Coordination Chemistry Reviews 138 (1995) 39-70

3. Tungsten

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CONTENTS

INTRODUCTION

This review covers the coordination chemistry of tungsten reported during the year 1992. Complexes have been classified according to the oxidation state of the tungsten atom(s) and the nature of the ligand donor atom type(s). A final section includes selected clusters with three or more metal atoms arranged by cluster type. References to purely organometallic compounds are avoided in this review, except in certain circumstances where there is significant metal-metal bonding. The analogous chemistry of chromium and molybdenum compounds has not been discussed.

The references for this article are based on a literature search of Vols. 116 and 117 of Chemical Abstracts. The following journals were also searched independently, *Acta Chem. Scand.; Acta Crystallogr., Sect. C; Angew. Chem. Int. Ed. Engl.; Bull. Chem. Soc. Jpn.; Chem. Lett.; Chem.*

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Ber.; Helv. Chim. Acta; Inorg. Chem.; J. Am. Chem. Soc.; J. Chem. Soc., Chem. Commun.; J. Chem. Soc., Dalton Trans.; J. Organomet. Chem.; Organometallics; Polyhedron; Z. Anorg. Allg. Chem.; Zh. Neorg. Khim. PLUTO diagrams were redrawn using the TEXSAN package of software by inputting the crystal parameters and atom coordinates from the original published work [1].

3.1 TUNGSTEN(VI)

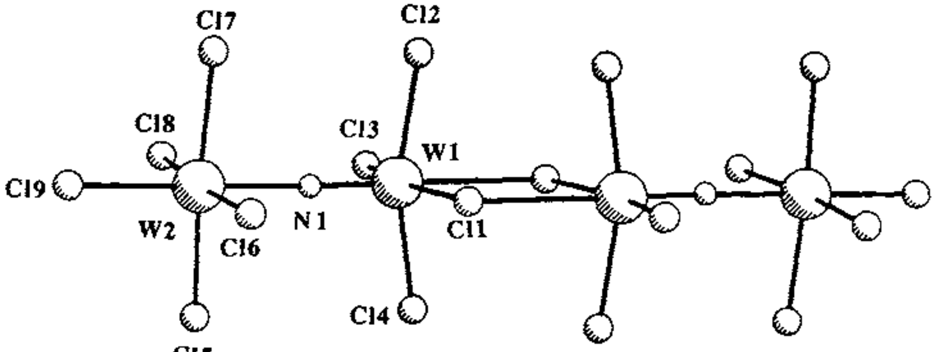
3.1.1 Complexes with halide ligands.

Reduction of mixture a of $MoCl_5$ and WCl_6 with aluminium in a NaCl-$AlCl_3$ melt produced mixed-metal clusters of the composition $[Mo_nW_{6-n}Cl_{14}]^{2-}$ (n = 0-6) as identified by liquid secondary ion mass spectrometry (LSIMS). The distribution of the two metals in the clusters depends on the ratio of molybdenum and tungsten in the starting melt, and is biased in favour of molybdenum [2].

3.1.2 Complexes with nitrogen donor ligands

The reaction of the tungsten(IV) silylimido complex $W(NSiMe_3)Cl_2(PMe_3)_3$ with excess Cl_2 yielded the W(VI) phosphoraniminato complex $W(NPMe_3)Cl_5$ with loss of $ClSiMe_3$ and PCl_2Me_3. Related tungsten(IV) phosphoraniminato complexes, $[W(NPR_3)Cl_2(PMe_3)_3]Cl$ (PR_3 = PMe_3, $PMePh_2$, PPh_3) are easily prepared by the addition of PCl_2Me_3 to $W(NSiMe_3)Cl_2(PMe_3)_3$ [3]. Using a limited amount of chlorine gas as oxidant, a tungsten(V) derivative $W(NPMe_3)Cl_4(PMe_3)$ was also synthesized and characterized. All of these complexes display approximately linear W-N-P geometries with short tungsten-nitrogen multiple bond distances of 1.736-1.79 Å. A high yield of the reduced mixed-valence nitride-bridged compound $[W_2NCl_9]_2[PClMePh_2]_2$ (**1**) is obtained from the reaction of WCl_6 with $Me_3SiNPMePh_2$. Interestingly, the highly oxidized tungsten phosphoraniminato complex $W(NPR_3)Cl_5$ containing W(VI) and P(V) centres can be further oxidized by oxygen atom sources producing W(VI) chloroimido complexes $W(NCl)Cl_4(OPR_3)$. The oxygen atom is attached to the P(V) in an organophosphine oxide form [4].

Addition of potassium hydrotris(1-pyrazolyl)borate (KTp) or potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate (KTp') to $W(CHC(Me_3)_2Ph)(NAr)(OTf)_2(dme)$ (Ar = 2,6-i-Pr_2-C_6H_3, OTf = $SO_3CF_3^-$, dme = $CH_3OCH_2CH_2OCH_3$) (**2**) yielded remarkably air-, moisture-, and heat-stable tungsten(VI) imido alkylidenes [5]. The complex $[Tp'W(CHC(Me_3)_2Ph)(NAr)(PyrH)][OTf]$ (PyrH = 3,5-dimethylpyrazole) (**3**), obtained from the reaction of (**2**) with KTp', is the first example of a crystallographically characterized d^0 cationic alkylidine. Compound (**2**) reacts with KTp to give $TpW(CHC(Me_3)_2Ph)(NAr)(OTf)$ (**4**), which exists in two isomeric forms as determined by ^1H NMR spectroscopy. Compound (**3**) catalyses the ring-opening metathesis polymerization of cyclooctene in the presence of $AlCl_3$, forming high molecular weight poly(1-octenylene) (M_n = 98,900, M_w/M_n = 1.2).



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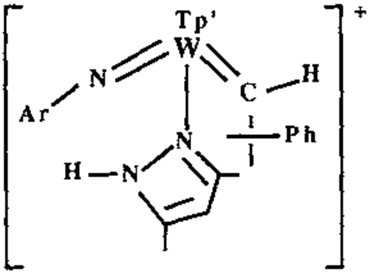

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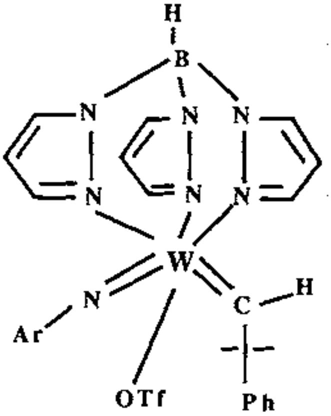

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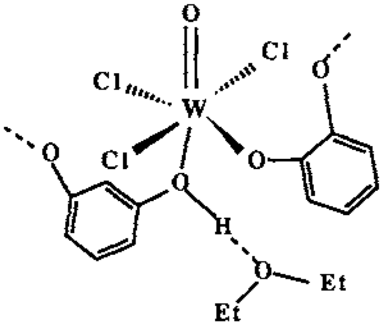
The complex WO_2Cl_2(tmen) (tmen = *N,N,N',N'*-tetramethylethylenediamine) has been prepared by two different methods [6]. A single crystal X-ray analysis showed that the tungsten atom is in an octahedral environment with *cis*-dioxo ligands, *cis*-chloro ligands and *cis* tmen nitrogen atoms resulting in an all *cis* configuration which is an unique feature of this complex. The *trans* influence of the oxo-ligands is evidenced by the two different W-N distances (2.249 Å *trans* to Cl and 2.458 Å *trans* to O) and two different W-Cl distances (2.336 Å *trans* to N and 2.458 Å *trans* to O) in the molecule and is discussed in relation to other multiply-bonded ligands. Analogous molybdenum complexes have also been prepared and characterized. Reaction of $WOCl_4$ with one equivalent of catechol in diethyl ether produced $[W(O)Cl_3(O, HO\text{-}C_6H_4)\cdot O(C_2H_5)_2]$ while reaction with two equivalents of catechol led to the formation of $[W(O)Cl(O_2\text{-}C_6H_4)(O,HO\text{-}C_6H_4)\cdot O(C_2H_5)_2]$ (5) in high yields [7]. A crystal structure analysis was performed on the latter compound. The tungsten atom is in an octahedral geometry and the diethyl ether molecule is strongly hydrogen-bonded to the hydroxy group with a short distance of 2.51 (2) Å between the ether oxygen atom and the hydroxy oxygen atom.



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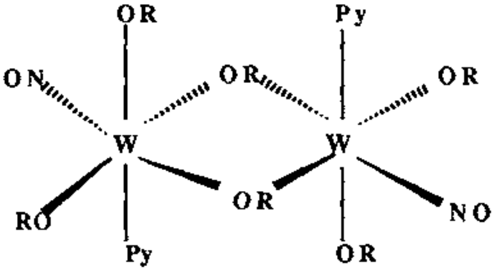

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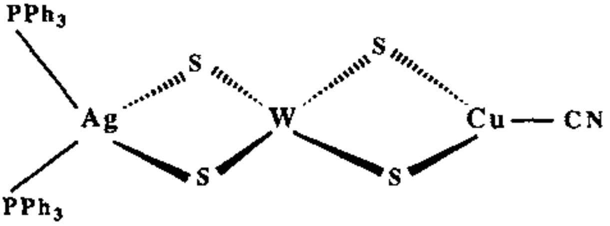
The reactions of the alkoxide-supported cluster $W_4(OR)_{12}$ (R = CH_2-*i*-Pr, CH_2-c-Pen, Pen = pentyl) with isonitriles RNC (R = ${}^tBu$, $PhCH_2$, mesityl) in hydrocarbon solvents at 22 °C produced the μ_4-carbido cluster $W_4(\mu_4\text{-}C)OR)_{14}$ by cleavage of the C≡N bond. However, $W_4(OR)_{12}$ clusters are inert to the nitriles MeCN and $NC(CH_2)_5CN$ and to the internal alkynes C_2Me_2 and C_2Et_2 under similar experimental conditions. In the presence of pyridine, $W_4(OR)_{12}$ reacts with nitric oxide to yield the dinuclear complex $[W(OR)_3(NO)(py)]_2$ (6) where each tungsten is in an octahedral coordination environment. The short W-N(nitrosyl) distance (1.75 Å) and the low value of $\nu(NO)$ = 1568 cm^{-1} supports extensive W d_π–NO π^* back-bonding [8].

3.1.3 *Complexes with sulfur donor ligands.*

A novel heterometallic cluster has been synthesized in 85 % yield obtained from the reaction of $[Et_4N]_2[WS_4Cu(CN)]$ with $(PPh_3)_2AgNO_3$ and characterized by elemental analysis, IR, UV-VIS spectroscopy and single crystal X-ray analysis [9]. The three different metals are nearly colinear with the cyanide ligand. The WS_2Ag *rhomb* and WS_2Cu *rhomb* units in (7) are planar. Hydrolysis and aerobic oxidation of $WS_3(S_2CNMe_2)_2$ and PPh_3 in acetonitrile at room temperature yields the complex $[W(S_2CNMe_2)_4]_2[W_6O_{19}]$ (8). The molecular structure shows that the tungsten atom is in a dodecahedral environment. The hexatungstate anion $[W_6O_{19}]^{2-}$ is located on an inversion centre [10].



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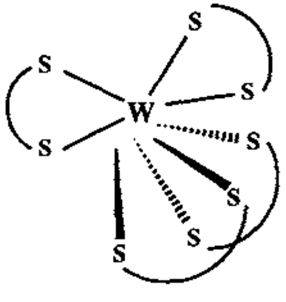
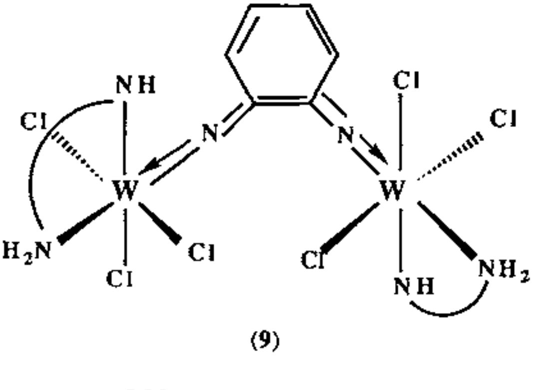


(8)

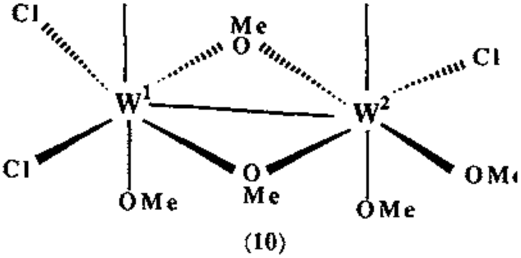
The reaction of $[MO_2S_2]^{2-}$ (M = Mo, W) with elemental sulfur in the presence of hydrazine hydrochloride in dmf at ambient temperature leads to the formation of $[Et_4N]_2[\{MO(S_2)_2\}_2(S_7)(NH_2NH_2)]\cdot MeCN$ in reasonable yields [11]. The solid state structure shows that the tungsten atoms are joined by both a S_7^{2-} and NH_2NH_2 bridge with each metal atom being further coordinated to two persulfide S_2^{2-} ligands and one double-bonded terminal oxo ligand. The two metals are in a *trans* disposition to each other. Furthermore, two types of conformations are observed for the bridging S_7^{2-} ligand that exhibit different torsion angles.

3.1.4 Complexes with mixed donor atom ligands

Reaction of WCl_6 and *o*-phenylenediamine (1,2-diaminobenzene, H_2pda) affords the dinuclear compound $[WCl_3\{1\text{-}(HN),2\text{-}(H_2N)(C_6H_4)\}]_2[\mu\text{-}1,2\text{-}(N)C_6H_4]$ (**9**) in ^{i}PrOH and the methoxide complex, $W_2Cl_3(OMe)_5(\mu\text{-}OMe)_2$ (**10**), when the reaction is carried out in MeOH. The metal centres in complex (**9**) are related by symmetry with each metal exhibiting a *mer*-arrangement of the three chlorides in an octahedral environment. The metal centres are inequivalent in complex (**10**), as W(1) is ligated by two terminal chlorides and two terminal methoxides (mutually *trans*) while W(2) contains one terminal chloride and three methoxide ligands. The W-W distance in (**10**) (2.733 (3) Å) is consistent with the presumed W-W single bond. The compound $WCl_4(PMe_3)_3$ reacts further with H_2pda to yield $WCl_2[1,2\text{-}(HN)_2(C_6H_4)](PMe_3)_3]$, while $WOCl_4$ reacts with the diamine and $LiNMe_2$ to give a 1,5-benzodiazepinium cation of $[W_2Cl_4O(NMe_2)_5]^-$ which exhibits bridging dimethylhydroxyl aminato groups. The products were fully characterized by single crystal X-ray analyses and IR and NMR spectroscopies [12].

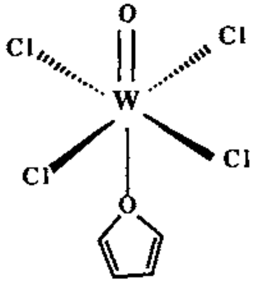


(**9**)



(**10**)

UV irradiation of a tetrahydrofuran solution of $W(CO)_6$ and $PPh_4[As_2SCl_4]$ resulted in the formation of $PPh_4[WOCl_4{\cdot}thf]$ **(11)** , $PPh_4Cl{\cdot}4As_4S_3$ and $PPh_4[Cl_2H]$ [13]. The crystal structure of **(11)** shows that the anion consists of a $WOCl_4$ group with a tetragonal pyramidal geometry and a short W=O bond distance of 1.69 Å. The thf molecule is associated with weak interactions (W-O = 2.36 Å). The reaction of $[WH_6(PMe_2Ph)_3]$ with $HBF_4{\cdot}Et_2O$ under a carbon monoxide atmosphere in tetrahydrofuran produced $[\{W(CO)_2(PMe_2Ph)_2\}_2(\mu\text{-}F)_3]{\cdot}BF_4$ **(12)** in low yield (32 %) [14]. The molecular structure of **(12)** was described as consisting of a basal plane containing three fluorine atoms bridging the two W atoms and a second parallel plane containing mutually *trans* carbon monoxide and two phosphine ligands.



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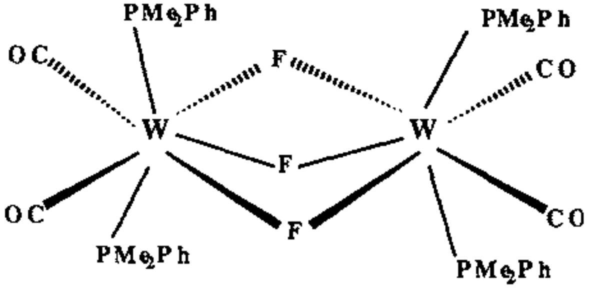


(12)

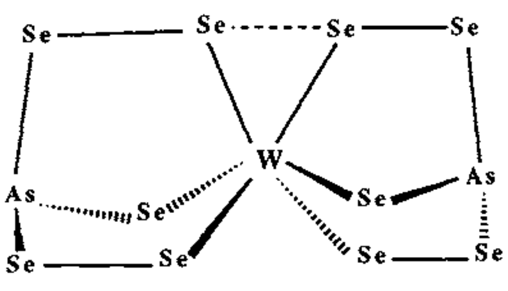
Mono- and bis-phenoxide compounds of tungsten are obtained from the reaction of WCl_6 with one or two equivalents of $Me_3Si[2,6\text{-}(CH_3)_2C_6H_3O]$ in toluene [15]. The products were characterized by elemental analysis, mass spectrometry, ^1H NMR spectroscopy and single crystal X-ray analysis. The two compounds $WCl_5[2,4\text{-}(CH_3)_2C_6H_3O]$ and $WCl_4[2,4\text{-}(CH_3)_2C_6H_3O]_2$ exhibit molecular symmetries of C_{2v} (*mm*) and C_{2h} (*2/m*) respectively. These are the first documented examples with linear W-O-C (phenoxy) bonds, the angles being 180° and 179° for the mono- and bis-phenoxide derivatives respectively.

3.2 TUNGSTEN(V)

Treatment of $[\{WCl_4\}_2(\mu\text{-}NC_6H_4N\text{-}1,4)]$ with PMe_2Ph results in the formation of the dinuclear d^1-d^1 tungsten(V) complex $[\{WCl_3(PMe_2Ph)_2\}_2(\mu\text{-}NC_6H_4N\text{-}1,4\}]$ [16]. The product was characterized by X-ray analysis and found to consist of two *mer, trans*-$WCl_3(PMe_2Ph)_2$ fragments linked in an eclipsed conformation by a linear, π-bonded 1,4-phenylenediimido ligand. Oxidative decarbonylation of the metal carbonyls $M(CO)_6$ (M = W, Mo) by the arsenic selenide anion $As_4Se_6^{2-}$ has been reported to lead to the formation of the compounds $[M(CO)_2(As_3Se_3)_2]^{2-}$ **(13)** and $[M(AsSe_5)_2]^{2-}$ **(14)** in moderate yields [17]. Complex **(14)** was also obtained from the addition of red selenium to complex **(13)**.

Reaction of $W(CO)_6$ with RNC (R = Et, ^{t}Bu) followed by treatment with bromine yields metal isocyanide complexes of general formula $W(CO)_2(CNR)_3(Br)_2$. These complexes react further with $Et_2NC{\equiv}CNEt_2$ to give the cationic alkyne derivatives *mer*-$[Br(CO)(RNC)_3W(\eta^2$-

$Et_2NC{\equiv}CNEt_2)]Br$. Thermal decarbonylation of the cations with RNC affords the carbonyl-free compounds *trans* $[Br(RNC)_4W(\eta^2\text{-}Et_2NC{\equiv}CNEt_2)]Br$ **(15)**. An X-ray diffraction analysis was performed on the PF_6 salt of **(15)**. The alkyne ligand acts a four-electron donor which gives the metal centre a closed-shell configuration. Spectroscopic data support substantial delocalization in the metal-alkyne fragment and restricted rotation of the diethylamino groups around the C_{alkyne}-N bonds. Complex **(15)** can also be obtained from the homoleptic isocyanide complex $W(CNEt)_6$ by a series of reactions involving coupling of two ethyl isocyanide ligands to give a bis(diethylamino)acetylene ligand. The molybdenum chemistry proceeds in an analogous fashion [18].



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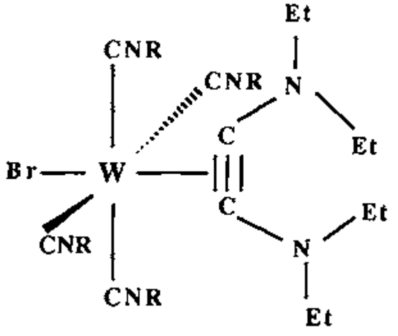

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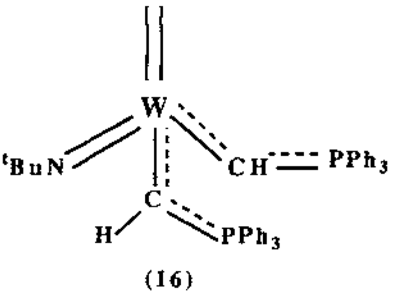
3.3 TUNGSTEN(IV)

Reduction of either $[WCl_4(PMe_2Ph)_2]$ or WCl_6 with sodium amalgam in thf in the presence of stoichiometric amounts of PMe_2Ph under varying pressures of dinitrogen leads to the formation of *cis* and *trans* -$[W(N_2)_2(PMe_2Ph)_4]$ [19]. Separation of the two isomers was achieved based on their different solubilities in pentane, with the *cis* isomer being more soluble than the *trans* isomer. Reaction of the *cis* complex with phenyl cyanide resulted in the substitution of one of the dinitrogen ligands to form $[W(N_2)(PhCN)(PMe_2Ph)_4]$, whereas the *trans*-isomer was found to be substitutionally inert. The two isomers have been characterized by IR, ^{31}P NMR spectroscopy and cyclic voltammetry. Transylidation of $[W(N^tBu)_2Cl_2]$ with four equivalents of methylenetriphenylphosphorane affords the highly reactive complex $[W(N^tBu)_2(CHPPh_3)_2]$ **(16)** in high yields [20]. Compound **(16)** is a tetrahedral mononuclear complex in the solid state as

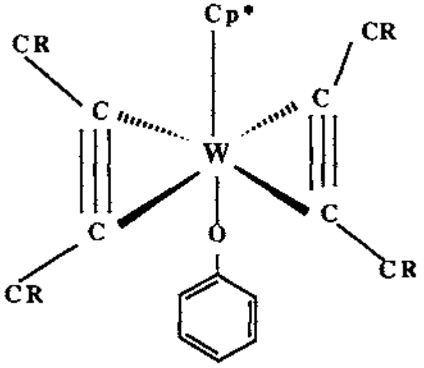


(16)

determined by single crystal X-ray analysis. Both W-C bond distances (2.043 (3) and 2.051 (3) Å) fall at the upper end of the range for W-C double bonds. The W-N bond distances are 1.773 (3) and 1.771 (3) Å.

The quadruply bonded heterometallic complexes $MoWCl_4(\mu\text{-dppm})_2$, $\beta\text{-}MoWCl_4(\mu\text{-dppe})_2$, $\alpha\text{-}MoWCl_4(dppe)_2$, $MoWCl_4(\mu\text{-dmpm})_2$ and $\alpha\text{-}MoWCl_4(dmpe)_2$, are produced in the reactions of $MoWCl_4(PMePh_2)_4$ with dppm, dppe, dmpm, dmpe, respectively [21]. These complexes are the first examples of heteronuclear quadruply bonded compounds of the type $MM'Cl_4(L\text{-}L)_2$, where L-L groups are didentate phosphines. The diphosphine ligands are bonded either in a chelating mode (denoted as α-complex), or in the more commonly encountered bridging mode (denoted as β-complex). All the complexes were fully characterized by single crystal X-ray analysis, as well as ^1H and ^{31}P NMR spectroscopies. The diamagnetic anisotropy of the Mo-W bond has been estimated from the ^1H NMR chemical shift data of the methylene or ethylene protons. The heterodimetallic edge-sharing bioctahedral complexes $MoWCl_6(dppe)_2$, $MoWCl_6(\mu\text{-dppm})_2$, and $MoWCl_6(\mu\text{-dmpm})_2$ were synthesized by oxidative addition reactions of the corresponding quadruply bonded M_2L_8 complex and $PhICl_2$ or CH_2Cl_2. These complexes represent the first examples of heteronuclear edge-sharing bioctahedral complexes of the form $MM'Cl_4(\mu\text{-Cl})_2(L\text{-}L)_2$, where L-L are didentate phosphines [22].

A series of mono-Cp* complexes of the type $WCp^*(OR)_3Cl$ and $WCp^*(OR)_4$ have been investigated [23]. Products obtained from the reduction of $WCp^*(OC_6H_5)_4$ using 0.5 % sodium amalgam under dinitrogen were intractable, but a single diamagnetic product of composition $WCp^*(OC_6H_5)(RC{\equiv}CR')_2$ (R = H, R' = H, TMS, C_6H_5; R = R' = Me) (**17**) was obtained in high yield. A single crystal X-ray diffraction analysis revealed a pseudotetrahedral environment around the tungsten atom. Based on the spectroscopic evidence, the oxidation state of the metal could be from W(II) to W(VI).



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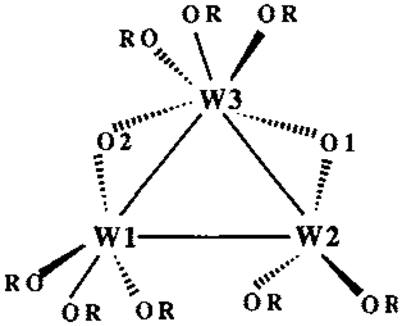
3.4 *TUNGSTEN(III)*

3.4.1 *Complexes with oxygen donor ligands*

The reaction of $W_2(O\text{-}^tBu)_6$ with two equivalents of N_2O in pentane at -15°C yields the complex $W_3O_2(O\text{-}^tBu)_8$ (**18**) in low yield (15 %). The molecular structure of (**18**) is unusual for several reasons: (i) there is no capping ligand (ii) there are two long (2.93 Å) and one short (2.45 Å) metal-metal bond distances and (iii) the two oxo ligands are in the W_3 plane and bridge the two long W-W distances while the short W-W edge of the triangle is unsupported. As a result, each tungsten atom is in a unique coordination environment. Complex **(18)** dissociates irreversibly in warm toluene (45°C) to form $W_2(O\text{-}^tBu)_6$ and $WO_2(O\text{-}^tBu)_2$ [24].



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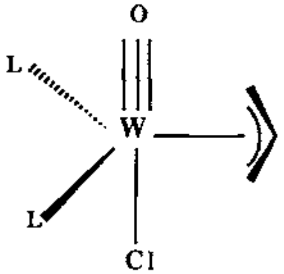
The X-ray structure of the compound, $(^tBuO)_3W{\equiv}C\text{-}C{\equiv}W(O\text{-}^tBu)_3$, obtained from the scission of 3,5-octadiene by $W_2(O\text{-}^tBu)_6$ has been determined at low temperature (-171°C). The compound crystallizes in the triclinic system P1 with two interstitial toluene molecules. The two $W(O\text{-}^tBu)_3$ groups are arranged in a staggered conformation. Cyclic voltammetry measurements in CH_2Cl_2 with $[n\text{-}Bu_4N][PF_6]$ as the supporting electrolyte reveal two irreversible oxidations at +0.36 and +0.82 V vs SCE [25]. Reactions of WCl_2L_4 (L = PMe_3, $PMePh_2$) with (allyloxy)trimethylsilane in toluene at 65 °C produced the tungsten-oxo-allyl complexes, $W(O)(\eta^3\text{-}C_3H_5)(L)_2Cl$ **(19)** in high yields. The tungsten atom abstracts the oxygen atom while retaining the organic fragment. The chloride is abstracted to form Me_3SiCl as a by-product of the reaction. The formation of a strong W=O multiple bond and coordination of the η^3-allyl group provides the driving force for cleavage of the Si-O bond. In the analogous reaction of $WCl_2(PMe_3)_4$ with vinyl- and allylsilane reagents, tungsten carbyne compounds, $W(CR)(PMe_3)_4Cl$ **(20)** are obtained; the vinyl group is transformed to methyl carbyne and allyl to ethylcarbyne, respectively [26].



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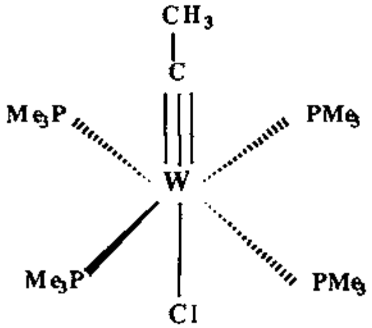
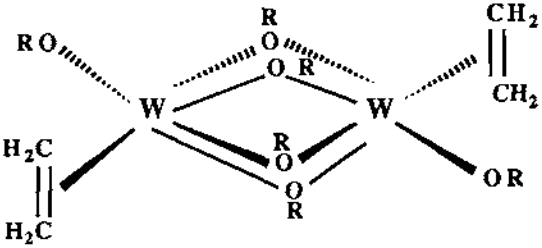


(20)

Reaction of hydrocarbon solutions of $W_2(OCH_2\text{-}^tBu)_6$ with two or more equivalents of ethylene at 0°C yields $W_2(OCH_2\text{-}^tBu)_6(\eta^2\text{-}C_2H_4)_2$, **(21)** which represents the first organometallic compound derived from the addition of an olefin to a compound containing a metal-metal triple bond [27]. In this compound, four bridging OR-ligands span a W-W bond separation of 2.533 (1) Å in an unsymmetrical arrangement; W-O(bridge) = 2.00 (1) and 2.31 (1) Å (average) for the four short and four long distances, respectively. The two olefinic C_2 axes are mutually orthogonal and perpendicular to the W-W axis. A salient feature of this chemistry is the reversible formation of **(21)** at ambient temperature conditions.



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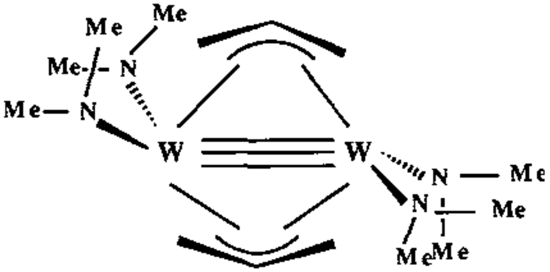
3.4.2 Complexes with nitrogen or sulfur donor ligands

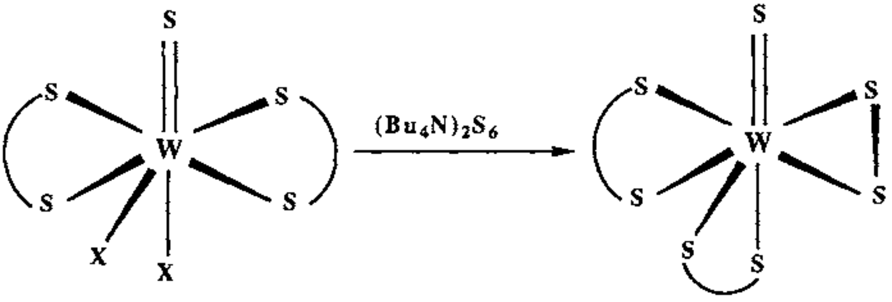
Two equivalents of RMgCl (R = allyl, 1-methylallyl, 2-methylalllyl) reacts with 1,2-$W_2Cl_2(NMe_2)_4$ in hydrocarbon solvents to afford the compounds $W_2R_2(NMe_2)_4$ [28]. The molecular structure of $W_2(C_3H_5)_2(NMe_2)_4$ **(22)** reveals bridging allyl ligands and terminal NMe_2 ligands. Molecular orbital calculations support an extensive mixing of the allyl π-MO's with the W≡W π-MO's, in agreement with the long W-W (2.481 (1) Å) and C-C (1.47 (1) Å) distances. Variable temperature ^1H and ^{13}C NMR studies show that both *anti-* and *gauche* -$W_2C_2N_4$ rotamers are present in solution, although the solid state structure indicates only a *gauche*-$W_2C_2N_4$ arrangement in $W_2(C_4H_7)_2(NMe_2)_4$.



(22)

Reactions of $(Et_2NCS_2)_2Se$ with anionic mononuclear WS_4^{2-} or trinuclear $W_3S_9^{2-}$ in acetonitrile give $WS_3(S_2CNEt_2)_2$, which yields thiohalogenide complexes, $WSX_2(S_2CNR_2)_2$ (R = Me, Et) upon treatment with HX (X = Cl, Br). The molecular structure of $WSCl_2(S_2CNMe_2)_2$ **(23)**

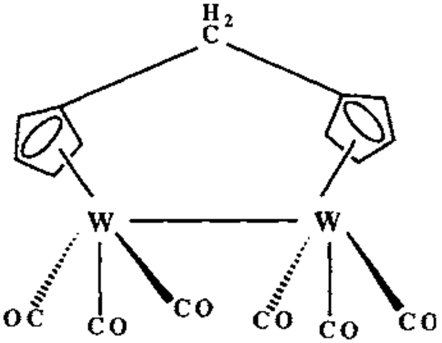
shows that the geometry about the tungsten atom is a slightly distorted pentagonal bipyramid whose equator is defined by the sulfur atoms of the dimethyldithiocarbamate ligands. Based on infrared spectral studies, the authors suggest that interaction of **(23)** with $[{}^tBu_4N)_2{}^{34}S_6$ leads to the formation of $W^{32}S(^{34}S\text{-}^{34}S)(S_2CNMe_2)_2$ **(24)** and $W^{34}S(^{32}S\text{-}^{34}S)(S_2CNMe_2)_2$ [29].



(23) (24)

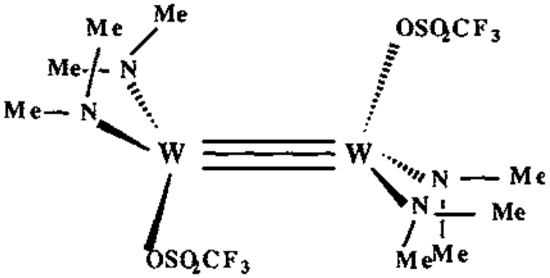
3.4.3 *Complexes with mixed donor atom ligands*

The complexes $[WI_2(NCMe)(\eta^2\text{-}RC_2R)_2]$ (R = Me or Ph) react with 1-5 equivalents of CN^tBu in CH_2Cl_2 at room temperature to give $[WI_2(CO)(CN^tBu)(\eta^2\text{-}RC_2R)_2]$, $[WI_2(CO)(CN^tBu)_2(\eta^2\text{-}RC_2R)]$, $[WI_2(CN^tBu)_3(\eta^2\text{-}RC_2R)]$, $[WI(CN^tBu)_4(\eta^2\text{-}RC_2R)]I$, and $[W(CN^tBu)_5(\eta^2\text{-}RC_2R)_2]I_2$. The identity of these complexes was established by ^1H and ^{13}C NMR spectroscopy [30]. Reaction of methylenedicyclopentadiene ($bcpmH_2$) with $(CH_3CN)_3W(CO)_3$ gives the dinuclear complex $(bcpm)W_2(CO)_6$ **(25)** in high yields [31]. An X-ray analysis of the analogous chromium complex exhibits a chiral structure which is a consequence of distortion of the bcpm ligand. Low temperature ^1H NMR measurements reveal a dynamic process analogous to that previously observed for the silyl-bridged complexes.



(25)

The compound $W_2(NMe_2)_4(OTf)_2$ ($OTf = O_3SCF_3^-$) **(26)** has been prepared from either the reaction of $W_2(NMe_2)_6$ with two equivalents of Me_3SiOTf in hexanes in quantitative yield (95 %) or from the reaction of $W_2Cl_2(NMe_2)_4$ with AgOTf (2 equivalents) in thf (15 %) yield [32]. A single crystal X-ray analysis showed that **(26)** contains an *anti*-$W_2O_2N_4$ core with a W-W distance of 2.29 (2) Å. Ligand redistribution occurs in the reaction of $W_2(NMe_2)_4(OTf)_2$ **(27)** with excess PMe_3 in toluene to yield $W_2(NMe_2)_3(OTf)_3(PMe_3)_2$ and $W_2(NMe_2)_6$. The molecular structure of **(27)** contains roughly square planar WON_2P and WO_2NP units united by a W≡W bond of 2.324 (1) Å. The $W_2O_3N_3P_2$ unit is staggered in the structure. In an attempt to prepare $W_2(O\text{-}^tBu)_4(OTf)_2$ from the reaction between $W_2(O\text{-}^tBu)_6$ and Me_3SiOTf, a thermally unstable polymeric compound formulated as $[W(O\text{-}^tBu)_2(OTf)]_n$ (*n* = even), was obtained. Addition of PMe_3 to this polymeric product gives $W_2(O\text{-}^tBu)_4(OTf)_2(PMe_3)_2$ in high yield.



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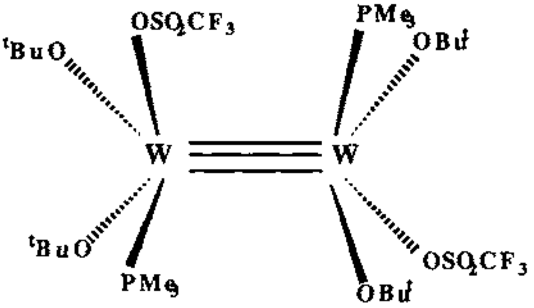
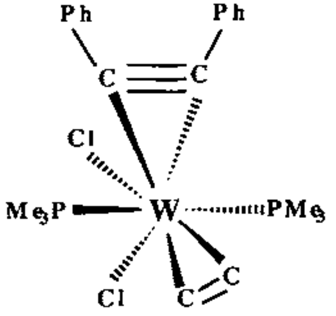


(27)

Reduction of $[WCl_3(PhC_2Ph)(PMe_3)_2]$ with Na/Hg amalgam in the presence of MeC_2Me and $Me(CH_2)_2C_2Me$ or substitution of a phosphine ligand in $[WCl_2(PhC_2Ph)(PMe_3)_3]$ by PhC≡CPh, PhC≡CH, and HC≡CH yield mixed bis-alkyne complexes; these complexes have been characterized by IR, ^1H NMR and ^{13}C NMR spectroscopy [33]. The mixed alkene-alkyne complex $[WCl_2(PhC_2Ph)(CH_2{=}CH_2)(PMe_3)_2]$ **(28)** is obtained in the reduction reaction using ethylene as an alkene source. The phosphine ligands are repelled by the alkyne and alkene ligands which straddle the respective P-W-P plane without any significant twists.

The triply bonded dimers $[W_2(\eta\text{-}C_5H_4R)_2X_4]$ (R = Me or ^iPr, X = Cl or Br) undergo addition reactions with a number of Lewis bases to give a variety of complexes including $[W_2(\eta\text{-}C_5H_4Me)_2Cl_2(\mu\text{-}Cl)_2(dmpe)]$, $[W_2(\eta\text{-}C_5H_4R)_2Cl_2(\mu\text{-}Cl)_2(CO)_2]$, *fac*-$[W(\eta\text{-}C_5H_4{}^iPr)Br_3(CO)_2]$, $[W_2(\eta\text{-}C_5H_4R)_2Cl_3(\mu\text{-}Cl)(\mu\text{-}\sigma{:}\eta^2\text{-}^tBuNC)(^tBuNC)]$, $[N(PPh_3)_2][W_2(\eta\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)]$ and $[W_2(\eta\text{-}C_5H_4R)_2Cl_3(\mu\text{-}Cl)(\mu\text{-}\sigma{:}\eta^2\text{-}R'CN)]$ (R' = Me, Et Ph; R = ^iPr, Me) [34]. These compounds were characterized by elemental analysis and ^1H and ^{31}P NMR spectroscopies; selected compounds were subjected to single crystal X-ray analysis. The complex [$W_2(\eta\text{-}C_5H_4{}^iPr)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}EtCNH)$] **(29)** constitutes the first crystallographically characterized example of a perpendicular bridging iminoacyl ligand.



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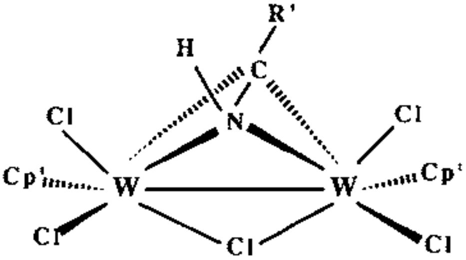


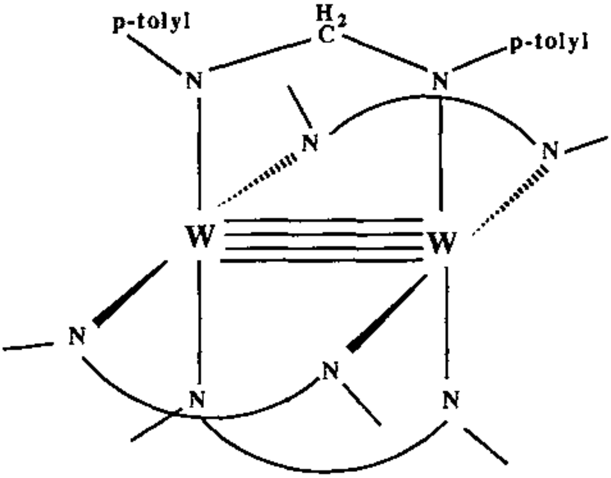
(29)

3.5 *TUNGSTEN(II)*

3.5.1 *Complexes with nitrogen or sulfur donor ligands*

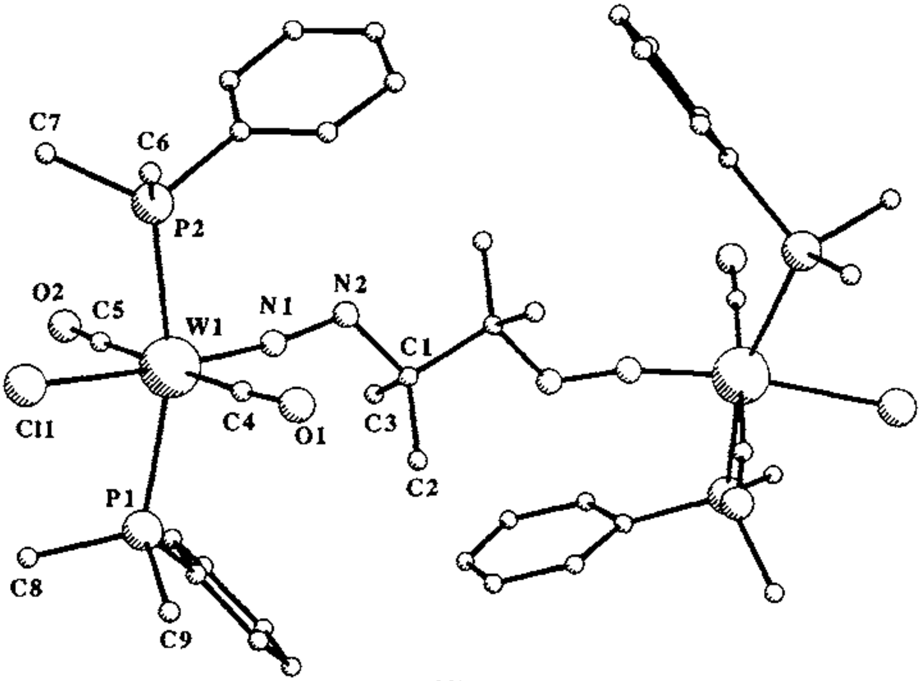
A number of hydrazine adducts are formed upon the addition of hydrazine, methylhydrazine, or 1,1-dimethylhydrazine to [Cp^*WMe_4]PF_6. These complexes are readily deprotonated to give hydrazido complexes of the type $Cp^*WMe_4(\eta^2$-hydrazidol), and decompose to yield complexes of the type [$Cp^*WMe_3(\eta^2$-hydrazido)]$^+$ while releasing methane [35]. The cations deprotonate at low temperatures to give complexes of the type $Cp^*WMe_3(\eta^2$-hydrazido), which rearrange readily to $Cp^*WMe_3(\eta^1$-hydrazido) at the temperature of approximately –20°C. The complexes characterized solely by IR and NMR spectroscopy were discussed in the context of dinitrogen reduction to ammonia at a high oxidation state tungsten centre. Synthesis and full characterization of two new compounds of the type $M_2(L)_4$ (M = Cr, W) (HL = di-*p*-tolylformamidine) completes the triad of group VI dinuclear complexes with formamidine ligands [36]. The complex $W_2(L)_4$ **(30)** is obtained from the reaction of LiL with $Na_4(thf)_xW_2Cl_8$ in thf in 45 % yield. The solid state structure shows that the complex has a crystallographically imposed C_4 symmetry with both W atoms residing on the four-fold axis. The assignment of a metal-metal quadruple bond is in accord with the W-W distance of 2.187 (1) Å. A cyclic voltammogram of **(30)** in CH_2Cl_2 exhibits a reversible oxidation at -0.28 V (vs Ag/AgCl) which suggests that $W_2(L)_4{}^+$ species are accessible.

Reaction of the diazoalkane complex *mer*-[$WCl_2(NN{=}CMe_2)(PMe_2Ph)_3$] with CO in the presence of $ZnCl_2$(dioxane) affords the cationic carbonyldiazoalkane complex [$WCl(CO)(N{=}NCMe_2)(PMe_2Ph)_3$][$ZnCl_3$(thf)] in high yield (75 %) [37]. Treatment of this complex with an excess of mercury in thf at ambient temperature under CO produces the ditungsten complex, [$WCl(CO)_2(PMe_2Ph)_2(NN{=}CMe_2CMe_2N{=}N)WCl(CO)_2(PMe_2Ph)_2$] **(31)** with a bridging $NN{=}CMe_2CMe_2N{=}N$ ligand. The tungsten atoms are in an octahedral geometry, in which the Cl ligand coordinates *trans* to the diazenido ligand.



(30)

Reactions of $[W(CO)(Ph_2PhC{\equiv}CPPh_2)(S_2CNEt_2)_2]$ with $[W(CO)_4(pip)_2]$ (pip = piperidine yield $[W(CO)\{Ph_2PC{\equiv}CPPh_2)W(CO)_4\}(S_2CNEt_2)_2]$ (**32**). A single crystal X-ray analysis shows that the acetylenic bond of $Ph_2PC{\equiv}CPPh_2$ is coordinated to the W(II) centre, while the two phosphorus atoms are coordinated to the tungsten tetracarbonyl fragment to form a five-membered chelate ring. ^{13}C NMR data are discussed in relation to the molecular structure; a variable temperature ^{31}P NMR spectroscopic study established the barrier to alkyne rotation [38].



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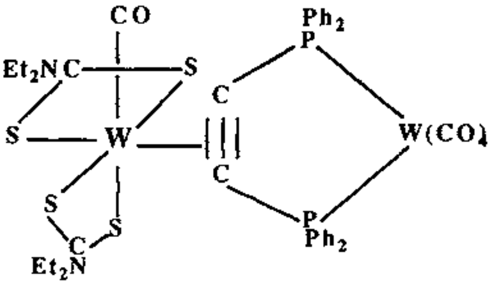
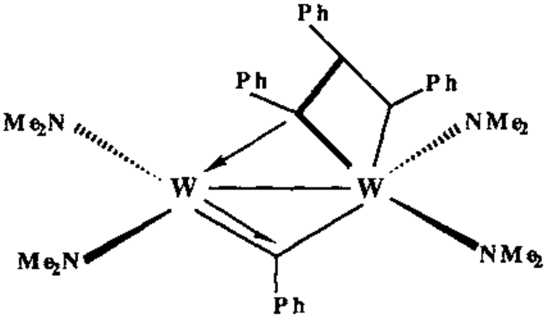


(32)

3.5.2 *Complexes with mixed donor atom ligands*

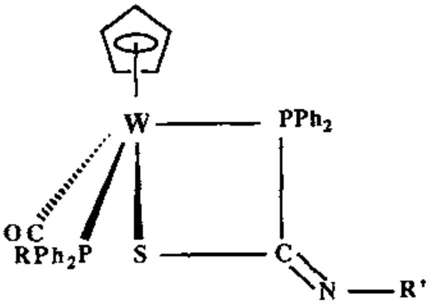
Reactions between 1,2-$W_2Cl_2(NMe_2)_4$ and two equivalents of a lithium organophosphide reagent, $LiPR_2$ (R = ^tBu, Et, $SiMe_3$, Ph, *p*-tol, *p*-C_6H_4F) in thf at 0 °C or below yield mixed-phosphido complexes 1,2-$W_2(PR_2)_2(NMe_2)_4$ [39]. Single crystal X-ray analyses revealed that both *anti*- and *gauche* -$W_2P_2N_4$ ethane-like cores with metal-metal distances typical of a W_2^{6+} core with $\sigma^2\pi^4$ triple bond character are observed (2.2 Å). Based on ^{31}P NMR chemical shifts and the measured barriers to rotation about the M-N and M-P bonds, it is concluded that a competition between metal-imido and metal-phosphido bonding exists which is controlled by the substituents on the phosphorus atom. Except for bulky R group systems (R = $SiMe_3$ and ^tBu), isomerization of these phosphido-bridged dimers occurs in hydrocarbon solution above 0 °C. The bridged isomers are characterized by lower field ^{31}P chemical shifts, *ca.* 180-280 ppm, and larger values for $J(^{183}W\text{-}^{31}P)$ *ca.* 250-350 Hz, relative to the unbridged isomers. Bridge formation is favored for the more Lewis-basic phosphide ligands. When 1,2-$W_2Cl_2(NMe_2)_4$ is allowed to react with 1,4-$Li_2C_4Ph_4$ in tetrahydrofuran at 0°C, a black compound of composition $W_2(\mu\text{-}C_3Ph_3)(\mu\text{-}CPh)(NMe_2)_4$ (**33**) is obtained in high yield. The molecular structure consists of two terminal amido ligands and bridging benzylidyne and a μ-metallacyclobutadiene ligands spanning a metal-metal distance of 2.67 Å. The air-sensitive compound is soluble in hydrocarbons [40].



(33)

The unprecedented asymmetric compound Cp*W(NO)(CH_2SiMe_3)R (R = alkyl or aryl) was synthesized in three steps from Cp*W(NO)(CH_2SiMe_3)$_2$[41]. The first step involves exposure of Cp*W(NO)(CH_2SiMe_3)$_2$ to H_2 at atmospheric pressure in acetonitrile to give Cp*W(NO)(CH_2SiMe_3)(N=C(H)CH_3). The second step requires treatment of this intermediate product with 2 equivalents of HCl in Et_2O to form Cp*W(NO)(CH_2SiMe_3)Cl. In the final step, a metathesis reaction of this complex with an organomagnesium reagent, R_2Mg (R = *o*-tolyl, CH_2CMe_2Ph, Me) produces the mixed allyl and alkyl-aryl complexes, Cp*W(NO)(CH_2SiMe_3)R (R = o-tolyl, CH_2CMe_2Ph, Me). The complexes have been characterized by spectroscopy and single crystal X-ray analysis. Complexes of the type Cp(OC)(RPh_2P)M-PPh_2-C(=N-R')S (M = W, Mo; R = H, Me; R' = Et, ^{t}Bu,Ph) (**34**) are obtained from the reaction of chiral phosphenium complexes Cp(OC)(RPh_2P)M=PPh_2 with the aryl- and alkylisothiocyanates *via* [2+2]-cycloaddition. The products were identified on the basis of IR and NMR spectroscopies [42].

Reactions of the alkylidyne complexes [W(CR)Br$(CO)_3$L] (L = CO, R = C_6H_4OMe-4, $C_6H_4NMe_2$-4; L = PPh_3, R = Ph, $C_6H_4NMe_2$-4) with methyllithium in thf at low temperature afford the alkylidyne acyl tungsten complexes Li[W(CR)(COMe)Br$(CO)_3$L] (**35**) in good yields [43]. Further reactions of these complexes with $C_2O_2Br_2$ in CH_2Cl_2 followed by addition of PPh_3 gives the alkyne complexes [WBr_2(CO)($CH_3C\equiv CR$)$(PPh_3)_2$] (**36**). The identity of these complexes have been established by a combination of spectroscopic methods. The formation of the alkyne ligands is believed to be a result of the coupling of two alkylidyne ligands.



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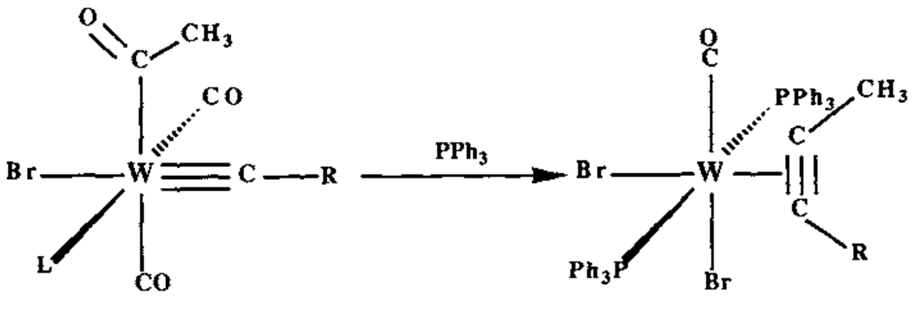

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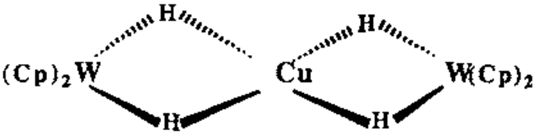
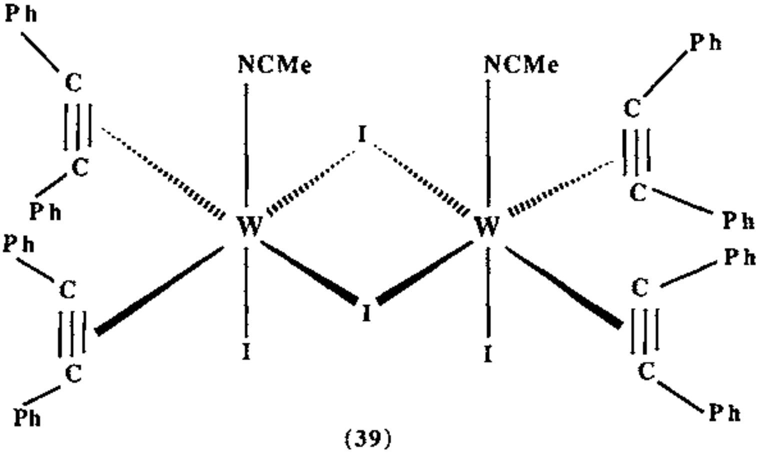
(36)

Reactions of Cp_2WH_2 with $[Cu(NCMe)_4]^+$ in a 2:1 molar ratio (thf) in a dry ice-isopropanol bath followed by warming of the solution to room temperature gives $[(Cp_2WH_2)_2Cu]^+$ (**37**). The molecular structure of the analogous molybdenum derivative has been studied by single crystal X-ray diffraction analysis. IR and ^1H NMR data are consistent with the solid state structure in which all the hydrides are bridging. Reaction of Cp_2WH_2 with $AgBF_4$ first gives $[(Cp_2WH_2)_2Ag]^+$, which is oxidized by additional Ag^+ in MeCN to give equimolar amounts of $[Cp_2W^{VI}H_3]^+$ and $[Cp_2W^{IV}H(NCMe)]^+$ *via* the adduct $[(Cp_2WH_2Ag)_2]^{2+}$. The adduct is believed to possess μ^3-hydrides as indicated by IR spectroscopy. Addition of $[Cu(NCMe_4)]^+$, however, has no effect on $[(Cp_2WH_2)_2Cu]^+$. A detailed mechanism has been proposed for these reactions [44].



(**37**)

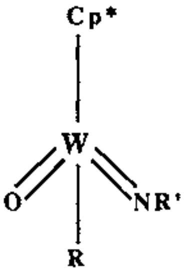
The mono(acetonitrile) complex $[WI_2(CO)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]$ reacts with PhC_2Ph in refluxing acetonitrile for 5 h to give the bis(acetonitrile) complex $[WI_2(NCMe)_2(\eta^2\text{-}PhC_2Ph)_2]$ (**38**) in high yield [45]. Acetonitrile-substituted products of composition $[WI_2(Ph_2P(CH_2)_nPPh_2)(\eta^2\text{-}PhC_2Ph)_2]$ are obtained from the reaction of (**38**) with equimolar quantities of $Ph_2P(CH_2)_nPPh_2$ (n = 1-3). When (**38**) is refluxed in $CHCl_3$ for three hours, the iodo-bridged dinuclear complex $[WI(\mu\text{-}I)(NCMe)(\eta^2\text{-}PhC_2Ph)_2]_2$, (**39**) is formed; the compound is proposed to have two possible structures. Iodo-bridged dinuclear complexes and bis(dithiocarbamate) complexes are obtained from the reaction of (**38**) with NaS_2CX (X = NMe_2 or NEt_2) under various experimental conditions. The identity of these compounds was established by elemental analysis as well as by IR, ^1H, and ^{13}C NMR spectroscopies.



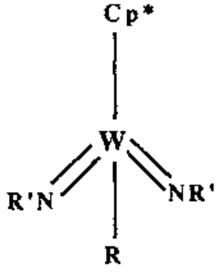
(**39**)

Treatment of $Cp^*W(O)_2(CH_2SiMe_3)$ with *p*-tolyl isocyanate leads to the formation of $Cp^*W(O)(NC_6H_4\text{-}p\text{-}Me)(CH_2SiMe_3)$ (**40**), $Cp^*W(NC_6H_4\text{-}p\text{-}Me)_2(CH_2SiMe_3)$ (**41**) and $Cp^*W(NC_6H_4\text{-}p\text{-}Me)[N(C_6H_4\text{-}p\text{-}Me)C(O)N(C_6H_4\text{-}p\text{-}Me)](CH_2SiMe_3)$ (**42**) [46]. Single crystal X-ray diffraction analyses of these organometallic imido complexes reveal three-legged (**40**) and (**41**) and four-legged (**42**) piano-stool structures. Each of these complexes is formed in a sequential manner from its precursor by incorporation of an additional *p*-tolyl isocyanate fragment.

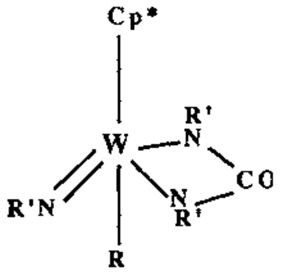
A novel disilylhydrazido (2-) complex, *mer*-$[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3]$ (**43**), is obtained from the reaction of $ClMe_2SiCH_2CH_2SiMe_2Cl$ with *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ and excess NaI. Compound (**43**) reacts with CH_2X_2 (X = Cl, I) to yield the paramagnetic disilylhydrazido (2-) complex $[WX_3(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2]$. Reactions of (**43**) with CO, $CH_2{=}CH_2$, and nitriles produce neutral disilylhydrazido(2-) complexes $[WI_2(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_2(L)]$ (L = CO, $CH_2{=}CH_2$, MeCN, EtCN, *p*-MeC_6H_4CN, *p*-$MeCOC_6H_4CN$) The reaction of (**43**) with ^tBuNC, however, produces the cationic complex *mer*-$[WI(NNSiMe_2CH_2CH_2SiMe_2)(PMe_2Ph)_3(^tBuNC)]I$ as a major product [47].



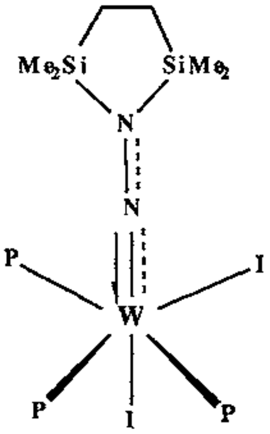
(**40**)



(**41**)

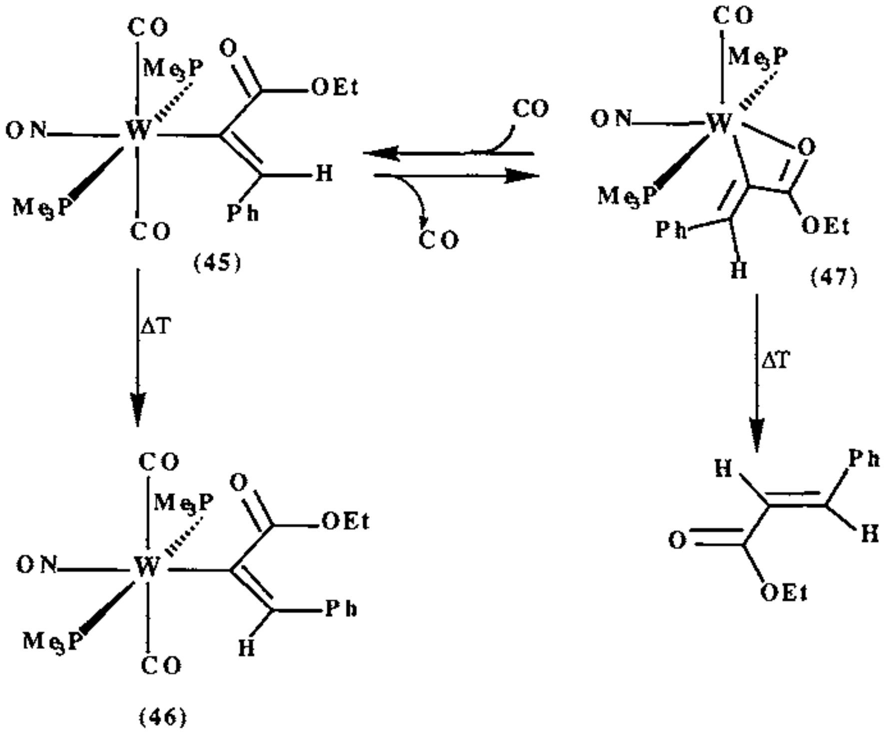


(**42**)



(**43**)

Selective α-metalation occurs in the insertion reactions of *trans*,*trans*-$WH(CO)_2(NO)(PMe_3)_2$ (**44**) with activated acetylenes of the type $RC{\equiv}CCO_2R'$ (R = H, Me, Ph, R'O_2C), affording tungsten vinyl compounds [48]. The reaction of PhC≡CCO_2Et with **(44)** initially yields the *trans*- and *cis*-products W[Z-C(CO_2Me)=CH(Ph)]$(CO)_2(NO)(PMe_3)_2$ **(45)**, W[*E*-C(CO_2Me)=CH(Ph)]-$(CO)_2(NO)(PMe_3)_2$ **(46)** in an 85:15 ratio. Compound **(44)** slowly and reversibly loses CO, leading to the complex W[Z-C{C(O)OEt}=CH(Ph)](CO)(NO)$(PMe_3)_2$ **(47)** which contains a four-membered metallacycle. Equilibrium solutions of **(44)** and **(47)** were heated in the presence of CO which resulted in irreversible conversion of these compounds to **(46)**. Reduction of simple and phenoxy-functionalized aldehydes and ketones occurs with the compound **(44)** [49].



3.6 TUNGSTEN(0)

3.6.1 Complexes with nitrogen donor ligands.

The mononuclear complex $[W(CO)_4(\eta^2\text{-}C_2O_4)]^{2-}$ is obtained in 56 % yield by addition of one equivalent of $[Et_4N]_2[C_2O_4]$ to $W(CO)_5(MeCN)$ in acetonitrile. This complex reacts slowly with an additional equivalent of $W(CO)_5(MeCN)$ to form the stable dinuclear species $[W_2(CO)_8(\eta^2\text{-}C_2O_4)]^{2-}$. Alternatively, the dinuclear complex can be prepared by addition of $[PPN]_2[C_2O_4]$ to an excess of $W(CO)_5$(thf) in thf. The authors proposed that the initial product of this reaction, $[W_2(CO)_{10}(\eta^1\text{-}C_2O_4)]^{2-}$, loses two CO molecules to yield the stable dinuclear product. The arrangement of ligands around the metal centre in both cases is a distorted octahedron

[50]. Reaction of $W(CO)_5(thf)$ with an equivalent of RCN (R = CH_2COOH, $(CH_2)_{10}COOH$, CH_3) at ambient temperature yields $W(CO)_5(NCR)$ in essentially quantitative yield [51]. In the solid state structure of $W(CO)_5NCCH_2COOH$ the W-N distance is 2.178 (2) Å. The carboxylate groups of two independent molecules are coupled by strong intermolecular hydrogen-bonding (O---H---O = 2.627(3) Å). The preservation of the hydrogen-bonded structure in solution is supported by infrared spectroscopy.

An electron transfer-induced isomerization occurs from the blue compound $(TCNE)W(CO)_5$ to give a yellow anion-radical in which $TCNE^{\cdot-}$ coordinates to the metal centre *via* a lone pair of electrons on the nitrile nitrogen [52]. The results obtained from EPR, UV-VIS and IR spectroscopies conducted on the reduced complex $[(TCNE)W(CO)_5]^{0/-}$ clearly show the expected lower symmetry and diminished π-back donation. Two distinctly separate second reduction processes are observed for the σ- and π-coordinated complexes based on variable scan mode cyclic voltammetric experiments. The kinetics of solvent (thf) and trimethylphosphine substitution with TCNE in a number of organometallic complexes e.g. $(thf)W(CO)_5$, $(thf)Cr(CO)_5$, $(thf)Mn(CO)_2(C_5H_4Me)$ and $[P(OMe)_3Cr(CO)_2(C_6Me_6)]$ were investigated in thf solution [53]. The kinetic data in conjunction with electrochemical studies support a self-induced homogeneous electron transfer mechanism, where electron transfer between TCNE and the organometallic precursor leads to substitutionally-labile 17 electron complexes as essential intermediates in the catalytic chain. An efficient oxidation of the precursors by TCNE-substituted 17 electron species is possible because of intramolecular metal-to-TCNE electron transfer, especially in the σ-coordinated products with mixed carbonyl/carbocycle ligands.

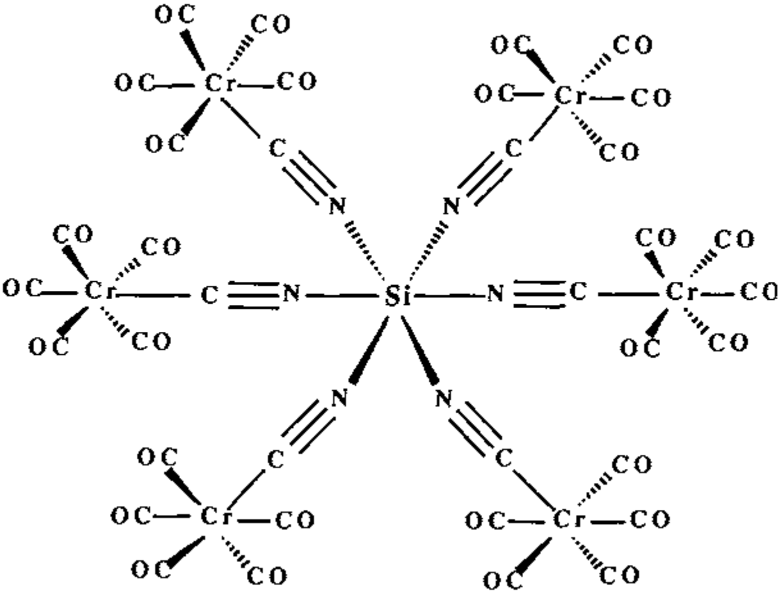
A number of homoleptic and heteroleptic "supercomplexes" have been synthesized and characterized wherein a first row transition metal (Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}) or central metalloid (Si^{IV}, Ge^{II}, Sn^{IV}) is coordinated by up to six ligand complexes, $[NCM'(CO)_5]^-$ (M' = Cr^0, Mo^0, W^0) [54]. Molecular structures of the heptanuclear six-coordinate $(NEt_4)_2[Si\{NCCr(CO)_5\}_6]$ (48), the hexanuclear five-coordinate $(NEt_4)_3[Ni\{NC(W(CO)_5\}_5]$, and the tetranuclear four-coordinate complex $(NEt_4)_2[CoCl\{NCCr(CO)_5\}_3]$ have been carried out. In general, the peripheral atoms and groups such as oxygen and methyl are in rather ill-defined positions due to their high thermal motion. The most striking feature of these complexes is the presence of both linear and bent M'-C=N-M linkages.

The mononuclear complex $W(CO)_5$(*N'*-benzoi[c]cinnoline) is obtained from the reaction of the Fischer carbene complex $(CO)_5W{=}C(OMe)(Me)$ with benzo[c]cinnoline. The ligand is essentially planar with a 1° twist angle between the phenyl rings. The distance between two nitrogen atoms (1.31 (1) Å) is intermediate between a single and a double bond [55].

3.6.2 Complexes with phosphorus donor ligands

The complex $W(CO)_4(dppb)$ (dppb = diphenylphosphino propane) is obtained by refluxing a stoichiometric amount of $W(CO)_6$ and $Ph_2P(CH_2)_4$ in purified *n*-decane under a nitrogen atmosphere [56]. The coordination environment of the tungsten atom is a distorted octahedron with a seven-membered chelating ring. The other homologues of this triad *i.e.* $Cr(CO)_4(dppe)$ and

$Mo(CO)_4(dppe)$ exhibit similar structures and are isomorphous with each other. Reduction of WCl_6 with Na/K alloy in neat PMe_3 produced $W(PMe_3)_6$ **(49)** in good yield [57]. Facile dissociation of one of the PMe_3 ligands gives the oxidative addition product $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ **(50)** which has been fully characterized. The kinetics and thermodynamics of the reaction are presented in detail. Compound **(49)** and **(50)** react with phenols to give four- and five-membered oxametallacycle derivatives as a result of competitive sp^2 vs sp^3 C-H bond activation. These oxametallacycle species react with hydrogen to establish an equilibrium with the aryloxide compounds $W(PMe_3)_4H_3(OAr)$. For most of the derivatives reported, the equilibrium is shifted strongly in favor of the alkoxide derivatives.



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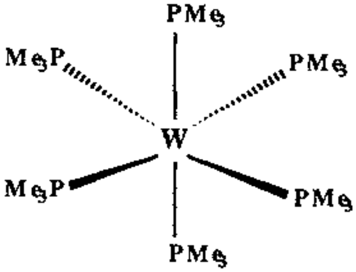

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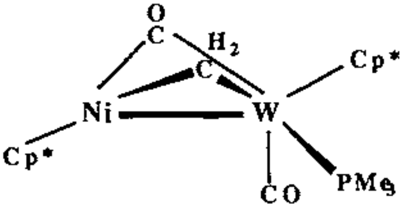
The unsaturated complex $(\eta\text{-}C_5Me_5)Ni\text{-}W(CO)_3(\eta\text{-}C_5H_5)$ reacts with two-electron donor ligands to give compounds of generic formula $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}L)W(CO)L'(\eta\text{-}C_5H_5)$ (L = CO; L' = CO, PMe_3, PMe_2Ph, $P(OMe)_3$, PPh_2Cl, PPh_2H; L = ^tBuNC, CH_2; L' = CO). The phosphine ligands PMe_3 and PPh_2H displace a carbonyl ligand in $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}CH_2)W(CO)_2(\eta\text{-}C_5H_5)$ to afford *cis* and *trans* isomers of $(\eta\text{-}C_5Me_5)Ni(\mu\text{-}CO)(\mu\text{-}CH_2)W(CO)L(\eta\text{-}C_5H_5)$ (L = PMe_3, PPh_2H) **(51a)** and **(51b)**. Several complexes of this type have been characterized by single crystal X-ray analysis and IR and NMR spectroscopies. All of these complexes exhibit dynamic behavior on the NMR spectroscopic time scale that has been rationalized on the basis of the observed structures [58].



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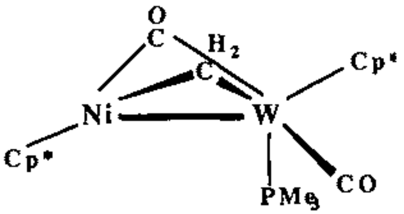


(51b)

3.6.3 Complexes with sulfur or selenium donor ligands

A complete decarbonylation of $NEt_4[\{HB(Me_2pz_3)\}W(CO)_3]$ ($HB(Me_2pz)_3^-$ = hydrotris(3,5-dimethyl-1-pyrazolyl)borate anion) by tetraalkylthiuram disulfide is achieved in refluxing acetonitrile. The intermediate $\{HB(Me_2pz)_3\}W(CO)_2(S_2CNEt_2)$, the mixed-valence complex $\{HB(Me_2pz)_3\}W^{II}(CO)_2(\mu\text{-}S)W^{IV}(S_2CNEt_2)_2(S(NEt_2)$, and the final products $\{HB(Me_2pz)_3\}WS(S_2CNEt_2)$, $W_2(\mu\text{-}S)_2(S_2CNEt_2)_4$, and $[W(S_2CNEt_2)_4]^+$ have been fully characterized [59].

The pentacarbonyltungsten coordinated selenetanes react with $SeCN^-$ and $TeCN^-$ to yield 1,2-diselenolanes and 1,2-selenatellurolane, respectively by insertion of the chalcogen into the Se-C bond of the selenetanes [60]. The diselenolane ring adopts the 'envelope' conformation with a dihedral angle of *ca.* 127°. The phenyl and the methoxy groups occupy equatorial positions, and Ph and $W(CO)_5$ are mutually *trans* to each other.

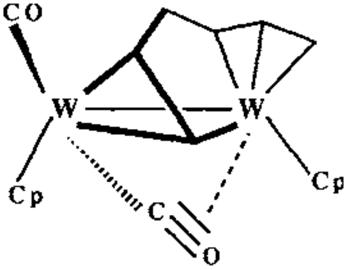
3.6.4 Complexes with mixed donor atom ligands

Photochemical reaction of $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{2:2}\text{–}C_2H_2)]$ **(52)** with 1,3-butadiene under UV radiation yields the products $[W_2(\eta^5\text{-}C_5H_5)_2(CO)(\mu\text{-}\eta^{1:2:1}$-3-oxo-1-propene-1,3-diyl)(η^4-1,3-butadiene)], $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}H)(\mu\text{-}\eta^{1:4}$-3-methylene-1,4-pentadiene-1-yl)], the two isomers $[W_2(\eta^5\text{-}C_5H_5)_2(CO)(\mu\text{-}\eta^{1:2}\text{-}CO)(\mu\text{-}\eta^{1:2:3}$-1,5-hexadiene-1,4-diyl)] **(53)**, $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_2(\mu\text{-}\eta^{1:2:3}$-1,5-hexadiene-1,4-diyl)], and $[W_2(\eta^5\text{-}C_5H_5)_2(CO)_4(\mu\text{-}\eta^{1:2:1}$-1,4-hexadiene-1,6-diyl)]. The main product of **(52)** with acetylene is the fly-over complex $[W_2(\eta^5\text{-}C_5H_5)_2(CO)(\mu\text{-}\eta^{1:3:3:1}$-1,3,5-hexatriene-1,6-diyl)]. Analogous molybdenum chemistry has also been reported. The identity of these products was established by IR and NMR spectroscopies [61].

Treatment of $(CO)_5W[C(N(CH_3)_2CH_3]$ **(54)** with ^{n}BuLi followed by 5-10 equivalents of diiodoalkanes (diiodomethane, 1,2-diiodoethane, 1,3-diiodopropane, 1,4-diiodobutane, or 1,5-

diiodopentane) yields the respective (iodoalkylaminocarbene)tungsten complexes $(CO)_5W[C(N)(CH_3)_2(CH_2)(CH_2)_nI)$ (n = 1-5) **(55)** in moderate to high yields [62]. When the α-lithio anion of **(54)** is treated with **(55)** (n = 3-5) in thf at low temperature, new (μ-bis(aminocarbene)ditungsten complexes $(CO)_5W[C(N(CH_3)_2)CH_2(CH_2)_nCH_2C(N(CH_3)_2)]W(CO)_5$ (n = 3-5) **(56)** are formed in high yields. The complexes have been characterized by mass spectrometry, elemental analysis, and IR and NMR spectroscopies.

The exact products obtained from the reaction of cyclodiphosphazanes $[PhNP(OR)]_2$ (R = CH_2CF_3 and C_6H_4Me-*p*) with metal carbonyl derivatives such as $[M(CO)_4(NHC_5H_{10})_2]$, $[M(CO)_4(NBD)]$ (M = W, Mo, NBD = norbornadiene) depend upon the stereochemistry of the ligands [63]. Cyclodiphosphazane, $[PhNP(OCH_2CF_3)]_2$, (isolated as the *trans*-isomer) affords dinuclear complexes **(57)** in which the two metal centres are bridged by the diphosphazane ligand. In contrast, cyclodiphosphazane $[PhNP(OC_6H_4Me$-$p)_2]$ (isolated as a 3:1 mixture of *cis*- and *trans*-isomers) yields the mononuclear complex $[W(CO)_4(NHC_5H_{10})\{(PhNP(OC_6H_4Me$-$p)_2\}]$ in which the ligand is coordinated in an η^1-fashion.



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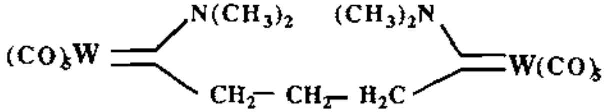

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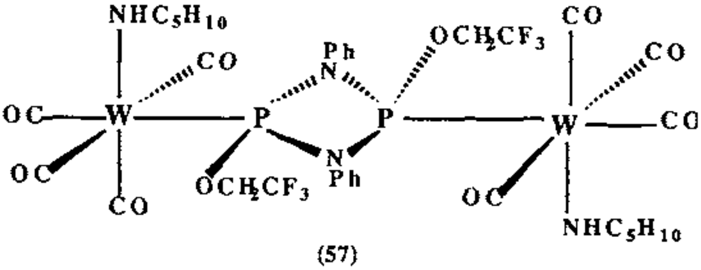

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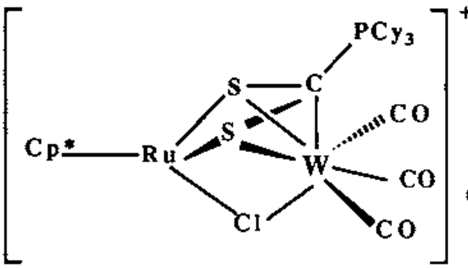
The first cationic heteronuclear complex containing S_2CPR_3 bridges $[(\eta^6$-$C_6Me_6)Ru(\mu$-$Cl)(\mu$-$S_2CPCy_3)W(CO)_3]$ **(58)** has been prepared from the reaction of $[(\eta^6$-$C_6Me_6)Ru(S_2CPCy_3)Cl]PF_6$ with $[W(CO)_3(NCR)_3]$. The two metal units are held together by one bridging chloride and a S_2CPR_3 ligand which acts as an η^2(S,S') chelate for ruthenium and as an

η^3(S,C,S') pseudoallyl to tungsten [64]. One of the carbonyl ligands in **(58)** has been replaced by various phosphines with retention of the basic structure of the complex. It is remarkable that the SCS chelate ring in the ruthenium starting material is sufficiently nucleophilic to bind to a tungsten metal fragment. Reaction of [Cp(CO)$_3$WH] with triflic acid, CF_3SO_3H, in acetone at ambient temperature leads to the formation of the alcohol complex, [Cp(CO)$_3$WOHCH(CH$_3$)$_2$][OTf] **(59)** in quantitative yields [65]. The results of kinetic studies point to hydride transfer from the metal complex to the protonated compound as the rate-determining step in the ionic hydrogenation of aldehydes or ketones. The O---O contact of 2.63 (1) Å between the oxygen of the coordinated acetone and the triflic anion confirms hydrogen-bonding exists in the solid state.



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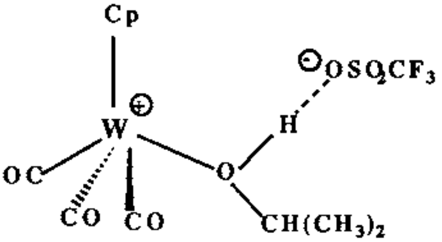

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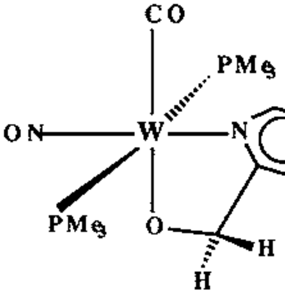
Two types of complexes, [W(CO)$_5${B$_2$H$_4$·2P(CH$_3$)$_3$}] and [W(CO)$_4${B$_2$H$_4$·2P(CH$_3$)$_3$}], are obtained from the photochemical reactions of W(CO)$_6$ with B$_2$H$_4$·2P(CH$_3$)$_3$ in toluene. The ligand bis(trimethylphosphine)diborane acts as an didentate chelate in the latter complex. These are the first examples wherein B$_2$H$_4$·2P(CH$_3$)$_3$ is coordinated to metals other than d^{10} systems. The complexes also exhibit a single M-H-B linkage between the metal and the polyboranes [66]. Similar results are obtained for chromium and molybdenum. Extensive coordination and organometallic chemistry has been carried out on the tungsten-alkylidyne and tungstacarborane system. The reader is referred to selected articles [67-72]

Reactions of water with W(CO)$_3$(PR$_3$)$_2$ and W(CO)$_3$(PR$_3$)$_2$(η^2-H$_2$) (R = Cy(cyclohexyl), ^{i}Pr) in various organic solvents have been reported [73]. Water instantaneously displaces the dihydrogen ligand in W(CO)$_3$(PR$_3$)$_2$(η-H$_2$) in thf solution to give the aqua complex, W(CO)$_3$(P-i-Pr$_3$)$_2$(H$_2$O)·thf which has been structurally characterized. A long W-O distance of 2.320 (5) Å was observed for the bound H$_2$O ligand, which also displays hydrogen-bonding interactions with both lattice thf and with a carbonyl ligand of an adjacent molecule. A ^{1}H NMR spectrum of the aqua complex showed rapid exchange between free and coordinated water at 298 K.

Reduction of (pyridin-2-yl)-substituted aldehydes and ketones, (pyridin-2-yl)C(O)R (R = H, Me, Ph, pyridin-2-yl, 6-methylpyridine-2-carbaldehyde) by *trans, trans*-[WH(CO)$_2$(NO)(PMe$_3$)$_2$] **(60)** has been studied in detail [74]. A key feature in this chemistry is the facile insertion of the CO ligand into the W-H bond with rapid subsequent extrusion of a coordinated carbonyl ligand, thereby forming O-N-didentate coordinated tungsten alkoxides. The initial η^1-*O*-bonded insertion product, which is an unstable intermediate, was characterized by low temperature NMR studies in the cases of the pyridin-2-carbaldehyde and bi(pyridin-2-yl)ketone compounds.



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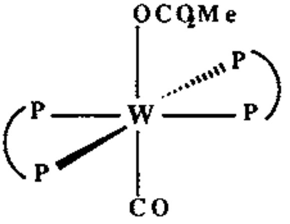
Reaction of *trans*-[W(CO)N_2(dppe)$_2$] with excess MeOH or HNR_2 (R = Me, Et; R_2 = $(CH_2)_4$, $(CH_2)_5$, $(CH_2)_2O(CH_2)_2$) under CO_2 at room temperature afforded a hydrido-carbonato complex [WH(η^1-OCO_2Me)(CO)(dppe)$_2$] (**61**) and a hydrido-carbamato complex {WH(η^2-O_2CNR_2)(CO)(η^1-dppe)(η^2-dpppe)]. When the hydrido-carbamato complex is treated with one equivalent of $AlEt_3$ under CO_2, a complex in which CO_2 is bonded in a η^2-mode, *trans*-[W(CO)(CO_2)(dppe)$_2$] (**62**), is obtained in 50 % yield [75]



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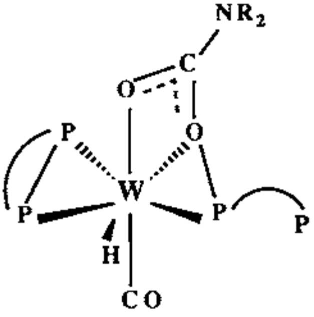

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3.7 SELECTED CLUSTERS

3.7.1 Polyoxotungstates

A novel polyoxotungstate complex containing a ferromagnetically coupled triangular Ni_3^{II} cluster, $K_6Na[Ni_3(H_2O)_3PW_{10}O_{39}H_2O]\cdot 12H_2O$ has been fully characterized by elemental analysis, IR spectroscopy, magnetic measurements, and single crystal X-ray crystallography [76]. Magnetic susceptibility measurements show that within the triangulated Ni_3^{2+} moiety, ferromagnetic exchange interactions occur (μ_{eff} increases with decreasing temperature), thereby supporting a ground state of S = 3. Heteropoly complexes $K_8[M(H_2O)CuW_{11}O_{39}]\cdot nH_2O$ (M = Zn, Cd, Ni) are obtained from the reaction of $Na_2WO_4\cdot 2H_2O$ with acidic solutions of various transition metals. The complexes are characterized by IR, UV spectroscopy, X-ray diffraction, and X-ray photoelectron spectroscopy. The structures of these complexes are similar to that of $NiSiW_{11}$ [77].

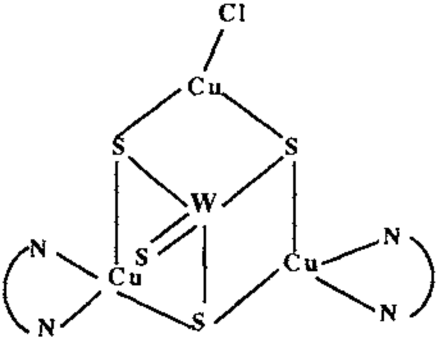
Phenylphosphonyl heteropolyundecatungstates of general formula $[PhP(O)]_2X^{n+}W_{11}O_{39}^{(8-n)-}$ ($X^{n+} = P^{5+}, S^{4+}$) have been synthesized and characterized by elemental analysis as well as IR, ^1H, ^{31}P, and ^{183}W NMR spectroscopies [78]. Reactions of $[Ru(H_2O)_6]^{2+}$ with $[PW_{11}O_{39}]^{7-}$, followed by oxidation with O_2 yield $[PW_{11}O_{39}Ru^{III}(H_2O)]^{4-}$ which has been isolated as a cesium salt [79]. Cyclic voltammetry indicates that this complex can be reduced and oxidized to the corresponding aquaruthenium(II), oxoruthenium(IV), and oxoruthenium(V) derivatives. Details of ^{31}P NMR, electronic spectroscopy and cyclic voltammetry are presented. A series of $H_3PW_{12}O_{40}$-SiO_2 catalysts with various polyanion loadings (ranging from 13 to 87 wt %) obtained by impregnating SiO_2 Aerosil ($S = 380$ m^2 g^{-1}) with a solution of $H_3PW_{12}O_{40}$, have been studied by ^{31}P MAS NMR spectroscopy [80]. A typical ^{31}P MAS NMR spectrum of these catalysts shows two peaks corresponding to the bulk $H_3PW_{12}O_{40}$ and to $(\equiv SiOH_2^+)(H_2PW_{12}O_{40}^-)$.

In an attempt to synthesize the lacunary Keggin species $(TBA)_3[PW_{12}(NR)O_{39}]$ (TBA = n-$(C_4H_9)_4N$) from the reaction of $(TBA)_4[H_3PW_{11}O_{39}]$ with $[W(NR)Cl_4]_2$, unexpected mononuclear W(VI) species $(TBA)[W(NR)Cl_5]$ (**63**) and the dinuclear W(VI) complex $(NBA)(C_7H_7NH_3)[W_2OCl_8(NR)_2]$ (**64**) were obtained. Reactions of (**63**) and (**64**) with H_2O yielded the tetranuclear complex $(TBA)_2[W_4O_4(NR)_4Cl_{10}]$ in low yield. An infrared spectrum of (**63**) exhibits a band at 1145 cm^{-1} which has been assigned to ν(W=N). An additional band at 775 cm^{-1} in (**64**) is attributed to the bridging W-O-W group. Both complexes have been characterized by single crystal X-ray analyses [81].

Reaction of Na_2MoO_4 and A-$Na_9[PW_9O_{34}]$ in HCl and 1,4-dioxane mixed solution resulted in the formation of the molybdenum-trisubstituted tungstaphosphate anion, $[PMo_3W_9O_{40}]^{3-}$, which was crystallized as its tetramethylammonium salt [82]. A single crystal X-ray structural analysis revealed that the compound is the first example of a heteropolyanion containing an A-type trisubstituted, β-isomer of a PW_9 unit. A ^{31}P NMR spectrum displayed only a single sharp peak at -7.88 ppm confirming a single mixed metal polyanion in solution and occurrence of neither lacunary polyanions nor other isomers.

3.7.2 Cubanes

Incomplete cubanes of composition $[WS_{3.4}O_{0.6}Cu_3(bpy)_2Cl]$ (**65**) are formed in the reaction of $[Fe(bpy)_3]Cl_2$ with $[WS_4Cu_4Cl_4]^{2-}$ in an acetonitrile-dichloromethane mixture [83]. The solid state structure shows that the overall geometry of (**65**) is a cubane with one missing corner. The empty coordination site in the cube is attributed to the poor ability of Cu(I) to form five-coordinate compounds. Infrared spectroscopy supports the oxygen/sulfur mixed occupancy for the terminal W=S bond. In the molybdenum analogue, the terminal double bond is entirely Mo=O. Syntheses and detailed electrochemistry of several incomplete cubane-type clusters with basic W_3S_4 cores have been reported. The redox chemistry of the cluster $[W_3S_4(Hnta)_3]^{2-}$ shows three consecutive one-electron reduction steps corresponding to the change in oxidation states of the three metals [84].



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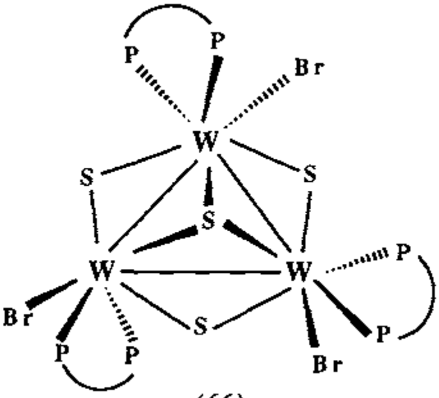
3.7.3 *Homo- and heteronuclear clusters*

The initial reaction of WBr_5 with $NaBH_4$ or $NaB(C_2H_5)_3H$ in refluxing thf, followed by subsequent addition of a methanolic solution of NaHS and dmpe, yields the triangular trinuclear cluster $[W_3S_4Br_3(dmpe)_3]^+$ **(66)** in high yield [85]. The cation **(66)** has been isolated as the bromide or fluorophosphate salt. A single crystal X-ray analysis established that each metal atom in **(66)** is attached to one capping and two bridging sulfur atoms, one terminal bromide and one chelating dmpe ligand. One P atom in the dmpe ligand is *trans* to the μ^3-S and the other P atom is *trans* to a bridging sulfur atom. UV-VIS and NMR spectra of these compounds are presented.



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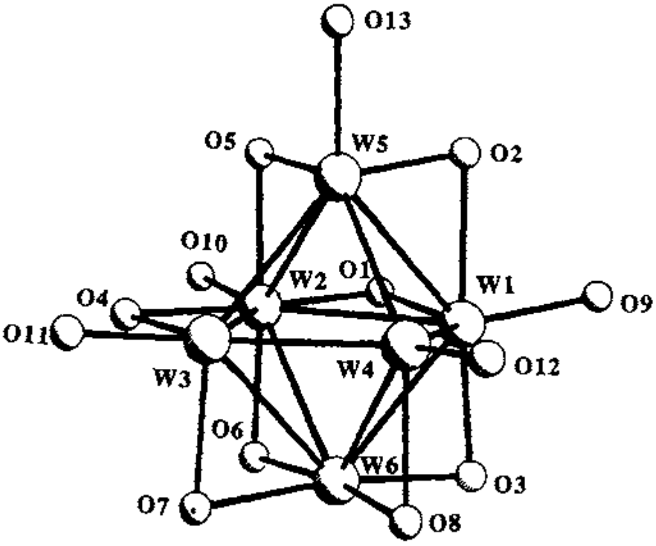
The polyhydride compound $W_6(H_5)(O\text{-i-Pr})_{13}$ is formed upon exposure of $W_2(\text{i-Bu})_2(O\text{-i-Pr})_4$ **(67)** to H_2 at 3 atm in a hydrocarbon solvent with concomitant elimination of isobutane [86]. Compound **(67)** is air-sensitive and soluble in hydrocarbons. The hexanuclear cluster is the first member of a group of complexes of general formula $M_6(H)_n(OR)_{18-n}$. A single crystal X-ray study revealed a distorted octahedron of W atoms with eight bridging and five terminal O-*i*-Pr ligands. ^1H NMR spectroscopy showed five signals in the range δ 9-15 ppm, which are assigned to the five hydrides. Each resonance exhibits coupling to ^{183}W (I = 1/2, 14.5 % natural abundance). Based on the relative intensities of the satellite signals, it was inferred that the compound possesses terminal hydride and four edge-bridging hydride ligands.

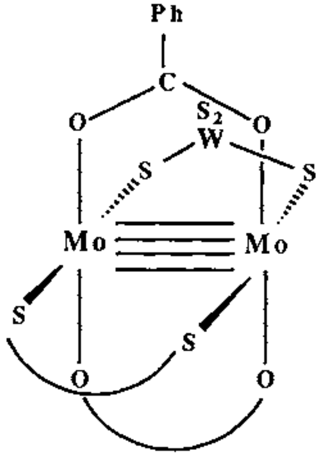


(67)

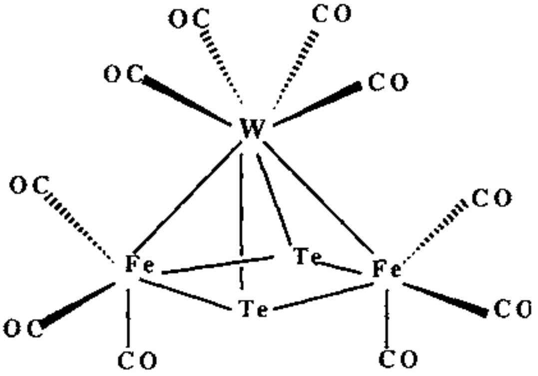
Reductive cleavage of carbon monoxide to carbide and oxide ligands by ditungsten and tetratungsten alkoxides has been explored [87]. Addition of 1-3 equivalents of CO to $W_4(OCH_2$-*c*-pen$)_{12}$ (pen = pentyl) leads to the formation of three carbonyl derivatives, $W_4(\mu_4$-C$)(OCH_2$-*c*-pen$)_{14}$, $W_4(\mu_4$-CO$)(CO)_2(OCH_2$-c-pen$)_2$ and an oxo-tungsten alkoxide, $W_4(\mu_4$-C$)(O)(OCH_2$-*c*-pen$)_{12}$. Reactions employing ^{13}CO indicate that C-O bond cleavage occurs prior to oxo/alkoxide exchange. The reaction between $W_2(\mu$-CO$)($O-t-Bu$)_6$ and $W_2($O-t-Bu$)_6$ in the presence of excess alcohol yields $W_4(\mu$-C$)(O)(OR)_{12}$ (R = CH_2-t-Bu, CH_2-i-Pr). These reactions are the first examples of carbon monoxide cleavage to carbido and oxo ligands in a homogeneous system. It has been concluded that the key feature in this process is the ability of the metal atoms within the cluster or on the metal surface to behave as a d_π-donors to the CO π^* MO's and as d_π-acceptors from the filled CO π MO's *via* a p_π-to-M d_π donation.

Addition of two equivalents of $(Pr_4N)_2(WS_4)$ to an acetone solution of $Mo_2(O_2CPh)_4$ afforded $(Pr_4N)_2[Mo_2(O_2CPH)_2(WS_4)_2]$ **(68)** in high yield (75 %) [88]. A single crystal X-ray analysis reveals a novel bonding mode for the WS_4^{2-} ligands which bridge two quadruply-bonded molybdenum atoms. The molecule resides on a centre of inversion while the two WS_4^{2-} ligands are *trans* to each other. Complex **(68)** represents a rare example of a stable complex containing two metals from the same group with different oxidation states *i.e.* Mo^{II} and W^{VI}.

Reaction of $Fe_2(CO)_6(\mu$-$M_2)$ (M = Te, Se) with an equimolar quantity of $W(CO)_5$(thf) in thf at ambient temperature yielded mixed-metal cluster complexes $[Fe_2W(\mu_3$-M$)_2(CO)_{10}]$ in moderate yields [89]. A single crystal X-ray structure reveals that the geometry of the metal core in $FeW(\mu_3$-Te$)_2$ $(CO)_{10}$ **(69)** is a Fe_2WTe_2 square pyramid with the tungsten atom occupying the apical site. This represents the first example of an iron-tungsten mixed-metal cluster capped by two tellurium functionalities.



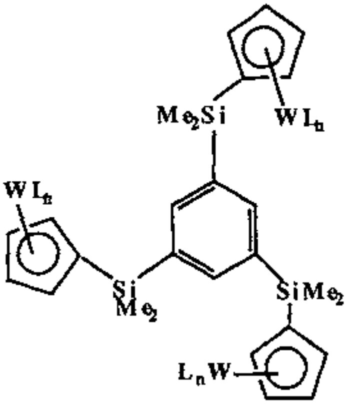
(68)



(69)

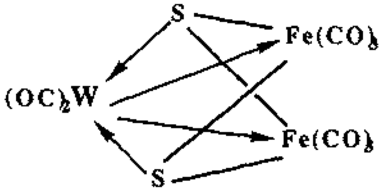
Heterometallic phosphinidene cluster complexes of the type $Cp^*WRu_3(CO)_{10}(\mu_3\text{-}H)(\mu_3\text{-}PPh)$ (**70**) and $CpWRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$ (**71**) are obtained in reasonable yields from the reaction of $Ru_3(CO)_{10}(\mu\text{-}H)(\mu\text{-}PPh_2)$ with an excess of the tungsten hydride species $LW(CO)_3H$ (L = Cp*, Cp) in refluxing toluene [90]. Further refluxing of (**70**) in toluene under CO induces cluster fragmentation to the phosphinidene derivative $Cp^*WRu_2(CO)_8(\mu\text{-}H)(\mu_3\text{-}PPh)$ (**72**) in high yield (72%). It was therefore concluded that complex (**70**) is an intermediate in the formation of the trinuclear cluster (**72**). Complex (**70**) represents the first tetrahedral cluster containing a μ_3-PR ligand to have been characterized by X-ray crystallography. In clusters (**71**) and (**72**), the phosphinidine ligand is triply bridging, but the two complexes differ from each other by the location of the edge-bridging hydride ligand.

A number of aryldimethylsilylcyclopentadienes of the general type $1,4\text{-}C_6H_4(SiMe_2Cp)_2$ and $1,3,5\text{-}C_6H_3(SiMe_2Cp)_3$ ($Cp = C_5H_5$, $C_5H_3(t\text{-}C_4H_9)_2$, C_5HMe_4) are obtained by substitution of the halides in the aryldimethylsilyl halides $1,4\text{-}C_6H_4(SiMe_2Br)_2$, $2,6\text{-}C_5NH_3(SiMe_2Br)_2$, $1,3,5\text{-}C_6H_3(SiMe_2X)_3$ (X = Br or Cl). Treatment of the aryldimethylsilylcyclopentadiene compounds with NaH, $(MeCN)_3W(CO)_3$ and MeI gave the η^5-C_5H_4 complexes, $C_6H_5(SiMe_2(C_5H_4)W(CO)_3Me)$, 1,4-$C_6H_4(SiMe_2(C_5H_4)W(CO)_3Me)_2$, and 1,3,5-$C_6H_3\{SiMe_2(C_5H_4)W(CO)_3Me\}_3$ (73) which contain up to three half-sandwich units within one molecule. The compounds were characterized by the usual spectroscopic methods [91].

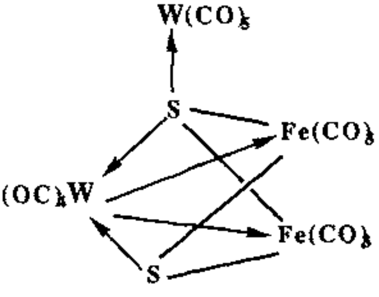


(73)

Reaction of the inorganic disulphide compound $S_2Fe(CO)_6$ with electron-deficient transition metal fragments such as $W(CO)_x$ (x = 4, 5) leads to the formation of $W(CO)_4(\mu_3\text{-}S)_2(Fe(CO)_6$ (74) and $W(CO)_4[\mu_4\text{-}S)W(CO)_5](\mu_3\text{-}S)[Fe_2(CO)_6]$ (75) in low yields [92]. In both cases, the Fe-Fe bond is cleaved at the expense of the new W-Fe bond. The W-S distances in both compounds are very similar (2.547 Å and 2.524 Å respectively).



(74)



(75)

REFERENCES

1. TEXSAN-TEXRAY Structure Analysis Package, Molecular Science Corporation, 1985.
2. H.A. Hodali, H. Hung and D.F. Shriver, *Inorg. Chem. Acta*, 198-200 (1992) 245.
3. J.D. Lichtenhan, J.W. Ziller and N.M. Doherty, *Inorg. Chem.*, 31 (1992) 2893.
4. J.D. Lichtenhan, J.W. Ziller and N.M. Doherty, *Inorg. Chem.*, 31 (1992) 4210
5. L.L. Blosch, A.S. Gamble, K. Abboud and J.M. Boncella, *Organometallics*, 11 (1992) 2342.
6. K. Dreisch, C. Andersson and C. Stålhandske, *Polyhedron*, 11 (1992) 2143.
7. C. Persson, Å. Oskarsson and C. Andersson, *Polyhedron*, 11 (1992) 2039.
8. M.H. Chisholm, V.J. Johnston and W.E. Streib, *Inorg. Chem.*, 31 (1992), 4081.
9. D. Shaowu, Z. Nianyong, C. Pengcheng, W. Xinato and L. Jiaxi, *Polyhedron*, 11 (1992) 109.

10. V.P. Fedin, Yu.V. Mironov, A.V. Chernobrivets, A.V. Virovets, N.V. Podberezskaya and V.E. Fedorov, *Zh. Neorg. Khim.*, 37 (1992) 547.
11. D. Shaowu, Z. Nianyong, W. Xinato and L. Jiaxi, *Inorg. Chem.*, 31 (1992) 2847.
12. C. Redshaw, G. Wilkinson, B. Hussain-Bates and M. B. Hursthouse, *J. Chem. Soc., Dalton Trans.*, (1992) 555
13. B. Siewet and U. Muller, *Z. Anorg. Allg. Chem.*, 609 (1992), 77.
14. D.M. Dawson, R.A. Henderson, A. Hills and D.L. Hughes, *J. Chem. Soc., Dalton Trans.*, (1992) 973.
15. N. Kanehisa, Y. Kai, N. Kasai, H. Tasuda, Y. Nakayama and A. Nakamura, *Bull. Chem. Soc. Jpn.*, 65 (1992) 1197.
16. W. Clegg, R. J. Errington, D.C.R. Hockless, J.M. Kirk and C. Redshaw, *Polyhedron*, 11 (1992), 381.
17. S.C. O'Neal, W.T. Pennington and J.W. Kolis, *Inorg. Chem.*, 31 (1992) 888.
18. A.C. Filippou, C. Völkl, W. Grünleitner and P. Kiprof, *J. Organomet. Chem.*, 434 (1992) 201.
19. T.A. George, J.R.D. Debord, B.B. Kaul, C.J. Pickett and D.J. Rose, *Inorg. Chem.*, 31 (1992) 1295.
20. J. Sundermeyer, K. Weber and O. Nürnberg, *J. Chem. Soc., Chem Comm.*, (1992) 1631.
21. F.A. Cotton and C.A. James, *Inorg. Chem.*, 31 (1992) 5298.
22. F.A. Cotton, J.L. Eglin, C.A. James and R.L. Luck, *Inorg. Chem.*, 31 (1992) 5308.
23. M.B. O'Regan, M.G. Vale, J.F. Payack and R.R. Schrock, *Inorg. Chem.*, 31 (1992) 1112.
24. M.H. Chisholm, C.M. Cook and K. Folting, *J. Am. Chem. Soc.*, 114 (1992) 2721.
25. K.G. Caulton, R.H. Cayton, M. H. Chisholm, J.C. Huffman, E.B. Lobkovsky and Z. Xue, *Organometallics*, 11 (1992) 321.
26. L.M. Atagi, S.C. Critchlow and J.M. Mayer, *J. Am. Chem. Soc.*, 114 (1992) 1483.
27. S.T. Chacon, M.H. Chisholm, O. Eisenstein and J.C. Huffman, *J. Am. Chem. Soc.*, 114 (1992) 8497.
28. R.H. Cayton, M.H. Chisholm, M.J. Hampden-Smith, J.C. Huffman and K.G. Moodley, *Polyhedron*, 11 (1992) 3197.
29. V.P. Fedin, Yu.V. Mironov, A.V. Virovets, N.V. Podberezskaya, V.Ye. Fedorov and P.P. Semtyannikov, *Polyhedron*, 11 (1992) 279.
30. E.M. Armstrong, P.K. Baker, T. Callow, K.R. Flower, P.D. Jackson and L.M. Severs, *J. Organomet. Chem.*, 434 (1992) 321.
31. H. Brunner, R. Graβl, J. Wachter, B. Nuber and M.L. Ziegler, *J. Organomet. Chem.*, 431 (1992) 143.
32. M.H. Chisholm, K.S. Kramer, J.D. Martin, J.C. Huffman, E.B. Lobkovsky and W.E. Streib, *Inorg. Chem.*, 31 (1992) 4469.
33. G.R. Clark, A.J. Nielson, A.D. Rae and C.E.F. Rickard, *J. Chem. Soc., Chem. Commun.*, (1992) 1069.
34. Q. Feng, M. Ferrer, M.L. H. Green, P. Mountford and V.S. B. Mtetwa, *J. Chem. Soc., Dalton Trans.*, (1992) 1205.
35. T.E. Glassman, M.G. Vale and R.R. Schrock, *J. Am. Chem. Soc.*, 114 (1992) 8098.
36. F.A. Cotton and T. Ren, *J. Am. Chem. Soc.*, 114 (1992) 2237.
37. T. Aoshima, T. Tanase, Y. Mizobe, Y. Yamamoto and M. Hidai, *J. Chem. Soc., Chem. Commun.*, (1992) 586.
38. A.K. Powell and M.J. Went, *J. Chem. Soc., Dalton Trans.*, (1992) 439.
39. W.E. Buhro, M.H. Chisholm, K. Folting, J.C. Huffman, J.D. Martin and W.E. Streib, *J. Am. Chem. Soc.*, 114 (1992) 557.
40. M.H. Chisholm, R.-M. Jansen and J.C. Huffman, *Organometallics*, 11 (1992) 2305.
41. J.D. Debad, P. Legzdins, R.J. Batchelor and F.W.B. Einstein, *Organometallics*, 11 (1992) 6.
42. H. Pfister and W. Malisch, *J. Organomet. Chem.*, 439 (1992) C11.
43. A. Mayr, C.M. Bastos, N. Daubenspeck and G.A. McDermott, *Chem. Ber.*, 125 (1992) 1583.
44. L.F. Rhodes, J.C. Huffman and K.G. Caulton, *Inorg. Chim. Acta*, 198-200 (1992) 639.
45. P.K. Baker, G.A. Cartwright, P.D. Jackson, K.R. Flower, N. Galeotti and L.M. Severs, *Polyhedron*, 11 (1992) 1043.
46. P. Legzdins, E.C. Phillips, S.J. Rettig, J. Trotter, J.E. Veltheer and V.C. Yee, *Organometallics*, 11 (1992) 3104.
47. H. Oshita, Y. Mizobe and M. Hidai, *Organometallics*, 11 (1992) 4116.
48. A.A.H. van der Zeijden, H.W. Bosch and H. Berke, *Organometallics*, 11 (1992) 563.
49. A.A.H. van der Zeijden, H.W. Bosch and H. Berke, *Organometallics*, 11 (1992) 2051.
50. D.J. Darensbourg, J.A. Chojnacki and J.H. Reibenspies, *Inorg. Chem.*, 31 (1992) 3428.
51. D.J. Darensbourg, E.V. Atnip and J.H. Reibenspies, *Inorg. Chem.*, 31 (1992) 4475.
52. T. Roth and W. Kaim, *Inorg. Chem.*, 31 (1992)1930.

53. B. Schwederski, W. Kaim, B. Olbrich-Deussner and T. Roth, *J. Organomet. Chem.*, 440 (1992) 145.
54. M. Fritz, D. Rieger, E. Bär, G. Beck, J. Fuchs, G. Holzmann and W.P. Fehlhammer, *Inorg. Chim. Acta*, 198-200 (1992) 513.
55. E.K. Pham and L. McElwee-White, *Acta Crystallogr., Sect. C*, 48 (1992) 1120.
56. C.-H. Ueng and G.-Y. Shih, *Acta Crystallogr., Sect. C*, 48 (1992) 988.
57. D. Rabinovich, R. Zelman and G. Parkin, *J. Am. Chem. Soc.*, 114 (1992) 4611.
58. M.J. Chetcuti, K.J. Deck, J.C. Gordon, B.E. Grant and P.E. Fanwick, *Organometallics*, 11 (1992) 2128.
59. C.G. Young, M.A. Bruck, P.A. Wexler, M.D. Carducci and J.H. Enemark, *Inorg. Chem.*, 31 (1992) 587; C.G. Young, M.A. Bruck and J.H. Enemark, *ibid*, 31 (1992) 593.
60. H. Fischer, C. Kalbas and J. Hofmann, *J. Chem. Soc., Chem. Commun.*, (1992) 1050.
61. C.G. Kreiter, A. Würtz and P. Bell, *Chem. Ber.*, 125 (1992) 377.
62. D.W. Macomber and P. Madhukar, *J. Organomet. Chem.*, 433 (1992) 279.
63. V.S. Reddy, S.S. Krishnamurthy and M. Nethaji, *J. Organomet. Chem.*, 438 (1992) 99.
64. J. Cuyas, D. Miguel, J.A. Perez-Martinez, V. Riera and S. Garcia-Granda, *Polyhedron*, 11 (1992) 2713.
65. J.-S. Song, D.J. Szalda, R.M. Bullock, C.J.C. Lawrie, M.A. Rodkin and J.R. Norton, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 1233.
66. K. Katoh, M. Shimoi and H. Ogina, *Inorg. Chem.*, 31 (1992) 670.
67. N. Carr, D.F. Mullica, E.L. Sappenfield and F.G.A. Stone, *Organometallics*, 11 (1992) 3697.
68. S.A. Brew, D.D. Devore, P.D. Jenkins, M.U. Pilotti and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1992) 393.
69. J.C. Jeffrey, S. Li and F.G.A. Stone, *Organometallics*, 11 (1992) 1902.
70. J.C. Jeffrey, S. Li, D.W.I. Sams and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1992) 877.
71. J.E. Goldberg, D.F. Mullica, E.L. Sappenfield and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1992) 2495.
72. J.A.K. Howard, J.C. Jeffery, S. Li and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1992) 627.
73. G.J. Kubas, C.J. Burns, G.R.K. Khalsa. L.S.V.D. Sluys, G. Kiss and C.D. Hoff, *Organometallics*, 11 (1992) 3390.
74. A.A.H. van der Zeijden and H. Berke, *Helv. Chim. Acta*, 75 (1992) 513.
75. T. Ishida, T. Hayashi, Y. Mizobe and M. Hidai, *Inorg. Chem.*, 31 (1992) 4481.
76. C.J.Gómez-García, E. Coronado and L. Ouahab, *Angew. Chem. Int. Ed. Engl.*, 31 (1992) 649.
77. Wu and E. Wang, *Zh. Neorg. Khim.*, 37 (1992) 787.
78. G.-S. Kim, K.S. Hagen and C.L. Hill, *Inorg. Chem.*, 31 (1992) 5316.
79. C. Rong and M.T. Pope, *J. Am. Chem. Soc.*, 114 (1992) 2932.
80. F. Lefebvre, *J. Chem. Soc., Chem. Comm.*, (1992) 756.
81. Q. Chen, D. McClinton and J. Zubieta, *Inorg. Chim. Acta*, 195 (1992) 163.
82. I. Kawafune and G. Matsubayashi, *Chem. Lett.*, 1992 1869.
83. S. Bernès, F. Sécheresse and Y. Jeannin, *Inorg. Chim. Acta*, 194 (1992) 105.
84. T. Shibahara, M. Yamasaki, G. Sakane, K. Minami, T. Yabuki and A. Ichimura, *Inorg. Chem.*, 31 (1992) 640.
85. F.A. Cotton and S.K. Mandal, *Inorg. Chim. Acta*, 192 (1992) 71.
86. M.H. Chisholm, K.S. Kramer and W.E. Streib, *J. Am. Chem. Soc.*, 114 (1992) 3571.
87. M.H. Chisholm, C.E. Hammond, V.J. Johnston, W.E. Streib and J.C. Huffman, *J. Am. Chem. Soc.*, 114 (1992) 7056.
88. M.A. Greaney and E. Stiefel, *J. Chem. Soc., Chem. Commun.*, (1992) 1679.
89. P. Mathur, D. Chakrabarty, M.M. Hossain, R.S. Rashid, V. Rugmini and A.L. Rheingold, *Inorg. Chem.*, 31 (1992) 1106.
90. R.-C. Lin, Y. Chi, S.-M. Peng and G.-H. Lee, *Inorg. Chem.*, 31 (1992) 3818.
91. H. Plenio, *J. Organomet. Chem.*, 435 (1992) 21.
92. A.A. Pasynskii, B.I. Kolobkov, I.L. Eremenko, S.E. Nefedov, S.B. Katser and M.A. Porai-Koshits, *Zh. Neorg. Khim.*, 37 (1992) 1278.