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Comprehensive Coordination Chemistry II

FROM BIOLOGY TO NANOTECHNOLOGY

EDITORS-IN-CHIEF
Jon A McCleverty
Thomas J Meyer

Edited by
A.G. Wedd

Volume 4
Transition Metal Groups 3 - 6

Introduction to Volume 4

In the 20 years since 1982, there has been, of course, an avalanche of activity in the coordination chemistry of the early transition metals, Groups 3–6. This has been driven by further fundamental study but also by strategic work in reactivity and catalysis (including biological chemistry) and in solid state and thin film technologies.

Chapters 1–8 cover mononuclear systems, together with polynuclear species in which intermetallic bonding is not important or which have particular connections to the mononuclear systems. Highlights include the new area of metallofullerene chemistry (Chapter 1), intensive development of the aqueous chemistry of vanadium (Chapter 4) and the spectacular performance of the Group 6 elements chromium, molybdenum, and tungsten, driven by technological and biological aspects. Group 6 chemistry accounts for nearly half of the present volume, when the polynuclear systems of Chapters 9–12 are included.

Chapter 9 covers binuclear metal–metal bonded systems and acts as a link between the mononuclear species and the cluster chemistries of Chapters 10–12. The rapid evolution of the latter aspects is another highlight of development of the chemistry of Groups 4–6.

A G Wedd
Parkville, Australia
April 2003

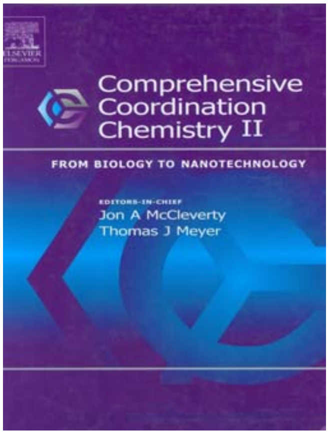
COMPREHENSIVE COORDINATION CHEMISTRY II

From Biology to Nanotechnology

Second Edition

Edited by

J.A. McCleverty, University of Bristol, UK
T.J. Meyer, Los Alamos National Laboratory, Los Alamos, USA



Description

This is the sequel of what has become a classic in the field, Comprehensive Coordination Chemistry. The first edition, CCC-I, appeared in 1987 under the editorship of Sir Geoffrey Wilkinson (Editor-in-Chief), Robert D. Gillard and Jon A. McCleverty (Executive Editors). It was intended to give a contemporary overview of the field, providing both a convenient first source of information and a vehicle to stimulate further advances in the field. The second edition, CCC-II, builds on the first and will survey developments since 1980 authoritatively and critically with a greater emphasis on current trends in biology, materials science and other areas of contemporary scientific interest. Since the 1980s, an astonishing growth and specialisation of knowledge within coordination chemistry, including the rapid development of interdisciplinary fields has made it impossible to provide a totally comprehensive review. CCC-II provides its readers with reliable and informative background information in particular areas based on key primary and secondary references. It gives a clear overview of the state-of-the-art research findings in those areas that the International Advisory Board, the Volume Editors, and the Editors-in-Chief believed to be especially important to the field. CCC-II will provide researchers at all levels of sophistication, from academia, industry and national labs, with an unparalleled depth of coverage.

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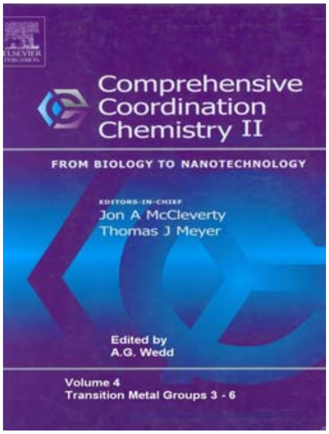
COMPREHENSIVE COORDINATION CHEMISTRY II



Volume 4
Transition Metal Groups 3 - 6

Edited by
A.G. Wedd

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4.1
Scandium and Yttrium

K. J. FISHER

*University of New South Wales and University of Sydney,
NSW, Australia*

4.1.1 INTRODUCTION

The chemistries of scandium and yttrium are often reported together (although yttrium is also often grouped with the lanthanides) so in this section they will be discussed together. Reference, where appropriate, will be made to the first volume in this series, *Comprehensive Coordination Chemistry: The Synthesis, Reactions, Properties and Applications of Coordination Compounds* (*CCC*, 1987). Volume 3 of *CCC* (1987) contained a chapter entitled *Scandium, Yttrium and the Lanthanides*,[1] and this chapter is designed to follow part of that chapter. The articles reviewed will cover the period 1982–2001 although earlier work may be cited. Volume 2 of *CCC* (1987), devoted to ligands, will also be referred to in this chapter.

Scandium and yttrium are almost exclusively observed in the +III oxidation state in condensed phase compounds, but there are some cluster and sandwich compounds that may be regarded as the metal having a reduced oxidation state; these compounds will be discussed in the relevant sections. Although the ionic radii of Sc^{3+} (0.68 Å) and Y^{3+} (0.88 Å) are significantly different their general coordination chemistries are similar. A whole range of coordination numbers from 3–12 are observed in the chemistry of scandium and yttrium and, in general, similar compounds of each element have similar coordination numbers with yttrium occasionally having a higher coordination number. Low coordination numbers are observed with very bulky ligands and the highest coordination numbers are observed where the metals are coordinated to small atoms such as hydrogen. These two elements are typical Chatt–Ahrland Class A metal ions and show ready coordination with ligands having oxygen and nitrogen donor atoms and also halides.

Since *CCC* (1987) was published there has been a greater use of X-ray crystallography resulting in a larger proportion of papers of these two elements containing structural data. The emphasis in the coordination chemistry has shifted away from simple monodentate and bidentate ligands, with the exception of the triflate (—O_3SCF_3), alkoxide (—OR), and amide (—NR_2), to polydentate ligands, particularly ligands having bulky groups. The triflates, particularly of scandium, have become important Lewis acid catalysts in synthetic organic chemistry and will be discussed in a later section. The alkoxides have strong M—O bonds and where volatile compounds can be made they are potentially useful in surface chemistry, particularly the MOCVD process. The alkoxides are also viewed as alternatives to cyclopentadienyl compounds (or other organometallic compounds) in solubilizing or stabilizing molecular precursors for materials applications. The amides are used in the same manner, to provide stable, volatile, or soluble precursors for use in producing materials. The yttrium compounds are used as precursors in the production of high-temperature superconductors.

Many of the macrocyclic ligands have been prepared so that the catalytic properties of metal complexes may be fine tuned by minor changes in the ligand design. Recent developments, that will continue to attract attention, have been the ability to bind metal complexes to surfaces so that they may be used in heterogeneous catalysis. The reactive alkoxide and amide groups are particularly useful in allowing the metal to form a bond with the surface (generally a M—O bond). The other groups attached to the metal influence the heterogeneous properties of the surface.

A whole new area of carbon chemistry has been developed since the publication of *CCC* (1987). This is fullerene chemistry and the related metallofullerene chemistry. Scandium and yttrium have featured prominently in metallofullerene chemistry as along with lanthanum these metals are easily encapsulated in the carbon cage. Later developments have allowed metal clusters and metal compounds to be trapped inside the carbon cage. The emphasis in this chemistry is now shifting to modifying the metallofullerenes by attaching groups to the outside of the carbon cage. The development of metallofullerene chemistry is being held back by the poor yields and difficult separation of pure products. This chemistry will be discussed in a following section.

Numerous reviews of the chemistries of scandium and yttrium (often with the lanthanides and actinides) have appeared since 1982. The Chemical Society Annual Reports on the Progress of Inorganic Chemistry contain a section on scandium and yttrium surveying the literature of selected years. These surveys by S. J. Lyle,[2,3] covering the period 1982–1983, J. D. Miller,[4–8] covering the period 1984–1988, C. J. Jones[9–11] covering the period 1989–1991, and S. A. Cotton[12–20] covering the period 1992–2000 have a separate section on scandium and then group yttrium with the lanthanides. Specific reviews on scandium and yttrium by E. C. Constable,[21,22] C. E. Housecroft,[23–32] and Z. Pikramenou[33,34] have been published in *Coordination Chemistry Reviews*. An article entitled *Scandium, Yttrium and the Lanthanides: Inorganic and Coordination Chemistry*, was featured in the *Encyclopedia of Inorganic Chemistry* that appeared in 1994.[35] More recent advances in the chemistry of scandium have also been reported.[36] This report highlights the aqueous chemistry, complexes with O-, N-, and P-donors and also the use of scandium complexes in synthetic organic chemistry.

The structural chemistry of scandium(III) has been reviewed[37] with emphasis on the coordination number and geometry of coordination complexes. This review covers the period 1926–1998.

4.1.2 COORDINATION NUMBERS

Coordination numbers from 3 to 12 have been observed in solid compounds of scandium and yttrium and some specific examples are given in Tables 1 and 2. Some discussion of these properties will be introduced in individual sections. The structural chemistry of scandium(III) has been reviewed with coordination numbers from 3 to 9 being highlighted.[37]

Table 1 Coordination numbers of scandium compounds.

Compound	*Coord. No.*	*References*
$Sc[N(SiMe_3)_2]_3$	3 [pyramidal(solid)planar (gas)]	1,42
$Sc[N(SiHMe_2)_2]_3(thf)$	4 (distorted T_d)	47
$Sc[N(CH_2CH_2NR_2]_3[ClLi(thf)_3]$	5 (distorted trigonal bipyramid)	48
$[Sc\{(CF_3)_2CHO\}_3(NH_3)_2]_2$	6 (O_h)	49
$Sc(Ph_3AsO)_3(NO_3)_2$	7	50
$Sc(12\text{-crown-}4)_2{}^{3+}$	8	51
$Sc(terpy)(NO_3)_3$	9	52
$Sc(BH_4)_3(thf)_2$	10	53

Table 2 Coordination numbers of yttrium compounds.

Compound	*Coord. No.*	*References*
$Y(OC_6H_5Bu^t{}_2\text{-}2,6)_3$	3 (trigonal planar)	54
$Y(OSiPh_3)_4(CuPMe_2Ph)$	4 (T_d)	55
$Y[N(SiHMe_2)_2]_3(thf)_2$	5 (distorted trigonal bipyramid)	47
$Y(Ph_2PO)_3C)_3$	6 (O_h)	56
$YCl[N(SiMe_2CH_2PMe_2)_2]_2$	7	57
$Y(H_2O)_8{}^{3+}$	8 (distorted dodecahedron)	58
$Y[C_6H_3(COO)_3(H_2O)_6]$	9	59
$[Y(BH_4)_2(thf)_4]^+$	10	60
$[Y(BH_4)_3(thf)_3]$	11	61
$[Y(BH_4)_4]^-$	12	60

A search of the Cambridge Structural Database (CSD)[38] for Sc—O bond lengths is shown in Figure 1. As the database only includes compounds having a carbon atom present in the molecule, some data from hydrated scandium halides[39,40] and hydroxylammonium sulfate have been added.[41] Sc—O bond lengths show a bimodal distribution centered at 2.07 Å and 2.17 Å. There are a few Sc—O bonds shorter than 2.0 Å with the three-coordinate $[Sc(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)_3]$ having a very short bond of 1.869 Å. Variation of Sc—N bond lengths are shown in Figure 2. The gas phase structure of the three-coordinate $Sc[N(SiMe_3)_2]_3$[42] has a short Sc—N bond length of 2.02 Å. Many more structural studies of yttrium compounds have been reported and this is revealed in Figures 3 and 4. Figure 3 shows the Y—O bond lengths, the data from the CSD[38] has been supplemented with data from the structures of $Y(HSO_4)_3$, $Y(HSO_4)_3{\cdot}H_2O$,[43] $Y(H_2O)_3[IO_4(OH)_2]$, $Y(H_2O)_2(IO_3)_3$,[43] $YCl(SiO_4)_2$, $Y_6Cl_{10}(Si_4O_{12})$,[44] and $YF_3(Si_3O_{10})$.[45] The Y—O bond lengths show a normal distribution centered at 2.34 Å with short bonds in the low-coordinate compounds such as $Y(OC_6H_3Ph\text{-}2,6)_3$,[46] which has a Y—O bond length of 2.05 Å. Figure 4 shows the broad distribution of Y—N bond lengths with the median at 2.44 Å. The Y—N and Y—O bond lengths are generally about 0.2 Å longer when compared with similar Sc—N and Sc—O bond lengths.

There have been several studies of coordination numbers in solution. These experiments generally involve the use of X-ray absorption fine structure (XAFS) or large-angle X-ray scattering. Seven water molecules with an average bond length of 2.18 Å are coordinated to the Sc^{3+} ion.[62] A more recent study also concludes that seven coordination occurs in solution.[63] A Raman study of scandium perchlorate solutions suggest that the coordination number six occurs in aqueous solution.[64] The hydrated Y^{3+} ion has eight coordination with an average Y—O bond length of ~2.4 Å.[65,66] In nonaqueous solvents such as dmso and dmf the complexes $[YL_8]^{3+}$ exist. These solutions have been studied by XAFS and large angle X-ray scattering. Comparing the solution measurements with solid-state measurements leads to the conclusion that there is an increase in the ionic radius of Y^{3+} as the coordination number increases from 6 to 8.[67] Solution measurements must take account of hydrolysis of the M^{3+} ion. The comparative hydrolysis of yttrium and the lanthanide ions has been measured:[68]

$$M^{3+} + H_2O \rightarrow MOH^{2+} + H^+$$

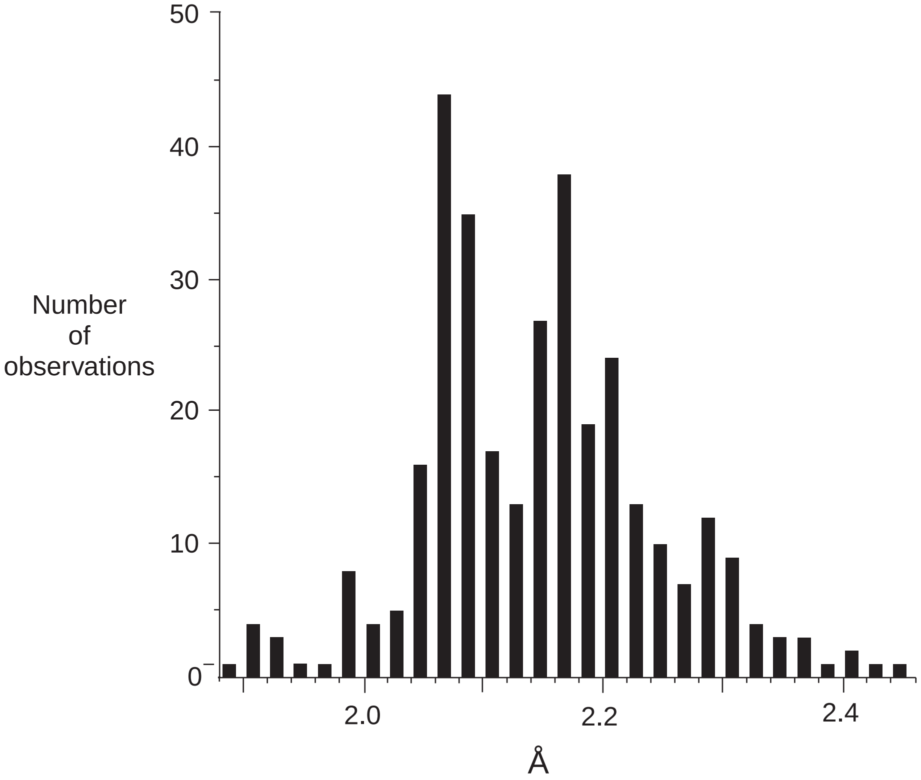


Figure 1 Variation of Sc—O bond lengths (*x*-axis) with the number of observations taken mainly from the CSD.

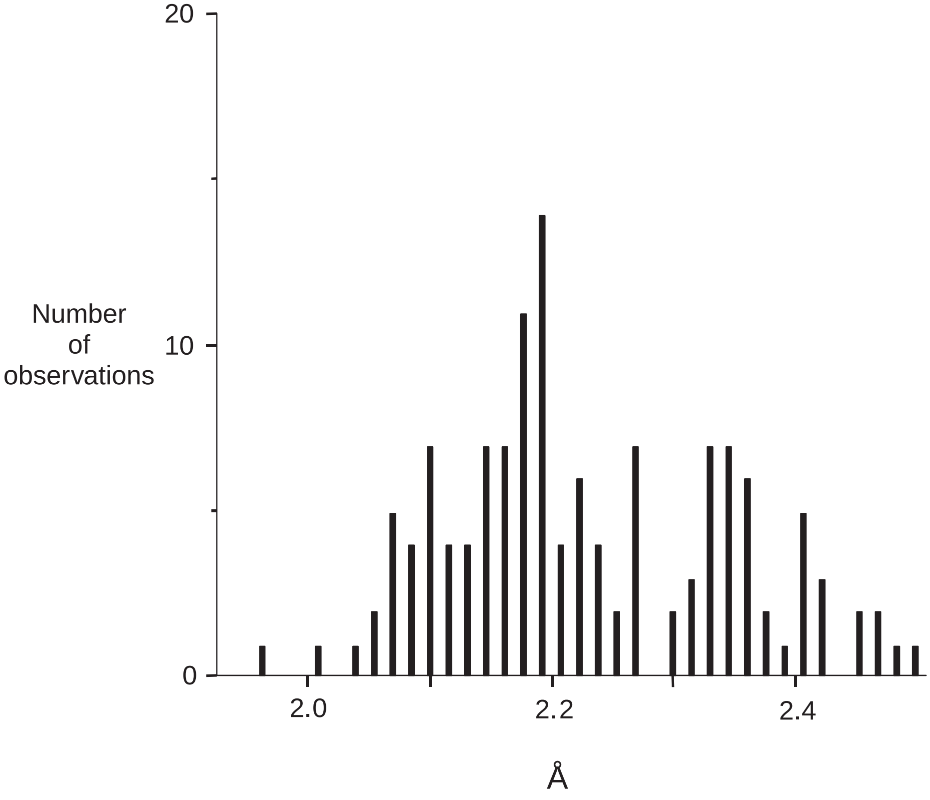


Figure 2 Variation of Sc—N bond lengths (*x*-axis) with the number of observations taken from the CSD.

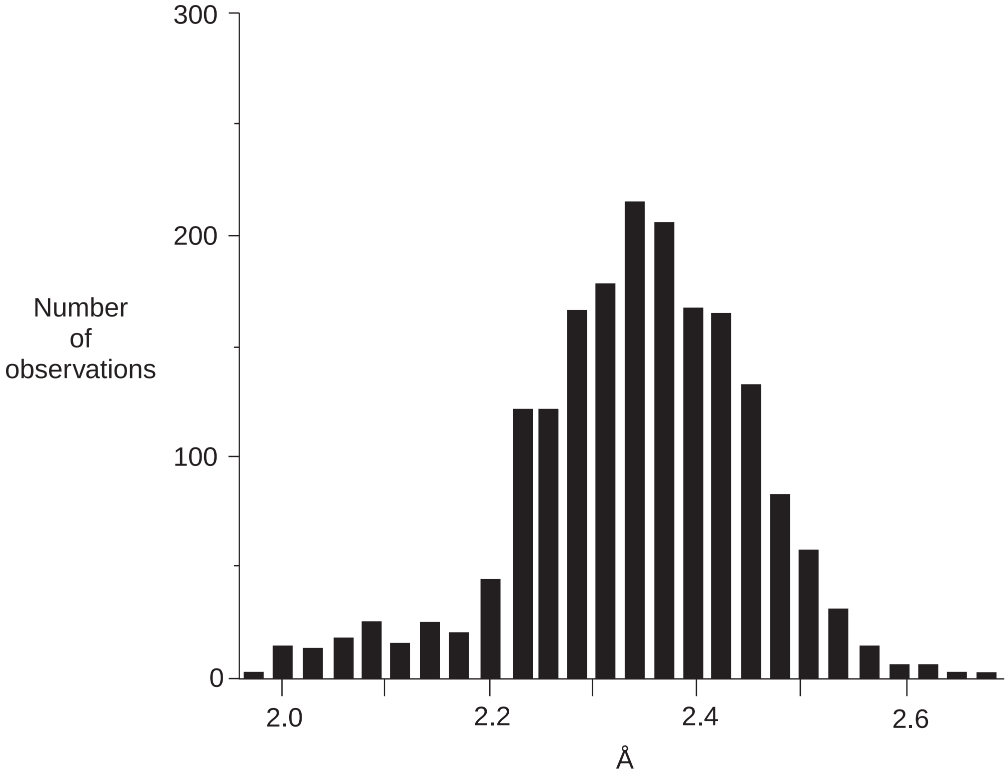


Figure 3 Variation of Y—O bond lengths (x-axis) with the number of observations taken mainly from the CSD.

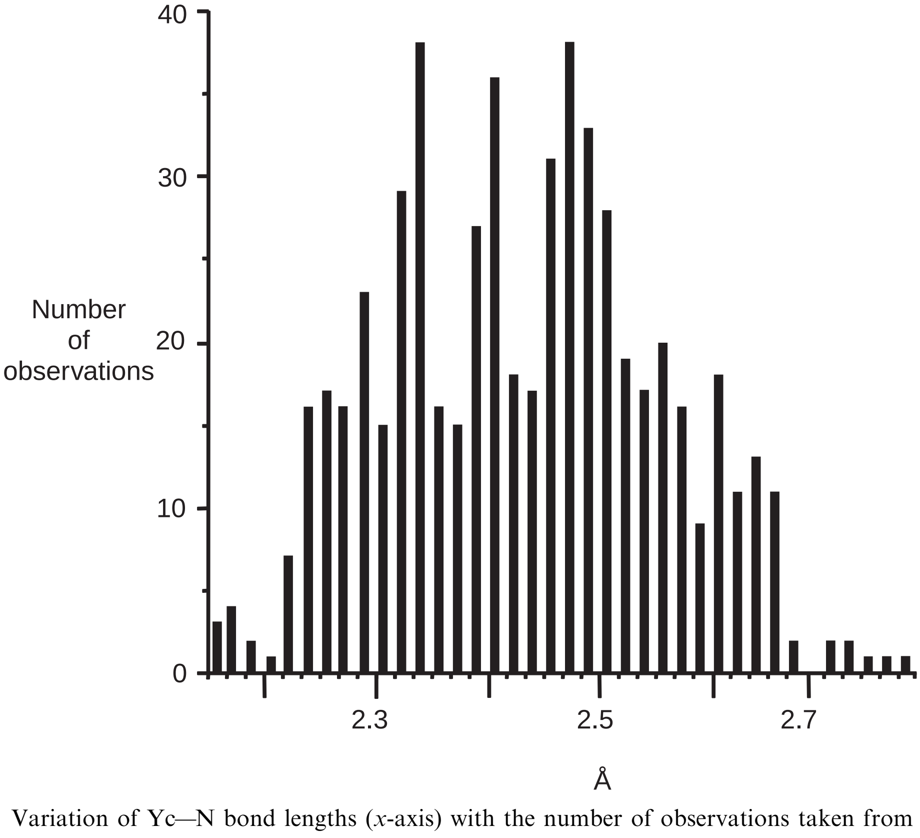


Figure 4 Variation of Yc—N bond lengths (x-axis) with the number of observations taken from the CSD.

4.1.3 ^{45}Sc AND ^{89}Y NMR

^{45}Sc and ^{89}Y both have 100% abundance with spins of 7/2 and 1/2 respectively. ^{45}Sc has a sensitivity of 0.3 compared with 1.0 for the ^{1}H and an NMR frequency of 24.29 MHz at 2.3488 T (100 MHz for ^{1}H). ^{89}Y has a much lower relative sensitivity of 1.18×10^{-4} and an NMR frequency of 4.899 MHz at 2.3488 T.

^{45}Sc NMR chemical shifts, linewidths, and relaxtion rates of scandium chloride and sulfate have been studied in aqueous solution.[69] Results in acid and basic solution are presented, as is the H_2O–D_2O isotope effect. ^{45}Sc NMR data of solutions of $ScCl_3$ in H_2O saturated with HCl indicate the formation of $[ScCl_4(H_2O)_2]^-$ whereas $[ScCl(H_2O)_5]^{2+}$ is present in 4 M HCl and $[ScCl_2(H_2O)_4]^+$ is present in 7 M HCl.[70] The interaction of alanine and small peptides with scandium nitrate has been investigated by ^{45}Sc NMR.[71,71] The complexes are labile but the oligopeptide complexes are shown to be more stable than the alanine complex. ^{45}Sc NMR data of ionic and covalent compounds, relative to external 1.5 M aqueous $ScCl_3$, has been presented.[73] The binding of Sc to a protein (chicken ovotransferrin) has been studied by ^{45}Sc NMR.[74]

There have been very few solid state NMR studies of scandium and yttrium compounds. A comparative study of the acetates and hydrated nitrates of scandium, yttrium, and lanthanum by magic angle spinning solid state ^{45}Sc, ^{89}Y, and ^{139}La NMR has been carried out.[75] The nuclear quadrupole coupling constant and the asymmetry parameter of the electric field gradient tensor for the scandium and lanthanum compounds was determined. Other compounds such as the hydrated chlorides and the oxides of scandium and yttrium were also measured. ^{89}Y magic angle spinning NMR has shown that the Y^{3+} ion in the oxide ion conductor $(Bi_2O_3)_{1-x}(Y_2O_3)_x$ (fluorite structure) is surrounded by six anions.[76] ^{89}Y magic angle spinning NMR has also been used to investigate the incorporation of paramagnetic ions in rare-earth pyrochlores $Y_{2-x}Ln_xM_2O_7$ (Ln = Ce, Pr, Nd, Sm, Eu, Yb; M = Sn, Ti).[77] The paramagnetic ions decrease the ^{89}Y relaxation time allowing spectra to be obtained in relatively short times and the paramagnetic shifts are proportional to the number of lanthanide ions substituted for yttrium.

^{89}Y solution measurements of simple yttrium salts have shown that the ^{89}Y chemical shift is dependent upon covalent interactions and solvent effects.[78] The long relaxation times were shortened by the addition of 1% (mole ratio) of gadolinium nitrate. Exchange processes in ions such as $YCl_6{}^{3-}$ were also investigated. ^{89}Y chemical shifts are normally measured relative to YCl_3 in D_2O (the concentration varies between 1M and 3 M) and the range is large as shown in Table 3. Generally the ^{89}Y chemical shifts vary with the donor ligand and the coordination number. The ranges are as follows: oxygen ligands from +270 ppm to +60 ppm, nitrogen ligands +570 ppm to +100 ppm, carbon ligands +40 ppm to −370 ppm, and halides from +10 ppm to −30 ppm.[79] These are only approximate and mixed donor ligands can be outside the normal ranges as shown by the last entry in Table 3.

4.1.4 BOROHYDRIDES

The scandium borohydride thf complex was mentioned in *CCC* (1987).[1] There have been more developments in the borohydride chemistries of scandium and yttrium and so some literature prior to 1982 has been included in this section.

Both scandium and yttrium form borohydride complexes $[M(BH_4)_3(thf)_n]$ with thf coordinated to the metal.[53] In each compound two borohydride groups are bound through three hydride bridges and one borohydride is bound through two hydride bridges. The scandium compound is

Table 3 ^{89}Y chemical shifts of compounds with oxygen and nitrogen donors.

Coordination number	*Compound*	δ (ppm)	*References*
3	$Y(O\text{-}2,6\text{-}Bu^t\text{-}4\text{-}C_6H_2)_3$	171	79
3	$Y[N(SiMe_3)_2]_3$	570	79
4	$Y[N(SiMe_3)_2]_3\ (OPPh_3)$	544	79
4	$[Y(OSiPh_3)_3]_2$	263	79
5	$Y_5O(OPr^i)_{13}$	223, 219	80
6	$Y(OSiPh_3)_3(thf)_3$	157	79
6	$Y_3(OBu^t)_9(Bu^tOH)_2$	167	81
6	$[Me_2Si(NBu^t)(OBu^t)]_2YCl(thf)$	458	82
5	$[Me_2Si(NBu^t)(OBu^t)]_2Y[CH(SiMe_3)_2]$	645	82

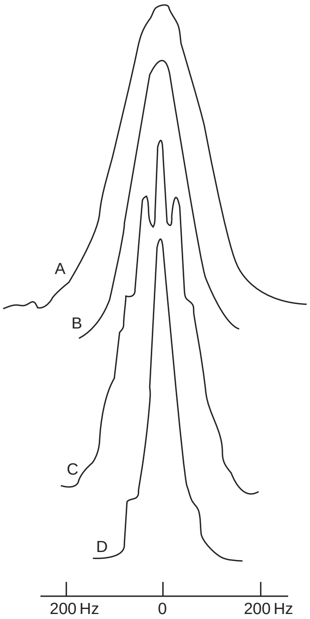


Figure 5 ^{45}Sc NMR spectra of [Sc(BH$_4$)$_3$(thf)$_2$].[87] (A) normal spectrum; (B) ^{1}H decoupled spectrum; (C) ^{11}B decoupled spectrum; (D) ^{1}H and ^{11}B decoupled spectrum (reproduced by permission of the American Chemical Society from *Inorg. Chem.*, **1984**, *23*, 1072–1078).

trigonal bipyramidal coordinating two thf molecules and is 10-coordinate.[83] A doubly bridged borohydride also occurs in the tetrahydridoboratometallocene [Sc{(SiMe$_3$)$_2$Cp}$_2$BH$_4$].[84] The yttrium compound [Y(BH$_4$)$_3$(thf)$_3$] coordinates three thf molecules and has a coordination number of 11.[61] There is also a second ionic form of the yttrium borohydride [Y(BH$_4$)$_2$(thf)$_4$][Y(BH$_4$)$_4$].[60] In the ionic compound [Y(BH$_4$)$_2$(thf)$_4$][Y(BH$_4$)$_4$] the yttrium is 10-coordinate in the cation and 12-coordinate in the anion. The scandium and yttrium borohydrides have also been prepared solvated with dimethoxyethane.[85,86] Solution multinuclear NMR studies[87] of the scandium and yttrium borohydrides have been carried out, including ^{45}Sc and ^{89}Y measurements. Figure 5 shows that [Sc(BH$_4$)$_3$(thf)$_2$] exhibits a broad ^{45}Sc resonance which is sharpened with ^{1}H and ^{11}B decoupling. Coupling constants were $J(^{45}\mathrm{Sc},^{11}\mathrm{B}) = 15.5$ Hz and $J(^{45}\mathrm{Sc},^{1}\mathrm{H}) = 30$ Hz. [Y(BH$_4$)$_3$(thf)$_3$] shows no hydrogen or boron coupling to ^{89}Y and this is attributed to the increased ionic bonding in the yttrium compound relative to the scandium compound.

4.1.5 CARBON LIGANDS

Organometallic compounds are not specifically discussed in this section.

No carbonyl chemistry of scandium and yttrium has been reported yet and there is also no cyanide chemistry of these two elements although thiocyanato complexes of scandium [Sc(NCS)$_6$]$^{3-}$ (bonded through nitrogen) are known.[88] The important developments involving scandium or yttrium with carbon have involved the fullerene derivatives of these elements. There have been some scandium carbide systems prepared but these will be highlighted in the chemistry of the halides.

4.1.5.1 Endohedral Fullerene Compounds of Sc and Y

The fullerenes were first discovered by laser ablation cluster ion formation in a mass spectrometer.[89] Soon after the identification of C$_{60}$ as a "magic number cluster," [LaC$_{60}$]$^+$ was also identified.[90] Later, macroscopic quantities of fullerenes were produced by the carbon arc method[91] soon followed by the macroscopic production of the lanthanum endohedral fullerenes.[92] Fullerene chemistry has developed rapidly since the preparation of macroscopic quantities of these compounds. The development of the metallofullerenes has been hampered by the low yield of these compounds in conventional syntheses. Newer and better synthetic routes to metallofullerenes will probably be found in the near future speeding up the investigation of the properties, particularly of the scandium and yttrium metallofullerenes. Laser vaporization and the arc method of metal-doped carbon have been used to produce endohedral Sc and Y compounds and a recent review has details of these methods.[93] The initial studies of metallofullerenes involved gas phase laser ablation, used to observe the ions by mass spectrometry.[94] Macroscopic quantities of scandium metallofullerenes are prepared by the arc method and although laser desorption of the soots formed in the preparation show the presence of $[ScC_{60}]^+$ and $[ScC_{70}]^+$ the extractable compounds typically give only one monoscandium fullerene ScC_{82}.[95,96] Di-, tri- and tetrascandium fullerenes such as Sc_2C_{84}, Sc_3C_{82}, and Sc_4C_{82}, are extractable. The extractable yttrium fullerenes are less extensive than the scandium counterparts and only YC_{82} and Y_2C_{82} have been recovered in small quantities.[97,98]

The endohedral (metal trapped inside the carbon cage) nature of the metallofullerenes has been questioned, but gas phase photofragmentation experiments of ions[99,100] and solid-state measurements indicate that the metals are endohedral not exohedral.[101] Exohedral metallofullerenes have been prepared in the gas phase but they have different properties to the endohedral metallofullerenes prepared by the arc or laser methods.[102–104] The symbol @ has been used to denote a species inside the fullerene cage and this symbol will be now used to denote endohedral metallofullerenes.

The solids produced by the arc method are often complex mixtures of fullerenes and metallofullerenes and an important part of this chemistry has involved the purification of the individual metallofullerenes and even isomers of a particular species. In general a two-stage HPLC method has been used to separate the metallofullerenes from the empty fullerenes and purify individual metallofullerenes.[105,106]

$Sc@C_{82}$ and $Y@C_{82}$ have both been investigated by synchrotron X-ray diffraction[107] and in each case the metal is inside the carbon cage; not in the center but close to one of the six-membered rings of the cage. The scandium atom in $Sc@C_{82}$ is shown to have 18.8 electrons and so the ion may be formulated as $Sc^{2+}C_{82}{}^{2-}$; this agrees with UPS measurements.[108] The Y atom in $Y@C_{82}$ is also close to one of the six-membered rings of the cage and at room temperature the Y is stationary with respect to the cage. This stationary state for the metals Sc and Y differs from lanthanum where the metal atom appears to be in motion. ESR and XPS measurements suggest that the formulation of $Y@C_{82}$ is best described as $Y^{3+}C_{82}{}^{3-}$.[97,98]

The discandium endohedral fullerenes $Sc_2@C_{74}$, $Sc_2@C_{82}$ and $Sc_2@C_{84}$ have been isolated and three isomers of $Sc_2@C_{84}$ have been separated. ^{45}Sc NMR of $Sc_2@C_{84}$ isomers indicates that the scandium atoms are separated and that motion of these atoms is restricted.[109] This is supported by theoretical and structural studies.[110] Synchrotron powder X-ray studies indicate that $Sc_2@C_{84}$ is best represented as $2(Sc^{2+})C_{84}{}^{4-}$. The Raman scattering and infrared absorptions of $Sc_2@C_{84}$ are consistent with a simple ionic picture of $Sc_2@C_{84}$.[111] The results for $Sc_2@C_{84}$ differ from $Sc_2@C_{66}$ that has since been characterized.[112] In this endohedral metallofullerene the two scandium atoms appear to form a dimer. The scandium atoms sit close to two pairs of fused five-membered rings in the C_{66} cage. This indicates that the size and structure of the fullerene influences the trapped species. The compound may be regarded as $(Sc_2)^{2+}C_{66}{}^{2-}$.

The triscandium endohedral fullerene $Sc_3@C_{82}$ has been isolated and studied by ESR.[96] Synchrotron X-ray studies indicate that the three scandium atoms form a triangle and this trimer has a formal charge of three allowing formulation of the compound as $(Sc_3)^{3+}C_{82}{}^{3-}$.[113] The temperature-dependent metal cluster position inside the C_{82} cage has been studied.[114]

One area of development of metallofullerene chemistry has been the synthesis of adducts by addition to the carbon cage.[115] Another advance in the endohedral metallofullerene area has been the identification of metal compounds inside the carbon cages. Introducing nitrogen (pressure, 1–3 mbar) into the arc process using a scandium-doped graphite rod results in the isolation of $Sc_3N@C_{80}$. Structural characterization of this endohedral fullerene has been accomplished by X-ray crystallography of a crystal formed when the endohedral fullerene co-crystallized with cobalt octaethylporphyrin.[116] A similar method has been used to crystallize $Sc_3N@C_{78}$.[117] The latter compound studied by synchrotron X-ray crystallographic analysis shows the Sc_3N as a planar group with nitrogen at the center bonded to three scandium atoms. There has also been an EPR study of $Sc_3N@C_{80}$ radical anions.[118] Recently $Sc_3N@C_{68}$ has been prepared and this compound has been studied by ^{13}C and ^{45}Sc NMR.[119] It is postulated that the Sc_3N group is planar and is inside a C_{66} cage of D_3 symmetry. The structure of a scandium carbide endohedral metallofullerene: $Sc_2C_2@C_{84}$ has been investigated by ^{13}C NMR and synchrotron X-ray diffraction on the powder sample.[120] The carbon atoms in Sc_2C_2 unit are shown to be equivalent by ^{13}C NMR. The diffraction study indicates that the ScC_2 unit has a C—C bond intermediate in bond length

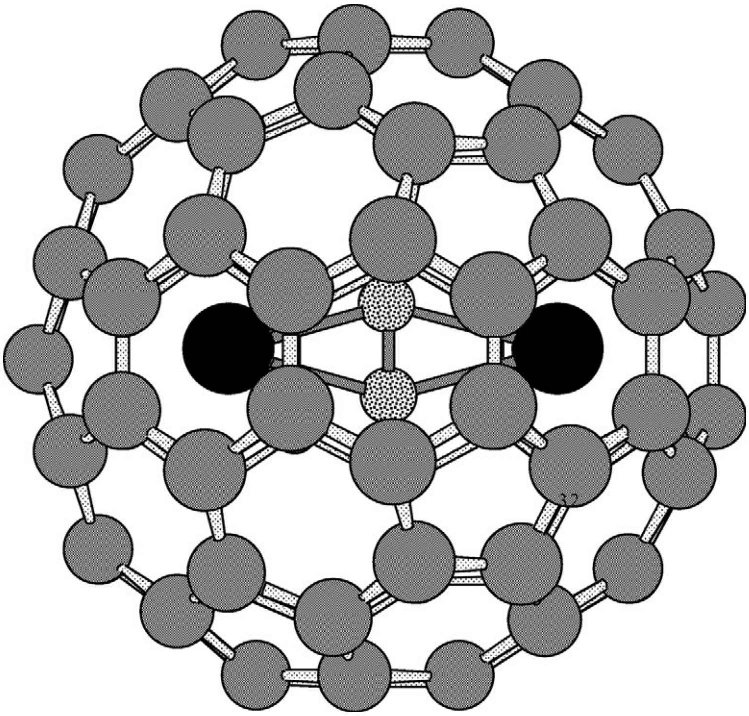


Figure 6 Schematic representation of $Sc_2C_2@C_{84}$ showing the planar Sc_2C_2 ring. The scandiums are shown in black and the carbons of the C_2 unit are stippled.

between a single and double bond. The scandium atoms are on opposite sides of the C—C unit and the Sc_2C_2 ring is planar. The structure is shown in Figure 6 along with the planar Sc_2C_2 ring.

4.1.6 NITROGEN DONOR LIGANDS

4.1.6.1 Amido Complexes

The simplest amide of yttrium $Y(NH_3)_2$ has been prepared by the reaction of $Y(SCN)_3$ with KNH_2 in liquid ammonia.[121] The amidometallates $K_3Y(NH_2)_6$ and $Rb_3Y(NH_2)_6$ may be prepared by dissolving the metals in supercritical ammonia.[122]

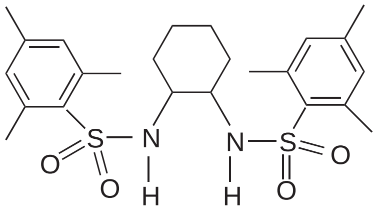
The volatile metal amido compounds $M(NR_2)_x$ are potential precursors for solid-state materials such as metal nitrides. The metal amido compounds have also become very important synthetic starting materials for many types of compounds. The low coordination of these compounds often allows addition of molecules with suitable donor ligands. The relatively weak M—N bond allows the NR_2 group to be replaced by other groups and in the case of scandium and yttrium the M—O bond is much stronger than the M—N bond.

As previously reported[1] the three-coordinate $Sc[N(SiMe_3)_2]_3$ has been known since 1972 and the similar yttrium compound $Y[N(SiMe_3)_2]_3$ was reported in 1980.[123] The scandium compound was reported to have ScN_3 with pyramidal geometry in the solid state, but the gas phase structure determined by electron diffraction[42] has a ScN_3 with planar structure. There is no significant change in the Sc—N bond length in the solid and gas phase and the Sc—N bond length is shorter than most other Sc—N bond lengths. The difference in configuration is attributed to the crystal packing forces in the crystalline state that are absent in the gas phase. The $M[N(SiMe_3)_2]_3$ compounds of scandium and yttrium have proved to be good starting materials in the preparation of coordination compounds of the two metals. Similar to all transition metal dialkylamino compounds, they may be used in alcoholysis or aminolysis reactions to form alkoxides or other Sc—N systems.

The reaction of $ScCl_3(thf)_3$ with $Sc[N(SiMe_3)_2]_3$ gives the dichloro complex $[ScCl_2\{N(SiMe_3)_2\}(thf)_2]$ which when heated to 400 °C is converted to scandium nitride ScN, with loss of thf and $ClSiMe_3$.[124] $Sc[N(SiMe_3)_2]_3$ undergoes deprotonation (and loss of $HN(SiMe_3)_2$) when reacted with $NaN(SiMe_3)_2$ in thf,[125] forming the complex $[Na(thf)_3Sc(CH_2SiMe_2NSiMe_3)\{N(SiMe_3)_2\}_2]$. The reaction of $M[N(SiHMe_2)_2]_3$ (M = Sc or Y) with a substituted bis-benzenesulfonamidocyclohexane (**1**) results in the replacement of two $N(SiHMe_2)_2$ groups.[126] The yttrium compound appears to have a coordinated thf molecule that is absent in the scandium compound. The ^1H and ^{13}C NMR are complex and a monomer–dimer equilibrium is suggested, complicated by the presence of *cis*- and *trans*- isomers. The yttrium compound is desolvated under vacuum to yield a less soluble compound that may be crystallized. The crystal structure reveals a dimer structure with unusual bridging S=O groups.

$Y[N(SiHMe_2)_2]_3$ has been used to attach a YNR_2 group to the surface of the mesoporous silica MCM-41. The NR_2 group may be replaced by other ligands. The catalytic reactivity of these modified surfaces in the Diels–Alder reaction has been investigated.[127]

The reaction of YCl_3 with $KNPPh_3$ and Baysilon paste, $(OSiMe_2)_n$, gives a dimer with a Y_2O_2 bridge in the compound $[Y(NPPh_3)_2(OSiMe_2NPPh_3)]_2$ (**2**).[128]



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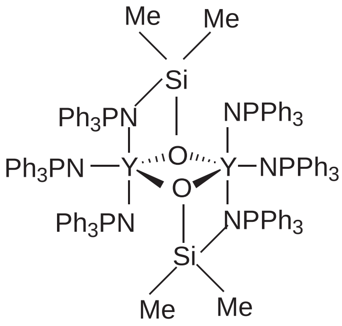


(2)

4.1.6.2 Bidentate Ligands

A useful compound for the preparation of organoscandium compounds is (β-diketiminato)scandium dichloride. This compound is prepared from the lithium salt of the aryl-β-diketiminate and $ScCl_3(thf)_3$; the product retains a thf ligand and is five-coordinate in the solid state. ^1H NMR shows that the compound is fluxional in solution.[129] The chlorides are easily replaced and alkylation with organolithium compounds has been investigated. Reaction of bis-trimethylsilylmethylscandium aryl-β-diketiminates with a phosphine telluride yields bis-tellurate complexes (**3**).[130] These complexes decompose to bridged Sc–Te–Sc species and the type of bridging is dependent upon the substituents on the aryl-β-diketiminates.

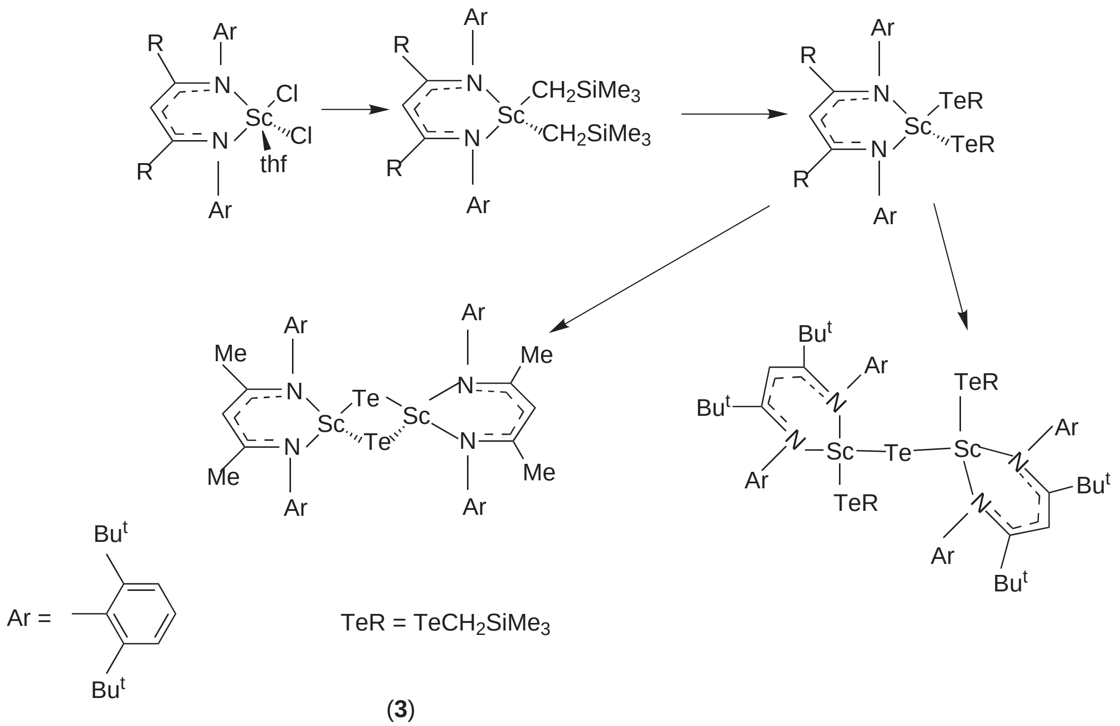
The bis(oxoazoline) ligand (**4**) acts as a bidentate ligand with yttrium.[131] The reaction of 2,2′-methylene-bis[(4S)-4-*tert*-butyl-2-oxazoline with $Y[N(SiHMe_2)_2]_3(thf)_2$ gave the mono or bis-oxoazoline complexes, $[(oxoazoline)Y\{N(SiHMe_2)_2\}_2]$ or $[(oxoazoline)_2YN(SiHMe_2)_2]$.

The bidentate ligand guanidine has been discussed in *CCC* (1987).[132] A guanidinate anion $(Me_3Si)_2NC(NPr^i)_2$ has since been used to prepare a dimeric yttrium complex, $[\{(Me_3Si)_2NC(NPr^i)_2\}_2YCl]_2$.[133] This complex has proved to be a useful starting material for the preparation of hydrocarbomyl and amide compounds that retain the guanidinate ligand. A similar ligand $Bu^tC(NPr^i)_2$ has also been used to prepare yttrium compounds.[134]

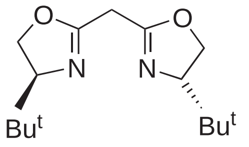
Eight-coordinate yttrium compounds having three pyrazolato ligands and two thf or two pyridine ligands may be prepared by the reaction of yttrium metal with $Hg(C_6F_5)_2$ and 3,5-$Bu^t_2C_3N_2H$.[135] The potential of using these compounds for chemical vapor deposition was investigated. The pyridine compound could be sublimed without visible residue whereas the thf complex sublimed as the tris-pyrazolato-yttrium(III), $Y(Bu^t_2C_3N_2)_3$ that appeared to be polymeric.

4.1.6.3 Amidines

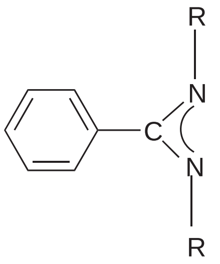
Amidines are nitrogen compounds of the general form RC(NR′)(NR″H) that can act as bidentate ligands. They have been discussed in *CCC* (1987).[132] Some of these ligands (**5**) have been used to stabilize unusual scandium and yttrium compounds. Much of the chemistry involving amidines



(**3**)



(**4**)



(**5**)

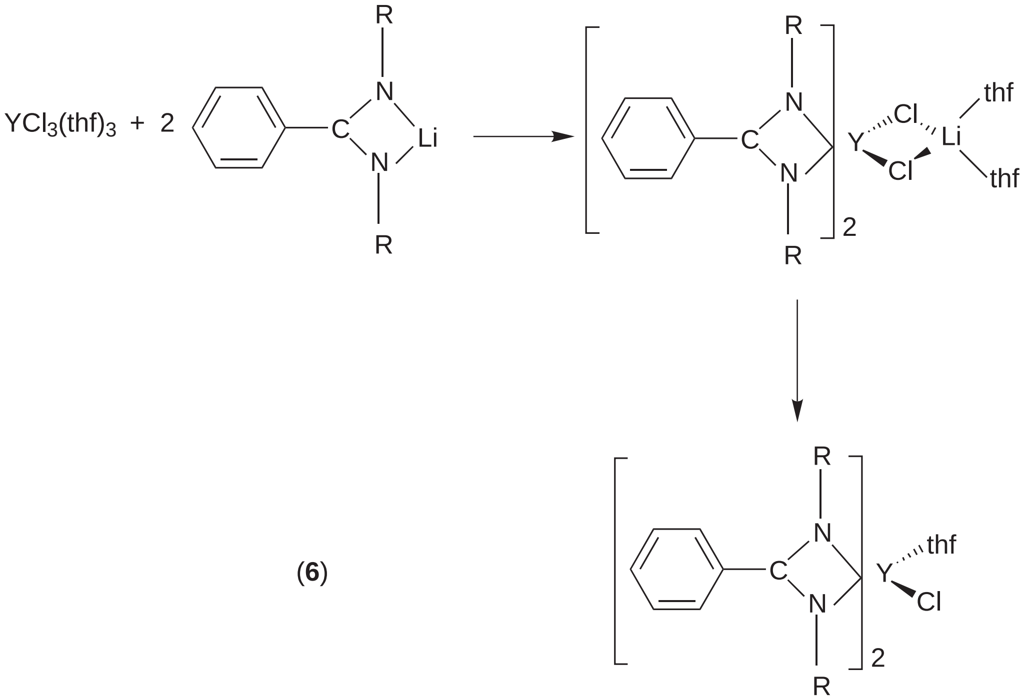
and group 3 elements has been directed towards finding alternatives to cyclopentadiene in the preparation of potential Ziegler–Natta type catalysts.

The coordination chemistry of the N-silylated benzimidines has been reviewed.[136] Many transition metal halides, acetates, and alkoxides react with silylated benzimidines or the anions $[RC_6H_4C(NSiMe_3)_2]^-$ to produce chelate complexes containing planar four-membered MNCN rings.

The reaction of $ScCl_3(thf)_3$ or $YCl_3(thf)_3$ with the sodium or lithium adduct $[RC_6H_4C(NSiMe_3)_2]M(Et_2O)_n$ yields $[RC(NSiMe_3)_2]_2MCl(thf)$ which may be used to prepare other derivatives (BH_4, NHR) by substitution of the chloride shown below (**6**).[136–138]

Yttrium triflate may also be used as a starting material to produce the derivative $[RC_6H_4C(NSiMe_3)_2]Y(thf)OSO_2CF_3$.[136] A similar complex having a coordinated Li(tmeda) species may also be prepared. One important derivative is the hydride $[\{RC(NSiMe_3)_2\}_2ScH]_2$ prepared via the trimethylsilylmethyl derivative $[RC(NSiMe_3)_2]_2ScCH_2SiMe_3$ by reaction with H_2. The hydride has two Sc—H bridges with each Sc having distorted octahedral symmetry. The Sc—H bond lengths vary from 1.87 to 2.00 Å.

The coordination chemistry of the aminotroponiminates has been reviewed.[139] A homoleptic aminotroponiminate complex of yttrium has been prepared and studied by X-ray crystallography and density functional theory calculations.[140]



(6)

4.1.6.4 Polydentate Nitrogen Ligands

The classical tridentate ligand terpyridyl (terpy) forms a nine-coordinate complex with scandium nitrate [Sc(terpy)$(NO_3)_3$].[52] This compound with chelating nitrates exhibits a relatively rare high coordination number for scandium.

1,4,7-Triazacyclononane is a tridentate ligand which may be converted to a hexadentate ligand by the addition of pendent amide groups to the nitrogens. One such ligand 1,4,7-tris(carbamoylmethyl)-1,4,7-triazacyclononane (tcmt) forms a complex with yttrium, [Y(tcmt)$(CF_3SO_3)_2$-(H_2O)]CF_3SO_3.[141] Yttrium is nine-coordinate in this complex, bound to the hexadentate tcmt, one water molecule and two triflate ions. 1,4,7-Triazacyclononane may also be modified by reactions with phenols to produce other hexadentate ligands. These ligands have been used to prepare scandium phenoxyl radical complexes.[142]

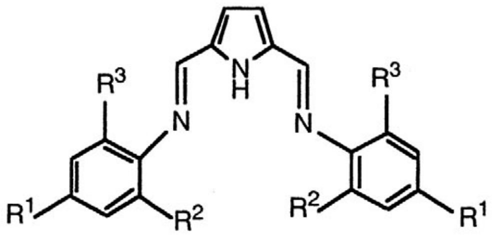
The bis(iminomethyl)pyrrolyl ligands (R-pyr) (**7**) are tridentate and these compounds react with $Y[N(SiMe_3)_2]_3$ to give five or nine-coordinate complexes depending upon the steric size of the aryl groups attached to two of the nitrogens.[143] When the *ortho* groups are large (e.g., the diisopropyl derivative), the pyrrolyl ligand is bidentate and the compound $(R\text{-pyr})_2Y[N\ (SiMe_3)_2]$ is formed, where Y has square pyramidal geometry. When the *ortho* groups are methyl the compound $(R\text{-pyr})Y[N(SiMe_3)_2]_2$ is formed, where the pyrrolyl ligand is tridentate and Y has a distorted trigonal bipyramidal geometry. When the *ortho* groups are hydrogen a nine-coordinate species $(R\text{-pyr})_3Y$ is formed.

The quadridentate triamidoamines $[N(CH_2CH_2NR)_3]^{3-}$ ($R = SiMe_3$) form complexes with scandium and yttrium.[48] These complexes are prepared by the reaction of the lithium triamidoamine thf complex with $MCl_3(thf)_n$ initially giving a lithium chloride adduct $M[N(CH_2CH_2NR)_3]$-$LiCl(thf)_3$. The adduct when heated at 140 °C at 10^{-6} mbar leads to the distillation of pure $M[N(CH_2CH_2NR)_3]$. The structure of the $Y[N(CH_2CH_2NR)_3]LiCl(thf)_3$ complex has been determined and the yttrium is bound through a chlorine bridge to the $Li(thf)_3$ unit.

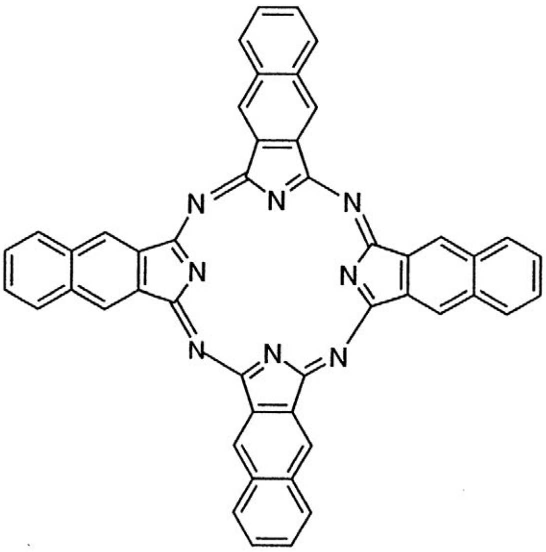
4.1.6.5 Porphyrin Compounds

Porphyrins, hydroporphyrins, azaporphyrins, phthalocyanines, corroles, corrins, and related macrocycles were discussed in *CCC* (1987).[144] The octaethylporphyrin complexes of scandium were also previously mentioned in *CCC* (1987).[1] The octaethylporphyrin (oep) scandium chloride complex (oep)ScCl, prepared by the reaction of the dilithium porphyrin with $ScCl_3(thf)_3$, has proved to be a good starting material for the preparation of a wide range of organometallic compounds.[145] This result contrasts with an earlier report that an oxide dimer $[Sc(oep)]_2O$ was produced by the action of H_2O on (oep)ScCl.[1] The reaction of the dilithiumoctaethylporphyrin with $YCl_3(thf)_3$ gives a yttrium octaethylporphyrin complex having an ethoxide group attached to the yttrium.[146] The ethoxide group is assumed to have been present due to the cleavage of thf.

Double decker complexes involving yttrium with a porphyrin and the 2,3-naphthalocyaninato (nc) group (**8**) have been prepared by the reaction of yttrium acac, porphyrin, and naphthalonitrile in the presence of 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU).[147,148] These complexes have been studied spectroscopically and electrochemically and in the case of the Y(nc)(oep) complex the crystal structure has been determined. In Y(nc)(oep) the yttrium is eight-coordinate and sits between the two ligand planes that are separated by 2.7 Å. The complex $Y(nc)_2$ has also been prepared by the reaction of yttrium acac and naphthalonitrile in the presence of DBU.[149]



(**7**)



(**8**)

The tetraphenylporphyrin scandium complexes were previously reported and now crystal structures have been determined for the *p*-toly derivatives (ttp). Both scandium and yttrium form (ttp)MCl complexes[150,151] but whereas the scandium compound is five-coordinate the yttrium compound coordinates solvent molecules forming seven or eight-coordinate complexes. Reaction of (ttp)ScCl with water forms an oxide dimer $[Sc(ttp)]_2O$,[151] whereas for yttrium the cation $[Y(ttp)(H_2O)_3]^+$ has been observed.[152] The structure of $[Sc(ttp)]_2O$ is shown in Figure 7, the bridging oxygen is disordered over two sites with 50% occupancy of each site. The reaction of

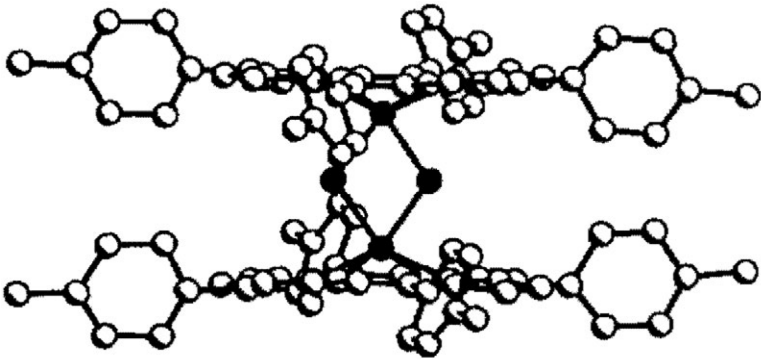
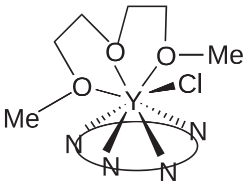


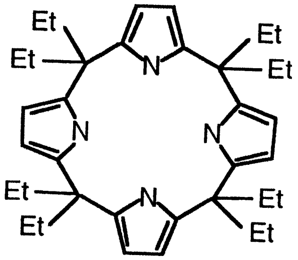
Figure 7 The structure of $[Sc(ttp)]_2O$. The bridging oxides are disordered over two sites at 50% occupancy for each site (reproduced by permission of Elsevier from *Inorg. Chim. Acta*, **1988**, *144*, 47–51).

$Y[N(SiMe_3)_2]_3$ with ttp in coordinating solvents such as thf or bis(2-methoxyethyl)ether (**9**) give complexes in which the yttrium lies well above the N_4 plane of the porphyrin.[150]



(**9**)

The porphyrin precursor octaethylporphrinogen (oepg) (**10**) has been used to form a yttrium complex $[Li(thf)_2][(oepg)Y(OEt)Li(thf)]$. The ethoxide group, which is believed to arise from cleavage of thf, acts as a bridge between the yttrium and one lithium cation.[146]

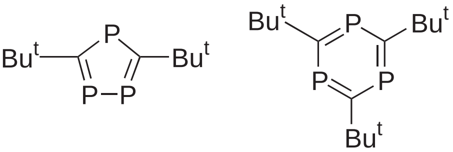


(**10**)

4.1.7 PHOSPHORUS DONOR LIGANDS

Phosphorus, arsenic, antimony, and bismuth ligands have been discussed in *CCC* (1987).[153] Complexes containing bonds between scandium, yttrium, and phosphorus or arsenic have been reviewed,[154] as have complexes with neutral phosphorus ligands.[155] Many of the complexes described in these reviews contain organic substituents such as cyclopentadienyl or alkyl groups.

Vaporized Sc atoms have been reacted with $Bu^tC{\equiv}P$ to give two unusual compounds, a triple decker sandwich compound of Sc^I, $Sc_2(P_2C_3Bu^t{}_3)_2(P_3C_3Bu^t{}_3)$[156] and a sandwich compound of Sc^{II} $[Sc(P_2C_3Bu^t{}_3)_2]$.[157] The $P_2C_3Bu^t{}_3$ and $P_3C_3Bu^t{}_3$ molecule are diphospacyclopentadienyl and triphosphabenzene molecules respectively (**11**).



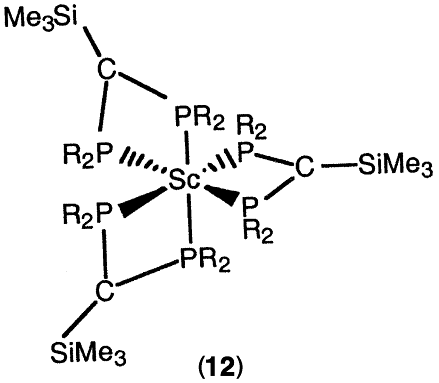
(**11**)

The reaction of scandium triflate with $Li[C(PMe_2)_2SiMe_3]$ gives a six-coordinate complex with a trigonal prismatic environment (**12**). There is an unusual ScP_2C four-membered ring in this compound.[158]

4.1.8 OXYGEN DONOR LIGANDS

4.1.8.1 Phosphine and Arsine Oxide

CCC (1987) contains a section on sulfoxides, amide, amine oxides, and related ligands that have sections on phosphine oxides and arsine oxides.[159] Phosphine and arsine oxide complexes of yttrium and the lanthanides were highlighted in *CCC* (1987).[1] Scandium and yttrium phosphine oxide complexes have been reinvestigated and characterized by multinuclear NMR and X-ray



(12)

crystallography.[160] Three phosphine oxides have been used, Ph_3PO, Ph_2MePO, and Me_3PO and four types of compounds of both scandium and yttrium prepared: $M(R_3PO)_2(NO_3)_3$, $M(R_3PO)_3(NO_3)_3$, $[M(R_3PO)_4(NO_3)_2]NO_3$, and $M(R_3PO)_2(EtOH)(NO_3)_3$. Scandium also forms a fifth complex $[M(Me_3PO)_6](NO_3)_3$. ^{45}Sc, ^{89}Y, and ^{31}P NMR have been used to characterize species in solution and these show a range of complexes having variations in M and R_3PO. The crystal structures of $[Sc(Ph_3PO)_2(NO_3)_3]$ and $[Sc(Ph_2MePO)_4(NO_3)_2]NO_3$ show that the scandium is eight-coordinate with bidentate nitrates. The yttrium complexes $Y(Ph_3PO)_2(EtOH)(NO_3)_3$ and $Y(R_3PO)_3(NO_3)_3$ ($R_3PO = Ph_3PO$, Ph_2MePO, and Me_3PO) all have nine-coordinate yttrium.

Arsine oxide complexes of scandium and yttrium nitrate have been synthesized and characterized by NMR and X-ray crystallography.[50] Me_3AsO produces one type of complex $[M(Me_3AsO)_6](NO_3)_3$ and the crystal structure shows six coordination at the metal. ^{45}Sc and ^{89}Y NMR indicates that the major species in solution is $[M(Me_3PO)_6]^{3+}$ but there are also the species $[M(Me_3AsO)_{6-n}(NO_3)_n]^{(3-n)+}$. Ph_3AsO forms $[Sc(Ph_3AsO)_2(NO_3)_3]$, $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$, $[Y(Ph_3AsO)_4(NO_3)_2]NO_3$, and $Y(Ph_3AsO)_2(EtOH)(NO_3)_3$. The crystal structure of $[Sc(Ph_3AsO)_3(NO_3)_2]NO_3$ shows the metal to be seven-coordinate and the crystal structure of $[Y(Ph_3AsO)_4(NO_3)_2]NO_3$ shows the metal to be eight-coordinate.

4.1.8.2 Alkoxides

The syntheses, physical properties, and molecular structures of alkoxides and aryloxides have been discussed in *CCC* (1987).[161] The alkoxides of scandium and yttrium were reviewed in *CCC* (1987).[1] There have been more recent developments in this area and the impetus for this chemistry has been the developments in materials research. Metal alkoxides and β-diketonates can be used as precursors for oxide and nonoxide thin films.[162] The stable M—O bond and the volatility of the metal alkoxides are important features of this area of chemistry. This has lead to more research in this area particularly in synthesis, NMR, and X-ray crystallography.

The three major preparative methods used to obtain the alkoxides of Sc and Y are:

(i) the reaction of the anhydrous metal halide with an alkalis metal alkoxide,
(ii) alcoholysis of a scandium or yttrium alkoxide, and
(iii) the reaction of the metal dialkylamides, principally the hexamethyldisilylamino compounds $M[N(SiMe_3)_2]_3$.[123]

The simple alkoxides of scandium $Sc(OR)_3$ ($R = Me$, Et, or Bu^n) prepared by alcoholysis of $Sc_5O(OPr^i)_{13}$ or anodic oxidation of scandium in alcohols are polymeric and do not contain the oxo ligand.[163] Attempts to prepare the simple iso-propoxides of Sc or Y always produce the oxoalkoxides $[M_5(\mu_5\text{-}O)(\mu_3\text{-}OPr^i)_4(\mu_2\text{-}OPr^i)_4(OPr^i)_5]$ that are volatile crystalline solids.[80,164,165] The stabilty of the $M_5O(OR)_8$ core is shown by the partial alcoholysis of $Sc_5O(OPr^i)_{13}$ by alcohols to produce $Sc_5O(OPr^i)_8(OR)_5$ compounds.[163] Metal oxoalkoxides have been reviewed[166] and included in the review are some scandium and yttrium alkoxides (such as the iso-propoxides) and mixed metal alkoxides (such as the yttrium barium oxoalkoxides).[167] $Sc_5O(OR)_{13}$ compounds have been prepared using an electrochemical synthesis.[163] In a variation of the normal reaction of the metal halide with sodium iso-propoxide, $Y_5O(OPr^i)_{13}$ may be prepared using anhydrous $(NH_4)_3Y(NO_3)_6$.[168] Two ^{89}Y solution NMR studies of $Y_5O(OPr^i)_{13}$ have been undertaken.[79,80]

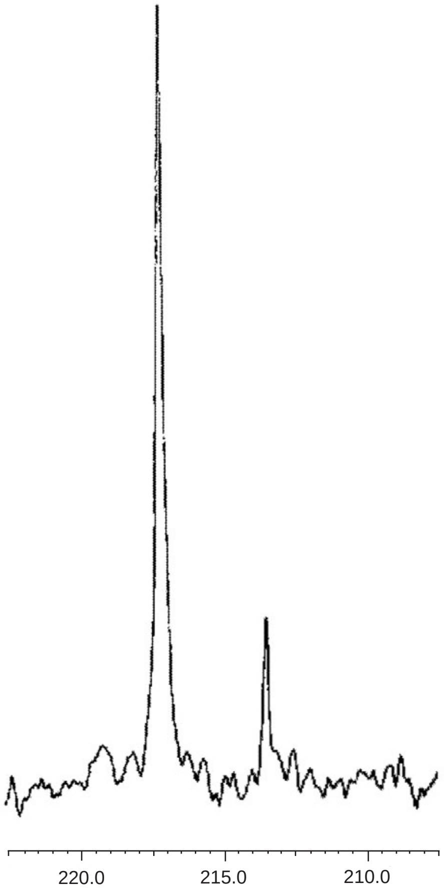


Figure 8 ^{89}Y NMR of $Y_5O(OPr^i)_{13}$ showing the presence of two inequivalent yttrium atoms in the molecule (reproduced by permission of the American Chemical Society from *Inorg. Chem.*, **1992**, *31*, 1262–1267).

The ^{89}Y solution spectrum (Figure 8) of $Y_5O(OPr^i)_{13}$ shows that there are two distinct yttrium sites, which is consistent with the solid-state structure. Figure 9 shows these sites are very similar, with the yttrium atoms being coordinated to six oxygens, showing the sensitivity of ^{89}Y chemical shifts to slight structural variations.[79]

Trimeric alkoxides of yttrium are formed where the R group is larger than Pr^i, e.g., $R = Bu^t$ or $CH_2C(CH_3)_3$ giving compounds such as $[Y_3(OBu^t)_9(Bu^tOH)_2]$ and with even larger alkyl groups such as CEt_3 dimers are obtained.[81]

Well characterized "simple" alkoxides of scandium and yttrium $M(OR)_3$ are rare. Three coordination about the metal requires a sterically large ligand such as the 2,6-di-*tert*-butylphenoxide, which does form both a scandium and yttrium monomeric alkoxide.[54,169] $Y(OC_6H_4Bu^t{}_2)_3$ has been used as an initiator in the polymerization of L-lactide.[170] The 2,6-diphenylphenoxide also forms a monomeric yttrium alkoxide[46] although thf adducts have been prepared for substituted 2,6-diphenylphenoxides of scandium and yttrium.[171] The sterically smaller 2,6-dimethylphenoxide does not form three-coordinate yttrium species and allows coordination of donor ligands such as thf in the yttrium compound $Y(OC_6H_3Me_2)_3(thf)_3$.[172]

Many other alkoxides show a tendency to polymerize, thus a toluene solution of $Y(OC_6H_3Me_2)_3(thf)_3$ produces a dimeric compound $[Y(OC_6H_3Me_2)_3(thf)_2]_2$ which when dissolved in thf reverts to the monomer $Y(OC_6H_3Me_2)_3(thf)_3$. This shows the facile interconversion of the two alkoxides.[172] The interconversion of yttrium alkoxides is also shown in the *tert*-butoxide compound $Y_3(OR)_7Cl_2(thf)_2$ which polymerizes in toluene solution to give the Y_{14} complex $[Y_7(OR)_{14}Cl_5O(thf)_2]_2$.[173] Substituted alcohols with potentially coordinating groups such as $HOCR_2CH_2OMe$ react with the metal or $Y[N(SiMe_3)_2]_3$. A decameric yttrium alkoxide $[Y(OR)_3]_{10}$ is formed by the reaction of 2-methoxyethanol with yttrium metal.[174] The compound has a cyclic structure where the alkoxy groups act as bridging bidentate ligands. More highly substituted alkoxy groups such as $OCEt_2CH_2OMe$ form dimeric compounds.[175]

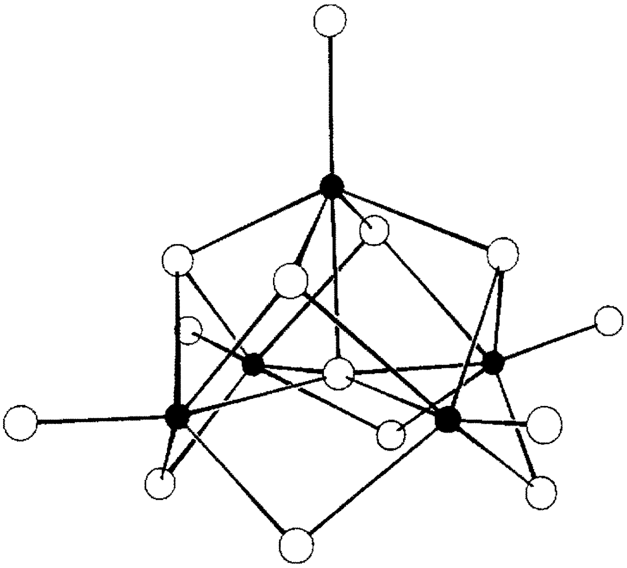


Figure 9 Structure of $Y_5O(OPr^i)_{13}$ showing only the yttrium atoms (black) and the oxygen atoms. (open circles) The structure shows the similarity of the yttrium atom environments (reproduced by permission of Wiley from *Mag. Res. Chem.*, **1991**, *29*, 1191–1195).

4.1.8.3 Fluorinated Alkoxides

The reactions of alcohols with $Sc[N(SiMe_3)_2]_3$ or $Y[N(SiMe_3)_2]_3$, may be used to prepare alkoxides but if excess alcohol is present the amine reacts to produce ammonia, which can act as a neutral ligand with the metal alkoxide:

$$(Me_3Si)_2NH + 2R'OH \rightarrow NH_3 + 2Me_3SiOR'$$

The scandium compounds $[Sc\{OCMe(CF_3)_2\}_3]_2$ and $[Sc\{OCH(CF_3)_2\}_3(NH_3)_2]_2$ have been prepared using the above method.[49] A more extensive series of yttrium compounds having fluorinated alkoxy ligands have been prepared. The compounds $[Y(OR_f)_3]_n$ (where $OR_f = OCMe(CF_3)_2$ or $OCMe_2CF_3$) appear to be trimers. Monomeric compounds $Y(OR_f)_3L_3$ are formed in the presence of neutral ligands such as thf, NH_3, diglyme, or Bu^tOH. $[Y\{OCH(CF_3)_2\}_3(NH_3)_2]_2$ has been prepared by the reaction of YCl_3 with hexafluoroisopropanol in the presence of anhydrous ammonia.[176] The alcoholysis of $Y_5O(OPr^i)_{13}$ with hexafluoroisopropanol has been used to prepare $[Y\{OCH(CF_3)_2\}_3L_3]$ where L = thf or Pr^iOH.[177]

4.1.8.4 Mixed Metal Alkoxides

The stability of the $M_5O(OR)_{13}$ structure is shown by the nonreactivity of the scandium compound with $Al(OR)_3$ whereas $Sc(OBu^n)_3$ reacts with $Al(OBu^n)_3$ to form $Sc[Al(OBu^n)_4]_3$. $Sc[Al(OPr^i)_4]_3$ may be prepared by the reaction of $ScCl_3$ with $KAl(OPr^i)_4$.[163] Alkalis metalate complexes $M'_xY(OR)_yL_z$ (where M' = Na or K and L = neutral ligand, generally having an oxygen donor atom) are formed where R = aryl or fluorinated group.[178–180] Examples of these complexes include $[(dme)Li]_2[Y(OAr)_5]$[178] shown in Figure 10, $[(thf)_3K][Y(OAr)_4(thf)_2]$ (where Ar = 2,6-$Me_2C_6H_3$),[178] $[NaY(OAr')_3Cl]$ and $[NaY_2(OAr'')_6Cl]$ (where $Ar' = C_6H_2$ $(CH_2NMe_2)_2Me$, $Ar'' = C_6H_4(CH_2NMe_2)$).[179] The sterically large ligands afford compounds with one yttrium atom but the smaller alkoxide $OC_6H_4(CH_2NMe_2)$ with only one ortho substituent allows self-assembly of a dimer structure. The fluorinated alkoxides $Na_3Y[(OCH(CF_3)_2]_6(thf)_3$ and $Na_2Y[(OCH(CF_3)_2]_5(thf)_3$ have six-coordinate yttrium atoms and are sublimable with loss of the thf ligand.[180]

Interest in barium yttrium alkoxides stems from metal organic vapor deposition experiments for the preparation of superconducting thin films. The compound $[Y_4Ba_2O(OEt)_8(dmp)_6]$ (where dmp = $Bu^tC(O)CHC(O)Bu^t$) has been prepared by the reaction of $Y_5O(OPr^i)_{13}$ with $Ba(OEt)_2$ $(Pr^iOH)_y$ in the presence of dmpH.[167] The structure contains seven-coordinate yttrium atoms with

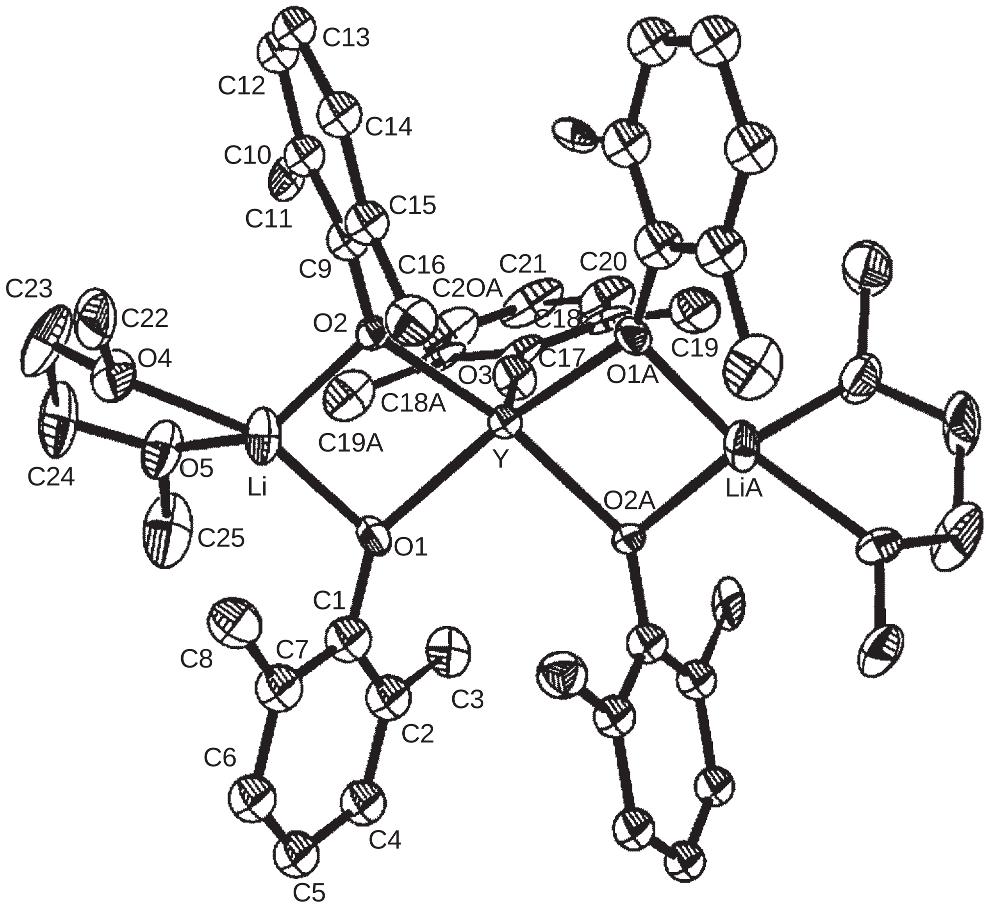


Figure 10 The structure of $[(\mathrm{dme})\mathrm{Li}]_2[\mathrm{Y}(\mathrm{OAr})_5]$ (where $\mathrm{Ar} = 2,6\text{-}\mathrm{Me}_2\mathrm{C}_6\mathrm{H}_3$) (reproduced by permission of Elsevier from *J. Organomet. Chem.*, **1998**, *553*, 141–148).

an unusual six-coordinate oxygen atom (coordinated to 4 Y and 2 Ba atoms) at the center of the molecule. The reaction of barium chips with $(\mathrm{CF}_3)_2\mathrm{CHOH}$ in thf and YCl_3 produced a volatile heterometallic species $\mathrm{YBa}[\mathrm{OCH}(\mathrm{CF}_3)_2]_7(\mathrm{thf})_3$.[181,182] The reaction of $\mathrm{YBa}[\mathrm{OCH}(\mathrm{CF}_3)_2]_7(\mathrm{thf})_3$ with $\mathrm{Y}(\mathrm{dpm})_3$ produced a compound $\mathrm{Y}_2\mathrm{Ba}[\mathrm{OCH}(\mathrm{CF}_3)_2]_4(\mathrm{dmp})_4$. The latter compound was purified by sublimation to produce the structure shown in Figure 11.

The reaction of anhydrous YCl_3 with $\mathrm{KTi}_2(\mathrm{OPr}^i)_9$ in molar ratios 1:1 and 1:2 gave two compounds, $\mathrm{Cl}_2\mathrm{YTi}_2(\mathrm{OPr}^i)_9$ and $\mathrm{ClY}[\mathrm{Ti}_2(\mathrm{OPr}^i)_9]_2$, respectively.[183] The molecular structure of $\mathrm{Cl}_2\mathrm{YTi}_2(\mathrm{OPr}^i)_9$ consisted of a six-coordinate yttrium bound to two chlorines and four oxygen atoms from the $\mathrm{Ti}_2(\mathrm{OPr}^i)_9$ ligand. Other mixed metal alkoxides are known including the yttrium copper compound with the alkoxide from 2-hydroxypyridine (Opy), $[\mathrm{Y}_2\mathrm{Cu}_8(\mathrm{Opy})_{12}(\mathrm{Cl})_2(\mathrm{O})_2(\mathrm{NO}_3)_4(\mathrm{H}_2\mathrm{O})_2\cdot 2\mathrm{H}_2\mathrm{O}]$[184] and the yttrium aluminum compound $\mathrm{Y}(\mathrm{OBu})_3(\mathrm{AlMe}_3)_2\mathrm{thf}$.[185] Other yttrium copper alkoxides are known including the siloxy bridged compound $[(\mathrm{Ph}_3\mathrm{SiO})_2\mathrm{Y}(\mu\text{-}\mathrm{OSiPh}_3)_2\mathrm{CuPMe}_2\mathrm{Ph}]$[55] and the β-diketonate alkoxides $\mathrm{YCu}_2(\mathrm{thd})_2(\mathrm{OR})_4$ and $\mathrm{YCu}(\mathrm{thd})_3(\mathrm{OR})_2$ (where thd = 2,2,6,6-tetramethylheptane-3,5-dionate and $\mathrm{OR} = \mathrm{OC}_2\mathrm{H}_4\mathrm{NMe}_2$).[186]

4.1.8.5 Siloxides

The synthesis, structure, and applications to catalysis of metal–siloxide complexes has been reviewed.[187] The preparation and NMR properties of $[\mathrm{Sc}(\mathrm{OSiBu}^t{}_3)_3\mathrm{NH}_3]3\mathrm{NH}_3$[188] and $\mathrm{Y}(\mathrm{OSiPh}_3)_3$,[189] was included. Structural details were also presented for the thf and the $\mathrm{Bu}^n{}_3\mathrm{PO}$ adducts of $\mathrm{Y}(\mathrm{OSiPh}_3)_3$,[79] as well as the structure of a four-coordinate yttrium siloxide $[\mathrm{Y}(\mathrm{OSiBu}^t\mathrm{Ar}_2)\{\mathrm{N}(\mathrm{SiMe}_3)_2\}_2]$ where $\mathrm{Ar} = \mathrm{OC}_6\mathrm{H}_4(\mathrm{CH}_2\mathrm{NMe}_2)$.[190] One of the nitrogens attached to the aryl group coordinates to the yttrium making the siloxide a bidentate ligand. Further coordination of the second nitrogen is inhibited by the steric hindrance caused by the disilylamino ligands.

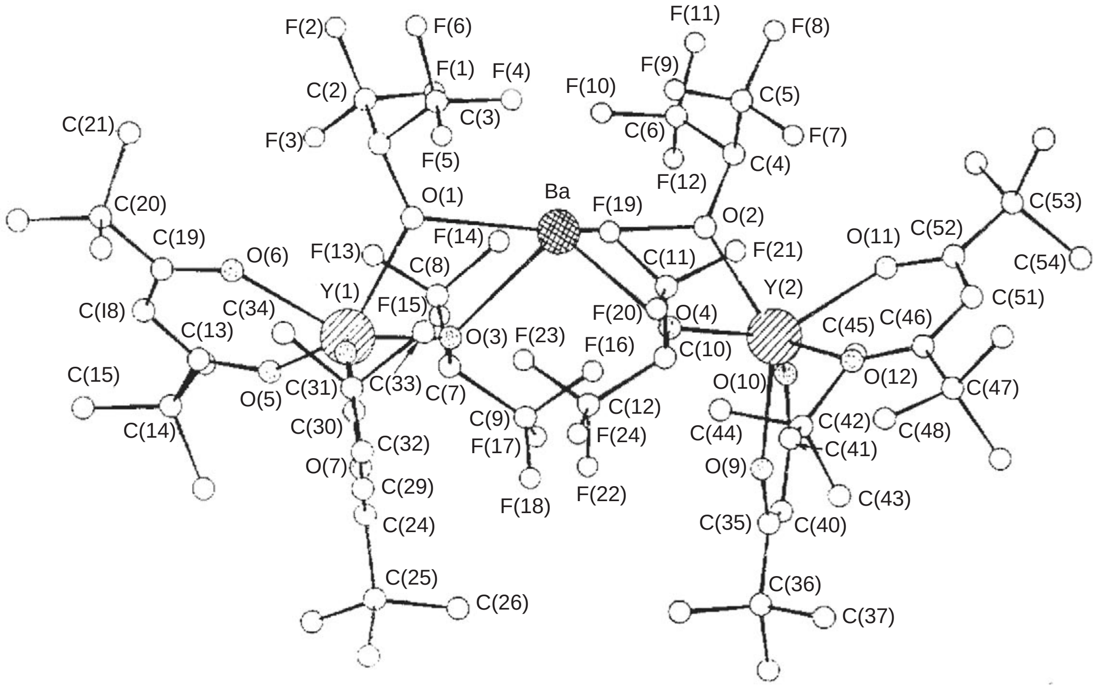


Figure 11 The molecular structure of $Y_2Ba[OCH(CF_3)_2]_4(dmp)_4$ (where dmp = $Bu^tC(O)CHC(O)Bu^t$) (reproduced by permission of The Royal Society of Chemistry from *J. Chem. Soc., Chem. Commun.*, **1993**, 1556–1558).

The reaction of a cyclopentadienyl scandium acac complex $[(C_5Me_5)Sc(acac)_3]$ with tetraphenyldisiloxanediol $(Ph_2SiOH)_2O$ results in displacement of the cyclopentaidiene group and the formation of a siloxane complex, $[\{(Ph_2SiO)_2OSc(acac)_2\}_2Sc(acac)]$.[191]

A combination of ^{89}Y and ^{29}Si has been used to observe the fluxionality of some yttrium alkoxides, siloxides, and adducts. Large ^{89}Y chemical shift changes have been observed on changing the coordination number of the yttrium.[79]

4.1.8.6 Triflate

One of the major developments in scandium chemistry has been the use of scandium salts, particularly scandium triflate, in organic synthesis. Kobayashi[192,193] found that scandium triflate was stable in water and acted in aqueous solution as a Lewis acid, which could activate carbonyl and related compounds. This activity in water contrasts with most Lewis acids and scandium triflate is a reusable catalyst. In general $Sc(OTf)_3$ acts as a better catalyst than $Y(OTf)_3$ or the lanthanide triflates. A brief review of the Lewis acid catalytic activity of scandium triflate[194] has appeared. $Sc(OTf)_3$ has now been used as a catalyst in numerous synthetic reactions including aldol reactions,[195] Meerwein–Ponndorf–Verley reductions,[196] glycosidation,[197] Friedel–Crafts,[198] and Michael additions.[199] $Sc(OTf)_3$ in CD_3OD is a very active catalyst for deuterium exchange of the aromatic hydrogens in 1,3,5-trimethoxybenzene.[200] An arylscandium species is postulated as an intermediate in the reaction. The use of scandium triflate in organic synthesis is now extensive and has been reviewed.[193] One more recent development has been the preparation of polymer supported scandium triflate catalysts.[201–203] This development of supported catalysts aids easy recovery, and is quantitative in many cases. A supported catalyst has been tested on the reaction of carbonyl compounds with tetraallyltin[202] and was shown to be most active with water as solvent.

Other scandium perfluoroalkanesulfonates such as the pentafluoroethanesulfonate and nonafluorobutanesulfonate have also been shown to be good catalysts.[204] Scandium salts such as the perchlorate and alkylsulfates[205] are also active catalysts.

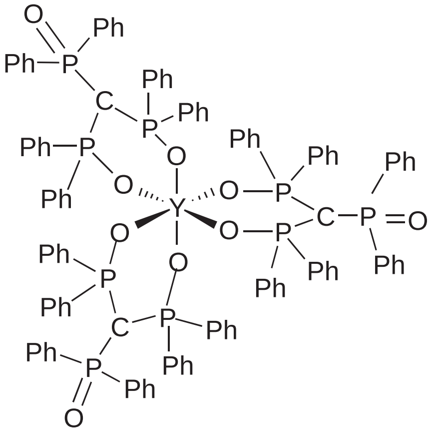
The crystal structure of the hydrated scandium triflate has been determined. Nine water molecules surround the scandium ion and the triflate anions are hydrogen bonded to the water molecules.[206] A structural analysis of anhydrous scandium triflate, using X-ray powder diffraction and IR spectroscopy, indicates that the triflate acts as a bidentate ligand with scandium in an octahedral environment.[207]

Scandium triflate has been used as a cross-linking agent for dendrimers producing a heterogeneous catalyst with Lewis acid properties.[208]

A related compound scandium tris(trifluoromethylsulphonyl)methanide, $Sc[(F_3CSO_2)_3C]_3$ (scandium triflide) has been prepared and used as a catalyst in the nitration of *o*-nitrotoluene.[209] Scandium triflide has proved to be a better catalyst than scandium triflate for the aromatic nitration of the electron deficient *o*-nitrotoluene.

4.1.8.7 Bidentate Oxygen Ligands

The reaction of a methanide ion $[(Ph_2PO)_3C]^-$ with the chlorides or nitrates of scandium or yttrium produce stable six-coordinate metal species (**13**) where the metal is coordinated to six oxygens in the form of three bidentate ligands.[56]



(13)

Many of the early reports of complexes with bidentate oxygen ligands involved acac complexes and the β-diketonate and related ligands were discussed in *CCC* (1987).[210] The β-diketonate complexes of scandium and yttrium and the lanthanides were also discussed in *CCC* (1987).[1] Many reported systems contained adducts formed by the metal β-diketonate complexes. In solution some of the complexes with bidentate ligands can expand their coordination number to seven by coordination to a suitable donor ligand. A solvent extraction method has been used to show that $Sc(acac)_3$ does not form an adduct with trioctylphosphine oxide but tris(tropolonato)scandium(III) and tris-(ethylmatolato)scandium(III) do coordinate with trioctylphosphine oxide.[211]

In a search for volatile scandium and yttrium compounds, as precursors for the MOCVD production of new materials such as high-temperature superconductors, acac type compounds with bulky end substituents have been investigated. Substituted β-diketonate complexes of scandium have been used in a liquid-injection MOCVD method to produce thin films of Sc_2O_3.[212] The vapor pressure of 2,2,6,6-tetramethylheptanedionatoyttrium, $Y(C_{11}H_{19}O_2)_3$ has been measured over a range of temperatures (361–387 K) and the molecular weight data indicate that the saturated vapor consists mainly of monomers.[213] A methylpivaloylacetate, $Bu^tCOCHCO(CH_2)_3OMe$(mpa), complex of yttrium has been prepared by reaction of mpa with $Y[N(SiMe_3)_2]_3$.[214] The complex $[Y(mpa)_3]_n$ is moisture sensitive and nonvolatile but reaction with Lewis bases gives two air-stable sublimable solids, $[Y(mpa)_3]$(tmeda) and $[Y(mpa)_3]$(bipy). The bipy complex has been structurally characterized by X-ray crystallography showing that the yttrium is eight-coordinate, bound to six oxygens and two nitrogens.

Not all substituted acac type complexes have simple structures. A nonanuclear clusters involving yttrium and the bidentate ligand allyl acetoacetate $[MeC(O)CHC(O)OCH_2{=}CH_2]$ has been observed.[215] Yttrium β-diketonate complexes have been reacted with mono-, di-, tri-, and tetraglyme resulting in eight and nine-coordinate yttrium complexes.[216]

Glycine (gly) can act as a bidentate ligand with the carboxyl groups bridging metal atoms. This occurs in the six-coordinate scandium complex $[Sc_2(gly)_6(ClO_4)_2]_n$ where an infinite chain of dimeric units with three bridging glycines per dimeric unit is formed.[217]

4.1.8.8 Crown Ethers

Crown ethers and the lanthanide complexes were extensively covered in *CCC* (1987)[218] but complexes of scandium and yttrium were not mentioned with the exception of $[Y(NCS)_3$(18-crown-6)].[1]

Several scandium chloride crown ether complexes $[ScCl_2(crown)]^+X^-$ have been structurally characterized. These include $[ScCl_2$(15-crown-5)$]_2[CuCl_4]$,[219] $[ScCl_2$(benzo-15-crown-5)$][SbCl_6]$,[220] $[ScCl_2$(18-crown-6)$][SbCl_6]$,[221] $[ScCl_2$(dibenzo-24-crown-8)$(H_2O)][SbCl_6]$,[222] and $[ScCl_2$(dibenzo-30-crown-10)$(H_2O)_2][SbCl_6]$.[222] The $ScCl_2^+$ unit is generated by the abstraction of a Cl^- ion by the Lewis acceptor $SbCl_5$ or $CuCl_2$. The removal of further chloride ions is effected by the addition of both $SbCl_5$ and $SbCl_3$ to $ScCl_3$ in the presence of 12-crown-4. This reaction produces a sandwich type cation where Sc^{3+} is bound to two 12-crown-4 molecules.[51] There are two anions, one antimony(V) ion, $[SbCl_6]^-$, and one antimony(III) ion, $[Sb_2Cl_8(MeCN)_2]^{2-}$. Although single-crystal X-ray structural determinations were the major characterization tool, ^{45}Sc NMR has been used to study most of the compounds in solution.[223] There is usually a Cl–Sc–Cl unit that fits within an embrace of five oxygen donor atoms forming a seven-coordinate pentagonal bipyramidal arrangement around the scandium. For the small crown ethers such as 15-crown-5 and related aza-crown ethers the ^{45}Sc resonance is a sharp singlet at room temperature. With the larger crowns such as dibenzo-24-crown-8 the scandium may bind to the crown in inequivalent positions. This results in more than one ^{45}Sc resonance and fluxional behavior in these molecules has been demonstrated by variable temperature ^{45}Sc NMR measurements.[223] The ^{45}Sc chemical shift of the eight-coordinate $[Sc(crown)_2]^{3+}$ ion differs from that of the $[ScCl_2(crown)]^+$ complexes.

A novel scandium complex formed from scandium triflate in the presence of 18-crown-6 and p-sulfonatocalix[4]arene has been investigated.[224] The crown ether resides in cavities created by two calixarenes from adjacent polymeric sheets. There are two types of scandium ions in the complex, one type is bound to the phenolic oxygen of the calixarene and the second exists as the hydroxide bound dimer ion $[Sc(OH)_2(H_2O)_{10}]^{4+}$. A similar complex may also be prepared without the crown ether.

There are several examples of crown ether complexes where yttrium is not bound to the crown ether. $[Y(H_2O)_8]Cl_3\cdot$(15-crown-5) has a $[Y(H_2O)_8]^{3+}$ cation (distorted dodecahedron) with the crown ether and chloride hydrogen bonded to the coordinated water molecules.[58,225] An aqueous solution containing yttrium triflate and 18-crown-6 produces crystals of $[Y(CF_3COO)_2(H_2O)_6](CF_3COO)\cdot$(18-crown-6) which have the crown ether hydrogen bonded to the coordinated water molecules.[226] The complex $[Y(NO_3)_3(H_2O)_3]\cdot$(dibenzo-24-crown-8) has a nine-coordinate yttrium formed by bonding to three bidentate nitrate groups and three water molecules. The crown ether is hydrogen bonded to the water molecules.[227]

4.1.9 SULFUR DONOR LIGANDS

There has been very little recent work on scandium or yttrium sulfur compounds. Only one system has been structurally characterized, $[Y(SCEt_3)_3(py)_2]_2$.[121] This compound was prepared by the reaction of yttrium amide $Y(NH_3)_2$ with Et_3CSH in pyridine. Poorer yields of $[Y(SCEt_3)_3(py)_2]_2$ could be prepared from yttrium metal, Et_3CSH and pyridine in the presence of ammonia. The crystal structure of $[Y(SCEt_3)_3(py)_2]_2$ has two six-coordinate yttrium atoms with distorted octahedral geometry bridged by two SR groups.

The reaction of $Y[N(SiMe_3)_2]_2Cl(thf)_2$ with $LiSBu^t$ in thf gave the compound $Y[N(SiMe_3)_2](SBu^t)_2$[228] Although this compound was not structurally characterized crystals of the similar gadolinium compound were reported.

4.1.10 HALIDES

Complex halides of scandium and yttrium have been discussed in *CCC* (1987).[1] Most halides and halide complexes reported are of Sc^{III} and Y^{III} but there are some reduced halide species such as the diiodide.[229]

The hexafluoroscandium compounds $(NH_4)_3(ScF_6)$ and $[Cu(NH_3)_4]_3(ScF_6)$ have been prepared by the action of ammonium fluoride on scandium in a copper tube heated to 330 °C or 400 °C.[230]

The structure of solid $ScCl_3$ has been refined from high-resolution powder neutron diffraction data. $ScCl_3$ has a BiI_3 structure with two-dimensional $ScCl_3$ layers and each $ScCl_6$ unit has a slightly distorted octahedral geometry.[231] The gas phase structure of $ScCl_3$ has been investigated by electron diffraction and density functional theory (dft) calculations. The electron diffraction favored a C_{3v} structure with Sc—Cl bond lengths of 2.291 Å whereas the dft calculations optimized the structure to D_{3h} symmetry with Sc—Cl bond lengths of 2.285 Å.[232]

Hydrated scandium chloride is a heptahydrate that is isomorphous with the scandium bromide whereas the iodide is an octahydrate.[39] Dehydrated forms of scandium chloride are important in many synthetic reactions. Scandium chloride hydrate may be dehydrated by thionyl chloride in the presence of thf to yield $ScCl_3(thf)_3$.[233] This compound is an important precursor for many scandium compounds, particularly organometallic species. Controlled hydrolysis of $ScCl_3(thf)_3$ results in the replacement of one thf by a water molecule.[234] The complex $ScCl_3(thf)_2(H_2O)$ has been structurally characterized and the scandium atoms are six-coordinate being bonded to three chlorines and three oxygen donor atoms in a *mer*-octahedral configuration. Me_3SiCl may also be used to dehydrate hydrated scandium chloride and if this is carried out in the presence of diglyme the adduct $ScCl_3$(diglyme) is formed. Hydrolysis of $ScCl_3$(diglyme) produces a hydroxide bridged dimer $[Sc_2(OH)_2\ (H_2O)_{10}]Cl_4{\cdot}2H_2O$. The crystal structures of $ScCl_3$(diglyme) and $ScCl_3$(dme)-(MeCN) show that the scandium is six-coordinate with a distorted octahedral geometry. In the hydrolysis dimer $[Sc_2(OH)_2(H_2O)_{10}]Cl_4{\cdot}2H_2O$ scandium is seven-coordinate.[233]

An unusual bimetallic oxychloro compound of scandium $[(thf)_3ScOCl_5Li(thf)]_2$ has been prepared by the reaction of $LiC_6H_3(C_{10}H_7)_2$, [lithium 2,6-di(1-naphthyl)phenyl] with $ScCl_3$.[235]

The reactions of $ScCl_3(thf)_3$ and $YCl_3(thf)_3$ with $SbCl_5$ give different products. Scandium chloride gives $[ScCl_2(thf)_4][SbCl_6(thf)]$ whereas yttrium chloride gives $[YCl_2(thf)_5][SbCl_6(thf)]$.[236] Anhydrous YCl_3 in thf yields a solid of formula YCl_3 3.5thf.[237] Recrystallization of this solid in thf gives a crystalline solid which has a *trans*-$YCl_2(thf)_5$ cation and a *trans*-$YCl_4(thf)_2$ anion. When this ionic compound is dissolved in CH_2Cl_2 a polymeric bis-thf $[YCl_3(thf)_2]_n$ adduct crystallizes. The polymer has seven-coordinate Y^{III} centers linked by double chlorine bridges.

Scandium forms a diiodide by the reaction of ScI_3 with Sc metal.[229] Reduced scandium iodides $LiScI_3$ and $NaSc_2I_6$ have been produced by the reactions of Sc metal with ScI_3 and LiI or NaI.[238] These compounds contain chains of ScI_6 octahedra. The scandium halides form a series of compounds with an interstitial element strongly bonded within the scandium halide cluster. Compounds such as Sc_4Cl_6B,[239] Sc_5Cl_8C,[240] Sc_5Cl_8N,[240] $Sc_6I_{11}C_2$,[241] $Sc_7Br_{12}C$,[242] $Sc_7I_{12}B$,[242] and $Sc_7I_{12}Co$,[243] have been prepared.

The periodates of Sc and Y, $M(H_2O)_3[IO_4(OH)_2]$, have been examined by ^{45}Sc and ^{89}Y NMR, and the crystal structure of the yttrium compound determined.[244] In the crystal eight water molecules surround the yttrium atom.

4.1.11 MIXED DONOR ATOM LIGANDS

Aqueous scandium chloride reacts with picolinic acid at pH 4.5 to yield a dimeric compound $[Sc(C_5H_4NCO_2)(OH)(H_2O)]_2{\cdot}4H_2O$.[245] The structure of an edta complex of scandium has been determined.[246] The compound $NH_4[Sc(edta)(H_2O)_2]{\cdot}3H_2O$ has scandium bonded to four oxygens and two nitrogens from the edta and also to two water molecules, making the scandium eight coordinate. The structure around the scandium is a distorted square antiprism.

Pyrazolylborates $H_2B(pz)_2$ and $HB(pz)_3$ were described in *CCC* (1987),[247] they act as tridentate ligands, the dihydrobis-pyrazolylborate binding through the two nitrogen atoms and hydrogen bonding to the metal forming a B—H—M bridge. The complex $Y[H(\mu\text{-}H)B(pz)_2]_3$ has six nitrogen donor atoms arranged in a trigonal prism around the metal atom.[248] A bridging three centered B—H—Y bond shown in Figure 12 caps the rectangular faces of the prism. This bonding survives in solution as shown by the B—H stretching frequency and the inequivalence of the BH_2 atoms in low temperature NMR spectra. The hydrotris-pyrazolylborate forms complexes with yttrium,[249,250] including the aquobis[hydrotris(pyrazolyl)borato]chloroyttrium, which has an

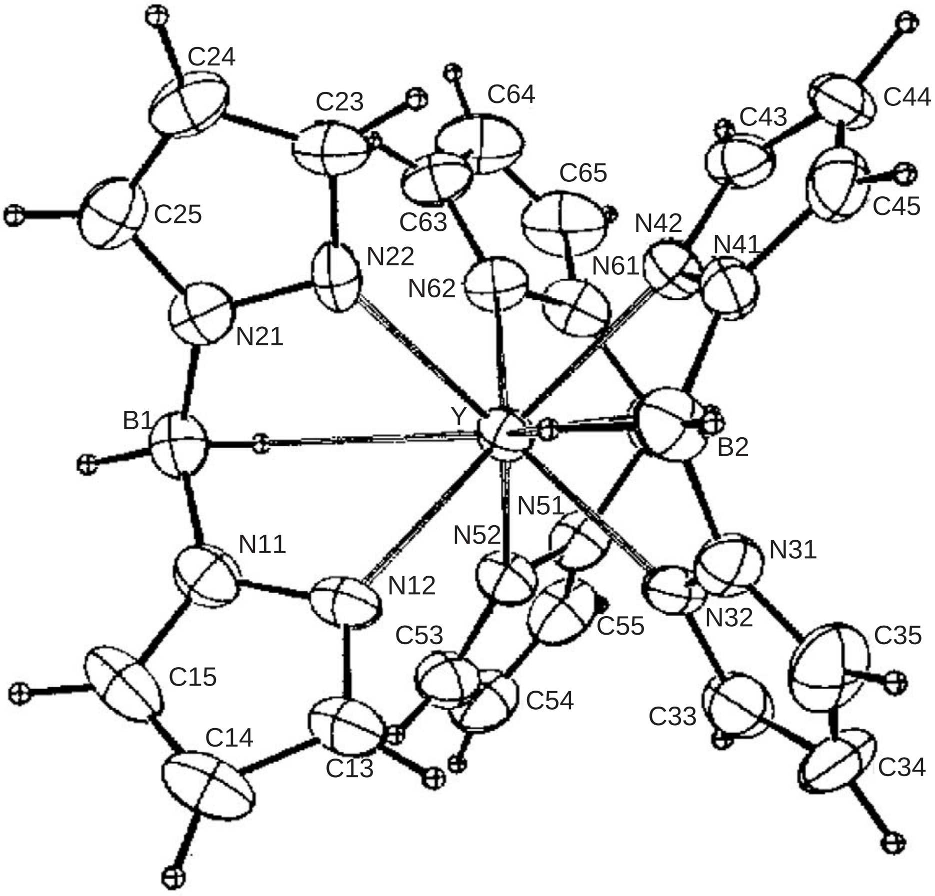


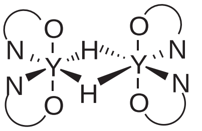
Figure 12 Yttrium surrounded by six nitrogens in a trigonal-prismatic arrangement with each rectangular face capped by a bridging B–H interaction in the compound, $Y[H(\mu\text{-}H)B(pz)_2]_3$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.*, **1988**, *27*, 1890–1896).

eight-coordinate yttrium where the pyrazolyl rings are inequivalent. ^1H and ^{13}C NMR show that at room temperature the pyrazolyl rings are equivalent but at low temperature they become inequivalent.[250]

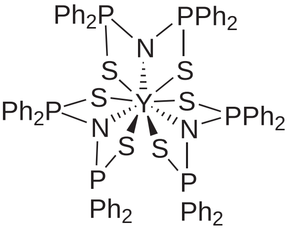
Aza-18-crown-6 reacts with $Y(CH_2SiMe_3)_3(thf)_2$ to produce a compound with yttrium bonded to the nitrogen and three oxygens of the aza-crown. The other two oxygens are ~0.5 Å more distant from the yttrium,[251] and the CH_2SiMe_3 group is almost vertical to the Y-crown plane. This compound reacts with CO, by insertion into the Y—C bonds forming two Y—O—C(CH_2)($SiMe_3$) groups. Reaction is favored by forming strong Y—O bonds.

The (alkoxysilyl)amido ligand $[Me_2Si(NBu^t)(OBu^t)]$ acts as a bidentate chelating group that is useful in stabilizing coordinatively unsaturated metal complexes.[82] The compound $[Me_2Si(NBu^t)(OBu^t)]_2YCl(thf)$ has been used in the preparation of several yttrium compounds.[82,252] Schiff base and acyclic polydentate ligands have been discussed in *CCC* (1987).[253] The salen ligand may be prepared with a variety of substituents and so the steric properties are easily tunable. There have been many studies of lanthanide Schiff-base complexes but few studies in nonaqueous media. $YCl_3(thf)_3$ reacting with the dipotassium salt of a bulky di-*t*-butyl substituted salen gave a chloride bridged dimer $[(salen)YCl(thf)]_2$, with each yttrium having seven coordination.[254] Yttrium compounds with a bulky salen ligand have also been prepared by the silylamide route.[255] The reaction of the salen with $Y[N(SiMe_3)_2]_3$ gave a polymeric compound where the salen group is coordinated to two yttrium atoms whereas reaction with $Y[N(SiHMe_2)_2]_3(thf)_2$ gave a monomeric compound, $Y(salen)[N(SiHMe_2)_2](thf)$. The yttrium is six-coordinate in a distorted trigonal-prismatic geometry.

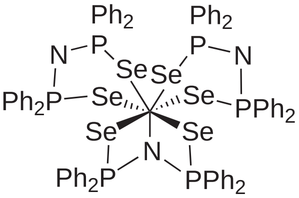
A bulky salicylaldiminato ligand, where the *ortho* positions on the benzene rings have *t*-butyl groups, reacts with the organoscandium or organoyttrium compound $M(CH_2SiMe_2Ph)_3(thf)_2$ to produce a compound where two of the organo groups have been replaced by the bidentate salicylaldiminato ligand (salen)$_2$MCH$_2$SiMe$_2$Ph.[256] The scandium and yttrium compounds react with H_2 by elimination of Me$_3$SiPh but give different final products. The scandium compound interacts with one of the Bu^t groups on the phenyl group attached to a nitrogen of one salicylaldiminato group, whereas the ytrium forms a hydrogen bridged dimer (**14**).



(14)



(15)



(16)

The bis(amidophosphine) ligand PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh (P$_2$N$_2$) is tetradendate, bonding through two nitrogens and two phosphorus atoms. Reaction of the P$_2$N$_2$ ligand with YCl$_3$(thf)$_3$ gives a dimeric chloro bridging complex [(P$_2$N$_2$)$_2$Y]$_2$(Cl)$_2$.[257] [(P$_2$N$_2$)$_2$Y]$_2$(Cl)$_2$ has been used as a starting material for the production of a variety of aryl complexes by reactions with aryllithium compounds. Interestingly the reaction with aryl Grignard bromides does not result in the replacement of the chlorides by aryl groups but the production of halide dimers [(P$_2$N$_2$)$_2$Y]$_2$(Br)$_2$ and [(P$_2$N$_2$)$_2$Y]$_2$(Cl)(Br).

The imidodiphosphinochalcogenido ligand $[N(EPPh_2)_2]^-$, where $E = S$ or Se, can act as a tridentate or bidentate ligand.[258] The reaction of Y[N(SiMe$_3$)$_2$]$_3$ with HN(SPPh$_2$)$_2$ gives a nine-coordinate complex Y[N(SPPh$_2$)$_2$]$_3$ (**15**) where each ligand coordinates through two sulfurs and a nitrogen. A similar reaction with HN(SePPh$_2$)$_2$ gives a seven-coordinate complex Y[N(SePPh$_2$)$_2$]$_3$ (**16**) where one ligand is tridentate bonding through two selenium atoms and nitrogen and the other two ligands bond only through the two selenium atoms. These complexes have been examined in solution by ^{89}Y, ^{77}Se, and ^{31}P NMR. The D$_3$ symmetry of the sulfur compound Y[N(SPPh$_2$)$_2$]$_3$ is maintained in solution whereas the selenium compound Y[N(SePPh$_2$)$_2$]$_3$ shows fluxional behavior.

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4.2
Titanium

S. B. SMITH and D. W. STEPHAN
University of Windsor, Ontario, Canada

4.2.1 INTRODUCTION

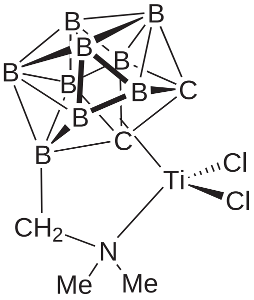
Titanium chemistry has seen a burgeoning growth since the early 1980s. Much of the effort in this area has been spurred by the potential for applications in stoichiometric synthesis, catalysis, and materials chemistry. For example, in recent years the push for "single-site" olefin polymerization catalysts has prompted the development of many new ligands and the resulting studies of Ti coordination chemistry. Similarly, efforts to uncover molecular precursors to TiN have led to the study of the chemistry of coordination compounds designed to degrade thermally. Applications aside, many studies of unique Ti coordination compounds have been prompted simply by intellectual curiousity and creativity.

In this chapter, we review the progress in coordination chemistry of Ti since the early 1980s. This chapter was written as an extension of the previous issue of Comprehensive Coordination Chemistry (*CCC*, 1987) and in defining the scope of this review, we have specifically limited the discussion to exclude compounds deemed to be principally organometallic in nature.

4.2.2 TITANIUM(IV)

4.2.2.1 Boron-based Ligand Complexes

Carborane ligand complexes $TiX_2(\eta^5\text{-}Et_2C_2B_4H_4)L_2$ ($X = Cl$, Me, OBu^t; $L_2 = 2PMe_3$, $Me_2P(CH_2)_nPMe_2$, $n = 2$, 3) were prepared from reaction of $TiCl_4(PMe_3)_2$, $Li[Et_2C_2B_4H_4]$ and phosphine.[1] Related Ti–dicarborollide complexes $Ti(\eta^5\text{-}C_2B_9H_{11})(NR_2)(NHR_2)$ ($R = Me$, Et) were prepared by amine elimination reactions of $Ti(NR_2)_4$ with $C_2B_9H_{13}$.[2] The related dianionic and trianionic amino and amido-bridged carborane ligands were incorporated into Ti complexes yielding $TiCl((NHCH_2)(\eta^5\text{-}C_2B_9H_{10}))$[3] and $TiCl_2((Me_2NCH_2)(\eta^5\text{-}C_2B_9H_{10}))$ (**1**).[4]



(**1**)

The latter compound showed moderate activity as an ethylene polymerization catalyst.

Azaborolinyl–Ti complexes have been reported, including $TiBr_2(\eta^5\text{-}(Bu^t)NB(Me)C_3H_3)$. X-ray data revealed an interaction between B and Br.[5]

4.2.2.2 Silicon-based Ligand Complexes

Isolable Ti–Si compounds that lack ancillary Cp-ligands are rare. The metathetical reaction of $TiCl(CH_2R)_3$ ($R = Bu^t$, $SiMe_3$) with $Li[Si(SiMe_3)_3]$ afforded the crystallographically characterized complexes $Ti(Si(SiMe_3)_3)(CH_2R)_3$.[6,7] *Ab initio* calculations suggested synthetic strategies to Ti—Si multiple bonds, although these have not been prepared as of yet.[8–10]

4.2.2.3 Nitrogen-based Ligand Complexes

4.2.2.3.1 Neutral nitrogen ligand complexes

A number of articles have focused on the general issues of structure, stability, donor properties, and ligand strength of neutral ligand–$TiCl_4$ adducts. Generally these works have involved use of various spectroscopic techniques including NQR, X-ray fluorescence, and NMR spectroscopy.[11–15]

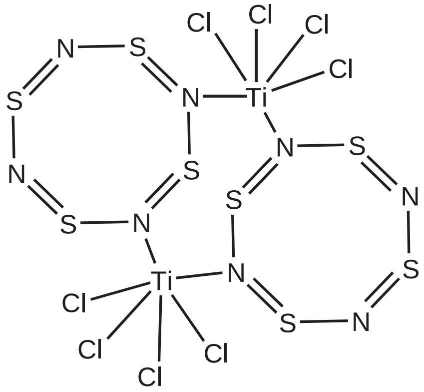
In more specific work, adducts of the form $TiCl_4L_2$ have been prepared and reported. These include complexes where L = TMEDA,[16] benzotriazole,[17] benzothiazole,[18] 2-aminobenzimidazole,[19] 2-methyl-2-oxazoline, thiazole and a variety of oxazole-derivatives.[20] Similarly, complexes of the form $TiCl_4L$ ($L = RC_6H_4NH_2$, $R = Bu^t$, Cl, NO_2, Me[21,22] isoxazole, 5-methylisoxazole,[20] 2-aminobenzimidazole, 2(2′-aminophenyl)benzimidazole,[19] 2-pyridylphenylacetonitrile[22]) have been reported. Schiff base adducts of $TiCl_4$ derived from *N*-methylpyrrole-2-carboxaldehyde, 4-methylbenzaldehyde, salicylaldehyde, and aromatic or aliphatic amines have also been characterized.[23–25] A variety of 2:1 substituted silyl-amine-Ti adducts have also been reported.[26–28]

Matrix isolation work and IR spectroscopy have identified the amine adducts $TiF_4(NH_3)$ and $TiF_4(NMe_3)$ at low temperature.[29] Winter and co-workers have prepared $TiCl_4(NH_3)_2$, and have used it as a single-source precursor for the deposition of TiN films.[30]

The reaction of $TiCl_4$ with $SbCl_5$ in MeCN afforded the salt *fac*-$[TiCl_3(MeCN)_3][SbCl_6]$. Crystallographic data revealed a distorted octahedral Ti environment.[31]

A number of related Ti/N-donor complexes have been synthesized and crystallographically characterized. These include monomeric adducts of $TiCl_4$ such as $TiCl_4(NC_5H_5)_2$,[32,33] $TiCl_4(NC_5H_3Me_2)$, $TiCl_4(NC_5H_4Me)$[34], $TiX_4(NC_5H_3Me_2)$, $TiX_4(NC_5H_4Me)$ (X = Cl, Br),[35–37] In contrast, the trimethylsilylimidazole adduct was confirmed as $Ti_2Cl_6(\mu\text{-}Cl)_2(NC_3H_3NSiMe_3)_2$.[38] In addition, the ionic complexes $[HNC_3H_3NMe]_2[TiCl_5(NC_3H_3NMe_2)][TiCl_6]_{0.5}$,[34] $[HNC_5H_4Me][TiCl_5(NC_5H_4Me)]$,[39] and $[TiL_2]Cl_4$ (L = furfuraldazine, 2-thiophenaldazine, 2-pyridinaldazine)[40] have been reported. $TiCl_4(Si(SCN)((OCH_2CH_2)_3N))$ was reported as the first example of a silatrane adduct. IR data suggested coordination via the thiocyanate nitrogen atom.[41]

S_4N_4 reacted with $TiCl_4$ forming what was thought to be the 1:1 adduct $TiCl_4(S_4N_4)$.[42] This complex was subsequently shown to be dimeric, forming an eight-membered $Ti_2N_4S_2$ ring (**2**).[43]



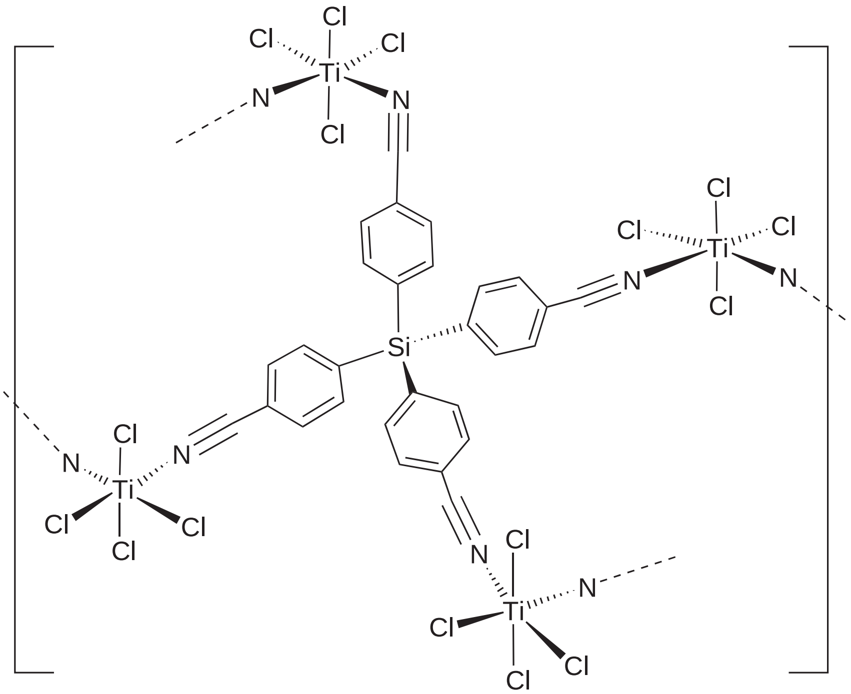
(**2**)

The related adduct $TiCl_4(S_2N_2)$[44] has also been reported.

Spectroscopic methods have probed the properties of N_2-bridged Ti complexes derived from the reaction of *trans*-$ReCl(N_2)(PMe_2Ph)_4$ with $TiCl_4$.[45,46] Raman and ^{15}N NMR spectral data for $TiCl_4((\mu\text{-}N_2)ReCl(PMe_2Ph)_4)_2$ indicate a TiN_2Re linkage.[45,46]

$TiCl_4$ adducts of acetyl and benzoyl nitrile ligands were isolated and formulated as chloro-bridged dimers.[47] Crystallographic studies established a *cis* arrangement of the nitrile ligands in $TiCl_4((Me_3Si)_2NC_6H_4CN)_2$.[48] The reaction of $TiCl_4$ with the dinitrile $NC(CH_2)_5CN$ resulted in the formation of a one-dimensional polymer.[49] The trimetallic complexes $TiCl_4(Fe(C_5H_4HgSCN)_2)$ and $TiCl_4\text{-}(Fe(C_5H_4HgSeCN)_2)$ were synthesized by reaction of $TiCl_4$ and $Fe(C_5H_4HgSCN)_2$.[50] Subsequently, use of the tetra-nitrile $Si(C_6H_4CN)_4$ was shown to form a coordination network. Within this network (**3**) each ligand coordinates to four Ti centers via the nitrile N atoms.[51]

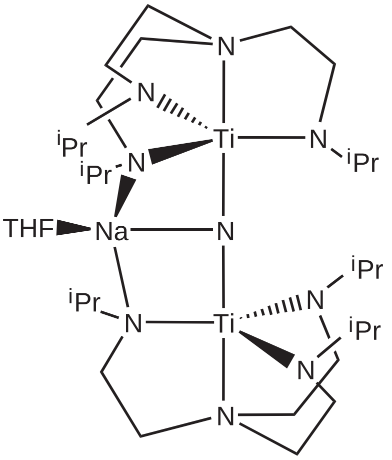
A recent study has shown the coordination of phosphinimine ligands in the complex $TiCl_4(SiMe_2(NPEt_3)_2)$ to be a pseudo-octahedral chelate.[52]

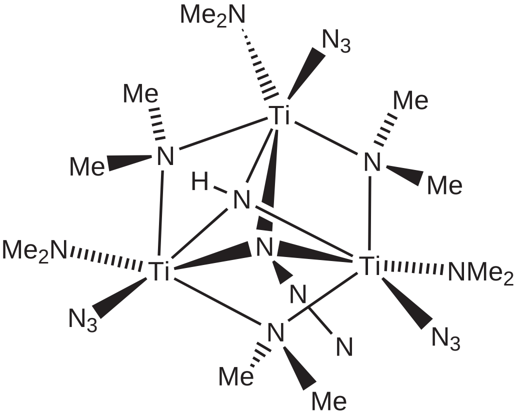


(**3**)

4.2.2.3.2 *Nitrido ligand complexes*

A review has described transition metal nitrides.[53] The majority of Ti nitrido compounds have been stabilized by somewhat sterically encumbering organometallic ligands.[54–56] However, $(Ti((Pr^iNCH_2CH_2)_3N))_2(\mu^3\text{-}N)Na(THF)$ (**4**) was unexpectedly synthesized by the reaction of $ClTi(Pr^iNCH_2CH_2)_3N)_3$ and $Na[NH_2]$ in THF. Structural evidence supports Ti—N π bonding.[57]





(**4**) (**5**)

In recent work, the Ti^{IV}/Re^{V} complexes $TiCl_5(\mu\text{-}N)ReCl(PMe_2Ph)_3(MeCN)$ and $TiCl_4((\mu\text{-}N)ReCl_2(PMe_2Ph)_3)_2$[58] have been prepared via reaction of Ti^{IV} precursors and $ReCl_2(N)(PMe_2Ph)_3(MeCN)$. Similarly, the simple nitrido coordination compound $(Ti_2Cl_5(NC_5H_3Me_2)_5)(\mu\text{-}N)$ has been recently reported from the reaction of $TiCl_4$ with $HN(SiMe_3)_2$ in the presence of a pyridine donor ligand.[59]

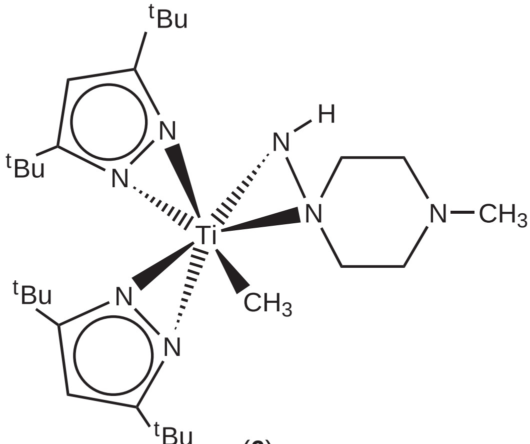
4.2.2.3.3 Azido and hydrazido ligand complexes

The explosive azide compounds $TiBr_2(N_3)_2$ and $TiI_3(N_3)$ were prepared from the reaction of TiX_4 (X = Br, I) with IN_3 and characterized by IR spectroscopy.[60] Alternatively, oxidation of $TiCl_3((MeNCH_2CH_2)_3)$ by NaN_3 followed by the addition of $Na[BPh_4]$ was reported to give $[TiCl_2((MeNCH_2CH_2)_3)(N_3)][BPh_4]$.[61] In the same year, Gross and Siegrist crystallographically characterized $(Ti(NMe_2)(N_3)(\mu\text{-}NMe_2))_3(\mu^3\text{-}N_3)(\mu^3\text{-}NH)$ (**5**), which was derived from the reaction of $Ti(NMe_2)_4$ and Me_3SiN_3.[62] In a similar synthesis, the oxidation of $Ti(N(Bu^t)C_6H_3Me_2)_2(CH(SiMe_3)_2)(NCMe)$ by Me_3SiN_3 gave $Ti(N_3)(N(Bu^t)C_6H_3Me_2)_2(CH(SiMe_3)_2)$.[63]

Roesky and co-workers isolated several Ti^{IV} azido complexes from the reaction of $Ti(NMe_2)_4$, Me_3SiN_3, and N-donors, including $Ti(NMe_2)_2(N_3)_2(NC_5H_5)_2$, $Ti(NMe_2)_2(N_3)_2$(bipy), and Ti $(NMe_2)_3(N_3)$(bipy). These complexes yielded TiN when heated to 300–400 °C.[64] In a similar vein, $(TiCl(NBu^t)(\mu\text{-}N_3)(NC_5H_5)_2)_2$ and $(Ti(NCy)(\mu\text{-}N_3)_2(NC_5H_5)_2)_2$ were prepared from $TiCl_2(NR)(H_2NBu^t)_3$.[65] Ti-azides have found applications as reagents for the regio-specific ring opening of 2,3-epoxy alcohols[66] or as catalysts for the syntheses of O-protected azidohydrins.[67]

Few Ti^{IV}–hydrazido complexes exist without Cp-ligands. The reactions of $HNMeNMe_2$ and $HNPhNH_2$ with $TiCl_3((N_2C_3H_2)_3BH)$ yielded the complexes, $TiCl_3((N_2C_3H_2)_3BH)(\eta^2\text{-}NMeNMe_2)$ and $TiCl_3((N_2C_3H_2)_3BH)(NPhNH_2)$. Both of these complexes were structurally characterized, confirming the η^2-bonding mode of the hydrazido ligand.[68] More recently, the reaction of two equivalents of $HNSiMe_3N(SiMe_3)_2$ with $TiCl_4$ yielded $TiCl_2(\eta^2\text{-}HNN\text{-}(SiMe_3)_2)_2$.[69] Addition of a third equivalent of hydrazine afforded $TiCl(\eta^2\text{-}HNN(SiMe_3)_2)_3$. Alternatively, treatment of $TiCl_4$ with dilithiated 1,1- and 1,2-substituted hydrazines afforded complexes such as $TiCl_2(\mu^2\text{-}NSiMe_3NSiMe_3)_2$. This complex was also structurally characterized.[69] Winter and co-workers synthesized and structurally characterized the first Ti^{IV}–triazenido complex $Ti(NR_2)_2(PhNNNPh)_2$ (R = Me, Et).[70]

The pyrazolate–hydrazido complex $TiMe(\eta^2\text{-}HNN(CH_2CH_2)_2NMe)(\eta^2\text{-}N_2C_3HBu^t{}_2)_2$ (**6**) was derived from the reaction 1-amino-4-methylpiperazine and $TiMe_2(\eta^2\text{-}N_2C_3HBu^t{}_2)_2$.[71] In a similar fashion, the porphyrin hydrazido complexes $Ti(TTP)(NNR_2)$ (R = Me, Ph) were synthesized by treatment of $TiCl_2(TTP)$ with H_2NNR_2 in the presence of piperidine.[72]



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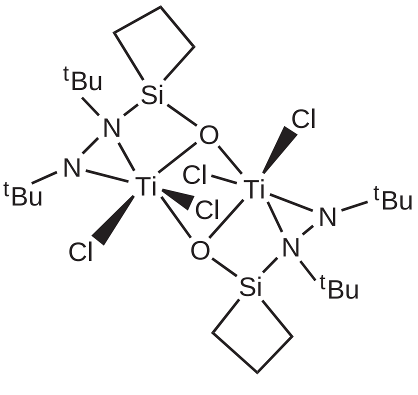

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While the complexes $TiMe_2((Bu^tN)_2Si(CH_2)_3)$ and $TiMeCl((Bu^tN)_2Si(CH_2)_3)$ react with O_2 to give the dimers $(TiX(\mu\text{-}OMe)((Bu^tN)_2Si(CH_2)_3))_2$ (X = Cl, Me), $TiCl_2((Bu^tN)_2Si(CH_2)_3)$ reacted with O_2 to give the hydrazido complex $(TiCl_2((Bu^tN)_2SiO(CH_2)_3))_2$ (**7**).[73]

4.2.2.3.4 Amido ligand complexes

In the early 1980s the adducts $Ti(NMe_2)_2(\mu\text{-}NMe_2)_2MX_4$ (M = Sn, Zr, Hf; X = Cl, Br) were isolated and characterized spectroscopically.[74] The complexes $TiX_2(N(SiMe_3)_2)_2$ (X = Cl, Me) were prepared via facile metathesis.[75] In a similar manner, $TiX(N(SiMe_3)_2)_3$ (X = Me,[76] F[77]) and $TiCl_n(N(SiCl_3)_2)_{4-n}$ ($n = 2,3$)[78,79] have been isolated and structurally characterized. A crystal structure of TiCl $(NEt_2)_3$ confirmed the expected pseudo-tetrahedral geometry about Ti and the planar nature of the N atoms.[80] Similar geometries were also confirmed for $TiCl(NCy_2)_3$,[81] $Ti(OC_6H_2Bu^t{}_2Ph)_2(NMe_2)_2$,[82] and $Ti(OC_6H_3Bu^t{}_2)_2(NMe_2)_2$.[83]

CVD techniques employing Ti-amides have been probed as routes to TiN films. Precursors include $Ti(NMe_2)_4$, $Ti(NEt_2)_4$, $TiBu^t(NMe_2)_3$, and $(Ti(\mu\text{-}NBu^t)(NMe_2)_2)_2$[84,85] and $(Ti(NMe_2)(N_3)(\mu\text{-}NMe_2))_3(\mu^3\text{-}N_3)(\mu^3\text{-}NH)$.[62] A related *ab initio* analysis of small-molecule (HX) elimination from Ti-amides ($TiH_2(NH_2)X$) to Ti-imides ($TiH_2(NH)$) suggested that precursors with higher Ti–H interaction led to lower activation barriers.[86]

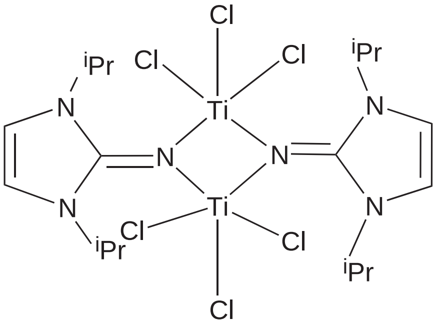
Cummins and co-workers showed that addition of $Li[Bu^t\text{-}d^6NC_6H_3Me_2]$ to $TiCl_2(NMe_2)_2$ afforded $Ti(NMe_2)_2(Bu^t\text{-}d^6NC_6H_3Me_2)_2$. This complex reacted subsequently with MeI affording $TiI_2(Bu^t\text{-}d^6NC_6H_3Me_2)_2$.[87] A variety of similar Ti–amido complexes containing halide or aryloxide ligands have been prepared. Alternatively, oxidation of $Ti((Me_2\ (Ph)C)NC_6H_3Me_2)_2(\mu\text{-}Cl)_2\text{-}Li(TMEDA)$ with $CHCl_3$ afforded the product $TiCl_2((Me_2(Ph)C)NC_6H_3Me_2)_2$.[88]

Ti^{IV} dialkylamide complexes have been utilized as reagents in organic transformations. For example, $Ti(NR_2)_4$ (R = Me, Et) have been used as chemoselective protecting agents for the addition of Grignard reagents to ketones in the presence of aldehydes.[89] Alternatively, the compounds $Ti(NR_2)_{4-n}Cl_n$ ($n = 0$, 2–4) have been used in dialkylamino/alkoxide group exchanges with phosphoryl substrates,[90,91] while the complex Ti $(OPr^i)_2(N(O_3SCF_3)_2)_2$ acts as a highly efficient catalyst for Friedel–Crafts acylations.[92]

More recently, plumbylene-amides were used as reagents to prepare $TiCl_3(NR(SiMe_3))$ (R = $SiMe_3$, Bu^t, 9-BBN).[93] In a similar manner, the bis(amide) derivatives $TiCl_2(N(9\text{-}BBN)(SiMe_3))_2$, $TiCl_2(NBu^t(SiMe_3))(NR(SiMe_3))$ (R = $SiMe_3$, 9-BBN) $TiCl_2(N(SiMe_3)_2)(N(9\text{-}BBN)SiMe_3)TiCl_2(N(SiMe_3)_2)_2$ were prepared.[94] The syntheses and spectroscopic data for the compounds $Ti(NMe_2)_3(N(B(NMe_2)_2)(Si(NMe_2)_3)$ and $Ti(NMe_2)_3)(N(SiMe_3)(Si(NMe_2)_3))$ have also been reported.[95]

4.2.2.3.5 *Carbimido ligand complexes*

The reaction of $Me_3SiNC(CF_3)_2$ with $TiCl_4$ afforded the complex $Ti(NC(CF_3)_2)_4(THF)$.[96] Subsequently, the related carbimide derivatives $(TiCl_3(\mu\text{-}NC(NMe)_2C_2H_2))_2$ (**8**) and $TiCl_3(NC(NMe)_2C_2H_2)(MeCN)_2$ were described. Crystallographic characterization confirmed the bridging and terminal nature of the carbimide ligands.[97]



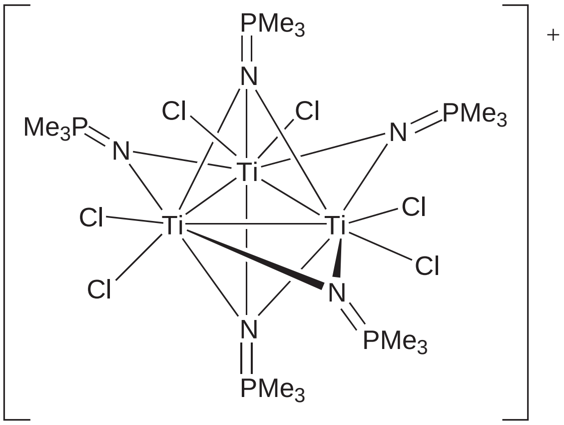
(**8**)

4.2.2.3.6 *Phosphinimido ligand complexes*

Dehnicke and co-workers have reported on the syntheses and crystallographic structures of the monometallic Ti^{IV} phosphinimide complexes $TiCl_3(NPPh_3)$,[98] $TiCl_2(NPPh_3)_2$,[99] $Ti(NPPh_3)_4$,[100] and $TiCl_3(NPEt_3)(THF)_2$.[52] While the Ti–N–P angle in $TiCl_2(NPPh_3)_2$ was found to be 166.6(2)°, steric crowding in $Ti(NPPh_3)_4$ accounted for the reduced average Ti–N–P angle of 150.4°. The bimetallic derivatives $(TiCl_2(\mu\text{-}Cl)(NPMe_2Ph)(MeCN))_2$,[99] and $(TiF_2(\mu\text{-}F)(NPPh_3)\text{-}(HNPPh_3))_2$[101] were found to be halide bridged whereas in the dimers $(TiCl_3(\mu\text{-}NPR_3))_2$, (R = Me,[102] Et[52]) and $Ti_2Cl_5(\mu\text{-}NPMe_2Ph)_2(NPMe_2Ph)$[102] phosphinimide groups linked the metal centers. In higher-order aggregates, $[Ti_3Cl_6(NPMe_3)_5][BPh_4]$ (**9**),[102] and $[Ti_3Cl_8(NPMe_3)_3][Cl]$[103] terminal, double and triple bridging phosphinimide ligands were confirmed crystallographically.

In related work, Roesky and co-workers showed that the reaction of $TiCl_4$ with an excess of $Me_3SiNPPh_2(N(SiMe_3)_2)$ gave $TiCl_2((Me_3SiN)_2PPh_2)(NPPh_2(NSiMe_3)_2)$.[104] Similarly, reaction of $Me_3SiNP(Ph)_2NP(Ph)_2N(SiMe_3)_2$ with $TiCl_4$ resulted in the formation of $TiCl_3(NP(Ph)_2NP(Ph)_2N(SiMe_3)_2)$.[105] A crystallographic study confirmed that this ligand was bound as a monodentate phosphinimide, with a dangling NPNPN backbone.

More recently, Stephan and co-workers have synthesized a series of compounds $TiCl_{4-n}(NPBu^t_3)_n$ ($n=1$, 2, 3), and $TiR_{4-n}(NPBu^t_3)_n$ (R = alkyl; $n=1$, 2).[106,107] Several of these complexes have been shown upon activation to yield remarkably active and thermally stable catalysts for the polymerization of olefins under commercially relevant conditions.



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4.2.2.3.7 *Imido ligand complexes*

This area of Ti chemistry has advanced rapidly in recent years and has been reviewed.[108–110] In addition, theoretical studies have probed in detail the nature of the Ti–imide bond.[111–115]

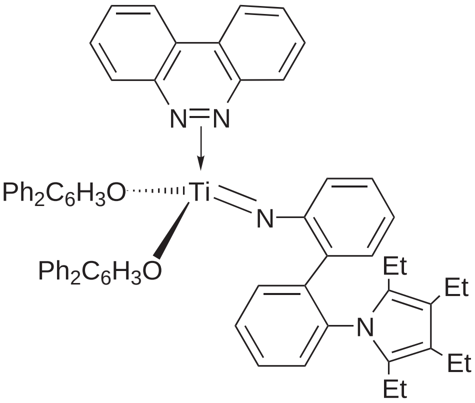
Before 1990 the Ti^{IV} imido derivatives, $(TiCl_2(NSiMe_3))_n$[116] and $(TiCl_2(NBu^t)(NH_2Bu^t)_2)_n$,[117] were reported but poorly characterized. Subsequently, reaction of $(TiCl_2(NSiMe_3))_n$ with PPh_4Cl gave $[PPh_4]_2[TiCl_3(\mu\text{-}NSiMe_3)]_2$ which has been crystallographically characterized.[118]

The first monomeric Ti–imido complex reported was the structurally characterized complex $Ti(NP(S)Ph_2)Cl_2(NC_5H_5)_3$ (Ti–N = 1.720(2) Å) by Roesky *et al.*[119] Subsequently they showed that reaction of $(SiMe_3)_2NP(S)Pr^i_2$ with $TiCl_4$ in MeCN yielded the dimeric species $(Ti(\mu\text{-}NP(S)Pr^i_2)Cl_2(MeCN))_2$ in which the imido groups bridge the two Ti centers.[120]

Also in 1990, Rothwell and co-workers reported the five-coordinate Ti–imido complex, $Ti(NPh)(OC_6H_3Pr^i_2)_2(py')_2$, (Ti–N = 1.719(3) Å) (py′ = 4-pyrrolidinopyridine) which was derived from thermolysis of $Ti(PhNNPh)(OC_6H_3Pr^i_2)_2(py')_2$[121] Similarly, thermolysis of $Ti(OC_6H_3Ph_2)_2(C_4Et_4)$ with two equivalents of benzo[*c*]cinnoline yielded the terminal arylimido complex $Ti(OC_6H_3Ph_2)_2(\eta^2\text{-}N_2C_{12}H_8)(NC_6H_4(C_6H_4(NC_4Et_4)))$ (**10**).[122] Subsequently, reaction of N donors with $Ti(OC_6H_3R_2)_2(NHPh)_2$ (R = Pr^i, Ph) generated terminal Ti–imido species $Ti(OC_6H_3R_2)_2(NPh)L_2$ (L = NC_5H_5, $NC_5H_4(NC_4H_8)$).[123]

Gambarotta and co-workers have also reported that the oxidative addition of azobenzene to $TiCl_2(TMEDA)_2$ afforded $TiCl_2(NPh)(TMEDA)$. In a similar reaction with MeCN, $(TiCl_2(TMEDA))_2(\mu\text{-}NC(Me)C(Me)N)$ (**11**) was isolated. This reaction was proposed to proceed through dimerization of a diradical.[124]

In 1991, Wolczanski and co-workers reported the transient imido species $Ti(NSiBu^t_3)(NHSiBu^t_3)_2$ from the reaction of $TiBr(NHSiBu^t_3)_3$ and MeLi, which was trapped as $Ti(NSiBu^t_3)(NHSiBu^t_3)_2(OEt_2)$. $TiX(NSiBu^t_3)(NHSiBu^t_3)(THF)$ (X = Cl, Br, Me, Bu^t) were obtained in an analogous manner. Subsequent hydrogenation afforded the imido bridged Ti^{III} complex $(Ti(NHSiBu^t_3)(\mu\text{-}NSiBu^t_3))_2$. The amido protons of $Ti(NSiBu^t_3)(NHSiBu^t_3)_2(OEt_2)$ were deuterated through addition/elimination of C_6D_6.[125] In a related system the putative complex $Ti(OSiBu^t_3)_2(NSiBu^t_3)$ was shown to activate hydrocarbons. This aspect has been studied in detail. $Ti(OSiBu^t_3)_2(NSiBu^t_3)$ also reacted with C_2H_4 to give the azametallocycle $Ti(OSiBu^t_3)_2(CH_2CH_2NSiBu^t_3)$. In addition, the donor adducts $Ti(OSiBu^t_3)_2(NSiBu^t_3)L$ (L = Et_2O or THF) were isolated and structurally characterized.[126,127]



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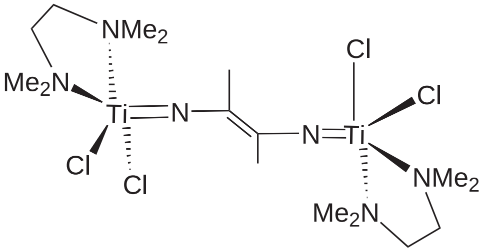

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The dimeric $(Ti(\mu\text{-}NBu^t)(NMe_2)_2)_2$ was used as a precursor for the CVD of TiN.[84] Subsequent work by Winter and co-workers led to a high-yield synthesis of $(TiCl_2(\mu\text{-}NBu^t)(H_2NBu^t)_2)_3$ from $TiCl_4$. This compound was converted to $TiCl_2(NBu^t)(L)$ ($L = Me_2NCH_2CH_2NMe_2$, $MeHNCH_2CH_2NHMe$), both of which have been crystallographically characterized.[128] Treatment with $OPPh_3$ afforded the bis-adduct $TiCl_2\ (NBu^t)(OPPh_3)_2$.[129] The related $TiCl_2(NH)(OPPh_3)_2$ was also prepared from treatment of $TiCl_4(NH_3)_2$ with NaH followed by addition of $OPPh_3$.[130]

In a more recent study, reaction of $(TiCl_2(NBu^t)(H_2NBu^t)_2)_3$ with Me_3SiN_3 gave the dimeric species $(TiCl(NBu^t)(\mu\text{-}N_3)(NC_5H_5)_2)_2$. Alternatively, reaction of $(Ti(NMe_2)_2(N_3)(\mu\text{-}N_3)(NC_5H_5)_2)_2$ and $CyNH_2$ resulted in the formation of $(Ti(NCy)(N_3)(\mu\text{-}N_3)(NC_5H_5)_2)_2$. The solid state structures of these dimers confirmed that the two Ti atoms are bridged by a pair of azide ligands. Pyrolysis studies showed that these materials were not effective TiN precursors.[65]

Reaction of $TiCl_4$ and $Li[N(SiMe_3)_2]$ produced $(TiCl(N(SiMe_3)_2)(\mu\text{-}NSiMe_3))_2$ and $TiCl(N(SiMe_3)_2)(\mu\text{-}NSiMe_3)(\mu\text{-}HNSiMe_2NMe(SiMe_3))TiN(SiMe_3)_2$ (**12**).[131] In a similar manner $(Ti(NMe_2)_2(\mu\text{-}NSi(NMe_2)_3))_2$ was prepared and characterized.[95]

In 1994, Mountford and co-workers synthesized the $TiCl_2(NBu^t)(NC_5H_4Bu^t)_2$ via the reaction of H_2NBu^t with $TiCl_4$ followed by addition of the pyridine donor. This compound was prepared on a relatively large scale in high yield. This product was used as a precursor to a variety of monomeric Ti–imido complexes including tris(pyrazolyl)borate,[132–134] macrocyclic ligand,[133,135] and porphyrin derivatives.[136] Alternatively, reaction of $TiCl_2(TTP)$ with two equivalents of $Li[NHR]$ ($R = Ph$, C_6H_4Me, Cy) yielded the corresponding imido complexes $Ti(TTP)NR$[137] (see Section 4.2.2.4.23).

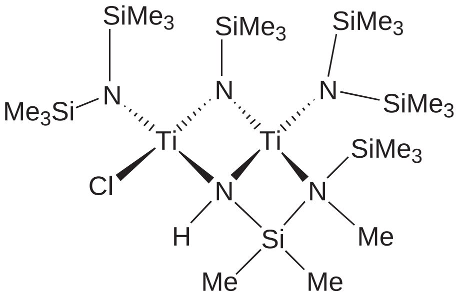
Exchange of the imido functionality of $TiCl_2(NBu^t)(NC_5H_5)_2$ with arylamines gave $TiCl_2(NR)(NC_5H_5)_n$ ($n = 2$, 3; $R = Ph$, C_6H_4Me, $C_6H_4NO_2$, $C_6H_3Pr^i{}_2$, $C_6H_3Me_2$, $C_6Me_4NH_2$, $C_6H_4N(SiMe_3)_2$).[132,138,139] It was proposed that the greater basicity of the Bu^tN group was a driving force in the exchange process.[132]

Diazabutadiene complexes of the form $TiCl_2(NR)L$ ($L = PhNC(Me)C(Me)NPh$, $R = C_6H_3Pr^i{}_2$, $C_6H_3Me_2$; $L = MeC_6H_4NC(Me)C(Me)NC_6H_4Me$, $R = C_6H_3Pr^i{}_2$, Bu^t) were prepared and characterized. In the absence of methyl groups on the butadiene backbone, imine–imide metathesis was observed. For example, reaction of $TiCl_2(NBu^t)(NC_5H_5)_2$ with $ArNCHCHNAr$ ($Ar = C_6H_3Pr^i{}_2$, $C_6H_3Me_2$) gave $TiCl_2(NAr)(NC_5H_5)_2$, $Bu^tNCHCHNAr$ and $Bu^tNCHCHNBu^t$.[140]

An attempt to uncover an alternative strategy to Ti–imido complexes involved the reaction of $(HNBu^t)_2SiMe_2$ with $TiCl_4$. This led to a mixture of products including the imido complex $(TiCl(\mu\text{-}Cl)(NBu^t)(H_2NBu^t)(MeCN))_2$ and the ketimido complex $TiCl_3(NC(Me)NHBu^t)(MeCN)_2$ (**13**).[141]

The triazacyclohexane and trithiacyclononane adducts $TiCl_2(NR)L$ ($L = (MeNCH_2)_3$, $(Bu^tNCH_2)_3$, $(SCH_2CH_2)_3$;[142] $R = Bu^t$, $C_6H_3Pr^i{}_2$,[143,144]) were prepared from $TiCl_2(NR)(NC_5H_5)_2$, and a number of these complexes have been structurally characterized. The related linked macrocyclic–imido complexes $TiCl_2((RNCH_2CH_2)_2N(CH_2CH_2)(CH_2)_3N)$ and $TiCl_2((RNCH_2CH_2)_2N(CH_2CH_2)CH_2C_6H_4N)$ (**14**) ($R = Me$, Pr^i) have been described[144,145] and shown to exhibit low ethylene polymerization activity.[145] More recently, related macrocyclic derivatives with pendent donors $TiCl(NR)((Pr^iNCH_2CH_2)_2N(CH_2CH_2)CH_2C_6H_2Bu^t{}_2O)$ and $[TiCl(NR)((Pr^iNCH_2CH_2)_2N(CH_2CH_2)CH_2C_5H_4N)]Cl$ ($R = Bu^t$, $SiMe_3$) have been reported.[146]

Substitution reactions of $TiCl_2(NR)L_3$ ($R = Bu^t$, $C_6H_3Me_2$, $C_6H_3Pr^i{}_2$; $L = NC_5H_5$, $NC_5H_4Bu^t$)[132] with $Li[OC_6H_3R'_2]$ ($R' = Me$, Pr^i, Bu^t) produced $Ti(OC_6H_4R'_2)_2(NR)L_2$. At



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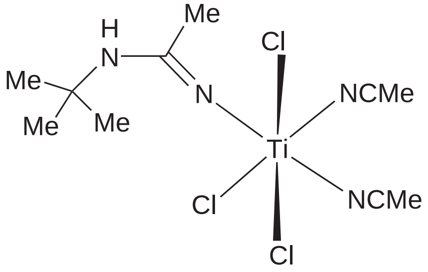

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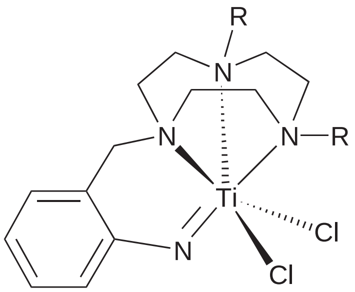
elevated temperatures, loss of pyridine afforded $(Ti(OC_6H_4Me_2)_2(NBu^t))_2$.[147] Similarly, reaction with amidinate salts afforded complexes of the form $TiCl(NR)((Me_3SiN)_2CPh)(NC_5H_5)_2$ and $(TiCl\text{-}(\mu\text{-}NR)((Me_3SiN)_2CPh))_2$ ($R = Bu^t$, $C_6H_4Me_2$, $C_6H_4Pr^i{}_2$)[148] Related amidinate derivatives $(Ti(\mu\text{-}NR)\text{-}(\mu\text{-}(PhN)_2CH)((PhN)_2CH))_2$[149] and $TiCl(NBu^t)((Pr^iN)_2CPh)(NC_5H_5)$,[150] the diiminophosphinate derivative $TiCl(NBu^t)((Me_3SiN)_2PPh_2)(NC_5H_5)$[150] and the related pyrollide derivative $TiCl(NBu^t)(NC_4H_3CH_2NMe_2)(NC_5H_5)$ have been reported.[151]

Cycloaddition of $Ti(Me_4taa)(NR)$ ($R = C_6H_3Me_2$, Ph) and isocyanates has been shown by Blake *et al.* to produce *N,N*-bound ureate complexes.[152] Similarly, they have described the use of $TiCl_2(NR)(NC_5H_5)_2$ to prepare the tridentate chelate derivative $Ti(NBu^t)((Me_3SiNCH_2)_2CMe(C_5H_4N))(NC_5H_5)$. This compound was shown to react with MeCN effecting cycloaddition to the imido group yielding $Ti(Bu^tNC_4H_3N_2Me(NMe))((Me_3SiNCH_2)_2CMe(NC_5H_4))$.[153] In subsequent work the complexes $TiCl_2(NR)(NC_5H_5)_2$ ($R = Ph$, Et, Pr^i) reacted with Bu^tCP to give $TiCl_2((Bu^tCP)NR(CBu^tP))$ in low yields.[154] In a related reaction, $Ti(NBu^t)((Me_3SiNCH_2)_2CMe(C_5H_4N))(NC_5H_5)$ reacted with Bu^tCP affording $Ti(C(Bu^t)PNBu^t)((Me_3SiNCH_2)_2CMe(C_5H_4N))$ (**15**). In this complex the geometry at Ti is pseudo-tetrahedral, as the pyridine group of the chelating ligand is pendent. Similarly, MeCN led to cycloaddition affording $(Ti(\mu\text{-}NC(Me)NBu^t)((Me_3SiNCH_2)_2C(Me)C_5H_4N))_2$.[155] Related cycloadditions of acetylenes, allenes, isocyanates, and isocyanides giving metallacycles have also been described recently.[156,157]

Winter and co-workers reacted the Ti-bis(pyrazolato) complex $TiMe_2(N_2C_3HBu^t{}_2)_2$ with Bu^tNH_2 in the presence of pyridine to obtain the $TiMe_2(NBu^t)(N_2C_3HBu^t{}_2)_2(NC_5H_5)$. In contrast, reaction of $TiCl_2(N_2C_3HBu^t{}_2)_2$ gave $(TiCl(\mu\text{-}NBu^t)(N_2C_3HBu^t{}_2))_2$. Both of these products were crystallographically characterized.[71]



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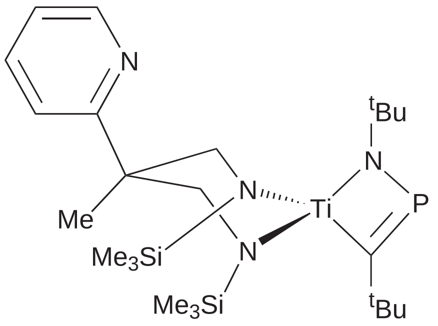

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4.2.2.3.8 *Miscellaneous monodentate ligands*

Ti–thiocyanate complexes $Ti(OR)_n(NCS)_{4-n}$, ($R = Pr^i$, Et, $n = 2$, 3) have been reported. IR data indicated coordination via N.[158]

4.2.2.3.9 Amidinato and guanidinato ligand complexes

In 1988, $(TiCl_2(\mu\text{-}Cl)((Me_3SiN)_2CPh))_2$ was prepared and structurally characterized.[159] In the same year, Roesky and co-workers reported the related monomeric complex $TiCl_2((Me_3SiN)_2CPh)_2$. X-ray data indicated a *trans*-octahedral geometry about Ti.[160] Subsequently the dimer $(TiCl_2(\mu\text{-}Cl)((MeN)_2CPh))_2$ was prepared and converted to the monomeric complexes $TiCl_3(MeN)_2CPh)(L)(L = THF, PMe_3)$ in the presence of donors. These species were only moderately active as olefin polymerization catalysts.[161] In a similar manner, the related complexes $TiCl_3((Me_3SiN)_2CPh)(L)$ ($L = THF, PMe_3$) were prepared while attempted methylations led to the formation of $TiMe_2$ $((Me_3SiN)_2CPh)_2$ and $TiMe_4$.[161] Similarly, $TiMe_2((Me_3SiN)_2CPh)_2$ was synthesized via protonolysis of $TiMe_4$ with the neutral ligand.[162] This bis-ligand complex was employed in the syndiospecific polymerization of styrene but exhibited low activity for ethylene polymerization.[161] Similarly, the complexes $(TiCl_2(\mu\text{-}Cl)((MeN)_2CC_6H_5Me))_2$ and $TiCl_3((MeN)_2C_6H_5Me)(L)$ ($L = THF, PMe_3$) showed moderate activity for styrene and ethylene polymerization.[163] Modification of the ligands as in $TiMe_2((CyN)_2CMe)_2$[164] or $TiCl_2((CyN)_2CPh)_2$ and $TiMe_2((Pr^iN)_2CPh)_2$[165] improved the catalytic activity. This was attributed to the steric inhibition of β-hydrogen elimination processes.

4.2.2.3.10 Bis-amino phosphinato ligand complexes

Reaction of $(Me_3SiN)PPh_2(N(SiMe_3)_2)$ with $TiCl_4$ in MeCN gave the complex $TiCl_3((Me_3SiN)_2PPh_2)(MeCN)$.[104] The related complexes $TiCl_3((Me_3SiN)_2PXY)$ ($X = OMe, Cl, Y = OMe, Cl, CCl_3, XY = (CF_3CS)_2$) and $TiCl_2((Me_3SiN)_2P(CF_3CS)_2)_2$ have also been prepared and reported.[166]

4.2.2.3.11 Sulfodiimido ligand complexes

The complex $TiCl_3((Bu^tN)_2SPh)$ contains a four-membered chelate ring[167] and reacts with H_2O to give $(TiCl_2((Bu^tN)_2SPh))_2(\mu\text{-}O)$. Crystallographic data confirmed that each of the sulfodiimido ligands remains chelated to Ti.[167]

4.2.2.3.12 Pyrazolyl ligand complexes

In recent years Winter and co-workers have described a number of Ti–pyrazolyl complexes. $Ti(NMe_2)_4$ reacted with $N_2C_3H_2R_2$ ($R = Me, Ph$) to give the monomeric complexes $Ti(N_2C_3HR_2)_4$ (**16**). Crystallographic characterization confirmed that the four ligands were bound in an η^2 fashion.[168] Similarly, treatment of $TiCl_4$ with $N_2C_3H_2Bu^t{}_2$ in the presence of NEt_3, or use of $K[N_2C_3HBu^t{}_2]$ or $Me_3SiN_2C_3HBu^t{}_2$ provided access to the complexes $TiCl_{4-n}(N_2C_3HBu^t{}_2)_n$ ($n = 1, 2, 3$).[169,170] Adducts of the general formula $TiCl_4(N_2C_3H_2R_2)_2$ were shown to be intermediates en route to these complexes.[168] Subsequent studies focused on the preparation of related imido derivatives.[71]

4.2.2.3.13 Amidopyridine ligand complexes

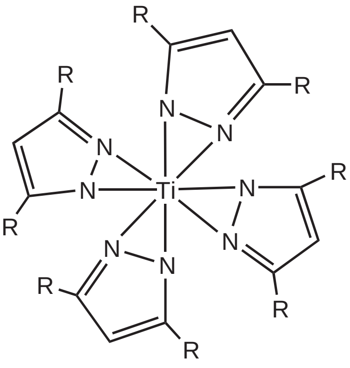
Reaction of $NC_5H_4(HNR)$ ($R = Me, Ph$) and $NC_5H_3Me(HNSiMe_3)$ with $TiCl(NMe_2)_3$ afforded $TiCl(NMe_2)(NC_5H_4(NR))_2$, $TiCl(NC_5H_4(NR))_3$, and $TiCl(NMe_2)(NC_5H_3Me(NSiMe_3))_2$. Several of these compounds were characterized crystallographically.[171] Similarly, $NC_5H_3Me(HNSiMe_3)$ reacted with $TiCl_2(NMe_2)_2$ to give $TiCl_2(NMe_2)(NC_5H_3Me(NSiMe_3))(HNMe_2)$.[172] In contrast, the reaction between $TiCl_4$ and $NC_5H_4(HNPh)$ produced the salt $[NC_5H_4(PhNH_2)][TiCl_4(NC_5H_4(NPh))]$.[173] A similar strained geometry was observed for the tetradentate bis(aminopyridinato) Ti complex $Ti(NMe_2)_2$ $(\mu\text{-}O$ $(SPr^{ii}{}_2(N(NC_5H_4Me))_2)$ (**17**).[174] The related ligand complexes $TiCl_3(NC_5H_4\ CH_2CH_2NR)$ ($R = SiMe_3, SiMe_2Bu^t, Ph$) have been prepared.[175]

4.2.2.3.14 Aminotroponiminato ligand complexes

The monoanionic bidentate ligand complex $TiCl_2((MeN)_2C_7H_5)_2$ was derived from reaction of $TiCl_2(NMe_2)_2$ with two equivalents of the aminotroponiminato ligand. Subsequent reactions afforded $Ti(OSO_2CF_3)_2((MeN)_2C_7H_5)_2$ as well as $Ti(NC_6H_3Pr^i_2)((MeN)_2C_7H_5)_2$ and $(Ti(\mu\text{-}O)\text{-}((MeN)_2C_7H_5)_2)_2$ (**18**).[176] The reduced Ti complex $Ti((MeN)_2C_7H_5)_2$ reacted with CO and carbonyl compounds to form Ti–diolate complexes of the form $Ti((MeN)_2C_7H_5)_2(OCR_2CR_2O)$. Subsequent acid hydrolysis liberated the diol.[177]

4.2.2.3.15 Miscellaneous monoanionic bidentate ligand complexes

Reaction of the amine–aminoborane $H_2NC_{10}H_8HN$(9-BBN) with $Ti(NMe_2)_4$ afforded $Ti(NMe_2)_3(HNC_{10}H_8HN(\mu\text{-}9\text{-}BBN))$. This complex contains an amine–amido ligand in which the boron atom of 9-BBN bridges the two nitrogen atoms.[178]



R = Me, Ph

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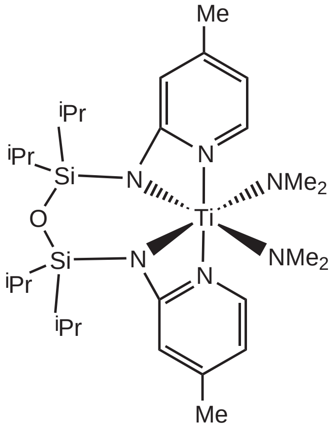

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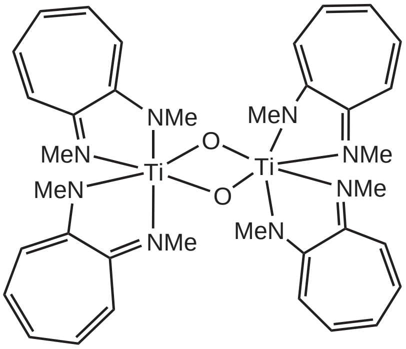

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Chiral bis(oxazoline) (BOX) complexes of the form $TiX_2(BOX)_2$ have been synthesized from Ti-halides. These complexes effected the reduction of ketones in the presence of silanes.[179]

4.2.2.3.16 Dianionic bidentate ligand complexes

Ti^{IV} complexes containing chelating bis(amido) ligands have continued to be explored over the last two decades. The general synthetic methods used to produce bis-amido chelate complexes involve reactions of dilithio salts or bis(Me_3Si) derivatives of the diamine with $TiCl_4$ or protonolysis of $Ti(NR_2)_4$ or TiR_4 with the parent amine. For example, reaction of $Li_2[(Me_3SiNCH_2)_2]$ and $TiCl_4$ gave the complex $Ti(Me_3SiNCH_2)_2)_2$.[180] The redistribution reaction of $Ti(Me_3SiNCH_2)_2)_2$ and $TiCl_4(THF)_2$ provided $TiCl_2((Me_3SiNCH_2)_2)$. This compound catalyzes olefin polymerization upon activation.[181]

McConville and co-workers utilized ligands with bulky alkylsubstituted aryl groups to create $TiCl_2(((C_6H_3R_2)NCH_2)_2CH_2)$ ($R = Pr^i$, Me).[182–184] The corresponding methyl derivatives, upon activation with $B(C_6F_5)_3$, formed TiMe $(MeB(C_6F_5)_3)((C_6H_3R_2)NCH_2)_2CH_2)$ which acted as a living catalyst for the polymerization of α-olefins. The complex $TiMe(MeB(C_6F_5)_3)(((C_6H_3R_2)\text{-}NCH_2)_2CH_2)$ slowly evolved CH_4 affording $Ti(C_6F_5)(CH_2B(C_6F_5)_2)(((C_6H_3R_2)NCH_2)_2CH_2)$.[185] Similarly, $TiCl_2((R_3SiN)_2C_6H_{10})$, $Ti((R_3SiN)_2C_6H_{10})_2$, ($R_3 = Me_3$, Me_2Ph, $MePh_2$)[186] $TiCl_2$(1,8-$(R_3SiN)_2$ $C_{10}H_6$) ($R_3 = Me_3$, $BuMe_2$, Pr^i_3)[187,188] and $TiCl_2((Bu^tPh_2SiNCH_2)_2$ $CMe_2)$[189] have been synthesized and characterized. Several of these systems have been assessed as potential olefin polymerization[188–190] and copolymerization[191] catalysts. A dissymmetric diamide ligand has been employed to prepare complexes of the form $TiCl_2(Me_3SiNC_6H_4(CH_2NSiMe_3)$. These proved to be only moderately active polymerization catalysts upon treatment with an activator.[192] Recently, the chelating aryl–diamido complexes $TiCl_2((HN)_2C_6H_4)(NC_5H_5)_n$ and $TiCl_2((HN)_2C_6H_4)$(TMEDA) were derived from $TiCl_2$ $(Bu^tN)(NC_5H_5)_2$.[139]

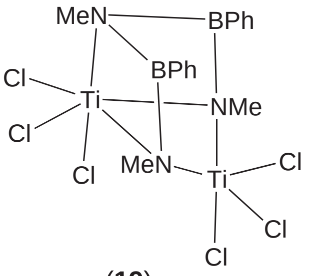
In efforts to increase the electrophilicity of the Ti center, π-accepting boryl–amide chelates were employed to prepare the complexes $TiCl_2(((R_2B)NCH_2)_2)$ ($R = C_6H_2Me_3$, Cy) and related alkyl derivatives. However, these compounds, upon activation with $B(C_6F_5)_3$, produced minimally active olefin polymerization catalysts.[193,194]

The related bidentate ligand $MeN(B(Ph)N(Me)SiMe_3)_2$ gave rise to the complexes $Ti_2Cl_4(\mu\text{-}NMe)(\mu\text{-}MeNB(Ph)NMe)$ and $Ti_2Cl_6(\mu\text{-}MeN(B(Ph)NMe)z)$ (**19**). In both dimers the bridging nature of the ligands was confirmed crystallographically.[195]

Boron-bridged diamide ligand complexes $Ti((RN)_2BPh)_2$ have also been derived from the reaction of $Li_2[(RN)_2BPh]$ ($R = Bu^t$, $SiMe_2Bu^t$) and $TiCl_4$.[196] The diborane-bridged bis-amido complex $TiCl_2((C_6H_3Pr^i_2)NB(NMe_2))_2$ was synthesized by reaction of the dilithio salt of the ligand with $TiCl_3(THF)_3$ followed by oxidation with $PbCl_2$.[197] These complexes provided active olefin polymerization catalysts upon activation. The disilyl-bridged complex $TiCl_2((Bu^tNSiMe_2)_2)$ was synthesized and converted to $(TiF(\mu\text{-}F)((Bu^tNSiMe_2)_2))_2$ via treatment with Me_3SnF.[198]

An early report described the synthesis and structure of $TiCl_2((NBu^t)_2SiMe_2)$, which was derived from the reaction of the silyldiamine with $TiCl_4$.[199] Thermolysis of $TiCl_3((Me_3SiN)_2PPh_2)(MeCN)$ afforded the dimeric derivative $(TiCl_2(\mu\text{-}NPPh_2(NSiMe_3)(MeCN))_2$ (**20**) with the elimination of Me_3SiCl.[104] The related ligand $HN(SiMe_3)SiMe_2Cl$ reacted with $TiCl_4$ yielding $(TiCl_2(\mu\text{-}Cl)(N(SiMe_2Cl)(SiMe_2NH_2)))_2$. The crystal structure indicated that the NH_2 group formed a weak coordinative bond to Ti yielding a planar four-membered N–Ti—N–Si ring.[200] Recently, related complexes of the form $TiX_2((NBu^t)_2Si(CH_2)_n)$ ($n = 3$–5) and $TiX_2((NBu^t)_2Si(CH_2CH)_2)$ ($X = Cl$, NMe_2)[201] and $(TiCl(\mu\text{-}OMe)_2((NBu^t)_2Si(CH_2)_n))_2$ were described.[73]

Siddiqi and co-workers have reported the heterobimetallic complexes $TiCl_2(CuCl_2(\mu\text{-}HNCH_2CH_2NCH_2)_2)$ and $TiCl_2(CuCl_2(\mu\text{-}HNCH_2CH_2NH_2)_2)$.[202,203] Related dithiocarbamate and borohydride derivatives have also been described.[204,205] The fused diferrocenyl diamine was used to prepare $TiCl_2(OAr)_2((NHMeCHC_5H_4FeCp)_2)$ (**21**). X-ray studies confirmed a distorted octahedral geometry about Ti.[206] Reaction of the related ferrocenyl–diamido ligand with $TiCl_4$ afforded the complex $TiCl_2(Me_3SiNC_5H_4)_2Fe$. The first two of these complexes have been crystallographically characterized and shown to adopt a pseudo-tetrahedral geometry at Ti.[207] Subsequently, the related compound $Ti(NMe_2)_2(PhNC_5H_4)_2Fe$ was described.[208]



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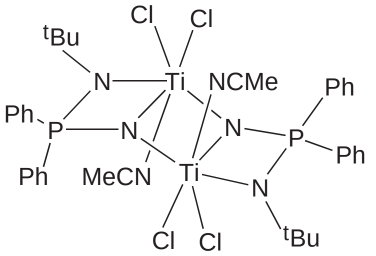

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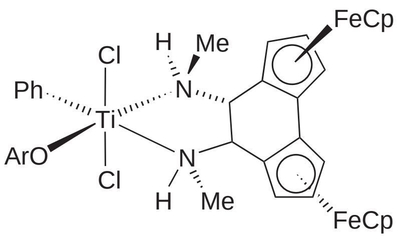

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4.2.2.3.17 Miscellaneous bidentate–dianionic ligand complexes

The reaction of $TiCl_4$ with $Ph_2S(NSiMe_3)_2$ yielded the dimeric species $(TiCl_3(THF)_2)_2(\mu\text{-}N_2SPh_2)$. Crystallographic data affirmed that the N_2S fragment linked the two metal centers.[105]

The ethylamido–pyridine complexes $TiCl_3(RNCH_2CH_2C_5H_4N)$ ($R = SiMe_3$, $SiMe_2Bu^t$) all converted to the dimer $(TiCl_2(\mu\text{-}NCH_2CH_2C_5H_4N))_2$ with the loss of trialkylsilyl chloride under thermolysis conditions. This species was crystallographically characterized, confirming the presence of the imido bridges. The corresponding phenyl amido complex $TiCl_3(PhNCH_2CH_2C_5H_4N)$ was thermally stable.[175]

4.2.2.3.18 Neutral tridentate ligand complexes

Coordination of the triazacyclononane ligand to $TiCl_4$ afforded $[TiCl_3(MeNCH_2CH_2)_3]Cl$. Oxidation of $TiCl_3((MeNCH_2CH_2)_3)$ by Me_3SiN_3 in the presence of $Na[BPh_4]$ afforded $[TiCl_2(N_3)(MeNCH_2CH_2)_3][BPh_4]$, whereas oxidation of $Ti(SCN)_3((MeNCH_2CH_2)_3)$ by O_2 gave $TiO(NCS)_2((MeNCH_2CH_2)_3)$.[61]

A variety of oxidations of $TiX_3((RNCH_2CH_2)_3)$ ($X = Cl$, Br; $R = Me$, Pr^i) have been used to prepare $[TiBr_n(OMe)_{3-n}((MeNCH_2CH_2)_3)][ClO_4]$ ($n = 0$–2), $TiCl_2(O_2)((MeNCH_2CH_2)_3)$, $TiCl_2O((MeNCH_2CH_2)_3)$, $Ti(NCO)_2(O_2)((MeNCH_2CH_2)_3)$, $Ti(NCS)_2O((Pr^iNCH_2CH_2)_3)$, and

$Ti(NCO)_2O((Pr^iNCH_2CH_2)_3)$. The six-coordinate geometry of a number of these complexes has been confirmed crystallographically.[209]

4.2.2.3.19 *Monoanionic tridentate ligand complexes*

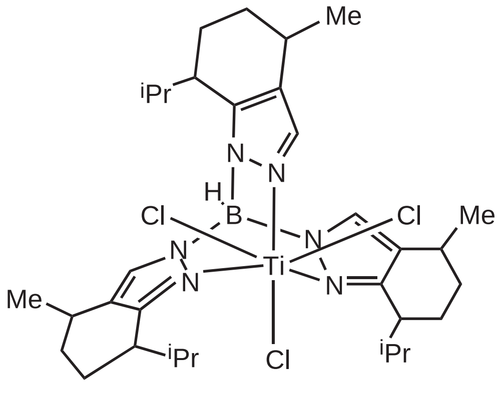
The salt metathesis reaction of $TiCl_4$ with $Li[N(SiMe_2CH_2NMe_2)_2]$ yielded $TiCl_3(N(SiMe_2CH_2NMe_2)_2)$. The crystal structure revealed a distorted octahedral geometry about Ti in which the ligand was bound in a *meridonal* fashion.[210]

4.2.2.3.20 *Tris(pyrazolyl)borato ligand complexes*

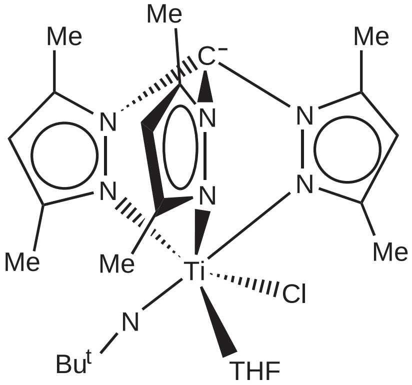
The monoanionic tris(pyrazolyl)borate ligand $((N_2C_3H_3)_3BH)$ binds strongly to Ti ions via three of the N atoms. Crystal structures of $TiCl_2((N_2C_3H_3)_3BH)(NMeNMe_2)$ and $TiCl_2((N_2C_3H_3)_3BH)(NPhNH_2)$ were published in 1989.[68] Tris(pyrazolyl)borate ligands have also been employed as ancillary ligands in Ti–imido complexes[133,134] (see Section 4.2.2.3.7). The chiral menthol derivatives $TiCl_3((N_2C_3HC_4H_6\ MeR)_3BH)$ ($R = Bu^t$, Pr^i) (**22**) have been prepared from the reactions of the corresponding Ti salts with $TiCl_4$.[211] While a variety of derivatives of $TiCl_3((N_2C_3H_3)_3BH)$ have previously been reported, a recent paper has described an alternative synthesis of this compound via reaction of $SnCl_3((N_2C_3H_3)_3BH)$ and $TiCl_4$.[212]

A series of related derivatives with the general formulas $TiCl_n(OR)_{3-n}((N_2C_3H_3)_3BH)$ ($n = 1, 2$), $TiCl(CH_2SiMe_3)(OR)((N_2C_3H_3)_3BH)$, and $TiCl_n(O(CH_2)_mPPh_2)_{3-n}((N_2C_3H_3)_3BH)$, ($n = 0$–2; $m = 1$–3) have been prepared.[213,214] The latter series have been employed to prepare the heterobimetallic complexes $TiCl((N_2C_3H_3)_3BH)(O(CH_2)_nPPh_2)_2Mo\ (CO)_4$.[214]

Very recently, $TiCl(NBu^t)((N_2C_3HMe_2)_3C)(THF)$ (**23**) was prepared via deprotonation of the corresponding tris(pyrazolyl)methane complex $TiCl_2(NBu^t)((N_2C_3HMe_2)_3CH)$. This species is the first structurally authenticated *sp*^{3}-hybridized carbanion derivative.[215]



(**22**)



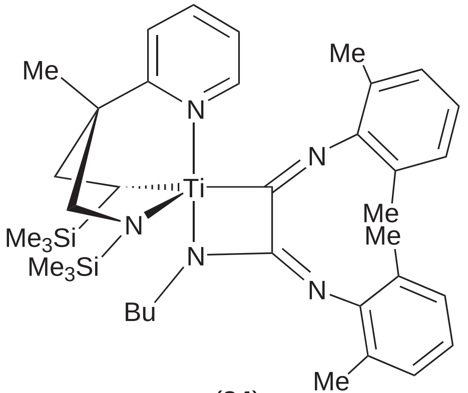
(**23**)

4.2.2.3.21 *Dianionic tridentate ligand complexes*

The syntheses and structures of the five-coordinate diamido–pyridine tripodal ligand complexes $TiX_2((Me_3SiNCH_2)_2CHC_5H_4N)$ ($X = Cl$, Br) were reported in 1993.[216] The related complexes $TiCl_2((RNCH_2)_2NC_5H_3)$ ($R = SiMe_3$, Bn, CH_2SiMe_3) and the corresponding alkyl analogues were prepared and reported.[217] Some of these derivatives were investigated as ethylene polymerization catalysts.[218]

The related amino–diamido complex $TiCl_2((Me_3SiNCH_2CH_2)_2NSiMe_3)$ and alkyl derivatives exhibit spectroscopic and structural data indicating weak coordination of the central amino N-atom to Ti.[219] The related dimethyl complex $TiMe_2((Me_3C_6H_2NCH_2CH_2)_2NH)$ was also obtained in a one-pot synthesis in low yield.[220] A related amino–dipyrrolylide ligand complex $Ti(NMe_2)_2((NC_4H_3CH_2)_2NMe)$ displayed a trigonal bipyramidal geometry.[221]

Complexes of tridentate dianionic donor ligands such as $Ti(NR)((Me_3SiNCH_2)_2C(Me)C_5H_4N)L$ and $Ti(NR)(Me_3SiN(CH_2CH_2NSiMe_3)_2)L$ ($L = NC_5H_5$, PMe_3, OC_4H_8; $R = Bu^t$, $C_6H_3Pr^i{}_2$, $C_6H_3Me_2$) have been reported.[222,223] Cycloadditions to the imido group with isocyanides, phosphaalkynes, and alkynes have been studied.[153–156,224] For example, $Ti(NBu^t)((Me_3SiNCH_2)_2C(Me)C_5H_4N)(NC_5H_5)$ reacted with $Me_2C_6H_3NC$ to effect double insertion affording $Ti(C(NC_6H_3Me_2)C(NC_6H_3Me_2)NBu^t)((Me_3SiNCH_2)_2C(Me)C_5H_4N)$ (**24**). Further reaction with RNC ($R = Et$, Pr^i, Bu, Bu^t, CH_2Ph, PhMe and CHMePh) afforded the related derivatives $Ti(N(C_6H_3Me_2)C(CNR)C(C_6H_3Me_2)NBu^t)((Me_3SiNCH_2)_2C(Me)C_5H_4N)$. Similar reactions with isocyanides containing H atoms α the CN group led to $Ti((CNCH_2R)(C_4H_2RN_2CH_2R)NCBu^t)((Me_3SiNCH_2)_2C(Me)C_5H_4N)$ ($R = H$, Me, Pr, Ph) and $Ti((NCHRR')(C_4HRR'N_2CHRR')NBu^t)((Me_3SiNCH_2)_2C(Me)C_5H_4N)$ (**25**) ($R = Me$, C_5H_{10}; $R' = Me$, Ph).[157]



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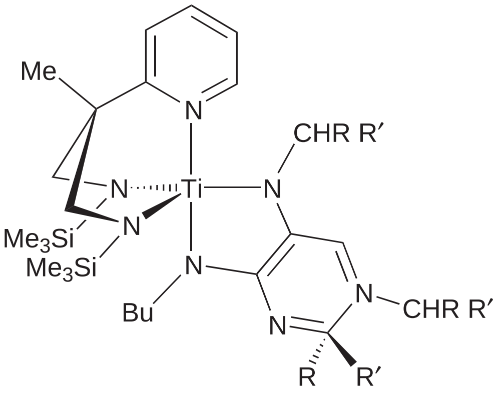

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4.2.2.3.22 *Trianionic tripodal ligand complexes*

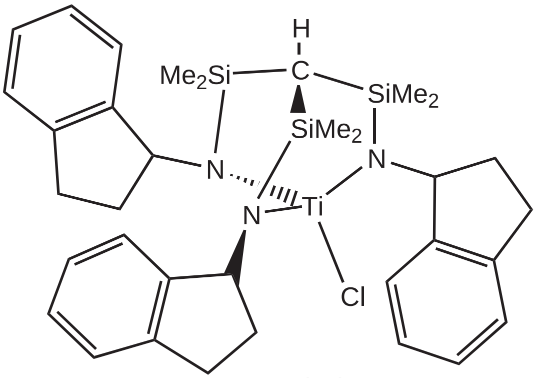
The first azatitanatrane, $Ti(NMe_2)((MeNCH_2CH_2)_3N)$, was prepared by the protonolysis of $Ti(NMe_2)_4$ with the $(MeHNCH_2CH_2)_3N$ by Verkade and co-workers.[225] Subsequently, related N-silylated[226,227] and N-alkylated azatitanatranes[228,229] have been prepared via salt metathesis reactions. Another synthetic pathway to azatitanatranes was demonstrated by the reaction of $B(MeNCH_2CH_2)_3N$ with $Ti(OPr^i)_4$ yielding $Ti(OPr^i)((MeNCH_2CH_2)_3N)$.[230] A variety of substituted derivatives of the form $TiX((RNCH_2CH_2)_3N)$ have also been characterized.[57,226,228,229,231]

Complexes containing similar tripodal ligands $(TiX((RNCH_2)_3CMe))_2$ ($X = Cl$, Br; $R = Me$, $SiMe_3$, $SiMe_2Bu^t$) have been reported and the Cl derivatives characterized crystallographically.[232] The related complexes $TiX((RC_6H_4NSiMe_2)_3CH)$ ($X = Cl$, Br; $R = Me$, F),[233] $TiX((MeC_6H_4NSiMe_2)_3SiMe)$ ($X = Cl$, Br), and $TiX((FC_6H_4NSiMe_2)_3SiMe)$ ($X = Cl$, O_3SCF_3, Me)[234] have also been reported.[235] In the latter compound weak ortho-F interactions with the Ti centers were implied. Hydrolysis of $TiX((RNCH_2)_3CMe)$ ($X = Cl$, Br) yielded the oxo-bridged complexes $(Ti((Me_3SiNCH_2)_3CMe))_2(\mu\text{-}O)$ and $(Ti(\mu\text{-}Cl)((PrNCH_2)_2(Pr^iNHCH_2)CMe))_2(\mu\text{-}O)$.[236]

Analogous complexes that incorporated chiral substituents on the N-atoms of the tridentate trianionic ligands have recently been reported. These include $TiCl(((Bu^t(Me)HC)NCH_2)_3CH)$[237] and $TiCl((C_9H_9NSiMe_2)_3CH)$ (**26**).[238]

4.2.2.3.23 *Dianionic tetradentate ligand complexes*

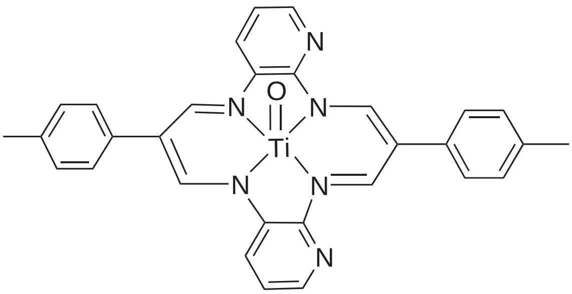
The macrocyclic Ti complex $TiCl_2(Me_4taa)$ was first synthesized by Goedken and Ladd via the reaction of $TiCl_4$ with the ligand under basic conditions.[239] Alternatively, the Li_2 salt of the ligand reacted with $TiCl_4$ to give $TiCl_2(Me_4taa)$, while the sandwich-type complex $Ti(Me_4taa)_2$ was prepared using a 2:1 ratio of ligand salt to metal.[240] Treatment of $TiCl_2(Me_4taa)$ with NH_4OH/MeCN gave $TiO(Me_4taa)$. This oxo complex and the corresponding sulfido complex were shown to react with a variety of reagents resulting in derivatives including $Ti(S_2C_6H_4)(Me_4taa)$, $Ti(O_2C_6H_4)(Me_4taa)$, $Ti(O_2C)_2(Me_4taa)$, $TiS(Me_4taa)$ $Ti(S_2)(Me_4taa)$,[239] $Ti(O_2SO)(Me_4taa)$, $Ti(O_2SO_2)(Me_4taa)$, $Ti(O_2CMe(CF_3))(Me_4taa)$, $Ti(OCF_2CF(CF_3)O)(Me_4taa)$, $Ti(OS_2PC_6H_4OMe)(Me_4taa)$, and $Ti(O_2C)_2C_6H_4(Me_4taa)$.[241,242] The oxo derivative was also employed to



(**26**)

generate a series of mixed metal oxo-bridged complexes such as Ti(μ-O)(Me_4taa)-($Fe(OC_6H_4NCH_2)_2$).[242,243] The heavier chalcogenide derivatives, TiSe(Me_8taa) and TiTe(Me_8taa), were prepared and the latter was crystallographically characterized.[244] In addition, the imido analogues Ti(NR)(Me_4taa) (R = Ph, C_6H_4Me) react with isocyanates to give *N*,*N*-bound ureate complexes.152 Aminopyridinato fragments have also been incorporated into a taa-type ligand derivative as in $TiO(NC_5H_4NHCHCRCHN)_2$ (R = Me, C_6H_4Me (**27**)).[245]

The piperazine derivatives $Ti(NR)((Me_3SiNC_6H_3R'CH_2NCH_2CH_2)_2)$ (**28**) (R = Bu^t, C_6H_4Me; R′ = H, Bu^t) were prepared from the precursor $TiCl_2(NBu^t)(NC_5H_5)_3$ and the corresponding piperazine Li salt. The chelating nature of this N_4 ligand was confirmed crystallographically.[246] The related tetradentate ligand complex $TiCl_2(((MeN)C_7H_5N)_2C_6H_{10})$ (**29**) was prepared and structurally characterized. Derivatives including $Ti(OCPh_2)_2(((MeN)C_7H_5N)_2C_6H_{10})$ and $Ti(Bu^tNCMe_2)(((MeN)C_7H_5N)_2C_6H_{10})$ were also reported.[247]



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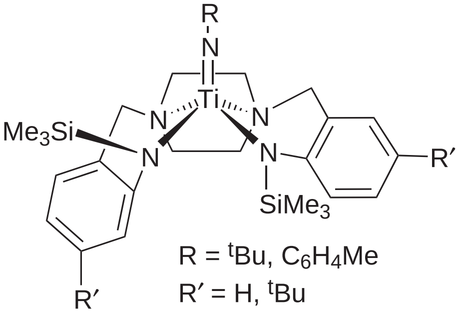

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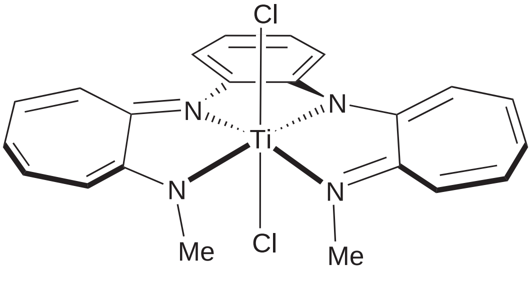
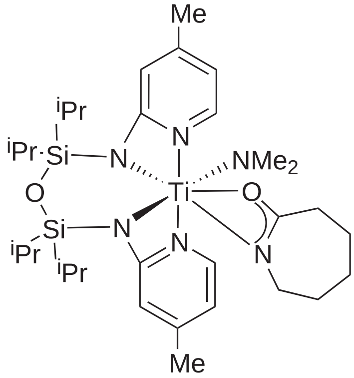


(**29**)

The tetradentate bis(aminopyridinato) ligands $(NC_5H_3RNHSiR'_2)_2O$ (R = Me, H; R′ = Me, Pr^i) reacted with $Ti(NMe_2)_4$ and $TiCl(NMe_2)_3$ to afford the siloxane-bridged Ti complexes $Ti(NMe_2)_2((NC_5H_3MeNHSiR'_2)_2O)$ and $TiCl(NMe_2)(NHMe_2)((NC_5H_3MeNHSiR'_2)_2O)$. The related derivatives based on pyrimidines, $Ti(NMe_2)_2((N_2C_4H_2MeNHSiR'_2)_2O)$ and $TiCl(NMe_2)(NHMe_2)((N_2C_4H_2MeNHSiR'_2)_2O)$, ($R' = Me$, Pr^i) have also been described.[174,248,249] The diamido derivative was shown to react with caprolactam to give $Ti(NMe_2)(NOC_6H_{10})((N_2C_4H_2MeNHSPr^i_2)_2O)$ (**30**).[174] A ferrocenyl backbone has also been incorporated into the bridge of a bis(aminopyridinato) ligand, affording the complexes $Ti(NMe_2)X(NC_5H_3MeNSiMe_2C_5H_4)_2Fe$ ($X = NMe_2$, Cl).[250]

More recently, the tripodal pyridyl–amino–bis(amido) ligand complex $Ti(NR)(NC_5H_4CH_2N(CH_2CH_2NSiMe_3)_2)$ was prepared, structurally characterized, and its chemistry examined. Crystallographic data showed a pseudo-trigonal bipyramidal geometry at Ti.[251]



(**30**)

4.2.2.3.24 *Porphyrin and porphyrinogen ligand complexes*

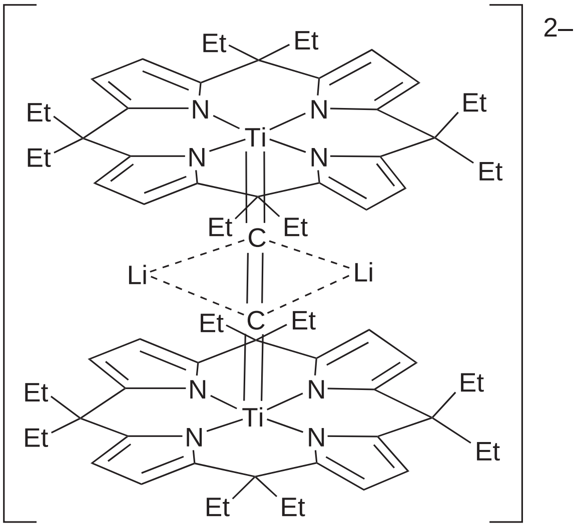
Continuing studies of porphyrin complexes have addressed the mechanism of the reaction of H_2O_2 with TiO(TPyP) to give $Ti(O_2)$(TPyP).[252–254] Similarly, $Ti(O_2)$(TPP) was formed from reaction of TiO(TPP) and ROOH.[255] The complexes $Ti(O_2)$(TPP) and $Ti(O_2)$(OEP) have also been shown to react with SO_2 to give $Ti(SO_4)$(TPP) and $Ti(SO_4)$(OEP) respectively.[256,257] Donors such as $BuNH_2$, Bu^tNH_2, and Et_2NH weakly coordinate to TiO(TPP).[258] TiO(TPP) has been employed as a catalyst for the oxidation of cyclohexene to cyclohexenone, cyclohexeneol, and cyclohexylepoxide.[259] It also has been investigated as an initiator in a variety of polymerization reactions.[260]

$Ti(O_2)$(TPP) did not react in the presence of electron-rich or electron-deficient olefins or BuLi, however, it did oxidize PPh_3 to give TiO(TPP) and $OPPh_3$.[261] The analogous complexes $Ti(E_2)$(TPP) ($E = S$, Se) have been prepared via reduction of TiF_2(TPP) and subsequent oxidation with Cp_2TiE_5.[262,263] The complexes TiX_2(TPP) ($X = F$, Cl, Br) were prepared via reaction of TiO(TPP) and HX. Similarly, $Ti(O_2C_6H_4)$(TPP) and $Ti(S_2C_6H_3Me)$(TPP) were derived from the reactions of (TPP)TiO with catechol or toluenedithiol.[264]

A series of derivatives of TiO(TTP) incorporating a variety of fluorinated and chlorinated-aryl rings has been synthesized and characterized. These include $TiO(TPPF_8)$, $TiO_2(TPPF_8)$, $TiO(TPPF_{20})$, $TiO_2(TPPF_{20})$, $TiO(TTPCl_8)$, and $TiO(TTPCl_{20})$.[265]

The imido derivatives, Ti(NR)(TTP) ($R = Ph$, C_6H_4Me, Cy), have also been prepared and crystallographically characterized. Hydrolysis or treatment with S_8 of this complex gave TiO(TTP) or $Ti(S_2)$(TTP) respectively.[137] More recently, the imido derivative $Ti(NPr^i)$(TTP) reacted with PhNO gave Pr^iNNPh and TiO(TTP).[72] The related hydrazido complexes $Ti(NNR_2)$(TTP) ($R = Me$, Ph) were shown to undergo reactions with PhOH or H_2O to give $Ti(OPh)_2$(TTP) and TiO(TTP). The related derivatives TiX_2(TTP) and TiClX(TTP) ($X = OPh$, OMe, OBu^t, NPh_2) were prepared via straightforward ligand replacement reactions. In addition, oxidation of the Ti^{II} species Ti(EtCCEt)(TTP) with PhNNPh afforded Ti(NPh)(TTP).[266]

Studies of the physical properties of Ti–porphyrin complexes have included examinations of the details of the photoexcitation of TiO(TPP),[267] and the electrochemical properties of $Ti(O_2)$(TPP) and TiO(TPP).[268] In addition, mass spectral studies of $Ti(O_2)$(TPP) and TiO(TPP),[269] synchrotron X-ray powder diffraction of $TiCl_2$(TPP),[270] crystallographic and EXAFS studies of



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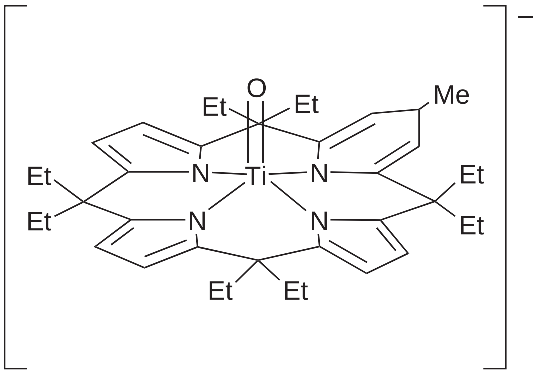

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$TiF_2(TPP)$,[264] optical absorption and laser photolysis of $Ti(O_2)(TPP)$,[271] and EXAFS studies of $Ti(O_2)(TPP)$[272] have been reported.

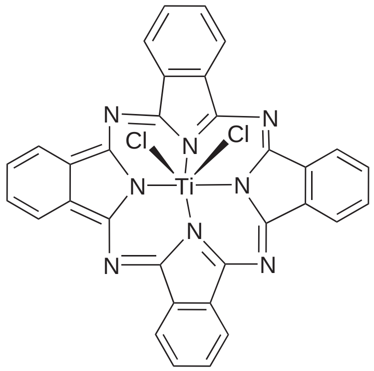
Floriani and co-workers established the synthesis of the porphyrinogen complex Ti(OEP′)$(THF)_2$ from the reaction of $TiCl_4$ with the Li salt of tetraanionic OEP′.[273] Ti(OEP′)$(THF)_2$ has been shown to react with PhCHO to add to the ring affording Ti(η^1-η^1-η^1-η^5-OEP′(OCPhH)).[274] Subsequent reaction with Li in the presence of ethylene gave $[Li(THF)_4]_2[(Ti(OEP')_2(\mu\text{-}C_2)]$ (**31**) which was characterized by X-ray crystallography.[273] The reaction of alkyl and aryl derivatives with CO resulted in the ring expansion of one of the pyrrole rings of OEP′ affording the dimer $Li_2[(TiO(Et_8(NC_4H_2)_3(NC_5H_2Me)))_2]$ which was transformed to the monomeric salt $[Li(NC_5H_5)_3][TiO(Et_8(NC_4H_2)_3(NC_5H_2Me))]$ (**32**) in the presence of pyridine.[275]

Subsequent liberation of the tris(pyrrole)pyridine ligand and complexation with Ti gave $TiCl(Et_8(NC_4H_2)_3(NC_5H_3))$. Alkylation and insertion of CO afforded the complex $TiO(Et_8(NC_4H_2)_2(NC_5H_3)_2)$.[276,277]

4.2.2.3.25 Phthalocyaninate ligand complexes

A variety of substituted phthalocyanine (PC) complexes of the form $TiCl_2(PC)$ (**33**), and TiL(PC) ($L = O_2C_6H_4$, C_2O_4, O_2) have been prepared and reported.[278] A structural study of $TiCl_2(PC)$ confirmed the *cis* arrangement of the Cl-ligands. The reaction of $TiCl_2(PC)$ with excess of the dianion of PC afforded the unique complex Ti(5,5′;19,19′-$(PC)_2$). This complex, which was described and crystallographically characterized, has two phthalocyanine rings linked by inter-ring C—C bonds.[279] When oxidized with iodine or nitric acid, the salts [Ti(5,5′; 19,19′-$(PC)_2$)]$[I_3]_{0.66}$ and [Ti(5,5′;19,19′-$(PC)_2$)]$[NO_3]$ were obtained. The electrical conductivity properties of these compounds were investigated.[280]

Related Ti complexes in which a variety of peripheral substituents were incorporated into the PC ligands have been described. For example, octa-substituted phthalocyanines have been used to prepare the analogous complexes $TiO(R_8PC)$ ($R = C_7H_{15}$, OC_5H_{11},[281] Bu^t [282]). Alternatively, replacement of the ancillary chloride ligands of $TiCl_2(PC)$ afforded a variety of derivatives including $Ti(O_2C_6HRR'R'')(PC)$ (R = H, CHO, Bu^t; R′ = H, CHO, Bu^t, CO_2H, CN; R″ = H, Bu^t), $Ti(S_2C_6H_4)(PC)$, and $Ti(O_2C_{10}H_6)(PC)$.[283] A more sophisticated analogue of the phenolate-substituted PC complexes has been recently reported by Kobayashi *et al.* They describe the reaction of $TiO(Bu^t{}_4PC)$ with an octahydroxy-substituted PC resulting in the tetrameric compound of the formula $(Ti(Bu^t{}_4PC))_4(O_8PC)$ (**34**).[284]



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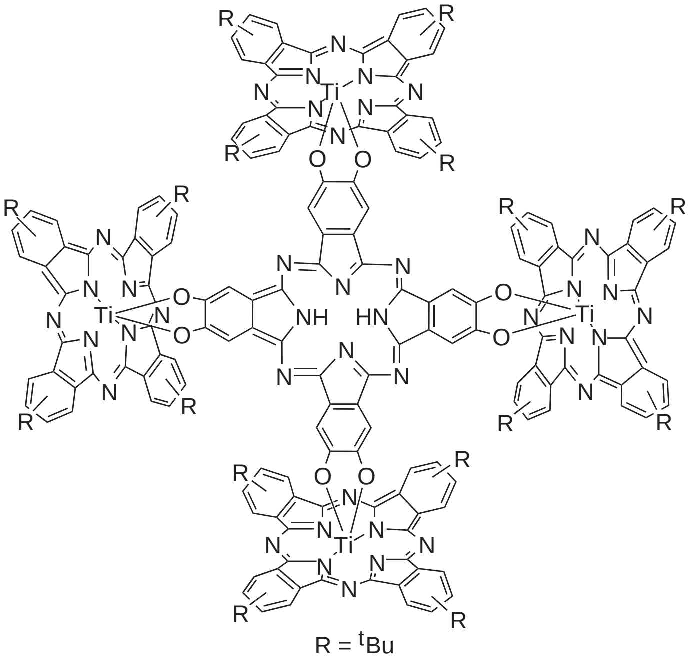

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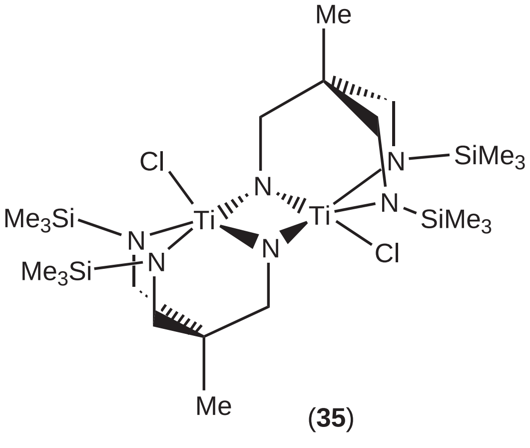
A variety of different studies involving the physical properties of TiO(PC) have been reported including absorption[285–289] thermochromic,[290,291] spectroscopic,[292] and photochemical properties,[293–296] and photoconductivity.[297–299]

Functionalized alkoxy derivatives of phthalocyanine complexes have been used to prepare polymeric PC materials and a number of studies have investigated the physical and mesomorphic properties of these and related polymers.[300–306]

4.2.2.3.26 *Tetraanionic tridentate ligand complexes*

The dimeric complexes (TiX((Me$_3$SiNCH$_2$)$_2$(μ-NCH$_2$)CMe))$_2$ (**35**) (X = Cl, Br) were isolated as by-products in the syntheses of TiX((Me$_3$SiNCH$_2$)$_3$CMe). A single-crystal X-ray structure confirmed the dimeric structure.[232]



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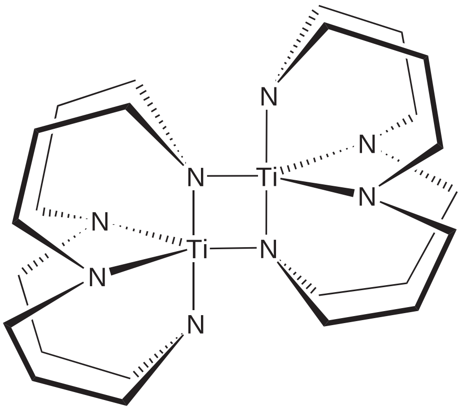
4.2.2.3.27 Tetraanionic tetradentate ligand complexes

The Ti complex $(Ti(NCH_2CH_2CH_2)_4)_2$ (**36**) was prepared via protonolysis of $Ti(NMe_2)_4$ with the neutral ligand. The crystal structure confirmed the dimeric nature in which one of the N-atoms from each ligand bridged the Ti centers. Hydrolysis of this compound afforded $(Ti(NCH_2CH_2CH_2)_3HNCH_2CH_2CH_2)_2(\mu\text{-}O)$.[307]



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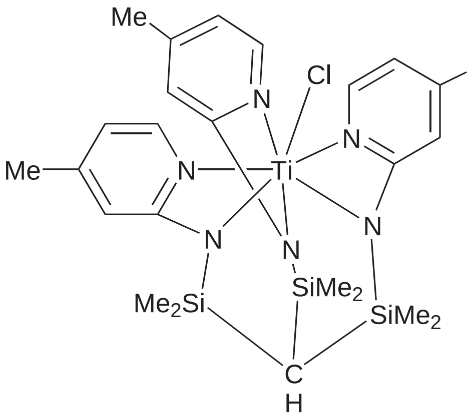

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The dissymmetric imido ligand complex $(Ti((N(CH_2CH_2CH_2NPr^i)_2)CH_2CH_2N))_2$ was derived from the reaction of $(N(CH_2CH_2CH_2NPr^i)_2)CH_2CH_2NH_2$ and $Ti(NMe_2)_4$. Crystallographic studies confirmed the dimeric nature in which the imido N atoms bridge the two Ti centers.[308]

4.2.2.3.28 Trianionic hexadentate ligand complexes

The tris(aminopyridinato) ligand complex $TiCl((NC_5H_3MeNSiMe_2)_3CH)$ (**37**) was prepared by reaction of the neutral ligand with $TiCl(NMe_2)_3$. Crystallographic data confirmed a seven-coordinate metal center.[309]

4.2.2.4 Phosphorus Ligand Complexes

4.2.2.4.1 Neutral phosphorus ligand complexes

The reaction of $TiCl_4$ and PH_2Cy afforded the octahedral $TiCl_4(PH_2Cy)_2$. Thermolysis of this compound between 350 °C and 600 °C showed that it was effective as a single-source precursor for the production of Ti—P films.[310]

The related monomeric complex $TiCl_4(DMPE)_2$ was unintentionally synthesized via reaction of the ligand and $TiCl_4$ in the presence of $ZnEt_2$.[311] In the solid state, $TiCl_4(DMPE)$ exhibited a distorted eight-coordinate geometry. This chelate complex was also readily alkylated.[312]

4.2.2.5 Oxygen-based Ligand Complexes

4.2.2.5.1 Neutral oxygen ligand complexes

Both *cis* and *trans* isomers of the THF adduct of $TiCl_4$ have been reported,[11,313,314] crystallographically characterized,[313] and commonly employed as starting materials for a variety of Ti compounds. The related adducts, $TiCl_4L_n$ ($L = EtO_2CR$ ($R = Me$, H, Ph),[315] $Me_3C_6H_2COH$, PhCOMe, PhSCOMe $EtCO(NCO_2CH_2CH(Pr^i))$),[316] ($n = 1, 2$) have also been characterized spectroscopically.

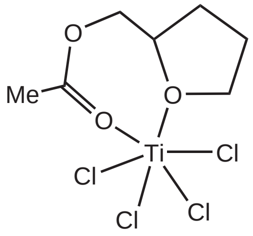
A number of crystallographic studies of $TiCl_4$ adducts of esters have been reported. The monomeric complexes $TiCl_4(CHCH_2CO_2CH(Me)CO_2Et)$,[317] $TiCl_4(C_6H_4\ (CO_2CH_2CHMe_2)_2)$,[318]

$TiCl_4(C_6H_4(CO_2CH_2CH_2Ph)_2)$, $TiCl_4(C_2O_4(CH_2CH_2Ph)_2)$,[319] $TiCl_4(CH_2(CO_2Et)_2)$, $TiCl_4(C_2H_4(CO_2CH_2OPh)_2)$,[320] $TiCl_4(\mathit{cis}\text{-}Me_2C_2(CO_2Et)_2)$, $TiCl_4(\mathit{cis}\text{-}Et_2C_2(CO_2Et)_2)$, $TiCl_4(\mathit{cis}\text{-}C_2H_2(CO_2Et)_2)$, $TiCl_4(CHCMe(CO_2Et)_2)$, $TiCl_4(C_6H_4(1,2\text{-}CO_2Me)_2)$, and $TiCl_4(C_6H_{10}(CO_2CH_2\text{-}CHMe_2)_2)$[321] have been characterized. The related monomer $TiCl_4(CH(CO_2Et)_3)$ formed a chelated six-coordinate complex with one pendent ester group.[322] Similarly, $TiCl_4(C_4H_7OCH_2CO_2Me)$ (**38**) was shown to be monomeric with the ligand chelated through both the ether and ester oxygen atoms.[323] In contrast $(TiCl_3(\mu\text{-}Cl)(MeCO_2CH_2CHCH_2))_2$ [324] was determined to be a chloro-bridged dimer and crystallographic studies showed that $(TiCl_4\ (\mu\text{-}C_6H_4(CO_2CH_2CH_2Ph)_2))_2$[325] and $(TiCl_4(\mu\text{-}C_6H_4(CO_2Et)_2))_2$[326,327] were ester-bridged dimers. Moreover, the reaction of $TiCl_4$ with $C_6H_4(CO_2Me)_2$ formed a polymeric chain with the formula $(TiCl_4(\mu\text{-}C_6H_4(CO_2Me)_2))_n$.[318] Similarly, the reaction of $TiCl_4$ with $C_6H_3(CO_2Me)_3$ in a 1:1 ratio in dichloromethane led to the dimeric compound $(TiCl_4(C_6H_3(CO_2Me)_3))_2$, while the analogous reaction using a 1:3.5 ratio in dichloroethane led to the two-dimensional polymer $(TiCl_4(C_6H_3(CO_2Me)_3))_n$.[328]

Monomeric ketone donor adducts such as $TiCl_4(Ph_3PCHC(O)R)(THF)$ ($R = Me$, Ph),[329] $TiCl_4(Me_2C(COMe)_2)$,[330] $TiCl_4(Ph_2CO)_2$[331] and $TiCl_4\ (C_{10}H_{14}O_2)$ (**39**)[332] have been described.

Solid state ^{13}C NMR spectroscopy was used to study the chelation in ketone,[333] diketone,[334] ethylacetate,[335] and dialkyl phthalate adducts of $TiCl_4$.[336] Related studies of such adducts employing EXAFS, XANES,[337,338] and theoretical calculations[339,340] have also been reported.

Treatment of $TiCl_4$ with 18-crown-6 formed the corresponding 1:1 adduct in which the crown coordinated to Ti in a bidentate fashion.[341] The reaction of $TiCp_2Cl_2$ with HCl and 18-crown-6 led to the isolation of $[(H_3O)(18\text{-crown-}6)][TiCl_5(H_2O)]$.[342] The ionic compound $[TiCl_3(15\text{-crown-}5)(MeCN)][SbCl_6]$ was prepared by the reaction of $TiCl_4$ with 15-crown-5, and $SbCl_5$. Crystallographic studies revealed an octahedrally coordinated Ti center, with the chloride ligands adopting a *facial* arrangement.[343] The corresponding reaction of 12-crown-4 with $[TiCl_3(MeCN)_3][SbCl_5]$ after inadvertent hydrolysis yielded the oxo dimer $[TiCl(\mu\text{-}O)(12\text{-crown-}4)]_2[SbCl_6]_2$ (**40**).[344]



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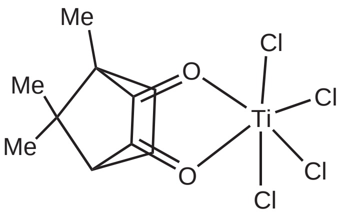

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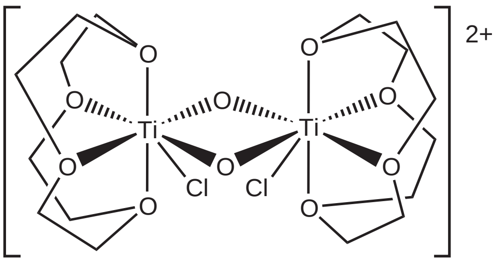

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A variety of neutral heteroatom-based oxygen donors have formed neutral adducts with $TiCl_4$. Such complexes include $TiCl_4(OP(NMe_2)_3)_2$,[345] $TiCl_4(OP(NC_5H_{10})_3)_2$,[30] $(Ti(\mu\text{-}Cl)Cl_3(SO_2))_2(C_6H_6)_2$, $(Ti(\mu\text{-}Cl)Cl_3(SO_2))_2(C_6H_2Me_4)_2$,[346] $(TiCl_4)_2(S_6N_4(\mu\text{-}O_4))$,[347] $TiCl_4(ONPh)_2$,[348] $TiCl_4(EtOCOC_5H_4NO)$, $TiCl_4(C_8H_6N_2O)$, $TiCl_4(C_{10}H_8N_2O)$, $TiCl_4(C_8H_6(NO)_2)$,[349] and the benzofuroxan derivatives $TiCl_4\ (C_6H_4N_2O_2)$, $TiCl_4(C_6H_3N_2O_2(OMe))$, $TiCl_4(C_6H_3N_2O_2(Me))$, $TiCl_4(C_6H_3N_2O_2(OMe))_2$, $TiCl_4(C_6H_3N_2O_2(Me))_2$, $TiCl_4(C_6H_3N_2O_2(Cl))_2$, $TiCl_4(C_6H_3N_2O_2Cl)_2$, and $TiCl_4(C_6H_4N_2O_2Me)_2$.[350] More recently, the X-ray crystal structure of the dimeric sulfoxide adduct, $(TiCl_3\ (\mu\text{-}Cl)(SOCl_2))_2$, was solved.[351] Co and Ni bis-dialkoxyphosphate complexes, $M(O_2P(OR)_2)_2$, also coordinate to $TiCl_4$. Coordination is thought to occur via the alkoxide oxygen atoms.[352]

Reaction of $TiCl_4$ and 4,4′-methylenebis(antipyrine) (also called diantipyrylmethane or dam) in perchloric acid afforded the salt $[Ti(dam)_3][ClO_4]_4$.[353] Crystallographic data revealed that this Ti cation was six coordinate with unusual eight-membered chelate rings. Aromatic ring stacking was presumed to be responsible for the orange color.

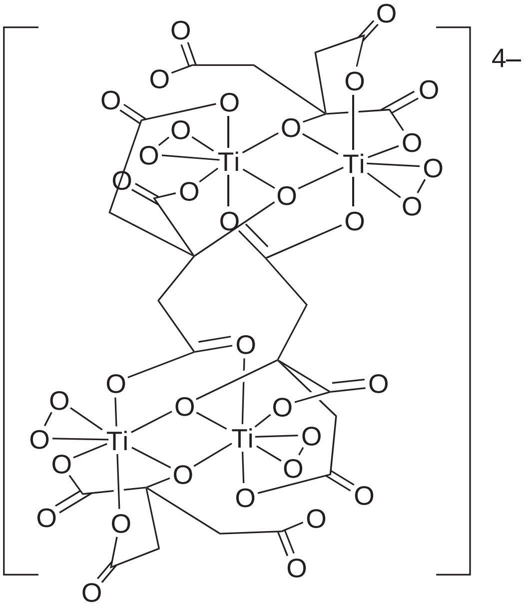
$TiCl_4$ is used extensively as a Lewis acid in numerous organic transformations, forming adducts that mediate reactivity. Such reactions include Diels Alder,[354,355] hetero Diels Alder,[356] cyclization of olefinic aldehydes,[357] Hosomi–Sakurai allylic coupling reactions,[358] cyclopropanations,[359] chalcogen-Baylis–Hillman,[360] Mukaiyama Aldol reactions,[361–363] reductions of ketones to alcohols,[364] and stereoselective nucleophilic additions to aldehydes.[365]

4.2.2.5.2 Oxide, hydroxide, and peroxo ligand complexes

Several peroxo complexes of the form $Ti(O_2)(X)_2(L)$ (X = monoanionic ligand and L = neutral ligand) have been prepared. Those that have been crystallographically characterized include $Ti(O_2)(C_6H_4NO_2)_2(OP(NMe_2)_3)$,[366] $Ti(O_2)(C_4H_4N_2(CO_2)(CO_2H))(OC(Me)CHC(Me)O)(OP(NMe_2)_3)$,[367] $Ti(O_2)(NCO)_2(MeNCH_2CH_2)_3$ and $Ti(O_2)Cl_2$ $(MeNCH_2CH_2)_3$.[209] A variety of ligands such as ethylenediamine and 2-aminopyridine aided in the stabilization of a number of Ti–peroxo and Ti–bis(peroxo) complexes.[368,369] Many of these peroxo complexes were found to react with phosphines and sulfides to affect phosphine and sulfide oxidations.[366,368,370]

A number of Ti–alkylperoxide complexes such as the Bu^t–peroxide complex $(Ti(O_2Bu^t)(N(CH_2\text{-}CH_2O)_3))_2$ have been structurally characterized and studied by ^{17}O NMR.[371–373]

The tetrameric salt $[NH_4]_8[Ti_4(C_6H_4O_7)(O_2)_4]$ (**41**) has been structurally characterized.[374] Peroxo complexes of porphyrins are described in Section 4.2.2.4.24.



(41)

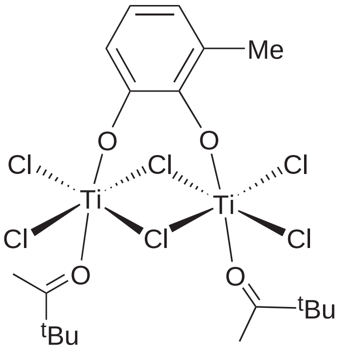
4.2.2.5.3 Alkoxide ligand complexes

The chemistry of mono[375–379] and hetero[376,380,381]-metallic alkoxides has been extensively reviewed. Such compounds have also been employed in a variety of organic transformations.[382–386]

Reaction of $Ti(OR)_4$ ($R = Pr^i$, Et) with excess fluoroalcohols (R^fOH ($R^f = CH(CF_3)_2$, C_6F_5, $C_6H_3F_2$, C_6H_4F)) yielded a series of complexes of the general formula $Ti(OR^f)_x(OR)_{4-x}(HOR)_n$ ($x = 2$–4, $n = 0$, 1).[387,388] X-ray crystallographic data of $Ti(OCH\ (CF_3)_2)_2(OEt)_2$ and $Ti(OC_6F_5)_3(OPr^i)$ confirmed dimeric complexes with two alkoxide bridges.[387] The monomeric complexes $TiCl_3(OCH_2CF_3)$ and $TiCl_3(OCH_2CF_3)(THF)_2$ were shown to polymerize alkyl isocyanates at 25 °C.[389–391]

The facile reactions of $TiCl_3(OPr^i)$, with a variety of O and N donors gave octahedral adducts.[392] In the case of pinacolone $(OC(Me)(Bu^t))$ a 1:2 adduct was formed and exchange of free and bound pinacolone was shown to proceed via a dissociative mechanism. An X-ray crystal structure established the dimeric nature of $(TiCl_2(\mu\text{-}Cl)(OC(Me)(Bu^t)))_2(\mu\text{-}O_2C_6H_9Me)$ (**42**).[393] Other dimeric derivatives of $TiCl_3(OPr^i)$ have also been described.[394,395]

The dimer $(TiCl_2(\mu\text{-}Cl)(OPr^i)(PhCHO))_2$ reacted with oxygen donors to give the monomeric derivatives $TiCl_3(OPr^i)(PhCHO)L$ (L = DMF, DMSO, Pr^iOH). The weakly coordinated PhCHO accounts for the highly dynamic nature of these compounds.[396] Similarly, dynamic interactions of $TiCl_3(OPr^i)$ with bidentate ligands containing methoxy and hydroxyl groups have been reported. The reaction of $TiCl_3(OPr^i)$ with $HOCH_2CH_2OMe$ in benzene yielded $TiCl_3(OPr^i)(HOCH_2CH_2OMe)$, while analogous reactions in the presence of NEt_3 in CH_2Cl_2 or in THF yielded $[HNEt_3][TiCl_3(OPr^i)(OCH_2CH_2OMe)]$ and $TiCl_3(OPr^i)(HOCH_2CH_2OMe)(THF)$ respectively. Similarly, when $TiCl_3(OPr^i)$ was reacted with DME, $TiCl_3(OPr^i)(DME)_2)$ formed. The solid



(**42**)

state structure of $TiCl_3(OPr^i)(HOCH_2CH_2OMe)$ showed the OH group *trans* to the OPr^i group.[397] The reaction of $TiCl_3(OPr^i)$ with $C_6H_4(NH_2)OH$ in CH_2Cl_2 gave the dimer $(TiCl_3(OPr^i)(OC_6H_4NH_3))_2$, however, when conducted in THF the monomeric zwitterionic product formulated as $TiCl_3(OPr^i)(OC_6H_4NH_3)(THF)$ formed. Addition of NEt_3 to the reaction mixture afforded the salt $[HNEt_3][TiCl_3(OPr^i)(OC_6H_4NH_2)]$.[398]

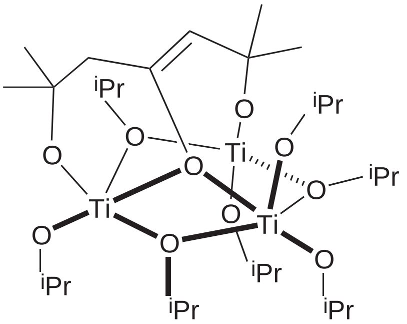
The Ti–tritox (tritox = tri-*tert*-butylmethoxide) complexes $TiCl_n(OCBu^t_3)_{4-n}$[399] when alkylated, reacted with O_2 to form $TiMe_n(OMe)_{3-n}(OCBu^t_3)$. A bimolecular methyl–methoxy exchange mechanism was proposed.[400] Theoretical and FTIR studies have probed the nature of Ti—O multiple bonding in Ti^{IV} alkoxide complexes.[401,402]

Titanium tetrabutoxide formed 1:2 adducts with $Si(OBu)_4$ and $(Me_3Si)_2O$.[403] Solid state structures of the six-coordinate complexes formed from reactions of $TiCl_3(OPr^i)$ with donor ligands such as aldehydes, chlorides, esters, THF, and diethyl ether indicated the bonding order: $OPr^{i-} > Cl^- > THF > Et_2O > PhCHO > \mu\text{-}Cl^- > RC(O)OMe$. This study suggested that the lability of ligands *trans* to the alkoxide may contribute to the efficiency of Ti alkoxides as catalysts or reagents.[392]

The alcoholysis of $Ti(OPr^i)_4$ gave a variety of dimeric trigonal bipyramidal complexes including $(Ti(\mu\text{-}OC_6H_3F_2)(OC_6H_3F_2)_2(OPr^i))_2$,[387] $(Ti(\mu\text{-}OCH_2Bu^t)(OCH_2Bu^t)_3)_2$,[404] and $(Ti(OC_6H_2Me_3)(\mu\text{-}OPr^i)(OPr^i)_2)_2$.[405] More recently the compound $[NBu_4][(Ti(OPr^i)_3)_2(\mu\text{-}F)_2(\mu\text{-}OPr^i)]$ was derived from the reaction of $Ti(OPr^i)_4$ and $[NBu_4][HF_2]$.[406]

Dimeric six-coordinate Ti complexes have also been structurally characterized including $(TiCl_2(\mu\text{-}OCH_2CH_2X)(OCH_2CH_2X)(HOCH_2CH_2X))_2$ (X = Cl, Br, I)[407] $(TiCl_2(\mu\text{-}OPr^i)(OPr^i)(HOPr^i))_2$, $(TiCl_3(\mu\text{-}Cl)(HOPr^i))_2$, $(TiCl_2(\mu\text{-}Cl)(OPr^i)(HOPr^i))_2$,[394] and $(TiCl_2(\mu\text{-}Cl)(OPr^i)(PhCHO))_2$.[396]

A number of Ti–oxo–alkoxide aggregates based on a triangular arrangement of three Ti atoms have been characterized. These include $Ti_3(\mu^3\text{-}O)(\mu\text{-}OPr^i)_3(\mu^3\text{-}X)(OPr^i)_6$, (X = OPr^i, OMe,[408] F[409]), $Ti_3(\mu^3\text{-}O)(\mu^3\text{-}Cl)(\mu\text{-}OCH_2Bu^t)_3(OCH_2Bu^t)_6$,[404] $Ti_3(\mu^3\text{-}O)(\mu^3\text{-}OPr^i)_2(OPr^i)_5(O_2CCCl_3)_3$,[410] $Ti_3(\mu^3\text{-}O)(\mu\text{-}OPr^i)_3(OPr^i)_4(Me_2C(O)CHC(O)CH_2C(O)Me_2)$ (**43**).[411] In contrast, both the complexes $Ti_3((OC_6H_4CH_2CH_2CHO)_2C_2H_2(O_2CEt_2))_3$[412] and $Ti_3(OPr^i)_6(C_6H_9O_3)_2$[413] adopted linear arrangements of Ti atoms. Other reports have described related Ti–oxo–alkoxide aggregates.[408,414]



(**43**)

More recently, the reaction of $[Ph_3PCH_2C(O)Ph]Br$ with $Ti(NMe_2)_4$ formed the zwitterionic Ti alkoxide $TiBr_2(NMe_2)_2(OC(Ph)CHPPh_3)$. This complex was shown to adopt a trigonal–bipyramidal geometry.[415]

The combination of $Ti(OPr^i)_4$ and $(Bu^tO)_2$ or Bu^tO_2H has been utilized in a number of organic transformations including the Sharpless epoxidation,[416] the conversion of alcohols to carbonyl compounds,[417] the oxidation of phenols to quinones or ketols,[418] and the oxidation of Ti enolates to α-hydroxyketones.[419]

4.2.2.5.4 *Aryloxide ligand complexes*

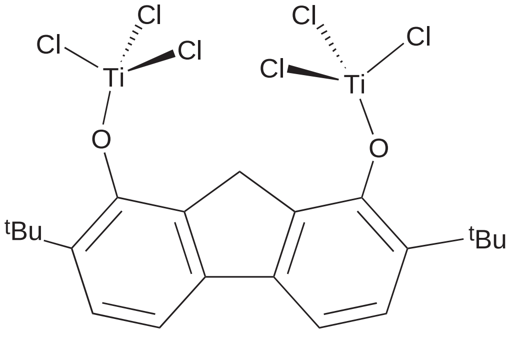
Aryloxide complexes have been studied for some time. In an early report, $Ti(CH_2CHCH\text{-}CH_3)(OPh)_3$ has been utilized as a catalyst for diastereoselective syntheses of alcohols.[420] The complexes $TiCl_{4-n}(OC_6H_4X)_n$ ($X = Cl$,[421,422] Bu^t, Ome[423]) and $TiCl_{4-n}(OC_6H_2Me_3)_n$ ($n = 1$–3)[424] were generated by the reaction of $TiCl_4$ with the corresponding phenol. The chlorophenoxy titanium derivative reacted with a variety of α-hydroxy aldehydes and ketones, whereas the latter compounds reacted with neutral donors (L = pyridine, THF, bipy, picoline) to form adducts of the form $TiCl_{4-n}(OC_6H_2Me_3)_nL_2$.[424,425]

A series of reports have described complexes incorporating varying stoichiometries of substituted phenolate ligands.[426–439] Alcoholysis of $Ti(OPr^i)_4$ by $HOC_6H_4NH_2$ yielded $Ti(OC_6H_4NH_2)_4$. Ligand redistribution reactions of this complex with $TiCl_4$ in varying ratios led to the mono-, di-, and tri-substituted aryloxide–Ti complexes $TiCl_n(OC_6H_4NH_2)_{4-n}$.[440] A number of these complexes were crystallographically characterized and were also observed to form adducts with donor ligands.[424,441,442] For example, the complexes $TiCl_{4-n}(OPh)_nL_2$ (L = PMe_3, PPh_3, PhCOMe, Ph_2CO) and $TiCl_{4-n}(OPh)_nL$ (L = $Me_2PCH_2CH_2PMe_2$, $Bu_2PCH_2CH_2PBu_2$, TMEDA)[443,444] have been prepared and characterized.

$Ti(NEt_2)_2(OC_6H_3MeBu^t)_2$ and $Ti(NMe_2)_2(OC_6H_2Bu^t{}_3)_2$ were synthesized by reacting $Ti(NR_2)_4$ with the corresponding phenol.[445,446] Procedures for converting these amido derivatives to the corresponding chloride derivatives were based on reactions with $SiCl_4$ and Me_3SiCl respectively. In a similar manner, $TiCl_2(OC_6H_3MeBu^t)_2$ was converted to $TiX_2(OC_6H_3MeBu^t)_2$ (X = Br, I) via reaction with BX_3.[447] Ti–oxo–aryloxide derivatives $TiO(OC_6H_3Pr^i{}_2)_2(NC_5H_4(NC_4H_8))$ and $(Ti(\mu\text{-O})(OC_6H_3Pr^i{}_2)_2(NC_5H_4(NC_4H_8)))_2$ containing terminal[448] or bridging[449] oxo groups, respectively, have also been characterized.

Similarly, the naphthoxide complexes $TiCl_{4-n}(OC_{10}H_7)_n$ ($n = 1$–4) have been prepared.[450] Formation of adducts with alcohols,[450] carbonyl compounds,[451] N bases,[452] formamides, acetamides, sulfoxides, phosphorous oxides,[453] amine oxides,[454] and acetoacetanilide[455] have been described. Complexes containing linked aryloxide fragments were derived from the reaction of bis(dimethylethyl)fluorene-1,8-diol with $TiCl_4$. The products $Ti_2Cl_6(O_2C_{13}H_6Bu^t{}_2)$ (**44**) and $Ti_2Cl_6(O_2C_{13}H_6Bu^t{}_2)(OC(C_6H_4Me)_2)$ were both crystallographically characterized.[456]

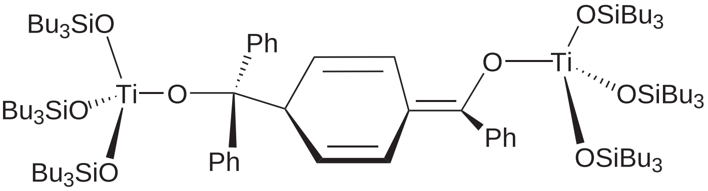
Titanium complexes containing polymerizable vinyl-substituted aryloxide ligands have been employed to prepare polystyrene/divinylbenzene-based polymers that incorporate Ti–aryloxide fragment into the matrix.[446] Such materials have been used to catalyze Diels–Alder reactions with high diastereoselectivity and at rates only three to five times slower than the corresponding homogeneous reactions.[446,447]



(**44**)

4.2.2.5.5 Siloxide ligand complexes

The addition of three equivalents of $Na[OSiBu^t_3]$ to $TiCl_4$ yielded $TiCl(OSiBu^t_3)_3$. Reduction with Na/Hg and subsequent oxidation with Ph_2CO gave the Ti–ketyl complex $Ti(OSiBu^t_3)_3(OCPh_2)$ in which dissymmetric dimerization afforded $Ti(OSiBu^t_3)_3(OCPh_2)C_6H_5C(Ph)OTi(OSiBu^t_3)_3$ (**45**). Subsequent addition of Ph_3SnH gave $Ti(OSiBu^t_3)_3(OCHPh_2)$.[457] In more recent work, it was shown that $Ti(OSiBu^t_3)_3$ could be readily oxidized in reactions with CCl_4. $RhCl(PPh_3)_3$, Br_2, I_2, MeI, *neo*-PnBr to $TiX(OSiBu^t_3)_3$ (X = Cl, Br, I, Me, *neo*-Pn) respectively. Similarly, reaction of $Ti(OSiBu^t_3)_3$ with THF gave the dimer $(Ti(OSiBu^t_3)_3)_2(\mu\text{-}OCH_2CH_2CH_2CH_2)$; however, when conducted in the presence of Ph_3SnH both the dimer and the monomeric complex $Ti(OSiBu^t_3)_3(OCH_2CH_2CH_2Me)$ were produced. Photolysis of $TiBn_2(OSiBu^t_3)_2$ in THF gave $(Ti(OSiBu^t_3)_2(OCH_2CH_2CH_2CH_2))_2$.[458]



(**45**)

The addition of two equivalents of $Na[OSiBu^t_3]$ to $TiCl_4$ yielded $TiCl_2(OSiBu^t_3)_2$. Subsequent reaction with $Li[NHSiBu^t_3]$ afforded $TiCl(OSiBu^t_3)_2(HNSiBu^t_3)$. An archive of alkyl, aryl, alkenyl, and hydrido derivatives $TiR(OSiBu^t_3)_2(HNSiBu^t_3)$ have been synthesized. Kinetic studies of 1,2-RH elimination reactions supported a first order process for the C—H activation and the equilibrium measurements allowed for the derivation of a relative free energy scale.[126,127] In related work, inter- and intramolecular equilibrium isotope effects and absolute Ti—R bond enthalpies for $TiR(OSiBu^t_3)_2(HNSiBu^t_3)$ have been reported.[459,460]

The complex $TiCl_3(OSiPh_3)$ was prepared by the protonolysis of $TiCl_4$ with $HOSiPh_3$. A comparison of the crystal structure of this complex to that of $TiCl_3(NPPh_3)$ showed that both contained tetrahedral Ti atoms.[98] The octahedral complex $TiCl_2(OSiPh_3)_2(THF)_2$ was prepared and activated to catalyze the selective formation of methylenecyclopentane from 1,5-hexadiene.[461] However, in the complexes $Ti(OSiPh_3)_4$ and $Ti(OGePh_3)_4$, steric congestion about the Ti atoms is believed to contribute to the catalytic inactivity toward the epoxidation of alkenes.[462]

$(Cy)_8Si_8O_{10}(OH)_2$ has been shown to react with TiX_4 (X = Cl, Bn) to give oligomeric materials formulated as $((TiX_3)_2(Cy)_8Si_8O_{12})_n$. These materials were active homogeneous catalysts for alkene epoxidation reactions.[463]

4.2.2.5.6 Miscellaneous anionic oxygen ligand complexes

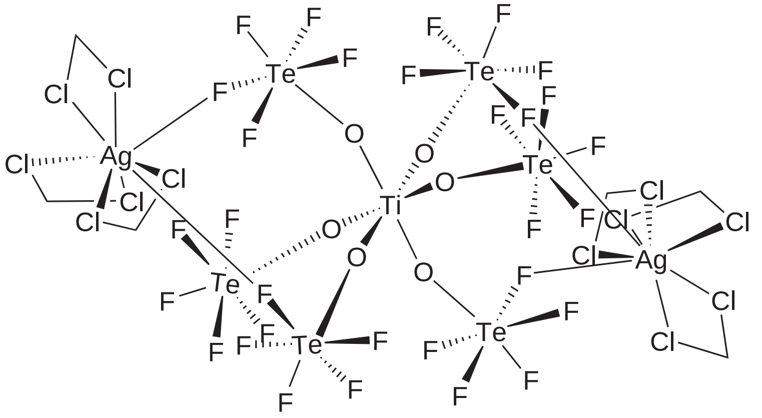
Ti–alkoxide complexes have been used to effect alkoxide group exchange with phosphorus diesters. For example, $Ti(OBu^t)_4$ reacted with $(MeO)_2P(O)H$ to give $(MeO)(Bu^tO)P(O)H$, while the analogous reaction with $Ti(OEt)_4$ gave $(EtO)_2P(O)H$.[464] The reaction of $Ti(OR)_4$ (R = Et, Pr^i) with $(OBu^t)_2P(O)(OH)$ yielded $Ti_2(OR)_6(O_2P(OBu^t)_2)_2$.[465]

Treatment of $TiCl_4$ with six equivalents of $AgOTeF_5$ afforded $[Ag]_2[Ti(OTeF_5)_6]$. A crystallographic study of $[Ag]_2[Ti(OTeF_5)_6]$ (**46**) revealed octahedral Ti and Te cores.[466] The reaction of $TiCl_4$ with $[Ph_4P][OSPCl_2]$ led to the formation of $[Ph_4P]_2[Ti(\mu\text{-}Cl)Cl_3(OSPCl_2)]_2$. Crystallographic data confirmed the dimeric nature of the complex and coordination of the oxygen atom to titanium.[118]

4.2.2.5.7 Heterometallic alkoxide complexes

A plethora of other heterometallic alkoxide complexes containing Ti have been reported and reviewed.[379,380,467–470]

Compounds with the general formula $M[Ti(OPr^i)_5]$ (M = Li, Na, K) have been reported.[471,472] Within this family of complexes only the Li salt, $(Li[Ti(OPr^i)_5])_2$, was isolated as a dimer. This compound contained two approximate trigonal–bipyramidal Ti centers.[471] In contrast, the Na and

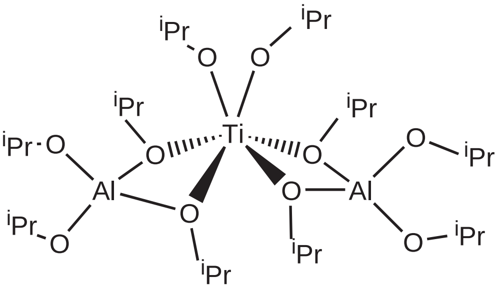


(**46**)

K analogues were linear and nonlinear polymers respectively.[472] All of the analogous *neo*-pentyloxide derivatives $(MTi(OCH_2Bu^t)_5)_2$ (M = Li, Na, K) were characterized as dimers, presumably as a result of the increased steric bulk of the ligand.[473] The related Al complex $Al_2Ti(\mu\text{-}OPr^i)_4(OPr^i)_6$ (**47**) was prepared from the reaction of Al turnings and $Ti(OPr^i)_4$.[475]

The mixed metal alkoxide $Bi(\mu\text{-}OPr^i)_2(\mu_3\text{-}O)(Ti_2(\mu\text{-}OPr^i)_2(OPr^i)_5)$ was obtained from the controlled hydrolysis of a reaction mixture of $Ti(OPr^i)_4$ and $BiO(OPr^i)$. Both Ti centers are six-coordinate while the Bi center is four-coordinate with a stereochemically active lone pair of electrons.[476]

A series of reactions have been carried out in which $K[Ti_2(OPr^i)_9]$ has been employed as a synthon for heterometallic alkoxides. For example, CdI_2 reacted with this complex to give the compound $[CdI][Ti_2(OPr^i)_9]$. Subsequent reaction of $[CdI][Ti_2(OPr^i)_9]$ with $K[Ba(OPr^i)_3]$ gave the heterometallic complex $(Cd[Ti_2(OPr^i)_9]Ba(OPr^i)_3)_2$ (**48**). Structural data revealed that metal rearrangements led to alkoxide bridging between Ba and Ti and between Ba and Cd.[477] Subsequent



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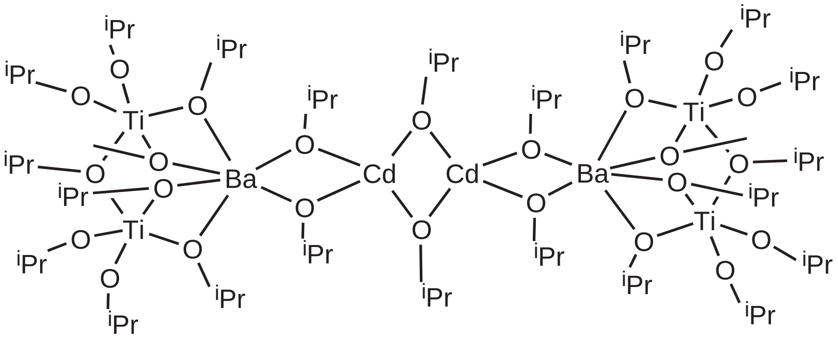
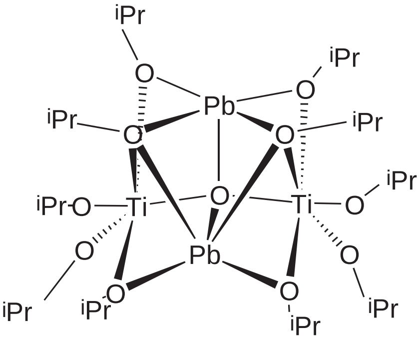


(**48**)

studies applied similar strategies to obtain $Cl_2Y(Ti_2(OPr^i)_9)$, $ClY(Ti_2(OPr^i)_9)_2$, $ClCu(Ti_2(OPr^i)_9)$, $(Ba(Ti_2(OPr^i)_{10}))_2$, $Ba(Ti(OPr^i)_5)(Ti_2(OPr^i)_9))$, $Ba(Ti_2(OPr^i)_9)_2$[478] The tin salt $[Ti_3(OPr^i)_{11}][(Sn_2I_6(\mu\text{-}OPr^i)_3]$ was obtained in the reaction of SnI_4 and $KTi_2(OPr^i)_9$. However, reaction of $[ClSn(Ti_2(O\text{-}Pr^i)_9)]_2$ with $SnCl_2$ afforded $[SnTi_2(OPr^i)_9][SnCl_3]$.[479]

Lead acetate ($Pb(O_2CMe)_2(H_2O)_3$) and Ti tetraalkoxides act as precursors to lead titanate, $PbTiO_3$, a ferroelectric material with applications in microelectronics.[480–485] A number of studies have attempted to identify precursors to $PbTiO_3$ in solution.[486–489] Related investigations have suggested the complexes $Pb_2Ti_2(O)(O_2CR)_2(OPr^i)_8$ ($R = C_3F_7$, Bu^t), $Pb_3Ti_3(O)_4(O_2CMe)_2(OPr^i)_7(OC(Me)\text{-}CHC(Me)O)$, $Pb_2Ti_2(O)(OEt)_8(OC\ (Me)CHC\ (Me)O)_2$, and $Pb_2Ti_2(O)(O_2CMe)_2(OPr^i)_8$.[490] Similarly, the reaction of $Ti(OPr^i)_4$ with $Pb_4O(OPr^i)_6$ or $Pb_6O_4(OPr^i)_4$ yielded $Pb_3TiO(OPr^i)_8$.[491] The X-ray crystallographic structures of the precursors to $PbTiO_3$, $Pb_2Ti_2(\mu^{\mathbf{4}}\text{-}O)(\mu^3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_4(OPr^i)_4$ (**49**),[492] and $Pb_2Ti_2(\mu^{\mathbf{4}}\text{-}O)(\mu\text{-}O_2CMe)_2(OPr^i)_8$[493] have been determined.

Transition-metal-based heterometallic alkoxide complexes have been prepared. For example, the heterometallic complex $Fe(Al(OBu^t)_4)(Ti_2(OPr^i)_9)$ was reported but not structurally characterized.[494] The reaction of $(Rh(\mu\text{-}OH)(COD))_2$ with $TiMe(OBu^t)_3$ at low temperatures afforded $(Ti(OBu^t)_2)_2\text{-}(\mu\text{-}O^3)(Rh(COD))_4$ (**50**)[495] In the same vein, the Ti/Rh complex $(Ti(OPr)_6Rh(COD))_2$ was obtained.[496]



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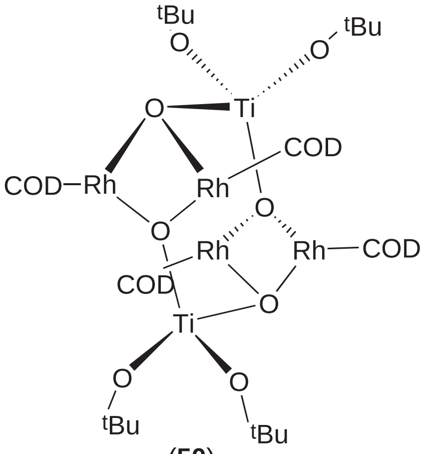
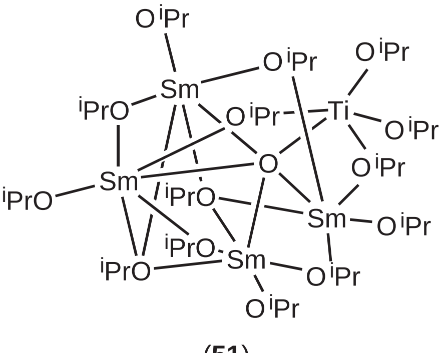


(**50**)

The protonolysis of $Ti(OR)_4$ with $Co_3(CO)_9(\mu^3\text{-}CCO_2H)$ led to a series of novel Co_3Ti clusters including $Ti_2Co_2((OCH_2)_3CMe)(OPr^i)_2(\mu\text{-}(CO)_9Co_3(\mu^3\text{-}CCO_2))_4$ and $(TiCo_3(OMe)_6(HOMe)(THF)\text{-}(\mu\text{-}(CO)_9Co_3(\mu^3\text{-}CCO_2)_3))_2$.[497] The Zr–Ti complex $TiZr_2(OCMe_2CMe_2O)_4(OCMe_2\ CMe_2OH)_2(OPr^i)_2$, and $Ti_2Zr_2(OCMe_2CMe_2O)_6(OPr^i)_4$ were derived from reactions of $Zr_2(OCMe_2\ CMe_2O)_2(OCMe_2C\text{-}Me_2OH)_4$ and $Ti(OPr^i)_4$ respectively.[498] The related Ti–Zr complexes $Ti_2Zr_4O_4\text{-}\ (OBu)_2(O_2C(Me)\text{-}CCH_2)_{14}$ and $Ti_2Zr_6O_6(O_2C(Me)CCH_2)_{20}$ were isolated from reactions of $Ti(OBu)_4$, $Zr(OBu)_4$ and methacrylic acid. The structures of these compounds are based on a zig-zag chain of TiO_6 and ZrO_8 or ZrO_7 units.[499]

The Sm–Ti complex $Sm_4Ti(\mu^{\mathbf{5}}\text{-}O)(\mu^3\text{-}OPr^i)_2(\mu\text{-}OPr^i)_6(OPr^i)_6$ (**51**) was derived from reaction of SmI_2 with $Na[Ti(OPr^i)_5]$.[500] The Ce–Ti mixed alkoxide complexes, $TiCe_2(OCMe_2\ CMe_2O)_2(OPr^i)_8$ and $Ti_2Ce_2O_2(OCMe_2CMe_2O)_4(OPr^i)_4(HOPr^i)_2$, were isolated and the latter compound has been structurally characterized.[501]



(**51**)

4.2.2.5.8 Diketonate ligand complexes

Various diketonate ligands, such as acetylacetone (acac), have been incorporated into Ti–halide,[502–508] Ti–alkoxide,[509–513] Ti–fatty acid[514] and Ti–oxo[515–517] complexes. Related tris(ketone) homometallic derivatives such as $Ti_2(OCMeCHC(CH_2COMe)O)_4(\mu\text{-}O)_2$ have been reported,[518] along with heterometallic derivatives such as $TiCl_2(OC(Bu^t)CHCO(C_6H_4PPh_2)_2PtCl_2$.[519]

For the symmetrically substituted complexes, $Ti(OCRCHCRO)_2(OR')_2$, ($R = Me$, Bu^t; $R' = Bn$, Pr^i, CH_2Pr^i, $C(Me)_2Ph$)) in the *cis*-geometry, there are two possible enantiomeric forms (Δ and Λ). These have been shown to interconvert at high temperatures.[520] Some of these derivatives were tested as photocatalysts for oxygenation of α-pinene with O_2[521] and as antitumor agents.[508]

4.2.2.5.9 O_2-monoanionic bidentate ligand complexes

Titanium complexes containing methylsalicylate, phenolphthalein,[522] furoic acid, isotan and picolinic acid ligands have been described.[523] Keto–alkoxide complexes such as $TiCl_3(O_2C_6H_7)$[524] and various maltolato derivatives[525,526] have been prepared and characterized.

Aryloxide–ether bidentate complexes such as $TiCl_2(OC_6H_4OMe)_2$, $(TiCl_2(\mu\text{-}Cl)(OC_6H_4OMe))_2$, $(TiCl(\mu\text{-}Cl)(OPr^i)(OC_6H_4OMe))_2$, $(TiCl(OC_6H_4OMe)_2)_2(\mu\text{-}O)$, and $TiCl_2(OPr^i)(OC_6H_4OMe)_2$ $(HOPr^i)$ were prepared via the reaction of the phenol with $TiCl_4$.[526,527] Crystallographic data confirmed a *cis* arrangement of the Cl atoms for $TiCl_2(OC_6H_4OMe)_2$ and $(TiCl_2(\mu\text{-}Cl)\text{-}(OC_6H_4OMe))_2$.

Other monoanionic bidentate oxygen-based ligand complexes include $TiCl_2((OPR_2)_2N)_2$ ($R = Cl$, Ph,[528] OPh,[529]), $TiCl_2(OPPh_2CH_2CH(Me)O)_2$, $TiCl_2(OPPh_2\ CH_2CH(Ph)O)_2$,[530] $TiCl_2(OC_{20}H_{12}P(O)Ph_2)_2$,[531] and $Ti(OPr^i)_3(OP(OMe)_2CH(OPr^i)O)$[532]. Similarly, a disulfone ligand has been used to prepare $Ti_2(\mu\text{-}OPr^i)_2(OPr^i)_4(HC(SO_2CF_3)_2)_2$ from $TiCl(OPr^i)_3$.[533] The reaction of $TiCl_4$ with Cl_2O_6 led to the formation of $Ti(ClO_4)_4$ in which the oxygen atoms of the perchlorate ligands bound to Ti in a bidentate fashion.[534]

Metal (Cu, Ni, Co) complexes containing ligands with pendent oxygen donors such as acids,[535] oxime donors,[536] enaminoketonates, or enaminoiminates,[537] have been reported to complex to titanium. Alternatively, the heterotrimetallic complex, $Ti(NMe_2)(OC(NMe_2))Fe(CO)_4(OC(NMe_2))_2Fe(CO)_3$, in which one of the two Fe centers forms a metallocyclic chelate ligand on Ti, was derived from the reaction of $Fe(CO)_5$ with $Ti(NMe_2)_4$.[538]

4.2.2.5.10 Carboxylate, carbamate, and oxolate ligand complexes

The reactions of several carboxylic acids (HCO_2R) or the corresponding alkali salts ($NaCO_2R$) yielded a series of derivatives of the form $Ti(O_2CR)_4$[539,540] and $TiX_{4-n}(O_2CR)_n$ ($X = OPr^i$, OC(Me)CHC(Me)O, OBu, Cl, aldehydes, ketones, Schiff bases).[410,541–547] The crystal structures of $(TiCl_3(O_2CBu^t))_3$, and $Ti_2Cl_7(O_2CR)(HO_2CR)$ ($R = C_6H_4Cl$, CHCHMe)[544,545] have been reported. The bonding modes observed for the carboxylate ligands included monodentate,[541,542] chelated bidentate,[539,540] or bridging bidentate.[545]

Similarly, the reaction of $Ti(OMe)_4$ with $O(OCCF_3)_2$ gave $Ti(OMe)_2(O_2CCF_3)_2$. Warming the analogous ethoxide derivative afforded $Ti_2O(O_2CCF_3)_6$.[548] The related oxo-bridged derivatives $(TiCl_2(\mu\text{-}O_2CR)(HO_2CR))_2(\mu\text{-}O)$ ($R = Me$, Et, Bu^t) and $(TiCl)_3(\mu\text{-}O_2CEt)_5(\mu^3\text{-}O)_2$ have also been structurally characterized.[549,550] The mononuclear oxo derivative $TiO(O_2CCH(Et)Bu)_2$ was prepared via treatment of $Ti(OR)_4$ ($R = n$Bu, Pr^i, $MeOC_2H_4$) with $HO_2CCH(Et)Bu)_2$.[551] Partial hydrolysis of $TiCl_n(O_2CR)_{4-n}$ gave $(TiCl_2(\mu\text{-}O_2CR))_2(\mu\text{-}O)$.[552] Similarly, the bridging oxo Ti^{III}/Ti^{IV} complex $Ti_2(\mu\text{-}O)Cl_3(O_2CPh)_2(THF)_3$ has been characterized.[553]

Ti complexes of Schiff-base carboxylate ligands,[554,555] isoindole–acetate ligands[556] and 2-furylacrylate ligands[557] have been described. Several examples of the applications of carbamate intermediate complexes in organic syntheses have also been reported.[558–560] Treatment of $TiCl_4$ with secondary amines and CO_2 yielded the monomeric eight-coordinate complexes $Ti(O_2CNEt_2)_4$ and $Ti(O_2CNPr^i{}_2)_4$.[561] Treatment of $Ti(O_2CNPr^i{}_2)_4$ with Ph_3SiOH afforded $Ti(O_2CNPr^i{}_2)_2(OSiPh_3)_2$.[562]

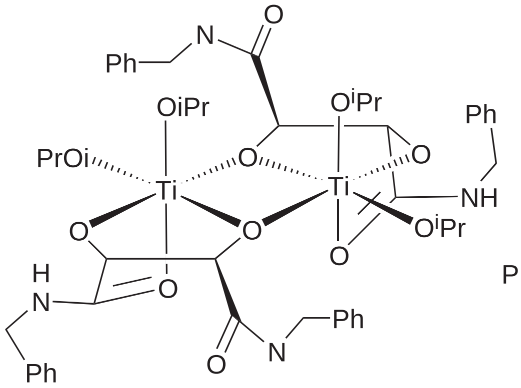
The oxolate salts $[NEt_4]_5[(TiO)_3(C_2O_4)_5(OH)]$, $[NEt_4]_6[(TiO)_4(C_2O_4)_6(OH)_2]$, and $[NEt_4]_8\text{-}[(TiO)_6(C_2O_4)_8(OH)_4]$ have also been characterized.[563]

4.2.2.5.11 Bidentate alkoxide ligand complexes

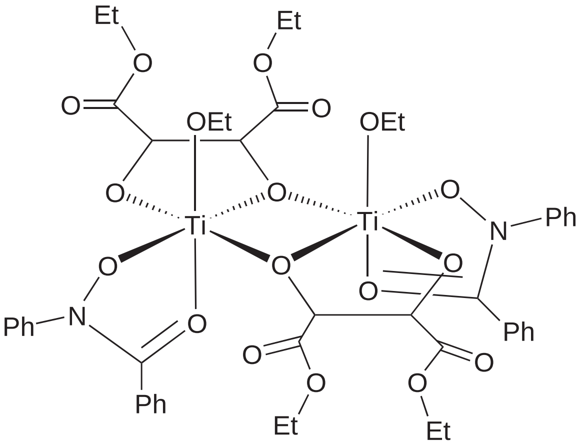
The first practical asymmetric epoxidation was reported by Katsuki and Sharpless.[416] The catalyst that was used in the epoxidation of allylic alcohols by $(\mathrm{Bu^tO})_2$ was prepared *in situ* with $\mathrm{Ti(OPr^i)_4}$ and diethyltartrate. Since then, synthetic applications and mechanistic details of these reactions have been widely explored and utilized.[564,565] Only a sampling of relevant reports have been cited.[416,566–575]

In 1984 the crystal structures of $\mathrm{(Ti(OPr^i)_2(OC(ONHCH_2Ph))_2)_2}$ (**52**) and $\mathrm{(Ti(OEt)(OC(OEt))_2)(ON(Ph)CPh))_2}$ (**53**) were determined.[576] Since then the propensity of the tartrate ligand to adopt multiple binding modes was confirmed by a number of other crystal structures.[577]

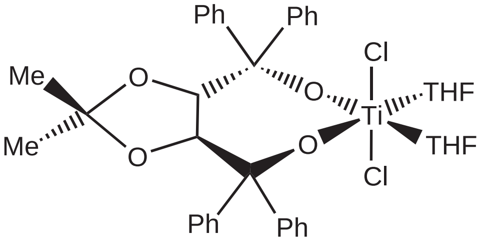
Various tetraaryl-1,3-dioxolane-4,5-dimethanol (TADDOL) ligands have been employed in the syntheses of a series of Ti–TADDOL derivatives[578] such as $\mathrm{TiCl_2(TADDOL)}$,[579] $\mathrm{TiCl_2(TADDOL)(THF)_2}$ (**54**),[515] and $\mathrm{Ti(OC(Ph)CHC(Ph)O)(TADDOL)(THF)_2}$.[580] Much of this chemistry has been reviewed.[383,386,581] Ti complexes of these ligands have been extensively used in asymmetric synthesis.[515,582–591]



(**52**)



(**53**)



(**54**)

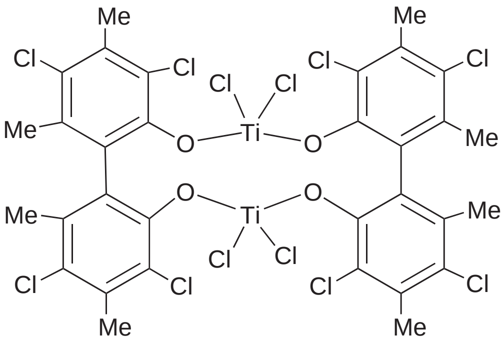
A variety of other titanium complexes containing dihydroxy ligands, such as dihydroxycoumarins,[592] glycolates,[593] arylbis(5-hydroxy-3-methyl-1-phenyl-4-pyrazolyl)methane,[594,595] 1-(*o*-hydroxybenzyl)-2-(*o*-hydroxyphenyl)benzimidazole,[596] and derivatives of ascorbic acid[597] have been described. The dimeric nature of the Ti–diolate complex $\mathrm{(Ti((OCHMe)_2CH_2)_2)_2}$ was determined by X-ray diffraction studies. In the gas phase this complex remained dimeric as shown by DCI–MS experiments.[598] Treatment of bis(dimethyldioxolanyl)ethanediol with $\mathrm{Ti(OPr^i)_4}$ afforded two dimeric species $\mathrm{Ti_2(OPr^i)_4(\mu\text{-diolate})_2}$ and $\mathrm{Ti(diolate)(OPr^i)(\mu\text{-}OPr^i)Ti(OPr^i)_3}$. These complexes catalyzed the enantioselective addition of $\mathrm{ZnEt_2}$ to aldehydes.[599] Related asymmetric diols were used *in situ* to prepare Ti complexes that were subsequently used in asymmetric reductions of ketones.[600,601]

4.2.2.5.12 Bidentate aryloxide ligand complexes

Neutral catechol derivatives of the form $\mathrm{TiCl_2(O_2C_6H_3R)L}$ ($\mathrm{R = H, Me, Bu^t}$; L = bipy, THF, $\mathrm{OEt_2}$)[602] have been prepared and used as catalysts in a variety of organic transformations.[603–606]

Synthetic methods used to prepare tris(catecholate)Ti salts have been standardized.[607] Related derivatives including $[NH_4]_2[Ti(O_2C_6H_4)_3]$, $Ba[Ti(O_2C_6H_4)_3]$,[608] $[HNEt_3]_2[Ti(O_2C_6H_4)_3]$, $K_4[TiO(O_2C_6H_4)_2]_2$, $[HNEt_3]_2[Ti(O_2C_6H_2Bu^t_2)_2(HO_2C_6H_2Bu^t_2)]_2$,[609] and $Cs_2[Ti(O_2C_6H_2PPh_2)_3]$[610] have been described. Several complexes with substituted biphenols of the form $(TiX_2(OC_6Me_2Cl_2)_2)_2$ (X = Cl, OPr^i) (**55**) have been structurally characterized illustrating that the biphenol ligands bridge the two Ti centers affording 14-membered rings.[611]

Several dicatechol derivatives with the general formula $1,2\text{-}(OH)_2C_6H_4RC_6H_4(OH)_2$ ($R = C_2H_4$,[612] C_6H_4,[613] CH_2,[614,615] $CH_2NHCOCHRNHCO$[616,617]) have been incorporated into Ti complexes of formulas $[M]_4[Ti_2L_3]$ or $[M]_2[Ti_2L_2(OMe)_2]$ (M = Li, Na, K). The former type of complex was described as having a triple-stranded dinuclear Ti center (**56**),[613] while the latter forms a double-stranded dinuclear Ti center.[616,617]



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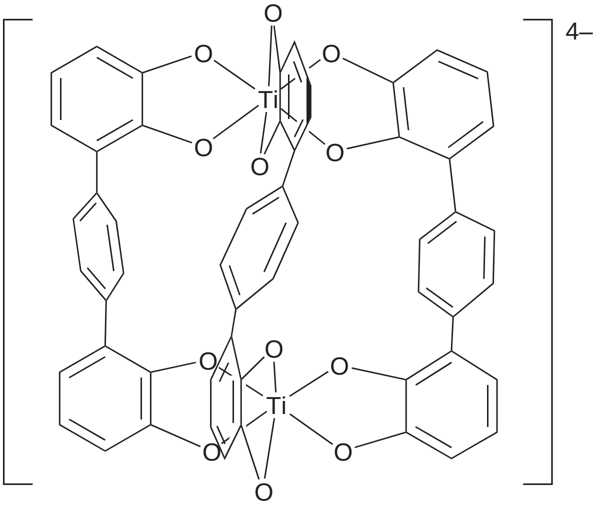


(56)

Naphthalenediols were used to prepare the dinuclear complexes $Ti_2Cl_6(C_{10}H_6O_2)$ and $(TiCl(\mu\text{-}Cl)(C_{10}H_6O_2)(OCPr^i_2))_2$.[618] Structural parameters of a few Ti binaphtholate complexes derived from the reaction of $Ti(OPr^i)_4$ and binaphthol have been determined by X-ray crystallography.[619,620] Ti derivatives of the chiral ligand 2,2′-dihydroxy-1,1′-binaphthol such as $(TiCl_2(O_2C_{20}H_{10}Me_2))_2$,[621] $TiCl_2(O_2C_{20}H_{12})$, and $(Ti(\mu\text{-}O)(O_2C_{20}H_{12}))_2$[622] have been prepared and employed in enantioselective catalysis of a number of organic reactions.[621,623]

A variety of Ti complexes with substituted binaphthalenediolate ligands have been reported.[624–629] Some of these derivatives have been employed in a variety of enantioselective catalytic reactions.[622,630–635] A related octahydrobinaphthol ligand has been employed to prepare $(TiCl_2(C_{20}H_{20}O_2))_2$ and $(Ti_2(OPr^i)_4(\mu\text{-}O)(C_{20}H_{20}O_2))_2$.[626]

A series of bis(phenol) complexes such as $TiCl_2((OC_6H_4)_2CMe_2)$, $TiX_2((OC_6H_2MeBu^t)_2CH_2)$ (X = Cl, Br, I, OMe, OPr^i, OBu^t), $TiCl_2((OC_6H_2MeBu^t)_2CH_2)(L)$ (L = THF, Bu^tNC), and $Ti((OC_6H_2RBu^t)_2CH_2)_2$ have been reported.[602,636–642] Subsequently, $Ti(\eta^3\text{-}BH_4)_2((OC_6H_2MeBu^t)_2CH_2)$ was prepared and structurally characterized.[643] A number of these complexes have been assessed as olefin polymerization pre-catalysts.[638,642]

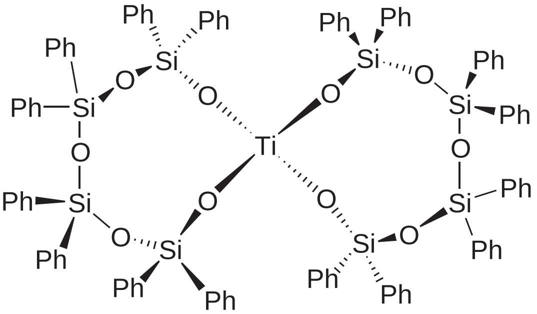
A relatively recent report has described the heterobimetallic diolate complex Ti $(OPr^i)_2((OCPh_2C_5H_4)_2Fe)$ derived from a substituted ferrocene ligand.[644]

4.2.2.5.13 Disiloxane ligand complexes

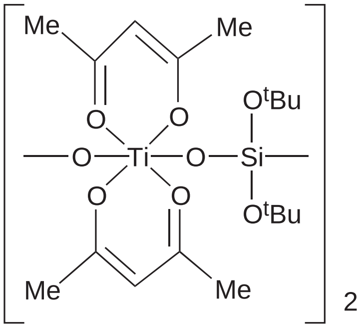
A number of Ti complexes containing di- or tri-siloxanediolate ligands have been obtained in metathesis reactions between $TiCl_4$ and the corresponding diolate. In this fashion the compounds *cis*-$Ti(OSiPh_2OSiPh_2OSiPh_2OSiPh_2O)_2$ (**57**),[645] and $Ti(OSiPh_2OSiPh_2OSiPh_2O)_2(NC_5H_5)_2$[646,647] were obtained. These complexes contain 10- and 8-membered titanasiloxane chelate rings respectively. In a more recent study the titanium salt $[Na(NC_5H_5)]_2[Ti(OSiPh_2OSiPh_2O)_3]$ was prepared.

The presence of three six-membered titanasiloxane chelate rings in this compound was confirmed crystallographically.[648]

The organosiloxane $Bu^t_2Si(OH)_2$ reacted with Ti halides to give the dimeric complexes $(TiX_2(\mu\text{-}O_2SiBu^t_2))_2$ (X = Cl, Br, I). X-ray data confirmed that these compounds contained eight-membered rings as a result of the bridging nature of the siloxane ligand.[649] Similarly, the reaction of $Ti(OC(Me)CHC(Me)O)_2(OPr^i)_2$ with $(Bu^tO_2)Si(OH)_2$ gave the cyclic compound $(Ti(OC(Me)CHC(Me)O)_2(\mu\text{-}O_2Si(OBu^t)_2))_2$ (**58**) in which the oxygen atoms of the silanediolate bridged the two Ti centers.[650]

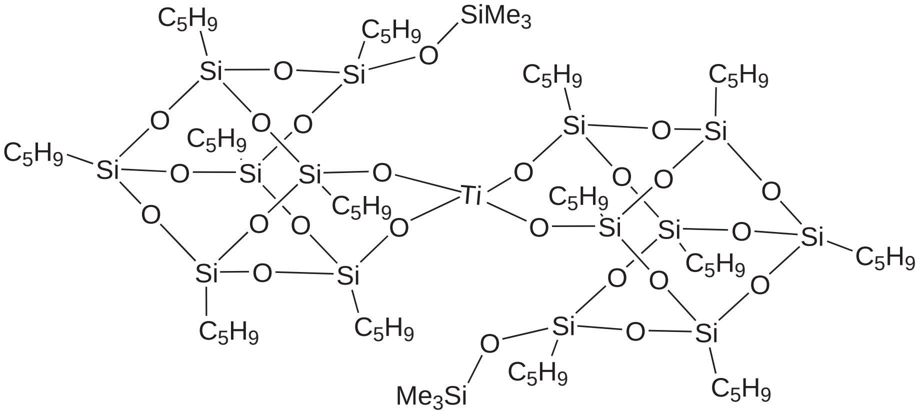


(**57**)



(**58**)

A more recent report has employed a silsesquioxane–disilanol ligand to prepare the complexes $Ti((Cy)_7Si_7O_{11}(OSiMe_3))_2$[651,652] and $Ti((C_5H_9)_7Si_7O_{11}(OSiMe_3))_2$ (**59**)[653] via reaction with $Ti(Bn)_4$ and $Ti(OPr^i)_4$ respectively.



(**59**)

4.2.2.5.14 *Borate ligand complexes*

The reaction of $(Ti(\mu\text{-}O)(OC(Me)CHC(Me)O)_2)_2$ with $B(C_6F_5)_3$ afforded the complex $Ti(OB(C_6F_5)_3)(OC(Me)CHC(Me)O)_2$.[654]

4.2.2.5.15 *Nitrate and sulfate ligand complexes*

The Ti sulfate complexes $TiCl_n(MeSO_3)_{4-n}$ ($n = 1$–3) were reported to react with mono-, di-, and trichloroacetic acids to give the corresponding complexes with the general formula $Ti(MeSO_3)_n(O_2CCl_mH_{3-m})_{4-n}$ ($n = 1$–3, $m = 1$–3). These complexes formed adducts with pyridine and bipyridine.[655] The complex $Ti(OMe)_2(SO_3F)_2$ was synthesized via the reaction between $Ti(OMe)_4$ and excess $S_2O_5F_2$.[656]

The triflate derivatives $TiCl_n(F_3CSO_3)_{4-n}$ ($n = 1$–3), $Ti(NO_2)_2(F_3CSO_3)_6$, and $Ti(OEt)_2(F_3CSO_3)_2$ were obtained from triflic acid hydrolysis of the appropriate Ti precursor.[548,657]

Thermal degradation led to the oxo compounds including $[(NO_2)NO)][TiO(F_3CSO_3)_4]$. Ti^{IV} triflate complexes efficiently catalyze a variety of reactions including the conversion of acetophenones to 1,3,5-triarylbenzenes,[658] the nucleophilic ring opening of epoxides,[659] Diels–Alder reactions,[660] selective Claisen and Dieckmann ester condensations,[661] esterification reactions,[662] Fries rearrangements,[663] homoaldol reactions,[664] sequential cationic and anionic polymerizations,[641] and the stereoselective synthesis of *cis*-arabinofuranosides.[606]

4.2.2.5.16 *Phosphate and phosphonate ligand complexes*

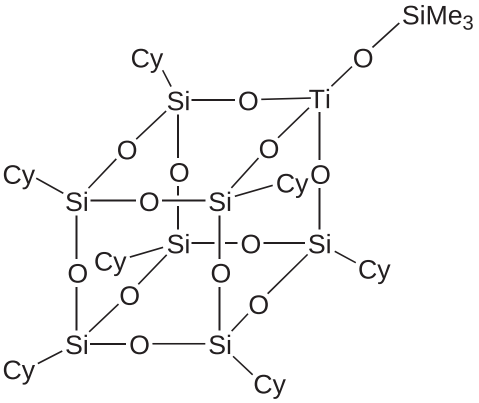
In 1986 the use of Ti phosphate ester derivatives as flame retardants and as hardening agents were patented.[665] In 1992, Thorn and Harlow synthesized the related compounds $Ti_2Cl_5(\mu\text{-}Cl)_2(\mu\text{-}O_2P(OSiMe_3)_2)(OP(OSiMe_3)_3)$ and $(TiNR'(\mu\text{-}O_2P(OR)_2)_2)_2$ ($R = Bu^t$, $SiMe_3$; $R' = Bu^t$, $C(Me)_2(Et)$).[666] The complex $(TiCl_3(\mu\text{-}O_2PCl_2)(OPCl_3))_2$ was shown to be a centrosymmetric dimer.[667] The related complexes $(Ti(OR)_3(\mu\text{-}O_2P(OR')_2))_2$ ($R = Et$, Pr^i; $R' = Bu^t$)[465] and $(Ti(OPr^i)_3(\mu\text{-}O_2P(R_2)_2$ ($R_2 = Ph_2$, $Bu^t/OSiMe_3$)[668] have also been prepared. Crystallographic data confirmed these complexes as centrosymmetric dimers with trigonal bipyramidal geometries at Ti.

4.2.2.5.17 *Dianionic tridentate ligand complexes*

Oxidation of the ligand $(HOC_6H_2MeBu^t)_2S$ permitted the preparation of the O_3 ligand complexes $(TiX_2(OC_6H_2MeBu^t)_2SO)_2$ ($X = Cl$, OPr^i) and $Ti((OC_6H_2MeBu^t)_2SO)_2$.[669] The related complex $TiCl_2((OCH_2CH_2)_2O)(THF)$ was prepared via the reaction of the diol with $TiCl_4$. This ligand was shown to bind in a *meridional* fashion.[670]

4.2.2.5.18 *Trianionic tridentate ligand complexes*

Complexes of the general form $(TiX((Cy)_7Si_7O_{12}))_n$ ($X = Bn$, NMe_2, $OSiMe_3$, OEt, OPr^i; $n = 1, 2$) were prepared and structurally characterized. $Ti(OSiMe_3)((Cy)_7Si_7O_{12})$ (**60**) was found to be monomeric[651] while $(Ti(\mu\text{-}OPr^i)((C_5H_9)_7Si_7O_{12}))_2$[671] and $(Ti(\mu\text{-}OEt)\ ((Cy)_7Si_7O_{12})\cdot HOEt)_2$ were found to be dimeric.[652] These compounds are models for heterogeneous titanosilicate catalysts and are active and selective catalysts for alkene epoxidation reactions.[651] Such compounds have been employed in high-speed catalyst optimization experiments.[672]

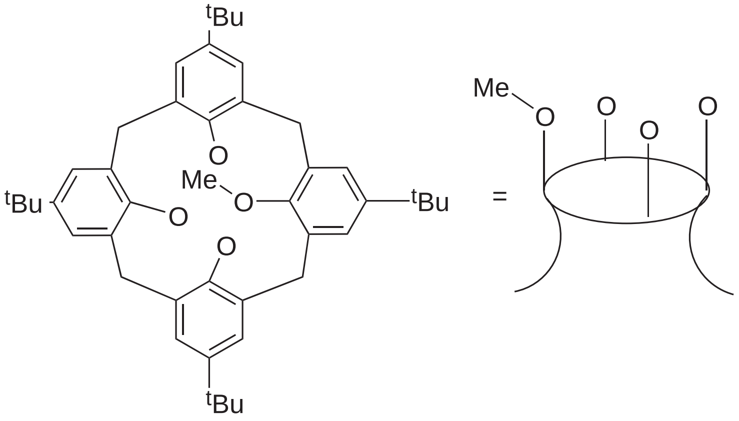


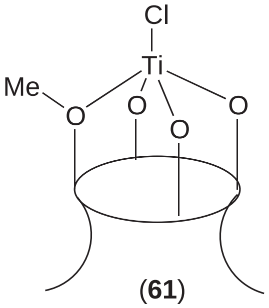
(**60**)

4.2.2.5.19 *Calix[n]arene complexes*

The macrocyclic calix[4]arene complex $(Ti(Bu^t\text{-}calix[4]arene))_2$ was prepared from $Ti(NMe_2)_4$ and the neutral ligand. One of the four O atoms of each ligand bridges the two titanium centers.[673] The related complex $TiCl(Bu^t\text{-}calix[4]arene(OMe)(O)_3)$ (**61**) was synthesized by a salt metathesis reaction. Subsequent displacement of the Cl by alkyl or aryl groups was readily accomplished.[674]

Similarly, Ti(NR)(calix[4]arene(OMe)$_2$)[675] and Ti(OC(Me)CHC(Me)O)(oxacalix[3]arene)[676] have been prepared. Related ligand complexes in which two of the adjacent calix[4]arene O atoms are functionalized by P and Si groups have also been reported.[677–679]

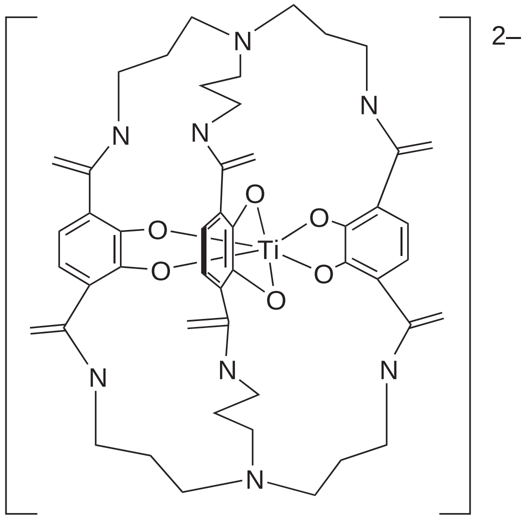




(**61**)

4.2.2.5.20 *Higher denticity ligand complexes*

A macrobicyclic tris(catecholate) bicapped cryptand ligand (BCT) was used to encapsulate the Ti ion in the complex K$_2$[Ti(BCT)] (**62**).[680,681]



(**62**)

4.2.2.6 Sulfur, Selenium, and Tellerium Ligand Complexes

4.2.2.6.1 *Neutral sulfur, selenium, and tellerium-based ligand complexes*

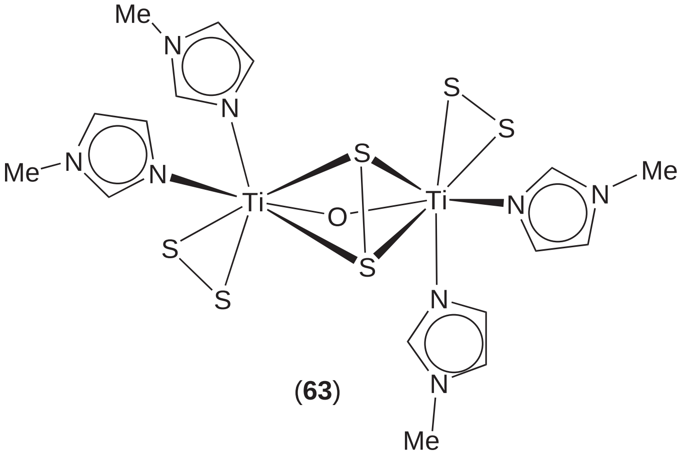
TiCl$_4$ adducts of thio-crown-ethers such as TiCl$_4$((SCH$_2$)$_3$)$_n$ ($n = 1$, 2),[682,683] TiCl$_4$((SCH$_2$CH$_2$)$_3$),[684] TiCl$_4$((SCH$_2$CH$_2$)$_2$)$_2$, TiCl$_4$(SCH$_2$)$_n$)$_m$ ($n = 4$, 5; $m = 1$, 2), and TiCl$_4$(SCHMe)$_3$[683] have been reported. Similarly, the neutral chelating bis(thiocarbamate) complex TiCl$_4$((S$_2$C(NC$_5$H$_{10}$))$_2$ CH$_2$),[685] and diphenylthiourea complexes TiCl$_4$(SC(NPh$_2$)$_2$)$_n$ ($n = 1$, 2)[686] have been described. The related dithiooxamide S$_2$-chelate complexes TiCl$_4$((SCNHR)$_2$) (R = Me, Et, CH(Me)$_2$Bu, Cy, Bn) have been described.[687] Moran and Cuadrado reported Ti adducts of several neutral phosphinosulfide ligands. Examples of these neutral ligands include Me$_2$P(S)NHP(S)Me$_2$, Ph$_2$P(S)NHC(S)NEt$_2$, and R$_2$P(S)SSP(S)R$_2$ (R = Et, OEt, OPr^i).[688] Similarly, dithiophosphoric acids reacted with TiCl$_4$ to give complexes of the form $TiCl_4(HS(S)P(O_2R)_2)_2$.[689] The adducts of bidentate sulfur donors $TiCl_4$-$(Et_2NC(S)NHC(S)Ph)$ and $TiCl_4((CH_2CH_2OCH_2CH_2N)C(S)$ $NHC(S)Ph)$ have also been characterized.[690]

Winter and co-workers have utilized the coordination chemistry of Ti–S compounds for applications in materials chemistry. Adducts of $TiCl_4$ with organothiols (HSR),[691,692] organosulfides (SR_2),[692] and organodisulfides (RSSR)[692] were prepared and characterized. The complexes $TiCl_4(HSCy)_2$ and $TiCl_4(HSC_5H_9)_2$ were employed as single-source precursors yielding high-quality TiS_2 films containing low C and Cl contaminants.[691]

Matrix isolation techniques have been employed to characterize 1:1 intermediate complexes in reactions between $TiCl_4$ and H_2S, MeSH, or Me_2S.[693] Organoselenide and organodiselenide adducts such as $TiCl_4(SeMe_2)_2$, $TiCl_4(SeEt_2)_2$, $TiCl_4(EtSeSeEt)$, and $TiCl_4(MeSeSeMe)$ have also been prepared by conventional methods. $TiCl_4(SeEt_2)_2$ was utilized as a precursor for the production of $TiSe_2$ films.[694] Related seleno–ether complexes with the general formula TiX_4 $(RSe)_2(CH_2)_n$ ($X = Cl$, Br; $R = Me$, Ph; $n = 1$, 2) and TiX_4 $(RSe)_2C_6H_4$ were also reported.[695]

4.2.2.6.2 *Sulfide, selenide, and telluride complexes*

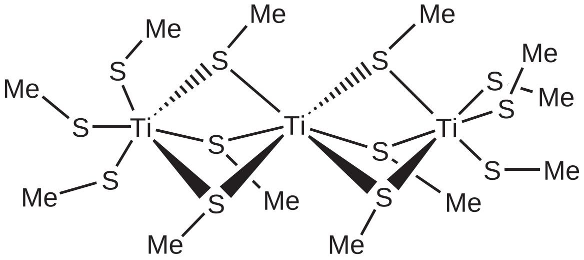
Examples of Ti/S complexes include the crystallographically characterized $[PPh_4]_2[TiSCl_4]$ and $[NEt_4]_2[TiSCl_4]$. In the presence of O_2, $[PPh_4]_2[Ti_3O(S_2)_3Cl_6]$ was obtained.[696] The complexes $Ti(S_2)_2(NC_5H_4R)_2$ ($R = H$, Bu^t) and $Ti(S_2)_2(N_2C_3H_3Me)_3$ were prepared from the reaction of $TiCl_4$ and ZnS_6 in the presence of a donor. The latter was oxidized to $(Ti_2S_6(O)(N_2C_3H_3Me)_4)$ (**63**) by O_2.[697]



(**63**)

4.2.2.6.3 *Thiolato, selenolato, and tellurolato ligand complexes*

$TiCl_4$ reacted with $Li[SBu^t]$ in the presence of a neutral chelating ligand (L) such as Me_2AsCH_2-CH_2AsMe_2, $Me_2PCH_2CH_2PMe_2$, or $Ph_2PCH_2CH_2PPh_2$ to give the complexes $TiCl_2(SBu^t)_2(L)$. X-ray diffraction studies showed that $TiCl_2(SBu^t)_2(Me_2AsCH_2CH_2AsMe_2)$ has a distorted octahedral geometry in which the Cl atoms are *trans* and the thiolate groups adopt a *cis* configuration.[698] A related series of complexes of the form $Ti(OPr^i)_2(SR)_2$ was derived from thiolysis of $Ti(OPr^i)_4$. These complexes formed adducts with N donors such NC_5H_5 and bipy.[699] $[NEt_4]_2$ $[Ti(SCH_2CH_2S)_3]$ was the first homoleptic thiolate Ti complex to be structurally characterized by X-ray crystallography. The geometry at Ti was found to be a trigonally distorted octahedral geometry.[700] A variety of studies including X-ray absorption, coulometry, and cyclic voltammetry have been performed on this compound.[701,702] The related homoleptic species $[NH_2Me_2]_2$ $[Ti(S_2C_6H_4)_3]$ was synthesized and characterized crystallographically. In the solid state this ionic molecule adopted a skewed trapezoidal bipyramidal geometry.[703] Analogous reactions of $Ti(NMe_2)_4$ with sterically less demanding thiols afforded dinuclear complexes such as $[NH_2Me_2]$ $[Ti_2(\mu\text{-}SMe)_3(SMe)_6]$ and the trinuclear complexes $Ti_3(\mu\text{-}SMe)_6(SMe)_6$ (**64**). In both cases three thiolate ligands bridged each pair of Ti centers.[704] Similar face-sharing bioctahedron motifs were determined for $[Li(C_4H_8O)_4][Ti_2(\mu\text{-}SC_6H_5)_3(SC_6H_5)_6]$[705] and $[NH_2Et_2]_2[Ti_2$-$(\mu\text{-}SBn)_3(SBn)_6]$.[706] Recently, an analogous homoleptic dianionic Ti complex containing monodentate thiolate ligands $[NEt_4]_2[Ti(SPh)_6]$ was synthesized and structurally determined.[707] Interest in Ti thiolate complexes as precursors to TiS_2 thin films has prompted the synthesis of the neutral homoleptic compound $Ti(SBu^t)_4$.[708,709] Ti thiolate derivatives have been reviewed.[710]



(**64**)

The reaction of $Ti(NEt_2)_4$ with excess HSC_6F_5 afforded the ionic complex $[NEt_2H_2]$ $[Ti(SC_6F_5)_5]$, which is the first confirmed 5-coordinate homoleptic Ti thiolate complex, whereas the reaction of four equivalents of thiol and $Ti(NEt_2)_4$ afforded the related salt $[NEt_2H_2]$ $[Ti(SC_6F_5)_4(NEt_2)]$.[711] A series of thiolate derivatives of the form $Ti(SR)(OCH_2CH_2)_3N$ were prepared by the thiolysis of $Ti(NMe_2)(OCH_2CH_2)_3N$.[225] Ti complexes containing (*S,S′*)-ferrocenyldithiolate ligands $Ti(NMe_2)_2(SC_5H_4)_2Fe$ were prepared by thiolysis of $Ti(NMe_2)_4$ with $(HSC_5H_4)_2Fe$. Treatment of this diamide complex with trimethylaluminum afforded the dimethyl species which reacted with MAO to form an ethylene polymerization catalyst that exhibited low activity.[712]

Selenolate and tellurolate Ti complexes are rare. To the best of our knowledge $Ti(SeSi(SiMe_3)_3)_4$, $Ti(TeSi(SiMe_3)_3)_4$, and $Ti(SeSi(SiMe_3)_3)_3(Bn)$ are the only selenolate and tellurolate Ti complexes reported in the last 20 years that do not contain a Cp-ligand.[713]

4.2.2.6.4 Dithiocarbamate and dithiophosphate ligand complexes

Ligand exchange or substitution reactions have been employed to prepare a variety of dithiocarbamate complexes of the forms $Ti(S_2CNR_2)_4$,[714–717]) $TiX_3(S_2CNR_2)$ (X = Cl, Br, I)[718] and $TiCl_2(S_2CN(CH_2)_4)_2$.[715] The oxo complex $TiO(S_2CNCH_2CH(Me)NCH_2CH_2)_2$[719] and the bimetallic complex prepared $TiCl_2(S_2CNC_4H_8)_2(CH_2N(CH_2CH_2NH_2))_2)Cu$[204], as well as a variety of related derivatives incorporating salicylate and dithiocarbamate ligands[720] have been described. The *N,N′*-dialkylmonothiocarbamate complexes $TiCl_2$ $(SOCNMe_2)_2$ and $TiCl_2(SOCNEt_2)$ have been reported.[721] Kinetic studies found that Ti-centered rearrangements and rotation about the C—N bonds in $Ti(OSCNMe_2)_4$ are much slower than in the analogous dithiocarbamate Ti complexes $Ti(S_2CNEt_2)_4$ and $Ti(S_2CNPr_2)_4$.[722]

The dithiophosphate complexes of the form $TiCl_{4-n}(S_2PR_2)_n$ ($n = 2$–4)[723] $Ti(OPr^i)_{4-n}$ $(S_2PR_2)_n$,[724] and $Ti(OR)_2(S_2P(OMe)_2)_2$[725] have been prepared and characterized. In addition, the oxo complex $TiO(S_2P(OMe)_2)_2$[719] was synthesized. Both this complex and $TiO(S_2CNCH_2CH(Me)NCH_2CH_2)_2$, when reacted with $HgCl_2$, formed the corresponding $HgCl_2$ adducts.[719]

4.2.2.7 Halometallate Complexes

In matrix isolation work, the dimerization of $TiCl_4$ has been shown to occur at 12 K. IR data suggested a bridged dimer with C_{2h} symmetry.[726]

The reaction of $TiCl_4(THF)_2$ with $[NBu_4][MgCl_4]$ in THF resulted in the formation of $[NBu_4]_2[TiCl_6]$.[727] Depending on the stoichiometric amounts used, treatment of a Grignard reagent or $[MgR_2(THF)_2]$ with $TiCl_4(THF)_2$ yielded $[Mg(THF)_6][TiCl_5(THF)]_2$, $[Mg(\mu\text{-}Cl)_2\ (THF)_4][TiCl_4]$, and $[Mg_2(\mu\text{-}Cl)_3(THF)_6][TiCl_5(THF)]$.[728]

The coordination of $TiCl_4$ with $MgCl_2$ and O donors gave products formulated as $TiCl_4(\mu\text{-}Cl)_2MgL_4$ (L = MeO_2CEt, HCO_2Et, THF) and $TiCl_4Mg(\mu\text{-}Cl)_2(MeO_2CEt)_2L_2$ (L = RCO_2Et, R = H, Ph, Me).[315] In the case of the related species $TiCl_3(\mu\text{-}Cl)_2(\mu\text{-}CO_2CH_2Cl)Mg(EtCO_2CH_2Cl)_3$, one of the ester ligands was also thought to be bridging.[729]

4.2.2.8 Metal—Metal Bonded Compounds

Studies showed that the Ti-ligand framework in $(TiX(RNCH_2)_3CMe)_2$ ($R = SiMe_3$, C_6H_4Me) was useful in the synthesis of heterobimetallic complexes such as $Ti(Co(CO)_3PPh_3)(RNCH_2)_3CMe$. These compounds are described as rare examples of thermally stable dinuclear complexes with highly polar unsupported metal—metal bonds.[730]

The complexes $Ti(NMe_2)_3Fe(CO)_2(Cp)$,[731] $Ti(NMe_2)(OC_6H_3Me_2)_2Ru(CO)_2(Cp)$, $Ti(NMe_2)_2(OC_6H_3Me_2)Ru(CO)_2(Cp)$,[732] $TiBn_3Co(CO)_4$, $TiBn_2(Co(CO)_4)_2$,[733] and $Ti(NPh_2)_2(Co(CO)_4)_2$[734] were prepared via protonolysis reactions, whereas $Ti(OBu^t)_3Co(CO)_4$,[735,736] $Ti(OR)_{4-n}(Co(CO)_4)_n$-($R = Pr^i$, Bu^t, $n = 1, 2$),[733] were prepared via metal anion displacement of Ti-bound halides.

More recently, a series of complexes incorporating a Ti-bound tripodal ligand afforded $Ti((SiMe_2N(C_6H_4Me))_3SiMe)(Co(CO)_3L)$ ($L = CO$, PPh_3, $P(C_6H_4Me)_3$). Crystallographic and theoretical data affirmed that the Ti—Co bond is highly polarized.[737] In a similar vein the complexes $Ti(SiMe_2N(C_6H_4Me))_3SiMe)(M(CO)_2Cp)$ ($M = Fe$, Ru) were described.[738,739]

4.2.2.9 Hydride Ligand Complexes

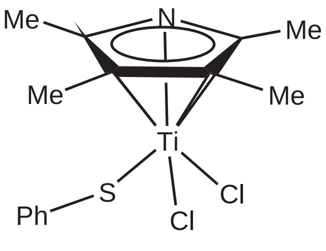
Ti–hydride complexes that do not contain Cp-ligands are rare. The reaction of $TiCl_2(OC_6H_3Pr^i_2)_2$ with $Li[BH_4]$ afforded $Ti(OC_6H_3Pr^i_2)_3(\eta^3\text{-}BH_4)$ and the Ti^{III} species $(Ti(OC_6H_3Pr^i_2)(\mu^3\text{-}BH_4)_2)_2$. In the presence of $PMe_3Ti(OC_6H_3Pr^i_2)_3(\eta^3\text{-}BH_4)$ lost BH_3 forming $TiH(OC_6H_3Pr^i_2)_3(PMe_3)$. PMe_3 dissociates reversibly from this product yielding $TiH(OC_6H_3Pr^i_2)_3$.[441] Subsequently, Bennett and Wolczanski reported the siloxy titanium hydride complex $TiH(OSiBu^t_3)_2(HNSiBu^t_3)$.[126]

4.2.2.10 Mixed Donor Ligand Complexes

4.2.2.10.1 C,N ligand complexes

Reduction of $TiCl_2(N(SiMe_3)_2)_2$ with Na resulted in C—H activation and the formation of the proposed dimer $Ti_2(\mu^2\text{-}CHSiMe_2N(SiMe_3))_2(N(SiMe_3)_2)_2$. The crystal structure of the Zr analogue was determined.[75]

Pyrrolyl ligands have been reported to mimic cyclopentadienyl ligands affording Ti-η^5-pyrrolyl complexes. Examples include $TiCl_3(\eta^5\text{-}NC_4H(Bu^t)_2SiMe_3)$, $TiCl_3(\eta^5\text{-}NC_4H_2Bu^t_2)$,[740,741] $TiX_3(\eta^5\text{-}NC_4Me_4)$ ($X = NMe_2$,[742] Cl, SPh), and $TiCl_2(\eta^5\text{-}NC_4Me_4)_2$ and $Ti(SPh)Cl_2(\eta^5\text{-}NC_4Me_4)$ (**65**).[743] These compounds were prepared via reactions of Li-pyrrolide with $TiCl_4$ or pyrroles with $Ti(NMe_2)_4$.



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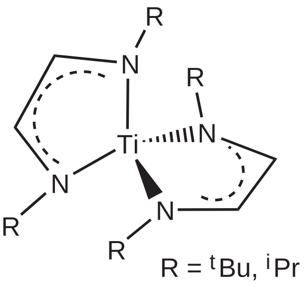


R = ᵗBu, ⁱPr

(66)

The complex $Ti(OC_6H_3Ph_2)_2(C_4Et_4)$ reacted with PhNNPh or $(PhNCMe)_2$ yielding $Ti(OC_6H_3Ph_2)_2(PhNCR)_2$ ($R = Me$, Et).[744] Similarly, reaction of $Ti(OC_6H_3Ph_2)_2(BnNCH(Ph)CH_2CH_2)$ with PhCN gave $Ti(OC_6H_3Ph_2)_2(BnNCH(Ph)C(Ph)N)$, which rearranged after two days to the ene–diamide complex $Ti(OC_6H_3Ph_2)_2$ $(BnNC(Ph)C(Ph)NH)$.[745] In related but more recent work, the bis(iminoacyl) complex $Ti(OC_6H_3Ph_2)_2((C_6H_3Me_2)NC(C_6H_3Ph_2))_2$ has been shown to rearrange over several days affecting C—C coupling and giving the ene–diamide complex.[746]

A series of ene–diamide complexes, $Ti(OC_6H_3Ph_2)_2(RNC(C_6H_3R'_2))_2$ ($R = Bu^t$, $C_6H_3Me_2$; $R' = Me$, Bu^t, Pr^i), were prepared via reaction of $TiMe_2(OC_6H_3Ph_2)_2$ with isocyanates.[747] The related ene–diamide complexes $TiCl_2((RN)_2C_2H_2)$ and $Ti((RN)_2C_2H_2)_2$ (**66**) were prepared via direct reaction of $Li[(RN)_2C_2H_2]$ ($R = Pr^i$, Bu^t) and $TiCl_4$. Substitution reactions afforded complexes of the form $TiClX((RN)_2C_2H_2)$ ($X = N(SiMe_3)_2$, CH_2Bu^t; $R = Pr^i$, Bu^t).[748] Similarly, $TiCl_2((Pr^i{}_3SiN)_2C_6H_4)$ and $TiMe_2((Pr^i{}_3SiN)_2C_6H_4)$[749] were prepared and shown to be fluxional due to arene ring flipping. In similar metathesis reactions the complexes $TiCl((Bu^tN)_2C_2H_2)(BH_4)$ and $Ti((Bu^tN)_2C_2H_2)(BH_4)_2$ were prepared.[750] More recently, $TiCl_2((RN)_2C_2H_2)$ ($R = Pr^i$, Cy) have been prepared and shown to be stabilized by intramolecular chlorine—hydrogen bonding.[751]

A molecular orbital analysis of the ene–diamide complex $TiCl_2((HN)_2C_2H_2)$ indicated that π interactions between the metal and the alkenyl linkage are negligible and that donation of two electrons from filled p_π N orbitals to the metal results in ligand folding.[752]

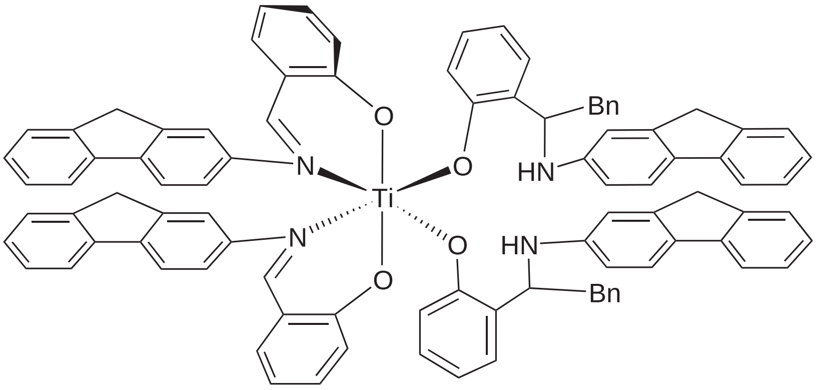
4.2.2.10.2 *Neutral N,O bidentate ligand complexes*

Neutral N,O adducts of $TiCl_4$ that were formed with Schiff bases derived from salicylaldehyde,[24] aminoethyltetrahydrofuran,[753] and phenoxyimines,[754] were thought to coordinate through both the pyridine N and phenolic O atoms. In the case of reactions of $TiCl_4$ with β-aminoketones the adducts $TiCl_4(Pr^iN(H)\ C(Me)CHC(Me)O)_2$ and $TiCl_4(CH_2CHCH_2N(H)C(Me)CHC(Me)O)_2$ were obtained and characterized crystallographically.[755]

4.2.2.10.3 *Monoanionic N,O bidentate ligand complexes*

A variety of monoanionic N,O-chelate complexes have been described. These include ligands derived from phenolic–diazo compounds,[756] a variety of Schiff-base derivatives,[757–761] aldehyde–hydrazone ligands,[762] thiazolidin-4-ones,[763,764] and salicylideneamino-3,5-dimercapto-1,2,4-triazoles.[760] Similarly, the complexes $Ti(OPr^i)_{4-n}(NHC(O)R)_n$ ($R = Me$, Ph, NC_5H_4, $n = 1$–4) are thought to be coordinated via the carbonyl group of the amide functional group.[765]

More recently, Ti complexes of β-aminoketonates, $TiCl_2(PhNCMeCHCMeO)_2$ and $TiCl_2(MeOC_6H_4NCMeCHCMeO)_2$, were synthesized via metathesis of the alkali metal salts of the β-aminoketones with $TiCl_4$.[755] Similarly, Schiff-base ligands derived from the condensations of salicylaldehyde or 3-methoxy-2-hydroxybenzaldehyde with 2-aminofluorene were used to prepare *N,O*-ligand complexes such as $TiCl_3((OC_6H_4CHNC_{13}H_9))$ when reacted with $TiCl_4$,[766] whereas the analogous reaction with $Ti(Bn)_4$ gave $Ti(OC_6H_4CHNC_{13}H_9)_2(OC_6H_4CH(Bn)NHC_{13}H_9)_2$ (**67**).[766] In addition, complexes of the Na salt of N-(salicylidene)anthranilic acid were thought to bind via N,O atoms.[767]



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Oxaazaphosphatitanetidine complexes of the form $Ti(OR)_{3-n}X_n(R'OP(NSiMe_3)_2NR)$ ($n = 1$–3) contain TiOPN-chelate rings and have been shown to react with amines and R_2NBr to give diiminophosphine derivatives.[768]

Hydroxylamido derivatives such as $Ti(ONR_2)_4$ ($R = Et$, Bn)[769] were prepared via protonolysis of $Ti(OPr^i)_4$ with $HONR_2$. The crystal structure of $Ti(ONEt_2)_4$ revealed a monomeric octacoordinated Ti center. More recently, the analogous compound $Ti(ONMe_2)_4$ was reported.[770]

The reactions of pyridine alcohols with $Ti(NMe_2)_4$ gave the complexes of the form $Ti(NMe_2)_2((NC_5H_4)C(C_6H_4R)_2O)_2$ ($R = Bu^t$, CF_3, Ph, NEt_2) and $Ti(NMe_2)_2((NC_5H_4)CR_2O)_2$

(R_2 = fluorenyl,($C_{12}H_8$) dibenzosuberyl). Single-crystal X-ray diffraction studies of the complexes $Ti(NMe_2)_2((NC_5H_4)CC_{12}H_8O)_2$ and $Ti(NMe_2)_2((NC_5H_4)C(C_6H_4NEt_2)_2O)_2$ revealed distorted tetrahedral geometries with the alkoxide ligands bound in a *trans* fashion.[771] These complexes provided active olefin polymerization catalysts.

Phenoxyimines formed adducts with $TiCl_4$ which upon treatment with base gave the complexes $TiCl_2(OC_6H_4CHNR)_2$ (R = Ph, $C_6H_3Pr^i_2$). While the crystal structures showed distorted octahedral Ti environments in both chelate complexes, in the $C_6H_3Pr^i_2$ derivative the N atoms were *cis* to one another while in the Ph derivative the O atoms were *trans*.[754] These complexes also yielded catalysts for olefin polymerization. Using a rapid screening process, it was found that $TiCl_2(OC_6H_4CHNC_6H_3Bu^t_2)_2$ was an effective catalyst for the production of syndiotactic polypropylene.[772] $TiCl_2(OC_6H_3Bu^tCHNC_6F_5)_2$ promoted the living polymerization of ethylene with high activity.[773]

The glycinate complex $(Ti(OEt)_2(\mu\text{-}OEt)(H_2NCH_2CO_2))_2$ was prepared via protonolysis of $Ti(OEt)_4$ with glycine. Crystallographic data confirmed the dimeric nature of this compound.[774]

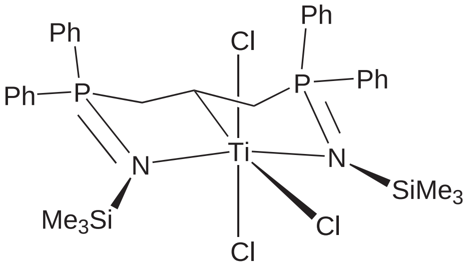
Bis(hydroxyphenyl)oxazoline Ti complexes were prepared via salt metathesis reactions of $TiCl_4$ with the corresponding salts.[775] The monoanionic bidentate nature of the ligands was confirmed in the crystal structure of $TiCl_2(OC_6H_4(CNOC(Me)_2CH_2))_2$, which revealed a *cis* arrangement of the N and Cl atoms.[775] Other Ti complexes containing N,O chelates include those derived from reactions of $Ti(NMe_2)_4$ with an assortment of N-substituted amino alcohols[776] such as $HOCH(Bu^t)CH_2NH(C_6H_3Me_2)$, and $HOCH_2CH_2\ NH(C_6H_3Me_2)$.[777]

4.2.2.10.4 *Dianionic N,O bidentate ligand complexes*

The eight-membered heterocyclic complex $(TiCl_2(\mu\text{-}OPPh_2N))_2$ was the unexpected product derived from the reaction of $SiMe_3NPPh_2(OSiMe_3)$ and $TiCl_4$.[778] Chiral N,O chelates have been implied as intermediates in stereoselective Aldol and Me_3Si cyanation reactions.[779,780] Complexes related to these intermediates, specifically $(TiX_2(\mu\text{-}OCHPhCHPhNR))_2$ (X = NMe_2, NEt_2; R = SO_2CF_3, $SO_2C_6H_2Me_3$, $CH_2C_6H_2Me_3$) and $Ti(NEt_2)_2(OCHPhCHPhNSO_2CF_3)$ $(NC_5H_4NMe_2)$, were derived from the protonolysis of $Ti(OR)_4$ (R = OPr^i, NMe_2 and NEt_2) with amino alcohols. A series of crystal structures of these complexes was also reported.[776] The similar dimers $(Ti(NMe_2)_2(\mu\text{-}OCHRCH_2NC_6H_3Me_2))_2$ (R = H, Bu^t) have also been described more recently.[777]

4.2.2.10.5 *N_2C tridentate ligand complexes*

The bis(phosphinimine) ligand $((SiMe_3N)Ph_2PCH_2)_2$ reacted with $TiCl_4$ resulting in metallation of one of the methylene groups affording $TiCl_3(((SiMe_3N)Ph_2PCH_2)_2)$ (**68**).[781] Cavell and co-workers reported a bis-phosphinimine ligand complex $TiCl_2(((SiMe_3NPPh_2)_2C))$ that was synthesized via salt metathesis of $TiCl_4$ with $Li_2[(SiMe_3NPPh_2)_2C]$. The bridged carbon atom within the ligand was found to be multibonded to the titanium atom.[782]



(**68**)

4.2.2.10.6 *N_2O tridentate ligand complexes*

A variety of N_2O-ligands are thought to bind titanium in a tridentate fashion in a number of complexes including pyridyl–hydrazone derivatives[762] and the histidine complex

$\mathrm{TiO(O_2CCH(NH_2)(CH_2N_2C_3H_2))}$.[783] Related compounds containing *N*-salicylidene–amino acid ligands were reported to catalyze the asymmetric oxidation of sulfides to sulfoxides by $\mathrm{Bu^tOOH}$.[784]

Titanium $\mathrm{N_2O}$ ligand complexes of the form $\mathrm{TiX_2((RNC_6H_4)_2O)}$ ($\mathrm{R = Bu^t\text{-}d^6}$, $\mathrm{SiMe_3}$, $\mathrm{C_6H_2Me_3}$)[785–788] and $\mathrm{TiX_2((RNCH_2CH_2)_2O)}$ ($\mathrm{R = C_6H_3Me_2}$, $\mathrm{C_6H_3Pr^i{}_2}$, $\mathrm{C_6H_3Et_3}$)[789,790] have been prepared by Schrock and co-workers. Several structural studies have confirmed the tridentate nature of the $\mathrm{N_2O}$-ligands. These complexes have also been examined as precursors to olefin polymerization catalysts.

4.2.2.10.7 $\mathrm{NO_2}$ tridentate ligand complexes

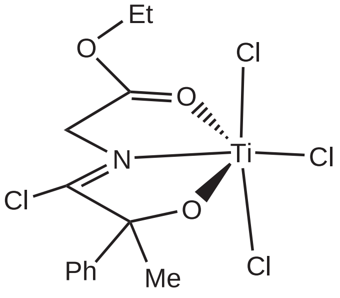
Many $\mathrm{NO_2}$-ligands are thought to chelate to titanium in a tridentate fashion. Such complexes include a series of Schiff-base derivatives,[791] alkylpyruvate–benzoylhydrazone derivatives,[792] and *N*-(*o*-hydroxy substituted benzyl) amino acid derivatives (namely alanines[793] and glycines[794]). Based on formulations, these ligands are thought to act as mono-, di- or tri-anions depending on the stoichiometric amounts used.[793,794] This, however, was not unambiguously confirmed.

The octahedral complexes containing tridentate dianionic benzoylhydrazone and benzoylhydrazine ligand derivatives $\mathrm{Ti(OC(Ph)CHNC(Me)CHC(Me)O)_2}$ and $\mathrm{Ti((OC(Ph)CHC(Me))_2N)_2}$ have been prepared and crystallographically characterized.[795] Ti complexes bearing related tridentate ligands include $\mathrm{(Ti(OH)(H_2O)(OC(Ph)NHNCHC_6H_4O))_2(\mu\text{-}O)}$,[796] $\mathrm{Ti(OC(Ph)NHNCHC_6H_4O)_2}$,[797,798] and $\mathrm{Ti(OC(Ph)NHNC(Ph)C_3MeN_2Ph)_2}$.[799]

Ti–pyridine diolate ligand complexes of the form $\mathrm{TiCl_2(C_5H_3N(CH_2CR_2O)_2)}$[800] and $\mathrm{Ti(C_5H_3N(CHC(Ph)O)_2)_2}$[801] have been prepared. The latter was structurally characterized revealing the six-coordinate nature of the complex with each ligand adopting a *meridional* geometry.[801] The related complex $\mathrm{Ti(OPr^i)_2(C_5H_3N(CHC(Bu^t)O)_2)}$ catalyzed the asymmetric epoxidation of (E)-α-phenylcinnamyl alcohol in 40% ee.[802]

A number of tridentate dianionic $\mathrm{NO_2}$–Schiff-base ligand Ti complexes of the form $\mathrm{TiCl_3(L)}$ have been readily prepared via conventional methods.[767,803–808] Structural data for $\mathrm{TiCl(OC(Me)CHC(Me)O)(OC_{10}H_6CHNCMe_2CH_2O)}$ confirmed a *meridional* geometry for the tridentate ligand.[808] Related alkoxy–ketoiminate ligand complexes have also been reported.[809] A number of these Schiff-base complexes catalyzed asymmetric organic transformations such as the $\mathrm{Me_3Si}$ cyanation of benzaldehydes,[803,805] the hydrocyanation of imines,[810] oxidation of sulfides,[784] the enantioselective reaction of diketenes with aldehydes,[804] and Diels–Alder reactions.[806]

Reaction of $\mathrm{TiCl_4}$ with a ketone and an isocyanide ester led to the formation of the anionic $\mathrm{NO_2}$ ligand complex $\mathrm{TiCl_3(\mu^3\text{-}OC(Me)(Ph)C(Cl)NCH_2CO_2Et)}$ (**69**). This complex, upon hydrolysis, gave the corresponding α-hydroxy amide.[811] Alternatively, reaction of dibutylcatechol with $\mathrm{NH_3}$ and $\mathrm{TiCl_3}$ afforded the tridentate diquinone ligand $\mathrm{Ti^{IV}}$ complex $\mathrm{Ti((OC_6H_2Bu^t{}_2)_2NH)_2}$.[812,813] Other tridentate diquinone ligand complexes have also been described and their electronic properties probed.[814,815] These complexes exhibit large intramolecular ferromagnetic interactions.



(**69**)

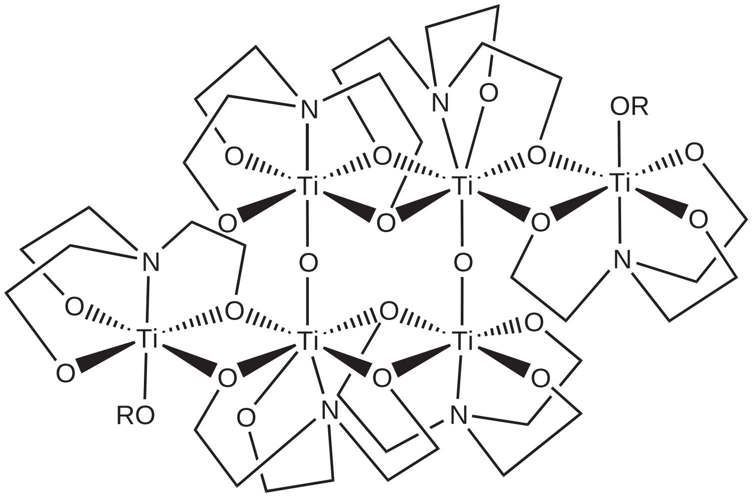
Protonolysis of $\mathrm{Ti(OPr^i)_4}$ was employed to prepare $\mathrm{Ti(OPr^i)_2((OC_6H_2R_2CH_2)_2NPr)}$ and $\mathrm{Ti((OC_6H_2R_2CH_2)_2NPr)_2}$ ($\mathrm{R = Me}$, $\mathrm{Bu^t}$). The octahedral nature of the latter was confirmed crystallographically.[816,817] The dibenzyl derivative $\mathrm{TiBn_2((OC_6H_2Bu^t{}_2CH_2)_2NPr)}$ was found to provide an active catalyst for the polymerization of 1-hexene.[818] The complex $\mathrm{Ti((OCH_2CH_2)_2NMe)_2}$ has been synthesized by reaction of hydrated titania with

$(HOCH_2CH_2)_2NMe$. X-ray crystallography showed that the tridentate ligands adopted a *facial* binding geometry.[819]

4.2.2.10.8 N,O tripodal ligand complexes

The reaction of $Ti(OPr^i)_4$ with triethanolamine afforded the dimeric complex $(Ti(OPr^i)(OCH_2CH_2)_3N)_2$. The crystallographic characterization of this complex revealed hexacoordinate Ti atoms asymmetrically bridged via one of the O atoms from each ligand.[820] A series of analogous complexes have been prepared via protonolysis of TiR_4 ($R = OBu^t$, NEt_2, $NPr^i{}_2$) with triethanolamine to give $Ti(R)((OCH_2CH_2)_3N)$ ($R = Me$, Et, Pr^i).[225,821,822] Several of these monomeric and dimeric products were structurally characterized.

Reactions with chiral trialkanolamine ligands afforded the complexes $Ti(OPr^i)((CH_2C(R)O)_3N)$ ($R = Me$, Ph), which were subsequently converted to $TiCl((CH_2C(R)O)_3N)$ via treatment with MeCOCl.[823] Similarly, reactions with ROOH afforded the complexes $Ti(OOR)((OC(R)CH_2)_3N)$. These complexes act as catalysts for the enantioselective oxidation of sulfides.[824,825] Partial hydrolysis of such complexes led to the isolation of $Ti_3(\mu_2\text{-}O)((HO(CH_2)_2)_2N(CH_2)_2O)\text{-}((O(CH_2)_2)_2(\mu_2\text{-}O(CH_2)_2)N)_2((O(CH_2)_2)(\mu_2\text{-}O(CH_2)_2)N)_2$ and $(Ti_3(\mu_2\text{-}O)(OCH(Me)_2)\text{-}((O(CH_2)_2)_2\text{-}(\mu_2\text{-}O(CH_2)_2)N)_2((O(CH_2)_2)(\mu^2\text{-}O(CH_2)_2)_2N))_2$ (**70**).[826] In addition, a number of salts of the dianion $[Ti(OCH_2CH_2)_3N)_2]^{2-}$ have also been reported.[827] Related chemistry has recently been extended to include the Ti–triphenolate amine complexes $Ti(OPr^i)(OC_6H_3R_2)_3N$-($R = Me$, Bu^t).[828]



$R = CH_2CH_2N(CH_2CH_2OH)_2$
$R = CH(CH_3)_2$

(**70**)

The N_3O and N_2O_2 tripodal ligand complexes of the form $TiX_2((OC_6H_2R_2)_2N(CH_2CH_2R))$-($R = NMe_2$, OMe)[816,817] were prepared and characterized. These compounds gave rise to living polymerization catalysis of 1-hexene.[818,829] Related N_2O_2 tripodal Schiff-base ligand complexes derived from the dissymmetric substitution of ethylenediamine $TiO(H_2NCH_2CH_2NC(C_6H_3(R)O)CHCH(C_6H_3(R)O))$ ($R = H$, Me, Cl) and $TiCl_2(H_2NCH_2CH_2NC(C_6H_3(R)O)CHCH(C_6H_3(R)O))$ have also been described.[830]

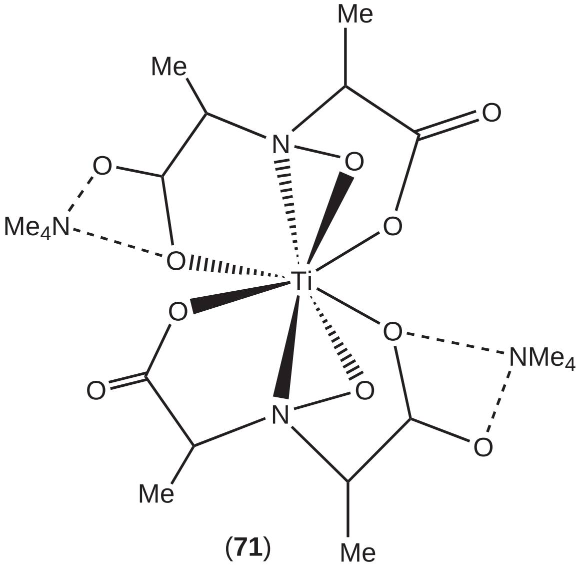
An amine oxide ligand has also been used as a tripodal-type ligand yielding the complex $[Ca(H_2O)_4][Ti((ON(CH_2CO_2)_2)_2]$.[831] The related tetramethylammonium salt $[NMe_4]_2$-$[Ti((ON(CH_2CO_2)_2)_2]$ (**71**) was synthesized via reaction of the ligand with $TiO(OC(Me)CHC(Me)O)_2$ and $[NMe_4][OH]$.[832]

A salt metathesis reaction was employed to prepare the N_3O tripodal ligand complex $TiCl_3((N_2C_3HMe_2)_2CHCO_2)$ in which the bis(3,5-dimethylpyrazoyl-1-ylacetate ligand binds in a N_3O tripodal fashion to Ti. Interestingly, when the compound was refluxed in THF, ring opening of the THF molecule occurred, forming $TiCl_2((N_2C_3HMe_2)_2CHCO_2)(O(CH_2)_4Cl)$.[833]

4.2.2.10.9 N,O tetradentate ligand complexes

The ligand $(HOC_6H_2(Bu^t)_2CH_2)_2NCH_2CH_2NMe_2$ was used to prepare $TiBn_2((OC_6H_2(Bu^t)_2CH_2)_2NCH_2CH_2NMe_2)$ (**72**). The crystal structure revealed a slightly distorted octahedral geometry about Ti. Upon activation by $B(C_6F_5)_3$, this complex provided a living catalyst for the polymerization of 1-hexene.[818]

A series of N_2O_2 Schiff-base mononuclear Ti imido complexes $Ti(NBu^t)(OC_6H_4CHNCH_2)_2$, $Ti(NBu^t)(OC_6H_3(Et)CHNCH_2)_2$, $Ti(NBu^t)((OC_6H_4CHN)_2C_6H_4)$, and $Ti(NBu^t)(OC_6H_3(Bu^t)C(Bu^t)NCH_2)_2$ and the binuclear Ti imido complex $(Ti(NBu^t)(OC_6H_3(OMe)CHNCH_2)_2)_2$ (**73**) have been prepared from $TiCl_2(NBu^t)(NC_5H_5)_3$. The monomeric complexes were shown to undergo imide/arylamine exchange reactions, whereas the dimeric complexes did not.[834]



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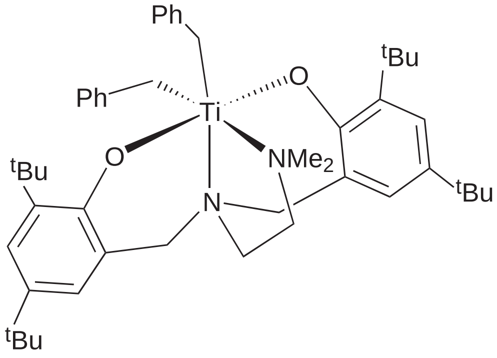
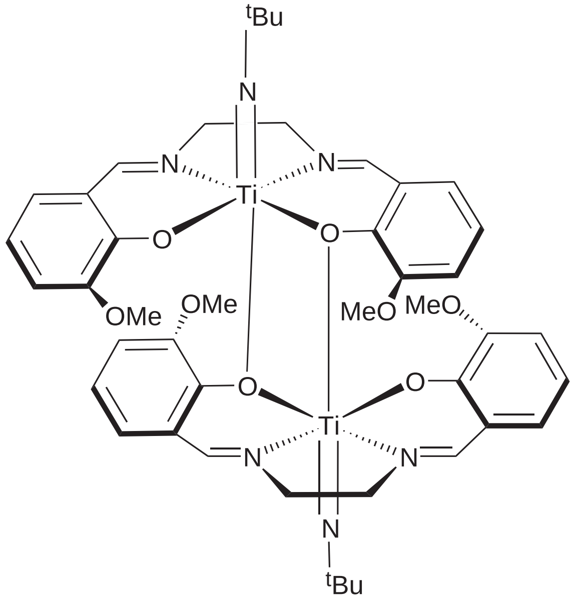
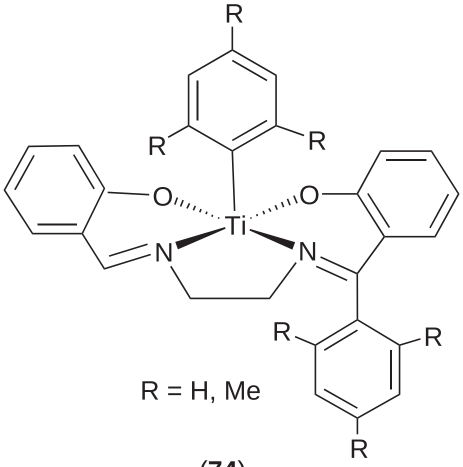




(72) **(73)**

A series of tetradentate Schiff-base ligands based on ethylenediamine have been used to form a variety of Ti complexes.[639,835–839] For example, the previously reported complex $TiCl_2(OC_6H_4CHNCH_2)_2$ reacted with $Li[BH_4]$ to give $(Ti(BH_4)_2(\mu\text{-}OC_6H_4CHNCH_2)_2)_2$.[840] X-ray data confirmed the dimeric formulation. The related complexes $Ti(OMe)_2(OC_6H_4CHNCH_2)_2$, Ti $(OMe)_2((OC_6H_4CHN)_2C_6H_4)$ were prepared via reaction of the Na salt of the ligand with $TiCl_2(OMe)_2$.[841] Methylation of $TiCl_2((OC_6H_4CHNCH_2)_2)$ afforded the analogous dimethyl species, whereas attempted arylations led to substitution on the imine C atom affording $Ti(C_6H_2R_3)(OC_6H_4CHNCH_2CH_2N(C_6H_2R_3)CHC_6H_4O)(THF)$ (**74**) (R = H, Me).[837,842]



(**74**)

Recently, it was found that the analogous complex $TiCl_2((OC_6H_4CHNCH_2)_2)$ adopted a *trans*-Cl geometry.[843] Reaction of $M((OC_6H_4CHNCH_2)_2)$ (M = Ge, Sn, Pb) with $TiCl_4$ gave the salts $[TiCl(OC_6H_2R_2HNCH_2)_2][MCl_3]$.[844]

Reactions of $TiCl_2((OC_6H_4CHNCH_2)_2)$ with chiral α-hydroxy-carboxylic acids proceeded to give complexes of the form $Ti(O_2CC(O)CH_2Ph)((OC_6H_4CHNCH_2)_2)$ in a stereoselective manner.[555] A variety of other substituted derivatives $TiX_2((OC_6H_2R_2CHNCH_2)_2)$ (X = Cl, Br; R = OMe, $SiMe_3$) have also been described.[845] The monomeric structures of $Ti(OC_6H_4Bu^t)_2((OC_6H_4CHNCH_2)_2)$[839] and $TiCl_2(OC_6H_2MeBu^tCHNCH_2)_2$[838] have been confirmed. The Ti^{III} complex TiCl $((OC_6H_4CHNCH_2)_2)$ was oxidized to give linear Ti—O oligomers and polymeric chains.[846]

The related chiral derivatives $(TiCl(OC_6H_4CHN)_2CHRCHR)_2(\mu\text{-}O)$ (R = Me, Ph) and $(TiCl((OC_6H_4CHN)_2C_6H_{10}))_2(\mu\text{-}O)$ were prepared, and the latter was structurally characterized.[847] These chiral derivatives were used to catalyze the oxidation of sulfides.[848] More recently, similar substituted ligand complexes with the general formula $Ti(OPr^i)_2((OC_6H_3RCHN)_2C_6H_3R)$ were tested for activity in olefin polymerization.[849] The related aryl analogues $TiCl_2((OC_6H_4C(R)N)_2C_6H_{10})$-(R = Et, Ph),[850] $Ti(OMe)_2((OC_6H_4CHN)_2C_6H_4)$,[851,852] and $TiCl_2((OC_6H_2(Bu^t)_2CHN)_2C_6H_{10})$[852,853] were characterized by X-ray crystallography. Complexes of the latter type were employed in the asymmetric addition of Me_3SiCN to PhCOH.[853]

Analogous ligand complexes based on binaphthyldiamine[854] and diamino–dimethylbiphenyl units[855] were prepared. In the latter case the dibenzyl derivative $TiBn_2((OC_6H_2Bu^t{}_2CHN)_2C_{12}H_6Me_2)$ was found to be thermally unstable. Benzyl group migration to one of the imine carbon atoms afforded $TiBn((OC_6H_2Bu^t{}_2CHN)(OC_6H_2Bu^t{}_2CH(Bn)N)(C_{12}H_6Me_2))$ (**75**) stereoselectively.

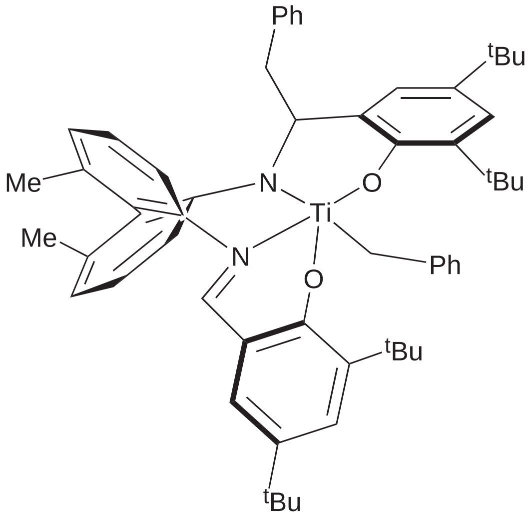
The diamido–diphenoxide chelate complex $Ti((OC_6H_4CH(Ph)NCH_2)_2)$ was prepared via reduction of the Schiff-base ligand followed by reaction with $TiCl_4$, while hydrolysis of the dianionic chelate complex gave $(TiO(OC_6H_4CH(R)NHCH_2)_2)_n$.[766] In a similar manner, diastereoselective reduction of the precursor Schiff-base ligands afforded the complexes $Ti(OPr^i)_2((OC_6H_2Bu^t{}_2CH_2NMeCH_2)_2)$ and $Ti(OPr^i)_2((OC_6H_2Bu^t{}_2CH_2NMe)_2C_6H_{10})$, which were characterized by X-ray methods.[856]

A variety of bis(sulfonamide) complexes of the form $TiX_2(C_6H_{10}(NSO_2R)_2)$,[857–861] $TiX_2(PhCH(NSO_2R))_2$, and $Ti((PhCH(NSO_2R)_2))_2$[862] have been prepared. A number of these complexes have been structurally characterized. In addition, these and related compounds have been used as catalysts for enantioselective addition of alkyl groups to aldehydes.

A trianionic tetradentate N,O ligand comprised of linked catechol and aminophenol fragments was used to prepare the Ti complex $K[Ti_2(O_2C_6H_3CH_2C_6H_3NO)_3]_2$. In the presence of $Ga(NO_3)_2$, $K_3[GaTi((O_2C_6H_3CH_2C_6H_3NO)_3)]$ was obtained. The latter was crystallographically characterized.[863]

A bis(amidate) ligand reacted with $Ti(NR_2)_4$ (R = Me, Et) to give the dimeric complex $(Ti(NR_2)_2(C_6H_4(NC(O)C_6H_4Bu^t)_2))_2$. Subsequent reaction with Me_3SiCl gave the analogous $TiCl_2$ derivative.[864]

A Schiff-base ligand, with a pendent phosphine donor bound to titanium, chelated to Pd affording the crystallographically characterized $(Ti(\mu\text{-}O)(PhCHNCHC_6H_3O(PPh_2))PdI_2)_2$.[865]



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The related Ti^{IV}/Rh^{I} complexes $TiCl_2(PhCHNCHC_6H_3O(PPh_2))_2Rh(CO)Cl$ and $[TiCl_2(PhCHNCHC_6H_3O(PPh_2))_2\text{-}Rh(COD)][BF_4]$ were employed in asymmetric hydroformylation.[866]

4.2.2.10.10 4 denticity N,O ligand complexes

A number of Ti complexes containing multidentate dihydrazone ligands $HOC_6H_4CHN_2\text{-}HC(O)CH_2(CH_2)_n)$ ($n = 1$, 2, 4, 8) have been synthesized although they have not been crystallographically characterized.[867,868]

In 1985, the seven-coordinate compound $Ti((O_2CCH_2)_2NCH_2)_2)(H_2O)$ containing the hexacoordinate ethylenediaminetetraacetate ligand (EDTA) was structurally characterized.[869] Similarly, the reaction of $Ti(OPr^{i})_4$ with $((HOCH(Me)CH_2)_2NCH_2)_2$ gave $(Ti((OCH(Me)\text{-}CH_2)_2NCH_2)_2)_2$. In this compound each Ti-atom is also seven-coordinate with one of the alkoxy groups of each ligand bridging the two Ti centers.[870] A related hexadentate ligand gave rise to the octahedral complex $Ti((OC_6H_4CH_2)_2NCH_2)_2$.[871]

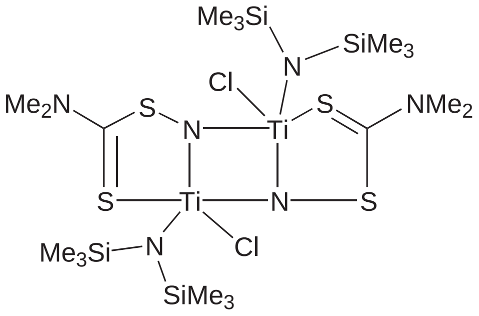
A derivative of triazacyclononane was used to prepare the titanium salt $[Ti((OC_6H_3\text{-}Bu^{t})NCH_2CH_2)_3)][BPh_4]$.[872] Most recently, the ligand (*N*-ethoxo)ethylenediaminetriacetate (EEDTA) was used to prepare the seven-coordinate compound (Ti(EEDTA) $(H_2O))(H_2O)_2$.[873]

4.2.2.10.11 N,S ligand complexes

A series of neutral *N*-alkylphenothiazine derivatives were proposed to chelate Ti through both the nitrogen and sulfur atoms.[874] The related thienylbenzylideneamines, N,S-chelate complexes $TiCl_4(SC_4H_3CH_2NCHC_6H_4R)$ have been prepared and reported.[875] A variety of thiocarbazone ligands have been incorporated into titanium isopropoxide and titanium chloride complexes.[876–878] The related tetradentate ligand complex $[TiCl_2(HONC(C\text{-}MeN_2HC(NH_2)S)_2)]Cl_2$[879] and a macrocyclic diaminodithiocarbamate titanium complex have also been described.[880]

Reaction of $Me_2NC(S)SN(SiMe_3)_2$ with $TiCl_4$ afforded $(TiCl(N(SiMe_3)_2)(\mu\text{-}NSC(S)(NMe_2)))_2$ (**76**),[881] $TiCl_2(NS(S)C(NMe_2))$, and $TiCl_2(NSC(S)(NMe_2))(NC_5H_5)_2$. The latter were crystallographically characterized.[882]

The Ti sulfenamido compounds $TiCl_2(\eta^2\text{-}Bu^{t}NSR)_2$ ($R = Ph$, $C_6H_2Me_3$) were prepared by ligand salt metathesis reactions with $TiCl_4$. The X-ray crystal structure of $TiCl_2(\eta^2\text{-}Bu^{t}NSPh)_2$ showed a tetrahedral $TiCl_2N_2$ core with weak Ti—S interactions.[88]



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4.2.2.10.12 *N,Se bidentate ligand complexes*

Bochmann and co-workers have described complexes derived from the ligand Li[$Bu^t{}_2$PSe(NR)]-(R = Pr^i, Cy). The selenophosphinic complexes $TiCl_2(Bu^t{}_2PSe(NCy))_2$ and $TiCl_3(Bu^t{}_2PSe(NPr^i))$ were prepared and the former complexes crystallographically characterized.[883]

4.2.2.10.13 *O,P bidentate ligand complexes*

The reaction of $TiCl_4$ with $BnP(CH_2CH_2OEt)_2$ resulted in the formation of $TiCl_4(BnP(CH_2CH_2OEt)_2)$. This species contained a distorted-octahedral geometry in which the ligand was coordinated to the Ti center via one of the O-atoms and the P-atom.[884]

4.2.2.10.14 *O,S bidentate ligand complexes*

Monothio-β-diketones have been used to prepare complexes of the form $Ti(OR)_2(R'CSCHCOR'')_2$-(R = Pr^i, Bu^t; R′ = Me, Ph; R″ = Me, Ph), which are thought to be mixtures of *cis* and *trans* isomers.[885] The mercaptophenol derivatives $[NBnMe_3]_2$ $[Ti(C_6H_4OS)_3]$, $[NEt_4]_2[(Ti(C_6H_4OS)_2(\mu\text{-}OMe))_2]$,[886] and $[NEt_4]_2[(Ti(C_6H_4OS)_3Na\ (MeOH)_2)_2]$[887] were prepared and fully characterized.

4.2.2.10.15 *O_2E (E = S,Te) tridentate ligand complexes*

The five-coordinate complexes $TiX_2((OC_6H_2MeBu^t)_2S)$ and $(TiX(\mu\text{-}Cl)(OC_6H_2MeBu^t)_2Te)_2$-(X = Cl, OPr^i) have been prepared and characterized.[888–890] Some of these compounds have been evaluated as catalysts in polymerization and copolymerization of olefins.[888,891–893]

The complexes $TiX_2((OC_6H_2MeBu^tS)_2)$ (X = I, Br), $(TiR(\mu\text{-}R)((OC_6H_2MeBu^tS)_2))_2$ (R = OPr^i, OBu), and $(Ti(OPr^i)_2(\mu\text{-}OPr^i))_2((OC_6H_2MeBu^tS)_2)$ have been prepared and structurally characterized. Interaction of the Ti with one or both of the S atoms was observed.[894]

4.2.2.10.16 *O,N,S tridentate ligand complexes*

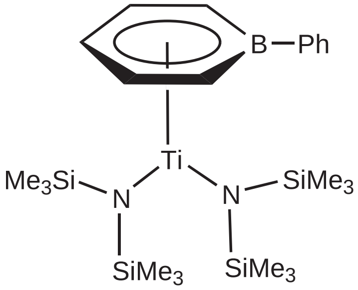
Schiff-base ligands coordinated to Ti via chelated S, N, and O-atoms are proposed in several systems including those derived from dithiocarbazates,[895–897] benzothiazoline,[898] and 2-(salicylideneamino)benzenethiol.[899]

4.2.3 TITANIUM(III)

Titanium(III) complexes have been shown to facilitate and catalyze a variety of organic transformations. This has been reviewed.[900–903]

4.2.3.1 Boron-based Ligand Complexes

The Ti–boratabenzene complex $Ti(C_5H_5BPh)(N(SiMe_3)_2)_2$ (**77**) was synthesized via reaction of $TiCl(N(SiMe_3)_2)_2$ and $Li[C_5H_5BPh]$ and has been crystallographically characterized.[904]



(**77**)

4.2.3.2 Borohydride Ligand Complexes

A series of Ti^{III} adducts $Ti(BH_4)_3(PR_3)_2$ ($R_3 = Me_3$, Et_3, Me_2Ph, $(OMe)_3$) have been prepared by Girolami and co-workers.[905,906] X-ray data established a *trans* arrangement of the phosphine ligands in $Ti(BH_4)_3(PMe_3)_2$ and suggested a $Ti\cdots HB$ agostic interaction. *Ab initio* calculations for $Ti(BH_4)_3(PH_3)_2$ predicted an η^2,η^2,η^3-coordination mode for the borohydrides although an η^1,η^1,η^2-coordination mode was observed experimentally.[907]

Electron diffraction and UV photoelectron spectroscopy indicated that gaseous $Ti(BH_4)_3$ contained three tridentate BH_4-ligands creating a monomeric compound with C_{3h} symmetry. In contrast, osmometry measurements inferred that this complex was dimeric in solution.[908] Studies of the reactions of $Ti(OR)_4$ ($R = CPh_3$, Bu^t, Pr^i, Et) with excess BH_4^- was shown to yield $Ti(BH_4)_3$. Nöth *et al.* have identified the $Ti(OR)(BH_4)_2$ as an intermediate in this process.[909] Subsequently, $Ti(OPr^i)_2(BH_4)$ was prepared from the reaction of $[NBnEt_3][BH_4]$ and $TiCl_2(OPr^i)_2$- and was employed to facilitate selective 1,2-reduction of α,β-unsaturated carbonyl complexes yielding the corresponding allylic alcohols.[910] Similarly, $Ti(BH_4)_3$, prepared via the reaction of $TiCl_4$ with $[NBnEt_3][BH_4]$, reacted with alkenes to effect anti-Markovnikov additions affording the corresponding alcohols upon aqueous workup.[911]

Reaction of $TiCl_2(OC_6H_3Pr^i{}_2)_2$ with $LiBH_4$ afforded $Ti(OC_6H_3Pr^i{}_2)_3(\eta^3\text{-}BH_4)$ and the Ti^{III} complex $(Ti(OC_6H_3Pr^i{}_2)(\eta^3\text{-}BH_4)_2)_2$. The latter reacted with PMe_3 to give $Ti(OC_6H_3Pr^i{}_2)(\eta^2\text{-}BH_4)_2(PMe_3)_2$.[441] Crystallographic structural data for $Ti(OBu^t)(BH_4)_2(THF)_2$ and $Ti(BH_4)_3(THF)_2$ indicates an η^2-coordination mode for the BH_4 groups to the Ti center. A similar bonding mode was observed for $Ti(N(SiMe_3)_2)_2(BH_4)(THF)$ crystallographically.[912] In the presence of pyridine, this complex underwent ligand redistribution yielding $Ti(N(SiMe_3)_2)(BH_4)_2(NC_5H_5)_2$.

4.2.3.3 Carbon-based Ligand Complexes

The synthesis and crystal structure of $[NEt_4]_3[Ti(CN)_6]$ was reported by Girolami and co-workers.[913] This complex was the first documented case where a d^1 ion exhibited an octahedral geometry in a strong ligand field.

4.2.3.4 Nitrogen-based Ligand Complexes

4.2.3.4.1 Neutral nitrogen ligand complexes

The pentacoordinate and hexacoordinate complexes, $TiCl_3((CH(CN)Ph(C_5H_4N))_2)$ and $TiCl_3((CH(CN)Ph(C_5H_4N))_3)$ respectively, were formed via reaction of $TiCl_3$ with $CH(CN)Ph(C_5H_4N)$. Based on IR data, the ligand was proposed to bind through the pyridine N-atom.[914] Similarly, binding in $TiCl_3((C(CN)Ph(C_5H_4N))_2)$ inferred a binuclear species,[914] while $TiCl_3(NC_5H_5)_3$[915] was monomeric. The ligand bis (vanillin)benzidine (vn_2bz) has six possible coordination sites; however, only the azomethine N atoms were proposed to coordinate to the Ti center in $[TiCl_2(vn_2bz)(H_2O)_2]_2Cl_2$.[916]

Coordination of triazacyclononane derivatives ($(RNCH_2CH_2)_3$) to $TiCl_3$ afforded $TiCl_3((MeNCH_2CH_2)_3)$ and $TiCl_3((Pr^iNCH_2CH_2)_3)$.[61,917] Subsequent derivatization gave $TiX_3((MeNCH_2CH_2)_3)$ ($X = O_3SCF_3$, NCS),[61] $Ti(NCS)_3((Pr^iNCH_2CH_2)_3)$, and $Ti(NCO)_2(OMe)((Pr^iNCH_2CH_2)_3)$.[917] Surprisingly, reaction of $TiBr_4$ with $((MeNCH_2CH_2)_3)$ in MeCN afforded the Ti^{III} species $TiBr_3$ $((MeNCH_2CH_2)_3)$.[61] Conversely, $TiCl_2$ reacted with NC_5H_5 and MeCN to give the Ti^{III} complex $TiCl_3(NC_5H_5)_3$.[918,919] Reaction of these complexes with H_2O resulted in the formation of $(TiCl_2((MeNCH_2CH_2)_3))_2(\mu\text{-}O)$[61] $(Ti(NCS)_2((MeNCH_2CH_2)_3))_2(\mu\text{-}O)$ and $(Ti(NCO)_2((MeNCH_2CH_2)_3))_2(\mu\text{-}O)$.[917]

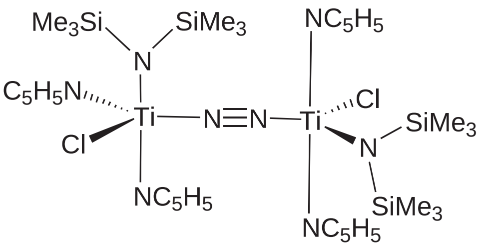
The 1,4,7-trimethyl–1,4,7-triazacyclononane Ti complex $(Ti_2Cl_4((MeNCH_2CH_2)_3)_2(\mu\text{-}O)$ was prepared from refluxing $TiCl_3((MeNCH_2CH_2)_3)$ and $Na(O_2CPh)$ in air and was shown to exhibit a temperature-independent magnetic moment corresponding to one unpaired electron.[920] This complex was reversibly oxidized in two one-electron steps. The mixed valent Ti^{IV}/Ti^{III} product $[Ti_2Cl_4((MeNCH_2CH_2)_3)_2(\mu\text{-}O)]Cl$ was crystallographically characterized.[921]

The ionic Ti^{III} compound $[NH_2Me_2][TiCl_4(HNMe_2)_2]$ was prepared by reacting $HN(SiMe_3)(SiMeCl_2)$ with $Ti(NMe_2)_4$. X-ray diffraction studies showed that the four Cl atoms occupied a planar arrangement about Ti.[922]

4.2.3.4.2 Amido ligand complexes

The majority of Ti amido complexes have been synthesized by the addition of amido salts to $TiCl_3(THF)_3$. For example, $TiCl(N(SiMe_3)_2)(THF)$,[912] $Ti(N(SiMe_3)_2)_3$,[76] and $TiCl_2(N(SiMe_3)_2)(THF)_2$[923] have been prepared in this fashion. Use of two equivalents of $Na[N(SiMe_3)_2]$ in the presence of 12-crown-4 ether afforded the ionic compound $[Na(12\text{-crown-}4)][TiCl_2(N(SiMe_3)_2)_2]$.[923] Similarly, $[Li(TMEDA)]$ $[TiCl_2(N(SiMe_3)_2)_2]$ has also been reported.[924] Alternatively, photolysis of $TiMe$ $(N(SiMe_3)_2)_3$ has been shown to give a product formulated as $Ti(N(SiMe_3)_2)_3$.[76]

Employing the precursor *trans*-$TiCl_2(TMEDA)_2$, reaction with $Li[N(SiMe_3)_2]$ and NC_5H_5 gave the thermally robust compound $(TiCl(N(SiMe_3)_2)(NC_5H_5)_2)_2(\mu\text{-}N_2)$ (**78**),[924] while reaction of $TiCl(N(SiMe_3)_2)_2(THF)$ or $[Li(TMEDA)_2][Ti(\mu\text{-}Cl)_2(NCy_2)_2]$ with CH_2PPh_3 yielded the zwitterionic complex $TiCl(NR_2)_2(CH_2PPh_3)$.[925]



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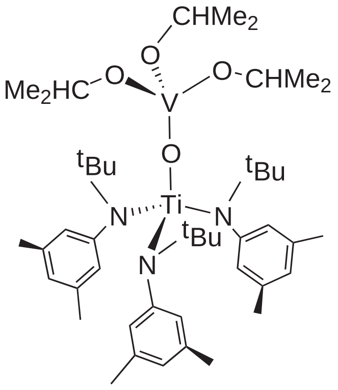

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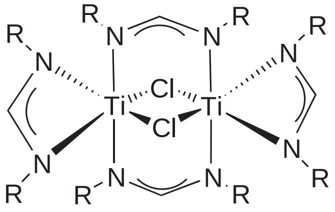
The reduction of $TiCl_2(N(SiMe_3)_2)_2$ by a Na/Hg amalgam yielded the Ti–carbene complex $(Ti((CHSiMe_2)NSiMe_3)N(SiMe_3)_2)_2$.[75] The complexes $Ti(RNC_6H_3Me_2)_2(\mu\text{-}Cl)_2Li(TMEDA)$ ($R = Bu^t\text{-}d^6$, $C(CD_3)_2Ph$) were derived directly from reaction of the amide salts with $TiCl_3(THF)_3$.[63] Alkylation of the former complex gave $Ti(Bu^t\text{-}d^6NC_6H_3Me_2)_2(CH(SiMe_3)_2)$, which contained an η^3-bound amido-aryl group. Subsequent reaction with pivalonitrile gave the corresponding Ti^{III}–pivalonitrile adduct, whereas the reaction with benzonitrile led to the dimeric complex $(Ti(Bu^t\text{-}d^6NC_6H_3Me_2)(CH(SiMe_3)_2))_2(\mu\text{-}NC(Ph)C(Ph)N)$. In a related effort, the complex $TiCl(Bu^t\text{-}d^6NC_6H_3Me_2)_3$ was reduced to $Ti(Bu^t\text{-}d^6NC_6H_3Me_2)_3$.[926] The addition of $V(O)(OPr^i)_3$ to $Ti(Bu^t\text{-}d^6NC_6H_3Me_2)_3$ afforded the bimetallic complex $(OPr^i)_3VOTi(Bu^t\text{-}d^6NC_6H_3Me_2)_3$ (**79**). Crystallographic studies revealed that the Ti–O–V connection was positioned on a three-fold axis.[926]

4.2.3.4.3 Imido ligand complexes

Recently, oxidation of $(Ti((OC_6H_4CHN)_2C_6H_4)THF)_2$ with N_3Ph or N_3SiMe_3 has been shown to provide an effective route to imido-bridged complex $(Ti((OC_6H_4CHN)_2C_6H_4))_2(\mu\text{-}NR)$ (R = Ph, $SiMe_3$).[927]

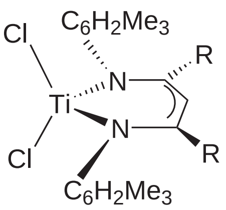
4.2.3.4.4 Amidinato ligand complexes

Synthetic routes to Ti^{III}–amidinato complexes involved either reduction of Ti^{IV} complexes or reaction of Ti^{III} chlorides with amidinato salts. Compounds prepared via one of these routes include $(Ti\text{-}(\mu\text{-}Cl)(HC(NR)_2)(\mu\text{-}HC(NR)_2))_2$ (**80**) (R = Ph, $C_{12}H_{10}$,[928] Cy[929]) and $Ti(HC(NPh)_2)_3$.[149] $Ti(PhC(NSiMe_3)_2)_2(\mu\text{-}Cl)_2Li(TMEDA)$ was prepared by the reaction of $TiCl_2(TMEDA)_2$ or $TiCl_3(THF)_3$ with $Li[PhC(NSiMe_3)_2]$. Subsequent reaction with $Li[BH_4]$ gave the monomeric species $Ti(BH_4)(PhC\ (NSiMe_3)_2)_2$; it was proposed that the steric hindrance precluded dimerization.[930] Reduction of the Ti^{IV} precursor under N_2 afforded $(Ti(PhC(NSiMe_3)_2)_2)_2(\mu\text{-}N_2)$ which was crystallographically characterized. This diamagnetic complex gave relatively short Ti–N distances; however, the oxidation state of Ti was not clear.[931] In contrast, reduction under CO afforded $(Ti(PhC(NSiMe_3)_2)_2)_2(\mu\text{-}O)$[931] while a Na/Hg reduction of $TiClMe(PhC(NSiMe_3)_2)_2$ gave $TiMe\text{-}(PhC(NSiMe_3)_2)_2$. In a more recent study, reaction of $TiCl_2(C_6H_4(Me)C(NSiMe_3)_2)_2$ with K in NH_3(l) produced the Ti^{III} complex $Ti(C_6H_4(Me)\text{-}C(NSiMe_3)_2)_3$.[932]



R = Ph, $C_{12}H_{10}$, Cy

(**80**)



R = Me, ^tBu

(**81**)

4.2.3.4.5 Diketinimato ligand complexes

The Ti^{III} complex $TiCl_2(THF)_2(PhNC(Me)CHC(Me)NPh)$ was prepared and the structure determined by X-ray crystallography.[933] In the presence of excess methylaluminoxane (MAO), this compound generates a catalyst for homo- and copolymerization of α-olefins. Also, the related compounds $TiCl_2((C_6H_2Me_3)NC(R)CHC(R)N(C_6H_2Me_3))$ (**81**) (R = Me, Bu^t) have been reported and have been shown to adopt tetrahedral metal environments. Reaction of the $TiMe_2$ derivatives with $B(C_6F_5)_3$ also produced catalysts for α-olefin polymerization.[934]

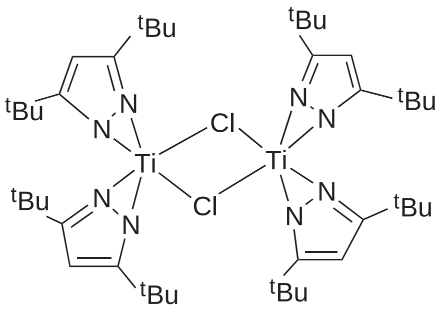
4.2.3.4.6 Miscellaneous bidentate ligand complexes

The chelate stabilized metal amide complex $Ti(NC_4H_7CH_2NMe_2)_3$ was synthesized employing amino–pyrrolide ligands.[935] Although crystallographic data was not reported, the structure of the Cr^{III} analogue was determined. A related amido–pyridine complex $Ti(NC_5H_3Me\ (NSiMe_3))_3$ was prepared via reduction of $TiCl(NMe_2)(NC_5H_3Me(NSiMe_3))_2$ by Na.[936]

Reduction of the pyrazolate complex $TiCl_2(N_2C_3HBu^t{}_2)_2$ by Na/Hg in THF or toluene gave $TiCl(N_2C_3HBu^t{}_2)_2(THF)_2$ or $(TiCl(N_2C_3HBu^t{}_2)_2)_2$ (**82**) respectively.[937] Structural data reported for both products confirmed the bidentate binding of the pyrazolato ligands to Ti.

NMR data for $Ti(bipy)_3$ was used to suggest that this species was best considered as a Ti^{III} complex of the bipyridyl anion.[938] Subsequent reaction with Ph_2CO led to a Ti^{IV} complex containing a pinacol dianion, further supporting this view.

Reduction of $TiCl_4(THF)_2$ with Mg in the presence of excess $(RNC(Ph))_2$ (R = Ph, C_6H_4Me, C_6H_4OMe) led to the formation of diaza–diene complexes $Ti(RNC(Ph))_2)_3$.[939] Alternatively, the analogous $Ti(Pr^iNCH)_2)_3$ was prepared by metathesis using the corresponding Li ligand salt.[940] The molecular structure of the latter octahedral complex was determined.[940]



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4.2.3.4.7 *Monoanionic tridentate ligand complexes*

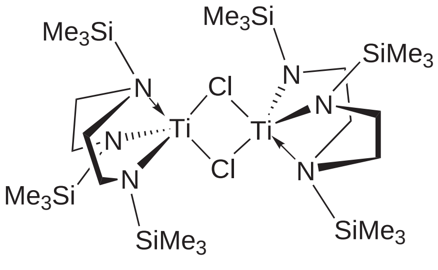
The ligand $[N(CH_2CH_2NEt_2)_2]^-$ was used to prepare $TiCl_2(N(CH_2CH_2NEt_2)_2)$.[941,942] Crystallographic data was reported for the V^{III} analogue.

4.2.3.4.8 *Tris(pyrazolyl)borate ligand complexes*

The Ti^{III} tris(pyrazolyl)borate ligand complexes $TiCl_2((N_2C_3HMe_2)_3BH)(C_3H_2Me_2N_2)$ and $[NHMe_2NHMe][TiCl_3((N_2C_3HMe_2)_3BH)]$ were prepared from $TiCl_3((N_2C_3HMe_2)_3BH)$ and hydrazines. These products were crystallographically characterized and were shown to exhibit a distorted octahedral geometry at Ti.[943]

4.2.3.4.9 *Dianionic tridentate ligand complexes*

The polydentate diamido–amine ligand $[Me_3SiN(CH_2CH_2NSiMe_3)_2]^{2-}$ has been used to prepare the Ti^{III} dimer $Ti_2(\mu\text{-}Cl)_2(Me_3SiN(CH_2CH_2NSiMe_3)_2)_2$ (**83**). Subsequent alkylation with $Li[CH(SiMe_3)_2]$ gave the monomeric species $Ti(CH(SiMe_3)_2)(Me_3SiN(CH_2CH_2NSiMe_3)_2)$ which was transformed to the stable diamagnetic Ti^{III}-hydride $Ti_2(\mu\text{-}H)_2(Me_3SiN(CH_2CH_2NSiMe_3)_2)_2$ upon hydrogenolysis.[944]



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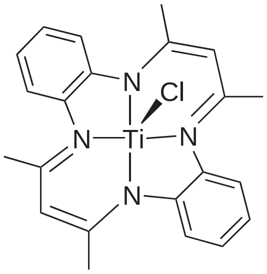

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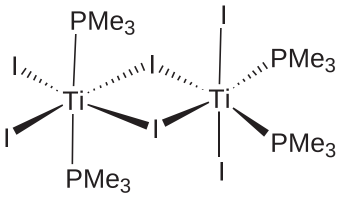

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4.2.3.4.10 *Dianionic tetradentate ligand complexes*

The Ti^{III} compound, $TiCl(Me_4taa)$ (**84**), was isolated and transformed to a variety of organometallic derivatives.[945]

4.2.3.4.11 *Porphyrin complexes*

Five-coordinate Ti porphyrin complexes are known to have an affinity for oxygen-based ligands. Reaction of TiF(TPP) with Na[SMe] and methanol yielded Ti(OMe)(TPP).[946]

4.2.3.5 Phosphorus-based Ligand Complexes

TiCl–phosphine complexes have the tendency to form dinuclear Cl-bridged complexes. For example, the series of compounds $(TiCl_2L)_2(\mu\text{-}Cl)_2$ ($L = Pr^i_2PCH_2CH_2PPr^i_2$,[947] $2PMe_3$,[928] $Et_2PCH_2CH_2PEt_2$ and DMPE[312]) consist of two octahedra that share a common edge. Alternatively, two octahedra fused by a common face are exemplified by the complexes $[PPh_4][(TiCl_2L)_2(\mu\text{-}Cl)_3]$ ($L = PEt_3$, PMe_2Ph,[915,948]). A dissymmetric bioctahedral analogue $Ti_2(\mu\text{-}I)_2I_4(PMe_3)_4$ (**85**) has also been reported.[949] In addition, the monomeric Ti^{III} adducts $TiCl_3(THF)(Pr^i_2PCH_2CH_2PPr^i_2)$[947] and $TiCl_3(P(SiMe_3)_3)_2$[950] have been synthesized.

4.2.3.6 Oxygen-based Ligand Complexes

4.2.3.6.1 Neutral oxygen donor ligand complexes

A number of THF adducts of Ti chlorides including $[TiCl_2(THF)_4][ZnCl_3(THF)]$,[951] $[TiCl_2(THF)_4][SnCl_5(THF)]$[952] and $(TiCl_2(THF)_2)_2(\mu\text{-}Cl)_2$[953] have been synthesized. Interestingly, reduction of $TiCl_4(THF)_2$ by Al in THF gave $TiCl_3(THF)_3$, while the same reaction in CH_2Cl_2 gave $(TiCl_2(THF)_2)_2(\mu\text{-}Cl)_2$.[953] In addition, the crystal structures of $TiCl_2(THF)_2(\mu\text{-}Cl)_2Li(THF)_2$,[954,955] $TiCl_3(THF)(OC_4H_7CH_2OH)$,[956] and $(TiCl_2(C_6H_4(CO_2Et)_2))_2$ $(\mu\text{-}Cl)_2$[957] have been reported.

The complex $[NBu_4]_2[TiCl_6]$ was reduced photochemically to the Ti^{III} complex $[NBu_4][TiCl_4(THF)_2]$. Alternatively, this anion was prepared directly from the reaction of $TiCl_3(THF)_3$ and $[NBu_4]_2[MgCl_4]$.[727]

Aqueous Ti^{III} has been utilized as a reducing agent in a wide variety of redox reactions.[958–969] In addition, a variety of tools have been employed to study Ti^{III} aqua complexes. For example, the reduction of H_2O_2 and O_2 by $[Ti(EDTA)(H_2O)]^-$ and $[Ti(H_2O)_6]^{3+}$ were studied using radical traps.[970] The SCF MS-Xα method suggested that the most stable configuration of *trans*-$[TiCl_2(H_2O)_4]^+$ was with the plane of each H_2O molecule oriented parallel to the Cl–Ti–Cl axis.[971] Magnetization and Raman studies of the $[Ti(H_2O)_6]^{3+}$ cation demonstrated the influence of Jahn–Teller coupling on the magnetic properties.[972] Finally, crystallographic studies have been performed on $[Ti(H_2O)_6][C_6H_4MeSO_3]_3$ and $[NMe_4][TiF_2(H_2O)_4][TiF_6]$.[973,974]

4.2.3.6.2 Hydroxide ligand complexes

Partial hydrolysis of Ti^{III} in the presence of $[PPh_4]Cl$ in acetone gave the dinuclear species $[PPh_4]_2[Ti_2(\mu\text{-}Cl)Cl_6(\mu\text{-}OH)(H_2O)(OCMe_2)]$ and the mononuclear compound $TiCl_3(H_2O)_3$.[975]

4.2.3.6.3 Alkoxide ligand complexes

A series of Ti^{III} alkoxides with the formulas $TiCl_2(OR)$ and $TiCl(OR)_2$ (R = Me, Et, Bu) were reported from the reactions of anhydrous $TiCl_3$ and trialkylorthoformates. These materials were thought to be polymeric in nature.[976] Reaction of $TiCl_3(THF)_3$ with $Na[OC_6H_3Bu^t_2]$ led to the monomeric five-coordinate Ti complex $TiCl_2(OC_6H_3Bu^t_2)(THF)_2$, which was shown to have trigonal bipyramidal coordination geometry.[977]

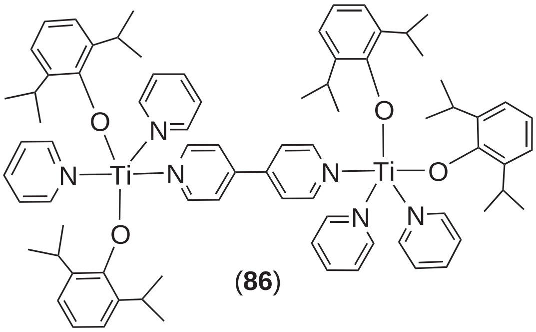
In related work, $Ti(OC_6H_3Bu^t_2)_3$ was obtained from $TiCl_3(NMe_3)_2$ and excess $Li[OC_6H_3Bu^t_2]$. An electrochemical study showed that $Ti(OC_6H_3Bu^t_2)_2X_2$ (X = Cl, Br) were reversibly reduced to the corresponding Ti^{III} monoanions.[426] In contrast, reduction of the Ti^{IV} precursor in a non-donor solvent led to the formation of the dimer $(Ti(OC_6H_3Ph_2)_2)_2(\mu\text{-}Cl)_2$.[978]

The complex $Ti(OC_6H_3Pr^i_2)_2Bn(Bu^tNCBn)$ reacted with pyridine effecting alkyl transfer, elimination of imine, and reductive coupling of a pyridine, affording the intermediate Ti^{III} complex $(Ti(OC_6H_3Pr^i_2)_2(NC_5H_5)_2)_2(\mu^2\text{-}NC_5H_4C_5H_4N)$ (**86**).[979]

Reactions of $TiCl_2(TMEDA)_2$ with $Na[OR]$ ($R = Ph$, $C_6H_3Bu^t_2$) formed the trimer $Ti_3(\mu\text{-}OPh)_4(OPh)_5(TMEDA)_2$ (**87**) and the dimer $(TiCl(OC_6H_3Bu^t_2)_2(TMEDA))_2(\mu\text{-}OC_6H_3Bu^t_2)_2$

respectively. Alternatively, the reaction of $Ti(N(SiMe_3)_2)_3$ with $HOC_6H_3Me_2$ gave $(Ti(OC_6H_3Me_2)_2(\mu\text{-}OC_6H_3Me_2))_2$, while the reaction of $Li[OC_6H_3Me_2]$ with $TiCl_3(THF)_3$ gave the monometallic salt $[Li(TMEDA)_2][Ti(OC_6H_3Me_2)_4]$.[980]

Floriani and co-workers have synthesized the Ti^{III} complex $Li_3[Ti(DAG)_6]$ (**88**) that contained ligand, di-*o*-isopropylidene-α-D-glucofuranose (DAG^-). The alkoxide fragments of the glucose ligands bridged the Ti and Li atoms and gave the pseudo-octahedral geometry about Ti.[981]



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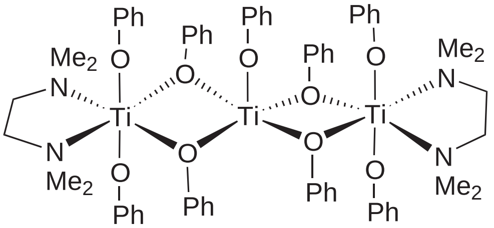

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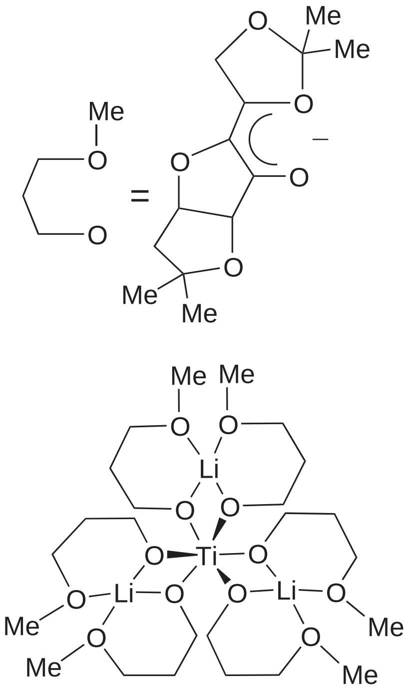

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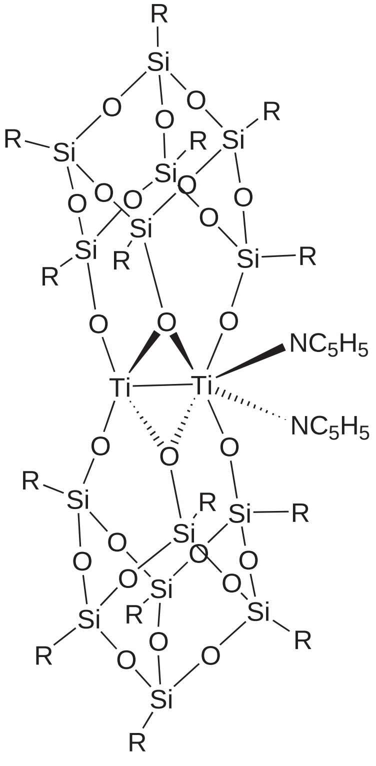

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4.2.3.6.4 *Siloxide ligand complexes*

The reduction of $TiCl(OSiBu^t{}_3)_3$ using a Na/Hg amalgam in DME yielded $Ti(OSiBu^t{}_3)_3(DME)$.[457] Reactions with a variety of Lewis bases were carried out in order to prepare $Ti(OSiBu^t{}_3)_3L$ ($L = Me_2O$, CNMe, $CNBu^t$, $NCBu^t$, PMe_3, NC_5H_5, NH_3)[982] In contrast, reaction with ketones and aldehydes gave ketyl derivatives via electron transfer.[983]

The Ti^{III} dimer $(Ti(Cy_7Si_7O_{12}))_2$ was derived from the reaction of the trisilanol $(Cy_7Si_7O_{12}H_2)$ with $TiCl_3(NMe_3)_2$ and characterized by X-ray crystallography.[984] This compound reacted with pyridine to give the dissymmetric dimer $Ti_2(Cy_7Si_7O_{12})_2(NC_5H_5)_2$ (**89**). In this latter complex the two Ti centers adopt distorted tetrahedral and octahedral geometries respectively.[984] An isomorphous siloxy bridged Ti^{III}–V^{III} dimer, $[Ti(Cy_7Si_7O_{12})(NC_5H_5)_2][V(Cy_7Si_7O_{12})]$ has also been reported.[985]

4.2.3.6.5 *Diketonate ligand complexes*

The compounds $Ti(OC(Me)CHC(Me)O)_3$ and $Ti(OC(CF_3)CHC(CF_3)O)_3$ have been studied by FT-ion cyclotron mass spectrometry. The trends in ligand binding energies in these complexes were analyzed in terms of ligand field theory.[986]

4.2.3.6.6 *Carboxylate, carbamate, and oxalate ligand complexes*

The carboxylate bridged dimer $[Ti_2(\mu\text{-}O_2CPh)_2((MeNCH_2CH_2)_3)_2(\mu\text{-}O)][PF_6]_2$ was prepared from a refluxing mixture of $TiCl_3((MeNCH_2CH_2)_3)$ and $Na[O_2CPh]$ in air followed by treatment with $Na[PF_6]$. A crystallographic study of this diamagnetic complex confirmed the linear arrangement of the Ti–O–Ti vector.[921]

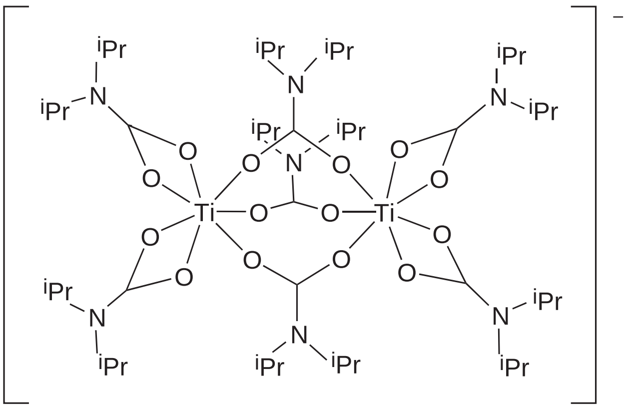
The reaction of $TiCl_3(THF)_3$ with $PhCO_2H$ gave the mixed valent compound $Ti_2Cl_3(\mu\text{-}O)(\mu\text{-}O_2CPh)_2(THF)_3$. Crystallographic data showed an unusual asymmetric Ti^{III}/Ti^{IV} bridged complex.[553] A series of Ti^{III} tetrachlorophthalate salts of the form $K[Ti(Cl_4C_6\ (CO_2)_2)_2(L)_2]$ have been prepared and characterized by conductivity and magnetic moment measurements.[987]

The complex $Ti(O_2CNPr^i{}_2)_4$ reacted with excess ligand to give the anionic dimer $[NH_2Pr^i{}_2][Ti_2(O_2CNPr^i{}_2)_4(\mu\text{-}O_2CNPr^i{}_2)_3]$ (**90**). The X-ray crystal structure revealed three bridging carbamate ligands and two terminal carbamate groups providing six-coordinate Ti centers.[988]

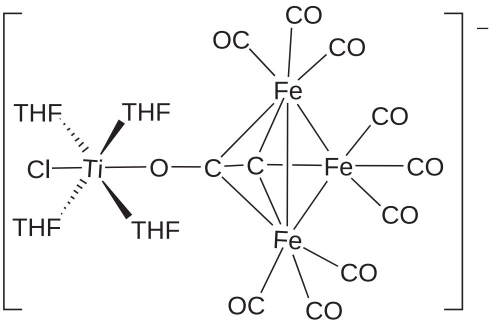
The oxalate complex $K_3[Ti(C_2O_4)_3(H_2O)]$ was prepared by the addition of excess $K_2[C_2O_4]$ to a solution of $[Ti((H_2N)_2CO)_6]Cl_3$. The crystal structure revealed a seven-coordinate pentagonal bipyramidal geometry about the Ti center.[989] The kinetics of electron transfer reactions between Ti^{III} oxalate complexes with Ru and Co complexes have been studied in detail.[969,990,991]

4.2.3.6.7 *Miscellaneous oxygen ligand complexes*

Treatment of $[(Ph_3P)_2N]_2[Fe_3(CO)_9(CCO)]$ with $TiCl_3(DME)_{1.5}$ in the presence of a Zn–Cu couple produced three products including $[(Ph_3P)_2N][(TiCl(CCO)(THF)_4)Fe_3(CO)_9]$ (**91**) in low yield.[992] This compound was characterized by X-ray crystallography, EPR spectroscopy, and magnetic susceptibility.[992]



(**90**)



(**91**)

The compound $Ti(H_3O)(SO_4)_2(H_2O)_3$ was obtained from reactions of the metal sulfate and SO_3 in water. The crystal structure revealed distorted TiO_6 octahedra which share corners with SO_4 tetrahedra.[993]

4.2.3.7 Sulfur-based Ligand Complexes

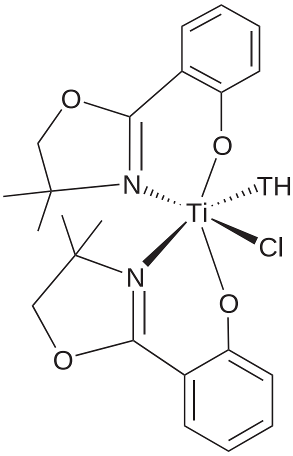
The addition of $TiCl_3$ to a solution of 1,4,7-trithiacyclononane $(SCH_2CH_2)_3$ was reported to yield $TiCl_3((SCH_2CH_2)_3)$.[684]

4.2.3.8 Mixed Donor Ligand Complexes

4.2.3.8.1 N,O bidentate ligand complexes

Reaction of equimolar amounts of 1,4-bis(2′-hydroxyphenylazomethine)phenylene and Ti^{III} cations resulted in a product which was proposed to be a coordination compound. IR data suggested N,O chelation to the Ti^{III} centers.[994] Similarly, the complex containing gallacetophenone–phenylhydrazone, $TiCl(OC_6H_2(OH)_2(CMeNNHPh))_2(H_2O)_2$, has been reported and proposed to bind in a bidentate N,O fashion.[995]

The metathesis reaction between the sodium salt of hydroxyphenyloxazoline with $TiCl_3(THF)_3$ yielded the complex $TiCl(OC_6H_4(C_3H_2Me_2ON)_2)(THF)$ (**92**) and the N,O chelation was verified crystallographically.[775]



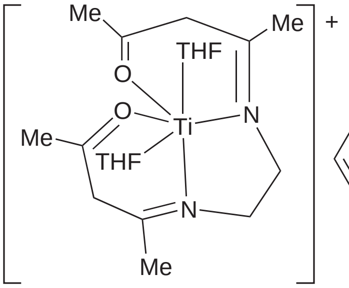
(**92**)

4.2.3.8.2 NO_2 tridentate ligand complexes

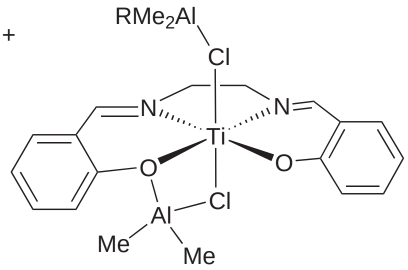
The ionic compound $K_2[Ti(C_{13}H_9NO_2)(SCN)_3]$, containing a dianionic tridentate Schiff-base ligand, has been reported recently and is presumed to adopt a pseudo-octahedral geometry.[996]

4.2.3.8.3 N,O tetradentate ligand complexes

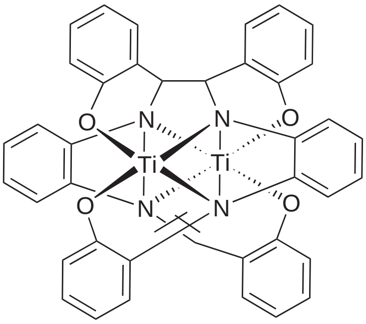
Reaction of $TiCl_3(THF)_3$ and $Na_2[(OC(Me)CH_2C(Me)NCH_2)_2]$ yielded $TiCl((OC(Me)CH_2C(Me)NCH_2)_2)(THF)$.[997] Crystallographic data confirmed the *trans* arrangement of the Cl and THF ligands in a pseudo-octahedral coordination geometry. Reactions involving $M[(OC(Me)CH_2C(Me)NCH_2)_2]$ ($M = Co$, Fe) with $TiCl_3(THF)_3$ gave the complexes $[Ti((OC(Me)CH_2C(Me)NCH_2)_2)(THF)_2][CoCl_3(THF)]$ (**93**) and $[Ti((OC(Me)CH_2C(Me)NCH_2)_2)(THF)_2]_2\ [Fe_3Cl_8(THF)_2]$.[998]



(**93**)



(**94**)



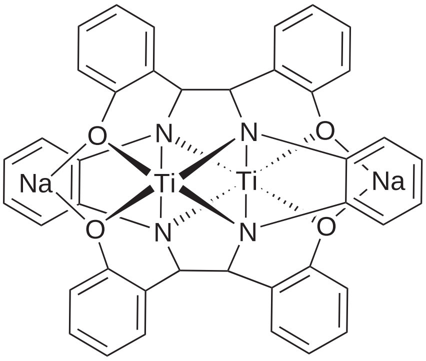
(**95**)

The reaction of the related Schiff-base complexes $TiX_2((OC_6H_4CNCH_2)_2)$ (X = Cl, Br) with $AlMe_3$ afforded the hetero-bimetallic Ti^{III} complex $Ti((OC_6H_4CNCH_2)_2)(\mu\text{-}X)(AlMe_2)(\mu\text{-}X)(AlMe_2R)$ (**94**) (R = Cl, Br).[835,836]

Ligand-based reduction occurred in the reaction of $TiCl((OC_6H_4CHN)_2C_6H_4)(THF)$ with Na. The product $Ti_2((OC_6H_4CHN)_2C_6H_4)_2)_2(THF)_2$ (**95**), in which the two ligands were coupled via C—C bond formation, exhibited temperature-dependent magnetic moments, typical of antiferromagnetic-coupled Ti^{III} centers.[927]

4.2.3.8.4 Hexa- and octadentate N,O ligand complexes

$Ti_2((OC_6H_4CHN)_2C_6H_4)_2)_2(THF)_2$ underwent an additional C—C bond formation upon further reduction. This yielded the ionic complex $Na_2[Ti_2(salophen^*)(THF)_6]$ (**96**) where salophen* is an octadentate, octaanionic ligand derived from the dimerization of two of the original ligands.[927] This latter compound showed a residual temperature-independent paramagnetism.



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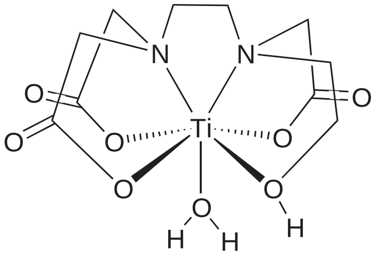


(97)

Initially, $(Ti(HEDTA)(H_2O))$ (**97**) was thought to have adopted a six-coordinate structure with the ligand binding in a pentadentate fashion.[960] However, a recent crystallographic study revealed a seven-coordinate complex in the solid state in which the ligand is hexadentate.[873]

4.2.3.8.5 N,S bidentate ligand complexes

Complexes of 3-(4-pyridyl)triazoline-5-thione[999] and thiobenzoylhydantoins[1000] have been reported and were presumed to chelate via N and S, although this was not confirmed unambiguously.

The Ti^{III} complexes $Ti(Et_2P(S)NR)_3$ (R = Me, Et, Bu^t, Cy, Ph) have been synthesized by a salt metathesis reaction between $Li[Et_2P(S)NR]$ and $TiCl_3$.[1001] These ligands formed four-membered chelate rings on Ti.

4.2.3.8.6 O,P bidentate ligand complexes

The alkoxy–phosphine complex $TiCl(OC(Bu^t)_2CH_2PMe_2)_2$ was prepared by the metathesis reaction of $TiCl_3$ and $Na[OC(Bu^t)_2CH_2PMe_2]$. Structural characterization revealed a trigonal bipyramidal geometry about Ti.[1002]

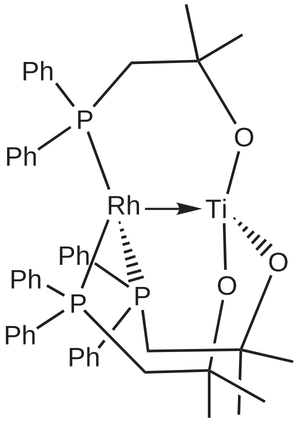
4.2.3.9 Halide Complexes

Reduction of $TiCl_4$ with $Me_3SiSiMe_3$ was suggested to yield $TiCl_2$.[1003] However, it has been shown that $TiCl_3$ is the major product based on the Ti:Cl ratio.[1004]

The reaction of $TiCl_3(THF)_3$ with chloride salts gave $[NEt_4]_3[Ti_2(\mu\text{-}Cl)_3Cl_6]$.[553] Reduction of $TiCl_4$ with $HSnBu_3$ followed by treatment with varying amounts of a chloride salt produced $[PPh_4]_3[Cl_3Ti(\mu\text{-}Cl)_3TiCl_3]$ and $[PPh_4]_3[Cl_3Ti(\mu\text{-}Cl)_3Ti(\mu\text{-}Cl)_3TiCl_3]$, which were determined crystallographically.[915]

4.2.3.9.1 Metal—metal bonded compounds

The reduction of $TiCl(\mu^2\text{-}OCMe_2CH_2Ph_2P)_3RhCl$ afforded the formally Ti^{III}/Rh(**0**) species $Ti(\mu^2\text{-}OCMe_2CH_2Ph_2P)_3Rh$ (**98**), which was reported to have a Ti—Rh bond distance of 2.2142(**11**) Å.[1005]



(**98**)

4.2.4 TITANIUM(II)

Transient Ti^{II} complexes have been inferred as reagents in a variety of organic transformations.[903,1006–1010] For example, the reactive species $(TiH(Cl)(THF)\sim0.5)_x$ was generated by the reduction of $TiCl_3(THF)_3$ with MgH_2 and shown to be the active species in the McMurry reaction.[1010–1013]

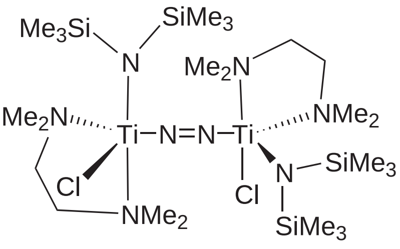
4.2.4.1 Nitrogen-based Ligand Complexes

4.2.4.1.1 Neutral nitrogen ligand complexes

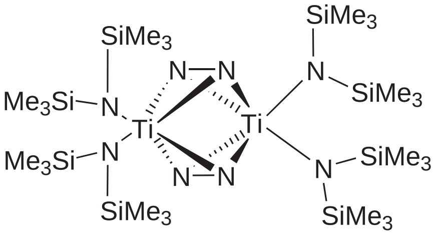
The reduction of $TiCl_3(THF)_3$ with Li in the presence of TMEDA (TMEDA = $Me_2NCH_2CH_2NMe_2$) yielded monomeric *trans*-$TiCl_2(TMEDA)_2$.[1014] Facile ligand exchange gave $TiCl_2L_2$-(L = $Me_2NCH_2CH_2NMeH$, bipy) and $TiCl_2(NC_5H_5)_4$. Alternatively, $TiCl_2(NC_5H_5)_4$[1015] was produced directly by reduction of $TiCl_4$ by Na in the presence of NC_5H_5.[1016]

4.2.4.1.2 Amido ligand complexes

The addition of $Li[N(SiMe_3)_2]$ to $TiCl_2(TMEDA)_2$ at −80 °C yielded the binuclear complex $(TiCl(TMEDA)(N(SiMe_3)_2))_2(\mu\text{-}N_2)$ (**99**). The bridging N_2 moiety adopted an end-on binding mode. Alternatively, two equivalents of the amide salt gave $(Ti(N(SiMe_3)_2)_2(\mu\text{-}N_2))_2$ (**100**), where the N_2 units were bound in a side-on fashion.[1017] The corresponding reaction with $LiNPh_2$ gave $[N,N'\text{-}(Ti((\eta^6\text{-}Ph)PhN)_2)Ti(NPh_2)_2]^-$ (**101**)[1018] whereas treatment of *trans*-$TiCl_2(TMEDA)_2$ with $NaPPh_2$ afforded the corresponding salt of $[Ti_3Cl_5(TMEDA)_3]^+$ (**102**),[1018] inferring a complicated ligand redistribution.



(99)



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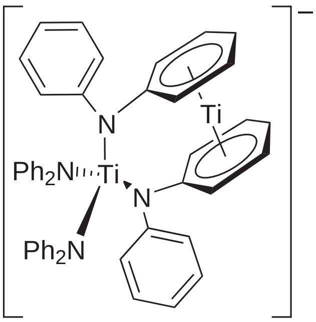

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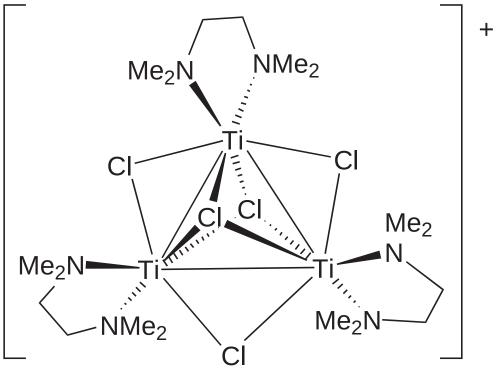
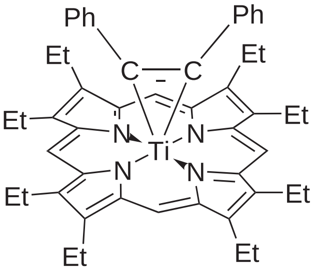


(102)

Reduction of $TiCl_4(THF)_2$ with Mg in the presence of RNC(Ph)C(Ph)NR (R = Ph, C_6H_4Me, C_6H_4OMe, Pr^i) gave $Ti(RNC(Ph)C(Ph)NR)_2$.[939] Coordination of the nitrogen atoms and the olefinic carbons to Ti were indicated crystallographically.

4.2.4.1.3 *Porphyrin complexes*

In 1991 the first Ti^{II} porphyrin complexes Ti(OEP)(η^2-PhCCPh) (**103**) and Ti(TTP)(η^2-PhCCPh) (OEP = octaethylporphyrinato, TTP = *meso*-tetra-*p*-tolyl-porphyrinato) were made and characterized by Woo *et al.*[1019] The syntheses involved reduction of $TiCl_2$–porphyrin complexes by $LiAlH_4$ in the presence of PhCCPh. Structural data confirmed a nearly planar porphyrin core for Ti(OEP)(η^2-PhCCPh).



(103)

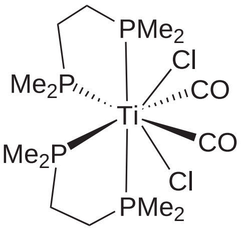
The Ti^{II} porphyrin complexes Ti(por)(η^2-RCCR) and $Ti(por)(L)_2$ (por = TTP, OEP; R = Me, Et, H; L = NC_5H_4Me, NC_5H_5, THF, Bu^tNC, PEt_3, $OP(C_8H_{18})_3$) have also been reported.[1020–1022] Ti(TTP)(η^2-EtCCEt) and $Ti(TTP)(THF)_2$ act as dechlorinating agents, reacting with chloroalkanes and chloroalkenes producing $TiCl_2(TTP)$. Ti(TTP)(η^2-EtCCEt) also deoxygenates sulfoxides or epoxides to form TiO(TTP) and the corresponding sulfides or olefins.[1023] Similarly, a variety of Ti–porphyrin complexes containing hydrazido, sulfido, persulfido, selenido, perselenido, oxo, peroxo, and imido ligands have been synthesized via oxidation of Ti^{II} porphyrin complexes[1020–1022] (see Section 4.2.2.3.24).

The reduction of $Ti(OEP)(THF)_2$ in THF with Li under C_2H_4 led to the formation of the dimeric Ti^{II} porphyrin complex with C_2-bridged Ti atoms and two Li cations supported by the porphyrin ligands.[273]

4.2.4.1.4 *Phosphine ligand complexes*

The monomeric *trans*-$TiCl_2(DMPE)_2$ was generated using a one-pot mixture of $TiCl_4$, DMPE, and Mg in THF.[1024] A series of derivatives—$TiX_2(dmpe)_2$ ($X = OPh$ and Cl, OPh,[1025] BH_4, Me)—have also been prepared.[1026] Interestingly, $TiCl_2(DMPE)_2$ and $Ti(BH_4)_2(DMPE)_2$ were found to be paramagnetic and thus had a triplet ground state, whereas $TiCl(OPh)(DMPE)_2$, $Ti(OPh)_2(DMPE)_2$, and $TiMe_2(DMPE)_2$ were diamagnetic complexes and correspondingly had a singlet ground state. These differences were attributed to the electronegativity and ligand field differences between the ancillary ligands.[1025,1027]

The thermally unstable carbonyl complex $TiCl_2(CO)_2(DMPE)_2$ (**104**) was prepared at −70°C from reaction of $TiCl_2(DMPE)_2$ with CO. NMR data suggested a bicapped octahedronal geometry about Ti.[1028] The reaction of $TiCl_4(DMPE)$ with Bu^tMgCl gave $(TiCl_2(DMPE))_3$ (**105**), which was the first Ti^{II} cluster isolated and structurally characterized.[312]



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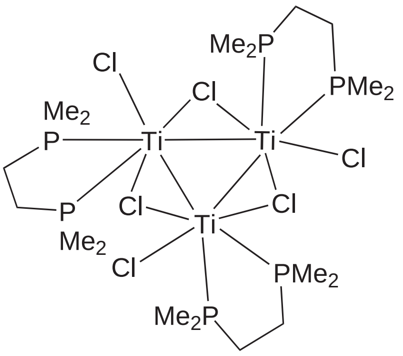


(105)

4.2.4.2 Oxygen-based Ligand Complexes

The complex $Ti(OC_6H_3Pr^i_2)_2(Bu^tNCBn_2)(NC_5H_5)$ reacted with bipy effecting elimination of imine affording $Ti(OC_6H_3Pr^i_2)_2(bipy)_2$.[979] Electrochemical and spectroscopic data support the Ti^{II} formulation.

The syntheses of the purported Ti^{II} complexes $TiX_2Y_2(H_2O)_z$ (X = hyrdoxamic acids, Y = RNCS, $H_2NCH_2CH_2NH_2$; $z = 0.5$, 1, 2, 3) were reported although these formulations were based only on IR data.[1029,1030]

4.2.5 TITANIUM(0)

The seven-coordinate complex $Ti(CO)_3(DMPE)_2$ was prepared by reduction of $TiCl_4(THF)_2$ by $Na[C_{10}H_8]$ in the presence of phosphine ligand, at −70 °C under Ar, followed by carbonylation.[1031,1032] Prolonged exposure to CO converted $Ti(CO)_3(DMPE)_2$ to $Ti(CO)_5(DMPE)$. Reaction with $K[(N_2C_3H_3)_3BH]$, $Na[SnPh_3]$, and $Na[GePh_3]$, followed by cation exchange afforded $[NEt_4][Ti(CO)_4(N_2C_3H_3)_3BH]$, $[AsPh_4][Ti(CO)_4(DMPE)SnPh_3]$, and $[AsPh_4][Ti(CO)_4(DMPE)GePh_3]$, respectively. Other Ti–CO complexes that have been synthesized recently include $Ti(CO)_4((Me_2PCH_2)_3CMe)$,[1033] $Ti(CO)_4((Me_2PCH_2)_3SiBu^t)$,[1034] $Ti(CO)_4((HNCH_2CH_2)_3)$, $Ti(CO)_4((MeNCH_2CH_2)_3)$,[1035] $Ti(CO)_3(C_6H_4(AsMe_2)_2)_2$, and $Ti(CO)_4((Ph_2PCH_2)_3CMe)$.[1036] Reductive carbonylation in the presence of PMe_3 followed by the addition of appropriate nucleophiles gave $[Ti(CO)_5(SnPh_3)_2]^{2-}$ and $[Ti(CO)_5(GePh_3)_2]^{2-}$,[1036] while $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$ reacted with $BH_3(THF)$ at −60 °C affording $[K(15\text{-crown-}5)_2][Ti(CO)_4(\eta^3\text{-}BH_4)]$. Subsequent reaction of

$[Ti(CO)_6(\eta^3\text{-}BH_4)]^-$ with $K[NC_4H_4]$ gave $[Ti(CO)_4(\eta^5\text{-}NC_4H_4)]^-$.[1037] Reaction of $[K(15\text{-crown-}5)_2]_2$-$[Ti(CO)_6]$ with $SnClR_3$ or PhNNPh generated the anions $[Ti(CO)_6SnR_3]^-$ (R = Ph, Me, Cy)[1038] and $[Ti(CO)_4(PhNNPh)]^{2-}$,[1039] respectively. Hydrolysis of $[Ti(CO)_4(PhNNPh)]^{2-}$ resulted in formation of $[Ti_2(\mu\text{-}OH)_2(CO)_8]^{2-}$.[1039] Similarly, $[K(15\text{-crown-}5)_2]_2[Ti(CO)_6]$ reacted with PhOH or MeOH to give $[Ti(CO)_4(OPh)]_2{}^{2-}$ and $[Ti(CO)_4\ (OMe)]_2{}^{2-}$.[1040]

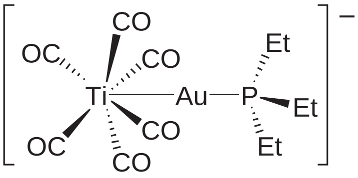
Metal vapor synthesis provided a synthetic route to $Ti(\mu^6\text{-}NC_5H_3Me_2)_2$.[1041,1042] Similarly, co-condensation of Ti vapor in the presence of an excess of $(Pr^iNCH)_2$ gave the six-coordinate Ti complex $Ti((Pr^iNCH)_2)_3$. The analogous reaction with the bulkier ligand $(Bu^tNCH)_2$ led to the four-coordinate complex $Ti((Bu^tNCH)_2)_2$.[1043] Altenatively, four- and six-coordinate diazadiene derivatives were obtained from reduction of $TiCl_4(THF)_2$ with Mg in the presence of $(RNCPh)_2$ (R = Ph, C_6H_4Me, C_6H_4OMe).[939]

Reduction of $TiCl_4(THF)_2$ with $[Et_3BH]^-$ was proposed to yield a Ti–H complex which under vacuum generated a Ti–THF complex ($Ti^0\cdot$THF). This was formulated based on IR data.[1044]

4.2.6 TITANIUM (-II)

Stable dianionic derivatives of the Ti carbonyl complex $[Ti(CO)_6]^{2-}$ have been synthesized, isolated, and characterized.[1045] The $[Ti(CO)_6]^{2-}$ ion was obtained via reductive carbonylation of $Ti(CO)_3(DMPE)_2$ or $TiCl_4(DME)$ by $KC_{10}H_8$ in the presence of a crown ether or cryptand.[1045] An octahedral environment about Ti in $[K(\text{cryptand }2.2.2)]_2[Ti(CO)_6]$ was confirmed both in solution by the observation of a septet resonance in the ^{49}Ti NMR spectrum for the ^{13}CO complex and crystallographically.[1046] Related complexes with weakly solvated alkali metal cations readily decomposed.[1047]

The reaction of $[K(15\text{-crown-}5)]_2[Ti(CO)_6]$ with $AuCl(PR_3)$ (R = Cy, Et) yielded $[K(15\text{-crown-}5)]$ $[Ti(CO)_6(AuPR_3)]$ (**106**).[1048] Structural data for the anion revealed a seven-coordinate geometry about Ti with a Ti—Au bond length of 2.719(1) Å. Distortion of the coordination sphere was attributed to the approach of a CO ligand to Au.



(**106**)

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4.3
Zirconium and Hafnium

E. HOLLINK and D. W. STEPHAN
University of Windsor, ON, Canada

4.3.1 INTRODUCTION

There has been tremendous growth in the chemistry of zirconium and hafnium since the 1960s. Many of the developments have been the result of efforts to uncover new applications. One of the major driving forces has been the rising importance of "single-site" alkene polymerization catalysis and catalysis in general. Other motivations have included a variety of strategies to develop molecular compounds as precursors to specific solid-state materials. In all cases, the fundamental chemical issues often are reduced to the development of new coordination chemistry.

In this chapter, we review the progress in coordination chemistry of zirconium and hafnium from the 1960s to 2002. Thus, this chapter was written as an extension of the previous issue of *Comprehensive Coordination Chemistry* (*CCC*, 1987). In defining the scope of this review, we have specifically limited the discussion to exclude compounds deemed to be principally organometallic in nature.

4.3.2 ZIRCONIUM(IV) AND HAFNIUM(IV)

4.3.2.1 Boron-based Ligand Complexes

4.3.2.1.1 Carborane ligand complexes

The zwitterionic complex $[Li(THF)_2]$ $[ZrCl\{C_2B_4H_4(SiMe_3)_2\}_2(THF)]$ (**1**) was prepared and characterized crystallographically. The carborane ligands were bound in a η^5-fashion, thus resembling a metallocene.[1] A subsequent study expanded the chemistry to include related carborane derivatives, as well as Hf analogs.[2]

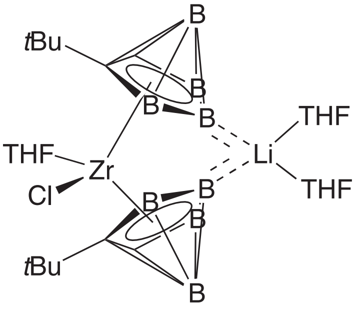
Related Zr carborane complexes $Zr(por)(\eta^5\text{-}1,2\text{-}C_2B_9H_{11})$ (por = TPP, octaethylporphyrin (OEP)) that incorporate porphyrin ligands were readily synthesized from reaction of the

$ZrCl_2$(por) precursor with the Tl or Na salt of the dianionic carborane.[3,4] X-ray structural data for Zr(OEP) (η^5-1,2-$C_2B_9H_{11}$) confirmed the η^5-bonding mode of the carborane.

Using an alternative synthetic approach, Zr(η^5-1,2-$C_2B_9H_{11}$)$(NEt_2)_2$($NHEt_2$) was derived from reaction of the neutral carborane ligand $C_2B_9H_{13}$ with $Zr(NEt_2)_4$. The amine donor was readily exchanged with THF or 4-picoline.[5] Alternatively, the amido ligands were replaced by Cl atoms upon reaction with $[NH_2Et_2]Cl$, providing $ZrCl_2$(η^5-1,2-$C_2B_9H_{11}$)($NHEt_2$). Upon activation, the bis-amido species Zr(η^5-1,2-$C_2B_9H_{11}$)$(NEt_2)_2$($NHEt_2$) exhibited good activity for the polymerization of C_2H_4 and copolymerization of C_2H_4/norbornene.[6,7]

The complexes M(η^5-η^1-$RC_2B_9H_9$-CH_2NMe_2)$_2$ (M = Zr (**2**), Hf) and *closo*-1-ZrCl[($NHCH_2$)-η^5-$C_2B_9H_{10}$](THF)[8,9] with chelating amino or amido groups were prepared. The former species were obtained by addition of the monoanionic ligand to MCl_4, whereas the latter was derived employing the dianionic salt of the ligand. Evaluation of these compounds as precatalysts for polymerization has yet to be reported.

The species $ZrCl_2(Et_2C_2B_4H_4)(PMe_3)_2$ was derived from the reaction of $ZrCl_4(PMe_3)_2$ with one equivalent of $Li_2[Et_2C_2B_4H_4]$.[10] Although it decomposed in solution, exchange of PMe_3 with $(Me_2PCH_2)_2CH_2$ gave the air-sensitive but thermally stable analog $ZrCl_2(Et_2C_2B_4H_4)[(Me_2PCH_2)_2$-$CH_2]$ (**3**).



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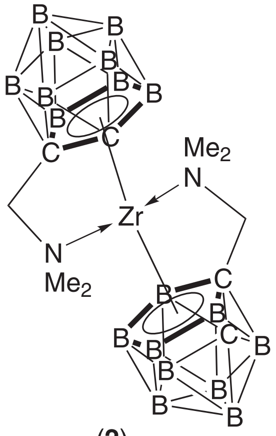

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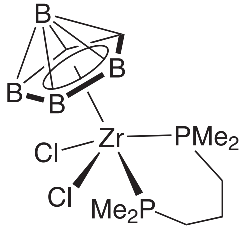


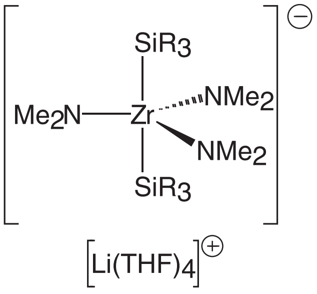
(**3**)

4.3.2.2 Silicon-based Ligand Complexes

Zr—Si bonds in the absence of anionic π-donor ligands are quite rare. The compound $Zr(OBu^t)_3$ $[Si(SiMe_3)_3]$[11] was prepared via treatment of $ZrCl(OBu^t)_3$ with $LiSi(SiMe_3)_3$. Subsequently, $ZrCl(OSiMe_3)_2(SiPh_2Bu^i)$[12] was also described. These compounds have been characterized structurally and the Zr—Si bond lengths were found to be 2.848(3) Å and 2.753(4) Å, respectively. It was suggested that the presence of the π-donating alkoxide ligands provided stability. This was consistent with preliminary results that indicated $Zr(OBu^t)_3$ $[Si(SiMe_3)_3]$ did not react with CO, C_2H_4, or $PhSiH_3$.[11] The compounds $ZrR_3[Si(SiMe_3)_3]$ (R = CH_2Bu^t, CH_2SiMe_3) were prepared and found to be photosensitive but thermally stable in the solid state.[13,14] RNC insertions into Zr—Si bonds of $ZrR_3[Si(EMe_3)_3]$ (E = C, Si) were found to depend on the steric properties of the ancillary ligands and the substrates.[15,16]

Amido ligands have also been exploited to stabilize Zr and Hf silyl complexes. Metathesis of halides with Li-silylides was used to prepare $M(NMe_2)_2(NR^1_2)(SiR^2_3)$ (M = Zr, Hf; R^1 = Me, $SiMe_3$; R^2 = $(SiMe_3)_3$, Ph_2Bu^t). Of these, only those containing the bulky silyl ligand $Si(SiMe_3)_3$ were thermally robust.[17] Reaction with excess $LiSiPh_2Bu^t$ afforded the salt $Li[Zr(NMe_2)_3(SiPh_2Bu^t)_2]$ (**4**), which was characterized crystallographically.[18] The two Si-groups adopted a *trans* disposition of a distorted trigonal bipyramidal geometry, with relatively long Zr—Si distances of 2.933,1(14) Å.

In a recent report, reaction of $M(NMe_2)_4$ (M = Zr, Hf) with SiR^1PhH_2 (R^1 = H, Me, Ph) yielded equilibria among $Zr(NMe_2)_3[Si(SiMe_3)_3]$, $Zr(NMe_2)_2[Si(SiMe_3)_3]H$, $SiPhR^2H_2$, and $SiPhR^2(NMe_2)H$.[19] It is noteworthy that the Zr—Si bonds in this series of compounds were unreactive.



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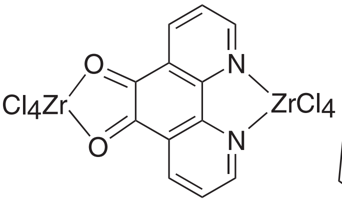

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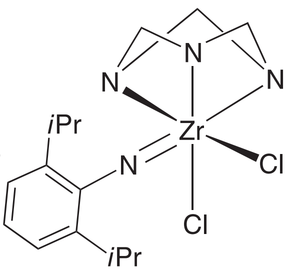

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4.3.2.3 Tin-based Ligand Complexes

Sn-based donor complexes are rare for Zr and Hf. However, $ZrCl_4[SnCl_2(NC_5H_5)]_2$ was prepared from the reaction of the Sn^{II} species with $ZrCl_4$. The Mössbauer spectrum of this product suggested that the 5*s* electron density of the Sn donors remained localized at the Sn sites.[20] A more recent report described the synthesis of the Zr–Sn complex $Zr[\{(MeC_6H_4)NSiMe_2\}_3SiMe](SnPh_3)$.[21]

4.3.2.4 Nitrogen-based Ligand Complexes

4.3.2.4.1 Neutral nitrogen ligand complexes

Simple amine adducts of Zr and Hf have been known for many years. A recent study has described the syntheses of $MF_4(NH_3)$ (M = Zr, Hf) via oxidation of the metal with NH_4HF_2.[22] Additional monodentate N-donors including benzothiazole[23] and 2-methylthiazoline[24] have been used to form adducts of the form MCl_4L_2. In a similar fashion, use of the sterically demanding amine $(TMS)_2NH$ formed $ZrCl_4[(TMS)_2NH]$.[25] Upon pyrolysis above 1,075 °C, this adduct gave ZrN.

Phosphinimine ligands have also been exploited to prepare $ZrCl_4(Ph_3PNSiMe_3)$. The five-coordinate nature of this species was attributed to the steric demands of the ligand, which presumably precluded coordination of a second equivalent of the phosphinimine to the metal center.[26] The related oxo-bridged product $Zr_2OCl_6(TMSNPMe_3)_2$ was also characterized structurally.[27] Very recently, a related bimetallic adduct $(ZrCl_4)_2[(SiMe_3NPPh_2)_2C_5H_3N]$ was prepared from the bis-phosphinimine-pyridine ligand.[28]

Other bidentate N-donor ligands such as 2,2′-bi-2-thiazoline (bt) and 2,2′-bi-thiazine (btz) formed adducts with $ZrCl_4$.[29] In the former case, $ZrCl_4(bt)_2$ was formally eight coordinate, while the latter $ZrCl_4(btz)$ adopted a more conventional pseudo-octahedral geometry. The difference was attributed to steric crowding. In the complex $Zr(NO_3)_4(PA)_2$ (PA = pyrrolealdazine), IR spectroscopy suggested that the N_4-ligand was in fact tridentate.[30]

The species $ZrCl_4{\cdot}1.5(Me_2NCH_2CH_2NMe_2)$ was described as a polymeric material.[31] Similarly, the Schiff-bases, 5,5′-methylene-bis(salicyaldehyde)[32] and *N*,*N*-bis(8-acetyl-7-hydroxy-4-methylcoumarin)hydrazone[33] were used to prepare complexes $MCl_4(L)$. A series of Schiff-bases derived from the condensation of acetylferrocene with diamines have also been used to complex $HfCl_4$.[34] Two additional reports described tetradentate macrocyclic Schiff-base complexes of $ZrOX_2$ formulated generally as $ZrOX_2(L)$ (X = ClO_4, NO_3, BF_4, Cl, SCN) and $Zr(OH)_2Cl_2(L)$.[35–38] Finally, the complex $ZrCl_4(DAD)$ (DAD = 1,4-diaza-1,2,3,4-tetraphenyl-1,3-butadiene)[39] was prepared and formulated as a typical pseudo-octahedral complex.

Complexation of MCl_4 (M = Zr, Hf) with the metal-amide complex $Ti(NMe_2)_4$ has been described. The products were thought to contain two bridging amide groups and thus *cis*-six-coordinate Zr or Hf centers.[40] Unique mixed-metal complexes were derived from coordination of *trans*-$ReCl(N_2)(PMe_2Ph)_4$ to MCl_4 (M = Zr, Hf). The derived compounds $MCl_4[(\mu\text{-}N_2)ReCl(PMe_2Ph)_4]_2$ were studied by ^{15}N NMR spectroscopy.[41] In more recent work, pseudo-octahedral

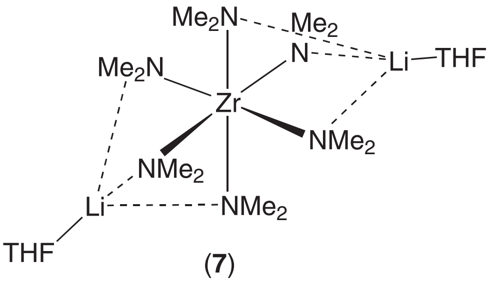
Zr and Hf adducts of 1,10-phenanthroline-5,6-dione were prepared. The accessible-ketonic O-atoms were then employed to bind a second metal fragment such as Cp_2Ti, Cp_2V, or MCl_4 (M = Zr, Hf) (**5**) providing electronic communication between the M-centers.[42]

The macrocyclic ligand 1,4,7-triazacyclononane was used to stabilize the eight-coordinate compounds $[\{M(MeCOCHCOMe)_2(NCH_2CH_2)_3\}_2(\mu\text{-}O)][ClO_4]_2$.[43] In a related approach, the smaller, substituted macrocycles $(RNCH_2)_3$ (R = Me, Bu^t) supported the imido complexes $ZrCl_2(NC_6H_3Pr^i{}_2)(RNCH_2)_3$ (**6**).[44] While preparative scale syntheses of the Zr complexes were difficult, Ti analogs were isolated, and several were characterized crystallographically.

4.3.2.4.2 Amido ligand complexes

Compounds of the form $Zr(NR_2)_4$ were detailed in the (*CCC*, 1987) although many contemporary advances have been reported.[45] Specifically, the structure of $Zr(NMe_2)_4$ has been detailed in two studies. In the gas-phase, electron diffraction showed this species was monomeric although the geometry of Zr remained unclear.[46] In contrast, a crystallographic study revealed a dimeric structure.[47] In both studies, the Zr-NC_2 units were planar, indicative of a considerable degree of π-bonding between N and the metal center. When excess $LiNMe_2$ was added, $Li_2[Zr(NMe_2)_6(ether)_2]$ (ether = Et_2O,[48] THF (**7**)[47]) were isolated as nonvolatile solids. The geometry about the Zr centers in these compounds approached octahedral symmetry, with each of the Li atoms bridging three N atoms.

In a recent report, reaction of $Fe(CO)_5$ with $[Zr(NMe_2)_4]_2$ resulted in the generation of $[(OC)_3Fe(\mu\text{-}OCNMe_2)_2]_2[Zr(NMe_2)]_2(\mu\text{-}NMe_2)(OCNMe_2)Fe(CO)_4$ (**8**).[49]



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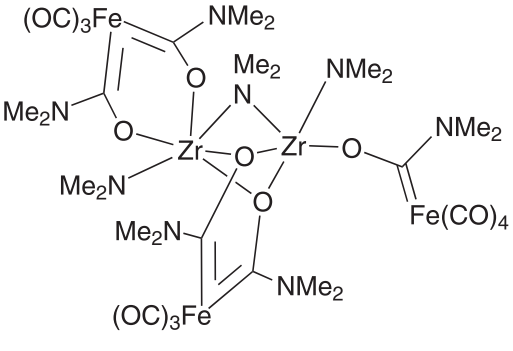

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A number of mixed chloro(*bis*alkyl)amido Zr and Hf compounds have been prepared and characterized, including $ZrCl_3(NEt_2)\cdot Et_2O$,[50] $[ZrCl(NMe_2)_3]_2$,[51] $ZrCl(NCy_2)_3$,[52] $MCl_2(NR_2)_2(THF)_2$ (M = Zr, Hf and R = Me; M = Zr and R = Et),[53] and the unusual bridged complexes $Zr(NMe_2)_3(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$ and $ZrCl(Me_2N)_2(\mu\text{-}Cl)_2(\mu\text{-}NMe_2)Zr(NMe_2)_2(THF)$.[54] Typically, these compounds were synthesized via ligand redistribution reactions or by traditional metathesis routes. In either case, the stoichiometry and reaction conditions were crucial. The most notable of this series of compounds were the asymmetric dimeric products. An alternative synthetic strategy involved the use of the amide transfer reagent $Mg(NBn_2)_2$. Reaction with $ZrCl_4(THF)_2$ afforded $ZrCl_2(NBn_2)_2(THF)_2$ which displayed a distorted octahedral geometry about the Zr center.[55]

The complex $ZrCl[N(C_6H_3Me_2)(adamantyl)]_3$, containing bulky amido ligands was prepared via a metathesis reaction involving the Li amide and $ZrCl_4(THF)_2$[56] Similarly, the species $ZrCl(NHSiBu^t{}_3)_3$ was prepared.[57] The complexes $MX_2[N(SiMe_3)(C_6H_3\ Pr^i{}_2)]_2$ (M = Zr, Hf; X = F, Cl) were also prepared and found to yield low activities for alkene polymerization catalysis upon activation.[58,59]

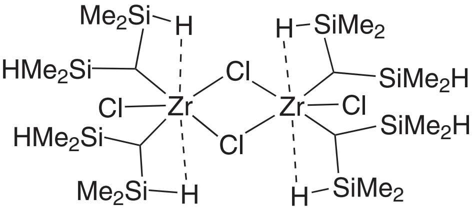
Efforts to study homoleptic complexes have drawn limited attention. The species $Zr[N(SO_2F)_2]_4$ formed adducts with NC_5H_5, MeCN, or Ph_3PO.[60] In contrast, the complexes $M(NPh_2)_4$ (M = Zr,[61] Hf[62]) and $M(NHC_6H_3\text{-}Pr^i{}_2)_4$[63] have been characterized crystallographically and confirmed to be monomeric. Transamination proved an unsuccessful route to homoleptic species, yielding instead $Zr(NMe_2)_2(carbazolide)_2(NHMe_2)$ (carbazolide = $C_{12}H_{10}N$, $Bu^tC_{12}H_9N$). However, protonolysis of $Zr(CH_2Ph)_4$ with carbazole successfully generated $Zr(carbazolide)_4$.[64]

The compounds $ZrR_2[N(SiMe_3)_2]_2$ ($R = Me$, Et, CH_2SiMe_3) were reported[65] to undergo thermolysis with elimination of alkane and formation of bridging carbene complexes. In an earlier report, use of a sterically less demanding amide gave rise to the species $[ZrCl(\mu\text{-}Cl)\{N(SiHMe_2)_2\}_2]_2$ (**9**). The dimeric formulation was confirmed crystallographically.[66] Of particular interest was the close approach of the Si—H to Zr (Zr$\cdots$H—Si 2.40(3) Å). Subsequently, reaction of $B(C_6F_5)_3$ with $Zr(CH_2Ph)_2[N(SiMe_3)_2]_2$ gave a cationic Zr species that cyclized to $Zr(TMSNSiMe_2CH_2)[N(SiMe_3)_2][PhCH_2B(C_6F_5)_3]$ and $[Zr(TMSNSiMe_2CH_2)\{N(SiMe_3)_2\}(THF)_2][PhCH_2B(C_6F_5)_3]$ with concurrent elimination of toluene.[67,68]

Cationic *tris*(amido) complexes of Zr and Hf have also been prepared. $[M\{N(SiMe_3)_2\}_3][MeB(C_6F_5)_3]$ ($M = Zr$, Hf) were generated by abstraction of a methyl group from the precursor complex.[69] This species has been used as an initiator for the cationic polymerization of isobutene and the co-polymerization of isobutene and isoprene.[70] An alternative synthetic approach involved protonolysis of *tetrakis*(amido) metal complexes with $[NHEt_3][BPh_4]$ yielding $[M(NMe_2)_3(THF)_2][BPh_4]$ ($M = Zr$, Hf).[71] The unexpected salt $[Zr(NEt_2)_3(THF)_2][(Et_2N)(TMS)_2B_{10}H_{10}]$ was formed from the reaction of the $(TMS)_2B_{10}H_{10}$ cluster with $Zr(NEt_2)_4$ in THF.[72]

A unique amido donor ligand is azacyclopentadienyl. Zr and Hf complexes of the formula $MCl_3(NC_4Bu^t{}_2RH)$ ($R = H$, $SiMe_3$) have been prepared and characterized by mass spectrometry. By analogy to the Ti compound, this ligand was presumed to bind in an η^5 fashion.[73]

The complex $Mg(THF)_2[Mo(N_2)\{(TMSNCH_2CH_2)_3N\}]$ reacted with $ZrCl_4$ to give the complexes $ZrCl_3[Mo(\mu\text{-}N_2)(TMSNCH_2CH_2)_3N]$, $ZrCl[Mo(\mu\text{-}N_2)\{(TMSNCH_2CH_2)_3N\}]_3$, and $ZrCl_2[Mo(\mu\text{-}N_2)(TMSNCH_2CH_2)_3N]_2$ (**10**). The latter species was characterized structurally.[74]



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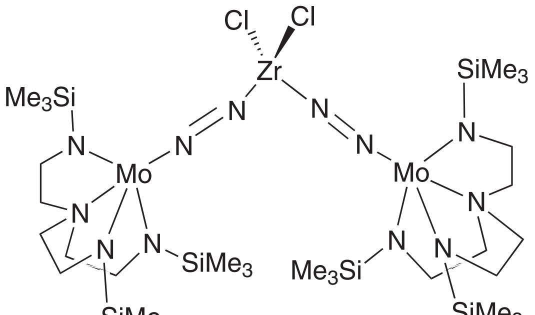

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4.3.2.4.3 Phosphinimido ligand complexes

Heating of MCl_4 with various stoichiometries of $Me_3PNSiMe_3$ or $(CsNPPh_3)_4$ resulted in the isolation of a series of phosphinimide complexes including: $[Zr_3Cl_6(NPMe_3)_5][Zr_2Cl_6(NPMe_3)_3]$ (**11**),[26] $[Hf_3Cl_6(NPMe_3)_5][Hf_2Cl_7(NPMe_3)_2]$,[26] $Zr_2Cl_4(\mu\text{-}NPMe_3)_2(NPMe_3)_2(\mu\text{-}HNPMe_3)$,[75] $Hf(NPPh_3)_4$,[76] and $HfCl_2(NPPh_3)_2(HNPPh_3)_2$.[76] The steric demands of the substituents on the phosphinimide appeared to impact on the degree of aggregation. This view was supported by the isolation of $ZrCl(NPBu^t{}_3)_3$. Facile ligand redistribution reactions in this case precluded the isolation of the mono- and disubstituted analogs.[77]

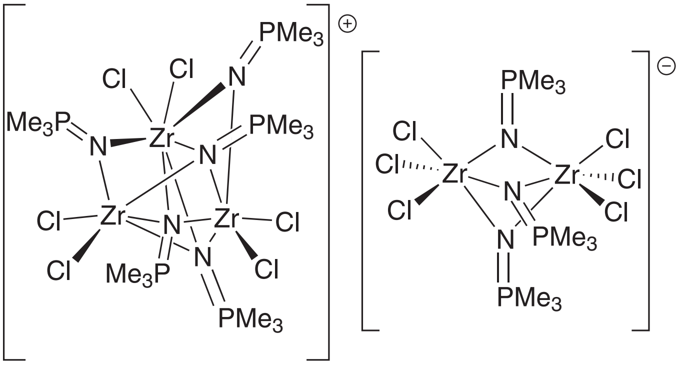
4.3.2.4.4 Imido ligand complexes

Synthetic methods to such species and their applications have been the subject of considerable experimental and theoretical interest.[78,79] Several terminal imido complexes that lack Cp-ligands have been synthesized and characterized, including $M(NR)(NHR)_2(py')_2$ ($M = Zr$, Hf; $R = C_6H_3Pr^i{}_2$,[63] Bu^t,[80] $SiBu^t{}_3$,[81,82]), $Zr(NAr)(NHAr)_2(NC_5H_5)_2$,[83] $ZrCl[N(Pr^i{}_2C_6H_3)][NH(C_6H_3Pr^i{}_2)](NC_5H_5)_2$,[84] $MCl_2[N(C_6H_3Pr^i{}_2)](L)_2$ ($M = Zr$, Hf; $L = THF$, NC_5H_5),[84] $Zr[N(C_6H_3Pr^i{}_2)](NHAr)[N(SiMe_3)_2](NC_5H_5)_2$,[84] $Zr(NPh)[NH(C_6H_3Pr^i{}_2)]_2(py')_2$,[63] and $Zr(NPh)[O(C_6H_3Pr^i{}_2)]_2(py')_2$[85] ($py' =$ 4-pyrrolidinopyridine). In general, structures of these species feature short M—N bonds. In the absence of bulky donor ligands, dimerization was observed as in $Zr_2Cl_4(\mu\text{-}NPh)_2(THF)_4$.[86] A list of crystallographically determined Zr-imido-N distances is compiled in Table 1.

Table 1 Zr—N bond distances in Zr and Hf imido compounds.

Formula	*M ··· N distance* (Å)
$\mathrm{Zr_2Cl_4(\mu\text{-}NPh)_2(THF)_4}$	2.068(2), 2.051(2)[123]
$\mathrm{Zr(OC_6H_3\text{-}2,6\text{-}Pr^i_2)_2(NPh)(NC_5H_5)_2}$[a]	1.844(9)[85]
$\mathrm{Zr(NHSiBu^t_3)_2(NSiBu^t_3)(THF)}$	1.978(8)[88]
$\mathrm{Zr(NHC_6H_3\text{-}2,6\text{-}Pr^i_2)_2(NC_6H_3\text{-}2,6\text{-}Pr^i_2)(NC_5H_5)_2}$	1.853(5)[198]
$\mathrm{Zr(NHC_6H_3\text{-}2,6\text{-}Pr^i_2)_2(NC_6H_3\text{-}2,6\text{-}\mathit{i}Pr_2)(Py')_2}$[a]	1.868(3)[85]
$\mathrm{Hf(NHC_6H_3\text{-}2,6\text{-}Pr^i_2)_2(NC_6H_3\text{-}2,6\text{-}\mathit{i}Pr_2)(Py')_2}$[a]	1.850(3)[63]
$\mathrm{Zr[(NC_6H_5)\text{-}2\text{-}CMe(CH_2NSiMe_3)_2](NC_6H_3\text{-}2,6\text{-}\mathit{i}Pr_2)(NC_5H_5)}$	1.976(4)[198]
$\mathrm{Zr(TTP)(\ NC_6H_3\text{-}2,6\text{-}Pr^i_2)}$	1.863(2)[252]
$\mathrm{Hf(TTP)(\ NC_6H_3\text{-}2,6\text{-}Pr^i_2)}$	1.859(2)[252]

[a] Py′ = 4-pyrrolidinopyridine.



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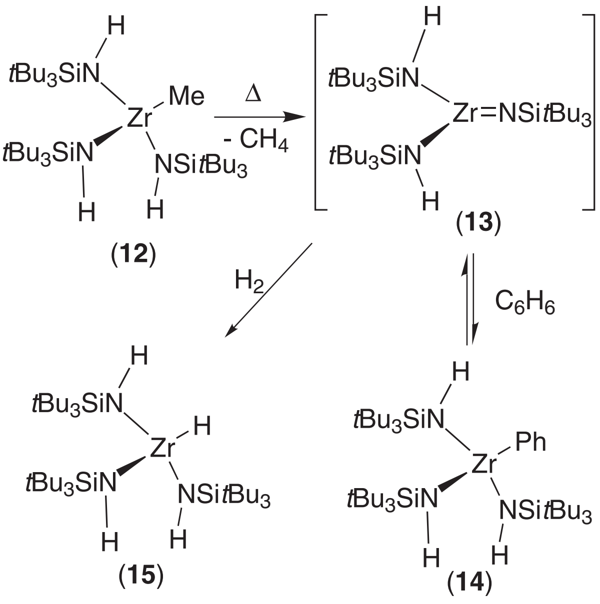
The unusual reactivity[87] of imide-complexes is exemplified by $\mathrm{Zr(NSiBu^t_3)(NHSiBu^t_3)_2}$ (**13**). This compound, generated from the thermolysis of $\mathrm{ZrMe(NHSiBu^t_3)_3}$ (**12**), activated C_6H_6 affording $\mathrm{Zr(NHSiBu^t_3)_3(Ph)}$ (**14**). Similar C—H activation reactions occurred with hydrocarbons. In inert solvents, the imido complex reacted with H_2 to generate $\mathrm{ZrH(NHSiBu^t_3)_3}$ (**15**).[82] Extensions of this work included an elegant study that investigated the kinetic isotope effect of the interaction of CH_4 with the transient imido complex,[81] as well as a thorough mechanistic study of hydrocarbon activation.[88]



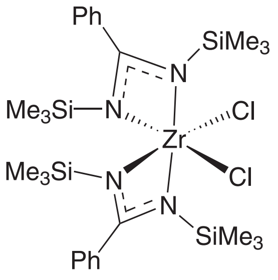
4.3.2.4.5 Aminidato and guanidinato ligand complexes

Since $[ZrCl_3\{PhC(NSiMe_3)_2\}]_2$ was first reported in 1988,[89,90] numerous studies of alkyl- and arylamidinate ligand complexes have emerged. The original synthesis involved the addition of $PhC(NSiMe_3)N(SiMe_3)_2$ to MCl_4,[90] with elimination of TMSCl. Later endeavors used the Li salt of the ligand resulting in the species $ZrCl_2[PhC(NSiMe_3)_2]_2$ (**16**)[91] and $ZrCl[PhC(NSiMe_3)_2]_3$.[92] Modification of the substituent on the backbone of the ligand was straightforward and exchange of the halide with alkyl, alkoxide-, amide, selenolate, and tellerolate ligands was also readily achieved.[92–94] Alterations of the *N*-substituents were accomplished affording $ZrCl_2[(CF_3)_3C_6H_2C(NCy)_2]_2$,[95] $ZrX_2[RC(NCy)_2]_2$ ($R = Me$, Bu^t; $X = Cl$, Me),[96] and $ZrCl[PhC(N\text{-myrtanyl})NSiMe_3]_3$.[97] Compounds of the form $ZrX_2[RC(NCy)_2]_2$ were found to be active as C_2H_4 polymerization catalysts[92,96–100] while the species $ZrCl[PhC(N\text{-myrtanyl})NSiMe_3]_3$ produced elastomeric polypropylene and syndiotactic $(PhCHCH_2)_n$. Of related interest were complexes containing aminophosphinimide ligands, $ZrCl_3R_2P(NSiMe_3)_2(MeCN)$ ($R = Ph$,[101] OMe[102]).

The benzamidinate complex $ZrCl_2[PhC(NSiMe_3)_2]_2$, was reduced with Na/Hg in the presence of PhCCPh to give the Zr^{IV} product $Zr(C_4Ph_4)[PhC(NSiMe_3)_2]_2$. In the absence of C_2H_2, the highly reactive intermediate oxidatively cleaved one of the C—N bonds of a benzamidinate ligand, yielding the dimeric species $[Zr\{PhC(NSiMe_3)_2\}(\eta^2\text{-}PhCNSiMe_3)(\mu\text{-}NSiMe_3)]_2$ (**17**).[103]

Related guanidinate complexes including $ZrBn_3[CyNC\{N(SiMe_3)_2\}NCy]$,[104] $MCl_2((NR^2_2)C(NR^1)_2)_2$ ($M = Zr$, Hf; $R^1 = Pr^i$ or Cy; $R^2 = SiMe_3$,[105] $M = Zr$; $R^1 = Pr^i$; $R^2 = Me$),[106] $Zr(Bn)_3[\{(SiMe_3)_2N\}C(CyN)_2]$,[105] and $[Li(L)_x][MCl_4\{(SiMe_3)_2N\}C(CyN)_2]$ ($M = Zr$, $(L)_x = (OEt_2)_2$; $M = Hf$, $(L)_x = (THF)_3$)[105] have also been prepared and characterized crystallographically.

In a recent effort, the amidinate-like complexes have been derived from oxalic acid.[107] The resulting ligand was used to prepare the mono- and bimetallic Zr complexes $ZrCl[\eta^2\text{-}(Bu^tN)C(NPh)C(NHBu^t)NPh][N(SiMe_3)_2]_2$ and $Zr_2[\eta^4\text{-}(Bu^tN)C(NPh)C(NHBu^t)NPh](NMe_2)_4$ (**18**), respectively.



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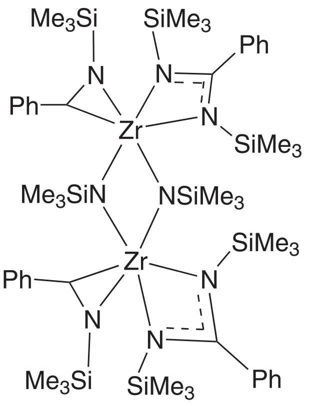

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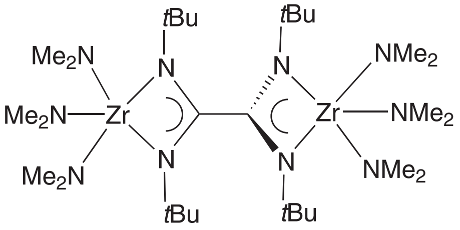
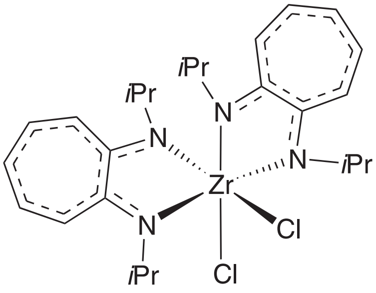


(**18**)

4.3.2.4.6 Diketinimato ligand complexes

The syntheses of the β-diketinimato complexes $MCl_3(RNCMeCHCMeNR)$ ($M = Zr$, Hf; $R = Me$, Ph, C_6H_4Me, $C_6H_3Me_2$, $C_6H_3Pr^i{}_2$,[108] $C_6H_4CF_3$[109]) were achieved via the reactions of the Li salts of the ligands with the appropriate MCl_4. The species $ZrCl_3[TMSNC(Bu^t)CHC(Ph)NSiMe_3]$ contained a five-coordinate Zr center with a distorted trigonal bipyramidal geometry,[110] whereas $ZrCl_3[(C_6H_3Pr^i{}_2)NC(Me)CHC(Me)N(C_6H_3Pr^i{}_2)](THF)$ exhibited a distorted octahedral geometry.[108] Alternatively, $ZrX_3[(Ar)NC(Me)CHC(Me)N(Ar)]$ and $ZrX_2[ArNC(Me)CHC(Me)NAr]_2$ ($X = NMe_2$, Bn; $Ar = Ph$, $C_6H_3Pr^i{}_2$, MePh, CF_3Ph) were prepared via protonolysis of $Zr(NMe_2)_4$ or $ZrBn_4$ with the parent diimine. Subsequently, these species were converted to the corresponding Zr—Cl species by reaction with TMSCl.[109,111] Several of these complexes have been characterized crystallographically and the conformation observed depended on the steric demands of the substituents. In general, these Zr species exhibited good activities for the polymerization of C_2H_4 when activated by methylaluminoxane (MAO).[108,112]

The related troponiminato complexes $MX_2[(Pr^iN)_2(C_7H_5)]_2$ (M = Zr (**19**), Hf) have been prepared via typical salt metathesis or protonolysis routes.[113] The NMR data for the dichloride derivatives indicated stereochemical nonrigidity and thus rapid interconversion of diastereotopic geometries.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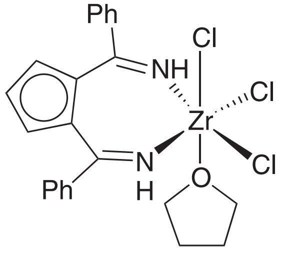
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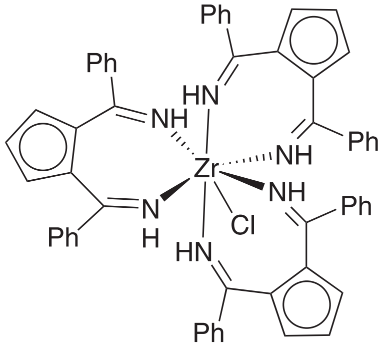
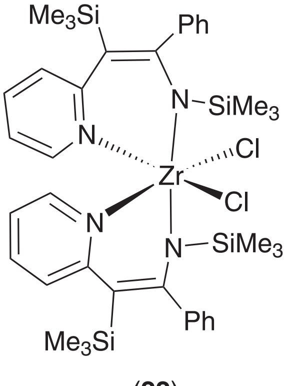

(**21**)

The reaction of $Mg(C_5H_5)_2$ with PhCN gave a novel bidentate–monoanionic–diketimine ligand. The resulting Zr complexes $ZrCl_3[C_5H_3\{C(Ph)NH\}_2](THF)$ (**20**) and $ZrCl[C_5H_3\{C(Ph)NH\}_2]_3$ (**21**) were isolated from a mixture of products originating from reaction of the zwitterionic ligand $H[C_5H_3\{C(Ph)NH\}_2]$ with $ZrCl_4(THF)_2$.[114] Structural data suggested a degree of formal charge separation that induced greater electrophilic character at Zr. A related complex of formula $ZrCl_2(NHCPhCMeCPhNPh)_2$ was subsequently reported.[115]

4.3.2.4.7 Amido-bidentate ligand complexes

Chelating pyridyl- and quinolyl-1-azaallyl ligands have also been used as β-diketinimato analogs to generate $ZrCl_2[N(SiMe_3)C(Ph)CR(C_5H_4N)]_2$ (**22**) and $ZrCl_2[N(SiMe_3)C(Ph)CR(C_9H_6N)]_2$ (R = H, $SiMe_3$ (**23**)).[116,117] Subsequent ligand redistribution reactions with $ZrCl_4$ afforded $ZrCl_3[N(SiMe_3)C(Ph)CR(C_9H_6N)]$.

Several iminopyrrolyl Zr complexes have been prepared either by transamination of the neutral ligand with $Zr(NR_2)_4$ (R = Me, Et) or by metathesis of $ZrCl_4$ with Li salts of the ligands. Complexes prepared in these ways include $ZrX_3[\{N(C_6H_3Pr^i_2)CH\}_2(C_4H_2N)]$, $ZrX_2[\{N(C_6H_3Pr^i_2)CH\}_2(C_4H_2N)]_2$, $ZrX_2[\{N(C_6H_3Pr^i_2)CH\}(C_4H_3N)]_2$,[118] $ZrX_2\{(NArCH)_2(C_4H_2N)\}_2$ (X = Cl, NEt_2 (**24**); Ar = $C_6H_3Me_2$, $C_6H_3Pr^i_2$, C_6H_4OMe, C_6H_4OMe),[119] and $ZrX_2[Me_2NCH_2(C_4H_3N)]_2$.[120] In all of these compounds the ligands were bound in a bidentate manner and NMR data revealed that these molecules were fluxional. Similarly, the bidentate ligand complexes adopted two geometric isomers, which interconverted at 70 °C.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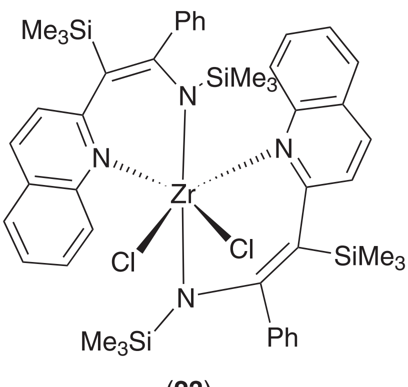
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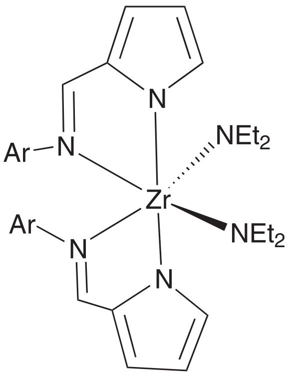
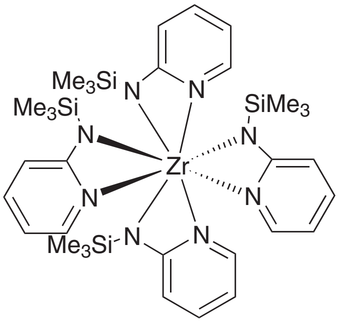

(**24**)

2-Amidopyridine ligands have been used to generate a series of complexes including ZrCl$_2$(NEt$_2$)[(TMSN)MeC$_5$H$_3$N],[121,122] Zr$_2$Cl$_2$(μ-Cl$_2$)[(PhN)C$_5$H$_4$N]$_4$,[123] ZrX$_2$[(adamantyl-N)RC$_5$H$_3$N]$_2$ (R = H, Me; X = Cl, NMe$_2$, CH$_2$Ph, CH$_2$Bu^t),[124] ZrX[(TMSN)MeC$_5$H$_3$N]$_3$ (X = Cl, Me, Ph, CCPh, NMe$_2$[125–127] C$_4$SiMe$_3$[128]), Zr[(TMSN)MeC$_5$H$_3$N]$_4$ (**25**),[128] and Hf[(PhN)C$_5$H$_4$N]$_4$.[129] The majority of these have been characterized crystallographically. The prevalence of *tris*-substituted complexes was attributed to kinetic stability provided by the propeller-like arrangement of the ligands. However, use of sterically more demanding ligands on N as in the adamantyl derivative, gave complexes of the form ZrCl$_2$L$_2$.[124] In these cases, the products demonstrated moderate activity for the polymerization of C$_2$H$_4$ when activated.[121,124]



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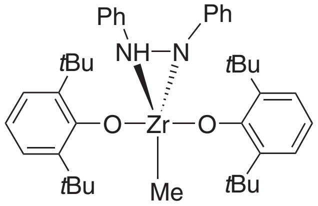
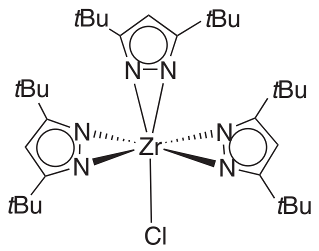


(**26**)



(**27**)

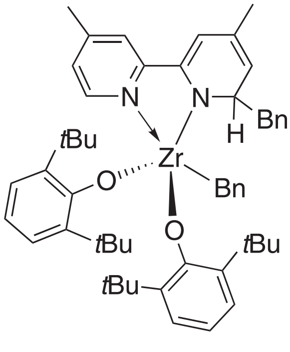
4.3.2.4.8 *Miscellaneous monoanionic bidentate ligand complexes*

A variety of complexes of unique monoanionic bidentate N-based ligands have also been prepared. For example, adducts of Zr(NCS)$_4$ have been reported.[130] The complex Zr(O-Bu$^t_2$C$_6$H$_3$)$_2$-Me(PhNNPhH) (**26**) was prepared and NMR data was consistent with η^2-bonding of the hydrazido ligand.[131] In a related study, the *tris*- and *tetrakis*(pyrazolato) compounds MCl(Bu$^t_2$C$_3$HN$_2$)$_3$ (M = Zr (**27**), Hf) and M(Bu$^t_2$C$_3$HN$_2$)$_4$ were obtained through reactions of K[Bu$^t_2$C$_3$N$_2$] with MCl$_4$.[132] The Hf species HfCl(Bu$^t_2$C$_3$HN$_2$)$_3$ was characterized crystallographically, revealing a seven-coordinate metal center, in which the pyrazolato ligands exhibited idealized η^2-bonding.

The homoleptic compound Zr(PhNNNPh)$_4$ was prepared via protonolysis of Zr(NR$_2$)$_4$ (R = Me, Et) with the parent triazene. Structural data showed the resulting complex had a distorted dodecahedral geometry, reminiscent of the analogous aminidinato complexes.[133]

Partial reduction of bipyridine or phenathroline ligands via intramolecular alkylation was observed upon reaction of ZrBn$_2$(OC$_6$H$_3$Bu$^t_2$)$_2$ with bidentate donors. The resulting amido–imine complexes ZrBn(OC$_6$H$_3$Bu$^t_2$)$_2$(C$_{10}$H$_6$R$_2$BnN$_2$) (R = H (**28**), Me) and ZrBn(OC$_6$H$_3$-Bu$^t_2$)$_2$(C$_{12}$H$_8$BnN$_2$) were characterized by NMR spectroscopy.[134]

Finally, 1,8-diamino-naphthalene reacted with 9-borobicycloborane (9-BBN) affording a novel diaminoborate ligand. Subsequent reaction with Zr(NMe$_2$)$_4$ gave the unusual complex Zr(NMe$_2$)$_3$[{(9-BBN)HN}C$_{10}$H$_6$NH] (**29**).[135]



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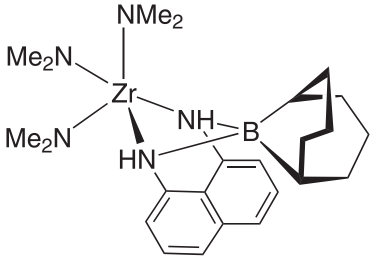
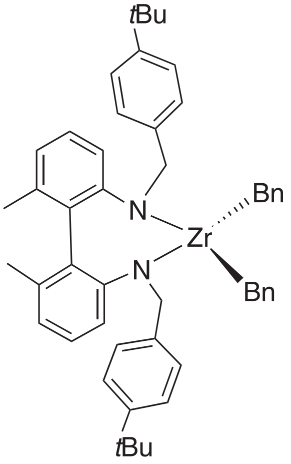


(**29**)

4.3.2.4.9 Dianionic bidentate ligand complexes

Zr complexes containing bidentate amido ligands have received recent attention. The complexes $ZrBn_2[(RC_6H_4CH_2N)_2C_{12}H_6Me_2]$ (R = Bu^t (**30**), Ph)[136] and $ZrBn_2[(C_6F_5N)_2(CH_2)_3]$ (**31**)[137] were prepared in quantitative yields via protonolysis of $ZrBn_4$. Crystallographic data revealed the close approach of an *ortho*-F to Zr (Zr···F: 2.511(1) Å) in the latter complex. This complex exhibited low C_2H_4 polymerization activity upon activation, and this was attributed to the persistence of a Zr—F interaction in solution.



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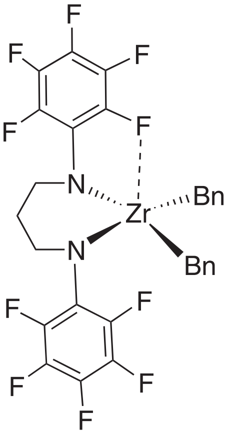
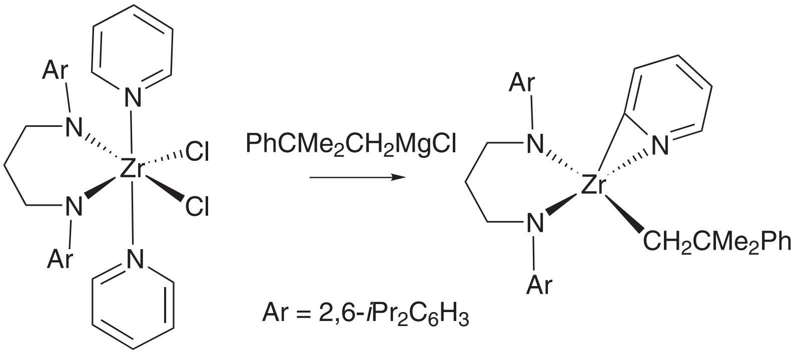


(31)

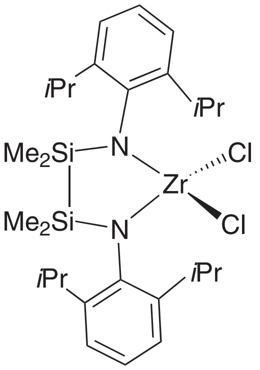
Following reports of living-polymerization with Ti-diamido complexes, transamination was used to prepare $Zr(NMe_2)_2[(Pr^i{}_2C_6H_3N)_2(CH_2)_3]$.[138] $ZrCl_2[(Pr^i{}_2C_6H_3N)_2(CH_2)_3]$ was obtained via reaction with TMSCl while alkyl derivatives and $ZrCl_2[(Pr^i{}_2C_6H_3N)_2(CH_2)_3](C_5H_5N)_2$ (**32**) were also synthesized.[139] Further reaction with two equivalents of Me_2PhCCH_2MgBr resulted in the ortho-metallation of a C_5H_5N ring, yielding $Zr(CH_2CMe_2Ph)[(Pr^i{}_2C_6H_3N)_2(CH_2)_3]$ (η^2-C_5H_4N) (**33**).



(32) **(33)**

Several examples of complexes of bidentate ligands incorporating silylamido groups including $MCl_2[(TMSN)_2(CH_2)_2]$ (M = Zr, Hf),[140] $Zr[(TMSN)_2(CH_2)_2]_2$,[140] $Zr[(MePh_2SiN)_2(CH_2)_3]_2$,[141] $Zr[(TMSN)_2C_6H_{10}]_2$,[142] and $MCl_2[(Bu^tPh_2SiN)_2(CH_2CMe_2CH_2)]$[143] have also been reported. Aryl spacers between the amido donors have also been exploited, as in $Zr[(NSiPr^i{}_3)_2C_6H_4]_2$, $Zr(OBu^t)_2[(NSiPr^i{}_3)_2C_6H_4]$,[144] $Zr_2(NMe_2)_2(\mu$-$NMe_2)_2[(RN)_2C_6H_4]_2$ (R = $SiMe_3$, $SiMe_2(CHCH_2)$), and $Zr_2Cl_2(\mu$-$Cl)_2[Me_2SiN(CHCH_2)_2C_6H_4]_2(THF)_2$.[145] Such ligands were observed to alternate between η^2 and η^4 donation as a result of coordination of phenylene C-atoms.[144] The species $Zr_2Cl_2(\mu$-$Cl)_2[Me_2SiN(CHCH_2)_2C_6H_4]_2(THF)_2$ was rendered monomeric by reaction with $Me_2NCH_2CH_2NMe_2$.[145] In a similar fashion, the compounds formulated as $ZrX_2[(NR)_2C_{10}H_6]$ (X = NMe_2, R = $SiMe_3$;[146] X = Cl, R = $SiMe_3$, $SiPr^i{}_3$)[147] and $Zr[(NR)_2C_{10}H_6]_2$ (R = Me, Pr^i) were prepared. Structural studies revealed that $Zr_2Cl_2(\mu$-$Cl)_2[(NSiR_3)_2C_{10}H_6]$ (R = Me, Pr^i) were dimeric in the solid state. In contrast, the structure of $ZrCl_2((Pr^i{}_3SiNCH_2)_2C_6H_4)$[148] was shown to be monomeric in the solid state. This species acted as a catalyst precursor for the polymerization of α-alkenes, generating polymers with relatively low polydispersities.

Bidentate ligands in which silyl groups are incorporated into the linking unit have also been prepared. An early report described the silyl-bridged complexes MCl$_2$[(TMSN)$_2$SiMe$_2$] (M = Zr, Hf), M[(TMSN)$_2$SiMe$_2$]$_2$ (M = Zr, Hf),[149] and Zr[(Bu^{t}N)$_2$SiMe$_2$]$_2$.[150] These species were thermally stable, presumably due to the bulky groups on N. A later report described the related compounds ZrCl$_2$[(RN)$_2$(SiMe$_2$)$_2$] (R = Bu^t, C$_6$H$_3$Pr$^i_2$ (**34**), 4F-C$_6$H$_4$).[151] Subsequently, the complexes ZrX$_2$(Me$_2$C$_6$H$_3$NSiMe$_2$CH$_2$)$_2$ (X = NMe$_2$ (**35**), Me) were reported. The related species Zr(NMe$_2$)$_2$[(Me$_2$C$_6$H$_3$N)$_2$(SiPh$_2$)](NMe$_2$H)[152] was prepared in a similar fashion and shown to be a five-coordinate monomer in the solid state. The complex Zr(NMe$_2$)$_2$[(Me$_2$C$_6$H$_3$)NSiMe$_2$CH$_2$)$_2$] also acted as an efficient C$_2$H$_4$ polymerization catalyst upon activation, whereas Zr(NMe$_2$)$_2$[(Me$_2$C$_6$H$_3$N)$_2$(SiPh$_2$)] (NMe$_2$H) (**36**) demonstrated negligible activity.[152]



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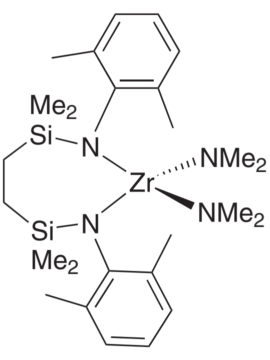

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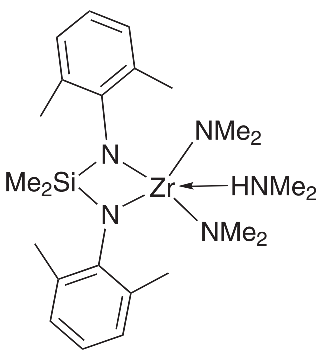
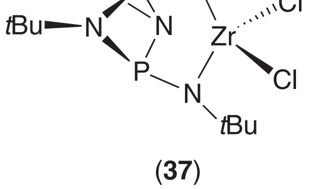


(36)

Horton *et al.* have described the syntheses of the related products formulated as Zr$_2$Cl$_2$(μ-Cl)$_2$[(Bu^{t}N)$_2$SiMe$_2$]$_2$(THF)$_2$ and ZrR$_2$[(Bu^{t}N)$_2$SiMe$_2$] (R = Bn, CH$_2$SiMe$_3$).[153] Zwitterionic and cationic derivatives were generated employing B(C$_6$F$_5$)$_3$ or [PhMe$_2$NH] [B(C$_6$F$_5$)$_4$], respectively. These products catalyzed the polymerization of MeCHCH$_2$ and EtCHCH$_2$, although the rates were found to be highly dependent on the nature of the anion.

A related but novel ligand was derived from a cyclodisilazane. Lithiation and reaction with MCl$_4$ afforded MX$_2$[(MeSiNBu^t)$_2$(NBu^t)$_2$] (M = Zr, Hf; X = Cl, Me).[154] A similar ligand geometry was derived from cyclodiphosphazane in the synthesis of MCl$_2$(Bu^{t}NP)$_2$(NBu^t)$_2$ (M = Zr , Hf).[155] These latter species were remarkably resistant to decomposition by O$_2$ or H$_2$O. In subsequent work, ZrCl$_2$[(Bu^{t}NP)$_2$(NBu^t)$_2$] (**37**) reacted with KH in liquid NH$_3$, affording the dimer [Zr(η^3-Bu^{t}NP)$_2$NBu$^t_2$(μ-NH)$_2$]$_2$ (**38**) in which the Zr atoms were bridged by imido groups.[156]

The borylamide bidentate complexes, ZrCl$_2$[(R$_3$C$_6$H$_2$)$_2$BNCH$_2$]$_2$ (R = Me (**39**), Pr^i)[157] and MI$_2$[(Cy$_2$BNCH$_2$)$_2$] (M = Zr, Hf)[158] were prepared and subsequently converted to a variety of alkyl and zwitterionic derivatives. Related species in which B was incorporated into the ligand backbone have also been reported. Reaction of the Li salt Li[C$_6$H$_3$Pr$^i_2$NB(NMe$_2$)] with ZrCl$_2$Bn$_2$ afforded the species ZrBn$_2$[C$_6$H$_3$Pr$^i_2$NB(NMe$_2$)]$_2$ (**40**). Upon activation, all of these species generated catalysts that showed only low polymerization activities.[159]



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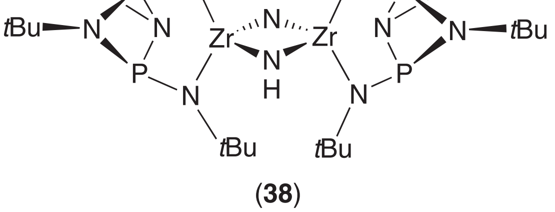

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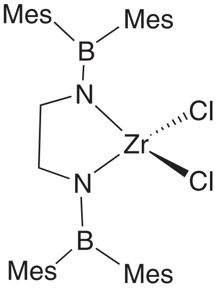
Dissymmetric chelating diamide ligands were used to prepare a number of complexes formulated as ZrX$_2$[C$_6$H$_4$(CH$_2$NR^1)NR^2] (X = NMe$_2$, Cl) and Zr[C$_6$H$_4$(CH$_2$NR^1)NR^2]$_2$ (R^1 = SiMe$_3$,

$SiMePh_2$, $R^2 = SiMe_3$, $SiMe_2Bu^t$, $SiMePh_2$).[160,161] Structural studies revealed that one of the Cl derivatives was actually the dimer $[ZrCl(\mu\text{-}Cl)\{C_6H_4(CH_2NSiMe_2Bu^t)(NSiMe_2Bu^t)\}]_2$ (**41**).



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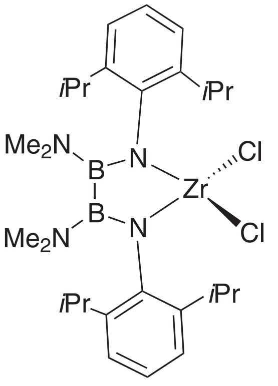

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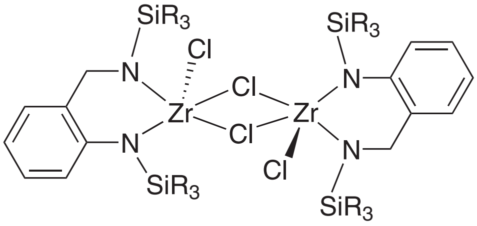
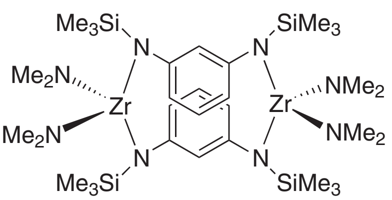


(41)

Binuclear products have been prepared from diamide ligands derived from the *meta*- and *para*-diamidobenzenes. Reaction of $Zr(NMe_2)_4$ with the appropriate diamines afforded the 1,3 (**42**) and 1,4 isomers of $[Zr(NMe_2)_2C_6H_4(NSiMe_3)_2]_2$. Both of these species were characterized crystallographically and exhibited a macrocyclic structure in which the arene rings were approximately parallel.[162]

Complexes of DAD ligands $(RNCR)_2$ were accessible via several different approaches. For example, the species $Zr(PhNCMe)_2(OC_6H_3Bu^t{}_2)_2$, derived from isocyanide insertion of $ZrR_2(OC_6H_3Bu^t{}_2)_2$, underwent thermolytic cyclization to give the mixed ligand complexes $[(R^1CNR^2)_2]M(OC_6H_3Bu^t{}_2)_2$ (M = Zr, Hf; R^1 = Me, CH_2Ph; R^2 = Ph, $C_6H_3Me_2$).[163] The kinetics for this process have also been reported.[164] Dilithio salts of DAD derivatives reacted with $MCl_4(DAD)$, giving the complexes $M[(RC_6H_4N)_2C_2Ph_2]_3$ (R = H (**42**) (**43**), Me, OMe).[39,165] The electronic nature of the three ligands was indistinguishable in the solid state, although charge balance dictates one of the ligands was formally a neutral donor.



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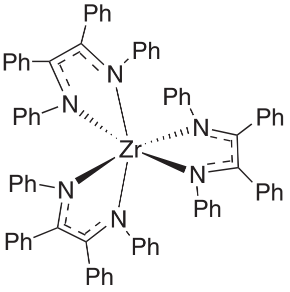

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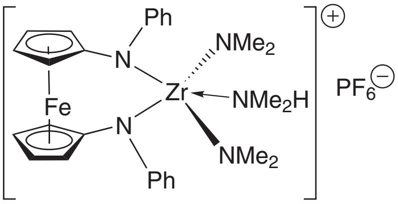


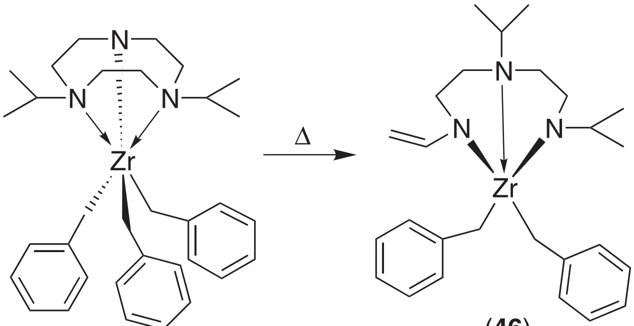
(44)

Heterobimetallic complexes of the form $ZrX_2(RNC_5H_4)_2Fe$ and $Zr[(RNC_5H_4)_2Fe]_2$ (R = $SiMe_3$, Ph; X = Bn, NMe_2, Cl) have been reported, and several of these ferrocene-based compounds were characterized crystallographically.[166,167] Oxidation of the Fe center with $[Cp_2Fe]$ $[PF_6]$ gave the species $[Zr(NMe_2)_2(NMe_2H)\{(PhNC_5H_4)_2Fe\}]$ $[PF_6]$ (**44**).[168] In another series of heterobimetallic compounds, Cu-ethylenediamine[169] or triethylene tetraamine (TETA) complexes reacted with $ZrCl_4$ to provide bridged Cu—Zr bi- and trimetallic species.[170,171] The structures of these compounds were proposed to be bis-amido-bridged compounds although evidence for this conclusion was limited.

4.3.2.4.10 *Monoanionic tridentate ligand complexes*

Several synthetic approaches to monoanionic-tridentate N_3-ligand complexes have been described. For example, salt metathesis was exploited to generate $ZrCl_3[N(CH_2CH_2NEt_2)_2]$ in low yield.[172] The same methodology was employed to prepare $MCl_3[N(Si\ Me_2CH_2NMe_2)_2]$ from $MCl_4(C_4H_8S)_2$ (M = Zr, Hf) in better yields. These compounds were isostructural with distorted bicapped tetrahedral geometries.[173] The related complex $Zr(NEt_2)_3[(CH_2NMe_2)_2(C_4H_2N)]$ was prepared via transamination. This species reacted with $CDCl_3$ at ambient temperatures to afford the corresponding trichloride derivative.[120]

Di-substituted triazacyclononane macrocycles have also acted as monoanionic ligands as in $ZrX_3[Pr^i{}_2(NCH_2CH_2)_3]$ (X = Cl, NEt_2, Bn (**45**)). Ring opening of the triazacyclononane ring occurred upon heating of the *tris*(benzyl) derivative, giving the species $ZrBn_2[CH_2CHN(CH_2)_2NPr^i(CH_2)_2NPr^i]$ (**46**).[174]



(45) **(46)**

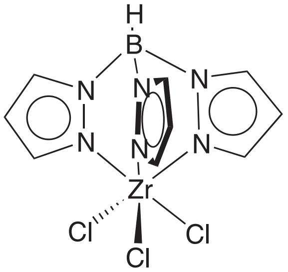
4.3.2.4.11 Pyrazolylborate ligand complexes

A number of complexes containing poly(pyrazolyl)borate ligands have been prepared including $ZrCl_3[R^1B(R^2{}_2C_3HN_2)_3]$ (R^1 = H, Pr^i, Bu^n; R^2 = H (**47**), Me)[175] and $ZrX_3[HB(Me_2C_3HN_2)_3]$ (X = Cl,[175,176] MeCOCHCOMe,[177] OC_6H_4R, R = H, NO_2, F, OBu^t).[178,179] Though such metal complexes were typically prepared from reaction of the lithiated ligand with MCl_4, an alternative strategy involved the use of $SnClBu_2[HB(Me_2C_3HN_2)_3]$ as a ligand-transfer reagent.[180] Complexes without methyl groups on the pyrazolyl rings decomposed on exposure to air, moisture, or heating, whereas additional steric protection enhanced stability. Substitution for chloride was readily achieved affording $ZrCl_2(OR)[HB(Me_2C_3HN_2)_3]$ (R = Me,[175] Bu^t [181]) and $ZrR_2(OBu^t)[HB(Me_2C_3HN_2)_3]$ (R = Me, CCPh).[182] Complexes of this series containing hindered hydrido-*tris*(pyrazolyl)borates effected C_2H_4 polymerization catalysis when activated by a Lewis acid.[183,184]

The related complex $ZrCl_3B(C_3H_3N_2)_4$ has been prepared. Although the ligand is potentially tetradentate, NMR evidence indicates that one of the pyrazolyl arms dangles free from coordination.[181]

4.3.2.4.12 Dianionic tridentate ligand complexes

The dilithio salt of a diamido-tridentate ligand reacts with $ZrCl_4(THF)_2$ to give the dimer $(ZrCl_2(TMSN(CH_2)_2)_2NSiMe_3)_2$.[185] This complex was readily functionalized to give monomeric derivatives, including $ZrX_2[SiMe_3N(CH_2)_2]_2(NSiMe_3)$ (X = BH_4,[185] Me, Bn[186]) and $ZrX[CH(SiMe_3)_2][TMSN(CH_2)_2]_2(NSiMe_3)$.[185] The dibenzyl derivative reacted with $B(C_6F_5)_3$, leading to C—H activation of one of the SiMe groups, ultimately giving the zwitterionic species $Zr[CH_2SiMe_2\text{-}NCH_2CH_2N(SiMe_3)CH_2CH_2N\ SiMe_3][BnB(C_6F_5)_3]$ (**47**) (**48**).[186]



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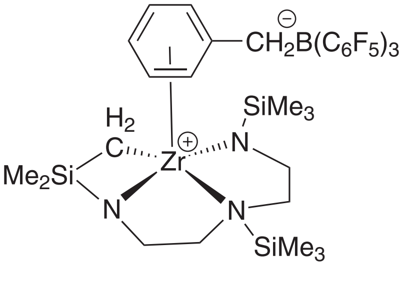
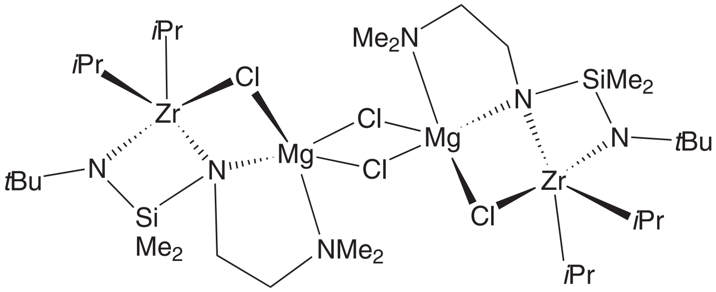


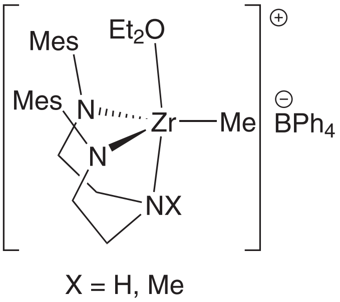
(48)

The related amido–amine ligand in which the amino donor is terminal has been employed to synthesize the species $ZrX_2[Me_2N(CH_2)_2N(SiMe_2)NBu^t]$ ($X = NMe_2$, Cl, Bn, CH_2SiMe_3).[187] It is noteworthy that the dichloride derivative was isolated as a dimeric $MgCl_2$-adduct $[ZrX_2\{MgCl_2Me_2N(CH_2)_2N(SiMe_2)NBu^t\}]_2$ (**49**), in which the neutral amine donor was bound to Mg.

Related tridentate ligand complexes such as $ZrCl_2[(Me_3C_6H_2)N(CH_2)_2]_2NR$ (R = H, Me) have been developed. The corresponding dimethyl derivatives, upon activation by $[Ph_3C][B(C_6F_5)_4]$, effectively polymerized 1-hexene.[188] The cationic species $[ZrMeL\{Me_3C_6H_2N(CH_2)_2\}_2NMe][BPh_4]$ ($L = Et_2O$ (**50**), $NHMe_2Ph$) and the neutral precursor $ZrMe_2[Me_3C_6H_2N(CH_2)_2]_2NMe$ was isolated and characterized crystallographically. Thermolysis of the etherate cation resulted in C—H activation of a methyl group of a *N*-bound mesityl substituent, although generation of the cation in the presence of 1-hexene resulted in living polymerization.[189–191]



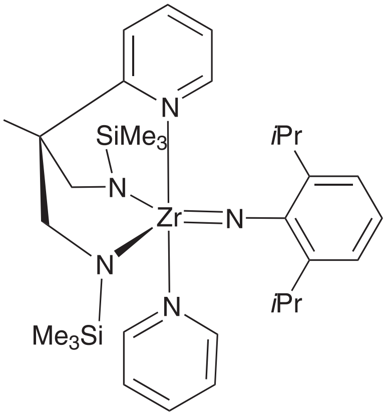
(**49**)



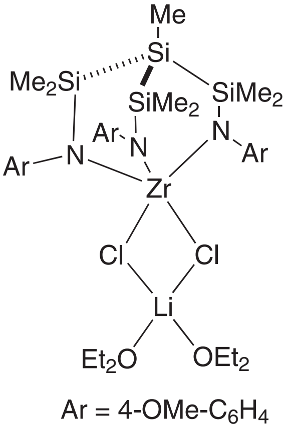
(**50**)

Pyridine–diamide ligands have been explored as alternative tridentate donors. McConville's group reported the preparation of the species $ZrX_2[(R_2C_6H_3NCH_2)_2C_5H_3N]$ (R = alkyl, X = Cl).[192–194] The related species $ZrBn_2[(C_6F_5NCH_2)_2C_5H_3N]$ possessed strong Zr–F interactions which were proposed to be responsible for diminished catalytic polymerization activity.[137]

Related tripodal dianionic ligands have also been exploited to prepare the pentacoordinate complexes $MX_2[MeC(C_5H_4N)(CH_2NR)_2]$ (M = Zr, $R = SiMe_3$;[195] M = Zr, Hf, $R = Me_3C_6H_2$[196,197]). These complexes were readily alkylated. A subsequently generated Hf cation showed remarkable stability to β-hydride elimination, even in the presence of 1-hexene.[197] The related complex $Zr[HC(C_5H_4N)(CH_2NSiMe_3)_2]_2$ has also been isolated.[195] A dianionic tripodal ligand has been employed in the stabilization of the monomeric imido complex $Zr(NPr^i{}_2C_6H_3)[MeC(C_5H_4N)(CH_2NSiMe_3)_2](NC_5H_5)$ (**51**).[198]



(**51**)



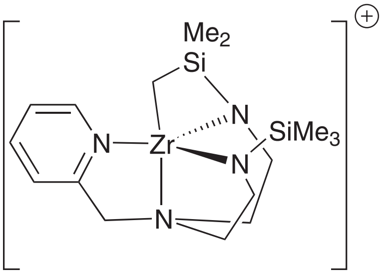
(**52**)

4.3.2.4.13 Trianionic tripodal ligand complexes

A number of compounds containing tripodal, trianionic ligands have been prepared in recent years. These were generally prepared via metathesis using the trilithio salts of the ligands. The LiCl adducts of $ZrX[HC(SiMe_2NR)_3][LiCl(THF)_2]$ (X = H, Cl (**52**); Me, O_3SCF_3, Bn; R = C_6H_4F, C_6H_4Me, $CHMeBu^t$),[199,200] $[LiCl(OEt_2)_3][ZrX\{(RNSiMe_2)_3CH\}]$,[201] and the related species $ZrCl(RNSiMe_2)_3SiMe$ (R = C_6H_4Me, C_6H_4OMe),[201–203] $MCl[MeSi\{SiMe_2N(C_6H_4Me)\}_3]$ (M = Zr, Hf)[204] and $Hf[HC(SiMe_2NR)_3](OEt_2)_2$[201] have been prepared and isolated. In the case of the C_6H_4F derivative, the F atoms provided weak donation to Zr, though these interactions were displaced by alkylation with bulky groups. In recent work, Gade and co-workers have described the complexes $[Li(OEt_2)_4][Zr_2Cl_3\{HC(SiMe_2NCHMePh)_3\}_2]$ and $ZrX[HC(SiMe_2NR)_3]$ (R = CHMePh, C_9H_9; X = Cl, alkyl; R = $CHMeBu^t$; X = Cl).[203,205] Alkyl derivatives of these chiral tripodal complexes effected stereoselective insertions, albeit with low enantioselectivity.

4.3.2.4.14 Dianionic tetradentate ligand complexes

The complexes of a related dissymmetric tripodal ligand $ZrX_2[N(CH_2CH_2NSiMe_3)_2(CH_2C_5H_4N)]$ (X = Cl, NMe_2) and $ZrCl(Bn)[N(CH_2CH_2NSiMe_3)_2(CH_2C_5H_4N)]$ were prepared via the metathetical reaction of the dithio-salt of the ligand with $ZrCl_4$.[206] Addition of $B(C_6F_5)_3$ to the dimethyl derivative afforded $[Zr\{CH_2SiMe_2N(CH_2CH_2NSiMe_3)(CH_2C_5H_4N)\}][BPh_4]$ (**53**), in which one of the $SiMe_3$ substituents was metallated. In contrast, the analogous reaction of the chloro-benzyl analog gave the stable cation, $[ZrCl\{N(CH_2CH_2NSiMe_3)_2(CH_2C_5H_4N)\}][BnB(C_6F_5)_3]$ (**54**).



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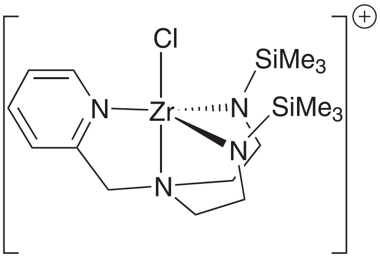


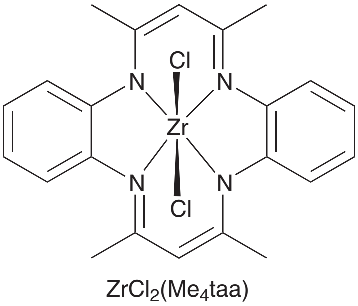
(54)

Macrocyclic Schiff-base ligands act as dianionic, tetradentate ligands.[207,208] Reaction of a variety of such macrocycles with metal precursors afforded the series of complexes of the general formula $MCl_2(L)$ (L = Me_4taa (**55**), Me_8taa, Me_4taen (**56**); where taa = dibenzotetraazaannulene and taen = tetraazacyclotetradecatraene). Floriani and co-workers reported the alkylation of such complexes affording $MR_2(Me_4taa)$.[209,210] Similarly, complexes of the form $MR_2(Me_4taen)$ (M = Zr, R = alkyl;[211] M = Zr, R = OBu^t; M = Hf, R = NMe_2;[212] M = Zr, R = NMe_2, Me[213]), $ZrR_2(Me_8taa)$ (R = Cl, Me, Bn, CH_2SiMe_3),[211,214] and $M(CCPh)_2(Me_4taen)(NHMe_2)$[212] were prepared employing standard salt metathesis procedures or by treatment of the neutral ligand with MR_4 precursors. The disubstituted products $Zr(Me_4taa)_2$[210] and $Zr(Me_4taen)_2$[213] were also prepared when two equivalents of the dilithio-salt of the ligand were employed.

Jordan and co-workers described the generation of cationic derivatives via protonolysis of dialkyl complexes with $[NHMe_2Ph]$ $[B(C_6F_5)_4]$.[211] Neutral and cationic complexes containing the $[Me_8taa]^{2-}$ ligand have been reported, including $MR_2(Me_8taa)$ (M = Zr, Hf; R = alkyl;[211] M = Zr, Hf; R = Cl, alkyl, NMe_2[214,215]).

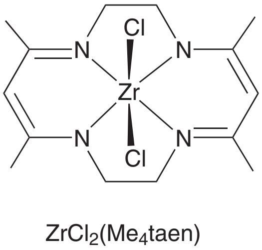
Reaction of $ZrCl_2(N\text{-}C_6H_3Pr^i_2)(C_5H_5N)_3$ with Me_4taaH_2 gave $Zr(N\text{-}C_6H_3Pr^i_2)(Me_4taa)(C_5H_5N)$, which in turn reacted with amine or isocyanate to give $Zr(NHC_6H_3Pr^i_2)_2(Me_4taa)$ and $Zr[Bu^tNC(O)NHC_6H_3Pr^i_2](Me_4taa)$, respectively.[216,217] In related work, reaction of $ZrCl_2(Me_4taa)$ with Li amides or alternatively, reactions of $Zr(CH_2SiMe_3)_2(Me_4taa)$ with amines, were used as synthetic routes to the diamide complexes $Zr(NHC_6H_3R_2)_2(Me_4taa)$ (R = Me, Pr^i).[218] The same product was obtained from reaction of the neutral ligand with $Zr(NC_6H_3Me_2)(NHC_6H_3Me_2)_2(C_5H_5N)_2$. In a related example, reaction of $[Zr(NHR)_2(\mu\text{-}NR)]_2$ with Me_4taaH_2 resulted in the isolation of $Zr(\mu\text{-}NR)_2$ $(Me_4taa)Zr(NHR)_2$ (R = Bu^t, $Me_2C_6H_3$).[218]

Complexes of macrocyclic ligands known as tropocoronands (TC) have also been described.[219] These were prepared by reaction of the Li_2-ligand salt with the corresponding MCl_4. A variety of macrocycles were prepared in a similar manner. The resulting species of the general formula $MCl_2(TC)$ were readily alkylated.[220] In a subsequent study, reactions involving alkyl and aryl isocyanides provided complexes of the general formula $M(RNCBn)_2(TC)$. Coupling or insertion reactions gave η^2-iminoacyl or enediamido products, respectively, which was confirmed by X-ray crystallography.[221] In a further study, reaction of Ph_2CO in the presence of a proton source with $HfBn_2(TC)$ yielded the cationic species $[Hf(TC)\{\eta^1\text{-}OCPh_2(CH_2Ph)\}][BPh_4]$ (**57**).[222]



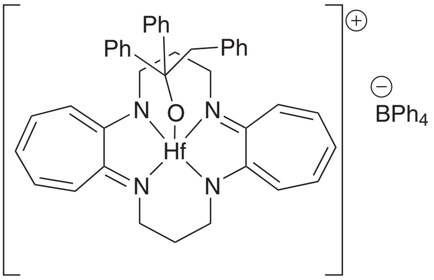
$ZrCl_2(Me_4taa)$

(55)



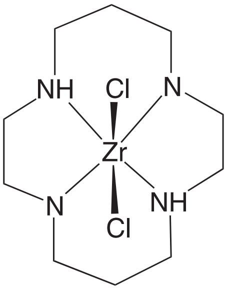
$ZrCl_2(Me_4taen)$

(56)



(57)

There are two Zr compounds reported that contain saturated tetradentate amido ligands. In an early report, complexes proposed to contain heptacoordinate Zr were formulated as $Zr(O)(O_2)[(H_2NCH_2CH_2)_3N]$.[223] In a later report in 1997, the complexation of the ligand 1,4,8,11-tetraazacyclotetradecane ($cyclamH_4$) yielded $ZrCl_2(cyclamH_2)$ (**58**), confirming the dianionic tetradentate nature of the ligand.[224]



(58)

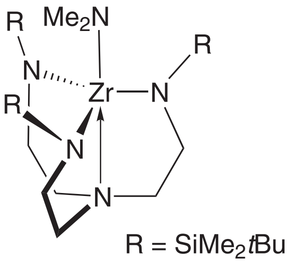
The preparation of the tetradentate ligand complex $ZrBn_2(NC_4H_3CHNCH_2)_2$ has been recently reported. It was derived from a di-pyrrolate Schiff-base, N_4-donor ligand.[142]

4.3.2.4.15 *Trianionic tetradentate ligand complexes*

Tripodal ligands incorporating a basal N-donor have been used to prepare the volatile products $M(NMe_2)[N(CH_2CH_2NR)_3]$ ($R = Pr^i$, $SiMe_3$, $SiMe_2Bu^t$ (**59**)), which acted as metalorganic chemical vapor deposition (MOCVD) precursors to metal nitrides.[225] Alternatively these ligands reacted with $ZrBn_4$ to give $ZrBn[N(CH_2CH_2NR)_3]$, the product of which was used to generate the corresponding chloride derivative via reaction with BCl_3. Treatment with H_2 resulted in C—H activation of a methyl group in the silyl substituent to generate $Zr[CMe_2C(Me)(Bu^t)]N(CH_2CH_2NSiMe_2Bu^t)_2$.[226] Attempts to prepare analogs with *N*-aryl substituents via reaction of the tri-amine with $ZrBn_4$ resulted in loss of only two equivalents of C_6H_5Me, affording $ZrBn_2[(ArNCH_2CH_2)_2NCH_2CH_2NHAr]$ (**60**).[227]

4.3.2.4.16 *Porphyrinato ligand complexes*

The bis(porphyrinate) complexes $M(OEP)_2$ and $M(TPP)_2$ ($M = Zr$, Hf) were reported by two groups independently.[228,229] Crystallographic characterization confirmed eight-coordinate, pseudo-sandwich-type structures. Characterization by spectroscopy,[228–232] cyclic voltammetry, [228,233] X-ray crystallography,[234] optical, IR, and Raman spectroscopy has also been performed. In addition, the radical cation $[Zr(por)_2][SbCl_6]$ was generated from reaction with $SbCl_5$. Spectroscopic analysis indicated that the charge was delocalized over the entire complex, consistent with an enhanced π–π interaction between the ligands.[230–234]



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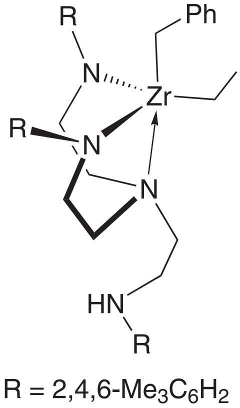


(60)

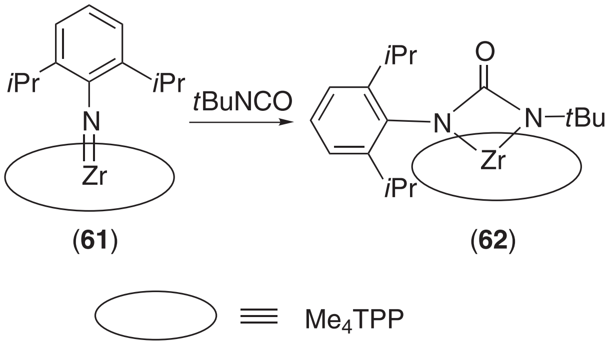
More recently, a variety of derivatives of TPP with substituted aryl groups have provided access to chiral bis(phorphyrinate) complexes. Such compounds were resolved by chiral chromatography.[235] The rates of racemization have been studied and revealed that the neutral species racemized at rates 21 and 99 times faster than the monocationic and dicationic derivatives, respectively.[236]

Porphyrin complexes have also been derivatized to give a variety of complexes in which ligands replace halides. In an early report, complexes of the form M(por)L, (M = Hf, Zr; por = OEP, TPP, L = ethylenebis(salicylaldimine) and analogs) were prepared from $Zr(OEP)(MeCOCH\ COMe)_2$. NMR data were consistent with a square antiprismatic geometry about the metal center. Electrochemical measurements demonstrated that the redox-active portion involved only the porphyrin ligand.[237] Monoporphyrinato complexes of the form $ZrCl_2(TPP)$,[238] as well as several of related *cis*-dialkyl or diaryl derivatives $ZrR_2(OEP)$[239–241] have been prepared. The related zwitterionic species [Li(THF)] $[Zr(OEP)(CCR)_3]$ (R = Ph, $SiMe_3$) have also been reported and characterized structurally.[242]

The compounds $[\{Zr(OEP)\}_2(\mu\text{-}OH)_3][C_2B_9H_{12}]$ and $[Zr(OEP)(\mu\text{-}OH)]_2(\mu\text{-}O)$[4,243] were obtained from reaction of the precursors with $Tl[C_2B_9H_{12}]$ and adventitous H_2O.[4] The related species $[Zr(TPP)(\mu\text{-}OH)_2]_2$ has also been characterized crystallographically.[244] Hf analogs[245] were prepared via analogous reactions, and the derivatives $(Hf(TPP)(\mu\text{-}OH))_2(\mu\text{-}O)$[246,247] and $Hf(TPP)(S_2C_6H_4)$[246] were isolated and characterized. Cationic complexes such as $[M(OEP)(CH_2SiMe_3)][BPh_4]$ (M = Zr, Hf) were prepared; however, these proved to be inactive as C_2H_4 polymerization catalysts.[245]

A variety of heteroatomic derivatives have been prepared. For example, the carborane derivative $Zr(OEP)(\eta^5\text{-}1,2\text{-}C_2B_9H_{11})$ has been described.[4] Other reports have shown that the *bis*-carboxylate derivatives $ZrX_2(TPP)$ (X = O_2CMe, O_2CBu^t, 1,2-$(O_2C)_2C_6H_4$) catalyzed the ethylalumination of alkynes with highly efficient regio- and stereoselectivity.[248] Subsequently, a number of *O*-ligated derivatives have been prepared, several of which have been characterized structurally. These compounds included: $ZrR_2(TPP)$ (R = O_2CMe,[249] OBu^t, $OSiMe_3$, OTf, OAc[240]), $[Zr(TPP)(\mu\text{-}OH)_2]_2$,[244] $Hf(TPP)(O_2C\ Me)_2$,[250] $Hf(H_2O)Cl_2(OEP)$, and $[NBu_4][Hf(OEP)(P_3O_9)]$.[246]

Metathesis of halides with amides gave the complex $ZrCl(TPP)N(SiMe_3)_2$ that was characterized structurally.[251] In related chemistry, reaction of $HfCl_2(TTP)$ (TTP = *meso*-tetra-*p*-tolylporphyrinate) with a Li amide reagent gave the diamido derivative $Hf(NHC_6H_3Pr^i{}_2)_2(TTP)$. Subsequent elimination of primary amine gave the imido species $Hf(NC_6H_3Pr^i{}_2)(TTP)$.[252] The analogous Zr chemistry proceeded directly to the imido-derivative (**61**). Structural data confirmed the monomeric nature of these imido complexes.[252] Reaction with isocyanate produced the insertion product $Zr[OC(NBu^t)N(Pr^i{}_2C_6H_3)](TTP)$ (**62**), while reaction with carbodimide afforded the related guanidinato-derivative. The imido species also reacted with pinacolone, yielding $Zr[OC(Bu^t)CHC(Bu^t)MeO](TTP)$. In contrast, reaction with PhNO afforded $[Zr(TTP)(\mu\text{-}O)]_2$, while reaction with H_2O directly gave $[Zr(TTP)(\mu\text{-}OH)]_2(\mu\text{-}O)$.[252,253]



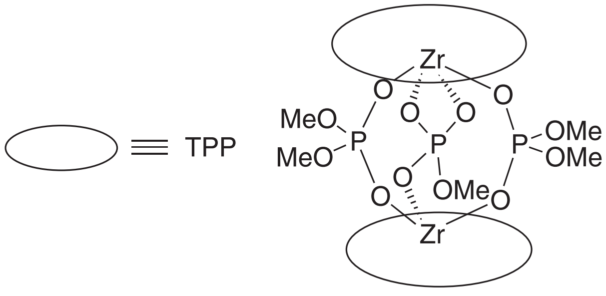
(61) **(62)**

Treatment of $Zr(TPP)_2$ with I_2 and $AgNO_2$ resulted in the monofunctionalization of one of the porphryin rings with a NO_2 group, giving $Zr(TPP)(TPP\text{-}NO_2)$. Subsequent reduction in the presence of Pd/C afforded the corresponding monoamino complex $Zr(TPP)(TPP\text{-}NH_2)$.[254] The asymmetry of these systems was expected to invoke nonlinear optical properties. Further functionalization incorporated anthraquinone and pyromellitimide units to give complexes of the form Zr(TPP)(TPP-quinone). These compounds were the first porphyrin sandwich complexes with electron acceptors bonded directly to the porphyrin ring[255] and were, therefore, examined as potential models for the photosynthetic reaction center. A related functionalized-OEP, octaethyl-5-methylporphyrin (OEMEP) was used to prepare the complex $Zr(OEMEP)_2$. This species was found to be more readily oxidized than $Zr(OEP)_2$, a feature attributed to the electron-donating methyl substituents present in the ligand.[256]

In a bioinorganic study, $ZrCl_2(TPP)$ complexes were used to mimic the reaction of nucleases in phosphate diester transesterification, as this species catalyzed solvolysis of model for RNA- and DNA-phosphates.[257,345] Kinetic and mechanistic studies suggested that the active species was dinuclear and it was likened to $[Zr(TPP)(\mu\text{-}Me_2PO_3)]_2(\mu\text{-}MePO_4)$ (**63**), which was characterized crystallographically.

4.3.2.4.17 *Porphyrinogen ligand complexes*

Disruption of the conjugation of porphyrin rings gave the tetraanionic phorphyrinogen ligands (Et_8N_4). The complex $Zr(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)$ (**64**) was prepared, and crystallographic data confirmed η^5- and η^1-bound pyrrolato groups.[258] This finding prompted theoretical[259] and reactivity studies.



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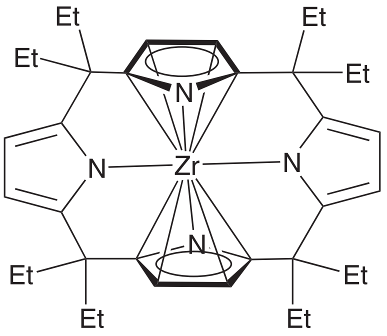


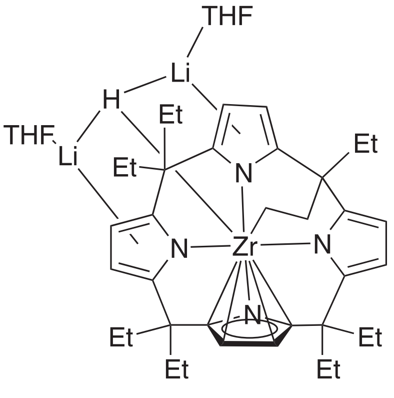
(64)

Porphyrinogen complexes acted as carriers for alkali metal hydrides as illustrated in $[Zr(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)(\mu\text{-}MH)]_2$ (M = Na,[260] K[261]). These species were stabilized by pyrrolyl interactions with the alkali metal ions. Subsequent crystallographic characterization of the LiH derivative revealed the formulation to be $[Zr(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)(\mu\text{-}Li_2H_2)]_2$, where $(LiH)_4$ was sandwiched between two porphyrinogen complexes.[262] In a similar manner, Zr-porphyrinogen complexes encapsulated Li_2O, affording the dimer $[Zr(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)Li_2O]_2$.

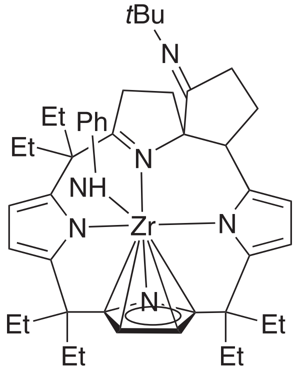
The KH derivative reacted with alkenes and alkynes to give the corresponding alkyl and vinyl derivatives,[260] while reaction with CO gave $[Zr(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)O(\mu\text{-}K)]_2$.[261] The related enolate adduct $[Zr(\eta^5\text{-}\eta^1\text{-}\eta^5\text{-}\eta^1\text{-}Et_8N_4)]_2[\mu\text{-}OCPh(CH_2)K]_2$ was derived from the reaction of

Zr(η^5-η^1-η^5-η^1-Et$_8$N$_4$) with K(PhCOCH$_2$). This species reacted with excess Ph$_2$CO to drive the Aldol condensation, affording [Zr(η^5-η^1-η^5-η^1-Et$_8$N$_4$)]$_2$ [μ-OCMe(Ph)CH$_2$C(Ph)O)K]$_n$.[263]

A study by Floriani and co-workers revealed a unique approach to the derivatization of porphyrinogen ligands.[264] The alkali metal-hydride adducts induced C–H activation of an Et-group from the porphyrinogen ligand to give [Zr(η^5-η^1-η^5-η^1-Et$_7$(CH$_2$CH$_2$)N$_4$]HM(THF)$_n$ and [Zr(η^5-η^1-η^5-η^1-Et$_6$(CH$_2$CH$_2$)$_2$N$_4$]HM(THF)$_n$ ($n=1$, M = Li (**65**), Na; $n=2$, M = K).[264] The former reacted with Bu^{t}NC, undergoing insertion into the Zr—C bond to yield Zr[η^5-η^1-η^5-η^1-Et$_7${CH$_2$CH$_2$CN (Bu^t)C$_4$H$_4$N}(C$_4$H$_2$N)$_3$](NHPh) (**66**). Similarly, it reacted with either CO or Mo(CO)$_6$ to give [Zr{η^5-η^1-η^5-η^1-Et$_7$(CH$_2$CH$_2$C$_5$H$_2$N)(C$_4$H$_2$N)$_3$}ZrOLi]$_2$, which contained one pyridine and three pyrrole rings.

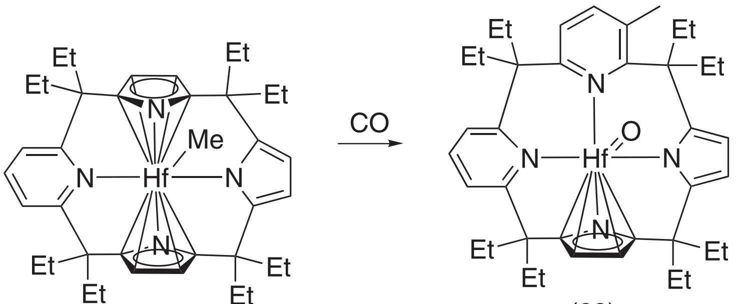


(**65**)



(**66**)

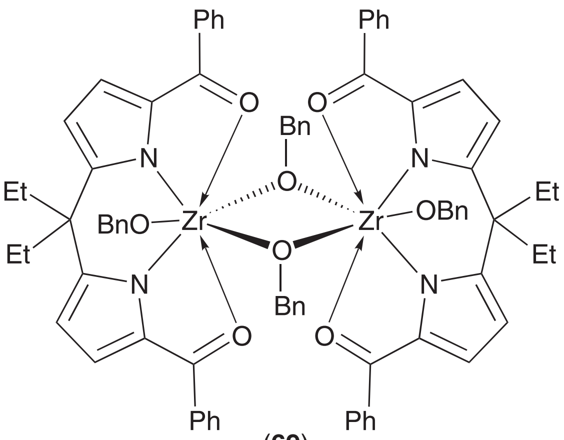
Treatment of [Zr(η^5-η^1-η^5-η^1-Et$_8$N$_4$)μ-MH]$_2$ with CO gave [Zr{η^5-η^1-η^5-η^1-Et$_8$(C$_5$H$_3$N)(C$_4$H$_2$N)$_3$} OM]$_2$, which contained an octaethyltrispyrrolemonopyridine ligand.[265] Alternatively, reaction of [ZrR(η^5-η^1-η^5-η^1-Et$_8$N$_4$)(μ-M)]$_2$ with CO gave the species [Zr{η^5-η^1-η^5-η^1-Et$_8$(C$_5$H$_2$RN)(C$_4$H$_2$N)$_3$}OM]$_2$ that contained the analogous alkylated pyridine. Isolation of the free ligand was achieved, and this was subsequently used to prepare HfX[η^5-η^1-η^5-η^1-Et$_8$(C$_5$H$_3$N)(C$_4$H$_2$N)$_3$] (X = Cl, Me (**67**)). Further reaction of the methyl derivative with CO afforded HfO[η^5-η^1-η^5-η^1-Et$_8$(C$_5$H$_3$N)(MeC$_5$H$_2$N)(C$_4$H$_2$N)$_2$] (**68**), which contained two adjacent pyridine groups in the ligand.[266,267]



(**67**) (**68**)

Related reactions of Zr(η^5-η^1-η^5-η^1-Et$_8$N$_4$) with PhCHO resulted in addition of the carbonyl-carbon to the pyrrolic rings. This prompted ligand cleavage and the isolation of (Zr{Et$_4$N$_2$-(PhCO)$_2$}(OCH$_2$Ph)$_2$]$_2$ (**69**).[268]

Two and four electron reductions of tetraethyl-porphyrinogen (**70**) ligands gave the porphomethene (Et$_4$H$_3$PM) (**71**) and porphodimethene (Et$_4$H$_2$PDM) (**72**) macrocycles.[269] The latter ligand was used to prepare complexes of the form ZrX$_2$(PDM) (X = Cl, Me, Bn, Ph). The derivative ZrMe$_2$(Et$_6$PDM) effected C—H bond activation of a peripheral Et-group upon thermolysis, affording Zr[Et$_4$(CHMe)PDM] (**73**). In contrast, the dibenzyl derivative ZrBn$_2$(Et$_6$PDM) gave Bn-group transfer to the ligand affording the product ZrBn(BnEt$_6$PM)(THF) (**74**).[270]



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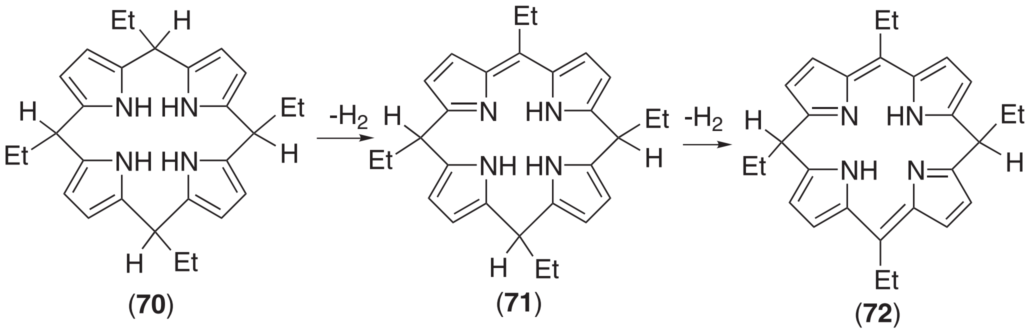
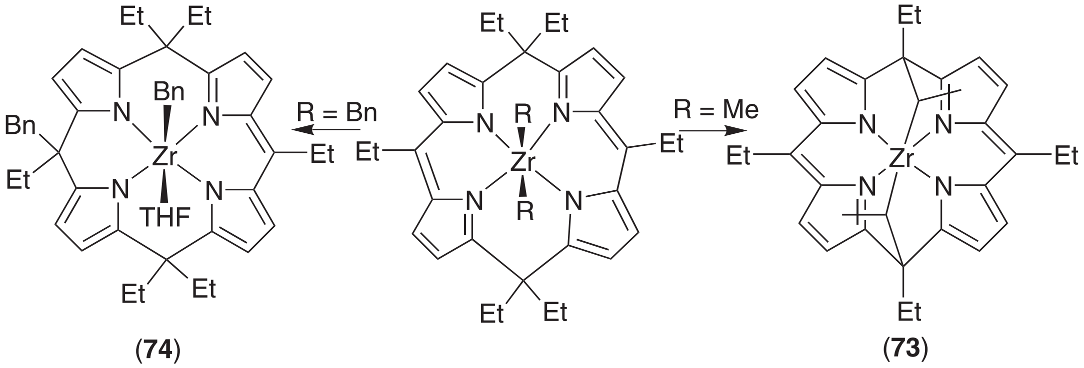




4.3.2.4.18 *Tetraazaporphyrin and phthalocyaninate ligand complexes*

The ligands octaphenyltetraaza-phorphyrin (OPTAP) and octaethylthiotetraaza-porphyrin (OETTAP) (**75**) are ligands that are related to porphyrinates. The corresponding *bis*-ligand complexes ML_2 have been prepared and characterized structurally.[271,272] In the case of $Zr(OETTAP)_2$, ligand-based oxidations gave radical cations, similar to those observed for porphyrinato-species.[272]

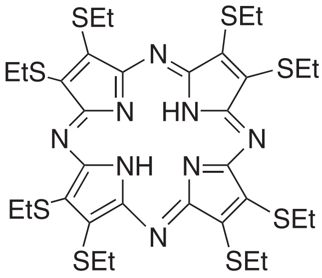
In recent work, $Zr(OETAP)_2$, Zr(OEP)(OETAP) and the related radical cations [Zr(OEP)(OETAP)][$SbCl_6$], and [$Zr(OETAP)_2$][$SbCl_6$] were prepared and characterized. The former cation possessed nonlinear optical properties. In related work, solvent-dependent charge-transfer complexes were prepared from the 1:1 co-crystallization of $Zr(OEP)_2$ with $M(OETAP)_2$ (M = Gd, Lu). The lanthanides partially oxidized the Zr complex in solution, and magnetic susceptibility measurements suggested weak intermolecular interactions.[273]

Related to these systems were those containing the phthalocyanin ligand (**76**). Though Ti phthalocyaninates (Pcs) are more common, several Zr and Hf Pcs have been reported in recent years. The *bis*-ligand product $Zr(Pc)_2$ was prepared from the reaction of diaminoisoindoline with $ZrCl_4$ in quinoline.[274] Monoligand complexes of the form $MCl_2(Pc)$ (M = Zr, Hf) were prepared from reaction of MCl_4 with phthalodinitrile in 1-chloronaphthaline at elevated temperatures.[275,276] The chloride substituents were replaced with bidentate O-ligands containing pendant sulfinate or carboxylic acid functional groups, yielding $M(O_2R)(pc)$. These species were stable in H_2O for an extended period of times.[277] Alternatively, the metallates $[Ph_3PNPPh_3][ZrCl_3Pc]$[275] or $[NBu_4][MF_3Pc]$ (M = Zr, Hf)[276] were isolated in the presence of halide salts and characterized crystallographically.

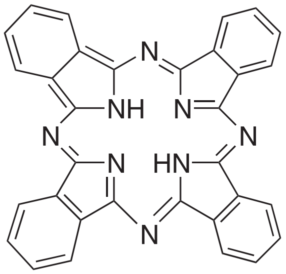
Mixed M(por)(Pc) (M = Zr, Hf; por = TPP, OEP) complexes have been prepared and studied electrochemically. All were found to undergo two reversible ring-centered oxidations and reductions.[278]

4.3.2.4.19 Tetraanionic tetradentate ligand complexes

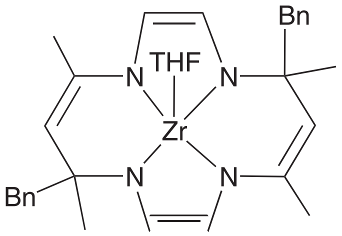
Tetradentate tetraanionic ligands are rare. However, Floriani's group has shown that the compounds $ZrR_2(Me_4taa)$ (R = Me, Bn) undergo successive migration of the alkyl groups into the macrocycle under thermal duress.[279] An intermediate trianionic species was isolated and converted to $Zr(R_2Me_4taa)(L)$ (**77**) in the presence of THF or C_5H_5N. This latter species contained a macrocyclic ligand which provided four amido donors to the metal center.



(**75**)



(**76**)



(**77**)

One other example of a tetradentate tetraanionic ligand complex has been reported. The ligand cyclamH_4 was used to prepare complexes in which the ligand acted as either a dianionic or tetraanionic donor, yielding $ZrCl_2(cyclamH_2)$ and Zr(cyclam) (see Section 4.3.2.4.14). The latter was prepared free of LiCl by reaction of the neutral ligand with $Zr(NMe_2)_4$.[224]

4.3.2.5 Phosphorus Ligand Complexes

4.3.2.5.1 Neutral phosphorus ligand complexes

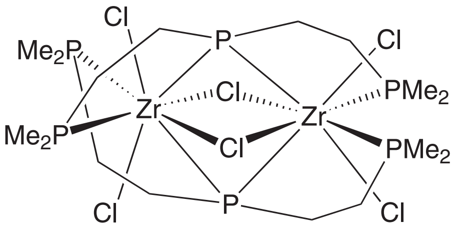
Mononuclear phosphine adducts of MX_4 have adopted several geometries. For example, $ZrCl_4(PEt_3)_2$,[31] *trans*-$ZrI_4(PMe_2Ph)_2$,[280] $ZrI_4(PMe_3)_3$,[281] and $HfI_4(PMe_3)_{2.5}$ have been characterized crystallographically. The latter species was a statistical mixture of two compounds incorporating either two or three equivalents of PMe_3 per Hf, thus generating six- and seven-coordinate Hf centers.[281] Analogous complexes containing bidentate phosphines such as $ZrCl_4(Bu_2PCH_2CH_2PBu_2)$, $HfCl_4(Ph_2PCH_2CH_2PPh_2)$, and $HfCl_4[Ph_2P(CH_2)_3PPh_2]$[282] possessed typical pseudo-octahedral geometries.

The eight-coordinate complex $ZrCl_4(Me_2PCH_2CH_2PMe_2)_2$ reacted with $MgMe_2$ to give $ZrCl_2Me_2(Me_2PCH_2CH_2PMe_2)_2$ or $ZrMe_4(Me_2PCH_2CH_2PMe_2)_2$.[283] It is noteworthy that the species $ZrMe_4$ is not readily accessible or stable in the absence of the phosphine donor. In a subsequent paper, reaction of $Zr(CH_2SiMe_3)_4$ with $Me_2PCH_2CH_2PMe_2$ gave $Zr(CH_2SiMe_3)_4(Me_2PCH_2CH_2PMe_2)$, which exhibited an agostic Zr···H interaction (2.48 Å).[284]

Dinuclear products have also been characterized from reactions of sterically less demanding phosphines with $ZrCl_4$. For example, use of PMe_3 resulted in the isolation of $Zr_2Cl_5(\mu\text{-}Cl)_3(PMe_3)_2$[285] and $Zr_2Cl_6(\mu\text{-}Cl)_2(PMe_3)_4$.[280] The former species was dissymmetric with three bridging Cl atoms, while the latter was a symmetric doubly bridged dimer. In a similar case, use of PPh_3 gave the dissymmetric product $Zr_2Cl_5(\mu\text{-}Cl)_3(PPh_3)_2$.[286]

4.3.2.5.2 Phosphido ligand complexes

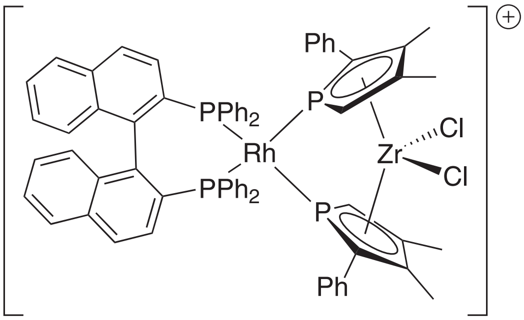
Few Zr phosphido complexes that lack a stabilizing cyclopentadienyl ligand have been reported. In 1983, Baker *et al.* described the synthesis of the homoleptic complexes [Li(DME)] [M(PCy$_2$)$_5$] (M = Zr, Hf) from the addition of excess LiPCy$_2$ to MCl$_4$. The Hf derivative was characterized crystallographically, revealing a five-coordinate metal center.[287] In a later study, Danopoulos *et al.* described a series of Zr phosphide complexes of the forms ZrCl$_2$[P(CH$_2$CH$_2$PR$_2$)$_2$]$_2$, [ZrCl$_2$(μ-Cl){P(CH$_2$CH$_2$PR$_2$)$_2$}]$_2$ (**78**), and Zr$_2$Cl$_5$(μ-H)[P(CH$_2$CH$_2$PR$_2$)$_2$]$_2$. These compounds were derived from the reaction of varying stoichiometries of LiP(CH$_2$CH$_2$PR$_2$)$_2$ (R = Me, Et) with ZrCl$_4$.[288]



(**78**)

A P-containing analog of the Cp-ligand is the phospholyl anion [C$_4$Me$_4$P]$^-$. The first Zr–phospholyl complex ZrCl$_2$(C$_4$Me$_4$P)$_2$ was prepared via reaction of the Li salt of the ligand with ZrCl$_4$. A crystallographic study confirmed the η^5-binding mode.[289] A number of related substituted bis(phospholyl) Zr compounds have been described in the literature.[290–292] Upon treatment with Lewis-acid activators, these compounds generally gave rise to only moderately active catalysts for MeCHCH$_2$ polymerization. Interestingly, when two very bulky groups were located adjacent P, the catalysts were inactive.

Coordination of another metal to the accessible lone pair of electrons on the P atom of the phospholyl ligand has also been exploited to prepare heterobimetallic complexes. In this fashion, the species [ZrCl$_2$(C$_4$HMe$_2$PhP)$_2$]Mo(CO)$_4$,[293] [ZrCl$_2$(C$_4$Me$_4$P)$_2$]M(CO)$_n$ (M = W, n = 4; M = Fe, n = 3),[294] [ZrCl$_2$(C$_4$Me$_4$P)$_2$]RuHCl(PPh$_3$)$_2$,[295] and [{ZrCl$_2$(C$_4$HMe$_2$PhP)$_2$}Rh(binap)]$^+$ (**79**)[296] (binap = 2,2′-bis(diphenylphosphino)-1,1′-binaphthylene) have been prepared. In the bimetallic Zr–Mo and Zr–Rh complexes, resolution of the *rac* and *meso* forms was realized. The applications of these species in catalysis have not been fully explored.



(**79**)

4.3.2.6 Oxygen-based Ligand Complexes

4.3.2.6.1 Neutral oxygen ligand complexes

Ether adducts of Zr and Hf halides have been characterized crystallographically. The coordination of a cyclic polyether to MCl$_4$, as in ZrCl$_4$(12-crown-4), was first prepared in 1986. This species was indefinitely stable in ethereal solvents.[297] The mononuclear complexes, *trans*-ZrCl$_4$(Et$_2$O)$_2$[50] and *cis*-MCl$_4$(THF)$_2$ (M = Zr,[298] Hf[299]) exhibited distorted octahedral geometries.

In all cases, coordination of the O donors rendered the complex more soluble in hydrocarbons, thus providing valuable precursors for organometallic syntheses. The symmetric dimer $Zr_2Cl_6(\mu\text{-}Cl)_2(THF)_2$[300] has been characterized structurally, although it was isolated in low yield. This stands in contrast to the monomeric adducts described above which were isolated in good yields in general.

Related oxo-bridged complexes of formulas $[ZrCl_3(MeOCH_2CH_2OMe)_2]_2(\mu\text{-}O)$[301] and $[ZrCl_3(THF)_2]_2(\mu\text{-}O)$[302] have also been synthesized and characterized. These dinuclear species were obtained only in low yields as the source of the oxo-bridge was inferred to be adventitious O_2.

$ZrCl_4$ has been used as a Lewis acid catalyst in a variety of organic transformations.[303–307] Intermediates in such reactions were proposed to be O-donor adducts. Several have been isolated, providing valuable mechanistic insight. For example, the stoichiometric reaction of $ZrCl_4$ with ethyl acetate[308] or *n*-hexyl acetate[309] gave $[ZrCl_2(\mu\text{-}Cl)_2(MeCO_2R)]_2$. These species have been tested as C_2H_4 oligomerization precatalysts and the catalyst derived from $[ZrCl_2(\mu\text{-}Cl)_2\{MeCO_2(CH_2)_5Me\}]_2$ displayed moderate activity upon activation.[309]

Coordination of ketonic O-donors gave $ZrCl_4(L)_2$ (L = phenazone, amidopyrine),[310] as well as $ZrOX_2[OP(NMe_2)_2]_2$ (X = Cl, Br, I, NO_3, NCS, NCSe, BPh_4).[311] A related 1:1 adduct was prepared via reaction of $ZrCl_4$ with $SOCl_2$, although this product was thought to be a dimer.[312] In a more recent study, reaction of $ZrCl_4$ with $SeOCl_2$ gave both 1:1 and 1:2 adducts.[313,314] Similarly, reaction of $ZrCl_4$ with poly(4-vinylpydridineNO) yielded what was proposed to be a *trans*-octahedral complex.[315] In the same way, R_3PO coordinated to MCl_4, affording both five- and six-coordinate adducts, MCl_4L_n ($n = 1, 2$; M = Zr, Hf). Studies of ligand exchange activation parameters, as well as relevant *cis*/*trans* isomerization processes have been reported.[316,317]

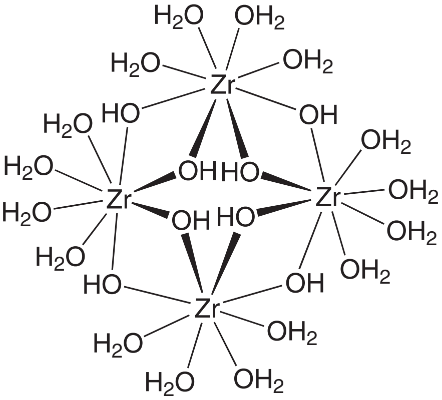
Other O-donor adducts have included species derived from α-keto-ylids and barbituric acid, $MCl_4[Ph_3PCHC(O)R]$ (M = Zr, Hf; R = Me, Ph)[318] and $ZrCl_4(C_4O_3N_2H_4)_2$,[319] respectively. Similarly, reaction of $Ph_3AsNSO_2(C_6H_5Me)$ with $ZrCl_4$ resulted in the formation of the dimeric adduct $[ZrCl_4(Ph_3AsNSO_2C_6H_5Me)]_2$ in which the ligand bridges the two metal centers.[320] Independent reports of the crystallographic characterizations of $[ZrF_4(Me_2SO)_2]_2$ have appeared.[321,322] The Zr centers were bridged by F-atoms and displayed pentagonal bipyramidal geometries. The related adduct $ZrF_4(Me_2SO)(H_2O)_2$ was also characterized, revealing a seven-coordinate mononuclear complex.[322] More recently, crystallographic characterization of the serendipitously obtained eight-coordinate species $[Zr(Me_2SO)_8]Cl_4$ was reported.[323] Heterobimetallic complexes obtained from the interaction of Cu^{II} Schiff-base complexes with $ZrCl_4$ were also described, and were proposed to involve O bridges.[324]

In recent studies, a series of ketone-bound adducts $ZrCl_4[R^2HNC(R^3)CHC(R^1)O]_2$ ($R^2 = Pr^i$, Ph, $R^3 = R^1 = Me$; $R^2 = C_6H_4OMe$, $R^3 = Me$; $R^1 = CF_3$) and $ZrCl_4[R^2{}_2NC(Me)CHC(Me)O]_2$ (R^2 = Et, Ph) were prepared.[325] $ZrCl_4[Pr^iHNC(Me)CHC(Me)O]_2$ was characterized crystallographically and it adopted a *trans* conformation, with intramolecular H-bonding between the amine groups and the O atoms. NMR spectroscopy, *ab initio* and DFT calculations suggested the formation of 1:1 and 2:1 formaldehyde:$ZrCl_4$ adducts.[326]

4.3.2.6.2 Oxide, hydroxide, and peroxo ligand complexes

Polymeric complexes of $ZrOX_2$ that contain substituted hydrazine donors have been described.[327,328] Similarly, Schiff-bases,[329–331] ethoxycarbonylaminopyridine,[332] 4-(*N*-benzoyl)-amino-antipyrine,[333] and aminopyridine[334] ligands have been used to generate adducts of $ZrOX_2$ (X = Cl, Br, I, NCS, BPh_4). Reaction of thionyl chloride with $ZrCl_4$ gave $ZrOCl_2(H_2O)_3$.[312] The related complexes $ZrOX_2$ (X = halogen, NCS, NO_3, ClO_4, BPh_4) were also reported but were poorly characterized. Similarly, $(Me_2N)_3PO$ coordinated to $ZrOX_2$ to provide compounds formulated as $ZrOX_2[(Me_2N)_3PO]_n$ ($n = 2, 4, 6$).[335]

The tetrameric Zr complexes $[Zr(OH)_2(H_2O)_2L]_4X_8$ (L = bipyridyl, phenanthroline, various Schiff-bases; X = Cl, NCS) were the presumed products from the reaction of $ZrOCl_2$ with various heterocyclic bidentate ligands.[336] The interaction of H_2O with $ZrO(ClO_4)_2$ or $ZrO(NO_3)_2$ was probed by NMR spectroscopy.[337,338] In the latter case, the cation $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$ (**80**) was proposed as the product.[338] The related trimer $[ZrO_2C_{12}H_8(\mu^2\text{-}OH)]_3(\mu^3\text{-}O)Li_5(THF)_8(H_2O)_5$ (**81**) was isolated from the hydrolysis product of an organometallic precursor. X-ray structural data confirmed the planarity of the six-membered $Zr_3(\mu^2\text{-}OH)_3$ core.[339] In related work, protometric studies of Zr hydroxide complexes have probed thermodynamic stability,[340] while FT IR and theoretical investigations have addressed the details of laser-ablated group IV metal atoms that co-deposited at 11 K with water. In the latter study, the species HMOH and $H_2M(OH)_2$ (M = Ti, Zr, Hf) provided H_2MO upon annealing.[341]



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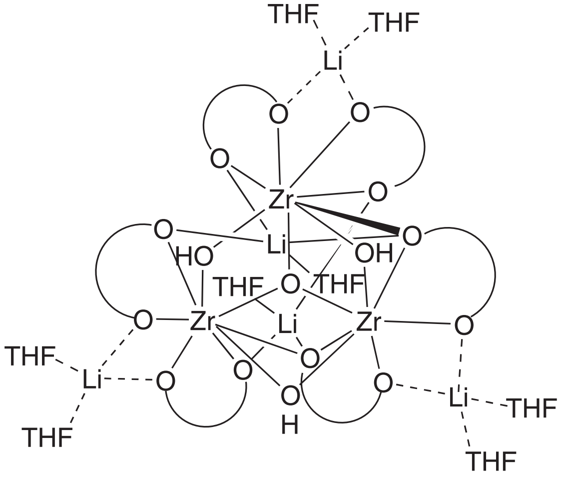


(81)

A series of papers have reported Zr peroxo derivatives.[334,342–352] While Raman, IR, and ^{13}C NMR data supported their structural formulations, no X-ray data have appeared.

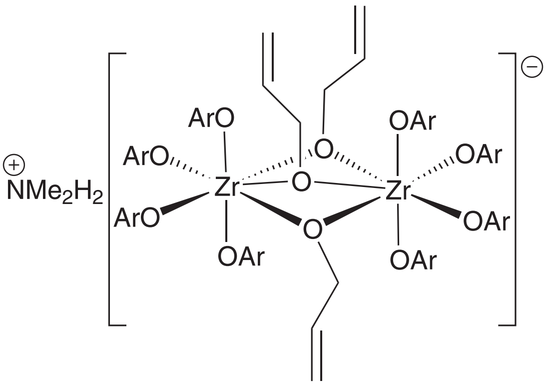
4.3.2.6.3 Alkoxide ligand complexes

The mixed amido alkoxide Zr complex $Zr(OC_6H_2Bu^t{}_3)_2(NMe_2)_2$ was prepared via protonolysis of $Zr(NMe_2)_4$ with the phenol.[353] Similarly, protonolysis has been used to synthesize hydroxychalcone and diactoneglucose complexes $Hf(OPr^i)_{4-n}(OR)_n$ ($n = 1$–3)[354] and $M(OR)_4$,[355] respectively. In contrast, treatment of MCl_4 (M = Zr, Hf) with $Li(O\text{-}Bu^t{}_2C_6H_3)$ gave only the species $MCl(OC_6H_3Bu^t{}_2)_3$, regardless of stoichiometry.[356,357] Salt metathesis was also exploited to generate the disubstituted product $ZrCl_2(OAr)_2$ ($Ar = C_6H_2MeBu^t{}_2$).[358] In later work, an alternate synthetic strategy using sterically less demanding aryloxide precursors was described. $Me_2C_6H_3O$ $SiMe_3$ reacted with MCl_4 to give the products $ZrCl_3(OC_6H_3Me_2)$ and $ZrCl_2(OC_6H_3Me_2)_2$ via TMSCl elimination.[359,360] The solvated adduct $ZrCl_2(OC_6H_3\ Me_2)_2(THF)_2$ was characterized crystallographically, revealing that Zr adopted a slightly distorted octahedral geometry. Reaction of trimethylphenol with $ZrCl_4$ generated $ZrCl_{4-n}(OAr)_n$ ($n = 1$–3), which were characterized as adducts with pyridine, bipyridine, or THF.[361] Protonolysis of $ZrBn_4$ with alcohols yielded $ZrBn_2(OC_6H_3Bu^t{}_2)_2$.[362] Subsequent thermolysis in the presence of pyridine resulted in C—H activation of one of the Me-groups on the Bu^t fragment.[362]

The sterically bulky alkoxide $[Bu^t{}_3CO]^-$ dubbed "tritox" has been described as a steric equivalent to Cp-ligand.[363] Salt metathesis of $ZrCl_4$ with the Li salt of tritox readily afforded $ZrCl_3(OR)_2{\cdot}Li(OEt_2)_2$ and $ZrCl_2(OR)_2$, while controlled hydrolysis of ZrR_4 ($R = Bn$, CH_2Bu^t) with the corresponding alcohol produced $ZrR_3(OR)$.[363] Reaction of MCl_4 (M = Zr, Hf) with three equivalents of LiOR, followed by *in situ* addition of $LiSi(SiMe_3)_3$ provided $Zr(OR)_3Si(SiMe_3)_3$.[11] Treatment of $ZrMe_2(OR)_2$ with dry O_2 afforded $Zr(OMe)_2(OR)_2$,[364] and mechanistic information was offered for this insertion process. Alcoholysis of ZrR_4 ($R = Bn$, $CH_2(FC_6H_4)$) with $HOC_6H_3\text{-}Bu^t{}_2$ generated the complexes $ZrR_3(OC_6H_3Bu^t{}_2)$ and $ZrR_2(OC_6H_3Bu^t{}_2)_2$.[365] Subsequent reaction of $ZrBn_2(OC_6H_3Bu^t{}_2)_2$ with the Lewis acid $B(C_6F_5)_3$ afforded a zwitterionic product that displayed η^6-coordination to the aryl ring of the $[BnB(C_6F_5)_3]^-$ anion. This was confirmed by X-ray crystallography.[366,367]

Employing protonolysis, complexes of the form $[Zr(OPr^i)_2\{OC_6H_3(OMe)(CH_2CHCH_2)\}\text{-}(\mu\text{-}OPr^i)]_2$ and $[Me_2NH_2][\{Zr(OC_6H_3Me_2)_3\}_2(\mu\text{-}OCH_2CHCH_2)_3]$ (**82**) have been isolated and characterized structurally.[368] In a related reaction of $Zr(OEt)_4$ with $K(O\text{-}C_6H_3Me_2)$, the cluster $[K_2Zr\{OC_6H_3(OMe)CH_2CHCH_2\}_4(OEt)]_2(\mu\text{-}O)$ (**83**) was produced.

The monomeric Zr enolate derivative, $ZrMe[N(SiMe_3)_2](OCMeCMe_2)$, was isolated as a by-product in the reaction of $ZrMe_2[N(SiMe_3)_2]$ with CO. The mechanism of formation of this species was not fully understood; however, labeling studies showed the enolate carbons were derived from CO. It should be noted that the major product of this reaction was $[ZrMe\{N(SiMe_3)_2\}]_2O$. Interestingly, no reaction occurred with the analogous Hf precursor.[369] A related report detailed the reaction of the allyl-species $Zr(C_3H_5)_4$ with CO_2 to result in the isolation of equimolar amounts of carboxylic acid and alcohol derivatives, which implied the formation of $[ZrO\{OC(C_3H_5)_3\}(O_2CC_3H_5)]_n$.[370] Similar organic products were isolated for the corresponding reaction of $ZrBn_4$. In contrast, $Zr(Bu^t)_4$ afforded predominantly $Bu^t{}_2CO$ with a smaller amount of Bu^tCO_2H, presumably reflecting steric congestion at the metal center.



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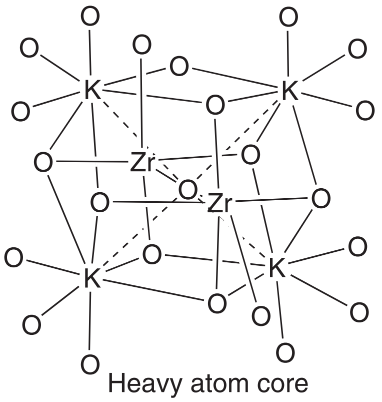
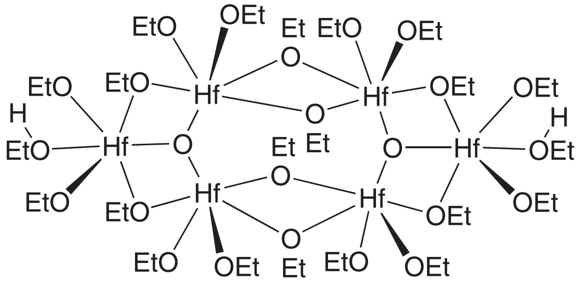


(83)

A unique approach to alkoxide derivatives was exemplified by the reaction of bulky phosphines with $ZrCl_4(THF)_2$. In these cases, simple ligand exchange products were not obtained, rather nucleophilic attack of coordinated THF afforded the dinuclear species $[ZrCl_4\{O(CH_2)_4PR_3\}]_2$ (R = Cy, Ph).[285]

The species $Zr_2(OPr^i)_8(Pr^iOH)_2$[371] and $[Zr_2(\mu\text{-}OCHMe_2)(OCH_2Bu^t)_3(HOCH_2Bu^t)]_2$[372] have been characterized spectroscopically and crystallographically. A combination of techniques demonstrated that H-bonding interactions between the coordinated alcohol and the alkoxide ligands persisted in solution and in the solid state. In addition, the alkoxide clusters $Zr_3(\mu^3\text{-}X)(\mu^3\text{-}O)(OCH_2Bu^t)_9$ (X = Cl, OH),[373] $Hf_6(\mu^3\text{-}O)_2(OEt)_{20}(EtOH)_2$ (**84**), and $Zr_3(\mu^3\text{-}O)(\mu^3\text{-}OBu^t)(OBu^t)_9$ (**85**)[374] have also been prepared and characterized structurally.



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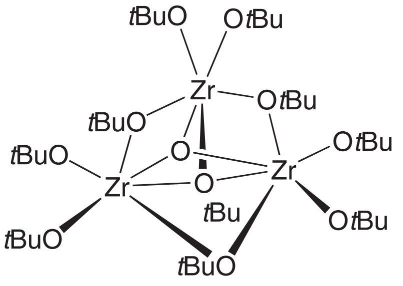


(85)

A variety of papers have described the applications of Zr and Hf alkoxides as precursors for metal oxide thin films and ceramics. In addition, these species have been used as Lewis acid catalysts in a variety of organic transformations.[375–381]

4.3.2.6.4 Siloxide ligand complexes

The homoleptic derivatives $M(OSiR_3)_4$ (M = Zr, R = Ph;[297] M = Zr, Hf, R = Bu^t) have been prepared from reaction of the MR_4 precursors with the appropriate silanol. Alternatively, the complexes $ZrCl_2(OSiPh_3)_2(MeOCH_2CH_2OMe)$,[297] $ZrX_2(OSiBu^t{}_3)_2$, $ZrX(OSiBu^t{}_3)_3$ (X = Cl, Bn),[382,383] $MCl_2(OSiPh_2Bu^t)_2(THF)_2$, and $MCl(OSiPh_2Bu^t)(OSiMe_3)_2(THF)_2$ (M = Zr, Hf)[12] were prepared from MCl_4 and the silyloxide ligand. Replacement of THF with donor ligands such as $MeOCH_2CH_2OMe$, $Ph_2PCH_2CH_2PPh_2$, and bipyridine was also described.[300] In a related example, the cyclozirconosiloxane was synthesized by the addition of $(Bu^tO)_2Si(OH)_2$ to $Zr(OPr^i)_2(MeCOCHCOMe)_2$. X-ray data confirmed the dimeric formulation $[Zr(MeCOCHCOMe)_2\{O_2Si(OBu^t)_2\}]_2$.[384]

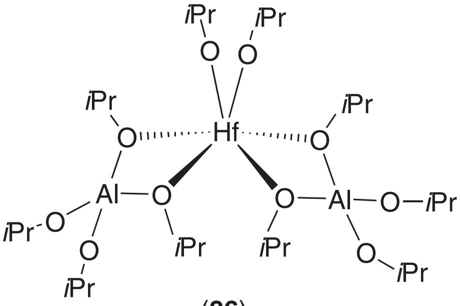
Heating of $M(OSiBu^t_3)_4$ afforded the materials $MO_2{\cdot}4SiO_2$ (M = Zr, Hf).[385] Alternatively, hydrolysis of $M[OSi(OBu^t)_3]_4$ was investigated, and with precise control of the stoichiometry of water, the adducts $M[OSi(OBu^t)_3]_4{\cdot}(H_2O)_n$ ($n = 1$, 2) were isolated. However, an excess of H_2O resulted in the formation of the gel $MO_x(OH)_y(OH_2)_z$.[386]

The interaction of Zr and Hf with silica has been probed via the study of well-defined silica- and alumina-[387] supported alkyl Zr complexes. This work has been reviewed recently.[388] Related organometallic Zr silsesquioxane compounds have also been prepared for grafting to silica and use in alkene polymerization catalysis.[389]

4.3.2.6.5 Heterometallic alkoxide complexes

Homo- and heteroleptic Zr or Hf alkoxide complexes have been employed to prepare mixed metal species incorporating Ba, Sr, Al, Tl, Sn, Pb, transition, or lanthanide metals. This area has been reviewed thoroughly.[390–392]

Building on earlier synthetic reports in this area, the Zr/Al bimetallic derivatives $ZrAl_2X_n(OPr^i)_{10-n}$, $[ZrAlX_3(OPr^i)_4]_3(Pr^iOH)_2$ ($n = 1$, 2; X = Cl, Br, MeCOCHCOMe),[393] and $ZrAl(OPr^i)_{7-n}L_n$ ($n = 1$, 2; L = RCOCHCOMe (R = Me, Ph), MeCOCH CO_2Me (R = Me, Et))[394] were prepared. However, it was not until the X-ray crystallographic study of the related Hf complex $Al_2Hf(OPr^i)_{10}$ (**86**) that the nature of these trimetallics was well understood.[395] This compound was prepared via prolonged refluxing of the respective metal alkoxides.



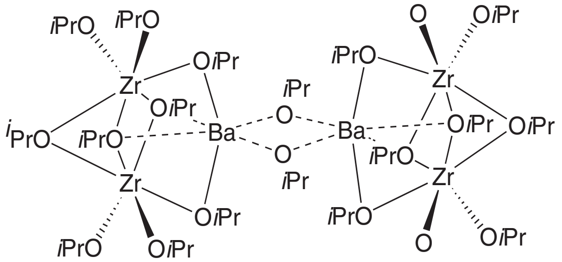
(**86**)

Related mixed metal species incorporating Ba have also drawn attention. Reaction of $Zr_2(OPr^i)_8(Pr^iOH)_2$ with Ba granules or $Ba[N(SiMe_3)_2]_2(THF)_2$ gave the complexes $[BaZr_2(OPr^i)_{10}]_2$ (**87**) and $Ba[Zr_2(OPr^i)_9]_2$.[396] Hydrolysis of the latter gave the cluster $BaZr_4(OH)(OPr^i)_{17}$.[397,398] Increasing the steric demands of the alkoxide precluded large cluster formation providing instead $BaZr_2(OBu^t)_{10}$, $Ba_2Zr(OBu^t)_8(Bu^tOH)(THF)$, and $BaZr(OBu^t)_6(THF)_2$. These compounds were shown to serve as precursors to morphologically pure $BaZrO_3$ ceramics.[399] Interestingly, hydrolysis of $[BaZr(OBu^t)_6]_n$ with H_2O and isopropanol afforded $[BaZr(OH)(OPr^i)_5(Pr^iOH)_3]_2$.

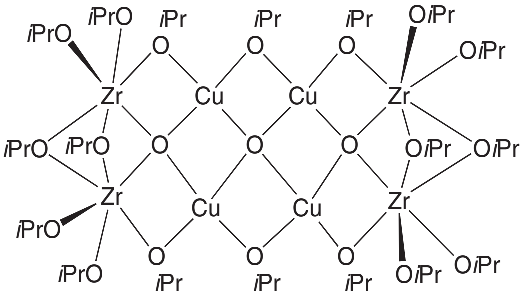
Reaction of the component metal alkoxides afforded the species $Tl_2Zr[OCH(CF_3)_2]_6$. X-ray data confirmed a hexacoordinate Zr center while the Tl atoms were coordinated to alkoxide O and F of the alkoxide substituents.[400] Variable-temperature ^{19}F and ^{205}Tl NMR spectroscopy indicated the F···Tl interactions persisted in solution although the structure was fluxional.

Employing metathesis methods, a series of other mixed-metal derivatives have been prepared. These included: $MXZr_2(OPr^i)_9$ and $M[Zr_2(OPr^i)_9]_2$; M = Cd (X = Cl,[401] I[402]), Mn (X = Cl, OPr^i, OBu^t),[403] Fe (X = Cl, OPr^i, OBu, OBu^t, MeCOCHCOMe),[404–406] Co (X = Cl, OMe, OPr, OPr^i, OBu, OBu^t,[407] MeCOCHCOMe[408]), Ni (X = Cl, OPr^i, OBu^t),[409] and Cu (X = Cl, MeCOCHCOR; R = Me, CF_3, $(CF_3CO)_2CH$, $OC_6H_3Me_2$, OC_6H_4Cl).[410–414] In addition, hydrolysis of $Cu_2Zr_2(OPr^i)_{10}$[410] afforded $Cu_4Zr_4O(OPr^i)_{18}$. Subsequent treatment with O_2 gave the Cu^{II} species $Cu_4Zr_4O_3(OPr^i)_{18}$ (**88**).[414,415]

Other oxo-containing aggregates have been characterized, including $Zr_2Co_4(\mu^6\text{-}O)(\mu^2\text{-}OPr^i)_8(OPr^i)_2(MeCOCHCOMe)_4$[416] and $FeZr_3O(OPr^i)_{10}(MeCOCHCOMe)_3$.[417] In both cases, the source of the oxide was not reported.



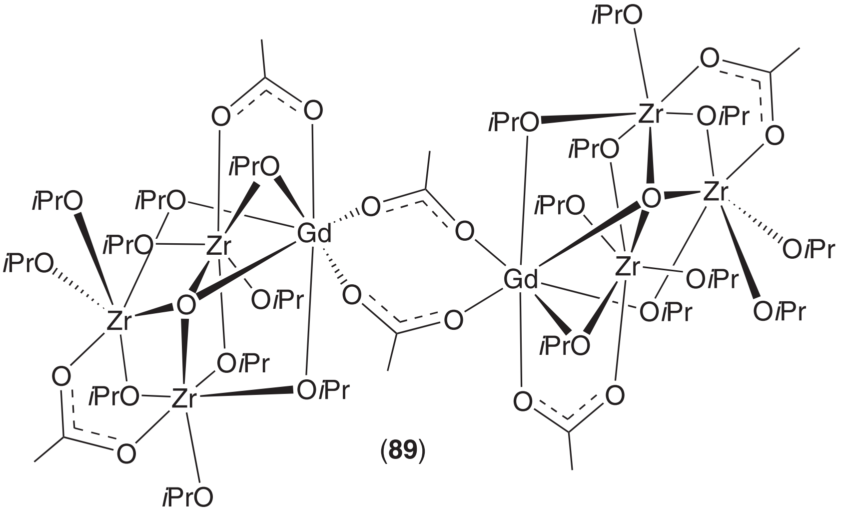
(**87**)



(**88**)

A collection of bimetallic compounds containing either Sn or Pb with Zr or Hf have been synthesized and their volatilities, thermal behavior, and aggregation tendencies have been summarized succinctly.[418] The Sn derivatives included $SnXM_2(OPr^i)_9$ (M = Zr, Hf; X = Cl,[419,420] Cp[420]), $SnI[Zr_2(OPr^i)_9]_2$,[421] $SnI_3Zr(OPr^i)_5(Pr^iOH)$,[422] and $Sn[M_2(OPr^i)_9]_n(OR)_{4-n}$ (n = 1–3, R = Pr^i, Bu^t).[423] X-ray data confirmed the monomeric nature of $SnCpM_2(OPr^i)_9$ and revealed that the species $[SnClM_2(OPr^i)_9]_2$ was in fact dimeric. Further reaction of $[SnClM_2(OPr^i)_9]_2$ with $SnCl_2$ gave the salt $[SnZr_2(OPr^i)_9]$ $[SnCl_3]$.[424] The simpler bimetallic species $MZr(OBu^t)_6$ (M = Sn, Pb) were prepared via the reaction of constituent alkoxides. Use of the smaller alkoxide afforded $Pb_4Zr_2(OPr^i)_{16}$ and $Pb_2Zr_4(OPr^i)_{20}$.[425–427] Subsequent work described a related product formulated as Pb_3ZrO $(OPr^i)_8$.[428–430] Use of these materials in chemical vapor deposition (CVD) gave crystalline lead metal deposits mixed with amorphous ZrO_2.[430]

The $[Zr_2(OPr^i)_9]^-$ anion has also been used to bind lanthanide halides.[431] A series of derivatives including $LnX_2[Zr_2(OPr^i)_9]$ (X = Cl, Ln = Er, Yb; X = I, Ln = Tm), $[Ln(\mu\text{-}I)Zr_2(OPr^i)_9]_2$ (Ln = Sm, Eu, Yb) and $[LnCl(\mu\text{-}Cl)Zr_2(OPr^i)_9]_2$ (Ln = Ce, Nd, Ho) have been prepared from the reaction of the appropriate LaX_3 with $KZr_2(OPr^i)_9$.[432,433] Analogous reactions in the presence of carboxylic acid salts gave $[Nd(\mu\text{-}Cl)(O_2CBu^t)Zr_2(OPr^i)_9]_2$[432] and $Zr_2(OPr^i)_4[Co(CO)_9(CCO_2)_2]$ $[Co_3(CO)_9(CCO_2)]$.[434] Alternatively, reaction of $Gd(O_2CMe)_3$ and $Zr_2(OPr^i)_8(Pr^iOH)_2$ afforded $Gd_2Zr_6(\mu^4\text{-}O)_2(\mu\text{-}O_2CMe)_6(\mu\text{-}OPr^i)_{10}(OPr^i)_{10}$ (**89**).[162,435]

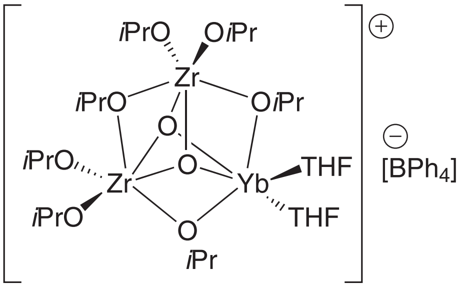


(**89**)

Reaction of $[Sm(\mu\text{-}I)Zr_2(OPr^i)_9]_2$ with $K_2C_8H_8$ afforded the related lanthanide species $Sm(C_8H_8)Zr_2(OPr^i)_9$,[436] while reaction of $[Yb(\mu\text{-}I)Zr_2(OPr^i)_9]_2$ with the appropriate amide gave $YbN(SiMe_3)_2Zr_2(OPr^i)_9$. Subsequent protonolysis gave the salt $[Yb(THF)_2Zr_2(OPr^i)_9][BPh_4]$ (**90**).[437] This and other work has lead to the comparison between the anion $[Zr_2(OPr^i)_9]^-$ and the Cp-ligand.

Early reports have described species of formulation $M[Al(OBu^t)_4]M'_2(OPr^i)_9$ (M = Fe,[438] Ni,[409] Co;[439] M′ = Zr, Hf) although none were characterized crystallographically. Complexes containing

Zr (or Hf), Ba, and Cd represented by $[Cd(OPr^i)_3BaM_2(OPr^i)_9]_2$ (M = Zr, Hf) were derived from the reaction of $XCd[M_2(OPr^i)_9]$[401,402] with $KBa(OPr^i)_3$.[402,440,441] The related Sr-containing species $Cd(OPr^i)_3Sr[M_2(OPr^i)_9]_2$ were obtained and characterized from the reaction of $ICdM_2(OPr^i)_9$ with $KSr(OPr^i)_3$.[442,443]



(**90**)

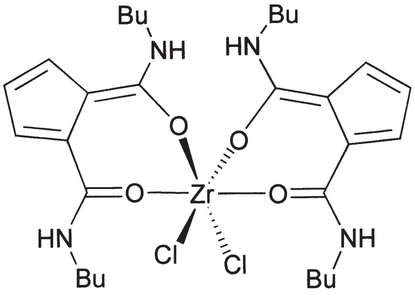
4.3.2.6.6 Diketonate ligand complexes

Acetylacetonate complexes have been studied at length and the previous issue of (*CCC*, 1987) summarized a vast number of derivatives. Since then, the homoleptic compounds $M(CF_3COCHCOMe)_4$ (M = Zr, Hf)[444] and $Zr(CF_3COCHCOCF_3)_4$[445] were prepared by metathesis. X-ray structural data for the latter compound confirmed an eight-coordinate geometry while electron diffraction has revealed D_2 symmetry in the gas phase.[446] The kinetics and mechanism of exchange of M(MeCOCH COMe)$_4$ (M = Zr, Hf) with free acetylacetone has been determined to proceed via a nine-coordinate intermediate.[447,448] The related *tris*-substituted complexes $ZrClL_3$ (L = $Bu^tCOCHCOBu^t$,[449] PhCOCHCOPh[450]) have also been characterized crystallographically, confirming a seven-coordinate, capped octahedral geometry. Contemporary investigations have utilized $Zr(MeCOCHCOMe)_4$ to effect copolymerization of biodegradable polymers,[451] as co-catalysts for the synthesis of poly(butylene terephthalate)[452] and polyurethanes[453] and to effect terpenic alkene epoxidation.[454] In addition, incorporation of long-chain substituents in $Zr(RCOCHCOR)_4$ complexes resulted in liquid crystalline materials.[455]

Numerous additional derivatives containing β-diketonate ligands have been prepared to compliment the already sizable inventory. Typically, syntheses involved the *in situ* generation of acetylacetonate anions and subsequent reaction with a metal halide precursor.[456] In this manner, β-diketonate ligands incorporating heterocyclic substituents have been employed to prepare Zr complexes.[457,458] In an unusual example, reaction of $MCl(MeCOCHCOMe)_3$ (M = Zr, Hf) with $NaCo(CO)_4$ gave $M(MeCOCHCOMe)_3[OCCo_3(CO)_9]$ (M = Zr, Hf).[459] The X-ray structure of this species confirmed the anticipated seven-coordinate geometry of Zr. An alternative synthetic strategy has exploited ligand exchange. For example, reaction of $Zr(PhCOCHCOMe)_4$ or $M(OR)_4$ (R = Pr, Bu^t) was used to prepare $Zr(PhCOCHCOMe)_n(OR)_{4-n}$ ($n = 2, 3$).[460] Protonolysis of acetylacetonate or alkoxide ligands was also used to prepare a variety of derivatives including $Zr(MeCOCHCOMe)_3[HB(3,5\text{-}Me_2C_3HN_2)_3]$,[177] $M_2(OPr^i)_6(Bu^tCOCHCOBu^t)_2$ (M = Zr, Hf),[461] $Zr(MeCOCHCOMe)_3(OC_6H_4NO_2)$, and $[Zr(MeCOCHCOMe)_3(OC_6H_4O)]_2$.[462] In a similar manner, reactions of catechol derivatives have yielded $Zr_3(MeCOCHCOMe)_4(O_2C_6H_4)(MeOH)_2$, $[Zr(MeCOCHCOMe)_2(O_2\text{-}3,5\text{-}Bu^t{}_2C_6H_2)]_2$, and the corresponding hydrolysis product $Zr_4(\mu^4\text{-}O)(MeCOCHCOMe)_4(O_2\text{-}3,5\text{-}Bu^t{}_2C_6H_2)_3(OMe)_4(MeOH)$.[463]

Activation of $ZrCl_2(MeCOCHCOMe)_2$ by MAO in the presence of alkenes gave an assortment of polymer products, including high molecular weight polyethylene[456] and syndiotactic $(PhCHCH_2)_n$.[464] In more recent work, an improved synthesis of $ZrCl_2$ $(MeCOCHCOMe)_2$ and its use as a catalyst precursor for the production of elastomeric $(MeCHCH_2)_n$ was reported.[465]

Complexes of a related anionic bidentate di-carboxamido-cyclopentadienyl ligand, $ZrCl_3[C_5H_3(CONHBu^t)_2](THF)$ and $ZrCl_2[C_5H_3(CONHBu^t)_2]_2$ (**91**) have also been described. This ligand chelates to Zr via the carbonyl O-atoms in a manner similar to diketonates. Structural data were consistent with π-delocalization of electron density in the ligand.[466]



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4.3.2.6.7 Keto-alkoxide bidentate ligand complexes

Chelating keto-alkoxide ligands complexes of dihydroxy-benzoquinone[467] and methylenebis(salicylaldehyde)[32] have been reported, although these compounds were poorly characterized. Subsequent studies have described the salicylaldehyde derivatives $ZrCl_3[OC_6H_23\text{-}Bu^t\text{-}5\text{-}Me(CHO)](THF)$ and $ZrCl_2[OC_6H_23\text{-}Bu^t\text{-}5\text{-}Me(CHO)]_2$.[468] In a related system, the keto-alkoxide adducts were thought to be intermediates in the Lewis acid catalysis of Diels-Alder cyclizations.[469] In a recent report, the compound $Zr(OPr^i)_2[(OC_6H_23\text{-}Bu^t\text{-}5\text{-}Me)C(Ph)O]_2$ was successfully employed as a Lewis acid catalyst for asymmetric allylations.[470]

A related ligand complex, $ZrCl_2[(OC_{10}H_6)(OPPh_2C_{10}H_6)]_2$ was derived from the monophosphine-oxide derivative of binaphthol. NMR and X-ray crystallographic data suggested an all-*cis* arrangement of the ligands.[471]

4.3.2.6.8 Carboxylate, carbamate, and oxylate ligand complexes

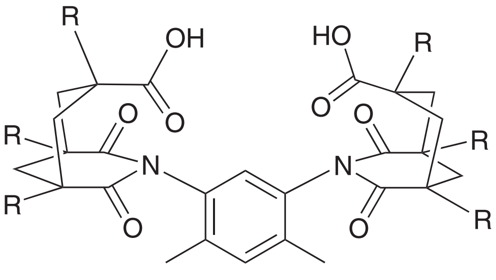
Carboxylate ligand complexes $Zr(OPr^i)_{4-n}(O_2CR)_n$ ($n = 1$–3) and $ZrCl_2(O_2CR)_2$ that have substituents comprised of heterocycles[472,473] or Schiff-base units[474] have been reported. Homoleptic Zr-carboxylates such as $Zr(CHBr_2CO_2)_4$ and $Zr(CBr_3CO_2)_4$ were obtained from the reaction of the appropriate acid with $ZrCl_4$ in the presence of base.[475,476] A variety of other carboxylate complexes have been reported, including: $Zr(O_2CMe)_2(SO_3F)_2$, $Zr(O_2CMe)_3(SO_3F)$,[477] $Zr(OMe)_2(O_2CCF_3)_2$, $Zr(O_2CCF_3)_4$,[478] $Zr_2O(OH)_5(O_2CC_6H_4NO_2)$, and $Zr_2O(OH)_4(O_2CC_6H_4NO_2)_2$,[479] as well as a series of heptafluorobutyric acid derivatives including $ZrF_2(C_3F_7CO_2)_2$,[480] the clusters $Zr_4(C_3F_7CO_2)_8(OH)_8$ and $Zr_4(C_3F_7CO_2)_{10}(OH)_6$, and the mixed-valent species $Zr_8(C_3F_7CO_2)_{14}(OH)_{16}$.[481,482] Although these formulations were not confirmed crystallographically, it is of interest to note that the formation of $ZrF_2(C_3F_7CO_2)_2$ implied C—F bond activation.[480]

Complexes incorporating a constrained bis-carboxylate ligand, $ZrX_2(XDK)$ ($X = Bn$, NMe_2; XDK = *m*-xylylenediamine bis(Kemp's triacid imide)) and $Zr(XDK)_2$ have been synthesized and characterized structurally. This ligand was derived from Kemp's tri-acid imide derivative of *m*-xylylenediamine (**92**) and shown to chelate through the two carboxylic acid fragments.[483]

The methacrylic acid derivatives $Zr(OPr^n)_3[O_2CC(Me)CH_2]$ and $Zr(OPr^n)_2[O_2CC(Me)CH_2]_2$ have been prepared and the subsequent hydrolysis products $[Zr_3O_3(OH)(OPr^n)_2\{O_2CC(Me)CH_2\}_3]_n$ and $[ZrO\{O_2CC(Me)CH_2\}_2]_n$ were characterized.[484] A closely related Zr complex $Zr(OPr)_3(O_2CCHCH_2)$ was prepared and functionalized by addition of $HPPh_2$ to the pendant alkene to give $Zr(OPr)_3(O_2CCH_2CH_2PPh_2)$ (**93**).[485] Alternatively, this species was obtained via reaction of $Zr(OPr)_3(O_2CCH_2CH_2Cl)$ with $LiPPh_2$. NMR data indicated that there was no significant interaction between the tethered phosphine and Zr.

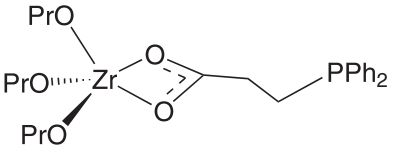
The propensity of carboxylates for bridging was demonstrated in the crystal structures of $Zr_6(OH)_8(OMe)_4(O_2CCHPh_2)_{12}$[486] and $Zr_6O_6(OH)_2(O_2CCHPh_2)_{10}(C_{14}H_8N_2)$.[487] Similarly, bridging ligands were observed in $[Zr_2(\mu\text{-}OH)_2\{\mu\text{-}CpMo(CO)_2Co_2(CO)_6(\mu^3\text{-}CCO_2)\}_2\text{-}\{\eta^2\text{-}CpMo(CO)_2Co_2(CO)_6(\mu^3\text{-}CCO_2)\}_4]$,[488] $[PbZr_2(\mu\text{-}O)(O_2CMe)_2(OCH_2Me)_6]_2$,[489] and

$Fe_2Zr_2(\mu^3\text{-}O)_2(O_2CPh)_6(OBu^t)_4(NC_5H_5)_2$.[490] The latter cluster was studied as a potential precursor for the deposition of metal-oxide films.[343]



R = Me, C_3H_7, Bn, CH_2OH

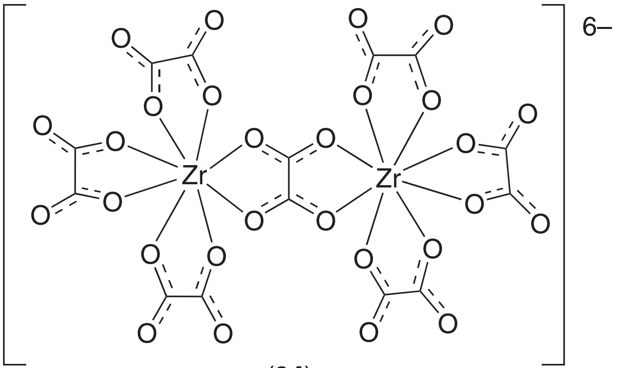
(92)



(93)

Carbamate complexes of the formula $M(O_2CNR_2)_4$ (M = Zr, Hf; R = Et,[445] Pr^i[491]) have been prepared by reaction of the $M(NR_2)_4$ with CO_2. Crystallographic studies have confirmed eight-coordinate geometry about Zr or Hf.

Several well-characterized Zr oxalate complexes have been reported recently, including $[K_2\{Zr(C_2O_4)_3\}H_2C_2O_4H_2O]_n$,[492] $K_6[\{Zr(C_2O_4)_3\}_2(\mu\text{-}C_2O_4)]$ (**94**),[493] and $Na_6[ZrOH(C_2O_4)_3]$.[494] All of these species were crystallized from reactions of $ZrOCl_2{\cdot}8H_2O$ with oxalic acid, potassium oxalate, or oxalic acid 2-hydrate in the presence of base. The oxalate ligand displayed both bidentate and bridging coordination modes.

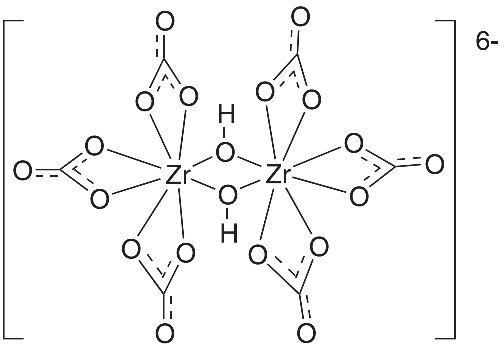


(94)

4.3.2.6.9 *Carbonate complexes*

Interest in Zr carbonates in part originates from their presence in nuclear waste.[495] Equilibrium constants for the formation of $[M(CO_3)_4]^{4-}$ have been measured,[496] and the coordination mode and kinetic behavior have been determined by dynamic NMR and Raman polarization studies.[495] The interactions of carbonate ions with Zr has been investigated by potentiometry, NMR spectroscopy,[497] and electrospray mass spectrometry.[498] Although four-coordination modes are possible, the data suggested a bidentate binding mode for the carbonates in $[Zr(CO_3)_4]^{4-}$.

The Zr carbonate complex $[C(NH_2)_3]_6[Zr(\mu\text{-}OH)(CO_3)_3]_2$ (**95**)[494] has been previously reported, however it has only been recently characterized crystallographically. The related derivative $[CN_3H_6]_2[Zr\{(O_2CCH_2)_2NCH_2\}_2CO_3]$[499] has also been characterized crystallographically. These structures revealed a bidentate binding mode of the carbonate ligands and formally eight-coordinate Zr metal centers.



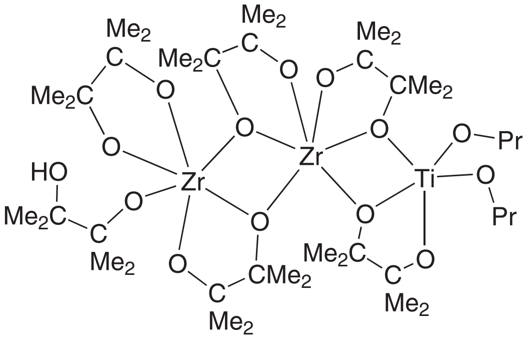
(**95**)

4.3.2.6.10 *Bidentate alkoxide ligand complexes*

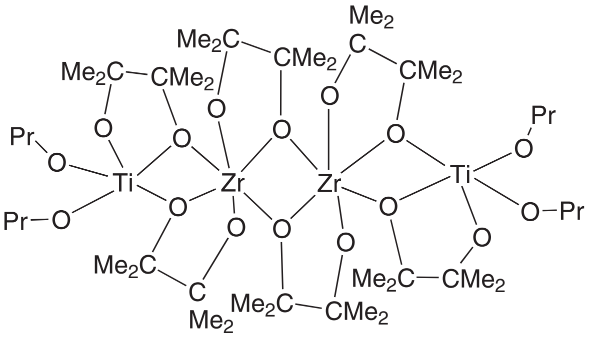
Typical metathesis, protonolysis, or alkoxide exchange methods have been used to obtain complexes containing dianionic O-ligands. For example, $MCl_2(O_2C_6H_4)$ (M = Zr, Hf),[500] $ZrMe_2(O_2C_6X_4)$ (X = H, Cl),[381] $Zr(NMe_2)_2[(OC_6H_2MeBu^t)_2CH_2]_2$, and $Zr_2[(OC_6H_2MeBu^t)_2CH_2]_2[(\mu\text{-}OC_6H_2MeBu^t)_2CH_2]$[501] have been prepared and characterized structurally. Partial hydrolysis of a related species afforded the cluster $Zr_3(\mu^3\text{-}O)$ $(OMe_2CCH_2CMe_2O)_4(HOMe_2CCH_2CMe_2O)_2$.[502] A related derivative of ethanediolate of the proposed formulation $[Zr(OCH_2CH_2O)(\eta^2\text{-}OCH_2CH_2O)(ROH)_2]_2$ (R = Pr, Bu) has been incorporated into hybrid materials that exhibited remarkable thermal stability.[503]

Another example of bidentate diphenoxide binding was demonstrated by the metallation of calix-4-resorcinarenes with zirconocene fragments. The resulting organometallic product contained four Zr atoms, each bound to the phenolate groups in a bidentate fashion.[504]

Ti has been incorporated into a Zr-pinacolate complex, affording the products $TiZr_2(OCMe_2CMe_2O)_4(OCMe_2CMe_2OH)_2(OPr^i)_2$ (**96**) and $Ti_2Zr_2(OCMe_2CMe_2O)_6(OPr^i)_4$ (**97**). Both of these species were characterized crystallographically, confirming that the pinacolate ligands acted in either terminal chelating or bridging fashion.[505] In a related system, two-dimensional diphenolate bridged networks were obtained from the reaction of $Zr(OEt)_4$ with $1,4\text{-}(HO)_2C_6H_4$ in the presence of base. The products were comprised of interpenetrating sheets, providing a dense material that precluded intercalation of simple aromatic hydrocarbons.[506] The related diolate complexes $Zr(OBu^t)_2(OCR_2CH_2CH_2CR_2O)$ (R = Me, Ph) have been used in the catalysis of the formation of β-cyanohydrins.[507]



(**96**)



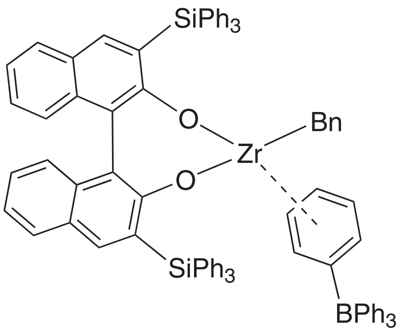
(**97**)

The binaphtholate and biphenolate complexes $ZrX_2(OC_{10}H_5SiR_3)_2$ (X = Cl, Bn, CH_2SiMe_3, $R_3 = Me_3$, $MePh_2$, Ph_3), $ZrX_2(OC_6H_2MeBu^t)_2$, and $ZrCl_2(THF)_2(OC_6H_2Bu^t{}_2)_2$ have been used as catalysts for polymerization. The species $[ZrBn(OC_{10}H_5SiPh_3)_2]$ $[BPh_4]$(**98**) and $ZrBn(OC_{10}H_5SiPh_3)_2(\eta^6\text{-}CH_2PhB(C_6F_5)_3)$ were made by treatment of the precursor with $[PhNMe_2H]$ $[BPh_4]$ and $B(C_6F_5)_3$, respectively. Upon activation with Al co-catalysts, the products served as active catalysts for the oligomerization of α-alkenes and butadiene, and for the catalytic cyclotrimerization of terminal alkynes. Steric modifications of the ligands exerted influence over the tacticity of poly(1-hexene).[508]

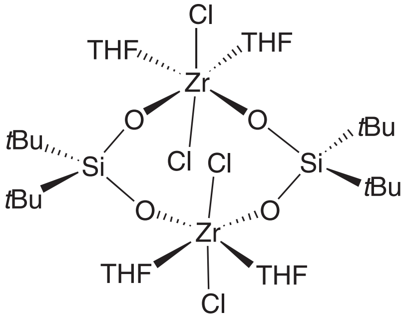
Complexes of a variety of binaphtholate derivatives of general formulas $Zr(OR)_2(OC_{10}H_5R)_2$, $Zr[(OC_{10}H_5R)_2]_2L_2$ (R = H, Br, Cl; L = donor),[470] and $Zr(OBu^t)_2(OPhBrC_{10}H_5)_2$[509] have been prepared. The chirality of these binaphthol derivatives has prompted applications as catalysts for enantioselective organic transformations. These included alkylation of aldehydes,[510] Mannich-type reactions,[511–513] allylation of imines,[514–517] aza-Diels-Alder reactions,[509,518] asymmetric prop-2-ynylation,[519] aldol reactions,[520,521] and alkene polymerization.[508,522,523]

4.3.2.6.11 *Disiloxane ligand complexes*

Bidentate siloxane ligands were used to prepare the octahedral complexes $Li_2[M(OSiPh_2OSiPh_2O)_3]$ (M = Zr,[524] Hf[525]). The related expanded chelate complex $Hf(OSiPh_2OSiPh_2OSiPh_2O)_2(C_5H_5N)_2$ was derived from the reaction of $Na_2[(OSiPh_2)_2O]$ with $HfCl_4$.[526] The related ligand $Bu^t{}_2Si(OH)_2$ reacted with $MCl_4(THF)_2$ to give $[MCl_2(O_2SiBu^t{}_2)(THF)_2]_2$ (M = Zr (**99**),[527] Hf[528]), which contained an eight-membered ring and octahedral metal centers.

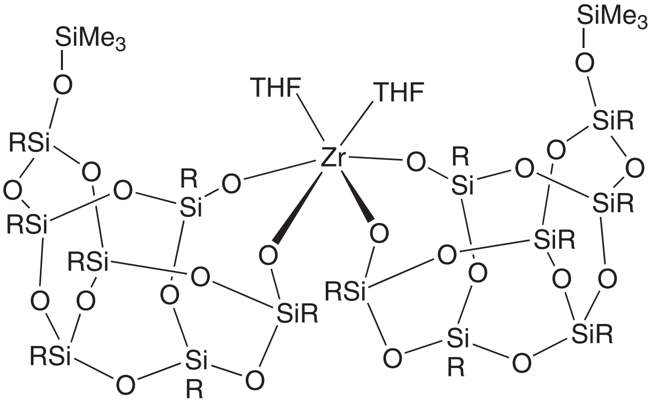


(**98**)



(**99**)

Monosubstituted silsesquioxane ligands also acted as bidentate dianionic ligands as in the complexes $Zr(THF)_2[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2$ (**100**), $Zr[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)]_2$, and $ZrCl_2[(c\text{-}C_5H_9)_7Si_7O_{11}(OSiMe_3)](THF)_2$.[529] In a related study of alumina-bound alkoxy Zr complexes, spectroscopy suggested bonding to the surface occurred in a bidentate fashion.[530,531]



(**100**)

The organometallic complexes of $(C_6H_3Pr^i{}_2)N(SiMe_3)Si(OH)_3$ such as $[ZrCp_2\{O_2Si\ (OH)NC_6H_3\text{-}Pr^i{}_2(SiMe_3)\}]_2$, in which the siloxane acted as a bidendate ligand have been reported.[532] However, no simple coordination compounds of this ligand have been reported to date.

4.3.2.6.12 Nitrate and sulfate ligand complexes

N-donor adducts of Zr-nitrate, $Zr(O)(NO_3)_2L_2$ have been reported.[533] The product of the reaction of N_2O_5 with $ZrCl_4$, $NO_2(NO)_3[Zr(NO_3)_5]_4$, has also been characterized, revealing both bidentate and monodentate coordination of the nitrate groups to Zr.[534]

The Zr-chlorosulfate and fluorosulfate complexes, $Zr(SO_3Cl)_4$, $Zr(SO_3Cl)_4L$, $Zr(O)(SO_3Cl)_2L$ (L = pyridine, pyridine *N*-oxide, phenanthroline), $Zr(O)(SO_3Cl)_2$,[535] $Zr(OH)_2(CF_3SO_3)_2$-$(H_2O)_4$,[536] $Zr(SO_3F)_4$, $Zr(O)(SO_3F)_2$, $Zr(O_2CMe)_2(SO_3F)_2$, $Zr(O_2CMe)_3$ (SO_3F), and $Zr(OMe)_2(O_3SCF_3)_2$[477] have been detailed. Although no X-ray structural data has been reported, IR spectroscopy suggested the chlorosulfate ligands were bridging. An improved synthetic route to a number of these species has been described employing the reaction of $Zr(OR)_4$ (R = Me, Et) with the corresponding anhyrides.[478] Two sulfate complexes, $[Zr(H_3O)_2(SO_4)_3]_\alpha$ and $[Zr(OPr)(O_3SMe)_3]_\alpha$, have been characterized crystallographically, and both form infinite arrays in the solid state.[537,538] In the former, three distinct SO_4 polyhedra and distorted ZrO_7 polyhedra are connected via common corners and edges, with the layers connected by H_3O^+ ions. In the latter species, sulfate groups adopted both bridging and bidentate coordination modes.

4.3.2.6.13 Phosphate and phosphonate ligand complexes

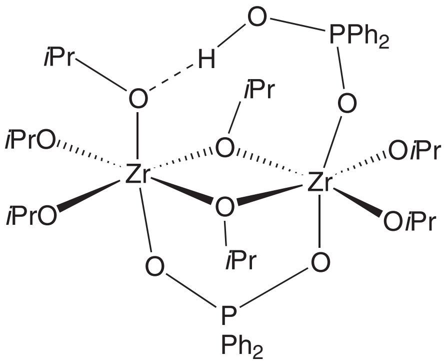
$Li[Zr_2(PO_4)_3]$ has been prepared, although the nature of phosphate binding is not clear.[539] The related complex $Zr(PO_4)F(OSMe_2)$ adopted a layered structure in the solid state and the phosphate was found to bridge four Zr centers.[540] The related derivatives $MH_2(PO_3E)_2$ (M = Zr, E = Se;[541] M = Zr, Hf, E = S[542]) have also been described. Edwards *et al.* have detailed the syntheses of the complexes $Zr(NO_3)_2[O_2P(OBu)_2]_2$ and $Zr(NO_3)_2[O_2P(OBu)_2]_2[OP(OH)(OBu)_2]_4$, which were proposed to contain eight-coordinate Zr centers.[543] The related phosphonate ligand $Ph_2P(O)(OH)$ was used in the synthesis of the species $M(OPr^i)_3(\mu\text{-}OPr^i)_2(\mu\text{-}O_2PPh_2)M(OPr^i)_2Ph_2\text{-}P(O)(OH)$ (M = Zr, Hf) (**101**).[544] Crystallographic data revealed that the phosphonate acted as both a bridging and terminal bidentate ligand.

Zirconium phosphate derivatives have been investigated for a number of applications. Thiophosphate derivatives,[542] as well as $[PhNH_3]_2[Zr(PO_4)_3]$,[545] have been employed as ion-exchange media. Similarly, a variety of materials derived from pillared Zr phosphates offered promise as selective ion-exchange materials.[546–549]

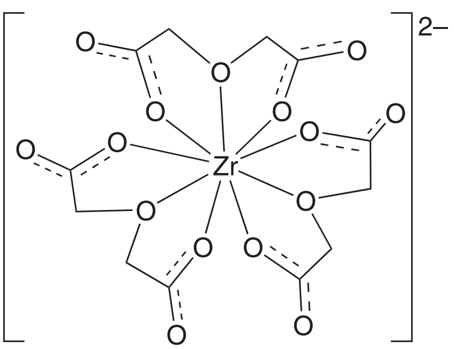
Zr phosphates and phosphites have played a variety of roles in organic transformations, acting as a catalyst support media,[550] as heterogeneous catalysts for tetrahydropyranylation of alcohols and phenols,[551] and as catalysts for the hydrolysis of phosphodiester compounds.[552–556]

4.3.2.6.14 Dianionic tridentate ligand complexes

Complexes of the dianionic tridentate ligand, oxydiacetic acid have been recently reported. The eight-coordinate Zr center in $Zr[(O_2CCH_2)_2O]_2(H_2O)_2$[557] has been confirmed crystallographically. The oxydiacetato ligands acted in a tridentate fashion. More recent work has described related oxydiacetic acid complexes $[Zr\{(O_2CCH_2)_2O\}]^{2+}$, $Zr[(O_2CCH_2)_2O]_2$, and $[Zr\{(O_2CCH_2)_2O\}_3]^{2-}$ (**102**) which exist in equilibrium. The nine-coordinate nature of the last dianion has also been characterized crystallographically.[558]



(**101**)

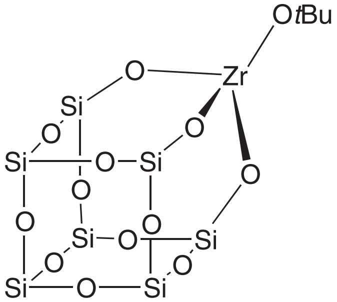


(**102**)

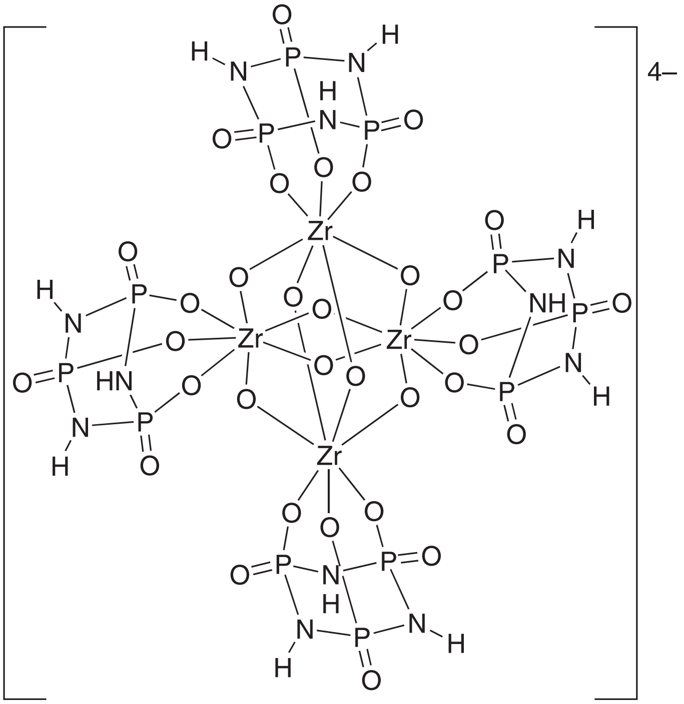
4.3.2.6.15 Trianionic tridentate ligand complexes

Few tridentate O-ligand complexes have been reported. Feher *et al.* originally developed organometallic Zr–silsesquioxane complexes which served as a model for silica-supported catalysts.[559] More recently, the coordination complexes $(MBn\{(c\text{-}C_5H_9)_7Si_7O_{12}\}_2)_2$ (M = Zr, Hf) have been reported by Duchateau *et al.* These species were effective catalysts for the polymerization of C_2H_4 when activated with $B(C_6F_5)_3$ and were considered as soluble models for silica-supported catalysts. In addition, the inorganic derivative $Zr(OBu^t)[(c\text{-}C_6H_{11})_7Si_7O_{12}]$ (**103**) has been synthesized and shown to exist as monomer–dimer equilibrium in solution.[560] In contrast to the Ti analog, this species exhibited minimal activity for the decomposition of Bu^tO_2H. This was attributed to the lower Lewis acidity of Zr.

A unique tridentate trianionic ligand derived from trimetaphosphimic acid has been reported. Reaction with $MOCl_2(H_2O)_8$ (M = Zr, Hf) gave the isotypic complexes $Na_4[M_4(\mu^4\text{-}O)(\mu\text{-}OH)_6(PO_2NH)_3]_4$ (M = Zr (**104**), Hf). These clusters adopted an adamantanoid M—O cage where the trimetaphosphimato ligand chelated each of the metal centers of the $[M_4(\mu^4\text{-}O)(\mu\text{-}OH)_6]^{8+}$ core.[561]



(**103**)



(**104**)

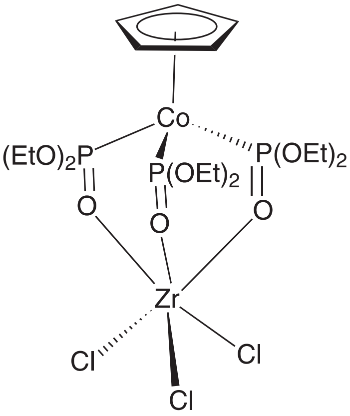
Zr and Hf nitrilotriacetate complexes have been prepared via addition of the neutral ligand to mixtures of $MOCl_2(H_2O)_8$ (M = Zr, Hf) and various alkali carbonates.[562] A series of these salts have been characterized crystallographically.[563–576] Typical of these structures was the species $[Me_2NH_2]_2[Zr\{N(CH_2CO_2)_3\}_2]$, in which the Zr center was coordinated to six O atoms of the two tridentate ligands.[576]

4.3.2.6.16 Monoanionic tripodal ligand complexes

The metal complexes $[CoCp(PR_2O)_3]^-$ (R = OEt, Et) have been used as a tripodal ligand to prepare complexes of the form $[Zr\{(OPR_2)_3CoCp\}_2][X]_2$ ($X = OSO_2C_6H_4Me$, Cl) and $ZrCl_3[\{OP(OEt)_2\}_3CoCp]$ (**105**).[577] In the reaction with $ZrCl_4(THF)_2$, the tripodal complex underwent an Arbuzov dealkylation to give the dimeric complex $Zr_2[\{OP(OEt)_2\}_2(O_2PR)\ CoCp]_4$, which contained seven-coordinate Zr centers. This dealkylation resulted in the formal conversion of the chelate to a dianionic ligand.

4.3.2.6.17 Trianionic tripodal ligand complexes

Two tripodal, O-donor ligands have been used to complex Zr. The ligand *tris*(hydroxymethylethane) produced $Zr_4[(OCH_2)_3CMe]_2(\mu\text{-}OPr^i)_2(OPr^i)_8$ (**106**). The central core consisted of a Zr_4O_8 ring, with eight O atoms supplied from two isopropoxide and two tripodal ligands.[578] This compound was used as a precursor to ceramic thin films which exhibited less macroscopic cracking and porosity relative to those derived from $Zr_2(OPr^i)_8(HOPr^i)_2$.



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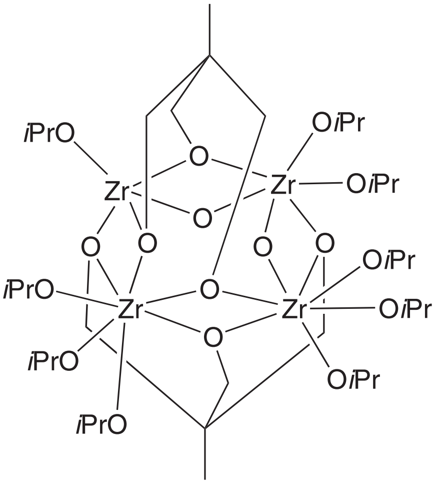
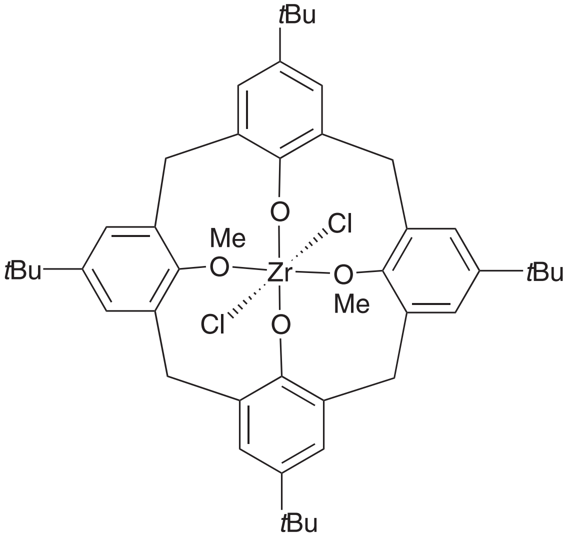


(**106**)

4.3.2.6.18 Dianionic tetradentate ligand complexes

Dimethylated calix-4-arenes have been used to prepare $ZrCl_2[OC_6H_2Bu^t(CH_2)]_2[MeOC_6H_2Bu^t\text{-}(CH_2)]_2$ (**107**).[579] The distortion of the structure from C_{2v} symmetry was addressed in a DFT study. The results suggested that packing effects were not the cause, but that the tethered calix-4-arene ligand imposed constraints on O—Zr—O bond angles.[580] Replacement of the metal chloride afforded a variety of dialkyl and alkyl-cation derivatives.[581] The corresponding butadiene derivative has also been prepared and its chemistry and bonding probed in detail.[582] Insertion reactions of the dialkyl derivatives with CO have been investigated via a theoretical study.[583]



(**107**)

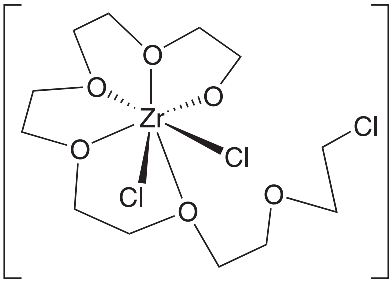
4.3.2.6.19 Trianionic tetradentate ligand complexes

A calix-8-arene complex, $[RNH_3][(ZrOPr^i)_2(Hcalix[8]arene)]$, has been synthesized. Although crystallographic data has only been obtained for the Ti analog, NMR data suggested that the Zr analog had a similar structure.[584,585]

The hydrolysis of dimethylated calix-4-arenes was used as a route to the trianionic monomethylated analog.[586] Complexation of this ligand by $ZrCl_4(THF)_2$ yielded a dimeric product formulated as $[ZrCl\{(OC_6H_2Bu^tCH_2)_3(MeOC_6H_2Bu^tCH_2)\}]_2$. Alternatively, the complex $ZrCl_2(OC_6H_2Bu^tCH_2)_2[MeOC_6H_2Bu^t(CH_2)]_2$ reacted with base, resulting in the loss of one of the ether methyl groups giving complexes containing a formally trianionic ligand as in the species $[MeNEt_3][ZrCl_2\{(OC_6H_2Bu^tCH_2)_3(MeOC_6H_2Bu^tCH_2)\}]$ or $Zr(O_3SCF_3)(C_5H_5N)(OC_6H_2Bu^tCH_2)_3(MeOC_6H_2Bu^tCH_2)$. Treatment of $ZrBn_2[(OC_6H_2Bu^tCH_2)_2(MeOC_6H_2Bu^tCH_2)_2]$ with base afforded $[ZrBn(OC_6H_2Bu^tCH_2)_3(MeOC_6H_2Bu^tCH_2)]_2$, with concurrent loss of EtC_6H_5.[586] In a related study, thiacalix-4-arenes were used to extract Zr or Hf from aqueous solution although the precise nature of the complexes was not determined.[587]

4.3.2.6.20 Higher denticity ligand complexes

Decyclization of 18-crown-6 with $ZrCl_4$ resulted in the isolation of a seven-coordinate Zr complex $[ZrCl_2\{O(CH_2CH_2O)_5CH_2CH_2Cl\}]$ $[ZrCl_5(THF)]$ (**108**).[588] In contrast, the analogous Hf reaction did not effect ring opening of the crown, yielding instead [Na(18-crown-6] $[HfCl_5(THF)]$.[589] Eight-coordinate Zr and Hf derivatives of the tetraanionic ligand ethylenedioxydiethylenedinitrilotetraacetic acid were synthesized from the reaction of $MOCl_2$ in NH_4OH solution.[590] The two compounds $M[(O_2CCH_2)_2NCH_2CH_2OCH_2]_2$ (M = Zr, Hf (**109**)) were found to be isostructural in the solid state, although NMR spectroscopy indicated that the Hf derivative had a higher degree of symmetry in solution.



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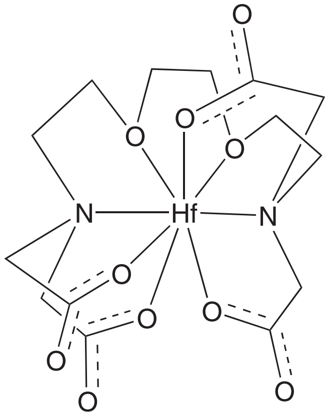


(**109**)

4.3.2.7 Sulfur, Selenium, and Tellerium Ligand Complexes

4.3.2.7.1 Neutral sulfur, selenium, and tellerium ligand complexes

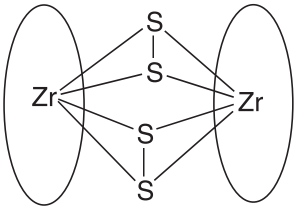
Metal halide adducts of S and Se of the general formula MCl_4L_2 (M = Zr, L = $SCNH_2Me$;[591] M = Zr, Hf; L = SMe_2, $SeMe_2$; M = Zr, L = SR_2, R = Et, Pr^i, Bu^{i316}) have been prepared in a straightforward manner. The relative stabilities of the *cis* vs. *trans* isomers of these complexes were examined in an NMR study.[316]

Accounts purporting the formation of disulfide adducts of $ZrOCl_2$ and $Zr(NO_3)_4$[592] or adducts of 2-thio-3-phenylquinazoline-4-one[593] have appeared, although the binding mode of these ligands was not confirmed unambiguously.

4.3.2.7.2 Sulfide, selenide, and telluride complexes

The S_2 bridged dimers $M_2(TPP)(\mu\text{-}\eta^2\text{-}X_2)_2$, were prepared via the reaction of $MCl_2(TPP)$ (M = Zr, Hf) with Li_2S_2 or Li_2Se_2. In these cases, the geometry of the M_2X_4 (X = S (**110**), Se) core was a distorted octahedron, with an unusual $M_2(\mu\text{-}\eta^2\text{-}X_2)_2$ core.[594] The reaction of the imido porphyrin derivatives $M(TTP)(NC_6H_3Pr^i{}_2)$ (M = Zr, Hf; TTP = *meso*-tetra-*p*-tolylporphyrinato) with Bu^tNCS or Bu^tNCSe generated $[Zr(TTP)(\mu\text{-}E)]_2$ (E = S, Se).[252]

Coucouvanis *et al.* have synthesized and characterized structurally Zr—S clusters. Reaction of $Zr(BH_4)_4$ with Bu^tSH resulted in the formation of $Zr_3(\mu\text{-}S)_3(SBu^t)_2(BH_4)_4(THF)_2$ and $Zr_6(\mu\text{-}S)_6(SBu^t)_4(BH_4)_8(THF)_2$.[595] The parallel reaction involving $ZrBn_4$ and Bu^tSH gave the species $Zr_3(\mu\text{-}S)(SBu^t)_{10}$ (**111**).[596,597] In each of these clusters the sulfide was derived via C—S cleavage.



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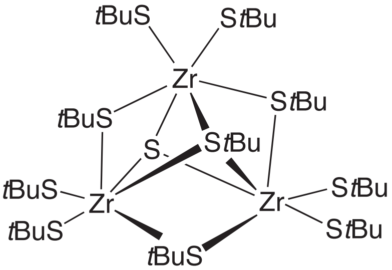
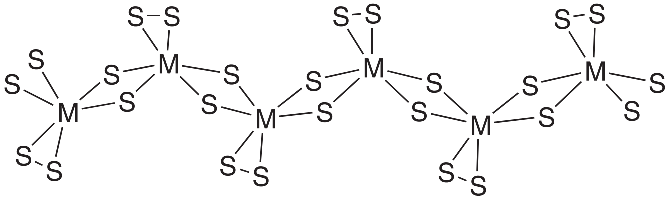


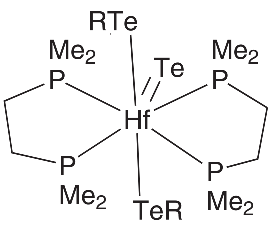
(**111**)

Recently, the crystal structures of Rb_2MS_4 (M = Zr, Hf) and K_2ZrS_4 have been determined showing an extended chain of S-bridged metal centers, with S_2 ligands bound to each metal center (**112**).[598] Gas phase experiments have also probed the interactions of Zr and Hf with S_8,[599] while Green *et al.* have investigated the intercalation of Mo organometallic species into ZrS_2.[600]



(**112**)

Treatment of the compound $M[TeSi(SiMe_3)_3]_4(Me_2PCH_2CH_2PMe_2)$ (M = Zr, Hf) with a second equivalent of phosphine prompted elimination of R_2Te and the formation of the terminal Te complex $MTe[TeSi(SiMe_3)_3]_2(Me_2PCH_2CH_2PMe_2)_2$ (**113**). Crystallographic data revealed Hf—Te and Zr—Te bond lengths of 2.637(2) Å and 2.650(1) Å, respectively.[601,602] Similarly, treatment of $M[SeSi(SiMe_3)_3]_4$ with phosphine prompted loss of R_2Se but gave $[M(\mu\text{-}Se)\{SeSi(SiMe_3)_3\}_2\text{-}(\mu\text{-}Me_2PCH_2CH_2PMe_2)_2]_2$ (**114**).



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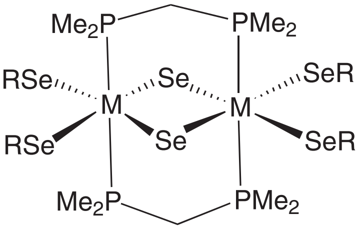


(**114**)

4.3.2.7.3 *Thiolato, selenolato, and tellurolato ligand complexes*

Reaction of $ZrBn_4$ with PhSH in the presence of BnMgCl afforded the disordered salt $[MgTHF_6][Zr_2(SPh)_{7.2}(Bn)_{1.8}]_2$.[597] The anion contains three bridging thiolate groups between the octahedral metal centers. Thiolate ligands have also been employed to replace the halides in OEP complexes. For example, the related dithiolate derivative $Hf(OEP)(1,2\text{-}S_2C_6H_4)$ has been reported.[603]

The homoleptic selenolate and tellurolate complexes $M[ESi(SiMe_3)_3]_4$ (M = Zr, Hf; E = Se, Te) were formed by straightforward protonolysis, yielding simple adducts with isocyanates. In addition, these species have been prepared via a salt metathesis reaction. The complexes $MBn[SeSi(SiMe_3)_3]_3$ were prepared in a similar manner with appropriate control of the stoichiometry.[602] Zr selenolate and tellurolate complexes with supporting benzamidinate ligands of the form $ZrCl[PhC(NSiMe_3)_2]_2ESi(SiMe_3)_3$ (E = Se, Te) were prepared via a metathesis route in moderate yields.[94]

Ferrocenyldithiol ligands have also been used to prepare $Zr(NMe_2)_2[(C_5H_4S)_2Fe]$ from $Zr(NMe_2)_4$.[604] Preliminary C_2H_4 polymerization experiments revealed that it was moderately active when activated with MAO.

4.3.2.7.4 *Dithiocarbamate and dithiophosphate ligand complexes*

Numerous reports describing the syntheses of complexes incorporating a variety of substituted monoanionic dithiocarbamate ligands of the form $MX_{4-n}(S_2CNR)_n$ ($n = 1$–4) and $MO(S_2CNR)_2$ have appeared.[605–613] NMR spectroscopic studies have determined the barriers to rotation about the C—N bond in $Zr(S_2CNPr^i{}_2)_4$.[614] A crystallographic study of $ZrCl_3(S_2CNMe_2)(C_5H_5N)_2$ confirmed the bidentate coordination mode of the dithiocarbamate ligand and the seven-coordinate nature of the Zr center.[615] One report proposed the formation of a heterobimetallic derivative in which a Schiff-base ligand bridges Cu and Zr-bis-dithiocarbamate fragments; however, this species was poorly characterized.[616]

Related dithiophosphate ligands have also been used to prepare complexes including as $ZrO[S_2P(OMe)_2]_2$,[617] $[Zr(OPr^i)_3(S_2PO_2R)]_2$,[618] and $ZrCl_{4-x}(S_2POR)_x$ ($x = 2$–4; R = CMe_2CMe_2, CHMeCHMe, $CH_2CMe_2CH_2$, $CH_2CEt_2CH_2$).[619]

A recent report has described the antifungal, antibacterial, and anticancer activity of a zirconyl-complex of the Schiff-base of *S*-benzyldithiocarbazate, although the exact nature of the product was not fully understood.[620]

4.3.2.7.5 *Selenocyanato complexes*

A series of adducts of $ZrO(SeCN)_2$ have been reported, however, the mode of coordination of the selenocyanate was not addressed.[621]

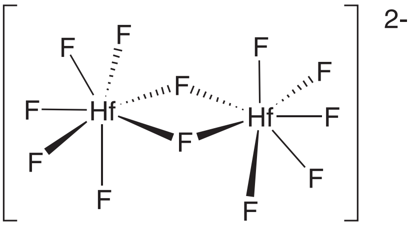
4.3.2.8 Halometallate Complexes

4.3.2.8.1 *Fluorometallate complexes*

A recent review has detailed stereochemical issues of Zr and Hf fluorometallate salts.[622] Synthetic advances in this domain focused mainly on the isolation of fluorometallate salts of N-based cations. The pyridinium salts of penta- and hexafluorozirconates, $[HNC_5H_5][ZrF_5]$ and $[HNC_5H_5]_2[Cu(NC_5H_5)_4][ZrF_6]_2$ have been reported.[623,624] Both are obtained from arduous synthetic procedures and were characterized by IR spectroscopy and crystallography. In the case of $[HNC_5H_5][ZrF_5]$, IR data were consistent with H-bonding between the cation–anion, which lowered the symmetry of the $[ZrF_5]^-$ ion in the crystal lattice. Alternatively, in $[HNC_5H_5]_2[Cu(NC_5H_5)_4][ZrF_6]_2$, the zirconate adopted an octahedral structure with coordination of one of the fluorine atoms to Cu^{II}, resulting in a comparatively long Zr—F bond. The electronic structure and solid-state vibrational transitions of $[ZrF_6]^{2-}$ have also been investigated at the SCF, MP2, and Becke3LYP levels of computational theory.[625]

In related work, the ammonium salts $[NH_4][MF_5]$ (M = Zr, Hf) have been prepared via oxidation of the metal with $[NH_4]$ $[HF_2]$, followed by pyrolysis in a sealed vessel.[626] Analysis of single crystals revealed that the structure is isotypic to $TlZrF_5$.

Mononuclear $[HfF_6]^{2-}$ and binuclear $[Hf_2F_{10}(H_2O)_2]^{2-}$ salts were isolated with a $[\{H_3N(CH_2)_3\}_2]^+$ counterion.[627,628] The $[HfF_6]^{2-}$ ion had an octahedral geometry, with all six F-atoms involved in H-bonding with ammonium centers of the counter ion. In contrast, $[Hf_2F_{10}(H_2O)_2]^{2-}$ adopted slightly distorted pentagonal bipyramidal coordination geometries with asymmetrically bridging F-atoms (**115**). In this species, H-bonding was also evident in the solid state between the cation and terminal F atoms and water molecules of the hafnate fragment. Recent solid-state VT-NMR studies of $[NH_4]_2[HfF_6]$, $Tl_2[HfF_6]$, and $[NH_4]Tl[HfF_6]$ have examined ionic mobility and the corresponding activation energies. In addition, the latter two salts underwent phase changes above 350 °C.[629]



(**115**)

4.3.2.8.2 *Chlorometallate complexes*

Monometallic chlorometallates are also well known. The anion $[ZrCl_5(THF)]^-$ was first characterized from the reaction of $ZrCl_4$ with 18-crown-6. This reaction resulted in C—O bond cleavage and the isolation of the species $[ZrCl_2(OCH_2CH_2)_5OCH_2CH_2Cl][ZrCl_5(THF)]$.[588] A mechanism for this reaction was proposed based on Lewis acid attack of the crown ether. Sobota *et al.* showed in the same year that the stoichiometry of the reaction of $ZrCl_4(THF)_2$ and $MgCl_2(THF)_2$ determined the formation of $[Mg(THF)_6][ZrCl_6]$ and $[Mg(THF)_6][ZrCl_5(THF)]_2$.[630] In a more straightforward synthesis, reaction of $ZrCl_4$(DAD) with HCl produced [DAD-H]$[ZrCl_5(THF)]$.[631] The analogous Li salt $[Li(THF)_4][ZrCl_5(THF)]$ was obtained from the reaction of $LiNPh_2$ with $ZrCl_4$ in THF. This species lost THF above −5 °C affording $[Li(THF)_3][ZrCl_5(THF)]$, which was stable at ambient temperatures.[632] In the former case where the Li atom was coordinatively saturated, the anion $[ZrCl_5(THF)]^-$ displayed only a slightly distorted octahedral geometry. However, in the latter cases where loss of THF has occurred, the Li coordination site was completed by a Zr—Cl interaction. A recent synthesis of the pentachlorozirconate derivative $[Ph_4P][ZrCl_5(NCMe)]$ from the reaction of $[Ph_4P]Cl$, acetonitrile, $ZrCl_4$, and S_2Cl_2 has also described by Rabe *et al.*[633]

In addition to the above pentachlorozirconates, hexachlorozirconates are also accessible. In earlier work conductiometric studies of SO_2Cl_2 solutions containing NH_4Cl and $ZrCl_4$ or $ZrOCl_2 \cdot 8H_2O$ suggested the presence of salts of both penta- and hexachlorozirconates.[634] Varying the protocols and stoichiometry resulted in the isolation of the species $[Me_4N][ZrCl_5]$ and $[Me_4N]_2[ZrCl_6]$.

The related complex, $[Ph_4P]_2[ZrCl_6]$ was isolated by combination of $[Ph_4P]Cl$ and $ZrCl_4$.[635] The related salt $[Ph_3PH]_2[ZrCl_6]$ was prepared from the reaction of $ZrCl_4$ with HCl, followed by exposure to $[Ph_3PH]Cl$.[636] This compound was seen to be remarkably resistant to decomposition, being destroyed only upon heating in H_2O. In 1996, Beck *et al.* reported the metallate $[SeCl_3]_2[MCl_6]$ (M = Zr, Hf) obtained from the reaction of the corresponding MCl_4 with $SeCl_4$.[637] Structural data showed that the metallate anion was very slightly distorted from octahedral symmetry, with each of the Cl atoms bridging to a $[SeCl_3]^+$ fragment, providing five-coordinate Se centers in the solid state. In subsequent work, reaction of $ZrCl_4(SeOCl_2)_2$ with $SOCl_2$ liberated SO_2, affording an alternate route to the chlorometallate salt $[SeCl_3]_2[ZrCl_6]$.[314]

As with the fluorometallates, dimeric chlorometallate salts are common. Reaction of $ZrCl_4$ with $(NSCl)_3$ afforded $[S_3N_3Cl_2]_2[Zr_2Cl_{10}]$. The crystallographic study of this species represented the first to confirm the dimeric nature of the dianion. In this salt, each Zr atom adopted a distorted octahedral geometry with two Cl atoms bridging the Zr centers.[638] The analogous salts $[Ph_3C]_2[M_2X_{10}]$ (M = Zr, X = Br; M = Hf, X = Cl, I) have been prepared from the reaction of excess Ph_3CX with the appropriate metal reagent $M(BH_4)_4$.[639] Crystallographic characterization of the Hf dianion $[Hf_2Cl_{10}]^{2-}$ confirmed the similarity to the Zr analog. In more recent studies, the related salts [bis(1,3,5-trimethoxyphenylium)] $[Zr_2Cl_{10}]$[640] and $[4\text{-Bu}^tPhCH_2PPh_2NH(SiMe_3)]_2[Zr_2Cl_{10}]$[28] were characterized.

Complex chlorometallates containing transition metal cations have also been prepared. The solvent dependence of interactions of *p* and *d*-block metals with Zr and Hf halides was reviewed.[641] In more recent studies, the compounds $[CoCp'_2][MCl_5(THF)]$ (Cp′ = Cp, Cp*; M = Zr, Hf) were synthesized by reaction of the metal tetrahalide with $CoCp_2Cl$ or $CoCp^*_2$.[642] The bimetallic Cu/Zr compound Cu_2ZrCl_6 was prepared by thermolysis of CuCl and $ZrCl_4$ at 450 °C. Heating this species in C_6H_6 afforded $Zr[(C_6H_6)CuCl_3]_2$, whereas reaction in the presence of $[H_2NMe_2]Cl$ gave $[H_2NMe_2][CuZrCl_6]$.[643,644] In these complexes, Cl atoms bridge the Cu and Zr. The solid-state structure of $Zr[(C_6H_6)CuCl_3]_2$ was analogous to corresponding phosphonate salt $Zr(O_3PR)_2$, whereas the structure of $[H_2NMe_2]Cu[ZrCl_6]$ was found to be analogous to that of $Zr(S_4P)_2$. The species $ZrCl_5(\mu\text{-N})ReCl(PMe_2Ph)_3(MeCN)$, in which a nitride bridged two metal centers, was derived from the reaction of $ZrCl_4$ with $ReNCl_2(PMe_2Ph)_3$.[645]

4.3.2.8.3 Mixed halide metallate complexes

Mixed halozirconates have also been reported. The species $[Na\text{-}15\text{-crown-}5]_2[ZrF_2Cl_4]$ was synthesized from the reaction of $[PhC(NSiMe_3)_2ZrCl_3]_2$ with NaF in the presence of 15-crown-5.[635] In this case, distortion from octahedral symmetry of the zirconate resulted from the interaction of the sodium ions with both F and Cl atoms of the anion.

4.3.2.9 Hydride and Borohydride Ligand Complexes

4.3.2.9.1 Hydride ligand complexes

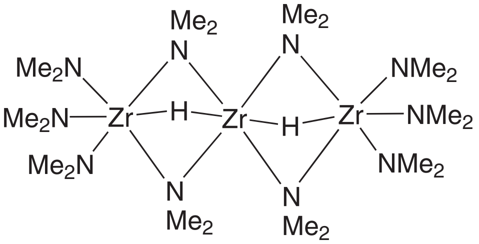
Significant progress in the domain of group IV metal-hydride complexes has been made in recent years. These have included a variety of theoretical and synthetic studies. Related but complex Zr—H clusters have been prepared and studied. These systems have been reviewed.[646–648]

Theoretical studies of simple homoleptic hydride derivatives MH_4 (M = Zr, Hf) have been addressed in an *ab initio* study. The rate of site exchange of the hydrogen atoms and the corresponding transition state energy in these species was interrupted by electrostatic interaction of the cationic metal center with a H_3^- fragment.[649] Theoretical studies have compared trends in bond energies, vibrational frequencies, metal-orbital hybridizations, and equilibrium geometries of ZrH^+ to those of other transition metal analogs.[650]

In synthetic efforts, hydrogenation of the transient imido complex $Zr(NSiBu^t_3)(NHSiBu^t_3)_2$ afforded the hydride $Zr(NHSiBu^t_3)_3H$.[82] In a subsequent study, the reaction of this hydride species and CO resulted in the isolation of $Zr(NHSiBu^t_3)_3(OCH)_2$. Mechanistic details were also investigated.[57] Related reactions of the amido-species $M(NMe_2)_4$ (M = Zr, Hf) with silanes, such as $SiPhH_3$, $SiPh_2H_2$, $SiPhMeH_2$, or $Si(NMe_2)Ph_2H$, gave the unusual trimer $M[(Me_2N)_3M(\mu\text{-H})(\mu\text{-NMe}_2)_2]_2$ (M = Zr, Hf) (**116**). Mechanistic studies that exploited isotope labeling with deuterium later confirmed the presence of an equilibrium between $Zr(NMe_2)_3Si(SiMe_3)_3$ and $SiPh_2H_2$ with $Zr(NMe_2)_2[Si(SiMe_3)_3]H$ and $Si(NMe_2)Ph_2H$. The implications of this chemistry with respect to the role of silanes in CVD of thin films of TiN from $Ti(NMe_2)_4$ was also considered.[19,651] Related tripodal amido ligands have been used to prepare the Zr—H species $[Zr(MeC_6H_4NSiMe_2)_3CH(\mu\text{-H})]_2$. The bridging nature of the hydrides was affirmed by a crystallographic study.[200] Recent advances in Zr porphyrinogen–hydride chemistry have been discussed above (see Section 4.3.2.4.17)

Fryzuk's group has also prepared and characterized the Hf-hydride compound, $[HfCl_2N(SiMe_2CH_2PMe_2)_2]_2(\mu\text{-H})_2$.[652] Using a related tridentate ligand, addition of the phosphide ligand to $ZrCl_4$ followed by exposure to Al_2Me_6 afforded $Zr_2Cl_4(\mu\text{-Cl})(\mu\text{-H})[P(CH_2CH_2PMe_2)_2]_2$. Although this species was isolated in low yield, it was characterized structurally.[288]

In ground-breaking work, Fryzuk *et al.* have developed related chemistry employing macrocyclic ligands. Interaction of molecular hydrogen or primary silanes with the N_2 complex $[Zr(P_2N_2)]_2(\mu\text{-}\eta^2\text{-}N_2)$ ($(P_2N_2) = PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$) produced what was initially proposed to be a bridging $N_2{-}H_2$ complex. This species isomerized in solution to the complex containing a $(\mu\text{-}\eta^2\text{-}N_2H)(\mu\text{-}H)$ bridging fragment.[653] A single-crystal neutron diffraction study subsequently confirmed the latter structure.[654,655] Theoretical considerations suggested that incorporation of one or two additional hydrogen molecules may also be possible.[656] Furthermore, the studies indicated that the formation of the isolable $[Zr(P_2N_2)]_2(\mu\text{-}\eta^2\text{-}N_2H)(\mu\text{-}H)$ (**117**) proceeded via a metathesis-like transition state, where Zr—H and N—H bonds were simultaneously formed with concurrent breakage of the H—H and N—N bonds.[654]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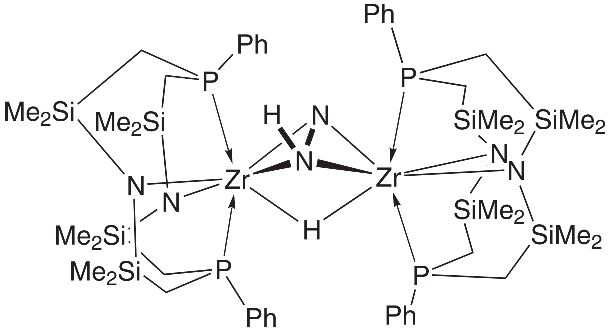

(**117**)

Zr and Hf hydrides have been proposed as intermediates or by-products in heterogeneous and homogeneous catalysis of alkene isomerization, polymerization, and trimerization reactions.[388,657–659] For example, heating the well-characterized silica-bound Zr(neopentyl)$_n$ ($n = 1, 2$) with dihydrogen afforded silica supported Zr-hydrides as indicated by IR spectroscopy.[658] Interestingly, this silica-supported Zr hydride exchanged via σ-bond metathesis with alkanes to produce the corresponding Zr alkyl derivatives.[388,660,661]

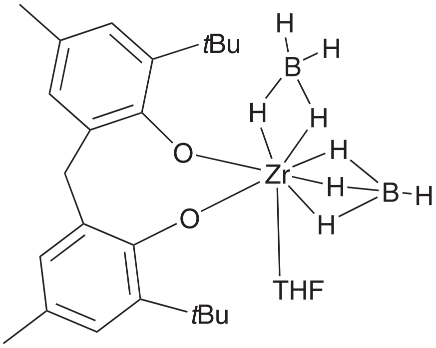
4.3.2.9.2 Borohydride ligand complexes

Zr and Hf tetrakis(tetrahydroborate) complexes are of interest due to their application in CVD of ZrB_2 and HfB_2 films.[662] Alternatively, these species acted as regenerable reducing agents when supported on polymers.[663] These applications have prompted theoretical,[664] and spectroscopic studies[665,666] as well as applications in hydroboration catalysis.[667] Synthetic efforts have targeted homoleptic Zr compounds of the formula $Zr(BH_3R)_4$ (R = Me,[668] H, Bu^t, $C(SiMe_3)_3$[669]). Structural studies have confirmed the expected symmetry of these species. A neutron diffraction study of $Hf(BH_4)_4$ confirmed the η^3-binding mode of the BH_4 ligands.[670]

Hf-BH_4 complexes of the formulas $Hf(BH_4)_3N(SiMe_2CH_2PR_2)_2$ (R = Me, Pr^i) and $Hf(BH_4)_2(CH_2SiMe_3)N(SiMe_2CH_2PR_2)_2$ have been synthesized and shown to be mononuclear.[652,671] NMR and IR data suggested η^2-binding of the BH_4 ligands. The related complex containing the tridentate diamido ligand $Zr(BH_4)_2(SiMe_3NCH_2CH_2)_2N\ SiMe_3$ was also prepared from the reaction of the corresponding dihalide with BH_4.[185] Crystallographic data suggested η^2-binding of the BH_4 ligands.

The complex $ZrCl[BH_3\{C(SiMe_3)_3\}]_3$ was synthesized and crystallographic evidence indicated the presence of η^3-bound borate ligands.[672] In contrast, the eight-coordinate BH_4 complex $Zr(\mu\text{-}BH_4)_2[CH_2(3\text{-Me-}6\text{-Bu}^tC_6H_2O)_2](THF)$ (**118**) was derived from the reaction of the dichloride precursor with $LiBH_4$.[673] Structural data showed that the BH_4 ligands were bound in η^2 and η^3 fashions. X-ray data confirmed the formulation of the related complex $Zr(Bu^tNCHCHNBu^t)(\eta^3\text{-}BH_4)_2$.[674] In more recent efforts, reaction of the sterically encumbered $ZrCl(NAdAr)_3$ (Ad = adamantyl, Ar = 3,5-Me_2Ph) with $NaBH_4$ resulted in the complex $Zr(\eta^3\text{-}BH_4)(NAdAr)_3$.[56]

Finally, one brief report has described a heterobimetallic derivative that was formulated as $Cu(TETA)(BH_4)_2Zr(BH_4)_2$. Based on IR data, the authors proposed η^2 coordination of the borate ligands.[675]



(**118**)

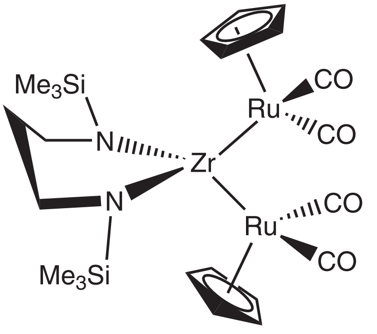
4.3.2.9.3 *Mixed hydride–borohydride complexes*

Addition of bases such PMe_3 or NMe_3 to $Hf(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]$ resulted in the generation of $Hf_2H_4(BH_4)_2[N(SiMe_2CH_2PMe_2)_2]_2$ and $Hf_2H_3(BH_4)_3[N(SiMe_2CH_2PMe_2)_2]_2$.[652,671] Spectroscopic data indicated that these molecules were fluxional in solution. Furthermore, it was shown that the mechanism of formation of these species did not involve simple dissociation of BH_3. A similar synthetic protocol was used to prepare a series of Zr and Hf hydride-BH_4 species including $M_2H_3(BH_4)_5(PMe_3)_2$, $M_3H_6(BH_4)_6(PMe_3)_4$, $M_2H_4(BH_4)_4(dmpe)_2$, $Zr_2H_4(BH_4)_4(PMe_3)_4$,[676] $MH(BH_4)_3(dmpe)$, and $MH_2(BH_4)_2(dmpe)_2$ (dmpe = 1,2-bis(dimethylphosphino)ethane). Complexes containing the bidentate phosphine ligands were conformationally stable at room temperature, despite the high formal coordination numbers. However these molecules did undergo an unusually high-energy intramolecular fluxional process.[677,678]

4.3.2.10 Metal–Metal Bonded Compounds

In a 1989 report, reaction of $ZrBn_4$ with $HCo(CO)_4$ yielded $ZrBn_3[Co(CO_4)]$ while subsequent reaction with PPh_3 gave $ZrBn_3[Co(CO)_3(PPh_3)]$.[679] A further study described related compounds of the general formulas $ZrR_{4-x}[Co(CO)_4]_x$ (R = Bn, NR_2 (R = Me, Et) and (R = Pr^i, Bu^n), $x = 1, 2$).[680]

Heterobimetallic bi- and trinuclear complexes $ZrCl[TMSN(CH_2)_2NSiMe_3][MCp(CO)_2]$, $Zr[TMSN(CH_2)_2NSiMe_3][MCp(CO)_2]_2$ (M = Fe, Ru (**119**)), and $ZrCl[TMSN(CH_2)_2NSiMe_3][Co(CO)_3PPh_3]$ have been prepared from $ZrCl_2[TMSN(CH_2)_2NSiMe_3](THF)_2$ via reaction with $K[CpM(CO)_2]$ (M = Fe, Ru) or $Na[Co(CO)_3(PPh_3)]$.[681,682] Crystallography has confirmed the presence of the metal–metal bond. Preliminary reactivity studies have demonstrated that these species react with MeNC to give $Zr[TMSN(CH_2)_2NSiMe_3]$ $[MCp(CO)_2]$ $[\eta^2\text{-}MeNC(MCo(CO)_2]$ (M = Fe, Ru).



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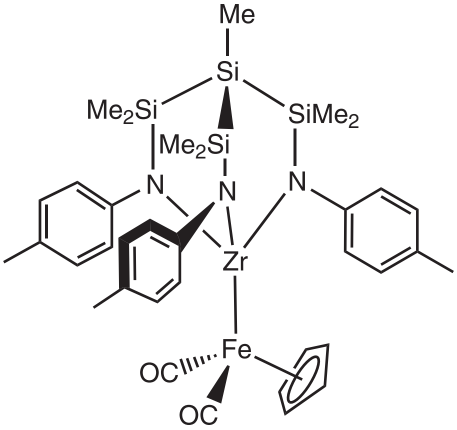


(**120**)

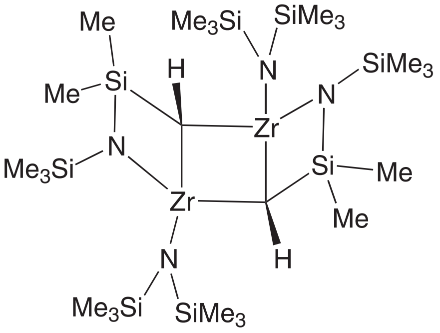
Tripodal ligands supporting analogous compounds of Zr and Hf have also been used to make complexes containing metal–metal bonds. For example, complexes of the form $Zr[(MeC_6H_4NSiMe_2)_3SiMe][MCp(CO)_2]$,[683,684] $Zr[(SiMe_2NAr)_3CH][MCp(CO)_2]$ ($Ar = MeC_6H_4$, M = Fe (**120**), Ru;[199,685] $Ar = C_6H_2F_3$, M = Fe, Ru;[686,687] $Ar = C_6H_3F$, M = Fe[688]), and $Zr[(MeC_6H_4NSiMe_2)_3CH][Co(CO)_3L]$ (L = CO, PPh_3, $P(MeC_6H_5)_3$)[689] have been prepared using methods analogous to those described above. These compounds also exhibited similar reactivity inserting a variety of organic unsaturates into the metal–metal bonds. For example, reaction with 1,2-diphenylcyclopropenone afforded $Zr[(ArNSiMe_2)_3CH][O_2CMCp(CO)(C_3Ph_2)]$, which contained a bridging μ^2-η^3-CO_2 ligand arising from O-atom migration.[687,688] Other work has shown that treatment of $Zr[(MeC_6H_4NSiMe_2)_3SiMe][Co(CO)_4]$ with Bu^tNC resulted in cleavage of the Zr—Co bond and subsequent formation of the salt $Zr[(MeC_6H_4NSiMe_2)_3SiMe(CNBu^t)_3]$-$[Co(CO)_4]$.[690]

4.3.2.11 Mixed Donor Ligand Complexes

4.3.2.11.1 C, N bidentate ligand complexes

A series of studies have examined complexes containing iminocacyl groups. The species $M(OAr)_2(\eta^2\text{-}BnCNBu^t)_2$, $Zr(OAr)(\eta^2\text{-}BnCNBu^t)_3$ (M = Zr, Hf, $Ar = Bu^t{}_2C_6H_3$, $Me_2C_6H_3$), and $M(OAr)_2(\eta^2\text{-}R^1CNR^2)_2$ (M = Zr, Hf, R^1 = Me, Bn, R^2 = Ph, MeC_6H_3, $C_3H_4F_3$, C_6H_4OMe, C_6H_4Cl, $C_6H_4NMe_2$) have been prepared by insertion of isocyanates into the precursor metal dialkyl derivatives. X-ray data has confirmed this mode of chelation. Intramolecular rearrangements affording enediamide derivatives have been studied in detail.[163,164,691–693] These processes have also been the subject of a theoretical investigation, which has demonstrated that these transformations are strongly exothermic.[694] Several other Zr-iminoacyl complexes have been characterized structurally by X-ray crystallography, including $Zr(\eta^2\text{-}Me_2PhNCCH_2Ph)_2(XDK)$ (see Section 4.3.2.6.8),[483] $ZrX_3[\eta^2\text{-}(TMS)_3SiCNC_6H_4Me_2]$, $ZrX_2[\eta^2\text{-}(TMS)_3SiCNC_6H_3Me_2](\eta^2\text{-}RCH_2CNC_6H_3Me_2)$, $ZrX[\eta^2\text{-}(TMS)_3SiCNC_6H_3Me_2](\eta^2\text{-}RCH_2CNC_6H_4Me_2)_2$, and $Zr[\eta^2\text{-}(TMS)_3SiCNC_6H_3Me_2](\eta^2\text{-}RCH_2CNC_6H_3Me_2)_3$ ($R = CH_2Bu^t$, CH_2SiMe_3, NMe_2; $X_2 = NMe_2$, $Si(SiMe_3)_3$).[15,16]

In 1983, the thermolysis of $ZrR_2[N(SiMe_3)_2]_2$ (R = Me, Et, CH_2SiMe_3) prompted elimination of alkane and the formation of the bridging carbene complex $[Zr\{N(SiMe_3)_2\}(CHSiMe_2NSiMe_3)]_2$ (**121**),[65] and addition of $Me_2PCH_2CH_2PMe_2$ generated $M(CH_2SiMe_2NSiMe_3)_2$ (dmpe).[65,695] In related chemistry, the compound $ZrCl_3[N(SiMe_3)_2]$[696] was prepared in a conventional manner. However, excess $Na[N(SiMe_3)_2]$ led to formation of the metallacycle, $ZrCl_2(CH_2SiMe_2NSiMe_3)$ (**122**). Similarly, the species $ZrMe\ N(SiMe_3)_2]_3$[697] was found to yield $Zr[N(SiMe_3)_2]_2(CH_2SiMe_2NSiMe_3)$.



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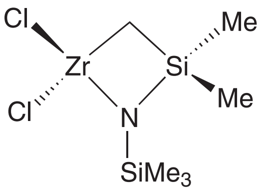
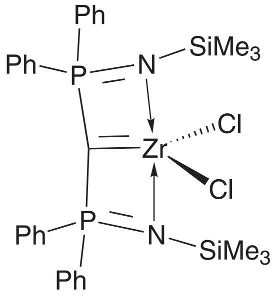


(**122**)

Another report in 1983 described metallation of quinolines to give complexes of the form $ZrCl_2(NC_9H_6)_2$.[698] In a related system, reaction of lithiated dimethylpyridine with $HfCl_2$-$(OBu^t{}_2C_6H_3)_2$ gave $Hf(OBu^t{}_2C_6H_3)_2(CH_2C_5H_3NMe)_2$.[699] C, N chelation and the six-coordinate geometry of the metal center was confirmed by X-ray methods. More recently, lithiation of benzyl or methyl-naphthalene substituents of amines has generated C_2N chelate complexes of the form $ZrBn_2(MeC_6H_3CH_2)_2NMe$ and $ZrBn_2(C_{10}H_6CH_2)_2NMe$.[700] Both of these species have been characterized crystallographically. The corresponding cations derived from reaction with borate salts have also been characterized.

Metallation of bis(phosphinimine) ligands has recently been employed to prepare a series of Zr and Hf carbene complexes. For example, the compounds $ZrBn_2C(Ph_2PNR)_2$ ($R = SiMe_3$, $C_{10}H_{16}$) were derived from the reaction of the neutral ligand with $ZrBn_4$.[701] Alternatively, reaction of the isolable dilithio salt of the ligand with $ZrCl_4$ has yielded $ZrCl_2C(Ph_2PNSiMe_3)_2$ (**123**).[702] X-ray crystallographic data confirmed the incorporation of the Zr—C bond in two adjacent four-membered rings. In a similar manner, reaction of $HfCl_2[N(SiMe_3)_2]_2$ with the ligand afforded the Hf complexes $HfCl_2C(R_2PNSiMe_3)_2$ ($R = Cy$, Ph).[703] The spirocyclic complex $Zr[C(Me_2PNSiMe_3)_2]_2$ has also been reported.[704] Both $Hf(CH_2Bu^t)_2C(R_2PNSiMe_3)_2$ and $MCl_2C(R_2PNSiMe_3)_2(L)$ ($M = Zr$, $L = CNMe_2C_6H_4$; Hf, $L = THF$, $C_{10}H_{16}$) have been prepared and characterized structurally. In addition, isocyanates and CO_2 undergo cycloaddition to the carbene, forming the complexes $MCl_2C(R_2PNSiMe_3)_2(YCX)$ ($M = Zr$, Hf; $X = O$, $NC_{10}H_{16}$, NCy; $Y = O$, $NC_{10}H_{16}$, NC_6H_4Me, NCy (**124**)) that contain new N_2CO and N_3O tripodal ligands.[705]



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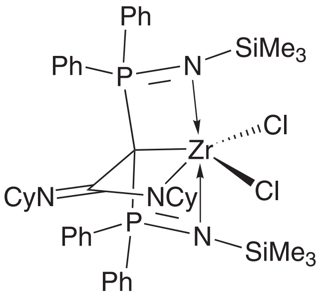


(**124**)

One other example of Zr-mediated C—H activation of a phosphinimine ligand has been described recently. The complex $ZrCl_3CHCH_2(Ph_2PNSiMe_3)_2$ was obtained from the reaction of the bis-phosphinimine with $ZrCl_4$.[28]

4.3.2.11.2 C, P bidentate ligand complexes

The phosphinomethanide complexes $ZrCl_{4-x}(CH(PMe_2)SiMe_3)_x$ ($x = 1$–4) have been synthesized.[706] Of these compounds, the symmetric *trans*-octahedral product $ZrCl_2[C(PMe_2)_2(SiMe_3)]_2$ was prepared in high yield. Interestingly, both η^1 and η^2 coordination was observed for P—C linkages in $Zr[CH(PMe_2)(SiMe_3)]_4$.

4.3.2.11.3 Monoanionic N, O bidentate ligand complexes

A variety of other monoanionic ligands that contain O and N functional groups have been reported to complex Zr and Hf. For example, hydroxy-pyridionate,[707] substituted-thiazolidin-4-ones,[708,709] cycloserine,[710] *N*-furfurylidnearylamines,[711] azopyrazolones,[712–714] substituted aroylhydrazone,[715] benzoyl hydrazones,[716–718] 6-amino-penicillinic acid,[719] aniline-carboxylate,[720] aminoantipyrine,[721] and bis-salicyloyl hydrazides[722] have been employed in the preparation of various halide and oxide derivatives. The majority of these complexes have been characterized by IR spectroscopy and elemental analysis alone.

Oximes were proposed to coordinate to group IV metals in a bidentate fashion, although the nature of binding was not unambiguously established.[723] In contrast, hydroxy-amides reacted with $Zr(OR)_4$ to give $Zr(ONR_2)_4$ ($R = Et$, Bn).[724] Crystallographic evidence later affirmed an eight-coordinate Zr center in the homoleptic $Zr(ONMe_2)_4$.[725]

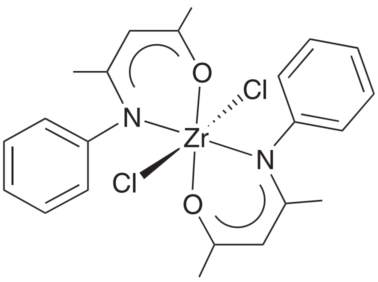
A series of amino-alkoxide ligand compounds of formulas $Zr(OR)_2(Me_2NCH_2CH_2O)_2$, $Zr_2(OR)_6(Me_2NCH_2CH_2CH_2O)_2$, $Zr_2(OR)_6[(Me_2NCH_2)_2CHO]_2$, and $Zr_2(OBu^t)_3[(Me_2NCH_2)_2CHO]_4(OH)$ ($R = Pr^i$, Bu^t) have been constructed in good yields from heating the neutral alcohol with the appropriate Zr tetraalkoxide precursor.[726] Structural studies revealed that the amino-alkoxide O atoms bridge the metal centers in the dimers. In the case of $Zr_2(OBu^t)_3[(Me_2NCH_2)_2CHO]_4(OH)$, the hydroxide group bridged the metals with one or two of the amino groups of the diamino-alkoxide ligands dangling free. Use of the related hydroxphenyl–oxazaoline ligands provided access to the species $ZrCl_2[OC_6H_4(CNOC(R^1)(R^2)CHR^3)]_2$ (R^1 = H, Me, Bn, Pr^i; R^2 = Me, H; R^3 = H, Ph). A crystallographic study has confirmed the bidentate ligands adopted a *cisoid* geometry.[727]

A variety of substitutents have been employed to prepare a number of phenoxy-imine chelate complexes of the form $ZrCl_2[(OC_6H_3R^1{}_2)CHNR^2]_2$ (R^1 = H, Me, cumyl, Pr^i, Bu^t, adamantyl; R^2 = Ph, C_6H_{11}, MeC_6H_4, $Pr^iC_6H_4$, $Bu^tC_6H_4$, $Pr^i{}_2C_6H_3$, $Bu^t{}_2C_6H_3$). Upon activation, these complexes catalyzed the polymerization of C_2H_4, and some exhibited extremely high turnover frequencies.[728–732]

Complexes containing pyridine-alkoxide ligands, $M(NMe_2)_2(OCAr_2C_5H_4N)_2$ (M = Zr, Hf; Ar = substituted arene) have been prepared and characterized.[733] Crystallographic data confirmed the chelating nature of these ligands. Related benzyl derivatives have also been prepared. Cationic analogs of these species were generated by reaction with $B(C_6F_5)_3$. These compounds acted as catalyst precursors for the polymerization of C_2H_4 and hexene, although the resulting polymers were of low molecular weight.[734]

Related 8-quinolinolato complexes of the form $ZrX_2(NC_9H_3MeR_2O)$ (X = Bn, CH_2Bu^t, CH_2SiMe_3, Cl; R = Me, H, Br)[735] have also been reported. NMR and X-ray crystallographic studies showed that the cations $[ZrBn(NC_9H_3MeR_2O)]^+$, derived from these species assumed a pseudo-square pyramidal structure with an η^2-bound benzyl ligand.[735] These compounds also exhibited low activities in alkene polymerization.

Salts of the anionic β-ketoiminato ligands were prepared by deprotonation of a β-aminoketone. A variety of complexes have been prepared, including $ZrCl_2(RNCMeCHCMeO)_2$ (R = Pr^i, Ph (**125**), C_6H_4Me, C_6H_4OMe).[325] Crystallographic analysis of $ZrCl_2(PhNCMeCHCMeO)_2$ indicated delocalization of the charge over the bidentate chelate. Protonolysis with the neutral ligand was employed to prepare $Zr(NMe_2)_2(RNCMeCHCMeO)_2$ and $Zr(NMe_2)_3(RNCMeCHCMeO)$ (R = p-MeC_6H_4, $Pr^i{}_2C_6H_4$ (**126**)). Subsequent conversion to the analogous Cl or alkoxide derivatives was straightforward.[736] Several complexes of the general formula $ZrCl_2(R^2NCRCHCR^1O)_2$, when activated with MAO, were moderately active catalysts for the polymerization of C_2H_4.[737,738] A density functional study demonstrated that the barrier for the insertion was lowered for ligands incorporating bulky substituents.[739]



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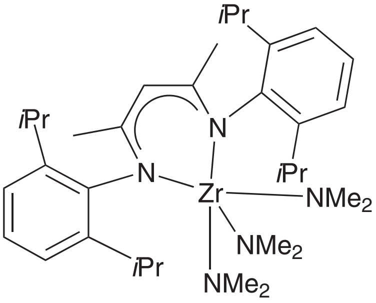

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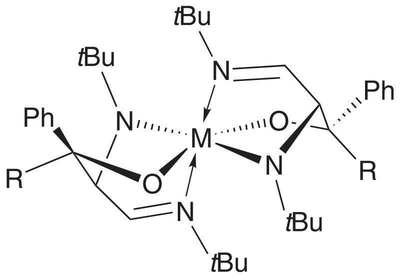
4.3.2.11.4 Dianionic N, O bidentate ligand complexes

The complex $Zr[OC(CH_2)SiMe_2N(SiMe_3)]_2(Me_2PCH_2CH_2PMe_2)$ containing a dianionic bidentate N, O ligand was derived from the insertion of CO into the precursor metallacycle.[65] Similarly, insertion of CO into Zr η^2-iminoacyl complexes afforded $Zr(OBu^t{}_2C_6H_3)_2$ $[OC(Bn)C(Bn)NBu^t]$.[691] Theoretical investigations of these coupling reactions indicated that the presence of the O atom directly influenced the activation barrier.[694]

4.3.2.11.5 N_2O tridentate ligand complexes

The reaction of $Hf(OPr^i)_4$ with semicarbazones was proposed to give five-coordinate complexes, in which the ligand acts in a tridentate fashion. However, this was not unambiguously confirmed.[740]

A tridentate ligand complex resulted from the reaction of 1,4-diaza-1,3-diene(DAD) Zr or Hf complex with Ph_2CO or MePhCO. This resulted in a [3 + 2] cycloaddition, giving $M[(Bu^tNCH)_2$-$(OCRPh)]_2$ (R = Me, Ph (**127**)).[741] Decomplexation and isolation of the newly formed tridentate ligand was readily achieved, although the mechanistic details of this unusual reaction have yet to be determined.



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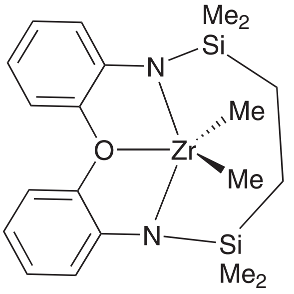
Schrock's group has detailed a series of tridentate diamido ligand complexes in recent years. Reaction of $O[C_6H_4N(Bu^t\text{-}d^6)H]_2$ with $Zr(NMe_2)_4$ gave the complex $Zr(NMe_2)_2(NBu^t\text{-}d^6C_6H_4)_2O$. Subsequent reaction with MeI gave the analogous iodide complex. N, O, N chelation was confirmed crystallographically. Generation of the zwitterion $[ZrMe(Bu^t\text{-}d^6NC_6H_4)_2O]$ $[MeB(C_6F_5)_3]$ was achieved via reaction with $B(C_6F_5)_3$ and this complex proved to be a living catalyst for the polymerization of 1-hexene.[742] NMR spectroscopy demonstrated that insertion of 1-hexene into the metal alkyl bond occurred in a 1,2 manner and that β-H elimination happened at a much slower rate than insertion. This was attributed to steric congestion at the metal center provided by the ligand.[743] A series of related complexes $MX_2[(RNC_6H_4)_2O]$ (M = Zr, X = Me, alkyl;[744] M = Zr, Hf, R = $SiMe_3$;[745] M = Zr, Hf, R = $C_6H_4Me_2$[746–748]) have also been prepared and studied. Methylation of $ZrCl_2(CH_2SiMe_2NC_6H_4)_2O(NC_5H_5)$ gave $ZrMe_2(CH_2SiMe_2NC_6H_4)_2O$ (**128**) while treatment with $Li[CH_2SiMe_3]$ led to double C—H bond activation giving the unusual dissymmetric product $Zr_2(CH_2SiMe_3)_2((CH_2SiMe_2NC_6H_4)_2O)(CH_2SiMe_2NC_6H_4)(CH_2SiMeCHNC_6H_4O)$ (**129**).[745] A series of related complexes derived from ligands that incorporated furan rings as the ether donor were also used to prepare analogous complexes, such as $ZrCl_2(Me_2C_6H_3NHCH_2)_2\text{-}(C_4H_6O)$.[749] In addition, the closely related species $ZrBn_2$ $(CyNSiMe_2)_2O$ and $Zr[(RNSiMe_2)_2O]_2$ (R = Bu^t, Cy)[142] have also been reported and characterized crystallographically.



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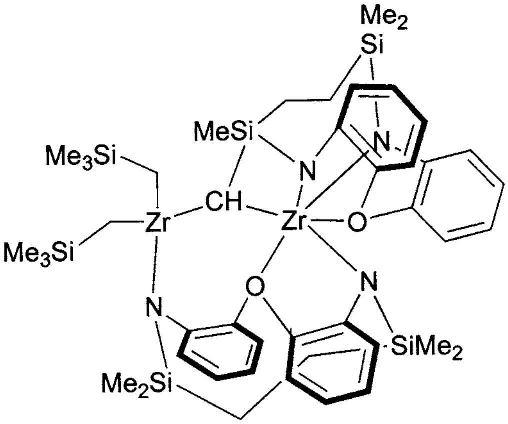

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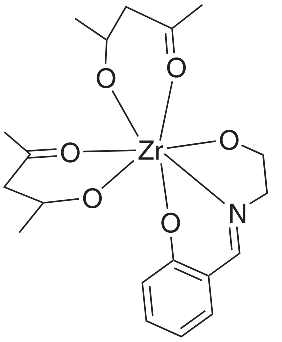
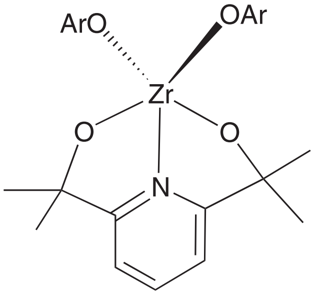
The dialkyl complexes $ZrX_2(RNC_6H_4)_2O$ (X = Et, Pr^i; R = Bu^t, CH_2CHMe_2) reacted with phosphine to give stable alkene complexes such as $Zr(CH_2CH_2)(RNC_6H_4)_2O$.[750] These Zr complexes also proved effective in alkene polymerization, although the Hf complexes were not well behaved.

4.3.2.11.6 NO_2 tridentate ligand complexes

A series of chelating ligand complexes derived from Schiff-base derivatives of salicylaldehyde,[751–757] anthranilic acid,[758] picoloylhydrazones,[759] and benzoylhydrazones[760] have been reported. These systems have not been characterized crystallographically. In contrast, tridentate O, N, O ligands based on the Schiff-base salicylidneaminoethanolate[761] reacted with $Zr(OCMeCHCMeO)_4$ to give the complex $[Zr(OCMeCHCMeO)_2(OCH_2CH_2NCHC_6H_4O)]_2$ (**130**). The dimeric formulation with bridging alkoxide O atoms was confirmed by X-ray crystallography.[762] In addition, it was demonstrated that this species was an active catalyst for the hydrolysis or transesterification of phosphate diesters.



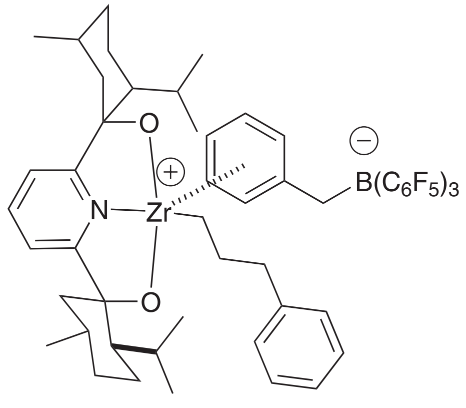
(**130**)



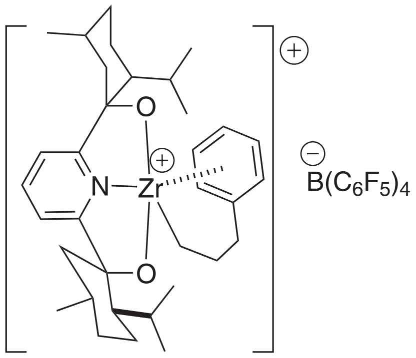
(**131**)

Acylation of substituted pyridines was achieved via insertion of CO into $MR_2(OC_6H_3Bu^t{}_2)_2$ ($R = Me$, Bn) to yield the O, N, O ligand complexes $Zr(OC_6H_3Bu^t{}_2)_2(OCHR)_2C_5H_2XN$ ($R = Me$ (**131**), Bn, $X = H$, Ph, Me) and $M(OC_6H_3Bu^t{}_2)_2[(OCHMe)_2C_5H_3N]_2$.[763]

A related ligand bis-menthoxo-pyridyl, has been employed to synthesize $ZrBn_2(OC_6H_8MePr^i)_2C_5H_3N$. This species reacted with $B(C_6F_5)_3$ or $[Ph_3C]$ $[B(C_6F_5)_4]$ to give $ZrBn[(OC_6H_8MePr^i)_2C_5H_3N][BnB(C_6F_5)_3]$ and $[ZrBn(OC_6H_8MePr^i)_2C_5H_3N][B(C_6F_5)_4]$, respectively.[764] These compounds undergo single insertions of C_2H_4 or alkenes to produce a diastereotopic mixture of $[Zr(\eta^1\text{-}\eta^6\text{-}CH_2CH_2CH_2Ph)\{(OC_6H_8MePr^i)_2C_5H_3N\}][BnB(C_6F_5)_3]$ (**132**) and $[Zr(\eta^1\text{-}\eta^6\text{-}CH_2CH_2CH_2Ph)(OC_6H_8MePr^i)_2C_5H_3N]$ $[B(C_6F_5)_4]$ (**133**). The authors attributed this phenomenon to the stabilizing effect of the benzyl group.



(**132**)



(**133**)

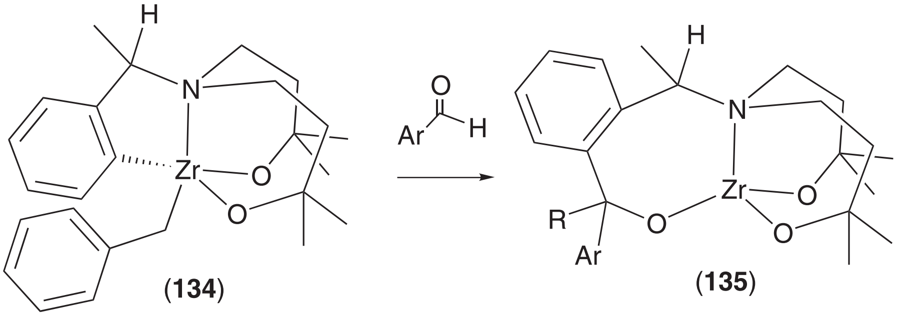
Zr complexes that contain amine-bis(phenolate) or aminodiolate ligands have been recently reported in the literature. For example, $ZrBn_2(OBu^t{}_2C_6H_2CH_2)_2NPr$,[765] $ZrX(OCR_2CH_2CH_2)_2NEt$ ($X = Me$, Bn, Cl, CH_2SiMe_3; $R = Me$, Ph),[766] and $Zr[(OCR^1{}_2CH_2CH_2)_2NR^2]_2$ ($R^1 = Me$, Ph; $R^2 = Me$, Bu^t, CHMe(Ph))[767] have been prepared. These products exhibited pseudo-trigonal bipyramidal geometries. A series of related ligands that incorporated a second N donor have also been developed. For example, in the complex $ZrBn_2(OBu^t{}_2C_6H_2CH_2)_2NCH_2CH_2CH_2NMe_2$, the dimethylamino group did not interact with the metal center. In contrast, $ZrBn_2(OBu^t{}_2C_6H_2CH_2)_2NCH_2CH_2NMe_2$ possessed a pendant amino group that did chelate to the metal center. These systems exhibited moderate utility as alkene oligomerization/polymerization catalysts.[768]

4.3.2.11.7 N, O tripodal ligand complexes

The complexes $ZrCl[(OCH_2CH_2)_3N]_n$ and $Zr(O_2CMe)(OCH_2CH_2)_3N$ were prepared from the reaction of $ZrCp_2Cl_2$ with the hydrochloride salt of the ligand in the presence of NEt_3.[769,770] During the 1990s, a number of research groups employed chiral tri(alkanol)amines to generate chiral Lewis acid catalysts. These were shown to effect a series of organic transformations, including enantioselective additions to epoxides[771–773] and stereoselective sulfoxidations.[774,775] Hydrolysis of $Zr(OBu^t)[CH_2CH(OH)Me]_3N$ resulted in the isolation of a hydroxy-bridged dimer.[771] Addition of $Zr[(OCH_2CH_2)_2NCH_2CH_2OH]_2$ to Al $(OPr^i)_3$ was proposed to give hetero-bimetallic derivatives, although the precise structural details were not determined.[776]

The complex of the ligand oxyiminodipropionate, $[Ca(H_2O)_5][Zr((O_2CCH_2)_2NO)_2(H_2O)]$, has been prepared and characterized crystallographically. The Zr was coordinated to one N and three O atoms of the ligand as well as to a water molecule, producing a formally nine-coordinate Zr center.[777]

As mentioned above, complexes derived from neutral $NN'O_2$ ligands reacted with $Zr(NMe_2)_4$, $ZrBn_4$, or $ZrCl_2(CH_2SiMe_3)_2$, bonding to Zr in a tripodal fashion. For example, the Zr complexes $ZrBn_2[(O\text{-}2,4\text{-}Bu^t{}_2\text{-}6\text{-}CH_2)_2NCH_2CH_2R]$ ($R = NMe_2$, C_5H_4N)[765,768] and $ZrBn[(OCMe_2CH_2CH_2)_2NCHMe(C_6H_4)CH(C_{10}H_7)O]$[766] have been prepared and characterized. The latter compound was derived from the insertion of aldehyde into $ZrBn[(OCMe_2CH_2CH_2)_2NCHMeC_6H_4]$ (**134**) yielding $Zr[(OCMe_2CH_2CH_2)_2NCHMeC_6H_4\ C(R)ArO]$ (**135**).[766]



(**134**) (**135**)

In another related and recent report, the ligand $NC_5H_4CH_2NH(CH_2CH_2NSiMe_3)_2$ was complexed to Zr, affording the octahedral species $ZrCl_2[NC_5H_4CH_2N(CH_2CH_2NSiMe_3)_2]$.[206]

4.3.2.11.8 N, O tetradentate ligand complexes

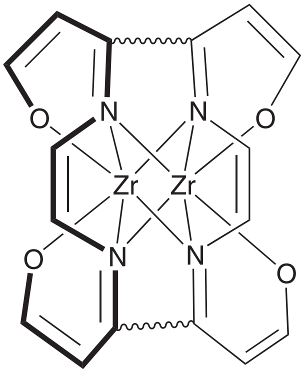
A variety of tetradentate Schiff-base-enolate ligands have been used to complex Zr. In an early study, Illingsworth and Archer described the coordination compound $Zr[(OC_6H_4CHN)_2C_6H_3(CO_2Et)]_2$. This species was proposed to be eight coordinate.[778] Using a closely related ligand, $Zr[(OC_6H_4CHN)_2C_6H_3R]_2$ ($R = NO_2$, NH_2) were prepared and the latter was confirmed crystallographically to contain an eight-coordinate Zr center.[779] Subsequent reactions of acid anhydrides or halides with the exo-cyclic amino group afforded preparation of oligomeric materials.[779,780] Block copolymers of organic segments and the Zr Schiff-base complexes have been prepared and characterized.[781] Related polymeric coordination compounds of formula $[Zr\{(OC_6H_4CHN)_4C_6H_2\}]_n$ were derived from the ligand based on tetra-aminobenzene.[782] The unique polymers have been characterized by a variety of techniques such as elemental analysis, gel-permeation chromatography (GPC), viscosity measurements, and IR spectroscopy.[782–784] Inclusion of a $Zr(OH)_2$ functionality at the end of these polymers permitted adhesion to silica and alumina.[785]

A series of closely related Schiff-base ligand complexes based on cyclohexyl- or alkyl diamines have been prepared and characterized.[786–789] Crystallographic studies have confirmed that the ML_2 complexes were eight coordinate,[790] while the related complexes MCl_2L and MCl_2L(donor) adopted *cis*- or *trans*-octahedral or seven-coordinate geometry.[791]

Several Schiff-base ligands derived from the condensation of diamines and 1,3-diones were employed as tetradentate ligands for Zr. For example, the complexes $ZrCl_2[OCRCHC(Me)NCH_2]_2$ ($R = CF_3$, Me) were derivatized and subsequently the salt $[Zr(CH_2CMe_3)\{OC(CF_3)CHC(Me)NCH_2\}_2(NMe_2Ph)]\ [B(C_6F_5)_4]$ was prepared and characterized crystallographically. Interestingly, in CH_2Cl_2 this species was unstable, affording instead a

Cl-bridged, cationic dimer $[\{Zr(CH_2CMe_3)(OC(CF_3)CHC(Me)NCH_2)_2\}_2(\mu\text{-}Cl)]$ $[B(C_6F_5)_4]$.[792] A separate report has detailed the structure of the complex $Zr[\{OC(CF_3)CHC(CF_3)NCH_2\}_2]_2$.[793]

The redox properties of the complexes $ZrCl_2(THF)[(OC_6H_4CHN)_2C_6H_4]_2$ and $Zr[\{(OC_6H_4CHN)_2C_6H_4\}_2]_2$ were investigated. Upon reduction with Mg, the former gave reductive C—C coupling of the Schiff-base ligands. The resulting binuclear complex was characterized crystallographically (**136**).[794]



(**136**)

The related complex $ZrCl_2(THF)(OC_6H_4CHNCH_2)_2$ lost THF upon heating. The resulting product was effective as a homogeneous alkene polymerization catalyst precursor. Alternatively, deposition on silica gave a moderately active heterogeneous catalyst.[795] A more recent study has evaluated a series of Schiff-base complexes for the polymerization of C_2H_4.[796] Suitable substitution of the Schiff-base afforded a C_2-symmetric complex of the formula $MCl_2(OC_6H_2\text{-}Bu^t_2CH_2NC_6H_3Me)_2$ (M = Zr, Hf). This species was likened to an *ansa*-metallocene. Although the Cl ligands could be replaced with hard donors such as amides and alkoxides, alkylation was unsuccessful.[797,798]

In a recent paper, zirconyl derivatives of tetradentate Schiff-base ligands have exhibited high activity for the inhibition of growth of a variety of organisms including *Escherichia coli*, *Staphylococcus aureus*, *Aspergillus niger*, and *Candida albicans*.[799]

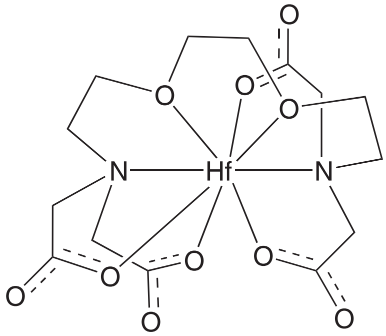
Reduction of Schiff-bases to the corresponding diamines yielded O_2N_2 donor complexes $ZrBn_2[OC_6H_2R_2CH_2N(Me)CH_2]_2$ (R = Me, Bu^t).[800] In a recent report, diamido-diether ligands have been used to form the complexes $ZrX_2(RNCH_2CH_2OCH_2)_2$ (X = Cl, Bn; R = C_6F_5, $C_6H_3(CF_3)_2$)[801] which were precursors to moderately active C_2H_4 polymerization catalysts.

4.3.2.11.9 >4 Denticity N, O ligand complexes

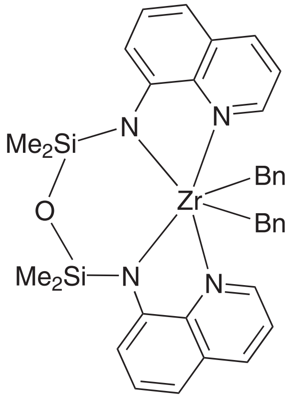
A report in 1984 described the coordination of the neutral ligand diacetylpyridine-bis-(semicarbazone) to Zr. This ligand was proposed to act in a pentadentate fashion in the complexes $[ZrO(H_2O)\{H_2NCONHNC(Me)\}_2C_5H_3N]Cl_2$ and $[Zr(OH)_2\{H_2NCONHNC(Me)\}_2C_5H_3N]Cl_2$.[802] Other reports have described multidentate phenoxy-imine Schiff-base ligand complexes of Zr, although the nature of the chelation has not been confirmed.[791,803–805]

The thermodynamically stable, triaqua adducts of $M[(O_2CCH_2)_2NCH_2CH_2OCH_2]_2$ (M = Zr, Hf (**137**)) have been synthesized. The Hf complex was characterized crystallographically, confirming the octadentate nature of this ligand.[590] A related octadentate ligand complex based on the tetraacetic acid derivative of tetraazacyclododecane was prepared. NMR data for $Zr(O_2CCH_2NCH_2CH_2)_4(H_2O)$ indicated two isomers in solution. Crystallographic data for the Zr complex was not obtained, although the structure of a Y analog was determined.[806]

The thermally stable $ZrBn_2[(NC_{10}H_6)NSiMe_2]_2O$ (**138**) was obtained from reaction of the pentadentate neutral ligand with $ZrBn_4$. Structural data revealed the ligand was bound in a pentadentate N_4O fashion.[142] The hexadentate (N_2O_4) 4,13-diaza-18-crown-6 ligand was used to prepare the complex $ZrBn_2(NCH_2CH_2OCH_2CH_2OCH_2)_2$, which existed as a mixture of the *cis* and *trans* isomers.[807] The zwitterionic species $[ZrBn(NCH_2CH_2OCH_2CH_2OCH_2)_2]$ $[BnB(C_6F_5)_3]$ catalyzed the dimerization of tolylalkyne to ditolylbutenyne.



(**137**)

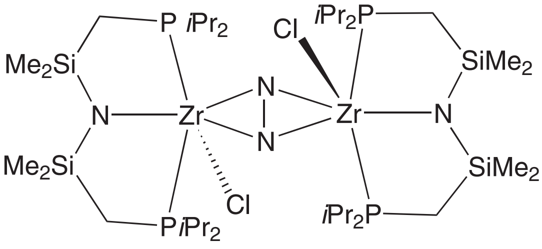


(**138**)

4.3.2.11.10 N, P ligand complexes

Tridentate amido-phosphine ligands have been used to prepare $MCl_2(SiMe_2CH_2PR_2)_2$ (R = Me, Ph),[808] $MCl_3N(SiMe_2CH_2PR_2)_2$ (R = Me, Pr^i, Bu^t; M = Zr, Hf),[809] and $ZrCl_2[N(CH_2CH_2PMe_2)_2]_2$.[810] The derivatives $MCl_3N(SiMe_2CH_2PR_2)_2$, $MMe_3[N(SiMe_2CH_2PR_2)_2]$, and $M(BH_4)_3N(SiMe_2CH_2PR_2)_2$ (R = Me, Pr^i, Bu^t) were readily prepared and characterized.[652,671,811]

Reduction of $ZrCl_3N(SiMe_2CH_2PPr^i{}_2)_2$ by Na/Hg under N_2 produced $[ZrClN(SiMe_2CH_2PR_2)_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$ (**139**), formally a Zr^{IV} product, since the N_2 was irreversibly reduced to an $(N_2)^{4-}$ hydrazido ligand.[812,813] A series of derivatives of the general formula $ZrCl_2XN(SiMe_2CH_2PR_2)_2$ (X = $OMe_2C_6H_3$, OBu^t, $OCHPh_2$, NPh_2) have also been prepared. Only in the case of X = $OMe_2C_6H_3$ was the analogous N_2 species, $[Zr(OMe_2C_6H_3)N(SiMe_2CH_2PR_2)_2]_2$-$(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$, accessible.[814]

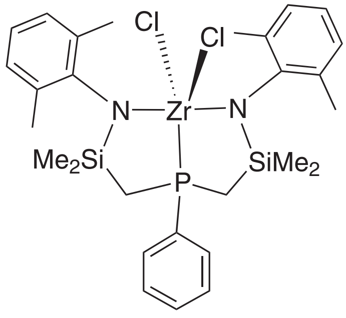


(**139**)

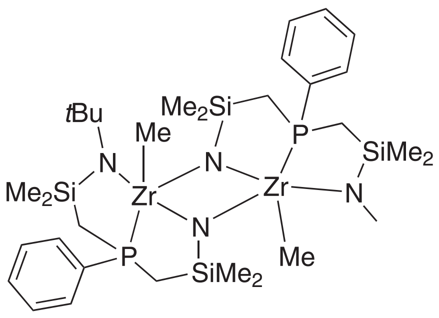
An extension of these efforts involved the preparation of the macrocyclic derivatives $ZrX_2PhP(CH_2SiMe_2NSiMe_2CH_2)_2PPh$ (X = Cl, Me, Bn, NBu^t).[815] Reduction of the dichloride complex by KC_8 under N_2 gave the species $[Zr(PhPCH_2SiMe_2NSiMe_2CH_2)_2]_2(\mu\text{-}\eta^2{:}\eta^2\text{-}N_2)$. This compound reacted with H_2 (see Section 4.3.2.9.1).[653–656,816]

The related diamido-phosphine ligand complexes $ZrX_2PhP(CH_2CH_2NSiMe_3)_2$ (X = Cl, Me, Bn, Bu^i) and $ZrX_2PhP(CH_2SiMe_2NR)_2$ (X = Cl, Me; R = Bu^t, $Me_2C_6H_3$) have also been prepared. The species $ZrCl_2PhP(CH_2SiMe_2NBu^t)_2$ (**140**) reacted with LiMe to effect N—C bond cleavage affording $[ZrMe\{PhP(CH_2SiMe_2NBu^t)CH_2SiMe_2N\}]_2$ (**141**).[817]

The homoleptic compound $Zr(NPhPPh_2)_4$ has been reported recently. Crystallography confirmed the eight-coordinate structure, with each of the ligands interacting with Zr via N and P. In solution, VT-^{31}P NMR experiments suggested six-coordinate geometry. This compound exhibited moderate activities for the polymerization of propylene, the isomerization and oligomerization of 1-octene, and the isomerization of allylbenzene to *trans*-methylstyrene.[818]



(**140**)



(**141**)

4.3.2.11.11 N, S bidentate ligand complexes

A series of complexes containing a variety of N and S heteroatomic ligands include systems based on thiotriazoles,[592] azinates,[819] dithiodianiline,[820] ferrocenylthiotriazoles,[821] dithiocarbazates,[822,823] tetrazoles,[824] phenothiozines,[825] dithiocarboxylic acids,[826] diacetylpyridinebis-(thiosemicarbazone),[827] thioamide,[824] amino-cyclopentenedithiocarboxylic acids,[740] quinoline sulphon-ates,[828] and thiazolidinones.[708] A macrocyclic compound containing the diamino-dithiocarbamate ligand was thought to yield a macrocyclic complex of Zr.[829] In these reports, the ligands were thought to be N, S chelates, although this was not confirmed unambiguously.

Extremely air-sensitive compounds, of formulation $ZrCl(NBu^tSPh)_3$ and $Zr(NBu^tSPh)_4$, were obtained from reaction of $ZrCl_4$ with the lithiated amide. Crystallographic characterization of the former species confirmed a bidentate N, S chelation and seven-coordinate Zr.[830]

The tridentate ligand complexes $ZrX_2(R_2C_6H_3NCH_2CH_2)_2S$ ($X = Cl$, Me, CH_2CHMe_2, NMe_2; $R = Me$, Et, Pr^i) and $ZrX_2(RNC_6H_4)_2S$ ($X = Cl$, NMe_2, Me; $R = Bu^t$, Pr^i) were reported.[748,831] X-ray data confirmed the tridentate nature of the ligand. Dialkyl and cationic derivatives appeared to be less stable than those derived from the ether analogs. Consequently, cationic complexes generated by reaction with $[Ph_3C]\,[B(C_6F_5)_4]$ exhibited only moderate activity for the polymerization of 1-hexene.

The pyrimidine-thiolate derivative $ZrCl_2HB(Me_2C_3HN_2)_3(Me_2C_2HN_2S)$ has been prepared and the barrier to rotation about the S bond studied in detail by ^1H NMR spectroscopy.[176]

4.3.2.11.12 O, P bidentate ligand complexes

The bidentate P, O ligand complexes $ZrX_2[OC(Bu^t)_2CH_2PPh_2]_2$ ($X = Cl$, Me, CH_2Bu^t) and $ZrX[OC(Bu^t)_2CH_2PPh_2]_3$ ($X = Cl$, Me) have been prepared and characterized by Baxter and Wolczanski. NMR spectroscopy revealed fluxional behavior in solution.[832]

4.3.2.11.13 O, S bidenate ligand complexes

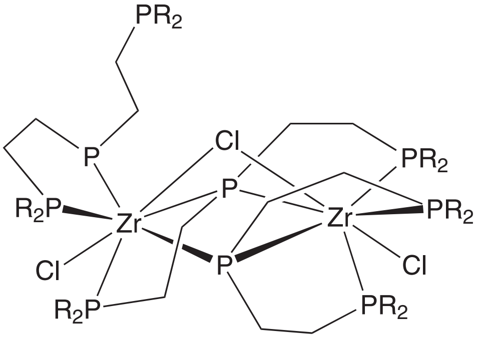
The compound $Zr(SCMeCHCMeO)_4$ was prepared from reaction of the monoanionic ligand with $ZrCl_4$.[833] Crystallographic data confirmed an eight-coordinate metal center, and solution NMR studies indicate that the molecule was fluxional. Thiocarbamate ligands have been used to prepare complexes of the form $Zr(OSCNR_2)_4$ ($R = Me$, Et, Pr^i). These eight-coordinate complexes rearranged more slowly than the analogous dithiocarbamates.[834] $Zr(O\ Pr^i)_2(OC_6H_2MeBu^t)_2S$ has been prepared and used as a precatalyst in alkene polymerization, though this species was only moderately active.[835]

4.3.2.11.14 O, N, S tridentate ligand complexes

A series of Zr and Hf complexes supported by dianionic phenolate-thiolate Schiff-base ligands have been reported.[825,827,836–840] While it is thought that these ligands give rise to O, N, S chelates, this has not been confirmed unambiguously.

4.3.3 ZIRCONIUM(III) AND HAFNIUM(III)

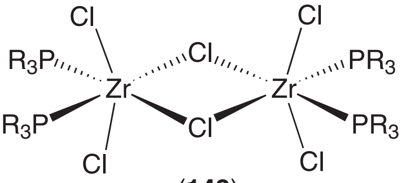
Few monomeric Zr^{III} coordination compounds are known. In 1983, Baker *et al.* reported the homoleptic phosphide Zr^{III}-metallate salt [Li(DME)] [$Zr(PCy_2)_4$], which exhibited a characteristic ESR spectrum.[287] The dissymmetric Zr^{III}-phosphide dimer $Zr_2Cl_3[P(CH_2CH_2PMe_2)_2]_3$ (**142**) was prepared via reaction of three equivalents of $Li[P(CH_2CH_2PMe_2)_2]$ with $ZrCl_4$. This compound featured two bridging phosphido groups in addition to a bridging Cl, presumably accounting for the diamagnetism of the compound.[841]



(**142**)

The reaction of ZrX_3 (X = Cl, Br) with NH_3 gave $ZrX_3(NH_3)_6$.[842] The Br adduct was relatively stable and the formulation was proposed to be $[Zr(NH_3)_6]Br_3$ based on IR data. The Cl analog, however, lost NH_3 at 25 °C, yielding a paramagnetic product formulated as $ZrCl_3(NH_3)_{2.5}$.

Dimeric Zr^{III} and Hf^{III} complexes of the form $M_2X_6L_4$(X = Cl, Br, I; L = various PR_3) (**143**) proved to be more stable. The general synthetic route to these compounds involved reduction of MCl_4 with Na/Hg (for Zr) or Na/K (for Hf) in the presence of a PR_3 ligand.[281,843–847] Crystallographic data revealed these dimers displayed edge-sharing bioctahedral geometry with M—M distances of 3.0–3.4 Å (**143**) (Table 2). Use of a bidentate phosphine as in $Zr_2Cl_6(Ph_2PCH_2CH_2PPh_2)_2$ and $Hf_2Cl_6(Pr^i{}_2PCH_2CH_2PPr^i{}_2)_2$ resulted in a reduced M—M distance. This was attributed to a decreased P–M–P bite angle.[843,849] Support for the presence of "super long" M—M single bonds in these compounds was derived from extended Hückel and *ab initio* self-consistent field theory calculations.[850]

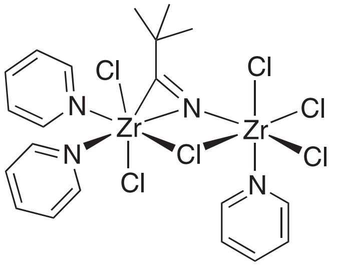


(**143**)

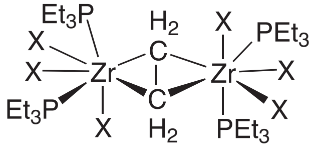
Table 2 Metal–metal distances for Zr and Hf^{III} dimers.

Formula	*M···M distance* (Å)	*Formula*	*M···M distance* (Å)
$Zr_2Cl_6(PMe_3)_4$	3.132(1)[847]	$Hf_2I_6(PMe_3)_4$	4.328(1)[281]
$Zr_2Cl_6(PEt_3)_4$	3.169(1)[843]	$Hf_2Cl_6(PEt_3)_4$	3.104(1)[846]
$Zr_2Br_6(PMe_3)_4$	3.200(1)[281]	$Hf_2Cl_6(PMe_2Ph)_4$	3.088,6(3)[844]
$Zr_2I_6(PMe_3)_4$	4.393(2)[845]	$Hf_2I_6(PMe_2Ph)_4$	4.394,8(6)[845]
$Zr_2Cl_6(PMe_2Ph)_4$	3.127(1)[843]	$Hf_2Cl_6[Pr^i{}_2PCH_2CH_2PPr^i{}_2]_2$	3.099(1)[849]
$Zr_2I_6(PMe_2Ph)_4$	3.439,0(6)[845]	Hf metal	3.159[849]
$Zr_2Cl_2(Ph_2PCH_2CH_2PPh_2)_2$	3.099(2), 3.109(2)[843]	Zr metal	3.118[848]

Ligand replacement reactions were employed to synthesize the analogous pyridine dimers $Zr_2Cl_6(NC_5H_4R)_4$ (R = H, Bu^t, $CHBu_2$) from $Zr_2Cl_6(P\text{-}Bu^n{}_3)_4$.[851] Subsequent reaction with MeCN resulted in formation of $Zr_2Cl_6(NC_5H_4R)_3(\sigma,\pi\text{–}NCBu^t)$ (**144**). The σ,π-bonding mode of nitriles has been rarely seen. In related work, the compounds $M_2X_6(PEt_3)_4$ (M = Zr, Hf; X = Cl, Br) reacted with C_2H_4 to give $M_2X_6(PEt_3)_4(CH_2CH_2)$ (**145**). These species were the first examples in which an alkene was bound orthogonally to the M–M axis.[852,853]



(144)

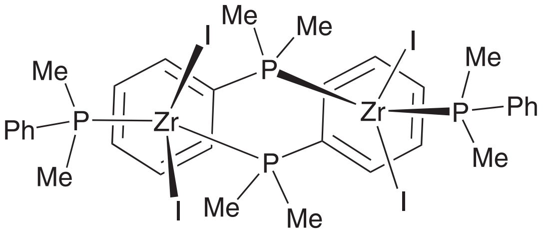


X = Cl, Br

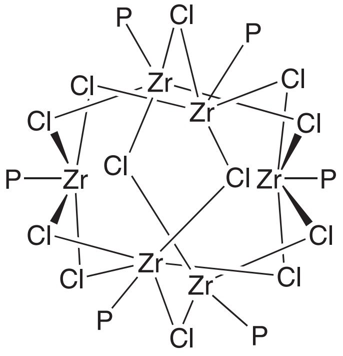
(145)

4.3.4 ZIRCONIUM(II) AND HAFNIUM(II)

The majority of coordination compounds of Zr^{II} and Hf^{II} utilize P-donor ligands to render them more stable. For example, $HfI_2(CO)_2(Me_2PCH_2CH_2PMe_2)_2$ was obtained by the reduction of $HfI_4(Me_2PCH_2CH_2PMe_2)_2$ with $K[C_{10}H_8]$ in the presence of CO.[854] While the Zr analog was not isolated, the Hf species was thermally stable in the solid state, decomposing in solution or on storage in the absence of a CO atmosphere.



(146)

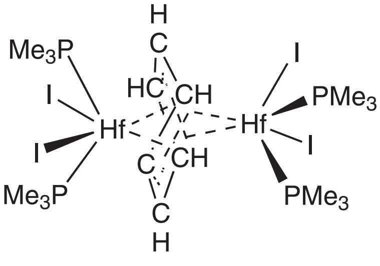


(147)

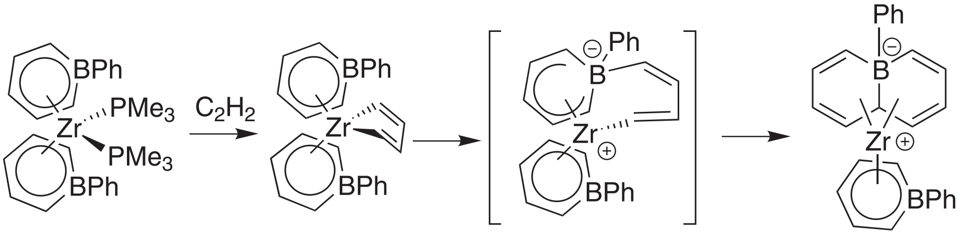
Coordination of arene rings with Zr^{II} or Hf^{II} has been reported for the species $M_2X_4(\eta^6\text{-}PhPMe_2)_2(PMe_2Ph)_2$ (**146**) (M = Zr, X = I; M = Hf, X = Br). In these dimers, the metals coordinate to both the P and the aryl substituent of a phosphine ligand.[855–857] Similarly, the hexameric species $Zr_6Cl_{12}(PMe_2Ph)_6$[855–857] was obtained, albeit in low yield. In this species, the higher degree of aggregation observed in the $Zr_6Cl_{12}P_6$ core (**147**) presumably precluded M-arene interactions.

An alternative mode of arene–M^{II} interaction was described for $Hf_2I_4(PMe_2Ph)_4(\mu\text{-}\eta^{12}\text{-Ar})$ (Ar = C_6H_6, MeC_6H_5) and $Hf_2I_4(PMe_3)_4(\mu\text{-}\eta^{12}\text{-}C_6H_6)$ (**148**) where two Hf^{II} atoms interact with either side of an arene ring resulting in a puckering of the ring. These species were obtained via reduction of $HfCl_4$ with Na/Hg in the presence of the arene and PR_3 donor.[281,858]

The bis-boratabenzene Zr^{II} complexes $Zr(C_5H_5BR)_2(PMe_3)_2$ (**149**) (R = $NPr^i{}_2$, Ph) were isolated as stable PMe_3 adducts.[859] Like the related Zr^{II} organometallic compound $ZrCp_2(PMe_3)_2$, the bis-boratabenzene derivatives were readily oxidized with reagents such as MeI or PhSSPh, while the P donors were readily displaced by bidentate phosphines. In contrast, reaction with alkynes resulted in an unusual addition to the boratabenzene affording $Zr(C_5H_5BR)(C_9H_5R^2{}_4BR)$ (R^2 = H, Me, Ph (**150**) that contained a newly formed boratanaphthalene ligand. The Zr centers of these zwitterionic molecules remained formally Zr^{II},[859–861] although this reaction was thought to be a Zr^{IV}-mediated transformation.



(148)



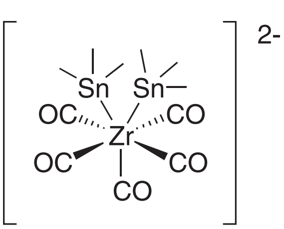
(149) **(150)**

Sn ligands complexes such as $[Pr^n_4N]_2[M(SnPh_3)_4(CO)_4]$ (M = Zr, Hf) were obtained via reduction with $K[C_{10}H_8]$ under CO in the presence of Ph_3SnNa,[862] followed by cation exchange. Crystallographic studies confirmed the eight-coordinate nature of the metal. Further, the analogous $SnMe_3$-complex $[Zr(SnMe_3)_4(CO)_4]^{2-}$ was uncovered as a decomposition product (see Section 4.3.5).[862]

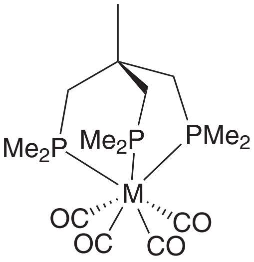
As a final example, the Zr^{II} species $Zr(TPP)Me_2$ (TPP = tetraphenylporphinato) was photochemically reduced in visible light to give $Zr(TPP)(OEt_2)_2$. This was a surprising result, given the thermal stability of the precursor.[238]

4.3.5 ZIRCONIUM(0) AND HAFNIUM(0)

The reduction of MCl_4 by Na/Hg in the presence of bipyridine, afforded $M(bipy)_3$ (M = Zr, Hf; bipy = 2,2′-bipyridyl).[863] In contrast, reduction of $ZrCl_4$ by vinyl-Li in the presence of bipyridine yielded a species formulated as $M(bipy)_4$.[864] However, the latter formulation was supported only by elemental analysis.



(151)



(152)

Subsequent work on M^0 compounds has been largely restricted to organometallic complexes; however, the seven-coordinate Zr^0 complex $[Zr(SnMe_3)_2(CO)_5]^{2-}$ (**151**) was prepared in moderate yield by reaction of $[Zr(C_{10}H_8)_3]^{2-}$ with Me_3SnCl, followed by carbonylation. Crystallographic data for $[K(15\text{-crown-}5)_2]_2[Zr(SnMe_3)_2(CO)_5]$, as well as the related anionic Zr^0 species $[K(15\text{-crown-}5)_2]$ $[ZrSnMe_3(CO)_4(Ph_2PCH_2CH_2PPh_2)]$ were reported. The former Zr^0 species is very air sensitive and readily decomposed to the more robust Zr^{II} anion $[Zr(SnMe_3)_4\ CO)_4]^{2-}$.[865] Employing a similar procedure, the complexes $M(CO)_4(Me_2PCH_2)_3CMe$ (**152**) containing a tripodal phosphine ligand were synthesized. The Zr derivative was confirmed crystallographically to have a seven-coordinate geometry.[866] The species $Zr(MeNCH_2CH_2)_3(CO)_4$ was prepared by ligand displacement of the tripodal phosphine ligand.[867] Attempts to prepare the Hf analog gave only intractable products. In contrast, the Ti analog $Ti(NCH_2CH_2)_3(CO)_4$ was characterized crystallographically.

4.3.6 NEGATIVE OXIDATION STATES OF ZIRCONIUM AND HAFNIUM

In pioneering work, Ellis and co-workers have prepared the CO complexes $[K(cryptand\ 2.2.2)]_2[M(CO)_6]$ (M = Zr, Hf) via reduction of $MCl_4(THF)_2$ with $K[C_{10}H_8]$ under CO.[868,869] The ^{91}Zr NMR spectrum provided evidence for a symmetric hexacoordinate compound. Later, crystallographic characterization confirmed the geometry.[869] The intermediate of this reaction, $[K(cryptand\ 2.2.2)]_2[Zr(C_{10}H_8)_3]$, was also characterized, although the formal oxidation state of the metal center could not be unambiguously assigned.[870] A complimentary theoretical investigation detailed the dissociation energy and vibrational frequencies of $[Hf(CO)_6]^{2-}$.[871] More recently, in matrix isolation work, IR data from laser excitation of Zr and Hf atoms in a CO/Ne environment were consistent with the formation of $M(CO)_2^-$.[872]

The syntheses of the related compounds $[Li_3(THF)_9Cl][Zr(bipyridine)_3]$, $[Li_3(THF)_9Cl][Hf(Me_4\text{-biphosphinine})_3]$, and $[Li_3(DME)_6Cl][Zr(Me_4\text{-biphosphinine})_3]$ were reported recently.[873] Crystallographic data implied that the (–II) oxidation state of the metal centers was merely a formality, as the aromaticity of the ligands was disrupted.

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4.4

Vanadium

D. C. CRANS and J. J. SMEE
Colorado State University, Fort Collins, CO, USA

4.4.1 INTRODUCTION, PERSPECTIVE, AND ORGANIZATION

Progress in the chemistry of vanadium in the IV, III, II, I, 0, and −I oxidation states has been exponential since the previous review on vanadium chemistry in *Comprehensive Coordination Chemistry* (*CCC*, 1987).[1,2] This growth is now reflecting the rich complexity of aqueous vanadium chemistry under a variety of conditions (see Figure 1).[3] Dramatic progress has been reported since the early 1980s, particularly in vanadium(V) chemistry, which presumably can be attributed to the fact that complexes with this oxidation state are diamagnetic and can readily be subjected to NMR analysis. Furthermore, the discovery of the haloperoxidases which involve peroxovanadium(V) compounds, the synthetic utility of some vanadium(V) complexes in catalysis and as materials, and the fact that contrary to previous expectations, vanadium(V) complexes have insulin-enhancing properties have all contributed to the rapid growth in this area of vanadium chemistry. However, progress has continued for vanadium(IV) and (III) chemistry and well over 3,000 papers have been reported since the mid-1980s for vanadium coordination chemistry as a whole. The coordination chemistry of the lower oxidation states (+2 and below), however, has failed to accumulate 100 papers over the same time period.

This review will summarize the progress in the coordination chemistry of vanadium in the V, IV, III, II, I, 0, and −I oxidation states. The coordination number of vanadium compounds varies from four to eight depending on the ligands used and the oxidation state of the metal. A number of complexes are illustrated and when one ligand type has been used the charges have been indicated (Figures 2–22, Structures **1–235**). Vanadium is typically found to have distorted coordination geometries. Since the area is too large to fully do justice to all the work, we must rely on previous reviews that have described various specialized areas of vanadium chemistry. Comprehensive reviews have been reported on bioinorganic vanadium chemistry,[4–17] vanadium compounds as insulin-enhancing compounds,[18–21] peroxovanadium(V) chemistry,[22] applications of vanadium compounds in organic synthesis[23] and in catalysis.[24–26] In addition, reviews on general vanadium chemistry,[2,3,5,8,27–29] structural advances,[30–32] and areas such as environmental vanadium chemistry,[33,34] aqueous vanadate chemistry,[35] vanadate as a phosphate analog and related biochemistry,[36,37] haloperoxidases,[38–40] and the modeling of nitrogenase and vanadium–nitrogenase.[8,41,42]

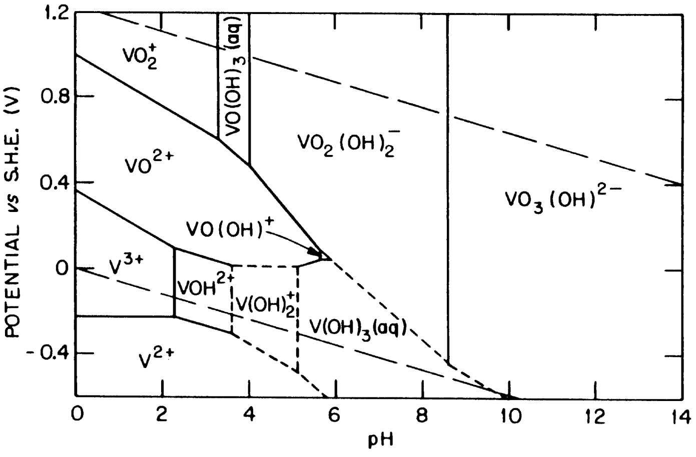

Figure 1 Diagram of potential (vs. SHE) vs. pH for vanadium species present in dilute solutions. The upper and lower dashed lines represent 1 atm O_2 and 1 atm H_2, respectively (reproduced with permission from Baes and Mesmer;[3] © 1976,Wiley. This material is used by permission of Wiley).

The organization of the main body of this review is structural in the sense that complexes are described in the order of mono-, bi- and polydentate ligands containing first O-donors, then N-donors and S-donors followed by halides and other donor atoms. The chemistry will be categorized based on the amounts of work carried out since the mid-1980s. Furthermore, since the previous review did not describe V^V chemistry, the review of this oxidation state has been made slightly more extensive. Attempts have been made to include the most significant contributions, however, in areas such as Schiff base complexes, this review focuses on a description of the diversity of vanadium compounds by the scientific community rather than a complete report of all the contributions from any particular research group. A section has been added at the end of this review with a topical perspective to enhance the coverage and usefulness of this review as a starting point for information to vanadium chemists. In view of the limited space, we refer the readers to the previous review by Vila Boras and Pessoa[2] and the many other reviews mentioned above because their excellent descriptions of many areas of vanadium chemistry go beyond the scope of this review.

4.4.2 VANADIUM(V)

4.4.2.1 Aqueous Vanadate (V^V) Chemistry

Vanadate in the solid state exists in four- and five-coordinate forms such as NH_4VO_3, $KVO_3{\cdot}2H_2O$ and V_2O_5.[27] In solution, all of these species will form oxometalates (see Figure 2) which are based on the $H_2VO_4^-$ anion (**1**) and can be dimeric (**2**), trimeric (only a very minor species in a limited pH range),[43,44] tetrameric (the major species under many conditions) (**3**), pentameric (**4**),[43–46] plus higher forms described elsewhere in this series. Some solid state characterization of trinuclear (**5**),[47] tetranuclear (4)[48] and pentanuclear (**6**)[45,49] species isolated from organic solvents have been reported and may be related to the species existing in aqueous solution.[47,48] The specific species that exist (see Figure 2) are best viewed in speciation diagrams and will vary with pH, ionic strength, concentration and temperature.[3,43–46,50] Although speciation diagrams of the simple vanadate system were reported some time ago, new studies have taken this speciation to the current level of accuracy.[43–46] Formation constants, pK_a values and ^{51}V NMR chemical shifts for the major V^V species in solution are shown in Table 1. Below pH 3 the anionic forms all convert to the hydrated form of VO_2^+, which is the fundamental *cis*-dioxovanadium unit often found in vanadium(V) complexes. Line-broadening of the ^{51}V NMR signal for VO_2^+ has been attributed to the exchange reaction between the VO_2^+ cation and a mixed-valence $VO_2^+{-}VO^{2+}$complex.[51] The cation VO_2^+ is redox active and the rate law of the reaction is sensitive to the nature of the acidic medium[52] and the reducing agent.[53] The $H_2VO_4^-$ anion is often referred to as a phosphate analog given the structural and electronic similarities with this anion.[9–12,29,35–37,54,55] In fact, the pK_a values for phosphate (2.1, 7.2, and 12.7) correspond closely with those of vanadate (3.5, 7.8, and 12.5).[9] In contrast to the high stability of H_3PO_4, the existence of H_3VO_4 was previously disputed.[45,46] Furthermore, thermodynamic evidence has recently been provided to support the high stability of VO_2^+ which arises from the increased coordination number of the hydrated form.[56]

^{51}V NMR spectroscopy is a particularly useful method for solution studies of vanadium(V) complexes. Several correlations of the shielding in vanadium(V) complexes have been reported and have been used as empirical guides to the coordination number of the vanadium.[57–64] Application of these correlations should, however, be used cautiously. ^{17}O NMR spectroscopy[65] and extended X-ray absorption fine structure (EXAFS) spectroscopy have been used for the characterization of solution complexes.[66] Methods including potentiometry, X-ray diffraction, and UV–visible and IR spectroscopic techniques are also widely used in the characterization of the properties of vanadium complexes. Other methods for the characterization of low-level (sub-microgram) vanadium complexes have been described.[67,68]

4.4.2.2 Oxygen Ligands

4.4.2.2.1 Monodentate, one oxygen donor

Vanadium(V) forms complexes with monodentate ligands such as alkoxides and carboxylates. Given the analogy between $H_2PO_4^-$ and $H_2VO_4^-$, vanadium(V) alkoxides are often referred to as

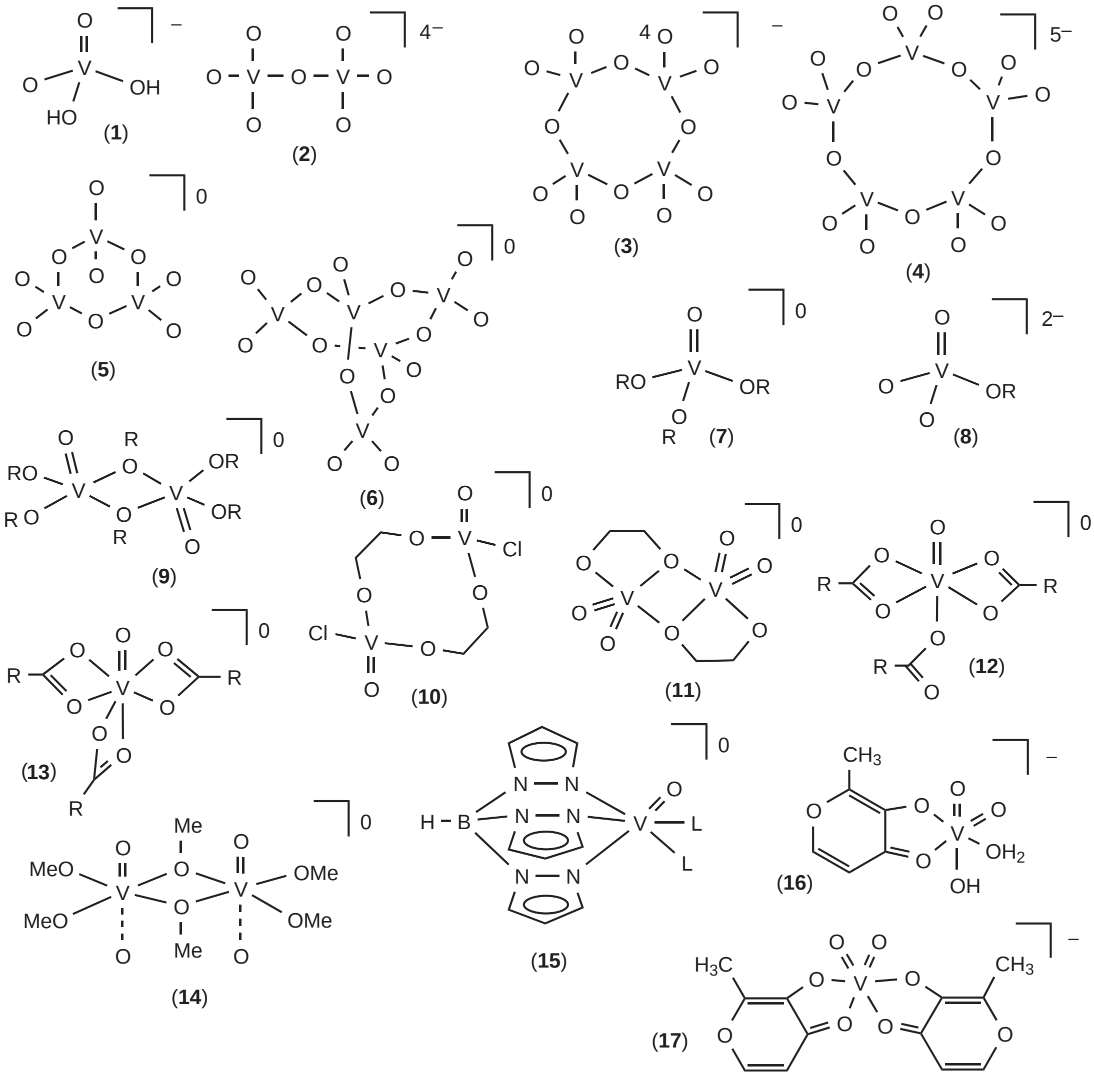

Figure 2 Structural illustrations of (**1**–**17**).

esters (**7**–**11**) and complexes with carboxylic acids (**12**,**13**) are referred to as carboxylates or anhydrides.

(i) Alkoxides and phenoxides (esters)

Vanadium(V) alkoxides have been known since 1913,[69] and in Table 2 we show some of the known alkoxides, the parent alcohol, and the nature of the complex in organic solvents and in aqueous solution. Alkoxides have been prepared from methanol, ethanol, isopropanol, *t*-butanol, silsequioxanes, cyclopentanol, cyclohexanol, norborneol, adamantanol, phenol, and other alcohols (see Table 2).[70–90] The simple complexes associate in organic solvents and dimerization in the presence of alkoxide is observed with the isopropanol complex.[70] The more sterically hindred alcohols are less reactive and do not hydrolyze completely in the presence of small amounts of water.[73] The first simple alkoxide to be structurally characterized was the methoxide complex (**14**) and the vanadium was found to be a six-coordinate dinuclear species; however, the structure of this compound did not refine very well.[91] This was the first report of the diamond core {V—O—V—O} unit, albeit associated with two six-coordinate vanadium atoms. The diamond core {V—O—V—O} (**11**), which has since then been found to be a typical structural unit for these complexes, was distinctly asymmetric revealing a difference in the interactions between the two mononuclear parts of the molecule. The first monodentate alkoxide found to contain

Table 1 Stoichiometry, formation constants, pK_a values and ^{51}V NMR chemical shifts for the major V^V species in aqueous solution (ionic strength = 0.6 M NaCl).[a]

Species	*Abbreviation*	*δ (^{51}V)*(ppm)[c]	pK_a	*p,q*	*log*β_{pq}[b]
VO_4^{3-}	V_1	−541.2		−2,1	−21.31
HVO_4^{2-}	V_1'	−538.8	14.4	−1,1	−7.91
$H_2VO_4^-$	V_1''	−560.4	7.91	0,1	
VO_2^+		−545		2,1	6.97
$V_2O_7^{4-}$	V_2	−561.0		−2,2	−15.13
$HV_2O_7^{3-}$	V_2'	−563.5	9.74	1,2	−5.39
$H_2V_2O_7^{2-}$	V_2''	−572.7	8.29	0,2	2.90
$V_4O_{13}^{6-}$		−566 to −585[d]		−2,4	−8.5
$HV_4O_{13}^{5-}$		−566 to −585[d]	8.9	−1,4	0.4
$V_4O_{12}^{4-}$	V_4	−577.6		0,4	10.04
$V_5O_{15}^{5-}$	V_5	−586.0		0,5	12.43
$V_{10}O_{28}^{6-}$	V_{10}	−422, −496, −513		4,10	51.98
$HV_{10}O_{28}^{5-}$	V_{10}'	−424, −500, −516	6.14	5,10	58.12
$H_2V_{10}O_{28}^{4-}$	V_{10}''	−425, −506, −524	3.68	6,10	61.80
$H_3V_{10}O_{28}^{3-}$	V_{10}'''	−427, −515, −534	1.57	7,10	63.37

[a] Data is taken from ref. 45. [b] log β for the equilibrium $pH^+ + qH_2VO_4^-$ $(H^+)_p(H_2VO_4^-)_q$. [c] Relative to $VOCl_3$. [d] A value within the indicated range has been reported.

five-coordinate vanadium was the 2-chloroethoxide derivative, which has a diamond core unit.[78] Mononuclear complexes have only been observed with sterically hindered, monodentate ligands such as cyclopentanol[71,74,87] and phenol[90,92] (see Table 2). Four-coordinate oxovanadium alkoxides have been prepared from monodentate alkoxides, including oxovanadium *t*-butyl,[69,73,78,84,88,89,93] adamantyl[74] and norbornyl[74] alkoxides (see Table 2). Examples of such complexes that have been structurally characterized involve aryloxide[94] and trisilyloxide[72] as ligands. Recently, the X-ray structure of tris(2,6-diisopropylphenoxo)oxovanadium(V) was reported to show a four-coordinate V^V center.[81]

In many cases the charged mono- and dialkoxides have been observed in aqueous solution and are often described as monoesters, and diesters.[73,93,95–100] These esters form upon mixing vanadate with alcohol in aqueous solution[95] and are characterized with ^{51}V NMR spectroscopy. The low stability of these esters precludes characterization with other routine methods. The formation constants for aliphatic and aromatic alcohols in aqueous solution are very small, typically about $0.2\,M^{-1}$ for the formation of alkyl esters[73,93,95–99] and about $1.0\,M^{-1}$ for phenyl and tyrosyl vanadate esters.[92] The formation of vanadate tyrosinate moieties by vanadylation of protein tyrosine hydroxyls may have some significance in cell signaling.[101] The phenoxide complex with the stabilizing tris(pyrazolyl)borate ligand (tpb) has been made as a model complex for the active site of bromoperoxidase.[102]

Stabilizing the vanadium with auxiliary ligands makes it possible to form complexes with various functionalities including the alkoxy functionality. Such classes of ligands include pyrazolyl borates (**15**)[102] and Schiff bases, and will be described in the appropriate multidentate ligand section.

(ii) Carboxylates (anhydrides)

The complexes derived from simple monodentate carboxylates are not stable, and only one mononuclear complex with a sterically hindered carboxylate has been successfully isolated, $[VO(O_2C^tBu)_3]$ (**13**).[103] Attempts to prepare carboxylates in organic solvents often led to the formation of oligomeric cluster compounds with a variety of interesting structural types.[103] In aqueous solutions, these vanadium complexes appear to contain six-coordinate vanadium.[60,104] Even carbonate has been found to form a weak vanadium(V) complex in solution.[105]

Weak complexes form between vanadate and phosphate,[59,99] pyrophosphate,[59] arsenate,[59] and chromate.[106] The formation constant for the simple phosphovanadate is about $20\,M^{-1}$.[99] Structural characterization has been reported for interesting cluster structures of vanadium with organophosphonates[107] and with sulfate.[108] Divanadium(V) complexes with either monodentate or bidentate nitrate (NO_3^-) groups have been reported.[109]

Table 2 Known alkoxide, dialkoxide, aryloxide, diaryloxide, and dicarboxylate vanadium(V) complexes and their characterization in both organic and aqueous solvent systems.

Ligand	*Species in organic solvents*	*Organic solvents (references)*	*Species in aqueous solution*	*Aqueous solution (references)*
$HOCH_3$	$[VO(OCH_3)_3]$	EA, X-ray, ^1H, ^{51}V NMR (69,82–84,91)	$[VO_2(OH)(OCH_3)]^-$, $[VO_2(OCH_3)_2]^-$	^{51}V NMR (99)
$HOCH_2CH_3$	$[VO(OCH_2CH_3)_3]$	EA, ^1H, ^{13}C, ^{51}V NMR (69,82,83,85)	$[VO_2(OH)(OCH_2CH_3)]^-$, $[VO_2(OCH_2CH_3)_2]^-$	^{51}V NMR (73,95)
$HOCH(CH_3)_2$	$[VO(OCH(CH_3)_2)_3]$ $[VOCl(OCH(CH_3)_2)_2]$ $[VOCl_2(OCH(CH_3)_2)]$ $[VO(OCH(CH_3)_2)_4]^-$	EA, ^1H, ^{51}V NMR (70,82-84)	$[VO_2(OH)(OCH(CH_3)_2)]^-$, $[VO_2(OCH(CH_3)_2)_2]^-$	^{51}V NMR (73,93)
$HOC(CH_3)_3$	$[VO(OC(CH_3)_3)_3]$	EA, ^1H, ^{13}C, ^{51}V NMR (69,78,84,88,89)	$[VO_2(OH)(OC(CH_3)_3)]^-$ $[VO_2(OC(CH_3)_3)_2]^-$	^{51}V NMR (73,93)
$HOCH_2CH_2Cl$	$[VO(OCH_2CH_2Cl)_3]$	EA, X-ray, ^{51}V NMR (78)	$[VO_2(OH)(OCH_2CH_3)]^-$	^{51}V NMR (73)
Cyclopentanol (C_5H_9OH)	$[VO(OC_5H_9)_3]$ $[VO(OC_5H_9)_3]_2$	X-ray, ^1H, ^{13}C, ^{51}V NMR (71,74,87)	$[VO_2(OH)(OC_5H_9)]^-$	^{51}V NMR (87)
Cyclohexanol	$[VO(OC_6H_{11})_3]$	EA, ^1H, ^{51}V NMR (74,82,84)	NA	NA
Adamantanol ($C_{10}H_{15}OH$)	$[VO(OC_{10}H_{15})_3]$	EA, ^1H, ^{13}C, ^{51}V NMR (74)	NA	NA
Norborneol ($C_7H_{11}OH$)	$[VO(OC_7H_{11})_3]$	EA, ^1H, ^{13}C, ^{51}V NMR (74)	NA	NA
Phenol (C_6H_5OH)	$[VO(OPh)_3]$	EA (90)	$H[VO_3(OC_6H_5)]^-$ $[VO_2(OC_6H_5)_2]^-$	^{51}V NMR (92)
2,6-diisopropyl-phenol ($C_{12}H_{17}OH$)	$[VO(OC_6H_3Pr^I{}_2\text{-}2,6)_3]$	EA, IR, ^1H, ^{51}V NMR, X-ray (81)	NA	NA
$HOSiPh_3$ ($C_{18}H_{15}SiOH$)	$[VO(OSiPh_3)_3]$	EA, IR, ^1H NMR, X-ray (72,86)	NA	NA

Ethanediol (ethylene glycol)	1:2 for both [VO_2] and [VOCl] units	EA, ^1H, ^{13}C, ^{17}O, ^{51}V NMR (112,113,126)	1:2[a]	^{51}V NMR (97)
Pinacol ($C_6H_{14}O_2$)	1:2 for [VOCl] unit	EA, X-ray, ^1H, ^{13}C, ^{51}V NMR (55)	NA	NA
1,2-Cyclohexanediol ($C_6H_{12}O_2$)	NA	NA	2:2	^{51}V NMR (110)
Sugars	NA	NA	2:2	EA, X-ray, ^1H, ^{13}C, ^{51}V NMR (110,121)
Adenosine	1:2	EA, X-ray, ^1H, ^{51}V NMR (115)	2:2[a]	^1H, ^{13}C, ^{51}V NMR (100,111,116,119,122)
Cytidine	NA	NA	2:2[a]	^1H, ^{13}C, ^{51}V NMR (116,119)
Guanosine	NA	NA	2:2[a]	^1H, ^{51}V NMR (119)
Inosine	NA	NA	2:2	^1H, ^{51}V NMR (54)
Uridine	NA	NA	2:2[a]	^1H, ^{13}C, ^{51}V NMR (116,117,119)
Glyceric acid ($C_3H_6O_4$)	NA	NA	1:1, 1:2[b]	^{51}V NMR (60)
Oxalic acid ($C_2H_2O_4$)	NA	NA	2:1[a]	^{51}V NMR (60)
Ethylhydroxybutanoic acid ($C_6H_{12}O_3$)	NA	NA	2:2	X-ray, IR, ^1H, ^{13}C, ^{51}V NMR (120)
Catechol ($C_6H_6O_2$)	[VO ($C_6H_4(O)OH)_3$][c]	EA (90)	NA	NA

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[a] 1:1 complex is a minor species in solution. [b] 2:2 complex is observed as a minor product. [c] Ligand is readily oxidized.

4.4.2.2.2 Bidentate, two oxygen donors

(i) Alkoxide ligands

Four-coordinate vanadium complexes (**7,8,10**) are structural models of the ground state product of phosphate ester hydrolysis while five-coordinate vanadium complexes (**9,11**) are structural models of the transition state. Vanadate reacts with 1,2-diols to form several products the major of which is a 2:2 complex (**11**)[97,110–113] (although one report has appeared to the contrary[114]). The structure of this basic unit has been characterized for a number of different diols both in the solid state and in solution (see Table 2). The 2:2 complex is significantly stabilized when the vanadium is complexed to the *cis*-coplanar arrangement of the 2′,3′-hydroxyls in a ribose ring or cyclohexane diols,[110] in pyranose forms of various protected monosaccharides[110] and in nucleosides.[54,73,115–117] The structure of these complexes is of interest because vanadate is a much more potent inhibitor for ribonuclease in the presence of a nucleoside[118] and complex formation is anticipated. Although the 2:2 complex is most stable, the complex binding to the enzyme is likely to be a 1:1 vanadium–nucleoside complex. Ternary ligands such as tris(hydroxymethyl)aminomethane[119] and imidazole[73] have been shown to effectively compete with the formation of the 2:2 complexes and generate stable vanadate–nucleoside–ligand complexes in aqueous solution. It is possible that the ribonucleoside in the vanadate–nucleoside–ribonuclease moiety is a stabilizing ternary ligand.

The first structural model complex for the ribonuclease system employed pinacol as a ligand;[55] several examples of this type of system, each focusing on different aspects of the complex, have now appeared.[115,120,121] The vanadium is five-coordinate with the diamond core {V—O—V—O} motif forming in all of these complexes (**11**).[115] Spectroscopic evidence suggests that the dimerization constant is on the order of $10^6\,M^{-1}$ or $10^7\,M^{-1}$ and accordingly the 1:1 species will exist in comparably low concentrations regardless of its formation constant.[122] Mono- and dinuclear complexes form with Schiff base ligands and serve to mimic the presumed transition state of vanadium complexes in ribonuclease.[123] Other systems are models for the nitrogenase active site and the reactivities of these complexes with cysteine and other biometabolites have been investigated.[124]

Oxovanadium(V) alkoxides have also been reported with bidentate alkoxy ligands. A ligand such as tris(pyrazolyl)borate (**15**)[125] can be used to help stabilize these complexes. The isolated ethylenediol compound does not contain the diamond core motif even though the complex is dinuclear (**10**).[126] *Ab initio* and electrostatic calculations were done on the pinacol and ethylenediol complexes[76] to investigate this structural preference. Relatively few simple complexes have been reported with diols (excluding the 1,2-diols) because they typically form oligomeric species such as that from 1,3-propanediolate;[127] however, an appropriately chosen ternary ligand will promote complex formation.[77,128–130] A monomeric complex was, however, found for an aryloxide with a C4-fragment (extending over two phenyl groups) between the OH groups.[94]

The aqueous speciation of the vanadate–maltol system has been characterized, describing complexes which chelate the vanadium(V) in a bidentate manner (**16**,**17**).[131] The formation of the corresponding vanadium(V) complex of 2-hydroxycyclohexanone (analogous to **17**) has been proposed as an intermediate in the oxidation of cyclohexanone.[132] Squaric acid forms a series of mono- and dinuclear complexes with vanadium(IV) and (V).[133] Subtle differences in the structure are observed depending on the oxidation state of the vanadium, and are induced by the rigid ligand structure.

(ii) Carboxylates

^{51}V NMR spectroscopic studies have been carried out with simple dicarboxylates and simple mixed alkoxide–carboxylate systems.[60] The complexes that form are generally stable in the acidic pH range. Recent investigations employ a combination of both solid state[124] and solution studies, and provide benchmark data for one of the classes of α-hydroxycarboxylate complexes which form in aqueous solution (VL^-, VL_2^-, $V_2L_2^{2-}$, and $V_3L_2^-$).[98]

A number of ternary complexes with simple dicarboxylic acid complexes supported by other ligands have been reported. These include the mixed valence $V^{IV,V}$ complex with 2,2′-bipyridine (bpy) as the supporting ligand[134] and the dinuclear vanadium(V) oxalate-bridged complex.[135] The structure–reactivity relationship in the redox series $V^{V,IV,III}$ chelated to 2-ethyl-2-hydroxybutanate differs from that which is observed for $Cr^{V,IV,III}$.[136] The structural change observed between the $V^{IV,III}$ are consistent with the expected change between oxidation states IV and III.[136] Vanadium-(IV) and (V) complexes with oxyoxime have been characterized in solution using EXAFS spectroscopy.[66]

(iii) Catechol complexes

Vanadium complexes with catechols have been of interest to chemists[80,98] due to the catalytic properties of such complexes,[137,138] and the possible involvement of catecholate complexes in the tunicate accumulation and reduction of vanadium.[40,63,139,140] Several new vanadium(V) catecholate complexes have been reported. Of particular interest are the non-oxovanadium(V) complexes with 2,2′-bipyridine and 1,10-phenanthroline (phen) serving as auxiliary ligands.[141]

(iv) Peroxovanadium complexes

Peroxovanadium complexes are among the most versatile vanadium complexes with regard to both structure and reactivity. In aqueous solution, a number of peroxovanadium(V) complexes are produced, including mono-, bis-, tris- and tetraperoxo complexes. Their reactivities have been investigated.[22] A number of these complexes have been structurally characterized (Table 3).[22,142] Mononuclear vanadium complexes have been described and contain one O_2^{2-} unit (**18**–**23**),[143–167] two O_2^{2-} units (**24**–**26**),[168–183] three O_2^{2-} units (**27**)[174,184] and four O_2^{2-} units (**28**).[185] Binuclear complexes include ones with two (**29**–**31**),[186–194] three (**32**,**35**),[195,196] and four O_2^{2-} units (**33**–**35**).[197–202] Their catalytic properties are of great interest because of their role in the oxidation catalyzed by haloperoxidases,[38,39] and their unsurpassed activation of insulin receptor-mediated protein phosphorylation.[21] In addition, some peroxo hetero ligand vanadate complexes have shown anti-tumor activity.[203]

In the absence of reducing substrates, diperoxovanadium(V) compounds are generally hydrolytically quite stable in the neutral and slightly alkaline pH ranges. Although most reported complexes contain one O_2^{2-} unit, the diperoxovanadium complexes (**24**–**26**) are the most stable under a range of conditions.[204,205] Compounds with O- and N- donor ligands make up the bulk of the monoperoxovanadium(V) complexes (**18**–**23**). These ligands include *N*-(carbamoylmethyl)iminodiacetate,[162,164] histidine and derivatives,[160,206] glycine,[207] and 3,5-dimethylpyrazole.[206] Peroxovanadates in aqueous solution coordinate a large number of ancillary ligands, including substituted carboxylic acids,[181,208,209] amino acids,[210] peptides,[143,211] nicotinic acid,[212] and nucleosides[213] to form both mono- and bisperoxovanadium–ligand complexes. These types have been studied even more extensively than the parent systems because of their favorable catalytic properties and their potent insulin-enhancing properties. The phenanthroline diperoxovanadium(V) complex has been reported to cleave DNA.[214] A few mono- and dinuclear complexes have been reported with all O-donors as the supporting ligand in addition to the O_2^{2-} unit.[194,215]

The dinuclear peroxo complexes exhibit an additional level of complexity (**29**–**35**). Their compositions are closely tied to the denticity of the coordinating ligand: bidentate and tridentate ligands tend to form complexes with a $V:O_2^{2-}$ ratio of 1:1,[186–194] whereas more complex systems form with monodentate ligands[195,197–202] (see Table 3). ^1H and ^{51}V NMR spectroscopic studies report the first dinuclear peroxovanadium complex containing an oxovanadium center on one of the vanadium atoms.[215] Interesting oligomeric systems include a tetranuclear vanadium(V) complex with eight peroxo groups.[216]

Aqueous–methanolic vanadate solutions (acidified by $HClO_4$) in the presence of hydrogen peroxide will mimic the reaction of the vanadium bromoperoxidase enzyme.[217] Mechanistic studies are in general complicated by the light- or metal ion-initiated disproportionation of peroxovanadium(V) centers which leads to the release of oxygen and water. However, peroxovanadates complexed to ternary ligands in aqueous solution are, in general, even better oxidants. Numerous studies have been carried out with simple systems, both on the complexation of vanadate by hydrogen peroxide[29,40,204,217–224] and on the oxidative reactivity of the peroxovanadium complexes formed.[225] Studies on various peroxo complexes[29,40,226,227] show that these complexes also are competent to alkylate,[228] iodinate[165,166,229,230] and brominate.[205,231] Mechanistic studies with the parent system[224] and with a series of tetradentate ligands (including *N*,*N*-bis(2-pyridylmethyl)glycine, *N*-(2-pyridylmethyl)imidodiacetic acid, *N*-(2-amidomethyl)iminodiacetic acid and nitrilotriacetic

Table 3 Summary of the structural features of the crystallographically characterized peroxo complexes.[a,b]

Peroxo ligands	*CN*	*Other ligand(s)*[a]	*Ligand denticity*	*Structural illustration*[b]	*References*
1	6	Glycylglycine	3	**18**	143
1	7[c]	Iminodiacetic acid	3	**19**	144
1	7	Picolinic acid, H_2O × 2/Bipyridine, Fluoride × 2/Phenanthroline, H_2O × 2	2,1,1	**20**	145–147
1	7	Oxalic acid × 2/Bipyridine × 2/ Phenanthroline × 2/Picolinic acid, Bipyridine/Picolinic acid × 2/ Picolinic acid, Phenanthroline/ Pyrazine-2-carboxylic acid × 2	2,2	**21**	147–151
1	7	Dipicolinicacid,H_2O/1-(2-pyridylazo-)-2-naphthol,pyridine/ Tris(3,5-diisopropyl-pyrazol-1-yl)borate, H_2O	3,1	**22**	152–154
1	7	Nitrilotriacetic acid (4 structures)/ D,L-*N*-Carboxymethyl-histidine/ Ethylenediamine-tetraacetic acid(2 structures)/*N*-(carbamoylethyl)-iminodiacetatic acid (2 structures)/ *N*-(carbamoylmethyl)-iminodiacetatic acid (2 structures)/*N*-(2-hydroxyethyl)-iminodiacetic acid/ *N*,*N*-bis(2-pyridylmethyl)-glycine/ *N*,*N*-bis(2-pyridylmethyl)-β-alanine	4	**23**	155–167
2	6	Ammonia/Fluoride (2 structures)/ Fluoride[c]/Imidazole	1	**24**	168–172
2	7	Fluoride × 2	1,1	**25**	173

2	7	Oxalic acid (3 structures)/Carbonate/Bipyridine (4 structures)/Picolinic acid/3-hydroxy-picolinic acid/2,4-pyridine dicarboxylic acid/3-acetatoxy-picolinic acid/5-nitro-phenanthroline	2	**26**	174–183
3	7	Hydroxide/Fluoride[d,e]	1	**27**	174,184
4	8	NA	NA	**28**	185
2	6,6	Glycolic acid × 2/D-lactic acid, L-lactic acid (2 structures)/L-lactic acid × 2/Mandelic acid × 2	2,2	**29**	186–189
2	7,7 or 6,6[f]	Citric acid (2 structures)/Malic acid (4 structures)	3,3	**30**	190–193
2	7,7	L-tartaric acid × 2,$H_2O(L')$	2,2,1	**31**	194
3	7,7	Fluoride ×3	1,1,1	**32**	195
4	6,6	H_2O (3 structures)	1	**33**	197–199
4	7,7	Oxide (2 structures)/Hydroxide	1	**34**	200–202
3	7,7	PO_4	2	**35**	196

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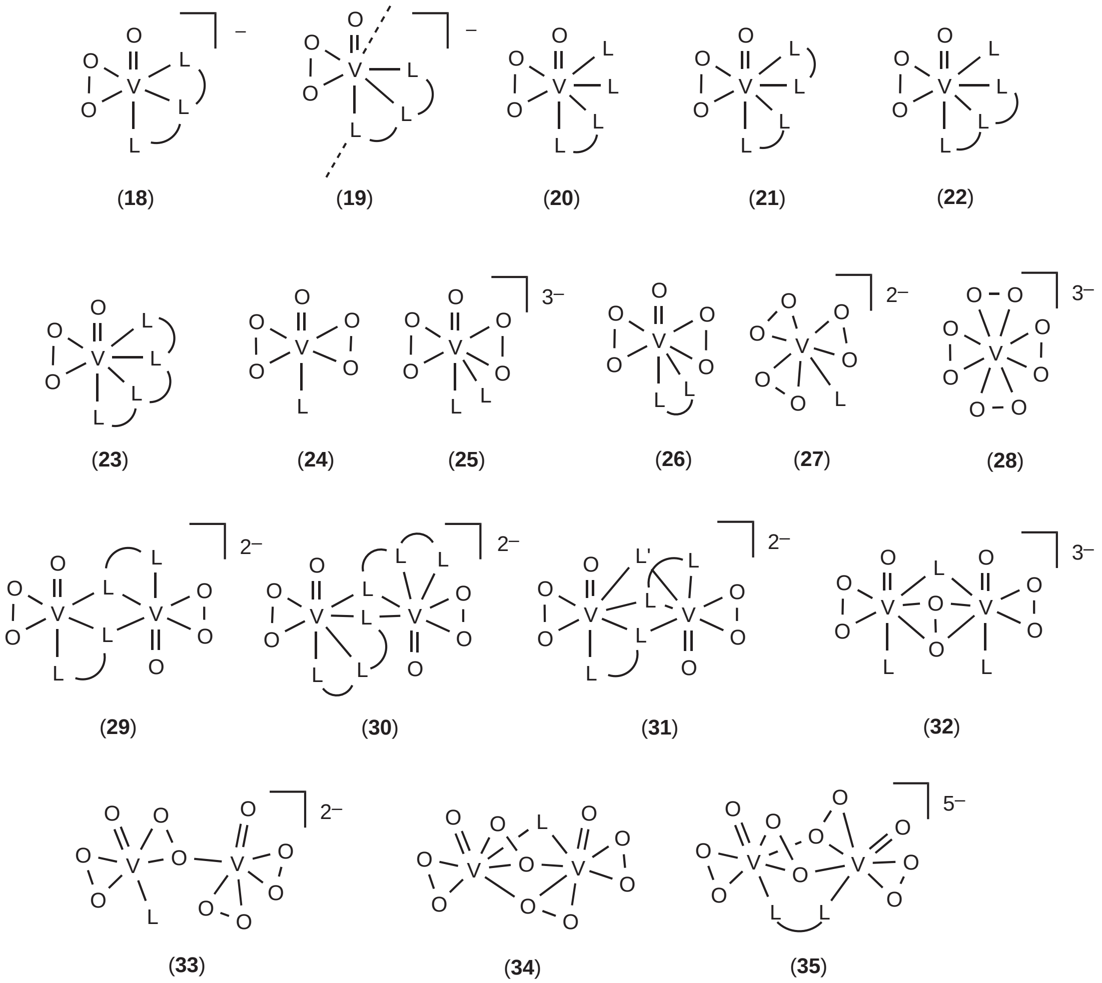
[a] The ligand sets of each structure are separated by a '/'. If two (or three) of the same ligands are present in a given structure, then the number of such ligands is denoted by ×2 or ×3; the number of structures of the same complex appear in parentheses. [b] The key to the structural illustrations is shown in Figure 3. [c] The complex forms an extended array with an adjacent V=O group serving as the seventh ligand. [d] The structure drawn is derived from diffraction data that is only refined to $R = 0.25$. [e] The complex crystallizes as polymeric chains linked by weak interactions between a carboxylate oxygen and an adjacent vanadium center. [f] The terminal carboxylate oxygens trans to the doubly bonded oxo ligands weakly interact with the vanadium ($V–O_{carboxylate}$ distance of ~2.5 Å).


(18) (19) (20) (21) (22)

(23) (24) (25) (26) (27) (28)

(29) (30) (31) (32)

(33) (34) (35)

Figure 3 Structural illustrations of vanadium peroxo compounds (**18**–**35**). The charges are given for structure types in which all the complexes have the same charge. For structure types that have differently charged ligands, no charge is given.

acid) showed that peroxide binds to a protonated form of the vanadium complex in an associative manner followed by the loss of hydroxide or water.[232] These studies were supported by recent investigations of the reaction of phenol red with simple peroxovanadates which suggested that the active species is the vanadium complex.[233]

The first evidence for activation of exogenous O_2 on a vanadium(IV) center was obtained recently.[154] The reaction of vanadium(IV) hydroxo tris(3,5-diisopropylpyrazol-1-yl)borate with O_2 resulted in the corresponding peroxo complex, which was structurally characterized and found to belong to the class of compounds illustrated in (**22**).[154]

4.4.2.2.3 *Bidentate, one oxygen donor*

Complexes of isoelectronic analogs of the peroxo ligand, mono-deprotonated hydroxylamines (NH_2O^-) and hydroxamic acids ($RC(=O)NHO^-$) have been characterized. The Wieghardt group studied several of these complexes more than two decades ago.[234–237] Since then the reaction of vanadate with hydroxylamine was investigated in aqueous solution,[238,239] and the structural characterization of several derivatives illustrates the rich coordination chemistry of these complexes.[240] Interestingly, with monodentate ligands, the NH_2 groups are coordinated cis (**36**), but when the auxiliary ligand is bidentate, the O^- groups are *cis* (**37**).[240] Differences in reactivity between the hydroxylamido and peroxo complexes are observed with sulfur-containing ligands such as cysteine.[241] Alkylated hydroxylamido vanadium(IV) complexes have been of long-standing interest due to the occurrence of the natural product amavadine.[242–247] Although the natural product contains V^{IV}, the corresponding V^{V} complexes have also been reported.[4,6,243,244] Vanadium complexes with hydroxylamido ligands have been shown to be potent inhibitors of several protein tyrosine phosphatases.[248]

Simple complexes of hydroxamic acids with vanadium(V) have been reported, including ones with a variety of nuclearities.[249,250] A wide range of *N*-substituted mono- and dihydroxamic acids undergo oxygen abstraction upon reaction with V^{III} and V^{IV} to form V^{V} hydroxamate complexes and the respective amides and diamides.[251]

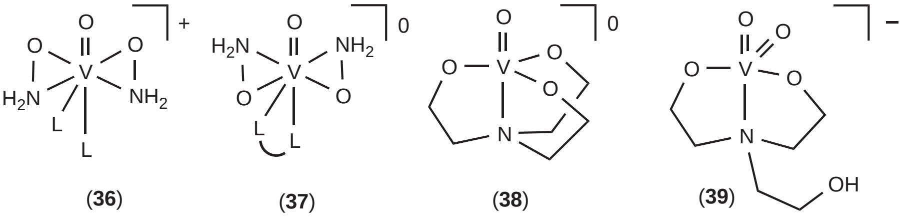
A variety of other NO donor ligands including pyrazine-2-carboxylate, *o*-amino-benzoate, picolinate and pyrazine-2-carboxylate have been prepared and their roles in catalysis discussed.[151] Amino acids and aminoethanol ligands only form weak complexes with vanadate.[252] However, simple amino acids have been investigated in detail.[210,253] With glycine (gly), potentiometric experiments suggest that two types of complexes form, $[VO_2(gly)]$ and $[VO_2(gly)_2]^-$.[253] The carbonyl amide oxygen binds to the vanadium center in organic solvents, and a series of these complexes have been structurally characterized.[254] Quinolate forms strong complexes with vanadate and a variety of complexes have been reported.[255,256] Complexes with a chiral alkoxide/quinolate ligand give rise to the observation of diastereomers.[256]

4.4.2.2.4 *Polydentate, three or more oxygen donors*

Relatively few complexes with this type of polydentate ligand have been reported. Citrate is found to form a dinuclear complex with the diamond core {V—O—V—O}.[190,191,257,258] A mixed valence V^{V}—V^{IV}—V^{V} trinuclear complex has been reported with quinic acid.[259] This compound contains one diamond core {V—O—V—O} bridged by an ethylenediol unit and a second one bridged by propylenediol.[259] It also features a distorted six-membered ring, propylenediol moiety (i.e., a metallo-1,3-diol chelate ring) that has remained elusive in aqueous solution. Another ligand used by several groups is tris(hydroxylmethyl)methane. The resulting complexes are usually polynuclear as seen in the isolated tetramers[260] and decamers.[261] The use of this ligand has revealed important information on the redox chemistry of these oxovanadate clusters.[261]

The natural product amavadine and its derivatives continue to generate interest due to their unique structures and reactivities. Besides the tetraperoxovanadium(V) complex,[185] these compounds are the only known octacoordinate vanadium(V) complexes. New analogs continue to be reported, such as complexes of *meso*-2,2′-(hydroxyimino)dibutyric acid.[243] The properties of the parent amavadine and analogs have been examined leading to the structural characterization of both monomeric[243] and cluster type derivatives containing vanadium(V).[243]

The solid-state and solution chemistry of triethanolamine complexes has been investigated. While the solid-state structure was maintained in organic solvent (**38**), a different structure was observed in aqueous solution.[262] ^{17}O NMR spectroscopy was used to demonstrate that the two oxo groups were different and in combination with ^{1}H and ^{13}C NMR data, defined the structure as (**39**).[262] Speciation studies and a detailed characterization of this class of compounds were important because the ligand is a commonly used buffer in biology and the complexes are model systems for interactions with proteins.[61,263] The thermodynamic parameters were determined for several derivatized diethanolamine ligand–vanadium(V) complexes, and represent some of the few vanadium complexes for which such parameters are known.[62] The structure of (nitrilotriacetato)dioxovanadate was reinvestigated.[264]



(36) **(37)** **(38)** **(39)**

Figure 4 Structural illustrations of (**36**–**39**).

4.4.2.2.5 Polydentate, two oxygen donors

Vanadium(V) complexes with derivatives of di- and triethanolamine (see also above)[61,62,252,262,265,266] and 1,1,1-tris(hydroxymethyl)aminomethane derivatives[266–268] are examples of complexes formed from simple O- and N- donor ligands. A series of vanadium(V) complexes with substituted diethanolamine ligands were found to show a pH-dependent stability.[252,263] Corresponding pyridine carboxylates or alkoxides have also been successfully investigated.[265,269] In contrast to the five-coordinate complexes with triethanolamine, substitution of one hydroxyl group with a carboxylate group leads to six-coordinate complexes. Complexes in which the hydroxyl groups have been substituted with carboxylate groups, a carboxyamide, amino, pyridine, benzimidazole and imidazole groups have also been reported.[270] By condensation of two such functionalities, extensive polydentate ligand frameworks result; such ligands lead to complexes of higher nuclearities, (e.g., tetranuclear).[271] Some of these complexes are chiral.[262,265] Others are linked by sodium cations in the solid state structures.[269] Vanadium(V) complexes with 2,2′-thiobis(4-methyl-6-tert-butylphenol) were prepared and the alkoxide or hydroxide dimers were structurally characterized.[272]

(i) Schiff base ligands

Schiff base complexes continue to intrigue chemists with regard to structure and reactivity. Their geometries are strongly influenced by the ligands and tend to be five- or six-coordinate. Mono- and dinuclear complexes are the most prevalent (**40**–**67** in Figure 5 and Table 4) and examples have been isolated with oxidation states V^{V},[77,123,128,268,273–310] V^{IV},[275–277,284,295,296,298,305,311–360] and V^{III}.[322,328,361–369] In this section progress with vanadium(V) systems is highlighted (**43**–**46**,**48**–**50**,**54**,**55**,**57**,**59**,**63**,**64** in Figure 5 and Table 4). Compounds of simple aromatic aldehydes and ketones with a range of diamines including aliphatic amines (**54**, **55**),[277,298] ethanolamines (**48**)[268] and simple amino acids[289] are known. Schiff base complexes with ethanolamines have higher aqueous stabilities compared to others (*vide infra*).[268] Alkoxo-rich Schiff bases of potentially tri-, tetra- and pentadentate alcohols such as 2-amino-2-methylpropan-1-ol, quinoline, triethanolamine, tris(hydroxymethyl)-aminomethane and *N*-[tris(hydroxymethyl)methyl]glycine have been reported.[266,370,371] Dioxovanadium(V) complexes of *N*,*N*-bis(2-pyridylmethyl)-glycine, N-(2-pyridylmethyl)imidodiacetic acid, *N*-(2-amidomethyl)iminodiacetic acid and nitrilotriacetic acid were characterized and their reactions with hydrogen peroxide investigated.[232]

The electrochemistry of dinuclear vanadium *o*-*N*-salicylideneamino-ethylphenyl complexes were investigated.[372] Conversion of $V^{IV}-V^{IV}$ dimers to $V^{V}-V^{V}$ dimers was reported and serves as a representative model system for oxidation reactions.[294,296] A related class of these dinuclear complexes form mixed valence vanadium(IV/V) complexes upon oxidation and exhibit an unusual electron delocalization over the $\{V_2O_3\}^{3+}$ core.[310] A $V^{III}-V^{IV}$ mixed valent, dinuclear bis(salicylidene)ethylenediamine (salen) complex underwent multielectron oxidation with dioxygen to yield a $V^{V}-V^{IV}$ mixed valence complex.[302]

Schiff base complexes have been extensively used to mimic the molecular reaction of bromoperoxidases by treating the pre-formed complex with hydrogen peroxide.[276,277,282] Decreasing the imine hydrolysis of the Schiff ligand base by reducing the imine functionality to an amine functionality promised to extend the lifetime of applications of this class of compounds. A series of such vanadium complexes have been prepared and evaluated;[373] they are very stable in aqueous solution, but so stable that they fail to exhibit the desired bromoperoxidase activity.[373] The reactions of these Schiff base complexes with L-ascorbic acid or L-cysteine ethyl ester were investigated.[371] Employing these types of complexes as catalysts for the selective epoxidation of olefins was reported to give yields ranging from 40% to 98%.[374]

New complexes containing azo- and hydrazinato-derivatized Schiff base ligands[298,375] continue to be used for the analytical determination of vanadium.[376] The vanadium complex was characterized for the Schiff base derived from the condensation reaction of benzoyl acetone and Girard's reagent P.[377] Azophenolates of mononuclear and mixed valence dinuclear species have been reported.[378] Naphthanol- or quinolinol-derivatized ligands prefer to chelate iron over vanadium.[379]

The first example of a μ-oxo-bis(μ-carboxylato)dioxovanadium(IV,V) complex has been reported (**68**).[380] Coupling reactions have been used in the preparation of ligands containing amide groups. One condensation reaction led to the first structurally characterized, deprotonated vanadium(V)–amide product (**69**).[381] This coordination mode was later observed for other amide

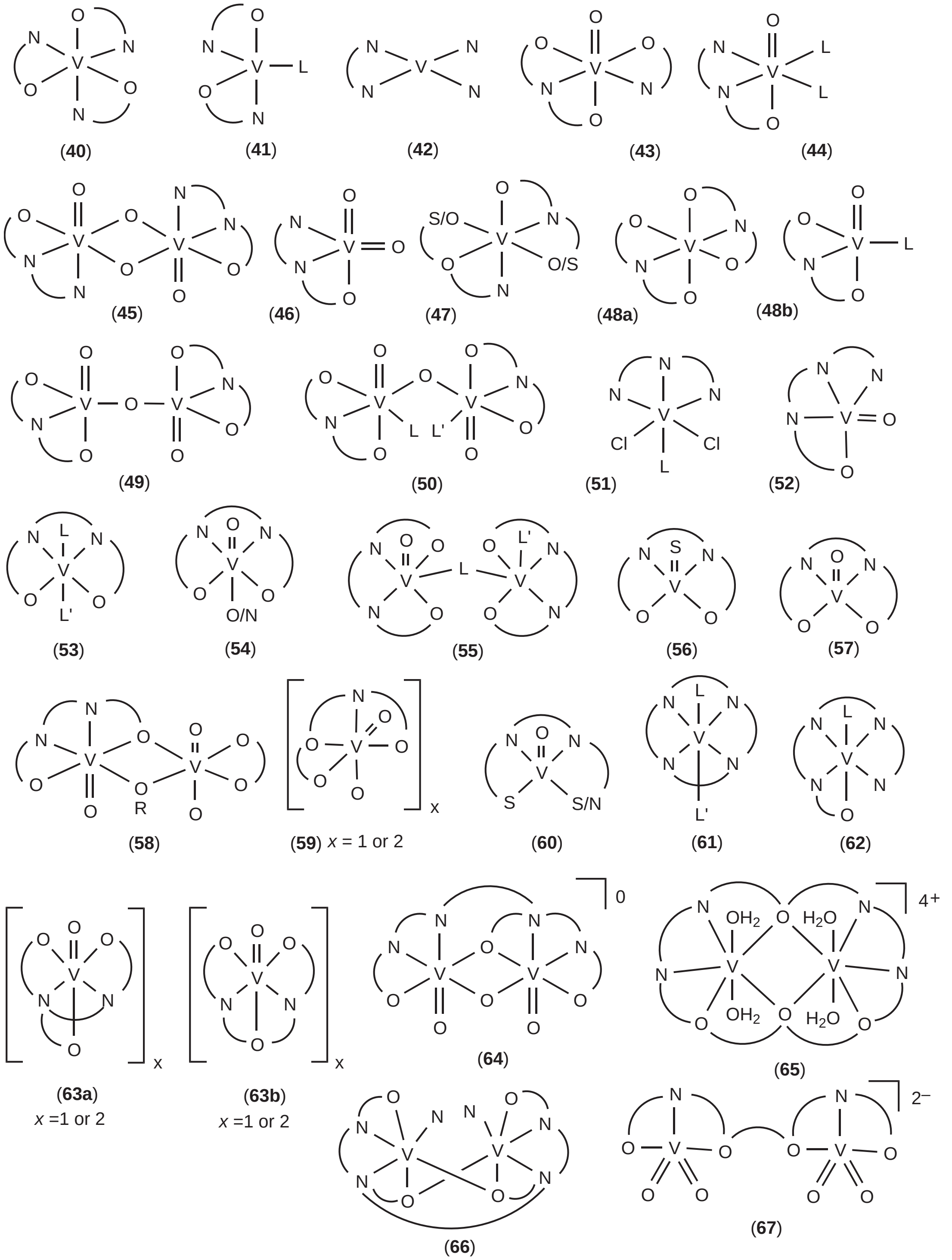


Figure 5 Structural illustrations of (**40**–**67**). Structures **43**–**46**, **48**–**50**, **54**, **55**, **57**, **59**, **63**, **64** contain V^V. The charges are given for structures and for structure types in which all the complexes have the same charge. For structure types that have differently charged ligands, no charge is given.

ligands[354] including those forming complexes in aqueous solution (**70**).[382–384] Extensive ligand frameworks were designed and the inclusion of an imidazole moiety was found to lead to very versatile ligands. A six-coordinate complex formed with the 4-(2-(salicylideneamino)ethyl)imidazole ligand and was the first reported vanadium(V)–imidazole complex (**71**).[385] A similarly constructed histidine–vanadium(V) complex contained a five-coordinate vanadium center, but

Table 4 Summary of the structural features of crystallographically characterized Schiff base complexes of V(V, IV, and III).[a,b]

Denticity	*Donor atom(s)*	*CN*	*Other ligands*[a]	*Structure (or motif)*[b]	V^V(references)	V^{IV}(references)	V^{III}(references)
Bidentate	ON × 3	6		**40**			361
	ON × 2	5	Oxo or Cl × 2	**41**		296,311,312	
	N_2	4	N	**42**			362
Tridentate/ Bidentate	ON_2/ON	6	Oxo	**43**	273,274	275,313	
Tridentate	ON_2	6	Oxo,O, N or Oxo, O, O_2	**44**	275	275,276,314	
		6,6	Oxo, μ-Oxo × 2	**45**	123,276–278		
		65	O × 2	**46**	123,279		
	ONS/O	6		**47**		315,316	
Tridentate	O_2N × 2	6		**48a**		316,617,618	
Tridentate	O_2N	6 or 5	Oxo,N,N Oxo,O,O Oxo,O Oxo,O,N	**48b**	77,128,268,280–291	284,296,317–320	
		5,5	Oxo, μ-Oxo	**49**	292–295		
		6,6 or 6,5	Oxo,μ-Oxo, or H_2O	**50**	296,297		
Tridentate	N_3 × 2	5	Cl × 2 or × 3	**51**			363

Tetradentate	ON_3	5	Oxo	**52**		321	
	O_2N_2	6 or 5	Cl×2 or Oxo or O or S, N×2	**53**		322,323	322,328,364,365
		5,5 or 6	Oxo, S or O or H_2O	**54**	277,300,303–305	277,325–328	366
		6,6 or 6,5	Oxo, μ-Oxo/μ-Oxo or μ-F Oxo, μ-Oxo/μ-Oxo	**55**	298–302	324	
		5	Sulfido	**56**		329	
		5	Oxo	**57**	303,306	295,298,305,312,325,327, 330–352,	
		6,5	Oxo, μ-Oxo	**58**		348	
	O_3N	6,6 or 6	Oxo or O,O	**59**	268,307		
	N_2S_2 or N_3S	5	Oxo	**60**		353,354	
	N_4	6 or 5	Cl × 2 or O, Cl	**61**		355–357	367
Pentadentate	O_2N_3	6	Cl or O	**62**		358,359	364
	O_3N_2	6 or 6,6 or 6,6,5	Oxo or N,O or μ_3-Oxo	**63a,b**	308,309	360	368
Heptadentate	O_3N_4	6,6	Oxo, μ-O	**64**	310		
Octadentate	O_2N_6	7,7	H_2O × 2	**65**			369
	O_4N_4	6,6	N	**66**			366

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[a] The donor atom(s) of each ligand is listed; oxo is indicated to differentiate between other O-donor ligands. [b] The structures/motifs are shown in Figure 5.

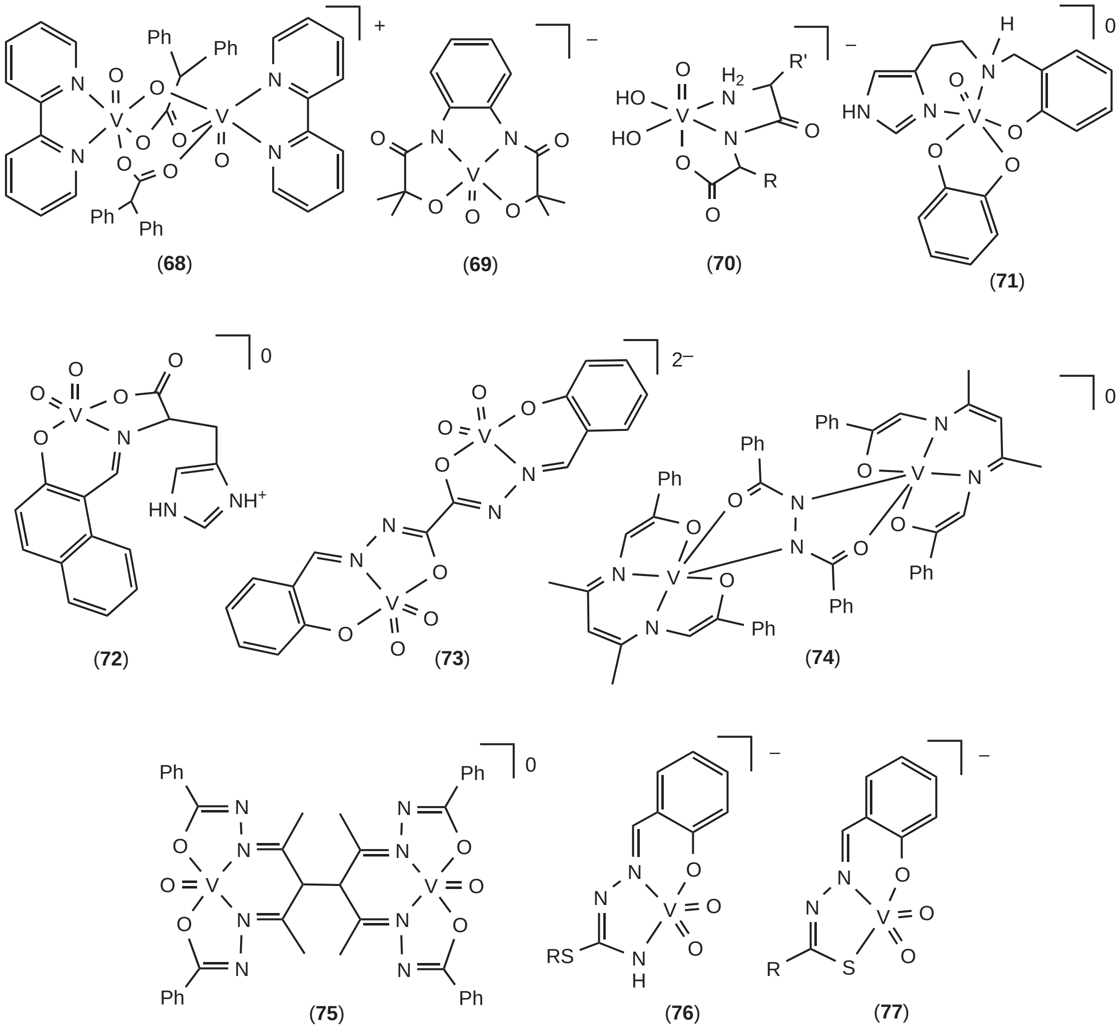


Figure 6 Structural illustrations of (**68–77**).

lacked coordination of the imidazole functionality (**72**).[290] By oxidative cyclization of the ligand, the vanadium(V) complex of 3-(2-hydroxyphenyl)-1-pyridin-2-yl-imidazo-[1,5,α]-pyridine was isolated and structurally characterized.[386] Although the vanadium(V) complex formed with *N*,*N*,*N*′,*N*′-ethylenediaminetetraacetic acid (EDTA) was characterized some time ago,[387] related complexes continue to provide fundamental information on the coordination chemistry of vanadium complexes. An asymmetric complex (β) retaining the *cis*-dioxo unit was structurally characterized with ethylenediamine-*N*,*N*′-diacetic acid.[388]

One subset of Schiff base complexes are the hydrazone complexes which have a R—C=N—N functional group instead of the R—C=N—C functionality. These compounds have been prepared as models for bromoperoxidase[389] and other biological systems.[390] In the solid state, the hydrazones have coordination patterns similar to those of the Schiff bases and the majority of the complexes are oxovanadium(V) hexadentate or pentacoordinate complexes with tridentate O_2N donor sets (see Table 5). While most structures contain alkoxide donors,[390–403] complexes have been reported with diols and catechols,[129,404,405] hydroxamic acids,[288,391] hydroxy quinolinate,[406,407] and benzoylhydrazine.[408] In addition, dioxo,[375,409–412] oxo-bridged dinuclear[393–395,413] complexes and a ligand-bridged dinuclear[410] complexe (**73–75**) have been isolated. Protonation of a *cis*-dioxovanadium(V) complex was found to preferentially take place at the hydrazide nitrogen atom over the oxo groups.[411] Thiocarbazone and semithiocarbazone derivative complexes of the type represented in (**76**,**77**) have also been isolated and structurally characterized.[414–421]

Table 5 Summary of the structural features of the crystallographically characterized hydrazone complexes.[a]

Denticity	*Donor atoms*	*CN*	*Other ligands*	*Structure (or motif)*[b]	*References*
Bidentate	ON × 3	6		**40**	763[c]
Tridentate	O_2N	6	Oxo, ON	**48**	408
Tridentate	O_2N	6	Oxo, O × 2	**48**	390–392
		6	Oxo, OO	**48**	129,288,391,404,405
		6	Oxo, ON	**48**	406,407
		5	Oxo, O	**48**	393–403
		5	Oxo × 2	**48**	409,411
Tridentate	ON_2	6,6	Oxo, μ-oxo	**45**	413
		5	Oxo × 2	**46**	375,412
	ONS × 2	6	NA	**47**	392[d]
Tetradentate	N_2O_2	6	ON	**53**	639[d]
Hexadentate	O_4N_2	5,5	Oxo	**67**	410
Octadentate	O_4N_4	5,5	Oxo	**66**	639[e]

[a] The donor atom(s) of each ligand is listed. To differentiate between oxo groups and other O-donor ligands, oxo is used to indicate the presence of an oxo group. [b] The structures/motifs are shown in Figure 5. [c] Vanadium(III) complex. [d] Non-oxovanadium(IV) complex. [e] Oxovanadium(IV) complex.

(ii) Hydroxamic acids

Hydroxamic acid complexes are used as reagents for the spectroscopic detection of vanadium,[376] and this ligand moiety is found in siderophores from microorganisms and tunicates and may be involved in the vanadium uptake and reduction by these organisms.[2,4,5,13,15,29,40,422,423] The first X-ray structures for vanadium hydroxamate complexes were reported in 1989 and demonstrated that the vanadium is six-coordinate in both mono- and dinuclear complexes.[424] A variety of hydroxamate and hydrazone ligands have been prepared and characterized.[391,425] The solution chemistry of a vanadium(V) complex with β-alaninehydroxamic acid was reported.[426] Using the hydroxamate as a stabilizing ternary ligand, nucleoside complexes yield spectroscopically characterizable products.[256] Tunichromes were found to be able to reduce vanadate to V^{IV} and V^{III}, supporting the hypothesis that tunichromes could generate V^{III} *in vivo* and that an oxidized form of tunichrome could sequester native V^{III}.[427] The vanadium(V) and (IV) complexes of desferrioxamine B have been characterized in aqueous solution[428] and desferrioxamine was used to reactivate vanadate-inhibited ATPase.[429] A vanadium(V) complex with a sulfonated hydroxamic acid was found to be a catalyst for the Stretford process.[430]

4.4.2.3 Nitrogen Ligands

4.4.2.3.1 Mono- and bidentate, one or two nitrogen donors

Aromatic amines, such as pyridine and imidazole, have been found to form weak complexes with vanadate.[100,104,267] The fact that no vanadium(V) complexes with aliphatic amines, in the absence of stabilizing ligands, have been reported supports the expectation that such complexes will have low stability in aqueous solution. In the presence of ancillary ligands, both aliphatic[119] and aromatic[73] amines form stable ternary complexes in solution.

(Arylimido)vanadium(V) complexes have been prepared from the reaction of $VOCl_3$ with various *para*-substituted aryl isocyanates. The reactivity and structure of some of these have been investigated (**78**).[431] The reactivities of a series of vanadium(V) chalcogens have been reported. The structure of $\{[(Me_3Si)_2N]_2V(Se)[SeSi(SiMe_3)_3]\}$[432] (**79**) shows that the V=Se double bond contracts by 8% compared to the single bond in a related dimeric vanadium(IV) structure (*vide infra*). The

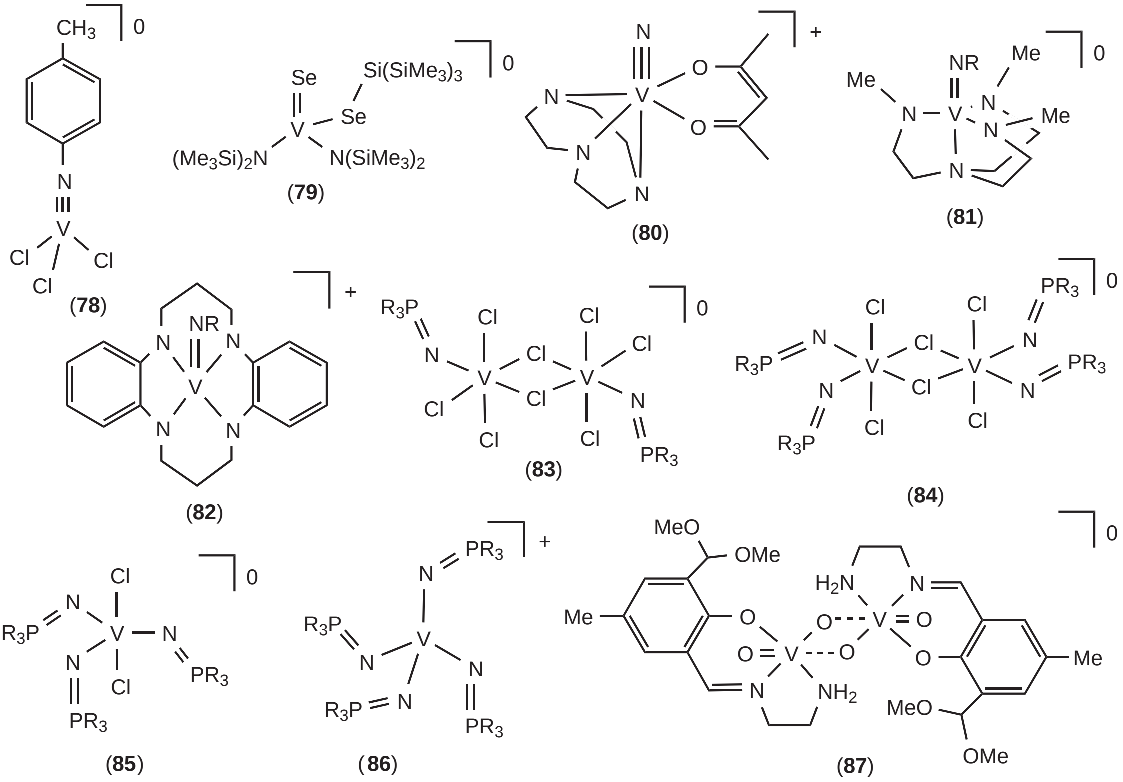


Figure 7 Structural illustrations of (**78**–**87**).

V^V—Se bond is slightly shorter than in the ethanedithiolate derivative as anticipated based on the observed $\nu_{V—Se}$ in the IR and the lower oxidation state of the vanadium.[433]

Vanadium(V) complexes of 1-oxa-4,7-diazacyclononane-*N*,*N*′-diacetate were prepared and undergo one-electron transfer to form the corresponding vanadium(IV) complexes.[434]

4.4.2.3.2 Polydentate, two or more nitrogen donors

Parent and derivatized vanadium(V)–tacn complexes (tacn = 1,4,7-triazacyclononane) have been prepared and structurally characterized.[435] Various auxiliary ligands have been used including acetylacetonate (acac), isothiocyanate ($^-$NCS), azide, and benzoic acid.[436] The acac derivative was used in the synthesis of a nitridovanadium(V) complex (**80**).[436]

A number of vanadium(V) complexes with the aliphatic ligand tri(ethyleneamine)amine (NN_3) have been investigated.[437,438] Vanadium(V) imido complexes (**81**) have been prepared by transmetalation from azastannatranes.[437] These complexes could also be prepared from the reaction of the four-coordinate vanadium complex with hydrazine.[438] An imidovanadium(V) complex containing the [1,4,8,11]tetraazacyclotetradecinato moiety was also reported (**82**).[439] One of these complexes was found to undergo cycloaddition with hexafluoroacetone, hexafluoropropene oxide, sulfur trioxide and triflic anhydride.[439] Chalcogenide vanadium(V) complexes of the type [LV=E] can be obtained from the reaction of trigonal pyramidal V^{III} complexes with S_8 or ethylene sulfide (E=S), with gray selenium (E=Se), or with propylene oxide (E=O).[438] The oxo derivative could also be prepared from $VOCl_3$.[440] A vanadium(III) complex with diazapyridinophane was oxidized to vanadium(V) with consecutive replacements of chloride ions by oxo donors while the remaining coordination environment was preserved.[441] Vanadium(V) oxidizes *meso*-octaethylprophyrinogen by one electron leading to a vanadium(IV) complex with an oxidized form of the porphyrinogen that has a cyclopropane unit.[442]

Vanadium(V) mono-, di-, tri-, and tetra(phosphoraniminato) complexes (**83**)–(**86**) have been prepared and an acetonitrile solvate of $[V(NPPh_3)_4]Cl$ structurally characterized.[443] A tridentate pyrazolylcyclohexanol complex of vanadium(V) has also been synthesized.[444] A derivatized pyridine ligand is chlorinated by $VOCl_3$ in the presence of *t*-BuOOH to yield the vanadium(V) alkoxo complex.[445] A dinuclear complex that has amino, imino, and phenolate coordinating functionalities has also been described (**87**).[278]

Numerous studies on the interactions of peptides and peptide-like ligands with vanadate have been reported.[68,382–384,446,447] Some of these ligands coordinate through the carboxylate, the amine functionalities and the deprotonated amide nitrogen of the peptide bond,[238,239,382,447,448] and some examples were described above in the section on polydentate ligands with two oxygen donor atoms.

4.4.2.4 Sulfur Ligands

Tetrasulfidovanadium(V) $[VS_4]^{3-}$, also referred to as thiovanadate, has been prepared[449] and its reactivity[449,450] and photochemistry have been explored.[451] Although it is generally believed that thiols reduce vanadate to give vanadyl cation and disulfides, recent reports of several V^V sulfide and thiol complexes document that many of these complexes are sufficiently stable for isolation and characterization.[7,452–460] That the accessibility of the thiol can be important has been illustrated by the addition of vanadate to glycerol-3-phosphate dehydrogenase.[452] Despite the presence of the thiol in the active site, the inhibition by vanadate is reversible and may not involve redox chemistry.[452] The redox chemistry between thiols and vanadate is dependent on the ligand itself, the concentrations of the ligand and metal ion, the pH, and other specific solution conditions, thus explaining the controversy in this area.[453] The reaction of vanadate with glutathione disulfide and the inhibition of gluthathione reductase activity by vanadate was investigated.[454]

Vanadium(V) persulfide complexes have been prepared and $(Me_3NCH_2Ph)_2[VS_2(S_2)(SPh)]$ (**88**)[455] and $(NEt_4)[VO(S_2)_2(bpy)]$ (**89**) have been structurally characterized.[456] In (**88**), the vanadium(V) center is ligated by three types of sulfur donors, one thiolate (PhS^-), one persulfido (S_2^{2-}) and two sulfido (S^{2-}) groups.[455] If the disulfide ligand (S_2^{2-}) is considered to be one functionality, the coordination geometry around the vanadium is approximately tetrahedral in analogy with the tetraperoxovanadium complex (**28**).[185]

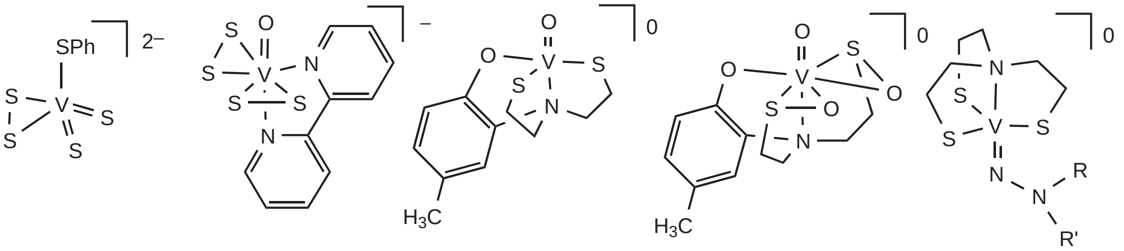
Vanadium(V) complexes of ligands with mixed thiolate–hydroxylate functionalities have been structurally characterized both in solution and in the solid state (**90**).[457] Oxidation of this complex resulted in a vanadium(V)–η^2,η^2–disulfenate complex with an unprecedented coordination mode (**91**).[457] Complexes with 2-thio-3-benzoylhydantoin have also been reported.[458] In addition, a recent solution study of vanadate with dithiothreitol (DTT) showed that the study of these complexes is quite tractable even in aqueous solution.[459] The first hydrazide vanadium complex with S-donor ligands was structurally characterized (**92**).[460]

4.4.2.5 Halides

The structure and electronic configuration of VF_5 was examined using SCF calculations.[461] A solution study of vanadium(V) fluoride and chloride complexes ($VOCl_3$, $VOCl_2F$, $VOClF_2$, VOF_3) in organic solvents was carried out using ^{51}V and ^{19}F NMR.[462]

4.4.2.6 Other Ligands

The geometries of VH_5 and VMe_5 do not conform to the valence shell electron pair repulsion (VSEPR) model, and self-consistent field (SCF) calculations show that the electron density of



(88) **(89)** **(90)** **(91)** **(92)**

Figure 8 Structural illustrations of (**88**–**92**).

the outer core has a square pyramidal arrangement corresponding to the geometries of these molecules.[461] Coordination of bridged phosphate was observed in a material formed by hydrothermal synthesis.[463] A complex with triphenylphosphine, *t*-butyl imine, and two chloride ligands was reported.[464] Silica-supported vanadium catalysts have led to the characterization of some vanadium-containing silsesquioxanes.[465]

4.4.3 VANADIUM(IV)

4.4.3.1 Aqueous Vanadyl (V^{IV}) Chemistry

Progress since the early 1990s in the area of aqueous vanadyl chemistry is limited and the previous review in *Comprehensive Inorganic Chemistry*[2] remains one of the premier sources for a summary of the state-of-the-art information on vanadyl solution chemistry. Here we will summarize the key points and highlights of the contributions that have appeared since that time. V^{IV} complexes are characterized in the solid state by X-ray crystallography and IR spectroscopy. In solution, the following spectroscopic techniques have been used in addition to potentiometric and electrochemical techniques: electron paramagnetic resonance (EPR), electron nuclear double resonance (ENDOR), UV-visible, EXAFS, electron spin echo envelop modulation (ESEEM), and X-ray absorption near-edge spectroscopy (XANES).

Dissolution of $VOSO_4$ in acidic aqueous solutions yields the hydrated vanadyl cation $[VO(H_2O)_5]^{2+}$ (**93**),[2] commonly abbreviated as VO^{2+}; its solvation structure was determined using ENDOR in frozen methanolic solutions.[466] This species has a pK_a value of 5.9 (**94**),[467,468] but after deprotonation, the V^{IV} species will either dimerize, form soluble and insoluble polymers, or oxidize.[2,9,10,469] Aqueous V^{IV} chemistry can be divided into three regimes: acidic ($pH < 6$), neutral (pH 6–8) and alkaline ($pH > 8$). The best understood regime of aqueous V^{IV} chemistry is the acidic region where the $[VO(H_2O)_5]^{2+}$ (**93**) and $[VO(OH)(H_2O)_4]^+$ (**94**) cations exist.[2,470] The alkaline pH region is governed by the presence of the EPR silent dimer $[(VO)_2(OH)_5]^-$ and other oligomers and polymers as well as the EPR active $[VO(OH)_3]^-$ species (**95**). The latter forms at about pH 9–10 and rapidly replaces the dimeric forms. However, precipitates do form in this pH region when the vanadyl hydroxide solubility product is exceeded ($K_{(sol,\ VO(OH)_2)} = 6.6 \times 10^{-23}\ M^3$).[467] In the neutral pH range, these same aqueous equilibria limit the concentration of hydrated monomeric VO^{2+} (in the form of (**93**) and (**94**)) to between 10^{-6} and 10^{-9} M, regardless of the amounts of $VOSO_4$ added to the solution.[469] Because of the high affinity of V^{IV} for most oxygen-, nitrogen- and sulfur-containing ligands, complexation can prevent the formation of the polymeric precipitates.[9,469] The limited progress in the areas of speciation and equilibria of the aqueous V^{IV} system since the review by Vilas Boas and Pessoa,[2] is in part due to the fact that few spectroscopic tools that can report on aqueous V^{IV} species because hydrated V^{IV} is EPR silent at neutral pH.

The kinetics of VO^{2+} oxidation in aqueous solution by $RuL_3{}^{3+}$ and $NiL_3{}^{3+}$ complexes (L = bpy, phen),[471] a Ni^{III} macrocycle,[472] metal polypyridines[471] and a carboxylato-bound Cr^V[473] have been reported. The reduction of V^{IV} has been demonstrated in aqueous solution by Vitamin B_{12} (Cob(I)alamin),[474] and by $OsL_3{}^{3+}$ (L = bipy, phen).[471]

4.4.3.2 Oxygen Ligands

4.4.3.2.1 Monodentate, one oxygen donor

Vanadium(IV) forms complexes with charged carboxylate, aryloxide and alkoxide functionalities as well as the neutral carbonyl group. The steric crowding of the *t*-butoxides allowed structural characterization of the tetraalkoxide (**96**) by gas-phase electron diffraction.[475] V^{IV} phenoxide complexes derived from ligands such as 2-(dimethylaminomethyl)phenol and 4-chloro-2-[(dimethylamino)methyl]phenol are active as ethylene and propylene copolymerization agents.[476] Complexes with silanoxides have been prepared by the oxidation of V^{III} complexes.[477]

A mononuclear complex with formate ligands has been structurally characterized (**97**).[478] Each unit of $K_2[VO(HCO_2)_4]$ has the vanadium in a pseudo-octahedral geometry, with the coordination of an adjacent molecule's free carbonyl (C=O) group serving as the sixth ligand.[478] The

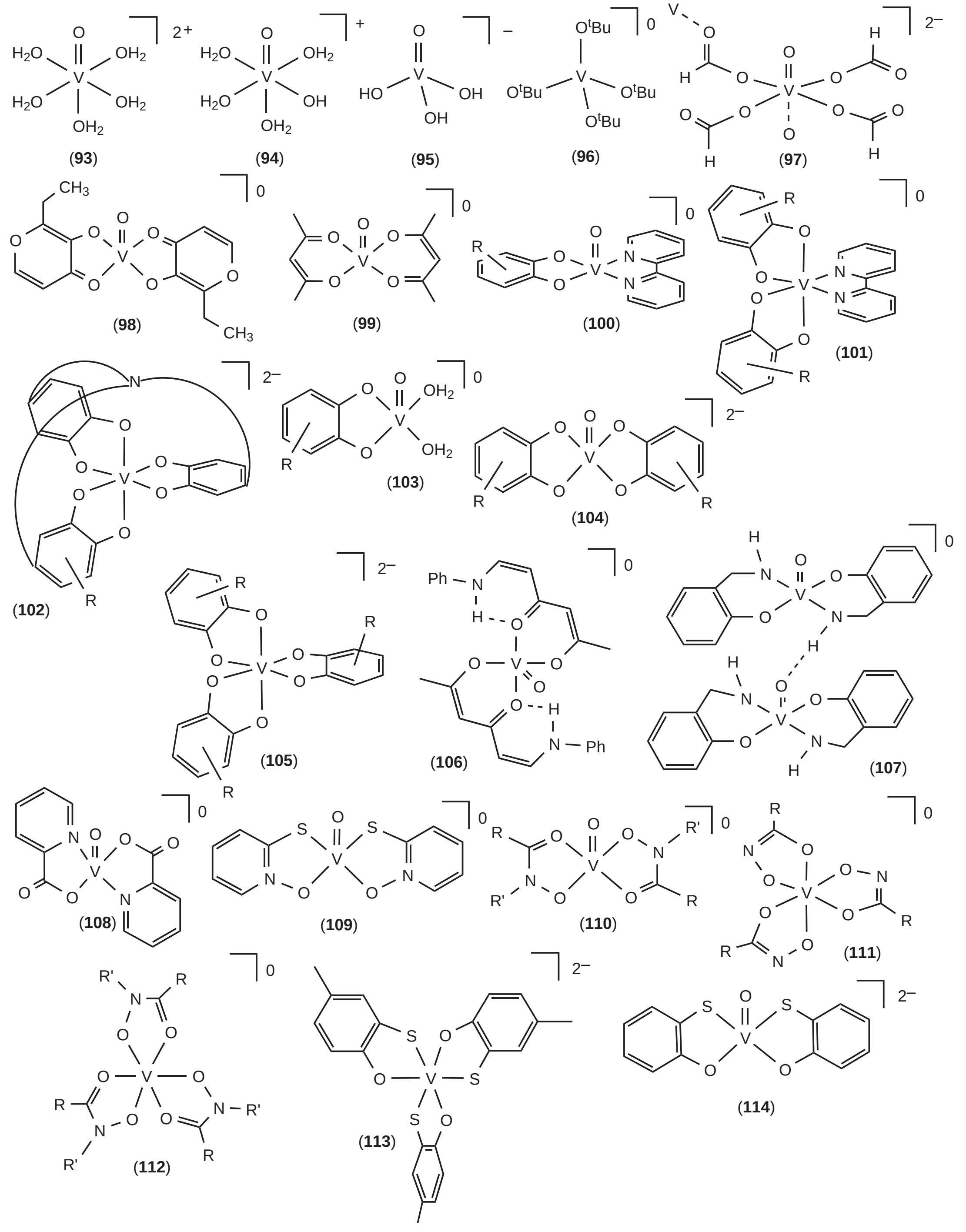


Figure 9 Structural illustrations of (**93–114**).

stability constants and heats of formation of V^{IV} complexes with acetate and glycolate have been determined in aqueous solution.[479] A binuclear V^{IV} complex has been described in which the carbonyl functionality of the isonicotinic acid hydrazide coordinates to the vanadium atom in a monodentate fashion.[480]

Several V^{IV} materials form via complexation with different protonation states of phosphate[481–484] and pyrophosphate[485,486] and have been characterized in the solid state. Corresponding studies with V^{IV} hypophosphites[487] and arsenates[488–490] have also been reported. Imidophosphinato complexes with the vanadyl cation are characterized in the solid state and in solution.[491] The

$[VO(H_2O)_2L]^{2+}$ moiety has a much lower affinity for sulfate[492,493] than the corresponding dehydrated unit $[VOL]^{2+}$.[492] This difference in selectivity was proposed to be a model for vanadyl–sulfate interactions in *Ascidians*.[492] Many such materials have been prepared by hydrothermal synthesis to generate materials with intriguing structures and interesting sorptive properties.[494]

4.4.3.2.2 Bidentate, two oxygen donors

Bidentate O,O-containing ligands include diols, catechols, acetylacetonates, hydroxycarboxylates, dicarboxylates, phosphocarboxylates, protected nucleosides and nucleotides. Only a few alkoxide complexes with V^{IV} have been reported and most of these include bifunctional ligands with an alkoxide group and some other functionality. A mononuclear complex of 2-ethyl-2-hydroxybutanate[495] was reported and is structurally similar to the corresponding mononuclear V^V complex characterized as a model for vanadium–nucleoside interactions (**11**).[120] The V^{IV} 2-ethyl-2-hydroxybutanate complex was found to inhibit Cr-mediated cleavage of DNA.[495] The speciation of vanadyl complexes with several ligands, including oxalic, malonic, and kojic acids as well as maltol have been recently reported.[496] One of the dinuclear complexes with 2-tetrahydrofurfuroxide[497] was found to be structurally analogous to the related dinuclear V^V diol complexes (**9,11**). More complex structures can also be obtained with this ligand.[497] A non-oxo-V^{IV} complex with two enediolate functionalities was formed in the redox reaction between benzil and $[VCl_2(tmeda)_2]$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine).[498]

The bis(ethylmaltolato)oxovanadium(IV) complex $[VO(malto)_2]$ (**98**) is currently in clinical trials for the treatment of diabetes.[18] *In vitro* studies with $[VO(acac)_2]$ demonstrated that this simple 1,3-diketonate V^{IV} complex (**99**) induced a significantly greater insulin-enhancing response on lipogenesis than vanadyl sulfate.[499] Animal studies have shown that this complex at low dosage has effects similar to those of $[VO(malto)_2]$ (**98**) in the treatment of diabetic rats.[500,501] These newly discovered biological effects show that more studies are warranted to explore the chemistry of related compounds. Solution studies of both $[VO(malto)_2]$[502] and $[VO(acac)_2]$[501] show that both complexes form cis and trans adducts in aqueous solution as well as undergo a slow redox reaction in the presence of oxygen.

Bridging oxalate groups have been found to form materials with a variety of different structural motifs and properties. A ferromagnetic- μ-oxalato $Cu^{II}-V^{IV}$ complex has been crystallographically and spectroscopically characterized.[503] Observations were also reported for an anti-ferromagnetically coupled $Mn^{II}-V^{IV}O$ pair.[504] A series of bimetallic vanadium complexes show weak anti-ferromagnetic pairwise interactions.[505] Other carboxylate ligands, such as isophthalate, have found similar uses.[506] Hydrogen peroxide does not form an isolable V^{IV} complex and any chemistry with V^{IV} involves redox chemistry. The oxidation of V^{IV} by alkyl hydroperoxides in acidic solutions has been characterized and the complexation of alkylperoxides by VO_2^+ was demonstrated.[154,507]

(i) Catechol ligands

A variety of catecholate complexes and their characterization have been reported (**100**)–(**105**).[137,140,508–511] While most catecholate complexes contain vanadium(IV), complexes with other oxidation states have been isolated (*vide infra*). Information on the kinetics of complex formation and ligand oxidation was reported in 1974 but still remains timely for current investigations.[512,513] Structural and electrochemical investigations of the simple V^{III} catecholate and semiquinone complexes lead to the formation of the dianionic V^{IV} complex of a 1:3 metal to ligand stoichiometry in organic solvents.[140] Aqueous speciation studies show formation of 1:1 (**103**), 1:2 (**104**), and 1:3 (**105**) species in various protonation states.[514–516] Ternary complexes containing catecholate and bipyridine have many properties analogous to those containing only catecholate ligands.[510,517] Studies have shown that the nature of the catechol does not significantly affect the magnitude of the formation constants.[514,515] In contrast, different g_o and A_o values are observed by EPR and ENDOR depending on the electronic structure of the chelating catecholate and the stoichiometry of the complex (1:1 or 1:2) suggesting that the complex is sensitive to small differences in catecholate structure.[518,519] Redox reactions in several cases resulted in ligand-based redox processes.[138,520] The ligand–metal electron transfer reaction can vary depending on the solvent and evidence for the oxidized metal, reduced quinone form is obtained in polar solvents; however, solid state studies support the reduced metal, oxidized ligand formulation.[137,140,520] Model complexes for Tunichrome B1 analogs have been prepared, and the catechol complexation is critical for these complexes.[509] The V^{IV} complexes with these ligands are often polymeric; monomeric complexes are only consistently observed for V^{III} derivatives.[509] Magnetic studies on model complexes and the whole and freeze-dried tunicate blood samples are consistent with V^{III} complexes being the major species in the tunicates.[508] The enterobactin V^{IV} complex was crystallized and in this complex the catecholate groups were found to be the coordinating functionalities; a similar observation was noted for the simplest geometrically unrestricted model complex with three *N*-ethyl-3,4-dihydroxybenzamide.[511] Spectroscopic characterization showed that the stability and Δ chirality of the complex originates from the preferential conformation of the trimeric serine backbone.[511]

(ii) Acetylacetonate ligands

Bis(acac)oxovanadium(IV) (**99**) complexes represent an important class of complexes that have existed for nearly a century.[2,521] The kinetics of ligand replacement in bis(malonato)oxovanadium(IV) has been investigated.[522] The mechanism proposed involves partial hydrolysis, followed by one slow step of ligand–H_2O substitution.[522] *Ab initio* theoretical methods,[523] UV-photoelectron spectroscopy[523] EPR/ENDOR spectroscopy,[524] symmetry correlations,[525] and electronic spectroscopy[523] have examined the bonding in this class of compounds. The vanadyl interaction is axial in nature and possesses partial triple-bond character. The equatorial bonding involves mostly sigma bonding between the lone pairs on the ligand oxygen atoms and the V $3d_{xy}$ orbital.[523] Investigations of the physical properties of these compounds include thermal and kinetic studies of adduct formation[526] oxidation in methanolic solutions[527] and thermal stability of pyridine adducts in the solid state.[528] New complexes containing the diketonate unit continue to be reported, including sterically hindered complexes with 2,2,6,6-tetramethyl-3,5-heptanedionate,[529] asymmetric complexes[530] and the tris(3,5-dimethylpyrazolyl)borate ligand.[531] In a melt reaction of $[VO(acac)_2]$ and *N*,*N*′-diphenylformamidine (phad) the corresponding $[VO(phad)_2]$ forms the less common trans isomer (**106**).[532] The first discotic di(oxovanadium(IV)) liquid-crystalline complexes have been prepared.[533]

A rapidly growing class of compounds is the ternary complexes in which one β-diketonato group, an oxo group and an additional ligand complete the coordination sphere of the vanadium complex.[534] The ternary ligands used include mono- and dialkoxides,[284,295,535,536] catechols,[534] purines and pyrimidines,[537] tris(pyrazolyl)borates[538,539] and other ligands.[540–544] These ternary complexes retain some of the favorable properties of the $VO(acac)_2$-type complex as well as showing additional hydrolytic and redox stability over the parent complexes.[534] When the supporting ligand is polydentate, di-, tri- and tetranuclear complexes have resulted[535] and distinctive differences between the $[V^{IV}O(acac)]^+$ unit and the $[V^{V}O(acac)]^{2+}$ unit are observed. Although most of the complexes with this class of ligand contain the $V=O$ unit, cationic V^{IV} acac-type complexes such as the non-oxo $[V(cat)_3]^{2-}$ (cat = catechol) complex have been prepared and characterized.[516,545] Given the unique structure of these V^{IV} complexes their redox chemistry is very versatile.[546]

4.4.3.2.3 Bidentate, one oxygen donor

Bidentate ligands in which one of the donor atoms is oxygen and the other is nitrogen have been reported in a variety of different types of V^{IV} complexes. A number of these complexes contain bidentate Schiff bases (**41**, **43**) (see Table 4).[292,317,361] In one of these compounds (**107**), hydrogen bonding between the V=O and the HN group resulted in the stabilization of the complex, which in contrast to similar V^{IV} complexes was not reduced to V^{III} complexes.[361] The solution interaction of V^{IV} with a series of amino acids and simple dipeptides has been characterized using potentiometry and EPR spectroscopy.[547–556] The 1:2 V^{IV}–picolinate complex (**108**) was synthesized in NaY zeolite cages; however, no difference in their catalytic activity was observed.[557] This complex is a key compound showing insulin-enhancing properties in diabetic animal model systems.[558–571] The related bis(1-oxy-2-pyridinethiolato)oxovanadium(IV) complex (**109**) also shows insulin-enhancing effects in diabetic rats.[559,568] A hydroxymentholpyridine ligand (1-pyridin-2-yl-menthol) was investigated for the preparation of a chiral V^{IV} complex.[572]

Diluting single crystals of oxobis(2-methylquinolin-8-olato)vanadium(IV) complexes in the solid state to overcome the difficulties of neighboring paramagnetic centers has allowed the determination of the *g* tensor and an estimation of the hyperfine coupling constant.[573] Four simple hydroxamates form six different types of complexes with V^{IV} in solution that were characterized by EPR spectroscopy.[574] The 1:2 complexes were also investigated in the solid state (**110**)–(**112**) and serve as important model systems for the amavadine complex which has been isolated from the mushroom *Amanita muscaria*.[574]

Several complexes with OS donor ligands have been prepared. The spectroscopic properties, magnetic properties and structures of the complexes with 2-mercaptophenol and the methyl-substituted derivative were determined (**113**,**114**).[575] Spectroscopic studies with 2-mercaptoethanol have also been carried out.[576]

4.4.3.2.4 Polydentate, three or more oxygen donors

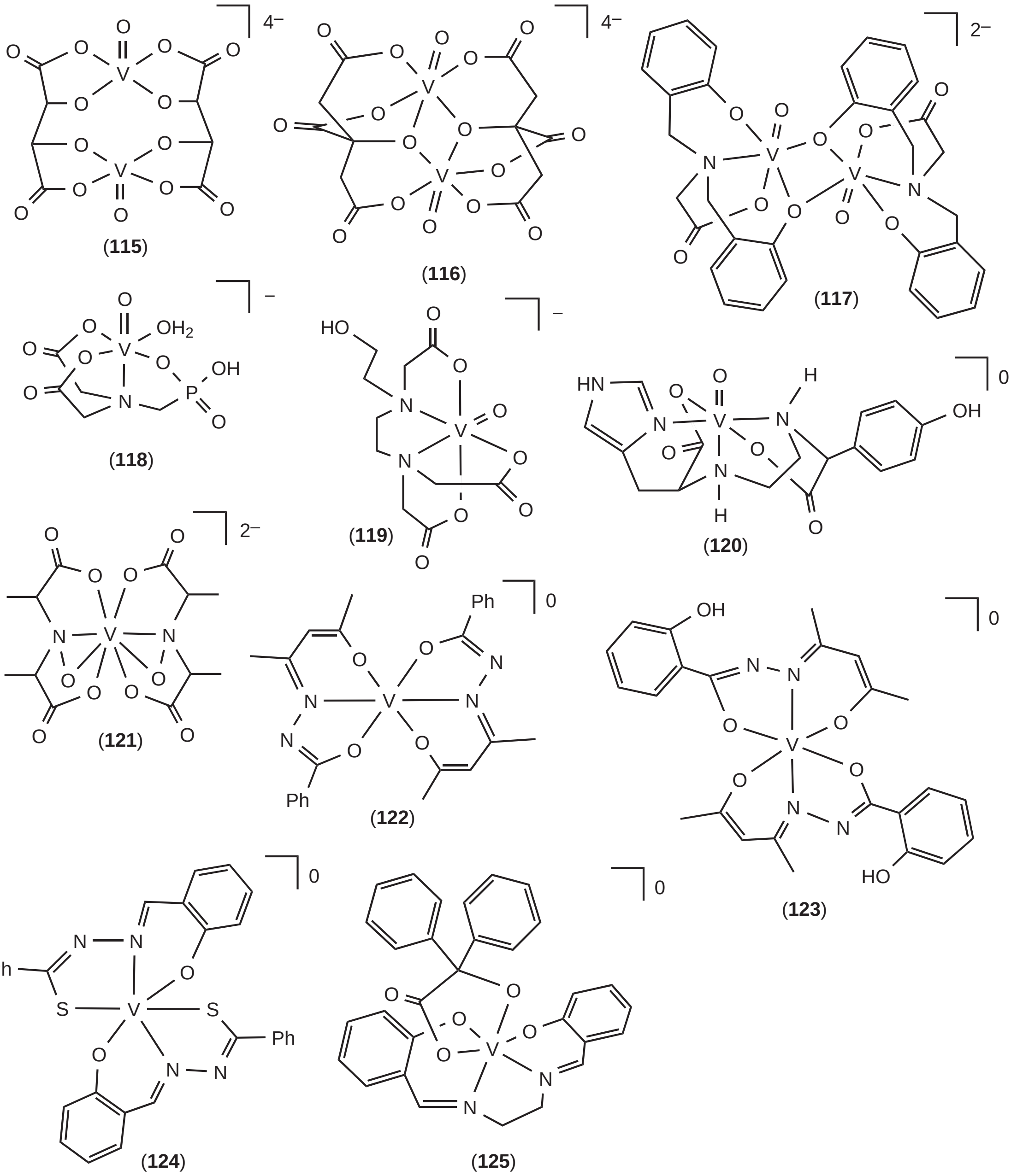
Vanadium(IV) tartrate complexes have been investigated, and the studies include structural characterization of a 2:2 complex in which the tetradentate ligand bridges two vanadium atoms (**115**).[577] An antiferromagnetically coupled, dinuclear V^{IV} complex with two tridentate 3-hydroxy-3-methylglutarate ligands was isolated.[578] A dinuclear complex (**116**) of the citrate ligand was characterized and the configuration of the anions was found to be anti-coplanar.[579] Low-temperature EPR spectra with zero-field splitting and 15 line hyperfine patterns on the parallel and perpendicular features, characteristic of two equivalent vanadium atoms, confirms the presence of a spin triplet.[579] A correlation was discovered between the structure and the magnetic properties of complexes with ligands containing O_3N-functionalities coordinating to the vanadium.[580]

Rhizoferrin is a carboxylate-containing siderophore, and has been found to form strong complexes with V^{IV}.[581] Solution studies of complexes formed with D-galacturonic,[519] polygalacturonic,[519] and lactobionic[582] acids were carried out using ENDOR spectroscopy or potentiometry. Representative potentiometric studies have been carried out for a variety of biologically interesting chelating ligands such as sugars[583] and sugar phosphates.[583,584] Some of these systems have been further characterized using EPR and ENDOR spectroscopic techniques.[585,586] A V^{IV} complex with 2,2′-oxydiacetic acid was synthesized and found to exhibit anti-apoptotic activity.[587]

The solid state properties of a complex with *N*,*N*-bis(2-hydroxybenzyl)aminoacetic acid (**117**) were investigated.[580] The kinetics of ligand substitution and oxidation of [((phosphonomethyl)-imino)diacetato]oxovanadium(IV) were found to be consistent with a hydrogen bond between a coordinated water molecule and the phosphonate arm.[588] Structural studies failed to confirm this interaction (**118**), however, several species exist under various conditions, showing the versatility of the system.[589] A range of oxovanadium(IV) complexes with ethylenediaminepolyacetic acid ligands have been prepared and their solution properties characterized (**119**).[590] Additional new members of this class of compounds and their structural characterization continue to be reported (**117**)–(**119**).[270,580,587,591-595] Spectroscopic studies have shown that stoichiometries, determined by potentiometry, and structural studies are needed to understand these systems fully. A pentadentate ligand generated by the functionalization of ethylenediamine with three phenolate coordinating moieties forms a complex that by UV-visible and EPR spectroscopy gives the same spectra as that of the vanadyl–transferrin complex.[596] Since 1998, several vanadium binding proteins, “vanabins,” have been isolated and show high selectivity for V^{IV}.[597–600]

4.4.3.2.5 Polydentate, two oxygen donors

Vanadium(IV) complexes with two dipeptides glycyl–tyrosine and glycyl–phenylalanine (Gly–Tyr and Gly–Phe, respectively) and their oxovanadium(IV) and (V) complexes have been observed.[382,601] The complex formed with Gly–Tyr showed coordination by the peptide backbone moieties, and no interaction from the distal phenolic hydroxy group.[601] A histidine–tyrosine derivatized peptide was shown to complex V^{IV} in a pentadentate manner (**120**).[564] The adduct between V^{IV} and a model of the active-site peptide of protein tyrosine phosphatases has been spectroscopically characterized.[602] Similar characterization of V^{IV} in serum suggests that protein complexes form, and that both V^{IV} and V^{V} can exist as complexes with transferrin and albumin.[603] ESEEM has been used to characterize the complexes of apoferritin with VO^{2+} and suggests that the carboxylates, one water molecule, and one histidine ligand fill the coordination sites of the vanadium.[604]



(**115**) (**116**) (**117**) (**118**) (**119**) (**120**) (**121**) (**122**) (**123**) (**124**) (**125**)

Figure 10 Structural illustrations of (**115–125**).

The coordination chemistry and oxidative reactivity of a series of mononuclear V^{IV} complexes containing nitriloacetate-derived ligands have been investigated.[64] Substituting an OH group in nitrilotriacetic acid with an NH_2 group gives *N*-(2-aminoethyl)iminodiacetic acid (see (**118**) where the PO_3H group would be substituted with a OH/NH_2 group). Substituting one carboxylic acid group with a hydroxyl group, an amino group, or a pyridyl group gives a wide range of ligands, all of which were found to form mononuclear V^{IV} complexes.[64] Using EPR and ESEEM to characterize the solution chemistry of these systems provided key information in understanding the EPR data for the reduced form of bromoperoxidase.[64]

It was found that the simple V^{IV} complex with *N*,*N*′-ethylenediaminediacetate (EDDA) had insulin-enhancing properties.[605] The corresponding complex with *N*,*N*′-ethylene bis(*S*)-methionine was found to have a lesser effect with regard to inhibition of the free fatty acid release from diabetic rat adipocytes.[605] The kinetics of the oxidation of V^{IV} complexes in solution with

$[IrCl_6]^{2-}$ were investigated[588,606] and the redox properties of the V^{IV} complex are different from those anticipated.[606,607] The structure of the *N*,*N′*,*N′*-ethylenediaminetriacetate was reported;[591] spectral properties of V^{IV} complexes with two spin-labeled derivatives of EDTA were described.[608] Vanadium(IV) complexes with tetraanionic diamidate–diphenolate ligands have been prepared and the strongly σ-donating ligands constructed on a disubstituted propanediamide backbone are found to stabilize the highly oxidized V^{IV} center.[609] Functionalization of the phenolato ring in the 5-position changes the reduction potential for the reversible VO^{3+}/VO^{2+} redox couple by ca. 0.5 V relative to that of the parent complex (−0.047 V vs. SCE).[609]

(i) Schiff base complexes

A large number of V^{IV} complexes have been reported with polydentate Schiff bases (**41, 43, 44, 47, 48**, **52**, **53**, **54–58, 60–63**, see Figure 5). The largest group of these complexes contains ligands with two oxygen donors (**48, 53, 54–58, 62, 63**, see Figure 5 and Table 4).[277,284,295,296,298,305,312,317–321,324–352,358–360] The V^{IV} Schiff base complexes are derived from the salen ligand,[295,298,305,312,325,327,330–352] and contain a five-[284,295,296,298,305,312,317–320,322,323,325,327,329–352] or six-coordinate[610] vanadium centers. Some of these complexes are mononuclear,[348,360] dinuclear,[275–277,284,295,296,298,305,311–323,325–360] chiral,[611] or Lewis acid complexes.[349] Examples of complexes with S-donor ligands,[315,316,329,353,354] water-soluble complexes,[612] and complexes with interesting reactivities and magnetic properties[323] have been reported.

The properties of the complexes are sensitive to the nature of the ligand, as exemplified by the reported magnetic properties of two diffferent series of complexes. Antiferromagnetic behavior is found for dinuclear Gd^{III}–V^{IV} complexes,[323] whereas ferromagnetic properties was found in macrocyclic dinuclear V^{IV} and dinuclear $V^{IV}-Ni^{II}$ complexes.[613] The magnetic properties of a Cu^{II}−vanadyl Schiff base system have been investigated.[614] Complexes often contain the Schiff base ligands and additional ligands such as 8-quinolinol,[610] and halides.[365] The iodide-containing complexes with N_2O_2 Schiff base ligands with hydrazines have an intramolecular H bond to an I^- counterion.[365] The elusive $[VI_2(salen)]$ and some of its homologs have been prepared and are found to undergo autoredox reactions (Equation (1)) in ionizing solvents.[347] Vanadium(IV) complexes with assymmetrical N_2O_2 Schiff bases have the vanadium atom displaced far from the basal plane and may, in part, explain the solvent-independence of the EPR parameters of a series of complexes.[331] A few dimethylsulfoxide adducts of V^{IV} Schiff base complexes have been structurally characterized.[277,326,360]

$$2V^{IV} + 2I^- \rightarrow 2V^{III} + I_2 \tag{1}$$

The redox reactivity of divanadium–salen[615] and other complexes[555] have been investigated. Disproportionation of $[\{V(salen)\}_2(\mu\text{-}O)]$ was observed under electrochemical conditions.[615] The reduced, $[V^{III}(salen)]^+$ complex was found to be the essential species in the catalysis of the electroreduction of O_2 by four electrons in CH_2Cl_2.[616] While $[\{V(salen)\}_2(\mu\text{-}O)]$ was proposed to be the active species in the redox reaction, more recently $[V^{III}(salen)]^+$ was identified as a reservoir from which the active species forms.[616] Schiff base complexes encapsulated in zeolite Y are catalytically active in the oxidation of thioanisole with H_2O_2.[14] Acid-promoted disproportionation of a V^{IV} phenolate under anaerobic conditions was proposed as a model reaction for the vanadium uptake in tunicates.[139]

(ii) Non-oxo- V^{IV} complexes

The vanadyl group is stabilized in high oxidation states by *pπ–dπ* interactions which facilitate the loss of electrons from the appropriate d orbital and shorten the V=O bond length.[617] It has been postulated that some multianionic ligands involved are modest π-donors and acceptors and thus can stabilize the V^{IV} oxidation state via *pπ–dπ* interactions.[617] In fact, increasing numbers of V^{IV} compounds have been reported with no V=O groups.[139,141,316,353,435,514,516,517,545,590,615,617–626] Initial reports in this area referred to these complexes as "bare vanadium(IV)" complexes due to the lack of an oxo ligand, but the more preferred term is "non-oxovanadium(IV)" which will be used throughout this review. Several classes of these complexes exist; the two largest are the hydroxamates (**111**,**112**) and the Schiff bases (**41**, **47**, **53**, **61**, **62**). However, a number of additional ligands have been found to generate non-oxovanadium(IV) complexes containing different supportive ligands and geometric environments.[627] None of the oxygen atoms in these supportive ligands can be assigned as part of a vanadyl group.

Non-oxovanadium(IV) complexes were first reported in complexes modeling the natural product amavadine (**121**) from the mushroom *Amanita muscaria*.[15] Although the biological role of the compound is not known, structurally this complex is of interest since amavadine is an example of an eight-coordinate non-oxovanadium(IV) complex.[619,628–630] Since the first discoveries of this class of V^{IV} complexes, a series of these non-oxo eight-coordinate vanadium-containing complexes have been reported.[246,619,628] They are unusually stable ($\log\beta_2 = 23$) and are surpassed in stability only by vanadyl porphyrins and some siderophore complexes.[247] The natural product amavadine consists of an almost equal mixture of the Δ and Λ isomers of the complex with each ligand containing two chiral centers with S stereochemistry.[631–633] The redox properties continue to be of interest, given the possibility that the role of this natural product involves redox chemistry.[634,635]

A number of non-oxovanadium(IV) complexes have been generated by Schiff base ligands containing O_2N donor sets. To date all the structurally characterized complexes contain two alkoxy or phenoxy functionalities and one imine-type functionality (**48**).[316,617,618] The effects on varying substituents on the phenoxo groups have been investigated.[620] The structure of bis[salicylaldehyde-2-hydroxyanilinato(2-)]V^{IV},[316] shows the vanadium to have a nearly octahedral coordination environment.

The vanadyl cation has been found to cleave DNA in the presence of hydroxamic acid.[636] Ligands with hydroxamic acid groups joined in the carbon framework furthermore have the possibility of creating polydentate ligands that will produce complexes with non-oxo-V^{IV} atoms.[15] Although no solid state structures have been reported for complexes with desferrioxamine B, this ligand has the potential to form such a vanadium complex and this is supported by spectroscopic data.[637] The kinetics and equilibria of the interaction between aqueous V^{IV} and desferrioxamine B methanesulfonate was characterized.[638] It was found that the unwrapping of the vanadyl tetradentate complex is about 50 times faster than that of the analogous ferric complex, and that the hydrolyzed form of V^{IV} reacts with the siderophore ca. 105 times faster than the vanadyl oligomeric and polymeric forms.[638]

The structures of bis(pentane-2,4-dione benzoylhydrazonato)V^{IV} (**122**) and bis(pentane-2,4-dione salicyloylhydrazonato)V^{IV} (**123**) show that the vanadium atom is in a trigonal–prismatic coordination geometry.[617] For these tridentate ligands, the four negatively charged enolic oxygen atoms effectively substitute for the $d\pi$–$p\pi$ interaction of the displaced oxo group. Evidence for such π interactions include V—O bond lengths which are shorter than 1.95–1.99 Å found in, for example, β-diketonato or diketonato-Schiff base complexes.[617] A tridentate NOS hydrazonato ligand was shown to produce a non-oxovanadium(IV) complex (**124**).[392] A dinuclear complex has been synthesized with three O_2N_2 hydrazonato ligands and has been structurally characterized (**74**).[639]

A related family of these non-oxovanadium complexes contains Schiff base ligands with O_2N_2 donor sets. Examples can be made from [VO(salen)] and $SOCl_2$ to generate *trans*-[VCl_2(salen)], which upon treatment with dilithium benzilate generates the benzilate–salen complex containing a non-oxovanadium(IV) center (**125**).[346] A μ-oxo dimer was prepared from [VO(salen)] by O atom extraction with Ph_3C^+ to yield $[\{V(salen)\}_2(\mu\text{-}O)\}]^{2+}$.[615]

N,*N*,*N*′,*N*′-tetrakis(2-hydroxybenzyl)ethylenediamine forms a non-oxovanadium derivative.[640] The electrochemical properties of this derivative have been determined in dimethylformamide and two well-defined reversible one-electron-transfer events were detected at +0.16 V for $E^1{}_{1/2}$ and at −0.84 V for $E^2{}_{1/2}$ (vs. Fc^+/Fc); these potentials correspond to the $V^{5+/4+}$ and $V^{4+/3+}$ redox couples, respectively.[640]

4.4.3.3 Nitrogen Ligands

4.4.3.3.1 Monodentate, one nitrogen donor

The tetrahedral complex tetrakis(dimethylamido)vanadium(IV) has been prepared (**126**).[641] The nitrogen and methyl groups of each ligand are nearly coplanar with the vanadium center. This versatile complex has been used as a precursor to other imido–V^{IV} complexes. Treatment with one equivalent of aniline generates $[V(NMe_2)_2(NHMe_2)_2(=NAr)]$, which upon treatment with excess Me_3SiCl produces $[V(NHMe_2)_2(=NAr)Cl_2]$ (**127**).[642] Other amido complexes have been

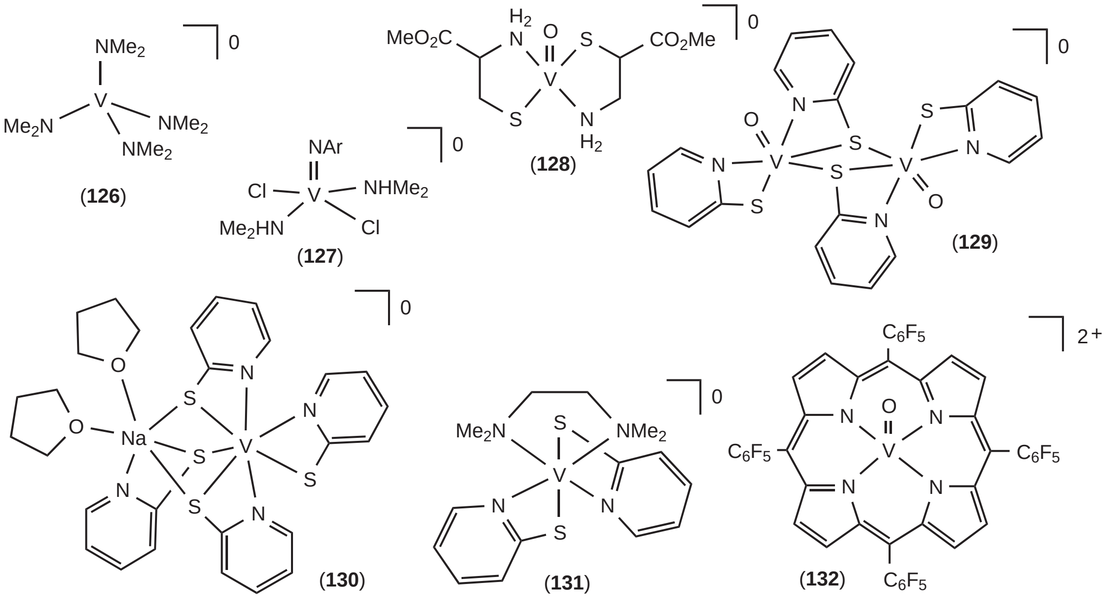


Figure 11 Structural illustrations of (**126–132**).

reported.[643–646] Imidodiphosphinoselenido complexes contain both five- and six-coordinate V atoms.[647] Several dinuclear V^{IV} complexes in which the two vanadium atoms are bridged by two single atoms are known. In one dinuclear compound, these two atoms are oxygen atoms utilizing bis(trimethylsilyl)amines as the supporting ligands.[648] Complexes of V^{IV} chlorides with acetyl and benzoyl cyanides have been prepared.[649]

4.4.3.3.2 *Bidentate, one and two nitrogen donors*

A number of V^{IV} and V^{V} complexes with the inorganic $H_3N_3S_2$ ($H_3N_3S_2$ = aminothiosulfur diimine) ligand have been prepared.[517,622–626] The α and β isomers of $[VCl_2(N_3S_2)]$ have been structurally characterized; the only structural difference is that the coordination polymer chains in the β form are rotated 11° relative to those in the α form.[622,623] In addition to the mononuclear species, a dinuclear complex has been isolated.[622] EPR spectroscopy detected superexchange coupling of the electron spins in some V^{IV}–V^{IV} dinuclear enaminoketone complexes.[650]

In addition to complexes with ON donor sets, complexes with bidentate N-donor atoms and other donors have been described. For example, after several solution studies the crystal structure of the bis(L-cysteine methyl ester)oxovanadium(IV) complex showed that the vanadium is coordinated by the amido nitrogens and thiolate sulfurs (**128**).[561] The complexes and reactivity of a series of pyridine-2-thiolate complexes of V(IV, III, and II) have been characterized (**129–131**).[651] The mass spectrometric fragmentation patterns of two of these complexes were investigated and show the formation of six 1:1 complexes and one 1:2 complex in the gas phase.[651]

4.4.3.3.3 *Polydentate, two or more nitrogen donors*

Mononuclear V^{IV} complexes of substituted hydroxamates have been characterized with 1,10-phenanthroline or 2,2′-bipyridine as supporting ligands. A seven-coordinate vanadium atom was proposed to exist in these complexes, although a six-coordinate complex may be more likely.[652] A range of hydroxamate-containing complexes have been prepared and were subsequently found to facilitate transport of V^{IV} into cells.[653]

Complexes with tetradentate N-donor ligands have been prepared. Although most of the studies reported for porphyrin-type complexes will be reviewed elsewhere, a few points regarding the properties of these complexes will be highlighted here. The structural characterization of V^{IV} porphyrin derivatives (**132**) has been reported.[654] The axial ligation of Lewis bases to the metalloporphyrins to explore the preferential sizes of ligands and specific steric restrictions has also been explored.[654] Resonance Raman analysis shows that the frequency of the V═O stretch is sensitive to interactions with a second axial ligand which weaken the V═O interaction.[655] Electrochemical studies in DMF have shown that porphyrin substituent groups strongly influence the redox chemistry of vanadyl porphyrins.[656] Spectroscopic techniques have been used to examine structural deformations in radical cation[657] or radical anion[658] vanadyl porphyrins. Vanadyl porphyrins can dimerize in solution and for one representative porphyrin the dimer formation constant was determined to be $1.7\,M^{-1}$.[659] A vanadium porphyrin complex with a hexadecylpyridiniumyl substituent formed micelles in ethanol–water or dimethylformamide–water mixtures.[660]

A complex containing macrocyclic diamidate ligands with the {VOCl} functionality and intramolecular hydrogen bonding has been reported.[661] A dimeric μ-oxo V^{IV} complex with tris(2-pyridylmethyl)amine has also been characterized.[662] Other V^{IV}–amide metallocyclic complexes have been prepared from ligands prepared by condensation of picolinic acid with 1,2-diaminobenzene (**133**) or 1,2-diaminocyclohexane.[663] Complexes with tris(3,5-dimethylpyrazolyl)borate have been isolated and resulted in a trigonally distorted octahedral geometry (**134**).[541,664–666] An unusual bidentate bonding mode was observed for the same tris(pyrazolyl)-borate ligand when solvents other than DMF were used; the use of non-DMF solvents led to the decomposition of the original complex (**134**) into (**135**).[667] One complex that contains a coordinating ferrocenecarboxylate ligand is EPR active; upon oxidation of the ferrocenecarboxylate ligand the complex becomes EPR silent.[664] Most of the dibridged V^{IV} tris(pyrazolyl)borate dimers are moderately antiferromagnetically coupled.[666]

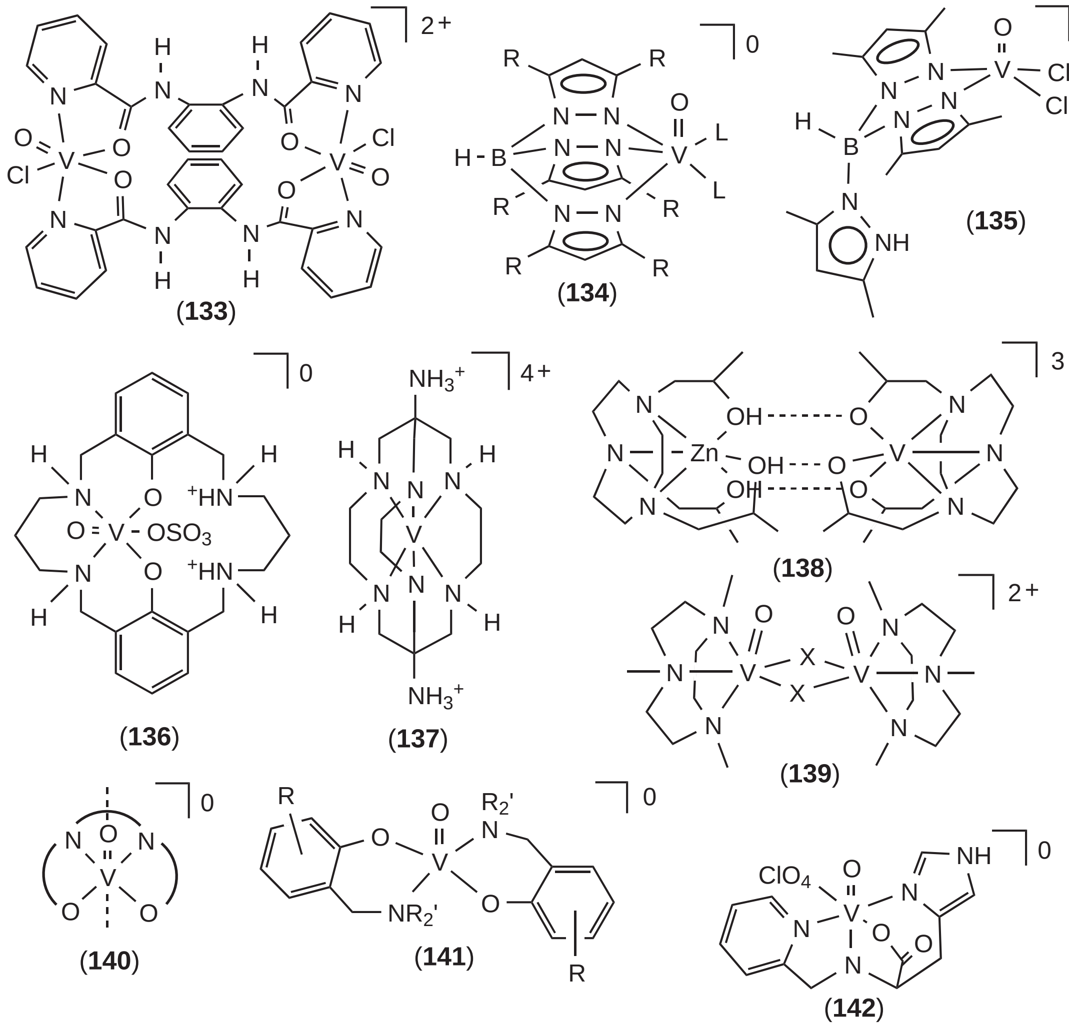


Figure 12 Structural illustrations of (**133–142**).

A pentadentate O_3N_2-donor ligand was found to bind two vanadyl ions. One amino and one alkoxy donor from each ligand bind to each vanadium while a third alkoxy donor bridges the two vanadium atoms; the square–pyramidal coordination spheres are completed by a bridging pyrazolate molecule.[668]

A number of macrocyclic ligands containing three N-donor and more functionalities have also been shown to bind V^{IV}. A macrocycle designed to bind two metals only complexed one oxovanadium(IV), however a sulfate moiety was associated with two protonated amine groups (**136**).[669] Examples of non-oxo-V^{IV} complexed to cage-like macrocycles have also been reported.[621,670] For the V^{IV} cage complex of the ligand derivative which contains two terminal $-NH_3^+$ groups, the X-ray crystal structure was determined and based upon charge considerations, two of the six coordinating amino groups must be deprotonated (**137**).[621] Because of the disorder in the crystal, spectroscopic studies were undertaken to establish which nitrogen donors were deprotonated, however these studies were inconclusive.[670] A non-oxo-V^{IV} ion bound to a pendant-arm macrocycle based on 1,4,7-triazacyclononane was found to co-crystallize with the analogous Zn^{II} complex to form a dimer linked by hydrogen-bonding interactions (**138**).[671] Complexes with two different, potentially hexadentate ligands (O_2N_4 and O_3N_3) containing phenolate, hydroxyl, imidazole, or pyridyl-type functionalities were investigated;[672] only five of the donor atoms in each ligand coordinate to the vanadium. Dinuclear μ-hydroxo, μ-oxo, and μ-carboxylato V^{IV} tacn complexes (**139**) show $d^1_{x^2-y^2}$–$d^1_{x^2-y^2}$ superexchange interactions via the bridging oxygen atom.[673,674]

Complexes of ligands with O-donors and two or three N-donors are known. The kinetics of the outer-sphere oxidation of *cis*-aquaoxovanadium(IV) complexes of [2-(pyridylmethyl)imino]diacetate and its derivatives were determined.[675] Complexes with Schiff bases have been used to mimic the structure and chemistry of vanadium bromoperoxidase.[275] The ligation of an imidazole functionality in the ligand has been found to readily dissociate, and is important to the functional aspects of this complex.[275] A variety of five-coordinate complexes with tridentate Schiff base complexes have been prepared, several of which have been found to form supramolecular polymeric structures through association between the V=O groups in a $\{V{=}O \cdots V{=}O \cdots V{=}O\}$ pattern (**140**).[627]

Several oxovanadium(IV) complexes (**141**) with ON-donor ligands were prepared from $[VOCl_2(thf)_2]$ (thf = tetrahydrofuran) and *ortho*-substituted phenols to study the electronic effects of *para* substituents in order to develop better $[VCl_2(OR)_2]$-type olefin polymerization catalysts.[676] The hyperfine coupling constants, the HOMO–LUMO transitions, and the oxidation potentials were all found to be linearly related to the Hammett σ constant of the substituent on the monoanionic aryloxy ring.[676]

A structurally characterized complex of *N,N′*-bis(2-pyridylmethyl)-(*S*)-histidine was also found to have insulin-enhancing properties (**142**).[564] Complexes with ligands such as pyrrolidine-*N*-carbodithioate[562] and *N*-2-(pyridylmethyl)-(*S*)-histidine[564] exhibited similar insulin-enhancing properties.

4.4.4.4 Sulfur Ligands

Only a few examples of monodentate S-donor ligands have been reported and include thiourea complexes with V^{IV}.[677] A simple coupling product from the reaction of terpyridine with the tetrathiolatovanadate anion has been prepared and structurally characterized (**143**).[678] The reactions of VO_2^+ with various phosphodithiolates have been reviewed.[679] The parent and V=S substituted complexes with ethane-1,2-dithiolate ligands have a square–pyramidal coordination geometry around the vanadium atoms (**144**).[680] The oxidation potentials of these systems were unusually low compared to $VS(acen)_2$ (acen = *N,N′*-ethylene-bis(acetylacetonylideneamine)).[681] Dithiocarbamate complexes (**145**) have been synthesized and tested for insulin-enhancing properties.[562,563] A tris(dithiolene)V^{IV} complex $[V(SC_2H_2S)_3]$ (**146**) was prepared and its structure was found to have D_{3h} symmetry; EPR measurements are consistent with a V^{IV} center, thus implying that a formal charge of -4 is delocalized over the three ligands.[682] Complexes derived from more bulky dithiolene ligands exhibited distorted octahedral geometries.[682] Compounds with ligands of even higher sulfur to carbon ratios have been described.[683] The reaction between the vanadyl cation and 1,2-dicyanoethylene-1,2-dithiolate forms a complex that has been characterized both in solution and in the solid state (**147**).[684] The synthesis of dihalobis(dialkyldithiocarbamato)vanadium(IV) complexes and their characterization has been reported for both the chloro and bromo derivatives.[685] The stoichiometric reaction of $[VCl(dipp)_2(thf)_2]$

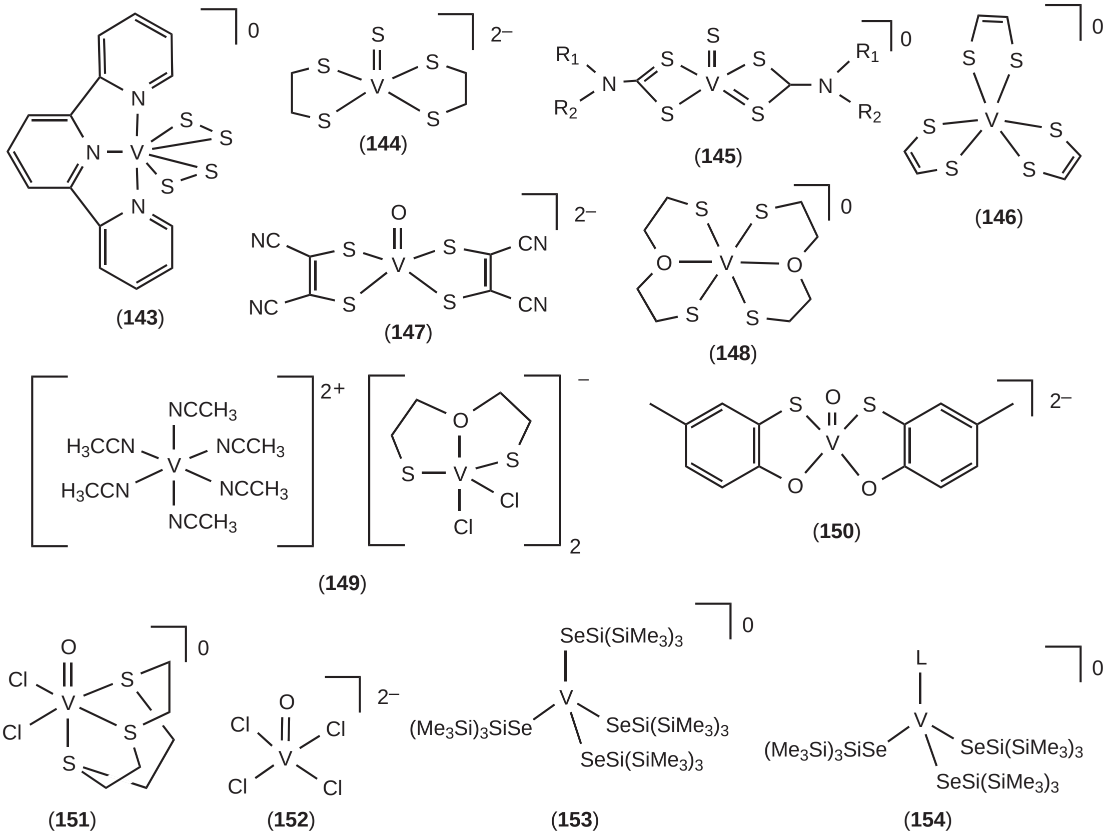


Figure 13 Structural illustrations of (**143–154**).

(dipp = 2, 6-diisopropylphenoxide) with 2,2′-oxydiethanethiol, $O(EtSH)_2$, forms an oxidized product $[V\{O(CH_2CH_2S)_2\}_2]$ (**148**) and a reduced product $[V(CH_3CN)_6][VCl_2\{O(CH_2CH_2S)_2\}]_2$ (**149**).[686]

Bidentate ligands containing OS donors, particularly in conjunction with carboxylate moieties, form strong complexes at pH values near the pK_a value for the thiol.[584,602,687–689] The reduction of V^{IV} to V^{III} by cysteine methyl ester in water has been found to be enhanced in the presence of amino polycarboxylates.[690] The ligand 2-mercapto-4-methylphenol forms a square–pyramidal five-coordinate complex with the vanadyl cation (**150**); the reported crystal structure is of the cis isomer.[691] The bidentate ligand 2-aminocyclopent-1-ene-1-carbodithioic acid forms non-oxo-V^{IV} complexes; based on spectroscopic studies and chemical precedence, an eight-coordinate vanadium atom is inferred.[692]

Contrary to hard and soft acid–base predictions, the first example of a vanadyl–thioether complex has been made (**151**).[693] The crown thioether 1,4,7-trithiacyclononane forms a stable 1:1 coordination complex upon reaction with VCl_3; the presence of adventitious water likely explains the hydrolysis/oxidation of V^{III} to form $V^{IV}O^{2+}$.[693] Complexes with a variety of bi- and tetradentate S-donor functionalities have been prepared as model complexes for nitrogenase.[498,694] These complexes have some structural similarities to the binding site of nitrogenase, however, in contrast to the cofactor they fail to convert N_2 to NH_3.

Glutathione is another ligand that has been investigated for complex formation.[689,695,696] Given the sensitivity of the EPR parameters to the equatorial coordination sphere of the vanadium atom, structural predictions have been made based on solution studies for a range of glutathione model complexes.[697]

4.4.3.5 Halides

The structure of a vanadyl tetrachloride salt has been characterized with the 1-ethyl-3-methylimidazolium cation (**152**).[698] The coordination chemistry of VO^{2+} with F^- was investigated in ionic melts.[699] X(α) calculations were carried out to characterize the electronic structures and *d–d* spectra of V^{IV} and VO^{2+} complexes; these calculations correctly predicted the energy level scheme for the $[VOCl_4]^{2-}$ species.[700] Monodentate and bidentate adducts of $[VOCl_2]$ with alkoxides and ketones were described and their solvation properties were documented.[701] The chlorination reactions of a number of tetra-, tri-, and bidentate Schiff base V^{IV} complexes with $SOCl_2$ and $SeOCl_2$ were characterized by EPR spectroscopy and their solvation properties investigated.[702]

4.4.3.6 Phosphorus and Other Ligands

Vanadium(IV) complexes with triphenylphosphine and dimethylphenylphosphine have been prepared and their properties evaluated.[703] The selenolates $\{V^{IV}[SeSi(SiMe_3)_3]_4\}$ (**153**) and $\{V^{II}[SeSi(SiMe_3)_2]_n\}$ were formed from a disproportionation reaction of the corresponding V^{III} dimer complex; the monomeric V^{III} complex could be isolated with an appropriate neutral monodentate ligand (**154**).[704] Vanadium(IV) complexes with 1,2-diselenosquarate have been prepared.[705] The topic of V^{IV}–C compounds has been described more thoroughly in the companion series *Comprehensive Organometallic Chemistry*; some examples include $[V(mes)_3(OSiMe_2{}^tBu)]$ and $[V(mes)_3(OSiPh_3)]$ (mes = mesityl).[477]

Dinuclear Cu^{II}–V^{IV} complexes exhibit ferromagnetic coupling for the single unpaired electron in the d^9 and d^1 ions.[706] Other heterodinuclear complexes in which superhyperfine coupling has been observed include the dinuclear V^{IV}–Tl^{I} enzyme complexes in pyruvate kinase[707] and *S*-adenosylmethionine synthase.[708]

4.4.4 VANADIUM(III)

4.4.4.1 Chemistry of Hydrated V^{III} Ions

Although water (and solvent) exchange is critical to understand complex formation and reactivity of metal ions in solution, experimental information with regard to the V^{III} and V^{II} systems has only recently emerged because of the difficulty of directly measuring water and solvent exchange for these ions. Experiments to measure the activation parameters by high-pressure NMR methods and theoretical methods have recently addressed these questions both in water[709,710] and in dimethylsulfoxide.[711] An associative (I_a) mechanism seems to be favored in general;[709–712] and an analysis of the ligand field stabilization energies has been carried out.[713] The stereochemistry and electronic structure of the $[V(OH_2)_6]^{3+}$ cation can result in structural abnormalities which may be observed in the solid state.[714]

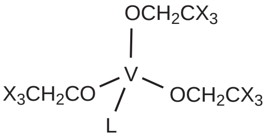
4.4.4.2 Oxygen Ligands

4.4.4.2.1 Monodentate, one oxygen donor

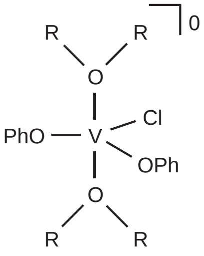
Vanadium(III) alkoxides with the formula $[V(OR)_3]$ tend to be inert and fail to react with ligands even under forcing conditions. However, ligands in which the alkoxide is derivatized with electronegative substituents, such as haloethoxides, result in $\{V(OR)_3\}$ species that forms complexes with pyridine, picolinic acid, and ethers (**155**).[715] The first homoleptic V^{III} complex with a derivatized D-glucofuranoside was structurally characterized and found to react with pyridine.[716] In the presence of alkali cations, this compound also adds an additional three ligands to generate a complex with pseudo-octahedral geometry.[717]

Phenoxide complexes have been of interest in catalysis because of their role as procatalysts for ethylene polymerization[25,718] and because in biology these complexes are found in certain organisms such as tunicates.[40,719–721] A variety of mononuclear (**156**,**157**)[81,718,722–724] and dinuclear (**158–161**)[718,722,725] V^{III} complexes have been made with simple[723] and sterically hindered[81,718,722] phenoxide ligands. The phenoxide can coordinate in a terminal (**158**) or bridging (**158**,**159**) manner. Complexes in which esters are bound through the C═O groups have also been reported (**160**).[725]

Two major groups of oxo-bridged dimers are the linear (μ-oxo) core (**162**) and the ligand-supported (μ-oxo)-bis(μ-carboxolato) core (**163**). The $\{V^{III}$–μ-O—$V^{III}\}$ complexes (**162**) show



(**155**)



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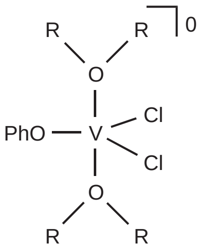

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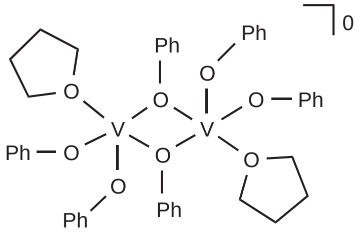
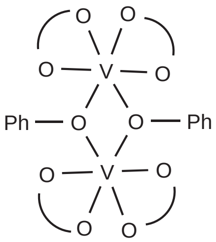


(**158**)



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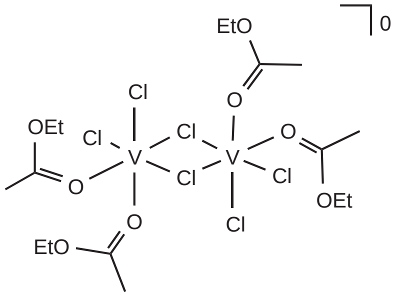
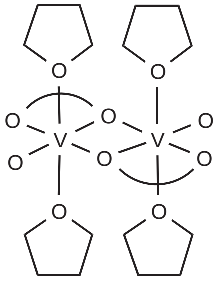
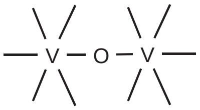


(**160**)



(**161**)



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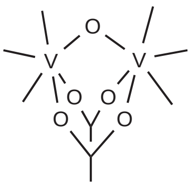
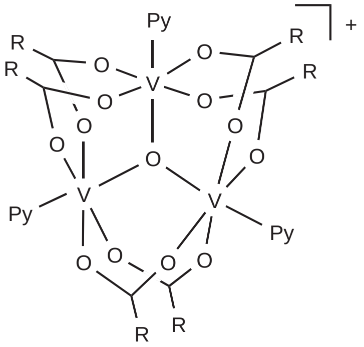
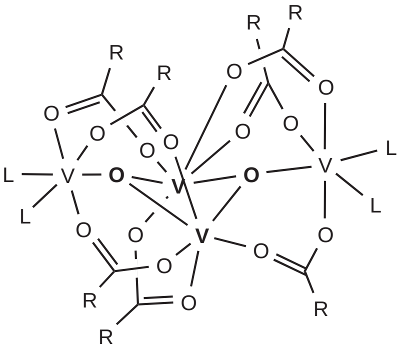


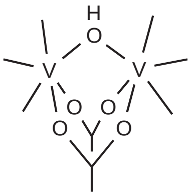
(**163**)



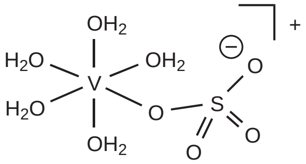
(**165**)



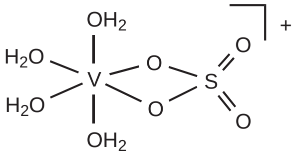
(**166**)



(**164**)



(**167a**)



(**167b**)

Figure 14 Structural illustrations of (**155–167**). The charges are given for structures and for structure types in which all the complexes have the same charge. For structure types that have differently charged ligands, no charge is given.

ferromagnetic coupling of the two V^{III} (d^2) ions. A theoretical study suggests that the occurrence of either ferromagnetism or antiferromagnetism is attributed to the balance of covalent and charge-transfer configurations.[726] Members of the class of compounds described by the structural motif in (**163**) show strong ferromagnetic coupling interactions. Protonation of (**163**) results in (**164**) which is now antiferromagnetically coupled.[727,728] To permit the structural characterization of these systems (**163**,**164**) a stabilizing ligand such as tris(pyrazolyl)borate ligand was used.[729] Additional structural motifs have been reported including (**165**,**166**). A particularly interesting example of (**164**) was reported in which H-bonding was observed between the bridging proton and a tetrahydrofuran molecule sandwiched between the stabilizing tris(pyrazolyl)borate ligand.[729] Several variations on the (**163**,**164**) motif have been reported,[730] including the class of complexes illustrated by the trinuclear structure (**165**).[731] The structural motif found in (**166**), coined the “butterfly” (or “diamond core”) structure of the {V—O—V—O} type, is described in detail for the analogous V^V complexes (*vide supra*). In (**166**) two additional vanadium atoms supported by a bidentate ligand make up the tetranuclear cluster with several carboxylate groups chelated to the various vanadium centers in pair-wise fashion.[732] In addition to representing a beautiful solid state structure, these compounds remain intact in solution, and exhibit out-of-phase a.c. susceptibility signals, a signature of single-molecule magnets.[732,733] Some of these compounds possess both ferro- and antiferromagnetic exchange interactions leading to spin-frustration effects and an $S = 3$ ground state.[732,733]

A number of phosphate and phosphonate complexes have been reported. These are important because of the role of $[(VO)_2P_2O_7]$ in the selective oxidation of *n*-butane to maleic anhydride.[734] Representative complexes include V^{III} bound to various protonation states of phosphate/pyrophosphate,[734,735] complexes containing additional cations,[736] and other anions.[737,738] A variety of structural motifs can form, and some of these are structural analogs of V^{III}–DNA interactions.[739] These types of complexes and interactions are of interest since it has been shown that various forms of vanadium can cleave DNA.[740,741]

The interaction of sulfate with V^{III} is of importance with regard to understanding the role of V^{III} in tunicates.[742–744] Various types of model complexes have been reported showing that the sulfate can be either monodentate or bidentate in the presence or absence of stabilizing ligands.[745,746] Spectroscopic studies have been carried out on the tunicate *Ascidia ceratodes* showing that V^{III} ions in the tunicates exist as a mixture of monomeric $[V(H_2O)_6]^{3+}$ and $[(VSO_4)(H_2O)_{4-5}]^+$ (**167**).[742] Recently a protein that complexes vanadium has been isolated from tunicates, and its selectivity for vanadium has been demonstrated.[17,214,740]

4.4.4.2.2 *Bidentate, one or two oxygen donors*

Adenine complexes forming with V^{III} were characterized using potentiometry and UV-vis spectroscopy.[747] In contrast to their mononuclear structure (**168**),[509] catecholate ligands form dinuclear complexes with V^{III} (**162**), which may be of interest because of their potential as ethylene polymerization catalysts.[25,718] Bidentate alkoxy ligands such as 2-tetrahydrofurfuroxide form complexes containing both V^{III} and Mg^{II} which may be potential polymerization procatalysts and N_2 activators.[748] A series of 1:3 (metal:ligand) complexes of acac have been reported (**168**).[749] The acac ligand serves to stabilize the vanadium, allowing a range of other heteroligand complexes to be isolated including ether[749] and halide[749,750] complexes. Small solvent guest molecules co-crystallize with these compounds,[751] and cluster compounds larger than the 1:3 complex were observed by mass spectroscopy.[752] Acac groups incorporated in a greater ligand framework can lead to dinuclear complexes,[753] but such ligand extensions do not enhance the Ziegler–Natta catalytic properties of these complexes.[754] A similar complex with the general structure (**168**) was reported with the ligand 2-(diphenylphosphinoyl)propanoic acid.[755] Oxalate forms a monomeric, six-coordinate complex with V^{III} (**169**);[756] however, if sulfate is present a coordination polymer is formed (**170**).[746]

The synthesis and characterization of a V^{III} complex with picolinic acid (**171**) showed that this complex remained stable in solution for several days and survived heating up to 180 °C without oxidative decomposition.[757] Complexes with amino acids including proline, phenylalanine, tryptophan, and valine have also been prepared and characterized.[758] The complex that forms with histidine was investigated in the solid state[759,760] and in solution by potentiometry.[761] A mixed complex with both picolinate and dipicolinate ligands containing seven-coordinate V^{III} was reported.[762] A V^{III} complex with a bidentate Schiff base hydrazone was prepared and represents a rare example of one of the few structurally characterized V^{III} Schiff base complexes and the only structurally characterized V^{III} hydrazone complex (**172** and see Tables 4 and 5).[763] (Hydroxyphenyl) oxazoline–vanadium(III) complexes have a high conformational rigidity in the oxazoline ligand which is attributed to an intramolecular H bond.[764]

4.4.4.2.3 *Polydentate, two or more oxygen donors*

The structure of a V^{III}–tetraethylene glycol complex was reported (**173**), and its V^V/V^{III} redox couple in acidic organic solutions was described.[765] Metalation of monomethoxycalix[4]arene with $[V(mes)_3thf]$ led to various derivatives which were characterized by X-ray crystallography.[766] The vanadium cap could be topped off with an oxo group, a diphenylhydrazine ligand, or by

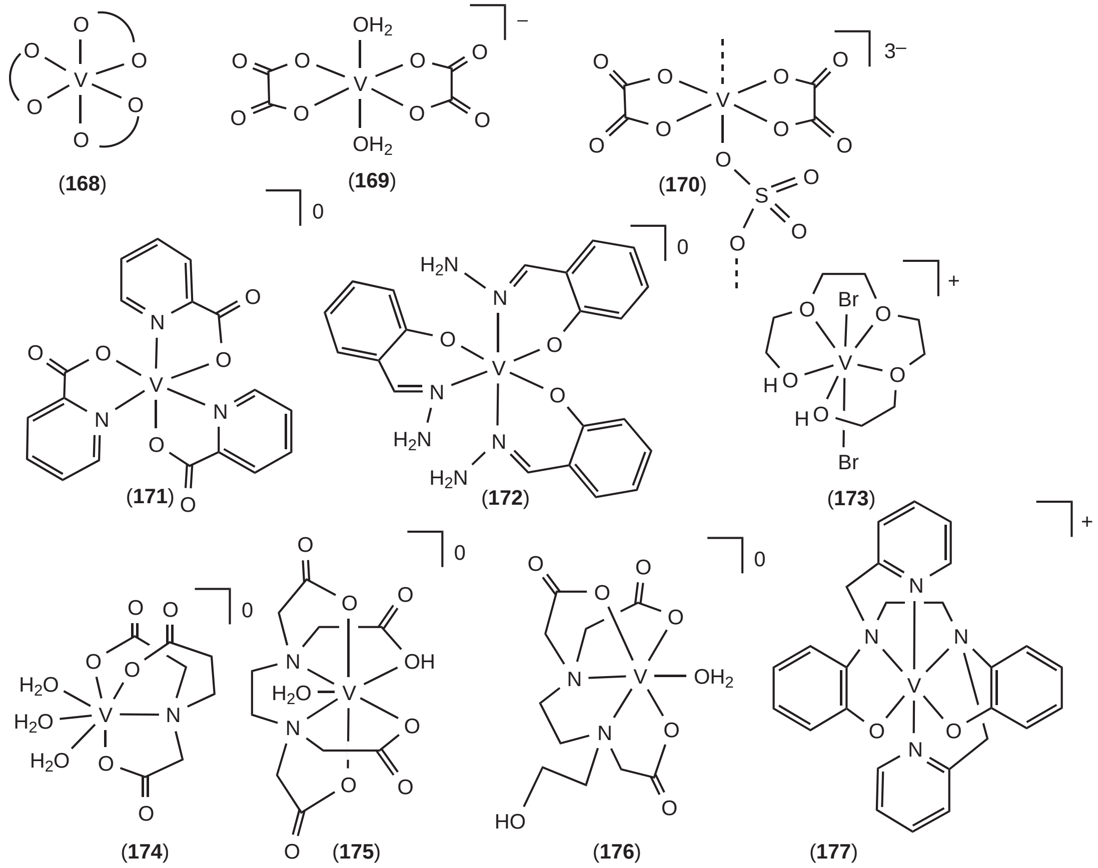


Figure 15 Structural illustrations of (**168–177**). The charges are given for structures and for structure types in which all the complexes have the same charge. For structure types that have differently charged ligands, no charge is given.

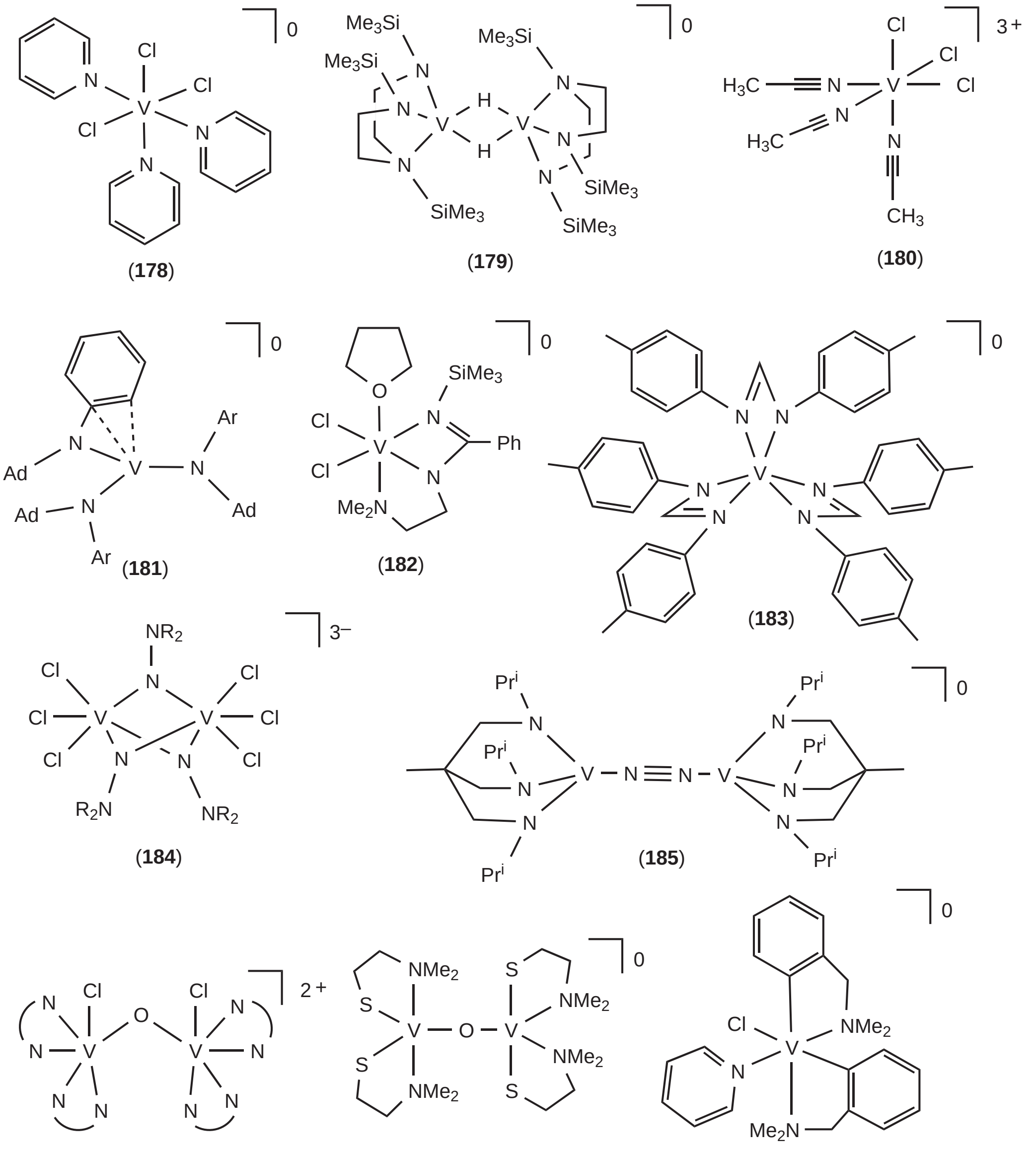
dimerization. These complexes were utilized to model the interaction of vanadium compounds with oxo surfaces.[766]

Nitrilotriacetate and related ligands form 1:1 V^{III} complexes with three water molecules completing the coordination sphere (**174**).[767–769] When one acetate group is exchanged with a pyridyl group, dinuclear complexes are isolated with ferromagnetically coupled spins.[769] A wide range of EDTA-related ligands have been used to form V^{III} complexes. The structure of the parent complex,[770] its monoprotonated form (**175**),[771] and a complex in which two propionate groups replace two of the acetate groups[768] have been structurally characterized. The two-electron transfer process was investigated for a complex in which one carboxylate group in the ligand was substituted with an alkoxy group; an intermediate species was characterized (**176**).[772] The ethylene diamine unit has also been substituted with propylenediamine,[773] 2-propanol-1,3-diamine,[773] and 1,3-propanediamine.[774] Other ligands with this basic structural motif but with important differences in coordinating donor atoms and their V^{III} complexes have been reported such as (**177**).[775] Some of these complexes yield oxo-bridged dinuclear complexes upon base hydrolysis.[768,774] In one complex a sulfate anion that is free in solution was found to coordinate to V^{III} in the solid state.[776] The spectral differences between six- and seven-coordinate complexes, particularly in the near-infrared region, are diagnostic in both the solid state and in solution.[777]

4.4.4.3 Nitrogen Ligands

4.4.4.3.1 Monodentate, one nitrogen donor

Three pyridine ligands coordinate to V^{III} in a meridional configuration with the pyridines planes twisted significantly from the metal–ligand planes (**178**).[778] The synthesis and structural



(178) (179) (180) (181) (182) (183) (184) (185) (186) (187) (188)

Figure 16 Structural illustrations of (**178–188**).

characterization of $N(SiMe_3)_2$–V^{III} complexes have been reported.[362] The silylamino(disilylamido) ligand was found to support a dimeric, non-metallocene V^{III} hydride-bridging structure (**179**).[779]

Vanadium(III) chloride in acetonitrile generates isomers of the $[VCl_3(CH_3CN)_3]$ adduct (the facial isomer is shown in (**180**)); solvent exchange takes place by two different mechanisms at two different types of CH_3CN sites in the complex.[780] The kinetics of formation and dissociation of $[V(H_2O)_5NCS]^{2+}$ are consistent with an associative interchange (I_a) mechanism;[781] these results are in agreement with kinetic data obtained for the hexahydrate complex (*vide supra*). A dinuclear isocyanide complex capped with two phenolate groups was isolated from the reaction of isocyanide with a chlorovanadium(III) precursor rather than the expected product which would result from the insertion of isocyanide into the V—Cl bond.[782] A bulky amide has been designed for the purpose of preparing a coordinatively unsaturated vanadium complex, which resulted in the first mononuclear, homoleptic V^{III} amide complex (**181**).[783] This complex reacts with chalcogens to yield diamagnetic, terminal chalcogenide derivatives.[783]

4.4.4.3.2 Bidentate, one or two nitrogen donors

(i) Amidinate ligands

A bidentate, amidinate ancillary ligand with a pendant tertiary amine functionality forms a complex with V^{III} in which the ligand adopts a facial geometry (**182**).[784] This type of complex, in the presence of a co-catalyst, is effective in ethylene polymerization catalysis. Related complexes have been reported with the formamidinate ligand[785,786] and a representative crystal structure shows the vanadium to have a severely distorted octahedral coordination environment (**183**).[786] Benzamidate ligands were also investigated with regard to the structure of the metal complex and its activity in catalytic ethylene oligomerization.[787] The pentafluorobenzamidinate ligand forms catalysts that are superior to the parent compounds.[787]

The vanadium-containing *Azotobacter vinelandii* nitrogenase enzyme reduces N_2 to produce NH_3 and trace amounts of N_2H_4. This enzymatic reaction prompted investigations of complex formation between V^{III} and N_2H_4 and its derivatives.[8] Substituted hydrazines form dinuclear V^{III} complexes in which the hydrazide bridges the two V atoms (**184**).[788] In mononuclear complexes, the two hydrazine groups are coordinated head-on in a trans configuration.[788] While most hydrazide complexes coordinate in a head-on fashion, some have been proposed to coordinate in a side-on manner.[789]

N_2 coordination by metal complexes is considered the first step in the N_2 fixation processes. The activation of N_2, by forming end-on or bridging N_2 adducts in dinuclear systems, has been studied for several years.[790] This reaction is particularly effective with early transition metal complexes where octahedral complexes tend to favor the high spin states of the metal.[790] In dinuclear complexes the N_2 can be poorly to strongly activated depending on the charge of the complex, the presence of alkali atoms, and the spin state of the complex.[791] In mononuclear complexes N_2 is always poorly activated[791] and not surprisingly, no mononuclear $\{V^{III}—N_2\}$ complexes have been observed. The preparation and characterization of a $\{V^{III}—N_2—V^{III}\}$ complex has been reported (**185**).[792]

Dimeric oxo-bridged V^{III} complexes with bipy or phen as supportive ligands (**186**) were found to cleave DNA without the addition of exogenous oxidants or reductants.[740] The dinuclear V^{III} complex formed from 2-(dimethylamino)ethanethiol has a linear $\{V—O—V\}^{4+}$ unit (**187**).[793] This compound was the first example of a class of dinuclear complexes containing NS donors.[793]

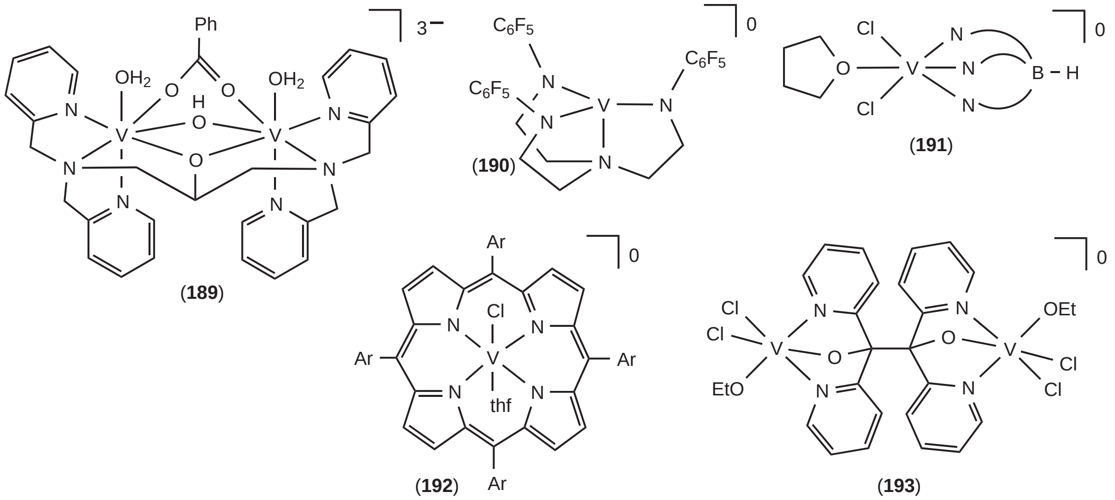
Although the description of most organometallic complexes is beyond the scope of this review, some of these types of complexes are relevant to the goal of developing catalysts that fix N_2. The V^{III} complex with the (dimethylamino)methylphenyl ligand (**188**) is an example of such a complex and is stable in solution.[794]

4.4.4.3.3 Polydentate, two or more nitrogen donors

A dinuclear V^{III} complex forms with the ligand 1,2-bis(2,2′-bipyridyl-6-yl)ethane and shows strong ferromagnetic coupling between the V atoms with $J > 100\,\mathrm{cm}^{-1}$ ($S = 2$ ground state).[795] A variety of heptadentate ligands designed to have bridging alkoxy groups were used to characterize binuclear V^{III} complexes; showing either ferromagnetic coupling (for the mixed alkoxide/carboxylate-bridged systems) or antiferromagnetic coupling (for the dialkoxide-bridged system).[796] The polydentate ligands serve as excellent supports for the metal ions as in, for example, the design of a μ-hydroxo dimer with three different functional groups coordinating the vanadium (**189**).[797]

A tetradentate N-donor ligand was used to form a monopyramidal V^{III} complex (**190**) that failed to bind even strong π acceptors such as CO; upon oxidation the complex dimerized.[798] An interesting structure is observed for the mixed valence complex $[V_3Cl_5(tmeda)][V(NPh_2)_4]$ in which the three vanadium(II) ions are coordinated by tmeda ligands and bridging chlorides while the single vanadium(III) ion is coordinated solely by four diphenylamido ligands.[799] A tridentate N-donor ligand such as 1,4,7-triazacyclononane facilitates self-assembly of the $\{V_2(\mu\text{-}O)(\mu\text{-}MeCO_2)_2\}^{2+}$ core.[800] The tris(pyrazolyl)borate complex (**191**), on the other hand, has been used in the preparation of the V^{III} half-sandwich complex $[\eta^5\text{-}CpVCl_2]$ (Cp = cyclopentadienyl).[801]

The first V^{III} porphyrin species was isolated by electrochemical reduction of the corresponding non-oxo-V^{IV} porphyrin[802] and shortly thereafter the first structure of a V^{III} porphyrin was reported (**192**).[803] These studies were supplemented by the structural characterization of a related V^{III} phthalocyanine complex.[804] Bis(pyridyl)ketone undergoes reductive coupling in the presence



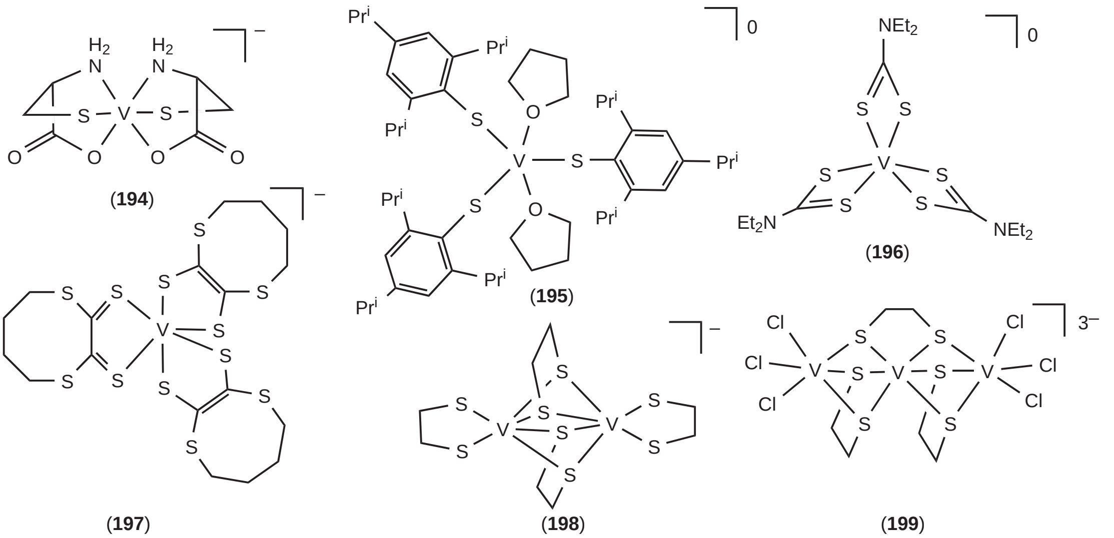
(189) (190) (191) (192) (193)

Figure 17 Structural illustrations of (**189–193**).

of vanadium[805] and forms the corresponding V^{III} complex with a hexadentate coupled ligand (**193**).[806] Coupling acac with ethylene diamine results in a tetradentate ligand that, upon complex formation, allows versatile chemistry to take place at the vanadium (**54**).[328] Vanadium(III) Schiff base complexes with the structural motifs found in (**40**,**42**,**51**,**53**,**54**,**61**–**63**,**65**,**66**) have been prepared generating mononuclear and polymeric arrays (see Tables 4 and 5).[364,807] A vanadium(III) dimeric μ-oxo Schiff base complex has been isolated.[807] Heptadentate and octadentate ligands formed by Schiff base coupling reactions are found to form either a mononuclear vanadium complex with an O_3N_3 coordination sphere,[808] or dinuclear vanadium complexes.[369,809]

4.4.4.4 Sulfur Ligands

The V^{III} complex with L-cysteine was prepared and characterized; the crystal structure shows a 1:2 stoichiometry and that the two S-donors are trans to one another while the O- and N-donors are cis to one another (**194**).[810] With three different donor functionalities, this 1:2 complex illustrates key aspects of V^{III} coordination chemistry. To identify the mode of action of cellular vanadium species and the roles of cysteine and glutathione in cellular redox chemistry, the redox and complexation chemistry of vanadium with sulfur-containing ligands must be better



(194) (195) (196) (197) (198) (199)

Figure 18 Structural illustrations of (**194–199**).

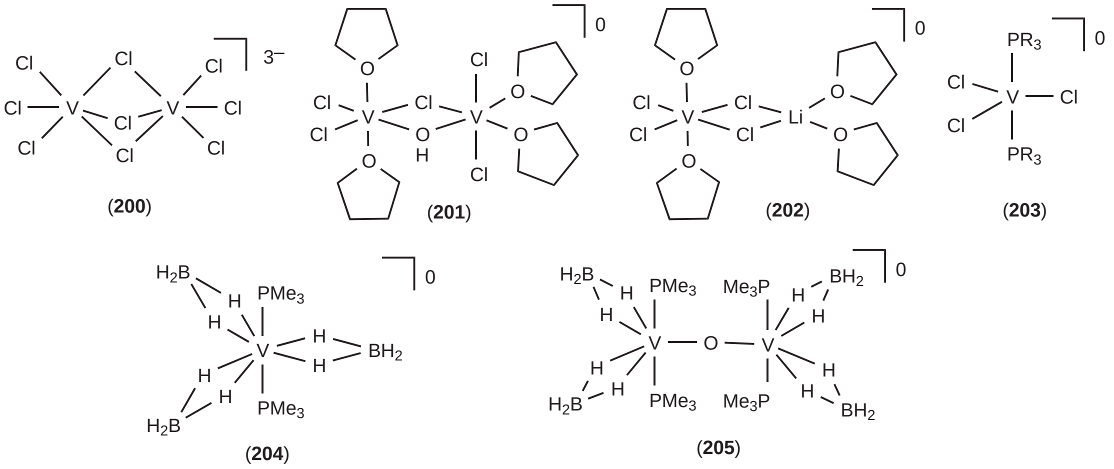
understood. A heteroleptic pentacoordinate V^{III} complex was obtained from the reaction of vanadium(III) and the bulky 2,4,6-tri(isopropyl)benzenethiolate in thf (**195**).[811] Vanadium(III) complexes with dithiocarbamate have been prepared and structurally characterized showing that the dithiocarbamate group acts as a bidentate ligand (**196**).[812]

The reactions of three different unsaturated vicinal thiolates with V^{III} led to several products, one of which was characterized by X-ray crystallography (**197**).[813] Extended Hückel molecular orbital calculations and structural data suggest that (**197**) is best described as a V^{III} complex with one oxidized ligand.[813] The reaction of V^{III} with ethanethiolate generates a mixed-valence binuclear complex (**198**) and a $\{V^{III}-\mu\text{–}S\text{–}V^{III}-\mu\text{–}S\text{–}V^{III}\}$ trinuclear complex (**199**).[814] The structural, spectroscopic, and magnetic properties of these complexes were characterized in great detail. In the dimer the electrons are coupled in an antiferromagnetic manner, whereas the trimer has an $S=3$ ground state that indicates ferromagnetic coupling between the V^{III} centers.[814]

The sulfur-containing analogs of acac (with either one or two S atoms) have been prepared, and the V^{III} complexes described.[815] Vanadium(III) forms a linear trinuclear complex with 2-aminoethanethiolate and Rh^{III} or Ir^{III}.[816] A new class of ethylene polymerization catalysts has been introduced, the parent complex being a V^{III} complex with the 2,2′-oxydiethanethiolate ligand.[817] The V^{III} complex with two 3-thiapentane-1,5-dithiolato ligands forms a zigzag chain structure in the presence of Li^+ ions.[818] These compounds were explored as potential ethylene polymerization catalysts in the presence of an aluminum co-catalyst; mechanistic studies suggest that when the $O(CH_2CH_2S)_2{}^{2-}$ ligand migrates to an aluminum ion, it produces an "inactive" V^{II} species.[686] When vanadium is incorporated into an iron–sulfur cluster $[VFe_3S_4]^{2+}$ moieties are generated; these species are capable of catalyzing the reduction of hydrazine by cobaltocene/lutidine hydrochloride.[819]

4.4.4.5 Halides

The $[V_2Cl_9]^{3-}$ anion has been prepared and the structure shows three bridging chlorides (**200**).[820] The six terminal chlorides of $[V_2Cl_9]^{3-}$ are readily exchanged with tetrahydrofuran to form $[(thf)_3V\text{–}\mu\text{–}Cl_3\text{–}V(thf)_3]^{3+}$ (**201**).[821] A dinuclear system with a bridging chloride and hydroxide demonstrates that even the bridging chlorides can be exchanged (**201**).[822] Mononuclear complexes have also been reported in which a $\{Li(thf)\}^+$ unit coordinates to two of the four chlorides that are bound to the vanadium (**202**).[823] VBr_3 was produced from the halide exchange reaction of VCl_4 with dry HBr at temperatures of ca. $-50\,°C$ to $+30\,°C$.[824] A trichlorodiphosphine V^{III} complex has been reported (**203**); upon long refluxing in toluene and PPh_2Me, the $[VCl_3(MeCN)_3]$ complex could be converted into $[VCl_3(MeCN)(PPh_2Me)]$.[825] Equilibrium studies on the complexation of Al^{III} and V^{III} by fluoride were investigated in molten KSCN.[826] $[VF_5O]^{2-}$ and $[(VF_3O_2)]$ have been structurally characterized.[827]



(**200**) (**201**) (**202**) (**203**)

(**204**) (**205**)

Figure 19 Structural illustrations of (**200–205**).

4.4.4.6 Phosphorus and Other Ligands

The complex *trans*-*mer*-[$VCl_3(OPMe_2Ph)(PMe_2PH)_2$] has been prepared and structurally characterized; in solution, the chloride ligands are rapidly displaced by solvent or phosphine molecules.[828] V^{III} reacts with aminotriphosphine to generate a complex which gives access to a new class of organometallic compounds (by reaction with alkyl or aryl lithium reagents).[829] Other V^{III} complexes with monodentate phosphines have been structurally characterized (**203**).[825,830]

V^{III} tetraborohydride complexes have been prepared and structurally characterized (**204**,**205**).[831] Mononuclear complexes[831,832] were prepared as well as one dinuclear complex (**205**) containing a linear μ-oxo bridge.[831] An unusual feature of this compound is that it contains both a μ-oxo bridge and BH_4^- ligands which would not seem very likely to coexist in the same molecule. The organometallic [$V_2N_2(mes)_6$] complex[833] produces NH_4^+ and/or $N_2H_5^+$ with protic reagents.

4.4.5 VANADIUM(II)

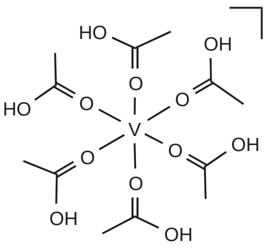
The known V^{2+} complexes thus far reported contain primarily N-, O-, P-, and halide donor ligands. The predominant coordination geometry is octahedral, although some four- and five-coordinate complexes have been reported (*vide infra*). Because most V^{II} complexes are rather air sensitive and require oxygen-free environments for both synthesis and storage, contamination of V^{II} compounds with higher oxidation states is a problem.[2] Accordingly, aqueous salts of V^{II}, including the hexahydrate salt of VSO_4,[834] were prepared initially from the electrolytic reduction of aqueous vanadyl sulfate solutions.[2] The production of V^{II} salts by treating vanadium metal with HCl or HBr in either water or acetic acid solutions were the first examples of chemically generated V^{II};[835] a Zn/Hg amalgam has also been used to reduce solutions of V^{III} to V^{II}.[836] The solid-state structures of several vanadium(II) hydrates have been determined either by X-ray crystallographic or neutron diffraction techniques.[834,837–841] A comparison of the $V—O_{H_2O}$ bond lengths[837] shows that these bonds range from 2.10 Å to 2.15 Å; the 0.05 Å difference is the smallest of all the metals in the first transition series.[839]

A theoretical study that calculated the volume of activation of the water exchange process in $[V(H_2O)_6]^{2+}$ led to the proposal that water exchange proceeds via an I_a mechanism[712,842] rather than a dissociative mechanism, the commonly accepted one.[843,844] Stopped-flow methods showed that when the concentration of $[V(H_2O)_6]^{2+}$ exceeded 0.1 M, V^{II} reacted with dioxygen to yield vanadyl cations.[845] Because no free peroxide was detected, the mechanism of this oxidation process was proposed to involve an equilibrium process between a V^{II}–dioxygen adduct and a μ-peroxo-V^{III} dimer (see Equation (2)). The one electron oxidation of $V(H_2O)_6^{2+}$ by cobalt(III) complexes with N-donor ligands[846] or with pentacyanocobalt(III) complexes[847] was found to involve outer-sphere mechanisms. In one of these systems the cobalt ion ligand framework contained a free phenanthroline unit,[848] and the two-step process for the reduction of the cobalt ion involved binding of the V^{2+} to the free phenanthroline unit followed by subsequent electron transfer via an outer sphere process.[848] Vanadium(II) hexahydrate ions have been shown to react with alkyl radicals to form alkanes and vanadium(III) hexahydrate ions.[849]

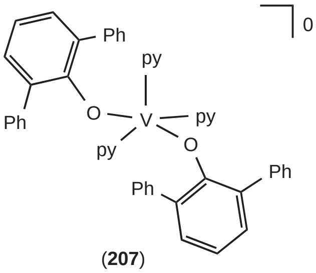
$$\{V^{II}O_2\}^{2+} + V^{II} \rightleftharpoons \{V^{III}—O—O—V^{III}\}^{4+} \rightarrow 2\{V^{IV}O\}^{2+} \qquad (2)$$

4.4.5.1 Oxygen Ligands

Mononuclear acetic acid complexes were prepared via the reaction of vanadium metal with acetic acid and HX gas (X = Br or Cl) giving a complex in which the carbonyl oxygens rather than the hydroxy oxygens of the acetic acid ligands bind to the vanadium (**206**).[835,850] A series of V^{II} complexes with sterically hindered phenoxides have been prepared by ligand exchange reactions and have been structurally characterized (**207**).[724] Nonaqueous sulfate salts of mono- and bidentate amino ligands are easily prepared from $[V(H_2O)_6]SO_4$ resulting in varying structural motifs; for example, $[V(bpy)_2SO_4]$ shows that the sulfate acts as a bidentate donor to the vanadium.[851] The first V^{II} ligated acac complex has been structurally characterized (**208**).[753] A carboxylate-bridged dinuclear vanadium complex with a small amount of antiferromagnetic



(**206**)



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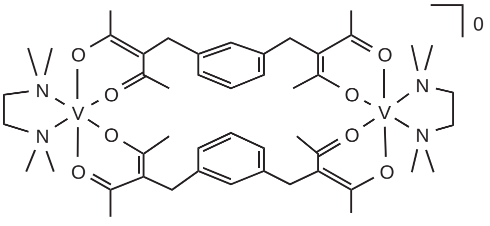
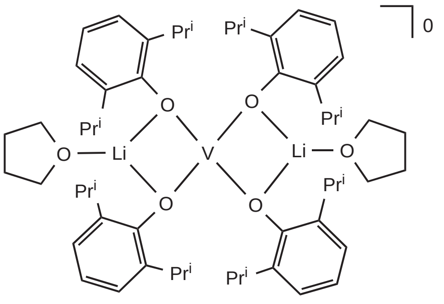
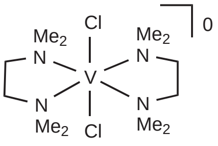


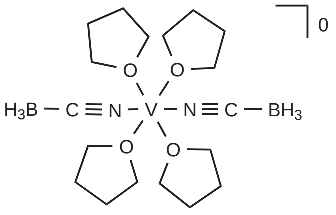
(**208**)



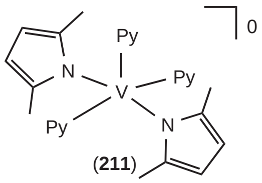
(**209**)



(**210**)



(**212**)



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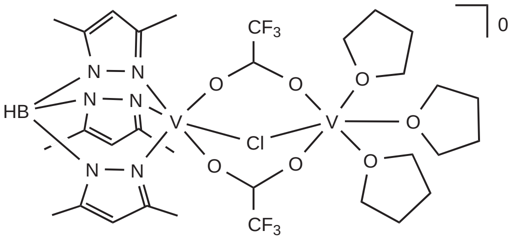
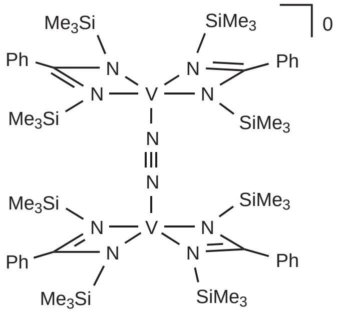
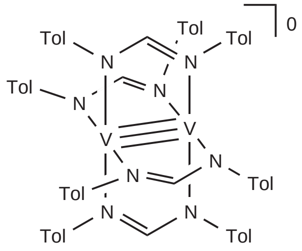


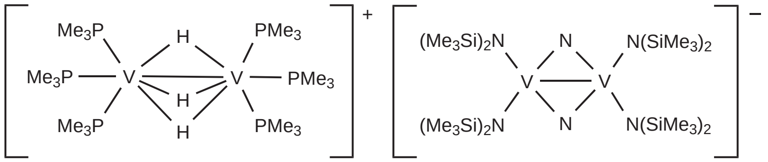
(**213**)



(**214**)



(**215**)



(**216**)

Figure 20 Structural illustrations of (**206–216**).

coupling ($J = -21\,\mathrm{cm}^{-1}$) was prepared from $[V_2(\mu\text{-}Cl_3)(thf)_6]_2[Zn_2Cl_6]_2$ and NaO_2CCF_3.[852] While most V^{II} complexes contain six-coordinate vanadium,[2] a four-coordinate complex was obtained with 2,6-diisopropylphenol (**209**).[853] This compound has a nearly square–planar vanadium atom with two pairs of *cis*-phenolate donors linked by a single $\{Li(thf)\}^+$ unit.[853] The V^{II} complex $[H(thf)_n][V(CF_3CO_2)_3]$ was formed from the reaction of dimesitylvanadium(0) with triflic acid.[854] Based upon IR and magnetic data, the complex was proposed to be mononuclear with a six-coordinate vanadium center. The triflate moiety was susceptible towards nucleophiles and its reaction with methyl iodide yielded the methylated complex $[V(CF_3CO_2)_2(CF_3CO_2CH_3)]$.[854]

4.4.5.2 Nitrogen Ligands

Monomeric V^{II} complexes with diamino, pyridyl, and pyrrolidyl ligands can be obtained from $[V_2(\mu\text{-}Cl_3)(thf)_6]_2[Zn_2Cl_6]$.[855] The well-characterized *trans*-$[V(tmeda)_2Cl_2]$ (**210**)[855] has been used as a starting material for several metal complexes, including those with organic amidinate ($RNC(R')NR^-$) and acetanilide ($PhNC(Me)O^-$) ligands.[856,857] A five-coordinate, square–pyramidal V^{II} complex was obtained with the 2,5-dimethylpyrrolyl ligand (**211**).[856]

A cyanohydridoborato vanadium(II) complex, *trans*-$[V(NCBH_3)_2(thf)_4]$, has been synthesized and structurally characterized (**212**).[858] Additional oligomeric complexes have been prepared; complexes that have been characterized include trinuclear vanadium complexes,[859–862] dinuclear V–Fe complexes,[863] and the first tetranuclear V^{II} species $[V_4(\mu_3\text{-}Cl)_2(\mu\text{-}Cl)_2(\mu\text{-}CF_3CO_2)_2(thf)_6]$.[864] The addition of tris(pyrazolyl)borate ligand to the tetranuclear species results in the dissociation of the complex to form a neutral dimeric species $[V(tpb)(\mu\text{-}Cl)(\mu\text{-}CF_3CO_2)_2V(thf)_3]$ (**213**) in which one of the vanadium centers is facially coordinated by tpb.[864]

Amides and amidinate ligands ($RNC(R')NR^-$) have been employed as precursors for dinuclear compounds with metal–metal bonds as well as N_2-bridged dinuclear vanadium complexes (**214–216**).[857,865–867] The strong metal–metal bonds (1.97 Å) are readily cleaved by pyridine to yield a mononuclear complex $[V(RNC(R')NR)_2(py)_2]$.[857] The dinitrogen-bridged complex (**214**) has V—N and N—N bond lengths of 1.76 Å and 1.24 Å, respectively; these dinuclear complexes can be easily cleaved by the addition of thf, which results in the release of N_2 gas and the formation of a monomeric complex with the formula $[V(RNC(R')NR)_2(thf)_2]$.[857] Restricted Hartree–Fock (RHF) and configuration interaction *ab initio* calculations on N_2-bridged V^{II} and V^{III} hydrido complexes suggested that N_2 activation is greater for V^{II} bimetallic systems.[791] In contrast, neither the V^{III} bimetallic nor the monomeric V^{II} and V^{III} complexes showed significant activation of N_2.[791] A later theoretical study suggested that pseudo-octahedral V^{II} centers should have a larger degree of N_2 activation than pseudo-tetrahedral centers.[790] This effect was attributed to the ability of an octahedral coordination environment to stabilize higher spin states that more easily facilitate N_2 activation.[790]

A vanadium(II) porphyrin complex was synthesized by the one-electron reduction of the corresponding V^{III} porphyrin with $NaBEt_3H$ in thf.[868] An octaethylporphyrinogen V^{II} complex was found to form a μ-N dinuclear V^{III} complex.[869] If this monomeric porphyrinogen complex is left in thf solution for extended periods of time, it will abstract an oxygen atom from the solvent and form a vanadyl porphyrinogen.[869]

Polypyridyl V^{II} complexes have been obtained from V^{III} precursors by the disproportionation of V^{3+} to V^{2+} and VO^{2+}[836] and by the one-electron chemical reduction of V^{3+} by reducing agents such as Zn/Hg amalgam.[836] Complexes reported include $[V(trpy)(bpy)Cl]^+$, $[V(trpy)(bpy)H_2O]^{2+}$, $[V(trpy)(bpy)CH_3CN]^{2+}$, and $[V(trpy)_3]^{2+}$ (trpy = 2,2′:6′,2″-terpyridine).[836] These ligands stabilize vanadium in the +3 to −1 oxidation states.[836] Reaction of these complexes[836] or of hexaaquavanadium(II) ions[845] with dioxygen led to the formation of mononuclear vanadyl complexes via a $\{V^{3+}\text{–}(\mu\text{-}O)\text{–}V^{3+}\}$ bimetallic species. Although the electronic absorbance spectra and one-electron reduction of V^{II} polypyridyl complexes are sensitive to ligand coordination, the one-electron oxidation process showed little ligand dependence.[870] Upon irradiation of $[V(phen)_3]^{2+}$, a short-lived (<2 ns) excited state is observed. This excited state then decays into either a $[V(phen)_3]^{3+}$ or a $[V^{3+}(phen)_2(\mu\text{-}OH)_2V^{3+}(phen)_2]^{4+}$ complex, depending on the oxidant used.[871] Studies have established that these lowest excited states are primarily metal to ligand charge transfer in character.[872] The first example of a photo-initiated two-electron oxidation in a d^3 metal was achieved by irradiating a solution of $[V(phen)_3]^{2+}$ and methyl viologen at pH 8; the resulting products are vanadyl cation and the reduced methyl viologen monocation.[873]

4.4.5.3 Sulfur Ligands

A vanadium(II)–tmeda complex with 2,6-dichlorothiophenolate has been reported with both S- and Cl-donor atoms (**217**).[874] The thiolate donor atoms are trans to each other while the Cl atoms are trans to the N atoms in the tmeda ligand.[874] The complex will react with azobenzene to give the phenylimido complex where one of the chloro-donor ligands is now trans to the imido nitrogen (**218**);[874] this complex is structurally similar to other imidovanadium(IV) complexes.[643–646] A V^{II} cysteine methyl ester complex has been shown to reduce water to H_2 but the mechanism of this process is not known.[875]

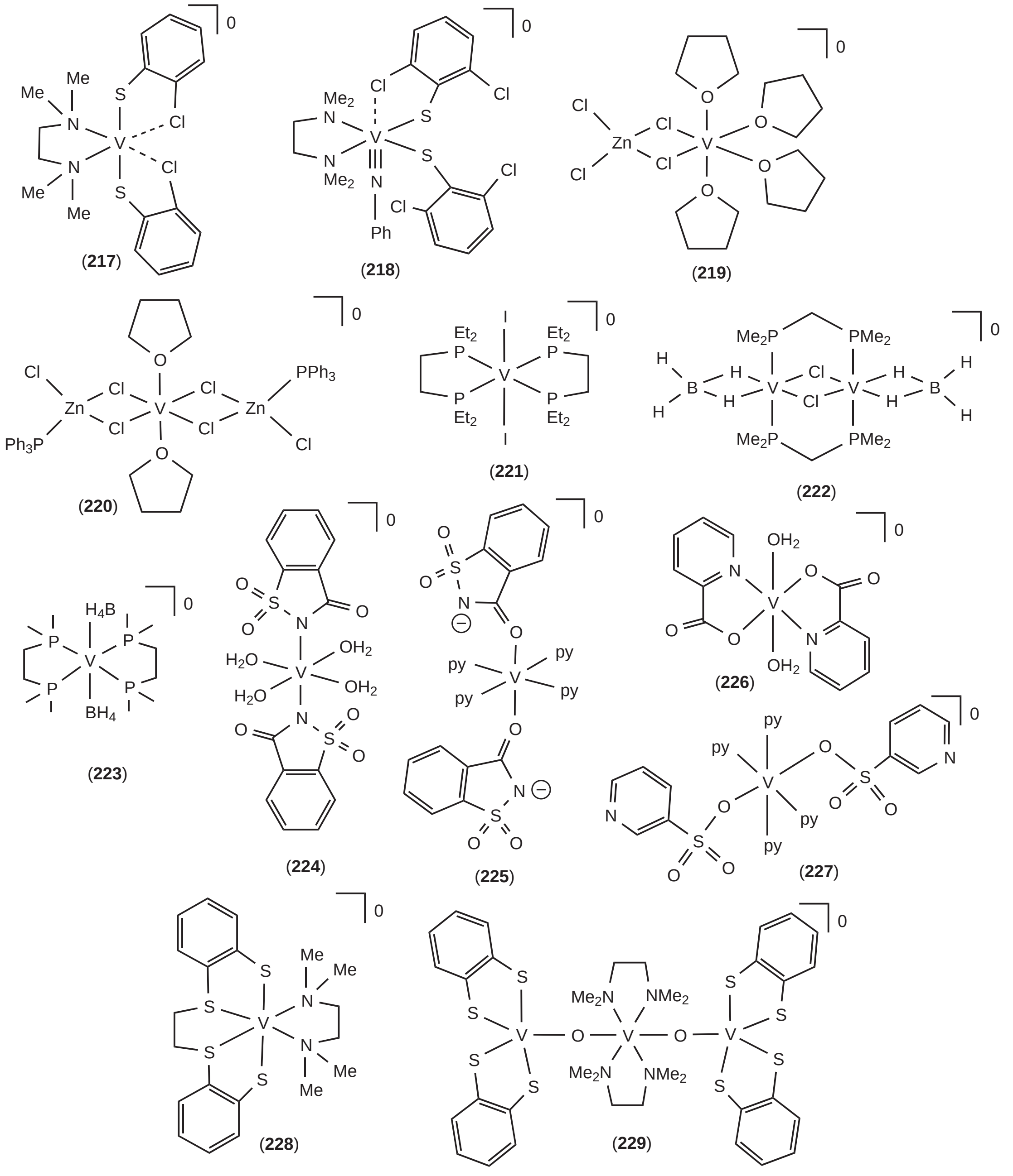


Figure 21 Structural illustrations of (**217–229**).

4.4.5.4 Halides

Complexes of the type $[L_3V(\mu\text{-}Cl)_3VL_3][BPh_4]$ (L = thf or 3-Me-thf) were synthesized from $[V_2(\mu\text{-}Cl_3)(thf)_6]_2[Zn_2Cl_6]$ and $NaBPh_4$ (L = thf) or from VCl_3, 3-Me-thf, $NaBPh_4$ and $AlEt_2(OEt)_2$ (L = 3-Me-thf).[876] The dimeric $[V_2Cl_3(thf)_6][AlCl_2Et_2]$ reacts with methanol to form either $[V(MeOH)_6]Cl_2$ or $[VCl_2(MeOH)_4]$, depending on the method of isolation.[877] Addition of trimethylphosphine (PMe_3) displaces the thf ligands without causing dissociation of the dimer as shown by X-ray crystallography.[877] Another useful starting material, $[V_2(\mu\text{-}Cl_3)(thf)_6]_2[Zn_2Cl_6]$, can be prepared by the reduction of $[VCl_3(thf)_3]$ with zinc powder.[878] This complex reacts with triphenylphosphine in benzene to form $[V_2(\mu\text{-}Cl_3)(thf)_5(PPh_3)]_2[Zn_2Cl_6]$,[878] in thf to form $[Cl_2Zn(\mu\text{-}Cl)_2V(thf)_4]$ (**219**) and in CH_2Cl_2 to form an oligomeric species containing one vanadium and two zinc centers, $[Cl(PPh_3)Zn(\mu\text{-}Cl)_2V(thf)_2(\mu\text{-}Cl)_2Zn(PPh_3)Cl]$ (**220**).[879] Each tetrahedral zinc center is bridged by two chloride ions to the octahedrally coordinated vanadium with two thf ligands.[879] In an attempt to synthesize a vanadium(II) iodide complex, $[V(MeCN)_6][I_4]$, with the unusual tetraiodide dianion (I_4^{2-}) was structurally characterized.[880] Utilizing $[V_2Cl_3(thf)_6][AlCl_2Et_2]$ as the vanadium precursor, $[VI_2(thf)_4]$ could be obtained; the complex is reactive and the thf ligands can readily be displaced by MeCN, MeOH, diamine, or diphosphine.[880] The diethylphosphinoethane (depe) complex, $[VI_2(depe)_2]$, was crystallized and the iodide ligands were found to be trans to one another (**221**).[880]

Addition of dimethylphosphinomethane (dmpm) to $[V_2(\mu\text{-}Cl_3)(thf)_6]_2[Zn_2Cl_6]$ in the presence of excess $LiBH_4$ leads to the formation of an edge-shared bioctahedron complex, $[VCl(dmpm)(BH_4)]_2$ (**222**).[881] The crystal structure shows each vanadium center to be bridged by two chlorides and the two diphosphine ligands; the BH_4^- ligand is presumed to be bidentate with the H-donors *trans* to the chloride bridges.[881] This structure is similar to one obtained earlier with diphenylphosphinomethane (dppm).[882] $[V_2(\mu\text{-}Cl_3)(thf)_6]_2[Zn_2Cl_6]$ is employed in organic synthesis. Some examples include the synthesis of HIV protease inhibitors,[883] the synthetic removal of an α-hydroxy group in acyloin and its derivatives,[884] and in the stereoselective synthesis of 1,2-diols via the pinacol cross-coupling of aldehydes.[805]

4.4.5.5 Other Ligands

The ability of phosphines to act as both a σ-donor to stabilize higher metal oxidation states and as a π acceptor to relieve electron density from lower metal oxidation states explains, in part, the observation that diphosphines stabilize the +3, +1, and 0 oxidation states at the expense of the +2 oxidation state.[870] Vanadium(II) diphosphine halides, $[V(dmpe)_2X_2]$ (dmpe = dimethyldimethylphosphinoethane, X = Br or I), were prepared as side products in the synthesis of $[XV(CO)_2(dmpe)_2]$.[885] The structurally characterized diphosphino V^{II} tetrahydroborate complex, *trans*-$[V(BH_4)_2(dmpe)_2]$, (**223**) was synthesized via the reduction of similar vanadium(III) precursors.[832] The reaction of a vanadium(II) chloride salt with dmpe afforded the *trans*-$[VCl_2(dmpe)_2]$ complex which can be alkylated with MeLi or $MgMe_2$ to afford the organometallic *trans*-$[V(Me)_2(dmpe)_2]$ compound, which in turn reacts with thiocyanate to form *trans*-$[V(NCS)_2(dmpe)_2]$.[886,887] Acetonitrile or propionitrile readily displace the chlorides from *trans*-$[VCl_2(dmpe)_2]$ to form *trans*-$[V(NCR)_2(dmpe)_2][BPh_4]_2$ (R = Me or Et); the acetonitrile derivative reacts with $HCPh(SO_2CF_3)_2$ in acetonitrile solvent to yield the hexaacetonitrile species $[V(NCMe)_6]^{2+}$.[887]

4.4.5.6 Mixed O-, N-, P-, and S-Donor Ligands

Saccharin and VSO_4 were employed to synthesize V^{II} complexes that could be employed as starting materials in different solvents.[834,888] In the 1:2 complex the saccharinate ligands bind via their nitrogen donor atoms in a trans configuration (**224**).[834] However, when (**224**) reacts with pyridine it generates an adduct with a ratio of V:saccharin:pyridine = 1:2:4 (**225**); the saccharin ligands are bound through a carbonyl oxygen donor presumably to lessen the steric crowding arising from the coordinated pyridine ligands.[834] Pyridine carboxylate and sulfonate ligands have been utilized to generate complexes containing six-coordinate V^{II} (**226**,**227**) which are relatively air stable.[841] In the case of the chelated picolinic acid, the ligand is bidentate whereas for pyridine-3-sulfonate, the ligand is monodentate.[841] The reduction of $[Co(en)_3]^{3+}$ by $[V(pic)_3]^-$ proceeds by an outer sphere mechanism with a rate constant of $3{,}100\,M^{-1}\,s^{-1}$.[889]

A mixed NS donor environment was obtained from the reaction of *trans*-$[V(tmeda)_2Cl_2]$ with 1,2-bis(2-sulfido-phenylsulfanyl)ethane(2–) to yield (**228**) which is the first thioether V^{II} complex isolated.[694] Due to a side reaction, a trimetallic complex was isolated (**229**). While this product would formally be considered to have a $V^{5+}/V^{2+}/V^{5+}$configuration, a $(V^{4+})_3$ configuration is also possible.[694]

A theoretical evaluation of ligands that would stabilize a vanadium–vanadium triple bond was undertaken and concluded that O- and N-donors in amidates would yield the greatest stability.[890] A lantern-type metal–metal bonded dinuclear V^{II} complex was synthesized by the reduction of $[VCl_3(thf)_3]$ with $NaHBEt_3$ followed by addition of the lithium salt of *N*,*N*′-di-*p*-tolylformamidate (**215**).[865] The crystal structure shows the $V\cdots V$ distance to be 1.98 Å, which is consistent with a fairly strong metal–metal triple bond.[865]

4.4.6 VANADIUM IN LOW OXIDATION STATES (BELOW +2)

The chemistry of vanadium in oxidation states lower than +2 is comprised primarily of organometallic compounds (described more thoroughly in the companion series *Comprehensive Organometallic Chemistry*). These compounds are generally air and moisture sensitive. There is a limited number of ligands that stabilize low-valent vanadium; these typically include ligands with some π-acceptor capability such as bipyridine, nitric oxide, and phosphines. Depending on their electronic structure, V^{I} and V^{-I} complexes may be diamagnetic, which permits their study by NMR spectroscopy.[891–896] EPR spectroscopy has been used to study paramagnetic V^{0} complexes.[897,898]

4.4.6.1 Vanadium(I)

A V^{I} nitrosyl complex was synthesized with triethanolamine (tea)[899] and was subsequently characterized by X-ray crystallography (**230**).[891,899] The product, while formally considered to have a V^{I} center, is better described as a $\{V(NO)\}^{5}$ species according to the Enemark–Feltham notation.[900] The vanadium in $[V(NO)(tea)]^{-}$ is in a distorted, trigonal–bipyramidal geometry with the amine and nitrosyl nitrogen donors in the axial positions and the three ethoxy oxygens in the meridional positions.[891,899] A series of complexes based on derivatized triethanolamine ligands was prepared and spectroscopically characterized.[891] The reaction between $[V(NO)(tea)]^{-}$ and CN^{-} initially formed a six-coordinate complex $[V(NO)(tea)(CN)]^{2-}$ (**231**);[891,899] additional equivalents of CN^{-} sequentially displaced all the oxygen donors to produce the previously isolated complex $[V(CN)_6(NO)]^{4-}$.[901]

4.4.6.2 Vanadium(0)

EPR spectroscopy was used to study the $[V(bpy)_3]$ complex.[897] The combined observation of an isotropic signal at ambient temperature,[898,902,903] and an axial signal in a frozen sample,[897] led to the conclusion that the single unpaired electron is extensively delocalized on the bipyridyl ligand and has ~30% 3d metal character.[897] The neutral V^{0} homoleptic hexakis(trifluorophosphine) complex $[V(PF_3)_6]$ (**232**) has been prepared via the oxidation of $[Na(diglyme)_2][V(PF_3)_6]$ with benzenediazonium tetrafluoroborate.[904] The $[V(PF_3)_6]$ complex was shown to oxidize sandwich compounds to form $[MCp_2][V(PF_3)_6]$ salts ($M = Fe^{3+}$, Co^{3+}, Ni^{3+}).[904]

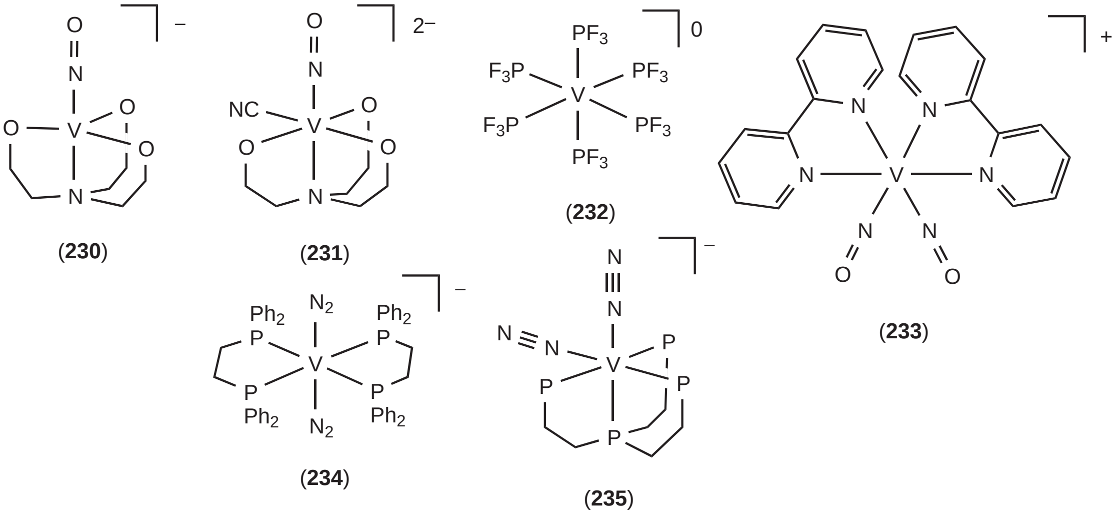


Figure 22 Structural illustrations of (**230**–**235**).

4.4.6.3 Vanadium(–I)

Nitrosyl ligands stabilize V^{-I} complexes because they are π acceptors which serve to remove electron density from electron-rich metals. Addition of bpy (or phen) to an aqueous solution of $[V(CN)_5(NO)]^{3-}$ produced a bis(bipyridyl) dinitrosyl complex $[V(NO)_2L_2][CN]$ (**233**).[905] Similar products were obtained from mixtures of $H_2VO_4{}^-$, hydroxylamine hydrochloride and pseudohalides such as NCS^- or $N_3{}^-$.[906] The vanadium centers having a formal -1 charge are also described as $\{V(NO)_2\}^6$ moieties using the Enemark–Feltham notation.[900]

Phosphine and diphosphine ligands are used to stabilize V^{-I} complexes produced from the reduction of V^{III} salts in the presence of N_2 to yield *cis*- and *trans*-bis(dinitrogen) complexes as well as mono(dinitrogen) complexes.[907–909] The *cis* isomers are the generally kinetic products while the trans isomers are typically the thermodynamically favored products, however most of the complexes are quite unstable in the solid state even under a dinitrogen atmosphere.[909] An X-ray crystal structure was obtained for the trans diphenylphosphinoethane derivative (**234**).[908] The series of V^{-I} complexes has been expanded to include systems with monodentate and tetradentate phosphine ligands; a *cis*-bis(dinitrogen) complex was obtained for (**235**).[909] Inspection of the spectroscopic data indicates an ion-pair interaction of the type $V{-}N{=}N\cdots M^+$.[909] Results from computational studies on the model complex $[V(PH_3)_4(N_2)_2]^-$ suggest that the anionic vanadium center favors metal to ligand π-back backbonding while hampering ligand to metal σ donation.[910] This is consistent with the observed reductive protonation of these types of complexes by acids to form NH_4^+[907–909] and the ability of CO and isocyanides to easily displace coordinated N_2.[909] These reactivity patterns are consistent with weak $V{-}N{\equiv}N$ interactions.

4.4.7 TOPICAL SUMMARY OF PROGRESS IN VANADIUM CHEMISTRY

As indicated by the preceding review of the literature, the knowledge and understanding of vanadium chemistry has undergone incredible growth since the early 1980s. In this review we have mainly described the advances in vanadium chemistry from a structural viewpoint, but in this section we will highlight areas in which important advances of relevance to vanadium chemistry occurred. This section will thus give the reader a topical overview with keywords and some surnames of contributing groups to provide rapid avenues of access into vanadium chemistry. Since the objective with this section is to expand the scope of the review, references will be made to scientists/teams in vanadium chemistry, biochemistry and/or biology, regardless of whether their recent work has been within the scope of this review.

Vanadium solution chemistry is very complex. Nevertheless, these reactions remain a crucial cornerstone because the species present in solution and their reactivity patterns are likely to affect the studies and properties of several other classes of compounds. Generally, the aqueous solution chemistry is more complex than the solution chemistry in organic solvents. Both environments, however, are relevant to bioinorganic chemistry and reactions catalyzed by vanadium or other transition metal catalysts. Solution studies investigating the different species that form in aqueous solution are often carried out using potentiometry. Several groups have been using this method for many years (Pettersson and Kiss). However, complementary methods such as NMR, EPR, and UV-visible spectroscopy as well as electrochemistry are being increasingly used for studies that characterize the species that exist in solution (Howarth, Tracey, Crans, Redher, Costa Pessoa, Pecoraro, Collison, de Silva, Kanamori, Cortizo, Etcheverry, and Williams). Furthermore, additional spectroscopic tools continue to provide fundamental information regarding the properties of vanadium compounds (le Brutto, Dikanov, Eaton, and Makinen).

Fundamental coordination chemistry has developed on many fronts. Peroxovanadium compounds have been the center of many studies (Conte, Butler, Pecoraro, Schwendt, Shaver, Sivak, Stomberg, Won, Sergienko and Kanamori) due to their intriguing structures and reactivities as well as their potential applications in catalysis. Coordination complexes continue to be reported by numerous groups, and include reactions with naturally occurring ligands such as amino acids as well as the gamut of synthetic ligands. Reactions of polydentate ligands with vanadium in various coordination environments have been tackled by many groups and resulted in many new classes of compounds. Of these classes the salen-type vanadium–ligand complexes are the largest group. Among the Schiff base vanadium complexes a great variety is found in reactivity although the structural changes are relatively small (see Table 4). Other new classes of compounds such as the vanadium–sulfur-type complexes have emerged as particularly interesting classes of compounds (Rehder, Cornman, and Sobota). The majority of contributions to vanadium chemistry each year is in the general area of coordination compounds (this review) and organometallic vanadium compounds (reviewed in the companion series *Comprehensive Organometallic Chemistry*). The groups involved with unraveling the fundamental vanadium chemistry and novel classes of coordination compounds are too many to name. Readers interested in this area should consult the body of this review and the original literature cited therein.

The bioinorganic chemistry and biochemistry of vanadium continues to grow and at this time contains several distinct, thriving areas worldwide. Perhaps the areas with greatest numbers of investigators are the modeling and studies of haloperoxidases (Vilter, Butler, Wever, Pecoraro, Rehder, Messerschmidt, Littlechild, Conte, and Plass), and the various aspects of studies with vanadium compounds as potential insulin enhancers (Shechter, Sakurai, McNeill/Orvig, Posner, Brichard and Crans/Willsky). Other areas of interest to the biochemist include the ability of vanadate to act as a phosphate analog (Gresser, Crans), to act as a phosphatase inhibitor (van Etten, Gresser, Tracey, Crans, Cornman, Rusnak, Shechter, and Posner), to act as an inhibitor for phosphorylases or ribonucleases (Cantley, Lindquist/Lienhard, and Berger) and the role of vanadium in vanadium-containing nitrogenases (Eady, Hales, Holm, Coucouvanis, and Armstrong). Some time ago, the investigation into the ability of vanadate to affect the Na^+-, K^+-ATPase was of interest to many biochemists (see reviews by Kustin and Nechay), considering its effect on transport and the reported affinity of about 10^{-9} M. The use of vanadate to photolytically cleave myosin at one specific amino acid (Cremo, Yount, and Mocz) and the NADPH-induced oxidase activity (Fridovich and Willsky) were also very active areas of research during the ten years up to 2002. Transferrin and human serum albumin binds vanadium both in oxidation states IV and V (Chasteen). Many additional areas have emerged, such as the identification of proteins that bind vanadium called vanabins (Michibata), anti-tumor properties of vanadium complexes (Marks, Djordevic and Chasteen), and the effects of vanadium compounds on cell growth and/or apoptosis (Willsky, Crans, Etcheverry, Galindo, Shi, Cortizo, Okazaki, and Sakurai). The inhibitory effects of vanadate on lactamases (Pratt) document that vanadate can also be inhibitory towards enzymes that do not catalyze reactions involving phosphate-containing substrates or co-factors. The ability of peroxovanadium compounds to react with DNA (Carrano and Ley) is likely to be investigated further now that the direct effects of metal ions on transcription factors have been reported. Thus, there is no doubt that the growth in this area is likely to continue to accelerate and as a deeper understanding of the mode of action of vanadium compounds is unraveled, applications of greater importance are to be anticipated.

Related areas include the investigations into the nutritional value of vanadium. Regardless of whether vanadium is essential, multiple researchers support the position that a low level of vanadium has beneficial effects, whereas others are convinced of its toxicity. Vanadium is present at low levels in most vitamins, however, the controversy regarding whether or not vanadium is a nutritional element continues to rage, with even the premier researchers in this area changing positions as new results come to light (Nielsen). High levels of vanadium are indeed toxic with the initial symptoms being diarrhea and "green tongue."

Environmental aspects of vanadium chemistry include vanadium chemistry in solution, gaseous, and solid states, and thus span a wide range of the properties of vanadium compounds. The recent compendium of reviews of the environmental chemistry of vanadium has shown that this area does have many contributors (contributed to and edited by Nriagu). Vanadium is a side product from refining coal, because vanadyl porphyrins are very stable (their stability is exceeded only by the nickel porphyrins).

In the *Amanita muscaria* mushrooms a naturally occurring vanadium-containing compound, amavadine, exists and the unusual structure and properties of this complex were elucidated in the last decade (Bayer, Carrondo, da Silva, Pombeiro, and Garner). Amavadine contains eight-coordinate vanadium with each of the two hydroxylamido ligands being tetradentate. However, amavadine is not the only type of naturally occurring vanadium complex; some siderophores have been shown to bind vanadium (Raymond, Carrano, Pecoraro and Butler). The most dramatic example of the accumulation of vanadium compounds is found for the ascidians, which are also referred to as tunicates. These organisms can accumulate vanadium up to about 200–300 mM, which is $\sim 10^6$ times the concentration of vanadium in seawater (Kustin, Frank, Hodgson, Hawkins, and Michibata). A vanadium accumulating polychaete worm has also been reported (Ishii).

In addition to the bulk industrial applications of vanadium oxides in preparation of maleic anhydride from *n*-butate, vanadium compounds have for some time been useful catalysts in organic synthesis. The number of contributions in this area has increased tremendously aided by key contributions from several synthetic groups (Hirao, Modena, Furia, Conte, Pedersen, Bolm, Yamamoto, Uang, Chen, Hessen, Feringa, and Hage). The most generally known agent, vanadyl acac, is still used successfully as an oxidizing agent although many more applications are now known with other vanadium compounds. The early applications of vanadium catalysts involved the oxidation of alcohols to ketones and oxidation reactions continue to be an important application of vanadium complexes, however the scope of the oxidation has dramatically expanded (Hirao, Bolm, and Yamamoto). At this time oxidation reactions being performed in the presence of vanadium complexes include dehydrogenation, oxygenation, oxidative coupling, oxidative decarbonylation, desilylation and oxidation of carbonyl compounds and heteroatom-containing compounds. The reductive chemistry reported includes dehalogenation, deoxygenation, hydrogenation, and coupling reactions such as C—C bond formation reactions between aldehydes, alkenes, alkynes and dienes, and organotin compounds (Pedersen, Hirao, Hage, Hessen, and Nishiguchi). Recent emphasis has also been on carrying out transformations in an enantiomeric manner; for example, strategies have been reported for enantioselective sulfide oxidations (Bolm) and enantioselective epoxidations of allylic alcohols (Bolm and Sharpless).

Applications of vanadium complexes in catalysis are well illustrated by the increasing number of reports involving vanadium complexes in various aspects of olefin polymerizations (Karol, Gambarotta, Green, Gibson, Sobota, Hessen, Sato, and Nomura). A variety of polymers and polymer molecular weights have been prepared using vanadium co-catalysts (Karol, Gambarotta, Hessen, Sobota, and Tsuschida). The objectives are to prepare polymers of desired and defined lengths, properties (e.g., tacticity) and purity. This area of vanadium chemistry is nonaqueous and often involves organometallic reagents, although vanadium coordination complexes are now solidifying a role in this chemistry, whether as co-catalysts (Gambarotta, Hessen, Sobota, Sato, and Nomura) or more recently as catalysts (Sobota). A wide variety of vanadium coordination complexes have been found to be effective in catalytic processes including imido, aryloxo and thiolato complexes. In general, these complexes contain vanadium(III), although vanadium(IV) catalysts have also been reported. The vanadium catalysts designed to activate N_2 (Schrock and Yamamoto) link the areas of catalyst development and bioinorganic modeling reactions of nitrogenase (Holm, Coucouvanis, Armstrong, and Rehder). At this stage both some structural and functional model systems have been prepared and the effects of compound nuclearity and ligand selection are being investigated.

Magnetic properties of vanadium compounds continues to be of interest (Wieghardt, Staemmler, Müller, Christou, Hendrickson, Hitchcock, Carrano, Costes, and Glebov) in part because the rich redox chemistry allows for a wide range of electronic states, supporting essentially all types of magnetic properties. V^{V} complexes are typically diamagnetic; V^{IV}, V^{II} and V^{0} complexes are generally paramagnetic, and V^{III}, V^{I} and V^{-I} complexes can be either diamagnetic or paramagnetic. The magnetism of the compounds has been examined both in the solid state and in solution, and complexes that have been of particular interest are dinuclear mixed valence complexes or larger mixed-valence clusters. Heterometallic complexes have also been investigated, which allowed the characterization of complexes with ferromagnetic and antiferromagentic properties (Wieghardt, Hitchcock, Staemmler, Costes, and Glebov). Studies on some $V^{III}-\mu\text{-O}-V^{III}$ complexes reveal that ferromagnetic coupling between the two V^{III} (d^2) ions is observed. However, when the balance of covalent and charge-transfer configurations is favorable, antiferromagnetic coupling can be observed by, for example, protonation of the bridging oxo ligand of the $V^{III}-\mu\text{-O}—V^{III}$ unit (Wieghardt). The "butterfly" (or diamond core) structures consist of a dinuclear $\{V_2O_2\}$ core to which two additional vanadium atoms are added, supported by a bidentate ligand (Christou). These compounds remain intact in solution, and exhibit out-of-phase a.c. susceptibility signals, a signature of single-molecule magnets. Some of these compounds possess both ferro- and antiferromagnetic exchange interactions leading to spin-frustration effects and an $S = 3$ ground state.

The solid state properties of vanadium-containing materials of which vanadium oxide (Kniep, Stiegman, Carrano, Zubieta, and Khan) is an important member due to its role in the oxidation of *n*-butate to maleic anhydride. Although many solid state systems are polymeric and cannot be characterized as coordination complexes, the determination of the solid state structures does provides clues to properties of the smaller unit. Important progress has taken place in the area regarding the development of new materials, their surface properties, and electron transfer processes. The areas of vanadium-containing organometallics, compounds in which the vanadium is part of an oxometalate cluster, and heteropolyoxometalates continue to grow. The vanadium can take on the role as a cluster scaffold or as a substituting metal ion and provides changes in the properties of the complexes as described by Pope and Hill elsewhere in this volume.

Many of the current studies on vanadium systems in the lower oxidation states (II, I, 0, −I) are addressing fundamental investigations regarding structure, complex formation, and solvent exchange. Applied studies have primarily focused on utilizing vanadium catalysts in organic synthesis and in nitrogen fixation (*vide supra*). The complexes are quite oxygen sensitive and are not stable unless appropriate precautions have been taken; while V^{II} complexes are moderately stable in aqueous solution, the lower oxidation state of vanadium tend to be much less stable. The number of studies investigating the coordination chemistry of these oxidation states (Cotton, Armstrong, Gambarotta, Rehder, Rotzinger, Wasada, Neves, Taube, Johnson, and Leigh) has so far been much smaller than the number of studies on vanadium complexes with higher oxidation states (+3 and higher).

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4.4.8 REFERENCES

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4.5
Niobium and Tantalum

T. WATERS and A. G. WEDD
The University of Melbourne, Parkville, Victoria, Australia
and
M. ZIOLEK and I. NOWAK
A. Mickiewicz University, Poznan, Poland

4.5.1 INTRODUCTION

In the fifteen years since publication of the first edition of *Comprehensive Coordination Chemistry* (*CCC*, 1987), group 5 chemistry has been part of the intensive development of ceramic, optical, and magnetic materials based upon metal borides, nitrides, phosphides, oxides, and sulfides. A major impetus came from the discovery of the high-temperature superconducting oxides. In addition, the search for new routes to these materials via sol–gel or chemical vapor deposition techniques has spurred growth in metal amido, oxo, alkoxo, thio, and carboxylato chemistry.

Such species are also part of the evolution of homogeneous and heterogeneous catalysts, including key oxidation and olefin polymerization processes. A burgeoning area is controlled immobilization of reactive centers on solid surfaces. In recognition, this Chapter concludes with a commentary on the development of heterogeneous catalysis and the synthesis of surfaces with controlled properties.

The Chapter covers the coordination chemistry of niobium and tantalum reported since 1984. Earlier work is described in *CCC* (1987).[1] Nb and Ta coordination chemistry has also been surveyed regularly in Coordination Chemistry Reviews (see, for example, ref. 2), and yearly reviews on the chemistry of V, Nb, and Ta have appeared in Annual Reports on the Progress of Chemistry (see, for example, ref. 3).

Detailed surveys of the organometallic chemistry of Nb and Ta can be found in *Comprehensive Organometallic Chemistry I* and *II*.[4,5] In addition, periodical reviews can be found in the series Organometallic Chemistry (see, for example,[6]).

Other useful reviews are referenced in the appropriate sections of this Chapter. The importance of metal–ligand multiple bonding in Nb and Ta chemistry makes the book by Nugent and Mayer a valuable resource.[7]

The use of M in the text implies both Nb and Ta. Common abbreviations are defined in the Abbreviations Section. They include $Cp = \eta^5\text{-}C_5H_5$ with superscripts to identify derivatized ligands (e.g., $Cp^* = \eta^5\text{-}C_5Me_5$). In the same way, Tp = hydrotrispyrazol-1-ylborate and Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate. Finally, common abbreviations for specialized ligands used by particular research groups (e.g., $[N_3N]^{3-}$, $[P_2N_2]^{2-}$, silox) are also employed and defined when first mentioned in the text and in the Abbreviations Section.

4.5.2 NIOBIUM(V) AND TANTALUM(V)

4.5.2.1 Carbon Donor Ligands

Discussion of the chemistry of carbon-based ligands is selective in order to emphasize more recent aspects of coordination chemistry. As a result, this section focuses on homoleptic alkyl complexes, as well as alkylidene and alkylidyne species that do not contain cyclopentadienyl or related ligands. Acyl (η^2-*C*,*O*-RCO) and iminoacyl (η^2-*C*,*N*-RCNR′) ligands are not discussed generally. These and other aspects of carbon-based ligands can be found in *Comprehensive Organometallic Chemistry I* and *II*.[4,5]

4.5.2.1.1 Homoleptic alkyl complexes

The structure of $TaMe_5(g)$ was studied by electron diffraction. A square pyramidal geometry was proposed with Ta—C bond lengths of 2.11(2) (ax) and 2.180(5)Å (eq).[8] Theoretical calculations suggested that this geometry is about $30\,kJ\,mol^{-1}$ more stable than the trigonal bipyramidal counterpart predicted by VSEPR theory, a consequence of a second order Jahn–Teller effect.[9] This result also correlates with the observation that $Ta(CH_2Ar)_5$ (Ar = 4-Me-C_6H_4) is square pyramidal in the solid state.[10] Elimination of methane from MMe_5 to form $M({=}CH_2)Me_3$ has been studied theoretically. The activation energy of an intermolecular mechanism was found to be much lower than that of a unimolecular mechanism.[11] The decomposition of penta-alkyl complexes $Ta(CH_2EMe_3)_5$ (E = C, Si) to alkylidene species $Ta({=}CHEMe_3)(CH_2EMe_3)_3$ via elimination of EMe_4 has been studied experimentally.[12] Steric crowding of the alkyl ligands appears to disfavor an intermolecular mechanism in these cases.

$[Li(OEt_2)_3][MMe_6]$ were prepared by addition of LiMe to M_4F_{20}.[13] Both species exhibited essentially trigonal prismatic stereochemistry. DFT calculations indicated that this geometry is favored over octahedral by more favorable M-CH_3 σ bonding and by core polarization effects.[14] $[Li(thf)_4][TaPh_6]\cdot 4C_6H_6$ was produced by reaction of Ta_2Cl_{10} with 12 eq LiPh in C_6H_6/ether and was also trigonal prismatic.[15] The polyacetylide species $A[Ta(C{\equiv}CSiBu^t{}_3)_6]$ (A = Li, K, [K(crypt-2.2.2)]) exhibited a twisted trigonal prismatic geometry (D_3).[16] The deviation from D_{3h} geometry was proposed to be due to steric factors.

4.5.2.1.2 Alkylidene ligands

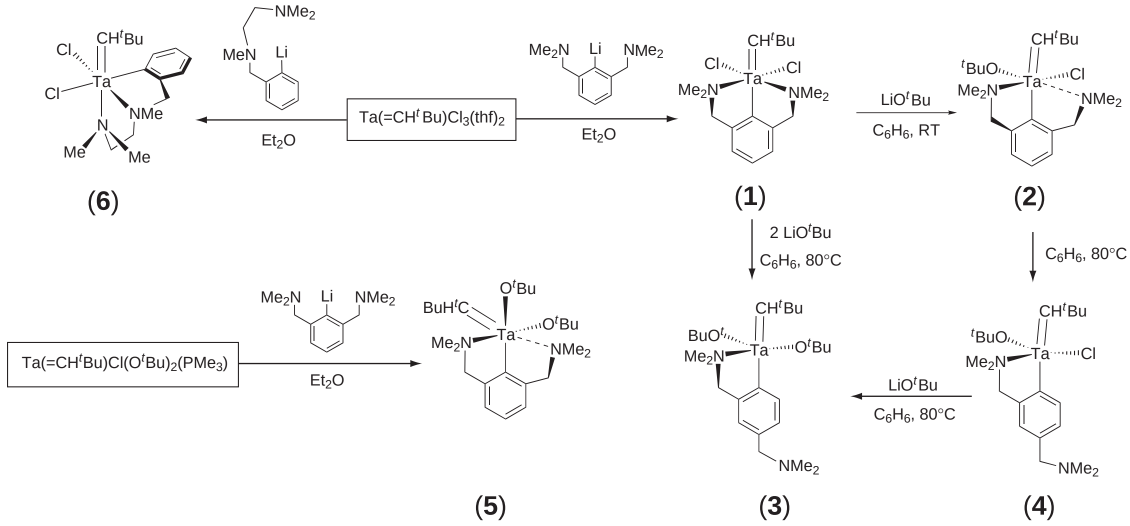
Sections on Nb and Ta were included in a review on high-oxidation-state species containing metal–carbon multiple bonds.[17] A perspective on metal–carbon multiple bonds is also available.[18]

The principle resonance contributions to the bonding in $(H)_3M({=}CH_2)$ were studied theoretically using a multi-reference wave function.[19] The thermochemistry of Ta^V-alkylidene formation was examined, revealing a very large Ta=C bond enthalpy.[20]

Reaction of $Ta({=}CHBu^t)Cl_3(thf)_2$ with the potentially tridentate aryldiamine ligand $LiL_{2,6}$ ($HL_{2,6}$ = 2,6-$(Me_2NCH_2)_2$-C_6H_4) in ether afforded *fac*-$L_{2,6}Ta({=}CHBu^t)Cl_2$ ((**1**); Scheme 1).[21] This reacted with acetone or benzaldehyde to provide binuclear $[L_{2,6}Cl_2Ta]_2(\mu_2\text{-}O)_2$, while reaction with PhCH=NMe produced $L_{2,6}Ta({=}NMe)Cl_2$.[21] The reactivity of (**1**) towards alkenes was investigated.[21,22]

Treatment of (**1**) with >1 eq of the bulky alkoxide $LiOBu^t$ in C_6H_6 at rt produced five-coordinate $L_{2,6}Ta({=}CHBu^t)(OBu^t)Cl$ (**2**) with a free CH_2NMe_2 substituent.[23] Reaction with 2 eq $LiOBu^t$ at 80 °C yielded the rearranged product $L_{2,4}Ta({=}CHBu^t)(OBu^t)_2$ (**3**).[24] This $6 \rightarrow 4$ rearrangement was shown to occur via isomerization of the intermediate monoalkoxo complex (**2**) to $L_{2,4}Ta({=}CHBu^t)(OBu^t)Cl$ (**4**), both of which were prepared and characterized independently.[24] Alternatively, the dialkoxo complex (**5**) could be prepared without rearrangement by reaction of $Ta({=}CHBu^t)Cl(OBu^t)_2(PMe_3)$ with $LiL_{2,6}$ (Scheme 1).[23] Both (**2**) and (**5**) reacted with $Me_3SiCH{=}CH_2$ to produce the (trimethylsilyl)methylidene analog via alkene metathesis reactions.[23] Ta^V–alkylidene complexes containing a related aryldiamine ligand have been prepared by similar methods (e.g., (**6**); Scheme 1).[25] Their activity as ring-opening metathesis polymerization catalysts was examined.

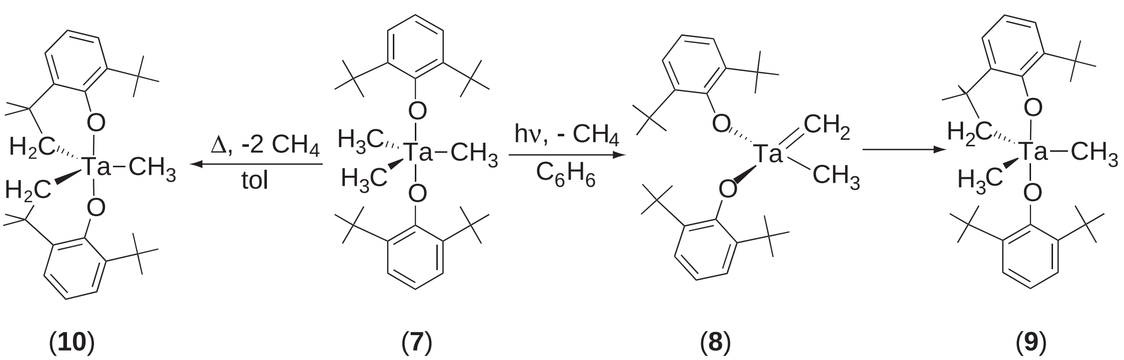
Addition of LiEAr (E = O, S) to $Ta({=}CHBu^t)Cl_3(thf)_2$ produced $Ta({=}CHBu^t)(EAr)_3(thf)$ (ArOH = 2,6-$Pr^i{}_2$-C_6H_3OH; ArSH = 2,4,6-$Pr^i{}_3$-C_6H_2SH).[26] The reactivity of these species as



Scheme 1

polymerization catalysts was examined.[26–28] Only Ta(=CHBu^t)(OAr)$_3$(thf) reacted cleanly with ethylene and 2-butyne to form the tantalacyclo–butane and –butene species, (ArO)$_3$Ta-CH$_2$CH$_2$CH$_2$] and (ArO)$_3$Ta-C(Me)=C(Me)CHBu^t, respectively.[26,28] Addition of py to the latter resulted in ring opening and formation of the vinylalkylidene complex (ArO)$_3$- Ta[=C(Me)C(Me)=CHBu^t], which was active in the polymerization of 2-butyne.[28]

The electronic absorption spectra and photochemical reactivity of the series MX$_2$(CH$_2$R)$_3$ (X = Cl, OPr^i, 2,6-disubstituted aryloxo; R = H, SiMe$_3$, Ph) have been studied.[29] The spectra were dominated by an intense band assigned as alkyl-to-metal charge transfer in character. Irradiation of this band for TaX$_2$(CH$_3$)$_3$ (X = 2,6-Bu^{t}C$_6$H$_3$O) ((**7**); Scheme 2) produced the alkyl–alkylidene complex TaX$_2$(=CH$_2$)(CH$_3$) (**8**) with a quantum efficiency of 0.9(1).[29] This rearranged on standing to the cyclometalated species (**9**).[30] In contrast to the photochemical reaction, thermolysis of (**7**) eliminated CH$_4$ with cyclometallation of both aryloxo ligands to form (**10**).[30] Alkyl–alkylidene species related to (**8**), Ta(=CHR) (CH$_2$R)(OAr)$_2$ (ArOH = 2,6-Pr^i$_2$- or 2,6-Bu^t$_2$-C$_6$H$_3$OH; R = SiMe$_3$, Ph), have also been prepared.[31] The effect of aryloxide substituents on the tendency of these species to undergo cyclometallation was examined (e.g., (**8**) → (**9**)).[32,33] A significant reduction in cyclometallation rates was observed with bulkier substituents at the *meta* position of the aryloxo ligands.



Scheme 2

Photolysis of [P$_2$N$_2$]TaMe$_3$ ([P$_2$N$_2$] = [PhP(CH$_2$SiMe$_2$NSiMe$_2$CH$_2$)$_2$PPh]$^{2-}$) produced themethyl–methylidene complex [P$_2$N$_2$]Ta(=CH$_2$)Me via elimination of methane.[34] In the presence of ethylene, this complex converted slowly to [P$_2$N$_2$]Ta(μ-C$_2$H$_4$)Et with [P$_2$N$_2$]Ta-(μ-C$_2$H$_4$)Me observed as a minor product only.[35]

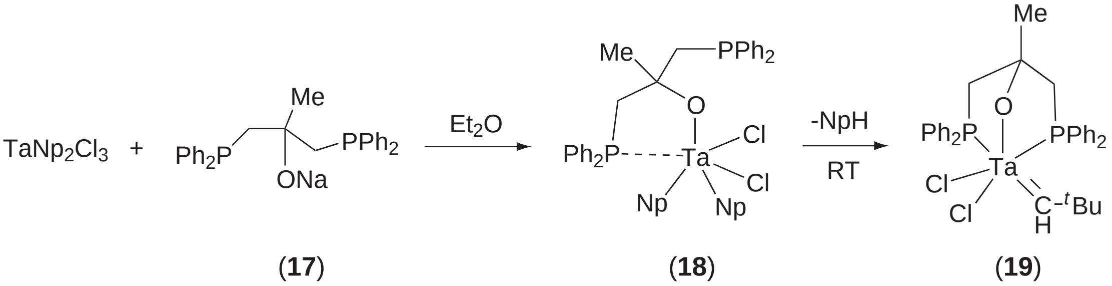
Nb^V–alkylidene species supported by the tetraanion $[p\text{-}Bu^t\text{-calix[4]arene-}(O)_4]^{4-}$ of calixarene (**11**) have been prepared (Scheme 32).[36] Ketones and aldehydes RR′CO reacted with binuclear (**12**) via metathesis of the C=O and $Nb^{III}{=}Nb^{III}$ double bonds to form equimolar quantities of the oxo- and alkylidene-Nb^V species, (**13**) and (**14**), respectively.[36] Interesting protonation equilibria are observed with (**14**) (Scheme 32) and the reactivity of the $Nb^V{=}CRR'$ bond was explored in some detail.[36] This chemistry has been reviewed.[37]

A variety of alkyl, alkylidene, alkene, and alkyne species supported by the triamido-amine ligand $[N_3N] = [(Me_3SiNCH_2CH_2)_3N]^{3-}$ have been prepared (Scheme 15). Alkylation of (**15**) with 2 eq CH_3CH_2MgCl produced the ethylene complex $[N_3N]Ta^{III}(\eta^2\text{-}H_2C{=}CH_2)$, presumed to be formed by β-hydrogen abstraction from an intermediate $[N_3N]Ta^V(CH_2CH_3)_2$ with elimination of ethane.[38,39] $[N_3N]Ta(\eta^2\text{-}H_2C{=}CH_2)$ was unstable and decomposed via cleavage of a C—N bond of the N_3N ligand to (**16**).[38] Isomerization of $[N_3N]Ta(\eta^2\text{-}H_2C{=}CH_2)$ to the alkylidene complex $[N_3N]Ta({=}CHCH_3)$ was catalyzed by $PhPH_2$ (Scheme 15).[38] Alkylation of (**15**) with $PhCH_2MgCl$ provided the related alkylidene species $[N_3N]Ta^V({=}CHPh)$. This was presumed to be formed by α-hydrogen abstraction from intermediate $[N_3N]Ta^V(CH_2Ph)_2$ with loss of CH_3Ph.[38,39]

Alkylation of (**15**) with 2 eq of bulkier alkyl Grignard reagents RCH_2CH_2MgX (R = Me, Et, Pr^i, Bu^t; X = Cl, Br) produced mixtures of alkylidenes $[N_3N]Ta({=}CHCH_2R)$ with other products whose NMR spectra were analogous to that of (**16**).[38] The relative yields were dependent on the steric bulk of R, consistent with competition between α- and β-hydrogen abstraction in intermediates $[N_3N]Ta(CH_2CH_2R)_2$. The alkene complexes $[N_3N]Ta(H_2C{=}CHR)$ formed by the β-hydrogen abstractions were proposed to decompose further to form species related to (**16**) (Scheme 15).[38] When the bulkier ligand $[N_3N^*] = [(Et_3SiNCH_2CH_2)_3N]^{3-}$ was used, β-hydrogen abstraction was suppressed and only alkylidene complexes were formed.[40] This was attributed to α-hydrogen abstraction in $[N_3N^*]Ta(CH_2CH_2R)_2$ being favored in the more crowded coordination pocket formed by the $SiEt_3$ substituents of $[N_3N^*]$.[40]

Alkyne complexes $[N_3N]Ta(\eta^2\text{-}HC{\equiv}CH)$ and $[N_3N]Ta(\eta^2\text{-}C_6H_4)$ were prepared via treatment of (**15**) with 2 eq $H_2C{=}CHMgBr$ and LiPh, respectively (Scheme 15).[38,39] In contrast, under the same conditions with $H_2C{=}CHMgBr$, $[N_3N^*]TaCl_2$ afforded an approximately equimolar mixture of $[N_3N^*]Ta(HC{\equiv}CH)$ and binuclear $[N_3N^*]Ta{=}CHCH_2CH_2CH{=}Ta[N_3N^*]$.[40]

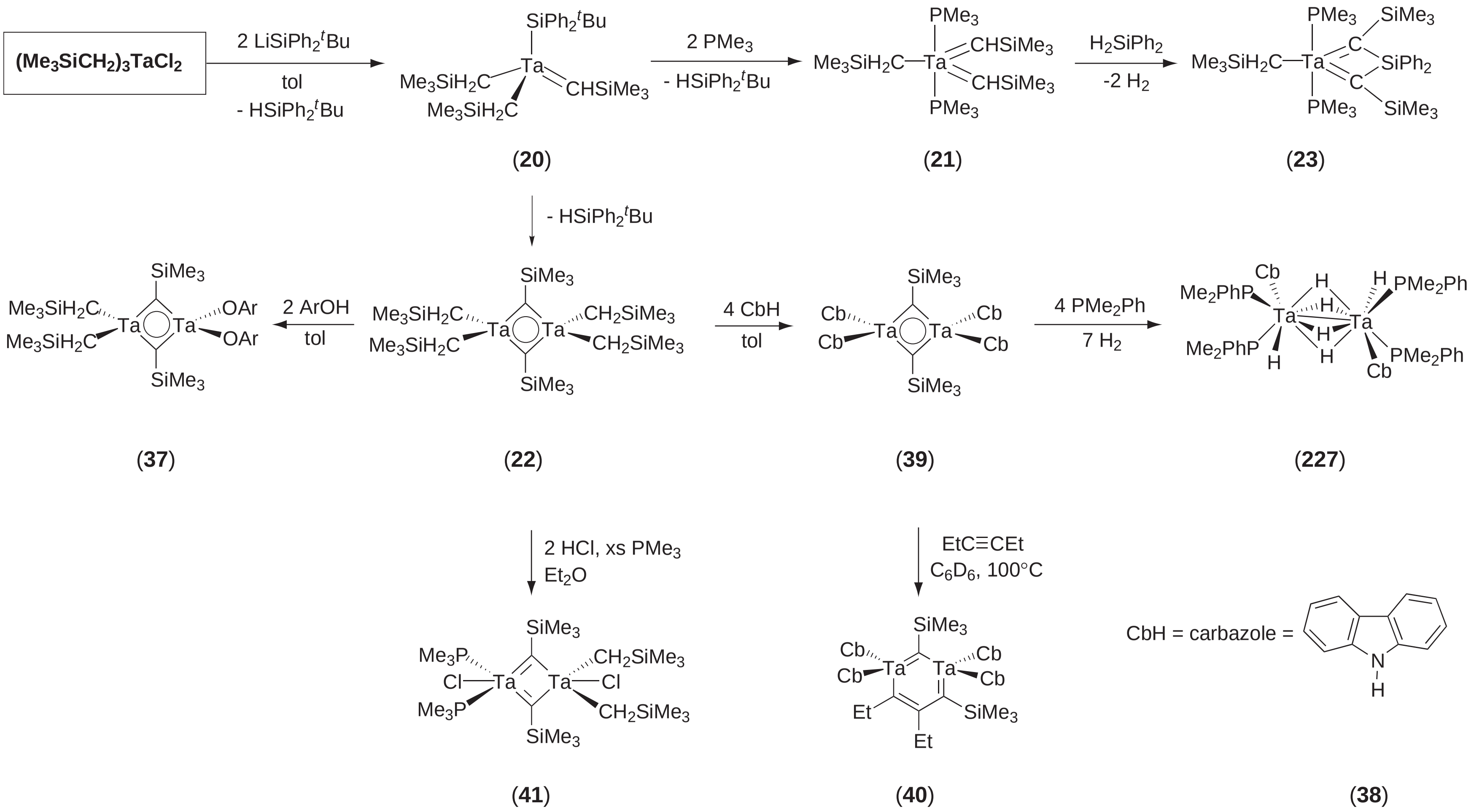
Treatment of $TaNp_2Cl_3$ (Np = neopentyl, CH_2Bu^t) with the phosphoranealkoxo ligand (**17**) in ether produced complex (**18**), which converted slowly in solution to the alkylidene species (**19**) with liberation of neopentane (Scheme 3).[41]



Scheme 3

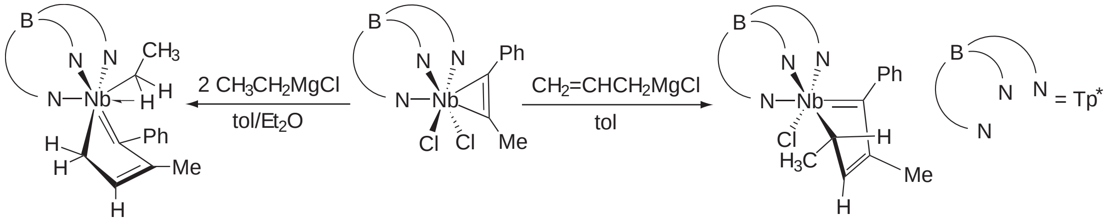
Ta–alkylidene complexes containing bidentate benzamidinato ligands $L = [PhC(NSiMe_3)_2]^-$ have been prepared.[42] Treatment of $LTa(CH_2Ph)_3Cl$ with $LiN(SiMe_3)_2$ afforded $LTa({=}CHPh)(CH_2Ph)_2$, while deprotonation of cationic $[L_2Ta(CH_3)_2]^+$ with $Me_3P{=}CH_2$ afforded the methylidene complex $L_2Ta({=}CH_2)(CH_3)$.

Reaction of $(RCH_2)_3TaCl_2$ (R = $SiMe_3$) with 2 eq $LiSiPh_2Bu^t$ in tol provided the silyl-alkylidene complex $(RCH_2)_2Ta({=}CHR)(SiPh_2Bu^t)$ ((**20**); Scheme 4) with elimination of silane $HSiPh_2Bu^t$.[43,44] Addition of 2 eq PMe_3 to (**20**) produced the bis(alkylidene) complex $(RCH_2)Ta({=}CHR)_2(PMe_3)_2$ (**21**) with trigonal bipyramidal geometry and axial PMe_3 ligands. In the absence of PMe_3, (**20**) decomposed to the alkylidyne complex $[(RCH_2)_2Ta]_2(\mu_2\text{-}CR)_2$ (**22**).[44] Treatment of (**21**) with diphenylsilane H_2SiPh_2 resulted in evolution of H_2 and formation of a novel metallasilacyclobutadiene complex (**23**).[45]


(Me$_3$SiCH$_2$)$_3$TaCl$_2$
2 LiSiPh$_2$^{t}Bu
tol
- HSiPh$_2$^{t}Bu
(20)
2 PMe$_3$
- HSiPh$_2$^{t}Bu
(21)
H$_2$SiPh$_2$
-2 H$_2$
(23)
- HSiPh$_2$^{t}Bu
2 ArOH
tol
(37)
(22)
4 CbH
tol
(39)
4 PMe$_2$Ph
7 H$_2$
(227)
2 HCl, xs PMe$_3$
Et$_2$O
(41)
EtC≡CEt
C$_6$D$_6$, 100°C
(40)
CbH = carbazole =
(38)

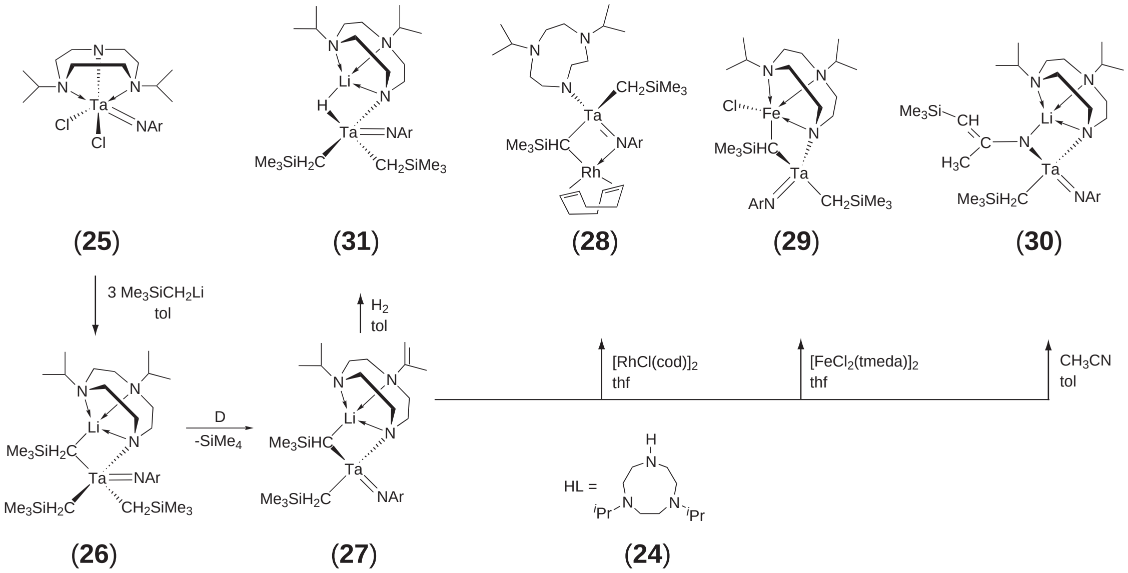
Scheme 4

Tp*Ta(=CHBu^t)X_2 (X = Cl, Br; Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) were prepared by reaction of KTp* with Ta(=CHBu^t)X_3(thf)$_2$ in thf.[46] A number of Tp*-supported complexes containing five-membered niobacycles have been prepared from Nb^{III} precursors with a coordinated alkyne ligand (see, e.g., Scheme 5).[47–50]



Scheme 5

Treatment of Ta(=NAr)Cl$_3$(thf)$_2$ (Ar = 2,6-Pr$^i_2$-C$_6$H$_3$) with 1 eq LiL (HL = 1,4-Pr$^i_2$-1,4,7-triazacyclononane, (**24**)) in thf produced LTa(=NAr)Cl$_2$ ((**25**); Scheme 6).[51–54] Ligand (**24**) offers the possibility of dissociation of amino nitrogens to expose additional coordination sites at the metal center for further reactivity. For example, (**25**) reacted with 3 eq Me$_3$SiCH$_2$Li in tol to give a heterobimetallic Ta–Li center with a bridging alkyl ligand and a μ_2-η^1:η^3 ligand L (**26**).[51] Gentle heating of (**26**) resulted in α-hydrogen abstraction to form a μ_2-alkylidene species (**27**).[51] This in turn reacted with [RhCl(cod)]$_2$ (cod = 1,5-cyclooctadiene) or [FeCl$_2$(tmeda)]$_2$ (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) to form binuclear complexes (**28**) and (**29**).[53] The reactivity of (**27**) towards a range of electrophilic organic substrates was examined, with insertion reactions observed for unsaturated substrates (e.g., reaction with CH$_3$CN produced (**30**)). Reaction with H$_2$ produced the bridging hydride (**31**).[54] Other heterobimetallic complexes with bridging alkylidene ligands (cf, (**28**), (**29**)) have also been described,[55,56] including a number of Cp-supported species (see, for example[57–59]).



Scheme 6

Wolczanski and co-workers have developed the chemistry of Nb and Ta centers supported by siloxo ligands.[60] Addition of 2 eq Na(silox) (silox = Bu$^t_3$SiO$^-$) to TaCl$_2$(CH$_2$Bu^t)$_3$ in C$_6$H$_6$ provided (silox)$_2$Ta(=CHBu^t)(CH$_2$Bu^t).[61] Treatment of (silox)$_3$Ta^{III} ((**32**); Scheme 44) with CO produced (silox)$_3$Ta=O and binuclear [(silox)$_3$Ta]$_2$(μ_2-η^1:η^1-C$_2$). Different reaction conditions also produced the ketenylidene complex (silox)$_3$Ta=C=C=O (Scheme 44).[62,63] The mechanism of formation of these species was studied in detail.

Binuclear [(silox)$_2$Ta^{IV}H$_2$]$_2$ ((**33**); Scheme 44) cleaved CO to give (**34**) which reacted further with CO to produce (**35**). The latter decomposed to [(silox)$_2$Ta^V]$_2$(μ_2-O)$_2$(μ_2-CHMe) (**36**) which contains a bridging ethylidene ligand.[64,65] This sequence of reactions was proposed as a model for Fischer–Tropsch chemistry.

4.5.2.1.3 Alkylidyne ligands

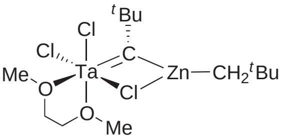
The reactivity of the alkylidyne-bridged binuclear species $[(RCH_2)_2Ta]_2(\mu_2\text{-}CR)_2$ ((**22**); R = $SiMe_3$, (Scheme 4) towards a variety of 2,6-disubstituted phenols and mono- and di-substituted 1-napthyl phenols has been examined.[66,67] For example, reaction with 2 eq ArOH = 2,6-Bu^t_2-C_6H_3OH yielded the asymmetric 1,1-disubstituted species $(RCH_2)_2Ta(\mu_2\text{-}CR)_2Ta(OAr)_2$ (**37**). Silica-supported (**22**) catalyzed the hydrogenation of benzene and substituted benzenes.[68]

Treatment of (**22**) with CbH = carbazole (**38**) in hydrocarbon solvents gave $[Cb_2M]_2(\mu_2\text{-}CR)_2$ ((**39**); Scheme 4). The reactivity of this species towards hydrogenation (M = Ta) and to organic isocyanides was studied.[69,70] Reaction of (**39**) with 1 eq EtC≡CEt produced the di-metallacyclic compound (**40**) by alkyne insertion into one of the bridging alkylidyne groups.[71,72]

Addition of 2 eq HCl to (**22**) in ether produced a thermally unstable bis(alkylidene) complex, which upon addition of excess PMe_3 generated binuclear (**41**). The bridging alkylidyne ligands of (**41**) exhibited inequivalent Ta—C bond lengths of 2.073(6)–2.099(6) Å and 1.922(6)–1.942(7) Å, consistent with the different nature of the Ta centers.[73,74]

A binuclear calixarene-supported niobium–alkylidyne complex ((**42**); Scheme 32) was prepared by deprotonation of a mononuclear alkylidene species (**14**).[36] The chemistry of calixarene-supported species containing metal–carbon bonds has been reviewed.[37]

Heterobimetallic Ta–Zn–alkylidyne complexes have been prepared via α-H abstraction from a Ta–alkylidene fragment by ZnR_2 or ZnClR (R = CH_2Bu^t, CMe_2Ph) ((**43**)–(**46**))[75–78] (**44**) reacted with acetylenes to yield products in which two acetylene molecules and an alkylidyne ligand were coupled to form a cyclopentadienyl ligand.[76] Species (**45**) was prepared via direct reaction of (**44**) with the Li^+ salt of the aryldiamine ligand or in higher yield via α-H abstraction from an alkylidene complex with the aryldiamine ligand already in place.[77]



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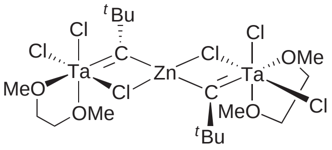

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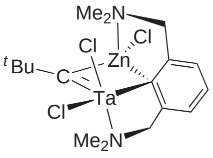

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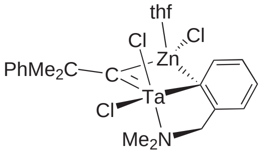


(46)

4.5.2.2 Nitrogen Donor Ligands

Nitrogen ligands are particularly versatile in high-valent, early transition metal chemistry. Deprotonation of amines, amides, and hydrazines generates multiply bonding ligands which help to stabilize the high oxidation states. Aspects of metal–amido and metal–imido chemistry have been reviewed.[79,80]

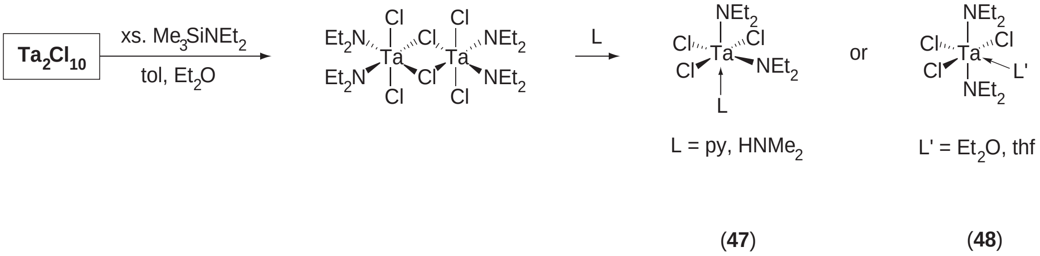
4.5.2.2.1 Amido ligands

A safer procedure for the synthesis of $Ta(NMe_2)_5$ has been described.[81] Electron diffraction indicated a square pyramidal stereochemistry with Ta—N bond lengths of 1.937 (ax) and 2.040 (eq) Å.[82] Its solid-state electronic spectrum exhibited absorption bands assigned to $N \rightarrow Ta^V$ ligand-to-metal charge transfer transitions.[83]

Treatment of $Ta(NMe_2)_5$ with two equivalents of CbH ((**38**), Scheme 4) generated trigonal bipyramidal *trans*-$Ta(NMe_2)_3Cb_2$.[81] Reaction of Ta_2Cl_{10} with excess Me_3SiL (LH = tetrahydro-tetrahydroquinoline) in tol produced TaL_3Cl_2, which could be converted to TaL_5 via reaction with 2 eq of LiL.[84]

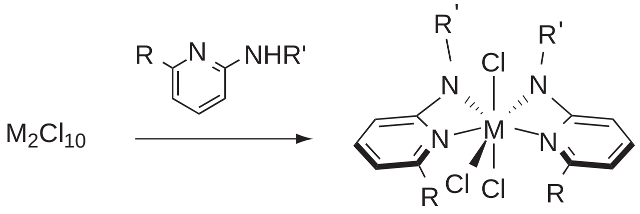
Homoleptic amido species $M(NR_2)_5$ have been used as precursors for chemical vapor deposition of metal-nitride thin films. For example, $Ta(NMe_2)_5$ and NH_3 afforded Ta_3N_5 thin films with low carbon contamination at temperatures between 200 °C and 400 °C.[85]

Reaction of M_2Cl_{10} with 2 eq Me_3SiNEt_2 in Et_2O produced six-coordinate $M(NEt_2)Cl_4(OEt_2)$, formulated as the *trans* isomers.[86] Reaction of Ta_2Cl_{10} with excess Me_3SiNEt_2 led to binuclear $[Cl_2(Et_2N)_2Ta]_2(\mu_2\text{-}Cl)_2$, which reacted with N-donor solvents L = py, $HNMe_2$ to form mononuclear *cis,mer*-$Ta(NEt_2)_2Cl_3L$ ((**47**); Scheme 7).[87] The corresponding reaction with O-donor solvents $L' = Et_2O$, thf generated *trans,mer*-$Ta(NEt_2)_2Cl_3L'$ (**48**).[86] Reaction of Ta_2Cl_{10} with 10 eq Me_2NH produced *cis,mer*-$Ta(NMe_2)_2Cl_3(HNMe_2)$ (isostructural with (**47**)), while reaction with 8 eq provided the salt *cis*-$[Me_2NH_2][TaCl_4(NMe_2)_2]$.[88]



Scheme 7

Treatment of M_2Cl_{10} with 4 eq substituted 2-aminopyridines in tol or under melt conditions produced *pseudo*-pentagonal bipyramidal complexes bis(amidopyridine)MCl_3 (Scheme 8).[89–92]



Scheme 8

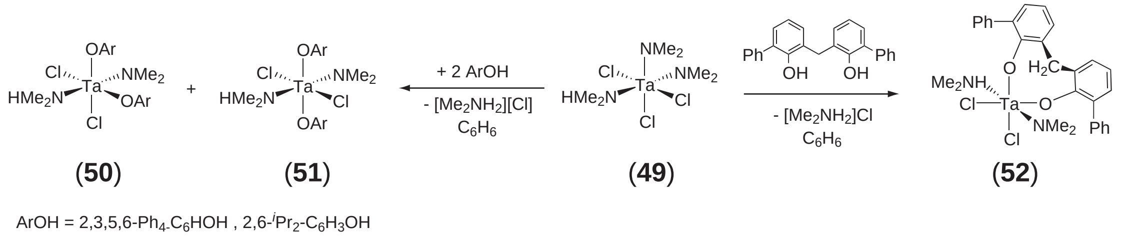
The series TaL_nCl_{5-n} (LH = tetrahydroquinoline, $n = 1$–5) was prepared from reaction of Ta_2Cl_{10} with Me_3SiL or LiL in tol.[84] TaL_2Cl_3 is trigonal bipyramidal with equatorial amido ligands. Related species $TaL'_nCl_{5-n}(thf)$ (L'H = indolene, $n = 1,2$) were also prepared.

Treatment of Ta_2Cl_{10} with the bulky diamine ligand $LH_2 = ArNH(CH_2)_3NHAr$ ($Ar = 2,6\text{-}Pr^i_2\text{-}C_6H_3$) in tol afforded six-coordinate $(LH)TaCl_4$. Further reaction with MeMgBr produced five-coordinate $LTaMe_3$.[93]

Amido–silyl complexes $(Me_2N)_4Ta(SiR_3)$ and $(Me_2N)_3Ta(SiR_3)Cl$ ($SiR_3 = Si(SiMe_3)_3$, $SiPh_2\text{-}Bu^t$) were synthesized from reaction of $Li(thf)_3SiR_3$ with $(Me_2N)_4TaCl$ and $(Me_2N)_3TaCl_2$, respectively.[94,95] These species adopted a trigonal bipyramidal geometry with the silyl ligand in an equatorial position. Reaction of $(Me_2N)_4Ta[Si(SiMe_3)_3]$ with 1 eq O_2 led to insertion into Ta—N and Ta—Si bonds to yield the oxidation product $(Me_2N)_3Ta(\eta^2\text{-}ONMe_2)[OSi(SiMe_3)_3]$.[95]

The groups of Rothwell and Wigley have prepared a number of mixed amido–aryloxo complexes with bulky aryloxo ligands. Treatment of $Ta(OAr)_nCl_{5-n}(OEt_2)$ ($ArOH = 2,6\text{-}Pr^i_2\text{-}C_6H_3OH$, $n = 1, 2$) with equimolar Me_3SiNEt_2 afforded $Ta(NEt_2)(OAr)_nCl_{4-n}(OEt_2)$.[86] Addition of 2 eq $Ar'OH = 2,4\text{-}Bu^t\text{-}6\text{-}Ph\text{-}C_6H_2OH$ to $Nb(NMe_2)_5$ in benzene produced $Nb(OAr')_2(NMe_2)_3$ with a severely distorted trigonal bipyramidal geometry ($\angle N_{ax}\text{–}Nb\text{–}N_{ax} = 169.1°$).[96] The reaction of $M(NMe_2)_5$ with 3 eq $Ar''OH = 2,6\text{-}Ph_2\text{-}C_6H_3OH$ in tol produced trigonal bipyramidal $M(OAr'')_3(NMe)(HNMe_2)$ with an equatorial imido group.[97] $TaL(OAr)Cl_3(OEt_2)$ (LH = tetrahytetrahydroquinoline) was prepared from reaction of $Ta(OAr)Cl_4(OEt_2)$ with Me_3SiL, while $TaL_2(OAr)_2Cl(OEt_2)$ was prepared from reaction of $TaL_2Cl_3(OEt_2)$ with excess LiOAr.[84]

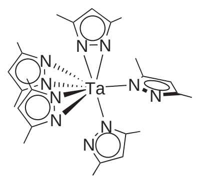
Reaction of *cis,mer*-$Ta(NMe_2)_2Cl_3(HNMe_2)$ ((**49**); Scheme 9) with 2 eq $ArOH = 2,3,5,6\text{-}Ph_4\text{-}C_6HOH$ or $2,6\text{-}Pr^i_2\text{-}C_6H_3OH$ in benzene produced a mixture of *cis,cis*- and *trans,trans*-$Ta(OAr)_2Cl_2(NMe_2)(HNMe_2)$ ((**50**), (**51**); Scheme 9).[88] The *cis,cis* isomer was found to convert thermally to the more stable *trans,trans* form, which could be prepared independently by addition of excess $HNMe_2$ to $Ta(OAr)_2Cl_3$. Addition of 2,2'-methylenebis(6-phenylphenol) to (**49**) produced (**52**).



Scheme 9

(i) Pyrazolato and related ligands

Winter and co-workers have prepared a number of complexes bearing η^1-, η^2-, and "slipped" η^2-pyrazolato ligands. Treatment of $Ta(NMe_2)_5$ with 5 eq LH = 3,5-Me_2-pyrazole in refluxing toluene produced TaL_5 (**53**) with two monodentate and three bidentate ligands, while 2 eq $L'H$ = 3,5-Bu^t_2-pyrazole yielded $TaL'_2(NMe_2)_3$ (**54**) with two bidentate pyrazolato ligands.[98] One of the pyrazolato ligands in the latter complex exhibited "slipped" η^2 binding, with the two Ta—N bond lengths differing by 0.17 Å.[98] Treatment of M_2Cl_{10} with 6 eq KL′ in tol produced ML'_3Cl_2 (**55**).[99] Low-temperature ^1H NMR revealed that (**55**) undergoes a Berry *pseudo*-rotation process that interconverts inequivalent Bu^t sites.[99] Complexes containing 1,2,4-triazolato or tetrazolato ligands have also been prepared (e.g., (**56**)).[100]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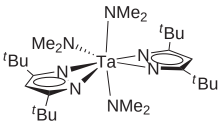
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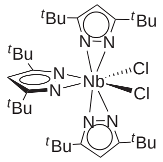
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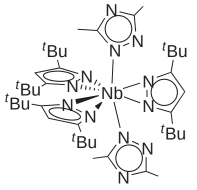
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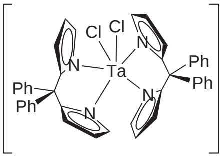

(57)

Reaction of Ta_2Cl_{10} with 4 eq of the diphenyldipyrrolide dianion L = $[Ph_2C(C_4H_3N)_2]^{2-}$ produced $[TaL_2Cl_2]^-$ (**57**).[101] Further reaction with $NaHBEt_3$ resulted in partial hydrogenation of one of the ligand phenyl rings.

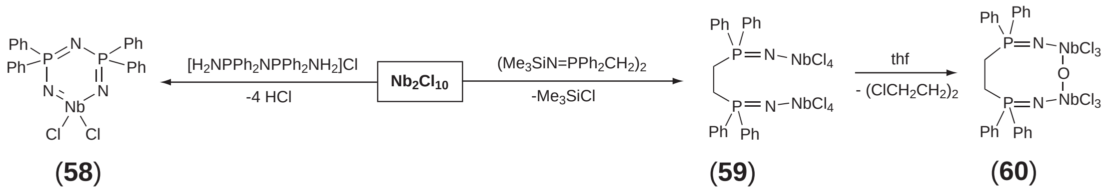
(ii) Phosphoraneiminato and related ligands

A common synthetic route involves reaction of the metal halides with silylated phosphoraneimines Me_3SiNPR_3. The chemistry of these ligands has been reviewed.[102] Treatment of Nb_2Cl_{10} with 4 eq $Me_3SiNPPh_3$ in MeCN produced $NbCl_3(NPPh_3)_2$,[103] while the analogous reaction with Ta_2Cl_{10} gave the salt $[Ta^V(NPPh_3)_4][Ta^VCl_6]$.[104] Reaction of 2 eq $Me_3SiNPPr^i_3$ with Ta_2Cl_{10} produced binuclear $[Cl_3(Pr^i_3PN)Ta]_2(\mu_2\text{-}Cl)_2$ and reaction with a further 2 eq formed mononuclear $TaCl_3(NPPr^i_3)_2$.[105] The equivalent Nb species resulted from reaction of $NbOCl_3$ with 2 eq $Me_3SiNPPr^i_3$ in CCl_4 with elimination of $O(SiMe_3)_2$.[105] Formation of *tris* derivatives $MCl_2(NPR_3)_3$ required 3 eq $LiNPR_3$ (R = Bu^t, NMe_2).[106] The phosphoraneiminato complex $TaCl_4(NPCl_3)$ was prepared from reaction of Ta_2Cl_{10} with 2 eq $Me_3SiNPCl_3$.[107] Redox-active ferrocene-functionalized phosphoraneiminato ligands have been incorporated at Nb centers.[108,109]

Reaction of Nb_2Cl_{10} with 2 eq of the bifunctional phosphazene salt $[H_2NPPh_2NPPh_2NH_2]Cl$ produced the metallacycle (**58**) (Scheme 10).[110] Reaction with 1 eq $(Me_3SiN{=}PPh_2CH_2)_2$ produced (**59**) which abstracted oxygen from thf to yield the nine-membered metallacycle (**60**).[111]

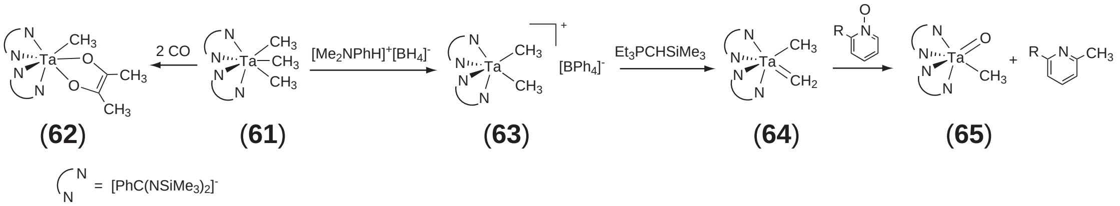
(iii) Amidinato, guanidinato, and related ligands

Amidinates $[RC(NR)_2]^-$ are isoelectronic with carboxylates. Reaction of Ta_4F_{20} with 8 eq LiL (L = $[PhC(NSiMe_3)_2]^-$) in tol yielded seven-coordinate L_2TaF_3 with distorted pentagonal



Scheme 10

bipyramidal geometry.[112] $TaMe_3Cl_2$ with 2 eq LiL yielded the equivalent trimethyl complex, L_2TaMe_3 ((**61**); Scheme 11).[42] Two equivalents of CO inserted into two Ta—Me bonds of (**61**) to form an ene-diolato ligand (**62**).[42] Reaction of (**61**) with $[Me_2NPhH][BPh_4]$ produced the salt $[L_2TaMe_2][BPh_4]$ (**63**). Deprotonation of (**63**) yielded $L_2Ta({=}CH_2)Me$ (**64**), which transferred methylidene to pyridine-N-oxides to form the oxo complex $L_2Ta({=}O)Me$ (**65**).[113] Related bis-benzamidinato complexes $L_2M({=}E)Cl$ (M = Nb, E = O, NBu^t; M = Ta, E = NAr) are also available.[42,114]

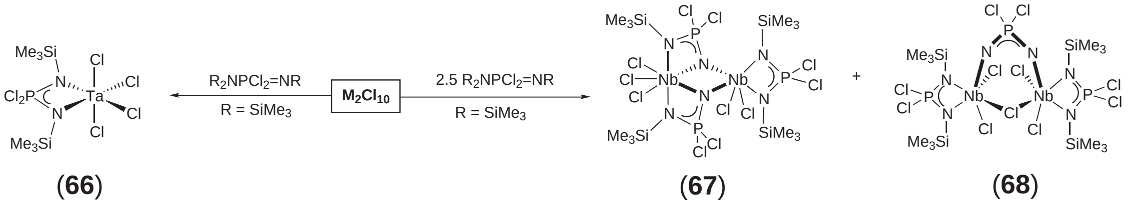


Scheme 11

Reaction of M_2Cl_{10} with the lithium salt of the bulky ligand $L = [2,4,6\text{-}Pr^i{}_3\text{-}C_6H_2C(NSiMe_3)_2]^-$ in tol produced the mono-benzamidinato complexes $LMCl_4$.[115] Other mono-amidinato complexes have also been prepared.[116,117]

The possibility of amidinates undergoing a variety of transformations under reducing conditions has been explored.[118] For example, treatment of Ta_2Cl_{10} with LiL ($L = [HC(NPh)]^-$) and excess $LiBH_4$ produced the seven-coordinate imido complex $L_3Ta(NPh)$, with the imido group derived from reduction and C—N bond cleavage of the amidinate.[119]

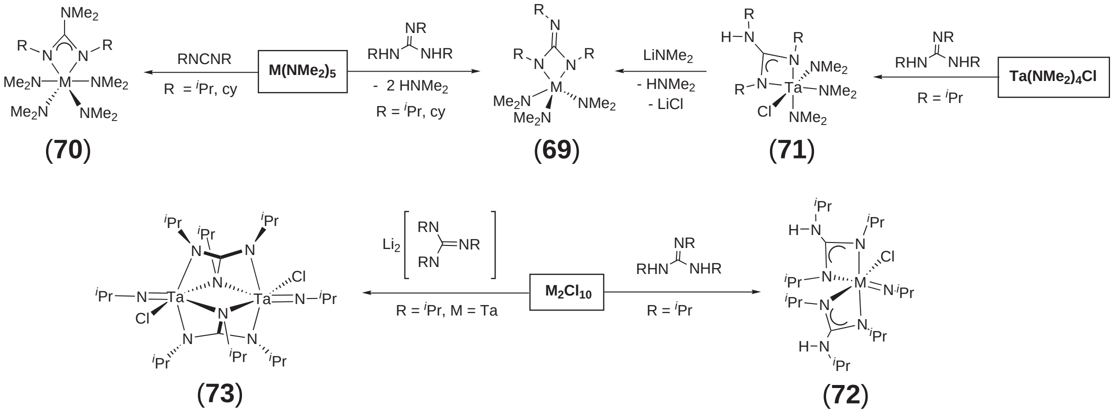
Treatment of M_2Cl_{10} with 2 eq of the phosphoranimine $Cl_2P(NR)(NR_2)$ ($R = SiMe_3$) yielded complexes $[Cl_2P(NR)_2]MCl_4$ (**66**) by desilylation (Scheme 12).[107,120] Reaction with 2.5 eq gave a complex series of products, from which the binuclear complexes (**67**) and (**68**) were identified.[120] (**67**) features a $Nb_2(\mu_2\text{-}N)_2$ core, with bridging desilylated nitrogen atoms, while (**68**) displayed a planar ClNbNPNNb metallacycle.



Scheme 12

$Ta(NMe_2)_5$ reacted with $O_2S(NHBu^t)_2$ in tol to produce five-coordinate $[O_2S(NBu^t)_2]Ta(NMe_2)_3$, with both nitrogen centers of the dianionic bis-sulfamide ligand coordinated to the metal center.[121]

Richeson and co-workers have studied the coordination chemistry of guanidinato ligands at Nb and Ta centers. Guanidinates are related to amidinates but can adopt monoanionic $[R_2N\text{-}C\text{-}(NR)_2]^-$ or dianionic $[RN{=}C(NR)_2]^{2-}$ forms. Reaction of $M(NMe_2)_5$ with trialkylguanidines $RN{=}C(NHR)_2$ ($R = Pr^i$, cy) resulted in release of two amide ligands as amine and formation of five-coordinate $[RN{=}C(NR)_2]M(NMe_2)_3$ (**69**) with a bidentate *dianionic* guanidinato ligand (Scheme 13).[122] On the other hand, the dialkylcarbodiimides $RN{=}C{=}NR$ ($R = Pr^i$, cy) inserted into a metal–amide bond of $M(NMe_2)_5$ to give six-coordinate $[Me_2NC(NR)_2]M(NMe_2)_4$ (**70**) with a bidentate *monoanionic* guanidinato ligand.[123] Protonation and elimination of an amido ligand of $Ta(NMe_2)_4Cl$ with triisopropyl guanidinate produced six-coordinate $[Pr^i(H)NC(NPr^i)_2]$-Ta-$(NMe_2)_3Cl$ (**71**).[124] Subsequent deprotonation of the monoanionic guanidinato ligand with $LiNMe_2$ provided a second route to five-coordinate (**69**).[124] The reactivity of (**69**) and (**71**) towards Me_3SiCl and ArNC ($Ar = 2,6$-$Me_2C_6H_3$) was studied.[125]

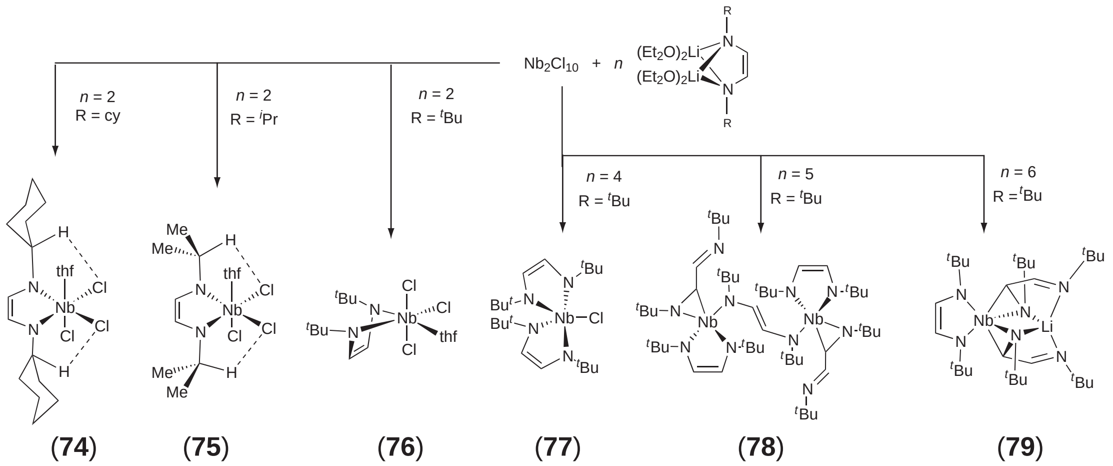


Scheme 13

In contrast to reaction with amide precursors, reaction of M_2Cl_{10} with $RN{=}C(NHR)_2$ ($R = Pr^i$) produced $[RN(H)C(NR)_2]_2M({=}NR)Cl$ ((**72**); Scheme 13), where the imido ligand resulted from cleavage of the parent guanidine.[126] Reaction between Ta_2Cl_{10} and $Li[(RN)_2C$-$NHR]$ yielded a binuclear species $[(RN)_3C)Ta({=}NR)Cl]_2$ (**73**) featuring two bridging guanidinato ligands.[126]

(iv) Ene-diamido ligands

Bidentate 1,4-diaza-1,3-diene ligands ($RN{=}C(R')$-$C(R'){=}NR$) are usually present at M^V centers in their reduced dianionic ene-diamide forms $[RN$-$C(R'){=}C(R')$-$NR]^{2-}$. Thermolysis of the bis(η^2-iminoacyl) complex $(ArO)_3Ta(\eta^2$-$R'C{=}NR)_2$ ($ArOH = 2,6$-Me_2-C_6H_3OH, $R = 2,6$-$Me_2C_6H_3$, $R' = C_6H_5CH_2$) afforded the enediamido complex $(ArO)_3Ta(\eta^2$-N,N-$RNCR'{=}CR'NR)$.[127,128] The two ligand nitrogen atoms occupy axial and equatorial positions of a trigonal bipyramid as part of an essentially planar five-membered chelate ring. Reaction of Nb_2Cl_{10} with 2 eq $Li_2[RNCH{=}CHNR]$ ($R = cy$, Pr^i) produced $Nb(\eta^2$-N,N-$RNCH{=}CHNR)Cl_3(thf)$ ((**74**), (**75**); Scheme 14), also with planar chelate rings.[129] In contrast, the ring is not planar in the Bu^t derivative (**76**). This variation in behavior may be related to hydrogen bonding interactions possible for the cy and Pr^i derivatives but not for the Bu^t analog.[130]



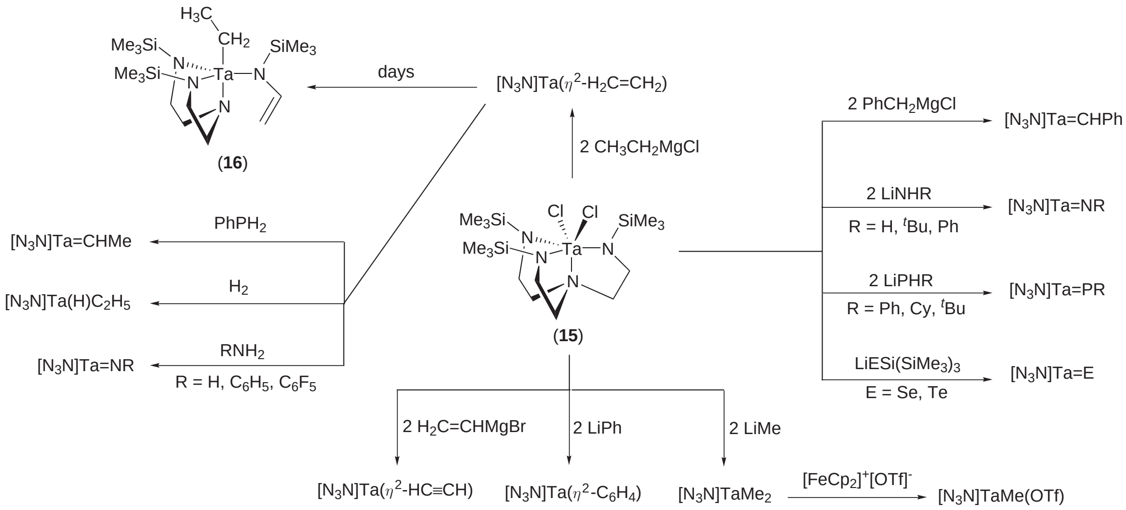
Scheme 14

Reaction of Nb_2Cl_{10} with 4 eq $Li_2[NRCH{=}CHNR]$ ($R = Bu^t$) provided the five-coordinate bis-enediamido derivative (**77**) (Scheme 14).[130] Reaction with 5 eq led to the binuclear complex (**78**), which features five $[RNCHCHNR]^{2-}$ ligands in three different bonding modes.[131] Reaction with 6 eq produced the hetero-binuclear complex (**79**).[131]

M_2Cl_{10} reacted with 4 eq Li_2L ($L^{2-} = 1,2\text{-}(Me_3SiN)_2\text{-}4,5\text{-}Me_2\text{-}C_6H_2$) at 90 °C in ether to afford the bis(phenylenediamido) compounds ML_2Cl.[132] The metal adopted a distorted square pyramidal geometry with two equatorial bidentate phenylenediamido ligands.

(v) Triamido-amine and related ligands

Arnold and Schrock pioneered the use of tetradentate triamidoamine ligands such as $[N_3N] = [(Me_3SiNCH_2CH_2)_3N]^{3-}$.[133,134] These ligands provide a protected pocket around the vacant coordination site of the metal atom. The $[N_3N]Ta^V$ group features (σ, 2π) frontier orbitals directed into this pocket for multiple bonding to small ligand fragments (e.g., oxo, imido, alkylidene, phosphinidene).[135] For example, $[N_3N]Ta{=}E$ (E = O, NR, CHR, PR, Se, Te) have all been prepared and are discussed elsewhere in this Chapter (Scheme 15).[38,39,133,134]

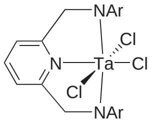


Scheme 15

The convenient starting material $[N_3N]TaCl_2$ ((**15**), Scheme 15) was prepared by addition of 2 eq $Li_3[N_3N]$ to Ta_2Cl_{10} in Et_2O.[133,134] Reaction of (**15**) with LiMe produced $[N_3N]Ta(CH_3)_2$ which could be converted to $[N_3N]Ta(CH_3)(OTf)$ (Scheme 15). This complex featured a long Ta—N—amine bond of 2.536 Å compared to 2.29 Å and 2.376 Å for $[N_3N]Ta(HC{\equiv}CH)$ and $[N_3N]Ta{=}Pcy$, respectively. This flexibility appears to be another significant feature of this ligand system, allowing variation of the effective size of the protected pocket.

The equivalent Nb chemistry is much less developed. $[N_3N]Nb{=}E$ (E = O, $NSiMe_3$) have been isolated. The oxo compound is nucleophilic and was converted to $[LNb(OR)]^+$ cations which could be reduced to $[N_3N]Nb(OR)$ (R = Me, $SiMe_3$).[136]

A variety of complexes supported by diamido–amine ligands have been prepared. These tridentate ligands can adopt either *fac* or *mer* geometries depending on the detailed ligand structure ((**80**)–(**84**)).[137–139] Interchange between diamido–amine and triamido coordination has been observed. For example, $TaMe_5$ reacted with $[(Ar_FN)_2N]^{2-} = (C_6F_5NCH_2CH_2)_2NH$ to yield first $[(Ar_FN)_2NH]TaMe_3$ (**83**) which then decomposed with loss of methane to produce $[(Ar_FN)_2N]TaMe_2$ (**84**).[139]



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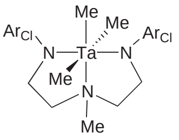

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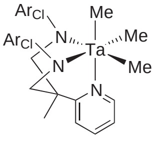

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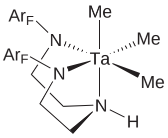

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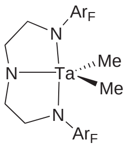


(84)

Ar = 2,6-$^iPr_2$-C_6H_3
Ar_{Cl} = 3,5-Cl_2-C_6H_3
Ar_F = C_6F_5

4.5.2.2.2 Imido ligands

Deprotonation of amine or amide reagents (NH_2R, Me_3SiNHR, LiNHR) interacting with M_2Cl_{10} provides a general entry into imido complexes $M{=}NR$. Intermediate binuclear imido complexes can be converted to their mononuclear counterparts by addition of appropriate neutral donor ligands. A review of organoimido complexes includes sections on Nb and Ta.[80]

(i) Mononuclear imido complexes

A variety of complexes of general formula *mer,cis*-$M(NR)X_3L_2$ (X = halide; L = neutral donor ligand) have been prepared. Reaction of M_2Cl_{10} with Me_3SiNHR ($R = Bu^t$) yielded species formulated as binuclear $[M(NR)Cl_3(NH_2R)]_2$.[140] Further reaction with excess L produced series of compounds formulated as *mer,cis*-$M(NR)Cl_3L_2$ ($L_2 = 2$ PMe_3, 2 picoline; tmeda, bipy = 2,2′-bipyridyl).[140,141] Related species $Ta(NAr)Cl_3L_2$ ($Ar = 2,6\text{-}Pr^i_2\text{-}C_6H_3$; $L_2 = 2$ thf, 2 py, 2 C_4H_8S; dme = 1,2-dimethoxyethane) were prepared directly from reaction of Ta_2Cl_{10} with $Me_3SiNHAr$ in benzene in the presence of L.[87] Addition of NHR'_2 ($R' = Me_3Si$) to M_2Cl_{10} produced binuclear $[M(NR')Cl_3(NH_2R')]_2$ which were converted to $M(NR')Cl_3(py)$ (M = V, Nb, Ta) in the presence of py.[142] Similarly, $[Nb(NAr')Cl_3\ (MeCN)_2]$ ($Ar' = p\text{-}Me_3SiOC_6H_4$) was prepared by reaction of Nb_2Cl_{10} with $Ar'N(SiMe_3)_2$ in MeCN.[143] A synthetic modification involved the use of an insoluble inorganic base or a soluble organic base and $ZnCl_2$ to remove by-product HCl from the reaction mixture.[144]

Related *mer,cis*-$M(NAr)X_3L_2$ complexes ($Ar = 2,6\text{-}Pr^i_2\text{-}C_6H_3$; M = Nb, X = Cl, L_2 = dme; M = Ta, X = Cl, Br, L_2 = dme, tmeda) have been characterized.[145] M—N bond lengths (M = Ta, 1.771(6)–1.785(6) Å; M = Nb, 1.746(4) Å) were relatively insensitive to the nature of M, X, and L and were characteristic of a formal metal–nitrogen triple bond. M–N–C angles were all close to linear (>174°). X-ray crystal structures of $Nb(NBu^t)Cl_3(dme)$ (Nb–N = 1.72 Å) and $Ta\text{-}(NBu^t)Cl_3(py)_2$ (Ta–N = 1.745(5) Å) have also been reported.[144,146]

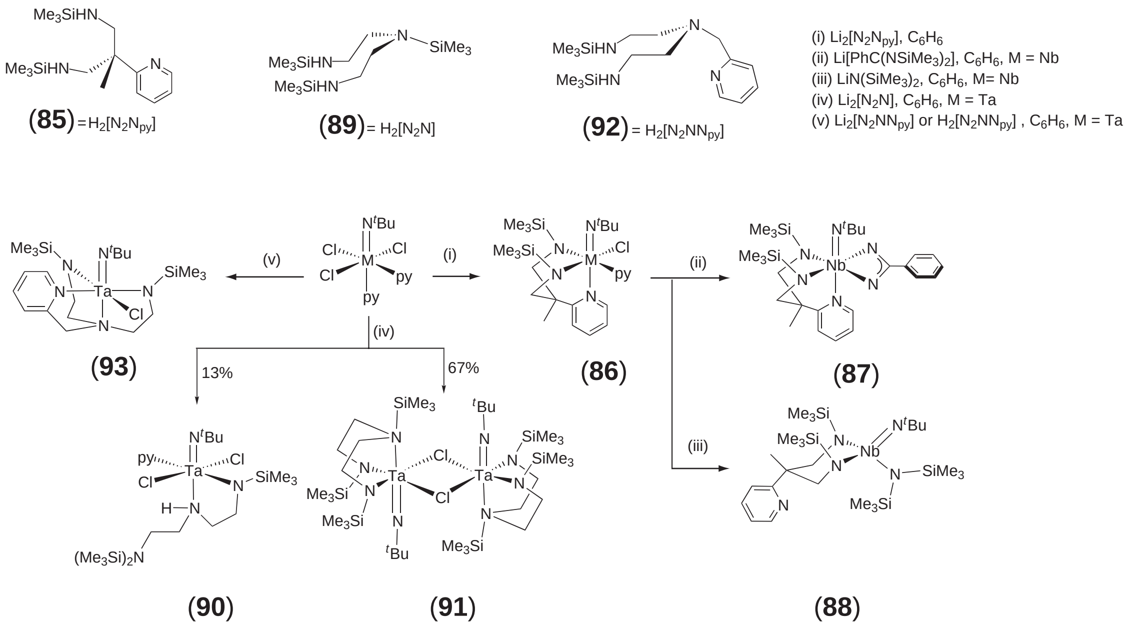
The luminescence properties of species of general formula *mer,cis*-$M(NAr)X_3L_2$ have been investigated.[144,145,147–149] Electronic absorption spectra exhibited a weak low-energy band in the range 19,000–22,000 cm^{-1} assigned to $\pi\text{-}(M{\equiv}NAr) \rightarrow d_{xy}$ due to its lack of sensitivity to changes in X and L.[147] The effect of variation of the imido substituent was also investigated.[148,149] A similar series of compounds has been investigated by FT-Raman spectroscopy, revealing bands attributed to M–X bending and stretching modes (160–360 cm^{-1}) and five bands associated with the MNAr fragment (990–1,600cm^{-1}).[145]

Reaction of *mer,cis*-$Ta(NAr)Cl_3L_2$ ($Ar = 2,6\text{-}Pr^i_2\text{-}C_6H_3$, $L_2 = 2$ thf, dme) with 1 eq LiOAr produced the imido alkoxo derivatives $Ta(NAr)(OAr)Cl_2L_2$ with *trans* Cl and *cis* L ligands.[87] On the other hand, treatment of $Ta(NAr)Cl_3(dme)$ with 3 eq $LiOBu^t$ gave $Ta(NAr)(OBu^t)_3$, which underwent imido/oxo exchange with OsO_2R_2.[150] Reaction of $M(NBu^t)Cl_3(py)_2$ with 2 or 3 eq KL′ ($L'H = 3,5\text{-}Bu^t_2$-pyrazole) in tol produced $M(NBu^t)L'_2Cl(py)$ and $M(NBu^t)L'_3$, respectively.[151]

Treatment of $(silox)_3Ta^{III}$ ((**32**), Scheme 44) with $PhNH_2$ resulted in oxidative addition of an N—H bond to afford the hydride $(silox)_3Ta(NHPh)(H)$. This in turn eliminated dihydrogen to form $(silox)_3Ta(NPh)$.[152] In contrast, the same reaction with $p\text{-}CF_3\text{-}C_6H_4NH_2$ produced $(silox)_3\text{-}Ta(NH_2)(C_6H_4\text{-}p\text{-}CF_3)$ from oxidative addition of a C—N bond (Scheme 44).[153] The competition between N–H and C–N activation was investigated for a variety of substituted anilines, with electron-withdrawing substituents found to favor C–N activation.

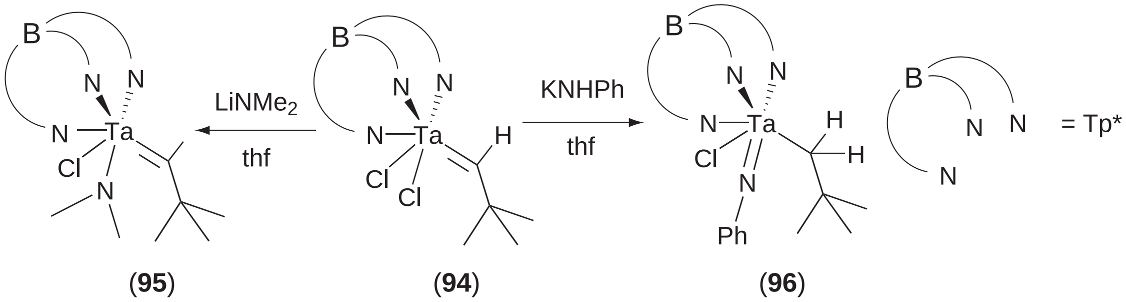
Ta–imido complexes supported by the triamido–amine ligand $[N_3N]^{3-}$ have been prepared. For example, $[N_3N]TaCl_2$ ((**15**), Scheme 15) reacted with LiNHR (R = H, Bu^t, Ph) to produce RNH_2 and the imido complexes $[N_3N]Ta{=}NR$.[38,39]

A number of imido complexes supported by diamido donor ligands have also been prepared. These systems have been reviewed.[154] Treatment of $M(NBu^t)Cl_3(py)_2$ with $Li_2[N_2N_{py}]$ ($H_2[N_2N_{py}]$ = (**85**); Scheme 16) in benzene yielded six-coordinate *fac*-$[N_2N_{py}]M(NBu^t)Cl(py)$ (**86**).[155] For M = Nb, (**86**) reacted with $Li[PhC(NSiMe_3)_2]$ to produce the six-coordinate benzamidinato complex (**87**), while reaction with $LiN(SiMe_3)_2$ yielded four-coordinate (**88**), with the pyridine of the $[N_2N_{py}]$ ligand unbound.[156] Reaction of $Ta(NBu^t)Cl_3(py)_2$ with $Li_2[N_2N]$ ($H_2[N_2N]$ = (**89**)) in benzene produced a mixture of (**90**) and (**91**).[157] (**90**) was characterized by X-ray crystallography and contained a bidentate modified ligand. (**91**) was assigned as binuclear by NMR. Finally, reaction of $Ta(NBu^t)Cl_3(py)_2$ with $H_2[N_2NN_{py}]$ (**92**) or its Li salt provided $[N_2NN_{py}]Ta(NBu^t)Cl$ (**93**).[158]



Scheme 16

A number of complexes containing imido ligands and an ancillary Tp* ligand have been reported. They are usually prepared from reaction of the parent metal–imido complex with KTp*. Thus, treatment of $Ta(NAr)Cl_3(thf)_2$ with KTp* yielded $Tp^*Ta(NAr)Cl_2$ ($Ar = 2,6\text{-}Pr^i{}_2\text{-}C_6H_3$).[159] Further reaction with Na/Hg in wet thf produced $Tp^*Ta(NAr)Cl(OBu^n)$, with the butoxo ligand proposed to arise from ring opening of solvent thf. Similarly, $Tp^*M(NBu^t)Cl_2$ was prepared by reaction of KTp* with $M(NBu^t)Cl_3(py)_2$.[160] Addition of the phosphido azide $N_3P(NPr^i{}_2)_2$ to $Tp^*NbCl(Et)(PhC{\equiv}CEt)$ in tol resulted in migratory insertion of the ethyl group onto the alkyne and N_2 extrusion to form the related phosphoranoimido complex $Tp^*Nb[NP(NPr^i{}_2)_2]Cl(\eta^1\text{-}CPh{=}CEt_2)$.[161] Finally, reaction of the alkylidene complex $Tp^*Ta({=}CHBu^t)Cl_2$ ((**94**); Scheme 17) with $LiNMe_2$ produced the alkylidene–amido complex (**95**) while reaction with KNHPh yielded the alkyl–imido complex (**96**).[46]



Scheme 17

Reaction of M_2Cl_{10} with H_2NAr ($Ar = 2,6\text{-}Pr^i{}_2\text{-}C_6H_3$) produced insoluble species formulated as $[H_3NAr]_2[M(NAr)Cl_5]$.[162] Treatment of these salts with 4-Bu^t-py afforded $[4\text{-}Bu^t\text{-}pyH]_2[M(NAr)Cl_5]$. The related anion $[Nb(NPh)Cl_5]^{2-}$ has been prepared from the reaction of *N*-allylphenylamine and Nb_2Cl_{10} in tol.[163]

Reaction of $Ta(NR_2)_2Cl_3$ ($R = SiMe_3$) with 3 eq $LiNHBu^t$ in pentane produced mononuclear $Ta(NBu^t)(NR_2)_2Cl$, while reaction with LiNHEt led to $Ta(NEt)(NR_2)_2(NHEt)$.[164,165]

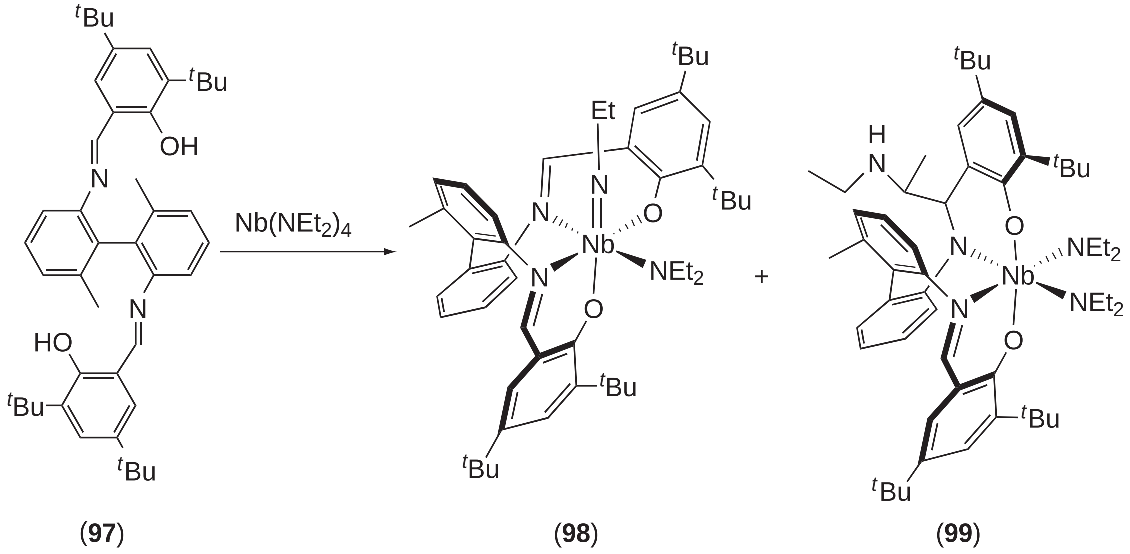
Treatment of $MOCl_3$ with 3 eq $LiNR_2$ ($R = SiMe_3$) in ether provided $M(NR)(NR_2)_2(OR)$, while reaction with $LiNR'_2$ ($R' = SiHMe_2$) yielded $M(NR')(NR')_3$.[166,167] Reaction of $NbOCl_3$ with Bu^tNH_2 in the presence of $[Ph_3PCH_2Ph]Cl$ and py in tol produced *trans*-[Ph_3PCH_2Ph][Nb(NBu^t)Cl_4(py)].[168] The related salt [pyH][Ta(NAr)Cl_4(py)] (Ar = 2-Bu^t-C_6H_4) was prepared by imido exchange between [Ta(NBu^t)$Cl_3$$(py)_2$] and $ArNH_2$.[169]

Reaction of Ta_2Cl_{10} with $NH_2(OCH_3)$ and bipy in CH_2Cl_2 produced the alkoxylimido complex Cl_3(bipy)Ta(NOMe).[170] A similar ligand was reported in $CpCl_2Nb(NOBu^t)$.[171]

Ta complexes containing imido and silyl ligands have been studied as potential precursors to Ta–Si–N ternary materials. Treatment of binuclear $[Cl(R_2N)(RN)Ta]_2(\mu_2\text{-}Cl)_2$ (R = $SiMe_3$) with 2 eq $LiNMe_2$ followed by 2 eq $LiSiPh_2Bu^t$ produced yellow $Ta(NR)(NR_2)(NMe_2)(SiPh_2Bu^t)$, characterized by X-ray crystallography.[172]

Tris(amido)–imido complexes $M(NAr)(NMe_2)_3$ (Ar = 2,6-Pr^i_2-C_6H_4) were prepared by reaction of $M(NMe_2)_5$ with NH_2Ar.[173] An X-ray structure of $Nb(NAr)(NMe_2)_3$ revealed Nb—N bond lengths of 1.794(2) Å and 1.974(2)–2.023(2) Å for the imido and amido ligands, respectively.

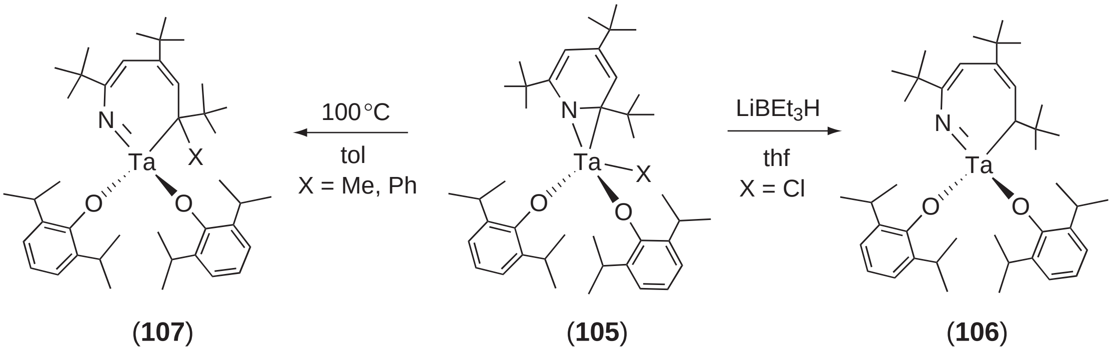
Reaction of the chiral Schiff-base ligand H_2L ((**97**); Scheme 18) with $Nb^{IV}(NEt_2)_4$ produced $LNb^V(NEt)(NEt_2)$ (**98**) (43%) and $L'Nb(NEt_2)_2$ (**99**) (16%) with modified ligand L′.[174] Radical pathways were suggested.



Scheme 18

Treatment of the binuclear nitride complex $\{Na[(N)NbL_3]\}_2$ (HL = $HNBu^tAr$, Ar = 3,5-Me_2-C_6H_3)[175] ((**100**); Scheme 20) with PCl_3 in thf produced the dichlorophosphinimido complex $L_3Nb(NPCl_2)$ (**101**).[176] Addition of excess Bu^tNH_2/NEt_3 to (**101**) modified the phosphinimido ligand to provide (**102**). Subsequent addition of excess Me_3SiCl led to (**103**).[176] Dehydrohalogenation of the latter with $LiN(SiMe_3)_2$ yielded the yellow *tert*-butyliminophosphinimido complex $L_3Nb(NP{=}NBu^t)$ (**104**).

Reaction of the η^2-N,C-pyridine complex (**105**) (Scheme 19, X = Cl) with $LiBEt_3H$ afforded the seven-membered metallocycle (**106**) (Ta–N = 1.779(8)Å) via C—N bond scission.[177,178] Thermolysis



Scheme 19

of (**105**) (X = Me, Ph) produced the related species (**107**) via intramolecular migration of ligand X.[178,179]

(ii) Binuclear imido complexes

Refluxing $TaCl_3(NR_2)_2$ (R = $SiMe_3$) in boiling tol produced binuclear $[Cl(R_2N)(RN)Ta]_2(\mu_2\text{-}Cl)_2$.[165] In the presence of Me_3SiX (X = Br, I) or LiX (X = OMe), the related $[X(R_2N)(RN)Ta]_2(\mu_2\text{-}X)_2$ species were generated.[164,165]

Reaction of M_2Cl_{10} and Bu^tNH_2 yielded binuclear $[Cl(Bu^tNH_2)(Bu^tNH)(Bu^tN)M]_2(\mu_2\text{-}Cl)_2$ which featured imido, amido, and amine ligands.[162,180] ^{13}C NMR indicated that these species exist as a number of isomeric forms in solution.[162] They have been examined as potential single-source precursors for metal–nitride thin films.[181] At 500–600 °C, the Nb analog decomposed to NbN, while the Ta analog gave Ta_3N_5.

Reaction of M_2Cl_{10} with $Me_3SiNHBu^t$ provided species formulated as binuclear complexes $[(Bu^tNH_2)Cl_2(Bu^tN)M]_2(\mu_2\text{-}Cl)_2$ which yielded the equivalent ethoxo-bridged species upon treatment with 2 eq EtOH.[140] $[Cl(R_2N)(RN)Nb]_2(\mu_2\text{-}OMe)_2$ (R = $SiMe_3$) was prepared by treatment of $NbCl_3(OMe)_2$ with $LiNR_2$.[182] Similar species $[(Me_2S)Cl_2(PhN)M]_2(\mu_2\text{-}Cl)_2$ have been prepared from reaction of $M^{III}{}_2Cl_6(SMe_2)_2$ with azobenzene PhN=NPh in reactions described as "double bond metathesis" between M=M and N=N to generate two M=N imido linkages.[183,184] The Nb compound has also been prepared by reaction of $Nb_2Cl_6(SMe_2)_2$ with PhN_3.[185]

Treatment of Nb_2Cl_{10} with *o*-, *m*-, or *p*-N-silylated phenylenediamines in MeCN produced binuclear $L_2Cl_3Nb{=}NC_6H_4N{=}NbCl_3L_2$ complexes (L = MeCN).[186]

(iii) Bis- and tris-imido complexes

Addition of 2 eq LiNHAr (Ar = 2,6-$Pr^i{}_2$-C_6H_3) to $Ta(NEt_2)_2Cl_3(OEt_2)$ in thf followed by py produced the bis(imido) complex $Ta(NAr)_2Cl(py)_2$.[187] The molecule is trigonal bipyramidal with axial py ligands. Analogous Nb complexes $Nb(NAr')_2Cl(py)_2$ (Ar′ = 2,6-$Pr^i{}_2$-C_6H_3, 2,4,6-Me_3-C_6H_2) were prepared in parallel procedures from binuclear $[Cl_2(Et_2N)_2Nb]_2(\mu_2\text{-}Cl)_2$.[187,188] This compound was also converted to $Nb(NAr)_2Cl(PMe_3)_2$ by sequential addition of 2 eq LiNHAr and PMe_3, and the same product was prepared by treatment of $Nb^{IV}Cl_4(PMe_3)_2$ with 2 eq LiNHAr.[189]

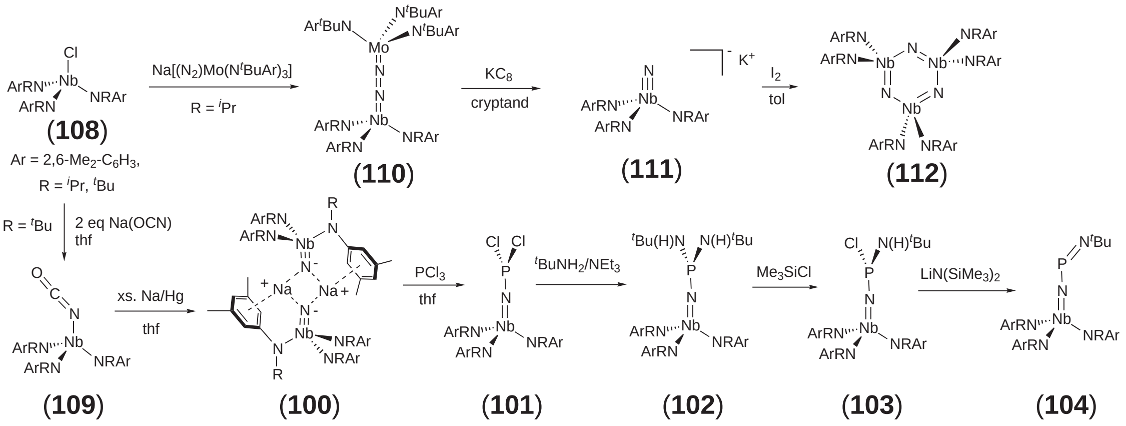
Thermolysis of $Me_2Ta(NR)(NHR)$ (R = $SiBu^t{}_3$) in either py or thf produced trigonal bipyramidal $MeTa(NR)_2L_2$ (L = py, thf) with elimination of CH_4.[190] The kinetics of alkane R′H elimination from mono(imido) $R'Ta(NR)(NRH)_2$ (R′ = Me, Ph, CH_2Ph, CH_2Bu^t) to form transient bis(imido) complexes $Ta(NR)_2(NHR)$ was studied in detail.[190] The reverse of this process, i.e., methane activation by bis(imido) complexes $M(NH)_2(NH_2)$, has been studied theoretically.[191]

Addition of ≥6 eq LiNHAr (Ar = 2,4,6-Me_3-C_6H_2) to binuclear $[Cl_2(Et_2N)_2M]_2(\mu_2\text{-}Cl)_2$ produced the tris(imido) anions $[M(NAr)_3(NHAr)]^{2-}$.[188] The amido ligand of the Nb anion could not be deprotonated with Bu^nLi.[188] Treatment of binuclear $[Cl(RNH_2)(RNH)(RN)Ta]_2(\mu_2\text{-}Cl)_2$ (R = Bu^t) with 10 eq LiNHR produced $\{M(NR)_3(NHR)]Li_2\}_2$, comprised of 2 tetrahedral $M(NR)_3(NHR)$ units linked by 6 Li···N···Li bridges with 2/3 occupancy.[192] Two of the three imido groups of each unit are involved in these bridging links (Nb–N = 1.949(6)–2.029(7) Å), while the third is a terminal ligand (Nb–N = 1.782(6)–1.810(6) Å).

4.5.2.2.3 Nitrido ligands

Reaction of $L_3Nb^{IV}Cl$ ((**108**); Scheme 20; HL = HNRAr; R = Bu^t, Ar = 3,5-Me_2-C_6H_3) with excess Na(OCN) in thf in the presence of 15-crown-5 produced $L_3Nb(NCO)$ (**109**).[175] Treatment of (**109**) with excess Na/Hg resulted in decarbonylation to form the binuclear anionic nitride $\{Na[(N)NbL_3]\}_2$ (**100**).[175]

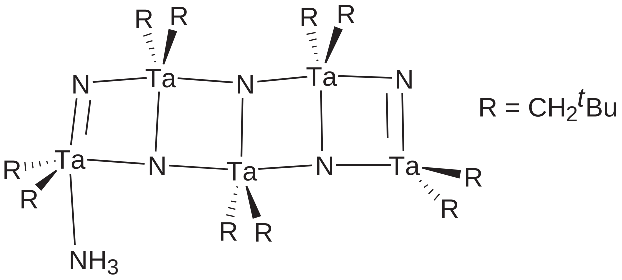
Treatment of (**108**) (R = Pr^i) with the dinitrogen compound $Na[(N_2)Mo(NBu^tAr)_3]$ provided the binuclear N_2-bridged complex (**110**) (Scheme 20).[193] Reduction of the latter produced the anion $[L_3NbN]^-$ (**111**) whose reaction with I_2 in tol yielded a mixture of products from which cyclic $[(L_2Nb(\mu_2\text{-}N)]_3$ (**112**) was isolated. The latter contained both "short" (1.791(7)Å) and "long" (2.004(6)Å) Nb—N bonds.[193]



Scheme 20

Ta species related to (**112**) have also been prepared. For example, ammonolysis of Cp^*TaMe_4 ($Cp^* = C_5Me_5$) resulted in release of 3 eq CH_4 per Ta and formation of trinuclear $[Cp^*MeTa(\mu_2\text{-}N)]_3$.[194] In contrast to (**112**), this complex featured equivalent Ta—N bond lengths of 1.89(2) Å.[194] $[Cp^*ClTa(\mu_2\text{-}N)]_3$ has been prepared as well, and also has equivalent Ta—N bond lengths (1.88(2) Å).[195]

Ammonolysis of $Ta(CHBu^t)(CH_2Bu^t)_3$ with 5 eq NH_3 in benzene produced pentanuclear $[(Bu^tCH_2)_2TaN]_5$ (**113**) which featured alternating $(Bu^tCH_2)_2TaN$ units in a roughly planar ladder structure.[196] Three triply bridging nitrido ligands adopt a T-shaped coordination geometry.



(**113**)

Addition of 6 eq $LiBHEt_3$ in thf to $[LNbCl_2]_2$ ((**114**); Scheme 31, $LH_3 =$ (**115**), $R = Bu^t$) in tol under N_2 produced binuclear $[Li(thf)]_2\{[LNb]_2(\mu_2\text{-}N)_2\}$ (**116**).[197]

Mononuclear and binuclear calixarene-supported nitrido complexes have been prepared ((**117**), (**118**); Scheme 32).[198,199] These species are discussed in Section 4.5.2.2.4 in the context of N_2 activation.

NH_4^+ salts of D_{4h} binuclear anions $\{[Cl_5M]_2(\mu_2\text{-}N)\}^{3-}$ were prepared by treatment of M_2Cl_{10} with NH_4Cl at 400 °C or by the prolonged high-temparature reaction of NH_4Cl with tantalum metal.[200,201]

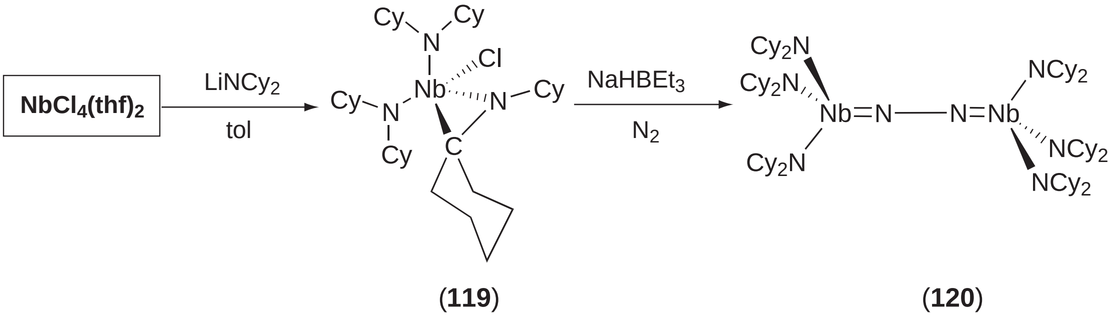
4.5.2.2.4 Hydrazido ligands

The reaction of excess $Me_3Si(Me)NNMe_2$ with L_3TaBr_2 ($L = Et_2NCS_2^-$) yielded the salt $[L_3Ta(MeNNMe_2)]Br$ containing an η^2-hydrazido(-1) ligand with Ta—N bond lengths of 1.932 Å and 2.209 Å.[202] Protonation with HBr gave trimethylhydrazine and $[L_3TaBr_2]$.

Reaction of Nb_2Cl_{10} with Me_2NNH_2 in benzene followed by addition of Me_3SiL ($L = Et_2NCS_2^-$) produced the η^1-hydrazido(2-) complex $[L_3Nb(NNMe_2)]$.[203] Its reaction with HBr in MeCN was proposed to proceed via $[L_3Nb(NHNHMe_2)]^{2+}$ which decomposed slowly to yield $[L_3NbBr_2]$ and Me_2NNH_2.[204]

Improved syntheses for the binuclear hydrazido(4-) complexes $[(thf)_2Cl_3M]_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}N_2)$ involved reaction of M_2Cl_{10} with $(Me_3Si)RNNR(SiMe_3)$ ($R = SiMe_3$, H) in CH_2Cl_2.[205] These complexes provide useful starting materials for species based upon the binuclear $\{[M]_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}N_2)\}^{6+}$ core. Reaction with 6 eq Me_3SiL ($L = Et_2NCS_2^-$) produced $[L_3M]_2(\mu_2\text{-}N_2)$, the first dinitrogen complexes in which the co-ligands are exclusively sulfur donors.[205] Reaction with HX (X = Cl, Br) yielded hydrazine and L_3MX_2. The kinetics and mechanisms of these reactions have been studied in detail.[206,207] Similarly, reaction of $[(thf)_2Cl_3Ta]_2(\mu_2\text{-}N_2)$ with 6 eq ArEH (ArEH = 2,6-Pr^i_2-C_6H_3OH, 2,6-Pr^i_2-C_6H_3SH, 2,4,6-Pr^i_3-C_6H_2SH) yielded the related complexes $[(ArE)_3Ta]_2(\mu_2\text{-}N_2)$.[208]

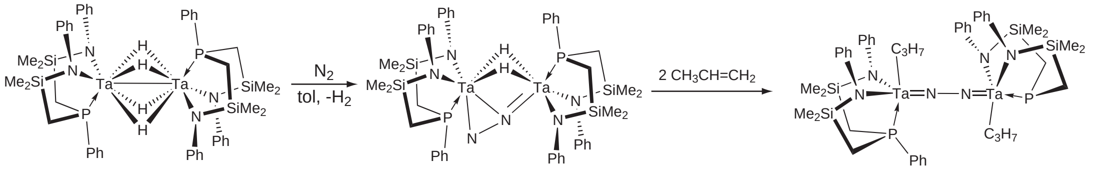
Reaction of $Nb^{IV}Cl_4(thf)_2$ with 3 eq $LiNcy_2$ in tol resulted in partial dehydrogenation of a cy ring and formation of diamagnetic $(cy_2N)_2ClNb(\eta^2\text{-}C,N\text{-}C_6H_{10}Ncy)$ ((**119**); Scheme 21) which contains a three-membered NbNC niobaaziridine ring.[209] Further reaction with $NaHBEt_3$ under N_2 produced binuclear $[(Cy_2N)_3Nb]_2(\mu_2\text{-}N_2)$ (**120**).[209]



Scheme 21

Aspects of N_2 activation by complexes containing tridentate or tetradentate amido-phosphorane ligands have been reviewed.[210] Reaction of $NbCl_3(dme)$ with $Li_2[NPN]$ ($[NPN] = [PhP(CH_2SiMe_2NPh)_2]^{2-}$) under N_2 produced $\{[NPN]ClNb\}_2(\mu_2\text{-}N_2)$.[211] Similarly, reaction of the Ta alkylidene complexes $[PNP]TaCl_2({=}CHR)$ (R = Bu^t, Ph; $[PNP] = [N(SiMe_2CH_2PPr^i_2)_2]^-$) with N_2 provided $\{[PNP]Ta({=}CHR)\}_2(\mu_2\text{-}N_2)$.[212]

Treatment of $TaMe_3Cl_2$ with $Li_2[NPN]$ yielded $[NPN]TaMe_3$, which reacted with H_2 to form diamagnetic binuclear $\{[NPN]Ta^{IV}\}_2(\mu_2\text{-}H)_4$ ((**121**), Scheme 22).[211] Reaction with N_2 displaced H_2 and formed $\{[NPN]Ta\}_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^2{:}\eta^1\text{-}N_2)$ (**122**), with the N_2^{4-} ligand bound in the unusual side-on, end-on mode.[211] Propene inserted into the Ta—H—Ta bonds of (**122**) to generate $\{[NPN]TaPr^n\}_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**123**) with the N_2^{4-} ligand adopting the more familiar end-on binding mode.[211] (**122**) was alkylated with $PhCH_2Br$ to form $\{[NPN]Ta\}(\mu_2\text{-}\eta^2{:}\eta^1\text{-}N_2CH_2Ph)(\mu_2\text{-}H)_2\{TaBr[NPN]\}$.[211] It also reacted with 9-borabicyclononane (HBC_8H_{14}) in thf to form $\{[NPN](H)Ta\}(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^2{:}\eta^1\text{-}N_2\text{-}BC_8H_{14})\{Ta[NPN]\}$, which was thermally unstable and gradually decomposed to an imido–nitrido complex.[213]



Scheme 22

Dinitrogen inserted into the $Nb^{III}{=}Nb^{III}$ bond of the calixarene supported species (**12**) (Scheme 32) as a four-electron reduced $[\mu_2\text{-}\eta^1{:}\eta^1\text{-}N_2]^{4-}$ ligand (**124**).[198,199] This interpretation is supported by short Nb—N (1.75(1) Å) and long N—N (1.39(2) Å) bonds and the fact that reaction with PhCHO gives 2 eq of the oxo derivative (**13**) and the expected azine PhCH=N-N=HCPh. Reduction of (**124**) with Na cleaved the N—N bond with formation of the $Nb^V_2(\mu_2\text{-}N)_2$ nitrido complex (**117**). The latter was proposed to be in equilibrium in solution with the mononuclear nitrido complex (**118**). Two distinct pathways for the transformation of (**12**) → (**117**) were identified as a function of the solvent used. These reactions have been discussed in detail.[199]

Exposure of seven-coordinate $Ta^{III}Cl(H)_2(PMe_3)_4$ to N_2 resulted in release of 1 eq PMe_3/Ta and formation of a product assigned as $[(PMe_3)_3ClTa(H)_2]_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}N_2)$ on the basis of IR and NMR measurements.[214] In contrast, the related species $TaCl(H)_2(dmpe)_2$ (dmpe = 1,2-bis-(dimethylphosphino)ethane) with bidentate phosphorane ligands was stable in the presence of N_2.

4.5.2.3 Phosphorous, Arsenic, Antimony, and Bismuth Donor Ligands

$[N_3N]TaCl_2$ ((**15**); Scheme 15) reacted with 2 eq LiPHR (R = Ph, cy, Bu^t) in ether to form the phosphinidenato complexes $[N_3N]Ta{=}PR$. An X-ray structure of the R = cy derivative revealed a Ta—P bond length of 2.145(7) Å and an approximately linear TaPR unit.[133] $[N_3N]Ta{=}PR$ reacted with aldehydes R′HCO to produce $[N_3N]Ta{=}O$ and the corresponding phosphaalkenes $RP{=}CHR'$.[133] Attempts to prepare the parent phosphinidenato $[N_3N]Ta{=}PH$ or the terminal phosphido $\{[N_3N]Ta{\equiv}P\}^-$ complexes were unsuccessful.[38]

Treatment of $(silox)_3Ta^{III}$ ((**32**); Scheme 44) with 1 eq $PhPH_2$ in benzene afforded the hydride $(silox)_3Ta(PHPh)(H)$ which eliminated dihydrogen to form $(silox)_3Ta{=}PPh$.[152] The phosphinidenato unit was bent (∠Ta—P—C = 110.2°) with a Ta—P bond length of 2.317(4) Å, longer than that reported for $[N_3N]Ta{=}Pcy$.[133] Related species $(silox)_3Ta{=}EPh$ (E = N, As) were prepared by similar methods.[152]

The series of compounds $Cp_2M(H)_2(ER_2)$ (M = Nb, E = As, R = Me, Et; E = Sb, R = Ph; E = Bi, R = Ph; M = Ta, E = P, R = Ph) have been prepared.[215–219] Synthetic routes involved reaction of XER_2 (X = Br, Cl) with the trihydride $Cp_2M(H)_3$ to generate the salt $[Cp_2M(H)_2(HER_2)]X$, which was deprotonated to yield $Cp_2M(H)_2(ER_2)$.

4.5.2.4 Oxygen Donor Ligands

Oxo complexes are important aspects of the high valent chemistry of Nb and Ta. Much of the interest derives from their use as soluble reactivity models of metal–oxo fragments relevant to heterogeneous oxidation catalysis. Volatile or hydrolysable alkoxo species have been explored as precursors for oxide films.

4.5.2.4.1 Mononuclear oxo complexes

(i) Halo co-ligands

Molecular cations of $TaOX_3$ (X = F, Cl) have been identified in the gas phase by mass spectrometry.[220]

$(NH_4)_3[NbOF_6]\cdot1.5H_2O$ was prepared by a solid state route and its structural and thermal stabilities compared with those of the vanadium analog.[221] The solids $K_2[MOF_5]$ resulted from thermal decomposition of the fluoroperoxo salts $K_2[M(O_2)F_5]\cdot H_2O$.[222] The structure of $Na_2[NbOF_5]$ is isomorphous with neither $Li_2[NbOF_5]$ nor $K_2[NbOF_5]$.[223] $[C(NH_2)_3]_2[NbOF_5]$ has been crystallized from an acid solution by addition of guanidinium fluoride.[224] The solids $A_3[MO_2F_4]$ (A = Na, K) result from thermal decomposition of the fluoroperoxo salts $A_3[M(O_2)_2F_4]$.[222]

Addition of oxide to the melt LiF-NaF-KF-$K_2[NbF_7]$ at 650 °C allowed detection of a $\nu(Nb{=}O)$ vibrational mode at 921 cm^{-1}.[225] The data are consistent with the presence of mononuclear $[NbOF_5]^{2-}$ (C_{4v}) and/or $[NbOF_6]^{3-}$ (C_s). A higher proportion of oxide led to bands at 878 and 815 cm^{-1}, consistent with the symmetric and asymmetric modes of a *cis*-Nb^VO_2 center.[225,226] The total data suggested the presence of mononuclear $[NbO_2F_4]^{3-}$ (C_{2v}). Melts saturated with oxide appeared to contain anions $[NbO_3F_n]^{(1+n)-}$ and/or $[NbO_4F_n]^{(3+n)-}$ which may be polymeric.[225–227] Equivalent Ta^V species were observed under similar conditions.[228,229]

Phase studies of metal oxides dissolved in $(HF)_x$/pyridine/water solutions under hydrothermal conditions have led to isolation of salts containing $[M'(py)_4]^{2+}$ (M′ = Cu, Zn, Cd) and $[MOF_5]^{2-}$.[230,231] Infinite chains of alternating cations and anions occur in $[M'(py)_4][MOF_5]$ with $[MOF_5]^{2-}$ anions supplying *trans*-fluoro ligands to square planar $[M'(py)_4]^{2+}$ units. Discrete "cluster" anions with equivalent stereochemistry were found in $(pyH)_2[M'(py)_4(MOF_5)_2]$. "Reverse clusters" exist in $\{(CuF(py)_4)_2[TaOF_5]\}(H_3O)_2F_2$ where the Ta anion supplies the sixth ligand to the Cu cations. The nature of local distortions and O/F ordering in the Cd compounds was examined by solid state ^{17}F, ^{93}Nb, and ^{113}Cd NMR.[232]

Aligned $[MOF_5]^{2-}$ (M = Nb, Ta) anions (a requirement for large, non-linear optical effects) were detected in $[CuL_2][MOF_5]\cdot2H_2O$ (L = 2,2′-dipyridylamine).[233,234] A linear chain structure is induced by the amine, which acts as a bidentate ligand to Cu^{II} and an H-bond donor to an F ligand of Nb^V.

The liquid system CsCl-$NbCl_5$-$NbOCl_3$ has been studied in the range 340–650 °C.[235] Molten $NbOCl_3$ exhibited Raman bands typical of both terminal and bridging oxo ligands. The mononuclear ions $[NbCl_6]^-$, $[NbOCl_5]^{2-}$, and $[NbOCl_4]^-$ have been identified in basic melts, and polymeric ions appear to be present in acidic melts. Interpretation of the vibrational spectra was assisted by *ab initio* calculations. The molecular and electronic structures of $[MOCl_5]^{2-}$ have also been calculated with DFT methods and compared with those of the group 6 analogs.[236]

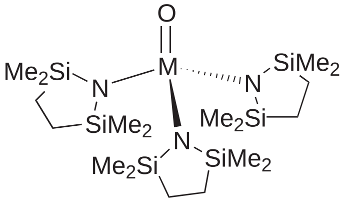
$NbECl_3$ (E = O, S) and their simple adducts remain very useful synthons (see, e.g., ref. 237–241). The systems $NbECl_3(PR_3)_{2,3}$ (E = O, S)[240,241] have been at the forefront of the controversy concerning distortional (bond stretch) isomers.[242–246]

Nb^VCl_5 and $Nb^{IV}Cl_4$ are sources of the $[Nb^VO]^{3+}$ center via oxygen abstraction from ether solvents such as thf or Et_2O. For example, *trans*-$[NbOCl_4(thf)]^-$ was synthesized in this manner for testing as a catalyst for alkene polymerization.[247] The structures of $[Mg(thf)_4][NbOCl_4(thf)]_2$. solvent and $[AlCl(thf)_3][NbOCl_4(thf)]_2$ revealed the presence of essentially linear Nb=O-M′-O=Nb fragments (M′ = Mg: Nb=O, 1.72; Mg—O, 2.11; M′ = Al: Nb=O, 1.74; Al—O, 1.90 Å).

Ph_4P^+ salts of six-coordinate *trans*-$[NbOCl_4(OH_2)]^-$ and -$[NbOCl_4(O_2PCl_2)]^{2-}$ have been characterized structurally.[248]

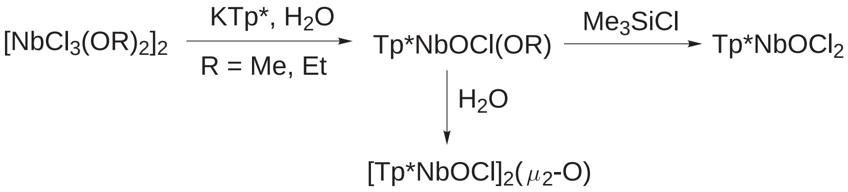
(ii) Nitrogen donor co-ligands

A four-coordinate $NbOL_3$ molecule resulted from the reaction of $NbCl_4(thf)_2$ and LiL = $LiN(SiMe_3)_2$ via oxygen abstraction from solvent thf. The low coordination number is imposed by the steric demands of the amido ligand.[249] An equivalent structure resulted from reaction of $MOCl_3$ with a lithiated aza-2,5-disila-cyclo-pentane ligand (**125**).[250]



(125)

The reaction of $MOCl_3$ with KTp* produced mononuclear six-coordinate complexes Tp^*MOCl_2.[160] Another route to the Nb complex is available (Scheme 23).[251] Controlled hydrolysis of Tp*NbOCl(OR) (R = Me, Et) produced binuclear $[Tp^*NbOCl]_2(\mu_2\text{-O})$ (Nb-O-Nb, 169.8(3)°).



Scheme 23

(iii) Oxygen donor co-ligands

The reaction of $NbOCl_3(MeCN)_2$ with LiOAr (Ar = 2,6-$R_2C_6H_3$; R = Me, Bu^t) produced four-coordinate $NbO(OAr)_3$ in good yield.[252]

$NbOL_3$ (L = bidentate tropolonato, $C_7H_5O_2^-$) is formed by hydrolysis of eight-coordinate $[NbL_4]^+$.[253] It is seven-coordinate with a distorted pentagonal bipyramidal stereochemistry.[254] The sulfur and selenium analogs are postulated to have equivalent structures.[254] The species $NbOL_3$ (L = 8-quinolinato-N,O) has a similar structure.[255]

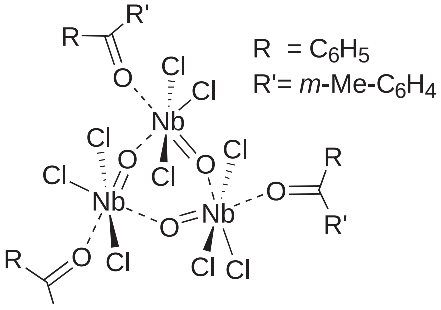
4.5.2.4.2 Polynuclear oxo complexes

(i) Homometallic complexes

Reaction of [Nb$^{IV}_2$(μ_2-η^2-S$_2$)$_2$]$^{4+}$(aq) and K$_3$L (LH$_3$ = N(CH$_2$CO$_2$H)$_3$) in aqueous solution followed by oxidation in air led to *anti*-K$_2${[NbOL]$_2$(μ_2-OH)$_2$}.[256]

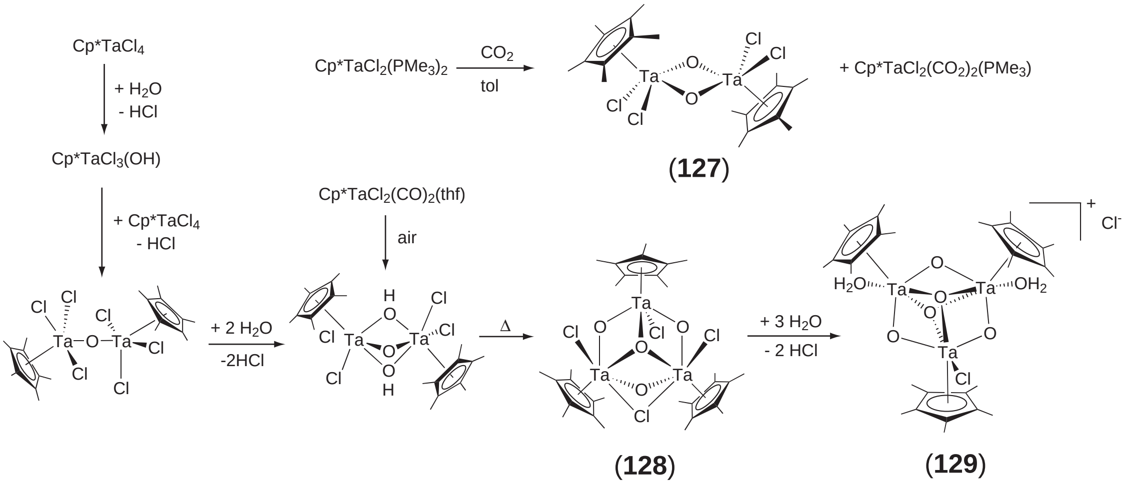
The salts A$_2${[NbCl$_5$]$_2$(μ_2-O)} (A = Te$_4^+$, A$_2$ = [Hg(PMe$_2$Ph)$_4$]$^{2+}$) contained linear Nb–O–Nb links.[257] [Ph$_4$P]$_2${[TaCl$_5$]$_2$(μ_2-O)} was a product of the reaction of Ta$_2$Cl$_{10}$ and Ph$_4$PCl in MeCN and featured a centrosymmetric anion with short Ta—O bonds (1.89 Å).[258] The source of oxygen appeared to be trace water. A Ph$_4$P$^+$ salt of [Ta$_2$OCl$_9$]$_2^{2-}$ was also isolated which displayed two [Ta$_2$OCl$_{10}$] fragments in which one Cl ligand from each unit acted as a bridge to the second unit. In this case, the essentially linear Ta–O–Ta moeity featured differing bond lengths of 1.79 Å and 2.03 Å. A K(18-crown-6)$^+$ salt of [Ta$_4$O$_6$Cl$_{12}$]$^{4-}$ was isolated from the reaction of Ta$_2$Cl$_{10}$, K$_2$S$_5$ and the crown ether in CH$_2$Cl$_2$. The anion featured an adamantane-like Ta$_4$O$_6$ core.

A trinuclear Nb$^V_3$(μ_2-O)$_3$ core is present in [NbOCl$_3$(OCRR′)$_3$]$_3$ ((**126**)R = C$_6$H$_5$, R′ = *m*-Me-C$_6$H$_4$) formed via reaction of Nb$^{III}_2$Cl$_6$(SMe$_2$)$_3$ with the ketone.[259] It featured a closed set of Nb=O—Nb bonds and is a rare example of a ketone bound directly to a metal atom.



(**126**)

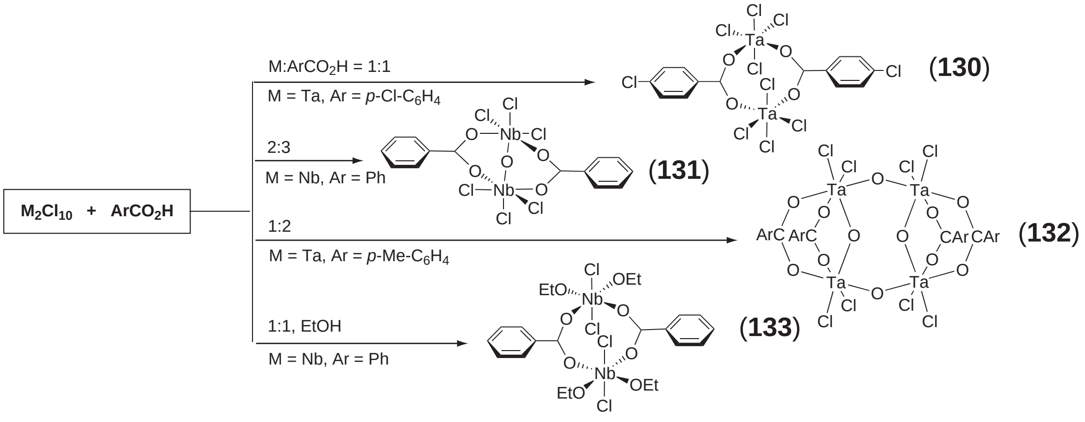
The classic vanadium organometallic oxides CpVOCl$_2$ and Cp*VOCl$_2$ are mononuclear while the Ta analog [Cp*Cl$_2$Ta]$_2$(μ_2-O)$_2$ is binuclear ((**127**), Scheme 24) and unstable to hydrolysis.[260,261] Hydrolysis of CpNbCl$_4$ in thf gave a mixture of products [CpNbX$_4$]$_2$(μ_2-O) where X$_4$ was a combination of H$_2$O and terminal or bridging Cl.[262] [CpNbCl$_3$(H$_2$O)]$_2$(μ_2-O) was characterized structurally.[262] Well-defined hydrolysis steps in the Cp*TaCl$_4$ system produced a series of bi- and tri-nuclear complexes (Scheme 24).[260,261,263] (**128**) and (**129**) feature Ta$_3$(μ_3-O)(μ_2-O)$_3$ and Ta$_3$(μ_3-O)$_2$-(μ_2-O)$_3$ cores, respectively.



Scheme 24

In addition, oxidation of $Cp^*{}_2Nb^{IV}Cl_2$ by O_2 in wet thf gave $[Cp^*Nb^VCl_2]_2(\mu_2\text{-}Cl)(\mu_2\text{-}OH)(\mu_2\text{-}O)$ which existed as two isomers distinguished by the relative orientation of the Cp* and bridging ligands.[264] Mixed-oxidation-state trinuclear species were derived from this system.

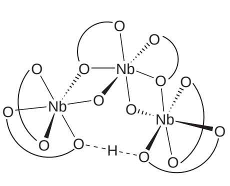
Reactions between M_2Cl_{10} and arylcarboxylic acids $ArCO_2H$ are complex and the products isolated are dependent upon M, Ar, and the reaction conditions (reactant ratios, solvent, temperature). Ta_2Cl_{10} reacted cleanly with 2 eq $ArCO_2H$ ($Ar = p\text{-}Cl\text{-}C_6H_4$) to generate binuclear $[Cl_4Ta]_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}O_2CAr)_2$ ((**130**); Scheme 25).[265] The $NbCl_5$ system is more complex, but an equivalent Nb compound ($Ar = C_6F_5$) was obtained. Under different conditions, oxo abstraction occurred with formation of aroyl chlorides. With the ratio $Nb{:}PhCO_2H = 2{:}3$, the oxo-bridged species $[Cl_3Nb]_2(\mu_2\text{–}O)(O_2CPh)_2$ resulted ((**131**); Scheme 25).[266] With the ratio $Ta{:}ArCO_2H = 1{:}2$ ($Ar = p\text{-}Me\text{-}C_6H_4$), tetranuclear $[TaOCl_2(O_2CAr)]_4$ was isolated ((**132**); Scheme 25).[267] In the presence of ethanol, oxo abstraction was suppressed in the Nb system and binuclear $[Cl_2(EtO)_2Nb]_2(O_2CPh)_2$ was isolated ((**133**); Scheme 25).[268]



Scheme 25

Reaction of $Nb_2(OPr^i)_{10}$ with acid led to tetranuclear clusters $[NbO(OPr^i)_2(O_2CR)]_4$ (R = Me, $C(Me)CH_2$).[269,270] The centrosymmetric $Nb_4(\mu_2\text{-}O)_4$ core supported by carboxylato bridges is related to (**132**). The structure of the acetato cluster was confirmed by NMR in solution and in the solid state.[269]

The products of reaction of $Nb_2(OR)_{10}$ (R = Et, Pr^i) and pinacol $LH_2 = HOCMe_2CMe_2OH$ in tol depended upon the stoichiometries employed.[271] A trinuclear cluster $[Nb_3O_2L_5(LH)]$ (**134**) featured a bent open-shell framework and an intramolecular hydrogen bond while tetranuclear $[Nb_4O_4L_2(OPr^i)_8]$ (**135**) contained an $Nb_4(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2$ rhombus.[272] In the presence of $Ce_2(OPr^i)_8(Pr^iOH)_2$, tetranuclear (**136**) was identified.



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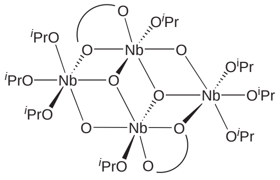

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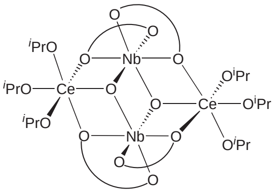
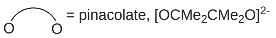


(136)

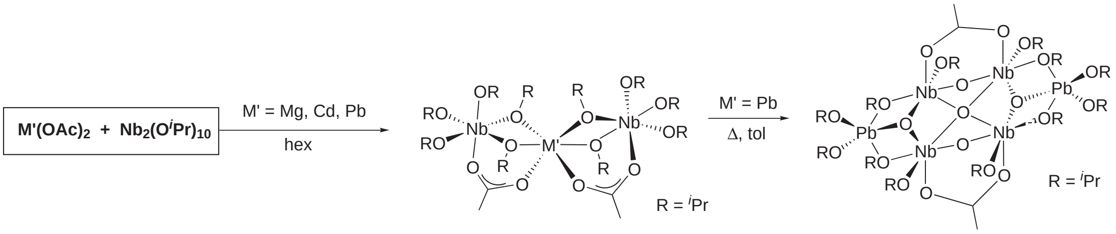

= pinacolate, $[OCMe_2CMe_2O]^{2-}$

A new route to $Nb_8(\mu_3\text{-}O)_2(\mu_2\text{-}O)_8(\mu_2\text{-}OEt)_6(OEt)_{14}$ based upon condensation of $NbO(OEt)_3$ is available and its structure has been confirmed.[273,274] The tantalum analog has an equivalent structure.[275] Three other oxo-alkoxo clusters of Ta have been characterized structurally: binuclear $Ta_2(\mu_2\text{-}O)(\mu_2\text{-}OPr^i)(OPr^i)_7(Pr^iOH)$, pentanuclear $Ta_5(\mu_3\text{-}O)_4(\mu\text{-}O)_3(\mu_2\text{-}OBu^t)(OBu^t)_{10}$, and heptanuclear $Ta_7(\mu_3\text{-}O)_3(\mu_2\text{-}O)_6(\mu_2\text{-}OPr^i)_4(OPr^i)_{13}$.[275,276]

(ii) Heterometallic complexes

Such species are potential precursors of mixed metal oxides and alloys.

Reaction of $M'(OAc)_2$ ($M' = Mg$, Cd, Pb) with $Nb_2(OPr^i)_{10}$ led to trinuclear clusters $M'Nb_2(\mu_2\text{-}OAc)_2(\mu_2\text{-}OPr^i)_4(OPr^i)_6$ ((**137**); Scheme 26).[277,278] Thermal decomposition in solution of (**137**) ($M' = Pb$) gave $Pb_2Nb_4O_5(OAc)_2(OPr^i)_{12}$ (**138**).

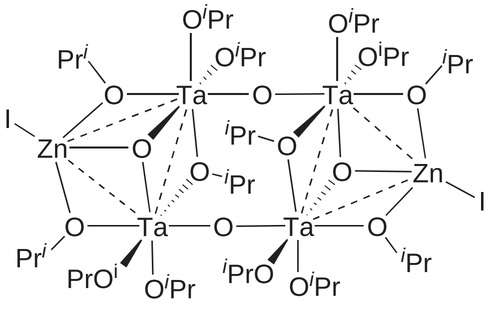


(137) **(138)**

Scheme 26

Tetranuclear clusters are observed in the reaction of $Ce_2(OPr^i)_8(Pr^iOH)_2$ and $Nb_2(OPr^i)_{10}$ in the presence of LH_2 = pinacol, $HOCMe_2CMe_2OH$.[272] Two products of stoichiometry Ce_2Nb_2 were isolated, one of which was positively identified as $Ce_2Nb_2O_2L_4(OPr^i)_6$ (**136**).

Reaction of ZnI_2 and $K[Ta(OPr^i)_6]$ in refluxing tol produced $[ZnTa_2IO_2(OPr^i)_7]_2$ (**139**) which features two triangular $ZnTa_2(\mu_3\text{-}O)(\mu_2\text{-}OPr^i)_3$ units linked by two linear oxo bridges involving the Ta centers on each unit.[279]



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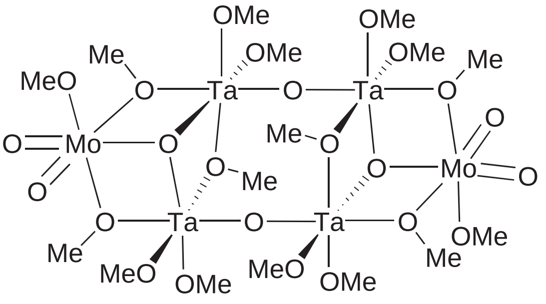


(140)

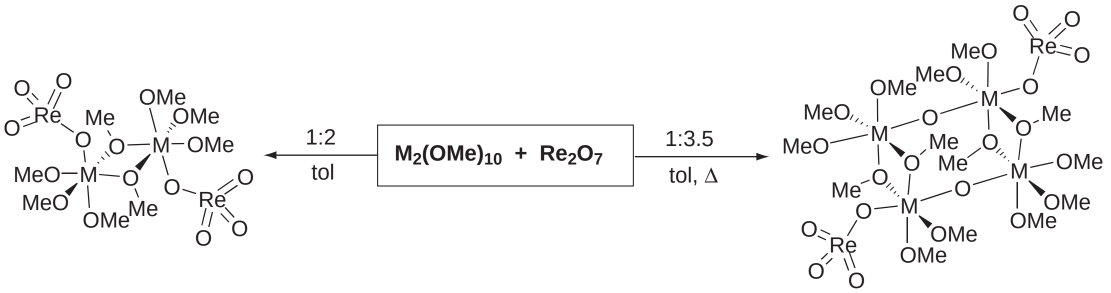
Partial hydrolysis of mixtures of $Mo^{VI}O(OMe)_4$ and $Ta_2(OMe)_{10}$ yielded centrosymmetric $Mo^{VI}{}_2Ta^{V}{}_4O_8(OMe)_{16}$ (**140**).[280] Reflux of the equivalent *iso*-propoxo starting materials led to $Mo^{V}{}_4M^{V}{}_2O_8(OPr^i)_{14}$ which contained two reduced *cis*-$[Mo^{V}{}_2O_2(\mu_2\text{-}O)_2]$ units bridged by two OPr^i ligands.[281] The molecules are capped at each end by $[(Pr^iO)_3M^{V}(\mu_2\text{-}OPr^i)_3]$ groups. Oxidation of the Ta species produced $Mo^{VI}{}_4Ta^{V}{}_4O_{16}(OPr^i)_{12}$ in which the metal atoms sit at the corners of a distorted cube.[280]

Reaction of $M_2(OMe)_{10}$ with $Re^{VII}{}_2O_7$ provided centrosymmetric $[(ReO_4)(MeO)_3M]_2(\mu_2\text{-}OMe)_2$ ((**141**), Scheme 27) whose structure is closely related to those of $M_2(OMe)_{10}$ and $M'_2O_2(OMe)_8$ ($M' = Mo$, W) due to the π bonding capabilities of the $[ReO_4]^-$ ligands.[282,283] Different reaction conditions produced $M^{V}{}_4O_2(OMe)_{14}(ReO_4)_2$ (**142**) whose $M^{V}{}_4(\mu_2\text{-}O)_2(\mu_2\text{-}OMe)_4$ core is derived from two units of (**141**).[283] The thermal decomposition and sublimation properties of these potential precursors of mixed oxides were examined.

Series of soluble bi- and tri-metallic species such as $M'[M(OR)_6]_n$ have been reported from reactions between the metal alkoxides or halides in alcohol solutions (e.g., see 284, 285 and refs. therein; Section 4.5.2.4.4 below). They are of interest as precursors for sol–gel procedures. A number of oxo clusters have been described, apparently products of hydrolysis or oxidation. $Pb^{II}{}_6Nb_4O_4(OEt)_{24}$ features an octahedral cluster $[Pb_6(\mu_3\text{-}O)_4(\mu_3\text{-}OEt)_4]$ whose faces are capped by the bridging ligands. The oxo ligands are also coordinated to $Nb(OEt)_5$ groups.[286]

$Li_2Nb_2O_2(OEt)_8(EtOH)_2$ has a metal–oxygen core similar to that in $Ti_4(OMe)_{16}$, while $[Ba_4Nb_4O_4(OEt)_{20}(EtOH)_4]$ features a $Ba_4(\mu_3\text{-}O)_4$ cubane unit whose O vertices are occupied by the oxo ligands of $[NbO(OEt)_5]$ octahedra.[285]

The cluster $Pb_2Nb_4O_5(OAc)_2(OPr^i)_{12}$ ((**138**), Scheme 26) was generated by thermal decomposition of $PbNb_2(OAc)_2(OPr^i)_{10}$ (**137**) in solution and characterized in solution by NMR.[277]



(141) **(142)**

Scheme 27

4.5.2.4.3 *Peroxo ligands*

Colorless $K_3[Ta(\eta^2\text{-}O_2)_4]$ was crystallized from solutions of Ta_2O_5.aq dissolved in basic H_2O_2.[287] The compound is isostructural with $K_3[Cr(\eta^2\text{-}O_2)_4]$.

γ-Irradiation of single crystals of $K_2[Nb(O_2)F_5]\cdot H_2O$ led to a paramagnetic species that was stable at room temperature.[288] EPR data were consistent with the primary reaction being loss of an electron, rather than reduction to Nb^{IV}. The stable "hole" species is the $[Nb(O_2)F_5]^-$ radical with the unpaired electron delocalized onto the peroxo ligand, i.e., it is formally a superoxo complex $[Nb^V(O_2^-)F_5]^-$.

A range of peroxo-carboxylato complexes $K_3[LM(O_2)_3]\cdot nH_2O$ (LH_2 = tartrate, glycolate, citrate, malate, etc.) have been synthesized and characterized spectroscopically.[289] Similar data is available for $K[L'Nb(O_2)_2(OH)]\cdot 2H_2O$ and $K[L'_2Nb(O_2)_2]\cdot nH_2O$ ($L'H$ = 8-quinolinate).[290]

4.5.2.4.4 *Alkoxo ligands*

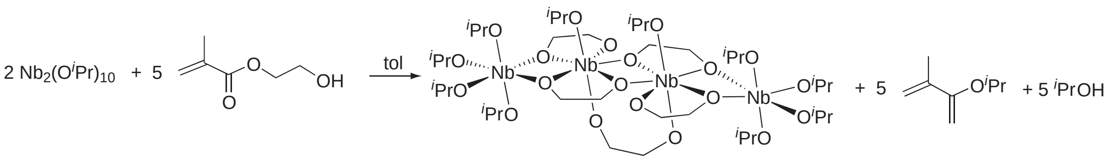
The structure and reactivity of metal alkoxo and aryl oxo compounds, including those of Nb and Ta, have been reviewed in detail.[291] The present account concentrates on more recent synthetic and structural aspects.

The key synthons $M(OR)_5$ are all dimeric in solution when R is primary but usually monomeric when R is secondary or tertiary.[292] A monomer–dimer equilibrium is present for $R = Pr^i$ at lower temperatures. Recent synthetic aspects include improved procedures for anodic dissolution of the metals into alcohols containing electrolytes. For example, binuclear $Ta_2(OR)_{10}$ (R = Me, Et, Bu^n) and $Ta_2O(OPr^i)_8\cdot Pr^iOH$ were isolated (electrolyte, LiCl).[276] The latter molecule features a $Ta_2(\mu_2\text{-}O)(\mu_2\text{-}OPr^i)$ core and may be hydrolyzed to heptanuclear $Ta_7O_9(OPr^i)_{17}$.

Metal–ethoxo cations derived from solutions of $B(C_6F_5)_3$ and $M_2(OEt)_{10}$ were observed in the gas phase by electrospray mass spectrometry.[293] They included $[M(OEt)_4]^+$, $[M_2(OEt)_9]^+$, and $[M_2O(OEt)_7]^+$ as well as heterometallic analogs when both metals were present in the sprayed solutions. Their fragmentation behavior under collision-induced dissociation was examined.

Six-coordinate complexes $Ta(OR)_4L$ and $TaCl_2(OR)_2L$ (LH = 2,2,6,6-tetramethylheptane-3,5-dione or 2,4-pentanedione(acacH)) have been characterized structurally and tested as precursors for the deposition of Ta_2O_5 films.[294,295]

The reaction of $Nb_2(OPr^i)_{10}$ and $CH_2{=}CMeCO(OC_2H_4OH)$ allowed isolation of $Nb_4(OC_2H_4O)_5(OPr^i)_{10}$ ((**143**), Scheme 28) containing two seven- and two six-coordinate niobium atoms.[296] The ethyleneglycolato ligands arise from activation of the methacrylate reactant by the metal.

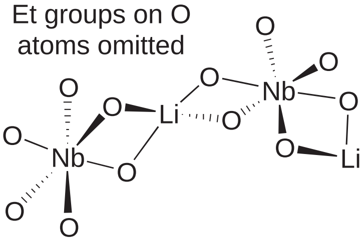


(143)

Scheme 28

Series of soluble bi- and tri-metallic species such as $M'[M(OR)_6]_n$ ($M' =$ Li-Cs, Mg-Ba, Al, Ga, Cr, Mn, Fe, Co, Ni, Cu; $R =$ alkyl) have been described (e.g., see 284,285,297, and refs. therein). They are of interest as precursors in the production of oxide materials by the sol–gel process. However, complex equilibria exist in solution and the exact nature of isolated products often depends upon conditions, especially the presence of trace O_2 or H_2O.[285] Limited structural information only is available.

$LiNb(OEt)_6$ (**144**) features a polymeric helix.[298] Alternating $Nb(OEt)_6$ octahedra are *cis*-linked to four-coordinate Li ions. It produced epitaxial $LiNbO_3$ films upon spray chemical vapor deposition.[299,300] The presence of H atoms β to O allowed production of water via the classic autocatalytic decomposition pathway. This in turn led to production of oxide via hydrolysis.[301] In contrast, although the binuclear analog $[LiNb(OCH_2SiMe_3)_6]_2$ (**145**) pyrolyzed to crystalline $LiNbO_3$, it did not deposit films upon spray deposition, apparently due to the lack of β H atoms.[301]



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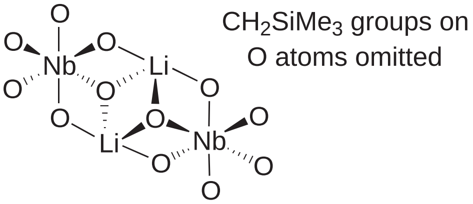
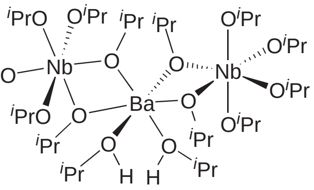


(145)

The anion in the salts $A[Nb(OCH(CF_3)_2)_6]$ ($A =$ Li, Ph_3C) has a single negative charge shared by 36 peripheral fluorine atoms. Consequently, it is weakly coordinating and the Li^+ salt exhibits useful properties as a Lewis acid catalyst.[302] Related salts of $[M(OC_6F_5)_6]^-$ are also available.[303]

Two trinuclear heterobimetallic molecules with alkoxo ligands are known: $BaNb_2(OPr^i)_{12}(Pr^iOH)_2$ (**146**) contains a non-linear $Nb(\mu_2\text{-}O)_2Ba(\mu_2\text{-}O)_2Nb$ core while $LaNb_2(OPr^i)_{13}$ (**147**) contains a non-linear $Nb(\mu_2\text{-}O)_3La(\mu_2\text{-}O)_2Nb$ core.[285]



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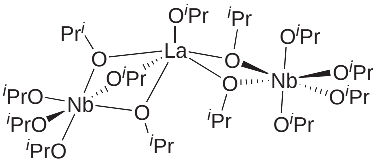

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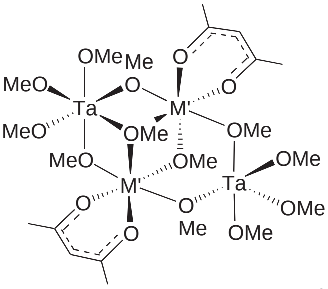


M' = Mg, Co, Ni, Zn

(148)

Bimetallic derivatives resulted from heating $M_2(OMe)_{10}$ and the acac complexes of $M' =$ Mg, Co, Ni, Zn in 1:3 proportions in tol.[304] The structure of centrosymmetric $M_2M'_2(acac)_2(OMe)_{12}$ (**148**) is based upon that of $Ti_4(OMe)_{16}$.

The use of multifunctional ligands allows generation of multinuclear species which may be tested as molecular precursors of mixed metal oxides. For example, $LH_2 =$ salicylaldehyde generated $Bi_2M_2L_4(LH)_4(OR)_4$ and $L'H =$ 1,3-bis(dimethylamino)propan-2-ol generated $SrTa_2(OEt)_6(\mu_2\text{-}OEt)_4(\mu_2\text{-}O\text{-}L')_2$.[305,306]

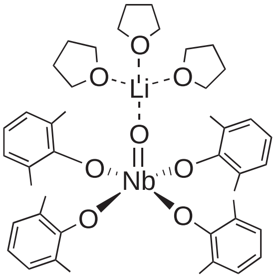
A soluble and volatile tetranuclear species $[La^{III}L_2\{Nb(OPr^i)_4\}_3]$ featured two tetradentate ligands $LH_3 =$ triethanolamine in bicapped trigonal antiprismatic coordination around the La ion.[307] The alkoxo substituents of L bridge the $Nb^V(OPr^i)_4$ fragments forming a cluster with threefold symmetry.

4.5.2.4.5 Aryloxo ligands

(i) Monodentate ligands

These ligands can be tuned both electronically and sterically via ring substitution. Consistently larger MOC bond angles are found in aryloxo relative to alkoxo complexes as ligand oxygen in the former is attached to two π-accepting groups that compete for its electron density. However, simple correlations between MO π bonding and the bond angles and bond distances are not apparent. For example, r(MO) = 1.9 Å is associated with MOC bond angles ranging from 135° to 180°.[308]

An extended range of synthons of stoichiometry $M(OAr)_5$ and $M(OAr)_{5-n}X_n$ (X = halo, alkyl; mono-, or binuclear depending upon ligand bulk) are available as well as six-coordinate complexes $M(OAr)_5L$ (L = neutral donor).[291,309] In addition, the reaction of bulky aryloxides such as LiOAr (ArOH = 2,6-Me_2-C_6H_3OH) with Nb_2Cl_{10} produced both mononuclear $[Li(thf)_3][Nb^V$-O-$(OAr)_4]$ (**149**) and binuclear $[Li(thf)_2]_2\{[Nb^{IV}(OAr)_2Cl_2]_2(\mu_2\text{-}Cl)_2\}$ (**150**) species.[310]



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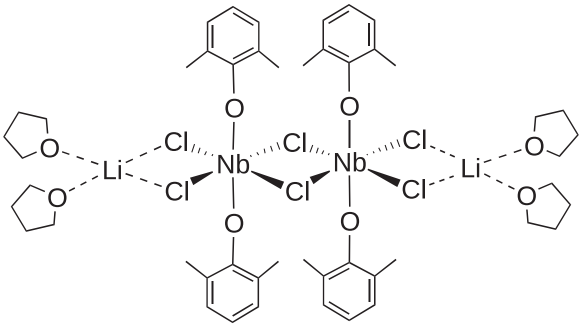
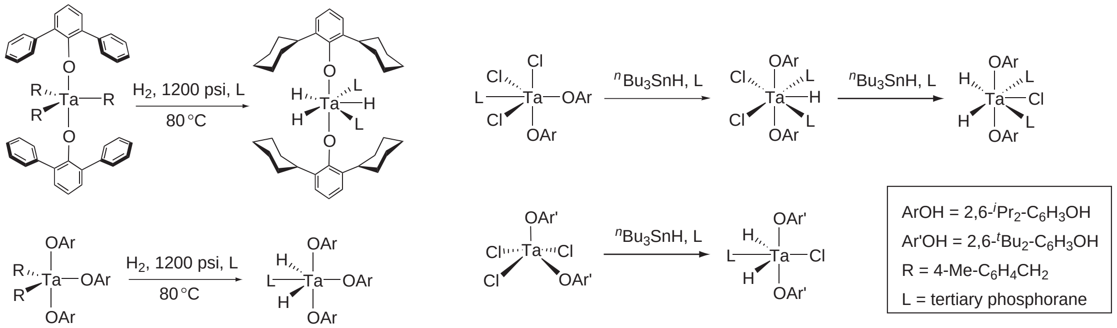


(150)

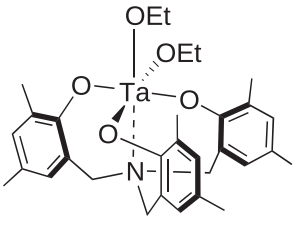
A significant development has seen the synthesis of aryloxo hydrido complexes and their application in homogeneous arene hydrogenation and related processes.[311,312] For Ta, these were formed by hydrogenolysis or reaction with Bu_3SnH in the presence of phosphorane ligands. The observed stoichiometry and the stereochemistry depend upon the steric properties of the aryloxo ligands (Scheme 29). These molecules are rigid on the ^1H NMR time scale.[313] Reduced species result from the equivalent reactions employing niobium. Complexes $Cp^*Ta(H)_2(OAr)_2$ result from the reaction of bulky ArOH with $Cp^*Ta(H)_2(PMe_3)(\eta^2\text{-}CH_2PMe_3)$.[314]



Scheme 29

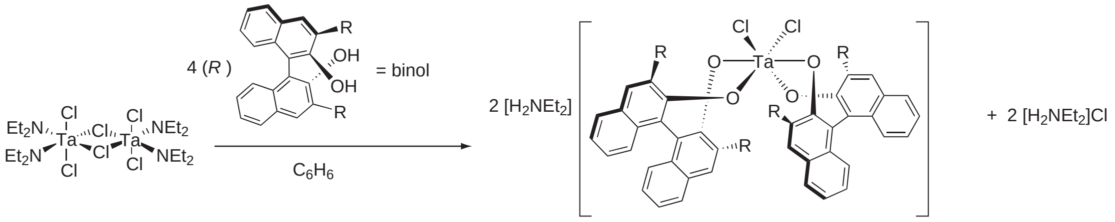
(ii) Multidentate ligands

The neutral mononuclear complexes *cis*-$TaLX_2$ ((**151**); X = OEt, NMe_2) result from reaction of Ta_2X_{10} with a *tris*(phenol)amine ligand LH_3.[315] The X ligands exhibit significant differences in substitutional lability attributed to the stronger *trans* effect induced by the phenolato functions of ligand L relative to the amino function.



(151)

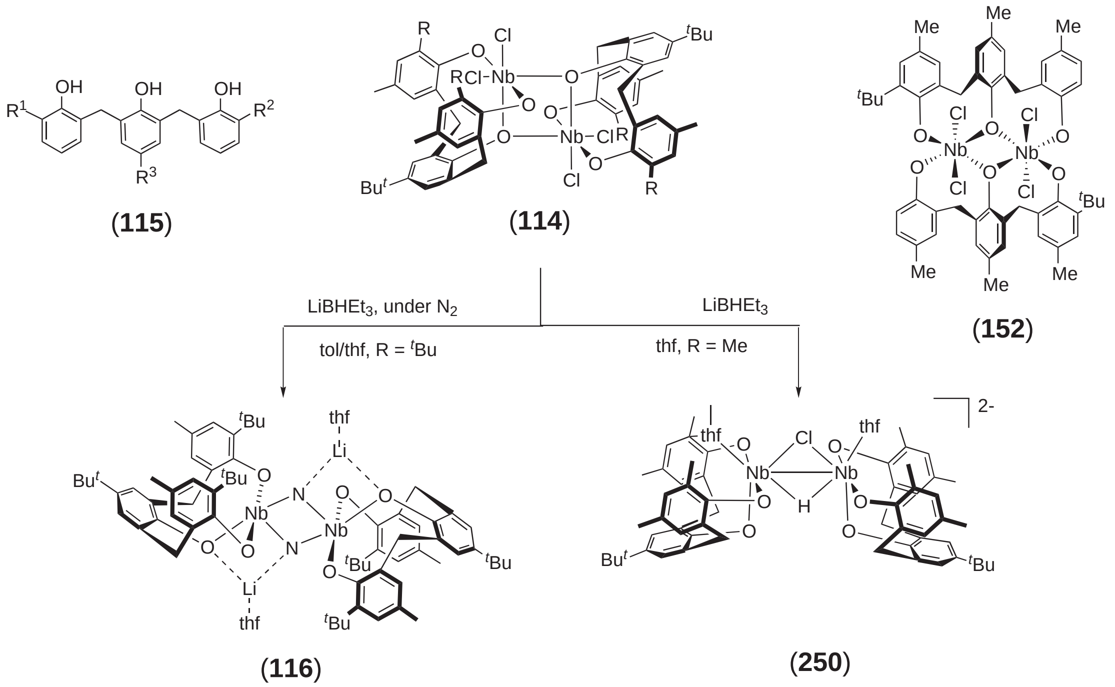
Derivatives of the chiral ligand binol have been introduced successfully to Ta chemistry by use of an amido precursor (Scheme 30).[316]



Scheme 30

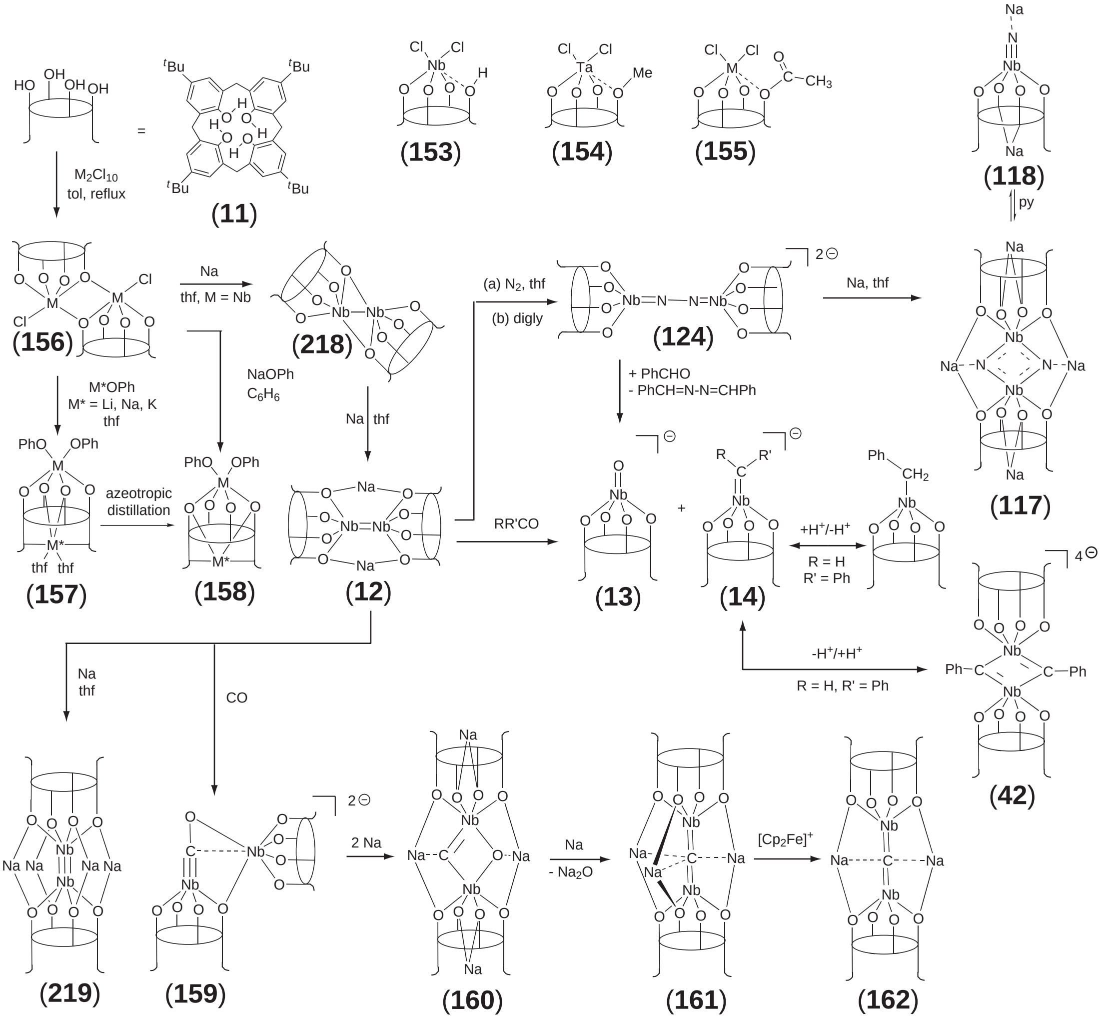
Reaction of Nb_2Cl_{10} with Li_2L ($LH_2 = 2,2'$-methylenebis(4,6-di-*t*-butyl-phenol) produced trigonal bipyramidal NbL_2Cl.[317] Each bidentate ligand provided one equatorial and one axial aryloxo ligand atom. On the other hand, reaction of Ta_2Cl_{10} or $Ta(NMe_2)_5$ with Li_2L' ($L'H_2 = 2,2'$-methylenebis(4-methyl-6-*t*-butylphenol)) provided $TaL'X_3$ ($X = Cl$, NMe_2).[318]

The products observed in the reaction of Nb_2Cl_{10} with linear aryloxo trimer ligands LH_3 ((**115**), Scheme 31) depend upon the nature of the aryl ring substituents and the solvent basicity.[319] For example, when $R = Bu^t$, the retro-Friedel–Crafts reaction can lead to loss of Bu^t substituent induced by HCl unless lithiated forms of the ligand are employed or basic MeCN is used as solvent. Complexes characterized in both the solid state and in solution included mononuclear species with a bidentate ligand, *mer*-$Nb(LH)Cl_3(MeCN)$ and *cis*-$Nb(LH)_2Cl(MeCN)$. A tridentate ligand was present in trigonal bipyramidal $NbL(SBu^t)_2$. Binuclear species $[NbLCl_2]_2$ featured different isomers. One was centrosymmetric with a planar $Nb_2(\mu\text{-}O)_2$ core and each tridentate ligand L bound *mer* to a single Nb center (**114**). One O ligand atom bridged to the second Nb center. A second isomer featured a *pseudo*-C_2 axis of symmetry with each ligand L spanning both Nb centers (**152**).



Scheme 31

The cavities of calixarenes can enclose small molecules ((**11**), Scheme 32). Electron-deficient fragments CpM^V were bound to calixarene ligands with the aim to produce cavities with enhanced nucleophile binding capabilities.[320] CpTaL for $LH_4 = p$-Bu^t-calix[4]arene (**11**) exhibited an eliptical distortion of the ligand fourfold symmetry, allowing an unusual sideways positioning of toluene in the *endo*-calix site. When a MeCN molecule was included in the cavity of CpTaL, it was bound via a Ta—N bond, an orientation inverted relative to that observed in a related calixarene in the absence of metal.



Scheme 32

Floriani has explored the way in which the calixarene skeleton can impose a quasi-planar O_4 donor set which allows the metal centers to provide (σ, 2π) frontier orbitals for M—X multiple bonding. Tuning the ligand charge via methylation of the ligating oxygen atoms was an additional design feature. Useful starting materials (**153**)–(**155**) (Scheme 32) were generated by reaction of M_2Cl_{10} with (**11**) or its derivatives. The di-methoxy form provided the demethylated product (**154**).[321] The reactivity of the ligand alkyl derivatives of the Ta systems was explored.[322,323]

Binuclear complexes (**156**) (Scheme 32) could be converted to mononuclear species (**157**) by interaction with alkali metal phenoxides.[321,324] The negatively charged calixarene ligand promoted binding of alkali metal cations M* in its cavity. Two calixarene and two thf oxygen atoms provided four ligand atoms for M* whose coordination environment was completed by cation–π–arene interactions. The nature of the latter varied with the size of M*, being bis-η^6 for K^+, η^6 for Na^+, and η^3 for Li^+. Non-interacting arene rings were pushed outwards to accommodate the coordination spheres of M*. Azeotropic distillation in hexane allowed removal of the thf ligands for M* = Na (**158**). These complexes acted as alkali metal ion carriers in hydrocarbon media.

Ketones and aldehydes RR′CO oxidatively added across the $Nb^{III}{=}Nb^{III}$ bond in (**12**) (Scheme 32) to form equimolar quantities of the oxo- and alkylidene-Nb^V species ((**13**),(**14**)) which were easily separated.[36] Dinitrogen inserted into the $Nb^{III}{=}Nb^{III}$ of (**12**) as the $4e^-$reduced hydrazido ligand (**124**).[198,199] Further reaction with PhCHO gave the oxo derivative (**13**) and the expected azine PhCH=N-N=HCPh. Reduction of (**124**) with Na cleaved the NN bond with formation of the $Nb^{V}_2(\mu_2\text{-}N)_2$ nitrido complex (**117**).[198,199]

(**12**) also reduced CO (1 atmos; −40 °C) by four electrons to form the oxyalkylidyne dianion (**159**) (Scheme 32).[325] Reduction of (**159**) with 2 eq Na cleaved the residual C—O bond to form (**160**) which contains μ_2-oxo and μ_2-carbido bridging ligands stabilized by interactions with sodium ions. Further reduction of (**160**) removed the oxo function and converted the unique bent mode of the bridging carbido ligand to the linear mode in (**161**). This species was paramagnetic and its spectroscopic properties were consistent with a $Nb^{V}=C=Nb^{IV}$ center with a delocalized unpaired electron. (**161**) was oxidized to (**162**) which contained an $Nb^{V}=C=Nb^{V}$ center.

4.5.2.4.6 Carboxylato and related ligands

Mononuclear dialkylcarbamato complexes $M(O_2CNR_2)_n$ ($n = 4, 5$) are eight coordinate, as demonstrated for $Nb^{IV}(O_2CNEt_2)_4$ and $Ta^{V}(O_2CNEt_2)_5$.[326] The niobium compound is dodecahedral with four bidentate ligands while the tantalum example is essentially square antiprismatic with three bi- and two monodentate ligands (as seen previously in $Nb^{V}(O_2CNMe_2)_5$[327]).

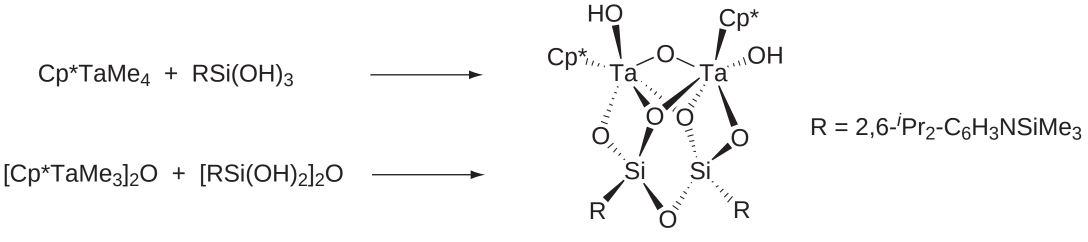
Reaction of $M_2(OEt)_{10}$ with $LH_3 =$ *N*-hydroxyiminodiacetic acid allowed isolation of salts of $[ML_2]^-$, isostructural with the V^{V} system.[328] The anion is eight coordinate with each ligand providing a η^2-NO group and two monodentate carboxylates. The anions are related to the V^{IV} centers present in the natural product amavadin isolated from mushrooms of the genus *Amanita*.

4.5.2.4.7 Oxyanion complexes

Oxidation of M(s) by the peroxide $S_2O_6F_2$ in HSO_3F formed acid solutions apparently containing $[H_2SO_3F]^+$ and $[M(SO_3F)_6]^-$ ions.[329] Supporting evidence included isolation of complexes $Cs_n[M(SO_3F)_{5+n}]$ ($n = 1, 2$).

Reaction of Nb_2Cl_{10} with $AgOTeF_5$ in 1,1,2-trichloritrifluorethane produced $AgNb(OTeF_5)_6$ which is soluble in chlorinated hydrocarbons and chorofluorocarbons.[330] The anion $[Nb(OTeF_5)_6]^-$ is useful as a weakly coordinating anion.

A tantalum–siloxane cage complex (**163**) has been synthesized by two routes and characterized structurally (Scheme 33).[331] A tetranuclear Ta_2Si_2 unit is the basis of a distorted bicapped cubane core $[Ta_2Si_2(\mu_3\text{-}O)_2(\mu_2\text{-}O)_4]^{6+}$.[331] Other cyclic Nb— and Ta— siloxanes based on $Bu^t_2Si(OH)_2$ have been prepared.[332]



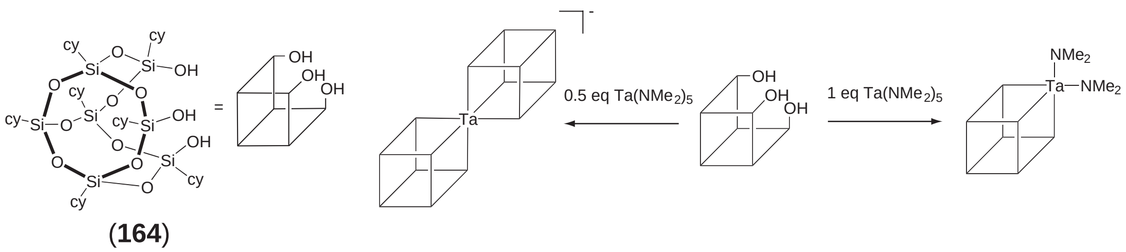
(163)

Scheme 33

Tantalasilsequioxanes based upon $LH_3 = cy_7Si_7O_{12}H_3$ ((**164**), Scheme 34) have been synthesized as structural models of silica-bound heterogeneous catalysts.[333] Compounds $LTa(NMe_2)_2$ and $[H_2NMe_2][TaL_2]$ were synthesized from $Ta(NMe_2)_5$ (Scheme 34).

4.5.2.5 Sulfur, Selenium, and Tellurium Donor Ligands

A number of useful reviews on chalcogenido species (E^{2-}, HE^-, RE^-) as ligands are available.[334–338] The versatility of these ligands may be appreciated from the observation of S^{2-} as a terminal



Scheme 34

or bridging ligand (μ_2, μ_3, μ_4, μ_6), S_2^{2-} as a terminal or bridging ligand (μ_2), and higher sulfides S_n^{2-} as bidentate or bridging ligands (μ_2, μ_3).

4.5.2.5.1 Chalcogenido ligands

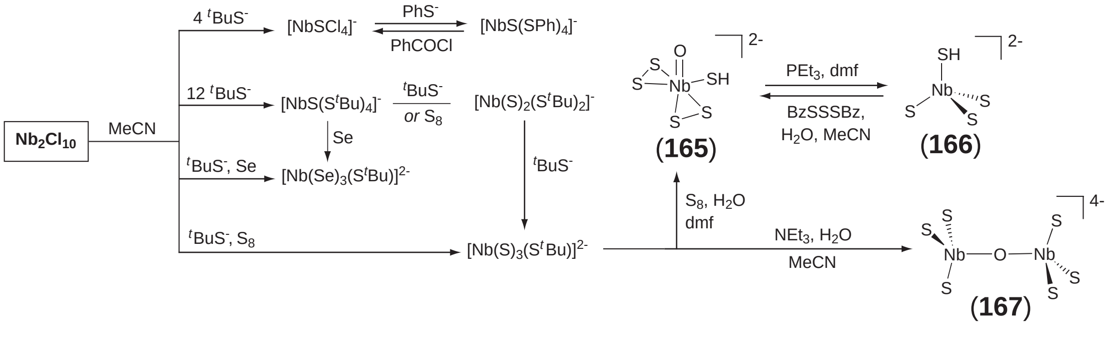
K^+ and Cs^+ salts of tetrathiometalates $[MS_4]^{3-}$ and tetraselenometalates $[MSe_4]^{3-}$ were formed by direct reaction of the elements at 850 °C.[339] Although these have some solubility in nonaqueous solvents, the more soluble salts $Li_3[MS_4]$solv (solv = 4 MeCN, 2 tmeda) were accessible in the system $M_2(OEt)_{10}/(Me_3Si)_2S/LiOMe$ (1:8:6) in MeCN.[340] These materials are useful precursors of metal cluster species (see Chapter 4.12).

The thiohalides MSX_3 (X = Cl, Br) were obtained by reaction of suspended M_2X_{10} and H_2S(g) in CCl_4 or $(Me_3Si)_2S$ in CH_2Cl_2.[341,342] When carried out in MeCN, the chloro systems provided the solvent adducts $MSCl_3{\cdot}2MeCN$.[341]

Treatment of $[N_3N]TaCl_2$ (**15**) with 2 eq $(thf)_2LiESi(SiMe_3)_3$ (E = Se, Te) eliminated neutral $E\{Si(SiMe_3)_3\}_2$ with formation of five-coordinate $[N_3N]Ta(=E)$ (Scheme 15).[343] The Ta=E bond lengths of 2.33 (Se) Å and 2.57 (Te) Å are consistent with the estimated difference in radii of E. Single resonances were observed in $^{77}Se\{^1H\}$ and $^{125}Te\{^1H\}$ NMR spectra in C_6D_6.

$Ph_4P[NbCl_6]$ reacted with $(Me_3Si)_2S$ in CH_2Cl_2 to produce $(Ph_4P)_2[NbSCl_5].2CH_2Cl_2$ while the equivalent bromo system led to $Ph_4P[NbSBr_4]$.[342] $(Ph_4P)_2[TaSCl_5].2CH_2Cl_2$ resulted from reaction of $TaSCl_3$ and Ph_4PCl in CH_2Cl_2. The salt $[Nb(S_2CNEt_2)_4]_2[NbSCl_5]$ has been characterized crystallographically.[205]

Although the reaction occurs rarely for arenethiolates, the alkylthiolate ion RS^- is a convenient source of thio ligand via metal-induced C—S bond cleavage. With Nb_2Cl_{10}:Bu^tS^- = 1:4 in MeCN, the $[NbSCl_4]^-$ anion formed and was readily converted to square pyramidal $[NbS(SPh)_4]^-$ (Scheme 35).[344] With increasing proportions of Bu^tS^-, trigonal bipyramidal $[NbS(SBu^t)_4]^-$ and then tetrahedral $[Nb(S)_2(SBu^t)_2]^-$ were obtained.[345] If elemental sulfur or selenium was included, tetrahedral $[Nb(E)_3(SBu^t)]^{2-}$ (E = S, Se) resulted (Scheme 35).[346] $[Ta(S)_3(SBu^t)]^{2-}$ was isolated from the equivalent route. These C—S bond cleavage reactions appear to involve generation of isobutene (via heterolytic β-elimination) or isobutane (via homolytic free radical formation and extraction of proton from solvent MeCN or trace H_2O).[346]

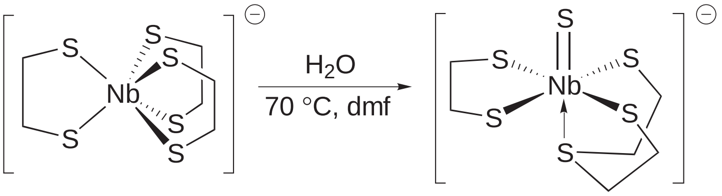


Scheme 35

$[Nb(S)_3(SBu^t)]^{2-}$ reacted with S_8 and stoichiometric H_2O in dmf to form pentagonal pyramidal $[NbO(\eta^2\text{-}S_2)_2(SH)]^{2-}$ (**165**) which was converted to tetrahedral $[Nb(S)_3(SH)]^{2-}$ by PEt_3 ((**166**); Scheme 35).[347] The thio donor BzSSSBz (Bz = benzyl, CH_2Ph) in wet MeCN reversed the latter reaction. ^1H resonances for the SH ligands were detected for both anions. In the presence of controlled concentrations of NEt_3 and H_2O in MeCN, $[Nb(S)_3(SBu^t)]^{2-}$ was converted to binuclear $\{[(S)_3Nb]_2(\mu_2\text{-}O)\}^{4-}$ (**167**) with a linear Nb–O–Nb bridge. In equivalent reactions, $[Nb(Se)_3(SBu^t)]^{2-}$ was the source of binuclear $\{[(Se)_3Nb]_2(\mu_2\text{-}O)\}^{4-}$ and pentagonal pyramidal $[NbO(\eta^2\text{-}Se_2)_2(SeH)]^{2-}$.[348] When oxidized by 2 eq Se, two units of the latter center became linked by an $Se_4{}^{2-}$ bridge in $\{[NbO(\eta^2\text{-}Se_2)_2]_2(\mu_2\text{-}Se_4)\}^{4-}$. $[NbO(\eta^2\text{-}S_2)_2(SPh)]^{2-}$ (isostructural with (**165**)) resulted from the interaction of $[NbO(SPh)_4]^-$ with S_8 under controlled conditions.[349] Unexpectedly, it reacted with $NaBH_4$ to produce the thio derivative $[NbS(\eta^2\text{-}S_2)_2(SPh)]^{2-}$.

The Nb=S bond distances in $[Nb(S)_2(SBu^t)_2]^-$, $[Nb(S)_3(SBu^t)]^{2-}$, and $[NbS_4]^{3-}$ show an essentially monotonic increase (2.187(2) < 2.230(6) < 2.274(1) Å), reflecting an increase in both anionic charge and the number of thio ligands.[346] The bond length of the Nb^V=S group in known systems varies within the range 2.09–2.28 Å, depending on its electronic environment.[346,350]

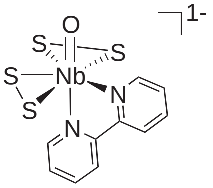
$[Nb(SCH_2CH_2S)_3]^-$ ((**168**), Scheme 36) underwent an unusual isomerization in the presence of trace water or MeOH.[351] Proton attack upon ligand thiolate appeared to induce C—S bond cleavage and subsequent rearrangement to (**169**).



(168) **(169)**

Scheme 36

In the reaction of $[NbO(SPh)_4]^-$ with S_8 in the presence of bpy in toluene, reduction of S_8 by ligand thiolate led to $[NbO(\eta^2\text{-}S_2)_2(bipy)]^-$ (**170**) with distorted pentagonal bipyramidal geometry.[352] The nucleophiles CS_2 and dimethyl ethynedicarboxylate added across one η^2-dithio ligand to produce anions containing, respectively, the ligands thiocarbonato $[NbO(CS_3)(S_2)(bpy)]^-$ and enedithiolato $[NbO\{S_2C_2(CO_2Me)_2\}(S_2)(bpy)]^-$.



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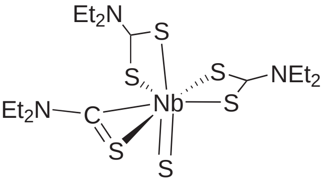

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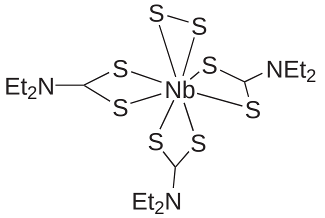

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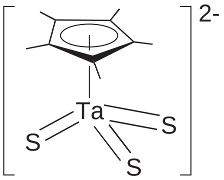


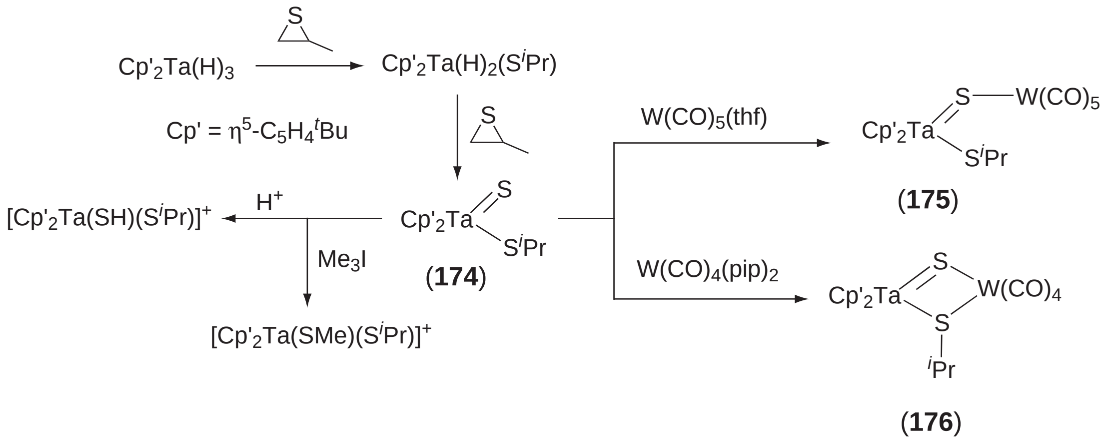
(173)

The reaction of NaL ($L = S_2CNEt_2$) with $M^{III}{}_2Cl_6(SC_4H_8)_3$ provided the pentagonal bipyramidal complexes $L_2M^VS(\eta^2\text{-}SCNEt_2)$ (**171**).[353] The thio and thiocarbamyl ligands appear to be generated by oxidative addition of a dithiocarbamato C—S bond to an M^{III} center with concomitant cleavage of the M=M bond in the precursor.

The eight-coordinate dithio derivative $L_3Nb(\eta^2\text{-}S_2)$ (**172**) was one of the products of the reaction of L_3NbO with B_2S_3 in CH_2Cl_2.[354] Similarly, $L_3Ta(\eta^2\text{-}S_2)$ was isolated in the reactions of NaL with $TaSBr_3$ in CS_2 and with Ta_2Cl_{10} in MeCN.[355,356]

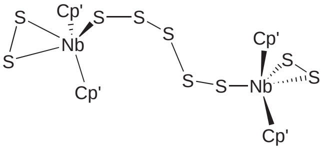
Reaction of Cp^*TaCl_4 with 4–5 eq of "Li_2S_2" or "Li_2S" produced $[Cp^*TaS_3Li_2(thf)_2]_2$ whose hexagonal prismatic $Ta_2S_6Li_4$ core contained the $[Cp^*Ta(S)_3]^{2-}$ unit (**173**), isostructural with $Cp^*Re(O)_3$.[357,358] This species is also formed if $Cp^*TaS(SCPh_3)Cl$ is treated with "Li_2S".[359]

The reaction of the trihydrido complex Cp'_2TaH_3 ($Cp' = C_5H_4Bu^t$) with propylene sulfide proceeded via a regioselective ring opening followed by desulfurization to yield the thio–thiolato complex $Cp'_2Ta(S)(SPr^i)$ ((**174**); Scheme 37).[360] Protonation and alkylation reactions occured at the thio ligand (Scheme 37), while the unsaturated fragments $W(CO)_5$ and $W(CO)_4$ bound at the thio and thio/thiolato sites, respectively ((**175**), (**176**)). Complexes $Cp'_2Ta(H)(S\text{-}M(CO)_5)$ ($M = Cr$, Mo, W) related to (**175**) are also known.[361]

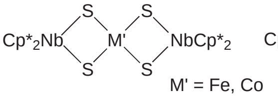


Scheme 37

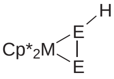
Reaction of $CpNb(\eta^7\text{-}C_7H_7)$ with $MeCS_2H$ in Et_2O led to $CpNb(\eta^2\text{-}S_2)(\eta^2\text{-}S_2CMe)_2$.[362] The S_2 ligand apparently arose from acid- and metal-induced C—S bond cleavage. In contrast, reduction of S_8 with Cp'_2NbH_3 in tol led directly to $\eta^2\text{-}S_2$ ligands and a polythio S_5^{2-} bridge in $Cp'_4Nb_2S_9$ (**177**).[363] A number of intermediates were observed and identified in subsequent work employing a range of cyclopentadienyl ligands. Reaction of $Cp^*_2NbBH_4$ with S_8 gave a complex with a planar NbS_3 core whose structural and spectroscopic properties supported the formulation $Cp^*_2Nb(\eta^2\text{-}S_2)$-(SH) (S-S = 2.17(1) Å).[364] The equivalent compound for $Cp^\dagger = C_5Me_4Et$ could be isolated as well as the structural isomers $Cp^\dagger_2Nb(\eta^2\text{-}S_2)H$ and $Cp^\dagger_2Nb(S)(SH)$ (Scheme 38).[365] Similar chemistry was found for Ta (Scheme 39).[364] The monohydride $Cp'_2Ta(S)H$ reacted with Na/Hg in thf in the presence of H_2O to produce the dihydride $Cp'_2Ta(SH)(H)_2$.[366] For both metals, these mononuclear complexes reacted further to produce clusters discussed in Chapter 4.12.[367] In addition, reactions between Me substituents on the Cp* ring and the metals and sulfur fragments were observed.[368,369]



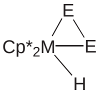
(**177**)



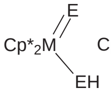
(**178**)



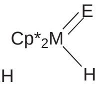
(**179**)



(**180**)

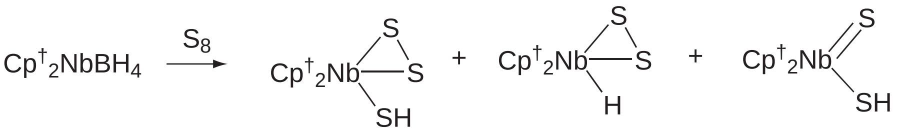


(**181**)



(**182**)

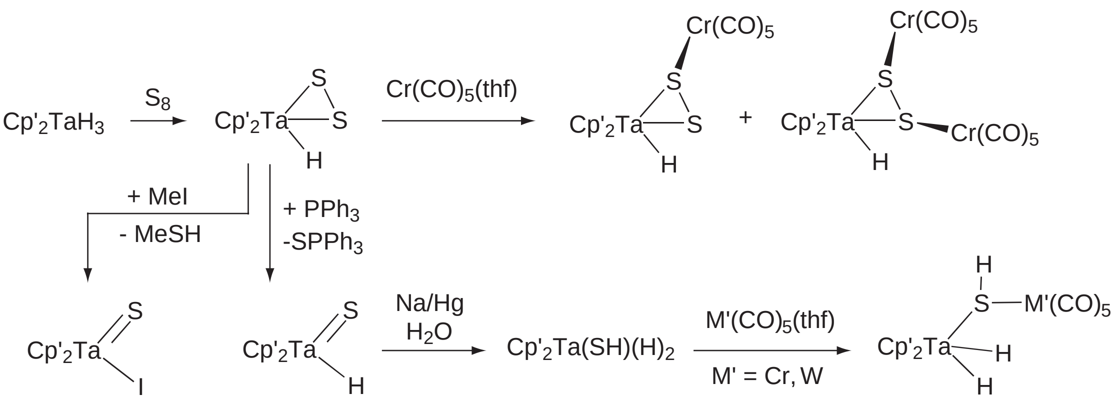
E = S, Se, Te



Scheme 38

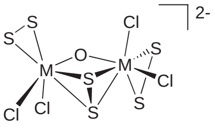
Mononuclear complexes $Cp^\dagger_2Nb(\eta^2\text{-}S_2)H$, $Cp'_2Ta(\eta^2\text{-}S_2)H$, and $Cp'_2Ta(SH)(H)_2$ added $M'(CO)_5$ ($M' = Cr$, Mo, W) fragments to their $\eta^2\text{-}S_2$ or SH ligands producing bi- and trinuclear species (e.g., Scheme 39).[366,370] In addition, $Cp^*_2Nb(\eta^2\text{-}S_2)H$ reacted with $Fe_2(CO)_9$ and $Co_2(CO)_8$ to produce trinuclear complexes with an $M'S_4$ tetrahedron ($M' = Fe$, Co) bound to two niobocene molecules (**178**).[371]

Chemistry related to that outlined in Schemes 38 and 39 led to equivalent species with selenium and tellurium replacing sulfur.[372–375] In addition, a selection of the molecular variants (**179**)–(**182**) have been characterized.



Scheme 39

Salts $[Ph_4P]_2\{[Cl_2(\eta^2\text{-}S_2)M]_2(\mu_2\text{-}O)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}S_2)\}$ (**183**) were produced by reacting Nb_2Cl_{10} with Li_2S_2 and by heating Ta_2Cl_{10} with Li_2S and S_8 in MeCN.[376]



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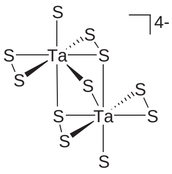

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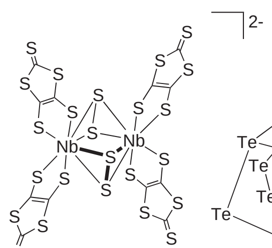

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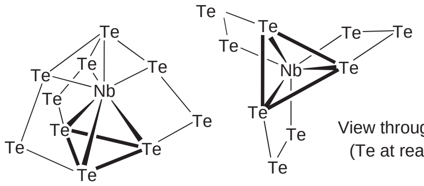


View through Te_3 ring (Te at rear omitted)

(186)

The ionic compound $[Ta(Se_2)_2]_2[TaBr_6]$ was prepared in high yield from the elements by stoichiometric reaction at 450 °C.[377] The positively charged polymeric component (formally $[Ta^{V}Ta^{IV}]$) is constructed from chains of $Ta(\mu_2\text{-}\eta^2\text{-}Se_2)_2Ta$ units. The ionic lattice is completed by $[Ta^{V}Br_6]^-$ anions.

$K_4Ta_2S_{11}$ was produced by interaction of K_2S, Ta, and S_8 at 800 °C. It contains the $\{[TaS(\eta^2\text{-}S_2)]_2(\mu_2\text{-}S)(\mu_2\text{-}\eta^2{:}\eta^1\text{-}S_2)_2\}^{4-}$ ion (**184**).[378] Bridging S_2 ligands are also seen in $[Bu_4N]_2\{[(C_3S_5)_2Nb]_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}S_2)_2\}$ (**185**), formed from the reaction of Nb_2Cl_{10} and $[Bu_4N]_2[Zn(C_3S_5)_2]$ in MeCN.[379]

The reaction of Nb_2Cl_{10} and K_2Te_4 in dmf followed by the addition of Ph_4PBr led to $[Ph_4P]_3[NbTe_{10}]$, a novel Zintl compound (**186**).[380] The anion features *pseudo*-C_3 point symmetry with distorted capped trigonal prismatic stereochemistry around the Nb atom. The compound is diamagnetic and its electronic structure was explored via Extended Huckel calculations.[381]

4.5.2.5.2 Thiolato ligands

Reaction of Ta_2Cl_{10} with LiSAr (ArSH = 2,3,5,6-Me_4-C_6HSH) or reaction of $Nb(NMe_2)_5$ with ArSH = 2,6-Me_2-C_6H_3SH led to $M(SAr)_5$.[382,383] While the MS_5 geometries were nominally trigonal bipyramidal, steric crowding induced substantial axial and equatorial distortions with bond angles $S_{ax}\text{–}M\text{–}S_{ax} \sim 156°$ and $105 < S_{eq}\text{–}M\text{–}S_{eq} < 130°$. Such distortions were not apparent in $Ta(SAr)_4(NMe_2)$, formed in the reaction of $Ta(NMe_2)_5$ with ArSH = 2,6-Me_2-C_6H_3SH.[384] The complex exhibits molecular C_2 symmetry with the ligand NMe_2 occupying an equatorial site.

Reaction of $Nb_2Cl_{10}$with NaSAr (ArSH = 4-Me-C_6H_4SH) in thf led to $[Na(thf)_3][Nb(SAr)_6]$ which features a nearly trigonal prismatic $[Nb(SAr)_6]^-$ unit, apparently stabilized against spontaneous reduction by significant interactions of the $Na(thf)_3{}^+$ cation with ArS^- ligands.[385] Reaction of $Ta_2Cl_{10}$with NaSPh and 15-crown-5 in Et_2O led to [Na(15-crown-5)][$Ta(SPh)_6$] which features an octahedral anion. The favored stereochemistry apparently depends on detailed electronic and crystal packing forces.[386]

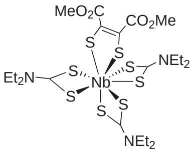
Cp*Ta(SPh)$_4$ was isolated from the reaction of Cp*TaCl$_4$ with NaSPh at −78 °C.[387] The molecule has a distorted four-legged piano-stool structure with two different sets of Cp*—Ta—S bond angles averaging 104.1° and 117.2°, respectively. These seem to be determined largely by electronic factors with a less important S···S repulsion effect.

Dimethyl ethynedicarboxylate added across the η^2-dithio ligand of Nb(S$_2$)L$_3$ (L = S$_2$CNEt$_2$) to create the mono(enedithiolato) complex Nb{S$_2$C$_2$(CO$_2$Me)$_2$}L$_3$ (**187**).[388]

Homoleptic tris-dithiolato complexes $[\mathrm{M^VL_3}]^-$ are formed typically by reaction of M_2X_{10} with Li$_2$L or of amides M(NR$_2$)$_5$ with H$_2$L.[386,389–391] Again, the tendency to the extremes of octahedral and trigonal trismatic geometries (related by a trigonal twist deformation) are determined by a complex mixture of electronic and crystal packing factors. The enedithiolato anions exhibit geometries closest to trigonal prismatic: ligand torsion angles ϕ average 0.7° for [Ph$_4$As][Nb(1,2-S$_2$C$_6$H$_4$)$_3$]. However, they are 30° and 43° for [Ph$_4$As][Nb(SCH$_2$CH$_2$S)$_3$] and [Ph$_4$As][Nb(SCH$_2$CH$_2$CH$_2$S)$_3$], respectively, which feature saturated ligands. The structural complexity is highlighted by the case of A[ML$_3$] (L = norbornane-*exo*-2,3-dithiolato).[386] The geometry observed is *synclastic* for (A$^+$ = Ph$_4$As, M = Ta; larger cation) and *anticlastic* for (A = Et$_4$N, M=Nb; smaller cation) ((**188**), (**189**)) although solution data indicate similar relative stabilities for these isomers. In addition, the TaS$_6$ core in (**188**) is trigonally twisted while the NbS$_6$ core in (**189**) is distorted towards a bicapped tetrahedron.

Reaction of Nb$_2$(OEt)$_{10}$ with LH$_2$ = 2-mercapto-4-methylphenol and Et$_3$N led to [Et$_3$NH][NbL$_3$].[392] Significant distortion (twist angle 41.5°) away from the trigonal prism was observed for this mixed O,S-arene donor ligand complex, in contrast with [Ph$_4$As][Nb-(1,2-S$_2$C$_6$H$_4$)$_3$] discussed above.

The chloro ligands in Cp*MCl$_4$ may be substituted by bidentate enedithiolato ligands L.[393,394] The presence in solution of orientationally inequivalent ligands L in Cp*ML$_2$ (**190**) was detected, the ligand folding being attributed to alkene-to-metal bonding interactions. The lack of such interactions accounts for the observation of a single coformer in solution for the dithiolato complex Cp*Ta(SCH$_2$CH$_2$S)$_2$ (**191**).[393] A single rigid geometry is also observed for the norbornane-*exo*-2,3-dithiolato complex with the dithiolato ligands assuming opposite orientations with respect to Cp* (**192**).[395] Related tridentate species (e.g., (**193**)) have been isolated.[396]



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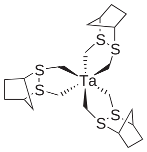

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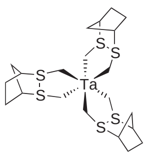

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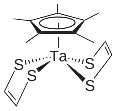

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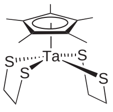

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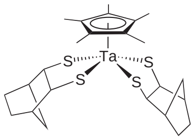

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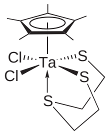

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4.5.2.5.3 *Thiocarbamato and related ligands*

Reaction of M_2X_{10} (X = Cl, Br) with NaL (L = *N*,*N*′-disubstituted dithiocarbamate) is complicated by side reactions and solvent dependency. In CH$_2$Cl$_2$, the two product salts [ML$_4$][MX$_6$] and [ML$_4$]X have similar solubilities.[397] A selection of both forms was isolated, as were the monothiocarbamato salts [M(OSCNMe$_2$)$_4$][MCl$_6$] which formed cleanly at −78 °C. Variable-temperature ^{1}H NMR was employed in a detailed study of the stereoisomerism and metal-centered rearrangements of the eight-coordinate $[\mathrm{ML_4}]^+$ ions.[397] The *mmmm* dodecahedral arrangement is present in [Nb(S$_2$CNEt$_2$)$_4$]Br.[356]

Use of the reagent SiMe$_3$L (L = S$_2$CNEt$_2$) with Nb$_2$Cl$_{10}$ in CH$_2$Cl$_2$ at 0 °C allowed separation of [NbL$_4$][NbCl$_6$] from its coordination isomer NbCl$_3$L$_2$.[398] The latter is pentagonal bipyramidal with one chloro and two L ligands in the equatorial plane. The same compound resulted from oxidative addition of tetraethyldithiuram disulfide to $\mathrm{Nb^{III}{}_2Cl_6(SMe_2)_3}$ with cleavage of the Nb=Nb bond.[399] A similar stereochemistry was present in solution in *trans*-Nb(OR)$_2$ClL$_2$ complexes obtained from the reaction of [NbCl$_3$(OR)$_2$]$_2$ with NaL.[400]

Cp*$_2$NbO(OH) reacted with PhNCS to form Cp*$_2$NbO{SC(O)NHPh} which features oxo and η^1-S-thiocarbamato ligands.[401]

4.5.2.6 Halo Ligands

A comprehensive review of the molecular structure of metal halides included sections on the tetrahalides and pentahalides of Nb and Ta.[402]

4.5.2.6.1 Fluoro ligands

TaF_5 and TaF_xCl_{5-x} have been identified in the gas phase by mass spectrometric detection of their primary ions.[220] The crystal structure of the salt $[Ph_3PMe][TaF_6]$ has been reported.[403] The gas-phase molecular structure, vibrational frequencies, and vertical electron detachment energy for $[TaF_6]^-$ were examined theoretically at HF, MP2, and DFT levels of theory.[404]

There has been an increasing interest in the chemistry of Nb and Ta in molten salts in the context of electrodeposition of these expensive metals. The salts $K_2[MF_7]$ are important precursors in the commercial manufacture of high-purity Nb and Ta, being employed as low-melting electrolytes. The anions are heptacoordinate with a capped trigonal prismatic stereochemistry.[405] $K_2[NbF_7]$ was studied by solid state ^{93}Nb and ^{17}F NMR, leading to chemical shielding and electric field gradient tensors and to the nuclear quadrupole coupling constant for ^{93}Nb.[406] An irreversible phase transition was observed at about 160 °C. Thermal vibrational amplitudes for $K_2[MF_7]$ have been defined and rationalized,[407] and luminescence properties reported.[405]

Vibrational spectroscopy of Ta^V in molten and solidified LiF-NaF-KF melts has confirmed the presence of the $[TaF_7]^{2-}$ ion and excluded the presence of $[TaF_8]^{3-}$.[228,229,408,409]

The spontaneous reduction of Nb^V in CsCl-KCl-NaCl-$K_2[NbF_7]$ melts at 973–1,073 K led to a decrease in the F:Nb mole ratio from the starting value of 7:1 to 6:1, consistent with F^-/F_2 being the reductive couple.[410]

4.5.2.6.2 Chloro ligands

The molecular structures of $MCl_5(g)$ have been redetermined by electron diffraction.[411,412] Structural refinements for $TaCl_5$ based upon models of D_{3h} point symmetry led to satisfactory agreement between experimental and calculated intensities, yielding bond distances r_{ax} 2.313(5), r_{eq} 2.226(4), and Δr 0.04(7) Å. The results were consistent with extensive HF and DFT calculations.[9,411] MX_5 (X = Cl, Br) molecules have been frozen out in argon and dinitrogen matrices at low temperature and probed by IR spectroscopy.[413] In argon, the matrix was found to play a significant role. For each system, initial deposition followed by controlled diffusion led to a mixture of isomers of D_{3h} and C_{4v} point symmetry, plus at least one other isomer of lower symmetry. In contrast, in the dinitrogen matrix, the square pyramidal (C_{4v}) isomer only was observed, apparently a consequence of stabilization by binding of N_2 at the sixth coordination site.

The crystal structures of two extra polymorphs of Nb_2Cl_{10} have been defined.[414,415] As for the original polymorph,[416] the molecules consist of edge-sharing bioctahedra $[Cl_4Nb]_2(\mu_2\text{-}Cl)_2$ but different three-dimensional packing leads to different crystal structures.

Detailed calorimetric data have been reported for M_2Cl_{10} and $AMCl_6$ (A = Rb, Cs).[417] Enthalpy contents and molar heat capacities were measured as functions of temperature. The ionic compounds underwent allotropic solid–solid transformations.

Nb_2Cl_{10} promotes the hydrolysis of MeCN to NH_4Cl. The reaction mechanism has been examined.[418] M_2Cl_{10} have proven to be versatile Lewis acids in organic synthesis (see refs. 419 and 420 for lead references) and in polymerization of alkenes (e.g., see ref. 421). They were included in a classification of Lewis acids that is based upon activity and selectivity.[422]

A new modification of $KNbCl_6$ has been obtained by crystallization from $SOCl_2$ solution.[423] The salts $[Al(MeCN)_6][MCl_6]_3$ were obtained from reaction of M_2Cl_{10} and $AlCl_3$ in MeCN.[424] Unusual problems of disorder and/or twinning were encountered in determination of their crystal structures due to the high symmetry of the space groups.

The electronic spectra of Nb^V and Ta^V chlorides and some reduced forms have been defined in alkali chloride and oxychloride melts.[425] Nb^V was detected as $[NbCl_6]^-$ in the basic ionic liquid medium $AlCl_3$-[emim]Cl (emim = 1-ethyl-3-methylimidazolium).[426] The addition of oxide produced $[NbOCl_5]^{2-}$. The nature of Ta^V in NaCl—$AlCl_3$ melts at 175 °C was studied by potentiometry and spectrophotometry.[427] For $1.1 < pCl < 4.5$ and $0 < [Ta^V] < 0.3$ M, the results were consistent with the following equilibrium: $[TaCl_6]^- \leftrightarrow TaCl_5 + Cl^-$. Reduction led to Ta^{IV}

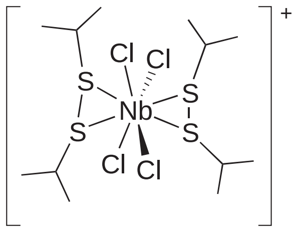
followed by dimerization and further reduction to Ta_6Cl_{14} and possibly other clusters. Formation of metallic Ta was not observed.

The six-coordinate synthon $NbCl_5(MeCN)$ has been characterized structurally.[428] Six-coordinate addition compounds MCl_5L also resulted from reaction of the halide with L = 7-azaindole.[429] $TaCl_5(OSCl_2)$ and $MCl_5(OSeCl_2)$ were prepared from M_2Cl_{10} and the chalcogen oxydichloride.[430] $NbCl_5(OSeCl_2)$ reacted with $SOCl_2$ to afford $[SeCl_3][NbCl_6]$ which contains trigonal pyramidal $[SeCl_3]^+$ cations and octahedral $[NbCl_6]^-$ anions. Additional interactions between Se and chloro ligands result in effective six-coordination of the Se atoms.

The electrochemical properties of the Nb^V systems $NbCl_5(MeCN)$ and $Et_4N[NbCl_6]$ have been determined in dried MeCN (10^{-3} M H_2O).[431] Two one-electron processes corresponding to the Nb^V/Nb^{IV} and Nb^{IV}/Nb^{III} couples were observed. The behavior of $NbCl_5(MeCN)$ is complicated by chemical reactions which follow the initial one-electron reduction.

^1H, ^{13}C, and ^{93}Nb NMR has identified the substitution products produced by reaction of M_2Cl_{10} with MeOH(D) in both coordinating and non-coordinating solvents.[432,433] Depending on conditions, all the mononuclear products $NbCl_{5-x}(OMe)_x$ ($x = 1$–5) were observed. Condensation to bi- or polynuclear species with bridging methoxo groups can lead to the elimination of products such as MeCl and Me_2O.

Reactions between Nb_2Cl_{10} and the disulfides S_2R_2 (R = Me, Pr^i) were examined in a search for precursors of NbS_2 films.[434] The products were hydrolysis-sensitive salts $[NbCl_4(\eta^2\text{-}S_2R_2)_2][NbCl_6]$ which could be purified by sublimation. Crystallization from CH_2Cl_2 led to salts containing the 8-coordinate cations $[NbCl_4(\eta^2\text{-}S_2R_2)_2]^+$ (**194**) and a tetranuclear dianion (**195**), apparently formed via hydrolysis with trace water.



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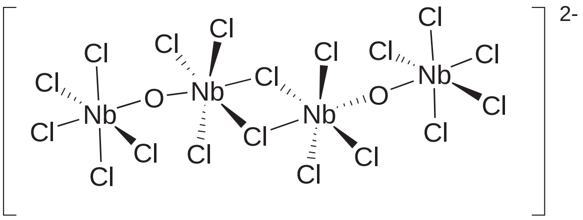

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Quantum chemical calculations were used to explore the initial reactions involved in chemical vapor deposition of Ta_2O_5 from $TaCl_5$ and H_2O.[435] The adduct $TaCl_5(OH_2)$ is predicted to eliminate HCl and convert to $TaCl_4(OH)$ which can react further with H_2O to form $TaCl_3(OH)_2$. Formation of $TaOCl_3$ in the unimolecular decompositions of $TaCl_4(OH)$ and of $TaCl_3(OH)_2$ had similar barriers of about 20 kcal mol^{-1}. However, the catalytic effect of an assisting H_2O molecule opened barrierless channels to $TaOCl_3$ from either of these precursors.

Nb_2Cl_{10} and Al_2Cl_6 reacted at ~200 °C to produce crystalline $Cl_4Nb(\mu_2\text{-}Cl)_2AlCl_2$.[436] Complexes of equivalent stoichiometry $MGaCl_8$ and point symmetry (C_{2v}) were identified by Raman spectroscopy in binary mixtures M_2Cl_{10}–$GaCl_3$ in the liquid and vapor states.[437] Similarly, a new component which appeared in vapor phase mixtures of Nb_2Cl_{10} and $SnCl_2$ was assigned to $Cl_4Nb(\mu_2\text{-}Cl)_2SnCl$.[438]

Conversion of Cp^*NbCl_4 to Cp^*NbF_4 has been reported.[439] $CpNbCl_4$ reacted with ligands PMe_xPh_{3-x} ($x = 1$–3) to form stable 1:1 adducts.[440] However, spontaneous subsequent reactions occur in solution (with rates increasing in the order $x = 1$–3) which led to the formation of Cl radicals and Nb^{IV} species. The solid state structures of adducts $CpNbCl_4(PMePh_2)_y$ ($y = 1$, 2) were defined. Cp^*MCl_4 also formed 1:1 adducts with a number of primary and tertiary phosphoranes.[441,442] The reagent $SbCl_5$ in MeCN was used to remove chloro ligands sequentially from $CpNbCl_4$.[443] The cations $[CpNbCl(MeCN)_4]^{3+}$ and $[CpNb(MeCN)_6]^{4+}$ were characterized structurally and exhibit distorted *pseudo*-octahedral and -pentagonal bipyramidal stereochemistries, respectively.

4.5.2.6.3 Bromo and iodo ligands

M_2Br_{10} and MI_5 were prepared by halide exhange from M_2Cl_{10} with either HX or Pr^iBr.[444] These syntheses offer an alternative to direct halogenation of the metal. The sublimation pressures of

Nb_2Br_{10} and MI_5 have been determined.[445] MX_5 ($X = Cl$, Br) molecules were studied in argon and dinitrogen matrices at low temperature and probed by IR spectroscopy (Section 4.5.2.6.2).[413]

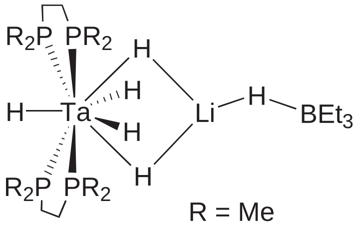
Photoelectron spectra (AlKα, HeI) of NbI_5, Nb_3I_8, Nb_6I_{11}, HNb_6I_{11}, $Nb_6I_8(MeNH_2)_6$, $Nb_6I_8(PrNH_2)_6$, and Nb(s) have been measured.[446] The binding energy of the Nb core levels depended linearly on the formal oxidation state of niobium, estimated as the ratio I/Nb.

4.5.2.7 Hydrido Ligands

A comprehensive review of early transition metal hydrides including those of Nb and Ta is available.[447] Hydrido-metallocene systems are discussed in detail there. The present account concentrates on other ligand systems, although mono- or polynuclear metallocene systems with interesting structural features are covered. Polyhydride systems have been reviewed from a theoretical standpoint.[448]

The square pyramidal (C_{4v}) form of TaH_5 is predicted to be 20 kcal mol^{-1} more stable than its trigonal bipyramidal (D_{3h}) isomer.[9] This contradicts the VSEPR rules, a consequence of second-order Jahn–Teller effects.

Treatment of $TaCl_4(dmpe)_2$ with $LiBHEt_3$ produced $TaH_5(dmpe)_2 \cdot LiBHEt_3$ (**196**) where the Li atom is linked to one H–B and two Ta–H fragments.[449]



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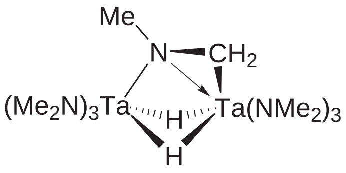

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Reaction of $Ta(NMe_2)_5$ with H_2SiRPh (R=Me, Ph) provided binuclear $[(Me_2N)_2Ta]_3(\mu_2\text{-}H)_2(\mu_2\text{-}N\text{-}\eta^2\text{-}N,C\text{-}CH_2NMe)$ (**197**) through C—H activation of an amide ligand via β–H abstraction.[450]

4.5.2.7.1 *Alkoxo or aryloxo co-ligands*

The dihydrido complex *trans*-$(silox)_3Ta(H)_2$ ((**198**); Scheme 44) was prepared by reduction of the equivalent chloro species under H_2.[65,451] It underwent reversible cyclometalation and reacted with MeI and C_2H_4 to yield monohydrido complexes ((**199**)–(**201**); Scheme 44). This chemistry was extended as a model of Ziegler–Natta copolymerizations.

Hydrogenation of $Ta(OAr)_3R_2$ ($Ar = 2,6\text{-}Pr^i_2\text{-}C_6H_3$; $R = p\text{-}Me\text{-}C_6H_4CH_2$) in the presence of phosphorane ligands L produced distorted six-coordinate dihydrido complexes $Ta(OAr)_3(H)_2L$ (Scheme 29).[452] Treatment of $Ta(OAr)_2Cl_3L$ with one or two eq of Bu_3SnH and L produced the seven-coordinate mono- and dihydrido compounds $Ta(OAr)_2Cl_2HL_2$ or $Ta(OAr)_2Cl(H)_2L_2$.[313] The latter features chemically equivalent hydrido ligands and is also produced via hydrogenation of $Ta^{IV}(OAr)_2Cl(CH_2SiMe_3)$ in the presence of L.[453] $Ta(OAr)_2(CH_2SiMe_3)_3$ provided the trihydride $Ta(OAr)_2(H)_3L_2$ for $L = PMe_2Ph$. Trihydrides were also produced for Ar = 2,6-diphenylphenyl but the phenyl substituents in the 2 and 6 positions were hydrogenated to cyclohexyl substituents (Scheme 29). These observations have been developed into procedures for the catalytic hydrogenation of arene rings.[311]

The "*trans*" hydrido ligands in *pseudo*-octahedral complexes $Ta(H)_2L(OAr)_2X$ ($L = PR_3$; $X = Cl$, OAr) are bent away from the sterically less-demanding ligand X towards the bulkier phosphorane ligand L (Scheme 29). *Ab initio* calculations indicate that this distortion arises form the relative π-acceptor ability of L relative to X.[454]

4.5.2.7.2 *Cyclopentadienyl co-ligands*

Photolysis of Cp_2MH_3 in Ar and N_2 matrices yielded the 16e species Cp_2MH.[455] In CO matrices, $Cp_2MH(CO)$ was formed which reacted further to $Cp_2M(CO)$ (17e).

Reaction of $Cp^*_2Ta(CH_2)H$ with water or aniline produced $Cp^*_2Ta(E)H$ ($E=O$, NPh) in which the reducing hydrido ligand co-existed with an oxo or phenylimido ligand.[456] Unexpectedly, the TaNC bond in the phenylimido species was linear, consistent with a 20-electron count and the presence of a $Ta{\equiv}N$ bond. However, the TaN and TaO bond distances are intermediate between the values expected for double and triple bonds, indicating that the second π interaction is relatively weak. This conclusion is supported by the low energy ($850\,cm^{-1}$) of the ν(TaO) stretching mode.

The formal 1σ, 2π donor analogy between cyclopentadienyl $[\eta^5\text{-}C_5R_5]^-$ and imido $[RN{=}]^{2-}$ has been used to synthesize isoelectronic analogs with differing overall charge. In particular, Tilley has explored certain Ta systems (see ref. 457 and refs therein). For example, $Cp^*(ArN)TaCl(SiR_3)$ ($ArNH_2=2,6\text{-}Pr^i_2\text{-}C_6H_3\text{-}NH_2$) underwent hydrogenolysis to yield binuclear $[Cp^*(ArN)ClTa]_2(\mu_2\text{-}H)_2$.

Reaction of $Cp_2Nb^V(H)_3$ or $Cp_2Nb^{III}BH_4$ with tertiary silanes $HSiR_3$ provided $Cp_2Nb^V(H)_2(SiR_3)$. The presence of base promoted the reactions and electron-accepting groups R provided more stable dihydrido compounds.[458,459] Two isomers were detected at 50 °C for $SiR_3=SiMe_2Cl$ with the silyl ligand in a lateral or a central position. At 90 °C, H_2 elimination yielded $Cp_2NbH(SiMe_2Cl)_2$. A neutron diffraction study of this complex, augmented by solution NMR measurements and DFT calculations, confirmed C_{2v} point symmetry with the hydrido ligand located in the central position with $r(NbH)=1.816(8)$ Å.[460] This long bond is apparently imposed by interligand interactions between the hydrido and silyl ligands. A non-classical hypervalent interaction was proposed in which the Nb—H bonding orbital overlaps with Si—Cl anti-bonding orbitals. This model can rationalize the observed structures in a number of the mono- and dihydrido complexes analogous to those described above.[459,461] An X-ray diffraction study reported that $Cp_2TaH(SiMe_2H)_2$ has an unsymmetrical structure,[462] but subsequent *ab initio* calculations favored a symmetric (C_{2v}) structure analogous to $Cp_2NbH(SiMe_2Cl)_2$.[461]

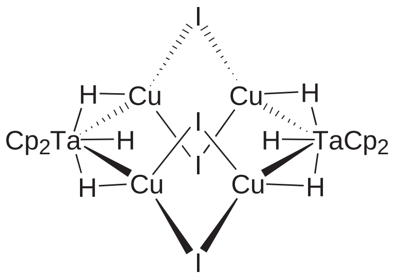
The (dihydrogen)hydrido C_s structures $(\eta^5\text{-}C_5H_{5-n}R_n)_2Nb^{III}H(\eta^2\text{-}H_2)$ ($R=SiMe_3$; $n=0\text{–}2$) are more stable than the trihydrido C_{2v} structures $(\eta^5\text{-}C_5H_{5-n}R_n)_2Nb^V(H)_3$ whereas the opposite is true for the Ta compounds.[463] In the mid-1980s, dihydrogen was discovered to act as a ligand,[464] and large temperature-dependent H—H couplings were observed in certain polyhydrido complexes. Systems derived from the complexes $(\eta^5\text{-}C_5H_{5-n}R_n)M^VH_3$ played important roles in understanding the latter phenomenon.[465–468] Further discussion is given in Section 4.5.4.5 for M^{III} hydrido complexes.

In related work, reduction of $(\eta^5\text{-}C_5H_3RR')_2Nb^{IV}Cl_2$ ($R, R'=H, SiMe_3$) (see, e.g., refs. 469 and 470) followed by hydrolysis gave trihydrido species $(\eta^5\text{-}C_5H_3RR')_2Nb^V(H)_3$ which reacted with sources of $M'=Cu^I$, Ag^I, and Au^I to provide trinuclear cations $\{[(\eta^5\text{-}C_5H_3RR')_2Nb(H)_3]_2M'\}^+$.[471,472] The magnitude of the H—H exchange couplings varied with M′. The observations were rationalized with a model proposing two isomeric states $(H)Nb(\mu_2\text{-}H)_2M'$ and $(\eta^2\text{-}H_2)Nb(\mu_2\text{-}H)M'$ that are close in energy. The results supported the proposal that rotational tunneling of coordinated H_2 ligands is the origin of the quantum mechanical H—H coupling in these systems.

Reaction of Cp_2TaH_3 with $[M'(PPh_3)][PF_6]$ ($M'=Cu$, Au) provided binuclear complexes $[Cp_2TaH(\mu_2\text{-}H)_2M'(PPh_3)][PF_6]$.[473] Detailed NMR studies revealed intramolecular exchange between the terminal and *one* of the bridging hydrido ligands as well as intermolecular exchange of phosphorane ligand.

Reaction of CuX ($X=Cl$, I) with $Cp_2Ta(H)_3$ or $Cp'_2Ta(H)_3$ produced adducts which IR spectroscopy indicated contained both terminal and bridging hydrido ligands.[474] Structural characterization of the iodo systems indicated the presence of $Cu(\mu_2\text{-}I)Cu$ fragments ((**202**), (**203**)). For the Cp system, two Cu_2I_2 fragments were connected to two Cp_2TaH_3 moieties by $Ta(\mu_2\text{-}H)Cu$ links (**202**). In contrast, for the Cp′ system, a single Cu_2I_2fragment was connected to two $Cp'_2Ta(H)_3$ moieties by $Ta(\mu_2\text{-}H)_2Cu$ links (**203**). Adducts were also formed in the reaction of $Cp_2Ta(H)_3$ with various M^{II} halides. The derivative $Cp_2HTa(\mu_2\text{-}H)_2ZnCl_2(thf)$ featured Zn in a distorted trigonal bipyramidal coordination sphere.[475]

The reaction of $Cp_2Ta^V(H)_3$ with $Ir^IX(CO)(dppe)$ ($X=Br$, I; dppe = 1,2-bis(diphenylphosphino)ethane) was rapid and led to clean formation of *fac*-$Ir^{III}(H)_3(CO)(dppe)$ and $Cp_2Ta^{III}X$ or $Cp_2Ta^{III}XL$ (in the presence of added $L=CO$, C_2H_4, $PrC{\equiv}CPr$).[476] The total results were consistent with the formation of hydrido- and halo-bridged intermediates in which transfer of all hydrido and halo ligands occurred before dissociation into the mononuclear products.



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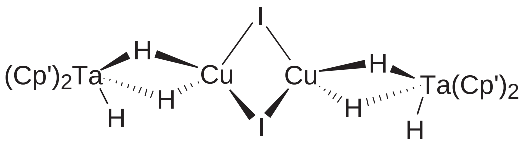

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4.5.3 NIOBIUM(IV) AND TANTALUM(IV)

4.5.3.1 Nitrogen Donor Ligands

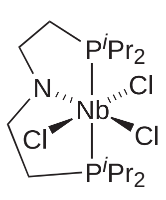
4.5.3.1.1 Amido ligands

A small number of M^{IV} amido complexes have been prepared, usually by metathesis reactions from synthons such as $MCl_4(thf)_2$. The homoleptic amido species $M(NMe_2)_4$ have been examined as precursors of metal nitride thin films.[85,477]

$NbCl_4(thf)_2$ reacted with 2 eq $LiNR_2$ ($R = Me_3Si$) to give $Nb(NR_2)_2Cl_2$ or with 4 eq $LiNPh_2$ to give $Nb(NPh_2)_4$.[189] $Nb(NR_2)_2ClPh$ resulted from reaction of $Nb(NR_2)_2Cl_2$ with $ZnPh_2$.[478] $NbCl_4(thf)_2$ reacted with 3 eq LiL (L = NArAd, Ar = 3,5-Me_2-C_6H_3, Ad = adamantyl) in ether to yield NbL_3Cl.[479] Further treatment with LiR produced NbL_3R (R = Me, Ph), while treatment with $LiCH_2CMe_2Ph$ produced the enolate $NbL_3(OCH{=}CH_2)$ from cleavage of solvent thf.[479] $Nb(NRAr)_3Cl$ was prepared by reaction of $NbCl_4(thf)_2$ with 3 eq Li(NRAr) ($R = Bu^t$, Ar = 3,5-Me_2-C_6H_3).[175] Similarly, treatment of $NbCl_4(thf)_2$ with either 1 or 2 eq of the terdentate diamino-amido ligand LiL′ (L′ = $(Et_2NCH_2CH_2)_2N$) in thf yielded $NbCl_3L'$ and $NbCl_2L'_2$, respectively.[480,481]

Reduction of $Ta^V(NR_2)_2Cl_3$ with excess Na/Hg in hexane produced $Ta^{IV}(NR_2)_2Cl_2$ ($R = SiMe_3$) while $Ta^V(NEt_2)_2Cl_3$ with Na/Hg and $LiNPh_2$ yielded $Ta^{IV}(NPh_2)_2(NEt_2)_2$.[482]

Nb complexes containing potentially tridentate diphosphorano-amido ligands have been prepared.[481] Treatment of $NbCl_4(thf)_2$ with 1 or 2 eq of Li[PNP] ([PNP] = $[N(CH_2CH_2PPr^i{}_2)_2]^-$) in tol produced *mer*-$LNbCl_3$ (**204**) and *trans*-L_2NbCl_2 (**205**), respectively. In contrast, when the Pr^i groups of ligand [PNP] were replaced with Me, reaction with 2 eq produced binuclear (**206**).[481]



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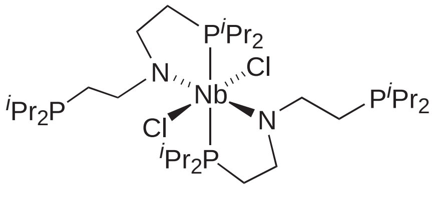

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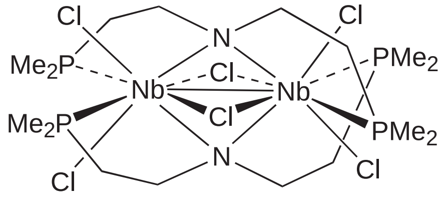

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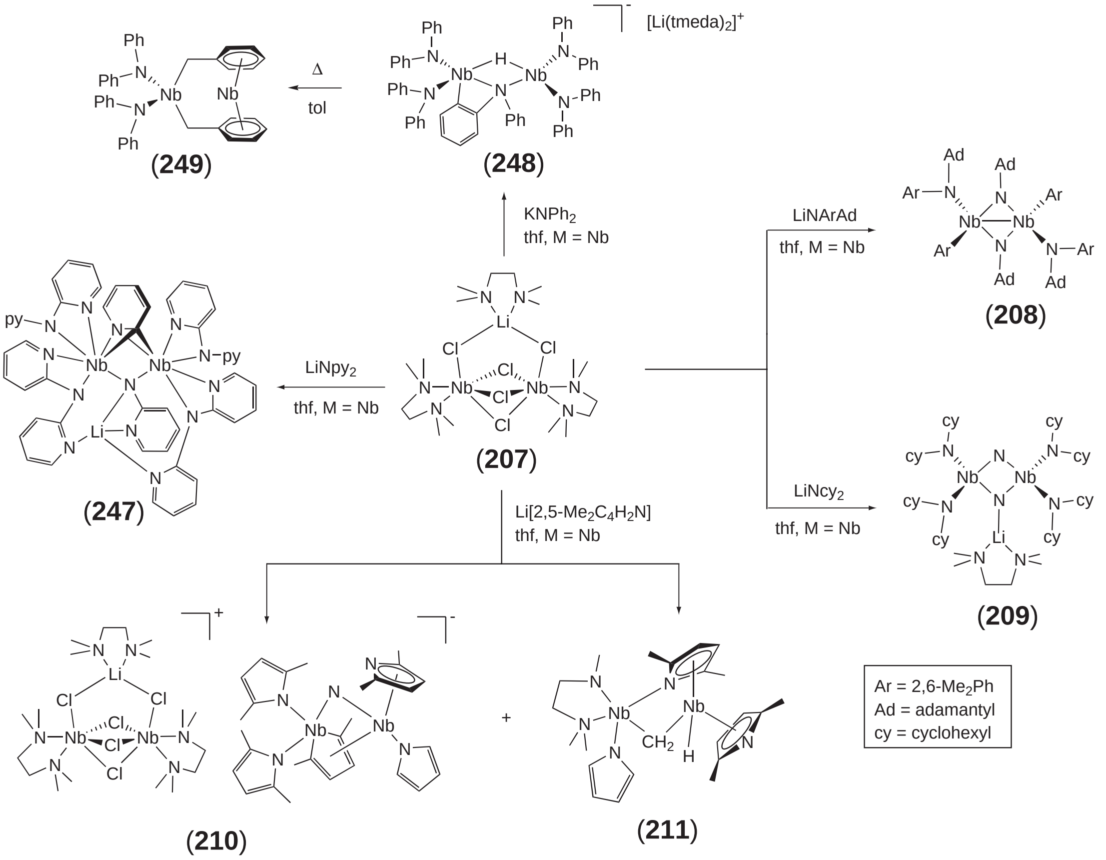
Benzamidinato and guanidinato complexes *trans*-$Cl_2Nb(\eta^2$-*N*,*N*-RNCR′NR$)_2$ ($R = SiMe_3$, R′ = p-tolyl; R = cy, R′ = $N(SiMe_3)_2$) were prepared by reaction of $NbCl_4(thf)_2$ with 2 eq Li[RNCR′NR] in tol.[117]

Reaction of $Nb^{III}{}_2Cl_6(tmeda)_2$ with the amide LiNArAd (Ar = 3,5-Me_2-C_6H_3) in refluxing thf produced the binuclear intermediate $(tmeda)_3Nb^{II}{}_2Cl_5Li$ ((**207**), Scheme 40) which reacted further to form $[(ArAdN)ArNb^{IV}]_2(\mu_2$-NAd$)_2$ (**208**).[483,484] The imido and aryl ligands of (**208**) were proposed to be generated by oxidative addition of the N—Ar bond of $[NArAd]^-$ to (**207**).

(**207**) reacted with a different amide, $LiNcy_2$, to produce the nitrido-bridged Nb^VNb^{IV} mixed-valence species (**209**).[484] The nitrido ligands were presumed to arise from N_2 activation. Treatment of (**207**) with the dimethylpyrrole lithium salt Li[2,5-Me_2-C_4H_2N] in thf yielded the salt (**210**) and neutral (**211**).[485] The anion in (**210**) contains two Nb centers ($Nb^{IV}{}_2$ or $Nb^{III}Nb^V$) linked by bridging nitrido and dienediyl ligands, both originating from denitrogenation of



Scheme 40

dimethylpyrrole. The cation is the one-electron oxidized form of (**207**). Neutral (**211**) is a mixed-valence $Nb^{III}Nb^{IV}$ species. The methylidine and hydrido ligands were presumed to arise from cleavage of a CH_3—N bond of tmeda followed by oxidative addition of the resultant CH_3.[485]

4.5.3.1.2 *Imido ligands*

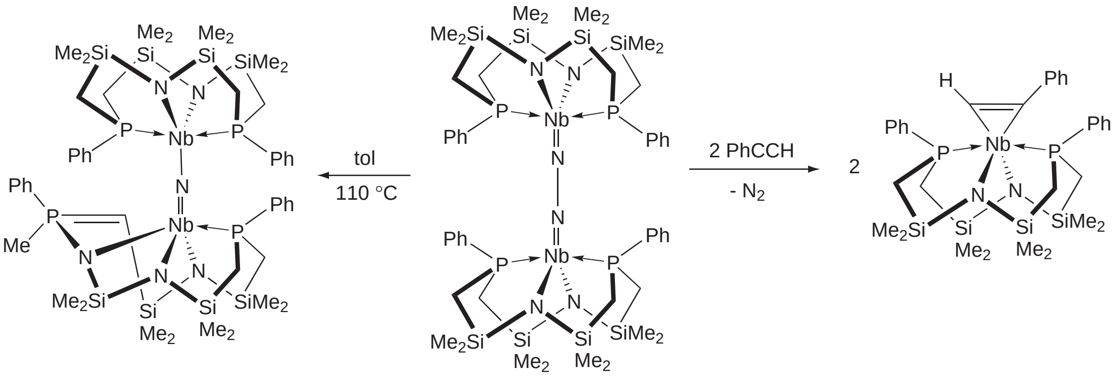
Reduction of $Ta(NR)(NR_2)Cl_2(thf)$ with Na/Hg yielded binuclear $[(R_2N)ClTa]_2(\mu_2\text{-}NR)_2$ (R = $SiMe_3$) with a Ta—Ta distance of 2.621(1)Å.[486] Treatment of $Nb(NBu^t)Cl_3(py)_2$ with the *ansa* ligand $[PhP(C_5Me_4)_2]Li_2$ in tol produced binuclear $[ClNb]_2(\mu_2\text{-}NBu^t)_2(\mu_2\text{-}\eta^5{:}\eta^5\text{-}(C_5Me_4)_2PPh)$.[487] Other Cp-supported binuclear M^{IV}–imido species have also been prepared.[488–490]

4.5.3.1.3 *Hydrazido ligands*

Reduction of $[P_2N_2]Nb^{III}Cl$ by KC_8 under N_2 produced $\{[P_2N_2]Nb^V\}_2(\mu_2\text{-}N_2)$ ((**212**), Scheme 41).[491] EPR and variable-temperature magnetic studies were consistent with the presence of two Nb^{IV} centers and a hydrazido N_2^{4-} bridging ligand. Thermolysis of (**212**) produced the Nb^VNb^{III} species (**213**) with a bridging nitride via insertion of nitrogen into the $[P_2N_2]$ ligand. Addition of 2 eq PhCCH to (**212**) resulted in displacement of the dinitrogen ligand to form (**214**).[491]

4.5.3.2 Phosphorous Donor Ligands

Compounds of general formula $MX_4(PR_3)_2$ (X = halo) display complex chemistry with stereochemistry and nuclearity often dependent on R. *trans*-$NbCl_4(PR_3)_2$ (R_3 = Et_3, $EtPh_2$) are both



(213) **(212)** **(214)**

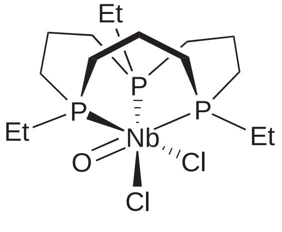
Scheme 41

mononuclear.[492] In contrast, although they may be mononuclear in solution, analogous species with less bulky ligands PMe_2R (R = Me, Ph) are binuclear in the solid state. $[(PMe_2R)_2Cl_2Nb]_2(\mu_2\text{-}Cl)_4$ are centrosymmetric with two square antiprismatic $Nb(PMe_2R)_2Cl_6$ units sharing a square Cl_4 face.[492–494] Related species with ligands PH_2R (R = Ph, cy) have been examined as potential precursors for niobium(III) phosphide films.[495] $[(PMe_3)_2Cl_2Ta]_2(\mu\text{-}Cl)_4$ has also been characterized.[494,496] *trans*-$TaCl_4(PEt_3)_2$ is homologous with its Nb counterpart, while *cis*-$TaCl_4(PMe_2Ph)_2$ displays different stereochemistry, and, in contrast with the Nb analog, is mononuclear in the solid state.[497] A species originally formulated as $Ta^{III}Br_3(PMe_2Ph)_2$[498] was proposed later to be $Ta^{IV}Cl_2Br_2(PMe_2Ph)_2$ on the basis of a reinterpretation of the original crystallographic data.[499]

HF and CI calculations were used to interpret the EPR spectra of mononuclear d^1 *pseudo*-D_{4h} species of general formula $NbCl_4(PR_3)_2$.[500] These calculations indicated that the previously reported spectra were inconsistent with such species. This conclusion was supported by a later study which suggested that the spectra may have been due to minor hydrolysis products such as $Nb^{IV}OCl_2(PEt_3)_2$.[501]

Seven-coordinate species $MCl_4(PMe_3)_3$ have also been prepared.[494,496,497] $NbBr_4(PMe_2Ph)_3$ was prepared from reaction of Nb_2Br_{10} with excess PMe_2Ph in tol.[502]

The reaction of $Nb^{III}Cl_3(dme)$ with the macrocycle L = [12]ane$(PEt)_3$ in CH_2Cl_2 in air provided $LNb^{IV}OCl_2$ (**215**).[503]



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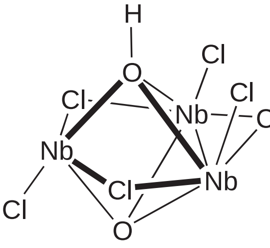
4.5.3.3 Oxygen Donor Ligands

4.5.3.3.1 Polynuclear oxo complexes

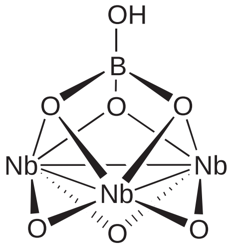
Reduction of $[CpNb^VX_4]_2(\mu_2\text{-}O)$ (X_4 is a combination of H_2O and terminal or bridging Cl) by Al in thf gave the cluster $Cp_3Nb^{IV}{}_3Cl_6O(OH)$.thf (**216**).[262] The compound features a Nb_3 isosceles triangle with one Nb—Nb bond (2.823(1) Å) and two non-bonding Nb···Nb distances (3.24–3.25 Å). This model was supported by a magnetic moment of 1.39 μ_B (295 K) and detection of an EPR spectrum. Analysis of the latter indicated that the unpaired electron is localized in the $d_z{}^2$

orbital of a single Nb^{IV} center. This orbital makes an angle of ~45° with the Nb_3 plane. Related compounds $Cp'_3Nb_3Cl_6OX$ ($X = OH, Cl$) were obtained by decarbonylation of $[Cp'Nb^{II}(CO)_2]_2(\mu_2\text{-}Cl)_2$.[504]



(Cp ligands on Nb not shown)

(**216**)



(triangular core only)

(**217**)

Hydrolysis of $Nb^{III}Cl_3(dme)$ in HCl provided the aqua cation $\{[(H_2O)_3Nb]_3(\mu_3\text{-}Cl)(\mu_2\text{-}O)_3\}^{4+}$, assigned as a $Nb^{IV}{}_2Nb^{III}$ cluster.[505] Water-exchange kinetic experiments identified two distinct aqua ligand environments consistent with an incomplete cuboidal triangular structure: ligands *trans* to the capping Cl (one per Nb) were more inert than those *trans* to the bridging oxo groups (two per Nb). Treatment of this cation with ethanolic KTp (Tp = hydrotrispyrazol-1-ylborate) provided the cluster $\{[TpNb^{IV}]_3(\mu_3\text{-}O)_3(\mu_3\text{-}BO_3(OH))\}$ (**217**).[506] The borate ligand was derived by degradation of Tp.

4.5.3.3.2 Alkoxo and aryloxo ligands

The complexes $(silox)_3M^VCl_2$ ($silox = Bu^t{}_3SiO$) undergo one-electron reduction to $[(silox)_3\text{-}M^{IV}Cl_2]^-$.[507] These anions are subject to loss of Cl^- but salts $[Bu_4N][(silox)_3M^{IV}Cl_2]$ were isolated in substance, as was $(silox)_3Nb^{IV}Cl$. The latter forms adducts $(silox)_3NbCl{\cdot}L$ (L = py, thf).

An extensive series of complexes *trans*-$M^{IV}(OAr)_2X_2L_2$ (ArOH = 2,6- or 2,4,6-substituted phenols; X = Cl, Br; L = py, PR_3) have been generated by reduction of the corresponding adducts $M^V(OAr)_2X_3L_2$ in the presence of excess L.[508]

Tetranuclear $[Li(thf)_2Nb^{IV}Cl_3(OAr)_2]_2$ (**150**) was obtained as one of the products in the reaction of LiOAr (ArOH = 2,6-Me_2-C_6H_3OH) with $Nb^V{}_2Cl_{10}$.[310]

4.5.3.3.3 Carboxylato and related ligands

The stereochemistry of $Nb(O_2CNEt_2)_4$ was essentially dodecahedral, as expected from the small bite angle of 1.01 Å for the ligand.[509]

Zinc reduction of Nb_2Cl_{10} in EtOH followed by the addition of LH = 2-pyridinecarboxylic acid provided $Nb^{IV}L_4{\cdot}2EtOH$ in good yield.[510] The four bidentate ligands spanned the *m* edges of a dodecahedron to give a D_{2d} *mmmm* stereoisomer. This complex provided the first experimental evidence for Orgel's postulate[511] that eight-coordinate d^1 $M(A\text{-}B)_4$ complexes will favor occupation of the A sites of the dodecahedron by the π-donor ligands while the B sites will favor π-acceptor ligands.

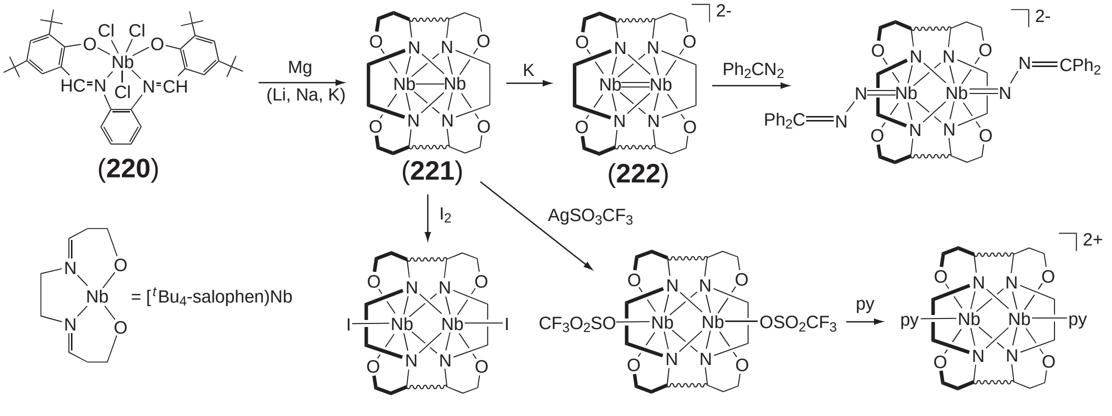
Depending upon the exact nature of the countercations A, the anion in $A_4[Nb(C_2O_4)_4]$ in the solid state can adopt distinctly different geometries intermediate between the square antiprismatic and dodecahedral extremes.[512] A convenient route to $K_4[Nb(C_2O_4)_4]$ involved adding oxalate to a solution of Nb_2Cl_{10} reduced with Zn in conc. HCl/EtOH.[513] A related synthesis produced $[Nb(edta)(OH_2)_2]{\cdot}2H_2O$ which featured a hexadentate $edta^{4-}$ ligand and two aqua ligands in a *pseudo*-square antiprismatic stereochemistry.[514]

The complex *trans*-$Nb^{IV}Cl_2L_2$ (LH = 2,2,6,6-tetramethylheptane-3,5-dione) was isolated as two polymorphs.[515] Both exhibited *pseudo*-D_{2h} point symmetry, but there were distortions in the chelate plane of one form, postulated to be due to packing forces. The EPR spectrum in solution was a decet (*g*, 1.930; *A*, 149 G) due to hyperfine interaction with ^{93}Nb ($I = 9/2$).

4.5.3.3.4 Multidentate ligands

Sequential two-electron reduction of calixarene-supported (**156**) by Na generated (**218**), (**12**), and (**219**) (Scheme 32) with bond distances 2.757(1), 2.659(1), and 2.385 Å, respectively, characteristic of $\mathrm{Nb^{IV}}$—$\mathrm{Nb^{IV}}$, $\mathrm{Nb^{III}}$═$\mathrm{Nb^{III}}$, and $\mathrm{Nb^{II}}$≡$\mathrm{Nb^{II}}$ bonds.[36,198,199]

The reduction of $\mathrm{LNb^{V}Cl_3}$ ((**220**), $\mathrm{LH_2}$ = a $\mathrm{Bu^t}$-substituted *N*,*N*′-*o*-phenylenebis(salicylideneamine)) led to the binuclear complex (**221**) (Scheme 42).[516] This neutral compound contained both an $\mathrm{Nb^{IV}}$—$\mathrm{Nb^{IV}}$ bond and two C—C bonds formed across the imino groups of ligands L which were converted to a binucleating ligand of charge 8-. (Scheme 42). Further reduction led to the $\mathrm{Nb^{III}}$═$\mathrm{Nb^{III}}$ compound (**222**). As outlined in Scheme 42, (**221**) and (**222**) could transfer one and two electrons pairs, respectively, with consequent cleavage of the Nb—Nb and Nb═Nb bonds. A theoretical treatment suggested that, while formation of the C—C bonds in (**221**) competed with that of the Nb—Nb bond during reduction of (**220**), the latter bond was the first one to be involved in electron transfer reactions.



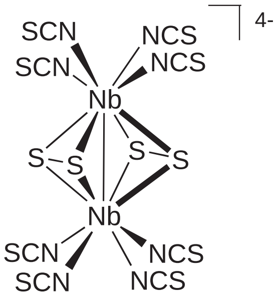
Scheme 42

4.5.3.4 Sulfur, Selenium, and Tellurium Ligands

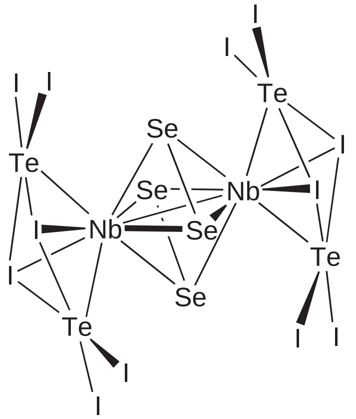
Additional bi- and polynuclear systems are discussed in Chapters 4.9 and 4.12, respectively.

$\mathrm{MS_2}$ molecules have been stabilized in Ar matrices at low temperature.[517] Analysis of IR spectra, augmented by DFT calculations, indicated bond angles of 107(3)°.

Fusion of KNCS and polymeric $\mathrm{NbS_2Cl_2}$ followed by dissolution of the melt in water and addition of cations led to isolation of salts of the centrosymmetric dithio anion $\{[\mathrm{(SCN)_4Nb^{IV}}]_2(\mu_2\text{-}\eta_2{:}\eta_2\text{-}\mathrm{S_2})_2\}^{4-}$ (**223**).[518,519] This species features eight-coordinate $\mathrm{Nb^{IV}}$ and a formal Nb—Nb single bond. One-electron oxidation provided a species whose EPR properties were consistent with an unpaired electron interacting with two equivalent Nb atoms in a $\mathrm{Nb^{V,IV}}_2$ core.



(**223**)



(**224**)

The NCS ligands in anion (**223**) were easily displaced by bidentate 1,1-dithio acid ligands R_2NCS_2, $ROCS_2$, or $(RO)_2PS_2$.[354,518] In addition, acid treatment of the anion allowed access to $[Nb_2(S_2)_2]^{4+}$(aq) which reacted with other bidentate ligands to produce $Nb_2(S_2)_2L_4$ (e.g., L = 1,3-enolato ligand such as acac, etc.) or $A_4[Nb_2(S_2)_2(C_2O_4)_4]$ (A = K, Cs, NH_4).[520,521] If the acid was concentrated aqueous HX (X = Cl, Br), double salts $A_5[Nb_2(S_2)_2X_8]X$ (A = Cs, H_3O) resulted.[522] The aqua cation itself was isolated as $[Nb_2(S_2)_2(OH_2)_8](pts)_4{\cdot}4H_2O$ (ptsH = *p*-toluenesulfonic acid) or as $[Nb_2(S_2)_2(OH_2)_8]Cl_4{\cdot}C^*{\cdot}15H_2O$ (C* = cucurbituril macrocyclic cavitand). The latter resulted from crystallization of $Cs_5[Nb_2(S_2)_2Cl_8]Cl$ and C* in aqueous HCl.[519,523] Substitution of aqua ligands is surprisingly slow, apparently due to the inhibitory effect of the bridging dithio ligands.[519]

However, those bridging dithio ligands are labile. For example, PEt_3 formally extracted 2 eq of sulfur from $[Nb_2(S_2)_2(OH_2)_8]^{4+}$ and $Nb_2(S_2)_2(acac)_4$ to provide the $Nb^{IV}{}_2(\mu_2\text{-}S)_2$ derivatives.[519,524] Reaction of $Nb_2(S_2)_2L_4$ (L = Et_2NCS_2) with chalcogen transfer reagents PEt_3Y (Y = Se, Te) allowed isolation of $Nb_2(Se_2)_2L_4$ and $[L_2Nb]_2(\mu_2\text{-}S)(\mu_2\text{-}\eta^2{:}\eta^2\text{-}Te_2)$.[524] One-electron oxidation of the former provided $[Nb_2(Se_2)_2L_4]^+$, characterized by EPR spectroscopy.

In related work, polymeric $[Nb_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}Se_2)_2]I_{8/2}$ underwent an extrusion reaction in the presence of elemental Te and I_2 at high temperature to form isolated molecules of $[(Te_2I_6)Nb]_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}Se_2)_2$ (**224**).[525] Similar compounds $Nb_2(Se_2)_2Cl_4L_4$ (L = Me_2S, C_4H_8S) were isolated by recrystallization of the products from the reaction of Nb^VSeCl_3 with L.[526,527]

The reaction of Nb_2Cl_{10} with 8 eq NaSPh in EtCN at 90 °C provided $[(EtCN)Cl(PhS)Nb^{IV}]_2(\mu_2\text{-}SPh)_4$ in 10% yield.[385] A similar reaction with 12 eq NaSPh and 2 eq Ph_4PBr in boiling MeCN provided paramagnetic, homoleptic $[Ph_4P]_2[Nb(SPh)_6]$ in 10% yield.

4.5.4.5 Halo Ligands

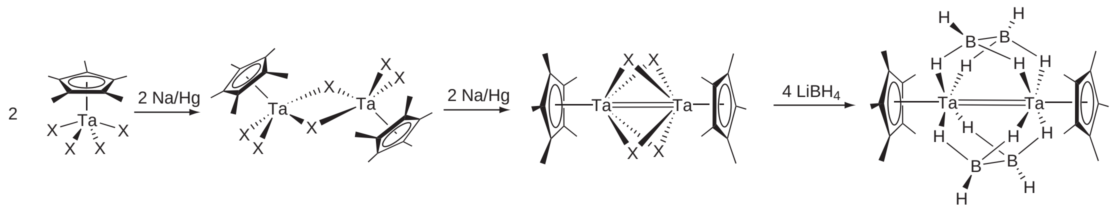
The vapor pressures of $NbCl_4$ and $NbBr_4$[528] and the enthalpies of formation of $NbBr_4$ and NbI_4[529] have been measured.

The nucleophilic stable carbene L = 1,3-dimethylimidazolin-2-ylidene displaced pyridine from $MCl_4(py)_2$ to form MCl_4L_2.[530]

The oxidation of six-coordinate $[MCl_{6-n}(NCMe)_n]^{n-2}$ complexes (n = 0–2) was studied using cyclic voltammetry.[531] Ease of oxidation decreased with increasing substitution of chloride.

In the presence of DBU = 1,8-diazabicyclo(5.4.0)undec-7-ene, $Cp^*Ta^VCl_4(PH_2R)$ species were reduced to the salt $[(DBU)H][Cp^*Ta^{IV}Cl_4]$ with production of the diphosphoranes $P_2H_2R_2$ or their decomposition products.[532]

The four-legged piano-stool complexes $Cp^*Ta^VX_4$ (X = Cl, Br) were reduced by Na/Hg to $[Cp^*Ta^{IV}X_2]_2(\mu_2\text{-}X)_2$ (**225**) and then to $[Cp^*Ta^{III}]_2(\mu_2\text{-}X)_4$ (**226**) which features a Ta═Ta bond (Scheme 43).[533] The Ta—Ta distance of 4.1230(9) Å in the related intermediate $[Cp^\dagger Ta^{IV}Br_2]_2(\mu_2\text{-}Br)_2$ suggested no intermetallic bonding interactions in the solid state. This was consistent with the observation of a triplet state in solution (μ_{eff}, 2.92 μ_B per Ta_2; no EPR signal at 8 K; single broad ^1H NMR resonance).



(225) **(226)** **(256)**

Scheme 43

$SnTa_4Cl_{18}$ was a minor product of the reaction of Ta_2Cl_{10} and $Bu^n{}_3SnH$.[534] Its constituents are Sn^{2+} and face-sharing bioctahedral $[Ta^{IV}{}_2Cl_9]^-$ ions. The latter are distorted from D_{3h} point symmetry by packing forces.

4.5.3.6 Hydrido Ligands

A comprehensive review on early transition metal hydrides including those of Nb and Ta is available.[447] Hydrido-metallocene systems are discussed in detail there.

Laser-vaporized Nb and Ta were condensed in D_2 or codeposited with H_2 in rare gas matrices at low temperature.[535] EPR spectra detected MH_4 as molecules of D_{2d} point symmetry in $^2B_1$ ground states imposed by a static Jahn–Teller effect. IR spectra indicated an H—Nb—H bond angle of 130°.

A compound originally formulated as $[Cl(cy_2N)_2Ta^{III}]_2$ with an unsupported Ta=Ta bond[536] was reformulated as $[Cl(cy_2N)_2Ta^{IV}]_2(\mu_2\text{-}H)_2$ with five-coordinate stereochemistry at the metal atoms.[537]

trans-$M^{II}Cl_2L_4$ ($L = PR_3$) oxidatively added H_2 in Et_2O under ambient conditions to form paramagnetic eight-coordinate complexes $M^{IV}(H)_2Cl_2L_4$ in good yields.[538] $Ta(H)_2Cl_2(PMe_3)_4$ adopted a distorted dodecahedral geometry in the solid state while $Ta(H)_2Cl_2(dmpe)_2$ was closer to square antiprismatic. EPR spectra were informative due to the presence of ^1H, ^{31}P, ^{93}Nb, and ^{181}Ta magnetic nuclei and demonstrated that the magnetic orbital was based upon the $d_{x^2-y^2}$ atomic orbital.[539]

$Ta(H)_2Cl_2L_4$ ($L = PMe_3$) decomposed in solution at elevated temperatures to binuclear $[L_2Cl_2Ta]_2(\mu_2\text{-}H)_4$ which features four bridging hydrido ligands.[540] The planar $(\mu_2\text{-}H)_4$ moeity is staggered by 45° relative to the eclipsed pyramidal L_2Cl_2Ta endgroups leading to D_{2d} point symmetry. The same compound resulted from oxidative addition of H_2 to $[L_2Cl_2Ta^{III}]_2(\mu_2\text{-}H)_2$ while addition of Cl_2 and HCl provided quadruply bridged $[L_2Cl_2Ta]_2(\mu_2\text{-}H)_2(\mu_2\text{-}Cl)_2$ and $[L_2Cl_2Ta]_2(\mu_2\text{-}H)_3(\mu_2\text{-}Cl)$, respectively.

The centrosymmetric, binuclear complex $[L_2CbTa^{IV}H]_2(\mu_2\text{-}H)_4$ ((**227**); Scheme 4, CbH = carbazole, (**38**); $L = PMe_2Ph$), was synthesized by reaction of the alkylidyne species $[Cb_2Ta^V]_2(\mu_2\text{-}CSiMe_3)_2$ (**39**) with H_2 in the presence of L.[70]

The methyl complex $[NPN]Ta^VMe_3$ underwent hydrogenolysis to produce $\{[NPN]Ta^{IV}\}_2(\mu_2\text{-}H)_4$ ((**121**); Scheme 22).[541] Reaction with N_2 led to loss of H_2 and incorporation of N_2 as an unsymmetrical bridging ligand in $\{[NPN]Ta\}_2(\mu_2\text{-}H)_2(\mu_2\text{-}\eta^1{:}\eta^2\text{-}N_2)$ (**122**).[542] Reaction of the latter with propene yielded $\{[NPN]TaPr^n\}_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-}N_2)$ (**123**) with an end-on bound N_2^{4-} ligand.[211]

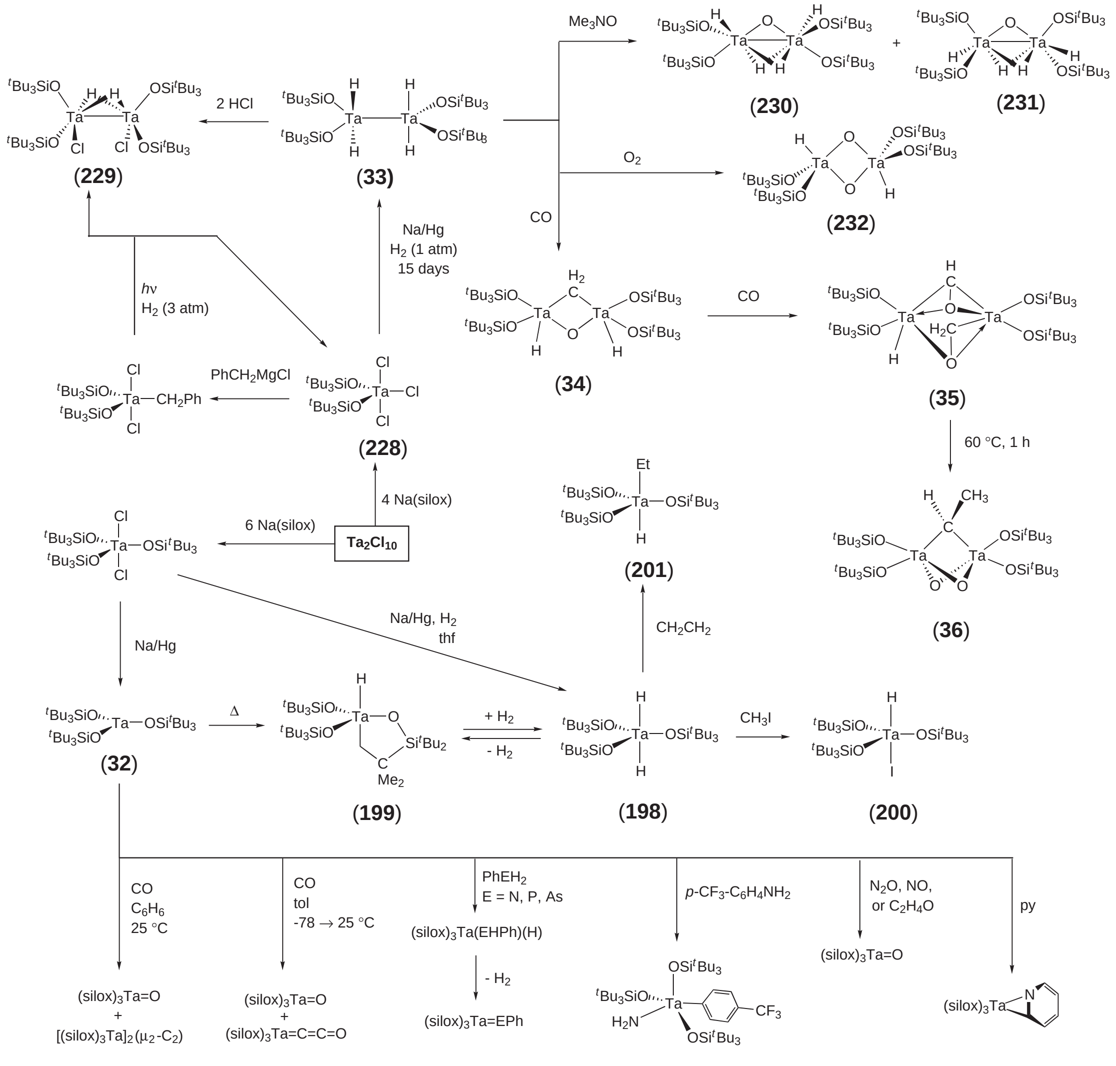
The harder, more electronegative character of silox = $Bu^t_3SiO^-$ ligands has allowed isolation of reactive Ta^{IV}– and Ta^V–hydrido complexes (see Section 4.5.2.7.1 for Ta^V).[65] Photolysis of $(silox)_2Cl_2Ta^VCH_2Ph$ under H_2 (3 atmos) afforded a mixture of $(silox)_2Ta^VCl_3$ and binuclear $[(silox)_2Ta^{IV}Cl]_2(\mu_2\text{-}H)_2$ ((**228**), (**229**); Scheme 44).[65] Reduction of (**228**) with Na/Hg under H_2 (1 atmos) for 15 days afforded (**229**) as an intermediate which reacted further to binuclear $[(silox)_2Ta^{IV}(H)_2]_2$ (**33**). The latter exhibited D_{2d} point symmetry and a direct Ta—Ta bond. (**33**) can be converted to (**229**) with HCl. Oxidation of (**33**) with Me_3NO furnished the μ_2-oxo binuclear hydrides (**230**), (**231**) (C_2 isomers). Oxidation of (**33**) with O_2 provided di-μ_2-oxo bridged (**232**). The reactivity of these binuclear hydrido complexes has been explored in the context of critical C—O bond-breaking and C—H and C—C bond-making events in the Fischer–Tropsch process for production of hydrocarbons from CO and H_2. The facile processes which interchange Ta—H and H—H bonds (Scheme 44) can be viewed as a σ-bond metathesis mechanism, driven by the electrophilicity of the $16e^-$ species *trans*-$(silox)_3Ta^VH_2$ (**198**) and the $14e^-$/Ta species $[(silox)_2Ta^{IV}(H)_2]_2$ ($14e^-$) (**33**), assuming silox to be a $3e^-$ donor.[65]

Reduction of $Ta^{III}{}_2Cl_6(SMe_2)_3$ by Na/Hg in the presence of 2 eq bidentate ligand dppp = $Pr^i{}_2P(CH_2)_3PPr^i{}_2$ under H_2 (4 atmos) provided $[(dppp)Ta^{IV}(H)Cl]_2(\mu_2\text{-}S)(\mu_2\text{-}H)_2$ in 70% yield (**233**).[543] Although the hydrido ligands were not detected crystallographically, NMR data supported the proposed structure. Product ethane was detected in the synthesis, indicating that S—C bond cleavage had occurred to convert a bridging SMe_2 ligand to a bridging thio ligand. On the other hand, an equivalent synthesis with the closely related tetrahydrothiophene reactant $Ta^{III}{}_2Cl_6(SC_4H_8)_3$ produced $[(dppp)Ta^{III}H_2]_2(\mu_2\text{-}H)_2$. NMR and IR spectral data is consistent with (**234**). These synthetic reactions are obviously complex.

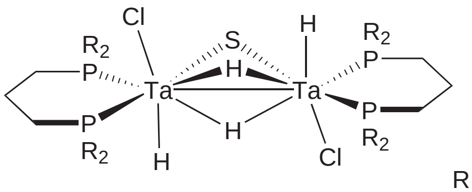
The reaction of Cp^*TaCl_4 with 2 eq Bu_3SnH provided $[Cp^*TaCl_2]_2(\mu_2\text{-}H)_2$ in high yield.[544]

4.5.4 NIOBIUM(III) AND TANTALUM(III)

Synthetic and structural aspects of many binuclear M^{III} species are discussed in Chapter 4.9.



Scheme 44



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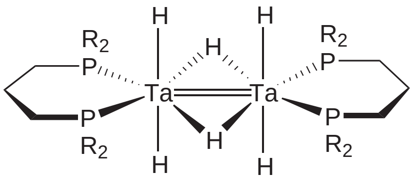


R = ^{i}Pr

(234)

4.5.4.1 Carbon Donor Ligands

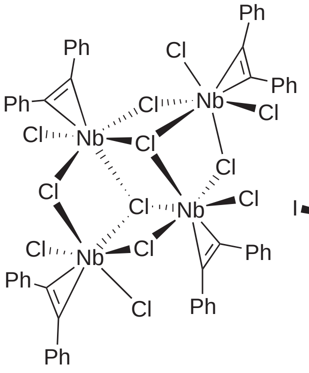
The reactions of $NbX_3(dme)_n$ (X = Cl, Br) with alkynes in solvents thf or dme led to $Nb^{III}X_3L_2(\eta^2\text{-RC}{\equiv}\text{CR})$ (L_2 = 2 thf, dme).[545] $NbCl_3(dme)(RC{\equiv}CR)$ reacted with $Na(S_2CNR'_2)$ to give $Nb(RC{\equiv}CR)(S_2CNR'_2)_3$.[546] The related complex $NbCl_3(dme)(\eta^2\text{-PhCH}{=}\text{NCH}_2\text{Ph})$ features a bidentate imine ligand.[547]

Reaction of $[\mathrm{Nb}^{-\mathrm{I}}(\mathrm{CO})_6]^-$, $\mathrm{F_3CC{\equiv}CCF_3}$, and pyHBr in thf led to $[\mathrm{Nb}^{\mathrm{III}}(\eta^2\text{-}\mathrm{F_3CC{\equiv}CCF_3})(\mathrm{py})\mathrm{Br_4}]^-$.[548] On the other hand, reaction of $\mathrm{Nb^{V}{}_2Cl_{10}}$ with $\mathrm{PhC{\equiv}CPh}$ provided $[\mathrm{Nb^{III}Cl_3}(\eta^2\text{-}\mathrm{PhC{\equiv}CPh})]_4$ (**235**).[549] The tetrameric structure of the $\mathrm{Nb_4Cl_6}$ core may be regarded as a distorted double hexahedron with two corners missing.

The salts $[\mathrm{M^{III}I_2L_6}]\mathrm{I}$ ($\mathrm{L = CNBu^t}$) resulted from the oxidation of $[\mathrm{M}^{-\mathrm{I}}(\mathrm{CO})_6]^-$ with $\mathrm{I_2}$ in the presence of L in dry thf.[550,551] The structures may be described as bicapped trigonal prisms with ligands I capping two of the tetragonal planes (**236**). In wet thf, protons induced formation of $[\mathrm{NbI_2L_4}(\eta^2\text{-}\mathrm{Bu^tHNC{\equiv}CNHBu^t})]\mathrm{I}$ where two of the isonitrile ligands may be considered to have approached sufficiently close to couple. Variation of conditions allowed isolation of $\mathrm{NbX_3L_3}$ ($\mathrm{X = Br, I}$).[551]

Treatment of $\mathrm{Na}[\mathrm{M}^{-\mathrm{I}}(\mathrm{CO})_2(\mathrm{dmpe})_2]$ with $\mathrm{Pr^i{}_3SiCl}$ produced the carbyne species $[\mathrm{M^{III}}({\equiv}\mathrm{COSiPr^i{}_3})(\mathrm{CO})(\mathrm{dmpe})_2]$, which reacted with an equivalent of $\mathrm{Me_3SiCl}$ to give the η^2-acetylene complex $[\mathrm{M^I}(\mathrm{Me_3SiOC{\equiv}COSiPr^i{}_3})(\mathrm{dmpe})_2\mathrm{Cl}]$ (see Section 4.5.6.1.3).[552–555] The Ta compound reacted with aqueous HCl to yield the salt $[\mathrm{Ta^{III}H}(\mathrm{HOC{\equiv}COH})(\mathrm{dmpe})_2\mathrm{Cl}]\mathrm{Cl}$ containing hydrido and dihydroxyacetylene ligands.[556]

Cotton and co-workers have reported a number of $\mathrm{Nb^{III}}$–alkyne complexes of varying nuclearity.[557–562] Clusters incorporating both cyclic (square) and "C-shaped" $\mathrm{C_4Ph_4}$ moieties have been observed. The anion $[\mathrm{Nb_4OCl_8(C_4Ph_4)_2}]^{2-}$ (**237**) was prepared by reduction of $\mathrm{NbCl_3(PhCCPh)(thf)_2}$ with Na/Hg or by reduction of $\mathrm{NbCl_4(thf)_2}$ with Mg in the presence of PhCCPh, yielding salts with $\mathrm{Na^+}$ or $[\mathrm{Mg_2Cl_3(thf)_6}]^+$ counterions, respectively.[557] The anion contains a rectangular $\mathrm{Nb_4}$ unit (Nb–Nb = 2.605(3), 3.340(3) Å) with an oxygen at the center of the rectangle (mean Nb–O = 2.118 Å). The longer Nb–Nb edges are bridged by two Cl ligands. The shorter Nb–Nb edges are clasped by a C-shaped PhC–C(Ph)C(Ph)–CPh chain that is perpendicular to the $\mathrm{Nb_4O}$ plane. The C—C distances in this chain are essentially equal at 1.458(9) Å.[557] The electronic structure and bonding in the anion (**237**) were considered by theoretical methods, and results were consistent with assignment of a formal oxidation state of III for each of the Nb atoms.[558]



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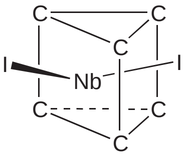

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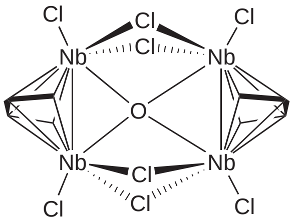

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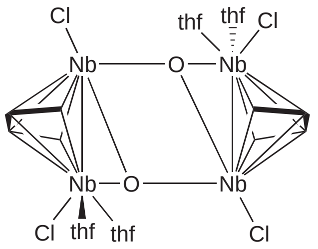


Ph groups on $\mathrm{C_4Ph_4}$ units not shown

(238)

The salt $[\mathrm{Nb_2Cl_3(C_4Ph_4)(thf)_4}]_2[\mathrm{Nb_4OCl_8(C_4Ph_4)_2}]$ contains an anion identical to (**237**). The cation incorporates major features of one half of anion (**237**).[559] A related species $[\mathrm{Nb_4O_2Cl_4(Ph_4C_4)_2(thf)_4}]$ (**238**), containing the $\mathrm{Nb_2(Ph_4C_4)}$ cores observed in (**237**), has also been prepared.[560] The two equivalent $[\mathrm{Nb_2(Ph_4C_4)Cl_2(thf)_2}]$ units of (**238**) are bridged by two oxo ligands.

Reduction of $\mathrm{Nb_2Cl_{10}}$ with $\mathrm{Bu^n{}_3SnH}$ followed by addition of PhCCPh produced the salt $[\mathrm{Bu^n{}_3Sn}][\mathrm{Nb_6Cl_{19}(Ph_4C_4)_3}]$ in moderate yield.[561] The anion features a central triangular $\mathrm{Nb_3}(\mu_3\text{-}\mathrm{Cl})(\mu_2\text{-}\mathrm{Cl})_3$ cluster (Section 4.5.4.4, c.f. (**254**)) with a $(\mu_2\text{-}\mathrm{Cl})_3\mathrm{NbCl_2}(cyclo\text{-}\mathrm{C_4Ph_4})$ unit attached to each of the central Nb atoms. Those units are *pseudo*-octahedral (assuming that the *cyclo*-$\mathrm{C_4Ph_4}$ ligand occupies a single coordination site).

The species $\mathrm{NbCl_3(dme)(PhC{\equiv}CR)}$[545,563] provide a convenient entry into tris (pyrazolyl)-borate-supported $\mathrm{Nb^{III}}$ complexes with alkyne ligands. Thus, reaction of $\mathrm{NbCl_3(dme)(PhC{\equiv}CR)}$ CR) (R = Me, Et, $\mathrm{Pr^n}$) with KTp* in thf produced $\mathrm{Tp^*NbCl_2(PhC{\equiv}CR)}$ in high yield.[49,564] An X-ray structure of $\mathrm{Tp^*NbCl_2(PhC{\equiv}CMe)}$ revealed that the alkyne ligand lies in a molecular mirror plane, consistent with solution phase NMR data. The barrier to alkyne rotation in these species was investigated.[565] $\mathrm{Tp^*NbCl_2(PhC{\equiv}CR)}$ reacted with 2 eq LiMe to give the methylated derivatives Tp*$NbMe_2$(PhC≡CR).[49,564] The activity of these species as ethylene polymerization catalysts was examined.[566]

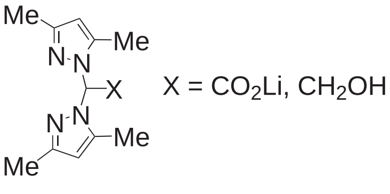
Tp*$NbCl_2$(PhC≡CMe) reacted with 1 eq RMgCl (R = Et, CH_2Ph) to yield Tp*NbCl(R)(PhC≡CMe).[161,567] Tp*NbCl(Et)(PhC≡CMe) featured an interesting α-agostic interaction in the ethyl group, apparently a result of the bulky Tp* ligand preventing a more conventional β-agostic interaction.[161,567] In contrast, Tp*NbCl(CH_2Ph)(PhC≡CMe) did not display the same α-agostic interaction. Thermolysis of Tp*NbCl(Et)(PhC≡CMe) led to Tp*NbCl(Me)(PhC≡CEt), formed via exchange of the α-agostic Et ligand and the Me substituent of the coordinated alkyne.[161,568] Significantly, Tp*NbCl(CH_2Ph)(PhC≡CMe), which did not display an α-agostic interaction, did not undergo the equivalent rearrangement.[161,568]

On the other hand, the complex Tp*NbCl($CHMe_2$)(PhC≡CMe) displayed evidence of both α- and β-agostic interactions.[569,570] X-ray diffraction revealed a β-agostic interaction in the solid state, while ^1H NMR in solution was consistent with the presence of a dynamic equilibrium between α- and β-agostic forms. This interpretation was supported by the observation of a thermodynamic isotope effect in favor of the α-agostic form in the partially deuterated species Tp*NbCl($CH(CD_3)_2$)(PhC≡CMe).[569,570] Finally, treatment of Tp*TaCl(Et)(PhC≡CMe) with LiMe in ether produced the mixed methyl–ethyl tantalum species Tp*Ta(Me)(Et)(PhC≡CMe).[571] This possessed a single α-agostic interaction occurring exclusively at the ethyl group.

4.5.4.2 Nitrogen and Phosphorous Donor Ligands

Reaction of $NbCl_3(dme)_n$ with an excess of bidentate bis(pyrazol-1-yl)methane ligands L provided binuclear complexes $[NbCl_3L]_2$.[572,573] Reaction with alkynes converted these species to mononuclear complexes $NbCl_3L(\eta^2$-RC≡CR). These, in turn, reacted with $Na(S_2CNR'_2)$ to give Nb(RC≡CR)$(S_2CNR'_2)_3$.[546] Reaction of $NbCl_3$(RC≡CR) with tridentate tris(pyrazol-1-yl) methane ligands L and one eq $AgBF_4$ provided salts [$NbCl_2L$(RC≡CR)][BF_4]. All species were characterized spectroscopically.

The anionic scorpionate ligand LiL (LH = bis(3,5-dimethylpyrazol-1-yl)acetic acid; (**239**)) and its reduced ethanol form reacted with $NbCl_3(dme)(\eta^2$-RC≡CR$'$) to produce $LNb^{III}Cl_2(\eta^2$-RC≡CR$'$).[574] The alkyne ligands are *trans* to one of the pyrazole rings of the tridentate ligands. Compounds proposed to have the binuclear structures $[LNbCl]_2(\mu_2\text{-}Cl)_2$ were also reported.



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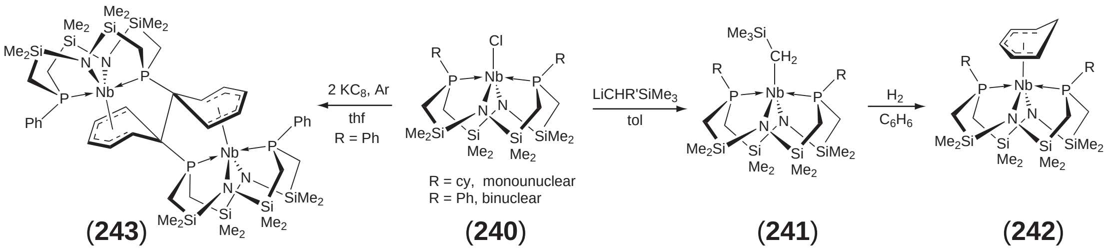
Reduction of *mer*-$[N_2N]Ta^VCl_3$ (**80**) with excess Na/Hg in the presence of alkynes produced $[N_2N]Ta^{III}Cl$(RC≡CR).[137,575]

Treatment of $Li_2{}^R[P_2N_2]$ ($^R[P_2N_2]^{2-}$ = $[RP(CH_2SiMe_2NSiMe_2CH_2)_2PR]$, R = cy, Ph) with $NbCl_3(dme)_2$ yielded species of stoichiometry $^R[P_2N_2]Nb^{III}Cl$ ((**240**); Scheme 45). The R = cy derivative was structurally characterized as mononuclear in the solid state, while the R = Ph derivative was proposed to exist as a Cl-bridged dimer in the solid state on the basis of magnetic susceptibility measurements.[576] The Cl ligand was substituted by reaction with $LiCH_2SiMe_3$ to provide $^R[P_2N_2]NbCH_2SiMe_3$ (**241**).[576] Hydrogenolysis of the latter in benzene resulted in formal hydride addition to a solvent molecule and formation of the π-complexes $^R[P_2N_2]Nb(\eta^5\text{-}C_6H_7)$ (**242**).[577] Reduction of $^{Ph}[P_2N_2]NbCl$ with KC_8 under N_2 produced dinitrogen complex $\{^{Ph}[P_2N_2]Nb\}_2(\mu\text{-}\eta^1{:}\eta^1\text{-}N_2)$ ((**212**); Scheme 41, Section 4.5.3.1.3). In the absence of N_2, the product was ((**243**), Scheme 45) where reduced phenyl rings from each $^{Ph}[P_2N_2]$ unit were coupled and also coordinated to the second Nb center.[578]

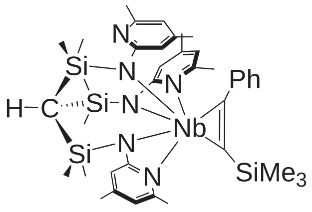
Treatment of $NbCl_3(PhC{\equiv}CSiMe_3)$ with Li_3L (LH_3 is a tris(amino-pyridine) ligand) in hex produced $LNb(PhC{\equiv}CSiMe_3)$ (**244**), with two of the aminopyridinato arms coordinated at the amido and pyridine N atoms, but the third coordinated at the amido N atom only.[579]

$Nb_2Cl_6(tmeda)_2$ reacted with 1 eq of the potassium salt of *tris*(2,2$'$,2$''$-pyrrolyl)methane K_3L to afford the novel binuclear species $[LNb(thf)]_2$ (**245**).[580] The salt $[Nb_4Cl_{11}(K(thf)_2)_2][L_2NbK]_2$ was also



Scheme 45

isolated and contains mixed-valence $[Nb_4Cl_{11}(K(thf)_2)_2]^{2+}$ cations and polymeric $[L_2NbK]^-$ anions. In contrast, reaction with the lithium salt Li_3L produced mononuclear $[Li(thf)_4]_2[L_2Nb^{IV}]$ (**246**).[580]



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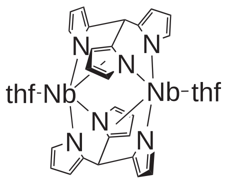

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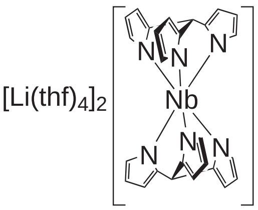

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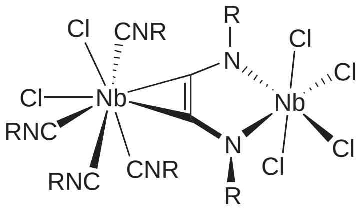
Reaction of the binuclear Nb^{II}-tmeda species (**207**) with the lithium salt of 2,2′-dipyridylamide in thf produced (**247**) (Scheme 40). The bridging μ_2-η^2:η^2-*C*,*N*-$[C_5H_4N]^-$ and μ_2-$[N\text{-}2\text{-}C_5H_4N]^{2-}$ ligands were formed from C—N bond cleavage.[581] In contrast, reaction with $KNPh_2$ produced (**248**) from ligand C—H bond cleavage.[581,582] Two other species were isolated from the reaction mixture: diamagnetic (**249**) (formally $Nb^{IV}Nb^0$) and $[(tmeda)ClNb]_2(\mu_2\text{-}Cl)_3$ ($Nb^{III}Nb^{II}$), which is related structurally to (**207**).[582]



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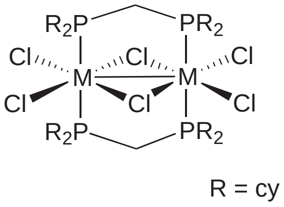

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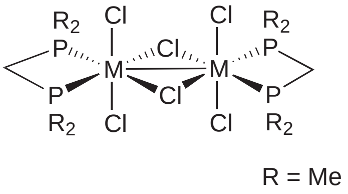

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4.5.4.3 Oxygen Donor Ligands

Reduction of $(silox)_3Ta^VCl_2$ (silox = $Bu^t{}_3SiO$) with Na/Hg in thf provided the synthon $(silox)_3Ta^{III}$ ((**32**), Scheme 44).[63,583] It cyclometalated thermally to (**199**), complicating some of its chemistry. It reacted readily with unsaturated ligands to provide $(silox)_3TaL$ ($L = RC{\equiv}CR$, $R_2C{=}CR_2$, H_2CO). Ligands L also included η^2-cycles such as py and benzene which were activated for reaction (Scheme 44). Reduction of $(silox)_3Nb^VCl_2$ with Na/Hg in the presence of 4-picoline afforded $(silox)_3Nb(\eta^2\text{-N,C-NC}_5H_4Me)$ which acts as an effective source of '$(silox)_3Nb^{III}$'.[507] For example, both this Nb complex and $(silox)_3Ta^{III}$ abstracted an O atom from N_2O, NO, and C_2H_4O to provide $(silox)_3M^VO$ (Scheme 44) and both compounds are useful deoxygenation reagents.[584] In these systems, Ta^{III} has a greater affinity for picolines than does Nb^{III}. Consequently, an equimolar solution of $(silox)_3Ta^{III}$ and $(silox)_3Nb(\eta^2\text{-N,C-NC}_5H_4Me)$ in benzene led to isolation of 1 eq of $(silox)_3Ta(\eta^2\text{-N,C-NC}_5H_4Me)$ and 0.5 eq of binuclear $[(silox)_3Nb]_2(\mu_2\text{-}\eta^2\text{:}\eta^2\text{-}C_6H_6)$.[507]

Reduction of $Nb^V{}_2(OAr)_{10}$ ($ArOH = 3,5\text{-}Me_2\text{-}C_6H_3OH$) with 1 eq Na/Hg in the presence of dmpe led to the salt *trans*-$[Nb^{III}(OAr)_2(dmpe)_2][Nb^V(OAr)_6]$ which featured a low-spin d^2 cation.[585] Oxidation of $Nb^{II}(OAr)_2(dmpe)_2$ provided the same product.

Binuclear $[L^{Me}Nb^{V}Cl_2]_2$ ((**114**), Scheme 31) which featured the linked trianionic aryl ligand H_3L^{Me} = (**115**) (R = Me) reacted with $LiBHEt_3$ in thf to form binuclear $[Li_4(thf)_4Cl_2]$ $\{[L^{Me}Nb^{III}(thf)]_2(\mu_2\text{-H})(\mu_2\text{-Cl})\}$ (**250**).[197] This contrasted with the analogous reaction with R = Bu^t when activation of N_2 occurred with formation of (**116**) (Scheme 31).

The ability of the calixarene complex (**12**) with its $Nb^{III}{=}Nb^{III}$ bond to induce four-electron reduction of N_2, aldehydes, and ketones has been discussed in Sections 4.5.2.1.2, 4.5.2.2.4, and 4.5.2.4.5.(ii) (Scheme 32).

4.5.4.4 Halo Ligands

Reduction of Ta_2Cl_{10} with the potassium graphite KC_8 in Et_2O in the presence of py provided *mer*-$TaCl_3(py)_3$.[586] The edge-sharing bioctahedral compound $[(SC_4H_8)(\eta^2\text{-PhC}{\equiv}\text{CPh})Cl_2Nb^{III}]_2(\mu_2\text{-Cl})_2$ reacted with py to produce $[pyH][Nb^{III}Cl_4(py)(PhC{\equiv}CPh)]$.[587]

Reduction of $[L_2Cl_2Ta^{III}]_2(\mu_2\text{-Cl})_2$ (L = 4-Me-py) by pulse radiolysis in O_2-free MeCN led to a transient $[Ta^{2.5+}]_2$ species of suggested bond order 1.5 ($\sigma^2\pi^2\delta^{*1}$).[588,589]

Reactions of $M_2Cl_6(SMe_2)$ with isocyanides RNC provided products of stoichiometry $M_2Cl_6(RNC)_6$. These contain, in fact, dimerized isocyanides as bridging ligands (**251**).[590]

Reduction of $Cp^*Ta^VX_4$ (X = Cl, Br) with 4 eq Na/Hg in tol produced $[Cp^*Ta^{III}]_2(\mu_2\text{-X})_4$ ((**226**), Scheme 43).[591]

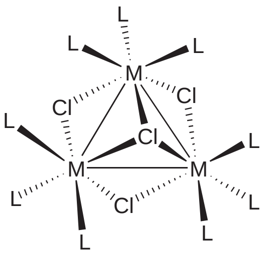
DFT calculations have been used to understand the detailed electronic and geometric structures of the binuclear d^2–d^2 anions $\{[M^{III}X_3]_2(\mu_2\text{-X})_3\}^{3-}$ (X = halo) which feature face-sharing bioctahedral stereochemistry.[592] The occupation of the trigonal $t_{2g}(a_1 + e)$ single-ion orbitals determined the geometry and the extent of MM bonding. The $[a_1e + a_1e]$ spin-triplet state (where complete delocalization of the σ and δ_π electrons occurs in a M═M bond) was found to be the global minimum. The predictions of relatively short MM internuclear distances were in good agreement with available structural data.

Binuclear compounds $M^{III}{}_2Cl_6L_4$ (L = neutral ligand) usually exhibit edge-sharing bioctahedral geometry. Thus, $[(SC_4H_8)(\eta^2\text{-PhC}{\equiv}\text{CPh})Cl_2Nb^{III}]_2(\mu_2\text{-Cl})_2$ has been isolated in the reaction of $Nb_2Cl_6(SC_4H_8)_3$ and $PhC{\equiv}CPh$.[587] Two isomeric forms have been observed with bidentate ligands. For example, reduction of M_2Cl_{10} with 4 eq Na/Hg in the presence of dcpm = bis (dicyclohexylphosphorano)methane provided $[Cl_2M]_2(\mu_2\text{-Cl})_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-dcpm})_2$ (**252**).[593] The steric size of the cyclohexyl substituents appears to favor isomer (**252**) rather than (**253**) (observed for L = dmpm [594]).

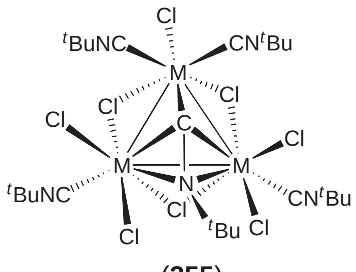
On the other hand, binuclear compounds $M^{III}{}_2Cl_6L_3$ (L = neutral ligand) exhibit face-sharing bioctahedral stereochemistry. The tetrameric compound $Ta_4Cl_{12}(SC_4H_8)_2(dppe)_2$ was comprised of two of these units linked by two dppe ligands, $\{[Cl_2Ta]_2(\mu_2\text{-Cl})_2(\mu_2\text{-SC}_4H_8)\}_2(\mu_2\text{-}\eta^1{:}\eta^1\text{-dppe})_2$.[595]

The complex pathways encountered in the use of $Nb^{IV}Cl_4(thf)_2$ under reducing conditions have been discussed. In particular, the conversion from edge-sharing bioctahedral $[(PR_3)_2Cl_2Nb^{III}]_2(\mu_2\text{-Cl})_2$ complexes to face-sharing bioctahedral $\{[(PR_3)Cl_2Nb^{III}]_2(\mu_2\text{-Cl})_3\}^-$ anions to triangular $\{[(PR_3)Cl_2Nb^{III}]_3(\mu_3\text{-Cl})(\mu_2\text{-Cl})_3\}^-$ anions was highlighted.[596]

The $M_3(\mu_3\text{-Cl})(\mu_2\text{-Cl})_3$ core (C_{3v}) in the latter anion is found in Nb_3Cl_8 and in clusters surrounded by nine terminal ligands, three per M atom (**254**).[597,598] In $\{[(PEt_3)Cl_2M^{III}]_3(\mu_3\text{-Cl})(\mu_2\text{-Cl})_3\}^-$, the six electrons from the $M^{III}(d^2)$ centers are involved formally in three M—M bonds. In $[(PMe_2Ph)_2ClNb]_3(\mu_3\text{-Cl})(\mu_2\text{-Cl})_3$, the intermetallic distances in the $Nb^{III}Nb^{II}{}_2$ core are ~0.15 Å shorter than in the above anions, consistent with the extra two electrons occupying a singly degenerate bonding orbital. An electronically dissimilar cluster $Nb_3Cl_8(CNBu^t)_5$ (**255**) featured a μ_3-$CNBu^t$ ligand.[599] Spectroscopic characterization favored the presence of a $Nb^{III}{}_2Nb^{II}$ core.



(**254**)



(**255**)

4.5.4.5 Hydrido Ligands

In the mid-1980s, dihydrogen was discovered to act as a ligand,[464] and at about the same time, large temperature-dependent H–H couplings were observed in certain polyhydrido complexes. Systems derived from the complexes $Cp_2M^VH_3$ played important roles in understanding the latter phenomenon.[466–468] For example, the Ta^{III} cation $[Cp_2Ta^{III}(\eta^2\text{-}H_2)(CO)]^+$ was a dihydrogen complex while $[Cp_2Ta^V(H)_2(P(OMe)_3))]^+$ was a dihydrido complex and exhibited exchange couplings. The greater electron-releasing tendency of the phosphite ligand favors the dihydrido tautomer. Cations such as $[Cp_2M(\eta^2\text{-HD})L]^+$ ($L = CO$, $P(OEt)_3$, PMe_2Ph) were synthesized from reactions of $Cp_2M^VH_3$ with L followed by deuteration with acid. For $[Cp_2Nb(\eta^2\text{-HD})(PMe_2Ph)]^+$, *endo* and *exo* isomeric forms (similar J_{HD}; very different J_{HP}) were observed at 203 K, consistent with freezing of the HD rotation ($\Delta G^{\neq}{}_C = 46$ kJ/mol). Detailed NMR studies for this and related systems such as $M = Ta$, $L = CO$ demonstrated that no kinetic isotope effect is observed for the classical rotation of H_2 in these complexes. This strongly suggested that rotational tunneling of coordinated H_2 ligands (whose classical rotation is blocked on the NMR timescale) is the origin of the quantum mechanical H–H coupling observed in d^2 metal polyhydrides in which one *d*-based orbital only is available for back-donation.

$Ta^{IV}(H)_2Cl_2L_4$ ($L = PMe_3$) was reduced by Na/Hg in the presence of additional L under Ar to $Ta^{III}(H)_2ClL_4$.[214] This exhibited pentagonal bipyramidal stereochemistry with axial ligands L and *cis* ligands H (HTaH, 66°; TaH, 1.8 Å). It reacted with N_2 to provide $[L_3ClH_2Ta^V]_2$ $(\mu_2\text{-}\eta^1{:}\eta^1\text{-}N_2)$. Reduction of $[L_2Cl_2Ta^{IV}]_2(\mu_2\text{-}H)_2(\mu_2\text{-}Cl)_2$ with Na/Hg gave $[L_2Cl_2Ta^{III}]_2(\mu_2\text{-}H)_2$ whose non-hydrogen framework exhibited D_{2d} point symmetry and resembles closely that of $W^{II}{}_2Cl_4L_4$ with its quadruple bond.[540]

Reaction of $[Cp^*Ta^{III}]_2(\mu_2\text{-}X)_4$ ($X = Cl$, Br) (**226**) with 4 eq $LiBH_4$ in Et_2O yielded $[Cp^*Ta^{III}]_2(\mu_2\text{-}\eta^2,\eta^2\text{-}B_2H_6)_2$ ((**256**), Scheme 43).[600] Intermediate species with one B_2H_6 ligand were detected. The free $[B_2H_6]^{2-}$ anion is unknown.

Reaction of $M^I(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl$ with aqueous HCl produced $[M^{III}H(HOC{\equiv}COH)(dmpe)_2Cl]Cl$ by hydrolysis of $Me_3SiOC{\equiv}COSiMe_3$ and oxidative addition of H^+ to the metal center.[556,601] The related species $Ta^{III}H(Me_3SiOC{\equiv}COBF_3)(dmpe)_2Cl$ with an anionic acetylene ligand was prepared from reaction of $Ta(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl$ with HBF_4.[601] Similarly, treatment of $Ta\{(Me_3Si)(Me)NC{\equiv}COSiMe_3\}(dmpe)_2Cl$ with aqueous acid produced $[TaH\ (MeHNC{\equiv}COH)(dmpe)_2Cl]Cl$.[602]

4.5.5 NIOBIUM(II) AND TANTALUM(II)

Using zero electron kinetic energy photoelectron spectroscopy, the structures of Nb_3N_2 and its cation were assigned as C_{2v}. The two N atoms bridge two sides of an isosceles triangle of Nb atoms.[603] Similar conclusions have been drawn for the Nb_3C_2 system and for $[M_3O]^x$ ($x = -1$, 0, +1).[604]

The synthon *trans*-$NbCl_2(py)_4$ was prepared by reduction of $NbCl_4(thf)$ in thf/py.[605] *trans*-MCl_2L_4 ($L = PMe_3$) were isolated from reduction of M_2Cl_{10} with Na/Hg in Et_2O in the presence of excess L.[538] Analogous species *trans*-$MCl_2(dmpe)_2$ resulted from reduction of $MCl_4(dmpe)_2$ in thf. The bromo complex $TaBr_2L_4$ ($L = PMe_2Ph$) displayed a *cis* geometry and was distorted significantly towards a bicapped tetrahedron.[606]

Reduction of $Nb^V(OAr)_5$ ($ArOH = 4\text{-}Me\text{-}C_6H_4OH$ or $3,5\text{-}Me_2\text{-}C_6H_3OH$) with 6 eq Na/Hg in the presence of 4 eq dmpe led to *trans*-$Nb^{II}(OAr)_2(dmpe)_2$.[585] Spectroscopic and magnetic characterization were consistent with low-spin d^3 centers.

Photolysis of $Cp^*Ta^I(CO)_4$ in solution in the presence of RSSR species produced diamagnetic $[Cp^*(CO)_2Ta^{II}]_2(\mu_2\text{-}SR)_2$.[607] For $R = Ph$, the $Ta_2(\mu_2\text{-}SPh)_2$ core is folded with *cis* Cp* ligands and *syn*-equatorial Ph substituents.

Diamagnetic, binuclear species $[Cp'(CO)_2M^{II}](\mu_2\text{-}Cl)_2$ were produced by reduction of M^{III} precursors by Na/Hg in thf.[608] Their structures feature folded $M_2(\mu_2\text{-}Cl)_2$ centers which contrast with the related species $[Cp(ArC{\equiv}CAr)_2Nb^{II}](\mu_2\text{-}Cl)_2$ ($Ar = 4\text{-}Me\text{-}C_6H_4$) whose $Nb_2(\mu_2\text{-}Cl)_2$ core is planar.

Heating of $[Nb^{III}Cl_3(tmeda)]_2$ with 6 eq $LiN(Pr^i)_2$ in thf produced $(tmeda)_3Nb^{II}{}_2Cl_5Li$ (**207**) whose Nb_2 core is based upon a face-sharing bioctahedron (Scheme 40).[483]

The classic cluster cores $[M_6X_8]^{x+}$ and $[M_6X_{12}]^{y+}$ contain an M_6 octahedron with halo ligands *X* bridging all faces or edges, respectively. They continue to be important building blocks for materials design (lead references for these and related clusters include).[609–611]

4.5.6 NIOBIUM(I) AND TANTALUM(I)

4.5.6.1 Carbon Donor Ligands

4.5.6.1.1 Carbonyl ligands

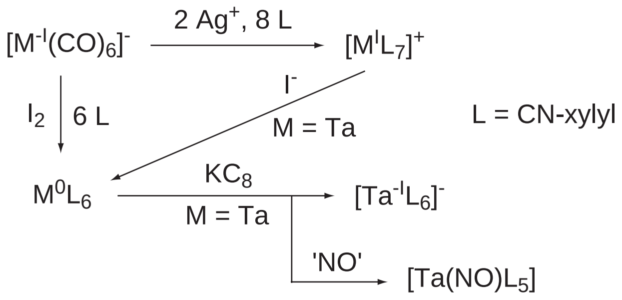
Gas phase photoelectron spectroscopy has investigated the bonding in $(\eta^5\text{-}C_5H_4R)M(CO)_4$ (R = H, $SiMe_3$, $COCH_3$).[612] The lowest energy ionizations arise from the two orbitals that are occupied by the electrons of the formal d^4 metal configuration. However, the absorption bands are dominated by extensive CO stretching vibrational progressions indicative of extensive carbonyl character in the valence electronic structure. This influence diminishes any trends in properties with metal substitution V → Nb → Ta down Group 5 or with substitutions in the Cp rings.

Photolysis of $LM(CO)_4$ (L = Cp or C_9H_7 (indenyl)) in polyethylene matrices under a high pressure of reactant gas provided a range of photoproducts.[613] Under helium, $LM(CO)_3$ and $LNb(CO)_2$ were observed while, under N_2, $LM(CO)_3(N_2)$ and $LNb(CO)_2(N_2)_2$ were seen. Under H_2, the classical dihydrides $LM^{III}(CO)_3(H)_2$ were observed for Cp, whereas the non-classical dihydrogen complex $(\eta^5\text{-}C_9H_7)Nb^I(CO)_3(\eta^2\text{-}H_2)$ was observed in the Nb-indenyl system. $CpM(CO)_3(Xe)$ was characterized in supercritical Xe solution at room temperature.[614]

The anions $[M^{-I}(CO)_6]^-$ are oxidized by H^+ and X_2 (X = Cl, Br, I) to the anions $\{[(CO)_4M^I]_2(\mu_2\text{-}X)_3\}^-$.[615]

4.5.6.1.2 Isocyanide ligands

Routes to homoleptic isocyanide complexes have been defined in thf (Scheme 46).[616] $[M^IL_7]^+$ (L = xylyl isocyanide) are fluxional in solution but do not exchange ligand with free L. The cation in $[ML_7][BF_4]$ is very crowded with the shortest Me···Me contact being 4.59 Å. The TaC_7 core has a geometry intermediate between the capped octahedron (C_{3v}) and capped trigonal prism (C_{2v}).



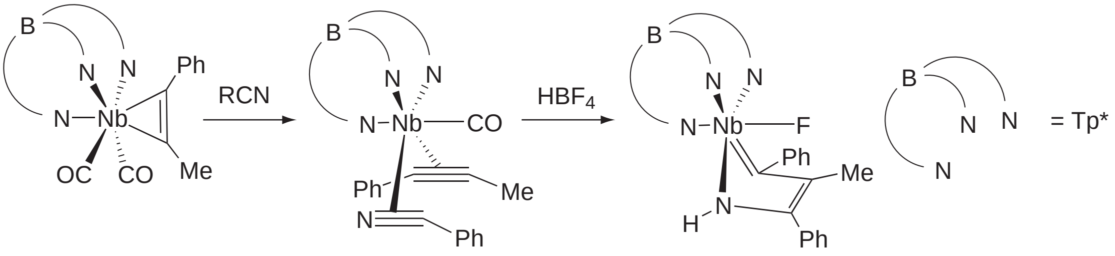
Scheme 46

Mixed carbonyl–isocyanide species $MCl(CO)(CNR)(dmpe)_2$ (M = Nb, R = Me, cy, Bu^t; M = Ta, R = Me, Et, Bu^t) were isolated from the photolysis of a suspension of $MCl(CO)_2(dmpe)_2$ in tol in the presence of CNR.[617–619] $NbCl(CO)(CNBu^t)(dmpe)_2$ exhibited Cl-capped trigonal prismatic stereochemistry with a severely bent CNC linkage (144°), consistent with a carbene-like isocyanide moiety (Nb—C=NR↔Nb=C=NR).[617] The bis(isocyanide) $TaCl(CNMe)_2(dmpe)_2$ was prepared by reduction of $TaCl_4(dmpe)_2$ in the presence of CNMe, and displayed bent CNC angles close to 120°.[618] Capped trigonal prismatic *cis*-$NbI(CO)_2(CNR)_2(dppe)$ (R = Bu^t, cy) were isolated by reaction of $NbI(CO)_4(dppe)$ with CNR in thf at low temperature.[550,620] Complexes $Nb^IX(CO)_2(CNR)_4$ have been identified in the systems $[Nb(CO)_6]^-/CNR/X_2$ which generate Nb^{III} systems (see Section 4.5.4.1).[551] The equivalent Ta system for R = Bu^t led to $TaI(CO)_3(CNR)_3$ and $TaI(CO)_3(CNR)(dppe)$.

4.5.6.1.3 Alkyne ligands

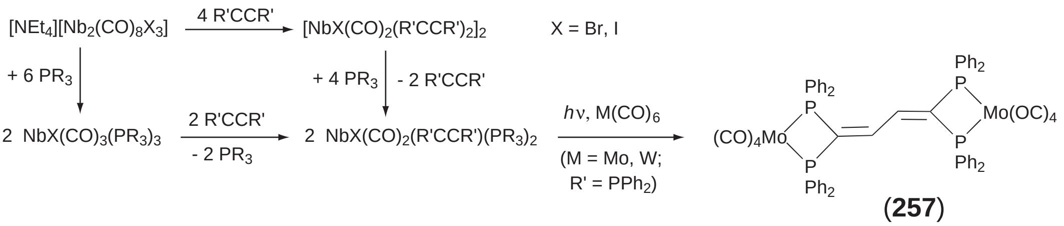
Treatment of the η^2(4e)-alkyne complex $Tp^*Nb(CO)_2(PhC{\equiv}CMe)$ with nitriles $RC{\equiv}N$ (R = Me, Et, Ph) led to the chiral mixed η^2(3e)-alkyne/η^2(3e)-nitrile complexes

$Tp^{*}Nb^{I}(CO)(PhC{\equiv}CMe)(RC{\equiv}N)$ (Scheme 47).[621] The assigned formal electron counts on the alkyne and nitrile ligands are compatible with detailed ^{13}C NMR data. Electrochemical studies indicated that an equilibrium existed in solution between the η^2(3e)-alkyne/η^2(3e)-nitrile and η^2(4e)-alkyne/η^1(2e)-nitrile complexes.[50] PhCN is displaced by PMe_2Ph or $PhC{\equiv}CMe$ to provide $Tp^{*}Nb(CO)(PhC{\equiv}CMe)(PMe_2Ph)$ and $Tp^{*}Nb(CO)(PhC{\equiv}CMe)_2$, respectively. Protonation of these species can induce intramolecular redox coupling reactions to produce Nb^V metallocycles (e.g., Scheme 47).



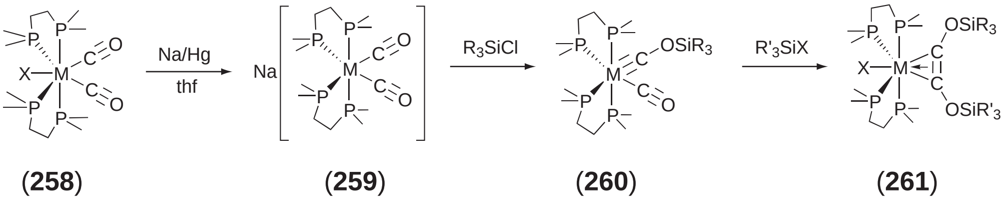
Scheme 47

Excess alkyne $RC{\equiv}CR$ reacted with $TaI(CO)_3L_3$ ($L = PR'_3$) to form six-coordinate complexes $TaI(CO)_2L_2(\eta^2\text{-}RC{\equiv}CR)$.[622] ^1H and ^{13}C solution spectra were compatible with the alkynes acting as 4e donors. The solid state structure of *all-trans*-$TaI(CO)_2(PMe_3)_2(\eta^2\text{-}RC{\equiv}CR)$ was established. Similar reactions produced equivalent Nb compounds (Scheme 48).[623–625] Although no unambiguous structural assignment was possible, ^{13}C NMR shift data favored halo-bridged binuclear structures for $[NbX(CO)_2(RC{\equiv}CR)_2]_2$. Each alkyne formally donates 3e for the metal to attain an 18e count. In a complex photo reaction, *all-trans*-$NbI(CO)_2(PMe_2Ph)_2(Ph_2PC{\equiv}CPPh_2)$ reacted with $M(CO)_6$ to form a bridging tetra-phosphorane ligand with a buta-1,3-diene backbone ((**257**); Scheme 48).[626]



Scheme 48

Lippard and co-workers have demonstrated the reductive coupling of CO ligands at M centers to generate coordinated alkyne ligands. Treatment of $[M(CO)_2(dmpe)_2Cl]$ ((**258**), Scheme 49) with 40% Na/Hg in thf followed by addition of Me_3SiCl produced $[M(Me_3SiOC{\equiv}COSiMe_3)(dmpe)_2Cl]$ (**261**). Earlier work in this area has been reviewed,[627] and similar chemistry has been observed for related vanadium species.[628–630]



Scheme 49

The mechanisms and intermediates involved in this process were investigated in detail.[552–555, 629–633] Two-electron reduction of (**258**) with 40% Na/Hg in thf produced the M^{-1} intermediate Na[M-$(CO)_2(dmpe)_2$] (**259**) with *cis*-carbonyl ligands.[553] Addition of 1 eq only of Pr^i_3SiCl to (**259**) afforded the M^{III} siloxycarbyne-carbonyl species $[M(CO)(\equiv COSiPr^i_3)(dmpe)_2]$ (**260**).[552,553] Further addition of Me_3SiCl caused coupling of the carbyne and carbonyl ligands of (**260**) to yield the asymmetric acetylene complex $[M(Me_3SiOC{\equiv}COSiPr^i_3)(dmpe)_2Cl]$ (**261**).[552,553] Ta forms of (**258**)–(**261**) were all characterized by X-ray crystallography.

The kinetics of reaction of the carbyne–carbonyl complex $[M(CO)(\equiv COSiPr^i_3)(dmpe)_2]$ (**260**) with Me_3SiCl were investigated in detail. The rate determining step was proposed to be electrophilic attack of the silyl reagent upon the terminal CO ligand.[554,555] The silylated intermediate was modeled by addition of $AlEt_3$ to a solution of (**260**) to generate the Lewis acid adduct $[M(COAlEt_3)(\equiv COSiPr^i_3)(dmpe)_2]$. A comparison of structural parameters for this adduct and for (**260**) ($R_3 = Bu^tPh_2$) revealed that addition of $AlEt_3$ to the terminal CO ligand resulted in a reduction in the C—Ta—C angle and a reduction in distance between the two metal-bound carbon fragments.[554,555]

The coupling of carbonyl–isocyanide and isocyanide–isocyanide ligands at Ta centers has also been demonstrated. Treatment of $[Nb(CNMe)(CO)(dmpe)_2Cl]$ with Na/Hg in thf followed by addition of 2 eq Me_3SiCl gave the cross-coupled product $[M\{(Me_3Si)(Me)NC{\equiv}COSiMe_3\}(dmpe)_2Cl]$, which contained the previously unknown $RR'NC{\equiv}COR$ ligand ($R = SiMe_3$, $R' = Me$).[602,619] The coupling of two isocyanide ligands has been demonstrated in similar systems.[602,618]

4.5.6.2 Nitrogen Donor Ligands

A range of seven-coordinate complexes $MX(CO)_4L$ (L = bidentate diamine; X = Cl, I) were prepared via oxidative halogenation of $[M^{-I}(CO)_6]^-$ anions with $[LH_2]Cl_2$ or with methyl viologen diiodide in the presence of L.[634] Similar species were obtained by oxidation of $[Ta(CO)_6]^-$ with I_2 also in the presence of L.[635]

Addition of $AgBPh_4$ to M^0L_3 ($L = Pr^iN{=}CH\text{-}CH{=}NPr^i$) led to $[M^IL_3]^+$ which exhibit distorted octahedral stereochemistries[636] However, these mononuclear 16e d^4 complexes are diamagnetic. A DFT study suggested that the t_{2g} orbitals are strongly split in the D_3 local symmetry with the e subset being stabilized strongly by π back-bonding. A configuration e^4 is consistent with the observed diamagnetism. The LUMO is a ligand-based orbital which is occupied in M^0L_3 (see Section 4.5.7.2).

4.5.6.3 Phosphorous Donor Ligands

4.5.6.3.1 *Polyphospho ligands*

Thermolysis of $LNb(CO)_4$ ($L = \eta^5\text{-}1,3\text{-}Bu^t\text{-}C_5H_3$) and P_4 in decalin afforded the triple-decker sandwich complexes $[LNb]_2(\mu_2\text{-}\eta^6{:}\eta^6\text{-}P_6)$ (**262**).[637,638] Although the P_6 ligand is essentially planar, it exhibits pronounced in-plane distortions with three pairs of P—P interatomic distances of 2.105(2), 2.116(3), and 2.347(3) Å. Extended Huckel calculations suggested that the distortion is due to the presence of two electrons in nearly degenerate $2e_2'$ antibonding orbitals.

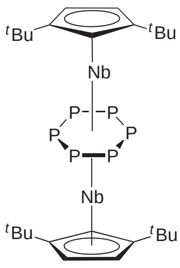
In contrast, photolysis of the equivalent Ta system produced $L(CO)_2Ta(\eta^4\text{-}P_4)$ (**263**), $[L(CO)Ta]_2(\mu_2\text{-}\eta^2{:}\eta^2\text{-}P_2)_2$ (**264**), and $[L_3(CO)_3Ta_3(P_2)_2]$.[639] In turn, photolysis of (**263**) and $Cp^*Nb(CO)_4$ allowed isolation of $Cp^*(CO)Nb(\mu_2\text{-}\eta^6{:}\eta^6\text{-}P_6)Ta(CO)L$ (c.f. (**262**)) and $[L(CO)Ta][Cp^*(CO)_2Nb][Cp^*Nb](\mu_3\text{-}\eta^2{:}\eta^1{:}\eta^1\text{-}P_2)_2$ (**265**) with its novel coordination mode for P_2.

$Cp^*Fe^{II}(\eta^5\text{-}P_5)$ contains the pentaphosphacyclopentadienyl ligand. Brief photolysis in the presence of $LTa(CO)_4$ led to $[Cp^*Fe](\mu_2\text{-}\eta^5{:}\eta^1\text{-}P_5)[Ta(CO)_2L]$ with the *cyclo*-P_5 ligand coordinated terminally to the Ta fragment.[640] Photochemical or thermal elimination of CO led to (**266**) with cleavage of a P—P bond.

Reaction of $LTa^I(CO)_4$ with P_4 in decalin at 190 °C provided $[LTa]_3(\mu_3\text{-}P_2)(\mu_3\text{-}P_4)$ which could be converted to $[LTa]_3(\mu_3\text{-}P_2)(\mu_3\text{-}P_4)\{Fe(CO)_4\}$ (**267**).[641] The latter features a P_2 ligand in the phosphido–phosphinidene coordination mode.

4.5.6.3.2 *Phosphorane ligands*

New or improved preparations have been reported for seven-coordinate complexes $MCl(CO)_2L_2$ (L = dmpe, depe, dppe, dbpe; depe = 1,2-bis(diethylphosphino)ethane, dbpe = 1,2-bis(dibutylphos-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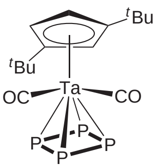
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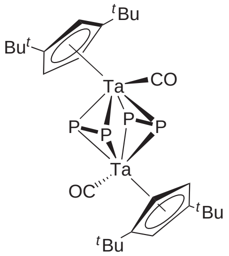
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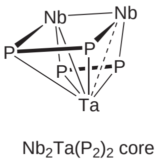

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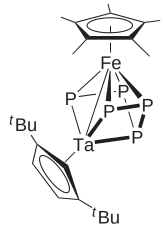
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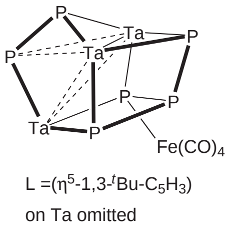


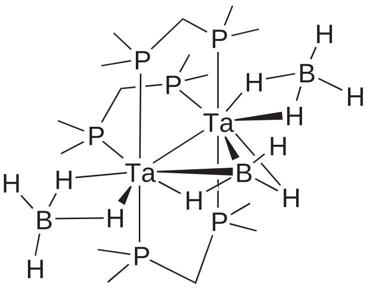
(267)

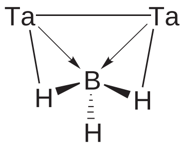
phino)ethane), $MCl(CO)_3L'$ ($L' = MeP(CH_2CH_2CH_2PMe_2)_2$), and $NbX(CO)_3(PMe_2Ph)_3$ (X = Cl, Br, I, CN).[629,642–644] The capped trigonal prismatic complex $Ta^{I}Cl(CO)_3L_3$ (L = PMe_3) was obtained in two ways: by elimination of H_2 from $Ta^{III}Cl(H)_2L_4$ in Et_2O in the presence of CO (3 atmos) or by oxidation of $[Ta^{-I}(CO)_6]^-$ by $Ta^{V}{}_2Cl_{10}$ in Et_2O in the presence of L.[645] In the latter reaction, the Ta^{V} chloride acted as a 2e oxidant and chloro ligand source and was converted to an uncharacterized Ta^{III} product. The bromo and iodo analogs $TaX(CO)_3L_3$ were obtained by oxidation of $[Ta^{-I}(CO)_6]^-$ by X_2 in Et_2O in the presence of L. Related compounds $MX(CO)_4$(dppe) and $MX(CO)_2(dppe)_2$ were synthesized similarly via oxidative halogenation with pyHX.[620,646] The Ta^{I} (d^4) complexes exhibited low levels of paramagnetism, possibly due to population of low-lying triplet states.[647] A wider series of Nb^{I} species $NbX(CO)_3(PR_3)_3$ (X = Cl, Br, I) was obtained by similar means.[620] Treatment of $\{[(CO)_4M^{I}]_2(\mu_2\text{-}X_3)\}^-$ with tripodal ligand $L = Bu^tSi(CH_2PMe_2)_3$ under reflux in dme/thf afforded $LM^{I}I(CO)_3$ of capped trigonal prismatic stereochemistry (cap = I).[648]

The electrochemistry of a range of these seven-coordinate species was explored.[649] Chemical reactions followed oxidation or reduction of most species. However, the more highly substituted complexes $MX(CO)_2(dppe)_2$ (X = H, Cl, Br, I) exhibited chemically reversible 1e⁻ oxidations in CH_2Cl_2/Bu_4NPF_6 and the 17e $[M^{II}X(CO)_2L_2]^+$ cations were characterized by EPR spectroscopy ($A(^{93}Nb) \sim 113$ G for X = Cl, H).

$Ta^{III}H_2ClL_4$ (L = PMe_3) reacted with C_2H_4 to furnish $Ta^{I}Cl(\eta^2\text{-}C_2H_4)L_4$ and with CO to provide $Ta^{I}Cl(CO)_3L_3$.[214] The latter is a capped trigonal prism with Cl capping a quadrilateral face comprised of one CO and the three ligands L.

The reaction of Ta_2Cl_{10} with $LiBH_4$ in the presence of dmpm produced the BH_3-bridged complex $[(\eta^2\text{- }BH_4)Ta^{I}]_2(\mu_2\text{-}BH_3)(\mu_2\text{-dmpm})_3$ (**268**).[650] The bonding scheme in (**269**) was suggested as the best description of the detailed structural features. It includes donation of *d*-electron density from the Ta^{I} centers to the electron-deficient bridging BH_3 ligand.


(268)


(269)

4.5.6.4 Oxygen Donor Ligands

Treatment of *trans*-$Nb^{II}(OAr)_2(dmpe)_2$ (ArOH = 3,5-Me_2-C_6H_3OH) with CO (1 atmos) led to $Nb^{I}(OAr)(CO)_2(dmpe)_2$.[585] The stereochemistry is monocapped trigonal prismatic with ArO as the capping group. The CNbC angle is only 66.7(2)°.

The anions $[M^{-I}(CO)_6]^-$ are oxidized by the acetylacetonato (acac) complexes of Ni^{II} and Fe^{III} in thf to seven-coordinate $M^{I}(acac)(CO)_4(thf)$.[651] The thf ligand is labile and easily substituted.

4.5.6.5 Hydrido Ligands

Protonation of $[M^{-I}(PF_3)_6]^-$ by conc. H_2SO_4 yielded volatile, thermally unstable species $[M^IH(PF_3)_6]$.[652,653] The formulation was consistent with ^1H NMR and mass spectrometric studies for M = Nb. For M = Ta, ^1H NMR detected a septet at δ, −8.7 ppm, consistent with coupling of six equivalent PF_3 ligands to ligand H in a fluxional seven-coordinate species.

UV irradiation of $[Ta^{-I}(CO)_6]^-$ in the presence of dppe provided, after chromatography on silica gel, the complex $Ta^IH(CO)_4(dppe)$ whose ^1H and ^{31}P NMR were interpreted in terms of an H-capped octahedral structure.[654] Photolysis converted this complex to $TaH(CO)_2(dppe)_2$ which, in the solid state, exhibited pentagonal bipyramidal stereochemistry with axial CO ligands.[644]

4.5.7 NIOBIUM(0) AND TANTALUM(0)

There has been a longstanding interest in readily available sources of Nb^0 and Ta^0. The failure to generate paramagnetic species $M^0(CO)_6$ contrasts with the stability of $V^0(CO)_6$ and also with the ready generation of $[M^{-I}(CO)_6]^-$ and $[M^{-III}(CO)_5]^{3-}$.

4.5.7.1 Carbon Donor Ligands

Co-condensation of M(g) with CO provided $M(CO)_6$ at 4 K.[655] Analysis of ^{93}Nb hyperfine structure in the EPR spectrum of $Nb(CO)_6$ indicated that this 17e species was axial, being distorted from octahedral by Jahn–Teller effects associated with the expected ${t_{2g}}^5$ low spin configuration. Spectra of the Ta system were very broad, apparently due to a significant quadrupolar interaction with ^{181}Ta allowing forbidden $\Delta M_I = \pm 2$ transitions to appear strongly. DFT calculations suggested that $Ta(CO)_6$ would also be axially distorted.[656]

Routes to homoleptic isocyanide complexes have been defined in thf (Scheme 46).[616] M^0L_6 (L = xylyl isocyanide) are fluxional in solution but do not exchange ligand with free L.

Co-condensation of Nb(g) with tol has allowed isolation of $Nb^0(\eta^6\text{-tol})_2$.[657] The tol rings are parallel with eclipsed Me groups.

4.5.7.2 Nitrogen Donor Ligands

Co-condensation of M(g) with N_2 provided $M(N_2)_6$ at 4 K.[655] Their EPR spectra were analyzed in the same manner as that described for the $M(CO)_6$ complexes discussed above (see Section 4.5.7.1).

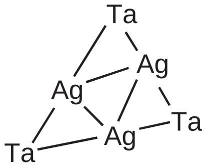
Reduction of Ta_2Cl_{10} with 10 eq sodium napthalenide in dme at −60 °C followed by addition of the bidentate α-diimine ligand $L = Pr^iN{=}CH\text{-}CH{=}NPr^i$ led to Ta^0L_3.[636] The Nb equivalent was more conveniently obtained from $NbCl_4(thf)_2$ and Na sand. These 17e complexes adopted D_3 stereochemistries (distorted octahedral) with planar ligands L and were paramagnetic (μ_{eff}, 1.66 down to 11 K for M = Ta). However, their EPR spectra were broad with no resolved hyperfine structure. This was consistent with a DFT investigation which indicated that the HOMO is ligand-based.

4.5.7.3 Phosphorous Donor Ligands

Co-condensation of M(g) and dmpe allowed isolation of *pseudo*-octahedral $M^0(dmpe)_3$.[658]

The 17e metal-based radical $Ta^0(CO)_4(dppe)$ was formed via hydrogen atom extraction from $Ta^IH(CO)_4(dppe)$.[659] In solution, this radical abstacted halogen atoms from many organic halides RX to give $Ta^IX(CO)_4(dppe)$. $Ta^0(CO)_4(dppe)$ existed in solution as an equilibrium mixture of monomer and dimer $[(dppe)(CO)_3Ta](\mu_2\text{-CO})_2$. The latter is the form stable in the solid state. While no crystal structures are available, DFT calculations indicated a stable *pseudo*-octahedral stereochemistry for the monomer and several possible $(\mu_2\text{-CO})_2$ structures for the dimer.[656] Each of the latter featured linear, semi-bridging carbonyls supporting a weak, delocalized Ta—Ta interaction.

Reaction of anions $[M^{-I}(CO)_4(dmpe)]^-$ with AgX (X = weakly coordinating anions $[NO_2]^-$, $[BF_4]^-$) provided hexanuclear clusters $Ag_3M_3(CO)_{12}(dmpe)_3$ (**270**) of D_3 point symmetry.[635] These clusters were proposed to feature novel $Ag^0{}_3M^0{}_3$ cores on the basis of (i) relatively high energy ν(CO) vibrational bands; (ii) the Ag–Ag separation being similar to that in the metal; and (iii) the following chemical reactivity: $Ag^0{}_3M^0{}_3(CO)_{12}(dmpe)_3 + 3\ HI(g) \rightarrow 3\ Ag^0(s) + 3\ M^{I}I(CO)_4(dmpe) + 3/2\ H_2(g)$. The alternative products $Ag^{I}I$ and $M^{I}H(CO)_4(dmpe)$ were expected for a $Ag^{I}{}_3M^{-I}{}_3$ cluster.



Ag_3Ta_3 core of $Ag_3Ta_3(CO)_{12}(dmpe)_3$

(270)

4.5.8 NIOBIUM(–I) AND TANTALUM(–I)

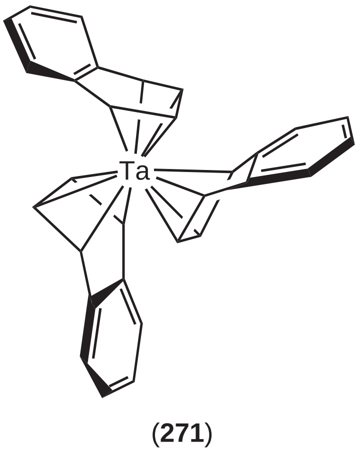
4.5.8.1 Carbon Donor Ligands

Detailed emission, excitation, and vibrational spectra have been reported for $[Ph_4P][Ta^{-I}(CO)_6]$.[660] The emission spectrum was assigned to a single ligand field transition and contained a resolved vibrational progression in the symmetric Ta–C stretching normal mode.

Reductive carbonylation of $Nb^{IV}Cl_4(thf)_2$ by NaAr (Ar = napthalenide, anthracenide) in the presence of CO (1 atmos) provided improved access to $[Nb^{-I}(CO)_6]^-$ as the $[NEt_4]^+$ salt.[653] An equivalent procedure is available for $[Ta^{-I}(CO)_6]^-$.[652] Reaction of $[M^{-III}(CO)_5]^{3-}$ with Ph_3SnCl provided salts $[NEt_4]_2[M^{-I}(CO)_5(SnPh_3)]$. Protonation of $[M^{-I}H(CO)_5]^{2-}$ in NH_3(l) provided $A[M^{-I}(CO)_5(NH_3)]$ (A = $AsPh_4$ or NEt_4) which could be converted to salts of $[M^{-I}(CO)_5(CNBu^t)]^-$. In addition, reaction of $[Ta(CO)_5(NH_3)]^-$ with L = PR_3, $AsPh_3$, $SbPh_3$ in NH_3/thf at 0 °C provided salts $[NEt_4][Ta^{-I}(CO)_5L]$.[661] Reaction with CN^- yielded $[NEt_4]_2[Ta^{-I}(CO)_5(CN)]$.

Routes to homoleptic isocyanide complexes have been defined in thf (Scheme 46).[616] Ta^0L_6 (L = xylyl isocyanide) was reduced by AC_8 (A = K, Cs) to $[Ta^{-I}L_6]^-$. This anion appears to be octahedral. Its ^{13}C NMR resonance occured at ~210 ppm, the most downfield shift observed for a diamagnetic homoleptic isocyanide complex. Reaction with the NO source N-methyl-N-nitroso-*p*-toluenesulfonamide provided $Ta^{-I}(NO)L_5$ whose essentially linear NbNO fragment is consistent with the formal presence of ligand NO^+. Direct nitrosylation of $[M^{-I}(CO)_6]^-$ with 2 eq $[NO][PF_6]$ in the presence of L in CH_2Cl_2 at −60 °C provided *cis*-$[M^{-I}(NO)_2L_4]^+$.[662] The reaction represents a rare example of non-oxidative displacement of all CO ligands from a homoleptic carbonylmetalate.

Reduction of $NbCl_4(thf)_2$ or Ta_2Cl_{10} with alkali metal arenides in ether solvents at −60 °C provided, after work-up, salts of the homoleptic arene complexes $[M^{-I}L_3]^-$ ((**271**); L = η^4-naphthalene, 1-4-η^4-anthracene).[663,664]



(271)

4.5.8.2 Phosphorous Donor Ligands

Reductive carbonylation of $NbCl_4(thf)_2$ or Ta_2Cl_{10} by NaAr (Ar = napthalenide, anthracenide) in the presence of PF_3 allowed isolation of salts of $[M^{-I}(PF_3)_6]^-$.[652,653] The observation of a doublet of decets in the ^{17}F NMR spectrum (^{31}P, $I = 1/2$; ^{93}Nb, $I = 9/2$) of the Nb anion was consistent with octahedral stereochemistry in solution. $[Nb(PF_3)_6]^-$ is almost one volt more difficult to oxidize than is $[Nb(CO)_6]^-$.

$CoCp^*_2$ reduced $M^{I}I(CO)_4(dppe)$ to form the salt $[CoCp^*_2][M^{-I}(CO)_4(dppe)]$.[635] Reduction of $LM^{I}I(CO)_3$ (L = tripodal ligand $Bu^tSi(CH_2PMe_2)_3$) with 2 eq NaH followed by the non-oxidative nitrosylating agent *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide provided *pseudo*-octahedral $LM^{-I}(CO)_2(NO)$.[648,665]

4.5.8.3 Hydrido Ligands

Protonation of $[M^{-III}(CO)_5]^{3-}$ in $NH_3(l)$ at −70 °C allowed isolation of the salts $[NEt_4]_2[M^{-I}H(CO)_5]$.[653] $^1H\{^{93}Nb\}$ NMR detected a sharp singlet at δ, −1.89 ppm for $[NbH(CO)_5]^{2-}$, a value similar to that observed for $[TaH(CO)_5]^{2-}$.[652] In addition, the $^{93}Nb\{^1H\}$ NMR spectrum of $[NbH(CO)_5]^{2-}$ (^{13}C, 99 atom%) was a well-resolved sextet, consistent with the presence of a fluxional pentacarbonyl.

4.5.9 NIOBIUM(–III) AND TANTALUM(–III)

Treatment of $[Nb^{-I}(CO)_6]^-$ with Na in $NH_3(l)$ allowed access to $[Nb^{-III}(CO)_5]^{3-}$.[653] Its solution properties are complementary to those of $[M^{-III}(CO)_5]^{3-}$ (M = V, Ta) which have been reported previously.[652,666,667]

4.5.10 ASPECTS OF HETEROGENEOUS CATALYSIS

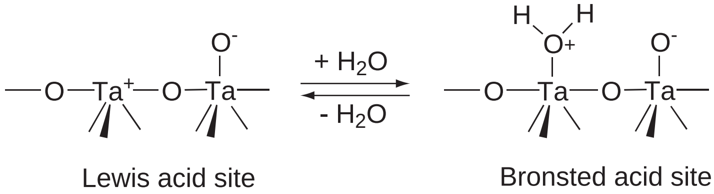
A most significant aspect of the chemistry of niobium and tantalum has been the development of heterogeneous catalysis and its relationship to the surface and bulk properties of the solid supports.[668–679] In this concluding section, molecular connections between fundamental coordination chemistry and surface and bulk properties of solids, particularly the oxides, are emphasized. A broad description of Nb compounds and heterogeneous catalysis is available.[670]

The oxides $M^{V}{}_2O_5$ have complex structures and display extensive polymorphism as a function of temperature. This highlights the challenge of obtaining molecular information about surface reactivity. Reduction leads to further complexity. For example, between $Nb^{V}{}_2O_5$ and $Nb^{IV}O_2$, there exists a homologous series of structurally related phases having the general formula $Nb_{3n+1}O_{8n-2}$ where $n = 5, 6, 7, 8$.[680] In addition, paramagnetic oxides of formula $Nb_{12}O_{29}$ ($12Nb_2O_5 - 2O$) and $Nb_{94}O_{232}$ ($47\ Nb_2O_5 - 3O$) have been reported.[681–683]

The melting points of Nb_2O_5 (1,785 K) and Ta_2O_5 (2,145 K) determine important catalytic properties as surface atoms on crystal planes begin to diffuse at the Tammann temperature, $T_{Tam} = \sim 1/2\ T_{mp}$. Consequently, under typical catalytic reaction conditions (473–873 K), the metal atoms cannot diffuse and so the bulk oxides exhibit acidic properties but not redox ones. In order to change the diffusion properties and reducibility, supported metal oxides or mixed oxides have been targeted.

Another important factor is surface area, as those of bulk $M^{V}{}_2O_5$ are very low (a few $m^2\ g^{-1}$). Therefore, since the early 1990s, there has been an emphasis on synthesis and catalytic testing of mesoporous oxides exhibiting high surface areas (a few hundred $m^2\ g^{-1}$).[684–689]

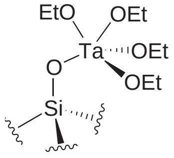
The acidity of bulk and supported Nb_2O_5 was probed by absorption of py. Raman and IR spectroscopy of the adsorbed pyridine indicated that highly distorted surface NbO_6 octahedral sites corresponded to Lewis acid sites (the Raman band between 850 and 1,000 cm^{-1}) and that slightly distorted surface NbO_6 sites, as well as NbO_7 and NbO_8 sites, corresponded to Brønsted acid centers (Raman bands between 500 and 700 cm^{-1}).[690,691] The acidic character of hydrated niobia (niobic acid $Nb_2O_5{\cdot}nH_2O$) depended on calcination temperature. Niobic acid calcined at moderate temperatures of 373–573 K showed acidic character but it became almost neutral when calcined at 873 K.[692] The presence or absence of water determines Lewis or Brønsted acidity of a given metal site (Scheme 50).[693]



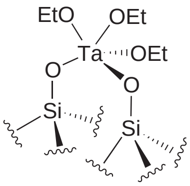
Scheme 50

When the oxides M_2O_5 are supported on other oxides or materials, surface M species can become either acidic or redox centers.[670,694] The supported oxide often shows different catalytic activity from its bulk form. The formation and location of surface oxo species are controlled usually by the substrate's surface hydroxyl chemistry. For example, Ta_2O_5 supported on silica via impregnation exhibited a tetrahedral $(\equiv Si{-}O)_3Ta{=}O$ species which was photoactive.[695] This center showed catalytic photoactivity in the oxidation of CO. The Ta=O bond was activated to an exciton $Ta^{4+}\text{-}O^-$ which reacted with O_2 to form a T-type ozonide $[Ta\text{-}O\text{-}O_2]^-$. This in turn reacted with CO forming the intermediate product $[O_3\text{-}CO]^-$.

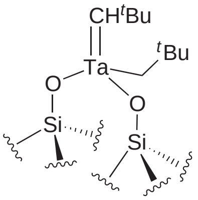
Tantalum can be grafted onto silica surfaces as Ta^V-alkoxo or organometallic species ((**272**)–(**275**)).[696–699] (**272**) is the active phase in epoxidation of allyl alcohols.[696] Similarly, the chemistry of Ta-alkylidene species on silica surfaces has been investigated to provide insights into the elementary reactions occurring at surfaces during heterogeneous catalysis.[699] The reaction of $Ta(=CHBu^t)(CH_2Bu^t)_3$ with a silica dehydroxylated at 500 °C produced a mixture of $(\equiv SiO)_2Ta(=CHBu^t)(CH_2Bu^t)$ and $(\equiv SiO)Ta(=CHBu^t)(CH_2Bu^t)_2$ ((**274**), (**275**), respectively) in an approximately 1:1 ratio.[698] This ratio was found to be dependent on the temperature used for silica dehydroxylation, with higher temperatures favoring the latter species with only one covalent bond to silica (**275**).[697] High-resolution, solid-state 1D and 2D NMR were used to investigate the structures of these surface complexes and results were compared with those for a silsesquioxane molecular analog (**276**).[700] The mixture of (**274**) and (**275**) was active for the stoichiometric cross-metathesis of alkenes.[701] The surface chemistries of $Ta(=CHBu^t)(CH_2Bu^t)_3$ and $Cp_2Ta(=CH_2)(CH_3)$ on partially dehydroxylated silica were compared.[702] The latter was proposed to be converted to the "cation-like" species $Cp_2Ta(CH_3)_2^+$ via addition of a proton from the silica surface.



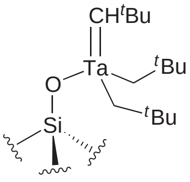
(**272**)



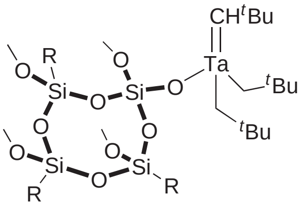
(**273**)



(**274**)



(**275**)

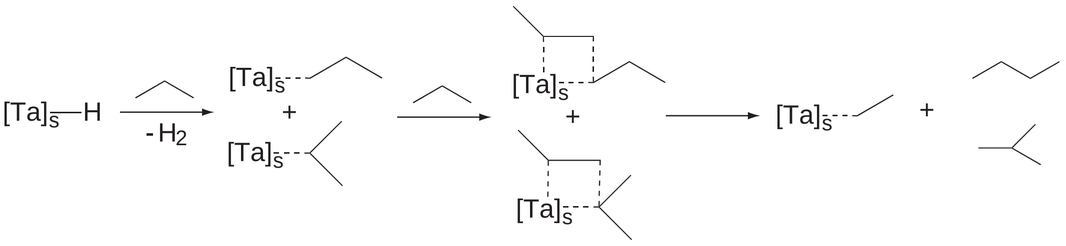


(**276**)

Generation of the surface-bound hydrido complex $(\equiv Si\text{-}O)_2Ta^{III}\text{-}H$ has been particularly well characterized. Treatment of a dehydroxylated silica with $Ta^V(=CHBu^t)(CH_2Bu^t)_3$ followed by H_2 (1 atmos) up to 200 °C provided this center as the major surface species.[703] The hydrido ligand could be exchanged with D by reaction with D_2. The center was highly electrophilic, eliminating CH_4 from MeI. It catalyzed H/D exchange between CH_4 and CD_4 at 150 °C leading to the statistical distribution of all methane isotopomers, indicative of an ability to cleave the C—H bonds of this most thermodynamically stable of alkanes.[704,705] The C—H bonds of cycloalkanes were also cleaved, leading to surface metal–cycloalkyl complexes.[703,706,707] Hydrogenolysis of alkanes was enhanced by $(\equiv Si\text{-}O)_2Ta^{III}\text{-}H$, most notably of ethane, which cannot be cleaved by the corresponding Group 4 metal hydrides.

In addition, the $(\equiv Si\text{-}O)_2Ta^{III}\text{-}H$ center catalyzed the metathesis of alkanes, an unprecedented process affording higher and lower homologs. For example, in the metathesis of propane to ethane and butanes, formation of four-centered intermediates was postulated (Scheme 51).[708] In the first step, the C—H bond is activated to yield $(\equiv Si\text{-}O)_2Ta^{III}\text{-}Pr^n$ and $(\equiv Si\text{-}O)_2Ta^{III}\text{-}Pr^i$

complexes. The subsequent transfer of a Me group from a second propane molecule to these intermediates evolves *n*-butane and *iso*-butane with the formation of ($\equiv$Si-O)$_2$Ta^{III}-Et. This, in turn, yields ethane, regenerating the active site.



Scheme 51

While Nb and Ta containing heterogeneous catalysts have been studied extensively, they have not been widely used as acid catalysts in practice. Recently, Tanabe reported the first application of niobic acid in industry.[709] The redox properties of catalytic materials containing niobium or tantalum are attractive and surely will be utilized in the future.

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4.6
Chromium

P. A. LAY and A. LEVINA
University of Sydney, NSW, Australia

4.6.1 INTRODUCTION

Chromium, molybdenum, and tungsten are the transition metals in Group 6 of the periodic table. Chromium metal has the outer electronic configuration $3d^5 4s^1$ and forms compounds in oxidation states II– to VI+.[1] The extensive organometallic chemistry of Cr is covered in the accompanying *Comprehensive Organometallic Chemistry* series, and this review is generally restricted to the coordination complexes (oxidation states 0 to VI+).

The previous review on Cr in *Comprehensive Coordination Chemistry*(*CCC*) was published in 1987,[1] and covered the literature until 1984 inclusive, as well as some articles published in 1985. Therefore, the current review will mainly consider the literature published between 1985 and 2001 inclusive (as well as some earlier works where appropriate); some important articles published in 2002 were added in revision. The primary literature search for this review was performed with the

SciFinder Scholar 2001 software, using the *Chemical Abstracts* database (with “chromium complexes” or “Cr complexes” as the main search concepts). Given the enormous progress in Cr chemistry since 1985, it will not be possible to cover all of the literature in a comprehensive manner, and only the more completely characterized systems will be discussed. More detailed coverage is provided by series of annual reviews on Cr coordination chemistry (although there are some significant gaps, particularly after 1996).[2–8] In addition, some important developments in Cr chemistry between 1985 and 1995 have been discussed elsewhere.[9] Gas-phase coordination chemistry of transition metal ions, including Cr, has been reviewed recently.[10] A detailed recent review on the relations between chemical properties and biological activities of Cr complexes is available.[11] More specialized reviews will be cited where appropriate.

Some of the major trends in Cr coordination chemistry since the mid-1980s have been the following:

(i) A decrease in the research activity on Cr^{II} complexes (except for the dimers with multiple Cr—Cr bonds, Chapter 4.9).
(ii) A shift of the main interest in Cr^{III} chemistry from the mechanistic studies of ligand-exchange reactions to the syntheses of materials with interesting properties (Volumes 6 and 7), as well as to a possible role of Cr^{III} as an essential micronutrient for humans.[12]
(iii) A dramatic increase of knowledge on the chemistry of Cr^{IV} and Cr^{V} complexes, particularly in relation to their possible roles in Cr^{VI}-induced genotoxicity and carcinogenicity.[13]

The ligand abbreviations[14] are explained in the text or in the footnotes to the tables.

4.6.2 CHROMUIM(VI)

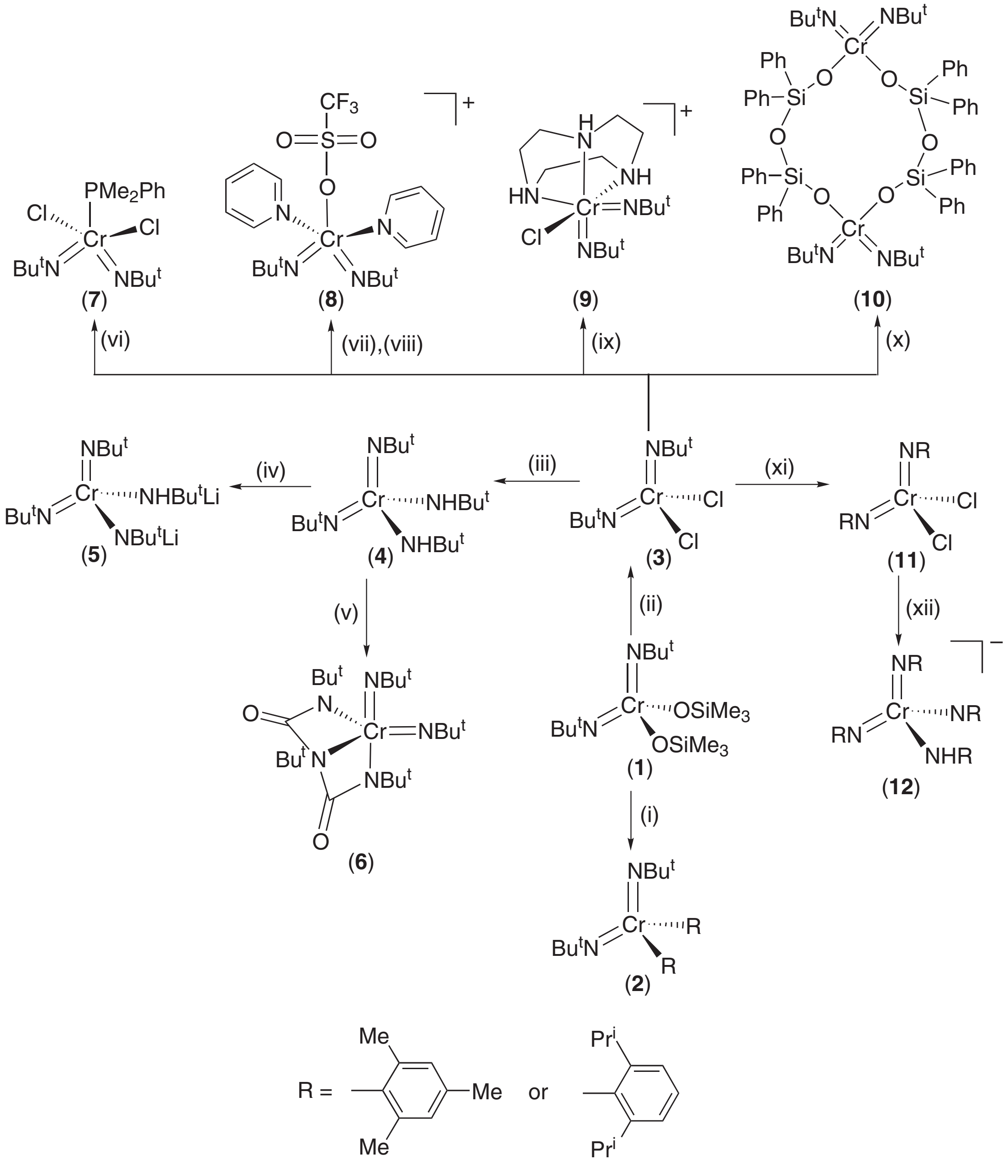
4.6.2.1 C-donor Ligands

Imido complexes of Cr^{VI}, containing alkyl,[15,16] aryl,[17] or alkylidene[18] ligands, are studied extensively as potential catalysts of alkene polymerization (see Section 4.6.5.1.2).[19–21] These complexes are described in the *Comprehensive Organometallic Chemistry* series, and some typical examples for their syntheses are given in Section 4.6.2.2.

4.6.2.2 N- and P-donor Ligands

Since the first synthesis of a Cr^{VI} diimido complex, (**1**) (Scheme 1; Conditions: (i) RMgBr (C_6H_{12}, ~20 °C);[22,23] (ii) BCl_3 (CH_2Cl_2, 0 °C);[24] (iii) $LiNHBu^t$ (MePh, −78 °C);[24] (iv) Bu^nLi (C_6H_{12}/Et_2O, −78 °C);[24] (v) Bu^tNCO (C_6H_{12}, reflux);[25] (vi) Me_2PPh (MePh, ~20 °C);[24] (vii) $Ag(OSO_2CF_3)$ (MeCN, ~20 °C);[24] (viii) Py, ~20 °C;[24] (ix) [9]aneN_3(tacn) (THF, −30 °C);[26] (x) $(Ph_2SiOH)_2O$ (Et_3N/MePh, ~20 °C);[27] (xi) RNCO (C_8H_{18}, reflux);[26] (xii) LiNHR (THF, −78 °C).[29]), by Nugent and Harlow in 1980,[1] extensive coordination chemistry of such complexes (e.g., (**2**)–(**12**) in Scheme 1) has been developed, primarily from studies by Wilkinson and co-workers.[22–28,30–33] Substitution reactions similar to those of (**3**) (Scheme 1) have been observed for diarylimido[26,29] and bis(adamantylimido)[32] Cr^{VI} complexes. Complex (**13**), synthesized from (**3**) via a ligand-exchange process (Scheme 2a), undergoes unusual imido-transfer reactions (e.g., Scheme 2b).[34] A mono-imido complex (**14**) has been synthesized by a nitrosyl-cleavage process (Scheme 2c).[16] Complexes (**2**), (**6**)–(**9**), and (**11**)–(**14**) have been characterized by X-ray crystallography; typical Cr^{VI}—N(imido) bond lengths are 1.62–1.65 Å.[16,22–28,31,32,34] Complex (**14**) is distinguished by a strongly bent imido group (the Cr—N—C angle, 146°; whereas this value is close to 180° for the other Cr^{VI} imido complexes), which was attributed to an oxo-imido π-conflict, based on the results of density functional theory (DFT) calculations.[16] Some of the Cr^{VI} diimido complexes, such as $[Cr(NR)_2Cl_2]$ ($R = 2,6\text{-}C_6H_3Cl_2$ or $2,4,6\text{-}C_6H_2Br_3$), have been used as catalysts for the cyclopropanation of activated monosubstituted alkenes.[35]

A general synthetic method for Cr^{VI} nitrido complexes (e.g., (**15**)–(**20**) in Scheme 3; Conditions: (i) Et_2O, 25 °C; (ii) $[V^{III}(mes)_3(THF)]$, MePh, 65 °C (mes $= 2,4,6\text{-}Me_3C_6H_2$);[36] (iii) $CHCl_3$, 30 °C; (iv) Et_2O, $-90 \rightarrow 28$ °C;[37] (v) MePh, $-35 \rightarrow 25$ °C; (vi) MePh, 30 °C; (vii) C_6H_{12}, $-90 \rightarrow 28$ °C;[38] (viii) C_6H_6, 28 °C; (ix) Et_2O, $-90 \rightarrow 28$ °C.[29]) involves the use of Cr^{III} amides (Section 4.6.5.2.2) and nitrosyls (Section 4.6.7.1) as precursors.[36–38] A slightly different method has been used for the



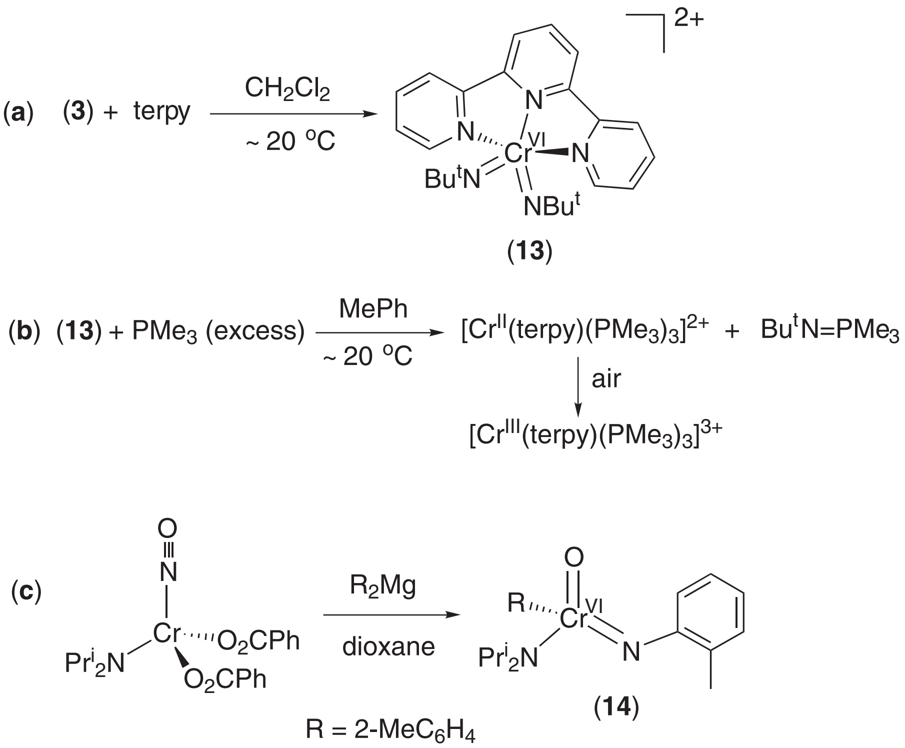
Scheme 1

syntheses of (**21**) and (**22**) (Scheme 3).[29] Complexes (**15**), (**17**), (**21**), and (**22**) have been characterized by X-ray crystallography; typical Cr^{VI}—N bond lengths are 1.54 Å and 1.82–1.84 Å for the nitrido and amido donors, respectively.[29,36,37] Several other Cr^{VI} complexes with amido, imido, and nitrido donors are mentioned in Section 4.6.2.3.1.

4.6.2.3 O- and S-donor Ligands

4.6.2.3.1 Oxo complexes: solution speciation and structural studies

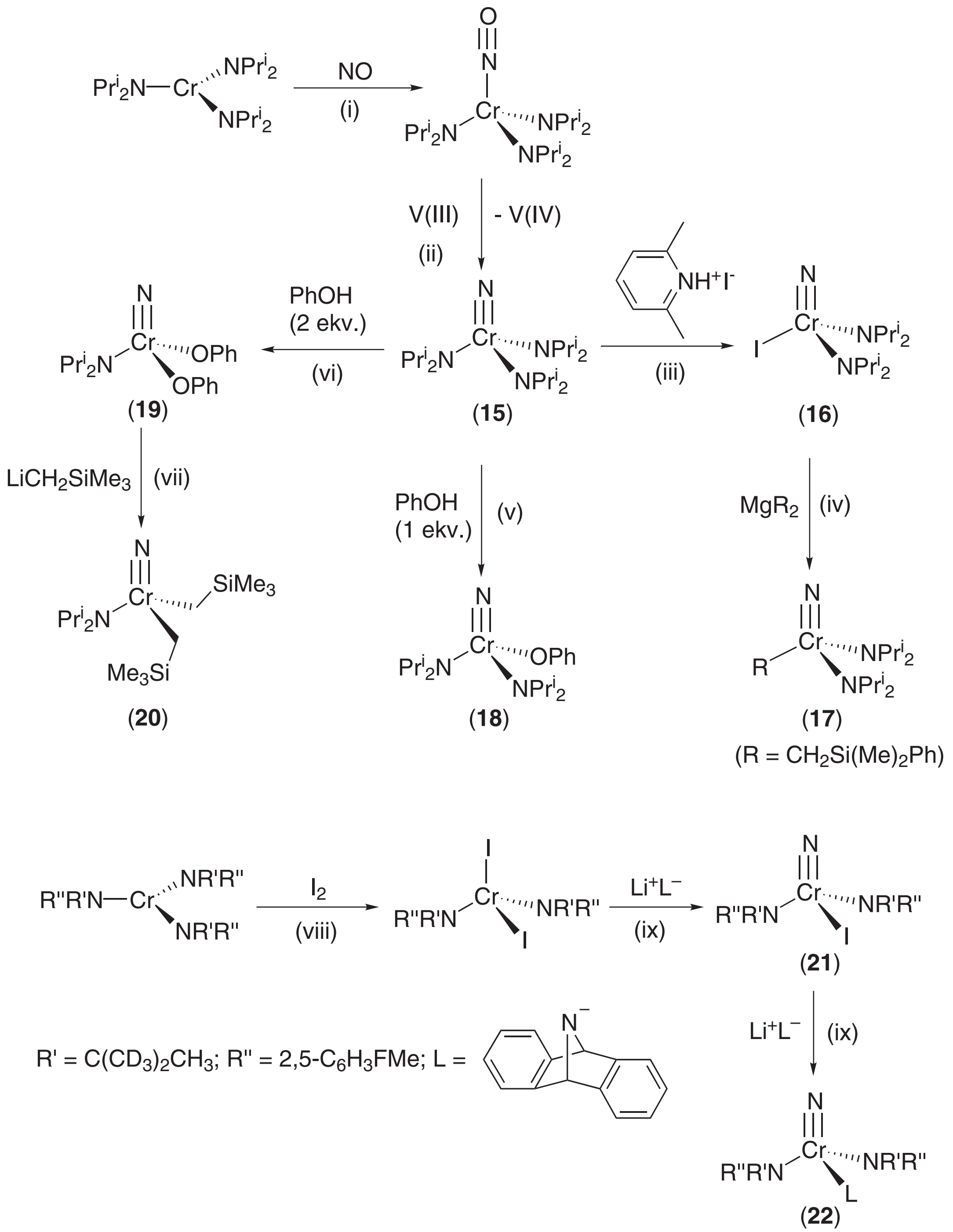
The pH- and concentration-dependent speciation in aqueous solutions involving $[CrO_4]^{2-}$, $[HCrO_4]^{-}$, and $[Cr_2O_7]^{2-}$ as the main components is a key factor in the biological activity of



Scheme 2

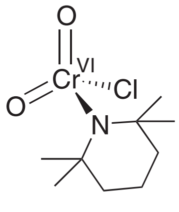
Cr^{VI}, as well as in many of its industrial applications (Sections 4.6.2.3.4 and 4.6.2.3.5). In addition to a large amount of early work (mainly by UV–visible spectroscopy),[1,39] several new methods have been applied recently to studies of this speciation, including: X-ray absorption fine structure (XAFS),[40,41] ^{17}O NMR[42] and Raman[43–45] spectroscopies, and electrospray mass spectrometry (ESMS),[46,47] as well as multivariate analysis of UV–visible spectroscopic data.[48] The recent debate in the literature on the existence of $[HCrO_4]^-$ has been reviewed.[9] The absence of detectable amounts of $[HCrO_4]^-$ in aqueous solutions of Cr^{VI} has been implied from some of UV–visible and Raman spectroscopic studies.[43,49] However, more recent studies by these and other instrumental methods are consistent with the presence of $[HCrO_4]^-$.[40–42,44,48,50,51] These species have also been directly detected by ESMS of aqueous and nonaqueous Cr^{VI} solutions.[46,47] A detailed study by ^{17}O NMR and UV–visible spectroscopies led to values of $pK_a = 5.80$ and $K_d = 81\,M^{-1}$ (both at $I = 1.0\,M$, 25 °C) for the deprotonation and dimerization of $[HCrO_4]^-$, respectively.[42] *Ab initio* molecular orbital calculations have been performed for $[CrO_4]^{2-}$, $[HCrO_4]^-$, $[Cr_2O_7]^{2-}$, $[H_2CrO_4]$, and $[HCr_2O_7]^-$,[51] and vibrational energies in $[CrO_4]^{2-}$ have been determined by DFT calculations.[52] A crystal structure of $(Ph_4P)[HCrO_4]$ (synthesized by decomposition of a Cr^{VI} peroxo complex in nonaqueous media)[53] has been reported.[54] The first applications of the X-ray emission (L-edge) and ^{53}Cr NMR spectroscopies for the studies of chromates(VI) in the solid state have been reported recently.[55,56]

Several Cr^{VI} oxo complexes have been characterized by X-ray crystallography since 1985 ((**23**)–(**28**)).[57–62] A general synthetic pathway to such complexes involves the reactions of the ligands with Cr^{VI} precursor compounds (CrO_3, CrO_2Cl_2, or $K_2Cr_2O_7$),[57,59–62] while the oxo-amido complexes (**24a,b**) are synthesized by the reactions of $Cr^{II/III}$ amido complexes with O_2.[58] The crystal structures of $(Me_4N)_2\,[Cr_2O_7]$ and $(Me_4N)_2[Cr_3O_{10}]$ have also been determined.[63] The formation of Cr^{VI} oxo-alkoxido complexes by the reactions of CrO_2Cl_2 with epoxides has been studied by NMR spectroscopy,[64] and $[CrO_3(OMe)]^-$, produced from the reaction of $K_2Cr_2O_7$ with MeOH, has been detected by ESMS.[47] Characterization of (**25**)–(**28**) is the first unambiguous evidence for the formation of chromate(VI) esters (or thioesters) as the first intermediates during the Cr^{VI} reduction by alcohols or thiols.[7] Complex (**26**) may serve as a model of catalytic Cr^{VI} sites at the surface of silica.[60] The formation of chromate thioesters (e.g., (**28**)) is probably relevant to the application of $K_2Cr_2O_7$ for "curing" of polysulfide prepolymers, used as

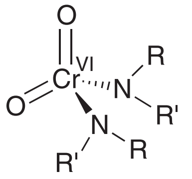


Scheme 3

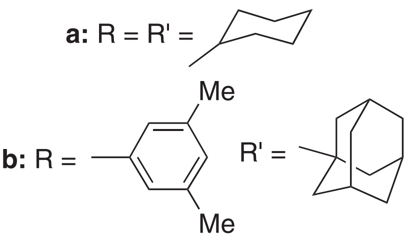
sealants.[62,65] Other crystallographically characterized Cr^{VI} complexes with monodentate thiolato donors contained nitrido or imido groups ((**29**) or (**30**)).[38,66] Reactions of $[HCrO_4]^-$ with glutathione (γ-Glu-Cys-Gly) (Cys = L-cysteine, Glu = glutamine, Gly = glycine) and other biological thiols (general formula RSH) in aqueous solutions at $pH \leq 6$ led to the formation of relatively stable $[CrO_3SR]^-$ species, characterized by multinuclear NMR, UV–visible, and Raman spectroscopies, as well as ESMS.[13,67–69] Complexation of Cr^{VI} by the ubiquitous biological ligand, glutathione, is likely to be relevant to the genotoxic effects of Cr^{VI} (Section 4.6.2.3.5).[13,67]

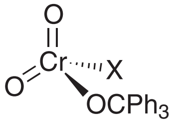


(**23**) (Ref. 57)



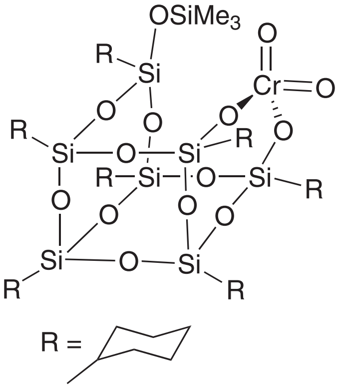
(**24a,b**) (Ref. 58)



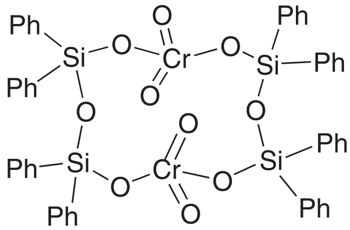


X = Cl or $OCPh_3$

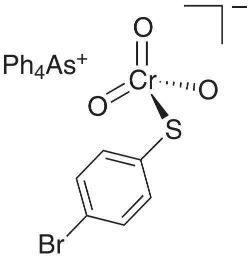
(**25**) (Ref. 59)



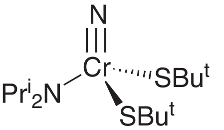
(**26**) (Ref. 60)



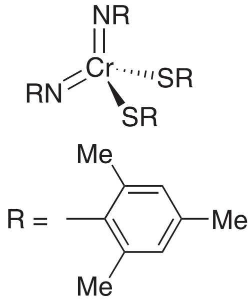
(**27**) (Ref. 61)



(**28**) (Ref. 62)



(**29**) (Ref.37)



(**30**) (Ref. 66)

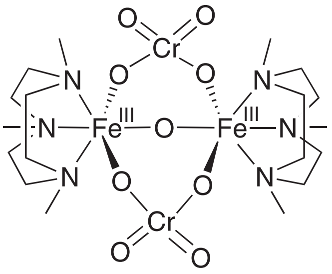
4.6.2.3.2 Peroxo complexes

The chemistry of Cr^{VI} peroxo complexes (general formula $[CrO(O_2)_2L]$, where L is a neutral uni- or bidentate ligand) was reviewed in 1994.[70] A recent XAFS spectroscopic study[71] of a species formed by the mixing of concentrated aqueous solutions of $Na_2Cr_2O_7$ and H_2O_2 supported the assignment of this complex as $[CrO(O_2)_2(OH_2)]$ (probably a pentagonal pyramid).[1,70] The Cr—O bond lengths, determined from the XAFS data, were 1.57 Å, 1.68 Å, and 1.93 Å for the oxo, peroxo, and aqua ligands, respectively.[71] Several kinetic and mechanistic studies of the $Cr^{VI} + H_2O_2$ reaction (where $[CrO(O_2)_2(OH_2)]$ or its deprotonated analogs are formed as intermediates) have been published.[72–74] The reaction of Cr^{VI} with H_2O_2 may be relevant to the toxic effects of Cr^{VI} (Section 4.6.2.3.5); for instance, it can occur during the phagocytosis of inhaled insoluble chromate particles by lung macrophages (which can be distinguished from most other mammalian cells by their relatively high H_2O_2 concentrations).[11,75] Peroxo complexes of Cr^{VI} (as well as those of Mo^{VI} and W^{VI}) are used as reagents for alkene epoxidation.[76] Recently, a comparative DFT study of the reaction pathways for these three metal ions has been performed.[76] Catalytic applications of Cr^{VI} peroxo complexes are discussed in Section 4.6.2.3.4.

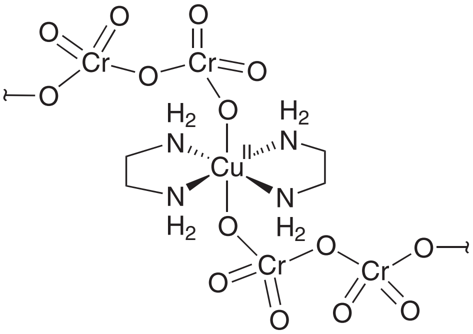
4.6.2.3.3 Chromates(VI) as ligands

A detailed review on the subject appeared in 1999.[77] Typical structures of metal complexes with chromato or dichromato bridges ((**31**) or (**32**)) have been determined by X-ray crystallography.[78,79] Some of the more recently reported complexes of these types are $[M^{II}(py)_4(Cr_2O_7)]$

(M = Cu, Zn, or Cd; py = pyridine),[80] [Ni (bpy)$_2$(OH$_2$)(Cr$_2$O$_7$)] (where bpy = 2,2′-bipyridine),[81] [NpO$_2$(CrO$_4$){OC(NH$_2$)$_2$}],[82] and [Ag$_3$Cl(CrO$_4$)][83] (all crystallographically characterized). Binding of $[CrO_4]^{2-}$ to transition metal complexes (e.g., $[Cu(bpy)_2]^{2+}$) markedly decreases the mutagenicity of Cr^{VI} in bacterial tests (probably because of the reduced permeability to the cells, Section 4.6.2.3.5),[84] but this is unlikely to be applicable to *in vivo* systems.[13] Formation of supramolecular adducts between $[CrO_4]^{2-}$ or $[HCrO_4]^-$ and calixarenes or crown ethers is used for the extraction of Cr^{VI} from aqueous solutions.[85,86]



(31)



(32)

4.6.2.3.4 Oxidations by Cr^{VI}: mechanistic studies and applications

General mechanisms of Cr^{VI} reduction to Cr^{III}, including the formation of Cr^{V}, Cr^{IV}, and Cr^{II} intermediates, have been reviewed.[9,13,87] Since 1985, the main focus of the mechanistic studies has shifted from the reactions of Cr^{VI} with model substances, such as alcohols in strongly acidic aqueous media,[87] to the reactions of biological substrates at pH ~ 7 (in relation to the genotoxicity of Cr^{VI}, Section 4.6.2.3.5).[13] Major developments in such studies are related to:

- (i) The availability of information on the structures and reactivities of the possible intermediates, including Cr^{VI} esters (Section 4.6.2.3.1) and Cr$^{V/IV}$ complexes (Sections 4.6.3.4 and 4.6.4.4).
- (ii) Application of new methods for the acquisition and analysis of kinetic data (e.g., global kinetic analysis).[13,88]

Since the structures of kinetically inert Cr^{III} products reflect those of labile Cr$^{V/IV}$ intermediates,[88] studies of the reaction products by ESMS can provide valuable information on the mechanisms of Cr^{VI} reduction.[89] The effects of micelle-forming reagents on the kinetics of Cr^{VI} reduction by organic substances in aqueous solutions have been investigated in relation to the biological and environmental processes involving Cr^{VI}.[90]

As the use of Cr^{VI} as a selective oxidant in organic synthesis[91] decreases due to environmental considerations, research efforts have focused on the applications of heterogeneous or catalytic Cr^{VI}-based reagents. Typical recent examples for the former include:

- (i) [CrO$_2$(OSiMe$_3$)$_2$] or (NH$_4$)[CrO$_3$Cl] supported on montmorillonite K-10.[92,93]
- (ii) Chromium(VI) trapped within a silica matrix by a sol–gel method.[94]
- (iii) Chromium(VI) peroxo complexes (Section 4.6.2.3.2), supported on poly(2-vinylpyridine) or poly(4-vinylpyridine).[95]

Applications of Cr^{VI} compounds as redox catalysts in organic synthesis were reviewed in 1992.[96] Typical recent examples include the selective oxidations of allylic alcohols,[97] alkenes,[98] arenes,[99] or adamantane[100] to carbonyl compounds by Bu^{t}OOH or H$_5$IO$_6$ in the presence of 5–10 mol.% of CrO$_3$ in organic solvents (such as CH$_2$Cl$_2$ or MeCN). The formation of [CrO$_2$(OH)(OOBu^t)] as an intermediate in such reactions has been proposed from the NMR- and UV–visible spectroscopic data.[101]

Gelatin, treated with (NH$_4$)$_2$Cr$_2$O$_7$, is widely used as a holographic recording material.[102] A recent study by X-ray photoelectron spectroscopy[102] suggested that microscopic grains of CrO$_2$ formed during the photo-assisted reduction of Cr^{VI} are the centers of a latent image. Further reduction during the development process leads to Cr^{III}-cross-linked sites in gelatin, which form a hologram.[102] Photo-catalytic oxidation of organic substances by Cr^{VI} in the presence of TiO_2 can be used in the treatment of waste waters.[103] Geochemical processes, leading to the conversion of Cr^{VI} to Cr^{III} and vice versa, were reviewed in 1999,[104] and detailed mechanistic studies on the role of the $Mn^{III/II}$ redox couple in these processes have been performed recently.[105,106] A characteristic high preedge absorbance peak in the XANES spectra of Cr^{VI} (due to the $1s \rightarrow 3d$ transition) is used for the quantitative determination of Cr^{VI} in environmental samples,[107,108] and to follow the intracellular reduction of carcinogenic Cr^{VI}.[109] Much attention has been paid recently to the possibilities of bioremediation of Cr^{VI}-contaminated soils and ground waters, using chromate-reducing bacteria or plants (reviewed in 2001).[110]

4.6.2.3.5 Toxicity of Cr^{VI}

The association between Cr^{VI} exposure and cancers of the respiratory tract has been acknowledged for over a century. Currently, Cr^{VI} compounds are among 87 recognized (class I) human carcinogens (only 33 of these are discrete chemicals or groups of chemicals), according to the classification of the International Agency for Research on Cancer.[111,112] Lung and nasal cancers, caused by exposure to Cr^{VI}, have been observed mainly in chrome electroplating, stainless steel welding, pigment production, and wood preservation industries.[111] Despite the implementation of workplace hazard reduction procedures[113] and extensive research towards replacement of Cr^{VI} in some industrial applications,[114,115] cancers and other adverse health effects arising from Cr^{VI} exposure in industry still remain a concern, as indicated by the results of recent epidemiological studies.[116,117]

In recent years, contamination of ground waters with Cr^{VI} and subsequent reported health problems, including cancers, in the exposed general population have received much public attention, as highlighted in the lawsuit against Pacific Gas & Electric (Hinkley, CA, USA), and in the film "Erin Brockovich."[118] However, there is ongoing debate as to whether the exposure to relatively low doses of Cr^{VI} in drinking water can lead to cancer.[119,120]

A framework for understanding the chemical mechanisms of Cr^{VI}-induced genotoxicity and carcinogenicity was conceived by Wetterhahn's uptake-reduction model in the early 1980s.[1,121] The current state of knowledge (reviewed in 2001 and 2003),[11,13] is that the following chemical properties of Cr are thought to be responsible for its mutagenicity and carcinogenicity. Tetrahedral $[Cr^{VI}O_4]^{2-}$ ions (resembling $[SO_4]^{2-}$ and $[HPO_4]^{2-}$) permeate easily across cell membranes through anion channels, while insoluble Cr^{VI} particles (such as $PbSO_4$) enter the cells by phagocytosis; however, Cr^{VI} itself is unreactive towards DNA or most proteins under physiological conditions. Once inside the cells, or while passing through the cell membranes, Cr^{VI} is reduced by a variety of compounds, such as ascorbate, glutathione, NADH, and tocopherols, resulting in the formation of highly reactive $Cr^{V/IV}$ and organic radical intermediates. These are capable of causing oxidative damage to DNA and proteins, as well as inducing chain reactions, leading to O_2 activation and oxidative stress. The $Cr^{V/IV}$ intermediates are capable of existing in cells as relatively long-lived species, stabilized by biological ligands such as 2-hydroxycarboxylates or 1,2-diolates, including carbohydrates and glycoproteins (Sections 4.6.3.4 and 4.6.4.4). Kinetically inert Cr^{III} complexes of DNA and proteins are formed as the products of Cr^{VI} intracellular reductions, leading to the lesions that may disrupt the function of the biomolecules. Finally, complexes of Cr^{III} with biomolecules may be reoxidized by cellular enzymatic systems with the formation of DNA-damaging $Cr^{V/IV}$ species.[11,13]

4.6.3 CHROMIUM(V)

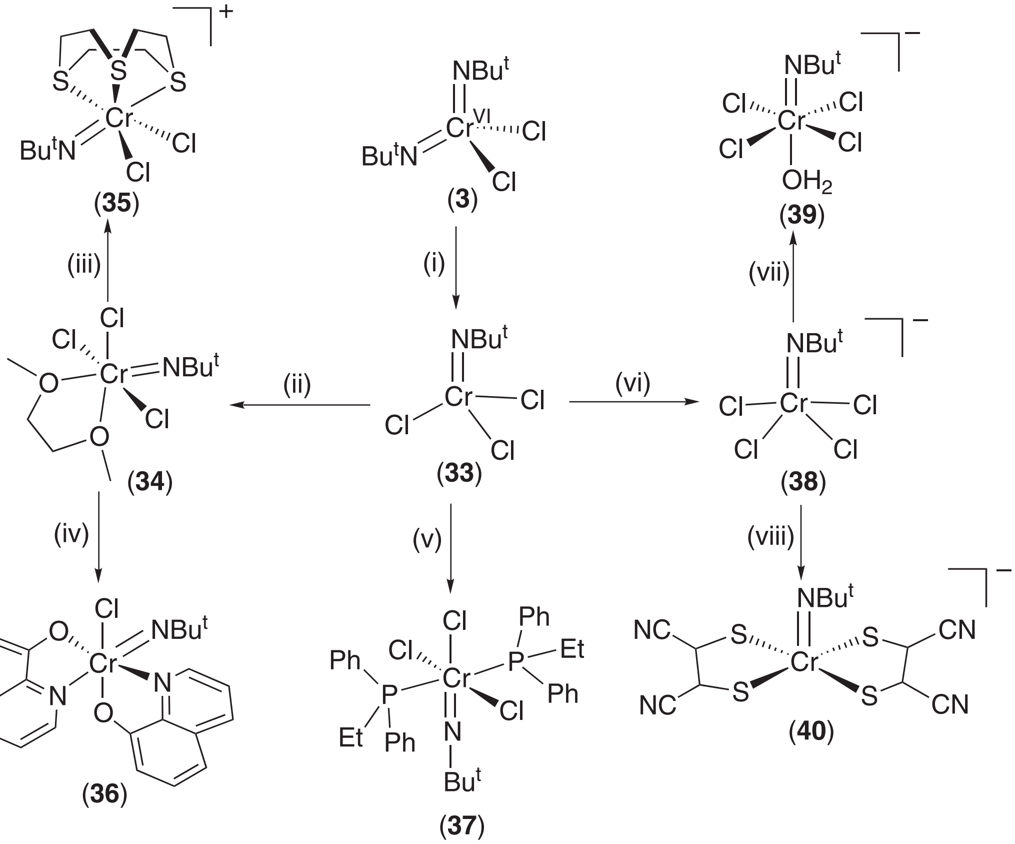
4.6.3.1 C-donor Ligands

Complexes of Cr^{V} with cyclopentadienyl ligands[31,122–124] are described in the *Comprehensive Organometallic Chemistry* series.

4.6.3.2 Imido Complexes

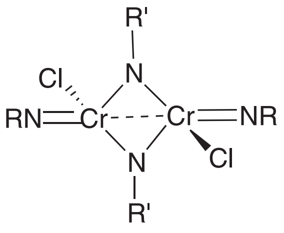
The first syntheses of monomeric Cr^{V} mono-imido complexes (starting from a Cr^{VI} diimido complex (**3**), Scheme 1) were reported in 1990.[125] Typical synthetic pathways to such compounds

((**33**)–(**40**)) are summarized in Scheme 4 (conditions: (i) Cl_2, CH_2Cl_2;[125,126] (ii) $MeO(CH_2)_2OMe$;[126] (iii) [9]aneS_3 in CH_2Cl_2, then $Ag(OSO_2CF_3)$ in MeOH;[127] (iv) 8-hydroxyquinoline, NEt_3, CH_2Cl_2;[126] (v) $PEtPh_2$, CH_2Cl_2;[125] (vi) $(Ph_4P)Cl$, CH_2Cl_2;[126] (vii) recrystallization from CH_2Cl_2/Et_2O;[128] (viii) $(HSCHCN)_2$, MeOH[126]). All the syntheses were performed under inert atmosphere at ambient temperature.[125–128] All the complexes except (**33**) and (**38**) have been characterized by X-ray crystallography; typical $Cr^V{=}N$ bond lengths are 1.58–1.64 Å.[125–128]



Scheme 4

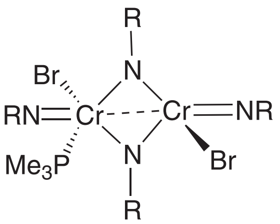
The crystallographically characterized dimeric (amido-bridged) Cr^V imido complexes ((**41**) and (**42**)) have been synthesized by reductions of Cr^{VI} diimido complexes ((**3**) or (**11**) in Scheme 1).[28,33] A dimeric Cr^V complex with imido and oxo donors is described in Section 4.6.3.4.1.



a: R = 2,6-$Pr^i_2C_6H_3$, R' = Bu^t

b: R = R' = 2,6-$Pr^i_2C_6H_3$

(**41a,b**)

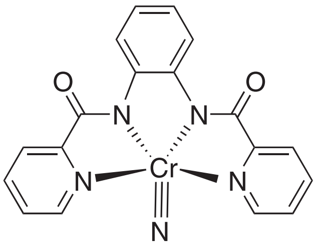


R = 2,4,6-$Me_3C_6H_2$

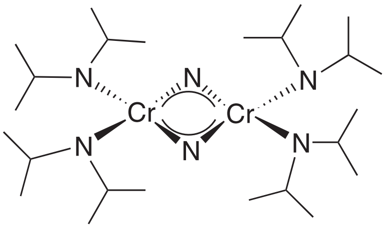
(**42**)

4.6.3.3 Nitrido Complexes

A list of crystallographically characterized Cr^V nitrido complexes is given in Table 1 and selected structures ((**43**) and (**44**)) are illustrated.[37,129–138] The most studied compounds of this type are the relatively stable complexes of general formula $[CrNL]^{n+}$ ($n = 0$ or 2), where L is a tetradentate open-chain ligand. These compounds are synthesized by oxidative photolysis of the corresponding Cr^{III} azido complexes.[132–138] The Cr^V nitrido complexes with substituted porphyrinato ligands react with Cr^{III} porphyrinates by the nitrido transfer mechanism (Section 4.6.5.2.10).[139] Studies on the electronic structure of the Cr≡N bond (by EPR spectroscopy and DFT calculations) revealed its strongly covalent nature, with the electron density being approximately equally distributed between the Cr and N atoms.[130,140]



(**43**)



(**44**)

4.6.3.4 Oxo and Peroxo Complexes

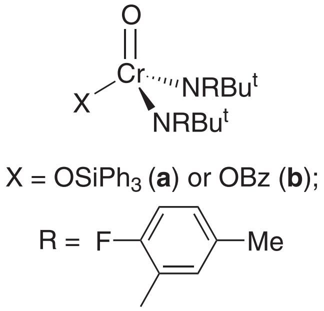
4.6.3.4.1 Syntheses and structural characterizations

Structurally characterized mono- and dinuclear Cr^V oxo complexes (as well as a tetraperoxo complex) are illustrated ((**45**)–(**57**)).[57,58,141–154] Such complexes have been synthesized either by reduction of Cr^{VI} compounds ((**45**)–(**50**), (**54**)–(**57**)),[57,58,141–149,154] or by oxidation of Cr^0, Cr^{II}, or Cr^{III} complexes ((**51**)–(**53**)).[150–153] The complexes were characterized by X-ray crystallography ((**45**)–(**48**), (**49a,b**), (**50**)–(**54**), (**56**)–(**57**)) or XAFS spectroscopy (**49c,55**). An unusual rearrangement of bisadamantylidene epoxide during its oxidation with Cr^{VI} led to a Cr^V complex (**50**).[149] Formation of six-coordinate adducts (e.g., (**51b**)) of Cr^V complexes with salen derivatives (e.g., (**51a**)) is important for the catalytic functions of such complexes (Sections 4.6.3.4.3 and 4.6.5.8.4).[150,151] Stabilization of Cr^V with a corrolato(3−) ligand in (**52**) has been reported recently[152] (by contrast, porphyrinato(2−) ligands preferentially stabilize Cr^{IV} oxo complexes, Section 4.6.4.2.2).

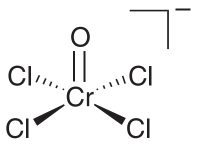
Table 1 Crystallographically characterized Cr^V nitrido complexes.

Complex[a]	*Geometry*	*Cr≡N(Å)*	*References*
$Ba_5[CrN_4]N$	Tetrahedral	1.75	129
$[CrN(CN)_5]^{3-}$	Octahedral	1.59	130,131
[CrN(bpb)] (**43**)	Square pyramidal	1.56	132
[CrN(salen)]	Square pyramidal	1.54	133,134
[CrN(salphen)]	Square pyramidal	1.55	135
[CrN(salpn)]	Square pyramidal[b]	1.56	136
trans-$[CrN(cyclam)(NCMe)]^{2+}$	Octahedral	1.56	137
$[\{trans\text{-}[CrN(cyclam)]\}_2(\mu\text{-}N_3)]^{3+}$	Octahedral	1.56	137
$[CrN(Me_4tpp)]$	Square pyramidal	1.565	138
$[\{Cr(NPr^i_2)_2\}_2(\mu\text{-}N)_2]$ (**44**)	Square planar	1.74	36

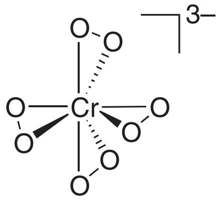
[a] Designations of the ligands: H_2bpb = 1,2-bis(2-pyridinecarboxamido)benzene; $H_2salophen$ = *N*,*N*′-bis(salicylidene)-1,2-phenylenediamine; H_2salpn = *N*,*N*′-bis(salicylidene)-1,3-propanediamine; cyclam = 1,4,8,11-tetraazacyclotetradecane; Me_4tpp = 5,10,15,20-tetrakis-*p*-methylphenylporphyrinato(2-); H_2salen = *N*,*N*′-bis(salicylidene)-1,2-ethanediamine. Typical structures are (**43**) and (**44**). [b] A linear Cr≡N···Cr≡N chain in the solid state.



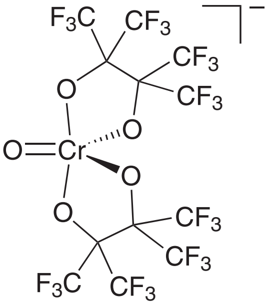
(**45a,b**) (Ref. 141)



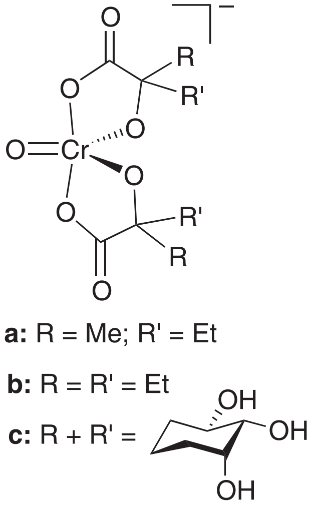
(**46**) (Ref. 142)



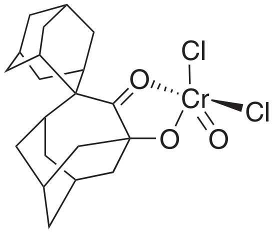
(**47**) (Ref. 143, 144)



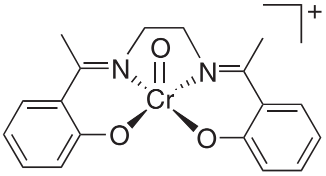
(**48**) (Ref. 145)



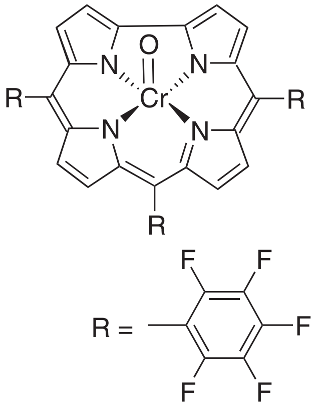
(**49a–c**) (Ref. 146–148)



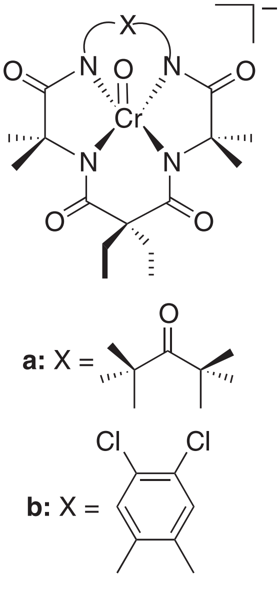
(**50**) (Ref. 146)



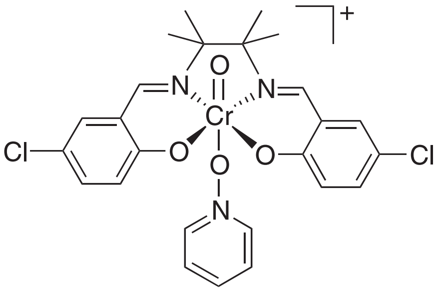
(**51a**) (Ref. 150)



(**52**) (Ref. 152)

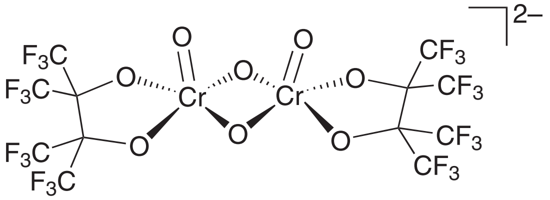


(**53a,b**) (Ref. 153)

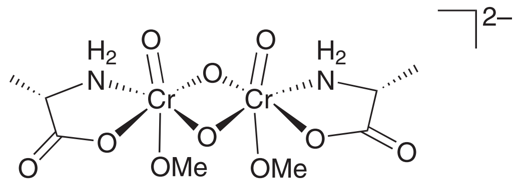


(**51b**) (Ref. 150, 151)

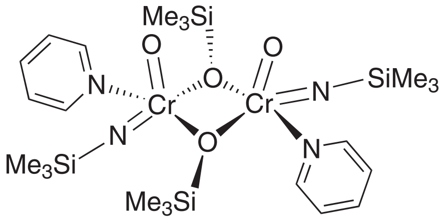
Many Cr^{V} complexes are difficult to crystallize due to their low stabilities in solution. In such cases, XAFS spectroscopy can be used for structural characterization of the complexes (which can be isolated as amorphous solids or snap-frozen in solutions).[11] Recently, this method has been applied for the first detailed characterizations of Cr^{V} complexes with natural ligands, quinic acid (**49c**)[148] and L-alanine (**55**).[154] The Cr=O bond lengths in (**45**)–(**57**) vary from 1.52 Å to 1.61 Å.[57,58,141–154] The values of Cr—O bond lengths in the complexes, containing only O-donors, can be used for the determination of the oxidation state of Cr by the bond valence sum method.[143]



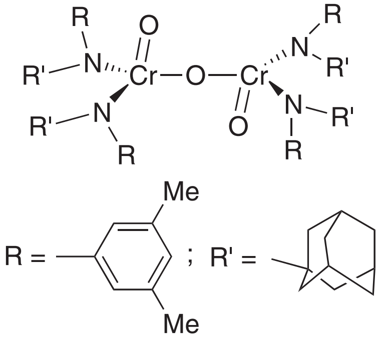
(**54**) (Ref. 145)



(**55**) (Ref. 154)



(**56**) (Ref. 57)



(**57**) (Ref. 58)

4.6.3.4.2 *Studies by EPR spectroscopy*

Mononuclear Cr^{V} complexes (d^1 species) usually possess intense sharp EPR signals at room temperature. Applications of EPR spectroscopy for the structural characterization of Cr^{V} complexes have been extensively reviewed.[11,13,155,156] By contrast, dinuclear Cr^{V} complexes are usually EPR-silent at room temperature due to the spin coupling of two unpaired *d*-electrons.[155] EPR spectroscopic methods are typically used in studies of reactive Cr^{V} intermediates, formed under biologically relevant conditions (e.g., during the reductions of Cr^{VI}, oxidations of Cr^{III}, or ligand-exchange reactions of relatively stable Cr^{V} complexes), in relation to Cr-induced genotoxicity and carcinogenicity (Section 4.6.2.3.5).[13,154,156–180] Numerous EPR-spectroscopic studies have been performed on the formation of Cr^{V} intermediates during the reactions of Cr^{VI} with biological media, including blood,[181,182] saliva,[183] mammalian tissues (such as liver or kidney),[184,185] whole living animals,[186,187] or plants.[188]

Although transient Cr^{V} species are formed during the reactions of Cr^{VI} with major cellular reductants, ascorbate and glutathione,[157–160,165,178] the most abundant Cr^{V} complexes in biological media are likely to be formed with 1,2-diolato ligands, such as carbohydrates (particularly D-glucose) and glycoproteins.[11,13] Various pH-dependent linkage isomerization reactions in aqueous solutions have been observed for the Cr^{V} complexes of the ligands, containing both the 2-hydroxycarboxylato and 1,2-diolato moieties, with the latter bound preferentially at $pH \geq 7$.[169] Detailed EPR-spectroscopic studies of the $Cr^{VI} + oxH_2$ and (**49b**) $+ oxH_2$ reactions (oxH_2 = oxalic acid) in acidic aqueous solutions revealed the formation of several mononuclear Cr^{V} species, as well as the mixed-oxidation-state (Cr^{V}–Cr^{VI} or Cr^{V}–Cr^{III}) oxalato complexes.[189] Photo-induced reductions of Cr^{VI} in acidic aqueous solutions[190] or in gelatin gels[191] led to detectable Cr^{V} intermediates. A quantitative EPR-spectroscopic method for the determination of Cr^{V}, formed in biological or environmental samples treated with Cr^{VI} (e.g., animal tissues or soil extracts) has been proposed.[192] A highly sensitive EPR-spectroscopic detection of the Cr^{V} species, bound to ion-exchanging resins, can be used to establish the presence of traces of toxic Cr^{VI} in water samples.[193]

Detailed analyses of EPR spectra have been performed for $[CrO(ehba)_2]^-$ (ehba = 2-ethyl-2-hydroxybutanoato(2−)) (**49b**),[155,194,195] $[CrO(hca)_2]^-$ ($hcaH_2$ = 1-hydroxycyclohexanecarboxylic-acid),[196] [CrN(bpb)] (**43**), [Cr(NBu^t)(bpb)Cl],[140] and Cr^{V} porphyrinato complexes.[197,198] Solution structures of the Cr^{V} complexes with 1,2-diolato or 2-hydroxycarboxylato complexes have been studied by ^{1}H ENDOR spectroscopy.[199,200] For the latter complexes, the existence of at least two geometric isomers in solutions has been detected,[200] in agreement with the EPR spectroscopic data.[148,155,169] An empirical correlation between the g_{iso} values for mononuclear Cr^V complexes (including imido, nitrido, and oxo species), and the nature of the ligands, has been proposed (Equation (1)):[11]

$$g_{iso} = 2.0023 - \Sigma\Delta g_{iso} \tag{1}$$

where 2.0023 is the g_{iso} value of a free electron and Δg_{iso} is a correction coefficient for each donor group (Table 2). This correlation can be used to predict the structures of unstable Cr^V complexes (particularly those formed in biological media) from their EPR spectra.[11,156] In recent years, ESMS has been used to assist in structural studies of Cr^V complexes generated in aqueous solutions in complex mixtures with other Cr species.[11]

4.6.3.4.3 Reactivities

A large majority of the reactivity studies have been performed using the well-characterized Cr^V complexes of 2-hydroxycarboxylates (particularly (**49b**)), or $[CrO(salen)]^+$ (salenH_2 = *N,N*′-bis(salicylidene)-1,2-ethanediamine). Krumpolc and Roček[201,202] developed a convenient method for the syntheses of Cr^V 2-hydroxycarboxylates and established that the decomposition of these complexes (such as (**49b**)) in aqueous solutions proceeds through parallel disproportionation (Equation (2), dominant in neutral and basic media) and ligand oxidation (Equation (3), dominant in acidic media):

$$3Cr^V \rightarrow 2Cr^{VI} + Cr^{III} \tag{2}$$

$$Cr^V - L \rightarrow Cr^{III} - L_{ox} \tag{3}$$

While the practically complete decomposition of (**49b**) in aqueous solutions at ambient conditions takes hours (at pH 3–5) or minutes (at pH 1–3 or 5–10),[202] this complex is stable for months in polar aprotic solvents (such as DMF or DMSO), or for years in the solid state.[147] The dependence of the redox potential of the $Cr^{V/IV}$ couple on the nature of the solvent has been studied for (**49b**).[147] A series of mechanistic studies of the electron-transfer reactions of (**49b**) with inorganic or organic reductants have been performed; several reviews of these studies are available.[13,155,203–205] Applications of (**49b**) for the selective oxidations of some alcohols or organic sulfides have been proposed.[202,206,207]

A detailed kinetic study on the disproportionation of (**49b**) in neutral aqueous solutions has been performed recently in relation to the mechanisms of oxidative DNA cleavage promoted by this complex.[208] Such Cr^V oxo complexes are among the few known types of metal complexes that cause oxidative DNA cleavage in the absence of reactive oxygen species.[209] The interactions of (**49b**) or $[CrO(salen)]^+$ with DNA have been studied in detail and several possible mechanisms of these reactions have been proposed (reviewed in 2000–2003).[11,13,210] Several mechanistic studies on the reactions of $[CrO(salen)]^+$ and related complexes with organic reductants have been performed in relation to the roles of these complexes in Cr^{III}–salen-catalyzed oxo-transfer reactions (Section 4.6.5.8.4).[211–215]

Table 2 Isotropic EPR Δg_{iso} parameters (Equation (1)) for different donor groups in Cr^V complexes.[a]

Donor group	Δg_{iso}	*Donor group*	Δg_{iso}
R_3P	−0.00625	RO^-	0.00505
R_2S	−0.00083	OH^-	0.00505
N^{3-}	0.00000	RCO_2^-	0.00593
$RNCOR^-$	0.00030	H_2O	0.00604
RS^-	0.00035	RN^{2-}	0.00630
Cl^-	0.00175	RNH_2	0.00667
O^{2-}	0.00210	$R_2C{=}NR$	0.00730
R_2O	0.00270	O_2^{2-}	0.00750
RO^-(enediol)	0.00475		

[a] Most of the Δg_{iso} values have been reported previously.[11] The values for the R_3P, R_2S, Cl^-, R_2O, and NR^{2-} donor groups have been calculated from the data of ref. 126.

4.6.4 CHROMIUM(IV)

4.6.4.1 C- and H-donor Ligands

Complexes of Cr^{IV} with alkyl,[216] alkylidene,[217] or η-carborane[218] ligands are extensively studied as model compounds for Cr-based alkene polymerization catalysts (Section 4.6.5.1.2). These complexes are described in detail in the *Comprehensive Organometallic Chemistry* series. A Cr^{IV} complex with isocyanide ligands is described in Section 4.6.4.2.1.

4.6.4.2 N-, P-, and S-donor Ligands

4.6.4.2.1 Open-chain ligands

Crystallographically characterized Cr^{IV} complexes ((**58**)–(**68**))[28,33,66,219–223] contain the following types of donor groups: imido ((**58**), (**60**)–(**63**)); amido ((**64**), (**65**), (**67**)); amine (**65**); imino (**59**); diazoalkane (**60**); tripyrazolylborato (**66**); phosphine ((**58**)–(**60**), (**63**), (**68**)); thiolato ((**61**), (**62**)); and sulfido ((**67**), (**68**)). Mixed-valence polynuclear compounds are represented by (**62**) and (**68**). Two other Cr^{IV} complexes with amido and/or amine ligands are described in Section 4.6.4.3.3. Typical synthetic methods include the reductions of Cr^{VI} ((**60**)–(**64**))[28,33,66] or the oxidations of Cr^{II} or Cr^{III} complexes ((**58**), (**59**), (**65**)–(**68**)).[219–223] Some Cr^{IV} complexes with amido ligands act as catalysts of alkene polymerization.[224]

4.6.4.2.2 Porphyrinates and related ligands

A stable prototype compound of this group, $[Cr^{IV}O(Me_4tpp)]$ (Me_4tpp = 5,10,15,20-tetrakis-*p*-methylphenylporphyrinato(2−)), was structurally characterized in the early 1980s.[1,225] Recently, a closely related complex, $[Cr^{IV}O\{(MeO)_4tpp\}]$, has been characterized by X-ray crystallography and DFT calculations,[226] and the redox chemistry of Cr^{IV} and Cr^{V} oxo-porphyrinato complexes has been reviewed.[227] A series of Cr^{IV} imido-porphyrinato complexes were characterized by spectroscopic methods, and the imido-transfer reactions of these compounds have been studied.[228] A Cr^{IV} corrolato complex has been generated by the reduction of its stable Cr^{V} analog (**52**) and characterized by ^1H NMR spectroscopy.[229] Complexes of Cr^{II}, Cr^{III}, and Cr^{IV} with a porphyrinogen ligand have been synthesized ((**69**)–(**71**) in Scheme 5) and characterized by X-ray crystallography.[230]

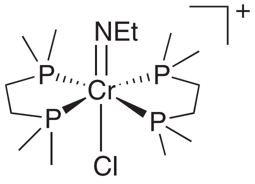
4.6.4.3 O-donor Ligands

4.6.4.3.1 Oxo and aqua ligands

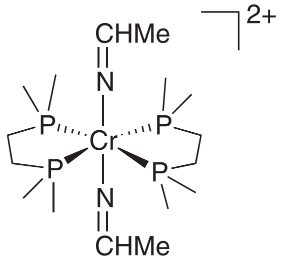
Generation and reactivity of a Cr^{IV} aqua complex (believed to be $[CrO(OH_2)_5]^{2+}$) in acidic aqueous solutions has been investigated.[231–235] Typical pathways for the formation and decay of $Cr^{IV}_{aq.}$ (which has a half-life time of ~20 s at pH 1 and 25 °C) are summarized in Scheme 6.[231–235] Kinetic studies of the reactions of $Cr^{IV}_{aq.}$ are complicated by:

(i) The absence of significant absorbance of this species in the UV–visible region (earlier statements to the contrary[236] were recently shown to be incorrect).[235]
(ii) The inevitable presence of other reactive species, such as $[Cr^{III}(O_2)(OH_2)_5]^{2+}$, in the reaction medium.[235]

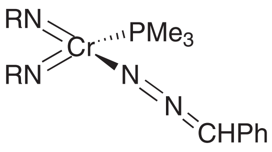
Nevertheless, the information obtained on the relative reactivities of $Cr^{IV}_{aq.}$ and other Cr species[232] is very important for understanding the general mechanisms of interconversions of various oxidation states of Cr, and the roles of O_2 in these reactions.[9] Generation of Cr^{IV} species by pulse radiolysis of Cr^{III} hydroxo-aqua complexes in alkaline aqueous solutions has also been described.[237]



(**58**) (Ref. 219)

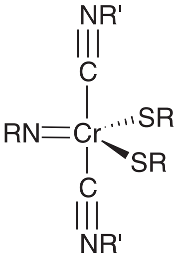


(**59**) (Ref. 219)



$R = 2,6\text{-}{}^{i}Pr_2C_6H_3$

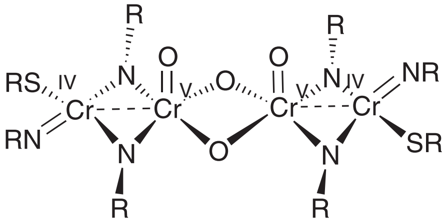
(**60**) (Ref. 30)



$R = 2,4,6\text{-}Me_3C_6H_2$;

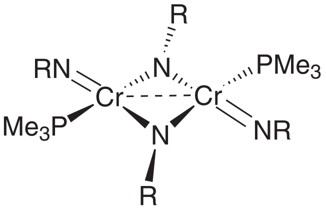
$R' = 2,6\text{-}Me_3C_6H_3$

(**61**) (Ref. 66)



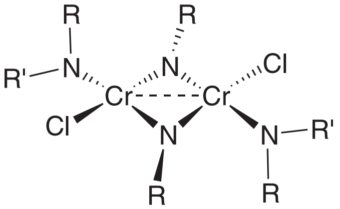
$R = 2,4,6\text{-}Me_3C_6H_2$

(**62**) (Ref. 66)



$R = 2,4,6\text{-}Me_3C_6H_2$

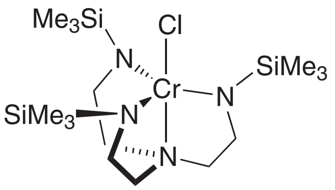
(**63**) (Ref. 26)



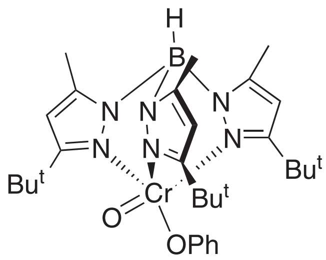
$R = 2,4,6\text{-}Me_3C_6H_2$

$R' = 4\text{-}{}^{t}BuC_6H_4$

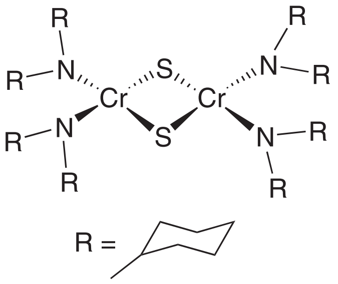
(**64**) (Ref. 26)



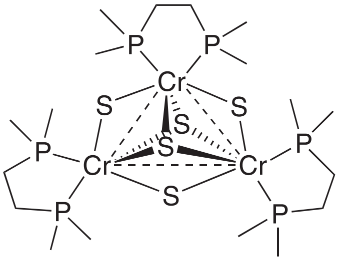
(**65**) (Ref. 220)



(**66**) (Ref. 221)



(**67**) (Ref. 222)

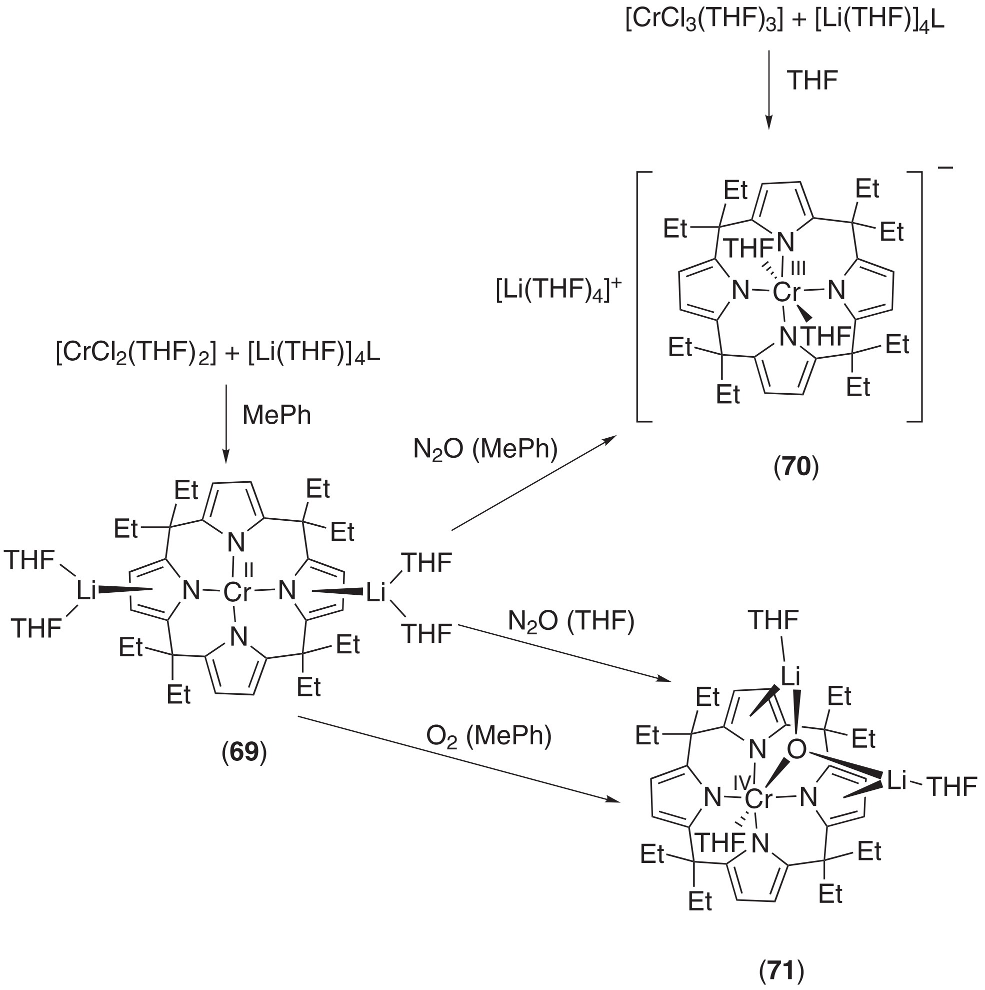


$Cr^{III,III,IV}$

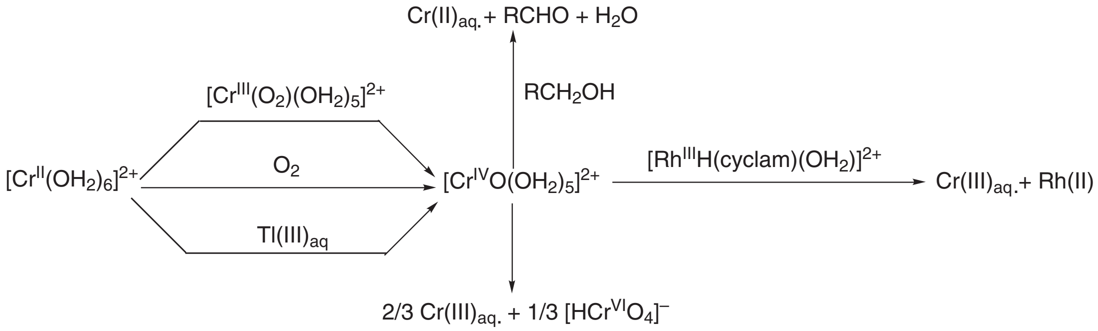
(**68**) (Ref. 223)

4.6.4.3.2 *Oxo and carboxylato ligands*

The statement made in 1987 that "Cr^{IV} does not have any aqueous solution chemistry,"[1] has been made redundant following extensive research in this area (see also Section 4.6.4.3.1). In 1991, Ghosh and Gould discovered a convenient method for quantitative generation of 2-hydroxycarboxylato Cr^{IV} complexes by the reactions of Cr^{VI} and As^{III} in the presence of an excess ligand in weakly acidic aqueous media (pH 2–4).[238] Such complexes could not be isolated due to their rapid decomposition in the absence of excess ligand.[239,240] More recently, Lay and co-workers used this



Scheme 5

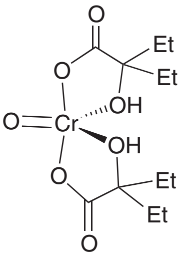


Scheme 6

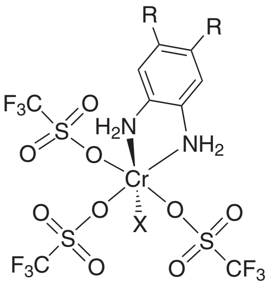
method for the first structural characterization of a Cr^{IV} complex ($[CrO(ehbaH)_2]$, (**72**)) in frozen aqueous solutions (by multiple-scattering analysis of XAFS spectroscopic data at 10 K).[13,241] Complex (**72**) is distinguished from its Cr^{V} analog, (**49b**), by protonation of the alkoxo donors, which is reflected in the elongation by 0.20 Å of the corresponding bond lengths, and explains the lower stability of (**72**) in solutions (the maximal half-life time is ~20 min at pH 3, [Cr] = 0.10 mM, 25 °C).[242] The availability of XAFS spectroscopic data on (**72**) solved the controversy[204,243] concerning the structure of this complex and the mechanisms of electron transfer in the $Cr^{V/IV/III}$–ehba complexes.[13]

In contrast to $[CrO(OH_2)_5]^{2+}$ (Section 4.6.4.3.1), the reactions of (**72**) (including the formation of deprotonated or partially aquated species), as well as those of the related Cr^{IV} oxo-carboxylato complexes, can be followed easily by UV–visible spectroscopy.[208,242] Detailed mechanistic studies of the reduction or disproportionation reactions of (**72**) in weakly acidic aqueous media have been performed (reviewed in 1994).[240] More recent studies include those of the reactions of (**72**) with Sn^{II}, In^{I}, Ge^{II},[244] hydrazine,[245] and hydroxylamine.[246]

The above-described method for the generation of Cr^{IV} seems to be specific for 2-hydroxycarboxylato complexes such as (**72**), $[CrO(hmbaH)_2]$ (hmba = 2-hydroxy-2-methylbutanoato(2−)) (related to (**49a**)) or $[CrO(qa)(qaH)]^-$ (qa = quinato(2−) = 1*R*,3*R*,4*R*-1,3,4-trihydroxycyclohexanecarboxylato(2−)) (related to (**49c**)), but the preformed Cr^{IV} species readily react with some other types of ligands, leading to the formation of Cr^{IV} oxalato or picolinato complexes ($[CrO(ox)_2]^{2-}$ or $[CrO(pic)_2]$) (ox = oxalato(2−); pic = picolinato(1−) = pyridine-2-carboxylato(1−)).[242] Complexes of Cr^{IV} with 2-hydroxycarboxylates are also generated as intermediates during the reduction of Cr^{VI} by anhydrous MeOH in the presence of the corresponding ligands.[148] A remarkable stability of $[CrO(qa)(qaH)]^-$ in neutral aqueous media (the maximal half-life time is ~1 h at pH 6, [Cr] = 0.10 mM, 25 °C)[242] has been used in the studies of Cr^{IV} reactions with DNA and other biomolecules.[89,209,247]



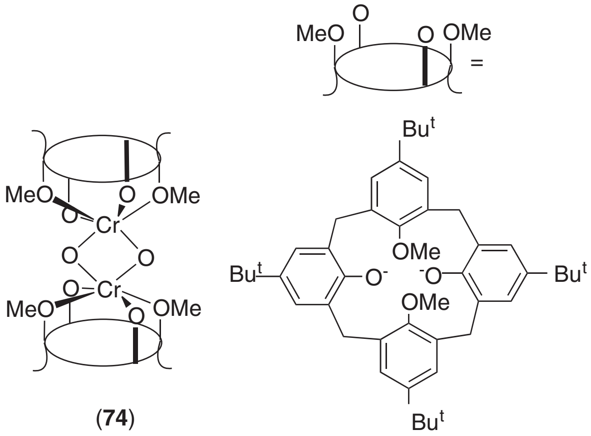
(**72**)



a: X = NH_2, R = Me

b: X = OSO_2CF_3, R = H

(**73a,b**)



(**74**)

4.6.4.3.3 *Other O-donor ligands*

A few Cr^{IV} complexes with O-donor ligands have been characterized by X-ray crystallography since 1985 ((**73**) and (**74**)).[248,249] An unusual dioxo-bridged complex of a calix[4]arene derivative (**74**) exhibits a ferromagnetic coupling between the two Cr^{IV} centers.[249] Mononuclear complexes of Cr^{III} and Cr^{II} with this ligand are described in Sections 4.6.5.1.2 and 4.6.6.4.2, respectively.

The first structural characterization of a volatile Cr^{IV} alkoxide, $[Cr(OBu^t)_4]$,[1] was performed in 1989, using gas-phase electron diffraction.[250] This complex is tetrahedral, with an average Cr—O distance of 1.75 Å,[250] and has found applications as a precursor for the syntheses of catalytic chromia-silica materials.[251]

The chemistry of Cr^{IV} peroxo complexes, $[Cr(O_2)_2L_3]^{n-}$(where L = H_2O, am(m)ine, or CN^-, and n = 0–3), has been reviewed extensively.[1,70,240] Recently, a long-range ferromagnetic ordering in the solid state at $T < 10$ K was observed for $[Cr(O_2)_2(en)(OH_2)]$ (en = 1,2-ethanediamine) and $[Cr(O_2)_2(NH_3)_3]$.[252,253] However, practical applications of such complexes are limited by their explosive nature.[1,70,240]

4.6.4.4 Cr^{IV} Intermediates in Reduction of Cr^{VI} or Oxidation of Cr^{III}

The presence of Cr^{IV} intermediates during the reactions of Cr^{VI} with two-electron reductants (e.g., alcohols) has been assumed since the 1940s (reviewed in 1985).[87] The first direct evidence for the formation of Cr^{IV} was obtained in the reductions of Cr^{VI} in the presence of Cr^{IV}-stabilizing ligands such as $ehbaH_2$ (the resulting Cr^{IV} complexes, such as (**72**), are strongly absorbing at

300–600 nm). Similar Cr^{IV} intermediates are formed during the reductions of relatively stable Cr^{V} complexes, such as (**49b**). The early work in this area was reviewed in 1994;[240] more recently, kinetics and mechanisms of the reactions of $[HCrO_4]^-$ with $H_2PO_2^-$,[254] HCO_2H,[255] or Ga^{I},[256] in the presence of ehbaH_2 (in weakly acidic aqueous solutions) have been studied. The formation of a highly colored intermediate (presumably a Cr^{IV} or Cr^{V} complex with edta) during the reaction of Co^{II}–edta with Cr^{VI} at pH 3–4 can be used for spectrophotometric determination of Co^{II} or Cr^{VI}.[257] Generally, studies of the transient Cr^{IV} species are more difficult than those for Cr^{V} (Section 4.6.3.4.2), as the former species are EPR-silent at room temperature.[11,13] Several proposed methods for the detection of such species, including the use of Mn^{II} as a selective trap for Cr^{IV},[258] or the measurements of dynamic magnetic susceptibility in solutions,[259] have been disputed recently.[11,13]

Formation of relatively stable Cr^{IV}-picolinato intermediates has been observed (by UV–visible spectroscopy) during the reduction of Cr^{VI},[260] oxidation of Cr^{III},[261,262] or ligand-exchange reactions of (**72**) and its analogs in the presence of excess picolinate.[242] This stabilization of potentially genotoxic[209] Cr^{IV} species may contribute to the adverse effects of high doses of a popular nutritional supplement, Cr^{III} picolinate (Section 4.6.5.8.1).[11,263] Some evidence for the formation of Cr^{IV} during the oxidation of $Cr^{III}_{aq.}$ on the surface of birnessite ($[Mn^{III/IV}O_{1.75}(OH)_{0.25}]$; a likely model for the oxidation of Cr^{III} in the environment) has been obtained by X-ray photoelectron spectroscopy.[106]

4.6.4.5 Solid-state Chemistry of Cr^{IV}

The Cr^{IV} dinitrogen or dihydrogen complexes, $(N_2)_xCrO_2$ or $(H_2)_xCrO_2$, ($x = 1$ or 2) have been generated from CrO_3 by laser ablation techniques in solid Ar at 11 K, and studied by IR spectroscopy and DFT calculations.[264,265] An understanding of the nature of H_2 or N_2 binding in such complexes is important for the development of Cr-based catalysts for hydrogenation or nitrogen activation.[264,265]

A well-known stable ferromagnetic Cr^{IV} oxide, CrO_2 (possessing a six-coordinate rutile-type structure) is widely used in magnetic memory devices.[1,266] The existence of Cr^{IV} in Cr-doped oxide minerals, Al_2O_3 (ruby) or $CaSnOSiO_4$ (malayaite), has been suggested from the EPR or Raman spectroscopic data, respectively.[267,268] Currently, significant attention is being paid to the use of Cr^{IV}-doped crystals in laser devices.[269]

4.6.5 CHROMIUM(III)

Since 1985 more than 3,000 publications on Cr^{III} coordination chemistry have appeared, including descriptions of hundreds of new complexes. Within the space limitations of this review, priority has been given to the publications including significant new information on Cr^{III} coordination chemistry, crystallographically characterized Cr^{III} compounds, and new practical applications of Cr^{III} complexes.

The majority of the Cr^{III} complexes described over the last 15–20 years are polynuclear or heteropolynuclear compounds. Such compounds are discussed in Section 4.6.5.9 and are classified by the type of bridging ligand(s). Typical synthetic methods for Cr^{III} complexes, including the ligand-exchange reactions of Cr^{III} precursors and oxidation of Cr^{II} complexes, have been described in detail previously.[1]

Kinetically inert Cr^{III} complexes (as well as those of Co^{III}) are extensively used in the mechanistic studies of conventional or photo-induced ligand-exchange reactions.[1] However, such studies are generally not included in this review. A general overview of the ligand-exchange and photochemical reactions of transition metal complexes, including those of Cr^{III}, is given in Volumes 1, 7, and 9 of this work. Most of the mechanistic studies of Cr^{III} ligand-exchange reactions were performed before 1991, and these are comprehensively covered in a series of annual reviews,[7] as well as in several other review articles.[270–272] Several recent reviews provide a detailed coverage of Cr^{III} photochemistry.[273–278]

4.6.5.1 C-donor Ligands

4.6.5.1.1 Cyanides

The most significant developments in the chemistry of a well-known[1] $[Cr(CN)_6]^{3-}$ complex are related to its use in the preparation of molecular magnets. The synthesis of a room-temperature magnetic material with a Prussian blue structure, $V^{II}_{0.42}V^{III}_{0.58}[Cr^{III}(CN)_6]_{0.86}\cdot 2.8H_2O$ ($T_c = 315$ K), was first reported in 1995.[279] This and related materials possess polynuclear, cyano-bridged structures, and are described in Section 4.6.5.9.1. A series of $[Cr(CN)_6]^{3-}$ salts with $[Ru^{II}(phen)_3]^{2+}$ (phen = 1,10-phenanthroline), $[Ru^{II}(bpy)_3]^{2+}$, or $[Os^{II}(phen)_3]^{2+}$ cations have been prepared, characterized by X-ray crystallography, and used for single-crystal photochemical studies.[280,281] Other mononuclear Cr^{III} cyano complexes, which have been crystallographically characterized since 1985, are the $(NMe_4)_2M^I[Cr(CN)_6]$ double salts (where M = K, Cs, Rb, or Tl).[282,283] Electron-density distributions in single- and double-complex salts ($Cs_2K[Cr(CN)_6]$ vs. $[Co(NH_3)_6][Cr(CN)_6]$) have been studied by polarized neutron diffraction experiments and DFT calculations.[284] The effective ionic charges of the $[Cr(CN)_6]^{3-}$ and $[Co(NH_3)_6]^{3+}$ units in the double-complex salt are significantly lower than the formal ±3 values due to the charge transfer through C—N···H—N hydrogen bonds.[284]

Binding of a paramagnetic, redox-inactive $[Cr(CN)_6]^{3-}$ anion to specific sites of a blue copper protein, amicyanin, has been used in NMR-spectroscopic studies of the protein structure in solutions.[285] *Ab initio* calculations of the ligand-field spectra of $[Cr(CN)_6]^{3-}$ have been performed and the results compared with those for cyano complexes of the other first-row transition metals.[286] The role of Cr—C—N bending vibrations in the $^2E_g \rightarrow {}^4A_{2g}$ phosphorescence spectra of $[Cr(CN)_6]^{3-}$ has been evaluated by computational methods.[287] A critical survey of stability constants of Cr^{III} cyano complexes is available.[288] Ligand-exchange reactions and photochemistry of some classes of mixed-ligand species, such as pentacyanochromates(III) or Cr^{III} cyano-ammine complexes, have been reviewed extensively.[289,290]

4.6.5.1.2 Alkyls and aryls

Most of the Cr complexes with the title ligands are described in the *Comprehensive Organometallic Chemistry* series. This section is limited to the Cr^{III} complexes containing a single alkyl or aryl ligand, acting as a σ-donor, in addition to N-, O-, or Hal-donor ligands (Hal = halide such as F^-, Cl^-, Br^-, or I^-).

(i) Aqua complexes

Data on the syntheses, structures, and reactivities of the $[Cr^{III}(OH_2)_5R]^{2+}$ complexes published before 1992 have been reviewed.[291] While no solids have been isolated as yet, these complexes are generated in acidic aqueous solutions by the reactions of $Cr^{II}_{aq.}$ with alkyl or aryl radicals $R^{\cdot}$ (Scheme 7a) and purified by column chromatography. Typical sources of these radicals are illustrated in Scheme 7b–d, and Scheme 7e–h summarizes the main reactions of the Cr—C bonds in the $[Cr(OH_2)_5R]^{2+}$ complexes.[291–293] Formation of transient complexes with Cr^{III}—C bonds in aqueous solutions and further reactions of such complexes (particularly those involving O_2, Scheme 7h) may be relevant to the biological activities of Cr^{III}.[11,292]

In contrast to the Werner-type complexes, such as $[Cr(OH_2)_6]^{3+}$ or $[Cr(OH_2)_5X]^{2+}$ (X = Hal or similar anion) where broad EPR signals with $g \sim 2$ are observed in the solids at ~295 K or in frozen aqueous solutions at 77 K, no EPR signals for $[Cr(OH_2)_5R]^{2+}$ could be detected at $T \geq 20$ K. This difference, together with the analysis of low-temperature EPR spectra, points to the predominantly covalent nature of the Cr—C bonds in the $[Cr(OH_2)_5R]^{2+}$ complexes.[293]

(ii) Complexes with other ligands

Reactions similar to those in Scheme 7a–d, in the presence of Cr^{III}-stabilizing ligands (such as polyazamacrocycles or β-ketoenolates), led to isolable complexes containing Cr^{III}—C bonds.[291] Several such complexes, including (**75**) and (**76**), have been characterized by X-ray crystallography, typical Cr—C bond lengths are 2.05–2.15 Å.[294–297] Mechanistic studies of the formation[298] and reactivity[294,299] of macrocyclic complexes related to (**75**) have been performed. A prominent feature of (**75**), (**76**), and related complexes is a significant elongation (by 0.10–0.20 Å compared with the usual values) of Cr-ligand bonds *trans* to the Cr—C bond (*trans*-effect), which leads to an increased reactivity of the *trans*-ligands in ligand-exchange reactions.[291,295]

Reactions of a well-known complex, $[Cr(Me)Cl_2(thf)_3]$,[300] with imidazole-based ligands in anhydrous solvents led to the isolation of new Cr^{III} methyl complexes (e.g., (**77**)).[301]

$$\textbf{a:}\quad [Cr^{II}(OH_2)_6]^{2+} + R^{\bullet} \rightleftharpoons [(H_2O)_5Cr^{III}\text{–}R]^{2+} + H_2O$$

$$\textbf{b:}\quad [Cr^{II}(OH_2)_6]^{2+} + CHX_3 \longrightarrow [Cr^{III}(OH_2)_5X]^{2+} + {}^{\bullet}CHX_2 \qquad (X = Cl, Br)$$

$$\textbf{c:}\quad [Cr^{II}(OH_2)_6]^{2+} + H_2O_2 + CH(CH_3)_2OH \longrightarrow [Cr^{III}(OH_2)_6]^{3+} + {}^{\bullet}C(Me)_2OH + H_2O + OH^{-}$$

$$\textbf{d:}\quad (CH_3)_2SO + {}^{\bullet}OH \longrightarrow {}^{\bullet}CH_3 + CH_3SO_2H \text{ (pulse radiolysis)}$$

$$\textbf{e:}\quad [(H_2O)_5Cr^{III}\text{–}R]^{2+} + {}^{\bullet}R' \xrightarrow{H_2O} [Cr^{II}(OH_2)_6]^{3+} + RR'$$

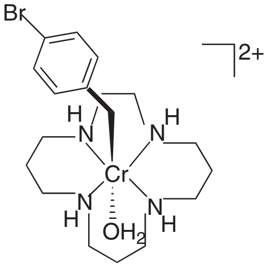
$$\textbf{f:}\quad [(H_2O)_5Cr^{III}\text{–}R]^{2+} \xrightarrow{H_2O,\ H^+} [Cr^{III}(OH_2)_6]^{3+} + RH$$

$$\textbf{g:}\quad [(H_2O)_5Cr^{III}\text{–}CH(Me_3)_2OH]^{2+} \longrightarrow [Cr^{III}(OH_2)_6]^{3+} + CH_2{=}CH(Me)$$

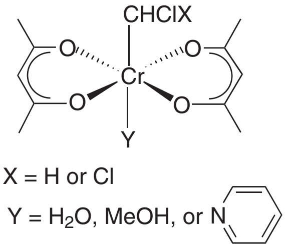
$$\textbf{h:}\quad [(H_2O)_5Cr^{III}\text{–}CH(Me_3)_2]^{2+} + O_2 \xrightarrow{H^+} [Cr^{III}(OH_2)_6]^{3+} + (Me)_2CO$$

Scheme 7

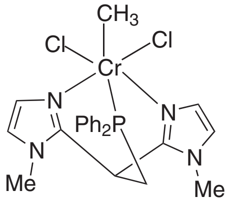
Five-coordinate Cr^{III} complexes of sterically crowded ligands ((**78**)–(**81**)) possessing distorted square-pyramidal or trigonal-bipyramidal geometries have been characterized by X-ray crystallography.[249,302–304]



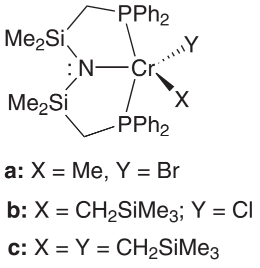
(**75**) (Ref. 294)



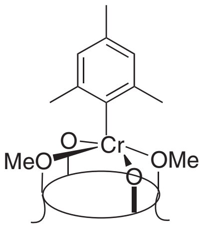
(**76**) (Ref. 295–297)



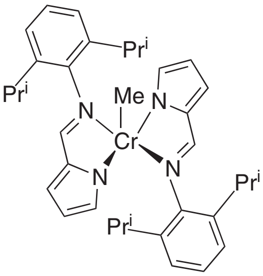
(**77**) (Ref. 301)



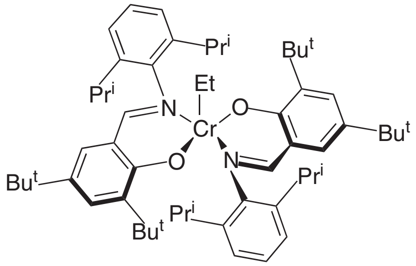
(**78a–c**) (Ref. 302)



(**79**) (see (**74**)
ref. 249)



(**80**) (Ref. 303)



(**81**) (Ref. 304)

(iii) Applications in catalysis

About one-third of all polyethylene is currently produced using the Cr-based Phillips catalyst.[305] Preparation of this heterogeneous catalyst consists of the following steps:

(a) Impregnation of SiO_2 with an inorganic Cr compound (e.g., CrO_3 or a Cr^{III} salt).
(b) Calcination in the presence of O_2.
(c) Reduction of the solid material with C_2H_4 or CO.[305]

Although the structures of the active centers and reaction mechanisms for the Phillips catalyst are uncertain, it is believed that the key species in the catalytic cycle are Cr^{II}-, Cr^{III}- or Cr^{IV}-alkene complexes.[305] Considerable effort has been devoted to studies of functional homogeneous catalytic models of the Phillips catalyst. A recent summary[305] shows that a majority of such models are the sandwich-type Cr complexes with cyclopentadienyl ligands, which are outside the scope of this review (see the *Comprehensive Organometallic Chemistry* series). The recently synthesized compounds (**77**)–(**81**) are among the noncyclopentadienyl-containing Cr complexes that act as homogeneous catalysts of alkene polymerization.[301,303,304] Other such complexes are mentioned in Sections 4.6.2.1, 4.6.4.1, 4.6.4.2.1, 4.6.5.2.6, 4.6.5.2.9, 4.6.5.8.1, 4.6.5.8.2, 4.6.6.2.1, 4.6.6.2.2, 4.6.6.4.2, and 4.6.6.8. A Cr^{III} complex of a calix[4]arene derivative (**79**) and the related Cr^{IV} and Cr^{II} compounds (Sections 4.6.4.3.3 and 4.6.6.4.2) have been designed to serve as models for the studies of Cr—C bonds over planar oxo surfaces (similar to those in SiO_2-supported Cr catalysts).[249]

4.6.5.2 N-donor Ligands

4.6.5.2.1 Ammonia, amines, and N-heterocycles as unidentate ligands

(i) Hexaamminechromium(III)

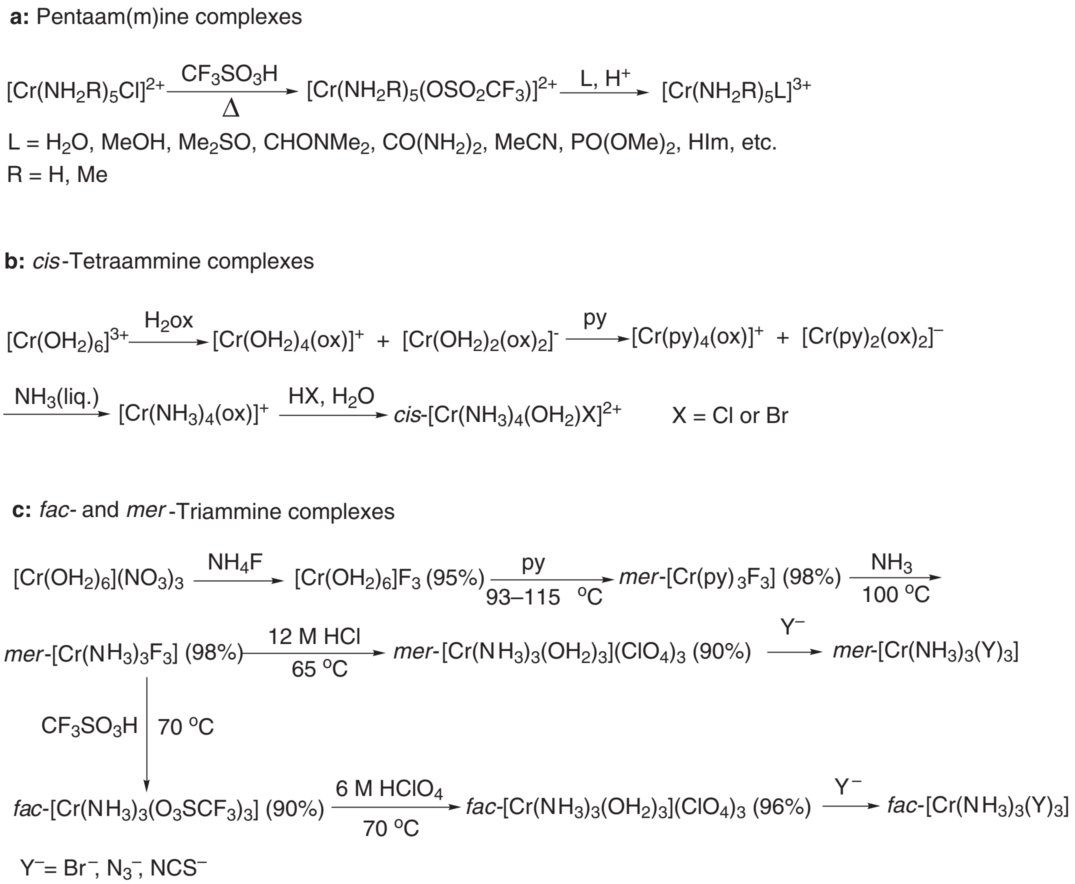
Since the beginning of the twentieth century, $[Cr(NH_3)_6]^{3+}$ remains one of the most thoroughly studied coordination compounds.[1] Several new compounds containing $[Cr(NH_3)_6]^{3+}$ have been synthesized and characterized by X-ray crystallography since 1985. Thus, the structures of the $Cs[Cr(NH_3)_6](ClO_4)_2X_2$ salts (where $X = Cl$ or Br) have been determined at different temperatures.[306] The average Cr—N distances in these compounds are 2.070(3) Å and 2.080(2) Å at 293 K and 10 K, respectively.[306] The bulky $[Cr(NH_3)_6]^{3+}$ cation has been used to assist in the crystallization and structural studies of some "exotic" anions, such as heptaiodide[307] or pentaazadienides.[308] Double-complex salts of $[Cr(NH_3)_6]^{3+}$ with $[CuCl_5]^{3-}$ or $[FeCl_6]^{3-}$ anions have been structurally characterized.[309–311] A crystal structure of $[Cr(NH_3)_6][Cr(CN)_6]$ was among the first to be determined with the use of short-wavelength synchrotron radiation.[312] Some of the double-complex salts may find use as magnetic materials,[311] but this area is currently dominated by cyano-bridged complexes (Section 4.6.5.1.1).

Numerous applications of $[Cr(NH_3)_6]^{3+}$ and its derivatives to mechanistic studies of conventional or photo-assisted ligand-exchange reactions have been extensively reviewed.[7,270–276] Among other common Cr^{III} complexes, $[Cr(NH_3)_6]^{3+}$ has been used for the studies of reactivities of muonium and positronium atoms in aqueous solutions.[313–315] Several computational methods, including DFT calculations,[316] a combination of molecular mechanics and angular overlap model calculations,[317,318] or vibrational analysis[319] have been used for the prediction and interpretation of electronic spectra and photochemical properties of $[Cr(NH_3)_6]^{3+}$.

(ii) Mixed-ligand species

Despite the enormous amount of early work,[1] the development of selective methods for the synthesis of Cr^{III} am(m)ine complexes with a predetermined structure (for use in mechanistic studies) has continued in recent years. Synthetic pathways to Cr^{III} cyano-am(m)ine complexes were reviewed in 1994.[290] Sargeson and co-workers[320,321] proposed a general method for the synthesis of pentaam(m)ine Cr^{III} complexes (Scheme 8a), based on the relative lability of the trifluoromethanesulfonato (triflato) ligand. This method has been subsequently used to synthesize the $[Cr(NH_3)_5(NH_2Bu^t)]^{3+}$ complex (characterized by X-ray crystallography), which is a rare example of the use of *tert*-butylamine as a ligand.[322]

Stereoselective synthetic schemes have been proposed for tetra- and triammine complexes (Scheme 8b,c).[323–325] Scheme 8b represents the first high-yield (~70%) synthesis of *cis*-tetraammine Cr^{III} complexes (published in 1997), while efficient synthetic methods for the corresponding *trans*-complexes have been known for decades.[325] Synthesis, structure determination (by X-ray crystallography), and ligand-exchange reactions of *trans*-$[Cr^{III}(NH_2R)_4Cl_2]^+$ complexes ($R = Et$ or Pr^n) have been reported.[326,327] Determination of the crystal structures of *mer*$[CrL_3Cl_3]$

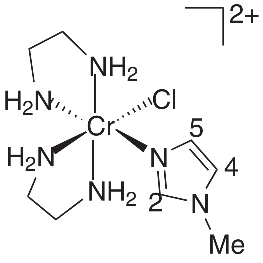


Scheme 8

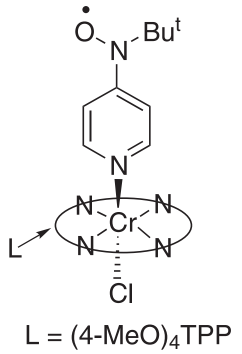
(L = pyridine or 4-ethylpyridine) has solved a long-standing controversy regarding the geometry of such complexes, which was based on different interpretations of their UV–visible spectra.[328,329] The average Cr—N bond distance for the pyridine ligands is 2.11 Å.[328,329]

A well-known complex, $[Cr^{III}(NH_3)_5Cl]^{2+}$, has been characterized by X-ray crystallography for the first time and used for the comparison of π- and H-bonding patterns in the isomorphous series of M^{III} complexes (M = Cr, Co, Rh, Ir, Ru, or Os).[330] Other long-known Cr^{III} complexes that have been crystallographically characterized since 1985 include *trans*-$[Cr(NH_3)_4Cl_2]^+$, *trans*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$,[331] *cis*-$[Cr(NH_3)_4(OH_2)Cl]^{2+}$,[332] and *cis*,*mer*-$[Cr(NH_3)_3(OH_2)_2Cl]^{2+}$.[333] The ability of en to act as a monodentate ligand (in intermediates formed during the acid hydrolysis of $[Cr(en)_3]^{3+}$) has been confirmed by solving the crystal structure of *cis*-$[Cr(en)_2(enH)Cl]^{3+}$.[334]

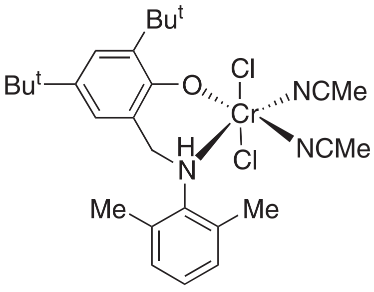
There is an ongoing controversy concerning the rates of isotopic H-exchange at C-2, C-4, and C-5 positions of *N*-methylimidazole in (**82**) and related species. Buncel and co-workers[335,336] reported an exceptionally high ability of Cr^{III} in (**82**) to promote such exchange (10^5–10^6-fold higher than for Co^{III}, and ~20-fold higher than for H^+). This outstanding Lewis acid capability of Cr^{III} could lead to its wider use in catalysis, as well as contribute to an understanding of the mechanisms of its biological activity.[11] However, Clark *et al.*[337] using a crystallographically characterized sample of (**82**), showed that the isotope exchange rates were comparable for the Cr^{III} and Co^{III} complexes, and attributed the results of Buncel and co-workers to erroneous experimental procedures.



(**82**)



(**83**)



(**84**)

(iii) Biochemical and medicinal applications

The $[Cr(NH_3)_6]^{3+}$ ion is widely used as a paramagnetic probe in structural studies of biomolecules (such as proteins, oligonucleotides, or enzyme cofactors) by NMR spectroscopy,[338–340] and as a promotor of electron transfer in the electrochemistry of redox-active proteins.[341–343] A series of kinetically inert Cr^{III} complexes, $[Cr(NH_3)_{6-x}(OH_2)_x]^{3+}$ ($x = 0$–6), have been used for activation of RNase H from *Escherichia coli* (in place of the natural activator, $[Mg(OH_2)_6]^{2+}$) to evaluate the role of hydrogen bonding and electrostatic factors in enzyme activation.[344] The $[Cr(NH_3)_5(az)]^{3+}$ complex (az = aziridine) has been synthesized as a part of the search for selective cytotoxic agents for hypoxic cells.[345] Aziridine is a potent DNA-alkylating agent, which can be released from $[Cr(NH_3)_5(az)]^{3+}$ in O_2-deficient cells (found in solid tumors but not in healthy tissue) following the conversion of kinetically inert Cr^{III} to labile Cr^{II} by intracellular reductants. However, the majority of work in this area has been performed with Co^{III}/Co^{II} aziridine complexes.[345]

(iv) Complexes of free radical ligands

Magnetic interactions of a paramagnetic metal center and a free radical ligand are of interest for the development of new types of molecular magnetic materials. Complexes of this type (such as (**83**)) change their magnetic properties upon irradiation by visible light and can serve as a basis for development of novel photo-activated memory units for electronic devices.[346,347]

4.6.5.2.2 Unidentate amido ligands

Air- and moisture-sensitive Cr^{III} complexes of a general formula $[Cr(NR_2)_3]$, possessing bulky dialkyl- or disilyl-amide ligands in a trigonal arrangement have been known since the 1970s,[1] but relatively little work has been done on these complexes since 1985. A theoretical study of the structure and bonding (e.g., metal–ligand π-bonding) in three-coordinate amido complexes of the first-row transition metal ions, including Cr^{III}, has been performed;[348] this work also provides a useful survey of crystal structures determined before 1999. A new high-yielding synthesis of $[Cr\{N(SiMe_3)_2\}_3]$ has been proposed recently, and an accurate crystal structure has been determined (the average Cr—N bond length is 1.889(2) Å).[349] Another crystallographically characterized compound, $[Cr(NRR')_3]$ (R = adamantyl; R′ = 3,5-dimethylphenyl), has been used in the syntheses of Cr^V and Cr^{VI} amido complexes (Sections 4.6.1.2 and 4.6.2.2).[58] Polymeric Cr^{III} complexes with simple amido ligands, such as $[Cr(NH_2)_3]$, are referred to in Section 4.6.5.9.2.

4.6.5.2.3 N-thiocyanates and N-cyanates

Well-known[1] Cr^{III} *N*-thiocyanate complexes, such as $[Cr(NCS)_6]^{3-}$, $[Cr(NCS)_4(NH_3)_2]^-$ (Reinecke anion), and their derivatives, are currently extensively used for the syntheses of charge-transfer salts of organic donors (tetrathiafulvalene derivatives) aimed towards the development of new conductive and magnetic molecular materials.[350–353] The ability of $[Cr(NCS)_4(NH_3)_2]^-$ and its analogs to form precipitates with protonated *N*-heterocycles is widely used in the analysis of pharmaceutical preparations.[354,355] A series of supramolecular adducts of $[Cr(NCS)_6]^{3-}$ with Na^+, K^+, or NH_4^+ crown-ether complexes have been studied recently.[356] The stereochemistry of the *mer*-$[Cr(NCS)_3(py)_3]$ complex has been established by ^2H NMR studies (contrary to its previous assignment as a *fac*-isomer, based on the UV–visible spectroscopic data).[357]

The first crystal structure of a Cr^{III} complex with *N*-cyanato ligand, $[Cr(NH_3)_5(NCO)]^{2+}$, has been determined and the ligand-field states of this complex have been calculated.[358] The cyanato ligand is linear, with Cr—N, N—C, and C—O distances of 2.09(1) Å, 1.16(1) Å, and 1.21(1) Å, respectively, and there is no significant structural *trans*-effect for the axial ammine ligand.[358] Time-resolved resonant emission spectra of $[Cr(NH_3)_5(NCO)]^{2+}$ have also been studied.[359]

4.6.5.2.4 Other unidentate N-donor ligands

(i) Azido complexes

The isomeric complexes, *fac*- and *mer*-$[Cr(NH_3)_3(N_3)_3]$, have been synthesized (Scheme 7c) and characterized by X-ray crystallography.[324] Nitrozation reactions (Equation (4); R = Me, Et, or $CHCH_2$) led to nitrile-substituted complexes:[324]

$$[Cr(NH_3)_3(N_3)_3] + 3\ NOBF_4 + 3\ RCN \rightarrow [Cr(NH_3)_3(NCR)_3]^{3+} + 3\ BF_4^- + 3\ N_2O + 3\ N_2 \quad (4)$$

A series of Cr^{III} azido-pyridine complexes has been prepared and characterized by spectroscopic methods.[360] Azido-bridged Cr^{III} complexes are described in Section 4.6.5.9.2. Azido complexes of Cr^{III} are widely used as precursors in photochemical syntheses of Cr^V nitrido complexes since the early 1980s (Section 4.6.3.3).[1] Photodecomposition of Cr^{III} complexes containing azido ligands (e.g., $[Cr(N_3)L(OH_2)_2]^{2+}$, where L = triethanolamine) has been used for deposition of thin films of metallic Cr on Si surfaces, with potential applications in the electronic industry.[361]

(ii) Nitrile complexes

Owing to the relative lability of the nitrile ligands, the $[Cr(NH_3)_3(NCR)_3]$ complexes (synthesized according to Equation (4) or Scheme 7a[321,324] can be used for the syntheses of the $[Cr(NH_3)_3L_3]$ complexes (where L are monodentate N- or O-donors) of predetermined geometry.[324] Recrystallization of Cr^{III} complexes from nitrile solvents can lead to coordination of nitrile ligands to the metal ion, as illustrated by a crystallographically characterized complex, (**84**), which is also catalytically active in ethylene polymerization (Section 4.6.5.1.2).[362]

(iii) Dinitrogen complexes

A series of articles on Cr^{III} dinitrogen complexes, stabilized by aminopolycarboxylato ligands (Section 4.6.5.8.4; general formula $[Cr(N_2)L]^-$), were published in 1984–1985.[363,364] Dinitrogen binding to Cr^{III} was suggested from the IR spectra.[363] However, to our knowledge, no crystal structures of mononuclear Cr^{III} dinitrogen complexes have been reported, and no such complexes have been mentioned in the literature since 1985. A dinitrogen-bridged Cr^{III}–Re^I complex has recently been described (Section 4.6.5.9.2).

(iv) Nitrosyl complexes

Nitrosyl complexes of Cr^{III} are described in Section 4.6.7.1.

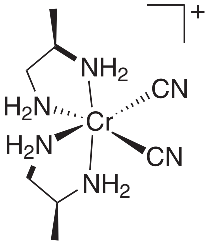
4.6.5.2.5 Polydentate (open-chain) amine ligands

(i) Bidentate ligands

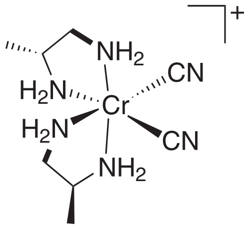
As a part of studies aimed towards magnetic molecular materials, the double complex salts $[Cr(en)_3]_3[FeCl_6]Cl_6{\cdot}H_2O$ and $[Cr(en)_3][FeCl_4]Cl_2{\cdot}9H_2O$ have been prepared and characterized by X-ray crystallography.[365] Ferromagnetic ordering in these compounds is achieved at very low temperatures (~1 K),[365] making their practical application unlikely (Section 4.6.5.9.1). Crystal structures have also been determined for the $[Cr(en)_3]^{3+}$ salts of the $[Hg_3Cl_{12}]^{6-}$ or $[ZnCl_4]^{2-}$ anions.[334,366] The crystal structure and electron density distribution at 120 K have been determined for $\Delta(\lambda,\lambda,\lambda)$-$[Cr(chxn)_3](NO_3)_3{\cdot}3H_2O$ (chxn = *trans*-1,2-cyclohexanediamine).[367]

Significant binding of $[Cr(en)_3]^{3+}$ to a human glycoprotein occurs *in vitro*, inducing a structural transition of the protein from the native twisted β-sheet to a more compact α-helix.[368] However, $[Cr(en)_3]^{3+}$ does not permeate into mammalian cells to any significant extent and is not genotoxic in the *in vitro* micronucleus assay.[176] Ligand-exchange reactions and photochemistry of $[Cr(en)_3]^{3+}$ and related complexes have been studied extensively (reviewed in 1997–2001).[273–276] The kinetics and mechanism of $[Cr(en)_3]^{3+}$ oxidation to Cr^{VI} by *N*-bromosuccinimide in neutral aqueous solutions have been studied and the importance of the partially aquated intermediate, $[Cr(en)_2(OH_2)_2]^{3+}$, has been emphasized.[369] Molecular-mechanical calculations, using a novel approach to model the angular geometry about the metal center, have been performed for $[Cr(en)_3]^{3+}$ and other Cr^{III} polyamine complexes.[317] Partial molar volumes in H_2O at infinite dilution (25 °C) have been calculated for Cr^{III} polyamine and polyimine complexes.[370]

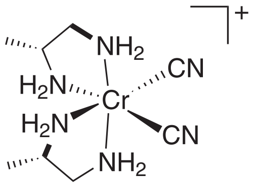
Separation of three geometric isomers of a cyano-amine complex, Λ-*cis*-$[Cr(CN)_2(d\text{-}pn)_2]Cl$ (pn = propylenediamine = 1,2-propanediamine) (**85a–c**), has been achieved by ion-exchange chromatography, and (**85a,b**) have been characterized by X-ray crystallography.[371] This is the first evidence for the existence of geometric isomers, distinguished by relative positions of the methyl groups, for the complexes of pn ligands.[371] The first crystal structure of a Cr^{III} complex with aromatic *o*-diamine, $[Cr\{1,2\text{-}(NH_2)_2C_6H_4\}Cl_4]^-$, has been reported.[248] Reactions of this and related complexes with mild oxidants led to unusual octahedral Cr^{IV} complexes (e.g., (**73**)).[248] A Cr^{III} complex of an antihistaminic drug, isothipendyl (proposed structure (**86**)), exhibited strong antibacterial properties.[372]



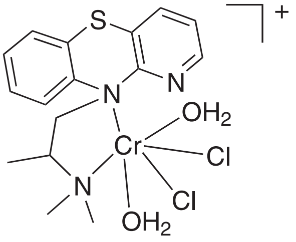
(**85a**)



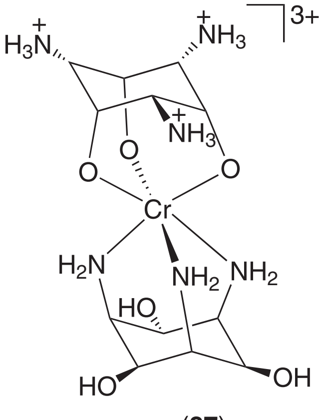
(**85b**)



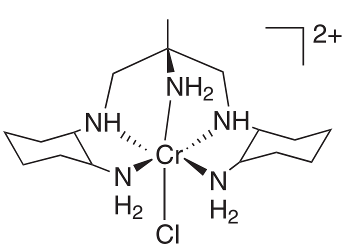
(**85c**)



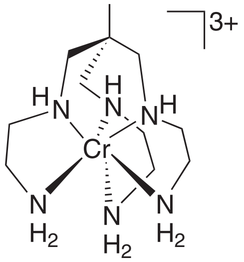
(**86**)



(**87**)



(**88**)



(**89**)

(ii) Tri-, tetra-, penta-, and hexadentate ligands

Stereoselective syntheses, crystallographic characterizations, and ligand-exchange studies of a series of $\mathrm{Cr^{III}}$ complexes with tri- and tetradentate aliphatic amines (such as $\mathrm{H_2N(CH_2)_{\mathit{n}}NH(CH_2)_{\mathit{n}}NH_2}$ or $\mathrm{H_2N(CH_2)_{\mathit{n}}NH(CH_2)_{\mathit{n}}NH(CH_2)_{\mathit{n}}NH_2}$, $n = 2$ or 3) have been performed by House and co-workers.[334,373–378] A series of crystallographically characterized $\mathrm{Cr^{III}}$ oxalato-tetraamine complexes have been prepared by the reduction of $\mathrm{Cr^{VI}}$ with oxalic acid in the presence of the corresponding amine.[379,380] Different binding modes of 1,3,5-trideoxy-*cis*-inositol-1,3,5-triamine have been observed in a single $\mathrm{Cr^{III}}$ complex ((**87**), characterized by X-ray crystallography) due to the presence of different geometric isomers of the ligand in solutions.[381] Several novel structurally characterized $\mathrm{Cr^{III}}$ complexes with penta- and hexadentate amine ligands have been reported (such as (**88**) and (**89**) in Scheme 19).[382,383] The $\mathrm{[Cr(tren)(OH)(OH_2)]^{2+}}$ complex (tren = $\mathrm{N(CH_2CH_2NH_2)_3}$) has been used as a slow dissociating model for $\mathrm{[Fe(OH_2)_6]^{2+}}$ in the mechanistic studies of biological iron storage in ferritin.[384]

4.6.5.2.6 Macrocyclic amine ligands

This has been one of the most dynamic areas of $\mathrm{Cr^{III}}$ chemistry in the past two decades owing mainly to the developments in $\mathrm{Cr^{III}}$ photochemistry,[273–276,278] and, more recently, to the interest in homogeneous catalysts of alkene polymerization (see below). A list of crystallographically characterized complexes is given in Table 3, and the ligand structures ($\mathrm{L^1}$–$\mathrm{L^{15}}$) are shown in Scheme 9.[294,385–414]

(i) Tridentate ligands: applications in catalysis

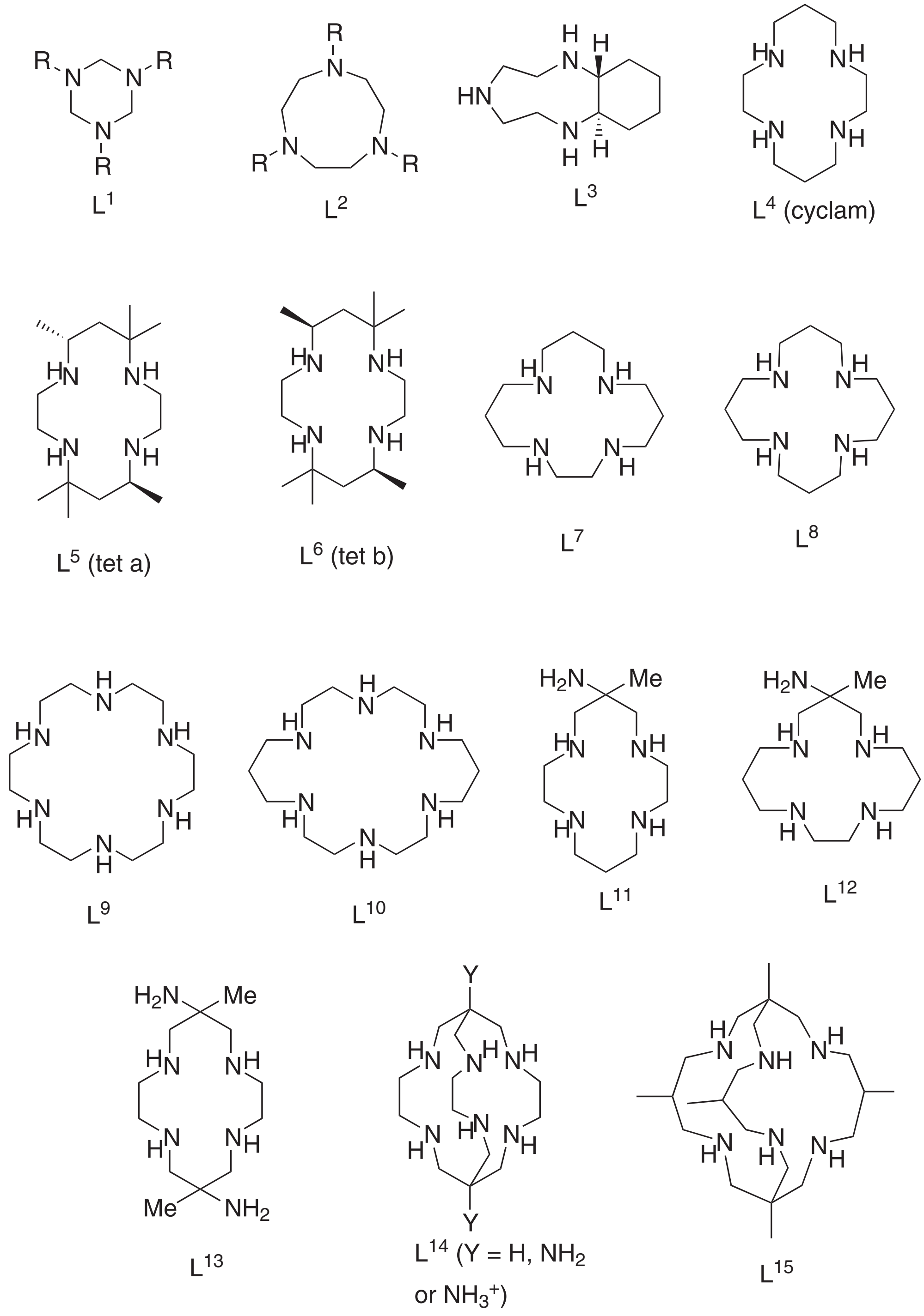
Recently, Köhn *et al.*[415] have discovered that the $\mathrm{Cr^{III}}$ complexes of [6]ane$\mathrm{N_3}$ derivatives ($\mathrm{L^1}$ in Scheme 9 and Table 3, where R is a $\mathrm{C_5}$–$\mathrm{C_{10}}$ alkyl residue) are efficient homogeneous catalysts of alkene polymerization, resembling the Phillips catalyst (Section 4.6.5.1.2). For instance, $\mathrm{[CrL^1Cl_3]}$ with R = n-$\mathrm{C_8H_{17}}$ is a selective catalyst for trimerization of α-alkenes.[416] Several patents for the use of such complexes have been issued,[417,418] and the catalytic applications were reviewed in 2001.[419]

Studies on $\mathrm{Cr^{III}}$ complexes of [9]ane$\mathrm{N_3}$ (1,4,7-triazacyclononane(tacn)) derivatives ($\mathrm{L^2}$ in Scheme 9 and Table 3) prior to 1987 have been reviewed.[420,421] Complexes of $\mathrm{Cr^{III}}$ with

Table 3 Crystallographically characterized $\mathrm{Cr^{III}}$ complexes of macrocyclic amines (since 1985).

Complex[a]	*References*	*Complex*[a]	*References*
cis-$\mathrm{[CrL^1X_3]}$[b]	385	*cis*-$\mathrm{[CrL^6(lact)]^{+}}$[g]	405
cis-$\mathrm{[CrL^2Cl_3]}$[c]	386,387	*trans*-$\mathrm{[CrL^7(NCS)(OH_2)]^{2+}}$	406
cis-$\mathrm{[CrL^2(acac)X]}$[d]	388	*trans*-$\mathrm{[CrL^7(R)(OH_2)]^{2+}}$[h]	294
$\mathrm{[Cr(L^3)_2]^{3+}}$[e]	389	*(s)-trans*-$\mathrm{[CrL^8Cl_2]^{+}}$	407
trans-$\mathrm{[CrL^4(ONO)_2]^{+}}$	390	$\mathrm{[CrL^9]^{3+}}$	408
cis- or *trans*-$\mathrm{[CrL^4(NH_3)_2]^{3+}}$	391–393	$\mathrm{[CrL^{10}]^{3+}}$	408
cis- or *trans*-$\mathrm{[CrL^4(NCS)_2]^{+}}$	394	*trans*-$\mathrm{[CrL^{11}Cl]}$	409,410
cis- or trans-$\mathrm{[CrL^4(CN)_2]^{+}}$	395,396	*trans*-$\mathrm{[CrL^{12}Cl]}$	409,410
trans-$\mathrm{[CrL^4(X)_2]^{+}}$[f]	397–402	$\mathrm{[CrL^{13}]^{3+}}$[i]	411,412
cis-$\mathrm{[CrL^4(en)]^{3+}}$	403	$\mathrm{[CrL^{14}]^{3+}}$	413,414
trans-$\mathrm{[CrL^4(OH)(OH_2)]^{2+}}$	404	$\mathrm{[CrL^{15}]^{3+}}$	413,414
trans-$\mathrm{[CrL^5(ONO)_2]^{+}}$	390		

[a] Designations of the ligands correspond to Scheme 9; acac = acetylacetonate(1−) = 2,4 pentanedionato(1−). [b] X = Cl, R = $\mathrm{-CH_2(CH_2)_2CCH}$; or X = Br, R = Me. [c] R = $\mathrm{Pr^i}$or $\mathrm{Bu^n}$. [d] X = F or $\mathrm{O_2PF_2}$, R = Me. [e] Crystal structure of a $\mathrm{Co^{III}}$ analog has been determined. [f] X = Cl or Br. [g] lact = lactate(2−) = 2-hydroxypropanoate(2−). [h] R = $\mathrm{4\text{-}BrC_6H_4CH_2}$ (**75**). [i] Complexes with two stereoisomers of the ligand.



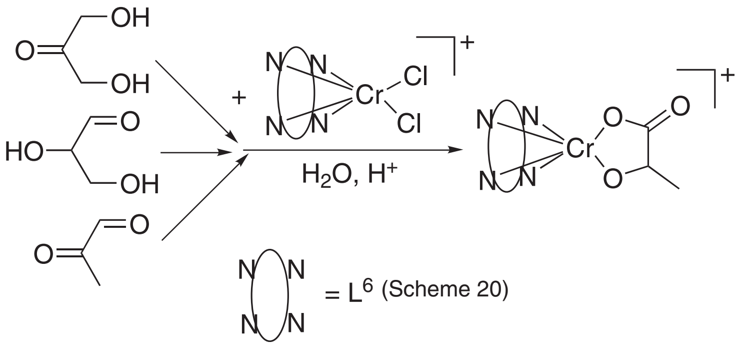
Scheme 9

[6]aneN$_3$ or [9]aneN$_3$ derivatives are widely used as building blocks for the syntheses of polynuclear and heteropolynuclear complexes (Section 4.6.5.9).[422–424] The chemistry of the related [Cr^{0}L(CO)$_3$] complexes (where L is a tridentate macrocyclic amine)[385,386] is described in the *Comprehensive Organometallic Chemistry* series.

(ii) Tetra-, penta-, and hexadentate ligands

General methods for the syntheses of *trans*- or *cis*-Cr^{III}–cyclam complexes with mono- or bidentate ligands were developed in the early 1980s.[1,425,426] Numerous Cr^{III} complexes of cyclam and its analogs (L^4–L^8 in Scheme 9) have been characterized by X-ray crystallography since 1985 (Table 3), typical Cr—N(macrocycle) bond lengths are 2.07–2.10 Å. Molecular mechanical calculations have been used[427] to explain the preference for *cis*- over *trans*-isomer formation in the syntheses of Cr^{III}–cyclam complexes.[1,425,426]

Complexes of Cr^{III} with tetradentate macrocyclic ligands are widely used to stabilize metal ion coordination to "unusual" unidentate ligands, such as alkyls (Section 4.6.5.1.2), superoxide (Section 4.6.5.4.2), nitrite, or hydrogen carbonate (Section 4.6.5.4.3), and to study the reactivities of such coordinated ligands, which are often biologically relevant. The chiral *cis*-$[CrL^6Cl_2]^+$ complexes induce the transformations of methylglyoxal, 1,3-dihydroxyacetone, or glyceraldehyde into Cr^{III}-bound *R*- or *S*-lactate (Scheme 10; confirmed by crystal structure determination for the Cr^{III} product).[405] This system mimics the action of a Zn^{II}-dependent glyoxalase I enzyme. The *cis*-$[CrL^6Cl_2]^+$ complexes also induce the transformations of carbohydrates into Cr^{III}-bound 2-hydroxycarboxylates.[428] Some complexes of a radioactive $^{51}Cr^{III}$ isotope with *N*-substituted cyclam have been patented as radiodiagnostic agents for the detection of hypoxia and radioresistance in tumor tissues.[429]



Scheme 10

Well-characterized Cr^{III} complexes with penta- or hexadentate macrocyclic and macrobicyclic amine ligands (L^9–L^{15} in Scheme 9, including "pendant-arm" macrocycles L^{11}–L^{13}) are listed in Table 3. Generally, the chemistry of Cr^{III} complexes with such ligands is much less developed than the corresponding Co^{III} chemistry.[414]

4.6.5.2.7 Polydentate and macrocyclic imine ligands

(i) Diimine ligands

Since 1985, research on the well-known Cr^{III} complexes of phen, bpy, and related ligands[1] has been dominated by their photo-induced reactions (reviewed in 1999 and 2001).[274,277] This section describes the related synthetic, structural, and analytical studies. Since 1996, much attention has also been paid to Cr^{III} dicarboxylato–diimine complexes as building blocks for molecular materials (described in ections 4.6.4.4.7 and 4.6.4.9.9.

Requirements for accurate structural data (to be used in computational studies of electron-transfer processes in $[Cr(diimine)_3]^{3+}$complexes) led to the determination of crystal structures of several compounds, including $[Cr(phen)_3](ClO_4)_3{\cdot}H_2O$,[430] *cis*-$[Cr(bpy)_2(OH_2)_2]$ $(NO_3)_3$,[431] $[Cr(bpy)_3](ClO_4)_3$,[432] and $[Cr(bpy)_3](PF_6)_3$.[433] Crystal structures and UV–visible spectroscopy of the $[Cr(dmb)_2(NCS)_2]I$, $[Cr(dmb)_2(NCS)_2](I_3)$, and $[Cr(bpy)_2(NCS)_2](I_3)$ complexes (dmb = 4,4′-dimethyl-2,2′-bipyridine) provided evidence for charge-transfer interactions between the complex cation and the iodide anion in the solid state and in solutions.[434] This aided in gaining a mechanistic insight into the redox interactions of structurally similar Ru^{III}/Ru^{II} diimine complexes with the I^-/I_3^- couple in photogalvanic cells.[434] A general method for the syntheses of heteroleptic $[Cr(diimine)_3]^{3+}$ complexes has been proposed recently.[435] Capillary electrophoresis has been applied as a powerful analytical method for $[Cr(diimine)_3]^{3+}$ complexes and their photoaquation products (including separations of enantiomers),[435,436] as well as for the studies of DNA binding of such complexes (see below).

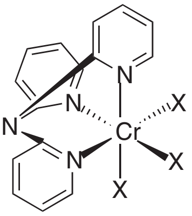
Quenching of the exited states of $[Cr(diimine)_3]^{3+}$ complexes by organic reductants can be used for quantitative generation of unstable $[Cr^{II}(diimine)_3]^{2+}$ complexes (Section 4.6.6.2.2),[437] or for oxidation of phenols in the presence of O_2 (with the potential application in treatment of waste waters).[438] Emission patterns of the $[Cr(diimine)_3]^{3+}$ complexes in aqueous solutions are modified by binding to anionic polyelectrolytes or to micelle-forming substances.[439,440] This feature can be used for tuning the photocatalytic properties of these complexes, as well as for probing the presence of hydrophobic sites in polyelectrolytes.[439] The encapsulation of $[Cr(phen)_3]^{3+}$ in zeolites has been studied as a means of producing a potential catalyst for cyclohexane oxidation.[441]

(ii) Biochemical applications

Extensive research has been performed on the DNA binding of $[Cr(diimine)_3]^{3+}$ complexes, leading to chiral separation of the complexes and to photo-catalyzed DNA cleavage; these data have been reviewed recently.[277] The complexes with an intercalating dipyridophenazine (dppz) ligand are particularly strong DNA binders.[442] The *cis*-$[Cr(phen)_2(OH_2)_2]^{3+}$ complex induced oxidative degradation of DNA *in vitro* in the presence of PbO_2 as an oxidant, due to the formation of Cr^V intermediates.[177] Reactions with $[Cr(phen)_3]^{3+}$ have been used in the mechanistic studies of electron transfer in metalloproteins, such as blue copper proteins[443] or ferredoxins.[444] Unlike the Cr^{III} complexes with aliphatic ligands, the complexes of phen or bpy ligands are genotoxic in bacterial and mammalian cell assays (in the presence of O_2).[176,445] This can be explained by the formation of highly genotoxic Cr^V intermediates,[176] as well as by the slightly higher permeability towards cell membranes, compared with the Cr^{III} complexes of less lypophilic ligands.[446]

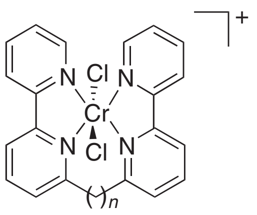
(iii) Tri- and tetradentate polypyridyl ligands

The complexes of tri(2-pyridyl)amine (**90**) and their analogs with deuterated pyridine rings have been characterized by spectroscopic methods.[357,447] Complex (**90**) with $X = F$ shows remarkable solvent dependencies of its UV–visible and ^2H NMR spectra, due to π-stacking interactions of the solvent molecules with the pyridyl groups of the ligands.[447] The *trans*-$[CrCl_2L]^+$ complexes with tetradentate polypyridyl ligands (**91**) have been characterized by X-ray crystallography.[448,449]



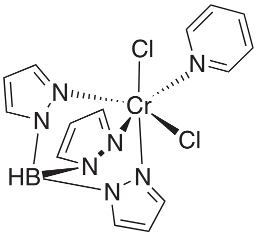
X = Cl or F

(**90**)

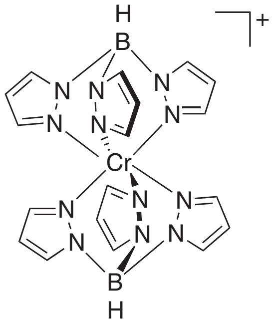


n = 0 or 2

(**91**)



(**92**)



(**93**)

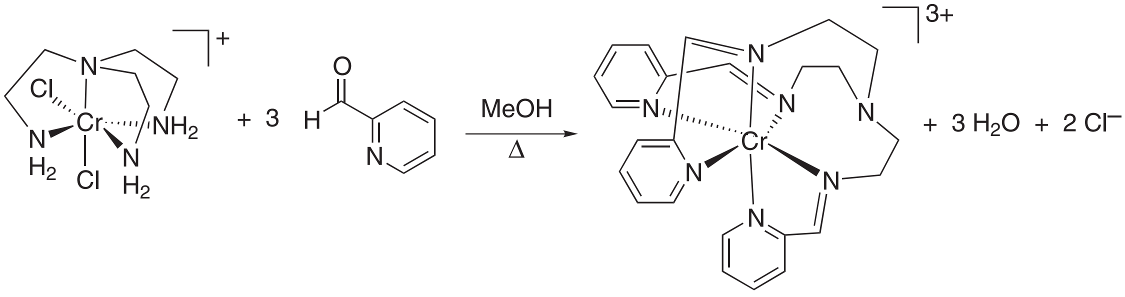
(iv) Polypyrazolyl ligands

The hydrotris(1-pyrazolyl)borato(1−) (Tp) ligand, known since 1966, is distinguished from "classical" polyimine systems (such as phen) by the presence of a delocalized negative charge.[450] The first crystallographically characterized Cr^{III} complex of the Tp ligand, (**92**), was synthesized in 1985.[451] This complex was not mutagenic in the Ames bacterial assay.[451] The $[Cr(Tp)_2]^+$

complex (**93**) was first synthesized in 1996,[452] and its crystal structure was reported subsequently.[453] Several complexes of a general formula $[Cr(Tp)X_nL_{3-n}]^{(2-n)+}$ ($X = Cl$ or I; $L = H_2O$, THF, or pyrazole; $n = 2$ or 3) have been characterized by spectroscopic methods.[451,453,454] A Cr^{III} complex of a substituted Tp ligand has been isolated from the decomposition products of the corresponding Cr^{II} complexes (Section 4.6.6.2.2) and characterized by X-ray crystallography.[455] The Cr—N distances in the Cr^{III}–Tp complexes (typically, 2.04–2.06 Å)[451,453,455] are similar to those in the $[Cr(phen)_3]^{3+}$ complex (2.040–2.055 Å).[430] The differences in energy level splittings of electronic states between $[Cr(Tp)_2]^+$ and the other types of $Cr^{III}N_6$ complexes have been discussed.[452] Stabilizing effect of a substituted Tp ligand has been used to isolate the first structurally characterized Cr^{III} superoxo complex (Section 4.6.5.4.2). Complexes of Cr^{III} with fluoroalkyl-substituted Tp ligands have been patented as catalysts of cyclohexane oxidation to cyclohexanone by organic peroxides.[456]

(v) Miscellaneous ligands

A crystallographically characterized complex (**94**) has been synthesized by a template method (Scheme 11).[457] Several other Cr^{III} complexes of polydentate heterocyclic ligands[458,459] or heterocycle-derived Schiff bases[460,461] have been characterized recently by spectroscopic methods. A Cr^{III} complex of 2-guanidinobenzimidazol (first reported in 1977, no crystal structure available)[462] acts as an inhibitor of photosynthetic system II in spinach thylakoids.[463]



(94)

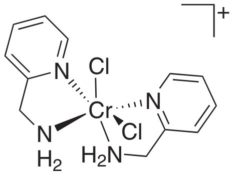
Scheme 11

4.6.5.2.8 Polydentate ligands with amine and imine donors

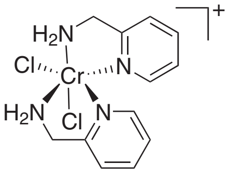
Typical crystallographically characterized complexes (**95**)–(**101**) are illustrated.[458,464–469] Complex (**96**) contains a ubiquitous biological ligand, histamine.[465] Complex (**99**) is distinguished by an unusually high (for a Cr^{III} species) rate of base hydrolysis (seconds timescale at pH ~ 7 and 25 °C).[470] A series of complexes with a hexadentate ligand, *N,N,N′,N′*-tetrakis(2-pyridylmethyl) ethane-1,2-diamine (tpen), have been prepared, including the crystallographically characterized species $[Cr(tpen)(OCOMe)]^{2+}$, $[Cr(tpen)]^{3+}$ (**100**), $[Cr(tpen)(OH)]^{2+}$, and $[Cr(tpen)(OH)_2]^{+}$.[468] The two latter complexes are among the few well-characterized monomeric Cr^{III} complexes with hydroxo ligands (Section 4.6.5.4.1). Some $^{51}Cr^{III}$ complexes with hexadentate macrocyclic ligands containing pyridine and amine donors have been patented for application in medical imaging and immunoassays.[471]

4.6.5.2.9 Polydentate N-donor ligands with amido donors

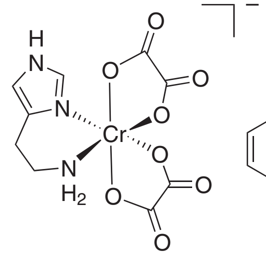
Structures of crystallographically characterized complexes (**102**)–(**108**) are illustrated.[220,472–476] Typical Cr—N(amido) bond lengths in such complexes are 1.88 Å (**102**),[220] 1.97 Å ((**107**) and (**108**)),[475,476] and 2.02–2.05 Å ((**103**)–(**106**)).[472–474] The four-coordinate triamidoamine Cr^{III} complex (**102**) reacts with mild Cl-containing oxidants, such as AgCl or $CuCl_2$, with the formation of the corresponding Cr^{IV} complex (**65**).[220,477] Complexes (**103**)–(**108**) are stabilized by delocalization of the negative charges on amido donors. Five- or six-coordinate Cr^{III} complexes of sterically demanding *β*-diketoiminates ((**103**) or (**104**)) act as alkene polymerization catalysts (Section



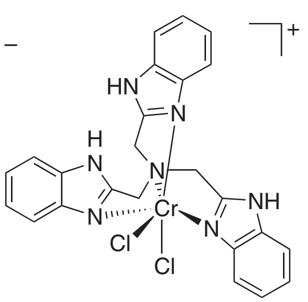
(**95a**)
(*cis*-α form; Ref. 464)



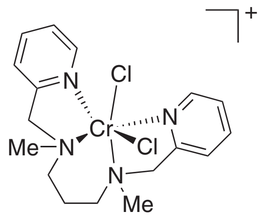
(**95b**)
(*cis*-β form; Ref. 464)



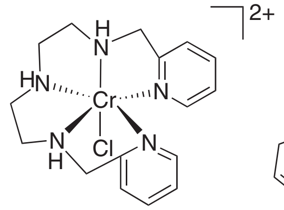
(**96**) (Ref. 465)



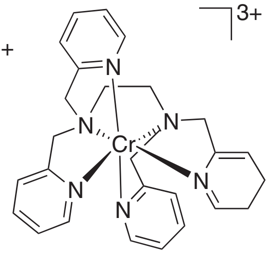
(**97**) (Ref. 458)



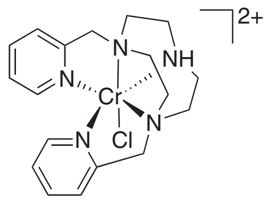
(**98**) (Ref. 466)



(**99**) (Ref. 467)

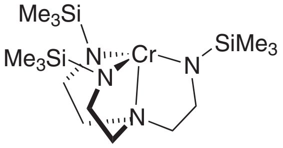


(**100**) (Ref. 468)

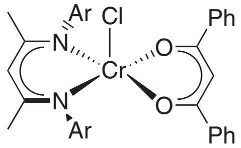


(**101**) (Ref. 469)

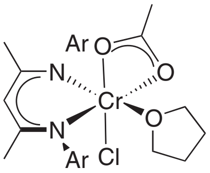
4.6.5.1.2).[303,472,478] For complexes (**103**) and (**104**), the presence of O-donor chelates (β-diketonates or carboxylates) was required to obtain mononuclear species. Dinuclear (chloro-bridged) β-diketoiminato complexes are described in Section 4.6.5.9.13. Similar, but less sterically crowded amidiminato ([ArNC(H)NAr]$^-$), 2-aminopyridinato, and 2-aminomethylpyrrolato ligands form tris-chelated Cr^{III} complexes (**105**),[473] (**106**),[474] and (**107**),[475] respectively. A five-coordinate (square-pyramidal, high-spin) complex (**108**) is formed with a macrocyclic β-diketoiminato donor ligand.[476]



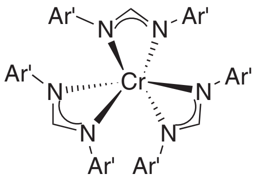
(**102**) (Ref. 220)



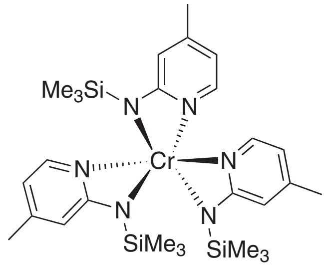
Ar = 2,6-Pr$^i_2$C$_6$H$_3$
(**103**) (Ref. 472)



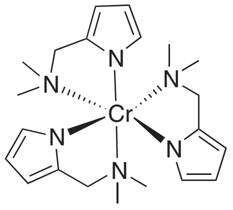
Ar = 2,6-Pr$^i_2$C$_6$H$_3$
(**104**) (Ref. 472)



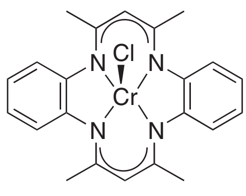
Ar' = 4-MeC$_6$H$_4$
(**105**) (Ref. 473)



(**106**) (Ref. 474)



(**107**) (Ref. 475)



(**108**) (Ref. 476)

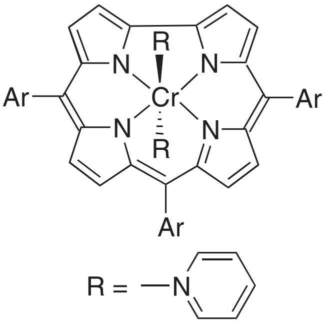
Several Cr^{III} complexes with activated amido donor ligands (e.g., amides of carboxylic or sulfonic acids) have been described, but none of them have been crystallographically characterized.[132,479] Complexes of Cr^{III} with 2-sulfonamide-1,3,4-thiadiazol derivatives act as potent inhibitors of carbonic anhydrases and may have potential use as anti-inflammatory or antidiabetic drugs.[479,480]

4.6.5.2.10 Porphyrins, corroles, and phthalocyanines

(i) Syntheses and characterizations of the complexes

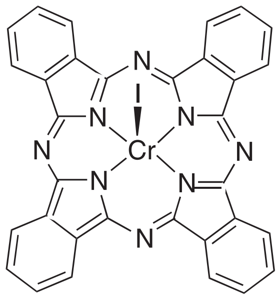
There have been relatively few developments in the chemistry of Cr^{III} porphyrinato complexes since 1985. Syntheses of new octahedral Cr^{III}–tpp derivatives (tpp = *meso*-tetraphenylporphyrinato(2−)) used the well-known reactions of a five-coordinate (square pyramidal) [Cr(tpp)Cl] complex, such as the exchange of Cl^- and/or the addition of a sixth neutral *N*- or O-donor ligand.[1,481] The following complexes have been characterized by X-ray crystallography: [Cr(tpp)Cl(py)],[482] [Cr(tpp)Cl(MeIm)] (MeIm = 1-methyl- or 1,2-dimethylimidazoles),[483] $[Cr(tpp)Cl(OH_2)]$,[484] [Cr(tpp)(OPh)(thf)],[485] [Cr(tpp)(OR)(thf)] (R = 2,4-$(NO_2)_2C_6H_3$),[486] and $[Cr(tpp)(N_3)(py)]$.[487] Formation and magnetic properties of Cr^{III} porphyrinato complexes with nitroxyl radicals as axial ligands (such as (**83**)) have been described in Section 4.6.5.2.1. A crystallographically characterized Cr^{III} complex with a porphyrinogen ligand, possessing a partially hydrogenated porphyrin ring, has been mentioned in Section 4.6.4.2.2 ((**70**) in Scheme 5).[230]

The first crystallographically characterized Cr^{III} corrolato complex, (**109**), has been recently reported.[229] The corrole ring in (**109**) is distinguished by the presence of formally three amido and one imine donors (rather than two amido and two imine donors in porphyrin derivatives), which leads to significantly shorter Cr—N(indole) bonds (1.93–1.95 Å in (**109**) vs. 2.03 Å in [Cr(tpp)Cl(py)]).[229,482]

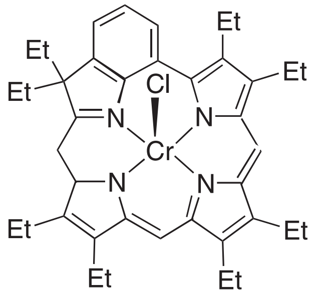


Ar = C_6F_5

(109)



(110)



(111)

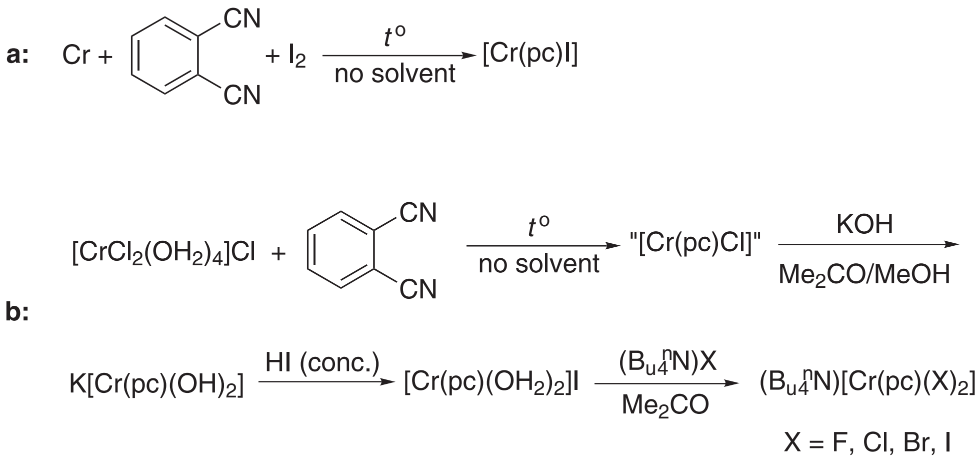
A new Cr^{III} phthalocyaninato complex [Cr(pc)I] (**110**) has been synthesized (Scheme 12a) and characterized by X-ray crystallography.[488] Another crystallographically characterized complex, *trans*-$[Cr(pc)(ONO)_2]^-$ (pc = phthalocyaninato(2−)), has been synthesized using $[Cr(pc)(OH_2)_2]^+$ as a precursor.[489] A general synthetic method for the $[Cr(pc)(X)_2]^-$ complexes has been developed (Scheme 12b), and spectral (electronic and vibrational) and electrochemical properties of these complexes have been compared.[490]

(ii) Reactivity

The relative lability of axial ligands in Cr^{III} porphyrinato complexes (leading to an increase in ligand-exchange rates by 1–2 orders of magnitude compared with usual Cr^{III} complexes) has been observed by many authors.[484,491] For instance, the influence of sterically hindered imidazole ligands on the rates of ligand-exchange reactions has been investigated.[483] Kinetics and mechanisms of photo-induced ligand exchange in five- or six-coordinate Cr^{III} porphyrinato complexes have also been studied extensively.[492–494] The photochemistry of Cr porphyrinato complexes was reviewed in 1992.[495]

The oxo-transfer reactions (illustrated by equations (i)–(iii) in Scheme 13) form the basis for the syntheses of stable Cr^{IV} porphyrinato complexes (equations (i) and (ii) in Scheme 13; see also Section 4.6.4.2.2), as well as for the use of [Cr(tpp)Cl] and related complexes in redox catalysis (Equations (ii) and (iii) in Scheme 13).[1,496,497] The related nitrido-transfer reactions (Equation (iv) in Scheme 13) have also been observed.[139,498,499]

Mechanistic studies of one-electron oxidations or reductions of Cr^{III} porphyrinato complexes have been performed by pulse-radiolysis and electrochemical methods.[500,501] The results (summarized in Equations (v)–(vii), Scheme 13) show that the reduction process can be directed either



Scheme 12

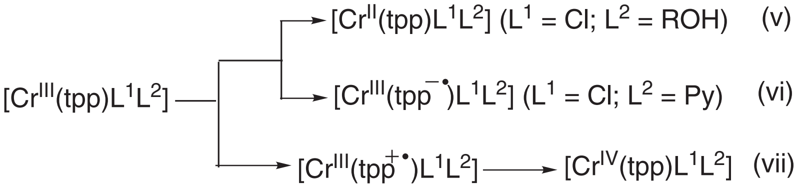
$$\mathrm{ROOH} + [\mathrm{Cr^{III}(tpp)Cl}] \longrightarrow \mathrm{ROH} + [\mathrm{Cr^{V}O(tpp)Cl}] \qquad \text{(i)}$$

$$[\mathrm{Cr^{V}O(tpp)Cl}] + [\mathrm{Cr^{III}(tpp)Cl}] \longrightarrow 2\,[\mathrm{Cr^{IV}O(tpp)}] + 2\,\mathrm{HCl} \qquad \text{(ii)}$$

$$[\mathrm{Cr^{V}O(tpp)Cl}] + \mathrm{R'H} \longrightarrow \mathrm{R'OH} + [\mathrm{Cr^{III}(tpp)Cl}] \qquad \text{(iii)}$$

$$[\mathrm{M^{V}N(p^1)}] + [\mathrm{Cr^{III}(p^2)Cl}] \rightleftharpoons [\mathrm{M^{III}Cl(p^1)}] + [\mathrm{Cr^{V}N(p^2)}] \qquad \text{(iv)}$$

M = Cr or Mn; p^1 and p^2 are different porphyrin derivatives



Scheme 13

to the ligand or to the metal ion, dependent on the complex used (Equations (v) and (vi) in Scheme 13).[501] By contrast, the first step in the oxidation process for all the studied complexes was the formation of a ligand-based cation-radical, followed (in some cases) by intramolecular electron transfer with the formation of a $\mathrm{Cr^{IV}}$ complex (Equation (vii) in Scheme 13).[500] The ligand-based oxidation step can lead to the formation of $\mathrm{Cr^{III}}$ complexes with oxidized porphyrin rings.[502] In a related study on phthalocyaninato complexes, the electrochemically oxidized derivative of $[\mathrm{Cr^{II}(pc)}]$ was isolated and described as $[\mathrm{Cr^{III}(pc^{\bullet +})Cl_2}]$ (rather than $[\mathrm{Cr^{IV}(pc)Cl_2}]$) on the basis of its crystal structure (see also Section 4.6.6.2.3).[503] Electrochemical studies of $\mathrm{Cr^{III/II}}$ porphyrinato and phthalocyaninato complexes were reviewed in 2001.[504]

(iii) Applications

The use of $\mathrm{Cr^{III}}$ porphyrinato complexes in catalysis became less prominent over the last 20 years due to developments in the $\mathrm{Cr^{III}}$–salen and related systems (Section 4.6.5.8.4). The most important recent applications of [Cr(tpp)Cl] as a catalyst include the synthesis of polycarbonates by copolymerization of 1,2-cyclohexene oxide derivatives and CO_2 (using supercritical CO_2 as a solvent),[505] and epoxidation of alkenes.[506,507] Patented technical applications of [Cr(tpp)Cl] include its use in the adsorbers of nitrogen oxides from air[508] and in photovoltaic devices.[509] Complex (**111**) has been patented (among the other metal ion complexes of porphyrin derivatives) as a photosensitizer in photodynamic therapy of cancer.[510] The [Cr(pc)F] complex has been patented as an inhibitor of viral reverse transcriptase and a potential anti-AIDS agent.[511]

4.6.5.3 P-, As-, and Sb-donor Ligands

Binding of "soft" P-, As-, or Sb-donors is uncommon for a "hard" acid, Cr^{III}.[1] In agreement with the known trend,[1] all the mononuclear Cr^{III} complexes with *P*-donor ligands, described since 1985,[512–514] are mixed-ligand species with halo or pseudo-halido (CN^-, NCS^-, or $N_3{}^-$) ligands. The following complexes have been characterized by X-ray crystallography: *trans*-$[CrCl_4(PMe_3)_2]^-$, *mer*-$[CrCl_3(PMe_2Ph)(OPMe_2Ph)]$,[512] *fac*-$[CrX_3\{MeC(CH_2PMe_2)_3\}]$ (X = Cl or CN),[513,514] and *trans*-$[CrI_2\{Me_2P(CH_2)_3PMe_2\}]^+$.[514] Typical Cr—P bond lengths in the Cr^{III} trialkylphosphine complexes are 2.45–2.48 Å.[512–514] Complexes with mixed-donor-atom ligands containing P-donors are mentioned in Sections 4.6.5.1.2 and 4.6.5.8.5, and dinuclear species with P-donor bridging ligands are described in Section 4.6.5.9.12. Electronic (UV–visible or MCD) spectra of Cr^{III} complexes with bi- or tridentate phosphine ligands have been compared.[514] To our knowledge, no nonorganometallic Cr^{III} complexes with As- or Sb-donors, apart from the few previously known species,[1] have been described.

4.6.5.4 O-donor Ligands

4.6.5.4.1 Aqua and hydroxo ligands

(i) Syntheses and structural characterizations

A crystal structure of a widely used commercial reagent, $[Cr(OH_2)_6](NO_3)_3 \cdot 3H_2O$, was first described in 1991; the Cr—O bond lengths were 1.95–1.97 Å.[515] The crystal structure of a supramolecular assembly, $[Cr(OH_2)_6][Na][calix[4]arenesulfonate](Me_2CO) \cdot 10.5H_2O$, revealed intercalation of $[Cr(OH_2)_6]^{3+}$ into the hydrophilic layer, which consisted of the sulfonate groups and water of crystallization.[516] The $[Cr(OH_2)_5R]^{2+}$ (R = C-donor ligand) complexes are described in Section 4.6.5.1.2.

Anionic Cr^{III} hydroxo complexes, $Na_9[Cr(OH)_6]_2(OH)_3 \cdot 6H_2O$ and $Na_4[Cr(OH)_6]Cl \cdot H_2O$, have been isolated from solutions of $Cr(OH)_3$ or $CrCl_3$ in concentrated aqueous NaOH and characterized by X-ray crystallography.[517] Other crystallographically characterized mononuclear Cr^{III} complexes with OH^- ligands are mentioned in Sections 4.6.5.2.6 and 4.6.5.2.8. Polynuclear OH- or H_3O_2-bridged Cr^{III} species are described in Sections 4.6.5.9.3–4.6.5.9.5.

(ii) Studies by instrumental and computational methods

Numerous studies on conventional and photo-assisted ligand-exchange reactions of Cr^{III} aqua and hydroxo complexes have been reviewed,[7,270,274] as have spectroscopic studies of the *trans*-$[CrCl_2(OH_2)_4]^+$ complex (the main constituent of the widely used commercial reagent, $CrCl_3 \cdot 6H_2O$).[518] Several analytical methods, including capillary electrophoresis linked to inductively coupled plasma mass spectrometry (ICPMS),[519] as well as ion-exchange chromatography, electrophoresis, dialysis, and ultrafiltration,[520] have been used to detect the formation of mononuclear hydroxo intermediates (e.g., $[Cr(OH_2)_5(OH)]^{2+}$) during the base hydrolysis of $[Cr(OH_2)_6]^{3+}$ (see also Section 4.6.5.9.4). Capillary electrophoresis has also been employed for the separation and detection of $[Cr(OH_2)_6]^{3+}$, $[Cr(OH_2)_5Cl]^{2+}$, and $[Cr(OH_2)_4Cl_2]^+$.[521]

The $[Cr(OH)(OH_2)_x(Solv)]^{2+}$ ions ($x = 0–3$, Solv = MeOH or MeCN) have been detected by ESMS in the gas phase, on fast evaporation of solutions of $[Cr(OH_2)_6](ClO_4)_3$ in MeOH or MeCN.[47] The $[Cr(NH_3)_5(OH)]^{2+}$ complex promotes the phosphorylation (by ATP) of serine and threonine OH-residues in bovine serum albumin *in vitro*.[522]

A methodology for structural studies of the first and second coordination shells in $[Cr(OH_2)_6]^{3+}$ and related complexes in aqueous solutions, based on multiple-scattering modeling of XAFS spectra, has been developed by Muñoz-Páez and co-workers.[523–525] Another technique, recently applied to studying of inner- and outer-sphere H_2O coordination in $[Cr(OH_2)_6]^{3+}$, is ^1H nuclear magnetic relaxation dispersion (NMRD).[526] Applications of different instrumental methods led to consistent results, indicating the presence of 13 ± 1 H_2O molecules with an average Cr···O distance of 4.02 Å in the second coordination shell of $[Cr(OH_2)_6]^{3+}$ in aqueous solutions.[9]

The $[Cr(OH_2)_6]^{3+}$ complex is among the most widely used models in theoretical studies of coordination compounds. Recent computational studies, performed mainly by the DFT or molecular dynamics methods, targeted the following problems:

(i) Electronic structure of the complex.[527]
(ii) Thermodynamics and kinetics of aquation of the Cr^{3+} ion.[528–531]
(iii) Kinetics and mechanisms of H_2O exchange in the inner and outer coordination spheres.[532,533]
(iv) Deprotonation and stability of $[Cr(OH_2)_6]^{3+}$.[534,535]
(v) Electron transfer within the $[Cr(OH_2)_6]^{3+/2+}$ couple.[536,537]

(iii) Applications

Replacement of H_2O ligands in $[Cr(OH_2)_6]^{3+}$ or $[CrCl_2(OH_2)_4]^+$ is widely used in the syntheses of new Cr^{III} complexes.[1] The $[Cr(OH_2)_6]^{3+}$ and $[Cr(OH_2)_5Cl]^{2+}$ complexes are among the key species in the redox cycles of the Fe/Cr redox flow storage batteries.[538,539]

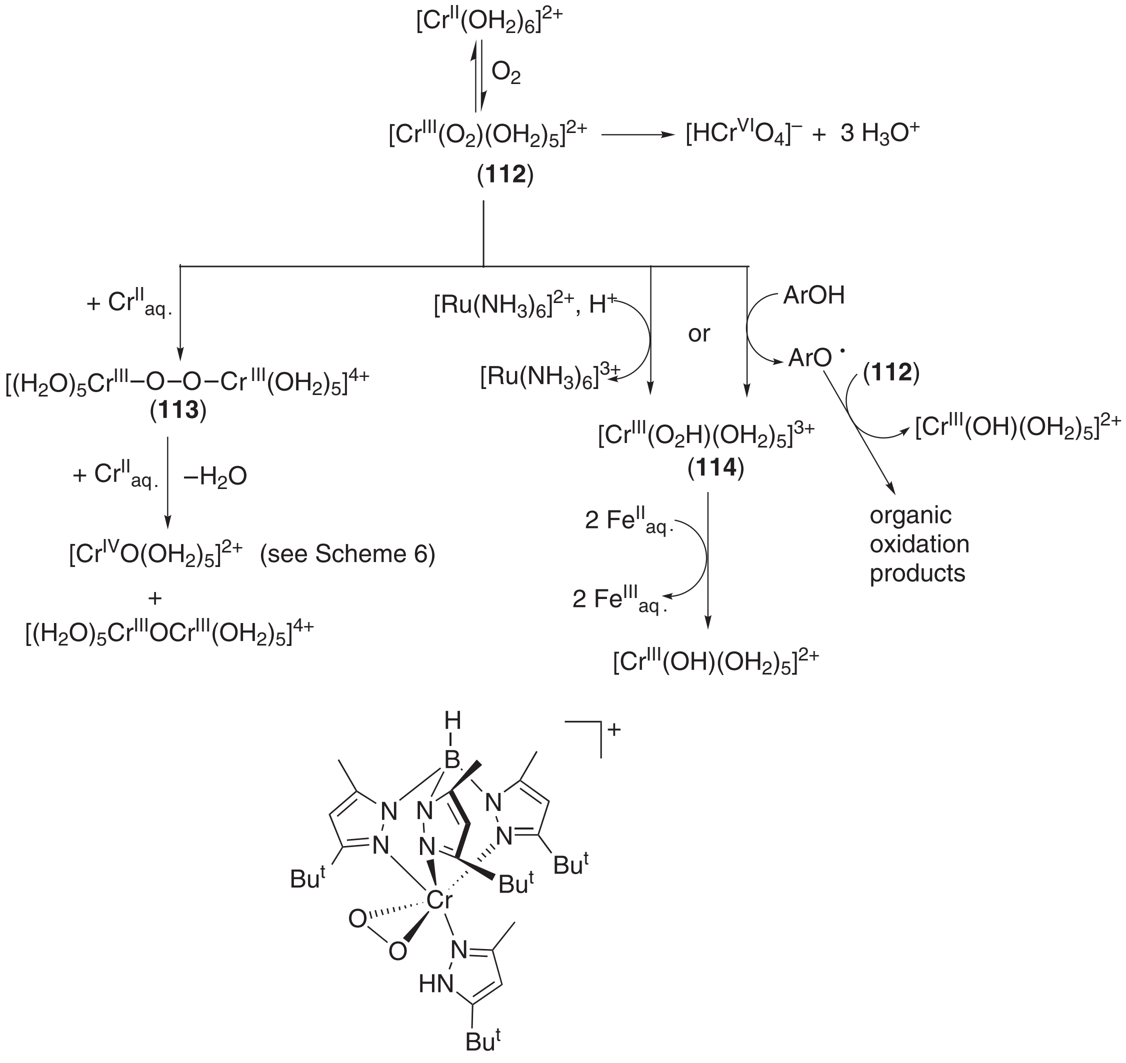
4.6.5.4.2 Superoxo and peroxo ligands

In the last 20 years, the chemistry of Cr^{III} complexes with O_2-derived ligands was developed mainly by Bakac *et al.* as outlined in two reviews (1993 and 1995).[231,232] Typical reactions of formation and decay of Cr^{III} superoxo, peroxo, and hydroperoxo complexes ((**112**), (**113**), and (**114**), respectively) in acidic aqueous solutions are summarized in Scheme 14.[231,232,234,540–542] The unstable complexes (**112**)–(**114**) have been generated in solutions and studied by spectroscopic (UV–visible, Raman) and kinetic methods. Recently, the first crystal structure of a Cr^{III} superoxo complex, stabilized with a substituted hydrotris (1-pyrazolyl)borato(1−) ligand ((**115**) in Scheme 14) has been reported, and the nature of the O_2^- ligand has been confirmed by IR spectroscopy.[543] An intramolecular rearrangement reaction of a Cr^{III} hydroperoxo complex, $[Cr^{III}(cyclam)(O_2H)(OH_2)]^{3+}$, has been used to generate a Cr^V complex, $[Cr^VO(cyclam)]^{3+}$.[164,174] Kinetics and mechanisms of the reactions of (**112**) with biological thiols (cysteine, glutathione, and penicillamine) in acidic aqueous solutions have been studied.[544]

4.6.5.4.3 Oxo anions as unidentate ligands

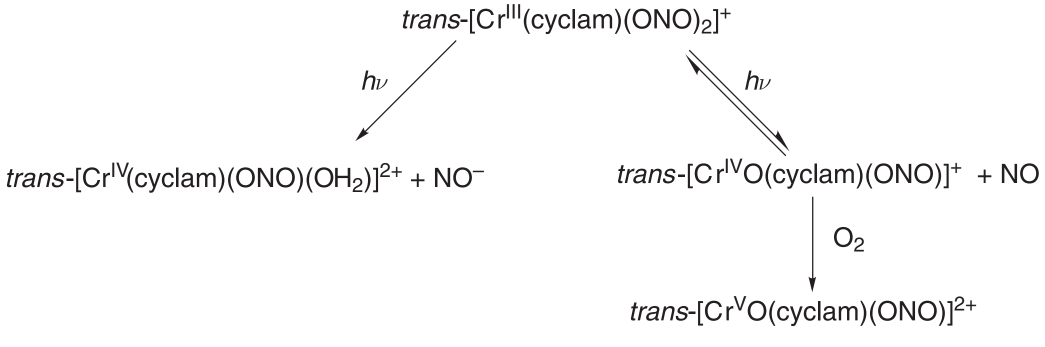
Carboxylates and other oxo anions have a strong tendency to form polynuclear Cr^{III} complexes (Section 4.6.5.9.8). A formato complex, $[Cr(OCHO)_6]^{3-}$, seems to be the only crystallographically characterized mononuclear Cr^{III} carboxylate.[545] This complex possesses a distorted octahedral geometry, with two Cr—O—C—O units in the *sp*- and four in the *ap*-conformation; the Cr—O bond lengths are 1.97–1.99 Å.[545]

Unidentate coordination of oxo anions can be readily achieved in Cr^{III} complexes with macrocyclic ligands. Thus, nitrito complexes, *trans*-$[Cr(cyclam)(ONO)_2]^+$ and *trans*-$[Cr(pc)(ONO)_2]^+$, have been characterized by X-ray crystallography (Sections 4.6.5.2.6 and 4.6.5.2.10, respectively).[390,489] The photo-induced labilization of a nitrito ligand in the former complex (Scheme 15) can potentially be used for the delivery of NO to biological targets.[546,547] A hydrogen carbonato complex, *cis*-$[CrL^6F(OCO_2H)]^+$ ($L^6 =$ *rac*-$Me_6[14]aneN_4$, see Scheme 9), has been generated in aqueous



(**115**)

Scheme 14



Scheme 15

solutions.[548] This complex undergoes decarboxylation (Equation (5)) in weakly acidic aqueous media, i.e., acts as a partial functional mimic of a Zn^{II}-dependent enzyme, carbonic anhydrase.[548]

$$[CrL^6F(OCO_2H)]^+ \rightarrow [CrL^6F(OH)] + CO_2 \tag{5}$$

The first crystallographically characterized Cr^{III} complex with a monodentate phosphate ligand, *cis*-$[Cr(phen)_2(OPO(OPh)_2)(OH_2)]^+$, was reported in 1998.[549] This complex is stable in neutral aqueous solutions (crystallizes as a H_3O_2-bridged dimer after several days at pH 7.4 and 22 °C, see Section 4.6.5.9.5; while the monomeric complex crystallizes at pH 3.0).[549] Coordination of a phosphate diester moiety to Cr^{III} is likely to mimic the binding mode in the Cr^{III}–DNA complexes, formed during the intracellular reduction of carcinogenic $[Cr^{VI}O_4]^{2-}$ (Sections 4.6.2.3.5 and 4.6.5.11.3).[11] Phosphonato complexes, $[Cr(NH_3)_5(OPHOPh)]^{2+}$ and $[Cr(NH_3)_5(OPO_2Ph)]^{2+}$, have been prepared by ligand-exchange reactions from $[Cr(NH_3)_5(OH_2)_5]^{3+}$.[550] Syntheses and applications of the $[Cr(NH_2R)_5(OSO_2CF_3)]^{2+}$ complexes are described in Section 4.6.5.2.1 (Scheme 8a).

4.6.5.4.4 Other unidentate O-donor ligands

The chemistry of Cr^{III} complexes with phenoxyl radicals (similar to that for other redox-active ligands, Section 4.6.5.4.6) has been reviewed recently.[551] Although the coordination of dmso to Cr^{III} had been known from spectroscopic studies since the 1950s,[1] the first crystal structures of such complexes were reported in 1998.[552] At present, the crystallographically characterized complexes include $[Cr(dmso)_6]^{3+}$ and mixed-ligand species with oxalato or polyamine ligands.[552,553] Several new crystallographically characterized compounds have been synthesized for the well-known urea complex, $[Cr(OC(NH_2)_2)_6]^{3+}$,[1] using $[Co^{III}(dimethylglyoximato)_2(NO_2)_2]^-$, $[ZnCl_4]^{2-}$, or $[Pt^{IV}Cl_5(OH)]^{2-}$ as counterions.[554–556] The first crystal structure of *mer*-$[CrCl_3(thf)_3]$ was reported in 1986;[557] this compound has been used extensively as a starting material for the syntheses of Cr^{III} complexes since the 1960s.[1] Similarly to amides (Section 4.6.5.2.2), sterically hindered siloxides form Cr^{III} complexes with low coordination numbers (three to five),[558,559] including a crystallographically characterized compound, $[Cr\{OSi(OBu^t)_3\}_3(NHEt_2)_2]$.[558] Thermal decomposition of Cr^{III} siloxide complexes is used for preparation of ultrapure Cr silicates (for applications in catalysis).[558]

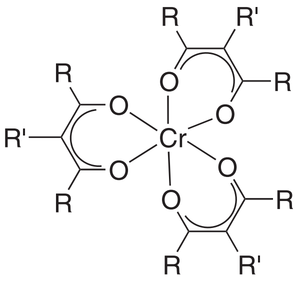
4.6.5.4.5 β-Ketoenolates (β-diketonates) and related ligands

Complexes of Cr^{III} with ligands possessing carbonyl donors in β-positions and a delocalized negative charge have been studied extensively since the 1930s.[1] The prototype compounds of this series are $[Cr(acac)_3]$ (acac = acetylacetonato(1−) = 2,4-pentanedionato(1−), (**116**)) and $[Cr(mda)_3]$ ((**117**); $mdaH_2$ = malonodialdehyde = propanedial). While many Cr^{III}β-ketoenolato complexes are known,[1] relatively few of them have been described since 1985 (e.g., (**118**)–(**123**); only (**119**) and (**120**) have been crystallographically characterized).[560–565] Nucleophilic substitution in the complexes of brominated ligands (e.g., (**116**) with R′ = Br) has been applied for the syntheses of new derivatives of (**116**).[566] Syntheses of polymeric compounds with the covalently bound substituted (**116**) units (such as (**123**)) may lead to the development of new materials with useful electrical, magnetic, photosensitive, or catalytic properties (Section 4.6.5.10).[565,567] Several new synthetic methods for (**116**) and related complexes, suitable for industrial conditions, have been developed recently, including mechanochemical reactions of solid Cr^{III} salts with the ligands,[568] and electrolysis of the ligands with a Cr anode and a Ni cathode.[569]

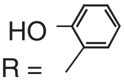
From all the coordination compounds of Cr^{III}, (**116**) and its analogs with fluoro-substituted ligands have probably the widest range of practical applications. Some of these, such as the formation of thin films of Cr oxides by thermal decomposition of the complexes,[570] or extraction of Cr^{III} into organic phases (used for Cr recovery from waste waters, as well as in analytical purposes),[571,572] have been known for decades. These applications employ the well-known general properties of metal β-ketoenolates, namely, the high volatility and solubility in organic solvents.[1] Some recent applications of (**116**) and its derivatives are summarized in Table 4.[96,573–580] Compound (**116**) is widely used as a starting material in the syntheses of Cr^{III} complexes,[1] and the coordination of Cr^{III} to β-ketoenolates is often used to stabilize complexes of less common ligands (e.g., (**76**) or (**103**)).

Table 4 Some recent applications of [Cr(acac)$_3$] and its derivatives.

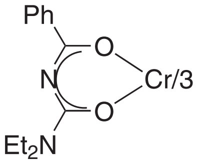
Application	*References*
Catalyst of alkene polymerization (grafted into molecular sieves)	573,574
Reagent in the preparation of Ziegler type catalysts	575
Oxidation catalyst in organic synthesis (review; 1992)	96
Catalyst of photo-induced oxidation (application in organic synthesis)	576
Promotor of extraction of lanthanoid(III) ions with β-diketonates	577
A component of liquid crystals (3-alkyl-substituted ligands)	578
Fire retardant and smoke suppressant (as an addition to polymers)	579
Calibrant for magnetic susceptibility measurements	580



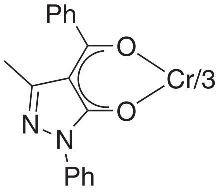
(116) R = Me; R' = H
(117) R = R' = H
(118) R = Me; R' = -CH$_2$CHCH$_2$
(Ref. 559)



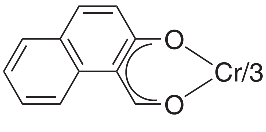
(119) R = ; R' = H
(Ref. 561)



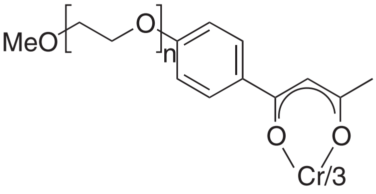
(120) (Ref. 562)



(122) (Ref. 564)



(121) (Ref. 563)

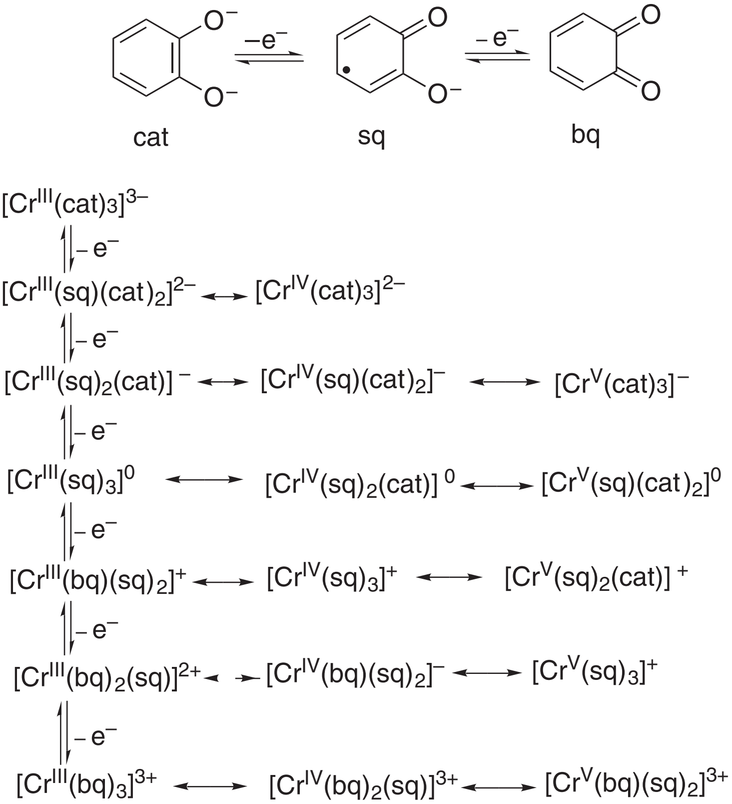


(123) (Ref. 565)

Numerous spectroscopic and theoretical studies of (**116**) and related complexes have been carried out (reviewed in 1997).[581,582] Recently, theoretical investigations of the electronic[583] and vibrational[584] spectra of (**117**) have also been performed. Ground and exited states of (**116**) doped into [Al(acac)$_3$] have been studied by time-resolved EPR spectroscopy at 77 K (as a model of ruby).[585] Ligand and solvent effects in the electrochemistry of Cr^{III} β-ketoenolates have been reported.[586] There have been many recent physicochemical studies relating to the main practical applications of (**116**) and its derivatives. For instance, thermodynamic parameters of bond cleavage and solvation of (**116**) in gas phase have been determined by mass spectrometry.[587] Solvation studies of (**116**) in the liquid phase have been performed by NMR spectrometry.[588–590] The ability of supercritical CO$_2$ to dissolve (**116**) has been studied (as an alternative to the use of organic solvents for the extraction of (**116**)).[591] A study mimicking the conditions of preparation of the Cr/SiO$_2$ catalysts (by the treatment of preheated SiO$_2$ with (**116**) at 160–240 °C) has been performed, and the possible nature of catalytic centers under various preparation conditions has been proposed.[592] Complex (**116**) was genotoxic in bacterial and mammalian cell assays; this was attributed to its relatively high permeability across cell membranes, due to its high lipophilicity.[593]

4.6.5.4.6 Dioxolene ligands

The chemistry of Cr^{III} complexes with catecholate (cat) and its oxidized forms (sq = semiquinonato(1−) and bq = benzoquinone in Scheme 16), as well as with substituted analogs of these ligands, was reviewed in 2001.[594] The most significant properties of these complexes are related to the redox activity of the ligands, and to the possibility of redox tautomerism of the complexes (Scheme 16). These features prevent an unambiguous assignment of the Cr oxidation state in the oxidized complexes. Thus, X-ray crystallographic and magnetic data support the structure $[Cr^{III}(sq)_2(cat)]^-$ for the monoanionic complexes of catechol and its substituted analogs.[595] Alternatively, the XANES spectra (featuring an increased preedge absorption and a shift of the edge to higher energy compared with typical Cr^{III} complexes) and EPR spectra (intense sharp signals with $g_{iso} \sim 1.972$ in solutions at room temperature) of such complexes are characteristic of Cr^{IV} and Cr^{V}, respectively.[596] Reduction of Cr^{VI} with catechol or its derivatives in aqueous solutions probably leads to a mixture of Cr^{III} complexes with sq and bq ligands (or their $Cr^{V/IV}$ tautomers, Scheme 16).[175,597]

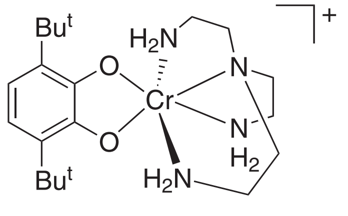


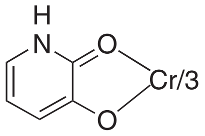
Scheme 16

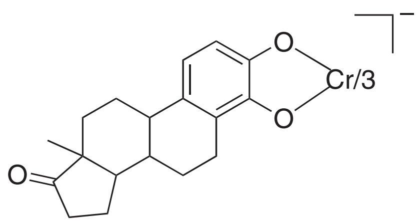
A catecholato-polyamine complex (**124**) and its semiquinonato analog have been characterized by X-ray crystallography and DFT calculations.[598,599] Several Cr^{III} complexes of the ligands, related to semiquinones, have been described, but only (**125**) has been crystallographically characterized.[600–602] Chromium(III) complexes of halogen-substituted 1,2-semiquinone ligands act as oxidants towards strong electron donors, with the formation of charge-transfer salts (Scheme 17).[603–605] Compounds shown in Scheme 17 have been characterized by X-ray crystallography,[603–605] and some of them possess semiconductor properties.[604] Complexes of Cr^{III} (or other transition metal ions) with catechol estrogens (such as (**126**)) have been patented as steroid receptor binders and potential antitumor agents.[606]

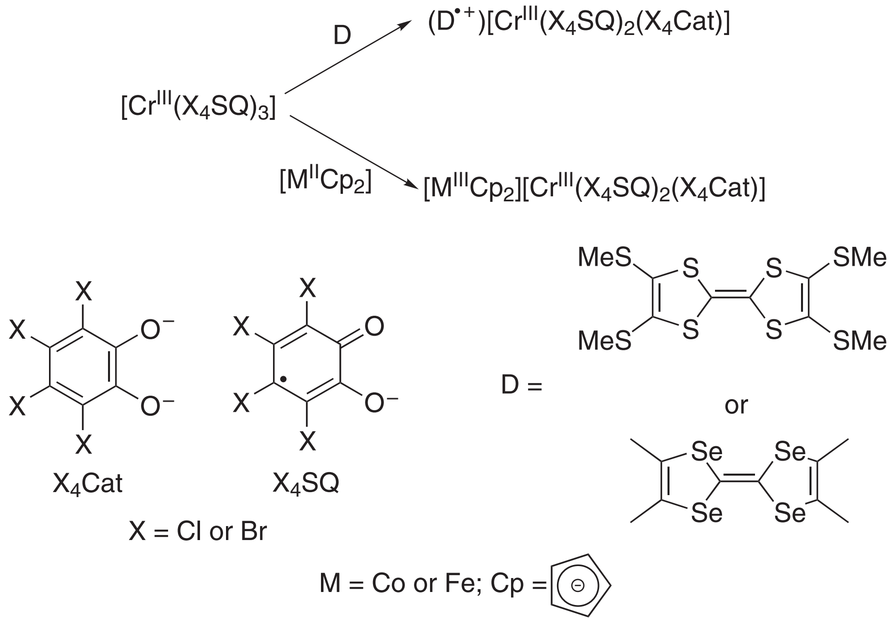
4.6.5.4.7 *Dicarboxylates*

In the last 15 years, the well-known $[Cr(ox)_3]^{3-}$ complex[1] has been used extensively in studies aimed towards the design of molecular materials with useful electric, magnetic, photophysical, adsorptive, or catalytic properties. Probably the first example of such a material, $Na_2(Me_3PhN)_5[Cr(ox)_3]_2Cl{\cdot}5H_2O$, was discovered by accident during attempts to isolate Cr^{V} oxalato complexes (first reported in 1987, published in 1995).[607] This compound has a two-dimensional


(**124**) (Ref. 598, 599)


(**125**) (Ref. 600)


(**126**) (Ref. 606)



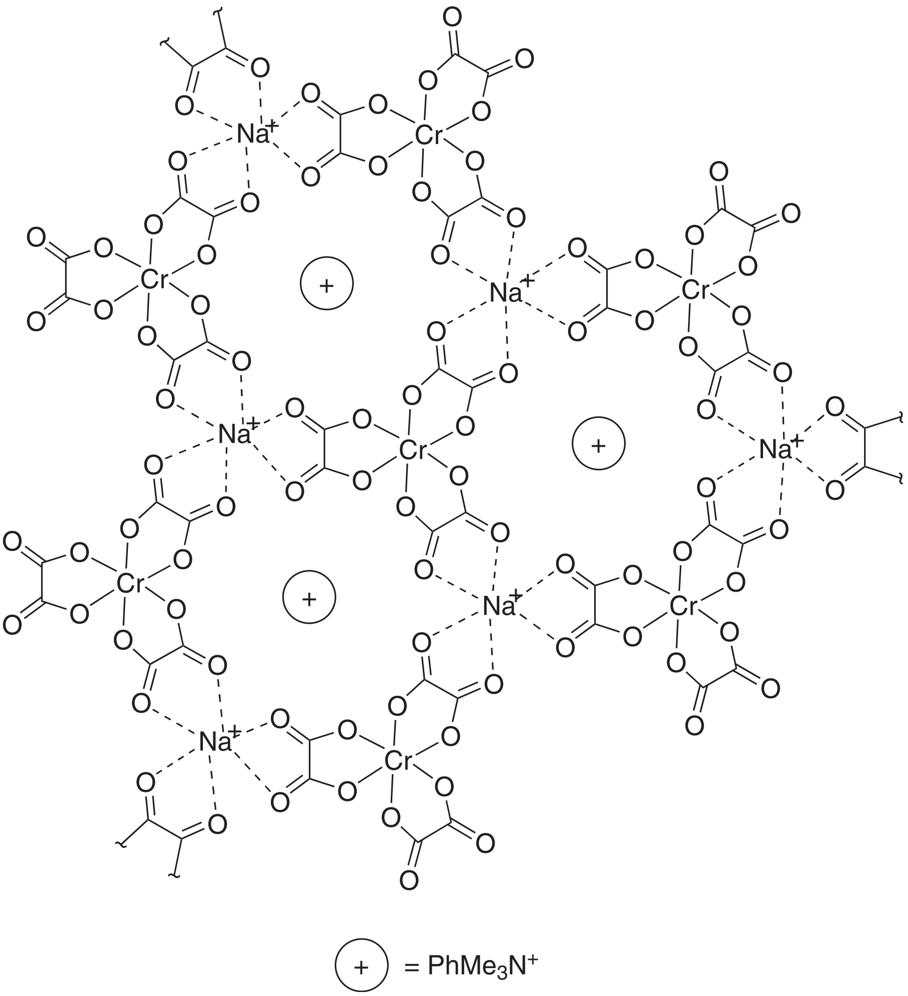
Scheme 17

(2D) achiral microporous structure, assembled by the electrostatic attraction of Na^+ cations to the carbonyl groups of the ligands, as well as by the host–guest interactions between the anionic network and the Me_3PhN^+ cations (Scheme 18). Subsequently, various types of 2D-networks were prepared using mixed-ligand Cr^{III} complexes with dicarboxylato (oxalato or malonato) and aromatic diimine ligands.[608–613] Importantly, the use of $[M(bpy)_3]^{2+/3+}$ complexes (where $M = Fe^{II}$, Ni^{II}, Cr^{III}, or Co^{III}) as counterions caused the crystallization of chiral, three-dimensional (3D) anionic networks of a general formula $[M'Cr(ox)_3]^{2-}$ ($M' = Li$ or Na).[614,615] Similar techniques have been used for the syntheses of 2D- or 3D-networks of a general structure $[N(Alk)_4][M^{II}Cr(ox)_3]$ (where M = Mn, Fe, Co, Ni, Cu, or Zn).[616] These oxalato-bridged complexes of two transition-metal ions are described in Section 4.6.5.9.9. In a search for molecular conducting materials, a series of charge-transfer salts of $[Cr(ox)_3]^{3-}$ and organic radical-cations have been prepared.[617–619] Some of these compounds exhibit superconducting properties at low temperatures ($T_c \sim 6\,K$).[618] These solids contain ion channels (e.g., H_2O/H_3O^+), and thus bestow both electronic and ionic conductivity.[617]

All the above-mentioned molecular materials have been characterized by X-ray crystallography. Other crystallographically characterized compounds (since 1985) include:

(i) Several $[Cr(ox)_3]^{3-}$ salts with simple or complex cations.[620–625]
(ii) A double-complex salt, $[Cr(mal)(OH_2)_4][Cr(mal)_2(OH_2)_2]$ (mal = malonato(2−)).[626]
(iii) Mixed-ligand complexes with oxalato and amine/imine ligands.[608,609,611,612,627]

Solvent effects on the Cr—O bond lengths in $[Cr(ox)_3]^{3-}$ have been studied by XAFS spectroscopy.[628] The Cr^{III} oxalato complexes are used in Cr^{III}-based chrome-electroplating solutions, avoiding the use of toxic and carcinogenic Cr^{VI}.[114,629]

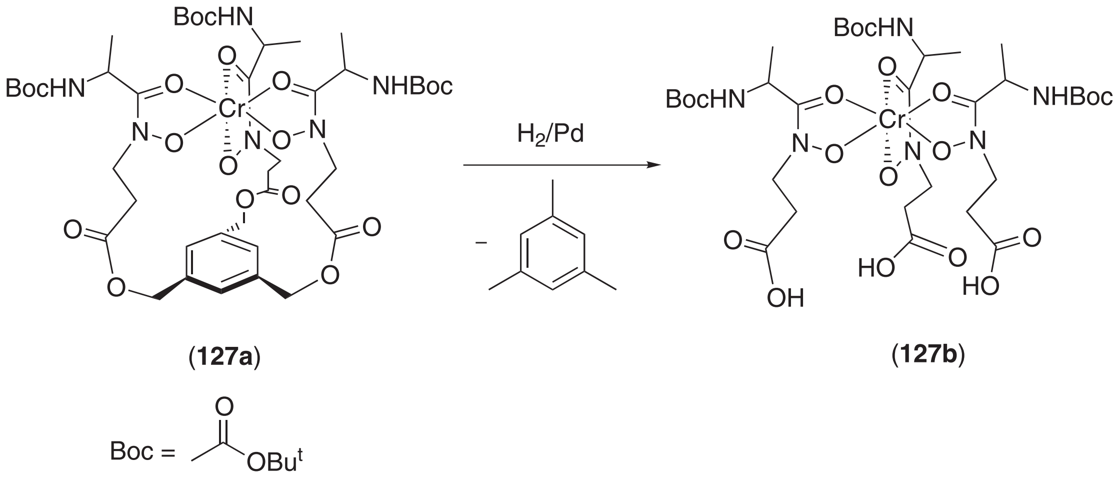


Scheme 18

4.6.5.4.8 *Other bidentate O-donor ligands*

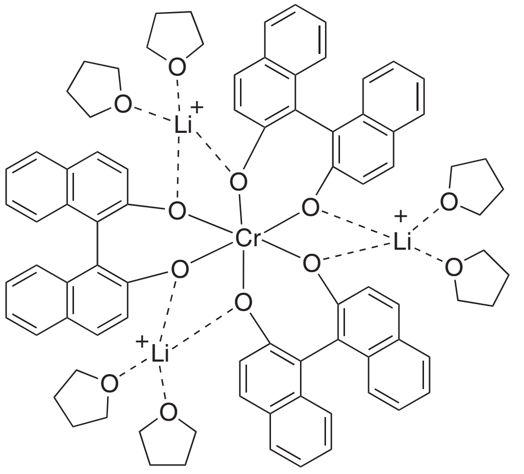
Typical structures of the complexes ((**127**)–(**132**)) are illustrated (see also Scheme 19). All the compounds have been characterized by X-ray crystallography, except for (**127**) and (**130**); for the latter, the crystal structure of a V^{III} analog is available.[630–636] In addition, a series of articles by Kanno *et al.* on isomerization and racemization of the Cr^{III} complexes of substituted 2,2′-bipyridine-1,1′-dioxide ligands[637–639] continued the earlier works of these authors on the stereochemistry of metal complexes with bidentate aromatic *N*-oxide ligands.[1]

A novel template method (Scheme 19) has been applied for the preparation of a Cr^{III} complex with oriented hydroxamate ($[RC(O)N(O)R']^-$) ligands, (**127b**); this approach can be used for the syntheses of models of biologically important hydroxamato complexes.[630] A model of biological enterobactin ligands, *R*-binaphtol, forms an unusual Cr^{III} complex (**128**), involving the coordination of $[Li(thf)_2]^+$ units.[631] A similar assembly, involving Li^+ cations, has been observed in the complex of 1,2:5,6-di-*O*-isopropylidene-α-Δ-glucofuranose (dagH; (**129**)).[632] Complexes (**128**) and (**129**) are among the first examples of the use of non-macrocyclic O-donors for the construction of host molecules (in this case, Cr^{III} complexes) for alkali metal ions.[631,632] Complex (**130**) possesses a rare phosphynoyl-carboxylato donor set.[633] Chiral Cr^{III} complexes of ATP and other nucleotide polyphosphates are used extensively as substrates in mechanistic studies of enzyme reactions (Section 4.6.5.11.3). To assist in the studies of stereochemistry of such Cr^{III} complexes, a series of model mixed-ligand compounds with pyrophosphato ligands have been prepared ((**131**) depicts one of the three crystallographically characterized stereoisomers).[634,635] A rare example of a bidentate ether donor coordination to Cr^{III} is shown in (**132**).[636]

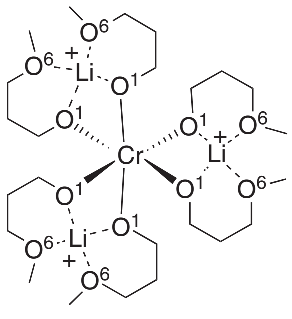


(127a) (127b)

Scheme 19

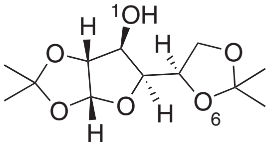


(128) (Ref. 631)

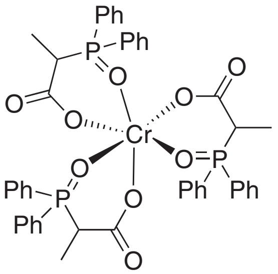


[Cr(dag)$_6$Li$_3$]

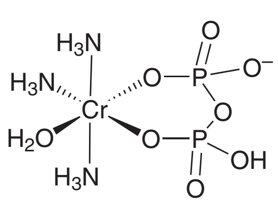
(129) (Ref. 632)



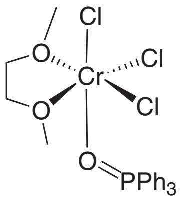
dagH



(130) (Ref. 633)



(131) (Ref. 634, 635)

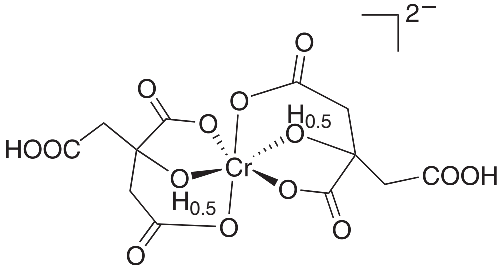


(132) (Ref. 636)

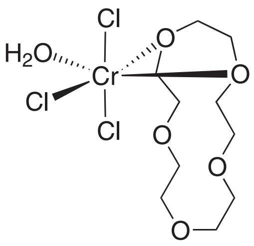
A crystallographically characterized Cr^{III} complex with lactate and cyclic polyamine ligands has been mentioned in Section 4.6.5.2.6. Well-known (but not fully characterized) Cr^{III} complexes of 2-hydroxycarboxylates (such as lactate, citrate, salicylate, or sulfosalicylate)[1] have been successfully applied as a replacement for toxic and carcinogenic Cr^{VI} compounds used as mordants in wool dyeing.[640]

4.6.5.4.9 *Polydentate and macrocyclic O-donor ligands*

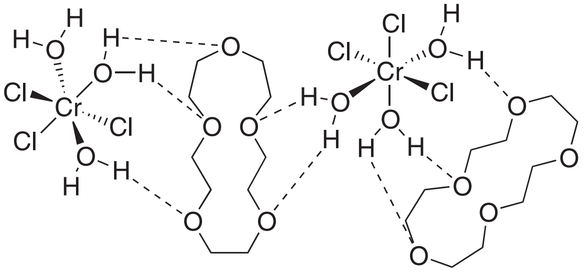
Typical complexes ((**133**)–(**137**)) are shown (crystal structures have been determined for all except (**137**)), see also (**79**) and (**87**).[641–645] The first crystallographically characterized Cr^{III} citrato complex, (**133**), has been isolated as a product of Cr^{VI} reduction by citric acid in weakly acidic aqueous solutions.[641] In contrast to the N-donors (Sections 4.6.5.2.6– 4.6.4.2.10), complexes of Cr^{III} with macrocyclic O-donor ligands are rare. Thus, reactions of Cr compounds with 15-crown-5 in the presence of water led either to a partial coordination of the O-donor atoms in the macrocyclic ring (**134**),[642] or to the formation of supramolecular structures with the macrocyclic molecules in the second coordination sphere of the metal ion (**135**).[643] Similar supramolecular structures have been reported for the adduct of $[Cr(NCS)_6]^{3-}$ with 18-crown-6 (Section 4.6.5.2.3),[356] or for that of $[Cr(OH_2)_6]^{3+}$ with calix[4]arenesulfonate (Section 4.6.5.4.1).[516] Syntheses under strictly anhydrous conditions led to Cr^{III} complexes of calixarene ligands ((**136**) and (**79**)),[249,644] as well as to a cage complex (**137**).[645] During the synthesis of (**136**), an unusual activation of a C—H bond in a methylene group of the ligand occurred, leading to the fusion of two calixarene ligands.[644] A helically chiral complex (**137**) has been studied as a model for the metal complexes of natural ligands, siderophores (see also Section 4.6.5.8.2).[645]



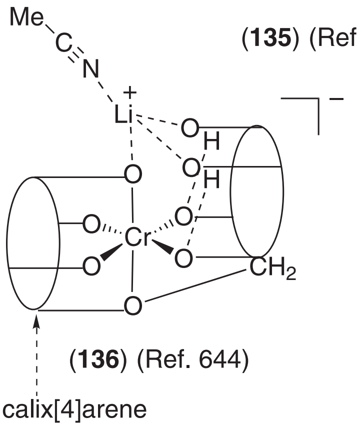
(**133**) (Ref. 641)



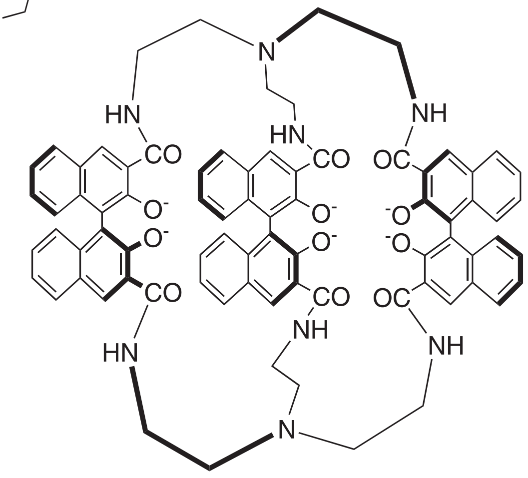
(**134**) (Ref. 642)



(**135**) (Ref. 643)



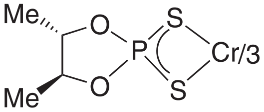
(**136**) (Ref. 644)

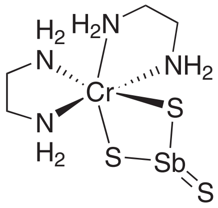


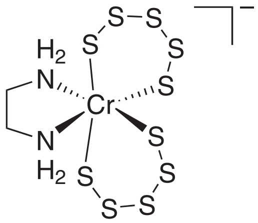
(**137**) $[CrL]^{3-}$; L = (Ref. 645)

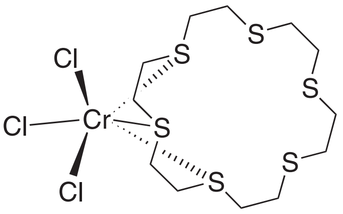
4.6.5.5 S- and Se-donor Ligands

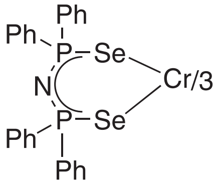
Coordination of a "hard" metal ion, Cr^{III}, to "soft" S- or Se-donors is regarded as unusual.[646] Typical structures of crystallographically characterized compounds ((**138**)–(**142**)) are illustrated.[647–651] By far the most numerous known mononuclear complexes of this type are those with 1,1-dithiolato(1−) ligands, including dialkyldithiocarbamates, xanthates, dithiocarboxylates, dithiophosphinates, and dithiophosphates.[1] One of the reasons for the ongoing interest in these compounds[647,652–660] is the wide use of dialkyldithiocarbamates ($[(Alk)_2NCS_2]^-$) and their metal complexes as analytical reagents, pesticides, fungicides, rubber vulcanization accelerators, and high-pressure lubricants.[661] Optically active dialkyldithiophosphate complexes (e.g., (**138**)) have been studied as typical examples of chiral discrimination in complexes with D_3 symmetry.[647,658,660]

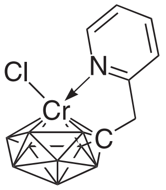

(**138**) (Ref. 647)


(**139**) (Ref. 648)


(**140**) (Ref. 649)


(**141**) (Ref. 650)


(**142**) (Ref. 651)


(**143**) (each unlabeled vertex is occupied by BH; ref. 678)

New types of Cr^{III} complexes with sulfide ligands ((**139**) and (**140**)) have been prepared by the solvothermal method.[648,649] Compound (**139**) is the first example of a transition metal complex with a $[SbS_3]^-$ ligand.[648] A series of Cr^{III} complexes with macrocyclic thio- or selenoethers have been prepared, including (**141**) ($[CrCl_3([18]aneS_6)]$), $[CrBr_2([14]aneS_4)]^+$, and $[CrCl_2([16]aneSe_4)]^+$ (the two latter complexes have been characterized by ESMS and XAFS spectroscopy).[646,650,662,663] The first Cr^{III} iminodiphosphinoselenido complex, (**142**), was described in 2000.[651] Typical Cr—S(Se) bond lengths are: 2.42–2.44 Å ((**138**) and other 1,1-dithiolato(1−) complexes),[647,652–659] 2.37–2.39 Å (**139**),[648] 2.39–2.42 Å (**140**),[649] 2.44–2.46 Å (**141**),[650] 2.57 Å ($[CrCl_2([16]aneSe_4)]^+$ determined by single-scattering modeling of XAFS data),[663] and 2.56 Å (**142**).[651] Complexes of Cr^{III} with mixed-donor ligands containing *S*-donors are described in Sections 4.6.5.8.1 and 4.6.5.8.5, and polynuclear Cr^{III} complexes with *S*-donor bridging ligands are described in Section 4.6.5.9.12.

4.6.5.6 Halide Ligands

There is relatively little new information on mononuclear Cr^{III} halido complexes since 1985 (polynuclear halido-bridged complexes are described in Section 4.6.5.9.13). The first crystal structures of $[CrCl_6]^{3-}$ and $[CrBr_6]^{3-}$ have been determined; the Cr—Cl and Cr—Br distances are 2.30–2.33 Å and 2.51–2.52 Å, respectively.[664,665] The latter anion, which is thermodynamically unstable at ambient conditions,[664] has been stabilized in an unusual compound, $[4\text{-}BrC_6H_4NH_3]_6[CrBr_6]Br_3\cdot 2MeCO_2H$.[665] The electronic structure of the $^4T_{2g}$ exited state of $[CrF_6]^{3-}$ has been studied by molecular orbital calculations.[666]

Since $CrCl_3$ (anhydrous, polymeric), $[CrCl_2(OH_2)_4]Cl$, and $[CrCl_3(thf)_3]$ are the most commonly used starting materials for the syntheses of new Cr^{III} compounds,[1] mixed complexes with chloro ligands are known for almost every other ligand type. Applications of $CrCl_3$ in organic synthesis were reviewed in 1999.[667] A series of fluoro-amine[668–671] and fluoro-oxalato[672] complexes have been studied by spectroscopic methods. A new efficient method for the synthesis of $[CrF(NH_3)_5]^{2+}$ (characterized by X-ray crystallography) has been developed.[673] A crystallographically characterized complex, *trans*-$[CrF_2(py)_4]^+$, has been obtained by disproportionation of $[Cr^I(\eta\text{-}C_6H_6)_2](PF_6)$ in pyridine (this also gave Cr^{II} and Cr^0 complexes).[674] Influences of various halo-donors on the spectroscopic and electrochemical properties of *cis*- and *trans*-$[CrX_2(cyclam)]^+$, and *trans*-$[CrX_2(pc)]^-$ have been investigated (X = F, Cl, Br, or I; see also Sections 4.6.5.2.6 and 4.6.5.2.10).[490,675]

4.6.5.7 H-donor Ligands

Most of the known Cr hydride complexes are the π-donor, sandwich-type carborane complexes,[676,677] which are described in the *Comprehensive Organometallic Chemistry* series. Recently, a "pendant-arm" Cr^{III} carborane complex containing a pyridine donor (**143**) has been prepared and characterized by spectroscopic methods.[678] Complexes of this type are of interest in the synthesis of new compounds for the treatment of cancer by boron neutron capture therapy and the development of new catalytic systems for alkene polymerization (Section 4.6.5.1.2).[678]

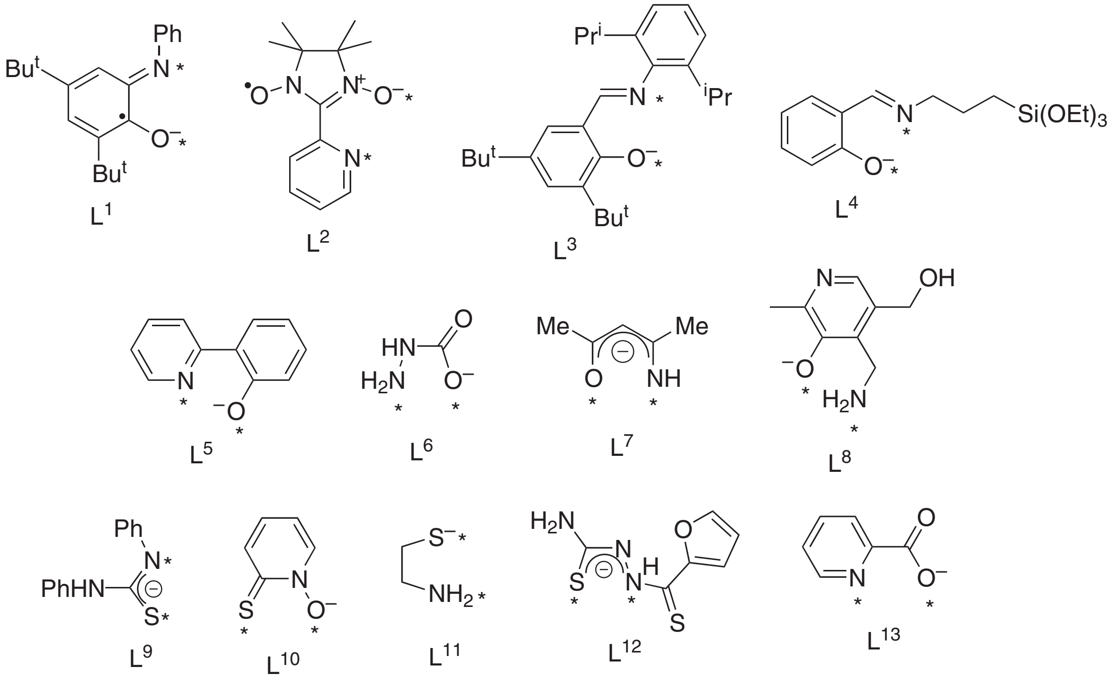
4.6.5.8 Mixed Donor Atom Systems

4.6.5.8.1 Bidentate N–O, N–S, and O–S donor ligands

Typical ligand structures (L^1–L^{13}) are shown in Scheme 20 (binding sites of the Cr^{III} ion are designated with asterisks); complexes of Cr^{III} with natural amino acids are described in Section 4.6.5.11.1. The redox chemistry of the Cr^{III} *o*-iminobenzosemiquinonato complexes (such as a crystallographically characterized complex $[Cr(L^1)_3]$) and their reduced analogs with *o*-aminophenolato ligands is similar to that of Cr^{III} semiquinonato/catecholato complexes (Scheme 16 in Section 4.6.5.4.6).[679] Spectroscopic studies (UV–visible, luminescence, MCD, and Raman) of a mixed-ligand complex with a chelating nitronyl nitroxyl radical, $[CrL^2(acac)_2]^+$, revealed exchange coupling between the Cr^{III} and organic radical centers (see also Section 4.6.5.2.1).[680] The compound $[Cr(L^3)_2Cl(NCMe)]$ (characterized by X-ray crystallography), as well as another complex of this salicylaldiminato ligand ((**81**)), acts as a catalyst of alkene polymerization.[304] The $[Cr(L^4)(OAc)_2]^-$ complex and its analogs have been patented as catalysts (supported on SiO_2) for the production of alcohol/ketone mixtures by the decomposition of alkyl hydroperoxides.[681] The $[Cr(L^5)_3]$ complex has been characterized by X-ray crystallography, EPR spectroscopy, and electrochemical techniques.[682] Hydrazidocarboxylato complexes, such as $[Cr(L^6)_3]$, have been studied as possible products of corrosion of stainless steel reservoirs for the storage of hydrazine and its analogs (used as components of rocket fuel).[683] A novel mechanochemical method for the synthesis of a β-iminoketonato complex, $[Cr(L^7)_3]$, has been proposed.[684] A mixed-ligand complex with a biological ligand ($[Cr(L^8)(ox)_2]^{2-}$, HL^8 = vitamin B_6, ox = oxalato(2−)) has been characterized by X-ray crystallography.[465]

The first Cr^{III} complexes with *N*,*N′*-diphenylthiourea ($[Cr(L^9)_3]$, characterized by X-ray crystallography),[685] 2-mercaptopyridine-*N*-oxide ($[Cr(L^{10})_3]$),[686] and 2-mercaptoethylamine (*fac*-*S*-$[Cr(L^{11})_3]$)[687] have been described. The latter complex has been used for the synthesis of *S*-bridged heteropolynuclear compounds (Section 4.6.5.9.12).[687] The recent interest in the Cr^{III} complexes of thiosemicarbazide derivatives (such as $[CrL^{12}(acac)_2]$) is related to their potential antibacterial, antiviral, or antitumor activities.[688–693]

Probably the most studied Cr^{III} complexes of this type were those with the picolinato (L^{13}) ligand. The prototype complex, $[Cr(L^{13})_3]$, has been widely used as a nutritional supplement since the early 1980s,[12,694,695] though its efficacy and safety have been questioned.[11,263,696,697] The crystallographically characterized *mer*-$[Cr(L^{13})_3]$ complex was isolated from acidic aqueous solutions (pH ~ 1),[698] and an increase in the pH value (to ~4.0) led to a hydroxo-bridged dimer (Section 4.6.5.9.3).[698,699] Detailed studies of the electronic, vibrational, and ^1H NMR spectra of $[Cr(L^{13})_3]$ have been reported.[699,700] The biological activities of $[Cr(L^{13})_3]$, including the potentially beneficial actions, such as stimulation of glucose and Ca^{II} metabolism, and adverse effects, such as DNA damage, have been reviewed recently.[11,12,694,695,697] One rather unusual application of $[Cr(L^{13})_3]$ was the generation of reactive Cr^{II} and Cr^{IV} picolinato complexes (see also Sections



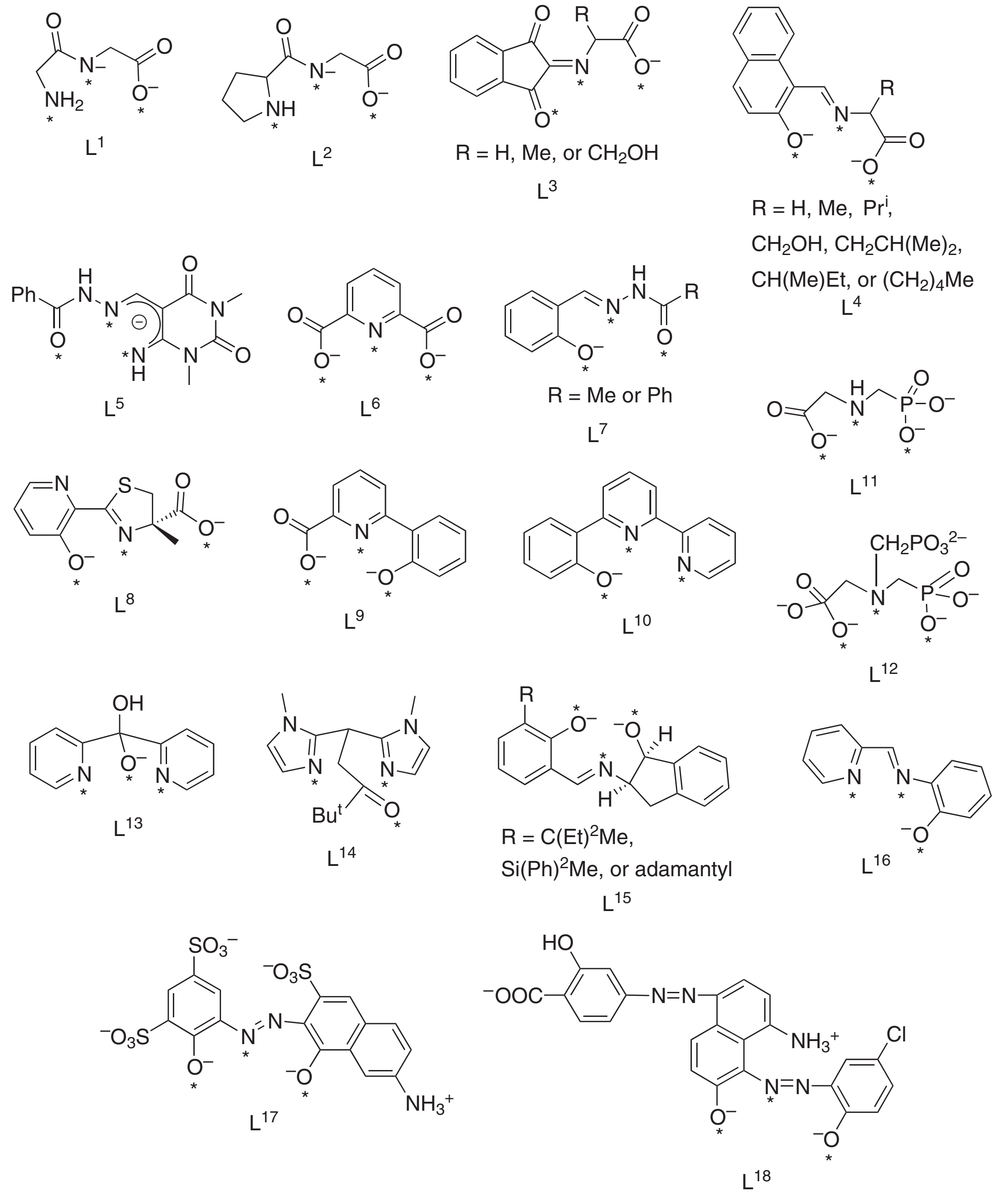
Scheme 20

4.6.4.4 and 4.6.6.8) in aqueous solutions by pulse radiolysis technique, with a potential use in decontamination of nuclear reactors.[262]

4.6.5.8.2 Tridentate N–O donor ligands

Typical ligand structures (L^1–L^{18}) are shown in Scheme 21 (binding sites of the Cr^{III} ion are designated with asterisks); in addition, some Cr^{III} complexes with aminodicarboxylates or tridentate amino acids are described in Sections 4.6.5.8.4 or 4.6.5.11.1, respectively. Complexes of Cr^{III} with amino acids, peptides, and their derivatives have been studied extensively as possible models of a natural Cr^{III}-containing compound, which is thought to be involved in glucose metabolism (Sections 4.6.5.11.1 and 4.6.5.11.2). Three mononuclear Cr^{III} complexes with synthetic dipeptides, *mer*-$[Cr(L^1)_2]^-$, *mer*-$[Cr(L^1)(3,3\text{-tri})]$ ($H_2L^1 = $ GlyGly; 3,3-tri $= H_2N(CH_2)_3NH(CH_2)_3NH_2$), and *mer*-$[Cr(L^2)_2]^-$ ($H_2L^2 = $ ProGly), have been characterized by X-ray crystallography.[701–703] A related dinuclear Cr^{III} dipeptido complex is described in Section 4.6.5.9.7. Several types of Cr^{III} complexes with amino acid-derived Schiff base ligands (such as $[CrL^3Cl(OH_2)_2$ or $[Cr(L^4)_2]^-$) have been described.[704,705]

Complexes of Cr^{III} with a benzoylhydrazone derivative (*mer*-$[CrL^5(OH_2)_3]^{2+}$),[706] or with dipicolinic acid ($[Cr(L^6)_2]^-$)[707] have been crystallographically characterized. A preliminary report[708] suggests that $[Cr(L^6)_2]^-$ is a potent insulin mimetic in animal models (unlike the Cr^{III} picolinato complex, Section 4.6.5.8.1, which acts as an insulin enhancer).[11,695] Complexes with salicylaldehyde hydrazone derivatives, such as $[Cr(L^7)_2]^+$, have been screened for cytotoxicity in human colon cancer and leukemia cell lines, but showed low activities compared with the corresponding Cu^{II} complexes.[709,710] Diastereomeric Cr^{III} complexes, $[Cr(L^8)_2]^-$, of a natural siderophore ligand (used by certain types of microorganisms for the uptake and transport of Fe^{III}) have been synthesized and characterized by X-ray crystallography.[711] Due to the similarity in chemical properties of Fe^{III} and Cr^{III}, these two ions can share metabolic pathways in biological systems.[11] Several Cr^{III} complexes with synthetic ligands, similar to siderophores (e.g., $[Cr(L^9)_2]^-$ and $[Cr(L^{10})_2]^-$), have also been crystallographically characterized.[682,712] Complexes such as $[Cr(L^{11})_2]^-$, where L^{11} is the active ingredient of glyphosate (a widely used herbicide), have been studied in relation to the mechanisms of immobilization and decomposition of the herbicide in soils.[713]



Scheme 21

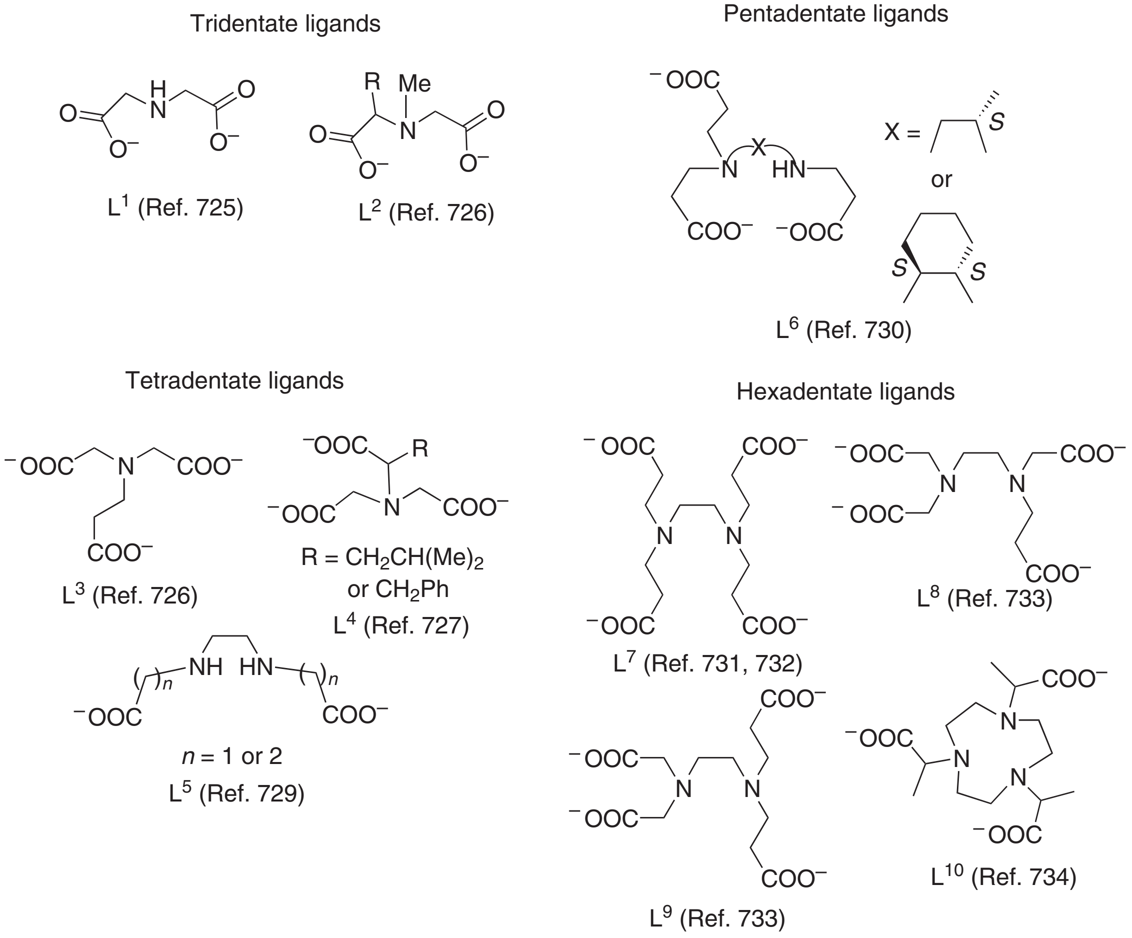
Many of the Cr^{III} complexes with tridentate N—O ligands possess notable reactivities or catalytic properties. For instance, $[Cr(L^{12})_2]^{9-}$ was used to promote the conversion of *ortho*-positronium to *para*-positronium.[714] The $[Cr(L^{13})_2]^+$ complex was formed (over a timescale of several weeks at ambient temperature) from $[CrCl_2(OH_2)_4]^{3+}$ and bipyridyl ketone in weakly acidic aqueous solutions (thus, the aquation of the ketone to give HL^{13} was promoted by coordination to Cr^{III}).[715] $[Cr(L^{14})Cl_3]$ was used as a catalyst of alkene polymerization (see also Section 4.6.5.1.2).[301] Chiral $[Cr(L^{15})X_3]$ complexes (the ligand X is not defined) have been patented as catalysts of asymmetric cycloaddition or of stereoselective epoxy ring opening (similar to the complexes of chiral salen derivatives, Section 4.6.5.8.4).[716,717] $[Cr(L^6)(bpy)Cl]^+$ and $[Cr(L^{16})(bpy)Cl]^+$ have been used as catalysts of oxidation of hydrocarbons by organic peroxides.[718,719]

The use of Cr^{III} complexes with azo dyes is well known (the stability of the dye increases due to the formation of a kinetically inert Cr^{III} complex).[720] Several Cr^{III}-containing special purpose dyes have been patented in recent years; some representative compounds are $[Cr(L^{17})_2]^{6-}$ (a water-soluble dye used in inkjet devices),[721] or $[Cr(L^{18})_2]^-$ (a dye for anodized Al).[722]

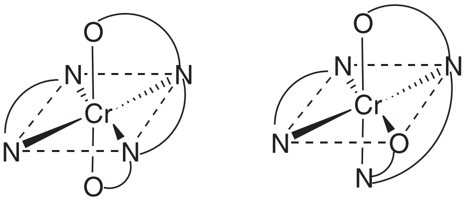
4.6.5.8.3 Aminopolycarboxylates (complexones)

(i) Syntheses and characterizations

The chemistry of Cr^{III} complexes with the title ligands, including edta, nitrilotriacetate (nta), and their derivatives, has been studied extensively since the 1940s.[1] The literature published before 1991 has been reviewed (including a detailed description of stereochemistry of the complexes).[9,723,724] More recently, crystallographic characterizations of the Cr^{III} complexes with L^1–L^{10} ligands (Scheme 22) have been reported.[725–734] The influence of the lengths of alkyl residues on the geometry of the complexes is illustrated in Scheme 23.[729] A solid-state synthesis of K[Cr(edta)] has been performed by the reaction of $KCr(SO_4)_2$ with Na_2H_2edta at 160 °C.[735] A semiempirical molecular orbital study of $[Cr(edta)]^-$ and related complexes has been performed recently.[736]



Scheme 22



trans-(*O*)-
$[CrL^5(phen)]^+$
($n = 1$)

cis-(*O*)-
$[CrL^5(phen)]^+$
($n = 2$)

Scheme 23

(ii) Reactivity

Although an anomalous lability of the unidentate ligands X in the $[Cr(HL)X]^-$ complexes (where L^{4-} is a hexadentate edta-type ligand) is well known,[1,9] mechanistic studies of this phenomenon are continuing. For example, recent results of variable-pressure kinetic studies point to the formation of $[CrL]^-$ intermediates as a reason for such lability.[491,737] The effects of geometric isomerism on the ligand-exchange kinetics in Cr^{III} aminopolycarboxylato complexes have been studied.[738] In a series of studies, the kinetics and mechanisms of oxidation of such Cr^{III} complexes to Cr^{VI} compounds in neutral and basic aqueous solutions have been investigated.[739,740]

Detailed studies of ligand and solvent effects on electrochemical reductions of Cr^{III} aminopolycarboxylates have been performed.[741,742] The observed differences in electrochemical behavior between *cis*- and *trans*-N_2O_4 Cr^{III} complexes have been explained by different Jahn–Teller distortions (JTD) of their Cr^{II} analogs (Section 4.6.6.8).[741] Electrochemical reduction of Cr^{III}–edta complexes has been used as a model reaction in studies of heterogeneous electron-transfer processes.[743]

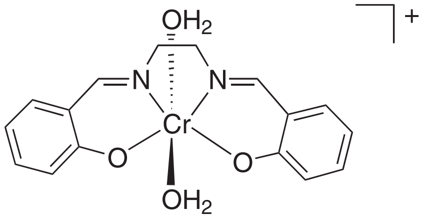
(iii) Applications and biological effects

Several new analytical methods for Cr^{III}, based on its complexation with classical aminopolycarboxylate reagents, have been developed recently, including capillary electrophoresis[744,745] and liquid chromatography coupled with atomic absorption spectroscopy.[746] The $^{51}Cr^{III}$–edta complexes are used in environmental analyses (e.g., as tracers in ground water studies)[747] and in medical tests (e.g., to assess the colonic permeability in ulcerative colitis).[748] Some Cr^{III} complexes of edta derivatives with lipophilic residues have been patented for use in magnetic resonance imaging.[749] Complexes of Cr^{III} with amino acid-derived ligands (such as L^4 in Scheme 22) have been used as selective noncovalent binders for NMR-spectroscopic studies of protein structures.[728] Interactions of Cr^{III}–edta complexes with lipid–water interfaces have been studied.[750] Additions of Na_2H_2edta to Cr^{III}-contaminated soils led to a dramatic increase in Cr^{III} bioavailability, resulting in high toxicity for plants.[751]

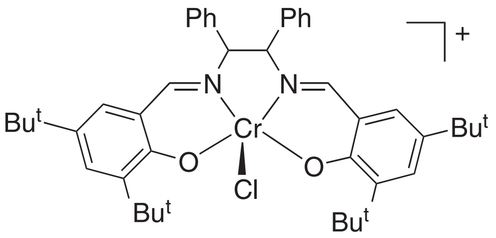
4.6.5.8.4 Tetradentate Schiff base N–O donor ligands (salen and its derivatives)

(i) Applications in catalysis

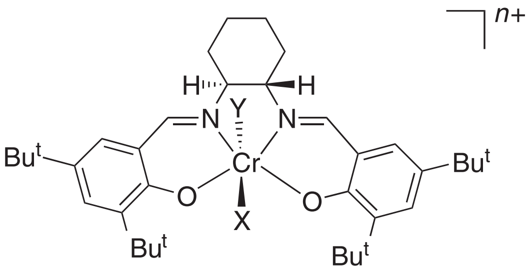
The first use of $[Cr(salen)(OH_2)_2]^+$ (**144**) as a catalyst of oxo-transfer reactions (similar to Equations (i) and (iii) in Scheme 13, Section 4.6.5.2.10) was reported by Kochi and co-workers in 1985.[1,151] This is now a rapidly developing area, described in several recent reviews.[214,752–755] In Section 4.6.5.8.4 "salen" is used as a generic name of tetradentate Schiff base ligands, such as those in (**144**)–(**148**). The main advantage of Cr^{III}–salen complexes as catalysts, compared with chemically similar Cr^{III} porphyrinato systems (Section 4.6.5.2.10), is the availability of versatile salen-type ligands through simple high-yield syntheses.[753] Syntheses of the corresponding Cr^{III} complexes usually involve reactions of Cr^{II} with the ligands, followed by exposure to air.[151]



(**144**)

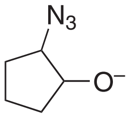


(**145**)



a: $n = 0$; X = THF; Y = N_3^-

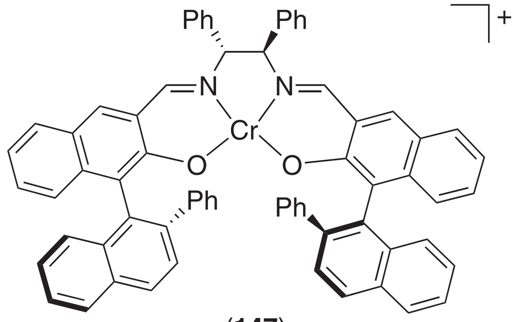
b: $n = 0$; X = THF; Y =



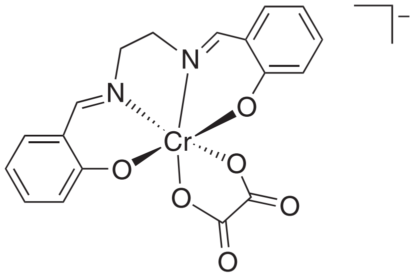
c: $n = 0$; X = SbF_6^-; no Y

d: $n = 1$; X and Y are not defined

(**146a–d**)



(**147**)

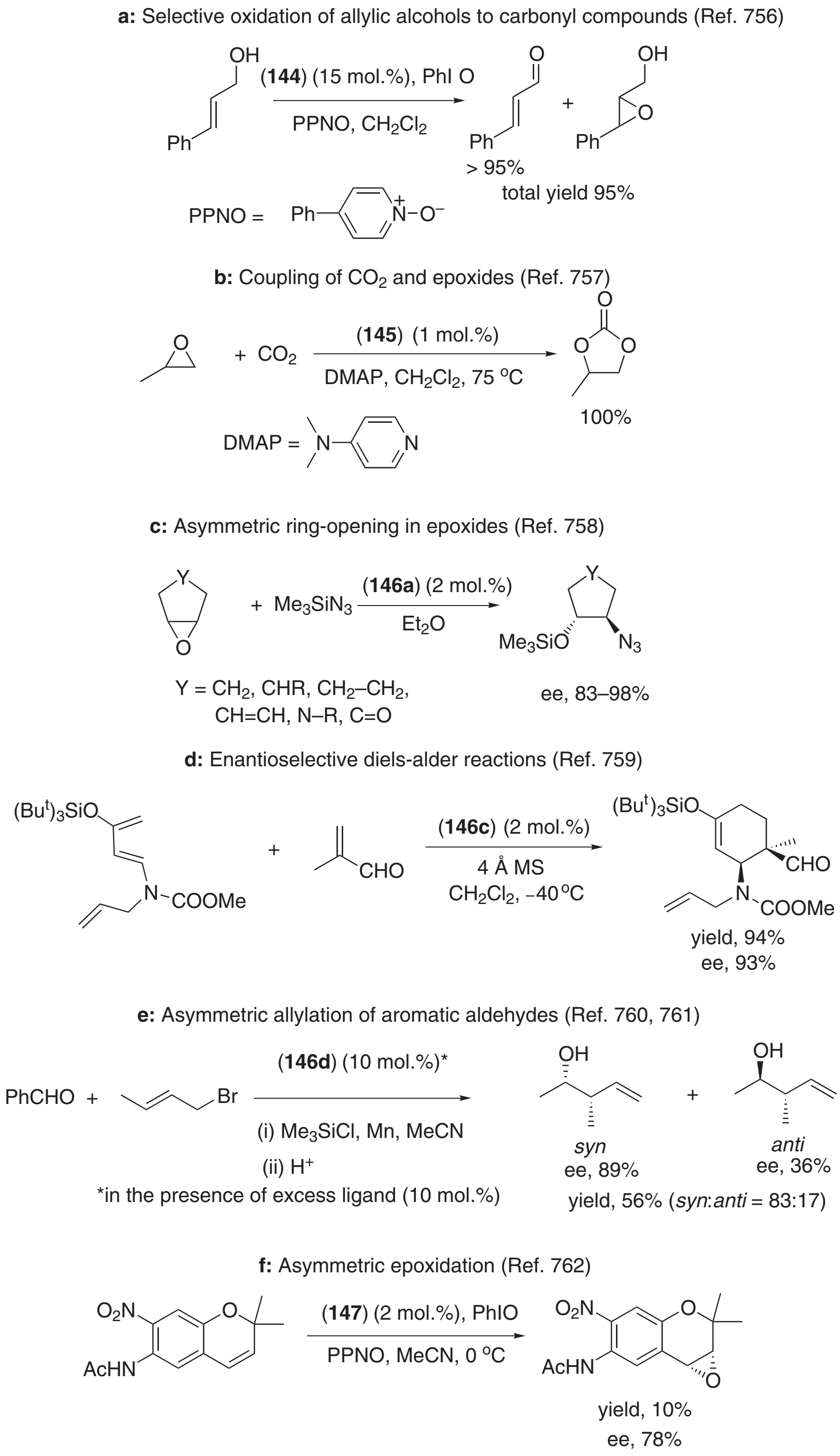


(**148**)

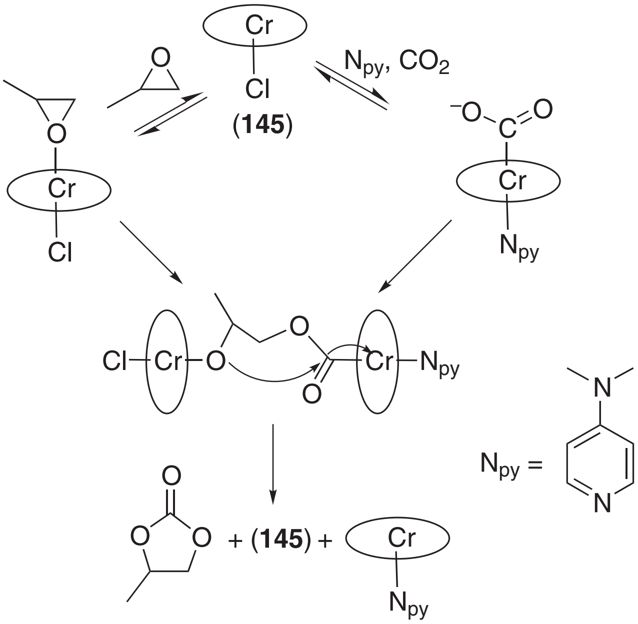
Typical recent examples of the applications of Cr^{III}–salen complexes as catalysts in organic syntheses are given in Scheme 24a–f.[756–762] For instance, a recently discovered reaction (Scheme 24b) provides the first efficient way of chemical CO_2 fixation under mild conditions.[757,763] The proposed mechanism of this reaction is shown in Scheme 25.[757] Such reactions have not been reported for the salen complexes of metal ions other than Cr^{III}. Great attention has been paid to the use of chiral Cr^{III}–salen complexes (e.g., (**146a–d**) or (**147**) in asymmetric catalytic syntheses (such as those in Scheme 24c–f).[214,752–754] Most of these processes are covered by patents,[716,717,764] which emphasizes their practical importance (mainly in the syntheses of biologically active compounds). Further developments in these catalytic systems include the use of dimeric Cr^{III}–salen complexes,[765] as well as the complexes covalently attached to polymer chains[766] or to the surface of SiO_2.[767] The use of room-temperature ionic liquids (such as 1-butyl-3-methylimidazolium salts) as solvents simplifies the recycling of the Cr^{III}–salen catalysts.[768]

(ii) Syntheses and characterizations of the complexes

Given the practical importance of the Cr^{III}–salen complexes, there have been surprisingly few recent studies on their structures. Apart from (**144**), known since the early 1970s,[1] only (**146a,b**)[758] and (**148**)[769] have been characterized by X-ray crystallography. Complex (**146a**) is used as a chiral catalyst for epoxide ring opening (Scheme 24c , and (**146b**) is an intermediate in the catalytic cycle.[758] Complex (**148**) is formed by a ligand-exchange reaction of (**144**) with oxalate in aqueous solutions.[769] Thus, all the structurally characterized Cr^{III}–salen complexes are six-coordinate. The kinetic lability of unidentate axial ligands in such compounds (similar to that in the


a: Selective oxidation of allylic alcohols to carbonyl compounds (Ref. 756)
OH
(144) (15 mol.%), PhI O
PPNO, CH2Cl2
Ph
O
Ph
> 95%
+
OH
O
Ph
total yield 95%
PPNO = Ph N-O
b: Coupling of CO2 and epoxides (Ref. 757)
O
+ CO2
(145) (1 mol.%)
DMAP, CH2Cl2, 75 °C
O
O O
100%
DMAP = N N
c: Asymmetric ring-opening in epoxides (Ref. 758)
Y
O
+ Me3SiN3
(146a) (2 mol.%)
Et2O
Y
Me3SiO
N3
Y = CH2, CHR, CH2–CH2,
CH=CH, N–R, C=O
ee, 83–98%
d: Enantioselective diels-alder reactions (Ref. 759)
(Bu^t)3SiO
N COOMe
+
CHO
(146c) (2 mol.%)
4 Å MS
CH2Cl2, -40 °C
(Bu^t)3SiO
CHO
N COOMe
yield, 94%
ee, 93%
e: Asymmetric allylation of aromatic aldehydes (Ref. 760, 761)
PhCHO +
Br
(146d) (10 mol.%)*
(i) Me3SiCl, Mn, MeCN
(ii) H+
*in the presence of excess ligand (10 mol.%)
OH
syn
ee, 89%
+
OH
anti
ee, 36%
yield, 56% (syn:anti = 83:17)
f: Asymmetric epoxidation (Ref. 762)
O2N
AcHN
O
(147) (2 mol.%), PhIO
PPNO, MeCN, 0 °C
O2N
AcHN
O
O
yield, 10%
ee, 78%

Scheme 24



Scheme 25

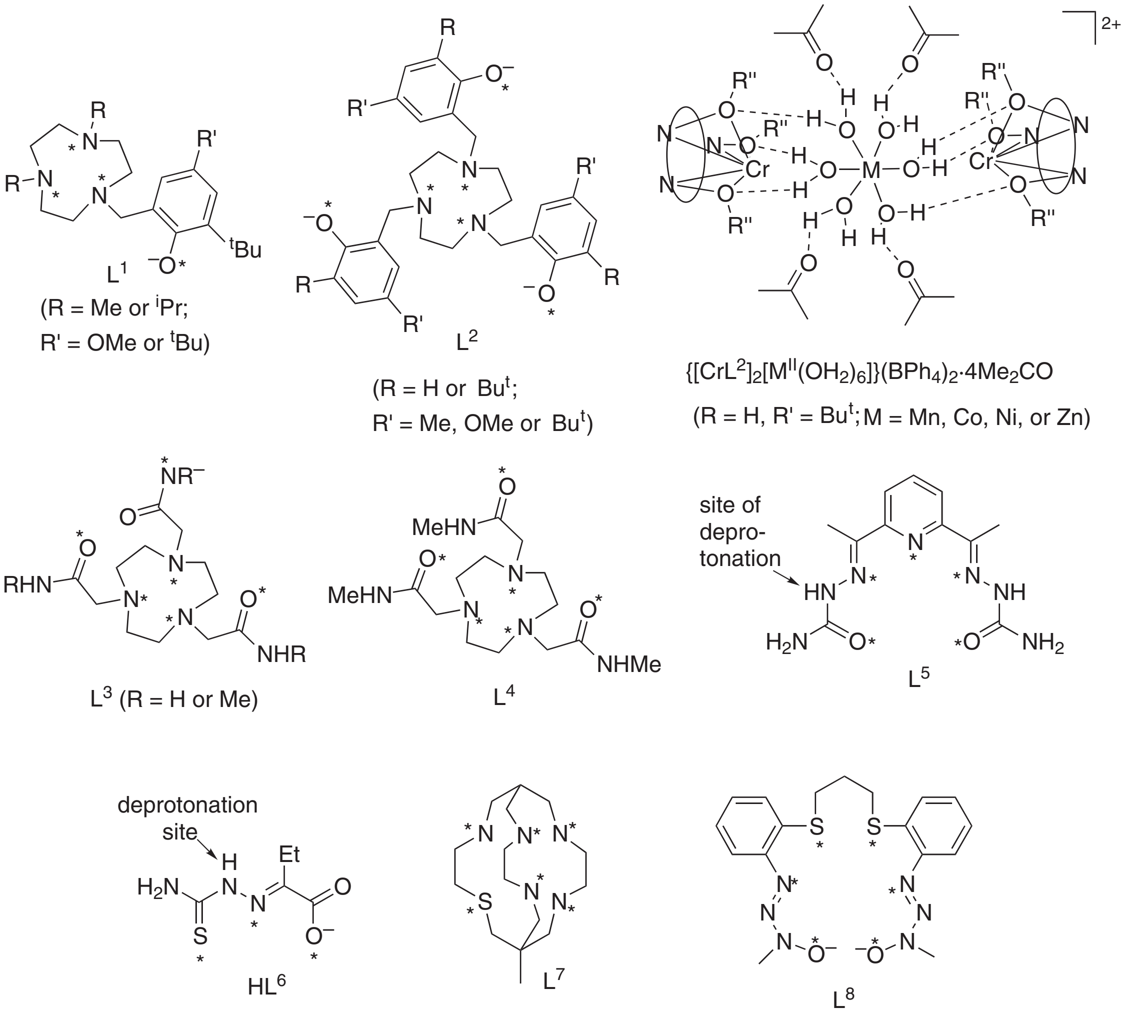
Cr^{III}–porphyrin complexes, Section 4.6.5.2.10) may lead to equilibria between five- and six-coordinate species in solution.[767] This suggestion is supported by the significant effects of added monodentate ligands (such as PPNO or DMAP, Scheme 24) on the activities and selectivities of the catalytic systems (illustrated by Scheme 25).[756,757,762] More sterically crowded species, such as (**147**) and its analogs (Katsuki's complexes), may be stable in solutions in a four-coordinate form.[752,762,770] Elimination of aqua ligands from (**144**) under conditions of ESMS has been used to study the metal–ligand interactions in this complex.[771]

(iii) Biochemical studies

Binding of Cr^{III}–salen complexes to DNA or nucleotides has been studied by UV–visible spectroscopy,[772] gel-shift assays,[177] and ESMS.[771] Complex (**144**) caused oxidative cleavage of a human glycoprotein *in vitro* in the presence of H_2O_2.[368] Alternatively, highly water-soluble analogs of (**144**) (with NR_4^+-substututed ligands) did not cleave DNA in the presence of H_2O_2 (in contrast to the corresponding Ni^{II} complexes).[774] Complex (**144**) was weakly genotoxic in bacterial or mammalian cell assays; however, its genotoxicity is significant, taking into consideration a very low permeability of (**144**) into cells.[11,176,177]

4.6.5.8.5 Other polydentate and macrocyclic mixed-donor ligands

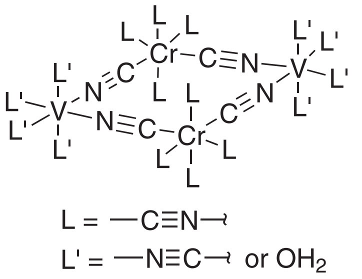
Structures of the ligands in crystallographically characterized Cr^{III} complexes (L^1–L^8) are shown in Scheme 26 (binding sites of the Cr^{III} ion are designated with asterisks). Extensive studies have been performed on the chemistry of Cr^{III} complexes with redox-active pendant-arm macrocyclic ligands (such as $[CrL^1(acac)]^+$ or $[CrL^2]$).[775–779] The redox chemistry of such complexes is similar to that of Cr^{III} catecholates (Scheme 16 in Section 4.6.5.4.6). The products of one-electron oxidations of Cr^{III}–L ($L = L^1$ or L^2, Scheme 26) have been assigned as Cr^{III}–$L^{\cdot +}$ (rather than Cr^{IV}–L) complexes, based on X-ray crystallographic, magnetic, and EPR spectroscopic data.[777,779] Such oxidized complexes may serve as models of active sites of enzymes, containing metal complexes of tyrosyl radicals (such as galactose or glyoxal oxidases).[777,779] Another notable feature of the $[CrL^2]$ complexes is their ability to form stable supramolecular assemblies with $[M^{II}(OH_2)_6]^{2+}$ (Scheme 26).[776]



Scheme 26

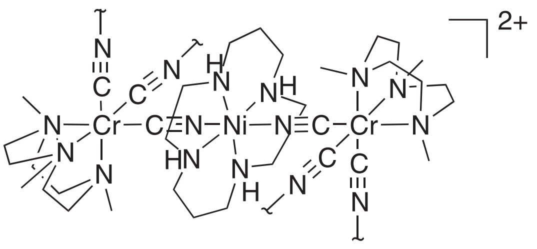
Two different coordination modes have been observed in Cr^{III} complexes with pendant-arm amide ligands, $[CrL^3]^{2+}$ and $[CrL^4]^{3+}$.[780] The ability to bind the ligands via three amine, two carbonyl, and one deprotonated amido donor (as in L^3) is unique for Cr^{III}; the other first-row transition-metal ions formed complexes with the protonated ligands via three amine and three carbonyl donors (as in L^4).[780] Structures of the seven-coordinate (pentagonal-bipyramidal) Cr^{III} complexes with L^5, first reported in 1975,[781] were reassigned in 1987.[782] The reaction of the ligand with $[Cr(OH_2)_6]^{3+}$ at pH ~ 3 led to a deprotonated form of the complex, $[Cr(L^5{-}H)(OH_2)_2](NO_3)_2$ (originally reported as $[CrL^5(OH_2)_2](OH)(NO_3)_2$),[781] while recrystallization of this product from 1 M HNO_3 led to a novel seven-coordinate complex, $[CrL^5(OH_2)_2](NO_3)_3$.[782] Binding of Cr^{III} to both protonated and deprotonated forms of a thiosemicarbazone ligand has been observed in $[Cr(L^6)(HL^6)]$.[783]

Complexes $[CrL^7]^{3+}$ and $[CrL^8]^+$ were the first crystallographically characterized Cr^{III} compounds with macrocyclic or acyclic ligands, respectively, containing thioether donors.[784,785] Several Cr^{III} complexes with acyclic or macrocyclic S_2P_2-donor ligands have been characterized by ESMS and spectroscopic methods.[786] In addition, two Cr^{III} complexes with N–P-donor ligands are mentioned in Section 4.6.5.2.1 ((**77**) and (**78**)), and the complexes of biological N,O,S-donor ligands, cysteine and penicillamine, are described in Section 4.6.5.11.1.



$V^{II}_{0.42}V^{III}_{0.58}[Cr(CN)_6]_{0.86}\cdot 2.8H_2O$

(149)



$[(Me_3tacn)_2(cyclam)NiCr_2(CN)_6]^{2+}$

(150)

4.6.5.9 Polynuclear and Heteropolynuclear Complexes

4.6.5.9.1 Cyano-bridging groups

Early studies of cyano-bridged Cr^{III} complexes[1] concentrated mainly on the mechanisms of photo-induced intramolecular energy transfer (reviewed in 1990).[787] The recent explosion of interest in such complexes is related to the discovery (published in 1995) of room temperature magnetic ordering ($T_c = 315\,K$) in a Prussian blue-type compound (**149**) (the structure is based on the XAFS spectroscopic data).[279] Compound (**149**) was obtained as an amorphous precipitate by mixing aqueous solutions of $K_3[Cr(CN)_6]$ and $(NH_4)_2[V^{II}(OH_2)_6](SO_4)_2$ under anaerobic conditions.[279] A modified sol–gel method led to the synthesis of a crystalline compound, $KV^{II}[Cr^{III}(CN)_6]\cdot 2H_2O\cdot 0.1KOSO_2CF_3$, which retains its magnetism at $\leq 380\,K$, and may serve as a prototype for a new class of practically useful molecular magnetic materials.[788]

A large number of heteropolynuclear Cr^{III} cyano complexes, containing chelating ligands (a typical example, (**150**), is shown)[423] has been synthesized in search of new materials with useful magnetic or photophysical properties. The data prior to 2000 have been reviewed,[789,790] and several crystallographically characterized compounds have been reported since then.[282,423,791–794] However, none of these compounds retains its magnetic properties at $>77\,K$.[282,423,789–794]

4.6.5.9.2 N-donor bridging groups

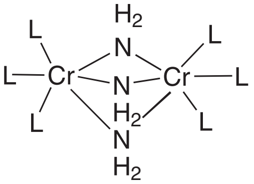
Typical structures ((**151**)–(**161**)) are shown; compounds (**151**), (**152**), (**153**), (**156**), and (**160**) have been characterized by X-ray crystallography.[360,795–806]

The formation of a polymeric compound, "$Cr(NH_2)_3$," during the reaction of $[Cr(NH_3)_6]^{3+}$ with KNH_2 in liquid NH_3, has been known since the 1940s.[807] In 1998, the first crystallographically characterized Cr^{III} amido complex, $Rb_3[Cr_2(NH_2)_9]RbNH_2$ (**151**), was synthesized by the reaction of "$Cr(NH_2)_3$" with $RbNH_2$ and NH_3 at high pressure.[795] The reactions of CrI_2 with supercritical NH_3 or those of Cr^{III} compounds with KNH_2 and NH_3 led to the amido-bridged am(m)ine complexes, (**152**) and (**153**).[796–798] Kinetics and mechanisms of the amido-bridge cleavage reactions of (**152**) or (**153**) in acidic aqueous solutions have been studied.[797,798]

In contrast to the Cr^{III}–cyclam complexes, where both *cis* and *trans* isomers could be obtained in high yields (Section 4.6.5.2.6), only *cis*-complexes (e.g., (**158**)) have been isolated for the *bis*-cyclam ligand.[427,803] Differences in complexation mechanisms of cyclam and *bis*-cyclam ligands to Cr^{III} have been studied by molecular mechanics methods.[427] A five-coordinate (square-pyramidal) coordination environment of Cr^{III} in (**159**) has been proposed from microanalytical data, and spectroscopic and magnetic measurements.[804] A polymeric complex (**160**) exhibited significant antibacterial activity (greater than that of the ligand alone).[802]

4.6.5.9.3 Hydroxo-bridging groups

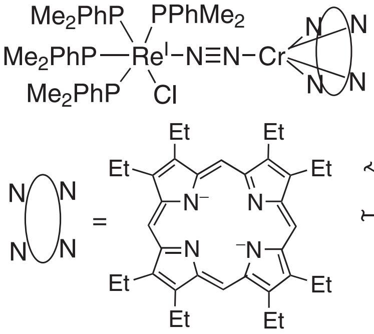
Dinuclear or oligonuclear OH-bridged complexes are ubiquitous in Cr^{III} chemistry.[1] Two reviews, although outdated (1988 and 1989), provide a useful introduction into the chemistry of such



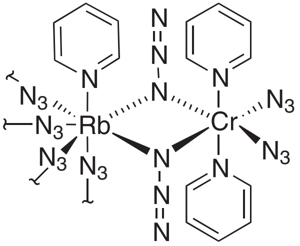
(**151**) $[Cr_2(NH_2)_9]^{3-}$ (Ref. 795)

(**152**) $[(H_3N)_3Cr(\mu\text{-}NH_2)_3Cr(NH_3)_3]^{3+}$ (Ref. 796, 797)

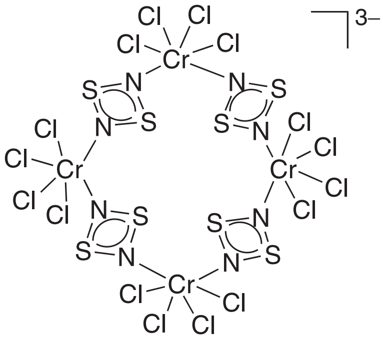
(**153**) $[(tacn)Cr(\mu\text{-}NH_2)_3Cr(tacn)]^{3+}$ (Ref. 798)



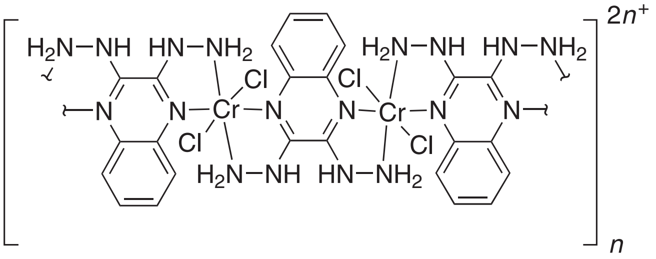
(**154**) (Ref. 799)



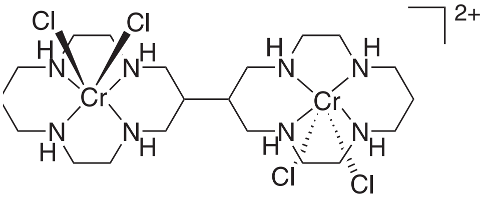
(**155**) (Ref. 360, 800)



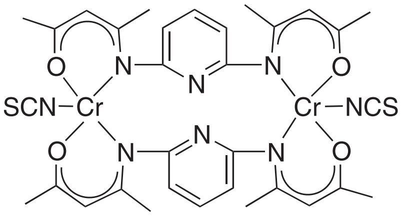
(**156**) (Ref. 801)



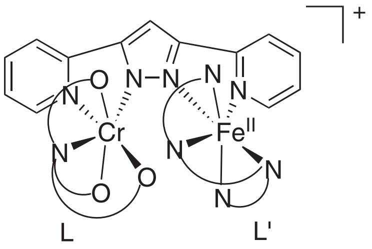
(**157**) (Ref. 802)



(**158**) (Ref. 803)



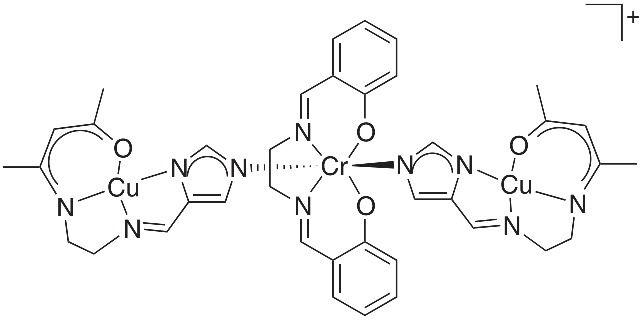
(**159**) (Ref. 804)



L = $[N(CH_2COO)_3]^{3-}$

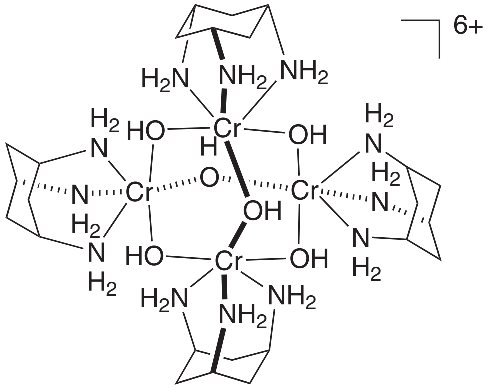
L' = $PhCH_2NH(CH_2)_2NHCH_2Ph$

(**160**) (Ref. 805)

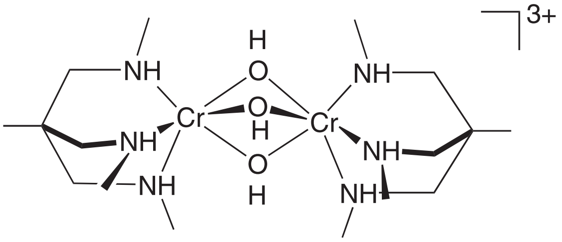


(**161**) (Ref. 806)

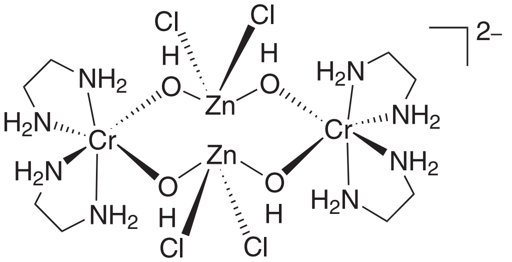
complexes.[808,809] A large number of crystallographically characterized compounds with two to six μ-OH groups (including heteropolynuclear species) have been reported since 1985, selected structures ((**162**)–(**164**)) are shown.[307,458,698,699,810–829] For many of the complexes, low-temperature (<50 K) antiferromagnetic[698,810,811,813–817,820,821] or ferromagnetic (for Cr^{III}–Cu^{II} or Cr^{III}–Zn^{II} complexes)[818,819,822] couplings have been reported. Complex (**162**) possesses a novel adamantane-like $Cr_4(OH)_6$ core; its magnetic properties have been studied in comparison with those



(**162**) (Ref. 820)



(**163**) (Ref. 821)



(**164**) (Ref. 825)

of dimeric and trimeric Cr^{III} complexes.[820] This is a further development of the Glerup–Hodgson–Pedersen (GHP) theory of magnetic interactions in polynuclear metal complexes.[809] Well-known model complexes,[1] $[Cr_2(\mu\text{-}OH)(NH_3)_{10}]^{5+}$ ("acid rhodo") and $[Cr_2(\mu\text{-}OH)_2(NH_3)_8]^{4+}$, have been used for detailed EPR-spectroscopic and computational studies of magnetic interactions in OH-bridged Cr^{III} dimers.[830–832] The OH-bridged species, formed during the base hydrolysis of $[Cr(OH_2)_6]^{3+}$, are described in Section 4.6.5.9.4.

4.6.5.9.4 Hydrolytic polymers

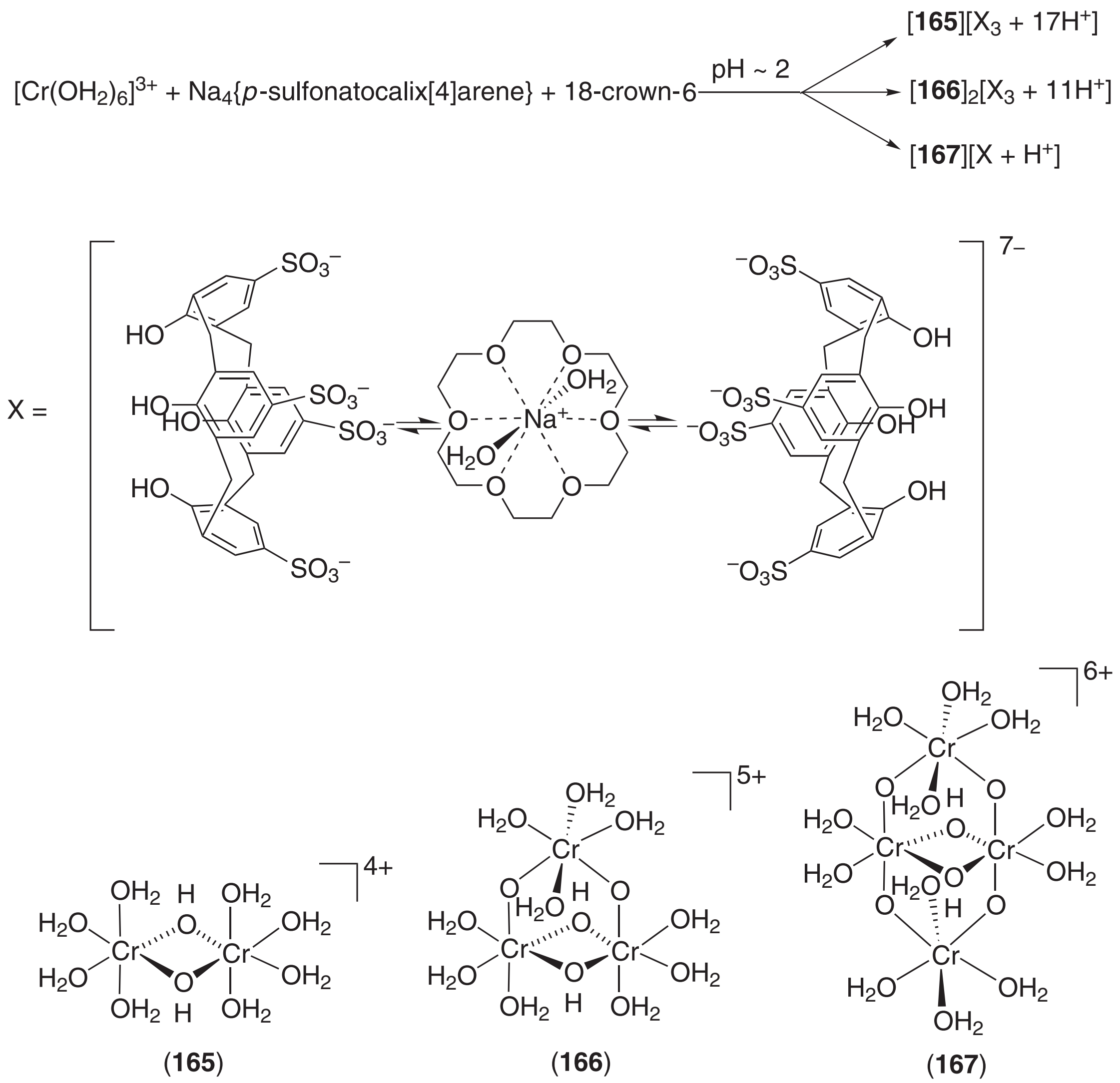
Polymeric Cr^{III} complexes with hydroxo and aqua ligands are the key species in the environmental chemistry of Cr,[104,833] as well as in industrial applications, such as leather tanning[834–836] or oil recovery (Section 4.6.5.10). Despite several decades of research (mainly by potentiometric methods), no unambiguous structural information on hydrolytic oligomers of Cr^{III} had been available prior to 1985.[1]

Stabilization and crystallization of $[Cr_x(\mu\text{-}OH)_y(OH_2)_z]^{(3x-y)+}$ cations have been achieved by exploiting the supramolecular interactions with large anionic assemblies: initially with mesitylene-2-sulfonate or its adduct with 18-crown-6,[837–839] and subsequently with the adducts of calixarene sulfonates with *N*- or *O*-macrocycles.[840,841] This approach, illustrated in Scheme 27, allowed the crystal structures of di-, tri- and tetrameric Cr^{III} complexes, (**165**)–(**167**),[837,839–841] as well as that of a heteropolynuclear complex, $[(H_2O)_4Rh(\mu\text{-}OH)_2Cr(OH_2)_4]^{4+}$,[838] to be determined.

Several new physicochemical methods have been used for the speciation of Cr^{III} hydrolytic oligomers in aqueous solutions. For instance, separation of the complexes (**165**)–(**167**) and related species has been achieved by capillary electrophoresis with ICPMS detection, and identification of the oligomeric species has been performed by ESMS.[519] A recent XAFS-spectroscopic study of a leather tanning solution (Cr^{III} sulfate at pH ~ 4) showed a predominance of tetrameric Cr^{III} complexes.[836] The mechanisms of formation of heteropolynuclear Cr^{III} hydroxo complyexes with various metal ions have been investigated by potentiometric methods.[842,843] Detailed kinetic studies of the early stages of Cr^{III} hydrolysis have been performed.[844]

4.6.5.9.5 H_3O_2- and related bridging groups

The concept of H_3O_2-bridging was first formulated by Ardon *et al.* in 1985–1987,[845,846] using Cr^{III} complexes with chelating N-donor ligands as examples. Deprotonation of *cis*-diaqua complexes (general structure (**168**) in Scheme 28) leads to dimeric species, (**169**), bridged by two short

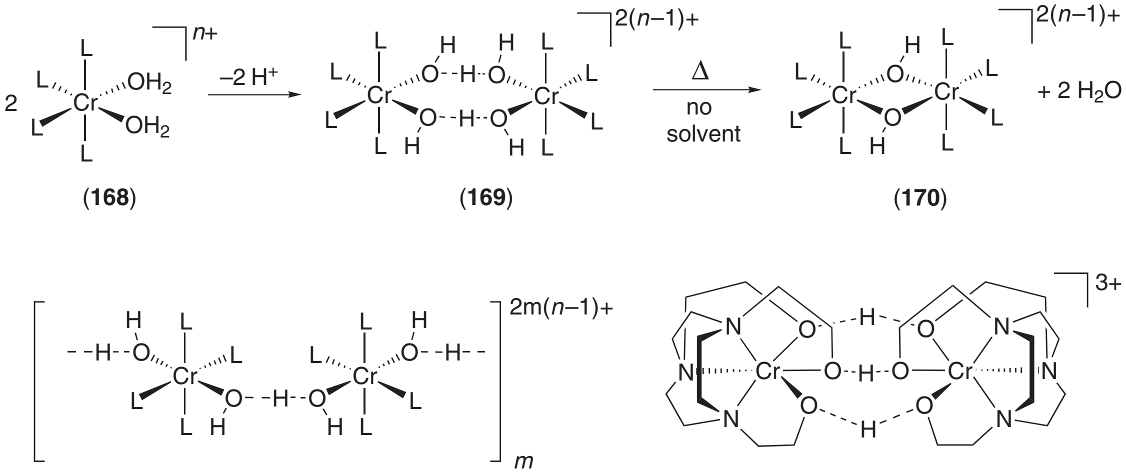


Scheme 27

(~2.5 Å), strong, and centered hydrogen bonds.[846] Heating of solid compounds (**169**) at ~150 °C leads to the formation of the dihydroxo-bridged dimers (**170**) (olation reaction; Scheme 28).[846] Stereoselectivity of the olation reactions for the $[Cr_2(chxn)_4(\mu\text{-}H_3O_2)_2]^{4+}$ complexes (chxn = (1*S*,2*S*)- or (1*R*,2*R*)-1,2-*trans*-cyclohexanediamine) has been discussed.[847]

Crystallographically characterized H_3O_2-bridged Cr^{III} complexes include dimeric species with one (e.g., $[\{Cr(en)_2(ONO)\}_2(\mu\text{-}H_3O_2)]^{3+}$),[388,549,848,849] two (e.g., *cis*-$[\{Cr(cyclam)\}_2(\mu\text{-}H_3O_2)_2]^{4+}$);[846,850,851], or three ($[(CrL)_2(\mu\text{-}H_3O_2)_3]^{3+}$; L = *N*,*N*′,*N*″-trimethyl-1,1,1-tris(aminomethyl)ethane)[852] H_3O_2-bridges, as well as infinite chain polymeric species (general structure (**171**) in Scheme 28).[853,854] The formation of chain structures seems to be dependent on the nature of counterions: for instance, a trifluoromethanesulfonate salt of *trans*-$[Cr(cyclam)(OH)(OH_2)]^{2+}$ forms such chains, while a perchlorate salt of the same complex exists in monomeric units.[854] Formation of the H_5O_3-bridging groups (with a second H_2O molecule intervening between the H_2O and OH^- ligands) has also been reported.[854]

The H_3O_2-bridged dimers (and to a lesser extent the chain polymers) exhibit magnetic exchange coupling between the Cr^{III} centers.[848,850,851,854] The extent of such coupling correlates with the Cr···Cr distances (typically, 4.8–5.1 Å for the diH_3O_2-bridged dimers and ~6.1 Å for the chain polymers).[848,850,851,854] The antiferromagnetic coupling in the diH_3O_2-bridged Cr^{III} dimers is reflected in their low-temperature (≤80 K) EPR spectra, which are typical for a quintet electronic



(**168**) (**169**) (**170**)

(**171**) (**172**)

Scheme 28

state.[851] Thus, the formation of H_3O_2-bridged dimers (Scheme 28) is the first step in polymerization of Cr^{III} complexes, containing aqua ligands.[846]

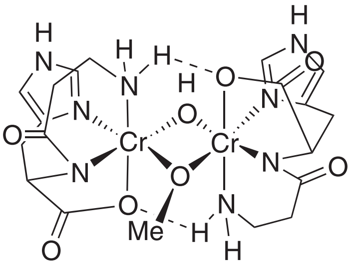
Hydrogen bonds are often important for crystallization or reactivity of Cr^{III} complexes; some examples are given in Sections 4.6.5.4.9, 4.6.5.8.5, 4.6.5.9.7, and 4.6.5.9.10. Formation of tri-Hbound dimeric Cr^{III} complexes with "pendant-arm" macrocyclic ligands, based on 1,4,7-triazacyclononane (e.g., (**172**) in Scheme 28, characterized by X-ray crystallography), has also been reported.[848,855] Similar to the "classical" OH-bridged Cr^{III} dimers (Section 4.6.5.9.3), complex (**172**) exhibits antiferromagnetic interactions between the metal centers.[848]

4.6.5.9.6 Oxo bridging groups

Oxo-bridged dimeric complexes of transition metal ions, including Cr^{III}, are of interest as possible models of intermediate states in enzymatic oxo-transfer reactions.[856] Studies on the chemistry of a well-known complex, $[Cr_2(\mu\text{-}O)(NH_3)_{10}]^{4+}$ ("basic rhodo"),[1] were continued by mechanistic investigations of its base hydrolysis,[857] as well as by calculations of its electronic structures in the ground and exited states.[858] A series of novel oxo-bridged Cr^{III} dimers with tetradentate N-donors and monodentate anionic ligands (such as $[\{Cr(tmpa)(NCS)\}_2(\mu\text{-}O)\}]$) (tmpa = tris-(pyridylmethyl)amine) have been synthesized and characterized by X-ray crystallography, magnetic measurements, and ligand-exchange studies.[859–863] Two oxo-bridged Cr^{III}–Fe^{III} complexes with porphyrinato ligands, $[(py)(tpp)Cr(\mu\text{-}O)Fe(tmtaa)]$[864] (tmtaa = 5,7,12,14-tetramethyldibenzo [*b*,*i*][1,4,8,11]tetraazacyclotetradeca-2,4,7,9,11,14-hexaneato(2−)) and $[(pip)(tpp)Cr(\mu\text{-}O)Fe(tpp)]$[482] (pip = piperidine), have been synthesized by the reactions of $[Cr^{IV}O(tpp)]$ with the corresponding Fe^{II} compounds, and characterized by X-ray crystallography. The former complex exhibits a strong antiferromagnetic coupling of the metal centers ($2J = -299\,cm^{-1}$).[864] For the latter complex, an unusual coordination environment has been found, with both Cr^{III} and Fe^{III} ions significantly protruding from the porphyrin planes.[482] The $[(tpp)Cr(\mu\text{-}O)Ru^{IV}(tpp)(\mu\text{-}O)Cr(tpp)]$ complex has been characterized by spectroscopic and magnetic measurements.[865] Polynuclear Cr^{III} complexes with oxo and carboxylato bridges are described in Section 4.6.5.9.8.

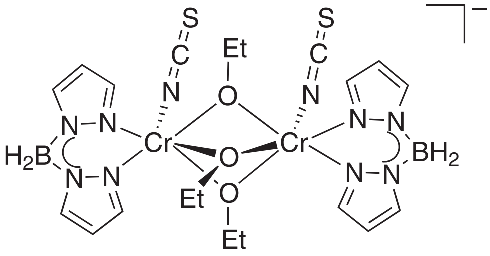
4.6.5.9.7 Alkoxo and aryloxo bridging groups

Typical structures of crystallographically characterized complexes ((**173**)–(**178**)) are shown (Cr^{III} binding sites in the ligands are designated with asterisks).[701,866–871] Compound (**173**) is one of the

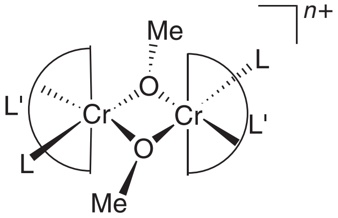


$[Cr_2(\beta\text{-Ala-L-H}_{-1}\text{-His})_2(\mu\text{-OH})(\mu\text{-OMe})]$

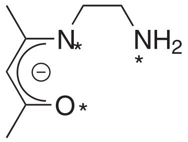
(**173**) (Ref. 701)



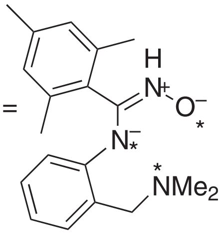
(**177**) (Ref. 859, 870)



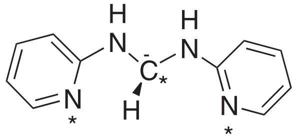
(**174**) $n = 2$; L = OH_2; L' =
(Ref. 866)

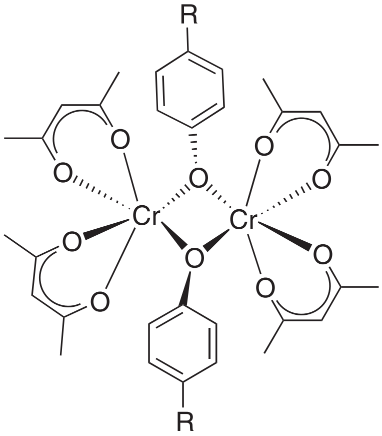


(**175**) $n = 0$; L = OMe; L' =
(Ref. 867)



(**176**) $n = 0$; L = Cl; L' =
(Ref. 868)



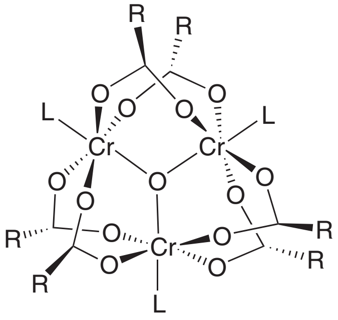


R = H or Me
(**178**) (Ref. 871)

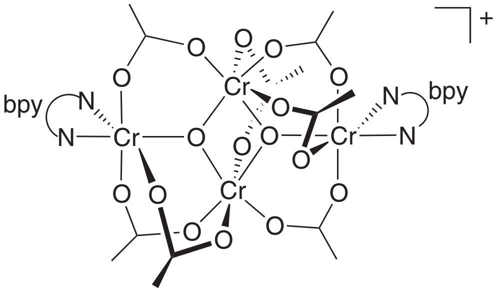
few well-characterized Cr^{III} complexes with dipeptide ligands (other examples are given in Section 4.6.5.8.2).[701] In (**175**), Cr^{III} is coordinated to an unusual protonated amidooximato ligand.[867] In (**176**), an unprecedented rearrangement of a formamidinato ligand occurs, leading to Cr—C binding.[868] Compounds (**177**) and (**178**) are among the few known transition metal complexes with three alkoxo bridges or with aryloxo bridges, respectively.[869–871]

4.6.5.9.8 Monocarboxylates and other oxo anions as bridging groups

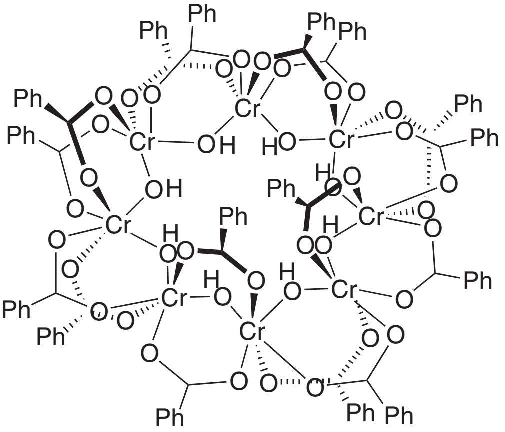
The most numerous Cr^{III} complexes of this type are the symmetric trinuclear oxo-carboxylates, $[Cr_3O(O_2CR)_6L_3]^+$ (general structure (**179**); the charge can vary depending on the nature of the ligands L). Structures of these complexes were first established in the 1960s.[1] Since 1985, more than 20 such compounds have been characterized by X-ray crystallography (typically with R = H, Me, Et, or Ph, and L = H_2O, Py, or F^-), this includes heteropolynuclear complexes with $Cr_nM_{(3-n)}O$ cores ($n = 1$ or 2; M = Fe^{III}, Co^{II}, Ni^{II}, or Mn^{II}).[872–893] Complexes (**179**) have been studied by kinetic methods (mechanisms of exchange of the ligands L),[888,894,895] magnetic



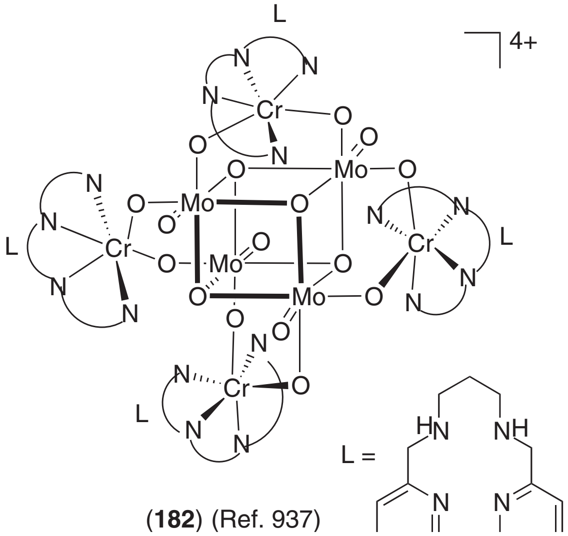
(**179**) (see text)



(**180**) (Ref. 922)



(**181**) (Ref. 890)

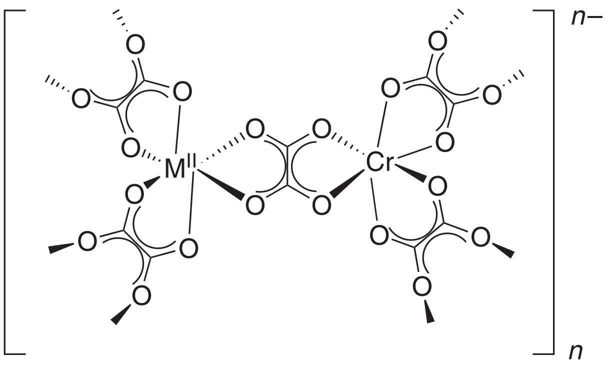


(**182**) (Ref. 937)

susceptibility measurements,[889] ^{1}H or ^{2}H NMR,[896] Raman[897] or XAFS[898] spectroscopies, mass spectrometry (fast-atom-bombardment or elecrospray ionization),[892,899–902] and neutron scattering analysis.[903,904]

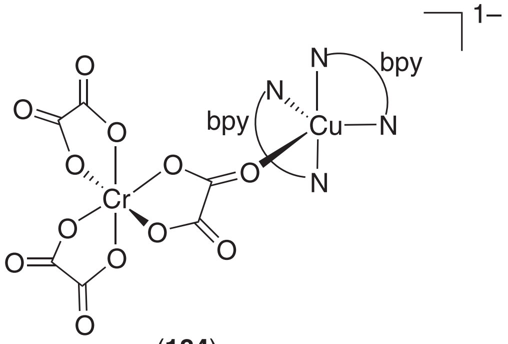
Applications of the complexes (**179**) as redox catalysts,[905] or as components of porous materials for gas storage[906] have been proposed. The greatest research effort has been focused on the possible use of (**179**) (R = Et, L = H_2O) as a nutritional supplement or therapeutic agent for improving glucose and fat metabolism (patented by Vincent *et al.* in 2000–2001).[907,908] This is the only Cr^{III} compound shown to decrease the levels of plasma cholesterol and triglycerides (in rats, intravenous administration).[909] A proposed mechanism of action of (**179**) (R = Et, L = H_2O) involves the promotion of insulin binding to the cellular insulin receptors,[910] and is thought to mimic the action of a putative natural Cr^{III}-containing factor (Section 4.6.5.11.2).[12] Interestingly, a closely related compound ((**179**) with R = Me and L = H_2O) was not active in insulin potentiation.[910]

Other polynuclear or heteropolynuclear Cr^{III} complexes, containing oxo anions as bridging ligands and characterized by X-ray crystallography since 1985, include carboxylato-bridged assemblies with 2–12 metal ions,[422,890,899,911–932] as well as the complexes bridged by carbonato,[862,933,934] dialkylcarbamato,[893] sulfato,[935,936] pyrophosphato,[634] and polyoxomolybdato (or tungstato)[937–939] anions. Some typical structures, (**180**)–(**182**), are shown. The carboxylato-bridged Cr^{III} assemblies with $n > 3$ (such as (**181**)) can be prepared by heating the complexes (**179**) (in the solid state or in aqueous solutions).[890,927–931] Most of the oxo-anion-bridged Cr^{III} complexes exhibit weak to moderate antiferromagnetic interactions between the adjacent metal ions. The dependencies of the magnetic exchange coupling constant (J) on the nature of the complexes have been studied.[862] In one case, an unusual alteration from antiferromagnetic to ferromagnetic coupling, depending on the nature of counterions, has been reported.[915] Carboxylato-bridged Cr^{III}–$Mn^{III/II}$ complexes have been examined as models for some structural and functional aspects of photosynthetic systems.[424,920]

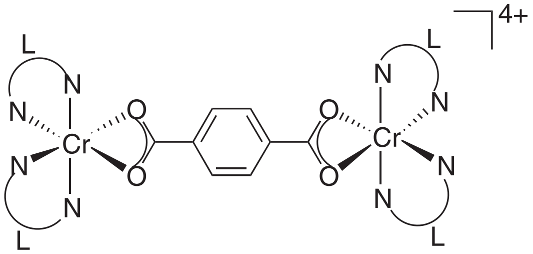


M = Mn, Fe, Co, Ni, Cu, or Zn

(**183**)



(**184**)



L = substituted bpy or phen

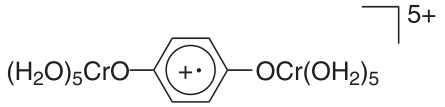
(**185**)

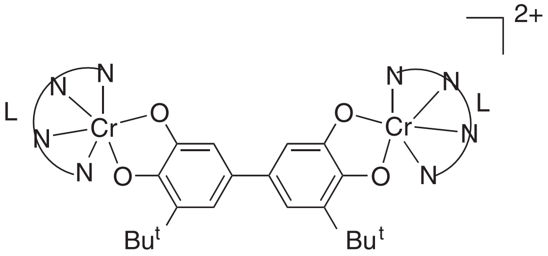
4.6.5.9.9 Dicarboxylates as bridging groups

This area is currently dominated by heteropolynuclear oxalato-bridged complexes, synthesized in the search for new molecular materials with useful conductive, magnetic, or nonlinear optical properties (see also Section 4.6.5.4.7).[940] The syntheses of polymeric compounds of the general formula $\{(NR_4)[M^{II}\text{-}Cr(ox)_3]\}_n$ (a typical structural unit is represented by (**183**)) were first reported in 1992;[616] about 20 such complexes have been characterized since then (by X-ray crystallography and magnetic measurements).[611,940–957] Three-dimensional architectures of the anionic assemblies are determined by the choice of counter-cations.[614] Recently, the first example of a monodentate coordination of the $[Cr(ox)_3]^{3-}$ unit to Cu^{II}, (**184**), has been reported.[957] A series of terephthalato-bridged dinuclear Cr^{III} complexes (**185**) have been characterized by spectroscopic and magnetic measurements.[958]

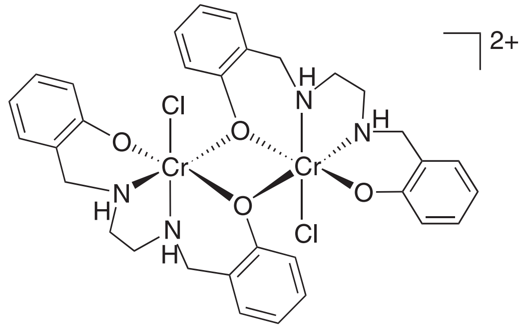
4.6.5.9.10 Other O-donor bridging groups

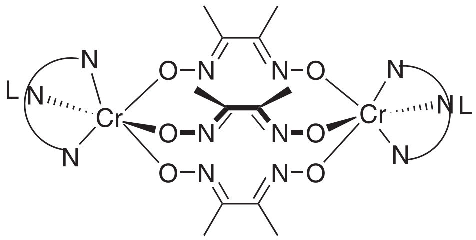
Typical structures of the complexes ((**186**)–(**193**)) are shown ((**188**), (**189**), and (**191**)–(**193**) have been characterized by X-ray crystallography).[959–966] Complex (**186**) is formed during the oxidation of Cr^{II} with 1,4-benzoquinone in acidic aqueous solutions (previously, it had been incorrectly assigned as $[(H_2O)_5CrOCr(OH_2)_5]^{4+}$).[959] Interest in the redox chemistry of Cr^{III} phenolato and catecholato complexes (Sections 4.6.5.4.4 and 4.6.5.4.6) on the one hand, and in the interactions of the metal centers in polynuclear complexes on the other, led to the syntheses and characterizations of several polynuclear Cr^{III} complexes with phenolato ligands, including (**187**) and (**188**).[960,961,967–969] Dimethyldioxime and its derivatives have been used as bridging groups in (**189**)[962] and in several related heteropolynuclear ($Cr^{III}\text{–}M^{II}$ or $Cr^{III}\text{–}M^{II}\text{–}Cr^{III}$) complexes.[970–973] The exchange interactions between the metal centers in such complexes have been studied by EPR spectroscopy.[970] Complex (**190**), supported on montmorillonites, is thermally stable up to 500 °C and can potentially be used as a catalyst in organic synthesis.[963]


(**186**) (Ref. 959)

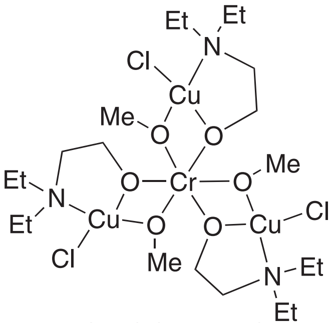

L: see L^6 in Chart 12

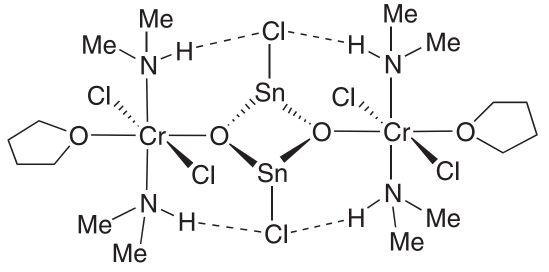
(**187**) (Ref. 960)

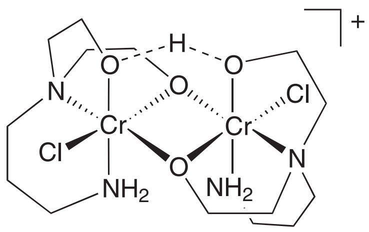

(**188**) (Ref. 961)

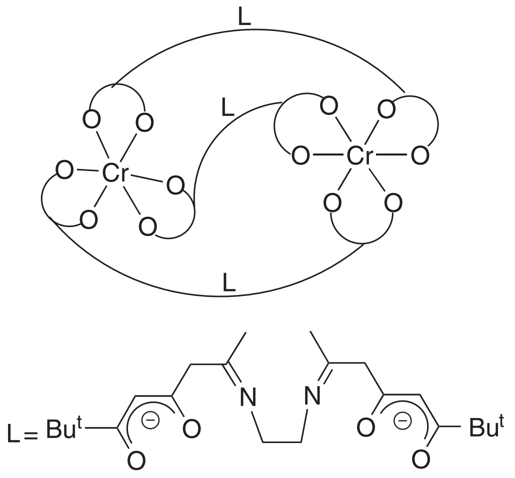

L = Me_3tacn

(**189**) (Ref. 962)


(**190**) (Ref. 963)


(**191**) (Ref. 964)


(**192**) (Ref. 965)


(**193**) (Ref. 966)

4.6.5.9.11 N–O donor bridging groups

Typical structures ((**194**)–(**201**)) are shown; (**194**)–(**198**) have been characterized by X-ray crystallography.[798,974–981] The exchange interactions between the metal centers in a series of heteropolynuclear complexes with the general structure (**194**) have been studied by magnetic susceptibility measurements and EPR spectroscopy.[974] Different stereoisomers of (**195**) are formed, depending on the alkyl chain lengths in the diamine–dicarboxylato ligands.[975,976] Complex (**196**), formed by an oxidative addition reaction from a corresponding Cr^{II} complex in the presence of traces of air and moisture, possesses an unusually short $Cr\cdots Cr$ distance (2.732 Å).[977] Complex (**199**) is formed as a result of an unusual Cr^{III} and nitrite-promoted hydration of MeCN.[979] A large series of oxamido-bridged Cr^{III}–Cu^{II} dimers (e.g., (**201**)), exhibiting ferromagnetic couplings at ≤ 50 K, have been described.[981–983]

4.6.5.9.12 Bridging groups containing P- or S-donors

Typical structures of the complexes ((**202**)–(**210**)) are shown (all the compounds, except (**205**), have been characterized by X-ray crystallography).[687,862,984–990] Among the few structurally characterized P-donor-bridged Cr^{III} compounds are (**202**),[984] as well as $[\{CrCl_3(L)\}_2(\mu\text{-}L)]$ ($L = Me_2P(CH_2)_nPMe_2$, $n = 1$ or 2).[991,992] A tetranuclear complex (**203**) ($[Cr_4S(OAc)_8(OH_2)_4]^{2+}$) is structurally similar to the well-known trinuclear oxo-carboxylates (**179**), but unlike those, (**203**) exhibits a strong ferromagnetic coupling between the Cr^{III} centers (maximum spin $S = 6$).[985] Potential biomedical applications of (**203**) as a spin label or a NMR contrasting agent have been proposed.[985] The Cr–S cluster complexes, such as $[Cr_2(PS_4)_4]^{6-}$ or $[Cr_{12}S_{16}(PEt_3)_{10}]$,[993,994] are described in Chapter 4.12 of this edition. The influences of thiolato donors on exchange interactions of the metal centers in the complexes (**204**)–(**206**) have been studied by electronic spectroscopy and magnetic measurements.[862,986,987]

Many heteropolynuclear Cr^{III} complexes with sulfur-containing bridging groups have been described (e.g., (**207**)–(**210**)).[687,988–990] Most of these complexes contain a second metal ion that is “softer” than Cr^{III} and hence has a higher affinity for S-donors (e.g., Ni^{II}, Pt^{II}, or Cu^{II} in (**207**), (**209**), or (**210**), respectively). Several crystallographically characterized compounds, related to (**207**) ($[Ni\{Cr(aet)_3\}]^{2+}$; aet = 2-amino-ethanethiolato(−)),[687] are also known, namely $[Zn_4O\{Cr(aet)_3\}_4]^{6+}$ and $[Cr\{M(aet)_3\}_2]^{3+}$ ($M = Rh^{III}$ or Ir^{III}).[687,995] A thiooxalato-bridged complex (**208**) is related to the numerous heteropolynuclear oxalato-bridged compounds (Section 4.6.5.9.9). An unusual five-coordinate Cr^{III} complex (**209**) has been synthesized by reduction of a five-coordinate Cr^{V} oxo complex.[989] The first crystallographic characterization of a thiocyanato-bridged Cr^{III} complex, (**210**), was reported in 2001.[990] Numerous related compounds have been synthesized previously by the reactions of $[Cr(NCS)_6]^{3-}$ and its derivatives with transition metal complexes, but the presence of thiocyanato bridges in such compounds was suggested mainly on the basis of IR spectroscopic data.[996]

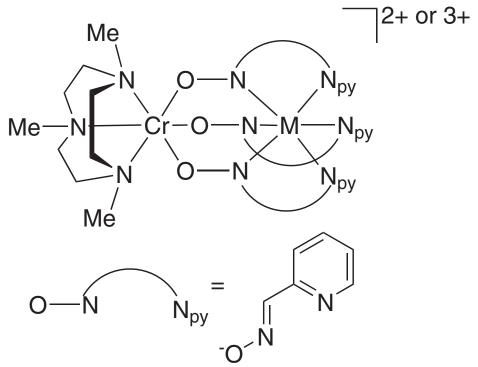
4.6.5.9.13 Halide bridging groups

Crystallographically characterized compounds (since 1985) include (**211**)–(**214**),[472,997–999] as well as $[Cr_8(\mu\text{-}F)_8(\mu\text{-}O_2CBu^t)_{16}]$ (the structure is similar to that of (**181**)).[1000,1001] A five-coordinate complex (**211**) is catalytically active in alkene polymerization (Section 4.6.5.2.1).[472]

Detailed studies of the well-known[1] trihalo-bridged $[Cr_2X_9]^{3-}$ complexes have continued in recent years. Crystal structures of $Cs_3[Cr_2Cl_9]$[664] and $(Et_4N)_3[Cr_2F_9]$[1002] have been reported, and single-crystal absorbtion spectra of the latter compound have been studied.[1003] The ligand dependence of metal–metal bonding in the $[Cr_2X_9]^{3-}$ complexes (X = F, Cl, Br, or I) has been investigated by DFT calculations.[1004] In addition, structures of the polymeric $K[CrF_4]$ and $K_2[Cr_3Cl_2F_6]$ compounds have been studied by X-ray crystallography.[1005]

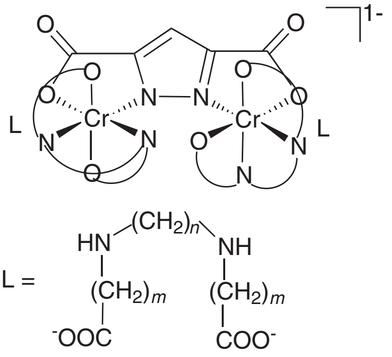
4.6.5.10 Polymers as ligands

Complexes of Cr^{III} with polymeric ligands have a wide range of practical applications in catalysis,[505,1006–1008] removal and recovery of Cr^{III},[1009–1012] and modification of polymeric materials;[1013–1020] typical recent examples are listed in Table 5. Complexes of Cr^{III} with biopolymers (proteins or nucleic acids) are described in Section 4.6.5.11.



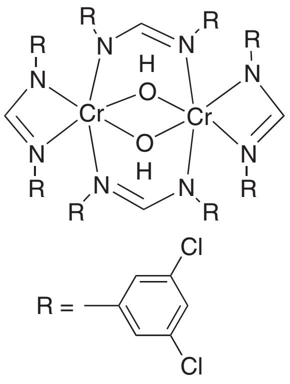
M = Fe^{II}, Ni^{II}, Cu^{II}, Zn^{II}, or Co^{III}

(**194**) (Ref. 974)

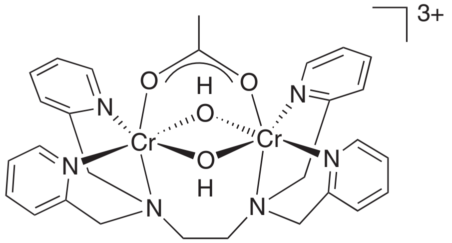


n, m = 1 or 2

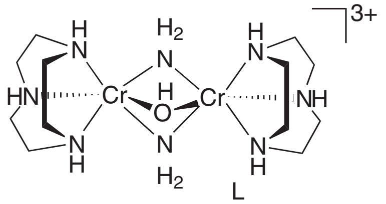
(**195**) (Ref. 975, 976)



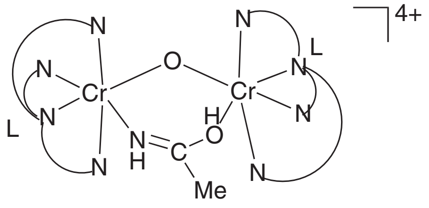
(**196**) (Ref. 977)



(**197**) (Ref. 978)

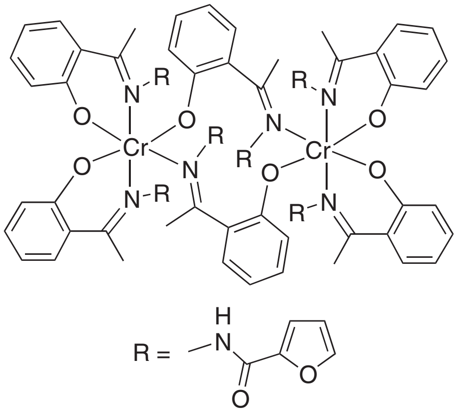


(**198**) (Ref. 798)

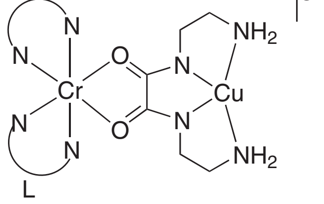


L = tmpa

(**199**) (Ref. 979)



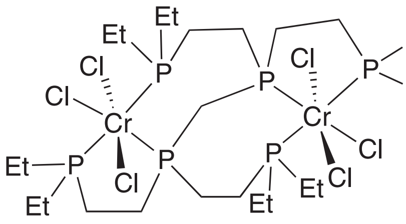
(**200**) (Ref. 980)



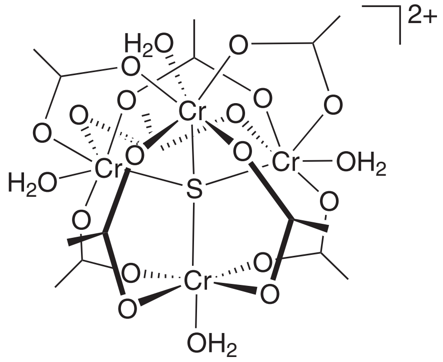
L = substituted bpy or phen

(**201**) (Ref. 981)

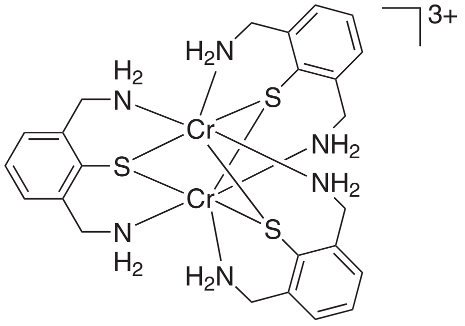
Apart from a simple addition of a Cr^{III} salt to a polymeric ligand, several synthetic methods for specific complexes have been developed. For example, S_2-linked tris-(β-diketonato) complexes (**215**) (Scheme 29a) have been synthesized by a reaction of a preformed Cr^{III} complex with S_2Cl_2.[1021] Similarly, preformed Cr^{III} complexes with porphyrin or salen ligands have been



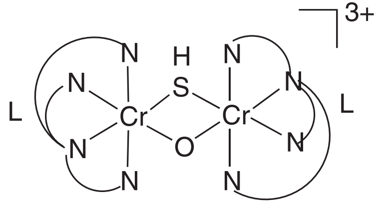
(**202**) (Ref. 984)



(**203**) (Ref. 985)

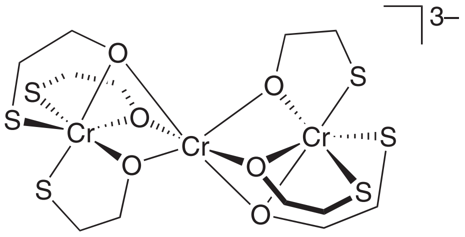


(**204**) (Ref. 862)

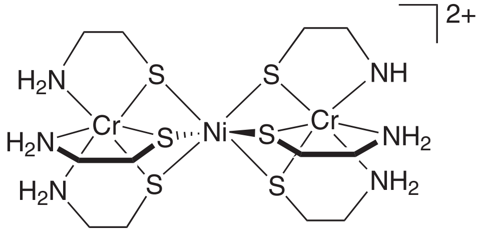


L = tmpa

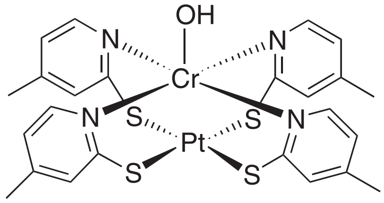
(**205**) (Ref. 986)



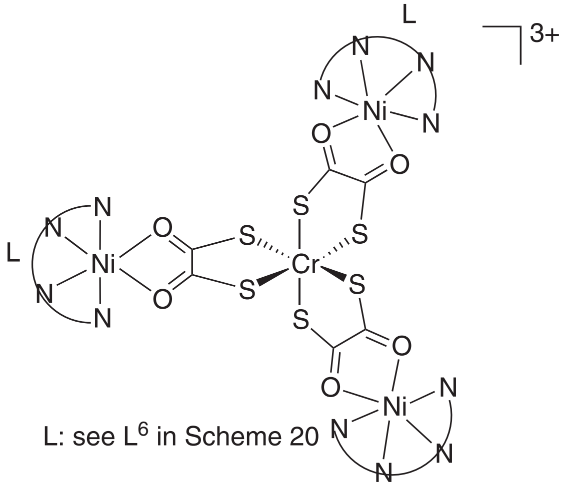
(**206**) (Ref. 987)



(**207**) (Ref. 687)

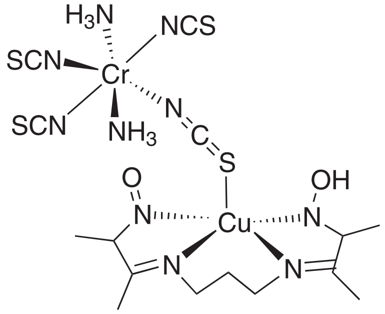


(**209**) (Ref. 989)

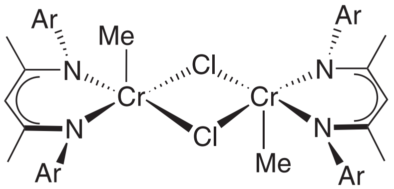


L: see L^6 in Scheme 20

(**208**) (Ref. 988)

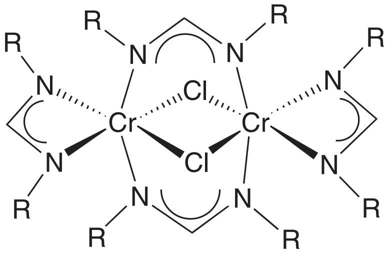


(**210**) (Ref. 990)



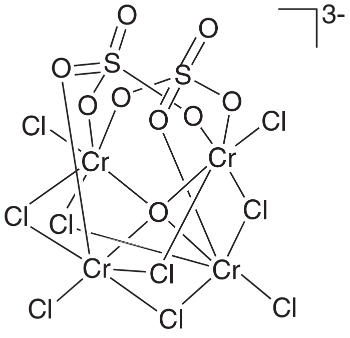
Ar = 2,6-$Pr^i_2C_6H_3$

(**211**) (Ref. 472)

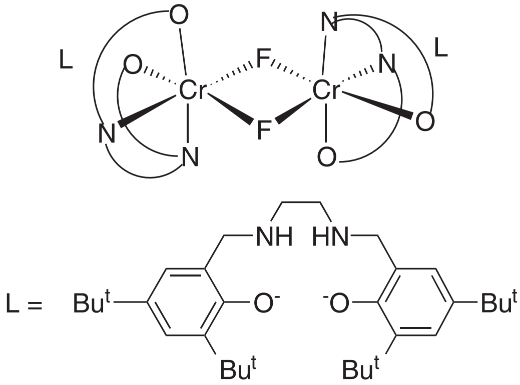


R = 4-MePh

(**212**) (Ref. 997)



(**213**) (Ref. 998)



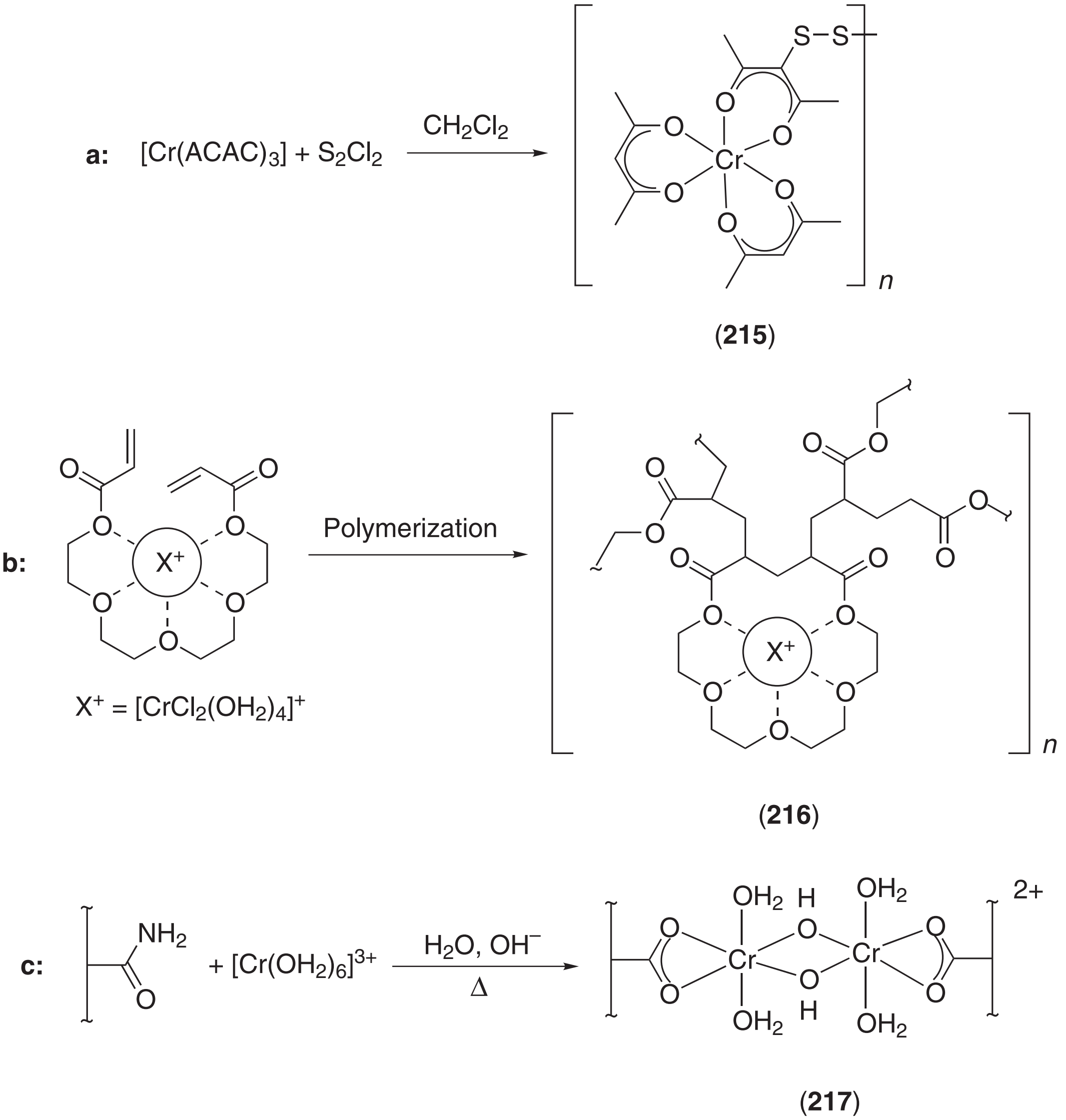
(**214**) (Ref. 999)

Table 5 Typical Cr^{III} complexes with polymeric ligands and their applications.

Ligand or complex	*Donor groups*	*Application*	*References*
[Cr(tpp)Cl], linked to Argogel chloride beads	see Section 4.6.5.2.10	catalyst for polycarbonate formation	505,1006
Cr^{III}–salen, linked to styrene-divinylbenzene	see Section 4.6.5.8.3	enantioselective catalyst of epoxide ring opening (low enantiomeric excess)	1007
Modified polyacrylamide	amido	catalyst of H_2O_2 decomposition	1008
Lactose-edta copolymer	amine + carboxylato	biodegradable chelator; potential for chelation therapy	1009
Modified cellulose	carboxylato	removal and recovery of Cr^{III} from waste waters	1010
Chitosan	amine + hydroxylato	removal and recovery of Cr^{III} from waste waters	1011
Poly[(2-hydroxyethyl)-DL-aspartamide]	amido + hydroxylato	separation and concentration of Cr^{III} by membrane filtration	1012
Copolymer of acrylic acid and tetrafluoroethylene-perfluorovinyl ether	carboxylato	antibacterial material (active against *E.coli* and *S.aureus*)	1013
Poly(*N*-isopropyl-acrylamides)	amido	regulation of swelling properties of hydrogels	1014
Partially hydrolyzed polyacrylamides	amido + carboxylato	cementing of oil wells to increase oil recovery	1015,1016
Polyaniline	imine	photosensitive materials	1017
Viscose or cellulose phosphates	phosphato	flame retardants	1018,1019
Methacrylate	carboxylato	promotor of adhesion of polymers to metal surfaces	1020

covalently attached to a polymer support.[1006,1007] Several Cr^{III}-containing polymers have been synthesized by polymerization of precursor complexes with acrylato ligands (such as $[Cr(phen)(acr)_3(OH_2)]$ or $[Cr_3O(acr)_6(OH_2)_3]^+$; acr = $CH_2CHCO_2^-$).[1022,1023] A template synthesis of a polymeric pseudo-crown ether (**216**) (Scheme 29b)[1024] used the ability of Cr^{III} aqua complexes to form hydrogen-bonded assemblies with polyether ligands (see (**135**)).[643] Mechanochemical syntheses of polymeric Cr^{III} complexes have been performed by mixing $[Cr(acac)_3]$ with a polymer ligand under an acoustic wave impact.[1025]

Probably the most important industrial application of Cr^{III}-containing polymers is the treatment of oil wells by a hydrophilic polymer (usually polyacrylamide) in the presence of a Cr^{III} salt as a cross-linking agent. This causes the formation of hydrogels, which decrease the permeability of surrounding rock formations, leading to enhanced oil recovery.[9,1015,1016] Recent thermodynamic studies[1026] suggested that the cross-links are likely to be formed by the coordination of dimeric Cr^{III} species to carboxylato groups of partially hydrolyzed polyacrylamide ((**217**); Scheme 29c).



(**215**)

(**216**)

(**217**)

Scheme 29

Although no crystallographic characterizations of Cr^{III} complexes with polymeric ligands are available to date, several new techniques have been applied recently for the determination of Cr^{III} coordination environments in such complexes. Energy-dispersive X-ray diffraction spectroscopy has been used in studies of Cr^{III} complexes with a widely used chelating resin, Chelex 100 (containing paired iminodiacetate ions coupled to a styrene–divinylbenzene support).[1027] Coordination of Cr^{III} in chrome-tanned leather has been studied by XAFS spectroscopy.[1028] Other characterization methods for Cr^{III} complexes with polymeric ligands include EPR[1029] and IR[1030] spectroscopies.

4.6.5.11 Biomolecules as Ligands

4.6.5.11.1 Amino acids

Despite several decades of extensive research,[1] there has been relatively little progress in structural characterizations of Cr^{III} complexes with amino acids. Crystallographically characterized complexes (since 1971) are listed in Table 6.[154,707,874,1031–1037] A series of mixed-ligand Cr^{III} complexes with deuterated amino acid and am(m)ine ligands have been prepared, and binding modes of the ligands have been studied by ^{2}H NMR (which is less sensitive than ^{1}H NMR to the presence of a paramagnetic Cr^{III} center).[1038] Complexes of Cr^{III} with amino acids have also been studied by fast atom bombardment mass spectroscopy.[1039,1040] The results of these studies,[1038–1040] together with the known crystal structures (Table 6), suggest that most amino acids bind to Cr^{III} in a bidentate fashion, through the carboxylato and α-amine groups, while those possessing an additional donor group (thiolato in Cys, carboxylato in Asp, or imidazole in His) bind in a tridentate mode.

The mode of coordination of amino acid ligands to Cr^{III} is determined by the preparation conditions (mainly the pH value). For example, trinuclear complexes of carboxylato-bound amino acids with protonated amino groups ($[Cr_3O(L)_6(OH_2)_3]^{7+}$; similar to (**179**)) have been isolated from aqueous solutions at pH $\sim$ 2 for Val, Ala, Leu, and Phe.[874] While a crystallographically characterized complex, $[Cr(cys)_2]^-$ (Table 6), possesses a tridentate (*O*,*N*,*S*-) binding mode of Cys,[1033] both bidentate (*O*,*N*-) and monodentate (*O*-) bindings have been proposed (based on IR spectroscopic data) for the complexes isolated under different conditions.[1041,1042] In acidic aqueous solutions in the presence of O_2, $[Cr(cys)_2]^-$ undergoes protonation of the Cys thiolato groups, followed by oxidation with the formation of S—S-bound polynuclear species.[1043,1044] Stereoselectivities of the syntheses of Cr^{III} complexes with amino acids have been studied.[1045–1047] Electronic spectra of a well-known complex, λ-*fac*-[Cr(ala)$_3$] (ala = *N*,*O*-L-alaninato(1−)),[1] have been investigated.[1048] A series of mechanistic studies on the anation of $[Cr(OH_2)_6]^{3+}$ with amino acid ions,[1049,1050] as well as on the oxidation of Cr^{III} amino acid complexes to Cr^{VI},[1051–1053] have been performed.

Many studies on Cr^{III} complexes with amino acids were related to the attempts to model the purported natural "glucose tolerance factor" (a compound isolated from yeasts, containing Cr^{III}, Gly, Glu, Asp, Cys, and nicotinate).[1,1054,1055] The experimental evidence available to date suggests that yeasts are unlikely to contain a well-defined Cr-dependent biologically active substance, but Cr^{III} amino acid complexes (which can accumulate naturally in plants or fungi, such as yeasts) may promote glucose metabolism in animals and humans.[11,12] This led to the recent patents on the use of Cr^{III} complexes with Met, His, or Thr as food supplements.[1056–1058] One of the main challenges in the studies of Cr^{III} complexes, related to biological systems, is the speciation of such complexes in aqueous solutions. The recently developed methods, ESMS and XAFS spectroscopy, are likely to become the major tools in such studies.[11]

Table 6 Crystallographically characterized Cr^{III} complexes with amino acids.

Complex[a]	*References*	*Complex*[a]	*References*
fac-[Cr(gly)$_3$]	1031	[Cr(cys)(his)]	1035
[Cr(his)(pen)]	1032	$[Cr_3(\mu_3\text{-}O)(\mu\text{-}val)_6(OH_2)_3]^{7+}$	874
$[Cr(cys)_2]^-$	1033	$[Cr(pen)_2]^-$	1036
$[Cr(his)_2]^+$	1034,1035	*fac*-[Cr(aib)$_3$]	154
		[Cr(acala)(his)]	1037
[Cr(asp)(his)]	1035	$[Cr(asp)(phen)(OH_2)]^+$	707

[a] Designations of the ligands: gly = *N*,*O*-glycinato(1–); his = *N*,*N*′,*O*-L-histidinato(1–); pen = *N*,*O*,*S*-D-penicillaminato(2–); cys = *N*,*O*,*S*-L-cysteinato(2–); asp = *O*,*O*′-L-aspartato(2–); val = *O*,*O*′-L-valinato (protonated amino group); aib = *N*,*O*-2-amino-2-methylpropanoato(1–); acala = *N*-acetyl-*N*,*O*-alaninato(2–).

4.6.5.11.2 Peptides and proteins

Several crystallographically characterized Cr^{III} complexes of synthetic dipeptides are known (Sections 4.6.5.8.2 and 4.6.5.9.7). The main attention [1,1059–1064] has focused on Cr^{III} complexes of a natural tripeptide, glutathione (γ-Glu-Cys-Gly). Glutathione is the most abundant intracellular reductant, and it is likely to play a key role in the conversion of carcinogenic Cr^{VI} into relatively nontoxic Cr^{III} complexes of small biomolecules, or to highly genotoxic DNA–Cr^{III}–DNA, protein–Cr^{III}–DNA, or amino acid–Cr^{III}–DNA cross-links (Sections 4.6.2.3.5 and 4.6.5.11.3).[11] No definitive structures of the Cr^{III}–glutathione complexes have been established to date. Reduction of Cr^{VI} with glutathione probably leads to a mixture of polynuclear (molecular mass 5–10 kDa)[1060] Cr^{III} complexes with the reduced GSH and oxidized GSSG forms of the ligand, where GSH and GSSG provide the *N*,*O*,*S*- and *N*,*O*-binding sites, respectively.[1059,1061–1064] The Cr^{III}–GSH–GSSG complexes do not bind to DNA to a significant extent and are not genotoxic in bacterial assays.[1065,1066]

The hypothesis that Cr^{III} is an essential micronutrient for humans (as an enhancer of the actions of insulin in glucose and fat metabolism) is currently under debate.[11,12,695,697,1067] Vincent and co-workers related the essentiality of Cr^{III} to the existence of a specific biomolecule, chromodulin, which is purported to be a tetranuclear Cr^{III} assembly (with oxo, hydroxo, or carboxylato bridging groups) bound to a small ($\sim$1.2 kDa) peptide, consisting of Cys, Glu, Asp, and Gly.[12,1068] Others questioned the existence of chromodulin,[11] based on the reported method of its isolation (a reaction of exogenous Cr^{VI} with bovine liver homogenate),[1068] and on the absence of definitive structural information (e.g., crystal structure of the complex or the polypeptide sequence).

Transferrin, one of the major transport proteins for metal ions,[1069] strongly binds to Cr^{III},[1070,1071] and is believed to be the main Cr^{III} carrier in human blood.[1072] One of the mechanistic hypotheses concerning the biological role of Cr^{III} suggests that binding of Cr^{III} to insulin stabilizes the protein structure and prevents its destruction by peptidase enzymes.[1073,1074] However, more recent evidence suggests that low-molecular-weight Cr^{III} complexes are likely to interact with cellular insulin receptors, rather than with insulin itself.[12,910,1075] The proposed role of Cr^{III} in the enhancement of insulin action[695,1067] led to the development of pharmaceutical formulations, including Cr^{III} complexes and insulin.[1076]

Insertion of the substitutionally inert[1] Cr^{III} ion into the active sites of metal ion-dependent enzymes provides a valuable tool in the mechanistic studies of enzyme actions.[1077] Recently, the first example of an active Cr^{III}-modified enzyme (phosphoenolpyruvate carboxykinase, normally a Mn^{II}-dependent enzyme) has been reported.[1078] Interactions of Cr^{III} with collagen have been studied in relation to the use of Cr^{III} in leather tanning.[1079] The use of low-molecular-weight Cr^{III} complexes as noncovalent binders in the structural studies of proteins (by NMR spectroscopy) is referred to in Sections 4.6.5.1.1, 4.6.5.2.1, and 4.6.5.8.3.

4.6.5.11.3 Nucleotides and nucleic acids

Disruption of DNA functions due to the formation of DNA–Cr^{III}–DNA, DNA–Cr^{III}–protein, or DNA–Cr^{III}–amino acid cross-links (caused by intracellular reduction of Cr^{VI}) is considered to be among the main reasons of Cr^{VI}-induced genotoxicity (Section 4.6.2.3.5).[11] Although it is well known that the addition of acidic Cr^{III} complexes (such as $[Cr(OH_2)_6]^{3+}$ or $[CrCl_2(OH_2)_4]^{+}$) to isolated DNA causes an extensive Cr^{III}–DNA binding, this effect is not biologically relevant, as Cr^{III} is likely to exist in biological media in the form of nonreactive anionic complexes.[11,1080] On the basis of equilibria studies and IR spectroscopic data, the most likely Cr^{III} binding sites in DNA and polynucleotides are the phosphate backbone and the *N*-7 atoms of guanine bases.[1081,1082] In a study directed towards the modeling of DNA–Cr^{III}–protein cross-links, a peptide-dinucleotide conjugate has been synthesized, but no well-defined Cr^{III} complexes of this ligand have been reported to date.[1083] A series of the Cr^{III}–nucleotide–amino acid[1084] and Cr^{III}–nucleotide–amine[1085] complexes have been synthesized and characterized by microanalytical data and spectroscopic methods. In all the reported complexes, the nucleotides appear to bind to Cr^{III} mainly through the phosphate groups.[1084,1085]

The well-known use of Cr^{III}–ATP complexes in studies of the active sites of kinase enzymes is based on a comparison of enzyme activities with the stereoisomeric Cr^{III}–ATP species (which can be easily resolved) as substrates.[1,1086] A recent development in this area has been the use of fluorescent labels attached to the Cr^{III}–ATP complexes for the mapping of ATP-binding sites of Na^+/K^+-ATPase.[1087,1088] Some recent examples of the use of Cr^{III}–nucleotide complexes in enzymology include the studies of DNA polymerase β,[1089,1090] or aminoglycoside nucleotidyltransferase.[1091]

4.6.5.11.4 Other biomolecules

Complexes of Cr^{III} with ascorbate, which are likely to form during the reactions of Cr^{VI} with this major intracellular reductant, have been studied (mainly by Cieślak-Golonka and co-workers),[1062–1064] but no definitive structural information has been obtained to date. Partially characterized Cr^{III} complexes with monosaccharides or their oxidized derivatives (e.g., aldonic acid) have been isolated from the reactions with either Cr^{III}[1092] or Cr^{VI}.[1093,1094]

Complexes of some natural antibiotics with metal ions, including Cr^{III}, are used for the detection of gram-negative bacteria.[1095] Some Cr^{III} complexes of natural polyphenols, such as lawsone (henna)[602] or tannins,[1096] have been prepared but not characterized fully. Crystallographically characterized Cr^{III} complexes with a natural siderophore ligand and some biological amines have been described in Sections 4.6.5.2.8, 4.6.5.8.1, and 4.6.5.8.2. Binding of Cr^{III} to humic acids in soil or ground water is important for Cr detoxification, either through the formation of kinetically inert Cr^{III} complexes[1097] or through the suppression of Cr^{III} oxidation to Cr^{VI} by MnO_2.[1098]

4.6.6 CHROMIUM(II)

The majority of the newly synthesized (since 1985) Cr^{II} complexes are dimers with quadruple Cr—Cr bonds.[1099,1100] These complexes are described in Chapter 4.9 of this edition. Comprehensive annual reviews are available (until 1991) on kinetic and mechanistic studies of electron-transfer reactions with a Cr^{II} complex as a reductant (including the numerous studies of the $Cr^{II}{}_{aq.} + Co^{III}$ reactions).[7,1101] Applications of Cr^{II} compounds (primarily $CrCl_2$) in organic syntheses were reviewed in 1999 and 2001.[667,1102] Unless stated otherwise, the Cr^{II} complexes described in this section have been prepared by the reactions of the ligands with Cr^{II} precursor compounds, such as $[CrCl_2(OH_2)_4]$, $[CrCl_2(thf)_2]$, or $[Cr_2(OAc)_4]$. Synthetic methods for these compounds have been reviewed previously.[1]

4.6.6.1 C-donor Ligands

Most of the Cr^{II} complexes with C-donor ligands are described in the accompanying *Comprehensive Organometallic Chemistry* series. Electron delocalization in the known[1] $[Cr(CN)_6]^{4-}$ complex has been evaluated recently using the *ortho*- to *para*-positronium conversion reaction.[1103] The thermal stability of $[Cr(CN)_5(CO)]^{3-}$ has been predicted from computational studies.[1104] Some Cr^{II} complexes with σ-bound alkyl ligands are described in Sections 4.6.6.2.2 and 4.6.6.3.

4.6.6.2 N-donor Ligands

4.6.6.2.1 Unidentate ligands

A list of crystallographically characterized Cr^{II} complexes with unidentate N-donor ligands (since 1985) is given in Table 7,[28,58,674,1105–1117] and typical reactions of Cr^{II} dialkyl (aryl)amido complexes are shown in Scheme 30.[58,1113,1114] The Cr^{II} dinitrogen complexes, $(NN)_xCrO$ ($x = 1, 2$), have been generated in solid Ar (at $\sim$10 K) by laser ablation techniques, and characterized by IR spectroscopy and DFT calculations.[265] Octahedral Cr^{II} complexes, such as *trans,trans*-$[CrCl_2(py)_2(OH_2)_2]$ (Table 7), have been used as convenient models for the experimental and computational studies of JTD.[1106] Some Cr^{II} complexes with pyrrolyl ligands have been applied as alkene polymerization catalysts (see also Section 4.6.5.1.2).[1118] Complexes of Cr^{II} with nitrosyl ligands are described in Section 4.6.7.1.

Table 7 Crystallographically characterized Cr^{II} complexes with unidentate *N*-donor ligands (since 1985).

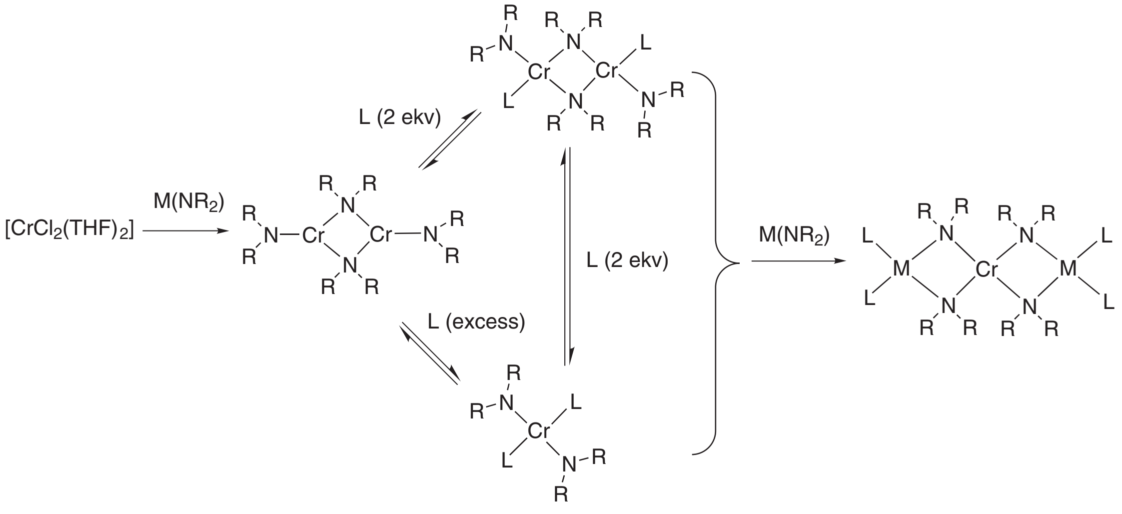
Complex[a]	*Type of N-donor*	*Geometry*	*Cr–N* (Å)	*References*
$[CrCl_2(Me_3SiNPMe_3)_2]$	Phosphaneimine	Square planar	2.12	1105
$[Cr(py)_4(PF_6)_2]$[b]	Imine	Octahedral	2.11	667
trans-trans-$[CrCl_2(py)_2(OH_2)_2]$	Imine	Octahedral	2.13	1106
trans,-$[CrCl_2(py)_4]\cdot(Me_2CO)$	Imine	Octahedral	2.13, 2.17[c]	1106
trans-$[CrBr_2(py)_4]\cdot 2py$	Imine	Octahedral	2.13, 2.16[c]	1107
$[CrBr_2(NCMe)_2]_n$	Nitrile	Octahedral[d]	2.07	1108
$[Cr(NCMe)_4(BF_4)_2](BF_4)_2$	Nitrile	Octahedral	2.06–2.07	1109
$(Bu^n{}_4N)_2[Cr(NCS)_4]$	Isothiocyanato	Square planar	2.01	1110
$[Cr(NCS)_2(opd)_2]$	Isothiocyanato + amine	Square planar	2.04,[e] 2.16[f]	1111
$[Cr(L^1)_2(py)_3]\cdot C_6H_5Me$	Amido + imine	Square pyramidal	2.06,[g] 2.17[h]	1112
$[Cr(L^2)_2(py)_2]$	Amido + imine	Square planar	2.04,[g] 2.14[h]	1113
$[Na_2Cr(L^2)_4(thf)_3]_n$	Amido	Square planar	2.07–2.09	1114
$[Cr(NPr^i{}_2)(\mu\text{-}NPr^i{}_2)]_2$[i]	Amido	Trigonal planar;[j] tetrahedral[k]	2.06,[j] 1.93[k]	58,1113,1114
$[Cr(NPh_2)(\mu\text{-}NPh_2)(thf)]_2$	Amido	Square planar	2.14,[j] 2.03[k]	1114
$[Cr(NPh_2)_2(py)_2]$[i]	Amido + imine	Square planar	2.06,[g] 2.15[h]	1114
$Na_2[Cr(NPh_2)_4(py)_2]$	Amido	Square planar	2.14	1114
$Li_2[Cr(NHAr)_4(thf)_2]$	Amido	Square planar	2.09–2.13	28
trans-$[Cr(nic\text{-}N)(OH_2)_4]$	Amido	Octahedral	2.13	1115
$[Cr/Zn(sac\text{-}N)_2(OH_2)_4]$[l]	Amido	Octahedral	2.20	1116
$[Cr(sac\text{-}N)_2(py)_3]$	Amido + imine	Distorted square pyramidal	2.12,[f] 2.33[g]	1117

[a] Designations of the ligands: opd = *o*-phenylenediamine = 1,2-benzenediamine (coordinated unidentately through one of the amine groups); L^1 = pyrrol-1-yl(1–); L^2 = 2,5-dimethylpyrrol-1-yl(1–); Ar = 2,6-$Pr^iC_6H_3$; R = 3,5-$Me_2C_6H_3$; R′ = adamantyl; nic = nicotinato = 3-pyridinecarboxylato(1–); sac = saccharinato = 1,2-benzisothiazol-3(2H)-one-1,1-dioxidato(1–). [b] Synthesized by disproportionation of $[Cr^I(C_6H_6)_2]^+$ in pyridine. [c] The longer Cr—N bonds are observed for the axial ligands (JTD). [d] Br-bridged linear polymer (Cr—Br distances, 2 at 2.54 Å and 2 at 2.98 Å). [e] For the isothiocyanato donor. [f] For the amine donor. [g] For the amido donors. [h] For the imine donor. [i] Several related complexes have been synthesized and characterized by X-ray crystallography. [j] For the bridging amido donors. [k] For the terminal amido donors. [l] Solid solutions with 33–69 at.% Cr.

4.6.6.2.2 Polydentate (open-chain) ligands

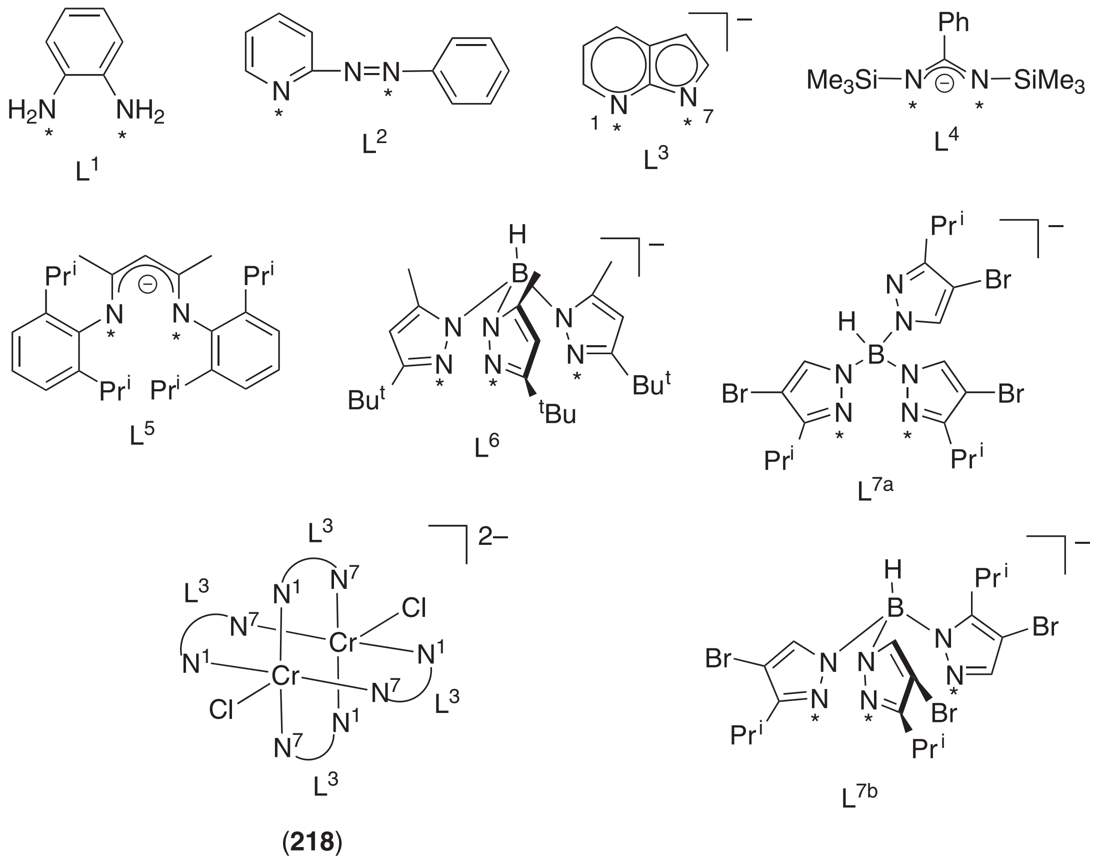
Structures of the ligands in crystallographically characterized complexes (L^1–L^7, binding sites of the Cr^{II} ion are designated with asterisks) are shown in Scheme 31. The $[Cr(L^1)_4]^{2+}$ (with two ligands bound bidentately and the other two monodentately) and $[CrCl_2(L^2)_2]$ complexes are octahedral;[1111,1119] the latter is distinguished by unusually low rates of Cl^- exchange (for kinetically labile Cr^{II}).[1119] The $[Cr_2(\mu\text{-}L^3)_4Cl_2]^{2-}$ complex ((**218**) in Scheme 31) possesses a classical paddlewheel geometry of Cr^{II} dimers, but the Cr···Cr distance is the longest known for this class of compounds (2.688 Å owing to the choice of bridging and axial ligands), which points to little or no Cr—Cr bonding.[1120] Sterically hindered square-planar complexes, $[Cr(L^4)_2]$ and $[Cr_2(L^5)_2(\mu\text{-}Cl)_2]$, are catalytically active in alkene polymerization.[472,1121,1122] No such activity was observed for $[Cr(L^6)R]$ (R = Et or Ph); an unusual geometry of these complexes has been described as *cis*-divacant octahedral.[1123] Isomerization of a substituted tri(pyrazolyl)borato ligand (L^{7a}) led to a square-pyramidal complex, $[Cr(L^{7a})(L^{7b})]$.[455]

Several methods for the generation (in dilute aqueous solutions) of Cr^{II} complexes with bpy, phen, and related chelating N-donor ligands have been outlined, including: (i) the reactions of the corresponding Cr^{III} complexes with aquated electron (generated by pulse radiolysis)[1124,1125] and (ii) the quenching of the exited states of the Cr^{III} complexes (generated by laser flash photolysis) with SO_2 or organic reductants.[1126,1127] Kinetics and mechanisms of the electron-transfer reactions of such Cr^{II} complexes with O_2, or with $[Ru(NH_3)_6]^{3+}$, have been studied.[437,1127] Thermal decomposition patterns of a series of known[1] Cr^{II} complexes with polyamine ligands have been determined.[1128,1129]

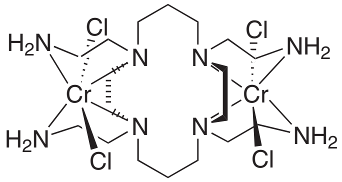


R = Alk or Ar; L = THF or Py; M = Li or Na

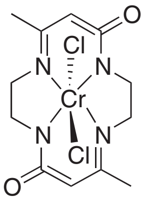
Scheme 30



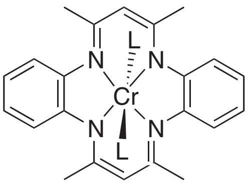
Scheme 31



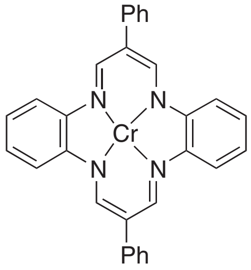
(**219**)
(Ref. 1130)



(**220**)
(Ref. 1131)



(**221**) (L = py)
(Ref. 1132)



(**222**)
(Ref. 1133)

4.6.6.2.3 *Macrocyclic ligands*

Several Cr^{II} complexes with macrocyclic N-donor ligands have been described since 1985, including those with saturated ((**219**)) or unsaturated ((**220**)–(**222**)) derivatives of [14]aneN_4,[1130–1133] as well as with porphyrinogen ((**69**) in Scheme 5, Section 4.6.4.2.2).[230] Only (**69**) and (**221**) have been characterized by X-ray crystallography.[230,1132] The Cr^{II}–cyclam complexes have been generated in aqueous solutions by chemical,[1134] electrochemical-,[1135] or photo-induced[1136] reductions of the corresponding Cr^{III} species, and ligand-exchange and redox reactions of these complexes have been studied.[298,1134] The latter reactions, including those with O_2 or with alkyl halides,[298,1134] are similar to those of $[Cr(OH_2)_6]^{2+}$ (see Scheme 7 and Scheme 14 in Sections 4.6.5.1.2 and 4.6.5.4.2, respectively). $[Cr([15]aneN_4)(OH_2)_2]^{2+}$ (generated *in situ*) has been used as a reductant to prepare the $Fe^{II}Fe^{II}$ forms of [2Fe–2S] ferredoxins.[1137] Typical redox reactions of the Cr^{II} complexes with macrocyclic N-donor ligands are shown in Scheme 32, as well as in Scheme 5 (Section 4.6.4.2.2).[228,230,503,1138]

a: (Ref. 228): $[Cr^{II}(TPP)] + N_3Ph \longrightarrow [Cr^{IV}(NPh)(TPP)] + N_2$

b: (Ref. 1137): $[Cr^{II}(oep)] + C_{60} \xrightarrow{\text{THF}} [Cr^{III}(oep)(thf)_2](C_{60}^{\bullet-})$

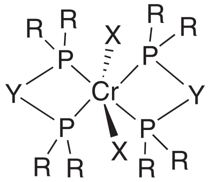
c: (Ref. 503): $[Cr^{II}(pc)] + Cl^{-} \xrightarrow{\text{electrolysis}} [Cr^{III}(pc^{+\bullet})Cl_2]$

Scheme 32

Complexes of Cr^{II} with porphyrinato or phthalocyaninato ligands have been known since the 1960s.[1] Recent studies of NO adsorption on solid [Cr(tpp)] by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy suggested the involvement of both the metal ion and the ligand in the adsorption.[1139] Electrochemical data on $Cr^{III/II}$ complexes with porphyrinato or phthalocyaninato ligands were reviewed in 2001, and correlations between the redox potentials and structures of the ligands have been established.[504] Molecular-orbital studies of the Cr^{II} complexes with these ligands have also been performed.[1140]

4.6.6.3 P-donor Ligands

Complexes of Cr^{II} with P-donor ligands are more diverse than those of Cr^{III} (Section 4.6.5.3). Structures of the crystallographically characterized (since 1985) (**223**)–(**228**) are shown;[513,1141–1147] another such complex is mentioned in Section 4.6.6.5. Unusually for Cr^{II} (a d^4 ion), the complex (**223c**) exhibits the spin cross-over from the high- to low-state with decreasing temperature ($\mu_{eff} = 4.84\mu_B$ at 295 K or $2.85\,\mu_B$ at 90 K).[1142,1148] Notably, closely related complexes with R = Me and X = Cl/Br/I, or with R = Et and X = Cl/Br possess temperature-independent low-spin states ($\mu_{eff} = (2.8–3.3)\,\mu_B$ at 90–295 K).[1141,1142,1148] Thus, relatively minor differences in the ligands can markedly affect the magnetic behavior of Cr^{II} phosphine complexes.[1142]

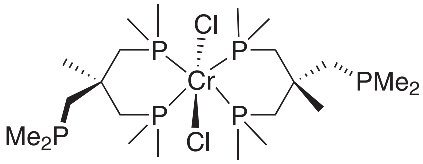


(**223a**) X = Cl; Y = $(CH_2)_2$; R = Me (Ref. 1141)

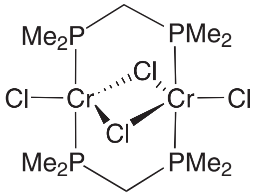
(**223b**) X = Me; Y = $(CH_2)_2$; R = Me (Ref. 1141)

(**223c**) X = I; Y = $(CH_2)_2$; R = Et (Ref. 1142)

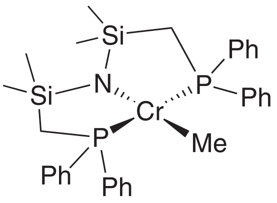
(**223d**) X = Cl; Y = C_6H_4; R = Me (Ref. 1143)



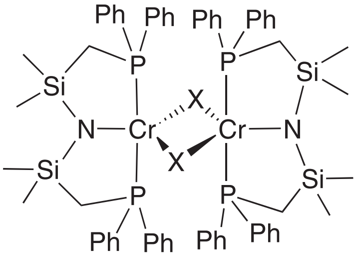
(**224**) (Ref. 513)



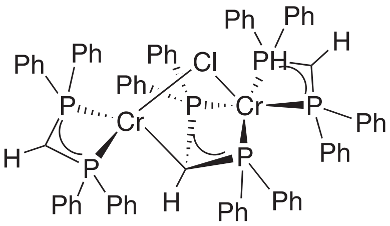
(**225**) (Ref. 1144)



(**226**) (Ref. 1145)



X = Cl (**227a**) or H (**227b**)
(Ref. 1146)



(**228**) (Ref. 1147)

Reduction of a Cl-bridged Cr^{III} phosphine complex led to an unusual Cr^{II} dimer (**225**) (Cr···Cr distance, 3.24 Å), instead of the expected paddlewheel complex with a short Cr—Cr bond.[1144] A series of Cr^{II} complexes with an amido-phosphine ligand ((**226**)–(**227**)) have been prepared, including a strongly antiferromagnetically coupled ($J = -139\,\mathrm{cm}^{-1}$) dihydrido-bridged dimer (**227b**) (Cr···Cr distance, 2.64 Å).[1145,1146] A three-center allylic-like ligand acts as both a P- and a C-donor in (**228**).[1147]

4.6.6.4 O-donor Ligands

4.6.6.4.1 Aqua ligands

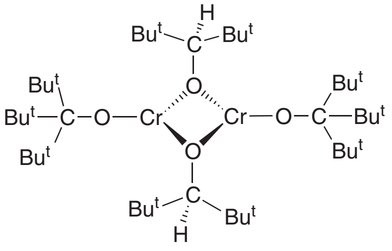
Structural studies of $[Cr(OH_2)_6]^{2+}$, as well as of other octahedral d^4 complexes, have attracted considerable attention because of the manifestations of the JTD effect.[1] Thus, a large difference in the lengths of the axial and equatorial Cr—O bonds (2.389 Å and 2.080 Å, respectively) has been detected in the deuterated Tutton salt, $(ND_4)_2[Cr(OD_2)_6](SO_4)_2$, by neutron diffraction studies at 4.3 K.[1149] Alternatively, the cation in $[Cr(OH_2)_6](SiF_6)$ presents an apparent case of suppressed JTD, being of an essentially regular octahedral structure (as determined by XRD at ~293 K).[1150] Other crystallographically characterized complexes (all exhibiting JTD) include $[Cr(OH_2)_4](SiF_6)$ (a chain octahedral complex with SiF_6^- occupying the axial positions; XRD at ~293 K)[1151] and $(NH_4)_2[Cr_xZn_{(1-x)}(OH_2)_6](SO_4)_2$ ($x = 0.10$ or 0.22; XRD at ~293 K or neutron diffraction at 11–17 K).[1152] Several computational studies on the geometry and dissociation energies of $[Cr(OH_2)_6]^{2+}$ have been published since 1985.[1153–1155]

The $[Cr(OH_2)_6]^{2+}$ ion has been among the most widely used reductants in kinetic and mechanistic studies of the electron-transfer reactions in metal complexes. Most of these studies were published before 1991, and have been covered by comprehensive annual reviews.[7,1101] Mechanistic studies of the $Cr^{II}_{aq.} + O_2$ reactions have also been reviewed (see Scheme 14 in Section 4.6.5.4.2).[231,232] Some of the more recent studies considered the reactions of $Cr^{II}_{aq.}$ with H_2O_2,[1156] 1,2-di(2-pyridyl)-ethylene,[1157] or blue copper proteins.[1158] A variable-pressure study of the oxidation of $Cr^{II}_{aq.}$ by aliphatic organic radicals (Scheme 7a in Section 4.6.5.1.2) led to the proposal of a dissociative interchange (I_d) mechanism for the $Cr^{II}–OH_2 \rightarrow Cr^{II}–R^{\bullet}$ ligand-exchange reaction (which is the first step of the redox process).[1159] *Ab initio* computational studies of ligand-exchange and electron-transfer reactions of $[Cr(OH_2)_6]^{2+}$ have been performed recently.[532,537]

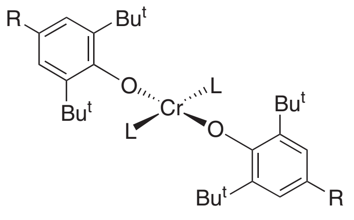
The reduction of $Hg^{II/I}$ to Hg^0 by $Cr^{II}_{aq.}$ is applied in analytical chemistry (including highly sensitive determination of mercury by atomic absorption spectroscopy in environmental samples).[1160] The well-known[1] catalysis by Cr^{II} of ligand-exchange reactions of Cr^{III} has been used to increase the efficiency of chrome-electroplating with environmentally acceptable Cr^{III}-based electrolytes.[1161] Photocatalytic H_2 generation by the CdS/Pd–Cr^{III}–EtOH–H_2O–H^+ system is based on the formation of $Cr^{II}_{aq.}$ (promoted by the accumulation of electrons in the conductance band of CdS during irradiation at 320 nm), which then reduces H_2O with the formation of H_2.[1162] Formation of $Cr^{II}_{aq.}$ during the reduction of $Cr^{III}_{aq.}$ is also a key step in the Fe–Cr redox energy storage cycle.[538]

4.6.6.4.2 *Other* O*-donor ligands*

Typical structures of crystallographically characterized complexes ((**229**)–(**236**)) are shown.[249,558,936,1163–1168] Complex (**229**) ($[Cr_2(OCBu^t_3)_2(\mu\text{-}OCHBu^t_2)_2]$) is formed by an unusual C—C bond cleavage reaction of $[Cr(OC\ Bu^t_3)_2(THF)(LiCl)]$ under mild conditions.[1163] The Cr—O bond

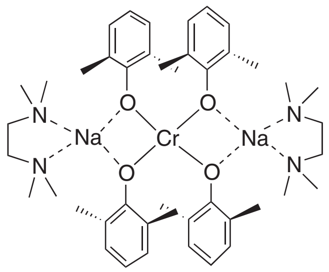


(**229**) (Ref. 1163)

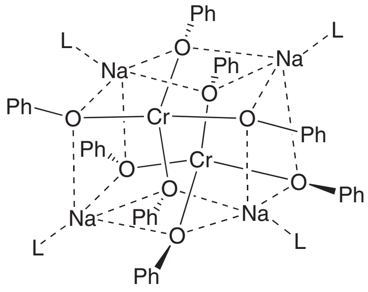


(**230a**) R = Me; L = THF (ref. 1164)

(**230b**) R = Bu^t; L = Py (ref. 1166)

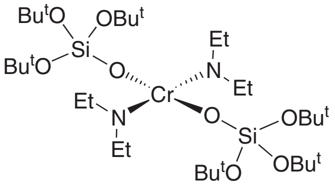


(**231**) (Ref. 1165)

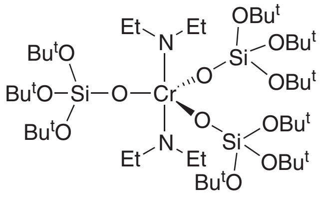


[(PhO)8Cr2][Na(py)]4

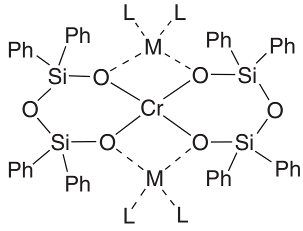
(**232**) (Ref. 1165)



(**233a**) (Ref. 558)

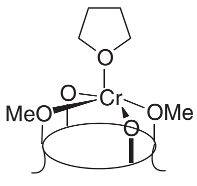


(**233b**) (Ref. 558)

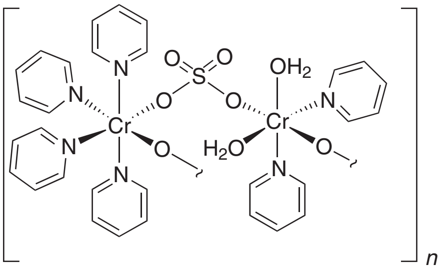


(**234a**) M = Na^+; L = THF (ref. 1167)

(**234b**) M = Li^+; L = Py (ref. 1168)



(**235**) (see (**74**), ref. 249)



(**236**) (Ref. 936)

lengths in (**229**) are 1.84 Å and 1.96 Å for the terminal and bridging alkoxo donors, respectively, and the Cr···Cr distance is 3.07 Å.[1163] Prior to the X-ray analysis, the structure of (**229**) had been wrongly assigned as $[Cr(OCBu^t{}_3)_2(THF)_2]$.[1] The structural complexity of the Cr^{II} aryloxides (**230**)–(**232**) increases with decreasing bulkiness of the ligands.[1164–1166] The Cr^{II} silyloxo complexes (e.g., (**233**) and (**234**)) have been studied as possible precursors of ultrapure Cr silicates (used in catalysis), and as homogeneous models of SiO_2-supported Cr catalysts.[558] Complex (**234a**) was catalytically active in alkene polymerization.[1167] A Cr^{II} complex with a calixarene derivative, (**235**) (synthesized by reduction of a Cr^{III} precursor), has been studied as a possible model of a catalytic Cr^{II} site over a planar oxo surface (see also Section 4.6.5.1.2).[249] Reaction of (**235**) with O_2 led to a Cr^{IV} dimer ((**74**), Section 4.6.4.3.3).[249] The complex (**236**) (a sulfato-bridged chain polymer with two different types of Cr^{II} coordination) crystallizes from a solution of $CrSO_4{\cdot}xH_2O$ in pyridine.[936]

New polymeric Cr^{II} phosphates, $MCrP_2O_7$ (M = Ca, Sr, or Ba) have been characterized by X-ray crystallography and phase transition equilibria studies.[1169] Formation of Cr^{II} carbazato complexes by the reactions of Cr^{II} salts with N_2H_4 and CO_2 has been studied in relation to the corrosion of stainless steel reservoirs used for the storage of rocket fuel (containing N_2H_4 or its derivatives).[683] Several Cr^{II} complexes with phosphato,[1170] phosphonato,[1170,1171] phosphinato,[1170] phosphoramide,[1172] and squarato[1173] ligands have been isolated and studied by spectroscopic methods.

4.6.6.5 S-donor Ligands

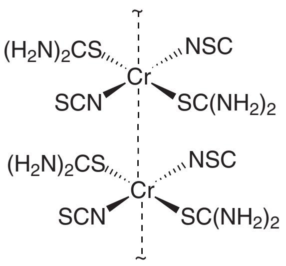
There are few known relatively stable complexes, containing Cr^{II}—S bonds.[1] Structures of the crystallographically characterized compounds ((**237**)–(**239**)) are shown.[1110,1174–1176] The isothiocyanato-thiourea complex (**237**) presents a previously unknown structural type of Cr^{II} with *trans*-planar units stacked in infinite parallel chains with a Cr···Cr separation of 3.97 Å.[1174,1175] Complex (**237**) is reasonably air-stable when dry; it possesses a high-spin electronic state ($\mu_{eff} = 4.53\mu_B$ at 291 K) and weak antiferromagnetic interaction between the Cr centers at low temperatures ($J = -2.7\,cm^{-1}$).[1174] Complex (**239**) is a dimeric (blue) form of Cr^{II} isothiocyanate; the monomeric (red) form has been referred to in Section 4.6.6.2.1.[1110]

4.6.6.6 Halide Donor Ligands

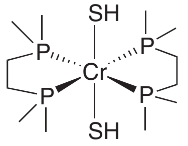
Complexes of Cr^{II} with halo ligands were studied most extensively in the 1960s and 1970s.[1] Crystallographically characterized compounds (since 1985) include $[PhCH_2NH_3][CrBr_4]$ (a ferromagnet with $T_c = 52\,K$),[1177] $[CrBr_2(thf)_2]$,[1178] $[Cr(\mu_4\text{-}O)(\mu\text{-}Cl)_6(thf)_4]$ (**240**),[1179] as well as numerous mono- and dinuclear mixed-ligand species with Cl^- ligands (derived from $CrCl_2$ as a synthetic precursor; Sections 4.6.6.2–4.6.6.5). Complex (**240**) is isostructural with the known tetramers of Cu^{II}, Mg^{II}, and Mn^{II}.[1179] A comparative analysis of the known crystal structures of CrX_n (X = F, Cl, Br, or I) for Cr^{II}, Cr^{III}, and Cr^{IV} has been performed, with a particular emphasis on the manifestations of JTD in the Cr^{II} compounds.[1180,1181] The reduction of polymeric[1] anhydrous $CrCl_2$ with $NaBH_4$ has been used recently for the preparation of Cr nanoparticles.[1182]

4.6.6.7 H-donor Ligands

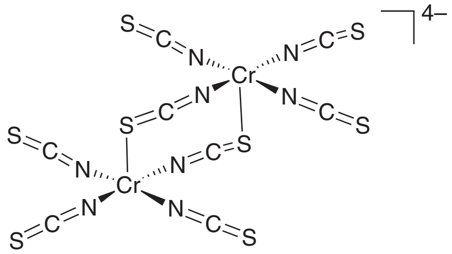
Only a few complexes with Cr^{II}—H bonds were known prior to 1985.[1] New crystallographically characterized complexes of this type (i.e., those with hydrido or borohydrido ligands) include $[CrH\{(Me_2PCH_2)_3CMe\}_2](BEt_4)$,[1183] $[CrH(\eta^2\text{-}BH_4)\{Me_2P(CH_2)_2PMe_2\}]$,[1184] $[Cr(\eta^2\text{-}BH_4)_2\{Me_2N(CH_2)_2NMe_2\}]$,[1185] $[Cr(BH_4)_2(py)_4]$,[1185] and a trimeric complex (**241**).[1185] An aluminohydrido complex, $[\{Me_2P(CH_2)_2PMe_2\}_2HCr(\mu\text{-}H)_2AlH(\mu\text{-}H)]_2$, has been characterized by multinuclear NMR spectroscopy.[1186] Such complexes are of interest as potential catalysts for hydrogenation or polymerization reactions.[1185]



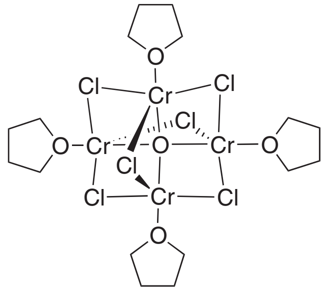
(**237**) (Ref. 1174, 1175)



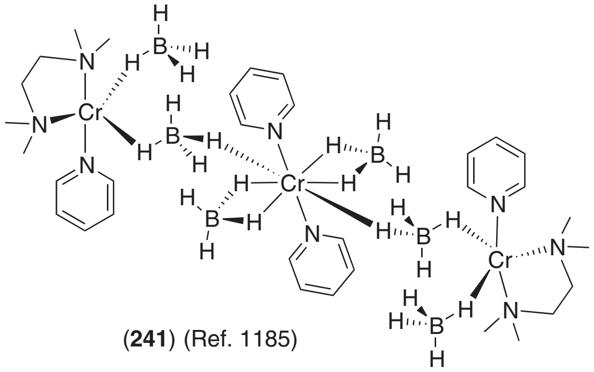
(**238**) (Ref. 1176)



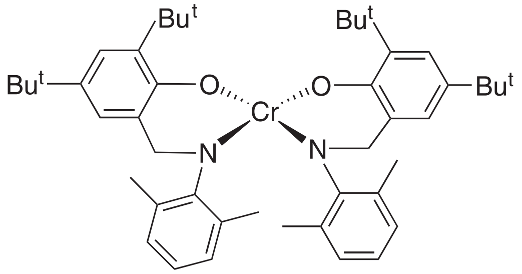
(**239**) (Ref. 1110)



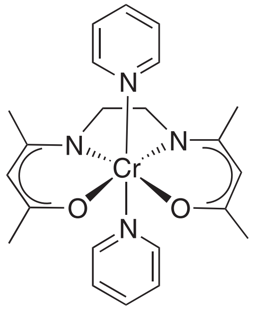
(**240**) (Ref. 1179)



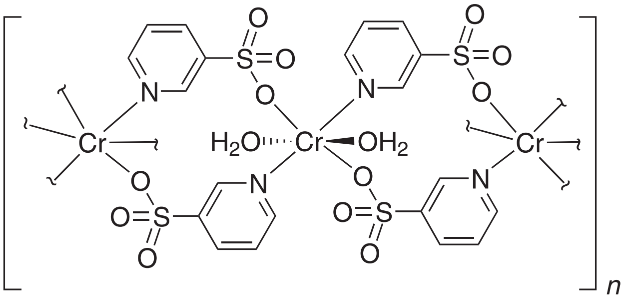
(**241**) (Ref. 1185)



(**242**) (Ref. 362)



(**243**) (Ref. 1187)



(**244**) (Ref. 1188)

4.6.6.8 N–O Donor Ligands

Structures of the crystallographically characterized complexes ((**242**)–(**244**)) are shown.[362,1187,1188] Complexes (**242**) and (**243**) were isolated in low yields from the reactions of Cr^{III} salts with the deprotonated ligands (where the ligand probably also acted as a reductant);[362,1187] (**242**) acts as a catalyst of alkene polymerization.[362] A polymeric complex (**244**), as well as a related monomeric species, $[CrL_2(py)_4]$ (L = 3-pyridinesulfonate), were crystallized from the aqueous solutions of the ligand and Cr^{II}; both complexes are relatively air-stable.[1188]

Stability constants of some Cr^{II} complexes with amino acids or aminopolycarboxylates have been compared with the corresponding values for Cu^{II} complexes.[1189] Known (though not fully characterized)[1] Cr^{II} complexes with edta or amino acids have been used as chemo- or enantioselective reductants in organic synthesis.[1190–1192] Complexes of Cr^{II} with aminopolycarboxylato ligands (generated in aqueous solutions) have also been used as redox mediators in the indirect electrochemical reductions of organic substances,[1193] and as components of electrochemical sensors for dissolved O_2.[1194] Complexes of Cr^{II} with picolinato ligand have been generated by pulse radiolysis from the corresponding Cr^{III} complex (Section 4.6.5.8.1).[262] Such generation of highly reactive Cr^{II} species in the presence of ionizing radiation may be used for chemical decontamination of nuclear reactor systems.[262]

4.6.7 CHROMIUM(I) AND CHROMIUM(0)

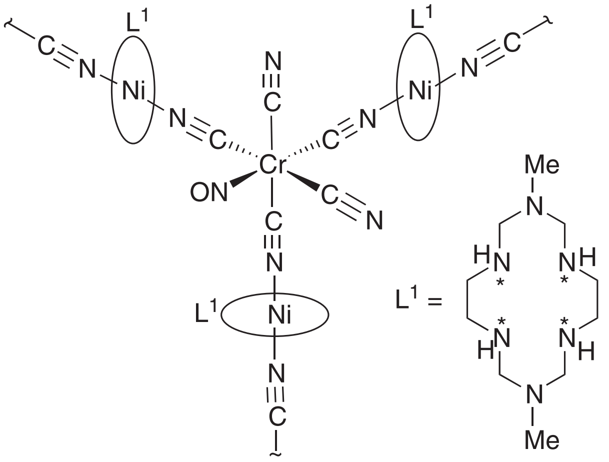
The great majority of Cr^I or Cr^0 complexes, including those with carbonyl, carbene, or η-hydrocarbon ligands, are described in the *Comprehensive Organometallic Chemistry* series.

4.6.7.1 Nitrosyl Complexes of $Cr^{I/II/III}$

The chemistry of transition metal nitrosyl complexes (including those of Cr) has been reviewed extensively.[1195–1197] Assignment of the metal oxidation state in the Cr–NO complexes is ambiguous (Cr^I–NO^+, Cr^{II}–$NO^\cdot$, or Cr^{III}–NO^-).[1] Crystallographically characterized complexes (since 1985) include (**245**)–(**247**),[1198–1200] as well as $[Cr(NO)(OH_2)_5]^{2+}$,[1201] $[Cr(NO)(NH_3)_5]^{2+}$,[1202,1203] and *mer*-$[Cr(NO)(CNCMe_3)_3(Ph_2PCH_2PPh_2)]$.[1204] A large series of Cr–NO complexes with N- or O-donor ligands have been characterized by spectroscopic methods.[1205–1207] Such complexes are also formed as intermediates in the syntheses of Cr^{VI} nitrido complexes (Scheme 3 in Section 4.6.2.2.3).[36] All the crystallographically characterized complexes possess octahedral coordination geometries and nearly linear (175–180°) Cr—N—O bond angles.[1198–1204] A polymeric cyano-bridged complex (**245**) is distinguished by a relatively long Cr–N(NO) bond (1.87 Å compared with 1.67–1.72 Å in the other compounds); it exhibits ferromagnetic interaction between the Cr and Ni^{II} centers.[1198] Compound (**248**) (characterized by NMR and other spectroscopic methods) is unusual as it can be formally described as a Cr^{II}–NO^+ complex.[867] General synthetic methods for the Cr–NO complexes have been reviewed previously.[1]

The $[Cr(NO)(OH_2)_5]^{2+}$ complex, first synthesized in 1962, was crystallographically characterized in 1993 by Ardon *et al.* It was described as being close to Cr^{III}–NO^-, based on the short Cr–N distance (1.68 Å) indicating a multiple Cr—N bonding, and on the elongation by 0.059 Å of a Cr—O bond *trans* to the NO group (while binding to NO^+ would lead to a shortening of this bond).[1201] Alternatively, *ab initio* calculations of the ground and exited electronic states in $[Cr(NO)(OH_2)_5]^{2+}$ led the values of the net charge on Cr atom in the range +1.65 to +1.84.[1208]

The Cr–NO complexes (possessing a d^5 electronic configuration) usually give sharp intense EPR signals at room temperature ($g_{iso} = 1.97$–1.99; reviewed in 1994).[1209] More recently, a detailed EPR spectroscopic study has been performed for $[Cr(NO)(OH_2)_5]^{2+}$, as well as for two Cr–NO–ehba complexes (generated in aqueous solutions by the reactions of $[Cr^VO(ehba)_2]^-$ with NH_2OH and separated by ion-exchange chromatography).[195] Kinetics and mechanisms of the redox reactions of $[Cr(NO)(OH_2)_5]^{2+}$ with BrO_3^-, IO_4^-, or U^{III} in acidic aqueous solutions, leading to $[Cr(OH_2)_6]^{3+}$ as a main product, have been examined.[1210] Comparative computational studies of the $[M(NO)(CN)_5]^{n-}$ complexes (M = Fe, Mn, or Cr) in relation to their reactivities with oxidants or nucleophiles have been performed.[1211,1212] The $[Cr(NO)(CN)_5]^{3-}$ complex is not pharmacologically active as a vasodilator (unlike the corresponding Fe^{III} complex).[1212]



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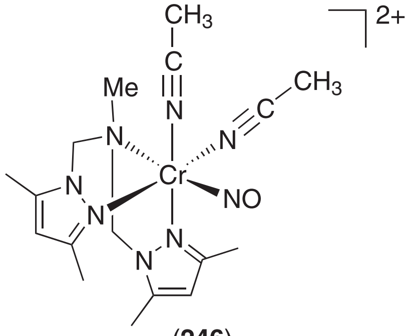

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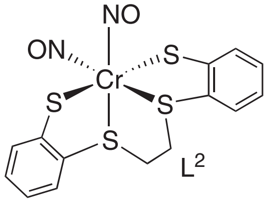

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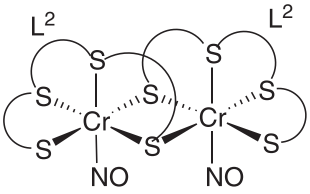
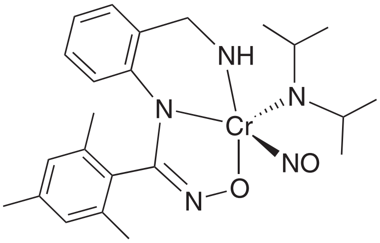


(247b)



(248)

4.6.7.2 Other Cr^I Complexes

A simple synthetic method for Cr^I complexes, based on the reaction of $CrCl_2$ with Ag^I complexes, has been proposed (it is believed that EtOH, used as a solvent, also acts as a reductant).[1213] Formation of $[CrL_3]^+$ complexes (where L is a bidentate N-donor ligand) has been supported by magnetic measurements ($\mu_{eff} \sim 1.9\,\mu_B$ at 298 K) and cyclic voltammetry.[1213] Studies of the

Table 8 Syntheses and/or characterizations of nonorganometallic Cr^0 complexes (since 1985).

Donor type	*Complex*	*Comment*[a]	*References*
Phosphine	$[Cr\{(Me_2PCH_2)_3CMe\}_2]$	Synt., cryst. str.	513
Phosphine, proton	$[CrH\{(Me_2PCH_2)_3CMe\}_2]^+$	Synt., cryst. str.	1183
Phosphine, protonated nitrile	*trans*-$[Cr(HNCMe)_2L]^{2+}$[b]	Synt., cryst. str.	219
Fluorophosphine	$[Cr(PF_2NMe_2)_4\{(PF_2)_2NMe\}]$	Synt., cryst. str.	1218
Nitrosyl, isocyanide, phosphine	*cis*-$[Cr(NO)(CNCMe_3)(PPh_3)]^+$	Synt., electrochem.	1204
Isocyanide	$[Cr(CN\text{-}2,6\text{-}Me_2Ph)_6]$	Synt.	1219
Isocyanide	$[Cr(CN\text{-}2,6\text{-}Pr^i{}_2Ph)_6]$	Electrochem.	1214
Isocyanide	$[Cr(CNPh)_6]$	Raman spectroscopy	1220
Isocyanide	$[Cr(CNAr)_6]$ [c]	Initiators of alkene polymerization	1221
Dinitrogen	$[Cr(N_2)]$ (in gas phase)	Laser ablation, IR spectroscopy, DFT calculations	1222
Carbonyl	$[Cr(OCMe_2)]$	Computational study	1223

[a] Synt. = synthesis; cryst. str. = determination of the crystal structure; electrochem. = electrochemical study. [b] $L = Me_2P(CH_2)_2PMe_2$; [c] Ar = Ph or its Cl- or Me-substituted derivatives.

known[1] $[Cr(bpy)_3]^+$ complex by EPR spectroscopy have been reviewed.[1209] Solvent effects on the electron self-exchange rates in the $Cr^{I/0}$ and $Cr^{II/I}$ couples have been studied using a Cr^I isocyanide complex, $[Cr(CN\text{-}2,6\text{-}Pr^i_2Ph)_6](BF_4)$.[1214] Formation of the bare Cr^+ ion and its adducts (such as $[Cr(MeOOMe)]^+$, $[Cr(OMe)_2]^+$, or $[Cr(NH_3)_2]^+$) in the gas phase has been studied by mass-spectrometric methods.[1215–1217]

4.6.7.3 Chromium(0) Complexes

Typical examples of nonorganometallic Cr^0 complexes, synthesized and/or characterized since 1985, are listed in Table 8.[219,513,1183,1204,1214,1218–1223] Generally, such Cr^0 complexes are generated by the reductions of the corresponding Cr^{II} or Cr^{III} complexes,[219,513,1183,1204] or, in some cases, by the reactions of Cr metal with the ligands.[1218] The former method led to the syntheses of two unusual cationic Cr^0 complexes (Table 8), probably involving the coordination of H^+ either to the Cr center or to the nitrile ligands (the Cr^0 oxidation state is confirmed by the diamagnetism of such complexes).[219,1183]

ACKNOWLEDGMENTS

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4.7
Molybdenum

C. G. YOUNG
University of Melbourne, Victoria, Australia

4.7.1 INTRODUCTION

This chapter covers mononuclear Mo chemistry reported from 1985 to late 2002, prior work being covered in a landmark review by Stiefel[1] and in *Comprehensive Coordination Chemistry* (*CCC*, 1987).[2–5] Prevalent high-valent Mo coordination chemistry is comprehensively reviewed but the treatment of low-valent chemistry, where the boundary between coordination and organometallic chemistry is often blurred, is selective rather than exhaustive (see also *Comprehensive Organometallic Chemistry*[6]). "Global" schemes are provided for systems boasting many species or spanning many oxidation states; presented as the systems are introduced, these act as guides to key papers and signposts to later sections. Communications of fully published work, reports of a purely crystallographic nature or *Inorganic Syntheses* are not cited; these can be located using the leads provided. ^{95}Mo NMR data are not specifically catalogued.

Molybdenum compounds are important catalysts in industry, finding applications in, inter alia, olefin metathesis, amm(on)oxidation, epoxidation, hydrodesulfurization, hydroformylation, and chemical and photo-oxidation processes.[7,8] The technological uses of Mo and its compounds are many and varied.[7,8] Molybdenum is also an essential trace element found in a wide variety of enzymes responsible for the growth and health of organisms and the cycling of nitrogen, sulfur, and carbon in the geo-bio-spheres; recent reviews of this important aspect of Mo chemistry are available.[9–11] Discernable trends in Mo chemistry since the early 1980s include: (i) the introduction of versatile tris(amido) and triamidoamine ligands supporting novel species and chemistry; (ii) an explosion in the chemistry and catalytic applications of imido and hydrazido complexes and chiral species (especially those with alkyl and alkylidene co-ligands); (iii) sustained development of oxo chemistry and the exploration of chiral dioxo and oxobis(peroxo) complexes for asymmetric synthesis; (iv) increased activity and sophistication in the chemical modeling of molybdoenzyme structure, function, and spectroscopy; (v) progress in the functionalization of dinitrogen at Mo centers (despite an overall decline in this area); and (vi) intense interest in the electro-optical and nonlinear optical behavior of Mo compounds and their use in the construction of devices and supramolecular assemblies. Molybdenum is a truly fascinating and versatile element and the full measure of its coordination chemistry is matched by few other elements.

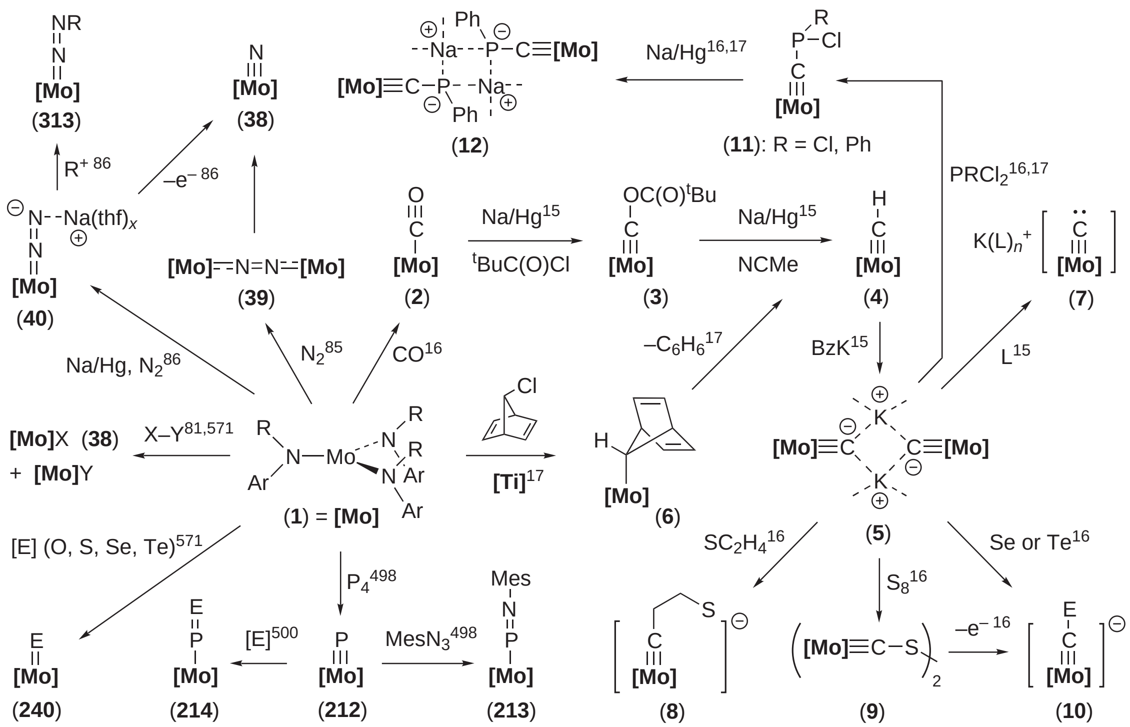
4.7.2 MOLYBDENUM(VI)

4.7.2.1 Complexes Containing Carbon-donor Ligands

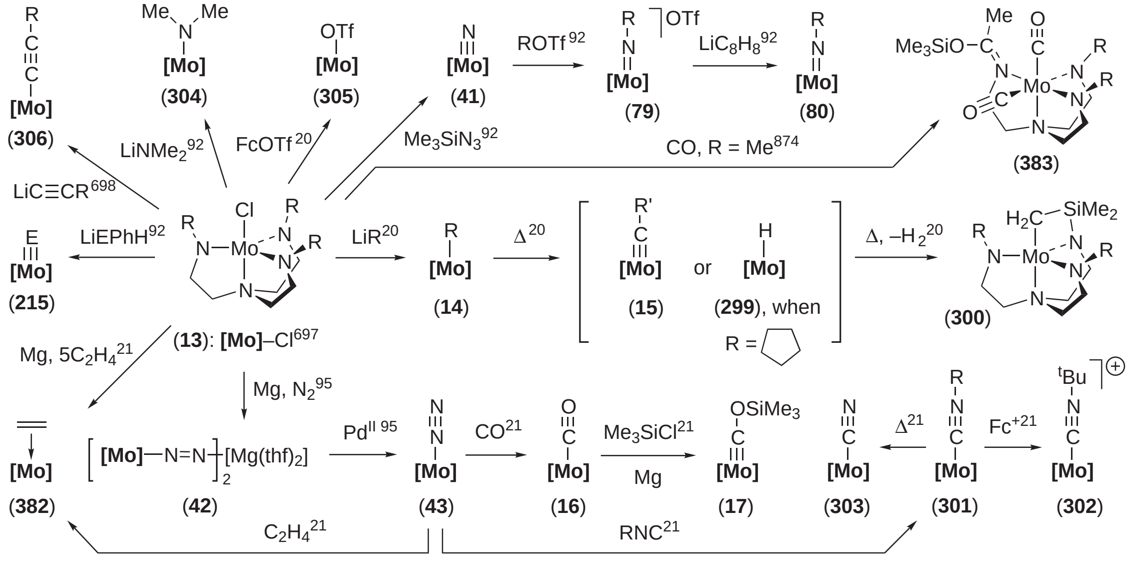
Complexes in this category include carbide ($Mo{\equiv}C{:}$), alkylidyne ($Mo{\equiv}CR$), alkylidene ($Mo{=}CRR'$), and alkyl ($Mo{-}R$) species (discussed in that order). Other perspectives on this area may be found in reviews by Schrock[12,13] and Nugent and Mayer,[14] and in *Comprehensive Organometallic Chemistry*.[6] From a practical standpoint, alkylidyne and alkylidene complexes are tremendously important as catalysts for olefin metathesis, "living" ring-opening metathesis polymerization (ROMP), ring-closing metathesis reactions, etc.

4.7.2.1.1 Carbide and alkylidyne complexes

Three-coordinate $Mo(NRAr)_3$ (**1** = [**Mo**], $R = C(CD_3)_2CH_3$, $Ar = C_6H_3Me_2$-3,5; Section 4.7.5.2.3) is pivotal to the exciting chemistry reported by Cummins and co-workers (Scheme 1). Conversion of (**1**) to $Mo(CO)(NRAr)_3$ (**2**) followed by reductive deoxygenation via $Mo\{COC(O)^tBu\}(NRAr)_3$ (**3**) produces $Mo(CH)(NRAr)_3$ (**4**) (pK_a ca. 30 in thf), that is deprotonated by BzK to yield $K[MoC(NRAr)_3]$ (**5**) (stabilized by π-arene-K^+ interactions).[15,16] A better route to (**4**) involves elimination of benzene from $Mo(\sigma\text{-}C_7H_7)(NRAr)_3$ (**6**).[17] Complex (**5**) is readily converted to crown ether derivatives $K(crown)_n[MoC(NRAr)_3]$ (**7**), the $K(benzo\text{-}15\text{-}C\text{-}5)_2{}^+$ salt exhibiting a tetrahedral structure with $d(Mo{\equiv}C)$ 1.713(9) Å (cf. $d(Mo{\equiv}C)$ 1.702(5) Å for (**4**)).[15] The $Mo{\equiv}{}^{13}C$ NMR signal of (**5**) is very deshielded (δ 501) and anisotropic (806 ppm) and carbide/methylidyne proton self-exchange is very fast ($k = 7 \times 10^6$ M^{-1} s^{-1}). The carbide anion is a strong reductant and nucleophile forming alkylidyne derivatives (**8**)–(**12**).[15,16] In broadly related work, Schrock and co-workers have defined the chemistry of the triamidoamine ligand, $N(CH_2CH_2NSiMe_3)_3{}^{3-}$($N_3N$, Scheme 2), and its arylamido analogs.[18,19] Reactions of $MoCl(N_3N)$ (**13** = [**Mo**]—Cl, Section 4.7.4.2.3) with alkyls lithium produce alkyl species, $MoR(N_3N)$ (**14**, R = alkyl, *c*-alkyl, *c*-C_5H_7, Bz, Ph), that are thermally unstable with respect to alkylidyne complexes such as $Mo(CR')(N_3N)$ (**15**, R′ = H, Pr, ^{t}Bu, for R = *c*-C_3H_5, *c*-C_4H_7, $CH_2{}^tBu$, respectively).[20] Reductive silylation of $Mo(CO)(N_3N)$ (**16**) also produces an alkylidyne complex, $Mo(COSiMe_3)(N_3N)$ (**17**).[21] Aryl analogs of these complexes and many W counterparts are known; $W(CSiMe_3)\{N(CH_2CH_2NC_6F_5)_3\}$ adopts a trigonal bipyramidal structure with an axial alkylidyne ligand.[22] Diamidoamine species are recent additions to this area.[23,24]



Scheme 1

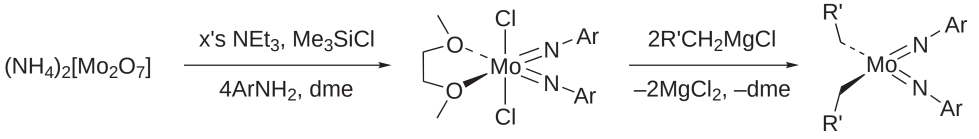


Scheme 2

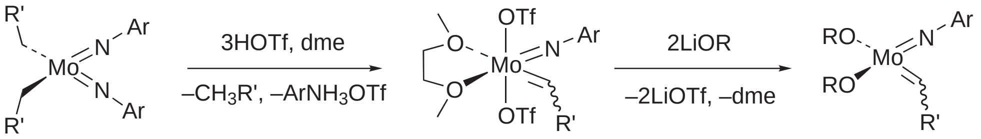
Convenient new syntheses for Mo(CR)(OAd)$_3$ (R = Me, Et, CH$_2$SiMe$_3$) from readily available Mo(N^{i}PrAr)$_3$[25] and the investigation of a silica-supported catalyst, ≡SiO—Mo(≡C^{t}Bu)(CH$_2{}^t$Bu)$_2$,[26] hint at a resurgence in interest in alkylidyne complexes such as Mo(C^{t}Bu)L$_3$ (L = CH$_2{}^t$Bu, OR, SR, O$_2$CR), last studied in the mid-1980s.[27] An alkylidyne, Mo(C^{t}Bu){N(Ar)P = CHR′}(OR)$_2$, has been identified as an intermediate in the formation of Mo{(η^2) = C(^{t}Bu)P(OR)CHR′}(NAr)(OR) in the reactions of ^{t}BuC≡P with Mo(NAr)(CHR′)(OR)$_2$ (R = CMe$_2$(CF$_3$), R′ = CMe$_2$Ph).[28] Finally, methoxide induces ligand and proton exchange at TpMo(CHCMe_2Ph)(NAr)(OTf) producing structurally characterized TpMo($CCMe_2$Ph)(NHAr)(OMe).[29]

4.7.2.1.2 Alkylidene complexes

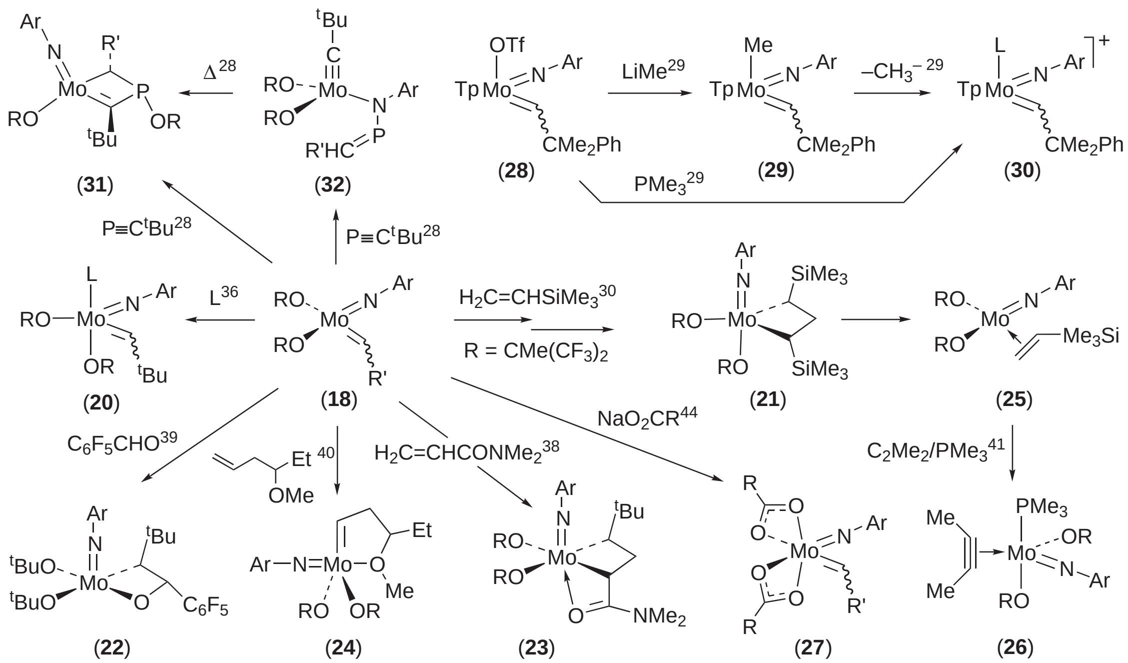
Virtually all chemistry in this area involves alkylidene imido complexes of the type Mo(CHR′)(NAr)$(OR)_2$ (**18**), prepared via Mo(CHR′)(NAr)$(OTf)_2$(dme) (**19**) using the synthetic protocol in Equations (1) and (2);[30,31] the use of py in place of dme and alternatives to step 3 enjoy niche applications.[32–34] The precursor, Mo(CH^{t}Bu)(NAr)$(OTf)_2$(dme), exhibits an octahedral structure with *cis* alkylidene (d(Mo=C)$_{av}$ 1.91 Å, ∠(Mo=C—C)$_{av}$ 141.5°) and imido (d(Mo=N) 1.72(1) Å, ∠(Mo=N—C)$_{av}$ 172.3°) groups.[30] The work-horses in this area are Mo(CHR′)(NAr)$(OR)_2$ (R′ = ^{t}Bu, CMe_2Ph; Ar = $C_6H_3{}^iPr_2$-2,6; R = $CMe(CF_3)_2$) and a detailed synthesis for popular Mo($CHCMe_2$Ph)(NAr)$\{OCMe(CF_3)_2\}_2$ has been published;[35] derivative chemistry is sampled in Scheme 3. Trigonal bipyramidal *syn* (kinetic) and *anti* (thermodynamic) adducts of L = PMe_3 (**20**), as well as *syn*/*anti* adducts of quinuclidine and py (Ar = $C_6H_3Cl_2$-2,6) have been prepared and structurally characterized.[36] The X-ray structures of Mo($CHCMe_2$Ph)(NAd)$\{OCH(CF_3)_2\}_2$(lutidine)[37] and several chiral derivatives (*vide infra*) confirmed the formation of solvent adducts in other derivatives (nb., these are often represented as 4-coordinate (**18**)). Reactions of (**18**) with ethene derivatives or aldehydes such as C_6F_5CHO produce unstable metallacyclobutane (e.g., (**21**))[30,38] or 2-oxametallacyclobutane (e.g., (**22**))[39] derivatives, respectively; metallacyclobutanes can be stabilized by pendent groups (e.g., (**23**)) but 5- and 6-coordinate alkylidene species (e.g., (**24**)) can also form.[40] Reduction by ethene derivatives results, e.g., in the formation of an η^2-vinyltrimethylsilane complex (**25**) that undergoes exchange producing alkyne and phosphine derivatives such as (**26**).[41] The interconversion and relative reactivities of *syn* and *anti* alkylidene imido complexes have been extensively probed due to their influence on polymerization reactions; high-*cis* polymers are obtained when *syn*/*anti* isomerization rates are negligible on the polymerization timescale, whereas high-*trans* polymers result when *syn*/*anti* isomerization rates are fast (*syn* and *anti* refer to the relationship of R′ and NAr across Mo=C).[42,43] Bis(carboxylate) derivatives, e.g., Mo($CHC_6H_4{}^t$Bu-2)(N^{t}Bu)$(O_2CCPh_3)_2$ (**27**), exhibit distorted octahedral structures and initiate cyclopolymerization of diethyldipropargylmalonate in a living manner giving a polymer containing only six-membered rings.[44] A silsesquioxane derivative is an efficient catalyst for the metathesis of terminal and internal olefins.[45] Reaction of (**19**) (R′ = CMe_2Ph) with KTp produces TpMo(CHR′)(NAr)(OTf) (**28**),[46] that can be alkylated to produce TpMo(CHR′)(NAr)(Me) (**29**); salts of $[TpMo(CHR')(NAr)L]^+$ (**30**, L = OEt_2, NCMe, thf, PMe_3) and structurally characterized *syn*-TpMo(CHR′)(NAr)(OMe) are also accessible from (**28**).[29] The reactions of (**18**) with ^{t}BuC≡P result in the formation of orange, phosphametallacyclobutene complexes, Mo$\{(\eta^2)$=C(^{t}Bu)P(OR)CHR′$\}$(NAr)(OR) (**31**), formed via unstable (**32**).[28] Finally, reaction of Mo($CHCMe_2$Ph)(NAr)(O^{t}Bu)$_2$ with pyridine-2,6-bis(2,2-diphenylethanol) yields structurally characterized Mo($CHCMe_2$Ph)(NAr)(pdpe):[47]



(44) **(46)** (1)

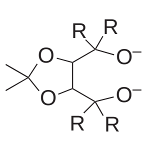


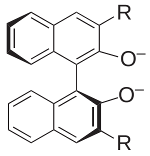
(46) **(19)** **(18)** (2)

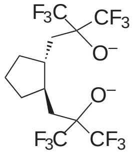


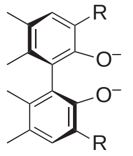
Scheme 3

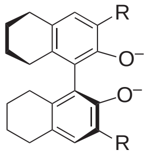
Much work has focused on the development of chiral catalysts incorporating optically pure bidentate –(OR)$_2$ ligands into (**18**) and related species. The first work in this area involved the use of chiral (+)- or (−)-R$_4$tart (**33**, R = Ph, Nap) and *rac*-bino (**34**, R = SiMe$_2$Ph) complexes in the production of all-*cis* highly tactic poly(2,3-norbornadiene).[48] Subsequently, complexes containing (*R*)- or (*S*)-bino (**34**, R = SiMe$_2$Ph, $C_6H_2{}^iPr_3$-2,4,6, Ph, Mes)[49–51] and their bisamido (bina) analogs,[52] (*R,R*)- or (*S,S*)-tbec (**35**),[53,54] (*R*)- or (*S*)-biphen (**36**, R = ^{t}Bu, Ad)[55] and related 3,3′,5,5′-tetra-*t*-butyl[49] and 6,6′-bis(silyl) and Si-linked derivatives,[56] and bitet (**37**)[57] were reported. Some of these complexes are now commerically available and many have been structurally characterized; four-coordinate species such as *syn*-Mo(CHCMe$_2$Ph)(NAr){(*S*)-^{t}Bu$_2$biphen} are tetrahedral while five-coordinate solvent adducts have trigonal bipyramidal structures. The properties of selected Mo(CHCMe$_2$Ph)(NAr)(L)(sol) complexes are summarized in Table 1. Chiral complexes have proven valuable in many applications including asymmetric ring-closing metathesis reactions (and associated kinetic resolutions) producing, e.g., dihydrofurans, small- and medium-ring carbocycles, heterocyclic ethers and siloxanes (and thence tertiary alcohols),[50,58,59] as well as tandem catalyzed asymmetric ring opening/cross metathesis reactions.[60] The vast literature relating to the catalytic properties and synthetic applications of alkylidene complexes has been reviewed by Schrock.[61,62] A unique bis(α-triphenylphosphonio)methylidene complex, Mo(N^{t}Bu)$_2$(CHPPh$_3$)$_2$, has been reported[63] and the chemistry of related species is discussed in Section 4.7.2.2.2(ii).


(**33**)


(**34**): (*S*)–form


(**35**): (*R,R*)–form


(**36**): (*S*)–form


(**37**): (*S*)–form

4.7.2.1.3 Alkyl complexes

Reaction of MoF$_6$ with the nonreducing methylating agent ZnMe$_2$ produces thermally unstable MoMe$_6$ that reacts with MeLi in diethyl ether to form red [Li(OEt$_2$)][MoMe$_7$]. In line with predictions for such σ-donor complexes, all three independent lattice molecules of MoMe$_6$ exhibit

Table 1 Properties of selected $Mo(CHCMe_2Ph)(NAr)(L)(solv)$ complexes ($Ar = C_6H_3{}^iPr_2$-2,6).

syn/anti-(L)(solv)	$\delta(={}^{13}C)^a$ (ppm)	$d(Mo{=}C)$ (Å)	$\angle(Mo{=}CC)$ (deg)	$d(Mo{=}N)$ (Å)	$\angle(Mo{=}NC)$ (deg)	*References*
syn-{*R*-$(C_6H_2{}^iPr_3)_2$bino}(py)	309.4	1.840(12)	149.5(10)	1.715(10)	158.6(8)	50
syn-(*S*-$^tBu_2$biphen)	277.1	1.885(10)	143.8(7)	1.738(6)	169.0(6)	55
anti-(*R*-Mes_2bitet)(thf)		1.882(1)	128.4(9)	1.721(9)	164.2(8)	57
syn-{*rac*-bina$(N^iPr)_2$}	268.8	1.904(3)	144.0(2)	1.747(2)	172.2(2)	52
anti-(*rac*-Mes_2bino)(thf)	315.0	1.909(7)	130.6(5)	1.734(5)	165.5(4)	51
syn-(*rac*-Me_2Sibiphen)	283.5	1.878(4)	151.1(3)	1.729(3)	172.6(3)	56
syn-{*rac*-$(Me_3Si)_2$biphen}	281.0	1.863(5)	147.0(5)	1.721(5)	171.9(4)	56
syn-(pdpe)	268.6	1.914(3)	141.0(2)	1.745(3)	172.5(2)	47
syn-Tp(OMe)	302.3	1.963(10)	136.8(10)	1.741(9)	169.7(8)	29

[a] ^{13}C signals may not arise from crystallographically characterized forms. For *syn*-$Mo(CHCMe_2Ph)(NAr)$(*rac*-Mes_2bino)(thf), $\delta = 298$. See literature for details of ^1H NMR studies of *syn* and *anti* isomers.

distorted trigonal prismatic (C_{3v}) structures. A capped octahedral geometry is adopted by the anion of $[Li(OEt_2)][MoMe_7]$.[64] Methylation of $MoOCl_4$ or $MoF_n(OMe)_{6-n}$ ($n \sim 5$) by $ZnMe_2$ yields $Mo(OMe)Me_5$ and, serendipitously, $Mo(OMe)_2Me_4$. Both complexes exhibit distorted trigonal prismatic geometries.[65] The distorted octahedral structure of $WCl(OMe)_2Me_3$ suggests a structural transition upon incorporation of three π-donor ligands into mixed σ(alkyl)/π-donor complexes.[65]

4.7.2.2 Complexes Containing Nitrogen-donor Ligands

4.7.2.2.1 Nitrido complexes

The structural, spectroscopic and bonding attributes of nitrido complexes are well established.[2,14,66] Only mono(nitrido)-Mo monomers are observed under normal circumstances but some melt products, e.g., $Ba_3[MoN_4]$ and $Sr_4[MoN_4]O$, contain tetranitrido-Mo^{VI} units. Four-, five-, and six-coordinate complexes adopt tetrahedral, square pyramidal, and octahedral geometries, respectively; the nitrido ligand occupies apical or axial positions and exerts a strong *trans* influence (>0.3 Å in some cases). Seven-coordinate species are also known. The interaction of nitrido ligands with neighboring metal centers, counterions, and lattice molecules is common.[66,67] The properties of selected nitrido compounds are presented in Table 2.

Nitrido complexes are usually prepared by metathesis of $MoNCl_3$ (itself tetrameric) or nitridochloromolybdate species; improved syntheses for $(NEt_4)_2[MoNCl_5]$ and $(NEt_4)_2[MoNCl_4]$ have been reported.[68] Chloride addition to $MoNCl_3$ occurs upon reaction with $[Cl_3PNPCl_3]Cl$, $MgCl_2$/thf and LiCl/12-crown-4, yielding $[Cl_3PNPCl_3][MoNCl_4]$, $Mg(thf)_4[MoNCl_4(thf)]_2$, and Li(12-C-4)-$[MoNCl_4]$, respectively. The first of these adopts a linear chain structure in the solid state and forms the isomeric phosphiniminate, $Mo(NPCl_2NPCl_3)Cl_5$, in solution.[69] A trimetallic unit, formed by association of $Mg(thf)_4{}^{2+}$ and *trans*-$[MoNCl_4(thf)]^-$ units, is present in the second, while the third contains square pyramidal anions weakly associated with $Li(12\text{-}C\text{-}4)^+$ units.[70] Reactions of $PPh_4[MoNCl_4]$ with tris(trimethylsilyl)benzamidine and $Me_3SiNPPh_3$ produce $PPh_4[MoNCl_3\{N(SiMe_3)_2\}]$[71] and $[Mo(NPPh_3)_4][MoNCl_3(NPPh_3)]_2$,[72] respectively; both contain square pyramidal anions. Diamagnetic Tp^*MoNCl_2 and paramagnetic $NEt_4[Tp^*MoNCl_2]$ (*g* 1.961) form in the reactions of $(NEt_4)_2[MoNCl_5]$ with KTp^* but only $Tp^*MoN(N_3)_2$ is isolated when $Na[MoN(N_3)_4]$ is reacted with $NaTp^*$. The azide complex, $Tp^*MoN(N_3)_2$, exhibits a distorted octahedral geometry with a nitrido *trans* influence of ca. 0.28 Å.[68] Reaction of $MoCl_4$-$(NCEt)_2$ with Me_3SiN_3 followed by addition of $NaTp^*$ produces mixed crystals of $Tp^*MoN(N_3)_2$ and $Tp^*MoNCl(N_3)$.[73] Pentagonal bipyramidal $MoN(N_3)_2Cl(terpy)$ has also been prepared and structurally characterized[74] and there is evidence for the formation of $NEt_4[MoNCl_3(OH)(NCMe)]$ in the reaction of $MoNCl_3$ with $NEt_4Cl{\cdot}H_2O$ in NCMe.[75]

Colorless $MoN(NPPh_3)_3$ is produced in the reactions of $[LiNPPh_3]_6$ with $[MoCl_3(N_3S_2)]_2$ or $MoNCl_3$ in toluene[76,77] or $MoOCl_4$ in thf;[77] the complex adopts a tetrahedral structure[76] as does the related amide, $MoN(NPh_2)_3$. An unusual mixed species, viz., $[MoN(N_3)_2(terpy)][MoN(N_3)_4]{\cdot}MoN(N_3)_3(terpy)$, was

Table 2 Properties of selected nitrido-Mo(VI) complexes.

Compound	ν(Mo≡N) (cm^{-1})	*Geometry*[a]	*d*(Mo≡N) (Å)	*d*(M—L) (Å)	*References*
$MoN(Mes)_3$	1104	T_d	1.649(4)	2.142(4), 2.100(5), 2.133(5)	100
$MoN(NPPh_3)_3$		T_d	1.666(4)	1.928(3), 1.939(3), 1.951(3)	76
$MoN(N^tBuPh)_3$		T_d	1.658(5)	1.979(2)	85
$MoN(O^tBu)_3$ (−160 °C)	1020	T_d	1.673(5)	1.888(3), *Mo···N* 2.844(5)	96
$MoN(SAd)_3$[b]		T_d	av. 1.625	2.304(7)–2.345(6)	84
$Li(12\text{-}C\text{-}4)[MoNCl_4]\cdot CH_2Cl_2$	1047	SP	1.628(6)	2.348(2), 2.331(2), 2.332(2), 2.357(2)	70
$[Mo(NPPh_3)_4][MoNCl_3(NPPh_3)]_2\cdot C_7H_8$[b]	1030	SP	av. 1.644	av. *N* 1.847, *Cl* 2.381(5)–2.461(4)	72
$[MoN(N_3)_2(terpy)][MoN(N_3)_4]\cdot[MoN(N_3)_3(terpy)]$ (AB·C)		A – PP	1.637(7)	$N_{av.}$ 2.238, N_3 2.106	78
		B – SP	1.649(7)	$N_{3\ av.}$ 2.077	
		C – PBP	1.656(1)	$N_{av.}$ 2.257, N_3 2.075(4), 2.120(3), 2.457(4)	
$MoN(OSiMe_3)_3(py)$[b]	1059	SP	av. 1.627	av. *O* 1.909, N_{py} 2.287	97
$MoN(OSiMe_3)_2\{N(SiMe_3)_2\}(py)$		SP	1.640(3)	$O_{av.}$ 1.922, *N* 1.973(3), N_{py} 2.334(3)	98
$PPh_4[MoNCl_3\{N(SiMe_3)_2\}]$	1059	SP	1.648(3)	*Cl* 2.425(1), $Cl_{t\ to\ N}$ 2.454(1), *N* 1.937(3)	71
$NEt_4[MoNCl_3(OH)(NCMe)]$	1055	O_h	1.680(3)	N_{trans} 2.420(4), $2Cl_{av.}$ 2.389, $Cl_{t\ to\ O}$ 2.4608(12), *O* 1.963(3)	75
$MoN(C_6H_4CH_2NMe_2\text{-}C,N)_2(O^tBu)$		O_h	1.663(2)	N_{trans} 2.742(2), *O* 1.886(2), $C_{av.}$ 2.182, *N* 2.434(2)	100
$Tp^*MoN(N_3)_2$	1023	O_h	1.646(4)	N_{trans} 2.449(3), $N_{av.}$ 2.168, $N_{3\ av.}$ 2.016	68
$MoN(N_3)_2Cl(terpy)$	1005	PBP	1.662(7)	$N_{av.}$ 2.258, $N_{3\ av.}$ 2.095, Cl_{trans} 2.719(2)	74

[a] Idealized geometry indicated: T_d = tetrahedral, SP = square pyramidal, PP = pentagonal pyramidal, PBP = pentagonal bipyramidal, O_h = octahedral. [b] Average of values for two independent molecules.

isolated from the reaction of $Mo(CO)_3(terpy)$ and Me_3SiN_3 and structurally characterized.[78] The "thermodynamic sink" in the $Mo(NRAr)_3/[N]$ system (Scheme 1) is four-coordinate $MoN(NRAr)_3$ (**38**);[79] the sources of the nitrido ligand include N_2O, aryl azides,[80,81] other metal–nitrido complexes (usually via isolable μ-nitrido complexes),[82–84] and N_2 itself (*vide infra*). The reaction of $Mo(NRAr)_3$ and N_2O (XY) produces equimolar amounts of (**38**) and $Mo(NRAr)_3(NO)$, the selective cleavage of the N—NO bond being under kinetic control.[81] Diamagnetic (**38**) ($\nu(Mo{\equiv}N)$ 1,042 cm^{-1}), $MoN(N^tBuAr)_3$,[85] $MoN\{N(2\text{-}Ad)Ar\}_3$,[81] and $MoN\{NR(C_6H_4F\text{-}4)\}_3$[83] have been thoroughly characterized. The X-ray structure of $MoN(N^tBuPh)_3$ revealed a tetrahedral geometry with a terminal nitrido ligand nestled in a pocket of *t*-butyl groups.[85] The reaction of (**1**) with N_2 proceeds through a μ-dinitrogen complex (**39**), shown by elegant EXAFS and Raman experiments to contain a linear Mo—N—N—Mo bridging unit.[85] Further, the cleavage of N_2 by $Mo(NRAr)_3$ is catalyzed by Na/Hg and the anionic dinitrogen complexes involved, e.g., $[Na(thf)_x][Mo(N_2)(NRAr)_3]$ (**40**), have been isolated, characterized and derivatized.[86] Reaction of $Mo(N^iPrAr)_3$ with N_2 results in the formation of $[Mo(N^iPrAr)_3]_2(\mu\text{-}N)$[87] that is reduced in situ by Na/Hg to $[Na(thf)_x][\{Mo(N^iPrAr)_3\}_2(\mu\text{-}N)]$.[88] The anion reacts with N_2 producing $[Na(thf)_x][Mo(N_2)\{N^iPrAr\}_3]$ and $MoN\{N^iPrAr\}_3$.[88] Theoretical studies of N_2O and N_2 cleavage by $Mo(NRAr)_3$ have been reported.[89,90] In related triamidoamine systems (Scheme 2),[91] $MoN(N_3N)$ (**41**, $\nu(Mo{\equiv}N)$ 1,001 cm^{-1}) and $MoN\{N(CH_2CH_2NAr)_3\}$ (Ar = aryl) can be generated by reacting $MoCl(N_3N)$ with Me_3SiN_3[92] or $MoCl\{N(CH_2CH_2NAr)_3\}$ with NaN_3,[19,93] respectively. Parent $MoN\{N(CH_2CH_2NMe)_3\}$ ($\nu(Mo{\equiv}N)$ 991 cm^{-1}) has been prepared by transmetallation between $Sn(Bu)\{N(CH_2CH_2NMe)_3\}$ and $MoN(O^tBu)_3$.[94] Reduction of (**13**) under N_2 followed by reaction of the product (**42**) with $PdCl_2(PPh_3)_2$ leads to stable $Mo(N_2)(N_3N)$ (**43**) without N_2 cleavage.[95] Related reactions occur in the tris(arylamido)amine systems.[93]

Reaction of $MoNCl_3$ with LiO^tBu yields colorless $MoN(O^tBu)_3$ that is amenable to ligand exchange giving $MoN(OR)_3$ (R = Et, ^{i}Pr, $CH_2{}^tBu$). The compounds are monomeric in solution but form linear polymers in the solid state.[96] Reaction of $MoO_2Cl_2(dme)$ with $HN(SiMe_3)_2$ in dme produces an oil that can be induced to form crystals of $MoN(OSiMe_3)_3(py)$; in this case, steric crowding in the square pyramidal complex prevents association.[97] Related complexes, e.g., $MoN(OSiMe_3)_2\{N(SiMe_3)_2\}(py)$, were isolated during the exploration of sol–gel syntheses for molybdenum nitride.[98] Orange $PPh_4[MoN(OPh)_4]$ ($\nu(Mo{\equiv}N)$ 1,033 cm^{-1}) is produced in the reaction of $PPh_4[MoNCl_4]$ with NaOPh.[99] Reaction of $MoN(O^tBu)_3$ with MesMgBr in diethyl ether at −78 °C produces $MoN(Mes)_3$, while pseudo-octahedral $MoN(C_6H_4CH_2NMe_2\text{-}C,N)_2(O^tBu)$ results from incomplete metathesis with $Li[C_6H_4CH_2NMe_2]$.[100] Related complexes, such as $MoN(CH_2{}^tBu)_3$ ($\nu(Mo{\equiv}N)$ 1,000 cm^{-1}), obtained from $MoN(O^tBu)_3$ and $^tBuCH_2MgBr$, behave as monomers in solution and react with HX to form $Mo(NH)(CH_2{}^tBu)_3X$ (Section 4.7.2.2.2(iii)).[101] Few nitrido thiolate complexes are known. The first reported, $(NEt_4)_2[MoN(bdt)_2Cl]$ ($\nu(Mo{\equiv}N)$ 1,010 cm^{-1}), resulted from the reaction of $(NEt_4)_2[MoNCl_4]$ and Li_2bdt at −70 °C (to prevent reduction).[102] The thiolate, $Ti(SAd)(O^iPr)_3$, and thiols, RSH (R = ^{i}Pr, ^{t}Bu), react with $MoN(O^tBu)_3$ to produce $MoN(SR)_3$. The Ad and ^{t}Bu derivatives exist as weakly associated pairs of "thiolate-bridged" pseudo-tetrahedral monomers in the solid state.[84,103] Sulfur lone pair combinations are identified as the frontier orbitals in such complexes.[103]

4.7.2.2.2 Imido complexes

This burgeoning field has been stimulated by the role of imido species in amm(on)oxidation reactions and the isolobal relationship of $Mo(NR)_2X_2$ to active Group 4 catalysts, Cp_2MX_2.[14,104] Synthetic strategies for imido–Mo complexes include: (i) N—H bond cleavage in amines and amides; (ii) N—Si bond cleavage in silyl-amines and -amides; (iii) imido metathesis involving [2 + 2] reactions with, e.g., isocyanates, phosphinimines, sulfinylamines, and metal–imido species; (iv) oxidations using organic azides or azo compounds; (v) electrophilic attack on nitrido ligands; and (vi) cleavage of hydrazines. The formation of very stable by-products (H_2O, Me_3SiX, $(Me_3Si)_2O$, CO_2, N_2, etc.) drives many of these reactions. Four-electron, π-donor imido ligands are isoelectronic with the ubiquitous oxo ligand and there are many parallels in their chemistries. There are differences, too, notably the large number of four-coordinate and low-valent imido complexes with no oxo–Mo counterparts. Imido ligands can be classified as bent ($\angle(Mo{=}N{-}R) < 150°$) with an sp^2 hybridized nitrogen atom or "linear" with an sp hydridized nitrogen. Only two bona fide cases of bent, nonchelating imido ligands, viz., $\mathrm{Mo(NPh)_2(S_2CNEt_2)_2}$[2,105] and $\mathrm{Mo(NAr)_2(pdpe)}$,[47] are known, although borderline cases exist (see Table 3). Bis- and mono(imido) species dominate $\mathrm{Mo^{VI}}$ imido chemistry. Bis(imido) complexes exhibit coordination numbers ranging from 4 to 6 and tetrahedral, trigonal bipyramidal, square pyramidal, and octahedral geometries. As with other π-donor ligand complexes of $\mathrm{Mo^{VI}}$, a *cis* arrangement of imido ligands allows effective π-donation from the ligands into empty metal orbitals. Further, π-donor ligands prefer to be *cis* to the imido ligands, the weakest π-donors being relegated to the sites *trans* to imido. Mono(imido) species may be 5, 6, or 7-coordinate with trigonal bipyramidal, octahedral, or pentagonal bipyramidal geometries. Steric and crystal packing interactions both impact on aryl orientation and substitutent regiospecificity in the solid state.[106] The structural and spectroscopic properties of imido complexes are well established.[14,104]

(i) Tetrakis- and tris(imido) complexes

These are limited in number. Deprotonation of $\mathrm{Mo(N^tBu)_2(NH^tBu)_2}$ with MeLi in diethyl ether produces moisture-sensitive $\mathrm{Li_2[Mo(N^tBu)_4]}$, proposed to be dimeric like its W analog; reaction with $\mathrm{AlX_3}$ (X = Me, Cl) produces $\mathrm{AlX_2^+}$-stabilized monomers, $\mathrm{Mo(\mu\text{-}N^tBu)_4(AlX_2)_2}$.[107,108] The kinetic product of the reaction of $\mathrm{Mo(NAr)_2Cl_2(thf)_2}$ with two equivalents of LiNHAr is unstable $\mathrm{[Li(thf)_4][Mo(NAr)_3Cl]}$, the thermodynamic product being $\mathrm{Mo(NAr)_2(NHAr)_2}$. Derivatives such as $\mathrm{Mo(NAr)_3(PMe_3)}$, $\mathrm{[Li(thf)_4][Mo(NAr)_3R]}$ (R = Me, $\mathrm{CH_2{}^tBu}$), and $\mathrm{NBu_4[Mo(NAr)_3Br]}$ can be prepared by reacting $\mathrm{[Li(thf)_4][Mo(NAr)_3Cl]}$ with $\mathrm{PMe_3}$, LiR, or $\mathrm{NBu_4Br}$, respectively.[109]

(ii) Bis(imido) complexes

Bis(imido) complexes, *cis*-$\mathrm{Mo(NR)_2Cl_2L_2}$ (R = alkyl, aryl) ((**44**), Equation (1)), are commonly prepared in "one-pot" reactions of molybdate, amines or anilines, $\mathrm{Me_3SiCl}$ and base ($\mathrm{NEt_3}$) in solvents like dme ($\mathrm{L_2}$), py, or thf (L).[31,109–111] The loss of thf from $\mathrm{Mo(NAr)_2Cl_2(thf)_2}$ is facile[109] and only $\mathrm{Mo(NAr)_2Cl_2(thf)}$ is isolated from the reaction of $\mathrm{MoO_2Cl_2}$ and ArNCO in thf.[112] The "one-pot" methodology can be adapted to the synthesis of chelate *ansa*-bis(imido),[113] mixed-imido and oxo-imido complexes[114,115] but is generally unsuccessful when functionalized anilines are employed (see Section 4.7.2.2.2(iii)).[115–117] Selected mixed-imido complexes, $\mathrm{Mo(NR)(NR')Cl_2(dme)}$, may be obtained by reacting $\mathrm{Mo(NR)_2Cl_2(dme)}$ or $\mathrm{Mo(NR)(O)Cl_2(dme)}$ with $\mathrm{H_2NR'}$[118,119] or by imido ligand exchange between $\mathrm{Mo(NR)_2Cl_2(dme)}$ and $\mathrm{Mo(NR')_2Cl_2(dme)}$.[33] Imido-for-oxo ligand exchange at $\mathrm{MoO_2Cl_2(dme)}$ or $\mathrm{Mo(NC_6F_5)(O)Cl_2(dme)}$ has also been demonstrated.[116] Structurally characterized *cis,trans,cis*-$\mathrm{Mo(NR)_2Cl_2L_2}$ complexes adopt distorted octahedral geometries.[33,114–116,120–122] Unusual *cis,cis,trans* structures are adopted by $\mathrm{Mo(N^tBu)_2(OTf)_2(NH_2{}^tBu)_2}$[107,108] and $\mathrm{Mo(NMes)_2Cl_2(PMe_3)_2}$.[120] The complexes $\mathrm{Mo(NR)_2Cl_2(dme)}$ (R = Ar, ^{t}Bu) and $\mathrm{Mo(NAr)_2(O^tBu)_2}$ catalyze imine metathesis reactions in benzene at ca. 80 °C.[123]

Many bis(imido) complexes may be prepared from $\mathrm{Mo(NR)_2Cl_2L}$ (L = dme, thf) by metathesis or ligand exchange. Four-coordinate, tetrahedral complexes such as $\mathrm{Mo(NR)_2(O^tBu)_2}$ (**45**, R = ^{t}Bu, Ar),[118] $\mathrm{Mo(NAr)_2Cl(NEt_2)}$, $\mathrm{Mo(NAr)_2(NHAr)_2}$,[112] and their alkyl analogs (*vide infra*) were among the first prepared; alternative routes to (**45**) include the reactions of $\mathrm{Mo_2(O^tBu)_6}$ with $\mathrm{RN_3}$[124] and $\mathrm{MoO_2Cl_2}$ with $\mathrm{{}^tBuN(SiMe_3)_2}$.[125] The production of mixed-ligand complexes by acid-catalyzed inter-metal ligand exchange was recently demonstrated.[126] Grignard reagents react with $\mathrm{Mo(NAr)_2Cl_2L}_n$ complexes to form air-sensitive $\mathrm{Mo(NAr)_2R_2}$ (**46**) (Step 2, Equation (1); R includes Me,[127,128] $\mathrm{CH_2{}^tBu}$, Mes, $\mathrm{CH_2CMe_2Ph}$[30,31,112]). The methyl derivative is stabilized by multiple α-agostic interactions but reacts with $\mathrm{PMe_3}$, $\mathrm{PMe_2Ph}$, thf, and py to form adducts of the type $\mathrm{Mo(NAr)_2Me_2L}$ (**47**)[127,128] and with $\mathrm{Me_3SnF}$ to give $\mathrm{Mo(NAr)_2F_2(thf)}$.[129] The reactions of $\mathrm{Mo(NAr)_2Cl_2(dme)}$ with $\mathrm{Li(thf)_3[E(SiMe_3)_3]}$ (E = Si, Ge) produce $\mathrm{Mo(NAr)_2Cl\{E(SiMe_3)_3\}}$, which react with AgOTf and $\mathrm{({}^tBuCH_2)MgCl}$ to give $\mathrm{Mo(NAr)_2(OTf)\{Si(SiMe_3)_3\}}$ and $\mathrm{Mo(NAr)_2(CH_2{}^tBu)\{E(SiMe_3)_3\}}$ (**48**), respectively. Reaction of $\mathrm{Mo(NAr)_2Cl\{Si(SiMe_3)_3\}}$ and CNR (R = $\mathrm{C_6H_3Me_2}$-2,6) gives the insertion product, $\mathrm{Mo(NAr)_2Cl\{\eta^2\text{-}C(NR)Si(SiMe_3)_3\}}$ (**49**). The X-ray structures of $\mathrm{Mo(NAr)_2Cl\{Si(SiMe_3)_3\}}$ and (**48**) (E = Si) revealed an α-agostic interaction in the latter.[130] Reaction of $\mathrm{Mo(NPh)_2Cl_2(dme)}$ with RMgCl produces four-coordinate $\mathrm{Mo(NPh)_2R_2}$ (R = $\mathrm{CH_2{}^tBu}$, $\mathrm{CH_2SiMe_3}$)[131] and related mixed imido complexes are known.[33,34] The 2,4,6-tris(trifluoromethyl)phenyl ($\mathrm{Mes^F}$) complex, $\mathrm{Mo(N^tBu)_2(Mes^F)_2}$ (**50**), produced in

Table 3 Structural data for selected bis(imido)–Mo^{VI} complexes containing NAr ($Ar = C_6H_3{}^iPr_2$-2,6).[a]

Compound	*Geometry*[b]	*d*(Mo=N) (Å)	∠(Mo=NC) (deg)	∠(N=Mo=N) (deg)	*d*(M—L_{trans}) (Å)	*d*(M—L) (Å)	*References*
$[Mo](NHAr)_2$	T_d	1.764(2)	155.7(3)	114.4(1)		*N* 1.987(2)	112
		1.753(2)	172.3(3)			*N* 1.975(2)	
$[Mo]Me_2$	T_d	1.749(4)	159.6(3)	112.6(2)		*C* 2.109(5)	128
$[Mo](\mu\text{-}C_6H_4CH_2NMe_2)_2Li$[c]	T_d	1.770(3)	162.3(4)	121.6(2)		*C* 2.159(5)	137
$[Mo]Cl\{Si(SiMe_3)_3\}$	T_d	1.753(4)	151.3(4)	109.3(2)		*Cl* 2.3093(14)	130
		1.748(4)	155.5(4)			*Si* 2.562(2)	
$[Mo](CH_2{}^tBu)\{Si(SiMe_3)_3\}$	T_d	1.752(2)	157.4(2)	112.68(11)		*C* 2.083(3)	130
		1.754(2)	161.6(2)			*Si* 2.6048(9)	
$[Mo]Cl\{C(CO_2Et)NMe_2\text{-}C,N\}$	$[T_d]$	1.746(4)		113.2(2)	*C* 2.149(6)[d]	*Cl* 2.336(1)	144
		1.753(4)	171.1(4)		*N* 2.198(4)[d]		
$[Mo]Cl\{CMe_2C(=O)O^tBu\text{-}C,O\}$	$[T_d]$	1.754(9)	157.6(8)	105.4(4)	*C* 2.208(11)[d]	*Cl* 2.362(3)	144
		1.730(9)	158.5(8)		*O* 2.370(6)[d]		
[Mo](pdpe)	TBP	e 1.771(4)	144.8(5)	105.0(3)		*O* 1.940(2)	47
		a 1.760(4)	164.7(4)		*N* 2.390(4)		
$[Mo]Cl(NC_4H_3CH_2NMe_2)$	TBP	e 1.766(2)	147.55(14)	108.36(8)		*Cl* 2.3911(6)	140
		a 1.762(2)	175.13(14)		*N* 2.360(2)		
$[Mo]Me(NC_4H_3CH_2NMe_2)$	TBP	e 1.759(4)	148.6(4)	109.3(2)		*C* 2.219(6)	140
		a 1.745(4)	177.4(4)		*N* 2.376(5)		
$[Mo]Cl\{NC_4H_2(CH_2NMe_2)_2\}$	TBP	e 1.757(2)	158.03(13)	110.39(7)		*Cl* 2.3834(5)	140
		a 1.762(2)	173.13(13)		*N* 2.362(2)		
$[Mo]Cl_2\{NH=C(C_6H_5)CH(SiMe_3)_2\}$	TBP	e 1.749(2)	151.1(2)	108.07(8)	*Cl* 2.3940(10)	*Cl* 2.4415(10)	141
		a 1.752(2)	176.6(2)		*N* 2.255(2)		
$[Mo]Me_2(PPhMe_2)$	TBP	e 1.759(3)	151.9(2)	111.61(13)		*C* 2.299(3)	128
		a 1.759(3)	175.9(3)		*P* 2.6793(10)	*C* 2.205(4)	
$[Mo](OCMe_2\text{-}2\text{-}py)(CH_2SiMe_3)$	TBP	e 1.7686(18)	152.52(15)	106.84(8)		*C* 2.156(2)	136
	(44.7%)	a 1.7529(19)	172.95(18)		*N* 2.346(2)	*O* 1.9504(19)	
$[Mo]Me(p\text{-}tol)(\mu\text{-}C_6H_4CH_2NMe_2)$-Li(dme)	TBP/SP	e 1.770(4)	156.7(4)	116.55(19)	C_{Ph} 2.239(4)[d]	CH_3 2.195(6)	137
	(54.9%)	e 1.772(4)	174.1(3)			C_{tol} 2.216(4)	

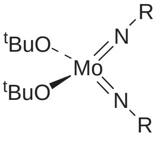
Table 3 continued

Compound	*Geometry*[b]	*d*(Mo═N) (Å)	∠(Mo═NC) (deg)	∠(N═Mo═N)(deg)	*d*(M—L$_{trans}$) (Å)	*d*(M—L) (Å)	*References*
[Mo]Me($C_6H_4CH_2NMe_2$-*C,N*)	SP	a 1.773(2)	150.37(16)	111.56(10)		*C*H$_3$ 2.177(2)	137
	(73.1%)	b 1.7495(13)	176.58(17)		*N* 2.383(2)	*C* 2.176(2)	
[Mo]Me{$C_6H_3(CH_2NMe_2)_2$}	SP	a 1.758(2)	151.4(2)	110.78(12)		*C* 2.205(3)	138
	(73.5%)	b 1.749(3)	174.5(2)		*N* 2.376(4)	*C*H$_3$ 2.194(3)	
[Mo]Cl{$C_6H_3(CH_2NMe_2)_2$}	SP	a 1.759(3)	150.2(3)	154.16(15)		*C* 2.184(5)	138
	(81.3%)	b 1.744(4)	172.0(3)		*N* 2.335(4)	*Cl* 2.413(2)	
[Mo]Me{$^iPr_2NC(NCy)_2$}	SP	a 1.756(3)	155.6(2)	109.56(13)		*N* 2.128(2)	141
		b 1.757(2)	175.5(3)		*N* 2.211(2)	*C* 2.172(3)	
[Mo]{PhNC(O^{t}Bu)O-*N,O*}$_2$	[O$_h$]	1.759(2)	159.1(2)	104.01(9)	*O* 2.304(2)	*N* 2.108(2)	142
		1.754(2)	171.9(2)		*O* 2.381(2)	*N* 2.103(2)	
[Mo]Cl$_2${$C_6H_3(CH_2NMe_2)_2H$}	O$_h$	1.768(6)	163.9(5)	101.8(3)	*Cl*···*H* 2.721(2)	*Cl* 2.4350(17)	138
		1.771(5)	168.9(6)		*N* 2.430(5)	*C* 2.198(7)	
[Mo]Cl($^iPr_2$-tcn)[c]	O$_h$	1.779(4)	154.6(3)	102.46(17)	*N*Pr 2.635(2)	*Cl* 2.4223(11)	147
		1.767(4)	161.5(3)		*N*Pr 2.530(4)	*N*$^-$ 2.003(4)	
[Mo]Cl$_2$(py)$_2$	O$_h$	1.773(10)	157.2(7)	102.1(4)	*N* 2.422(6)	*Cl* 2.395(3)	122
		1.758(9)	166.1(7)		*N* 2.396(5)	*Cl* 2.397(3)	

---

[a] Arranged in order of increasing coordination number, [Mo] = Mo(NAr)$_2$. The values of *d*(Mo═N), ∠(Mo═NC), and *d*(Mo—L$_{trans}$) for each imido ligand (identified as follows: a = axial/apical, b = basal, e = equatorial) are collected in individual rows, e.g., for the axial imido ligand of trigonal bipyramidal Mo(NAr)$_2$Me$_2$(PPhMe$_2$), d(Mo═N) 1.759(3) Å, ∠(Mo═NC) 175.9(3)° and *trans* d(Mo–P) 2.6793(10) Å. Other M—L values are in no particular order. [b] Idealized geometry indicated: T$_d$ = tetrahedral, [T$_d$] = pseudo-tetrahedral, SP = square pyramidal, TBP = trigonal bipyramidal, O$_h$ = octahedral, [O$_h$] = pseudo-octahedral. The percentages quoted refer to the distortion along the Berry pseudo-rotation coordinate from TBP (0%) to SP (100%). [c] Data for one of two independent molecules only. [d] These ligands not strictly *trans* to imido.

the reaction of $Mo(N^tBu)_2Cl_2(dme)$ with $LiMes^F$, is stabilized by close $Mo\cdots F$ interactions at ca. 2.47 Å.[132] Four-coordinate imido thiolates, $Mo(NR)_2(SAr)_2$ (R = Mes, Ar), have been briefly reported.[133] The α-triphenylphosphoniomethylidene complex, $Mo(N^tBu)_2(CHPPh_3)Cl$,[63] reacts with $Ph_2C{=}C{=}O$ giving $Mo(N^tBu)_2Cl\{OC({=}CHPPh_3)CPh_2\text{-}C,O\}$[134] and with axially pro-stereogenic biaryl lactones giving ring-expanded biaryloxo species.[135]



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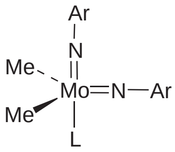

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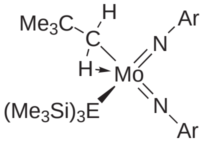
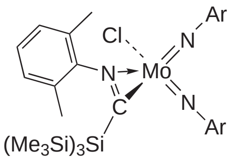


(48): E = Si, Ge



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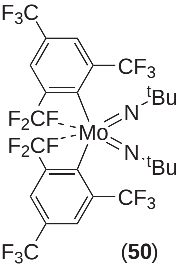
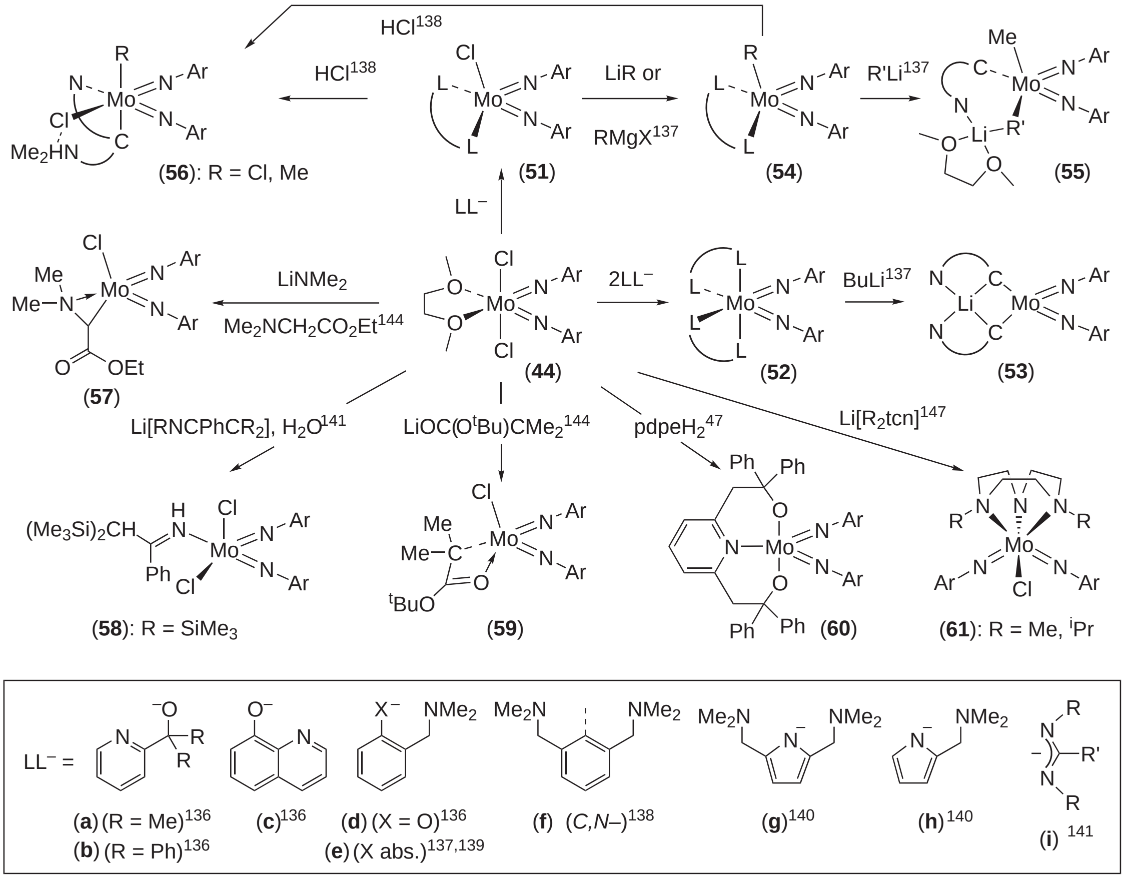


(50)

The scope of $[Mo(NAr)_2]^{2+}$ chemistry is summarized in Scheme 4; selected structural data are presented in Table 3. Five-coordinate $Mo(NAr)_2Cl(L\text{-}L)$ (**51**) are generated in the reactions of (**44**) with *one* equivalent of the bidentate ligands **a**–**h** (excluding **d**) and amidinates and guanidinates **i** (R = Cy, R′ = Me, N^iPr_2, $N(SiMe_3)_2$, etc.), whereas six-coordinate $Mo(NAr)_2(L\text{-}L)_2$ (**52**) are produced with *two* equivalents of **a**–**e**.[136–141] A bis(carbamate) complex, $Mo(NAr)_2\{PhNC(O^tBu)O\text{-}N,O\}_2$, is also known.[142] These complexes react with Grignard or organolithium reagents to produce 4- (**53**) or 5-coordinate (**54**, **55**) alkyl or aryl complexes, or 6-coordinate H-bond-stabilized species (**56**) when L–L is **f**-*C,N*.[137,138] Direct protonation of the uncoordinated amine in $Mo(NAr)_2R(\mathbf{f}\text{-}C,N)$(R = Cl, Me) also produces (**56**).[138] A related 8-hydroxyquinolinate (**c**) complex, $Mo(N^tBu)_2(Mes)(quin)$, is known.[143] Ligand exchange reactions at

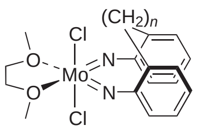


Scheme 4

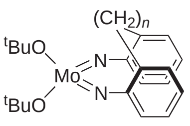
$Mo(NAr)_2Cl_2(dme)$ produce a variety of products (**57**)–(**61**) ((**60**), via $Mo(NAr)_2(O^tBu)_2$);[141,144] the carbophilic character of $[Mo(NAr)_2]^{2+}$ is indicated by the formation of (**57**) and (**59**).[144] Comparison of the structures of (**60**) and the alkylidene imido complex, $Mo(CHCMe_2Ph)(NAr)(pdpe)$, supports the presence of a bent sp^2-hybridized imido ligand in (**60**).[47] Bis(acetylacetonate) complexes include $Mo(NMes)_2(acac)_2$, formed in the reaction of $Mo(NMes)_2Cl_2(dme)$ with Tl(acac).[145] Trispyrazolylborate complexes such as $Tp^*Mo(N^tBu)_2Cl$ and $[Tp^*Mo(N^tBu)(NH^tBu)Cl]BF_4$ are known and the structure of $Tp^*Mo(N^tBu)_2Cl$ has been determined.[146] Triazacyclononane derivatives include (**61**) ($R = Me$, ^iPr)[147] and salts of $[Mo(N^tBu)_2ClL]^+$ ($L = tcn$, Me_3tcn).[148] Imido complexes bearing $CpCo\{P(OEt)_2O\}_3^-$ [145] and $PhSN^tBu$-*N,S*$^-$ co-ligands are among the others reported.[149]

Bis(imido) dithiocarbamate species of the type $Mo(NR)_2(S_2CNEt_2)_2$ ($R =$ aryl, ^tBu, Ad, C_6F_5, $SO_2C_6H_4Me$) are prepared by: (i) reaction of $MoO_2(S_2CNEt_2)_2$ with RNCO, (ii) reaction of $Mo(NR)_2Cl_2(dme)$ with dithiocarbamates,[105] or (iii) nitrene transfer from organic azides and other reagents to $Mo(CO)_2(S_2CNEt_2)_2$ (for $R = SO_2C_6H_4Me$).[150] New X-ray structures[105,150] are concordant with previous results.[2] A ^{13}C NMR method for assessing the difference in the bond angles of imido ligands at $[Mo(NR)_2]^{2+}$ centers has been developed.[105] Complexes of this type participate in catalytic imido transfer reactions.[150]

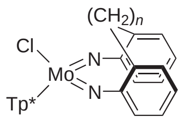
The efficacy of *ansa* metallocenes as polymerization catalysts has stimulated research into chelating bis(arylimido) complexes, including those with chiral ligands. The first of these, (**62**), and derivatives (**63**) and (**64**) ($n = 1$, 2) were reported by Gibson et al. in 1996.[121] The complexes display distorted octahedral structures with $d(Mo{=}N)$, $\angle(Mo{=}N{-}C)$ and $\angle(N{=}Mo{=}N)$ in the ranges 1.725–1.754 Å, 155–162° and 100–103°, respectively. Complexes featuring strained, seven-membered, unsymmetrical *ansa* bis(imido ligands), e.g., (**65**), have also been reported.[113] The first chiral bis(imido)-Mo^{VI} complex, C_2-symmetric (**66**), catalyzes the kinetic resolution of styrene oxide and enantioselective trimethylsilylcyanation of benzaldehyde with 30% and 20% e.e., respectively.[151]



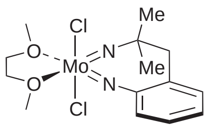
(**62**)



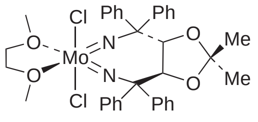
(**63**)



(**64**)



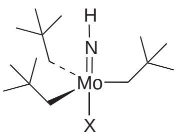
(**65**)



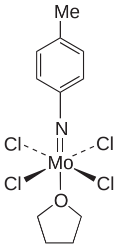
(**66**)

(iii) Mono(imido) complexes

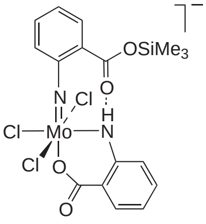
Mono(imido) complexes featuring alkylidene co-ligands were discussed in Section 4.7.2.1.2. Our treatment of other mono(imido) compounds begins with *trans*-$Mo(NH)X(CH_2{}^tBu)_3$ (**67**, $X = F$, Cl, Br, I, OTf, OPh, $OSiR_3$), formed in the reactions of $MoN(CH_2{}^tBu)_3$ with HX. Trigonal bipyramidal $Mo(NH)Br(CH_2{}^tBu)_3$ ($d(Mo{=}N)$ 1.692(3) Å, $\angle(Mo{=}N{-}H)$ 179.5(26)°) associates via NH···Br interactions in the solid state and affords olefin metathesis and ROMP catalysts when supported on silica.[101,152] Related complexes, including $Mo(N^tBu)X(CH_2{}^tBu)_3$ ($X = Cl$, OC_6F_5), $Mo(N^tBu)(OCH_2{}^tBu)_2(CH_2{}^tBu)_2$, and $Mo(N^tBu)(OSiMe_3)(Mes)_3$, are formed by alkylation of imido starting materials.[153,154] Yellow $Mo(N^tBu)(OSiMe_3)(Mes)_3$ displays a perfect trigonal bipyramidal structure, with $d(Mo{=}N)$ 1.786(10) Å, $d(Mo{-}O)$ 1.904(10) Å and $d(Mo{-}C)$ 2.138(8) Å, and reacts with Me_3SiBr to give the bromo analog.[154] With respect to other halo complexes, reaction of $MoCl_4(thf)_2$ with *p*-tolylazide in 1,2-dichloroethane at 40 °C yields (**68**), possessing an octahedral structure with $d(Mo{=}N)$ 1.717(3) Å.[155,156]



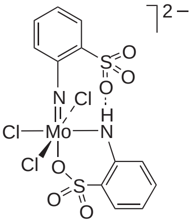
(**67**)



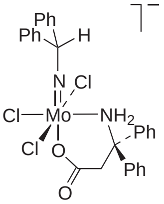
(**68**)



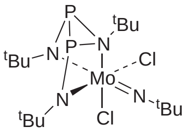
(**69**)



(**70**)

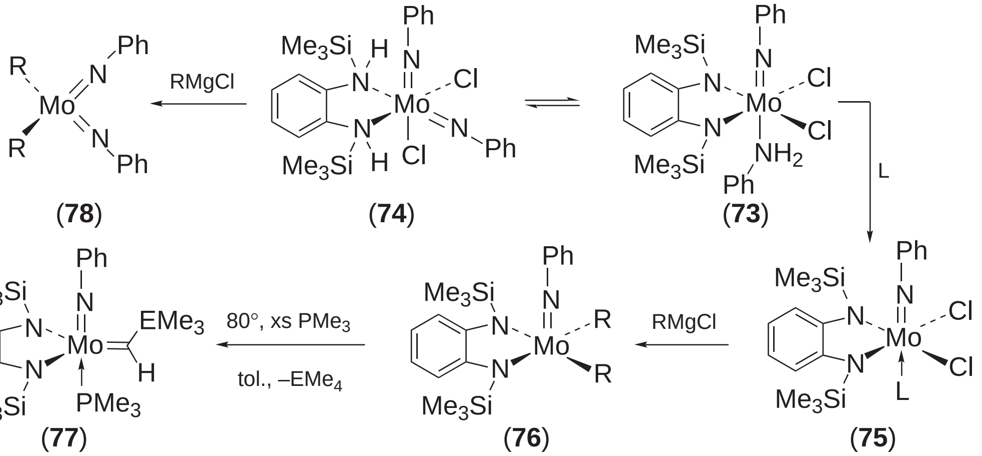


(**71**)



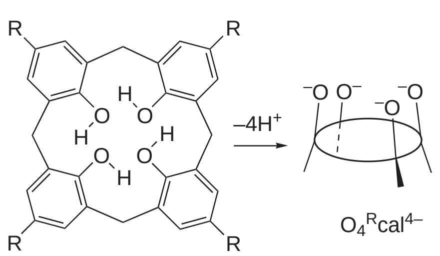
(**72**)

Salts containing anionic, monoimido complexes bearing bidentate amido/amino-carboxylate/sulfonate co-ligands, e.g., (**69**)–(**71**), are produced when the "bis(imido)" synthesis in step 1 of Equation (1) is performed with functionalized anilines.[115] An unusual N_3-donor co-ligand is found in (**72**), produced in the reaction of $Li_2[Mo(N^tBu)_4]$ with PCl_3.[157] Phenylimido complexes of the diamide ligand, *o*-$(Me_3SiN)_2C_6H_4^{2-}$, have been reported by Boncella and co-workers (Scheme 5). Reaction of $Mo(NPh)_2Cl_2(dme)$ with the ligand free acid produces (**73**), which participates in an equilibrium with (**74**) and undergoes aniline displacement giving (**75**) (L = PMe_3 and thf). Purple (**75**) (L = thf) reacts with Grignard reagents to produce dialkyl complexes, (**76**) (R = Me, Ph, Bz, $CH_2{}^tBu$, CH_2SiMe_3), several of which convert to imido–alkylidene species (**77**) (E = C, Si).[131] A metallacyclopentane derivative, (**76**) ($R_2 = (CH_2)_4$), is conveniently prepared by reacting (**75**) with either $BrMg(CH_2)_4MgBr$ *or* EtMgCl and ethene while square pyramidal, oxometallacyclic (**76**) ($R_2 = OCMe_2CH_2CHPh$) forms in the reaction of $Mo(NPh)\{(Me_3SiN)_2C_6H_4\}(\eta^2\text{-}PhCH{=}CH_2)$ with acetone.[158] Complex (**74**) affords a route into complexes (**78**) ($R = CH_2EMe_3$ (E = C, Si), cf. (**46**)) upon alkylation. Related chemistry is described in Section 4.7.4.2.2(ii). Imido—Mo^{VI} (**79**) and -Mo^V (**80**) triamidoamine complexes are available from (**41**) (Scheme 2).[92]

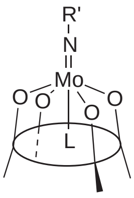


Scheme 5

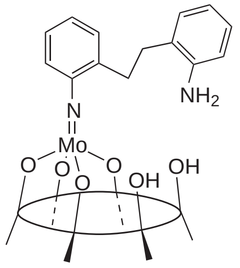
The calixarenes known to form mononuclear Mo complexes are limited to calix[4]arenes, $(HO)_4{}^Rcal$ (**81**), 1,3-dialkylcalix[4]arenes, $(HO)_2(RO)_2{}^{Bu}cal$, and the larger unsubstituted calix[6]-arene. Calix[4]arenes usually act as tetraanionic, quasi-planar O_4-donor ligands, the phenol groups commonly adopting the so-called "cone conformation". The denticity, charge, and conformation of the ligands can be tuned by selective *O*-alkylation. The complexes, $Mo(NAr)_2(O^tBu)_2$, $Mo(N^tBu)_2(NH^tBu)_2$, $Mo(NMes)_2Cl_2(dme)$, and (**63**) ($n = 2$), react (variously) with $(HO)_4{}^Rcal$ giving $Mo(NR')(O_4{}^Rcal)L$ (**82**; R = H, R′ = Ar or 2-$NC_6H_4CH_2CH_2C_6H_4NH_2$-2, L = NCMe;[159,160] R = ^tBu, R′ = Ar, ^tBu or Mes, L = NCMe, CN^tBu or OH_2).[161] These exhibit octahedral structures, the coordination spheres being defined by equatorial phenoxide groups and axial imido and *endo* solvent ligands. Reaction of (**63**) ($n = 2$) with calix[6]arene in toluene produces (**83**), that converts into an 11-membered, amidine(imido) chelate complex (**84**) upon workup in NCMe.[162]



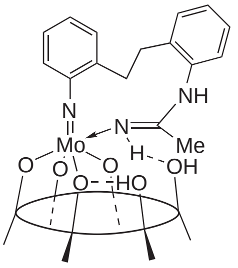
(**81**): $(HO)_4{}^Rcal$, R = H, ^tBu



(**82**)



(**83**)



(**84**)

Extending previous work,[2] imido-Mo^{VI} complexes, $Mo(NR)Cl_2(S_2CNEt_2)_2$ (R = Ph, $C_6H_4NH_2$-2, etc.), have been prepared by reacting substituted anilines with $MoOCl_2(S_2CNEt_2)_2$.[163,164] The X-ray structure of $Mo(NC_6H_4NH_2\text{-}2)Cl_2(S_2CNEt_2)_2$ confirmed the expected pentagonal bipyramidal geometry (*d*(Mo=N) 1.700(16) Å, ∠(Mo=N—C) 178.0(11)°).[163] Analogous reactions with 2-aminothiophenol are condition dependent, producing pentagonal bipyramidal $Mo(NC_6H_4S)Cl(S_2CNEt_2)_2$, with axial bent imido (*d*(Mo=N) 1.744(6) Å, ∠(Mo=N—C) 137.7(7)°) and equatorial thiolate donors,[165] or unstable $Mo(NC_6H_4S)(OMe)(S_2CNEt_2)_2$. Related reactions with alkyl substituted anilines ($ArNH_2$) yield $Mo(NAr)Cl_2(S_2CNEt_2)_2$, $[Mo(NAr)(S_2CNEt_2)_3]_2[Mo_6O_{19}]$, or $[Mo(NAr)(S_2CNEt_2)_3]_4[Mo_8O_{26}]$, depending on conditions and substitution patterns; the mononuclear complexes exhibit pentagonal bipyramidal structures.[166] Seven-coordinate $Mo(NR)(S_2)(S_2CNR'_2)_2$ (R = aryl (many), ^{t}Bu, Ph, Ad; R′ = Me, Et) result from the reactions of $MoO_2(S_2CNR'_2)_2$ with RNCO[167] or $Mo(NR)_2(S_2CNEt_2)_2$ with H_2S or Lawesson's reagent.[168] Pentagonal bipyramidal structures with axial imido (*d*(Mo=N) 1.713(2)–1.759(4) Å, ∠(Mo=N—C) 164.9(8)–179.1(3)°) and equatorial, side-on bonded disulfido ligands pertain.[167,168] Closely related oxo complexes are well known.[2]

Finally, reactions of F_2 with $Mo(NSCl)Cl_4$, $[Mo(N_3S_2)Cl_3]_2$, or $MoNCl_3$ produce the *N*-chloroimido complex, $Mo(NCl)F_4$ (ν(Mo≡N) 1,121 cm^{-1}), that converts to $Mo(NCl)F_4$(sol) (sol = NCMe,[169] thf[170]) upon dissolution; $Mo(NCl)F_4(NCMe)$ exhibits an octahedral structure with *d*(Mo=N)$_{av.}$ 1.720 Å, ∠(Mo=N—Cl)$_{av.}$ 176.6°.[169] An octahedral anion is also observed for the ionic derivative $[Na(15\text{-}C\text{-}5)][Mo(NCl)F_5]$ (*d*(Mo=N) 1.729(3) Å, ∠(Mo=N–Cl) 175.8(2)°).[170] Reaction of $MoCl_5$ or $MoCl_4$ with $(NSCl)_3$ in CH_2Cl_2 produces low yields of black $[N(SCl)_2][Mo(NSCl)Cl_5]$ and $Mo(N_3S_2)Cl_3$. The anionic chlorothioimido complex has an octahedral geometry with *d*(Mo=N) 1.75(1) Å and ∠(Mo=N=S) 171.2(9)°.[171]

(iv) Imido oxo complexes

Imido oxo complexes are relatively rare compared to bis(imido) or dioxo species. Compounds in this class are yellow–orange in color, exhibit ν(Mo=O) at 890 cm^{-1} and adopt distorted octahedral structures with *cis* imido and oxo ligands and *d*(Mo=O)$_{av}$ 1.70 Å, *d*(Mo=N)$_{av}$ 1.77 Å, ∠(O=Mo=N)$_{av}$ 104.3°, and ∠(Mo=N—X) > 153.5° (most > 168°). Complexes of the type *cis,-trans*-$Mo(NR)OCl_2L_2$ can be accessed through: (i) "incomplete" reaction of some amines and anilines with molybdate, Me_3SiCl, and NEt_3 in dme or py (L_2 = dme, R = $C_6H_2Ph_3$-2,4,6,[117] C_6F_5[116] (both structurally characterized), Ad;[114] L = py, R = $CMe(CF_3)_2$[119]), (ii) reaction of $MoO_2Cl_2(NCMe)_2$ with one equivalent of RNCO followed by derivatization,[153] or (iii) oxo/imido ligand metathesis of $Mo(NMes)_2Cl_2(dme)$ and $MoO_2Cl_2(dme)$.[145] Derivatives of $Mo(NMes)OCl_2(dme)$ include $Mo(NMes)OClL$ (L = Tp*, Cp), $Mo(NMes)OCl_2(bpy)$, $Mo(NMes)O(acac)_2$,[145] and $Mo(NMes)O(S_2CNR_2)_2$ (R_2 = C_4H_4, C_5H_{10}, $^iPr_2$).[172] Other dithiocarbamate derivatives, $Mo(NXC_6H_4Me\text{-}4)O(S_2CNEt_2)_2$ (X = absent, SO_2), can be prepared by autoxidation of $Mo(NXC_6H_4Me\text{-}4)_2(S_2CNEt_2)_2$ or nitrene transfer from RN_3 and other reagents to $MoO(S_2CNEt_2)_2$.[150,173] These complexes participate in oxygen or nitrene transfer reactions and catalysis with tertiary phosphines, nitrene transfer being favored with more basic substrates.[150,173,174] The complex, $Mo(NSO_2C_6H_4Me\text{-}4)O(S_2CNEt_2)_2$, is isostructural with its dioxo and bis(imido) analogs.[150] Other trispyrazolylborate complexes, $TpMo(NAr)O(CH_2CMe_2Ph)$ and Tp*Mo(NR)OCl (R = C_6H_4X-4 (X = Me, NH_2, NMe_2), Fc derivatives), have been prepared by hydrolysis of (**28**) (Scheme 3)[46] or reaction of primary amines with Tp*$MoOCl_2$ in the presence of NEt_3 and air,[175] respectively. The X-ray structure of octahedral $TpMo(NAr)O(CH_2CMe_2Ph)$ has been determined.[46] Reaction of MoO_2Cl_2 with two equivalents of $NH^tBu(SiMe_3)$ in refluxing hexane produces unstable $Mo(N^tBu)O(OSiMe_3)Cl$, that is also formed in the reaction of $Mo(N^tBu)_2(OSiMe_3)_2$ with an equivalent each of H_2O and HCl.[154] Reaction of $Mo(N^tBu)_2(OSiMe_3)_2$ with 8-hydroxyquinoline forms $Mo(N^tBu)O(quin)_2$ through elimination of H_2N^tBu and $(Me_3Si)_2O$.[143]

4.7.2.2.3 Amido and phosphiniminato complexes

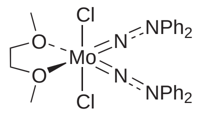
Reaction of $Mo(NMe_2)_4$ with four equivalents of dry O_2 produces a rare homoleptic amido complex, blue $Mo(NMe_2)_6$, and an oxide by-product. The octahedral complex has been characterized by ^1H (δ 3.22) and ^{13}C (δ 51.8) NMR and X-ray diffraction (T_h symmetry, *d*(Mo—N) 2.0338(14) Å).[176] Reaction of $MoNCl_3$ with Me_3SiNPR_3 (R = Me, Ph) produces

$[\mathrm{Mo(NPMe_3)_4]Cl_2}$[177] and $[\mathrm{Mo(NPPh_3)_4][MoNCl_3(NPPh_3)]_2}$,[72] respectively, while reaction of $\mathrm{MoN(NPPh_3)_3}$ with $\mathrm{BF_3{\cdot}OEt_2}$ in toluene yields $[\mathrm{Mo(NPPh_3)_4](BF_4)_2}$.[178] All three compounds have been structurally characterized and contain tetrahedral dications with $d(\mathrm{Mo{=}N})$ 1.769–1.840 Å, $d(\mathrm{N{-}P})$ 1.595–1.624 Å, and $\angle(\mathrm{Mo{=}N{-}P})$ 142.8–172.8°. Dissolution of $[\mathrm{Cl_3PNPCl_3}][\mathrm{MoNCl_4}]$ in $\mathrm{CD_2Cl_2/NCMe}$ produces isomeric $\mathrm{Mo(NPCl_2NPCl_3)Cl_5}$ according to ^{31}P NMR data.[69] Transition metal phosphiniminato complexes were reviewed by Dehnicke.[179]

4.7.2.2.4 Hydrazido and organohydrazido complexes

Hydrazido and organohydrazido ligands are intermediates in the reduction or utilization of dinitrogen in biological and chemical systems and are potential catalysts for alkene polymerization and metathesis reactions (cf., related imido species).[180] High-valent (organo)hydrazido(2-) complexes are commonly formed by the condensation of aryl/alkyl hydrazines with dioxo precursors (the stoichiometry providing access to hydrazido–oxo or bis(hydrazido) complexes) or protonation/alkylation of dinitrogen or diazenido species. The bonding and spectroscopic properties of these and allied ligands are discussed elsewhere.[14,181] Spectroscopic and structural data for representative complexes are summarized in Table 4.

Parallels between imido and hydrazido chemistries have been under examination for some years. Thus, $\mathrm{Mo(N^tBu)_2Cl_2(dme)}$ undergoes ligand exchange with $\mathrm{H_2NNPh_2{\cdot}HCl}$ in refluxing dme to produce *cis,trans*-$\mathrm{Mo(NNPh_2)_2Cl_2(dme)}$ (**85**), that exhibits an octahedral structure like its precursor. Treatment of (**85**) with Mg in the presence of $\mathrm{PMe_3}$ produces $\mathrm{Mo(NNPh_2)_2Cl_2(PMe_3)_2}$; this complex possesses an unusual *cis,cis,trans* structure with linear hydrazido(2-) ligands (cf. $\mathrm{Mo(NMes)_2Cl_2(PMe_3)_2}$ (Section 4.7.2.2.2(ii)) and $\mathrm{Mo(NNMePh)_2Cl_2(PPh_3)_2}$ (*vide infra*)). Attempts to prepare the complex using the "one-pot" synthesis in step 1 of Equation (1) yielded $\mathrm{NHEt_3[Mo(NNPh_2)(NHNPh_2)Cl_4]}$ (**86**), containing both hydrazido(2-) and H-bonded hydrazido(1-) ligands.[182] Likewise, all attempts to prepare $\mathrm{Mo(NNPh_2)_2R_2}$ (R = alkyl, aryl) have failed but species such as $\mathrm{Mo(NNPh_2)_2(OTf)_2(py)_2}$ (**87**), $[\mathrm{Mo(NNPh_2)_2(bpy)_2](PF_6)_2}$ (**88**), $\mathrm{LMo(NNPh_2)_2Cl}$ (L = Tp, Tp*), and $\mathrm{Mo(NNPh_2)(OTf)Cl(pdpe)}$ (**89**) have been prepared and structurally characterized.[183] Mono(hydrazido)-Mo$^{\mathrm{VI}}$ complexes, $\mathrm{Mo(NNRR')Cl_4}$ (cf. (**68**)), form upon reaction of $\mathrm{MoCl_5}$ with $\mathrm{H_2NNMePh}$ or $\mathrm{H_2NNPh_2{\cdot}HCl}$ in $\mathrm{CH_2Cl_2}$ at −78 °C; the complexes are sometimes formulated as $\mathrm{Mo(NNRR')Cl_3}$, their exact nature being uncertain.[184,185]



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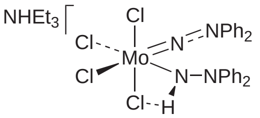

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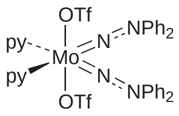

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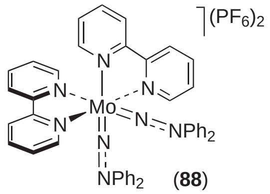

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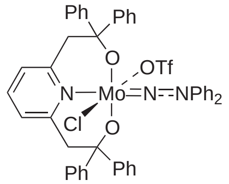

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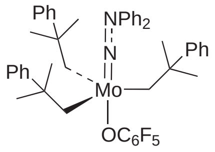

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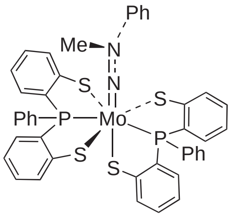

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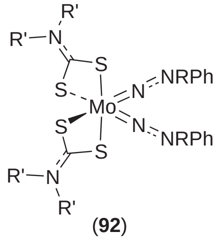

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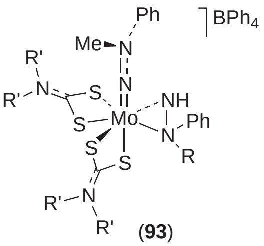

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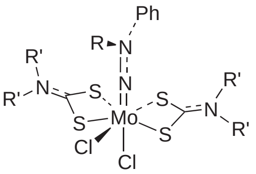

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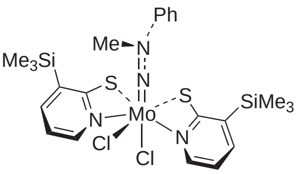

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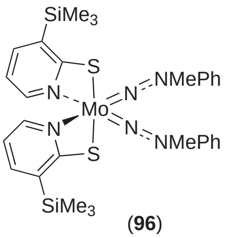


(**96**)

Table 4 Structural data for selected hydrazido–Mo^{VI} complexes.[a]

Compound	*IR*[b] (cm^{-1})	*d*(Mo=N) (Å)	*d*(N—N) (Å)	∠(Mo=N—N) (deg)	*d*(M—L_{trans}) (Å)	*d*(M—L) (Å)	*References*
$Mo(NNPh_2)(CH_2CMe_2Ph)_3(OC_6F_5)$	1588	1.746(2)	1.333(4)	174.5(2)	*O* 2.011(2)	$C_{av.}$ 2.140	180
cis-$Mo(NNMePh)(NHNMePh)Cl_2(acac)$	1590	(2-) 1.750(2)	1.301(3)	173.8(2)	*O* 2.108(2)	*Cl* 2.4102(8)	192
		(1-) 1.948(2)	1.339(3)	142.9(2)	*O* 2.103(2)	*Cl* 2.4336(8)	
cis-$NHEt_3[Mo(NNPh_2)(NHNPh_2)Cl_4]$	1585	(2-) 1.748(2)	1.304(3)	174.4(2)	2.4788(7)	2.4448(7)	182
		(1-) 1.958(2)	1.358(3)	136.0(2)	2.4641(7)	2.4213(7)	
cis,cis,trans-$Mo(NNPh_2)_2Cl_2(PMe_3)_2$	1587	1.793(3)	1.306(4)	175.2(2)	*Cl* 2.5625(11)	*P* 2.5141(12)	182
cis,trans-$Mo(NNPh_2)_2Cl_2(PPh_3)$	1595	1.76(1)	1.30(1)	172.9(9)	*Cl* 2.384(3)[c]	*Cl* 2.448(4)	193
		1.76(1)	1.33(1)	176.8(8)		*P* 2.526(4)	
cis,trans-$Mo(NNPh_2)_2Cl_2(dme)$	1586	1.771(2)	1.326(3)	154.6(2)	*O* 2.331(2)	*Cl* 2.4451(9)	182
		1.749(2)	1.324(3)	173.4(2)	*O* 2.322(2)	*Cl* 2.4380(9)	
cis,cis,trans-$Mo(NNPh_2)_2(OTf)_2(py)_2$	1588	1.768(7)	1.328(10)	164.2(6)	*O* 2.266(6)	*N* 2.212(8)	183
		1.765(8)	1.299(11)	171.7(7)	*O* 2.203(7)	*N* 2.216(8)	
cis,trans-$Mo(NNPh_2)_2Cl_2(phen)$	1589	1.773(4)	1.319(5)	170.1(2)	*N* 2.310(4)	*Cl* 2.461(1)	194
		1.779(3)	1.309(4)	171.3(4)	*N* 2.309(3)	*Cl* 2.457(1)	
cis-$Mo(NNPh_2)_2(acac)_2$	1590	1.781(3)	1.310(5)	171.3(3)	*O* 2.141(3)	*O* 2.093(3)	191
$TpMo(NNMePh)_2Cl$	1587	1.771(4)	1.308(5)	169.4(3)	*N* 2.294(4)	*N* 2.174(5)	195
						Cl 2.435(2)	
cis-$Mo(NNMePh)_2(SC_5H_3NSiMe_3)_2$	1595	1.782(4)	1.310(5)	172.3(3)	*N* 2.276(4)	*S* 2.496(1)	188
$Mo(NNMePh)Cl_2(SC_5H_3NSiMe_3)_2$	1563	1.75(1)	1.30(2)	171.3(11)	*Cl* 2.451(4)	$N_{av.}$ 2.21	188
					Cl 2.416(4)[d]	$S_{av.}$ 2.502	
cis-$Mo(NNMePh)O(acac)_2$[e]	1600	1.789(3)	1.281(4)	175.6(2)	*O* 2.145(2)	*O* 2.047(2)	201
	[915]	1.701(2)			*O* 2.207(2)	*O* 2.056(2)	
cis,trans-$Mo(NNPh_2)OCl_2(phen)$[e]	1587	1.791(4)	1.276(5)	173.1(2)	*N* 2.286(3)	*Cl* 2.425(1)	194
	[901]	1.691(2)			*N* 2.342(3)	*Cl* 2.419(1)	

[a] The values in each row pertain to a particular hydrazido or oxo ligand in the complex. Parameters for the *trans* and non-*trans* donors of bidentate co-ligands are placed in the same row. [b] Data for ν(NN) mode, except for ν(Mo=O) in brackets. [c] Value for the third donor in the trigonal plane defined by $Mo(NNPh_2)_2Cl$. [d] Value for chloride in pentagonal plane of seven-coordinate complex. [e] Values in the second row of each entry pertain to the oxo ligand.

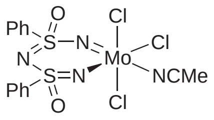
Alkylation of $Mo(NNPh_2)Cl_4$ with $PhMe_2CCH_2MgCl$ followed by the addition of HOC_6F_5 produces trigonal bipyramidal $Mo(NNPh_2)(CH_2CMe_2Ph)_3(OC_6F_5)$ ((**90**), cf. (**67**)), an active catalyst precursor in the ROMP of norbornene.[180] A similar reaction with MesMgCl produces $Mo(NNPh_2)(NPh_2)(Mes)_2(OC_6F_5)$, containing an amido ligand formed by hydrazido N—N bond cleavage.[186] Distorted pentagonal bipyramidal structures with apical hydrazido(2-) ligands are observed for $Mo(NNMeR)\{PhP(C_2H_4S)_2\text{-}P,S,S'\}_2$ (R = Me, Ph)[187] and $Mo(NNMePh)\{PhP(C_6H_4S)_2\text{-}P,S,S'\}_2$ (**91**),[188,189] produced in the reactions of $[Mo(NNMeR)_2\ Cl(PPh_3)_2]Cl$ or $Mo(NNMePh)Cl_4$ with the ligand free acids.[187–189] More recently, the reactions of $[MoO(\mu_S\text{-}tmea)]_2$ with H_2NNHR (R = Me, Ph) then HBF_4 or $[Me_3O]BF_4$ were reported to yield $[Mo(NNHR)(tmea)]BF_4$.[190] The reaction of $MoO_2(acac)_2$ with H_2NNRPh in the presence of Na_2SO_4 results in the formation of *cis*-$Mo(NNRPh)_2(acac)_2$ (R = Me, Ph) (nb. hydrazido oxo species form in the absence of drying agent, *vide infra*). The distorted octahedral complexes feature nearly linear hydrazido ligands ($\angle(Mo{=}N{-}N) > 171°$).[191] In contrast, $H_2NNRPh{\cdot}HX$ (R = Me, Ph; X = Cl, Br, I) react with $MoO_2(acac)_2$ to produce octahedral *cis,trans*-$Mo(NNRPh)(NHNRPh)X_2(acac)$ with linear hydrazido(2-) and bent hydrazido(1-) ligands in the same molecule.[192] The chloro complex serves as an entry to PR_3, dppe, bpy, phen, and Tp derivatives.[193–195] Unusual trigonal bipyramidal and *cis,cis,trans* octahedral structures pertain to $Mo(NNPh_2)_2Cl_2(PPh_3)$ and $Mo(NNMePh)_2Cl_2(PPh_3)_2$ (cf. $Mo(NMes)_2Cl_2(PMe_3)_2$ (Section 4.7.2.2.2(ii)) and $Mo(NNPh_2)_2Cl_2(PMe_3)_2$ (*vide supra*)).[193]

Additional derivatives of the type *cis*-$Mo(NNRPh)_2(S_2CNR'_2)_2$ (**92**, R = Me, Et, Pr, Bz, allyl, $CH_2C{\equiv}CH$, Ph; R′ = Me) have been reported.[196] Reactions of (**92**, R = Me, Ph; R′ = Me, Et) with one equivalent of $HX/NaBPh_4$ produce $[Mo(NNRPh)(NHNRPh)(S_2CNR'_2)_2]BPh_4$ (**93**), while an excess of acid produces $Mo(NNRPh)Cl_2(S_2CNR'_2)_2$ (**94**); the novel cationic complexes exhibit pentagonal bipyramidal structures with axial hydrazido(2-) and equatorial side-on bonded hydrazido(1-) ligands.[197] Treatment of (**94**, R = R′ = Me) with $AgNO_3$ in alcohols results in N—N bond cleavage and production of substituted *p*-alkoxyanilines.[196] Related pyridine thiolate derivatives, $Mo(NNMePh)Cl_2(SC_5H_3NSiMe_3)_2$ (**95**) and $Mo(NNMePh)_2(SC_5H_3NSiMe_3)_2$ (**96**) are produced in the reactions of $MoCl_4(SC_5H_3NSiMe_3)_2$ with one or more equivalents of $H_2NNMePh$, respectively.[188] The reactions of hydroxamate, thiohydroxamate,[198] and Schiff base[199] complexes with hydrazines are known to produce mixed-ligand diazenido and hydrazido(1-) species.

Hydrazido oxo complexes, $Mo(NNRPh)OR'_2(phen)$ (R = Me, Ph; R′ = Me, Ph), have been prepared by reacting $Mo(NNRPh)OBr_2(phen)$ with R′MgX in thf at 0 °C; $Mo(NNPh_2)OR'_2(phen)$ adopt distorted octahedral structures with $d(Mo{=}N)$ 1.770(3) Å, $d(Mo{=}O)$ 1.711(4) Å, near-linear hydrazido units ($\angle(Mo{=}N{-}N) > 171°$) and *trans* R′ groups ($\angle(C{-}Mo{-}C)$ ca. 150°).[200] Related species, e.g., *cis,trans*-$Mo(NNRPh)OX_2(bpy)$ are produced upon hydrolysis of bis(hydrazido) species.[194] In the absence of a drying agent, reaction of H_2NNRPh with $MoO_2(acac)_2$ at room temperature yields $Mo(NNRPh)O(acac)_2$ (R = Me,[201] Ph[202]) (nb. bis(hydrazido) species form in the presence of drying agent, *vide supra*). The X-ray structure of octahedral $Mo(NNMePh)O(acac)_2$ revealed *cis* hydrazido(2-) and oxo ligands exerting *trans* influences of ca. 0.1 and 0.16 Å, respectively.[201] This complex reacts with triethylammonium mercaptobenzoate producing octahedral $(NHEt_3)_2[Mo(NNMePh)O(SC_6H_4CO_2)_2]$. Further derivatives of the type $Mo(NNMe_2)O(S_2CNR_2)_2$ (R = ^{i}Bu, Cy, Bz; NR_2 = piperidinyl, etc.) have been prepared and $Mo(NNMe_2)O(S_2CN^iBu)_2$ has been structurally characterized.[203] Earlier work includes the synthesis and characterization of trigonal bipyramidal $Mo(NNMePh)O\{Me_2NCH_2CH_2N(CH_2CH_2S)_2\}$, $[Mo(NNMe_2)O(SPh)_3]^-$, and $Mo(NNMe_2)O\{S(CH_2CH_2S)_2\}$.[204] The X-ray structure of $Mo(NNMePh)O(SC_5H_3NSiMe_3)_2$ has also been determined.

4.7.2.2.5 Molybdacyclothiazene, molybdaphosphazene, and related complexes

Early metallacyclothiazene chemistry was reviewed in 1986.[205,206] Since then, an improved synthesis for $[Mo(N_3S_2)Cl_3]_2$ from $MoCl_5$ and $(NSCl)_3$ has been devised[207] and ligand addition and substitution reactions have produced derivatives such as *mer*-$Mo(N_3S_2)Cl_3L$ (L = py, thf),[207] $AsPh_4[Mo(N_3S_2)Cl_4]$,[208] $[Na(15\text{-}C\text{-}5)][Mo(N_3S_2)Cl_2F_2]$,[209] $Cat[Mo(N_3S_2)(dbc)_2]$ (Cat = Na^+, PPN^+), $Mo(N_3S_2)(dbc)Cl(phen)$, and $Mo(N_3S_2)(dbc)Cl(bpy)$.[210] The molybdacyclothiazene fragments are invariably planar with $d(Mo{-}N)$ in the range 1.778(3) (*trans* to thf) to 1.973(9) Å (*trans* to dbc) and almost equivalent N—S distances (av. 1.59 Å). An oxidized molybdacyclothiazene ligand is present in (**97**), the product of the reaction of $Mo(NCl)Cl_4$ with $PhS(O)N(SiMe_3)_2$ in NCMe.[211]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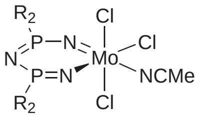
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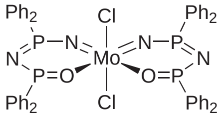
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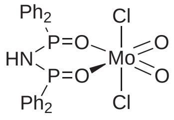
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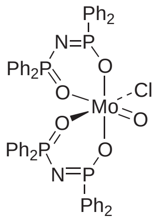

(101)

Metallacyclophosphazanes and -phosphazenes have been reviewed by Witt and Roesky.[212] Phosphazene salts react with $MoNCl_3$ producing yellow $Mo\{N_3(PR_2)_2\}Cl_3$ (R = Ph, C_6H_4Cl-4, $N[(CH_2)_2]_2O$, NMe_2), that were structurally characterized as their NCMe adducts, (**98**) (R = Ph, NMe_2);[213,214] mixtures of $Mo\{N_3(PPh_2)_2\}Cl_3$ and (**99**) result from similar reactions with $MoOCl_4$.[215] Modification of the heterocycle of $Mo\{N_3(PPh_2)_2\}Cl_3$ is common and reactions with, e.g., Ph_3SiOH and ^tBuOH, give (**100**) and (**101**), respectively. Electrochemical and theoretical studies of both classes of compound above have been reported.[216,217]

4.7.2.3 Chalcogenido (Oxo, Thio, Selenido) Complexes

Oxo complexes continue to dominate high-valent Mo chemistry. Previous reviews by Stiefel[1,2] and Nugent and Mayer[14] provide essential background to this section, which describes molybdate and related species, then trioxo-, dioxo-, mono-oxo, and oxo-thio complexes in that order.

4.7.2.3.1 Molybdate and related complexes

The colorless, tetrahedral molybdate ion, $[MoO_4]^{2-}$, lies at the epicenter of high-valent Mo chemistry and biochemistry, being an important starting material and the principal bio-available form of Mo. A timely review of molybdate transport, processing and gene regulation in biological systems has appeared.[218] Molybdate's size and shape, as well as its ability to participate in strong hydrogen bonding, is essential to its selective binding and transport by proteins. Indeed, hydrogen bonding pervades molybdate and related trioxo–Mo chemistry, a fact reflected in recent X-ray structures of the tris(2-ammonioethyl)amine and guanidinium salts of molybdate, where $d(Mo{=}O) = 1.728–1.776$ Å and $\angle(O{=}Mo{=}O) = 108.5–112.2°$ depending on the extent of hydrogen bonding. The multiple, simultaneous protonation equilibria of $[MoO_4]^{2-}$ have been extensively studied.[219] The tetrahedral oxyanion is stable and inert under basic conditions but is readily protonated upon acidification. The first protonation, with log K_1 3.47, generates $[HMoO_4]^-$. The second, occurring with log K_2 4.74 (∼log K_1 due to an accompanying increase in coordination number) yields $MoO_3(OH_2)_3$, $MoO_2(OH)_2(OH_2)_2$, or $Mo(OH)_6$. Subsequent protonation produces $[MoO_2(OH)(OH_2)_3]^+$ and $[MoO_2(OH_2)_4]^{2+}$ but these species are observed only at very low Mo concentrations ($<10^{-4}$ M). At higher concentrations, condensation leading to polyoxomolybdates occurs (see Chapter 4.10). The nature of the solution species and the role of $MoO_2(OH)_2(OH_2)_2$ or $Mo(OH)_6$ in condensation reactions have been probed by theoretical studies.[220] The existence of six-coordinate, dioxo-Mo^{VI} species in strong acid is supported by EXAFS studies[221] and the isolation of $MoO_2X_2(OH_2)_2$ (X = Cl, Br) from these solutions (Section 4.7.2.3.3(i)). Molybdenum(VI) equilibria in different ionic media and in the presence of organic and amino acids have been extensively studied; lead-in references provide an introduction to relevant literature.[222,223]

Intensely yellow/red-colored, tetrahedral thiomolybdates, $[MoO_xS_{4-x}]^{2-}$ ($x = 0–3$), are formed in the reactions of molybdate with H_2S or sulfiding agents in basic solutions. These complexes and their many homo- and heterometallic derivatives have been extensively studied and reviewed.[5,224,225] Interest in them stems, *inter alia*, from their roles in Cu–Mo antagonism in ruminants and their potential as treatments for Wilson disease.[226,227] Catalytic, industrial (e.g., lubricants), materials, and electronics applications also stimulate work in this area. The extension of thiomolybdate chemistry to nonaqueous media is facilitated by access to soluble alkylammonium salts and methods for the synthesis of $(NH_2R_2)_2[MoS_4]$ (R = Me, Et)[228] and $(NR_4)_2[MoS_4]$ (R = n-alkyl)[229] have been reported. Thiomolybdate salts, including $Cs_2[MoS_4]$, $[Ni(en)_3][MoS_4]$, and $[Co_2L_3][MoS_4]_2$ ($L = N(CH_2CH_2NH_2)_3$), have been structurally characterized. Photolysis of $[MoS_4]^{2-}$ in air produces $[MoO_2S_2]^{2-}$ and S_2 and accounts for the slow deterioration of $[MoS_4]^{2-}$ salts upon storage.[230] Contrary to earlier reports, the one-electron electrochemical reduction of $[MoS_4]^{2-}$ is reversible in dry dmf.[231,232] Spectroscopic (^{33}S, ^{17}O, and ^{95}Mo NMR) and theoretical studies of thiomolybdates have added to earlier insights.[1,5] *Ab initio* MO studies suggest that shielding of ^{95}Mo in the series $[MoO_xS_{4-x}]^{2-}$ ($x = 0$–4) is dominated by paramagnetic contributions arising from increased population of the 5p and 4d orbitals of Mo as x decreases.[233,234] The bonding and extent of electron delocalization in species of this type continue to elicit much interest.[235] Early transition metal thiometallates participate in induced internal redox reactions. For example, the reactions of $[MoS_4]^{2-}$ and tetraalkylthiuram disulfides afford $Mo(S_2)(S_2CNR_2)_3$,[236] while reactions with disulfides (RSSR) produce dinuclear $[Mo_2S_2(\mu\text{-}S)_2(S_2)_2]^{2-}$.[237] These reactions underscore the facile redox interplay of Mo and S.[225,238,239] Conversion of $(PPh_4)_2[MoS_4]$ to reduced polythiometalates is promoted by a variety of conditions and reagents, including alkyl halides, and intermediates such as $PPh_4[MoS_3(S^tBu)]$ appear to play a role in these reactions; this unstable compound contains a pseudo-tetrahedral anion with $d(Mo{=}S)_{av}$ 2.148 Å, d(Mo–S) 2.341(2) Å and ∠(Mo–S–C) 111.8(2)°.[240] Tatsumi and co-workers have recently used similar methods to prepare related complexes.[241]

Improved syntheses for purple $(NEt_4)_2[MoSe_4]$ from Na_2MoO_4, NEt_4Cl, and $[Me(CH_2)_7SiMe_2]_2Se$ in basic (NEt_3) acetonitrile,[242] and blue $(PPh_4)_2[MoSe_4]$ from $Mo(CO)_6$ and K_2Se_3 in dmf at 90 °C, followed by precipitation with PPh_4Br,[243] have been reported. The anion in $(PPh_4)_2[MoSe_4]$ has a tetrahedral structure with $d(Mo{=}Se)$ 2.293(1) Å.[243]

The pseudo-tetrahedral complexes, $MoE_2(ONR_2)_2$ (E = O, S, Se),[2,5] are closely related to the tetrahedral anions above. New dioxo complexes include $MoO_2(ONR_2)_2$ (NR_2 = 2,2,6,6-tetramethylpiperidine) but thio or seleno derivatives have not been reported since the 1980s.[244] The thio derivative, $MoOS(ONC_5H_{10})_2$, reacts with cyanide to produce $MoO_2(ONC_5H_{10})_2$ (50–60%) and SCN^- (65–80%) along with free HNC_5H_{10} and $HONC_5H_{10}$; the X-ray structure of $MoOSe(ONC_5H_{10})_2$ was also reported.[245] A detailed electrochemical examination of $MoE_2(ONC_5H_{10})_2$ derivatives revealed complex behavior, including ligand dissociation and reduction as well as interconversion of species, upon reduction.[246] The reactions of $MoO_2(ONHMe)_2$ with alkylnitriles, thiocyanate, CS_2, and isocyanates have been explored and octahedral *cis*-$MoO_2\{ON(Me)C(NH^tBu)O\text{-}O,N\}_2$ has been structurally characterized.[247] Attempted conversion of isocyanides (R = Bu, ^{t}Bu, Cy) to isothiocyanates by sulfur atom transfer from $MoS_2(ONEt_2)_2$ generated thioureas, $RHNC({=}S)NEt_2$, with cleavage of the hydroxylamido ligands.[248] Reactions of $MoO_2(ONC_5H_{10})_2$ with catechol and its derivatives ($catH_2$) produce $MoO(cat)(ONC_5H_{10})_2$. The parent complex exhibits a pentagonal bipyramidal solution and solid state structure with an axial oxo group ($d(Mo{=}O)$ 1.688(6) Å) and equatorial hydroxylamido ligands. The complexes undergo an irreversible reduction at potentials more positive than the dioxo–Mo^{VI} precursor (cf. the reversible reduction of dithiocarbamate and Schiff base analogs, Section 4.7.2.3.4(ii)).[249] Reaction of $MoO_2(ONR_2)_2$ (R = Et, Bz) with the strong Lewis acid $B(C_6F_5)_3$ produces pseudo-octahedral $MoO\{OB(C_6F_5)_3\}(ONR_2)_2$, with $d(Mo{=}O)$ 1.683(1) Å, d(Mo–OB) 1.808(1) Å and ∠(Mo—O—B) 170.09(8)° (for R = Et).[250]

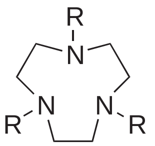
4.7.2.3.2 Trioxo complexes

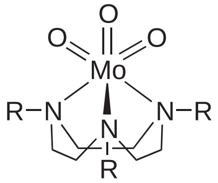
fac-Trioxo–Mo^{VI} complexes are generated under strongly oxidizing conditions in the presence of robust or chelating ligands. Complexes of this type are colorless and exhibit four-coordinate tetrahedral or six-coordinate distorted octahedral structures with $d(Mo{=}O)$/∠(O=Mo=O) in the ranges 1.718–1.746 Å/110.0–113.0° and 1.725–1.759 Å/103.3–107.7°, respectively. The pyramidal MoO_3 unit is invariably "flattened," resulting in disparate O—Mo—O and L—Mo—L angles and a "relative shift" of Mo toward the plane of oxo ligands. IR spectra typically exhibit two MoO_3 stretching modes, A_1 (polarized in Raman) and E (depolarized in Raman) under local C_{3v} symmetry, although solid state (H-bonding) effects commonly split the E mode. These bands are observed in the 820–920 cm^{-1} region. 17-Oxygen and ^{95}Mo NMR signals appear at δ 680–710 and δ 65–100, respectively.[251] Electrochemical studies reveal that trioxo complexes undergo a proton-assisted, two-electron reduction producing hydroxy/aqua–Mo^{IV} species that comproportionate with starting material to produce electroactive Mo^V dimers.[252,253]

Redistribution of oxygen in the reaction of $MoO_2(Mes)_2$ with the ylide $H_2C{=}C(H)PEt_3$ followed by cation exchange yields $PPh_4[MoO_3(Mes)]$,[254] whereas reaction of $MoO_2(Mes)_2$ with

$MgMes_2$ produces $[\{MoO_3(Mes)\}_2\{Mg_2Cl_2(thf)_5\}_2][MoOCl_3(Mes)]_2{\cdot}2thf$.[255] Both trioxo moieties exhibit tetrahedral geometries, the $Mo{=}O$ distances of the latter (av. 1.737 Å) being longer than those of the former (av. 1.720 Å) due to Mg^{2+} interactions.

A wealth of Mo chemistry (Scheme 6) is supported by triazacyclononane ligands (**102**, R_3tcn; R = H (tcn), Me, ^iPr, Bz). Colorless *fac*-$(R_3tcn)MoO_3$ (**103**) are prepared from MoO_3 and R_3tcn in hot water[252,256] or by oxidative decarbonylation of *fac*-$(R_3tcn)Mo(CO)_3$ (**104**) using nitric acid[257] or H_2O_2/thf at 50 °C.[251] The X-ray structures of octahedral $(tcn)MoO_3{\cdot}3H_2O$,[258] $(^iPr_3tcn)MoO_3{\cdot}3H_2O$, and $(^iPr_3tcn)MoO_3{\cdot}(PhNH)_2CO$ confirmed the molecular C_{3v} symmetry inferred by spectroscopic studies.[257] In aqueous protic media (**103**) (R = H, Me) undergo quasi-reversible $(2e^-,4H^+)$ reduction to $[(R_3tcn)Mo^{IV}O(OH_2)_2]^{2+}$, that undergo further reduction and di- and trimerization; the complexes are redox-inactive in aprotic media.[252] They function as O-donor ligands to Co^{II} and Fe^{II} and abstract BPh_3 and BPh_2^+ from BPh_4^-.[251,259] The X-ray structures of mono-*N*-functionalized derivatives, $(Rtcn)MoO_3{\cdot}nH_2O$ ($R = CH_2CH{=}CH_2$ ($n = 1$), $CH_2CH_2CH{=}CH_2$ ($n = 2$), CH_2CH_2OH ($n = 1$), CH_2-2-C_5H_4N ($n = 3$)) reveal intricate H-bonding networks.[258] The triazacyclohexane (R_3tch (**105**)) derivative, $(^tBu_3tch)MoO_3$ (**106**), formed by peroxide oxidation of $(^tBu_3tch)Mo(CO)_3$, crystallizes as the pentadecahydrate, $(^tBu_3tch)MoO_3{\cdot}15H_2O$.[260] In a similar fashion, oxidative decarbonylation of $NEt_4[LMo(CO)_3]$ (L = Tp, Tp*) by dimethyldioxirane, $Tm^*Mo(CO)_3$ by nitric acid, or $Mo(CO)_3(tpa)$ (tpa = tris(2-pyridylmethyl)amine) by O_2, produces $NEt_4[LMoO_3]{\cdot}2H_2O$ (see **107**, E = B, $n = 1$),[261] Tm^*MoO_3 (see **107**, E = C, $n = 0$),[262] and $MoO_3(tpa){\cdot}H_2O$ (**108**),[263] respectively. The anion of $NEt_4[TpMoO_3]{\cdot}2H_2O$ exhibits a distorted octahedral geometry and a network of H bonds involving all three oxo ligands. In (**108**), tpa binds in a tridentate fashion, the pendent pyridyl group and lattice water being H bonded to the oxo ligands. The X-ray structure of $MoO_3(dien)$ (dien = diethylenetriamine) has been redetermined.


(**102**)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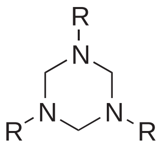
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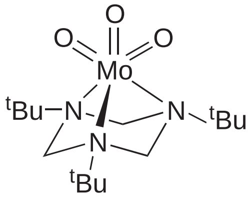
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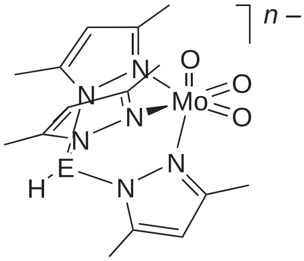
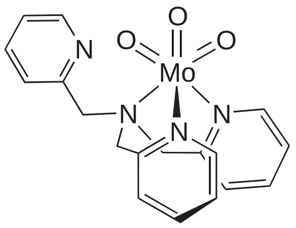
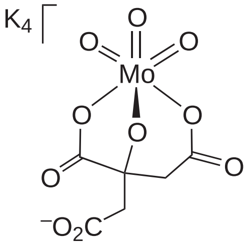

(**107**)

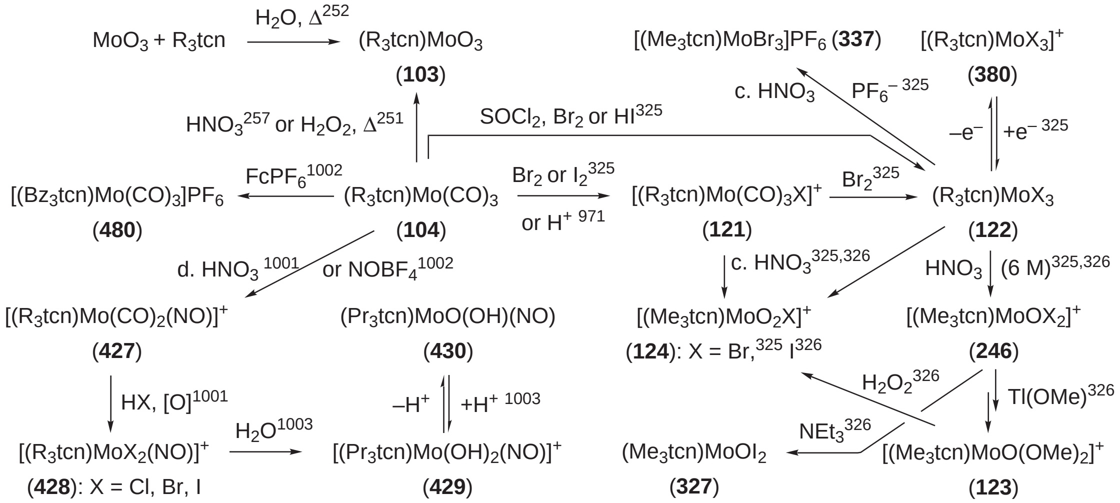

(**108**)


(**109**)

Complex formation between molybdate and citrate has been investigated by a variety of techniques; mononuclear, dinuclear, and tetranuclear complexes in six different Mo:citrate (cit) ratios and levels of protonation are observed.[264] The 1:1 complex, *fac*-$K_4[MoO_3(cit)]{\cdot}2H_2O$ (**109**), features a six-coordinate anion containing tridentate citrate bound through alkoxide, α-carboxylate, and (one) β-carboxylate groups.[265]

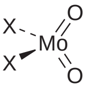
4.7.2.3.3 Dioxo complexes

Innumerable dioxo—Mo^{VI} complexes, having applications as oxidation catalysts, enzyme and metal oxide surface models, sensors, drugs, etc., have been reported since 1985. These are typically prepared by ligand addition, exchange, and/or metathesis at *cis*-$[MoO_2]^{2+}$ starting materials such as MoO_2X_2, $MoO_2X_2L_2$ (X = halide, L = H_2O, dmso, $OPPh_3$, etc.), or

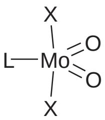


Scheme 6

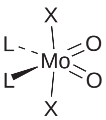
$MoO_2(acac)_2$. They are diamagnetic and generally colorless or yellow–orange, although deep red/purple complexes are known; blue or green "dioxo—Mo^{VI}" complexes are suspect. The π-donor oxo ligands are invariably *cis* in order to maximize donation into empty metal orbitals; the resultant complexes are characterized by two $\nu(MoO_2)$ IR bands in the region 800–970 cm^{-1}. Coordination numbers range from 4 to 6 and coordination geometries (**110**)–(**113**) are heavily represented; structural data for representative complexes are summarized in Table 5. Tetrahedral complexes (**110**) are restricted to those bearing π-donor co-ligands and examples include: $[MoO_2S_2]^{2-}$, $MoO_2(Mes)_2$,[266] $MoO_2(Mes)\{{=}C(Mes)PBu_3\}$,[267] $MoO_2(NPPh_3)_2$,[77] $MoO_2(OSiPh_3)_2$,[268] $MoO_2(OC_6H_3{}^tBu_2\text{-}2,6)_2$,[269] and the silsesquioxane, $MoO_2\{Cy_7Si_7O_9(OSiMe_3)(O\text{-})_2\}$.[270] Five-coordinate complexes are also relatively rare and include trigonal bipyramidal (**111**, L/X variously charged/uncharged) $MoO_2(Mes)_2(OPPh_3)$,[271] $MoO_2(Mes)_2(CH_2PBu_3)$,[272] $[Li(OEt_2)_2][MoO_2(Me)_2(Mes)]$,[273] $MoO_2(OSiPh_3)_2(PPh_3)$,[268] $MoO_2\{Cy_7Si_7O_9(OSiMe_3)(O\text{-})_2\}L$ ($L = py$, $OPPh_3$),[270] and NO_2- and NS_2-donor ligand complexes,[274–277] as well as square pyramidal $MoO_2L(bdt)$ ($L = OSiPh_3$, $SC_6H_2{}^iPr_3\text{-}2,4,6$).[278] The majority of dioxo—Mo complexes are six-coordinate species with distorted octahedral geometries. Further, due to the strong *trans* influence of the π-donor oxo ligands, the weakest π-donor ligands (L) coordinate preferentially to the sites *trans* to the oxo ligands, stronger π-donor ligands (X) being mutually *trans* and *cis* to the oxo groups. Thus, almost all 6-coordinate complexes can be described in terms of the *cis,trans,cis*-$MoO_2X_2L_2$ structure (**112**).[2,14] In rare instances, e.g., $MoO_2Cl_2(tmeda)$[279] and $MoO_2Cl_2(Me_4cyclam)$,[280] steric demands force the adoption of the electronically unfavorable *cis,cis,cis* structure (**113**).[281] A second, less common skew trapezoidal bipyramidal geometry is observed for *N*-substituted cysteamine complexes;[2] these can be distinguished from octahedral complexes by vibrational spectroscopy.[282]



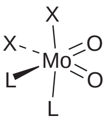
(**110**)



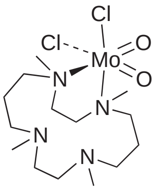
(**111**)



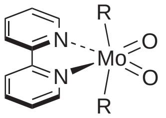
(**112**)



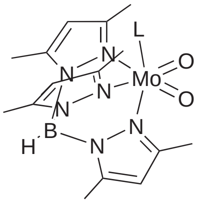
(**113**)



(**114**)



(**115**)



(**116**): (L = R, X)

(i) Complexes containing halide ligands

Compounds such as MoO_2X_2 and $MoO_2X_2L_2$ ($X = halide$, $L = neutral\ ligand$) are key starting materials in dioxo—Mo chemistry and discussion ahead of their derivatives is warranted.

Table 5 Selected structural data for *cis*-dioxo–Mo^{VI} complexes.[a]

Compound	*d*(Mo═O) (Å)	*d*(Mo—L)[b] (Å)	*d*(Mo—X)[c] (Å)	∠(O═Mo═O) (deg)	∠(L—Mo—L)[d] (deg)	∠(X—Mo—X)[d] (deg)	*References*
$MoO_2(Mes)_2$	1.699(3)		*C* 2.101(3)	109.5(1)		112.5(2)	266
$MoO_2(NPPh_3)_2$	1.712(3)		*N* 1.859(3)	108.2(1)		107.7(1)	77
$MoO_2(OSiPh_3)_2$	1.692(7)		*O* 1.815(5)	106.4(5)		110.0(4)	268
$MoO_2(Mes)_2(CH_2PBu_3)$	1.688(5)	*C* 2.227(7)	*C* 2.224(6)	113.5(3)		151.0(2)	272
	1.706(5)		CH_2 2.249(7)				
$MoO_2(OSiPh_3)_2(PPh_3)$	1.688(7)	*O* 1.922(6)	*O* 1.903(6)	110.0(4)		166.5(2)	268
	1.678(7)		*P* 2.759(3)				
MoO_2(**169**)[e]	1.698(4)	*N* 2.163(5)	*O* 1.898(4)	109.7(3)		144.8(2)	275
	1.696(4)		*O* 1.919(4)				
MoO_2(**178**)	1.691(6)	*N* 2.244(7)	*S* 2.412(2)	110.5(3)		156.4(1)	276
	1.696(6)		*S* 2.419(2)				
$MoO_2\{HN(CH_2CH_2S)_2\}$	1.697(4)	*N* 2.333(4)	*S* 2.361(1)	110.8(2)		137.8(1)	277
	1.687(4)						
$PPh_4[MoO_2(OSiPPh_3)(bdt)]$	O_{ax} 1.698(4)		*O* 1.916(4)	109.2(2)	79.9(1)[f]	152.27(8)[g]	278
	O_{eq} 1.710(4)	*S* 2.467(5)	*S* 2.452(4)		77.4(2)		
MoO_2Cl_2(tmeda) [**113**]	1.681(4)	*N* 2.464(4)	*N* 2.278(4)	103.1(2)	82.1(1)	165.2(1)	279
	1.697(4)	*Cl* 2.449(2)	*Cl* 2.338(2)				
$MoO_2Cl_2(Me_4cyclam)$ [**113**]	1.673(7)	*N* 2.478(8)	*N* 2.289(8)	101.5(3)	84.2(2)	163.9(3)	280
	1.701(7)	*Cl* 2.486(3)	*Cl* 2.331(3)				
$Na_2[MoO_2(bdbax)]\cdot 3dmso$	1.707(2)	m-*O* 2.186(2)	m-*O* 2.012(2)	101.87(9)	84.19(7)	151.40(7)	343
(bdbax = **134**) [**113**]	1.734(2)	o-*O* 2.125(2)	o-*O* 1.998(2)				
$MoO_2F_2(thf)_2$	1.682(3)	*O* 2.292(3)	*F* 1.884(2)	103.4(2)	77.52(11)	150.75(12)	170
	1.680(3)	*O* 2.275(3)	*F* 1.887(3)				
MoO_2Cl_2(diglyme)	1.688(2)	*O* 2.268(2)	*Cl* 2.363(1)	104.7(1)	70.96(8)	159.75(3)	288
	1.695(2)	*O* 2.327(2)	*Cl* 2.368(1)				
$MoO_2Br_2(NCMe)_2$	1.682(3)	*N* 2.326(3)	*Br* 2.5119(4)	104.4(1)	75.75(9)	156.52(2)	289
	1.682(3)	*N* 2.326(3)	*Br* 2.5119(4)				
$MoO_2Cl_2(OH_2)_2\cdot 2H_2O\cdot 18\text{-}C\text{-}6$	1.677(3)	*O* 2.210(3)	*Cl* 2.3682(9)	103.5(3)	75.8(2)	159.90(5)	300
$MoO_2(Me)_2$(bipyrimidine)	1.699(2)	*N* 2.336(2)	*C* 2.187(3)	110.26(9)	67.41(7)	148.00(12)	307
	1.717(2)	*N* 2.364(2)	*C* 2.190(2)				
$MoO_2\{NC_5H_3(NR)Me\text{-}2,6\}_2$	1.692(2)	*N* 2.350(2)	*N*R 2.077(2)	105.13(7)	76.19(5)	143.52(6)	316
($R = SiMe_3$)	1.694(2)	*N* 2.334(2)	*N*R 2.076(2)				

Tp*MoO$_2$(SPh)	1.696(4)	*N* 2.301(4)	*S* 2.402(2)	102.6(2)	79.9(2)	157.5(1)	319
	1.702(4)	*N* 2.346(2)	*N* 2.169(4)				
Tp$^{\mathrm{Pr}}$MoO$_2$(OMe)	1.705(2)	*N* 2.338(2)	*O* 1.865(2)	104.78(8)	78.52(6)	158.69(6)	319
	1.697(2)	*N* 2.346(2)	*N* 2.209(2)				
[(Me$_3$tcn)MoO$_2$(OMe)]BPh$_4$	1.792(4)	*N* 2.306(4)	*N* 2.258(3)	105.9(2)	75.0(1)	159.7(1)	326
	1.783(4)	*N* 2.318(4)	*O* 1.895(3)				
MoO$_2$(OSiPh$_3$)$_2$(py)$_2$	1.695(2)	*N* 2.404(4)	*O* 1.931(1)	104.5(1)	75.1(2)	151.7(9)	333
MoO$_2$(dag)$_2$	1.687(2)	*O* 2.568(2)	*O*R 1.909(2)	105.0(1)	79.2(1)	143.9(1)	334
	1.683(2)	*O* 2.484(2)	*O*R 1.924(2)				
MoO$_2${O$_2$(OMe)$_2$$^{\mathrm{Bu}}$cal}	1.694(3)	*O*$_{\mathrm{Me}}$ 2.394(3)	*O* 1.916(3)	101.47(15)	101.55(10)	137.16(12)	337
	1.690(3)	*O*$_{\mathrm{Me}}$ 2.559(3)	*O* 1.920(3)				
K$_2$[MoO$_2$(btrencam)]·dmf·5H$_2$O	1.722(7)	*O* 2.176(7)	*O* 1.991(7)	99.14(4)	89.54(4)	148.93(4)	342
(btrencam = **132**)	1.709(8)	*O* 2.167(7)	*O* 1.997(8)				
MoO$_2$(**137**-H)$_2$ (R = H)	1.705(2)	=*O* 2.207(2)	*O* 1.997(2)	104.8(1)	77.4(1)	154.5(1)	357
	1.697(2)	=*O* 2.242(2)	*O* 1.986(2)				
MoO$_2$(**139**-H)$_2$ (R = Et)	1.691(5)	*O*$_{\mathrm{pz}}$ 2.209(6)	*O* 1.981(4)	103.5(4)	77.8(3)	155.4(3)	361
(PPh$_4$)$_2$[MoO$_2$(mnt)$_2$]	1.721(6)	*S* 2.635(3)	*S* 2.439(2)	104.7(4)	83.3(1)	158.3(1)	362
MoO$_2$(Bu$_4$dttd) (Bu$_4$dttd = **147**)	1.702(10)	*S* 2.657(5)	*S*$^-$ 2.413(6)	108.5(7)	79.7(2)	150.2(2)	382
MoO$_2$(**154**)$_2$	1.684(4)	*N* 2.382(5)	*O* 1.957(3)	106.22(28)	76.16(20)	150.95(21)	386
MoO$_2$(**159**)$_2$	1.705(3)	*N* 2.363(3)	*O* 1.938(3)	104.5(1)	89.2(1)	146.3(2)	390
MoO$_2$(**164**)(HOMe)	1.705(5)	*O*H 2.349(4)	*O* 2.016(4)	106.4(2)	77.6(2)	148.2(2)	399
(R = C$_6$H$_4$OH-2)	1.692(4)	*N* 2.234(4)	*O* 1.927(4)				
MoO$_2$(pdc)(dmf) (pdc = **170**)	1.674(2)	*O*$_{\mathrm{dmf}}$ 2.308(2)	*O* 2.009(2)	105.5(1)	71.76(8)	144.68(9)	407
	1.702(2)	*N* 2.190(2)	*O* 2.010(2)				
MoO$_2$(**177**)$_2$	1.696(4)	*N* 2.411(5)	*S* 2.418(2)	107.7(3)	76.2(2)	159.8(1)	420
MoO$_2$(**183**)(HOMe)	1.709(4)	*N* 2.304(4)	*S* 2.389(1)	105.7(2)	77.2(1)	150.3(1)	433
	1.699(3)	*O* 2.322(4)	*S* 2.442(1)				
K[MoO$_2$(btap)] (btap = **184**)	1.715(4)	*N* 2.387(5)	*S* 2.4406(16)	105.3(2)	74.13(16)	155.17(6)	434
	1.742(4)	*O* 2.079(4)	*S* 2.4729(16)				
MoO$_2$(L-N$_2$S$_2$) (L-N$_2$S$_2$ = **186**)	1.697(2)	*N* 2.441(2)	*S* 2.414(1)	107.4(1)	74.52(5)	159.91(2)	435
	1.697(2)	*N* 2.460(2)	*S* 2.413(1)				

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[a] Representative complexes in order of increasing coordination number, with octahedral all-*cis* structures (**113**) ahead of *cis,trans,cis* structures (**112**). With some exceptions (e.g., angles in **113**), the donor atoms X and L are those indicated in structures (**110**)–(**113**). The donor atoms are indicated in italics. [b] d(Mo—L) pertains to donor atoms *trans* to the oxo ligands in (**112**) or their counterparts (L and X) in (**113**). Parameters for individual oxo/*trans* donor atom pairs are listed in the same row. [c] d(Mo—X$_c$) pertains to the mutually *trans* donor atoms *cis* to the oxo ligands in (**111**)–(**112**) or their counterparts (L and X) in (**113**). Parameters for the *trans* and non-*trans* donors of bidentate ligands are listed in the same row. [d] The angles identified in structures (**110**)–(**112**) or their counterparts in (**113**). [e] Data for one of two independent molecules. [f] For this square pyramidal complex, these values represent ∠(S—Mo—S) and (the smaller) ∠(S—Mo—OR), respectively. [g] Larger ∠(S—Mo—OR).

Exchange of oxide for chloride forms the basis of a new synthesis of MoO_2Cl_2 from $MoOCl_4$ and $(Me_3Si)_2O$;[283] addition of bpy to the reaction yields MoO_2Cl_2(bpy) but the scope of this "modification" has not been explored.[284] The gas-phase structures of MoO_2X_2 (X = Cl, Br) have been redetermined using electron diffraction, and molecular C_{2v} symmety is indicated.[285] The electrochemistry of MoO_2Cl_2 at Pt in NCMe and methylene or propylene carbonates has been investigated, and MoO_2^{2+}(sol), $[MoO_2Cl_4]^{2-}$, and $[MoO_2Cl_3]^-$ are implicated in the behavior observed.[286] A theoretical study of oxohalo–Mo anions (citing additional references) has appeared.[287]

Dissolution of MoO_2X_2 in coordinating solvents (L) produces distorted octahedral complexes, *cis,trans,cis*-$MoO_2X_2L_2$ (**112**). Complexes prepared in this manner include MoO_2Cl_2(diglyme),[288] MoO_2Cl_2(dme) (n.b., alternative synthesis from Na_2MoO_4 and Me_3SiCl in dme[116]), $MoO_2Br_2(NCR)_2$ (R = Me, Ph), and $MoO_2Br_2(NC^tBu)$.[289] Hydrolysis also affords complexes of this type; e.g., hydrolysis of $Mo(NCl)F_4$ in thf produces $MoO_2F_2(thf)_2$.[170] The ready displacement of water from $MoO_2Cl_2(OH_2)_2$ (*vide infra*) by dmso provides a reliable route to $MoO_2Cl_2(dmso)_2$ (see *Inorg. Synth., Vol. 31, p. 246*) and related species. Other complexes, such as $MoO_2X_2L_2$ (X = F, Cl, Br; L = picoline *N*-oxide, pentene-2-ones, L_2 = bpy, phen, bis(oxazoline), and 1,4-diazabutadiene derivatives),[290,291] $MoO_2Cl_2(pzH)_2$ and $MoO_2Cl_2(Me_2Cpz_2)$ (pz = pyrazolyl),[292] may be prepared through ligand exchange. These have been structurally characterized and tested as epoxidation catalysts, the chloro and aromatic N-donor complexes being more active than their bromo or aliphatic analogs.[290] Dioxo-dichloro-Mo^{VI} complexes also serve as precursors to active, heterogeneous, epoxidation catalysts.[293] The oxidation of PPh_3 by dmso or azoxybenzene is catalyzed by $MoO_2X_2(dmso)_2$ (X = F, Cl, Br).[294] Phosphoryl and carbonyl complexes, as well as $MoO_2Cl_2(Me_4cyclam)$ (**114**), are produced in the direct reactions of MoO_2Cl_2 and ligand in a suitable solvent; the latter exhibits the rare all-*cis* ligand configuration (**113**).[280] Related complexes formed in unusual ways include $PPh_4[MoO_2Cl_2\{HON{=}C(Me)CO_2\text{-}O,N\}]$, produced by ligand fragmentation in the reaction of H_3hidpa (see Section 4.7.3.6.3) with $PPh_4[MoOCl_4(OH_2)]$,[295] and $NEt_4[MoO_2F_2(acac)]$, prepared by reacting $MoO_2(acac)_2$ with $[NEt_4][HF_2]$ in NCMe.[296]

Spectroscopic evidence[297] for the existence of aqua complexes in solutions of MoO_3 or $M^I_2MoO_4$ in concentrated hydrohalic acids was corroborated by the isolation of *cis,trans,cis*-$MoO_2X_2(OH_2)_2$ (**112**, L = OH_2), in H-bonded solids. Early examples included $MoO_2Cl_2(OH_2)_2{\cdot}H_2O{\cdot}NEt_4Cl$[298] and polyether stabilized $MoO_2Cl_2(OH_2)_2{\cdot}(diglyme)_2$.[299] Subsequently, extraction of K_2MoO_4/HX solutions with diethyl ether, followed by addition of crown ethers to the organic phase, yielded $MoO_2X_2(OH_2)_2{\cdot}2H_2O{\cdot}$18-C-6, $MoO_2Cl_2(MeOH)_2{\cdot}$18-C-6 (after recrystallization from methanol) and $[K(18\text{-}C\text{-}6)][MoO_2Cl_3(OH_2)]$ (when 18-C-6 was present *in* the extractant).[300] Crystals of $MoO_2X_2(OH_2)_2{\cdot}2H_2O{\cdot}$18-C-6 comprise distorted octahedral complexes H-bonded through bound and lattice water to the crown ether moiety. In the lattice of $MoO_2Cl_2(MeOH)_2{\cdot}$18-C-6, the weakly coordinated methanol hydroxy groups H-bond to the crown ether.[300]

(ii) Complexes containing carbon-donor ligands

Virtually all the work in this area builds on the seminal contributions of Heyn, Hoffman, Schrauzer and their co-workers;[2] an alternative synthesis for $MoO_2(Mes)_2$[255] and the X-ray structures of $MoO_2(Mes)_2$ and $[Li(OEt_2)_2][MoO_2(Me)_2(Mes)]$[273] augment earlier work. In new chemistry, reactions of $MoO_2(Mes)_2$ with the phosphonium ylide, H_2CPBu_3, yield trigonal bipyramidal $MoO_2(Mes)_2(CH_2PBu_3)$[272] or tetrahedral $MoO_2(Mes)\{{=}C(Mes)PBu_3\}$,[267] depending on reaction temperature. Reactions with $H_2C{=}C(H)PEt_3$ produce $PPh_4[MoO_3(Mes)]$ (Section 4.7.2.3.2) while other ylides induce polyoxomolybdate formation.[254] The reactivity of $MoO_2(Mes)_2$ toward CO, isocyanates, and isocyanides has also been investigated.[301]

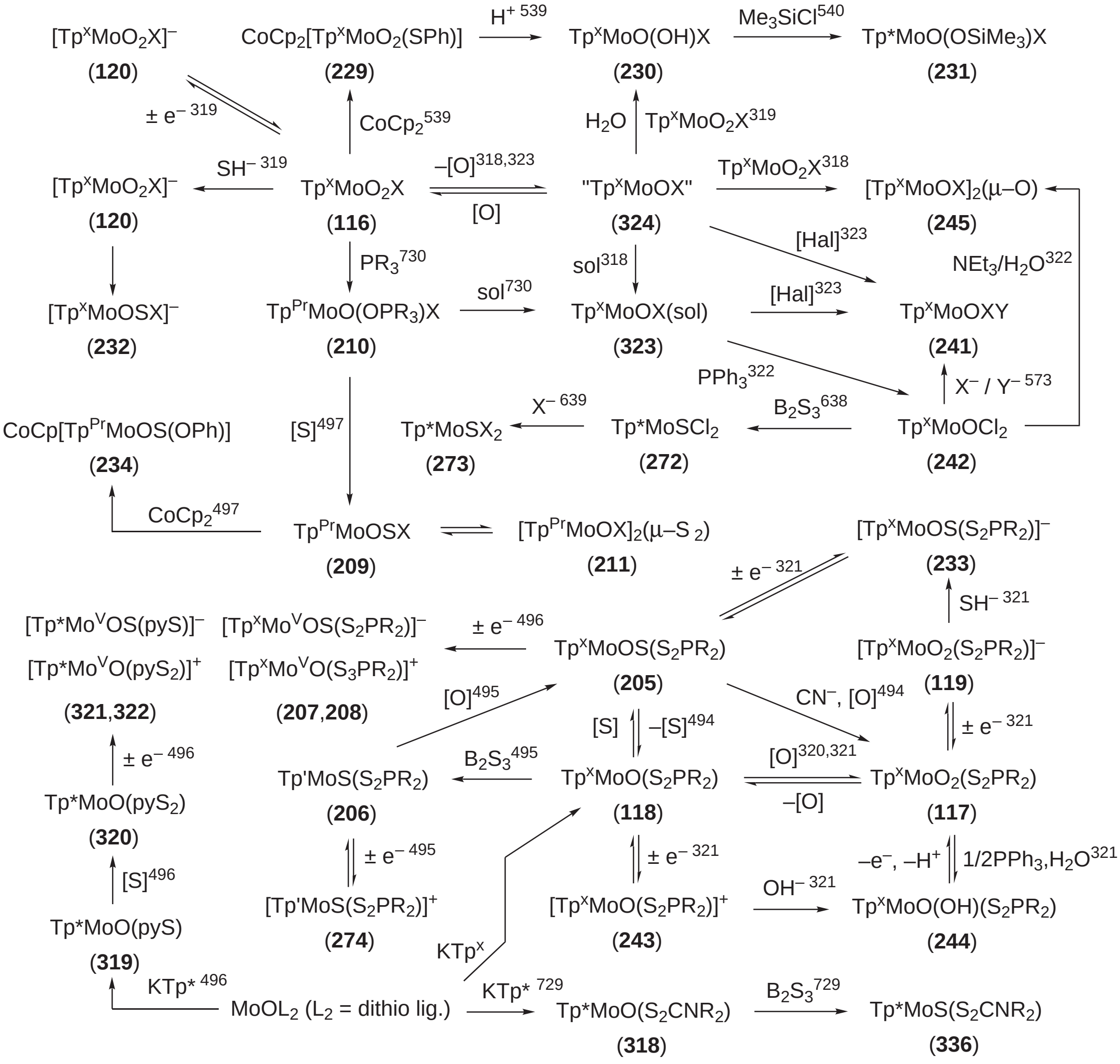
Complexes of the type MoO_2R_2(bpy) are prepared by reacting MoO_2Br_2(bpy) with Grignard or organolithium reagents in cold thf, and many new alkyl,[302–304] and aryl[305] derivatives have been prepared since 1985. Bipyridine has also been replaced by substituted bpy, phen, and 1,4-diazabutadiene ligands (L) to produce MoO_2R_2L (R = alkyl and Bz derivatives).[306–308] Structurally characterized species exhibit distorted octahedral structures (**115**) with *cis* oxo ligands (*d*(Mo=O) 1.695–1.74 Å, ∠(O=Mo=O) 110.3–113.1°), N-donors *trans* to oxo, and mutually *trans* organyl ligands positioned back from the oxo groups (*d*(Mo—C) 2.187–2.235 Å, ∠(C—Mo—C) 148.0–153.6°). Decomposition pathways are sensitive to the nature of the organyl ligand.[306,309] The methyl and ethyl derivatives are efficient catalysts for the ROMP of norbornene with MeMgBr co-catalyst or alone when supported on Montmorillonite K10.[310] Catalysis of olefin epoxidation by ^{t}BuOOH has also been demonstrated for MoO_2Me_2L (L = bpy, phen, or 1,4-diazabutadiene derivatives);[307] seven-coordinate $MoO(Me)_2(OH)(OO^tBu)L$ are believed to be the active catalysts in these systems.[308] Related but ill-defined methyl or μ-methylene species, formed in the reactions of MoO_2Cl_2 and $AlMe_3$, and their synthetic applications have been reviewed by Kauffmann.[311] Trispyrazolylborate complexes, Tp^*MoO_2R (**116**, R = Me, CH_2SiMe_3), are produced in the reactions of Tp^*MoO_2Cl with RMgX at $<-10\,°C$ in diethyl ether[312] or $AlMe_3$ in toluene followed by oxidation.[313] An X-ray structure of $Tp^*MoO_2(Me)$ revealed a distorted octahedral geometry.[313]

(iii) Complexes containing nitrogen-donor ligands

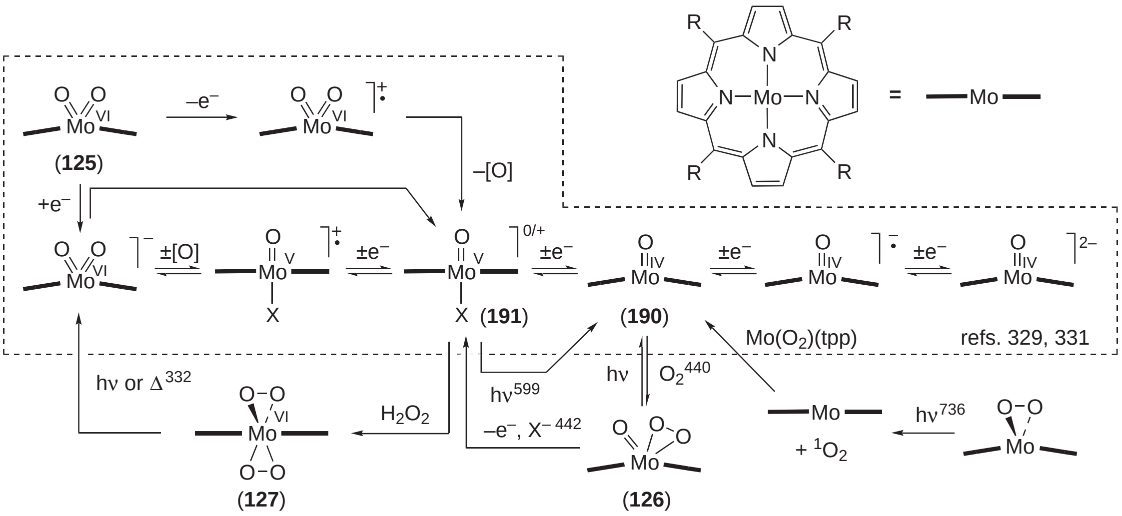
Dioxo complexes with monodentate N-donor ligands are rare but include tetrahedral $MoO_2(NPPh_3)_2$, produced in the reaction of MoO_2Cl_2 and $LiNPPh_3$ in thf or through hydrolysis of $MoN(NPPh_3)_3$,[77] and known $(PPh_4)_2[MoO_2(NCS)_4]$. The thiocyanate complex is an active oxygen atom transfer (OAT) catalyst[314] but the 4,4′-di-*t*-butyl-2,2′-bipyridine derivative, $MoO_2(NCS)_2(^tBu_2bpy)$, is even more active.[315] Amido-pyridine complexes, $MoO_2\{C_5H_3N(NR)Me\text{-}2,6\}_2$ (R = $SiMe_3$, $SiMe_2{}^iBu$, $SiPh_2{}^iBu$),[316] and bis(amido) species, $MoO_2\{PhC(NSiMe_3)_2\}_2$,[317] exhibit distorted octahedral structures; the small bite angles of the amido ligands (ca. 60°) exacerbate the canting of "equatorial" MoO_2 and MoN_2 planes.

Many dioxo—Mo^{VI} complexes containing trispyrazolylborate (Tp^x) ligands have been prepared and characterized as part of a broad exploration of bio-relevant Mo^{VI}–Mo^{IV} chemistry (Scheme 7). Reaction of MoO_2X_2 (X = Cl, Br), $MoO_2X_2L_2$ (X = F, Cl, Br; L = $OPPh_3$, dmso), or $(NEt_4)_2[MoO_2(NCS)_4]$ with KTp*, KTp^{Pr}, or KTz* yields *fac*-Tp^xMoO_2X (**116**) (X = F, Cl, Br, NCS). Related complexes (X variously OMe, OEt, OPh, S^iPr, SPh, SBz, and others) may be generated through methathesis with HX/NEt_3 or alkali metal salts.[318,319] Complexes of ambidentate ligands, $Tp^xMoO_2(S_2PR_3\text{-}S)$ (**117**, R = alkyl, alkoxy[320,321]), can be accessed by metathesis but oxidation of the corresponding Mo^{IV} complexes, $Tp^xMoO(S_2PR_2)$ (**118**), provides more reliable syntheses. The X-ray structures of Tp^*MoO_2X (X = $S_2P(OEt)_2$-*S*,[320] NCS,[318] SPh[319]), $Tp^{Pr}MoO_2(OMe)$ and $Tz^*MoO_2(SPh)$ reveal distorted octahedral geometries defined by *fac* Tp^x and mutually *cis* oxo and X ligands. Unlike most dioxo—Mo^{VI} complexes, Tp^x complexes generally undergo reversible or pseudo-reversible, one-electron reductions producing stable EPR-active Mo^V species (**119**/**120**) (see Section 4.7.3.3 for a description of isolable species). Redox potentials are influenced greatly by the nature of X and correlate with Hammett functions.[319,322] These Mo^{VI} complexes are the cornerstones of synthetic enzyme models encompassing many biologically relevant oxidation states, oxo centers, and reactions, and informing electronic structure (Scheme 7).[323] The OAT and coupled electron–proton transfer chemistries of this and related systems have been reviewed.[324] More recently, $[TmMoO_2X]X$ (X = Cl, Br), $[Bm^*MoO_2Cl]Cl$, and $TpMoO_2Cl$ were prepared and tested as epoxidation catalysts.[292] Oxidation of Mo^{II} (**121**), Mo^{III} (**122**), or Mo^V (**123**) complexes with nitric acid or H_2O_2 permits isolation of salts of *fac*-$[(Me_3tcn)MoO_2X]^+$ (**124**, X = Br, I, OMe) (Scheme 6). These were characterized spectroscopically, electrochemically, and crystallographically, the cation in $[(Me_3tcn)MoO_2(OMe)]BPh_4$ having an octahedral geometry defined by *facial* Me_3tcn and mutually *cis* oxo and methoxide ligands.[325,326] More recently, pseudo-octahedral $[(tcn)MoO_2(MeHNO)]ClO_4$ has been isolated and structurally characterized.[327]

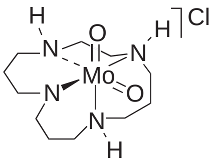
Molybdenum porphyrin chemistry spans a range of oxidation states, most notably +VI through +IV, and has been reviewed.[328–330] Three types of Mo^{VI} porphyrin complexes are known, viz., *cis*-$MoO_2(por)$ (**125**), *cis*-$MoO(O_2)(por)$ (**126**), and *trans*-$Mo(O_2)_2(por)$ (**127**) (por = 5,10,15,20-R_4-porphyrinato(2-); R = Mes (tmp), Ph (tpp), tol (ttp) etc).[2] The chemistry, electrochemistry, and photochemistry of these complexes are summarized in Scheme 8 (electrochemical interconversions[331] lie inside the dashed boundary, chemical transformations outside). Pyrolysis rather than photolysis of $Mo(O_2)_2(tpp)$ provides better access to bulk quantities of $MoO_2(tpp)$.[332] The tetradentate amido complex, $[MoO_2([15]aneN_4\text{-}H)]Cl$ (**128**), is produced in the reactions of MoO_2Cl_2 and 1,4,8,12-tetraazacyclopentadecane ($[15]aneN_4$) in CH_2Cl_2.[280]



Scheme 7



Scheme 8



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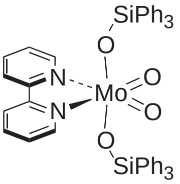

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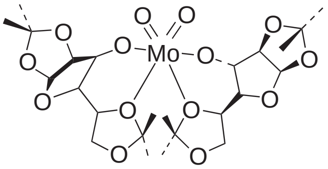

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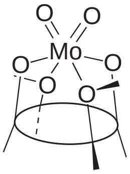
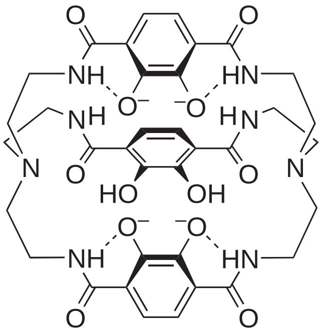


(131)

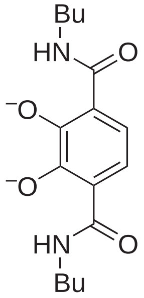
(iv) Complexes containing oxygen-donor ligands

(a) Alkoxide, aryloxide, and catecholate complexes. Two four-coordinate, tetrahedral complexes in this class have been structurally characterized. The first, $MoO_2(OSiPh_3)_2$, was prepared by silylation of Ag_2MoO_4 using Ph_3SiCl and reacts with PPh_3 to form trigonal bipyramidal $MoO_2(OSiPh_3)_2(PPh_3)$.[268] The second, $MoO_2L_2{\cdot}2HL$ ($L = OC_6H_3{}^tBu_2$-2,6), is produced in the reaction of MoO_2Cl_2 and Li(L).[269] Both complexes appear to be stabilized by significant π donation from the OR^- ligands, the Mo—O—Si/C angles being ca. 163° and 170°, respectively. Derivatives such as $MoO_2(OSiPh_3)_2L$ (L = phen (**129**), Me_4phen, 4,4′-Me_2bpy, 5,5′-bpy, and py_2) are also known.[333] Related oxo–thio complexes are described in Section 4.7.2.3.5. Reaction of $MoOCl_4$ or MoO_2Cl_2 with Li(dag) in diethyl ether yields $MoO(dag)_4$ and *cis*-$MoO_2(dag)_2$ (**130**), respectively; these react with bases producing $MoO(dag)_4(py)$ and $MoO_2(dag)_2(phen)$.[334] Reaction of $MoO(OEt)_4$ with excess $MeOC_2H_4OH$ (ROH) produces liquid $MoO(OR)_4$, which converts to $MoO_2(OR)_2$ (with the expected distorted octahedral structure) upon standing.[335] Reaction of tetraalkylammonium 1,1′-bi-2-naphtholate (bino) with $MoO_2(acac)_2$ results in the generation of $NR_4[MoO_2(bino)(acac)]$, which possesses a severely distorted octahedral structure with asymmetrically coordinated bidentate ligands.[336] Oxo calixarene complexes are of interest as models of heterogeneous metal–oxide catalyst surfaces, centers capable of supporing organometallic transformations, and as building blocks for supramolecular structures. However, only one dioxo-Mo^{VI} derivative, $MoO_2\{O_2(OMe)_2{}^{Bu}cal\}$ (**131**), has been reported.[337]

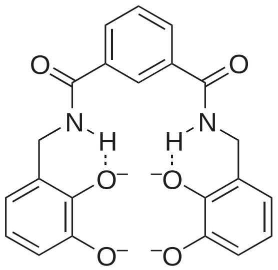
More "mononuclear" trioxo and dioxo catecholate complexes have been reformulated as dinuclear species but mononuclear catecholate or pyrogallolate complexes do exist.[338,339] Insights into monomer–dimer interconversions, especially through ligand autoxidation, have been provided by Pierpont and co-workers.[340] Complexes of the catechol amines, adrenaline (H_2ad), noradrenaline (H_2nad), dopa (H_2dp), dopamine (H_2dpm), and isoproterenol (H_2prot) have been prepared and characterized. Bidentate coordination was established for $Na_2[MoO_2L_2]{\cdot}H_2O$ (L = nad, dopa, prot), $(PPh_4)_2[MoO_2(prot)_2]{\cdot}H_2O$, and $MoO_2(Hdpm)_2{\cdot}H_2O$.[341] Siderophore complexes of Mo include $K_2[MoO_2(btrencam)]$, $Na_2[MoO_2(bta)_2]$,[342] and $Na_2[MoO_2(bdbax)]{\cdot}3dmso$[343] (see (**132**)–(**134**) for ligand structures). The *cis*-$[MoO_2]^{2+}$ unit in $K_2[MoO_2(btrencam)]$ is coordinated "outside" the macrobicyclic cavity by two catecholate units H bonded to adjacent amido NH groups; the third catecholate unit is protonated and is directed away from the octahedral Mo center. A distorted octahedral anion with planar intramolecularly H-bonded catecholamine units was established for $Na_2[MoO_2(bdbax)]{\cdot}3dmso$.[343] A similar H-bonded motif is observed in $(NH_4)_2[MoO_2(dhb)_2]{\cdot}1.5H_2O$ (H_2dhb = 2,3-dihydroxybenzoic acid), formed similarly.[344] Molybdate binding to the aminochelin siderophore of *Azotobacter vinelandii* quenches the fluorescence of attached Ru(bpy)-chromophores, affording a sensitive probe for the oxyanion.[345]



(**132**): btrencam



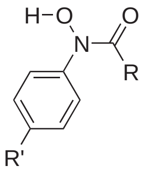
(**133**): bta



(**134**): bdbax

(b) Other O-donor ligand complexes. A detailed synthesis of $MoO_2(acac)_2$, a central precursor for synthesis and catalysis, can be found in *Inorg. Synth. (Vol. 29, p. 129)*. New catalytic applications for the complex include the Meyer–Schuster rearrangement[346] and the selective oxidation of alcohols to aldehydes.[347,348] The Lewis acid adduct, $MoO\{OB(C_6F_5)_3\}(acac)_2$, has been prepared and structurally characterized.[349] An unusual feature of the solid state structure of pyH[MoO_2(sal)(Hsal)] is the coordination of one of the bidentate ligands through the carbonyl group of a protonated carboxylate moiety.[350] A carbonyl group also assists bidentate coordination of (1*R*)-*endo*-(+)-3-(diethoxyphosphoryl)camphor (L) in MoO_2Cl_2L but it is easily displaced by a second phosphoryl group, forming $MoO_2Cl_2L_2$.[351] Four- and five-coordinate silsesquioxane complexes, $MoO_2\{Cy_7Si_7O_9(OSiMe_3)(O\text{-})_2\}$ and $MoO_2\{Cy_7Si_7O_9(OSiMe_3)(O\text{-})_2\}L$ (L = py, $OPPh_3$), have been characterized by spectroscopy and X-ray diffraction.[270]

Hydroxamic acids form very stable metal complexes, a feature making them attractive as siderophores and metal-chelating drugs.[2] The free acids (LH), (**135**, R = alkyl, R′ = H, Me),[352,353] and the amino acid derivatives (**136**)[354] form complexes of the type, *cis*-MoO_2L_2. These possess distorted octahedral structures with bidentate, uninegative hydroxamate ligands bound with their carbonyl oxygens *trans* to oxo. The mixed hydroxamato/hydroximato compound, $NH_2Et_2[MoO_2\{MeC(O){=}N(O)\}\{MeC(O)N(O)H\}]$, is the unexpected product of the reaction of $MoO_2(S_2CNEt_2)_2$ with acetonehydroxamic acid.[355] Boration of hydroxamato–Mo complexes has been described.[250] Complexes containing (deprotonated) hydroxy-4-pyrones (**137**, R = H (maltol), CH_2OH (kojic acid)) or hydroxy-4-pyridinones (**138**, R = H, CH_2OH; R′ = Me, Pr, Bz, Ph, and long chains) may be generated by reactions with molybdic acid or ligand elaboration at Mo through double Michael-type addition of the appropriate amine to *cis*-MoO_2-(pyronate)$_2$.[356–359] These complexes are of interest as treatments for iron overload, thalassemia, and heart dysfunction in diabetics.[357,358] Complexes derived from 3-hydroxy-2-pyridinone[356] and tropolone[360] are also known. A bis(3-H-pyrazol-3-onato) complex, *cis*-MoO_2L_2, is formed when ethanol solutions of (**139**, R = Et) are mixed with molybdate in acid. The X-ray structure of the octahedral complex revealed C_2 symmetry, with the acyl oxygens bound *trans* to oxo. The product of the same reaction with (**139**, R = CCl_3) is modified by ethoxylation at an acyl group, the pyrazolyl hydroxy group of the new ligand (**140**) being bound *trans* to oxo.[361]



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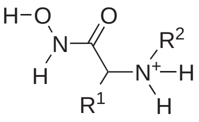

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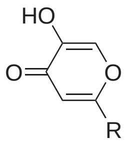

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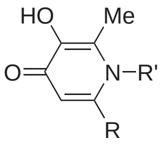

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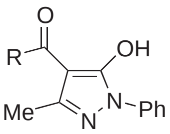

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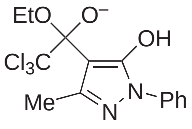
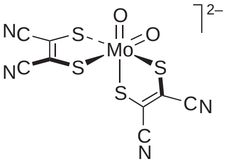


(140)

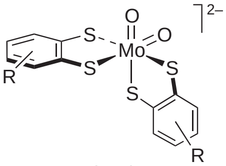
(v) Complexes containing sulfur-donor ligands

(a) Dithiolene complexes. Modeling of the pterin–dithiolene center in Mo and W enzymes has stimulated work on Mo^{VI}—Mo^{IV} dithiolene complexes, the contributions of Garner, Holm, Sarkar, Ueyama, and their co-workers being particularly noteworthy (see also Sections 4.7.3.4.3(ii) and 4.7.4.3.4(i)). Complexes such as $[MoO_2(mnt)_2]^{2-}$ (**141**), $[MoO_2\{S_2C_2(CO_2Me)_2\}_2]^{2-}$, and $[MoO_2L_2]^{2-}$ (**142**, L = bdt (R absent), tdt (R = Me-4), $S_2C_6H_3SiPh_3$-3) are prepared by OAT to the corresponding oxo—Mo^{IV} complexes,[362] although (**141**) is more conveniently obtained by reacting Na_2MoO_4 with Na_2mnt in aqueous buffer at pH 6.[363] These red–brown salts are characterized by low-energy $\nu_s(MoO_2)$ and $\nu_{as}(MoO_2)$ IR modes at ca. 890–850 and 850–820 cm^{-1}, respectively. Interestingly, resonance Raman studies suggest that the dithiolenes may exert a *trans* influence *on* the oxo ligands, not vice versa.[362,364] The anions of $(PR_4)_2[MoO_2(mnt)_2]$ (R = Bu,[363] Ph[362]) and $(PPh_4)_2[MoO_2(bdt)_2]$[362] exhibit distorted octahedral structures with *cis* oxo groups and very different Mo—S distances (ca. 2.6 vs. 2.4 Å), the longer being *trans* to the oxo ligands. Mo K- and $L_{2,3}$-edge XAS data for these and related complexes have been reported,[365] as have kinetics studies of the reactions of $[MO_2(mnt)_2]^{2-}$ (M = Mo, W) with hydrogensulfite/dimethylsulfite,[363,366–368] phosphines,[366] and phosphites ($k_{Mo}/k_W \sim 10^2-10^3$).[369] Selected compounds are known to react with silyl chlorides to produce mono(oxo) silyloxo derivatives, e.g., $NEt_4[MoO(OSi^tBuPh_2)(bdt)_2]$ (see (**143**)),[370] while $NEt_4[Mo(OPh)(S_2C_2Me_2)_2]$ reacts with Me_3NO to produce $NEt_4[MoO(OPh)(S_2C_2Me_2)_2]$ (detected in solution).[371] The mono(dithiolene) complex, $NEt_4[MoO_2(bdt)(OSiPh_3)]$, prepared by reacting $MoO_2(OSiPh_3)_2$ with Li_2bdt, undergoes ligand

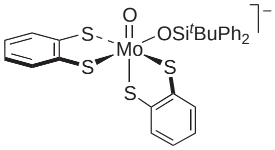
exchange producing NEt_4 [$MoO_2(bdt)(SC_6H_2{}^iPr_3$-2,4,6)], an advanced structural model for sulfite oxidase. Both anions exhibit square pyramidal (pseudo-tetrahedral) structures (see (**144**)).[278]



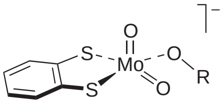
(**141**)



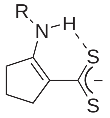
(**142**)



(**143**)



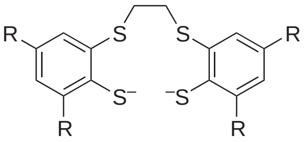
(**144**)



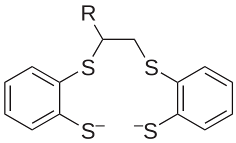
(**145**)

(b) Other sulfur-donor ligand complexes. Work in this mature area was reviewed by Stiefel[1,2] and lead-in references only are cited. Recent reports describe new derivatives of $MoO_2(S_2CNR_2)_2$ and structural, electrochemical, and (OAT) kinetics studies.[324,372] Reactions of $MoO_2(S_2CNR_2)_2$ (R = alkyl) with silanes produce silyloxo, halide, pseudo-halide, and tris(dithiocarbamato) species including $MoOX_2(S_2CNEt_2)_2$ (X = I, NCS), [$MoO(OSiMe_3)(S_2CNEt_2)_2$]OTf, and pentagonal bipyramidal $MoO(OSiMe_3)(CN)(S_2CNEt_2)_2$.[373] New derivatives of well-known $MoOCl_2(S_2CNR_2)_2$[203] and an undergraduate experiment exploring the chemistry of $MoO_2(S_2CNEt_2)_2$[374] have been published. The synthesis and characterization of $MoO_2\{S_2P(OEt)_2\}_2$ has also been reported.[375] Bidentate 2-aminocyclopent-1-ene-1-dithiocarboxylate (**145**, R = H, acda) and its *N*-alkyl derivatives form many complexes of Mo^{VI}–Mo^{III}; a summary of acda chemistry follows. The central starting material in this area, maroon $MoO_2(acda)_2$, reacts with excess Hacda, HX (X = F, Cl, Br, I), HX′ (X′ = BF_4, PF_6), catechols, and arylhydrazines to give $MoO(acda)_3$, $MoOX_2(acda)_2$, [$MoO(acda)_3$]X′, $MoO(cat)(acda)_2$, and $Mo(N_2R)(acda)_3$, respectively.[376,377] Complexes such as $Mo(acda)_4$, $MoO(SR)(acda)_2$ (R = Ph, $C_6H_4NH_2$-2, $CH_2CH_2NH_2$), $Mo(ONR)X_2(acda)_2$, and $Mo(NR)X_2(acda)_2$ are formed when $MoOX_2(acda)_2$ reacts with Hacda, RSH, RNHOH, and Ph_3PNR, respectively.[378] Reaction of [$MoO(acda)_3$]X′ with Hacda, $HSC_6H_4NH_2$-2, or PPh_3 results in $Mo(acda)_4$, $Mo(SC_6H_4NH_2$-2$)(acda)_3$, and $Mo(PPh_3)(acda)_3$, respectively,[376] while Hacda reacts with $MoOCl_2(S_2CNR_2)_2$ and [$MoO(S_2CNR_2)_3$]BF_4 to produce $Mo(acda)_2(S_2CNR_2)_2$ and $Mo(acda)(S_2CNR_2)_3$ species, respectively;[379] $MoOCl(Racda)_2$ and mixed-ligand complexes such as $MoO(acda)(Racda)_2$, $Mo(acda)_2(Racda)_2$, and Mo(ox)(acda)(Racda) are also accessible.

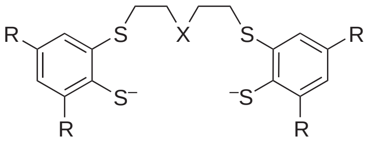
The Mo chemistry of the multidentate S- and mixed-donor ligands (**146**)–(**152**) has been defined by Sellmann *et al.* Orange, diamagnetic *cis*-MoO_2L (L = dttd, Bu_4dttd, Medttd) exhibit distorted octahedral structures with *cis* oxo groups, *trans* thiolate donors, and thioether donors *trans* to oxo. The electrochemistry and OAT reactions of the complexes have been investigated and related oxo—Mo^V and —Mo^{IV} species are known.[380–383] The extensive low-valent Mo chemistry of dttd, Bu_4dttd, and related ligands is described in Section 4.7.6.5.4.



(**146**): R = H (dttd)
(**147**): R = ^{t}Bu (Bu_4dttd)



(**148**): R = Me (Medttd)

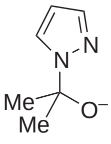


(**149**): X = S, R = H; (**150**): X = S, R = ^{t}Bu
(**151**): X = O, R = H; (**152**): X = NH, R = H

(vi) Complexes containing N/O-donor ligands

A range of simple bidentate N/O-donors form *cis*-MoO_2L_2 complexes. These include aminophenolate,[384] pyrazolyl alcoholate (**153**),[385] pyrazolyl phenolate (**154**),[386] benzimidazolyl alcoholate (**155**),[386,387] and Schiff base ligands (where claims of 8-coordination are doubtful).[388] Interest in asymmetric epoxidations has led to the recent investigation of complexes containing chiral NO-donor ligands such as oxazolines (**156**)[389] and pyridyl alcoholates including (**157**)–(**159**).[291,390–393] The complexes display good activity and variable (<26%) optical induction in the asymmetric epoxidation of *trans*-β-methylstyrene.

Schiff base (SB) complexes of the type, *cis*-MoO_2(SB)L (L = neutral donor), have attracted much attention and early work has been reviewed.[394] These complexes generally exhibit distorted octahedral geometries with *mer*-Schiff base ligands. Complexes containing NO_2-donor ligands derived from salicylaldehyde, 3-methoxysalicylaldehyde, and 2-hydroxy-1-naphthaldehyde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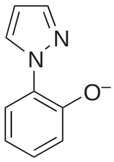
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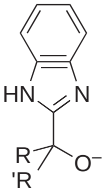
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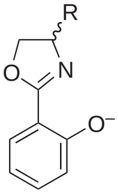
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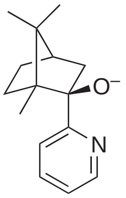
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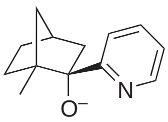
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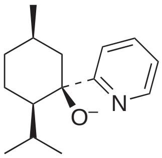
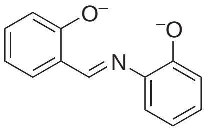

(159)

(**160**)–(**162**)[395–398] have been prepared and structurally characterized, as have complexes containing the hydrazones (**163**)–(**166**).[395,399–403] The Schiff bases formed from salicylaldehyde and Girard Reagents T and P (**166**) are unusual in forming cationic complexes, $[MoO_2(SB)(MeOH)]^+$.[402,403] NO_2-Donor Schiff base complexes are generally poor OAT agents (cf. N/O/S-donors, Section 4.7.2.3.3(vii)).[324] Indeed, some Schiff base complexes inhibit rather than accelerate the aerial oxidation of aldehydes, presumably by scavenging radicals.[396] Some potentially quinquidentate Schiff bases also form *cis*-MoO_2L complexes, where L acts as a tridentate ligand.[404] Electrochemical, spectroscopic, and kinetics studies have been reported for many of the complexes above.[405] Related amino alcoholate and phenolate ligands, (**167**) (R var. Me, CH_2OH)[397] and (**168**),[406] form similar complexes. The reaction of $MoO_2(acac)_2$ with the free acid of (**168**) produces $[MoO_2(\mathbf{168})]_2(\mu\text{-}O)$, that is converted to $MoO_2X(\mathbf{168})$ ($X = Cl$, N_3) upon treatment with Me_3SiX; these complexes are efficient epoxidation catalysts.[406]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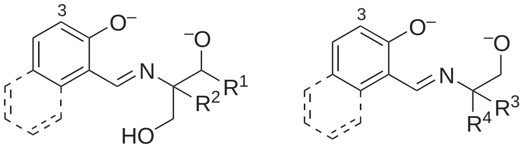
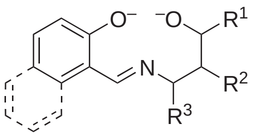
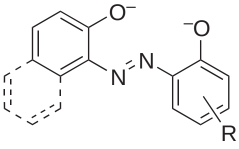
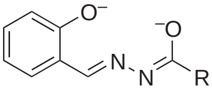
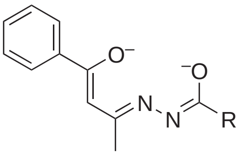
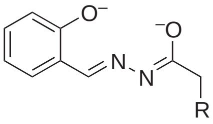

(161): R^{1-4} variously H, Me, Et, Ph, CH_2OH

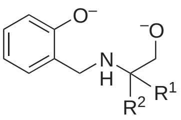

(162): $R^{1/2}$ or $R^{2/3} = C_4H_4$


(163)


(164): R = Ph, Bz, py, C_6H_4OH–2


(165): R = Ph, Nap


(166): $R = NMe_3^+$ (T) or $NC_5H_5^+$ (P)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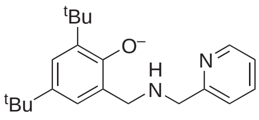
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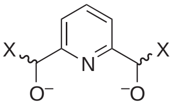
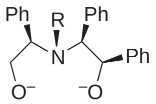

(169): R = ^tBu

(170): R = (=O) (pdc)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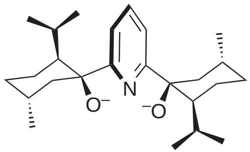
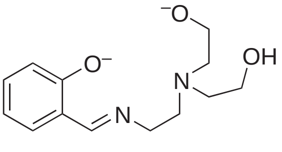
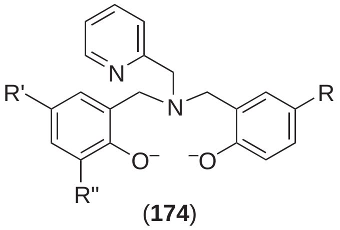

(172)

Dioxo complexes of 2,6-pyridinedimethanolates (**169**) are mononuclear in the solid as well as solution states and exhibit trigonal bipyramidal structures with axial alcoholate donors.[275] Related complexes, $MoO_2(pdc)L$ (pdc = (**170**); L = O- or N-donor), are efficient catalysts for the deoxygenation of azoxybenzene with PPh_3 in boiling toluene. Indeed, their reactivity and stability at high temperatures make them valuable in effecting "difficult" OAT reactions.[407] Many five-coordinate NO_2-donor complexes participate in $Mo{=}O \rightarrow Mo$ interactions in the solid state.[1,2] This is the case for *cis*-$MoO_2(\mathbf{171})$ ($R = H$, Me), that adopt linear polymeric $Mo{=}O \rightarrow Mo$ structures ($d(Mo{=}O)$ 1.739(4) Å, $d(O \rightarrow Mo)$ 2.246(4) Å, for $R = H$),[408] and $MoO_2(\mathbf{172}) \cdot C_6H_{14}$, that crystallizes as a "diamond core" dimer having $Mo{=}O \rightarrow Mo$ character ($(d(Mo{=}O))_{av}$ 1.768 Å, $d(O \rightarrow Mo)_{av}$ 2.432 Å).[409]

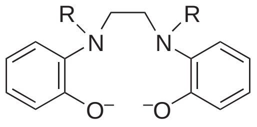
The ligands (**173**) (and its saturated analog),[410] (**174**) and (**175**)[411,412] react with $MoO_2(acac)_2$ to produce *cis*-dioxo complexes with N bound *trans* to oxo.[410] The complex of (**174**) ($R = R' = NO_2$, $R'' = H$) catalyses the oxidation of dmso with benzoin with high efficiency.[411,412] These and other results[407] challenge the requirement of S-donors for effective OAT catalysis.



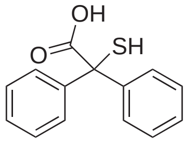
(**173**)



(**174**)



(**175**): R = H, Bz, sub. Bz

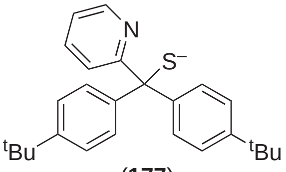


(**176**)

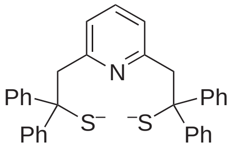
(vii) Complexes containing N/S-donor and mixed chalcogen ligands

N/S-donor ligands like pyridine- or pyrimidine-2-thiolate and ^{t}BuNSPh-*N,S*$^-$ form severely distorted complexes as a result of the small bite angles of the ligands; the S-donors are observed to bind *cis* to oxo in the former but *trans* to oxo in the latter.[149] Yellow, diamagnetic $(NH_4)_2[MoO_2\{O_2CC(S)Ph_2\text{-}O,S\}_2]$ is produced in the reaction of ammonium molybdate with 2,2-diphenyl-2-mercaptoacetic acid (**176**); the anion possesses a distorted octahedral structure in the NH_4^+ and $NHEt_3^+$ salts.[413] Electrochemical studies of solution and hydrotalcite-intercalated forms of the complex have been reported,[414] as has the electrocatalytic reduction of nitrite to ammonia by the complex.[415] Moreover, the hydrotalcite-intercalated form is an efficient catalyst for the oxidation of thiols by dioxygen, dmso and aromatic nitro compounds.[416,417] The reduction of nitrate (or nitrite) by thiols[418] and various OAT reactions are catalyzed by $(NBu_4)_2$-$[MoO_2\{O_2CC(S)MePh\}_2]$.[419]

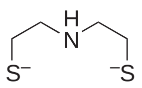
Dioxo complexes of the sterically bulky (thiolato)pyridine and bis(thiolato)pyridine ligands (**177**) and (**178**) have been described by Holm and co-workers; a distorted octahedral structure is observed for *cis*-MoO_2(**177**),[420] whereas MoO_2(**178**) adopts a trigonal bipyramidal structure with axial thiolate donors.[276] The desire to prevent comproportionation and maintain mononuclearity upon OAT was realized in the (thiolato)pyridine system[420,421] but not the bis(thiolato)pyridine system.[422] A trigonal bipyramidal structure is adopted by related NS_2-donor ligand complexes, e.g., *cis*-MoO_2(**179**).[277] Schiff base (SB) and related ligands such as (**180**) and derivatives,[423–426] (**181**) (R = NHPh, NH_2, Ph, SR etc),[427–431] (**182**),[432] and (**183**)[433] form complexes of the type *cis,mer*-MoO_2(SB) (associated in the solid state) and *cis,mer*-MoO_2(SB)L (L = neutral donor) that closely resemble the NO_2-donor complexes discussed in Section 4.7.2.3.3(vi). The structural, electrochemical, and chemical properties of these complexes have been well defined[423–433] and their OAT chemistry reviewed.[324] They are generally more active catalysts than their NO_2-donor counterparts but contrary to earlier reports, dinuclear Mo^V species rather than monomeric Mo^{IV} species appear to be the products of reactions with, e.g., phosphines.[423,433] The multidentate ligand btap (**184**) in distorted octahedral K[MoO_2(btap)] is positioned such that the O- and N-donors are *trans* to the *cis* oxo groups, the S- donors being *trans* and mutually *cis* to the other ligands.[434]



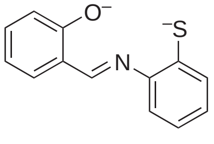
(**177**)



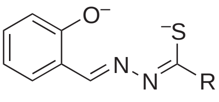
(**178**)



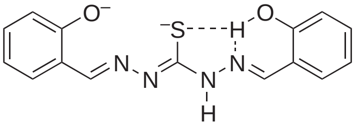
(**179**)



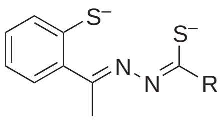
(**180**)



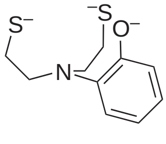
(**181**)



(**182**)

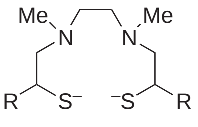


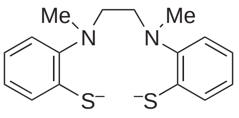
(**183**)

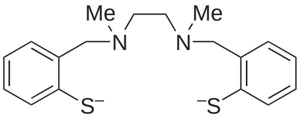


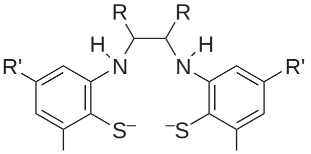
(**184**)

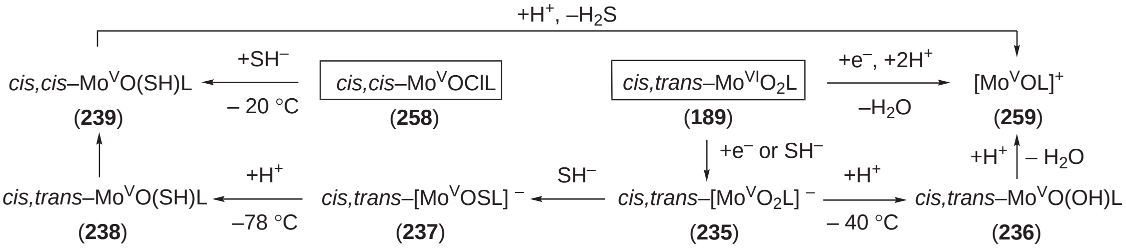
The genesis of research on tetradentate, N_2S_2-donor complexes has been summarized.[2] Since 1985, dioxo—Mo^{VI} complexes bearing the ligands (**185**)–(**188**) have been reported and many have been structurally characterized.[435–437] The structure of *cis,trans*-$MoO_2(L\text{-}N_2S_2)$ (**189**, Scheme 9; boxed species have been isolated and structurally characterized) is typical, with *cis* oxo and *trans* thiolate donors (hence the *cis,trans* designation). There has been intense study of the electrochemistry of these complexes[435,437] and of accessible Mo^V species (Section 4.7.3.3).


(**185**)


(**186**)


(**187**)


(**188**)



Scheme 9 ($L = L - N_2S_2 =$ **186**)

4.7.2.3.4 Monooxo complexes

(i) Porphyrin complexes

Oxo—Mo^{IV} porphyrin complexes, MoO(por) (**190**), react with O_2 in solution or the solid state forming dark-red $MoO(O_2)$(por) (**126**), exhibiting $\nu(Mo{=}O)$ and $\nu(O–O)$ IR bands at ca. 910 and 926 cm^{-1}, respectively (see Scheme 8 and Section 4.7.2.3.3(iii).[438–440] The compounds are stable in the dark but lose O_2 with full or partial regeneration of MoO(por) upon irradiation.[440] The X-ray structure of *cis*-$MoO(O_2)$(tmp) reveals *cis* oxo and peroxo ligands and a saddle-shaped porphyrin with Mo 1.0 Å above the N_4-plane. The molecule has effective C_s symmetry with $d(Mo{=}O)$ 1.697(13) Å and $d(O–O)$ 1.42(3) Å.[441] The structure is retained in solution and appears to be shared by all derivatives.[440] Chemical or electrochemical oxidation of $MoO(O_2)$(tmp) results in reduction of the metal center, producing $[MoO(tmp)]^+$ or *trans*-MoO(tmp)X (**191**) (in the presence of X^-) and O_2. Initial formation of a superoxo species that reduces Mo^{VI} to Mo^V with concomitant production of O_2 is proposed.[442]

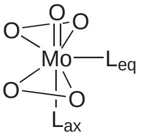
(ii) Diolate, catecholate, and calixarene complexes

Ligand-centered redox has stimulated interest in species containing catecholate and its derivatives (L). Seven-coordinate $MoOL(S_2CNEt_2)_2$ are produced in the reactions of $MoO_2(S_2CNEt_2)_2$ with catechols or upon oxidative addition of *o*-quinones to $MoO(S_2CNEt_2)_2$.[443] Pentagonal bipyramidal structures with apical oxo ($\nu(Mo{=}O)$ 922–906 cm^{-1}) and equatorial dithiocarbamate groups are postulated. Related, hydroxylamido complexes, $MoOL(ONR_2)_2$ (R = Me, Et, Bz; $\nu(Mo{=}O)$ 930–915 cm^{-1}) are produced in the reactions of $MoO_2(ONR_2)_2$ and catechols in methanol.[444] The complex electrochemical behavior of these and related dithiocarbamate complexes spans $Mo^{VI,V,IV}$ and (where applicable) catecholate, semiquinone, and quinone oxidation levels.[443–445] Blue–green MoOL(SB) (SB = (**160**),[446] (**180**),[447] (**181**) (R = NHPh)[448]) and MoOL(tbp) (tbp = 2,2′-thiobis (phenolate)s),[449] are also known. These 6-coordinate complexes display a $\nu(Mo{=}O)$ IR band at 950–930 cm^{-1} and are notable for the reversibility of their Mo^{VI}/Mo^V redox couple (cf. 7-coordinate species). The first mononuclear Mo calixarene complexes reported were oddly colored $MoO(O_4{}^{Bu}\text{-cal})\cdot\{(HO)_4{}^{Bu}cal\}\cdot 2CH_2Cl_2$ and $MoO(O_4{}^{Bu}cal)(H_2O)\cdot\{(HO)_4{}^{Bu}cal\}\cdot PhNO_2$. The X-ray structure of the latter revealed discrete $MoO(O_4{}^{Bu}cal)(H_2O)$ and $(HO)_4{}^{Bu}cal$ molecules arranged to resemble a Fabergé egg encapsulating a nitrobenzene molecule H-bonded to the aqua ligand.[450] Related phenyldiazenyl functionalized oxo—Mo^{VI} complexes have recently been reported.[451] Red–purple $MoOCl_2\{O_2(OR)_2{}^{Bu}cal\}$ ($R = Me$, Et) are formed in the reactions of $MoOCl_4$ with 1,3-dialkyl *p-tert*-butylcalix[4]arenes in hexane.[452] The X-ray crystal structure of $MoOCl_2\{O_2(OEt)_2{}^{Bu}cal\}\cdot CHCl_3$ confirmed the monomeric nature of the complexes and revealed a novel *fac*-tridentate, "collapsed" calixarene moiety. Finally, the synthesis and X-ray structure of $MoO(OTeF_5)_4$ (d(Mo=O) 1.66(2) Å) has been reported by Turowsky and Seppelt.[453]

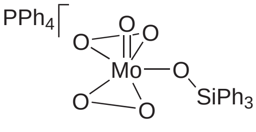
(iii) Peroxide complexes

Peroxide complexes are intermediates in industrially important epoxidation reactions and research in this area is focused on mechanism and the development of regioselective, stereoselective, and environmentally benign industrial processes. Oxodiperoxo and oxoperoxo complexes will be discussed in that order. Reviews by Dickman and Pope[454] and Caradonna[455] provide full accounts of peroxo complexes and their use as oxidants in the period prior to 1994.

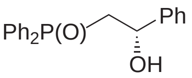
So-called "Mimoun-type" peroxo complexes, $[MoO(O_2)_2L_{eq}L_{ax}]^{0/n-}$ (**192**), are produced by the addition of ligands to solutions of MoO_3 in 30% H_2O_2, acidification of molybdate/ligand solutions in 30% H_2O_2,[2] or electrosynthesis;[456] water, amides, ureas, phosphoramides, amino acids, pyridines, N-, P- and As-oxides or combinations thereof, along with bidentate N-, P-, O-, and mixed-donor (ax/eq) ligands are all known to form complexes of this sort and many have been structurally characterized. Mimoun complexes generally exhibit pentagonal bipyramidal structures, with axial oxo (d(Mo=O) 1.659–1.682 Å) and L_{ax} ligands and equatorial side-on bound peroxo and L_{eq} ligands; the peroxide ligands are asymmetrically coordinated, the Mo—O bond proximal to L_{eq} being longer (by $<3\%$) than the other (both in the range 1.898–1.974 Å), while d(O—O) and $\angle$(O—Mo—O) fall into narrow ranges ca. 1.47 Å and 44.5°, respectively. Six-coordinate, pseudo-tetrahedral (or pentagonal pyramidal) $PPh_4[MoO(O_2)_2(OSiPh_3)]$ (**193**), with symmetrically bound peroxo ligands and a vacant site *trans* to oxo, is structurally unique.[457] The complexes exhibit three IR bands assignable to ν(O—O) and $\nu_s(MoO_2)/\nu_{as}(MoO_2)$ modes in the regions 950–800 cm^{-1} and 660–500 cm^{-1}, respectively; the ν(Mo=O) IR band appears at ca. 970–950 cm^{-1}.[458] Mimoun complexes are effective reagents for the selective oxidation of alcohols to aldehydes, amines to nitroso compounds, sulfides to sulfoxides (and thence sulfones), phenols to *o*-quinones, and in the sulfoxidation of thianthrene 5-oxide, etc.[455] Computional studies of olefin epoxidation by Mimoun complexes support a mechanism involving direct transfer of a peroxide oxygen atom to olefin via a *spiro* transition state.[459–461] Kinetics studies of the oxidation of bromide[462] and OAT[463] by oxo(peroxo) complexes have been reported.



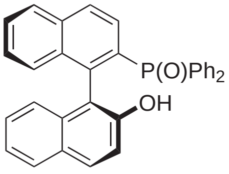
(192)



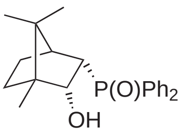
(193)



(194): *R* isomer

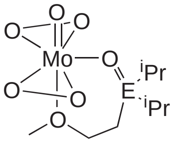


(195): *S* isomer

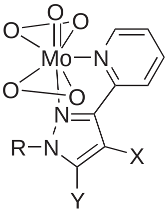


(196): *R,R,S* isomer

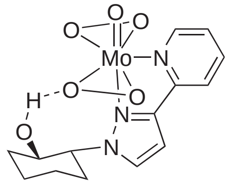
Djordjevic *et al.*[464] have described the synthesis and characterization of amino acid complexes $MoO(O_2)_2L_{eq}(OH_2)$ (**192**) and the X-ray structures of the Gly, Ala, and Pro derivatives. Chiral ligands such as (*R*)/(*S*)-(**194**), (*R*)/(*S*)-(**195**), and (*R,R,S*)/(*R,S,R*)-(**196**) form Mimoun complexes, $MoO(O_2)_2L$ and $MoO(O_2)_2L(OH_2)$. IR and ^{31}P NMR data, as well as the X-ray structure of pentagonal bipyramidal $MoO(O_2)_2$(*R,R,S*-**196**)(OH_2), indicate the presence of equatorial phosphoryl donors.[465,466] Enantioselectivity in the stoichiometric epoxidation of pro-chiral olefins was marginal ($<10\%$) except in the case of the binaphthyl derivatives ($L = $ **195**) where e.e.'s of up to 39% were recorded.[466] Related structures are observed for phosphine oxide[458,467] and chelate complexes such as $MoO(O_2)_2\{OE(^iPr)_2CH_2CH_2OMe\}$ (**197**, $E = P$, As).[458,468] An efficient biphasic catalytic epoxidation system based on $MoO(O_2)_2(OPR_3)$ ($R = n$-dodecyl) has been developed and the activity of related complexes assessed.[460] Earlier attempts to produce aqueous oxidants included the synthesis of water-soluble bpy derivatives.[469,470]



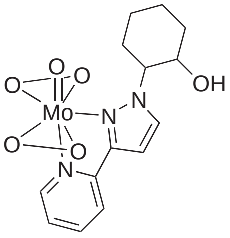
(**197**)



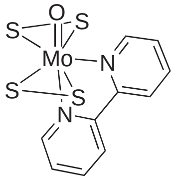
(**198**)



(**199**): isomer A



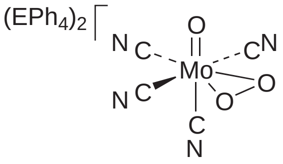
(**199**): isomer B



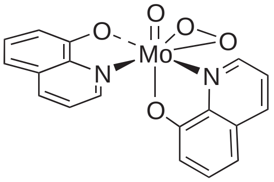
(**200**)

Complexes containing bidentate 2-(pyrazol-3-yl)pyridine ligands (**198**; R = alkyl; X/Y var. H, Cl, Br, Me, NO_2, CF_3, Ph) have been extensively studied by Thiel and co-workers.[471–477] In the solid state, the pentagonal bipyramidal complexes invariably bind the pyridine and pyrazole units at equatorial and axial sites, respectively, but isomerism is detectable. The stability of isomers A and B of *rac*-$MoO(O_2)_2$(ppc) and (1*S*,2*S*)-$MoO(O_2)_2$(ppc) (**199**) is dictated by the H-bonding capabilities of solvents and crystal lattices.[477] The observation of isomer A is consistent with NMR and theoretical studies supporting the preferential protonation of peroxo rather than oxo atoms in Mimoun complexes.[474,477] The complexes are effective epoxidation catalysts and the mechanisms of the reactions have been probed.[471–476] Pyrazolyl–pyridine complexes are also photoactive and produce both singlet and triplet O_2 upon irradiation.[478] A pentagonal bipyramidal persulfido analog, $MoO(S_2)_2$(bpy) (**200**), with ν(Mo═O) 930 cm^{-1}, ν(S—S) 540 cm^{-1}, *d*(Mo═O) 1.69(1) Å and *d*(S–S) 2.038(6)/2.055(6) Å, has also been reported.[479]

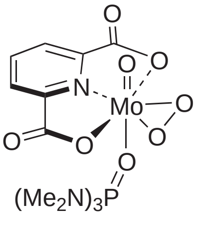
Oxoperoxo complexes, $[MoO(O_2)L_n]^{0/n-}$, are relatively rare. The salts, $(EPh_4)_3[MoO(CN)_5]$ (E = P, As), react with O_2 to produce $(EPh_4)_2[MoO(O_2)(CN)_4]$ (**201**), that in turn react with $AgBF_4$ and PPh_3BzCl in hmpa to yield *mer*-$PPh_3Bz[MoO(O_2)(CN)_3(hmpa)]$; autoxidation of $(PPh_4)_2[MoO(CN)_4(pyrazine)]$ also yields $(PPh_4)_2[MoO(O_2)(CN)_4]$.[480] Hydrogen bonding to lattice or solvent water is thought to prevent the autoxidation of other salts of $[MoO(CN)_5]^{3-}$.[481] The anionic complexes exhibit pseudo-octahedral structures with orthogonal Mo═O and O–O units and variously facilitate the oxidation of PPh_3 and epoxidation of cyclooctene.[482] Yellow, ill-defined $MoO(O_2)_2\cdot 2quinH$, formed in the reaction of MoO_3 with 8-hydroxyquinoline in 30% H_2O_2, converts to orange, pentagonal bipyramidal $MoO(O_2)(quin)_2$ (**202**) upon slow recrystallization. The compounds are active catalyst or catalyst precursor, respectively, for the autoxidation of methylbenzenes (e.g., toluene, *o*-xylene, and *p*-xylene) to carboxylic acids.[483] The formation constants of $MoO(O_2)$(pdc) (log K_f ca. 23) and $[MoO(O_2)(nta)]^-$ (nta = nitrilotriacetate; log K_f ca. 28) have been measured[463] and the X-ray structures of $MoO(O_2)$(pdc)(hmpa) (**203**)[484] and $K[MoO(O_2)(nta)]\cdot H_2O$ (**204**)[463] determined. Both exhibit pseudo-octahedral geometries with a symmetrical, side-on bound peroxide ligand *cis* and orthogonal to the Mo═O group. An experimental and theoretical electron density distribution study of $MoO(O_2)$(pdc)(hmpa) revealed significant covalency in the Mo–peroxide unit.[484] Related oxaziridine complexes, MoO(ONR)(pdc)(hmpa) (R = 4-aryl derivative) are also known.[2] These thermally unstable complexes are effective catalysts for the oxidation of aryl amines to nitroso compounds by H_2O_2.[485] Reaction of *o*-nitrosotoluene with $(PPh_4)_3[MoO(CN)_5]$ at −30 °C produces pentagonal bipyramidal $(PPh_4)_2[MoO(ONAr)(CN)_5]$, having an axial oxo group and a side-on-bonded $[ONAr]^{2-}$ lying in the equatorial plane.[486] Finally, incorporation of multidentate ligands into peroxo complexes such as $MoO(O_2)L$ (L = Schiff base) or $MoO_2(O_2)L$ (L = diethylenetriamine, etc.) renders them inactive as oxidants for alkenes, phosphines, and related substrates.[487]



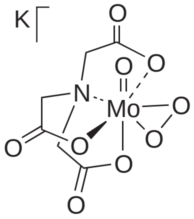
(**201**)



(**202**)



(**203**)



(**204**)

(iv) Dithiocarbamate complexes

Most monooxo, S-donor ligand complexes are dithiocarbamate species. However, $MoO(SC_6H_2{}^iPr_3\text{-}2,4,6)_4$[488] and a few dithiolene complexes (Section 4.7.2.3.3.(v)(a)) have been reported. Convenient syntheses and additional characterization data for $MoO(S_2)(S_2CNR_2)_2$- (R = alkyl) have been reported by Yan and Young,[489] complexes of this type being effective catalysts for the episulfurization of (*E*)-cycloalkenes by elemental sulfur.[490] Oxidation of $MoO(S_2)(S_2CNEt_2)_2$ with 3-chloroperoxybenzoic acid or reaction of $Mo_2O_3(S_2CNEt_2)_4$ or $MoO(S_2CNEt_2)_2$ with the S_2O source 4,5-diphenyl-3,6-dihydro-1,2-dithiin 1-oxide produces pentagonal bipyramidal $MoO(S_2O\text{-}S,S')(S_2CNEt_2)_2$, having axial oxo (*d*(Mo═O 1.681(3) Å) and equatorial, side-on bonded S_2O^{2-} ligands (*d*(S–S) 2.029(1) Å, *d*(O—S) 1.454(1) Å, $d(\text{Mo—S})_{av}$ 2.45 Å).[491] A related Mo^V complex, $Mo(S_2O)(S_2CNR_2)_3$, is discussed in Section 4.7.3.6.2. TCNQ radical anion salts of $[MoO(S_2CNR_2)_3]^+$ can be prepared by anion exchange at $[MoO(S_2CNR_2)_3]BF_4$, reaction of $Mo_2O_3(S_2CNR_2)_4$ with TCNQ or reaction of $MoO(S_2CNR_2)_2$ with thiuram disulfides and TCNQ.[492] The X-ray structure of $[MoO(S_2CNR_2)_3]TCNQ$ reveals a pentagonal bipyramidal cation with an apical oxo group (*d*(Mo═O) 1.678(2) Å) and dimeric, eclipsed $(TCNQ)_2{}^{2-}$ anion aggregates. Seven-coordinate catecholate derivatives, $MoOL(S_2CNEt_2)_2$, were described in Section 4.7.2.3.4(ii).

4.7.2.3.5 Oxo–thio complexes

Work in this area is motivated by a desire to understand the unique oxo—thio—Mo^{VI} active site in the Mo hydroxylases. Considerable synthetic challenges arise from the redox incompatibility of Mo^{VI} and sulfide and the reactivity of thio—Mo^{VI} moieties.[239] Pseudo-tetrahedral oxo—thio complexes were discussed in Section 4.7.2.3.1. Reaction of $MoOCl_4$ with $(Me_3Si)_2S$ provides access to $MoOSCl_2$ but this compound has not been exploited in the synthesis of oxo–thio complexes.[283] The red solutions and isolated solids from the reactions of $Na_2[MoO_3L]$ (L = *N,N*-bis(ethanoate)-1-amino-2-methylthioethane(2-)) with B_2S_3 in methanol are purported to contain $[MoO_2SL]^{2-}$ and $[MoOS_2L]^{2-}$.[493] The crystallographic characterization of $[MoO_2Cl_2(OPPh_3)_2{\cdot}MoOSCl_2(OPPh_3)_2]$ has also been reported. The above systems are not particularly well characterized. Orange $MoOS(OSiPh_3)_2L$ (L = phen or bpy derivatives, cf. **129**) are formed in the reactions of $K_2[MoO_3S]$ with Ph_3SiCl and L in basic (NEt_3) acetonitrile. X-ray diffraction confirmed the presence of monomers in the disordered phen and Me_4phen derivatives while EXAFS provided accurate metrical data, viz., *d*(Mo═O) 1.71–1.72 Å, *d*(Mo═S) 2.18–2.19 Å.[333] Sulfur atom transfer from propylene sulfide to green $Tp^xMoO(S_2PR_2)$ (**118**, R = alkyl, Ph) produces red $Tp^xMoOS(S_2PR_2)$ (**205**), OAT to $Tp'MoS(S_2PR_2)$ (**206**) providing an alternative route to related complexes (Scheme 7).[494,495] Available spectroscopic and structural data, including *d*(Mo═S) 2.227(2) Å and *d*(S···S) 2.396(3) Å for octahedral $Tp^*MoOS(S_2P^iPr_2)$, are consistent with the stabilization of the oxo–thio center by an S···S interaction.[495] Reduction or oxidation of the complexes produces Mo^V species (**207**/**208**) with concomitant S—S redox.[496] A related, unperturbed oxo–thio complex, $Tp^{Pr}MoOS(OPh)$ (**209**), is generated in the reaction of $Tp^{Pr}MoO(OPh)(OPEt_3)$ (see **210**) with propylene sulfide. The properties of the complex, especially the observation of strong 1s → π*(Mo═S) S K pre-edge XAS features, are consistent with the presence of a monomer in solution but only a redox dimer, $[Tp^{Pr}MoO(OPh)]_2(\mu\text{-}S_2)$ (**211**), has been isolated in the solid state (however, selected derivatives are monomeric in the solid state).[497] Oxo—thio complexes undergo sulfur rather than oxygen atom transfer to tertiary phosphines and to cyanide.

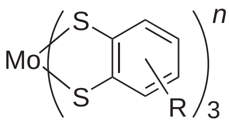
4.7.2.4 Phosphido and Arsenido Complexes and Derivatives

The first terminal phosphido complexes of Mo were reported simultaneously by groups at MIT.[498,499] Cummins and co-workers prepared $MoP(NRAr)_3$ (**212**) by reacting (**1**) with P_4 in diethyl ether (Scheme 1),[498] a method extended to the synthesis of $MoP(N^tBuPh)_3$,[79,83] $MoP\{N(2\text{-}Ad)Ar\}_3$[81] and (indirectly) $MoP\{N^iPrAr\}_3$.[88] The complexes exhibit pseudo-tetrahedral structures with terminal phosphido ligands, *d*(Mo≡P) 2.107(3)–2.119(4) Å. Archetypal $MoP(NRAr)_3$ reacts with mesityl azide to produce (**213**)[498] and with dimethyldioxirane[500] and sulfur or episulfides[498] to give (**214**) (E = O, S, respectively). Schrock and co-workers prepared related complexes, $MoE(N_3N)$ (**215**, E = P, As), by reacting (**13**) with LiEHPh (Scheme 2).[92,499] These have been variously characterized by IR (ν(Mo≡P) 521 cm^{-1}, ν(Mo≡As) 374 cm^{-1}),[501] ^{31}P NMR ($\delta > 1{,}200$ with large CSA),[502] computational,[503] and crystallographic studies; trigonal bipyramidal $MoAs(N_3N)$ possesses an axial terminal arsenido ligand with *d*(Mo≡As) 2.252(3) Å.[92]

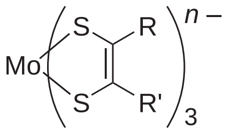
4.7.2.5 Non-oxo Complexes

Detailed analyses of the IR and Raman spectra of known $Mo(OMe)_6$ have been reported;[504] related distorted octahedral species, viz., $Mo(OCH_2CH_2O)_3$ and $Mo(OC_2Me_4O)_3$, are produced in the reactions of nitrido—Mo^{VI} complexes with 1,2-ethanediol or 2,3-dimethyl-2,3-butanediol/base, respectively.[99] The calixarene complexes $Mo(O_4{}^{Bu}cal)\{O_2(OH)_2{}^{Bu}cal\}$ and $(NHEt_3)_2[Mo_2(O_4{}^{Bu}cal)_2]$ are produced in the reactions of $MoCl_4L_2$ ($L = OEt_2$, SEt_2) with $(HO)_4{}^{Bu}cal$ and NEt_3 in toluene at 100 °C. The octahedral coordination geometry of $Mo(O_4{}^{Bu}cal)\{O_2(OH)_2{}^{Bu}cal\}$ is defined by alkoxide donor atoms from tetradentate $O_4{}^{Bu}cal^{4-}$ and bidentate 1,2-$O_2(OH)_2{}^{Bu}cal^{2-}$ ligands. This complex reacts with two equivalents of HCl to give violet *cis*-$MoCl_2(O_4{}^{Bu}cal)$, a potentially valuable starting material for new calixarene chemistry.[505] The synthesis and X-ray structure of octahedral $Mo(OTeF_5)_6$ has also been reported.[453]

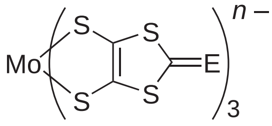
Tris(dithiolene) complexes[5] are potential radical scavengers, photostabilizers, photocatalysts, and components of electro- and photochemical devices. These dark-red or green complexes are produced by reacting dithiolenic precursors with Na_2MoO_4, $MoO_2(acac)_2$ (including a convenient synthesis for $Mo(bdt)_3$[506]), $MoCl_5$ or $MoCl_4(thf)_2$, or via oxidation of Mo^V and Mo^{IV} counterparts. Complexes of this type now include bdt (**216**),[507] ethene-1,2-dithiolate (**217**),[508–511] thioether/thiocarbonate ((**217**), R=R′=SR″; (**218**), E=O, S (dmit)),[512] Diels–Alder (**219**),[513] and crown ether (e.g., (**220**))[507] derivatives (the charge on Mo^{VI} complexes, n, is zero). These are well known for their trigonal prismatic structures, characterized by a twist angle, ϕ(**221**), approaching 0° as observed for $Mo\{S_2C_2(CF_3)_2\}_3$ (ϕ ca. 0°)[514] and $Mo(S_2C_2Me_2)_3$ (ϕ 5.4°).[515] The electronic origins of the trigonal prismatic geometry and discernable bend of the S—C=C—S ligand away from the MoS_2 plane have been assessed by theoretical studies.[514,516] NMR has been used to probe the fluxional behavior and isomer distribution of asymmetric (**217**) (R = H, R′ = Ph and *p*-derivatives).[517] ^{95}Mo NMR and associated studies support extensive electron delocalization and an M^{VI} oxidation state in neutral tris(dithiolene)–Mo/W complexes.[510] Tris(dithiolene) complexes are members of a reversible, three-member electron-transfer series, $[Mo(dithiolene)_3]^{0/1-/2-}$, redox potentials being sensitive to the ligand present.[506–513] Variations in the structural, spectral, and electrochemical properties across the series, $[Mo(S_2C_2Me_2)_3]^{0/1-/2-}$, are consistent with a principally (ca. 80%) ligand-based redox orbital in all members of the series. Complexes such as $Mo(bdt)_3$ and $Mo(tdt)_3$ are susceptible to reduction to Mo^V and Mo^{IV} species by organic bases[518] and NBu_4OH.[519]



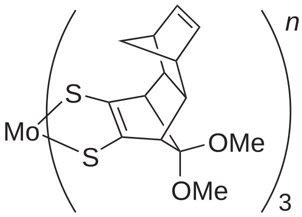
(**216**)



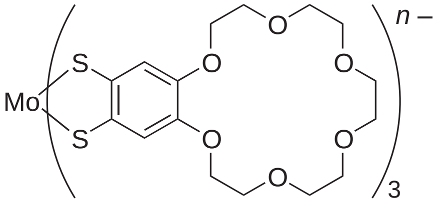
(**217**)



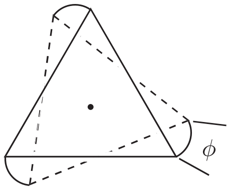
(**218**): E = O, S



(**219**)



(**220**)



(**221**)

Very few non-oxo Mo^{VI} halides are known. These include $Cs[MoF_7]$ and $NO[MoF_7]\cdot MeCN$, prepared by reacting MoF_6 with CatF;[520] the anions exhibit capped octahedral structures in line with theoretical predictions.[521] ^{18}F-radiotracer experiments have revealed rapid and complete intermolecular fluoride exchange between $[MF_7]^-$ and MF_6 (M = Mo, W).[522]

4.7.3 MOLYBDENUM(V)

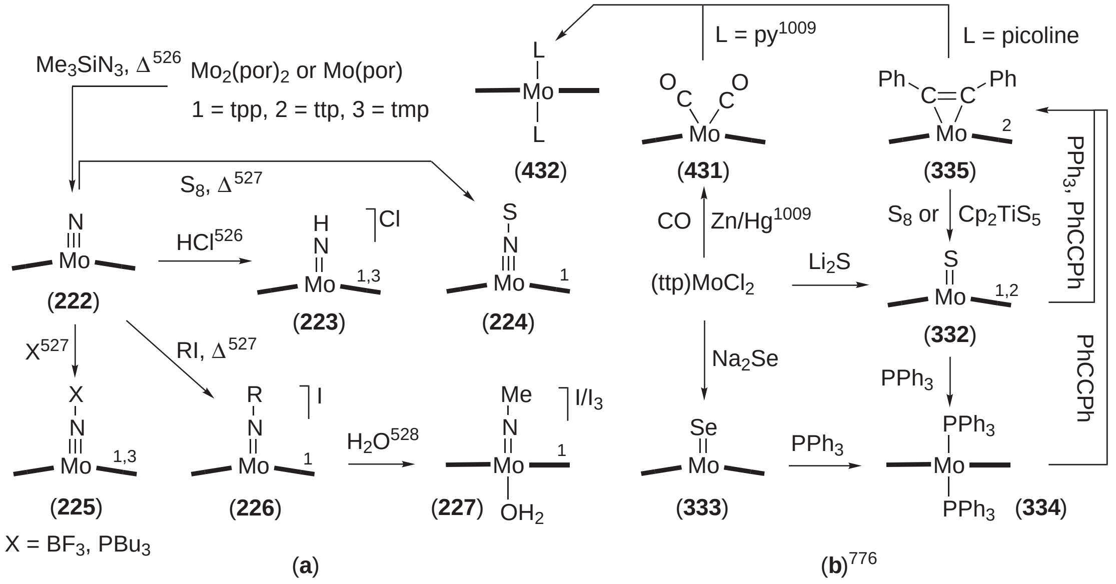
Mononuclear M^V complexes are relatively rare due to the propensity of Mo^V to form di- or polynuclear species. They possess a d^1 electron configuration, are paramagnetic (μ_B 1.65–1.73), and generally exhibit room-temperature EPR spectra featuring clearly resolved Mo hyperfine coupling.[3] The magnetic orbital is orthogonal to strong field ligands such as oxo groups. The observation of EPR active enzyme states has stimulated much of the work in this area.[10,11]

4.7.3.1 Complexes Containing Carbon-donor Ligands

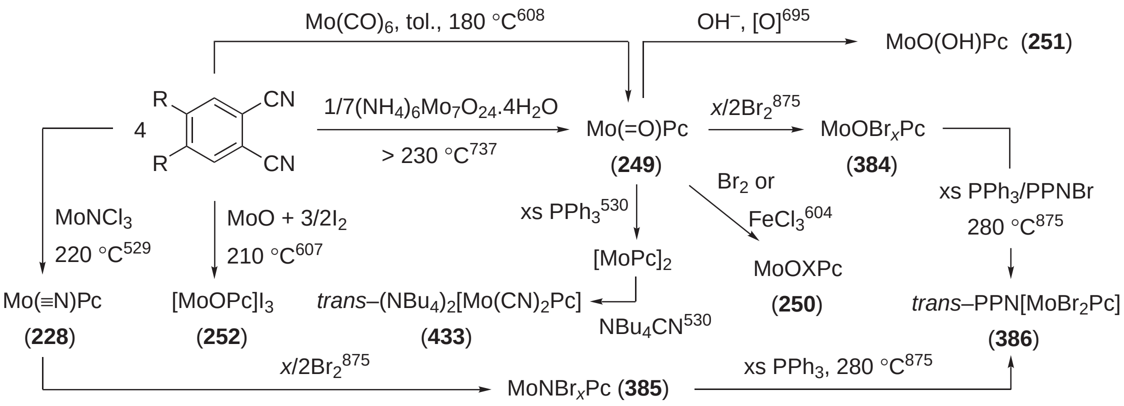
Thermally unstable $MoMe_5$, prepared by reacting $MoCl_5$ with $ZnMe_2$ in diethyl ether below −20 °C, exhibits a square pyramidal structure and an EPR spectrum (g 1.993) with well-resolved superhyperfine coupling to the basal CH_3 groups; these data are consistent with a magnetic orbital of d_{z^2} and d_{xy} character.[523] The alkylidyne and alkylidene complexes, *trans*-$[Mo(CCH_2{}^tBu)F(dppe)_2]BF_4{\cdot}OEt_2$ ($d(Mo{\equiv}C)$ 1.821(7) Å),[524] $Mo(CHSiMe_3)(CH_2SiMe_3)_3$, and $Li[Mo(CHSiMe_3)(CH_2SiMe_3)_4]$, represent earlier contributions to this area.[525]

4.7.3.2 Complexes Containing Nitrogen-donor Ligands

Complexes in this category include limited numbers of nitrido, imido, phosphiniminato, and amido/hydrazido(2-) species (discussed in that order). Nitrido—Mo^V complexes are restricted to porphyrin and phthalocyanine derivatives. Red–purple MoN(por) ((**222**), Scheme 10(a); $\nu(Mo{\equiv}N)$ ca. 1,040 cm^{-1}) are conveniently prepared by reacting Me_3SiN_3 with $[Mo(tpp)]_2$, $[Mo(ttp)]_2$, or Mo(tmp) in refluxing α-chloronaphthalene (T = 259 °C); MoN(tmp) exhibits a square pyramidal structure with $d(Mo{\equiv}N)$ 1.630(4) Å.[526] The nitrido ligand undergoes the reactions in Scheme 10(a), producing (**223**)–(**226**).[527,528] The imido aqua complexes, *trans*-$[Mo(NMe)(tpp)(H_2O)]X$ (**227**), were isolated from attempts to recrystallize [Mo(NMe)(tpp)]I (**226**) from wet benzene ($X = I_3^-$) or toluene ($X = I^-$) and the X-ray structure of octahedral *trans*-$[Mo(NMe)(tpp)(H_2O)]I_3$ was determined.[528] The melt reactions between phthalonitriles and $MoNCl_3$ yield dark-green phthalocyanine complexes, $MoN(R_8Pc)$ ((**228**), Scheme 11);[529] MoNPc (R = H) is also a by-product in the reaction of ammonium molybdate with 1,2-dicyanobenzene in a sealed tube.[530] Low $\nu(Mo{\equiv}N)$ values in the range 974–953 cm^{-1} are consistent with solid state stacking interactions but the complexes are monomeric in solution, with the exception of unsubstituted MoNPc, which forms exciton dimers. EPR spectra (g 1.97) exhibit rich superhyperfine coupling to the five nitrogen donor atoms.[529]



Scheme 10



Scheme 11

The most common imido—Mo^V complexes are of the type, *mer*-$Mo(NR)Cl_3L_2$ (L = neutral ligand). Structural parameters for such complexes include *d*(Mo=N) ca. 1.70–1.73 Å and ∠(Mo=N—C) > 175°, the imido *trans* influence being ca. 0.06–0.15 Å. A potentially general synthesis is exemplified by the comproportionation of $Mo(NMes)_2Cl_2(dme)$ with $MoCl_4(thf)_2$ in dme giving *mer*-$Mo(NMes)Cl_3(dme)$. This complex serves as a starting material for Mo(NMes) $Cl(acac)_2$, *mer*-$Mo(NMes)Cl_3(dppe)$, and $Mo(NMes)Cl_2[CpCo\{P(OEt)_2O\}_3]$.[145] Reduction during the reaction of $MoOCl_4$, Me_3SiCl, $ArNH_2$, and 2,6-lutidine in dme leads to the formation of Mo(N-Ar)Cl_3(dme) whereas octahedral $Mo(NAr)Cl_3L_2$ (L = *N*-2′,6′-diisopropylphenyl-2,5-dimethylbenzamide-*O*) forms in the reaction of $MoOCl_4$ and ArNCO in refluxing *p*-xylene.[531] Recrystallization of $Mo(NC_6H_4CN\text{-}2)Cl_3$, the product of the reaction of $MoCl_5$ and $(Me_3Si)_2NC_6H_4CN\text{-}2$, from NCMe yields *mer*-$Mo(NC_6H_4CN\text{-}2)Cl_3(NCMe)_2$[532] while reduction of $Mo(NC_6H_4Me\text{-}4)Cl_4(thf)$ with phosphines (L) produces $Mo(NC_6H_4Me\text{-}4)Cl_3L_2$ (L = PMe_3, PPh_3, $PEtPh_2$; L_2 = dppe; μ_B 1.73). The X-ray structure of $Mo(NC_6H_4Me\text{-}4)Cl_3(PEtPh_2)_2$ revealed a *mer,trans* configuration but EPR spectra of the dppe derivative indicate a *mer,cis* structure.[156] A related complex, *mer,trans*-$Mo(NC_6H_4NH_2\text{-}2)Cl_3(PMePh_2)_2$, is produced in the reaction of $MoOCl_2(PMePh_2)_3$ with excess *o*-phenylenediamine and NEt_3.[533] Unstable $Mo(NCH_2CH{=}CH_2)Cl_4(thf)$ reacts with $OPPh_3$ to yield structurally characterized *mer,cis*-$Mo(NCH_2CH{=}CH_2)Cl_3(OPPh_3)_2$; air oxidation leads to $MoOCl_3(OPPh_3)_2$.[534] Thermal activation or BuLi reduction of lithium molybdates(VI) leads to lithium molybdate(V) complexes, e.g., $Mo(NAr)_2$(**e**-*C,N*) (see Scheme 4 for structure of **e**-*C,N*), instead of the anticipated alkylidene species. These paramagnetic, EPR-active (*g* 1.97) species are active polymerization and ROMP catalysts.[137,139]

Phosphiniminato Mo^V complexes are uncommon. They include octahedral *trans*-$Mo(NPPh_3)$ $Cl_4(py){\cdot}CH_2Cl_2$ (*d*(Mo=N) 1.719(9) Å, *d*(N—P) 1.653(9) Å, ∠(Mo=N—P) 176.6(6)°), isolated from the reaction of $Mo(N_3S_2)Cl_3(py)$ with PPh_3 in CH_2Cl_2,[535] and $PPh_4[Mo(NPPh_3)Cl_5]{\cdot}CH_2Cl_2$, produced in the reaction of $[MoCl_4(NPPh_3)]_2$ with PPh_4Cl.[536] The crystal structure of *trans*-Mo(N-$PPh_3)Cl_4(OPPh_3)$, a by-product in the reaction of $MoCl_2(NO)_2$ and PPh_3, has been determined.[537]

Hydrazido(2-)–Mo^V complexes are also uncommon and are restricted to $Mo(NNRR')X_3$ species and their phosphine adducts. Purple/black $Mo(NNRR')Cl_3$ (R = R′ = Me, Ph; R = Ph, R′ = H, Me) (alternatively formulated as $Mo(NNRR')Cl_4$, Section 4.7.2.2.4) react with phosphines producing EPR-active species such as $Mo(NNMePh)Cl_3(PPh_3)$, Mo(N-NMePh)$Cl_3(PMe_3)_2$, and $Mo(NNPh_2)Cl_3(dppe)$.[184,185] Red $Mo(NNH_2)X_3(dppe)$ (X = Cl, Br), were prepared from $Mo(N_2)_2(dppe)(PPh_2Me)_2$ upon reaction with HX/ZnX_2; *fac*-$Mo(NNH_2)Br_3(dppe)$ adopts an octahedral geometry with a linear hydrazido(2-) ligand (∠(Mo=N—N) 173(2)°) and reacts with further acid yielding N_2, NH_3, and NH_2NH_2.[538]

4.7.3.3 Dioxo and Oxo–Thio Complexes and their Conjugate Acids

Work involving trispyrazolylborate (Scheme 7) and N_2S_2-donor complexes (Scheme 9) is discussed in that order. Electrochemical or chemical ($CoCp_2$ or SH^-) reduction of Tp^xMoO_2X (**116**) yields long-lived, dioxo–Mo^V anions, $[Tp^xMoO_2X]^-$ (**120**) that can be isolated in some cases, e.g., $CoCp_2[Tp^xMoO_2(SPh)]$ (**229**).[319,539] These complexes exhibit broad anisotropic EPR signals at

g ca. 1.92 and very low energy $\nu(MoO_2)$ IR bands (ca. 870 cm^{-1} and 770 cm^{-1}). They readily protonate forming the conjugate acids, $Tp^xMoO(OH)X$ (**230**), with less anisotropic, doublet EPR signals (g ca. 1.94, A_H ca. $11 \times 10^{-4}\,cm^{-1}$) and $\nu(Mo{=}O)$ and $\nu(Mo{-}O)$ IR bands at 915 cm^{-1} and 535 cm^{-1}, respectively. The anion of $CoCp_2[Tz^*MoO_2(SPh)]$ displays a distorted octahedral structure with d(Mo=O) (1.742(9) Å) and ∠(O=Mo=O) (112.1(4)°) values larger than those of the Mo^{VI} analog (1.700(6) Å and 103.9(2)°, respectively). These data are consistent with a magnetic orbital of significant $MoO_2\ \pi^*$ character. The anions can be trapped as isolable $Tp^*MoO(OH)X$ (**230**)[539] or $Tp^xMoO(OSiMe_3)X$ complexes (**231**).[540] Oxo—thio—Mo^V complexes, $[Tp^xMoOSX]^-$ (**232**) and $[Tp^xMoOS(S_2PR_2)]^-$ (**233**), are the eventual products of the reaction of Tp^xMoO_2X species with SH^-; these are characterized by a larger g and reduced anisotropy compared to their dioxo analogs.[319,321,496] Significantly, brown $CoCp_2[Tp^{Pr}MoOS(OPh)]$ (**234**) has now been isolated from the reaction of $CoCp_2$ with monomeric $Tp^{Pr}MoOS(OPh)$;[497] unlike $PPh_4[MoOS(L\text{-}N_2S_2)]$ (*vide infra*), the S K-edge X-ray absorption spectrum of the complex exhibits strong pre-edge features consistent with the presence of a terminal sulfido ligand.

Reduction of aminothiolate complexes such as MoO_2(**188**) induces proton transfer from the amine units to an oxo group, with concomitant formation of oxo—Mo^V or —Mo^{IV} amidothiolate complexes and water.[437] However, reduction of *N*-protected complexes permits *in situ* generation of dioxo— and oxo—thio—Mo^V complexes and/or their conjugate acids. For example, electrochemical reduction of (**189**) (Scheme 9) produces *cis,trans*-$[MoO_2(L\text{-}N_2S_2)]^-$ (**235**) or *cis,trans*-$MoO(OH)(L\text{-}N_2S_2)$ (**236**), the dioxo anion being characterized by a broad, highly anisotropic EPR signal at g 1.9007, its conjugate acid by a doublet signal at g 1.957 (A_H $15.1 \times 10^{-4}\,cm^{-1}$).[435,436] However, chemical reduction of (**189**) with excess SH^- eventually produces the oxo–thio anion, *cis,trans*-$[MoOS(L\text{-}N_2S_2)]^-$ (**237**); protonation of the anion at low temperature yields *cis,trans*-$MoO(SH)(L\text{-}N_2S_2)$ (**238**), an isomer of which is known (**239**). The EPR signal of (**237**) (g 1.9435) is less anisotropic than that of its dioxo analog. Elegant isotope labeling and multi-frequency EPR studies of these compounds have provided important insights into the electronic structure and mechanism of various molybdoenzymes.[541–543] Singh et al.[544] have reported the isolation of PPh_4[**237**] (devoid of S K pre-edge XAS features) and (**238**) and the geometry, electronic structure, and EPR g-tensors of these and related complexes have been examined by molecular orbital methods.[545]

4.7.3.4 Oxo (Molybdenyl) Complexes

4.7.3.4.1 Halide and pseudohalide complexes

Compounds containing six-coordinate, octahedral $[MoOX_5]^{2-}$ (X = F, Cl, Br, NCS) and $[MoOX_4L]^-$ (X = Cl, Br, I; L = OH_2, ROH, thf, dmf, NCMe, PMe_3) and five-coordinate, square pyramidal $[MoOX_4]^-$ (X = Cl, Br, I) have been extensively studied, some for more than a century.[3] Rational syntheses include: (i) the reduction of molybdate in aqueous HX (X = Cl, Br) by hydrazine hydrate followed by addition of ligand/counterion (see *Inorg. Synth., Vol. 26, p. 36*, for a synthesis of $(NH_4)_2[MoOCl_5]$), and (ii) ligand exchange, e.g., addition of chloride salts to $MoOCl_3(SPPh_3)$ in CH_2Cl_2.[546,547] The thermodynamic stability of the complexes also leads to their frequent isolation following adventitious hydrolysis or oxidation reactions. The EPR-active complexes exhibit strong $\nu(Mo{=}O)$ IR bands in the 1,020–940 cm^{-1} region, with predictable halogen dependences, e.g., for $PPh_4[MoOX_4]$, X = Cl (1,015 cm^{-1}) > Br (1,005 cm^{-1}) > I (970 cm^{-1}).[548] Syntheses for $LH_2[MoOX_5]$ (X = Cl, Br; L = diamine) and their thermal decomposition to "$MoOX_3L$" and HX have been reported.[549] Reaction of $MoOCl_3(PMe_3)_2$ with HCl or CH_2Cl_2 yields $(PHMe_3)_2[MoOCl_5]$ or $PHMe_3[MoOCl_4(PMe_3)]$, respectively,[550] whereas the photolytic reaction of $PPh_4[MoOCl_4(OH_2)]$ with PEt_3 produces $(PPh_4)_2[MoOCl_5]$.[551] Photolysis of *anti*-$(NR_4)_4[Mo_2O_2(\mu\text{-}O)(NCS)_8]$ (R = Me, Et) in NCMe in the presence of O_2 affords $(NR_4)_2[MoO(NCS)_5]$.[552] The crystal structures of $(PHPh_3)_2[MoOCl_5]$ (d(Mo=O) 1.647(5) Å, $d(Mo{-}Cl_{cis})_{av}$ 2.39(1) Å, $d(Mo{-}Cl_{trans})$ 2.563(2) Å),[553] $(PPh_4)_2[MoOCl_5]\cdot 2CH_2Cl_2$ (disordered),[551] and $(NMe_4)_2[MoO(NCS)_5]$ (d(Mo=O) 1.646(5) Å, $d(Mo{-}N_{cis})_{av}$ 2.054 Å, $d(Mo{-}N_{trans})$ 2.228(5) Å) revealed distorted octahedral anions.

A heroic study has defined the difficult chemistry involved in the reaction of $MoCl_5$ with ethanol (and subsequently with other ligands). The products of the reaction depend on stoichiometry and temperature, the unstable monomers $H[MoOCl_4]\cdot 2EtOH$ and $MoOCl_3(HOEt)$ being isolated and structurally characterized. The anion of $H[MoOCl_4]\cdot 2EtOH$ and neutral $MoOCl_3$

(HOEt) adopt square pyramidal structures with apical oxo groups (d(Mo=O) 1.668(4) and 1.641(2) Å, respectively). In the absence of ligands, these eliminate HCl ultimately producing dinuclear $Mo_2O_2Cl_4(\mu\text{-}OEt)_2(\mu\text{-}HOEt)$. Ligand ($MeCH{=}CH_2$, $CH_2{=}CH_2$, CO, $OPPh_3$) addition to $MoOCl_3(HOEt)$ produces $MoOCl_3L(HOEt)$ that also eliminates HCl to produce dinuclear species.[554] The PPN^+ (d(Mo=O) 1.646(6), d(Mo–Cl) 2.342 Å) and $Me_2C{=}NH_2^+$ (d(Mo=O) 1.641(4) Å, $d(\text{Mo–Cl})_{av}$ 2.355 Å) salts of $[MoOCl_4]^-$ have also been structurally characterized; the unusual air stability of $PPN[MoOCl_4]$ is attributed to encapsulation of the anions in hydrophobic channels. Dimers, linear polymers, and clusters are observed in solid state materials such as $KMoOCl_4$, $E_4[MoOCl_4]_2$, $(ECl_3)[MoOCl_4]$ (E = Se, Te), and $[Te_{15}X_4][MoOX_4]_2$ (X = Cl, Br).[555] Air oxidation of $[Mo_3X_{12}]^{3-}$ yields $PPN[MoOBr_4]$, $PPh_4[MoOI_4]$, or $PPh_4[MoOI_4(OH_2)]$, all of which were structurally characterized.[548]

Complexes of the type $[MoOX_4L]^-$ are generated by ligand association or displacement reactions, and numerous salts containing $[MoOCl_4L]^-$ (L = OH_2, thf, dmf, NCMe) and $[MoOX_4L]^-$ (X = Br, I; L = OH_2, thf) have been reported. These exhibit distorted octahedral geometries characterized by short Mo=O bonds (1.62–1.67 Å), long Mo—L_{trans} bonds (>2.3 Å) and the displacement of Mo from the equatorial plane (by ca. 0.3 Å toward oxo). Liquid clathrates are the initial products of the reactions of HCl with $M(CO)_6$ (M = Cr, Mo, W) in the presence of PPh_3 or crown ethers; compounds isolated from these clathrates include structurally characterized $(PHPh_3)_2[MoOCl_5]$, $[H_5O_2{\cdot}15\text{-C-}5][MoOCl_4(OH_2)]$, and $[H_3O{\cdot}18\text{-C-}6][MoOCl_4(OH_2)]$. Bromo compounds such as $(H_3O{\cdot}\text{tetraglyme})[MoOBr_4(OH_2)]$ are also known and a review of such species is available.[556] Reaction of $MoOCl_3(thf)_2$ with $MgCl_2(thf)_2$ produces $[Mg(thf)_x][MoOCl_4(thf)]_2$ ($x = 4$ (CH_2Cl_2 solvate), 6) or $[Mg_2(\mu\text{-}Cl)_3(thf)_6][MoOCl_4(thf)]$ depending on solvent and stoichiometry. All three compounds have been structurally characterized; the anions in the $[Mg(thf)_x]^{2+}$ salts are coordinated to Mg^{2+} through their oxo groups (d(Mo=O) 1.634(6)–1.674(5) Å, d(Mo–O) 2.308(7)–2.376(6) Å).[557,558] The charge-transfer salt $(DT\text{-}TTF^+)[MoOCl_4(OH_2)]$ (DT-TTF = bis(ethylenedithio)tetrathiafulvalene) was prepared by anodic electrocrystallization of mixtures of DT-TTF and $NEt_4[MoOCl_4(OH_2)]$ or $NEt_4[MoOCl_4]$ (with addition of water) in 1,1,2-trichloroethane. The semiconducting, magnetic material crystallizes with chains of H-bonded (Mo—O—H···O=Mo) anions sandwiched between edge-linked ribbons of $DT\text{-}TTF^+$ cations.[559]

Molybdenyl chloro complexes are typically green–blue in color, with absorption bands at 600–800 nm (usually vibronically coupled to ν(Mo=O)) and 400–530 nm. The assignment of these bands to $d_{xy} \rightarrow d_{xz},d_{yz}$ and $d_{xy} \rightarrow d_{x^2\text{-}y^2}$ ligand field transitions is supported by polarized, single-crystal electronic spectral[546] and MCD studies.[547,560] Higher energy bands are assigned to LMCT transitions.[547,560] Pioneering ENDOR/EPR studies by Attanasio *et al.*[561] set the scene for later work on oriented single crystals, solutions, and powders of, *inter alia*, $[MoOX_4(OH_2)]^-$ (X = F (g 1.902, A_{Mo} $68 \times 10^{-4}\,cm^{-1}$), Cl ($g$ 1.944, A_{Mo} $45 \times 10^{-4}\,cm^{-1}$), Br ($g$ 1.985, A_{Mo} $44 \times 10^{-4}\,cm^{-1}$))[562] and the use of density functional theory in the computation of g values.[563,564] The electronic structures of molybdenyl complexes have also been probed by Mo K-edge XAS.[565] Bromo and iodo complexes are brown/yellow to purple in color due to low-energy LMCT transitions. Complexes such as $[MoOX_4L]^{n-}$ (L = MeCN, H_2O, absent), $[(Me_3tcn)MoOX_2]^+$, and Tp^*MoOX_2 fluoresce in solution with excited state lifetimes favorable to bimolecular redox reactions.[566]

Ligand exchange at molybdenyl centers constitutes a general synthetic route for $MoOCl_3L_2$ complexes. However, complications can arise, as exemplified by the production of oxo—Mo^V, Mo^{IV}, and Mo^{III} species in the thermal and photochemical reactions of $PPh_4[MoOCl_4(NCMe)]$ with phosphines.[551] A *mer* structure is commonly adopted by $MoOCl_3L_2$ complexes.[3] Reaction of $MoOCl_3(dme)$ with 9,10-phenanthrenequinone (L) gives $MoOCl_3L$ with the ligand in the original quinone state. The semiquinone complex, Mo^VCl_4L, and related Mo^{VI} complexes are also accessible.[567] The X-ray structures of *mer*-$MoOCl_3\{C_6H_4(CO_2Et)_2\text{-}1,2\}$,[568] *mer*-$MoOCl_3\{Et_2PCH_2CH_2\text{-}P(O)Et_2\text{-}P,O\}$,[569] *mer,cis*-$MoOCl_3(OPPh_3)_2$, and *mer,cis*-$MoOCl_3(PMe_3)(OPMe_3)$[550] have been reported. The uncharacteristic spectral and photochemical properties of purple $MoOCl_3(PMe_3)_2$[550] and red $MoOCl_3(dppe)$[570] are ascribed to their unusual *fac* structures.

4.7.3.4.2 Complexes containing nitrogen-donor ligands

(i) Tris(amido) complexes

Oxidation of (**1**) with py-O yields brown, paramagnetic (μ_B 1.63), tetrahedral $MoO(NRAr)_3$ (**240**, E = O), characterized by IR (ν(Mo=O) 893 cm^{-1}) and EPR (g 1.96) spectroscopy and X-ray diffraction (d(Mo=O) 1.706(2) Å). The reactions of this complex include t-butyl elimination giving $\mathrm{MoO(NAr)(NRAr)_2}$ and oxidation to $\mathrm{[MoO(NRAr)_3]OTf}$ (ν(Mo=O) 972 cm^{-1}).[571] Reaction of $\mathrm{MoCl_3(thf)_3}$ with Li{N^{t}Bu(C$_6$H$_4$CF$_3$-3)} produces traces of the non-oxo Mo^{V} complex MoF$_2${N^{t}Bu(C$_6$H$_4$CF$_3$-3)}$_3$.[572]

(ii) Pyrazolylborate and related complexes

An extensive range of complexes, Tp*MoOXY (**241**), has been prepared and studied by Enemark and co-workers. The central starting material in this area is green, air-stable Tp*MoOCl$_2$ ((**242**), Scheme 7) prepared by reacting MoCl$_5$ with thf (giving MoOCl$_3$(thf)$_2$) and KTp* (see *Inorg. Synth., Vol. 33, p. 39*).[573] Metathesis can be effected by reacting Tp*MoOCl$_2$ with HX/NEt$_3$ or NaX and the derivatives listed in Figure 1 have been prepared in this fashion.[540,573–579] Others, like (**231**)[540] and Tp*MoOI$_2$,[580] are notable for their alternative syntheses. *In situ*-generated, [Tp^{x}MoO(XY)]$^+$ (**243**, XY = S$_2$PR$_2$$^-$ or S$_2$CNEt$_2$$^-$) and hydroxo species (**244**) are accessible from Mo$^{VI/IV}$ species.[321,495,581] A related complex, [Tp*MoO(OC$_6$H$_4$OEt-4)$_2$]NO$_3$, has been isolated from the reaction of Tp*MoO(OC$_6$H$_4$OEt-4)$_2$ with (NH$_4$)$_2$Ce(NO$_3$)$_6$; it is a component of an OAT cycle featuring oxo—Mo^{VI} and desoxo–Mo^{IV} Tp* species.[582] X-ray structures are available for the derivatives underlined in Figure 1. Distorted octahedral structures with a facial Tp* ligand and mutually *cis* oxo (d(Mo=O)$_{av}$ 1.674 Å) and X/Y ligands are observed in all cases. Spectroscopic studies, including IR (ν(Mo=O) 960–945 cm^{-1}), EPR,[540,573–578,581] single crystal EPR,[583,584] resonance Raman,[585,586] MCD,[560,586,587] photoelectron spectroscopy[588] and L-edge XAS,[565] have contributed to a detailed understanding of the electronic structure of such complexes, particularly those with biologically relevant dithiolene ligands. The complexes generally undergo a quasi-reversible, one-electron reduction at potentials (spanning ca. 1,500 mV!) sensitive to the type, size, conformation, and substituents of X/Y.[573–575,589] For Tp*MoOCl(OC$_6$H$_4$X-4) and Tp*MoO(OC$_6$H$_4$X-4)$_2$, Mo^V/Mo^{IV} potentials correlate with ligand Hammett σ_p parameters while Mo^{VI}/Mo^V potentials correlate with gas phase ionization energies.[590] More recently, McDonagh *et al.* reported the synthesis and spectroelectrochemical properties of 1- and 2-naphtholate complexes and observed marked differences in the energy and intensity of the lowest-energy LMCT band of Tp*MoOCl(OAr) and [Tp*MoOCl(OAr)]$^+$.[591] The synthesis and characterization of Tp^{Pr}MoOCl$_2$ has also been reported.[495] Limited studies of TpMoOCl$_2$ have appeared as it is prone to dinucleation to (**245**).[592] The complex, [Tm*MoOCl$_2$]Cl (ν(Mo=O) 979 cm^{-1}), and related catecholate and ethanedithiolate derivatives have been reported.[262] Very recently, studies of *cis* and *trans* (re phenolate and oxo donors) LMoOCl$_2$ (L = bis(3,5-dimethylpyrazolyl)(2-phenolato)-methanes) inspired a "serine gate" hypothesis for dmso reductase function.[593]

A range of di- and trinuclear complexes containing {Tp*MoOCl} fragments connected by bis- or tris-phenolato bridging ligands has been studied by McCleverty, Ward, and co-workers. The

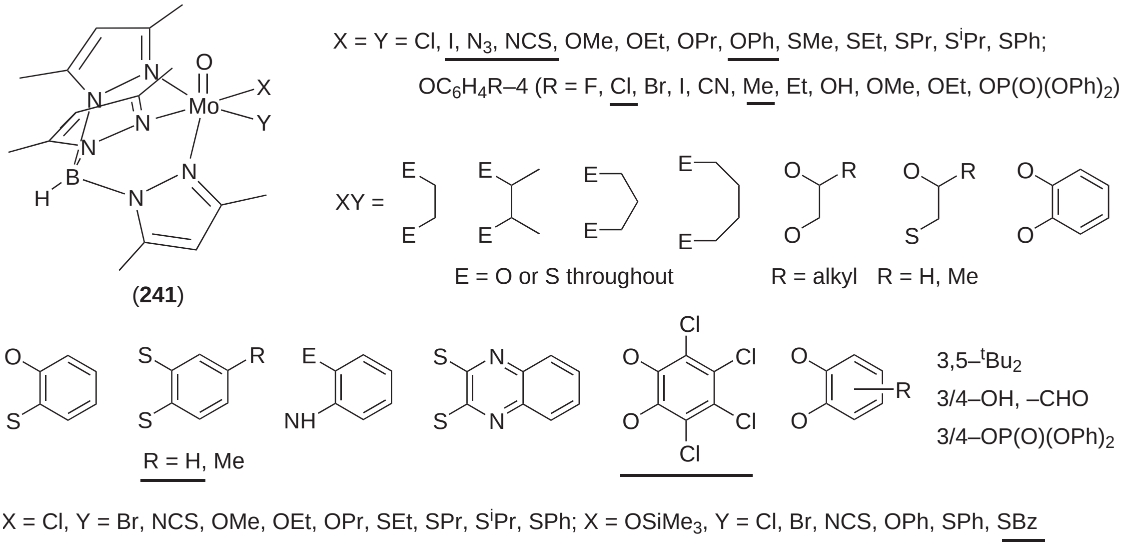


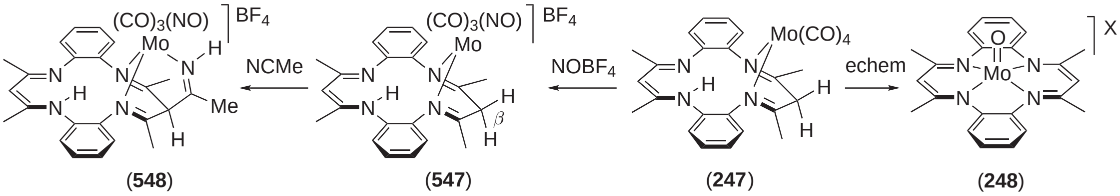
Figure 1 Molybdenyl complexes of T$_p$*.

main thrust of this work has been to investigate how the strong electronic and magnetic interactions between the metal centers are controlled by the structure and properties of the bridging ligand. This work is summarized in Chapter 2.63 and will not be discussed here. The polynuclear complexes can also show remarkable electronic spectroscopic properties with intense near-IR absorptions in their oxidized forms. This near-IR electrochromic behavior and its possible applications are described in Chapter 9.13.

Nitric acid oxidation of (**122**) produces green $[(Me_3tcn)MoOX_2]^+$ (**246**), characterized by IR (ν(Mo=O) ca. 960 cm^{-1}) and magneto- (μ_B ca. 1.9), and electrochemical data (Scheme 6).[325,326] Alkoxy derivatives are known and X-ray structures are available for $[(Me_3tcn)MoOX_2]PF_6$ (X = I, OMe).[326] Related dinuclear Mo^V and mixed-valence species have also been reported.[326,594]

(iii) Porphyrin and phthalocyanine complexes

A wide range of five- and six-coordinate porphyrin complexes of the types $[MoO(por)]^+$ and *trans*-$[MoO(por)X]^{0/+}$ ((**191**), Scheme 8; X including OH^-, Cl^-, Br^-, NCS^-, OR^-, ^-O_2CMe, ^-O_3SPh, NO_3^-, H_2O, dmso) have been reported. These exhibit axial EPR spectra, with *g* ca. 1.965–1.977 and A_{Mo} ca. 55×10^{-4} and 46×10^{-4} cm^{-1} for five- and six-coordinate species, respectively; theoretical calculation of the *g* tensors has advanced considerably.[595] In six-coordinate species, superhyperfine coupling to the porphyrin nitrogens ($A_N \sim 2 \times 10^{-4}$ cm^{-1}) leads to characteristic nine-line resonances. The chemistry, electrochemistry, photochemistry, and catalytic properties of oxo–Mo^V porphyrins have been reviewed (see Scheme 8).[328–330] The structures of six-coordinate *trans*-MoO(tpp)X (X = F^-, NCS^-, NO_3^-) and *trans*-MoO(tmp)(O_3SPh) are typical of MoO(por)X complexes, the Mo atom lying more than 0.3 Å out of the porphyrin plane toward the oxo ligand (d(Mo=O) ca. 1.67 Å).[596,597] The X-ray structure of MoO(ttp)(ClO_4) reveals a six-coordinate structure with a weakly bound perchlorate (*d*(Mo—O) 2.379(2) Å) *trans* to oxo (*d*(Mo=O) 1.658(2) Å); the perchlorate is displaced by water in *trans*-$[MoO(ttp)(OH_2)]ClO_4$ (*d*(Mo=O) 1.658(2) Å, *d*(Mo–O) 2.301(2) Å).[598] Photoreduction of MoO(ttp)X results in homolytic cleavage of the Mo—X bond producing MoO(ttp) (**190**) and a radical derived from the ligand X.[599] The hydroxy complex, MoO(OH)(tpp), has been incorporated into a hydroxide-selective coated wire electrode.[600] Compounds containing *meso*-octamethylporphyrinogen have also been described.[601] Electrochemical oxidation of *cis*-$Mo(CO)_4(tmtaaH_2)$ ((**247**), from $Mo(CO)_6$ and dibenzotetramethyltetraaza[14]annulene) in wet benzonitrile produces $[MoO(tmtaa)]^+$ (**248**) possibly via *trans*-$Mo(PhCN)_2(tmtaa)$ and MoO(tmtaa) (Scheme 12);[602] reaction of $Mo_2(R_2tmtaa)_2$ (R = H, Me, Cl on aryl) with excess TCNE in air permits the isolation of 1,1,2,3,3-pentacyanopropenide salts (ν(Mo=O) 950 cm^{-1}, $g = 1.958$, A_{Mo} 34.9 G).[603] The $[MoO(tmtaa)]^+$ cation features a square pyramidal structure with *d*(Mo=O) 1.670(3) Å and exhibits complicated electrochemical behavior.[603]



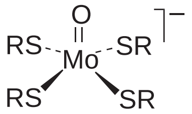
Scheme 12

Molybdenum phthalocyanine (Pc) chemistry is summarized in Scheme 11. The metal-based oxidation of MoOPc (**249**) by $FeCl_3$ or Br_2 produces MoOXPc (**250**, X = Cl, Br), the reaction being reversed by addition of $NaBH_4$.[604] Oxidation of MoOPc in the presence of OH^- yields MoO(OH)Pc (**251**).[605] Photophysical studies of Mo^V tetrasulfophthalocyanine are consistent with reversible dehydrogenation of the ligand upon irradiation.[606] Black–purple $[MoOPc]I_3$ (**252**) is produced in the reaction of 1,2-dicyanobenzene, molybdenum oxide, and iodine at 210 °C. The square pyramidal cations in (**252**) contain an axial oxo ligand (*d*(Mo=O)1.748(3) Å) and are packed in linear arrays with intervening I_3^- anions. The compound is paramagnetic ($\mu_B = 1.72$) and exhibits a solid state conductivity 10^6 times greater than unoxidized (**249**).[607] Earlier, partial oxidation of (**249**) was reported to yield semiconducting $MoOI_xPc$ ($x = 1.4$–2.6).[608]

4.7.3.4.3 Complexes containing sulfur-donor ligands

(i) Thiolate complexes

Compounds containing $[MoO(SR)_4]^-$ (**253**; R = Ph, C_6H_4Me-2) were first reported by Wedd and co-workers in 1978.[3] Synthetic approaches to these and related complexes now include: (i) reaction of thiols with Mo^V starting materials such as $MoOCl_3(thf)_2$ (as employed by the original workers),[609,610] (ii) thiol exchange at $[MoO(SPh)_4]^-$,[610,611] (iii) reaction of $MoO_2(acac)_2$ or $MoOCl_4$ with thiolates,[488,612–614] (iv) reaction of $MoCl_3(thf)_3$ with thiols and 4-methylpyridine *N*-oxide,[615] or (v) reaction of $MoCl_4(NCMe)_2$ with thiolates in wet NCMe.[488] New complexes include: (i) $[MoO(SR)_4]^-$, where R = Ph, Nap, C_6H_4X-4 (X = F, Cl, Me), C_6H_4Cl-3, $C_6H_3Cl_2$-2,6, C_6F_5,[615] C_6HMe_4-2,3,5,6, $C_6H_2X_3$-2,4,6 (X = Me, ^{i}Pr),[488] and $C_6H_4NHC(O)R$ (**254**, R = Me, CF_3, ^{t}Bu);[611] (ii) $[MoOL_2]^-$, where $L = S(CH_2)_nS$ ($n = 2$ (**255**), 3),[612,613] α-2-toluenedithiolate (**256**),[610] tri- and tetrapeptides,[609] and 2,2′-dimercaptobiphenyl (**257**).[614] The deep blue–purple complexes display intense low-energy (500–650 nm) charge-transfer bands comprising multiple $S \rightarrow Mo(d_{xy})$ transitions, as revealed by electronic, MCD, and resonance Raman spectral analysis; the transition energies are strongly dependent on the orientation of the S lone-pair orbitals with respect to the magnetic orbital.[616,617] They are paramagnetic (μ_B ca. 1.9) and EPR-active, with isotropic g and A_{Mo} values in the ranges 1.97–2.00 and $30–35 \times 10^{-4}\,cm^{-1}$, respectively ($g_{||} > 2.01$, $A_{||}$ and $A_{\perp}$ ca. 52–57 and $21–24 \times 10^{-4}\,cm^{-1}$, respectively).[618] The electronic structures of $[MoO(SR)_4]^-$ (R = Ph, C_6H_4Cl-4) were very recently probed by anionic photoelectron spectroscopy.[619] The oxo-tetrathiolate anions exhibit square pyramidal geometries with apical oxo groups; IR spectroscopic and structural data for selected compounds are presented in Table 6. The complexes typically undergo a reversible electrochemical reduction, at potentials spanning ca. 1,000 mV depending on R (alkyl < alkyl-arenes < fluoro derivatives < bdt < H-bonded); some complexes belong to the three-member electron-transfer series, $[MoO(SR)_4]^{0/1-/2-}$.[488] The influence of intra- and intermolecular NH···S hydrogen bonding on the properties and reactivity of such complexes has been assessed.[611,614] In related chemistry, reduction of $[MoO_2\{O_2CC(S)Ph_2\}_2]^{2-}$ with thiols results in the formation of square pyramidal, EPR-active (g 1.985, A_{Mo} $36 \times 10^{-4}\,cm^{-1}$) $[MoO\{O_2CC(S)Ph_2\}_2]^-$, isolated and structurally characterized as the NBu_4^+ salt.[620] The reduction of nitrate (or nitrite) by thiols is catalyzed by $NBu_4[MoO\{O_2CC(S)MePh\}_2]$.[418]



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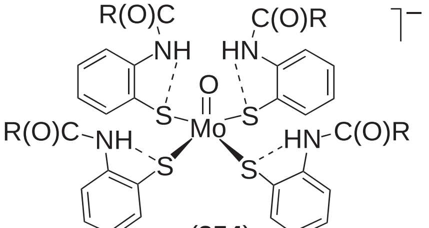

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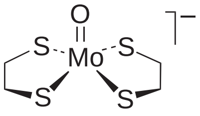

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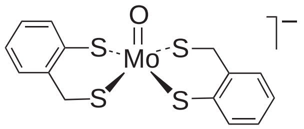

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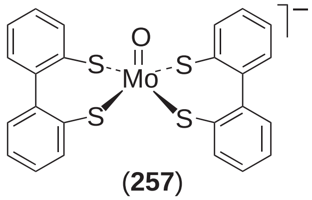


(257)

The synthesis of *cis,cis*-$MoOCl(L\text{-}N_2S_2)$ ((**258**), Scheme 9) and its thermal isomerization to the *cis,trans* isomer has been reported by Barnard *et al.* A number of derivatives, including *cis,cis*-$MoOX(L\text{-}N_2S_2)$ (X = Br, NCS, OMe, OEt) and *cis,trans*-$MoOX(L\text{-}N_2S_2)$ (X = Br, NCS, $OSiMe_3$, OPh, SPh), are accessible via metathesis. Related $[MoO(L\text{-}N_2S_2)]^+$ species (**259**) can be accessed in a number of ways. The spectroscopic and structural attributes of these paramagnetic complexes have been fully defined, providing an interesting example of isomerism in Mo^V chemistry.[621] A trace of *mer*-$[^tBu_2C_3HS_2][MoO(SH)_3(tdpm)]$, characterized by IR spectroscopy (ν(Mo=O) 950 cm^{-1}, ν(S—H) 2,600 cm^{-1}) and X-ray crystallography, is produced in the reaction of $Mo_2O_3(O_2CMe)_4$ and thiodipivaloylmethane (Htdpm).[622] Reaction of $(NH_4)_2[MoOCl_5]$ with $dttdH_2$ (dttd = (**146**))

Table 6 Properties of selected square pyramidal Mo^{V} and Mo^{IV} thiolate and dithiolene complexes.

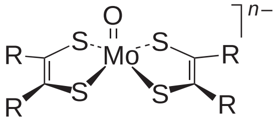
Compound	ν(Mo=O) (cm^{-1})	$Mo^{VI/V}$ (mV)	$Mo^{V/IV}$ (mV)	*d*(Mo—E)[a] (Å)	*d*(Mo–S) (Å)	∠(E—Mo—S)[b] (deg)	Δ[c] (Å)	*References*
$PPh_4[MoO(SC_6H_4NHCOMe)_4]$	937[d]		−360[e]	1.679(4)	2.383(2)–2.407(2)	108.7		611
$PPh_4[MoO(SCH_2CH_2S)_2]$				1.678(5)	av. 2.372(3)	108.8	0.76	612
$PPh_4[MoO(SCH_2CH_2CH_2S)_2]$	930		−615[e]	1.667(8)	2.376(3)–2.398(3)	108.3		613
$NEt_4[MoO(\alpha\text{-tdt})_2]$	940	650[g]	−730[f]	1.688(18)	2.366(7)–2.431(7)	108.4		610
$NHEt_3[MoO(S_2C_{12}H_8)_2]$	944	560[g]	−900[e]	1.684(8)	2.387(4)–2.406(4)	107.1	0.703	614
$NEt_4[MoO(S_2C_2H_2)_2]$	917			1.677(5)	2.362(3)–2.386(2)	108.6	0.757	370
$NEt_4[MoO(S_2C_2Me_2)_2]$	910	150	−620[e]	1.677(3)	2.365(1), 2.371(1)	109.0	0.773	515
$PPh_4[MoO(bdt)_2]$	944		−350[f]	1.668(3)	av. 2.377	108.1	0.74	623
$NEt_4[MoOCl_2(S_2C_2Me_2)]$	962	570	−730[e]	1.679(2)	2.3500(8), 2.3620(7)	106.5	0.712	278
$NEt_4[MoO(S\text{-}2\text{-}Ad)_2(S_2C_2Me_2)]$	924		−1000[e]	1.692(2)	2.391(1), 2.395(1)	109.3	0.790	278
$(PPh_4)_2[MoO(SC_6H_4Cl\text{-}4)_4]$	932	540[d,g]	−650[d,e]	1.690(9)	2.395(3)–2.431(3)	107.7	0.73	753
$(PPh_4)_2[MoO(SC_6H_4NHCOMe)_4]$	902[d]			1.689(5)	2.401(2)–2.421(2)	106.5		611
$(NEt_4)_2[MoO(\alpha\text{-tdt})_2]$	922	650[g]	−730[f]	1.686(4)	2.362(2)–2.433(2)	111.0	0.752	754
$(NEt_4)_2[MoO(S_2C_2H_2)_2]$ [h]	916		−610[e]	1.739(2)	2.394(1)–2.406(1)	108.8	0.774	370
$(NEt_4)_2[MoO(S_2C_2Me_2)_2]$	889			1.712(2)	2.3781(6)–2.3946(6)	108.7	0.765	515
$(NEt_4)_2[MoO(mnt)_2]$	932		480[e]	1.674(11)	2.376(5)–2.390(6)	108.3	0.749	370
$(NEt_4)_2[MoO\{S_2C_2(CF_3)_2\}_2]$	917			1.684(3)	2.365(2)–2.371(2)	109.1		514
$(NEt_4)_2[MoO\{S_2C_2(CO_2Me)_2\}_2]$	914		18	1.686(6)	2.370(2)–2.388(2)	108.9	0.71	744/5
$(NPr_4)_2[MoO\{S_2C_2(CONH_2)_2\}_2]$[i]	915		536	1.682(6)	2.368(3)–2.384(3)	108.8		745
$(NEt_4)_2[MoO(bdt)_2]$	905		−350[f]	1.699(6)	2.388(2)	108.2	0.75	623
$(NEt_4)_2[MoO(tdt)_2]$[h, j]	905		−460[f]	1.665(5)	2.371(3)–2.536(4)	107.5	0.71	742
$(NEt_4)_2[MoO(S_2C_6H_3SiPh_3)_2]\cdot dmf$[h, j]	910		−450[f]	1.677(4)	2.368(2)–2.404(2)	108.6	0.76	742
$(PPh_4)_2[MoO(S_2C_2HPh)_2]\cdot EtOH$[k]	879		−480[f]	1.700(5)	2.366(2)–2.385(2)	109.1	0.78	624
$NEt_4[Mo(O\text{-}2\text{-}Ad)(S_2C_2Me_2)_2]$				1.839(3)	2.3266(9)–2.2291(9)	109.1	0.762	371
$NEt_4[Mo(S\text{-}2\text{-}Ad)(S_2C_2Me_2)_2]$				2.312(1)	2.310(1)–2.318(1)	108.8	0.746	371
$NEt_4[Mo(Se\text{-}2\text{-}Ad)(S_2C_2Me_2)_2]$				2.4387(6)	2.314(1)–2.328(1)	108.6	0.740	371

[a] Distance from Mo to apical donor atom (=O, OR, SR, or SeR). [b] Angle between apical donor and in-plane sulfur atoms. [c] Displacement of Mo from basal plane. [d] Value for NEt_4^+ salt. [e] Versus SCE in MeCN. [f] Versus SCE in dmf. [g] Irreversible. [h] Data for one of two independent molecules. [i] As the $0.5^{i}PrOH\cdot dmf$ solvate. [j] *anti* isomer. [k] *syn* isomer.

produces green, EPR-active MoOCl(dttd)[380] while reactions of $NMe_4[MoO(SR)_4]$ with *N*-salicylidene(2-mercaptoaniline) yield dark-green $NMe_4[MoO(\mathbf{180})(SR)_2]$ (R = Ph, C_6H_4Me-4).[424] Oxo–Mo^V complexes of 2-aminocyclopent-1-ene-1-dithiocarboxylate (**145**) were discussed in Section 4.7.2.3.3(v)(b).

(ii) Dithiolene complexes

Complexes of the type $[MoOL_2]^-$ ((**260**)–(**263**), $n = 1$) are closely related to the thiolate complexes discussed above; they are EPR-active (g ca. 1.98–2.00, A_{Mo} ca. $30 \times 10^{-4}\,cm^{-1}$) and exhibit strong ν(Mo═O) IR bands, reversible electrochemical reductions and square pyramidal structures with apical oxo ligands (Table 6). They are accessed via ligand exchange at $[MoO(SPh)_4]^-$, as in the synthesis of $PPh_4[MoO(bdt)_2]$ (**262**, R = H),[623] or more commonly by oxidation of Mo^{IV} analogs. Thus, iodine oxidation of $(NEt_4)_2[MoO(S_2C_2R_2)_2]$ yields blue/black $NEt_4[MoO(S_2C_2R_2)_2]$ (R = P, Me, Ph (**260**); H/CN (**261**)), the central members of the three-member electron-transfer series, $[MoO(S_2C_2R_2)_2]^{0/1-/2-}$.[371,515] Similarly, ferrocenium oxidation of $[MoO\{SC(H)C(R)S\}_2]^{2-}$ and $[MoO(qdt)_2]^{2-}$ produces $[MoO\{SC(H)C(R)S\}_2]^-$ ((**261**), as *syn (cis)* and *anti (trans)* isomers; R = Ph, pyridin-*n*-yl ($n = 2$, 3, 4), quinoxalin-2-yl and 2-(dimethylaminomethyleneamino)-3-methyl-4-oxopteridin-6-yl)[624] and $[MoO(qdt)_2]^-$ (**263**),[625] respectively. The thermochromism of the latter is assigned to a thermally driven intramolecular charge transfer transition.[625] However, chemical or electrochemical oxidation of $[MoO(mnt)_2]^{2-}$ to $[MoO(mnt)_2]^-$ (**260**, R = CN; g 1.991, A_{Mo} $28.3 \times 10^{-4}\,cm^{-1}$) is followed by disproportionation yielding $[Mo(mnt)_3]^{2-}$ and MoO_3; in the presence of chloride, salts of $[MoOCl(mnt)_2]^{2-}$ are isolated.[363] Similarly, oxidation of $(NBu_4)_2$-$[MoO(dmit)_2]$ produces $NBu_4[MoO(dmit)_2]$;[626] fully or partially oxidized salts exhibit interesting electrical properties.[627,628] The electronic structure of $[MoO(bdt)_2]^-$ has been probed by Mo K- and $L_{2,3}$-edge X-ray absorption,[365] electronic,[629] and anionic photoelectron[619] spectroscopies. The compounds, $NEt_4[MoOL_2]$, react with PhSeCl to produce $NEt_4[MoOCl_2L]$ (L = $S_2C_2Me_2$, bdt), that in turn undergo ligand exchange to yield black–violet $NEt_4[MoO(S\text{-}2\text{-}Ad)_2(S_2C_2Me_2)]$, $NEt_4[MoO(SR)_2(bdt)]$ (R = 2-Ad, $C_6H_2{}^iPr_3$-2,4,6), and $NEt_4[MoOCl(SC_6H_2{}^iPr_3\text{-}2,4,6)(bdt)]$ (**264**), with ν(Mo═O) 924–962 cm^{-1}. These novel Mo^V–dithiolenes exhibit square pyramidal geometries with apical oxo groups and rhombic EPR spectra; they also undergo reversible electrochemical reduction.[278]



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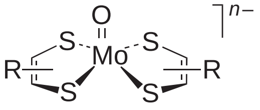

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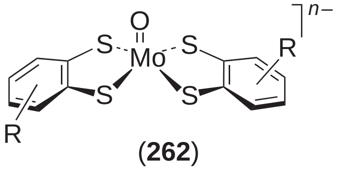

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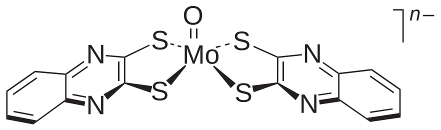

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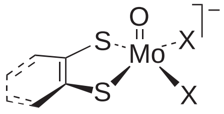
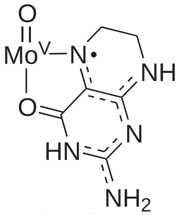


(264)

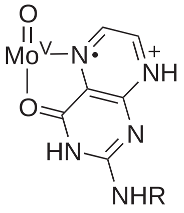
4.7.3.4.4 Pterin complexes

The presence of a pterin moiety in mononuclear Mo enzymes has stimulated work in this area. Concensus has replaced earlier confusion and controversy concerning the formulations, metal and pterin oxidation states, and electronic descriptions of Mo—pterin complexes. High-valent, monomeric oxo—Mo pterin complexes are diamagnetic yet they are formulated, on the basis of X-ray photoelectron and NMR spectroscopic data, as Mo^V species! This formulation and (partial) representations like (**265**) and (**266**) attempt to reflect the extent of electron pair delocalization in these non-innocent (buffered[588]) systems, not the existence of metal- and pterin-based diradicals.[630]

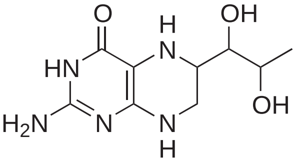
Reactions of MoO_2Cl_2 with the dihydrochlorides of 6*R*-tetrahydro-L-biopterin, H_4P^1 (**267**),[631] tetrahydropterin, H_4P^2 (**268**, R = H),[632] or tetrahydro-6,7-dimethylpterin, H_4P^3 (**268**, R = Me)[633,634] produce red–purple complexes, now formulated as trihydropterin species, *mer*-$MoOCl_3(H_3P^n)$ (cf. (**265**)); these are characterized by ν(Mo=O) ca. 985 cm^{-1} and λ_{max} ca. 485 nm. They exhibit distorted octahedral structures with the pterin carbonyl bound *trans* to the oxo ligand and metrical data indicative of trihydropterin coordination, viz., $d(Mo{=}O)_{av}$ 1.658 Å, $d(Mo{-}O)_{av}$ 2.249 Å, and $d(Mo{-}N)_{av}$ 2.014 Å.[631–633] Blue complexes, formulated as *mer*-$MoOCl_3(HP^n)$ (cf. (**266**)) and protonated at N-8 by virtue of pterin reduction and oxidation of Mo^{IV}, form in the reactions of $MoCl_4(NCMe)_2$ with fully oxidized 6,7-dimethylpterin, P^4 (**269**, R = NH_2), or 2-pivalolyl-6,7-dimethylpterin, P^5 (**269**, R = $NHC(O)^tBu$) in the presence of trace H_2O; these are characterized by ν(Mo=O) ca. 990 cm^{-1} and λ_{max} ca. 560 nm. The complex, *mer*-$MoOCl_3(HP^5)\cdot OEt_2$, exhibits a structure similar to the aforementioned but with d(Mo–N) 2.082(2) Å, indicative of pterin reduction.[633] Pterin complexes with S-donor co-ligands include $[MoO\{C_6H_3N(CH_2S)_2\text{-}2,6\}(H_3P^2)]Cl$, produced in the reaction of $MoO_2\{C_6H_3N(CH_2S)_2\text{-}2,6\}$ with $H_4P^2\cdot 2HCl$, and red dithiocarbamate derivatives, $MoOCl_2(S_2CNEt_2)(H_3P^n)$ and $[MoOCl(S_2CNEt_2)(H_3P^n)]Cl$, formed by reacting $H_4P^3\cdot 2HCl$ or H_4P^6(**270**)$\cdot 2HCl$ with $MoO_2(S_2CNEt_2)_2$ or $MoOCl_2(S_2CNEt_2)_2$.[634–637] The cations of $[MoO\{C_6H_3N(CH_2S)_2\text{-}2,6\}(H_3P^2)]Cl$[636] and $[MoOCl(S_2CNEt_2)(H_3P^3)]Cl\cdot MeOH$[637] are octahedral with a carbonyl oxygen *trans* to oxo and short Mo–N distances (cf. (**265**)). Hydrogen bonding, particularly in the pseudo-dimer units of $[MoOCl(S_2CNEt_2)(H_3P^3)]Cl\cdot MeOH$, and chloride association/dissociation in the S-donor complexes, impact on solution behavior. Related chemistry, including the X-ray structure of $MoOCl_3(HF^1)$ (protonated at uncoordinated N), has been described for 1,3,7,8-tetramethylalloxazine (**271**) and a dispute over the formulation of Mo–flavin complexes has been resolved.[633] For completeness, we mention here Mo^0 complexes, MoL_3, produced from oxidized pterins and $Mo(CO)_6$ in refluxing NCMe. Photoelectron spectra are consistent with considerable π-acid character in the ligands present.[630]



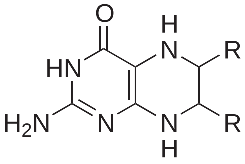
(**265**)



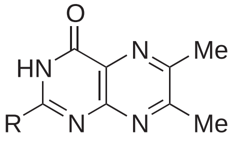
(**266**)



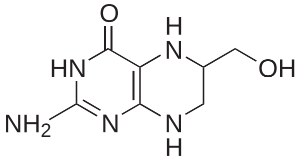
(**267**): H_4P^1



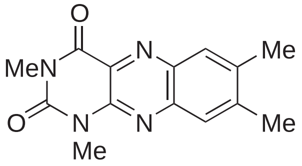
(**268**): $H_4P^{2/3}$



(**269**): $P^{4/5}$



(**270**): P^6



(**271**): F^1

4.7.3.5 Thio, Selenido, and Tellurido Complexes

Thio–Mo^V centers are implicated in the turnover of industrial catalysts and enzymes but mononuclear thiomolybdenyl complexes are rare. The first complex of this type, Tp^*MoSCl_2 (**272**), was prepared by sulfidation of Tp^*MoOCl_2 (**242**) using B_2S_3 (Scheme 7);[638] it has been characterized by IR, UV–visible, EPR,[638] resonance Raman,[585] and X-ray absorption spectroscopy.[544] More recently, derivatives such as Tp^*MoSX_2 (**273**, X = OPh, OC_6H_4X-2 (X = SEt (etp), Pr); X_2 = cat, tdt, bdt) were described.[639] These exhibit a single, strong ν(Mo=S) IR band at 505–490 cm^{-1} and distorted octahedral structures with short Mo=S bonds (2.1279(10) Å for $Tp^*MoS(etp)_2$). The S K-edge X-ray absorption spectra of all derivatives exhibit intense pre-edge $S(1s) \rightarrow \pi^*$ Mo=S transitions characteristic of terminal sulfido ligation.[544,639] Related cationic complexes, e.g., $[Tp'MoS(S_2PR_2)]^+$ (**274**), have been prepared in situ.[321,495]

The reactions of (**1**) with sulfur or ethylene sulfide, Se, and Te/PEt_3 produce $MoE(NRAr)_3$ (**240**) (Scheme 1), E = S, Se, Te, respectively). The tetrahedral complexes were characterized by IR (ν(Mo=E) 492, 342, 286 cm^{-1}, respectively), EPR, magnetochemical (μ_B 1.6–1.9), and crystallographic data (d(Mo=E) 2.1677(12) Å, 2.3115(6) Å, 2.5353(6) Å, respectively). The Mo=S bond dissociation enthalpy of $MoS(NRAr)_3$ was determined at 104.4 ± 1.2 kcal mol^{-1}.[571]

4.7.3.6 Non-oxo Complexes

4.7.3.6.1 Halide and cyanide complexes

Liquid MoF_6 is a powerful oxidant and its reduction with KBr in anhydrous HF or I_2 in NCMe produces $K[MoF_6]$[640] and $[I(NCMe)_2][MoF_6]$,[641] respectively. Oxidation of Ag by MoF_6 in *dry* NCMe produces yellow $[Ag(NCMe)_2][MoF_6]$ rather than the previously reported Ag^{II} salt, while ligand exchange yields $[AgL_4][MoF_6]$ ($L = P(OMe)_3$, py). Further oxidation of $[Ag(py)_4][MoF_6]$ by MoF_6 gives orange $[Ag(py)_4(NCMe)][MoF_6]_3$.[642] A convenient synthesis for $MoF_5(NCMe)$ from MoF_6 and Mo in NCMe has been reported.[643]

Molybdenum pentachloride, a widely used starting material in Mo chemistry, has a solid state structure comprised of edge-shared bioctahedra.[3] However, in the gas and low-temperature matrix phases monomeric units with C_{4v} symmetry are observed;[644] these are unstable with respect to, e.g., $[MoCl_6]^-$. Oxidation of $(\eta^6\text{-}C_6Et_6)Mo(CO)_3$ by Cl_2 or $PhICl_2$ produces EPR-active $[(\eta^6\text{-}C_6Et_6)Mo(CO)_3][MoCl_6]$ (g 1.980, A_{Mo} $45.7 \times 10^{-4}\,cm^{-1}$), containing an octahedral anion with d(Mo—Cl) 2.471(2) Å.[645] The redox potentials of $[MCl_6]^{n-}$ complexes, including the $Mo^{VI/V}$, $Mo^{V/IV}$, and $Mo^{IV/III}$ couples, display periodic trends related to metal core-charge and inter-electron correlation.[646]

The $OPCl_3$ adduct, $MoCl_5(OPCl_3)$, has been prepared and structurally characterized; the complex reacts with urea eventually yielding tetranuclear $[MoNCl_3(OPCl_3)]_4$.[647] Reaction of $MoCl_5$ with di-*i*-propylcarbodiimide in CCl_4 results in the production of dark-green $MoCl_4\{ClC(N^iPr)_2\}$. The complex exhibits a severely distorted octahedral (pseudo-trigonal bipyramidal) geometry with a small ligand bite angle of 63.0(2)° and a "*trans*" Cl—Mo—Cl angle of only 114.0(1)°.[648] Bromine oxidation of $Mo(CC_6H_4Me\text{-}4)(CO)_2[CpCo\{P(O^iPr)_2O\}_3]$ produces red, paramagnetic (μ_B 1.94) $MoBr_4[CpCo\{P(O^iPr)_2O\}_3]$.[649]

Improved syntheses for $[Mo(CN)_8]^{3-}$ salts based on the use of $NaNO_2$ in mineral acid as oxidant have appeared; nitrosonium ion, NO^+, is believed to be the active agent in this proton-assisted reaction.[650] Thiols such as L-cysteine, penicillamine, and thioglycolic acid are oxidized to disulfides by $[Mo(CN)_8]^{3-}$, with concomitant formation of $[Mo(CN)_8]^{4-}$; kinetics studies of these reactions have been reported.[651] The structural and chemical properties of $[Mo(CN)_8]^{3-}$ and related species have been reviewed.[652]

4.7.3.6.2 Complexes containing sulfur and mixed sulfur/nitrogen-donor ligands

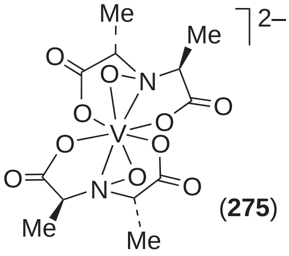
The central members of the three-electron-transfer series, $[Mo(dithiolene)_3]^{0/1-/2-}$ ((**216**)–(**220**), $n = 1$), are conveniently prepared from their Mo^{VI} (Section 4.7.2.5) or Mo^{IV} (Section 4.7.4.6.5(iii)) counterparts.[5] The complexes are EPR active (g ca. 2.002, A_{Mo} $26\text{–}33 \times 10^{-4}\,cm^{-1}$) and exhibit distorted trigonal prismatic structures with d(Mo–S) ca. 2.33–2.38 Å. Compounds such as $NEt_4[Mo(S_2C_2Me_2)_3]\cdot NCMe$ (twist angle, ϕ, 1.6°),[515] $NBu_4[Mo(bdt)_3]$ (ϕ 33.5°)[506,519] and salts of $[Mo(tdt)_3]^-$,[518] are formed by reducing Mo^{VI} species with BH_4^-, EH^- ($E = O$, S), and organic bases, respectively. Iodine or ferrocenium oxidation of Mo^{IV} species produces $Fc[Mo\{S_2C_2(CF_3)_2\}_3]$ (ϕ ca. 0°),[653] $Cat[Mo(qdt)_3]$ ($Cat^+ = PPh_4^+$ (ϕ 14.6°), NEt_4^+),[654] and conducting $Fc[Mo(dmit)_3]$.[655] Insights into the ground electronic state of such complexes were provided by a multifrequency EPR study of related $[Mo(abt)_3]^-$ (abt = *o*-aminobenzenethiolate)[618] and by recent computational studies.[511] Finally, *in situ* electrochemical or chemical oxidation of trigonal prismatic $[Mo\{O_2CC(S)Ph_2\}_3]^{2-}$ is reported to produce $[Mo\{O_2CC(S)Ph_2\}_3]^-$ (g 1.968, A_{Mo} $36 \times 10^{-4}\,cm^{-1}$).[656]

Reaction of $(NEt_4)_2[MoS_4]$ with $(S_2CNEt_2)_2$ produces brown, EPR-active (g 1.977, A_{Mo} 38 G) $Mo(S_2)(S_2CNEt_2)_3$, that exhibits a pentagonal bipyramidal structure with an apical disulfide ligand; the ^iBu derivative is also known.[236,657] The complex reacts with 3-chloroperoxybenzoic acid in CH_2Cl_2 at 0 °C to yield green $Mo(S_2O)(S_2CNEt_2)_3$ (g 1.982, A_{Mo} 39 G), having a pentagonal bipyramidal structure with an asymmetrically bound apical S_2O^{2-}-*S,S′* ligand (a related Mo^{VI} complex, $MoO(S_2O)(S_2CNEt_2)_2$, was described in Section 4.7.2.3.4(iv)). Ferrocenium oxidation of $Mo(S_2)(S_2CNEt_2)_3$ in dry or wet solvents yields $[Mo(S_2CNR_2)_4]^+$ or $[MoO(S_2CNR_2)_3]^+$, respectively.[657] Charge transfer and donor–acceptor coordination compounds of TCNQ and TCNE exhibit unusual magnetic and electrical properties with many potential applications. Reactions of $Mo(S_2CNR_2)_4$ ($R = Me$, Et) with TCNQ or TCNE produce the radical cation–anion salts $[Mo(S_2CNR_2)_4]TCNQ$, $[Mo(S_2CNR_2)_4]TCNE$, and $[Mo(S_2CNR_2)_4][C_3(CN)_5]$

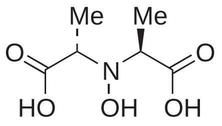
(from TCNE reaction in air). The TCNQ$^-$ salts react with additional TCNQ forming $[Mo(S_2CNR_2)_4](TCNQ)_2$, containing neutral and anionic forms of TCNQ.[658,659] The X-ray structures of $[Mo(S_2CNR_2)_4]TCNQ$ (R = Me,[659] Et[658]) reveal similar eight-coordinate, dodecahedral cations but distinctly different anion packings. A regular dodecahedral geometry is also displayed by the anion of paramagnetic $(NEt_4)_3[Mo(CS_3)_4]$.[660] Reaction of $[MoCl_3(N_3S_2)]_2$ with dithioimidophosphinates produces green, EPR-active $Mo(N_3S_2)\{R_2P(O)NP(S)R_2\}_2$ (R = ^{i}Pr, Ph); both complexes exhibit octahedral structures with planar, bidentate $N_3S_2{}^{3-}$ ligands with O-donors *trans* to the *cis* N donor atoms.[661]

4.7.3.6.3 Complexes containing mixed oxygen/nitrogen-donor ligands

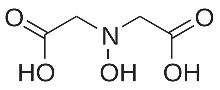
Mushrooms of the genus *Amanita* accumulate vanadium in the form of Amavadin, Δ,Λ-[V(*S,S*-hidpa)$_2$]$^{2-}$ (**275**), a 1:2 complex of V^{IV} and the proligand *S,S*-2,2′-(*N*-hydroxyimino)dipropionic acid (*S,S*-H$_3$hidpa, (**276**)).[662] Molybdenum(V) analogs of Amavadin have now been reported by Garner and co-workers; these brown/purple compounds include Δ,Λ-PPh$_4$[Mo(hida)$_2$]·CH$_2$Cl$_2$ (H$_3$hida = (*N*-hydroxyimino)diacetic acid (**277**)), Δ-PPh$_4$[Mo(*R,R*-hidpa)(*R,S*-hidpa)] (see (**278**) (R = Me) for proligands), H$_5$O$_2$[Mo(*R,R*-hidpa)$_2$], PPh$_4$[Mo(*R,S*-hidba)$_2$]·2H$_2$O, and Δ,Λ-Na[Mo(*R,S*-hidba)$_2$]·0.25^{i}Pr$_2$O (H$_3$hidba = 2,2′-(*N*-hydroxyimino)dibutyric acid, (**278**) (R = Et)).[663,664] Structurally characterized complexes exhibit the eight-coordinate geometry found in Amavadin, the ligands being bound by *trans* κ^2-NO and unidentate carboxylate groups. Absorption bands at ca. 550 nm (ε 10–47 M^{-1} cm^{-1}) and 380 nm (ε 60–134 M^{-1} cm^{-1}) are assigned to $d_{x^2-y^2} \rightarrow (d_{yz},d_{xz})$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transitions, in keeping with the qualitative "electronic equivalence" of *trans*-Mo(κ^2-NO)$_2$ and *trans*-MoO$_2$ moieties. EPR spectra are consistent with a $d_{x^2-y^2}$ ground state and a strong axial ligand field. The complexes are characterized by a reversible oxidation at 0.77–0.96 V vs. SCE, depending on the extent of solvent H-bonding.



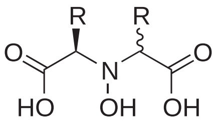
(**275**)



(**276**): *S,S*–H$_3$hidpa



(**277**): H$_3$hida



(**278**): *R,R*–, *R,S*– forms

4.7.4 MOLYBDENUM(IV)

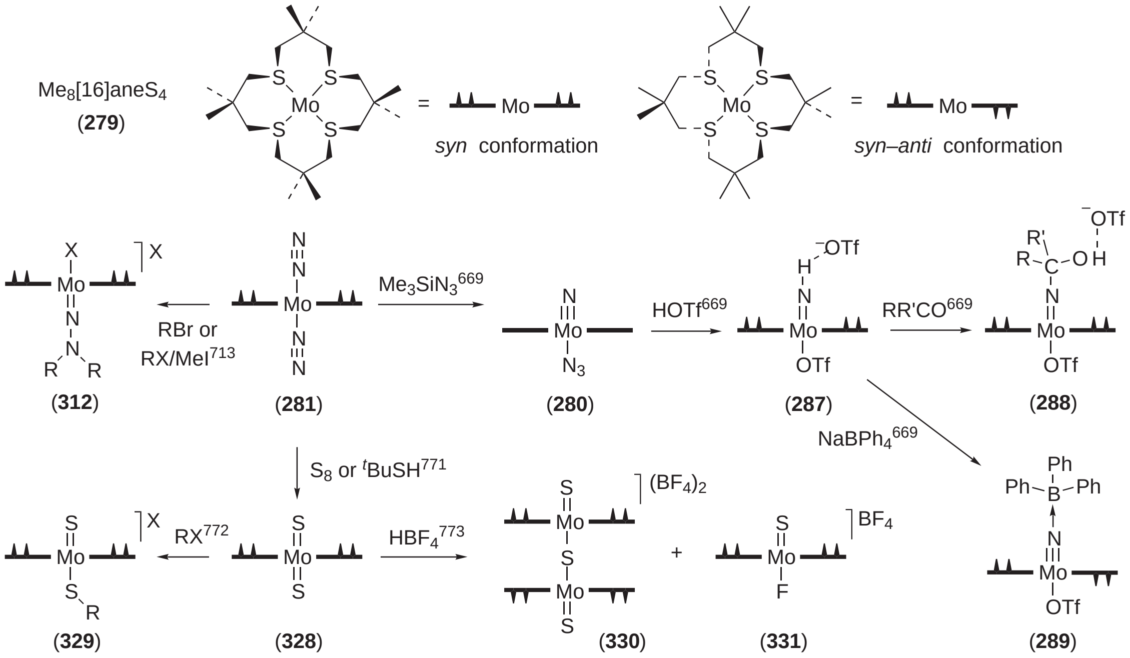
4.7.4.1 Alkyl and Aryl Complexes

New homoleptic compounds include red/purple MoR$_4$ (R = 1-norbornyl, C$_6$H$_4$Me-2) produced in the reactions of LiR/ether and MoCl$_3$(thf)$_3$[665] or MoCl$_4$(thf)$_2$,[666] respectively, at low temperature. These high-spin d^2 complexes are EPR-active and exhibit tetrahedral structures concordant with computational results.[667] Aryne complexes, Mo(η^2-C$_6$H$_3$Me-2)(C$_6$H$_4$Me-2)$_2$L$_2$ (L = PMe$_3$, PMe$_2$Ph), are formed when Mo(C$_6$H$_4$Me-2)$_4$ reacts with L; the PMe$_3$ derivative exhibits a pseudo-trigonal bipyramidal structure with axial phosphine ligands.[668] Paramagnetic, trigonal bipyramidal alkyl derivatives are recent additions to di- and triamidoamine systems.[18,23,24]

4.7.4.2 Complexes Containing Nitrogen-donor Ligands

4.7.4.2.1 Nitrido complexes

Yoshida and co-workers have described many Mo complexes containing tetradentate 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane (Me$_8$[16]aneS$_4$, **279**); Scheme 13 summarizes known Mo^{IV} chemistry and presents the structures and representations used for *syn* and *syn–anti* ligand conformations (see also Sections 4.7.6.5.3 and 4.7.8.5). The nitrido complex, *trans*-MoN(N_3)(Me_8[16]aneS_4) (**280**), prepared by reacting *trans*-Mo(N_2)$_2$(Me_8[16]aneS_4) (**281**) with Me_3SiN_3, is characterized by ν(Mo$\equiv$N) and ν(N_3) IR bands at 999 cm^{-1} and 2,040 cm^{-1}, respectively.[669] A related reaction between *trans*-Mo(N_2)$_2$(depe)$_2$ and Me_3SiN_3 produces *trans*-MoN(N_3)(depe)$_2$ and mixed-valence [MoN(N_3)(depe)$_2$]$_2${μ-MoN(N_3)$_2$}.[670] The X-ray structures of *trans*-MoN(NCCHCOPh)(dppe)$_2$[671] and *trans*-MoN{NCC(CN)COMe}(dppe)$_2$, two of many derivatives produced by dealkylation of β-ketonitriles by Mo(N_2)$_2$(dppe)$_2$, have been reported; the zwitterionic complexes feature anionic enolate ligands and octahedral geometries with d(Mo$\equiv$N) 1.704(3) Å and 1.704(6) Å, respectively. The mechanism of the dealkylation reactions has been probed.[672] Cationic complexes, [MoN(NCR)(dppe)$_2$]BPh$_4$ (R = Me, Et, Ph, ν(Mo$\equiv$N) 998–1,030 cm^{-1}), are produced when *trans*-[Mo(NH)Cl(dppe)$_2$]Cl reacts with NEt$_3$ in NaBPh$_4$/nitrile solutions.[673]



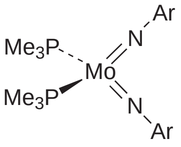
Scheme 13

4.7.4.2.2 *Imido complexes*

(i) Bis(imido) complexes

Although parallels exist, there are stark differences in imido and oxo chemistries at the Mo^{IV} level. The most obvious difference is the formation of many tetrahedral bis(imido)—Mo^{IV} complexes with but one oxo counterpart (Section 4.7.4.3). The imido ligands are linear (>160°) with d(Mo=N) 1.76–1.83 Å and ∠(N=Mo=N) 110–145°. Green Mo(NAr)$_2$(PMe$_3$)$_2$ (**282**) is produced in the reduction of (**44**) (Equation (1)) by Mg in the presence of PMe$_3$ in thf. This remarkable complex exhibits a distorted tetrahedral geometry with linear imido ligands; it reacts with phosphines and alkenes producing species such as Mo(NAr)$_2$(PMe$_2$Ph)$_2$ and Mo(NAr)$_2$(PMe$_3$)$_2$(η^2-CH$_2$CHR) (**283**, R = H, CH=CH$_2$);[674] the mesityl analog, Mo(NMes)$_2$(PMe$_3$)$_2$, reacts similarly.[675] Red–purple Mo(NR)$_2$(PMe$_3$)$_2$(η^2-C$_2$H$_4$) (R = Ar, Mes) adopt trigonal bipyramidal structures with equatorial imido and ethene ligands and axial phosphines, the ethene unit being perpendicular to the equatorial plane.[675,676] These and related alkene complexes, Mo(NR)$_2$(PMe$_3$)(η^2-CH$_2$CHR′) (**284**, R = ^{t}Bu, Ad; R′ = H, Me), may be prepared in a one-pot synthesis from Mo(NR)$_2$Cl$_2$(dme), R′CH$_2$CH$_2$MgCl, and PMe$_3$ in diethyl ether. Reactions of Mo(NAr)$_2$(PMe$_3$)$_2$ or Mo(NR)$_2$(PMe$_3$)(η^2-CH$_2$CHR′) with alkynes at room or elevated temperatures, respectively, produce alkyne complexes, Mo(NR)$_2$(PMe$_3$)(η^2-R′C$\equiv$CR″) (**285**, R = ^{t}Bu, Ar, Ad; R′/R″ = H/Ph).[111,674] η^2-Diphosphene complexes, Mo(NR)$_2$(PMe$_3$)(Mes^{F}P=PMes^F-*P,P′*) (**286**, R = Ar, ^{t}Bu; Mes^F = 2,4,6-tris(trifluoromethyl)phenyl), may be similarly prepared.[677] The Mo

$(NR)_2(PMe_3)(\eta^2\text{-L})$ complexes exhibit pseudo-tetrahedral structures with the η^2-ligand aligned with the Mo–P vector (PMe_3 being the weakest π-donor ligand). An unusual "bis(imido)" complex containing *trans* cyanamide ligands, *trans*-$Mo(NCN)_2(dppe)_2$, is produced in the reaction of *trans*-$Mo(N_2)_2(dppe)_2$ with $N{\equiv}CNH_2$.[678]



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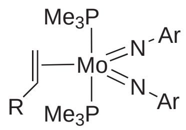

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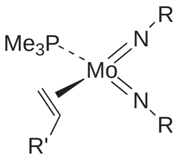

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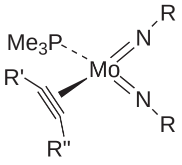

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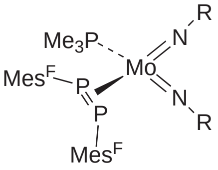
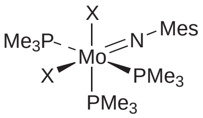


(286)

(ii) Mono(imido) complexes

Both *trans*-$MoN(N_3)(depe)_2$ and $[MoN(N_3)(depe)_2]_2\{\mu\text{-}MoN(N_3)_2\}$ serve as precursors for imido complexes such as *trans*-$[Mo(NH)X(depe)_2]BPh_4$ (X = Cl, N_3) and *trans*-$[Mo(NMe)(N_3)(depe)_2]BPh_4$;[670] an elegant electrochemical study of related dppe complexes revealed a (total) $4e^-$ reduction liberating amine RNH_2 and producing *trans*-$Mo(N_2)_2(dppe)_2$.[679] Protonation of (**280**) by HOTf in dme produces orange, air-stable *trans*-$[Mo(NH)(OTf)(Me_8[16]aneS_4)]OTf$ (**287**), that reacts reversibly with acetone or PhCHO in thf to afford red α-hydroxyalkylimido complexes (**288**) and with BPh_4^- to produce a yellow BPh_3 adduct (**289**) (Scheme 13). All three complexes have been spectroscopically and structurally characterized, giving $d(Mo{=}N)$ 1.695–1.718 Å and $\angle(Mo{=}N\text{–}E) > 174°$.[669] Protonation of the nitrile α-carbon of $Mo(N_2)(NCR)(dppe)_2$ complexes also permits the isolation of alkyl- and benzylimido complexes such as $[Mo(NCH_2R)X(dppe)_2]PF_6$.[671]

Diamagnetic complexes, *cis,mer*-$Mo(NR)Cl_2(PR'_3)_3$, are produced upon reduction of $Mo(NR)Cl_3L$ ($L = (PR'_3)_2$, dme) by Na/Hg in the presence of PR'_3.[156,174,531,680] Several, including $Mo(NC_6H_4Me\text{-}4)Cl_2(PMe_3)_3$[174] have been structurally characterized. Derivatives of $Mo(NMes)Cl_2(PMe_3)_3$ include halide and pseudo-halides (**290**, X = Br, NCS), dppe and $L = P(OR)_3$, alkenes, alkynes, CO, and CNR complexes (**291**), as well as xanthate (**292**–**293**, R = Me, ^{i}Pr), dithiocarbamate, and phosphonium dithiocarboxylate (**294**) species.[680,681] An octahedral geometry has been established for (**291**) ($L = PhC{\equiv}CPh$); here, the linear imido ligand ($d(Mo{=}N)$ 1.751(4) Å, $\angle(Mo{=}N\text{—}C)$ 176.9(4)°) exerts a minimal *trans* influence (ca. 0.07 Å) and the alkyne is bonded roughly orthogonal to the imido ligand.[680] Oxidative addition of RNCO ($R = {}^tBu$, $C_6H_4Me\text{-}4$) or $^tBuCNC^tBu$ to $MoCl_2(PMePh_2)_4$ produces $Mo(NR)Cl_2(CO)(PMePh_2)_2$ and $Mo(N^tBu)Cl_2(CN^tBu)(PMePh_2)_2$, respectively, but $MoCl_2(PMe_3)_4$ reacts with $4\text{-}MeC_6H_4NCO$ to form an equilibrium mixture of $Mo(NC_6H_4Me\text{-}4)Cl_2(CO)(PMe_3)_2$ and $Mo(NC_6H_4Me\text{-}4)Cl_2(PMe_3)_3$.[682] A mono(silylimido) complex, $Mo(NSiMe_3)Cl_2(PMe_3)_3$, is produced when $MoCl_2(PMe_3)_4$ reacts with Me_3SiN_3; a *cis,mer* structure is supported by spectroscopic data.[683] The ethylimido complex, $[Mo(NEt)Cl(dmpe)_2]BPh_4$, is reported to form when *trans*-$[MoCl(\eta^x\text{-}NCMe)(dmpe)_2]BPh_4$ ($x = 1, 2$) in heated in methanol.[684]



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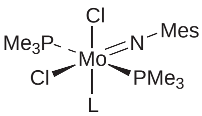

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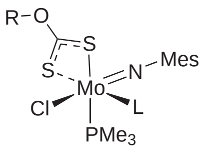

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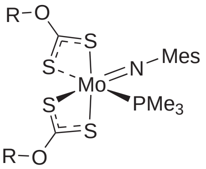

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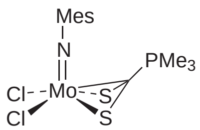
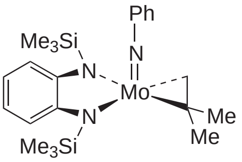


(294)

In contrast to earlier results (Section 4.7.2.2.2(iii)), reaction of $Mo(NPh)Cl_2\{(Me_3SiN)_2C_6H_4\}(thf)$ with Grignard reagents bearing β-hydrogens results in the formation of green alkene (metallacyclopropane) derivatives, exemplified by (**295**); the styrene derivative has been structurally characterized as the *anti* isomer (with reference to alkene phenyl and imido groups).[158] The alkenes are easily displaced by pyridine and imines $ArRC{=}NPh$ (R = H, Me; Ar = Ph, *p*-C_6H_4OMe) producing $Mo(NPh)\{(Me_3SiN)_2C_6H_4\}(py)_2$,[685] (**296**) or (**297**) (with less hindered imines).[686] Organometallic (arene, butadiene, and thence alkyne) complexes are also accessible.[687,688] In more recent work, *mer*-Mo(NPh){$(Me_3SiN)_2C_6H_4$}$(PMe_3)_3$ was reacted with H_2 at −10 °C to produce (**298**), which transforms to *mer*-Mo(NPh)$(PMe_3)_3${$(Me_3SiN)(NH)C_6H_4$} and $HSiMe_3$ at 30 °C. NMR evidence supports the formulation of (**298**) as a stretched dihydrogen complex with *d*(H—H) = 1.17 Å.[689]



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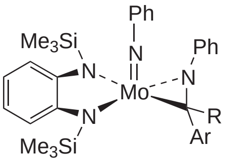

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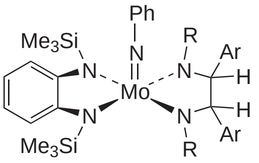

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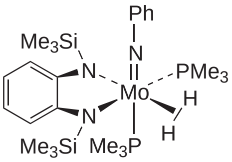

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By analogy with related oxo–dithiocarbamate systems, reaction of $MoO(NC_6H_4Me\text{-}4)(S_2CNEt_2)_2$ with one-half an equivalent or excess of PPh_3 or $PEtPh_2$ produces purple $[Mo(NC_6H_4Me\text{-}4)(S_2CNEt_2)_2]_2(\mu\text{-}O)$ (that disproportionates) and $Mo(NC_6H_4Me\text{-}4)(S_2CNEt_2)_2$, respectively.[173,174] The imido—Mo^{IV} complex has not been isolated but has been trapped with RC≡CR, (dmac, R = CO_2Me) producing pentagonal bipyramidal $Mo(NC_6H_4Me\text{-}4)(dmac)(S_2CNEt_2)_2$.[173,690] The complexes catalyze the oxidation of tertiary phosphines by O_2 or dmso.[173]

4.7.4.2.3 Amido complexes

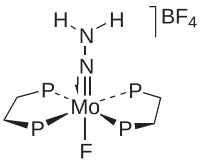
Direct protonation of *trans*-$MoN(N_3)(dppe)_2$ or *trans*-$[Mo(NH)(OMe)(dppe)_2]OTf$ by triflic acid produces purple *trans*-$[Mo(NH_2)(OH)(dppe)_2](OTf)_2$; this octahedral complex, with *d*(Mo—N) 2.053(11) Å, is a rare example of NH_2^- coordination.[691] Known $Mo(NMe_2)_4$ reacts with $LiNMe_2$ (>2 equivalents) to produce red $[Li(thf)]_2[Mo(NMe_2)_6]$, wherein isolated octahedral $Mo(NMe_2)_6$ units are associated with two (opposite) face-capping Li(thf) units; in solution, $Mo(NMe_2)_4$ is regenerated through elimination of $LiNMe_2$.[692] However, reaction of $Mo(NMe_2)_4$ with Ph_2PH or LiP^tBu_2 produces air-sensitive, red $Mo(NMe_2)_2(PR_2)_2$, with monomeric, tetrahedral structures related to $Mo(NMe_2)_4$ and $Mo(PCy_2)_4$.[693] The π- and δ-bonding in these complexes has been assessed by structural[694] and spectroscopic[695] methods. Reaction of $Mo(NMe_2)_4$ with $CNC_6H_3Me_2\text{-}2,6$ gives the homoleptic metallaamidine $Mo(Me_2NCNC_6H_3Me_2\text{-}2,6)_4$, characterized by IR, ^1H, and ^{13}C NMR spectroscopy and X-ray crystallography; the side-on bonded, bidentate ligands are arranged in a distorted dodecahedral array.[696]

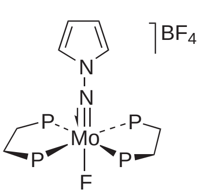
Red, paramagnetic $MoX(N^tBuAr)_3$ (X = Cl, Br) form in the reactions of $Mo(N^tBuAr)_3$ with X_2 or CH_2Cl_2, while $MoCl[N^tBu\{C_6H_3(OMe)_2\text{-}3,5\}]_3$ can be generated from $MoCl_3(thf)_3$ and $Li[N\text{-}^tBu\{C_6H_3(OMe)_2\text{-}3,5\}]$. These tetrahedral complexes are active catalysts for an impressive variety of alkyne metathesis reactions.[572] Related triamidoamine complexes, including (**13**) (Scheme 2) and many derivatives, are prepared by reacting $MoCl_4(thf)_2$ or $MoCl_3(thf)_3$ with ligand lithium salts under argon.[18,20,697] Purple, paramagnetic (μ_B 2.92) (**13**) exhibits contact shifted NMR spectra and a trigonal bipyramidal structure with an axial chloro ligand;[20,697] it supports the chemistry previously summarized (Scheme 2). Alkyl–Mo^{IV} derivatives (**14**) are generated upon reaction with LiR; the purple/black, paramagnetic complexes have been thoroughly characterized and the X-ray structures of trigonal bipyramidal $Mo(CD_3)(N_3N)$ and $Mo(C_6H_{11})(N_3N)$ determined. Decomposition to alkylidyne (**15**), hydride (**299**), and ligand-activated (**300**) species is summarized in Scheme 2. Isocyanide (**301** (R = ^tBu, $C_6H_3Me_2\text{-}2,6$) and **302**) and cyano (**303**) species are accessible via (**43**). Dimethylamido complexes (e.g., **304**) can be prepared from $MoCl(N_3N)$ and $LiNMe_2$[92] or from $Mo(NMe_2)_4$ and arylated N_3N analogs.[18] Ligand exchange permits the synthesis of other derivatives, e.g., $Mo(OTf)(N_3N)$ (**305**)[20] and $Mo(CCR)(N_3N)$ (**306**).[698] Various Mo^{IV} complexes containing diamidoamine have now been reported.[23,24] The complex, $Mo(NMe_2)_2(NHMe_2)\{MeN(CH_2C_4H_4N)_2\}$, derived from $Mo(NMe_2)_4$ and di-*N*,*N*-(pyrrolyl-α-methyl)-*N*-methylamine, readily inserts 3-hexyne forming a new C—N bond.[699]

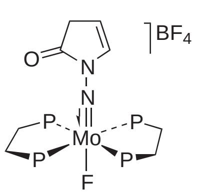
4.7.4.2.4 Hydrazido(2-) and diazenido complexes

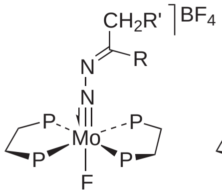
Much of the work in this area builds on earlier results.[3] Continued study of the protonation of dinitrogen complexes has led to the isolation of complexes such as *syn,trans*-[Mo

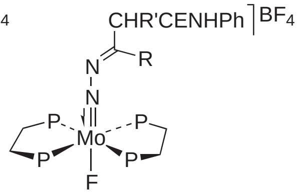
$(NNH_2)X(bdpe)(PPh_3)]X$, *anti,trans*-$[Mo(NNH_2)X(bdpe)(PPh_2Me)]X$, $[Mo(NNH_2)X(bdpe\text{-}P,P')(PMe_2Ph)_2]X$, and *syn,mer*-$[Mo(NNH_2)X(bdpe)(PMe_2Ph)]X$ ($X = Cl$, Br)[700,701] and the development of electrochemical methods for the cleavage of hydrazido ligands to form ammonia.[702] Several of these complexes, along with *trans*-$[Mo(NNH_2)F(dippe)_2]BF_4$, have been structurally characterized, with d(Mo–N) 1.69–1.78 Å, d(N–N) 1.31–1.34 Å, and $\angle$(Mo–N–N) > 172°.[700,703] The chemistry of related species, viz., *cis,mer*-$Mo(NNH_2)X_2(PMe_2Ph)_3$ and *trans*-$[Mo(NNH_2)X(dppe)_2]BF_4$, has been explored by Hidai and co-workers.[704–706] Reactions of $[Mo(NNH_2)F(dppe)_2]BF_4$ (**307**) include those with 2,5-dimethoxytetrahydrofuran[707] and 2,5-dimethoxy-2,5-dihydrofuran[708] to give (**308**) and (**309**), respectively, the latter converting to the α,β- isomer with time; development of a system for the conversion of dinitrogen to pyrrole and *N*-aminopyrrole was a significant outcome of related work.[707] Reaction of (**307**) with carbonyl compounds $RCOCH_2R'$ provides access to complexes such as (**310**) ($R/R' = H/Me$, Me/H), which can be elaborated by reactions with, for example, PhNCE ($E = O$, S)/$NaBF_4$ giving (**311**).[709] β-Monoalkylation and α,β-difunctionalization of α,β-unsaturated diazoalkane ligands by organocuprates has also been demonstrated.[710] Analogous depe chemistry has been reported.[711] Alkylation and benzylation of (**281**) (Scheme 13) produces various hydrazido (and diazenido) species (**312**), consistent with effective p_π donation from the thioether to the Mo—N_2 unit.[712,713] Likewise, alkylation of (**40**) (Scheme 1) produces $Mo(NNR)(NRAr)_3$ (**313**).[86]


(**307**)


(**308**)


(**309**)

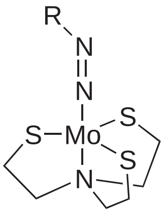

(**310**)


(**311**)

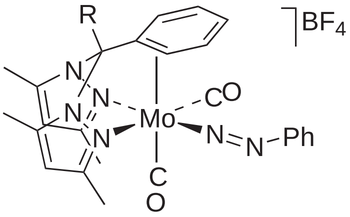
Octahedral, *cis*-bis(diazenido) complexes bearing bidentate S_2-, NS-, SO-, NO-, and O_2-donor ligands or tetradentate N_2S_2-donor and porphyrin ligands are well known.[3] *cis*-Bis(aryldiazenido) complexes are prepared from dioxo precursors and phenyl hydrazines; new examples include $Mo(NNPh)_2\{Me_2NCH_2CH_2N(CH_2CH_2S)_2\}$,[204] $Mo(NNC_6H_4R\text{-}4)_2(H_2NCH_2CH_2S)_2$ ($R = H$, NO_2),[714] and $Mo(NNPh)_2(Bu_4dttd)$ ($Bu_4dttd = \mathbf{147}$),[382] having distorted octahedral structures with N- or thioether-donors *trans* to diazenido ligands, and octahedral $Mo(NNC_6H_4R\text{-}4)_2(acac)_2$ ($R = H$, Me, OMe, F, NO_2).[715] Mono(diazenido) species include pentagonal bipyramidal $Mo(NNPh)L_3$ ($L = 2\text{-}SC_5H_3N\text{-}3\text{-}SiMe_3$), prepared in the reaction of $Mo_2Cl_4(\mu\text{-}S_2)(\mu\text{-}L)L_2$ with H_2NNHPh,[716] and Mo(NNR)(tmea) (**314**, $R = H$, Me, Ph), produced in the reaction of $[MoO(\mu_S\text{-}tmea)]_2$ with H_2NNHR.[190] Reaction of $PPh_4[Mo(SC_6H_2{}^iPr_3\text{-}2,4,6)_3(CO)_2]$ with $[N_2Ph][BF_4]$ in NCMe yields green Mo(NNPh) $(SC_6H_2{}^iPr_3\text{-}2,4,6)_3(NCMe)$; a trigonal bipyramidal structure with *trans* NNPh and NCMe ligands pertains.[717] The unusual η^2-$RCPh(Me_2pz)_2$-N,N'($R = H$, Ph) ligands in *fac*-$Mo(CO)_3L$ are retained in reactions with diazonium salts giving, *inter alia*, structurally characterized $[Mo(N_2Ph)(CO)_2L]BF_4$ (**315**, $R = Ph$).[718] Complexes of the type $Mo(NNPh)Cl_3L$ and $Mo(NNPh)Cl_2L$ ($L =$ depe, dppe) have been prepared.[719] Various mixed diazenido hydrazido(1-) complexes are formed in the reactions of alkyldithiocarbazates with dioxo–Mo^{VI} starting materials.[720,721]

4.7.4.3 Oxo Complexes

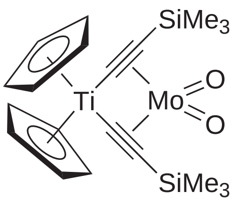
The spectroscopic and structural attributes of oxo—Mo^{IV} compounds have been documented elsewhere.[3,14] Dioxo–Mo^{IV} complexes are extremely rare and almost invariable adopt *trans* octahedral structures.[722] Examples include matrix-isolated *trans*-$MoO_2(CO)_4$, cyanide and phosphine complexes such as *trans*-$[MoO_2(CN)_4]^{4-}$ (Section 4.7.4.3.1), and *trans*-$MoO_2(dppe)_2$ (Section 4.7.4.3.3). Only one "*cis*" dioxo—Mo^{IV} complex, viz., brown–red $(\eta\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}CCSiMe_3)_2MoO_2$ (**316**) has been reported.[723] Five-coordinate, square pyramidal and six-coordinate, distorted octahedral oxo—Mo^{IV} complexes are most prevalent. These exhibit ν(Mo=O) IR bands in the range 960–900 cm^{-1}. The terminal oxo group is invariably apical or axial with d(Mo=O) ca. 1.66–1.70 Å and exerts a strong *trans* influence.



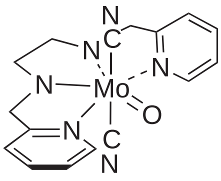
(**314**)



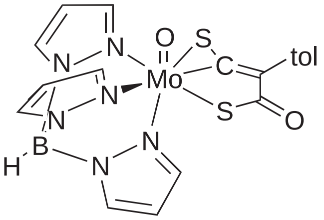
(**315**)



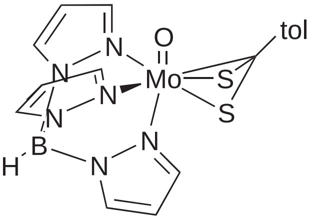
(**316**)



(**317**)



(**325**)



(**326**)

4.7.4.3.1 Cyanide complexes

Oxo cyano—Mo^{IV} complexes are well known and their chemistry has been extensively reviewed.[652,724,725] Recent work has included the measurement of the proton, oxygen, and cyanide exchange rates for archetypal (all *trans*) $[MoO_2(CN)_4]^{4-}$, $[MoO(OH)(CN)_4]^{3-}$, and $[MoO(OH_2)(CN)_4]^{2-}$ by NMR spectroscopy,[725] the synthesis and characterization of blue/green $Cat_3[MoO(CN)_5]$ ($Cat^+ = K^+$, PPh_4^+, $AsPh_4^+$)[482] and the X-ray structures of octahedral $(PPh_4)_3[MoO(CN)_5]\cdot PPh_4Cl\cdot 2MeCN$, $(PPh_4)_2[MoO(CN)_4(OH_2)]\cdot 6H_2O$, and $(PPN)_2[MoO(CN)_4(NCMe)]$.[481] Salts of the complex anions, *mer*-$[MoO(CN)_3L]^{n-}$ (L = bpy, phen, pic, acac, salicylaldehyde, and Schiff bases) are prepared by a general method involving adjustment to pH ca. 8 of aqueous solutions of $K_3Na[MoO_2(CN)_4]\cdot 6H_2O$ and ligand, followed by addition of precipitating cations.[726,727] The complexes exhibit $\nu(Mo{=}O)$ and $\nu(CN)$ IR bands in the ranges 973–932 cm^{-1} and 2,116–2,088 cm^{-1}, respectively, and feature six-coordinate, distorted octahedral structures with $d(Mo{=}O)$ 1.66–1.70 Å.[727] Interest in these compounds is stimulated by the characteristic solvatochromism and piezochromism of their MLCT bands. Pentagonal bipyramidal $MoO(CN)_2(bped)$ (**317**, bped = *N,N′*-bis[1-(pyridin-2-yl)ethylidene]ethane-1,2-diamine) is formed when $K_4[MoO_2(CN)_4]$ reacts with 2-acetylpyridine and ethylenediamine; the equatorial oxo group is characterized by a low $\nu(Mo{=}O)$ (909 cm^{-1}) but normal $d(Mo{=}O)$ (1.689(2) Å).[728]

4.7.4.3.2 Complexes containing nitrogen-donor ligands

Diamagnetic, green Tp*MoOL ($L = S_2CNR_2$ (**318**; R = Me, Et),[729] S_2PR_2 (**118**, R = alkoxy, alkyl, Ph),[320,321] pyridine-2-thiolate (pysS) (**319**)[496]), are conveniently produced by reacting $MoOL_2$ with KTp* in refluxing toluene (Scheme 7). Attempts to prepare related complexes of Tp^{Pr} were accompanied by a borotropic shift leading to $Tp'MoO(S_2PR_2)$ (**118**, R = ^iPr, Ph).[495] Reaction of (**319**) with propylene sulfide forms the pyridine-2-dithio complex, $Tp^*MoO(pyS_2)$ (**320**), that can be reduced *or* oxidized to Mo^V species (**321**/**322**) with concomitant S—S redox.[496] Reaction of Tp^*MoO_2X with one equivalent of PR_3 in donor solvents such as py, lutidine, NCMe, and dmf produces green Tp*MoOX(sol) (**323**) via a transient OPR_3 complex (**210**) or unsaturated intermediate (**324**).[318,323] The phosphine oxide complex, $Tp^{Pr}MoO(OPh)(OPEt_3)$, has been isolated and structurally characterized while unstable complexes of Tp* have been detected by mass spectrometry.[730] These complexes exhibit a single $\nu(Mo{=}O)$ IR band in the region 950–960 cm^{-1}, the species bearing monodentate ligands being unstable with respect to molybdenyl complexes, $Tp^xMoOXCl$ (**241**), in chlorinated solvents. The X-ray structures of $Tp^*MoO(S_2CNEt_2)$,[729] $Tp^*MoO\{S_2P(OEt)_2\}$,[320] Tp*MoOX(py) (X = Cl,[318] SPh[323]), $Tp'MoO(S_2P^iPr_2)$,[495] and $Tp^{Pr}MoO(OPh)(OPEt_3)$[730] reveal distorted octahedral complexes with short Mo=O bonds (generally < 1.68 Å) associated with a significant (0.1–0.3 Å) *trans* influence. Many of the complexes above are important in enzyme model systems, the trispyrazolylborate ligands ensuring mononuclearity at $\mathrm{Mo^{VI}}$, $\mathrm{Mo^{V}}$, and $\mathrm{Mo^{IV}}$ levels during biologically relevant OAT and CEPT reactions (Scheme 7); this area was recently reviewed by Young.[324] Dinuclear complexes, $\mathrm{[Tp^{*}MoOCl]_2(\mu\text{-}L)}$ (L = dipyridines), have also been structurally, spectroscopically, and electrochemically characterized by McCleverty and co-workers.[731] Red–brown $\mathrm{NEt_4[Tp^{*}MoO(S_4)]}$ (ν(Mo=O) 912 cm^{-1}) is a hydrolysis by-product in the reaction of $\mathrm{NEt_4[Tp^{*}Mo(CO)_3]}$ and $\mathrm{S_8}$ in dmf/ether.[732] Hydrolysis also accounts for the unexpected products, TpMoO{$\mathit{SC}\mathrm{C(C_6H_4Me\text{-}4)C(O)}\mathit{S}$} (**325**) and $\mathrm{TpMoO(\kappa^3\text{-}S_2CC_6H_4Me\text{-}4)}$ (**326**), obtained in the reactions of $\mathrm{TpMo(CC_6H_4Me\text{-}4)(CO)L}$ (L = CO, $\mathrm{PPh_3}$) with $\mathrm{CS_2}$[733] and $\mathrm{S_8}$ in refluxing thf,[734] respectively. Bis(pyrazolyl)borate oxo—$\mathrm{Mo^{IV}}$ complexes include square pyramidal $\mathrm{Bp^{*}MoO(S_2P^iPr_2)}$ (ν(Mo=O 980 cm^{-1}).[735] The triazacyclononane complex, $\mathrm{(Me_3tcn)MoOI_2}$ (**327**, Scheme 6) has been structurally characterized.[326]

Oxo–$\mathrm{Mo^{IV}}$ porphyrin complexes, MoO(por) (**190**), are formed by chemical,[736] electrochemical,[328] or photochemical[599] reduction (through Mo–X homolysis) of *trans*-MoO(por)X (**191**) species (Scheme 8). These compounds were fully described in previous reviews.[3,330] Börschel and Strähle prepared a violet form of MoOPc (**249**) from the reaction of $\mathrm{Mo(CO)_6}$ and 1,2-dicyanobenzene in a sealed tube (Scheme 11). A square pyramidal structure with an apical oxo group (d(Mo=O) 1.668(6) Å) was established.[608] A second blue modification, prepared by reacting ammonium molybdate or $\mathrm{MoO_2Cl_2}$ with 1,2-dicyanobenzene in a sealed tube, and the interconversion of the two forms, has been reported.[530,737]

4.7.4.3.3 *Complexes containing phosphorus-donor ligands*

Phosphine ligands such as $\mathrm{PMe_3}$, dppe, and dppee stabilize bis(chalcogenido)–$\mathrm{Mo^{IV}}$ complexes, *trans*-$\mathrm{MoE_2P_4}$, and their derivatives, *trans*-$\mathrm{[MoEXP_4]^+}$ (E = O (this Section), S, Se, Te (Section 4.7.4.4); P = donor atom of mono- or bidentate phosphine). Pink $\mathrm{[MoOXL_2]^+}$ (L = dppe, X = F, Cl; L = dppee; X = Cl) undergo hydrolysis in aqueous or alcoholic media to yield disolvates of $\mathrm{MoO_2L_2}$.[738,739] The X-ray crystal structures of $\mathrm{MoO_2L_2{\cdot}2MeOH}$ (L = dppee,[738] dppe[739]) revealed tetragonally compressed octahedral complexes with equatorial phosphorus donor atoms and axial oxo groups (d(Mo=O) 1.804(2)/1.8184(8) Å, ∠(O=Mo=O) 180°). Reactions of $\mathrm{MoO_2(dppe)_2}$ with noncoordinating acids (HX) produce $\mathrm{[MoO(OH)(dppe)_2]X}$, while reactions with coordinating acids or acid/$\mathrm{X^-}$ mixtures permit the isolation of salts of $\mathrm{[MoOX(dppe)_2]^+}$ (X = Br, I, NCS, $\mathrm{N_3}$, OMe).[739] An accurate X-ray structure of $\mathrm{[MoO(OH)(dppe)_2]ClO_4}$ was facilitated by $\mathrm{ClO_4^-\cdots HO\text{-}Mo}$ H-bonding; metrical data include, d(Mo=O) 1.7471(11) Å, d(Mo—O) 1.9044(12) Å, $d(\mathrm{Mo\text{–}P})_{\mathrm{av}}$ 2.533 Å, and ∠(O=Mo—O) 178.88(5)°. The X-ray crystal structures of $\mathrm{[MoO(OMe)(dppe)_2]OTf}$, prepared serendipitously from $\mathrm{[Mo(NH)(OMe)(dppe)_2]OTf}$,[691] as well as $\mathrm{[MoOCl(dmpe)_2]Cl}$[740] and $\mathrm{[MoOI(dmpe)_2]I}$, have been reported. Finally, $\mathrm{MoO(SeMes)_2}$(bdpeO-*P,P′,O*) was isolated from the reaction of $\mathrm{MoCl_3(bdpe)}$ with NaSeMes and structurally characterized.[741]

4.7.4.3.4 *Complexes containing sulfur-donor ligands*

(i) Dithiolene complexes

Square pyramidal complexes, $\mathrm{[MoO(dithiolene)_2]^{2-}}$ (**260**–**263**, $n = 2$), are accessible by a range of synthetic routes, including: (i) reaction of ligand with $\mathrm{Mo^{IV}}$ starting materials such as $\mathrm{K_4[MoO_2(CN)_4]}$,[624] $\mathrm{(NEt_4)_2[MoO(SC_6H_4Cl\text{-}4)_4]}$,[742] and $\mathrm{[MoOCl(CNMe)_4]PF_6}$,[370] (ii) reaction of ligand with $\mathrm{Mo^{VI}}$ or $\mathrm{Mo^{V}}$ complexes in the presence of reducing agents (including excess ligand),[363,366,626,743] (iii) induced internal redox between $\mathrm{(NEt_4)_2[MoO_2S_2]}$ and the oxidant $\mathrm{(CF_3)_2C_2S_2}$,[514] (iv) reaction of alkynes with $\mathrm{(NEt_4)_2[MoO(S_4)_2]}$,[744,745] (v) reduction of oxo—$\mathrm{Mo^{V}}$ or dioxo—$\mathrm{Mo^{VI}}$ counterparts,[362] (vi) reaction of $\mathrm{Mo(CO)_2(S_2C_2R_2)_2}$ with $\mathrm{NEt_4OH}$ solution,[515] and (vii) reaction of nitrido complexes with dioxygen.[102] Route (i), coupled with versatile methodologies for the *in situ* generation of dithiolene salts, has been exploited in the synthesis of salts of well-known $\mathrm{[MoO(mnt)_2]^{2-}}$ and $\mathrm{[MoO(bdt)_2]^{2-}}$, $\mathrm{[MoO(S_2C_2R_2)_2]^{2-}}$ (R = H, $\mathrm{CF_3}$), $\mathrm{[MoO(S_2C_2H_2)(mnt)]^{2-}}$,[370] $\mathrm{[MoO(tdt)_2]^{2-}}$, $\mathrm{[MoO(S_2C_6H_3SiPh_3\text{-}3)_2]^{2-}}$,[742] $\mathrm{[MoO\{SC(H)C(R)S\}_2]^{2-}}$ (R = Ph, pyridin-n-yl ($n = 2, 3, 4$), quinoxalin-2-yl, 2-(dimethylaminomethyleneamino)-3-methyl-4-oxopteridin-6-yl),[624] and $[MoO(qdt)_2]^{2-}$.[625] Spectroscopic and structural data for selected compounds are collected in Table 6. The complexes are reversibly oxidized to Mo^V counterparts and some belong to the three-member electron-transfer series, $[MoO(dithiolene)_2]^{0/1-/2-}$.[370,515] Many of these complexes participate in OAT reactions yielding dioxo—Mo^{VI} complexes and reduced "substrates"; these reactions and associated kinetics studies have been reviewed.[324] The influence of NH···S(dithiolene) H-bonding on structure and reactivity has been probed by the synthesis and study of $(NPr_4)_2[MoO\{S_2C_2(CONH_2)_2\}_2]$, the rate of OAT from Me_3NO to the complex being enhanced by 10^4–10^5 through H-bonding.[745] The Mo K- and $L_{2,3}$-edge X-ray absorption spectra of $(NEt_4)_2$-$[MoO(bdt)_2]$ have also been reported.[365]

Rare oxo—Mo^{IV} monodithiolene complexes, $MoO(mnt)L_2(thf)$ ($L_2 = (PPh_3)_2$, dppe, tmeda), are generated by reacting MoO_2Cl_2 with Na_2mnt in thf at $< -45\,°C$, followed by addition of ligand. The X-ray structure of an acetone adduct, $MoO(mnt)(dppe)(Me_2CO)$, confirmed a distorted octahedral geometry, with acetone weakly bound (d(Mo—O) 2.333(2) Å) *trans* to the oxo ligand (d(Mo=O) 1.682(2) Å).[746] The ditelluroene, $(PPh_4)_2[MoO\{Te_2C_2(CO_2Me)_2\}_2]$ (ν(Mo=O) 950 cm^{-1}; d(Mo=O) 1.683(6) Å) has also been prepared from $(PPh_4)_2[MoO(Te_4)_2]$ and $RC\equiv CR$ ($R = CO_2Me$).[747]

(ii) Other sulfur-donor ligand complexes

Dithio acid ligand complexes of the type $MoOL_2$ are well known.[3] In line with earlier work,[3] cyclooctyne reacts with $MoO(S_2CNR_2)_2$ (R = Me, Et) to form yellow $MoO(S_2CNR_2)_2(\eta^2\text{-}C_8H_{12})$, while halogen oxidation of $Mo(S_2CNR_2)_2(CO)(\eta^2\text{-}C_8H_{12})$ yields brown $MoX_2(S_2CNR_2)_2(\eta^2\text{-}C_8H_{12})$.[748] The reductive coupling of terminal alkynes,[749] intramolecular cyclization of diynes,[749] stereoselective epoxidation of alkenes,[750] and episulfurization of (*E*)-cycloalkenes[490] are all promoted by $MoO(S_2CNEt_2)_2$. Yellow $MoO\{S_2C(PMe_3)ER\}(S_2CER\text{-}C,S,S')$ (E = O, R = Me, Et, ^{i}Pr;[751] E = S, R = ^{i}Pr[752]), featuring oxo (ν(Mo=O) ca. 950 cm^{-1}), bentainic phosphonium and η^3-xanthate ligands, result from the reactions of $MoOCl_2(PMe_3)_3$ with KS_2COR or KS_2CSR/CS_2 in thf. The *i*-propyl derivatives are square pyramidal with an apical oxo ligand and basal S- and C-donors (d(Mo—C) ca. 2.25 Å).[751] Related phosphonium and η^3-dithio ligand complexes are described in Sections 4.7.6.1.1, 4.7.6.5.1, and 4.7.8.3.2.

New diamagnetic thiolate complexes, $[MoO(SR)_4]^{2-}$ (cf. (**253**)), have been prepared by: (i) NEt_4BH_4 reduction of the corresponding Mo^V species to produce $(NEt_4)_2[MoO\{SC_6H_4NHC(O)R\text{-}2\}_4]$ (R = Me, CF_3, ^{t}Bu),[611,753] (ii) thiol exchange at $(NEt_4)_2[MoO(SC_6H_4Cl\text{-}4)_4]$ (itself prepared by method (i)) yielding $(NEt_4)_2[MoO(\alpha\text{-tdt})_2]$,[754] and (iii) reaction of $MoOCl_2(PPh_2Me)_3$ with HSC_6F_5/NEt_3 to give $(NHEt_3)_2[MoO(SC_6F_5)_4]$.[615] The X-ray structures of $(PPh_4)_2[MoO\{SC_6H_4NHC(O)Me\text{-}2\}_4]$,[611] $(PPh_4)_2[MoO(SC_6H_4Cl\text{-}4)_4]$,[753] and $(NEt_4)_2[MoO(\alpha\text{-tdt})_2]\cdot OEt_2$[754] reveal a slight expansion in the coordination sphere compared to Mo^V analogs (Table 6). In a related system, the generation of $[MoO\{O_2CC(S)MePh\}_2]^{2-}$ and its participation in catalytic OAT reactions have been reported.[419] The thiolate–thioether complexes MoO(dttd) (dttd = (**146**)) and $MoO(dttd)(PPh_2Et)$ are formed in the reactions of $MoO_2(dttd)$ with PPh_3[381] and PPh_2Et,[380] respectively. Related complexes, $MoO(SC_6H_4SMe\text{-}2)_2$ and MoOL (L = (**149**)–(**152**)) are formed upon reaction of $MoCl_4(NCMe)_2$ with free ligand or NiL in wet thf[381,755] or upon aerial oxidation of $Mo(CO)_2L$.[756] The complexes are characterized by ν(Mo=O) IR bands at 950–920 cm^{-1} and adopt a common distorted octahedral structure, with X *trans* to oxo and mutually *trans* thiolate and thioether groups ($d(Mo{=}O)_{av}$ 1.688 Å).[755,756]

4.7.4.3.5 Halide complexes

New syntheses for *mer*-$MoOCl_2L_3$ (L = PMe_3, $PMePh_2$) and novel *cis,cis,trans*-$MoO(CO)Cl_2L_2$ include oxidation of $MoCl_2L_4$ with ethylene oxide or CO_2, respectively.[682] The reaction of $Mo_2O_2Cl_4(\mu\text{-OEt})_2(\mu\text{-HOEt})$ with PMe_3 also produces structurally characterized *cis,mer*-$MoOCl_2(PMe_3)_3$.[550] Related species, e.g., $MoOCl_2(dmpe)(PMe_3)$, $[MoOCl(dmpe)_2]Cl$, $MoOCl_2(PMe_3)_2(CNR)$ (R = ^{t}Bu, Cy),[757] and structurally characterized $MoOCl_2(dppe)(py)$[758] and $MoOX_2(bdpeO)$ (X = Br,[759] I[760]) are also known. Careful crystallographic[761] and spectroscopic[762] studies have revealed the "green" bond-stretch isomer of *cis,mer*-$MoOCl_2(PMe_2Ph)_3$ to be a binary mixture of blue *cis,mer*-$MoOCl_2(PMe_2Ph)_3$ and yellow *mer*-$MoCl_3(PMe_2Ph)_3$. Another case of bond-stretch isomerism proved to be a ternary mixture.[763] The broader implications of compositional disorder, clearly articulated by Parkin,[764,765] have not quelled interest in bond-stretch isomerism.[766] The separation of conformational isomers of *cis,mer*-$MoOBr_2(PMe_2Ph)_3$[767] or their co-existence in samples of *cis,mer*-$MoO(NCO)_2(PEt_2Ph)_3$[768] adds another dimension to distortional isomerism.

4.7.4.4 Thio, Selenido, and Tellurido Complexes

Bis(chalcogenido)–Mo^{IV} complexes, *trans*-$MoE_2(PMe_3)_4$ ($E = S$, Se, Te), are formed in the reactions of $Mo(PMe_3)_6$ with H_2S, H_2Se, Se, or Te/PMe_3 and exhibit distorted octahedral geometries with *d*(Mo═E) 2.254(2) Å, 2.383(2) Å, and 2.597(1) Å, respectively; characteristic ^1H, ^{13}C and ^{31}P NMR signals are observed at ca. δ 1.6, 22–29, and –15, respectively.[769] Analogous MoE_2L_2 ($L =$ bidentate diphosphine) complexes, as well as $MoOSL_2$ and $Mo(SO_2)_2L_2$, are also accessible from the reactions of $Mo(N_2)_2L_2$ with chalcogen atom sources or SO_2.[738,770] The Mo═E distances observed for structurally characterized $MoE_2(dppee)_2$ are 2.2280(14) Å, 2.356(2) Å, and 2.5615(10) Å, for $E = S$, Se, Te, respectively, the E═Mo═E units being strictly linear. The bonding in these complexes has been probed by computational studies.[722]

Elemental sulfur or ^tBuSH react with (**281**) to produce *trans*-$MoS_2(Me_{18}[16]aneS_4)$ (**328**), that exhibits a distorted octahedral structure with *d*(Mo═S) 2.232(9) Å and 2.245(8) Å for sulfido groups at the open and ligand encumbered sites, respectively (see Scheme 13).[771] Alkylation of (**328**) produces *trans*-$[MoS(SR)(Me_{18}[16]aneS_4)]X$ (**329**, $R = Me$, $X = I$; $R = Bz$, $X = Br$; ν(Mo═S) ca. 485 cm^{-1}). Red (**329**) ($R = Me$, $X = I$) adopts a *syn* ligand conformation, with sulfido (*d*(Mo═S) 2.140(5) Å) and thiolate (*d*(Mo—S) 2.440(6) Å) ligands in the encumbered and open axial sites, respectively.[772] Protonation with HBF_4 produces a sulfido bridged dinuclear species (**330**) and *trans*-$[MoSF(Me_{18}[16]aneS_4)]BF_4$ (**331**) with *d*(Mo═S) 2.118(3) Å.[773] Reactions of salts of $[MoS(S_4)_2]^{2-}$ with CS_2 under different conditions yield salts of orange *syn*- and *anti*-$[MoS(CS_4)_2]^{2-}$. The five-coordinate anions exhibit square pyramidal structures with apical sulfido groups and *d*(Mo═S) 2.126 Å, *d*(Mo—S)$_{av}$ 2.383 Å, and *d*(S—S)$_{av}$ 2.103 Å.[774] The complex solution behavior of these and related species has been reviewed.[225]

Porphyrin complexes, MoE(ttp) ($E = S$ (**332**), Se (**333**)), are prepared according to Scheme 10(b).[775] These undergo atom transfer reactions with PPh_3 forming $EPPh_3$ and $Mo(ttp)(PPh_3)_2$ (**334**) or $Mo(\eta^2\text{-}PhC{\equiv}CPh)(ttp)$ (**335**). The X-ray structure of (**332**) reveals a square pyramidal geometry with an apical sulfido ligand (*d*(Mo═S) 2.100(1) Å, ν(Mo═S) 542 cm^{-1}).[776] Yellow–brown $Tp^*MoS(S_2CNR_2)$ (**336**, $R = Me$, Et)[729] and (**206**) ($R = {}^iPr$, Ph)[495] are produced in the reactions of oxo–Mo^{IV} analogs with B_2S_3 (Scheme 7). The distorted octahedral complexes exhibit ν(Mo═S) IR bands at 510–515 cm^{-1} and *d*(Mo═S) 2.129(2) Å and 2.126(3) Å for (**336**) ($R = Et$) and (**206**) ($R = Ph$), respectively. Reaction of $NEt_4[LMo(CO)_3]$ ($L = Tp$, Tp^*) with an equivalent of S_8 yields red–brown $NEt_4[LMoS(S_4)]$ (ν(Mo═S) 491 cm^{-1} and 473 cm^{-1}, respectively). The complexes exhibit distorted octahedral geometries with terminal sulfido (*d*(Mo═S) 2.144(2) Å and 2.172(1) Å, respectively), bidentate tetrasulfido (*d*(Mo–S)$_{av}$ 2.247 Å and 2.294 Å, respectively) and *facial* L ligands.[732]

4.7.4.5 Complexes Containing Polychalcogenide Ligands

Salts containing $[MoE(Se_4)_2]^{2-}$ ($E = O$, S, Se) have been isolated from the reactions of $(NEt_4)_2[MoSe_4]$ with adventitious water, SeS_2, and Se_8, respectively.[242,243] The complexes have been characterized by ^{77}Se NMR and IR spectroscopy (ν(Mo═E) 928 cm^{-1}, 515 cm^{-1}, 360 cm^{-1}, respectively). The anions of $(NEt_4)_2[MoO(Se_4)_2]$[242] and $(PPh_4)_2[MoSe(Se_4)_2]$[243] possess square pyramidal geometries with apical oxo (*d*(Mo═O) 1.690(6) Å) or selenido (*d*(Mo═Se) 2.270(4) Å) ligands. Polytellurides react with $MoCl_5$ in dmf to form square pyramidal $[MoO(Te_4)_2]^{2-}$ isolated and characterized as the PPh_4^+ salt (ν(Mo═O) 950 cm^{-1}; *d*(Mo═O) 1.679(20) Å). Previously reported tetrasulfido species, e.g., $[MoE(S_4)_2]^{2-}$ ($E = O$, S), are described elsewhere.[3,225] Non-oxo, mixed-cage ligand complexes such as $(NBu_4)_2[Mo(AsSe_5)_2]$,[777] $(NBu_4)_2[Mo(CO)_2(As_3Se_5)_2]$, and $(NBu_4)_2[Mo(AsSe_5)_2]$ have also been reported;[778] the first of these contains a long intramolecular Se···Se interaction indicative of partial internal redox.

We also mention here blue/green, non-oxo complexes, $Tp^*MoX(S_4)$ ($X = F$, Cl, Br, NCS), produced by reacting Tp^*MoO_2X with B_2S_3 and H_2S mixtures. The very short Mo—S distances (av. 2.192 Å, X = Cl), alternating S—S distances, planarity, and ring current of the tetrasulfido ligand are suggestive of strong Mo—S π-bonding.[779]

4.7.4.6 Non-oxo Complexes

4.7.4.6.1 Halide complexes

Reduction of $K[MoF_6]$ with KI in anhydrous HF produces $K_2[MoF_6]$[640] while reduction of $MoOCl_3$ or $MoCl_5$ with TlCl at 350 °C yields $Tl_2[MoCl_6]$.[780] Related compounds, including $(SeCl_3)_2[MoCl_6]$ ($\mu_B = 2.5$), $(TeCl_3)_2[MoCl_6]$, and $(TeCl_3)_3[MoCl_6]Cl$, are obtained from ECl_4 (E = Se, Te) and $MoCl_4$.[781] Reaction of $MoX_2(CO)_2(PPh_3)_2$ (X = Cl, Br) with S_2Cl_2 produces yellow $[PClPh_3]_2[MoCl_6]$. A convenient synthesis for $MoBr_4$, from $MoCl_5$ and dry HBr, has been reported;[782] it reacts with PPh_3MeBr in CH_2Br_2 to yield $(PPh_3Me)_2[MoBr_6]\cdot 2CH_2Br_2$.[783] All hexahalide–$Mo^{IV}$ anions, including those in ternary solid state materials, exhibit octahedral structures.

In donor solvents, $MoCl_5$ and $MoCl_4$ are readily converted to octahedral Mo^{IV} complexes of the type $MoCl_4L_2$ (L = NCR, thf, OEt_2, 1/2dme, SEt_2); these are important starting materials in Mo chemistry. Improvements to the original syntheses for three widely utilized complexes, $MoCl_4(NCR)_2$ (R = Me, Et) and $MoCl_4(thf)_2$, have appeared in *Inorg. Synth. (Vol. 28, p. 34).* Electrocrystallization of $MoCl_4(NCMe)_2$ from $MoCl_5$/NCMe solutions yields the structurally characterized *trans* isomer.[784] Other new N-donor adducts of MoX_4 include yellow, paramagnetic *cis*/*trans*-$MoCl_4(NH_2{}^tBu)_2\cdot 2NH_2{}^tBu$,[785] $MoBr_4(NCMe)_2$, and $PPh_3Me[MoBr_5(NCMe)]$ (μ_B 2.65).[786]

Ether adducts of $MoCl_4$ are versatile starting materials and orange $MoCl_4(OEt_2)_2$ may be prepared by reacting $MoCl_5$ (and olefinic chlorine atom acceptors[787] or Sn[788]) or $MoCl_4$[789] with diethyl ether; the first of these methods has been extended to the synthesis of $MoCl_4$(dme) and related W complexes.[790] The diethyl ether ligands are readily displaced by thf, py, pentamethylene oxide, nitriles, phosphines, arsines, bpy, etc., while metathesis or reduction yields $Mo(O^tBu)_4$ and $MoCl_3(thf)_3$.[788] Complete loss of diethyl ether produces amorphous $MoCl_4$,[788] a stated but unrealized aim of early work.[787] The dark-red thioether analog, *trans*-$MoCl_4(SEt_2)_2$, is produced in the reaction of $MoCl_4$ with SEt_2 at 50 °C; the paramagnetic ($\mu_B = 2.81$) complex exhibits the expected octahedral geometry with $d(Mo–Cl)_{av}$ 2.331 Å and d(Mo–S) 2.534(2) Å. Dark-brown $MoCl_4$(dme) is also produced when $MoCl_5$ reacts with dme in toluene or with NaSi/15-crown-5/dme in toluene, whereupon it crystallizes as $MoCl_4(dme)\cdot$(15-C-5). The paramagnetic complex (μ_B 2.29) exhibits an octahedral geometry and associates with the crown ether through (dme) CH···O interactions.[791] The structure of *cis*-$MoCl_4(OPPh_3)_2$, in a mixed crystal of $[MoCl_3(OPPh_3)_2(NO).MoCl_4(OPPh_3)_2]$, has been determined.[537]

Non-oxo alkyne Mo^{IV} complexes are rare but diphenylacetylene reacts with $MoCl_5(OPCl_3)$ in CH_2Cl_2 forming $MoCl_4(\eta^2\text{-}PhC{\equiv}CPh)(OPCl_3)$ and $PhC(Cl){=}C(Cl)Ph$.[792] Reaction of $MoCl_4(SEt_2)_2$ with $PhC{\equiv}CSeBu$ produces *trans*-$MoCl_4(SEt_2)(\eta^2\text{-}PhC{\equiv}CSeBu)$, having a pseudo-octahedral geometry.[793] Finally, oxidation of $(Me_3tcn)MoBr_3$ with nitric acid produces red, paramagnetic (μ_B 2.2) *fac*-$[(Me_3tcn)MoBr_3]^+$ (**337**), isolated and structurally characterized as the $PF_6{}^-$ salt (Scheme 6).[325] Related compounds are electrochemically accessible from Mo^{III} counterparts.[257,325]

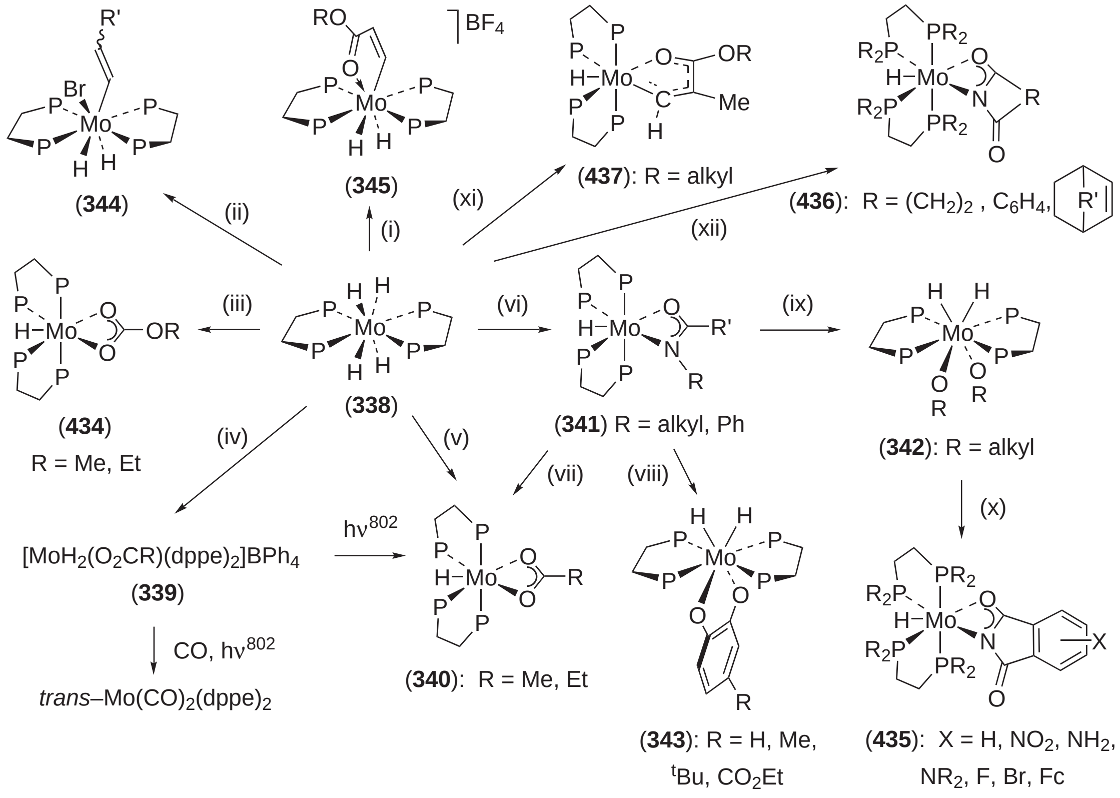
4.7.4.6.2 Cyanide complexes

Acidification of ice-cold solutions of $K_5[Mo(CN)_7]$ with acetic, hydrochloric, or ascorbic acids, or hydrogen sulfide, produces green, diamagnetic $K_4[MoH(CN)_7]\cdot 2H_2O$, characterized by ^1H (δ 2.3) and ^{13}C (δ 162.9, J_{CH} 11.3 Hz) NMR and IR (ν(Mo—H) 1,830 cm^{-1}) spectroscopy. The pK_a of the complex was estimated to be ca. 16.6. The electrochemical and chemical reactions of the complex, including catalytic alkene hydrogenation and SO_2 insertion into the Mo—H bond, have been studied.[794] The $[Mo(CN)_8]^{4-}$ anion exhibits distorted dodecahedral or distorted square antiprismatic geometries in its structurally characterized salts.[795] Variable-temperature ^{95}Mo and ^{14}N relaxation time measurements are consistent with a dodecahedral (D_{2d}) geometry in aqueous solution.[796] Magnetic materials such as $[Mn^{II}L]_6[Mo^{III}(CN)_7]\ [Mo^{IV}(CN)_8]_2\cdot 19.5H_2O$ (L = N_5-donor) are currently under study.[797]

4.7.4.6.3 Phosphido and hydrido–phosphine complexes

The homoleptic phosphido complex, $Mo(PCy_2)_4$, is produced by reacting $LiPCy_2$ with $MoCl_4(thf)_2$ in thf at −80 °C. A distorted tetrahedral structure, with planar $MoPC_2$ units and an average Mo—P distance of 2.265(2) Å, has been established by X-ray diffraction.[693]

Improved syntheses for $MoH_4(PR_3)_4$ ($PR_3 = PEt_3$, PBu_3, $PMePh_2$) and $MoH_4(dppe)_2$ (**338**, Scheme 14), based on reduction of $MoCl_4(thf)_2$ with $Li[BHEt_3]$ rather than $NaBH_4$, have been reported (see also *Inorg. Synth., Vol. 27, p. 8*).[798] Protonation of these compounds by anhydrous HX yields paramagnetic derivatives, $PHR_3[MoHX_4(PR_3)_2]$ with ν(Mo—H) ca. 1,850 cm^{-1}. The anion of $PHBu_3[MoHCl_4(PBu_3)_2]$ exhibits a pentagonal bipyramidal structure with apical chlorides and a hydride positioned between equatorial phosphine ligands.[798] Reduction of $MoCl_3(bdmp)/PMe_3$ under H_2 produces $MoH_4(PMe_3)(bdmp)$.[799] Oxidation of $Mo(dmpe)_3$ with HCl/NH_4PF_6 produces $[MoH_2(dmpe)_3](PF_6)_2$[800] while co-condensation of Mo with excess dippe yields $MoH_4(dippe)_2$ rather than desired $Mo(dippe)_2$.[801] The X-ray structures of $MoH_4\,(dippe)_2$[801] and $MoH_4(dppe)_2{\cdot}thf$ have been reported; the complexes are dodecahedral with H and P atoms in the A and B sites and Mo—L distances of ca. 1.67 Å and 2.42 Å, respectively.



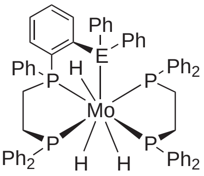
Reagents. (i) $HC{\equiv}CCO_2R$, HBF_4, $-H_2$;[804] (ii) $HC{\equiv}CCO_2R$, HBr, $-CO_2$, $-H_2$;[804] (iii) $RO_2COCH_2CCH_2$, hν;[1019] (iv) RCO_2H, $NaBPh_4$;[802] (v) $RCO_2CH_2CHCH_2$, hν;[1018] (vi) RNHCOR', hν or Δ;[803] (vii) $MeCO_2H$;[803] (viii) catechols;[803] (ix) 2ROH;[803] (x) phthalimides;[1020] (xi) $CH_2{=}CMeC(O)OR$, Δ or hν;[1022] (xii) $HN(C{=}O)_2R$.[1021]

Scheme 14

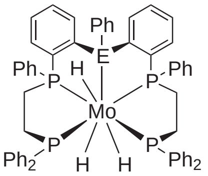
Protonation of (**338**) by carboxylic acids produces cationic $[MoH_2(O_2CR)(dppe)_2]^+$ (R = alkyl, alkenyl) that can be isolated as BPh_4^- salts (**339**) (Scheme 14). The acetate complex is photochemically unstable with respect to $MoH(O_2CMe)(dppe)_2$ (**340**) or, in the presence of CO, to *trans*-$Mo(CO)_2(dppe)_2$.[802] Tetrahydride (**338**) also reacts with *N*-alkylamides forming $MoH\{N(R)C(R')O\}(dppe)_2$ (**341**; R/R′ = H, $(CH_2)_3$, Me, Ph), that react with alcohols producing $MoH_2(OR)_2(dppe)_2$ (**342**)[803] and with catechol derivatives to give $MoH_2(cat)(dppe)_2$ (**343**);

complexes (**342**) are also unstable with respect to *trans*-$Mo(CO)_2(dppe)_2$.[803] Structural characterization of several catecholate derivatives revealed eight-coordinate distorted dodecahedral geometries.[803] Earlier, reactions involving alkynyl esters, $HC\equiv CCO_2R$ (R = Me, Et) and coordinating and noncoordinating acids were reported to produce organometallic derivatives (**344**) and (**345**), respectively.[804] Related Mo^{II} complexes are discussed in Section 4.7.6.3.2. The complex reaction between $MoH_4(dmpe)_2$ and CO_2 leads to the formation of formate, CO_2, and carbonate complexes such as $MoH_3(O_2CH)(dmpe)_2$, $MoH_2(O_2CH)_2(dmpe)_2$, and $MoH_2(CO_3)(dmpe)_2$.[805] An analogous carbonate, $MoH_2(CO_3)(PMe_3)_4$, results from the reaction of $Mo(\eta^2\text{-}C_2H_4)_2(PMe_3)_4$ with H_2/CO_2 mixtures.[806]

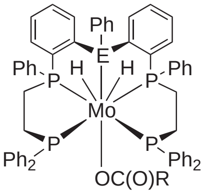
The reactions of (**338**) and Ph_2EH_2 (E = Si, Ge unless indicated) produce (**346**); at 100 °C, the Ge derivative eliminates benzene forming (**347**) (E = Ge), complexes (**347**) being directly accessible by reaction of $MoH_4(dppe)_2$ and $PhEH_3$.[807,808] Related alkyl and *o*/*p*-tolyl silyl complexes have also been prepared and the reactivity of the various series investigated.[808–810] Complexes (**347**) react with HO_2CR (R = H, Me, Ph) to produce monodentate carboxylate complexes (**348**), while the silyl derivative of (**347**) reacts reversibly with CO_2 to produce the formate complex (**348**) (E = Si, R = H). Significantly, complexes (**347**) and (**348**) (E = Si) catalyze the formation of dmf from $HNMe_2$ and CO_2/H_2 ($-H_2O$) in benzene at 110 °C.[810] Finally, the silyl derivative (**347**) reacts with dioxygen,[809] $PhSiH_3$,[807] and Hacac[811] to produce κ^2-peroxo (**349**), silane (**350**), and dangling-phosphine complexes, respectively. The X-ray structures of many of the complexes above have been determined.[807–811]



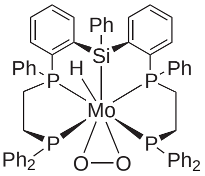
(**346**)



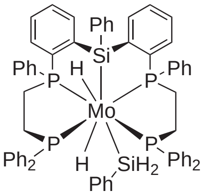
(**347**)



(**348**)



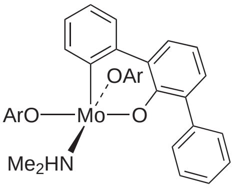
(**349**)



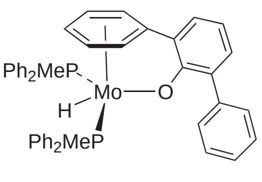
(**350**)

4.7.4.6.4 *Complexes containing aryloxide and related ligands*

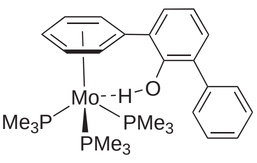
Mononuclear complexes are formed when $Mo(NMe_2)_4$ reacts with aryloxides (cf. formation of dinuclear species with alkoxides). The products formed depend on the steric bulk of the aryloxide and include $Mo(OAr)_4(HNMe_2)_2$ ($Ar = C_6H_4Me\text{-}4$, $C_6H_3Me_2\text{-}3,5$, $C_6H_3Me_2\text{-}2,6$), $Mo(OC_6H_3{}^tBu\text{-}Me\text{-}2,6)_3(NMe_2)(HNMe_2)$, $Mo(OC_6H_3{}^iPr_2\text{-}2,6)_3(NMe_2)(HNMe_2)$, and $Mo(OC_6H_4Me\text{-}4)_4(PMe_2Ph)_2$ (formed from $MoH_4(PMe_2Ph)_4$).[812] Reaction of 2,6-diphenylphenol (dppH) with $Mo(NMe_2)_4$ in benzene produces red, paramagnetic $Mo(OC_6H_3PhC_6H_4\text{-}C,O)(dpp)_2(NHMe_2)$ (**351**), that reacts with pyridine to form $Mo(OC_6H_3PhC_6H_4\text{-}C,O)(dpp)_2(py)$. Amide assisted cyclometallation of dpp was confirmed by X-ray crystallography, the aryl ligand (Mo—C_{av} 2.075 Å) occupying the apical site in these square pyramidal complexes.[813] In related chemistry, $MoH_4(PMePh_2)_4$ reacts with dppH to produce (**352**).[814] Paramagnetic *trans*-$Mo(OPh)_4(PMe_3)_2$ is produced in the reaction of $Mo(PMe_3)_6$ with excess phenol in benzene; increasing the steric demands of the aryloxide ligand induces partial oxidation to diamagnetic $MoH(OAr)(PMe_3)_4$ ($Ar = Mes$, $C_6H_3R_2\text{-}2,6$ ($R = {}^iPr$, Ph))[815] via species containing nonclassical H-bonds, exemplified by structurally characterized (**353**).[816] Density functional calculations on $Mo(OPh)_4$ are indicative of a pseudo-tetrahedral (flattened) D_{2d} structure.[817]



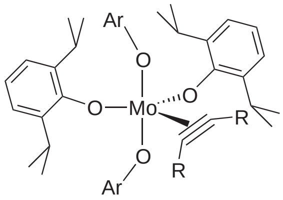
(**351**): OAr = dpp



(**352**)



(**353**)



(**354**): OAr = $OC_6H_3{}^iPr_2$

Trigonal bipyramidal η^2-alkyne aryloxide complexes such as $Mo(OAr)_2Cl_2(EtC{\equiv}CEt)$, $Mo(OAr)_3Cl(EtC{\equiv}CEt)$, and $Mo(OAr)_4(RC{\equiv}CR)$ (**354**; R = Et, Ph) can be prepared by reacting $MoCl_4(\eta^2\text{-}RC{\equiv}CR)(OEt_2)$ with $LiOC_6H_3{}^iPr_2$-2,6 (analogous thiolate complexes are described in the next section).[818] Addition of $MoCl_4(thf)_2$ to a suspension of $(NaO)_4{}^{Bu}cal{\cdot}2thf$ and alkynes in thf at −30 °C, followed by warming, provides access to η^2-2-metallacyclopropene complexes that are versatile synthons for anionic 1-metallacyclopropene, metallaalkylidyne, and dimetallic–dialkylidene complexes.[819] Oxidative addition of *p*-*tert*-butyltetrathiacalix[4]arene (L) to *cis*-$Mo(N_2)_2(PMe_2Ph)_4$ yields $MoH_2(PMe_2Ph)_3$(L-*S,O,O′*), characterized by dynamic NMR spectroscopy and X-ray crystallography.[820]

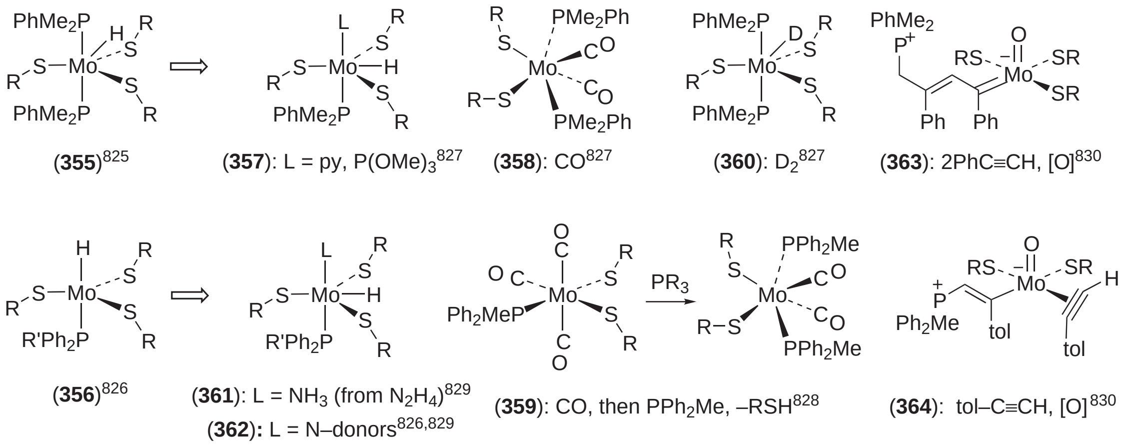
Dark-purple $Mo\{TeSi(SiMe_3)_3\}_4$ is produced in the reaction of $Mo(C_6H_4Me\text{-}2)_4$ and $HTeSi(SiMe_3)_3$ at low temperature. The diamagnetic complex exhibits a flattened tetrahedral structure with *d*(Mo—Te) 2.562(1)–2.582(1) Å.[821]

4.7.4.6.5 Complexes containing sulfur-donor ligands

(i) Thiolate complexes

Sterically hindered thiols form a variety of Mo^{IV} complexes. These include black/brown $Mo(SC_6H_2R_3\text{-}2,4,6)_4$ (R = Me, ^iPr) formed by reaction of $MoCl_4(thf)_2$ or $MoCl_4(NCMe)_2$ with sodium thiolates[822,823] or by Na/Hg reduction of $MoCl(SAr)_4$ (formed from $MoCl_4$ and Me_3SiSAr).[789] A flattened tetrahedral structure has been established for $Mo(SAr)_4$, which reacts with ethyne, 2-butyne, 3-hexyne, ^tBuNC, CO, and diphenyldiazomethane (L) to produce complexes of the type $Mo(SAr)_4L$.[789] Red $Mo(SAr)_4(\eta^2\text{-}RC{\equiv}CR)$ (R = Me, Et) are also accessible via reaction of $MoCl_4(\eta^2\text{-}RC{\equiv}CR)(OEt_2)$ with LiSAr, the X-ray structure of $Mo(SAr)_4(\eta^2\text{-}EtC{\equiv}CEt)$ revealing a distorted trigonal bipyramidal geometry with an axial η^2-alkyne on a pseudo-mirror plane.[818] Reaction of $MoCl_3(NCMe)_3$ with $HSAr/NEt_3$ in NCMe produces dark-brown, air-sensitive, diamagnetic $Mo(SAr)_4(NCMe)$, possessing a trigonal bipyramidal structure with an apical NCMe ligand.[823] Introduction of CO following the reaction of $MoCl_4(NCMe)_2$ with NaSAr produces $[Mo(SAr)_3(CO)_2]^-$.[824]

Hindered thiols also stabilize two types of hydrido–Mo^{IV} complex. The first, six-coordinate, 14-electron $MoH(SR)_3(PMe_2Ph)_2$ (**355**, R = Mes, $C_6H_2{}^iPr_3$-2,4,6), are formed in the reactions of $Mo(NNH_2)Br_2(PMe_2Ph)_3$ and RSH/NEt_3.[825] The second, five-coordinate, 12-electron complexes containing bulkier phosphines, $MoH(SR)_3(PR'Ph_2)$ (**356**, R = Mes, R′ = Me; R = $C_6H_2{}^iPr_3$-2,4,6, R′ = Et), are prepared from $MoH_4(PR'Ph_2)_4$ or $Mo(N_2)_2(PR'Ph_2)_4$ and RSH.[826] Compounds of the first type are characterized by hydride (^1H) and ^{31}P NMR signals at ca. δ 2.5 ($J_{HP(A)}$ ca. 100 Hz, $J_{HP(B)} < 10$ Hz) and δ ca. −110 and −147, respectively, and ν(Mo–H) IR bands at 1,902–1,926 cm^{-1}. The second type exhibit corresponding spectral features at δ ca. 3.3 (J_{HP} ca. 87 Hz), δ −69 to −78, and 1,858–1,940 cm^{-1}. The X-ray structure of $MoH(SC_6H_2{}^iPr_3)_3(PMe_2Ph)_2$ revealed a trigonal bipyramidal geometry with apical phosphine and equatorial thiolate ligands but failed to locate the hydride. Complexes (**355**) and (**356**) provide access to a variety of species by phosphine displacement (e.g., **357**), thiol elimination (**358**, **359**), hydride exchange (**360**), hydrazine disproportionation (**361**), and/or ligand addition (**362**) reactions, as shown in Scheme 15 (reagents are shown below each product). The electronic and steric determinants of structure and reactivity in these compounds have been extensively probed by spectral, electrochemical, and X-ray structural studies. The structures reported include those of (**357**) (L = py, R = $C_6H_2{}^iPr_3$ in all cases),[826] (**358**),[827] (**359**),[828] (**361**),[829] and (**362**) (R′ = Me, L = NH_2NHPh).[829] Typically, trigonal bipyramidal structures with an equatorial girdle comprised solely of thiolate ligands are observed. Complex (**355**) catalyzes the disproportionation or reduction of anhydrous hydrazine, lending support to the possibility of similar reactions at the Mo—S center of nitrogenase.[829] Recent work includes the reactions of (**355**) and (**356**) with alkynes, yielding structurally characterized phosphonium—alkylidene (**363**) and alkyne—ylide (**364**) oxo—Mo^{IV} complexes, respectively.[830] Related thiolato—Mo^{II} compounds are described in Section 4.7.6.5.2. Red, six-coordinate, distorted octahedral $Mo(dmsp)_2(S^tBu)_2$ (dmsp = 2-(diphenylphosphino)ethanethiolate), generated by bmsp-for-thiol exchange at $Mo(S^tBu)_4$, is effective in forming heterobimetallic cluster compounds with iron and copper species.[831]

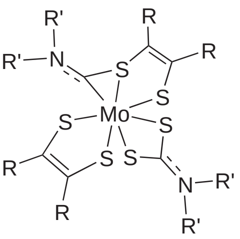


Scheme 15

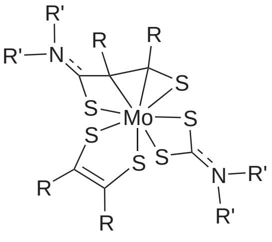
Tridentate $PhP(CH_2CH_2SH)_2$ and $PhP(C_6H_4SH)_2$ react with $MoCl_4(PPh_3)_2$ in methanol/NEt_3 to produce brown, air-stable, diamagnetic $Mo\{PhP(CH_2CH_2S)_2\}_2$[187] and $Mo\{PhP(C_6H_4S)_2\}_2$,[189] respectively; a distorted octahedral geometry with *facial P,S,S′*-bound ligands has been established for the former.[187] Diamagnetic $Mo\{PhP(C_6H_4S)_2\}_2(NCMe)$ is obtained when the latter reaction is performed in acetonitrile.[189] Reaction of $MoCl_2(CO)_2(PPh_3)_2$ with $PhP(C_6H_4SH)_2$ in methanol/base produced $Mo\{PhP(C_6H_4S)_2\}_2(CO)$ (ν(CO) 1,900 cm^{-1}).[189] Reaction of $MoCl_4(thf)_4$ with dttdH_2 produces violet, paramagnetic (μ_B 2.61) $MoCl_2$(dttd) that undergoes metathesis with thiolates (bdt^{2-}, edt^{2-}, SEt$^-$) producing, e.g., Mo(bdt)(dttd).[832]

(ii) Dithiocarbamate and related complexes

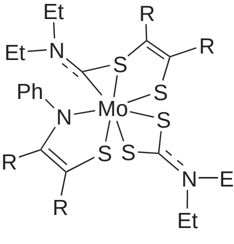
Novel ligands formed from the melding of dithiocarbamate, sulfur co-ligands, and alkyne units on Mo (and W) have been reported by Young and co-workers.[833–835] Thus, reactions of disulfido complexes $[Mo_2(\mu\text{-}S_2)_2(S_2CNR'_2)_4]^{2+}$, $MoO(S_2)(S_2CNR'_2)_2$ (R′ = Me, Et), or $Mo(S_2)(S_2CNEt_2)_3$ with RC≡CR (dmac, R = CO_2Me) produce isomeric orange (**365**) and green (**366**) complexes, characterized by spectroscopic and crystallographic methods.[833,834] The same melded ligands are proposed to exist in orange (**367**) and blue (**368**) 1-thio-2-iminoene complexes produced in the reaction of $Mo(NPh)(S_2)(S_2CNEt_2)_2$ with dmac. The presence of a melded ligand in (**368**) was confirmed by X-ray crystallography.[167,836] Dithiolenic species are the thermodynamic products of these and related reactions.[835] The reaction of $MoCl(S_2CNR_2)_3$ (R = Me,Et) with silver triflate results in the formation of brown, diamagnetic $[Mo_2(S_2CNR_2)_6](OTf)_2$, that acts as a source of the tris(dithiocarbamato)–Mo^{IV} cations $[Mo(S_2CNR_2)_3]^+$ in the synthesis of $[MoL(S_2CNR_2)_3]^{n+}$ (L = Cl, I, N_3, $n = 0$; L = O, NCMe, PR_3, $n = 1$). Structural characterization of paramagnetic, seven-coordinate $[Mo(S_2CNEt_2)_3(PMe_2Ph)]OTf$ revealed a pentagonal bipyramidal coordination geometry with an apical phosphine ligand.[837] Molybdenum(IV) 2-aminocyclopent-1-ene-1-dithiocarboxylate (**145**) complexes were discussed in Section 4.7.2.3.3(v)(b).



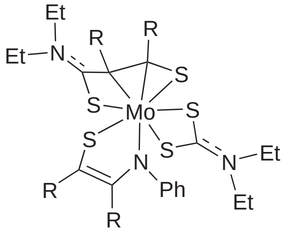
(**365**)



(**366**)



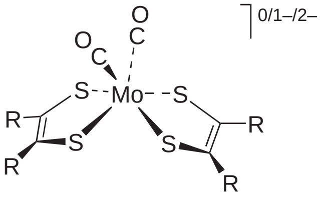
(**367**)



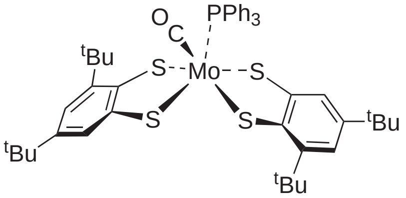
(**368**)

(iii) Dithiolene complexes

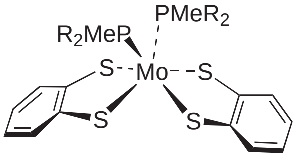
Improved syntheses for $Mo(CO)_2(S_2C_2R_2)_2$ (R = alkyl, Ph), from $Mo(CO)_3(NCMe)_3$ and $Ni(S_2C_2R_2)_2$, have underpinned recent developments. Potassium anthracenide reduction of $Mo(CO)_2(S_2C_2Me_2)_2$ produces $[Mo(CO)_2(S_2C_2Me_2)_2]^{2-}$ that comproportionates with $Mo(CO)_2(S_2C_2Me_2)_2$ to yield $[Mo(CO)_2(S_2C_2Me_2)_2]^{-}$. This allows the isolation of all three members of the series $(NEt_4)_n[Mo(CO)_2(S_2C_2Me_2)_2]$ ($n = 0, 1, 2$). The complexes exhibit trigonal prismatic structures (**369**) and structural, spectral, and electrochemical properties consistent with a principally ligand-based (>80%) redox orbital (also probed by DFT calculations).[511] Related complexes, $Mo(CO)_2(Bu_2bdt)_2$, $Mo(CO)(PR_3)L_2$, and $Mo(PMe_3)_2L_2$ (R = Me, Ph, Cy; L = bdt, Bu_2bdt), are produced upon thioether *S*-dealkylation of $Mo(CO)_3(Bu_4dttd)$ or $Mo(CO)_2(PR_3)L'$ (L′ = dttd (**146**), Bu_4dttd (**147**))[838–840] and in related reactions, e.g., those of PMe_3 with $Mo(CO)(PMe_3)$(**149**)[756] and $MoO_2(Bu_4dttd)$,[382] which produce $Mo(PMe_3)_2L'_2$ (L′ = bdt and Bu_2bdt, respectively). Trigonal prismatic strutures are adopted by $Mo(CO)(PPh_3)(Bu_2bdt)_2$ (**370**)[839] and $Mo(PMe_3)_2(bdt)_2$ (**371**)[756] in the solid state although octahedral *trans*-$Mo(CO)(PR_3)(Bu_2bdt)_2$ may exist in solution.[839] Further, $Mo(PMePh_2)_2(bdt)_2$ (**371**) and isocyanide complexes such as $Mo(CN^tBu)_2(S_2C_2H_2)_2$ and $Mo(CNMe)_2(bdt)_2$ (**372**) can be prepared by reacting $MoCl_4(NCMe)_2$ with dithiolene (L) salts and co-ligands; these complexes all adopt trigonal prismatic structures.[370]



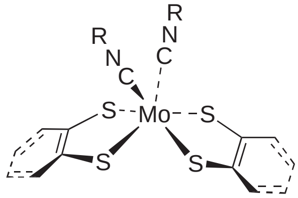
(**369**)



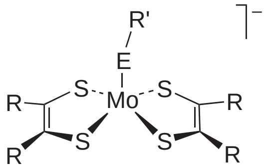
(**370**)



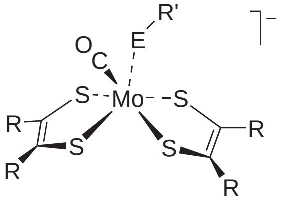
(**371**): R = Me, Ph



(**372**)



(**373**): E = O, S, Se



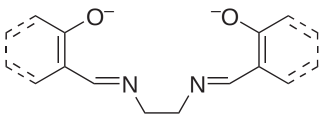
(**374**): E = S, Se

The reactions of $Mo(CO)_2(S_2C_2R_2)_2$ with $R'O^-$ and NEt_4^+ salts produce orange/brown $NEt_4[Mo(OR')(S_2C_2Me_2)_2]$ (R′ = ^{i}Pr, Ph, Ar, 2-Ad, C_6F_5) and $NEt_4[Mo(OR')(S_2C_2Ph_2)_2]$ (R′ = Ph, Ar) while reactions with NEt_4OH produce $(NEt_4)_2[MoO(S_2C_2R_2)_2]$ (R = Me, Ph);[371,515] related silyloxo complexes are produced in the reactions of $[MoOL_2]^{2-}$ (L = edt, bdt) with $ClSi^tBuPh_2$.[370] The complex anions all exhibit square pyramidal structures with basal dithiolene ligation (**373**). Kinetics and isotope-labeling studies of the OAT reactions of $NEt_4[Mo(OR')(S_2C_2Ph_2)_2]$ with Se-, N-, and S-oxides are consistent with initial formation of $NEt_4[MoO(OR')(S_2C_2Ph_2)_2]$ (cf. (**143**)) that decay by internal redox to the final product, $NEt_4[MoO(S_2C_2Ph_2)_2]$. These complexes and reactions are excellent models for the dmso reductases.[371] The large negative potentials required to reduce $NEt_4[Mo(OR')(S_2C_2R_2)_2]$ account for the absence of Mo^{III} enzyme states. The reactions of $Mo(CO)_2(S_2C_2R_2)_2$ with thiolates and selenolates are more complicated and two types of product, salts of $[Mo(ER')(CO)(S_2C_2R_2)_2]^-$ (R = Me, ER′ = SPh, SePh; R = Me, Ph, ER′ = $SeC_6H_2{}^iPr_3$-2,4,6)[515] or $[Mo(ER')(S_2C_2R_2)_2]^-$ (R = Me, Ph, ER′ = $SC_6H_2{}^iPr_3$-2,4,6; R = Me, ER′ = S-2-Ad, Se-2-Ad)[371,515] are isolated depending on ligand and conditions. The carbonyl anions exhibit trigonal prismatic structures (**374**) while the non-carbonyl complexes are square pyramidal (**373**). Molybdenum K- and $L_{2,3}$-edge X-ray absorption spectra of the compounds have been reported.[365,841] Blue/green $Tp^*MoX(S_4)$ (X = F, Cl, Br, NCS) (Section 4.7.4.5) react with alkynes to yield mono(dithiolene) complexes such as structurally characterized $Tp^*Mo(NCS)\{S_2C_2(CO_2Me)_2\}$.[842]

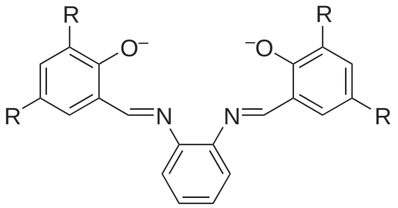
Trigonal prismatic tris(dithiolene) complexes, including representatives from (**216**)–(**220**) ($n = 2$) are also well known.[5] These are typically prepared by reacting a ligand salt or precursor mixture with $[MoS_4]^{2-}$[512,514,744] or $MoCl_5$[655] or by reduction of Mo^{VI} or Mo^{V} counterparts. Alternative syntheses include the reaction of $MoO_2(acac)_2$ with H_2qdt in 98% H_2SO_4, followed by hydrolytic workup and cation exchange to give $Cat_2[Mo(qdt)_3]$ ($Cat = PPh_4^+$, NEt_4^+).[843] As noted previously, complexes of this type are typically members of a reversible three-membered electron-transfer series $[Mo(dithiolene)_3]^{0/1-/2-}$. Trigonal prismatic structures have been confirmed by the X-ray structures of $(PPh_4)_2[Mo\{S_2C_2(CO_2Me)_2\}_3]$ (ϕ 10.6°),[744] $(NBu_4)_2[Mo(dmit)_3]$ (ϕ 11°),[655] $(PPh_4)_2[Mo(qdt)_3]$ (ϕ 4.5°),[843] $(NEt_4)_2[Mo\{S_2C_2(CF_3)_2\}_3]$ (ϕ 16°),[514] $Fc_2[Mo\{S_2C_2(CF_3)_2\}_3]$ (ϕ 0°),[653] and $(NEt_4)_2[Mo(S_2C_2Me_2)_3]$ (ϕ 2.6°).[511] A spectroelectrochemical study of $[Mo(mnt)_3]^{n-}$ species has probed the nature of highly reduced $[Mo(mnt)_3]^{n-}$ ($n = 3, 4$).[844] The qdt ring nitrogens of $(PPh_4)_2[Mo(qdt)_3]$ undergo reversible protonation reactions that impact markedly on electrochemical behavior.[845] Finally, red, diamagnetic $(NBu_4)Na[Mo\{O_2CC(S)Ph_2\text{-}O,S\}_3]\cdot H_2O\cdot MeOH$ crystallizes from partially neutralized solutions of $(NBu_4)_2[MoO_2\{O_2CC(S)Ph_2\}_2]$ and $HO_2CC(SH)Ph_2$ (**176**); the anion exhibits a trigonal prismatic structure (ϕ 4.7°) and is readily oxidized to the Mo^V analog.[656]

4.7.4.6.6 *Complexes containing nitrogen/oxygen/sulfur-donor ligands*

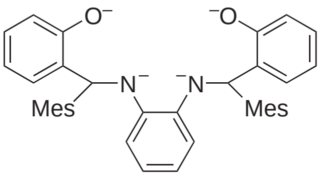
Paramagnetic *trans*-$MoCl_2L$ (L = acen, salen, salophen, and Bu_4salophen, (**375**)–(**378**)) precipitate when $MoCl_4(NCMe)_2$ is reacted with LH_2/NBu_3 in thf.[846,847] The acen[846] and Bu_4salophen[847] complexes both exhibit octahedral structures although the N_2O_2 equatorial girdle of the latter is tetrahedrally distorted. Reaction of *trans*-$MoCl_2$(salophen)·thf with Bz_2Mg produces brown $Mo(Bz)_2$(salophen), while reaction with MesMgBr results in oxidation to Mo^V and arylation at Mo *and* the ligand, producing green–brown Mo(Mes)(Mes_2salophen) (Mes_2salophen = (**379**)). The geometry of the latter is "square pyramidal" with an apical mesityl group.[847] Pentadentate bis(hydrazone) ligands are also observed to form pentagonal bipyramidal complexes of the type $MoCl_2L$.[848]



(**375**): acen (rings absent)
(**376**): salen (rings present)



(**377**): salophen (R = H)
(**378**): $^tBu_4$salophen (R = ^tBu)



(**379**): Mes_2salophen

Reaction of pyrimidine-2-thiol/NEt_3 with $MoCl_4(thf)_2$ in thf produces green–brown $Mo(pymS)_4$ that features bidentate pyrimidine-2-thiolate (pymS) ligands and a dodecahedral structure. The ligands can be protonated by $HBF_4\cdot OEt_2$ or methylated by Me_3OBF_4 to produce intensely colored $[Mo(RpymS)_4](BF_4)_4$ (R = H, Me). Electrochemical and spectroscopic data for these and related compounds have been reported.[849] Silylated pyridine-2-thiol complexes such as $Mo(SC_5H_3N\text{-}3\text{-}SiMe_3)_4$ are also known.[188]

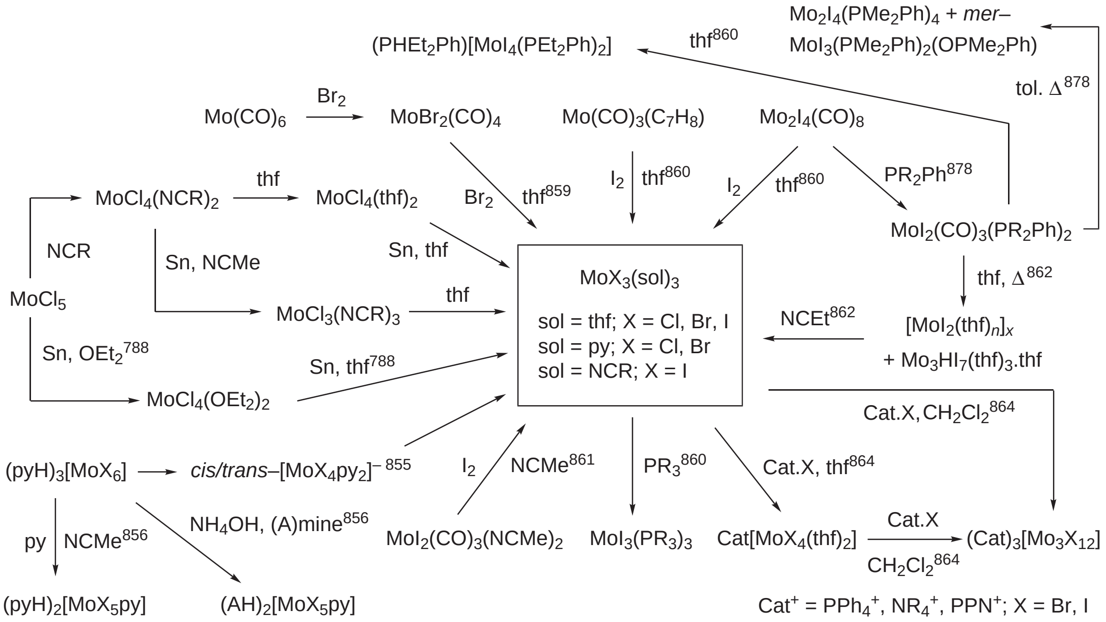
4.7.5 MOLYBDENUM(III) COMPLEXES

In contrast to the plethora of Cr^{III} complexes, mononuclear Mo^{III} species are rare due to their susceptibility to oxidation and proclivity for dinucleation. However, like their Cr^{III} counterparts they are almost invariably octahedral in geometry and paramagnetic due to a high-spin d^3 electron configuration. Halide complexes dominate this oxidation state and *mer*-trihalide species are heavily represented. Consequently, halide complexes are discussed ahead of other species.[3]

4.7.5.1 Halide and Cyanide Complexes

Most Mo^{III} complexes contain halide ligands and those bearing easily displaced solvent ligands are key starting materials. Indeed, as shown in Scheme 16, most "roads" in Mo^{III}

chemistry lead to or from *mer*-$MoX_3(sol)_3$ species (boxed). It is convenient to discuss the majority of halide complexes under a single heading, working from hexahalides down to dihalides. Other Mo^{III} complexes, many bearing halide co-ligands, are then discussed under the usual ligand categories.



Scheme 16

A convenient synthesis of $(NH_4)_3[MoCl_6]$ from ammonium molybdate and Sn in hydrochloric acid has been reported in *Inorg. Synth. (Vol. 29, p. 127)*. A related synthesis and the X-ray structure and catalytic properties of $(dppeH_2)_3[MoCl_6]_2 \cdot 12H_2O$ have been reported.[850] Hexahalo complexes are photochemically active and the absorption and luminescence spectra of $K_3[MoX_6]$ ($X = Cl^-$ (λ 1,095 nm, τ 480 ns),[851] NCS^- (λ 1,350 nm, τ 760 ns)[852]) have been probed by magneto-optical studies of Mo^{III} doped in Cs_2NaYCl_6.[853] Stepwise exchange of the halide ligands of $(pyH)_3[MoX_6]$ by pyridine, followed by cation metathesis, yields salts of $[MoX_5py]^{2-}$, *cis*/*trans*-$[MoCl_4py_2]^-$, and ultimately *mer*-MoX_3py_3.[854–856] The many structurally characterized compounds in this class include: $(Cat)_2[MoCl_5py]$ ($Cat = NH_2Me_2^+$, NMe_4^+, pyH^+), *cis*-$Rb[MoCl_4py_2] \cdot H_2O$, *cis*-$PPh_4[MoBr_4py_2]$, *trans*-$Cat[MoCl_4py_2]$ ($Cat = C_{10}H_9N_2^+$, NH_4^+), and *trans*-$[MoCl_2py_4](Br_3)$.

Improved syntheses for $MoCl_3(thf)_3$ have been reported. The reduction of readily prepared $MoCl_4(OEt_2)_2$[789,790] by Sn in thf offers a convenient alternative[788] to traditional syntheses employing nitrile and thf complexes (see *Inorg. Synth., Vol. 28, p. 36*). The X-ray structure of $MoCl_3(OEt_2)_3$, prepared by reducing $MoCl_4(\eta^2\text{-}PhC{\equiv}CPh)$ by sodium naphthalide in thf, has been determined.[857] It is relatively unstable and is readily converted to edge- and face-shared bioctahedral species in dichloromethane.[858] Reliable syntheses for $MoBr_3(thf)_3$, by bromine oxidation of $MoBr_2(CO)_4$ in thf[859] or dissolution of $MoBr_4$ in thf,[782] and of $MoI_3(thf)_3$,[860] by iodine oxidation of $Mo(CO)_3(C_7H_8)$ or $Mo_2I_4(CO)_8$, are also available (see *Inorg. Synth., Vol. 32, p. 198*). Iodine oxidation of $MoI_2(CO)_3(NCMe)_2$ provides a convenient route to air-sensitive, red-brown *mer*-$MoI_3(NCMe)_3$,[861] the propionitrile analog being a minor product in the reaction of $[MoI_2(thf)_n]_x$ with NCEt. The X-ray structures of (all *mer*) $MoI_3(thf)_3$,[860] $MoI_3(NCMe)_3$,[861] and $MoI_3(NCEt)_3$[862] have been determined. The chloride, *mer*-$MoCl_3(NCMe)_3$, is conveniently prepared by reducing $MoCl_4(NCMe)_2$ with Sn in NCMe (see *Inorg. Synth., Vol. 28, p. 37*). Air-stable salts of *trans*-$[MoCl_4(thf)_2]^-$ may be generated by reducing $MoCl_4(thf)_2$ with Zn metal in alcohol in the presence of base followed by cation metathesis. These compounds undergo ligand exchange producing, e.g., salts of $[MoCl_4(PMe_2Ph)_2]^-$, $[MoCl_4(dppe)]^-$, and $[MoCl_4(py)_2]^-$.[863] The reactions of $MoX_3(sol)_3$ with halides also produce $Cat[MoX_4(sol)_2]$ species, e.g., $Cat[MoX_4(thf)_2]$ ($X = Cl$, Br, I),[864] and the X-ray structure of *trans*-$PPh_4[MoCl_4(thf)_2]$ has been determined.[863] A compound containing a cyano–Mo^{III} complex, $[Mn^{II}L]_6[Mo^{III}(CN)_7][Mo^{IV}(CN)_8]_2 \cdot 19.5H_2O$ ($L = N_5$-donor), has also been reported.[797]

4.7.5.2 Complexes Containing Nitrogen-donor Ligands

4.7.5.2.1 Ammine, cyclam, and related complexes

Few ammine–Mo^{III} complexes have been reported. Treatment of $MoCl_3(thf)_3$ with NH_3, followed by triflic acid, yields yellow *fac*-$Mo(OTf)_3(NH_3)_3$;[865] halide derivatives, *fac*-$MoX_3(NH_3)_3$ (X = Cl, Br, I), can be prepared by metathesis.[866] The air-sensitive, paramagnetic (μ_B 3.61–4.75) halides display spectral bands due to spin-forbidden ${}^4A_{2g} \rightarrow {}^2T_{2g}$ (λ 649, 660, 690 nm, respectively) and spin-allowed ${}^4A_{2g} \rightarrow {}^4T_{2g}$ (Δ_o, λ 405, 420, 450 nm, respectively) and ${}^4A_{2g} \rightarrow {}^4T_{1g}$ transitions (ca. 350 nm). Complexes of the type $MoCl_3(NH_2R)_3$, $NH_3R[MoCl_4(NH_2R)]$ (R = Et, Pr, ${}^tBu$, Cy), and $(NH_2Et_2)_{n-3}[MoCl_n(NHEt_2)_{6-n}]$ (n = 4, 5) are formed in the reactions of $Mo_2Cl_6(thf)_3$ with amines.[867,868] Reaction of $MoCl_3(thf)_3$ with cyclam (and selected methyl derivatives) in refluxing thf produces *cis*-$[MoCl_2(cyclam)]Cl$ that reacts with triflic acid forming $[Mo(OTf)_2(cyclam)]OTf$, a source of $[Mo(OH_2)_2(cyclam)]^{3+}$ in solution. Green *cis*-$[MoCl_2(cyclam)]Cl$ exhibits a distorted octahedral structure and spin-allowed transitions at 370 nm and 310 nm.[869] A structurally related complex, *cis*-$[MoCl_2([15]aneN_4)]Cl{\cdot}2H_2O$, with λ 640(w), 363 and 319 nm, was subsequently prepared from $MoCl_3(thf)_3$ and 1,4,8,12-tetraazacyclopentadecane ($[15]aneN_4$).[870] Complexes of imidazole and its derivatives (L), viz., MoX_3L_3 (X = Cl, Br, NCS), have been partially characterized[871] and the X-ray structures of $PPh_4[MoCl_4(bpy)]$ and *mer*-$MoBr_3$(1,3-thiazole-*N*)$_3$ determined.

4.7.5.2.2 Triaza and tris(pyrazolyl) ligand complexes

Oxidation of (**104**) by $SOCl_2$, Br_2, or HI produces paramagnetic (μ_B 4.7–3.9) (**122**) (X = Cl, Br, I; R = Me,[325] ${}^iPr$[257]); a thiocyanate analog is also known[325] (Scheme 6). Dinuclear Mo^{III} species form with less sterically hindered triazacyclononane and triazacyclododecane ligands.[594] The phosphorescence of $(Me_3tcn)MoX_3$ (X = Cl, Br, I), $MoCl_3py_3$, and $[Tp^*MoCl_3]^-$ is assigned to the $\{{}^2E_g, {}^2T_{1g}\} \rightarrow {}^4A_{2g}$ transition, excited at ca. 1,050–1,250 nm. Complexes (**122**) undergo reversible electrochemical[325] and (ir)reversible photochemical oxidations to produce $[(Me_3tcn)MoX_3]^+$ (**380**) and $[(Me_3tcn)MoOX_2]^+$ (**246**).[872] Related complexes, $({}^tBu_3tch)MoX_3$ (X = Cl, Br, see (**105**) for ligand structure), may be similarly prepared.[260] Oxidation of $Tm^*Mo(CO)_3$ with $SOCl_2$, Br_2, or I_2/HI provides access to Tm^*MoX_3 (X = Cl, Br, I). These undergo a reversible oxidation to Mo^{IV} species and possess distorted octahedral structures, as evident from the X-ray structure of Tm^*MoI_3.[262] Oxidation of $NEt_4[Tp^*Mo(CO)_3]$ with thiuram disulfides produces orange, paramagnetic (μ_B ca. 3.9) $Tp^*Mo(S_2CNR_2)_2$ (R = Me, Et), containing both mono- and bidentate dithiocarbamate ligands.[873]

4.7.5.2.3 Tris(amido) complexes

Orange–red, air- and moisture-sensitive (**1**) is the key starting material for the chemistry summarized in Scheme 1.[79] The complex is conveniently prepared by reacting $MoCl_3(thf)_3$ with Li(N-RAr)(OEt_2) in diethyl ether under an argon atmosphere;[80] relatives such as $Mo(N^tBuPh)_3$,[85,572] $Mo\{N(Ad)Ar\}_3$,[86] $Mo\{N(2\text{-}Ad)Ar\}_3$,[81] $Mo\{NR(C_6H_4F\text{-}4)\}_3$,[83] and $Mo\{N^tBu(C_6H_4F\text{-}4)\}_3$[572] may be similarly prepared but the reaction is not universal.[572] Three-coordinate (**1**) exhibits a trigonal planar structure with d(Mo—N) 1.960(7)–1.977(7) Å and ∠(N—Mo—N) ca. 120°; the nitrogen atoms are also trigonal planar with like substituents in the same hemispheres.[85] Related structures have been established for $Mo\{N(Ad)Ar\}_3$[86] and $Mo\{N(2\text{-}Ad)Ar\}_3$.[81] The steric bulk of the ligands is critically important in preventing dinucleation and the formation of Mo≡Mo bonded species.[89] The complexes are paramagnetic (μ_B 3.4–3.9) consistent with an $a(n)^1e(n)^2$ configuration.[85] Interestingly, a cyclometallated resting state (**381**) is observed for the *i*-propyl "analog." This paramagnetic (μ_B 2.1) monohydride exhibits a five-coordinate structure with a side-on bonded metallaziridine ligand.[87] Chemically, it behaves as a source of $Mo(N^iPrAr)_3$, the hydride migrating back to carbon during the course of reactions. The complex induces the cleavage of N_2 (Section 4.7.2.2.1) and reductive coupling of nitriles, and binds $Ph_2C{=}O$ and $PhC{\equiv}CPh$ in a side-on η^2 fashion.[87] Related Mo^{III} complexes include brown, paramagnetic (**2**) with ν(CO) 1,797 cm^{-1} (Scheme 1).[15] Attempts to prepare analogous $Mo(N_3N)$ complexes have to date failed. However, Mo^{III} complexes such as $MoL(N_3N)$ (L = CO (**16**), N_2 (**43**), RNC (**301**), C_2H_4 (**382**)),

$[Mo(N_2)(N_3N)]_2[\mu\text{-}Mg(thf)_2]$ (**42**) (Scheme 2) and $MoL\{N(CH_2CH_2NC_6F_5)_3\}$ (L = CO, RNC) have been described.[21] Also, a carbonyl complex (**383**) containing a "tren" ligand modified by net insertion of COMe into an N—Si bond, has been produced in the reaction of (**14**) (R = Me) with CO.[874] The susceptibility of N_3N^{3-} to undesired side reactions has encouraged the study of $N(CH_2CH_2NAr)_3{}^{3-}$ (Ar = aryl) complexes, and dinitrogen, diazenido, and hydrazido complexes are known.[19]

4.7.5.2.4 Phthalocyanine complexes

Reaction of bromine-activated MoOPc (**384**) or MoNPc (**385**) with molten PPh_3/PPNBr yields purple *trans*-PPN[$MoBr_2Pc$] (**386**) (Scheme 11). The paramagnetic (μ_B 3.84) compound undergoes metal- then Pc-centered reductions and metal-centered oxidations. The anion has an octahedral geometry with *d*(Mo—N) 2.034(10) Å and *d*(Mo—Br) 2.588(1) Å. Spectral studies of the compound confirmed the existence of exotic trip-multiplet transitions.[875]

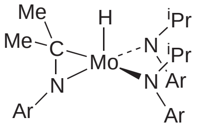
4.7.5.3 Complexes Containing Phosphorus-donor Ligands

Chloro phosphine Mo^{III} complexes are produced by ligand exchange at $PPh_4[MoCl_4(thf)_2]$ or by phosphine reduction and ligand exchange at $MoCl_4(thf)_2$.[876] The X-ray structures of *trans*-$PPh_4[MoCl_4(PR_3)_2]$ ($PR_3 = PMePh_2$, PMe_2Ph, PEt_3), *cis*-$PHEt_2Ph[MoCl_4(PEt_2Ph)_2]$, $(PHMe_2Ph)_2[MoCl_5(PMe_2Ph)]$, and *trans*-$MoCl_3(NCMe)(PEtPh_2)_2$ have been determined by Cotton and Vidyasagar.[876] Orange, $PMe_4[MoCl_4(PMe_3)_2]$, produced by decomposition of $Mo(\eta^3\text{-}C_3H_5)_2(PMe_3)_3$ in CH_2Cl_2, has also been structurally characterized.[877] Mononuclear species isolated from the iodide/phosphine/Mo^{III} system are shown in Scheme 16; the structures of *mer*-$MoI_3(PMe_2Ph)_2(OPMe_2Ph)$ and *trans*-$PHEt_2Ph[MoI_4(PEt_2Ph)_2]$ have been determined.[878]

Bidentate dppe reacts with $MoX_3(thf)_3$ to produce paramagnetic (μ_B 3.13–3.81) *mer*-MoX_3(dppe)(thf) (X = Cl, Br, I), the iodide being crystallographically characterized. The thf is readily displaced by NCMe or PMe_3 and $MoI_3(dppe)(PMe_3)$ adopts a rare *fac* structure (cf. *mer*-$MoI_3(PMe_3)_3$).[859] Tridentate and potentially tetradentate phosphines react with $MoX_3(thf)_3$ to produce yellow *mer*-$MoCl_3L$ (L = bdmp, bdpp,[879,880] tdea, tdep[881]) and *mer*-$MoBr_3$(tdea);[882] several of these have been structurally characterized. Oxidation of *trans*-$MoCl_2(dmpe)_2$ with $AgPF_6$ or $SnCl_2$ yields paramagnetic *trans*-$[MoCl_2(dmpe)_2]X$ (X = $PF_6{}^-$ (μ_B 3.61), $SnCl_3{}^-$).[740] The X-ray structure of *trans*-$(NBu_4)_2[MoCl_2(dppe)_2](BF_4)_3$, produced by electrochemical oxidation of $MoCl_2(dppe)_2$, has been reported and variations in the M—P and M—Cl distances in this and related Re complexes have been interpreted in terms of π-effects.[883] Finally, chemical oxidation of *trans*-$Mo(SR)_2(dppe)_2$ (R = alkyl, C_6F_5, C_6H_4X-4) produces rare EPR-active, low-spin d^3 (μ_B ca. 1.3) complexes, $[Mo(SR)_2L_2]^+$, isolated as $BPh_4{}^-$ salts.[884]

4.7.5.4 Complexes Containing Oxygen-donor Ligands

Light-green crystals of $Na_3[Mo(HCO_2)_6]$ (λ 383, 357 nm) precipitate over a period of days from solutions of $(NH_4)_2[MoCl_5(OH_2)]$ in 7 M $NaHCO_2/HCO_2H$.[885] The compound contains an octahedral anion featuring six monodentate formate ligands with $d(Mo\text{–}O)_{av}$ 2.113 Å. It is a precursor for cesium molybdenum alum, $Cs[Mo(OH_2)_6](SO_4)_2{\cdot}6H_2O$, a β-alum containing a perfectly octahedral hexaaqua-Mo^{III} cation (point symmetry S_6, *d*(Mo—O) 2.089(1) Å).[886] The trigonal planar structure of the $Mo(OH_2)$ units, confirmed by neutron diffraction, provides strong evidence for the presence of structurally significant Mo—O $d_\pi\text{–}p_\pi$ interactions.[887] Indeed, a beautiful, single-crystal polarized neutron diffraction study of $Cs[Mo(OD_2)_6](SO_4)_2{\cdot}6D_2O$ has revealed anisotropic spin transfer from the metal to the ligand, principally through $d_\pi\text{–}p_\pi$ interactions normal to the plane of the water molecules.[888] The X-ray structure of $(pyH)_2[MoCl_5(OH_2)]$ has been determined. Well-known $Mo(acac)_3$ continues to demand the attention of parties interested in epoxidation, hydrotreating, packaging, composites, ballistics, and waste conversion technologies.



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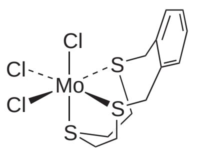

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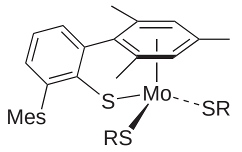
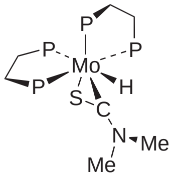


(388): R = $C_6H_3Mes_2$–2,6



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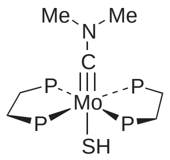

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4.7.5.5 Complexes Containing Sulfur-donor Ligands

Reactions of $MoCl_3(thf)_3$ with thioethers produce $MoCl_3(ttcn)$[889] and $MoCl_3(ttob)$ (**387**)[890] but ligand dissociation thwarts their derivatization.[890] Reaction of $MoCl_3(thf)_3$ with neat tetrahydrothiophene (tht) produces octahedral *mer*-$MoCl_3(tht)_3$ that reacts with alkynes to give pseudo-octahedral *mer,trans*-$MoCl_3(tht)_2(\eta^2\text{-PhC}\equiv\text{CR})$ (R = Me, Et). These are active catalysts for the selective polymerization and cyclotrimerization of alkynes.[891] A bromo derivative, *trans*-$(SMe_3)[MoBr_4(SMe_2)_2]$, is generated by reduction of $MoBr_4$ using excess SMe_2.[892]

A unique homoleptic molybdenum thiolate, $Mo(\eta^6\text{-dmpt})(dmpt)_2$ (**388**), is produced in the reaction of $MoCl_3(thf)_3$ with Li(2,6-dimesitylphenylthiolate) in diethyl ether at 0 °C. The paramagnetic ($\mu_B = 3.6$), pseudo-tetrahedral complex features two monodentate thiolates, the third being bound through sulfur and π-arene interactions.[893] The investigation of Mo^{III} and Mo^{IV} dithiocarbamates as oil additives and lubricant precursors continues.

4.7.6 MOLYBDENUM(II) COMPLEXES

Molybdenum(II) chemistry is dominated by six- to eight-coordinate mononuclear complexes and quadruply bonded Mo_2^{4+} species. Seven-coordinate complexes having a stable 18-electron count are most common. Easily interconvertible capped octahedral, capped trigonal prismatic, pentagonal bipyramidal, and 4:3 structures are observed for species of this type; they are frequently fluxional in solution. Examples of coordinatively and electronically unsaturated, six-coordinate, 16-electron complexes are also well represented. Dicarbonyl complexes of this type usually exhibit distorted octahedral structures with unusually large C—Mo—C angles (ca. 106°) and small *trans* X—Mo—X angles (140–150°). Work in this area has been reviewed in *Comprehensive Organometallic Chemistry*[6] and elsewhere.[894] A report of tetrahedral "$MoCl_2(PMe_3)_2$" was challenged by Cotton and Schmid[895] leading to the compound's reformulation as the corresponding Zn complex.[896] The organometallic chemistry of Mo^{II} is extensive and the reader is referred to *Comprehensive Organometallic Chemistry* for a description thereof.[6]

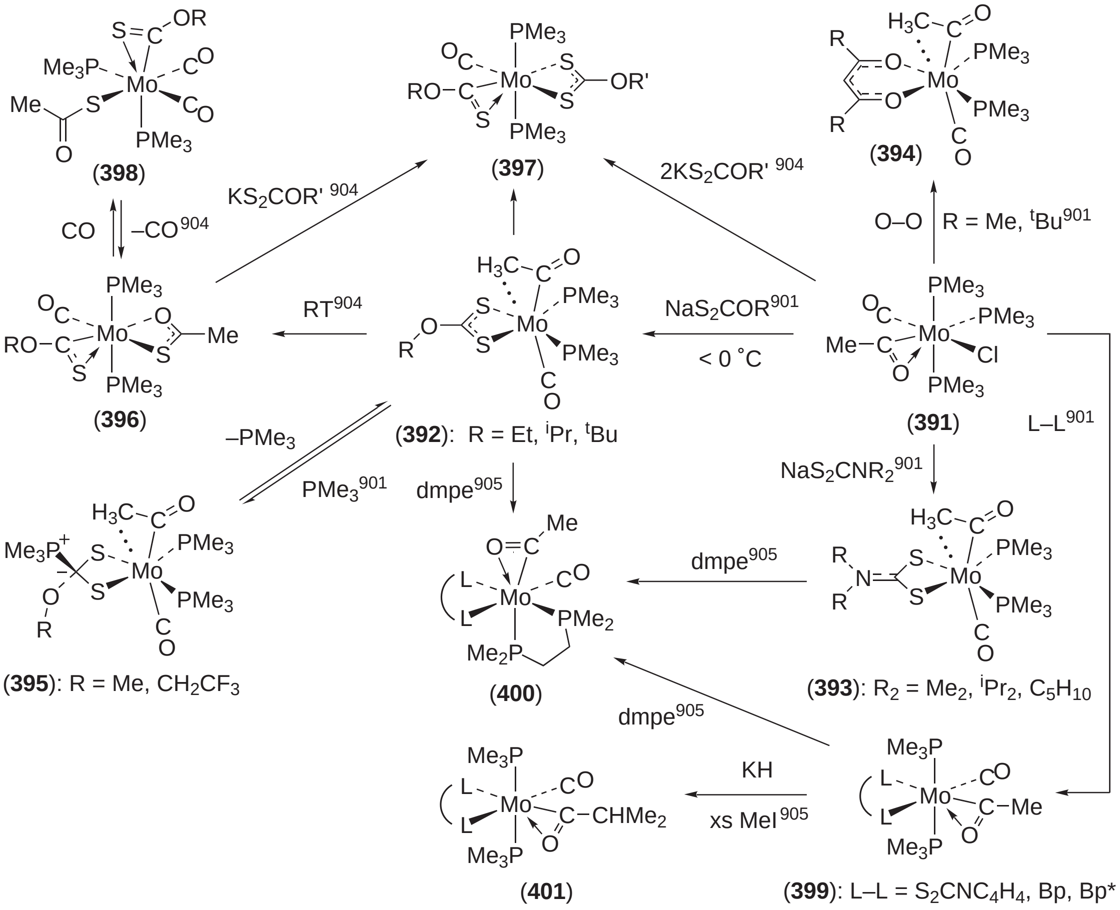
4.7.6.1 Complexes Containing Carbon-donor Ligands

4.7.6.1.1 Alkylidyne and acyl complexes

The alkylidyne complexes, $L_nMo(CR)$ ($L_n = Tp(CO)_2$, $(bpy)Br(CO)_2$; R, e.g., Ph derivatives), react with one equivalent of propylene sulfide to form thioacyl complexes, $L_nMo(\eta^2\text{-SCR})$. In the case of $Tp(CO)_2Mo(\eta^2\text{-SCC}_6H_4Me\text{-}4)$ conversion into dithiocarboxylate, mixed thioselenocarboxylate/thiolatocarbene, α-thiolatoalkyl, and α,α-bis(thiolato)alkyl species has been demonstrated.[897] More recently, related thiocarboxamide and alkoxythiocarbonyl chemistry has been reported.[898] Moreover, $Mo(CO)L_2$ (L = depe, dppe) react with $HC(S)NMe_2$ to produce thiocarboxamide hydrides (**389**) that convert at 125 °C to aminomethylidyne hydrosulfides (**390**).[899]

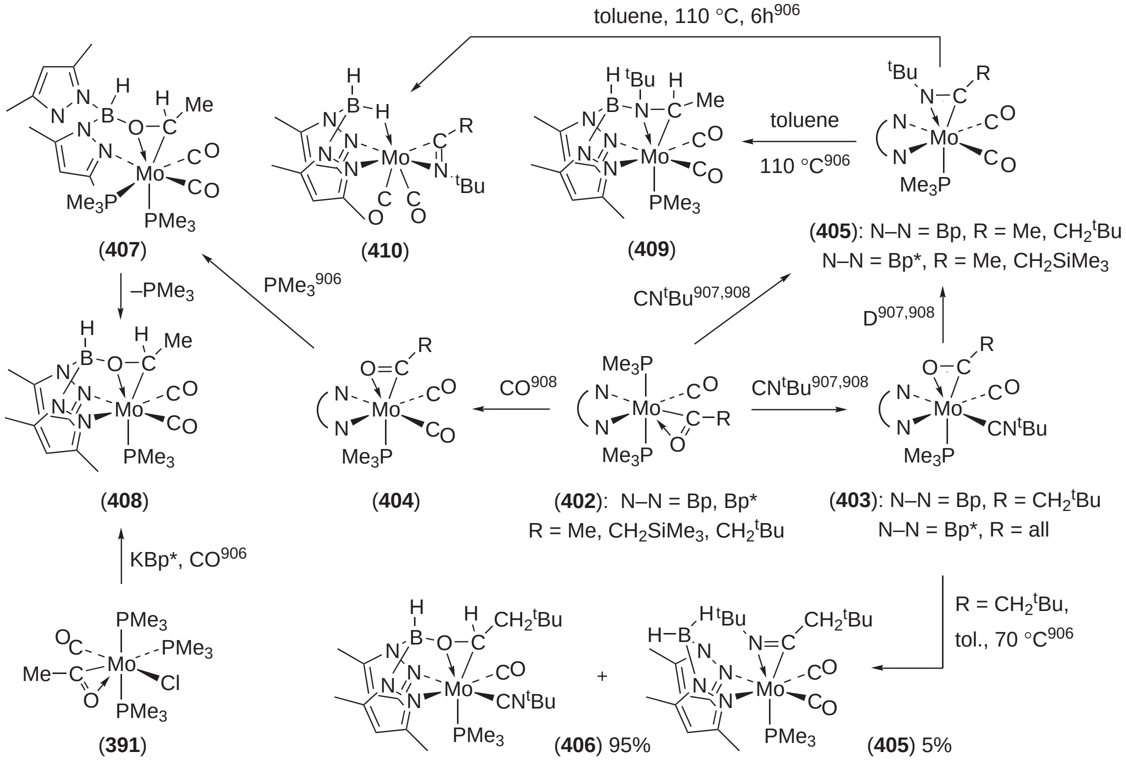
The chemistry of unusual agostic and η^2-acyl complexes is defined in Scheme 17.[900] Ligand exchange at $Mo\{\eta^2\text{-C(O)R}\}Cl(CO)(PMe_3)_3$ (R = Me (**391**), CH_2SiMe_3) produces $Mo\{C(O)Me\}L(CO)(PMe_3)_2$ (L = dithio acid or acac derivative) ((**392**)–(**395**)),[901,902] the silyl derivatives converting to methyl counterparts through C—Si bond heterolysis.[903] The equilibria between (**392**) and the phosphonium xanthates (**395**) lie well to the right except when R = Me or CH_2CF_3 (permitting isolation of (**395**)) (other phosphonium species are described in Sections 4.7.4.3.4(ii) and 4.7.6.5.1). The X-ray structures of (**393**) ($R_2 = Me_2$,[903] C_5H_{10}[901]), (**395**) ($R = CH_2CF_3$)[901] and

Mo{η^2-C(O)CH_2SiMe_3}(S_2CNMe_2)(CO)$(PMe_3)_2$[902] confirm the presence of an agostic interaction and its enhancement by electron-donating co-ligands.[902] Complexes (**392**) (and related dppe species) are unstable with respect to (**396**), containing η^2-alkoxythiocarbonyl and monothioacetate ligands. Chemical, spectroscopic, and structural evidence supports the translocation of a sulfur atom through C—S bond breaking/making processes. Reaction of (**396**) with KS_2COR' and CO permits the isolation of (**397**) and (**398**), respectively, the structural characterization of octahedral (**397**) ($R = R' = {}^tBu$) and (**398**) ($R = {}^iPr$) confirming the presence of the η^2-alkoxythiocarbonyl ligands.[904] The acac derivatives (**394**) are unstable with respect to disproportionation.[901] Interestingly, the pyrrole-based dithiocarbamate and Bp and Bp* derivatives (**399**) contain η^2- rather than agostic acyl ligands.[905] A variety of species bearing bidentate phosphine (**400**) and/or elaborated acyl ligands (**401**) have been prepared therefrom.[905]



Scheme 17

The Bp and Bp* complexes (**402**) (cf. **399**/**401**) are central to some intriguing reactions shown in Scheme 18 (for CN^tBu only).[900,906–908] These include: (i) ligand exchange at (**402**) to produce isocyanide (**403**) and carbonyl (**404**) complexes, (ii) thermal isomerization of (**403**) to give iminoacyl-carbonyls (**405**), (iii) intramolecular acyl and iminoacyl hydroborations producing (**406**)–(**408**) and (**409**), respectively, and (iv) generation of species with nonclassical B—H—Mo interactions (**410**). The chemistry in Scheme 18 is supported by spectroscopic and kinetics studies and the X-ray structures for key compounds, e.g., (**403**) and (**405**) ($R = CH_2SiMe_3$),[907] (**408**),[906] and (**410**) (R = Me).[900] Red Mo(η^2-$OCCH_2{}^tBu$)X$(PMe_3)_4$ (X = Cl, Br) are formed in the reactions of $Mo(CO_3)(CO)(PMe_3)_4$ with ${}^tBuCH_2MgX$; derivatives of these unstable species include Mo(η^2-$OCCH_2{}^tBu$)Cl(CO)$(PMe_3)_3$ and Mo(η^2-$OCCH_2{}^tBu$)Cl$(CO)_2(PMe_3)_2$.[909] Finally, η^2-acyl complexes, $LMo(CO)_2(\eta^2\text{-}OCR)$ (L = Tp, Tp*; R = Me, Et, Ph), are produced in the reactions of $NEt_4[LMo(CO)_3]$ with, e.g., RI and RCOBr.[910,911] The elaboration of the acyl ligand by deprotonation and electrophilic attack at the resultant enolate has been extensively explored by Templeton and co-workers.[911]



Scheme 18

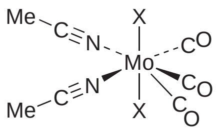
4.7.6.1.2 Carbonyl halide complexes

Work in this expansive area has been reviewed by Baker[894,912] and the literature cited herein is selective rather than exhaustive. The pivotal synthons in this area, $MoX_2(CO)_3(NCMe)_2$ (**411**; $X_2 = I_2$, Br_2, ICl, IBr), are prepared by low-temperature reactions of $Mo(CO)_3(NCMe)_3$ with halogens or interhalogens,[913,914] ligand exchange providing access to nitrile derivatives.[915] Archetypal $MoI_2(CO)_3(NCMe)_2$ adopts a distorted capped octahedral structure with CO atop a $(CO)_2I$-face.[861] Complexes (**411**) react with a wide variety of neutral and anionic mono-, bi-, and polydentate, C, N, P, As, Sb, Bi, O, and S-donor ligands, leading to seven-coordinate mono- and dinuclear species.[912] The catalytic properties of the complexes have been the focus of more recent studies.[916,917]

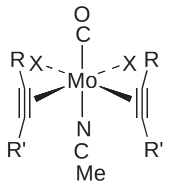
Alkynes react with (**411**) to form bis(alkyne) complexes, *cis,trans,cis*-$MoX_2(CO)(NCMe)(\eta^2\text{-}RC{\equiv}CR')_2$ (**412**; R = R′ = Me, Et, Ph; R/R′ = Me/Ph), possessing pseudo-octahedral structures with *cis*-aligned alkynes bound *trans* to halide.[918,919] These react with N- and P-donor ligands to form mixed-ligand complexes such as *cis*-$MoI_2(CO)(Me_2phen)(\eta^2\text{-}PhC{\equiv}CPh)$, *cis,trans*-$MoI_2(CO)(NCMe)\{P(OPh)_3\}(\eta^2\text{-}MeC{\equiv}CPh)$ (**413**), *cis,cis*-$MoI_2(CO)\{P(OMe)_3\}_2(\eta^2\text{-}MeC{\equiv}CMe)$ (**414**), *cis,trans*-$MoI_2\{P(OPh)_3\}_2(CO)(\eta^2\text{-}MeC{\equiv}CPh)$ (**415**), and *cis*-$MoI_2(CO)(dppe)(\eta^2\text{-}EtC{\equiv}CEt)$; again, the CO and alkyne ligands adopt a *cis*-aligned configuration in these pseudo-octahedral complexes.[919–921] Related species, *cis,trans*-$MoX_2(PR_3)_2(CO)(\eta^2\text{-}RC{\equiv}CR')$ (cf. (**415**)), are generated when $MoX_2(CO)_n(PR_3)_2(NCMe)$ ($n = 1$, 2) react with alkynes.[922,923] Brown $Mo(OTf)_2(CO)_2(PPh_3)_2$ reacts with nitriles and alkynes to give $[Mo(CO)_2(PPh_3)_2(NCMe)_3](OTf)_2$ and $Mo(OTf)_2(CO)(PPh_3)_2(MeC{\equiv}CR)$ (R = Me, Ph), respectively; bis(alkyne) complexes such as $[Mo(OTf)(CO)(PPh_3)_2(MeC{\equiv}CMe)_2]OTf$ are also accessible.[924]

N-donor ligands including pyridine, imidazole, pyrazole (L), RN=CHCH=NR (R = ^{i}Bu, Cy Ph, C_6H_4OMe), bpy, phen (L_2), and their various derivatives react with (**411**) to form $MoX_2(CO)_3(NCMe)L$, $MoX_2(CO)_3L_2$ and $[MoI(CO)_3L_3]I$;[925–927] the mono-substituted species dimerize to $[Mo(\mu\text{-}I)X(CO)_3L]_2$. Yellow/orange $MoBr_2L(CO)_2$, $MoI_2L(CO)_3$ ($L = Bm$, Bm^*, $H_2C(Me_3pz)_2$), and related complexes are formed when (**411**) reacts with L or when $Mo(CO)_4L$ react with X_2. The dicarbonyls are paramagnetic with contact-shifted NMR spectra, while the tricarbonyls are diamagnetic; $Bm^*MoBr_2(CO)_2$ (**416**) exhibits an octahedral geometry.[928] The complexes, $MoX_2(CO)_3(NCMe)(ER_3)$ and $MoX_2(CO)_3(ER_3)_2$ ($ER_3 = PPh_3$ etc., $AsPh_3$, $SbPh_3$, $BiPh_3$),[929,930] as well as mixed-ligand[931] and phosphite analogs[932] have been synthesized and characterized; the mono- and disubstituted complexes slowly convert to $[Mo(\mu\text{-}I)X(CO)_3L]_2$ and $PR_3H[MoI_3(CO)_3(ER_3)]$ (more basic phosphine is protonated), respectively.[929–931] Flash photolysis of $MoBr_2(CO)_3(PR_3)_2$ generates *cis,cis,trans*-$MoBr_2(CO)_2(PR_3)_2$ (that recombine with CO)[933] while decarbonylation in NCMe produces $MoX_2(CO)_2(NCMe)(PR_3)_2$ (e.g., $X = Br$; $PR_3 = PMePh_2$, $PEtPh_2$); the latter convert to $MoX_2(CO)_2(PR_3)_2$ in other solvents.[934] Complexes such as $MoBr_2(CO)_2L_2(PPh_3)$ ($L = PH_3$; $L_2 =$ bpy, dppm) and $[MoBr(CO)_2\{P(OCH_2)_3CMe\}_4]Br$ are formed when $MoBr_2(CO)_2(PPh_3)_2$ reacts with selected ligands; $MoBr_2(CO)_2(dppm)(PPh_3)$ adopts a bromide capped trigonal prismatic structure.[935] A similar structure is observed for $MoI_2(CO)_2(dppm)(dppm\text{-}P)$, prepared by reacting $NEt_4[MoI_3(CO)_4]$ with dppm.[936] However, $Mo(NCS)_2(CO)_2(dppm)(dppm\text{-}P)$, produced in the reaction of *fac*/*mer*-$Mo(CO)_3(dppm)(dppm\text{-}P)$ with $Hg(NCS)_2$, exhibits an intermediate geometry.[937] The structures of $MoX_2(CO)_3(R_2POPR_2)$ ($X = I$, $R = Ph$; $X = Br$, $R = C_6H_4Me\text{-}4$), prepared by halogenation of tetracarbonyl-Mo^0 species, are described as pentagonal bipyramidal with apical carbonyl ligands.[938] The reaction of $[MoI_2(CO)_4]_2$ with smaller, more basic dmpm in refluxing toluene permits the isolation of a pentagonal bipyramidal (CO and I apical) monocarbonyl, $MoI_2(CO)(dmpm)_2$.[939] Ready displacement of Bm^* from $Bm^*MoBr_2(CO)_2$ yields the phosphine complexes $MoBr_2(CO)_2L_n$ ($L = PMe_3$, $P(OMe)_3$, $n = 3$; $L =$ dppm, dppe, $n = 2$); $MoBr_2(CO)_2(dppm)_2$ exhibits an intermediate geometry and mono- and bidentate dppm ligands.[940] The reactions of $MoX_2(CO)_3(NCMe)(ER_3)$ with N-donors result in nitrile and/or iodide displacement giving complexes of the type $MoX_2(CO)_3L(PR_3)$ ($L =$ py, pzH) or $[MoI(CO)_3L]I$ ($L = py_2$, $(pzH)_2$, bpy, phen, etc).[927,941,942] Orange, light-sensitive $MoBr_2(CO)_2L(dppm\text{-}P)$ ($L =$ bpy, phen) are formed by reacting $MoBr_2(CO)_3L$ with dppm; irradiation produces green $MoBr_2(CO)(bpy)(dppm)$ that serves as a starting material for $[MoBr(CO)(bpy)(dppm)L']BPh_4$ ($L' = CO$, PR_3 ($R = H$, OMe, O^iPr, OPh)) and $[Mo(CO)(bpy)(dppm)\{P(OCH_2)_3CMe\}_2](BPh_4)_2$; $MoBr_2(CO)(bpy)(dppm)$ adopts a pentagonal bipyramidal structure, with equatorial bromo, dppm-*P,P′*, and bpy-N-donor atoms.[943] Diphosphazanes, $MoI_2(CO)_3[RN\{P(OPh)_2\}_2]$ ($R = Me$, Ph), are proposed to have pentagonal bipyramidal structures with carbonyl, iodide, and diphosphazane ligands at equatorial sites.[944] The X-ray structure of $MoI_2(CO)_2\{^iPrN(PPh_2)(PPh(Me_2pz))\}$ revealed an iodo capped trigonal prismatic geometry and confirmed coordination of the pyrazolyl β-nitrogen atom.[945] Bidentate and tridentate phosphines have also been incorporated into complexes of the type $MoI_2(CO)_3\{Ph_2P(CH_2)_nPPh_2\}$ ($n = 1$–6) and $MoI_2(CO)_3(bdpe)$; more recently, the syntheses and X-ray structures of mixed phosphite/phosphine complexes were reported.[946,947]

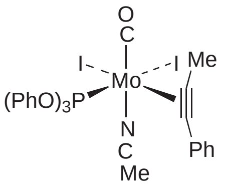
Neutral O- and S-donor ligands such as $OPPh_3$, $SPPh_3$, and thiourea derivatives react with (**411**) or $MoI_2(CO)_3(NCMe)(EPPh_3)$ forming complexes of the type $MoI_2(CO)_3(NCMe)L$, $MoI_2(CO)_3L_2$, and $MoI_2(CO)_3(EPPh_3)L$ (or μ-iodo complexes).[948–950] Reactions of (**411**) ($X = I$) with phosphines, then acetylacetonates yield $MoI(acac)(CO)_3(PPh_3)$ or $MoI(acac)(CO)_2(PR_3)_2$ ($R = Ph$, Et). The X-ray structure of $MoI(acac)(CO)_2(PEt_3)_2$ (**417**) revealed a pentagonal bipyramidal geometry.[951] The complexes $MoI(CO)_3L(S_2CNR_2)$ may be prepared by reacting *in situ*-generated $MoI_2(CO)_3(NCMe)L$ with NaS_2CNR_2 ($L = PPh_3$, $AsPh_3$, $SbPh_3$; $R = Me$, Et, Bz);[952] similar reactions have been demonstrated for ethyl xanthate and pyridine- and pyrimidine-2-thiolates.[953] Reaction of (**411**) ($X = I$) with two equivalents of dithioacid ligand produces $Mo(S_2CX)_2(CO)_n$ complexes; the most recent addition to this class, orange $Mo\{S_2P(OEt)_2\}_2(CO)_3$, reacts with phosphines such as dppm, dppe, and PPh_3 to form $Mo\{S_2P(OEt)_2\}_2(PPh_3)(CO)_2$, $Mo\{S_2P(OEt)_2\}_2L(CO)$ ($L =$ dppm, dppe), and $MoOI(dppe)\{S_2P(OEt)_2\}$.[954] Similar reactions with S_2CPCy_3 produce species of the type $MoI_2(CO)_3(S_2CPCy_3)$, $[Mo(CO)_3(S_2CPCy_3)_2]I_2$, and $[MoI(CO)_3(S_2CPCy_3)(PPh_3)]I$.[955] Unusual hydrides, $MoH(S_2CX)(CO)_2(PMe_3)_2$ ($X = NMe_2$, O^iPr, OMe) and $MoH(acac)(CO)_2(PMe_3)_2$, are produced in the reactions of $MoHCl(CO)_2(PMe_3)_3$ and salts of the bidentate ligands.[956] Neutral di- and tridentate S-donor ligands including $RS(CH_2)_2SR$ ($R = Ph$, $C_6H_4Me\text{-}4$, $C_6H_4F\text{-}4$),[957] ttn,[957] ttcn,[958] and 2,5,8-trithia[9]orthocyclophane[958] react with (**411**) to produce air-stable di- and tricarbonyls (**418**)–(**421**), respectively (structures inferred from W analogs). The alkyne derivatives, $MoI_2(CO)(NCMe)(\eta^2\text{-}RC{\equiv}CR)_2$, also react with a variety of sulfur-donor ligands giving, e.g., (**422**)–(**425**).[959,960]



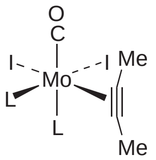
(**411**)



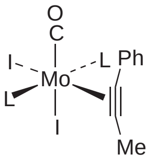
(**412**)



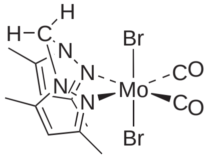
(**413**)



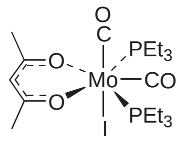
(**414**)
L = P(OMe)$_3$



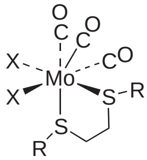
(**415**)
L = P(OPh)$_3$



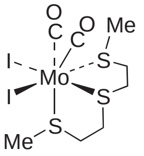
(**416**)



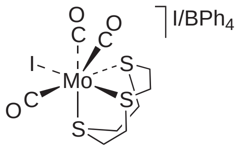
(**417**)



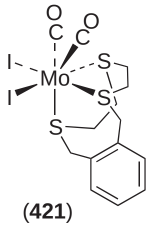
(**418**): X = I, Br



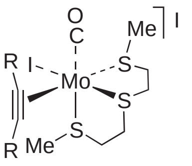
(**419**)



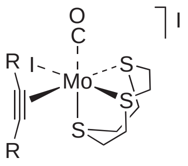
(**420**)



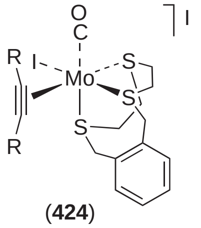
(**421**)



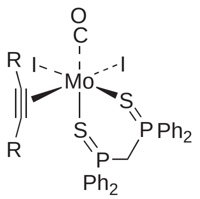
(**422**)



(**423**)



(**424**)



(**425**)

4.7.6.2 Complexes Containing Nitrogen-donor Ligands

4.7.6.2.1 Imido, amido, and diazenido complexes

These are relatively rare for Mo^{II} and are treated collectively. The electrochemical reduction of *trans*-[Mo(NR)X(dppe)$_2$]X′ (X = halide, R = alkyl, X′ = X or BPh$_4$) in the absence of protons produces five-coordinate Mo(NR)(dppe)$_2$.[679] Brown *cis,cis,trans*-Mo{1,2-(NH)$_2$-C$_6$H$_4$}(CO)$_2$(PPh$_3$)$_2$ (ν(CO) 1,913 cm^{-1}, 1,826 cm^{-1}) is produced in the reaction of MoBr$_2$(CO)$_2$-(PPh$_3$)$_2$ and 1,2-diaminobenzene under basic conditions. The six-coordinate complex is proposed to possess a pseudo-dodecahedral structure with two phenyl group hydrogens acting as "token ligands." Phosphine displacement is effected by PEt$_3$, P(OEt)$_3$, and dppe.[961] The reaction of MoCl$_2$(dmpe)$_2$ with LiNEt$_2$ at −78 °C is reported to produce orange *trans*-Mo(NEt$_2$)$_2$(dmpe)$_2$.[684]

3,5-Dimethylpyrazole-4- and antipyrene-4-diazonium salts react with TmMo(CO)$_3$, NEt$_4$[Tp-Mo(CO)$_3$], and Mo(CO)$_4$L (L = bpy, phen) producing red [TmMo(CO)$_2$(NNR)]BF$_4$, TpMo(CO)$_2$ (NNR), and [Mo(CO)$_3$L(NNR)]BF$_4$, respectively. The diazenido ligand in [TmMo(CO)$_2${NN-(Me$_2$pz)}]BF$_4$ is bent with ∠(Mo—N—N) 164.5(8)°.[962] Complexes containing pyridinium-diazenido and chelating pyridylhydrazinium and pyridinediazenido ligands have been reported by Rose et al.[963]

4.7.6.2.2 Tris(pyrazolyl) and triaza ligand complexes

The reader is referred to *Comprehensive Organometallic Chemistry*[6] for a description of alkyne, ketenyl, vinylidene, alkylidyne, and allyl Tp^x complexes prepared and exploited in elegant ligand elaborations and organic syntheses by Templeton, Liebeskind and others. Only selected "coordination chemistry" will be presented here. Halogen oxidation of NEt$_4$[TpMo(CO)$_3$] produces TpMoX(CO)$_3$ (X = Br, I) characterized by IR (3 ν(CO) for C_s symmetry), ^{1}H and ^{13}C NMR spectroscopy and X-ray crystallography; TpMoBr(CO)$_3$ possesses a 4:3 piano stool[964] (or alternatively, a capped octahedral[965]) structure. Oxidation of NEt$_4$[Tp*Mo(CO)$_3$] by PhICl$_2$ or I$_2$ yields unstable Tp*MoX(CO)$_3$ (ν(CO) ca. 2,025, 1,930 cm^{-1}), that convert to paramagnetic (μ_B 2.8–3.0)

Tp*MoX(CO)$_2$ (X = Cl, I; ν(CO) ca. 2,000, 1,922 cm^{-1}) upon standing.[580,966] Tris(triazolyl)-borate[967,968] and W[965] halocarbonyl complexes have also been prepared and structurally characterized. As originally reported by Trofimenko, seven-coordinate hydrides, Tp^{x}Mo(CO)$_3$H, result from the protonation of [Tp^{x}Mo(CO)$_3$]$^-$. The hydride ligand of Tp*Mo(CO)$_3$H (ν(Mo—H) ca. 1,886 cm^{-1}, δ(Mo—^{1}H) –3.41) was located between a pair of CO ligands giving a 4:3 structure.[969] The rates of the degenerate H$^+$ and H transfers between Tp*Mo(CO)$_3$H, Tp*Mo(CO)$_3$, and NBu$_4$[Tp*Mo(CO)$_3$], as well as the Mo—H bond dissociation energies of various complexes, have been measured.[969,970]

Halogenation of (**104**) yields salts of [(R$_3$tcn)MoX(CO)$_3$]$^+$ (**121**, R = H (tcn), Me, X = Br, I);[325,971] all the cations are proposed to have the 4:3 piano stool geometry established in the case of [(tcn)MoBr(CO)$_3$]ClO$_4$·H$_2$O.[971] A hydrido complex, [(tcn)MoH(CO)$_3$]$^+$, results from oxidation of (tcn)Mo(CO)$_3$ by HCl(aq).[971] Related complexes, [(^{t}Bu$_3$tch)MoX(CO)$_3$]X$_3$ (X = Br, I) and [(^{t}Bu$_3$tch)MoH(CO)$_3$]OTf, have also been reported.[260]

4.7.6.2.3 Nitrosyl and nitrito complexes

Nitrosyl–Mo^{II} complexes of the type Tp^{x}MoXY(NO) ((**426**), Figure 2) have been described by McCleverty and co-workers. These are accessed via metathesis of Tp^{x}MoX$_2$(NO) (X = Cl, Br, I), prepared by halogenation of Tp^{x}Mo(CO)$_2$(NO) (Tp^x = Tp* (*vide infra*)[4] and to a lesser extent 4-R-Tp* (R = Me, Bu,[972] Bz[973]), B(4-Rpz)$_4$ (R = C$_6$H$_4$OMe-4, Cy),[974] Tp^{Pr}, Tp′,[975,976] and HB(pz-C$_6$H$_4$OMe-4)$_3$[977,978]). The dihalides react smoothly with alcohols, phenols, alkyl- and arylamides, and thiols (with added base as necessary) generating the air- and water-stable, mono- (X ≠ Y) and di-substituted (X = Y) complexes in Figure 2 and elsewhere.[4] The monohalides serve as precursors for further mixed-ligand complexes; procedures for the synthesis of frequently used starting materials (X = I; Y = I, OEt, NHEt) can be found in *Inorg. Synth. (Vol. 23, p. 4)*. Recent additions to this class include: (i) complexes with redox active pendent ligands such as ferrocenyl and retinal derivatives,[979,980] (ii) complexes containing chiral ligands such as glucofuranose derivatives,[981] (+)/(−)-mentholate,[982] (+)/(−)-NHCH(Me)Ph,[983] and (−)-cholesterol,[980] (iii) cationic acetylacetonate derivatives, [Tp*Mo(acac)(NO)]$^+$, isolated as triiodide salts,[984] (iv) a variety of cyclic polyether[985] and cyclophane[986] derivatives, some containing 25(!)-membered chelate rings, (v) pentachalcogenido species, Tp*Mo(E$_5$)(NO) (E = S, Se),[987] (vi) a rare dihydroxo

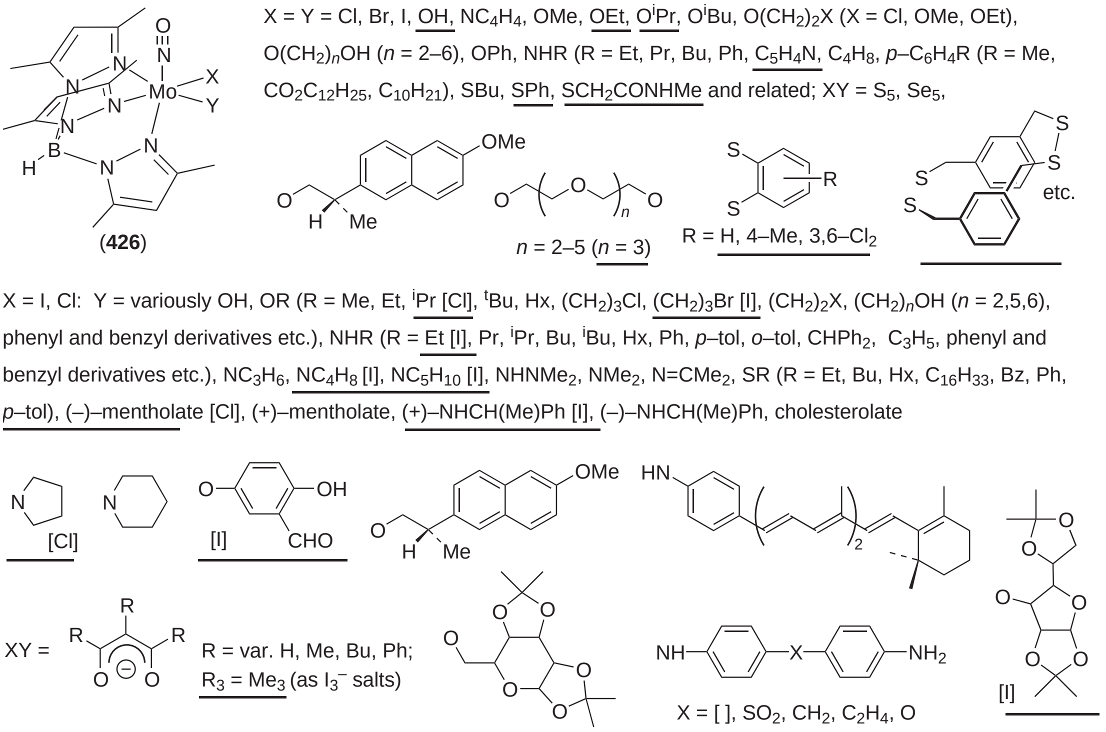


Figure 2 Nitrosyl-Mo^{II} complexes of T$_p$*.

complex, Tp*Mo(OH)$_2$(NO), structurally characterized as the H-honded bis(acetone) solvate (d(Mo—O) 1.928(2) Å),[988] and (vii) structurally characterized dithiolene complexes, Tp*MoL(NO) (L = bdt, tdt, S$_2$C$_6$H$_2$Cl$_2$-3,6), examined to define the electronic nature of biologically relevant Mo—dithiolene units.[989] Complexes containing potentially bridging ligands have also been prepared as precursors and spectral benchmarks for di- and trinuclear species with interesting electronic, spectral, and nonlinear optical properties.[990,991] Dozens of compounds have been structurally characterized and many of these are underlined in Figure 2 (where necessary, co-ligands are specified in square brackets); distorted octahedral structures with *facial* Tp* ligands and linear nitrosyls are invariable observed. The Mo—X/Y bond distances are shorter and the Mo—X/Y—C(R) angles wider than expected for singly bonded ligands, consistent with considerable p_π–d_π bonding between these ligands and the electron-deficient [Tp*Mo(NO)]$^{2+}$ center. The presence of linear NO$^+$ ligands is confirmed by the observation of ν(NO) IR bands between 1,730 and 1,600 cm^{-1}. The intense colors of the complexes, ranging from blue (X = Cl, Y = OR) through green (X = I, Y = OR) to red (X = Y = OR) and orange (X = I, Y = NHR), also reflect facile p_π–d_π LMCT. The complexes are readily reduced to 17-electron species and extensive electrochemical studies have been reported; reduction is sometimes reversible but more often pseudo-reversible or irreversible. Potentials are ligand dependent in the order: I > Br > Cl > NC$_4$H$_4$ > SPh > OPh > NHPh.[992–994] More subtle substituent and electronic effects have been probed by electrochemistry[995–997] and ^{95}Mo NMR spectroscopy.[998] Comparisons of the redox and electronic properties of Tp*MoOX$_2$ (Section 4.7.3.4.2(ii)) and Tp*MoX$_2$(NO) complexes have been presented.[999,1000] Like Tp*MoOX$_2$, the redox potentials of Tp*MoX$_2$(NO) species (and related Mo$^{\mathrm{I}}$ and Mo^0 complexes) can be fine tuned over an impressive range of ca. 2,000 mV. Chemical reduction is associated with displacement of halide producing Tp*MoXL(NO) or [Tp*MoL$_2$(NO)]$^+$ (L = neutral ligand) (Section 4.7.7).

Nitrosylation of (**104**) by 0.5 M HNO$_3$ (R = H (tcn),[971] Me,[1001]) or NOBF$_4$ (R = Bz)[1002] produces [(R$_3$tcn)Mo(CO)$_2$(NO)]$^+$ ((**427**), Scheme 6), from which orange [(R$_3$tcn)MoX$_2$(NO)]$^+$ (**428**), colorless (tcn)Mo(CN)$_3$(NO), and blue/green [(Me$_3$tcn)MoX(OEt)(NO)]$^+$ are accessible.[971,1001,1003] The preparation of [(Me$_3$tcn)MoCl(OMe)(NO)]PF$_6$ and addition of amines to [(Me$_3$tcn)MoBr$_2$(NO)]$^+$ have been reported.[1004] Nitrosylation of MoO$_3$ in the presence of tcn yields structurally characterized [(tcn)MoCl(H$_2$NO)(NO)]ClO$_4$.[327] Interestingly, hydroxo and oxo nitrosyl complexes such as [(^{i}Pr$_3$tcn)Mo(OH)$_2$(NO)]PF$_6$ (**429**) and (^{i}Pr$_3$tcn)MoO(OH)(NO) (**430**, formally an oxo–Mo$^{\mathrm{II}}$ species!) are produced in the reactions of [(^{i}Pr$_3$tcn)MoBr$_2$(NO)](Br$_3$) with H$_2$O.[1003] Other triazacyclononane—Mo$^{\mathrm{II}}$ chemistry is summarized in Section 4.7.6.2.2. Derivatives such as MoCl(OMe)$_2$L$_2$(NO) (L = py, L$_2$ = phen) may be obtained from MoCl(OMe)$_2$-(MeOH)$_2$(NO), prepared by nitrosylation of molybdate in refluxing methanol.[1005] Nitrosyl complexes of 1,5,9-triazacyclododecane are also known.[594]

An improved synthesis of yellow MoCl$_3$(PMe$_3$)$_3$(NO) from MoCl$_3$(PMe$_3$)$_3$ and NO at low temperature has been reported.[1006] Reaction of Mo(acac)$_2$(NO)$_2$ with salicylaldehyde-2-mercaptoanil and PPh$_3$ in refluxing methanol produces octahedral Mo(SB)L(NO), possessing an apical nitrosyl, a *fac* tridentate Schiff base (SB), and a bidentate 2-hydroxyphenylbenzthiazolate(1-)-*O,N* ligand (L) formed upon Schiff base oxidation.[1007] The extensive nitrosyl chemistry of S$_4$-donor ligand complexes is summarized in Section 4.7.6.5.4. Nitrito–Mo species are unstable and appear to be limited to Mo(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$, prepared by metathesis of MoBr$_2$(CO)$_2$(PPh$_3$)$_2$ and NaNO$_2$ in methanol.[1008]

4.7.6.2.4 Porphyrin and phthalocyanine complexes

Reduction of MoCl$_2$(por) (por = tpp, ttp) with Zn/Hg under an atmosphere of CO produces red, diamagnetic *cis*-Mo(por)(CO)$_2$ ((**431**), see Scheme 10(b), for por = ttp). A trigonal prismatic geometry with *cis* CO ligands staggered with respect to the Mo–N vectors is observed for Mo(ttp)(CO)$_2$. An additional ligand (L = 1-methylimidazole, py, OMe$^-$, N$_3$$^-$, $^-$O$_2$CMe) is observed to bind *trans* to the CO ligands to form [Mo(por)(CO)$_2$L]$^{n-}$. Displacement of the organometallic ligands from (**335**) or (**431**) produces *trans*-Mo(por)L$_2$ (**432**, L = py, 4-picoline); structurally characterized Mo(ttp)(py)$_2$ possesses an octahedral structure.[776,1009] The metal–metal bonded dimer, [MoPc]$_2$, formed in the reaction of MoOPc with molten PPh$_3$, reacts with molten NBu$_4$CN producing unstable, red–brown, paramagnetic (μ_{B} = 3.15) *trans*-(NBu$_4$)$_2$[Mo(CN)$_2$Pc] ((**433**), Scheme 11). The UV–vis–NIR spectrum of the complex is highly structured with an intense triplet–triplet transition at 7,780 cm^{-1}.[530]

4.7.6.3 Complexes Containing Phosphorus-donor Ligands

4.7.6.3.1 Halide complexes

Studies of complexes of the type *trans*-MoX_2P_4 ($X = Cl$, Br, I; $P_4 =$ monodentate, bidentate, or tridentate phosphine ligand combinations) have continued.[4] Red–purple, *trans*-$MoCl_2L_4$ ($L = PMe_3$, $PMePh_2$) can be prepared by Na/Hg[1010] or Mg[682] reduction of $MoCl_4L_3$ in thf; the complexes are stable in solution up to 80 °C but thereafter convert to quadruply bonded $Mo_2Cl_4L_4$.[682] The half-life for the first phosphine exchange at $MoCl_2(PMe_3)_4$ has been measured at 18 min ($k = 6.6 \times 10^{-4}$ s^{-1}) at 24 °C.[682] Experimental observations and theoretical analyses indicate that the exothermicity of oxidative addition of H_2 to $MX_2(PMe_3)_4$ depends on the nature of the metal and halogen as follows: Mo < W and I < Br < Cl < F. Moreover, oxidative addition of H_2 to $WI_2(PMe_3)_4$ is characterized by an *inverse* deuterium isotope effect ($K_H/K_D = 0.063(5)$ at 60 °C) and occurs at a five-coordinate complex formed by dissociation of PMe_3.[1011] The PMe_2Ph analog, $MoCl_2(PMe_2Ph)_4$ (μ_B 2.84), has also been prepared by reacting $MoCl_5$ with Mg or $MoCl_3(PMe_2Ph)_3$ with BuLi in the presence of PMe_2Ph.[1012] Thermogravimetric studies have shown that $MoCl_2(PMe_3)_4$ decomposes to $MoCl_2$ under an inert atmosphere.[1013] Reaction of $MoCl_2(PMePh_2)_4$ with amines results in phosphine displacement and the formation of red $MoCl_2(NH_2R)(PMePh_2)_3$ ($R = H$, Me, Pr, ${}^iPr$, Cy, CH_2CF_3, $CH_2CH{=}CH_2$) or $MoCl_2(en)(PMePh_2)_2$, characterized by spectroscopic and mass spectrometric studies.[1014]

A bromo complex, $MoBr_2(dppe)_2$, has been obtained in low yield from the prolonged reaction of $(NH_4)_4[Mo_2Br_8]$ and dppe in refluxing alcohols[1015] while $MoX_2(dppb)_2$ and $[MoOX(dppb)_2]X$ are produced when $K_4[Mo_2Cl_8]$, $(NH_4)_5[Mo_2Cl_9]{\cdot}H_2O$ or $(NH_4)_4[Mo_2Br_8]$ react with dppb in refluxing 1-propanol; reactions at room temperature in methanol produce dinuclear species.[1016] The paramagnetic complexes (μ_B ca. 2.8–3.0) have been characterized by IR and UV–vis spectroscopy, cyclic voltammetry, and X-ray crystallography. In $MoBr_2(dppe)_2$ and $MoCl_2(dppb)_2$, steric influences prevent the linear X–Mo–X unit from standing perpendicular to the equatorial P_4 plane. Additional structures have also been reported for known *trans*-$MoCl_2(dppe)_2$. Reaction of $MoCl_2$ with dmpe yields paramagnetic (μ_B 2.65) *trans*-$MoCl_2(dmpe)_2$ while reaction of $MoCl_2(CO)_4$ with dmpe yields $[MoCl(CO)_2(dmpe)_2]PF_6$ after anion exchange. Both complexes have been structurally characterized, the cation of the latter exhibiting a capped trigonal prismatic geometry.[740] Isomers of *trans*-$[MoCl(\eta^x\text{-}NCMe)(dmpe)_2]BPh_4$ ($x = 1$, 2), as well as *trans*-$[Mo(NCMe)_2(dmpe)_2](BPh_4)_2$, are formed when $MoCl_2(dmpe)_2$ is refluxed in NCMe in the presence of $NaBPh_4$; the η^2-acetonitrile complex was structurally characterized.[684] Reaction of *cis*-$Mo(N_2)_2(tppea)$ with MeI produces $MoI_2(tppea)$.[1017]

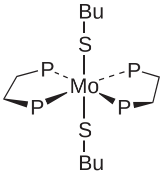
4.7.6.3.2 Hydride and other complexes

Attempts to prepare dinitrogen complexes by the Na/Hg reduction of $MoCl_3(bdmp)$ in the presence of PR_3 produced only chloro—Mo^{II} species, *trans*-$MoCl_2(bdmp)(PR_3)$ ($PR_3 = PMe_3$, PMe_2Ph).[880] The use of dispersed Na or Li as reducing agent yields *trans*-$Mo(N_2)_2(bdmp)(PMe_3)$ but under argon $MoH(\eta^2\text{-}CH_2PMe_2)(PMe_3)(bdmp)$ or $Mo(PMe_3)_3(bdmp)$ are produced. A hydrogen atmosphere allows the isolation of $MoH_2(PMe_3)_2(bdmp)$. Molybdenum(II) complexes, $Mo(CO_3)(CO)(PMe_3)_n(bdmp)$ ($n = 0$, 1), are formed in the reactions of CO_2 with related dinitrogen complexes.[799]

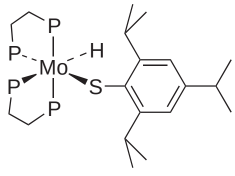
Tetrahydride (**338**) (Scheme 14) reacts with *N*-alkylamides to form seven-coordinate $MoH\{N(R)C(R')O\}(dppe)_2$ (**341**) through elimination of H_2 and oxidative addition of the N—H bond. A pentagonal bipyramidal structure, with apical P- and N-donor atoms, has been established for $MoH\{N(Me)C(Me)O\}(dppe)_2$.[803] These complexes react with carboxylic acids giving $MoH(O_2CR)(dppe)_2$ (**340**). Carboxylates (**340**)[1018] and related carbonates, $MoH(O_2COR)(dppe)_2$ (**434**),[1019] can be prepared directly from $MoH_4(dppe)_2$ by irradiation in the presence of allyl esters or allyl carbonates, respectively; pentagonal bipyramidal structures are indicated by spectroscopic and/or crystallographic studies, e.g., of $MoH(O_2COEt)(dppe)_2{\cdot}C_6H_6$.[1019] Alkoxide (**342**) ($R = Me$) reacts with functionalized phthalimide derivatives to produce (**435**).[1020] Related, more robust phthalimide derivatives (**436**) can be accessed directly from (**338**).[1021] Distorted pentagonal bipyramidal (**436**) ($R = (CH_2)_2$) features an equatorial, bidentate O,N-donor phthalimido ligand.[1021] Complexes (**437**) are also produced in thermal or photochemical reactions involving (**338**) and methacrylic esters.[1022] The complicated reaction between $MoH_4(dmpe)_2$ and CO_2 leads to the formation of formate, CO_2, and carbonate complexes such as

$MoX(O_2CH)(dmpe)_2$ ($X = H$, O_2CH) and $MoH(O_2CH)(CO_2)(dmpe)_2$.[805] Other hydrido–Mo^{II} phosphine complexes are described in Section 4.7.4.6.4.

Reaction of $Mo(N_2)_2L_2$ ($L = dmpe$, dppe) and RSH ($R = alkyl$, C_6F_5, C_6H_4X-4 ($X = H$, F, Cl, Me, NH_2, OMe) with elimination of N_2 and H_2 produces *trans*-$Mo(SR)_2L_2$, characterized by spectroscopic and, in the case of *trans*-$Mo(SBu)_2(dppe)_2$ (**438**), structural methods.[684,884] The complexes undergo a reversible electrochemical oxidation at potentials correlated with substituent Hammett functions. Chemical oxidation produces EPR-active, low-spin d^3 complexes, $[Mo(SR)_2L_2]^+$, isolated as BPh_4^- salts.[884] In contrast, the reactions of $Mo(N_2)_2(dppe)_2$ with sterically bulky RSH ($R = {}^iPr$, ${}^tBu$, $C_6H_2Me_3$-2,4,6, $C_6H_2{}^iPr_3$-2,4,6, $C_6H_2Br{}^iPr_2$-4,2,6) yields green hydride thiolates, *cis*-$MoH(SR)(dppe)_2$, that react with CO, $CN{}^tBu$ (L), and PhSH (LH) to give $MoL_2(dppe)_2$ species. An octahedral structure has been established for *cis*-$MoH(SC_6H_2{}^iPr_3$-2,4,6)$(dppe)_2$ (**439**).[1023] Other notable Mo^{II} complexes prepared from $Mo(N_2)_2(dppe)_2$ (via $Mo(N_2)(CNR)(dppe)_2$) include diaminoacetylene complexes (**440**),[1024] an agostic aminoalkylidene (**441**), and a novel hydrido aqua complex (**442**).[1025]



(**438**)



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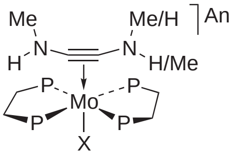

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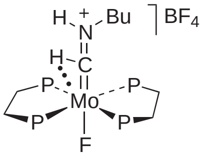
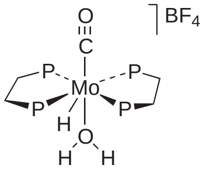


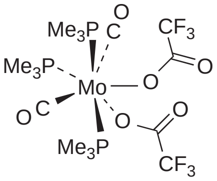
(**441**)



(**442**)

4.7.6.4 Carboxylate Complexes

Carboxylate complexes of Mo^{II} are uncommon. Protonation of $Mo(CO)_3(PR_3)_3$ ($R = Me$, Et) by trifluoroacetic acid produces $[HMo(CO)_3(PR_3)_3]O_2CCF_3$ that convert in solution to seven-coordinate $Mo(O_2CCF_3)_2(CO)_2(PMe_3)_3$ (**443**)[1026] and $Mo(O_2CCF_3)_2(CO)_2(PEt_3)_2$ (**444**),[1027] respectively; capped trigonal prismatic (or 4:3) structures pertain. Reaction of $Mo(CO)_3X_2(PR_3)_2$ with NaO_2CR produces $Mo(O_2CR')X(CO)_2(PR_3)_2$ or $Mo(O_2CR')_2(CO)_2(PR_3)_2$ ($X = Cl$, Br; $R = Et$, Ph; $R' = H$, Me, Ph, CCl_3 etc).[1028,1029] The X-ray structure of seven-coordinate $Mo(O_2CH)_2(CO)_2(PEt_3)_2$ (**445**) revealed a 4:3 piano stool structure with mono- and bidentate formate ligands on the trigonal face.[1028] Related complexes, $Mo(O_2CCF_3)Br(CO)_2(PR_3)_2$ and $Mo(O_2CCF_3)_2(CO)_2(PR_3)_2$, are similarly prepared; $MoBr(O_2CCF_3)(CO)_2(PPh_3)_2$ (**446**) adopts a 4:3 piano stool structure with bromide and bidentate carboxylate ligands on the trigonal face.[1030] The bis(formate) complex, *trans*-$Mo(O_2CH)_2(dmpe)_2$, is a product of the reaction of $MoH_4(dmpe)_2$ with CO_2,[805] whereas $MoH(O_2CEt)(PMe_3)_4$ results from hydrogenation of $[MoH(O_2CCH{=}CH_2)(C_2H_4)(PMe_3)_2]_2$ in the presence of PMe_3.[806] Finally, *cis*-$Mo(N_2)_2(tppea)$ reacts with HO_2CCF_3 to produce $Mo(O_2CCF_3)_2(tppea)$.[1017]



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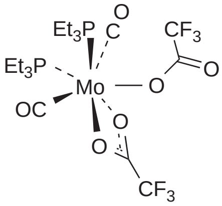
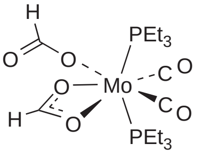
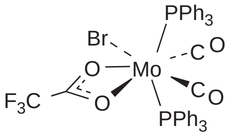


(**444**)



(**445**)



(**446**)

4.7.6.5 Complexes Containing Sulfur-donor Ligands

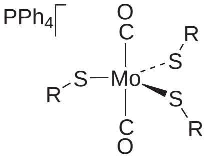
4.7.6.5.1 *Dithiocarbamate and related dithio-ligand complexes*

The dithiocarbamate system pioneered by Colton and co-workers has undergone further development and a complete review of this area has been prepared by Baker.[894] Reports since 1985 describe new syntheses for $Mo(S_2CNR_2)_2(CO)_2$ ($R = Me$, Et), the assessment of their ligand affinities (halides < NCMe < thiophene < py < $P(OR)_3$ < PR_3), and the isolation of reactive adducts such as orange

$NEt_4[MoX(S_2CNR_2)_2(CO)_2]$ (X = F, N_3). The fluoro complex exhibits a fluoro-capped trigonal prismatic structure with an acute $\angle$(C—Mo—C) of 68.20(6)°.[1031] Pyrrole-*N*-carbodithioate complexes, $Mo(S_2CNC_4H_4)_2(CO)_2L$ (L = PEt_3, $P(OMe)_3$, EPh_3 (E = P, As, Sb), OC_4H_8, SC_4H_8), $Mo(S_2CNC_4H_4)_2(CO)L_2$ (L = PEt_3, $P(OMe)_3$; L_2 = dppe) and $NEt_4[MoX(S_2CNC_4H_4)_2(CO)_2]$ (X = F, Cl, Br) have also been reported.[1032,1033] The bonding and stereochemistry in these and related complexes have been addressed theoretically.[1031] The X-ray structure of $Mo(NS)(S_2CNEt_2)_3$ has been determined.[1034] A description of new alkyne and organometallic chemistry supported by dithiocarbamate ligands may be found in *Comprehensive Organometallic Chemistry*.[6] Other dithiocarbamate—Mo^{II} complexes are described in Section 4.7.6.1. Complexes containing ligands derived from head-to-tail dimerization of CS_2 and η^3-trimethylphosphonium dithioformate derivatives (and their protonated and alkylated forms) have been described by Carmona and co-workers; the most recent work involved a theoretical study of such complexes.[1035] See also *Comprehensive Organometallic Chemistry*.[6]

4.7.6.5.2 Thiolate complexes

Reaction of $[MoBr_2(CO)_4]_2$ with sterically hindered thiols RSH (R = substituted aryl) in the presence of NEt_3 yields $PPh_4[Mo(SR)_3(CO)_2]$ (**447**) after cation exchange with PPh_4Br. A single ν(CO) IR band at 1,865–1,846 cm^{-1} is indicative of *trans* carbonyl groups, a fact confirmed by the X-ray structure of $PPh_4[Mo(SC_6H_2{}^iPr_3\text{-}2,4,6)_3(CO)_2]$. This complex reacts with CO and a range of ligands L to produce $PPh_4[Mo(SC_6H_2{}^iPr_3)_3(CO)_3]$ and $PPh_4[Mo(SC_6H_2{}^iPr_3)_3(CO)L]$ (L = NCR (R = Me, Et, ^{t}Bu), PMe_2Ph, CNMe and CN^tBu). Related thiolate chemistry is described in Section 4.7.4.6.5(i).[717] However, reaction of 2,6-diphenylthiophenol with $[MoX_2(CO)_4]_2$ (X = Cl, Br) in dme produces $Mo(SC_6H_3Ph_2\text{-}2,6)_2(CO)$ (**448**). The complex possesses a pseudo-tetrahedral structure with a phenyl group from one of the thiolates bound at one site in an η^6-fashion. The η^6-phenyl group is displaced in the formation of, e.g., *trans,cis*-$Mo(SC_6H_3Ph_2\text{-}2,6)_2(CO)_2L$ (L = bpy (**449**), phen) or $Mo(SC_6H_3Ph_2\text{-}2,6)_2(CO)(dppe)$.[1036] Complexes such as $Mo(SR)_2(CO)_2(PR_3)_2$ (R = Mes, $C_6H_2{}^iPr_3\text{-}2,4,6$; PR'_3 = $PMePh_2$, PMe_2Ph)[828] and trigonal prismatic (ϕ = 13.7°) $Mo(SCH_2CH_2S)(CO)_2(PEt_3)_2$ (**450**) have also been reported.[1037]



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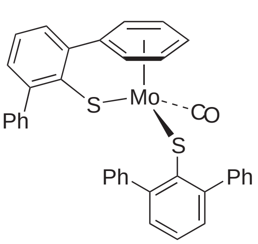

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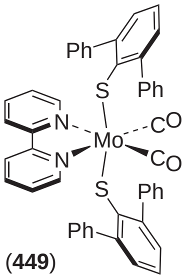

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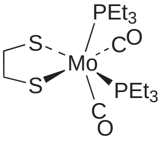

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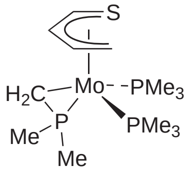
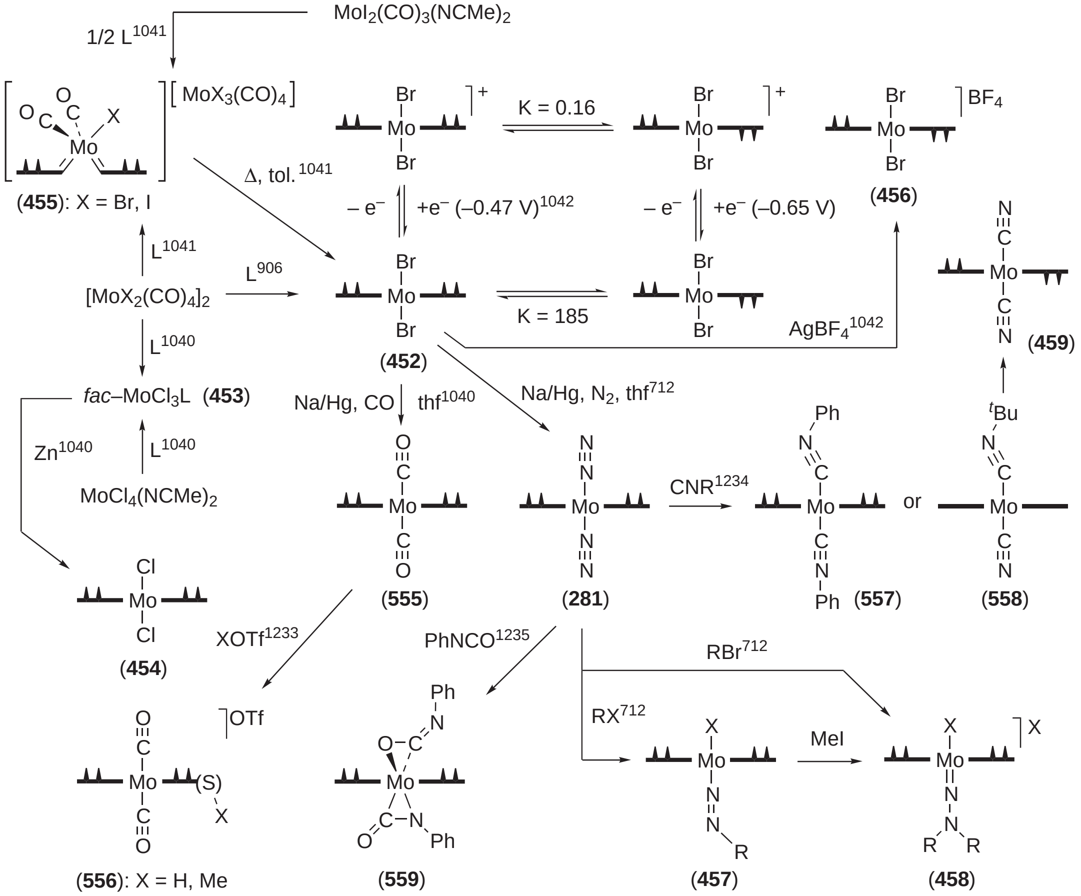


(451)

Dark-red $Cat[Mo(SR)_4(NO)]$ (Cat^+ = $NHEt_3{}^+$, $PPh_4{}^+$; R = Ph, $C_6H_4Me\text{-}2$, $C_6H_4Cl\text{-}4$, $C_6H_2Me_3\text{-}2,4,6$) are produced in the reactions of either $MoCl_3(PPh_3)_2(NO)$ or $[Mo(NH_2O)(H_2O)_x(NO)]_n$ with thiolates in methanol. Related reactions produce $Cat[MoCl(S^tBu)_3(NO)]$ and $Mo(SC_6H_2{}^iPr_3)_3(NH_3)(NO)$. Structurally characterized $NHEt_3[Mo(SPh)_4(NO)]$, $PPh_4[WCl(SPh)_3(NO)]$, and $Mo(SC_6H_2{}^iPr_3)_3(NH_3)(NO)$ all exhibit trigonal bipyramidal structures with equatorial thiolate ligands and linear, axial nitrosyl ligands.[1038] Reaction of $NHEt_3[Mo(SPh)_4(NO)]$ with $PhP(C_6H_4SH)_2$ in refluxing methanol produces diamagnetic $NHEt_3[Mo\{PhP(C_6H_4S)_2\}_2(NO)]$.[189] Recently, the synthesis of $Mo(\eta^5\text{-}C_4H_4S)(\eta^2\text{-}H_2CPMe_2)(PMe_3)_2$ (**451**) from $Mo(PMe_3)_6$ and thiophene and its conversion to $Mo(\eta^5\text{-}C_4H_5S)(OTf)(PMe_3)_3$ upon reaction with HOTf were described.[1039]

4.7.6.5.3 Thioether complexes

The Mo^{II}/Mo^0 coordination chemistry of $Me_8[16]aneS_4$ is summarized in Scheme 19. Reaction of $[MoBr_2(CO)_4]_2$ and $Me_8[16]aneS_4$ in refluxing toluene produces *trans*-$MoBr_2(Me_8[16]aneS_4)$ (**452**), whereas $[MoCl_2(CO)_4]_2$/refluxing toluene and $MoCl_4(NCMe)_2/CH_2Cl_2$ react with $Me_8[16]aneS_4$ to give *fac*-$MoCl_3(Me_8[16]aneS_4)$ (**453**), which is reduced by Zn to *trans*-$MoCl_2(Me_8[16]aneS_4)$ (**454**); all three orange/yellow complexes are paramagnetic.[1040] A possible intermediate in the first reaction, viz., green $[MoBr(CO)_2(Me_8[16]aneS_4)][MoBr_3(CO)_4]$ (**455**), has been isolated and structurally characterized along with an iodide analog; it converts to (**452**) upon heating. The $[MoBr(CO)_2(Me_8[16]aneS_4)]^+$ cation exhibits a 4:3 piano stool structure with Mo 1.488(2) Å out of the S_4-plane of a *syn*-$Me_8[16]aneS_4$ ligand.[1041] A *syn* conformation is also adopted by the equatorial $Me_8[16]aneS_4$ ligand of *trans*-$MoBr_2(Me_8[16]aneS_4)$ but the *syn–anti* conformation is observed in the salt (**456**) produced upon oxidation with $AgBF_4$. A rationalization of the anomalous[1040] electrochemical behavior of (**452**) (Scheme 19) rests on this observation.[1042] Diazenido (**457**), hydrazido (**458**), and cyano (**459**) Mo^{II} complexes of $Me_8[16]aneS_4$ are also known.[712,713]

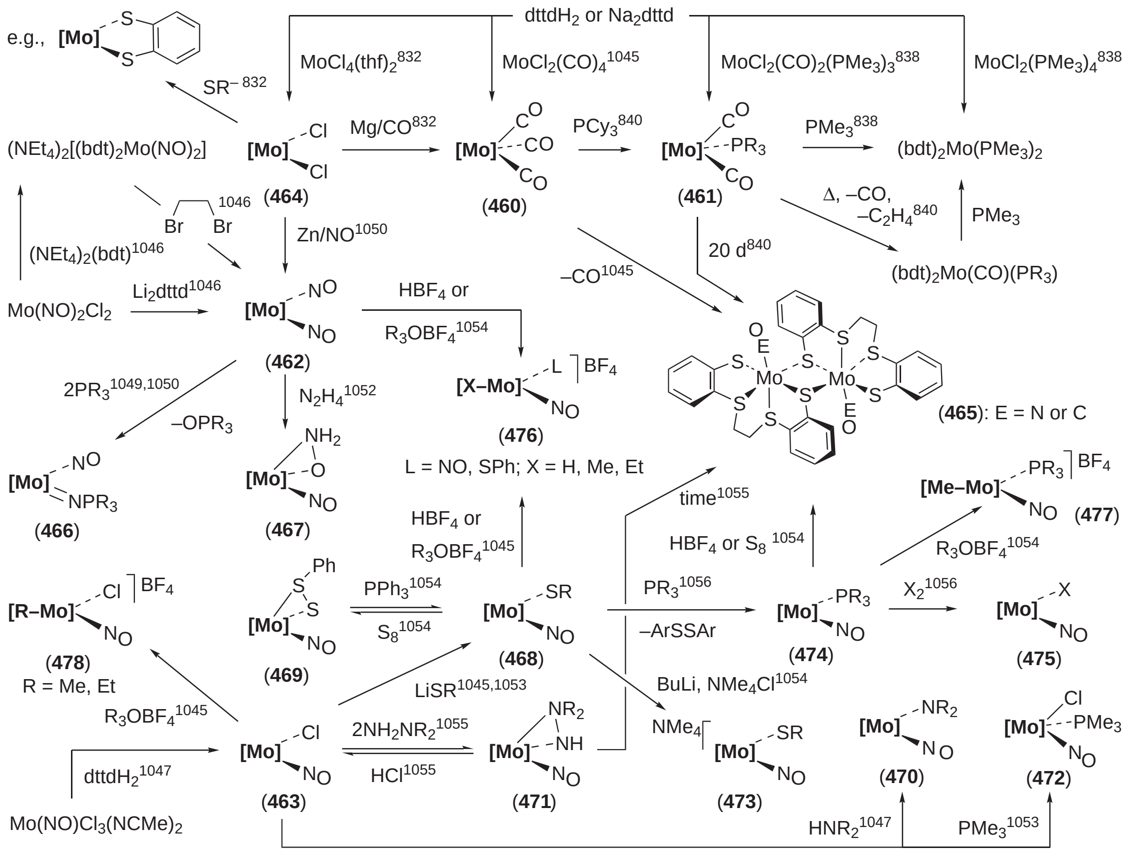


Scheme 19 (L=$Me_8[16]aneS_4$ 279)

Dithiooxamides react with $Mo(CO)_2(PR'_3)_2(NCMe)_2$ (R′ = Bu, Ph) producing violet complexes *cis,cis,trans*-$Mo\{S_2C_2(NR)_2\}(CO)_2(PR'_3)_2$ (R_2 = H/alkyl or dialkyl). A dithiolenic (reduced ligand) formulation is supported by IR and NMR data and the X-ray structure of *cis,cis,trans*-$Mo\{S_2C_2(NC_5H_{10})_2\}(CO)_2(PBu_3)_2$.[1043,1044]

4.7.6.5.4 Mixed thiolate/thioether complexes

The Mo chemistry of dttd (**146**) (Scheme 20), Bu_4dttd (**147**) and related ligands has been defined by Sellmann and co-workers. The free ligands or alkali metal salts react with key starting materials producing, e.g., $Mo(dttd)(CO)_3$ (**460**),[1045] $Mo(dttd)(CO)_2(PMe_3)$ (**461**),[838] $Mo(dttd)(NO)_2$ (**462**),[1046] and Mo(dttd)Cl(NO) (**463**),[1047] as well as related Bu_4dttd derivatives.[839,1048] Reduction of $MoCl_2$(dttd) (**464**) by Mg under CO provides alternative syntheses for the tri- and dicarbonyls[832,840] and Bu_4dttd derivatives;[839,840] seven-coordinate (**461**) (R = Me,[1049] Cy[840]) have been structurally characterized. The carbonyl complexes convert to bis(benzenedithiolate) derivatives upon thermal dealkylation (Section 4.7.4.6.5(iii)) or slowly transform into dimeric $[Mo(CO)(\mu\text{-dttd})]_2$ (**465**, E = C) in solution at room temperature.[840,1045] The former feature trigonal prismatic structures, the latter distorted octahedral Mo centers bridged via thiolate sulfur atoms in both the *syn*[840] and *anti*[1045] isomers. Dinitrosyl (**462**) is also accessible through Zn reduction of (**464**) under NO[1050] or via a template reaction involving alkylation of $[Mo(bdt)_2(NO)_2]^{2-}$;[1046] diastereospecific alkylations using substituted 1,2-dibromoethanes produce chiral derivatives.[383,1051] The dinitrosyl[1050,1051] and chloro nitrosyl[1047] complexes exhibit distorted octahedral structures with linear (>172°) nitrosyl groups; dttd invariably adopts a *cis* (thioether) *trans* (thiolate) binding mode. Reactions of (**462**) with two equivalents of PR_3 produce $Mo(NPR_3)(dttd)(NO)$ (**466**, R = alkyl, Ph; $PR_3 = PMePh_2$ (structurally characterized), $PEtPh_2$) and OPR_3, while dppe gives $Mo\{NPPh_2C_2H_4P(O)Ph_2\}(dttd)(NO)$.[1049,1050] The reactions of (**462**) with N_2H_4 or $NaBH_4$ produce seven-coordinate, pseudo-octahedral Mo $(ONH_2)(dttd)(NO)$ (**467**) (d(Mo—O) 2.053(3) Å, $d(Mo—NH_2)$ 2.103(3) Å, ∠(O—Mo—N) 38.6(1)°) in a process modeling a key step in the biological reduction of NO_3^- to NH_3.[1052] Metathesis and/or addition at (**463**) allows thiolate (**468**, R = Me, Pr, Bu, Ph, $C_6H_4SMe\text{-}2$),[1045,1053] phenyldithio (**469**),[1054] amido (**470**, R = H, Me, Et),[1047] side-on bonded hydrazido(1-) (**471**)[1055] and chloro phosphine (**472**)[1053] derivatives to be prepared. Subsequent redox reactions yield EPR-active Mo^I species, including $NMe_4[Mo(SR)(dttd)(NO)]$ (**473**),[1054] $Mo(dttd)(PR_3)(NO)$ (**474**, R = Me, Et, Pr; $PR_3 = PMe_2Ph$),[1056] as well as $Mo(dttd)X(NO)$ (**475**, X = Br, I).[1056] Structurally characterized six-coordinate derivatives, e.g., (**470**) and (**474**) (R = Me),[1047,1056] exhibit distorted octahedral structures whereas seven-coordinate (**471**) (R = Me) adopts a pseudo-octahedral structure with d(Mo—NH) 2.099(11) Å, $d(Mo—NMe_2)$ 2.172(12) Å, and ∠(N—Mo—N) 38.3(4)°;[1055] all contain linear nitrosyl ligands. Co-ligand loss from several of these species produces dimeric (**465**) (E = N) structurally characterized as the *anti* isomer.[1055] Protonation or alkylation of the nitrosyl complexes invariably occurs at *one* of the thiolate sulfur atoms leading to cationic species (**476**–**478**).[1045,1054] The chemistry of related carbonyl and nitrosyl complexes containing backbone[383,838] and donor-modified[1057] tetradentate ligands and pentadentate ligands[756,1058] is less extensive.



Scheme 20 [Mo]=Mo(dttd) fragment; [X-Mo]=S-alkylated or S-protonated Mo(dttd) fragment

4.7.7 MOLYBDENUM(I) COMPLEXES

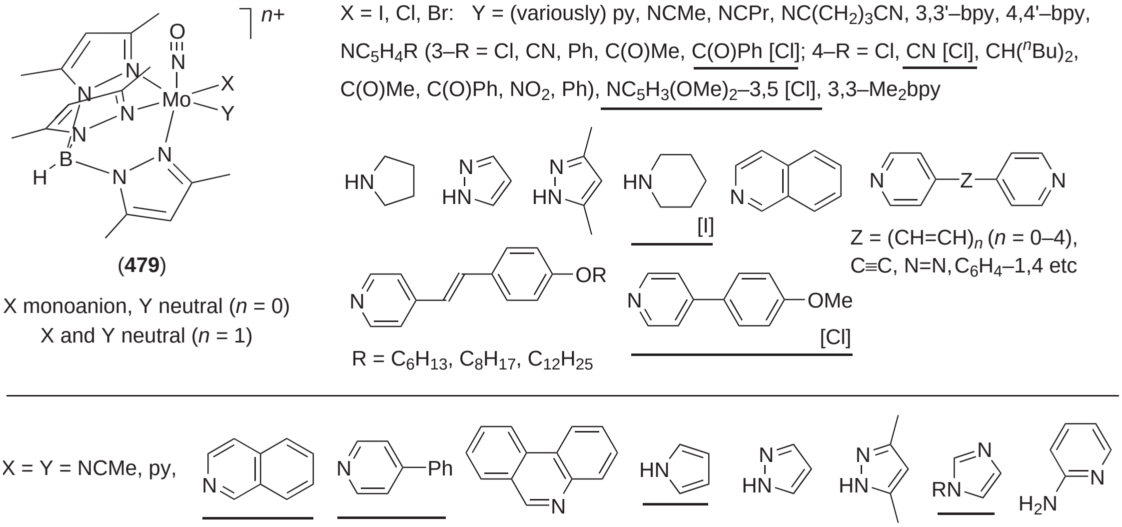
Most of the relatively few monomeric, 17-electron Mo^{I} complexes known contain trispyrazolylborate or triazacyclononane ligands. Oxidation of $NEt_4[Tp^*Mo(CO)_3]$ with $FcPF_6$ produces red, paramagnetic (μ_B 2.13) $Tp^*Mo(CO)_3$;[1059] unstable $TpMo(CO)_3$ and $(Bpz_4)Mo(CO)_3$ are also accessible.[1060] Octahedral $Tp^*Mo(CO)_3$ possesses pseudo-C_{3v} symmetry and undergoes degenerate electron transfer with $NBu_4[Tp^*Mo(CO)_3]$ ($k_2 = 1.4 \times 10^6$ M^{-1} s^{-1} at $-34\,°C$).[969] The redox behavior of the $LMo(CO)_3/[LMo(CO)_3]^-$ ($L = Tp$, Tp^*) couples has been investigated by cyclic voltammetry[970] and the factors affecting the redox equilibria between $[Tp^*Mo(CO)_3]^-$/triarylpyrylium cations and $Tp^*Mo(CO)_3$/pyranyl radicals have been examined.[1061] The less sterically encumbered complexes react with phosphines producing brown, octahedral $TpMo(CO)_2(PR_3)$ ($R = Me$, Bu; $R_3 = Me_2Ph$, Et_2Ph, $MePh_2$, $EtPh_2$).[1060] A variety of complexes, $Tp^*MoXL(NO)$ and $[Tp^*MoL_2(NO)]^+$ (**479**, Figure 3) can be prepared by reducing $Tp^*MoX_2(NO)$ in the presence of neutral unsaturated N-heterocycles (L).[990,1062–1066] Salts of $[Tp^*MoX_2(NO)]^-$ ($X = Cl$, I) can also be prepared by reduction of $Tp^*MoX_2(NO)$ in the absence of added ligand.[1063,1067] These complexes are EPR-active (g 1.97–2.07, A_{Mo} ca. $43–46 \times 10^{-4}\,cm^{-1}$) and exhibit novel magnetic behavior. The complexes underlined in Figure 3 have been structurally characterized, the Mo–N(amine) bonds being ca. 0.3 Å longer than the Mo—N(amido) bonds in their Mo^{II} counterparts, consistent with the switching off of p_π—d_π interactions upon reduction. The nitrosyl ligands are linear and produce ν(NO) IR bands in the range 1,600–1,700 cm^{-1}. The complexes undergo further reduction to 18-electron species (Section 4.7.8.3.2). While $[(R_3tcn)Mo(CO)_3]^+$ complexes may be generated electrochemically, oxidation of $(Bz_3tcn)Mo(CO)_3$ with $FcPF_6$ produces air- and light-sensitive, paramagnetic (μ_B 1.94) $[(Bz_3tcn)Mo(CO)_3]PF_6$ (**480**), structurally characterized as the dmf solvate (Scheme 6).[1002] The complexes, $(Me_3tcn)MoX_2(NO)$ ($X = Cl$, Br, I), have been briefly described.[1001]

Other new Mo^{I} complexes are restricted to nitrosyl and phosphine complexes. These include (**473**)[1054] and (**474**)[1056] (Section 4.7.6.5.4, Scheme 20) and *trans,trans,trans*-$MoCl_2(PPh_3)_2(NCMe)(NO)$ isolated from the reaction of $MoCl_2(NO)_2$ with PPh_3.[537] Orange, paramagnetic (μ_B 1.87) *fac*-MoBr(bdpe)(dmpm) is generated in the reaction of HBr with $Mo(N_2)$(bdpe)(dmpm)[701] while oxidation of $Mo(dmpe)_3$ by I_2(or MeI)/NH_4PF_6 produces $[Mo(dmpe)_3]PF_6$.[800] The reactions of $M(CO)_3(PR_3)_2$ ($M = Cr$, Mo, W) with HSR, H_2S, RSSR, HI, and I_2 produce some interesting Mo^{I} compounds, e.g., $Mo(SPh)(CO)_3(PR_3)_2$ ($R = {}^{i}Pr$, Cy).[1068]

4.7.8 MOLYBDENUM(0) COMPLEXES

4.7.8.1 Complexes Containing Carbon-donor Ligands

Zero- and lower-valent Mo chemistry is dominated by organometallic species, mostly metal carbonyls and their derivatives. A wide variety of other complexes, including σ-aryl, σ-alkynyl,



(**479**)

X monoanion, Y neutral ($n = 0$)
X and Y neutral ($n = 1$)

Figure 3 Nitrosyl-Mo^{I} complexes of T_p*.

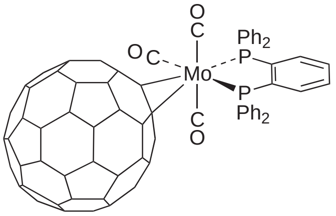
alkyne, and Fischer-type alkylidyne complexes, some with a significant complement of non-organometallic ligands, also exist. These will not be discussed here as a treatment can be found in *Comprehensive Organometallic Chemistry*.[6] A discussion of tricarbonyl species is included, as these incorporate ligands and/or undergo reactions of interest to coordination chemists.

4.7.8.2 Tricarbonyl Complexes and their Derivatives

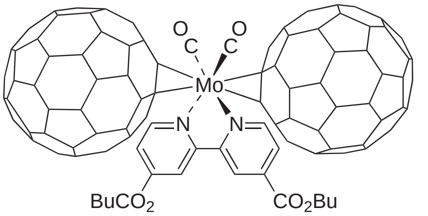
Tricarbonyl complexes are nearly always prepared by the thermal or photochemical reactions of $Mo(CO)_6$ or *fac*-$Mo(CO)_3L_3$ ($L = NCMe$, thf, dmf; $L_3 = \eta^6$-C_7H_8, η^6-$C_6H_3Me_3$, etc.) complexes with the ligand of interest. The use of other starting materials, e.g., *fac*-$Mo(CO)_3(NCEt)_3$ (*Inorg. Synth., Vol. 28, p. 29*) and $Mo(CO)_3(py)_3$[1069] has also been advocated. Tricarbonyl complexes are usually yellow/orange in color, diamagnetic and octahedral with either *fac*- (most commonly) or *mer*- carbonyl ligand arrangements. With the exception of fullerene complexes, we restrict our treatment to ternary (Mo/CO/L) species only.

4.7.8.2.1 Fullerene complexes

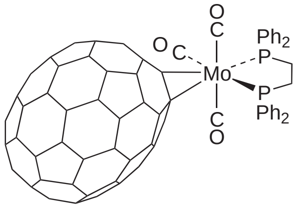
Molybdenum and tungsten (M) η^2-fullerene complexes are readily prepared by reacting carbonyl precursors with the appropriate fullerene. Known compounds include: $Mo(\eta$-$C_5H_4R)_2(C_{60})$ ($R = H$, Bu),[1070] *fac*/*mer*-$[M(CO)_3(dppe)_2]_x(C_{60})$ ($x = 1$, 2),[1071,1072] *mer*-$M(CO)_3(dppb)(C_{60})$,[1073] *fac*/*mer*-$M(CO)_3(dppf)(C_{60})$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene),[1074] $[M(CO)_3(ddh)]_2(C_{60})\cdot 2.5C_6H_6$ (ddh = diacetyl dihydrazone),[1075] $[M(CO)_2(phen)(dbm)]_n(C_{60})$ (dbm = dimethyl maleate; M = Mo, $n = 1$–3;[1076,1077] M = W, $n = 1$[1076]), $Mo(CO)_3(dppe)_2(C_{70})$,[1071] $Mo(CO)_2(phen)(dbm)(C_{70})$,[1077] and $Mo(CO)_2\{bpy(CO_2Bu)_2\}(C_{60})_2$.[1078] In the C_{60} complexes, the metal is dihapto linked to a [6:6] bond as evident in the structures of $Mo(CO)_3(dppb)_2(C_{60})$ (**481**)[1073] and dumb-bell-shaped $Mo(CO)_2\{bpy(CO_2Bu)_2\}(C_{60})_2$ (**482**).[1078] The binding of C_{70} in the predominant isomer (80%) of $Mo(CO)_3(dppe)_2(C_{70})$ (**483**) is via one of the most geometrically polar [6:6] bonds.[1071] Binding of the metal leads to pyramidalization of the bonded carbon atoms and a lengthening of the bound and proximal C—C bonds, to ca. 1.48 vs. 1.36(1) Å for [6:6] C_{60}. An increase in electron density over the fullerene ligand as a result of metal → ligand π back-bonding makes multi-electron reductions more difficult, typically by 150–200 mV, compared to the parent fullerene.[1074,1077,1079]



(**481**)



(**482**)

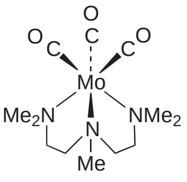


(**483**)

4.7.8.2.2 Complexes containing nitrogen-donor co-ligands

New reports in this area include an improved synthesis for *fac*-$Mo(CO)_3\{MeN(CH_2CH_2NMe_2)_2\}$ (**484**)[1080] and the description of new complexes containing R_3tch ((**105**, R = Me, ^{t}Bu, Bz)[1081] and (**485**)[1082]), a variety of substituted triazacyclononanes ((**102**, R = ^{i}Pr,[257] Bz,[1002]), (**486**, $R = CH_2CH{=}CH_2$, $CH_2CH_2CH{=}CH_2$),[258] (**487**, R = H, Me, Ph)[1083]), triazacyclododecane (**488**)[594] and triaminomethanes derived from 1,5,9-triazacyclododecane (**489**, R = H, Me).[1084] Structurally characterized complexes exhibit an octahedral geometry with *fac* tricarbonyl ligands (ν(CO) ca. 1,880 cm^{-1}, 1,700–1,785 cm^{-1}). The *fac*-$Mo(CO)_3(R_3tach)$ complexes are touted as useful synthons in tricarbonyl-Mo^0 chemistry.[1085]

Linear and cyclic polyamines generally react with $Mo(CO)_6$ to afford *fac*-$Mo(CO)_3L$ complexes despite the potential for greater denticity (larger rings/chains and permethylation even favor the formation of tetracarbonyl complexes[1086,1087]). Tricarbonyl complexes are known for cyclen (**490**, R = H, Me), cyclam (**491**),[1087] (**492**)[1088] and *meso*- and *rac*-(**493**).[1089] Available



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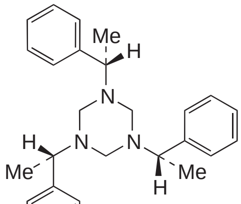

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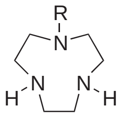

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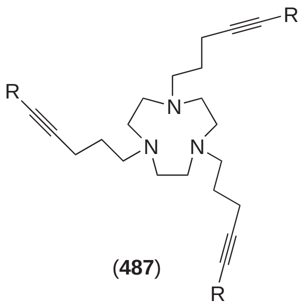

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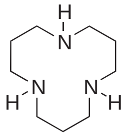

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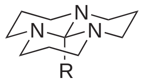
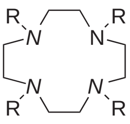
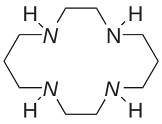


(489)

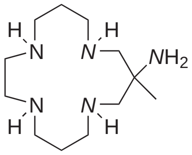
X-ray structures reveal tridentate coordination of L (through the italicized donors) and the existence of intramolecular H-bonding.[1088,1089] Interestingly, dinuclear *cis*-$[Mo(CO)_4]_2L$ is produced when (**494**) reacts with $Mo(CO)_6$.[1088] Although displaying a quasi-reversible electrochemical oxidation, complexes of (**493**) are not amenable to chemical oxidation.[1089] Selective mono-alkylation of cyclen and cyclam is facilitated by binding to the $Mo(CO)_3$ moiety (see lead-in references for details[1090,1091]).



(490): cyclen



(491): cyclam



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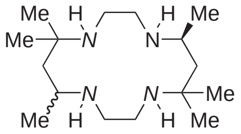

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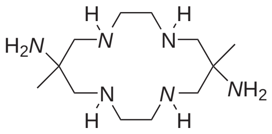
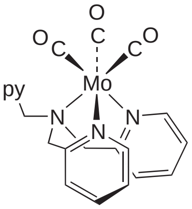


(494)

Complexes containing trispyridyl- and related heterocyclic N-donor ligands include (**495**),[263] *fac*-$Mo(CO)_3(Xpy_3)$ (**496**; X = HC,[1092] BuSn,[1093] P, EP where E = O, S, AuCl, $Au(C_6F_5)$) and (**497**) (E = O, S).[1094,1095] The X-ray structures of (**496**) (X = P,[1094] BuSn[1093]) and (**497**) (E = S)[1095] confirmed the expected octahedral geometries. An example of tridentate coordination of potentially tetradentate *N,N′*-dimethyl-2,11-diaza[3.3](2,6)pyridinophane (dap) is observed in octahedral *fac*-$Mo(CO)_3$(dap) (**498**); low-energy ν(CO) IR bands are attributed to the strong σ-donor and weak π-acceptor capacity of dap.[1096] Finally, mixed bis(benzimidazolyl)amine tricarbonyl complexes have been reported by Crane and Fenton.[1097]



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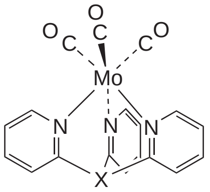
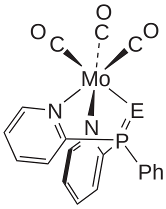
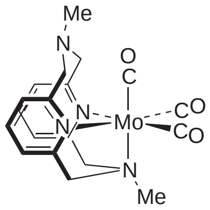


(496): X = CH, P, PE, BuSn



(497): E = O, S



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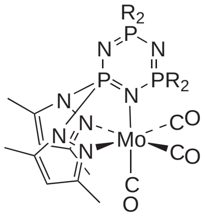


(499)

C-Phenyl bis(pyrazolyl)methane complexes, *fac*-$Mo(CO)_3\{\eta^2$-$RCPh(Me_2pz)_2$-*N,N′*$\}$ (R = H, Ph), are formed upon decarbonylation of *cis*-$Mo(CO)_4\{RCPh(Me_2pz)_2$-*N,N′*$\}$ in refluxing dme[1098] or reaction of $Mo(CO)_6$ and $RCPh(Me_2pz)_2$ under the same conditions.[718] The X-ray structures of both derivatives revealed an unusual η^2-interaction between a phenyl group and Mo, with *d*(Mo—C) 2.46–2.70 Å (cf. **315**).[718,1098] Mixed pyrazole/phosphazene complexes (**499**) (R = Ph, $R_2 = N(Me)CH_2CH_2O$) have also been prepared and structurally characterized.[1099] The thermal reactions of $Mo(CO)_6$ or $Mo(CO)_3(NCMe)_3$ with Tm* or $MeSi(Me_2pz)_3$ (L) produce neutral tricarbonyls *fac*-$LMo(CO)_3$;[262,1100] Mo^{III}, Mo^V, and Mo^{VI} complexes of the former are also known. While new trispyrazolylborate ligands are routinely incorporated into complexes such as $Tp^xMo(CO)_2(NO)$ or $Tp^xMo(CO)_2(\eta^2$-allyl), only hydrotris(2H-benzo[*g*]-4,5-dihydroindazol-2-yl)borate has been fashioned into an *isolated* tricarbonyl, $NEt_4[Tp^xMo(CO)_3]$.[1101] However, tris(triazolyl)borate complexes of this type have been prepared[967,968,1102] and the X-ray structures of $(MeNC_5H_4CN\text{-}4)[Tp^*Mo(CO)_3]$[1061] and $NEt_4[TpMo(CO)_3]$[1102] have been reported.

4.7.8.2.3 Complexes containing phosphorus-donor co-ligands

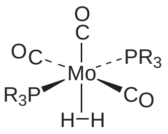
Tricarbonyl complexes containing monodentate P-donors are relatively rare. They include *mer*-$Mo(CO)_3(PR_3)_2$, formed in the reactions of *fac*-$Mo(CO)_3(\eta^6\text{-}C_7H_8)$ with PR_3 ($PR_3 = P^iPrCy_2$, PCy_3) or by elimination of N_2 from $[Mo(CO)_3(P^iPr_3)_2]_2(N_2)$; the presence of an agostic interaction (ν(CH) 2,613–2,710 cm^{-1}) was confirmed by the X-ray structures of *mer*-$W(CO)_3(PR_3)_2$ (R = ^{i}Pr, Cy).[1103] Adducts of the type *mer*-$Mo(CO)_3(PR_3)_2L$ (L = H_2 (**500**), N_2, C_2H_4, H_2O, Me_2CO, SEt_2, NCMe, NH_3, NH_2Bu, py, py-O) are readily formed;[1103] thermodynamic data are available from H_2, N_2, and py binding studies.[1104] The dihydrogen complexes (**500**) are conveniently prepared by performing the reaction of $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ and PR_3 under an atmosphere of H_2[1105] (see *Inorg. Synth., Vol. 27, p. 1*). Complexes of this type have been extensively characterized by complete IR and NMR studies (that provide evidence for equilibria involving dihydride species)[1105] and by X-ray structures of W analogs.[1106] Dihydrogen–Mo complexes containing diphosphine ligands are discussed in Section 4.7.8.4.2. The structure, theory, and reactivity of dihydrogen complexes are the topics of a complete treatise by Kubas.[1107] *fac*-Tricarbonyl complexes containing the ligands (**501**) (X = NH, R = Me; X = O, R = $N(Me)(CH_2)_2NMe_2$),[1108,1109] (**502**), (**503**),[1110] P(*c*-C_2H_4)Ph, and P(*c*-C_3H_6)Ph[1111] are also known. Substituted 2-phosphaindolizines (**504**) form *fac*/*mer*-$Mo(CO)_3L_3$, the ligands acting as monodentate P-donors rather than η^5 π-donors.[1112] Alkenyl- and alkynyl-phosphine complexes, *fac*-$Mo(CO)_3L_3$ (L = $H_2PCH_2CH{=}CH_2$, $H_2PCH_2CH_2CH{=}CH_2$, $H_2PCH_2C{\equiv}CH$), have been reported by Diel *et al.*;[1113] the alkenyl complexes undergo radical or photo-initiated cyclotrimerization yielding structurally characterized *fac*-$Mo(CO)_3$(tpcd) (**505**, tpcd = 1,5,9-triphosphacyclododecane) and *fac*-$Mo(CO)_3$(tpcp) (tpcp = 1,6,11-triphosphacyclopentadecane), respectively. Protocols for alkylating the secondary phosphorus atoms of *fac*-$Mo(CO)_3$(tpcd) have been described, as has the X-ray structure of *fac*-$Mo(CO)_3(^iPr_3\text{tpcd})$.[1114] Photolysis of 1:2 mixtures of $Mo(CO)_6$ and $Ph_2PCH{=}CH_2$ (L) in thf at 0 °C produces mixtures of $Mo(CO)_5L$, *cis*/*trans*-$Mo(CO)_4L_2$, $Mo(CO)_4$(dppe), and $Mo(CO)_3$(dppe)L, rather than the anticipated *trans*-1,2-bis(diphenylphosphino)cyclobutane complexes.[1115] Claims that *fac*-$Mo(CO)_3$(dmpm-*P*)$_3$ is produced in the reaction of $Mo(CO)_3(NCMe)_3$ and dmpm have been challenged.[1116]

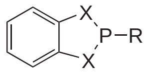
A wide variety of tripodal diarylphosphine ligands, $MeC(CH_2PAr_2)_3$ (**506**, Ar = Ph derivative, 1-Nap; PAr_2 = dibenzophospholyl) and $RCH_2C(CH_2PPh_2)_3$ (R = $PhCO_2$, many R′O) form *fac*-tricarbonyl complexes.[1117–1119] These have been spectroscopically characterized and the X-ray structures of the $MeC(CH_2PR_2)_3$ (R = Me, $C_6H_4{}^t$Bu-4, 1-Nap)[1117] and $PhCO_2CH_2C(CH_2PPh_2)_3$[1118] complexes have been determined. A stibine derivative, *fac*-$Mo(CO)_3\{MeC(CH_2SbPh_2)_3\}$, has also been reported.[1120] Tripodal ligands containing three different phosphine moieties have been incorporated into tricarbonyl complexes[1121] and the diastereoselectivity of alkylations at $MeC[CH_2PPh(Li)]_3$ and Mo-coordinated $RCH_2C[CH_2PAr(Li)]_3$ have been thoroughly investigated; the X-ray structures of the tricarbonyl complexes of $MeC(CH_2PPhR)_3$ (R = Ph, Et, Bz), (*RRR*/*SSS*)-$RCH_2C(CH_2PPhBz)_3$ (R = Me, Ph) and $MeC[CH_2P(C_6H_3Me_2\text{-}3,5)Bz]_3$ were determined in conjunction with these studies.[1122,1123] The conformational enantiomerization of complexes of $MeC(CH_2PPh_2)_{3-n}\{CH_2P(C_6H_4Me\text{-}2)_2\}_n$ (n = 1–3) has been probed by force field calculations and 1D and 2D NMR experiments.[1124,1125] Colorless, *fac*-$Mo(CO)_3\{(S,R)$-tdpox-$P,P',P''\}$ forms in the reaction of $Mo(CO)_3(NCMe)_3$ with (S,R)-tdpox (**507**) in CH_2Cl_2. Bidentate-P,P' binding is observed in the two isomers of *fac*-$Mo(CO)_3(NCMe)\{(S,R)$-tdpox$\}$.[1126] Cyclohexane-based tripodal ligands (**508**) react with $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ to produce *fac*-$Mo(CO)_3L$ complexes[1127,1128] and cyclophosphasilanes (**509**)[1129] and the larger macrocycles (e.g., (**510**)[1130]) form similar compounds. Tricarbonyl complexes containing the pentaphosphacyclopentadienyl ligand, viz. $[(\eta^5\text{-}P_5)Mo(CO)_3]^-$ (**511**), have been briefly reported.[1131] A number of phosphenium complexes are known and their properties and reactions have been the subject of recent studies[1132,1133] and reviews.[1134,1135]

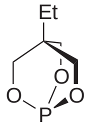
4.7.8.2.4 Complexes containing sulfur-donor co-ligands

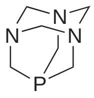
(i) Thiolate and thioether complexes

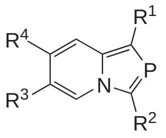
Thiolates, including NEt_4SR (R = H, Ph), react with $Mo(CO)_6$ to yield $NEt_4[Mo(CO)_5(SR)]$. These decarbonylate to give $(NEt_4)_2[Mo_2(CO)_8(SR)_2]$ and react with phosphines to produce *fac*-$NEt_4[Mo(CO)_3L_2(SR)]$ (L = PMe_3, $P(OMe)_3$; L_2 = dppe). The dinuclear complexes are cleaved by phosphines yielding *cis*-$NEt_4[Mo(CO)_4L(SR)]$ (L = PMe_3, $P(OMe)_3$, PPh_3, $P(OPh)_3$).[1136]


(**500**)


(**501**): X = NH, O


(**502**)


(**503**)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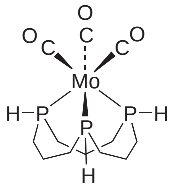
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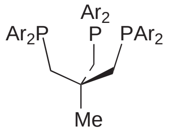
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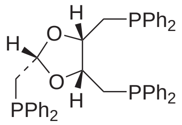
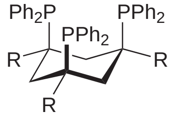
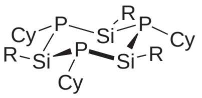
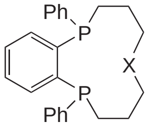
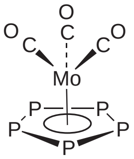

(**507**)

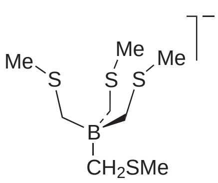

(**508**): R = H, CN

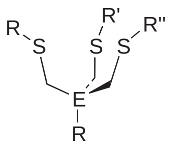

(**509**)

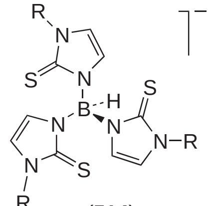

(**510**): X = PH, NMe

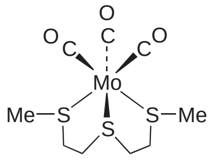

(**511**)

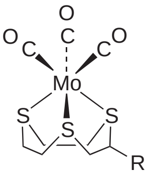
The chemistry of tripodal S_3-donor ligands has developed rapidly in recent years. The first work in this area involved the synthesis of yellow $NBu_4[TtMo(CO)_3]$ (Tt (**512**) = tetra(methylthiomethyl)borate).[1137] This was followed by the synthesis of octahedral tricarbonyl complexes of the neutral thioether podands (**513**) (RE = MeC,[1138] MeSi,[1139] BuSn;[1093] R-R″ = alkyl (mostly Me), aryl). Long Mo—S bonds (>2.6 Å) and facile ligand substitution reactions are both indicative of weak binding of the S-donor ligands in these complexes. Thione ligands including (**514**) are also known and have been incorporated via the *in situ*-generated tricarbonyl anions into complexes of the type Mo(**514**)$(CO)_2(\eta^3\text{-}C_3H_5)$.[1140]

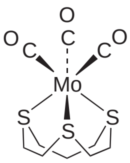

(**512**)

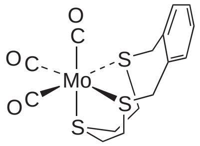

(**513**)

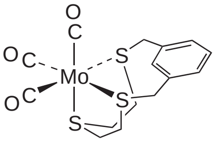

(**514**)

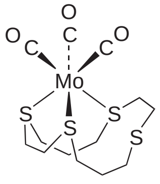

(**515**)

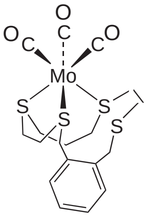

(**516**)


(**517**)


(**518**)


(**519**)


(**520**)


(**521**)

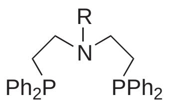
A variety of linear and macrocyclic thioethers, including potentially tetradentate ligands, form *fac*-tricarbonyl complexes with ν(CO) 1,910–1,940 cm^{-1} and 1,780–1,830 cm^{-1}. Reactions of $Mo(CO)_3(NCMe)_3$ with ttn and ttcn in acetonitrile yield (**515**)[1141] and (**516**) (R = H),[1142] respectively. The reactions of $(NMe_4)_2[Mo(CO)_3\{S(CH_2CH_2S)_2\text{-}S,S',S''\}]$ with 1,2-dibromoethane or substituted 1,2-dibromoethanes provide template syntheses for ttcn[889] and C-functionalized ttcn complexes, (**516**) (R = Me, CH_2OH, $CH_2OCH_2C_6H_4R'$-4 (R′ = H, Br, CO_2H, CN)).[1143] The complexes (**517**),[1144] (**518**), and (**519**)[1145] were subsequently described whereas tridentate coordination of potentially tetradentate ligands in (**520**) and (**521**) had been reported earlier.[1146] Potentially hexadentate thioethers also fail to displace CO from $Mo(CO)_3(NCMe)_3$ binding instead in a tridentate fashion.[1144,1147] The kinetics of thioether decomplexation in dmso has been studied by Durrant et al.[890]

(ii) Sulfur dioxide complexes

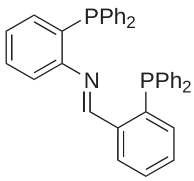
Red *mer,trans*-$Mo(CO)_3(PR_3)_2(SO_2\text{-}S)$ are formed in the reactions of $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ with PR_3 (R = ^{i}Pr, Cy) and SO_2; the *i*-propyl derivative exhibits an octahedral geometry. However, a side-on bonded SO_2–*S,O* complex, lavender-colored *cis,trans*-$Mo(CO)_2(PPh_3)_2(SO_2)(NCMe)$, is produced from $Mo(CO)_2(PPh_3)_2(NCMe)_2$ and SO_2; displacement of NCMe and/or PPh_3 provides access to *cis,trans*-$Mo(CO)_2(PPh_3)_2(SO_2)L$ (L = py, CNCy, CN^tBu, CNC_6H_4Me-4),[1148] mixtures of *cis,mer*- and *cis,fac*-$Mo(CO)_2(PR_3)_3(SO_2$-*S*) and *cis,mer*-$Mo(CO)_2(PR_3)_3(SO_2$-*S,O*) ($PR_3 = PMe_3$, PMe_2Ph, $PMePh_2$, $P(OMe)_3$), or related tridentate phosphine complexes.[1149] Octahedral *cis,mer*-$Mo(CO)_2(PMe_3)_3(SO_2$-*S,O*) has been structurally characterized.[1149] Reactions of $Mo(CO)_3L(NCMe)$ with SO_2 provide access to red/purple *fac*-$Mo(CO)_3L(SO_2$-*S,O*) and red *mer*-$Mo(CO)_3L(SO_2$-*S*) (L = bpy, phen, dppm, dppe, dppp, etc.).[1148,1150] The reaction of $Mo(CO)_2(PPh_3)_2(SO_2)(NCMe)$ with dppe or dmpe (L) produces $Mo(CO)_2$(L-*P*)$(PPh_3)_2(SO_2)$ that undergoes slow associative substitution of PPh_3 giving octahedral *trans*-$Mo(CO)_2$(L-*P,P′*)$(PPh_3)(SO_2$-*S*).[1150,1151] Displacement of SO_2 from *fac*-$Mo(CO)_3L(SO_2)$ (L = bpy, dppe) proceeds by both associative and dissociative mechanisms.[1151] Reaction of SO_2 with $Mo(CO)(Ar_2PC_2H_4PAr_2)_2$ (Ar = benzyl derivative) produces $Mo(CO)(SO_2$-*S*)$(Ar_2PC_2H_4PAr_2)_2$.[1152] The reactions of $Mo(CO)_3L(SO_2)$ (L = bidentate phosphine) with diazomethane at 0 °C produce beige sulfene complexes, *mer*-$Mo(CO)_3(CH_2SO_2$-*C,S*)L.[1150] Several reviews relating to the coordination chemistry of sulfur dioxide are available.[1153,1154]

4.7.8.2.5 Complexes containing mixed-donor co-ligands

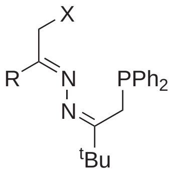
The open and cyclic NP_2-donor ligands (**510**) (X = NMe)[1155] and (**522**)–(**527**) have been incorporated into $Mo(CO)_3L$ complexes. These include yellow *fac*-$Mo(CO)_3$(**522**) (R = Et)[1156] and *fac*/*mer*-$Mo(CO)_3$(**522**) (R = Bz), that reacts with PPh_3 to give *trans,mer*-$Mo(CO)_2$(**522**)(PPh_3).[1157] Crimson *fac*-$Mo(CO)_3$(**523**) is the kinetic product in the reaction of (**523**) and $Mo(CO)_3(\eta^6\text{-}C_7H_8)$ in toluene at < 0 °C, dark-purple *mer*-$Mo(CO)_3$(**523**) being the thermodynamic product obtained upon reflux; the *fac* → *mer* isomerism is first order in acetone, with $k_1 = 1.22 \times 10^{-5}\ s^{-1}$ at 19.5 °C.[1158] Related hydrazone derivatives (**524**)[1159,1160] bind in a tridentate-*N,P,P′* fashion to the $Mo(CO)_3$ fragment; halogen oxidation produces seven-coordinate Mo^{II} derivatives,[1159–1162] sometimes with cleavage of the N—N bond.[1163] Species such as *fac*-$Mo(CO)_3$(**525**-*N,P,P′*) and *fac*-$Mo(CO)_3(NCMe)$(**525**-*P,P′*) are produced in the reactions of (**525**) with $Mo(CO)_3(NCMe)_3$ or upon heating $Mo(CO)_4$(**525**) in heptane; the latter reacts with the diphosphines dppm, dppe, bis(diphenylphosphino)amine, and dppmO (L) to produce *mer*-$Mo(CO)_3$(**525**-*P,P′*)(L-*P*) via *fac* intermediates and is oxidized to Mo^{II} species.[945] The coordination chemistry of diphosphinoamines and cyclodiphosphazanes up to 1994 has been reviewed.[1164] Tridentate coordination of acriphos (**526**) is observed in conformationally constrained *mer*-$Mo(CO)_3$(acriphos).[1165] More recently, mixed phosphine–pyrazole ligands such as (**527**) have been incorporated into tricarbonyl species.[1166]



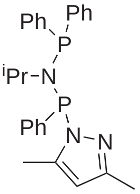
(**522**): R = Et, Bz



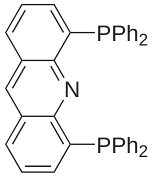
(**523**)



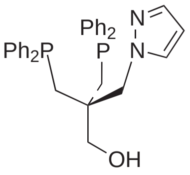
(**524**): X = PPh_3, R = ^tBu
X = SC_6H_4Me–4, R = Me



(**525**)

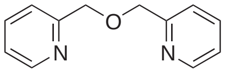


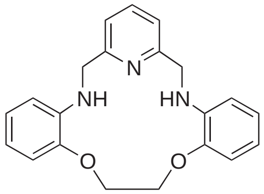
(**526**)



(**527**)

Ether groups generally coordinate weakly to Mo^0, making them potential hemi-labile ligands. Ether coordination is observed in the *fac*-tricarbonyl complexes of (**528**)–(**530**).[1167,1168] The major diastereomers of $Mo(CO)_3L$(**530**) produced in the reactions of *fac*-$Mo(CO)_3$(**530**-*P,P′,O*) with NCMe, py, $P(OCH_2)_3CMe$, and CO, etc. (L) result from displacement of the ether donor from the coordination sphere.[1169] Mixed-donor tricarbonyl complexes are formed by the ligands (**531**)-*N,N′,S*,[1170] (**532**)-*S,P,P′*,[1171] and (**533**)-*P,S,S′*.[189] A wide variety of P/S-donor ligands, (**534**)–(**537**), have been incorporated into octahedral *fac*-tricarbonyl complexes,[1138,1172] $Mo(CO)_3$(**537**-*S,S′,P*) reacting with CO (1 atm) to form $Mo(CO)_4$(**537**-*S,P*) with dangling thioether groups.[1138] Salts of (**534**) and (**535**) react with $Mo(CO)_3(NCMe)_3$ to produce unstable M[$Mo(CO)_3$(**534**)] (M = Li^+ and Na^+) and Na_2[$Mo(CO)_3$(**535**)], respectively, the former being stabilized as M(cryptand) [$Mo(CO)_3$(**534**)] or through alkylation to produce $Mo(CO)_3$(**536**) (R = Me, Et, Bz). A wide variety of open and cyclic tcn and ttcn analogs also form *fac*-tricarbonyl complexes; a calorimetric study of these complexes revealed that the basicity of the metal center increases with ligand donor groups in the order $\mathrm{S} \leq \mathrm{PPh} << \mathrm{NR}$ (R = Me, Et) and cyclic < open.[1156] The template synthesis and X-ray structure of $Mo(CO)_3$(**538**) and related species were reported earlier by Blower et al.[1173] The highly enantio- and regioselective alkylation of 1- and 3-monosubstituted allylic substrates is catalyzed by molybdenum complexes containing bis(pyridine) and bis(dihydrooxazole) ligands.[1174]


(**528**)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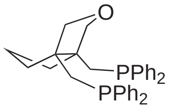
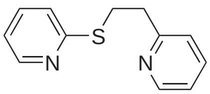
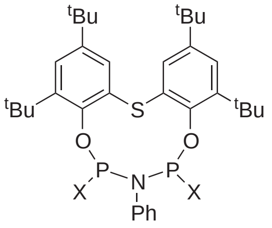
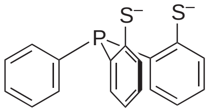
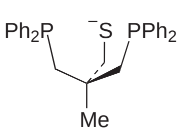
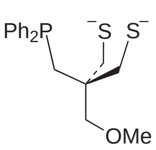

(**530**)

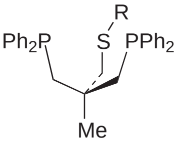

(**531**)

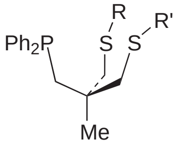

(**532**): X = F, Cl

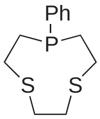

(**533**)


(**534**)


(**535**)


(**536**)


(**537**)


(**538**)

Interest in thiophene complexes[1175] stems from a desire to understand industrial hydrodesulfurization processes catalysed by Co-promoted Mo and W sulfide catalysts. However, surprisingly few Mo–thiophene complexes are known. These include yellow, *fac*/*mer*-$Mo(CO)_3[2,5\text{-}(Ph_2PCH_2CH_2)_2C_4H_2S]$, where the thiophene unit is tethered to the metal by two phosphine side-chains (d(Mo–S)2.569(1) Å),[1176] unstable $Mo(CO)_5$(dbt-*S*) and $Mo(CO)_3(\eta^6$-dbt) (dbt = dibenzothiophene),[1177] and $Mo(\eta^5\text{-}C_4H_4S)(PMe_3)_3$.[1039]

4.7.8.3 Nitrosyl Complexes

4.7.8.3.1 Dinitrosyl complexes

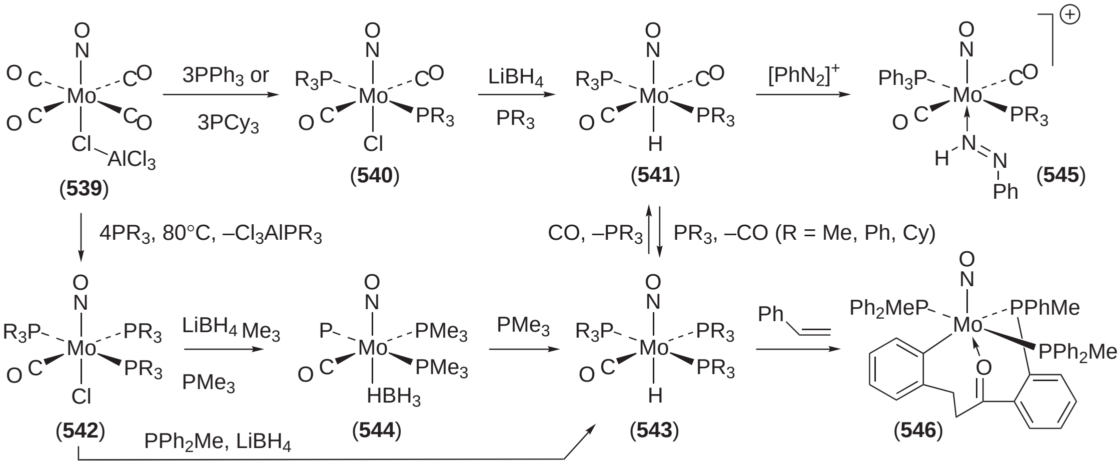
The dinitrosyl halides, $[MoX_2(NO)_2]_n$, and their many ligand adducts and derivatives are well known and have been reviewed.[4] In new work, $[Na_2(15\text{-}C\text{-}5)_2(NCMe)][MoCl_4(NO)_2]$ (ν(NO) 1,769 cm^{-1} and 1,639 cm^{-1}) and $[Na(15\text{-}C\text{-}5)]_2[MoF_4Cl(NO)]$ (ν(NO) 1,628 cm^{-1}), were isolated from the reaction of $[MoCl_2(NO)_2]_n$ with NaF and 15-crown-5 in NCMe. Close association of the $Na(15\text{-}C\text{-}5)^+$ units to the chloro and fluoro ligands, respectively, was established by X-ray crystallography.[1178] An analogous reaction with $Me_3SiNPPh_3$ produces $MoCl_2(OPPh_3)_2(NO)_2$, the source of $OPPh_3$ being uncertain.[537] The versatile starting materials, *cis*-$[MoL_4(NO)_2]X_2$ (L = NCMe (see *Inorg. Synth., Vol. 28, p. 63*), $MeNO_2$, thf; X = PF_6^-, BF_4^-), are produced in the reactions of $Mo(CO)_6$ and NOX or $MoCl_2(NO)_2$ and AgX in L. Derivatives such as $[MoL_4(NO)_2]X_2$ (L = $OPPh_3$; L_2 = bpy, dppe)[1179] and *cis*-$Mo(O_2CR)_2(NO)_2$ (R = alkyl, Ph)[1180,1181] are readily prepared. The carboxylate complexes are precursors for active olefin polymerization and metathesis catalysts such as $Mo(CHMe)(O_2CR)_2(AlCl_2)_2(NO)_2$[1182] and $Mo(CHMe)(ROAlCl_2)_2(NO)_2$.[1183] A theoretical study of these complexes has been published.[1184]

Dinitrosyl complexes are also accessed via reduction of molybdate by hydroxylamine in the presence of added ligands. Complexes prepared in this fashion include $MoL_2(NO)_2$ (L = $S_2CNR_2^-$, S_2COR^-, OR^-, 2-picolinate (structurally characterized), quin, $2\text{-}H_2NC_6H_4O^-$, $2\text{-}H_2NC_6H_4S^-$, hydroxamic acids) and $MoCl_2L_2(NO)_2$ (L = HO^iPr, py).[1005,1185–1187] Schiff base complexes of the type *trans*-$Mo(SB)_2(NO)_2$ result from reactions of *cis*-$Mo(acac)_2(NO)_2$ and ligand free acids.[1188] A synthesis of $Mo(S_2CNEt_2)_2(NO)_2$ has been described in *Inorg. Synth. (Vol. 28, p. 145*) and related complexes, e.g., $Mo(MeSC_6H_4S)_2(NO)_2$, are known.[1046] The chemistry of *cis*-Mo(dttd)$(NO)_2$ is described in Section 4.7.6.5.4. Pyridine- and pyrimidine-thiolate complexes, *cis*-$MoL_2(NO)_2$, adopt distorted octahedral geometries.[1189]

Orange (**496**) (X = CH) reacts under different conditions with $NOSbF_6$ to form $[Mo(CO)(HCpy_3)(NO)_2](SbF_6)_2$ (ν(CO) 2,159 cm^{-1}! cf. CO gas 2,143 cm^{-1}) or $[MoL(HCpy_3)(NO)_2](SbF_6)_2$ (L = NCMe, $Me_2C{=}O$). The carbonyl ligand of $[Mo(CO)(HCpy_3)(NO)_2](SbF_6)_2$ is extremely labile and is displaced by aldehydes, ketones (e.g., $Me_2C{=}O$), and esters; the conformational equilibria and relative Lewis acidities of the complexes have been probed.[1092] Similarly, (**496**) (X = P) reacts with successive equivalents of $NOBF_4$ to form *fac*-$[Mo(CO)_{3\text{-}n}(Ppy_3)(NO)_n](BF_4)_n$ ($n = 1, 2$) or *fac*-$[MoL(Ppy_3)(NO)_2](BF_4)_2$ in the presence of NCMe, NCEt, and $CH_3CH{=}CHCH{=}O$ (L). The Lewis acidity of $[M(Ppy_3)(NO)_2]^{2+}$ is comparable to that of $TiCl_4$.[1094] A few tcn dinitrosyls, e.g., $[(tcn)MoX(NO)_2]^+$ (X = Br, H), are also known.[971]

4.7.8.3.2 *Mononitrosyl complexes*

Ligand exchange at *trans*-$[Bm^*Mo(CO)_2(MeOH)(NO)]BF_4$ produces derivatives such as *trans*-$[Bm^*Mo(CO)_2(py)(NO)]BF_4$, *trans*-$Bm^*MoX(CO)_2(NO)$ (X = monoanion), *trans*-$[Bm^*Mo(CO)(PR_3)_2(NO)]BF_4$, $Mo(CO)L_2(NO)$ (L = bpy, phen, Me_2bpy, dppm) and dimeric $[Mo(S_2CNR_2)(CO)_2(NO)]_2$ (R = alkyl).[1190] Facile dithiocarbamate-bridge cleavage of $[Mo(S_2CNEt_2)(CO)_2(NO)]_2$ by a variety of nucleophiles yields Cat$[Mo(S_2CNEt_2)X(CO)_2(NO)]$ ($Cat^+ = PPN^+$, $NEt_4{}^+$; $X = NCS^-$, $NO_3{}^-$, $N_3{}^-$, Br^-, Cl^-) and $Mo(S_2CNEt_2)(CO)L_2(NO)$ (L = PPh_3, PMe_3, $P(OMe)_3$; L_2 = CO/py, dppe). All complexes, except the dppe derivative, have a *cis,trans*- structure with a linear NO ligand ($\angle$(Mo—N—O) > 175°) and S-donors *trans* to the π-acceptor CO/NO ligands.[1191] Hydridonitrosyl complexes have been studied by Hillhouse, Berke, and co-workers; selected reactions, centered on the hydride ligand, are shown in Scheme 21. The reactions of (**539**) with three equivalents of PR_3 (R = Ph, Cy) produce (**540**), which are converted into the corresponding hydrides (**541**) by $LiBH_4$. However, reactions involving four equivalents of PMe_2Ph or PMe_3 produce (**542**); these react with $LiBH_4$ to give (**543**) via an isolable borohydride (**544**) when $PR_3 = PMe_3$. The carbonyls (**541**) and (**543**) may be interconverted, the former reacting with diazonium salts and acids HX to form phenyldiazene (**545**) or conjugate base complexes.[1192] The reactions of (**543**) include alkene-induced coupling of hydride, CO, olefin, acyl, and alkyl ligands[1193] and the insertion of aldehydes, CO_2, Fe, and Re carbonyls and bisdihydroproline ester into the Mo—H bond giving, e.g., (**546**).[1194] The X-ray structures of (**543**) ($PR_3 = PMe_3$), (**544**), and many organometallic derivatives have been determined.[1194] Reduction of $MoCl_3(PMe_3)_3(NO)$ with Na/Hg in the presence of PMe_3 affords yellow *trans*-$MoCl(PMe_3)_4(NO)$. Metathesis permits the preparation of $MoI(PMe_3)_4(NO)$ and $Mo(S_2CX)(PMe_3)_3(NO)$ (X = NMe_2, OMe), which react with CN^tBu and CO to give $Mo(S_2CX)(CN^tBu)(PMe_3)_2(NO)$ and $Mo(S_2CX)(CO)(PMe_3)_2(NO)$, respectively. Direct reaction of $MoCl(PMe_3)_4(NO)$ with CN^tBu and CO yields $MoCl(CN^tBu)_n(PMe_3)_{4-n}(NO)$ ($n = 1, 2$) and $MoCl(CO)(PMe_3)_3(NO)$, respectively. These complexes contain linear nitrosyl ligands with ν(NO) 1,590–1,530 cm^{-1}. Reaction of $MoCl(PMe_3)_4(NO)$ with CS_2 produces off-white $MoCl(\eta^3\text{-}S_2CPMe_3)(PMe_3)_2(NO)$, possessing a linear nitrosyl in a pseudo-square pyramidal structure with an apical η^3-ligand.[1006] Brown $MoBr(\eta^3\text{-}S_2CPCy_3)(CO)_2(NO)$ has been synthesized in three steps from $Mo(CO)_3(NCMe)_3$ and is used as a building block for bimetallic speces.[1195] Related η^3-dithio ligand complexes are described in Section 4.7.4.3.4(ii).



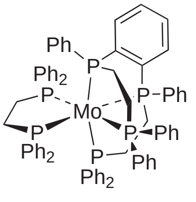
Scheme 21

A preparation for orange Tp*Mo(CO)$_2$(NO) has been published in *Inorg. Synth. (Vol. 23, p. 4)* and related complexes bearing 3-R-Tp (R = ^{t}Bu, Ph,[1196] C$_6$H$_4$OMe-4[977]), 4-R-Tp* (R = Me, Et, Bu,[972] Bz[973]), B(3-R-pz)$_4^-$ (R = ^{t}Bu, Ph,[1196] C$_6$H$_4$OMe-4, Cy[974]), Tp^{Pr} and Tp′ have been reported. Several of these have been structurally characterized, disorder of NO and CO being commonly observed; linear nitrosyl ligands are indicated, in keeping with ν(NO) ca. 1,670 cm^{-1}.[974] Tris(triazolyl)borate complexes of this type have also been prepared,[967,1102] as has the thionitrosyl analog Tp*Mo(NS)(CO)$_2$.[1197] The nitrosyl-Tp^x complexes are starting materials for Mo^{II} species (Section 4.7.6.2.3) that can in turn be reduced back to Mo^0 complexes of the type [Tp*MoClL(NO)]$^-$. Spectroelectrochemical studies of Tp*MoClL(NO) (L = substituted pyridine) have revealed a reversible reduction to [Tp*MoClL(NO)]$^-$ complexes with intense, low-energy MLCT transitions. Near-IR electrochromism in some 3-substituted pyridine complexes (λ ca. 1,510 nm, ε 12,000 M^{-1} cm^{-1}) has potential applications in electrochromic dye and electro-optical switching technologies.[1198] Nitrosylation of (**104**) by 0.5 M HNO$_3$ (R = H (tcn),[971] Me[1001]) or NOBF$_4$ (R = Bz)[1002] produces [(R$_3$tcn)Mo(CO)$_2$(NO)]$^+$ ((**427**), Scheme 6). Related 1,5,9-triazacyclododecane complexes are also known.[594] Reaction of *mer*-[Mo(CO)$_3$(dppe)(NO)]BF$_4$ with hot NCMe produces orange [Mo(CO)$_{2-n}$(NCMe)$_n$(dppe)(NO)]BF$_4$ (n = 0, 1) that are useful synthons for [Mo(CO)$_2$(PMe$_3$)(dppe)(NO)]BF$_4$, [Mo(CO)(NCMe)(PPh$_3$)(dppe)(NO)]BF$_4$, Mo(SC$_6$H$_4$-Me-2)(CO)$_2$(dppe)(NO), etc.[1199] Bidentate binding of the N-donor ligand of (**247**) persists upon nitrosylation by NOBF$_4$ to form (**547**) (Scheme 12) and in its reversible deprotonation at the β-carbon. However, a novel tridentate scorpiand ligand is observed in (**548**) (W analog structurally characterized), formed when (**547**) reacts with NCMe.[602]

4.7.8.4 Complexes Containing Phosphorus-donor Ligands

4.7.8.4.1 *"Homoleptic" phosphine complexes*

The organometallic chemistry of pyrophoric Mo(PMe$_3$)$_6$ and related complexes up to 1995 has been surveyed in *Comprehensive Organometallic Chemistry*.[6] Now, a convenient synthesis for Mo(PMe$_3$)$_6$ from MoCl$_5$ and Na/K in PMe$_3$[769] has superseded the original metal-vapor synthesis described by Brookhart and co-workers.[4] In solution, Mo(PMe$_3$)$_6$ is in equilibrium with MoH(CH$_2$PMe$_2$)(PMe$_3$)$_4$, with $K = 8.6(4) \times 10^{-3}$ in C$_6$D$_6$.[769] Some chemistry of this complex is described in Section 4.7.4.6.4; the arene/heteroarene chemistry currently emerging from Parkin's laboratory is beyond the scope of this review. Co-condensation of Mo vapor with excess dmpe yields Mo(dmpe)$_3$[800] while Mo(tmbp)$_3$ is produced upon reduction of MoCl$_5$ by Mg in thf solutions of 4,4′,5,5′-tetramethyl-2,2′-biphosphine (tmbp).[1200] Contrary to expectations, these complexes adopt trigonal prismatic structures and significant Mo → L electron transfer is inferred from structural and computational studies.[1200] Red Mo(tdep)$_2$ has also been isolated from the reaction of Mo(N$_2$)$_2$(PPh$_2$Me)$_4$ with tdep; the octahedral complex contains two opposed *fac*-tridentate tdep ligands, each with a pendent arm.[1201] The dinitrogen complex, Mo(N$_2$)$_2$(dppe)$_2$, decomposes to (**549**) in refluxing benzene, the yield being enhanced by added dppe. The dppe ligand of (**549**) is displaced by CO (1 atm) forming the corresponding *cis*-dicarbonyl complex.[1202] Reduction of MoCl$_3$(bdpe) in the presence of P(OMe)$_3$ or PMe$_3$ (L) produces Mo(bdpe)L$_3$.[1203] The thermally stable phosphinine complex, Mo(PC$_5$H$_5$)$_6$, is prepared from MoCl$_5$, Mg, and ligand in thf; it exhibits an almost ideal octahedral coordination geometry with d(Mo—P) 2.381(16) Å. Studies of the series M(PC$_5$H$_5$)$_6$ (M = Cr, Mo, W) have been reported.[1204]



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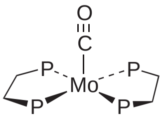

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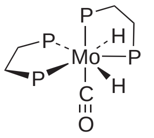

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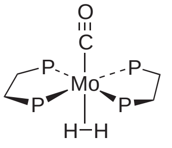

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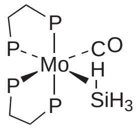

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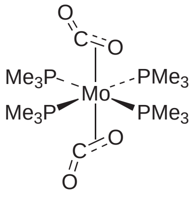

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4.7.8.4.2 Complexes with carbonyl or organometallic co-ligands

Yellow *cis*-$Mo(CO)_2L_2$ (L = dppm, dppe, dppp) are produced in the reactions of $Mo(CO)_2(\eta^4\text{-}C_7H_8)_2$ with phosphines, and a number of crystal structures are available from the late 1970s onward.[1205] Protonation by $HBF_4{\cdot}OEt_2$[1206] or HOTf[1207,1208] yields pentagonal bipyramidal hydrides, $[HMo(CO)_2L_2]X$ ($X^- = BF_4^-$, OTf^-; $\delta(^1H)$ −3 to −7). Kinetics studies of the deprotonation of the hydrides by amines are consistent with anion-assisted reactions[1206] while electrochemical studies point to an ECEC oxidation and reduction forming H_2.[1208]

Reactions of *trans*-$Mo(N_2)_2(R_2PC_2H_4PR_2)_2$ (R = Et, ^{i}Bu, Ph, Bz, $CH_2C_6H_4Me$-3) with ethyl acetate in refluxing toluene/benzene under argon produce $Mo(CO)(R_2PC_2H_4PR_2)_2$ ((**550**), R groups excluded in (**550**)–(**553**)).[1152,1209] These compounds feature an agostic interaction between Mo and a γ—C—H bond at the site *trans* to the carbonyl ligand, as evidenced by NMR[1152] and X-ray diffraction studies (d(Mo···C) 3.007(4) Å for R = ^{i}Bu,[1209] 3.50(2) Å for R = Ph[4]). They react rapidly with H_2 producing (**551**) (R = Et, ^{i}Bu; ν(M–H) ca. 1,650 cm^{-1}; $\delta(^1H)$ ca. −5, $J_{HD} < 2$ Hz) or (**552**) (R = others, ν(H—H) ca. 2,650 cm^{-1}, $\delta(^1H)$ ca. −5, J_{HD} 30–35 Hz); some derivatives participate in a tautomeric equilibrium between (**551**) and (**552**) in solution.[1210] The dihydride $MoH_2(CO)(depe)_2$ exhibits a pentagonal bipyramidal structure[1210] while octahedral structures with square pyramidal heavy atom cores are observed for $Mo(H_2)(CO)(R_2PC_2H_4PR_2)_2$ (R = Ph,[1210] $CH_2C_6H_4Me$-3[1152]). Neutron diffraction and inelastic neutron scattering experiments have probed the structure and dynamics of the dihydrogen ligand in perdeuterated $Mo(H_2)(CO)(dppe)_2$, where d(H—H) = 0.82 Å.[1210] Isocyanide analogs, *trans*-$Mo(H_2)(CNR)(dppe)_2$ (R = Bu, Ph, $C_6H_4NMe_2$-4, $\delta(H_2)$ ca. −5), are accessible from *trans*-$Mo(N_2)(CNR)(dppe)_2$.[1211] Related σ-bonded silane complexes, e.g., (**553**), have been reported (some of these equilibrate with oxidative addition products).[1212,1213] A complete treatise on dihydrogen and σ-bond complexes has been provided by Kubas.[1107] The X-ray structure of *fac*-Mo(CO)(bdpe)(dppm) and known *trans*-$Mo(CO)(dmf)(dppe)_2$[1214] have been determined. A rare trigonal bipyramidal, 4-electron-donor mono(acetylene) complex, $Mo(HC{\equiv}CH)(dppe)_2$, forms upon reaction of *trans*-$Mo(N_2)_2(dppe)_2$ with HC≡CLi.en in thf.[1215] Details of the reactions of *trans*-$Mo(N_2)_2(dppe)_2$ and related species with alkynes may be found in *Comprehensive Organometallic Chemistry*[6] and a review by Henderson.[1216]

4.7.8.4.3 Carbon dioxide complexes

Interest in CO_2 binding and activation by transition metals is piqued by the potential of the molecule as a C_1 feedstock. The first bis(carbon dioxide) metal complex, *trans*-$Mo(\eta^2\text{-}CO_2)_2(PMe_3)_4$ (**554**), was prepared by reacting *cis*-$Mo(N_2)_2(PMe_3)_4$ with CO_2;[4] $MoH(\eta^3\text{-}C_3H_5)(PMe_3)_4$ reacts with CO_2 to give the same product.[806] IR/Raman studies have shown that the energies of the ν(CO) (1,155 cm^{-1}) and γ(C=O) (ca. 550 cm^{-1}) modes are sensitive to ligand geometry;[1217] ^{13}C ($\delta(CO_2)$ 206) and ^{31}P NMR spectra are in accord with staggered CO_2 ligands. The compound reacts with MeI or I_2, CO, COS, and CNR (R = Me, ^{i}Pr, ^{t}Bu, Cy, Bz) to produce $MoI_2(PMe_3)_4$, *cis*-$Mo(CO)_2(PMe_3)_4$, $Mo(S_2C{=}O)(CO)_2(PMe_3)_3$, and *trans,mer*-$Mo(CO_2)_2(CNR)(PMe_3)_3$, respectively. X-ray structures of the latter (R = ^{i}Pr, Bz) confirmed the presence of η^2 *trans* staggered CO_2 ligands in this class of compound,[1218] a result in line with computational studies.[1219] Irradiation of (**554**) produces *cis*-$Mo(CO)_2(PMe_3)_4$ and $OPMe_3$ along with small amounts of *fac*-$Mo(CO)_3(PMe_3)_3$ and $Mo(CO)(PMe_3)_5$.[1220] Diphosphine derivatives, *trans*-$Mo(CO_2)_2(PMe_3)_2L$ and *trans*-$Mo(CO_2)_2L_2$ (L = dmpe, depe, and dmpm), have been prepared and probed by dynamic NMR spectroscopy.[1221] The Mo^{II} complex, $MoH(O_2CH)(CO_2)(dmpe)_2$, is formed in the reaction between $MoH_4(dmpe)_2$ and CO_2.[805]

4.7.8.4.4 Dinitrogen complexes

The desire to understand and harness dinitrogen fixation and functionalization has sustained research in this area.[4,1222] Mononuclear dinitrogen complexes containing phosphine co-ligands are typically prepared via reduction of high-valent chloro species under dinitrogen in the presence of added phosphine or by ligand displacement reactions; complexes of the type *fac*-$Mo(N_2)_3P_3$, *cis*/*trans*-$Mo(N_2)_2P_4$, and *cis,mer*- and *cis,fac*-$Mo(N_2)P_5$ (P = phosphine donor) are well known (see *Inorg. Synth., Vol. 28, p. 38*, for a synthesis of *trans*-$Mo(N_2)_2(dppe)_2$). The dinitrogen ligand is invariably bound in a linear end-on fashion, with d(N≡N) close to or slightly longer than free

N_2 (1.09–1.15 Å, cf. 1.0976(2) Å for N_2). The spectroscopic characteristics of dinitrogen complexes include ν(NN) IR bands between 1,880 and 2,110 cm^{-1} (2,331 cm^{-1} for N_2), ^{15}N NMR resonances at −35 ppm to −55 ppm ($N_\alpha > N_\beta$)[4] and co-ligand dependent ^{95}Mo chemical shifts.[1223]

Sodium reduction of $MoCl_3(PEt_3)_3$ under N_2 yields $[Mo(N_2)_2(PEt_3)_3]_2(\mu\text{-}N_2)$ that reacts with PMe_3 to give known *trans*-$Mo(N_2)_2(PMe_3)_4$.[1224] The *cis*- and *trans*- isomers of a related complex, $Mo(N_2)_2(PMe_2Ph)_4$, have been separated[1225] and a kinetics study of the decomposition of *trans*-$Mo(N_2)_2(PMePh_2)_4$ has been reported.[1226] New derivatives of *trans*-$Mo(N_2)_2L_2$ (L = bidentate diphosphine) incorporate ligands such as (–)-(2*S*,3*S*)-bis(diphenylphosphino)butane (*S,S*-chiraphos),[1227] dmpe,[740] $Bz_2PCH_2CH_2PBz_2$ derivatives[1152] and dippe.[703] Reduction of MoX_3(tppea) (X = Cl, Br) under similar conditions produces unstable *cis*-$Mo(N_2)_2$(tppea); subsequent reactions with CO or PMe_3 (L) yield MoL_3(tppea).[882,1017] The phosphorus analog, *cis*-$Mo(N_2)_2$(tppep), is also known.[1017] Complexes such as *trans*-$Mo(N_2)_2(PR_3)L$ ($L = E\{(CH_2)_nPPh_2\}_2$ ($n = 2$, 3; E = O, S, NH, NMe, PPh),[1228,1229] $MeP\{(CH_2)_3PMe_2\}_2$[1230]) are produced by reducing $MoCl_3L$ under N_2 in the presence of one equivalent of PR_3 ($R_3 = Me_3$, Ph_3, $MePh_2$, Me_2Ph, etc). Similar reactions employing two equivalents of PR_3 and limited N_2 produce isomeric mono(dinitrogen) complexes, $Mo(N_2)(tppep)L_2$ (L = PMe_2Ph; L_2 = dmpm, dppm, dppe, etc),[1231] while addition of N_2 to $MoH(CH_2PMe_2)(PMe_3)$(bdmp) produces $Mo(N_2)(PMe_3)_2$(bdmp).[799] Reaction of *trans*-$Mo(N_2)_2(PMe_3)_4$ with PMe_3, dmpm, dmpe, depe, or $N(CH_2CH_2PMe_2)_3$ provides an alternative route to mono(dinitrogen) complexes bearing mono-, bi-, and tridentate co-ligands; the X-ray structure of known $Mo(N_2)(PMe_3)_5$ has been determined.[1224] NMR studies and the X-ray structures of *cis,mer*-$Mo(N_2)(PMe_3)_2$(bdmp)[1230] and *cis,fac*-$Mo(N_2)$(dppm)(bdpe)[1232] have defined the isomers present in this system. Ready loss of N_2 from mono(dinitrogen) complexes yields dihydrides (from H_2) and CO and ethene adducts.[1231] The condition-dependent reactions of dinitrogen complexes with acids, producing ammonia, hydrazine, etc, may be found in the references cited.

4.7.8.5 Complexes Containing Sulfur-donor Ligands

Macrocyclic, $Me_8[16]aneS_4$ ((**279**) Scheme 13) supports the Mo^0 chemistry shown in Scheme 19. Sodium amalgam reduction of (**452**) in thf under CO or N_2 produces *trans*-$Mo(CO)_2(Me_8[16]aneS_4)$ (**555**, ν(CO) 1,902, 1,767 cm^{-1})[1040] and *trans*-$Mo(N_2)_2(Me_8[16]aneS_4)$ (**281**, ν(NN) 1,955 cm^{-1}, 1,890 cm^{-1}),[712] respectively. The octahedral complexes feature an equatorial *syn* S_4-donor and axial CO or N_2 ligands. Alkylation and protonation of the dicarbonyl takes place at sulfur giving (**556**).[1233] The dinitrogen complex undergoes alkylation and arylation reactions consistent with effective p_π donation from the thioether to the Mo—N_2 unit;[712,713] it is a versatile starting material for isocyanide (**557**, **558**),[1234] phenylisocyanate (**559**),[1235] and oxidized cyano (**459**), nitrido, thio, and hydrosulfido species, etc. (see Scheme 13). Therewith ends this review of mononuclear Mo chemistry!

4.7.9 ABBREVIATIONS

acac = acetylacetonate(1-) = 2,4-pentanedionate(1-)
Ad = 1-adamantyl (2-Ad = 2-adamantyl)
Ar = generally $C_6H_3Me_2$-3,5 and $C_6H_3{}^iPr_2$-2,6 in triamido and imido ligands, respectively
bdme = bis(dimethylphosphinoethyl)methylphosphine
bdmp = bis(dimethylphosphinopropyl)methylphosphine
bdpe = bis(diphenylphosphinoethyl)phenylphosphine
bdpp = bis(diphenylphosphinopropyl)phenylphosphine
bdt = benzene-1,2-dithiolate
Bm = bispyrazolylmethane
Bm* = bis(3,5-dimethylpyrazolyl)methane
Bp = dihydrobispyrazolylborate
Bp* = dihydrobis(3,5-dimethylpyrazolyl)borate
bpy = 2,2′-bipyridine
Bu_2bdt = 3,5-di-*tert*-butylbenzene-1,2-dithiolate
Bu_4dttd = 1,2-bis(2-mercapto-3,5-di-*t*-butylphenylthio)ethane(2-)
cyclam = 1,4,8,11-tetraazacyclotetradecane
dbc = 3,5-di-*tert*-butylcatecholate

dippe = 1,2-bis(diisopropylphosphino)ethane
dmit = 4,5-dimercapto-1,3-dithiole-2-thionate
dppb = 1,2-bis(diphenylphosphino)benzene
dppe = 1,2-bis(diphenylphosphino)ethane
dppee = 1,2-bis(diphenylphosphino)ethene
dppm = bis(diphenylphosphino)methane
dttdH$_2$ = 1,2-bis(2-mercaptophenylthio)ethane(2-)
Fc = ferrocenium ion, $[Fe(\eta^5\text{-}C_5H_5)_2]^+$
hmpa = hexamethylphosphoramide
MCD = magnetic circular dichroism
Me$_4$cyclam = 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane
Me$_8$[16]aneS$_4$ = 3,3,7,7,11,11,15,15-octamethyl-1,5,9,13-tetrathiacyclohexadecane
Mes = 2,4,6-trimethylphenyl (mesityl)
Nap = 1-naphthyl
N$_3$N = triamido ligand, $N(CH_2CH_2NSiMe_3)_3{}^{3-}$
OAT = oxygen atom transfer
OTf = trifluoromethanesulfonate (triflate) anion
Pc = phthalocyaninate(2-)
pdc = pyridine-2,6-dicarboxylate(2-)
pdpeH$_2$ = pyridine-2,6-bis(2,2-diphenylethanol)
phen = 1,10-phenanthroline
PPN = bis(triphenylphosphine)iminium cation
py = pyridine
quin = 8-quinolinolate (8-hydroxyquinolate)
ROMP = ring opening metathesis polymerization
TCNE = tetracyanoethylene
TCNQ = 7,7,8,8-tetracyano-*p*-quinodimethane
tdea = tris(diphenylphosphinoethyl)amine
tdep = tris(diphenylphosphinoethyl)phosphine
terpy = 2,2′:6,2″-terpyridine
Tm = trispyrazolylmethane
Tm* = tris(3,5-dimethylpyrazolyl)methane
tmeaH$_3$ = tris(2-mercaptoethyl)amine
tmeda = *N,N,N′,N′*-tetramethylethylenediamine
tmp = 5,10,15,20-tetramesitylporphyrinato(2-)
Tp = hydrotripyrazolylborate
Tp* = hydrotris(3,5-dimethylpyrazolyl)borate
Tp^{Pr} = hydrotris(3-isopropylpyrazolyl)borate
Tp′ = hydrobis(3-isopropylpyrazolyl)(5-isopropylpyrazolyl)borate
tpp = 5,10,15,20-tetraphenylporphyrinato(2-)
ttcn = 1,4,7-trithiacyclononane
ttp = 5,10,15,20-tetra-*p*-tolylporphyrinato(2-)
Tz* = hydrotris(3,5-dimethyl-1,2,4-triazolyl)borate
XAS = X-ray absorption spectroscopy

4.7.10 REFERENCES

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4.8
Tungsten

T. OKAMURA and N. UEYAMA
Osaka University, Osaka, Japan

4.8.1 INTRODUCTION

Since the first edition of *Comprehensive Coordination Chemistry* (*CCC*, 1987), the border line between coordination chemistry and organometallic chemistry has became obscure. Generally metal–carbon bonds had been distributed to organometallic chemistry but recently they have been found in biological systems, i.e., hydrogenases have CO and CN^- ligands in the active center.[1] Isoelectronic NO has been known to play a significant biological and physiological role in the central nervous system.[2] The coordination chemistry of such small molecules, including H_2, O_2, N_2, and CO_2 is very important and is discussed here. In this chapter, tungsten coordination chemistry since 1982 is described, except that of W—W triple-bonded complexes (described in Chapter 4.9) and chalcogeno and halo clusters (Chapters 4.10 and 4.12). The compounds shown here are limited to those whose structures have been confirmed by X-ray crystallography.

4.8.2 THE CHEMISTRY OF W^{VI}

The fundamental chemistry and compounds reported prior to 1984 are summarized in *CCC* (1987). The development and expansion of coordination chemistry provided many possibilities and opportunities for the selection of ligands. Many combinations of coordinated atoms have been reported including halogen, chalcogen, nitrogen, phosphorus, carbon, and hydrogen. Initially, classical halides and their derivatives are described, followed successively by less electronegative atoms.

4.8.2.1 W^{VI} Halides and Derivatives

Tungsten hexahalides are well-known starting materials for the synthesis of W^{VI} or related reduced derivatives. Substitution of ligands or hydrolysis sometimes gave derivatives $[WX_nL_{6-n}]$ (X, halogen; L, any ligand; $n = 1$–5) by incomplete replacement of the halo ligands.

4.8.2.1.1 Complexes containing oxygen and sulfur

Controlled hydrolysis gave oxohalide derivatives. Using anhydrous HF and boric acid, WF_6 was hydrolyzed uniquely to oxonium (μ-fluoro)bis(tetrafuluorooxotungstate(VI), $[H_3O][W_2O_2F_9]$, where an W=O bond was found *trans* to bridging F^-.[3] $[W(CO)_6]$ and 21-crown-7 in the presence of water and gaseous HCl in toluene gave $[H_5O_2{}^+(21\text{-crown-7})][WOCl_5{}^-]$ under UV-irradiation conditions.[4] The coordinated halide allows coordination to another metal ion. The F atom of [*cis*-$WO_2F_4]^{2-}$ coordinates to Cu in the crystal of $(pyH)_2[Cu(py)_4(WO_2F_4)_2]$.[5]

The halide ligand of oxohalides is easily replaced by alkoxide, phenoxide, or thiolate. Calix[4]-arene is a polyphenoxo ligand. Reaction of 1,3-dialkyl *p*-*tert*-butylcalix[4]arene (R_2calH_2; R = Me, Et) with $WOCl_4$ in hexane gave $[(R_2cal)WOCl_2]$.[6] When normal calix[4]arene was used, four chloride ions were replaced completely to give a mononuclear monooxocalix[4]arene W^{VI}

complex.[7] The 1:2 reaction between $WOCl_4$ and phenol derivatives (ArOH) gave $[WOCl_2(OAr)_2]$.[8] In the case of aromatic diols, the formation of phenol–phenolate complexes from $WOCl_4$ was dependent on solvent. Alcoholysis reactions in THF generated the dianionic aryloxide, $[WO(OArO)Cl_2(thf)_2]$, while $[WOCl_3(OArOH{\cdot}OEt_2)]$ was produced in Et_2O.[9] Hexamethyl disiloxane effectively removes chloride ion from $WOCl_4$ via elimination of Me_3SiCl in DME (1,2-dimethoxy ethane) or diglyme to give $[WO_2Cl_2(solv)]$ (solv = DME[10] or $C_6H_{14}O_3$[11]). Tungsten oxo salicylate was obtained by the reaction of WCl_6 and salicylic acid.

The chloride ligand is introduced by the addition of equivalent Me_3SiCl to the complex having no chlorine. By this procedure, $(Et_4N)[WO(bdt)_2Cl]$ (bdt = 1,2-benzenedithiolato) was obtained from $(Et_4N)[WO(bdt)_2(OSiBu^tPh_2)]$. This compound is also prepared from $WOCl_4$ and $Li_2(bdt)$.[12]

Mixed ligand complexes having halide and alkoxo or phenoxo were synthesized by two procedures. One was incomplete replacement of WCl_6 and the other was introduction of halide by halogenated reagent. The fist method gave $[W(OAr)_4Cl_2]$ (Ar = pentafluorophenyl, 2,6-dichlorophenyl),[13] $[W(p\text{-}Bu^t\text{-calix[4]arene})Cl_2]$,[7] and $[W(O\text{-}2,6\text{-}C_6H_3R_2)_2Cl_4]$ (R = *i*-Pr, Ph).[14,15] Tungsten hexachloride reacts with salicylic acid to produce an oxochloride complex with evolution of gaseous HCl.[16] Slow recrystallization from THF/hexane gave $[W(O)Cl(Hsal{\cdot}THF)(sal)]$ (H_2sal = salicylic acid). Reaction of $WOCl_4$ and salicylic acid in a 1:2 molar ratio gave the same product. The second method gave *trans*-$[WCl_2(eg)(OAr)_2]$ (eg = 1,2-ethanediolate dianion; OAr = $OC_6H_2Me_2$-2,6, $OC_6H_2Pr^i_2$-2,6, $OC_6H_2Me_2$-2,6,-Br-4)[17] and *trans*-$[WI_2(OCMe_3)_4]$, which revealed the first characterized structurally W^{VI}-I bonds.[18] The former is produced by the reaction of $[W(eg)_2(OAr)_2]$ and gaseous HCl in CH_2Cl_2. When Br_2 was used, bromination was observed at the 4-position of the coordinated phenolate ligand.

A mononuclear octahedral tungsten halide having a terminal sulfide ligand was prepared from $W_2Cl_8S_2$ and S_8. The resulting crystal was a *cyclo*-octasulfur adduct, $[WSCl_4(thf)]{\cdot}S_8$, with the S ligand *trans* to THF.[19]

4.8.2.1.2 *Complexes containing chalcogen and nitrogen group (N, P)*

Heating a suspension of WOF_4 in pyridine at ca. 60 °C gave a pyridine adduct, $WOF_4{\cdot}2C_5H_5N$, which decomposed to produce $WOF_4{\cdot}C_5H_5N$ (Figure 1). The latter adduct was also obtained by the reaction of WOF_4 with equimolar pyridine in dichloromethane.[20] When 2-fluoropyridine (F-py) was used, the reaction proceeded at room temperature to give a similar product, $WOF_4{\cdot}$F-py.[21]

Polymeric $[WO_2Cl_2]_x$ reacted with neutral ligands, 1,3-dimethylalloxazine (DMA) and bis (1-methylimidazol-2-yl)ketone (BIK) to give monomeric compounds, $[(DMA)WO_2Cl_2]$ and $[(BIK)WO_2Cl_2]$ (Figure 2).[22]

Mononuclear phenylimido tungsten(VI) phenoxide, $[WCl_3({=}NPh)\{OC_6H_2(CH_2NMe_2)_2\text{-}2,6\text{-}Me\text{-}4\}]$, was synthesized by a ligand-exchange reaction between $[WCl_4({=}NPh)(OEt_2)]$ and the lithium phenoxide derivative. One of the two NMe_2 groups is coordinated to W at the position *trans* to the imido ligand.[23]

The chloroimido complexes, $[W(NCl)Cl_4(OPR_3)]$ (R = Me, Ph), were produced from $[W(NPR_3)Cl_5]$[24] by oxidation on the nitrogen atom. The complexes were also prepared by the reaction of $[W(NCl)Cl_4]_2$ and $R_3P{=}O$ in a good yield (Scheme 1).[25]

Oxidative addition of cyclopentanone or acetone to the tungsten(II) complex $[WCl_2(PMePh_2)_4]$ gave an oxo–alkylidene tungsten(VI) complex, $[W(O{=}C_5H_8)Cl_2(PMePh_2)]$ and $[W(O{=}CMe_2)Cl_2(PMePh_2)]$ as shown in Scheme 2.[26,27] The carbonyl moiety coordinates to tungsten ion as an η^2-ligand and the C—O distance is lengthened and similar to a C—O single bond. The subsequent elimination reaction provided an alkylidene complex. Similar η^2-carbonyl compounds having chalcogenide ligand have been reported,[28] as described in Section 4.8.2.2.3.

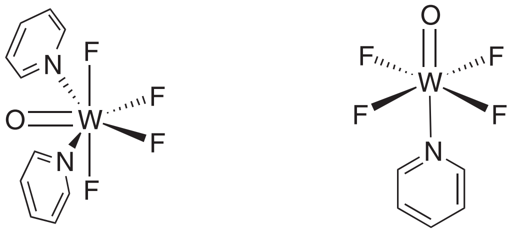


Figure 1 Schematic drawing of $WOF_4{\cdot}2C_5H_5N$ and $WOF_4{\cdot}C_5H_5N$.

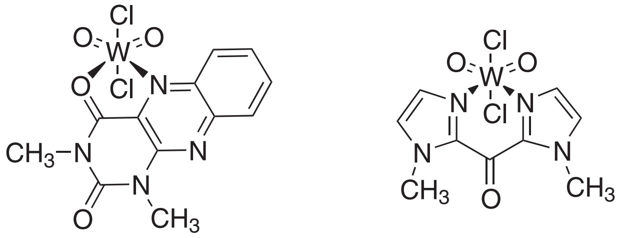
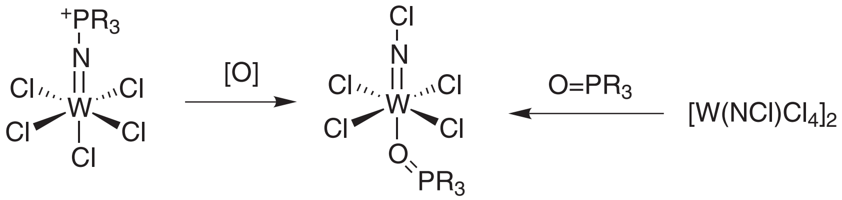
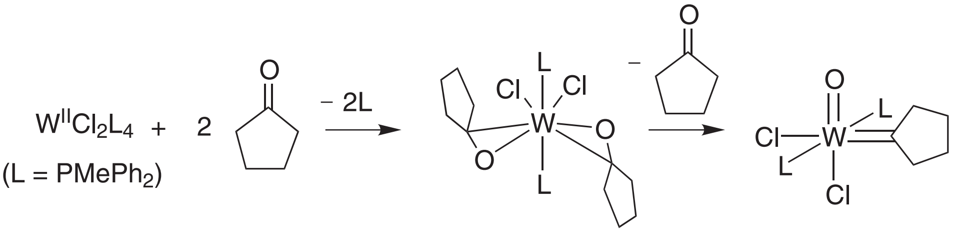


Figure 2 The compounds of $\mathrm{WO_2Cl_2}$ with dimethylalloxazine (DMA) and bis(1-methylimidazol-2-yl)-ketone (BIK).



Scheme 1



Scheme 2

4.8.2.1.3 *Complexes containing nitrogen groups*

The nitrogen atom provides a variety of ligands in the form of amine, amido, imido, nitrido, etc., functions. Combination with tungsten halides provided various derivatives. Tungsten(VI) amide–chloride complexes, *fac*-[$\mathrm{WCl_3(NR_2)}$] (Me, Et, pyrrolidine), were synthesized from $\mathrm{WSCl_4}$ and *N,N*-dialkyl(trimethylsilyl)amine. Interestingly the use of $\mathrm{WCl_6}$ was not successful.[29] The reaction of a half equivalent of 2-fluoropyridine with $\mathrm{WF_6}$ gave mononuclear 7-coodinated $\mathrm{WF_6{\cdot}F\text{-}py}$.[21]

Phosphoraniminato complexes were produced by the reaction of [$\mathrm{W(NSiMe_3)Cl_2(PMe_3)_3}$][30] and $\mathrm{Cl_2}$ at −196 °C and followed by warming up to 22 °C accompanied by the elimination $\mathrm{Me_3SiCl}$ and $\mathrm{PMe_3Cl_2}$. The speed of the warming determines the product, [$\mathrm{W(NPMe_3)Cl_5}$] (20 min) or [$\mathrm{W(NPMe_3)Cl_4(PMe_3)}$] (rapid warming).[24] The stoichiometric reaction of $\mathrm{WCl_6}$ and 1 or 2 equiv. of $\mathrm{Cl_3P{=}NSiMe_3}$ gave [$\mathrm{WCl_5(N{=}PCl_3)}$] and [$\mathrm{WCl_4(N{=}PCl_3)_2}$] with elimination of $\mathrm{Me_3SiCl}$.[31] Crystallographically characterized *cis*-[$\mathrm{WCl_4(N{=}PCl_2Ph)_2}$] was synthesized in a similar procedure. Reaction of [$\mathrm{WCl_5(N{=}PCl_3)}$] with $\mathrm{GaCl_3}$ gave [$\mathrm{Cl_4WNPCl_3}$][$\mathrm{GaCl_4}$], where the chloride of the $\mathrm{GaCl_4^-}$ anion coordinates weakly to the octahedral tungsten ion (W—Cl = 2.704(4) Å) at the position *trans* to the nitrogen atom.

Trimethylsilyl derivatives are also useful for the introduction of the imido groups. On the reaction of [$\mathrm{W(NAr)Cl_4(thf)}$] (Ar = 2,6-diisopropylphenyl) with 2 equiv. of $\mathrm{Me_3SiNHAr}$ in THF, [$\mathrm{W(NAr)_2Cl_2(thf)_2}$] was obtained in 87% yield. Reaction of [$\mathrm{W(NAr)_2Cl_2(thf)_2}$] and 2 equiv. of LiNHAr gave [$\mathrm{Li(thf)_4}$][$\mathrm{W(NAr)_3Cl}$] in high yield (Figure 3).[32] The coordinated imido ligand retains coordination ability to the other metal ion = basicity. When protonic acids are used,

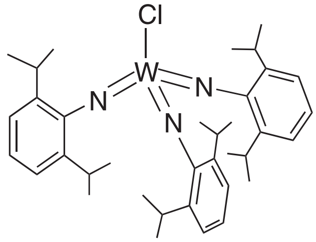


Figure 3 Schematic drawing of [W(NAr)$_3$Cl]$^-$.

protonation of the imido nitrogen occurred. Upon addition of HCl to [W$_2$(NBut)$_8$Li$_4$] in Et$_2$O, the μ-Cl dimeric amino compound, [{W(NBu^t)$_2$(NH$_2$Bu^t)Cl(μ-Cl)}$_2$], was isolated.[33] The chemistry of the imido compound is described in Section 4.8.2.3. Reaction of the organoimido chloro complex, [W(NR)Cl$_4$(L)] (R = Et, L = none; R = C$_6$H$_4$Me-p, L=OEt$_2$) with N(SiMe$_3$)$_3$ in a 2:1 ratio yielded the hexanuclear nitrido complex [W$_2$(N)(NR)$_2$Cl$_5$]$_3$ shown in Figure 4. In the (RN)W(N)W(NR) unit, two imido groups show nearly orthogonal orientation, allowing the central nitride to achieve maximum tungsten–nitrogen π-bonding.

The reaction of [W$^{\mathrm{II}}$Cl$_2$(PMe$_4$)$_4$] with 2 equiv. of trimethylsilyl azide produced a bis(silylimino) tungsten(VI) complex, [W(NSiMe$_3$)$_2$Cl$_2$(PMePh$_2$)] with evolution of N$_2$. When 1 equiv. of trimethylsilyl azide was used, oxidative replacement gave the six-coordinate tungsten(IV) mono (silylimido) complex, [W(NSiMe$_3$)Cl$_2$(PMePh$_2$)$_3$].[30] A bis(hydrazido) complex, [WCl(NNMe$_2$)$_2$(PR$_3$)$_2$]Cl, was obtained from [WCl$_4$(PR$_3$)$_2$] and 2 equiv. of Me$_3$SiNHNMe$_2$.[34] Reaction of [WCl$_4$(NNPh)] with Me$_3$SiCH$_2$MgCl followed by the addition of C$_6$F$_5$OH afforded the trialkyl complex, [W(CH$_2$SiMe$_3$)$_3$(NNPh$_2$)(OC$_6$F$_5$)]. However, an analogous reaction using PhCH$_2$MgCl gave [WCl$_2$(NNPh$_2$)(OC$_6$F$_5$)$_2$(thf)].[35]

The hydrazido(1-) tungsten(VI) shown in Figure 5 was produced from the triflate complex [W(NAr){2,6-NC$_5$H$_3$(CH$_2$NTosyl)$_2$}{(OTf)Cl}] (Ar = 2,6-C$_6$H$_3$-i-Pr$_2$) and 2 equiv. of hydrazine.

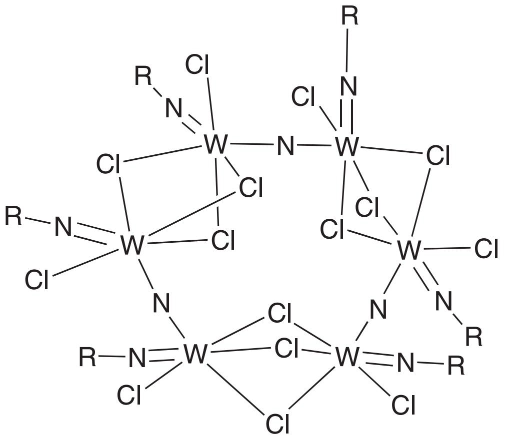


Figure 4 Schematic drawing of [W$_2$(N)(NR)$_2$Cl$_5$]$_3$ (R = Et, C$_6$H$_4$Me-p).

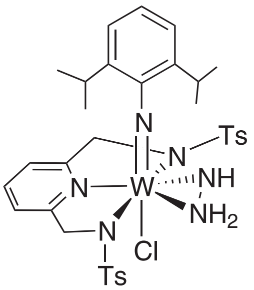


Figure 5 Representation of [WCl(N-2,6-C$_6$H$_3$-i-Pr$_2$){2,6-NC$_5$H$_3$(CH$_2$NTosyl)$_2$}(μ^2-NHNH$_2$)].

The triflate complex was prepared by the reaction of $[WCl_4NAr]$ with the tridentate ligand following elimination of Cl^- using silver triflate.[36]

4.8.2.2 W^{VI} Chalcogenides and Derivatives

Tungsten trioxide or tungstic acid and the metal salts are very stable but their derivatives have been investigated as synthetic or biological catalysts. Tungstoenzymes catalyze O atom transfer redox reactions using the tungsten(VI) and (IV) oxidation states and are similar to analogous molybdoenzymes.[37] The related model compounds have been reported and are also described in this section.

4.8.2.2.1 Complexes containing only oxygen

Monooxotungsten(VI) phenoxide, $[WO\{L(O)_4\}]$ ($L(OH)_4$ = calix[4]arene), was prepared by the heating $WOCl_4$ with $L(OH)_4$.[7] One acetic acid molecule weakly coordinated at the position *trans* to the terminal oxo ligand. In the case of siloxide, reaction of 4 equiv. of $NaOSiPh_3$ with $WOCl_4$ failed to generate $[WO(OSiPh_3)_4]$ whereas 3 equiv. of siloxide afforded $[WO(Cl)(OSiPh_3)_3]$. Use of cyclic $(Ph_2SiO)_3$ gave a spirocyclic tungstasiloxane $[WO\{O(Ph_2SiO)_3\}_2(thf)]$.[38]

The electron-rich oxo anion $[WO_4]^{2-}$ easily reacts with Lewis acids. Reaction with $[B(C_6F_5)_3]$ produced tetrahedral $(^nPr_4N)_2[WO\{OB(C_6F_5)_3\}_3]$.[39] $WO_3{\cdot}H_2O$ reacted with 30% hydrogen peroxide following addition of $Ph_2Si(OH)_2$ or $[Ph_2Si(OH)_2]_2O$ affording dimeric peroxo compounds $[Ph_2SiO_2\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}^{2-}$ or $[(Ph_2SiO\{WO(O_2)_2\})_2O]^{2-}$ which were isolated as PPh_4^+ salts (Figure 6).[40,41]

Anodic oxidation of metallic tungsten in methanol afforded a mixture of $[W(OMe)_6]$ and $[WO(OMe)_4]$. After purification and treatment with $MeOC_2H_4OH$, crystals of $[\{LiWO_2(OC_2H_4OMe)_3\}_2{\cdot}2Li(HOC_2H_4OMe)_2][W_6O_{19}]$ were obtained.[42] Single crystals of $W(OMe)_6$ were also prepared by anodic oxidation and subsequent separation from by-product, $[WO(OMe)_4]$.[43]

Reaction of WCl_6 with salicylic acid produced an oxochloride complex with evolution of gaseous HCl as mentioned in Section 4.8.2.1.1. Reaction of $WOCl_4$ with 3 equiv. of salicylic acid gave the μ-oxo dimer, $[W(=O)(Hsal)(sal)]_2O$.[16]

Tungsten(VI) pinacolate $[W(OCMe_2CMe_2)_3]$ was produced by the reaction of $W(NMe_2)_6$ with 3 equiv. of pinacol in high yield.[44] The dimeric catecholate derivative $[W_2(Cl_4Cat)_6]$ (Cl_4Cat = tetrachlorocatecholato) was synthesized by the redox reaction between $W(CO)_6$ and tetrachloro-1,2-benzoquinone.[45] The bis(sisesquinoxane)tungsten complex $[\{(C_6H_{11})_7Si_7O_9(O)_3\}_2W]$, shown in Figure 7, was afforded by the reaction of WCl_6 with 1 or 2 equiv. of silsesquioxane $(C_6H_{11})_7Si_7O_9(OH)_3$.[46]

4.8.2.2.2 Complexes containing oxygen and nitrogen groups (nitrogen and phosphorus) and carbon

Tridentate nitrogen ligand is one of the useful ligands capping coordination sites of metal ions. Hydrotris(pyrazolyl)borate derivatives have been used for this purpose. The starting material, $[LWO_2(OH)]$ (L = hydrotris(3,5-dimethylpyrazol-1-yl)borate) was prepared from $[LWI(CO)_3]$ via transfer of two oxygen atoms from dimethyl sulfoxide. This reaction required water as the source

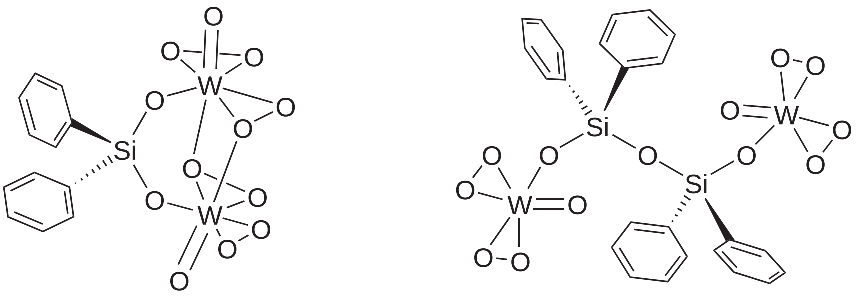


Figure 6 $[Ph_2SiO_2\{W_2O_2(\mu\text{-}O_2)_2(O_2)_2\}^{2-}$ and $[(Ph_2SiO\{WO(O_2)_2\})_2O]^{2-}$.

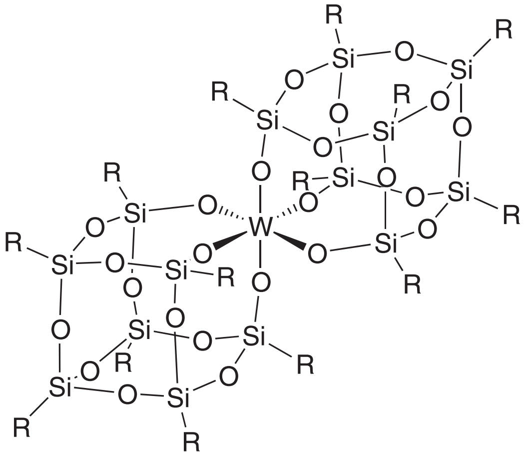


Figure 7 Schematic drawing of $[\{(C_6H_{11})_7Si_7O_9(O)_3\}_2W]$ where R indicates cyclohexyl group.

of hydroxo ligand. The starting material was reacted with NEt_4OH to give $(NEt_4)[LWO_3]\cdot4H_2O$ and the anion is shown in Figure 8. Reaction of $[LWO_2(\mu\text{-}O)WO(CO)L]$[47] with *tert*-butyl hydroperoxide afforded $[LWO_2]_2(\mu\text{-}O)$.[48] Triazacyclohexane derivatives present facial tridentate coordination. The oxidation reaction of $[(t\text{-}Bu_3tach)W(CO)_3]$ ($t\text{-}Bu_3tach = 1,3,5$-tri-tert-butyl-1,3,5-triazacyclohexane) with H_2O_2 gave $[(t\text{-}Bu_3tach)W(O)_3]$ (Figure 8) in high yield.[49]

The reaction of $[WO_2(acac)_2]$ and the Schiff base ligand, $H_2(5\text{-}t\text{-}Busap)$ (2-(5-*tert*-butylsalicylideneamino)phenol), afforded $[WO_2(5\text{-}t\text{-}Busap)]$ in yields exceeding 90%.[50]

A linear O═W—O—W═O unit was found in $[W_2O_3(CH_2CMe_3)_6]$ which was prepared from the reaction of $[W(CCMe_2)Np_3]$ ($Np = CH_2CMe_3$) and a large excess of H_2O in tetrahydrofuran.[51]

Mononuclear *cis*-dioxo-amido tungsten(VI) compounds were prepared by the reaction of $[WO_2Cl_2(dme)]$ (dme = 1,2-dimethoxyethane) and lithium amide. For pyridine functionalized amido ligands $L = {}^-N(SiMe_3)(2\text{-}C_5H_3N\text{-}6\text{-}Me)$, ${}^-N\{Si(t\text{-}Bu)Me_2\}(2\text{-}C_5H_3N\text{-}6\text{-}Me)$, $[WO_2(L)]$ were isolated.[52] Similar *cis*-dioxo, oxosulfido, and disulfido complexes, $[WQ_2(OSiPh_3)_2(Me_4phen)]$ ($Q_2 = O_2$, OS, S_2, Me_4phen = 3,4,7,8-tetramethyl-1,10-phenanthroline) were prepared by the reaction between $K_2[WO_2Q_2]$, Me_4phen and Ph_3SiCl in acetonitrile.[53]

Reaction of triplebonded dimeric $W_2(O\text{-}t\text{-}Bu_2)_6$ with acetonitrile or benzonitrile afforded alkylidyne and nitride compounds.[54] The nitride compound, $[W(N)(O\text{-}t\text{-}Bu)_3]$, was easily separated and the polymeric structure was determined X-ray analysis.[55] The terminal nitride ligand is triply bonded to W and interacts to the neighboring W via a weak dative bond. An analogous compound, $[W_2\{OC(CH_2)_2(CF_3)\}_6]$, did not react with acetonitrile but reacted with benzonitrile to give the trinuclear triangular complex, $[NW\{O(CH_2)_2CF_3\}]_3$, having nitride bridge. The W—N bond lengths alternate between 1.72(2) (average) and 2.14(2) Å (average).[56]

Calixarene compounds bearing hydrazido(2-) or isodiazene complexes were produced by the ligand exchange reaction between $[W(NNPh_2)(OBu^t)_4]$ and calixarenes. The near-linear W—N—N angles, short W—N (1.74–1.75 Å) and long N—N (ca. 1.32–1.33 Å) distances indicate the W═N—N bond character.[57] The related compound having alkyl groups, $[W(NNPh_2)(CH_2SiMe_3)(OC_6F_5)]$, was isolated by the reaction of $[WCl_4(NNPh_2)]$ and $MeSiCH_2MgCl$ following the addition of C_6F_5OH.[35] The calix[5]arene derivative bearing a Me_2NP moiety reacted with

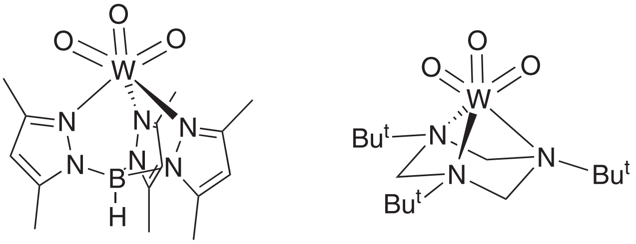


Figure 8 Schematic drawing of $[LWO_3]^-$ (L = hydrotris(3,5-dimethylpyrazol-1-yl)borate) and $[(t\text{-}Bu_3tach)W(O)_3]$ ($t\text{-}Bu_3tach$ = 1,3,5-tri-tert-butyl-1,3,5-triazacyclohexane).

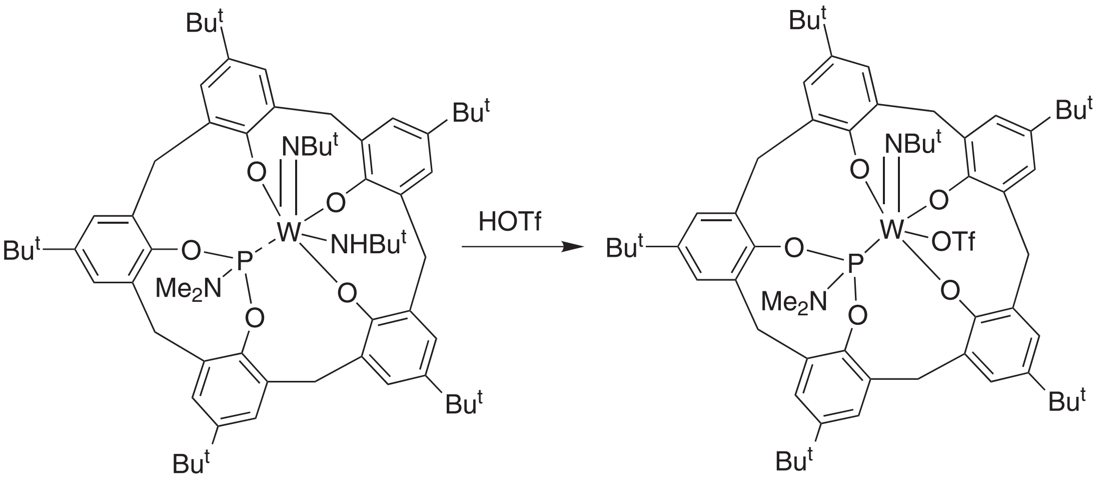


Figure 9 Change of W—P interaction in the *p-tert*-butylcalyx[5]arene imido complex.

[(Bu^{t}N)$_2$W(NHBu^t)$_2$] to give the imidoamido complex shown in Figure 9. This complex was refluxed with HOTf to give a triflate accompanied with an increased W—P interaction.[58]

The four-coordinate tungsten(IV) complex, [W(NAr)$_2$(PMe$_2$Ph)$_2$] (Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$), reacted with acetone in pentane to give [W(NAr)$_2$(PMe$_2$Ph)(η^2-OCMe$_2$)] quantitatively. This compound has a long C—O bond (1.39(1) Å) and no ν(CO) stretch above 1,400 cm^{-1} features which are characteristic for an oxametallopropane tungsten(VI) complex (Figure 10). Bis(imino)tungsten(VI) Schiff-base complexes were synthesized by alcoholysis of [W(NBu^t)$_2$(NHBu^t)$_2$] using diprotonated Schiff-base.[59] A schematic drawing of the complex [W(NBu^t)$_2${(3,5-Bu$^t_2$)$_2$salen}] is shown in Figure 10. The reaction of [W(NBu^t)$_2$(NHBu^t)$_2$] with (Ph$_2$SiOH)$_2$O gave an imido metallasiloxane, [W(NBu^t)(NH$_2$Bu^t)(OSiPh$_2$OSiPh$_2$O)$_2$].[60] Two nitrogen atoms are *trans* to each other and the two *tert*-butyl groups are distinguishable by ^{1}H NMR.

4.8.2.2.3 Complexes containing sulfur, selenium, or tellurium

A few examples only of tungsten(VI) telluride or selenide compounds are known. The tungsten (IV) bis(chalcogenido) complexes, *trans*-[W^{IV}(PMe$_3$)$_4$(E)$_2$] (E = S, Se, Te) were treated with aldehyde to give the η^2-aldehyde complexes, [W^{VI}(PMe$_3$)$_2$(E)$_2$(η^2-OCHR))] shown in Scheme 3. The structural parameters indicate that this complex is a W^{VI} metallaoxirane derivative rather than a W^{VI} aldehyde adducts.[28,61] Convenient preparation of WSe$_4$$^{2-}$ from W(CO)$_6$ and Se$_3$$^{2-}$ has been reported.[62]

Treatment of (Et$_4$N)[Me$_2$TpW(CO)$_3$] (Me$_2$Tp = tris(3,5-dimethylpyrazol-1-yl)borate) with 1 equiv. of S$_8$ in DMF gave the mononuclear tris(sulfide) complex, (Et$_4$N)[Me$_2$TpWS$_3$]. A similar reaction using the Tp (hydrotris(pyrazol-1-yl)borate) derivative in acetonitrile provided (Et$_4$N)$_2$ [{WO(S$_2$)$_2$}$_2$S] as a by-product.[63] The starting materials of *cis*-bis(thio) and -oxothio derivatives

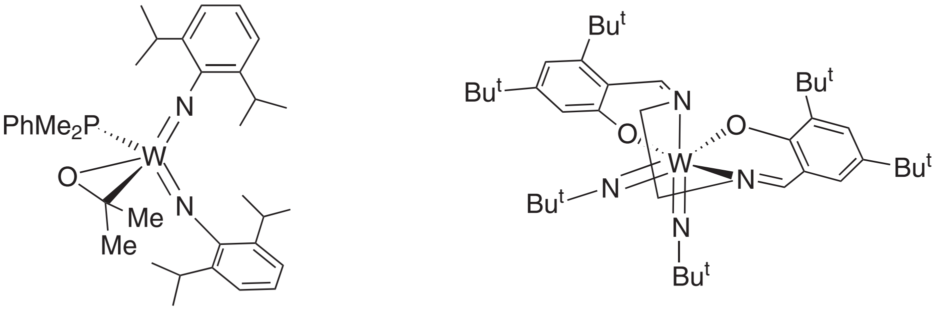
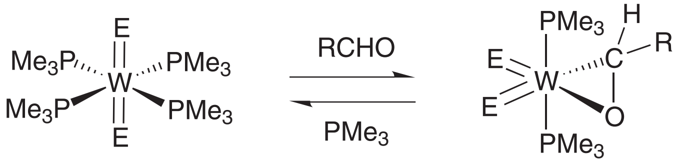


Figure 10 Schematic drawing of [W(NAr)$_2$(PMe$_2$Ph)(η^2-OCMe$_2$)] (Ar = 2,6-C$_6$H$_3$-*i*-Pr$_2$) and [W(NBu^t)$_2${(3,5-Bu$^t_2$)$_2$salen}].



E = S, R = H, Me, Ph, C_6H_4Me, C_6H_4OMe
E = Se, R = H, Ph
E = Se, R = H, Ph

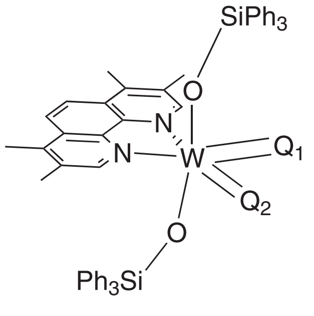
Scheme 3

having Tp* (=Me_2Tp) were synthesized from Tp^*WO_2Cl and B_2S_3 or P_4S_{10}. The isolated $[Tp^*WS_2Cl]$ and $[Tp^*WOSCl]$ reacted with NaOPh, NaSPh, NaSePh, or sodium (−)-mentholate to give the corresponding products. Molecular structures of $[Tp^*WS_2(OPh)]$ and (*R,S*)-[Tp*WOS{(−)-mentholate}] were determined.[64,65] The reaction between $[WO_{4\text{-}n}S_n]^{2-}$ ($n = 0$–2), Ph_3SiCl, and Me_4phen (3,4,7,8-tetramethyl-1,10-phenanthroline) gave $[WO_{2\text{-}n}S_n(OSiPh_3)_2(Me_4\text{-}phen)]$ as shown in Figure 11.[53] The dimeric disulfide complex $[(S)_2W(\mu\text{-}S)_2W(NNMe_2)_2(PPh_3)]$ was prepared from $[WCl(NNMe_2)_2(PPh_3)_2]Cl$ and $(NBu^n{}_4)_2[WS_4]$ in acetonitrile.[66]

Oxidative addition of sulfur to tungsten(IV) complexes afforded sulfido tungsten(VI) derivatives. A solution of $(Et_4N)[W(OPh)(S_2C_2Me_2)_2]$ reacted with dibenzyl trisulfide to produce $(Et_4N)[WS(OPh)(S_2C_2Me_2)_2]$.[67] A similar procedure using $(Et_4N)[W(bdt)_2(OSiBu^tPh_2)]$ gave $(Et_4N)[WS(bdt)_2(OSiBu^tPh_2)]$. The same product can be prepared by the reaction between $(Et_4N)[WO(bdt)_2(OSiBu^tPh_2)]$ and $(Me_3Si)_2S$.[12]

Dioxotungsten(VI) thiolates have been reported in relation to the active sites of tungstoenzymes in the oxidized state. Dithiolene derivatives, especially, are good models for the pterin cofactor. The first reported dioxotungsten(VI) dithiolate was $(PPh_4)_2[WO_2(bdt)_2]$ (bdt = 1,2-benzenedithiolate), shown in Figure 12, which was synthesized by the oxidation of $(PPh_4)_2[WO^{IV}(bdt)_2]$ by trimethylamine *N*-oxide.[68] The *trans* influence means that the W—S bonds at the *trans* position (mean 2.597(4) Å) *trans* to the oxo ligand are significantly longer than those at the *cis* position (mean 2.425(4) Å). Similar reactions were effective for analogous compounds. $(Et_4N)_2[WO_2(S_2C_2Me_2)_2]$ was produced by the oxidation of $(Et_4N)_2[WO(S_2C_2Me_2)_2]$ using Me_3NO.[67] The reaction of aqueous $Na_2WO_4{\cdot}2H_2O$ and Na_2nmt (nmt^{2-} = 1,2-dicyanoethylenedithiolate) in the presence of excess $NaHSO_3$ at pH = 5.5 by the addition of acetic acid gives *cis*-$[W^{VI}O_2(nmt)_2]^{2-}$. The tungsten(IV) complex $(Et_4N)_2[W^{IV}O(nmt)_2]$ was oxidized by elemental sulfur under reflux to $(Et_4N)_2[W^{VI}O(\eta^2\text{-}S_2)(nmt)_2]$.[69] A dioxotungsten(VI) selenophenolate complex, $[Tp^*WO_2(SePh)]$ (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate) was obtained by the reaction of $[Tp^*WO_2Cl]$ and LiSePh in tetrahydrofuran.[70]

A solution of $[W(CO)(phen)(SPh)_2(\eta^2\text{-}SO_2)]$ (formal oxidation state is II or IV) in dichloromethane converted spontaneously to $[W^{VI}(phen)(SPh)_2(O)_2]$ as shown in Scheme 4.[71]



$Q_1Q_2 = S_2, OS, O_2$

Figure 11 Schematic drawing of $[WO_{2\text{-}n}S_n(OSiPh_3)_2(Me_4phen)]$ ($n = 0$–2).

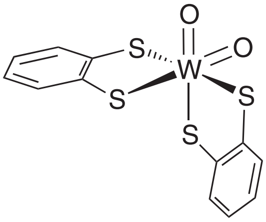
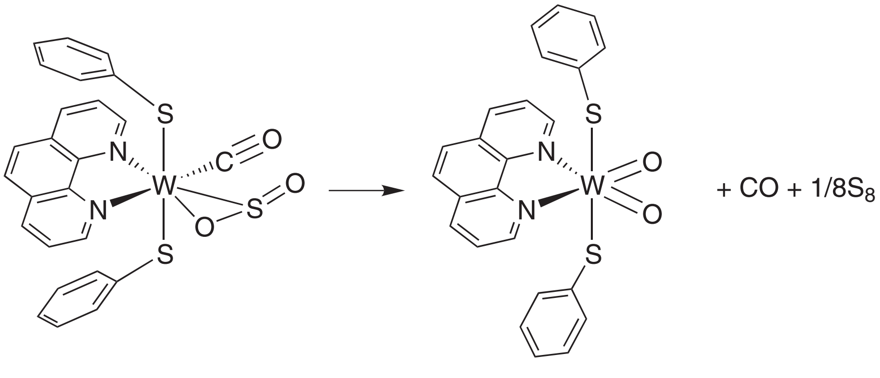


Figure 12 The anion part of $(PPh_4)_2[W^{VI}O_2(bdt)_2]$.



Scheme 4

Recent crystallographic studies of the active sites of tungstoenzymes suggests the possibility of desoxotungsten(IV) and monooxotungsten(VI) bis(dithiolate) centers with an additional coordination of serine. Some model compounds mimicking the coordination environment around the tungsten atom have been reported. Treatment of $(Et_4N)[W^{IV}(OSiPh_2But)(bdt)_2]$ with 3-fold excess of Me_3NO led to $(Et_4N)[W^{VI}O(OSiPh_2But)(bdt)_2]$.[12,72] A similar reaction between $(Et_4N)[W^{IV}(OPh)(S_2C_2Me_2)_2]$ and Me_3NO afforded $(Et_4N)[W^{VI}O(OPh)(S_2C_2Me_2)_2]$.[73]

Reaction of WO^{3+} species with aqueous $(NH_4)_2S_x$ in the presence of 2,2′-bipyridine (bpy) gave the discrete mononuclear complex $[WO(\eta^2\text{-}S_2)_2(bpy)]$.[74] The reaction between $(NH_4)_2[WO_2S_2]$, elemental sulfur and $NH_2NH_2\cdot 2HCl$ following addition of Et_4NBr gave $(Et_4N)_2[\{WO(\eta^2\text{-}S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}NH_2NH_2)]$. The anion is shown in Figure 13.[75] The reaction between $(Et_4N)_2[WS_4]$ and $(C_6H_5CS_2)_2$ gave $(Et_4N)[WO(S_2)_2(S_2CC_6H_5)]$ (as minor product) and $(Et_4N)[W^{VI}S(S_2)_2(S_2CC_6H_5)]$.[76]

The tungsten(IV) complex $[W(NPh)\{o\text{-}(Me_3SiN)_2C_6H_4\}(py)_2]$ (py = pyridine) reacted with 2 equiv. of thiophene to give the S,C-chelate tungsten(VI) complex, $[W(NPh)\{o\text{-}(Me_3SiN)_2C_6H_4\}(SC_4H_4)]$, shown in Scheme 5.[77]

A sulfenamide complex $[W(NBu^t)_2(\eta^2\text{-}PhSNBu^t)_2]$ was produced by the interaction of $Li_2W(NBu^t)_4$ with PhSCl. The molecular structure with distorted bicapped tetrahedral geometry is shown in Figure 14.[78]

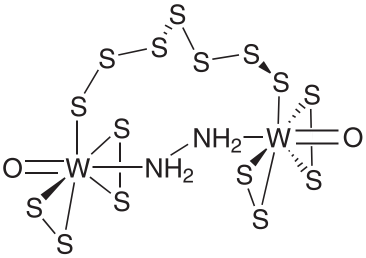
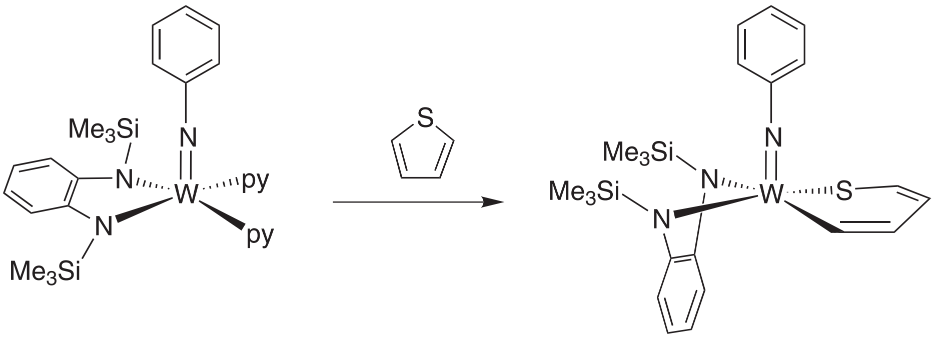


Figure 13 Representation of $[\{WO(\eta^2\text{-}S_2)_2\}_2(\mu_2\text{-}S_7)(\mu_2\text{-}NH_2NH_2)]^{2-}$.



Scheme 5

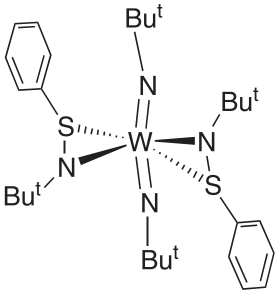
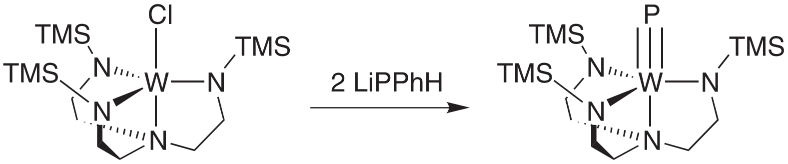


Figure 14 Molecular structure of [W(NBu^t)$_2$(η^2-PhSNBu^t)$_2$].

4.8.2.3 W^{VI} Complexes Containing Only Nitrogen Groups' Ligands and Hydride

The phosphido triamideamine tungsten complex [([N$_3$N])W$\equiv$P] ([N$_3$N] = Me$_3$SiNCH$_2$CH$_2$)$_3$N) was prepared by the reaction of [([N$_3$N])WCl] and LiPPhH as shown in Scheme 6. The analogous reaction using LiAsPhH gave only trace of [([N$_3$N])W$\equiv$As] with [([N$_3$N])WPh] as main product. However [([N$_3$N])W$\equiv$As] was obtained by the reaction of [([N$_3$N])WPh] and a slight excess of PhAsH$_2$. In this reaction approximately 2 equiv. of benzene were formed. The nitrido compound was produced by the reaction of [([N$_3$N])WCl] and NaN$_3$. The nitrido, phosphido, and arsenido complexes reacted readily with methyl triflate in toluene to give the imido, phosphinidene, and arsinidene complexes [{([N$_3$N])W=EMe}](OTf) (E = N, P, As), respectively in quantitative yield. The arsinidene complex was characterized crystallographically.[79]



Scheme 6

Treating [W(NPh)Cl$_4$] with 1 equiv. of MeOH gave [W(NPh)(OMe)Cl$_3$] that reacts with 4 equiv. of LiNMe$_2$ to afford [W(NPh)(NMe$_2$)$_4$].[80]

Deprotonation of (Bu^{t}NH)$_2$W(NBu^t)$_2$ by methyl lithium gave dimeric [W$_2$(NBu^t)$_8$Li$_4$], as shown in Figure 15.[81] The bridging NBu^t ligands are coordinated as amido rather than imido. The terminal imido, Bu^{t}N, exhibits a reasonably short W—N bond (1.723(8) Å). Reaction of [W$_2$(NBut)$_8$Li$_4$] with Lewis acids gave monomeric [W{(μ-NBu^t)$_2$AlCl$_2$}$_2$] as shown in Figure 15.[33]

Hydrazo compounds are reported as intermediates in nitrogen fixation by molybdenum-containing nitrogenase. Tungsten chemistry has been reported for comparison with molybdenum. Addition of methyl lithium to [W(NPh)Me$_3$Cl] followed by 1 equiv. of hydrazine afforded [{W(NPh)Me$_3$}$_2$(μ-η^1,η^1-NH$_2$NH$_2$)(μ-η^2,η^2-NHNH)] in good yield.[82]

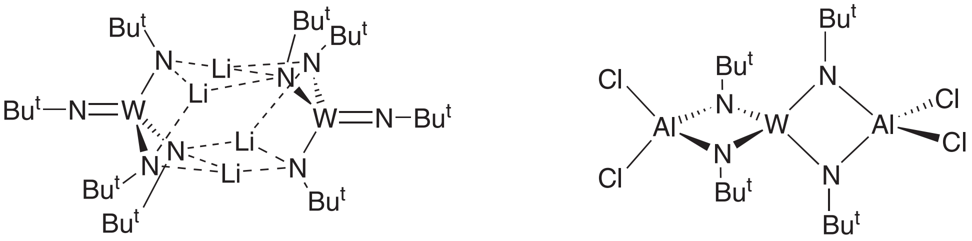


Figure 15 Representation of $[W_2(NBu^t)_8Li_4]$ and $[W\{\mu\text{-}NBu^t\}_2AlCl_2]_2]$.

The structure of tris(phenyldiisopropylphosphine)tungsten hexahydride $[WH_6(PPh\text{-}i\text{-}Pr_2)_3]$ was determined by X-ray and neutron diffraction.[83]

4.8.3 THE CHEMISTRY OF W^V

4.8.3.1 W^V Halides and Derivatives

The addition reaction of KWF_6 and KF at elevated temperature under vacuum gave seven-coordinate K_2WF_7.[84] Reduction of $[W^{VI}(O\text{-}2,6\text{-}C_6H_3Cl_2)_4Cl_2]$ by sodium amalgam produced $[W^V(O\text{-}2,6\text{-}C_6H_3Cl_2)_4Cl(Et_2O)]$, where the ether molecule occupies the position *trans* to chloride.[13] Bis(aryloxide)tungsten(VI) $[WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2]$ is reduced by excess $LiBH_4$ or an equivalent of sodium amalgam in the presence of PMe_2Ph to give $[WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)]$.[15] $[WCl_3(OAr\text{-}2,6\text{-}Ph_2)_2(thf)]$ was obtained by treatment with magnesium butadiene in THF.

The reaction between dibenzo-30-crown-10, $[W(CO)_6]$, water, and gaseous HCl in toluene gave oxonium ion complex of the crown, $[2H_3O^+(\text{dibenzo-30-crown-10})][W^{II}(CO)_4Cl_3]_2$ and $[2H_3O^+(\text{dibenzo-30-crown-10})][WOCl_4(H_2O)]_2$.[4]

Binuclear complexes $\{W^VOLCl\}_2(\mu\text{-}OO)$ (μ-OO = *p*-diphenolato) exhibit both reduced electronic and magnetic exchange interactions compared to the Mo analogues. This was ascribed to poorer d_π—p_π W—O overlap involving the bridging ligands.[85]

4.8.3.2 W^V Chalcogenides and Derivatives

Some dimeric tungsten(V) selenides have been reported. While tungsten(V) is essentially paramagnetic (d^1). Antiferromagnetc interactions within the dimeric core enabled the use of ^1H and ^{77}Se NMR. Acidification of $(NH_4)_2[WSe_4]$ with acetic acid in methanol followed by addition of PPh_4Cl afforded $(PPh_4)_2[W_3Se_9]$, i.e., $[(\eta^2\text{-}Se_2)(Se)W(\mu\text{-}Se)_2W(Se)(\eta^2\text{-}Se_3)]$. The thermal reaction of $[WSe_4]^{2-}$, PPh_4Cl and black selenium gave two isomers of $(PPh_4)_2[W_2Se_{10}]$, i.e., $[(\eta^2\text{-}Se_2)(Se)W(\mu\text{-}Se)_2W(Se)(\eta^2\text{-}Se_4)]^{2-}$ and $[(\eta^2\text{-}Se_3)(Se)W(\mu\text{-}Se)_2W(Se)(\eta^2\text{-}Se_3)]^{2-}$. These isomers may be distinguished by ^{77}Se NMR.[86] The complex $(PPh_4)_2[W_2Se_{10}]$ reacts with dimethyl acetylenedicarboxylate to give the di(μ-Se) diselenene compound, $(PPh_4)_2[W_2Se_2\{Se_2C_2(COOCH_3)_2\}_4]$.[87] $(PPh_4)_2[W_2Se_{10}]$ reacted with $NaBH_4$ to produce $(PPh_4)_2[W_2Se_6]$, i.e., the $[(Se)_2W(\mu\text{-}Se)_2W(Se)_2]^{2-}$ anion.[88]

The terminal sulfide thiolate complex $[W_2(S)_2(\mu\text{-}S)_2\{S_2P(OEt)_2\}_2]$, was prepared from $[WS_4]^{2-}$ and $HS_2P(OEt)_2$ or WS_2Cl_2 and $(NH_4)[S_2P(OEt)_2]$. The complex reacted with $Na(S_2CNEt_2)$ to produce the ligand-substituted product $[W_2S_2(\mu\text{-}S)_2(S_2CNEt_2)_2]$, which may also be prepared by the oxidation of $[W(CO)_6]$ with $[Et_2NC(S)S\text{-}]_2$.[89]

Treatment of sodium tungstate with NH_4SCN in aqueous HCl produced oxotungsten(V) species. The reaction of this solution with polysulfide afforded $[(S_4)(O)W(\mu\text{-}S)_2W(O)(S_2)]^{2-}$ and $[(S_4)(O)W(\mu\text{-}S)_2W(O)(S_4)]^{2-}$.[90]

Monooxotungsten(V) thiolates have been synthesized as models for the ESR-active species of tungstoenzymes or as analogues of molybdoenzymes. The square-pyramidal alkanedithiolate derivative, $(PPh_4)[WO(SCH_2CH_2S)_2]$ was produced by the ligand exchange reaction between $(PPh_4)[WO(SPh)_4]$[12,91] and ethanedithiol.[92] The substituted arenethiolate compound, $[(n\text{-}Pr)_4N][WO(S\text{-}2,3,5,6\text{-}Me_4C_6H_4)_4]$ showed similar geometry around the metal center.[93] Chelate compounds, $(Et_4N)[WO(bdt)_2]$[68] and $(Et_4N)[WO(S_2C_2Me_2)_2]$,[67] also exhibit similar structures.

The reaction of $(Et_4N)[W^{IV}(OPh)(S_2C_2Me_2)_2]$ with 2 equiv. of benzenethiol or benzeneselenol gave $(Et_4N)[W^V(QPh)_2(S_2C_2Me_2)_2]$ (Q = S, Se). When 1 equiv. of Ph_3CSH is added instead of benzenethiol, the dimeric compound, $(Et_4N)_2[W_2(\mu\text{-}S)_2(S_2C_2Me_2)_4]$ was obtained. This compound was also produced by the reaction of $[W(CO)_2(S_2C_2Me_2)_2]$ and S_2^{2-} or the oxidation of $[W^{IV}(S)(S_2C_2Me_2)_2]^{2-}$ by I_2.[67] For the synthesis of $(Et_4N)_2[W_2(\mu\text{-}S)_2(S_2C_2Ph_2)_4]$, tropylium hexafluorophosphate was used as oxidizing agent.[94] Reductive desulfurization of $[WS(S_2)(S_2CNEt_2)_2]$ using Me_3SiI afforded $[W^V{}_2(\mu\text{-}S_2)_2(S_2CNEt_2)_4]I(I_3)$.[95] $[W^V(S_2CNR_2)_4][TCNQ]$ was obtained from $[W^V(S_2CNR_2)_4]I$ and Li[TCNQ].[4]

$[W_2(OCH_2\text{-}t\text{-}Bu)_8]_n$ reacted with pyridine-*N*-oxide, elemental sulfur, selenium, and tri(*n*-butyl)phosphine telluride to give $[W_2(\mu\text{-}E)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_2(OCH_2\text{-}t\text{-}Bu)_6]$ (E = O, S, Se, Te).[96] The linear oxo-bridged complex, $[(WO\{S_2CN(CH_2Ph)_2\}_2)_2O]$ was obtained by the oxidation of $[W(CO)_3\{S_2CN(CH_2Ph)_2\}_2]$ under oxygen.[97] $Na_2[W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}edta)]$ (edta = ethylenediaminetetraacetate) was separated by chromatography of the reaction mixture of $(NH_4)_2[WOCl_5]$ and $Na_2(edta)$ in aqueous H_2S solution.[98] Asymmetric analogues, $[MoW(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}edta)]^{2-}$[99] and $[W_2(O)_2(\mu\text{-}O)(\mu\text{-}S)(\mu\text{-}R\text{-}pdta)]^{2-}$ (*R*-pdta = (*R*)-propylenediamine)[100] show similar structures.

The macrocyclic *meso*-octaethylporphyronogen-lithium derivative $[Et_8N_4Li_4(THF)_4]$ reacted with $WOCl_4$ to give $[(Et_8N_4)W^V{=}O\text{-}Li(THF)_4]$ and oxidized ligand, $[(Et_8N_4)(\Delta)Li_2(THF)_2]$.[101]

4.8.3.3 $[W(CN)_8]^{3-}$ salts

Because the $[W(CN)_8]^{3-}$ anion has nitrogen atoms on the surface, it retains the capability of coordination or interaction to neighboring metal ions. Recently, some adducts or clusters have been reported. The ternary adduct, $[Pt(en)_2]_3[W(CN)_8]_2$, exhibited electronic coupling in solution and in the solid state.[102] Combination with manganese(II) ions produced magnetically interesting $[Mn^{II}{}_6(H_2O)_9\{W^V(CN)_8\}_4\cdot 13H_2O]_n$[103] and $[Mn_9\{W(CN)_8\}_6\cdot 24C_2H_5OH]\cdot 12C_2H_5OH$.[104] The latter was high spin ($S = 39/2$).

4.8.4 THE CHEMISTRY OF W^{IV}

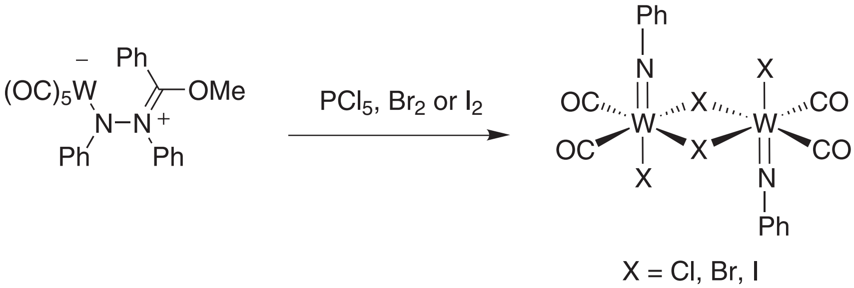
4.8.4.1 W^{IV} Halides and Derivatives

4.8.4.1.1 Complexes containing oxygen coordination

Oxidative addition of CO_2 to $[W^{II}Cl_2(PMePh_2)]$ yielded the oxotungsten(IV) carbonyl complex, $[W(O)Cl_2(CO)\ (PMePh_2)]$. Related reactions afforded imido and sulfido complexes.[105] A similar reaction to that described in Section 4.8.3.1 for the tungsten(V) complex was performed. Reduction of $[WCl_4(OAr\text{-}2,6\text{-}Ph_2)_2]$ by 2 equiv. of sodium amalgam in the presence of PMe_2Ph produced $[WCl_2(OAr\text{-}2,6\text{-}Ph_2)_2(PMe_2Ph)_2]$.[15] Reaction of $[WCl_4(PMe_2Ph)_2]$ with 2 equiv. of $TlOCH_2CF_3$ gave $[W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2]$.[106] *trans*-$[W(O)(F)(dppe)_2](BF_4)$ (dppe = $Ph_2PCH_2CH_2PPh_2$) was prepared by the reaction of *trans*-$W(PPh_3)_2Cl_4$ and dppe followed by addition of BF_4^- anion. The reaction of $[W(O)(F)(dppe)_2](BF_4)$ and NEt_4OH afforded *trans*-$[W(O)_2(dppe)_2]$. Addition of $HClO_4$, Cl^-, Br^-, NCS^-, CH_3I to *trans*-$[W(O)_2(dppe)_2]$ gave protonated, substituted, or methylated compounds, *trans*-$[W(O)(X)\ (dppe)_2]$ (X = Cl, Br, NCS, OCH_3).[107]

4.8.4.1.2 Imido, hydrazido amido, and the related complexes

The zwitterionic tungsten(0) complex $[(CO)_5WNPhNPhC(OMe)Ph]$[108] reacted with PCl_5, Br_2, or I_2 to give the tungsten(IV) imido complex $[(CO)_2W(NPh)_2(X)(\mu\text{-}X)]_2$ shown in Scheme 7.[109,110] The dimeric complex reacted with donor ligands such as pyridine, phosphine, and acetonitrile to give monomeric imido complexes. Di-imido-bridged tungsten(IV) complexes $[\{WCl_2(PMePh_2)_2(CO)\}_2(\mu\text{-}N\text{–}X\text{–}N)]$ (X = *p*-phenylene or the other rigid groups) were synthesized via oxidative addition of diisocyanates (OCN–X–NCO) to two equiv. of $[WCl_2(PMePh_2)]$.[111] An analogous reaction using $Ar'P{=}C{=}O$ ($Ar' = 2,4,6\text{-}t\text{-}Bu_3C_6H_2$) was effective for the synthesis of the phosphinidene complex. $[WCl_2(PMe_3)_4]$ reacted with Ar'PCO to give $[W(PAr')(CO)Cl_2(PMe_3)]$ where the W—P—C bond is essentially linear (168.2(2)°).[112]

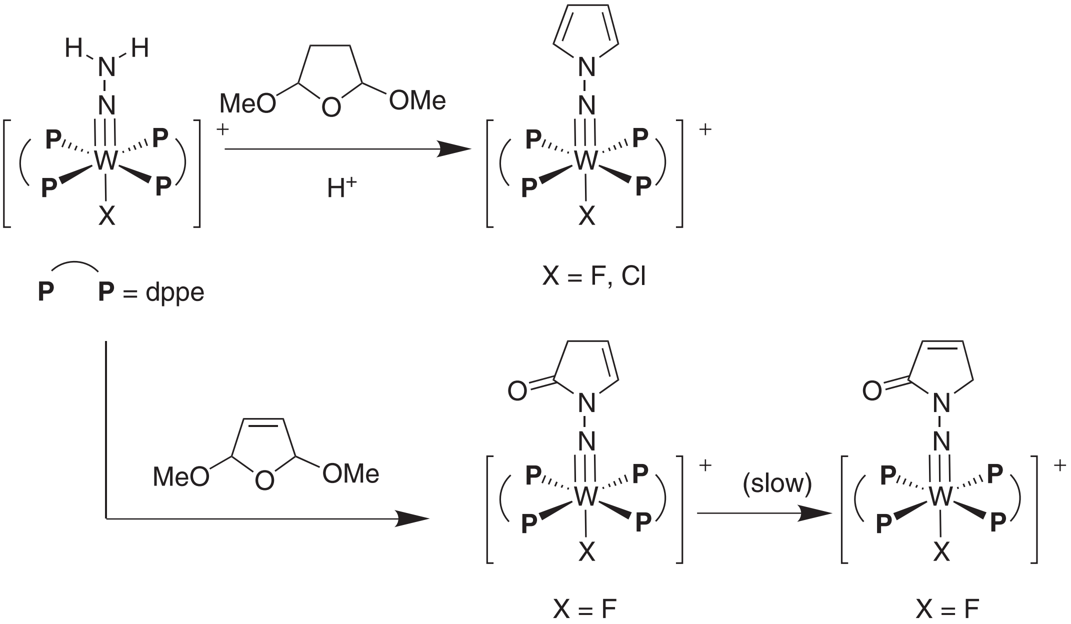


Scheme 7

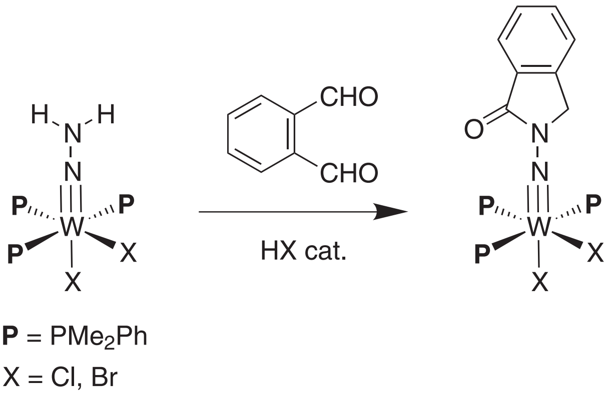
Hydrazido tungsten(IV) derivatives have been reported as intermediates in the conversion of dinitrogen to ammonia. Substituted hydrazido compounds have been isolated and characterized crystallographically. [$W^{IV}Cl_2(NNPh_2)(PMe_2Ph)_3$] was synthesized by Na/Hg-reduction of [$W^{VI}(NNPh_2)Cl_4$] prepared from WCl_6 and $Ph_2NNH_2{\cdot}HCl$. The resulting hydrazido complex reacted with HCl or water to yield ammonia and diphenylamine.[113]

The reaction of *trans*-[$W(N_2)_2$(dtpe)] (dtpe = 1,2-bis(di-*p*-tolylphosphino)ethane) with one equiv. of 1,3-dibromopropane yielded the azetidinylimido complex [$WBr(NNC_3H_6)$(dtpe)] featuring a 4-membered $N(CH_2)_3$ ring.[114]

The acid-catalyzed reaction of the hydrazido(2-) complex [$WF(NHNH_2)(dpp)_2$](BF_4) (dppe = $Ph_2PCH_2CH_2PPh_2$; readily derived from *trans*-[$W(N_2)_2(dppe)_2$] by protonation with HF) condensed with 2,5-dimethoxytetrahydrofuran to afford the pyrrolylimido complex shown in Scheme 8.[115,116] When the complex was reacted with 2,5-dimethoxy-2,5-dihydrofuran under similar conditions, the kinetic product formed initially gradually isomerized to the thermodynamically more stable compound shown in Scheme 8.[117] Related reactions of *cis*,*mer*-[$WX_2(NHNH_2)(PMe_2Ph)_3$] (X = Cl, Br) with phthalaldehyde gave the (phthalimidin-2-yl)imido complexes shown in Scheme 9. Treatment of [$W(N_2)_2(PMe_2Ph)_4$] with HCl under CO afforded [$WCl_2(NNH_2)(CO)(PMe_2Ph)_2$]. This complex reacted with 2,4,6-trimethylpyrylium tetrafluoroborate to give the (1-pyridinio)imino complex [$WCl_2(NNC_5H_2Me_3)(CO)(PMe_2Ph)_2$]($BF_4$) in the presence of HCl.[118,119] Analogous derivatives were synthesized similarly.



Scheme 8



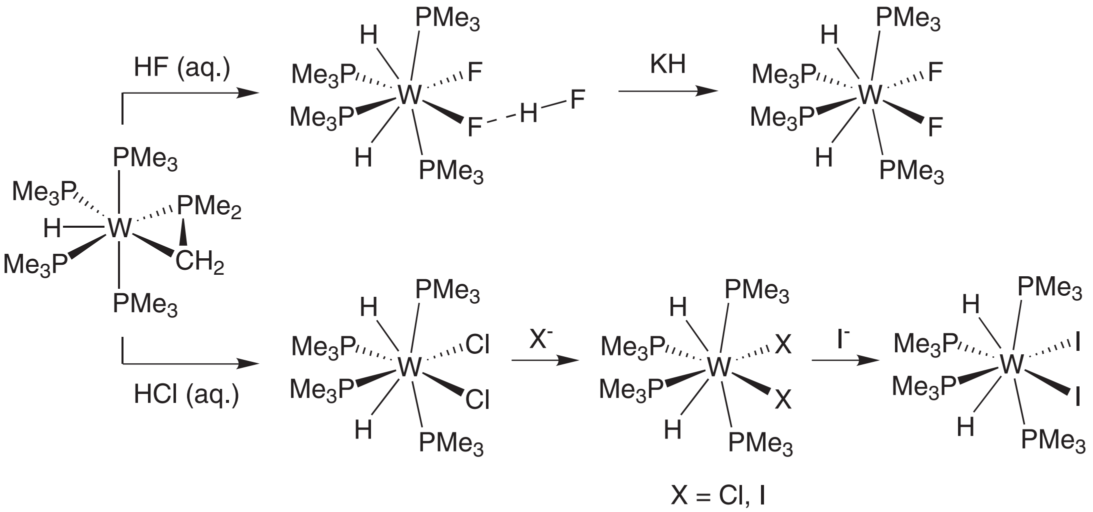
Scheme 9

The silylimido complex [W(NSiMe$_3$)Cl$_2$(PMe$_3$)$_3$] was prepared by the reaction of [MCl$_2$(PMe$_3$)$_4$] and trimethylsilyl azide.[30] Treatment with PCl$_2$R$_3$ (R$_3$ = Me$_3$, MePh$_2$) yielded the phosphoamininato compound [W(NPR$_3$)Cl$_2$(PMe$_3$)$_3$]Cl. The complex is diamagnetic with an electronic structure analogous to that of the closely related tungsten(IV) imido complex [WCl$_2$(NR)(PR$_3$)$_3$].[24]

Reaction of the tetradentate triamidoamine ligand (C$_6$F$_5$NHCH$_2$CH$_2$)$_3$N with [WCl$_4$(Et$_2$S)$_2$] gave a distorted trigonalbipyramidal compound [W^{IV}Cl{(C$_6$F$_5$NCH$_2$CH$_2$)$_3$N}].[120]

4.8.4.1.3 Hydride complexes

Some crystallographically characterized hydrido tungsten(IV) complexes have been reported. Reduction of WCl$_6$ by sodium–potassium alloy in PMe$_3$ gave [W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)H]. This complex was treated with aqueous HF to afford [W(PMe$_3$)$_4$H$_2$(OH$_2$)F]F.[121,122] The structure of this compound has been corrected to W(PMe$_3$)$_4$H$_2$F$_2$(H$_2$O) or W(PMe$_3$)$_4$H$_2$F$_2$(FHF).[123] A similar procedure gave eight-coordinate [W(PMe$_3$)$_4$H$_2$Cl$_2$]. Anion exchange using LiBr and NaI provided [W(PMe$_3$)$_4$H$_2$Br$_2$] and [W(PMe$_3$)$_4$H$_2$I$_2$]. The reaction is shown in Scheme 10.[123,124]



Scheme 10

4.8.4.2 W^{IV} Chalcogenides and Derivatives

4.8.4.2.1 Complexes containing only chalcogen

Tungsten(VI) hexachloride reacted readily with polytelluride anions (Te_3^{2-}, Te_4^{2-}, Te_5^{2-}) in DMF to form $[W^{IV}O(\eta^2\text{-}Te_4)_2]^{2-}$ in good yield. Use of WCl_4 or $WOCl_4$ instead of WCl_6 as the starting material gave the same product in lower yield.[125]

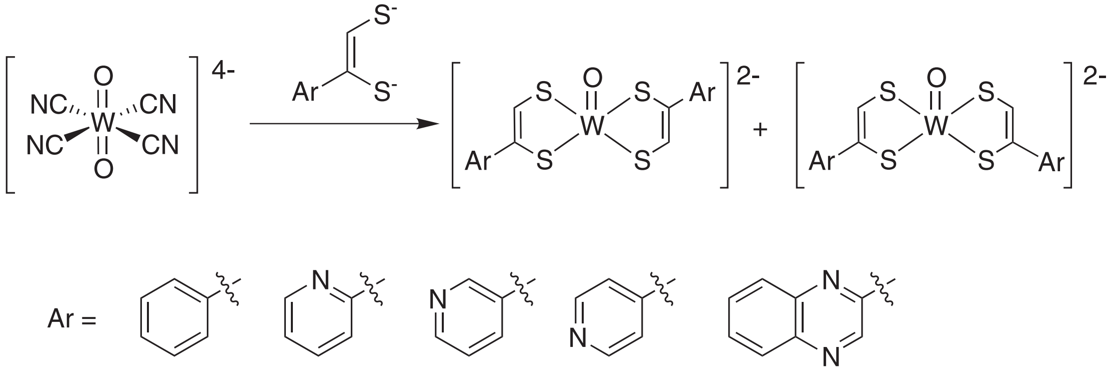
Monomeric polyselenide anions $[WQ(Se_4)_2]^{2-}$ with Q = Se, S, O were synthesized by the reaction of $[WSe_4]^{2-}$ and Se_8, SeS_2, or $Se_4(NC_5H_{10})_2$, respectively. The crystal structure of $[WS(Se_4)_2]$ was determined by X-ray analysis. The starting material $[MSe_4]^{2-}$ was prepared from WO_4^{2-} and bis(dimethyloctylsilyl) selenide.[126]

$(Ph_4P)_2[WSe_4]$ and phosphorus selenide glass, "P_2Se_4", reacted readily to give the $[(PSe_2)W(Se)(PSe_4)]^{2-}$ anion containing terminal selenide, tetrahedral PSe_4^{3-} and heteroallylic PSe^{2-}, as shown in Figure 16.[127] Oxidative decarbonylation of $[W(CO)_6]$ by As_4Se_4 and K_2Se_3 afforded $[W(AsSe_5)_2]^{2-}$ as shown in Figure 16, which was also prepared from $[W(CO)_2(As_2Se_3)]^{2-}$.[128] $[WSe_9]^{2-}$ or $[W(Se)(\eta^2\text{-}Se_4)_2]^{2-}$ reacted with dimethyl acetylenedicarboxylate to yield the tris(diselenene) complex $[W\{Se_2C_2(COOCH_3)_2\}_3]^{2-}$.[87]

Tetrathiapentalenedione $C_2S_4(CO)_2$ reacted with $[WS_4]^{2-}$ to give $[W(S_2C_2S_2CO)_3]^{2-}$.[129] The tris(dithiolene) complex $[W(S_2C_2Me_2)_3]^{2-}$ was prepared by reduction of $[W(S_2C_2Me_2)_3]$ by Et_4NBH_4.[130]

Dicarbonyl bis(dithiolene) compounds $[W^{IV}(CO)_2(S_2C_2R)_2]$ (R = Me, Ph) reacted with OH^-, S^{2-}, or Se^{2-} to yield the terminal chalcogenides $[W^{IV}Q(S_2C_2R_2)_2]^{2-}$ (Q = O, S, Se).[94]

Bis(dithiolene) and bis(benzenedithiolato) tungsten(IV) complexes have been synthesized for comparison with the active sites of tungstoenzymes. The oxotungsten(IV) complexes $[WO(bdt)_2]^{2-}$ (bdt = 1,2-benzenedithiolato) was synthesized by a simple borohydride reduction of $[W^VO(bdt)_2]^-$.[68] This compound readily reacted with trimethylamine-*N*-oxide to give $[W^{VI}O_2(bdt)_2]^{2-}$. The analogous complex $[W^{IV}O(mnt)_2]^{2-}$ was prepared by the reduction of $[W^{VI}O(\eta^2\text{-}S_2)(mnt)_2]^{2-}$.[69] $[W^{IV}O(sdt)_2]^{2-}$ (sdt = styrenedithiolato) and derivatives are synthesized by the reaction of $K_3Na[WO_2(CN)_4]\cdot 6H_2O$ and the corresponding dithiolate as shown in Scheme 11. The products are mixtures of *cis*- and *trans*-isomers, as established by ^1H NMR spectroscopy, but only the *cis*-isomer was crystallized and characterized crystallographically.[131] Treatment of $[WO(bdt)_2]^{2-}$ with 1 equiv. of R_2Bu^tSiCl (R = Ph, Me) afforded the desoxo compound $[W^{IV}(OSiR_2Bu^t)(bdt)_2]^-$.[12,72]



Scheme 11

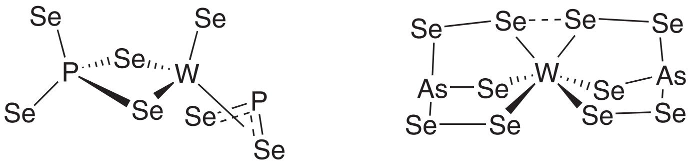
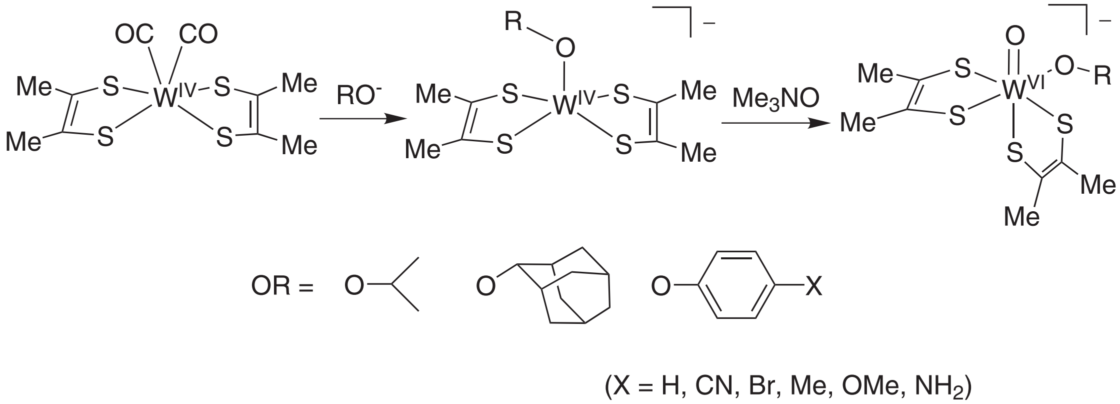


Figure 16 Schematic drawing $[(PSe_2)W(Se)(PSe_4)]^{2-}$ and $[W(AsSe_5)_2]^{2-}$.

Desoxo tungsten(IV) compounds have been reported with an additional phenolate, thiolate, or selenolate ligand related to serine, cysteine, or selenocysteine in the enzyme active sites. The reaction of [W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$] with PhO$^-$ gave [W(OPh)(S$_2$C$_2$Me$_2$)$_2$]$^-$ but with ArQ$^-$ (Ar = Ph, C$_6$H$_2$-2,4,6-Pr$^i_3$; Q = S, Se) gave [W(CO)(QAr)(S$_2$C$_2$Me$_2$)$_2$]$^-$.[132] Analogous reactions were effective for alkoxide and substituted phenols to give [W^{IV}O(OR)(S$_2$C$_2$Me$_2$)$_2$] (R = Pr^i, 2-adamantyl, *p*-C$_6$H$_4$X where X = CN, Br, Me, OMe, NH$_2$). The desoxo tungsten(IV) complexes were oxidized to the corresponding oxotungsten(VI) complexes by trimethylamine-*N*-oxide as shown in Scheme 12.[73] Treatment of [W(CO)$_2$(S$_2$C$_2$Me$_2$)$_2$] with (Et$_4$N)(O$_2$CPh) afforded the noncarbonyl compound (Et$_4$N)[W(O$_2$CPh)(S$_2$C$_2$Me$_2$)$_2$].[67,132]



Scheme 12

The monomeric tungsten(IV) phenoxide and thiolate complexes [W(O-2,6-C$_6$H$_3$R$_2$)]$_4$] (R = Me, *i*-Pr) and [W(S-*t*-Bu)$_4$] were produced by the reaction of [WCl$_4$(Et$_2$S)$_2$] and the corresponding phenolate or thiolate anion.[133,134] The phenolate complexes exhibited nearly square planar geometry.

The trinuclear bioxocapped cluster [W$^{IV}_3$(μ-O)$_2$(μ-OCOR)$_6$(H$_2$O)$_3$]$^{2+}$ was prepared from W(CO)$_6$ and carboxylic acid. The elution using cation-exchange column afforded hydrogen oxide (H$_3$O$_2^-$) bridging dimeric compound [{W$^{IV}_3$(μ-O)$_2$(μ-OCOEt)$_6$(H$_2$O)$_2$}$_2$(H$_3$O$_2$)]Br$_3$.[135] In the case of the benzoate compound, the cluster showed stability under strongly acidic conditions and nitration on the benzene ring was achieved with maintenance of the trinuclear unit.[136] Mixed metal (W$_2$Mo and WMo$_2$) derivatives were also prepared by careful and assiduous separation.[137]

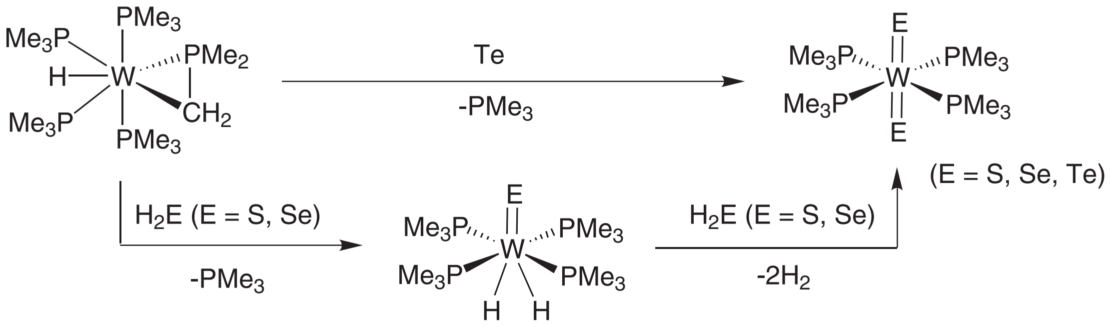
4.8.4.2.2 Complexes containing nitrogen groups

The terminal tellurido tungsten(IV) complex [W(PMe$_3$)$_2$(Te)$_2$] was synthesized by the reaction of [W(PMe$_3$)$_4$(η^2-CH$_2$PMe$_2$)$_2$(H)] and elemental tellurium while the analogous reaction with elemental sulfur resulted in complete decomposition of the complex. For synthesis of the sulfido and selenido derivatives, H$_2$E (E = S, Se) was used instead by elemental Te as shown in Scheme 13. The reaction proceeded via intermediate [W(PMe)$_4$(E)(H$_2$)], which was characterized crystallographically in the case of E = Se.[28,138] When pentane was used as the solvent, intermediate [W(PMe$_3$)$_4$(H)$_2$(SH)$_2$] was isolated and characterized by IR spectra.[61] The η^2-ditelluride derivative [W(PMe$_3$)$_4$(η^2-Te$_2$)$_2$(H)$_2$] was synthesized by the reaction of [W(PMe$_3$)$_4$(H)$_2$] with elemental tellurium. The Te—Te bond in the complex was cleaved oxidatively to give the terminal tellurido compound [W(Te)$_2$(PMe$_3$)$_4$].[139]

The terminal sulfido complex [{HB(Me$_2$pz)$_3$}W(S)(S$_2$CNEt$_2$)] was obtained by the oxidative decarbonylation of (NEt$_4$)[{HB(Me$_2$pz)$_3$}W(CO)$_3$] by tetraethylthiuram disulfide followed by separation from by-product [W$_2$(μ-S)(S$_2$CNEt$_2$)$_4$].[140]

The bis(thio)tungsten(VI) complex [{HB(Me$_2$pz)$_3$}WS$_2$(OPh)] was combined with dicarbomethylacetylene to produce [{HB(Me$_2$pz)$_3$}W(OPh){S$_2$C$_2$(CO$_2$Me)$_2$}].[115] The analogous complex [WS$_2$(OSiPh$_3$)$_2$(Me$_4$phen)], which is illustrated in Figure 11, reacted readily with dicarbomethylacetylene or diphenylacetylene to afford [W(OSiPh$_3$)$_2$(Me$_4$phen)(S$_2$C$_2$R$_2$)] (R = CO$_2$Me or Ph) with dithiolene ring closure.[53]

The reaction of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] and *tert*-butanethiol in THF gave the dinuclear compound [{W(SBu^t)$_2$(PMe$_2$Ph)}$_2$(μ-S)$_2$].[66]



Scheme 13

The tungsten(VI) complex $[WO(bdt)_2Cl]^-$ was reducible by $P(OEt)_3$ to afford the tungsten(IV) complex $[W(bdt)_2\{P(OEt)_3\}_2]$.[12]

The S,N_3-tetradentate ligand $N(CH_2CH_2SH)_3$ reacted with $[WI_2(CO)_3(MeCN)]$ in the presence of triethylamine to give the dinuclear complex $[\{W[N(CH_2CH_2S)]\}_2\{\mu\text{-}SCH_2CH_2N(CH_2CH_2SH)_2\}_2]$.[141] The S,$P_2$-tridentate ligand $PhP(2\text{-}C_6H_4SH)_2$ reacted with $[WCl(NNMePh)_2(PPh_3)_2](BPh_4)$ to give $[W\{PhP(2\text{-}C_6H_4S)_2\}_2(NNMePh)]$.[142]

The phosphido-capped tritungsten(IV) alkoxide $[W_3(\mu^3\text{-}P)(\mu\text{-}OCH_2\text{-}t\text{-}Bu)_3(OCH_2\text{-}t\text{-}Bu)_3]$ was prepared by the reaction between $[W_2(OCH_2\text{-}t\text{-}Bu)_6(HNMe_2)_2]$ and P_4 in hydrocarbon solvents.[143] This reaction gave another product $[(HNMe_2)(t\text{-}BuCH_2O)W(\eta^3\text{-}P_3)]$, which had been characterized previously.[144]

The reaction of *trans*-$[W(N_2)_2(dpe)]$ (dpe = 1,2-bis(diphenylphosphino)ethane) with $HFeCo_3(CO)_{12}$ in methanol afforded methoxide complex *trans*-$[W(OCH_3)(NNH_2)(dpe)_2][FeCo_3(CO)_{12}]$.[145] The dinitrogen complex *cis*-$[W(N_2)_2(dpe)]$ reacted with acetylacetone in methanol to give an alkenyldiazenido complex *mer*-$[W(acac)(NNCMeCHCOMe)(PMe_2Ph)_3]$, which when treated with gaseous HBr in CH_2Cl_2 yielded *mer*-$[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)_3]Br$, as shown in Figure 17.[146] Treatment of *cis*-$[W(N_2)_2(dpe)]$ with HOTf afforded *trans*-$[W(OTf)(NNH_2)(PMe_2Ph)_4](OTf)$, which was also prepared from the reaction of *cis*-$[W(N_2)_2(dpe)]$ and 2 equiv. of *trans*-$[RuCl(\eta^2\text{-}H_2)(dppe)_2](OTf)$ under an atmosphere of H_2.[147]

The cyclopentoxyditungsten compound $[W_2(\mu\text{-}H)(\mu\text{-}O\text{-}c\text{-}C_5H_9)_2(O\text{-}c\text{-}C_5H_9)_5(NHMe_2)]$ was prepared by extended reaction of $[W_2(O\text{-}c\text{-}C_5H_9)_6(NHMe_2)_2]$ with cyclopentanol in hexane. $[W_2(O\text{-}c\text{-}C_5H_9)_6(NHMe_2)_2]$ was obtained by interaction of $W_2(NMe_2)_6$ and excess cyclopentanol for a short time.[148] Controlled potential electrolysis of $[WH_2(\eta^2\text{-}OCOMe)(dppe)]^+$ containing one equiv. of MeCOOH afforded $[WH_3(\eta^1\text{-}OCOMe)(dppe)]$ in excellent yield.[149]

4.8.4.2.3 *Complexes having a W—C bond*

Treatment of *trans*-$[W(E)_2(PMe_3)_4]$ (E = S, Se) with RNC gave *trans*-$[W(PMe_3)_2(RNR)(E)_2]$ whereas the reaction between *trans*-$[W(E)_2(PMe_3)_4]$ (E = S, Se) and Bu^tNC gave $[W(PMe_3)(CNBu^t)_4(\eta^2\text{-}Te_2)]$ by reductive coupling of the two tellurido ligands as shown in Scheme 14.[28,61]

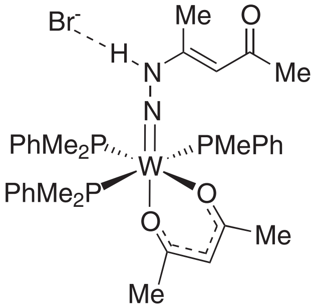
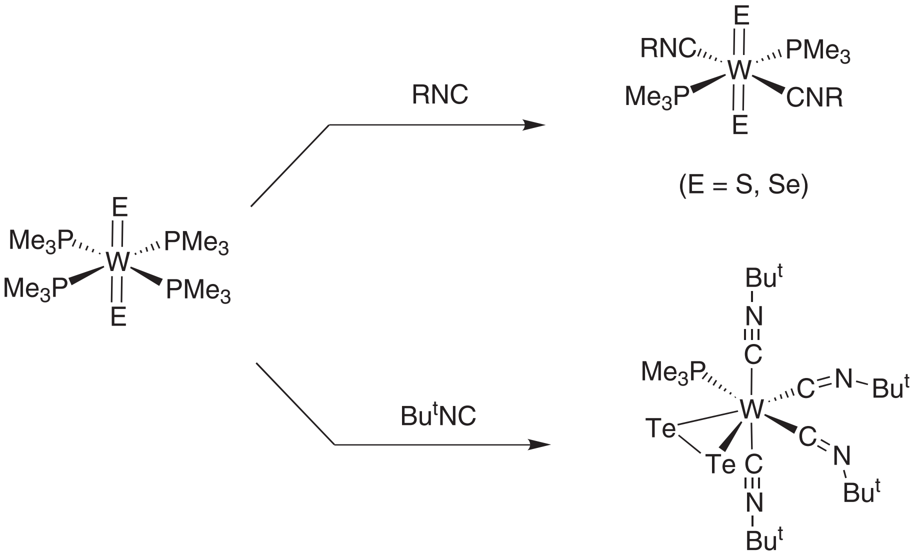


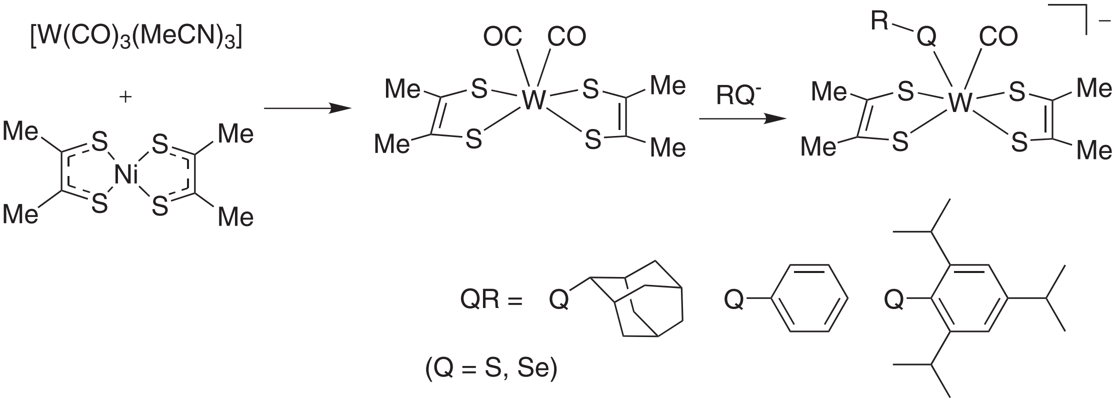
Figure 17 Schematic drawing of *mer*-$[W(acac)(NNHCMeCHCOMe)(PMe_2Ph)_3]Br$.



Scheme 14

The reaction of $[W(CO)_6]$ and $As_4Se_6{}^{2-}$ generated $[W(CO)_2(As_3Se_3)_2]^{2-}$ in reasonable yield. The molecular structure is shown in Figure 18. Addition of red selenium converted this complex to $[W(AsSe_5)_2]^{2-}$.[128]

$[W(CO)_2(S_2C_2R_2)_2]$ (R = Me, Ph)[150] has been prepared by an improved method, reaction between $[W(CO)_3(MeCN)_3]$ and $[Ni(S_2C_2R_2)_2]$ in 1:2 proportion with formation of $[Ni^{II}(S_2C_2R_2)]$ as by-product (Scheme 15).[94] $[W(CO)(QAr)(S_2C_2Me_2)_2]^-$ (R = Ph, C_6H_2-2,4,6-$Pr^i{}_3$; Q = S, Se) were prepared by the reaction between $[W(CO)_2(S_2C_2Me_2)_2]$ and ArQ^-, as described in Section 4.8.4.2.1.[132] Adamantane-2-thiol and -selenol derivatives showed analogous reactions (Scheme 15)[67,132] Reduction of the tungsten(VI) complex $[WO(bdt)_2Cl]^-$ by $P(OEt)_3$ in the presence of Bu^{t}CN yielded the tungsten (IV) complex $[W(bdt)_2(Bu^tCN)_2]$.[12]



Scheme 15

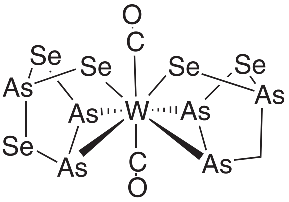


Figure 18 Molecular structure of $[W(CO)_2(As_3Se_3)_2]^{2-}$ anion.

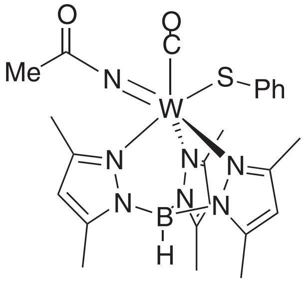


Figure 19 [LW^{IV}{NC(O)Me}(SPh)(CO)] (L = hydrotris(3,5-dimethylpyrazol-1-yl)borate).

Air oxidation of [LW$(CO)_3$I] (L = hydrotris(3,5-dimethylpyrazol-1-yl)borate) in toluene under reflux conditions yielded [LWO(CO)I].[151] The reaction of the κ^2N,C nitrile compound [LW^{II}I (MeCN)(CO)][152] with pyridine *N*-oxide afforded the acylimino tungsten(IV) complex [LW{NC(O)-Me}I(CO)] while [LW(S)I(CO)] was generated in high yield by sulfur atom transfer to [LWI (η^2-MeCN)(CO)] using propylene sufide.[153] Sodium benzenethiolate reacted with [LW{NC(O)-Me}I(CO)] to afford [LW^{IV}{NC(O)Me}(SPh)(CO)] as shown in Figure 19.[154] The sulfide derivative crystallized as the dithiophosphinate derivative [LW^{IV}(S)(S_2PPh_2-*S*)(CO)], which was prepared from [LW^{II}(η^2-MeCN)(S_2PPh_2-*S*)(CO)] and propylene sulfide. The analogous [LW^{IV}(O)(S_2PPh_2-*S*)-(CO)] was obtained via the oxidation of [LW^{II}(S_2PPh_2-*S*)$(CO)_2$] pyridine *N*-oxide.[153]

The reaction of [$WOCl_2(PMe_3)_2$] with potassium *O*-alkyl xanthates, KS_2COR (R = ME, Et, *i*-Pr) in tetrahydrofuran gave [WO{$S_2C(PMe_3)OR$-*S,S'*}(S_2COR-*S,S',C*)]. The zwitterionic ligands, $ROC^-(^+PMe_3)S^-{}_2$ are formed by nucleophilic attack of triphenylphosphine on the carbon atom of the CS_2 moiety. Two isomers were found in solution (Figure 20) and the structure of isomer A was determined for the molybdenum analog (R = *i*-Pr).[155]

Reduction of the 2,6-diphenylphenoxide complex [$W(OC_6H_3\text{-}2,6\text{-}Ph_2)_2Cl_4$] by sodium amalgam in hydrocarbon solvent gave the tungsten(IV) complex [$W(OC_6H_3Ph\text{-}C_6H_4$-*O,C*)$(PMePh_2)_2$] featuring two cyclometallated 2,6-diphenylphenoxide ligands with mutually *trans* oxygen atoms and *cis* $PMePh_2$ ligands.[156] Treatment of this compound with pyridine afforded isostructural [$W(OC_6H_3Ph\text{-}C_6H_4$-*O,C*)$(py)_2$] by replacement of $PMePh_2$.[157]

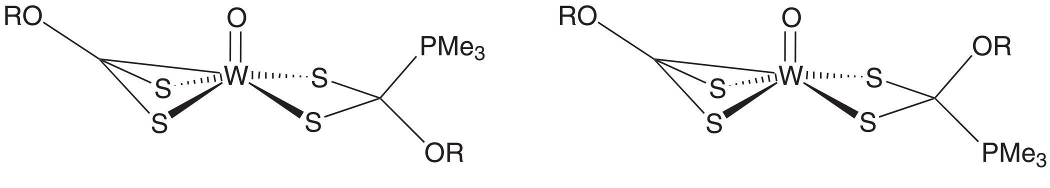
The oxocyano tungsten(IV) complex $(PPh_4)_2[WO(CN)_3(ensal)]$ (ensal = *N*-salicylideneethylenediaminonato) resulted from reaction between $K_3Na[W(CN)_3O_2]\cdot 6H_2O$, salicylaldehyde and ethylenediamine.[158]

4.8.4.3 W^{IV} Compounds Lacking Coordination of Halogen and Chalcogen

4.8.4.3.1 Complexes containing nitrogen and phosphorus

[W(NPh){*o*-$(Me_3SiN)_2C_6H_4$}(*p*-$CH_3C_5H_4N)_2$] was prepared by the reaction of [W(NPh)(η^4-C_6H_5-*n*-Pr){*o*-$(Me_3SiN)_2C_6H_4$}] and 4-picoline. The reduction of [W(NPh)$Cl_2(Me_3SiN)_2C_6H_4$}] by sodium in the presence of 4-picoline gave the same product. This square pyramidal 5-coordinate compound reacted with CO in toluene to form octahedral 6-coordinate *trans*-[W(NPh) {*o*-$(Me_3SiN)_2C_6H_4$}(*p*-$CH_3C_5H_4N)_2$(CO)].[159]

Treatment of [$W(PMe_3)_3H_6$] with Bu^{n}Li, NaH or KH gave [$W(PMe_3)_3H_5M$] (M = Li, Na (15-crown-5) or K(18-crown-6)). The tetranuclear compound [$W(PMe_3)_3H_5Li$}]$_4$ (with bridging by



A **B**

Figure 20 Two isomers of [WO{$S_2C(PMe_3)OR$-*S,S'*}(S_2COR-*S,S',C*)] (R = ME, Et, *i*-Pr).

lithium ion) and the mononuclear compounds [Na(15-crown-5)][W(PMe$_3$)H$_5$] and [K(18-crown-6)][W(PMe$_3$)H$_5$] were characterized crystallographically. The hydride ligands in the latter salts interacted weakly with K$^+$ and Na$^+$ ions in the crystal.[160,161]

4.8.4.3.2 CO complexes

The dicarbonylamidotungsten(II) complexes [Tp′(CO)$_2$W(NHR)] (Tp′ = hydrotris(3,5-dimethylpyrazoyl)borate; R = Bu^t, Ph) were oxidized by I$_2$ or trityl hexafluorophosphate to the cationic nitrene tungsten(IV) complex [Tp′(CO)$_2$W(NR)]$^+$.[162] The related carbene compound [Tp′(CO)$_2$W{=C(Ph)Me}]$^+$ with β-agostic interaction has been reported.[163] Treatment of the amido complex [Tp′(CO)$_2$W^{II}{N(H)Ts}] (Ts = tosyl) with AgOTf or I$_2$ yielded the tosylnitrene complexes [Tp′(CO)$_2$W^{IV}(NTs)][X] (X = OTf, I$_3$). These reacted with trimethylphosphine to give the phosphinimine TsN=PMe$_3$, [Tp′(CO)$_2$W(PMe$_3$)$_2$]X and [Tp′(CO)$_2$(PMe$_3$)W(NTs)]X.[164]

4.8.4.3.3 [W(CN)$_8$]$^{4-}$ salts

[W^{IV}(CN)$_8$]$^{4-}$ is used as a building block for the construction of oligomeric or polymeric structure. Polymeric [(MeSn)$_4$W(CN)$_8$] was formed in a straightforward way by the reaction of K[W(CN$_8$)] and 4 equiv. of Me$_3$SnCl.[165] The hexanuclear complex [{Mn(bpy)$_2$}$_2$ (μ-NC)$_2${W(CN)$_6$}$_2$(μ-CN)$_2${Mn(bpy)$_2$}$_2$] was prepared by the addition of [Mn(bpy)$_2$Cl$_2$]·2H$_2$O·EtOH to K$_4$[W(CN)$_8$]·2H$_2$O in an aqueous medium.[166]

4.8.5 THE CHEMISTRY OF W^{III}

Many tungsten(III) complexes have been reported as W–W triple-bonded derivatives, which are described in Chapter 4.9. The other compounds are discussed here, including dimeric tungsten (III) complexes containing bridging ligands are described.

4.8.5.1 W^{III} Halides and Derivatives

Tungsten(III) fluoride K$_3$WF$_6$ was obtained as a mixture with K$_3$WF$_6$ and K$_2$WF$_7$ by the reduction of K$_3$WF$_8$ with tungsten metal.[84]

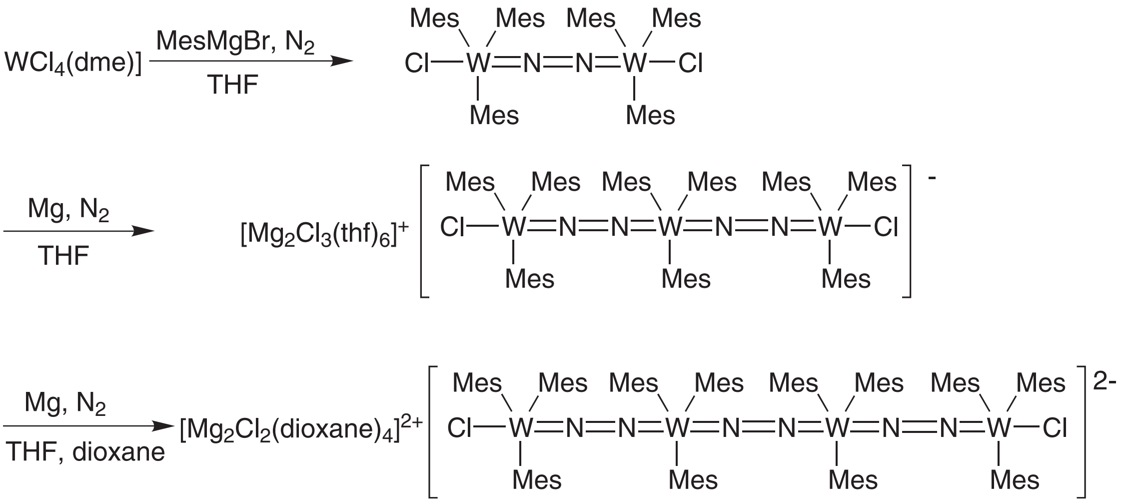
The monomeric tungsten(III) anion [(HBpz$_3$)WCl$_3$]$^-$ was prepared by chemical (hydrazine) or electrochemical reduction of [(HBpz$_3$)W^{IV}Cl$_3$] (prepared from (Et$_4$N)[(HBpz$_3$)W(CO)$_3$] and thionyl chloride). A mixed cation salt (NH$_4$)$_{0.5}$(Et$_4$N)$_{0.5}$[HBpz$_3$)WCl$_3$] was isolated and the structure was determined.[167]

Halogen-bridged dinuclear tungsten(III) complexes containing the PMe$_2$Ph ligand have been isolated. The reduction of WCl$_4$ by 1 equiv. of reducing agent (sodium amalgam or NaB(C$_2$H$_5$)$_3$H) in toluene followed by the addition of excess PMe$_2$Ph produced [(PMe$_2$Ph)$_2$Cl$_2$W(μ-Cl)$_2$WCl$_2$(PMe$_2$Ph)$_2$]. When 1 equiv. of reducing agent and 1.5 equiv. of PMe$_2$Ph were used, [(PMe$_2$Ph)$_2$ClW(μ-Cl)$_3$WCl$_2$(PMe$_2$Ph)] was obtained. The analogous bromide complex [(PMe$_2$Ph)$_2$BrW(μ-Br)$_3$WBr$_2$(PMe$_2$Ph)] was obtained by the reduction of WBr$_5$ with 2 equiv. of reducing agent followed by 1.5 equiv. of PMe$_2$Ph.[168]

Monomeric [WCl$_3$(PMe$_2$Ph)$_3$] was synthesized by the comproportionation reaction between equimolar WCl$_4$L$_2$ (L = PMe$_2$Ph) and *trans*-WCl$_2$L$_4$. The stable *mer*-isomer was obtained as major product with the *fac*-isomer being isolated from the mother liquor as minor product. The *mer* to *fac* isomerization was catalyzed by WCl$_4$L$_2$ but not by WCl$_2$L$_4$. Photolysis of a mixture of [WCl$_3$(PMe$_2$Ph)]$_2$ in the presence of excess PMe$_2$Ph completely converted the dimer to *mer*-[WCl$_3$(PMe$_2$Ph)$_3$]. The reverse conversion was not successful.[169]

The reaction of [W(N$_2$)(dpe)$_2$] (dpe = 1,2-bis(diphenylphosphino)ethane) with HFeCo(CO)$_{12}$ in water–tetrahydrofuran formed [W(OH)(NNH$_2$)(dpe)$_2$][FeCo$_3$(CO)$_{12}$]. The anion could be exchanged by suitable anions to give the hydroxo compounds [W(OH)(NNH$_2$)(dpe)$_2$](X) (X = BPh$_4$, PF$_6$, BF$_4$). When the reaction between [W(N$_2$)(dpe)$_2$] and HFeCo(CO)$_{12}$ was performed in dichloromethane, [WCl$_2$(dpe)][FeCo$_3$(CO)$_{12}$], lacking an hydrazido ligand, was obtained. Anion-exchange yielded [W^{III}Cl$_2$(dpe)$_2$]BF$_4$·1/3(CH$_2$Cl$_2$) whose structure was determined by X-ray analysis. The condensation reaction of $[W(OH)(NNH_2)(dpe)_2]PF_6$ and acetone in the presence of a catalytic amount of $HFeCo(CO)_{12}$ proceeded readily to form $[W(OH)(NNCMe_2)(dpe)_2]PF_6$.[170]

The alkylation of $[WCl_4(dme)]$ (DME = 1,2-dimethoxyethane) using MesMgBr (Mes = 2,4,6-$(CH_3)_3C_6H_3$) under nitrogen atmosphere resulted in the intermediate formation of a red solid, which was then extracted with toluene to give a green crystalline material that was characterized as the dimeric compound shown in Scheme 16. Stepwise elongation using controlled stoichiometry successfully produced the tetranuclear compound.[171]



Scheme 16

The tungsten(II) complex $[WCl_2(PMe_3)_4]$ reacted with $SPMe_3$ at 80 °C to give dinuclear complex $[W_2(\mu\text{-}S)(\mu\text{-}Cl)Cl_3(PMe_3)_5]$, which was also obtained by the reaction between $[WCl_2(PMe_3)_4]$ and $[W(S)Cl_2(PMe_3)_2]$.[172]

4.8.5.2 W^{III} Thiolates and Derivatives

The tungsten(III) thiolate compound $(Et_4N)[W^{III}(CO)_2(S_2C_2Me_2)_2]$ was synthesized by the redox reaction between $(Et_4N)_2[W^{IV}(CO)_2(S_2C_2Me_2)_2]$ and $[W^{II}(CO)_2(S_2C_2Me_2)_2]$. This reaction occurred instantly and the structure of the product was determined by X-ray analysis.[130]

4.8.6 THE CHEMISTRY OF W^{II}

4.8.6.1 W^{II} Complexes Lacking CO Ligands

4.8.6.1.1 NO^+ complexes

Synthesis of the formally 16 e^- species W(NO)LXY (L = tris(3,5-dimethylpyrazolyl)borate; X, Y = monoanionic ligand) was reviewed in 1983.[173] Diastereoisomers of $[W(NO)LCl(G_f)]$ (HG_f = 1,3:5,6-di-*O*-isopropylidene-D-glucofuranase) were generated.[174] The thermodynamically stable isomer exhibits S absolute configuration at the W atom.

The reaction of $[W(NO)LCl_2]$ (L = hydrotris(3,5-dimethylpyrazol-1-yl) with excess 2-aminopyridine in the presence of NaH yielded $[W(NO)L(2\text{-}NHC_5H_4N)_2]$ while, due to the difference in reduction potential, similar reactions with molybdenum derivatives afforded the paramagnetic complex $[Mo(NO)L(2\text{-}NHC_5H_4N)_2]^+$.[175] $[W(SBu^t)_3(NO)(py)]$ was synthesized by the reaction of $[W(OBu^t)_3(NO)(py)]$ and excess Bu^tSH in toluene. The molecular structure showed trigonal bipyramidal geometry with py and NO^+ ligands in the axial positions. The linear W—NO bond indicated NO^+ coordination and an oxidation state of +2. The NO stretching mode ν(NO) was found at 1,604 cm^{-1}.[176] [W(NO)LI$_2$] reacted with NEt$_3$ and 1,4-dihydroxybenzene and the resulting product separated by column chromatography to give *anti,syn*-[W(NO)L(1,4-O$_2$C$_6$H$_4$)]$_3$ in 11% yield.[177,178] Analogous reactions using various diols gave cyclic compounds. In the purification process, an unanticipated dimeric compound [W(L)(NO)(OC$_6$H$_4$NO$_2$-4-CH$_2$CH$_2$O-3)]$_2$ was isolated and characterized by X-ray analysis.[179]

The electrochemical properties of mononuclear species W(NO)LXY and various binuclear forms have been examined. Mononuclear W forms undergo 1 e$^-$ reduction at potentials about 0.45 V more cathodic than those of the Mo analogues.[180,181] Binuclear species featuring bridging *p*-diphenyl ligands such as [HN-C$_6$H$_4$-NH]$^{2-}$ exhibited two 1 e$^-$ reductions steps separated by up to 138 mV, indicative of weak interactions mediated by the bridging ligand.[182]

Linking of donors such as ferrocenyl, OMe or NMe$_2$ to a {W(NO)LX}$^{2+}$ acceptor via azo or stilbene groups has produced interesting nonlinear optical effects.[183,184]

The tetranuclear alkoxide cluster [W$_4$(OCH$_2$-*i*-Pr)$_{12}$][185] reacted with NO to produce the dimeric compound [W(μ-OCH$_2$-*i*-Pr) (OCH$_2$-*i*-Pr)$_2$(NO)(py)]$_2$. The value of ν(NO) was 1,568 cm^{-1} and a short W—NO distance (1.75(1) Å) indicated extensive Wdπ-to-NOπ* back-bonding.[72]

4.8.6.1.2 Complexes lacking CO and NO$^+$ Ligands

The tungsten(II) complex [W(PMe$_3$)(CNBu^t)$_2$(η^2-Te$_2$)] was prepared by the treatment of *trans*-[W^{IV}(PMe$_3$)$_4$Te$_2$] in benzene with excess Bu^{t}CN. The coupling of two tellurido ligands to an η^2-ditellurido moiety proceeds as shown Scheme 14.[28] The reaction of [WH(tipt)$_3$(PMe$_2$Ph)$_2$] (tipt = SC$_6$H$_3$Pr$^i_3$-2,4,6) with MeNC in THF yielded *cis*-[W(tipt)$_2$(CNMe)$_4$].[186]

4.8.6.2 W^{II} Halides with CO Ligands

The dimeric halo carbonyl tungsten(II) compounds [{WBr(CO)$_4$}$_2$(μ-Br)$_2$] and [(CO)$_4$W(μ-Br)$_3$WBr(CO)$_3$] were obtained by the reaction of [W(CO)$_6$] with Br$_2$ in dichloromethane at low temperature. The structural variation was induced by filtration through Celite, which was accompanied by copious evolution of CO gas.[187] The reaction of tungsten hexacarbonyl W(CO)$_6$ with antimony(V) fluoride SbF$_5$ in the conjugate Brønsted-Lewis superacid HF-SbF$_5$ afforded [W(CO)$_6$(FSbF$_5$)][Sb$_2$F$_{11}$] as the main product without any loss of CO.[188]

4.8.6.2.1 Complexes containing chalcogen

The tungsten(II) dithiocarbamate complex [W(CO)$_3$(S$_2$CNR$_2$)$_2$] (R = Me, Et, *i*-Pr) was prepared from (Et$_4$N)[W(CO)$_4$I$_3$] by the improved route of oxidation of (Et$_4$N)[W(CO)$_5$I] by elemental iodine. The reaction of [W(CO)$_3$(S$_2$CNR$_2$)$_2$] and excess (Et$_4$N)F·2H$_2$O gave (Et$_4$N)[W(CO)$_3$(S$_2$CNR$_2$)$_2$F]. The structure of the molybdenum derivative (R = Et) was determined by X-ray analysis to be a capped trigonal prism. A similar reaction using stoichiometric PPN azide (PPN = bis(triphenylphosphine)nitrogen) yielded (PPN)[W(CO)$_3$(S$_2$CNR$_2$)$_2$N$_3$].[189]

4.8.6.2.2 Complexes containing nitrogen group, isocyanido, and aryl ligands

[WI$_2$(CO)$_3$(NCMe)$_2$] was reacted with SbPh$_3$ in CH$_2$Cl$_2$ with PPh$_2$(C$_6$H$_{11}$) being added after 5 min. After 25 min the seven-coordinate complex [WI$_2$(CO)$_3${PPh(C$_6$H$_{11}$)$_2$}(SbPh$_3$)] was obtained. A solution in a mixture of CH$_2$Cl$_2$ and diethyl ether deposited single crystals of the disproportionated product [PPh$_2$(C$_6$H$_{11}$)H][WI$_3$(CO)$_3$ (SbPh$_3$)] over a period of two months. The structure exhibited an approximate capped octahedral geometry.[190] The reaction of WBr$_2$(CO)$_4$ with triphenylphosphine initially produced the seven-coordinate 18-electron species [WBr$_2$(CO)$_3$(PPh$_3$)$_2$], which was converted to the 16-electron compound [WBr$_2$(CO)$_2$(PPh$_3$)$_2$] by refluxing for 3d in dichloromethane.[191]

The addition of TlPF$_6$ to an acetonitrile solution of [W(bpy)(PMe$_3$)$_2$Cl$_2$] produced [W(bpy)(PMe$_3$)$_2$Cl(η^2-NCCH$_3$)](PF$_6$) as shown in Figure 21. The acetonitrile molecule is highly nonlinear (129.6°) with a long C—N bond (1.26 Å) and acts as a four-electron donor.[192] The seven-coordinate isocyanide tungsten(II) complex [WCl$_2$(CNBu^t) (CO)(PMe$_3$)$_3$] was synthesized

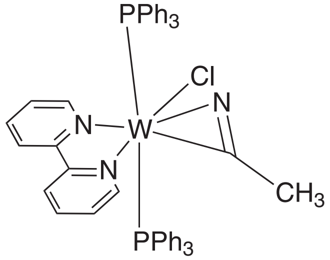
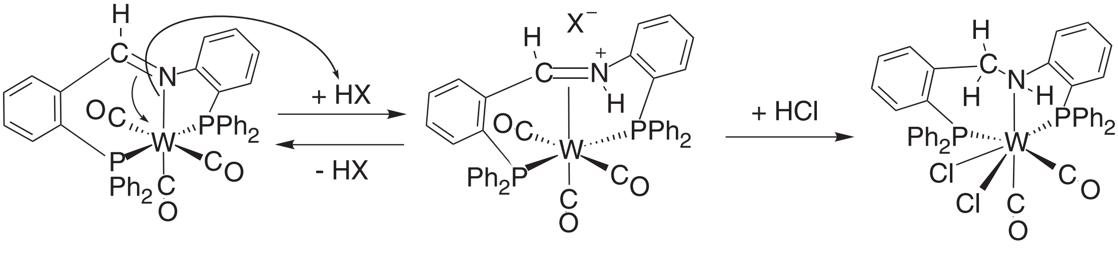


Figure 21 Schematic drawing of [W(bpy)$(PMe_3)_2$Cl(η^2-$NCCH_3$)](PF_6).

by the reaction of [$WCl_2(CO)_2(PMe_3)_2$] with $CNBu^t$ at room temperature in the presence of 1 equiv. of PMe_3. When the reaction was carried out at low temperature without PMe_3, another compound [$WCl_2(CNBu^t)(CO)_2(PMe_3)_2$] was obtained in 90% yield.[193] Previously, seven-coordinate tungsten(II) iodocarbonylisocyanide complexes have been characterized structurally. [$W(CO)_2I_2$(t-BuNC)] exhibits the C_s 4:3 tetragonal base-trigonal cap piano-stool structure. [$W(CO)I_2$(t-BuNC)$_4$] shows capped-octahedral geometry.[194] The seven-coordinate aryl-Schiff base-amine tungsten(II) complex [$W(CO)_3$Cl(2-C_6H_4-CH=N-2-$C_6H_4NH_2$-C,N,N')] associates with γ-valerolactam by intermolecular NH $\cdots$ Cl hydrogen bonds in solution and in the crystal.[195]

Addition of $HBF_4{\cdot}Et_2O$ to a solution of [$W(CO)_3(PCy_3)_2$] in toluene-d_8 yielded [$W(H)(BF_4)(CO)_3(PCy_3)_2$]. The BF_4^- anion acts an η^1 ligand to W. The hydride ligand was not detected by X-ray analysis because of the disordered CO group but was established by ^1H and ^{31}P NMR.[196]

When the Schiff base tungsten(0) compound mer-[W(CO)(L)] (L = $Ph_2PC_6H_4CHNC_6H_4PPh_2$; Scheme 17) was exposed to HCl gas, it converted to cis-[$W^{II}Cl_2(CO)_2(L')$] (L' = $Ph_2PC_6H_4CH_2NHC_6H_4PPh_2$) as the final product. The π-iminium intermediate, i.e., the protonated complex mer-[$W(CO)_3(LH)$]BF_4, and the final product were both characterized structurally. In this reaction, the metal center has undergone a two-electron oxidation (W^0 to W^{II}) and the original imine bond has been reduced to a secondary amine, as indicated by X-ray analysis and spectroscopic measurements.[197]



Scheme 17

The reaction of tertiary phosphines (PR_3) and organic azides ($R'N_3$) is known to proceed via a reactive intermediate, $R'NNNPR_3$, which decomposes in a bimolecular process to dinitrogen and the corresponding phosphoramine ($R'N{=}PR_3$). The reactive intermediate is stabilized in the tungsten complex. The reaction of $R'N_3$ (R' = Ph, p-$CH_3C_6H_4$) with [$WBr_2(CO)_3(PPh_3)_2$] in dichloromethane at RT afforded [$WBr_2(CO)_3(R'N_3PPh_3)$], N_2 and $R'N{=}PPh_3$. The molecule [$WBr_2(CO)_3$(p-$CH_3C_6H_4N_3PPh_3$)] exhibited capped octahedron geometry as shown in Figure 22.[198]

The oxidation reaction of [W([9]aneN_3)$(CO)_3$] ([9]aneN_3 = 1,4,7-triazacyclononane) with iodine followed by the addition of $NaPF_6$ gave [W^{II}([9]aneN_3)$(CO)_3I$](PF_6). The structure of the analogous molybdenum complex [Mo^{II}([9]aneN_3)$(CO)_3Br$](ClO_4) was determined by X-ray analysis. The starting material [W([9]aneN_3)$(CO)_3$] was obtained via the reaction of [$W(CO)_6$] and [9]aneN_3.[199] Analogous halocarbonyltungsten(II) complexes containing the tripodal tris(pyrazolyl)borate ligand [$LWX(CO)_3$] (L = hydrotris(3,5-dimethylpyrazol-1-yl)borate; X = Br, I) were obtained by the oxidation of (NEt_4)[$LW(CO)_3$] with iodine or bromine in acetonitrile. In the

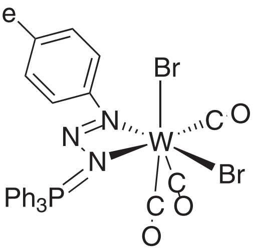


Figure 22 Molecular structure of [$WBr_2(CO)_3(p\text{-}CH_3C_6H_4N_3PPh_3)$] where each bond order does not represent the real valence bond structure.

case of bromine, bromination of the ligand gave [$L^{Br}WBr(CO)_3$] (L^{Br} = hydrotris(4-bromo-3,5-dimethylpyrazol-1-yl)borate) and [$LWBr(CO)_3$] in a 1:1 ratio. [$LWBr(CO)_3$] was also obtained from (NEt_4)[$L^{Br}W(CO)_3$]. [$L^{Br}BrW(CO)_3$] converted to [$L^{Br}WBr(CO)_2$] by heating in acetonitrile at 70 °C for 30 min and to [$L^{Br}BrW(MeCN)(CO)$] by refluxing in acetonitrile for 1 h. The molecular structures of [$L^{Pr}WI(CO)_3$]·MeOH (L^{Pr} = hydrotris(3-isopropylpyrazol-1-yl)borate) and [$L^{Br}Br(CH_3CN)(CO)$] have been determined by X-ray analysis (Figure 23). The acetonitrile molecule coordinates to W ion in side-on mode with a C—N bond length of 1.10(2) Å.[200]

The Schiff base ligand prepared from pentafluorobenzaldehyde and 1,2-diaminobenzene reacted with [$W(CO)_3(EtCN)$] to give [$W^0(CO)_3(NH_2C_6H_4NCHC_6F_5\text{-}N,N')(EtCN)$] immediately and then the metallacycle [$W^{II}F(CO)_3(NH_2C_6H_4NCHC_6F_4\text{-}N,N',C)$] by cleavage of a C—F bond. The cleaved fluoride atom coordinated to tungsten ion.[201]

4.8.6.3 W^{II} Chalcogenides with CO Ligands and the Related Compounds

4.8.6.3.1 Complexes containing phosphine ligands

Treatment of [$W^{IV}H\{SC_6H_2(i\text{-Pr})_3\text{-}2,4,6\}_3(PMe_2Ph)_2$][202] with CO led to loss of the thiolate and formation of [$W^{II}\{SC_6H_2(i\text{-Pr})_3\text{-}2,4,6\}_2(CO)_2(PMe_2Ph)_2$]. Solid-state samples contained crystalline forms (green, 90%; red, 10%) of two isomers. ^{1}H NMR spectra also indicated fluxional isomers in solution. The determined structure (red) exhibited trigonal-prismatic geometry.[203] The structure of the green compound was identified for the analogous [$W(SC_6H_2Me_3\text{-}2,4,6)_2(CO)_2(PMe_2Ph)_2$], which exhibited a twisted (35°) trigonal prismatic or distorted octahedral geometry. A similar reaction of [$WH(SeC_6H_3Pr^i{}_2\text{-}2,6)_3(PMe_2Ph)_2$] with CO afforded [$W(SeC_6H_3Pr^i{}_2\text{-}2,6)_2(CO)_2(PMe_2Ph)_2$]. Care was necessary to prevent the formation of [$W(CO)_4(PMe_2Ph)_2$]. The structure of the selenolate derivative is similar to that of the red isomer mentioned above, being close to a trigonal prism with the same twist angle of 12°.[204] The reaction of [$WI_2(CO)_3L_2$] ($L_2 = (PEt_3)_2$, $(PPh_3)_2$, $Ph_2P(CH_2)_2PPh_2$) with Na_2S_2R ($S_2R^{2-} = C_3S_5{}^{2-}$ (4,5-disulfanyl-1,3-dithiole-2-thionate), mnt (maleonitriledithiolate) or H_2bdt (1,2-benzenedithiolate) gave the six-coordinate complexes [$W(S_2R)(CO)_2L_2$].[205] A similar reaction for [$WI_2(CO)_3(PEt_3)_2$] with either 2 equiv. of NaSPh or 1 equiv. of $Na_2[S(CH_2)_nS]$ ($n = 2,3$) yielded analogous complexes [$W(SPh)_2(CO)_2(PEt_3)_2$] and [$W\{S(CH_2)_nS\}(CO)_2(PEt_3)_2$]. The benzenethiolate complex exhibits octahedral geometry.[206]

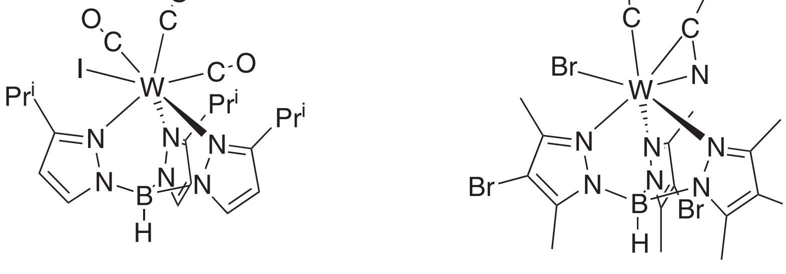


Figure 23 Molecular structures of [$L^{Pr}W^{II}I(CO)_3$] and [$L^{Br}W^{II}Br(CH_3CN)(CO)$].

4.8.6.3.2 Complexes lacking phosphine ligands

The reaction between PySeSePy (2,2′-dipyridyl diselenide) and [W(C_7H_8)(CO)$_4$] (C_7H_8 = norbornadiene) yielded the seven-coordinate complex [W^{II}{C_5H_4N(2-Se)-*N,Se*}$_2$(CO)$_3$].[207] Oxidative addition of 2,2′-pyridine disulfide to [$L_3W(CO)_3$] (L_3 = (pyridine)$_3$, cycloheptatriene) in dichloromethane gave the seven-coordinate [W(η^2-mp)$_2$(CO)$_3$] (mpH = 2-mercaptopyridine). This complex reacted with NO in the presence of additional pyridine disulfide to yield the seven-coordinate tungsten(II) nitrosyl complex [W^{II}(η^2-mp)$_3$(NO)], as well as [W(η^2-mp)$_2$(NO)$_2$] and a trace amount of [W^{IV}(η^2-mp)$_4$].[208]

Oxidative decarbonylation of (NEt_4)[LW(CO)$_3$] (L = hydrotris(3,5-dimethyl-1-pyrazoyl)borate) by tetraethylthiuram disulfide (S_2CNEt_2)$_2$ gave [LW^{II}(CO)$_2$(S_2CNEt_2)]. The seven-coordinate monomeric complex exhibited a distorted pentagonal bipyramidal structure with a carbonyl ligand and one nitrogen donor atom of the L occupying the axial positions.[209] The related hydrotris(3,5-dimethyl-1-pyrazoyl)borate tungsten(II) thiolate compounds [LW^{II}(CO)$_2$(SR)] (R = Me, Et, Pr^i, CH_2Ph, *p*-$C_6H_4NO_2$) were synthesized by the reaction of [LW^{II}(CO)$_2$I] and the corresponding thiol or sodium thiolate. Metathesis of the thiolate complexes was possible by thiolate exchange reactions using the sodium thiolates. The starting material [LW^{II}(CO)$_2$I] was prepared from [LW^{II}(CO)$_3$I] by reflux in THF for 20 h.[210] When the latter was refluxed in acetonitrile, the η^2-acetonitrile complex [LW^{II}(η^2-MeCN)(CO)I] was obtained. This reacted with (NH_4)[$S_2PR^*_2$] (R* = (−)-mentholate) to give air-stable [LW^{II}($S_2PR^*_2$-*S*)(η^2-MeCN)(CO)] as an 8:1 diastereomeric mixture. The structure of the (*R*)-isomer was determined by X-ray analysis.[153] (μ-Thio)ditungsten(II) complexes [{LW(CO)$_2$}$_2$(μ-S)] (L = hydrotris(3,5-dimethyl-1-pyrazoyl) borate, hydrotris(3-isopropyl-1-pyrazoyl)borate) were synthesized by the reaction of [{HB(Me_2pz)$_3$}WBr(CO)$_2$] or [LWH(CO)$_3$] with propylene sulfide in refluxing 1,2-dichloroethane. The W—S—W angles (171.6(1)°, 175.3(1)°) are nearly linear suggesting multiple bond character which is consistent with the short W—S bonds (2.173–2.184 Å).[211]

The tungsten(0) complex [W(CO)$_3$(phen)(EtCN)] underwent oxidative addition with disulfides forming [W(CO)$_2$(phen)(SR)$_2$] (R = Ph, CH_2Ph, Me, ^{t}Bu). The rate of the reaction was in the order Ph > CH_2Ph > Me >> ^{t}Bu. [W(CO)$_2$(phen)(SPh)$_2$] reacted with P(OMe)$_3$ to give [W(CO){P(OMe)$_3$}(phen)(SPh)$_2$]. The structures of [W(CO)$_2$(phen)(SPh)$_2$] and [W(CO)-{P(OMe)$_3$}(phen)(SPh)$_2$] were determined by X-ray analysis. These molecules exhibit octahedral geometry with the two thiolate ligands in the axial positions.[212] Treatment of [W(CO)$_2$(phen)(SPh)$_2$] or [W(CO){P(OMe)$_3$}(phen)(SPh)$_2$] with SO_2 gave a tungsten(II) sulfur dioxide complex [W(CO)(phen)(SPh)$_2$(η^2-SO_2)]. The distance (1.588(14) Å) between the coordinated S and O atoms is long indicating the coordination is expressed as oxidative addition. The activated S—O bond is cleaved to afford the dioxotungsten(VI) compound as shown in Scheme 4.[71]

The bis(carbonyl)-bis(dithiolene) tungsten(II) complex (Et_4N)$_2$[W^{II}(CO)$_2$($S_2C_2Me_2$)$_2$] was synthesized by reduction of [W^{IV}(CO)$_2$($S_2C_2Me_2$)$_2$] with K(anthracene) in THF followed by addition of Et_4NCl.[130]

The tungsten carbyne complex [Cl(CO)$_2$(py)$_2$W(≡CPh)] reacted with (H_2NEt_2)[S_2CNEt_2] to yield a neutral thioaldehyde compound [(Et_2NCS_2)(Et_2NCS-*C,S*)W^{II}(CO)(PhCHS-*C,S*)]. This η^2-PhCHS tungsten(II) complex can also be formulated as a metallacycle tungsten(IV) complex analogous to η^2-aldehyde and η^2-ketone compounds.[27] The thioaldehyde ligand was generated by cleavage of a diethyldithiocarbamate ligand to diethylthiocarboxamide and sulfide.

4.8.6.4 W^{II}–CO Complexes Lacking Halogen and Chalcogen

A series of tungsten(II) phosphine complexes [Tp′W(CO)$_3$L](PF$_6$) (Tp′ = hydrotris(3,5-dimethyl-1-pyrazoyl)borate, L = PMe$_3$, PEt$_3$, PPh$_3$, PMe$_2$Ph) were synthesized by oxidation of the Tp′W(CO)$_3$ radical with ferrocenium followed by addition of phosphine. The complexes [Tp′W(CO)$_3$PMe$_2$R](PF$_6$) (R = Me, Ph) exhibit a capped octahedral geometry as shown in Figure 24.[213] Treatment of [Tp′W(CO)$_2$I] with ammonia in dichloromethane at low temperature afforded [Tp′W(CO)$_2$(NH$_2$)]. Methylation using lithium diisopropyl amide (LDA) or Bu^{t}Li and MeI gave [Tp′W(CO)$_2$(NMe$_2$)], which was characterized structurally. The amido complex [Tp′W(CO)$_2$(NH$_2$)] was treated with [Ph$_3$C][PF$_6$] to produce nitrene products [Tp′W(CO)$_2$(NR)](PF$_6$) (R = H, CPh$_3$) in a 4:1 ratio. The former reacted with base (KH, LDA or NEt$_3$) to yield the nitrido tungsten(IV) complex [Tp′W(CO)$_2$(≡N)]. Treatment of this complex with MeOTf and CH$_3$COCl gave [Tp′(CO)$_2$W(NMe)]$^+$ and [Tp′WCl{NC(O)CH$_3$}], respectively.[214] Heating the tricarbonyl hydride complex [Tp′WH(CO)$_3$] and tosyl azide TsN$_3$ in THF

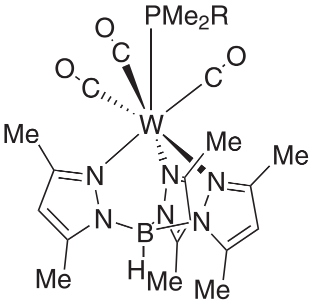


Figure 24 Capped octahedral geometry in [Tp'W(CO)$_3$PMe$_2$R](PF$_6$) (R = Me, Ph).

produced the tosylamido complex [Tp′W^{II}(CO)$_2${N(H)Ts}].[164] The related reactions are described in Section 4.8.4.3.2. The photolysis of [Tp′WH(CO)$_3$] in the presence of PhCH$_2$CN afforded an azavinylidene complex [Tp′W^{II}(N=CHCH$_2$Ph)(CO)$_2$] via insertion of nitrile into the W—H bond. Analogous compounds were prepared in a similar manner. The neutral compounds [Tp′W^{II}(N=CHR)(CO)$_2$] (R = Me, Et, CH$_2$Ph) were treated with HBF$_4$ at low temperature to give cationic nitrene compounds [Tp′W^{IV}(=NCH$_2$R)(CO)$_2$](BF$_4$). When (Ph$_3$C)(PF$_6$) was used instead by HBF$_4$, [Tp′W^{IV}(=NCH(R)CPh$_3$)(CO)$_2$](PF$_6$) was obtained. [215] The reaction between [Tp′W(CO)$_3$Br] and NaS-*i*-Pr in acetonitrile produced the dimeric compound [{Tp′W(CO)$_2$}$_2$ {μ-NC(Me)C(Me)N-*N:N'*}] which features a bridging *anti*-butane-2,3-diimino-(2-)-*N:N'* ligand produced by the coupling of two acetonitrile molecules.[216]

The reaction of *trans*-[W(CO)(N$_2$)(dppe)] (dppe = Ph$_2$PCH$_2$CH$_2$PPh$_2$) with excess MeOH or HNR$_2$ (R$_2$ = (CH$_2$)$_4$, (CH$_2$)$_5$, (CH$_2$)$_2$O(CH$_2$)$_2$) under CO$_2$ afforded the hydrido–carbonato complex [W^{II}H(η^1-OCO$_2$Me)(CO)(dppe)$_2$] or hydrido–carbamato complexes [W^{II}H(η^2-O$_2$CNR$_2$)(CO)(η^1-dppe)(η^2-dppe)], respectively. The structures of [WH(η^1-OCO$_2$Me)(CO)(dppe)$_2$] and [WH(η^2-O$_2$CNC$_4$H$_8$)(CO)(η^1-dppe)(η^2-dppe)] were determined by X-ray analysis but the hydride ligands were not located. Treatment of the latter compound with 1 equiv. of AlEt$_3$ in THF under CO$_2$ afforded *trans*-[W(CO)(η^2-CO$_2$-*C,O*)(dppe)].[217]

The reaction between K$_3$P$_7$, 2,2,2-crypt and [{C$_6$H$_3$(CH$_3$)$_3$}W(CO)$_3$] in ethylenediamine (en) formed [(η^4-P$_7$)W(CO)$_3$]$^{3-}$ species and the subsequent following addition of Et$_4$NBr gave [K(2,2,2-crypt)]$_2$[((η^4-EtP$_7$)W(CO)$_3$]·en. Schematic drawings of these anions are shown in Figure 25 (a)–(c). The P—P bonds rearranged in the formation of the complex. The oxidation state of the tungsten center was considered to be 2+ formally.[218] NO complexes show ambiguous metal oxidation states. Linear W—NO bond has been formulated as W—NO$^+$ species, analogous to W—CO. Some bent NO complexes have been formulated as M—NO$^-$ complexes.[219,220] According this classification, the bent W—NO (W—N—O = 156(2)°, 160(2)°, two disordered positions) complex [W(CO)$_3$ (NO)(C$_{24}$H$_{27}$N$_5$)](BF$_4$) should be classified as W^{II}—NO$^-$. However, ν(NO) was found at 1,670 cm^{-1}, which is common for W^0—NO$^+$ complexes. In this complex, the contribution of W^0—NO$^+$ is large.[221]

Bismuthine (MeSi)$_2$CHBiCl$_2$ was treated with Na$_2$[W(CO)$_5$] to afford [{W(CO)$_5$}$_3$(μ_3-η^2-Bi$_2$)] and [W$_2$(CO)$_8$(μ-η^2-Bi$_2$)(μ-BiMe)W(CO)$_5$]. The structures of these compounds are shown in Figure 26. The latter complex features a Bi$_2$ moiety bridging two tungsten ions. If the Bi—Bi bond is a single bond, the formal oxidation state of tungsten is +2. However, the Bi—Bi distance

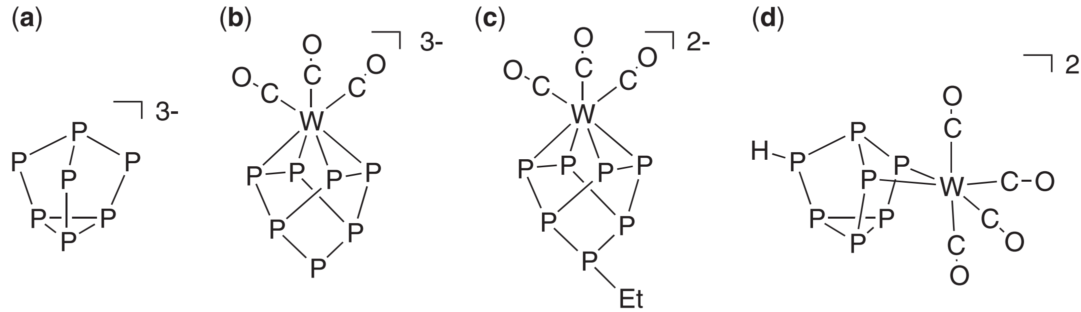


Figure 25 Schematic drawing of (a) P$_7$$^{3-}$, (b) [($\eta^4$-P$_7$)W(CO)$_3$]$^{3-}$, (c) [($\eta^4$-EtP$_7$)W(CO)$_3$]$^{2-}$ and (d) [(η^2-HP$_7$)W(CO)$_4$]$^{2-}$.

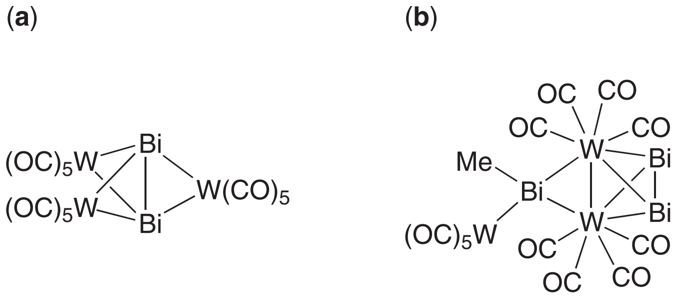


Figure 26 Schematic drawing of (a) $[\{W(CO)_5\}_3(\mu_3\text{-}\eta^2\text{-}Bi_2)]$ and (b) $[W_2(CO)_8(\mu\text{-}\eta^2\text{-}Bi_2)(\mu\text{-}BiMe)W(CO)_5]$.

(2.795(3) Å) is short and corresponds to a bond order of approximately 2. The actual oxidation state is considered to be between +1 and +2.[222,223]

The terminal borylene complex $[(CO)_5W\{{=}BN(SiMe_3)_2\}]$ was obtained by the reaction between $Na_2[W(CO)_5]$ and $Br_2BN(SiMe_3)_2$. The octahedral structure shows linear W—B—N (177.9(5)°) and short B—N bonds (1.338(8) Å).[224]

4.8.7 THE CHEMISTRY OF W^I

Tungsten(I) complexes are rare but are found as dimeric compounds or as reactive species generated by one-electron oxidation of 18-electron compounds.

Treatment of $(Me_3Si)_2CHSbCl_2$ with $Na_2[W(CO)_5]$ followed by purification using column chromatography gave the dimeric compounds $[W(CO)_5]_2\{\mu\text{-}SbCH(SiMe_3)]_2$. The W—W distance is too long (4.907(1) Å) for a W—W single bond.[223] The analogous reaction using $(Me_3Si)_2CH\text{-}BiCl_2$ gave quite different results. The compounds isolated are described in Section 4.8.6.4.

The tungsten(0) complex $[W(CO)_3\{P(i\text{-}Pr\}_3\}_2]$ reacted with diphenylsilane to give the dimeric compound $[\{W^I(CO)_3[P(i\text{-}Pr\}_3]\}_2(\mu\text{-}SiHPh_2)_2]$, which contains W—H agostic interactions.[225]

The air- and light-sensitive but thermally stable monomeric tungsten(I) complex $[LW(CO)_3](PF_6)$ (L = 1,4,7-tribenzyl-1,4,7-triazacyclononane) was synthesized by the oxidation of $[LW(CO)_3]$ by $[Cp_2Fe^{III}]PF_6$. The structure of the molybdenum analogue $[LMo(CO)_3](PF_6)\cdot dmf$ is known (Figure 27(a)).[226]

Oxidative addition of disulfide (PhSSPh) or iodine into $[W(CO)_3\{P(i\text{-}Pr\}_3)_2]$ afforded tungsten(I) complexes $[W^I(CO)_3\{P(i\text{-}Pr\}_3)_2(X)]$ (X = SPh, I). The iodo example $[W^I(CO)_3\{P(i\text{-}Pr\}_3)_2I]$ was characterized structurally (Figure 27(b). The structure shows octahedral geometry without any intermolecular interactions in the solid state.[129]

4.8.8 THE CHEMISTRY OF W^0

An equilibrium between dihydrogen and dihydride forms in solution was observed by ^1H NMR for $[W(CO)_3\{P(i\text{-}Pr)_3\}(H_2)]$ in methylcyclohexane-d_{14}.[227] Consequently, the formal oxidation state

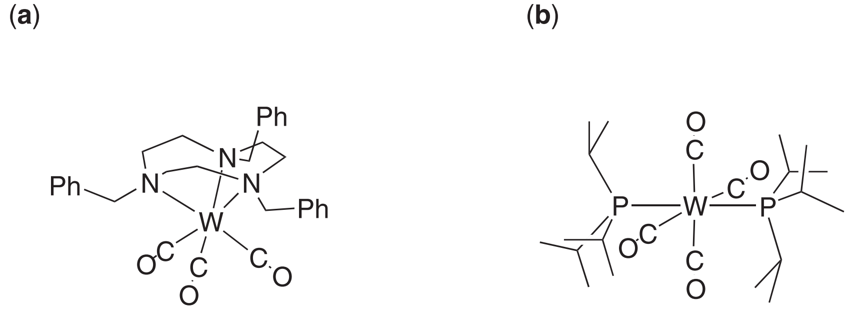


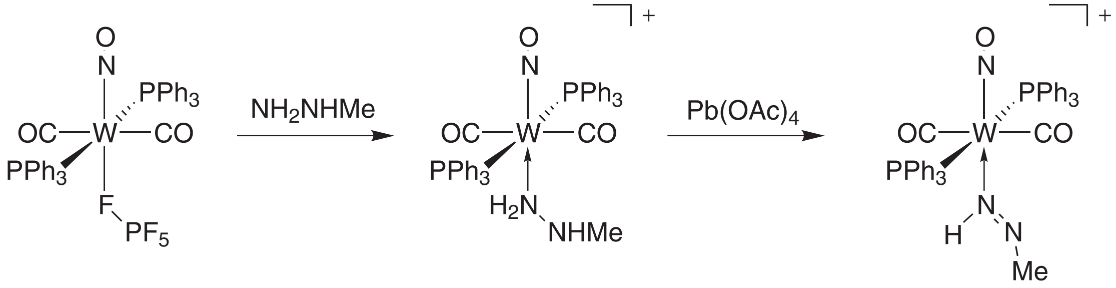
Figure 27 Isolated mononuclear tungsten(I) complexes (a) $[LW(CO)_3](PF_6)$ (L = 1,4,7-tribenzyl-1,4,7-triazacyclononane) and (b) $[W^I I(CO)_3\{P(i\text{-}Pr)_3\}_2]$.

is not determined exactly. This section includes some compounds formed by oxidative addition of ligand to tungsten(0) centers.

4.8.8.1 W^0 Complexes Lacking CO Ligands

4.8.8.1.1 NO$^+$ complexes

As mentioned in Section 4.8.6.4, linear W—N—O coordination has been classified as a W—NO$^+$ bond by an analogy with CO compounds. Use of NO$^+$ salts is one of the most convenient methods for the introduction of NO$^+$ ligand to low-valent tungsten compounds. The reaction of $[W(PMe_2Ph)(CO)_5]$ with 1 equiv. of $(NO)[SbF_6]$ in dichloromethane gave $[W(PMe_2Ph)(CO)_3(NO)(\eta^1\text{-}FSbF_5)]$, where the SbF_6^- anion is coordinated to W by an F atom in the position *trans* to the NO$^+$ ligand.[228] Similar reactions of $[W(PMe_3)(CO)_5]$ with (NO)X (X = BF_4 or PF_6) gave the corresponding F-coordinated compounds $[W(PMe_3)(CO)_3(NO)(\eta^1\text{-}X)]$.[229] *trans,-trans*-$[W(\eta^1\text{-}FPF_5)(CO)_2(NO)(PPh_3)_2]$ was prepared in high yield by the reaction of $[Ph_3C^+][PF_6^-]$ with *trans,trans*-$[W(H)(CO)_2(NO)(PPh_3)_2]$.[230] The weakly coordinated PF_6^- anion was replaced by methylhydrazine to give *trans,trans*-$[W(NH_2NHMe)(CO)_2(NO)(PPh_3)_2](PF_6)$. The oxidation of the complex by $Pb(OAc)_4$ selectively occurred at the ligand to afford *trans,trans*-$[W(NH{=}NMe)(CO)_2(NO)(PPh_3)_2](PF_6)$ as shown in Scheme 18.[231] The hydrido complexes *trans,trans*-$[W(H)(CO)_2(NO)(PR_3)_2]$ (R = Et, Me, Ph, O^{i}Pr) reacted with $BH_3{\cdot}L$ (L = THF, SMe_2) to yield air-sensitive *trans*-$[W(\eta^2\text{-}BH_4)(CO)(NO)(PR_3)_2]$. In the case of R = Me, the molecular structure with octahedral geometry was determined by X-ray analysis.[232] The tungsten hydride *trans,trans*-$[W(H)(CO)_2(NO)(PMe_3)_2]$ reduced β-diketotones selectively to β-hydroxyketones with concomitant formation of *trans*-$[W(\beta\text{-diketonate})(CO)(NO)(PMe_3)_2]$ in most cases. For example, *trans*-$[W\{CF_3(CO)CH(CO)CH_3\text{-}O,O'\}(CO)(NO)(PMe_3)_2]$ was characterized by X-ray analysis.[233]



Scheme 18

$[LW(CO)_2(NO)]PF_6$ (L = 1-thia-4,7-diazacyclononane) was obtained by the reaction of $[LW(CO)_3]$ with $NaNO_2$/HCl in water. Prolonged reaction using a source of excess NO$^+$ gave the dinitrosylchloro compound $[LWCl(NO)_2]PF_6$. The molybdenum analogues have been characterized structurally.[234]

Mono- or disubstituted compounds were obtained from $HW_2(CO)_9(NO)$ and phosphine or pyridine derivatives. Two isomers exist for each compound, but one isomer only was isolated successfully by the column chromatography. $[(CO)_5W(\mu\text{-}H)W(CO)_3\{P(p\text{-}C_6H_4F)_3\}(NO)]$ and $[(CO)_5W(\mu\text{-}H)W(CO)_2L_2(NO)]$ ($L_2 = (py)_2$, $\{P(p\text{-}C_6H_4F)_3\}_2$, bipy) were characterized structurally. The latter complexes were also obtained from $HW_2(CO)_7(THF)_2(NO)$.[235] When a sterically more bulky phosphine P^tBu_3 was used, other compounds were isolated. Treatment of $HW_2(CO)_7(THF)_2(NO)$ with $P(t\text{-}Bu)_3$ gave $HW_2(CO)_8\{P(t\text{-}Bu)_3\}(NO)$ (25%), $[HP(t\text{-}Bu)_3][(\mu H)W_2(CO)_{10}]$ (10%) and $[HP(t\text{-}Bu)_3][(\mu\text{-}H)_2W_3(CO)_{13}(NO)]$ (18.5%). The anion $[(\mu\text{-}H)_2W_3(CO)_{13}(NO)]^-$ was also obtained conveniently from the reaction of $HW_2(CO)_9(NO)$ and $[PPN][HW(CO)_5]$ ($PPN^+ = (Ph_3P)_2N^+$). This trinuclear compound reacted with the nucleophile PMe_3 to afford $[HP(t\text{-}Bu)_3][(\mu\text{-}H)_2W_3(CO)_{12}(PMe_3)(NO)]$ as shown Figure 28.[236]

The reaction of gaseous NO with $[W^{II}(phen)(CO)_2(SPh)_2]$ gave $[W^0(phen)(NO)(CO)_2(SPh)]$ and PhSNO where NO is *trans* to the SPh ligand. When the toluene-3,4-dithiolate *cis*-$[W(phen)(CO)_2(S_2C_6H_3CH_3)]$ was used, the dinitrosyl compound *cis*-$[W(phen)(NO)_2(S_2C_6H_3CH_3)]$ was obtained. $[W(phen)(CO)_3(EtCN)]$ was combined with RSH (R = *t*-Bu, Ph) to give the thiol adduct

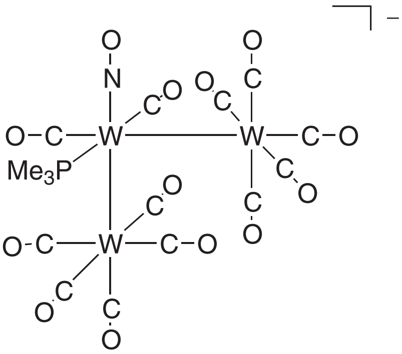


Figure 28 Anion part of $[HP(t\text{-}Bu)_3][(\mu\text{-}H)_2W_3(CO)_{12}(PMe_3)(NO)]$. Hydride atoms were not determined by X-ray analysis but ^1H NMR spectra suggest the presence of two bridging H atoms each site between two W atoms.

$[W(phen)(CO)_3(t\text{-}BuSH)]$ or the thiolate hydride $[W(phen)(CO)_3(SPh)(H)]$. This latter compound reacted with NO to yield $[W(phen)(NO)(CO)_2(SPh)]$ and HNO, which decomposed to detectable N_2O and HNO_2.[237] The analogous compound $[W(\eta^2\text{-mp})_2(CO)_3]$ (mpH = 2-mercaptopyridine) reacted with NO to afford the dinitrosyl $[W(\eta^2\text{-mp})_2(NO)_2]$.[208]

4.8.8.1.2 *Complexes lacking CO and NO^+ ligands*

The dinitrogen complexes *cis*-$[W(N_2)_2(Ph_2PCH_2PPh_2)_2]$ and *trans*-$[W(N_2)_2(Ph_2PCH{=}CHPPh_2)_2]$ were obtained by the reduction of, respectively, WCl_6 and $[WCl_4(Ph_2PCH{=}CHPPh_2)]$ by Mg under N_2 in the presence of the corresponding phosphine. The structure of the analogous monomeric complex *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ was determined by X-ray analysis.[238] The reaction of *trans*-$[W(N_2)_2(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) with 1,4-diisocyanobenzene or 4-isocyanobenzonitrile under irradiation afforded isostructural *cis*-$[(CNC_6H_4NC)_2W(dppe)_2]$ or *cis*-$[(NCC_6H_4NC)_2W(dppe)_2]$, respectively. The isocyanide ligands exhibit bent C—N—C bond (mean, 139°), long C—N bonds (mean, 1.30 Å) and short W—C bonds (mean, 1.86 Å) which indicate substantial back-donation from the electron-saturated tungsten atom.[239]

$[W(tmbp)_3]$ (tmbp = 4,4′,5,5′-tetramethyl-2,2′-biphosphinine) was obtained by the reduction of WCl_6 by excess magnesium powder in the presence of 3 equiv. of the ligand. The molecular structure with trigonal geometry is shown in Figure 29. The twist angle θ is calculated to be $15 \pm 0.6°$. Octahedral geometry ($\theta = 60°$) is usual for tungsten(0) compounds. The results of an *ab initio* calculation suggested a contribution from the partially oxidized state $[W^n\{(tmpy)_3{}^{n-}\}]$.[240]

4.8.8.2 W^0 Halides with CO Ligands

The addition of $W(CO)_5THF$ to 1 equiv. of anhydrous Et_4NF in THF resulted in the insoluble product $(Et_4N)_3[W_2(CO)_6(\mu\text{-}F)_3]$, which has been characterized structurally. The reaction of this dinuclear complex with excess CO produced the unstable anion $[W(CO)_5F]^-$ with labile CO

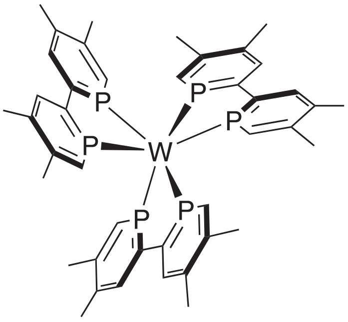


Figure 29 Molecular structure of $[W(tmbp)_3]$ with a triginal prismatic geometry.

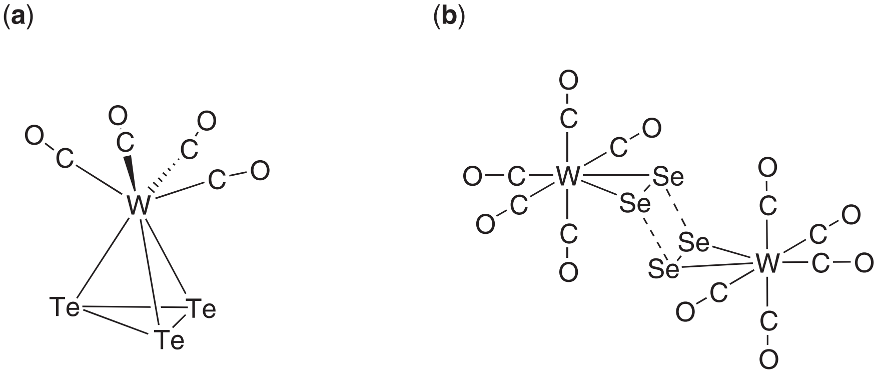


Figure 30 The structure of the cation part in (a) $[W(CO)_4(\eta^3\text{-}Te_3)](SbF_6)_2$ and (b) $[W_2(CO)_{10}Se_4](AsF_6)_2$.

ligands This complex converted easily back to the dimeric compound in the absence of CO or to $W(CO)_6$ with prolonged exposure to CO.[241] $[W(CO)_5I]^-$ ion was generated easily by very simple reaction between $W(CO)_6$ and $LiI{\cdot}Et_2O$. The structure of $[Li(dime)_2][W(CO)_5I]$ (dime = diethylene glycol dimethyl ether) was determined.[242]

4.8.8.3 W^0 Chalcogenides with CO Ligands and Related Compounds

4.8.8.3.1 Complexes containing tellurium and selenium

The reaction of $Te_4(SbF_6)_2$ with $W(CO)_6$ in SO_2–AsF_3 produced $[W(CO)_4(\eta^3\text{-}Te_3)](SbF_6)_2$ having a triangular Te_3^{2+} moiety. The molecular structure exhibits 'piano stool' geometry as shown in Figure 30 (a).[243] Anionic polytelluride K_2Te_4 reacted with $W(CO)_6$ to afford $(Ph_4P)_2[(CO)_4W(\eta^2\text{-}Te_4)]$ containing a five-membered chelate ring involving Te_4^{2-}.[244] The iron telluroether compound $[(Ph_2Te)Fe^{II}(CO)_3I_2]$ transferred the coordinated telluroether to $W(CO)_5THF$. The resultant $[(Ph_2Te)W(CO)_5]$ exhibited octahedral geometry.[245] The tellurophosphorane complex $[W(CO)_5\{(t\text{-}Bu)_3PTe\}]$ was synthesized by photolysis in the presence of $(t\text{-}Bu)_3P{=}Te$.[246]

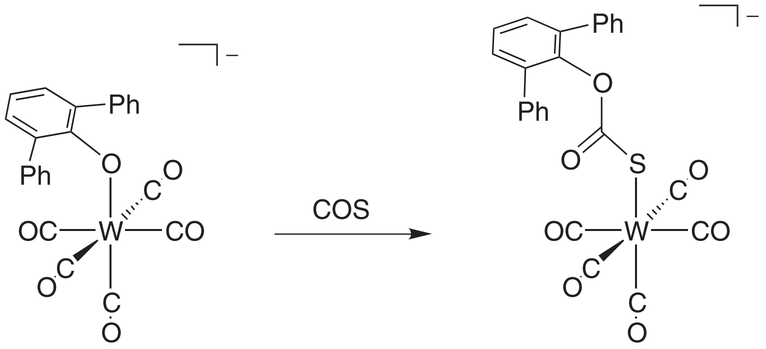
In the case of selenium, the chemistry is slightly different. The reaction of $Se_4(AsF_6)_2$ or $Se_8(AsF_6)_2$ with $W(CO)_6$ in liquid SO_2 gave the diamagnetic product $[W_2(CO)_{10}Se_4](AsF_6)_2$. The structure indicated $\mu\text{-}Se_4^+$ coordination as shown in Figure 30(b). The shorter Se—Se bond lengths (2.286(2) Å) are close to the value of 2.19 Å found for gaseous Se_2. The longer Se—Se bonds (3.015(2) Å) suggest that the complex may be formulated as dimeric $[W(CO)_5(\eta^2\text{-}Se^+)]$.[247]

The reaction of $[W(CO)_4(TMPA)]$ (TMPA = *N,N,N,N'*-tetramethyl-1,3-propanediamine) with $[8]aneSe_2$ (1,5-diselenacyclooctane) yielded the *cis*-disubstituted tetracarbonyl compound $[W(CO)_4([8]aneSe_2)]$.[248]

4.8.8.3.2 Complexes containing sulfur

The reaction of $[W(CO)_3(NCMe)_3]$ with $P(i\text{-}Pr)_3$ followed by the addition of excess SO_2 gave *mer,trans*-$[W(CO)_3\{P(i\text{-}Pr)_3\}_2(\eta^1\text{-}SO_2\text{-}S)]$.[249] Treatment of $[W(CO)_4\{PPh_2(CH_2)_2SCH_3\}]$ with $[(CH_3)_3O]BF_4$ resulted in methylation of the ligand sulfur to yield $[W(CO)_4\{\eta^2\text{-}PPh_2(CH_2)_2S(CH_3)_2\text{-}P,S\}]BF_4$. This compound reacted with donors L to form six-coordinate $[W(CO)_4(L)\{\eta^1\text{-}PPh_2(CH_2)_2S(CH_3)_2\text{-}P\}]BF_4$ (L = CO, $P(OCH_3)_3$, CH_3CN).[250] The sulfide osmium cluster $[Os_5(CO)_{15}(\mu_4\text{-}S)]$ contains a square pyramidal Os_5 core and a quadruply bridging sulfido ligand. When this cluster reacted with $[W(CO)_5PPh_3]$, the apical sulfido ligand coordinated to the tungsten ion to yield $[Os_5(CO)_{15}(\mu_5\text{-}S)\{W(CO)_4(PPh_3)\}]$.[251] The tungsten(0) thiolate compound $(Et_4N)[W(CO)_5(SPh)]$ (obtained by the reaction of $[W(CO)_5(thf)]$ with Et_4NSPh) converted slowly to $(Et_4N)[W(\mu\text{-}S)_2(CO)_8]$ upon gentle heating.[252] The tungsten(0) complex *mer*-$[W(CO)_3(dppe)(2,3\text{-}DHT)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$; 2,3-DHT = 2,3-dihydrothiophene) was obtained by the reaction of 2,3-DHT and $W(CO)_3(dppe)(thf)$ (prepared from $W(CO)_4(dppe)$ by irradiation with 254-nm light).[253] The insertion of COS to the W—O bond in $(Et_4N)[W(CO)_5(O\text{-}2,6\text{-}Ph_2C_6H_3)]$ afforded $(Et_4N)[W(CO)_5\{SC(O)O\text{-}2,6\text{-}Ph_2C_6H_3\}]$ as shown in Scheme 19.[254]

The cyclic polythioether complex $[W(CO)_4(L)]$ (L = 2,5,8,11-tetrathia[12](2,5)thiophenophane) was prepared by the reaction of $W(CO)_6$ and the ligand with irradiation. The ^1H NMR spectra of the complex show fluxional conformations and the derived molecular structure indicates η^2-L-S^5,S^8 coordination.[255] The trimethylphosphonium dithiocarboxylate compound $[W(CO)_2(PMe_3)_2(\eta^3\text{-}S_2CPMe_3\text{-}S,S',C)]$ is obtained by HCl elimination from $[WH(Cl)(CO)_2(PMe_3)_2]$ upon treatment with CS_2 and PMe_3. The complex was treated with the protic acid HBF_4 to afford the dithioformate species $[W\{\eta^2\text{-}S_2C(H)PMe_3\}(CO)_2(PMe_3)_2]BF_4$ and with MeI to yield the *S*-methylated compound $[W(CO)_2(PMe_3)_2\{\eta^3\text{-}SC(SMe)PMe_3\text{-}S,S',C\}(CO)_2(PMe_3)_2]I$.[256] *mer*-$(NMe_4)_2[W(CO)_3L]$ (L = η^3-(S-(2-$C_6H_4)_2$PPh-*S,S',P*) was obtained by the reaction of $(NMe_4)[L]$ and $[W(CO)_3(CH_3CN)]$, which is prepared from $[W(CO)_6]$.[141] The reaction of $[W(CO)_5(NCMe)]$ with 2(*R*),3(*S*)-dimethylthiirane (*cis*-DMT=$SC_2H_2Me_2$)) afforded $[W(CO)_5(\eta^1\text{-}cis\text{-DMT-}S)]$. When excess thiirane reacted with $[W(CO)_5(NCMe)]$, cyclic polysulfides $(CH_2CH_2SS)_n$ and ethylene were formed catalytically.[257] In the case of vinylthiiranes, 3,6-dihydro-1,2-dithiine ($S_2C_4H_6$) was obtained. The tungsten compound $[W(CO)_5(\eta^1\text{-}S_2C_4H_6\text{-}S)]$ was isolated and characterized structurally.[258] The monoanion of 1,2-disubstituted benzene [PPN][HX] (PPN^+ = bis(triphenylphosphoranylidene)ammonium, X = S,S-C_6H_4, O,S-C_6H_4, NH,S-C_6H_4) reacted with $[W(CO)_5(thf)]$ to afford $[PPN][W(CO)_5HX]$, which were treated with NaOMe and PPNCl to produce $[PPN]_2[W(CO)_4(X)]$. The tetracarbonyl compounds were slowly converted to tricarbonyl complexes $[PPN]_2[W(CO)_3(X)]$ by bubbling argon into acetonitrile at 40 °C. $[PPN]_2[W(CO)_4(PH_2C_6H_4PH_2)]$ was prepared from $[W(CO)_4(piperidine)_2]$ and dishosphinobenzene. Trigonal bipyramidal structures for $[PPN][W(CO)_3(S,NH\text{-}C_6H_4)]$ and $[PPN][W(CO)_3(S,O\text{-}C_6H_4)]$ and octahedral structures for $[W(CO)_4(S,S\text{-}C_6H_4)]$ and $[W(CO)_4(PH_2C_6H_4PH_2)]$ were determined by X-ray analysis.[259] $(NEt_4)[W(CO)_5(\eta^1$-2-thiouracylato-*S*)] was prepared by the reaction of $[W(CO)_5(MeOH)]$ and (Et_4N)[2-thiouracilate]. The pentacarbonyl complex loses one CO ligand to yield $(NEt_4)[W(CO)_4(\eta^2$-2-thiouracylato-*S,N*)].[260] The thioether compound μ-hexakis(pentylsulfanylmethy)benzene- or μ-hexakis(propylsulfanylmethy)benzene-bis(tetracarbonyltungsten) $[\{W(CO)_4\}_2L]$ was prepared from $[W(CO)_4(MeCN)]$ and the corresponding thioether.[261] A similar reaction using $[W(CO)_5(thf)]$ and 4-methylthiazole-2-dithiocarboxylate methyl ester (L) afforded a *S,N*-chelate compound $[W(CO)_4(L)]$.[262]



Scheme 19

4.8.8.3.3 *Complexes containing oxygen*

The carbonyl acetato tungsten(0) complex $[PNP][W(CO)_5(O_2CCH_3)]$ was prepared by the reaction of $[PNP][W(CO)_5Cl]$ and AgO_2CCH_3. The resultant complex reacted with triethylphosphine to yield *cis*-$[PNP][W(CO)_4(PEt_3)(O_2CCH_3)]$. The pentacarbonyl complex in solution was shown to dissociate an equatorial CO ligand but the tetracarbonyl complex was inert towards dissociative CO loss.[263] $(Et_4N)[W(CO)_5OR]$ (R = Ph, $C_6H_4CH_3$-*m*), prepared from the reaction of $[W(CO)_5(thf)]$ and $(Et_4N)[OR]$), reacted with CO_2 to afford the carbonate species $(Et_4N)[W(CO)_5\{OCO(O)OR\}]$. Hydrolysis of these compounds, accompanied by loss of CO ligand led to the η^2-carbonate complex $(Et_4N)_2[W(CO)(\eta^2\text{-}CO_2\text{-}O,O')]$. While the structures of salts of $[W(CO)_5OR]^-$ (R = Ph, O-2,6-$Ph_2C_6H_3$) were determined by X-ray analysis,[254,264] this anion is extremely CO labile, decomposing readily to $[W_4(CO)_{12}(\mu_3\text{-}OR)_4]^{4-}$ in the absence of a CO atmosphere.[264,265] In the case of $[W(CO)_5(OSiMe_3)]^-$, an intermediate dimeric compound was isolated as the salt $[K(18\text{-crown-}6)]_2[W_2(CO)_8(OSiMe_3)_2]$.[266] An analogous compound

$[PPN][W(CO)_8(\mu\text{-}OCH_2CF_3)_2]$ was produced from $[PPN][W(CO)_5(OCH_2CF_3)]$ (prepared from $[PPN][W(CO)_5CH_3]$ and $HOCH_2CF_3$).[267] When excess OPh^- was present, another dimeric compound $(Et_4N)_3[W_2(CO)_6(\mu\text{-}OPh)_3]$ was obtained.[266] The reaction of the oxalate anion, $(Et_4N)_2(C_2O_4)$ with $[W(CO)_5(CH_3CN)]$ afforded monomeric $(Et_4N)_2[W(CO)_4(\eta^2\text{-}O_2CCO_2)]$. A similar reaction using 2 equiv. of $[W(CO)_5(CH_3CN)]$ gave a dimeric compound initially $[PPN][W_2(CO)_{10}(\mu\text{-}\eta^1\text{-}O_2CCO_2)]$ and then $[PPN][W_2(CO)_8(\mu\text{-}\eta^2\text{-}\ O_2CCO_2)]$ by removal of two labile CO molecules.[268] Bicarbonato compound $[PPN][W(CO)_5(\eta^1\text{-}HCO_3)]$ was synthesized by the reaction of $[W(CO)_5(\text{acetone})]$ and $[PPN](HCO_3)$, which was also produced by the treatment of $[W(CO)_5(OH)]^-$ and CO_2.[269,270] The glycine derivatives of tungsten(0) complexes $(Et_4N)[W(CO)_4(\eta^2\text{-}O_2CCH_2NRR'\text{-}N,O)]$ ($RR' = H_2$, HMe, Me_2) were synthesized by the reaction of $[W(CO)_5(thf)]$ and the corresponding glycine derivatives.[271] Analogous amino acid and phosphino acid derivatives $(Et_4N)[W(CO)_4L]$ ($L = \eta^2\text{-}O_2CCH(C_6H_5)NH_2\text{-}O,N$, $\eta^2\text{-}O_2CCH_2PPh_2\text{-}O,P$) were obtained in similar methods.[272] The orotate ($C_5H_2N_2O_4{}^{2-}$), L-dihydroorotate ($C_5H_4N_2O_4{}^{2-}$) and uracilate derivatives $(Et_4N)[W(CO)_4(L)]$ ($L = \eta^2$-orotato-*N,O*, η^2-L-dihydroorotato-*N,O*, η^1-uracilato-*N*) were prepared in a similar way.[273] The reaction of 2 equiv. of di-*tert*-butylcatecholate (DTBCat) $(Et_4N)[DTBCat]$ with $[W(CO)_5(THF)]$ afforded $(Et_4N)_2[W(CO)_3(DTBCat)]\cdot[DTBCatH_2]$, which was converted, to $(Et_4N)_2[W(CO)_3(DTBCat)]$[274] and $(Et_4N)_2[W(CO)_4(DTBCat)]$ by treatment of five-fold excess of MeONa.[275] Binuclear complex bridging by NCH_2CH_2N unit in *N,N'*-ethylenebis(salicylideneamine) (H_2salen), $(Et_4N)_2[W_2(CO)_8(salen)]$, was obtained by the reaction of 2 equiv. of $[W(CO)_5(thf)]$ and doubly deprotonated salen.[276]

4.8.8.4 CO Complexes Lacking Halogen and Chalcogen

4.8.8.4.1 Complexes containing arsenic and antimony

Isostructural pentacarbonyl tungsten(0) compounds $[W(CO)_5(EPh_3)]$ (E = P, As, Sb) were prepared by photolysis of $[W(CO)_6]$ in the presence of the corresponding EPh_3.[277] The bis(dimethylstibino)methane $Me_2SbCH_2SbMe_2$ (dmsm) and bis(diphenylstibino)methane $Ph_2SbCH_2SbPh_2$ (dpsm) tungsten(0)complexes were prepared by the ligand-exchange reaction of appropriate starting materials. Monomeric complexes $[W(CO)_5(\eta^1\text{-dpsm})]$ and *fac*-$[W(CO)_3(\eta^1\text{-dpsm})_3]$ are prepared from $(NEt_4)[W(CO)_5Br]$ and *fac*-$[W(CO)_3(CH_3CN)_3]$, respectively. Dimeric $[(CO)_5W(\mu\text{-dpsm})W(CO)_5]$, $[(CO)_5W(\mu\text{-dmsm})W(CO)_5]$ and *cis*-$[\{W(CO)_4(L\text{-}L)\}_2]$ (L-L = dpsm, dmsm) were obtained from $[W(CO)_5(thf)]$, $[W(CO)_6]$ and $[W(CO)_4(Me_2NCH_2CH_2CH_2NMe_2)]$, respectively.[278] Antimony-containing cage compound $[\{W(CO)_5\}_2(\eta^1{:}\eta^1\text{-}P_4Sb_2C_4Bu^t{}_4\text{-}P,Sb)]$ was also produced from $[W(CO)_5(thf)]$.[279]

4.8.8.4.2 Complexes containing phosphorus

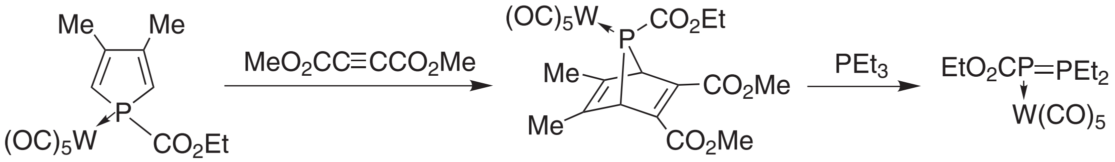
Anionic $PR_2{}^-$ ligand is found in dimeric compound. The dinuclear W^I–W^I compound $[W_2(CO)_8(\mu\text{-}PPh_2)_2]$ was synthesized by the reaction of $[W(CO)_5(PPh_2H)]$ with *n*-BuLi. The reduction by 2 equiv. of $LiBEt_3H$ gives tungsten(0) complex $[Li(thf)_3]_2[(CO)_4W(\mu\text{-}PPh_2)W(CO)_4]$ accompanying cleavage of W—W bond.[280]

Ligands having P—O bond coordinated to tungsten(0) by phosphorus to form compounds. The previously known compound $[W(CO)_5\{P(OCH_2)_3CMe\}]$ was characterized structurally for molybdenum analogue.[281] The Δ^3-1,4,2-oxazaphospholene complex having five-membered ring $[(CO)_5W\{\eta^1\text{-}P[CH(SiMe_3)_2]OC[(CH_2)_5]N{=}CPh\text{-}P\}]$ was produced by regioselective ring expansion of the *2H*-azaphosphirene tungsten complex $[(CO)_5W\{\eta^1\text{-}P[CH(SiMe_3)_2]N{=}CPh\text{-}P\}]$ using cyclohexanone.[282]

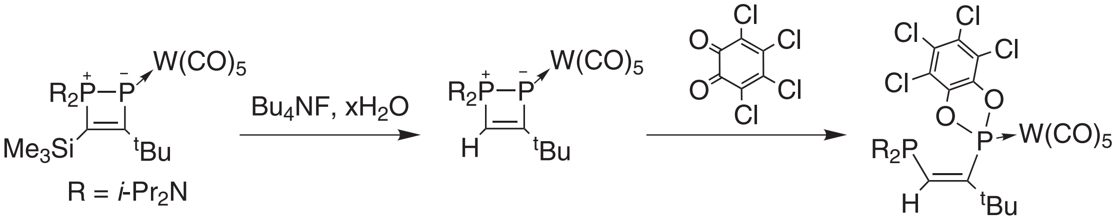
Some tungsten(0) complexes with ligands having P—N bonds have been reported. Cyclic ligand $[P(Ph)N(Me)N\{P(OCH_2CF_3)_2\}]_2$ reacted with $[W(CO)_4(NHC_5H_{10})_2]$ to yield dimeric complex $[\{W(CO)_4\}_2\{\mu\text{-}\{PhPN(Me)N[P(OCH_2CF_3)]\}_2\}]$ where the ligand formed four-membered P—N—P—W chelate ring but not P—N—N—P—W.[283] The P—N—N—P chelate $P(OPh)_2N(Me)N(Me)P(OPh)_2$ is found in $[W(CO)_4\{P(OPh)_2N(Me)N(Me)P(OPh)_2\}]$, which was prepared by the reaction of the ligand and *cis*-$[W(CO)_4(NHC_5H_{10})_2]$.[284] Photochemical ring opening of *2H*-azaphosphirene complex $[(CO)_5W\{\eta^1\text{-}P[CH(SiMe_3)_2]N{=}C(Ph)\text{-}P\}]$ in the presence of 2 equiv. of ethyl cyanoformate EtO_2CCN afforded 2H-1,4,2-diazaphosphole complex $[(CO)_5W\{\eta^1\text{-}P[CH(SiMe_3)_2]N{=}C(Ph)N{=}C(CO_2Et)\text{-}P\}]$.[285]

Ethylenediamine solution of $[(\eta^4\text{-}P_7)W(CO)_3]^{3-}$, which was mentioned in Section 4.8.6.4, reacted under 1 atm CO to form $[(\eta^2\text{-}P_7)W(CO)_4]^{3-}$. This complex was protonated by methanol to yield $[(\eta^2\text{-}HP_7)W(CO)_4]^{2-}$ as shown in Figure 25.[286] Ring opening reaction of the cyclic $[(Bu^tP)_3As]^-$ anion by electrophiles RX (RX = H_2O, MeI, $CH_2{=}CHCH_2I$, $PhCH_2Br$) yielded triphosphine ligands of the type $[(Bu^tP)(Bu^tRP)_2]$. In the case of R = H, the ligand was combined with $[W(CO)_5(thf)]$ to afford $[W(CO)_4\{\eta^2\text{-}(P^tBu)_2P^tBu\text{-}P,P'\}]$.[287] Treatment of the *cyclo*-P_3 complexes $[(triphos)RhP_3]$ (triphos = 1,1,1-tris(diphenylphosphinomethyl)ethane) with stoichiometric amounts of $[W(CO)_5(thf)]$ gave $[(triphos)Rh](\mu,\eta^{3:1}\text{-}P_3)\{W(CO)_4(PPh_3)\}]$.[30] Dichlorodiphosphene moiety Cl—P=P—Cl was found in the complex $[W(CO)_5\{\mu,\eta^2{:}\eta^1{:}\eta^1\text{-}P_2Cl_2[W(CO)_5]\}]$, which is prepared by the reaction of $Na_2[W_2(CO)_{10}]$ with PCl_3 accompanying the formation of $[\{W(CO)_5\}_2(\mu\text{-}PCl)]$ and $[(CO)_5WPCl_3]$.[288]

The reaction of $[\eta^1$-3,4-dimethyl-1-(ethoxycarbonyl)phosphole-*P*]pentacarbonyltungsten with dimethyl acetylenedicarboxylate gave the 7-phosphanornadiene complex as shown in Scheme 20.[289] The complex reacted with triethylphosphine to affords phosphoranylidenephosphine complex (Scheme 20).[290] The P—P bond (2.156(2) Å) was closer to a single bond than to a double bond, which indicates its zwitterionic character $[(CO)_5W\{EtO_2P^-\text{-}P^+Et_3\}]$. A similar P=P bond was found in the diphosphete derivative[291] as shown in Scheme 21 (left), which was prepared from the reaction of $[W(CO)_5(thf)]$ and the corresponding ligand. The trimethylsilyl group is replaced by H and the following addition of tetrachloro-*o*-benzoquinone resulted in the cleavage of P=P bond.[292] Symmetric coordination $(CO)_5WPPh(R)\text{-}PPh(R)W(CO)_5$ was prepared from the reaction of $[(PhP{=})W(CO)_5]$ and phospha[3]radialene.[293] Two equiv. of the diphosphastibolyl five-membered ring anion $[1,4,2\text{-}P_2SbC_2Bu^t{}_2]^-$ reacted with $FeCl_3$ to produce and antimony-containing cage compound $P_4Sb_2C_4Bu^t$, which reacted with $[W(CO)_5(thf)]$ to give $[\{W(CO)_5\}(\eta^1\text{-}P_4Sb_2C_2Bu^t{}_4\text{-}P)]$. The crystal structure exhibits a three-membered PPC diphosphirane ring.[294]



Scheme 20

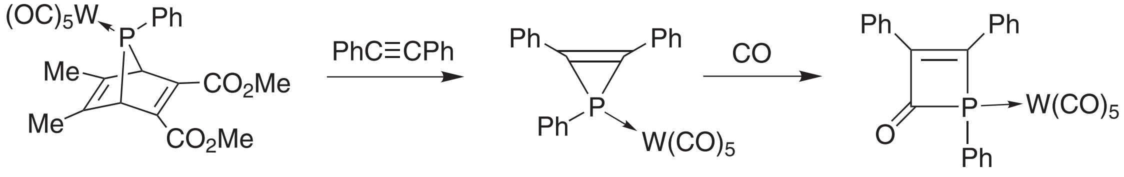


Scheme 21

The compounds with ligands having P=C bonds have been reported. Treatment of 2,4,6-tris(2,4,6-tri-tert-butylphenyl)-1,3,6-triphosphafulvene with $[W(CO)_5(thf)]$ afforded the corresponding monomeric η^1-complex.[295] The diphoshinidenecyclobutene derivative with 2,4,6-triisopropylphenyl group (Tip), *cyclo*-(TipP=C-C(=PTip)-C(Ph)=C(Ph)), reacted with $[W(CO)_5(thf)]$ to give doubly tungsten-coordinated complex. One is η^2-chelate (*P,P*) and the other is organometallic π-type coordination.[296] Treatment of (*Z*)-2-chloro-3,3-diphenyl-1-(2,4,6-tri-*tert*-butylphenyl)-1,3-diphosphapropene $^tBu_3C_6H_2P{=}C(Cl)PPh_2$ with $[W(CO)_5(thf)]$ afforded monodentate compound $[(CO)_5W\{\eta^1\text{-}PPh_2C(Cl)PC_6H_2{}^tBu_3\text{-}P\}]$. The photolysis of this complex produces $[(CO)_4W\{\eta^2\text{-}PPh_2C(Cl)PC_6H_2{}^tBu_3\text{-}P,P'\}]$ which was also obtained from $[W(CO)_4(cod)]$ (cod = cycloocta-1,5-diene).[297]

The phosphirene compound was prepared from the 7-phosphanorbornadiene complex as shown in Scheme 22.[298] The complex converts to 2-keto-1,2-dihydrophosphete complex by insertion of CO into P—C bond via metallacycle intermediates.[299] Analogous phosphirene,[300] phosphirane,[301] and the related alkenylidenephosphirane[293] derivatives have been reported.

Dimeric 2,2′-biphosphirirene[302] and 2,2′-bisphosphirane[303] derivatives were characterized structurally. Treatment of 2,5-di(2-pyridyl)phosphole (L) with $[W(CO)_5(thf)]$ affords monodentate (*P*) complex $[(CO)_5W(L)]$.[304]



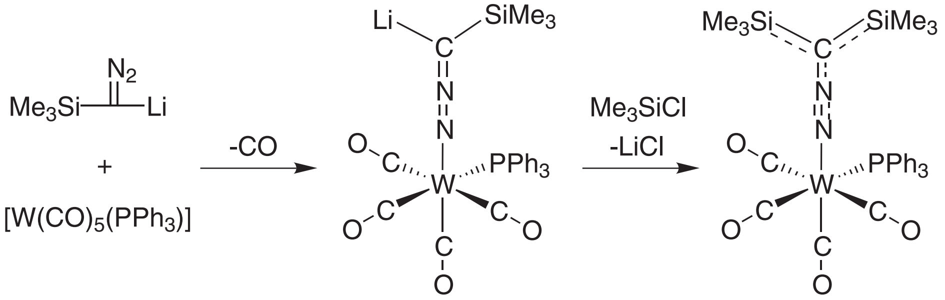
Scheme 22

Many carbonyltungsten(0) compounds containing only phosphine derivatives PR_3 have been reported,[146,305–317] however, the structures exhibit normal octahedral geometry so further discussions are not shown here.

Treatment of phosphirene compound $[(CO)_5W(\eta^1\text{-}P(Ph)C(Ph){=}CPh)]$ reacted readily with $M(PEt_3)_2(C_2H_4)]$ to result the insertion of $[M(PEt_3)_2]$ fragment into the P—C bond. The obtained metallacycle $[(CO)_5W\{P(Ph)C(Ph)C(Ph)Pt(PEt_3)_2\}]$ was characterized structurally.[318] The phosphoriranepentacarbonyltungsten complex (*E*)-and (*Z*)-$[W(CO)_5\{\eta^1\text{-}P(Ph)CH(Ph)CHPh\}]$ with PCC three-membered ring converted to (*2R,3S,4R*)- and (*2R,3S,4S*)-$[(CO)_5W\{P(Ph)CHCH(Ph)\}Pd(dppe)]$ (dppe = 1,2-bis(diphenylphosphanyl)rthane) with PCCPd four-membered ring by insertion of Pd fragment into the P—C bond.[319]

4,5-Dimethyl-2-(2-pyridyl)phosphorin ($C_{12}H_{12}NP$) which is the analogy of 2,2′-bipyridine reacted with $[W(CO)_6]$ under UV irradiation to afford $[W(CO)_4(\eta^2\text{-}C_{12}H_{12}NP\text{-}N,P)]$.[320] Tridentate 11-membered phosphino macrocyclic ligand reacted with $[W(CO)_6]$ to give octahedral tri(carbonyl-*κC*)[*meso-cis*-2,6,10-triphospha-κ^3P-bicyclo[9.4.0]pentadeca-11(1),12,14-triene]tungsten(0) ($C_{33}H_{31}O_3P_3W$).[321] The solution of $[(\eta^4\text{-}P_7)W(CO)_3]^{3-}$ anion (Figure 25(b)) in ethylenediamine (en) reacted with $[(mesitylene)W(CO)_3]$ to produce dimeric $[(en)(CO)_3W(\eta^1,\eta^4\text{-}P_7)W(CO)_3]^{3-}$. The $W(CO)_3(en)$ fragment coordinated η^1 to the apical P of $[(\eta^4\text{-}P_7)W(CO)_3]^{3-}$.[143] The reaction of trimethylsilyldiazomethane anion with $[W(CO)_5(PPh_3)]$ in the presence of Me_3SiCl gave $[W(CO)_4(PPh_3)\{\eta^1\text{-}N_2C(SiMe_3)_2\}]$ as shown in Scheme 23. The W—N bond (2.161(11) Å) is long and N=N and N—C of 1.165(15) and 1.34(1) Å are intermediate between double and triple, and single and double bonds, respectively.[322] The bent nitrene or hydrazido coordination in *fac*-$[(CO)_3(dppe)W{=}NNMe_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) is considered a neutral 2 e$^-$ donor which is resemble the zero-valent Fischer carbenes than the linear imido complexes. The W=N—N angle is 139(1)°. The complex was prepared by the reaction between $[(CO)_5W{=}NNMe_2]$[323] and dppe.[324] $[W(CO)_3(CH_3CN)]$ reacted with bis(diphenylphosphino)methane (dppm) to yield *fac*-$[W(CO)_3(CH_3CN)(dppm)]$.[325] Treatment of (1*R*)-(+)-camphor azine with 2 equiv. of BuLi followed by PPh_2Cl gave azine diphosphines *Z,Z*-3,3′-$Ph_2P^nC_{10}H_{15}{=}N\text{-}N{=}C_{10}H_{15}P^xPh_2$ and *Z,Z*-3,3′-$Ph_2P^xC_{10}H_{15}{=}N\text{-}N{=}C_{10}H_{15}P^xPh_2$ (*x* = *exo*, *n* = *endo*). Reaction of *Z,Z*-3,3′-$Ph_2P^xC_{10}H_{15}{=}N\text{-}N{=}C_{10}H_{15}P^xPh_2$ and $[W(CO)_5(nbd)]$ (nbd = norbornadiene) yielded *fac*-$[W(CO)_3(\eta^3\text{-}Ph_2P^xC_{10}H_{15}{=}N\text{-}N{=}C_{10}H_{15}P^xPh_2\text{-}P,N,P')]$.[38] Analogous compound $[W(CO)_3\{\eta^3\text{-}PPh_2CH_2C(Bu^t){=}N\text{-}N{=}C(Bu^t)CH_2PPh_2\}]$ was treated with 4 equiv. of $LiBu^n$ followed by methyl iodide to give dimethylated complex $[W(CO)_3\{\eta^3\text{-}PPh_2CH(Me)C(Bu^t){=}N\text{-}N{=}C(Bu^t)CH(Me)PPh_2\}]$.[326] The μ-N_2 dinuclear complex $[\{W(CO)_3(P^iPr_3)_2\}(\mu\text{-}N_2)]$ was obtained by the reaction of $[W(CO)_3(P^iPr_3)]$ and N_2.[225] The Schiff base tungsten(0) compound *mer*-$[W(CO)(L)]$ ($L = Ph_2PC_6H_4CHNC_6H_4PPh_2$, Scheme 17) mentioned in Section 4.8.6.2.2 was prepared from the ligand and *cis*-$[W(CO)_4(pip)_2]$.[197,317]

The compound *cis*-$[PNP][(CH_3)W(CO)_4(PMe_3)]$ was prepared by the alkylation of $Na_2[W(CO)_4(PMe_3)]$ by methyl tosylate followed by addition of [PNP][tosylate]. The phosphine ligand expedited CO_2 insertion into the W—C bond.[327] The bimetallic compounds containing 1,4-diisocyanatobenzene as a bridging ligand $[\{W(CO)_4(PR_3)\}_2(\mu\text{-}CNC_6H_4NC)]$ were prepared by the reaction of the bridging ligand and $(Et_4N)[W(CO)_4(PEt_3)Cl]$.[328] Aromatic isocyanide *p*-RC_6H_4NC reacted with *trans*-$[W(dppe)_2(N_2)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane) to produce *cis*- or *trans*-$[(p\text{-}C_6H_4NC)_2W(dppe)_2]$ depending on the R group. Subtle differences of π-acidity or steric repulsion determine the structure. The ligands CNC_6H_4NC, $CF_3C_6H_4NC$, $NO_2C_6H_4NC$ and *p*-$CNC_6H_2(CH_3)_2NC$ give *cis*-isomers while FC_6H_4NC, $CH_3C_6H_4NC$, and *p*-$CNC_6(CH_3)_4NC$ afforded *trans*-isomers.[329]



Scheme 23

The first structure of isolable H_2 tungsten complex *mer,trans*-$[W(CO)_3\{P\text{-}(i\text{-}Pr)_3\}_2(\eta^2\text{-}H_2)]$ shows slightly longer H—H distance than free H_2. The complex was prepared readily and cleanly by the reaction of $[W(CO)_3\{P(i\text{-}Pr)_3\}_2]$ with hydrogen (1 atm).[330] ^1H NMR spectra indicated dynamic equilibrium between the H_2 complex $[W(CO)_3\{P\text{-}(i\text{-}Pr)_3\}_2(\eta^2\text{-}H_2)]$ and dihydride complex $[W(H)_2(CO)_3\{P\text{-}(i\text{-}Pr)_3\}_2]$.[227] The structure of $[N(PPh_3)_2][W(CO)_4(H)\{P(OMe)_3\}_3]$ [331] indicated *cis* arrangement of the hydride and phosphine ligands.[332]

4.8.8.4.3 *Complexes containing nitrogen*

Monomeric and dimeric pyridine compounds containing alkyne moiety have been reported. The ligands 1,4-bis(4′-pyridylethynyl)benzene, ferrocenyl-4-pyridylacetylene, (4-nitorphenyl)-4′-pyridylacetylene, 4,4′-dipyridylbutadiene reacted with $[W(CO)_4(L)]$ (L = CO, PEt_3, PPh_3, $P(OEt)_3$, $P(OPh)_3$ to give the required complexes. The coordinated pyridine groups were found at *cis* position to L.[333] Treatment of 1,2,3,4λ^5-triazaphosphinine with $[W(CO)_5(pip)]$ (pip = piperadine) gave a five-membered cyclophosphazene bonded to $[W(CO)_5(pip)]$ via hydrogen bond.[334] The formally 16-electron compound $(Et_4N)_2[W(CO)_3(OC_6H_4\text{-}2\text{-}NH)]$ and $(Et_4N)_2[W\ (CO)_3(NHC_6H_4\text{-}2\text{-}NH)]\cdot(NH_2C_6H_4NH_2)$ were produced by the reaction of $[W(CO)_5(thf)]$ and $(Et_4N)\ [OC_6H_4\text{-}2\text{-}NH]$ with subsequent deprotonation by $(Et_4N)OH$ and the reaction between $[W(CO)_5(thf)]$ and 2 equiv. of $(Et_4N)[NH_2C_6H_4NH_2]$. These compounds exhibited trigonal bipyramidal geometry. The coordinatively and electrochemically unsaturated tungsten(0) complexes were stabilized by π-donating amido ligands.[335] The tungsten(0) complex of 1,3,5-tri-*tert*-butyl-1,3,5-triazacyclohexane (t-Bu_3tach) was obtained by the photolysis of $[W(CO)_6]$ in the presence of the ligand. The reaction of 2-aminopyridine (2PAH) with $[W(CO)_5(thf)]$ afforded $[W(CO)_5(2APH)]$. Deprotonation of the complex by NaH gave dimeric $Na_2[W(CO)_4(\mu\text{-}2AP)]_2$ and monomeric $[Na_2(18\text{-crown-}6)][W(CO)_5(\eta^1\text{-}2AP)]$.[336] The compound *fac*-$[W(CO)_3(tbtach)]$ exhibit piano-stool conformation, which is similar to $[WO_3(t\text{-}Bu_3tach)_3]$ as shown in Figure 8.[337] The reaction of $[W(CO)_4(pip)_2]$ (pip = piperidine) with 2,6-bis[(4S)-isopropyloxazolin-2-yl] (L) yields *cis*-$[W(CO)_4(L)]$. The ligand coordinates η^2 to tungsten ion by one N of pyridine and one N of oxazoline. The ^1H NMR spectra showed the presence of fluxional rearrangement by exchange of the two N atoms of the oxazoline.[338]

4.8.8.4.4 *Complexes containing carbon groups*

The tetranuclear tungsten(0) compound containing diatomic Pb_2^{2-} ligand $(Ph_4P)_2[\{W(CO)_5\}_4Pb_2]$ was produced by the reaction of $K_2[W_2(CO)_{10}]$ and $Pb(NO_3)_2$. A schematic drawing of the molecular structure is shown in Figure 31. The Pb—Pb distance of 2.816(8) Å is short.[339]

Salts of $[Ph_3SnW(CO)_5]^-$ are quite stable and readily prepared by the reaction of $Na_2[W(CO)_5]$ and Ph_3SnCl or $(Et_4N)[ClW(CO)_3]$ and $LiSnPh_3$. The compound was also prepared from Ph_3SnOH and $[PPN][HW(CO)_5]$ accompanying the production of water. The isolated complex exhibits octahedral structure.[340] The octahedral compound $[(CO)_5W\{SnCl_2(thf)_2\}]$[341] reacted with $[Fe(CO)_4]^{2-}$ to afford $[Na_2(OEt_2)_4(thf)][\{W(CO)_5Sn(Cl)[Fe(CO)_4]\}_2]$. The $[W(CO)_5]$ moieties are bridged by Sn atoms of dimeric $[\{Fe(CO)_4\}_2(\mu\text{-}SnCl)_2]$. The carbonyl groups of the anion interact with Na ion of the cation resulting 2-dimensional sheet.[342]

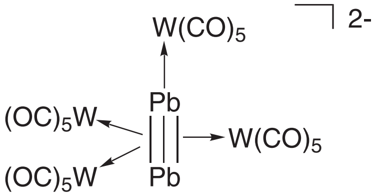


Figure 31 Schematic drawing of $(Ph_4P)_2[\{W(CO)_5\}_4Pb_2]$.

The crystal structure of $[PPN][W(CO)_5(SiMe_3)]$ indicates octahedral geometry. This compound was obtained by the reaction of $Na_2W(CO)_5$ and trimethylsilyl chloride. While the complex is inert toward CO_2, the insertion of SO_2 into W—Si bond was occurred resulting $[PPN][W(CO)_5\text{-}SO_2SiMe_3]$.[343]

The cyanide-bridged compound $[(CO)_5W(CN)Cu(PPh_3)_3]$ was produced by the reaction of $Na[W(CO)_5(CN)]$ with $[Cu(CH_3CN)_4]BF_4$ and PPh_3. The analogous isocyanide-bridging compound $[(CO)_5W(NC)Cu(PPh_3)_3]$ was prepared by the addition of $[Cu(CN)(PPh_3)_3]$ to $[W(CO)_5(thf)]$ at −78 °C, which was slowly converted to the rearranged cyanide-bridging compound.[344]

Photochemical reaction of $W(CO)_6$ in the presence of $B_2H_4{\cdot}2PMe_3$ gave $[W(CO)_5(\eta^1\text{-}B_2H_4{\cdot}2PMe_3)]$ and $[W(CO)_4(\eta^2\text{-}B_2H_4{\cdot}2PMe_3)]$ as shown in Figure 32. Both compounds indicate the presence of W—H—B linkage that is a three-center two-electron bond.[345] Analogous reaction in the presence of $BH_3{\cdot}PR_3$ (R = Me, Ph) or $BH_3{\cdot}NMe_3$ afforded $[W(CO)_5(\eta^1\text{-}BH_3{\cdot}PR_3)]$ or $[W(CO)_5(\eta^1\text{-}BH_3{\cdot}NMe_3)]$, respectively. The determined structure is shown in Figure 32(c).[346]

4.8.9 MIXED VALENCE COMPLEXES

4.8.9.1 W^{VI} and W^{V} Mixed Complexes

The nitride-bridged complex $(PClMePh_2)_2[\{W_2(N)Cl_9\}_2]$ contains formally tungsten(VI) nitride $[W(N)Cl_4]^-$ and neutral tungsten(V) fragment WCl_5 as shown in Figure 33. Two distinct W—N bonds were found in the crystal structure, one is triple bond (1.682(10) Å) and the other is single bond (2.050(10) Å) with almost linear WNW angle (177.6(6)°). This compound was prepared by the reaction of WCl_6 and $Me_3SiNPMePh$ while the reaction WCl_6 and Me_3SiNPh_3 afforded $[W(NPPh_3)Cl_5]$ in high yield.[24]

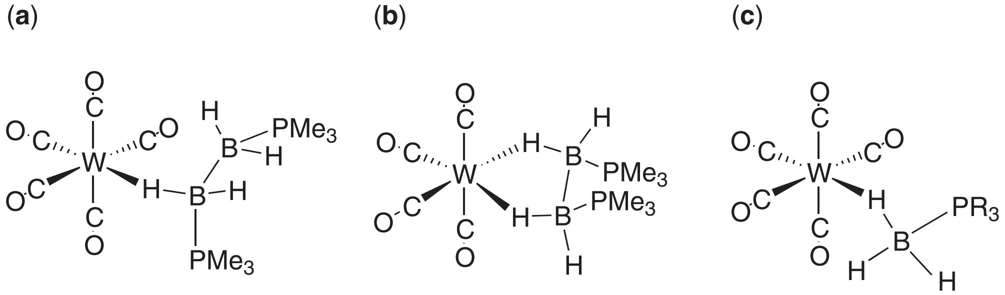


Figure 32 Schematic drawing of (a) $[W(CO)_5(B_2H_4{\cdot}2PMe_3)]$, (b) $[W(CO)_4(B_2H_4{\cdot}2PMe_3)]$ and (c) $[W(CO)_5(BH_3{\cdot}PR_3)]$ (R = Me, Ph).

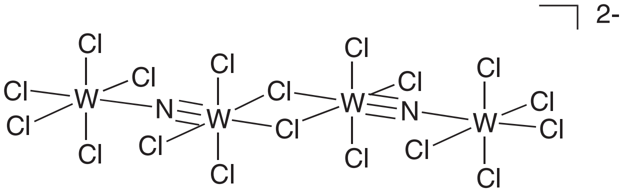


Figure 33 Mixed-valence W^{VI}-W^{V} nitride-bridged complex $(PClMePh_2)_2[\{W_2(N)Cl_9\}_2]$.

4.8.9.2 W^{VI} and W^{IV} Mixed Complexes

The mixed valence tungsten complexes containing VI and IV are rare. The compound $[\{HB(Me_2pz)_3\}W^{VI}O_2(\mu\text{-}O)W^{IV}O(CO)\{HB(Me_2pz)_3\}]$ ($HB(Me_2pz)_3$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate)) was formed upon oxidative hydrolysis of $(NEt_4)[\{HB(Me_2pz)_3\}W(CO)_3]$. The *cis*-dioxo-$W^{VI}$ moiety observed in this complex is a common feature in W^{VI} chemistry.[47]

4.8.9.3 W^{IV} and W^{III} Mixed Complexes

The hemicapped structure was found in $[W_3(\mu_3\text{-}O)(O_2CCH_3)_6(H_2O)_3][ZnBr_4]\cdot 8H_2O$ as shown in Figure 34. The complex was obtained as a by-product in the preparation of the well-known $[W_3(\mu_3\text{-}O)_2(O_2CCH_3)_6(H_2O)_3]^{2+}$ cation from $W(CO)_6$, acetic acid and acetic anhydride in a very low yield after separation by cation-exchange column. The W—W distances (mean 2.710(4) Å) are longer in comparison to the corresponding bicapped compounds. The W—(μ_3-O) distance is similar to the bicapped compounds. The formal oxidation number is 10/3 (average).[347] The improved preparation procedure employed $Na_2WO_4\cdot 2H_2O$ instead by $W(CO)_6$ and granular zinc as reductant. The resultant $[W_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(H_2O)]^{2+}$ was refluxed in methanol to give $[W_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_5(\mu\text{-}OCH_3)(H_2O)]^{2+}$, which was isolated $[ZnCl_4]^{2-}$ salt.[348] The dimeric tungsten(III/IV) complex $[(Me_2S)Cl_2W(\mu\text{-}Cl)(\mu\text{-}SPh)_2WCl_2(SMe_2)]$ was prepared by the reaction of $[WCl_4(SMe_2)_2]$ and exact 1 equiv. of $SiMe_3(SPh)$. The obtained very air-sensitive compound was treated with Ph_4AsCl to afford $(Ph_4As)_2[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SPh)_2WCl_3]\cdot 1.4(CH_2Cl_2)$ as crystals.[349] Analogous W^{III}–W^{IV} compound $(Ph_4P)_2[Cl_3W(\mu\text{-}Cl)(\mu\text{-}SePh)_2WCl_3]$ was cocrystallized in the crystal of W^{IV}–W^{IV} compound $(Ph_4P)_2[Cl_3W(\mu\text{-}Se)(\mu\text{-}SePh)_2WCl_3]\cdot 2CH_2Cl_2$. Both complexes were obtained as a mixture by the reaction of $WCl_4(SMe_2)_2$ and $Me_3SiSePh$ followed by addition of PPh_4Cl. The ESR spectra of the single crystal indicate the presence of paramagnetic species in a diamagnetic matrix.[350]

4.8.10 METAL-COORDINATED COMPLEXES

4.8.10.1 Clusters

The reaction of $[PPN]_2[Fe_3(CO)_{11}]$ with $Cr(CO)_3(CH_3CN)$ afforded $[PPN]_2[FeW(CO)_{14}]$ with pseudotetrahedral Fe_3W core.[351] Tungsten-centered gold cluster $[W(CO)_4(AuPPh_3)_5](PF_6)$ and $[W(CO)_3(AuPPh_3)_7](PF_6)$ were prepared by the reaction of $[Au(PPh_3)(AuPPh_3)_7](PF_6)_2$ with $[W(CO)_3(C_2H_5CN)_3]$. The former complex reacted with 1 equiv. of $AuPPh_3NO_3$ to give $[W(CO)_4(AuPPh_3)_6](NO_3)_2$.[352]

4.8.10.2 Linear and Binuclear Complexes

The reaction of $[(n\text{-}Bu)_4N][\{HB(pz)_3\}(CO)_2W(CS)]$ with $ClAuPPh_3$ afforded $[\{HB(pz)_3\}(CO)_2(CS)WAu(PPh_3)]$, which have a semibridging CO and a semibridging CS. The W—C—O (173.4(7)°) and W—C—S 165.9(5)°) are bent.[353]

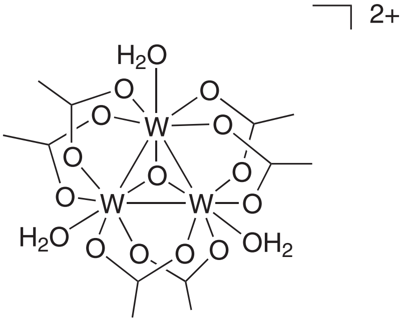


Figure 34 Hemicapped trinuclear structure in $[W_3(\mu_3\text{-}O)(O_2CCH_3)_6(H_2O)_3][ZnBr_4]\cdot 8H_2O$.

The 18-electron compound $[Os(CO)_4(PMe_3)]$ acts as a donor ligand to $W(CO)_5$ unit in $[W(CO)_5(thf)]$ to produce $[(Me_3P)(OC)_4OsW(CO)_5]$ without any bridging ligand, which was established by X-ray analysis. The Os—W bond length is 3.0756(5) Å.[354] Similar compound $[(L)(OC)_4OsW(CO)_5]$ ($L = P(OCH_2)_3CMe$) reacted with $[Os(CO)_4(L)]$ to give linear (Os—Os—W = 172.07(4)°) $[(OC)_3(L)_2OsOs(CO)_4W(CO)_5]$ having two dative bonds Os—Os (2.940(1) Å) and Os—W (3.039(1) Å).[355] Analogous tandem structure with isonitrile $[(OC)_4(Bu^t NC)OsOs(CO)_3(CNBu^t)W(CO)_5]$ was successfully determined.[356]

The reaction of $(Et_4N)[HFe(CO)_4]$ and $[W(CO)_5(thf)]$ gave $(Et_4N)[HFeW(CO)_9]$, which was treated with $(Et_4N)OH$ to yield $(Et_4N)_2[FeW(CO)_9]$. This complex reacted with Ph_3PAuCl to afford $(Et_4N)[Ph_3PAuFeW(CO)_9]$ where Au—Fe—W bond is bent (82.7(1)°).[357] The related compounds, $[PPN][HFeW(CO)_9]$ and $[PPN][(OC)_3\{(MeO)_3P\}Fe(H)W(CO)_5]$, were characterized structurally, where the phosphorus atom is *trans* to W.[358]

$K_2[W(CO)_5]$ reacted with $EXCl_2$ (E = Al, Ga; X = Cl, Et, ^iBu) followed by addition of chelating Lewis base, e.g., tmeda (*N,N,N'N'*-tetramethylethylenediamine) and tmpda (*N,N,N',N'*-tetramethylpropylenediamine), to yield neutral compound with a W—E bond $[(OC)_5WE(X)(L)]$ (L = tmeda, tmpda). The structures $[(CO)_5WAl(Et)(tmeda)]$ and $[(CO)_5WAl(Cl)(tmpda)]$ were determined by X-ray analysis.[359]

4.8.11 REFERENCES

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4.9
Dinuclear Metal–Metal Bonded Systems

J. L. EGLIN
Los Alamos National Laboratory, New Mexico, USA

4.9.1 INTRODUCTION

Dinuclear group 3–6 metal–metal bonded systems encompass a wide range of compounds with a variety of ligand types. With the use of innovative starting materials or novel synthetic methods, the number of new complexes continues to expand. Several general trends are apparent for known metal–metal bonded systems of group 3–6. The number of metal–metal bonded complexes increases as one moves across the periodic table from group 3 to group 6. Sulfur-based ligands tend to dominate in higher oxidation state complexes, while nitrogen, phosphorus, and oxygen are more common for lower oxidation states. Overall, cyclopentadienyl ligands play a significant role in the design of metal–metal bonded complexes regardless of the oxidation state.

The present review of metal–metal bonded systems focuses primarily on complexes that are supported by structural evidence. Information for group 6 compounds concentrates on complexes synthesized since 1990. Although several organometallic complexes are discussed, their inclusion is primarily a result of either their use as a starting material or an unusual oxidation state or structure.

Metal–metal bonded dinuclear complexes are absent for the group 3 metals scandium, yttrium, and lanthanum while dititanium chemistry is truly in its infancy.

4.9.2 DITITANIUM COMPLEXES

Dititanium(III, III) edge-sharing bioctahedral complexes have been synthesized from $TiCl_4$ using formamidinate ligands to result in $Ti_2(\mu\text{-}Cl)_2(\mu\text{-}H_5C_6NC(H)NC_6H_5)_2(H_5C_6NC(H)NC_6H_5)_2$ and $Ti_2(\mu\text{-}Cl)_2(\mu\text{-}H_9C_{12}NC(H)NC_{12}H_9)_2(H_9C_{12}NC(H)NC_{12}H_9)_2$.[1] With Ti—Ti bond lengths of 2.890(8) Å and 2.916(3) Å respectively, the formamidinate ligands both chelate to the titanium metal centers and bridge the dinuclear core. Other researchers have successfully investigated the use of $TiCl_3(THF)_3$, $Ti_2Cl_6(THF)_4$, and $TiCl(tmeda)_2$, where tmeda is *N,N,N′,N′*-tetramethylethylenediamine, as starting materials in the synthesis of the dicyclohexylformamidinate derivative, $Ti_2(\mu\text{-}Cl)_2(\mu\text{-}H_{10}C_6NC(H)NC_6H_{10})_2(H_{10}C_6NC(H)NC_6H_{10})_2$ with a Ti—Ti bond length of 2.942(2) Å.[2]

A few unrelated complexes with $Ti_2^{II,III}$ mixed oxidation states are known. Addition of two equivalents of C_3H_5MgCl in toluene to $TiCl_4(dmpe)$, where dmpe is $(CH_3)_2PCH_2CH_2P(CH_3)_2$, at low temperature results in the formation of the mixed valent species $Ti_2(\mu\text{-}Cl)_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ shown in Figure 1.[3] The allyl ligand symmetrically bridges the two titanium centers with Ti—C bond lengths to the terminal carbons of 2.154(6) Å and a Ti—Ti bond length of 2.908(1) Å. The mixed valence hydride complex (η^5-indenyl)Ti(μ-indenyl)(μ-H)$_2$Ti(η^5-indenyl) has a Ti—Ti bond length of 2.745 Å, averaged from the two geometries with the terminal indenyl ligands in either the *syn* or *anti* positions.[4]

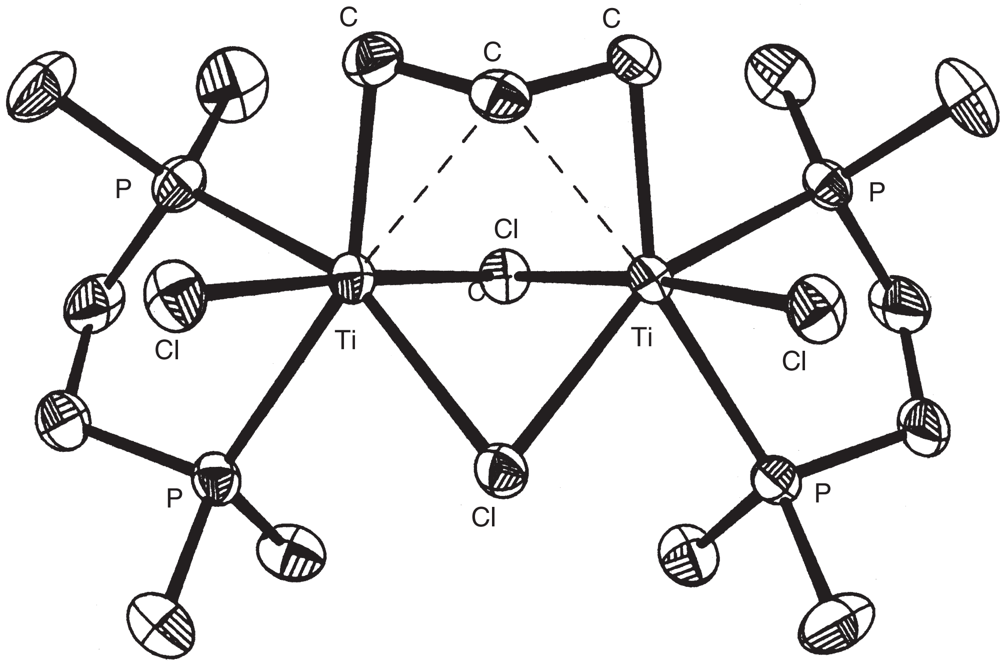


Figure 1 ORTEP drawing of $Ti_2(\mu\text{-}Cl)_2Cl_2(dmpe)_2(\mu^2\text{-}\eta^3\text{-}C_3H_5)$ (reproduced by permission of Elsevier Science from *J. Organomet. Chem.* **2000**, *593–594*, 1–6).

While predominantly coordinated by cyclopentadienyl ligands, the molecular structure of $(\eta^5\text{-}C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O){\cdot}C_4H_8O$ provides an example of a Ti—Ti bond (3.336(4) Å) containing a coordinated tetrahydrofuran ligand with the structure shown below in Figure 2.[5] The basic synthetic pathway, reduction of a Ti^{II} mononuclear complex, is repeated for the synthesis of the compound $[(2,6\text{-}(C_6H_5)_2C_6H_3O)_2Ti(\mu\text{-}Cl)_2Ti(OC_6H_3(C_6H_5)_2\text{-}2,6)_2]$ upon the sodium amalgam reduction of $Ti(OC_6H_3(C_6H_5)_2\text{-}2,6)_2Cl_2$ where $OC_6H_3(C_6H_5)_2\text{-}2,6$ is 2,6-diphenylphenoxide.[6] The core structure is described as an edge-sharing *bis*-tetrahedron with a Ti—Ti bond length of 2.9827(7) Å.

4.9.3 DIZIRCONIUM COMPLEXES

Metal–metal bonds between zirconium atoms are limited effectively to $Zr_2^{III,III}$ species, with coordination spheres primarily composed of phosphine ligands and halide atoms. In $Zr_2^{III,III}$ compounds, one of the critical characteristics of the Zr—Zr σ^2 bond is the resulting diamagnetism of these complexes. *Ab initio* self-consistent field/configuration interaction calculations indicate that a significant metal–metal bonding interaction is present at Zr—Zr distances greater than 3.5 Å for $[ZrCl_3(PH_3)_2]_2$ and $[(\eta^5\text{-}C_5H_5)_2Zr(\mu\text{-}PH_2)]_2$.[7] The first example of an edge-sharing bioctahedral $Zr_2^{III,III}$ complex was reported in 1981, $[ZrCl_3(PBu_3)_2]_2$.[8] The Zr—Zr bond length in this compound is 3.182(1) Å, and the general preparative route to $[ZrCl_3L_2]_2$ complexes, where L is a monodentate phosphine ligand is shown in Equation (1).

$$\mathrm{ZrCl_4 + 2\,L} \xrightarrow[\mathrm{Na/Hg}]{\mathrm{toluene}} \mathrm{0.5[ZrCl_3L_2]_2} \tag{1}$$

$$\mathrm{L = PMe_3,\ PEt_3,\ PPr_3,\ PBu_3}$$

The basic synthetic method has been expanded to include both the synthesis of $[ZrBr_3L_2]_2$ and $[ZrI_3L_2]_2$ compounds and the use of bidentate phosphine ligands. There is a significant variation in the metal–metal bond lengths observed for these complexes with a lengthening of the Zr—Zr bond length with an increase in the size of the bridging halide; Cl through I. A representative structure, $Zr_2I_6(P(CH_3)_3)_4$,[9] is shown in Figure 3 with two bridging halides and the phosphine ligands in the plane of the bridging halides. In the following series, the Zr—Zr distances for the structurally characterized complexes are $Zr_2Cl_6(P(CH_3)_3)_4$ (3.132(1) Å),[1] $Zr_2Cl_6(P(CH_2CH_3)_3)_4$ (3.169(1) Å),[10] $Zr_2Cl_6(P(CH_3)_2(C_6H_5))_4$ (3.127(1) Å),[10] $Zr_2Br_6(P(CH_3)_3)_4$ (3.200(1) Å),[11] $Zr_2I_6(P(CH_3)_3)_4$ (3.393(2) Å),[9] and $Zr_2I_6(P(CH_3)_2(C_6H_5))_4$ (3.490(6) Å).[9]

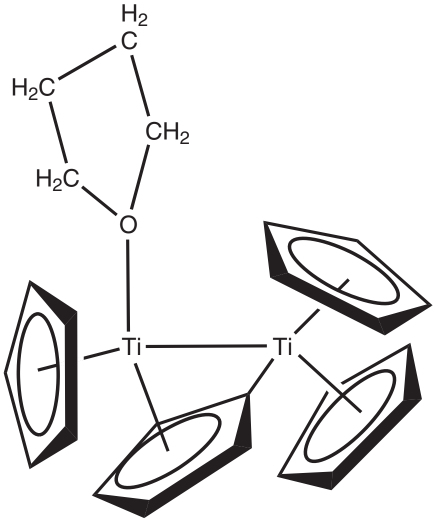


Figure 2 Drawing of the bonding in $(\eta^5\text{-}C_5H_5)_3(C_5H_4)Ti_2(C_4H_8O)\cdot C_4H_8O$.

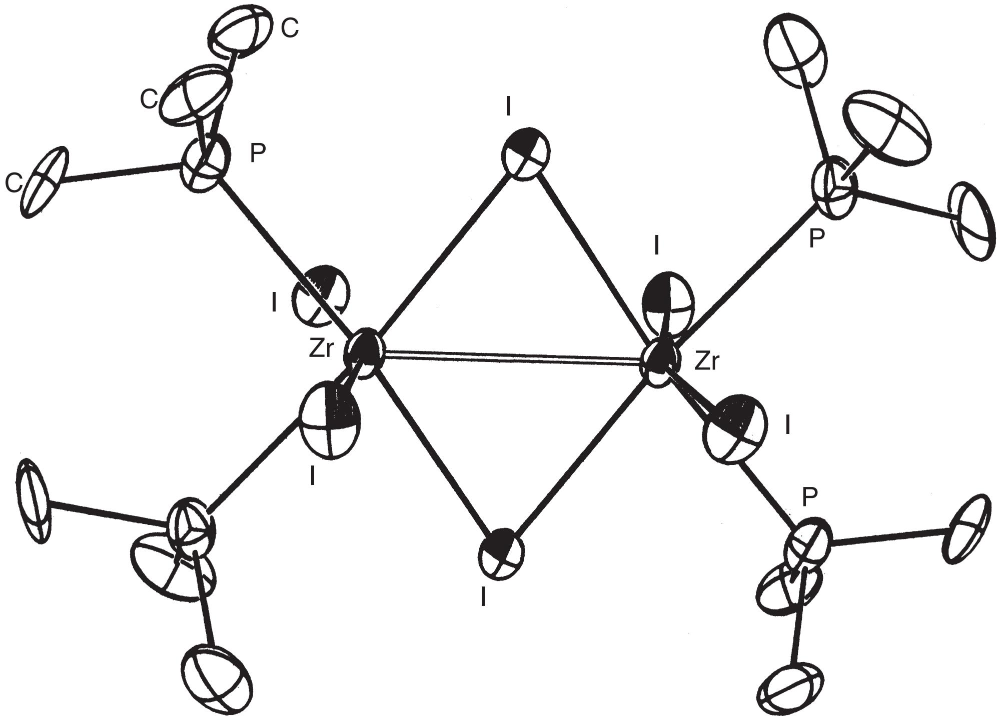


Figure 3 ORTEP drawing of $Zr_2I_6(P(CH_3)_3)_4$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1991**, *30*, 3670–3675).

There are few exceptions in zirconium/phosphine compounds to the basic $[ZrCl_3L_2]_2$ structural motif. The presence of the chelating phosphine ligand dppe [bis(diphenylphosphino)ethane] in a toluene solution of $ZrCl_4$ results in the formation of the green compound, $Zr_2Cl_6(dppe)_2{\cdot}2C_2H_4Cl_2{\cdot}1.5C_6H_5CH_3$, upon addition of dichloroethane.[10] Two independent dinuclear molecules are present in the unit cell with Zr—Zr bond lengths of 3.099(2) Å and 3.109(2) Å, respectively. The chelating phosphine ligand forms a puckered 5-membered ring; ZrP_2C_2. The related compound $Zr_2Cl_6(dippe)_2$ where dippe is $(Pr^i)_2PCH_2CH_2P(Pr^i)_2$ has been synthesized, but not characterized structurally.[12]

Using $HSn(^nBu)_3$ as the reducing agent, the face-sharing bioctahedral compound $[NBu_4][Zr_2I_7(P(CH_2CH_3)_3)_2]$ is prepared in low yield from reduction of ZrI_4 followed by the subsequent addition of $P(CH_2CH_3)_3$ and $[NBu_4]I$.[13] The Zr—Zr bond length of 3.171(3) Å is significantly shorter than the edge-sharing bioctahedral complexes with bridging iodides.

Another significant area of research in zirconium chemistry is the use of cyclopentadienyl ligands in the synthesis of dinuclear complexes.[14–18] However, only the fulvalene zirconium(II) derivative shown in Figure 4, $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2$ contains a Zr—Zr bond.[19] $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2$ (3.233(1) Å] results from the comproportionation reaction between Zr^{IV} and Zr^{II} reagents, $(\eta^5\text{-}C_5H_5)_2ZrCl_2$ and $(\eta^5\text{-}C_5H_5)_2Zr[P(CH_3)_3]_2$.

4.9.4 DIHAFNIUM COMPLEXES

Metal–metal bonded complexes of dihafnium are similar to dizirconium complexes in regard to both the ligand types used in the synthesis and the structural geometry of the resultant complexes. Compounds have been synthesized from the reduction of the Hf^{IV} halide with Na/Hg amalgam in toluene and the addition of monodentate or bidentate phosphine ligands.[9,12,20] Rather surprisingly, the first compound containing a Hf—Hf bond was not identified until 1990[20] and there remains only a handful of structurally characterized complexes. The structure of the olive–green diamagnetic crystals of $Hf_2Cl_6(P(CH_3)_2(C_6H_5))_4$ contains a Hf—Hf bond length of 3.0886(3) Å,[20] 0.038 Å shorter than the Zr—Zr analog, $Zr_2Cl_6(P(CH_3)_2(C_6H_5))_4$.[10] As in the case of the $Zr_2^{III,III}$ analogs, there is an increase in the Hf—Hf bond length with an increase in the size of the bridging halide, chloride versus iodide. The phosphorus atoms are found to lie in the same plane as the

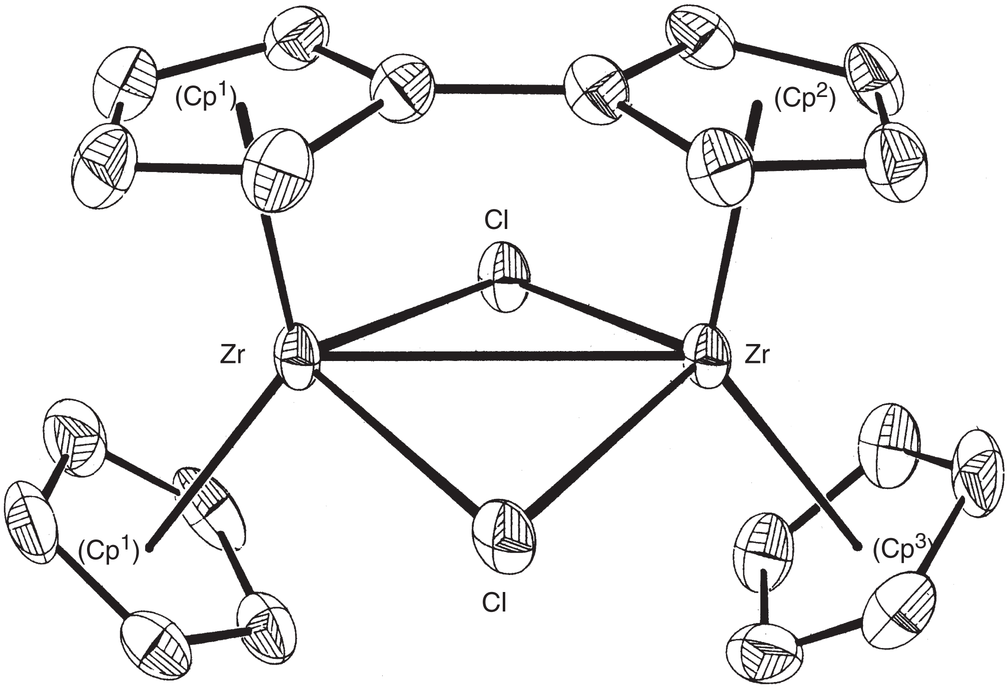


Figure 4 ORTEP drawing of $(\eta^5{:}\eta^5\text{-}C_{10}H_8)[(\eta^5\text{-}C_5H_5)Zr(\mu\text{-}Cl)]_2$ (reproduced by permission of the American Chemical Society from *Organometallics* **1987**, *6*, 897–899).

bridging halides in these edge-sharing bioctahedral structures. For $Hf_2I_6(P(CH_3)_2(C_6H_5))_4$, the Hf—Hf bond length increases from the chloro analog to 3.3948(6) Å with the structure shown in Figure 5.[9] The highest yield synthesis of a $Hf_2^{III,III}$ complex is $Hf_2Cl_6(dippe)_2$, 57%.[12] In contrast to the synthesis of the monodentate phosphine analogs where the phosphine ligand is added 24 hrs after Na/Hg reduction, the bidentate phosphine ligand is present in the suspension of $HfCl_4$ upon addition of the amalgam.[12]

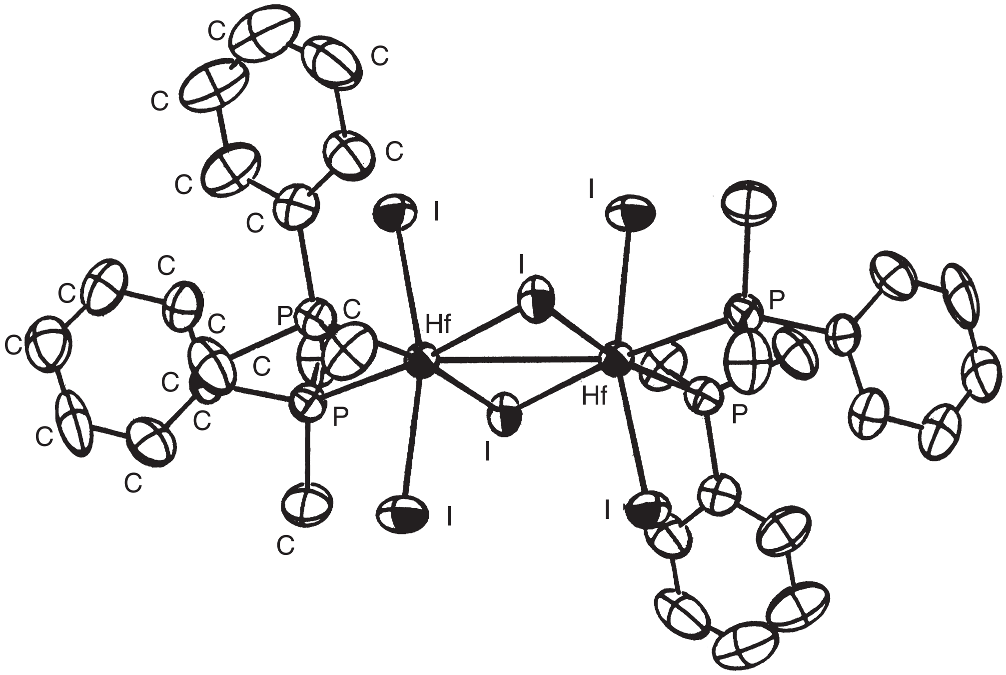


Figure 5 ORTEP drawing of $Hf_2I_6(P(CH_3)_2(C_6H_5))_4$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1991**, *30*, 3670–3675).

4.9.5 DIVANADIUM COMPLEXES

4.9.5.1 $V_2^{IV,IV}$ Complexes

Unlike group 4 dinuclear metal complexes, metal–metal bonded divanadium complexes span a wide range of oxidation states and ligand types. McCarley presents a nice literature review of dinuclear vanadium(IV) complexes with two single-atom bridges, but only a handful with V—V bond lengths between 2.459 Å and 2.970 Å possess metal–metal single bonds.[21] One of the high-oxidation-state examples is the $V_2^{IV,IV}$ diamagnetic complex $V_2(\mu\text{-N}^t\text{Bu})_2(\eta^2\text{-CH}_2\ (2,4\text{-}(CH_3)_2C_6H_2)CH_2N^t\text{Bu})_2$ with a vanadium—vanadium single bond, 2.460(1) Å.[22] A weak V—V bond is present in the dark green compound $V_2(\mu\text{-O})_2[N(Si(CH_3)_3)_2]$ (2.612(2) Å)[21] with two bridging oxides. $V_2(\mu\text{-O})_2[N(Si(CH_3)_3)_2]$ is synthesized by the reduction of vanadyl trichloride upon addition of $LiN(Si(CH_3)_3)_2$. The deep red sulfur analog, $V_2(\mu\text{-S})_2[N(Si(CH_3)_3)_2]$,[23] is synthesized by a slightly different route: the addition of S_8 to a suspension of $[((CH_3)_3Si)_2N]_2VCl(THF)$. The structure of $V_2(\mu\text{-S})_2[N(Si(CH_3)_3)_2]$ with a distorted tetrahedral geometry at the vanadium core is shown in Figure 6 and contains a V—V bond length of 2.857(1) Å.

Sulfur-based ligands play a more dominant role in $V_2^{IV,IV}$ complexes. A weak metal–metal bond is proposed in the structure of $[V_2(\mu\text{-}\eta^2\text{-S}_2)_2(CS_3)_4]^{4-}$ (2.8720(59) Å).[24] Similar $V_2(\mu\text{-}\eta^2\text{-S}_2)_2$ core structures are observed in the analogous compounds $V_2(\mu\text{-}\eta^2\text{-S}_2)_2((CH_3CH_2)_2NCS_2)_4$ (2.884(4) Å),[25] $V_2(\mu\text{-}\eta^2\text{-S}_2)_2(CH_3CS_2)_4$ shown in Figure 7 (2.800(2) Å),[26] and $V_2(\mu\text{-}\eta^2\text{-S}_2)_2({}^i\text{Bu}_2NCS_2)_4$ (2.851(1) Å).[27] This series of structural analogs is the product of a surprising variety of synthetic methods: $V_2(\mu\text{-}\eta^2\text{-S}_2)_2(CH_3CS_2)_4$[26] is synthesized from $(\eta^6\text{-C}_6H_6)_2V$ and dithioacetic acid in 56% to 62% yields while $V_2(\mu\text{-}\eta^2\text{-S}_2)_2({}^i\text{Bu}_2NCS_2)_4$[27] results from the treatment of a $(NH_4)_3VS_4$ solution with tetraisobutylthiuram disulfide in 22% yield.

Further investigations of synthetic routes to the $V_2(\mu\text{-S})_2(\mu\text{-}\eta^2\text{-S}_2)$ core resulted in a complex containing a vanadium—vanadium single bond, $(\eta^5\text{-C}_3H_7C_5H_4)_2V_2(\mu\text{-S})_2(\mu\text{-}\eta^2\text{-S}_2)$, from the mononuclear starting material $(\eta^5\text{-C}_3H_7C_5H_4)_2V_2Cl_2$.[28] The $V_2^{IV,IV}$ bond length of 2.610(1) Å shortened

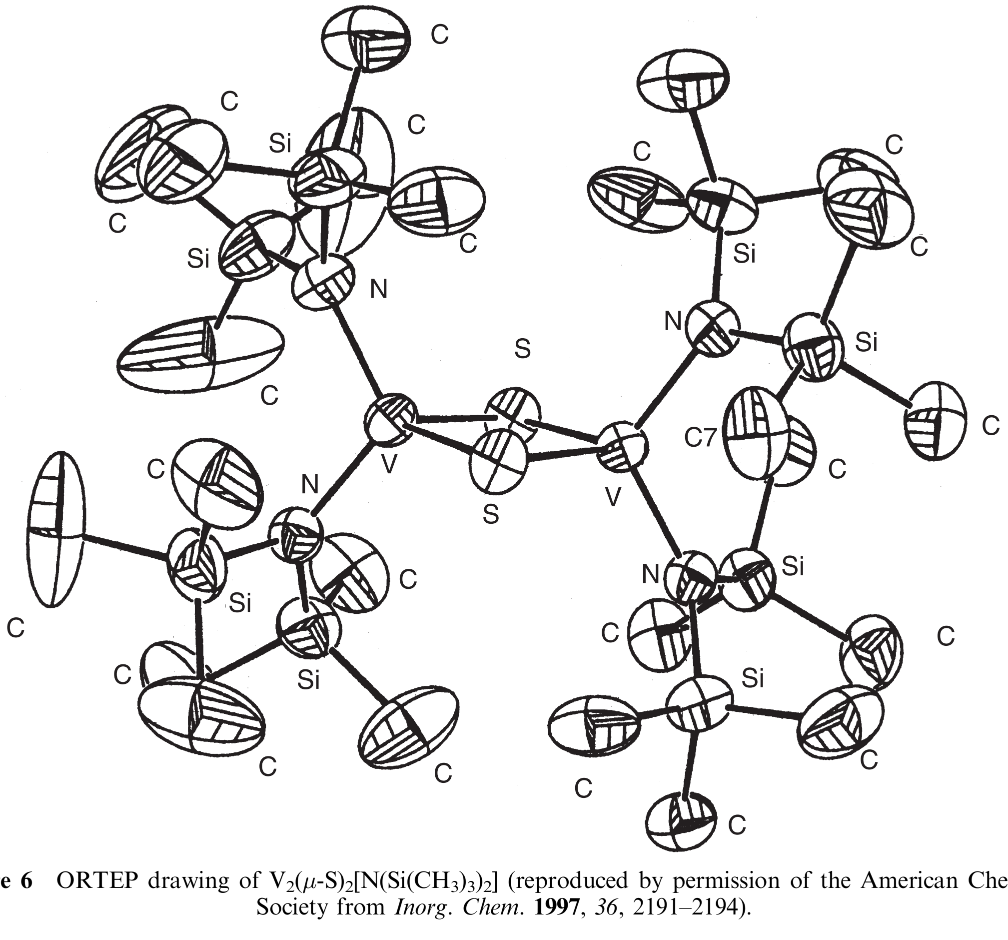


Figure 6 ORTEP drawing of $V_2(\mu\text{-S})_2[N(Si(CH_3)_3)_2]$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1997**, *36*, 2191–2194).

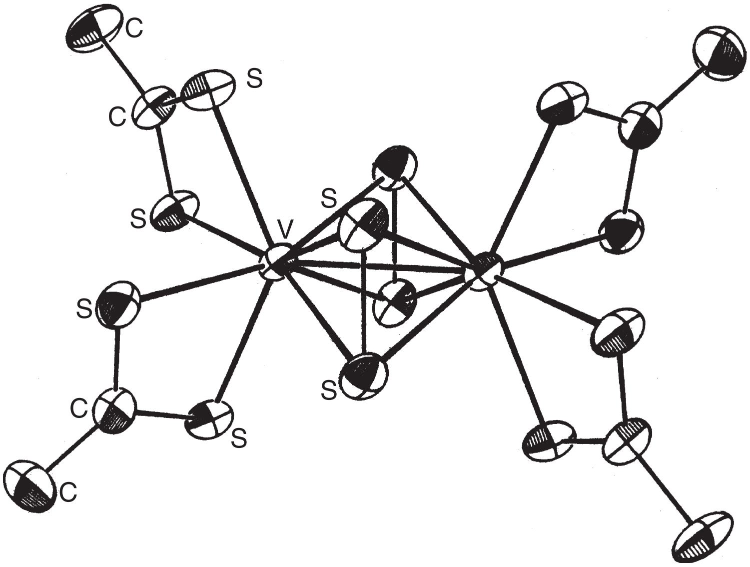


Figure 7 ORTEP drawing of the molecule $V_2(\mu-\eta^2-S_2)_2(CH_3CS_2)_4$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1990**, *29*, 1232–1234).

to 2.574(3) Å upon addition of hexafluoro-2-butyne in the synthesis of the dark green complex $(\eta^5-C_3H_7C_5H_4)_2V_2(\mu-\eta^2-S_2C_2(CF_3)_2)(\mu-\eta^2-S_2)$. A related selenium derivative with a $V_2^{IV,IV}$ core synthesized from the reaction of $(\eta^5-CH_3C_5H_4)_2V_2Cl_2$ with H_2Se is shown in Figure 8.[29] The V—V bond length in $(\eta^5-CH_3C_5H_4)_2V_2(\mu-Se)(\mu-\eta^2-Se_2)(syn-\mu-Se_2)$ of 2.779(4) Å is elongated in comparison to the sulfur derivative, $(\eta^5-CH_3C_5H_4)_2V_2(\mu-S)(\mu-\eta^2-S_2)(syn-\mu-S_2)$ (2.658(1) Å).[30]

4.9.5.2 $V_2^{III,III}$ Complexes

The vanadium—vanadium bond length in the organometallic complex $(\eta^5-C_5H_5)_2V_2(C_4H_8)_2$ (Figure 9) of 2.315(1) Å is somewhat controversial.[31,32] Similar to μ-(η^5:η^5-cyclooctatetraene)bis[(η^5-cyclopentadienyl)divanadium][33,34] with a metal–metal distance of 2.439(1) Å, the interpretation of the interaction between the two vanadium centers has been proposed to be a triple bond, a very short single bond,[33] or a weak double bond.[35]

From the reaction of VO(salophen), where salophen is *N,N′*-*o*-phenylenebis(salicylideneiminato), in THF with an equimolar solution of $TiCl_3(THF)_3$ followed by treatment with sodium

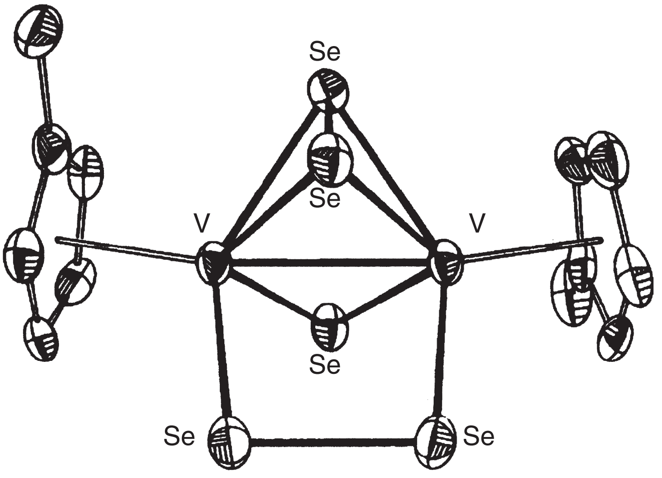


Figure 8 ORTEP drawing of $(\eta^5-CH_3C_5H_4)_2V_2(\mu-Se)(\mu-\eta^2-Se_2)(syn-\mu-Se_2)$ (reproduced by permission of the International Union of Crystallography from *Acta Crystallogr.* **1986**, *C42*, 1878–1880).

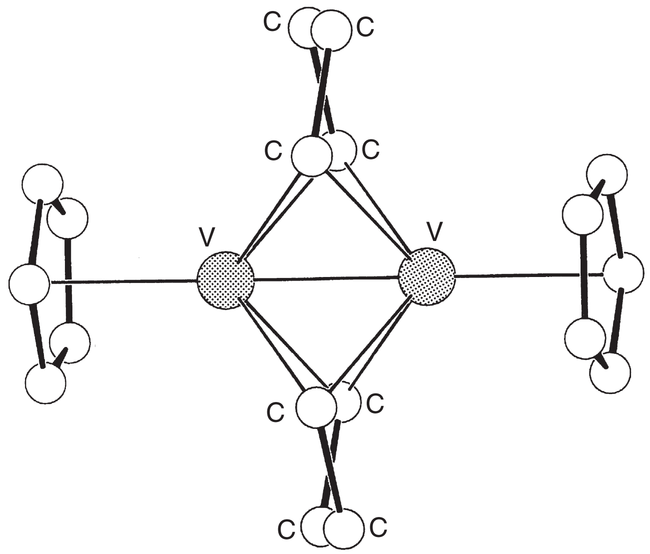


Figure 9 Crystal structure of (η^5-C_5H_5)$_2V_2(C_4H_8)_2$ (reproduced by permission of Wiley-VCH from *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 925–927).

sand, [V_2(salophen)$_2Na_2(THF)_6$] crystallizes upon addition of ether.[36] The V—V bond length of 2.406(3) Å is interpreted as a V—V double bond in this diamagnetic complex. In contrast, a "significantly elongated" single V—V bond is proposed for the paramagnetic dication in [(η^5:η^5-$C_{10}H_8$)$_2(NCCH_3)_3V_2$][PF_6]$_2$ with a V—V separation of 3.329(4) Å.[37]

For vanadium—vanadium bonds, 1983 was the year of the ethane-1,2-dithiolato (edt) ligand with papers received in June, July, and August containing the core anion [$V_2(edt)_4$]$^{2-}$.[38–40] The anion is prepared by either the reaction of VCl_3 with Na_2(edt) or 1,2-ethanedithiolate[38,39] or the reaction of VO(acac)$_2$ [Hacac is pentane-1,4-dione] with Na_2(edt).[40] The color of the crystals varies depending on the cation used in the preparation, $P(C_6H_5)_4{}^+$: red–brown,[39] $N(CH_3)_4{}^+Na^+$: green,[40] and $(CH_3CH_2)_4N^+$: green.[38] The diamagnetic compounds have slightly different V—V bond lengths: 2.616(2) Å for [$(CH_3CH_2)_4N$]$_2$[$V_2(edt)_4$],[38] 2.575(1) Å for [$P(C_6H_5)_4$]$_2$[$V_2(edt)_4$]·4CH_3OH, and 2.600(2) Å for [$N(CH_3)_4$]Na [$V_2(edt)_4$]·4CH_3CH_2OH.[40] With two terminal and two chelating edt ligands, the structure of [$(CH_3CH_2)_4N$]$_2$[$V_2(edt)_4$] is shown in Figure 10.[38]

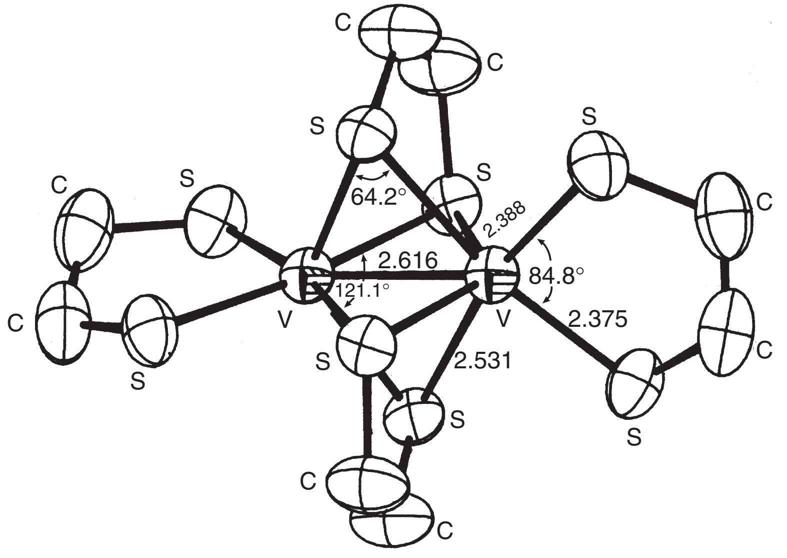
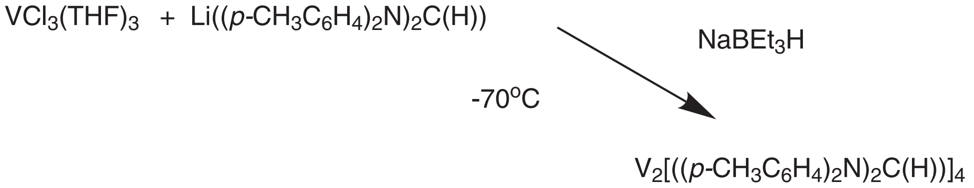


Figure 10 ORTEP drawing of [$(CH_3CH_2)_4N$]$_2$[$V_2(edt)_4$] (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1983**, *22*, 3179–3181).

4.9.5.3 $V_2^{II,II}$ Complexes

The ability to synthesize triply bonded divanadium complexes was transformed in 1992 with the development of a new synthetic pathway shown in Equation (2).[41] The use of $NaB(CH_3CH_2)_3H$ as the reducing agent with the lithiated ligand precursor provided the route to the first complex with a vanadium—vanadium triple bond possessing fourfold symmetry; the classic paddlewheel complex had been achieved. $V_2[((p\text{-}CH_3C_6H_4)_2N)_2C(H))]_4$ has a vanadium—vanadium bond length of 1.978(2) Å. An ORTEP drawing of the diamagnetic copper-colored compound $V_2[((p\text{-}CH_3C_6H_4)_2N)_2C(H))]_4$ is shown in Figure 11.[41,42]



(2)

In the further investigation of divanadium paddlewheel complexes, 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (Hhpp) shown in Figure 12 coordinated as an anion to form

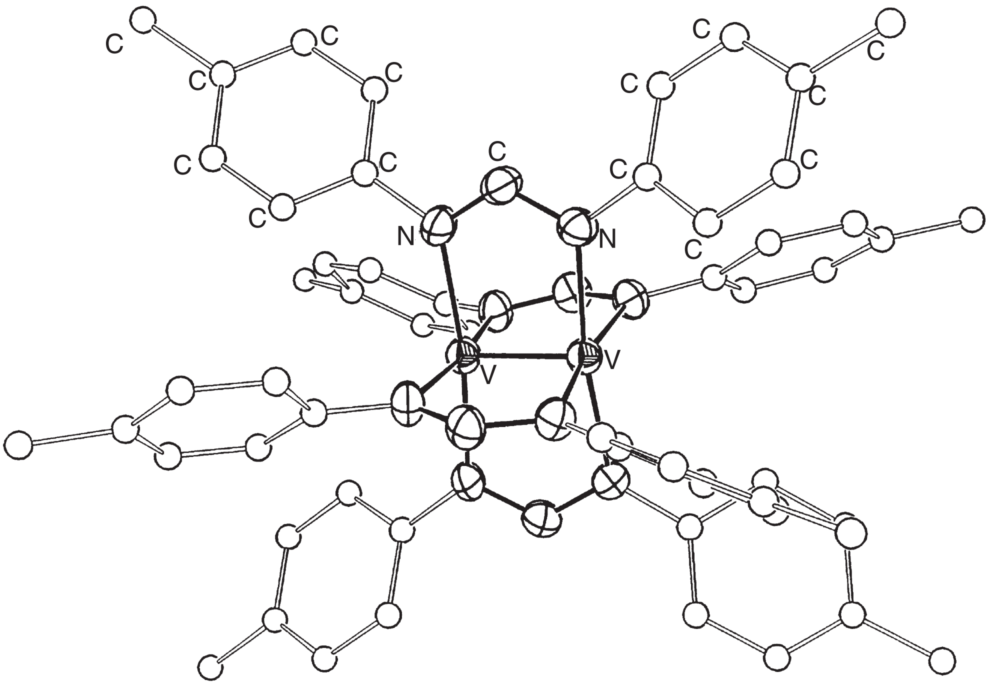


Figure 11 ORTEP drawing of $V_2[((p\text{-}CH_3C_6H_4)_2N)_2C(H))]_4$ (reproduced by permission of Wiley-VCH from *Angew. Chem., Int. Ed. Engl. Engl.* **1992**, *31*, 737–738).

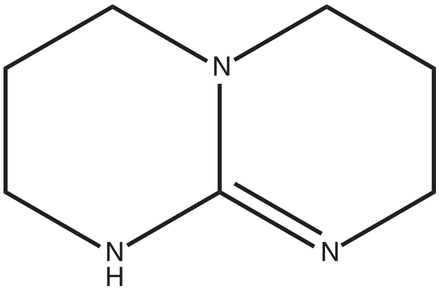


Figure 12 The neutral ligand 1,3,4,6,7,8-hexahydro-2H-pyrimido[1,2-a]pyrimidine (Hhpp).

$V_2(hpp)_4$ (1.932(1) Å) with the shortest V—V bond length in a complex of this type.[43] Other complexes in the series include the green compound $V_2[((C_6H_{10})_2N)_2C(H))]_4$ with a V—V bond length of 1.968(2) Å, prepared by several methods in an expansion of the general synthetic route.[44] While nitrogen-based ligands provided the example of an unbridged vanadium—vanadium triple bond, the use of oxygen-based anionic ligands such as 2,6-dimethoxyphenyl[45] (2.200(2) Å) and 2,4,6-trimethoxyphenyl[46] (2.223(2) Å) provided the first examples of divanadium triple bonds $(\sigma^2\pi^4)$[47] with the ligand arrangement shown in Figure 13.

4.9.5.4 $V_2^{I,I}$ Complexes

The structure of dicyclopentadienylpentacarbonyldivanadium elucidated in 1973 with a V—V bond length of 2.463(2) Å, contained two vanadium atoms with 16 (η^5-C_5H_5 and three CO groups) and 14 electrons (η^5-C_5H_5 and two CO groups).[48] Substitution of a carbonyl with the triphenylphosphine ligand on the more electron-deficient vanadium center results in minimal changes in the structure such as the V—V bond length of 2.466(1) Å,[49] and the work was expanded to include other monodentate and bidentate phosphine ligands.[50]

Upon reacting $[V_2(\mu\text{-Cl})_3(THF)_6]_2ZnCl_6$ with $P(CH_3)(C_6H_5)_2$ in THF followed by the addition of $LiBH_4$ and subsequent removal of solvent, a red residue, $V_2Zn_2H_4(BH_4)_2(P(CH_3)(C_6H_5)_2)_4$, is formed.[51] With a $V_2^{I,I}$ double bond $(\sigma^2\pi^2)$ of 2.400(2) Å in length, the coordination sphere of each of the vanadium atoms is VP_2H_2 in this diamagnetic molecule.[51]

4.9.5.5 $V_2^{0,0}$ Complexes

Although an organometallic complex, a triple bond is predicted for the carbonyl compound $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$ (2.388(2) Å) shown in Figure 14 formed in the reaction of $V(CO)_6$ with toluene.

4.9.6 DINIOBIUM COMPLEXES

4.9.6.1 $Nb_2^{V,V}$ Complexes

The addition of trimethylsilylmethylmagnesium chloride to $NbCl_5$ results in the formation of $Nb_2(CSi(CH_3)_3)_2(CH_2Si(CH_3)_3)_4$ with a $—CSi(CH_3)_3$ bridging group as shown in Figure 15[52] In this reddish-brown complex, the Nb—Nb bond length of 2.897(2) Å with a Nb—C—Nb—C core is described as a quasi-aromatic ring. Addition of two equivalents of 2,6-diphenylphenol to a toluene solution of the complex results in the substitution of two of the $—CH_2Si(CH_3)_3$ groups for $—OC_6H_3(C_6H_5)_2$. With the aryloxide ligands *trans* in the Nb—C—Nb—C ring, the product $Nb_2(CSi(CH_3)_3)_2(CH_2Si(CH_3)_3)_2(OC_6H_5(C_6H_5)_2\text{-}2,6)_2$ has a Nb—Nb bond length of 2.9082(8) Å.[53]

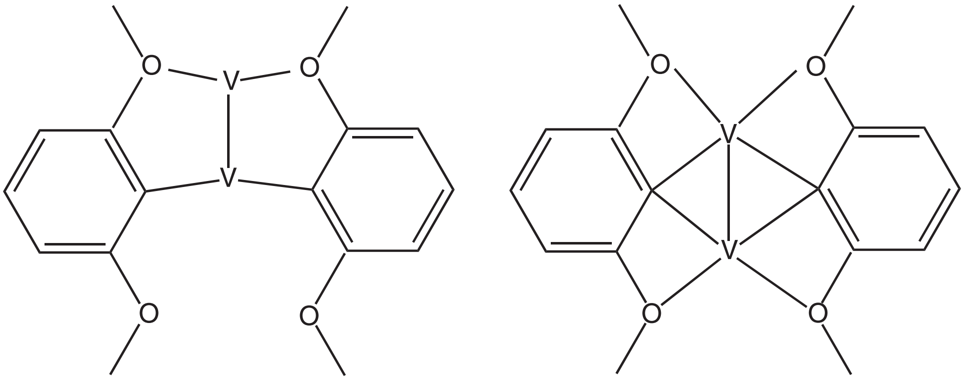


Figure 13 Diagrams of the bidentate and tridentate ligand arrangements in V_2(2,6-dimethoxyphenyl)$_4$.

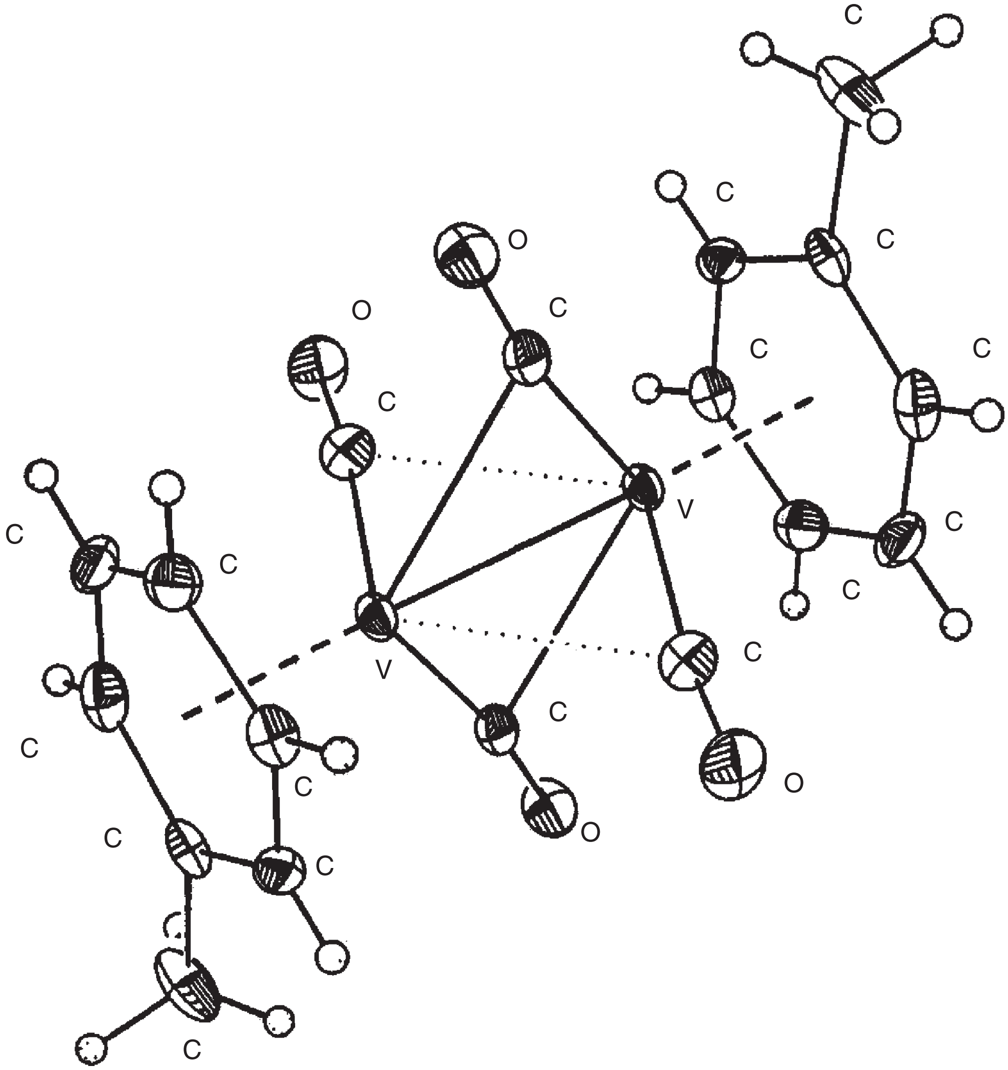


Figure 14 Crystal structure of the triply bonded $V_2(0, 0)$ complex $[(\eta^6\text{-}C_6H_5CH_3)V(CO)_2]_2$ (reproduced by permission of the American Chemical Society from *Organometallics* **1993**, *12*, 1682–1685).

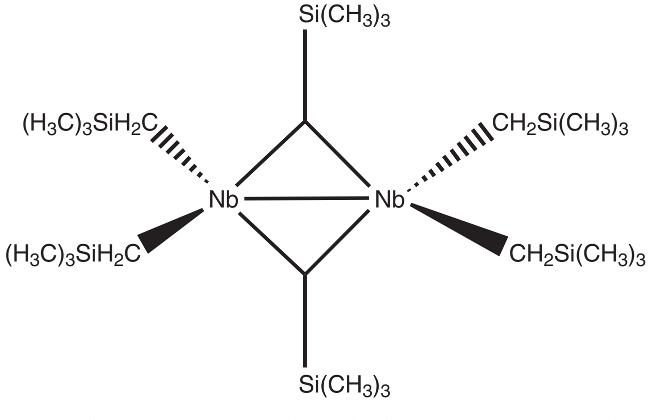


Figure 15 Schematic representation of $Nb_2(CSi(CH_3)_3)_2(CH_2Si(CH_3)_3)_4$.

4.9.6.2 $Nb_2^{IV,IV}$ Complexes

While metal–metal bonded $Nb_2^{IV,IV}$ complexes are dominated by sulfur ligands, a few complexes with nitrogen and phosphorus ligands have been synthesized. Red crystals of $Nb_2Cl_6(S(CH_3)_2)(NCH(C_6H_5)CH(C_6H_5)NNCH(C_6H_5))$ result upon the addition of benzaldehyde azine to $Nb_2Cl_6(S(CH_3)_2)_3$[54] at room temperature.[55] The Nb—Nb bond length, 2.681(1) Å, is short in comparison to other $Nb_2^{IV,IV}$ species. Two coordination geometries exist for the metal centers; one six-coordinated Nb(μ-N)(μ-Cl)$_2$Cl$_2$S and the other seven-coordinated Nb(μ-N)(μ-Cl)$_2$N$_2$Cl$_2$.[55] The red–brown complex $[NbCl_2(P(CH_3)_2(C_6H_5))_2]_2(\mu\text{-}Cl)_4$ shown in Figure 16 contains a Nb—Nb single bond, 2.838(1) Å.[56] The complex is synthesized by the reduction of $NbCl_5$ in toluene by sodium amalgam in the presence of the monodentate phosphine ligand. Upon dissolution of the molecule in CH_2Cl_2 or THF, the solution becomes green with a 10-line ESR

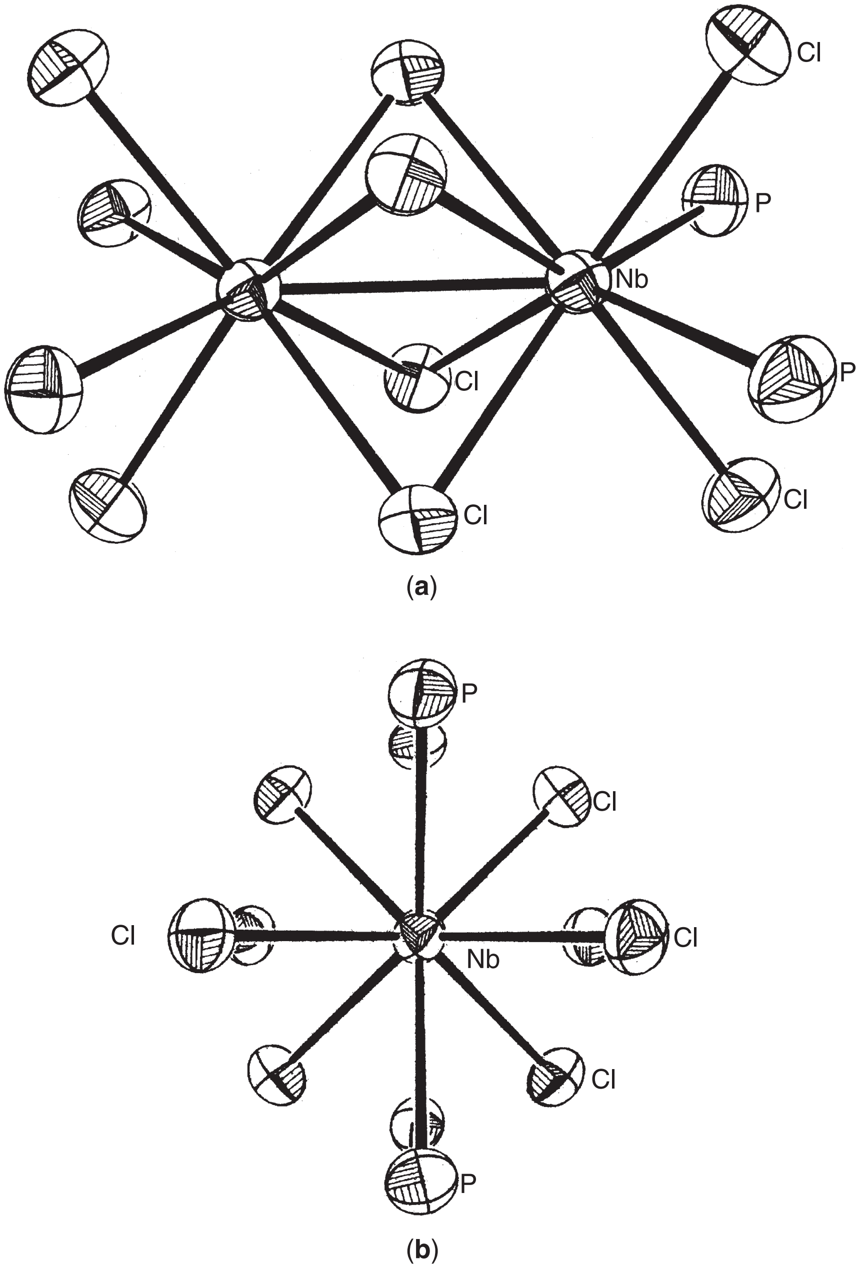


Figure 16 ORTEP drawing of the core structure of the $[NbCl_2(P(CH_3)_2(C_6H_5))_2]_2(\mu\text{-}Cl)_4$ molecule both perpendicular to and along the Nb—Nb axis (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1984**, *23*, 945–947).

spectrum consistent with the presence of mononuclear $NbCl_4(P(CH_3)_2(C_6H_5))_2$ and reflecting the instability of the molecule $[NbCl_2(P(CH_3)_2(C_6H_5))_2]_2(\mu\text{-}Cl)_4$ in solution. The trimethylphosphine analog $[NbCl_2(P(CH_3)_3)_2]_2(\mu\text{-}Cl)_4$ has been synthesized. The Nb—Nb bond length of 2.833(1) Å is comparable to the dimethylphenylphosphine analog, and the compound exhibits a similar solution behavior.[57] The purple complexes $[NbCl_2(PH_2(C_6H_5))_2]_2(\mu\text{-}Cl)_4$ (2.7949(10) Å) and $[NbCl_2(PH_2C_6H_{11})_2]_2(\mu\text{-}Cl)_4$ (2.809(1) Å) are synthesized by the addition of cyclohexylphosphine and phenylphosphine to dichloromethane solutions of $NbCl_5$ without the addition of a reducing agent.[58]

With Nb—Nb single bonds, the edge-sharing bioctahedral complexes $Nb_2Cl_4(OCH_3)_4(CH_3OH)_2$ and $Nb_2Cl_4(OCH_3)_4(CH_3CN)_2$ are shown in Figure 17.[59,60] Purple crystals of $Nb_2Cl_4(OCH_3)_4(CH_3OH)_2$ form upon dissolving $NbCl_4(CH_3CN)_3$ or $NbCl_4(THF)_2$ in methanol. Addition of acetonitrile to $Nb_2Cl_4(OCH_3)_4(CH_3OH)_2$ (2.781(1) Å) results in the formation of $Nb_2Cl_4(OCH_3)_4(CH_3CN)_2$ (2.768(2) Å). Addition of methanol to the salt $[(C_6H_5)_4P]_2[Nb_2(SCH_2CH_2CH_2S)_5]$[61] results in the formation of the triply bridged $Nb_2^{IV,IV}$ complex, $[(C_6H_5)_4P][Nb_2(OCH_3)_3(SCH_2CH_2CH_2S)_3]$ with a Nb—Nb bond length of 2.901(1) Å. The blue–purple niobium$^{(IV)}$ nonamethoxide anion, $Nb_2(OCH_3)_9^-$, is prepared by the magnesium reduction of $NbCl_5$ in methanol or the addition of sodium methoxide to $Nb_2Cl_4(OCH_3)_4(CH_3OH)_2$.[62] Three salts of the face-sharing bioctahedral anion have been characterized by X-ray crystallographic methods with an average Nb—Nb bond length of 2.640(6) Å: $[Mg(CH_3OH)_6]_2[Nb_2(OCH_3)_9]Cl_3$, $[Mg(CH_3OH)_6][Nb_2(OCH_3)_9]I{\cdot}CH_3OH$, and $[Na(CH_3OH)_6][Nb_2(OCH_3)_9]$.

Several niobium sulfidohalide complexes have been synthesized with the use of the starting materials $NbX_3S{\cdot}2tht$ producing mononuclear $NbX_5{\cdot}(tht)_2$ or $NbX_5(tht)$ complexes in addition to $Nb_2X_4S_3{\cdot}4tht$ where X is the halide Br or Cl and tht is tetrahydrothiophene.[63] The green complexes $Nb_2Cl_4S_3{\cdot}4tht$ (2.844(2) Å)[63] and $Nb_2Br_4S_3{\cdot}4tht$ (2.830(5) Å[63] or 2.8371(7) Å[64]] contain a Nb—Nb single bond with the sulfur atoms bridging the niobium metals centers, μ-S and μ-S_2. Replacement of the reagent CS_2 with Sb_2S_3 results in the preparation of a single niobium-containing product as shown in Equations (3) and (4).[65] The reaction of $Nb_2Cl_4S_3{\cdot}4tht$ with triphenylphosphine resulted in the extraction of a sulfur atom and the formation of the edge-sharing bioctahedral complex $Nb_2Cl_4S_2{\cdot}4tht$ (2.868(2) Å) shown in Figure 18.[65] $Nb_2Cl_4S_2{\cdot}4THF$ is prepared by the reaction of $NbCl_4(THF)_2$ with $S(Si(CH_3)_3)_2$ in tetrahydrofuran.[66] The thiophosphate, $Rb[Nb_2(S_2)_3(PS_4)]$ (2.888(2) Å) is prepared by the reaction of Nb, P, and S in the ratio 2:1:10 in RbCl/LiCl.[67]

$$3NbX_3S{\cdot}2tht \xrightarrow{CS_2} Nb_2X_4S_3{\cdot}4tht + NbX_5.n\text{tht} \; (n = 1 \text{ or } 2) \tag{3}$$

$$2NbX_5 + Sb_2S_3 \longrightarrow Nb_2X_4S_3 + 2SbX_3 \tag{4}$$

Variations in the mononuclear niobium starting materials lead to the syntheses of other edge-sharing bioctahedral complexes.[68,69] $[\{NbCl_2S(NCCH_3)_2\}_2]$ and $[\{NbBr_2S(NCCH_3)_2\}_2]$ are prepared by placing $NbCl_4(NCCH_3)$ or $NbBr_4(NCCH_3)_2$ in an ampoule with SbS_3 and $NCCH_3$ and heating for 2 days.[68] The crystals structures of the brown complex $[\{NbCl_2S(NCCH_3)_2\}_2]{\cdot}2NCCH_3$ and the green complex $[\{NbCl_2S(NCCH_3)_2\}_2]{\cdot}NCCH_3$ vary in

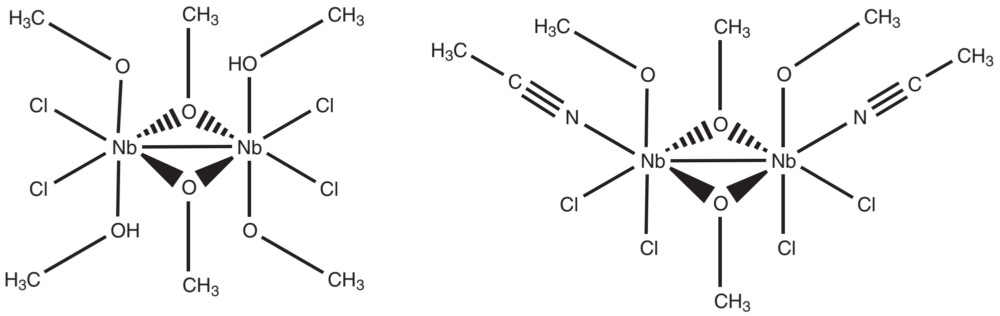


Figure 17 The edge-sharing bioctahedral complexes, $Nb_2Cl_4(OCH_3)_4(CH_3OH)_2$ and $Nb_2Cl_4(OCH_3)_4$-$(CH_3CN)_2$.

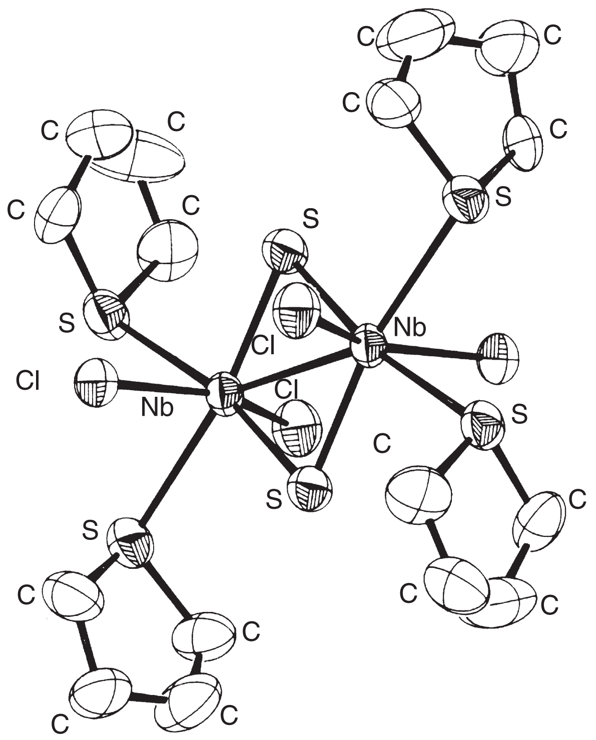


Figure 18 ORTEP drawing of $Nb_2Cl_4S_2{\cdot}4tht$ (reproduced by permission of the Royal Society of Chemistry from *J. Chem. Soc. Dalton* **1985**, 417–421).

the number of acetonitrile molecules in the lattice with only a slight variation in the Nb—Nb bond lengths of 2.862(2) Å and 2.872(3) Å, respectively. When $NbCl_4(THF)_2$ is reacted with Li_2S in THF followed by the subsequent addition of $P(CH_3)_3$, the orange–brown complex $Nb_2S_2Cl_4(P(CH_3)_3)_4$ with a Nb—Nb single bond (2.869(1) Å) results.[69] As in the case of $[\{NbCl_2S(NCCH_3)_2\}_2]{\cdot}2NCCH_3$ and $[\{NbCl_2S(NCCH_3)_2\}_2]{\cdot}NCCH_3$, the neutral ligands, $NCCH_3$ or $P(CH_3)_3$, occupy the equatorial sites.

$(\eta^5{:}\eta^1\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Nb_2H_2$ is an unusual diamagnetic complex synthesized from $(\eta^5\text{-}C_5H_5)_2NbH_3$,[70] possessing two bridging C_5H_4 ligands and terminal hydrides. The Nb—Nb bond length of 3.105(6) Å and Nb—H bond length of 1.70(3) Å have been determined from X-ray crystallographic data.[71,72] A two-electron reduction in the related system $[(\eta^5\text{-}C_5H_4Si(CH_3)_2OSi(CH_3)_2\text{-}\eta^5{:}\eta^1\text{-}C_5H_3)Nb_2H_2][Na(O(CH_2CH_3)_2)_2]_2$ results in the cleavage of the Nb—Nb bond.[73]

The interaction of $(\eta^5{:}\eta^1\text{-}C_5H_4)(\eta^5\text{-}C_5H_5)Nb_2H_2$ with azoaromatic compounds provides a synthetic route to the $Nb_2^{III,III}$ complexes $(\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)(\eta^5\text{-}C_5H_5)_2Nb_2(\mu\text{-}NC_6H_4R)_2$ where R is H or OCH_3.[74] Subsequent oxidation of these complexes with either $AgBF_4$ or HgX_2 results in the formation of the paramagnetic salts, $[(\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)(\eta^5\text{-}C_5H_5)_2Nb_2(\mu\text{-}NC_6H_4R)_2]BF_4$ and $[(\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)(\eta^5\text{-}C_5H_5)_2Nb_2(\mu\text{-}NC_6H_4R)_2]_2(HgX_4)$ where X is Cl or Br. The Nb—Nb bond length increases slightly upon oxidation from 2.834(5) Å for $(\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)(\eta^5\text{-}C_5H_5)_2Nb_2(\mu\text{-}NC_6H_4OCH_3)_2$ to 2.921(1) Å for $[(\eta^5{:}\eta^5\text{-}C_5H_4C_5H_4)(\eta^5\text{-}C_5H_5)_2Nb_2(\mu\text{-}NC_6H_4OCH_3)_2]^+$.[74] $[(\eta^5\text{-}C_5(CH_3)_5)_2Nb_2Cl_4]$ is oxidized upon addition of $LiP(C_6H_5)_2$ to form the oxo/phosphido bridged complex $((\eta^5\text{-}C_5(CH_3)_5)_2Nb_2)(\mu\text{-}P(C_6H_5)_2)(\mu\text{-}O)$ (2.625(5) Å).[75]

4.9.6.3 $Nb_2^{III,III}$ Complexes

Edge-sharing and face-sharing bioctahedral geometries predominate the structural chemistry of $Nb_2^{III,III}$ complexes, regardless of the ligand types. Neutral $Nb_2^{III,III}$ complexes are synthesized from $Nb_2Cl_6(S(CH_3)_2)_2$ or $Nb_2Cl_6(SC_4H_8)_3$ and the appropriate chelating phosphine ligand in toluene solutions, forming red or red–purple crystals. The chelating phosphine ligands used to date include $(CH_3CH_2)_2PCH_2P(CH_2CH_3)_2$ (depe),[76] $(CH_3)_2PCH_2P(CH_3)_2$ (dmpm),[77] dppe,[78] and $(C_6H_5)_2PCH_2P(C_6H_5)_2$ (dppm).[79] The Nb—Nb doubly bonded complexes, $\sigma^2\pi^2$, form $Nb_2Cl_6(depe)_2$,

$Nb_2Cl_6(dppm)_2$, $Nb_2Cl_6(dppe)_2$, and $Nb_2Cl_6(\mu\text{-dmpm})_2$ with bond lengths of 2.741(3) Å,[76] 2.696(1) Å,[79] 2.7383(3) Å,[78] and 2.711(3) Å, respectively.[77] Analogous to bidentate phosphine ligands, $(CH_3CH_2)_2NCH_2CH_2N(CH_2CH_3)_2$ (dene) coordinates to the $Nb_2^{III,III}$ core to form $Nb_2Cl_6(dene)_2$, with a Nb—Nb bond length of 2.764(1) Å.[76] Only the $(CH_3)_2PCH_2P(CH_3)_2$ derivative, $Nb_2Cl_6(\mu\text{-dmpm})_2$, contains a bidentate ligand that bridges the two niobium metal centers as shown in Figure 19.[77]

For the monodentate phosphine ligands $P(CH_3)_3$ and $P(CH_2CH_3)_3$, $Nb_2Cl_6(SC_4H_8)_3$, in the presence of Na/Hg, reacts to result in the simple substitution of monodentate phosphine ligands for the terminal SC_4H_8 ligands.[80] In addition to the synthesis of monodentate phosphine derivatives, $Nb_2Cl_6(SC_4H_8)(P(CH_2CH_3)_3)_2$ (2.718(1) Å) and $Nb_2Cl_6(SC_4H_8)(P(CH_3)_3)_2$, tetrahydrofuran undergoes a similar reaction to form $Nb_2Cl_6(SC_4H_8)(OC_4H_8)_2$ (2.684(2) Å) as shown in Figure 20.[80]

Use of an alternate starting material, $NbCl_4(THF)_2$, in a reaction mixture comprised of Mg turnings, Bu_4NBF_4, and the monodentate phosphine ligands $P(CH_3)_3$ or $P(CH_2CH_3)_3$, results in the edge-sharing anionic complexes $[Nb_2Cl_7(P(CH_3)_3)_2]^-$ or $[Nb_2Cl_7(P(CH_2CH_3)_3)_2]^-$, respectively.[81] As in the case of the neutral complexes discussed previously containing these monodentate phosphine ligands, the terminal phosphine ligands are in the *syn* configuration with Nb—Nb bond lengths of 2.683(1) Å and 2.708(3) Å for the trimethylphosphine and triethylphosphine derivatives. The anion $Nb_2Cl_9^{3-}$ is prepared by the reaction of either $Nb_2Cl_4(tht)_2$ or $Nb_2Cl_6(S(CH_3)_2)_2$ with $(CH_3CH_2)_4NCl$ or $(CH_3CH_2CH_2)_4NCl$ with the two resultant salts, $((CH_3CH_2)_4N)_3[Nb_2Cl_9]$ and $((CH_3CH_2CH_2)_4N)_3[Nb_2Cl_9]$, having slightly different metal–metal bond lengths, 2.7413(3) Å and 2.691(2) Å.[82]

The addition of an excess of tetramethylammonium acetate to $Nb_2Cl_6(SC_4H_8)_3$ in dichloromethane results in the formation of the diamagnetic purple compound $(N(CH_3))_4$-

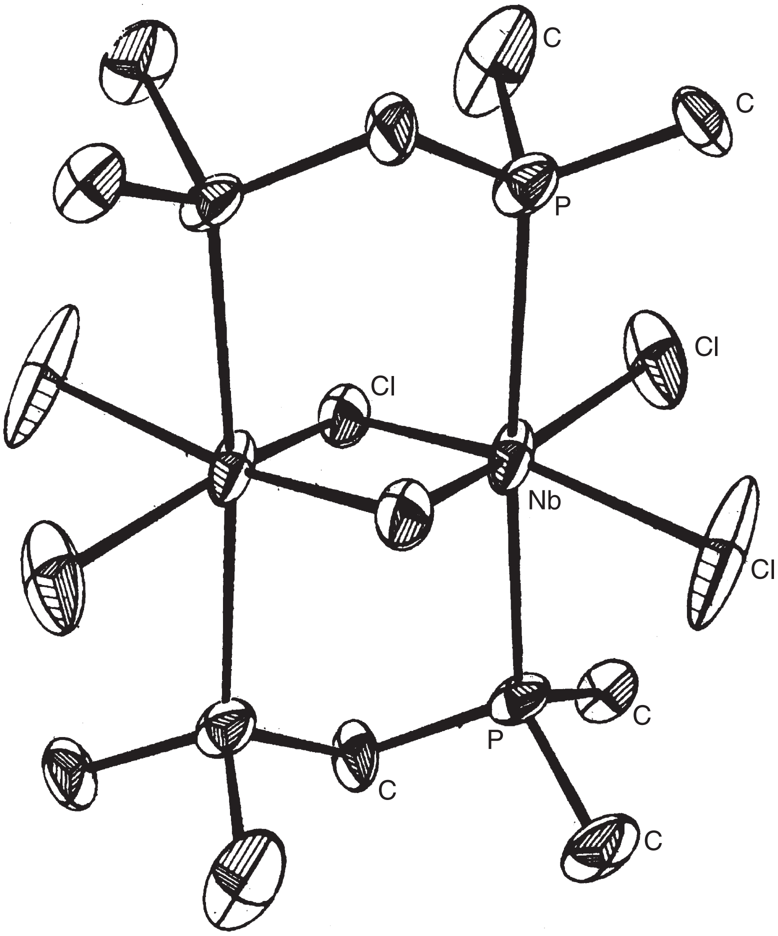


Figure 19 ORTEP drawing of the $Nb_2Cl_6(\mu\text{-dmpm})_2$ molecule (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1985**, *24*, 4389–4393).

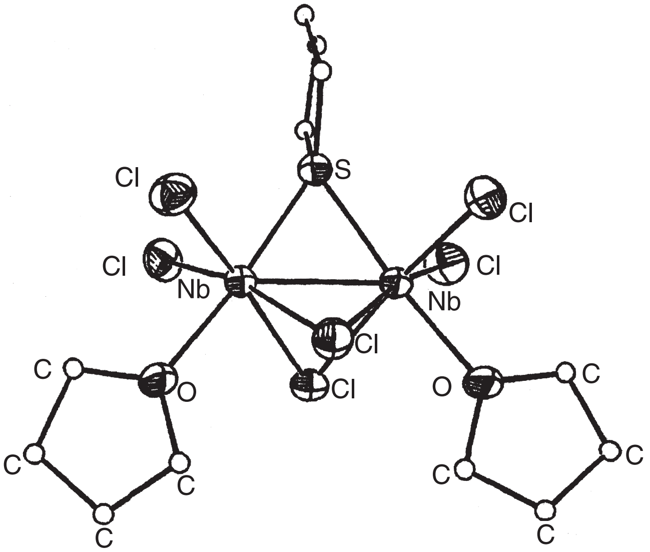


Figure 20 ORTEP drawing of $Nb_2Cl_6(SC_4H_8)(OC_4H_8)_2$ (reproduced by permission of the International Union of Crystallography from *Acta Crystallogr.* **1991**, *C47*, 1617–1621).

$[Nb_2Cl_2(SC_4H_8)(CH_3CO_2)_5]$.[83] The five acetato ligands coordinate to the Nb—Nb core (2.764(1) Å) in three different modes: two bridge the dinuclear core, two chelate to each of the metal centers in a *cis* fashion, and one bridges the core through a single oxygen atom to result in seven-coordinate niobium centers. Other examples of oxygen-based ligands include alkoxides.[59,84] In toluene, addition of CH_3CH_2OH or $(CH_3)_2CHOH$ to $Nb_2Cl_6(SC_4H_8)_3$ generates yellow–brown products upon removal of solvent. With Nb—Nb bond lengths of 2.891(1) and 2.611(3) Å respectively, $Nb_2Cl_5(OCH_2CH_3)(HOCH_2CH_3)_4$ and $Nb_2Cl_5(OCH(CH_3)_2)(HOOCH(CH_3)_2)_4$ are edge-sharing bioctahedral complexes with one bridging chloride, a bridging alkoxide, two equatorial chlorides *cis*, and two axial chlorides, *trans* at the dinuclear core.[59,84]

Green–brown crystals of $Nb_2Cl_4(OC_4H_8)_4(C_6H_5CCC_6H_5)$ and brown crystals of $[Mg_2Cl_3(OC_4H_8)_6][NbCl_4(OC_4H_8)_4(C_6H_5CCC_6H_5)(OC_4H_8)]$ both form in a 1:3 mass ratio upon the reaction of $NbCl_4(OC_4H_8)_2$ with magnesium turnings and $C_6H_5CCC_6H_5$.[85] The C$\equiv$C bond in $C_6H_5CCC_6H_5$ is slanted relative to the Nb—Nb axis with Nb—C bond lengths of 2.014(6) Å and 2.453(7) Å and a Nb—Nb bond length of 2.737(1) Å.

The common starting material, $Nb_2X_6(SC_4H_8)_3$, where X is Cl, Br, or I,[86] is prepared by the reaction of $NbX_4(SC_4H_8)_2$[87] with sodium amalgam in benzene. The edge-sharing bioctahedral complex $Nb_2Br_6(SC_4H_8)_3$ with a Nb—Nb bond length of 2.728(5) Å is diamagnetic with two bridging chlorides, a bridging tht ligand, and terminal tht ligands in a *cis* configuration. The dimethylsulfide complex, $Nb_2X_6(S(CH_3)_2)_3$, is synthetically accessible via the Na/K reduction of the appropriate pentahalide in the presence of borane-dimethylsulfide.[54] Green crystals of the edge-sharing bioctahedral complex, $Nb_2Cl_6(S(CH_3)_2)_4$ (2.836(2) Å), were obtained by the addition of $S(CH_3)_2$ and $(CH_3)_2SS(CH_3)_2$ to $Nb_2Cl_6(S(CH_3)_2)_3$.[88] Dark purple crystals of $Nb_2Cl_6(dto)_2$ where dto is 3, 6-dithiaoctane ($CH_3CH_2SCH_2CH_2SCH_2CH_3$) result from the addition of a hexane solution of dto to a toluene solution of $Nb_2Cl_6(S(CH_3)_2)_3$.[88] As in the case of $Nb_2Cl_6(S(CH_3)_2)_4$, $Nb_2Cl_6(dto)_2$ (2.688(2) Å[88] or 2.682(3) Å[89]) is an edge-sharing bioctahedral complex with the neutral ligands at the axial coordination sites as shown in Figure 21. Addition of tetrahydrofuran to $Nb_2Cl_6(S(CH_3)_2)_3$ results in the face-sharing bioctahedral complex $Nb_2Cl_6(S(CH_3)_2)(OC_4H_8)_2$ (2.684(2) Å) with two μ-Cl ligands, a μ-$S(CH_3)_2$ ligand, and the two OC_4H_8 ligands in a *cis* configuration.[90]

4.9.6.4 $Nb_2^{II,II}$ Complexes

With the exception of $[(\eta^6\text{-}C_5H_3(Bu^t)_2)Nb_2(\mu\text{-}\eta^6{:}\eta^6\text{-}P_6)]$ (2.828(1) Å),[91] low oxidation state Nb—Nb triply bonded complexes fall primarily into two categories, anionic face-sharing bioctahedral or paddlewheel complexes. In 1997, $NbCl_3(DME)$, where DME is dimethoxyethane, was reacted with

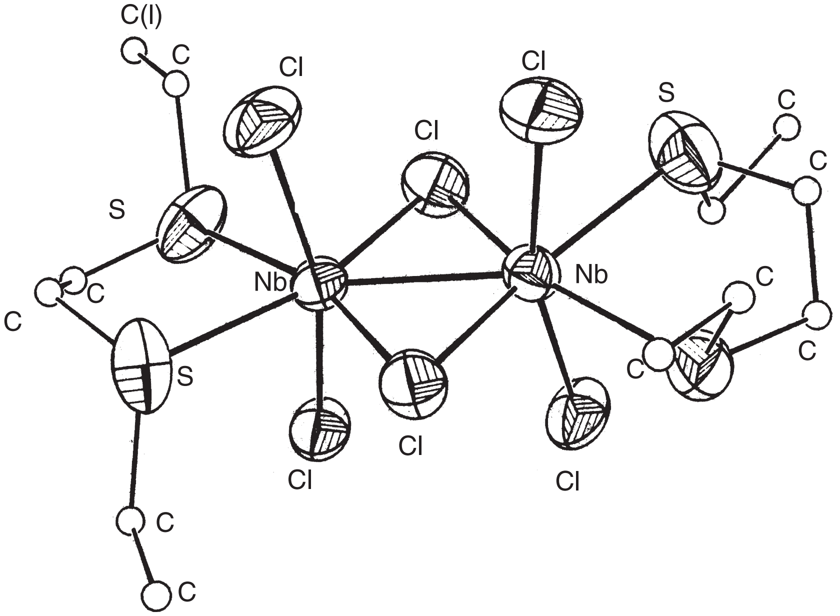


Figure 21 ORTEP diagram of $Nb_2Cl_6(dto)_2$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1990**, *29*, 4002–4005).

Li(hpp) in THF using KC_8 as the reducing agent.[92] Shown in Figure 22, the green paddlewheel complex $Nb_2(hpp)_4$ with a Nb—Nb bond length of 2.2035(9) Å ($\sigma^2\pi^4$) has a metal–metal bond length 0.27 Å longer than the isostructural vanadium complex. Other reducing agents have been investigated such as lithium naphthalenide and sodium triethylborohydride, $NaB(CH_3CH_2)_3H$.[93]

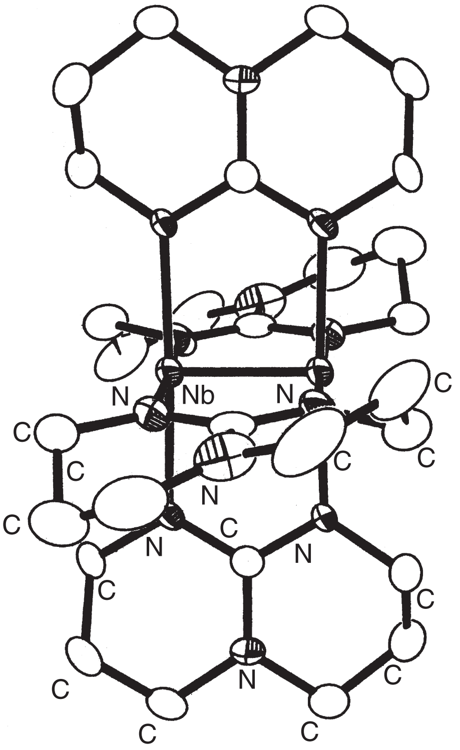


Figure 22 ORTEP drawing of the paddlewheel complex $Nb_2(hpp)_4$ (reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.* **1997**, *119*, 7889–7890).

Attempts to reduce the $Nb_2^{II,II}$ species further with $NaB(CH_3CH_2)_3H$ result in the incorporation of the reducing agent in the crystal structure and the resultant bond lengths are 2.2064(6) Å and 2.2187(7) Å for $Nb_2(hpp)_4{\cdot}2NaB(CH_3CH_2)_3H$ and $Nb_2(hpp)_4{\cdot}NaB(CH_3CH_2)_3H$, respectively.[93] In addition to the hpp ligand, the lithium salt of 7-azaindole, Li(azin) (Figure 23), was synthesized and reacted with $NbCl_3(DME)$ and lithium naphthalenide to form the blue–green complex $Nb_2(azin)_4{\cdot}2LiCl{\cdot}4THF$ with a Nb—Nb bond length of 2.278(2) Å. Weak interactions between the Nb center and the axial chloro ligands are observed in the $Nb_2(azin)_4{\cdot}2LiCl{\cdot}6THF$ complex (Nb—Nb 2.2683(13) Å and Nb—Cl 2.733(2) Å) synthesized from the alternative Nb^{II} starting material $[Nb_2Cl_5Li(TMEDA)_3]$.[93,94]

Reduction of the neutral molecule $Nb_2Cl_6(SC_4H_8)_3$ using sodium amalgam in the presence of the appropriate cation leads to the synthesis of the $Nb_2^{II,II}$ anionic complexes: $[Li(THF)_2]_2$-$[Nb_2Cl_6(SC_4H_8)_3]$, $Na_2[Nb_2Cl_6(SC_4H_8)_3]$ (2.610(3) Å), and $[(CH_3CH_2)_4N]_2[Nb_2Cl_6(SC_4H_8)_3]$ (2.632(1) Å).[95] Reduction of the bromide analog, $Nb_2Br_6(SC_4H_8)_3$, results in the synthesis of $Na_2[Nb_2Br_6(SC_4H_8)_3]$. Reduction of the tetrahydrofuran adduct, $Nb_2Cl_6(SC_4H_8)(OC_4H_8)_2$, provides a synthetic route to the $[Nb_2(\mu\text{-}Cl)_2Cl_3(SC_4H_8)(NC_5H_5)_3]^-$ monoanion (Nb—Nb 2.6054(5) Å) with two chlorine atoms and a sulfur atom from the tetrahydrothiophene ligand bridging the Nb—Nb core.[96]

4.9.7 DITANTALUM COMPLEXES

4.9.7.1 $Ta_2^{IV,IV}$ Complexes

Carbon-based ligands in $Ta_2^{IV,IV}$ systems include the 1,3 dimetallacyclobutadiene derivatives such as $Ta_2(\mu\text{-}CSi(CH_3)_3)_2(OC_6HNp\text{-}2\text{-}(C_6H_5)_3\text{-}3,5,6)(CH_2Si(CH_3)_3)_3$ (2.8943(6) Å), where OC_6HNp-2-$(C_6H_5)_3$-3,5,6 is 2-(1-naphthyl)-3,5,6-triphenylphenol, synthesized from the reaction of $Ta_2(\mu\text{-}CSi(CH_3)_3)_2(CH_2Si(CH_3)_3)_4$ with the *o*-arylphenol and one equivalent of $Si(CH_3)_4$.[97] The reaction of $Ta_2(\mu\text{-}CSi(CH_3)_3)_2(CH_2Si(CH_3)_3)_4$ with 9H-carbazole (cbH) results in the deprotonation of the carbazole ligand and the formation of the metallacycle $Ta_2(\mu\text{-}CSi(CH_3)_3)_2(cb)_4$.[98] Hydrogenation of $Ta_2(\mu\text{-}CSi(CH_3)_3)_2(cb)_4$ in the presence of $P(CH_3)_2(C_6H_5)$ leads to the green compound $(cb)(P(CH_3)_2(C_6H_5))_2(H)Ta(\mu\text{-}H)_2Ta(H)(P(CH_3)_2(C_6H_5))_2(cb)$ with a Ta—Ta bond length of 2.184(4) Å.

From the $Ta_2^{III,III}$ starting material $Ta_2Cl_6(S(CH_3)_2)_3$ in a tetrahydrofuran solution with the lithium salt of *N*,*N*′-diphenylformamidinate, reduction by Zn and Na/Hg results in a diamagnetic $Ta_2^{IV,IV}$ singly bonded compound.[99] In the presence of zinc metal, the red complex $(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)_2Ta(\mu\text{-}NC_6H_5)(\mu\text{-}\eta^2\text{-}CNC_6H_5)Ta(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)_2$ with a Ta—Ta bond length of 2.9411(7) Å is synthesized. In this molecule, the four formamidinate ligands chelate (two to each metal center) to the Ta metal center with the dinuclear core bridged by an imido and a CNC_6H_5 dianion. As shown in Figure 24, a simple change in the reducing agent from zinc metal to Na/Hg results in the formation of a similar compound, but with a change in the coordination geometry of the formamidinate ligands; two formamidinate ligands chelate while two bridge the dinuclear core in the dark purple complex $(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)Ta(\mu\text{-}NC_6H_5)(\mu\text{-}\eta^2\text{-}C_6H_5NC(H)NC_6H_5)_2(\mu\text{-}\eta^2\text{-}CNC_6H_5)Ta(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)$. The Ta—Ta single bond is significantly shorter, 2.7825(6) Å, due to the presence of the bridging formamidinate ligands. Formed upon insertion of a $B_2H_5^-$ molecule into the formamidinate ligand, the reaction of potassium metal with $Ta_2(\mu_2\text{-}\eta^4\text{-}B_2H_6)(CH_3C_6H_4NC(H)NC_6H_4CH_3)_4$ produces $[(B_2H_5)N(CH_3C_6H_4)C(H)NC_6H_4CH_3]Ta(\mu_2$-

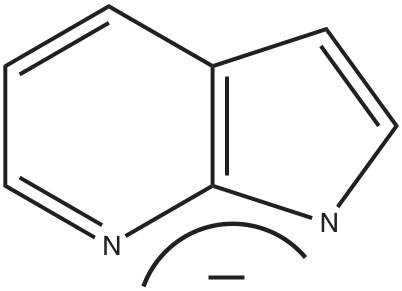


Figure 23 7-azaindolate ligand, azin

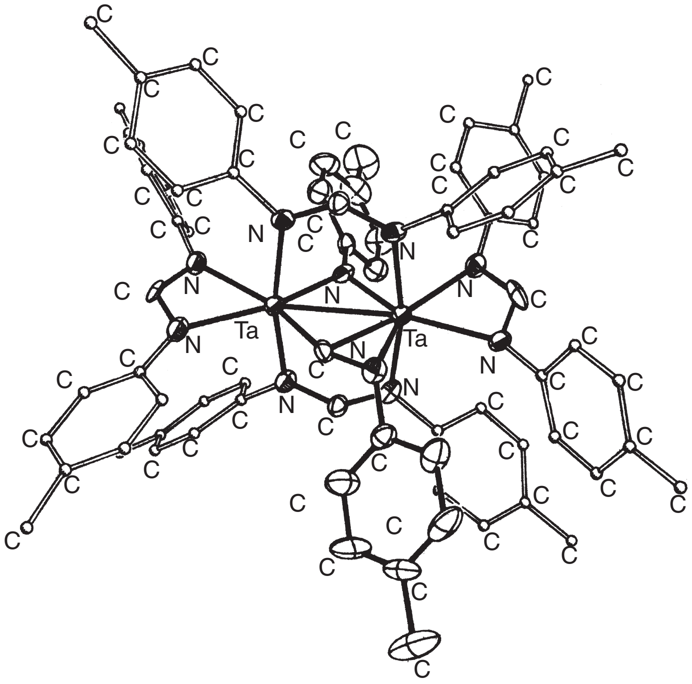


Figure 24 ORTEP drawing of $(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)Ta(\mu\text{-}NC_6H_5)(\mu\text{-}\eta^2\text{-}C_6H_5NC(H)NC_6H_5)_2(\mu\text{-}\eta^2\text{-}CNC_6H_5)Ta(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1997**, *36*, 896–901).

$NC_6H_4CH_3)_2(\mu_2\text{-}CH_3C_6H_4NC(H)NC_6H_4CH_3)_2Ta[(CH_3C_6H_4)NC(H)N(C_6H_4CH_3)B_2H_5]$ (2.6608(7) Å).[100] Using the mononuclear starting material $TaCl_5$ with $LiBH_4$ followed by the addition of the lithium salt of N,N′-diphenylformamidinate results in the cleavage of the formamidinate ligand, but a more symmetric complex, $(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)Ta(\mu\text{-}NC_6H_5)_2(\mu\text{-}\eta^2\text{-}C_6H_5NC(H)NC_6H_5)_2Ta(\eta^2\text{-}C_6H_5NC(H)NC_6H_5)$ (2.6608(5) Å), is synthesized.

Edge-sharing bioctahedral complexes with sulfur-based ligands are prepared either from $TaCl_5$[69,89] or $Ta_2Cl_6(S(CH_3)_2)_3$.[101] Oxidative addition of diphenyldisulfide to $Ta_2Cl_6(S(CH_3)_2)_3$ yields the green complex, $[TaCl_3((CH_3)_2S)]_2(\mu\text{-}S(C_6H_5))_2$ with a Ta—Ta single bond (3.165(1) Å).[101] A deep blue, mixed valent $Ta_2^{IV,III}$ complex is synthesized when diethylsulfide is added to a toluene solution of $Ta_2Cl_6(S(CH_3)_2)_3$ to form the face-sharing bioctahedral compound $Ta_2(\mu\text{-}SCH_2CH_3)_2(\mu\text{-}Cl)Cl_4(S(CH_3)_2)_2$ with a Ta—Ta bond length of 2.758(1) Å.[102] Addition of the appropriate phosphine ligand to a tetrahydrofuran solution of $TaCl_5$, Na/Hg, and either diphenyldisulfide or Li_2S, produces μ-S ligands in the complexes $Ta_2(\mu\text{-}S)_2Cl_4(P(CH_3)_3)_4$ (2.865(1) Å)[69] and $Ta_2(\mu\text{-}S)_2Cl_4(P(CH_3)_2(C_6H_5))_4$ (2.8757(4) Å).[89] Addition of di-*tert*-butylacetylene (DTBA) to $Ta_2Cl_6(SC_4H_8)_3$ results in oxidative addition to the $Ta_2^{III,III}$ core and the formation of a bridging DTBA ligand.[103] Subsequent exchange of tetrahydrothiophene for tetrahydrofuran occurs upon dissolving the reaction mixture in THF to form $Ta_2Cl_6(DTBA)(OC_4H_8)_2$ as shown in Figure 25.[103]

$Ta_2^{IV,IV}$ complexes with bridging hydrides are synthetically accessible using $Ta_2Cl_6(P(CH_3)_3)_4$ as the starting material.[104] The emerald green diamagnetic compound $Ta_2Cl_6(P(CH_3)_3)_4H_2$ (2.721(1) Å) with two bridging chlorides and two bridging hydrides is produced by the addition of molecular hydrogen to $Ta_2Cl_6(P(CH_3)_3)_4$. An alternative synthetic route to $Ta_2Cl_6(P(CH_3)_3)_4H_2$ is the oxidative addition of Cl_2 to $Ta_2Cl_4(P(CH_3)_3)_4H_2$.[105] A variation of the oxidizing agent from Cl_2 to HCl or H_2 produces $Ta_2Cl_5(P(CH_3)_3)_4H_3$ and $Ta_2Cl_4(P(CH_3)_3)_4H_4$ (2.511(2) Å),[106] respectively. The related complex $Ta_2Cl_8(P(CH_3)_3)_4$ (2.830(1) Å)[107] has been synthesized as a minor side product[108] and more systematically by the Na/Hg reduction of a toluene slurry of $TaCl_5$ and trimethylphosphine.[107]

A high-yield preparative route[109] to $(\eta^5\text{-}(C_5(CH_3)_4R))Ta_2(\mu\text{-}H)_2Cl_4$ (2.854(1) Å for R = $—CH_2CH_3$)[110] where R is $—CH_3$ or $—CH_2CH_3$ has been developed based on the addition of hydridotri(butyl)tin to the mononuclear complex, $(\eta^5\text{-}(C_5(CH_3)_4R))TaCl_4$. A dark green diamagnetic complex, $(\eta^5\text{-}(C_5(CH_3)_5))_2Ta_2(\mu\text{-}H)_2(\mu\text{-}2,6\text{-}Pr^i_2C_6H_3NSiHC_6H_5)_2$ (2.88472(5) Å), is one of three products

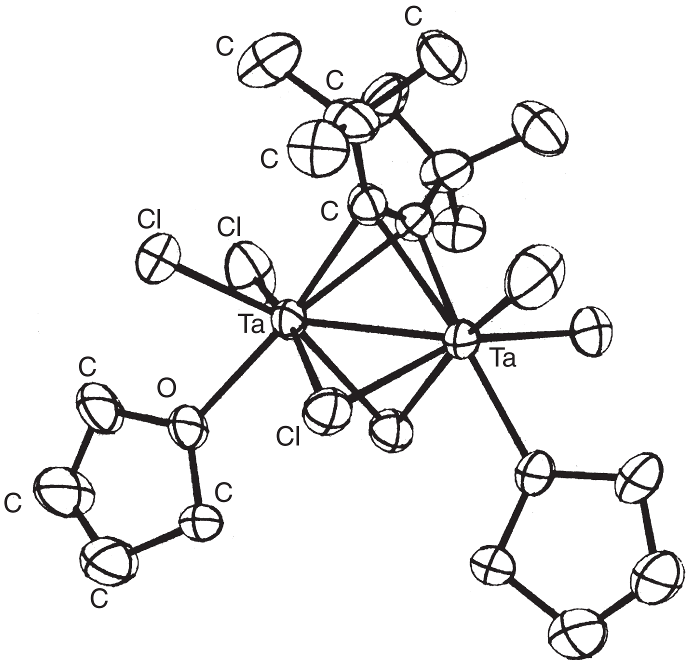


Figure 25 ORTEP drawing of $Ta_2Cl_6(DTBA)(OC_4H_8)_2$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1980**, *19*, 2354–2356).

formed in the reaction of $(\eta^5\text{-}(C_5(CH_3)_5))(2,6\text{-}Pr^i{}_2C_6H_3N)Ta(Si(Si(CH_3)_3)H$ with $C_6H_5SiH_3$.[111] Based on a theoretical analysis of the Ta—Ta bonding, a weak σ bond is predicted.

One of the more controversial cases of a ditantalum hydride complex is $[((H_{10}C_6)_2N)_2ClTa(\mu\text{-}H)]_2$.[112,113] Originally believed to be the first $Ta_2{}^{III,III}$ complex without bridging ligands and a Ta—Ta bond length of 2.8484(7) Å,[113] re-evaluation of the structure and ^1H NMR spectroscopy indicated the presence of two bridging hydride ligands.[112] A Ta—Ta bond length of 2.720(4) Å has been determined for the unsupported $Ta_2{}^{IV,IV}$ core in $[(Bu^t{}_2SiO)_2TaH_2]_2$.[114]

4.9.7.2 $Ta_2{}^{III,III}$ Complexes

Reduction of $(\eta^5\text{-}(C_5(CH_3)_4R))_2TaX_4$ where R is —CH_3 or —CH_2CH_3 and X is Cl or Br with Na/Hg in toluene provides a high-yield (70%) synthetic route to the ditantalum doubly bonded complexes $(\eta^5\text{-}(C_5(CH_3)_4R))_2Ta(\mu\text{-}X)_4$.[115] The crystal structure of $(\eta^5\text{-}(C_5(CH_3)_5))_2Ta(\mu\text{-}Br)_4$ with a Ta—Ta double bond length of 2.748(2) Å bridged symmetrically by four bromo ligands is shown in Figure 26. Reactions of $(\eta^5\text{-}C_5H_4CH_3)_2TaCl_4$ with $KP(C_6H_5)_2(dioxane)_2$ led to the phosphanido-bridged complex $[(\eta^5\text{-}C_5H_4CH_3)Ta(\mu\text{-}P(C_6H_5)_2)(P(C_6H_5)_2)]_2$ with an extremely long Ta—Ta double bond length of 3.024(2) Å.[116] The use of 2,4,6-triisopropylphenylphosphine in a similar reaction results in a mononuclear complex, $[(\eta^5\text{-}C_5H_4CH_3)TaCl_4\{PH_2(2,4,6\text{-}Pr^i{}_3C_6H_2)\}]$, and attempts to remove HCl result in the oxidation of the tantalum and the formation of $[(\eta^5\text{-}C_5H_4CH_3)TaCl\{\mu\text{-}P(2,4,6\text{-}Pr^i{}_3C_6H_2)\}]$ with a Ta—Ta single bond, 3.100(3) Å.[116]

As in the case of niobium, ditantalum complexes with sulfur-based ligands play a key role as starting materials for other $Ta_2{}^{III,III}$ complexes. Brown crystals of the face-sharing bioctahedral complex $Ta_2(\mu\text{-}NC_6H_5)(\mu\text{-}Cl)_2Cl_4(H_2NC_6H_5)_2$ (2.644(1) Å) are formed upon the addition and subsequent nitrogen bond cleavage of benzaldehyde azine to a benzene solution of $Ta_2Cl_6(S(CH_3)_2)_3$.[55] When *N,N,N′,N′*-tetraethylethylenediamine (dene) is added slowly to a toluene solution of $Ta_2Cl_6(S(CH_3)_2)_3$, the green edge-sharing bioctahedral complex $Ta_2Cl_6(dene)_2$ (2.7776(6) Å) is synthesized with each of the two ethylenediamine ligands chelating to a single tantalum metal center as shown in Figure 27.[76]

Addition of pyridine to a benzene solution of $TaCl_5$ reduced by $LiBH_4$ results in the formation an edge-sharing bioctahedral complex, but two of the pyridine ligands are in axial positions and two are in equatorial positions.[117] The purple crystals of $Ta_2Cl_6(NC_5H_5)_4$ (2.740(1) Å) have a slightly shorter Ta—Ta bond length than the $Ta_2Cl_6(dene)_2$ derivative. Unfortunately, reduction of $TaCl_5$

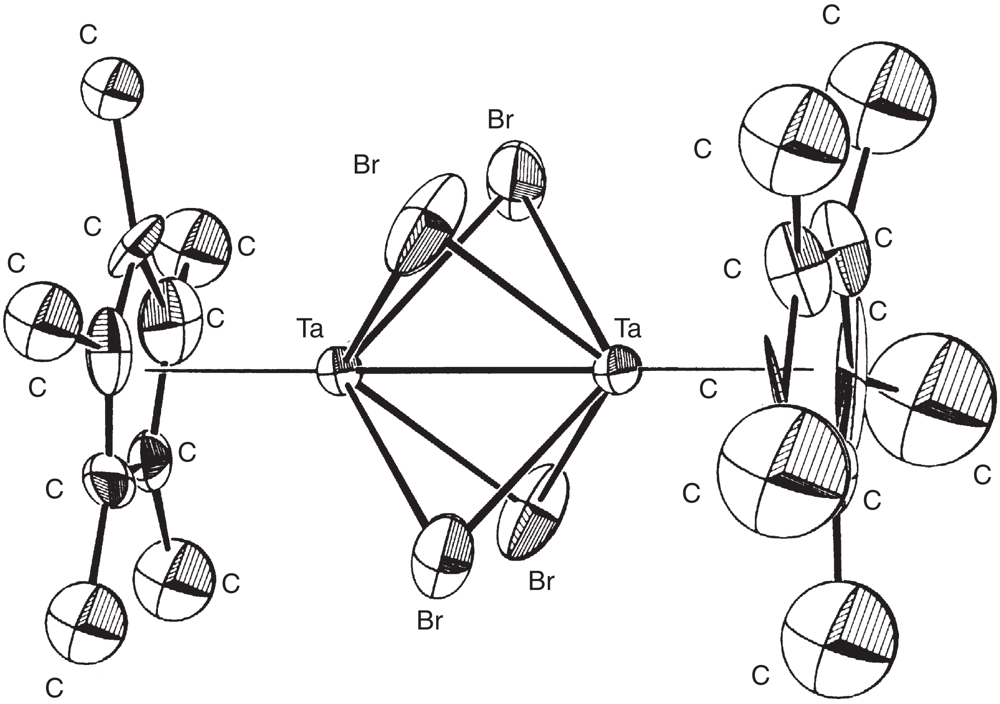


Figure 26 ORTEP drawing of $(\eta^5\text{-}(C_5(CH_3)_5))_2Ta(\mu\text{-}Br)_4$ viewed perpendicular to the Ta—Ta axis (reproduced by permission of the Royal Society of Chemistry from *J. Chem. Soc. Chem. Commun.* **1988**, 1133–1135).

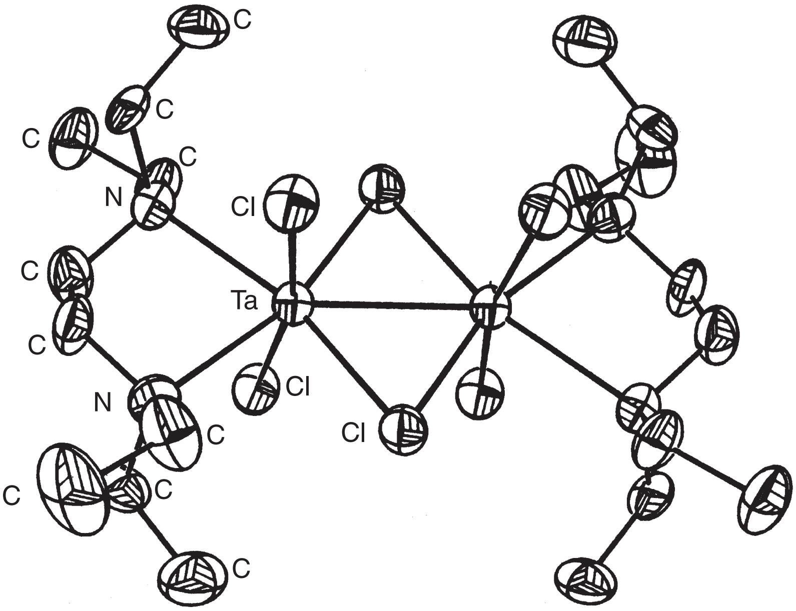


Figure 27 ORTEP drawing of $Ta_2Cl_6(dene)_2$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1987**, *26*, 4236–4240).

by $LiBH_4$ can lead to the incorporation of borane by-products in the ditantalum core.[118] Reduction of $TaCl_5$ by $LiBH_4$ followed by addition of the formamidinate ligands $Li[(C_6H_5)NC(H)N(C_6H_5)]$ and $Li[(CH_3C_6H_4)NC(H)N(C_6H_4CH_3)]$ yields the ditantalum complexes $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)((C_6H_5)NC(H)N(C_6H_5))_4$ (2.736(1) Å) and $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)((CH_3C_6H_4)NC(H)N(C_6H_4CH_3))_4$ (2.7251(11) Å).[118] As shown in Figure 28, the B_2H_6 anion bridges the ditantalum core symmetrically via Ta—H bonds.

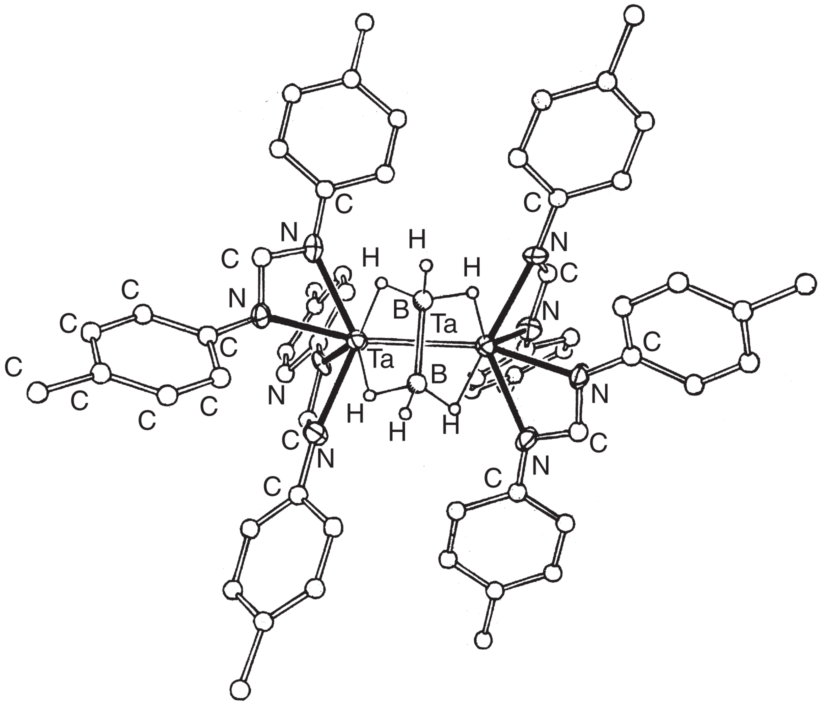


Figure 28 ORTEP drawing of $Ta_2(\mu_2,\eta^4\text{-}B_2H_6)((CH_3C_6H_4)NC(H)N(C_6H_4CH_3))_4$ (reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.* **1996**, *118*, 4830–4833).

Several ditantalum complexes have been synthesized with either monodentate or bidentate phosphine ligands; dmpm,[119] depe,[120], dmpe,[121] and trimethylphosphine.[105,122] For two of the phosphine complexes, the synthetic route involves the addition of the appropriate phosphine ligand, dmpe[121] or dmpm,[119] to a solution of either $Ta_2Cl_6(S(CH_3)_2)_3$ or $Ta_2Cl_6(SC_4H_8)_3$, respectively. In the case of $Ta_2Cl_6(dmpe)_2$ (2.710(1) Å), each of the phosphine ligands chelate to a single metal center and lie in the equatorial plane with the bridging chlorine atoms. For $Ta_2Cl_6(dmpm)_2$ (2.692(2) Å) shown in Figure 29, the phosphine ligands bridge the dinuclear core. While Ta_2Cl_6 $(depe)_2$[120] (2.737(1) Å) is prepared by the addition of tri-*n*-butylphosphine and sodium amalgam to

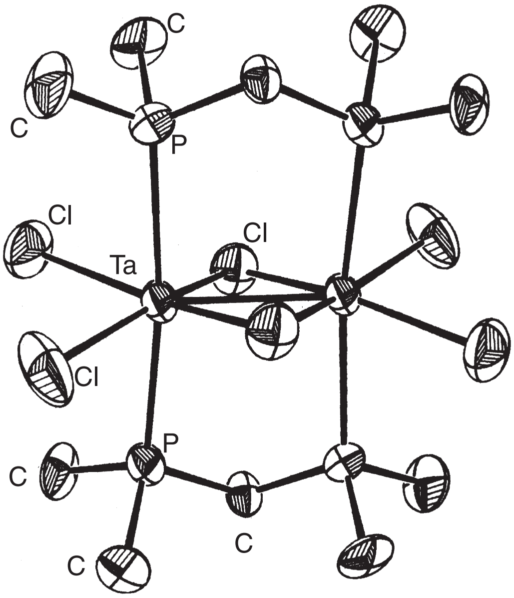


Figure 29 ORTEP drawing of $Ta_2Cl_6(dmpm)_2$ (reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.* **1986**, *108*, 971–976).

a toluene slurry of $Ta_2Cl_6(\mu\text{-}SC_4H_8)(OC_4H_8)_2$ then subsequent addition of the chelating phosphine ligand depe, the complex produced is the same as the one synthesized by direct addition of a chelating phosphine ligand to $Ta_2Cl_6(S(CH_3)_2)_3$ or $Ta_2Cl_6(SC_4H_8)_3$.

Burgundy red crystals of $Ta_2Cl_6(P(CH_3)_3)_4$ (2.721(1) Å) are obtained by the addtion of $TaCl_5$ and Na/Hg to a toluene solution of $P(CH_3)_3$.[122] Shown in Figure 30, the edge-sharing bioctahedral structure has two phosphine ligands in the equatorial plane on one tantalum metal center and two in the axial plane on the other tantalum metal center. Addition of H_2 to $Ta_2Cl_6(P(CH_3)_3)_4$ results in $Ta_2Cl_6(P(CH_3)_3)_4H_2$, discussed earlier.[105] Subsequent reduction of the $Ta_2^{IV,IV}$ complex using sodium amalgam leads to the reductive elimination of chloride and the formation of $Ta_2Cl_4(P(CH_3)_3)_4H_2$ (2.545(1) Å) with two bridging hydrides. Upon reduction of the dinuclear complex $Ta_2Cl_6(SC_4H_8)(OC_4H_8)_2$ with sodium amalgam and addition of trimethylphosphine, the tetrahydrofuran ligands are replaced with trimethylphosphine ligands, $Ta_2Cl_6(SC_4H_8)(P(CH_3)_3)_2$ (2.682(3) Å).[80] $Ta_2Cl_6(S(CH_3)_2)_2$ and $P(N(CH_3)_2)_3$ were mixed in a dichloromethane solution to produce the related red complex $Ta_2Cl_6(S(CH_3)_2)(P(N(CH_3)_2)_3)_2$ (2.704(1) Å).[123]

Addition of one equivalent of $C_4H_9CO_2Li$ to $Ta_2Cl_6(tht)_3$ results in the formation of a complex with a bridging carboxylate, $Ta_2Cl_5(O_2CC_4H_9)(S(CH_3)_2)(OC_4H_8)_2$ that crystallizes in two different forms with Ta—Ta double bonds, 2.766(1) Å. and 2.779(1) Å.[124] A minor product in the synthesis of $Ta_2Cl_6(dmpe)_2$ is the dark green complex $Ta_2Cl_4(dmpe)_2(\mu\text{-}O)(\mu\text{-}S(CH_3)_2)$ (2.726(1) Å).[125] When $Ta_2Cl_6(tht)(OC_4H_8)_2$ is reduced by sodium amalgam with the subsequent addition of pyridine, red crystals of $Ta_2Cl_4(\mu\text{-}O)(\mu\text{-}S(tht)(NC_5H_5)_4$ are formed with the ligand geometry shown in Figure 31.[126]

Common ditantalum starting materials include the face-sharing bioctahedral species $Ta_2Cl_6(S(CH_3)_2)_3$ (2.691(1) Å)[127] and $Ta_2Cl_6(SC_4H_8)_3$ (2.681(1) Å)[127] with Ta—Ta double bonds. The brown crystals of $Ta_2Cl_6(S(CH_3)_2)_3$ (Figure 32) are synthesized by the reduction of a $TaCl_5$ and $S(CH_3)_2$ mixture using sodium amalgam.[127] The Ta—Ta bond length increases slightly for $Ta_2Br_6(SC_4H_8)_3$ (2.710(2) Å) in comparison to the chloro analogs.[128] The sulfur ligands are relatively easy to replace since $Ta_2Cl_6(SC_4H_8)(OC_4H_8)_2$ (2.6695(5) Å) is synthesized simply by layering a tetrahydrofuran solution of $Ta_2Cl_6(SC_4H_8)_3$ with hexanes.[90] In fact, the tetrahydrothiophene ligands are replaced with chlorides when $Ta_2Cl_6(SC_4H_8)_3$ is layered with $(CH_3CH_2)_4NCl$ in a 1:4 ratio to result in $((CH_3CH_2)_4N)_2[Ta_2Cl_8(SC_4H_8)]$ (2.688(1) Å).[82]

Addition of excess $S(CH_3)_2$ to a toluene solution of $Ta_2Cl_6(S(CH_3)_2)_3$ followed by layering of the reaction filtrate with $(CH_3)SS(CH_3)$ converts the face-sharing bioctahedral complex to the edge-sharing bioctahedral complex $Ta_2Cl_6(S(CH_3)_2)_4$ with a Ta—Ta bond length of 2.829(1) Å.[88] The bidentate sulfur-based ligand 3,6-dithiaoctane (dto) coordinates in a manner similar to the

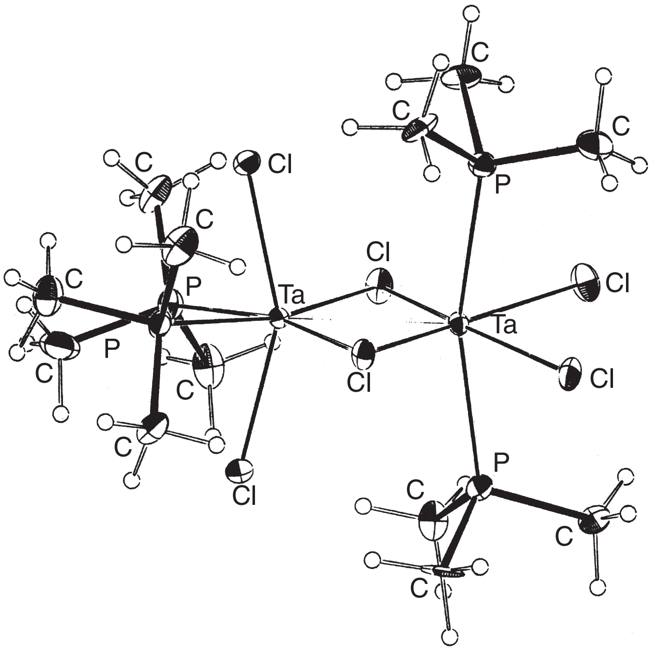


Figure 30 ORTEP drawing of $Ta_2Cl_6(P(CH_3)_3)_4$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1982**, *21*, 2392–2396).

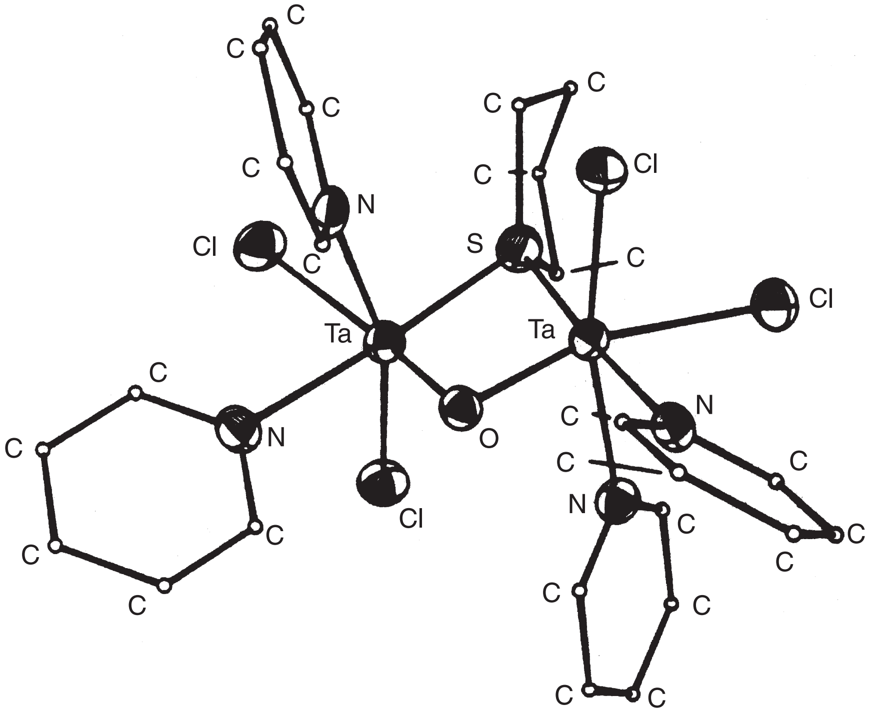


Figure 31 ORTEP drawing of $Ta_2Cl_4(\mu\text{-}O)(\mu\text{-}S(tht)(NC_5H_5)_4$ (reproduced by permission of Elsevier Science from *Inorg. Chim. Acta* **1988**, *149*, 105–110).

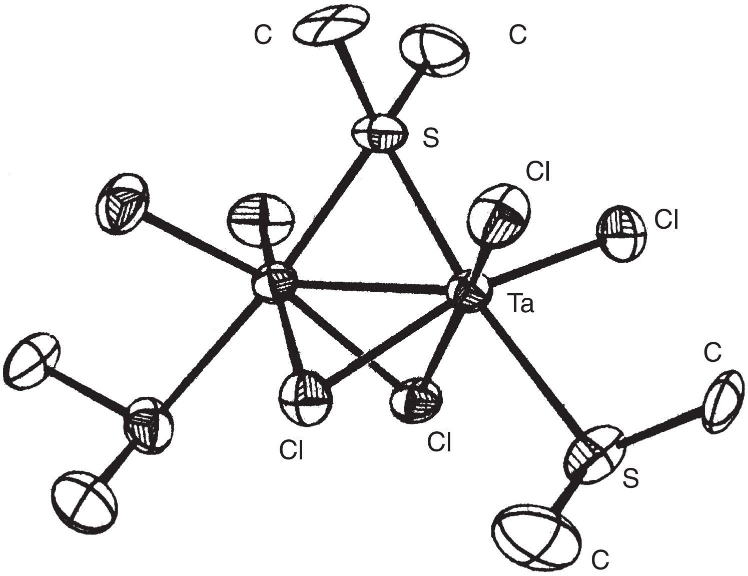


Figure 32 ORTEP drawing of $Ta_2Cl_6(S(CH_3)_2)_3$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1981**, *20*, 2716–2719).

bidentate phosphine ligands described earlier to result in $Ta_2Cl_6(dto)_2$ (2.841(1) Å and 2.852(1) Å for the two independent molecules in the unit cell).[88]

4.9.7.3 $Ta_2^{II,II}$ Complexes

There are only a few ditantalum complexes with the metal centers in lower oxidation states, such as the triply bonded anionic complexes $[Ta_2Cl_6(SC_4H_8)_3]^{2-}$ synthesized by the reduction of either

$Ta_2Cl_6(SC_4H_8)_3$ or $TaCl_5$ with sodium amalgam.[95] In the presence of LiCl, $[Li(THF)_2]_2$-$[Ta_2Cl_6(SC_4H_8)_3]$ is formed with a Ta—Ta bond length of 2.626(1) Å. Considering the BH_3 group as a 2-electron donor, the purple $Ta_2^{II,II}$ complex $Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3(\eta^2\text{-}BH_4)_2$ (2.7708(5) and 2.7875(5) Å for the unsolvated and solvated forms) is synthesized from the $LiBH_4$ reduction of $TaCl_5$ followed by the addition of dmpm.[129] As shown in Figure 33, the tantalum metal centers bond to two of the hydrogen atoms of the bridging BH_3 moiety.

4.9.8 DICHROMIUM COMPLEXES

4.9.8.1 $Cr_2^{III,III}$ Complexes

$(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$, synthesized from $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_6$, reacts with 2 molar equivalents of $Cr(CO)_5(OC_4H_8)$, $Mo(CO)_5(OC_4H_8)$, or $W(CO)_5(OC_4H_8)$ to yield the brown-to-brownish-red diamagnetic di-metallated complexes, $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$, $(\eta^5\text{-}C_5H_5)_2Cr_2$-$(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Mo(CO)_5]_2$, and $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2))[W(CO)_5]_2$, respectively.[130] An ORTEP drawing of the structure of $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ is shown in Figure 34.[130] The Cr—Cr bond length of the di-metallated species $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (3.003(1) Å) decreases only slightly from the parent compound $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)$ (3.011(1) Å).

The $Cr_2^{III,III}$ starting material $(\eta^5\text{-}C_5H_5)_2Cr_2(SC(CH_3)_2)_2S$ reacts with metal carbonyls such as $(\eta^5\text{-}C_5H_5)Mn(CO)_3$, $(\eta^6\text{-}C_6H_6)Cr(CO)_3$, $Fe_3(CO)_9S_2$, and $Re_2(CO)_9$, to form cluster complexes with the retention of the Cr—Cr bond in the $(\eta^5\text{-}C_5H_5)_2Cr_2(SC(CH_3)_3)$-core.[131–134] An example of the "Bow-Tie" framework is shown in Figure 35 for $[(\eta^5\text{-}C_5H_5)_2Cr_2(SC(CH_3)_3)(\mu_3\text{-}S)_2]_2Mn$.[131] The length of the Cr—Cr double bond is 2.690(4) Å with only a slight change for $[(\eta^5\text{-}C_5H_5)_2Cr_2(SC(CH_3)_3)(\mu_3\text{-}S)_2]_2Cr$ (2.655(1) Å).[132] $(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}OC(CH_3)_3)_2[OCCo_3(CO)_9]$ is synthetically accessible through the room-temperature interaction of $(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}OC(CH_3)_3)_2$ with $Co_2(CO)_8$ and contains a Cr—Cr bond length of 2.766(1) Å.[135]

4.9.8.2 $Cr_2^{II,II}$ Complexes

$Cr_2^{II,II}$ complexes can be separated into two primary categories: organometallic complexes with carbon-based ligands such as indenyl,[136] fulvalene,[137] and cyclopentadienyl ligands[135,138,139] and

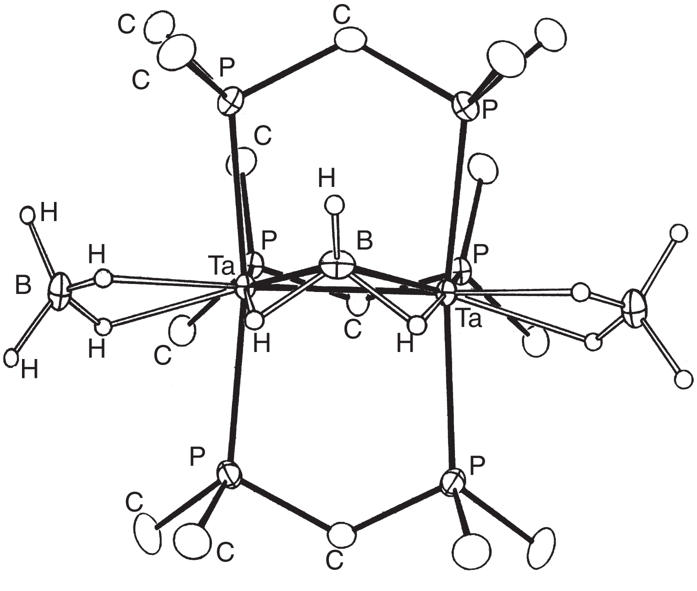


Figure 33 ORTEP drawing of viewed perpendicular to the Ta—Ta axis in $Ta_2(\mu\text{-}BH_3)(\mu\text{-dmpm})_3$ $(\eta^2\text{-}BH_4)_2$ (reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.* **1998**, *120*, 9594–9599).

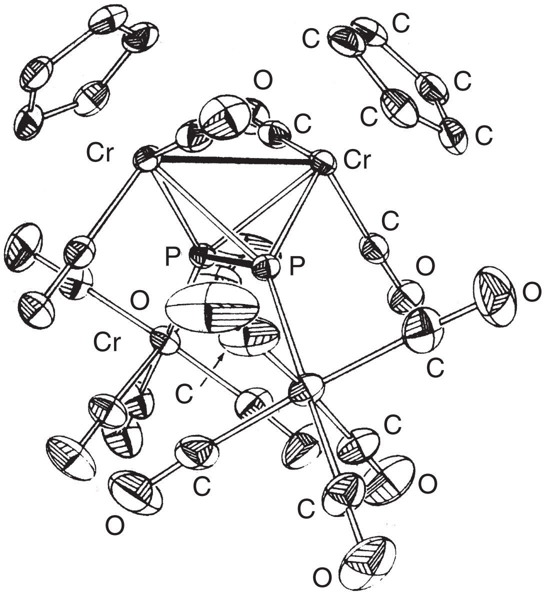


Figure 34 ORTEP drawing of $(\eta^5\text{-}C_5H_5)_2Cr_2(CO)_4(\mu\text{-}\eta^2\text{-}P_2)[Cr(CO)_5]_2$ (reproduced by permission of Elsevier Science from *J. Organomet. Chem.* **1989**, *364*, 363–371).

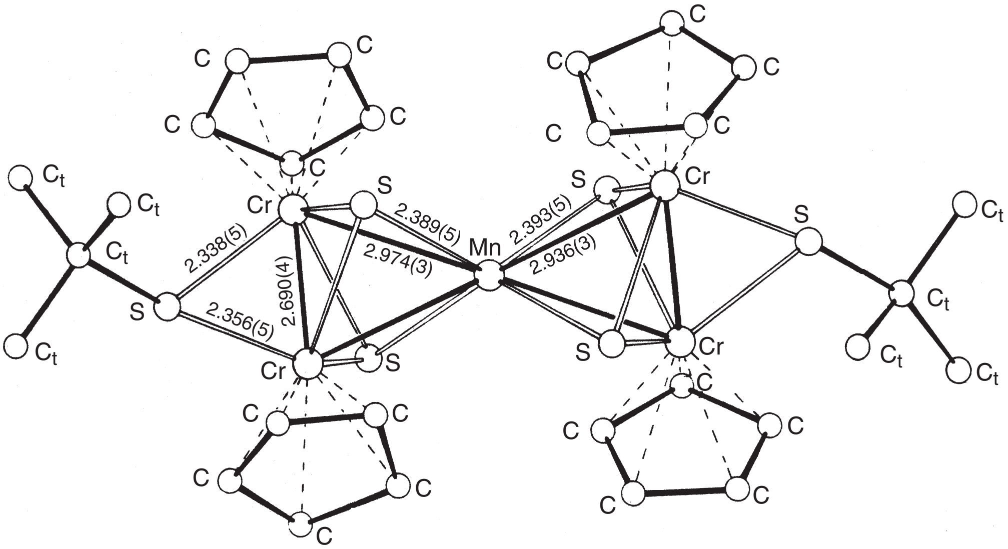


Figure 35 The structure of $[(\eta^5\text{-}C_5H_5)_2Cr_2(SC(CH_3)_3)(\mu_3\text{-}S)_2]_2Mn$ (reproduced by permission of Elsevier Science from *J. Organomet. Chem.* **1984**, *275*, 183–189).

quadruply bonded paddlewheel complexes.[140] With an excellent history of dichromium complexes already available,[140] new Cr—Cr bonded compounds synthesized since 1990 will be the focus of the $Cr_2^{II,II}$ section.

The dark red complex $(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}OC(CH_3)_3)_2$ is prepared by refluxing $(\eta^5\text{-}C_5H_5)_2Cr$ with *tert*-butyl alcohol in toluene.[139] The Cr—Cr bond length is 2.632(5) Å and 2.669(6) Å for the two independent molecules in the crystal lattice. Further reaction of $(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}OC(CH_3)_3)_2$ with $Co_2(CO)_8$ in benzene results in a cluster compound $(\eta^5\text{-}C_5H_5)_2Cr_2(\mu\text{-}OC(CH_3)_3)_2[OCCo_2(CO)_9]$ with a slight increase in the Cr—Cr bond length to 2.766(1) Å.[135] The Cr—Cr bond length of $(\text{indenyl})_3Cr_2Cl$ (shown in Figure 36) formed from the reaction of $CrCl_2$ with only one equivalent of sodium indenyl in THF is 2.317(1) Å.[136] In addition to bridging oxygen-based ligands, the reaction of $[(\eta^5\text{-}C_5H_5)Cr(CO)_2]_2$ with $(C_6H_5)_2S_2$ in toluene at elevated temperature yields the purple complex $[(\eta^5\text{-}C_5H_5)Cr(\mu\text{-}S(C_6H_5))_2]_2S$[141] (2.676(1) Å) as a secondary product.

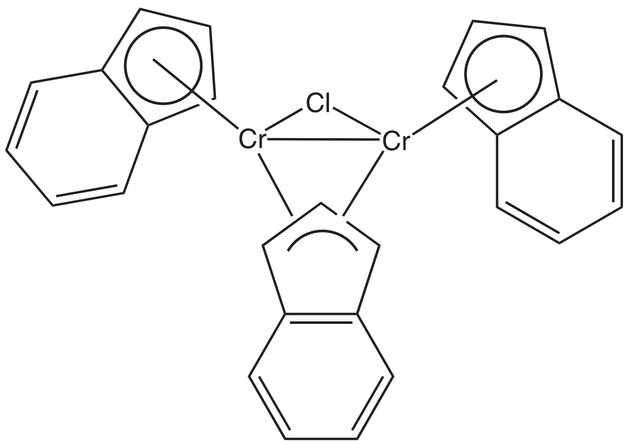


Figure 36 Structure of (indenyl)$_3$Cr$_2$Cl.

The unusual structure shown in Figure 37 results from the reaction of CrCl$_2$(THF)$_2$ with LiCH$_2$N(CH$_3$)$_2$ in ether.[142] The red diamagnetic Cr$_2^{II,II}$ salt [{Li(THF)}$_2$Cr$_2$(CH$_2$N(CH$_3$)$_2$)$_6$] has a Cr—Cr bond length of 1.844(1) Å. In a similar reaction using LiCH$_2$Si(CH$_3$)$_3$, two of the six —CH$_2$Si(CH$_3$)$_3$ ligands are proposed to bridge the Cr—Cr bond, based on NMR spectroscopy of the orange–brown complex.[143] Although the anionic complex [Li(DMF)$_6$][Cr$_2$(azin)$_4$Cl$_2$] where Hazin is 7-azaindole with a Cr—Cr distance of 2.688(2) Å is diamagnetic, the presence of a Cr—Cr bond has not been confirmed for this red compound.[144] However, a single or triple bond is proposed based on a metal–metal interaction comprised of both bonding and exchange coupling.

One of the dominant ligand groups in recent Cr$_2^{II,II}$ chemistry is the amidinate anion. The guanindinate anion [(C$_6$H$_5$N)$_2$CN(CH$_2$)$_4$]$^-$ reacts with CrCl$_2$ to result in the classic paddlewheel complex, Cr$_2$[(C$_6$H$_5$N)$_2$CN(CH$_2$)$_4$]$_4$ (1.9049(7) and 1.9025(7) Å).[145] With the addition of AgPF$_6$, the yellow solution of Cr$_2$[(C$_6$H$_5$N)$_2$CN(CH$_2$)$_4$]$_4$ becomes dark blue upon formation of the Cr$_2^{II,III}$ complex [Cr$_2$[(C$_6$H$_5$N)$_2$CN(CH$_2$)$_4$]$_4$]PF$_6$ with a slight increase in the Cr—Cr bond length to 1.9249(9) Å. A series of twenty tetraformamidinate[146] dichromium complexes have been synthesized over the last ten years.[147–150] Of note in the series is the lengthening of the Cr—Cr bond upon coordination of a substituent of the phenyl ring of formamidinate ligand to an axial coordination site of the dichromium core.[147,148] As shown in Figure 38 for Cr$_2$[(C$_6$F$_5$N)$_2$C(H)]$_4$,

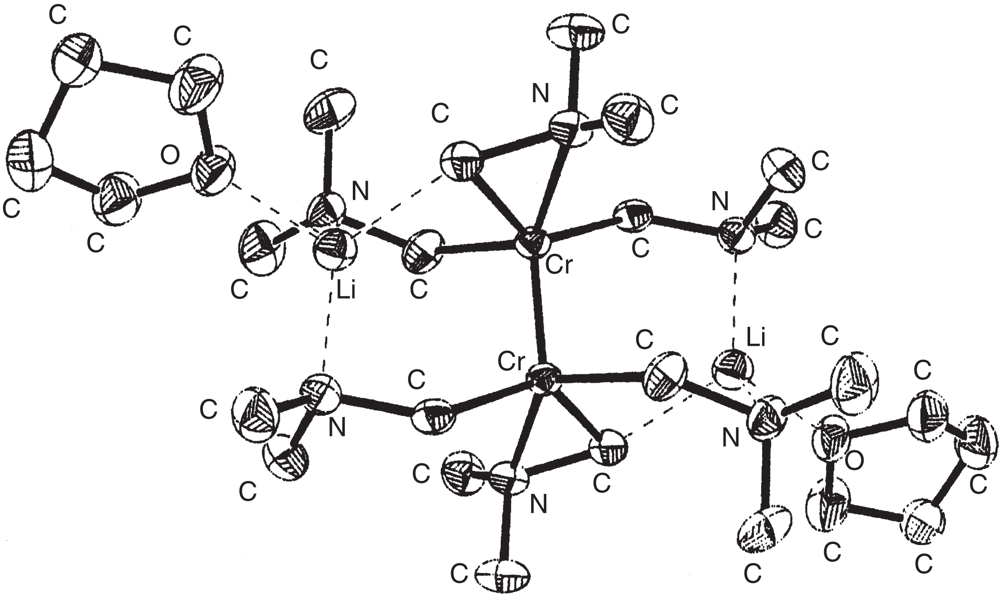


Figure 37 ORTEP drawing of [{Li(THF)}$_2$Cr$_2$(CH$_2$N(CH$_3$)$_2$)$_6$] (reproduced by permission of the American Chemical Society from *Organometallics* **1998**, *17*, 475–478).

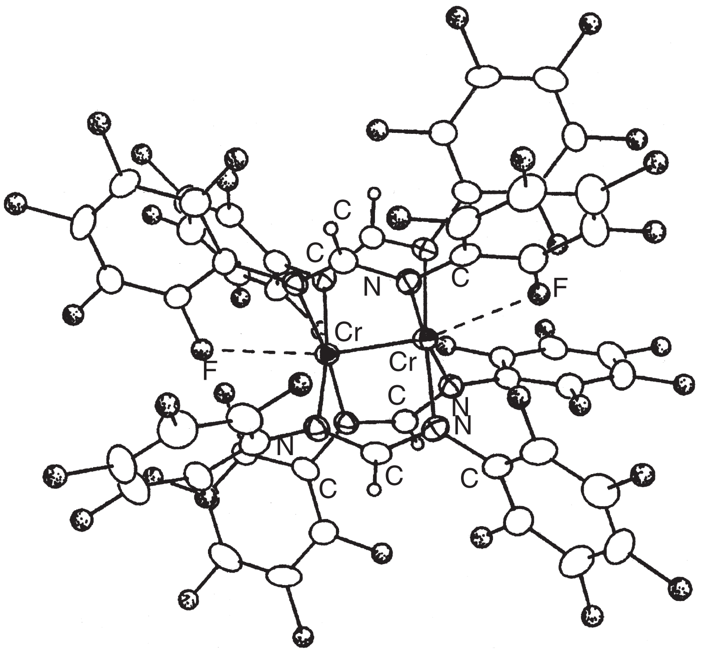


Figure 38 Drawing of the structure of $Cr_2[(C_6F_5N)_2C(H)]_4$ showing the Cr—F interactions (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1999**, *38*, 2182–2187).

the Cr—Cr bond length 2.0121(11) Å has lengthened rather significantly from the more typical value of 1.93 Å for complexes of this type.[148]

With the expansion of the use of nitrogen-based ligands, more complex ring systems have been used in the synthesis of $Cr_2^{II,II}$ complexes such as the hpp^- ligand discussed previously for the divanadium paddlewheel complex.[43] $Cr_2(hpp)_4$ has a Cr—Cr bond distance of 1.8517(7) Å[43] in comparison to complexes made with the anions of 2,6-di(phenylimino)piperdine,[146] 2,2′-dipyridylamine,[146] 2,6-bis(phenylamino)pyridine,[151] and 1′,3′-dihydrospiro[cyclohexane-1,2′-[2H]imidazo[4,5-*b*]pyridine][152] with Cr—Cr bond lengths of 2.2652(9), 1.858(1), 1.873(2), 2.016(1), and 2.016(1) Å, respectively. Note the lengthening of three of the Cr—Cr bond lengths due to either axial coordination to the dichromium core or divergent angles on the coordinated ligands. Without a bridging bidentate ligand, the bond lengths increase as demonstrated by the Cr—Cr bond length of $Cr_2(tmtaa)_2$ (2.101(1) Å) where tmtaa is the dianion of tetramethyldibenzotetraaza[14]-annulene[153] where a triple bond is predicted as a result of the loss of δ bonding.

In a typical synthesis of $Cr_2^{II,II}$ paddlewheel complexes with nitrogen-based ligands, $CrCl_2$ and the appropriate salt of the anion react together in the appropriate stoichiometry.[140] When $CrCl_2$ and $Li[o\text{-}ClC_6H_4N)_2CH]$ are reacted in a 2:3 ratio, three formamidinate ligands bridge and one chloro ligand bridge the dinuclear core.[154] The green diamagnetic solid $Cr_2[o\text{-}ClC_6H_4N)_2CH]_3(\mu\text{-}Cl)$ (1.940(1) Å) has an acute Cr—Cl—Cr bond angle of 46.67(2) degrees. In the case of the anion of α-carboline (Hcarb), the reaction of excess lithium salt of the anion with $CrCl_2$ yields the dark red anionic complex $[Cr_2(carb)_4Cl]^-$ (Cr—Cr 2.530(1) Å and Cr—Cl 2.509(2) Å) shown in Figure 39.[152] The sterically demanding *N,N*′-bis(2,6-xylyl)formamidinate ligand reacted in a 1:1 ratio with $CrCl_2$ provides a synthetic route to $Cr_2(\mu\text{-}Cl)_2((2,6\text{-}(CH_3)_2C_6H_3N)_2C(H))_2(THF)_2$ (2.612(1) Å), a molecule without significant metal–metal bonding interaction.[155] Subsequent addition of sodium acetate to a blue solution of $Cr_2(\mu\text{-}Cl)_2((2,6\text{-}(CH_3)_2C_6H_3N)_2C(H))_2(THF)_2$ results in a mixed acetate:formamidinate quadruply bonded complex with the acetate ligands in a *trans* configuration, $Cr_2((2,6\text{-}(CH_3)_2C_6H_3N)_2C(H))_2(O_2CCH_3)_2$ (2.342(1) Å).[155] Use of $Cr_2(O_2CCH_3)_4$ as the starting material followed by the addition of the formamidinate ligand results in $Cr_2((2,6\text{-}(CH_3)_2C_6H_3N)_2C(H))_2(O_2CCH_3)_2$ (2.037(1) Å) with the acetate ligands in a *cis* configuration.[155] Nitrogen-based tri- and tetradentate ligands yield linear chains containing chromium atoms appropriate for building blocks in the synthesis of large extended arrays.[156-164]

Dichromium tetracarboxylates typically contain axially coordinated ligands.[140] Indeed, even benzene, $p\text{-}C_6H_4F_2$, and $p\text{-}C_6H_4(CH_3)_2$ will form axial adducts with $Cr_2(O_2CC(C_6H_5)_3)_4$ to result in Cr—Cr bond length changes based on the ionization potentials of the axially coordinated arene ring; $Cr_2(O_2CC(C_6H_5)_3)_4{\cdot}(p\text{-}C_6H_4F_2)$ (2.176(3) Å) and $Cr_2(O_2CC(C_6H_5)_3)_4{\cdot}(p\text{-}C_6H_4(CH_3)_2)$

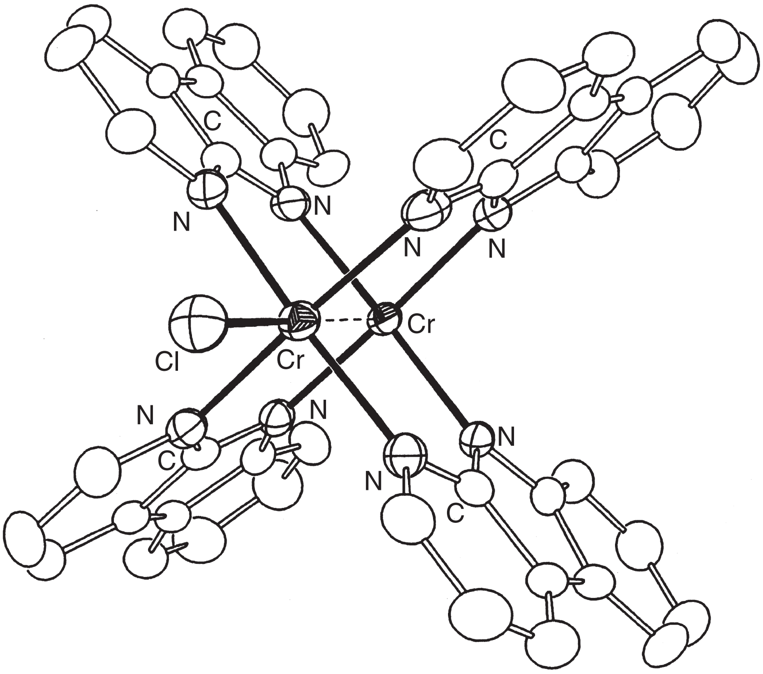


Figure 39 Drawing of the molecular structure of the anion, $[Cr_2(carb)_4Cl]^-$ (reproduced by permission of Elsevier Science from *Inorg. Chim. Acta* **2000**, *300–302*, 319–327).

(2.291(3) Å).[165] Variable temperature ^{1}H NMR studies of a series of dichromium tetraacetate complexes with different axially coordinated ligands provides an experimental method to easily probe the singlet–triplet separation.[166] To eliminate the coordination of axial ligands, 2,4,6-triisopropylbenzoic acid is refluxed in toluene with $(\eta^5\text{-}C_5H_5)_2Cr$ to result in the first crystalline dichromium tetracarboxylate with a supershort Cr—Cr bond (1.9662 (5) Å).[167] Coordination of acetonitrile in the axial positions results in an increase in the Cr—Cr bond length to 2.3892(2) Å.[167]

Using the dichromium core as a template, several unusual tetracarboxylate complexes have been synthesized as in the case of the iron-containing anion $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2CO_2)^-$.[168] Synthesized by the addition of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2CO_2H)$ to $CrCl_2$ prepared *in situ*, the red–orange diamagnetic product $Cr_2[(O_2CCH_2)(CO)_2Fe(\eta^5\text{-}C_5H_5)]_4{\cdot}[(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2CO_2H)]_2$ (2.3070(8) Å) has two neutral $(\eta^5\text{-}C_5H_5)Fe(CO)_2(CH_2CO_2H)$ ligands coordinated in the axial positions.[168] Using four zwitterionic betaine ligands in the synthesis of $[Cr_2(O_2CCH_2N(CH_3)_3)_4(OH_2)_2]^{4+}$ (2.446(2) Å)[169] from $CrCl_2$, $[ZnCl_4]^{2-}$ acts as the counter anion with only the typical electrostatic interactions between the ions in the solid state.

4.9.9 DIMOLYBDENUM COMPLEXES

4.9.9.1 Introduction

Since excellent reviews of compounds with multiple bonds between dimolybdenum and ditungsten atoms before 1990 exist,[140,170–172] attention to new complexes synthesized and structurally characterized with the exclusion of organometallic and cluster complexes is the main focus in the review of dimolybdenum metal–metal bonded compounds.

4.9.9.2 $Mo_2^{V,V}$ Complexes

Unlike chromium, dimolybdenum complexes exist in higher oxidation states primarily coordinated by nitrogen-, oxygen-, and sulfur-based ligands. The reaction of $[Mo_2(CO)_6(\eta^5\text{-}C_5H_5)_2]$ with excess $C_2(C_6H_5)_2$ in boiling octane to result in the formation of $[Mo_2(CO)(\eta^5\text{-}C_5H_5)_2\text{-}(\mu\text{-}C_4(C_6H_5)_4)]$ begins a progressive increase in the oxidation state of the metal center. When dissolved in dichloromethane and subsequently exposed to air, $[Mo_2(CO)(\eta^5\text{-}C_5H_5)_2\text{-}(\mu\text{-}C_4(C_6H_5)_4)]$ is oxidized to form the brown complex $Mo_2^{IV,IV}$ complex $[Mo_2(O)(\mu\text{-}O)\text{-}(\mu\text{-}C_4(C_6H_5)_4)(\eta^5\text{-}C_5H_5)_2]$.[173] Subsequent reaction with $(C_6H_5)NCO$ in refluxing toluene results in the loss of CO_2 and the formation of $[Mo_2(O)(\mu\text{-}NC_6H_5)(\mu\text{-}C_4(C_6H_5)_4)(\eta^5\text{-}C_5H_5)_2]$ (2.7654(3) Å) shown schematically in Figure 40a.[174] Alternatively, reaction of $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}C_4(C_6H_5)_4)(\eta^5\text{-}C_5H_5)_2]$ with Pr^iSH yielded a mixture of products, the sulfido species $[Mo_2(S)(\mu\text{-}O)(\mu\text{-}C_4(C_6H_5)_4)(\eta^5\text{-}C_5H_5)_2]$ and the Mo_2(V, V) species $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4(C_6H_5)_4)(\eta^5\text{-}C_5H_5)_2]$ (2.8129(9) Å) shown in Figure 40b.[174] Other oxidants have been used to add either oxygen or sulfur, such as air oxidation to form μ-O species or S_8 in the synthesis of μ-S complexes. With the solvent acetonitrile in the presence of trimethylamine N-oxide, $[Mo_2(CO)_4(\mu\text{-}CH_3O_2CC_2\text{-}CO_2CH_3)(\eta^5\text{-}C_5H_5)_2]$ is oxidized to $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}CH_3O_2CC_2CO_2CH_3)(\eta^5\text{-}C_5H_5)_2]$ (2.7875(6) Å).[175] Warming the substituted cylopentadienyl complex $[C_5(CH_2CH_3)(CH_3)_4]_2Mo_2(CO)_4$ in toluene in the presence of S_8 results in the formation of three isomers: $[C_5(CH_2CH_3)(CH_3)_4]_2Mo_2(\mu\text{-}\eta^2\text{-}S_2)(\mu\text{-}S)_2$, *syn*-$[C_5(CH_2CH_3)(CH_3)_4]_2Mo_2(\mu\text{-}S)_2S_2$ (2.895(1) Å), and *anti*-$[C_5(CH_2CH_3)\text{-}(CH_3)_4]_2\ Mo_2(\mu\text{-}S)_2S_2$.[176]

In a direct route to the formation of complexes with two bridging imido groups, $[Mo_2(CO)_6\text{-}(\eta\text{-}C_5H_4(CH_3))_2]$ is reacted with $(C_6F_5)NO_2$ in refluxing toluene to yield $[Mo_2O_2(\mu\text{-}N(C_6F_5)_2\text{-}(\eta\text{-}C_5H_4(CH_3))_2]$ (2.686(1) Å).[177] The use of other fluorinated nitrobenzenes such as $(C_6H_4F_2)NO_2$ or $(C_6H_5(CF_3))NO_2$ yields $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}N(C_6H_4F_2)(\eta\text{-}C_5H_4(CH_3))_2]$ (2.6499(5) Å), and $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}NC_6H_4CF_3)_2(\eta\text{-}C_5H_4(CH_3))_2]$ (2.6591(8) Å), respectively, in low yield (1–2%).[178] When $[Mo_2(CO)_6(\eta\text{-}C_5H_4(CH_3))_2]$ is reacted with $(C_6H_5)NO_2$, three products are formed: $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}NC_6H_5)(\eta\text{-}C_5H_4(CH_3))_2]$ (2.645(1) Å), $[Mo_2O_2(\mu\text{-}NC_6H_5)_2(\eta\text{-}C_5H_4(CH_3))_2]$ (2.691(1) Å), and $[Mo_2O(\mu\text{-}O)(NC_6H_5)(\mu\text{-}NC_6H_5)_2(\eta\text{-}C_5H_4(CH_3))_2]$ in the ratio 3:1:1 with yields of 56%, 18%, and 20% respectively.[179] More elaborate nitrobenzene groups have also been used such as 4′-nitrobenzo-15-crown-5 to form imido complexes.[180] Higher-yield preparative methods (20–65%) involve the use of phenylisocyanate instead of nitrobenzene to yield $[Mo_2(N(C_6H_5)_2)(\mu\text{-}N(C_6H_5)_2)(\eta\text{-}C_5H_4(CH_3))_2]$ (2.7175(5) Å).[181] Heating the mononuclear Mo^{IV} starting material $[Mo(NC_6H_5)(NC_5H_5)_2\{o\text{-}((CH_3)_3SiN)_2C_6H_4\}]$ in toluene results in C—N bond cleavage to form $[Mo_2(NC_6H_5)(\mu\text{-}NC_6H_5)_2\{\mu\text{-}(CH_3)_3SiNC_6H_4\}((CH_3)_3SiN)\{o\text{-}((CH_3)_3SiN)_2C_6H_4\}]$ (2.5669(4) Å) shown in Figure 41.[182] Heating $Mo_2(\mu\text{-}NC_6H_5)_2O_2(S_2CN(CH_2CH_3)_2)_2$ in the presence of phenyl isocyanate results in insertion of an isocyanate into a bridging (μ-NC_6H_5) to form $Mo_2(\mu\text{-}NC_6H_5)(\mu\text{-}C_6H_5NC(O)NC_6H_5)(NC_6H_5)_2(S_2CN(CH_2CH_3)_2)_2$ (2.625(3) Å).[183] Phenyl isocyanate also reacts with $[Mo_2(\mu\text{-}O)_2O_2(\eta\text{-}C_5H_4(CH_3))_2]$ in THF at elevated temperatures to form the orange complex $Mo_2(\mu\text{-}NC_6H_5)_2(NC_6H_5)_2(\eta\text{-}C_5H_4(CH_3))_2$ (2.7175(5) Å).[184]

Starting with the mononuclear Mo^V compound $[N(CH_2CH_3)_4][MoOI_4(H_2O)]$, a reaction with $OP(C_6H_5)_3$ in acetonitrile leads to a mixture of compounds, $[MoOI_3(OP(C_6H_5)_3)_2]$ and $[Mo_2O_4I_2(OP(C_6H_5)_3)_3]$ (2.557 (1) Å).[185] In the dinuclear compound, each metal center is coordinated to two bridging and one terminal oxo ligand with the iodo ligands and the three phosphine ligands unsymmetrically coordinated to result in coordination environments about the central

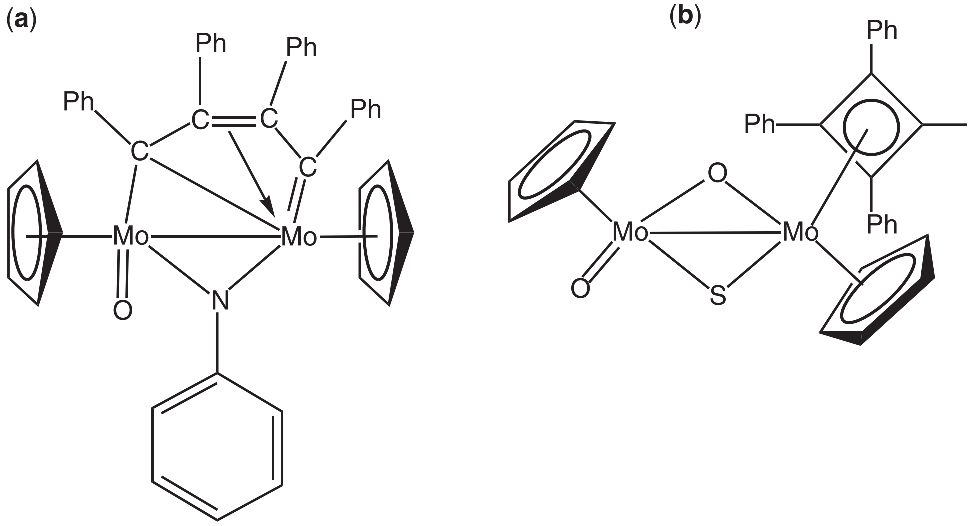


Figure 40 The structures of $[Mo_2(O)(\mu\text{-}N(C_6H_5)(\mu\text{-}C_4(C_6H_5)_4)(\eta^5\text{-}C_5H_5)_2]$ and $[Mo_2(O)(\mu\text{-}O)(\mu\text{-}S)(\eta\text{-}C_4(C_6H_5)_4)(\eta^5\text{-}C_5H_5)_2]$

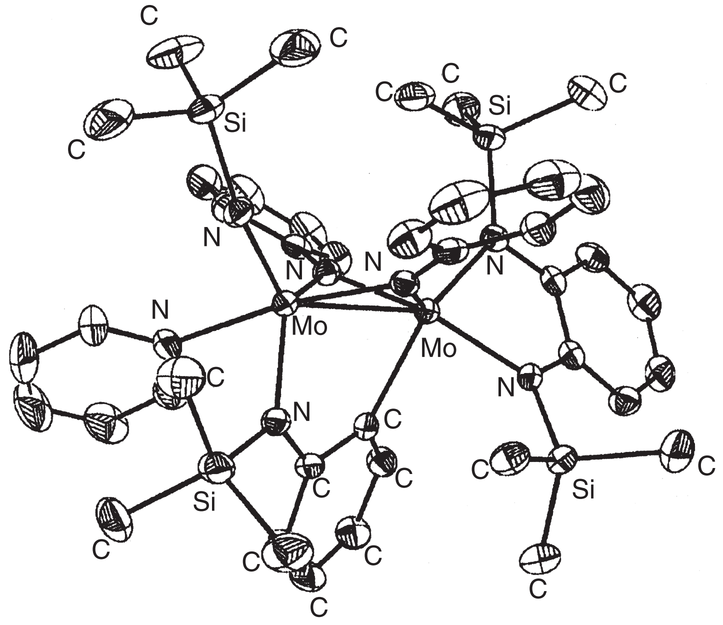


Figure 41 ORTEP drawing of $[Mo_2(NC_6H_5)(\mu\text{-}NC_5H_5)_2\{\mu\text{-}(CH_3)_3SiNC_6H_4\}((CH_3)_3SiN)\{o\text{-}(CH_3)_3SiN)_2\text{-}C_6H_4\}]$ (reproduced by permission of the Royal Society of Chemistry from *J. Chem. Soc. Chem. Commun.* **2001**, 1224–1225).

metal ions of MoO_3I_2 and $MoO_3(OP(C_6H_5)_3)_3$. Using $Mo_2O_3(acac)_4$, where acac is acetylacetonate, as the starting material, the two different ligands ethyl 4-hydroxy-3-[3-(4-methoxyanilino)-2-butenoyl]-2*H*-pyran-2-on-6-carboxylate (Mo-Mo 2.549(1) Å) and ethyl 4-(4-hydroxy-6-methyl-2*H*-pyran-2-on-3-yl)-2-(4-methoxyanilino)-4-oxo-2-butenoate (2.556(1) Å) react to result in complexes of the general type $Mo_2O_4L_2(HOCH_3)_2$ where L represents the two carboxylate ligands.[186] Complexes with the Mo_2O_4 core have also been prepared from either mononuclear Mo^{V}, triply bonded $Mo_2^{III,III}$, or quadruply bonded $Mo_2^{II,II}$ starting materials. Using $(C_5H_5NH)_2[MoCl_5O]$ and a series of diamine ligands, the dicationic complexes $[Mo_2O_4(tpen)]^{2+}$ (2.546(1) Å) and $[Mo_2O_4(tppn)]^{2+}$ (2.541(2) Å) where tpen and tppn are *N,N,N,N*-tetrakis(2-pyridylmethyl)ethylenediamine and *N,N,N,N′*-tetrakis(2-pyridylmethyl)propylenediamine respectively have been prepared and structurally characterized.[187] $Mo_2(N(CH_3)_2)_6$ is reacted with C_6F_5OH to form the anion $[Mo_2O_2(\mu\text{-}O)_2(OC_6F_5)_4]^{2-}$ (2.556(1) Å).[188] In the case of the reaction of $Mo_2(O_2CCH_3)_4$ with 2-pyridyl(diisopropylphosphino)methane in a THF:dichloromethane solvent mixture, an orange–yellow complex $Mo_2O_4Cl_2(\eta^2\text{-}2\text{-pyridyl(diisopropylphosphino)methane})_2$ (2.5700(8) Å) shown in Figure 42 results.[189] Simply heating $Mo_2Cl_4(4,4'\text{-dimethyl-}2,2'\text{-dipyridyl})_2$ in *o*-dichlorobenzene provides the red complex $Mo_2O_4Cl_2(\eta^2\text{-}2\text{-pyridyl(diisopropylphosphino)-methane})_2$ (2.562(2) Å).[190]

There is a wide variety of both mono-, di-, and trinuclear complexes used in the synthesis of Mo_2(V,V) sulfur-containing complexes. $Mo_2(O_2CCH_3)_4$ is reacted with $Na_2[S_2C_2(CN)_2]$ and subsequently $(C_4H_9)_4NBr$ in dry methanol to result in the red complex $[Mo_2(\mu\text{-}S)_2(O)(S)(S_2C_2(CN)_2)_2]^{2-}$ with a Mo—Mo bond length of 2.858(1) Å.[190] The reaction of $[Mo_2O_2(\mu\text{-}O)(\mu\text{-}NC_6H_5)(\eta\text{-}C_5H_4(CH_3))_2]$ with hydrogen sulfide leads to the substitution of a terminal oxo ligand by a sulfido ligand to form $[Mo_2O(S)(\mu\text{-}O)(\mu\text{-}NC_6H_5)(\eta\text{-}C_5H_4(CH_3))_2]$ (2.660(1) Å) as shown in Figure 43.[191] The $Mo_2(\mu\text{-}S)(\mu\text{-}O)O_2$ core in the anion $[Mo_2(\mu\text{-}S)(\mu\text{-}O)O_2(\mu\text{-}N,N'\text{-}C_{10}H_{12}N_2O_8)]^{2-}$ (2.6655(7) Å) is formed by the reduction of $[(MoO_3)_2(\mu\text{-edta})]^{4-}$, where edta is ethylenediaminetetracetate, by dithionite at pH 6.[192] Both *trans*-$Mo_2O_2(\mu\text{-}Te)(\mu\text{-}O)(\eta^5\text{-}C_5H_5)_2$ (2.068(7) Å) and *cis*-$Mo_2O_2(\mu\text{-}S)(\mu\text{-}O)(\eta^5\text{-}C_5H_5)_2$ (2.08(1) Å) are formed upon refluxing $(\eta^5\text{-}C_5H_5)_2Mo_2Fe_2(CO)_7(\mu_3\text{-}S)(\mu_3\text{-}Te)$ in the presence of air.[193] The $[Mo_2(\mu\text{-}S)_2O_2Br_4]^{2-}$ (2.857(2) Å) core is synthesized by simply refluxing $Mo_2S_7Br_4$ in tri-*n*-butylphosphine.

A high-yield preparation of the complex $[Mo_2S(SC(H){=}C(H)S)(\mu\text{-}S)_2(\eta^5\text{-}C_5H_5)_2]$ (2.984(1) Å) has been developed using $[Mo_2(\mu\text{-}HCCH)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ and S_8.[194] Both of the anions $[Mo_2S_4(S_2C_6H_4)_2]^{2-}$ (2.865(2) Å) and $[Mo_2S_4(S_2)_2]^{2-}$ (2.821(1) Å) are prepared by the addition of benzenethiol to $(NH_4)_2Mo_2(S_2)_6{\cdot}H_2O$ under slightly different reaction conditions.[195] Crystallographic

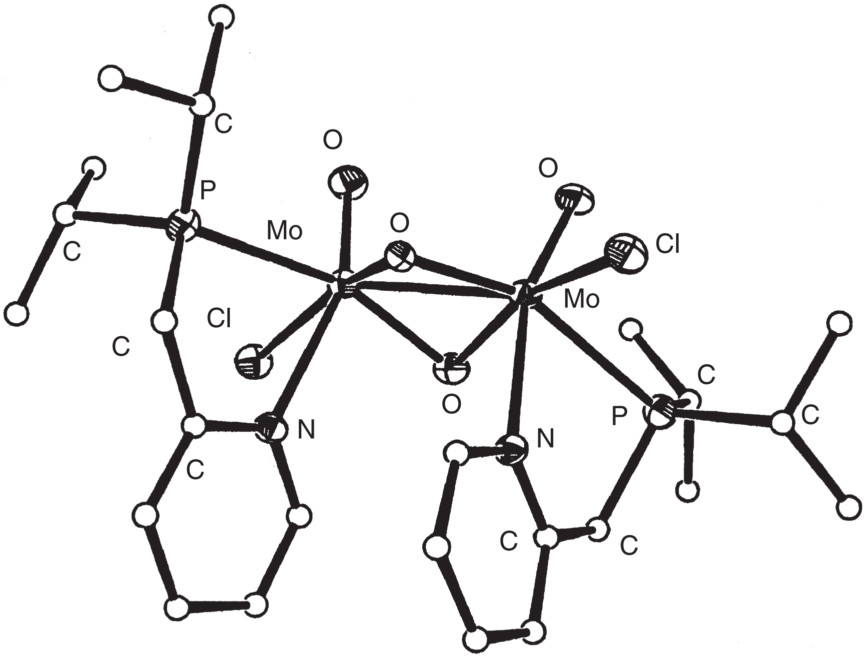


Figure 42 ORTEP drawing of the structure of $Mo_2O_4Cl_2(\eta^2\text{-}2\text{-pyridyl(diisopropylphosphino)methane})_2$ (reproduced by permission of Elsevier Science from *Inorg. Chim. Acta* **2002**, *328*, 232–236).

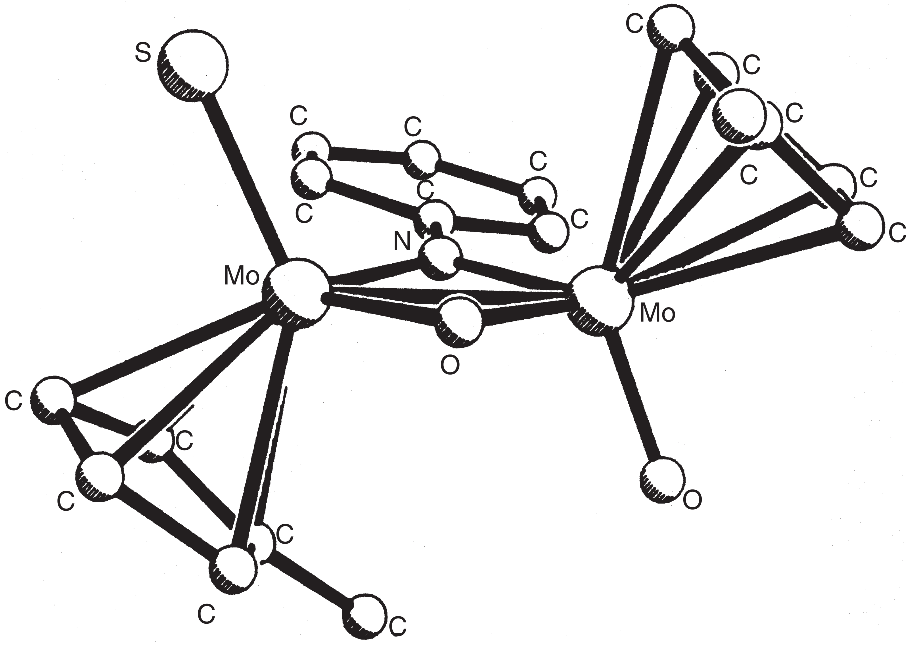


Figure 43 Structure of $[Mo_2O(S)(\mu\text{-}O)(\mu\text{-}N(C_6H_5)(\eta\text{-}C_5H_4(CH_3))_2]$ (reproduced by permission of Elsevier Science from *J. Organomet. Chem.* **1991**, *405*, 207–215).

studies of the MoS_2 core in $[Mo_2(NC_6H_4CH_3)_2(S_2P(OCH_2CH_3)_2)_2(O_2CCH_3)(\mu\text{-}S)(\mu\text{-}SCH_3)]$ (2.8347(5) Å), $[Mo_2(NC_6H_4CH_3)_2(S_2P(OCH_2CH_3)_2)_2(O_2CCH_3)(\mu\text{-}SCH_3)_2]^+$ (2.878(1) Å) shown in Figure 44, and $[Mo_2(NC_6H_4CH_3)_2\text{-}(S_2P(OCH_2CH_3)_2)$ $(S_2P(O)(OCH_2CH_3)_2)$ $(O_2CCH_3)(\mu\text{-}SCH_2CH_3)_2]$ (2.8948(9) Å) were undertaken to compare the cationic complex that is activated towards heterolytic C—S and C—O cleavage and the neutral complexes.[196] The related complex $[Mo_2(NC_6H_4CH_3)_2(S_2P(OCH_2CH_3)_2)_2(\mu\text{-}O_2CCH_3)(\mu\text{-}S)$ $(\mu\text{-}SI_3)]$ (2.878(1) Å) has also been structurally characterized.[197]

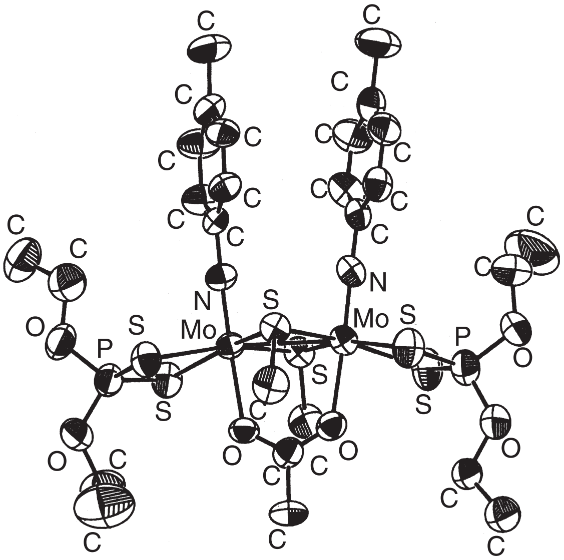


Figure 44 ORTEP drawing of the cationic complex $[Mo_2(NC_6H_4CH_3)_2(S_2P(OCH_2CH_3)_2)_2(O_2CCH_3)(\mu\text{-}SCH_3)_2]^+$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1999**, *38*, 802–813).

4.9.9.3 $Mo_2^{IV,IV}$ Complexes

In comparison to the variety of Mo_2(V, V) complexes, only several $Mo_2^{IV,IV}$ compounds with predominately cyclopentadienyl- and sulfur-based ligands have been structurally characterized. Synthesized from the $Mo_2^{II,II}$ anion $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}PH_2)]^-$,[198] $[Mo_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu,\eta^2\text{-}PE)]$ where E is As (Mo—Mo bond length 3.0191(9) Å) or Sb (Mo—Mo bond length 3.0563(11) Å) form upon addition of one equivalent of $AsCl_3$ and $SbCl_3$ respectively. The phosphorus:arsenic and phosphorus:antimony are disordered 50:50 over the two crystallographic sites. In related chemistry, the $Mo_2^{II,II}$ core is oxidized by the addition of 4-$(CH_3)C_6H_4CCH$ to an ethylenediamine (en) solution of $Mo_2(\mu\text{-}O_2CCH_3)_4$ to result in the formation of the cation $[Mo_2(\mu\text{-}O_2CCH_3)(\mu\text{-}4\text{-}(CH_3)C_6H_4CCH)(en)_4]^{3+}$ (2.486(3) Å).[199]

The reaction of $[Mo_2(\mu\text{-}C_2(CO_2CH_3)_2)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ with $(CH_3S)_2C{=}S$ results in the insertion of a $—CSCH_3$ fragment in the bridging alkyne to produce $[Mo_2(\mu\text{-}C(CO_2CH_3)C(SCH_3)C(CO_2CH_3))(\mu\text{-}S)(\mu\text{-}SCH_3)(\eta^5\text{-}C_5H_5)_2]$ (2.5605(1) Å).[200] Note that the reaction can be generalized to other trithiocarbonates. The reaction of $[Mo_2(\mu\text{-}H)(\mu\text{-}P(C_6H_5)_2)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ with Pr^iSH leads to the dealkylation of the thiol to result in the quadruply bridged green product $[Mo_2(\mu\text{-}S)_2(\mu\text{-}SPr^i)(\mu\text{-}P(C_6H_5)_2)(CO)_4(\eta^5\text{-}C_5H_5)_2]$ (2.623(2) Å).[201] The red–purple cationic complex $[Mo_2(\mu\text{-}S)(\mu\text{-}S_2C_4H_2S)(S_2CH_2)\{\eta^5\text{-}C_5H_4(CH_3)\}_2]Br$ (2.608(1) Å) forms upon addition of 2-bromothiophene to $[Mo_2(\mu\text{-}S)_2(S_2CH_2)\{\eta^5\text{-}C_5H_4(CH_3)\}_2]$.[202] $[(\eta^5\text{-}C_5H_5)_2(CO)_4Mo_2]$ reacts with $HSCH_2CO_2CH_2CH_3$ to yield $[(\eta^5\text{-}C_5H_5)_2(CO)_4Mo_2(\mu\text{-}S)_2(\mu\text{-}SCH_2CO_2CH_2CH_3)_2]$ (2.590(1) Å).[203]

Imido complexes are synthetically accessible by the addition of ethylene to a toluene solution of $Mo(CHBu^t)(NC_6H_3(CH_3)_2\text{-}2,6)(OBu^t)_2$ in a pressure vessel to result in the purple–red complex $[Mo(\mu\text{-}NC_6H_3(CH_3)_2\text{-}2,6)(OBu^t)_2]_2$ (2.654(1) Å).[204] Imido complexes have also been synthesized as a result of cleavage of formamidinate ligands as in the case of the reaction of $MoCl_3(THF)_3$ with diphenylformamidine and $(C_6H_5)_4PCl$ in refluxing *o*-dichlorobenzene.[205] The red anion $[Mo_2\{((C_6H_5)_2N)_2C(H)\}_2(\mu\text{-}NC_6H_5)Cl_5]^-$ (2.527(1) Å) can also be synthesized by refluxing $MoCl_4(CH_3CN)_2$ with diphenylformamidine and $(C_6H_5)_4PCl$ in *o*-dichlorobenzene. The starting material $Mo_2S_2Cl_6$ reacts with tetrahydrothiophene to yield the green diamagnetic $Mo_2^{IV,IV}$ complex $Mo_2(\mu\text{-}S_2)(\mu\text{-}SC_4H_8)Cl_6(SC_4H_8)_2$ (2.769(3) Å).[206] Upon reacting $Mo_2S_2Cl_6$ with $S(CH_3)_2$ the brown paramagnetic mixed valent complex $Mo_2(\mu\text{-}S)(\mu\text{-}S_2)Cl_5(S(CH_3)_2)_3$ (2.742(1) Å) is formed.[206]

4.9.9.4 $Mo_2^{III,III}$ Complexes

Thiolate-bridged $Mo_2^{III,III}$ complexes play a key role in synthesizing cluster compounds in addition to their biological and catalytic applications as outlined in an extensive review of the field.[207] $[Mo_2(\eta^5-C_5H_5)_2(\mu-\eta^1-\eta^2-C_2C_6H_4CH_3)(\mu-S(CH_3))_3]$ (2.616(1) Å) has been synthesized via deprotonation of $[Mo_2(\eta^5-C_5H_5)_2(HCCC_6H_4CH_3)(\mu-S(CH_3))_3](BF_4)$ with $N(CH_2CH_3)_3$ as part of a study of the activation of alkynes at a sulfur-rich $Mo_2^{III,III}$ core.[208] Subsequent protonation of the phenyl derivative, $[Mo_2(\eta^5-C_5H_5)_2(\mu-\eta^1-\eta^2-C_2C_6H_5)(\mu-S(CH_3))_3]$, using $HBF_4{\cdot}(CH_3CH_2)_2O$ yields the vinylidene complex $[Mo_2(\eta^5-C_5H_5)_2(\mu-\eta^1-\eta^2-CC(H)C_6H_5)(\mu-S(CH_3))_3](BF_4)$ (2.622(1) Å). $[Mo_2(\eta^5-C_5H_5)_2(HCCC_6H_5)(\mu-S(CH_3))_3](BF_4)$ also reacts with isocyanide and carbon disulfide to result in $[Mo_2(\eta^5-C_5H_5)_2(\mu-\eta^1-\eta^3-CH{=}CC_6H_5-SCH_3)(\mu-SCH_3)_2](BF_4)$ (2.825(1) Å). Addition of $NaBH_4$ to μ-vinylidene complexes such as $[Mo_2(\eta^5-C_5H_5)_2(\mu-\eta^1-\eta^2-CC(H)(CH_2CH_2CH_3))(\mu-S(CH_3))_3](BF_4)$ results in the μ-alkylidyne species $[Mo_2(\eta^5-C_5H_5)_2(\mu-CCH_2CH_2CH_2CH_3)(\mu-S(CH_3))_3]$ (2.5846(2) Å) as blue diamagnetic powders.[209] However, the reaction of $NaBH_4$ with $[Mo_2(\eta^5-C_5H_5)_2(CH_3CN)(\mu-S(CH_3))_3](BF_4)$ produces the orange diamagnetic tetrahydroborato complex $[Mo_2(\eta^5-C_5H_5)_2(\mu-S(CH_3))_3(\mu-BH_4)]$ (2.653(1) Å) shown in Figure 45.[210]

S-methylthiophenium derivatives such as $[Mo_2(\eta^5-C_5H_5)_2(\mu-\eta^2-\eta^4-C_4H_2(CF_3)_2(SCH_3))-(\mu-S(CH_3))_2](BF_4)$ (2.604(1) Å), shown in Figure 46, and the metallocycle $[Mo_2-(\eta^5-C_5H_5)_2(\mu-\eta^2-\eta^4-C(C_6H_4CH_3){=}CHC(C_6H_4CH_3){=}C(H)SCH_3)(\mu-S(CH_3))_2](BF_4)$ (2.761(2) Å) result from the addition of terminal alkynes to $[Mo_2(\eta^5-C_5H_5)_2(CH_3CN)-(\mu-S(CH_3))_3](BF_4)$.[208,211] The green, diamagnetic, cationic complex, $[Mo_2(\eta^5-C_5H_4CH_3)_2(\mu-SCH_3)_2(\mu-SI)(CO)_2]I_5$ (2.7735(12) Å), is synthesized from the reaction of $[Mo_2(\eta^5-C_5H_4CH_3)_2(\mu-SCH_3)_2(\mu-S)(CO)_2]$ with excess I_2 in methylene chloride.[212]

The irradiation of a benzene solution of $[Mo_2(\eta^5-C_5H_5)_2(CO)_6]$, S_8, and dimethyl acetylenedicarboxylate produces the bridging ligand $\mu-S_2C_2(CO_2(CH_3)_2)_2$ in $[Mo_2(\eta^5-C_5H_5)_2(CO)_2-(\mu-S_2C_2(CO_2(CH_3)_2)_2)_2]$ (3.040(2)Å).[213] $[Mo_2(\mu-S)(\mu-SCH_3)(\mu-C(CO_2CH_3)C(SCH_3)C(CO_2CH_3))(\eta^5-C_5H_5)_2]$ reacts with dimethylacetylenedicarboxylate to yield $[Mo_2(\mu-C(CO_2CH_3)C(SCH_3)C(CO_2CH_3)))(\mu-SC(CO_2CH_3){=}C(CO_2CH_3)SCH_3)(\eta^5-C_5H_5)_2]$ (2.7201(6) Å).[214] $[Mo_2(\mu-S)(\mu-SCH_2CH_2SCC(CO_2CH_3){=}C(CO_2CH_3))(\eta^5-C_5H_5)_2]$ reacts with dimethyl acetylenedicarboxylate but two isomers, $[Mo_2(\mu-SC(CO_2CH_3){=}C(CO_2CH_3)-SCH_2CH_2SCC(CO_2CH_3){=}C(CO_2CH_3))(\eta^5-C_5H_5)_2]$ and $[Mo_2(\mu-SCH_2CH_2SCC\ (CO_2CH_3){=}C(CO_2CH_3)C(CO_2CH_3){=}C(CO_2CH_3)S)(\eta^5-\ C_5H_5)_2]$ (2.7677(8) Å), are formed.[214] Attempts to crystallize $[Mo_2(\mu-SC(CO_2CH_3){=}C(CO_2CH_3)SCH_2CH_2SCC(CO_2CH_3){=}C(CO_2CH_3))(\eta^5-C_5H_5)_2]$ led to the oxidized product $[Mo_2(\mu-SC\ (CO_2CH_3){=}C(CO_2CH_3)S({=}O)CH_2CH_2S({=}O)_2CC(CO_2CH_3){=}C(CO_2CH_3))(\eta^5-C_5H_5)_2]$ (2.727(2) Å). The reaction of $[Mo_2(\mu-S)(\mu-SCH_2CH_2SCC(CO_2CH_3){=}C(CO_2CH_3))(\eta^5-C_5H_5)_2]$ with methyl propiolate yields $[Mo_2(\mu-SCH{=}C(CO_2CH_3)SCH_2CH_2SCC(CO_2CH_3){=}C(CO_2CH_3))(\eta^5-C_5H_5)_2]$ (2.7245(14) Å).

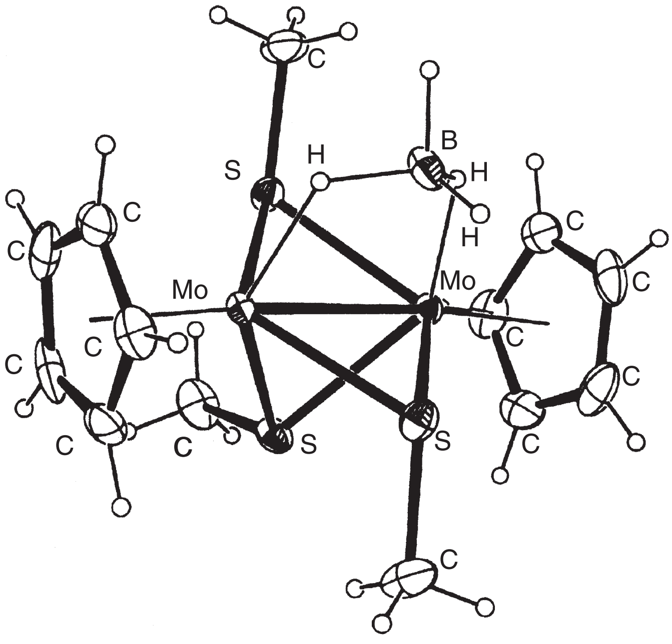


Figure 45 ORTEP drawing of $[Mo_2(\eta^5-C_5H_5)_2(\mu-S(CH_3))_3(\mu-BH_4)]$ (reproduced by permission of the Royal Society of Chemistry from *J. Chem. Soc. Chem. Commun.* **2000**, 2137–2138).

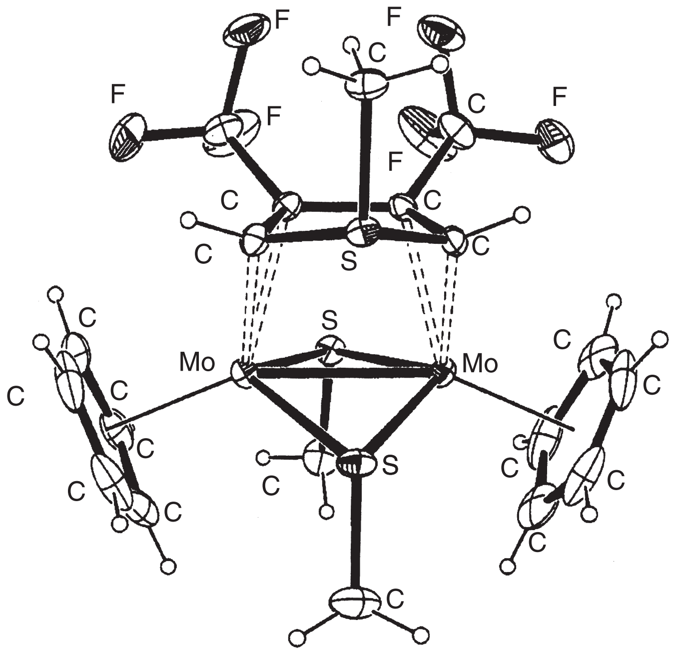


Figure 46 ORTEP drawing of $[Mo_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}\eta^2\text{-}\eta^4\text{-}C_4H_2(CF_3)_2(SCH_3))(\mu\text{-}S(CH_3))_2](BF_4)$ (reproduced by permission of the American Chemical Society from *Organometallics* **2001**, *20*, 1230–1242).

The reactivity of $[Mo_2(CO)_4(\mu\text{-}(CO_2CH_3)CC(CO_2CH_3))(\eta^5\text{-}C_5H_5)_2]$ has been investigated with 1,3-dithiole-2-thiones. C$=$S bond cleavage results in the formation of the green diamagnetic product $[Mo_2(\mu\text{-}S)(\mu\text{-}SC(CO_2CH_3){=}C(CO_2CH_3)SCC(CO_2CH_3){=}C(CO_2CH_3))(\eta^5\text{-}C_5H_5)_2]$ (2.5825(7) Å) upon reacting $[Mo_2(CO)_4(\mu\text{-}(CO_2CH_3)CC(CO_2CH_3))(\eta^5\text{-}C_5H_5)_2]$ with 4,5- bis(methoxylcarbonyl)1, 3-dithiole-2-thione.[215] $[Mo_2(CO)_4(\mu\text{-}(CO_2CH_3)CC(CO_2CH_3))(\eta^5\text{-}C_5H_5)_2]$ reacts with dimethyl trithiocarbonate to form $[Mo_2(\mu\text{-}S)(\mu\text{-}SCH_3)\text{-}(\mu\text{-}C(CO_2CH_3)C(SCH_3)C(CO_2CH_3))(\eta^5\text{-}C_5H_5)_2]$ (2.5605(10) Å).[215] $[Mo_2(\mu\text{-}S)\text{-}(\mu\text{-}SC\text{-}(CO_2CH_3){=}C(CO_2CH_3)SCC(CO_2CH_2CH_3){=}C(C_6H_5))(\eta^5\text{-}C_5H_5)_2]$ (2.5770(6) Å) and $[Mo_2(\mu\text{-}S)(\mu\text{-}SC\text{-}(CO_2CH_3){=}C(CO_2CH_3)SCC(C_6H_5){=}C(CO_2CH_2CH_3))(\eta^5\text{-}C_5H_5)_2]$ (2.5700(7) Å) are the mixture of products synthesized from the reaction of $[Mo_2(CO)_4\text{-}(\mu\text{-}(C_6H_5)\text{-}CC(CO_2CH_2CH_3))(\eta^5\text{-}C_5H_5)_2]$ with 4,5-bis(methoxylcarbonyl)1,3-dithiole-2-thione.[215]

After reacting the mononuclear Mo^{III} complex $(\eta^5\text{-}C_5H_5)Mo(\eta^4\text{-}C_4H_6)(CH_3)$ with one equivalent of $B(C_6F_5)_3$, extraction with CH_2Cl_2 results in the red paramagnetic complex $[(\eta^5\text{-}C_5H_5)Mo(\eta^4\text{-}C_4H_6)(\mu\text{-}Cl)(\mu\text{-}CH_2)(O)Mo(\eta^4\text{-}C_4H_6)][CH_3B(C_6F_5)_3]$ (2.8801(5) Å) after borane attack at the methyl position.[216] The complex bis(η^5-indenyl)tetrakis(μ-iodo)dimolybdenum, $Mo_2I_4(C_9H_7)_2$ (2.720(4) Å), is also formed from the reaction of a mononuclear starting material, $MoI_3(THF)_3$, with sodium indenyl and subsequently tetraphenylphosphonium iodide.[217] $MoCl_3(THF)_3$ forms red crystals of $Mo_2Cl_6(THF)_3$ (2.602(1) Å) upon standing in a methylene chloride for several hours.[218]

In terms of more unusual bridging ligands, the reaction of $(C_6H_5)_2Te_2$, $(\eta^5\text{-}C_5H_5)_2ZrCl_2$, and $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(CO)_4]$ results in the formation of three separate products $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(\mu\text{-}TeC_6H_5)_4]$ and two isomers of $[(\eta^5\text{-}CH_3O_2CC_5H_4)_2Mo_2(\mu\text{-}TeC_6H_5)_3(\mu\text{-}Cl)]$ with either one or two (2.714(6) Å) of the phenyl groups of the bridging μ-TeC_6H_5 moiety parallel to the Mo—Mo axis.[219] $[(\eta^5\text{-}1,2,4\text{-}Bu^t{}_3C_5H_2)_2Mo(\mu\text{-}\eta^5\text{-}Sb_5)Mo(\eta^5\text{-}1,2,4\text{-}Bu^t{}_3C_5H_2)_2]$ shown in Figure 47 is formed upon the reaction of *cyclo*-$Bu^t{}_4Sb_5$ with $[(\eta^5\text{-}1,2,4\text{-}Bu^t{}_3C_5H_2)(CO)_3Mo(CH_3)]$ in decaline.[220]

Quadruply bonded $Mo_2{}^{II,II}$ compounds undergo oxidative addition to form a range of products.[140] For example, the reaction of $Mo_2(\mu\text{-}O_2CCH_3)_4$ with $K(\eta^5\text{-}C_5H_5)$ in the presence of trimethylphosphine results in the $Mo_2{}^{III,III}$ complex $Mo_2(\mu\text{-}O_2CCH_3)_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CH_3)(\mu\text{-}P(CH_3)_2)$ (2.8447(5) Å).[221] Addition of $AgBF_4$ to a solution of $Mo_2(hpp)_4$ leads to the oxidation of the dimolybdenum core and the formation of $Mo_2(hpp)_4(BF_4)_2$ with a molybdenum—molybdenum bond length of 2.142(2) Å.[222] The reaction of the cation $[Mo_2(CH_3CN)_8](BF_4)_4$ with bis(diphenylphosphino)amine (dppa) in acetonitrile results in

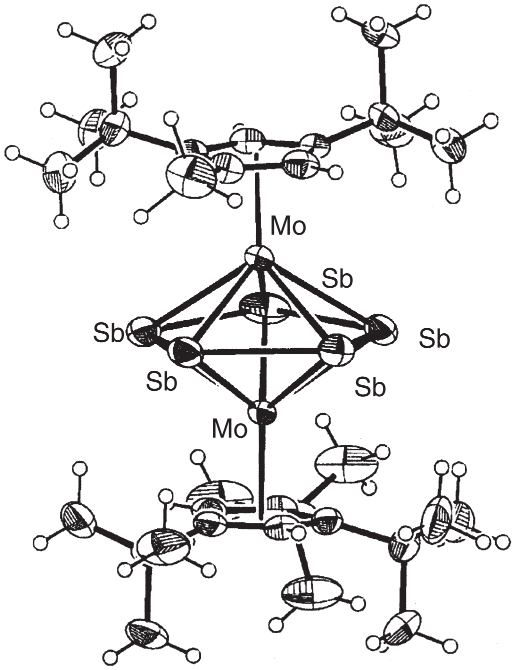


Figure 47 Molecular structure of $[(\eta^5\text{-}1,2,4\text{-}Bu^t{}_3C_5H_2)_2Mo(\mu\text{-}\eta^5\text{-}Sb_5)Mo(\eta^5\text{-}1,2,4\text{-}Bu^t{}_3C_5H_2)_2]$ (reproduced by permission of Wiley-VCH from *Angew. Chem., Int. Ed. Engl.* **2000**, *39*, 4148–4150).

bridging acetonitrile species both with $\{Mo_2(\mu\text{-}\eta^2\text{-}CH_3CN)(\mu\text{-}O))(\mu\text{-dppa})_2(CH_3CN)_4](BF_4)_2$ (2.4174(8) Å)} and without $\{[Mo_2(\mu\text{-}\eta^2\text{-}CH_3CN)(\mu\text{-}NC(CH_3)P(C_6H_5)_2NP(C_6H_5)_2)$ (μ-dppa) $(CH_3CN)_5](BF_4)_3$ (2.493(15) Å)} the presence of water in the reaction mixture.[223]

A common structural motif in $Mo_2^{III,III}$ complexes is the edge-sharing bioctahedral geometry shown in Figure 48 that can be synthesized directly or by oxidative addition across a $Mo_2^{II,II}$ quadruple bond.[140] A variety of both bridging and terminal ligands has been studied and recent examples include complexes with bridging $\mu\text{-}SCH_2CH_2CH_3$[224] and μ-O[225,226] ligands such as in $[Mo_2(\mu\text{-}O)(\mu\text{-}OCH_3)(en)_4]^{3+}$ (2.442(1) Å).[225]

One of the most common bridging ligands is a halide atom[205,227–231] as in the case of $Mo_2Cl_4(\mu\text{-}O_2CCH_3)_2(P(CH_2CH_3)_3)_2$ (2.612(1) Å) shown in Figure 49.[228] Recent studies include determining the energy of the singlet–triplet gap for edge-sharing bioctahedral complexes using NMR spectroscopy techniques[227,228,232] and the synthesis of heterobimetallic, $MoW^{III,III}$, edge-sharing bioctahedral complexes.[227,232,233]

One of the classic types of triply bonded $Mo_2^{III,III}$ compounds is the ethane-like d^3—d^3 molecules shown in Figure 50.[140,234] Alkyl groups are common ligands.[140,234,235] For example, the red diamagnetic compound 1, $2\text{-}Mo_2(N(CH_3)_2)(P(C_6H_5)_2)(CH_2Si(CH_3)_3)_4$ (2.1911(9) Å) is synthesized from addition of the lithium reagent $Li(P(C_6H_5)_2)$ to a hexane solution of $1,1\text{-}Mo_2(N(CH_3)_2)Br(CH_2Si(CH_3)_3)_4$.[236] Neutral ligands such as phosphine ligands will also coordinate, and thereby increase the coordination number at the metal center without changing the bond order as in the case of $Mo_2(CH_2C_6H_5)_2(O^iPr)_4(dmpm)$ (2.2540(11) Å).[237] In contrast, the reaction of $Mo_2(\mu\text{-}O_2CH_2Bu^t)_6$ with trimethylphosphine leads to the mixed valent compound, $Mo_2^{II,VI}$ $Mo_2(\mu\text{-}O_2CH_2Bu^t)(O_2CH_2Bu^t)_3(\mu\text{-}O)(P(CH_3)_3)_4$ (2.4931(9) Å).[238]

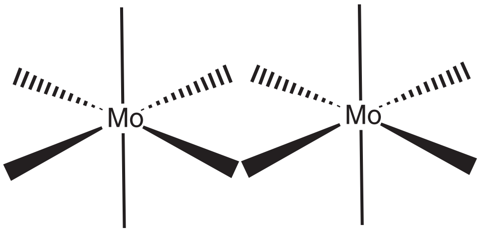


Figure 48 Edge-sharing bioctahedral geometry at a $Mo_2^{III,III}$ core.

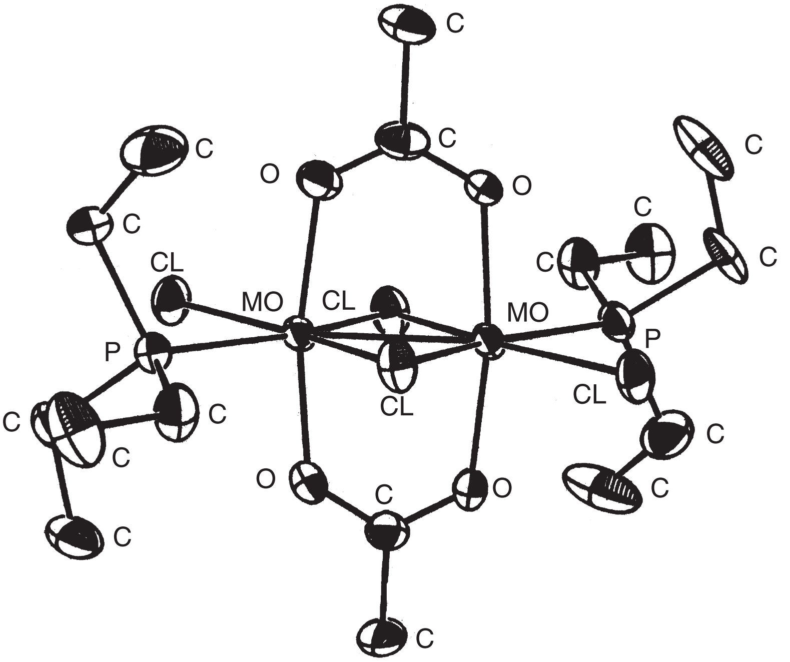


Figure 49 ORTEP drawing of $Mo_2Cl_4(\mu\text{-}O_2CCH_3)_2(P(CH_2CH_3)_3)_2$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1993**, *32*, 4871–4875).

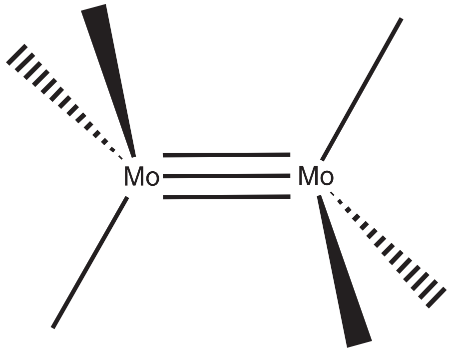


Figure 50 Triply bonded ethane-like d^3—d^3 molecules

Common ligands include nitrogen-based ligands[239] such as —$N(CH_3)_2$[240–245] in the complex $Mo_2(C_9H_7)_2(N(CH_3)_2)_4$ (2.2516(5) Å).[240] Other ligand types in triply bonded ethane-like molecules include oxygen-based ligands[238,246-252,253] such as the homoleptic alkoxide complex $Mo_2(OC(CH_3)_2C_6H_5)_6$ (2.2388(6) Å)[254] shown in Figure 51. In the absence of dinitrogen, $Mo(NC(CD_3)_2CH_3)(3,5\text{-}C_6H_3(CH_3)_2)_2$ reacts with $NMo(OC(CH_3)_3)_3$ with nitrogen atom transfer from $NMo(OC(CH_3)_3)_3$ to $Mo(NC(CD_3)_2CH_3)(3,5\text{-}C_6H_3(CH_3)_2)_2$ and the formation of the triply bonded complex $Mo_2(OC(CH_3)_3)_6$.[255]

4.9.9.5 $Mo_2^{II,II}$ Complexes

The reaction of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}C_2(CO_2(CH_3)_2)_2]$ with $[NO][BF_4]$ leads to the formation of the cation $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_3(NO)(\mu\text{-}C_2(CO_2(CH_3)_2)_2][BF_4]$ (2.9762(9) Å) with loss of a carbonyl ligand.[256] The salt $[C_7H_7][BF_4]$ reacts with the mononuclear anion $[(\eta^5\text{-}C_5H_5)Mo(CO)_2(CH_3CHO)]^-$ to form three different species, $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4\text{-}(\mu\text{-}\eta^2\text{-}CH_3CHO)]$ (2.9670(8) Å), $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6]$, and $[(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_7H_7)Mo(CO)_2]$.[257] However, phosphido-bridged complexes dominate dimolybdenum(II, II) complexes containing the $(\eta^5\text{-}C_5H_5)_2Mo_2$ core with Mo—Mo bond lengths in the range 2.593–3.333 Å.[258-264] The chelating

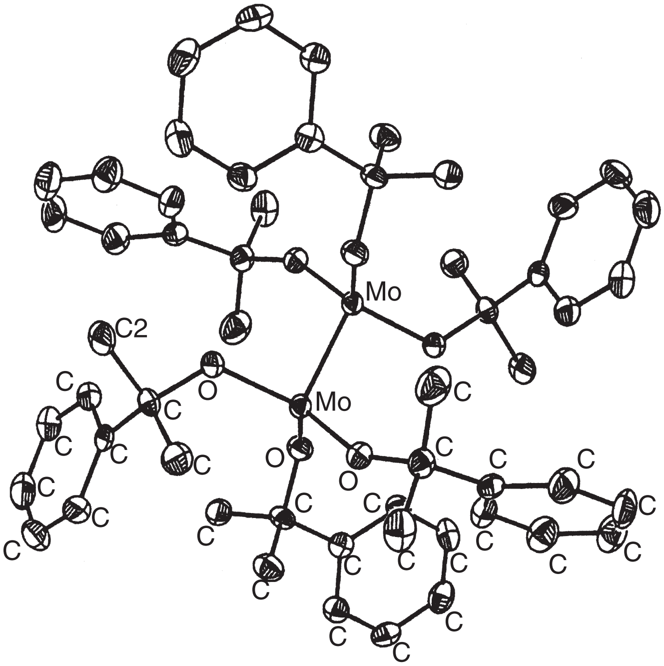


Figure 51 ORTEP drawing of the structure of $Mo_2(OC(CH_3)_2C_6H_5)_6$ (reproduced by permission of Elsevier Science from *Polyhedron* **1999**, *18*, 1293–1301).

phosphine ligand dppm undergoes a ring-opening reaction in the presence of $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-dppm})$ and $CNBu^t$ with the loss of a carbonyl group to form $(\eta^5\text{-}C_5H_5)_2Mo_2(\mu\text{-}\sigma, \pi\text{-}CNBu^t)(CO)_3(\mu\text{-dppm-P})$ (3.1950(5) Å).[265]

Thiolato-bridged $Mo_2^{II,II}$ [207] compounds such as $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2(\mu\text{-}SCF_3)_2]$ react with KCN in acetonitrile with subsequent addition of $[(CH_3)_3O][BF_4]$ resulting in the formation of the red compound $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)(CNCH_3)(\mu\text{-}SCF_3)_2]$ (2.597(1) Å).[266] The reaction of alkyne complexes such as $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\mu\text{-}C_2CO_2CH_3)]$ with thiols, with the exception of $HSBu^t$,[267] provides synthetic access to the vinyl complexes.[261] The structure of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2(\mu\text{-}SPr^i)(\mu\text{-}C(CO_2CH_3){=}C(H)CO_2CH_3)]$ (2.8621(5) Å) is shown in Figure 52.[261] $[(\eta^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4]$ reacts with $(C_6H_5)_2Te_2$ in toluene to result in the brown complex $[(\eta^5\text{-}C_5H_4CH_3)Mo_2(CO)_4(\mu\text{-}TeC_6H_5)_3]$ (2.9354(8) Å).[268]

The eclipsed geometry of the eight coordination sites in quadruply bonded $Mo_2^{II,II}$ complexes is shown in Figure 53 with the normal range of Mo—Mo bond lengths between 2.06 Å and 2.17 Å.[269] Nitriles and cyano ligands[270,271] have become more common as either neutral or anionic substituents coordinated to the $Mo_2^{II,II}$ core. Of particular note is the octakis(acetonitrile)dimolybdenum(II) cation, $[Mo_2(NCCH_3)_8](BF_4)_4$, for which structures have been determined with both two (2.187(1) Å)[272] and one (2.180(1) Å: shown in Figure 54)[273] axially coordinated acetonitrile ligands. Acetonitrile ligands have been coordinated to $Mo_2^{II,II}$ compounds containing phosphine,[274,275] formamidinate,[276] acetamidate,[277] and acetate ligands.[274] Other monodentate nitrogen-based ligands incorporated in $Mo_2^{II,II}$ compounds include pyridine,[278] 4-picoline, 3,5-lutidine, 4-*tert*-butylpyridine,[279,280] and primary[281,282] and secondary[283] amines.

As in the case of $Cr_2^{II,II}$ chemistry, a variety of $Mo_2^{II,II}$ paddlewheel complexes with formamidinate ligands[284–288] have been synthesized. The oxidative potentials of the complexes can be tuned by changing the electron-donating or withdrawing ability of the remote substituents of the formamidinate ligands as gauged by the Hammett constants.[284–288] Mixed oxidation state complexes have been synthesized with formamidinate ligands by the addition of ferrocenium chloride to the tetraformamidinate complex, as in the synthesis of $Mo_2((CH_3C_6H_4)NC(H)N(C_6H_4CH_3))_3Cl_2$ (2.1510(5) Å).[289] Dimolybdenum complexes have been synthesized with other bidentate or tetradentate nitrogen-based ligands such as $Mo_2(hpp)_4$,[43] $Mo_2(tmtaa)_2$,[153] and $Mo_2((C_5H_5N)NC(O)CH_2CH_3))_4$.[269] Other ligands used in the synthesis of $Mo_2^{II,II}$ paddlewheel complexes include the monoanion of 2,6-bis(phenylamino)pyridine,[151] 1′,3′-dihydrospiro-[cyclohexane-1,2′-[2*H*]imidazo[4,5-*b*]pyridine,[152] and 7-methyl-1,8-naphthyridin-2-one.[290] From the paddlewheel $Mo_2^{II,II}$ complex synthesized using the anion of 2,6-diphenyliminopiperdine,

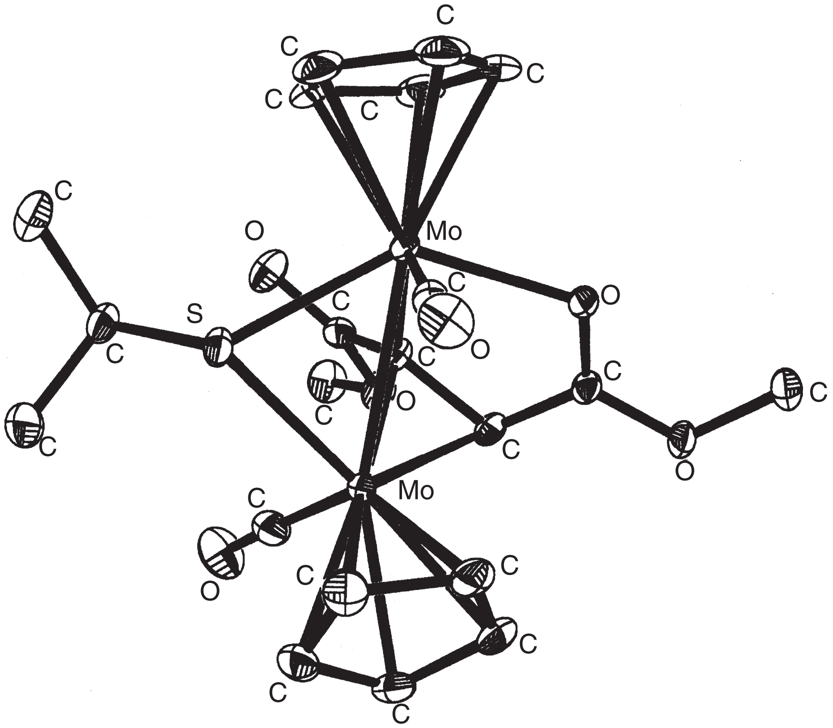


Figure 52 Structure of $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_2(\mu\text{-}SPr^i)(\mu\text{-}C(CO_2CH_3){=}C(H)CO_2CH_3)]$ (reproduced by permission of the Royal Society of Chemistry from *J. Chem. Soc. Dalton Trans.* **2000**, 2983–2989).

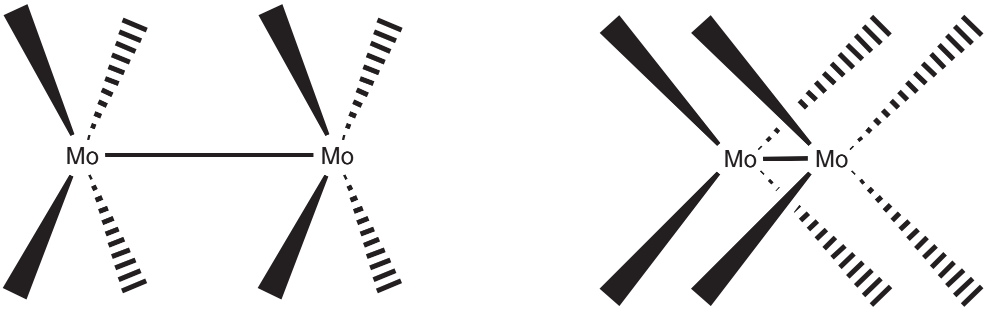


Figure 53 Structural motif of $Mo_2^{II,II}$ complexes both perpendicular to and along the metal–metal axis.

the mixed valent cation, $Mo_2^{III,II}$ has been structurally characterized, and the metal–metal bond length found to increase slightly upon oxidation from 2.085(4) Å to 2.122(3) Å.[291]

Mixed-ligand sets such as nitrogen and oxygen[292–295] are also common as in the case of $[Mo_2(O_2CCH_3)_2(en)_4](O_2CCH_3)_2]$ (2.125(1) Å) with both ethylenediamine and acetate ligands.[296] Other nitrogen-containing ligands include the anion of 2-mercaptoquinoline[297] or 2-imidazolinethione,[298] and the tridentate ligand 2,6-bis(diphenylphosphino)pyridine (bdppp) that forms $Mo_2Cl_4(bdppp)_2$ (2.149(1) Å), shown in Figure 55, upon reacting with $K_4Mo_2Cl_8$ in refluxing methanol.[299] $Mo_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}2\text{-chloro-6-(diphenylphosphino)pyridine})_2](BF_4)_2$ and $Mo_2(\mu\text{-}O_2CCH_3)_2(\mu\text{-}2\text{-(diphenylphosphino-6-(pyrazol-1-yl)- pyridine})_2](BF_4)_2$ are synthesized upon reacting the respective derivatives of 2-(diphenyl-phosphino)pyridine with $Mo_2(\mu\text{-}O_2CCH_3)_4$.[300]

The mixed nitrogen:phosphorus ligand bis(diphenylphosphino)pyridine bridges the gap between nitrogen-based and phosphorus-based ligand types. Monodentate phosphine ligands typically coordinate to a $Mo_2^{II,II}$ core to maintain a total of eight ligands, four neutral and four anionic, as in the example $Mo_2(CCH)_4(P(CH_3)_3)_4$ (2.134(1) Å).[301–303] Other anionic ligands include alkoxides,[304] acetates,[305] and halides.[306–310] A synthetic route to mixed metal $MoW^{II,II}$ complexes with monodentate phosphine ligands and halides has been developed and expanded to include both the chloride and bromide derivatives.[311,312]

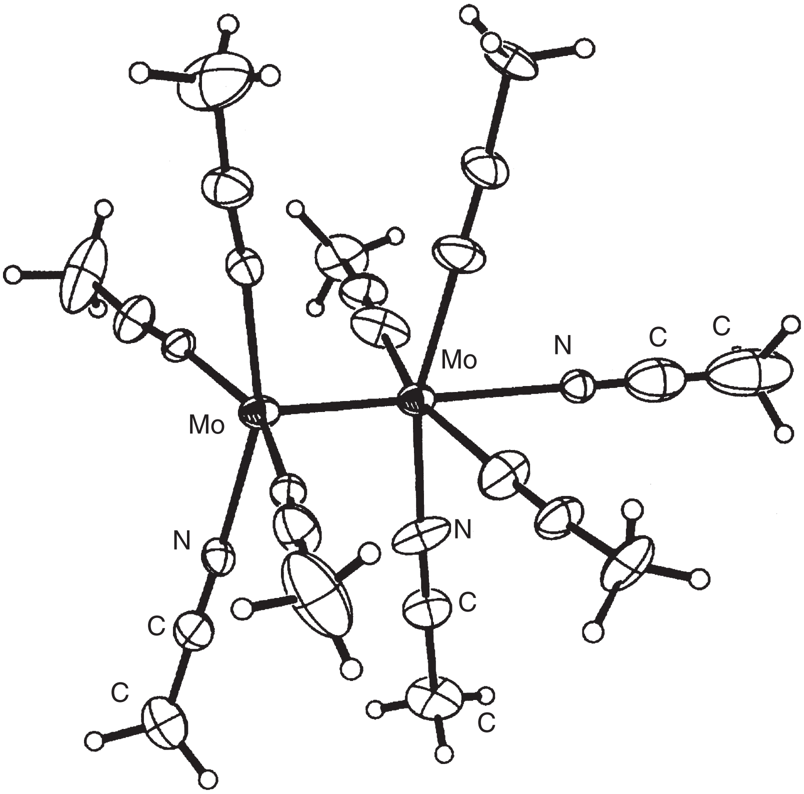


Figure 54 ORTEP drawing of the $[Mo_2(NCCH_3)_8(ax\text{-}NCCH_3)]^{4+}$ cation (reproduced by permission of Elsevier Science from *Polyhedron* **1998**, *17*, 2781–2793).

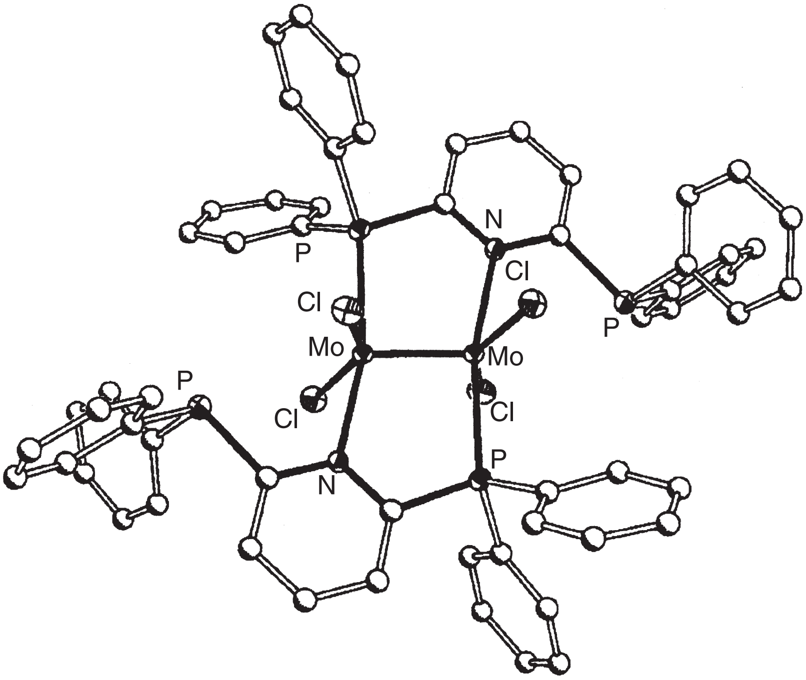


Figure 55 Perspective drawing of $Mo_2Cl_4(bdppp)_2$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1998**, *37*, 4611–4616).

As outlined for $Mo_2^{III,III}$ edge-sharing bioctahedral complexes, variable-temperature ^{31}P NMR spectroscopy provides a technique to probe the singlet–triplet energy gap in dimolybdenum complexes.[313,314] Combined with other theoretical and spectroscopic techniques the δ bond energy manifold for quadruply bonded dimolybdenum compounds can be fully explored.[315,316] The ^{31}P NMR spectroscopy technique has been explored for $Mo_2^{II,II}$ compounds with bidentate phosphine ligands.[313,314] As in the case of $Mo_2Cl_4(\mu\text{-dppa})_2$ shown in Figure 56, bidentate phosphine ligands have been widely utilized in the synthesis of quadruply bonded dimolybdenum compounds in combination with anionic ligands such as an acetate[317–322] or halide atoms.[319–321,323–333] Mixed-metal $MoW^{II,II}$ complexes with bidentate phosphine ligands and halide atoms have also been synthesized and structurally characterized.[333,334]

Dimolybdenum tetracarboxylate plays not only a key role as a synthetic precursor to other complexes but also in understanding structural and spectroscopic properties and correlations.[140,335–345] $Mo_2^{II,II}$ compounds with oxygen-based ligands include the cation $Mo_2[O_2P(OC_6H_5)_2]_4^+$ (2.190 Å) shown in Figure 57, prepared from the addition of $NOBF_4$ to a methylene chloride solution of $Mo_2[O_2P(OC_6H_5)_2]_4$.[346] Alkoxide ligands have also been used to synthesize both cationic[347] and neutral $Mo_2^{II,II}$ complexes.[348] Carboxylate, calixarene, and formamidinate ligands have played a key role in the design of supramolecular assemblies based on Mo_2^{4+} building blocks.[159,349–372]

4.9.9.6 $Mo_2^{I,I}$ Complexes

The reaction of the anion of 2,6-bis(diphenylphosphino)-*N*-methylaniline [Hdppman] with excess $Mo(CO)_6$ results in a binuclear complex $\{[\mu\text{-}P,N\text{:}P',N\text{-dppman}][Mo(CO)_4]_2\}^-$.[373] Treatment of the anion $\{[\mu\text{-}P,N\text{:}P',N\text{-dppman}][Mo(CO)_4]_2\}^-$ with Br_2 leads to the synthesis of the neutral $Mo_2^{I,I}$ complex $\{[\mu\text{-}P,N\text{:}P',N\text{-dppman}][\mu\text{-Br}][Mo(CO)_3]_2\}$(2.987(2) Å) shown in Figure 58. The related complex, deep violet $[(\eta^5\text{-}C_5H_5)_2(CO)_4Mo_2(\mu\text{-}P(C_6H_5)_2)]^-$ (3.185(1) Å), is synthesized by the addition of $[(\eta^5\text{-}C_5H_5)_2(CO)_4Mo_2(\mu\text{-}P(C_6H_5)_2)(\mu\text{-H})]$ to a THF solution containing potassium hydride.[264] Deprotonation of $[(\eta^5\text{-}C_5H_5)_2(CO)_4Mo_2(\mu\text{-}P(C_6H_5)H)(\mu\text{-H})]$ upon the addition of butyllithium at low temperatures followed by the subsequent addition of acryloyl chlorides provides a high-yield synthetic route to *trans*-$[(\eta^5\text{-}C_5H_5)_2(CO)_4Mo_2(\eta^1\text{-}\eta^2\text{-}P(C_6H_5){=}CH(CH_3))]$ (3.240(1) Å).[374] Upon thermolysis, the *trans* isomer converts to the *cis* isomer with a concurrent shortening of the Mo—Mo bond length to 3.220(1) Å. The red–purple diamagnetic compounds $[(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{—}CH_2\text{—}C_5H_4)(CO)_5Mo_2(P(C_6H_5)_3)]$ (3.173(2) Å) and $[(\mu\text{-}\eta^5,\eta^5\text{-}C_5H_4\text{—}CH_2\text{—}C_5H_4)$

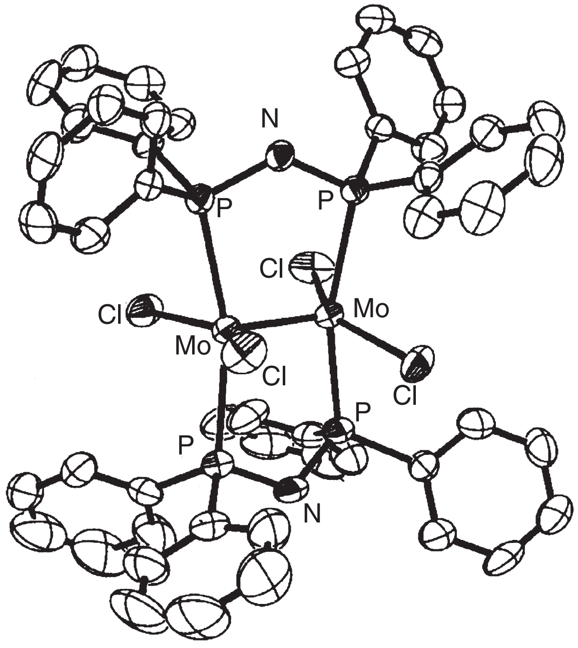


Figure 56 ORTEP drawing of $Mo_2Cl_4(\mu\text{-dppa})_2$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1996**, *35*, 5764–5769).

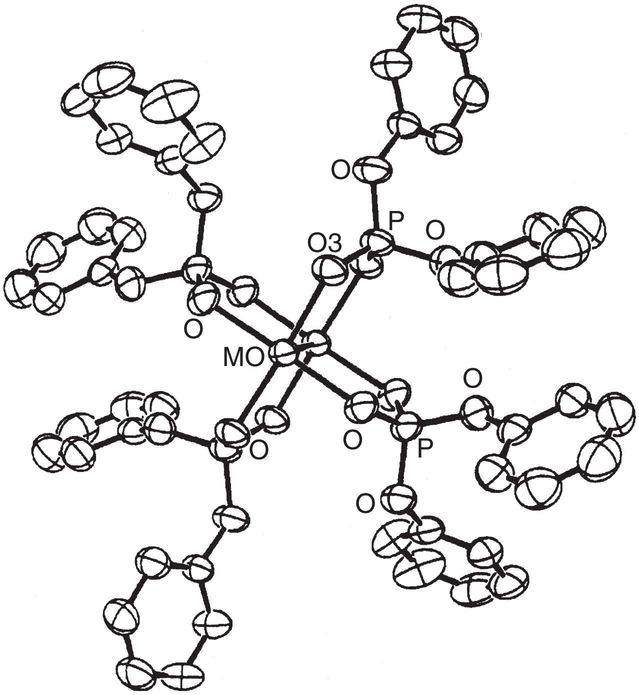


Figure 57 ORTEP drawing of the structure of $Mo_2[O_2P(OC_6H_5)_2]_4^+$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1994**, *33*, 2932–2937).

$(CO)_5Mo_2(P(CH_2)_3)_2]$ (3.1341(12) Å) are synthesized by the photolysis of $[(\mu\text{-}\eta^5, \eta^5\text{-}C_5H_4\text{—}CH_2\text{—}C_5H_4)(CO)_5Mo_2]$ in the presence of the appropriate phosphine ligand.[375]

4.9.10 DITUNGSTEN COMPLEXES

4.9.10.1 $W_2^{V,V}$ Complexes

The blue homoleptic alkoxide $W_2(OCH_3)_{10}$ is synthesized by the addition of lithium powder to a THF solution of *cis*-$WF_2(OCH_3)_4$, followed by the addition of excess sodium methoxide.[376] The edge-sharing bioctahedral structure has a W—W bond length of 2.7897(8) Å. The triply bonded complex $W_2(OCH_2Bu^t)_6(NC_5H_5)_2$ reacts with cyclopropanecarboxaldehyde in hexane to form dark red $W_2(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_4(\mu\text{-}CH(C_3H_5))(O)(NC_5H_5)$ (2.6586(6) Å),[377,378] similar to the complex $W_2(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_4(\mu\text{-}CH(C_6H_4CH_3))(O)(NC_5H_5)$ (2.655(1) Å).[379] The reaction of $W_2(OCH_2Bu^t)_6(NC_5H_5)_2$ with aldehydes has been extended, and the structure of $W_2(OCH_2Bu^t)_6(\mu\text{-}CH(C_6H_4CH_3))(O)(NC_5H_5)$ determined.[378] Subsequent addition of pyridine results in the loss of one equivalent of $HOCH_2Bu^t$ and the formation of $W_2(\mu\text{-}O)(\mu\text{-}OCH_2Bu^t)(OCH_2Bu^t)_4(\mu\text{-}CH(C_3H_5))(NC_5H_5)_2$ (2.4456(7) Å) shown in Figure 59.

$W_2(\mu\text{-}O)(\mu\text{-}OCH_2Bu^t)(OCH_2Bu^t)_4(\mu\text{-}CH(C_6H_4OCH_3))(NC_5H_5)_2$ (2.4507(6) Å) as products of the reductive cleavage of the C=O bond.[378] The reaction of $W_2(OCH_2Bu^t)_6(NC_5H_5)_2$ with cyclohexenone yields $W_2(O)(OCH_2Bu^t)_6(\mu\text{-}OC_{12}H_{16})$ (2.8247(5) Å).[377] Studies of the reactivity of $W_2(OCH_2Bu^t)_6(NC_5H_5)_2$ with acrolein (2.6478(6) Å), methyl vinyl ketone (2.792(1) Å), and crotonaldehyde (2.621(2) Å) yielded W_2(V, V) species.[379]

Upon warming a frozen solution of $W_2(\mu\text{-}H)(\mu\text{-}O\text{-}c\text{-}C_5H_9)_2(O\text{-}c\text{-}C_5H_9)_5(HN(CH_3)_2)$ to room temperature in the presence of four equivalents of ethane, the brown diamagnetic compound $W_2(\mu\text{-}O\text{-}c\text{-}C_5H_9)_3(O\text{-}c\text{-}C_5H_9)_4)((\eta^1\text{-}C_2H_5)(\eta^2\text{-}C_2H_4)$ (2.6684(12) Å) is formed.[380] When two equivalents of cyclopentanone are added to $W_2(\mu\text{-}H)(\mu\text{-}O\text{-}c\text{-}C_5H_9)_2(O\text{-}c\text{-}C_5H_9)_5(HN(CH_3)_2)$ in hexanes, $W_2(\mu\text{-}O\text{-}c\text{-}C_5H_9)_3(O\text{-}c\text{-}C_5H_9)_5(\eta^2\text{-}O\text{-}c\text{-}C_5H_8)$ (2.6738(1) Å) is isolated, but will decompose after several days at room temperature under a nitrogen atomosphere.[380] With the reaction of $W_4(H)_2(OPr^i)_{14}$ and benzophenone in pentane, a dark green diamagnetic W_2(V, V) complex, $W_2(H)(\mu\text{-}OPr^i)_3(OPr^i)_4(\eta^2\text{-}OC(C_6H_5)_2)$ (2.650(3) Å), is synthesized.[380] The reaction of

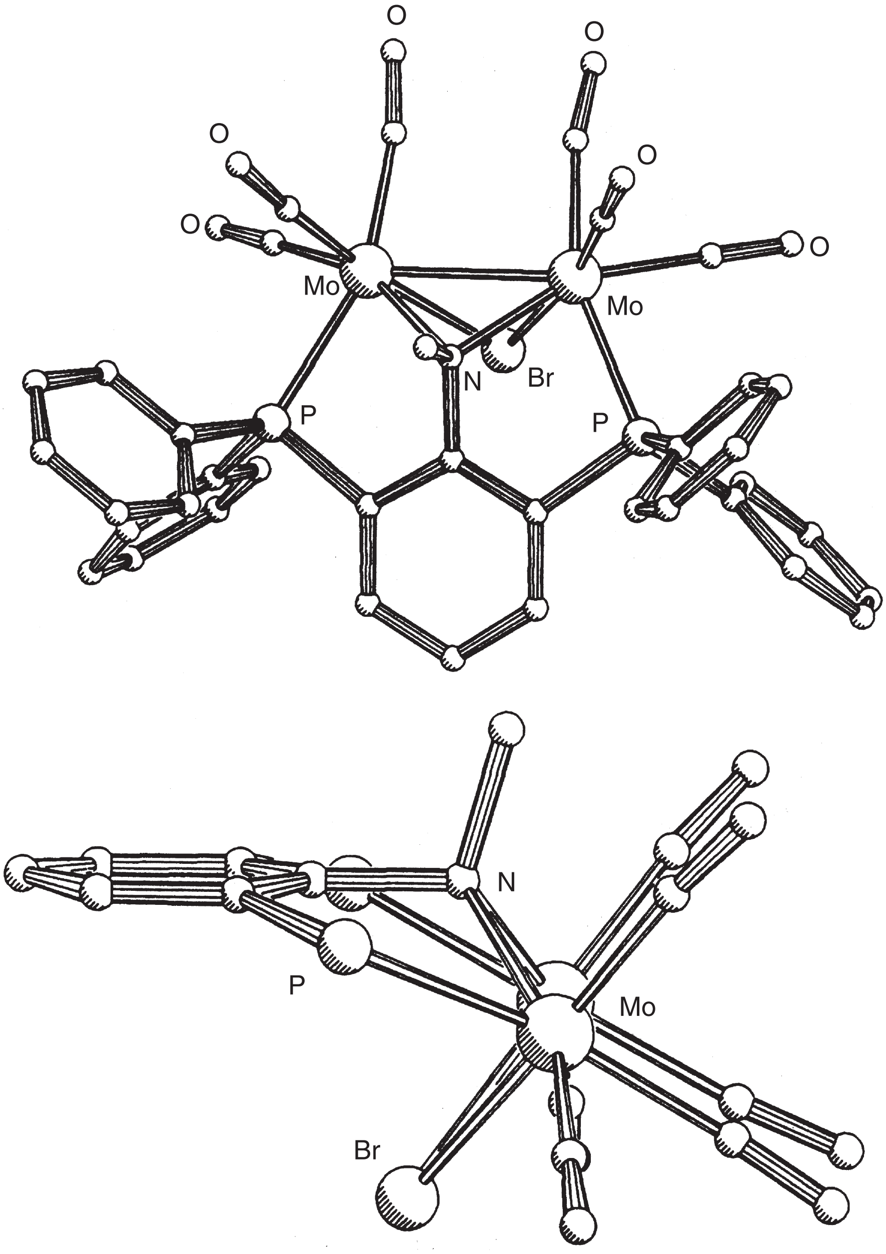


Figure 58 ORTEP diagram of $\{[\mu\text{-}P,N{:}P',N\text{-dppman}][\mu\text{-Br}][Mo(CO)_3]_2$ (reproduced by permission of Elsevier Science from *J. Organomet. Chem.* **1990**, *396*, 33–47).

$W_4(H)_2(OPr^i)_{14}$ with benzonitrile leads to coupling of the nitriles and the formation of green diamagnetic $W_2(\mu\text{-}OPr^i)_2(OPr^i)_5(\mu\text{-}\eta^1\text{-N}, \eta^1\text{-N-NC}(C_6H_5)C(C_6H_5)N(H))$ (2.5909(21) Å).[380]

The reactivity of $W_2^{III,III}$ complexes with ethylene has also been investigated with $W_2(\mu\text{-}CCH_3)(OCH_2Bu^t)_6(OBu^t)$ (2.644(1) Å) formed as a minor product in the reaction between $W_2(OCH_2Bu^t)_6$ and ethylene.[381] An orange solution of $W_2(OCH_2Bu^t)_6$ $(NC_5H_5)_2$ turns blue–black upon stirring under an atmosphere of butadiene with the formation of $W_2(OCH_2Bu^t)_6(\mu\text{-}\eta^1{:}\eta^4\text{-}C_4H_6)(NC_5H_5)$ (2.4706(8) Å).[382] $W_2(OCH_2Bu^t)_6$ reacts with allene to form a variety of products such as $W_2(OCH_2Bu^t)_6(\mu\text{-}C_2H_4)$ (2.5828(5) Å)[383] or $W_2(OCH_2Bu^t)_6(\eta^2\text{-}C_2H_4)$ (2.5331(9) Å)[384] with the allene acting as a four-electron donor or green $W_2(OCH_2Bu^t)_6(C_2H_4)_2$ (2.8548(10) Å) with the allene as a neutral ligand.[383] $W_2(OCH_2Si(CH_3)_2Bu^t)_6(\mu\text{-}C_2H_4)(NC_5H_5)$ undergoes a reaction with allene in hydrocarbon solvents at low temperature to form the deep red diamagnetic W_2(V, V) compound with a terminal hydride, $HW_2(OCH_2Si(CH_3)_2Bu^t)_6(\mu\text{-CCH=CHCH}_3)$ (2.658(1) Å).[385]

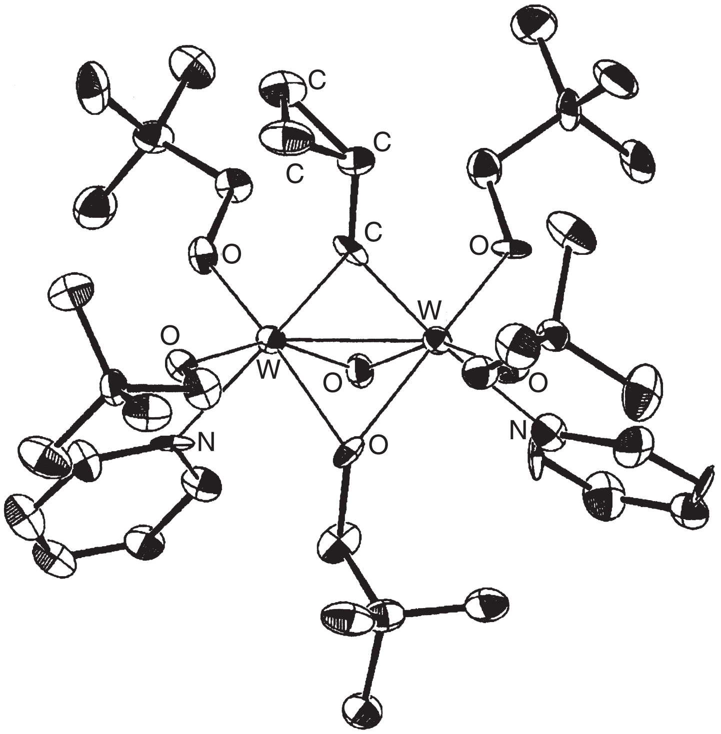


Figure 59 ORTEP drawing of $W_2(\mu\text{-}O)(\mu\text{-}OCH_2Bu^t)(OCH_2Bu^t)_4(\mu\text{-}CH(C_3H_5))(NC_5H_5)_2$ (reproduced by permission of the American Chemical Society from *Organometallics* **2000**, *19*, 884–892).

The blue complex $W_2(H)(\mu\text{-}CCH{=}CHCH_3)(OSi(Bu^t)(CH_3)_2)_6$ (2.658(1) Å) is synthesized in the reaction between ethylene and $W_2(\mu\text{-}C_2H_2)(OSi(Bu^t)(CH_3)_2)_6(NC_5H_5)$ in hexane. When the anion $Li_2C_4(C_6H_5)_4$ is added to 1,2-$W_2Cl_2(N(CH_3)_2)$ the black crystalline compound $W_2(\mu\text{-}C_3(C_6H_5)_3)(\mu\text{-}CC_6H_5)(N(CH_3)_2)$ (2.6709(11) Å) is formed.[386]

The yellow–brown diamagnetic complex $W_2(O_2CCF_3)_2(OCH_2Bu^t)_4(NC_5H_5)(O)(\mu\text{-}C(CH_3)_2)$ (2.7046(6) Å) is synthesized by the simple addition of HO_2CCF_3 to a hexane solution of $W_2(OCH_2Bu^t)_6(NC_5H_5)_2(C(CH_3)_2)$.[387] The reaction of $W_4(H)_2(OPr^i)_{14}$ with benzonitrile leads to coupling of the nitriles and the formation of green diamagnetic $W_2(\mu\text{-}OPr^i)_2(OPr^i)_5)(\mu\text{-}\eta^1\text{-}N, \eta^1\text{-}N\text{-}NC(C_6H_5)C(C_6H_5)N(H))$ (2.5909(21) Å).[380] The red–purple diamagnetic compound $W_2(OBu^t)_5(\mu\text{-}SC_4H_4)(\eta^1\text{-}2\text{-}SC_4H_3)$ (2.633(6) Å) is formed by the addition of *tert*-butyl alcohol to a hydrocarbon solution of 1,2-$W_2\text{-}(\eta^1\text{-}2\text{-}SC_4H_3)_2(N(CH_3)_2)_4$.[388] The reaction of $[W_2(OCH_2Bu^t)_8]_n$ with pyridine *N*-oxide and elemental sulfur, elemental selenium, and tellurium, provides the complexes $W_2(\mu\text{-}O)(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_6$, $W_2(\mu\text{-}Se)(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_6$ (shown in Figure 60), and $W_2(\mu\text{-}Te)(\mu\text{-}OCH_2Bu^t)_2(OCH_2Bu^t)_6$, respectively with W—W bond lengths ranging from 2.55 Å to 2.66 Å.[389] $[W_2Cl_2(HNSiBu^t{}_3)_4]$ reacts with pyridine to form the dark purple species, $[W_2(\mu\text{-}H)_2(\mu\text{-}Cl)HCl_2(HNSiBu^t{}_3)_3(NC_5H_5)_2]$ (2.7878(6) Å).[390]

Analogous to the dimolybdenum chemistry, the reaction of $[C_5(CH_2CH_3)(CH_3)_4]_2\text{-}W_2(CO)_4$ with S_8 results in the formation of two different isomers: *syn*-$[C_5(CH_2CH_3)\text{-}(CH_3)_4]_2W_2(\mu\text{-}S)_2S_2$ (2.891(1) Å) and *anti*-$[C_5(CH_2CH_3)(CH_3)_4]_2W_2(\mu\text{-}S)_2S_2$.[176] The blue diamagnetic compound $W_2(\eta^2\text{-}S_2CN(CH_2CH_3)_2)_2(\mu\text{-}CN(CH_2CH_3)_2)(\mu\text{-}S)(\mu\text{-}S_2CN(CH_2CH_3)_2)(\mu\text{-}S_2SnCH(Si(CH_3)_3)_2)$ (2.614(2) Å) is synthesized by refluxing the mononuclear compound $W_2(CO)_2(\eta^2\text{-}S_2CN(CH_2CH_3)_2)$ $(SnCH(Si(CH_3)_3)_2)$ in benzene.[391] The sulfur-bridged species $[W_2(NC_6H_4CH_3)_2(S_2P(OCH_2CH_3)_2)_2$ $(\mu\text{-}O_2CCH_3)(\mu\text{-}S)(\mu\text{-}SBr)]$ (2.8315(6) Å) is synthesized by the addition of *N*-bromophthalimide to a cold solution of $[W_2(NC_6H_4CH_3)(S_2P(OCH_2CH_3)_2S)_2]_4$, acetic acid, and triethylamine in chloroform.[197] The $W_2S_4{}^{2+}$ core in $W_2(\mu\text{-}S)_2S_2Br_2(P(C_6H_5)_3)_2$ (2.813(3) Å) is a result of the addition of triphenylphosphine to the anion $W_2S_4Br_4{}^{2-}$.[392] The $[WSe_4]^{2-}$ anion is the precursor to $[(CH_3CH_2)_4N]_2[W_2Se_6]$ (2.8529(8) Å) formed by simply stirring the anion in an acetonitrile–methylene chloride solution containing triphenylphosphine.[393] Further reaction of $[(CH_3CH_2)_4N]_2[W_2Se_6]$ with tricyclohexylphosphine in the presence of copper chloride results in cluster compounds.

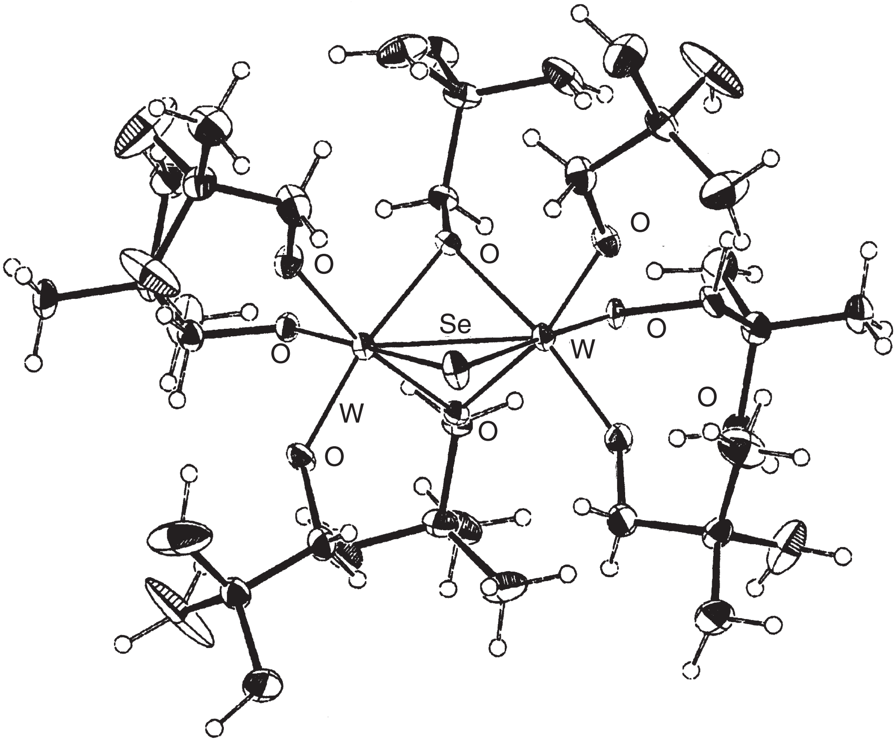


Figure 60 ORTEP drawing of the molecule $W_2(\mu\text{-Se})(\mu\text{-OCH}_2Bu^t)_2(OCH_2Bu^t)_6$ (reproduced by permission of the Royal Society of Chemistry from *J. Chem. Soc. Dalton Trans.* **2001**, 2074–2082).

4.9.10.2 $W_2^{IV,IV}$ Complexes

The tungsten triple bond in $[W_2(\eta^5\text{-}C_5H_4Pr^i)_2Cl_4]$ undergoes an oxidative addition reaction with diphenylphosphine to form the bridging hydride compound $[W_2(\mu\text{-H})(\mu\text{-P}(C_6H_5)_2)(\eta^5\text{-}C_5H_4Pr^i)_2Cl_4]$ (2.6558(3) Å).[394] $[W_2(\mu\text{-H})(\mu\text{-P}(C_6H_5)_2)(\eta^5\text{-}C_5H_4Pr^i)_2Cl_4]$ reacts further with $P(CH_3)_3$ to provide the μ-Cl compound $[W_2(\mu\text{-H})(\mu\text{-Cl})\ (\mu\text{-P}(C_6H_5)_2)(\eta^5\text{-}C_5H_4Pr^i)_2Cl_3(P(CH_3)_3)]$ (3.1165(2) Å).[394] Complexes with bridging chloro ligands can also be synthesized directly from $[W_2(\eta^5\text{-}C_5H_4Pr^i)_2Cl_4]$ by the addition of CH_3CH_2CN followed by HCl gas to form $CH_3CH_2CNH^-$ as a perpendicular bridging ligand as in $[W_2(\mu\text{-CH}_3CH_2CNH)(\mu\text{-Cl})(\eta^5\text{-}C_5H_4Pr^i)_2Cl_4]$(2.9359(4) Å).[395]

Methylation of $[W_2(\mu\text{-CO})(\eta^5\text{-}C_5H_5)_2(\mu\text{-P}(C_6H_5)_2)_2]$ with $CH_3SO_2CF_3$ provides the methoxycarbyne complex $[W_2(\mu\text{-COCH}_3)(\eta^5\text{-}C_5H_5)_2(\mu\text{-P}(C_6H_5)_2)_2]SO_2CF_3$ (2.5324(8) Å).[396] The *nido*-icosahedral 7,8-$C_2B_9C_{11}$ cage provides a variation in carbon-based ligands for Group 6 (IV, IV) complexes. Shown in Figure 61, $\{MoW(\mu\text{-}\eta^3{:}\eta^2\text{-C}(Bu^t)CC[{=}C(H)C_6H_4CH_3])\ (CO)_4(\eta^5\text{-7,8-}C_2B_9C_{11})(\eta^5\text{-}C_5H_5)\}$(3.031(2) Å) is produced by the protonation of equivalent amounts of the mononuclear compounds $[Mo(CC_6H_4CH_3)(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[(CH_3CH_2)_4N][W(CCCBu^t)(CO)_2(\eta^5\text{-7,8-}C_2B_9C_{11})]$ using $HBF_4{\cdot}(CH_3CH_2)_2O$.[397] Several ditungsten complexes with boron-containing ligands have been synthesized such as $[W_2(\mu\text{-CC}_6H_4CH_3)(CO)_3(PCH_3)\ (\eta^5\text{-}C_5H_5)\{\eta^5\text{-2,8-}C_2B_9H_8\text{-10-}(CH_2C_6H_4CH_3)\text{-2,8-}(CH_3)_2\}]$ (2.798(1) Å) shown in Figure 61,[398] $[W_2(\mu\text{-CCH}_3)(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_2B_9H_8\text{-}(CH_2C_6H_4CH_3)\ (CH_3)_2\}]$ (2.651(1) Å),[399] $[W_2(\mu\text{-CC}_6H_4CH_3)(CO)_3(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_2B_9H_8\ (CH_3)_2\}]$ (2.657(1) Å),[399] $[Au(P(C_6H_5)_3)_2][W_2\{\mu\text{-}\eta^2\text{-C}(CH_3)\text{-CO}\}(CO)_3\{\eta^6\text{-7,9-}(CH_3)_2\text{-7,9-}C_2B_{10}H_{10}\}\{\eta^6\text{-7,9-}(CH_3)_2\text{-7,9-}C_2B_{10}H_9\text{- 11-}(CH_2CH_3)\}]$ (2.778(1) Å),[400] and $[MoW(\mu\text{-CC}_6H_4CH_3)(CO)_2(PCH_3)(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}C_2B_{10}H_{10}\ (CH_3)_2\}]$ (2.702(1) Å).[399]

As in the case of $W_2^{V,V}$ complexes, $W_2(OCH_2Bu^t)_6$ and related compounds are precursors to dinuclear $W_2^{IV,IV}$ materials. $W_2(OCH_2Bu^t)_6(NC_5H_5)_2$ reacts with both 1,3-butadiene and isoprene to form the adducts $W_2(OCH_2Bu^t)_6(NC_5H_5)$(butadiene) (2.4706(8) Å) shown in Figure 62 and $W_2(OCH_2Bu^t)_6(NC_5H_5)$(isoprene) (2.4644(9) Å), respectively.[401] $W_2Cl_2(N(CH_3)_2)_4$ reacts with Li_2COT, where COT is c-C_8H_8, with the COT ligand acting as a 4^- anion bridging the ditungsten core in $W_2(COT)(N(CH_3)_2)_4$ (2.4297(5) Å).[402] The reaction of $W_2(OCH_2\ Si(CH_3)_2Bu^t)_6$ with NO

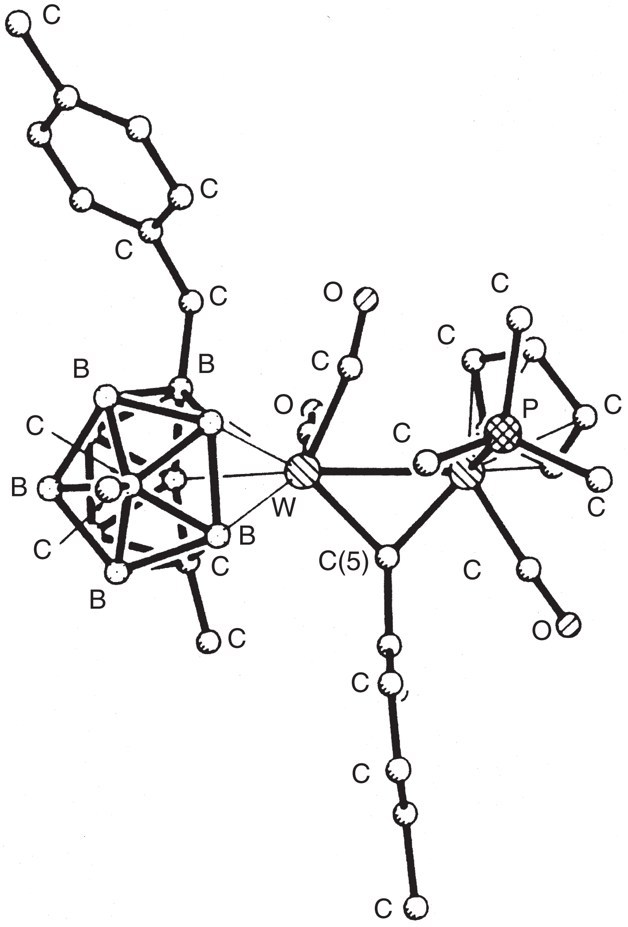


Figure 61 Crystal structure of $[W_2(\mu\text{-}CC_6H_4CH_3)(CO)_3(PCH_3)(\eta^5\text{-}C_5H_5)\{\eta^5\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}(CH_2C_6H_4CH_3)\text{-}2,8\text{-}(CH_3)_2\}]$ (reproduced by permission of the Royal Society of Chemistry from *J. Chem. Soc. Dalton Trans.* **1992**, 867–875).

in hydrocarbon solvents in the presence of pyridine leads to the formation of tungsten oxo species and loss of W—W bonding.[403] An intermediate in the reaction has been isolated, $W_2(\mu\text{-}O)(\mu\text{-}OCH_2Si(CH_3)_2Bu^t)(OCH_2Si(CH_3)_2\ Bu^t)_5(NC_5H_5)_2$ (2.488(1) Å), formed upon coupling of two nitrosyl ligands.[403] *Tert*-butoxide ligands also undergo decomposition to form hydride and oxo ligands as in the case of $[W_2(OCH_2Bu^t)_7]^-$ to form the red anion $[W_2(\mu\text{-}O)(\mu\text{-}H)(OCH_2Si(CH_3)_2Bu^t)_6]^-$ (2.4447(10) Å) with concurrent formation of $(CH_3)_2C{=}CH_2$.[404] Other bridging hydride species are formed over time[405] as in the case of $W_2(O\text{-}c\text{-}C_5H_9)_6(HN(CH_3)_2)_2$ stirred for four days in the presence of cyclopentanol to yield green $W_2(\mu\text{-}H)(\mu\text{-}O\text{-}c\text{-}C_5H_9)_2(O\text{-}c\text{-}C_5H_9)_5(HN(CH_3)_2)$ (2.4380(14) Å).[406]

4.9.10.3 $W_2^{III,III}$ Complexes

The triply bonded starting materials $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4]$ and $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Br_4]$ react with alkynes and form demetallatetrahedrane complexes such as $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4\ (\mu\text{-}C_4(CH_3)_4]$ (2.9295(7) Å) and $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4(\mu\text{-}C_2(C_6H_5)_2]$ (2.795(3) Å).[407] $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4(\mu\text{-}C_4(CH_3)_4]$ is hydrolyzed by wet acetone to form the oxo complex $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_2O(\mu\text{-}C_4(CH_3)_4]$ (2.9097(6) Å).[407,408] The μ-alkyne species $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_4(\mu\text{-}C_2(CH_2CH_3)_2)]$ reacts with the monodentate phosphine ligand $P(CH_3)_3$ to form $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2\ (\mu\text{-}Cl)(P(CH_3)_3)Cl_3(\mu\text{-}C_2(CH_2CH_3)_2)]$ (2.814(2) Å).[409] $[(\eta^5\text{-}C_5H_4Pr^i)_2W_2Cl_2\ (\mu\text{-}NC_6H_5)(\mu\text{-}C_2(CH_2CH_3)_2)]$ (2.5923(5) Å) is synthesized when three equivalents of aniline are used in place of the monodentate phosphine ligand.[409] Several mixed-metal, $WMo^{III,II}$ or $WMo^{III,III}$ complexes have recently been prepared

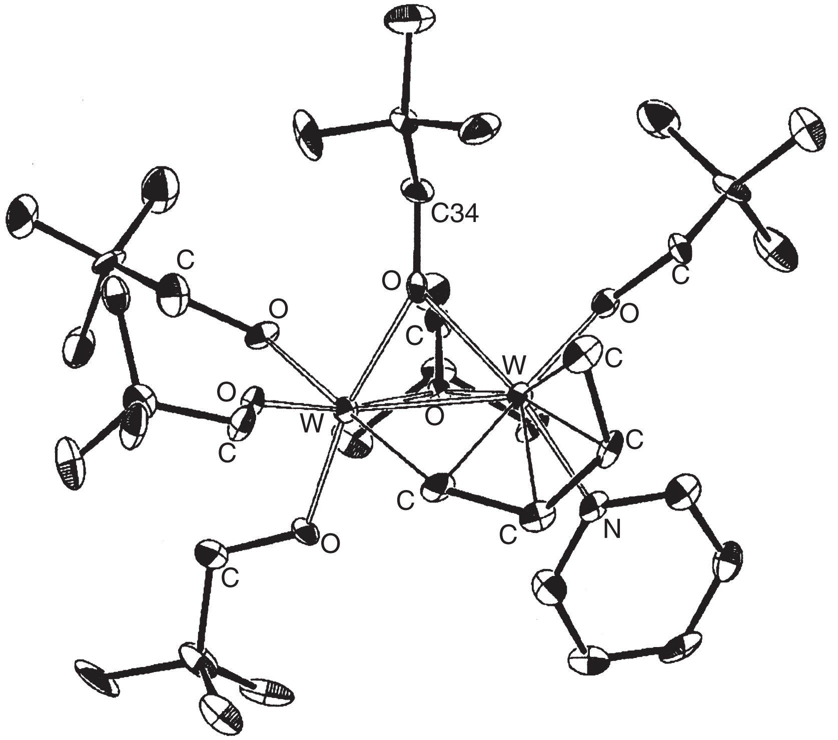


Figure 62 ORTEP drawing of the structure of $W_2(OCH_2Bu^t)_6(NC_5H_5)$(butadiene) (reproduced by permission of the American Chemical Society from *Organometallics* **1999**, *18*, 2300–2308).

such as $[(\eta^5\text{-}C_5H_5)_2MoWCl_2(\mu\text{-}(C_6H_5)PC{=}CH(C_6H_5))(\mu\text{-}P(C_6H_5)_2)]$ (2.772(3) Å)[410] and $[(\eta^5\text{-}C_5H_5)_2MoWCl(\mu\text{-}HC{=}CH(C_6H_5))]$.[411]

The brown diamagnetic cation $[W_2(\mu\text{-}COCH_3)(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-dppm})]BF_4$ (2.781(3) Å) with a W—W double bond is synthesized by the addition of $(CH_3)_3OBF_4$ to a methylene chloride solution of $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-dppm})]$.[412,413] Subsequent reaction of $[W_2(\mu\text{-}COCH_3)(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-dppm})]BF_4$ with $BH_3{\cdot}THF$ yields the methylidyne–borane complex $[W_2(\mu\text{-}CHBH_3)(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-dppm})]BF_4$ (3.074(1) Å) with a W—W single bond.[412] $[W_2(\mu\text{-}COCH_3)(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-dppm})]BF_4$ also reacts with CH_2N_2 to yield the orange diamagnetic complex shown in Figure 63, $[W_2(\mu\text{-}CH_2)\{\mu\text{-}\eta^1{:}\eta^2\text{-}C(OCH_3)CH_2\}(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-dppm})]BF_4$ (2.965(1) Å).[414]

For edge-sharing bioctahedral, face-sharing bioctahedral, and ethane-like molecules, ditungsten$^{(\text{III III})}$ chemistry parallels the dimolybdenum$^{(\text{III III})}$ chemistry outlined previously. One of the drawbacks to low-oxidation-state dinuclear tungsten complexes is their susceptibility to oxidation.[140,415–420] However, $W_2(\mu\text{-}Cl)_2Cl_4(P(CH_3)_2(C_6H_5))_4$ (2.6950(9) Å),[421] $W_2(\mu\text{-}Cl)_2Cl_4(P(CH_2CH_3)_3)_4$ (2.7397(7) Å),[422] and $W_2(\mu\text{-}Cl)_2Cl_4(P(CH_3)_3)_4$ (2.7113(8) Å)[422] are synthesized by the reduction of WCl_4 using sodium amalgam and subsequent addition of excess monodentate phosphine ligand. Face-sharing bioctahedral complexes are synthesized by the same general procedure by limiting the monodentate phosphine ligand to tungsten ratio to 1.5:1 as in the case of $W_2(\mu\text{-}Cl)_3Cl_3(P(CH_3)_2(C_6H_5))_3$ (2.4433(4) Å) and $W_2(\mu\text{-}Cl)_3Cl_3(P(CH_2CH_3)_3)_3$ (2.4705(7) Å).[421,422] Of note is the synthesis of $W_2(\mu\text{-}Br)_3Br_3(P(CH_3)_2(C_6H_5))_3$ (2.4768(9) Å) using WBr_5 as the starting material[421] and the formation of the anion $[W_2(\mu\text{-}Cl)_3Cl_4(P(CH_2CH_3)_3)_2]^-$ (2.4377(22) Å) upon addition of water to the neutral species.[422]

The halides bridge the two metal centers in both the edge-sharing and face-sharing bioctahedral geometries in the presence of monodentate phosphine ligands, but the halides are the terminal atoms in the presence of sulfur-based ligands.[423,424] Synthesized by the addition of the appropriate ligands, $S(CH_2CH_3)_2$, 1,4-dithiane, 1,4-thioxane, or pentamethylene sulfide, to WCl_4 reduced by sodium amalgam, the dark red complexes $W_2(\mu\text{-}S(CH_2CH_3)_2)_3Cl_6$ (2.4990(9) Å),[423] $W_2(\mu\text{-1,4-dithiane})_3Cl_6$ (2.507(1) Å),[424] $W_2(\mu\text{-1, 4-thioxane})_3Cl_6$ (2.529(1) Å),[424] and $W_2(\mu\text{-pentamethylene sulfide})_3Cl_6$ (2.506(2) Å) shown in Figure 64[424] have been structurally characterized. The anions, $[W_2(\mu\text{-}Cl)(\mu\text{-1,4-dithiane})_2Cl_6]^-$ (2.481(2) Å)[424] and $[W_2(\mu\text{-}Cl)(\mu\text{-1,4-thioxane})_2Cl_6]^-$ (2.496(4) Å),[424] are formed as side products in the reactions of 1,4-thioxane and 1,4-dithiane, respectively.[424] When $S(CH_3)_2$ is used in the reaction, the sole product is the anion $[W_2(\mu\text{-}Cl)$

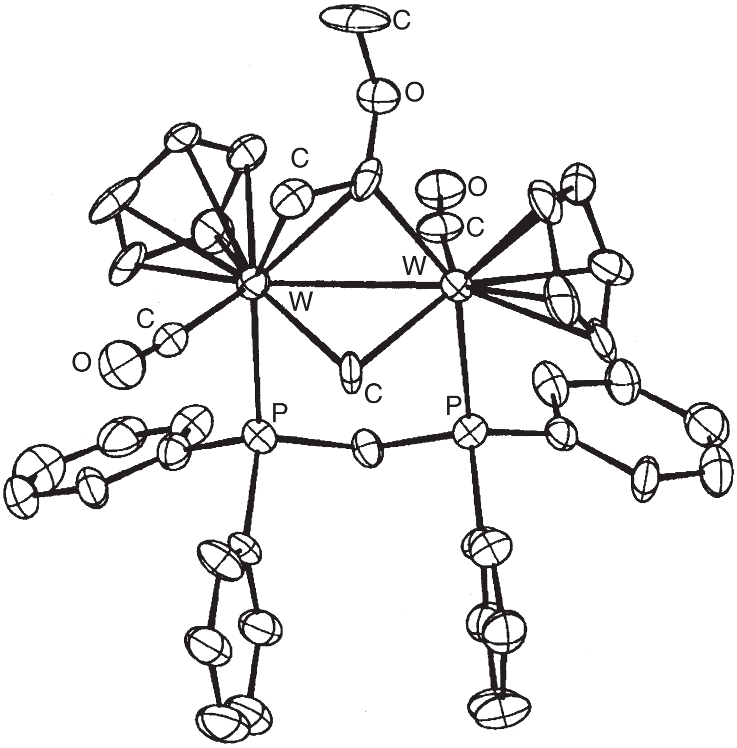


Figure 63 CAMERON drawing of the structure of the cation of $[W_2(\mu\text{-}CH_2)\{\mu\text{-}\eta^1\text{:}\eta^2\text{-}C(OCH_3)CH_2\}(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-dppm})]BF_4$ (reproduced by permission of the American Chemical Society from *Organometallics* **2002**, *21*, 1177–1183).

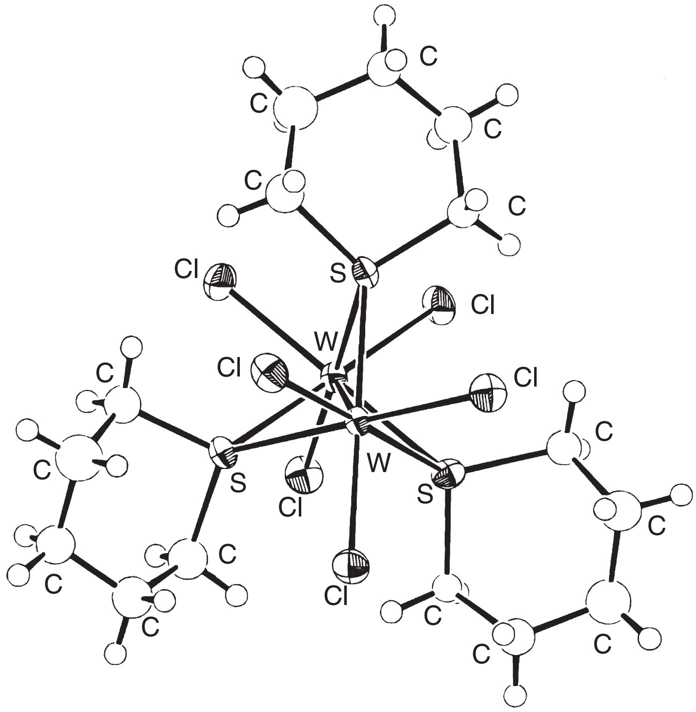


Figure 64 ORTEP drawing of $W_2(\mu\text{-pentamethylene sulfide})_3Cl_6$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1998**, *37*, 6023–6029).

$(\mu\text{-S(CH}_3)_2)_2\text{Cl}_6]^-$ (2.4752(8) Å).[423] Subsequent studies indicate that the products may vary depending on both the temperature of the reaction and the WCl_4 sample.[425] The anions, such as $[\text{W}_2(\mu\text{-Cl})(\mu\text{-S(CH}_2\text{CH}_3)_2)_2\text{Cl}_6]^-$, are susceptible to nucleophilic attack at the *S* center that results in either displacement of $\text{—CH}_2\text{CH}_3$ to yield $[\text{W}_2(\mu\text{-Cl})(\mu\text{-S(CH}_2\text{CH}_3))(\mu\text{-S(CH}_2\text{CH}_3)_2)\text{Cl}_6]^-$ (2.4418(6) Å)[425,426] or ring opening of bridging tetrahydrothiophene ligands upon addition of Cl^- to yield $[\text{W}_2(\mu\text{-Cl})(\mu\text{-SC}_4\text{H}_8)(\mu\text{-S(CH}_2)_4\text{Cl})\text{Cl}_6]^-$ (2.4846(8) Å).[426]

$\text{W}_2^{\text{III,III}}$ ethane-like molecules provide precursors in the synthesis of complexes for almost every oxidation state discussed.[234,427] As outlined previously for $\text{Mo}_2^{\text{III,III}}$ ethane-like molecules, ditungsten ethane-like molecules contain six anionic ligands such as alkyls[428] as in the case of $\text{W}_2(\text{CH}_2\text{Si(CH}_3)_2(\text{C}_6\text{H}_5))_6$ (2.2587(5) Å) or a bridging 1,1′-ferrocenyl as in $\text{W}_2(\text{N(CH}_3)_2)_4(\mu\text{-(C}_5\text{H}_4)_2\text{Fe})$ (2.2877(21) Å).[242,428] Other ligands include the anions of amines,[239,240,242,243,245,390,429–432] calixarenes,[248,433] binaphthol,[434] diols,[435] phenols,[241] allyls,[429] thiols,[436] thienyls,[388,437] alkoxides,[239,245,430–432,436,438–440] siloxides,[245,441] selenolates,[246] germanides,[243,442] cyclopentadienyl,[240] phosphido,[242,443] or halides.[242,390]

In addition to ethane-like molecules, there are several $\text{W}_2^{\text{III,III}}$ complexes that are more difficult to classify. Instead of the classic six anionic ligands, these compounds contain a W_2 core supported by eight or nine ligands, six anionic and two or three neutral.[431,444,445] Examples of complexes of this type have been synthesized by the addition of neutral ligands such as the chelating phosphine ligand dmpm, $\text{P(CH}_3)_3$ or quinuclidine to ethane-like $\text{W}_2^{\text{III,III}}$ starting materials to form $\text{W}_2(\text{CH}_2\text{C}_6\text{H}_5)_2(\text{OPr}^{\text{i}})_4(\text{dmpm})$ (2.3476(13) Å), $\text{W}_2(^t\text{Bu})_2(\text{OPr}^{\text{i}})_4(\text{dmpm})$ (2.3490(7) Å), $\text{W}_2(\mu\text{-CC}_6\text{H}_5)(\mu\text{-H})(\text{OPr}^{\text{i}})_4(\text{P(CH}_3)_3)_3$ (2.5374(14) Å), $\text{W}_2(\mu\text{-CPr}^{\text{i}})_2(\mu\text{-H})(\text{OPr}^{\text{i}})_4(\text{P(CH}_3)_3)_3$ (2.5030(13) Å), $\text{W}_2(\mu\text{-CC}_6\text{H}_5)_2(\mu\text{-H})(\text{OPr}^{\text{i}})_4(\text{P(CH}_3)_3)_2$ (2.4697(21) Å), and $\text{W}_2(\text{OPr}^{\text{i}})_4(\mu\text{-CC}_6\text{H}_5)_2(\mu\text{-H})(\text{quinuclidine})_2$ (2.4425(10) Å).[446] While complexes of this type have an overall W_2^{6+} core, the tungsten atoms may be in different oxidation states.[446] Ligand types vary as in the cases of $\text{W}_2\text{Cl}_3(\text{OC(CH}_3)_3)_3(\text{NH(CH}_3)_2)_2$ (2.3155(5) Å), $\text{W}_2\text{Cl}_4(\text{NHC}_6\text{H}_{11})_2(\text{NH}_2\text{C}_6\text{H}_{11})_2$ (2.2884(9) Å),[447] $\text{W}_2\text{Cl}_4(\text{NH}^s\text{Bu})_2(\text{P(CH}_3)_3)_2$ (2.320(1) Å),[447] $\text{W}_2\text{Cl}_4(\text{NHC}_6\text{H}_{11})_2(\text{P(CH}_3)_3)_2$ (2.3229(5) Å),[447] $\text{W}_2\text{Cl}_4(\text{NHCH}_2\text{CH}_3)_2(\text{P(CH}_3)_3)_2$ (2.3066(6) Å) shown in Figure 65.[448] Other complexes of this type have been synthesized with halides, amido ligands, and either monodentate[449,450] or bidentate[451,452] phosphine ligands.[448]

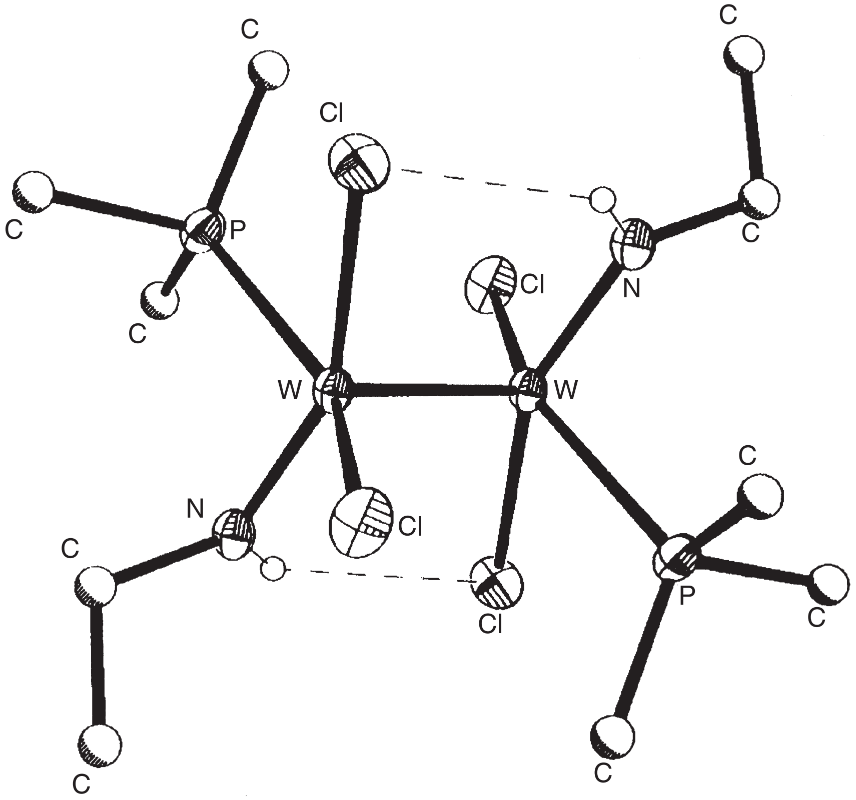


Figure 65 ORTEP drawing of $\text{W}_2\text{Cl}_4(\text{NHCH}_2\text{CH}_3)_2(\text{P(CH}_3)_3)_2$ (reproduced by permission of the American Chemical Society from *Inorg. Chem.* **1997**, *36*, 2670–2677).

Other complexes containing the W_2^{6+} core include the brown diamagnetic complex $W_2(hpp)_4Cl_2$ (2.250(2) Å) synthesized by the reduction of WCl_4 with one equivalent of sodium triethylborohydride followed by the addition of the Lihpp salt.[453] A mixed valent complex with a W_2^{6+} core is synthesized by the addition of carbon dioxide to $(Pr^iO)_4W(\mu\text{-}H)_2W(\eta^2\text{-dmpe})_2$ to result in the formation of the green compound $(\eta^2\text{-}O_2CH)(Pr^iO)_4WW(\eta^2\text{-dmpe})_2H$ (2.5242(9) Å).[454]

4.9.10.4 $W_2^{II,II}$ Complexes

The $W_2^{III,II}$ and $W_2^{II,II}$ compounds $[(\eta^5\text{-}C_5H_5)_2(CO)W_2Cl(\mu\text{-}P(C_6H_5)_2)_2(\mu\text{-}C_6H_5C_2C_6H_5)]$ (2.660(1) Å) and $[(\eta^5\text{-}C_5H_5)_2(CO)W_2Cl(\mu\text{-}P(C_6H_5)_2)(\mu\text{-}C_6H_5C_2C_6H_5)]$ (2.654(1) Å) are prepared by the addition of $PCl(C_6H_5)_2$ to a refluxing xylene solution of $[(\eta^5\text{-}C_5H_5)_2(CO)_4W_2(\mu\text{-}C_6H_5C_2C_6H_5)]$.[455] The molecular structure of the cation $[(\eta^5\text{-}C_5H_5)_2W_2(\mu\text{-}Cl)(\mu\text{-}CO)(CO)_2(\mu\text{-dppm})]^+$ (3.040(3) Å) contains a W—W single bond and is one of several complexes synthesized from the dicationic starting material $[(\eta^5\text{-}C_5H_5)_2W_2(\mu\text{-}CO)_2(CO)_2(\mu\text{-dppm})]^{2+}$.[456] In the synthesis of $[(\eta^5\text{-}C_5H_5)_2W_2(\mu\text{-}CO)_2(\mu\text{-dppm})]$, the brown complex $[(\eta^5\text{-}C_5H_5)_2W_2(\mu\text{-}CH_2P(C_6H_5)_2)(O)(\mu\text{-}P(C_6H_5)_2(CO)]$ (2.9500(7) Å) is produced as a secondary product.[457] Refluxing $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_2(P(C_6H_5)_3)(SCH(CH_3)_2)]$ in THF provides a synthetic route to the dark green complex $[(\eta^5\text{-}C_5H_5)_2W_2(CO)_2(\mu\text{-}SCH(CH_3)_2)_2]$ (2.602(5) Å) with a tungsten—tungsten double bond.[458]

The dominant structural motif in $W_2^{II,II}$ chemistry is the quadruply bonded complex with either monodentate or bidentate ligands providing a total negative charge of four about the dinuclear core. As a result of the extreme sensitivity of the ditungsten core to oxidative addition, the field of quadruply bonded ditungsten complexes is less developed than the analogous dimolybdenum complexes.[140] An example of a $W_2^{II,II}$ complex containing monodentate ligands is $W_2(CCCH_3)_2Cl_2(P(CH_3)_3)_4$ (2.268(1) Å) shown in Figure 66, synthesized by reacting $W_2Cl_4(P(CH_3)_3)_4$ with $LiCCCH_3$.[459] Other monodentate and bidentate ligands include carboxylates,[354,460–462] phosphines,[309,311,314,461–465] halides,[309,311,314,461,462,464–467] amines,[466,467] and formamidinates and other nitrogen-based chelating ligands.[149,415,468] The brown $W_2^{III,II}$ species $W_2Cl_5(P(CH_3)_3)_3$ (2.433(1) Å) is synthesized by the addition of $C_6H_5I{\cdot}Cl_2$ to $W_2Cl_4(P(CH_3)_3)_4$.

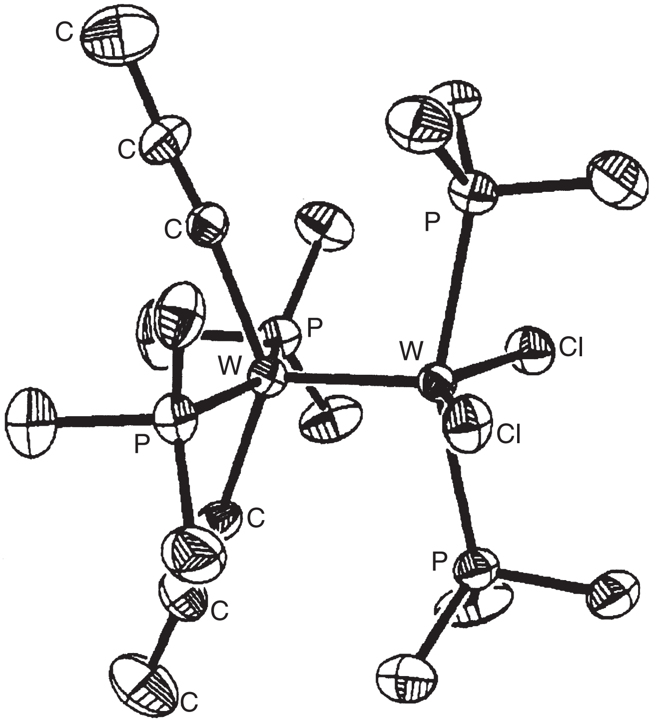


Figure 66 ORTEP drawing of $W_2(CCCH_3)_2Cl_2(P(CH_3)_3)_4$ (reproduced by permission of the American Chemical Society from *J. Am. Chem. Soc.* **1992**, *114*, 4201–4204).

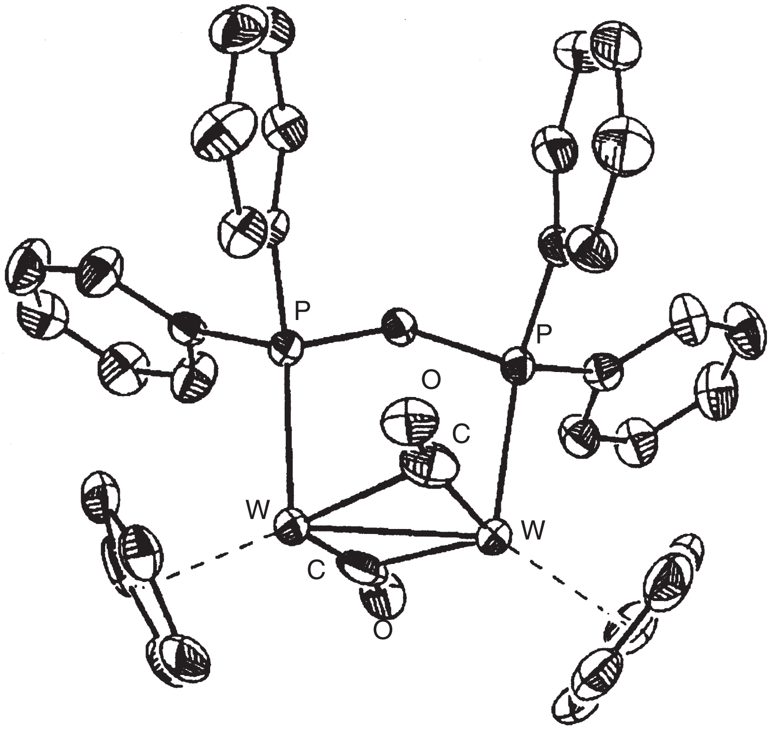


Figure 67 ORTEP drawing of the structure of [(η^5-C_5H_5)$_2$$W_2$($\mu$-CO)$_2$($\mu$-dppm)] (reproduced by permission of the American Chemical Society from *Organometallics* **1997**, *16*, 354–364).

4.9.10.5 $W_2^{I,I}$ Complexes

With a W—W bond length of 3.2731(6) Å, [(η^5-C_5H_5)$_2$$W_2(CO)_4$($\mu$-($CH_3CH_2O$)$_2$POP($OCH_2CH_3$)$_2$)] is synthesized by the addition of the neutral ligand (CH_3CH_2O)$_2$POP(OCH_2CH_3)$_2$ to [(η^5-C_5H_5)$_2$$W_2(CO)_4$].[469] An analogous reaction can be performed using other chelating phosphine ligands such as dppm and dmpm, and the structure of [(η^5-C_5H_5)$_2$$W_2$($\mu$-CO)$_2$($\mu$-dppm)] (2.5144 (5) Å) is shown in Figure 67.[457] The subsequent reaction of [(η^5-C_5H_5)$_2$$W_2$($\mu$-CO)$_2$($\mu$-dppm)] with Bu^{t}NC results in the oxidation of the ditungsten core and the formation of [W_2(μ-η^1:η^5-C_5H_4)(η^5-C_5H_5)(μ-H)(Bu^{t}NC)(CO)$_2$(μ-dppm)] (3.179(2) Å).[457]

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4.10

Polyoxo Anions: Synthesis and Structure

M. T. POPE

Georgetown University, Washington, DC, USA

4.10.1 INTRODUCTION

4.10.1.1 Definitions and Scope

The explosion of activity and subsequent literature in the polyoxometalate field during the past two decades may reflect the increasing access to reliable methods of characterization in solution (multinuclear NMR) and the solid state (X-ray diffraction), but is certainly stimulated by the realization that there are few fields of science to which these complexes do not have important applications. One result of this expansion has been the necessity to devote two chapters to the chemistry of polyoxometalates—one focusing on structure and one on reactivity—instead of the single chapter in the original *Comprehensive Coordination Chemistry* (*CCC*, 1987).

Polyoxometalates encompass complexes known historically as heteropoly- and isopolyanions (or acids). Other labels, e.g., heteropoly electrolytes, metal–oxygen cluster anions, have also been applied from time to time. The present chapter will discuss only those complexes containing V, Nb, Ta, Mo, and/or W as the major component (the addenda atoms). The relatively small number of polyoxochromates is excluded, since Cr^{VI} is restricted to tetrahedral four-coordination by oxide, and these complexes are if anything more closely related to the nonmetal polyoxoanions like sulfates.

To a large extent the discussion will be limited to those complexes that have a discernible solution chemistry (e.g., by spectroscopy). The boundary between metal-oxide lattices and solid-state materials incorporating known and new polyoxometalate structures is becoming less and less well defined. Although this is an interesting and important area, with many potential applications, it is beyond the scope of the present endeavor.

Since the publication of *CCC* (1987), various aspects of the chemistry of polyoxometalates have been reviewed or assembled in symposia proceedings; see Table 1. Within the same time period, three volumes of *Inorganic Syntheses* have included sections on polyoxometalates (**1985**, *25*, 186–191; **1990**, *27*, 71–135; **1997**, *31*, 167–201).

4.10.2 ISOPOLYANIONS

4.10.2.1 Vanadates(V)

4.10.2.1.1 Aqueous solution species

Aqueous vanadate(V) solutions contain anions with structures based on both four- and six-coordinate vanadium centers. After decades of investigations, the speciation in such solutions has finally been established by a combination of precise EMF measurements and NMR spectroscopy (^{51}V and ^{17}O).[1–4] Changes in ionic medium (0.6 M Na(Cl) vs. 3.0 M $Na(ClO_4)$) have relatively minor effects upon the distribution of species, as shown by the predominance diagrams in Figure 1. In weakly acidic solution ($pH < 6$) the orange decavanadate anions, $[H_xV_{10}O_{28}]^{(6-x)-}$ ($x = 0–3$) are the major species. The decavanadate anion's D_{2d} arrangement of ten edge-shared VO_6 octahedra has been identified in dozens of X-ray structural investigations since 1966. The protonation sites of the anion can be detected by ^{17}O NMR, and correspond to bridging oxygen atoms.[5,6] Slowly established equilibria connect the decavanadates to the metavanadate domain ($pH \sim 6–8$). NMR evidence points to the presence of cyclic $[V_4O_{12}]^{4-}$ and $[V_5O_{15}]^{5-}$ in such solutions, and the exchange rates between these species and $[V_2O_7]^{4-}$ and $[VO_4]^{3-}$ have been probed by ^{51}V EXSY.[7] Attempts to crystallize metavanadates from aqueous solution lead to polymeric structures (chains of linked VO_4 or VO_5 polyhedra). Salts of the cyclic tetravanadate have been isolated only from nonaqueous media.

Table 1 Recent general references on polyoxometalates.

Year	*Title*	*Citation*
1987	Oxomolybdenum(VI) species in aqueous solution	Tytko, K. H. *Gmelin Handbook of Inorganic Chemistry*, 8th ed., Molybdenum Suppl. B, 3a, 67–358.
1989	Reactions of oxomolybdenum(VI) species in aqueous solution	Tytko, K. H. *Gmelin Handbook of Inorganic Chemistry*, 8th.ed., Molybdenum Suppl. B, 3b, 1–207.
1989	Oxomolybdenum(VI) species in nonaqueous (organic) solvents	Tytko, K. H. *Gmelin Handbook of Inorganic Chemistry*, 8th.ed., Molybdenum Suppl. B, 3b, 209–266.
1991	Polyoxometalate chemistry: an old field with new dimensions in several disciplines	Pope, M. T.; Müller, A. *Angew. Chem. Int. Ed. Engl.*, 30, 34–48.
1991	Molybdenum oxygen chemistry: oxides, oxocomplexes, and polyoxoanions	Pope, M. T. *Prog. Inorg. Chem. 30*, 181–257.
1992	Zeolite, Clay, and Heteropoly Acid in Organic Reactions	Izumi, Y.; Urabe, K.; Onaka, M., VCH: Weinheim, Germany, pp 1–106.
1994	Polyoxometalates: From Platonic Solids to Anti-retroviral Activity	Pope, M. T.; Müller, A., Eds. Kluwer Academic, Dordrecht, Netherlands, pp 1–411.
1994	Polyoxoanions	Pope, M. T. In *Encyclopedia of Inorganic Chemistry*, King R. B., Ed.; Wiley, Chichester, UK; pp 3361–71.
1996	Polyoxometalates in catalysis	Hill, C. L., Ed. *J. Mol. Catal., 114*, 1–371.
1996	Catalytic chemistry of heteropoly compounds	Okuhara, T.; Mizuno, N.; Misono, M. *Adv. Catal. 41*, 113–252.
1998	Polyoxometalate complexes in organic oxidation chemistry	Neumann, R. *Prog. Inorg. Chem. 47*, 317–370.
1998	Polyoxometalates	Hill, C. L., Ed. *Chem. Rev. 98*, 1–387.
1999	Bond length–bond valence relationships, with particular reference to polyoxometalate chemistry	Tytko, K. H.; Mehmke, J.; Kurad, D. *Struct. Bonding (Berlin) 93*, 1–66.
1999	A bond model for polyoxometalate ions composed of MO_6 octahedra (MO_k polyhedra with $k > 4$)	Tytko, K. H. *Struct. Bonding (Berlim) 93*, 67–127.
1999	Bonding and charge distribution in isopolyoxometalate ions and relevant oxides – a bond valence approach	Tytko, K. H.; Mehmke, J.; Fischer, S. *Struct. Bonding (Berlin) 93*, 129–321.
2000	Acid catalysts for clean production. Green aspects of heteropolyacid catalysts	Misono, M. *C. R. Acad. Sci., Ser. IIc: Chim. 3*, 471–475.
2001	Unique acid catalysis of heteropoly compounds	Misono, M. *Chem. Commun.* 1141–1152.
2001	Metal-Oxygen Clusters. The Surface and Catalytic Properties of Heteropoly Oxometalates	Moffat, J. B. Kluwer Academic: Dordrecht, Netherlands; pp 1–320.
2001	Polyoxometalate Chemistry : from Topology via Self-assembly to Applications	Pope, M. T., Müller, A., Eds. Kluwer Academic: Dordrecht, Netherlands; pp 1–467.
2002	Polyoxometalate Chemistry for Nano-composite Design	Yamase, T., Pope, M. T., Eds. Kluwer Academic/Plenum Publishers, pp 1–235.

Two metastable aqueous polyvanadates have been identified. Acidification of neutral vanadate solutions yields a solution with the expected V and O NMR spectra of the decavanadate anion and with additional resonances (two V, 1:12; three O, 1:1:1) that decay with a half-life of 80 min at 25 °C. The spectra are consistent with either a protonated α-Keggin anion or its ε-isomer, $[H_{12}V_{13}O_{40}]^{3-}$.[8,9] Reaction of VO^{2+} with 50% H_2O_2 and subsequent treatment with tetramethylammonium ion leads to black $(NMe_4)_3H_6[V_{15}O_{42}]$ in 36% yield. The anion has a *trans* bicapped Keggin structure analogous to that of $[PV_{14}O_{42}]^{9-}$ (see below) and has the expected four-line ^{51}V NMR spectrum (1:2:8:4). At pH 3.5, solutions of the anion are stable for a week at room temperature, and exhibit an initial reduction potential of 0.23 V vs. Ag/AgCl. Acidification leads irreversibly to VO_2^{+}.[10]

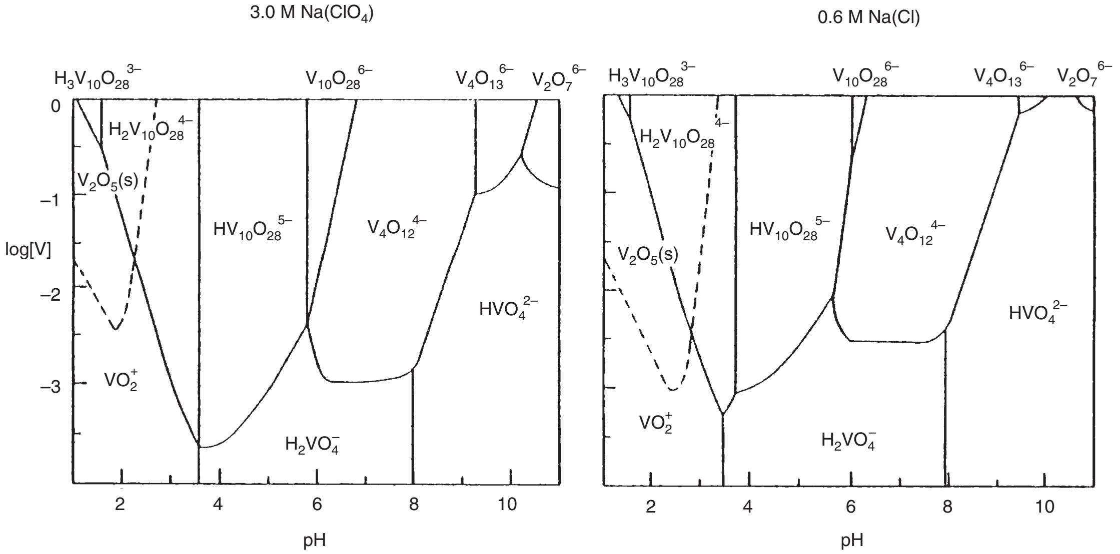

Figure 1 Predominance diagrams for aqueous polyvanadate species (reproduced by permission of Kluwer Academic Press from Pettersson, L. *Mol. Eng.* **1993**, *3*, 29–42).

4.10.2.1.2 Non-aqueous polyvanadates(V)

Tetrabutylammonium salts of the decavanadate anion are sources of new organic-solvent-soluble polyvanadates. Neutralization of $(Bu_4N)_3H_3[V_{10}O_{28}]$ in acetonitrile yields $[V_5O_{14}]^{3-}$, with a structure based on a trigonal-bipyramidal arrangement of VO_4 tetrahedra (Figure 2a).[11] The bowl-shaped anion, $[V_{12}O_{32}]^{4-}$, incorporating a guest acetonitrile molecule (Figure 2b), resulted from refluxing a solution of $(Bu_4N)_4H_2[V_{10}O_{28}]$ in that solvent.[12] The selectivity of this inorganic cavitand for other nitriles has been investigated.[13] Prolonged reflux of $(Bu_4N)_3H_3[V_{10}O_{28}]$ in acetone leads to the highly condensed anion $[V_{13}O_{34}]^{3-}$, with a structure of nominal C_{3v} symmetry based on 13 edge-shared VO_6 octahedra (Figure 2c). The anion undergoes a quasi-reversible, one-electron reduction at +0.228 V vs. ferrocinium/ferrocene.[9] The V_{12} and V_{13} anions have also been prepared from controlled hydrolyses of $VO(OMe)_3$.[14] In the presence of $[Pd(1,5\text{-}COD)Cl_2]$ in acetonitrile solution, the same decavanadate salt yields a mixed-valence V_{17} anion (Section 4.10.2.6.1) in high yield.[15]

4.10.2.2 Niobates(V) and Tantalates(V)

The aqueous solution chemistry of pentavalent niobium and tantalum, which is limited to highly basic media, is dominated by the hexametalate anions, $[Nb_6O_{19}]^{8-}$ and $[Ta_6O_{19}]^{8-}$, first identified by Lindqvist. A more recent X-ray investigation identifies protonation sites in $[H_2Nb_6O_{19}]^{6-}$.[16] The decaniobate anion, $[Nb_{10}O_{28}]^{6-}$, isostructural with decavanadate, was adventitiously obtained by a nonaqueous route, and has recently been confirmed. Although all known heteropoly niobates (see below) contain the hexaniobate structure as a component, it is possible that other structural types might be accessible under appropriate conditions. Limited numbers of niobium atoms have been incorporated into polytungstate structures; these species are discussed in Sections 4.10.2.5 and 4.10.6.

4.10.2.3 Molybdates(VI)

4.10.2.3.1 Aqueous-solution species

Based on precise EMF measurements and analysis of ^{17}O and ^{95}Mo NMR spectra, the speciation in alkali-metal molybdate solutions is dependent upon the ionic medium.[17–20] Distribution diagrams for 0.6 M Na(Cl) and 3.0 M $Na(ClO_4)$ are shown in Figure 3.[21] The predominant species are the heptamolybdates, $H_xMo_7O_{24}^{(6-x)-}$ ($x = 1$–3). The octamolybdates, $Mo_8O_{26}^{4-}$ and $HMo_8O_{26}^{3-}$, are detected in 0.6 M $Na(ClO_4)$, but not in 0.3 M $Na_2(SO_4)$.[22] The equilibrium

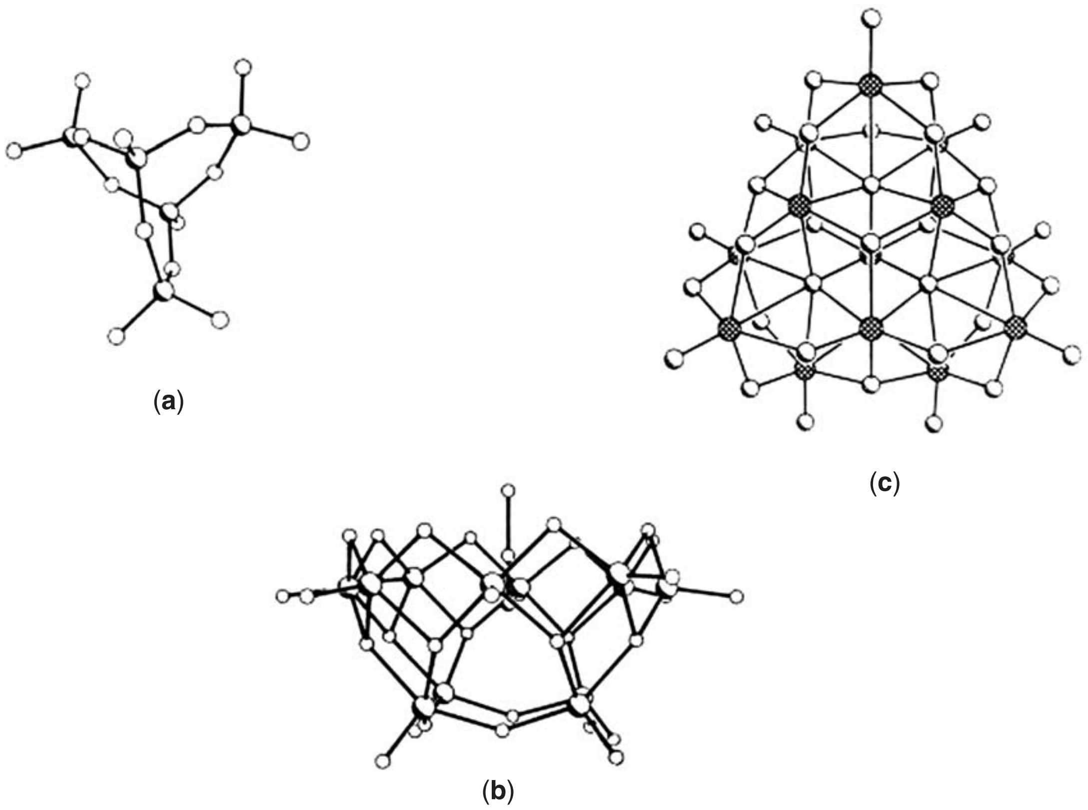

Figure 2 (a) $[V_5O_{14}]^{3-}$; (b) $[V_{12}O_{32}]^{4-}$ (showing included acetonitrile molecule); (c) $[V_{13}O_{34}]^{3-}$ (reprinted with permission from (a) Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 4518–4519; (b) Day, V. W.; Klemperer, W. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1989**, *111*, 5959–5961; (c) Hou, D.; Hagen, K. S.; Hill, C. L. *J. Am. Chem. Soc.* **1992**, *114*, 5864–5866. © 1989, 1992 American Chemical Society).

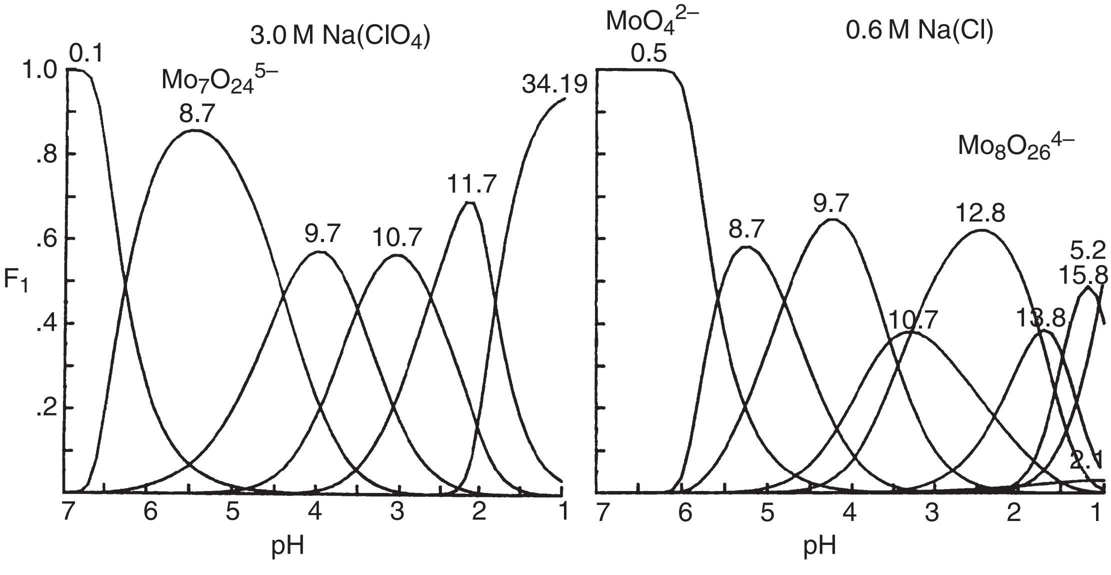

Figure 3 Distribution diagrams of polymolybdate species in two different ionic media (reproduced by permission of Kluwer Academic Press from Pettersson, L. *Mol. Eng.* **1993**, *3*, 29–42).

Table 2 Examples of octamolybdate salts.

$Mo_8O_{26}{}^{4-}$ isomer	Cation	Anion structure	References
α	$n\text{-}Bu_4N^+$	$2\ \{MoO_4\} + 6\ \{MoO_6\}$	492
β	$NH_4{}^+$	$8\ \{MoO_6\}$	493
γ	$[Me_3NCH_2CH_2NMe_3]^{2+}$	$2\ \{MoO_5\} + 6\ \{MoO_6\}$	24
δ	$[(RhCp^*)_2(\mu_2SCH_3)_3]^+$	$4\ \{MoO_4\} + 4\ \{MoO_6\}$	494
ε	$\{[Ni(H_2O)_2(4,4'bpy)_2]^{2+}\}_x$	$6\ \{MoO_5\} + 2\ \{MoO_6\}$	495
ξ	$[(Ni(phen)_2)_2Mo_8O_{26}]$	$4\ \{MoO_5\} + 4\ \{MoO_6\}$	496

species present in more acidic solutions ($pH < 2$) cannot be reliably identified, although salts of $[Mo_{36}O_{110}(H_2O)_{16}]^{8-}$ (see below) have been isolated from such solutions.

In spite of its rarity as an equilibrium species in aqueous media, many salts of the octamolybdate anion have been crystallized. Six different structural forms of the anion have been characterized (Table 2). These differ in the linkage and types of MoO_n coordination polyhedra. In 1976 Klemperer and Shum had proposed a nondissociative process for the interconversion of the α- and β-isomers.[23] An intermediate in this mechanism was a γ-structure, which was later isolated by Cruywagen and co-workers.[24] Other potential intermediates, the so-called α-γ and β-γ structures, are closely related to the observed δ-structure. The final structures listed in Table 2, ε and ξ, have been isolated from hydrothermal processes and appear to be controlled by the coordination demands of the lattice or the countercations.

The large anion $[Mo_{36}O_{110}(H_2O)_{16}]^{8-}$ has been structurally characterized in both potassium and sodium salts.[25,26] The structure contains four pentagonal-bipyramidal Mo centers, and is loosely described as a centrosymmetric dimer of $\{Mo_{17}\}$ units linked by two *cis*-MoO_2 groups. The nitrosyl-containing anion $[Mo_{36}(NO)_4O_{108}(H_2O)_{16}]^{12-}$ is isostructural with $\{(MoNO)^{3+}O_6\}$ in place of $\{(MoO)^{4+}O_6\}$.[27] Other nitrosyl polymolybdates are discussed in Section 4.10.3.8.

4.10.2.3.2 Non-aqueous isopolymolybdates

The vibrational spectra of the well-characterized hexamolybdate anion, $[Mo_6O_{19}]^{2-}$ of O_h point symmetry, and of the related species $[W_6O_{19}]^{2-}$ and $[Mo^VMo^{VI}{}_5O_{19}]^{3-}$, have been subjected to a normal coordinate analysis based on total isotopic substitution for the first case.[28,29] Derivatization of the hexamolybdate anion is discussed in Section 4.10.6. The dimolybdate, $Mo_2O_7{}^{2-}$, as a tetrabutylammonium salt, continues to be a valuable and convenient synthon for new organic-solvent-soluble derivatives. The unstable and amorphous salt $(Bu_4N)_3\ [Mo_5O_{17}H]$ was originally thought to have an anion structure isotypic with that of $[Me_2AsMo_4O_{15}H]^{2-}$. However the structurally characterized anion $[Mo_3O_8(OMe)(MoO_4)_2]^{3-}$ (Figure 4) has an IR spectrum that is almost identical with that of $[Mo_5O_{17}H]^{3-}$, suggesting structural similarity.[30]

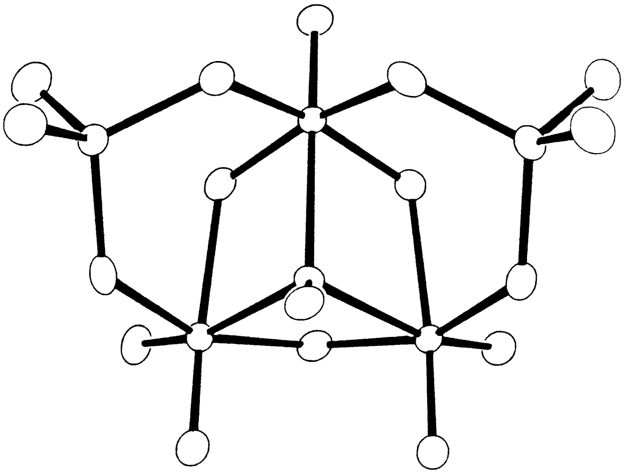

Figure 4 $[Mo_3O_8(OMe)(MoO_4)_2]^{3-}$ (reprinted with permission from Chen, Q.; Ma, L.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1989**, *111*, 5944–5946. © 1989 American Chemical Society).

4.10.2.4 Tungstates(VI)

Nuclear magnetic resonance studies[31,32] of aqueous tungstate solutions confirm that above pH 6 the major polytungstate species are $[W_7O_{24}]^{6-}$ (paratungstate-A) and $[H_2W_{12}O_{42}]^{10-}$ (paratungstate-B) which have been isolated in numerous salts. Tungsten NMR chemical shifts are given in Table 3.

Below pH 5.5 equilibria are very slowly established and most polytungstate species, with the exception of the Keggin anion α-$[(H_2)W_{12}O_{40}]^{6-}$ (metatungstate), are metastable. Acidification of paratungstate solutions leads to "pseudometatungstate(s)", which ultimately lead to the stable metatungstate anion. The composition of pseudometatungstate has been problematical. From solutions believed to contain this anion, the salt $K_6H_4W_{11}O_{38}.11H_2O$, with an anion of C_s symmetry, has been crystallized.[33] However, the W-NMR spectrum of similar solutions shows a species with 11 resonances of equal intensity, which has tentatively been assigned to $[H_7W_{11}O_{40}]^{7-}$, a lacunary version of paratungstate-B. This solution also shows a two-line NMR spectrum attributable to $[W_{10}O_{32}]^{4-}$, once known as tungstate-Y, a species that is stabilized in nonaqueous solvents, and which has a rich photochemistry.[34–47] The NMR spectra (^{183}W, ^{17}O, ^{1}H) also reveal the presence of minor amounts of β-$[(H_2)W_{12}O_{40}]^{6-}$ (tungstate-X in the early literature) and α- and β-$[(H)W_{12}O_{40}]^{7-}$ with single central protons. Recently, Himeno *et al.* have reported $[(H_4)W_{12}O_{40}]^{4-}$, believed on the basis of W- and H-NMR measurements to contain four central protons, and which was isolated as a tetra-*n*-propylammonium salt from aqueous acetonitrile solutions.[48] Salts containing fragments of the heptatungstate structure, $Na_5[H_3W_6O_{22}]$ and $K_7[HW_5O_{19}]$, have been isolated from concentrated aqueous tungstate solutions, but there is no evidence to suggest that the anions are stable in solution.[49,50]

In nonaqueous solutions, the hexa- and decatungstate anions are well characterized (Table 3). In an attempt to synthesize the currently unknown $[W_2O_7]^{2-}$ anion, e.g., by protonation of $(Bu_4N)_2WO_4$, Errington discovered a new polytungstate with a clean, five-line W-NMR spectrum, but was unable to obtain crystals for structure determination.[51] A polytungstate formulated as $[H_6W_{18}O_{60}]^{6-}$ was isolated in small yield as a tetra-*n*-propylammonium salt from aqueous tungstate solutions at pH 4. In acetonitrile solution the anion exhibits reversible voltammetric behavior, and the W-NMR spectrum in propylene carbonate consists of three lines of equal intensity (Table 3).[52]

4.10.2.5 Mixed-metal Isopolyanions

4.10.2.5.1 Molybdovanadates

The aqueous system H^+–HVO_4^{2-}–MoO_4^{2-} has been investigated by EMF methods and NMR spectroscopy (^{51}V, ^{95}Mo, ^{17}O) in 0.6 M Na(Cl) at pH 1.4–7.[53–55] A very large number of species is involved. The major anions detected are listed in Table 4. Several of these have been independently isolated as crystalline salts and structurally characterized. Other structural types of molybdovanadates have been crystallized from aqueous solutions, e.g., $[V_2Mo_6O_{26}]^{6-}$ (α-octamolybdate structure), $[V_5Mo_8O_{40}]^{7-}$ (*not* a Keggin structure), and $[V_8Mo_4O_{36}]^{8-}$[56–58]

The Keggin anions $[(V)Mo_{12}O_{40}]^{3-}$, $[(V)V_xMo_{12-x}O_{40}]^{(3+x)-}$ ($x = 1$–3) with a central V atom, have been prepared in nonaqueous solution and isolated as tetrabutylammonium salts. Their electrochemical behavior has been briefly investigated.[59]

Table 3 Tungsten-183 chemical shifts of some isopolytungstates.[a]

Anion	*δ(ppm. vs. external 2M Na_2WO_4)*
$[WO_4]^{2-}$	−9.5
$[W_7O_{24}]^{6-}$	+268 (1W), −106 (2W), −189 (4W)
$[H_2W_{12}O_{42}]^{10-}$	−109 (2W), −114 (2W), −116 (4W), −147 4W)
α-$[(H_2)W_{12}O_{40}]^{6-}$	−123
β-$[(H_2)W_{12}O_{40}]^{6-}$	−112 (3W), −127 (6W), −136 (3W)
α-$[(H_4)W_{12}O_{40}]^{4-}$	−92[b]
$[W_6O_{19}]^{2-}$	+59[c]
$[W_{10}O_{32}]^{4-}$	−105 (2W), −118 (8W) {−98, −105}[b]
"$[H_6W_{18}O_{60}]^{6-}$"	−111 (6W), −147 (6W), −161 (6W)[d]

[a] in aqueous solution unless otherwise specified. [b] in acetonitrile. [c] in dimethylformamide. [d] in propylene carbonate.

Table 4 Major molybdovanadate anions.

Formula	$\delta(^{51}V)$	*Structure type*
$[MoV_9O_{28}]^{5-}$	−425–525 (2:2:2:1:1:1)	decavanadate
cis-$[Mo_2V_8O_{28}]^{4-}$	−424–525 (2:4:2)	decavanadate
trans-$[Mo_2V_8O_{28}]^{4-}$	−427−516 (2:4:2)	decavanadate
$[Mo_4V_5O_{27}]^{5-}$	−440.0–518.6 (1:1:1:1:1)	Figure 5
cis-$[Mo_4V_2O_{19}]^{4-}$	−498.0	Hexamolybdate
$[Mo_5VO_{19}]^{3-}$	−506.4	Hexamolybdate
$[Mo_7VO_{26}]^{5-}$	−537.2	β-octamolybdate

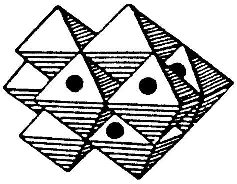

Figure 5 $[Mo_4V_5O_{27}]^{5-}$.

4.10.2.5.2 *Tungstovanadates*

The major confirmed and isolated species are the hexametalate $[V_xW_{6-x}O_{19}]^{(2+x)-}$ ($x = 1$–3) and Keggin anions $[(V)V_xW_{12-x}O_{40}]^{(3+x)-}$ ($x = 1$–4), and $[(H_2)W_{11}VO_{40}]^{7-}$. A ^{51}V NMR investigation of vanadate–tungstate mixtures has revealed the existence of $[WV_9O_{28}]^{5-}$ as a significant component at pH 5, and of the second (*mer*) isomer of $[V_3W_3O_{19}]^{5-}$ at pH 6.5.[60]

4.10.2.5.3 *Molybdotungstovanadates*

All nine possible anions/isomers of *cis*-$[V_2Mo_xW_{6-x}O_{19}]^{4-}$ have been detected in aqueous solution by ^{183}W-NMR spectroscopy.[61]

4.10.2.5.4 *Niobotungstates*

These are all hexametalates, $[Nb_xW_{6-x}O_{19}]^{(2+x)-}$ ($x = 1$–4). Derivatives of the anions with $x = 1$ and 2 are discussed in Section 4.10.9. A normal coordinate analysis of the vibrational spectra of $[NbW_5O_{19}]^{3-}$ and $[MoW_5O_{19}]^{2-}$ has been reported.[62]

4.10.2.5.5 *Molybdotungstates*

By means of ^{183}W and ^{95}Mo NMR, it has been established that all possible mixtures of $[(Mo,W)_7O_{24}]^{6-}$ are formed, but that molybdenum substitution into paratungstate-B, $[H_2W_{12}O_{42}]^{10-}$, and metatungstate, α-$[(H_2)W_{12}O_{40}]^{6-}$, is limited to a single site in both cases.[63]

4.10.2.6 Reduced and Mixed-valence Isopolyanions

4.10.2.6.1 *Vanadates*

A bewildering variety of reduced and mixed-valence polyvanadates has been reported (Table 5). Several of these can be viewed as clathrates that encapsulate a guest anion or water molecule within a hollow shell (entries 2, 4, 8, 10–14). Technically, some of the entries in Table 5 should be regarded as heteropolyanions, but it is more convenient to discuss them here, in view of their structural similarities. The guest anions in the clathrate structures have been regarded as templates that control the overall structure shape, and these structural data have been successfully used to generate force-field

Table 5 Some reduced and mixed-valence polyvanadates.

	Anion	*X*	*V^{IV} centers*	*References*
1	$[V^{IV}{}_2V^V{}_8O_{26}]^{4-}$		2	64–66
2	$[V^{IV}{}_{12}O_{42}(H_2O)]^{12-}$		12	67
3	$[H_6V^{IV,V12}O_{30}F_2]^{6-}$		10	68
4	$[As^{III}{}_8V^{IV,V}{}_{12}O_{40}(HCO_2)]^{n-}$		6, 8	69,70
5	$[KH_3As^{III}{}_3V^{IV,V}{}_{12}O_{39}(As^VO_4)]^{6-}$		4	71,72
6	$[KH_6(CH_3PO_3)_3V^{IV,V}{}_{12}O_{27}(V^VO_4)]^{5-}$		9	73
7	$[As^VV^{IV}{}_2V^V{}_{12}O_{40}]^{7-}$		2	74
8	$[H_4V^{IV,V}{}_{14}O_{26}(H_2O)_2$ $(C_6H_5PO_3)_8\text{-}\{2NH_4{}^+,2Cl^-\}]^{6-}$		12	75
9	$[V^{IV,V}{}_{17}O_{42}]^{4-}$		5	15
10	$[As^{III}{}_6V^{IV}{}_{15}O_{42}(H_2O)]^{6-}$		15	76
11	$[V^{IV,V}{}_{15}O_{36}(X)]^{n-}$	Cl^-, Br^-, $CO_3{}^{2-}$	6–12	66,77–80
12	$[V^{IV,V}{}_{18}O_{42}(X)]^{n-}$	Cl^-, Br^-, I^-, $SO_4{}^{2-}$, $PO_4{}^{3-}$, $VO_4{}^{3-}$	12	77,81–84
13	$[V^{IV,V}{}_{18}O_{44}(X)]^{n-}$	$N_3{}^-$, $NO_3{}^-$	9, 15	82,84
14	$[V^{IV,V}{}_{22}O_{54}(X)]^{n-}$	$ClO_4{}^-$, SCN^-, $CH_3CO_2{}^-$	8	68,82,85
15	$[V^{IV,V}{}_{34}O_{82}]^{10-}$		16	86

parameters.[87] Most of these species listed in Table 5 were first isolated from aqueous solutions at ambient temperatures, but more recently photochemical and hydrothermal processes have been found to yield such anions. The V_{15} and V_{18} species (11–13) are often produced, but with variable numbers of V^{IV} centers. The magnetic properties of these substances have attracted much attention.[70,72,88–92]

4.10.2.6.2 *Molybdates and tungstates*

The mixed-valence species (heteropoly blues and -browns) generated by reduction of stable polyoxomolybdates and -tungstates are discussed in Section 4.10.3.7.

Since about 1990, several reduced polymolybdates have been isolated from aqueous solution or via hydrothermal synthesis. Some of these (see Table 6) have structures based on six diamagnetic $\{Mo^V{}_2O_4\}^{2+}$ units assembled into an ε-Keggin conformation (see Figure 6). Recently, a partially-reduced ε-$PMo_{12}O_{40}$ core has been identified in some lanthanum derivatives.[98] Even larger species, some with more than 350 metal centers and with dimensions in the multinanometer range, are accessible by similar processes. Discussion of these and other very large polyoxometalates is deferred to Section 4.10.3.8.

4.10.3 HETEROPOLYANIONS

4.10.3.1 Keggin and Related Plenary Structures

The Keggin-structure anions (α-$XM_{12}O_{40}$), particularly the tungsto- and molybdophosphates and -silicates, continue to be the most frequently investigated polyoxometalates, almost always for potential and realized catalytic applications.

Table 6 Some reduced polymolybdates incorporating the ε-Keggin $Mo^V{}_{12}$ core.

	Formula	*Mo^V centers*	*References*
1	$[(H_2)Mo_{12}O_{28}(OH)_{12}(Mo^{VI}O_3)_4]^{6-}$	12	93
2	$[(H_2)Mo_{12}O_{30}(OH)_{10}\{Ni(H_2O)_3\}_4]$	12	94
3	$[H_{14}Mo_{37}O_{112}]^{14-}$	26	95
4	$[Na(H_2O)_3H_{13}Mo_{42}O_{109}\{(OCH_2)_3C\text{-}CH_2OH\}_7]^{9-}$	38	96,97
5	$[H_{13}Mo_{43}O_{112}\{(OCH_2)_3CH_3\}_7]^{10-}$	36	96,97
6	$[PMo_{12}O_{36}(OH)_4\{La(H_2O)_4\}_4]^{5+}$	8	98

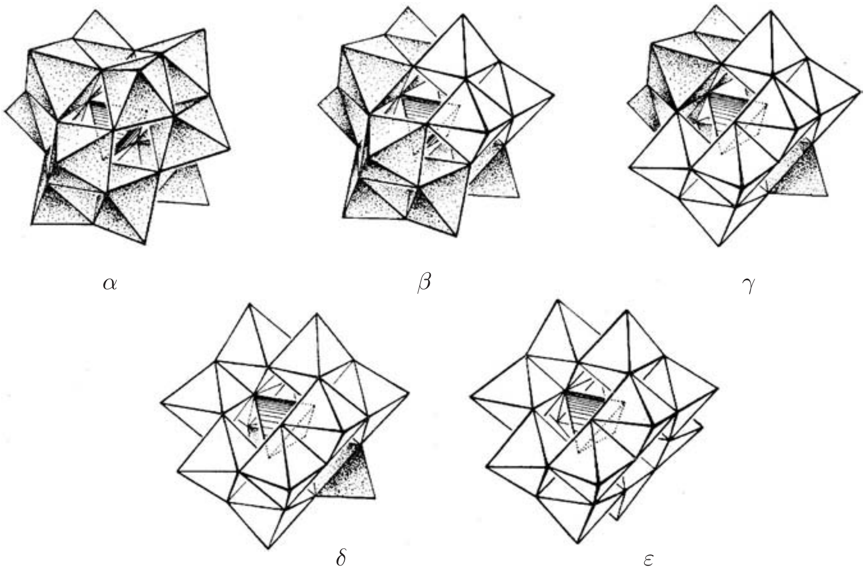

Figure 6 The Baker–Figgis isomers of the Keggin anion.

4.10.3.1.1 Keggin isomers

Polyhedral representations of the Keggin structure and its possible skeletal ("Baker–Figgis"[99]) isomers are shown in Figure 6, and a list of confirmed species is given in Table 7.

Detailed vibrational (infrared and Raman) spectra of multiple salts of many of the anions listed in the Table have been reported and analyzed.[107,108] As will be seen from Table 7, the α-isomer is the most common and presumably the thermodynamically stable form, at least for oxidized anions with all addenda (M) atoms identical. In the molybdate system, reduction of the α-anions results in spontaneous isomerization to the β-isomers, since the latter have more positive reduction potentials: see Section 4.10.3.7. Rates of isomerization in the tungstate system are exceedingly slow, so that β-isomers possess considerable kinetic stability. A recent density functional theory treatment[109] of Keggin tungstates with central P, As, Si, Ge, Al, and Ga concludes that the β-isomer becomes relatively more stable as the oxidation state of the central atom decreases; see Table 8.

Table 7 Central heteroatoms, X, in Keggin and isomeric anions, $[XM_{12}O_{40}]^{n-}$.

Isomer	*molybdates*	*tungstates*
α	Ga,[100,101] Si, Ge, P^V, As^V, Sb^V, V,[102] S^{VI} [103,104]	H_2*, Be, B, Al, Ga, Si, Ge, P^V, As^V, V,[105]Cr^{3+}, Fe^{3+}, $Co^{2+,3+}$, $Cu^{1+,2+}$, Zn
β	Si, Ge, P^V, As^V	H_2, Al, Ga(?), Si, Ge, P^V[100]
γ		Si

*See Section 4.10.2.4 for metastable Keggin anions with one and four central protons.

Table 8 Computed relative stabilities (eV) of α- and β-isomers of oxidized Keggin anions.[a]

Central atom	$\Delta E(\beta-\alpha)$ *Mo*	$\Delta E(\beta-\alpha)$ *W*
P	+0.21	+0.28
Si	+0.14	+0.26
Al	+0.08[b]	−0.35
As	+0.11	+0.16
Ge	+0.01	+0.21
Ga	−0.02	−0.19

[a] Lopez, X.; Maestre, J. M.; Bo, C.; Poblet, J.-M. *J. Am. Chem. Soc.* **2001**, *123*, 9571–9576. [b] anion is currently unknown.

This is consistent with the following experimental observations:

(i) in aqueous solution an equilibrium is established between α- and β-isomers of $[AlW_{12}O_{40}]^{5-}$.[110,111] Based on ^{27}Al-NMR measurements of 0.1 M solutions of the free acids at 200 °C, K_{eq} $(\beta/\alpha) = 0.11 \pm 0.01$. This value indicates that the α-isomer is more stable than the β-isomer by 2.1 ± 0.5 kcal mol^{-1}. First-order rate constants for approach to equilibrium at 200 °C were $k(\alpha \rightarrow \beta) = 7.68 \times 10^{-7}\,s^{-1}$ and $k(\beta \rightarrow \alpha) = 6.97 \times 10^{-6}\,s^{-1}$.

(ii) The β-isomers of the Si- and Ge-centered anions have considerable kinetic stability and can be synthesized in high yield[112], but there is no evidence of an equilibrium concentration in aqueous solution.

(iii) The β-isomer of $[PW_{12}O_{40}]^{3-}$ appears to be unstable in aqueous solution,[113] but has been isolated as a tetra-*n*-butylammonium salt from aqueous acetonitrile.[106]

The structure of the γ-isomer involves an additional coulombically unfavorable, edge-shared contact between MO_6 octahedra than do the structures of the α- and β-forms. Examples of γ-structure e anions have been synthesized from the lacunary anion (γ)-$[SiW_{10}O_{36}]^{8-}$ of C_{2v} symmetry, which is lacking the two edge-shared octahedra. Reaction with $[M^{V}{}_2O_4(aq)]^{2+}$ (M = Mo, W) and subsequent oxidation leads to metastable γ-Keggin anions which have been structurally characterized.[112,114,115] A P-centered analogue of the (γ)-decatungstate precursor anion is also known, but it is less stable.

4.10.3.1.2 Capped Keggin anions

So-called capped Keggin structures were first observed with the vanadophosphate and -arsenate anions, $[(T)V_{14}O_{42}]^{9-}$. These anions contain an α-Keggin core to which are attached two VO^{3+} groups, as shown in Figure 7. The phosphate anion has received the most attention.[116] In 0.6 M Na(Cl) at $1.3 < pH < 4.0$, the major solute species is $[H_4PV_{14}O_{42}]^{5-}$ and the transient existence of

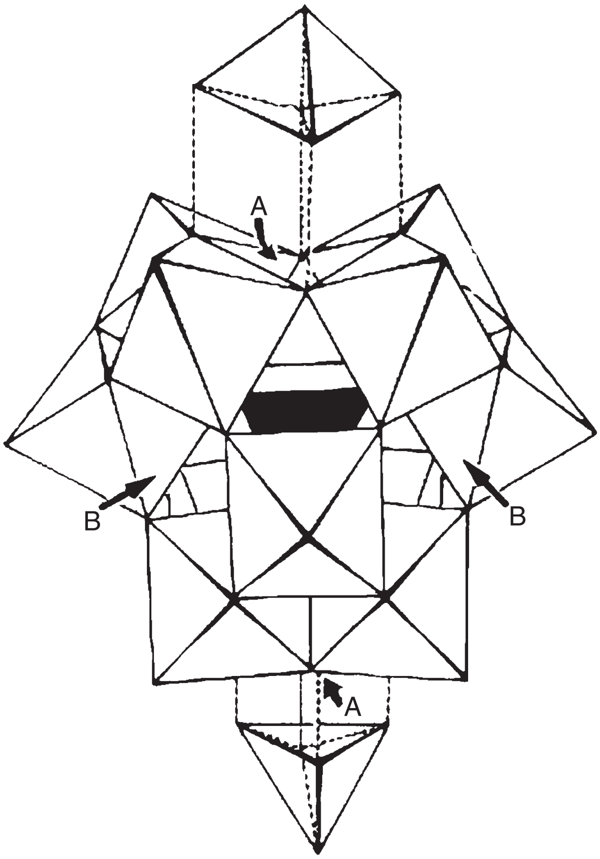

Figure 7 Bicapped Keggin anion (reprinted with permission from Kato, R.; Kobayashi, A.; Sasaki, Y. *Inorg. Chem.* **1982**, *21*, 240–246. © 1982 American Chemical Society).

the monocapped anion, $[H_xPV_{13}O_{41}]^{(12-x)-}$, was detected.[117] Phosphorus-, vanadium-, and oxygen-NMR have been recorded, and oxygen exchange with solvent is most rapid for the oxygens in the VO caps.[6] Other examples of the capped structure are adopted by $[V_{15}O_{42}]^{9-}$ (Section 4.10.2.1.1) and by mixed-addenda and partially reduced anions, some of which have been formed via hydrothermal methods. Examples include dicapped $[PMo^{V}{}_{6}Mo^{VI}{}_{6}O_{40}(V^{IV}O)_2]^{5-}$[118], mono-capped $[PMo_5V_7O_{40}(VO)]^{7-}$[119], and the extended (chain) structure of $[\{(V^{V}O_4)Mo^{VI}{}_{8}V^{IV}{}_{4}O_{36}(V^{IV}O)_2\}_n]^{7n-}$ [120,121] has been reported. Hydrothermal syntheses also lead to a tetracapped anion,[122] $[PMo^{V,VI}{}_{8}V^{IV}{}_{4}O_{40}(V^{IV}O)_4]^{5-}$, and to species capped by As^{III}, $[H_4As^{V}Mo^{V}{}_{8}Mo^{VI}{}_{4}O_{40}As^{III}{}_{2}]^{-}$,[123] and by *cis*-$(MoO_2)^{2+}$ groups, $[SiMo^{V}{}_{4}Mo^{VI}{}_{8}O_{40}(Mo^{VI}O_2)_2]^{4-}$ and $[\{SiMo^{V}{}_{4}Mo^{VI}{}_{8}O_{40}(Mo^{VI}O_2)(Mo^{VI})\}_2\{\mu\text{-}(H_2O)_2\}]^{6-}$.[124] That no capped polytungstate anions have so far been reported presumably reflects the lower nucleophilicity of oxygens attached to W compared with V and Mo(V).

No examples of anions containing the δ-Keggin core have been reported, but several are known to contain the ε configuration. All involve V and or Mo(V): examples of molybdates are listed in Table 6. Vanadates include mixed-valence $[K(AsO_4)V^{IV,V}{}_{12}O_{36}(AsOH)_3]^{6-}$,[71] and $[H_6K(V^{V}O_4)V^{IV,V}{}_{12}O_{36}(PCH_3)_3]^{5-}$[73] with capping As(III) and phosphonate groups, respectively, and the vanadomanganate, $[Mn^{IV}{}_{3}V^{V}{}_{12}O_{40}H_3]^{5-}$.[125]

4.10.3.1.3 *Mixed-addenda Keggin anions*

Incorporation of more than one type of addendum atom (V, Mo, W) into the Keggin structure raises the issue of isomerism based upon the distribution of the like addenda ("positional isomers"). The numbering scheme for the α and β Keggin frameworks is shown in Figure 8. The theoretical numbers of positional isomers are very large (Table 9), and these have been confirmed in some of the simpler cases by NMR spectroscopy.[126] Although some of the isomers can be synthesized in pure form by the reaction of appropriate lacunary anions, e.g., the formation of 1,2,3-$[SiW_9V_3O_{40}]^{7-}$ from A-$[SiW_9O_{34}]^{10-}$ (Section 4.10.3.2) and VO_3^{-}, in general mixtures of all possible isomers are generated, and these have so far proved to be impossible to separate. An even more intractable situation occurs with the molybdotungstate anions $[(T)Mo_xW_{12-x}O_{40}]^{n-}$, which bear the same charge for every value of x.

A quantitative NMR and EMF investigation of the quaternary system H^+–MoO_4^{2-}–HVO_4^{2-}–MoO_4^{2-} in 0.6 M Na(Cl) at 25 °C and 90 °C, with $(Mo+V):P=12:1$ and $Mo:V>9:3$, reveals

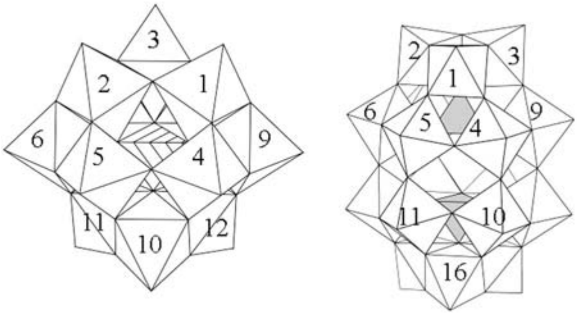

Figure 8 Numbering scheme for the α isomers of the Keggin and Wells–Dawson anions. The numbering is retained for the β-isomer of the Keggin anion with the "rotated" triad containing atoms 10, 11, and 12.

Table 9 Numbers of positional isomers for Keggin anions $[(T)M_xMN_{12-x}O_{40}]^{n-}$.

x	*α-isomer*	*β-isomer*
1	1	3
2	5	14
3	13	43
4	27	90
5	38	142
6	48	166

the existence and pK_a values of all five isomers of α-$[PV_2Mo_{10}O_{40}]^{5-}$ to be close to their expected statistical abundances. Two other isomers, presumably based on the β-framework, were also detected in small quantities.[127] In solutions where Mo:V = 3.8, several isomers of $[PV_3Mo_9O_{40}]^{6-}$ could be identified.[128]

Vanadium-centered Keggin molybdo- and tungstovanadates were mentioned in Sections 4.10.2.5.1 and 4.10.2.5.2. The corresponding P- and Si-centered tungstovanadates have received attention.[126,129–131]

4.10.3.1.4 Keggin anions with inversion disorder

Several salts of Keggin anions, especially those with mixed addenda (Mo, V) or capped species, crystallize with the anion on an inversion center, i.e., with the central (tetrahedral) atom appearing to be eight-coordinate. This type of disorder, unless carefully analyzed,[132] leads to erroneous conclusions regarding bond lengths and coordination environments of the addenda atoms.

4.10.3.2 Wells–Dawson and Related Plenary Structures

4.10.3.2.1 Isomers

Baker and Figgis originally proposed six possible skeletal isomers for anions with the so-called Wells–Dawson structure, typified by the tungstophosphates, $[P_2W_{18}O_{62}]^{6-}$. Examples of four of these have now been identified and these are illustrated in polyhedral form in Figure 9. As for the Keggin anions, β- and γ-isomers have structures in which one and two W_3 groups, respectively, have been rotated by 60°. Structures in which the central W_6 belts are staggered rather than eclipsed are denoted with an asterisk; of these, only the γ^*-isomer has been confirmed: see Table 10. The α- and β-isomers of $[P_2W_{18}O_{62}]^{6-}$ are formed simultaneously in the conventional synthesis of this anion and can be separated by fractional crystallization of the ammonium salts.[133] Note that in the early literature these were known as the A- (β) and B- (α) forms.

Although the P- and As-centered anions and their isomers are synthesized and are stable (at least kinetically) in aqueous solution,[136] the sulfate anions, as a consequence of their lower charge (4−), are prepared in aqueous acetonitrile and have been structurally characterized as tetraalkylammonium salts. The molybdate is an α-isomer,[135] but the tungstate isolated proved to be the γ^*-isomer.[141] The one-electron reduced anion, $[S_2W_{18}O_{62}]^{5-}$, isolated as a tetra-*n*-butylammonium salt,

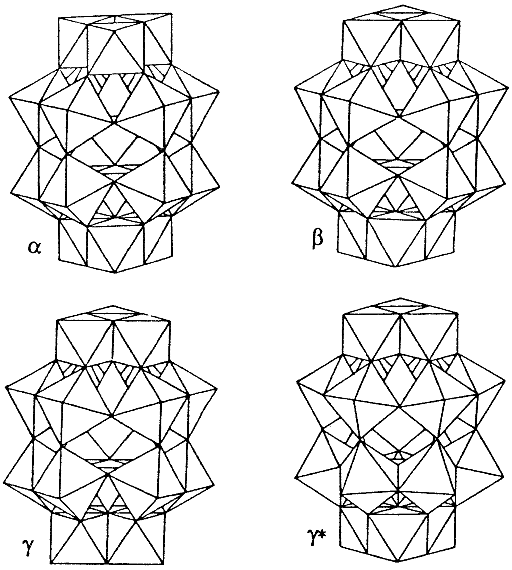

Figure 9 Four Isomers of the Wells–Dawson anion (reprinted with permission of Elsevier from Contant, R.; Thouvenot, R., *Inorg. Chim. Acta* **1993**, *212*, 41–50).

Table 10 Isomers of Wells–Dawson polyoxometalates, $[X_2M_{18}O_{62}]^{n-}$.

Isomer	*M = Mo*	*M = W*
α	P, As, S[134,135]	P, As
β	see text	P, As
γ		P,[136–139] As[136]
γ*		As[136,137,140] S[141]

was found to have the α-configuration, but no electrochemical distinction could be made between the two isomers.[142]

Early polarographic studies of the (α) molybdodiphosphate and -arsenate anions showed that upon reduction they were slowly transformed into "β" isomers in an analogous manner to the behavior of the corresponding Keggin molybdates.[143] It has been reported, however, that the P-NMR spectrum of a reduced "β"-$[P_2Mo_{18}O_{62}]$ has one line which is consistent only with an α*-, γ-, or γ*-structure.[136]

4.10.3.2.2 Mixed-addenda Dawson Anions

As for the Keggin anions (Section 4.10.3.1.3), there are numerous possibilities for positional isomers, and mixtures are frequently encountered. Almost all of these have been derived from the P- and As-centered tungstates, but a tungstovanadosulfate, $[S_2V_2W_{16}O_{62}]^{6-}$, has been structurally characterized.[144] Individual isomers can often be prepared from appropriate lacunary species, and these are discussed in Section 4.10.3.3.

4.10.3.2.3 Semi-vacant Wells–Dawson anions

The Wells–Dawson tungstophosphate and -arsenate anions are synthesized using a large excess of phosphoric or arsenic acids and, especially for the phosphate isomers, prolonged boiling.[133,136] When the tungstate is in molar excess (e.g., W/P = 20) new anions $[H_4XW_{18}O_{62}]^{7-}$ (X = P, As) are produced. Based on P-NMR, three isomers of the phosphate are formed initially, but boiling for 60 h yields a single product. No crystallographic investigation has yet been reported, but based upon NMR analysis (Table 11) it was concluded that the anions have the α-Wells–Dawson structure with one phosphorus site vacant.[145] The location of the anion protons is uncertain; no separate ^{1}H-NMR signal is observed, implying that exchange with solvent is rapid, but this does not rule out the possibility that they are attached to internal oxygen atoms.

Table 11 W-NMR chemical shifts for Wells–Dawson tungstates.

	α-XW_9 group	*β-XW_9 group*	*α-$\square W_9$ group*
α-$[P_2W_{18}O_{62}]^{6-}$	−126.5 (6W), −172 (12W)		
β-$[P_2W_{18}O_{62}]^{6-}$	−129.9 (3W), −170.1 (6W)	−110.6 (3W), −190 (6W)	
γ-$[P_2W_{18}O_{62}]^{6-}$		−110.4 (6W), −190.8 (12W)	
α-$[H_4PW_{18}O_{62}]^{7-}$	−144.9 (3W), −181.3 (6W)		−135.7 (3W), −127.8 (6W)
α-$[As_2W_{18}O_{62}]^{6-}$	−120.8 (6W), −144.1 (12W)		
β-$[As_2W_{18}O_{62}]^{6-}$	−123.4 (3W), −140.6 (6W)	−106.6 (3W), −160.1 (6W)	
γ-$[As_2W_{18}O_{62}]^{6-}$		−106.3 (6W), −160.1 (12W)	
γ*-$[As_2W_{18}O_{62}]^{6-}$		−109.7 (6W), −166.0 (12W)	
α-$[H_4AsW_{18}O_{62}]^{7-}$	−134.6 (3W)[a], −161.3 (6W)		−134.1 (3W)[a], −112.4 (6W)

[a] The relative assignment of these two lines is uncertain.

4.10.3.3 The "Preyssler" Anion

This anion, originally described by Preyssler as a P_3W_{18} species,[146] is formed as a by-product in the standard synthesis of the Wells–Dawson tungstophosphates, and was later shown to be $[Na(H_2O)P_5W_{30}O_{110}]^{14-}$ with the structure illustrated in Figure 10.[147,148] This structure can be related to the Keggin and Wells–Dawson structures in the following manner. Removal of a group of three corner-shared WO_6 octahedra from the Keggin structure yields A-type $[PW_9O_{34}]^{9-}$ (see Section 4.10.3.4), two of which can be combined to form the Wells–Dawson anion. If two groups of corner-shared octahedra are removed from the Keggin anion, the remaining $\{PW_6O_{26}\}$ fragment forms one-fifth of the complete structure. The Keggin, Wells–Dawson, and Preyssler structures are topologically analogous to a tetrahedron (methane), two face-shared tetrahedra (ethane), and five face-shared tetrahedra (cyclopentane). A notable feature of this anion is the tightly encapsulated (on the ^{23}Na NMR timescale) sodium cation and coordinated water molecule. Under forcing conditions the central sodium cation can be replaced by Ca^{2+}, trivalent lanthanide cations, and some tetravalent actinides, all of which have similar ionic radii (ca. 1 Å).[147–152] Spectroscopic, luminescence, and ESR studies have been reported for some of the lanthanide-encrypted anions.[153–158] All the anions show reversible tungsten-reduction processes, and there is some evidence to suggest that divalent europium is generated in partially reduced $[Eu(H_2O)P_5W_{30}O_{110}]^{n-}$.[159] Proton exchange on the internal water molecule has been traced by NMR measurements.[148] The remarkable hydrolytic (pH 0–11) and thermal stability of the anion has attracted investigations of its catalytic activity, discussed in Chapter 4.11.

No lacunary versions of this anion have been unambiguously identified, but a monosubstituted vanadium(IV) derivative has been isolated and characterized by ESR spectroscopy. Attempts to prepare molybdate or arsenate analogues have been unsuccessful.

4.10.3.4 Lacunary Forms of Keggin and Wells–Dawson Anions

The main lacunary versions of Keggin- and Dawson-type structures that can be isolated as pure salts, and that have kinetic stability in solution, are summarized in Table 12. Some molybdate analogues have been isolated[160] or otherwise identified in equilibrium studies.[19,161,162] All these lacunary anions have structures in which no MO_6 octahedron has more than two (*cis*) terminal oxygens, and are convenient synthetic precursors of substituted "plenary" anions and functionalized species.

The monovacant anions (entries 1–4, 9–11 in Table 12) generate a vast number of species in which the substituent atom is a metal cation bearing a variety of terminal ligands, or in some cases none (e.g., Sn^{2+},[163] Co^{2+},[164]). These complexes may well be regarded as coordination complexes with the polyoxometalate functioning as a tetra- or pentadentate ligand. If the substituent metal cation is "octahedral" with a small terminal ligand, crystallographic disorder

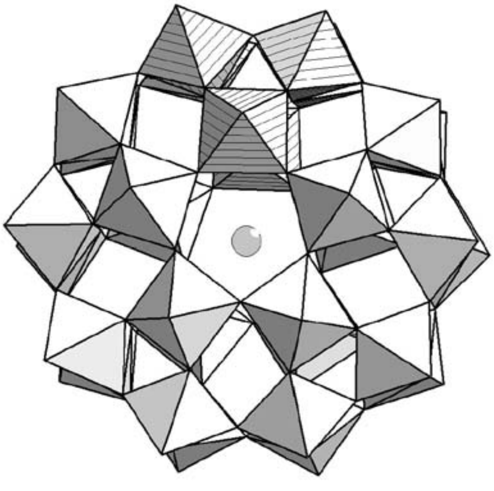

Figure 10 The "Preyssler" anion, $[Na(H_2O)P_5W_{30}O_{110}]^{14-}$. The central sphere locates the water molecule and eclipsed sodium cation.

Table 12 Some isolable lacunary anions derived from Keggin- and Wells–Dawson-type structures.

	Formula	*"Missing" octahedra*	*X*
1	α-$[XW_{11}O_{39}]^{n-}$	1	P, As, Si, Ge, B, Al, Ga, Fe^{III}, Co^{III}
2	β_1-$[XW_{11}O_{39}]^{n-}$	1	Si, Ge
3	β_2-$[XW_{11}O_{39}]^{n-}$	4	Si, Ge
4	β_3-$[XW_{11}O_{39}]^{n-}$	10	Si, Ge
5	γ-$[XW_{10}O_{36}]^{n-}$	1, 2	P, Si
6	A-α-$[XW_9O_{34}]^{n-}$	1, 2, 3	P, As, Si, Ge
7	A-β-$[XW_9O_{34}]^{n-}$	1, 2, 3	P, As, Si, Ge
8	B-α-$[XW_9O_{34}]^{n-}$	1, 4, 9	P
9	α_1-$[X_2W_{17}O_{61}]^{10-}$	4	P
10	α_2-$[X_2W_{17}O_{61}]^{10-}$	1	P, As
11	α_2-$[H_4XW_{17}O_{61}]^{11-}$	1	P, As
12	α-$[X_2W_{15}O_{56}]^{12-}$	1, 2, 3	P, As
13	α-$[X_2W_{12}O_{48}]^{14-}$	1, 4, 5, 10, 11, 16	P

generally prevents characterization by X-ray crystallography, but W-NMR has proved to be a reliable alternative.[165] By virtue of the reducibility of the addenda metal atoms adjacent to the substituent, the polyoxometalate exhibits properties commonly associated with pi-acceptor ligands.[166] Since the polyoxometalate ligands are fully oxidized, the potential exists for such complexes with the appropriate substituent metal center to act as particularly robust oxidation catalysts ("inorganic metalloporphyrins").

The divacant anions (5) can in principle be converted to complete γ-Keggin structure types, and this has been achieved with $[SiW_{10}O_{36}]^{8-}$ (the phosphate is less stable and has not yet been intensely investigated), yielding γ-$[SiW_{10}M_2O_{40}]$ (M = W,[114] Mo,[115] V (the last readily isomerizes to β anions),[167] Mn(III),[168], Fe(III),[169] and η^5-(C_5H_5)Ti). [170] Attempts to convert $[SiW_{10}O_{36}]^{8-}$ to γ-$[SiW_{12}O_{40}]^{4-}$ in aqueous solution lead to $[Si_2W_{23}O_{77}(OH)]^{9-}$, an anion with only C_s symmetry that incorporates both SiW_{10} and SiW_{11} fragments.[171] Chromium(III) derivatives with bridging hydroxo and acetate (formate) groups, $[SiW_{10}O_{36}\{(H_2O)Cr\text{-}\mu(OH)(OAc)_2\text{-}Cr(OH_2)\}]^{5-}$ are also known.[172] See Tables 25 and 27 for other complexes incorporating the SiW_{10} group.

The trivacant lacunary anions A-$[XW_9O_{34}]^{n-}$ and $[X_2W_{15}O_{56}]^{12-}$ have been used as precursor species for the formation of substituted plenary Keggin and Wells–Dawson anions; see Table 13. In some cases the resulting anions dimerize via oxo or hydroxo bridging between the substituent metal atoms. Examples include the Cr^{III} and Ti^{IV} derivatives; see Figure 11. A hexabromo derivative, β-$[PW_9O_{27}Br_6]^{3-}$, has been prepared as a tetrabutylammonium salt by reaction of PW_{11} and PW_9 precursors with $SOBr_2$.[173]

Several solid-state polyoxometalate structures that incorporate $PW_9M^{II}_3$ Keggin units (with edge-shared $M^{II}O_6$ octahedra, and thus formally derived from the A-PW_9O_{34} anion) have been described and their magnetic properties have been reported. These include $[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]^{7-}$,[194]

Table 13 Plenary structures derived from A-type trivacant lacunary anions.

	X	*M*	*References*
1,2,3-XW_9M_3	Si (α, β)	Cu, Mn, Ni^{II}; Al,Ga,Cr,Fe^{III}	174
	Si(α)	Cr^{III}	175
	Si(α)	Cr, Al (dimers)	176
	Ga	V	177
	Si(β)	Nb, Nb(dimer)	178
	Si(β) Ge(β)	Ti (dimer)	179–181
	Si(α, β)	$\{RSn\}^{3+}$	182
	P(α, β)	V, Mo	183–187
	Si(α, β)	$\{CpTi\}^{3+}$	170
1,2,3-XMo_9M_3	P	$\{BuSn\}^{3+}$	188
$X_2W_{15}M_3$	P	V	189,190
	P	Nb, Nb (dimer)	191,192
	P	$\{RSn\}^{3+}$	193

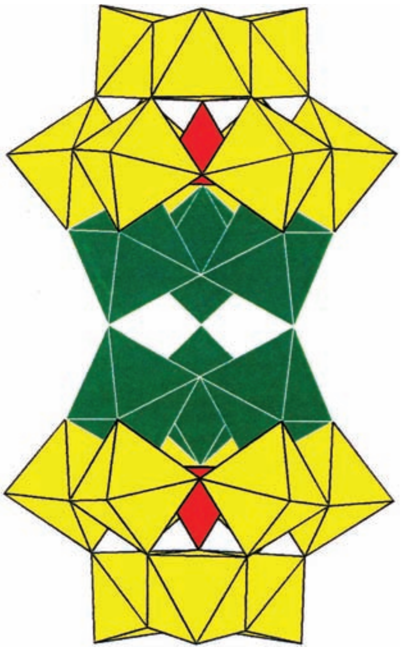

Figure 11 $[\{SiW_9O_{34}(OH)_3Cr_3\}_2(\mu\text{-}OH)_3]^{11-}$, i.e., all [Cr–O–Cr junctions are protonated.

$[PW_9O_{34}Ni_4(OH)_3(H_2O)_6]^{4-}$,[195] $[M_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$ (M = Ni, Co),[196] and $[Co_7(H_2O)_2(OH)_2(PW_9O_{34})_2(W_7O_{26})]^{16-}$.[197]

4.10.3.5 Sandwich-type Structures Based on Trivacant Lacunary Anions

A large number and variety of polytungstate complexes incorporate pairs of trivacant lacunary anions that sandwich three or four metal atoms. Three types of lacunary anions involved in such sandwich structures are shown in Figure 12.

4.10.3.5.1 *Derivatives of A-$[XW_9O_{34}]^{n-}$*

These complexes are generally prepared by direct reaction of the appropriate lacunary anion, in the form of a solid salt, with a solution containing the desired heteroatoms. The variety of heteroatoms that have been incorporated is summarized in Table 14. The first entry in the table is the long-known (1896) $[P_2W_{21}O_{71}]^{6-}$ anion, which was structurally characterized some 90 years later.[198] Lacunary versions, $[P_2W_{20}O_{70}]^{10-}$ and $[P_2W_{19}O_{69}]^{14-}$, in which one or two of the "sandwiched" tungsten atoms have been lost, have also been characterized[210,211] and these offer routes to numerous mixed (W_2M and WM_2) species. The equatorial M (or W) atoms have nominal octahedral or square-pyramidal coordination geometries, and the central cavity of the anion is normally occupied by H_2O or OH^- ligands. In the case of the W_{21} anion, one of the internal ligands is an oxo group. The Pd and Cu derivatives have been shown to incorporate NO_3^- or trigonally disordered NO_2^- in the internal cavity, if such anions are present in the synthesis solutions.[200]

4.10.3.5.2 *Derivatives of B-$[XW_9O_{34}]^{n-}$ and $[X_2W_{15}O_{56}]^{n-}$*

The divalent metal derivatives of the A-type sandwich complexes (Table 14) are readily converted, e.g., by boiling aqueous solutions, to new sandwich species with the general formula $[(XW_9O_{34})_2M_4(H_2O)_2]^{n-}$ that incorporate B-type lacunary anions. The first example of this type of anion, with X = P and M = Co^{II}, had been reported in 1973[212], but the range of heteroatoms

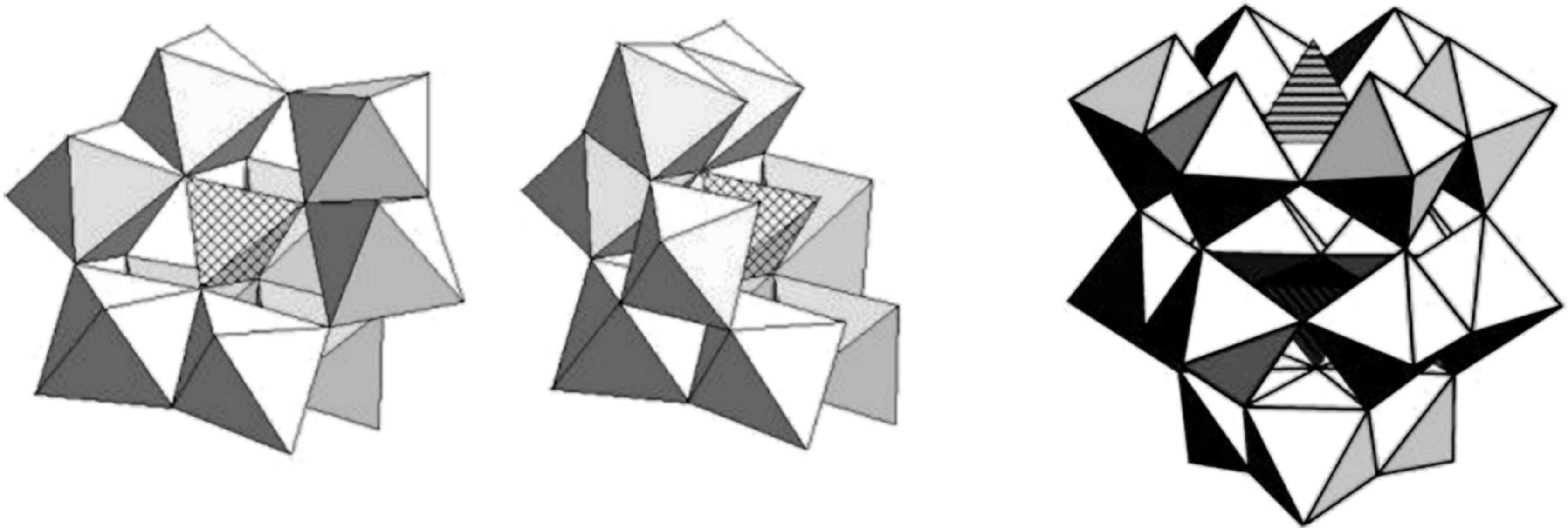

Figure 12 Trivacant α-Keggin (A- and B-type) and Wells–Dawson structures.

Table 14 Sandwich complexes derived from A-type trivacant lacunary anions.

	X	*M*[a]	*References*
$[(XW_9O_{34})_2M_3]^{n-}$	P, As	WO^{4+}	198
	P	$M^{II} = Mn, Fe, Co, Ni, Cu, Zn, Pd$	199,200
	P, Si	$\{Ce_3O_3\}^{6+}$, $\{Zr_3(OH)_3\}^{9+}$, $\{Ln_3O_3\}^{3+}$	200–203
	P, Si	$\{RSn\}^{3+}$ $\{RSi\}^{3+}$	182,199,204,205
	P, Si	Sn^{II}	206,207
$[(XMo_9O_{34})_2M_3]^{n-}$	P	$\{BuSn\}^{3+}$	188
$[(XW_9O_{34})_2M_2]^{n-}$	P, Si	UO_2^{2+}	208,209

[a] Unless specified otherwise the oxidation state of M is 2^+.

and oxidation states has since been extended; see Table 15. With the exception of the tungstophosphate, which has been identified as a component in a mixture resulting from thermolysis of the sodium salt of the A-PW_9 anion, none of the B-XW_9 groups incorporated in the complexes listed in Table 15 is known to exist as an independent anion, and the process by which the sandwich complexes are formed is unclear. Since many of these complexes contain isolated clusters of four adjacent transition-metal cations in octahedral coordination, their magnetic properties are of interest.[213–218] In 1991 Tourné reported a less symmetrical (chiral) variant of the sandwich structure in which one of the M-cations was a tungsten(VI) atom. The tungsten atom forms a more inert link between the two lacunary anion layers and makes it possible to exchange two (or all three) of the remaining M-cations to yield a variety of mixed anions: see Table 15.[219] Neumann has investigated the catalytic activity of several of these species for oxidations with dioxygen and hydrogen peroxide.[220–225]

A closely related series of sandwich complexes (also shown in Table 15) is formed with the anions derived from the Wells–Dawson structure, $[X_2W_{15}O_{56}]^{12-}$ (X = P, As), since these possess a lacunary surface identical to that of B-$[PW_9O_{34}]^{9-}$. Since the precursor lacunary anions are easily isolated, the synthesis of the sandwich complexes is straightforward. Although several Baker–Figgis-type isomeric possibilities exist for anions of this composition,[233] until recently all confirmed structures have been found to be identical. The exception is $[(P_2W_{15}O_{56})_2Fe^{III}{}_2Na_2(H_2O)_2]^{16-}$, which has a different connectivity of the lacunary components.[235]

4.10.3.5.3 *Derivatives of B-α-$[XW_9O_{33}]^{n-}$*

When the heteroatom X has a stereochemically active, unshared pair of electrons, a complete Keggin structure cannot be formed and the trivacant lacunary species must adopt a B-type structure. The As^{III} and Sb^{III} derivatives were first reported in 1930 and have been confirmed more recently.[238] Krebs has described the bismuth analogue and reported the structure of the

Table 15 Sandwich complexes derived from B-type trivacant lacunary anions.

	X	*M*[a]	*References*
$[(XW_9O_{34})_2M_4(H_2O)_2]^{n-}$	P, As	Co, Cu, Zn, Mn	212,214,226–228
	P	Fe^{III}	229
	Zn, Co^{II}	$\{WX_3\}$, $\{WZnM_2\}$(M = VO^{2+}, $Mn^{II,III}$, $Fe^{II,III}$, Co, Ni, Pd, Pt)	219,230
	Zn	$\{WZnRh^{III}{}_2\}$, $\{WZnRu^{III}{}_2\}$	222,225
	Si	Mn, Cu, Zn	231
	Cu^{II}, Fe^{III}	X	232
$[(X_2W_{15})_2M_4(H_2O)_2]^{n-}$	P	Co, Cu, Zn, Mn, Ni	213,217,227,233
	P	Fe^{III}	234
	P	$Fe^{III}{}_2Na_2$	235
	P	Al^{III}, Cd, Ga^{III}, Fe^{III}	236
	As	Zn, Cu, Co, Ni, Mn, Cd	237

[a] Unless specified otherwise the oxidation state of M is 2^+.

Table 16 Sandwich complexes derived from α-$[XW_9O_{33}]^{n-}$ units.

	X	*M*[a]	*References*
B-α-$[(XW_9O_{33})_2M_3]^{n-}$	As^{III}	WO^{4+}	241
	As^{III}, Sb^{III}	Cu, Zn	242,243
	Se^{IV}, Te^{IV}	Cu	243
	Sb^{III}, Bi^{III}	VO^{2+}	244,245
	Sb^{III}	U^{IV}, Mn	246,497
	Bi^{III}	Cu	247
	As^{III}	$\{(Hg^{I}_2)_2(WO)\}$	248
	Te^{IV}	Pd	230
	Se^{IV}	Cu	230
	As^{III}	$\{BuSn\}^{3+}$, $\{RSi\}^{3+}$	205
	Sb^{III}	$\{PhSn\}^{3+}$	249

[a] Unless specified otherwise the oxidation state of M is 2^+.

sodium salt of the antimonite, which reveals pairs of the lacunary anions sandwiching six sodium cations in an assembly of approximate D_{3h} symmetry.[239] The tendency of these XW_9 anions to form sandwich-type complexes with three divalent metals is pronounced, and the recognition of analogous structures based on the so-far-hypothetical Se^{IV} and Te^{IV} derivatives—see Table 16—suggests that this family of complexes will be further expanded. The all-tungsten version of this structure, $[As_2W_{21}O_{69}]^{6-}$, (or $[(AsW_9O_{33})_2(WO)_3(H_2O)]^{6-}$),[240,241] yields upon partial hydrolysis the lacunary As_2W_{20} and As_2W_{19} derivatives, in an analogous fashion to the $P^{V}{}_2W_{21}$ anion described in Section 3.4.1.[238,240]

As will be evident in Section 4.10.3.9 below, the $X^{III}W_9$ anions are found to be components of much larger, composite polyoxoanion assemblies.

4.10.3.5.4 Derivatives of B-β-$[XW_9O_{33}]^{n-}$

Under mildly acidic conditions the (α)-SbW_9 and BiW_9 anions react with excess tungstate to yield new complexes, originally formulated as "$[XW_{11}O_{38}H]^{8-}$"[250,251], but more recently shown to have the composition $[X_2W_{22}O_{74}(OH)_2]^{12-}$.[239,252] The sandwich nature of these anions is emphasized in Figure 13. Two of the four sandwiched tungsten atoms appear to have three terminal oxygen atoms, in violation of the so-called Lipscomb criterion,[253] but two of these are in fact OH groups. The XW_9 units are derived from a β-Keggin structure, i.e., with one group of three edge-shared WO_6 octahedra rotated by $\pi/3$. An unsupported, unprotonated β-XW_9 structure has not yet been identified, presumably because it too is "anti-Lipscomb". It is relatively straightforward to replace the two external, $WO_2(OH)$, tungstens with di- and trivalent metal cations; see Table 17. As shown in that table, the structural type has recently been extended to incorporate Te^{IV} as the central atom of the lacunary fragments, and to involve replacement of all four sandwiched tungstens with divalent cations.

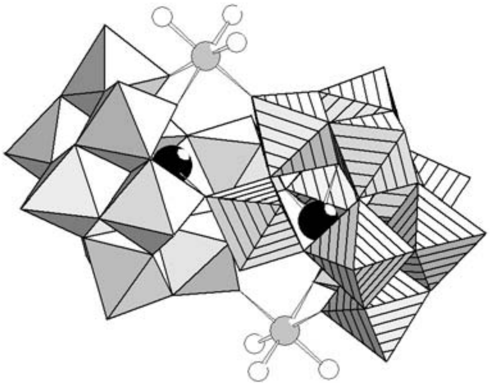

Figure 13 The structure of $[X_2W_{22}O_{74}(OH)_2]^{12-}$. Two (or all four) of the sandwiched tungsten atoms can be replaced by other metal cations; see Table 17.

Table 17 Sandwich complexes derived from β-$[XW_9O_{33}]^{n-}$ units.

	X	*M*	*References*
$[(\beta\text{-}XW_9O_{33})_2(WO_2)_2M_2]^{n-}$	Sb, Bi	$\{WO_2(OH)\}^{+}\}$, Fe^{III}, Co^{II}, Zn	239,252,254
	Sb, Bi	Sn^{II}	255
	Bi	$\{WO_2(OH)\}^{+}\}$, Ni^{II}, Mn^{II}	256,497
	Bi	Cu	247
	Te^{IV}	$\{WO_2(OH)\}^{+}\}$, Zn	257
$[(\beta\text{-}XW_9O_{33})_2M_4]^{n-}$	Te^{IV}	Mn^{II}, Co^{II}	257,497
	Bi	Cu	247

4.10.3.6 Augmented Versions of B-α-$[XW_9O_{33}]^{n-}$:XW_{18} Anions

The anion $[H_2AsW_{18}O_{60}]^{7-}$, first prepared and structurally characterized several years ago (1979) by Jeannin,[258] has the structure shown in Figure 14(a). Subsequently, other examples of this class of structures have been reported, some with the isomeric (b) structure; see Table 18. In much the same way that the Wells–Dawson structure may be considered to be formed by fusion of two A-$[PW_9O_{34}]^{9-}$, the structures shown in Figure 14 are based upon fusion of two B-$[XW_9O_{33}]^{9-}$ groups. However, the presence of a lone pair on X requires that the second X-site is vacant, and is probably occupied by two or three protons (compare with the metatungstate structures (Table 3)). When the syntheses are carried out in the presence of divalent metal cations (Mn, Co, Ni, Cu, Zn), the Sb- and Bi-centered anions incorporate an additional heteroatom in place of a tungsten, e.g., $[H_3SbW_{17}Co(H_2O)O_{59}]^{8-}$. The heteroatom is believed to occupy one of the "belt" tungsten sites.[259]

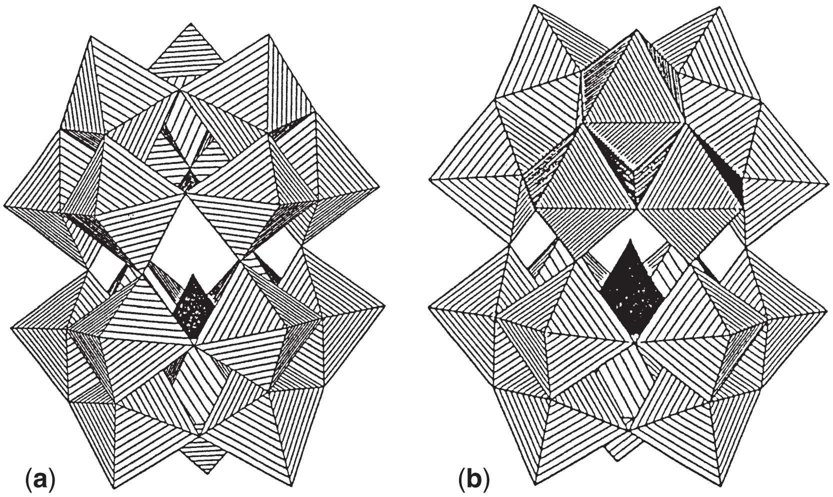

Figure 14 (a) Staggered, and (b) eclipsed forms of $[H_2X^{III}W_{18}O_{60}]^{7-}$ (reproduced by permission of Kluwer Academic Press from Krebs, B.; Klein, R. *Mol. Eng.* **1993**, *3*, 43–59).

Table 18 $[H_pXW_{18}O_{60}]^{n-}$ anions.

X	*p*	*Structure type*	*References*
As^{III}	2	A	258
Sb^{III}	2	B	254
Bi^{III}	3, 2	B	260,261
Sn^{II}	3	A & B	255
Te^{IV}	?	?	262

4.10.3.7 Other Heteropolyanions with Tetrahedrally-coordinated Heteroatoms

4.10.3.7.1 Tungstophosphates

The existence of well-defined tungstophosphate complexes with W/P ratios of 2:1, 3:1, and 3.5:1 has long been indicated in the early literature. More recently, these species have been further characterized by crystallographic and spectroscopic methods: see Table 19. All of the anions were isolated as sodium salts from relatively concentrated solutions, acidified to pH ~ 6 with acetic acid. The exact conditions required for the isolation of each specific complex do not appear to have been established.

No solution chemistry of $[P_4W_8O_{40}]^{12-}$ has been reported, but W- and P-NMR spectra of the other two anions are consistent with the structures revealed by crystallography. The structure of the anion in crystals of $Na_{20}[P_6W_{18}O_{79}].xH_2O$ ($x = 12, 32, 41$) reported by Fuchs and Palm[264] is identical to that found in $Na_{14}H_6[P_6W_{18}O_{79}].37.5H_2O$ by Acerete *et al.*[265] and is not an isomeric version as previously supposed. The P_6W_{18} anion has a pronounced chiral (C_2) structure, based on two $\{PW_8O_{33}\}$ groups that are derived from an A-type β-$[PW_9O_{34}]^{9-}$ anion by loss of a WO_6 octahedron from the edge-shared W_3O_{13} triad in the latter. The two PW_8 groups are linked though pairs of additional (nonequivalent, one μ_3 and one μ_4) PO_4 tetrahedra to a central pair of corner-shared WO_6 octahedra. In the presence of L-lysine hydrochloride the three P-31 NMR lines are each split into doublets, indicating that racemization of the enantiomers is slow on the NMR timescale. A lacunary version of this structure, $[P_5W_{18}O_{78}H_3]^{20-}$, in which one of the linking phosphate groups is missing, has been structurally characterized by Fuchs.[264] Simultaneous reports of the structure of $[P_4W_{14}O_{58}]^{12-}$ appeared in 1988.[264,266] This structure is also based upon a lacunary derivative of the A-β-$[PW_9O_{34}]^{9-}$ anion; two PW_7O_{29} units are linked by two PO_4 tetrahedra into an assembly of C_{2h} symmetry. In addition to P- and W-NMR, the Raman and infrared spectra have been recorded.[266]

4.10.3.7.2 Anions with diphosphate hetero groups

The diphosphate anion and its hydrolytically inert analogue methylene diphosphonate, $[[O_3PCH_2PO_3]^{4-}$, have been incorporated into polymolybdate and polytungstate structures. The anions $[(O_3PXPO_3)_4W_{12}O_{36}]^{16-}$ ($X = O, CH_2$)[267] have a folded cyclic structure of linked WO_6 octahedra, stapled into shape by external diphosphate groups (Figure 15). The polymetalate core of this structure is analogous to that observed in the molybdosquarate complex, $[Mo_{12}O_{36}(C_4O_4H)_4]^{4-}$, reported by Zubieta.[268] The polytungstates have been shown to inhibit HIV-1 Reverse Transcriptase, probably by blocking the DNA-binding cleft of the enzyme.[269] The molybdates $[(O_3PXPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ have an unsymmetrical structure in which one PO_3 group is centered in a ring of six corner- and edge-shared MoO_6 octahedra (Figure 16).[270,271] It has been proposed that this complex is an intermediate in the molybdate-catalyzed hydrolysis of $[P_2O_7]^{4-}$. In aqueous–organic solvents, Hori *et al.* reported that the diphosphate anion reacts with molybdate to yield yellow, electrochemically active $(P_2)Mo_{18}$, $(P_2)Mo_{15}$, and $(P_2)Mo_{12}$ complexes.[272–274] The first of these was subsequently shown to have a structure based on fusion of two B-type $[PMo_9O_{34}]$ units, i.e., $[P_2Mo_{18}O_{61}]^{4-}$ containing an internal $[P_2O_7]^{4-}$ group with enforced D_{3h} symmetry.[275] The anion formulated by Hori *et al.* as $[H_6(P_2O_7)Mo_{15}O_{48}]^{4-}$ has been shown to be a dimer of the proposed lacunary anion, i.e., $[(P_2O_7)_2Mo_{30}O_{90}]^{8-}$ (Figure 17) in the solid state.[276]

4.10.3.7.3 $[As^{III}{}_2Mo_{12}O_{42}]^{6-}$ and related anions

Acidic solutions of As^{III} and molybdate yield yellow crystals containing the anion $[As_2Mo_{12}O_{42}]^{6-}$.[277] The same anion, formulated as an $AsMo_6$ species, had probably been isolated

Table 19 Tungstophosphate complexes with high phosphorus content.

W/P	*Formula*	*Anion symmetry*	*References*
2	$[P_4W_8O_{40}]^{12-}$	C_{2v}	263
3	$[P_6W_{18}O_{79}]^{20-}$	C_2	264,265
3.5	$[P_4W_{14}O_{58}]^{12-}$	C_{2h}	264,266

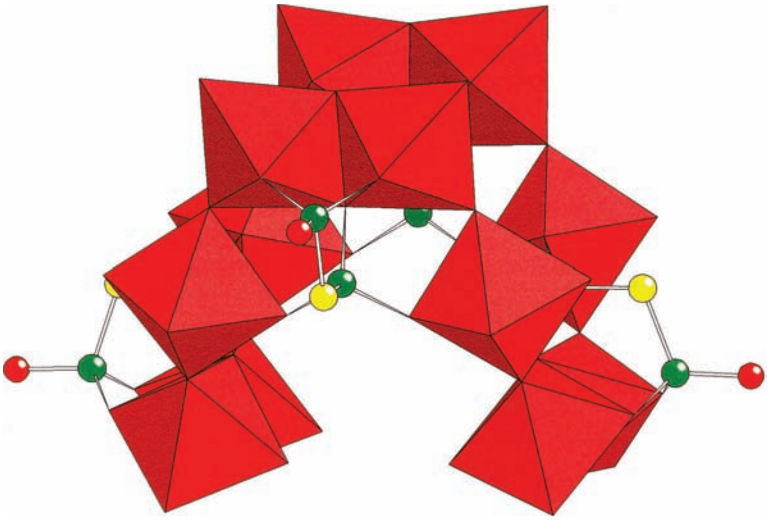

Figure 15 $[(O_3PXPO_3)_4W_{12}O_{36}]^{16-}$ (X = O, CH_2).

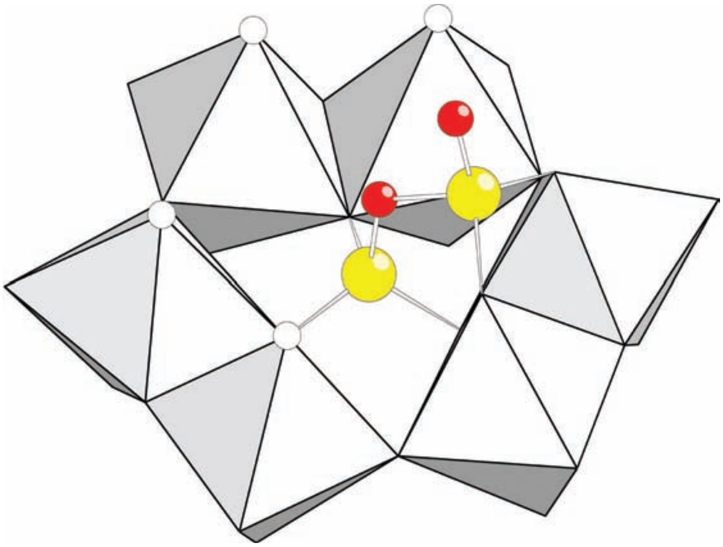

Figure 16 $[(O_3PXPO_3)Mo_6O_{18}(H_2O)_4]^{4-}$ (X = O, CH_2).

some 70 years earlier by Rosenheim. Although appearing to have some symmetry, e.g., three slabs of four edge-shared MoO_6 octahedra linked by vertices, the anion structure (Figure 18) possesses no symmetry element other than the identity. The molybdophosphite anion $[(HP)_2Mo_{12}O_{42}]^{4-}$, first reported by Rosenheim and later investigated by Hori *et al.*[278], and $[Se_2Mo_{12}O_{42}]^{4-}$ and $[Te_2Mo_{12}O_{42}]^{4-}$,[279] may prove to be isostructural with the molybdoarsenite.

4.10.3.8 Anderson and related (small) polyoxometalates

Apart from several new structure determinations (Table 20), the chemistry of polyoxoanions incorporating rings of five and six MO_6 octahedra, $[(XO_3)_2M_5O_{15}]^{n-}$, $[(XO_3)_2M_6O_{18}]^{n-}$, $[(XO_6)M_6O_{18}]^{n-}$, and $[\{X(OH)_6\}M_6O_{18}]^{n-}$, has not developed significantly since about 1980. The majority of these complexes are relatively labile molybdates, and the hexamolybdo anions are occasionally isolated in nonplanar protonated forms.

Bi-capped versions of the Anderson structure are found with $[(As^{III}{}_3O_3)_2(Co^{II}Mo_6O_{24})]^{4-}$[307] and $[H_xXMo_6O_{18}\{RC(CH_2O)_3\}_2]^{(6-m-x)-}$ ($X^{m+} = Fe^{3+}, Ni^{2+}, Zn^{2+}$).[308] The arsenite complex was isolated from a reaction between $Co(H_2O)_6{}^{2+}$ and $[As^{III}{}_3Mo_3O_{15}]^{3-}$, an anion that was probably first reported in the nineteenth century. The structure of the latter and its tungstate analogue, of

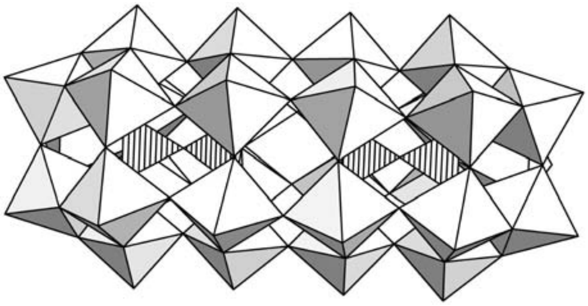

Figure 17 $[(P_2O_7)_2Mo_{30}O_{90}]^{8-}$.

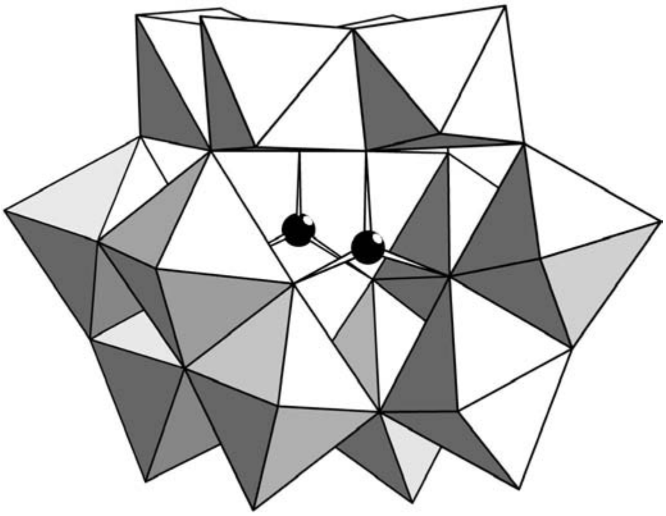

Figure 18 $[As_2Mo_{12}O_{42}]^{6-}$.

Table 20 Recent structure determinations of penta- and hexametalate heteropolyanions.

Formula	*X*	*References*
$[X_2Mo_5O_{15}]^{4-}$	$HOPO_3$	280
	HPO_3	281
	RPO_3	282–284
	$RAsO_3$	285
	OSO_3	286–288
	SeO_3	289
$[XMo_6O_{18}]^{n-}$	$Cu(OH)_6$	290
	$Al(OH)_6$	291
	$Co^{III}(OH)_6$	292–294
	$In^{III}(OH)_6$	295
	$Pt^{IV}O_6$[a]	296–298
	Sb^VO_6[b]	299
$[XW_6O_{18}]^{n-}$	$Mn^{IV}O_6$	300
	$Pt^{IV}O_6$	301,302
	Sb^VO_6[b]	303
	Te^{VI}	304
$[X_2Mo_6O_{25}H]^{5-}$	$RAsO_3$	305
$[X_2W_6O_{25}H]^{5-}$	$RAsO_3$	306

[a] Both D_{3d} (Anderson) and C_{2v} (heptamolybdate) structures have been observed. [b] The molybdate has the C_{2v} structure and the tungstate has the Anderson (D_{3d}) structure.

approximate C_s symmetry, incorporates a trigonal assembly of three edge-shared MO_6 octahedra to which is attached a "linear" As_3O_4 group.[307]

The ring of six edge- and corner-shared MoO_6 octahedra observed in the diphosphate complexes, described in the previous section, has also been found recently in an extensive class of amino-acid derivatives $[XMo_6O_{21}(O_2CC(R)NH_3)_3]^{2,3-}$ ($X = As^{III}$, Sb^{III}, Bi^{III}, Se^{IV}, Te^{IV}).[309]

4.10.3.9 Lanthanide and Actinide Heteroatoms

Polyoxometalates incorporating lanthanide (Ln) and actinide (An) heteroatoms were, by about 1980, represented by (i) $[LnL_2]^{n-}$ complexes (L = monovacant lacunary anion, $[W_5O_{18}]^{6-}$, $[XM_{11}O_{39}]^{n-}$, and α_2-$[X_2M_{17}O_{61}]^{n-}$; M = Mo, W) that were initially characterized by Weakley; and (ii) the dodecamolybometalates $[(Ln/An)^{IV}Mo_{12}O_{42}]^{8-}$. In the Weakley-type complexes, the Ln (and subsequently, An^{IV}) heteroatoms adopt an approximately square-antiprism coordination geometry, whereas the heteroatoms in the dodecamolybdates have approximate icosahedral coordination (Figure 19).

In the last two decades, since about 1980, there has been an explosion of papers on these and other lanthanide/actinide polyoxometalates driven by several interests, e.g., radioactive-waste teatment, luminescence and emission, and other solid-state properties.

The Weakley complexes (i) can be viewed as 1:2 coordination complexes of tetradentate lacunary anion ligands. Structural investigations of the decatungstometalates are summarized in Table 21, and the paramagnetic shifts of tungsten NMR lines have been recorded for several of these complexes.[310] Since about 1990 the variety of monovacant lacunary anion ligands in such complexes has been extended; see Table 22. Some conditional formation constants have been determined, (Table 23) and the 1:1 complexes, $[Ln(L)(H_2O)_x]^{n-}$, where L is a Keggin- or Wells–Dawson-derived lacunary anion, have been characterized in solution by electrochemistry[348] and by NMR spectroscopy[349–351]; the number of coordinated water molecules, x, has been determined by luminescence-lifetime measurements[345,351,352]. The 1:1 complexes are prone to association in solution[353] and yield dimeric anions or extended chain structures upon crystallization (Figure 20).[349,354] Tungsten-NMR investigations of the 1:2 complexes of the Keggin- and Wells–Dawson-derived lacunary anions which have molecular C_2 point symmetry in the solid state reveal that ligand rotation occurs in solution to introduce additional mirror symmetry. The rotation is restricted for complexes of the smaller lanthanides[355] and for complexes of the α_1 isomer of $[P_2W_{17}O_{61}]^{10-}$.[341] Ligand-exchange reactions have been observed, leading to mixed-ligand complexes such as $[U(PW_{11}O_{39})(P_2W_{17}O_{61})]^{13-}$, $[U(\alpha_1\text{-}P_2W_{17}O_{61})(\alpha_2\text{-}P_2W_{17}O_{61})]^{16-}$, and $[Eu(BW_{11}O_{39})(W_5O_{18})]^{10-}$.[356–358]

Studies of the interaction of lanthanide cations with multivacant lacunary tungstates have shown that a variety of "composite" polyoxoanions are formed. There is currently no end in sight to the range of compositions and structures possible. Although fairly simple sandwich complexes are formed (Table 14) with A-$[XW_9O_{34}]^{n-}$, more elaborate assemblies have been produced, especially from precursors such as B-$[X^{III}W_9O_{33}]^{9-}$, or directly from the components, e.g., AsO_3^{3-},WO_4^{2-}, and Ln^{3+}. Table 24 lists some structurally characterized behemoths that have been shown to possess solution integrity by NMR spectroscopy.

The incorporation of the uranyl cation UO_2^{2+} into polytungstate structures has recently been investigated. In all cases so far reported (Table 25), the uranium atoms adopt a pentagonal-bipyramidal coordination geometry.

Apart from some Weakley-type complexes (Table 22), there has been little systematic investigation of lanthanide–molybdate complexes. Multinuclear NMR studies of solutions of the well-established dodecamolybdates $[M^{IV}Mo_{12}O_{42}]^{8-}$ (M = Ce, U), with a range of di- and trivalent transition-metal and lanthanide cations, show the formation of complexes incorporating two metal cations. In most cases these complexes are labile on the NMR timescale.[368–370]

Several examples of anions with the stoichiometry Ln:Mo = 4:29 have been reported. The structures reveal an assembly of four heptamolybdate anions bridged to a central MoO_4^{2-} group by the lanthanide cations, i.e., $[Ln_4(H_2O)_{16}(MoO_4)(Mo_7O_{24})_4]^{14-}$ (Figure 27).[371–374] It is unclear whether this assembly survives in solution.

4.10.4.10 Peroxo, Fluoro, and Thio Derivatives

Peroxo derivatives of polymolybdates and polytungstates were reviewed in 1994.[375] The solution chemistry of isopolyoxo(peroxo)molybdates and -tungstates has recently been investigated by ^{17}O

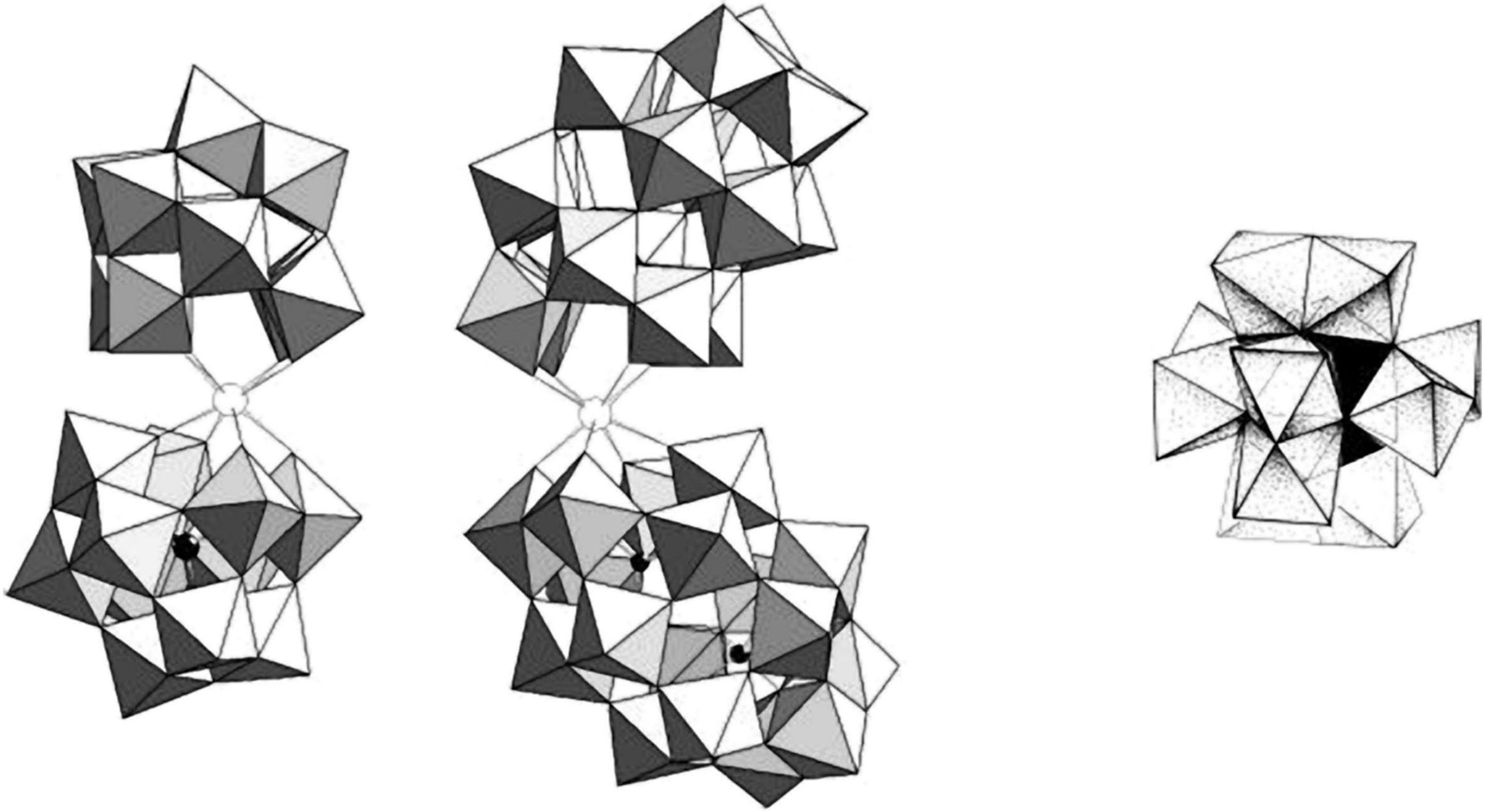

Figure 19 (a) Weakley-type $[\mathrm{LnL_2}]^{n-}$ complexes; (b) $[\mathrm{X^{IV}Mo_{12}O_{42}}]^{8-}$.

Table 21 Decatungstolanthanates and -actinates.

Formula	*Heteroatom*	*References*
$[Ln(W_5O_{19})_2]^{9-}$	Ln^{III} = Pr, Nd, Sm, Eu, Gd, Tb, Dy	311–319
$[An(W_5O_{19})_2]^{8-}$	An^{IV} = Np, Th	320,321

Table 22 Recent examples of Weakley-type polyoxometalate complexes, $[(Ln,An)L_2]^{n-}$.

L	*X*		*References*
$[X^{x+}\ Mo_{11}O_{39}]^{(12-n)-}$	P^V, As^V, Si	Ln^{III}	322–325
α-$[X^{x+}\ W_{11}O_{39}]^{(12-n)-}$	P^V, As^V, Si, Ge^{IV}, Ti^{IV}(?), Zr^{IV}(?), Mn(?), B, Ga^{III}, Cu^{II}	Ln^{III}	326–335
β_n-$[SiW_{11}O_{39}]^{8-}$		Ln^{III}	331,332
α_2-$[X_2M_{17}O_{61}]^{10-}$	P (Mo, W), As (W)	Ln^{III}	336–341
α_1-$[P_2W_{17}O_{61}]^{10-}$		Ln^{III}, Th^{IV}, U^{IV}	341
β-$[P_2W_{17}O_{61}]^{10-}$		Ln^{III}	342

Table 23 Formation constants for $[(Ln,An)L_x]^{n-}$ ($x = 1, 2$).

	log β_1	*log β_2*	*Medium*	*References*
$[PW_{11}O_{39}]^{7-}$				
Ce^{III}	6.2 ± 0.2	10.2 ± 0.2	?	343
	8.7	15.4	1 M $LiNO_3$	344
Ce^{IV}	22.9	33.5	1 M $LiNO_3$	344
$[SiW_{11}O_{39}]^{8-}$				
Ce^{III}	9.4	15.8	1 M $LiNO_3$	344
Ce^{IV}	24.6	35.0	1 M $LiNO_3$	344
α_1-$[P_2W_{17}O_{61}]^{10-}$				
Ce^{III}	6.6	8.1	1 M $LiNO_3$	344
Ce^{IV}	21.7	27.9	1 M $LiNO_3$	344
α_2-$[P_2W_{17}O_{61}]^{10-}$				
Ce^{III}	8.8	14.8	1 M $LiNO_3$	344
	1.74 ± 0.05	0.3 ± 0.5	1 M HNO_3	344
Nd^{III}	1.54		2 M HNO_3	345
Am^{III}		5.4	1 M HNO_3	346
	1.9	3	2 M HNO_3	345
Ce^{IV}	23.1	33.6	1 M $LiNO_3$	344
	15.1 ± 0.3	19.6 ± 0.3	1 M HNO_3	344
U^{IV}	7	11.4	2 M HNO_3	345
Np^{IV}	≥ 7		2 M HNO_3	345
Pu^{IV}	≥ 8	≥ 13	2 M HNO_3	345
Am^{IV}		32	pH 0.5–6.0	346
		9	1 M HNO_3	347
Am^{V}		6	pH 0.5–6.0	346

NMR spectroscopy and electrospray mass spectrometry.[376] Other research in this area has focused mainly on the catalytic activities of the Venturello anion, $[PO_4\{WO(O_2)_2\}_2]^{3-}$,[377] and complexes that are structurally related to this. These and other peroxo-containing heteropolyanions that have been reported recently are summarized in Table 26.

Polyoxotungstates in which internal oxygen atoms of Keggin and Wells–Dawson structures had been replaced by one or more fluorines were first described by Chauveau and by Baker in the 1970s. In 1990, Baker *et al.*[391] showed that the hexafluoro-substituted Wells–Dawson anion contained a nonexchangeable sodium cation at the center of the structure (trigonal prismatic NaF_6 coordination site); a proton is incorporated in each of the two OF_3 central tetrahedra, $[(HOF_3)_2NaW_{18}O_{56}]^{7-}$. Several transition-metal-substituted versions of this anion have been

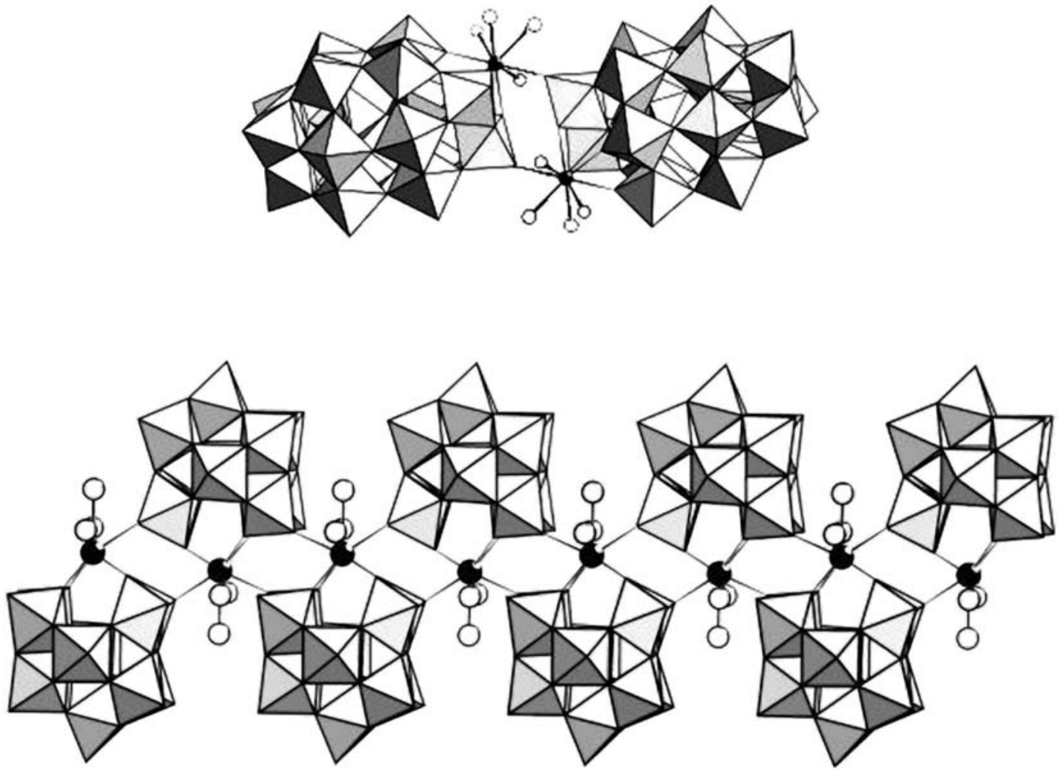

Figure 20 Association of 1:1 Weakley complexes: $[\{Ce(H_2O)_4(\alpha_2\text{-}P_2W_{17}O_{61})\}_2]^{14-}$ and $\{[Ce(H_2O)_3(\alpha\text{-}SiW_{11}O_{39})]^{5-}\}_\infty$.

Table 24 Examples of large polyoxometalate–lanthanide complexes.

Formula		*Molar mass*	*References*
$[Ln_2(H_2O)_2(SbW_9O_{33})(W_5O_{18})_2]^{15-}$ (Ln = Y, Sm, Er)		5,056	359
$[\{Ln_3O(OH)_3(H_2O)_3\}_2Al_2(Nb_6O_{19})_5]^{26-}$ (Ln = Eu, Er, Lu)		5,531	360,361
$[Ce_3(CO_3)(SbW_9O_{33})(W_5O_{18})_3]^{20-}$		6,406	362
$[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$	Figure 21	6,436	363
$[Ce_2(H_2O)_7(WO_2)_2(AsW_9O_{33})_3]^{17-}$		7,611	364
$[Ce_4(OH)_2(H_2O)_9(P_2W_{16}O_{59})_2]^{14-}$	Figure 22	8,652	365
$[Y_8(PW_{10}O_{37})_4(W_3O_{18})]^{30-}$		8,997	354
$[Ln(Ln_2OH)(H_2O)_{11}(WO_2)_4(AsW_9O_{33})_4]^{20-}$ (Ln = Ce, Nd, Sm, Gd)		10,529	366
$[Ln_{16}(H_2O)_{36}(WO_2)_4(W_2O_6)_8(AsW_9O_{33})_{12}(W_5O_{18})_4]^{76-}$ (Ln = Ce, La)	Figure 23	39,383	367

Table 25 Some polyoxotungstates incorporating uranyl heterogroups.

Formula		*References*
$[(UO_2)_2(XW_9O_{34})_2]^{n-}$ (X = P, Si)	Figure 24	208,209
$[(UO_2)_3(AsW_9O_{33})_3(W_3O_6)(H_2O)_6]^{15-}$	Figure 25	491
$[(UO_2)_3(H_2O)_3(AsW_9O_{33})(AsW_8O_{30})_2\{WO(H_2O)\}]^{17-}$		209
$[\{M(OH_2)\}_4(UO_2)_4(OH)_2(\gamma\text{-}SiW_{10}O_{36})_4]^{22-}$ (M = Na, K)	Figure 26	209
$[Na(UO_2)_3(OH)(H_2O)_6(As_4W_{40}O_{140})(WO)]^{18-}$		209

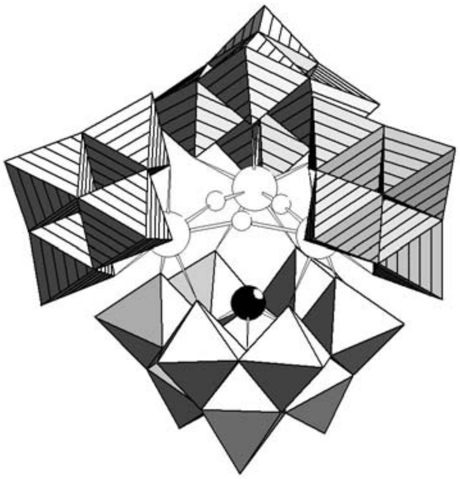

Figure 21 $[Eu_3(H_2O)_3(SbW_9O_{33})(W_5O_{18})_3]^{18-}$.

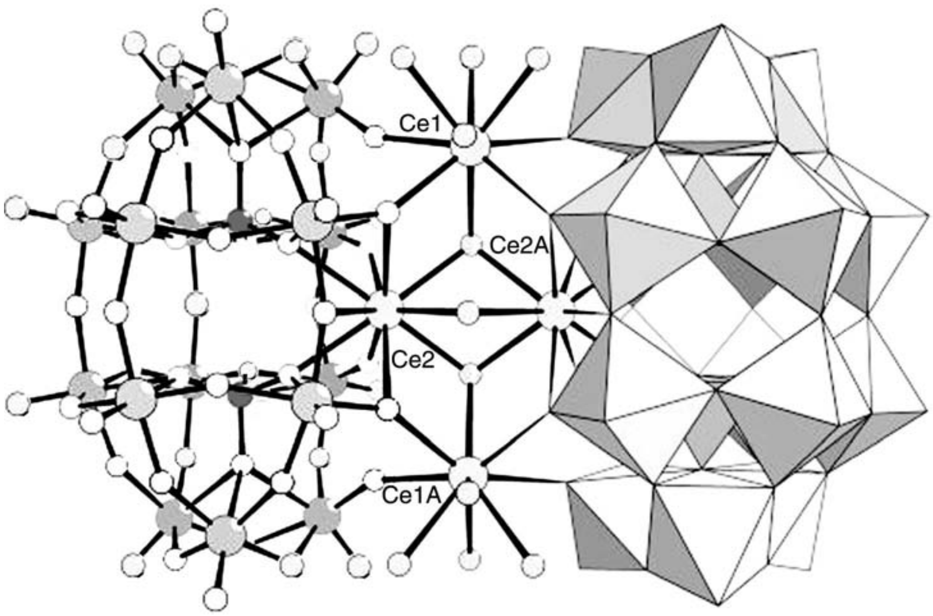

Figure 22 $[Ce_4(OH)_2(H_2O)_9(P_2W_{16}O_{59})_2]^{14-}$.

reported by different groups.[392–398] Unequivocal structural characterization (location of the substituent atom) of these complexes is denied by crystallographic disorder and (especially for corresponding substituted Keggin anions) nonseparable mixtures of complexes with different numbers of fluorines.[399] Terminal fluoro ligands are found in the complexes $[SiW_{11}O_{39}(MF)]^{5-}$ (M = Zr, Hf).[400]

Systematic investigation of polyoxo(thio)metalates has followed two routes. The first involves incorporation of thiometal groups into lacunary anions. Examples are $[PW_{11}O_{39}(MX)]^{4-}$ (M = Nb, Ta; X = S, Se)[401,402], γ-$[SiW_{10}O_{38}M_2S_2]^{6-}$ (M = Mo, W), $[(PW_{11}O_{39})_2\ (Mo_2S_2(OH)_2O_2)]^{10-}$, $[(PW_9O_{34})_2\{Mo_2S_2(OH)_2O_2\}_3]^{10-}$,[403] and $[(SiW_{11}O_{39})_2\ \{Mo_3S_4(H_2O)_3(OH)\}_2]^{10-}$.[404] The second route involves condensation reactions incorporating the $[M^V{}_2S_2O_2]^{2+}$ (M = Mo, W) building block. The latter process leads to a variety of cyclic structures that are templated by oxoanions and carboxylates.[403,405–408]

4.10.4 REDUCTION: HETEROPOLY BLUES AND BROWNS

The reducibility of type-I polyoxometalates, notably the Keggin, Wells–Dawson, and Lindqvist (hexametalate) structures, to mixed-valence heteropoly blues was well established in the 1960s and

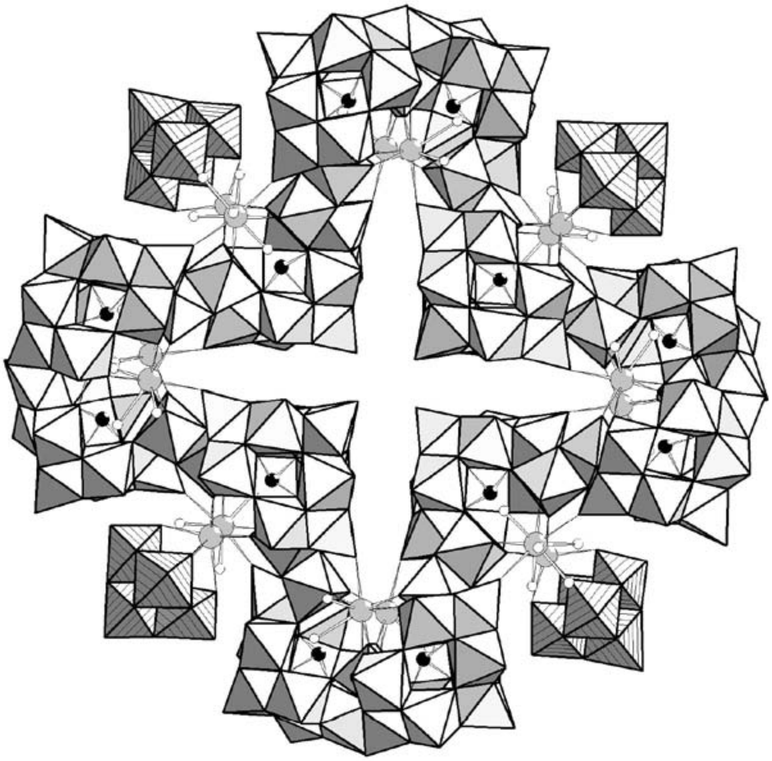

Figure 23 $[Ln_{16}(H_2O)_{36}(WO_2)_4(W_2O_6)_8(AsW_9O_{33})_{12}(W_5O_{18})_4]^{76-}$.

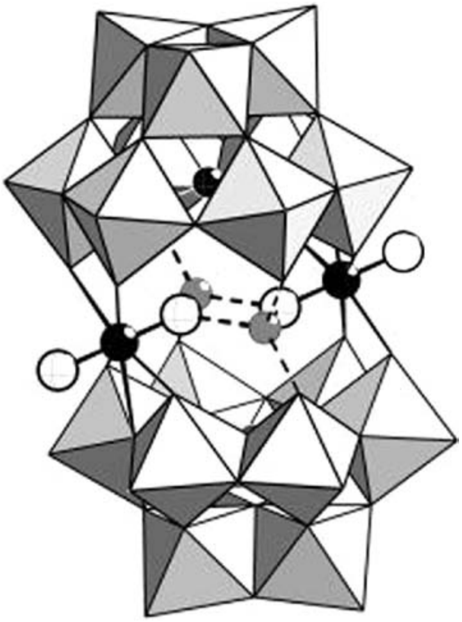

Figure 24 $[Na_2(UO_2)_2(SiW_9O_{34})_2]^{14-}$. The incorporated sodium cations are shown as gray spheres.

1970s. Investigation of the one-electron reduced anions by ESR spectroscopy showed that these species could be viewed as Robin–Day Class II mixed-valence systems with a "hopping" electron becoming trapped on a single metal center at low temperatures.[409] The short residence time of the electron on a particular metal site at room temperature leads to well-resolved ^{31}P- and ^{17}O-NMR spectra from which the rates of intra- and intermolecular electron transfer were estimated and, for

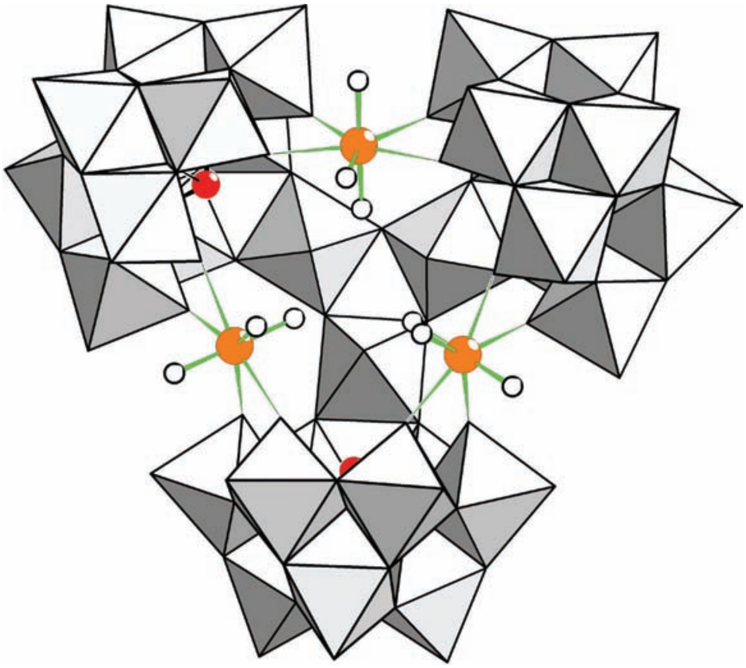

Figure 25 $[(UO_2)_3(AsW_9O_{33})_3(W_3O_6)(H_2O)_6]^{15-}$.

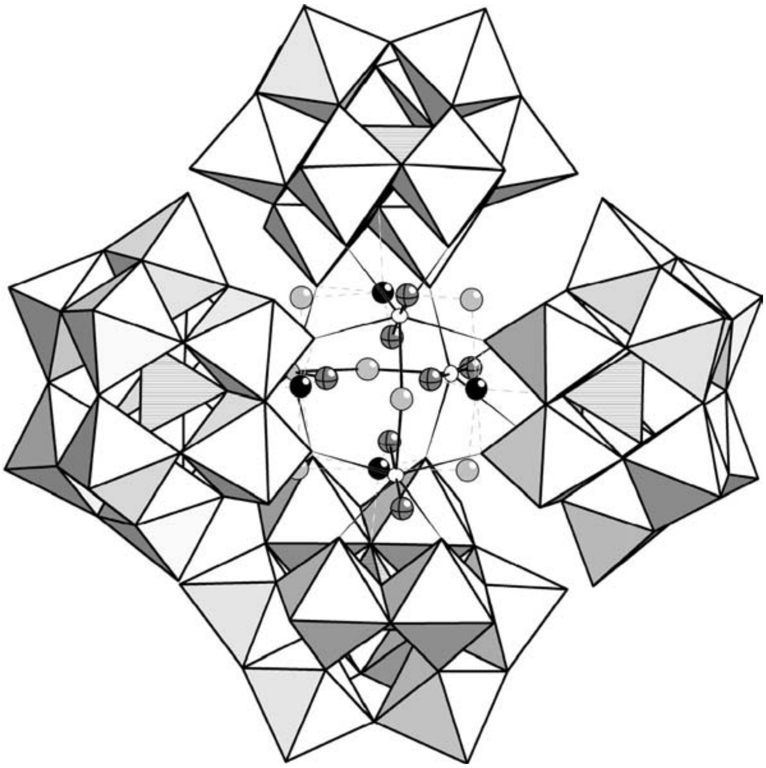

Figure 26 $[\{M(OH_2)\}_4(UO_2)_4(OH)_2(\gamma\text{-SiW}_{10}O_{36})_4]^{22-}$.

$[PW_{12}O_{40}]^{3/4-}$, compared with Marcus-theory predictions.[410–414] With the use of mixed-metal polytungstates such as 1,4,9-$[PW_9V^{IV,V,V}{}_3O_{40}]^{7-}$, the number of sites with which the unpaired electron can interact is limited, and a detailed understanding of the factors affecting activation energies has been determined from variable-temperature ESR studies.[189,415–420] The general area of

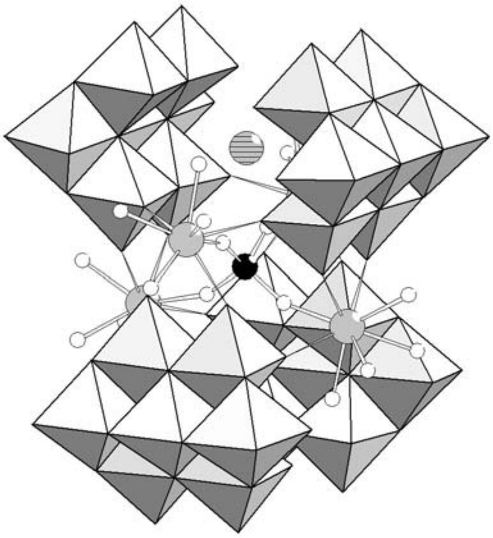

Figure 27 $[Ln_4(H_2O)_{16}(MoO_4)(Mo_7O_{24})_4]^{14-}$.

homogeneous electron transfer between polyoxometalates has been comprehensively reviewed,[421] and the consequences of ion pairing upon electron-transfer rates have been examined.[422]

The two-electron reduced anions are diamagnetic as a result of multipath antiferromagnetic coupling and are therefore ESR-silent, permitting observation of W-NMR spectra from which the time-averaged distribution of the "blue" electrons can be inferred.[423] Circulation of the pairs of blue electrons over the polyanion structures give rise to increased diamagnetic susceptibilities that are attributed to ring currents.[424] The magnetic properties of the one- and two-electron blues of Keggin and Wells–Dawson anions that contain paramagnetic ions in the central site and/or in one of the tungsten sites have been investigated, and these show a complicated variation in antiferromagnetic behavior.[425,426]

Earlier electrochemical investigations had shown that reductions can proceed beyond the two-electron stage; a recent example is the behavior of $[S_2Mo_{18}O_{62}]^{4-}$ which, like other molybdates, can be reduced by up to six electrons.[141,427–430] Density functional theory calculations have been reported for Keggin anions treated as clathrates of XO_4^{n-} in a neutral $M_{12}O_{36}$ shell; these provide satisfactory explanations for the relative stabilities of the α- and β-structures (see Table 8) and for the first reduction steps of 2, 2, and 2 electrons.[109,431] Several structure determinations of heteropoly blues have now been reported but, as expected, none can unambiguously locate the

Table 26 Polyoxo(peroxo)metalates.[a]

Formula	*References*
$[PO_4\{WO(O_2)_2\}_4]^{3-}$	377
$[HPO_4\{WO(O_2)_2\}_2]^{2-}$	378
$[PO_4\{VO(O_2)_2\}_4]^{7-}$	379
$[(PhPO_3)\{MoO(O_2)_2\}_2\{MoO(O_2)_2(H_2O)\}]^{2-}$	380
$[Ph_2PO_2\{WO(O_2)_2\}_2]^{-}$	381
$[Ph_2PO_2\{MoO(O_2)_2(H_2O)\}]^{-}$	381
$[Me_2AsO_2\{MoO(O_2)_2\}]^{-}$	381
$[Ph_2PO_2\{MoO(O_2)_2\}]^{-}$	381
$[W_4O_6(O_2)_6(OH)_2(H_2O)_2]^{2-}$	380
$[MePO_3\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2]^{3-}$	382
$[XW_{11}O_{39}(NbO_2)]^{n-}$ $(X = P, Si)$	383,384
$[SiW_9O_{37}(NbO_2)_3]^{7-}$	383,385
α_2-$[P_2W_{17}O_{61}(MO_2)]^{n-}$ $(M = Ti, Nb, Ta)$	386–388
α-$[P_2W_{15}O_{59}(MO_2)_3]^{n-}$ $(M = Ti, Nb)$	387,388
$[P_2W_{12}O_{56}(NbO_2)_6]^{12-}$	389
β_3-$[CoW_{11}O_{35}(O_2)_4]^{10-}$	390

[a] See also Dickman, M. H.; Pope, M. T. *Chem. Rev.* **1994**, *94*, 569–584.

reduced metal centers.[142,432–435] Tsukerblat *et al.*[436–438] have described a theoretical treatment of the delocalization of electron pairs in reduced Keggin and Wells–Dawson anions.

Under acidic conditions, certain Keggin polytungstate anions (with central H_2, B, Si) are reduced to heteropoly "browns" in which one or more of the triads of edge-shared WO_6 octahedra are reduced to metal–metal-bonded W^{IV} clusters. Confirmation of this composition has been provided by W-NMR spectroscopy,[439,440] and by a crystal-structure determination of $K_5[BW_9O_{37}\{W^{IV}{}_3(OH_2)\}_3]$.aq [441] in which the anion was not disordered, in contrast to an earlier investigation of reduced metatungstate.[442] The reduced anions have been shown to undergo oxygen-atom-transfer reactions, e.g., with sulfoxides, in nonaqueous media.[443] Reaction with excess tungstate(VI) in neutral solution leads to novel complexes in which the $W^{IV}{}_3$ cluster is capped by a W_8 group (Figure 28), $[(XO_4)W^{IV}{}_3W^{VI}{}_{17}O_{62}H_x]^{n-}$ (X = B, Si, H_2).[444]

4.10.5 COMPOSITE AND MESOSCOPIC POLYOXOMETALATES

Recent years have seen the reports of increasing numbers of very large polyoxometalate anions. These may be divided into two classes: (i) "composite" anions constructed of assemblies of simpler, usually lacunary, polyanions; and (ii) mixed-valence polymolybdate anions which comprise common building blocks, e.g., Mo_8, Mo_6, and Mo_2 clusters that have no separate, stable existence.

In keeping with the defined scope of the present review, it would be desirable to limit discussion of these species to those which are known to remain stable in solution. While that is possible in principle for many of the polytungstates, the reduced molybdates present difficulties, as a consequence of the quadrupolar nature of ^{95}Mo.

The field was comprehensively reviewed in 1998[445] and more focused reviews of the large polymolybdates have been published since.[446–449]

In addition to the composite anions listed in Tables 24 and 25, other complexes include $[(BiW_9O_{33})_3Bi_6(OH)_3(H_2O)_3V_4O_{10}]^{12-}$ [450] and $[As_6W_{65}O_{217}(H_2O)_7]^{26-}$, with a structure based on six $As^{III}W_9$ units (Figure 29).[451] The tetrameric (tetrahedral) assembly $[(P_2W_{15}Ti_3O_{60.5})_4]^{36-}$ proposed by Nomiya *et al.*[452] has been confirmed.[453] A similar type of tetrahedral assembly has recently been reported for $[(UO_2)_{12}(\mu_3\text{-}O)_4(\mu_2\text{-}H_2O)_{12}(P_2W_{15}O_{56})_4]^{32-}$ by Gaunt *et al.*[454]

By far the most intriguing types of mesoscopic polyoxometalates are the ring-shaped and hollow polymolybdate assemblies that have been reported by Müller and colleagues during the 1990s (Table 27). These are reproducibly generated, by self-assembly processes, by reduction of aqueous molybdate solutions. The common building block in these anions is a cluster formed by an $MoO_4(NO)$ or MoO_5 pentagonal bipyramid surrounded by five edge-shared MoO_6 octahedra. Depending upon the solution acidity, the degree of reduction, and the presence of appropriate linker groups, the pentagonal $\{Mo_6\}$ clusters can be induced to form spherical (icosahedral) $\{Mo_{72}(Mo^V{}_2)_{30}\}$[456] or $\{Mo_{72}(Fe^{III}{}_{30})\}$[457] "Keplerates" (Figure 30) or the cyclic $\{Mo_{154}\}$,$\{Mo_{176}\}$ structures (Figure 31) that were described earlier.[445] More recent developments in this area include: (i) the formation and characterization of

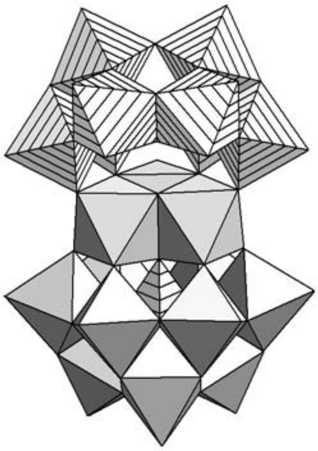

Figure 28 $[(XO_4)W^{IV}{}_3W^{VI}{}_{17}O_{62}H_x]^{n-}$.

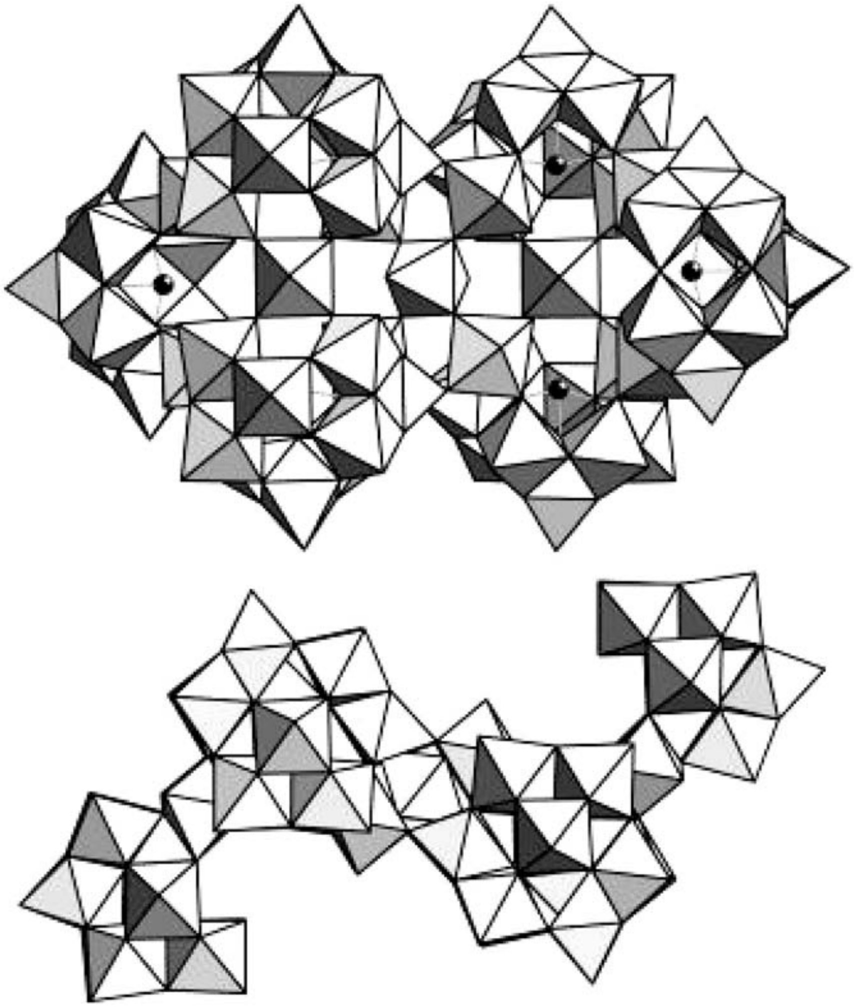

Figure 29 $[As_6W_{65}O_{217}(H_2O)_7]^{26-}$.

surfactant-encapsulated $\{Mo_{132}\}$ and $\{Mo_{57}V_6\}$ clusters using dimethyldioctylammonium (DODA);[462–464] (ii) the observation that a Keggin molybdophosphate anion can be incorporated within the $\{Mo_{72}(Fe^{III}{}_{30})\}$ cluster;[465] and (iii) the formation of a two-dimensional layer structure of $\{Mo_{72}(Fe^{III}{}_{30})\}$ linked by Fe–O–Fe bridges.[466] The magnetic properties of $\{Mo_{72}(Fe^{III}{}_{30})\}$ (thirty $S = 5/2$ centers) have been satisfactorily explained using classical and quantum Heisenberg models.[467]

Even larger species have been described: the $\{Mo_{176}\}$ anion, in aged solutions, can acquire two $\{Mo_{36}\}$ "hubcaps" to yield an $\{Mo_{248}\}$ cluster,[468] and recently the $\{Mo_{368}\}$ "hedgehog" (Figure 32) has been crystallized from an acidified solution of sodium molybdate and sodium dithionite.[469]

Table 27 Examples of mesoscopic polyoxomolybdates.

Formula		*References*
$[X_6\{Mo^V(\mu\text{-}H_2O)_2(\mu\text{-}OH)Mo^V\}_3\{Mo^{VI}{}_{15}(MoNO)_2O_{58}(H_2O)_3]^{21-}(X = V^{IV}O(H_2O);\ Fe^{III}(H_2O)_2\ )$	$\{Mo_{57}X_6\}$	455
$[\{Mo^V{}_2O_4(CH_3COO)\}_{30}\{(Mo)Mo_5O_{21}(H_2O)_6\}_{12}]^{42-}$	$\{Mo_{132}\}$	456
$[Mo_{72}Fe_{30}O_{252}(CH_3COO)_{12}\{Mo_2O_7(H_2O)\}\{H_2Mo_2O_8(H_2O)\}(H_2O)_{91}]$	$\{Mo_{72}Fe_{30}\}$	457
$[\{Mo^{VI}O_3(H_2O)\}_{10}\{V^{IV}O(H_2O)\}_{20}\{(Mo^{VI})Mo^{VI}{}_5O_{21})(H_2O)_3\}_{10}(\{Mo^{VI}O_2(H_2O)_2\}_{5/2})_2\ (\{NaSO_4\}_5)_2]^{20-}$	$\{Mo_{75}V_{20}\}$	458
$[Mo_{154}O_{420}(NO)_{14}(OH)_{28}(H_2O)_{70}]^{28-}$	$\{Mo_{154}\}$	459
$[(MoO_3)_{176}(H_2O)_{80}H_{32}]$	$\{Mo_{176}\}$	460,461
$[H_xMo_{368}O_{1032}(H_2O)_{240}(SO_4)_{48}]^{48-}$	$\{Mo_{368}\}$	469

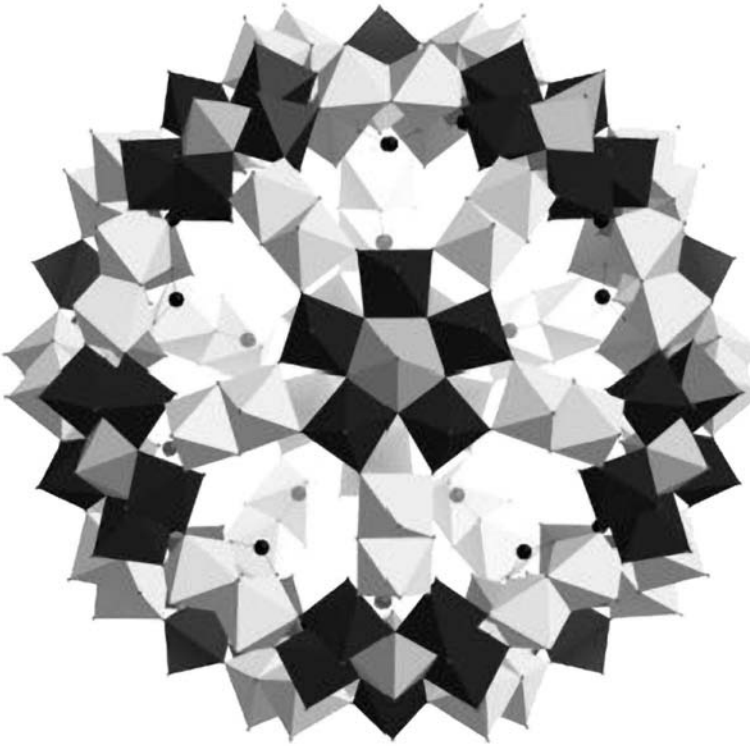

Figure 30 {Mo$_{132}$} (reproduced by permission of Wiley–VCH Verlag from Müller, A.; Krickemeyer, E.; Bögge, H.; Schmidtmann, M.; Peters, F. *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 3360).

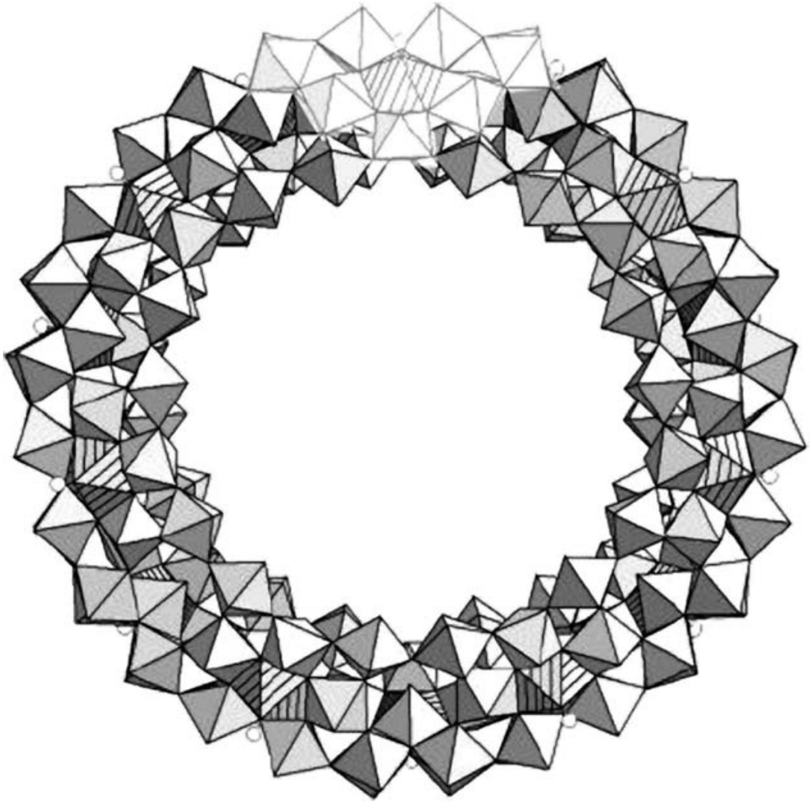

Figure 31 {Mo$_{154}$} (reproduced by permission of Wiley–VCH Verlag from Müller, A.; Krickemeyer, E.; Meyer, J.; Bögge, H.; Peters, F.; Plass, W.; Diemann, E.; Dillinger, S.; Nonnenbruch, F.; Randerath, M.; Menke, C. *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2122).

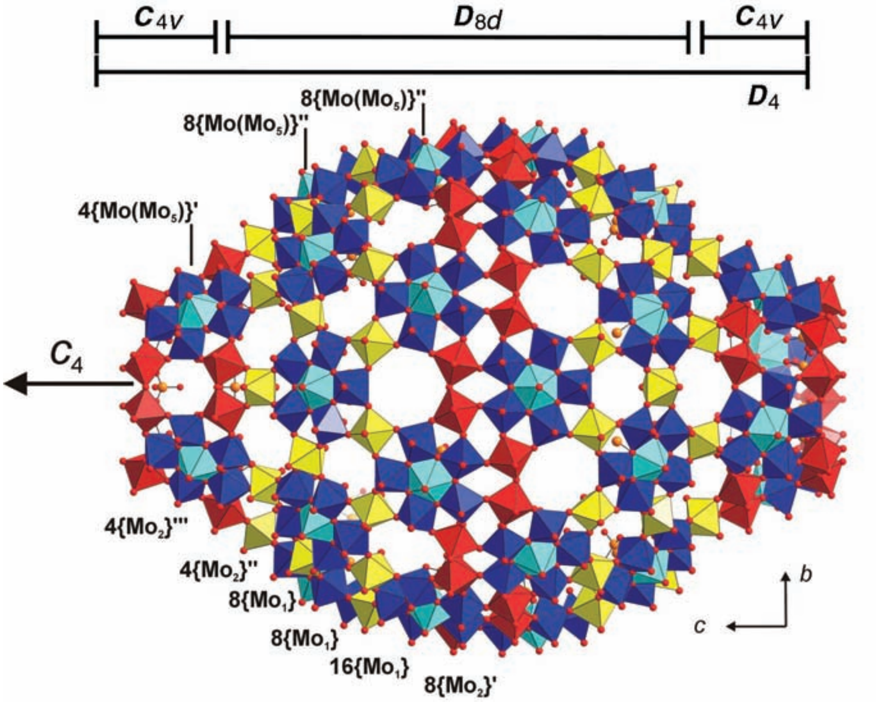

Figure 32 $\{Mo_{368}\}$ (reproduced by permission of Wiley–VCH Verlag from Müller, A.; Beckmann, E.; Bögge, H.; Schmidtmann, M.; Dress, A. *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 1162–1167).

4.10.6 ORGANOMETALLIC AND FUNCTIONALIZED DERIVATIVES

The field of organometallic and functionalized polyoxometalates is enormous and was thoroughly reviewed by Gouzerh and Proust in 1998.[308] Subsequent, briefer reviews have focused on functionalized polyoxoanion clusters,[470,471] and the direct functionalization of $[M_6O_{19}]^{2-}$ (M = Mo, W) by replacement of terminal oxygens with isoelectronic NAr groups has been further developed.[472–476] The analogous Nb_6 and Ta_6 anions have been derivatized under aqueous conditions to yield $[M_6O_{19}\text{-}\{MN(CO)_3\}_n]^{(8-n)-}$ (M = Nb, Ta; MN = Mn,Re) and $[Nb_6O_{19}\{Ru(p\text{-cymene})\}_2]^{4-}$.[477] Errington has explored the synthesis of polyoxometalates via controlled hydrolysis of metal alkoxides, and has reported several new "nonaqueous" species, including $[\{MeOMW_5O_{18}\}_2]^{6-}$ (M = Zr, Hf), $[W_3Nb_3O_{17}(OMe)_2]^{3-}$, $[V_6O_{11}(O_3PPh)_5]^{-}$, and $[V_9O_{19}(O_3PPh)_4Cl]^{2-}$.[14] Complexes formed by incorporation of $\{RSn\}^{3+}$ and $\{CpTi\}^{3+}$ into lacunary anions are listed in Tables 13, 14, and 16. The products of reaction of organophosphonyl and organosilyl precursors with a variety of lacunary anions lead to a class of organic–inorganic hybrids, Table 28, that have been used for grafting into polymer matrices and the incorporation of magnetic nanoparticles.[478,479]

Table 28 Organophosphonyl and organosilyl derivatives of lacunary polyoxotungstates.

Formula	*References*
$[\{PhP(O)\}_2XW_{11}O_{39}]^{n-}$ (X = P, Si)	480
$[\{C_6H_{11}P(O)\}_2XW_{11}O_{39}]^{n-}$ (X = P, Si, B, Ga)	481
$\alpha_2\text{-}[Q_2P_2W_{17}O_{61}]^{6-}$ {Q = PhP(O), PhP(S), $C_6H_{11}P(O)$, $C_6H_{11}P(S)$}	482
$[\{RP(O)\}_2(\gamma\text{-}SiW_{10}O_{36})]^{4-}$	483
$[\{RSi_2O\}(\gamma\text{-}SiW_{10}O_{36})]^{4-}$	484
$[\{RSiO\}_4(\gamma\text{-}SiW_{10}O_{36})]^{4-}$	484
$[\{t\text{-}BuSiOH\}_2(\gamma\text{-}SiW_{10}O_{36})]^{3-}$	485
$[\{RP(O)\}_2PW_9O_{34}]^{5-}$	480–482
$\alpha\text{-}[Q_2PW_9O_{34}]^{5-}$ {Q = PhP(S), $C_6H_{11}P(O)$}	489
$[SiW_9O_{34}(SiR)_3(O_3SiR)]$	490

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4.11

Polyoxometalates: Reactivity

C. L. HILL
Emory University, Atlanta, GA, USA

4.11.1 INTRODUCTION

4.11.1.1 Definitions

Polyoxometalates (POMs) are discrete molecular structures composed of metal cations bridged by oxide anions. They are not multi-metal species with metal–metal bonding, one conventional definition of "clusters," but they are clusters in the generic sense of the word. A number of general reviews on POMs have appeared in recent years.[1–13] Since a great majority of these structures are anionic, and thus salts with obligatory cations, and constituted primarily of early-transition-metal (*d*-block) elements in their highest oxidation states, the name early-transition-metal-oxygen-anion clusters is generally viewed as appropriate. However, the literature on molecular polyanions is now so large that there are exceptions to each component of this description of POMs. For example, many polyanions are now known with sulfido,[14–18] alkoxo,[19,20] or peroxo ligands[21–28] in place of some or all of the conventional oxo ligands. A review by Dickman and Pope on peroxo and superoxo complexes of chromium, molybdenum, and tungsten with overlap with the POM literature appeared in 1994.[29] In addition, there are metal oxide cluster species that are neutral or cationic. Most of these are polyalkoxyoxometalates (polyalkoxyoxoanions)[19] or polyhydroxoaluminum cluster cations.[30–33] This review focuses on early-transition-metal polyanions. The term POM or polyoxoanion is in most frequent use, as are the terms heteropolyanions (HPAs) or heteropoly compounds which refer to the largest sub-family of POMs. For convenience, the term "POM" will be used in this review.

4.11.1.2 Literature and Topics Covered

There has been such a dramatic increase in the number of publications on POMs since the first edition of *Comprehensive Coordination Chemistry* (*CCC*, 1987), that the single chapter in *CCC* by Pope[3] has now become two in *Comprehensive Coordination Chemistry II* (*CCC-II*). *CCC-II* is mandated to cover the literature starting in 1982. Since POM reactivity was not covered as such in *CCC* a few seminal papers in this area published prior to 1982 are cited in this review. A search solely on the terms "POM" and "heteropoly" from 1982 to 2002, the years addressed in *CCC-II*, identified 11,378 publications. The literature on the synthesis and physical properties of POMs, the subject of Chapter 4.10 by Michael Pope, has increased several-fold since 1982, and the literature on the dynamic properties (reactivities, mechanisms, etc.), the subject of this chapter, has increased by a comparable or even greater percentage over this time interval. While there have been edited volumes on POMs (effectively "proceedings" of meetings),[4,7,10–12] the last monograph on the subject was that by Pope completed 20 years ago.[1] To cover the current literature comprehensively would require a multi-volume series, which would be out of date shortly after it was published.

Given the space limitations, this review is confined to the reactivity of the POM units themselves and reactivity in solution, including processes facilitating catalysis. A mitigating factor in this selective coverage is that recent reviews in several areas of POM chemistry other than the above that loosely fall under the rubric of "POM reactivity" have appeared. The following topics are beyond the purview of this article: (i) reactivities that arise in context with routine POM synthesis, including preparation of inorganic–organic nanocomposites, Langmuir–Blodgett films, and other POM-containing materials;[34–38] (ii) electron delocalization in POMs ("heteropoly blue" chemistry)[39–48] and the somewhat related area of electron donor–acceptor salts with noteworthy magnetic properties,[36,49–51] (iii) POM electrochemistry (electrode modification, electrocatalysis, electroactive, or electrochromic materials, etc.);[52–56] (iv) thermodynamic speciation studies,[57–59] except in cases where actual kinetic information on intermediates (and hence insight regarding POM reactivity) are reported; and (v) heterogeneous catalysis by POMs.[60,61]

Pope addresses POM synthesis, heteropoly blue chemistry, and speciation work in Chapter 4.10. Recent reviews on inorganic–organic nanocomposites, including those containing POMs, by Sanchez *et al.*[34] and Stein *et al.*[62] as well as a review on porous materials[63] have appeared. These complement recent reviews on POM electrocatalysis,[54] electrochromism,[52] and electrode modification.[53,64,65] In addition, the use of POMs in heterogeneous catalysis has been repeatedly reviewed by Misono[60,66–74] and a recent monograph on this subject by Moffat just appeared.[61,75] A very thorough and informative but not entirely complete review on the routes of formation of heteropolytungstates and their structures by Contant and Hervé appeared while this article was nearing completion.[13] Many other review articles on POMs that relate indirectly to the subject matter of this review have appeared and these will be cited in each of the appropriate sections below. However, the majority of these reviews cannot claim to be either comprehensive or critical. A consequence of this limited coverage and analysis is that such reviews have proportionally limited "shelf lives."

This review chapter has three sections. The first involves reactions of the POM units themselves, including ion-pairing interactions with POM surface oxygens, rearrangements, isomerizations, and reaction of these oxygens with organic groups. The second involves thermal reactions with external reagents, primarily oxidants, and the role of POMs in homogeneous catalysis. The third involves the role of POMs in photochemical and photocatalytic processes. The first section constitutes the bulk of this review, in part because the data therein are fundamental to all POM chemistry, including that in the latter two sections. In this chapter, a great majority of the relevant articles are cited but emphasis will be placed on those that are the most insightful and informative. Only a modest percentage of the multitude of publications on POMs probes the basic properties of this large and growing class of compounds. Our understanding of POM reactivity (and associated potential utility and application) derives from a relatively modest percentage of the papers, those that address fundamental properties in a rigorous way. This follows, in part, because most investigators working with POMs are structurally oriented and not trained to investigate dynamic chemistry, including reaction mechanisms. Before we turn to these three sections, we will review some general properties of POMs that relate directly or indirectly to reactivity.

4.11.1.3 Polyoxometalate Properties

Isopolyanions ("IPAs;" generic formula: $\mathrm{H}_x\mathrm{M}_q\mathrm{O}_y{}^{z-}$) form from stoichiometric quantities of hydrogen ion (p) and a monomeric oxometal form of the d-electron early-transition-metal ion (q), typically $\mathrm{MO}_4{}^{\mathrm{r}-}$ (Equation (1)). The starting ratio of reactants, p/q ($=Z$ value) defines the stoichiometry. Pope has noted that the Z value has been used to mean three different things: (i) the above (mole ratio of reactants), (ii) the p/q value for a solution at equilibrium, and (iii) the p/q value for POM(s) that crystallize(s) from that solution.[1] These are not necessarily the same. The p/q value dictates the POM, or more accurately in most cases, the distribution of POMs formed. (Clearly an isolated POM will have one precise p/q value.) HPAs contain one or more "heteroatoms," X^{n+}, in addition to the metal centers, M (Equation (2)):

$$p\mathrm{H}^+ + q\mathrm{MO}_4^{\mathrm{r}-} \rightarrow \mathrm{H}_x\mathrm{M}_q\mathrm{O}_y{}^{z-} + (4q-y)\mathrm{H}_2\mathrm{O} \qquad (1)$$

$$p\mathrm{H}^+ + q\mathrm{MO}_4^{\mathrm{r}-} + \mathrm{XO}_4{}^{n-} \rightarrow (\mathrm{H}_x\mathrm{X}^{n+}\mathrm{M}_q\mathrm{O}_y)^{n-} + q\mathrm{H}_2\mathrm{O} \qquad (2)$$

The heteroatoms can be p-, d-, or f-block elements, and they are present in lesser quantities than M. They typically occupy a single location, as in the common Keggin family of complexes, $\mathrm{X}^{n+}\mathrm{M}_{12}\mathrm{O}_{40}{}^{(8-n)-}$, or one type of location based on the symmetry of the parent (unsubstituted) POM. Figure 1 illustrates four parent (nondefect or nonsubstituted) POMs in polyhedral notation. The Keggin structure, which dominates catalytic applications and, to a lesser extent, reactivity studies of the polyanion units themselves, contains one central heteroatom and 12 "addenda" atoms that surround it in four $\mathrm{M}_3\mathrm{O}_{13}$ triads. The POM reactivity addressed in this review can involve either the heteroatom(s) or the addenda atoms. These addenda atoms can be either the d^0 early-transition-metal ions that form POMs such as W^{VI}, $\mathrm{Mo}^{\mathrm{VI}}$, and V^{V}, they can be d-electron-containing, or occasionally f-electron-containing ions.

In practice, POMs are most frequently prepared by one-pot, proton-induced condensation-dehydration reactions in water. Unfortunately, these self-assembly processes are almost never monitored with time, so information regarding the POM formation subset of "POM reactivity" is minimal. Typical reactions are given in Equations (3)–(5) for preparation of a representative isopolyanion, heptamolybdate, an unsubstituted HPA, dodecatungstophosphate, and a substituted HPA (a "mixed addenda HPA"), undecatungstodicobaltate(III), respectively:

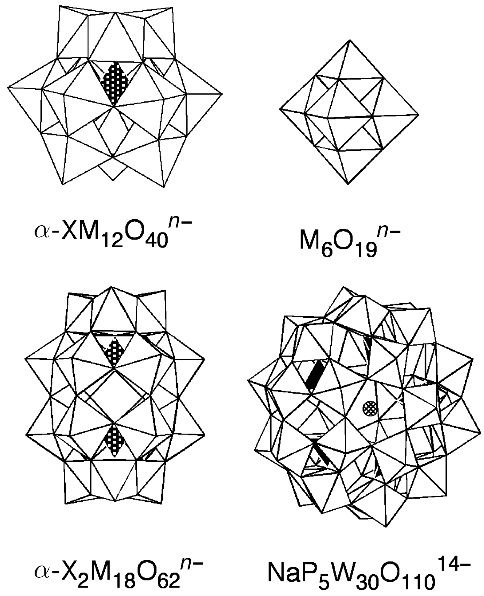
$$7\mathrm{MoO}_4^{2-} + 8\mathrm{H}^+ \rightarrow \mathrm{Mo}_7\mathrm{O}_{24}{}^{6-} + 4\mathrm{H}_2\mathrm{O} \qquad (3)$$

$$12\mathrm{WO}_4^{2-} + \mathrm{HPO}_4^{2-} + 23\mathrm{H}^+ \rightarrow \mathrm{PW}_{12}\mathrm{O}_{40}{}^{3-} + 12\mathrm{H}_2\mathrm{O} \qquad (4)$$

$$2\mathrm{Co}^{2+} + 11\mathrm{WO}_4^{2-} + 10\mathrm{H}^+ \rightarrow (\mathrm{Co})\mathrm{CoW}_{11}\mathrm{O}_{39}{}^{8-} + 5\mathrm{H}_2\mathrm{O} \qquad (5)$$

d- or f-Electron ions in addenda positions, such as in $(\mathrm{Co})\mathrm{CoW}_{11}\mathrm{O}_{39}{}^{8-}$ in Equation (5), can be incorporated into the POM structure either in the initial one-pot self-assembly synthesis or by preparing a defect ("lacunary") structure first, and then treating this compound in solution in a subsequent step with one equivalent of the final metal to be substituted in the surface site. A great majority of the time, this final metal incorporation involves reaction of aquated first-row and occasionally second-row d-block metal ions, $\mathrm{M(H_2O)}_6{}^{z+}$, with a lacunary POM derived from the Keggin (as in Equation (6)), Wells–Dawson, or, less frequently, other POM families:

$$\mathrm{M(H_2O)}_6^{z+} + \mathrm{X}^{n+}\mathrm{W}_{11}\mathrm{O}_{39}{}^{(4-n)-} \rightarrow (\mathrm{MOH}_2^{z+})\mathrm{X}^{n+}\mathrm{W}_{11}\mathrm{O}_{39}{}^{(12-n-z)-} \qquad (6)$$



α-$XM_{12}O_{40}{}^{n-}$ $M_6O_{19}{}^{n-}$

α-$X_2M_{18}O_{62}{}^{n-}$ $NaP_5W_{30}O_{110}{}^{14-}$

Figure 1 Representative POM structures in polyhedral notation. Top left: the common Keggin structure; top right: the hexametalate structure; bottom left: the Wells–Dawson structure; bottom right: the Pope–Jeannin–Preyssler structure. In polyhedral notation, the center of each MO_6 unit is a metal nucleus and each vertex is an oxygen nucleus.

The principal reactions of POMs are those in which the POM functions as a Brønsted or Lewis acid, or as an oxidant. Acid–base interactions involving POMs not only induce many important reactions by themselves but also influence the redox reactions of POMs. Figure 2 illustrates the cation–polyanion interactions and loci of reactivity in a typical POM, in this case, a mixed acid–metal salt of a HPA. These reactive locations include the oxygens, and perhaps in rare cases the metals, in the POM unit as such as well as sites on the cations. Brønsted acidity derives from POM proton counterions residing on solvent molecules, or if these solvent molecules are removed by high temperature and/or vacuum, protons on the actual POM oxygens. If solvent molecules are present, including H_2O molecules, the protons reside on these because the heteroatom lone pairs of most solvent molecules are more basic, and in most cases far more basic, than the oxygens of most POMs. Nearly all heteropoly acids are prepared in water, in which case the protons are on the H_2O molecules. Protonated water is structurally complex in general[76] and likely is for heteropolyacids in water, but simple protonated dimers, $[H_2O–H–OH_2]^+$, are a common structural motif for the proton counterions in crystalline heteropolyacids based on several X-ray structures.[77] Heteropolyacids are soluble in polar aprotic solvents and crystal

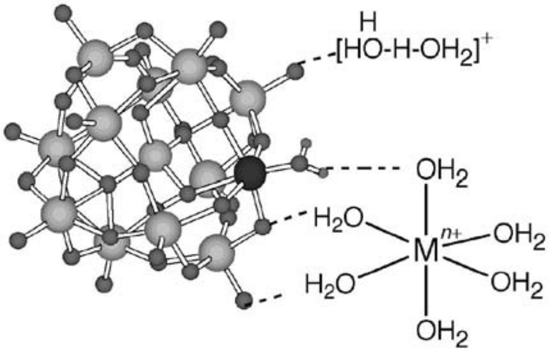


Figure 2 Cation–polyanion interactions and loci of reactivity in a typical POM. The black addenda atom (frequently a *d*-electron-containing metal) on the right of the POM has the terminal H_2O ligand.

structures of these molecules crystallized from DMA[78] and tetramethylurea[79,80] confirm in all cases that the protons exist as protonated dimer counterions, $[\text{Sol–H–Sol}]^+$; they do not reside on the less basic POM oxygens. POM X-ray structures indicate that some complex cations comprised of protonated solvent molecules also involve hydrogen bonding to POM oxygens, while some do not. Where hydrogen bonding to POM oxygens is operable, either the less basic terminal oxo groups or the more basic bridging oxo groups can be involved. Heteropolyacids are typically isolated as etherates, and most frequently complexes of diethyl ether. There is less hard structural information on etherates because they are nearly always noncrystalline oils, but it is likely that protonated dimers are present in most of these cases as well. The same goes for solutions of heteropolyacids in the other oxygenated solvents in which they are highly soluble, including acetone. The case of acetonitrile is less clear because the lone pairs on acetonitrile, like the those on the POM oxygens, are extremely weak bases (the pK_a value for the acetonitrilium ion, $[\text{MeCNH}]^+$, is ~ -9).[81]

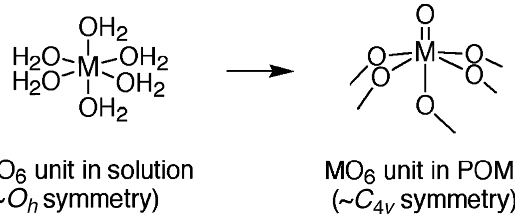
Because Brønsted acidity correlates inversely with the negative charge density of the conjugate base, and POMs have lower negative charge densities than the conjugate bases of even the strongest conventional acids such as $HClO_4$ or CF_3SO_3H (HOTf or triflic acid), the acid forms (protic "salts") of POMs are extremely strong acids. If the solvent molecules (most commonly the water molecules of heteropolyacids) are driven off by the application of heat and/or vacuum, the proton counter cations of the POM no longer reside on the solvent molecules but now reside on the POM oxygens. Thus, the desolvation process produces a much stronger acid, typically one with a Hammett acidity function value in the superacid range. Superacidity is not limited to dehydrated heteropoly acids but also to mixed proton–metal salts of POMs such as $Cs_xH_x[\text{POM}^{n-}]$.[61,82,83] The acid forms of isopolyanions as well as HPAs have also been studied, but less so simply because there are fewer of them and they are less useful in catalysis. One study involving the tetra-*n*-butylammonium (TBA) salt of decavanadate, $TBA_3[H_3V_{10}O_{26}]^{3-}$, revealed the protons were on the bridging oxygens.[84]

Acidity in the useful (functional superacid) POMs can derive not only from the protons in the acid salts but also from the metal counter cations in two respects (Figure 2). These cations can function as Lewis acid sites and/or Brønsted acid sites in that the cations facilitate hydrolysis of their own aqua (H_2O) ligands.[66] The latter process is enhanced upon oxidation of the cations (for many *d*- and *f*-block cations that have a redox capability). In addition, hydrogen bonding between the cation aqua ligand protons and the POM oxygens can labilize and increase the acidity of these aqua protons. Since hydrogen bond energies correlate with negative electron density on the acceptor, such $\text{M—OH}_2 \cdots \text{O(POM)}$ hydrogen bonding interactions, not surprisingly, are weak and probably perturb the acidity minimally. For *d*-metal-substituted POMs, which have been referred to, among other ways, as "transition-metal-substituted POMs" (TMSPs),[85–87] the terminal aqua ligand on the *d*-metal center(s) can also undergo hydrolysis and this process is impacted by the oxidation state of the *d*-metal center.[88–91]

Within the polyanion units themselves, the bridging oxygens are generally more basic than the terminal oxygens. This correlates with the degree of donation of the oxygen-lone-pair electron density to the metal center(s). In the Keggin (general formula, $X^{n+}M_{12}O_{40}{}^{(8-n)-}$), Wells–Dawson (general formula, $X^{n+}{}_2M_{18}O_{62}{}^{(16-2n)-}$), and several other structural classes of POMs there are also internal (and often solvent inaccessible) oxygens in addition to the bridging and terminal oxygens. The internal oxygens are almost always trans to a terminal oxygen and thus exhibit the longest M—O bonds and presumably the highest negative charges of the POM oxygens (the word "presumably" is used because the negative charge densities cannot usually be measured experimentally but only assessed computationally).

The ability of most families of POMs, including most isopolyanions and effectively all heteropolyacids and mixed addenda HPAs, to undergo reversible reduction and reoxidation plays an even more significant role in POM reactivity than acidity. Several factors influence POM redox reactivity, but none are more important than reduction potentials of the polyanion unit itself. These potentials depend on, in decreasing order of impact, the particular metal that is involved in the redox process, the charge on the polyanion unit, the degree of ion pairing, and the solvent. For the principal d^0 metal centers that constitute the polyanion units, the potentials are in the order $V^{V/IV}$ (highest potential) $> Mo^{VI/V} > W^{VI/V}$ (lowest potential). There is little or no redox chemistry documented for the Ti^{IV}, Nb^V, and Ta^V centers in POMs, because the reduced forms of these species are generally inaccessible by either conventional electrochemical or common chemical methods of reduction. The reason for this is not clear, but more than likely reflects thermodynamic rather than kinetic barriers. For the most common *d*-metals substituted in surface sites (defining mixed addenda POMs or TMSPs), the standard reduction potentials for the corresponding

$\sim O_h$ symmetry hexaaquo complex cations are as follows: $Co^{III/II} = 1.84\,V > Mn^{III/II} = 1.51\,V > Fe^{III/II} = 0.770\,V > Cu^{II/I} = 0.158\,V$. Perturbation of the local O_h symmetry of the O_6 coordination polyhedra of such *d*-metal centers upon incorporation from aqueous solution into POMs (e.g., Equation (6)) can change the reduction potential of this metal center by several hundred millivolts. This incorporation results in a lowering of the local symmetry of this *d*-metal center from $\sim O_h$ to $\sim C_{4v}$ as depicted in Scheme 1 but rarely results in a spin state change of the incorporated metal for the first-row *d*-block metals.



Scheme 1

Ion pairing between the polyanion unit and the counterions in POMs varies greatly with the medium, and to a lesser extent, negative charge density on the POM, but when present can change the potential of a redox-active metal center in a POM by 150 mV or more.[92,93] These and solvent effects are addressed in Section 4.11.2.1. The general reactions of POMs with reductants and oxidants are summarized in Section 4.11.3.1.

A detailed knowledge of the electronic structure of POMs, and in particular the Keggin structure, has been sought for years. Such information would be insightful in understanding structural features, assessing spectroscopic signatures, characterizing the delocalization and behavior of added electrons, evaluating the relative energies of different POM structural isomers and electronic configurations, probing electron transfer to other species, and other issues. Needless to say, the complexity of POM structures coupled with the difficulty of parametrizing heavy metals for quantum mechanical and other calculations has made such research problematical at best until recently. Thankfully, the marked advances the last few years in computer hardware and software for density functional theory (DFT) and other calculations is starting to make important calculations on POMs fairly viable. Recent calculations by Poblet and co-workers have been noteworthy.[94–96] These investigators have used DFT methods to probe the electronic and magnetic properties of Keggin POMs. For example, their work to date indicates that atomic populations and the distribution of the electron density computed for Keggin polyanions support the hypothesis that the oxidized structure is an XO_4^{n-} clathrate inside a neutral $M_{12}O_{36}$ cage,[95] a proposal popularized years ago by Day and Klemperer.[2] Their calculations indicate that the energy gap between the band of occupied orbitals and the unoccupied *d*-metal orbitals is independent of the central ion. (The former and latter orbitals are formally delocalized over the oxo ligands and delocalized over the addenda, respectively.) Recent experimental work by Weinstock, Hill, and co-workers is consistent with these findings.[97,98]

4.11.2 BASIC THERMAL REACTIONS

4.11.2.1 Ion Pairing in POMs

4.11.2.1.1 General aspects

The interactions of the polyanion units in POMs with the counterions underlies and impacts both the physicochemical and the reactivity properties of POMs. We address these interactions in this section because they can have considerable bearing on processes formally associated with the polyanions. While it has been known for some time that POM counterions impact POM formation and POM distributions in solution,[99–101] ion pairing interactions in reacting POM systems have largely been ignored until recently. One likely explanation for this is that such interactions are hard to investigate and even harder to quantify meaningfully. They involve potentially complex stoichiometries (ratios of cations to the polyanion), small association constants, and short cation–polyanion association lifetimes in solution. Another general reason they have been largely ignored is that the main focus of much of POM chemistry has been the structurally and dynamically rich polyanion unit itself.

Reports of ion pairing can be loosely grouped into investigations that focus on the structural and, to a lesser extent, other physical properties of POMs and those that focus on the dynamic properties of POMs. In context with the dynamic properties, a number of studies of POM reduction by electron transfer from a suitable donor (organic or inorganic) have been studied and are reviewed in subsequent sections. One can also define two categories of POMs with respect to cation association: POMs that do not have specific and structurally well-defined metal binding pockets, which includes the majority of POMs; and those which do contain one or more such metal-binding pockets. Ion pairing in the common and general structures, including Keggin and Wells–Dawson complexes, and cation association in POMs with specific structurally well-defined cation binding sites are covered in the next two sections in that order.

4.11.2.1.2 Cation association in POMs without specific metal binding sites

For these general and commonly occurring POMs, ion pairing studies that focus primarily on structural and static POM properties are addressed first, followed by ones that encompass both structural and reactivity properties.

Two studies prior to the start date of this review (1982) should be mentioned as they impact the work after 1982. Contant and Ciabrini in 1977 demonstrated that in the preparation of the monodefect Wells-Dawson complex, $P_2W_{17}O_{61}^{10-}$, the α_1 (or belt defect) isomer is formed in the presence of Li^+ whereas the α_2 (or cap) isomer is formed in the presence of K^+.[102,103] Subsequently Knoth and Harlow showed that $P_2W_5O_{23}^{6-}$, $PW_9O_{34}^{9-}$, and $PW_{11}O_{39}^{7-}$, form in the presence of Cs^+, K^+, and Li^+, respectively, under otherwise identical conditions.[104] Although crystal packing forces cannot be ruled out as partly controlling the ultimate structures that form, the different POMs do persist in solution prior to precipitation and/or crystallization. In 1985, Contant and Tézé showed that the large donut structure, $P_8W_{48}O_{184}^{40-}$, a tetramer of the hexadefect Wells-Dawson POM, $P_2W_{12}O_{48}^{12-}$, is dependent on the presence of K^+.[105] The following year, Canny *et al.* reported that $SiW_{10}O_{36}^{8-}$ is stable with K^+, Rb^+, and Cs^+ but not Na^+ or Li^+ counterions.[106] Day *et al.* conducted an NMR and X-ray study on the TBA_3H_3 salt of decavanadate that indicated the three protons reside on the POM oxygens.[84] A thorough review of the consequences of cations on heteropolytungstate formation modes and final structures by Contant and Hervé appeared recently.[13] All these publications address the structural consequences of ion pairing in POMs. However, static structures, while informative regarding some physicochemical properties, reveal little about dynamic properties. Isolable POM salt structures including those in X-ray crystallographic investigations, given the intrinsic time scale for data collection in crystallography, may not reside along the reaction coordinate for either an intramolecular process such as isomerization or an intermolecular process such as reaction with an organic molecule or a reductant.

In 1991, Fournier *et al.* investigated solutions of Keggin heteropolytungstates by IR, Raman, and electronic absorption spectroscopies.[107] This effort was a logical application of the vibrational spectroscopy studies of POMs by Rocchiccioli-Deltcheff and Thouvenot that provide most of our current understanding of this subject. They assigned the principal stretching modes of Keggin and hexametalate POMs,[108,109] and conducted a normal coordinate analysis of $Mo_6O_{19}^{2-}$ based on total isotopic (^{18}O, ^{92}Mo, ^{100}Mo) substitution.[110] Subsequent work provided vibrational spectroscopic evidence for polyanion–polyanion electrostatic interactions in solid Keggin heteropolymolybdates and tungstates,[111] correlations between structural and vibrational features in Keggin ions,[112] and a confirmation of the rigidity of the polytungstates from a subsequent normal coordinate analysis of $W_6O_{19}^{2-}$.[113] In the 1991 paper with Fournier, who has extensively studied POMs of value in heterogeneous catalysis (and thus POMs in the solid state), this collaborative team found evidence for aggregation of the counterions in tetraalkylammonium POM salts and polyanion–polyanion interactions in solution (H_2O, MeCN and $(Me)_2CO$)[107] like those previously documented in the solid state.[111] In a sidebar, these authors used the absorption maxima of $SiM_{12}O_{40}^{4-}$ ($M = Mo$ or W) to assess the effect of cation and solvent on the electronic structure (oxygen-to-metal charge-transfer states) of these POMs and concluded there was almost no effect of either because the maxima (λ_{max} values) were nearly independent of both solvent and counterion. However, caution should be exercised here as Hill and co-workers have quantified substantial effects of cations and solvent, not only on the λ_{max} values, but also on the overall oxygen-to-metal absorption manifold of d^0 POMs. Nearly all the solvent-dependent changes in the UV–visible spectra occur in the absorption tails.[78–80,114]

In 1995, Finke and co-workers garnered direct, although qualitative, evidence for pairing of Na^+ with the polyanion unit in the air-sensitive POM-supported organometallic complexes, $TBA_5Na_3[(1,5\text{-COD})M\cdot P_2W_{15}Nb_3O_{62}]$ (COD = cyclooctadiene; M = Ir and Rh), in DMSO solution. Addition of the diazabicyclic crown-ether alkali metal chelating agent, Kryptofix[2.2.2], resulted in a sharpening and/or increasing of the signal to noise of the peaks in ^{31}P and ^{183}W NMR spectra of these complexes in DMSO. This is consistent with Na^+ complexation by the chelating agent and consequent severing of the ion pairing interaction with the polyanion unit.[115] However, the observed spectral changes upon addition of the Na^+ counterion-chelating agent are complicated by the possibility of positional (point of attachment) isomerism of the $(1,5\text{-COD})M^+$ caps. The most probable metal binding coordination polyhedron in this POM, $P_2W_{15}Nb_3O_{62}{}^{9-}$, based on electron density clearly should be the facial κ_3-O-support site of effective C_{3v} symmetry presented by the $Nb_3O_9{}^{3-}$ end unit of this POM. In subsequent work, this group prepared the $TBA^+{}_8$ and mixed TBA^+/Na^+ salts of $[Re(CO)_3\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ and $[Ir(CO)_2\cdot P_2W_{15}Nb_3O_{62}]^{8-}$ and examined the coordination chemistry of the cationic organometallic capping units, $Re(CO)_3{}^+$ or $Ir(CO)_2{}^+$, by ^{31}P and ^{183}W NMR and IR.[116] While this was a spectroscopic, not a kinetics study, the spectra in the absence and presence of Kryptofix[2.2.2], provide clear evidence of pairing between the polyanion units and the Na^+ counterions. This ion pairing directly impacts positional isomerism with respect to the capping organometallic units (see below; Section 4.11.2.2.5). In the most recent study (1999), Weiner *et al.* prepared a third class of POM derivatives involving the attachment of complex cationic species to $P_2W_{15}Nb_3O_{62}{}^{9-}$.[117] The complexes entail covalent (or more accurately, dative) bonding (vs. ion pairing via simple electrostatic association) of acetonitrile ligated first-row transition metal cations to this POM. They were prepared as outlined in Equation (7) (M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Cu^{II}, and Zn^{II}). The number of solvated cationic units per complex (the value of m), depends of the metal and the reaction stoichiometry (ratio of POM to $[M^{n+}(NCMe)_y](BF_4)_n$ reactants). Ion pairing (electrostatic "outer sphere" association), vs. dative bonding, of the solvated transition metal cations was convincingly demonstrated using ion exchange chromatography. The cationic caps datively bound to the POM were not exchanged with cations on the column and remained firmly bound to the POMs. In contrast, the column quantitatively retained the electrostatically associated cations. For some of the product complexes, $(TBA)_{(9-nxm)}[m\{(MeCN)_xM^{n+}]/P_2W_{15}Nb_3O_{62}{}^{9-}]$, both types of solvated cationic units were present:[117]

$$\begin{aligned}&(TBA)_9P_2W_{15}Nb_3O_{62} + m[M^{n+}(NCMe)_y](BF_4)_n \xrightarrow[2\,h,25\,^\circ C]{MeCN,N_2} (TBA)_{(9-nxm)}\\ &[m(MeCN)_xM^{n+}/P_2W_{15}Nb_3O_{62}{}^{9-}] + nxmBF_4\end{aligned} \quad (7)$$

In 1998, Baker and Kirby conducted a ^{31}P NMR investigation of electron exchange in the two-electron reduced heteropoly blue complex of $[(P_2W_{17}O_{61})_2Th]^{18-}$ (which contains an equilibrium mixture of oxidized, two-electron- and four-electron-reduced species) as a function of alkali metal counterion, concentration, and temperature. They interpreted their data in terms of Equation (8) in which the more strongly pairing alkali metals (M in Equation (8) = K^+, Rb^+, and Cs^+ but not Li^+) form an ion bridge between the two defect HPA units in the *syn* isomer. This interaction stabilizes the *syn* isomer and drives an apparent *syn–anti* equilibrium, Equation (8), to the left.[118] The change in chemical shifts and other features of the ^{31}P NMR spectra of these Th sandwich POM complexes as a function of the counterion defined a qualitative method to estimate the association of monocations with POM polyanions:

$$syn\text{–}[M(P_2W_{17}O_{61})_2Th]^{17-} \rightarrow M(H_2O)_n{}^+ + \underset{\text{(primarily } anti)}{[(P_2W_{17}O_{61})_2Th]^{18-}} \quad (8)$$

where M = alkali metal.

In 2000, experiments were conducted that defined the stoichiometry and association of cations with polyanion units undergoing reduction in solution. Grigoriev *et al.* prepared a series of nine 1:1 association complexes between alkali-metal cations (M = Li^+, Na^+, or K^+) and three representative vanadium(V)-substituted α-Keggin heteropolytungstates, α-$X^{n+}VW_{11}O_{40}{}^{(9-n)-}$ (X = P^V, Si^{IV}, and Al^{III}) (Equation (9); $y = 1$). The medium used was acetate-buffered 2:3 (v/v) H_2O/Bu^tOH at 60 °C which facilitated control of pH, temperature, and ionic strength.[92] Three lines of evidence are consistent with the formation of 1:1 ion pairs, Equation (9). First, the potentials of the POMs

$$X^{n+}V^VW_{11}O_{40}{}^{(9-n)-} + yM^+ \rightarrow [(M^+)_y(X^{n+}V^VW_{11}O_{40})]^{(9-n-y)-} \quad (9)$$

as a function of M^+ concentration can be fit to the rectangular hyperbolic function in Equation (10), where E_{POM} is the formal one-electron potential of the unpaired polyanion unit (i.e., the $X^{n+}V^VW_{11}O_{40}{}^{(9-n)-}/X^{n+}V^{IV}W_{11}O_{40}{}^{(10-n)-}$ couple), E_{MPOM} is the reduction potential of the 1:1 ion pair, and K_{MPOM} is the association

$$E = (E_{POM} + E_{MPOM}K_{MPOM}[M^+])/(1 + K_{MPOM}[M^+]) \qquad (10)$$

constant (Equation (9), where $y = 1$ or $[\{(M^+)(X^{n+}V^VW_{11}O_{40})\}^{(8-n)-}]/[M^+][X^{n+}V^VW_{11}O_{40}{}^{(9-n)-}]$) (Figure 3). Second, as the concentration for all three alkali metal cations $[M^+]$ decreases, the nine curves converge to three E_{POM} values. These represent one limiting case of the hyperbolic function of $[M^+]$ and Figure 3, where there is no pairing, and the reduction potentials are those of the unpaired POMs. The other limiting case for the Figure 3 curves is the plateau at high $[M^+]$ where nearly all the POM is present as the 1:1 ion pair. Third, plots of E_{POM} vs. the ion-pair charge are linear (Figure 4). The data in this figure follow a relationship noted by Pope that reduction potentials of isostructural Keggin anions in solution decrease linearly with whole-number increments in anion charge.[119,120] This, combined with the other two lines of evidence, confirm the presence of 1:1 ion pairs. In addition, Grigoriev *et al.* used single-step chronoamperometry to calculate the diffusion coefficients, D, for these 1:1 ion pairs which enabled the effective radius of all nine 1:1 reacting ion pairs to be calculated for the first time by using the Stokes–Einstein equation (Equation (11)) where D is the diffusion coefficient of a sphere of radius r in a solvent of viscosity η (k is the Boltzmann constant and T is absolute temperature):

$$D = k\mathrm{T}/6\pi\eta \mathrm{r} \qquad (11)$$

In subsequent work, the effect of the sizes of the cation and the associated $[(M^+)(SiVW_{11}O_{40}{}^{5-})]^{4-}$ ($M^+ = Li^+$, Na^+, K^+) ion pairs—the same ion pairs in Equation (9) above—on both the rate of oxidation of an organic substrate and the energy of electron transfer to these ion pairs was addressed.[93] The organic substrate used was a diphenol (DPH_2) because it is oxidized cleanly by these ion pairs to the corresponding diphenoquinone (DPQ) (Equation (12))

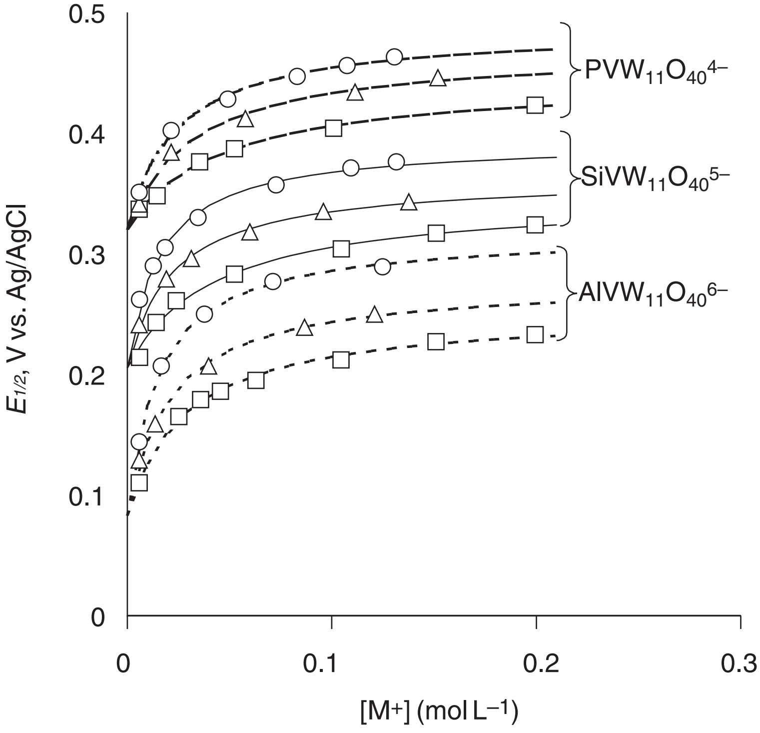
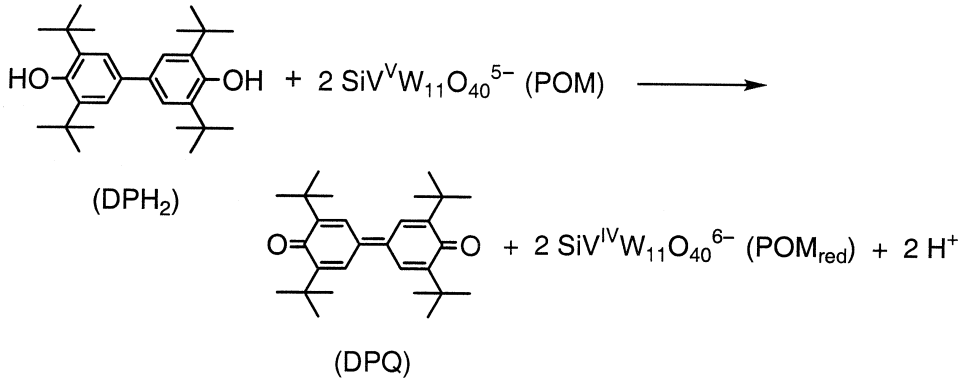


Figure 3 Plot of $E_{1/2}$ vs. $[M^+]$: $M^+ = Li^+$ (squares), Na^+ (triangles), and K^+ (circles) $[M^+]$ = total cation concentration from MCl, POM countercations, and buffer (reprinted with permission of *J. Am. Chem. Soc.* **2000**, *122*, 3544–3545; © American Chemical Society).

maximizing the accuracy of kinetics measurements including a full rate law. The general rate law for this oxidation involves a first term for DPH_2 oxidation by the unpaired polyanion and a second term for DPH_2 oxidation by the 1M:1polyanion pair (Equation (13)). Combining Equation (13) with a mass action equation, Equation (14), provides an



(12)

$$\frac{1}{2}\frac{\mathrm{d}[\mathrm{POM_{red}}]}{\mathrm{d}t} = k_{\mathrm{POM}}[\mathrm{POM}][\mathrm{DPH_2}] + k_{\mathrm{MPOM}}[\mathrm{MPOM}][\mathrm{DPH_2}] \tag{13}$$

$$K_{\mathrm{MPOM}}[\mathrm{M^+}][\mathrm{POM}] = [\mathrm{MPOM}] \tag{14}$$

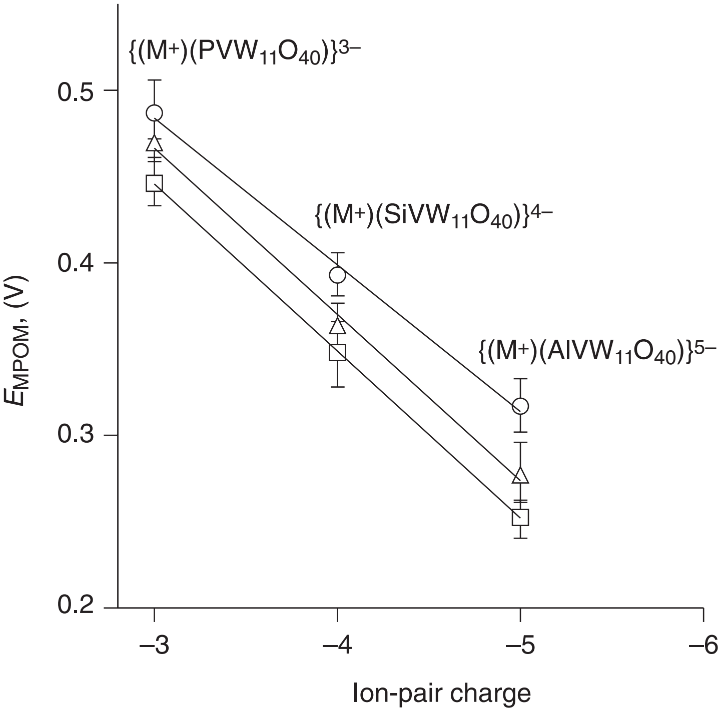


Figure 4 Plot of E_{MPOM} vs. ion-pair charge; $M^+ = Li^+$ (squares), Na^+ (triangles), and K^+ (circles) (reprinted with permission of *J. Am. Chem. Soc.* **2000**, *122*, 3544–3545; © American Chemical Society).

expression for the rate as a function of metal cation concentration, $[M^+]$ (Equation (15)). This, as for the reduction potential data as a function of $[M^+]$ discussed above, is a rectangular hyperbolic function that gives the rate for DPH_2 oxidation by the unpaired POM, k_{POM}, at low $[M^+]$, while the rate for DPH_2 oxidation by the 1M:1POM pair, k_{MPOM}, is asymptotically approached at high $[M^+]$:

$$\frac{1}{2}\frac{d[POM_{red}]}{dt} = \left(\frac{k_{POM} + k_{MPOM}K_{MPOM}[M^+]}{1 + K_{MPOM}[M^+]}\right)[POM][DPH_2] \qquad (15)$$

The factors of 1/2 in Equations (13) and (15) derive from the 2:1 stoichiometry (Equation (12)). The thermodynamic association constants (K_{MPOM}, where $M^+ = Li^+$, Na^+, K^+) and the rate constants for diphenol oxidation (k_{MPOM}, where $M^+ = Li^+$, Na^+, K^+) associated with each 1:1 ion pair were calculated by simultaneous nonlinear fitting of kinetic data (obtained by using all three cations) to Equation (15). The data and the fits to Equation (15) are shown in Figure 5.[93]

Formation constants for the 1:1 ion pairs between the same alkali metal cations and the one-electron reduced form of the POM, $SiV^{IV}W_{11}O_{40}{}^{6-}$, were obtained by using the association constant values for the oxidized POMs (from k_{obs} data) and simultaneously fitting the reduction potential ($E_{1/2}$) values (from cyclic voltammetry) of this POM containing varying concentrations of all three cations to a Nernstian equation describing the dependence of $E_{1/2}$ values on the ratio of thermodynamic formation constants for the 1:1 ion pairs of both the oxidized and reduced POM. These formation constants, K_{MPOM} and $K_{MPOMred}$, and rate constants for diphenol oxidation, k_{MPOM}, all increase with the size of M^+. $K_{LiPOM} = 21 < K_{NaPOM} = 54 < K_{KPOM} = 65\,M^{-1}$; $K_{LiPOMred} = K_{NaPOMred} = 570 < K_{KPOMred} = 2{,}000\,M^{-1}$; and $k_{LiPOM} = 0.065 < k_{NaPOM} = 0.137 < k_{KPOM} = 0.225\,M^{-1}\,s^{-1}$.

The trend in the crystallographic radii of the alkali metal cations ($Li^+ < Na^+ < K^+$) is opposite the trend in their hydrodynamic radii ($Li(H_2O)_n{}^+ > Na(H_2O)_n{}^+ > K(H_2O)_n{}^+$). The larger, less hydrated cations associate more strongly with the polyanion unit, and consequently lower the negative charge density more effectively than the smaller, more hydrated, cations. On this point, it is significant to make clear that the impact of ion pairing on the potential, the driving force for the reaction (and ultimately the rate for electron transfer) depends on not only the pairing of the oxidized species with the counterions but also the pairing of the reduced species with the counterions.[97,121]

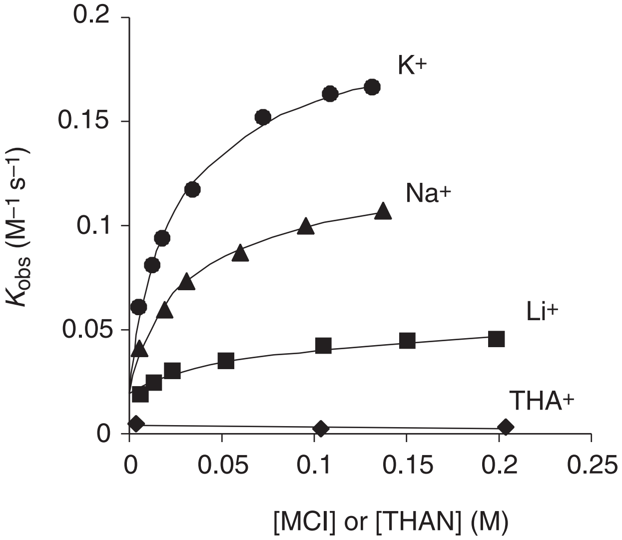


Figure 5 Rate of the outer-sphere electron-transfer oxidation of an organic substrate by a POM (oxidation of 3,3′,5,5′-tetra-Bu^t-biphenyl-4,4′-diol by α-$SiVW_{11}O_{40}{}^{5-}$ to form α-$SiV^{IV}W_{11}O_{40}{}^{6-}$ and the DPQ in ~100% selectivity; Equation (12)) as a function of the cation concentration (counterions + added MCl), $M^+ = K^+$ (top curve); Na^+ (second curve from top); Li^+ (third curve from top), and THAN (the nitrate salt of the nonpairing cation, tetra-*n*-heptylammonium; bottom curve) (reprinted with permission from *J. Am. Chem. Soc.* **2001**, *123*, 5292–5307; © American Chemical Society).

Finally, evidence for the presence of solvent separated ion pairs in the case of the $Li(H_2O)_n^+$ salts of both POM and POM_{red} was obtained from the changes in the ^7Li NMR chemical shifts as a function of the concentrations of the two salts, $Li_5(SiV^VW_{11}O_{40})$ and $Li_6(SiV^{IV}W_{11}O_{40})$.[93]

Thus, work to date is beginning to supply viable experimental approaches and data of value to investigators working with POMs in solution, including information on cation–polyanion association stoichiometries, association constants, and the impact of this pairing on potentials and reactivity. While 1:1 alkali metal–POM pairs can be induced to form when some organic solvent is added to water, it is likely that ion pairing of POMs with typical negative charge densities, including the much-studied Keggin heteropolytungstates, in pure water is minimal. Pairing of divalent cations with POMs in water and pairing of quaternary ammonium or other large hydrophobic cations with the polyanion units in organic solvents has not been examined yet in a compelling or quantitative manner.

4.11.2.1.3 Cation association in POMs with specific metal binding sites

The lacunary or defect forms of most common structural families of POMs have well-defined metal binding sites. Many of the pioneers of POM chemistry in 1950s through the early 1980s including Baker, Souchay, and co-workers; Tourné and Tourné; Pope, Weakley; and others studied the stability of lacunary heteropolytungstates and heteropolymolybdates in the presence of first-row *d*-block metal cations. Many of these early studies provided information, frequently indirectly and most commonly of a qualitative or semi-quantitative nature, on metal ion binding in structurally defined POM sites. A few articles and reviews are noteworthy.[88–90,122–128] Some data on association of simple inorganic ligands such as SO_3^{2-}, $Fe(CN)_6^{4-}$, halides, SCN^-, thiourea, with the *d*-electron-metal sites in these POMs are also given in these early papers.[89] One recent study of ligand binding to *d*-electron addenda atoms is of note as it provides more information on the electronic nature of such interactions than previous studies. Woo *et al.* investigated the binding of pyridine and picoline to the paramagnetic POM $SiW_9O_{37}Cu_3^{10-}$ by ^1H NMR. The complexes with one, two, or three bound picolines could be distinguished and the isotropic shifts of these bound ligands were primarily contact (vs. dipolar) in character. The longitudinal relaxation times (T_1 values) were measured and rationalized in terms of the electronic structure of the three interacting Cu^{II} centers.[129] Metal binding in the conventional (Keggin, etc.) lacunary POMs or ligand association with the related *d*-metal-containing (TMSP) species will not be discussed further here as much of this chemistry predates 1982. It should be noted, however, that there are many metal and ligand binding processes in such systems of considerable fundamental interest and practical value in context with applications that have yet to be investigated.

POMs with specific and structurally well-defined cation binding sites include but are not limited to $[As_4W_{40}O_{140}]^{28-}$,[130,131] $[NaSb_9W_{21}O_{86}]^{18-}$,[132–135] and the Pope–Jeannin–Preyssler ion, $[NaP_5W_{30}O_{110}]^{14-}$.[136,137] Leyrie *et al.* showed that $[As_4W_{40}O_{140}]^{28-}$ exhibits several types of coordination sites that can lead to multi-nuclear complexes of formula $M_1M_{2m}Z_2(H_2O)_2As_4W_{40}O_{140}^{x-}$ where M_1 and M_2 ($m=0$ or 1) are alkali metal and/or alkaline earth cations, and Z is a first-row transition metal cation, particularly Co^{II}.[130] Mononuclear complexes ($m=0$) are obtained with $M_1=Na^I$, Ca^{II}, Cs^I, Sr^{II}, and binuclear ones ($m=1$) are obtained with $M_1=Na^I$ or Ca^{II} and $M_2=K^I$, Rb^I, NH_4^+, Ba^{II}, or $M_1=M_2=Sr^{II}$. The formation of all these complexes in solution was demonstrated and their relative stability constants were assessed by spectrophotometric measurements. Substitution of carboxylated ligands, pyrimidine or adenosine for the aqua ligands in the coordination sphere of the two Co centers was documented for various complexes. The equilibrium constants for binding of adenosine to the mononuclear complexes where $M_1=Na^I$, Ca^{II}, Sr^{II}, are 5×10^3, 3×10^3, and 1.6×10^3, respectively. Association of the alkali metal or alkaline earth cations modulates the reactivity of the Co^{II} center. A structural model was proposed in this early article for the location of the cations M_1 and M_2. This location depends mainly on their size; the cations Na^I, Ca^{II}, and Sr^{II} have no interaction with the oxygens in the coordination sphere of the Co^{II} center. The larger cations are bound to oxygens cis to the H_2O units. The latter cations can be substituted. This research group subsequently studied the metal binding chemistry of these POMs by ^{183}W NMR (the six lines were assigned via one-dimensional-COSY and homonuclear $2J_{W-W}$ coupling values).[131] These authors noted the chemical shift of the resonance line of the tungsten centers near the cryptand site correlates with increasing stability of the M-bound cryptate, and they were able to qualitatively document M exchange rates for the different complexes.

The complex $[NaSb_9W_{21}O_{86}]^{18-}$, first structurally characterized by Weiss and co-workers as the $(NH_4)_{17}Na$ salt,[132] was initially shown by Michelon *et al.* to bind several alkali metal and alkaline earth cations.[133] Subsequently (1992), Liu *et al.* showed this complex binds lanthanide ions by replacing the central clathro-chelated Na^I ion.[135] Contemporaneously, this group reported that this same complex binds Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, and Cu^{II} in the outer sites of this multi-vacant ("multi-nucleating") POM to yield complexes of formula $[NaSb_9W_{21}O_{86}M_4]^{n-}$. Both the *d*-block and *f*-block metal derivatives were fairly well characterized despite the lack of X-ray structures (elemental analysis, visible and IR spectroscopy, magnetic susceptibility, and cyclic voltammetry).[134] Shortly thereafter (1994), Thouvenot and colleagues characterized the alkali metal and alkaline earth derivatives, $[MSb_9W_{21}O_{86}]^{n-}$ (M = alkaline or alkaline earth cation) by ^{183}W NMR.[131] None of these studies entailed full quantitative determination of metal association constants. Such measurements are hard to make in this system. This family of complexes ($[NaSb_9W_{21}O_{86}]^{18-}$ and its metal derivatives) have garnered considerable attention as antiviral agents; however, the role of metal binding in the antiviral activity has been minimally addressed in these biological (*in vitro* and *in vivo*) studies.[138–144]

Jeannin's 1985 X-ray crystal structure of the $[NaP_5W_{30}O_{110}]^{14-}$ showed that the Na ion is encrypted (clathro-chelated) in the central cavity of this complex.[136] Its off-center location reduces the symmetry of this aesthetically appealing polyanion from D_{5h} to the observed C_{5v}, and this, in turn explains the ^{183}W NMR spectrum of the complex in solution.[136] In subsequent work, Pope and his co-workers demonstrated that the weakly bound Na cation in the sterically protected central cavity can be exchanged (120–180 °C for several hours in a sealed vessel) for Ca^{II}, Y^{III} the trivalent lanthanide ions of Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, or the tetravalent ions of Ce and U. The divalent ions of Cd, Sn, Hg, the trivalent ions of Ce and Tl, and the tetravalent ion of Th do not exchange for extended periods up to 180 °C.[137] The exchanged complexes, characterized by cyclic voltammetry, IR spectra, and ^{31}P NMR, are stable from pH 0 to pH 9–10. The biggest single factor in the selectivity of cation binding by this POM appears to be the ionic radius.

In 1999, Kim and Pope prepared the first POMs with uranyl heterogroups. The counterions in these POMs pair with the polyanion units but also control the actual isomers of the POMs that are present. This study is addressed below (Section 4.11.2.2.4).[145]

4.11.2.2 Rearrangements and Isomerizations

4.11.2.2.1 General points

The lability of bonds between d^0 transition metals and oxygen that constitute metal oxides and nearly all POMs, underlie nearly all rearrangement and isomerization reactions of POMs. Unfortunately, despite the ubiquity of these bonds in POMs and the importance of their reactions to a host of POM-related or -dependent phenomena, including but not limited to catalysis, this chemistry has largely been ignored in general inorganic texts including Cotton and Wilkinson,[146] Kepert's book on the early transition metals,[147] and Baes and Mesmer's book on the speciation chemistry of coordination complexes in water.[148] These and similar informative books do not significantly address the structural and electronic basis of the relative reactivities of different oxygens or the mechanism of processes involving exchange of these bonds. Fortunately useful reviews on oxygen exchange in low nuclearity oxoanions by Murmann and others have been published.[149–151]

The lability of these early transition metal–oxygen bonds relates to one fairly general experimental observable, the rate of oxo exchange between POMs and H_2O. In consequence, we will first address these processes (Section 4.11.2.2.2) with the understanding that in many studies of POM oxo-H_2O oxygen exchange, they cannot reasonably and should not be separated from intramolecular POM oxygen exchange ("atom scrambling") processes (Section 4.11.2.2.3). Indeed, rapid intramolecular oxygen exchange can, in principle, transpire subsequent to bimolecular reaction with water en route to the final products actually observed by ^{17}O NMR. If this does happen, a misleading distribution of isotopically labeled POMs could well be generated. Similarly, it is hard to rule out the involvement of some intermolecular POM oxo-H_2O oxygen exchange in processes that appear to involve strictly intramolecular oxygen scrambling in POMs. Oxygen-17 NMR has been the dominant technique used to probe and quantify both POM oxo-H_2O oxygen exchange and intramolecular POM oxygen exchange processes. It also is the most suitable technique for other aspects of POM chemistry including the interpretation of dynamic NMR spectra, determination of protonation sites, and structure determination of mixed metal POMs.[152]

Unfortunately, the lack of a systematic comparison of the rates of various processes in different POM systems under the same experimental conditions hampers attempts to understand POM reactions, let alone quantitatively predict them.

4.11.2.2.2 Polyoxometalate–water oxygen exchange

General trends and points are first presented followed by discussion of specific literature studies in roughly chronological order. The bonds between d^0 transition metals and oxygen typically increase in strength and decrease in lability as one goes down each column in the *d*-block. This important kinetic phenomenon has been known for some time, but little quantified in POM systems. In particular, Mo^{VI}—O bonds are a little weaker and thus more labile than corresponding W^{VI}—O bonds.[1,153,154] Although less documented, Nb^V—O bonds are, likewise, more labile than the corresponding Ta^V—O bonds in identical clusters (e.g., $M_6O_{19}{}^{8-}$).[152] This greater lability of d^0 transition metal–oxygen bonds in the lighter transition metals has been seen in oxygen exchange between POMs and water,[152] POM substitution reactions,[155] and in the hydrolytic or acid–base chemistry of POMs in general.[57,156–158]

A related and well-known but effectively unquantified phenomenon is that POM lability is greatly reduced in organic solvents. The addition of even small percentages of either polar protic solvents such as alcohols or polar aprotic solvents such as acetonitrile, DMF, and DMSO to aqueous solutions of POMs greatly reduces the rate of POM reactions.[107,152,159–162] The medium one is using impacts the rates of intramolecular processes such as rearrangements and isomerizations as well as intermolecular processes.

Specific literature studies begin with that of Geier and Brubaker who used ^{18}O to probe POM oxo-H_2O oxygen exchange in orthotungstate and $CoW_{12}O_{40}{}^{5-}$. They reported that in aqueous solution at 25 °C, oxygen exchange in the former is complete in minutes but negligible in the latter.[163] The most studied POM with respect to POM oxo-H_2O oxygen exchange is decavanadate, $V_{10}O_{28}{}^{6-}$. First, Harrison and Howarth[164] pointed out that Klemperer and Shum in their ^{17}O NMR study of the protonation and negative charge distribution in $V_{10}O_{28}{}^{6-}$ showed data that indicated all the oxo ligands in $V_{10}O_{28}{}^{6-}$ exchanged at the same rate.[165] Shortly thereafter, Murmann and Giese studied both oxygen exchange and POM decomposition for $V_{10}O_{28}{}^{6-}$.[166] Oxygen exchange and decomposition kinetics in $V_{10}O_{28}{}^{6-}$ was followed using $H_2{}^{18}O$. First, the labeled $V_{10}O_{28}{}^{6-}$ in exchanging or reacting aliquots was precipitated as the Cs^+ salt. Next, the Cs^+ salt was dried, and all its oxygen atoms were converted to CO_2. Finally, the isotopic composition of the CO_2 was quantified by mass spectrometry. Given the complexity of the decavanadate structure and the difficulty in getting extensive kinetic data using such a laborious data collection procedure, it would be reasonable to expect that minimal insights regarding oxygen exchange and decomposition could be derived from the kinetic data. However, like Klemperer and Shum, these investigators found that all the oxygens exchanged at essentially the same rate. This allowed rate constants and activation parameters to be estimated under pseudo-order conditions. Oxygen exchange for 0.01 M solutions of $V_{10}O_{28}{}^{6-}$ in the pH range 4.0–6.3 has a half-life of ~15 h at 25 °C with a small ionic strength dependence. The rate increases dramatically below pH ~ 4.0, and decreases above pH ~ 6.3, reaching essentially zero at $pH > 10.0$. At $pH \sim 6.3$, $\Delta V^\ddagger = -5.0 \pm 2\,cm^3\,mol^{-1}$, $\Delta H^\ddagger = 31 \pm 0.5\,kcal\,mol^{-1}$, and $\Delta S^\ddagger = -7 \pm 0.5\,cal\,mol^{-1}\,K^{-1}$. The authors' interpretation of the similar ^{18}O exchange and POM decomposition kinetics led them to propose a mechanism involving a partially bonded intermediate common to both pathways. A $^{49}VO_4{}^{3-}$ transfer experiment during oxygen exchange and POM dissociation was in agreement with this mechanism.[166]

There was some controversy over the protonation sites in $V_{10}O_{28}{}^{6-}$,[165,167] but a combination X-ray diffraction, vapor pressure osmometry, and multinuclear solution NMR study indicated the protons reside on two OV_2 (doubly bridging) and one OV_3 (triply bridging) oxygens that are roughly colinear in the structure.[84] However, this work used quaternized organic salts and acetonitrile or mixed acetonitrile/H_2O solutions; whereas, a great majority of the other studies of POMs–water oxygen exchange used purely aqueous media. Extrapolating results from organic media or mixed aqueous–organic media to purely aqueous media could be problematical.

In 1981, Fedotov *et al.* reported the observed rate constants for exchange of the different oxygens in $PW_{12}O_{40}{}^{3-}$ and $PV_XW_{12-X}O_{40}{}^{(3+X)-}$ ($X = 1$–4) under pseudo-order conditions in H_2O by ^{17}O NMR at two different temperatures (20 °C and 70 °C). Unfortunately, neither the POM concentrations nor the pH values were stated, and the exchange rates could well vary with these parameters. Given this uncertainty, however, the following reactivity order and rates of exchange ($k_{ex} \times 10^6$ s^{-1} at 70 °C) were found for $PVW_{11}O_{40}^{4-}$: V═O fastest (104) > W═O (97) ~ V—O—W (97) > W—O—W (51). All rates decrease substantially and the rate differences for the different oxygens increase modestly as the vanadium content (the value of x) increases. Exchange in the W—O—W groups of $PV_{2-4}W_{8-10}O_{40}^{(5-7)-}$ is very slow (no values given). The parent compound, $PW_{12}O_{40}^{3-}$, shows very little oxygen exchange at 20 °C after 1 year indicating that the V—O bonds have a labilizing role. The authors also state, although no specific data are provided, that the corresponding vanadopolymolybdates, $PV_xW_{12-x}O_{40}^{(3+x)-}$ ($x = 1$–4), are about two orders of magnitude more labile than their vanadopolytungstate analogues.[154]

A subsequent (1984) study, that of Besecker *et al.* on the isomers of $[\{(Me)_5C_5\}Rh(cis\text{-}Nb_2W_4O_{19})]^{2-}$, also provides data, qualitative in this case, on the relative rates of POM oxo-H_2O oxygen exchange for oxygens in the same POM but bound to different d^0 metals. In the *cis*-$Nb_2W_4O_{19}^{2-}$ (C_{2v} symmetry) unit, the terminal Nb^V—O oxygens and the Nb^V—O—Nb^V oxygens exchange with H_2O in MeCN solution in less than 10 min at 25 °C, while the Nb^V—O—W^{VI} oxygens require many hours to exchange. The W^{VI}—O—W^{VI} oxygens exchange more slowly still. These highly variable oxygen exchange rates in the POM unit prevented more quantitative investigation of the isomerism of the organometallic unit (see below).[168] Pettersson and co-workers have indicated that equilibrations in the vanadophosphate system in 0.6 M Na(Cl) medium at 25 °C require months to years to reach equilibrium. This is significantly slower than equilibration in mixed vanadomolybdate systems.[59]

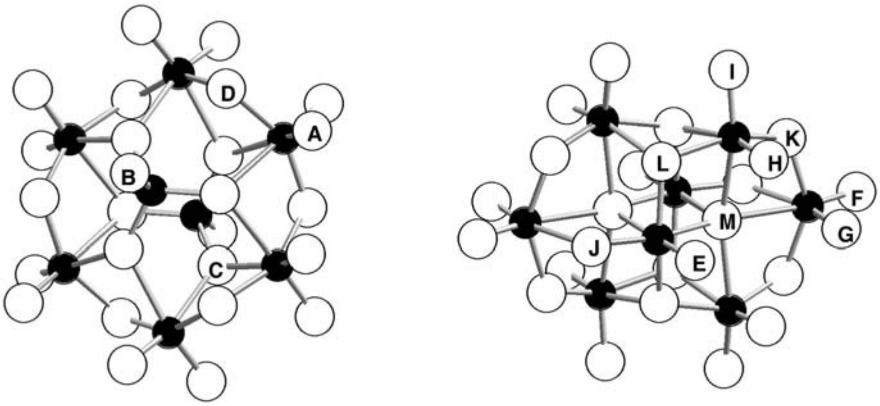
In 1985, using ^{17}O NMR, Harrison and Howarth showed that, in contrast to $V_{10}O_{28}^{6-}$, $HPV_{14}O_{42}^{8-}$ (a dicapped Keggin complex first published by Sasaki and co-workers[169]), exchanges different oxygens at different rates like the common Keggin HPAs.[164] They reported rate constants under pseudo-first-order conditions (large excess of H_2O) for POM oxo-H_2O oxygen exchange for all the symmetry distinct oxygens at pH 2, 3, 5.5, and 7. Not surprisingly, the oxygens associated with the cap exchange fairly rapidly at all pH values consistent with these caps being cationic components added to stabilize the Keggin structure by reducing the excessive negative charge.[169,170] The relative reactivities of the different oxygens are consistent with the likely protonation sites on $HPV_{14}O_{42}^{8-}$ suggested by these investigators. The relative exchange rates of the different oxygens change as the pH is lowered. Interestingly, the terminal oxygens exchange very slowly at all pH values. The authors propose that this is because the labilization process(es) involving these oxo ligands simultaneously labilizes other oxygens that exchange more rapidly than the terminal oxo ligands themselves.[164]

In 1996, Kozhevnikov *et al.*[153] conducted a revealing ^{17}O MAS NMR study of oxygen exchange between solid ^{17}O-labeled $H_3PMo_{12}O_{40}$ and H_2O at 200–250 °C. Since the ratio of enrichment of the different oxygens in the POM appeared to be independent of temperature and the same within experimental error as that for the fully equilibrated POM in labeled water, they inferred that an intramolecular (intra-Keggin) scrambling process was proceeding far faster than the intermolecular POM oxo-H_2O oxygen exchange process itself. Interestingly, the internal oxygens exchanged far slower under these conditions. The rates of POM oxo-H_2O oxygen exchange for the corresponding heteropolytungstate, $H_3PW_{12}O_{40}$, were far lower but unfortunately, no ratio of rates can be inferred from their data.[153]

In summary, with the limited data currently available, the rates of POM oxo-H_2O oxygen exchange processes appear to depend most of all on the metal to which the oxygen is bound (Mo^{VI} faster > W^{VI}, $Nb^V > Ta^V$, and + 5 metals > + 6 metals). They also depend significantly on the structure and composition of the POM. Mixed addenda POMs (more than one d^0 metal in the external or solvent accessible sites) usually but not always exchange more rapidly than POMs with a single metal in these sites. Exceptions are cases where oxygen is bound to at least two fairly labile metal centers. Higher negative charges on the polyanion unit appear to slow exchange. However, studies that report (control) all factors that likely impact these oxygen exchange rates including pH, POM concentration, ionic strength, and metal counterion concentration are needed to be sure of some of these trends and certainly to quantify them. The possibility (probability) of specific or general acid or base catalysis has not been addressed fully. Finally it is unequivocal that organic solvents slow these exchanges as they do other reactions associated with polyanion units.

4.11.2.2.3 Intrapolyoxometalate oxygen exchange

Nearly all quantitative data in this area have appeared in the time-window of this review. In early work, Klemperer and Shum conducted an IR study that indicated both α and β isomers of



α-$Mo_8O_{26}^{4-}$ β-$Mo_8O_{26}^{4-}$

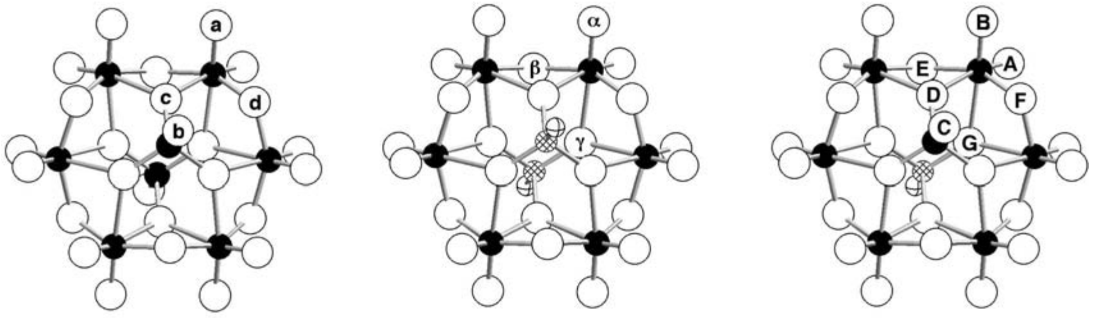
Figure 6 The two isomers of octamolybdate with the symmetry-distinct oxygens labeled.

$Mo_8O_{26}^{4-}$ (Figure 6) equilibrate in acetonitrile solution and at higher temperatures convert irreversibly to $Mo_6O_{19}^{2-}$. A mechanism for the α–β isomerization of $Mo_8O_{26}^{4-}$ that preserved the center of inversion was proposed but no experimental evidence for it was offered.[171] Subsequently, Day *et al.* conducted a variable temperature ^{17}O NMR study of α-$Mo_8O_{26}^{4-}$ and showed that the resonances of two of the four symmetry-distinct oxygens (O_B and O_C; see Figure 6) broadened with increasing temperature while those of O_A and O_D did not. They also reported that the H_2O peak remained a triplet even at the highest temperature of the investigation (30 °C).[172] Since line broadening for resonances of different quadrupolar nuclei such as ^{17}O ($I = 5/2$) in a single molecule (i.e., different symmetry distinct oxygens in a POM) should not change with temperature by differing amounts if the broadening is associated with spin–spin splitting or quadrupolar effects, then the temperature-dependent changes in the line widths in the spectrum of α-$Mo_8O_{26}^{4-}$ are very likely due to chemical exchange. The temperature dependence of peak widths for quadrupolar nuclei is expressed in Equation (16), where η is the electric field gradient asymmetry parameter, ($e^2Qq/\hbar$) is the quadrupolar coupling constant and τ_c is the correlation time for molecular rotation. The only temperature dependent term is τ_c and this is constant

$$\upsilon_{1/2} = \frac{1}{\pi T_2} = \frac{1}{\pi T_1} = \frac{3}{125\pi}\left(1 + \frac{\eta^3}{3}\right)\left(\frac{e^2Qq}{\hbar}\right)^2 \tau_c \qquad (16)$$

for different nuclei in the same molecule. In other words, if there is no chemical exchange in a rigid molecule isotropically tumbling in a homogeneous medium, the temperature-dependent change in peak widths for all symmetry equivalent ^{17}O resonances should be the same. Since the water oxygen peak remained a triplet indicative of no exchange with the POM oxygens, and the terminal and bridging oxygens in the apical or "cap" MoO_4^{2-} units in this POM (O_B and O_C, respectively) were changing with temperature and the terminal and bridging oxygens of the central $(MoO_3)_6$ ring (O_A and O_D, respectively) were not, these authors concluded that the former POM oxygens were exchanging and the latter POM oxygens were not. This is reasonable given that the cap MoO_4^{2-} units, based on Mo—O bond distances from X-ray structures, are more weakly bound to the $(MoO_3)_6$ ring portion of the POM than the ring MoO_3 units in the ring are bound to each other.[172] There are a number of POMs based on the mono- or dicapping of $(MoO_3)_n$ rings for which this finding is likely relevant including $(AsO_4^{3-})_2(Mo_6O_{18})$,[173,174] $(C_6H_5AsO_3^{2-})_2(Mo_6O_{18})$,[174,175] $(RAsO_3^{2-})_2(Mo_6O_{18})$ (R = Me, *p*-$C_6H_4NH_2$),[175] $(PO_4^{3-})_2(Mo_5O_{15})$,[176] and $(RPO_4^{2-})_2(Mo_5O_{15})$, R = $NH_3C_2H_4$, the first zwitterionic HPA, and Me.[177]

Pope and co-workers contemporaneously prepared and investigated organoarsonate- and organophosphonate-capped hexamolybdates,[178] hexatungstates,[179] and pentatungstates.[180] They investigated interconversion of two such structures in acetonitrile solution and suggested a new pathway for the hydrolysis of polyoxoanion units.[178] They also used NMR line shape analysis to investigate the protonation of bridging hydroxo oxygens and subsequent H_2O exchange in these compounds.[179] Much of this initial work was summarized in a short review article.[181]



α-$Mo_8O_{26}{}^{4-}$ α-$(RAs)_2Mo_6O_{24}{}^{4-}$ α-$(RAs)Mo_7O_{25}{}^{4-}$

Figure 7 Three dicapped-ring polymolybdates whose rearrangements have been studied by variable temperature ^{17}O NMR. Only the ipso (connecting) carbon of the phenyl rings is shown (spheres with cross lines).

Subsequently, Pope, Brévard, and co-workers examined isomerization in the organophosphonates, $(C_6H_5PO_3)_2W_5O_{15}{}^{4-}$ by dynamic ^{183}W NMR as well as ^{17}O NMR.[180] NMR, IR, and X-ray power diffraction data indicated these polytungstates were isostructural to the polymolybdates investigated by the other groups. The ^{183}W NMR of this complex in acetonitrile at 235–306 K is a single 1:2:1 triplet ($^2J_{W—O—P} = 1.95\,Hz$) which is consistent with a rapid intramolecular rearrangement of the POM structure. The authors propose a pseudorotation of the nonplanar five-membered ring of corner-shared WO_4 tetrahedra capped on both sides by fluxional $PhPO_3$ groups.[180]

In 1985, Klemperer and co-workers followed up their preliminary report of a variable-temperature NMR and structural study on α-$Mo_8O_{26}{}^{4-}$ with a more detailed ^{17}O NMR study of the intramolecular rearrangements of the capping polymolybdates. They examined α-$Mo_8O_{26}{}^{4-}$ as before but now also two other POMs constituted by cap units on a Mo_6O_{18} ring, $(C_6H_5As)_2Mo_6O_{24}{}^{4-}$ and $(C_6H_5As)Mo_7O_{25}{}^{4-}$ (Figure 7).[174] In addition to the line broadening experiments they addressed in the earlier report, they also conducted ^{17}O spin saturation transfer techniques, and ^{17}O label crossover experiments on all three of these POMs. $(C_6H_5As)Mo_7O_{25}{}^{4-}$ exhibits two types of fluxional behavior, a low temperature process that involves Mo_6O_{18} ring inversion accompanied by twisting of the $C_6H_5AsO_3{}^{2-}$ subunit and twisting of the capping $MoO_4{}^{2-}$ subunit, and a higher temperature process that involves cleavage of stronger Mo—O bonds. The latter process is mechanistically undefined.

In 1988, Howarth and Kelly, using a partially selective ^{17}O inversion sequence (T_1 and T_2 values were too short to render two-dimensional NOESY and DANTE methods practical) demonstrated that oxygen exchange in the common isopolyanion, $Mo_7O_{24}{}^{6-}$, does not involve the H_2O solvent but rather exchange of terminal and bridging oxygens of the POM.[182] In 1990, these investigators, in a collaboration with Pettersson, used ^{17}O and ^{95}Mo NMR to study Mo^{VI} in aqueous solution from pH 6 to pH 1.2 and obtained evidence for the conversion of $Mo_7O_{24}{}^{6-}$ to β-$Mo_8O_{26}{}^{4-}$ via observing the sequential intermediates in this transformation: monoprotonated $Mo_7O_{24}{}^{6-}$, a second intermediate, and then $H_3Mo_8O_{28}{}^{5-}$, a third intermediate.[183]

In 1996, Andersson *et al.* studied oxygen and vanadium exchange in linear vanadate oligomers at pH 10–12.3.[184] They confirmed the existence of V_3 and V_4 species. Peak broadening was largely but not exclusively due to chemical exchange. Line widths and magnetization transfer experiments indicated that oxygen and vanadium exchange is independent of the solvent and the monomeric or the dimeric vanadates also present. The broadenings are consistent with the presence of an intermediate, probably a cyclic structure. Interestingly, simple proton transfer between the oxygens in the monoprotonated monovanadate anion is sufficiently slow to be detectable by NMR spectroscopy.[184]

4.11.2.2.4 Isomerization of polyanion units

There have been studies of polyanion unit isomerization in the solid state but such isomerizations are more problematical to quantify and unequivocal inferences from them are harder to come by than from the analogous studies in solution. The difficulty derives in part because high-quality kinetics data are hard to obtain for reactions in the solid state. Nonetheless, some reports on solid-state POM isomerization in the time period of this review afford valuable insights.

In 1995, Wachs and co-workers disclosed that exposure of MoO_3 on silica to water-saturated air for several hours leads to the formation of surface $H_4SiMo_{12}O_{40}$. This process was followed by *in situ* Raman spectroscopy, TGA, and selective oxidation of MeOH to $CH_2{=}O$.[185] A significant and phenomenologically related but hard to categorize investigation by Lambert, Che, and co-workers should be noted here. These chemists demonstrated that suspending alumina in a tungstate solution, even at near-neutral pH values, leads to the formation of polytungstoaluminate species in solution.[186,187] In 1996, Trifirò, Finke, and co-workers documented (FTIR, XRD, TGA, and TEM) evidence for the solid-state rearrangement of the Wells-Dawson POM, $K_6P_2W_{18}O_{62}\cdot 10H_2O$, to a stable Keggin-type HPA phase.[188] Also in 1996, Kawafune and Matsubayashi gave the rate constants, activation parameters, and the kinetic impact of some ion pairing effects on the solid-state isomerization of A-β-$PV_3W_9O_{40}{}^{6-}$ to its corresponding α isomer.[189]

There have been many attempts to rationalize the structure and isomers of Keggin HPAs, the most common and investigated class of POMs. Since component substructures in the Keggin ion, including but not limited to the M_3O_{13} triad, are common to most POMs, understanding the Keggin structure would be insightful to the study of POMs in general. The principal isomers of the Keggin structure result from 60° rotation and re-attachment of one, two, three, and four M_3O_{13} triads that comprise the overall polyanion. These different compounds were referred to as the β, γ, δ, and ε isomers, respectively, by Baker and Figgis.[190] There has been disagreement regarding the relative stabilities of the two most common isomers, α and β, in the regular (fully oxidized) Keggin POMs. The simple electrostatic assessment of bonding in POMs argues that the α and β isomers should be the most stable and of similar energies because all four M_3O_{13} triads in both structures are connected by corner-shared contacts; whereas, the γ, δ, and ε isomers should be less stable because the intertriad corner-sharing linkages are replaced successively with edge-sharing linkages. This follows because the main electrostatic component in the energy of the polyanion unit is M^{VI}—M^{VI} ($M = Mo$ or W) repulsion and corner-sharing (μ-oxo linked) MO_6 octahedra have longer M—M distances than edge-sharing (di-μ-oxo linked) MO_6 octahedra ($d_{W—W} = \sim 3.7$ Å and ~ 3.4 Å, respectively).[191] However, experimental evidence indicates that α isomers are more stable than β isomers.[91,192,193] For example, isomerization always proceeds β to α.[13,106] Indeed, one reason equilibrium concentrations of α and β isomers have not been determined until recently is that these isomerizations proceed to completion (i.e., there is not enough of the less stable β isomer remaining at equilibrium to quantify its concentration). Quantitative experimental data to address this and other stability and lability issues associated with the different isomers of the Keggin and other POM structures have been lacking until recently.

In 1983, Kircher and Crouch conducted a stopped flow kinetics investigation of the formation and decomposition of $PMo_{12}O_{40}{}^{3-}$ at 25 °C and 3.0 M ionic strength as a function of solution pH and Mo(VI) concentration. The kinetics are complex which prohibited many molecular aspects of the mechanism to be unequivocally determined. They proposed that isomerizations of Keggin species take place through lacunary (defect) intermediates.[194] In 1986, Canny *et al.* also made this proposal based on the isolation of many thoroughly characterized Keggin lacunary and other derivatives.[106]

In 1999, Weinstock *et al.* quantified the equilibria between the α and β isomers of a Keggin complex, $AlW_{12}O_{40}{}^{5-}$, and the α and β isomers of the corresponding lacunary form, $AlW_{11}O_{39}{}^{9-}$ in solution. Pure α and β isomers of $H_5AlW_{12}O_{40}$ were first prepared and then aqueous solutions of each heated to form the same ratio of products. The equilibrium ratio of β to α (k_1/k_{-1}), K_{eq}(473 K, 0.1 M), is 0.11 ± 0.01. This translates (via $\Delta G = -RT \ln K_{eq}$) to the α isomer being more stable than β isomer by 2.1 ± 0.5 kcal mol^{-1}.[97] First-order rate constants for the approach to equilibrium of α- and β-$H_5AlW_{12}O_{40}$ at 473 K are $k_{1\alpha\rightarrow\beta} = 7.68 \times 10^{-7}\ s^{-1}$ and $k_{-1\beta\rightarrow\alpha} = 6.97 \times 10^{-6}\ s^{-1}$ (see Figure 8). Likewise, the pure α and β isomers of $K_9AlW_{11}O_{39}$ were prepared and solutions of each were equilibrated (0.13 M in D_2O, 333 K at natural pH values of ca. 7) to produce a 60:40 molar α:β mixture which translates to a $K_{Equation} = 1.5$, and an energy difference of 0.3 kcal mol^{-1}. A trend was established in the relative stabilities of the β isomers: $X = Al^{III}$-β most stable $> Si^{IV} > P^{V}$.[97] Subsequent work by Cowan *et al.* further established the roles of kinetic and thermodynamic control in the formation and isomerization of Keggin polytungstoaluminates.[91]

Independently, theoretical work by Poblet and co-workers on the relative energies of α and β Keggin isomers as a function of the heteroatom and other parameters of the polyanion ion unit also indicated that the stability of the β isomer relative to the α isomer decreases in the order $Al^{III} > Si^{IV} > P^{V}$.[95,195] The higher stability of β-$Al^{III}W_{12}O_{40}{}^{5-}$ is attributed to an electronic effect of a large, electron-donating heteroatom moiety ($AlO_4{}^{3-}$) encapsulated inside a polarizable fixed-diameter β-$W_{12}O_{36}$ shell. No unique structural distortion of the β Keggin structure (or β-$W_{12}O_{36}$

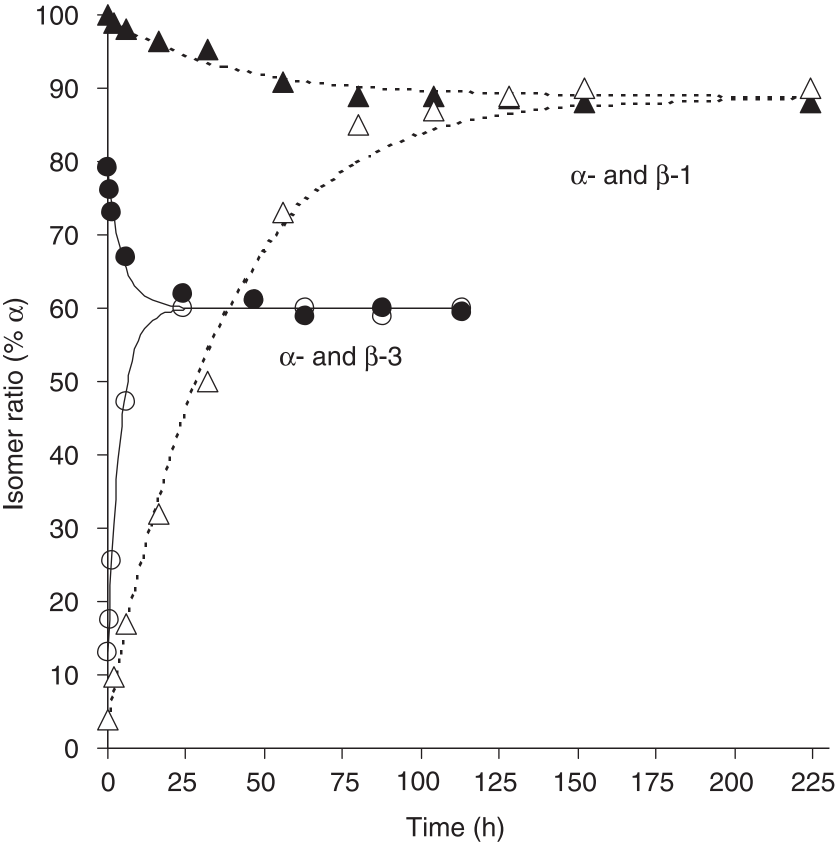


Figure 8 Isomerization of α-$AlW_{12}O_{40}^{5-}$ (α-(**1**); black triangles) and β-$AlW_{12}O_{40}^{5-}$ (β-(**1**); open triangles) and of α-$Na_9AlW_{11}O_{39}$ (α-(**3**); black circles) and β-$Na_9AlW_{11}O_{39}$ (β-(**3**); open circles). Approach to equilibrium between α-(**1**) and β-(**1**) shown by dashed curves; approach to equilibrium between solutions initially containing mostly α-(**3**) (82% α, 18% β) and mostly β-(**3**) (87% β, 13% α) in D_2O is shown by solid curves (reprinted with permission from *J. Am. Chem. Soc.* **1999**, *121*, 4608–4617; © American Chemical Society).

neutral shell) is needed to explain the observed β:α ratios in the series of Keggin POMs. These specific structural findings from the DFT computations were confirmed by a detailed analysis of the X-ray crystal structure of the β-$Cs_{4.5}K_{0.5}Al^{III}W_{12}O_{40}\cdot 7.5H_2O$ with previously published structures of the α isomer of $Al^{III}W_{12}O_{40}^{5-}$ and the α and β isomers of $Si^{III}W_{12}O_{40}^{4-}$.[98]

In 1999, Kim and Pope prepared the first POMs with uranyl hetero groups. Solid Na_9 [A-PW_9O_{34}] was added to aqueous $UO_2(NO_3)_2$ (0.2 M in NaCl). Adding additional NaCl, KCl, or NH_4Cl produced crystals of formula $[M_2(UO_2)_2(A\text{-}PW_9O_{34})_2]^{12-}$, where $M = Na^+$, K^+, or NH_4^+, respectively.[145] X-ray crystallography established that the Na^+ salt is of C_i symmetry with equivalent tetrahedrally coordinated Na^+ centers in the central cavity. In contrast, the K^+ and NH_4^+ salts are of C_s symmetry with one cation in a central site and one external to the structure. Both ^{31}P and ^{183}W NMR show the solid state structures for all three compounds persist in solution and that addition of either K^+ or NH_4^+ salts to the disodium POM results in formation of the C_s symmetry potassium or ammonium POMs.[145] The NMR spectra indicate that the external cation in the latter POMs is in rapid exchange so as not to lower the symmetry of the POMs in solution below C_s. These cation-induced rearrangements are defined by the equilibria in Equation (17), and the equilibrium constants for these processes, K_{eq}, assessed by the same techniques, are 128 ± 12 and 1.8 ± 0.8, for K^+ and NH_4^+, respectively. The presence of calcium ions produces a POM with C_i symmetry based on the NMR spectra but the resulting calcium complex was not studied further:

$$[Na_2(UO_2)_2(A-PW_9O_{34})_2]^{12-} + 2M^+ \rightarrow [M_2(UO_2)_2(A-PW_9O_{34})_2]^{12-} + 2Na^+ \qquad (17)$$

where $M = K^+$ or NH_4^+.

M_3O_{13} triad attachment (Baker–Figgis) isomerization has also been repeatedly addressed in the Wells–Dawson polyoxotungstates. However, nearly all these studies, like those involving Keggin complexes, are purely structural in nature (synthesis coupled with spectroscopic and/or X-ray crystallographic data).[13] Quantitative thermodynamic or kinetic information was not reported. Purely structural studies are not the focus of this review but some of these informative studies have been and will be mentioned here to put the reactivity studies in full context.

In 2002, a full kinetic investigation of the Baker-Figgis (β to α) isomerization in the classical polytungstophosphates, α- and β-$P_2W_{18}O_{62}^{6-}$, was undertaken.[196] The α isomer was determined to be more stable than the β isomer in the solid state by differential scanning calorimetry (4.36 ± 0.64 kcal mol^{-1}) and in solution by ^{31}P NMR (3.80 ± 0.57 kcal mol^{-1}). The k_{obs} for conversion of β-$P_2W_{18}O_{62}^{6-}$ to α-$P_2W_{18}O_{62}^{6-}$ at 343 K in pH = 4.24 acetate buffer, followed by ^{31}P NMR, is $5.3 \pm 0.4 \times 10^{-5}$ s^{-1}.

Several lines of evidence establish the validity of proposals in the literature that isomerization goes through a lacunary (defect) intermediate.[106,194] First, the rate is proportional to [OH$^-$]. Second, isomerization increases at higher ionic strengths, and a Debye–Hückel plot is consistent with a rate limiting reaction between β-$P_2W_{18}O_{62}^{6-}$ and OH$^-$ (two species with a charge product = six). Third, alkali metal cations stabilize the bimolecular transition state ($K^+ > Na^+ > Li^+$) consistent with recent ion pairing studies in POM systems. Fourth, the mono-vanadium substituted products, α_1- and α_2-$P_2VW_{17}O_{62}^{7-}$ (^{51}V NMR, $\delta = -554$ ppm), form during isomerization in the presence of VO^{2+} (yield 19%). The known lacunary compounds (α_1- and α_2-$P_2W_{17}O_{61}^{10-}$) also react rapidly with the same vanadium precursor. Fifth, solvent studies establish that isomerization does not occur when OH$^-$ is absent. A mechanism is proposed involving attack of OH$^-$ on β-$P_2W_{18}O_{62}^{6-}$, loss of monomeric W^{VI} from the M_3 (M_3O_{13}) terminal cap, isomerization of the resulting lacunary compound to α-$P_2W_{17}O_{61}^{10-}$, and finally reaction of this species with monomeric W^{VI} to form the thermodynamic and observed product, α-$P_2W_{18}O_{62}^{6-}$.

4.11.2.2.5 Isomerization of surface bound organometallic units

The 1984 study of Besecker *et al.* on the isomers of $[\{(Me)_5C_5\}Rh(cis\text{-}Nb_2W_4O_{19})]^{2-}$ was mentioned in Section 4.11.2.2.2 as providing information on POM oxo-H_2O oxygen exchange. This complex was prepared by a simple displacement reaction in CH_2Cl_2 solution, Equation (18), and

$$2Nb_2W_4O_{19}^{4-} + [\{(Me)_5C_5\}RhCl_2]_2 \rightarrow 2[\{(Me)_5C_5\}Rh(Nb_2W_4O_{19})]^{2-} + 2Cl^- \qquad (18)$$

the ^{1}H NMR indicates that only two of the possible diastereomers of the product are formed.[168] However, in $MeNO_2$ or MeCN solution in the presence of $[\{(Me)_5C_5\}RhS_3]^{2+}$ (S = $MeNO_2$ or MeCN) at ambient temperature, a third diastereomer is formed. The mechanism proposed for this involves association of a second $[(Me)_5C_5]Rh^{2+}$ with the POM via Equations (19) and (20). Two possible geometries for the 2:1 adduct intermediate, $[\{(Me)_5C_5\}Rh(Nb_2W_4O_{19})Rh\{(Me)_5C_5\}]$, were proposed based on spectral data and steric arguments. While is it reasonable that this adduct would be more labile than the 1:1 complex of the reactants, $[\{(Me)_5C_5\}Rh(Nb_2W_4O_{19})]^{2-}$, based on electrostatic arguments, no direct kinetic or other hard evidence for it was provided. Multiple detailed mechanisms could proceed by the general processes in Equations (19) and (20):[168]

$$[\{(Me)_5C_5\}Rh(Nb_2W_4O_{19})]^{2-} + [\{(Me)_5C_5\}RhS_3]^{2+} \rightarrow$$

two diastereomers

$$[\{(Me)_5C_5\}Rh(Nb_2W_4O_{19})Rh\{(Me)_5C_5\}] + 3S \qquad (19)$$

$$[\{(Me)_5C_5\}Rh(Nb_2W_4O_{19})Rh\{(Me)_5C_5\}] + 3S \rightarrow$$

third diastereomer

$$[\{(Me)_5C_5\}Rh(Nb_2W_4O_{19})]^{2-} + [\{(Me)_5C_5\}RhS_3]^{2+} \qquad (20)$$

Two subsequent studies by Finke and co-workers also addressed isomerism or potential isomerism of organometallic units bound to the surfaces of POMs. In 1995, Pohl *et al.* studied the ^{1}H, ^{13}P, ^{31}P, and ^{183}W NMR of TBA$_5$Na$_3$[(1,5-COD)M·P$_2$W$_{15}$Nb$_3$O$_{62}$] (M = Ir and Rh) in DMSO solution in the presence and absence of a bicyclic crown chelating agent.[115] The spectral changes are likely due to some fluxionality in the binding position of the (1,5-COD)M$^+$ unit. A main argument for this fluxionality was indirect, namely Day *et al.* had previously demonstrated that (1,5-COD)IrP$_3$O$_9$$^{2-}$, although its cation binding P$_3$O$_9$$^{3-}$ surface unit is very similar to that in P$_2$W$_{15}$Nb$_3$O$_6$$^{29-}$ (a local κ_3-O-support site of effective C_{3v} symmetry), does not bind the Ir$^+$ moiety symmetrically. That is, the local IrO$_3$ unit in (1,5-COD)IrP$_3$O$_9$$^{2-}$ has a lower symmetry than C_{3v}. Furthermore this complex is fluxional in solution down to −75 °C.[197] Since the two κ_3-O-support sites are so structurally and electronically similar in P$_3$O$_9$$^{3-}$ and P$_2$W$_{15}$Nb$_3$O$_6$$^{29-}$, it is a reasonable inference that a similar fluxionality may be present in [(1,5-COD)Ir·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$. In subsequent work, this group prepared two organometallic POM derivatives, [Re(CO)$_3$·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$ and [Ir(CO)$_2$·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$ as both the TBA$^+$-only salts and as the mixed TBA$^+$/Na$^+$ salts. When TBA$^+$ is the only counterion, the ^{31}P NMR and ^{183}W NMR spectra of these complexes are consistent with the presence of only the maximally symmetrical (C_{3v}) isomer in which the organometallic units are centrally bound to the electron dense Nb$_3$O$_9$$^{3-}$ end of the POM.[116] However, the ^{31}P NMR and ^{183}W NMR spectra, and by comparison the IR spectra, of the mixed TBA$^+$/Na$^+$ salts indicate they do not have C_{3v} symmetry. Addition of an equivalent amount of the alkali metal chelating agent, Kryptofix[2.2.2], to solutions of these mixed salts results in immediate complexation of the Na based on the ^{1}H NMR, but the ^{31}P and ^{183}W NMR spectra indicate the organometallic units are still bonded to the supporting POM in a nonsymmetrical way(s). However, heating the solution results in the high yield and selective production of the more stable C_{3v} isomers of both [Re(CO)$_3$·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$ and [Ir(CO)$_2$·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$. This isomerization chemistry is depicted in the Scheme 2 below taken directly from this reference.[116]

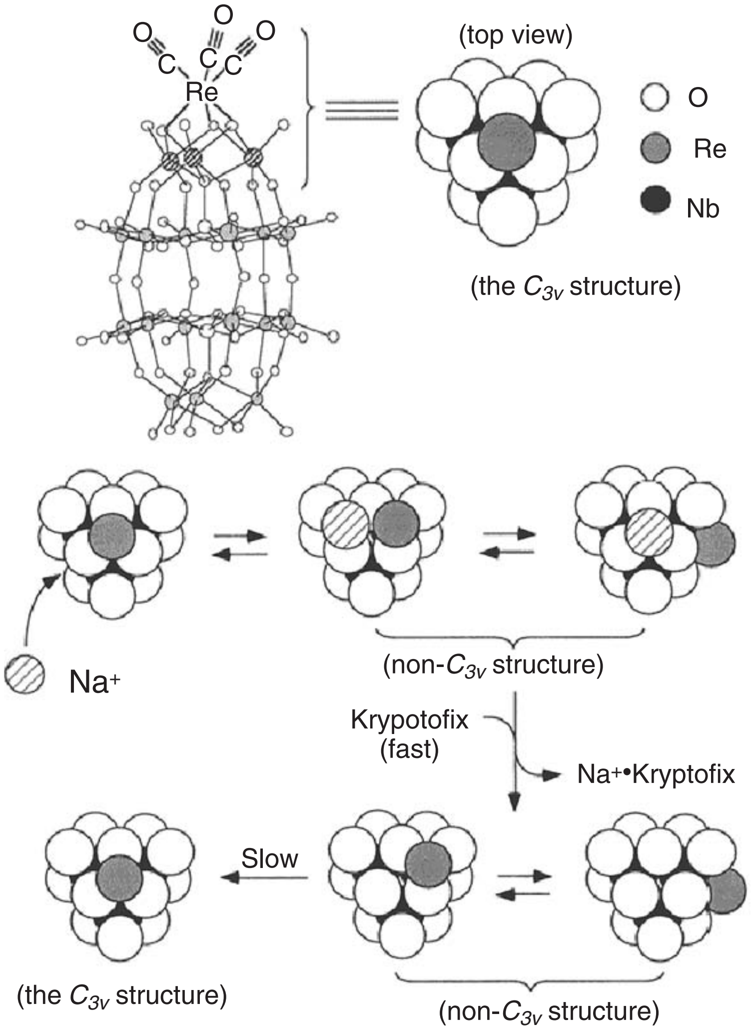
The isomerism in the previously studied organometallic POM derivative, [(1,5-COD) M·P$_2$W$_{15}$Nb$_3$O$_{62}$]$^{8-}$ (M = Ir and Rh), is very likely analogous to that in the "Re(CO)$_3$$^+$" and "Ir(CO)$_2$$^+$" derivatives, but equilibration of the nonsodium-paired species is significantly faster for the former. The lower mobility of Re(CO)$_3$$^+$ and Ir(CO)$_2$$^+$ vs. the Ir(1,5-COD)$^+$ on the Nb$_3$O$_9$$^{3-}$ unit surface was attributed to the greater binding affinity of the former organometallic cations vs. the latter. (The CO ligands make the former units significantly better acceptors of the electron density on the Nb$_3$O$_9$$^{3-}$ oxygens.)[116] In 1999, Weiner *et al.* prepared a third class of POM derivatives involving the attachment of complex cationic species to P$_2$W$_{15}$Nb$_3$O$_{62}$$^{9-}$. However, there is no experimental evidence thus far that the cationic units in these complexes of formula (TBA)$_{(9-nxm)}$ [m{(MeCN)$_x$M^{n+}}/P$_2$W$_{15}$Nb$_3$O$_{62}$$^{9-}$] (see above; Section 4.11.2.1) are mobile.[117]

4.11.2.3 Reactions of Surface Groups

4.11.2.3.1 Formation of p-block organometallic derivatives of POMs

There is very little dynamic or mechanistic data currently available on the formation or subsequent reactions of POMs containing appended *p*-block organometallic groups other than what can be inferred from the fully characterized product complexes. However, the formation of these complexes itself constitutes a fairly general type of POM reactivity and is thus included in this review. Gouzerh and Proust have written a thorough and authoritative review (several hundred references) on organic, *p*-block organometallic and *d*-block organometallic derivatives of POMs covering the literature through early 1998.[20] This should be consulted for the synthetic and structural chemistry in this area.

There is a substantial literature on reactions of electrophilic species with POMs or POM precursors such as MoO$_4$$^{2-}$ or WO$_4$$^{2-}$ to form stable adducts. The electrophilic groups can be *p*-block-based organometallic compounds, organic compounds, or in some instances, *d*-block-based organometallic compounds. Some of the latter were addressed above (Section 4.11.2.2.5 and elsewhere) but these complexes are not addressed in this section. The organic compounds, particularly alcohols or carboxylic acids, are, of course, *p*-block-based species because carbon is a *p*-block element. However, organic POM derivatives are discussed separately below (Section 4.11.2.3.2) because of the unique nature of carbon and potential diversity and utility of such complexes. In nearly all cases, the formation of *p*-block organometallic POM derivatives involves the formation of M^1—O—M^2 linkages, where M^1 = *p*-block element and



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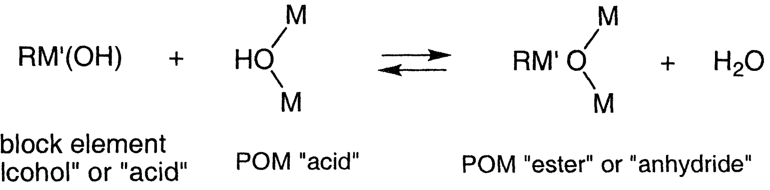
Scheme 2

M^2 =*d*-block (POM forming) element. Two different general synthetic approaches, each with its own implications for POM reactivity, have been used. The first general approach entails reaction with *p*-block acids, most commonly arsonates and phosphonates, with a POM or POM precursor. Although few investigators have addressed it experimentally, such reactions are, in principle, reversible. Evidence of reversibility has been established for alkoxy POMs[198,199] (species with C—O—M linkages that are covered in Section 4.11.2.3.2 below). If the M—OH group of the *p*-block reagent is viewed as an alcohol analogue, then reaction with the POM "acid" leads to an "ester" where both alcohol and acid component units are inorganic. By the same analogy, if the M—OH group of the *p*-block reagent is viewed as an acid (analogous to a hydroxy group of a carboxylic acid), then its reaction with the POM produces an "anhydride" (Equation (21)). Given that many esters of inorganic acids are effectively metal alkoxides, and such species in most cases are very unstable to hydrolysis, the hydrolytic stability of several *p*-block-element-based organometallic derivatives of POMs is noteworthy. Indeed many are prepared in water. Actual equilibrium constants in general have not been measured, but the generic equilibrium in Equation (21) lies well to the right in many cases. This fact suggests potential utility and applications based on POMs:



(21)

The earliest work on formation of organometallic POM species involved this condensation–dehydration approach (Equation (21)) and typically produced capped ring structures in which a ring of 4–6 W^{VI} or Mo^{VI} octahedra bears one cap centrally located above the ring or two caps, each centrally located, one above and one below the ring. The typical pH range of stability of these complexes in aqueous solution is 2–6. First, Pope and co-workers prepared dialkyl- and diarylarsinate adducts of tetramolybdate in which a Me_2AsO_2 tetrahedron caps the Mo_4 moiety. The ^1H NMR and IR spectra of $(CN_3H_6)_2[Me_2AsMo_4O_{14}(OH)]$ are consistent with a proton localized on the oxygen that bridges the four Mo atoms. About the same time, the group also prepared and characterized the pentamolybdobisphosphonates, $(RP)_2Mo_5O_{21}{}^{4-}$, where R = H, Me, C_2H_5, C_6H_5, $C_2H_4NH_3{}^+$, and p-$CH_2C_6H_4NH_3{}^+$.[200,201] The following year, Filowitz and Klemperer published the preparation and solution structures (by ^{17}O NMR) of $As_2Mo_6O_{26}{}^{6-}$ and $(PhAs)_2Mo_6O_{24}{}^{4-}$,[173] while Kwak *et al.* also synthesized several derivatives of this same organoarsonate dicapped POM, $(RAs)_2Mo_6O_{24}{}^{4-}$ (R = Me, Ph, p-$NH_2C_6H_4$) and an X-ray structure of the $[(Me)_4N]_2Na_2$ salt of the MeAs derivative.[175] Pope and co-workers followed this investigation with a synthesis and dynamic study of $(PhAs)_2Mo_6O_{25}H_2{}^{4-}$,[178] and $(PhAs)_2Mo_6O_{25}H_2{}^{4-}$, as detailed above in Section 4.11.2.2.3.[179,181]

Subsequently, Pope's group published three other studies involving preparation and characterization of three more capped POMs. Sethuraman *et al.* described the synthesis and isomerization of heteropolypentatungstobisphosphonates,[180] Barkigia *et al.* reported a neutral zwitterionic-derivatized POM, $(p\text{-}H_3N^+C_6H_4As)_4Mo_{12}O_{46}{}^{4-}$, and related derivatives,[202] and Katsoulis *et al.* noted organophosphate-capped ring-type POMs of formula $(ROPO_3)_2Mo_5O_{15}{}^{4-}$, where $ROPO_3H_2$ = riboflavin 5′-monophosphate, AMP, UMP, and glycerophosphoric acid.[203]

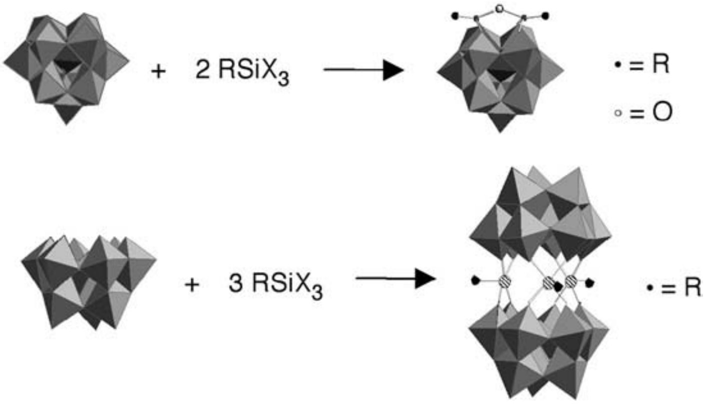
In the 1990s, Zubieta and co-workers found a variety of novel organophosphonate POMs as well as solid metal phosphonate phases using this general p-block acid + POM (or POM precursor) approach (Equation (21)). Some of the reactions were conducted under typical solution conditions and others under hydrothermal conditions. Like the great majority of the publications in this area, dynamic (kinetic and mechanistic) data as such are not given, but the products provide insight into self-assembly and stability issues. In 1993, Chen and Zubieta documented that reaction between $PhPO_3H_2$ and $TBA_4V_5O_{14}$ in methanol produced TBA $[V_5O_7(OMe)_2(PhPO_3)_5]$, a POM with alkoxy and organophosphonate ligands, with a vanadyl (V^{IV}=O) group directed into the interior of the cluster space.[204] Both protonation and reduction of this structurally unique POM produce other structures. In 1993, this group also demonstrated the hydrothermal synthesis and structural characterization of $(NH_4)_5Na_4\text{-}[Na\{Mo_6O_{15}(HO_3PC_6H_5)_3(O_3PC_6H_5)\}_2]$, a polyoxomolybdenum(V) complex with several organophosphonate ligands,[205] and followed up this work in 1995 with additional phenylphosphonate Mo^V-based POMs prepared the same way.[206] In 1994, they reported the preparation $(Ph_4P[VO_2Cl_2] + PhPO_3H_2$ in acetonitrile or methanol) and structure of $[ClV_7O_{12}(O_3PC_6H_5)_6]^{2-}$, an oxovanadium(V) organophosphonate cluster encapsulating a chloride ion, and other complexes.[207] Khan and Zubieta reviewed much of this work (oxovanadium and oxomolybdenum clusters and solids incorporating oxygen-donor ligands) in 1995, and this publication should be consulted for further chemistry in this area.[8]

In the late 1990s, Thouvenot and co-workers published studies involving the condensation approach (Equation (21)) to make p-block organometallic derivatives of Keggin POMs. In 1998, Mayer *et al.* reported the preparation of organophosphoryl polyoxotungstate derivatives $TBA_3Na_2[A,\alpha\text{-}PW_9O_{34}(RPO)_2]$ (R = Et, Bu^n, Bu^t, allyl, or Ph) by reaction of the organophosphonic acids $RPO(OH)_2$ with the trivacant polytungstophosphate, $Na_8[A,\beta\text{-}HPW_9O_{34}]$ in acetonitrile solution.[208] An earlier (1992) synthesis of phosphonyl Keggin derivatives used a different procedure (irreversible reaction with phosphonyl chlorides; see below).[209] In 1999, the Thouvenot group also disclosed the preparation of C_{2v} bis(organophosphoryl) decatungstosilicates of formula $SiW_{10}O_{36}(RPO)_2{}^{4-}$ (R = H, Et, Bu^n, Bu^t, $C_2H_4CO_2H$, and Ph) using the same synthetic procedure they used in the 1998 study but starting with the divacant $[\gamma\text{-SiW}_{10}O_{36}]^{8-}$ anion.[210] The diphenyl derivative was characterized by X-ray crystallography, and multinuclear NMR (^{1}H, ^{29}Si, ^{31}P, and ^{183}W) confirmed the same structures existed in solution.

This *p*-block acid + POM condensation approach (Equation (21)) was used to graft polymerizable groups, particularly alkenes, to POMs following by polymerization of the functionalized POMs to make network materials.

The second general approach to POMs bearing *p*-block organometallic groups entails reaction of POMs with *p*-block species that are higher energy than hydroxy compounds (acids). Most frequently acid chlorides have been used. Although rarely if ever addressed, these reactions are, in most cases and under most synthetic conditions used, doubtless irreversible. This attribute distinguishes them from the reactions discussed in the preceding section. Monomeric POM precursor compounds are generally not used in these preparations but rather lacunary (defect) POMs. Both these measures, use of acid chlorides and use of highly charged and consequently more reactive, nucleophilic POMs, usually ensure reaction completion. A noteworthy and related point regarding reactivity is that despite the hydrolytic lability of MCl (M = *p*-block element) bonds, these reactions have frequently been conducted in water. Indeed, many of them have been conducted in the absence of base to consume the HCl by-product as well.

The groups of Knoth, Klemperer, and Pope first described reactions of organosilyl or organotin chlorides or comparably reactive reagents with POMs, and primarily with lacunary POMs.[211–214] The products, as in the case of the reactions involving *p*-block hydroxy bearing reactants, are POMs with pendant organometallic groups. Scheme 3 illustrates two typical syntheses involving organometallic acid chlorides and POM fragments and is constructed using coordinates from actual X-ray structures. The top equation illustrates the usual reaction of an organosilyl trichloride with a lacunary POM ($XM_{11}O_{39}{}^{n-}$) to form a 2:1 adduct, and the bottom equation illustrates a reaction between an organotin trichloride with a trivacant POM to form a 3:2 sandwich complex.



Scheme 3

In these early publications, the hybrid *p*-block and *d*-block compounds were touted as models for possible intermediates in catalytic reactions, models for some materials, and simply as new synthetic inorganic chemistry. The work garnered considerable attention from both the organometallic and inorganic communities at the time because both cluster chemistry and exploration of the interface between homogenous and heterogeneous catalysis were very hot topics at that time. (Both topics have continued to be very active in the interim with activity increasing in the last few years. A special journal issue covering the 10th International Symposium on the Relations between Homogeneous and Heterogeneous Catalysis has been published recently.)[215]

More recently (1991), Thouvenot and co-workers reported the reaction of $RSiCl_3$ (R = alkyl or aryl) in dry acetonitrile with the trivacant heteropolytungstate $A,\alpha\text{-}[SiW_9O_{34}]^{10-}$.[216] The resulting complex has three $HSiO_3$ centers. Each of these centers shares two oxygens with two WO_6 units in the POM framework and a third oxygen with a fourth HSi center which symmetrically caps the other three and the overall polyanion. In 1994, Pope and co-workers demonstrated that the reaction of organotin trichlorides with $Na_8H[A\text{-}PW_9O_{34}]$ and $Na_{12}[\alpha\text{-}P_2W_{15}O_{56}]$ produces the tris(organotin)-substituted Keggin and Wells-Dawson polytungstophosphates of formula $[(PhSnOH)_3(PW_9O_{34})_2]^{12-}$,

$[(BuSnOH)_3(PW_9O_{34})_2]^{12-}$, $[(PhSn)_3P_2W_{15}O_{59}]^{9-}$, and $[(BuSn)_3P_2W_{15}O_{59}]^{9-}$, respectively.[217] The X-ray structure of $K_{11}H[(PhSnOH)_3(PW_9O_{34})_2]$ shows a polyanion of approximate D_{3h} symmetry with three PhSnOH groups sandwiched between two A,β-$PW_9O_{34}{}^{9-}$ units, a structure which is isomerically similar to the sandwich compounds first published by Knoth in 1985 (see Scheme 3 above).[218] In 1996, Xin *et al.* published the full characterization of eight tris(organotin)-substituted Keggin polytungstosilicates.[219] Extensive characterization including X-ray structures indicated these POMs were of two basic structural types, tri-substituted Keggin monomers of approximate C_{3v} symmetry with three corner-shared WO_6 octahedra of the β-Keggin anion replaced by three $PhSnO_5$ groups (typical formula, $(PhSn)_3SiW_9O_{37}{}^{7-}$), and sandwich structures including $[(BuSnOH)_3(SiW_9O_{34})_2]^{14-}$, of approximate D_{3h} symmetry with three BuSnOH groups sandwiched between two A,α-$SiW_9O_{34}{}^{10-}$ polyanions. Also in 1996, Mazeaud *et al.* disclosed the reaction of Bu^tSiCl_3 with A,α-$[PW_9O_{34}]^{9-}$ and B,α-$[HAsW_9O_{33}]^{8-}$ to form A,α-$[PW_9O_{34}(Bu^tSiOH)_3]^{3-}$ and B,α-$[AsW_9O_{33}(Bu^tSiOH)_3]^{3-}$, respectively.[220]

Organophosphonate POMs were prepared via this acid chloride + POM route by Kim and Hill in 1992.[209] The product complexes $[C_6H_5P(O)]_2X^{n+}W_{11}O_{39}{}^{(8-n)-}$ ($X^{n+} = P^{5+}, Si^{4+}$) were characterized by multinuclear NMR, X-ray crystallography, and other methods. $TBA_2H\ [PhP(O)]_2PW_{11}O_{39}$ converts cleanly to the partially hydrolyzed complex $TBA_2H_2[PhP(O)]\ [PhP(O)(OH)]PW_{11}O_{39}$ when dissolved in wet DMSO, and the latter reversibly reverts to the former when placed back in anhydrous acetonitrile. Phosphorus-31 NMR shows that the partially hydrolyzed complex slowly hydrolyzes further to several products in DMSO-d_6. The rate is dependent on the H_2O concentration with half-lives in dry DMSO and wet DMSO (10 equivalents of H_2O) at 296 K of 312 h and 55 h, respectively.[209] The Si-based analogue does not exhibit this reversible hydrolysis chemistry. In 2000, Mazeaud *et al.* prepared some of their organic derivatized POMs using *p*-block acid chlorides and POMs under phase transfer conditions. Reaction of Bu^tSiCl_3 with $Cs_7[(\gamma\text{-}PW_{10}O_{36})]$ under such conditions affords $[(\gamma\text{-}PW_{10}O_{36})\ (Bu^tSiOH)_2]$.[221] The X-ray structure of the TBA_3 salt of this complex shows it has C_s symmetry in the solid state with an open structure in which two structurally nonequivalent Bu^tOH groups are anchored to the POM unit framework. In solution, however, ^{29}Si and ^{183}W NMR, indicate the complex adopts the symmetrical C_{3v} conformation. It reacts cleanly in anhydrous solution with Me_2SiCl_2 to yield $TBA_3[(\gamma\text{-}PW_{10}O_{36})(Bu^tSiO)_2(SiMe_2)]$. Also in 2000, Pope and co-workers published the synthesis and thorough characterization of additional organotin POM derivatives.[222] Phenyltin trichloride reacts with $Na_9[\alpha\text{-}SbW_9O_{33}]$ and $Na_9[\alpha\text{-}AsW_9O_{33}]$ to produce $Cs_6[(PhSn)_3Na_3\ (\alpha\text{-}SbW_9O_{33})_2]$ (D_{3h} symmetry) and $Na_9[\{(PhSn)_2O\}_2\ H(\alpha\text{-}AsW_9O_{33})_2]$ (nominal C_{2h} symmetry), respectively. The latter complex contains four $PhSn^{3+}$ groups sandwiched between two $[\alpha\text{-}AsW_9O_{33}]^{9-}$ units.

In 2000, Mayer and co-workers used trialkoxysilanes and not trichlorosilanes as the electrophilic *d*-block organometallic precursors to functionalize the surface oxygens of POMs. The M—OR bond, like the M—Cl bond, generally reacts irreversibly with nucleophiles including the oxygens in POMs, alcohols, and water. These investigators prepared two types of functionalized POMs, $[\gamma\text{-}SiW_{10}O_{36}(RSi)_2O]^{4-}$ and $[\gamma\text{-}SiW_{10}O_{36}(RSiO)_4]^{4-}$, and characterized the complexes by multinuclear NMR and matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectrometry.[223]

A 1987 paper by Chorghade and Pope involved a new approach to the irreversible covalent modification of POMs. They incorporated an atom with a reactive lone pair of electrons, namely Sn^{II}, into an external position of a POM (an addenda atom on a Keggin ion), and subsequently used this lone pair as a nucleophile for irreversible displacement reactions with organic and organometallic electrophiles.[224] They prepared the polytungstostannate(II) POMs, $PSn^{II}W_{11}O_{39}{}^{5-}$, $SiSn^{II}W_{11}O_{39}{}^{6-}$, $GeSn^{II}W_{11}O_{39}{}^{6-}$, $BSn^{II}W_{11}O_{39}{}^{7-}$, $GaSn^{II}W_{11}O_{39}{}^{7-}$, and α_2-$P_2SnW_{17}O_{61}{}^{8-}$ and the corresponding polytungstostannate(IV) POMs of formula $XSn^{IV}OHW_{11}O_{39}{}^{n-}$, and characterized them by ^{11}B, ^{31}P, and ^{119}Sn NMR spectroscopy, cyclic voltammetry, and other methods. $K_6SiSn^{II}W_{11}O_{39}$ and the corresponding P- and Ga-centered POMs react with a range of primary and secondary organic halides and one secondary (cholesteryl) tosylate to form products with stable Sn—C bonds. The following POMs were realized: $Si(SnR)W_{11}O_{39}{}^{5-}$ ($R = CH_2C_6H_5$, $(CH_2)_3Br$, $(CH_2)_4Cl$, $(CH_2)_{11}Me$, $(CH_2)_6Br$, $C_{27}H_{45}$ and α_2-$P_2[Sn(CH_2)_{11}Me]W_{17}O_{61}{}^{7-}$). There is no reaction between these Sn^{II}POMs and the aryl halides, 1-bromonaphthalene and 4,4′-dibromobiphenyl under identical conditions. The reactivity of all the primary and second substrates and the lack of reactivity of the aryl halides argue strongly that these alkylation reactions proceed by a classical S_N2 mechanism. The product organotin POMs are soluble in aqueous buffer (pH 4.5–5.5) as well as DMSO. Reaction of $K_6SiSn^{II}W_{11}O_{39}$ with the electrophilic organotransition metal iodide, $IFe(CO)_2(C_5H_5)$, produces $SiW_{11}O_{39}SnFe\ (CO)_2(C_5H_5)^{5-}$.[224] The functionalization of nucleophilic lone pairs on POM addenda atoms, as exemplified by this work, offers considerable potential for attaching POMs to biological and synthetic molecules, macromolecules and surfaces.

4.11.2.3.2 Organic esters and anhydrides of POMs

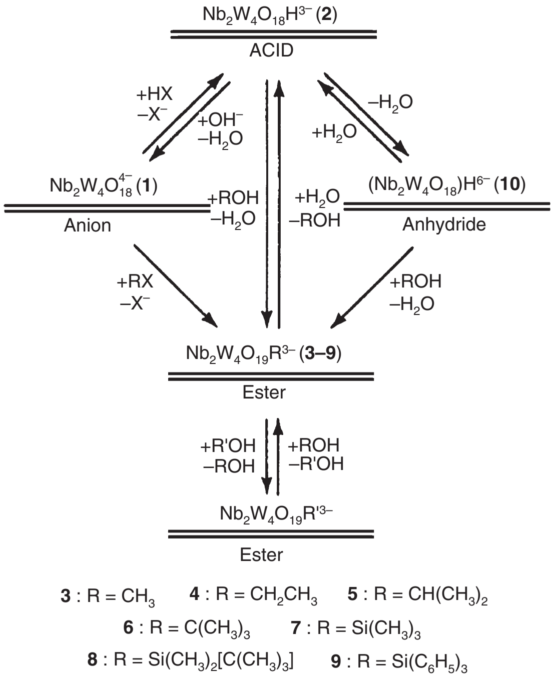
A host of reactions are now known in which alcohols react with a POM or monomeric POM precursors such as MoO_4^{2-} or WO_4^{2-} to form POMs where one or all of the oxo ligands have been replaced by alkoxo ligands. Again, the alkoxypolyoxometalates or polyalkoxyoxometalates can be viewed as organic esters of the POM acids. As for the POM functionalization using *d*-block-element acids, acid chlorides, or acid alkoxides (organic esters) addressed in the preceding section, the great majority of papers on POM functionalization by alcohols do not contain kinetic or other mechanistic data *per se*. However, the syntheses themselves constitute an important and general type of POM reactivity. The papers in this area typically report thorough spectroscopic or X-ray crystallographic characterization of the products but some reactivity information can be inferred from the isolated esterified POM products.

The groups of Zubieta, Gouzerh and Proust, Hill, Müller, Klemperer and others have made contributions in this area. Zubieta and co-workers have prepared and structurally characterized a large number of such complexes and reviewed this literature recently.[8,19] Klemperer and co-workers have developed the chemistry of polyalkoxypolytitanates (titanium oxoalkoxides),[225–228] including a cluster bearing a terminal organotransition metal group, (1,5-COD)Rh.[229] The review of Gouzerh and Proust is quite comprehensive for the synthesis and structures of organic POM derivatives up to early 1998. This research group has reported many polyalkoxy POMs, including some with both alkoxy and *d*-block organometallic ligands since 1998,[230] and recently addressed the structural relationships, structural preferences, and stereochemical nonrigidity in the organometallic subunits and oxo(alkoxo)molybdenum or tungsten subunits in the appropriate structures.[231]

The groups of Zubieta, Gouzerh and Proust, Müller, Hill and others have researched the chemistry of one subset of polyalkoxy POMs in particular: the triesters derived from reaction of tris(hydroxymethyl)methane ("tris") derivatives, $RC(CH_2OH)_3$ (R = organic group such as alkyl or an inorganic group such as NO_2) with POMs or POM precursors. Zubieta alone has published many syntheses, most frequently using monomeric or low-nuclearity POM precursors to generate polytris derivatives of V_6,[232–235] V_{10},[236,237] mixed valence $Mn^{II,III}{}_{10}$,[238] neutral V_{16},[239] Fe_6 and Fe_{10},[240] and Mo_{42}, a large cluster with three structural components prepared by hydrothermal synthesis.[241] Müller and co-workers explored the cis/trans isomers of bis(trisalkoxy)hexavanadates using UV/visible-, IR- and EPR-spectroscopy, magnetic measurements, cyclic voltammetry, and a single-crystal X-ray crystallography, but not actual isomerization by kinetics.[242] This group also addressed the possibility of template effects and nucleation involving tris ligands.[243] Chelate effects are clearly operable in the chemistry of these triester (trisester) POMs but they have yet to be quantified.

The most insightful paper on POM esterification processes (reactions with alcohols and POMs) not involving kinetics is that of Day *et al.* in which the synthesis, characterization, and interconversion of the alkyl and silyl monoesters of *cis*-$Nb_2W_4O_{19}H^{3-}$ were disclosed.[198] The transformations are summarized in Scheme 4 taken from this article. Specifically $TBA_3Nb_2W_4O_{19}R$ (R = Me, Et, $CHMe_2$, CMe_3, $SiMe_3$, $SiMe_2[CMe_3]$, and $SiPh_3$) were prepared via $Nb_2W_4O_{19}H^{3-} + ROH \rightarrow Nb_2W_4O_{19}R^{3-} + H_2O$ (TBA = Bu_4N^+). The alkoxy group bridges the two Nb atoms in the case of the methyl and ethyl esters. The more sterically encumbered alkoxy/siloxy groups bond to one terminal $oxoNb^V$ group. When $TBA_3Nb_2W_4O_{19}H$ is dissolved in dry CH_2Cl_2, the anhydride $(Nb_2W_4O_{18})_2O^{6-}$ is formed. Reaction of $TBA_4Nb_2W_4O_{19}$ with RX (R = Me, Et; X = OSO_2R) yields $TBA_3Nb_2W_4O_{19}R$ as a mixture of five diastereomers in which the R groups around bound to five nonequivalent types of doubly bridging oxygens in the POM unit. Similar reactions of $Nb_2W_4O_{19}{}^{4-}$ with RX (R = $CHMe_2$, $SiMe_2[CMe_3]$; X = O_3SCF_3; R = $SiMe_3$, X = Cl, $NHSiMe_3$) afford $Nb_2W_4O_{19}R^{3-}$ where the R groups are bonded solely to a terminal ONb oxygen in $Nb_2W_4O_{19}{}^{4-}$. Protonation of the $Nb_2W_4O_{19}{}^{4-}$ is predominantly at the unique bridging Nb—O—Nb oxygen. From the extensive structural data, the authors can make a strong case that the structure and reactivity of the $Nb_2W_4O_{19}{}^{4-}$ polyanion and its esters and anhydrides reflect the relative labilities of different types of metal–oxygen bonds, the steric environments of different surface oxygens, and the surface charge distribution in the polyanion unit.[198] The Nb—O bonds are far more labile than W—O bonds, the bridging oxygens occupy a more sterically congested environment than terminal oxygens, the bridging oxygens are more basic/nucleophilic than terminal oxygens, the Nb—O—Nb oxygens are marginally the most basic/nucleophilic bridging oxygens, and the ONb oxygens are by far the most nucleophilic terminal oxygens.

Hou and Hill studied the actual mechanism of ester formation and transesterification using kinetics coupled with a range of spectroscopic methods. Stoichiometric condensation of 1,1,1-tris(hydroxymethyl)ethane compounds with $TBA_5H_4[V_3P_2W_{15}O_{59}]$ in MeCN yield the tris- (or triester)-capped complexes of formula $RC(CH_2O)_3V_3P_2W_{15}O_{59}{}^{6-}$, where R = Me, NO_3, and



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Scheme 4

CH_2OH, in yields up to 90%. The triester POMs have substantial kinetic stability with respect to hydrolysis (e.g., $\tau_{1/2} \sim 912$ h for 40 mM $[MeC(CH_2O)_3V_3P_2W_{15}O_{62}{}^{6-}]$ in D_2O, pD = 0 at 100 °C). No POM intermediates were detectable (^1H, ^{31}P, and ^{51}V NMR) during the synthesis (POM + triol) of these capped complexes. Tungsten-183 NMR and IR coupled with ^1H, ^{31}P, and ^{51}V NMR confirm that the only detectable product in each case is the local-C_{3v}-symmetry regioisomer involving replacement of the three μ_2-oxo edge-bridging oxygens of the V_3 cap in the starting POM, the most basic oxide ions in the complex, with the three μ_2-oxo-alkoxy groups of the triols. Competitive kinetics methods indicate the relative reactivities of MeOH, $MeC(CH_2OH)_3$, $(HOCH_2)C(CH_2OH)_3$, and $(NO_2)C(CH_2OH)$ with this POM are 6:6:5:1, respectively, consistent with the alcohol group functioning as a nucleophile for an electrophilic POM-based species in the rate-limiting step of the esterification process. Triester cap-(triester cap') exchange (or triple transesterification) reactions of the type $R^1C(CH_2OH)_3 + [R^2C(CH_2O)_3HV_3P_2W_{15}O_{59}]^{5-} = [R^1C(CH_2O)_3HV_3P_2W_{15}O_{59}]^{5-} + R^2C(CH_2OH)_3$, where R^1, $R^2 = NO_2$ or CH_2OH also proceed both readily and in high selectivity at 50 °C in DMF solution (full equilibration in 3 days or less). They indicate a 35-fold preference for binding of the $HOCH_2C(CH_2–)_3$ cap relative to the $NO_2C(CH_2–)_2$ cap. The triester-capped complexes can be reduced by one electron provided the medium is dry. However, the resulting triester-reduced-POMs, unlike their oxidized counterparts, do hydrolyze fairly readily. Elemental analysis, potentiometric titration, and chemical reactivity confirmed that two different protonation states of the methyl-capped triester-POM, $TBA_5H[MeC(CH_2O)_3HV_3P_2W_{15}O_{59}]$ and $TBA_2H_4[MeC(CH_2O)_3HV_3P_2W_{15}O_{59}]$ can be prepared. The complexes catalyze oxygenation of sulfides by iodosylbenzene, H_2O_2, and Bu^tOOH. (All such reactions are summarized in Tables 1 and 2 in Section 4.11.3 below.)

The irreversible route to POM esters—alkylation of intact POMs by high-energy electrophilic species—has been attempted rarely. Apart from the work from the Klemperer group discussed above ($TBA_4Nb_2W_4O_{19} + RX$, where X = Cl or OSO_2R),[198] Knoth reported the direct alkylation of a $PMo_{12}O_{40}{}^{3-}$ using trimethyl and triethyl oxonium ions.[244] While the product alkylated Keggin complexes are highly unstable to hydrolysis, these investigators successfully obtained a X-ray structure of the methyl derivative, $THA_2(MeO)PMo_{12}O_{39}$ (THA = $(n\text{-}C_6H_{13})_4N^+$), which revealed the methyl is bound to an oxygen which is bridging two edge-shared MoO_6 units.

Finally, there is one classic example of anhydride formation involving an organic acid and a POM under equilibrium conditions (i.e., reaction of a carboxylic acid with a POM in water). Adams, Klemperer, and Liu isolated the diformyl POM (formally a mixed carboxylic-POM anhydride), $[(HCO)_2(Mo_8O_{28})]^{6-}$, from reaction of $(NH_4)_6Mo_7O_{24}$ and formic acid in water.[245] The $[(HCO)_2(Mo_8O_{28})]^{6-}$ polyanions are isostructural with the protonated $H_2Mo_8O_{28}{}^{6-}$ with formyl groups replacing the protons.

4.11.2.4 Electron Transfer Reactions

There is now a sizable literature on the electron transfer reactions of POMs. An authoritative and comprehensive review in this area but one limited to those papers with hard kinetics data in them (306 references) was written by Weinstock in 1998.[246] As a consequence, this section will be brief. Those interested in the electron transfer chemistry of POMs should consult this review.

Most of the research involving detailed kinetics studies of electron transfer both in the early period (1980s) and more recently has centered around the use of $Co^{III/II}W_{12}O_{40}{}^{5-/6-}$ because this POM has the redox active center (Co^{II} or Co^{III}) completely encapsulated by the polyoxotungstate framework. In consequence, it has been assumed that reactions with this POM approach the outer sphere limit for which Classical Marcus Theory is optimally applicable. Much of the early work involved reductions of $Co^{III}W_{12}O_{40}{}^{5-}$ by a range of substrates conducted by three research groups, that of Eberson,[247–252] Banerjee,[253–263] and Ayoko.[264–274] All three research groups also examined electron transfer oxidations of the corresponding reduced complex, $Co^{II}W_{12}O_{40}{}^{6-}$[275] and many reactions involving other outer sphere reagents (including oxidations by the POM $Ce^{IV}Mo_{12}O_{42}{}^{8-}$).[276] These papers generally provide some structure-activity and kinetics information. Both uncatalyzed and metal-ion-catalyzed reactions are addressed. Selected studies are now elaborated in a very brief format.

In 1983, Eberson published a thorough mechanism study of the oxidation of *p*-methoxytoluene by $Co^{III}W_{12}O_{40}{}^{5-}$.[247] The reaction was first order each in *p*-$MeOC_6H_4Me$ and $[AcO^-]$ (at $[AcO^-] < 0.25$ M) and inverse first order in the final concentration of the reduced POM product, $Co^{II}W_{12}O_{40}{}^{6-}$. Cations strongly affect the observed rate constant (k) which decreases in the order $Sr^{2+} > Cs^+ > Ca^{2+} > Rb^+ > K^+ > Li^+ > Na^+ > R_4N^+$ ($R = Me > Bu > Pr >$ hexyl $>$ decyl). The rate constant, k, increases with the solvent dielectric constant, and shows a positive salt effect. The isotope effect, $k_H/k_D = 5$–7, indicates the rate-limiting step involves proton transfer. The data are consistent with a mechanism involving an initial reversible electron-transfer, followed by rate-limiting deprotonation of the radical cation. The authors attributed the specific cation effect to the cation acting as an electron mediator in the transition state of the electron-transfer step.[247] In subsequent work, Eberson noted and analyzed sizable solvent and counter cation effects on the rates of electron transfer reactions involving $Co^{III}W_{12}O_{40}{}^{5-}$.[252] Banerjee's extensive work on electron transfer reactions of POMs was largely in the 1980s. He reported the oxidation of several substrates by $Co^{III}W_{12}O_{40}{}^{5-}$: oxalate,[253] formate,[253] *d*-fructose, *d*-glucose, and *d*-mannose,[254] citric acid (catalyzed by alkali metals),[255] amine-*N*-carboxylates,[256] sulfur(IV),[256] ethyl acetoacetate and diethyl malonate,[257] cyclic and acyclic ketones,[260] thiosulfate,[259] α-hydroxyacids,[260] histidine,[261] vanadyl ion,[262] octacyanomolybdate(IV), and octacyanotungstate(IV).[263] Banerjee also reviewed electron transfer reactions of POMs in 1993.[277] Ayoko and co-workers started their research in ~1983 and disclosed oxidation of the following substrates by $Co^{III}W_{12}O_{40}{}^{5-}$: thiols,[264,265] thiocyanate and iodide,[266] nitrous acid,[267] hydroxyammonium ion,[268] butane-1,4- and pentane-1,5-diols,[269] hydrazinium ion,[270] hypophosphorus and arsenious acids,[271] nitrilotriacetate (rates of oxidation compared to rates of oxidation by poly(pyridyl)iron(III) complexes),[272] *N*-(2-hydroxyethyl)ethylenediamine triacetate,[273] thiourea, and 1,1,3,3-tetramethyl-2-thiourea;[274] they demonstrated reduction of the following substrates by the corresponding reduced complex, $Co^{II}W_{12}O_{40}{}^{6-}$: $BrO_3{}^-$,[278] $IO_4{}^-$ (catalyzed by Cu^{II}),[279] $ClO_3{}^-$ (catalyzed by AgI),[280] and $MnO_4{}^-$.[281]

After the initial reports of thermal electron transfer processes involving POMs by Eberson, Banerjee, and Ayoko, Bacciochi conducted similar studies involving many organic substrates and POMs (again primarily using $Co^{III}W_{12}O_{40}{}^{5-}$).[282–288] In 1992, Bacciochi *et al.* published a kinetic study of electron-transfer-initiated carbon–silicon bond cleavage reactions of benzyltrialkylsilanes promoted by $Co^{III}W_{12}O_{40}{}^{5-}$.[282,283] The rate law and cation effects were similar to that documented by Eberson for methoxytoluene oxidation by this POM.

Other research groups who have contributed either directly or indirectly to our current understanding of electron transfer processes involving POMs include (alphabetically by correspondence author(s)): Anson (reduction of O_2 to H_2O_2 by $PRu^{II}(H_2O)W_{11}O_{39}{}^{5-}$ in good agreement with Marcus theory[289] and related work[290–294]), Balzani (electron-transfer quenching of the luminescence emission of $Ru(bpy)_3{}^{2+}$ (bpy = 2,2′-bipyridine) by Si $CoW_{11}O_{39}{}^{6-}$)[295] and related work,[296,297] Bond and Wedd (electrochemical investigations including proton coupled electron transfer[56,298,299]), Darwent,[300] Fox (photooxidation of organic substrates; see Section 4.11.4 below),[301] Nadjo (NADH oxidation by Wells-Dawson POMs),[302,303] Neumann (electron transfer oxidations of arenes and other classes of organic compounds,[304,305] and work on other systems[306–310]), and Hill and Weinstock (oxidation of organic substrates with simultaneous quantification of ion pairing effects).[92,93,311–313] Again the reader is referred to the recent review of Weinstock for discussion of all the papers in this area with kinetics data in them.

4.11.2.5 Adduct Formation and Atom Transfer Reactions

There are a growing number of examples of adduct formation and atom transfer reactions involving POMs. These necessarily involve surface or solvent-accessible sites in the polyanion units.

4.11.2.5.1 Adduct formation

In 1984, Katsoulis and Pope demonstrated that the extraction of $XCo^{II}(H_2O)W_{11}O_{39}{}^{n-}$, X = Si^{IV} or B^{III} and $XMn^{II}(H_2O)W_{11}O_{39}{}^{n-}$, X = Si^{IV} or Ge^{IV} into toluene using the highly hydrophobic quaternary ammonium cation, tetra-*n*-heptylammonium ion results in loss of the terminal aqua ligand on the *d*-electron transition metal center (Equation (22)).[314] The ease of dehydration to the five-coordinate species depends on the central metal, the heteroatom, and the temperature. The electronic absorption spectra strongly suggest that extraction into toluene forms the five-coordinate species as the does the reactivity. The coordinately unsaturated Co POMs bind donor substrates, D in Equation (23), where D = alcohols, acetone, acetonitrile, pyridine, and chloride ion. The coordinately unsaturated

$$M^{II}(H_2O)W_{11}O_{39}{}^{n-}(aq) + THA'Br\ (toluene) \rightarrow (THA')_nM^{II}W_{11}O_{39}(toluene) + Br^-(aq) \qquad (22)$$

$$(THA')_nM^{II}(H_2O)W_{11}O_{39} + D \rightarrow (THA')_nM^{II}(D)W_{11}O_{39} \qquad (23)$$

Mn POMs reversibly bind O_2 at low temperature (many cycles are possible), but undergo irreversible oxidation to the Mn^{III} complexes at higher temperature. Addition of H_2O results in complete conversion of the five-coordinate Mn and Co POMs to the conventional six-coordinated aqua complexes, $M^{II}(H_2O)W_{11}O_{39}{}^{n-}$.[314] Similar chemistry was shown to be operable for other Co-containing POMs. Subsequently, this group disclosed that toluene solutions of THA'-extracted and dehydrated salts of the $PCo^{II}W_{11}O_{39}{}^{5-}$, $SiM^{II}W_{11}O_{39}{}^{6-}$ (M = Mn, Co, Ni, Cu), α_2-$P_2CoW_{17}O_{61}{}^{8-}$, and $Co_4(PW_9O_{34})_2{}^{10-}$, react rapidly (1–2 min) with gaseous SO_2. The electronic absorption and IR spectra of the resulting solutions are consistent with the presence of metal-coordinated SO_2. The passage of a stream of dry N_2 through the solution converts the SO_2 adduct of $Co_4(PW_9O_{34})_2{}^{10-}$ to the dehydrated form, but this action has no effect on the more strongly bound adducts of the other POMs. Addition of water to the solutions of the SO_2 adducts displaces the SO_2 and restores the original six-coordinate aquated POMs in all cases.[315]

Two years later (1989), the same authors reported the oxygenation and oxidation chemistry of the Mn-substituted POMs $XMn^{II}W_{11}O_{39}{}^{n-}$ (X = P, Si, Ge, or B) and α_2-$P_2Mn^{II}W_{17}O_{61}{}^{8-}$.[316] These POMs undergo reversible oxygenation at low temperature in toluene or benzene solution but irreversible oxidation above ~22 °C. The O_2 adduct can be intercepted by the spin trap 5,5-dimethyl-1-pyrroline *N*-oxide (DMPO). EPR spectra indicate formation of a polyanion-O_2-DMPO intermediate that decomposes to the oxidized POM. The nonpolar organic solutions of these POMs catalyze the oxidation of 2,6- and 2,4,6-substituted phenols to benzoquinones or polyphenyl ethers, and a POM-O_2-phenoxy radical intermediate can be detected by EPR.

Other adduct formation reactions involving *d*-electron centers in POMs have been addressed in the preceding sections of the review (e.g., Section 4.11.2.1.3*),* in the following section, or in various papers in Table 1 (Section 4.11.3.2 below).

Day *et al.* published the synthesis and structural characterization of an inclusion complex $[\mathrm{MeCN}{\cdot}(\mathrm{V_{12}O_{32}}^{4-})]$ in which one MeCN molecule was noncovalently bound inside the central bowl-shaped cavity of the isopolyvanadate, $\mathrm{V_{12}O_{32}}^{4-}$.[317] This novel inclusion complex was characterized in solution by Wagner using ^{17}O–^{51}V heteronuclear shift correlation NMR spectroscopy on the ^{17}O-enriched inclusion complex.[318] This provocative bowl-shaped polyvanadate is one of many isopolyvanadate structures known, including cages, baskets, belts, bowls, and barrels, that are based on the folding of planar sheets comprised of linked $\mathrm{VO_5}$ square pyramids.[319]

4.11.2.5.2 Oxo transfer from d-electron centers

The *d*-electron centers in TMSPs react with oxygen donors, including but not limited to iodosylarenes, various peroxides, *N*-oxides, and $\mathrm{N_2O}$, to form the corresponding high valent species, and quite frequently oxometal species (Equation (24)). Many of the resulting oxometal POM species ("OM(POM)" in Equations (24) and (25)) can transfer their terminal oxo groups to a variety of inorganic (e.g., halide) or organic (e.g., alkenes, phosphines, etc.) acceptor molecules (Equation (25)). Evidence for Equations (24) and (25) comes from stoichiometric reactions combined with spectroscopic studies and from product and other studies in TMSP-catalyzed processes. Key papers on this chemistry are summarized below in Table 1 or in references contained in these key papers. To avoid redundancy and for sake of simplicity, all the individual POM systems exhibiting this chemistry (Equations (24) and (25)) are neither elaborated nor referenced here. Indirect evidence for these oxo transfer processes also derives from the very extensive studies of analogous reactions involving metalloporphyrins.[320] The thermodynamics of oxo transfer involving many *p*-block and *d*-block has been effectively summarized by Holm:[321]

$$\mathrm{M_{red}(POM)} + \mathrm{DO} \rightarrow \mathrm{OM(POM)} + \mathrm{D}\ (\mathrm{DO} = \text{the oxygen donor}) \qquad (24)$$

$$\mathrm{OM(POM)} + \mathrm{A} \rightarrow \mathrm{M_{red}(POM)} + \mathrm{AO}\ (\text{oxygen atom acceptor}) \qquad (25)$$

There is one case where both Equations (24) and (25) are facile under mild conditions, where the high valent oxometal species have been isolated and fully characterized,[322,323] and where their oxo transfer to substrates (alkenes) has been studied in depth. This is the case where $\mathrm{M_{red}(POM)} = \mathrm{Cr^{III}X^{n+}W_{11}O_{39}}^{(9-n)-}$ and $\mathrm{OM(POM)} = (\mathrm{OCr^{V}})\mathrm{X}^{n} + \mathrm{W_{11}O_{39}}^{(9-n)-}$, $\mathrm{X} = \mathrm{P^{V}}$ or $\mathrm{Si^{IV}}$.[323]

Neumann and co-workers reported a catalytic variation of this chemistry. Labile Keggin heteropolymolybdates such as $\mathrm{K_5PV_2Mo_{10}O_{40}}$ after activation by $\mathrm{H_2}$ catalyze the deoxygenation of aldehydes and ketones. For example, PhCOMe is deoxygenated to PhEt in ~100% yield in the presence of $\mathrm{K_5PV_2Mo_{10}O_{40}}$ supported on $\mathrm{Al_2O_3}$.[324]

4.11.2.5.3 Oxo transfer from d^0 POMs during catalytic turnover

In recent work (2000 and 2001) Khenkin, Neumann, and co-workers convincingly demonstrated that the $\mathrm{O_2}$-based oxidation of alkyl and aromatic compounds catalyzed by the much studied HPA $\mathrm{H_5PV_2Mo_{10}O_{40}}$ proceeds by initial electron transfer followed by rate-limiting oxygen transfer from the POM to the substrate cation radical intermediate. The obligatory defect POM is subsequently reoxygenated by the terminal oxidant, $\mathrm{O_2}$.[310,325] This is the general Mars-van Krevelen mechanism that has been a mainstay in heterogeneous catalytic oxidations for many years.[326,327] These investigators used a combination of EPR and NMR spectroscopies and a range of kinetics experiments, including kinetic isotope effect studies, to rule out two well-documented alternative mechanisms for homogeneous catalytic $\mathrm{O_2}$-based oxidations in these $\mathrm{H_5PV_2Mo_{10}O_{40}}$-catalyzed reactions, namely autooxidation and oxidative nucleophilic substitution and to provide evidence for the Mars-van Krevelen mechanism. When the more easily oxidized substrate xanthene was used, the radical cation intermediate could not be detected. Instead, the radical

Table 1 Homogeneous catalysis by *d*-electron-metal-substituted POMs.[a]

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comment*	*References*
$THA'_6MnSiW_{11}O_{39}$	Alkylphenol	Dione, dimer	O_2	C_6H_5Me, C_6H_6	25 °C, phase transfer, mechanism study	316
$PW_{11}Fe(H_2O)O_{39}{}^{5-}$ where M = Fe, Co, Ni	H_2S	S_8	O_2	H_2O, pH 3.5–5.0	Initial report of aerobic H_2S oxidation by POMs	395
$Na_5P(FeH_2O)W_{11}O_{39}$	NO, H_2S	HNO_3, S_8	O_2	H_2O	Successful membrane separation of a soluble catalyst from a soluble reaction product; 20 °C	396,397
Supported $Pd(OAc)_2$ + $PV_xMo_{12-x}O_{40}{}^{n-}$	CO	CO_2	O_2	H_2O vapor	Effect of Al_2O_3, TiO_2, and SiO_2 supports on the POM and POM/Pd catalysis studied	398
$Na_{10}X_2Fe^{II}{}_3W_{18}O_{66}$, where X = As, Se, or Te	NO (coordinated to Fe atom)	HNO_2	O_2	H_2O	Primarily a POM synthesis paper; 22 °C	399
$PCoW_{11}O_{39}{}^{5-}$	(R)-(+)-limonene, 4-vinyl-1-cyclohexene, 1-methyl-1,4-cyclohexadiene	Epoxides	O_2	MeCN or CH_2Cl_2	Aldehyde reductant; quite selective	400
$[\{Fe_2Ni(OAc)_3\}PW_9O_{37}]^{10-}$	Adamantane, ethylbenzene, cyclohexane	Alcohols, ketones	O_2	No solvent used except for adamantane rxns.	Modest selectivities	401
$TBA_5PMW_{11}O_{39}$, where M = Co, Mn, Cu, Ni, or Fe	Alkenes	Epoxide, allylic ketone, allylic alcohol	O_2	MeCN and aldehyde	Aldehyde reductant; quite selective; 303 K	402
$TBA_4H_6(Fe_2–Ni(OAc)_3)PW_9O_{37}$	Alkane	Alcohol, ketone	O_2 or H_2O_2	MeCN	82 °C or 50 °C	403
	Alkene	Allylic alcohol, allylic ketone, epoxide	O_2		30 °C	
	Aldehyde	Carboxylic acids	O_2		30 °C	
$[WZnRu^{III}{}_2(OH)(H_2O)(ZnW_9O_{34})_2]^{11-}$	Alkanes	Alcohols, ketones	O_2	$ClCH_2CH_2Cl$	Catalytic nonradical alkene functionalization	404

Table 1 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comment*	*References*
$PPdW_{11}O_{39}[PW_{11}O_{39}Pd\text{-}O\text{-}PdO_{39}W_{11}P]^{n-}$	Benzene	Phenol	O_2/H_2	H_2O/C_6H_6	Pd^0 forms and plays key catalytic role	405
$H_{3+x}PV_xM_{12-x}O_{40}$, where M = Mo, W, or both and $x = 0–5$	Sulfide (THT)[b]	Sulfoxide (THTO)	O_2	MeCN	First combinatorial library of POMs; 99% selectivity for sulfoxide	406
$TBA_5Na_3[(1,5\text{-COD})IrP_2W_{15}Nb_3O_{62}]$	Cyclohexene	Epoxides	O_2	MeCN, CH_2Cl_2, $ClCH_2CH_2Cl$ $Cl_2CHCHCl_2$	Several control reactions done but presence of Ir^0 nanoclusters not yet realized	407
Pd^{II} complexes of $PW_{11}O_{39}{}^{7-}$ and $PW_9O_{34}{}^{9-}$, bimetallic $Pd^{II}–Fe^{III}$ complexes with $PW_9O_{34}{}^{9-}$	Benzene, cyclohexane	Oxygenated organic products	O_2/H_2		Bimetallic $Pd^{II}–Fe^{III}$ POM species supported on silica	408
$[\{Fe_{3-x}Ni_x(OAc)_3\}PW_9O_{37}]^{(9+x)-}$ where x = predominantly 1	Alkanes	Alcohols, ketones, acids	O_2	MeCN	With and without isobutyraldehyde reductant	409
$[\{WZnRu_2(OH)(H_2O)\}ZnW_9O_{34})]^{1-}$	Alkene	Epoxide	O_2	$ClCH_2CH_2Cl$	Initial report of nonradical O_2 activation and selective oxygenation	361
Tetra-*n*-alkylammonium salts of $PCoW_{11}O_{39}{}^{5-}$, $CoW_{12}O_{40}{}^{6-}$	Alkenes	Epoxides	O_2	MeCN	Isobutyraldehyde reductant; the superior activity of Co in these reactions is due to its ability to catalyze the chain branching which yields acylperoxy radicals for alkene epoxidation with high selectivity	410
$[WZnRu^{III}{}_2(XW_9O_{34})_2]^{11-}$, where X = Zn^{II} or Co^{II}	Adamantane, Alkenes	1-Adamantanol, 2-adamantanol, 2-adamantanone	O_2	$ClCH_2CH_2Cl$	Nonradical-chain aerobic alkane hydroxylation	28

$TBA_5[(MeCN)_xFeSiV_3W_9O_{40}]$ $TBA_5[(MeCN)_xFeP_2V_3W_{15}O_{62}]$	3,5-Di-Bu^t-catechol	Muconic acid anhydride; 4,6-di-Bu^t-2H-pyran-2-one; spiro[1,4-benzodioxin-2(3H),2′-[2H]-pyran]-3-one, 4′,6,6′,8-tetrakis(1,1-dimethylethyl); 3,5-di-Bu^t-5(carboxymethyl)-2-furanone; 3,5-di-Bu^t-1,2-benzoquinone	O_2	$ClCH_2CH_2Cl$	Catalyst precursors well characterized; true catalysts less clear	411
$(n\text{-}Bu_4N)_7[(MeCN)_xFe^{II}\cdot P_2W_{15}Nb_3O_{62}]$	3,5-Bu^{t}catechol	Extradiol products	O_2	MeCN or $ClCH_2CH_2Cl$	Complex oxidation processes catalyzed by new class of POMs	412
$[XMLW_{11}O_{39}]^{8-n}$, where X = P and Si, M = Co^{II}, Cu^{II} and Mn^{II} and L = H_2O	*p*-Xylene	*p*-Toluic acid, *p*-terephthalic acid, *p*-tolualdehyde, *p*-Me benzyl alcohol	O_2	H_2O	Halide free and using only air	413
$[Pd_3(PW_9O_{34})_2]^{12-}$ $[Pd_3(PW_9O_{34})_2Pd_nO_xH_y]^{q-}$, where $n = 3$; $[Pd_2Cu(PW_9O_{34})_2]^{12-}$, $[Pd_2Fe(PW_9O_{34})_2]^{11-}$, $[PdFe_2(PW_9O_{34})_2]^{10-}$, $[Pd_3(PW_9O_{34})_2\text{-}Pd_nO_xH_y]^{q-} + [(VO)_3(PW_9O_{34})_2]^{9-}$	Benzene	Phenol	O_2/H_2	H_2O, C_6H_6	Bimetallic Pd^{II}–Fe^{III} complexes proposed to be key; Pd^0 involved	414
$PV_nMo_{12-n}O_{40}{}^{x-}$, where $n = 1$–3; also cites $PMW_{11}O_{39}$, where M = Ni^{II}, Co^{II}, Cu^{II}, Fe^{III}, Ru^{III}	Methyl isobutyrate	Methyl α-hydroxyisobutyrate, isobutyric acid	O_2	MeCN	Isobutyraldehyde reductant, thus isobutyric acid and acetone by-products	415
	Isobutyraldehyde	Acetone				

Table 1 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comment*	*References*
$PW_{11}O_{39}^{7-}$, $PM(L)W_{11}O_{39}^{n-}$,where $L = H_2O$, OH^-, O^{2-} and $M = Ti^{IV}$, V^V, Cr^{III}, Mn^{II}, Fe^{III}, Ni^{II}, Cu^{II}, Ru^{IV}, Co^{II}	Cyclohexene	Cyclohexene oxide, cyclohexanol, cyclohexenone, 1,2-cyclohexane diol, hydroperoxides	H_2O_2	MeCN, C_6H_6	One-phase system	416
$Fe^{II}{}_4[(B\text{-}PW_9O_{34})_2]^{10-}$	Alkene	Epoxide	H_2O_2	MeCN	Initial report of highly selective H_2O_2-based epoxidation catalyzed by a *d*-electron–metal sandwich-type POM	417
Layered double hydroxides pillared with $SiW_{12}O_{40}^{4-}$	2-Hexene, cyclohexene, cyclododecene	Epoxides and other oxidation products	H_2O_2	H_2O/alcohol	Some size selectivity	418
$WZnM_2(ZnW_9O_{34})_2^{12-}$ where M = Mn, Ni, Cu, Co, Fe	Alkene	Epoxide, allylic ketone	H_2O_2	$ClCH_2CH_2Cl$	Highly selective epoxidation	419
$K_{12}[\{WZnPd^{II}{}_2(H_2O)_2\}(ZnW_9O_{34})_2]$, $K_{12}[\{WZnPt^{II}{}_2(H_2O)_2\}(ZnW_9O_{34})_2]$, $Na_{11}[\{WZnRu^{III}{}_2(OH)(H_2O)\}(ZnW_9O_{34})_2]$	Alkenes, alkanes	Epoxides	H_2O_2, Bu^tOOH	$ClCH_2CH_2Cl$	Transfer to chlorocarbon using $(Cap)_3MeN^+$; very selective epoxidation	420
Silica particles derivatized with POMs	Alkenes	Epoxide, diol, benzaldehyde, enol, enone, ketone	H_2O_2	No organic solvent	Oxidation rates and selectivities depend on how silica support is derivatized	421
$[WZnMn_2(ZnW_9O_{34})_2]^{12-}$	Alkenes, secondary alcohols	Epoxides, ketones	H_2O_2	$ClCH_2CH_2Cl$	99% selective epoxidation	422
Range of POMs on high-surface-area supports	Penicillin-G, K^+ salt	Sulfoxide	H_2O_2	H_2O or H_2O/alcohol media	Some catalysts very selective	423

$TBA_{8-n}[PM^{n+}BrMo_{11}O_{39}]$, where $M^{n+} = Mn^{II}$, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}	Cyclohexene	Cyclohexene epoxide, cyclohexen-1-ol, cyclohexen-1-one	H_2O_2	$ClCH_2CH_2Cl$	Conversion ranges 6.4–20.0%; focus of this paper is a reaction mechanism study; the results suggested that the substituted heteropolyoxometalate reacts with H_2O_2 to form an intermediate, and the substituted transition metal ion seems to be the center of activating H_2O_2	424
$[WZnMn^{II}_2(ZnW_9O_{34})_2]^{12-}$	Alkenes, dienes, alkenols, sulfides	Expected epoxidation and other oxidation products	H_2O_2	$ClCH_2CH_2Cl$	Summary of reactions with this POM and H_2O_2	425
$[PFe(H_2O)W_{11}O_{39}]^{4-}$ $[PFe(SO_4)W_{11}O_{39}]^{6-}$ $[PFe(OH)W_{11}O_{39}]^{5-}$ $[PW_{11}O_{39}Fe_nO_xH_y]^{m-}$, where $n = \sim 8$	Benzene	Phenol	H_2O_2	MeCN	Significant H_2O_2 decomposition	426
$PCrW_{11}O_{39}{}^{n-}$	Cyclohexene Benzene	Cyclohexenone, cyclohexenol, cyclohexene oxide; Phenol	H_2O_2	MeCN	Some characterization of high-valent CrPOM intermediates (see ref. 324); oxidations not highly selective	427
$Na_xM_2Zn_3W_{19}O_{68}$, where M = Ru, Mn, Zn, Pd, Pt, Co, Fe, Rh	Organic substrates	Epoxy alcohols, ketones, ketols, hydroxy amines	H_2O_2, Bu^tOOH	$ClCH_2CH_2Cl$ and other media	Survey rather than mechanism paper; many substrates, oxidants and sandwich POMs evaluated	428
$[Fe^{III}{}_4(H_2O)_4(P_2W_{15}O_{56})_2]^{12-}$, $[Fe^{III}{}_4(H_2O)_4(PW_9O_{34})_2]^{6-}$	Alkenes	Epoxides	H_2O_2	MeCN	Low to moderate epoxide selectivities depending on alkene	429,430
$XM(H_2O)W_{11}O_{39}{}^{n-}$, where M = Fe, Co, Cu, Mn and X = Si, P; 1-hexadecylpyridinium salt	1,3-Dimethyladamantane	Oxidations at tertiary and other carbons	H_2O_2		Selectivity varies considerably with POM	431

Table 1 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comment*	*References*
d-Electron-TMSP complexes	*R*-(+)-limonene	1-Methyl-4-(1-methyethenyl)-1,2-cyclohexanediol	H_2O_2	Acetone	Highly selective; only indicated diastereomer produced	432
$[Fe^{III}_4(H_2O)_2(P_2W_{15}O_{56})_2]^{12-}$ $[Fe^{III}_2(NaH_2O)_2(P_2W_{15}O_{56})_2]^{16-}$	Alkenes	Epoxides	H_2O_2	MeCN	Modest to high epoxide selectivities depending on alkene	433
γ-Si$[Fe(OH_2)]_2W_{10}O_{38}{}^{6-}$	Alkanes, cyclohexane, *n*-hexane, *n*-pentane, adamantane	Oxygenated products	H_2O_2	MeCN	Low oxygenation selectivity, but ~100% selectivity for H_2O_2 utilization in some cases; (Is O_2 from H_2O_2 disproportionation involved? see ref. 363)	434
$[(Mn^{II}(H_2O)_3)_2(WO_2)_2(BiW_9O_{33})_2]^{10-}$, $[(Mn^{II}(H_2O)_3(SbW_9O_{33})_2]^{12-}$, $[(Mn^{II}(H_2O)_3)_2(Mn^{II}(H_2O)_2)_2(TeW_9O_{33})_2]^{8-}$	Dienes, (e.g., (*R*)-(+)-limonene)	Epoxides (e.g., 1,2-limonene oxide)	H_2O_2	H_2O/CH_2Cl_2	Regioselective epoxidation of disubstituted alkenes	435
$PTiW_{11}O_{40}{}^{5-}$	Methyl phenyl sulfide	Sulfoxide, sulfone	H_2O_2	MeCN	Nearly quantitative yield of sulfoxide and sulfone together	436
β_3-$[(Co^{II}O_4)W_{11}O_{31}(O_2)_4]^{10-}$	2-Cyclohexenol	*Cis*- and *trans*-2,3-epoxycyclohexen-1-ol, 2-cyclohexen-1-one (28.3, 59.3 and 3.6% yields, respectively)	H_2O_2	H_2O, $CHCl_3$	1 M pH 5 acetic acid buffer/$CHCl_3$ biphasic system	437
Cetylpyridinium salts of $LnW_{10}O_{36}{}^{9-}$ $Ln(PW_{11}O_{39})_2{}^{n-}$ $Ln(PW_9O_{34})_2{}^{n-}$	Cyclooctene, cyclohexanol, methyl menthol	Oxidation products	H_2O_2		Extensive H_2O_2-based degradation of POM	438

$K_{0.5}(NH_4)_{5.5}MnMo_9O_{32}$	Phenol	Hydroquinone	H_2O_2	MeOH	39% yield, 86% selectivity; optimized solvent	439
γ-$Si[Fe(OH_2)]_2W_{10}O_{38}{}^{6-}$	Methane, ethane, cyclooctane, *n*-hexane, *n*-pentane, adamantane	Oxygenated products	H_2O_2	H_2O	High rates at low temperature	440
$K_{10}[Mn^{II}{}_4(PW_9O_{34})_2$-$(H_2O)_2]$ $K_{10}[Co^{II}{}_4(PW_9O_{34})_2$-$(H_2O)_2]$ $Na_{12}[Zn_3W(ZnW_9O_{34})_2$-$(H_2O)_2]$ $Na_{12}[Co^{III}{}_3W$-$(Co^{II}W_9O_{34})_2(H_2O)_2]$ $K_6Na_2[Mn^{IV}W_6O_{24}]$	Methyl orange, crocetin	Bleached products	H_2O_2	H_2O	Ten POMs catalyze peroxide bleaching; kinetic data given	441
$CuCl_2$ or $CuCO_3 + H_4SiW_{12}O_{40}$	Phenol	Dihydroxybenzene	H_2O_2	H_2O	39% phenol conversion	442
$NaH_8[PDA]_5[PCo_3$-$W_9O_{37}]$ where PDA = *p*-pheylenediamine	Acetaldehyde	Acetic acid	H_2O_2	H_2O	20–50 nm nanoparticles	443
α-$K_6SiTiW_{11}O_{40}$ α-,β_i-$K_6[Si(TiO_2)$-$W_{11}O_{39}]$, where $\beta_i = \beta_1\beta_2\beta_3$	Maleic acid	Maleic acid oxide	H_2O_2	H_2O	Primarily a POM synthesis and characterization paper; the peroxotitanium groups increased reactivity	444
$THA_5MPW_{11}O_{39}$, where M = Co, Mn, Cu, or Fe	Alkane	Alcohol, ketone, *N*-alkylacetamides, alkyl halides	Bu^tOOH	C_6H_6, $ClCH_2CH_2Cl$, or MeCN	Early papers in this area; some mechanistic information	445,446
$SiMW_{11}O_{39}{}^{5-}$, where M = Ru, Rh	Cyclohexane, *n*-decane, ethylbenzene	Cyclohexanone, cyclohexanol alcohols, ketones	Bu^tOOH	C_6H_6	Compared to corresponding Co- and Fe-substituted POMs	447
$PCoW_{11}O_{39}{}^{n-}$ $PFeW_{11}O_{39}{}^{4-}$ $PCrW_{11}O_{39}{}^{n-}$	Cyclohexane, adamantane	Cyclohexanol, cyclohexanone, chlorocyclohexane, adamantane-1 and 2-ols	Bu^tOOH in presence of O_2	CCl_4, CH_2Cl_2	Radical chain oxidation mechanisms	448

Table 1 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comment*	*References*
$NaN_3 + POM$, where POM = $K_3PW_{12}O_{40}$, $K_4PCrW_{11}O_{39}$, $K_5PCrW_{11}O_{39}N_3$, $K_5PVW_{11}O_{40}$, $K_5PVW_{11}O_{40}N_3$, $H_6PFe_3W_9O_{37}$, $H_6PCr_3W_9O_{37}$, $H_7PFe_2MnW_9O_{37}$, $H_7PFe_2CoW_9O_{37}$, or $H_6PFe_2VW_9O_{38}$	Light alkanes	"Valuable oxygenates"	O_2 Bu^tOOH	C_6H_6 MeCN	Catalysis promoted by Group 1 metal azides over a range of conditions	449
$H_5PV_2Mo_{10}O_{40}$ and $[ZnWMn_2^{II}(Zn\ W_9O_{34})_2]^{12-}$ on PEO/PPO[b]-modified cationic SiO_2	Dihydroanthracene alkenes	Anthracene epoxides	Bu^tOOH	Toluene	POMs bound to silica with PEO,[b] PPO,[b] and quaternary ammonium groups	450
$TBA_4HMPW_{11}O_{39}$, where M = Mn or Co	Alkane	Alcohol, ketone	$[PhIO]_n$ or PFIB[b]	MeCN	Early paper on TMSP-type catalysis; primarily product studies	360
$TBA_4HMPW_{11}O_{39}$, where M = Fe or Cr	Alkane	No rxn				
$TBA_4PMnW_{11}O_{39}$	Alkane, alkene	Ketone, alcohol Epoxide, and other products	$[PhIO]_n$	$MeCN/CH_2Cl_2$	Comparisons with corresponding metalloporphyrin catalysts (MPor); some mechanistic information	451
β-$SiM_3(H_2O)_3W_9O_{39}{}^{n-}$, where M = first-row *d*-electron transition metals; $ZnTiW_{11}O_{40}{}^{8-}$	Alkenes	Epoxides and/or cleavage products	$[PhIO]_n$, IO_4^-		Cleavage products in high selectivity with IO_4^-	452

α-$(XO_4)MnW_{11}O_{36}{}^{n-}$, where X = P, Si, B, Zn; γ-$[(SiO_4)Mn_2{}^{III}$-$W_{11}O_{36}H_6]^{4-}$,$[Mn_4{}^{II}$-$(H_2O)_2(PW_9O_{34})_2]^{10-}$	Cyclohexene, *cis*-stilbene	Cyclohexene oxide, *cis*/*trans*-stilbene epoxides	$[PhIO]_n$	$CH_2Cl_2/MeCN$	Products vary with POM charge; products from catalytic and stoichiometric reactions are different	453
$[(MeCN_xM]^{n+}$ + $P_2W_{15}Nb_3O_{62}{}^{9-}$ where M = Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{I}, Cu^{II}, Zn^{II}	Norbornene, cyclohexene	Epoxides	$[PhIO]_n$	MeCN	Evidence for POM-supported, *d*-electron center as active catalyst	117
Cr- and Mn-substituted Keggin heteropolytungstates	2-Cyclohexenol	2-Cyclohexanone	$[PhIO]_n$[b]	MeCN or CH_2Cl_2	Selectivity varies with catalyst	454
$THA_5(RuH_2O)SiW_{11}O_{39}$	Alkene	Alcohol, ketone, acid, aldehyde	Bu^tOOH	$ClCH_2CH_2Cl$	Second paper is mechanism study of $IO_4{}^-$ -based oxidative cleavage of alkenes	455,456
		Acid, aldehyde, epoxide	$KHSO_5$	$H_2O/ClCH_2$-CH_2Cl		
		Aldehyde, acid	$NaIO_4$	$H_2O/ClCH_2$-CH_2Cl		
		Alcohol, ketone, acid, epoxide aldehyde	$[PhIO]_n$	$ClCH_2CH_2Cl$		
$K_5(RuH_2O)PW_{11}O_{39}$	Alkane	Alcohol + ketone	NaClO or Bu^tOOH	CH_2Cl_2/H_2O	22 °C, biphasic reaction; some mechanistic information given	457
$K_2Ru(OH)Cl_5$ + $Na_7PW_{11}O_{39}$	Primary alcohols Aldehydes, acrolein	Carboxylic acids Acrylic acid	$KClO_3$	H_2O, pH 2	Very high yields of the acids	458
$THA'{}_5(CrO)SiW_{11}O_{39}$			H_2O_2 or $[PhIO]_n$ OCl^-	C_6H_6	Mechanism of alkene oxidation elucidated; comparison to corresponding metalloporphyrins made	323
$TBA_4(CrO)PW_{11}O_{39}$	Alkene	Epoxide, allylic alcohol, allylic ketone		MeCN		

Table 1 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comment*	*References*
$THA_4(CrO)PW_{11}O_{39}$	Alkene	Epoxide, allylic alcohol, allylic ketone		MeCN or C_6H_6		
$THA'_5(CrO)SiW_{11}O_{39}$	Alkene	Epoxide, allylic alcohol, allylic ketone		MeCN or C_6H_6		
	Allylic alcohol	Allylic ketone		MeCN		
	Triphenylphosphine	Triphenylphosphine oxide		C_6H_6		
$Co_4P_2W_{18}O_{68}{}^{10-}$, $CoPW_{11}O_{39}{}^{5-}$, $Mn^{III}PW_{11}O_{39}{}^{4-}$, $Mn^{II}PW_{11}O_{39}{}^{5-}$, $Fe^{III}PW_{11}O_{39}{}^{4-}$, $NiPW_{11}O_{39}{}^{5-}$	Cyclohexene	Epoxide, enol, enone	CDMANO[b]	MeCN	Mechanism study	459,460
$Li_{12}[Mn^{II}{}_2ZnW(ZnW_9O_{34})_2]$	Alkanes, alkylarenes	Ketones, α-oxidation products	Ozone	H_2O	Likely metal-ozonide intermediate	461
$K_7AlCoW_{11}O_{39}$	Ascorbic acid, phenol, peroxynitrite	Dehydroascorbic acid, nitrated phenol, nitrate	Peroxynitrite	H_2O, pH 7.0 buffer	Initial report of POM catalysis of these reactions; comparison to metalloporphyrin catalysts made	462
$HPW_{11}O_{39}{}^{6-}$ modified with Fe^{II}, Fe^{III}, Mn^{II}	Propane	Oxydehydrogenation products	O_2		Heterogeneous reaction involving high-temperature treatment and transformation of POM	463

[a] Entries are grouped by oxidant. A few reactions conducted under heterogeneous conditions, when the conditions are unusual, are included. Review articles and nonpeer-reviewed publications such as conference proceedings, are not generally included.

[b] CDMA = *p*-cyano-*N*,*N*-dimethylaniline; CDMANO = *p*-cyano-*N*,*N*-dimethylaniline-*N*-oxide; PEO = polyethylene oxide; PFIB = pentafluorobenzene; $[PhIO]_n$ = iodosylbenzene; PPO = polypropylene oxide; TBA, THA, THA′ = tetra-*n*-butylammonium, tetra-*n*-hexylammonium, and tetra-*n*-heptylammonium, respectively; TMA = tetramethylammonium; TBHP = Bu^thydroperoxide; THT = tetrahydrothiophene.

cation undergoes fast proton and electron transfer (or hydrogen atom transfer) to yield a stable benzylic cation which is observable by ^{1}H NMR. Again in this case, the kinetics data are consistent with a rate-limiting oxygen transfer from the POM to the xanthenyl cation, with formation of xanthen-9-one as the only product.

4.11.2.5.4 Oxo transfer to reduced POMs

Most POM reductions (chemical, photochemical or electrochemical) result in the production of "heteropoly blue" species that involve reduction of M^{VI} to M^{V}, M = Mo or W, and some coupling of spins (frequently antiferromagnetic coupling in polyanions with an even number of electrons). Single-electron-reduced species are by far the most common, but two- and four-electron species are not uncommon, and there are several examples of heteropoly blue compounds with six or more electrons. Despite the implication of the name "heteropoly blue," there are several examples of reduced isopolyanions (isopoly compounds) that have similar properties. The structural and electronic properties of these reduced complexes are addressed in older reviews cited in the Introduction (Section 4.11.1) and also in the accompanying chapter by M. T. Pope (Chapter 4.10).

Distinct from these common heteropoly blue complexes are POMs that are reduced by several electrons where the formal oxidation state of M (W or Mo) has now dropped to (IV) and M—M bonding is extant. These compounds have been referred to as "heteropoly browns" from their color, and they are good reducing agents. The best characterized of such species to date are Keggin polyoxotungstates where one edge-sharing triad is reduced and exhibits M—M bonding. Launay initially disclosed the synthesis of the metatungstate derivative by preparative electroreduction of metatungstate $H_2W_{12}O_{40}{}^{6-}$,[328] then three other groups further characterized the six-electron-reduced complex $[H_2W_{12}O_{40}]^{12-}$: Kazansky and Launay published the X-ray photoelectron spectra,[329] Jeannin and co-workers reported a disordered X-ray structure of the Rb_4H_8 salt,[330] and Piepgrass and Pope disclosed the ^{183}W NMR spectra.[331] The latter group also prepared the six-electron-reduced heteropoly browns α-$H_6SiW_{12}O_{40}{}^{4-}$ and α-$H_6BW_{12}O_{40}{}^{5-}$ and characterized them.[331] Yamase and Ishikawa subsequently prepared the diamagnetic six-electron-reduced form of α-$K_5BW_{12}O_{40}$ by prolonged photolysis of an aqueous MeOH solution of this POM at pH 0.1.[332]

The W^{IV} centers in these complexes have terminal aqua ligands coordinated in place of oxo groups. Piepgrass and Pope demonstrated that in nonaqueous solutions, the terminal aqua ligands on the W^{IV} centers in the Keggin heteropoly browns $XW^{VI}{}_9O_{37}W^{IV}{}_3(OH_2)_3{}^{n-}$ ($X = H_2$, B, Si; $n = 6, 5, 4$, respectively) are lost and the resulting apparently five-coordinate metal centers deoxygenate AO (e.g., Me_2SO, Ph_2SO, Ph_3AsO). The corresponding "A" products are formed in moderate to high yields and the oxidized (W^{VI}) HPAs are quantitatively regenerated.[333] The oxygen from Me_2SO is transferred to the terminal oxo positions of $SiW_{12}O_{40}{}^{4-}$ based on isotope-labeling studies. These experiments represent the first examples of a general oxygen atom transfer involving more than one center in unsubstituted HPAs and the first example of oxygen atom transfer to W^{IV}.

A nonredox reactivity of heteropoly browns is the condensation of the terminal aqua ligands on the W^{IV} centers with additional tungstate in aqueous solution between pH = 4 and 6.5 to form the species of formula, $[(XO_4)W^{IV}{}_3W^{VI}{}_{17}O_{62}H_x]^{n-}$, where $X = B^{III}$ (the best characterized) and H_2 (the metatungstate analogue).[334]

4.11.3 CATALYSIS OF THERMAL REACTIONS

4.11.3.1 Basic Modes of POM Redox Reactivity

POMs exhibit two dominant modes of reactivity in redox processes. There are well-documented variations for each mode. Mode 1, which is the most frequent one when O_2 is used as the oxidant, involves initial substrate oxidation (Equation (26)) followed by reoxidation of the reduced POM (Equation (27)). The net reaction is Equation (28). Mode 2, which is most frequent with oxygen donor oxidants including peroxides, involves initial activation of the oxidant, OX, by the POM with formation of a POM-OX complex (Equation (29)). There are three general fates of these complexes. They can directly react with substrate to form product (Equation (30)), transform to another complex, [POM-OX]′ (Equation (31)) which then oxidizes the substrate (Equation (32)), or form freely diffusing oxidizing intermediates that are not bound to the POM catalyst

(Equation (33)), which then oxidize substrate. A prominent example of Equations (29), (31), and (32) is formation of a POM-bound oxygen atom donor, which transforms to a POM oxometal intermediate, which then oxidizes the substrate. The last mode (generation of metal-free oxidizing intermediates) can involve oxygen donors, such as iodosylarenes, peroxides (formation of alkylperoxy, alkoxy radicals, etc.), or O_2 (formation of all the radicals associated with radical chain oxidation or "autoxidation").[335–338]

$$2\,\mathrm{POM_{ox}} + \mathrm{SubH_2} \rightarrow 2\mathrm{POM_{red}} + \mathrm{Sub} + 2\mathrm{H^+} \tag{26}$$

$$2\mathrm{POM_{red}} + 1/2\,\mathrm{O_2} + 2\mathrm{H^+} \rightarrow \mathrm{H_2O} + 2\mathrm{POM_{ox}} \tag{27}$$

$$\mathrm{SubH_2} + 1/2\,\mathrm{O_2} \xrightarrow{\mathrm{POM(catalyst)}} \mathrm{Sub} + \mathrm{H_2O} \tag{28}$$

$$\mathrm{POM} + \mathrm{OX} \rightarrow \mathrm{POM{-}OX} \tag{29}$$

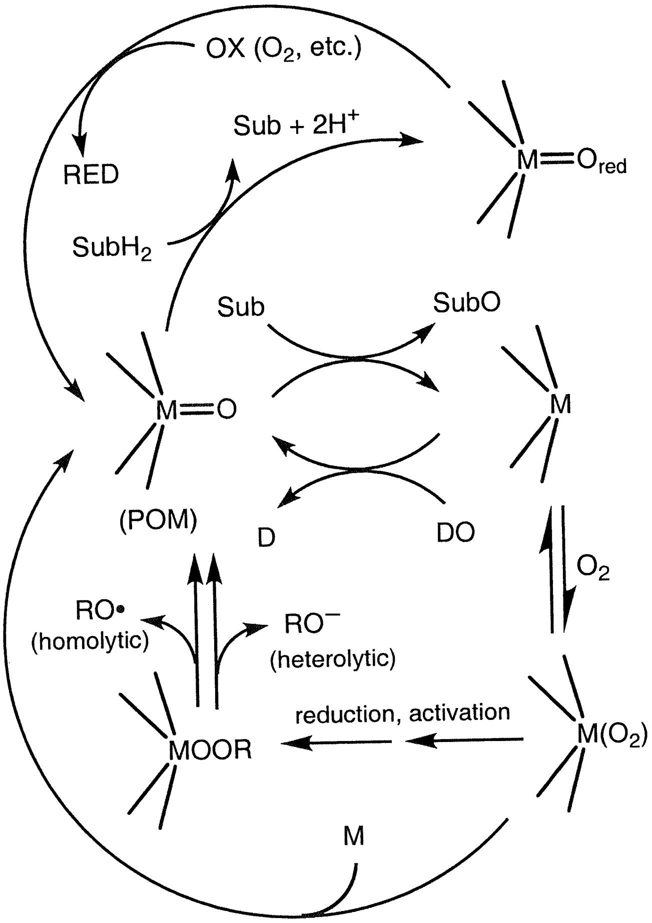
$$\mathrm{POM{-}OX} + \mathrm{SubH_2} \rightarrow \mathrm{POM} + [\mathrm{SubH_2}]_{\mathrm{ox}} \tag{30}$$

$$\mathrm{POM{-}OX} \rightarrow [\mathrm{POM{-}OX}]' \tag{31}$$

$$[\mathrm{POM{-}OX}]' + \mathrm{SubH_2} \rightarrow \mathrm{POM} + [\mathrm{SubH_2}]_{\mathrm{ox}} \tag{32}$$

$$\mathrm{POM{-}OX} \rightarrow \text{metal-free substrate-oxidizing intermediates} \tag{33}$$

These and other basic modes of reactivity are summarized in Scheme 5.



Scheme 5

The bottom process in the scheme represents reaction of a metallodioxygen complex with another molecule of a coordinately unsaturated POM to generate two reactive POM molecules.

If these product POMs can oxidize the desired substrate directly without simultaneous generation of oxy radicals and consequent minimally selective autoxidation, an attractive O_2-based POM-catalyzed chemistry is realized.

Most "homogeneous catalysts" taken from repository containers (bottles, vials, flasks, Schlenkware, etc.) are actually catalyst precursors ("pre-catalysts" in the terminology of Finke), but such materials are referred to as "catalysts" in this review because this is the general convention in the homogenous catalysis literature. In other words, no distinction is made between catalyst precursors and actual catalysts, because it is generally understood the active form(s) of the catalyst are only generated in low concentration during turnover, and that the material in the proverbial bottle is as close to an isolable active catalyst as one typically gets.

The next two sections (Sections 4.11.3.2 and 4.11.3.3) are tables of reactions involving homogeneous catalysis by POMs. The great majority of these reactions are oxidations but some involve acid-dependent or other processes. The coverage is not comprehensive (indeed some of author's own papers are not cited), but it is nearly so. As stated out the outset, this review article does not cover heterogeneous catalysis. A few examples of heterogeneous catalysis by POMs are included in Tables 1 and 2 but only those that entail unusual catalyst immobilization chemistry. The reactions involving homogeneous catalysis by POMs have been divided up into two groups: Table 1 summarizes the reactions catalyzed by POMs that contain one or more *d*-electron-containing active site(s), and Table 2 summarizes the reactions catalyzed by d^0 POMs (most frequently mixed addenda HPAs). Several reviews have appeared on portions of this chemistry.[86,87,307,339–356] Three other references are pertinent.[357–359]

The purpose of this review is not to critically analyze this now substantial body of work or to discuss mechanism in detail but to present a reasonably comprehensive tabulation of the reactions. While fairly in-depth analyses of many of these reactions have been published recently,[86,352] a truly critical review of the mechanisms in POM-catalyzed oxidations that is also reasonably comprehensive would require a book-sized review. Such a review is needed.

4.11.3.2 Homogeneous Catalysis by *d*-electron-metal-substituted Polyoxometalates

The initial impetus for the development of such catalysts was that they represent oxidatively resistant versions of the much-studied metalloporphyrins.[320] In short, both the *d*-electron-containing TMSPs and metalloporphyrins share key positive features pertinent to oxo transfer oxidation (oxygenation). These include but are not limited to a redox-functional active site firmly held by a chelating ligand that simultaneously has a redox capacity.[343] The redox chemistry of the multidentate ligand facilitates formation of highly reactive (and frequently quite selective) high-valent oxometal species (e.g., M$=$O, where $M = Fe^{IV}$, the equivalent of Fe^V, Mn^{IV}, Mn^V, Cr^{IV}, Cr^V, and others). Importantly however, TMSPs unlike metalloporphyrins and metal complexes of other macrocyclic ligands, are oxidatively resistant and, in most cases, readily prepared in quantity. The initial reports of adduct formation were by Katsoulis and Pope and other groups (addressed in Section 4.11.2.5.1 above and elsewhere in the review), and the initial report of a TMSP catalyzing substrate oxygenation (oxygen atom rebound oxidation from a formal oxygen donor, analogous to the shunt mechanism with the cytochrome P-450 enzymes) was by Brown and Hill in 1986.[360] Since then the groups of Neumann, Finke, Pope, Lyons, and Ellis, and others have contributed to this approach. The findings in the principal papers involving catalysis by TMSPs are summarized in Table 1.

The principal mechanistic paradigm in such POM-catalyzed oxidations is that of oxo transfer via high-valent oxygenated TMSPs (Equations (24) and (25), which are subsets of the general processes in Equations (29) and (30) above). However, with all oxygen donor oxidants, including those that appear to be optimally constrained to follow an oxo rebound mechanism such as *N*-oxides or iodosylarenes, the mechanisms are frequently more complex. Reactions with most peroxo species and even more so with O_2 as terminal oxidant, are almost always more complex. The detailed mechanistic aspects of TMSP-catalyzed H_2O_2 activation and H_2O_2-based oxidations have been thoroughly addressed, but many questions remain. The same is true for the one oxidant that is more environmentally and economically attractive—O_2. While POMs are known that activate O_2 and facilitate oxidations of organic substrates that proceed with minimal or no intervention of radical chain processes[361,362] the development of this promising area is in its infancy.

4.11.3.3 Homogeneous Catalysis by d^0 Polyoxometalates

This class of catalyzed oxidations dates to the mid-1970s and the research of Matveev and co-workers. Articles by Matveev and Kozhevnikov in the early part of the time period of *CCC II* (early 1980s) review this early work.[339,340] The most prominent and attractive general process catalyzed by these d^0 POMs is the O_2-based oxidation of organic substrates. Most frequently H_2O is the by-product (thus the overall process is oxidative dehydration; net reaction is Equation (28)), but other overall processes (stoichiometries) can be observed. The principal mechanistic paradigm associated with homogeneous catalysis by d^0 POMs involves an initial oxidation of the substrate by the POM, followed by reoxidation of the reduced POM with O_2 (Equations (26) and (27)). As for the TMSP-catalyzed reactions addressed in the previous section and in Table 1; however, the mechanisms of these processes can be quite complex. The substrate oxidation step (Equation (26)) can proceed by different mechanisms although outer sphere electron transfer followed by deprotonation of the substrate cation radical appears to be the most common. In addition, the second step ($POM_{red} + O_2$; Equation (27)) can proceed either by an outer sphere or inner sphere process. The reduced forms of the minimally labile polyoxotungstates appear to be reoxidized by O_2 by outer sphere processes, or more rigorously, processes that do not involve exchange of POM oxo oxygens with O_2 oxygen.[363] In contrast, the reduced forms of the more labile and also heavily investigated mixed addenda vanadopolyoxomolybdates appear to be reoxidized by inner sphere processes, and in some cases by donation of a POM oxygen atom to the substrate followed by replenishment of the POM oxo oxygen by oxygen from O_2 (the Mars-van Krevelen mechanism).[310,325] The findings in the principal papers involving catalysis by d^0 POMs are summarized in Table 2.

4.11.4 PHOTOCHEMICAL PROCESSES

4.11.4.1 Some History

Reports of the photosensitivity of POMs in the presence of organic compounds date to at least 1916;[364] however, the first systematic study of POM photochemistry was the work of Yamase who studied the photochromism of alkyl- and dialkylammonium polymolybdates[365,366] and subsequently the structural and spectroscopic (largely EPR) properties of irradiated alkylammonium molybdates.[367–372] In key early work involving POMs as photocatalysts, Papaconstantinou reported the photocatalytic oxidation of alcohols by O_2 in 1982 (Equation (34)),[373] Darwent published the anaerobic photocatalytic production of H_2 from alcohols later that same year (Equation (35)),[374] and Hill showed the breadth of the photocatalytic oxidation of organic compounds by POMs in 1985.[375] In the intervening years, many features of POM photochemistry have been elucidated. The key papers in this and other areas and their principal findings are summarized in Table 3:

$$R^1R^2CHOH + 1/2\ O_2 + h\nu \xrightarrow[H_2O,air,25\,^\circ C]{H_3PW_{12}O_{40}(cat)} R^1R^2CO + H_2O \tag{34}$$

$$R^1R^2CHOH + h\nu \xrightarrow[H_2O,25\,^\circ C]{H_3PW_{12}O_{40}(cat)} R^1R^2CO + H_2 \tag{35}$$

where R^1 and R^2 = alkyl or hydrogen.

A number of reviews on POM photochemistry and photocatalysis have appeared over the years by the principal investigators in this area (alphabetically): Ferry, a recent arrival to this field,[376] Giannotti,[377,378] Hill,[342,343,345,347,379–383] Maldotti,[384] Papaconstantinou,[385–390] Tanielian,[391] Yamase,[52,392,393] and others. Most of these reviews target, understandably and conventionally, the work of the researcher's group itself, but a few are comprehensive[382] or at least comprehensive for a particular subtopic, e.g., alkane functionalization,[383] intermediates in decatungstate photochemistry,[391] or photochemistry of composite systems.[384]

4.11.4.2 General Features of Reactivity

Most organic molecules and many inorganic ones can function as electron donors (reductants) to POMs of many structural classes (generic acceptors and oxidants). Indeed a multitude of processes

Table 2 Homogeneous catalysis by d^0 POMs.[a]

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comments*	*References*
$Na_5H_2PV_4Mo_8O_{40}$	CO	CO_2, Me_2CO_3, Et_2CO_3, EtO_2CCO_2Et	O_2	MeCN, EtOH, H_2O	Co-catalysis by Pd^{II} salts	464
Vanadomolybdophosphates	Toluene, *p*-xylene, mesitylene, durene, pentamethylbenzene, hexamethylbenzene	Alcohols, aldehydes diarylmethanes	O_2		Cation radical intermediates demonstrated	465
Vanadomolybdophosphoric acid	CO	CO_2	O_2		Aqueous Pd^{II}; POM + Pd^{II} salts; increase in H_2O concentration increases yield of CO_2	466
$H_5PV_2Mo_{10}O_{40}$	Phenolic compound, alkene, ketone	*p*-Bromo derivative, vicinal dibromide α-bromoketone	O_2/HBr	$ClCH_2CH_2Cl$ tetraglyme	Effective oxybromination catalyzed by a POM; tetraglyme was used as a complexing agent to enable dissolution of $PV_2Mo_{10}O_{40}{}^{5-}$ in its acidic form in nonpolar organic solvents; several other complexing agents were examined	467
$H_4PVW_{11}O_{40}$ $H_6PV_3W_9O_{40}$	CO	CO_2	O_2		Catalysis occurs in presence of aqueous $PdSO_4$; article concentrates on rate data	468
$Na_3H_3PV_3Mo_9O_{40}$	Larixol	Acetate, dienes	O_2	Acetic acid	Oxidation studied under three conditions; yield and selectivity good with optimal system	469

Table 2 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comments*	*References*
$H_{3+n}PV_nMo_{12-n}O_{40}$, where $n = 0$–3 $H_{3+n}PV_nW_{12-n}O_{40}$, where $n = 0$–1	Benzylic ketone	Acid, benzaldehyde; for $n = 0$, only trace amounts of products were observed; for $n = 1$, benzoic acid, a dione, and *trans*-stilbene were produced as minor products	O_2	MeCN or substrate	High yield oxidative cleavage of ketones	470
$H_5PV_2Mo_{10}O_{40}$	α-Substituted cyclic ketone	Ketoacid	O_2	MeCN, H_2O, or $AcOH/H_2O$	High selectivity oxidative cleavage under mild (60 °C, MeCN, 2–6 h) conditions	471
$H_6PV_3Mo_9O_{40}$	4-Oxoalkyl-substituted 2,6-di-Bu^t-phenol	Dienones, quinones	O_2	C_6H_6, MeOH	Acidic conditions due to presence of heteropolyacid; reaction is sensitive to the solvent used; oxidation occurs via differing routes depending on whether one-electron oxidants, dioxygen, or photochemical irradiation is used	472
$H_6PV_3Mo_9O_{40}$	4-(3,5-Di-Bu^t-4-hydroxyphenyl)butan-2-one,	4-Hydroxy-4-(3-oxobutyl)-2,6-di-Bu^t-2,5-cyclohexadien-1-one and *p*-benzoquinone	O_2	C_6H_6	Catalyzed and uncatalyzed reactions proceed by different mechanisms	473
	methyl ester of β-(3,5-di-Bu^t-4-hydroxyphenyl)propionic acid	*p*-benzoquinone, spirolactone, dienone, and quinol		C_6H_6 or MeOH		
$TBA_5Na_3(1,5\text{-COD})IrP_2W_{15}Nb_3O_{62}$	Alkene	No rxn	O_2/H_2, H_2O_2	CH_2Cl_2	POM-supported Ir^+ complexes are precatalysts; later research showed Ir^0 nanoclusters are formed	474
$H_5PV_2Mo_{10}O_{40}$	Dialkyl phenols	Diphenoquinones	O_2	*n*-Hexanol or CH_3CH_2OH	Rate depends on oxidation potential of substrate and proceeds by electron transfer	304

$H_{3+n}PV_nMo_{12-n}O_{40}$ where $n = 2, 4$, or 6	2,4,6-Trimethylphenol, 2,3,6-trimethylphenol	2,3,5-Trimethyl-1, 4-benzoquinone	O_2	$AcOH/H_2O$, CH_3OH/H_2O, CH_3CN/H_2O, $(CH_3)_2CO/H_2O$, CH_2Cl_2, or $CHCl_3$	86% yields at 100% conversion of substrate; VO^{2+} proposed to be the oxidizing intermediate	475,476
$H_5PV_2Mo_{10}O_{40}$	*d*-Terpinene	*p*-Cymene	O_2	MeCN	Early kinetics and mechanism study of Keggin polymolybdates catalyzing O_2 oxidations	305
$(NH_4)_5H_4PV_6W_6O_{40}$, $(NH_4)_3PW_{12}O_{40}$, $(NH_4)_3PMo_{12}O_{40}$, or $(NH_4)_7HPV_4W_8O_{40}$	Alkene, aldehyde	Epoxide	O_2	$ClCH_2CH_2Cl$	Aldehyde co-reductant	477
$H_3PW_{12}O_{40}$, or $H_3PMo_{12}O_{40}$	Alkene, aldehyde	No reaction				
$(NH_4)_5H_4PV_6Mo_6O_{40}$	Aldehyde Ketone Thianthrene 5-oxide	Acid or ester Ester Thianthrene dioxides				
$(NH_4)_5H_4PV_6Mo_6O_{40}$,	Indan isochroman benzylamine	1-Indanone 3,4-dihydroisocoumarin Schiff-base imine	O_2	$C_6H_5CH_3$	High-selectivity reactions; 100 °C	478
$(NH_4)_5H_4PV_6W_6O_{40}$, $(NH_4)_3HPVMo_{11}O_{40}$, $H_4PVMo_{11}O_{40}$, $H_3PMo_{12}O_{40}$ $H_3PW_{12}O_{40}$, $H_5PV_2Mo_{10}O_{40}$	Benzylamine	Schiff-base imine				
$H_7PV_4Mo_8O_{40}$	α-Subst. cyclic ketone	Ketoacid	O_2	H_2O	Product distribution is very dependent on solvent	479
	Cyclic ketone	Acid		$AcOH/H_2O$		
$TBA_5PV_2Mo_{10}O_{40}$	α-Subst. cyclic ketone	No rxn		MeCN	60 °C	
$H_5PV_2Mo_{10}O_{40}$	Cyclic ketone	Acid		MeCN, H_2O, Bu^tOH, C_2H_5OH, $AcOH/H_2O$	65–70 °C	
$K_{14}NaP_5W_{30}O_{110}$, $K_7PW_{11}O_{39}$, $K_8SiW_{11}O_{39}$	H_2S	S_8	O_2	H_2O	60 °C; highly selective and stable catalysts	480

Table 2 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comments*	*References*
$TBA_5P(Z^{n+}L)M_{11}O_{39}$, where M = Mo, W; Z = Mn^{II}, Fe^{III}, Co^{II}, Ni^{II}, Cu^{II}; L = unknown	Cyclohexene	Epoxide, allylic alcohol, allylic ketone	O_2	$ClCH_2CH_2Cl$	Mild reaction conditions; transition-metal center responsible for activation of dioxygen	481
$TBA_5P(Z\text{–}L)Mo_{11}O_{40}$, where Z = Mn, Fe, or Cu and L = unknown	Cyclohexene	Cyclohexene epoxide, cyclohexen-1-ol, cyclohexen-1-one	O_2	CH_2Cl_2	Conversion of cyclohexene 50–70%; product ratios are typical for autoxidation	482
Hydrotalcites intercalated with TMSP	Cyclohexene	2-Cyclohexene-1-one, 2-cyclohexene-1-ol	O_2		Heterogeneous catalyst	483
$H_{3+n}PV_nMo_{12-n}O_{40}$	2-Methyl-1-naphthol	2-Methyl-1,4-naphthoquinone (menadione, or vitamin K3)	O_2	Benzene, hexane, other organic solvents	'Vikasib' technology overcomes problem of hard-to-procure raw material through use of naphthol-1; ways to increase catalyst selectivity are presented; biphasic solvent system	484
Soluble and supported vanadomolybdophosphates	Benzylic and allylic alcohols 2,3,6-trimethylphenol, amines, alkyl-substituted phenols, alkanes	Aldehydes, ketones trimethyl-*p*-benzoquinone	O_2	Several used	Catalytic activity enhanced using charcoal support	485
$H_5PV_2Mo_{10}O_{40}$	THT[b]	THTO[b]	O_2	MeCN	Initial report of a combinatorial approach for POM catalysts	406
$Na_5PV_2Mo_{10}O_{40}$	Lignin, polysaccharide fragments	CO_2, H_2O	O_2	H_2O	Wet oxidation (oxidative mineralization) via radical-chain autoxidation	486
$PV_5Mo_7O_{40}{}^{8-}$	Lignin	CO_2	O_2	H_2O	Pulps of commercially acceptable quality are produced using this system; technology is fairly environmentally benign; retention of viable pulp viscosities requires EtOH as co-solvent	487,488

$H_5PV_2Mo_{10}O_{40}$-SiO_2 $H_5PV_2Mo_{10}O_{40}$-$SiO_2 \cdot NH_3^+$	Cyclohexene adamantane arylalkane	Cyclohexene oxide1- and 2-substituted alcohols benzylic ketones	O_2	$ClCH_2CH_2Cl$	Isobutyraldehyde coreductant; POM supported on mesoporous MCM-41, and amino-modified MCM-41; acylperoxy radical intermediates oxidize substrate	489
$TBA_7SiV_3W_9O_{40}$ $TBA_9P_2V_3W_{15}O_{62}$ $TBA_5[(MeCN)_xFeSiV_3W_9O_{40}]$ $TBA_5[(MeCN)_xFeP_2V_3W_{15}O_{62}]$	3,5-Di-*t*-Butylcatechol	Muconic acid anhydride; 4,6-di-*t*-Butyl-2H-pyran-2-one; spiro [1,4-benzodioxin-2(3H), 2′-[2H]pyran]-3-one; 4′,6,6′,8-tetrakis (1,1-dimethylethyl); 3,5-di-*t*-butyl-5 (carboxymethyl) -2-furanone; 3,5-di-*t*-butyl-1,2-benzoquinone	O_2	$ClCH_2CH_2Cl$	Four new polyoxoanion-based dioxygenase precatalysts described; very high turnover numbers	411
$H_5PV_2Mo_{10}O_{40}$	Aldehydes, alkanes	Ketones	O_2	Acetone, MeCN, acetic acid	Aldehyde coreductant; POM-aldehyde interaction examined; system has high selectivity for ketone formation; acylperoxy radical intermediates oxidize substrate	490
Vanadomolybdophosphoric acids	2,6-Dimethyl- and 2,6-di-*t*-Butylphenols	2,6-Dialkyl-1,4-benzoquinones	O_2	11 different solvents	Organic (substrate)—aqueous (POM) biphasic system	491
$M_5PV_2Mo_{10}O_{40}$, where $M = Na^+$ or TBA^+	Benzylic and allylic alcohols	Aldehydes	O_2	A range of solvents	Quinones are effective co-catalysts for both homogeneous and supported POM-based catalytic oxidative dehydrogenation of alcohols	309
$H_5PV_2Mo_{10}O_{40}$	Anthracene xanthene fluorene diphenylmethane	Anthraquinone xanthone fluorenone benzoquinone	O_2	MeCN	Electron transfer oxidation; evidence for Mars-van Krevelen mechanism (see ref. 311)	325

Table 2 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comments*	*References*
$H_5PV_2Mo_{10}O_{40}$	Acetaldehyde 1-propanethiol THT[b]	Acetic acid dipropyl disulfide THTO[b]	O_2	Chlorobenzene	POM deposited on cotton cloth, polyacrylic fiber, nylon fiber, Ambersorb™, and Smoklin™; facile reaction at 25 °C with 1 atm of O_2	492
$H_2F_6NaV^{V}W_{17}O_{56}{}^{8-}$ $XV^{IV}W_{11}F_nO_{40-n}$, where $X = H_2$, V, W and $n = 1$–4	Alkyl aromatic compounds	Oxydehydrogenation products	O_2	No solvent	Biphasic (water-catalyst and substrate) media. The ratio of autoxidation to oxydehydrogenation depends on substrate, T and O_2 pressure	493
$H_5PV_2Mo_{10}O_{40}$ + TEMPO	Primary and secondary alcohols	Aldehydes, ketones	O_2	Acetone	Synergistic co-catalysis; selectivities very high; some mechanistic features established	494
$H_5PV_2Mo_{10}O_{40}$	Anthracene, xanthene	Anthraquinone, xanthen-9-one	O_2	MeCN	Mars-van Krevelen thoroughly established; mode of substrate oxidation more likely electron transfer than H transfer	310
Library of POMs	Alcohols	Aldehydes, ketones	O_2	*t*-Butanol, EtOAc,[b] MeCN, MIBK;[b] 15 different solvents	High throughput screening of combinatorial library; supported catalysts included	495
$AlV^{V}W_{11}O_{40}{}^{6-}$ as component of equilibrating POM ensemble	Lignin in wood	CO_2, H_2O	O_2	H_2O	Self-buffering, thermodynamically stable catalyst	496
$SiV^{V}W_{11}O_{40}{}^{5-}$	Phenolic lignin	CO_2, H_2O	O_2	H_2O	Self-buffering, stable catalyst	311
$H_5PV_2Mo_{10}O_{40}$	Alcohols	Aldehydes	O_2	Polyethylene glycol	Catalyst-solvent phase can be recovered and re-used	497
	Cyclic dienes	Dehydrogenation products				
	Sulfides	Sulfoxides				

$PV_xMo_{12-x}O_{40}^{3+x-}$, where $x = 0$, 2	Benzylic, allylic and aliphatic alcohols	Aldehydes, ketones	O_2	DMSO	Sulfoxide is shown to be the oxygen donor; mechanism and kinetics given	498
$H_3PW_{12}O_{40}$	Allyl alcohol	Glycerol	H_2O_2		Peroxotungstate intermediates	499
$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $K_4SiMo_{12}O_{40}$, $H_4GeMo_{12}O_{40}$, $H_3PMo_{10}W_2O_{40}$, $H_5PV_2Mo_{10}O_{40}$	Cyclopentene	61% glutaraldehyde	H_2O_2	Tributylphosphate solution	35 °C; mixed-addenda heteropoly acids of Mo and W are particularly effective	500
$H_{3,4}XM_{12}O_{40}$, where $X = P$ or Si $Na_3PM_{12}O_{40}$, where $M = W$ or Mo	2,6-Di-*t*-Butyl-4-methylphenol	2,6-Di-*tert*-Butyl-4-hydroperoxy-4-methyl-2,5-cyclohexadien-1-one, 2,6-di-*tert*-butyl-4-hydroxy-4-methyl-2,5-cyclohexadien-1-one, 2,6-di-*tert*-Butyl-*p*-benzoquinone	H_2O_2	$MeCO_2H$	30 °C, N_2	501,502
$H_3PMo_{12}O_{40}$, $H_4SiMo_{12}O_{40}$, $H_3PW_{12}O_{40}$	3,4,5-Trimethoxytoluene	2,6-Dimethoxy-*p*-benzoquinone	H_2O_2	$MeCO_2H$, MeOH, MeCN, or HCO_2H	50–60% yields at 30 °C, N_2	503
CP salts of uncharacterized polyperoxotungstates	*Vic*-diols	α-Hydroxy ketones	H_2O_2	$CHCl_3$	Biphasic conditions	504
$TBA_6H_2Si_2Nb_6W_{18}O_{77}$	Alkene allylic alcohol maleic acid	No rxn triol *d,l*-$HO_2CCH(OH)$-$CH(OH)CO_2H$	H_2O_2	MeCN	The POM breaks down to form the actual catalyst	505
$H_3PMo_{12}O_{40}$	Cyclohexene	Cyclohexene oxide, *trans*-1,3-cyclohexanediol	H_2O_2		Reaction affected by concentration of H_2O and POM redox potential	506
$H_5BW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_6P_2W_{18}O_{62}$	Alkene	No rxn	H_2O_2	$CHCl_3$	Degradation of $H_3PW_{12}O_{40}$ by H_2O_2 to form polyperoxometalates clearly shown; biphasic medium	507
$H_3PMo_{12}O_{40}$, $H_3PW_{12}O_{40}$, $K_4W_{10}O_{32}$, $(NH_4)_{10}H_2W_{12}O_{42}$, $(NH_4)_6Mo_7O_{24}$	Alkene	Epoxide				

Table 2 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comments*	*References*
$TBA_3PW_{12}O_{40}$, $TBA_5H_2PW_{11}O_{39}$	Alkene	Epoxide	H_2O_2	MeCN	H_2O_2 decomposition as well as cyclohexene epoxidation studied	416
Uncharacterized polyperoxotungstates (CP salt)	Primary and secondary aliphatic and aromatic amines	Oximes, nitrones, nitroso compounds and nitrobenzene	H_2O_2	$CHCl_3$	Biphasic or homogeneous conditions; the catalytically active intermediates were correctly identified by other groups later	508
$H_5PV_2Mo_{10}O_{40}$,	Alkyl aromatic compounds	Ketone acetate	H_2O_2	MeCOOH	110 °C or 60 °C; POM not degraded during catalytic cycles; benzyl radicals are intermediates	509
	Alkyl benzene	Ketone		DMF, CH_3OH, or formic acid		
$H_5PV_2W_{10}O_{40}$	Alkyl aromatic compounds	Ketone acetate		MeCOOH		
$H_4PVMo_{11}O_{40}$	Alkyl aromatic compounds	Ketone acetate		MeCOOH		
$H_5SiV_2Mo_{10}O_{40}$	Alkyl aromatic compounds	Ketone acetate		MeCOOH		
$H_3PMo_{12}O_{40}$ or $H_3PW_{12}O_{40}$	Alkyl aromatic compounds	Ketone		MeCOOH		
$THA_5PV_2Mo_{10}O_{40}$	Alkyl benzene	Ketone		$ClCH_2CH_2Cl$		
$H_5PV_2Mo_{10}O_{40}$	Alkyl benzene	Ketone alcohol		MeCN, ethylene glycol, $(CH_3)_2CO$, or sulfolane		
Uncharacterized polyperoxotungstates (CP salt)	Anilines	Nitroso- or nitrobenzenes	H_2O_2	$CHCl_3$, Bu^tOH, or MeOH	25 °C; reasonable yields of oxidized nitrogen compounds; in the case of methanol solvent, nitrosobenzene is the only product	510
CP salts of uncharacterized polyperoxomolybdates and polyperoxotungstates	Sulfide	Sulfoxide, sulfone	H_2O_2	$CHCl_3$	25 °C; different catalyst preparation protocols give quite different selectivities; nitrosobenzene is the only product	511

$H_3PM_{12}O_{40}$	Alkenes	Epoxides	H_2O_2	$H_2O/CHCl_3$ with biphasic conditions	Mechanistic information on formation and reactivity of polyperoxometalate intermediates	24
$TMA_4[(Me_2AsO_2)\{MoO(O_2)_2\}_2]$, $TBA_4[(Ph_2PO_2)\{WO(O_2)_2\}_2]$, $TMA_4[(Ph_2PO_2)\{MoO(O_2)_2\}_2]$, $NH_4[(Ph_2PO_2)\{MoO(O_2)_2(H_2O)\}]$	Alkenes, alcohols, tertiary amines	Epoxides aldehydes, ketones *N*-oxides	H_2O_2 H_2O_2 H_2O_2	Benzene benzene toluene	Second paper in a series; investigates influence of η^2,η^1-peroxo groups on the catalytic oxidation properties of title compounds	512
$H_5PV_2Mo_{10}O_{40}$—PEO-$SiO_2THA_3PO_4$ $[W(O)(O_2)]_4$—PEO/PPO-SiO_2	Ayclooctene cyclooctene	Cyclooctene oxide cyclooctene oxide	IBA[b]/O_2, H_2O_2	1,2-Dichloroethane no org. solvent	Solvent-anchored, supported, liquid-phase catalysts	513
$H_7P_2VMo_{17}O_{62}$, $Cpyr_8P_2V_2Mo_{16}O_{62}$	Ethylbenzene	Acetophenone	H_2O_2	Various solvents used, including DMF,[b] MeCN, MeOH, acetone, acetic acid, formic acid, ethylene glycol, $ClCH_2CH_2Cl$	Role of intermediate peracid is not clear; V in POM is important for reaction; highest conversion was obtained in acetic acid, which is 29.4%; selectivity for acetophenone can reach up to 100%	514
"$PVMo_{11}O_{40}{}^{4-}$" prepared 3 different ways	Benzene	Phenol	H_2O_2, $MeCO_3H$	Biphasic reaction system; organic layer contains C_6H_6 and CH_3CN, and aqueous layer contains MeCN and 30% H_2O_2	Different activities attributed to different isomers (mono- vs. di- and tri-vanadium POMs and different positional isomers)	515
Vanadium-substituted heteropolymolybdates	Alkylbenzenes	Range of oxidation products, aromatic ring hydroxylation products	H_2O_2, Bu^tOOH	MeCN	H_2O_2 leads to both allylic and ring oxidation products; Bu^tOOH leads primarily to allylic products	516
A,β-$(NbO_2)_3PW_9O_{37}{}^{6-}$	Alkenes	Epoxides	H_2O_2		The active catalyst is shown to be a low nuclearity tungstate from peroxide degradation of the reactant POM	517

Table 2 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comments*	*References*
$PZnMo_2W_9O_{39}{}^{5-}$	Alkenes, alkylaromatic compounds	Epoxides	H_2O_2	Chloroform	Epoxide selectivity ranges from 80% to 100%	518
$H_3PMo_{12}O_{40}$ $H_3PVMo_{11}O_{40}$ $H_5PV_2Mo_{10}O_{40}$ $H_6PV_3Mo_9O_{40}$ $H_3PMo_6W_6O_{40}$ $K_7PTi_2W_{10}O_{40}$	Organic sulfides	Phenyl sulfoxide, propyl and phenyl sulfone	H_2O_2	MeCN	Comparison of reactivities of unsubstituted and V/Ti-substituted heteropolycompounds vs. substituted silicalites for oxidation of organic sulfides	519
$Q_3\{PO_4[WO(O_2)_2]_4\}$, where $Q = C_{18}H_{37}(CH_3)_3N^+$, $C_{16}H_{33}(CH_3)_3N^+$, $C_{16}H_{33}C_5H_5N^+$, $(C_8H_{17})_3CH_3N^+$	Octadecanol	Octadecanoic acid	H_2O_2	No solvent	Conversion ranges from 20% to 70%; yield of octadecanoic acid ranges from 16% to 53%, depending on the quaternary alkyl ammonium cation, the pH of solution, and temperature; H_2O_2 decomposed completely after 6 h under reaction conditions	520
Heteropolyacids + phase transfer catalysts	Benzyl alcohol	Benzaldehyde	H_2O_2	H_2O/organic solvent	Biphasic with phase-transfer catalysts	521
$H_3PW_{12}O_{40}$ $H_6P_2W_{18}O_{62}$	Hexanol	Hexanal	H_2O_2	H_2O, hexanol	Biphasic liquid-liquid system	522
Keggin-type heteropolyacids	Hexanol	Hexanal	H_2O_2	H_2O, hexanol	Biphasic liquid-liquid system	523
Vanadium-substituted molybdophosphoric acids	Benzene	Phenol	H_2O_2, AcOOH	MeCN	Nearly quantitative selectivity to phenol at reasonable conversions of benzene	524
$K_{15}[La(PMo_9V_2O_{39})_2]$	Toluene	Benzoic aldehyde	H_2O_2	Different solvents were used, including acetic acid, methanol, THF, DMF, acetone, acetonitrile, etc.	Reactions were carried out under both homogeneous and heterogeneous conditions; the best results were in homogeneous acetonitrile (19% yield and 25% selectivity)	525

$Y_4PVMo_{11}O_{40}$, $Y = TBA^+; K^+; Na^+$ $Y_4KPV_2W_{10}O_{40}$, $Y = TBA^+; K^+$ $K_7P_2VMo_2W_{15}O_{62}$	Toluene, nitrobenzene	*o*-Cresol, *m*-cresol, *p*-cresol, benzyl alcohol, benzaldehyde	H_2O_2	Substrate and MeCN in organic layer; MeCN + 30% H_2O_2 in aqueous layer	Mechanism and side-chain vs. ring oxidation of toluene addressed	526
$K_{15}H_2[Ce(P_2W_{15}Mo_2O_{61})_2]$	Glyoxal	Allantoin	H_2O_2	No solvent	Highest yield is 27.2%, selectivity not reported	527
$HPDA[H_2PDA]_2[As_2^{III}AsV_4Mo_8O_{40}]$	Benzaldehyde	Benzoic acid	H_2O_2		Liquid-solid biphasic system	528
$H_3PM_{12}O_{40}$, $H_4SiM_{12}O_{40}$, where M = W or Mo	*p*-Substituted phenols	Peroxy ketone, quinone, dimer derived from substrate	Bu^tOOH	MeCOOH	30 °C	529
$TBA_2H_4[CH_3C(CH_2O)_3P_2V_3W_{15}O_{59}]$ $TBA_5H_4P_2V_3W_{15}O_{62}$, $TBA_6P_2W_{18}O_{62}$, $TBA_5H[CH_3C(CH_2O)_3P_2V_3W_{15}O_{59}]$	Thioether	Sulfoxide	Bu^tOOH, H_2O_2, PhIO	MeCN	Triester linkage to POM stable under turnover conditions	199
$H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$, $H_5PV_2Mo_{10}O_{40}$	Sulfides	Sulfoxides	Bu^tOOH	MeCN	99.9% selective; reaction inhibited by H_2O	530
$H_4PVMo_{11}O_{40}$	α-Terpinene	*p*-Cymene	Bu^tOOH	MeCN	Correlating catalytic activity with catalyst self-assembly	531
$H_5PV_2Mo_{10}O_{40}$	Sulfides	Sulfoxides	Bu^tOOH	Toluene	POM supported on carbons; 99% selective for sulfoxide	532
$H_5PV_2Mo_{10}O_{40}$ and $[ZnWMn_2^{II}(ZnW_9O_{34})_2]^{12-}$—PEO/PPO cationic SiO_2	Dihydroanthracene	Anthracene	Bu^tOOH	Toluene	POMs bound to silica with PEO, PPO, and quaternary ammonium groups	450
$Na_4PTlW_{11}O_{39}$	Sclareol	Oxetane, epoxides, diol	Tl^{III}	MeOH	Reactions proceed under ambient conditions	533
$H_6PV_3Mo_9O_{40}$	γ-(3,5-Dialkyl-4-hydroxyphenyl)propanols	Oxaspirodecadienone (major), 2,6-di-Bu^t-*p*-benzoquinone (minor)		Benzene, MeOH	Biphasic (POM in H_2O, substrate in benzene)	534

Table 2 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*	*Solvent*	*Comments*	*References*
$H_5PV_2Mo_{10}O_{40}$ $H_5SiVW_{11}O_{40}$	CH_4 and CO	Acetic acid	$K_2S_2O_8$	CF_3COOH	Catalytic system that converts methane and CO to acetic acid almost quantitatively	535
$PMo_{12}O_{40}{}^{3-}$	Alkylarenes	Oxygenated products	Sulfoxides	$ClCH_2CH_2Cl$	A good correlation of heterolytic benzylic C—H bond energies and alkylarene oxidation rates; the formation of 9-phenylfluorene from triphenylmethane and other data imply rate-limiting hydride abstraction by POM-sulfoxide complex	536
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$ $H_3PW_{12}O_{40}$	Alkene	H_2O and alcohol addition products		H_2O, C_6H_6	Biphasic liquid–liquid and solid catalyst–liquid reactions (“water-tolerant” catalysts)	537
	Esters and oligosugars nitrile + alcohol formalin + benzene	Hydrolysis products *N*-alkylamide diphenylmethane				
$H_3PW_{12}O_{40}$	17-α-hydroxyprogesterone	17-α-Capronate, 3,17-α-dicapronate	N/A[c]	MeCN, or CH_2Cl_2	POM-acid catalyzed esterification and acetylization of steroids; 40 °C; $(AmCO)_2O$ was added as a reactant	538
$H_3PM_{12}O_{40}$, where M = Mo or W $H_4SiW_{12}O_{40}$	Aldehyde	Trioxane	N/A[c]	Substrate, hexane, or diethyl ether	Cyclotrimerization of aliphatic aldehydes catalyzed by POM acids (25 °C)	539
$H_mXW_{12}O_{40}$, where X = P, Si, Ge, B, or Co	Isobutyl propionate	Isobutylene + propionic acid	N/A[c]		POM acid catalyzed reactions; PTS,[b] 128 °C, N_2 for esterification	540
$H_6P_2W_{18}O_{62}$	Isobutyl propionate, MeCOOH isobutyl propionate, *n*-propyl alcohol	Isobutyl acetate + propionic acid propyl propionate + isobutyl alcohol				
	Propionic acid	Isobutyl propionate		Isobutyl alcohol		

$H_mXW_{12}O_{40}$, where X = P, Si, Ge, B, Fe, or Co	isobutyl propionate		N/A[c]		Direct correlation of POM acidity with other catalytic activity	541
$(NH_4)_6Mo_7O_{24}$	D-mannose, D-xylone, D-lyxose	D-glucose	N/A[c]	MeCN-H_2O mixtures	POM-acid catalyzed epimerization of *d*-mannose to *d*-glucose; binding and rate constants given	542,543

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[a] A few reports involving heterogeneous catalysts are included. These involve unusual or noteworthy POM immobilization chemistry. No reactions involving standard heterogeneous catalytic oxidation (gaseous reactants and/or products over solid catalyst at high temperature) are included. [b] 2-PrOH = 2-propanol; AcOH = acetic acid; Bu^tH = *t*-butanol; Cpyr = hexadecylpyridinium; EtOAc = ethyl acetate; HD = thioether mustard; IBA = isobutryaldehyde; IBP = isobutyl propionate; MIBK = methyl isobutyl ketone; NHPI = *N*-hydroxyphthalimide; PDA = propanediamine (HPDA and H_2PDA are mono- and diprotonated forms of PDA); PhIO = iodosylbenzene, PTA = phase transfer agent; PTS = *p*-toluenesulfonic acid; TBA = tetra-*n*-butylammonium; THA = tetra-*n*-hexylammonium; TEMPO = 2,2,6,6-tetramethylpiperidine-1-oxy; THT = tetrahydrothiophene; THTO = tetrahydrothiophene oxide; TMA = tetramethylammonium; TMSP = *d*-electron-transition-metal-substituted POM. [c] N/A = not applicable.

Table 3 Photocatalytic and photoassisted reactions of POMs.[a]

Catalyst[b]	*Substrate*	*Products*	*Oxidant*[c]	*Solvent*	*Comments*	*References*
$H_4SiW_{12}O_{40}$	Methanol	Organic oxidation products + H_2	Protons from medium	H_2O	Initial report of POM-photocatalyzed dehydrogenation of an organic substrate (H_2 evolution)	374
$TBA_4W_{10}O_{32}$	TDA counterion	1-Butene, butyraldehyde (after addition of H_2O)	Protons from medium (RuO_2, IrO_2 and Pt^0 used as H_2 evolution catalysts)	MeCN MeCN-H_2O, MeCN-alcohols	Initial time-resolved flash photolysis study of $W_{10}O_{32}{}^{4-}$ (microsecond time frame); early spectroscopic and electrochemical study of the photoredox chemistry	544
	MeCN	Succinonitrile				
$XW_{12}O_{40}{}^{n-}$, where X = P, Si, Fe, Co or H_2	Methanol, ethanol, 1-propanol, 2-propanol	Aldehydes, ketone	Protons from medium or O_2	H_2O	Quantum yields and reaction rates measured; microsecond flash photolysis data	300
$H_3PW_{12}O_{40}$	Alkanes	Methyl ketones, *N*-alkylacetamides and alkenes	Protons from medium	MeCN	Initial report of alkane and unactivated C—H bond oxidation by POM excited states; some mechanistic information	545
$BW_{12}O_{40}{}^{5-}$	Methanol	Formaldehyde + H_2	Protons from medium	H_2O (pH 2–9) medium	Energetic and chemical properties of reduced POM characterized	546
$(NMP_2H)_3PW_{12}O_{40}$	NMP[b]	NMP-derived oxidation products	Protons from medium	NMP[b]	Early report of time-resolved photoredox behavior of organic donor-POM acceptor complexes; reduced POM appears to be generated ~90 ps after irradiation	114

$H_3PW_{12}O_{40}$	Alkanes	Tri- and tetra-substituted alkenes	Protons from medium	MeCN	Initial report of high-selectivity alkane dehydrogenation by photoexcited POM	547
$H_3PW_{12}O_{40}$ $TBA_3PW_{12}O_{40}$ $H_3PMo_{12}O_{40}$ $TBA_3PMo_{12}O_{40}$ $(NH_4)_6P_2W_{18}O_{62}$ $TBA_2W_6O_{19}$ $TBA_4W_{10}O_{32}$	Alkanes cycloalkanes	Alkenes, *N*-alkylacetamides, alkylmethylketone, alkylalkane (dimer)	Protons from medium	MeCN with or without acid (TFA[b] or $HClO_4$)[b]	Yields and quantum yields for photooxidation of alkenes as a function of solution conditions	548
$(DP_2H)_3PW_{12}O_{40}$, where DP = NMP, TMU or DMEU	NMP, TMU, or DMEU	Oxidation including demethylation products derived from substrate	Protons from medium	NMP, TMU, DMEU or MeCN	Organic substrate donor-POM acceptor complexes; irradiation of EDA band shows at least two distinct species formed in <80 ps	80
$TBA_4W_{10}O_{32}$	Alkenes	Primarily dimers from coupling of allylic radicals	Protons from medium (RuO_2 and Pt^0 used as H_2 evolution catalysts)	MeCN	Early report of time-resolved flash photolysis data on $W_{10}O_{32}^{4-}$ (transient absorbance on nanosecond time scale); $HW_{10}O_{32}^{4-}$ disproportionates to $H_2W_{10}O_{32}^{4-}$ and $W_{10}O_{32}^{4-}$; NMR data on electron-hopping rates in reduced POM	549
α-$PW_{12}O_{40}^{3-}$ $W_{10}O_{32}^{4-}$	Cyclooctane, 2-butanol Cyclooctane, 2-butanol	Cyclooctene, 2-butanone Cyclooctene, dimer 2-butanone	Protons from medium	MeCN	Photocatalytic transformation of unactivated C—H bonds by POMs varies greatly with the POM and its post-irradiation thermal chemistry; comparative vs. competitive kinetics indicate alcohol-POM precomplexation	550

Table 3 continued

Catalyst[b]	Substrate	Products	Oxidant[c]	Solvent	Comments	References
$TBA_4W_{10}O_{32}$ $H_3PW_{12}O_{40}$	Cyclooctane	Cyclooctene, cyclooctyl cyclooctane (dimer)	Protons from medium	MeCN	Unconventional intermolecular selectivities (alkane more reactive than alcohol in some solutions under some conditions), and intramolecular selectivities (selective epimerization of a saturated unactivated C—H bond in a ketone, 2-decalone)	45
	Cis-2-decalone	*Trans*-2-decalone				
$Na_4W_{10}O_{32}$, $TBA_4W_{10}O_{32}$	Caged hydrocarbon derivatives	Acylated hydrocarbons	Protons from medium; Pt^0 facilitates POM re-oxidation	MeCN	Demonstration that alkyl radical from POM-catalyzed photooxidation of alkenes could be reduced *in situ* to carbanions	551
$W_{10}O_{32}{}^{4-}$	Cyclohexene	3,3′-Dicyclohexene	Protons from medium	Organic solvents	Theoretical study of allylic H abstraction by photo-excited $W_{10}O_{32}{}^{4-}$ and dimerization of resulting radicals; substrate oxidation is atom transfer, not electron transfer	552
$TBA_4W_{10}O_{32}$, $Na_4W_{10}O_{32}$, α-$H_3PW_{12}O_{40}$	Alkanes	Alkenes and other organic oxidation products	Protons from medium	MeCN	Protonation of the reactant (oxidized) and product (reduced) forms of the POM takes place in the presence of strong acids; solvent-induced perturbations of the POM complex do not affect the photoredox chemistry as much as protonation-induced ones	553

$W_{10}O_{32}^{4-}$, α-$P_2W_{18}O_{62}^{6-}$, α-$PW_{12}O_{40}^{3-}$	Cis-2-decalone, cis-decalin	Octalones, trans-decalin	Protons from medium	MeCN	Photocatalytic transformation of unactivated C—H bonds by POMs varies greatly with the POM and its post-irradiation thermal chemistry	554
$TBA_4W_{10}O_{32}$ $TBA_3PW_{12}O_{40}$ $TBA_6P_2W_{18}O_{62}$ $TBA_3PMo_{12}O_{40}$ $TBA_5HP_2Mo_{18}O_{62}$ $TBA_4Mo_8O_{26}$ $TBA_3H_3V_{10}O_{28}$ $TBA_2W_6O_{19}$ $TBA_2Mo_6O_{19}$	Cyclohexane, cyclohexanol	Usual products of these substrates (not focus of article)	Protons from medium	MeCN	Four types of experiments are consistent with radical abstraction (hydrogen atom transfer) as the usual rate-limiting process between POM and alkane	555
$TBA_4W_{10}O_{32}$ $TBA_3PW_{12}O_{40}$	Alkanes	Ethylated and vinylated alkanes	Protons from medium	MeCN	Effective trapping of intermediate alkyl radicals by ethylene or acetylene affords the respective products in high selectivity	556
$V_4O_{12}^{4-}$	Alcohols	α-Hydroxy radicals	Protons from medium	H_2O, MeOH	Upon irradiation of $V_4O_{12}^{4-}$, CO_3^{2-} in medium becomes incorporated into $V_{15}O_{36}$-type POM	557

Table 3 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*[c]	*Solvent*	*Comments*	*References*
$TBA_4W_{10}O_{32}$ $TBA_3PW_{12}O_{40}$	Alkanes	Aldehydes	Protons from medium	MeCN	Effective trapping of intermediate alkyl radicals by CO affords aldehydes in high selectivity	558
$TBA_4W_{10}O_{32}$ $Na_4W_{10}O_{32}$	MeCN 2-butanol, cyclohexene	Oxidized products	Protons from medium	MeCN	Initial picosecond study of $W_{10}O_{32}{}^{4-}$; transients of <30 ps and many nanoseconds	559
$W_{10}O_{32}{}^{4-}$	Alkanes	Usual products	Protons from medium or O_2	MeCN	Photoexcited $W_{10}O_{32}{}^{4-}$ transients of <30 ps and ~55 ns	560
$TBA_4W_{10}O_{32}$	Propan-2-ol, adamantane	Acetone, H_2O_2, hydroperoxides	O_2	MeCN	Laser flash photolysis, pulse radiolysis and continuous photolysis information on $W_{10}O_{32}{}^{4-}$ excited state	561
$TBA_4W_{10}O_{32}$	MeCN	Cyanomethyl	Protons from medium	MeCN	Use of CW-EPR spectroscopy and time-resolved laser flash photolysis in the microsecond time range to show high yields of cross-disproportionation products result from the persistency of the $H^+W_{10}O_{32}{}^{5-}$ intermediate	562
	Toluene	Benzyl				
	Ethylbenzene	1-Phenylethyl				
	Diphenylmethane	Diphenylethyl				
	Cyclopentane	Cyclopentyl				
	t-Butylbenzene	Neophyl				
	Diethyl ether	1-Ethoxyethyl				
	Tetrahydrofuran	2-Tetrahydrofuryl				
	p-Cresol	4-Hydroxybenzyl				
	Methanol	Hydroxymethyl				
	and others					
$TBA_4W_{10}O_{32}$ $Na_4W_{10}O_{32}$	Aromatic amines, thianthrene, thiocyanate, alkenes		Protons from medium	MeCN	First three substrates quench photoexcited $W_{10}O_{32}{}^{4-}$ by diffusion-controlled electron transfer and last three quench by slower (10^7–10^8 M^{-1} s^{-1}) atom transfer	563

$W_{10}O_{32}^{4-}$, $PW_{12}O_{40}^{3-}$	Alkane	Nitriles and α-iminoesters	Protons from medium	MeCN	Irradiation of $W_{10}O_{32}^{4-}$ or $PW_{12}O_{40}^{3-}$, alkanes, and methyl cyanoformate in MeCN solution produces either the corresponding nitriles or α-iminoesters with high selectivity, depending on the temperature, via a mechanism involving two roles for the polyoxotungstate	564
$W_{10}O_{32}^{4-}$	MeCN	Usual products		MeCN, H_2O	Initial report on sub-picosecond flash photolysis characterization of POM photoredox chemistry (nanoseconds to femtoseconds); clarification of some early events	378
$Na_4W_{10}O_{32}$					Further characterization of the photoredox dynamics of $W_{10}O_{32}^{4-}$ on the ns time scale	565
$PW_{12}O_{40}^{3-}$	2-propanol	Acetone	O_2	H_2O	Initial report of O_2 oxidation of organic compounds photocatalyzed by a POM	373
$Nb_6O_{19}^{8-}$, $Ta_6O_{19}^{8-}$, $V_{10}O_{28}^{6-}$, $PW_{12}O_{40}^{3-}$	Alcohols, ethers, amides, aldehydes, carboxylic acids, ketones, nitriles	Oxidized products	O_2 or protons from medium	Various	Paper showing diversity of POM-based photocatalysis with respect to organic substrate and POM	375

Table 3 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*[c]	*Solvent*	*Comments*	*References*
$TBA_4W_{10}O_{32}$	Isopropyl alcohol	Acetone	O_2	MeCN	The catalytic cycle and photochemistry of $W_{10}O_{32}^{4-}$ and Keggin heteropolytungstates are compared	566
$H_3PW_{12}O_{40}$, $K_4W_{10}O_{32}$, $TBA_3PW_{12}O_{40}$, $TBA_4W_{10}O_{32}$	Secondary alcohols	Ketones	O_2	H_2O, MeCN	Effect of counterions on the redox cycle is examined	567
$PW_{12}O_{40}^{3-}$ $WO_2(OR)_2$ $FeW_{12}O_{40}^{5-}$ $CoW_{12}O_{40}^{6-}$ $(NH_4)_6P_2W_{18}O_{62}$ $(NH_4)_{14}[NaP_5W_{30}O_{110}]$ $TBA_4H_3SiV_3W_9O_{40}$	Methanol 1-propanol 2-butanol cyclobutanol *t*-butanol benzhydrol toluene benzyl methyl ether diphenyl methane	Formaldehyde 1-propanal 2-butanone cyclobutanone acetone, formaldehyde benzophenone benzaldehyde, benzyl alcohol methyl benzoate benzophenone	O_2	H_2O, MeCN, DMF	An early paper comparing the photocatalytic properties of POMs and semiconductor metal oxides; photooxidation of alcohols involves preassociation with the POM	301
$TBA_4W_{10}O_{32}$	Isobutane	TBHP, cyclohexane, cyclohexene, ethylbenzene	O_2	MeCN	Demonstration that POMs can be catalytic initiators of radical-chain autoxidation processes in the presence of light	568
$H_3PW_{12}O_{40}$, $(Bu_4N)_3PW_{12}O_{40}$	*p*-Xylene	*p*-Tolualdehyde, *p*-toluic acid (aerobic conditions),1,2-di-*p*-tolylethane (anaerobic conditions)	O_2 or protons from medium	MeCN	PtO_2 used as hydrogen evolution co-catalyst	569

$TBA_4W_{10}O_{32}$, α-TBA_3P-$W_{12}O_{40}$, α-$H_3PW_{12}O_{40}$, $TBA_2W_6O_{19}$, α-$(NH_4)_6P_2$-$W_{18}O_{62}$	Alkanes	Thermodynamic (most substituted) and nonthermodynamic (least substituted) alkenes	O_2, Ar	MeCN	Characterization of photochemical and subsequent thermal processes leading to various alkene products; selectivity for products systematically controlled	570
$W_{10}O_{32}{}^{4-}$	Thioethers	Sulfoxides, sulfones hydrocarbon, dimer	O_2 or protons from medium	MeCN	Redox catalysis involving substrate photooxidation (by POM) with catalyst regeneration by substrate reduction	571
$W_{10}O_{32}{}^{4-}$	Alkylbenzenes	Carbonyl derivatives, carboxylic acid and other minor products	O_2	MeCN	Allylic products in good yield; $TBA_3VW_5O_{19}$ and $TBA_2W_6O_{19}$ reported to be photocatalytically inactive	572
$W_{10}O_{32}{}^{4-}$, $PW_{12}O_{40}{}^{3-}$, $Cu^{II}PW_{11}O_{39}{}^{5-}$, $P_2W_{18}O_{62}{}^{6-}$	Thiother	Range of oxidized and other degradation products	O_2 or protons from medium	MeCN	Early paper on use of POMs as catalysts for photodegradation of organic compounds; comparison of metal oxides and POMs as photocatalysts	394
$P_2W_{18}O_{62}{}^{6-}$, $SiW_{12}O_{40}{}^{6-}$, $H_2W_{12}O_{40}{}^{6-}$	Organic compounds	Oxidized products (not focus of study)	O_2, H_2O_2	H_2O	Rate study of reaction of reduced POMs in aqueous solution with O_2 and H_2O_2	573
$TBA_4W_{10}O_{32}$	1,8-Cineole	5- and 6-keto derivatives of 1,8-cineole	O_2	MeCN	Successful application of POM photochemistry to the synthesis of a natural product; workup involves chlorochromate	574
$W_{10}O_{32}{}^{4-} + Pt^0$	Cyclooctane, tetrahydrofuran	Cyclooctene, 2,3-dihydrofuran, tributyl amine, bicyclooctyl, and other products	O_2, Ar	MeCN, H_2O	Emission of $W_{10}O_{32}{}^{4-}$ measured; mechanistic information (kinetics and product studies) given	381

Table 3 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*[c]	*Solvent*	*Comments*	*References*
$TBA_4W_{10}O_{32}$	Cyclohexylamine	44% $C_6H_{10}{=}NOH$, 18% $C_6H_{10}{=}O$, 22% $C_6H_{11}NO_2$, ~1% $C_6H_{10}{=}NC_6H_{11}$, 14% $C_6H_{11}NHOH$	O_2	MeCN	Aminium cation radical and HO radical intermediates detected by EPR	575
W- and Mo-containing POMs with cations containing petroleum sulfide fragments: $C_{50.7}H_{78.6}Mo_{12}O_{46}PS_3$, $C_{50.7}H_{78.6}O_{46}PS_3W_{12}$, $C_{67.6}H_{116.8}O_{40}S_4W_{10}$	Adamantane	Adamantan-1-ol, adamantan-2-ol	H_2O_2	$ClCH_2CH_2Cl$	New sulfonium salts of POMs catalyze the photooxidation of adamantanes by H_2O_2; neither POMs nor oxidation mechanisms significantly characterized	576
$W_{10}O_{32}{}^{4-}$, $PW_{12}O_{40}{}^{3-}$, $SiW_{12}O_{40}{}^{4-}$	Chlorophenols	CO_2, Cl^-	O_2	H_2O	Some mineralization in the absence of O_2; efficiency of photocatalytic degradation comparable to TiO_2	577
$W_{10}O_{32}{}^{4-}$, $PW_{12}O_{40}{}^{3-}$, $SiW_{12}O_{40}{}^{4-}$	Phenol, *p*-cresol	CO_2, hydroxylation products, dimerization products	O_2	H_2O	Complete mineralization achieved	578
$TBA_9P_2W_{15}Nb_3O_{62}$ $TBA_6P_2W_{18}O_{62}$ $TBA_9H_{19}P_4W_{32}Ti_6O_{132}$	Cyclohexanol 1-Hexanol 2-Hexanol Cyclohexanol	Cyclohexanone Hexanal 2-Hexanone Cyclohexanone	O_2	MeCN	Pseudo-first-order rate constants for these processes were compared; no POM significantly more active than the others	579

$K_4W_{10}O_{32}$, $H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $K_6H_2SiCu^{II}$-$W_{11}O_{40}$, $K_6H_2SiMn^{II}$-$W_{11}O_{40}$	4-Nitrophenol, 2,4-dimethylphenol, acetic acid, 1,1,2-trichloroethane	CO_2, H_2O, Cl^-	O_2	H_2O	These POMs are at least as effective as TiO_2 as catalysts for photodegradation of these organics; the *d*-electron metals Cu^{II} and Mn^{II} reduce the effectiveness 10-fold	580
$H_3PW_{12}O_{40}$	4-Chlorophenol	Hydroquinone	O_2	H_2O	Kinetics suggest complex formation between POM and substrate	581,582
$W_{10}O_{34}{}^{4-}$, $PW_{12}O_{40}{}^{3-}$, $SiW_{12}O_{40}{}^{4-}$	Chlorophenols	CO_2, HCl	O_2	H_2O	Complex homogeneous reactions; some organic intermediates detected; OH radicals inferred	583
$X^{n+}W_{12}O_{40}{}^{8-n}$, where X = Si, Co^{II}, Co^{III}	Adamantane	Adamantan-1-ol, adamantan-2-ol, adamantanone	O_2	MeCN-H_2O (98:2 v/v)	Conventional radical mechanism involving ROOH intermediates proposed	584
$Q_4W_{10}O_{32}$, where Q = TMA, TPA, TBA, THA, and Na	Adamantane	Adamantan-1-ol, adamantan-2-ol, adamantanone	O_2	MeCN-H_2O	Nitrile solvents and the organic counterions compete with alkane for POM excited state	585
$TBA_3PW_{12}O_{40}$, $TBA_4W_{10}O_{32}$, $TEA_4W_{10}O_{32}$	Cyclohexane	Cyclohexanol, cyclohexanone	O_2	MeCN/2-propanol, CH_2Cl_2/MeCN	POM–Fe^{III} porphyrin complexes photooxidize alkanes with higher selectivity for alcohols (vs. POMs only); Fe^{II} porphyrin intermediates reduce O_2	586
$Cs_3PW_{12}O_{40}$	*N*-methylpyrrolidinone	*N*-methylsuccinimide and succinimide	O_2	H_2O	Colloids of solid POM and TiO_2 compared	587
$PW_{12}O_{40}{}^{3-}$	Propan-2-ol	CO_2, H_2O	O_2, Ar	H_2O	Hydroxylated products, EPR spin trapping experiments and potential of POM excited state lead to proposal of HO radical intermediates	588

Table 3 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*[c]	*Solvent*	*Comments*	*References*
$Na_4W_{10}O_{32}$	Atrazine, including ^{14}C ring-labeled derivative	Primarily dealkylated products	O_2	$H_2O + HClO_4$ (pH 2.4)	Like TiO_2, $Na_4W_{10}O_{32}$ partially degrades the persistent pesticide atrazine upon irradiation but by a different mechanism than TiO_2	589
$Na_4W_{10}O_{32}$	Phenol, 4-chlorophenol, 2,4-dichlorophenol, bromoxynil, atrazine, imidachloprid, oxamyl	Oxidative degradation products	O_2	H_2O	Photodegradation studied by nanosecond laser flash photolysis; photodegradation chemistry different from that of TiO_2; effects of formulation using SDS and Triton X100 on photodegradation noted	377
$H_3PW_{12}O_{40}$–SiO_2, $H_4SiW_{12}O_{40}$–SiO_2	Hexachlorocyclohexane, pentachloronitrobenzene	Ultimately, CO_2 and HCl	O_2	H_2O	Complete mineralization of trace quantities of organochlorine pesticides by irradiation of silica-entrapped POMs	590
$HNa_2PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$	1,2-Dichlorobenzene	Oxidized products	O_2		Effect of scavengers Br^-, 2-propanol, acetone and acetone-d_6 studied; limited product analysis	591
$PW_{12}O_{40}^{3-}$–TiO_2, $SiW_{12}O_{40}^{4-}$–TiO_2, $W_{10}O_{32}^{4-}$–TiO_2	1,2-Dichlorobenzene	Chlorophenols	O_2	H_2O	Additions of POMs to TiO_2 suspensions significantly increased photooxidation of substrate	592
$PW_{12}O_{40}^{3-}$, $SiW_{12}O_{40}^{4-}$	Atrazine (CIET)[b]	Cyanuric acid, NO_3^-, Cl^-, H_2O	O_2	H_2O	Intermediates: OIET, CIAT, CAET, OAAT, OOAT[b]	593

$XW_{11}O_{39}$ units bound to silica, where X = Si, Ge or P (POM-silica composite films)	Formic acid	$CO_2 + H_2O$	O_2	H_2O	Focus of article is material preparation and characterization (spin-coated co-gels from POM + TEOS[b])	594
$Na_6W_7O_{24}$–SiO_2 $H_4W_{10}O_{32}$–SiO_2 $H_3PW_{12}O_{40}$–SiO_2 $H_6P_2W_{18}O_{62}$–SiO_2	Aqueous 4-chlorophenol	Hydroquinone, *p*-benzoquinone; ultimately CO_2, Cl^-	O_2	H_2O	POM-silicates made by hydrolysis of solutions of TEOS and POM; hydroquinone and *p*-benzoquinone intermediates detected	595
$H_2NaPW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$	1,2-Dichlorobenzene	2,3-Dichlorophenol, 3,4-dichlorophenol, in <5% yields	O_2	H_2O	Keggin POMs supported on NaY zeolite; photooxidation rates higher for supported POMs than POMs alone	596
$H_3PW_{12}O_{40}$–SiO_2, $H_4SiW_{12}O_{40}$–SiO_2, $Na_4W_{10}O_{32}$–SiO_2	Hydroxy butanedioic acid (malic acid, MA)	CO_2, H_2O	O_2	H_2O	Oxalic acid, glyceric acid, tartaric acid, butenedioic acid, acetic acid, and formic acid intermediates were detected	597
Alkylammonium polymolybdates	Usually counterion	Reduced POM	Anaerobic reactions	H_2O	Series of early papers on the EPR and other spectroscopic properties of photoexcited alkylammonium polymolybdates	371,372
$H_3PW_{12}O_{40}$ $Na_4W_{10}O_{32}$ $TBA_4W_{10}O_{32}$	2-Propanol or DMF (reductant) and CCl_4 (oxidant)	Acetone, N-methylformamide, $CHCl_3$ and C_2Cl_6	See “comments”	Alcohol or DMF	Photoexcited POM oxidizes alcohol or DMF and resulting reduced POM reductively dehalogenates CCl_4 (i.e., POM catalyzes reductive dehalogenation by alcohol or DMF)	598
$W_{10}O_{32}^{4-}$	Nitroxyl radical	Nitrosonium salt		MeCN	Photoinduced electron transfer followed by EPR	599

Table 3 continued

Catalyst[b]	*Substrate*	*Products*	*Oxidant*[c]	*Solvent*	*Comments*	*References*
$W_{10}O_{32}^{4-}$ $PW_{12}O_{40}^{3-}$	Secondary alcohols or tertiary amides (reductant) and aliphatic or aromatic halocarbon (oxidant)	Oxidized alcohol products (aldehydes, ketones, etc.) and dehalogenated hydrocarbons + HCl	See "comments"; most reactions run under anaerobic conditions, some under aerobic conditions	MeCN or 100% substrate reductant (alcohol or DMF)	Three modes for catalytic dehalogenation of halocarbons established, one thermal and two photocatalytic; mechanistically complicated chemistry	600
$(TMU_2H)_3PMo_{12}O_{40}$	TMU[b]	TMU-derived oxidation products	Reduced POM not re-oxidized	TMU[b]	Initial report of organic substrate donor-POM acceptor photoredox-active complex	79
$(DMA_2H)_3PMo_{12}O_{40}$	DMA[b]	DMA-derived oxidation products	Reduced POM not re-oxidized	DMA[b]	The second report of organic substrate donor-POM acceptor photoredox-active complex	78
W- and Mo-containing POMs with cations containing petroleum sulfide fragments: $C_{50.7}H_{78.6}Mo_{12}O_{46}PS_3$, $C_{50.7}H_{78.6}O_{46}PS_3W_{12}$, $C_{67.6}H_{116.8}O_{40}S_4W_{10}$	Adamantane	Adamantan-1-ol, adamantan-2-ol	H_2O_2	$ClCH_2CH_2Cl$	New sulfonium salts of POMs catalyze the photooxidation of adamantanes by H_2O_2; neither POMs nor oxidation mechanisms significantly characterized	576

[a] Reports involving supported POM catalysts are included. The type of immobilization is addressed in the "catalyst" or "comments" columns. [b] CAET = 2-chloro-4-amino-6-(ethylamino)-*s*-triazine; CIAT = 2-chloro-4-(isopropylamino)-6-amino-*s*-triazine; CIET = 2-chloro-4-(isopropylamino)-6-(ethylamino)-*s*-triazine; DMA = *N*,*N*-dimethylacetamide; DMEU = "dimethylethylene urea" = 1,3-dimethyl-2-imidazolidinone; DP = dipolar aprotic solvent; NMP = *N*-methyl pyrrolidinone; OAAT = 2-hydroxy-4,6-diamino-*s*-triazine; OIET = 2-hydroxy-4-(isopropylamino)-6-(ethylamino)-*s*-triazine; OOAT = 2-hydroxy-4-hydroxy-6-amino-*s*-triazine; PS = petroleum sulfide; TBA = tetra-*n*-butylammonium; TEA = tetraethylammonium; TEOS = tetramethylorthosilicate; TMA = tetramethylammonium; TMU = tetramethylurea. [c] For reactions photocatalyzed by POMs under anaerobic conditions, the reduced POM resulting from photooxidation of the substrate is reoxidized by reduction of protons generated in this initial substrate photooxidation step, forming H_2.

involving the oxidation of an organic or inorganic substrate and reduction of a POM oxidant take place thermally, as we have seen in the preceding sections. Upon absorption of light by a POM (irradiation of the oxygen-to-d^0-metal charge transfer transition), however, a great many more substrate oxidation–POM reduction processes (photoredox processes) become both thermodynamically and kinetically favorable. The absorption of light adds the energy intrinsic in the wavelength of light to the ground state potential of the POM, and most photoexcited POMs are sufficiently reactive to oxidize even conventionally inert compounds such as alkanes at room temperature.

The partitioning of the POM excited state between productive processes (photoredox reactions involving substrate) and nonproductive processes (radiationless decay including internal conversion, bimolecular quenching, or emission) depends on the structure and elemental composition of the POM, and to a lesser extent other parameters. The quantum yields for the photoredox processes of POMs in solution can be quite high (well over 50%). The presence of *d*-electron containing metal centers lowers the quantum yields for substrate oxidation by quenching the excited states.

The photoredox process generally proceeds by atom transfer from the substrate to the photoexcited POM for organic molecules with relatively high ionization potentials and C—H bonds. This is basically a hydrogen atom abstraction process (or proton coupled electron transfer). This mechanism is definitely operable for alkane oxidation by photoexcited POMs. In contrast, electron transfer from the substrate to the photoexcited POM appears to be the dominant mechanism for the oxidation of electron rich aromatics and other organic substrates with low ionization potentials and strong C—H bonds. One caveat: some substrates that are easily oxidized by electron transfer likely quench POM excited states by back electron transfer (i.e., the reduced ground-state POM resulting from substrate photooxidation transfers its electron back to the substrate cation radical).

Much of our quantitative knowledge of POM excited states is based on time-resolved photolysis studies of decatungstate, $W_{10}O_{32}^{4-}$. The groups of Yamase, Duncan, and Hill; Duncan and Fox; Tanielian; and Giannotti (roughly in chronological order of initial research activity) using increasingly rapid (microsecond to femptosecond) laser systems, have all contributed to our understanding in this area. The nature of POM excited states, their partitioning between different pathways, their perturbation by solvent and counterions, and their mechanisms of substrate oxidation are also now fairly clear. The same is true for the rich thermal chemistry in substrate-POM systems following photooxidation of the substrate. The publications summarized and footnoted in Table 3 address all the above issues.

The view that POMs might represent molecular versions of semiconductor metal oxide particles has been addressed repeatedly by several groups.[301,389,394] While POMs and colloidal semiconductor metal oxide particles have some features in common, some features of the both the excited states and the reduced ground states resulting from photoredox chemistry of the two types of clusters are clearly distinct.

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4.12
Chalcogenide-containing Metal Clusters

M. N. SOKOLOV and V. P. FEDIN
Russian Academy of Sciences, Novosibirsk, Russia
and
A. G. SYKES
University of Newcastle upon Tyne, UK

4.12.1 INTRODUCTION

This chapter is devoted to clusters of early transition elements (Groups 3–6), with elements of the oxygen group referred to as the chalcogens ($Q = O$, S, Se, Te) in the core. We find it appropriate to apply the term "cluster" in a broader sense and clusters without M-bonding, e.g., Ti and Zr are included. Trinuclear upward (not binuclear) complexes are considered. The reader will see that the same structural type may or may not include M—M bonding. As this chapter needs to fall within the scope of coordination chemistry, the coverage of organometallic examples is restricted. However, for Group 4, to a lesser degree Group 5, and for Cr, almost all known chalcogenide clusters include η^5-cyclopentadienyl ligands, and some coverage of the published data is included. Studies on early transition-metal chalcogenide clusters are relatively new, and most of the research has been carried out since the mid 1980s, with almost all compounds routinely characterized by X-ray structural analysis. Spectroscopic methods have usually played a secondary role. The main emphasis is on synthesis, yields, structure, stability, reactivity, core rearrangements and interconversions; while spectroscopic and other information is given more selectively. The area has been the subject of several reviews since 1990.[1–9] Other reviews albeit not strictly dedicated to the present topic are also of interest.[10–12] Though not covered in this chapter, chalcogenide rhenium clusters show some strong similarities. A review covering this aspect of rhenium chemistry has appeared recently.[13]

4.12.2 YTTRIUM

The only relevant Group 3 polynuclear complex, $[Y_8(\mu_4\text{-}O)(\mu_3\text{-}OH)_{12}(\mu\text{-}Se_4)_4Cl_2(DMF)_{10}]\cdot 6DMF$ is prepared from YCl_3 and polyselenide in DMF. It has an octanuclear core, supported by oxo, hydroxo, and tetraselenido bridges with no Y—Y bonds. No Sc or actinide chalcogenide clusters are known. Lanthanide/selenido clusters have recently been isolated.[14]

4.12.3 TITANIUM AND ZIRCONIUM

4.12.3.1 Trinuclear Clusters

Very few examples of this type are known in Group 4. Reaction of $TiCl_4$ with $(Me_3Si)_2S$ in CH_2Cl_2 gives a black precipitate, formulated as "$TiSCl_2$," which reacts with PPh_4Cl or Et_4NCl to

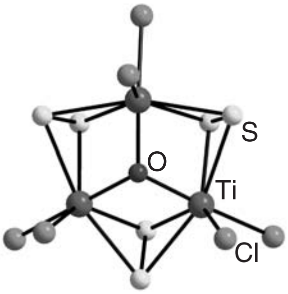


Figure 1 Structure of the $[Ti_3(\mu_3{-}O)(\mu{-}S_2)_3Cl_6]^{2-}$ cation.

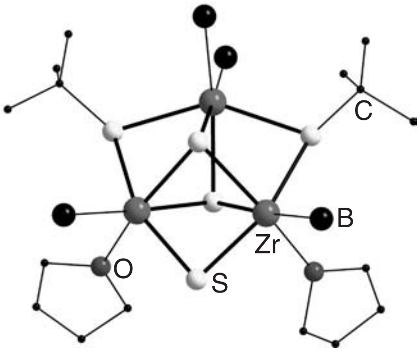


Figure 2 Structure of the $[Zr_3(\mu_3{-}S)_2(\mu{-}^tBuS)_2(\mu{-}S)(BH_4)_4(THF)_2]$ molecule.

give $[TiSCl_4]^{2-}$ salts as the major products, with small yields of red $(Et_4N)_2[Ti_3O(S_2)_3Cl_6]$ and $(Ph_4P)_2[Ti_3O(S_2)_3Cl_6]$. The X-ray structure of the latter shows the $Ti_3(\mu_3{-}O)(\mu{-}S_2)_3{}^{4+}$ core, more typical of Mo, W, Re clusters. A long Ti–Ti distance of 3.16 Å indicates the absence of Ti—Ti bonding, consistent with Ti^{IV}. The S—S bonds are 2.04 Å (Figure 1). No similar Zr or Hf complexes are known.[15,16]

The reaction of $Zr(CH_2Ph)_4$ with ^tBuSH in toluene (~20 °C) gives the Zr^{IV} complex $[Zr_3(\mu_3{-}S)(\mu_3{-}^tBuS)(\mu{-}^tBuS)_3(^tBuS)_6]$ as yellow needles, 75% yield.[17,18] Attempts to substitute the capping thiolate result in rapid decomposition. Another $Zr_3{}^{IV}$ cluster with three bridging sulfides is a product of $Zr(BH_4)_4$ with ^tBuSH in THF at 50 °C. This yellow compound has the composition $[Zr_3(\mu_3{-}S)_2(\mu{-}^tBuS)_2(\mu{-}S)(BH_4)_4(THF)_2]$ (Figure 2). The structure shows an equilateral triangle with long Zr–Zr distances (3.47 Å), and no M—M bonding. The complex is extremely moisture sensitive. On leaving a concentrated CH_2Cl_2 solution (~20 °C) for 24 h, one THF dissociates and dimerization of the trinuclear units gives hexanuclear $[Zr_3(\mu_3{-}S)_2(\mu{-}^tBuS)_2(\mu{-}S)(BH_4)_4(THF)]_2$ (Figure 3).[17,19]

4.12.3.2 Tetranuclear Clusters

The $Ti_4S_4{}^{4+}$ core exists in Ti^{III} cuboidal clusters $[(\eta^5{-}RC_5H_4)_4Ti_4S_4]$ (R = H, Me, ^iPr). The complex $[(\eta^5{-}C_5H_5)_4Ti_4S_4]$ forms in the reaction of $[(\eta^5{-}C_5H_5)_2Ti(CO)_2]$ with H_2S at 80 °C in the presence of water, 50% yield.[20] Cuboidal clusters are also obtained by reacting $[(\eta^5{-}RC_5H_4)TiCl_2(THF)_2]$ with $(Me_3Si)_2S$. All these clusters are air-sensitive brown solids, extremely reactive towards protic solvents. The structure of $[(\eta^5{-}MeC_5H_4)_4Ti_4S_4]$ shows a distorted cubic core (symmetry D_{2d}) with Ti–Ti distances of 2.93–3.01 Å. The clusters give molecular peaks in mass spectra. The ^iPr derivative does not show reversible redox behavior between +0.6 V and −0.6 V.[21]

Group 4 metals have little affinity for S, Se, and Te, which is confirmed in the aqueous solution chemistry. However, when oxygen is excluded, a variety of chalcogenide derivatives can be incorporated via, e.g., RSH scission. The presence of small amounts of O_2 or H_2O can lead to incorporation of oxygen, and Ti clusters containing O alongside S, Se are formed extensively in processes difficult to control. There are several examples of $Ti_4(\mu_4{-}O)^{14+}$ with O at the center of the Ti_4 tetrahedron. When metallic Ti reacts with S and S_2Cl_2 at 160 °C, red air-sensitive $[Ti_4(O)(S_2)_4Cl_6]$ is isolated, 25% yields. Raising the temperature to 425 °C gives the adduct $[Ti_4(O)(S_2)_4Cl_6]{\cdot}2S_8$. Both

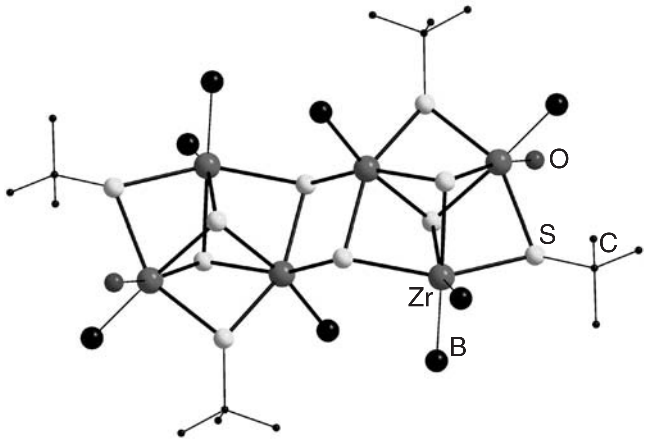


Figure 3 Structure of the $[Zr_3(\mu_3-S)_2(\mu-{}^tBuS)_2(\mu-S)(BH_4)_4(THF)]_2$ molecule. Only oxygen and boron donor atoms of THF and BH_4 ligands are shown.

have essentially the same geometry with distorted tetrahedral arrangement of Ti (idealized symmetry D_{2d}). Four short Ti–Ti edges of the tetrahedron (4.12 Å) are bridged by S_2 groups, and the other two bridged by μ-Cl are longer (3.56 Å). In the absence of Ti—Ti bonding, Fenske–Hall calculations attribute the Ti—Ti shortening to the strong bonding between Ti^{IV} and bridging S_2. Mass spectrometry on $[Ti_4(O)(S_2)_4Cl_6]$ shows a monoprotonated molecular peak at 485 °C.[22]

The same Ti_4O^{14+} core is present in $[(\eta^5-C_5H_5)_4Ti_4O_2(S_2)_4]$, (5% yield), when products of the reaction of $[(\eta^5-C_5H_5)_2Ti(CO)_2]$ with H_2S are allowed to stand for eight days after separation of $[(\eta^5-C_5H_5)_4Ti_4S_4]$.[20] The core here is again asymmetrical with one of the Ti–Ti edges bridged by μ_2–O. The proton NMR in CD_2Cl_2 shows two types of resonances (1:1, 6.21 ppm and 5.65 ppm), and in the mass spectrum the molecular peak appears at 740 m/e.[20] The MeC_5H_4 analog, $[(\eta^5-MeC_5H_4)_4Ti_4O_2(S_2)_4]$ was prepared by treatment of $[(\eta^5-MeC_5H_4)TiCl_3]$ with 1.5 eq. of Li_2S_2 in THF, followed by exposure to O_2, 15% yield. The structure shows essentially the same geometry (Figure 4). The H^1 NMR spectrum has two non-equivalent MeC_5H_5 rings invariable +80 to –70 °C.[23] Olive-green $[(\eta^5-C_5H_5)_4Ti_4(\mu_4-O)(Se_2)_2(Se)_3]$ is more distorted, where the Ti_4O^{14+} core has two μ_3–Se_2 bridges, two μ_3–Se bridges and one μ_2–Se (Figure 5). It forms as one of the products when $[(\eta^5-C_5H_5)_4Ti_4Se_6]$ is reduced with Bu_3SnH or PBu_3[24] or from $(Me_3Si)_2Se$ with $[(\eta^5-C_5H_5)TiCl_3]$.[25]

Another Ti_4 cluster is better viewed as a derivative of the hypothetical trinuclear "crown-shaped" unit $(\eta^5-C_5H_5)_3Ti_3(\mu_2-Q)_6$, Q = S, Se. Capping the three chalcogen atoms from one side with a $(\eta^5-C_5H_5)Ti$ group gives $[(\eta^5-C_5H_5)_4Ti_4Q_6]$ (Ti_4^{16+} core, no Ti—Ti bonding). Here, the Se derivative $[(\eta^5-C_5H_5)_4Ti_4Se_6]$ is the only real example.[26] Substituting μ–QR for some of μ–Q bridges, while keeping the molecule neutral, gives mixed Ti^{III}–Ti^{IV} clusters, of which $[(\eta^5-C_5H_5)_4Ti_4S_4(SEt)_2]$ is known. It is formed from $[(\eta^5-C_5H_5)TiMeCl_2]$, EtSH, and Et_3N in pentane, 5% yield. This very oxophilic product has an ESR spectrum ($g = 1.998$ in C_6H_6 at 25 °C). The Ti atoms are clearly non equivalent. The unique capping Ti atom has greater Lewis

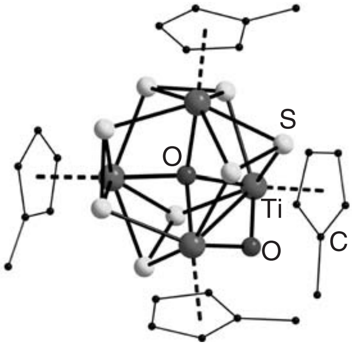


Figure 4 Structure of the $[(\eta^5-MeC_5H_4)_4Ti_4(\mu_4-O)(\mu_2-O)(S_2)_4]$ molecule.

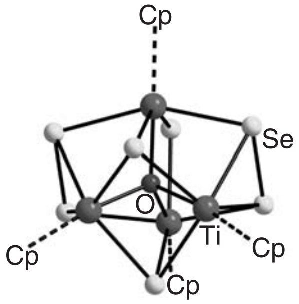


Figure 5 Structure of the $[(\eta^5{-}C_5H_5)_4Ti_4(\mu_4{-}O)(Se_2)_2(Se)_3]$ molecule.

acidity (Ti—S 2.29 Å) and may be regarded as Ti^{IV}, and the three basal Ti have longer Ti—S bonds, 2.38–2.52 Å. The $Ti^{III}{-}Ti^{III}$ distances do not reflect significant M−M interaction.[27] The core in this family $Ti_4(\mu_3\text{-}S)_3{}^{7+}$ is unique, formula $[(\eta^5\text{-}C_5H_5)_4Ti_4\ S_3(2,6\text{-}{}^iPr_2C_6H_3O)_3]$.[28]

4.12.3.3 Pentanuclear Clusters

Capping the $[(\eta^5{-}C_5H_5)_4Ti_4Q_6]$ clusters with another $(\eta^5{-}C_5H_5)Ti$ unit gives pentanuclear clusters incorporating pentagonal bipyramidal $Ti_5{}^{17+}$. Here, all three derivatives are known, Q = S, Se, and Te. The cluster $[(\eta^5{-}C_5H_5)_5Ti_5S_6]$ (Figure 6) is made from $[(\eta^5{-}C_5H_5)_2Ti(CO)_2]$ and H_2S in toluene (80 °C), yield 73%. This green–brown, moderately air-sensitive product is very soluble in toluene. Its structure shows two sorts of Ti atoms, the apical ones Ti^{IV}—S at 2.28 Å, and three equatorial Ti^{III}—S bonds, 2.47 Å. There are only three electrons available for M—M bonding and they are localized between the equatorial atoms, (Ti—Ti 3.21 Å). The $Ti_{ap}{-}Ti_{eq}$ distance is 3.08 Å, possibly a secondary effect due to the shortness of the Ti_{ap}—S bonds. The ESR spectrum in toluene (20 °C) gives $g = 1.993$, and μ_{eff} is only 1.25 B.M., which is low compared to the expected 1.73 B.M. This is attributed to the lack of diamagnetic correction for any of the ligands at the Ti.[29] The reaction of $[(\eta^5{-}C_5H_5)TiCl_3]$ with $PhCH_2SH$ (1:3) and Et_3N in benzene gives also $[(\eta^5{-}C_5H_5)_5Ti_5S_6]$ as one of the products.[27] The Se analog is obtained from $[(\eta^5{-}C_5H_5)_4Ti_4Se_6]$ and Bu_3SnH or PBu_3.[24] It is also prepared by incubation of $[(\eta^5{-}C_5H_5)TiCl_2(THF)_2]$ with Et_3N and H_2Se for 24 h, yield 71%.[24] Its crystal structure shows the same features as the S analog, with two sets of Ti–Ti distances of 3.37 Å and 3.32 Å and Ti–Se 2.42 Å and 2.64 Å. Two types of cyclopentadienyl protons can be seen in the NMR (15.88 ppm and 9.01 ppm), and the ESR spectrum in toluene gives a single narrow line, $g = 1.979$ (293 K). The compound $(Me_3Si)_2Se$ can be used as a source of Se in the case of $[(\eta^5\text{-}MeC_5H_4)TiCl_3]$.[30] The Te analog can also be prepared from $[(\eta^5\text{-}MeC_5H_4)TiCl_3]$ and $(Me_3Si)_2Te$, 68% yield. Both clusters have been structurally characterized and are paramagnetic.[30]

The structure of $[(\eta^5{-}C_5H_5)_5Ti_5(S_2)(S)_5(O)]$ (Figure 7) is made from $[(\eta^5{-}C_5H_5)_2Ti(SH)_2]$ and Zn powder in toluene (~20 °C) alongside $[(\eta^5{-}C_5H_5)_5Ti_5S_6]$, is related to the type of compound just discussed, yields 10%. It has one S_2 bridge instead of S, and an interstitial μ_4-oxygen atom. Thus we have a Ti_5O^{17+} core, which is paramagnetic with ESR spectrum in toluene, $g = 1.980$.[20]

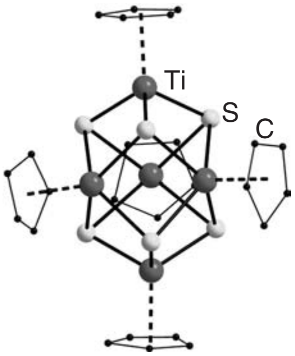


Figure 6 Structure of the $[(\eta^5{-}C_5H_5)_5Ti_5S_6]$ molecule.

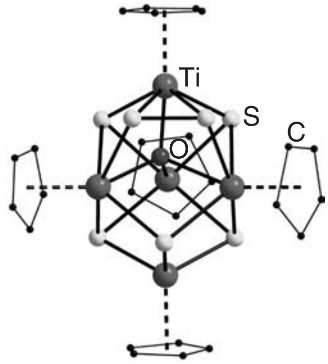


Figure 7 Structure of the $[(\eta^5-C_5H_5)_5Ti_5(S_2)(S)_5(\mu_4-O)]$ molecule.

4.12.3.4 Hexanuclear Clusters

Examples are almost exclusively cyclopentadienyl derivatives of the very common octahedral core $M_6(\mu_3\text{-}Q)_8$. With Ti the compound $[(\eta^5-C_5H_5)_6Ti_6S_4O_4]$ (Figure 8) and $[(\eta^5-C_5H_5)_6Ti_6Te_6O_2]$ have been prepared, but no corresponding selenide is known. The pure oxo-cluster $[(\eta^5-C_5H_5)_6Ti_6O_8]$ also exists.[31] A dark-red sulfide cluster is obtained in low yield from $[(\eta^5-C_5H_5)TiMeCl_2]$ and $PhCH_2SH$ in pentane, which with LiOH deprotonates the thiol, and oxygen is incorporated. The structure of this very oxo-philic product indicates an octahedral Ti_6 core with partially disordered O and S atoms.[27] Black platelets of $[(\eta^5-(C_5H_5)_6Ti_6Te_6O_2]$ were obtained in low yield by treating $[(\eta^5-C_5H_5)_2Ti(TeSiPh_3)_2]$ with PPh_3. The Ti–Ti distances vary from 3.27 Å to 3.99 Å,[32] and the oxidation state is less than Ti^{IV}, with electrons available for M—M bonding. In the case of Zr, which is bigger and less easy to reduce, the product $[(\eta^5-C_5H_5)_6Zr_6S_9]$ is obtained where one S acts as interstitial μ_6 ligand inside the Zr_6 octahedron.[33] No electrons are available for M—M bonding in the Zr^{IV} derivative.

Black $K_4Ba[Ti_6OS_8(S_2)_6$ prepared in a 70% yield from K_2S, BaS, Ti, TiO_2, and S in the molar ratio of 1:0.25:1:0.25:7 at 550–600 °C, has an octahedral core $Ti_6(\mu_6-O)(\mu_3-S)_8{}^{6+}$ with interstitial oxygen. Each titanium has $S_2{}^{2-}$ bound sideways on the outside. The oxidation state is Ti^{IV} with no Ti—Ti bonds (Ti–Ti $\sim$ 3.23 Å).[34]

No hafnium chalcogenide clusters have yet been reported.

4.12.4 VANADIUM, NIOBIUM, AND TANTALUM

4.12.4.1 Trinuclear Clusters

The only cluster in this group having the incomplete cuboidal core $V_3S_4{}^{3+}$ was isolated from a reaction mixture of $Na_2S_2C_2H_4$ (Na_2edt), Et_4NBr, VCl_3, and sulfur as black $(Et_4N)_3[V_3\ S_4(edt)_3]\cdot 2CH_3CN$. The yield was 20%. Its structure shows a triangular arrangement of vanadium atoms (V—V bonds

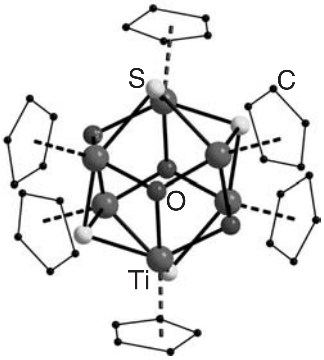


Figure 8 Structure of the $[(\eta^5-C_5H_5)_6Ti_6(\mu_3-S)_4(\mu_3-O)_4]$ molecule.

2.89–2.92 Å), and the core possesses idealized C_{3v} symmetry. The coordination around each V, neglecting V—V bonds, is close to a trigonal bipyramid. The structure shows no evidence to justify a trapped-valence assignment ($V^{III}V^{IV}{}_2$). The cluster can be oxidized and reduced reversibly in CV experiment, in CH_3CN, which give reduction potentials (vs. NHF): 3−/4− (−1.51 V) 2−/3− (−0.63 V) both reversible, and 1−/2− (0.00 V) irreversible.[35] No Nb or Ta analogs are known, although in the black compound $(Me_4N)_3(NH_4)_3[Nb_3\ SO_3(NCS)_9]$ a $Nb_3(\mu_3\text{-}S)(\mu\text{-}O)_3{}^{3+}$ core is present (Nb—Nb 2.763 Å) (Figure 9). It was prepared by the aquation of tetrahydrothiophene (THT) of $Nb_2Cl_6(THT)_3$ in HCl and subsequent treatment with NH_4NCS in a 60% yield. Without counting the Nb—Nb bonds the metal has an octahedral coordination.[36]

The closely related chalcogen-rich cluster core $M_3(\mu_3\text{–}S)(\mu\text{–}S_2)_3$ is known for vanadium. Reaction of $[V(SPh)_2(bpy)_2]PF_6$ with sulfur in acetonitrile gives $[V_3S_7(bpy)_3]PF_6$ in a 35–40% yield. In this V^{III} derivative, the V–V distances are 2.75–2.77 Å, and six electrons are available to give three single V—V bonds (Figure 10). The calculations show that indeed the HOMO and LUMO are almost pure M—M bonding and antibonding orbitals, respectively. The cluster is diamagnetic both in the solid state and in solution. Cyclic voltammetry shows one-electron reversible oxidation at −0.47 V vs. Fc^+/Fc in acetonitrile.[37] The oxidized $V_3S_7{}^{2+}$ core is found in black $(Et_4N)[V_3S_7\ (Me_2NCS_2)_3]$ which forms from $(NH_4)_3[VS]_4$, CuCl, PhSNa, $Na(Me_2NCS_2)$, and Et_4NCl in DMF in only 3% yield. The cluster is very stable and the solutions are not air sensitive. It is paramagnetic, $\mu_{eff} = 1.76$ B.M. at 300 K. An IR band of 442 cm^{-1} was assigned to μ_3–S, and that of 554 cm^{-1} to S−S of the disulfido bridge, while $V{-}S_{dtc}$ appears at only 354 cm^{-1}. The vanadium atoms are identical and no separate oxidation states can be ascribed to them, the V–V distances are 2.74–2.75 Å. Cyclic voltammetry shows a reversible reduction at −1.09 V, and a reversible oxidation at 0.04 V.[38] The presence of Cu^I is in fact not necessary for the assembly of the V_3S_7 core. The compound $(NH_4)_3[VS_4]$ reacts with $(HOCH_2CH_2)_2NCS_2Na$ and Et_4NCl in CH_3OH to give black $(Et_4N)[V_3S_7((HOCH_2\text{-}$

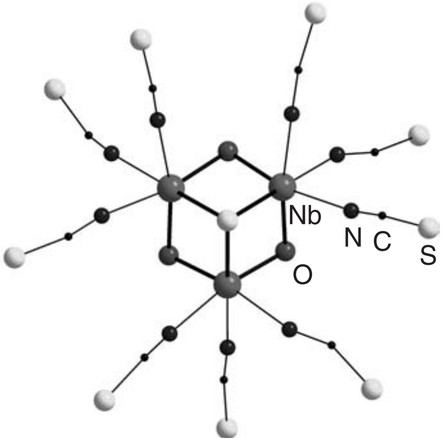


Figure 9 Structure of the $[Nb_3(\mu_3\text{—}S)(\mu\text{—}O)_3(NCS)_9]^{6-}$ anion.

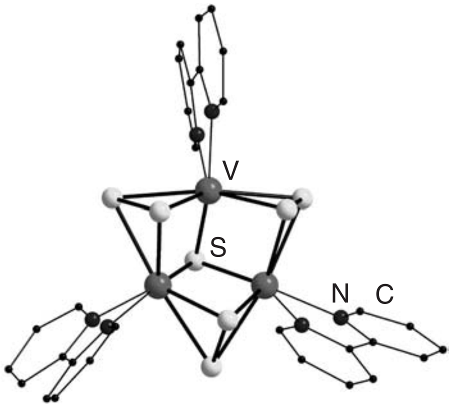


Figure 10 Structure of the $[V_3S_7(bpy)_3]^+$ cation.

$CH_2)_2NCS_2)_3]$ in 19% yield. The yield increases when a stream of H_2S is passed through the reaction mixture and a thiol is added. Thus $(Et_4N)[V_3S_7(Et_2NCS_2)_3]$ forms from $(NH_4)_3[VS_4]$, Nadtc, Et_4NCl, and dithiothreitol ($C_4H_{10}O_2S_2$) under these conditions. It has also been structurally characterized. The redox behavior of all the three dithiocarbamates is very similar.[39]

In the black air-sensitive compound $(Et_4N)[V_3(\mu{-}O)_2(\mu{-}S)_2(O)(Et_2NCS_2)_3]$ only two of the vanadium(IV) atoms are close enough (2.715 Å) to form a single metal–metal bond and they are spin-coupled. The third V atom is present as a typical tetragonal pyramidal vanadyl, VO^{2+}, and the ESR spectrum resembles that of $[VO(edt)_2]^{2-}$. In the IR spectrum a band at 971cm^{-1} was assigned to the V=O group, and another band at 844 cm^{-1} to the V—O—V. The compound was made from VCl_3, Li_2S, Et_4NBr, and Nadtc·$3H_2O$ (1:2:1:1 molar ratio) in acetonitrile. The ^{51}V NMR gives two signals with chemical shifts −389 ppm and −519 ppm.[40]

The congeners Nb and Ta do not resemble V in its tendency to form trinuclear chalcogenide clusters. An unusual Nb cluster is obtained from $[(\eta^5{-}EtMe_4C_5)_2Nb_2(B_2H_6)_2]$ and S_8 in decane at 170 °C in a 26% yield (Figure 11). An equilateral triangle Nb_3 is capped by a $[BS_3(SH)]^{4-}$ anion in a symmetrical way (Nb—S 2.55 Å), so that this unusual anion is able to act as a donor of 12 electrons. There are only 2e to fill M—M bonding orbitals. The S−H group shows a weak band in the IR spectrum at 2,560 cm^{-1} . If the same reaction is done in xylene at 144 °C, the same product forms along with a more sulfur-rich cluster $[(\eta^5{-}EtMe_4C_5)_3Nb_3S_8]$ of unknown structure.[41] A very similar cluster is known also for Ta except the capping ligand here is a hydridotrithioborate anion, $[BS_3(H)]^{4-}$. It was prepared from the mononuclear complex $[(\eta^5{-}C_5Me_5)Ta(S)(SCPh_3)_2]$ and $NaBH_4$ as a green product (plates) in 70% yield. The ^{11}B NMR gives a sharp resonance at −21.3 ppm. The Ta—S (thioborate) distance is 2.54 Å and the Ta—S (bridging sulfide) is shorter, 2.36 Å.[42] Treatment of $[(\eta^5{-}C_5Me_5)TaCl_4]$ with Li_2S (THF, 0 °C) gives another Ta triangular cluster, isolated as $Li_2[(\eta^5{-}C_5Me_5)_3Ta_3S_6]$·2THF.[43]

There are also less symmetrical triangular cores which contain bridging disulfido or trisulfido ligands, often as a part of complex product mixtures. The corresponding $[(\eta^5{-}C_5H_5)MCl_4]$ (M = Nb, Ta) reacts with $(Me_3Si)_2Q$ (Q = S, Se) to form black $[(\eta^5{-}C_5H_5)_3Nb_3Se_5Cl_2]$, red $[(\eta^5{-}C_5H_5)_3Ta_3S_7Cl_2]$, brown $[(\eta^5{-}C_5H_5)_4Ta_4S_{13}]$, and black $[(\eta^5{-}C_5H_5)_8Ta_6S_{10}][TaSCl_5]_2$.[44] The Nb cluster has a chain of three Nb atoms bridged by Se and Se_2 (Figure 12). The trinuclear Ta^V cluster shows a triangle of three Ta atoms bridged by μ_2−S, μ_3−S, and μ_2−S_2 (Figure 13). Long Ta–Ta

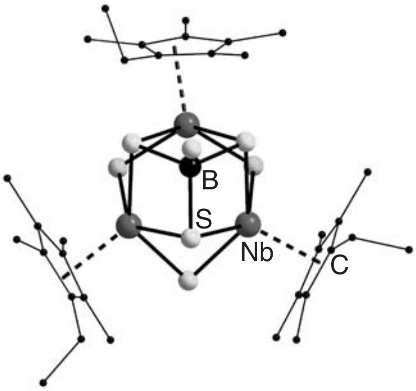


Figure 11 Structure of the $[(\eta^5{-}EtMe_4C_5)_3Nb_3(S_3BSH)(\mu{-}S)_3]$ molecule.

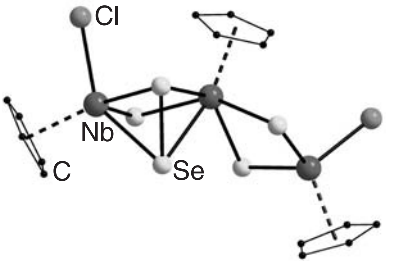


Figure 12 Structure of the $[(\eta^5{-}C_5H_5)_3Nb_3Se_5Cl_2]$ molecule.

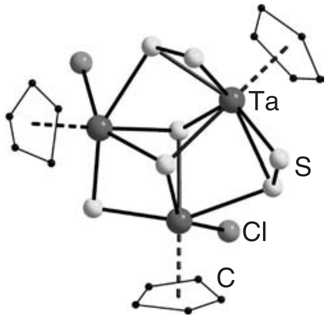


Figure 13 Structure of the $[(\eta^5{-}C_5H_5)_3Ta_3S_7Cl_2]$ molecule.

distances of 3.24–3.60 Å indicate no M—M bonding, in agreement with the oxidation state formalism.[44] The group Nb_3^{15+} gives even more chalcogen-rich cores. Thermolysis of a polysulfide mixture of $[(\eta^5{-}^tBuC_5H_4)_4Nb_2(S_n)]$ ($n = 8$, 9) in toluene (1 h, 100 °C) gives a mixture of four products: red–orange structurally characterized as $[(\eta^5{-}^tBuC_5H_4)_3Nb_3S_{12}]$ and $[(\eta^5{-}^tBuC_5H_4)_3$-$(O)S_{10}]$, and $[(\eta^5{-}^tBuC_5H_4)_4Nb_4S_{13}]$ of unknown structure. The first cluster has a $Nb_3(\mu_3{-}S)(\mu_3{-}S_2)(\mu{-}S_2)_2(\mu{-}S_3)(S_2)^{3+}$ core with three different types of Nb atoms, and in solution its proton magnetic resonance spectrum indicates three different $^tBuC_5H_4$ rings (Figure 14). The Nb–Nb distances range from 3.61 to 4.08 Å. The structure of $[(\eta^5{-}^tBuC_5H_4)_3Nb_3(O)S_{10}]$ is similar, with $\mu_3{-}O$ instead of $\mu_3{-}S$ (Nb–O 2.07−2.12 Å) and a $\mu_3{-}S_2$ ligand instead of S_3 (Figure 15). The Nb atoms here are not equivalent and they remain so in solution, as can be seen from ^1H NMR. The Nb–Nb distances are 3.33–3.74 Å.[45]

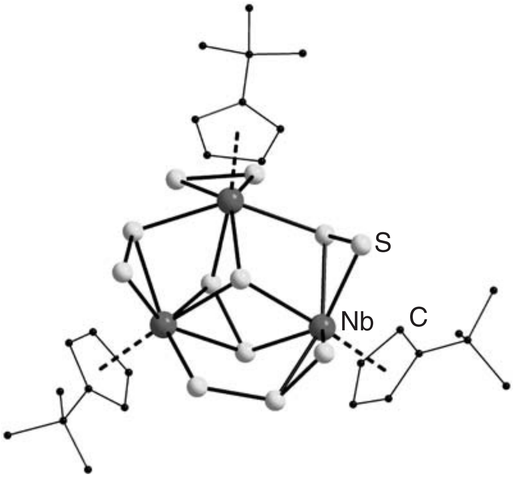


Figure 14 Structure of the $[(\eta^5{-}^tBuC_5H_4)_3Nb_3(\mu_3{-}S)(\mu_3{-}S_2)(\mu{-}S_2)_2(\mu{-}S_3)(S_2)]$ molecule.

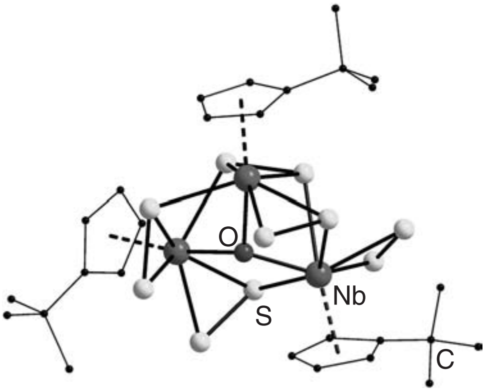


Figure 15 Structure of the $[(\eta^5{-}^tBuC_5H_4)_3Nb_3(\mu_3{-}O)(S_2)_5]$ molecule.

A mixed chalcogenide halide bridged cluster core $Nb_3(\mu_3{-}S)(\mu_3{-}I)(\mu{-}I)_3^{4+}$ is encountered in a layered compound $Nb_7S_2I_{19}$, that is present as $[Nb_3SI_7]_2[NbI_5]$. This compound forms nearly level sheets of Nb_3 triangular clusters. Each Nb is octahedrally coordinated by one S and five I atoms. The sulfur atom and one of the iodine atoms cap the triangle (Nb–Nb 2.776 Å). The two-dimensional network forms through intercluster bridging iodine atoms, forming nearly hexagonal channels along the *c* axis. In these channels are isolated NbI_5 molecules. This inclusion compound was made by heating the elements in a molar ratio 7Nb:2S:19I in a quartz ampoule at 1,100 K for 2 days. Another triangular cluster compound, Nb_3IS_7, formed under these conditions as an impurity. Two-probe electrical resistivity measurements indicated $\rho(300\,K) > 10^4\ \Omega\,cm$.[46] A series of polymeric chalcohalides M_3QX_7 (M = Nb, Ta; Q = S, Se, Te; X = Cl, Br, I) with a $M_3(\mu_3{-}Q)(\mu{-}X)_3^{4+}$ core as common unit was prepared by solid-state reactions[47,48] In a cluster $[Nb_3O(Te_4)(Te_2)_2I_6]I$ the metal core is arranged in the form of an isosceles triangle with the Nb–Nb distances 3.013 Å, 3.048 Å, and 3.861 Å. The core is capped by a $\mu_3{-}O$ atom. Each of the two short sides if the triangle is bridged by one Te_2 group, while a similar planar Te_4 group (Te—Te 2.797 Å) is bonded in a $\mu{-}\eta^2{:}\eta^2$ fashion to the longer side. The bonding is rationalized in terms of the formalism $[(Nb^{3+})(Nb^{4+})_2(O^{2-})(Te_2^{2-})_2(I^-)_6]^+$, thus leaving four electrons to form two localized Nb—Nb bonds. The compound, which is black, is obtained in a moderate yield from Nb, $NbOI_3$, Te, and I_2 (2:1:8:2 molar ratio). It can also be made in low yield directly from the elements (3Nb, 11Te, $2I_2$, at 680 °C).[49]

4.12.4.2 Tetranuclear Clusters

The tetrahedral M_4 unit is present in cuboidal clusters M_4Q_4, and these are well known for V, Nb, and to a lesser extent, Ta. Vanadium forms a dithiocarbamate $(Et_4N)[V_4S_4(C_4H_8NCS_2)_6]$ in a 67% yield from $(NH_4)_3[VS]_4$, ammonium pyrrolidine dithiocarbamate $NH_4C_4H_8NCS_2$ and PPh_3, in the presence of Et_3N in acetonitrile at room temperature. The V–S distances vary 2.27–2.33 Å, and V–V distances in the $V_4S_4^{5+}$ core (2.77–3.00 Å) indicate M—M bonding, with the involvement of seven electrons.[50] The cyclopentadienyl derivatives have been long known and can be accessed by various routes. The oxidative sulfurization of $[(\eta^5{-}MeC_5H_4)_2V]$ with ^tBuSH under reflux in heptane gives relatively air-stable $[(\eta^5{-}MeC_4H_5)_4V_4S_4]$, with small amounts of penta-nuclear $[(\eta^5{-}MeC_5H_4)_5V_5S_6]$ (Figure 16).[51] The unsubstituted less soluble $[(\eta^5{-}C_5H_5)_4V_4S_4]$ is made from vanadocene and $CH_3C(S)SH$ (yield 47%, reaction takes four days).[52] This cluster can also be made from $[(\eta^5{-}C_5H_5)_2V]$ and H_2S in THF at room temperature.[53] Another approach involves a condensation of two V_2 units. Desulfurization of S_2 bridged $[(\eta^5{-}MeC_5H_4)_2V_2(\mu{-}\eta^1{-}S_2)(S)_2]$ with PBu_3 gives a mixture of $[(\eta^5{-}MeC_5H_4)_4V_4S_4]$ and $[(\eta^5{-}CH_3C_5H_4)_5V_5S_6]$.[54] The cube of $[(\eta^5{-}C_5H_5)_4V_4S_4]$ is made from the corresponding $[(\eta^5{-}C_5H_5)_2V_2S_4]$ and PBu_3. Reaction of $[(\eta^5{-}C_5H_5)_2V]$ with $[(\eta^5{-}CH_3C_5H_4)_2V_2S_4]$ gives the mixed species $[(\eta^5{-}C_5H_5)_x(MeC_4H_5)_{4-x}V_4S_4]$, which have been characterized by ^1H NMR and mass spectroscopy.[21,54] Similarly, selenium-rich $[(\eta^5{-}C_5H_5)_2V_2Se_5]$ reacts with PBu_3 to give $[(\eta^5{-}C_5H_5)_4V_4Se_4]$ (72%, 2 h in CH_2Cl_2).[55] The MeC_5H_4 analog is obtained in a 46% yield from $[(\eta^5{-}MeC_5H_4)_2V_2Se_4]$ and PBu_3 (46%, 4 h in CH_2Cl_2).[55] The tellurides $[(\eta^5{-}RC_5H_4)_4V_4Te_4]$ (R = H, Me) are obtained by heating $[(\eta^5{-}RC_5H_4)_2V_2(CO)_4(Te)_2]$ in toluene at 50–60 °C in almost quantitative yields (R = H, Me).[55] These cuboidal clusters have 8e available for M—M bonding and are paramagnetic, in agreement with the orbital population pattern $a_1^2 + e^4 + 1t_2^2$. The cube $[(\eta^5{-}MeC_5H_4)_4V_4S_4]$ gives the molecular peak in the mass spectrum, with subsequent loss of all the cyclopentadienyl ligands, when the "naked" $V_4S_4^+$ ion appears. X-ray analysis of this cluster shows a regular tetrahedron with V—V bonds 2.88 Å, and V—S 2.30 Å.[51,56] The cube $[(\eta^5{-}C_5H_5)_4V_4S_4]$ has a very similar structure.[52] Although cyclic voltammetry experiments

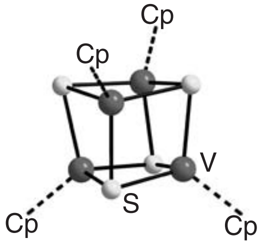


Figure 16 Structure of the $[(\eta^5{-}MeC_5H_4)_4V_4]$ molecule.

show that $[(\eta^5{-}MeC_5H_4)_4V_4S_4]$ loses reversibly four electrons in four consecutive 1e oxidation steps, only the first oxidation gives a product stable enough to be isolated. It was obtained as $[(\eta^5{-}MeC_5H_4)_4V_4S_4]BF_4$ by oxidation with Ph_3CBF_4. The V–V and V–S distances in this cation are very similar to those in the neutral molecule, 2.86 Å and 2.30 Å, respectively.[21]

The $Nb_4Q_4{}^{4+}$ core is found only in the solid state, in chalcohalides $Nb_4Q_4X_4$ (Q = S, Se; X = Br, I). They are prepared by high-temperature synthesis from the elements. Only the seleno-iodide $Nb_4Se_4I_4$ could be obtained pure by heating the elements in a sealed quartz ampoule in a 880/850 °C temperature gradient. It is built from the cuboidal units Nb_4Se_4 and I atoms in such a way that a cubic NaCl-type lattice is formed. Each Nb atom is connected to three I's and each I is triply bridging. The Nb–I distance is 3.01 Å and Nb–Nb 2.96 Å, which is appreciably longer than in the isoelectronic V_4S_4 cubes. The $Nb_4S_4Br_4$, $Nb_4Se_4Br_4$, and $Nb_4S_4I_4$ compounds are also known but could not be prepared pure.[57] The cubes GaM_4Q_8 (M = Nb, Ta; Q = S, Se) are prepared by high-temperature reactions from the elements; their structures resemble that of $Nb_4Se_4I_4$, but with the M_4Q_4 units interconnected by the extra chalcogenide ions instead of iodine.[58]

Examples of incorporation of a $\mu_4{-}O$ atom at the center of an M_4 tetrahedron M = Nb, Ta are also known. Both the cluster anions $[M_4(\mu_4{-}O)Te_4(CN)_{12}]^{6-}$ are made by heating MTe_4 with KCN at 350–450 °C. They are relatively air stable and have been structurally characterized. The Nb–Nb distances in dark-brown $K_6[Nb_4(O)Te_4(CN)_{12}]KOH{\cdot}K_2CO_3{\cdot}8H_2O$ are 3.20 Å, with only four electrons available for M—M bonding. The cluster undergoes a quasi-reversible oxidation at 309 mV followed by irreversible oxidation at 900 mV in 0.1 M Na_2SO_4 solution (vs. NHE).[59,60]

The tetrahedral arrangement of Ta atoms is also found in $[(\eta^5{-}C_5H_5)_4Ta_4S_{13}]$, where the Ta atoms are bridged by four $\mu_2{-}S_2$, two $\mu_3{-}S$, and one $\mu_4{-}S$ ligands (Figure 17). The quadruply bridging sulfide forms rather long bonds with Ta ranging from 2.62 Å to 2.67 Å. No Ta—Ta bonding exists in this Ta^V compound.[44] The compound $[(\eta^5{-}{}^tBuC_5H_4)_4Nb_4S_{13}]$ may have the same structure.[45]

Opening up the M_4 tetrahedron gives square–planar units, represented here by a $Nb_4(\mu_4{-}S)_2{}^{8+}$ core. The first cluster of this type to be prepared was black $Li_4[Nb_4(S)_2(SPh)_{12}]$, made from $[Nb_2Cl_6(Me_2S)_3]$ and LiSPh (taken in a large excess) in toluene, 55–60% yield. In this diamagnetic cluster, four Nb^{III} atoms have 8e, sufficient to satisfy the requirement of four single metal–metal bonds (Figure 18). The Nb–Nb distances are 2.83 Å. This cluster is rather robust and cannot be oxidized with PhSSPh, nor does it reacts with PPh_3 in a hot toluene.[61] Orange $[Nb_4(S)_2(SPh)_8(PMe_2R)_4]$ (R = Me, Ph) were prepared by reducing $NbCl_5$ with Na/Hg, adding PhSSPh and then the phosphine, in about 20% yields. The Nb—Nb bonds are somewhat shorter, 2.82 Å (in both clusters), and the Nb—P bonds are rather long (2.69 Å).[62]

Reduction of a mixture of $TaCl_5$ and Li_2S with Na/Hg initially gives a green solution, which turns dark orange. Addition of PMe_3 gives a binuclear Ta^{IV} complex $[Ta_2(\mu{-}S)_2Cl_4(PMe_3)_4]$ (20%), together with 2% of green tetranuclear $[Ta_4S_4Cl_8(PMe_3)_6]$ (Figure 19). In the latter Ta^{IV} cluster only four electrons are available for M—M bonding, and this is realized within a zigzag chain Ta(1)–Ta(2)–Ta(2)–Ta(1) with Ta(1)–Ta(2) 3.09 Å, and Ta(2)–Ta(2) 2.90 Å.[63] Tetranuclear $[Nb_4Se_3Br_{10}(CH_3CN)_4]$ (Figure 20) is obtained from $[NbBr_4(CH_3CN)_2]$ and Sb_2Se_3 in acetonitrile (50 °C, seven days). Two of its Nb atoms are Nb^{IV}, bridged by Se_2, and form a Nb—Nb bond (2.886 Å). The other two Nb atoms are Nb^{III} and are surrounded with 5Br + 1Se (C_{3v} symmetry). They have a low-lying and doubly occupied d_{z^2} orbital and do not participate in M—M bonding ($Nb^{III}{-}Nb^{IV}$ 3.1 Å). The cluster is ESR silent over the −195.8 °C to 20.0 °C temperature range, and is diamagnetic.[64]

On carrying out the reaction between VCl_3, Li_2S, Et_4NBr, and Na_2edt in CH_3CN in a reagent ratio different from that used to obtain the trinuclear cluster $[V_3S_4(edt)_3]^{3-}$,[35] the tetranuclear

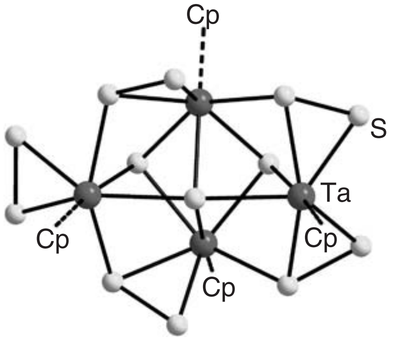


Figure 17 Structure of the $[(\eta^5{-}C_5H_5)_4Ta_4(\mu_4{-}S)(\mu_3{-}S)_2(\mu_2{-}S_2)_4(S_2)]$ molecule.

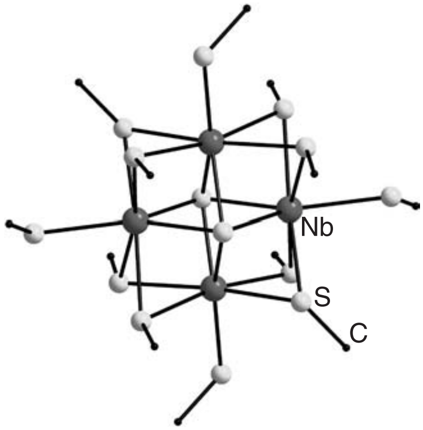


Figure 18 Structure of the $[Nb_4(S)_2(SPh)_{12}]^{4-}$ anion. Only C atoms bonded to S are shown.

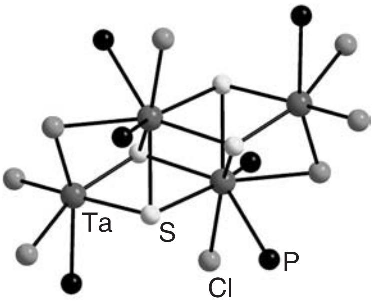


Figure 19 Structure of the $[Ta_4(\mu_3{-}S)_4Cl_8(PMe_3)_6]$ molecule; Me groups are omitted for clarity.

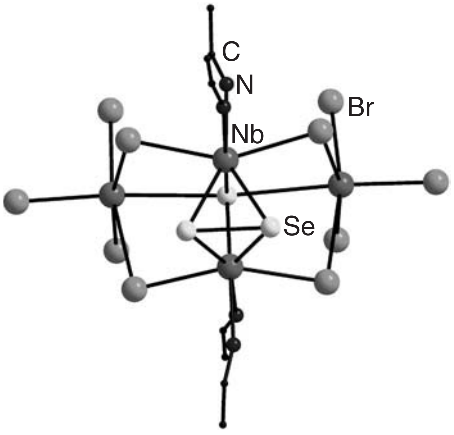


Figure 20 Structure of the $[Nb_4(\mu_4{-}Se)(\mu_2{-}Se_2)Br_{10}(CH_3CN)_4]$ molecule.

vanadium cluster $[V_4S_2(SCH_2CH_2S)_6]^{2-}$ is obtained. In this cluster four vanadium atoms are bonded to two $\mu_3{-}S$ bridges. The V–V distances range from 2.77 Å to 3.30 Å. The resulting V_4S_{14} fragment is very close to a discrete portion of the Li_xVS_2 phase and displays similar redox chemistry. The cluster can be oxidized at 0.00 V and reduced in two consecutive one-electron steps at −0.41 V and −0.97 V (vs. SCE).[65]

4.12.4.3 Pentanuclear Clusters

These are represented only by cyclopentadienyl derivatives of the V_5S_6 core. The compound $[(\eta^5{-}MeC_5H_4)_5V_5S_6]$ can be prepared in low yields either from $[(\eta^5{-}MeC_5H_4)_2V]$ and

$CH_3C(S)SH$ or from $[(\eta^5-MeC_5H_4)_2V_2S_4]$ and PBu_3, the second (major) product always being the cuboidal cluster $[(\eta^5-MeC_5H_4)_4V_4S_4]$. The V_5 core is trigonal bipyramidal and each triangular face is capped by a μ_3–S atom. Two types of V–V and V–S distances are observed: V_{ax}–S 2.23 Å; V_{eq}–S 2.39 Å; V_{ax}–V_{eq} 3.07 Å; V_{eq}–V_{eq} 3.21 Å. Treatment of a toluene solution of the pentanuclear cluster with TCNQ precipitates dark green crystals of $[(\eta^5-MeC_5H_4)_5V_5S_6](TCNQ)_2]$.[54]

4.12.4.4 Hexanuclear Clusters

Molecular octahedral clusters are represented here by the octahedral V_6 core only with an interstitial oxygen atom inside, $[(\eta^5-C_5H_5)_6V_6Se_8(O)(PMe_3)_6]$. This was prepared from $[(\eta^5-C_5H_5)VCl_2(PMe_3)_2]$ and $(Me_3Si)_2Se$. The V–V distances range from 2.79 Å to 2.84 Å, V–Se 2.52 Å. The cluster is V^{IV} and is diamagnetic[33] High-temperature reactions of Nb_6I_{11} or of Nb_3I_8 plus niobium with sulfur in a sealed niobium container afford Nb_6I_9S in high yields. It takes up hydrogen to form $Nb_6(H)I_9S$, with the hydrogen atom probably inside the Nb_6 octahedron. Both clusters are isostructural (Nb_6I_8 type), and can be described as one-dimensional polymeric $[(Nb_6I_6)S_{2/2}I_{6/2}]$, with Nb–Nb 2.92 Å. The octahedra in Nb_6I_9S are tetragonally compressed, whereas in the hydride a more regular arrangement is observed. The product Nb_6I_9S is a one-dimensional semiconductor, with room-temperature conductivity of $30\,\Omega^{-1}cm^{-1}$.[66]

A prismatic Nb_6 cluster having a μ_6–S as an interstitial atom is found in $Rb_3[Nb_6SBr_{17}]$. It was made by heating together RbBr, Nb, $NbBr_5$, and S at 800 °C for five days.[67] Here the $Nb_6SBr_{18}{}^{4-}$ units are linked through two terminal bromine atoms to form chains. Six bromine atoms lie above the six edges of the triangular faces of the prism (Nb—Br 2.57–2.61 Å), and further six μ_2–Br lie above the rectangular faces (Nb–Br 2.68–2.79 Å). The S atom is located almost exactly in the center of the prism (Nb–S 2.37 Å). The Nb–Nb distances along the edges of the rectangles (3.28 Å) are longer than along the edges of the triangles (2.95–2.98 Å). A MO treatment has been given to explain the M—M bonding in this cluster.[67]

An interesting hexanuclear vanadium cluster was obtained by treatment of$(Et_4N)Na[VS(edt)_2]$ with wet Et_3NHCl. Black, diamagnetic, extremely air-sensitive $(Et_4N)_3[V_6S_4(edt)_6(O)_2]$ was isolated from this reaction in a 5–10% yield (Figure 21). It has an open V_6 core, which can be rationalized in terms of a planar V_4 core with two μ_3–S above and below, and two VO^{2+} groups attached to the core via sulfido bridges and sulfur atoms of some edt ligands. The V–V interactions can be traced along a zigzag chain of all the six vanadium atoms. Their lengths vary from 2.758 Å for the central pair of V atoms to 2.82–2.86 Å for the peripheral bonds. All the other V–V distances are of the order of 3.3 Å. The cluster is ESR silent, and shows reversible redox behavior with reduction wave at −1.82 V and two oxidation waves at −1.01 V and −0.56 V (CH_3CN, vs. SCE). Apparently the vanadyl group is not involved in the redox changes.[68]

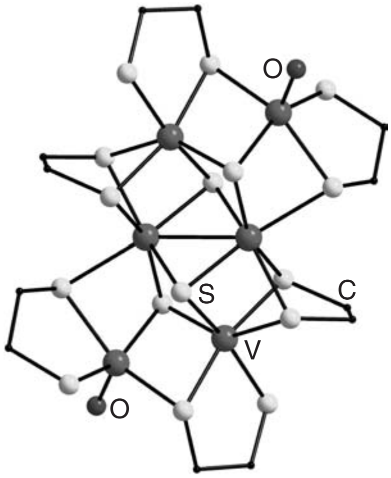


Figure 21 Structure of the $[V_4(V{=}O)_2(\mu_3-S)_4(edt)_6]^{3-}$ anion.

4.12.5 CHROMIUM

4.12.5.1 Trinuclear Clusters

A bicapped Cr_3 cluster is found in $[Cr_3S_5(dmpe)_3]$ (Figure 22). It was obtained in the reaction of anhydrous $CrCl_2$ with NaSH (−78 °C, methanol) followed by addition of an excess dmpe. A distorted Cr_3 triangle (Cr–Cr 2.647 Å, 2.552 Å, and 2.565 Å) is capped on each side by two sulfur atoms and is bridged by another three sulfides. A second-order Jahn–Teller effect may be responsible for this distortion in the cluster core.[69] Another bicapped cluster $(Et_4N)_2[Cr_3(\mu_3-Se)_2(CO)_{10}]$ (Cr–Cr 2.85–2.92 Å) was obtained from SeO_2 and $[Cr(CO)_6]$ in a strongly alkaline methanol, followed by addition of Et_4NBr in a 52% yield. This core is asymmetric since two Cr atoms have three terminal CO groups and one has four.[70]

Trinuclear Cr complexes $(Ph_4P)_3[Cr_3Q_{24}]$ (Q = Se, Te) are also known, where a linear array of three Cr atoms is held by six $Q_4{}^{2-}$ ligands. The Cr–Cr distances are quite long, 3.21 Å for the selenide and 3.41 Å for the telluride. A strong antiferromagnetic coupling is observed between the Cr^{III} centers (Q = Se, $\mu_{eff} = 5.25$ B.M.; Q = Te, 5.74 B.M., both at 300 K).[71]

4.12.5.2 Tetranuclear Clusters

The cuboidal $Cr_4S_4{}^{4+}$ core is found only in cyclopentadienyl derivatives, which can be accessed by a number of different synthetic procedures. $[(\eta^5-RC_5H_4)_4Cr_4S_4]$ (R = H, CH_3) are made from corresponding $[(\eta^5-RC_5H_4)_2Cr]$ and Me_3CSH or S_8 in organic solvents with high boiling point.[72,73] Thermolysis of $[(\eta^5-C_5H_5)_2Cr_2(S)_2(CO)_5]$ in toluene at 100 °C (or other dimeric carbonylcyclopentadienyl chromium complexes with sulfido bridges) gives $[(\eta^5-C_5H_5)_4Cr_4S_4]$. The cluster $[(\eta-C_5H_4)_5Cr_4(\mu_3-S)_2(\mu_3-CO)_2(CO)_6]$ is also formed in these reactions.[74–76] Passing H_2S through a THF solution of $[(\eta^5-RC_5H_4)_2Cr]$ (R = H, CH_3) converts the latter into the cuboidal clusters.[77] In addition, $[(\eta^5-MeC_5H_4)_4Cr_4S_4]$ is obtained by thermolysis of $[(\eta^5-Me_3C_5H_4)_2Cr_2(\mu-SCMe_3)_2(\mu-S)]$ or by reacting it with $CuBr_2$ in THF in the presence of Et_3N.[73]

The clusters are diamagnetic and contain 60e, with sufficient electrons to fill all six M—M bonding orbitals. The tetrahedron is distorted in such a way that there are two long and four short M–M distances. An electronic density map was obtained from X-ray diffraction experiments on $[(\eta^5-C_5H_5)_4Cr_4S_4]$.[78] A mixed S/O bridged core exists in the adduct $[(\eta^5-C_5H_5)_4Cr_4S_3O]\cdot CuBr_2$, where one of the sulfur atoms acts as a donor toward the $CuBr_2$ molecule.[73] The $[(\eta^5-C_5H_5)_4Cr_4S_2O_2]$ cluster has never been isolated in the free state, only as a component of the crystal lattice of ternary molecular adducts with ratios $[(\eta^5-C_5H_5)_4Cr_4S_4]\cdot 0.4[(\eta^5-C_5H_5)_4Cr_4S_3O]\cdot 0.6[(\eta^5-C_5H_5)_4Cr_4S_2O_2])$.[74]

The corresponding Se and Te bridged cuboidal Cr clusters also exist. Black $[(\eta^5-RC_5H_4)_4Cr_4Se_4]$ (R = CH_3, H) are obtained from $[(\eta^5-C_5H_5)_2Cr_2(CO)_6]$ or $[(\eta^5-CH_3C_5H_4)_2Cr]$ and gray Se, via isolatable intermediates $[(\eta^5-C_5H_5)_2Cr_2(Se)(CO)_4]$ and $[(\eta^5-C_5H_5)_2Cr_2(CO)_4Se_2]$.[75,76] The cluster $[(\eta^5-CH_3C_5H_4)_2Cr]$ with H_2Se in toluene also give $[(\eta^5-CH_3C_5H_4)_4Cr_4Se_4]$ in a 90% yield.[77,78] In addition $[(\eta^5-C_5H_5)_4Cr_4Se_4]$ is obtained from $[(\eta^5-C_5H_5)_2Cr_2(CO)_6]$ and Ph_2Se_2 via $[(\eta^5-C_5H_5)_2Cr_2(SePh)_2(\mu-Se)]$.[79,80] The X-ray structure of $[(\eta^5-CH_3C_5H_4)_4Cr_4Se_4]$ shows almost no distortion of the Cr_4 tetrahedron. The distances Cr–Cr differ by no more than 0.066 Å from the average value 3.008 Å.[78] With Te, only mixed Te/O

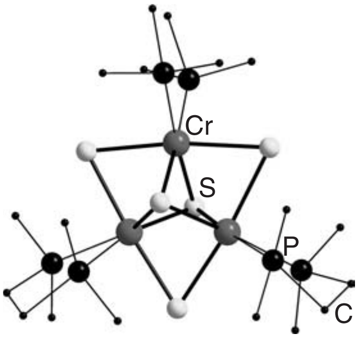


Figure 22 Structure of the $[Cr_3S_5(dmpe)_3]$ molecule.

bridged clusters are known: [(η^5–C_5H_5)$_4$$Cr_4Te_3O$] (Cr–Cr 3.191 Å), [($\eta^5$–$C_5H_5$)$_4$$Cr_4Te_2O_2$] (Cr–Cr 3.033 Å) and [($\eta^5$–$C_5H_5$)$_4$$Cr_4TeO_3$] (Cr–Cr 2.90 Å), prepared by thermolysis of [(η^5–C_5H_5)Cr(CO)$_3$TePh].[81]

Electrochemical studies on [(η^5–$CH_3C_5H_4$)$_4$$Cr_4Q_4$] (Q = S, Se) show that the cluster cores are capable of losing one or two electrons. For the methycyclopentadienyl derivatives, $E_{1/2}$ values are −0.66 V and −0.06 V (Q = S); −0.52 V and +0.31 V (Q = Se) for +1/0 and +2/+1 couples respectively (vs. Fc^+/Fc). These Cr clusters are more difficult to oxidize than their Mo analogs. Oxidation of [(η^5–MeC_5H_4)$_4$$Cr_4Q_4$] (Q = S, Se) with TCNQ, [(η^5–C_5H_5)$_4$$Fe_4(NO)_4$] or [Mo($S_2C_2$($CF_3$)$_2$)$_3$] gives the 1:1 charge-transfer salts. In the case of TCNQ, [(MeC_5H_4)$_4$$Cr_4Q_4$](TCNQ)$_2$ also forms.[77] Paramagnetic salts of 59e [(η^5–RC_5H_4)$_4$$Cr_4S_4$]$^+$ (R = H, CH_3) were also prepared directly by cluster assembly reactions from [(η^5–C_5H_5)$_2$$Cr_2$($SCMe_3$)$_2$(S)] and $SnCl_4$ or $SnCl_2$ (20 °C, using a C_6H_6/THF mixture), or from [(η^5–C_5H_5)$_2$$Cr_2$($SCMe_3$)$_2$(S)] and [($\eta^5$–$C_5H_5$)Re(CO)(NO)($PEt_3$)$_2$]($CF_3SO_3$). They were isolated and structurally characterized as salts with [$SnCl_5$(THF)]$^-$ and triflate, respectively. X-ray structure of the pentachlorostannate salt shows that the Cr_4 tetrahedron is distorted: there are five short Cr—Cr bonds (2.80 Å) and one long at 2.84 Å.[82–84] The structure of [(η^5–MeC_5H_4)$_4$$Cr_4S_4$]$^+$ [(η^5–MeC_5H_4)$CrBr_3$]$^-$ has been determined.[83]

The reaction of [(η^5–C_5H_5)$_2$$Cr_2(CO)_6$] with 1eq. of tetraethylthiuramdisulfide (Et_2NC(S)S)$_2$ in toluene (90 °C, 2 h) gives a dark-brown mixture, from which six products were isolated by column chromatography (in the order of elution): [(η^5–C_5H_5)Cr(CO)$_2$)$_2$S] (1%), [(η^5–C_5H_5)$_6$Cr(CO)$_2$(S_2CNEt_2)] (22%), [(η^5–C_5H_5)$_4$$Cr_4S_4$] (22%), [($\eta^5$–$C_5H_5$)$_6$$Cr_8S_8$(C(S)$NEt_2$)$_2$] (6.8%, brown solid), [Cr(S_2CNEt_2)$_3$] (19%) and [(η^5–C_5H_5)$_6$$Cr_8S_8$($S_2CNEt_2$)$_2$] (11%, dark-brown solid).[84] The structures of both Cr_8 clusters consist of two (η^5–C_5H_5)$_3$$Cr_3CrS_4$ cubes, linked at Cr atoms from which the cyclopentadienyl ligands have been cleaved. In the last product, the double cube is bridged by two dithiocarbamate ligands in a μ–η^1–S, η^2–S,S mode which act as 5e donors. Thus each Cr_4 unit has 60 electrons with Cr–Cr distances 2.87 Å. The other Cr_8 cluster has a thiooxamide ligand Et_2NC(S)–C(S)NEt_2 that links the two cubes in a μ–η^2, η^4–bridging mode, and a weak Cr—Cr bond (3.101 Å and 3.118 Å for two crystallographically independent anions) between the two cubes. Counting the thioamidic bridge as an eight-electron donor, each cuboidal Cr_4 fragment reaches the 60e configuration with Cr—Cr bond lengths of 2.83 Å. Both clusters are diamagnetic, as follows from the normal chemical shifts in their ^{1}H NMR spectra.[85]

Some heterometallic cuboidal clusters with the $Cr_3M'S_4$ core have been reported. The reaction of (η^5–C_5H_5)$_2$$Cr_2$($SCMe_3$)$_2$(S) with [($\eta^5$–$MeC_5H_4$)$_2$V] gives the 59e cluster [(η^5–C_5H_5)$_3$$Cr_3$($\eta^5$–$CH_3C_5H_4$)$VS_4$], which co-crystallizes with [(η^5–C_5H_5)$_4$$Cr_4S_4$] as a 1:1 molecular adduct.[83] Iron gives the 58e clusters [(η^5–C_5H_5)$_3$$Cr_3$ ((^{t}Bu COO) Fe)S_4][86] and [(η^5–C_5H_5)$_3$$Cr_3$((PhS)Fe)$S_4$],[87] while for Co, 60e clusters [(η^5–RC_5H_5)$_3$$Cr_3$((CO)Co)$S_4$] (R = H, CH_3) are known.[51,88] It appears that these heterometallic cubes follow the pattern set by homometallic Cr_4Q_4 clusters, i.e., where 58, 59, and 60e cluster states are accessible, at least by electrochemistry. The 64e cluster [(η^5–C_5H_5)$_3$$Cr_3$((CO)$_3$Co)$S_4$] is no longer a cube: two M—M bonds are broken to give a butterfly-type shape, in accordance with electron count rules.[89]

The reaction of Cr metal powder or [Cr(CO)$_6$] with S in refluxing AcOH/Ac_2O yields a mixture of soluble cationic species, from which blue [Cr_4(μ_4–S)(μ–OAc)$_8$(H_2O)$_4$(BF_4)]·H_2O has been isolated. The sulfur atom is located inside an approximately tetrahedral Cr_4 array (Cr–S 2.35 Å). Each metal is hexacoordinated. Although the Cr–Cr edges in the octahedron are bridged by acetates, the M–M distances are long, 3.72–3.91 Å. The spins of the four Cr^{III} are ferromagnetically coupled to give an $S = 6$ ground state. The ESR of the cluster (in frozen methanol solution, at 15 K) shows a single broad peak with $g = 1.983$.[90]

4.12.5.3 Pentanuclear Clusters

Chromium does not form pentanuclear clusters with a trigonal bipyramidal core, as do Ti and V. The only pentanuclear cluster reported here is a spirane [(η^5–C_5H_5)$_4$$Cr_5$($\mu_3$–S)$_4$($\mu$-S^{t}Bu)$_2$] (Figure 23), which can be regarded as Cr^{2+} coordinated by two ligands [(η^5–C_5H_5)$_2$$Cr_2(S)_2$(S^{t}Bu)]$^-$.[91]

4.12.5.4 Hexanuclear Clusters

An octahedral cluster with a Cr_6(μ_3–Te)$_8$ core has been synthesized by two routes. The complex [$CrCl_2$(PEt_3)$_2$] made *in situ*, was treated with allylmagnesium chloride, to which $TePEt_3$ was

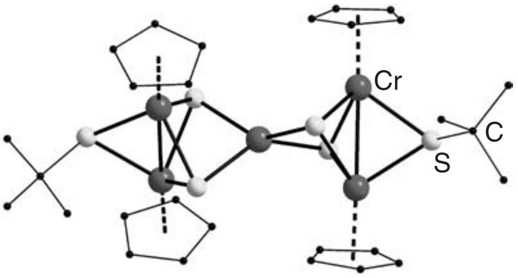


Figure 23 Structure of the $[(\eta^5{-}C_5H_5)_4Cr_5(\mu_3{-}S)_4(\mu{-}S^tBu)_2]$ molecule.

added. Alternatively, and apparently in somewhat better yield (38%), this dark-brown cluster can be made from bis(2,4–dimethylpentadienyl)- chromium $[Cr(\eta^5{-}C_7H_9)_2]$, by treating with $TePEt_3$ and an excess PEt_3. The cluster $[Cr_6Te_8(PEt_3)_6]$ is obtained with Cr–Cr distance 2.94 Å, and C–Te 2.65 Å (Figure 24). The cluster is paramagnetic with μ_{eff} of 2.8 B.M. This means that in the 84e cluster the ground state is a triplet, in agreement with theoretical models. Heating the cluster in a sealed evacuated Pyrex tube (315 °C, 19 h) gives the known binary telluride Cr_3Te_4. The Cr_6Te_8 core is therefore not preserved in the transformation.[92] The reaction of anhydrous $CrCl_2$ with Na_2Se or NaSH with subsequent treatment with PEt_3 in methanol was initially reported to give $[Cr_6Q_8(PEt_3)_6]$ (Q = S, Se). However, a later careful reexamination of the data led the authors to reformulate the sulfido cluster as $[Cr_6S_8(H)(PEt_3)_6]$, with a hydrogen atom incorporated inside the Cr_6 octahedron. An improved method to make this cluster using NaS_xH ($x = 1.33$) instead of NaSH gives the black crystalline material, 21% yield. With d^4-methanol as solvent, a partially deuterated cluster $[Cr_6S_8(D)_{0.8}(H)_{0.2}(PEt_3)_6]$ was the product. In the case of the selenide, it was shown to be actually a mixture of both $[Cr_6Se_8(PEt_3)_6]$ and $[Cr_6Se_8(H)(PEt_3)_6]$. The initial reaction of $CrCl_2$ with Na_2Se_x ($x = 1.33$) in CH_3OH followed by addition of PEt_3 and extraction gives the mixture indicated. Due to a large difference in the ox–red potentials of $[Cr_6Se_8(PEt_3)_6]$ (oxidation at −0.50 V, reduction at −1.75 V) and $[Cr_6Se_8(H)(PEt_3)_6]$ (oxidation at −0.81 V and reduction at −1.48 V, vs. Fc^+/Fc in acetonitrile) it was possible to oxidize only the hydrido cluster with a stoichiometrical amount of the ferricinium compound $FcPF_6$, and to separate $[Cr_6Se_8(PEt_3)_6]$ (4% yield) and $[Cr_6Se_8\ (H)(PEt_3)_6]PF_6$ making use of their different solubilities. The PF_6^- salt was then reduced with cobaltocene in acetone to give the neutral hydrido cluster (8% yield). The Cr—Cr bond distances in the hydrido cluster are 0.13−0.16 Å shorter than in the hydrogen-free cluster (2.66 Å vs. 2.80 Å) indicating bonding interaction between interstitial hydrogen and chromium atoms. The average Cr–Cr distance in the sulfido cluster $[Cr_6S_8(H)(PEt_3)_6]$ is 2.59 Å. All the three clusters are paramagnetic between 200 and 300 K, with μ_{eff} for $[Cr_6Se_8(PEt_3)_6]$ is 0.2 B.M. (2 K), thus indicating zero ground state. For $[Cr_6Se_8\ (H)(PEt_3)_6]$ μ_{eff} was found to be 2.0 B.M. (2 K), and for $[Cr_6S_8(H)(PEt_3)_6]$ 1.7 B.M. at 4.5 K, which are close to the spin-only magnetic moment for the $S = 1/2$ state. There are intracluster magnetic interactions between the spins on six Cr atoms.[93]

Oxidation of 21e $[Cr_6S_8(H)(PEt_3)_6]$ with $FcBF_4$ gives $[Cr_6S_8(H)(PEt_3)_6](BF_4)$ with Cr–Cr distances of 2.81–2.85 Å, ca. 0.2 Å longer than in the starting neutral cluster. The oxidation weakens the antiferromagnetic interaction, and at 0 K the ground state $S = 0$ must apply to this

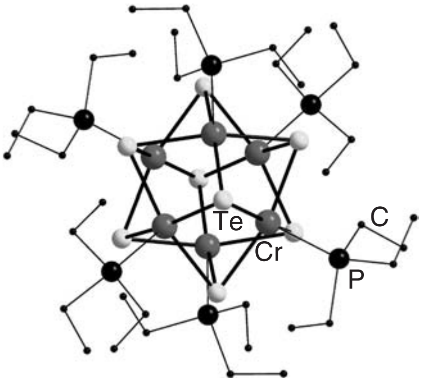


Figure 24 Structure of the $[Cr_6Te_8(PEt_3)_6]$ molecule.

20e cluster. Attempts to remove hydrogen from the cluster by deprotonation with n-BuNH$_2$ resulted in the recovery of only the reduced cluster, [Cr$_6$S$_8$(H)(PEt$_3$)$_6$].[94] Treatment of [Cr$_6$S$_8$(H)(PEt$_3$)$_6$] with S$_8$ removes one PEt$_3$ (as PEt$_3$S) to give a dodecanuclear [Cr$_{12}$S$_{16}$(H)$_2$(PEt$_3$)$_{10}$] in a 39% yield, characterized by FAB–mass spectroscopy and X-ray analysis. Here, two Cr$_6$S$_8$ units are linked by a Cr—Cr and two Cr—μ_4S bonds. The intercluster Cr–Cr distance is 2.952 Å, while the intra-cluster Cr—Cr bonds vary: those including the Cr atom participating in the intercluster bonding are longer (av. 2.79 Å) and the others shorter –2.63 Å. The cluster shows antiferromagnetic behavior with the antiferromagnetism enhanced at lower temperatures, and $S = 0$ is expected to be the ground state.[95]

4.12.6 MOLYBDENUM AND TUNGSTEN

4.12.6.1 Trinuclear Clusters with $M_3Q_4^{4+}$ Core

This is the most-studied family of clusters of all the early transition metals, M = Mo, W. The first cluster reported as having this core was the cyclopentadienyl derivative [(η^5–C$_5$H$_5$)$_3$-Mo$_3$S$_4$](Me$_3$SnCl$_2$).[96] Subsequently, clusters with three anionic or neutral ligands instead of the cyclopentadienide ligands coordinated to each M of Mo$_3$Q$_4$ were prepared. If the M—M bonds are ignored, the metal is hexacoordinated and in a distorted octahedral environment. The three M^{IV} atoms possess the required number of electrons to give three single M—M bonds, forming a very stable framework. There is one μ_3–Q atom capping the M$_3$ core, and the three M—M edges are bridged by the other chalcogen atoms. Alternatively, the M$_3$Q$_4$ core can be referred to as a one-metal depleted or incomplete cube.

4.12.6.1.1 *Aquacomplexes [$M_3Q_4(H_2O)_9$]$^{4+}$*

Green [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ can be prepared in a 15% yield; together with some 20% of the [Mo$_4$S$_4$(H$_2$O)$_{12}$]$^{5+}$ cube (also green) by the reaction of [Mo(CO)$_6$] with anhydrous Na$_2$S in acetic anhydride, followed by dissolution in water and cation-exchange chromatography.[97] An alternative procedure employs the electrochemical reduction of a cysteinato complex of Mo^V, [Mo$_2$O$_2$S$_2$(cys)$_2$]$^{2-}$, in 2 M HCl using a Hg pool electrode at a constant potential or electrochemically to give a mixture of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ and [Mo$_4$S$_4$(H$_2$O)$_{12}$]$^{5+}$.[98] The reduction of [Mo$_2$O$_2$S$_2$(cys)$_2$]$^{2-}$ with NaBH$_4$ in HCl solution followed by air oxidation of the reaction mixture (90 °C) to convert the cube into the trinuclear cluster has been much used, ~20% yield.[99] The aqua ion is isolated from a solution in 4 M Hpts as [Mo$_3$S$_4$(H$_2$O)$_9$](pts)$_4$·9H$_2$O (Mo–Mo 2.732 Å) (Figure 25).[100] A 20% yield of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ is also achieved by reducing (NH$_4$)$_2$[Mo$_2$(S$_2$)$_2$Cl$_8$] with Pb or In in conc. HCl.[101] When (NH$_4$)$_2$[MoS$_4$] is reduced with aqueous NaBH$_4$, [Mo$_3$S$_4$-(H$_2$O)$_9$]$^{4+}$ is obtained in a 50% yield after air oxidation and Dowex columning.[102] A very efficient way to make the aqua ion involves sulfur abstraction from S$_2$ bridges in [Mo$_3$(S)(S$_2$)$_3$Cl$_6$]$^{2-}$ with PPh$_3$, followed by cation-exchange chromatography. The yields here are almost quantitative.[103] In 2 M non-complexing acidic solutions [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ is stable over long periods (>2 years).

The whole range of mixed [Mo$_3$O$_n$S$_{3-n}$(H$_2$O)$_9$]$^{4+}$ ($n = 0–4$) aqua ions is also known. They are obtained as by-products from the preparations of [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ by reduction of [Mo$_2$O$_2$S$_2$(cys)$_2$]$^{2-}$ or [MoS$_4$]$^{2-}$ as indicated above.[102] Comproportionation reactions between

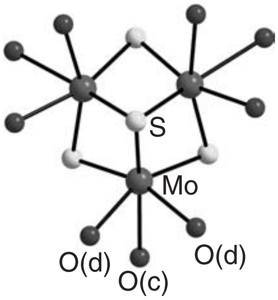


Figure 25 Structure of the [Mo$_3$S$_4$(H$_2$O)$_9$]$^{4+}$ cation showing c- and d-positions of coordinated H$_2$O ligands.

$Mo_2O_2S_2^{2+}$ and $[MoCl_6]^{3-}$, or between $Mo_2O_3S_2^{2+}$ and $[MoCl_6]^{3-}$, in 2 M HCl or 2 M Hpts are the best ways to make gray $[Mo_3O_2S_2(H_2O)_9]^{4+}$ and red $[Mo_3O_3S(H_2O)_9]^{4+}$ respectively in 70–80% yields.[104] The yields of green $[Mo_3OS_3(H_2O)_9]^{4+}$ are especially high upon electrolytical reduction of $Mo_2O_2S_2^{2+}$.[105] Treatment of the binuclear complex $[Mo_2O_3S(edta)]^{2-}$ with a solution of K_2CO_3, followed by acidification and column purification, gives trinuclear $[Mo_3O_3S(H_2O)_9]^{4+}$, 20% yield.[105] The $[Mo_3S_4(H_2O)_9]^{4+}$ product can be a source of the mixed O/S bridged species since it reacts with a large excess of $NaBH_4$ to give predominantly $[Mo_3OS_3(H_2O)_9]^{4+}$ together with smaller amounts of the other species.[106] In all these mixed O/S clusters the capping position is occupied by a sulfur atom. The crystal structure of $[Mo_3OS_3(H_2O)_9](pts)_4{\cdot}7H_2O$ has been determined.[107]

Similarly, brown $[Mo_3Se_4(H_2O)_9]^{4+}$ is obtained by a $NaBH_4$ reduction of $[Mo_2O_2Se_2(cys)_2]^{2-}$ in hydrochloric acid solutions. The products from cation-exchange chromatography give several bands corresponding to trinuclear green $[Mo_3O_2Se_2(H_2O)_9]^{4+}$, yellow–brown $[Mo_3OSe_3(H_2O)_9]^{4+}$, $[Mo_3Se_4(H_2O)_9]^{4+}$ and a green cuboidal $[Mo_4Se_4(H_2O)_{12}]^{5+}$ with the total yield of all products about 10%. The cluster $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ is better prepared by an alternative procedure involving reduction of $[Mo_2O_2Se_2(cys)_2]^{2-}$ with $[MoCl_6]^{3-}$ (90 °C, 1 h, 1 M HCl, 70% yield), and red $[Mo_3O_3Se(H_2O)_9]^{4+}$ has been obtained by electrochemical reduction of $[Mo_2O_4(cys)_2]^{2-}$ in the presence of gray Se powder in 3% yield. It also forms from $[Mo_3O_2Se_2(H_2O)_9]^{4+}$ with a 30-fold excess of $NaBH_4$.[108,109] More recently, a much more efficient way to make $[Mo_3Se_4(H_2O)_9]^{4+}$ has been identified by a procedure involving aquation of $(Ph_4P)_2[Mo_3Se_7Br_6]$ in 4 M Hpts and subsequent selenium abstraction from the resulting aqua complex $[Mo_3Se_7(H_2O)_6]^{4+}$ with PPh_3.[110] The crystal structure of $[Mo_3Se_4(H_2O)_9](pts)_4{\cdot}10H_2O$ has been determined.[111] In air, $[Mo_3Se_4(H_2O)_9]^{4+}$ decays (days) with the formation of red selenium.

Purple $[W_3S_4(H_2O)_9]^{4+}$ can be prepared by $NaBH_4$ reduction of $(NH_4)_2[WS_4]$ in HCl solutions. Using Dowex column purification, different products including red $[W_3O_2S_2(H_2O)_9]^{4+}$ (0.3%), $[W_3OS_3(H_2O)_9]^{4+}$ (red-purple, 5%) and $[W_3S_4(H_2O)_9]^{4+}$ were separated. In this preparation the yield of the latter was about 25%.[104] All three mixed O/S species $[W_3O_xS_{4-x}(H_2O)_9]^{4+}$ can be made by comproportionation of $(NH_4)_2[WS_4]$ with $K_3[W_2Cl_9]$.[112] The complex $[W(CO)_6]$ reacts with Na_2S in acetic anhydride to give the $W_3O_3S^{4+}$ core as the only isolatable product, characterized as the di-propyl- ammonium salt of $[W_3O_3S(NCS)_9]^{5-}$ (W–W 2.612 Å).[114] A far more efficient route to $[W_3S_4(H_2O)_9]^{4+}$ employs heating of the polysulfido complex $[W_3S_4(S_4)_3(NH_3)_3]^{2-}$ with conc. HCl,[114] or treatment of polymeric $\{W_3S_7Br_4\}_x$ with H_3PO_2 (in hot conc. HCl), in the yield 60–70%. Two solid hydrates $[W_3S_4(H_2O)_9](pts)_4{\cdot}xH_2O$ ($x = 7$, 9) have been isolated and structurally characterized with W–W (2.723 Å), identical to Mo—Mo in analogous aqua ion.[102]

The last cluster in this series to be identified was green $[W_3Se_4(H_2O)_9]^{4+}$. It was originally made in a low yield (about 5%) by treatment of polymeric $\{W_3Se_7Br_4\}_x$ with aqueous ammonium polysulfide $(NH_4)_2S_x$, followed by heating with conc. HCl.[115] Later, a better way was identified, involving reaction of $[W_3Se_7(H_2O)_6]^{4+}$ (aquation product of $(Ph_4P)_2[W_3Se_7Br_6]$ in 4 M Hpts) with PPh_3.[110] Even more efficient (yield ~60%) is the reaction of $\{W_3Se_7Br_4\}_x$ with H_3PO_2 in conc. HCl.[116] The aqua ion has been structurally characterized as $[W_3Se_4(H_2O)_9](pts)_4{\cdot}12H_2O$.[111]

Reduction of an equimolar mixture of $(NH_4)_2[WS_4]$ and the Mo^V-complex $Na_2[Mo_2\ O_2S_2(cys)_2]$ with excess $NaBH_4$ gives a mixture of sulfido-bridged clusters, which on chromatographic separation yields the mixed-metal incomplete cubes $[Mo_2WS_4(H_2O)_9]^{4+}$ (green, yield 17%) and $[MoW_2S_4(H_2O)_9]^{4+}$ (gray, yield 3%).[117,118] The structures of isomorphous $[MoW_2\ S_4(H_2O)_9](pts)_4{\cdot}9H_2O$ and $[Mo_2WS_4(H_2O)_9](pts)_4{\cdot}9H_2O$ have been determined.[118] An alternative method to prepare these mixed-metal clusters makes use of selective oxidative degradation of mixed-metal cubes $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{5+}$, where always only one W atom is lost. In this way the tedious column separation of the trinuclear aqua ions is avoided.[119]

4.12.6.1.2 Reactivity of the aqua ions

Water-exchange ligand substitution studies on the $[Mo_3S_4(H_2O)_9]^{4+}$ ion using ^{17}O NMR show that there are two types of kinetically distinct water ligand. Those *trans* to the capping sulfur (designated as c-H_2O), which exchange about 10^5 times more slowly than those *trans* to the bridging sulfur and *cis* to the capping sulfur (d-H_2O) (Figure 25). Explanation was given in terms of activation at the d-H_2O sites via $[Mo_3S_4(H_2O)_8(OH)]^{3+}$, whereas exchange at the c-H_2O is not similarly activated. The K_a value for acid dissociation to $[Mo_3S_4(H_2O)_8(OH)]^{3+}$ was found to be 0.18 M at 25 °C, I = 2.00 M.[120]

The substitution of a single H_2O by NCS^- has been studied for species $[Mo_3O_nQ_{4-n}(H_2O)_9]^{4+}$ (Q = S, Se), and also for $[W_3O_nS_{4-n}(H_2O)_9]^{4+}$ (Tables 1 and 2).[109] Different M = Mo, W

Table 1 Comparisons of forward (k_f) and back (k_b) rate constants (25 °C) for the 1:1 equilibration of NCS^- at d-H_2O (as defined, Figure 25) with $[Mo_3O_nQ_{4-n}(H_2O)_9]^{4+}$ (Q = S, Se) in 2.00 M $HClO_4$. Equilibrium constants K_{eq} (k_f/k_b) are also given.

	Mo—S			*Mo—Se*		
n	k_f ($M^{-1}s^{-1}$)	10^2 k_b(s^{-1})	K_{eq} (M^{-1})	k_f ($M^{-1}s^{-1}$)	10^2 k_b(s^{-1})	K_{eq} (M^{-1})
4	2.13	0.22	970	2.13	0.22	970
3	0.37	0.016	3210	0.19[a]	0.0125[a]	1520[a]
2	Not determined			2.8	0.062	4250
	7.7	0.27	2850	13.5	0.59	2290
1	23	1.4	1640	52	3.0	1730
	82	2.4	3420	131	9.3	1410
0	212	9.2	2300	480	20	2400

[a] 2.00 M Hpts

Table 2 Comparisons of forward (k_f) and back (k_b) rate constants (25 °C) for the 1:1 equilibration of NCS^- at d-H_2O (as defined, Figure 25) with $[W_3O_nS_{4-n}(H_2O)_9]^{4+}$ ions in 2.00 M $HClO_4$. Equilibrium constants K_{eq}(k_f/k_b) are also given.

n	k_f ($M^{-1}s^{-1}$)	10^2 k_b (s^{-1})	K_{eq} (M^{-1})
4	0.110	0.0035	3140
3	0.0080	0.00054	1480
2	0.045	0.006	750
	0.50	0.013	3820
1	0.212	0.041	520
	1.24	0.23	540
0	38.4	2.5	1520

environments give rise to more than one rate constant. From these studies a number of definitive trends have emerged. The replacement of μ_3-O by μ_3-S and then by μ_3-Se on $[Mo_3O_4(H_2O)_9]^{4+}$ results in a retardation in substitution (at d-H_2O), by factors of 6 and 11, respectively. However, replacement of μ-O by μ-S and μ-Se results in labilization, with a factor of 10(S) and 20(Se) for each μ-O replaced.[120] For mixed-metal $[Mo_2WS_4(H_2O)_9]^{4+}$ and $[MoW_2S_4(H_2O)_9]^{4+}$ the first stage is the substitution at Mo.[116] Despite the X-ray crystal structures showing a strong affinity of Mo and W for N-bonded NCS^-, kinetic studies of the reaction of $[W_3S_4(H_2O)_9]^{4+}$ with NCS^- suggest that an S-bonded isomer is formed, which then isomerizes into the more stable N-bonded product.[111] Chloride coordination to $[Mo_3S_4(H_2O)_9]^{4+}$ is weak, and the equilibrium constant for the formation of $[Mo_3S_4(H_2O)_8Cl]^{3+}$ is only 3.0 M^{-1}.[119]

The clusters $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3OS_3(H_2O)_9]^{4+}$ react with acetylene in 1 M HCl with C—S bond formation, giving new clusters with alkenedithiolate ligands, $[Mo_3(\mu_3{-}S)(\mu{-}Q)(\mu S{-}C_2H_2{-}\mu S)(H_2O)_9]^{4+}$ (Q = O, S). The crystal structure of $[Mo_3(\mu_3{-}S)(\mu{-}Q)$ $(\mu S{-}C_2H_2{-}\mu S)(H_2O)_9](pts)_4{\cdot}7H_2O$ indicates considerable changes in the core structure of Mo_3OS_3 except in the $Mo{-}\mu_3{-}S$ distances.[107] Neither $[W_3S_4(H_2O)_9]^{4+}$ nor $[W_3OS_3(H_2O)_9]^{4+}$ react with acetylene but a reaction with $[W_3OS_3(NCS)_9]^{5-}$ is observed.[121]

4.12.6.1.3 Complexes with halides (Cl^-)

No $[M_3Q_4Cl_9]^{5-}$ species has been detected or isolated (S = Se, S) even from conc. HCl. In 1–3 M HCl, some Cl^- coordination takes place to $[M_3Q_4(H_2O)_6Cl_3]^+$. Using cucurbituril (Cuc, $C_{36}H_{36}N_{24}O_{12}$) as a second coordination sphere ligand to promote crystallization through formation of complementary hydrogen bonds between carbonyl groups of Cuc and the water molecules in d-positions of the clusters, it was possible to isolate and determine the crystal structures of the following: (i) monosubstituted $\{[W_3S_4(H_2O)_8Cl](pyH \subset Cuc)\}Cl_4{\cdot}15.5H_2O$ and $\{[W_3Se_4(H_2O)_8Cl]_2(Cuc)\}Cl_6{\cdot}12H_2O$; (ii) disubstituted $\{[W_3S_4(H_2O)_7Cl_2](Cuc)\}$ $Cl_4{\cdot}10H_2O$;

(iii) trisubstituted $\{[Mo_3S_4(H_2O)_6Cl_3]\ [Mo_3S_4(H_2O)_7Cl_2](pyH \subset Cuc)\}Cl_4 \cdot 17H_2O$ and $\{[W_3S_4(H_2O)_6Cl_3]_2(pyH \subset Cuc)\}Cl_3 \cdot 18H_2O$. The barrel-shaped cucurbituril molecule is effectively closed by one or two cluster "lids"; in some cases a small molecule (pyH^+) can be included and retained inside the cucurbituril inner cavity. The chloride substitution is always at the *c*-positions, and *d*-H_2O ligands are retained and used for complementary hydrogen bonding.[122–125] No complexes with other halides (F^-, Br^-, I^-) have been reported.

4.12.6.1.4 Complexes with O- and N-donors

Formato complexes $K_4[Mo_3S_4(HCO_2)_8(H_2O)]$ and $K_6[W_3S_4(HCO_2)_9](HCO_2) \cdot 3H_2O$ were obtained by elution of $[M_3S_4(H_2O)_9]^{4+}$ absorbed on a Dowex-cation column with 5 M $KHCO_2$ in 5 M formic acid, and precipitation with alcohol. The crystal structure of $K_6[W_3S_4(HCO_2)_9](HCO_2) \cdot 2.27H_2O \cdot 0.73CH_3OH$ shows that all the formato ligands are monodentate, (W–O 2.138 Å). The formato ligands are weakly bound and in, e.g., aqueous CF_3SO_3H the clusters $[M_3S_4(H_2O)_9]^{4+}$ readily reform.[126]

Oxalate complexes $[M_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$ have been prepared and structurally characterized as $Cs_2[Mo_3S_4(C_2O_4)_3(H_2O)_3] \cdot 3H_2O$[97] and $(4,4'\text{-bipyH}_2)[W_3S_4(C_2O_4)_3(H_2O)_3] \cdot 5H_2O$[127] by direct addition of oxalic acid to aqueous solutions of the corresponding aqua ions, followed by the respective cations. The reaction of $(NH_4)_2[Mo_3S_{13}]$ with oxalic acid in DMF also gives the oxalato complex.[128] Interestingly, attempts to isolate an oxalato complex of the $[Mo_4S_4(H_2O)_{12}]^{5+}$ cube by adding oxalic acid and CsCl produces only crystals of $Cs_2[Mo_3S_4(C_2O_4)_3(H_2O)_3] \cdot 3H_2O$.[97] In all these oxalato complexes the water ligands are trans to the capping (μ_3) sulfur atoms, while the oxygen atoms of oxalates are trans to μ_2–S.

Acetylacetonato complexes such as $[M_3Q_4(acac)_3(py)_3]PF_6$ are known for all M = Mo, W and Q = S, Se. They are prepared by treating the aqua ions (in HCl) with Hacac, followed by neutralization with $NaHCO_3$, addition of pyridine and NH_4PF_6. X-ray structures have been solved for all cases except the Mo_3Se_4 derivative. In these isostructural compounds py is *trans* to the μ_3–S. In the FAB–MS the peaks of $[M_3Q_4(acac)_3(py)_3]^+$ are observed with subsequent stepwise loss of the py molecules. ^1H NMR indicates the conservation in solution of the molecular structure found in the solid state. CV studies show two quasi-reversible reduction steps attributed to stepwise metal reduction: $M_3^{IV} \rightarrow M_2^{IV}M^{III} \rightarrow M^{IV}M_2^{III}$ with the ease of reduction diminishing in the range $Mo_3S_4 > Mo_3Se_4 > W_3Se_4 > W_3S_4$.[129] The complex $[W_3S_4(acac)_3(NH_3)_3]Cl$ has also been prepared and its FAB–MS recorded.[130]

In an acidic medium (pH = 1.8) $[Mo_3S_4(H_2O)_9]^{4+}$ reacts with monovacant lacunary anions $[SiW_{11}O_{39}]^{8-}$ and $[P_2W_{17}O_{61}]^{10-}$ to yield nanosized cluster species $[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{–}OH)\}_2]^{10-}$ and $[\{(P_2W_{17}O_{61})Mo_3S_4(H_2O)_3(\mu\text{–}OH)\}_2]^{14-}$, isolated as $Me_2NH_2^+$ salts in high yields and structurally characterized (Figure 26). The central core is built up by two $Mo_3S_4(H_2O)_3^{4+}$ fragments, connected through 2 OH^- (*cis* to μ_3–S). These large clusters are stable in solutions at pH between 1 and 7, quantitatively converting into $[Mo_3S_4(H_2O)_9]^{4+}$ in more acidic media.[149]

Complexes of iminodiacetate (ida^{2-}), are also known. A crystalline sample $Ca[Mo_3S_4(ida)_3] \cdot 11.5H_2O$ was prepared from the aqua ion and H_2ida, followed by addition of $CaCl_2$. The X-ray structure shows that the nitrogen atoms of the three ida groups are trans to μ_3–S. Cyclic

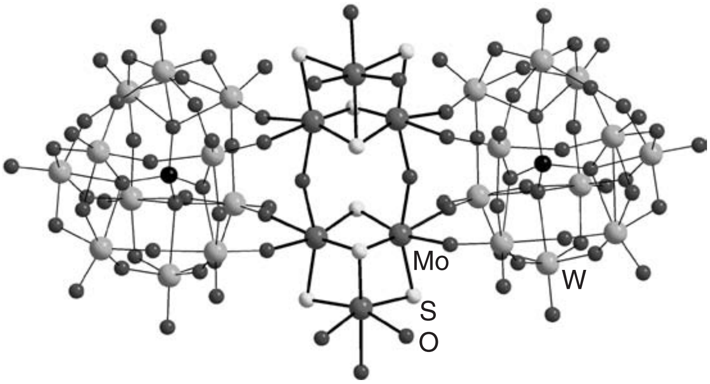


Figure 26 Structure of the $[\{(SiW_{11}O_{39})Mo_3S_4(H_2O)_3(\mu\text{–}OH)\}_2]^{10-}$ anion.

voltammetry experiments show two reversible one-electron reduction waves and another ill-defined process.[99] Later this reaction was re-examined and using ion-exchange chromatography followed by crystallization of Ca salts, four isomers were isolated. The first one, now reformulated as $Ca[Mo_3S_4(ida)_3]\cdot12H_2O$ (isomer 1) was found to be identical with that reported in the earlier work. The second, $Ca[Mo_3S_4(ida)_3]\cdot21H_2O$ (isomer 2) is a *trans*, *trans*, *cis*-isomer with respect of the mutual positions of capping sulfur and nitrogen. The structure of isomer 3, $Ca[Mo_3S_4(ida)_3]\cdot10H_2O$ has not been established, and isomer 4, $Ca[Mo_3S_4 (ida)_3]\cdot14H_2O$ was found to be the *cis*, *cis*, *cis* form. Analysis by HPLC reveal that *cis* → *trans* isomerization of the ida ligands occurs one by one, and that at equilibrium 1(18%), 2(68%), and 3(14%) are present, but not 4.[131] The core $Mo_3O_3S^{4+}$ coordinates ida to give dark-red products $Ca[Mo_3O_3S(ida)_3]\cdot7H_2O$ and $Na_2[Mo_3O_3S(ida)_3]\cdot3H_2O$. Cyclic voltammetry of $[Mo_3O_3S(ida)_3]^{2-}$ at a hanging drop electrode shows three quasi-reversible waves.[132] The complex $Ba[Mo_3OS_3(ida)_3]\cdot7H_2O$ has also been reported.[133]

Nitrilotriacetates can be prepared by addition of H_3nta to the aqua ions, followed by careful adjustment of the pH with NaOH or KOH. In this way, crystalline $K_2[Mo_3S_4(Hnta)_3]\cdot9H_2O$,[102] $Na_2[Mo_3S_4(Hnta)_3]\cdot5H_2O$,[102,134] $Ca_{1.5}[Mo_3S_4(Hnta)_2(nta)]\cdot12H_2O$,[135] $Na_2[W_3S_4(Hnta)_3]\cdot5H_2O$,[102] as well as mixed-metal $Na_2[Mo_2WS_4(Hnta)_3]\cdot5H_2O$[118] and $Na_2[MoW_2S_4(Hnta)_3]\cdot5H_2O$[118] have been prepared. All of these clusters have been structurally characterized except the K^+ salt. Similarly, $Mo_3O_3S^{4+}$ derivatives $Na_2[Mo_3O_3S(Hnta)_3]\cdot10H_2O$ and $Ba[Mo_3O_3S(Hnta)_3]\cdot10H_2O$ are prepared.[132] The coordination mode of the $Hnta^{2-}$ ligand in all structurally investigated cases is tridentate with one COOH group remaining free. The nitrogen atoms are invariably *trans* to the capping sulfur. Preparation and X-ray structures of complexes of mixed O/S tungsten clusters with $Hnta^{2-}$ have also been reported as $K_2[W_3O_3S(Hnta)_3]\cdot9H_2O$,[136] $Ba[W_3O_2S_2(Hnta)_3]\cdot9H_2O$[137] and $K_2[W_3OS_3(Hnta)_3]\cdot KCl\cdot7H_2O$ (Figure 27).[138] In the case of Mo/W mixed-metal clusters the metals are randomly disordered in the crystalline state. Cyclic voltammetry on $[Mo_nW_{3-n}S_4(Hnta)_3]^{2-} (n = 0–3)$ shows three consecutive one-electron steps corresponding to changes from M_3^{IV} to M_3^{III}. The clusters are more readily reduced with increasing number of Mo atoms.[118] The reaction of $(NH_4)_2[Mo_3S_{13}]$ with H_3nta in DMF under reflux gave $(NH_4)_3[Mo_3S_4(Hnta)_2(nta)]$ EtOH.[128] Aquation of $[Mo_3S_4(Hnta)_3]^{2-}$ in 2 M HCl (8 h) gives a clear green solution of $[Mo_3S_4(H_2O)_9]^{4+}$.[128]

Complexes of $W_3S_4{}^{4+}$ and $W_3O_3S^{4+}$ with a number of polyaminopolycarboxylate ligands have been prepared, and evaluated as potential water-soluble X-ray contrast agents. Reaction of $[W_3S_4(H_2O)_9]Cl_4$ with ethyleneglycol-bis(2-aminoethyl)tetraacetic acid (H_4egta) in DMF gives a number of products, of which a purple $Na_4[(W_3S_4)_2(egta)_3]\cdot16H_2O$ was crystallized in a 25–40% yields after size-exclusion chromatography. For each egta ligand, an iminodiacetate (ida) component coordinates a W atom of one cluster unit, while another ida coordinates a W in the second cluster unit. Each ida coordinates in the usual tripodal fashion so that its nitrogen is trans to μ_3–S.[139] Red $Na_4[(W_3OS)_2(egta)_3]\cdot10H_2O$ was obtained from the aqua complex and egta ligand in DMF in a 14% yield.[140] Under similar conditions triethylentetraminehexaacetic acid, H_6ttha, gives at least three well-defined species: $[W_3S_4(ttha)]^{2-}$, $[(W_3S_4)_2(ttha)_2]^{4-}$, and $[(W_3S_4)_2(ttha)_3]^{10-}$. It was possible to isolate solid $Na_2[W_3S_4(ttha)]$ in a 17% yield. It has been supposed that the $ttha^{6-}$ would be nano-coordinated in this complex, with one free carboxylate group. However, single crystals from aqueous solutions gave $Na_3H [(W_3S_4)_2(ttha)_2]\cdot16H_2O$, the structure of which shows a decadentate ttha, coordinating one cluster in a hexadentate fashion and the other in a tetradentate fashion.[141]

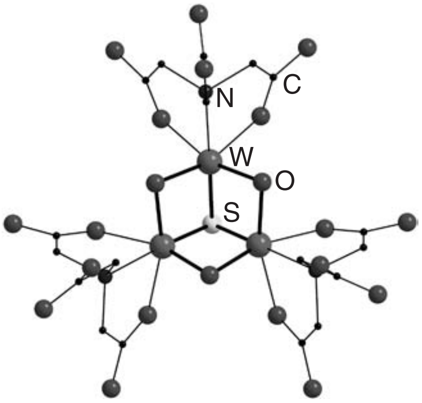


Figure 27 Structure of the $[W_3SO_3(Hnta)_3]^{2-}$ anion.

The $W_3O_3S^{4+}$ core coordinates a number of long-chained polyaminopoly carboxylates, leading to stable products consisting of two cluster units bonded to three deprotonated ligands. In all cases, solid products could be obtained. Thus, with oxybis (ethylamine)tetraacetic acid (H_4obeta) $Na_4[(W_3O_3S)_2(obeta)_3]\cdot 10H_2O$ (35% yield) was obtained, while 1,4-butylendiaminetetraacetic acid (H_4bdta) gave $Na_4[(W_3O_3S)_2(bdta)_3]\cdot 12H_2O$. With 1,3-propylendiaminetetraacetic acid (H_4pdta) and its 2-methoxy (H_4MeO-pdta), 2-carboxymethyl (H_5CM-pdta) and 2-hydroxy (H_4HO-pdta) derivatives gave $Na_4[(W_3O_3S)_2(pdta)_3]\cdot 11H_2O$ (46% yield), $Na_4[(W_3O_3S)_2(HO\text{-}pdta)_3]\cdot 6H_2O$, $Na_4[(W_3O_3S)_2(MeO\text{-}pdta)_3]\cdot 7H_2O$ (53% yield) and $Na_7[(W_3O_3S)_2(CM\text{-}pdta)_3]\cdot 7H_2O$ (18% yield). X-ray crystal structures were determined for $(PPh_4)_4[(W_3O_3S)_2(pdta)_3]\cdot 39H_2O$ and for $(PPh_4)_4[(W_3O_3S)_2(HO\text{-}pdta)_3]\cdot 27.5H_2O$. In both these salts two cluster units are linked by three ligands with local coordination of W atoms by three ida subunits similar to that discussed earlier for the ida complexes.[140]

Coordination of $Mo_3S_4{}^{4+}$ to 1,3,5-triamino-1,3,5-trideoxy-cis-inositol (taci) and with its methylated derivative 1,3,5-tris(dimethyamino)-1,3,5-trideoxy-cis-inositol (tdci) has been studied. The $Mo_3S_4{}^{4+}$ core was generated *in situ* from $(Et_4N)_2[Mo_3S_7Br_6]$ and PPh_3 in ethanol. A 1:3 complex forms, and for $[Mo_3S_4(taci)_3]^{4+}$ it was shown that in aqueous solution isomerization occurs, supported by conformational changes in the ligand to give isomers with N,N,N; N,N,O and N,O,O bonding modes of the ligand. The bonding mode O,O,O was not observed. Attempts to grow single crystals from a water–acetone mixture led to a formation of a Schiff-base from the attack of acetone on one of the amino groups, giving a new ligand 1,3-diamino-5-(isopropylidenamino)-1,3,5-trideoxy-cis-inositol(L). Finally, a complex of composition $Mo_3S_4(L\text{-}4H)_4\cdot 20H_2O$ was obtained and its crystal structure determined. This showed an N,N,O coordination mode of the partially deprotonated ligand (Figure 28). With tdci, green $[Mo_3S_4(tdci)_4]\,Br_4\cdot 9.5EtOH\cdot 5H_2O$ was prepared. The ligand coordinates through two deprotonated hydroxo and one NMe_2 groups to each metal, while the other two uncoordinated dimethylamino groups are protonated.[142]

A tacn complex of composition $[Mo_3S_4(tacn)_3](ZnCl_4)(ZnCl_3OH_2)_2\cdot 3H_2O$ was prepared as blue–green crystals in a 60% yield from the cube $[Mo_4S_4(H_2O)_{12}]^{5+}$, with amine in excess, followed by adjustment to $pH = 2$ and addition of $ZnCl_2$. Its crystal structure was determined.[143] The open-chain tridentate amine dien reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_3OS_3(H_2O)_9]^{4+}$ in HCl to give $[Mo_3S_4(dien^-)(dien)_2]Cl_3\cdot 4H_2O$ and $[Mo_3OS_3(dien^-)(dien)_2]\,Cl_3\cdot 3H_2O$ respectively, where each cluster has one deprotonated dien. An X-ray crystal structure of the latter shows that the Mo—N(amido) bonds are much shorter than the Mo—N(amino) bonds, 1.99 Å vs. 2.23–2.28 Å. In D_2O solutions NMR indicates that the deprotonated amine receives a D^+ from D_2O.[144]

Reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ and $KBHpz_3$ leads to a partial hydrolysis of both the ligand and the cluster to give $[\{(HBpz_3)_2Mo_3S_4\}_2(\mu\text{-}O)(\mu\text{-}pz)_2]$, where two cluster units are bridged by a triple bridge of one oxide and two deprotonated pyrazolates (Figure 29).[145]

Pyridine (py) complexes are also known. Thus, polymeric $\{Mo_3S_7Cl_4\}_x$ reacts slowly under reflux with PPh_3 in py to give green $[Mo_3S_4(py)_5Cl_4]$ in a 33% yield.[146] Treatment of this cluster with I_2 gives $[Mo_3S_4(py)_6Cl_3]I\cdot 0.5py$. Crystal structures have been determined.[146,147]

Thiocyanate complexes are easily obtained from the aqua ions and NCS^-, which coordinate exclusively through the nitrogen. The following compounds have been prepared and structurally characterized: $(pyH)_5[Mo_3S_2O_2(NCS)_9]\cdot 2H_2O$,[148] $(bpy)_5[W_3S_4(NCS)_9]\cdot 3H_2O$,[102] $(Me_3NH)_5[W_3Se_4(NCS)_9]$,[115]

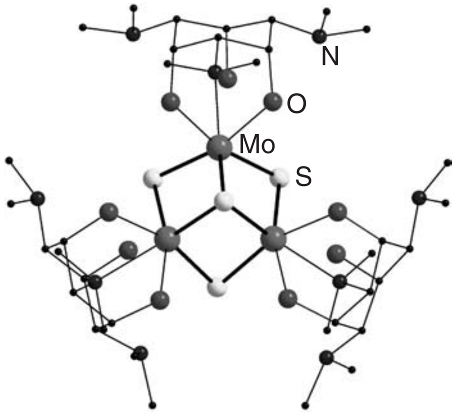


Figure 28 Structure of the $[Mo_3S_4(L\text{-}4H)_4]$ (L = 1,3-diamino-5-(isopropylidenamino)-1,3,5-trideoxy-cis-inositol) molecule.

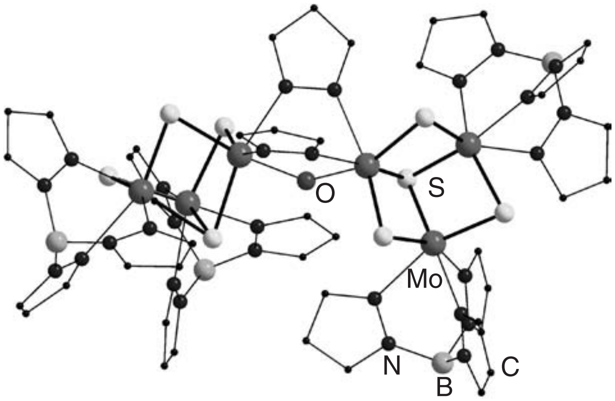


Figure 29 Structure of the $[\{(HBpz_3)_2Mo_3S_4\}_2(\mu-O)(\mu-pz)_2]$ molecule.

$(Me_4N)_5[Mo_3Se_4(NCS)_9]$.[108,109] Isolation of $(Me_4N)_5[Mo_3S_4(NCS)_9]$ was briefly mentioned.[98] Heating of polymeric $\{W_3S_7Br_4\}_x$ in a KNCS melt gives green $[W_3S_4(NCS)_9]^{5-}$ in high yield. From this reaction, Cs^+ and Et_4N^+ salts were obtained. The complex $[W_3S_4(NCS)_9]^{5-}$ also forms from $[W_3S_7Br_6]^{2-}$ and NCS^- under reflux in CH_3CN solutions.[114] Heating $\{W_3Se_7Br_4\}_x$ with KNCS leads to stepwise S for Se substitution giving initially a mixture of all possible $[W_3S_nSe_{4-n}(NCS)_9]^{5-}$ forms, finally converting into $[W_3S_4(NCS)_9]^{5-}$ in high yield.[150]

Green $[W_3OS_3(NCS)_9]^{5-}$ reacts with acetylene in 1 M HCl (in the presence of excess NCS^-) with the formation of μ_2-vinylsulfido complex, $[W(\mu_3-S)(\mu-O)(\mu-S)(\mu-SCHCH_2)(NCS)_9]^{5-}$, isolated and structurally characterized as a mixed K^+/pyH$^+$ salt.[122]

4.12.6.1.5 *Sulfur-containing ligands*

Reaction of $(NH_4)_2[Mo_3S_{13}]$ and excess (>9 equivalent) Na_2edt with Et_4NBr in CH_3CN at room temperature gives a deep-violet solution, from which violet–black, moderately air-stable crystals of $(Et_4N)_2[Mo_3S_4(edt)_3]$ can be isolated, 50% yield. This compound features a five-coordinated Mo with Mo—Mo bonds 2.78 Å. Treatment of the product with sulfur gives red $(Et_4N)_2[Mo_3S_7(edt)_3]$, which again regenerates the starting material with CN^- and PPh_3.[151]

Another compound with an M_3S_7 core, polymeric $\{W_3S_7Br_4\}_x$, reacts slowly with $(NH_4)_2S_x$ at room temperature, giving black needles of $(NH_4)_2[W_3S_4(S_4)_3(NH_3)_3]\cdot H_2O$. The tetrasulfido ligand is coordinated in a bidentate fashion, and a rather long (2.5 Å) W–S distance explains the easy reaction with conc. HCl to give $[W_3S_4(H_2O)_9]^{4+}$ in high yield.[114,152]

There exists an extensive series of dithiophosphato ester complexes (dtp, $(EtO)_2PS_2$) of the cuboidal clusters, especially of the $Mo_3S_4{}^{4+}$ core. Treatment of $MoCl_3\cdot 3H_2O$ with $(EtO)_2PS_2H$ in ethanol gives $[Mo_3S_4(dtp)_3(\mu-dtp)(H_2O)]$, which is a valuable starting material.[153] Its W analog has also been prepared.[154] The water ligand is only weakly bound and undergoes an easy substitution with other bidentate ligands oxazole,[156] bpy,[157] imidazole,[158] $PhCH_2CN$,[159] $PhCH_2SH$,[160] PPh_3,[160] thiourea,[161] allyl-thiourea[160] to give corresponding $[Mo_3S_4(dtp)_4L]$, all of which have been structurally characterized. The unique bridging dtp is also liable to substitution by other bidentate ligands, such as formate,[162] acetate,[162] propionate,[163] salicylate,[164] phthalate,[164] and nitro-benzoate.[187] The structures of $[Mo_3S_4(dtp)_3(RCO_2)(py)]$ (R = H,[162] CH_3,[161] C_2H_5[163]) and of $[Mo_3S_4(dtp)_3(O\text{-}HOC_6H_4CO_2)(py)]$[164] have been determined, as well as of $[W_3S_4(dtp)_3(CH_3CO_2)(py)]$[165] and $[Mo_3Se_4(dtp)_3(CH_3CO_2)(py)]$.[166] The structure of the *O*-nitrobenzoate complex is shown in (Figure 30). Even weakly nucleophilic *P*-toluene-sulfonate $CH_3C_6H_4SO_3{}^-$ is capable of acting as the bridging ligand in $[Mo_3S_4(dtp)_3(\mu\text{-pts})(py)]$.[167] Substitution of more then one dtp is also possible. The structures of $[Mo_3(\mu_3-O)(\mu-S)_3(dtp)_2(\mu-RCO_2)_2(py)]$ (R = CH_3, C_6H_5) show that the two carboxylates are bridging while the dtp ligands form bidentate chelates.[168] Monodentate imidazole (Im) appears to be a rather efficient ligand to compete with dtp in the structure of $[Mo_3S_4(dtp)_3(Im)_3](dtp)$, where each of the three imidazole ligands is coordinated to one Mo, leaving one dtp uncoordinated to act as a counterion.[169] Treatment of $[Mo_3S_4(dtp)_3(\mu-dtp)(H_2O)]$ with Fe^{III} perchlorate and oxazole led to a partial hydrolysis of the bridging ligand, and a monothiophosphato bridged complex $[Mo_3S_4(dtp)_3(\mu-SOP\ (OEt)_2)(oxazole)]$ was obtained.[170] Reaction of the hydrate $MoCl_3\cdot 3H_2O$

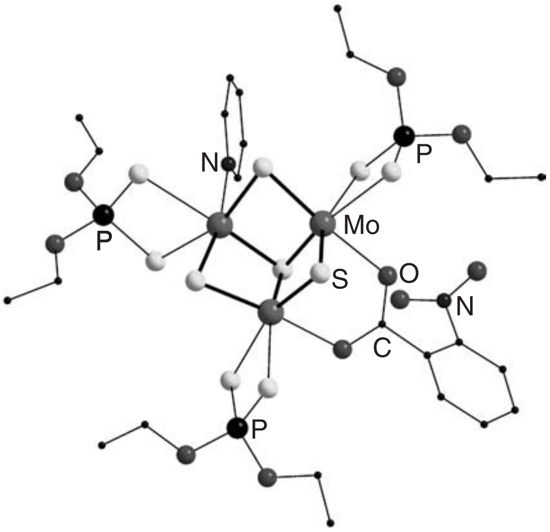


Figure 30 Structure of the $[Mo_3S_4(dtp)_3(o\text{-}O_2NC_6H_4CO_2)(py)]$ molecule.

with $(EtO)_2PS_2H$ in ethanol in the presence of oxazole gave also $[Mo_3OS_3(dtp)_4(oxazole)]$.[156] The cluster $[Mo_3(\mu_3-S)(\mu-Se)_3(dtp)_3(\mu-dtp)(py)]$, which represents a very rare type of incomplete cuboidal cluster with two different chalcogen atoms in the core, is also known.[171]

The complexes $[Mo_3S_4(dtp)_4(CH_3CN)]$ and $[Mo_3OS_3(dtp)_4(CH_3CN)]$ can be made in 80% yield by reacting the corresponding aqua ions with $(EtO)_2PS_2H$ followed by recrystallization from CH_3CN. Black crystals of $[Mo_3OS_3(dtp)_4(H_2O)]$ can be detected before treatment with acetonitrile. Similarly, $[Mo_3O_3S(dtp)_4(H_2O)]$ was obtained (44% yield). Green $[Mo_3O_2S_2(dtp)_4(py)]$ is prepared by treating the aqua ion with $(EtO)_2PS_2H$, followed by recrystallization from CH_3CN in the presence of small amounts of pyridine. Refluxing $[Mo_3OS_3(dtp)_4(CH_3CN)]$ in ethanol with acetic anhydride and pyridine gave crystals of $[Mo_3OS_3(dtp)_2(OAc)(py)_2(OEt)]$. This has a structure with both dtp ligands chelated to a single metal and acetate bridging the $Mo(\mu-O)Mo$ edge. From ^{31}P NMR studies on the $[Mo_3O_nS_{4-n}(dtp)_4(L)]$ ($n = 0$–3) the monodentate ligand is very labile and can easily be exchanged with the bulk solvent used for the NMR studies with the result that the dtp at the same Mo fluctuates around the coordination site.[172]

The reaction between $MoCl_3\cdot 3H_2O$, P_4S_{10} and H_2S in ethanol under less acidic conditions than used for preparation of $[Mo_3S_4(dtp)_3(\mu\text{–}dtp)(H_2O)]$ gives $[Mo_3OS_3(dtp)_3(\mu\text{–}dtp)(H_2O)]$. In this case the cluster core is $[Mo(\mu_3-O)(\mu-S)_3]^{4+}$, which can be regarded as isomeric with the more common $[Mo(\mu_3-S)(\mu-O)(\mu-S)_2]^{4+}$. Alternatively, $[Mo_3OS_3(dtp)_3(\mu\text{–}dtp)(H_2O)]$ is obtained when $[Mo_3S_4(dtp)_3(\mu\text{–}dtp)(H_2O)]$ is refluxed in acidic solutions for a long time. Crystal structures have been determined for some mixed-ligand derivatives of the $Mo(\mu_3-O)(\mu-S)_3{}^{4+}$ core. These are for $[Mo_3OS_3(\mu\text{–}OAc)_2(dtp)_2(py)]$, $[Mo_3OS_3(\mu\text{–}OAc)(\mu\text{–}dtp)_3(py)]$, and $[Mo_3OS_3(dtp)_3(py)_3](CdI(dtp))_2$.[173–176]

Dithiophosphinates (R_2PS_2) and dithiocarbamates (R_2NCS_2) have been less extensively studied. The reaction of sulfur-rich $[Mo_3S_7(Et_2PS_2)_3](Et_2PS_2)$ with PPh_3 leads to sulfur abstraction with $[Mo_3S_4(Et_2PS_2)_3(\mu\text{–}Et_2PS_2)]$ as the product.[177] The cluster $[Mo_3S_4(Et_2PS_2)_3(py)_3](ZnI_3py)$ is also known (Figure 31).[178] Analogously, $[Mo_3Se_7(Et_2NCS_2)_3]$ (Et_2NCS_2) reacts with PPh_3 to give $[Mo_3Se_4(Et_2NCS_2)_4(PPh_3)]$.[180] Crystal structures of $[Mo_3S_4(dtc)_3(\mu\text{–}dtc)(py)]\cdot 2py\cdot H_2O$ and of $[Mo_3S_4(dtc)_3(\mu\text{–}dtc)(DMF)$ (dtc is Et_2NCS_2)] demonstrate much similarity in the coordination behavior of the dtp and dtc ligands.[155]

The reaction of $[Mo_3Te_7((^iPrO)_2PS_2)_3]I$ with Bu_3P in the presence of benzoate or *o*-aminobenzoate gave the first Mo_3Te_4 cluster, which was isolated and structurally characterized as $[Mo_3Te_4((^iPrO)_2PS_2)_3(\mu\text{–}RC_6H_4CO_2)(PBu_3)]$ (Figure 32).[180]

4.12.6.1.6 Complexes with phosphines

Polymeric forms $\{M_3Q_7X_4\}_x$ (M = Mo, W; Q = S, Se; X = Cl, Br) react with mono and bidentate phosphines to give phosphine complexes with the $M_3Q_4{}^{4+}$ cores. In the case of $\{Mo_3S_7Cl_4\}_x$ with

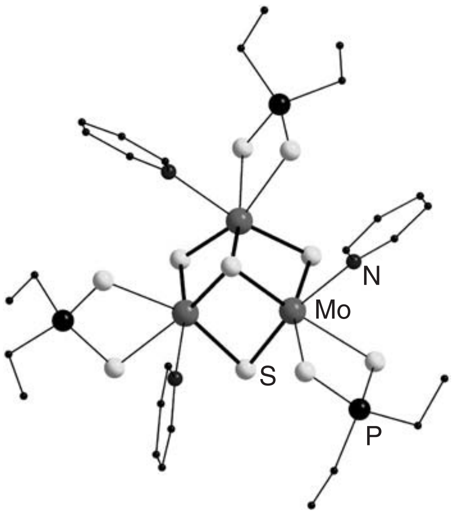


Figure 31 Structure of the $[Mo_3S_4(Et_2PS_2)_3(py)_3]^+$ cation.

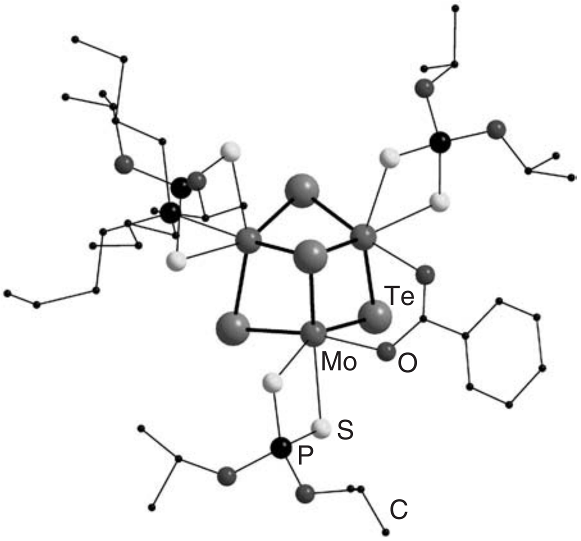


Figure 32 Structure of the $[Mo_3Te_4((^iPrO)_2PS_2)_3(\mu\text{—}C_6H_5CO_2)(PBu_3)]$ molecule.

PEt_3 in MeOH at ~20 °C two products are obtained: $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$ (Figure 33) in a 24% yield, and $[Mo_3S_4Cl_4(PEt_3)_4(MeOH)]$ in a 46% yield,[181] while slow reactions of $\{M_3S_7Br_4\}_x$ (M = Mo, W) with PEt_3 in THF at room temperature led to a partial P—C bond scission and phosphine oxidation, giving $[M_3S_4Br_4(PEt_3)_3(OEt_2PH)(H_2O)]$ as products (M = Mo, 32%; M = W, 20%).[182] Reaction of $Mo_3S_7Cl_4$ with PPh_3 in THF (48 h) produces dark-green crystals of $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]\cdot 3THF$ (Figure 34), 35% yield.[183] The structure of the W analog $[W_3S_4Cl_4(PPh_3)_3(H_2O)_2]\cdot 2THF$ has also been structurally characterized.[184] The compounds $(Et_4N)_2[Mo_3S_7X_6]$ (X = Cl, Br) react with PPh_3 in CH_3OH much faster than $\{Mo_3S_7X_4\}_x$ to give $[Mo_3S_4Cl_4(PPh_3)_3]$ in good yields.[185]

Bidentate phosphines (dmpe, dppe) react with polymeric $\{M_3S_7X_4\}_x$(M = Mo, W; X = Cl, Br) in different solvents to give $[M_3S_4X_3(dmpe)_3]^+$ and $[M_3S_4X_3(dppe)_3]^+$. When this reaction is carried out in a halogenated solvent, halogen exchange occurs: Thus, from $\{W_3S_7Br_4\}_x$ in CH_2Cl_2, the formation of $[W_3S_4Br_2Cl(dmpe)_3]^+$ and $[W_3S_4BrCl_2(dmpe)_3]^+$ has been observed, together with the expected product $[W_3S_4Br_3(dmpe)_3]^+$. It seems from these studies that dmpe is more reactive than dppe (as expected), $\{Mo_3S_7Cl_4\}_x$ is more reactive than the corresponding bromide, and halogenated solvents are more efficient than THF or acetonitrile. Crystal structures of $[Mo_3S_4Cl_3(dppe)_3]Cl$ and $[Mo_3S_4Cl_{2.25}Br_{0.75}(dppe)_3](BF_4)_{0.5}Cl_{0.5}$ have been determined. Other

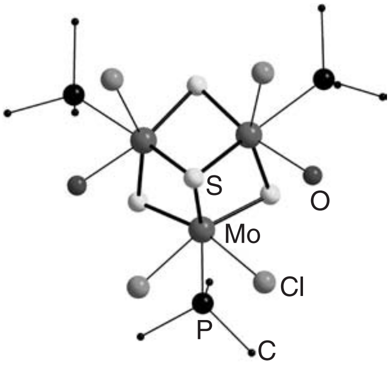


Figure 33 Structure of the $[Mo_3S_4Cl_4(PEt_3)_3(MeOH)_2]$ molecule. Only C atoms bonded to P and O of methanols are shown.

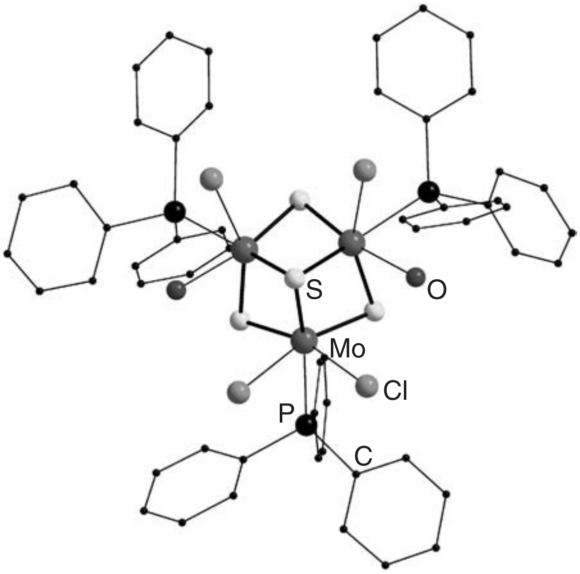


Figure 34 Structure of the $[Mo_3S_4Cl_4(PPh_3)_3(H_2O)_2]$ molecule.

products isolated from these reactions and characterized by ^{31}P NMR and FAB–MS are $[M_3S_4X_3(dmpe)_3]PF_6$ (M = Mo, W; X = Cl, Br), $[Mo_3S_4X_3(dppe)_3]PF_6$ (X = Cl, Br) and $[W_3S_4Br_3(dppe)_3]X$ (X = Br, PF_6).[183,186] Similarly, from $\{Mo_3Se_7Cl_4\}_x$, brown $[Mo_3Se_4Cl_3(dppe)_3]Cl$ was obtained,[179] and from $\{W_3Se_7Br_4\}_x$, green products $[W_3Se_4Br_3(dppe)_3]X$ (X = Br, ReO_4, PF_6, BF_4, BPh_4) were obtained, 50–70% yields.[130] The cluster $[W_3S_xSe_{4-x}(NCS)_9]^{5-}$ undergoes ligand substitution with dppe to give $[W_3S_xSe_{4-x}(dppe)_3(NCS)_3]^+$, the formation of which was studied by FAB–MS.[150] The cluster $(Et_4N)_2[Mo_3S_7X_6]$ reacts rapidly with dppe in CH_3OH with the formation of $[Mo_3S_4X_3(dppe)_3]X$ (X = Cl, Br) in high yields.[185]

Cluster core self-assembly gives an alternative route to access the incomplete cuboidal cluster complexes with bidentate phosphines. Thus, $[MoCl_3(THF)_3]$ with NaSH in THF, followed by addition of dmpe, gives on silica gel column purification (and addition of NH_4PF_6 in methanol) the green compound $[Mo_3S_4Cl_3(dmpe)_3]PF_6$ in 40% yield.[188] Both WCl_4 and WBr_5 can serve as starting compounds in the reaction with NaSH and a phosphine, but WBr_5 requires an extra reducing agent such as $NaBH_4$ or $NaBEt_3H$. With WCl_4, $[W_3S_4Cl_3(dmpe)_3]PF_6$ (20%) and $[W_3S_4Cl_3(depe)_3]PF_6$ (15%) were obtained. In the case of WBr_5 the products $[W_3S_4Br_3(phosphine)_3]X$ (phosphine = dmpe, depe; X = Br, PF_6), have been structurally characterized.[189–192] All the complexes $[M_3Q_4X_3(diphosphine)_3]^+$ have diphosphine ligands with one P atom trans to the capping μ_3–Q, and the other trans to the bridging μ_2–Q, thus giving chiral cations.

Reactions of $[W_3S_4Cl_3(dmpe)_3]BPh_4$ with $LiBH_4$, or of $[W_3S_4Br_3(dppe)_3]PF_6$ with $NaBH_4$, give the corresponding hydrido complexes $[W_3S_4H_3(dmpe)_3]BPh_4$[190] and $[W_3S_4H_3(dppe)_3]PF_6$.[186] The latter hydride is a pink air-stable solid with ^1H NMR signal at 0.97 ppm.

It is possible to reduce the core $Mo_3S_4^{4+}$ to $Mo_3S_4^{3+}$ in a phosphine complex. Thus, on treating $\{Mo_3S_7Cl_4\}_x$ with PEt_3, reducing with Mg at −20 °C, and addition of dppe, paramagnetic $[Mo_3S_4Cl_3(dppe)_2(PEt_3)]$ is obtained. The Mo—Mo bonds (2.806 Å) are longer than in analogous complexes of $Mo_3S_4^{4+}$ with phosphines.[193]

4.12.6.1.7 Cyanide and η^5-cyclopentadienyl complexes

Cyanide has a high affinity for the M_3Q_4 core, and $[M_3Q_4(CN)_9]^{5-}$ complexes are very stable. The cluster $(NH_4)_2[Mo_3S_{13}]$ reacts with KCN (with the formation of SCN^-), giving green $[Mo_3S_4(CN)_9]^{5-}$, which can be isolated as the double salt $K_5[Mo_3S_4(CN)_9]\cdot 3KCN\cdot 4H_2O$ (70% yield).[194] The same product is obtained from MoS_3 and KCN.[195] The product $K_5[Mo_3S_4(CN)_9]\cdot 7H_2O$ has also been identified.[196]

The cyano complexes of the incomplete cubes $[Mo_3Se_4(CN)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$ have been prepared by reacting polymeric $\{M_3Se_7Br_4\}_x$ with KCN in hot aqueous solution. The products have been isolated as isostructural double salts $Cs_5[M_3Se_4(CN)_9]\cdot CsCl\cdot 4H_2O$. Reduction potentials for $[M_3Se_4(CN)_9]^{5-}$ associated with reduction to the $M^{III}M_2^{IV}$ state are −0.63 V (Mo) and −0.97 V (W) vs. NHE, indicating that the W derivative is more strongly reducing.[197]

A high yield conversion of $[Mo_3S_4(H_2O)_9](pts)_4$ into $[(\eta^5{-}C_5H_5)_3Mo_3S_4](pts)$ and $[(\eta^5{-}CH_3C_5H_4)_3Mo_3S_4](pts)$ has been reported.[198,199] Cyclopentadienyl derivatives of the reduced core $Mo_3S_4^{3+}$ are also known. The reaction of propylenesulfide with $H[Mo(\eta^5{-}C_5H_5)(CO)_3]$ (1:2 ratio), or with $H[Mo(\eta^5{-}C_5H_5)(CO)_2(P(OPh)_3)]$ (1:1 ratio) in THF at room temperature gives black oxygen-sensitive $[(\eta^5{-}C_5H_5)_3Mo_3S_4]$, which has been characterized spectroscopically. Recently it was reported that reduction of $[(\eta^5{-}C_5Me_5)Mo(S^tBu)_3]$ with Na/Hg gives green, paramagnetic $[(\eta^5{-}C_5Me_5)_3Mo_3S_4]$. Its structure shows elongation of both Mo—S and Mo—Mo bonds, compared to $[(\eta^5{-}C_5H_5)_3Mo_3S_4]$ (Me_3SnCl_2).[200]

4.12.6.2 Chalcogen-rich Clusters with M_3Q_7 Cores

Polymeric forms $\{M_3Q_7X_4\}_x$ (M = Mo, W; Q = S, Se; X = Cl, Br) are prepared by high-temperature reactions (ca. 350 °C) of the elements in a sealed tube. The crystal structures of isostructural $\{Mo_3S_7Cl_4\}_x$ and $\{W_3S_7Br_4\}_x$ have been determined and consist of $M_3(\mu_3{-}S)(\mu{-}S_2)_3^{4+}$ units, bridged by four halide atoms forming an extended zigzag chain.[201,202] This cluster core has the same features, e.g., asymmetrical coordination of the S_2 units, as the Ti and V clusters already described. The metal is in oxidation state IV and thus six electrons are available to form three single metal–metal bonds in the triangle. It is believed that the selenides have similar structures. The polymeric structure can be broken under various conditions (some of them are not found in the traditional inventory of inorganic chemistry due to inertness of the starting polymers) to give discrete anions $[M_3Q_7X_6]^{2-}$. They can in turn be aquated in 4 M Hpts into corresponding aqua ions $[M_3Q_7(H_2O)_6]^{4+}$, which are quite stable in acidic solutions but are yet to be isolated as solids.[110] The cluster $Mo_3Te_{10}I_{10}$, made by heating the elements at 395 °C, contains the Mo_3Te_7 core, three TeI_3^- ligands and one I^- as counter ion, interacting strongly with axial Te atoms from the Te_2 units (Te···I, 3.26–3.35 Å). The new TeI_3^- ligand is coordinated via both Te and one of its I atoms; two other iodine atoms remain free.[203]

Clusters with two different chalcogen atoms (or with oxygen) in the core are known. Thus, clusters with the following cores: $Mo_3(\mu_3{-}O)(\mu{-}S_2)_3^{4+}$,$Mo_3(\mu_3{-}S)(\mu{-}Se_2)_3^{4+}$, $M_3(\mu_3{-}S)(\mu{-}SSe)_3^{4+}$, $M_3(\mu_3{-}Se)(\mu{-}SSe)_3^{4+}$(M = Mo,W), $Mo_3(\mu_3{-}S)(\mu{-}Te_2)_3^{4+}$ and $Mo_3(\mu_3{-}O)(\mu{-}Te_2)_3^{4+}$ have been reported.

4.12.6.2.1 Mo_3S_7 clusters

Air stable, crystalline $[Mo_3S_7X_6]^{2-}$ (X = Cl, Br, I) (Figure 35), can be made either by melting the polymeric $\{Mo_3S_7X_4\}_x$ with PPh_4X (X = Cl, Br) at 300 °C,[204] or mechanochemical reaction with Et_4NBr in a vibration mill.[205] The $\{Mo_3S_7X_4\}_x$ is known to be insoluble in organic solvents and requires drastic conditions for the halide group to be replaced, and the cluster core to be excised. Gamma-radiolysis has also been found to be an efficient way of breaking up the $\{Mo_3S_7Br_4\}_x$ and from the irradiated material $[Mo_3S_7Br_6]^{2-}$ can be extracted into hot conc. HBr in high yield.[206]

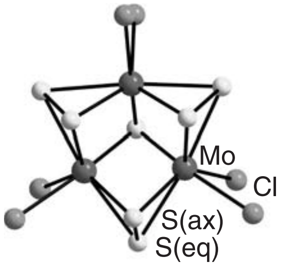


Figure 35 Structure of the $[Mo_3S_7Cl_6]^{2-}$ cation showing equatorial and axial sulfur atoms of the bridging μ–S_2 ligands.

The ionic form are readily accessible, from $(NH_4)_6[Mo_7O_{24}]$ and $(NH_4)_2S_x$ at 90 °C, or $\{Mo_3S_7X_4\}_x$ (X = Cl, Br) and $(NH_4)_2S_x$,[207,208] red $(NH_4)_2[Mo_3S_7(S_2)_3]$ reacts with hot conc. HX acids (X = Cl, Br, I) to give the corresponding $(NH_4)_2[Mo_3S_7X_6]$ salts,[185,210] and the chloride and bromide (but not the iodide) are also obtainable by treatment of $(NH_4)_2[Mo_3S_7(S_2)_3]$ with Br_2 or Cl_2 in CH_3CN.[209] A high-yield access route to $[Mo_3S_7Br_6]^{2-}$ is to treat $(NH_4)_2[Mo_3S_7(S_2)_3]$ with $(CH_3)_3CBr$ (50 °C, DMF).[211] Crystal structures have been determined for $(Ph_4P)_2[Mo_3S_7Cl_6]$,[204] $(Et_4N)(H_9O_4)[Mo_3S_7X_6]$ (X = Cl, Br),[206,210] $(Et_4N)_2[Mo_3S_7Br_6]$[210] and $(N_2H_5)_2$ $[Mo_3S_7I_6]$.[212] In certain conditions, one more additional Cl^- or Br^- is weakly bound to the three axial sulfur atoms of the S_2 groups, as has been crystallographically verified for $(pyH)_3\{[Mo_3S_7Cl_6]Cl\}$,[213] $(C_5H_7S_2)_3\{[Mo_3S_7Cl_6]Cl\}$ ($C_5H_7S_2$ is 3,5–dimethyl-2–dithiolium),[214] $(Et_4N)_3\{[Mo_3S_7Cl_6]Cl\}$,[215] $[Pr(DMSO)_6\,(H_2O)_2]\{[Mo_3S_7Br_6]Br\}$, $[Eu(DMSO)_7(H_2O)]\{[Mo_3S_7Br_6]Br\}$, and $[Tm(DMSO)_6(H_2O)]\{[Mo_3S_7Br_6]Br\}$.[216] This secondary halogen coordination leads to S···Cl distances around 2.9 Å and S···Br around 3.1 Å.

These salts, in particular $(Et_4N)_2[Mo_3S_7Br_6]$, are good starting materials for preparation of other Mo_3S_7 derivatives by ligand substitution. Thus NCS^- converts it into $(Et_4N)_2$ $[Mo_3S_7(NCS)_6]$,[217] and aniline into $\{[Mo_3S_7Br_3(PhNH_2)_3]Br\}\cdot Et_4NBr$ (Figure 36).[218] Dithiocarbamates $[Mo_3S_7(Et_2NCS_2)_3]X$ (Figure 37) (X = Br, Et_2NCS_2),[153,219] $[Mo_3S_7\,(pipCS_2)_3]Br$[219] (pip is piperidyl) are obtained in this way. When treated with $(Et_2NCS_2)_2$ and NaI the compound $(NH_4)_2[Mo_3S_7(S_2)_3]$ yields $[Mo_3S_7(Et_2NCS_2)_3]I$.[211] An extended list of dialkyldithiocarbamate salts $[Mo_3S_7(Et_2NCS_2)_3]X$ (X = Cl,[220] I,[211,221,222] ClO_4,[225] TCNQ,[223] Et_2NCS_2,[152,224] S,[225,226] $C_2H_{11}B_9$,[227] as well as other dithiocarbamates $[Mo_3S_7(PyrrCS_2)_3]I$[228] and $[Mo_3S_7(pipCS_2)_3]I$[221] have been prepared with strong interactions between the axial sulfur atoms and X^- donor atoms. A theoretical treatment has been presented for $[Mo_3S_7(Et_2NCS_2)_3]X$. The covalency of this interaction strongly increases on going from perchlorates (almost pure Coulombic) to sulfide (covalent): $ClO_4^- < Cl^- < I^- < S^{2-}$. A decrease in S–S Raman frequency and S–S distance has been noted for the S_2 ligand.[225] Another interesting example in this series of salts is $[Mo_3S_7(Et_2NCS_2)_3]_4(SO_4)_2$, where the four oxygen atoms of one sulfate interact with four different Mo_3S_7 units, while the other SO_4^{2-} remains free,[225] and cationic $\{[Mo_3S_7(Et_2NCS_2)_3]_2Cl\}^+$, where Cl^- is sandwiched between two Mo_3S_7 units, like S^{2-} in $[Mo_3S_7(Et_2NCS_2)_3]_2S$.[229]

Complexes with dithiophosphate ligands $(RO)_2PS_2^-$(R = Et, ^iPr) are obtained by substitution,[219] or by sulfur addition to $[Mo_3S_4((EtO)_2PS_2)_4(H_2O)]$. Several crystal structures $[Mo_3S_7(dtp)_3]X$ have been reported, showing short S···X contacts.[230,231] Closely related dithiophosphinates $[Mo_3S_7(R_2PS_2)_3]^+$(R = Et, n–Pr) have been prepared by cluster self-assembly from $[Mo(CO)_6]$ and $R_2P(S)SSP(S)R_2$ (reflux in toluene, 4 h).[232,233]

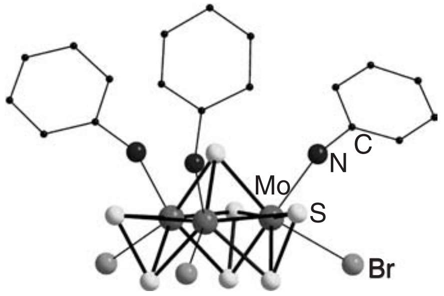


Figure 36 Structure of the $[Mo_3S_7Br_3(PhNH_2)_3]^+$ cation.

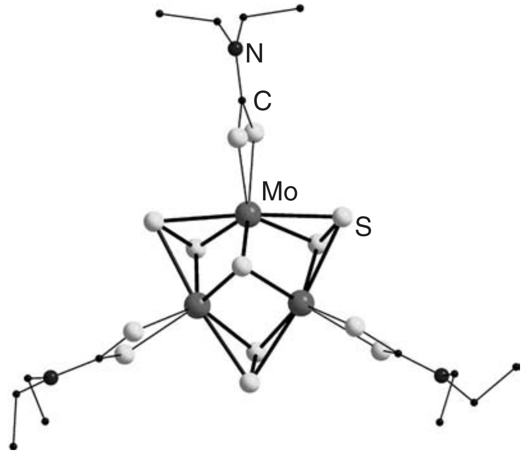


Figure 37 Structure of the $[Mo_3S_7(Et_2NCS_2)_3]^+$ cation.

Reactions of $(Et_4N)_2[Mo_3S_7Br_6]$ with $K[(Ph_2P(Q))_2N]$ ($Q = S$, Se) give $[Mo_3S_7\{(Ph_2P(Q))_2N\}_3]Br$ containing six-membered chelate rings.[234] A 3,4-toluenedithiolate complex has been structurally characterized as $(Et_4N)_2[Mo_3S_7(CH_3C_6H_3S_2)_3]$,[235] and the brown catecholate analog from $(Et_4N)_2[Mo_3S_7Br_6]$, Et_3N and H_2cat has also been prepared, yield 75%.[211] The disulfonated catecholate $(OH)_2C_6H_2(SO_3)_2{}^{2-}$ also gives a tris-complex, which is too soluble for a well-defined product to be isolated.[237]

Reaction of $(NH_4)_2[Mo_3S_7(S_2)_3]$ with C_5H_4N-S-S-C_5H_4N (tpy_2) in DMF gives an orange solution, from which a tris-complex $[Mo_3S_7(tpy)_3]I$ is isolated in 11% yield upon addition of NaI; and a dark solid, converted by treatment with dtc_2 and NaI into a mixed-ligand complex $[Mo_3S_7(tpy)_2(dtc)]I$. This latter product, however, exhibits in the FAB–mass spectra molecular peaks corresponding to $[Mo_3S_7(tpy)_3]^+$, $[Mo_3S_7(tpy)_2(dtc)]^+$ and $[Mo_3S_7(tpy)(dtc)_2]^+$, interpreted as ligand redistribution products under mass spectrometry conditions.[211] Tris-chelated complexes of Mo_3S_7 with bidentate ligands 2-mercapto succinic acid (H_3msa), meso-2,3-dimercapto succinic acid (H_4dsa), 2-mercapto benzoic acid (H_2mba), 3,4-dihydroxybenzoic acid (H_3dba), 8-oxyquinoline (Hoxq) and 6-mercapropurine (Hmp) have been prepared from $(Et_4N)_2[Mo_3S_7Br_6]$ in CH_3CN or DMF and isolated as solids with appropriate counterions.[211,228,237,238] FAB–MS was applied to study fragmentation patterns of $[Mo_3S_7Br_6]^{2-}$, $[Mo_3S_7(cat)_3]^{2-}$, $[Mo_3S_7(oxq)_3]^+$, $[Mo_3S_7(mba)_3]^{2-}$ and $[Mo_3S_7(mp)_3]^+$.[211,236–238] As in the Mo_3S_7 core each Mo atom has two non-equivalent coordination sites with respect to the capping sulfide, and formation of different isomers is possible. Crystal structures of $(Et_3NH)_2[Mo_3S_7(mba)_3]$ reveal only one isomer in the solid state with all sulfur atoms *cis* to μ_3–S (Figure 38).[237] Potentiometric titrations of $[Mo_3S_7(H_2dsa)_3]^{2-}$ with KOH indicate chelating formation of a less symmetrical isomer, with two ligands S,S′ and one S,O.[237] Electrochemical reduction of $[Mo_3S_7(mba)_3]^{2-}$, $[Mo_3S_7(Hdba)_3]^{2-}$, $[Mo_3S_7(H_2dsa)_3]^{2-}$ and

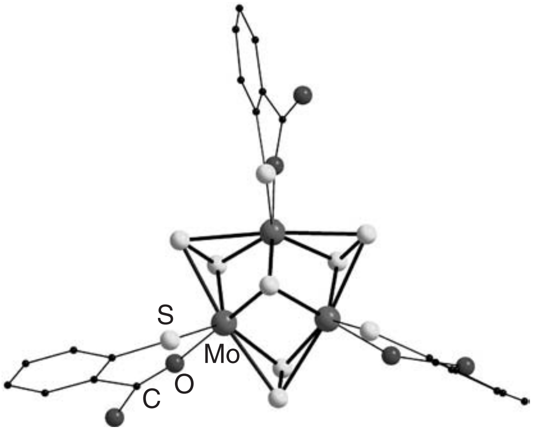


Figure 38 Structure of the $[Mo_3S_7(mba)_3]^{2-}$ anion incorporating the mba^{2-} anion of 2-mercaptobenzoic acid (H_2mba).

$[Mo_3S_7(Hmsa)_3]^{2-}$ occurs in the range −0.2 V to −0.9 V vs. Ag/AgCl and is irreversible, due to sulfur loss from the S_2 bridges and formation of $Mo_3S_4^{4+}$.[237]

The main characteristic of the M_3Q_7 core is found in the distinction between the equatorial and axial chalcogen atoms in the $\mu_2{-}Q_2$ ligands (Figure 35). Thus the Mo—S_{eq} bond distance (2.485 Å) in $(Ph_4P)_2[Mo_3S_7Cl_6]$ is longer than Mo—S_{ax} (2.391 Å).[204] Consequently, the bond force constant for Mo—$S_{eq.}$ is smaller,[185] and equatorial sulfur is more labile toward abstraction and substitution. This was shown by preparation of a unique series of six isotopomers of $(NH_4)_2[Mo_3S_7(S_2)_3]$ with ^{92}Mo, ^{100}Mo, ^{34}S isotopes. The reaction of $(Et_4N)_2[Mo_3{}^{34}S_7Br_6]$ with $(NH_4)_2{}^{32}S_x$ gives the expected $[Mo_3S_{13}]^{2-}$ where not only terminal ligands are exchanged, but (selectively) equatorial sulfur atoms, and a unique isotopomeric $^{32}S{-}^{34}S$ product is obtained $[Mo_3(\mu_3{-}^{34}S)(\mu{-}^{34}S_{ax}{-}^{32}S_{eq})_3(^{32}S_2)]^{2-}$.[239] With conc. HCl this gives $[Mo_3(\mu_3{-}^{34}S)(\mu{-}^{34}S_{ax}{-}^{32}S_{eq})_3Cl_6]^{2-}$, which reacts with PPh_3 to generate the $Mo_3S_4^{4+}$ core. Exclusive formation of $^{32}SPPh_3$ demonstrates that sulfur abstraction takes place at the equatorial position.[185] However, when $(Et_4N)_2[Mo_3{}^{34}S_7Br_6]$ is treated with $(NH_4)_2{}^{32}S_x$ saturated with ^{32}S, no $^{32}S/^{34}S$ exchange occurs within the bridging S_2 ligands. This difference in reactivity between sulfur-saturated and unsaturated $(NH_4)_2S_x$ is explained by a reversible elimination–addition mechanism. Saturated polysulfide S_x^{2-} cannot add any more sulfur, no attack of the S_2 ligands is observed, and the first elimination step is effectively blocked.[152] Reaction of $(Et_4N)_2[Mo_3S_7Br_6]$ with $[(\eta^5{-}C_5H_5)_2TiS_5]$ proceeds without isotopic exchange in the core, and $[Mo_3S_{13}]^{2-}$ is the product.[152]

Vibrational spectra (IR and Raman) have been studied in detail for $(NH_4)_2[Mo_3S_{13}]$, $(Ph_4As)_2[Mo_3S_{13}]$ and $(Et_4N)_2[Mo_3S_7Cl_6]$, using isotope substitution. For the first of these only Mo$-\mu_3$S (462 cm^{-1}) and S–S vibrations (bridging 541, 552 cm^{-1}; terminal 506, 513 cm^{-1}) are clearly defined, and Mo$-$S, Mo—Mo and Mo–Cl vibrations are mixed.[185,239,240] The structure of $(Me_4N)_2[Mo_3S_7(S_2)_3]$ has been determined.[240]

A 50% yield of $K_2[Mo_3S_{13}]\cdot xH_2O$ is obtained from amorphous polymeric MoS_3 (of unknown structure) with 5% aqueous KOH. When a mixture of $^{92}MoS_3$ and $^{100}MoS_3$ is used, homoisotopic $[^{92}Mo_3S_{13}]^{2-}$ and $[^{100}Mo_3S_{13}]^{2-}$ are products. From this it is concluded that MoS_3 is built up of cluster aggregates M_x with $x \geq 3$.[241]

Orange $[Mo_3S_7(H_2O)_6]^{4+}$ reacts with PR_3^{3-} ($R = C_6H_4SO_3$) giving green $[Mo_3S_4(H_2O)_9]^{4+}$ according to a rate law $k = k_1[H^+] + k_{-1}[H^+]^{-1}$ which was interpreted as involvement of a protonated S_2 and an H_2O conjugate-base form; k_1 was found to be 3.14×10^4 M^{-2}s^{-1} and $k_{-1} = 2.78 \times 10^4$ s^{-1}. Equilibration rate constants for Cl^- or Br^- substitution of H_2O are independent of $[H^+]$ and their values are: (10^4 k_{eq} (M^{-1}s^{-1})) 1.83 (Cl^-) and 2.07 (Br^-). These uniphasic reactions are assigned as substitution of the H_2O *cis* to μ_3–S at each Mo, giving $[Mo_3S_7Cl_3(H_2O)_3]^+$.[110]

4.12.6.2.2 W_3S_7 clusters

Clusters with this core are scarce. Polymeric $\{W_3S_7Br_4\}_x$,[114,183] orthe chloride, (made from WS_3 and PCl_5} are believed to have the same structure.[114] In a melt (ca. 290 °C) $\{W_3S_7Br_4\}_x$ reacts with PPh_4Br to give bright red $(Ph_4P)_2[W_3S_7Br_6]$, the crystal structure of which has been determined.[114] The structural parameters of the $W_3S_7^{4+}$ core are very close to those of $Mo_3S_7^{4+}$. Detailed IR and Raman studies on $[W_3S_7Br_6]^{2-}$, including bonds force constants calculations, have been reported.[114] Conversion of $\{W_3S_7Br_4\}_x$ into $(Et_4N)_2[W_3S_7Br_6]$ by heating with Et_4NBr in hot conc. HBr (low yields, poor reproducibility),[114] or better by mechanochemical reaction with an excess of solid Et_4NBr is possible.[242] The chlorides are known, and crystal structures of $(PPN)_2[W_3S_7Cl_6]$[242] and a cucurbituril derivative $(H_3O)_4[W_3S_7Cl_6]_2$ $(C_{36}N_{24}O_{12}H_{36})\cdot 8H_2O$ have been described.[243] With ammonium polysulfide $\{W_3S_7Br_4\}_x$ is transformed into $W_3S_4^{4+}$ as black $(NH_4)_2[W_3S_4(S_4)_3(NH_3)_3]$.[114,152]

4.12.6.2.3 M_3Se_7 clusters

These are accessed from $\{M_3Se_7X_4\}_x$ by reaction with PPh_4X (melts) or Et_4NX (vibration mill), X = Cl, Br, leading to $[M_3Se_7X_6]^{2-}$ salts.[179,242] With Nadtc these are converted into red crystalline dithiocarbamates $[M_3Se_7(dtc)_3](dtc)$ which give strong contacts between Se_{ax} and an S atom of dtc, the Se—Se distance is 2.31 Å (M = Mo, W).[179] Similarly, $(Et_4N)_2[W_3Se_7Br_6]$ is converted into red $[W_3Se_7((EtO)_2PS_2)_3]Br$ by reaction with potassium diethyldithiophosphate in CH_3CN (74%). Solutions in DMF have non-electrolyte properties, indicating short $Se_{ax}\cdots$Br–contacts (3.07–3.08 Å) as in the solid state.[244] Melting $\{M_3Se_7X_4\}_x$ with 1,10-phenanthroline gives red $[M_3Se_7\,(phen)_3]^{4+}$, isolated as X^- or ZnX_4^{2-} salts after extraction with hot conc. HX (X = Cl, Br).[179]

Self-assembly of the M_3Se_7 core has been reported on refluxing $[M(CO)_6]$ ($M = Mo$, W) with Se and in dtc_2 in 1,2-dichlorobenzene; when red $[M_3Se_7(Et_2NCS_2)_3]_2Se$ products are isolated in ~50% yields as structural analogs of $[Mo_3S_7(Et_2NCS_2)_3]_2S$.[245]

Ligand substitution on $(Ph_4P)_2[Mo_3Se_7Br_6]$ gives $[Mo_3Se_7\{(Ph_2P(Se))_2N\}_3]Br$ and $[Mo_3Se_7((EtO)_2PSe_2)_3]Br$. The crystal structure and ^{77}Se and ^{31}P NMR spectra have been reported.[246]

An interesting series of polyselenido complexes of $Mo_3Se_7^{4+}$ has been prepared from MoO_3 and an alkali metal polyselenide under hydrothermal conditions (135 °C), in the presence of K^+, Me_4N^+, or Et_4N^+. Dark-red $(Me_4N)_2[Mo_3Se_7(Se_2)_3]$ has a structure similar to $(Me_4N)_2[Mo_3S_7(S_2)_3]$. In $K_2Mo_3Se_{12.5}O_{0.5}$ both $[Mo_3OSe_6(Se_2)_3]^{2-}$ and $[Mo_3Se_7(Se_2)_3]^{2-}$ are present in a 1:1 ratio. Black $K_6[Mo_6Se_{27}]\cdot 6H_2O$ has a Se^{2-} ion sandwiched between two $[Mo_3Se_{13}]^{2-}$ units, as in $[M_3Se_7(Et_2NCS_2)_3]_2Se$ ($Se^{2-}\cdots Se_{ax}$ 2.81–3.04 Å).[245] Calculations show a significant electron transfer from Se^{2-} to the anti-bonding orbitals of the $\mu{-}Se_2$ group.[247,248]

Clusters $[Mo_3Se_{13}]^{2-}$ are present in black $K_8[Mo_9Se_{40}]\cdot 4H_2O$, obtained from MoO_3, K_2Se_2 and H_2O at 135 °C. This compound contains an aggregate of three trinuclear $Mo_3Se_7^{4+}$ units, linked by two Se^{2-}. One of the latter is the capping μ_3 atom of an Mo_3Se_7 cluster ($Se\cdots Se$, 3.13 Å). Another Se^{2-} is sandwiched between two Mo_3Se_7 clusters as in the above-mentioned $Mo_6Se_{27}^{6-}$ aggregate. Thus, the cluster can be described as three $[Mo_3Se_{13}]^{2-}$ and one Se^{2-}, linked by short $Se\cdots Se$ contacts.[249] Another cluster, $K_2[Mo_3Se_{18}]$, obtained under the same conditions but with a different reagent ratio, has the $Mo_3Se_7^{4+}$ core, coordinated by a Se_3^{2-} and bridging Se_4^{2-}, with infinite chains $[Mo_3Se_7(Se_3)(Se_4)_{4/2}]_n^{2n-}$.[249]

The reaction of Mo metal with K_2Se_4 in H_2O (140 °C) gives black $K_{12}[Mo_{12}Se_{56}]$. Here, $Mo_3Se_7^{4+}$ cluster units are bound into tetrameric aggregates (clusters of clusters) via Se_3 bridges; the Mo atoms, which do not participate in the intercluster bridging, are coordinated by terminal Se_2^{2-}, and there are four Se^{2-}, each of them bound to the three axial Se atoms in the cluster.[249] Even more complicated polymeric structures involving the bridging of $Mo_3Se_7^{4+}$ via Se_4^{2-} and Se_5^{2-} are found in $[NEt_4]_6[\{Mo_3(\mu_3{-}Se)(\mu{-}\eta^2{-}Se_2)_3(\eta^2{-}Se_2)\ (\mu{-}\eta^2{-}Se_5)(\eta^1{-}Se_5)\}_2(\mu{-}\eta^2{-}Se_4)]$.[250]

Orange $[Mo_3Se_7(H_2O)_6]^{4+}$ reacts with PR_3^{3-} ($R = C_6H_4SO_3$), giving yellow–brown $[Mo_3Se_4(H_2O)_9]^{4+}$, $\sim 10^3$ times more slowly than $[Mo_3S_7(H_2O)_6]^{4+}$. Equilibration rate constants for the Cl^- or Br^- substitution of H_2O are independent of H^+, and $10^4\ k_{eq}$ ($M^{-1}\ s^{-1}$) is 6.7 (Cl^-) and 33 (Br^-). These uniphasic reactions are assigned as substitution of the H_2O *cis* to $\mu_3{-}Se$ at each Mo.[110]

4.12.6.2.4 Mo_3Te_7 clusters

Heating Mo, Te and I_2 in an atomic ratio 3:7:4 at 380 °C (98 h) gives an amorphous powder which dissolves in aqueous KCN, producing brown $[Mo_3Te_7(CN)_6]^{2-}$. The Mo_3Te_7 in this cluster has a strong affinity for I^-, forming $\{[Mo_3Te_7(CN)_6]I\}^{3-}$ through $Te_{ax}I$ contacts (3.576 Å). In the crystal structure of $Cs_{4.5}[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ the Mo—Mo distance was found to be 2.891 Å, Te—Te 2.688 Å.[251] Structures of $K_{4.5}[Mo_3Te_7(CN)_6]I_{2.5}\cdot 3H_2O$ and $Cs_3\{[Mo_3Te_7(CN)_6]I\}I\cdot 2H_2O$ have also been reported.[252] With solid $KS_2P(OR)_2$ ($R = Et$, *i*-Pr) at 100 °C under N_2, the cluster $Mo_3Te_{10}I_{10}$ gives the product $[Mo_3Te_7((RO)_2PS_2)_3]I$, 20% yield. Short contacts $Te_{ax}\cdots I$, 3.30–3.40 Å, were found, whereas the sum of Te and I van der Waals radii is 4.35 Å (Figure 39).[253] Trinuclear $[Mo_3Te_7(CN)_6]^{2-}$ is inert to Te abstraction, in stark contrast to its S and Se analogs, and no reaction with PR_3^{3-} ($R = C_6H_4SO_3$; in H_2O) or PEt_3 (in CH_3OH) is observed at 130 °C.[251]

4.12.6.2.5 $Mo_3O(S_2)_3$ clusters

These are known only as diethyldithiophosphates $[Mo_3O(S_2)_3((EtO)_2PS_2)_3]X$ ($X = Cl$, I, I_3). An O instead of S caps the trinuclear Mo_3 and shortens the Mo—Mo bonds significantly, from 2.723 Å to 2.626 Å in the iodide.[254] The triiodide made from $[Mo_3\ OS_3((EtO)_2PS_2)_4(H_2O)]$ and CuI in air has the composition $[Mo_3(O_{0.58}S_{0.42})(S_2)_3((EtO)_2\ PS_2)_3]I_3$ and is a semiconductor.[255]

4.12.6.2.6 $Mo_3O(Te_2)_3$ clusters

This core is found in α and β modifications of $[Mo_3O(Te_2)_3(en)_3]In_2Te_6$, prepared by solvothermal reaction of Li_2Te, K_2Te, $MoCl_5$, $InCl_3$ and Te in ethylenediamine (180 °C, 7 days). The only

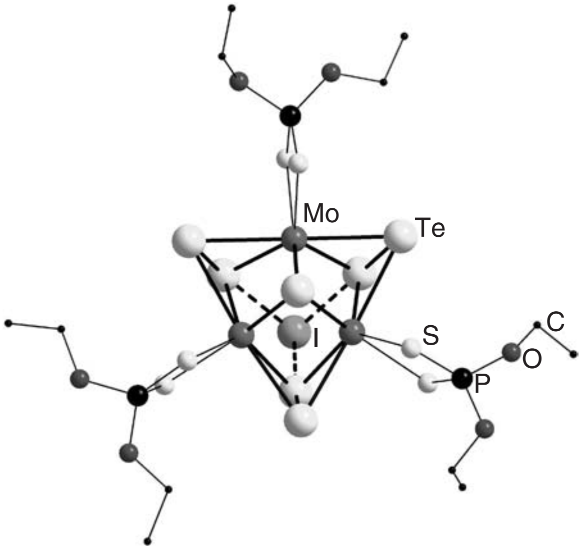


Figure 39 Structure of the $[Mo_3Te_7((EtO)_2PS_2)_3]I$ molecule.

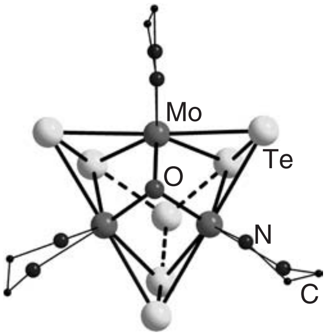


Figure 40 Structure of the $[Mo_3O(Te_2)_3(en)_3]Te$ molecule.

difference between these modifications is the different ways of puckering and disposition of the In_2Te_3 rings along the polymeric $In_2Te_6^{2-}$ chains. Capping with O instead of Te draws the Mo atoms nearer (Mo—Mo 2.72 Å) (Figure 40).[256]

4.12.6.2.7 $Mo_3S(Se_2)_3$ cluster

This core is only found in $[Mo_3(S_{0.65}Se_{0.35})(Se_2)_3((EtO)_2PS_2)_3]Cl$, obtained from $MoCl_3 \cdot 3H_2O$, ZnSe and $Me_4N(S_2P(OEt)_2)$.[171]

4.12.6.2.8 $M_3S(S_{eq}-Se_{ax})_3$ clusters

Chalcogen-exchange reactions between $[Mo_3S_7Cl_6]^{2-}$ and PPh_3Se or KNCSe result in a selective substitution of the equatorial sulfur atoms. With PPh_3Se, $[Mo_3S_7X_6]^{2-}$ (X = Cl, Br) is converted into $[Mo_3S(SSe)_3X_6]^{2-}$; the W analog has also been prepared.[257] Reaction with KNCSe gives (in the presence of excess KNCS) $[M_3S(SSe)_3(NCS)_6]^{2-}$ (M = Mo,[217] W[257]). This reaction is irreversible, and the $Mo_3S(SSe)_3$ core does not revert to $Mo_3S(S_2)_3$ even when treated with excess PPh_3S or KNCS.[217,252] Crystal structures were determined for PPN and PPh_3Et salts of $[Mo_3S(SSe)_3Cl_6]^{2-}$.[217,257] Though $[Mo_3S_7(dtc)_3](dtc)$ does not react with PPh_3Se, it can be converted with KNCSe into $[Mo_3S(SSe)_3(dtc)_3]SeCN$, which contains practically linear polymeric chains $(S–Se\cdots Se\cdots S–Se\cdots Se\cdots)_n$ due to short (2.9–3.3 Å) cation–anion contacts. Bond lengths S—Se are 2.16–2.23 Å.[258] *In situ* $Mo_3S_4^{4+}$, generated from $(Et_4N)_2[Mo_3S_7Br_6]$, reacts with $Se(dtc)_2$ to give $[Mo_3S(SSe)_3(dtc)_3]Br$.[259] Aquation of $[Mo_3S(SSe)_3Br_6]^{2-}$ in 4 M Hpts gives

$[Mo_3S(SSe)_3(H_2O)_6]^{4+}$, which reacts with PPh_3 to generate $[Mo_3S_4(H_2O)_9]^{4+}$, rate constant $1.48 \times 10^5\,M^{-1}s^{-1}$ in 2.0 M Hpts.[110]

4.12.6.2.9 $M_3S(S_{eq}-Se_{ax})_3$ and $M_3Se(S_{eq}-Se_{ax})_3$ clusters

Initially both cluster cores were found in red–orange $[Mo_3(S_{0.65}Se_{0.35})(SSe)_3((EtO)_2PS_2)_3]I$, prepared by treatment of $[Mo_3S_{0.65}Se_{0.35}Se_3((EtO)_2PS_2)_4(py)]$ with H_2S in the presence of iodine.[171] Aqua ions $[M_3Se_4(H_2O)_9]^{4+}$ (M = Mo, W) react with P_4S_{10} in an EtOH/HCl mixture to give red sulfur addition products, $[M_3Se(S_{eq}-Se_{ax})_3((EtO)_2\,PS_2)_3]Cl$. The S–Se distances are ~2.20 Å in both clusters.[166]

4.12.6.3 Mo_3S_5 Core Clusters

Reaction of $(NH_4)_2[Mo_3S_{13}]$ with excess PMe_3 in THF at ~20 °C gives black crystalline $[Mo_3(\mu_3-S)_2(\mu-S)_3(PMe_3)_6]$, yield 26%. In this symmetrical structure an equilateral triangle of Mo atoms (Mo—Mo 2.714 Å) is capped by two sulfur atoms (Mo–S 2.421 Å) and bridged by three other sulfur atoms (Mo—S 2.393 Å). All six PMe_3 ligands are equivalent, and give only one sharp ^{31}P NMR signal in solution (30.4 ppm). Cyclic voltammetry shows a quasi-reversible reduction ($E_{1/2} = -1.16$ V) and oxidation ($E_{1/2} = +0.06$ V) vs. $Ag/AgNO_3$ in CH_3CN.[260]

The self-assembly reaction of $MoCl_3{\cdot}3H_2O$ and H_2S in HCl/EtOH gives $[Mo_3(\mu_3-S)_2(\mu-Cl)_3Cl_6]^{3-}$, isolated and structurally characterized as the 3,5-dimethyldi-thiolium salt, $(C_3H_7S_2)_2[Mo_3S_2Cl_9]$.[214] Its electronic structure has been studied.[261] The latter can be converted into the neutral dithiophosphate, $[Mo_3S_2(dtp)_3]$.[262]

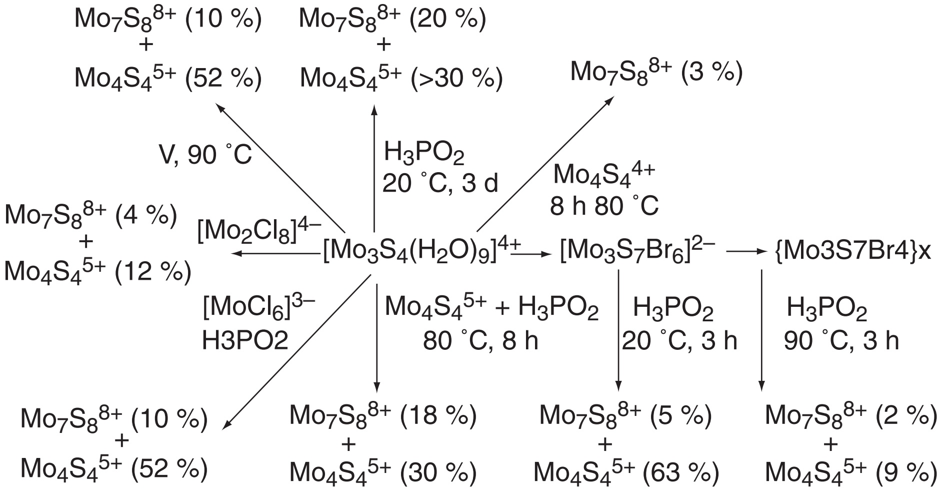
4.12.6.4 M_4Q_4 Cubes (M = Mo, W; Q = S, Se, Te)

4.12.6.4.1 Aqua ions

Green $[Mo_4S_4(H_2O)_{12}]^{5+}$ is made (i) either by electrochemical or chemical reduction ($NaBH_4$) of $[Mo_2O_2S_2(cys)_2]^{2-}$ (ca. 20% yield);[104] (ii) from Na_2S and $[Mo\,(CO)_6]$ in acetic anhydride (up to 30%);[263] (iii) by reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ with H_3PO_2 (up to 60%).[103] Reactions are summarized in (Scheme 1).[103] None of these gives $[Mo_4S_4(H_2O)_{12}]^{5+}$ as sole product. Methods (i) and (ii) also give $[Mo_3S_4(H_2O)_9]^{4+}$ and/or Mo_3 mixed O/S bridged analogs, whereas (iii) generates $[Mo_7S_8(H_2O)_{18}]^{8+}$. Reduction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Mg[264] or V[103] gives a mixture of $[Mo_4S_4(H_2O)_{12}]^{5+}$ and $[Mo_7S_8(H_2O)_8]^{8+}$. Finally, reactions of quadruple bonded $[Mo_2Cl_8]^{4-}$ with $[Mo_3S_4(H_2O)_9]^{4+}$ or with $[Mo_2(\mu-S_2)_2Cl_8]^{2-}$ give moderate yields of the cuboidal aqua ion, in the latter case together with $[Mo_3S_4(H_2O)_{12}]^{4+}$.[101,103] At 4 °C in 2 M Hpts $[Mo_4S_4(H_2O)_{12}]^{5+}$ is stable for weeks when stored O_2-free. Heating in air at 50 °C gives $[Mo_3S_4(H_2O)_9]^{4+}$, with a half-life of 4 days. In 1 M HCl the same reaction has a half-life ($t_{1/2}$) of 10 h.[265]

The crystal structure of $[Mo_4S_4(H_2O)_{12}](pts)_5{\cdot}14H_2O$, (from 4 M Hpts) gives an average Mo—Mo of 2.802 Å (Figure 41).[266] The cube consists of two interpenetrating Mo_4 and S_4 tetrahedra of different sizes. The cube is therefore distorted and hence the cuboidal description applies. The cluster has 59 electrons and is paramagnetic showing Curie-like behavior with μ_{eff} constant at 1.78 B.M. between 300 K and 20 K, and 1.73 B.M. at 4.2 K.[267] The ESR spectrum is shown in (Figure 42).

Green $[Mo_4Se_4(H_2O)_{12}]^{5+}$ is made in a low yield by $NaBH_4$ reduction of $[Mo_2O_2Se_2(cys)_2]^{2-}$; it is less stable than the sulfido cluster and decays at 20 °C in air to give $[Mo_3Se_4(H_2O)_9]^{4+}$ ($t_{1/2} = 7$ d). The crystal structure was determined for $[Mo_4Se_4(H_2O)_{12}((pts)_5{\cdot}14H_2O)$.[108,109] Both cuboidal aqua ions can be reversibly reduced from 5+ to 4+ state (at 0.21 V for S, at 0.19 V for Se), and reversibly oxidized to 6+ state (0.86 V for S, 0.79 V for Se; all values are vs. NHE).[108,109,265] Orange air-sensitive $[Mo_4S_4(H_2O)_{12}]^{4+}$ can be prepared quantitatively by reduction of the 5+ state electrochemically or by $NaBH_4$, $[V(H_2O)_6]^{2+}$, or $[Cr(H_2O)_6]^{2+}$ reduction. The kinetics of last two reaction shows first-order dependence in the presence of a large excess of the reductant, and outer-sphere mechanism was deduced, with $k = 0.61 \times 10^3\,M^{-1}s^{-1}$ (Cr) and $24.5 \times 10^3\,M^{-1}s^{-1}$ (V).[265] Red $[Mo_4S_4(H_2O)_{12}]^{6+}$ is prepared by oxidation of $[Mo_4S_4(H_2O)_{12}]^{5+}$ by controlled stoichiometric amounts of *cis*-$[VO_2(H_2O)_4]^+$.[265,268] It is not very stable and decays spontaneously with the formation of $[Mo_3S_4(H_2O)_9]^{4+}$. Attempts to prepare the 6+ cube by controlled electrolysis of



Scheme 1

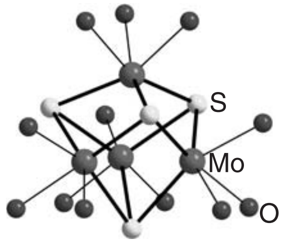


Figure 41 Structure of the $[Mo_4S_4(H_2O)_{12}]^{5+}$ cation.

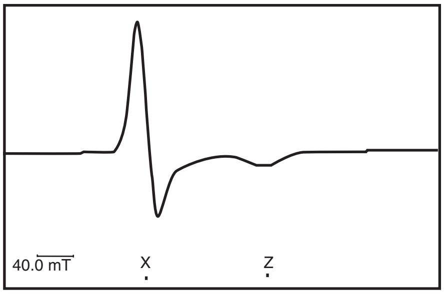


Figure 42 ESR spectrum of $[Mo_4S_4(H_2O)_{12}]^{5+}$ (2 mM) in 2.0 M Hpts at 3.8 K, with microwave frequency 9.25 GHz, power 20 mV and gain 1.25×10^{-3}.[6]

$[Mo_4S_4(H_2O)_{12}]^{5+}$ gave $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Mo_2O_2S_2(H_2O)_6]^{2+}$.[9] The $[Mo_4OS_3(H_2O)_{12}]^{5+}$ cube has been prepared by reduction of $[Mo_3OS_3(H_2O)_9]^{4+}$ with Fe wire. The X-ray structure of $[Mo_4OS_3(H_2O)_{12}]$ $(pts)_5 \cdot 14H_2O$ has been reported.[269]

The quadruply bonded Mo^{II}_2 complex $K_4[Mo_2Cl_8]$ reacts with $[W_3S_4(H_2O)_9]^{4+}$, $[Mo_2WS_4(H_2O)_9]^{4+}$, $[MoW_2S_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$, giving the heterometallic cubes $[MoW_3S_4(H_2O)_9]^{5+}$, $[Mo_3WS_4(H_2O)_9]^{5+}$, $[Mo_2W_2S_4(H_2O)_9]^{5+}$ and $[MoW_3Se_4(H_2O)_9]^{5+}$, respectively. Trends in UV–vis spectra are shown in (Figure 43). The crystal structure of red $[MoW_3S_4(H_2O)_{12}](pts)_5 \cdot Hpts \cdot 16H_2O$ exhibits a random occupancy of metal sites (due to similar Mo and W radii). Air oxidation or oxidation by $[Fe(H_2O)_6]^{3+}$, gives first the 6+ cubes, which then fragment by losing exclusively one tungsten atom, e.g., $[MoW_3S_4(H_2O)_9]^{5+}$ gives $[MoW_2S_4(H_2O)_9]^{4+}$, etc. Electrochemical studies of these heterometallic cubes indicate two reversible redox processes, corresponding to the 5+/4+ and 6+/5+ couples.[119]

Trends in $E^{o\prime}$ values and in UV–vis spectra for these $Mo_xW_{4-x}S_4{}^{5+}$ cubes allowed predictions to be made for $[W_4S_4(H_2O)_{12}]^{5+}$ (Figure 44).[120] Recently, brown—red $[W_4S_4(H_2O)_{12}]^{6+}$ was

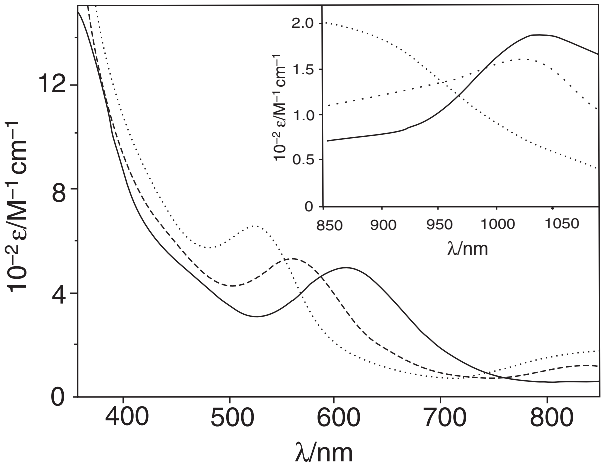


Figure 43 Trends in UV–vis spectra of $[Mo_3WS_4(H_2O)_{12}]^{5+}$ (———) $[Mo_2W_2S_4(H_2O)_{12}]^{5+}$ (– – –) and $[MoW_3S_4(H_2O)_{12}]$ (····) in 2 M Hpts.[119]

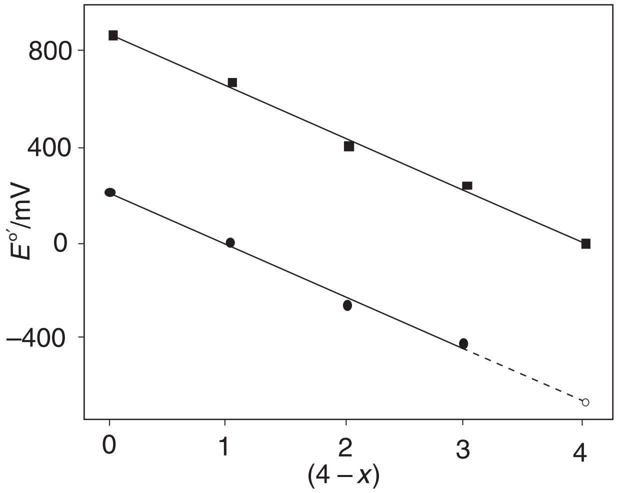


Figure 44 Reduction potentials $E^{o\prime}$ vs. nhe for $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{6+/5+}$ (■) and $[Mo_xW_{4-x}S_4(H_2O)_{12}]^{5+/4+}$ (●) couples, $x = 0$–4.[119,270]

prepared by the [3 + 1] reaction of $[W_3S_4(H_2O)_9]^{4+}$ with $[W(CO)_6]$ in 2 M HCl under hydrothermal conditions (130 °C).[270] The 5+ reduced form (red–brown) is obtained by controlled potential voltammetry, $E^{o\prime}$ for $[W_4S_4(H_2O)_{12}]^{6+/5+}$ 35 mV (vs. nhe). An estimate of $E^{o\prime}$ for $[W_4S_4(H_2O)_{12}]^{5+/4+}$ of −627 mV accounts for the difficulty in preparing $[W_4S_4(H_2O)_{12}]^{4+}$.

Extensive kinetics studies on water substitution by thiocyanate in $[Mo_4Q_4(H_2O)_{12}]^{5+}$ (Q = S, Se), $[Mo_4S_4(H_2O)_{12}]^{4+}$ and $[Mo_4S_4(H_2O)_{12}]^{6+}$ have been reviewed recently.[6] Chloride coordinates to $[Mo_4S_4(H_2O)_{12}]^{5+}$, equilibration constant 1.98 M^{-1}, which is $\sim 10^3$ times less than for thiocyanate.[271]

A double cube in which an Mo is bonded to two Mo_3S_4 units to give an $Mo_3S_4(Mo)S_4Mo_3$ core, overall composition $[Mo_7S_8(H_2O)_{18}]^{8+}$, has been prepared.[103] Distance from the nodal Mo to other Mo's, 3.026–3.060 Å, are longer than other Mo–Mo distances 2.766–2.773 Å. Analogs $[Mo_7Se_8(H_2O)_{18}]^{8+}$, $[MoW_6S_8(H_2O)_{18}]^{8+}$ and $[MoW_6Se_8(H_2O)_{18}]^{8+}$ have also been prepared, but less extensively studied. Other corner-shared double cube derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$, with a heterometal M′ at the nodal position giving $[Mo_6M'S_8(H_2O)_{18}]^{8+}$, are considered in later sections.

4.12.6.4.2 *Derivatives of $[Mo_4S_4(H_2O)_{12}]^{5+}$*

The water molecules in $[Mo_4S_4(H_2O)_{12}]^{5+}$ can be substituted by NCS^-. In air this reaction is accompanied by cluster core oxidation, the product being purple 58e $[Mo_4S_4(NCS)_{12}]^{6-}$, isolated as NH_4^+[262] or pyH^+[265] salts. X-ray analysis of $(NH_4)_6[Mo_4S_4(NCS)_{12}]\cdot 10H_2O$ revealed C_{3v} symmetry in the cuboidal core with two sets of Mo–Mo distances, 2.791 Å and 2.869 Å.[263] Using similar procedures, Mo/W mixed-metal $[Mo_xW_{4-x}(NCS)_{12}]^{6-}$ cubes ($x = 1,2,3$) have been prepared. X-ray analysis of $(Me_2NH_2)_6[MoW_3S_4(NCS)_{12}]\cdot 0.5H_2O$ revealed T_d symmetry of the core with M–M distances (the positions of Mo and W are occupied almost statistically) 2.83–2.85 Å.[119]

Reaction of the $Mo_4S_4^{4+}$ aqua ion with concentrated aqueous ammonia gives 60e $[Mo_4S_4(NH_3)_{12}]Cl_4\cdot 7H_2O$ (Mo—Mo 2.79–2.89 Å) isolated in a 33% yield. In air (and with acid) $[Mo_4S_4(H_2O)_{12}]^{5+}$ is restored.[266]

Reaction of $[Mo_4S_4(H_2O)_{12}]^{5+}$ with $KHB(pz)_3$ is not accompanied by a redox process, and gives red–brown $[Mo_4S_4(HB(pz)_3)_4(pz)]$ as the product (80%). The core has C_{2v} symmetry and the Mo_4 tetrahedron is compressed along the pyrazolyl-bridged edge (Mo—Mo 2.659 Å), while five other Mo—Mo are 2.92 Å.[272]

In the presence of some ligands, cluster degradation may take place. Thus, an attempt to coordinate oxalate to $[Mo_4S_4(H_2O)_{12}]^{5+}$ gives only $[Mo_3S_4(C_2O_4)_3(H_2O)_3]^{2-}$.[97] Reaction with tacn depends strongly on pH: at $pH \leq 2$, triangular $[Mo_3S_4(tacn)_3]^{4+}$ forms, whereas without acidification, anti-$[Mo_2O_2S_2(tacn)_2]^{2+}$ is obtained.[143]

4.12.6.4.3 Complexes with edta

Reduction of $Na_2[Mo_2O_2S_2(edta)_2]$ with $NaBH_4$ in aqueous solution, followed by acidification and air-oxidation, gives dark-green crystals of $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$. The hexadentate ethylenediaminetetraacetate (edta) ligands are tridentate to each of two Mo's. The Na^+ counter ion can be exchanged for Ca^{2+}, and the crystal structure of $Ca_{1.5}[Mo_4S_4(edta)_2]\cdot 13H_2O$ has been determined (Mo—Mo 2.76–2.88 Å). In the same way green $Na_{2.5}H_{0.5}[Mo_4Se_4(edta)_2]\cdot 10H_2O$ was obtained from $[Mo_2O_2Se_2(edta)_2]^{2-}$ (Mo—Mo 2.81–2.92 Å). The 3− ion is reduced by $NaBH_4$ into orange $[Mo_4S_4(edta)_2]^{4-}$, of which Na^+, Mg^{2+} and Mn^{2+} salts could be obtained. In $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ the Mo—Mo distances were found to fall in a narrow range of 2.77–2.79 Å. Bromine water oxidizes the 3− ion into red $[Mo_4S_4(edta)_2]^{2-}$, isolated in the form of Na^+, NH_4^+ and Ca^{2+} salts (Mo—Mo 2.74–2.87 Å) in $Na_2[Mo_4S_4(edta)_2]\cdot 6H_2O$. The mean values of Mo—Mo bond lengths and volumes of Mo_4 tetrahedral decrease on going from a 58e to 60e cluster. Both $Mg_2[Mo_4S_4(edta)_2]\cdot 20H_2O$ and $Mg[Mo_4S_4(edta)_2]\cdot 12H_2O$ were found to be diamagnetic whereas $Na_3[Mo_4S_4(edta)_2]\cdot 10H_2O$ is paramagnetic ($S = 1/2$ ground state). Aquation of $[Mo_4S_4(edta)_2]^{3-}$ in conc. HCl gives $[Mo_4S_4(H_2O)_{12}]^{5+}$.[266] The $[Mo_4Se_4(edta)_2]^{3-}$ complex is oxidized electrochemically into the unstable brown 2-cluster, and is reduced with $Na_2S_2O_4$ into orange–red $[Mo_4Se_4(edta)_2]^{4-}$.[267] Studies on the ^{77}Se NMR of the mixed valence cluster $[Mo_4Se_4(edta)_2]^{3-}$ are consistent with the presence in solution of a valence-trapped species Mo^{III}_3-Mo^{IV} with a lifetime in excess of 10^{-5}s. However, studies on the ^{95}Mo and ^{77}Se NMR of $[Mo_4Se_4(edta)_2]^{n-}$ need also to be considered.[267]

4.12.6.4.4 Complexes with S-donors

These ligands all have a strong tendency to stabilize the 58e cluster cores with 6+ charge. Dithiophosphates $(RO)_2PS_2^-$ are available through self-assembly reactions. Thus, $MoCl_3\cdot 3H_2O$ reacts with P_4S_{10} in EtOH to give $[Mo_4OS_3(\mu\text{–}dtp)_3(dtp)_3]$ (designated as the 3:3 isomer), whereas in the presence of HCl, a mixture of another isomer, $[Mo_4OS_3(\mu\text{–}dtp)_2(dtp)_4]$ (2:4), and $[Mo_4S_4(\mu\text{–}dtp)_2(dtp)_4]$, is obtained. Treating a mixture of $[Mo(CO)_6]$ and $[MoCl_5]$ with P_4S_{10} in ethanol gives $[Mo_4O_{0.4}S_{3.6}(\mu\text{–}dtp)_3(dtp)_3]$. Comproportionation of $[W(CO)_6]$ with $Na_2[WO_4]$ in ethanol in the presence of P_4S_{10} gives the $W_4S_4^{6+}$ cluster, $[W_4S_4(\mu\text{–}dtp)_2(dtp)_4]$, whereas when $[W_2Cl_9]^{3-}$ serves as the unique W source, with the same reagents, the 3:3 isomer is obtained. Crystal structures of all these clusters have been determined.[273] The cluster $[Mo_4S_4(\mu\text{–}dtp)_2(dtp)_4]$ can also be made by refluxing $[Mo(CO)_6]$ with $(EtO)_2P(S)S\text{-}S(S)P(OEt)_2$ diethyldithiophosphate disulfide (dtp_2) in toluene, 20% yield.[274]

The bridging dtp ligand in $[Mo_4S_4(\mu\text{–}dtp)_2(dtp)_4]$ was found to be labile enough to be substituted by acetate, thus generating paramagnetic $[Mo_4S_4(\mu\text{–}O_2CMe)_2(dtp)_4]$.[273] A benzoate derivative $[Mo_4S_4(\mu\text{–}O_2CPh)_2(dtp)_4]$ was prepared in a similar manner.[275] A [3 + 1] cluster assembly from $[Mo_3S_4(\mu\text{–}dtp)(dtp)_4(H_2O)]$ and $[Mo(CO)_6]$ in an acetic acid/acetic anhydrate mixture, or from $[Mo_3S_7(dtp)_3]Cl,PPh_3$, $[Mo(CO)_6]$ and NH_4dtp, gives a 59e $Mo_4S_4^{5+}$ derivative, formulated as $H[Mo_4S_4(\mu{-}O_2CMe)_2(dtp)_4]$.[276] X-ray crystal structure analysis of this product and its 1:1 acetone solvate failed to localize the extra hydrogen atom, but the formulation given is supported by ^1H NMR (including H^+/D^+ exchange observation), ESR and XPS data.[276] Quantum chemical treatment of the bonding in these cluster has been given.[273,274]

The [3 + 1] assembly strategy of cuboidal clusters was also successful in preparation of black, air-stable $[Mo_4S_4(\mu{-}R_2PS_2)_2(R_2PS_2)_4]$ from $[Mo_3S_4(R_2PS_2)_4]$, $[Mo(CO)_6]$ and $(R_2PS_2)_2$ (R = Et, 37%; *n*-Pr, 31%), in toluene. The clusters are paramagnetic with $\mu_{eff} = 1.05$ B.M. for R = Et, and $\mu_{eff} = 1.40$ B.M. for R = *n*-Pr. The cube $[Mo_4S_4(\mu{-}Et_2PS_2)_2(Et_2PS_2)_4]$ is antiferromagnetic with μ_{eff} only 0.54 B.M. at 80 K. In the case of Mo/W mixed clusters, 3:3 isomers $[Mo_3WS_4(\mu{-}dtp)_3(dtp)_3]$ and $[Mo_2W_2\ S_4(\mu{-}dtp)_3(dtp)_3]$ have been prepared.[277–279]

Heating $[Mo(CO)_6]$ with thiuramdisulfides $[R_2NCS_2]_2$ in toluene in 1:2 ratio gives $[Mo_4S_4(\mu{-}R_2NCS_2)_2(R_2NCS_2)_4]$ (R = Et; *n*-Oct).[274] Prolonged heating of $Mo_2(dtc)_6$ (structure unknown) in toluene gives the same cuboidal cluster, 20–30% yield. The crystal structure of $[Mo_4S_4(\mu{-}Et_2NCS_2)_2\ (Et_2NCS_2)_4]$ shows that the two Mo—Mo bonds, spanned by the dtc ligands, contract to 2.74 Å, while the other four bonds are 2.85–2.87 Å. The ^1H NMR spectrum in solution shows two non-equivalent dtc, thus indicating retention of the solid state structure in solution. It is paramagnetic ($\mu_{eff} = 2.96\ \mu_B$).[280]

Other synthetic routes to dithiocarbamates $Mo_4S_4L_6$ are: (i) from $[MoCl_3(CH_3CN)_3]$ and R_2NCS_2K (R = Et, *n*-Oct), ~50% yield; (ii) from $(NH_4)_2[MoCl_5(H_2O)]$ and Et_2NCS_2Na (25%); (iii) thermolysis of $[Mo(Et_2NCS_2)_4]$ in toluene; (iv) reduction of $[Mo_2S_4(R_2NCS_2)_2]$ with $NaBH_4$ or $LiBEt_3H$ (R = *n*-Pr, *n*-Bu, *n*-Oct, yields vary); (v) [3 + 1] cluster assembly from $[Mo_3S_4\ (n\text{-}Pr_2NCS_2)_4]$, $[Mo(CO)_6]$ and $(n\text{-}Pr_2NCS_2)_2$ (70%).[274] One or both bridging ligands in $[Mo_4S_4(\mu{-}Et_2NCS_2)_2(Et_2NCS_2)_4]$ can be exchanged for $EtOCS_2^-$, giving a mixture of $[Mo_4S_4(\mu{-}Et_2NCS_2)(\mu{-}EtOCS_2)(Et_2NCS_2)_4]$ and $[Mo_4S_4(\mu{-}EtOCS_2)_2(Et_2NCS_2)_4]$. Xanthates of the type $[Mo_4S_4(\mu{-}ROCS_2)_2\ (ROCS_2)_4]$ are made by: (i) reaction of $[Mo(CO)_6]$ with $(ROCS_2)_2$ (R = Et, *n*-Oct); (ii) refluxing $[Mo(ROCS_2)_4]$ in toluene (R = *n*-Oct). The formation of the 2:4 isomer for R = Et is confirmed by an incomplete X-ray study and ^1H NMR data. A green thioxanathate, $[Mo_4S_4(n\text{-}C_{12}H_{25}SCS_2)_6]$, was prepared in a low yield (11%) from $[Mo(CO)_6]$ and $(n\text{-}C_{12}H_{25}SCS_2)_2$.[274]

Cyclic voltammograms of $Mo_4S_4L_6$(L = dithiophosphate, dithiocarbamate, xanthate, thioxanthate) reveal two quasi-reversible one-electron reduction waves, corresponding to the formation of the $Mo_4S_4^{5+}$ and $Mo_4S_4^{4+}$ states, and two quasi-reversible one-electron oxidation waves suggesting the formation of $Mo_4S_4^{7+}$ and $Mo_4S_4^{8+}$ cores. The potentials vary as much as 670 mV depending on the ligand bridging the cube with the relative ease of reduction as follows: $RSCS_2^- > ROCS_2^- > (RO)_2PS_2^- > R_2NCS_2^-$.[274]

4.12.6.4.5 Cyanides

High-temperature reactions of polymeric $\{M_3Q_7Br_4\}_x$ (M = Mo, W; Q = S, Se) or $[Mo_3Te_7I_4]$ with KCN give cuboidal clusters in high yields as cyano complexes $[M_4Q_4(CN)_{12}]^{6-}$ (M = Mo, W; Q = S, Se) or $[Mo_4Te_4(CN)_{12}]^{7-}$. The latter is oxidized by bromine water into $[Mo_4Te_4(CN)_{12}]^{6-}$. The tungsten analog $[W_4Te_4(CN)_{12}]^{6-}$ is made by heating WTe_2 with KCN, while in a KNCS melt chalcogen exchange takes place and $[W_4S_4(CN)_{12}]^{6-}$ is formed.[281] The products can be extracted into water and crystallized as K^+, Cs^+ or NH_4^+ salts. Insoluble precipitates are obtained immediately with 3*d* metal cations, and well-shaped single crystals grown by the gel diffusion technique. The structures of $[M(H_2O)_4][W_4Q_4(CN)_{12}]\cdot xH_2O$ (M = Co, Q = Te; M = Mn, Q = S)[282,283] are polymeric (M is octahedral) with a high degree of porosity. All these cyanide clusters have been structurally characterized. It was found that the M—M bonds decrease systematically on going from M_4Te_4 to M_4S_4. The symmetry of the cluster core was found to be sensitive to the nature of the counter ion. In isostructural $(NH_4)_6\ [M_4Q_4(CN)_{12}]\cdot 6H_2O$ (M = Mo, W; Q = S, Se)[284] the cores have ideal T_d symmetry (W—W is 2.845 Å); in $KCs_5[W_4S_4(CN)_{12}]\cdot 2H_2O\cdot CH_3OH$ lower C_1 symmetry is observed (W—W 2.80–2.90 Å),[281] and in $K_6[W_4S_4(CN)_{12}]\cdot 2H_2O\cdot 2CH_3OH$ the core is C_2 (W—W 2.83–2.91 Å).[285] While $K_6[W_4Se_4(CN)_{12}]\cdot 6H_2O$ provides an example of a cuboidal core with C_{2v} symmetry (W—W 2.88 Å),[281] C_s symmetry is found in $K_7[Mo_4Te_4(CN)_{12}]\cdot 12H_2O$ (Mo—Mo bonds 2.97–3.00 Å),[281] and in $Cs_6[Mo_4\ Te_4(CN)_{12}]\cdot 6H_2O$ (C_1 symmetry) the Mo—Mo bonds vary within the range 2.860–3.055Å.[281] CV experiments on the cyanide clusters show two reversible or quasi-reversible redox waves corresponding to the 6−/7− and 7−/8− couples. The ease of reduction decreases from Mo to W and from S to Te.

All these clusters are stable in air both as solids and in solutions (pH 2–10 at 95 °C) with no tendency to lose core atoms. Despite the distortions observed in the solid state, the ^{77}Se, ^{125}Te, ^{183}W NMR studies on $[W_4Q_4(CN)_{12}]^{6-}$ demonstrate the equivalence of metal and chalcogen atoms in solution.[281] It seems that $[Mo_4S_4(CN)_{12}]^{8-}$, reported as a product from reaction between MoS_3 and aqueous KCN, must now be reformulated as the 6-charged cluster.[195]

4.12.6.4.6 Cyclopentadienyls

Several η^5–cyclopentadienyl derivatives of Mo_4S_4 and Mo_4Se_4 clusters have been prepared. The complex $[(\eta^5\text{–}{}^iPrC_5H_4)MoCl_2]_2$ reacts with LiHS[286] or LiH Se,[77] giving $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4Q_4]$ in high yields. Another route makes use of the [2 + 2] approach, based on reaction of $[(\eta^5\text{–}C_5H_5)_2Mo_2(\mu\text{–}CH_3CHCH_2S_2)_2]$ with 2–3 equivalents of $[(\eta^5\text{–}C_5H_5)_2Mo_2(CO)_4]$; an attempt to make a $Mo_2W_2S_4$ derivative using $[(\eta^5\text{–}C_5H_5)_2W_2(CO)_4]$ failed. Yields vary between 20% and 40%, $[(\eta^5\text{–}MeC_5H_4)_2(\eta^5\text{–}C_5H_5)_2Mo_4S_4]$ (from $[(\eta^5\text{–}MeC_5H_4)_2Mo_2(CO)_4)]$; $[(\eta^5\text{–}MeC_5H_4)_4$-$Mo_4S_4]$ and $[(\eta^5\text{–}MeC_5H_4)_2\ (\eta^5\text{–}C_5Me_5)_2Mo_4S_4]$ from $[(\eta^5\text{–}C_5Me_5)_2Mo_2(CO)_4]$. The cube $[(\eta^5\text{–}MeC_5H_4)_2(\eta^5\text{–}C_5H_5)_2Mo_4S_4]$ is also obtained from $[(\eta^5\text{–}C_5H_5)Mo(S)(SH)]_2$ and $[(\eta^5\text{–}MeC_5H_4)_2\ Mo_2(CO)_4]$ in 41% yield.[287] It was possible to generate mixed $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4S_nSe_{4-n}]$ in solution but individual members could not be isolated.[76] The cube $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4S_4]$ (Mo—Mo 2.887 Å) can be further oxidized by treatment with dilute acids to $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4Q_4](BF_4)$ (Mo—Mo 2.856 Å) or, with iodine, one step further, into $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4Q_4](I_3)_2$ (Mo—Mo 2.749 Å).[286] Electrochemically, both the sulfide and selenide clusters undergo reversible redox interconversions between 58e, 59e and 60e clusters; with the Se species the more readily oxidized. Measured against Fc^+/Fc couple in THF, $E_{1/2}$ values for $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4S_4]$ clusters are −0.82 V (+1/0), −0.22 V (+2/+1); and for $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4Se_4]$ −0.91 V and −0.32 V.[77,286]

An interesting series of "soft" salts with big cations and big anions was prepared by oxidation of $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4Q_4]$ (Q = S, Se) with $[Os_6(CO)_{18}]$, $[Fe_4S_4(NO)_4]$, $[Mo(S_2C_2(CF_3)_2)_3]$, $[Ni(S_2C_2(CN)_2)_2]$ and TCNQ. In all cases transfer of only one electron takes place. Crystal structures of $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4S_4](TCNQ)$, $[(\eta^5\text{–}{}^iPrC_5H_4)_4Mo_4S_4][Fe_4S_4(NO)_4]$ and $[(\eta^5\text{–}\ {}^iPr\text{-}C_5H_4)_4Mo_4S_4]_2[Os_6(CO)_{18}]$ were determined. The geometry of the Mo—Mo core depends very much on the crystal packing forces and it seems that the non-bonding S···S distances are more important than Mo—Mo interactions.[77]

Reactions of $[(\eta^5\text{–}C_5H_5)_3Mo_3S_4](pts)$ with $[M(CO)_3(CH_3CN)_3]$ (M = Cr, Mo, W) were reported to give moderate yields of $[(\eta^5\text{–}C_5H_5)_3Mo_3M(CO)_3S_4](pts)$ ($pts^- = p\text{-}CH_3C_6H_4SO_3^-$), which can be regarded as derivatives of $Mo_4S_4^{4+}$. A crystal structure of the Mo_3WS_4 cluster indicates Mo—Mo 2.87–2.88 Å, Mo—W 2.96–2.98 Å.[198]

4.12.6.4.7 Solid-state chalcogenides and chalcohalides

Solid-state compounds $Mo_4S_4X_4$ (X = Cl, Br, I) and $M'Mo_4Q_8$ (M′ = Al, Ga, Q = S; M′ = Ga, Q = Se) are known to contain the $Mo_4Q_4^{4+/5+}$ cores, with each Mo octahedrally coordinated by three chalcogen and three halogen atoms, or six chalcogen atoms. Their tungsten analogs are not known.[288–291]

4.12.6.4.8 Electron-poor and electron-rich cube clusters

Electron depletion beyond 58e (i.e., $M_4Q_4^{7+}$ and higher) generally leads to degradation of the cuboidal core. However, a unique series of 52e cuboidal clusters has been made, based on (p-tolylimido)derivatives of Mo^V and W^V. In the structure of $[Mo_4S_4(tolN)_4(S_2P(OEt)_2)_4]$ each metal atom is bound to one terminal group $CH_3C_6\ H_4N$=, one chelating dtp and three sulfur atoms of the core. As there are only four electrons to form M—M bonds, the two such bonds (2.862 Å) are localized on the opposite edges of the Mo_4 tetrahedron, while the other four distances are non-bonding at 3.69 Å. There is a marked tendency to dissociate in solution into two dimeric molecules $[Mo_2(tolN)_2(\mu\text{–}S)_2(S_2P(OEt)_2)_2]$; the dissociation constant was determined to be 0.00063 M^{-1} in CH_2Cl_2.[292] In the case of $[Mo_4S_4(tolN)_4(S_2CN({}^iBu)_2)_4]$ this tendency to dissociate is so high that it allowed isolation and crystal structure determination of both the Mo_4S_4 cluster and its dissociation product, $[Mo_2S_2(tolN)_2(S_2CN({}^iBu)_2)_2]$. The dissociation is facilitated not only by the lack of M—M bonding between the two dimeric units within the cluster, but also by long Mo–S distances (2.7–2.8 Å) uniting them.[293] Treatment of $[Mo_4S_4(tolN)_4(S_2P(OEt)_2)_4]$ with CF_3COOH leads to similar dissociation, the product being an SH-bridged dimer, $[Mo_2(tolN)_2(\mu{-}S)(\mu{-}SH)(\mu{-}CF_3COO)(S_2P(OEt)_2)_2]$.[295] An oxo/imido cluster, $[Mo_4S_4(tolN)_2O_2(S_2P(OEt)_2)_4]$ has also been prepared.[294] The structure of $[W_4S_4(tolN)_4(S_2P(OEt)_2)_4]$ has been determined.[296]

As an example of a 54e cluster, $[W_4S_4(en)_4(S)_4]S$ has been prepared by a solvento-thermal reaction from $[W(CO)_6]$, K_2S_4 and ethylenediamine at 300 °C. It gives air-stable black–red crystals (31% yield), insoluble in DMF and water. It has a W_4S_4 cuboidal skeleton (W—W, 2.801–2.878 Å; W—μ_3S, 2.36–2.41 Å) and unusually S^{2-} as counter ion (there are contacts with en through hydrogen bonds, N—H···S, 2.36–2.41 Å). Although the W–S distances (2.54 Å) to the terminal sulfur are long for what is supposed to be a double bond, an alternative formulation as 58e $[W_4S_4(en)_4(SH)_4]S$, which is more consistent with the observed geometry, was not favored as no S—H bands appeared in the IR spectrum. The magnetic susceptibility of the cluster obeys the Curie–Weiss law with $\mu_{eff} = 2.67$ BM at 400 K.[297]

An example of a 68e electron-rich cube is red $K_8[Mo_4S_4(NO)_4(CN)_8]\cdot 4H_2O$, obtained in a low yield from $[Mo_4(NO)_4(S_2)_6(\mu_4{-}O)]^{2-}$ and KCN. The electron count leaves the possibility of formation of two Mo—Mo bonds, and this is supported by two short (2.99 Å) Mo–Mo distances on opposite edges of the tetrahedron Mo_4; the other four distances are non-bonding (3.67 Å).[298] The anion $[Mo_4(NO)_4(S_2)_6(\mu_4{-}O)]^{2-}$ is a 72e species, and the 18e rule is fulfilled here without the necessity of M—M bonding (Mo—Mo 3.31 and 3.94 Å).[299]

4.12.6.4.9 Raft-type$[M_4(\mu_3{-}S)_2(\mu{-}S)_4]^{2+}$ clusters and their derivatives

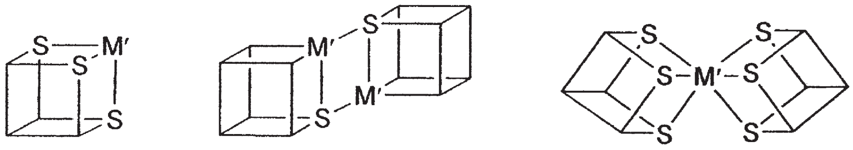
Treatment of $(NH_4)_2[Mo_3S_7(S_2)_3]$ by PMe_3 in butylamine gives a raft-type Mo_4 cluster $[Mo_4(\mu_3{-}S)_2(\mu{-}S)_4(SH)_2(PMe_3)_6]$.[300] Its tungsten analog has been obtained by treating *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with 2-equivalents of $(Me_3Si)_2S$ in methanol as $[W_4(\mu_3{-}S)_2$-$(\mu{-}S)_4(SH)_2(PMe_2Ph)_6]$.[301] These 58e clusters have 10e sufficient to form five M—M bonds, including one between the hinge atoms. There is little variation between Mo—Mo (2.83–2.85 Å); and W—W (2.81–2.84 Å) distances. The presence of an S–H ligand coordinated to two opposite wingtip metal atoms is deduced from: (i) observation of ν(S–H) in the IR spectra (2,516 cm^{-1} for Mo_4, 2,512 cm^{-1} for W_4); (ii) long M—SH bond distances (2.410 Å for Mo_4, 2.390 Å for W_4); (iii) in the case of the W_4 cluster, the position of the hydrogen atom was determined from X-ray data (S–H 1.28 Å, angle W–S–H 116.4°).[300,301]

The SH group can be exchanged for chlorine by heating with $SnCl_2$ in THF, giving $[Mo_4(\mu_3{-}S)_2(\mu{-}S)_4Cl_2(PMe_3)_6]$ and $[W_4(\mu_3{-}S)_2(\mu{-}S)_4Cl_2(PMe_2Ph)_6]$.[302] This transformation causes only small changes in the M_4 skeleton. The $[W_4(\mu_3{-}S)_2(\mu{-}S)_4Cl_2\ (PMe_2Ph)_6]$ product undergoes 2e oxidation by Ag^+ triflate, and $[W_4(\mu_3{-}S)_2(\mu{-}S)_4Cl_2\ (PMe_2Ph)_6](CF_3SO_3)_2$ was isolated. Although for this 56e cluster a raft-type metal connectivity is preserved, the core no longer has C_{2h} symmetry, but is distorted, with a pair of opposite W—W bonds elongated to 2.937 Å, another pair shortened to 2.738 Å, and only the W—W hinge essentially unchanged at 2.833 Å.[301] Reduction of $[W_4(\mu_3{-}S)_2(\mu{-}S)_4Cl_2(PMe_2Ph)_6]$ with an excess of sodium amalgam gives $[W_4(\mu{-}S)_6(PMe_2Ph)_4]$ in a low yield. It contains an adamantane-like core, unprecedented for transition-metal chalcogenide clusters. There are 12 electrons in this W^{III} derivative giving six M—M bonds (W—W 2.634 Å). Disregarding the W—W bonds, tungsten is tetrahedrally coordinated (angle S–W–P 89.2°, S–W–S 120.0°).[301]

4.12.6.5 Heterometallic Derivatives of $[Mo_3Q_4(H_2O)_9]^{4+}$ and $[W_3Q_4(H_2O)_9]^{4+}$

Cube derivatives of the incomplete cubes $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) formed by the uptake of a heterometal have been prepared. Those of $[Mo_3S_4(H_2O)_9]^{4+}$ are most extensive, with exceptions metals from Groups 3–5, Mn/Tc (Group 7), Ag/Au (Group 11), and Zn (Group 12). Fewer derivatives (about half the number) are obtained from $[W_3S_4(H_2O)_9]^{4+}$.

In this chemistry the heteroatoms M′ can occupy the vacant single cube site of $[Mo_3S_4(H_2O)_9]^{4+}$ to give **A**. When M′ is tetrahedral an edge-linked double cube **B** can form. When M′ is octahedral a corner-shared double-cube **C** is redox accessible.[7] Key atoms only are used to illustrate these different structures **A**–**C** (Scheme 2).



A B C

Scheme 2

The reaction giving **B** is a dimerization process. Known examples are with M′ = Co, Pd, Cu and Ni (the latter with W containing trinuclear clusters). The conversion **A** → **B** occurs when the accompanying anions are non-complexing, e.g., pts^-, ClO_4^- and M′ is weakly coordinated by solvent H_2O. Reformation of **A** occurs on addition of, e.g., CO, PR_3, Cl^-, NCS^- to coordinate to M′ in **B**. Excess $[Mo_3S_4(H_2O)_9]^{4+}$ and a reducing agent (BH_4^- or H_3PO_2) are required for the conversion of **A** → **C**, and with oxidants, e.g., $[Fe(H_2O)_6]^{3+}$ and $[Co(dipic)_2]^-$ the reverse action is observed. From X-ray crystallography short Mo—Mo or W—W bonds (2.5–2.8 Å) are present in all **A**, **B**, and **C** cases. Whereas short Mo/W to heterometal M′ bonds ~2.7 Å are observed for transition metals in **A** and **B**, long non-bonding >3.5 Å separations are a feature of **A** and **C** when M′ is from Groups 12–15, as will emerge in different sections considered below.

Because all known corner-shared double cubes **C** are 8+ in charge, a formalism $Mo_3S_4^{4+}M'^0Mo_3S_4^{4+}$ has been found to be a useful approximation.[303] Such cubes are most common for M′ from Groups 12–15, and $[Mo_7S_8(H_2O)_{18}]^{8+}$ (already considered) is an exception in that an alternative distribution of charge seems to apply. In an extension to this approach, single cubes (M′ = Co, Ni, Pd, Cu) have short Mo—M′ consistent with metal–metal bonding and the formalism $Mo_3S_4^{4+}M'^0$. Assignments M'^0 are consistent with the use of the metallic state in preparative procedures. Single cubes with M′ from Groups 12–13 are written as, e.g., $Mo_3S_4^{4+}Hg^0$, $Mo_3S_4^{4+}Ga^I$, $Mo_3S_4^{4+}Ge^{II}$ and $Mo_3S_4^{4+}Sb^{III}$.[7] Three categories of M′ are apparent, those of Group 6, late transition metals, and post-transition metals.

Extensive use is made of Dowex 50W-X2 cation-exchange column chromatography in the purification of aqua ion derivatives of $[M_3Q_4(H_2O)_9]^{4+}$. Acidic solutions are required to avoid acid dissociation steps involving H_2O ligands, which can result in aggregation steps. Acids such as Hpts (*p*-toluenesulfonic acid) are widely used, where the weakly coordinating properties of pts^- approach those of ClO_4^-, which is generally regarded as the weakest common donor anion, but can also function as an oxidant. Almost all heterometallic cubes are air-sensitive, and need to be handled e.g., under N_2.

4.12.6.5.1 Group 6 (Cr)

Group 6 examples with M′ = Mo, W, i.e., the Mo_4S_4 and Mo_3WS_4 cubes, have already been considered. Although $[Mo_3S_4(H_2O)_9]^{4+}$ does not react with Cr metal, it reacts with $[Cr(H_2O)_6]^{2+}$ giving brown $[Mo_3CrS_4(H_2O)_{12}]^{4+}$, UV–vis peaks λ(nm) ($\varepsilon(M^{-1}\,cm^{-1})$) at 255 (12,000), 510 (387) in 2 M Hpts.[304] It is air-sensitive and decays into $[Mo_3S_4(H_2O)_9]^{4+}$ and $[Cr(H_2O)_6]^{3+}$. The aqua ions $[Cr(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ are known for their extreme lability and inertness, and H_2O-exchange rate constants with solvent H_2O are $\sim 10^9\,s^{-1}$ and $\sim 10^{-6}\,s^{-1}$ respectively. An assignment $[Mo^{III}_3Cr^{III}S_4(H_2O)_{12}]^{4+}$, analogous to the well-characterized $[Mo^{III}_4S_4(H_2O)_{12}]^{4+}$ is considered here. Kinetic studies on the NCS^- substitution of H_2O assigned to reactions at the Cr were found to be quite fast ($25.2\ M^{-1}\,s^{-1}$), suggesting labilization of the Cr^{III} by three attached μ_3–sulfido ligands.[304] The $[H^+]^{-1}$ dependence indicates an involvement of a second H_2O on the Cr, which is therefore assigned an octahedral coordination. The reaction of $[(\eta^5\text{–}C_5H_5)_3Mo_3S_4](pts)$ with $[Cr(CO)_3(CH_3CN)_3]$ produces $[(\eta^5\text{–}C_5H_5)_3Mo_3Cr(CO)_3)S_4](pts)$.[198]

4.12.6.5.2 Group 7 (Re)

No Mn (or Tc) derivatives have been prepared. The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Re(CO)_5Br]$ yields $[Mo_3Re(CO)_3S_4(H_2O)_9]^{5+}$ in small yields.[305] Analyses and the X-ray crystal structure of

$(Me_2NH_2)[Mo_3Re(CO)_3S_4(NCS)_6]$ are consistent with formation of an Mo_3ReS_4 single cube. On heating $[Mo_3S_4(H_2O)_9]^{4+}$ is reformed and can be recovered by Dowex chromatography.

4.12.6.5.3 Group 8 (Fe, Ru, Os)

The reaction of Fe wire with $[Mo_3S_4(H_2O)_9]^{4+}$ in HCl or $HClO_4$ gives red–purple $[Mo_3FeS_4(H_2O)_{10}]^{4+}$, UV–vis peaks λ(nm) ($\varepsilon(M^{-1}\,cm^{-1})$) in 2 M $HClO_4$ 236 (10,390), 503 (730), 603 (448), 970 (122).[306,307] The crystal structure of $[Mo_3FeS_4(H_2O)_{10}]$ $(pts)_4\cdot 7H_2O$ has been determined confirming a tetrahedrally coordinated Fe site.[308] The kinetics of the O_2 oxidation have been interpreted in terms of a spectrophotochemically detected intermediate $Mo_3Fe(O_2)S_4{}^{4+}$, which decays further to give Fe^{2+} and $[Mo_3S_4(H_2O)_9]^{4+}$.[309] No reaction is observed between $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and CO[310] or the water-soluble phosphine $P(C_6H_4SO_3)_3{}^{3-}$.[311] In HCl solutions, the Fe site coordinates Cl^- to give $[Mo_3(FeCl)S_4(H_2O)_{10}]^{3+}$ in a fast reaction (complete within 2–3 ms); stability constant 560 M^{-1}.[307] The air-sensitivity can result in handling difficulties. Although no ESR spectrum is observed down to 4.2 K in 2M HCl or 2M Hpts,[307] a solid sample of $[Mo_3FeS_4(H_2O)_{10}](pts)_4\cdot 7H_2O$ was found to be paramagnetic (μ_{eff} 2.83 BM at 22 °C). Magnetic susceptibility data, at temperatures 2–270 K, were fitted to a model having a $Fe^{II}Mo^{IV}$-$Mo^{III}{}_2$ core with $J_1(Mo—Mo)/k_B = -25$ K, $J_2(Mo–Fe)/k_B = -75$ K (k_B is the Boltzmann constant).[312] However, Mössbauer spectra at 4.2 K (frozen solutions in 2 M $HClO_4$) give a chemical isomer shift $\delta = 0.52$ mm s^{-1}, quadrupole splitting $\Delta Eq = 0.22$ s^{-1} and linewidth $\Gamma = 0.29$ mm s^{-1} suggesting the presence of Fe^{III} and $S = 3/2$, effectively spin-coupled at 4.2 K.[307] With conc. NH_3, black–purple crystals of $[Mo_3Fe(H_2O)S_4(NH_3)_9]Cl_4$ separate, and give Mo—Mo 2.68–2.69 Å and Mo—Fe 2.77–2.83 Å (Figure 45).[306]

A butterfly-type cluster $[(\eta^5{-}C_5H_5)_2Mo_2(CO)_2(\mu_3{-}S)_2Fe_2(CO)_6]$ reacts with thiophene (large excess) at 150 °C, giving a low yield of cuboidal $[(\eta^5{-}C_5H_5)_3Mo_3Fe(SH)S_4]$ (Mo—Mo 2.8–2.87 Å, Mo—Fe 2.7–2.81 Å).[313]

No Ru or Os derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$ have been prepared. However, the cluster $[(\eta^5{-}MeC_5H_4)_3Mo_3S_4](pts)$ reacts with $[Ru(CO)_3(COD)]$, generated *in situ* from $[Ru_3(CO)_{12}]$ and 1,5-COD (cyclooctadiene), to give the brown 60e cuboidal $[(\eta^5{-}MeC_5H_4)_3Mo_3Ru(CO)_2S_4](pts)$, (Mo—Mo 2.85 Å, Mo—Ru 2.88 Å). Solutions in CH_2Cl_2 gradually lose CO to give $[(\eta^5{-}MeC_5H_4)_3Mo_3S_4Ru_2(\mu{-}CO)_3](pts)_2$, with two Mo_3RuS_4 units held together by a Ru—Ru bond (2.70 Å) bridged by three CO groups.[314]

Similarly, $[(\eta^5{-}MeC_5H_4)_3Mo_3Os(CO)_2S_4](pts)$ has been prepared and characterized by ^1H NMR, FAB–MS and IR spectra.[314]

4.12.6.5.4 Group 9 (Co, Rh, Ir)

Metallic Co reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ to give a brown air-sensitive solution, from which crystals of the edge-linked double cube $[\{Mo_3CoS_4(H_2O)_9\}_2](pts)_8\cdot 20H_2O$ have been obtained (Co—Co 2.498 Å).[315] No clear-cut distinction between the single and double cubes has been possible in solution, e.g., by UV–vis spectra.[316] Notably in cation-exchange chromatography $[Mo_3S_4(H_2O)_9]^{4+}$ is eluted prior to the Co derivative, indicating retention of the double cube in solution. However, CO gives brown $[Mo_3Co(CO)S_4(H_2O)_9]^{4+}$ which is stable in air.[310] It has been demonstrated that $[Mo_2(\eta^5{-}C_5H_5)_2Co_2(CO)_4(\mu_4{-}S)(\mu_3{-}S)_2]$ undergoes transformation into a 60e cube $[(\eta^5{-}C_5H_5)_3\,Mo_3(CoCO)S_4]$ (Mo—Mo 2.83–2.84 Å, Co—Mo 2.74–2.76 Å) on treatment with

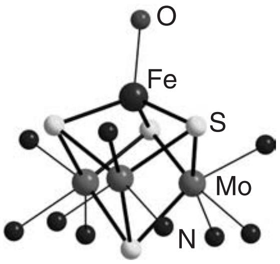


Figure 45 Structure of the $[Mo_3Fe(H_2O)S_4(NH_3)_9]^{4+}$ cation.

a CO/H_2 mixture (1:4, 150 °C, 200 psi, yield 15–30%), or by heating with py (150 °C, 15% yield).[313]

A color change to brown is observed on heating $[Mo_3S_4(H_2O)_9]^{4+}$ in 4 M HCl with $RhCl_3$ on a hotplate (~3 h).[303] The chloro product $[Mo_3RhCl_3S_4(H_2O)_9]^{4+}$ can be separated by Dowex cation-exchange chromatography. On diluting to 0.5M HCl and leaving to stand for a few days $[Mo_3RhS_4(H_2O)_{12}]^{7+}$ forms and is no longer eluted from a Dowex column.[315] A similar reaction is observed with $[W_3S_4(H_2O)_9]^{4+}$.[303] Other examples of Rh incorporation are with $[Mo_3(\eta^5\text{—}C_5Me_5Rh)S_4(H_2O)_9]^{4+}$, and $[Mo_3(\eta^5\text{—}C_5\ Me_5Rh)S_4(H_2O)_7O]_2{}^{4+}$.[317,318]

The reaction between $[M'(\mu\text{-}Cl)(cyclooctene)_2]_2$, $M' = Rh, Ir$, with $[(\eta^5\text{—}Me\ C_5H_4)_3Mo_3S_4]$ (pts) in the presence of PPh_3 in boiling methanol gives a mixture of cationic components, which were identified by FAB^+ mass-spectroscopy as, e.g., $[(\eta^5\text{—}MeC_5H_4)_3Mo_3(RhCl)S_4]^+$ and $[(\eta^5\text{—}MeC_5H_4)_3Mo_3Rh(pts)S_4]^+$.[314]

4.12.6.5.5 Group 10 (Ni, Pd, Pt)

Blue–green $[Mo_3NiS_4(H_2O)_{10}]^{4+}$, UV–vis spectrum in 2 M Hpts, λ(nm) (ε($M^{-1}cm^{-1}$)): 500 (200), 680 (610) can be prepared as follows: (i) reaction of metallic Ni with $[Mo_3S_4(H_2O)_9]^{4+}$ (in HCl, hours/days);[319] (ii) reaction of metallic Ni with $[Mo_3S_7Cl_6]^{2-}$;[323] (iii) reduction of Ni^{2+} with $NaBH_4$ in the presence of $[Mo_3S_4(H_2O)_9]^{4+}$;[320] (iv) one-pot synthesis from $(NH_4)_2MoS_4$ and Ni powder in 2 M HCl.[321] Method (i) has been used to prepare green $[W_3NiS_4(H_2O)_{10}]^{4+}$, and mixed Mo/W metal cubes $[Mo_2WNiS_4(H_2O)_{10}]^{4+}$ and $[MoW_2NiS_4(H_2O)_{10}]^{4+}$. The Ni is tetrahedral. All four aqua ions have been isolated as pts^- salts. Whereas Mo_3Ni and Mo_2WNi crystallize as single cubes $[M_3NiS_4(H_2O)_{10}](pts)_4{\cdot}7H_2O$, the two more tungsten-rich clusters give edge-linked double cubes, $[\{M_3NiS_4(H_2O)_9\}_2](pts)_8{\cdot}20H_2O$ (Ni—Ni 2.549 Å for MoW_2Ni; 2.560 Å for W_3Ni).[322]

Solutions of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ are stable in air over periods ~1 h. On heating in air Ni^{2+} and $[Mo_3S_4(H_2O)_9]^{4+}$ are obtained.[320] In hydrochloric acid Cl^- coordination to Ni occurs with the formation of green $[Mo_3(NiCl)S_4(H_2O)_9]^{3+}$ ($K = 97\,M^{-1}$),[320] which has been isolated as the supramolecular adduct with cucurbituril ($C_{36}H_{36}N_{24}O_{12}$), $\{[Mo_3(NiCl)S_4(H_2O)_7Cl_2](C_{36}H_{36}N_{24}O_{12})\}Cl{\cdot}13H_2O$ (Ni—Cl 2.238 Å).[323] When a solution of $[Mo_3(NiCl)S_4(H_2O)_9]^{3+}$ is treated with nitrilotriacetate, the Cl^- remains coordinated at the Ni site, and complexation proceeds at the Mo to give, after crystallization in the presence of Ca^{2+}, green $Ca_{2.5}[Mo_3(NiCl)(Hnta)(nta)_2]{\cdot}14H_2O$ (Ni—Cl 2.240 Å).[319]

Derivatization of the $Mo_3NiS_4{}^{4+}$ core is also achieved by reacting solid $[Mo_3(NiCl)S_4(H_2O)_9]Cl_3$ with dppe in methanol, giving dark-brown $[Mo_3(NiCl)S_4Cl_3\ (dppe)_3]$, 43% yield. The Cl coordinated at the Ni could not be replaced by CO, PMe_3 or PMe_2Ph.[324]

Substitution of seven different ligands including two water-soluble phosphines at the Ni site of $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ have been studied.[311] Formation rate constants ($M^{-1}s^{-1}$) monitored by stopped-flow spectrophotometry are: Cl^-, 9.4; Br^-, 14.6; I^-, 32.3; NCS^-, 44; CO, 0.66; $P(3\text{-}SO_3C_6H_4)_3{}^{3-}$, 58; 1,3,5-triaza-7-phosphaadamantane (PTA), 119. With the exception of CO these are consistent with an I_d dissociative interchange mechanism. From $H_2{}^{17}O$ studies it is concluded that $Ni{-}H_2O$ water-exchange rate constant on $[Mo_3NiS_4(H_2O)_{10}]^{4+}$ is $<10^3\,s^{-1}$. Similarly, formation equilibrium constants are (M^{-1}): Cl^-, 9.4; Br^-, 150; NCS^-, 690; CO, 5,150; $P(3\text{-}SO_3C_6H_4)^{3-}$, 8,900; PTA, 2,040. The Ni behaves as a soft metal,[311] in its coordination of C_2H_4[322] as well as CO[320,325] to give $[Mo_3(Ni(L))S_4(H_2O)_9]^{4+}$. The crystal structure of $[Mo_3Ni(CO)S_4(H_2O)_9]\ (pts)_4{\cdot}7H_2O$ has been determined.[325] Reaction of $[Mo_3NiSe_4(H_2O)_{10}]^{4+}$ with CO to give $[Mo_3\ Ni(CO)Se_4(H_2O)_9]^{4+}$ has also been reported.[310] The IR spectrum of $[Mo_3Ni(CO)S_4(H_2O)_9]^{4+}$ has a CO stretching band at 2,077 cm^{-1} (for the W analog), 2,045 cm^{-1}. On passing N_2 through solutions loss of CO and reformation of the aqua complex is observed.[321]

The coordination of ethylene is favored with an increasing number of tungsten atoms in the cores, and crystal structures of isostructural $[Mo_xW_{3-x}Ni(C_2H_4)S_4(H_2O)_9]\ (pts)_4{\cdot}0.5Hpts{\cdot}6H_2O$ ($x = 0{-}2$) have been determined.[322] ^1H NMR spectra show that the increase in the number of W atoms causes an upfield chemical shift, as electron density increases due to the weaker electron-withdrawing nature of the W atoms.[322]

The cluster $[Mo_3NiS_4(H_2O)_{10}](pts)_4{\cdot}7H_2O$ is antiferromagnetic ($\mu_{eff} = 0.11$ B.M. at 2.0 K, and 1.26 B.M. at 260.7 K). In terms of a $Ni^{II}Mo^{IV}Mo^{III}{}_2$ formalism, $J_1(Mo\text{—}Mo)/k_B = -35\,K$, $J_2(Mo{-}Ni)/k_B = -60K$.[312] However, from other studies the behavior of the tetrahedral Ni is closer to that of Ni^0 (substitution properties, coordination of π-acids). These contradictory interpretations reflect the difficulty in assigning classical oxidation states to metal atoms involved in M—M

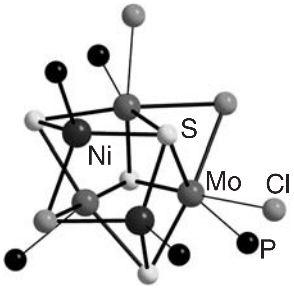


Figure 46 Structure of the [$Mo_3(NiPEt_3)_2S_4Cl_4(PEt_3)_3$] molecule. All carbon atoms are omitted for clarity.

bonding. Indeed, DV-Xα calculations on [$Mo_3NiS_4(H_2O)_{10}$]$^{4+}$ show that the magnitude of the Ni—Mo bond order is approximately 2/3 of the value for Mo—Mo bonds.[312]

The reaction of [$Mo_3S_4Cl_4(PEt_3)_4(MeOH)$] with $Ni(COD)_2$ generates a penta-nuclear cluster [$Mo_3(NiPEt_3)_2S_4Cl_4(PEt_3)_3$].[326] X-ray structure determination reveals a square – pyramidal core with an Mo_2Ni_2 base and third Mo at the apex. Short metal–metal distances (Mo—Mo 2.65–2.67 Å; Mo—Ni 2.5–2.67 Å; Ni—Ni 2.71 Å) are indicated. The XPS spectrum is consistent with a formulation as $Mo_3Ni^0_2$ (Figure 46).

The cube [$Mo_3NiS_4(H_2O)_{10}$]$^{4+}$ has been incorporated into zeolites by an ion exchange procedure, which lead to catalysts for benzothiophene hydrodesulfurization as well as highly selective catalysis for the formation of C_2 species from CO and H_2.[327,328]

The incomplete cubes [$Mo_3Q_4(H_2O)_9$]$^{4+}$ (Q = S, Se) in 2 M HCl, but not their W analogs, give with Pd black–blue solutions of [$Mo_3(PdCl)Q_4(H_2O)_9$]$^{3+}$ (yields ~90%).[329,330] Crystal structures of the supramolecular adducts with cucurbituril {[$Mo_3(PdCl)S_4(H_2O)_6Cl_3$](pyH $\subset$ $C_{36}H_{36}N_{24}O_{12}$)} $Cl\cdot 14H_2O$[331] and {[$Mo_3(PdCl)Se_4$ $(H_2O)_7Cl_2$]($C_{36}H_{36}N_{24}O_{12}$)}$Cl\cdot 7H_2O$ have been determined.[332] When Cl^- is removed and replaced with Hpts (using ion-exchange chromatography), dimerization to the edge-linked double cubes occurs (purple for Q = S),[329,333] [{$Mo_3PdS_4(H_2O)_9$}$_2$](pts)$_8\cdot 20H_2O$ (Mo—Mo 2.78, Pd—Mo 2.80, Pd—Pd 2.79 Å).[329] Solutions of both the single and double cubes are more air stable than, e.g., M′ = Ni, with [{$Mo_3PdQ_4(H_2O)_9$}$_2$]$^{8+}$ in Hpts stable for 3–4 weeks. UV–vis spectra are given in (Figure 47).[332] The double cube [{$Mo_3PdS_4(H_2O)_9$}$_2$]$^{8+}$ in Hpts reacts with L = Cl^-, Br^-, NCS^-, CO, $P(C_6H_4SO_3)_3{}^{3-}$ and 1,3,5-triaza-7-phospha adamantane (PTA), with fast stopped-flow cleavage of the intercube Pd—S bonds to give [$Mo_3(PdL)S_4(H_2O)_9$]$^{n+}$.[332] Equilibration constants K(M^{-1}) were determined: Cl^- 490, Br^- 8,040, NCS^- 630, with CO and the two phosphines binding even more strongly.[332]

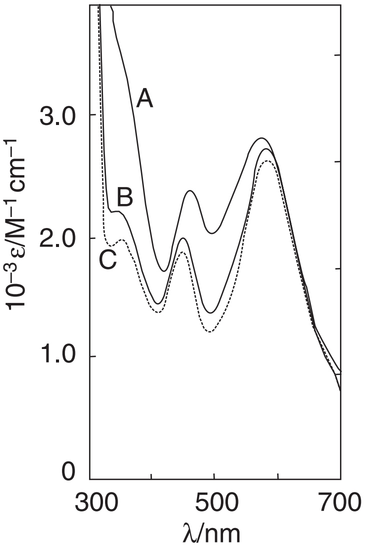


Figure 47 UV–vis spectra (1 cm path length) of: (A) the purple double cube [{$Mo_3PdS_4(H_2O)_9$}$_2$]$^{8+}$ (0.23 mM), (B) the effect of addition of a 10-fold excess of Cl^- giving predominantly blue [$Mo_3(PdCl)S_4(H_2O)_9$]$^{3+}$, and (C) the further effect of increasing the Cl^- to 1.0 M.

The single cube $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ coordinates $HP(O)(OH)_2$ as the tautomeric form $P(OH)_3$, confirmed by the crystal structure of the cucurbituril adduct of $[Mo_3(PdP(OH)_3)S_4(H_2O)_9]^{4+}$, which is the first structurally confirmed example of $P(OH)_3$ as a ligand.[334] Similarly, $As(OH)_3$ has been isolated as $[Mo_3(PdAs(OH)_3)\ S_4(H_2O)_9]^{4+}$.[334] The single cubes $[Mo_3(PdCl)Q_4(H_2O)_9]^{4+}$ (Q = S, Se) react 1:1 with excess $SnCl_3^-$ to give $[Mo_3(PdSnCl_3)Q_4(H_2O)_9]^{3+}$ with Pd—Sn bonding.[330] Formation constants $K(25\,°C)$ are $1.15 \times 10^3\,M^{-1}$ (Q = S) and 9.5×10^3 (Q = Se) in 2 M HCl. On mixing the heterometal cubes $[Mo_3PdS_4(H_2O)_{10}]^{4+}$ and $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ in 2 M HCl, no Pd—Sn interaction occurs. With $[Pd(H_2O)_4]^{2+}$ and $[Mo_3SnS_4(H_2O)_{10}]^{6+}$ in 2 M $HClO_4$ reaction steps $Mo_3SnS_4^{6+} \rightarrow Mo_3S_4^{4+} + Sn^{II}$ followed by $Sn^{II} + Pd^{II} \rightarrow Sn^{IV} + Pd^0$ are observed with the precipitation of Pd^0. Treatment of $[Mo_3(PdCl)S_4(H_2O)_9]^{3+}$ with 3.3 equivalents of 1,4,7-triazacyclononane (tacn) gives dark-blue $[Mo_3(PdCl)S_4(tacn)_3]Cl_3$, 40% yield. The product is stable enough to re-crystallize from 2 M HCl without ligand loss.[329] Derivatization is also achieved with dppe in methanol, when brown $[Mo_3(Pd(\eta^1{-}dppe))S_4Cl_3(dppe)_3]Cl$ is obtained, 50% yield. Its structure was deduced from ^{31}P NMR data.[324]

The Pd site in $[Mo_3(PdCl)S_4(tacn)_3]^{3+}$ is able to bind π-acids such as CO, isonitriles, alkenes and alkynes. With CO, brown $[Mo_3(PdCO)S_4(tacn)_3]^{4+}$ is obtained, which reforms the chloro complex in the presence of excess Cl^-. Solid $[Mo_3(PdCO)S_4(tacn)_3]Cl(PF_6)_3$ was obtained ($\nu(CO) = 2{,}087\,cm^{-1}$) and the crystal structure determined (Pd—CO, 1.95 Å). A dark-red isonitrile complex $[Mo_3(Pd(t{-}BuNC))S_4(tacn)_3]Cl(BF_4)_3$ was also isolated ($\nu(CN) = 2{,}202\,cm^{-1}$). Coordination of alkenes seems to be not very strong, and there is a strong competition by Cl^- for the Pd site. By UV–vis, and in some cases by ^1H NMR, alkene coordination of COD, $4\text{-}MeC_6H_4CH{=}CH_2$, *trans*-PhCH=CHMe, PhCH=CH_2, and C_2H_4 has been monitored. Crystals of X-ray quality of $[Mo_3(Pd(\textit{cis}\text{-}OHCH_2CH{=}CHCH_2OH))S_4(tacn)_3]Cl(ClO_4)_3$ were obtained.[329]

Attempts to coordinate activated alkynes (e.g., HC≡COOMe, MeOOCC≡CCOOMe) to $[Mo_3(PdCl)S_4(tacn)_3]^{3+}$ gave unstable products which could not be isolated. In the presence of CH_3OH, nucleophilic and selective addition of methanol to the activated alkyne was observed, and (Z)-MeOCH=CHCOOMe obtained (97%, 6 h, 40 °C). The reaction is believed to involve a transformation of the π-bonded alkyne complex into a π-bonded vinyl derivative. This and other processes are catalytic,[329] and can be more efficient than the traditional mononuclear Pd^{II} catalysts.[9]

The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[PtCl_4]^{2-}$ (with H_3PO_2 as reductant) gives on standing for 2–3 days the brown edge-linked cube $[\{Mo_3PtS_4(H_2O)_9\}_2]^{8+}$, which is difficult to elute in cation-exchange chromatography.[305] As compared to the Ni and Pd heterometal cubes, the Pt cube is much more inert, and air stable. The $[W_3S_4(H_2O)_9]^{4+}$ analog has been prepared. No reaction of the incomplete cubes with Pt black is observed.[305]

Reaction of solid $[Mo_3S_4(H_2O)_9]Cl_4$ with $Pt(dba)_2$ (dba = 1,5-diphenyl-1-4-pentadiene-3-3-on) in methanol gives a brown precipitate, which can be treated with 3- equivalents of dppe yielding 60e $[Mo_3(PtCl)S_4Cl_3(dppe)_3]$ (37%).[324] When the amount of dppe is increased $[Mo_3(Pt(\eta^1{-}dppe))S_4Cl_3(dppe)_3]Cl$ is obtained, 29% yield. X-ray crystallography on the first of these clusters gives Mo—Mo, 2.81–2.82 Å; Pt—Mo 2.74–2.76 Å (Figure 48); ^{31}P NMR on the second cluster gave a signal at $\delta = -10.3$ ppm ascribed to the uncoordinated PPh_2. While $[Mo_3(PtCl)S_4Cl_3(dppe)_3]$ shows one reversible oxidation wave at 0.67 V (in CH_2Cl_2, vs. Hg_2Cl_2), $[Mo_3(Pt(\eta^1{-}dppe))S_4Cl_3\ (dppe)_3]Cl$ is oxidized irreversibly at 1.41 V. The Pt-coordinated Cl of $[Mo_3(PtCl)S_4Cl_3(dppe)_3]$ could not be replaced with CO, PMe_3, PMe_2Ph or dppe.[324]

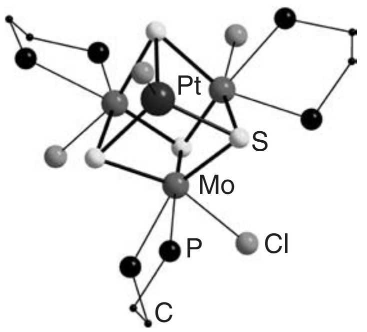


Figure 48 Structure of the $[Mo_3(PtCl)S_4Cl_3(dppe)_3]$ molecule, only C atoms bonded to P are shown.

4.12.6.5.6 Group 11 (Cu)

Metallic Cu reacts with $[Mo_3S_4(H_2O)_9]^{4+}$, forming an air-sensitive brown solution of the paramagnetic 61e cluster $[Mo_3CuS_4(H_2O)_{10}]^{4+}$. On crystallization from 4 M Hpts, the edge-linked $[\{Mo_3CuS_4(H_2O)_9\}_2](pts)_8\cdot20H_2O$ (Mo—Mo, 2.73 Å; C—Mo, 2.78–2.93 Å; Cu—Cu, 2.43 Å) is obtained (Figure 49).[335] The salt is ESR silent in solid state (77–290 K) and has μ_{eff} of only 0.48 B.M. Solution ESR measurements have proved difficult because of air-sensitivity with tendency to release Cu^{II}.[337] Elution from a Dowex cation-exchange column with HCl or Hpts occurs before green $[Mo_3S_4\ (H_2O)_9]^{4+}$, indicating formation of the single cube.[336] The opposite is true for M′=Co, when there appears to be retention of the double cube.[316]

When $[Mo_3S_4(tdci)_3]Br_4$ reacts with Cu in ethanol at room temperature, reddish-brown $[Mo_3(CuBr)S_4(tdci)_3]Br_3\cdot11H_2O\cdot EtOH$ has been isolated, 55% yield, tdci = 1,3,5-tris(dimethylamine)-1,3,5-trideoxy-cis-inositol. The presence of a single cube $Mo_3CuS_4^{4+}$ was demonstrated by X-ray diffraction (M—Mo, 2.82 Å; Mo—Cu, 2.90 Å).[142]

The cluster $[Mo_3CuS_4(H_2O)_{10}]^{5+}$ is obtained by Cu^+ addition (as CuCl or metastable Cu^+_{aq}), or by reduction of Cu^{2+} salts with BH_4^- in the presence of $[Mo_3S_4(H_2O)_9]^{4+}$.[336] In non-complexing Hpts it tends to disproportionate into aqua Cu^{2+} and $[Mo_3CuS_4\ (H_2O)_{10}]^{4+}$.[337] In HCl it is more stable, due to Cl^- coordination and formation of $[Mo_3(CuCl)S_4(H_2O)_9]^{4+}$. Oxidation of $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ by various oxidants also produces the 5+ state as the first step.[336] The cluster $[Mo_3(FeCl)S_4(H_2O)_9]^{3+}$ reacts with 10:1 excess of aqua Cu^{2+}, giving a mixture of $[Mo_3(CuCl)S_4(H_2O)_9]^{3+}$(5%), $[Mo_3(CuCl)S_4(H_2O)_9]^{4+}$(37%), and $[Mo_3S_4(H_2O)_9]^{4+}$(21%).[336] By adding nitrilotriacetate to $[Mo_3(CuCl)S_4(H_2O)_9]^{4+}$ it is possible to crystallize K^+ and NH_4^+ salts of $[Mo_3(CuCl)S_4(Hnta)_3]^{2-}$, the structures of which have been determined.[337] The core in the 5+ cluster (Mo—Mo 2.75 Å; Mo—Cu 2.85 Å) has been formulated as $Mo_3^{IV}Cu^I$, and is isoelectronic with Mo_3Ni^0. The Cu^+ can be taken out of the cluster by coordination with CO.[310] When the CO of aqua $Cu(CO)^+$ is removed by an N_2 stream, $[Mo_3(CuCl)S_4(H_2O)_{10}]^{4+}$ reforms.

Trinuclear $[W_3S_4(H_2O)_9]^{4+}$ reacts with Cu metal with the formation of green, air-sensitive $[W_3CuS_4(H_2O)_{10}]^{5+}$, UV–vis peaks λ(nm) ($\varepsilon(M^{-1}cm^{-1})$) at 288(5,500), 384(1,940), 570 (342).[338] No 4+ W_3CuS_4 core is known. On addition of Cu^I to $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo, W) the kinetics indicate first-order dependencies for each reactant, with Cu^+ attachment to one S atom occurring in the rate-limiting step. At 25 °C, rate constant $M^{-1}s^{-1}$ are: 980 (Mo), 1,820 (W).[338] Subsequent reorientation and attachment to other μ–S core atoms occurs. In the case of Mo, a second Cu^+ independent step is observed.

An attempt to derivatize $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ by NH_3 substitution of H_2O in concentrated ammonia led to one-electron oxidation to the $Mo_3CuS_4^{5+}$ cluster, isolated as black $[\{(NH_3)_6(H_2O)(OH)Mo_3CuS_4(\mu{-}O)\}_2]Cl_4\cdot8H_2O$. The structure reveals two cubes with Mo—O—Mo bridges (Mo—O, 1.90–1.93 Å; Mo—O—Mo, 159°).[339]

The trinuclear clusters $[Mo_3Q_4X_3(dmpe)_3]PF_6$ (Q = S, Se; X = Cl, Br), and $[W_3S_4X_3(dmpe)_3]PF_6$ (X = Cl, Br) react with Cu^I halides, or with $[Cu(CH_3CN)_4]PF_6$ in the presence of Bu_4NX, to give the corresponding air-stable cuboidal clusters.[340,341] Crystal structures were determined for $[Mo_3(CuCl)S_4Cl_3(dmpe)_3]PF_6$ (Mo—Mo, 2.78; Cu—Mo, 2.82 Å); for $[W_3(CuBr)S_4Br_3(dmpe)_3]PF_6$ (W—W, 2.78; Cu—W, 2.88 Å), and for $[Mo_3CuSe_4Cl(dmpe)_3]PF_6$ (Mo—Mo, 2.84; Cu—Mo, 2.84 Å).[340,341]

Thiophosphate complexes of $M_3CuS_4^{5+}$ (M = Mo, W) have been prepared. Reported structures are $[Mo_3(CuI)S_4(\mu{-}OAc)((EtO)_2PS_2)_3L]$ (L = DMF,[342] DMSO (Figure 50),[343] $[Mo_3(CuI)S_4(\mu{-}O_2CCF_3)((EtO)_2PS_2)_3(CH_3CN)]$,[344] $[W_3(CuI)S_4(\mu{-}O_2CCl_3)((EtO)_2PS_2)_3(CH_3CN)]$,[345]

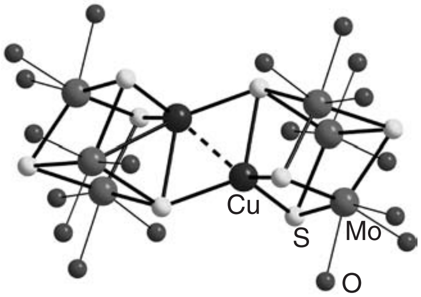


Figure 49 Structure of the $[\{Mo_3CuS_4(H_2O)_9\}_2]^{8+}$ cation.

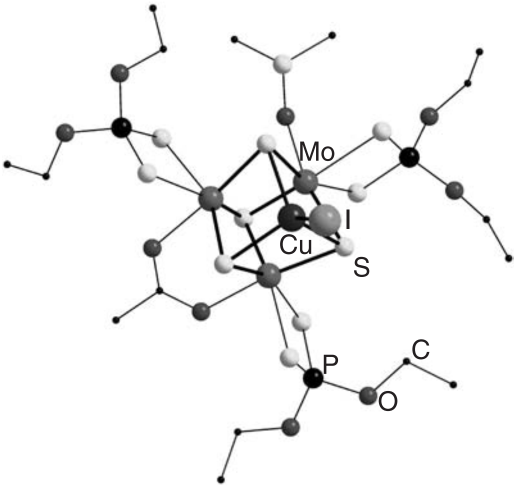


Figure 50 Structure of the $[Mo_3(CuI)S_4(\mu{-}OAc)((EtO)_2PS_2)_3(DMSO)]$ molecule.

$[W_3(CuI)S_4(\mu{-}OAc)((EtO)_2PS_2)_3py]$,[346] and $[Mo_3(CuI)(\mu_3{-}O)S_3(\mu{-}OAc)((EtO)_2PS_2)_3L]$ (L = py, DMF).[347]

The preparation and structure of the dithiocarbamate, $[Mo_3(CuI)S_4(\mu{-}Et_2NCS_2)(Et_2NCS_2)_3py]$, has been reported. In the case of pyrrolydinedithiocarbamate (pyrrdtc), a closely related oxidized product with one broken Mo—Mo bond results $[Mo_3(CuI)(O)_2S_4(\mu{-}OAc)(pyrrdtc)_3py]$.[348]

Diamagnetic dithiophosphinates $[Mo_3(CuI)S_4(\mu{-}R_2PS_2)(R_2PS_2)_3py]$ (R = Et, *n*-Pr) are obtained by reacting trinuclear $[Mo_3S_4(\mu{-}R_2PS_2)((R_2PS_2)_3]$ with CuI and py. For R = *n*-Pr: Mo—Mo, 2.76–2.78 Å; Mo—Cu, 2.84–2.87 Å. A temperature-dependent ^{31}P NMR study indicates a possible isomerization around the unique Mo atom bound to py, which becomes frozen out at low temperature.[349] Using a similar procedure, trimetallic cuboidal clusters $[Mo_2W(CuI)S_4(\mu{-}R_2PS_2)((R_2PS_2)_3py]$ (R = Et, *n*-Pr) have been obtained.[350]

4.12.6.5.7 Group 12 (Cd, Hg)

A Cd derivative of $[Mo_3S_4(H_2O)_9]^{4+}$ has been prepared by (a) reaction with Cd^{2+} in the presence of H_3PO_2 as reductant in 2M HCl, and (b) addition of Cd granules to $[Mo_3S_4(H_2O)_9]^{4+}$ in 0.5 M Hpts and heating ~70 °C for 1 h.[351] The orange–brown product is eluted from a Dowex cation-exchange column at low H^+ using a mix of 2.9 M Lipts + 0.1 M Hpts, and has been characterized as $[Mo_3CdS_4(H_2O)_{12}]^{4+}$. With $[Co(dipic)_2]^-$, O_2 and H^+ as oxidants, the incomplete cube $[Mo_3S_4(H_2O)_9]^{4+}$ is re-formed. The reaction with H^+ is much faster in Cl^- than pts^-, and the pts^- appears to act as an outer-sphere H-bonded protective sheath as in corner-shared double cube crystal structures. The reaction with H^+ yields H_2, and in 1 M HCl the half-life is ~5 min. The kinetics of the reaction with H^+ suggests a dominant $[H^+]^2$ dependence.[351]

Corner-shared double cubes $[CdMo_6S_8(Hnta)_6]^{4-}$ and $[CdMo_6S_8(dtp)_8(CH_3CN)_2]$ are obtained by reacting metallic Cd with $[Mo_3S_4(Hnta)_3]^{2-}$ or $[Mo_3S_4(dtp)_4(CH_3CN)_2]$ respectively. The structures have been confirmed by X-ray crystallography. No Mo—Cd bonding is apparent.[352]

Metallic Hg reacts with $[M_3S_4(H_2O)_9]^{4+}$ to give the intense purple corner-shared double cube $[Mo_6HgS_8(H_2O)_{18}]^{8+}$.[315,353] For conditions specified the reaction requires ~40 h in 2 M HCl, is less rapid in 2 M Hpts (120 h), and extremely slow in 2 M $HClO_4$ (days). From solutions in 4 M Hpts crystals $[Mo_6HgS_8(H_2O)_{18}](pts)_8{\cdot}20H_2O$ were obtained (Hg—S, 2.84 Å).[315] In HCl a partial substitution of Cl^- for coordinated water takes place, and with the addition of cucurbituril to facilitate crystallization, the blue supramolecular adduct $[Mo_6HgS_8Cl_4(H_2O)_{14}](C_{36}H_{36}N_{24}O_{12})Cl_4{\cdot}14H_2O$ is obtained in (Figure 51) and extended structure as in (Figure 52).[354] Cucurbituril has an annular shape with six carboxyl groups exposed in either side of the ring, and these serve to H-bond to H_2O ligands on the cluster to give an extended supramolecular arrangement (Figure 52). The crystal structure indicates Mo—Mo but no Mo—Hg bonding. The coordination around the Hg atom is distorted octahedral, with two short bonds trans to each other (Hg—S, 2.768 Å); and four long bonds (Hg—S, 2.902 Å).[354] The long Hg—S bonds favor an Hg^0 assignment, with the latter

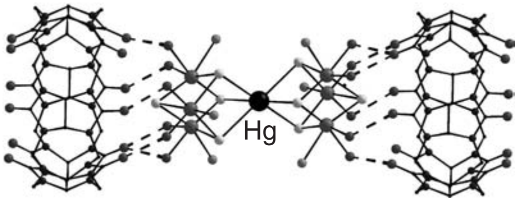


Figure 51 Structure of the $[Mo_6HgS_8Cl_4(H_2O)_{14}]^{4+}$ double cube, and its interaction with cucurbituril $C_{36}H_{36}N_{24}O_{12}$.[353,354]

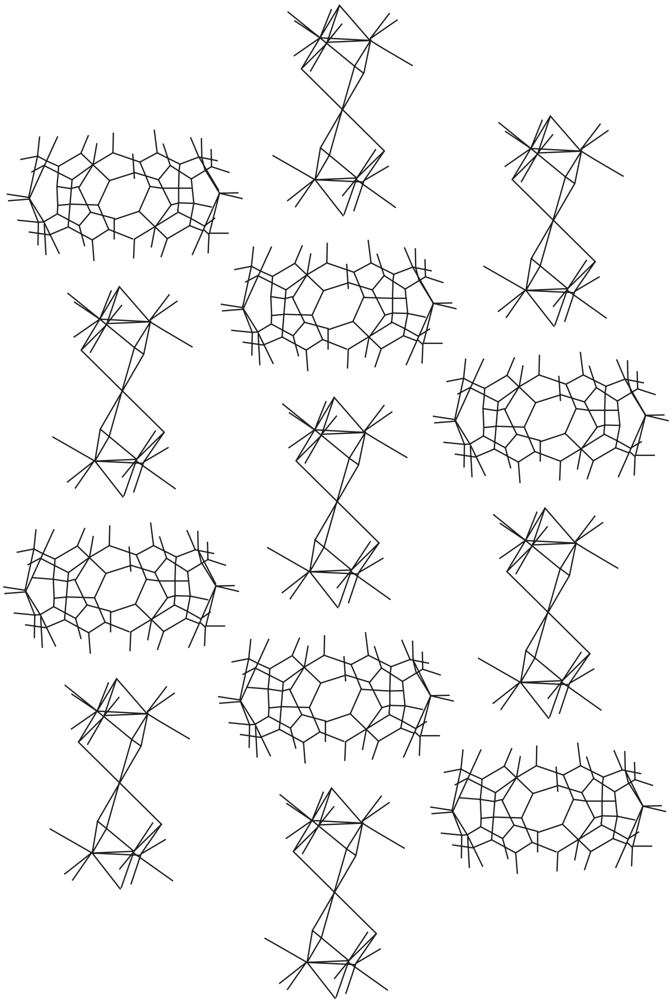
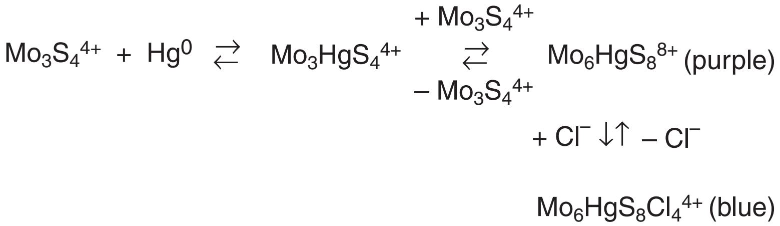


Figure 52 Supermolecular arrangement of cucurbituril and the corner-shared double cube.

sandwiched between two $Mo_3S_4{}^{4+}$ moieties. Kinetic studies favor a rate determining step first-order in $[Mo_3S_4(H_2O)_9]^{4+}$ and formation of the single cube, $Mo_3HgS_4{}^{4+}$, which reacts rapidly with a second $[Mo_3S_4(H_2O)_9]^{4+}$[354]. Equilibrium studies including a Beer's Law plot on $[Mo_6HgS_8(H_2O)_{18}]^{8+}$ indicate an $[Mo_3S_4(H_2O)_9]^{4+}$ square dependence.[354] The interconversions in (Scheme 3) are unique in that the second stage giving the double cube does not involve redox changes. Mercury also reacts with $[Mo_3Se_4(H_2O)_9]^{4+}$ and $[W_3Se_4(H_2O)_9]^{4+}$ (but not $[W_3S_4(H_2O)_9]^{4+}$), to give cucurbituril adducts isostructural with the $[Mo_3S_4(H_2O)_9]^{4+}$ derivative.[353,354]

A particularly striking feature of the supermolecular cucurbituril double-cube structures is that they are isostructural with assemblies incorporating, e.g., two $[W_3Se_4(H_2O)_8Cl]^{3+}$ units as in $[W_3Se_4(H_2O)_8Cl]_2(C_{36}H_{36}N_{24}O_{12})Cl_6{\cdot}12H_2O$. Here, the two W_3Se_4 units are held together by Se—Se interactions (3.617–3.740 Å), and are embedded between cucurbituril molecules in exactly



$$\begin{array}{ccccc} Mo_3S_4^{4+} + Hg^0 & \rightleftarrows & Mo_3HgS_4^{4+} & \underset{-\,Mo_3S_4^{4+}}{\overset{+\,Mo_3S_4^{4+}}{\rightleftarrows}} & Mo_6HgS_8^{8+}\text{ (purple)} \\ & & & & +\,Cl^- \downarrow\uparrow -\,Cl^- \\ & & & & Mo_6HgS_8Cl_4^{4+}\text{ (blue)} \end{array}$$

Scheme 3

the same way as the double cubes.[353] Similar dimeric interactions have been reported previously for $[W_3Se_4(NCS)_9]^{5-}$ and $[W_3Se_4(CN)_9]^{5-}$ as well as in other M_3Q_4 (M = Mo, W; Q = S, Se) structures.[197] Of interest, in binary MQ_2 chalcogenides of early transition metals, the chalcogenide atoms of neighboring layers interact with each other in a similar manner.[7] Thus, the structures are formally related to those of a matrix and intercalator (e.g., Hg), and the two W_3Se_4 units mimic closely the QMQ—QMQ layered structure in MQ_2. The results suggest that structures of MQ_2 are related to the chemistry of small molecular clusters in a way not previously recognized.

4.12.6.5.8 Group 13 (Ga, In, Tl)

In this group the single cubes $[Mo_3GaS_4(H_2O)_{12}]^{5+}$, $[Mo_3InS_4(H_2O)_{12}]^{5+}$, and double cubes $[Mo_6InS_8(H_2O)_{18}]^{8+}$, $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ have been prepared from $[Mo_3S_4\ (H_2O)_9]^{4+}$.[355] No evidence for $[Mo_3TlS_4(H_2O)_{12}]^{5+}$, $[Mo_6GaS_8(H_2O)_{18}]^{8+}$, or confirmation of the 6+ analog of $[Mo_3GaS_4(H_2O)_{12}]^{5+}$ has been obtained.[355,356] Of the nine Group 13–15 heteroatoms studied, Ga is the only one that does not give a double cube using existing procedures.

Metallic Ga reacts with $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M HCl (at 90 °C), giving the red–brown cuboidal cluster $[Mo_3GaS_4(H_2O)_{12}]^{5+}$, which can be crystallized from 4 M Hpts as $[Mo_3Ga\ S_4(H_2O)_{12}](pts)_5{\cdot}14H_2O$ (Mo—Mo 2.71 Å; Ga—Mo 3.52 Å).[356] Alternatively, Ga can be dissolved in 4 M HCl as Ga^{III} and added to $[Mo_3S_4(H_2O)_9]^{4+}$ in the presence of $NaBH_4$.[355] In 4 M HCl a low yield (10%) of H_2 gas was evolved over 3 days from H^+ oxidation, and was determined by gas chromatography over 3 days. No reaction is observed between Ga and $[W_3S_4(H_2O)_9]^{4+}$, or of $GaCl_3$ and $NaBH_4$ with $[W_3S_4(H_2O)_9]^{4+}$.[7]

Similar procedures can be used to prepare $[Mo_3InS_4(H_2O)_{12}]^{5+}$. Thus, when metallic In is treated with $[Mo_3S_4(H_2O)_9]^{4+}$ in 4 M Hpts, brown needle-like crystals of the single cube $[Mo_3In(\eta^1{-}pts)_2H_2O)S_4(H_2O)_9](pts)_3{\cdot}13H_2O$ separate. The structure gives Mo—Mo 2.69 Å; Mo—In 3.72 Å.[357] Dark-blue $[W_3InS_4(H_2O)_{12}]^{5+}$ and its blue–green Se analog are obtained in the same way.[355,358,359] Quantitative additions of aqua In^+ to $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo, W) is fast.[355,358] When In^{3+} is reduced with H_3PO_2 in the presence of $[M_3S_4(H_2O)_9]^{4+}$ (M = Mo, W), the W reactant gives $[W_3InS_4(H_2O)_{12}]^{5+}$, but the Mo reaction proceeds to $[Mo_6InS_8(H_2O)_{18}]^{8+}$, which is stable only in the presence of excess H_3PO_2.[355] (Figure 53) illustrates typical UV–vis spectra of single and double cube derivatives.

Red–orange $[Mo_6InS_8(H_2O)_{18}]^{8+}$ is also obtained by a reductive addition of $[Mo_3S_4(H_2O)_9]^{4+}$ to $[Mo_3InS_4(H_2O)_{12}]^{5+}$ in the presence of $NaBH_4$. Attempts to elute from a cation-exchange column at $[H^+] \geq 1$ M result in rapid oxidation to $[Mo_3In\ S_4(H_2O)_{12}]^{5+}$.[355] At a lower $[H^+]$ (0.1 M Hpts) crystals of $[Mo_6InS_8(H_2O)_{18}](pts)_8{\cdot}xH_2O$ were isolated, but only the geometry of the cluster core could be established due to severe disorder.[360] Less reactive $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ is obtained from In metal and $[Mo_3OS_3(H_2O)_9]^{4+}$ in 4 M Hpts, and crystallizes as $[Mo_6InO_2S_6(H_2O)_{18}](pts)_8{\cdot}30H_2O$, 54% yield. The latter is not stable in HCl solutions when, as a result of H^+ oxidation, it decays into In^{3+} and $[Mo_3OS_3(H_2O)_9]^{4+}$ with the transient formation of $[Mo_3InOS_3\ (H_2O)_{12}]^{5+}$.[355,360]

The double and single In cubes react with H^+ to give H_2 determined by GC. The reaction of $[Mo_6InO_2S_6(H_2O)_{18}]^{8+}$ is first order in $[H^+]$ ($k = 4.9\times10^{-3}\ M^{-1}\,s^{-1}$). When equimolar amounts of $[W_3InS_4(H_2O)_{12}]^{5+}$ and $[Mo_3S_4(H_2O)_9]^{4+}$ are mixed, a rapid and quantitative In^+ transfer takes place with the formation of $[W_3S_4(H_2O)_9]^{4+}$ and $[Mo_3InS_4\ (H_2O)_{12}]^{5+}$.[358]

Blue–green $[Mo_6TlS_8(H_2O)_{18}]^{8+}$ is formed in the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Tl metal in 2 M $HClO_4$, or more effectively by addition of TlCl with BH_4^- or H_3PO_2 as reductant.[361] The product

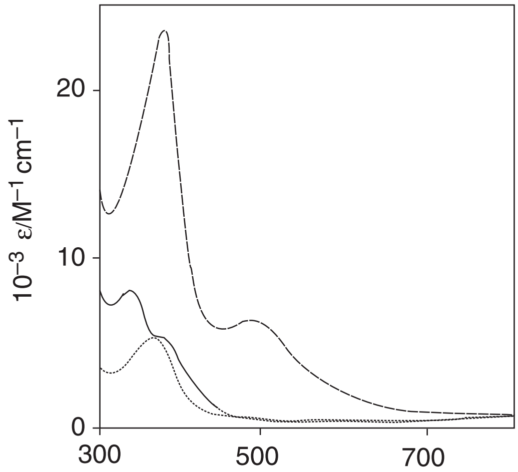


Figure 53 UV–vis spectra of red–brown $[Mo_3InS_4(H_2O)_{12}]^{5+}$ (——) (ε's per Mo_3), and red–orange $[Mo_6InS_8(H_2O)_{18}]^{8+}$ (- - -) (ε's per Mo_6) in 2 M HCl. The spectrum of green $[Mo_3S_4(H_2O)_9]^{4+}$ (····) (ε's per Mo_3) is also given.

is air-sensitive, and is oxidized by H^+ to Tl^+ and $[Mo_3S_4(H_2O)_9]^{4+}$. Column purification is carried out preferably at 0 °C. The reaction with H^+ is first-order in $[H^+]$, $k = 0.25 \times 10^{-3}\ M^{-1}\ s^{-1}$.[355,361]

4.12.6.5.9 *Group 14 (Ge, Sn, Pb)*

All three heterometals give corner-shared double cubes with $[Mo_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se). Single cubes have been characterized for Ge and Sn.

The red–purple Ge double cube is obtained by the reaction of GeO with $[Mo_3S_4(H_2O)_9]^{4+}$, by heating with Ge powder at 90 °C, or by heating with GeO_2 in the presence of H_3PO_2 at 90 °C.[362] Reaction with GeO is almost quantitative and most likely proceeds by disproportionation of the Ge^{II} to give reactive Ge^0 *in situ* along with Ge^{IV}. The crystal structure of $[Mo_6GeS_8(H_2O)_{18}]$ $(pts)_8{\cdot}28H_2O$ indicates Mo—Mo (2.69 Å) but no Mo—Ge bonding (3.56 Å). Difference in UV–vis spectra in 2.0 M HCl and 2.0 M Hpts are illustrated in (Figure 54). The dark-green Se analog $[Mo_6GeSe_8(H_2O)_{18}]^{8+}$ displays similar properties. In the case of the trinuclear clusters $[W_3Q_4(H_2O)_9]^{4+}$(Q = S, Se) with GeO or GeO_2/H_3PO_2 the single cubes $[W_3GeQ_4(H_2O)_{12}]^{4+}$ are obtained. Conversion to the double cubes is achieved by reductive addition with BH_4^- in the presence of a further equivalent of $[W_3Q_4(H_2O)_9]^{4+}$. Crystals of $[W_6GeS_8\ (H_2O)_{18}](pts)_8{\cdot}23H_2O$ were obtained from 4 M Hpts and give W—W 2.67 Å, W—Ge 3.60 Å.[362]

Studies on $[W_3GeS_4(H_2O)_{12}]^{6+}$ in aqueous solution suggest that three H_2O's are coordinated to the Ge and can be replaced by Cl^-, with formation of $[W_3(GeCl_3)S_4(H_2O)_9]^{3+}$ approaching

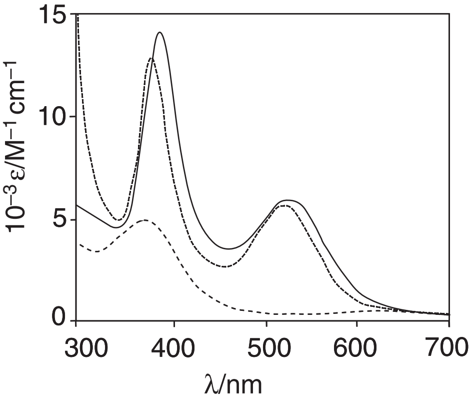


Figure 54 UV–vis spectra of $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ in 2 M HCl (——) and 2 M Hpts (- - -), ε's per Mo_6. The spectrum of $[Mo_3S_4(H_2O)_9]^{4+}$ (–•–) is also given, ε's per Mo_3.

completion at 2.0 M Cl^- levels. UV–vis spectra in 2.0 M HCl, Hpts and $HClO_4$ respectively, are shown in (Figure 55). Rate constants for the $[Co^{III}(dipic)_2]^-$ oxidation of single (two Co^{III} equivalents) and double cubes (four Co^{III} equivalents), rate laws first-order in Co^{III} indicating rate controlling first stages, are of interest (Table 3). The rate constants for $[W_6GeS_8(H_2O)_{18}]^{8+}$ are $\sim 10^5$ times bigger than those for $[Mo_6GeS_8(H_2O)_{18}]^{8+}$, and $[W_3GeS_4(H_2O)_{12}]^{6+}$. For the double cube $[Mo_6GeS_8(H_2O)_{18}]^{8+}$ and (for comparison) $[Mo_6SnS_8(H_2O)_{18}]^{8+}$ the ratio of rate constants in 2.0 M Cl^- and 2.0 M pts^- exhibit large 160-fold differences favoring Cl^-. A possible explanation is that pts^- and solvent H_2O form some sort of protective hydrogen-bonded sheath around the 8+ ions, as in the crystal structures (Figure 56). The effect is not as apparent with $[W_6GeS_8(H_2O)_{18}]^{8+}$ possibly due to the much faster reaction at the limit of the stopped-flow range.

A comparison of rate constants for the oxidation of $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ is given in (Table 4), showing that the Ge cube is the least reactive, with Sn next. Both are Group 14 and have an even number of electrons.[363] A molecular orbital treatment has been considered for $[Mo_6SnS_8(H_2O)_{18}]^{8+}$. Group 13, (In, Tl) containing double cubes have one electron less, and the Group 15 cubes (As, Sb, Bi) one electron more in LUMO, orbitals. Both effects result in increased reactivity.

Metallic tin shot reacts with $[Mo_3Q_4(H_2O)_9]^{4+}$ (Q = S, Se) to give purple $[Mo_6SnS_8(H_2O)_{18}]^{8+}$,[364] and brown $[Mo_6SnSe_8(H_2O)_{12}]^{8+}$, and pts^- crystals are obtained salts from 4 M Hpts solutions. The X-ray crystal structure of $[Mo_6SnS_8(H_2O)_{18}](pts)_8$ gives Mo—Mo 2.69 Å and Mo—Sn 3.71 Å.[364] X-ray crystal structure of double cubes have been determined.[359,364] The single and not double cube is obtained in the reaction of tin shot with $[W_3S_4(H_2O)_9]^{4+}$. Purple–red, extremely air-sensitive $[W_6SnS_8(H_2O)_{18}]^{8+}$ is obtained by $NaBH_4$ reductive addition of $[W_3(SnCl_3)S_4(H_2O)_9]^{3+}$ and $[W_3S_4(H_2O)_9]^{4+}$. Reductive coupling has also been used to prepare $[Mo_3W_3SnS_8(H_2O)_{18}]^{8+}$, $[Mo_6SnS_4Se_4(H_2O)_{18}]^{8+}$, and $[Mo_3W_3SnS_4Se_4(H_2O)_{18}]^{8+}$ (Scheme 4).[358,359] All the tin double cubes are oxidized by O_2, $[Fe(H_2O)_6]^{3+}$ or $Co(dipic)_2^-$ in two steps, giving first

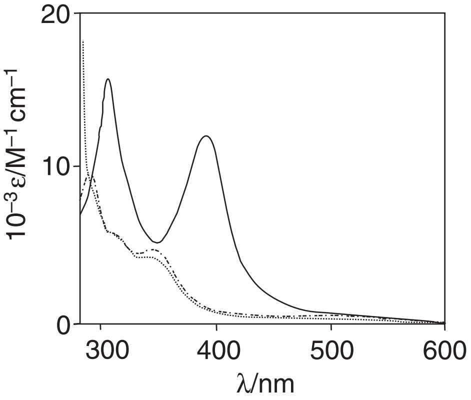


Figure 55 UV–vis spectra of $[Mo_3GeSe_4(H_2O)_{12}]^{6+}$ in 2 M HCl (——), 2 M Hpts (- - -) and 2.0 M $HClO_4$ (–•–).

Table 3 Rate constants k_{Co} (25 °C) for the oxidation of germanium containing single and double cubes in aqueous solutions, (1–6) × 10^{-5} M, with $[Co(dipic)_2]^-$ in large excess, $[H^+]$ = 0.5–2.0 M, I = 2.00 M (LiCl) and 2.0 (Lipts) as indicated.[362]

	k_{Co} ($M^{-1}s^{-1}$) (2.0 MCl^-)	k_{Co} ($M^{-1}s^{-1}$) (2.0 M pts^-)	*Ratio*[a]
$[Mo_6GeS_8(H_2O)_{18}]^{8+}$	12.8	7.7×10^{-2}	166
$[W_6GeS_8(H_2O)_{18}]^{8+}$	2.8×10^4	7.3×10^3	3.8
$[Mo_6GeSe_8(H_2O)_{18}]^{8+}$	>145	6.9	>21
$[Mo_3GeS_4(H_2O)_{12}]^{6+}$	3.2×10^{-2}	4.6×10^{-2}	0.70
$[W_3GeS_4(H_2O)_{12}]^{6+}$	1.17	1.49	0.79
$[W_3GeSe_4(H_2O)_{12}]^{6+}$	1.04		
$[Mo_6SnS_8(H_2O)_{18}]^{8+}$	2.32×10^{3}[b]	14.9[c]	156

[a] k_{Co} in 2.0 M Cl^-: k_{Co} in 2.0 M pts^-. [b] Seo M.-S. and Sykes A. G., unpublished work. [c] Ref [359].

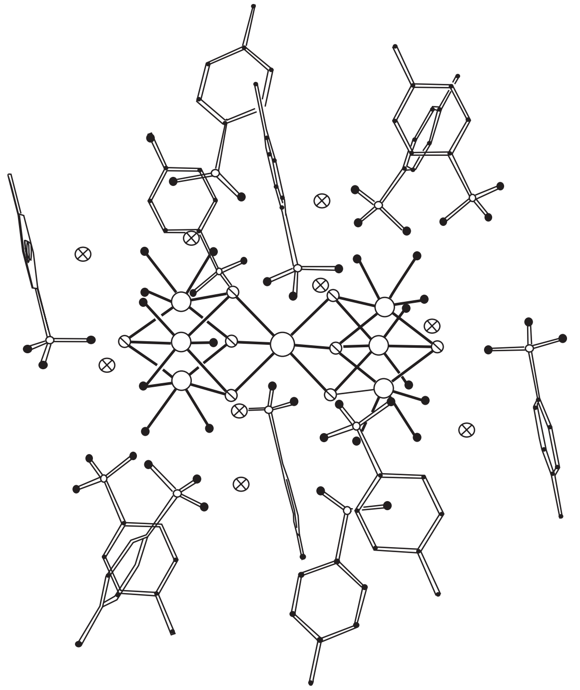


Figure 56 Arrangements of *p*-toluenesulfonate (pts$^-$) anions (hollow bonds), and water molecules (cross-hatched circles), hydrogen-bonded to a corner-shared double cube, to give a protective sheath around the double cube.

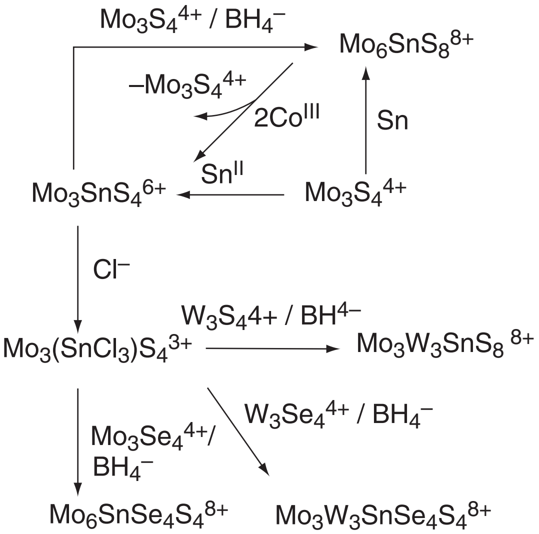
Table 4 Summary of rate constants k_{Co} (25 °C) for the $[Co(dipic)_2]^-$ oxidation of heterometal (M′) corner-shared derivatives $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ of $[Mo_3S_4(H_2O)_9]^{4+}$ at $[H^+] = 0.5–2.0$ M, I = 2.0 M (pts$^-$).[362]

M′	k_{Co} ($M^{-1}s^{-1}$)[a]
In	3.09×10^4
Tl	very fast
Ge	very fast
Sn	14.9
Pb	2.76×10^5
As	2.10×10^4
Bi	3.6×10^4

[a] Rate constants independent of [H$^+$] in range 0.5–2.0 M.

$[M_3SnQ_4(H_2O)_{12}]^{6+}$, and then (with excess oxidant) $[M_3Q_4(H_2O)_9]^{4+}$ and Sn^{IV}.[359,365] The yellow–green single cube $[Mo_3SnS_4(H_2O)_{12}]^{6+}$ is prepared by direct addition of Sn^{II} to $[Mo_3S_4(H_2O)_9]^{4+}$. Different spectra are observed in 2.0 M HCl from those in 2.0 M Hpts and 2.0 M $HClO_4$. The affinity of Sn for Cl^- is high and $[Mo_3(SnCl_3)S_4(H_2O)_9]^{3+}$ is formed when 0.05 M Cl^- is added to a 0.13 mM solution. Addition of excess NCS^- to these solutions does not affect the Sn-coordinated Cl^-, substitution takes place only at the Mo, and in the presence of $Me_2NH_2^+$, crystals of e.g., $[Me_2NH_2]_6[Mo_3(SnCl_3)S_4(NCS)_9]\cdot 0.5H_2O$ are obtained. Structures have been determined for the four cases with M = Mo, W and Q = S, Se.[116,359,365,366]

Transfer of $SnCl_3^-$ can be monitored by UV–vis spectrophotometry on the reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ or $[W_3(SnCl_3)Q_4(H_2O)_9]^{3+}$ (Q = S, Se). No corresponding reactions of $[W_3S_4(H_2O)_9]^{4+}$ with $[W_3(SnCl_3)Se_4(H_2O)_9]^{3+}$, or of $[W_3Q_4(H_2O)_9]^{4+}$ with $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ are observed. The reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with $[Mo_3(SnCl_3)Se_4(H_2O)_9]^{3+}$ gives an equilibrium mix, with $K = 4.0$. From these studies the affinities of a triangular cluster towards $SnCl_3^-$ are: $Mo_3S_4^{4+} > Mo_3Se_4^{4+} > W_3Se_4^{4+} > W_3S_4^{4+}$.[358,359]



Scheme 4

Non-aqueous chemistry of $Mo_3SnS_4^{6+}$ clusters has also received attention. When Sn powder is heated with a toluene solution of $[Et_2P(S)S]_2$ and $[Mo_3S_4(Et_2PS_2)_4]$, black, air stable $[Mo_3SnS_4(Et_2PS_2)_6]$ is obtained, 50% yield. Its crystal structure shows the presence of three bridging and three chelating dithiophosphinate ligands. Direct addition of $Sn(Et_2P(S)S)_2$ to $[Mo_3S_4(Et_2PS_2)_4]$ gives the same product.[367]

A series of $[Mo_3(\mu_3{-}O)(\mu{-}S)_3]^{4+}$ derivatives, $[Mo_3OS_3(SnCl_3)(dtp)_3py_3]$, $(PPN)[Mo_3OS_3(SnCl_3)(\mu{-}OAc)(dtp)_3py]$, and $(Et_4N)[Mo_3OS_3(SnCl_3)(\mu{-}OAc)_2(dtp)_2py]$ have been prepared and characterized by IR, UV–vis, ^{31}P and ^{95}Mo NMR and X-ray structure analysis. The addition of $SnCl_3^-$ shortens the Mo—Mo bonds by 0.03–0.04 Å. Reactions of $[Mo_3QS_3(dtp)_4(H_2O)]$ with $SnCl_3^-$ (Q = O, S; X = Cl, Br, I) and py yield $[Mo_3QS_3(SnX_3)(dtp)_3py_3]$.[368–370]

Extremely air-sensitive, blue–green $[Mo_6PbS_8(H_2O)_{18}]^{8+}$ is obtained when Pb shot is allowed to react with $[Mo_3S_4(H_2O)_9]^{4+}$ in 2 M Hpts or 2 M $HClO_4$.[371,372] Similarly, $[Mo_3Se_4(H_2O)_9]^{4+}$ gives dark-green $[Mo_6PbSe_8(H_2O)_{18}]^{8+}$, and $[W_3Se_4(H_2O)_9]^{4+}$ the wine-red $[W_6PbSe_8(H_2O)_{18}]^{8+}$.[111] However, no reaction is observed with $[W_3S_4\,(H_2O)_9]^{4+}$ under similar conditions. The oxidants O_2, $[Fe(H_2O)_6]^{3+}$, and $[Co^{III}(dipic)_2]^-$ oxidize the double cubes rapidly with the formation of Pb^{2+} and trinuclear cluster.

No single-cube derivatives $[M_3PbS_4(H_2O)_{12}]^{6+}$ have been prepared.[111] However, in non-aqueous media Pb^{II} (as PbI_3^-) adds to the $Mo_3S_4^{4+}$ core in the presence of dtp. The single-cube product $[Mo_3(PbI_3)S_4(dtp)_3(py)_3]$ has been confirmed by crystal structure determination.[373] Syntheses and structures of $[Mo_3(PbI_3)S_4(dtp)_3(C_3H_4N_2)_3]$, $[W_3(PbI_3)\,S_4(dtp)_3(py)_3]$, $[Mo_3(PbI_3)OS_3(dtp)_3(py)_3]$ and $\{[Mo_3(PbI_3)OS_3(OAc)_2(dtp)_2\,(py)_3](\mu{-}O)_2\}$ have also been reported.[371]

4.12.6.5.10 Group 15 (As, Sb, Bi)

The isolation of the corner-shared double cube $[Mo_6AsS_8(H_2O)_{18}]^{8+}$ is of considerable interest because of the largely non-metallic properties of arsenic. Although gray arsenic does not react with $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) blue–green $[Mo_6AsS_8(H_2O)_{18}]^{8+}$, green $[Mo_6AsSe_8(H_2O)_{18}]^{8+}$ and red $[W_6AsSe_8(H_2O)_{18}]^{8+}$ (yields approaching 100%) are obtained by reduction of $NaAsO_2$ and $[M_3Q_4(H_2O)_9]^{4+}$ (M = Mo, W; Q = S, Se) with H_3PO_2.[111,303] Crystal structures give $[Mo_6AsS_8(H_2O)_{18}](pts)_8{\cdot}28H_2O$ (Mo—Mo, 2.72 Å; As—S, 2.46 Å).[303] and $[Mo_6AsSe_8(H_2O)_{18}](pts)_8{\cdot}8H_2O$ (Mo—Mo, 2.76 Å; As—Se, 2.61 Å).[111] Mo—As separation of 3.55 Å indicates the absence of Mo—As bonds. Oxidants O_2, $[Fe(H_2O)_6]^{3+}$ and $[Co(dipic)_2]^-$ react with the double cubes with formation of As^{III} and trinuclear $[M_3Q_4(H_2O)_9]^{4+}$. No single-cube products are observed as intermediates.[111,303] The redox chemistry is adequately described by the $Mo_3S_4^{4+}As^0Mo_3S_4^{4+}$ formalism.

Green $[Mo_6SbS_8(H_2O)_{18}]^{8+}$ and dark-green $[Mo_6SbSe_8(H_2O)_{18}]^{8+}$ are obtained in 40% yields when Sb powder is allowed to react with $[Mo_3Q_4(H_2O)_9]^{4+}$ for 7 days.[111,374] A crystal structure of

$[Mo_6SbS_8(H_2O)_{18}](pts)_8{\cdot}24H_2O$ (Mo—Mo, 2.72 Å; Mo—Sb, 3.68 Å) shows an absence of direct Mo—Sb bonding. The ^{121}Sb Mössbauer spectrum of this compound ($\delta = -2.64$ mm s^{-1}, $e^2qQ = 18.1$ mm s^{-1}, $\eta = 0.29$), together with the XPS data, were interpreted in terms of an Sb^{3+} component.[375] Much of the redox chemistry is, however, better described using the $Mo_3S_4{}^{4+}Sb^{o}Mo_3S_4{}^{4+}$ approximation, with $Mo_3S_4{}^{4+}$ Sb^{III} applying in the case of the single cube. Green–blue $[W_6SbSe_8(H_2O)_{18}]^{8+}$ is best obtained from $SbCl_3$, H_3PO_2 and $[W_3Se_4(H_2O)_9]^{4+}$. Again, O_2, $[Fe(H_2O)_6]^{3+}$, and $[Co(dipic)_2]^-$ oxidize the double cubes to Sb^{III} and $[M_3Q_4(H_2O)_9]^{4+}$. No single-cube intermediates were observed in these interconversions.[111,374]

Solutions of $[W_3Se_4(H_2O)_9]^{4+}$ react with $SbCl_3$ to give a yellow–brown adduct believed to be the single-cube $[W_3(SbCl_3)Se_4(H_2O)_9]^{4+}$. The same product is observed with Sb shot, prior to formation of the green–blue double cube.[111] Also, in organic solvents, addition of Sb^{III} (as SbX_3, X = Cl, Br, I) to the dtp complexes of $[M_3S_4\ (H_2O)_9]^{4+}$ (M = Mo, W) is observed. Reported products are $[Mo_3(SbCl_3)S_4(dtp)_4L]$ (L = EtOH, oxazole),[374] $[Mo_3(SbX_3)OS_3(OAc)(dtp)_3(py)]$ (X = Cl, Br, I), $[Mo_3(SbI_3)OS_3(OOCCH_2Cl)(dtp)_3(py)]$, $[Mo_3(SbBr_3)OS_3(OAc)_2(dtp)_2(py)]$, $[W_3(SbI_3)S_4(OAc)\ (dtp)_3(DMF)]$, and $[Mo_3(SbI_3)S_4(pyrrdtc)_4(py)]$.[369] The $SbCl_3$ unit is readily replaced by $SnCl_3{}^-$. In some cases, self-assembly of the cubes is possible. Thus, on mixing P_4S_{10}, $MoCl_3{\cdot}3H_2O$, H_2S and $SbCl_3$ in ethanol, and treatment with acetic acid and pyridine, $[Mo_3(SbCl_3)OS_3(OAc)(dtp)_3(py)]$ is obtained, yield 10%.[370]

Rapid reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with Bi^{III} in the presence of $NaBH_4{}^-$, or with Bi metal shot (3–4 days at room temperature) gives turquoise–blue $[Mo_6BiS_8(H_2O)_{18}]^{8+}$.[376] Reduction of Bi^{III} citrate with H_3PO_2 in the presence of $[M_3Se_4(H_2O)_9]^{4+}$ affords green $[Mo_6BiSe_8(H_2O)_{18}]^{8+}$ (λ (nm) (ε(M^{-1} cm^{-1})) at 447(12,830), 736(7,120), 800sh(7,000) in 2 M Hpts), and green–blue $[W_6BiSe_8(H_2O)_{18}]^{8+}$ (λ(nm)-(ε(M^{-1} cm^{-1})) at 360(16,160), 581(8,244), 706(5,407) in 2 M Hpts).[111] Oxidants such as O_2, $[Fe(H_2O)_6]^{3+}$, and $[Co(dipic)_2]^-$ oxidize the double cube with the formation of Bi^{III} and the corresponding $[M_3Q_4(H_2O)_9]^{4+}$. No single-cube intermediate has been observed.[111,376]

Dtp complexes of M_3S_4 (M = Mo, W) have been shown to form single cubes with BiI_3. Two crystal structures $[M_3(BiI_3)S_4(OAc)(dtp)_3L]$ (M = Mo, L = py; M = W, L = H_2O) have been determined. The W/S cube was obtained in a 8% yield by reaction of BiI_3 with $[W_3S_4(dtp)_4H_2O]$, followed by addition of acetic acid.[369] The bridged cube $[\{Mo_3(BiI_3)\text{-}OS_3(\mu\text{–}OAc)_2(dtp)_2(py)\}_2(\mu\text{–}O)]$, was obtained from BiI_3 and $\{[Mo_3OS_3(OAc)_2\ (dtp)_2(py)]$ in the presence of some water.[377]

4.12.6.5.11 Postscript

All corner-shared double cubes $[Mo_6M'S_8(H_2O)_{18}]^{8+}$ (>10 characterized by crystallography) have an 8+ charge. Similarly, the W_6 corner-shared double cubes are 8+, and the one crystal structure on $[W_6GeS_8(H_2O)_{18}]^{8+}$ shows similar features to the Mo_6 clusters with virtually identical bond lengths. In the case of single as well as corner-shared double cubes, heteroatom derivatives of $[W_3S_4(H_2O)_9]^{4+}$ are less common, and to date only eight derivatives (Mo, Rh, Ni, Pt, Cu, In, Ge, Sn) have been identified, with no reaction in other cases (Fe, Co, Pd, Pb, Sb, Bi, Hg). All sixteen $[Mo_3S_4(H_2O)_9]^{4+}$ derivatives and others also have been prepared.

(Table 5) summarizes Mo—Mo and Mo—M′ bond lengths. For those cases in which the Mo—M′ separation is >3.0 Å a non-bonding situation applies. Behavioral aspects can be summarized in terms of at least three categories: those involving early transition metals (Group 6), late transition metals, and post-transition elements. Understandably metal–metal bonding is more likely for transition metals M′ with outer-electron configuration of d^{10} or less. The non-bonding situations apply for post-transition elements when M′ has $>d^{10}$ outer electrons, general formula $Mo_3S_4{}^{4+}M'^{n+}$ ($n = 0$–3) and $Mo_3S_4{}^{4+}M'Mo_3S_4{}^{4+}$.

The double-cube $[Mo_7S_8(H_2O)_8]^{8+}$ is at present the only corner-shared example with M′ a transition metal. In this structure each cube has three short (2.77 Å) and three long (3.05 Å) Mo—Mo distances, the latter involving the nodal Mo. Here, a structure approximating to $Mo_3S_4{}^{4+}Mo'^{0}Mo_3S_4{}^{4+}$, with adjacent Mo's assigned as Mo^{IV} and Mo is less satisfactory.

4.12.6.6 Octahedral Clusters M_6Q_8

These clusters are found in Chevrel phases, i.e., solids containing Mo_6Q_8 (Q = S, Se, Te) and ternary phases $M'Mo_6Q_8$.[378] No solid-state (non-molecular) tungsten analogs have been

Table 5 Summary of metal–metal distances from X-ray crystallography for aqua ions of double and single cube heteroatom (M′) derivatives of $[Mo_3S_4(H_2O)_9]^{4+}$, and related structures.

Core	*Mo—Mo* (Å)	*Mo—M′* (Å)
Corner-shared double cubes $[Mo_6M'S_8(H_2O)_{18}]^{8+}$		
$Mo_6HgS_8{}^{8+}$	2.713	3.830
$Mo_6InS_6O_2{}^{8+}$	2.627	3.583
$Mo_6GeS_8{}^{8+}$	2.689	3.556
$Mo_6SnS_8{}^{8+}$	2.688	3.713
$Mo_6AsS_8{}^{8+}$	2.716	3.554
$Mo_6SbS_8{}^{8+}$	2.717	3.680
Edge-linked double cubes $[\{Mo_3M'S_4(H_2O)_9\}_2]^{8+}$		
$\{Mo_3CoS_4\}_2{}^{8+}$	2.744	2.643
$\{Mo_3PdS_4\}_2{}^{8+}$	2.773	2.799
$\{Mo_3CuS_4\}_2{}^{8+}$	2.730	2.887
Single cubes		
$Mo_3FeS_4{}^{4+}$	2.793	2.683
$Mo_3NiS_4{}^{4+}$	2.744	2.678
$Mo_3PdS_4{}^{4+}$ [a]	2.819	2.793
$Mo_3GaS_4{}^{5+}$	2.713	3.520
$Mo_3InS_4{}^{5+}$	2.682	3.720
$Mo_3SnS_4{}^{6+}$ [b]	2.730	3.732
$Mo_3PbS_4{}^{6+}$ [c]	2.747	4.207
$Mo_3BiS_4{}^{7+}$ [c]	2.732	4.132
Others		
$Mo_7S_8{}^{8+}$ [d]	2.770	3.046
$Mo_3S_4{}^{4+}$	2.732	
$Mo_4S_4{}^{5+}$	2.802	
$Mo_4S_4{}^{4+}$	2.797	

[a] tacn ligands. [b] NCS^- and Cl^- ligands. [c] dtp ligands. [d] Mo is at nodal postion of double cube.

clearly identified. The compounds have structures in which the Mo_6Q_8 clusters are tightly cross-linked by Mo—Q bonds into three-dimensional networks. In the 1970s and 1980s they attracted interest because they exhibit diverse physical and chemical properties, such as high-critical-field (H_{c2}) superconductivity,[379] magnetic ordering,[380] fast ion conductivity,[381] and catalytic activity for hydrodesulfurization.[382]

The literature dealing with this subject is enormous, and the reader should consult the references cited rather than any attempt be made to cover the subject in this review. Given the interesting properties of Chevrel phases, a considerable effort has recently been made to prepare molecular complexes with M_6Q_8 cluster cores. These serve both as molecular models and (in the case of tungsten) molecular precursors of solid-state materials.

4.12.6.6.1 Mo Clusters

Reductive coupling of $[Mo_3Q_4Cl_4(PEt_3)_x]$ ($x = 3, 4$; Q = S, Se) with Mg as the reductant gave the first molecular clusters Mo_6Q_8 as air-stable $[Mo_6S_8(PEt_3)_6]$ (red–violet, 32%) and $[Mo_6Se_8(PEt_3)_6]$ (blue, 21%). These 20e clusters possess a regular octahedral core with Mo—Mo distances 2.662–2.664 Å in the case of S and 2.697–2.708 Å in the case of Se.[383] A transformation of $Mo_6Cl_8{}^{4+}$ into Mo_6S_8 is also achieved by treatment of Mo_6Cl_{12} with NaSH, NaO^{t}Bu and pyridine. A product of composition $Na_{0.8}Mo_6S_{8.4}(py)_2$ was isolated and converted upon prolonged extraction with py into dark-brown $Mo_6S_8(py)_6{\cdot}2py$ (Mo—Mo, 2.644 Å). The same product, when treated with $PrNH_2$ gives amorphous $[Mo_6S_8(PrNH_2)_{6-x}]$, which can be converted into $[Mo_6S_8(pyrr)_6]$ pyrr (Mo—Mo, 2.648 Å) or $[Mo_6S_8(pip)_6]{\cdot}7pip$ (Mo—Mo, 2.649 Å) upon treatment with pyrrolidine and piperidine, respectively.[385]

The above-mentioned PEt_3 complexes in THF solution exhibit a single oxidation and two reduction steps. The one-electron reduced 21e clusters obtained by Na/Hg reduction have been isolated as $(PPN)[Mo_6Q_8(PEt_3)_6]$ (Q = S, orange; Q = Se, red), and their structures determined.

The metal octahedron of the 21e clusters is distorted to a measurable degree, and the Mo—Mo distances are slightly longer than in the neutral clusters.[384] Reaction of $[Mo_6S_8(PEt_3)_6]$ with $NOBF_4$ in CH_2Cl_2 gives green $[Mo_6S_8(NO)(PEt_3)_5]$ (21%) and brown $[Mo_{12}S_{16}(PEt_3)_{10}]$ (15%) as products. The former has a distorted octahedral metal core: the Mo—Mo bonds involving the unique Mo atom bound to NO (Mo—N, 1.795 Å; Mo—N—O 175.3°) are much longer than between the rest of Mo atoms (2.63 Å). A detailed MO treatment of the bonding within the nitrosyl cluster is given.[386] The second, dodecanuclear cluster has two octahedral Mo_6S_8 cores connected to each other by two $Mo{-}\mu_4{-}S$ bonds, which is a similar connection to that mode found in solid-state Chevrel phases.[386] This cluster can also be obtained from $[Mo_6S_8(PEt_3)_6]$ by PEt_3 abstraction (as $SPEt_3$) with 1 eq. of sulfur.[387] The Se analog $[Mo_{12}Se_{16}(PEt_3)_{10}]$ is made by a similar procedure from $[Mo_6Se_8(PEt_3)_6]$ and S_8.[387]

The Chevrel phase Mo_6Se_8 reacts with KCN (650 °C) to give three products: the water-soluble blue 21e cluster $K_7[Mo_6Se_8(CN)_6]$ (Figure 57), which is oxidized in air into brown 20e $[Mo_6Se_8(CN)_6]^{6-}$, and as main product (up to 85%) black insoluble $K_6[Mo_6Se_8(CN)_5]$. An X-ray study of the latter shows that the Mo atoms in the basal plane of each Mo_6Se_8 cluster are bound to four terminal CN– ligands, with the clusters linked by CN groups into linear chains, $\{Mo_6Se_8(\mu{-}CN)^{6-}\}_x$ This 21e cluster gives an EPR spectrum (T = 10 K) characteristic of axial system, $g_{av} = 2.2891$. The Curie–Weiss law is obeyed over the 1.8–400 K range, with $\mu_{eff} = 1.99$ B.M.. The same products are also obtained by heating KCN with ($KMo_3Se_3 + MoSe_2$), ($KMo_3Se_3 +$ Se) or (Mo + $MoSe_2$) mixtures.[389,390]

Octahedral cluster groups M_6Q_8 with mixed chalcogen–halogen core are found in 23e $(Et_4N)_3$ $[(Mo_6Se_2Cl_6)Cl_6]$, 24e $(Ph_4P)_2(H_3O)_2((Mo_6Se_2Cl_6)Cl_6]$[391] and 24e $(Et_4N)_3$ $[(Mo_6TeCl_7)Cl_6]$.[392]

4.12.6.6.2 W Clusters

Reaction of polymeric W_6Cl_{12} with NaSH and NaO^nBu in py is complex, and gives dark-red $[W_6S_8(py)_6]$ only if molar ratio W:S is at least 1:12. This diamagnetic product is very insoluble in common solvents, and single crystals were grown only by heating in py at 200 °C for 5 days. At lower W:S ratios (1:8), and longer reaction times, red insoluble 22e $[W_6S_6Cl_2(py)_6]$ was the product, while for 1:6–1:8 ratio (and shorter reaction times in the latter case) red soluble 24e $[(W_6Cl_6S_2)Cl_2(py)_6]\cdot 5py$ is obtained.[393] A more soluble cluster is obtained when 4-tert-butylpyridine (^{t}Bupy) is substituted for py in a procedure using W_6Cl_{12}, KSH, KO^nBu and the ligand in DMF.[394] Even better yields of this orange cluster are obtained from $(Bu_4N)_2[W_6Cl_{14}]$ instead of polymeric W_6Cl_{12}. The ^{t}Bupy can then be quantitatively exchanged with pip or PEt_3, to give $[W_6S_8(pip)_6]$ (isostructural with the corresponding Mo cluster), or $[W_6S_8(PEt_3)_6]$.[395] This PEt_3 complex was the first W_6Q_8 cluster to be made and was prepared by a reductive dimerization reaction of trinuclear $W_3S_4Cl_4(PEt_3)_n]$ ($n = 3$–4) using Mg in THF.[396]

The cluster $[W_6S_8L_6]$ (L = PEt_3, $E_{1/2} = 0.11$ V; L = ^{t}Bupy, $E_{1/2} = 0.13$ V vs. Ag/AgCl) is oxidized by $FcPF_6$ into green paramagnetic 19e $[W_6S_8L_6]PF_6$. The products have $S = 1/2$ ground state with $\mu_{eff} = 1.71$ MB for L = PEt_3 and 1.60 MB for L = ^{t}Bupy. For L = PEt_3, the W—W distance (2.681 Å) is only marginally longer than in the neutral cluster (2.679 Å).[395] The ^{t}Bupy ligand can be replaced by cyanide by heating with KCN or NaCN in dimethyl sulfoxide (DMSO), and X-ray structures of $Na_6[W_6S_8(CN)_6]\cdot 18DMSO$ and $K_6[W_6S_8(CN)_6]\cdot 10H_2O$ have been carried out.[397] When $[W_6S_8(^tBupy)_6]$ reacts with the more sterically hindered PCy_3, the substitution stops with only four PCy_3 molecules entering the cluster, and *cis*-$[W_6S_8(PCy_3)_4(^tBupy)_2]$ is the

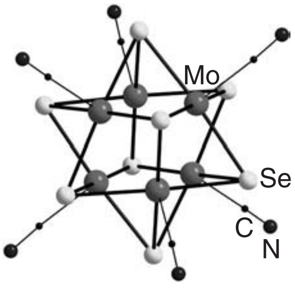


Figure 57 Structure of the $[Mo_6Se_8(CN)_6]^{7-}$ anion.

only product isolated from this reaction. In order to access the fully substituted $[W_6S_8(PCy_3)_6]$, more weakly bound *n*–BuNH$_2$ must be used as the ligand to be substituted. Prolonged heating of *cis*-$[W_6S_8(PCy_3)_4(^tBupy)_2]$ in benzene solution at 100 °C gives the following mixture of ligand redistribution products: *fac*-$[W_6S_8(PCy_3)_3\ (^tBupy)_3]$ (5.3%), *mer*-$[W_6S_8(PCy_3)_3\ (^tBupy)_3]$ (5.7%), *trans*-$[W_6S_8(PCy_3)_4\ (^tBupy)_2]$ (4.4%), *cis*-$[W_6S_8(PCy_3)_4(^tBupy)_2]$ (73.6%), $[W_6S_8(PCy_3)_5(^tBupy)]$ (11%).[398]

From substitution studies with various N, P and C donors it has been shown that the binding free energies increase in the following series: $PhNH_2$, $t\text{–}Bu_3P \ll Et_2NH$, $Bu_2NH < {}^tBuNH_2 <$ morph, pip $\leq n\text{–}BuNH_2$, $MeNH_2 \leq {}^tBupy$, py $< {}^tBuNC < PCy_3 < PPh_3$, $P^nBu_3 \leq PEt_3$. Crystal structures were determined for all the $W_6S_8L_6$ members of this series, with the exception of $L = PhNH_2$, Et_2NH, Bu_2NH and $^tBu_3P$.[399]

Red $[W_6Se_8L_6]$ clusters (L = pip, 74%, L = py, 56%) are accessed by the standard route from W_6Cl_{12}, Na_2Se and L both as ligand and solvent (reflux 3–4 days).[400] By contrast, reaction of W_6Cl_{12} with Na_2Se and PEt_3 (W:Se ratio 1:8) in toluene gives only the red—brown 20e mixed Se/Cl cluster $[W_6Se_7Cl(PEt_3)_6]Cl(CHCl_3)_6]$. In the core, the Cl and Se are randomly distributed over all the eight positions (W—W, 2.699 Å). The chloride is bound through hydrogen bonds to six $CHCl_3$ molecules (H···Cl 2.41 Å; Cl···C 3.33 Å). Using the Se reagent K_2Se (W:Se 1:10), crystals of $[W_6Se_{6.4}Cl_{1.6}(PEt_3)_6]Cl(CHCl_3)_6]$ are obtained. The cationic part was shown to be a mixture of diamagnetic 20e $[W_6Se_7Cl(PEt_3)_6]^+$ and paramagnetic 21e $[W_6Se_6Cl_2\ (PEt_3)_6]^+$ in a ratio 40:60.[401]

The W_6Te_8 core has been obtained using Na_2Te in the reaction with W_6Cl_{12} (3d, reflux in pip or py), and in the case of py, gives the 21e reduced cluster, characterized as $[Na(py)_6][W_6Te_8(py)_6]\cdot py$ (W—W 2.718–2.746 Å), and in the case of pip, the 20e cluster dark-blue $[W_6Te_8(pip)_6]\cdot 6pip$ (W—W 2.742 Å). The latter can be transformed into $[W_6Te_8(py)_6]$ by treatment with py (black powder), and the py complex, by treatment with PEt_3, into dark-purple $[W_6Te_8(PEt_3)_6]$ (W—W, 2.770 Å).[402,403]

4.12.6.6.3 Hexanuclear raft-type clusters with $Mo_6Q_8^{6+}$ cores

Reaction of $[Mo_3Q_4Cl_4L_5]$ (Q = S, Se; L = PEt_3 and/or THF) with Mg in THF at −20 °C gives brown $[Mo_6Q_8Cl_6(PEt_3)_6]$ (Q = S, 26%; Q = Se, 11%) (Figure 58). In this structure four Mo_3 triangles are aligned linearly by a process involving edge-sharing. There are 7 Mo—Mo single bonds (14e), and the structure may be viewed as formed by two reduced $Mo_3Q_4^{3+}$ triangular clusters united via a Mo—Mo bond (Q = S, 2.996 Å; Q = Se, 3.062 Å).[404]

A similar structure holds for $[Mo_6S_{10}(SH)_2(PEt_3)_6]$, obtained in a 11% yield from $(NH_4)_2[Mo_3S_{13}]$ and PEt_3 in THF. Here, each of four linearly aligned Mo_3 units is capped by a μ_3–S, while each peripheral Mo—Mo edge is bridged by a μ–S. The Mo—Mo bonding is again localized in two triangles (6 bonds, 12e) bound through a single bond (2.948 Å) (2e).[405]

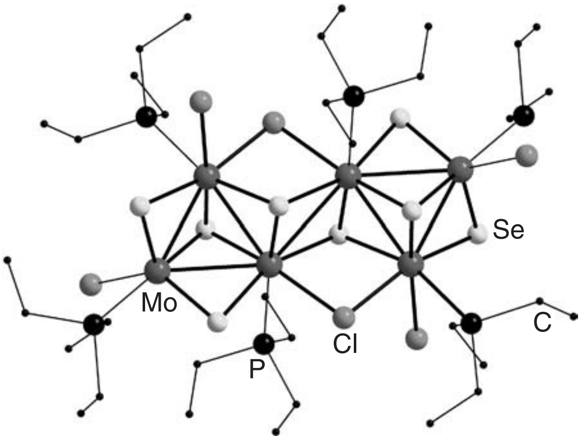


Figure 58 Structure of the $[Mo_6Se_8Cl_6(PEt_3)_6]$ molecule.

4.12.7 REFERENCES

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