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3. Tungsten

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CONTENTS

INTRODUCTION

This chapter surveys the coordination chemistry of tungsten reported during the year 1991. Complexes of tungsten have been categorized by oxidation state of the tungsten atom(s) and further subdivided according to the ligand donor atom type(s). Complexes with three or more metal atoms are included in the final section of this survey and are arranged by cluster type. References to purely organometallic compounds have been omitted from this review, except in certain circumstances where there is a significant metal-metal bonding interaction. No effort was made to discuss analogous molybdenum complexes in this work.

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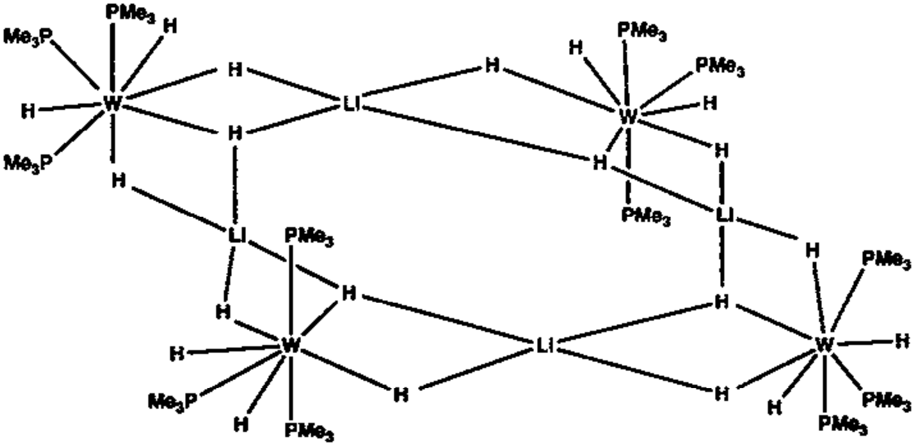
The references for this review were located by a search of Vols. 114 and 115 of *Chemical Abstracts*. The following journals were also searched independently: *Inorg. Chem.*; *J. Am. Chem. Soc.*; *J. Chem. Soc., Dalton Trans.*; *J. Chem. Soc., Chem. Commun.*; *Organometallics*; *J. Organomet. Chem.*; *Chem. Ber.*; *Angew. Chem. Int. Ed.*; *Z. Anorg. Allg. Chem.*; *Inorg. Chim. Acta*; *Polyhedron*; *Zh. Neorg. Khim.*; *Acta Crystallogr., Sect. C*; *Helv. Chim. Acta*; and *Acta Chem. Scand.* X-ray structural figures for this work were redrawn using the TEXSAN package of software by inputting the crystal parameters and atom coordinates from the original published work [1].

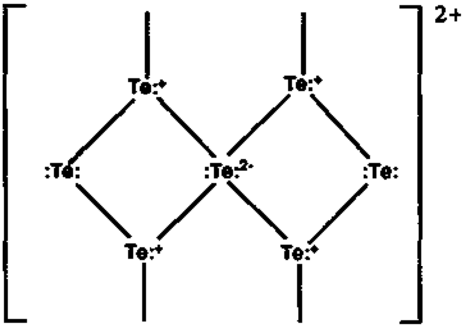
3.1 TUNGSTEN (VI)

3.1.1 Complexes with halide and hydride ligands

The tungsten(VI) hydride complex [$W(PMe_3)_3H_6$] has been found to undergo reactions with a variety of alkali-metal containing species to produce complexes wherein hydrogen atoms bridge the tungsten centre and the alkali metal ion [2]. Reaction of the hydride complex with KH produces K[$W(PMe_3)_3H_5$] which contains three bridging hydride ligands. It was further demonstrated that the potassium is readily complexed by 18-crown-6 without affecting the hydride bridges; analogous chemistry occurs with NaH and 15-crown-5. Reaction of [$W(PMe_3)_3H_6$] with ^{n}BuLi results in the formation of the octanuclear species (**1**), with lithium atoms tetrahedrally coordinated to hydrides and the tungsten atoms coordinated to three phosphines and five hydrides (three bridging and two terminal). Reaction of K[$W(PMe_3)_3H_5$] with $^nBu_3SnCl$ produces [$W(Sn^nBu_3)(PMe_3)_3H_4$]; reactions of the potassium complex with zirconocene dichloride [Cp_2ZrCl_2] and zirconocene chloride hydride [Cp_2ZrHCl] lead to the formation of dinuclear ZrW complexes with three bridging hydrides. The structures of these complexes were determined by ^1H and ^{31}P NMR spectroscopy as well as by single crystal X-ray and neutron diffraction studies.



(**1**)



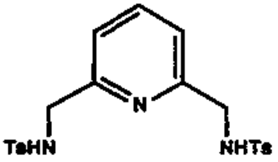
(2)

Tellurium reacts with a mixture of WBr_5 and $WOBr_4$ to yield a compound with the empirical formula Te_7WOBr_5 [3]. A single crystal X-ray study of the compound reveals that the structure of the compound, best formulated as $Te_7[WOBr_4]Br$, consists of one-dimensional polymeric tellurium cations (Te_7^{2+}), one-dimensional $(WOBr_4)_n$ chains and free bromide ions. The $(WOBr_4)_n$ chains are comprised of square-planar WBr_4 moieties bridged by oxygen atoms. Three different types of Te atoms are evident in the tellurium polymer (2). The central tellurium atom carries a 2- charge and is nearly square planar ($Te\text{-}Te_{ave}$=2.957Å). The four bridging tellurium atoms carry a 1+ charge and form bonds to neighboring Te_7 groups (2.881(1)Å), as well as to neutral tellurium atoms (2.760(1)Å) for an overall pseudo-trigonal planar geometry.

3.1.2. Complexes with nitrogen donor ligands

The reaction of $[W(NAr)Cl_4]$ (Ar=2,6-diisopropylphenyl) with one equivalent of 2,6-pyridinebis(tosylmethylamine) (3) in the presence of two equivalents of triethylamine (NEt_3) produces *trans*-$\{W(NAr)[N(NTs)_2]Cl_2\}$ and two equivalents of $[NHEt_3]Cl$ [4]. Further reaction with AgOTf results in the substitution of one Cl with OTf. Reaction of this triflate complex with two equivalents of hydrazine yields $\{W(NAr)[N(NTs)_2](\eta^2\text{-}NHNH_2)Cl\}$ (4), which is believed to form via a hydrazine adduct intermediate. This hypothesis is supported by the protonation reaction of (4) with triflic acid which produces the hydrazine adduct. The X-ray crystal structure of (4) revealed that the W atom is situated 0.23 Å above the plane defined by the five planar nitrogen atoms.

$[W(NAr)Cl_4(thf)]$ reacts with two equivalents of $Me_3SiNHAr$ in thf to produce $[W(NAr)_2Cl_2(thf)_2]$ [5] which further reacts with Me_3SiNEt_2 to form $[W(NAr)_2(NEt_2)Cl]$ and with LiNHAr to give $Li[W(NAr)_3Cl]$. Spectroscopic studies of the lithium salt indicate an absence of N-H stretches in the infrared region and N-H resonances in the ^1H NMR spectrum. An X-ray crystal structure of this complex shows the tungsten is in a tetrahedral coordination environment with W-N$_{ave}$=1.782 Å and W-N-C$_{ipso}$=170.8°. Due to the symmetry of the complex, only 10 of the 12 available Nπ electrons are used for bonding, rendering $[W(NAr)_3Cl]^-$ an eighteen electron complex.



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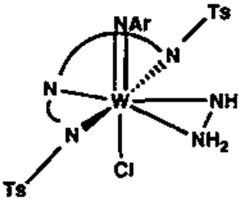
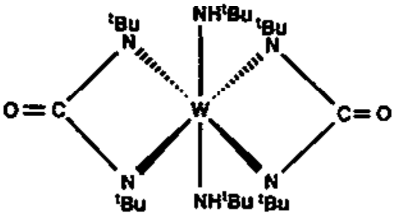


(4)

The reaction of $[W(N^tBu)_2(NH^tBu)_2]$ with ^tBuNCO produces the six-coordinate tungsten(VI) complex (5) [6]. The direct interaction of the M-NR group with ^tBuNCO leads to the formation of the ureato-N,N complex, whose formula is postulated on the basis of NMR and mass spectrometry data.

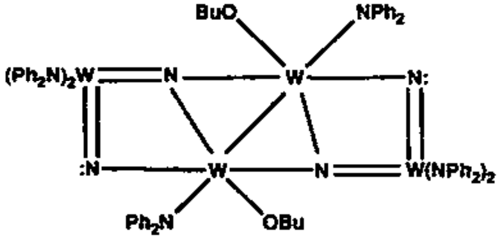


(5)

$[W(N^tBu)_2(NH^tBu)_2]$ is also known to react with secondary and tertiary alcohols to form amide/alkoxide complexes of the type $[W(N^tBu)_x(OR)_y]$ (R = ^iPr, ^tBu, x = 1, y = 4; R = Ph_3C, x = 2, y = 2). $WOCl_4$ reacts with $^tBu(Me_3Si)NH$ to yield $[WO(N^tBu)(NH^tBu)(NH_2{}^tBu)Cl]$ which was shown to react with PMe_3 to give the four-coordinate complex $[WO(N^tBu)_2(PMe_3)]$. Reaction of $[WO(N^tBu)(NH^tBu)(NH_2{}^tBu)Cl]$ with ^tBuOH leads to the isolation of two products, $[WO(N^tBu)(O^tBu)_2(NH_2{}^tBu)]$ and $[W(N^tBu(O^tBu)_3(NH_2{}^tBu)Cl]$; an X-ray crystal structure was reported for the latter compound [7].

A series of compounds involving nitrogen donors have been synthesized beginning with the $[Cp^*WMe_4]^+$ species [8]. The reversible reaction of $[Cp^*WMe_4]^+$ with NH_3 produces $[Cp^*WMe_4(NH_3)]^+$, which expels $NH_4{}^+$ in the presence of excess NH_3 to form $[Cp^*W(=NH_2)Me_4]$. This second reaction is easily reversed with the addition of strong acid. The cation $[Cp^*WMe_4(NH_3)]^+$ releases methane at –10°C to give $[Cp^*WMe_3(=NH_2)]^+$, which can also be prepared by oxidation of [Cp*WMe_3(=NH_2)] with ferrocenium. The tris-methyl complex [Cp*WMe_3(=NH_2)]$^+$ loses ammonium to form {[Cp*WMe_3]$_2$(μ-N)}$^+$ and reacts with NEt_3 to yield [Cp*W(NH)Me_3] reversibly with gain and loss of a H^+. The neutral species [Cp*WMe_3(=NH_2)] undergoes a reaction with ammonium to form [Cp*WMe_3(NH_3)$_2$]$^+$, which reverts to the parent complex with release of NH_3 upon reaction with DBU (1,8-diazobicyclo[5.4.0]undec-7-ene). The complex [Cp*WMe_3(NH_3)]$^+$ was synthesized by reaction of [Cp*WMe_3(=NH_2)] or [Cp*WMe_3(NH_3)$_2$]$^+$ with strong acid; in the presence of excess triflic acid the product is [Cp*WMe_3(OTf)]. These reactions are reversible upon addition of base such as NH_3 or DBU. All species were characterized by IR and ^{15}N NMR spectroscopies.

$WNCl_3$ reacts with lithium diphenyl amide to form the four-coordinate complex $WN(NPh_2)_3$, [9]. When the reaction is carried out in the presence of ^{n}BuLi, the tetranuclear mixed valence cluster (6) is formed. The compound crystallizes in the space group $P2_1/n$ with a W-W bonding distance of 2.535(1)Å and a W-W non-bonding distance of 2.789(1)Å.



(6)

The reaction of 1,1-dimethylalkylhydrazines (Me_2NNHR) with WOF_4 produces two isomeric hydrazine adducts as shown by ^{19}F NMR spectroscopy [10]. The more stable isomer has the R group positioned towards the oxygen atom, as in similar compounds containing dialkyldimethylhydrazines described by the same authors wherein the bulkier substituent is oriented toward the oxygen atom [11].

3.1.3. Complexes with oxygen donor atoms

The complex [Cp*WO_3]$^-$, much like the isoelectronic species [Cp*ReO_3], exhibits enhanced nucleophilicity which makes it a useful precursor for the synthesis of heterobimetallic complexes with μ-oxo bridges [12]. Reaction of this complex with Cp_2MCl_2 (M=Ti, Zr, V) produces complexes of the type [Cp*WO_2(μ-O)MClCp_2]. Reaction of [Cp*WO_2(μ-O)VClCp_2] with KOH and O_2 gives [Cp*WO_2(μ-O)VOCp_2]. Reaction of [Cp*WO_3]$^-$ with [Cp(CO)$_2$Re(CTol)] results in the formation of [Cp(CO)$_2$Re{=C(Tol)O}WO_2Cp*]. Addition of strong acid to $[Cp^*WO_3]^-$ results in the formation of the dinuclear tungsten complex $[(Cp^*WO_2)_2(\mu\text{-}O)]$.

The reaction of vanadium trichloride(1,4,7-trimethyl-1,4,7-triazacyclononane) $[VCl_3L]$ with trioxotungsten(1,4,7-triazacyclononane) $[WO_3L']$ in $MeOH/H_2O$ (4:1) in the presence of air yields the paramagnetic complex $[LO(H_2O)V(\mu\text{-}O)WO_2L]Cl(ClO_4)$ after addition of $NaClO_4$ [13]. This complex is soluble in water, methanol, and acetonitrile.

3.1.4. *Complexes with sulfur donor atoms*

The reaction of $[WO_4]^{2-}$ with $[SCN]^-$ and H^+ results in the formation of the $[WO(NCS)_5]^{2-}$ anion. Reaction of the tungsten-thiocyanate anion with aqueous polysulfides yields complexes with η^2-polysulfido ligands and a bridging S, S $[W_2O_2S_2]^{2+}$ core [14]. The two tungsten centres are further ligated by either two $\eta^2\text{-}S_4{}^{2-}$ groups as in $[W_2O_2S_{10}]^{2-}$ or one $\eta^2\text{-}S_4{}^{2-}$ and one $\eta^2\text{-}S_2{}^{2-}$ moiety, *i.e.* $[W_2S_2O_8]^{2-}$. The cyclic voltammograms of the complexes each show a two-electron reduction wave at −1.30V vs. SCE followed by two one-electron oxidations (−1.22 and −0.76V) at scan rates equal to or greater than 100 mV s^{-1}. At 50 mV s^{-1}, however, two separate one electron reductions are observed.

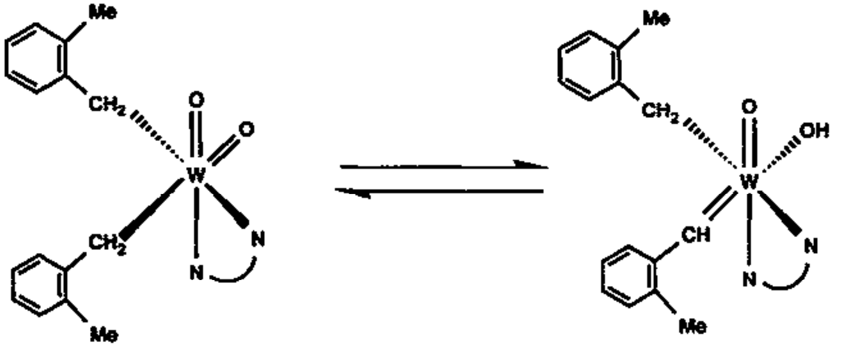
The reaction of $W(CO)_6$ with S_2Cl_2 in CH_2Cl_2 produces $WCl_4S \cdot S_8$ [15]. The presence of the S_8 group was originally based on the IR spectroscopic data ($\nu(S\text{-}S)_{complex}$ = 467, 379, 307, 269, 236 cm^{-1} vs. $\nu(S\text{-}S)_{free}$ = 465, 389, 306, 270, 235 cm^{-1}). The $\nu(W{=}S)$ mode occurs at 551 cm^{-1}. An X-ray crystal structure analysis shows that the tungsten centre exhibits a square pyramidal geometry, with a sulfur atom in the apical position. The tungsten atom is 0.45 Å above the plane defined by the four chlorine atoms. The W-S distance for the closest member of the eight-membered ring is 3.189(2)Å, which is approximately equal to the metallic radius of tungsten plus the van der Waals radius of sulfur, therefore the authors concluded that the proximity of the sulfur atom to the tungsten centre is due mainly to crystal packing forces. It was pointed out, however, that several S(ring)-Cl distances are significantly shorter (0.4 Å shorter) than the sum of the van der Waals radii of sulfur and chlorine, indicating that some weak intermolecular interactions are present. Attempts to remove S_8 by sublimation were unsuccessful, as the complex melts at *ca.* 120°C.

Reactions of $W(1,2\text{-}S_2C_6H_4)_3$ with alkylating reagents have been attempted in an effort to alkylate the metal centre [16]. In most cases alkylation reactions of the ligand occurred as in the reaction of $W(1,2\text{-}S_2C_6H_4)_3$ with MeLi in the presence of NR_4Cl (R = Me, Et) to give $[NR_4][W(S_2C_6H_4)_2(MeSC_6H_4S)]$ in which the methylated sulfur is coordinated to the pseudo-octahedral tungsten centre. Dropwise addition of MeLi or reaction of Li metal with $W(1,2\text{-}S_2C_6H_4)_3$ reduces W^{VI} to W^V to give $Li[W(S_2C_6H_4)_3]$. The identical product has been formed in the analogous reaction with EtLi which first produces the alkylated complex $Li[WEt(S_2C_6H_4)_3]$ which then readily undergoes β-elimination followed by reductive elimination of H_2. Addition of two equivalents of ^nBuLi to $W(1,2\text{-}S_2C_6H_4)_3$ leads to the formation of the W^{IV} complex $[W(S_2C_6H_4)_3]^{2-}$ which reacts with two equivalents of R_3OBF_4 (R=Me, Et) to yield [$W(S_2C_6H_4)(RSC_6H_4S)_2$]. This product has also been synthesized by the reaction of [NR_4][$W(S_2C_6H_4)_2(MeSC_6H_4S)$] with one equivalent of Me_3OBF_4.

3.1.5. Complexes with mixed donor atom ligands

^{183}W NMR shifts were measured for a large number of organometallic oxo-, sulfido-, and imidotungsten(VI) methyl complexes by using indirect methods such as $^1H\{^{183}W\}$ double resonance and $^1H\{^1H,^{183}W\}$ triple resonance techniques [17]. For complexes of general formula Cp*W(=E)MeL (E = O, S; L = O^{2-},S^{2-}, PhN^{2-}, $[Cl^-]_2$, $[Br^-]_2$, η^2-O_2^{2-}, η^2-S_2^{2-}), the W^{VI} nucleus becomes more deshielded with increasing ligand polarizability and W-E bond multiplicity.

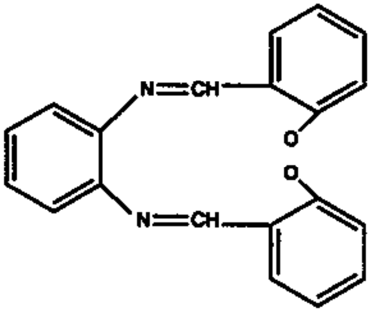
The decomposition of bipyridylbis(2-methylbenzyl)dioxotungsten (**7**) was followed by gas chromatography and ^1H NMR [18]. Products observed from the room temperature decomposition in CH_2Cl_2, CH_3CN, thf, dioxane or dmf include 2-MeC_6H_4CHO, 2-$MeC_6H_4CH_2OH$, and traces of o-xylene and (2-MeC_6H_4)CH_2CH_2(2-MeC_6H_4). The reaction is believed to proceed via a dialkyldioxo- to alkylalkylideneoxohydroxometal tautomerism to form (**8**).



(**7**) (**8**)

The stabilization of peroxo moieties bound to W^{VI} with quadridentate Schiff bases as co-ligands has been reported (**9, 10, 11**) [19]. Molecules of the type [$W(O)(O_2)L$], where the oxo and peroxo ligands are *trans*, are inert toward the oxidation of olefins. When L=(**10**), the complex failed to oxidize allyl alcohol after heating at 90°C for 48 hours.

The reaction of WCl_6 with three equivalents of 2,2-dimethylpropylidynephosphine [$(CH_3)_3CCP$:] produces three mononuclear tungsten complexes [20]. The compounds [$WCl_5P_2(C_5H_9)_3$] (**12**), [$WCl_4P_5(C_5H_9)_5$] (**13**) and [$C_3(C_4H_9)_3$][$WCl_5(C_4H_9CCC_4H_9)$] (**14**) were fully characterized by single crystal X-ray studies. As can be clearly seen, considerable fragmentation of the propylidyne phosphine occurs in the formation of (**12**) and (**13**). In the case of compound (**14**), phosphorus has been eliminated altogether, and major C-C bond formation has occurred between the cyclopropenium cation and the coordinated 2,2,5,5-tetramethyl-3-hexyne.



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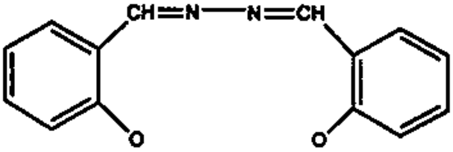

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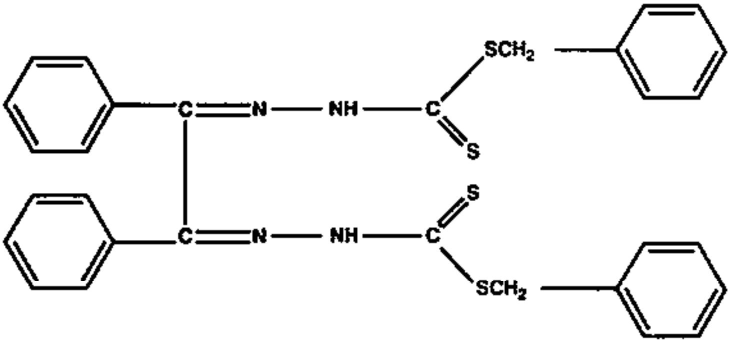

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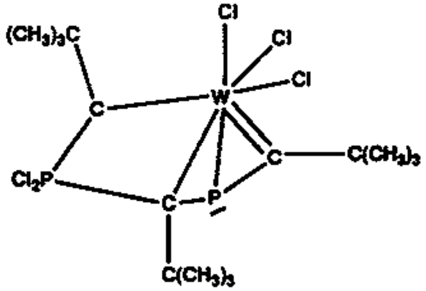
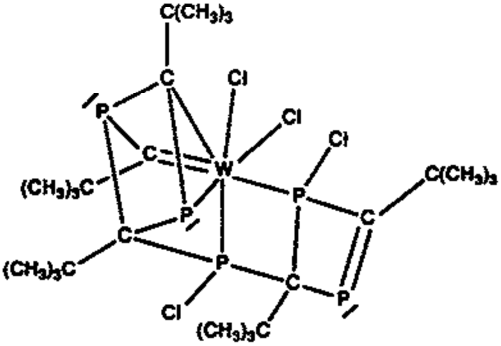
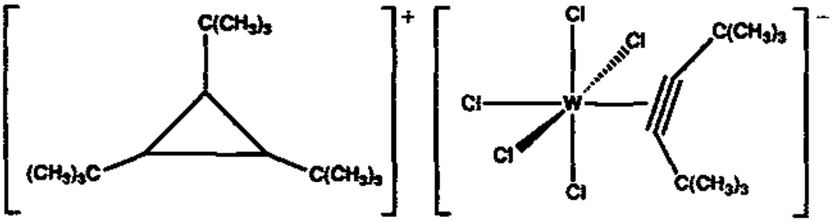




(12) **(13)**



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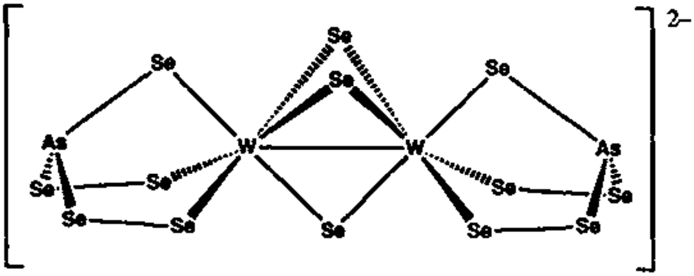
3.2 *TUNGSTEN(V)*

The reaction of $[WSe_4]^{2-}$ with excess As_4Se_4 produces the dinuclear $W^{V,V}$ complex $[W_2As_2Se_{13}]^{2-}$ (**15**). The molecule possesses a confacial bioctahedral geometry, where three selenium atoms bridge the two metal centres and one $AsSe_5^{3-}$ ligand occupies the other three coordination sites on each metal. A single bond is assigned based on the W-W distance of 2.903(2) Å [21].



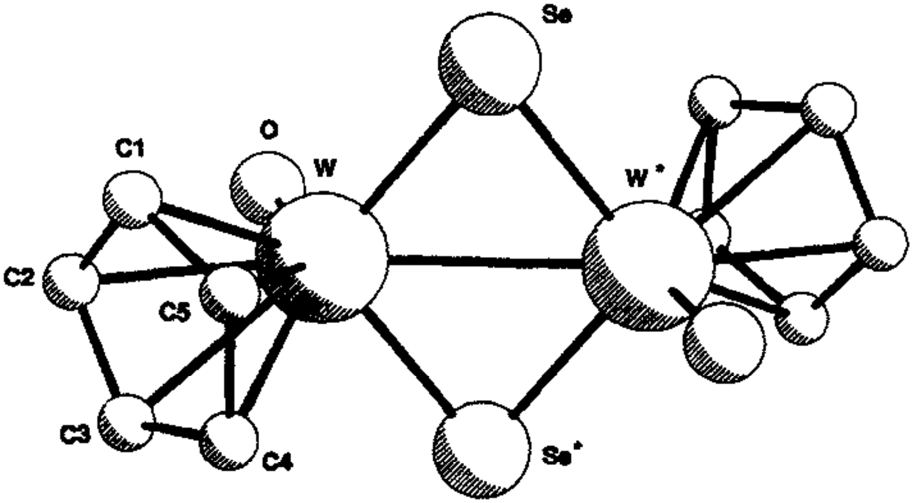
(15)

The reaction of WF_6 with four equivalents of Me_3SiOMe results in the formation of [*cis*-$WF_2(OMe)_4$], which can be reduced by lithium metal in thf to form $[W_2F_x(OMe)_{10-x}]$ (x = 1-3) [22]. Reaction of this mixed fluoride-alkoxide complex with NaOMe in thf leads to the isolation of the highly air-sensitive complex $W_2(OMe)_{10}$, which constitutes the first example of a homoleptic tungsten(V) alkoxide complex. This complex exhibits the familiar edge-sharing bioctahedral geometry with W-W = 2.7897(8) Å, $W\text{-}O_{ax}$ = 1.887(6) Å, $W\text{-}O_{eq}$ = 1.963(6) Å, and $W\text{-}O_{bridge}$ = 2.028(6) Å.

The reaction of WCl_6 with excess allyltrimethylsilane at low temperature in diethyl ether proceeds with reduction of W^{VI} to W^V and formation of $WCl_5(OEt_2)$, which is both air and moisture sensitive [23]. This compound is a convenient starting material to react with Lewis bases in the formation of new W^V complexes.

A variety of dinuclear tungsten(V) complexes have been prepared by the reaction of $[WO_4]^{2-}$ with ethyl xanthate [24]; among these are the compounds {$[W_2O_3(S_2COC_2H_5)_4]$, $[W_2O_4(S_2COC_2H_5)_2]$, $[W_2O_2S_2(S_2COC_2H_5)_2]$ and $[W_2O_3S(S_2COC_2H_5)_2]$} whose identities were established by IR and UV-vis spectroscopies. The thermal decomposition of $[W_2O_2X_2(S_2COC_2H_5)_2]$ (X = O, S), where the X groups bridge the two $[WO(S_2COC_2H_5)]$ cores, was monitored by TGA. At temperatures between 110°C and 330°C, the compound decomposes to give $[W_2O_2X_2S_2]$, followed by the formation of W_2O_6 at 530°C and finally WO_3 at 560°C.

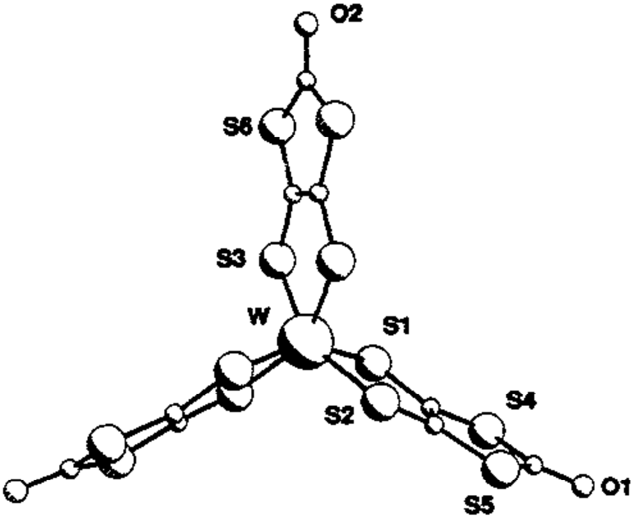
Oxidation of $[CpW(CO)_3]^-$ with $SeOCl_2$ results in the formation of $[(CpWO)_2(\mu\text{-}Se)_2]$ (**16**) as well as $[Cp_2W_2(CO)_6]$, $[Cp_2W_2(CO)_4]$ and $[Cp_2W_2(CO)_6Se]$ [25]. The bridging telluride complex analogous to (**16**) is formed from the reaction of tellurium metal with $[Cp^*{}_2W_2(CO)_4]$. Compound (**16**) crystallizes in the space group $P2_1/c$ with a W-W distance of 2.962(1) Å. The analogous tellurium complex crystallizes in the P1(bar) space group with a W-W distance of 3.075(1) Å.



(16)

3.3. TUNGSTEN(IV)

The anion $[WS_4]^{2-}$ reacts with $C_2S_4(CO)_2$ to yield $[W(S_2C_2S_2CO)_3]^{2-}$ (**17**), with COS as the major byproduct [26]. Similar reactions of $[WS_4]^{2-}$ with $C_2S_4(CO)(CS)$ have produced two complexes, $[W(S_2C_2S_2CS)_3]^{2-}$ and $[W_2S_4(S_2C_2S_2CS)_2]^{2-}$; the latter compound consists of a $[(WS)_2(\mu\text{-}S)_2]$ core. Electrochemical studies performed on (**17**) indicate that the complex undergoes two one-electron oxidations at mild potentials ($E_{1/2}$ vs. Ag/AgCl = −0.07V [−2/−1] and +0.27V [−1/0]).



(17)

The synthesis of [*trans*-W(PMe_3)$_4$(S)$_2$] has been reported from the reaction of [W(PMe_3)$_4$ (η^2-CH_2PMe_2)H] with H_2S [27]. When the reaction is carried out in pentane, the dihydrido, bis-hydrosulfido species [W(PMe_3)$_4$(H)$_2$(SH)$_2$] is isolated from protonation of the CH_2PMe_2 ligand to form PMe_3 by H_2S. Dissolution of the product in solvents other than saturated hydrocarbons is immediately followed by hydrogen elimination. The compound [*trans*-W(PMe_3)$_4$(S)$_2$] readily reacts with isocyanides to form [*trans, trans, trans*-W(PMe_3)$_2$(CNR)$_2$(S)$_2$] or with aldehydes to form η^2-aldehyde complexes of the form [*trans, cis*-W(PMe_3)$_2$(S)$_2$(η^2-OCHR)] whose formation is supported by X-ray crystal analysis.

[W(PMe_3)$_4$(η^2-CH_2PMe_2)H] has been found to produce [*trans*-W(PMe_3)$_4$(Te)$_2$] with elimination of PMe_3 upon addition of two equivalents of solid tellurium [28]. The reaction mechanism is believed to involve tellurium atom transfer via Me_3P=Te, where PMe_3 is acting as a transfer catalyst. The reaction to form [*trans*-W(PMe_3)$_4$(Te)$_2$] is instantaneous when Me_3P=Te is added. Structural characterization of the product reveals a W-Te distance of 2.596(1) Å. The complex was further characterized by ^{125}Te{^{1}H} and ^{31}P{^{1}H} NMR spectroscopy.

The compound [WH($SC_6H_2R_3$-2,4,6)$_3$(PMe_2Ph)$_2$] has been prepared from reaction of the tungsten(VI) hydride complex [WH_6(PMe_2Ph)$_3$] with three equivalents of [$HSC_6H_2R_3$-2,4,6] (R=Me, ^{i}Pr) following the elimination of four equivalents of H_2 [29]. X-ray crystal analysis of the complex (R=^{i}Pr) shows that the molecule exhibits a pseudo-octahedral geometry, with three sulfur ligands in a meridonal conformation. The hydride ligand in each complex was detected by

^{1}H NMR as a doublet of doublets due to the inequivalent phosphines arising from steric hindrance in the molecule (δ +9.08 [R=^{i}Pr] and δ +8.86 [R = Me]).

The reaction of [(^{t}BuNH)$_2$W(=N^{t}Bu)$_2$] with two equivalents of ^{t}Bu$_3$SiOH (silox-H) in benzene leads to release of ^{t}BuNH$_2$ and formation of the colorless compound [(silox)$_2$W(=N^{t}Bu)$_2$] in 81% yield. Further treatment with three equivalents of HCl in benzene results in the elimination of ^{t}BuNH$_3$Cl with concomitant formation of the light yellow compound [(silox)$_2$Cl$_2$W=N^{t}Bu] (88%). Reduction of this complex with magnesium dust in diethyl ether yields the green product [(silox)$_2$W = N^{t}Bu], the first example of a three-coordinate mononuclear tungsten species [30]. The complex is unstable in hydrocarbon solvents, but ^{1}H spectroscopic NMR and IR data support the assignment of the complex as a diamagnetic mononuclear species. A single crystal X-ray structure shows that the complex is nearly trigonal planar with a slight distortion towards T-shaped due to the bulk of the t-butyl groups on the silox ligand. The pertinent bond distances (W-O$_{ave}$=1.820(16) Å and W-N=1.658(17) Å) are consistent with the electrophilic nature of the tungsten atom. The complex does not react with σ-donors (thf, etc.,) due to the four-electron repulsion between the σ-donor orbital and the filled d_{z^2} orbital on the metal centre, but the complex reacts with π-acceptors (*e.g.* ethylene, 2-butyne) to form adducts.

3.4 TUNGSTEN (III)

3.4.1 Complexes with oxygen donor ligands

The reaction of [W$_2$(O^{t}Bu)$_6$] with the silyl alcohol reagent (c-C$_6$H$_{11}$)$_7$Si$_7$O$_9$(OH)$_3$ has been shown to give the dinuclear tungsten complex {[(c-C$_6$H$_{11}$)$_7$Si$_7$O$_{12}$]$_2$W$_2$(μ-H)(O^{t}Bu)}, where the silyl reagent occupies three coordination sites, bonding via the deprotonated oxygens [31]. The structure of the compound is postulated on the basis of ^{1}H, ^{13}C, ^{29}Si, and ^{183}W NMR spectroscopic data.

The reaction of [W$_2$(O^{t}Bu)$_6$] with six equivalents of ^{t}BuMe$_2$SiOH leads to the formation of ^{t}BuOH and [W$_2$(OSi^{t}Bu$_2$Me)$_6$] [32]. Further reaction of this complex with acetylene in the presence of pyridine in hexane at −10°C gives [W$_2$(OSi^{t}Bu$_2$Me)$_6$(μ-C$_2$H$_2$)(py)], which goes on to eliminate pyridine and ^{t}BuMe$_2$SiOH at room temperature to yield [W$_2$(OSi^{t}Bu$_2$Me)$_5$(μ-CCH)] as the major product. [W$_2$(OSi^{t}Bu$_2$Me)$_7$(μ-CHCH$_2$)] and [W$_2$(OSi^{t}Bu$_2$Me)$_7$(μ-CCH$_3$)] are minor products in the reaction; neither of these species were isolated, but their presence was confirmed by ^{1}H and ^{13}C NMR spectroscopies. The vinyl complex is formed independently from the reaction of [W$_2$(OSi^{t}Bu$_2$Me)$_6$(μ-C$_2$H$_2$)(py)] with ^{t}BuMe$_2$SiOH. The authors conclude that the vinyl complex and the ethylidyne complex are not interconverted in the reaction. The formation of the ethylidyne complex is thought to proceed via a vinylidene intermediate.

When [W$_2$(O^{t}Bu)$_6$] reacts with dinitriles NC(CH$_2$)$_n$CN (n = 3-6), the W-W triple bond is ruptured with the formation of [(^{t}BuO)$_3$WC(CH$_2$)$_n$CW(O^{t}Bu)$_3$] and two equivalents of [(^{t}BuO)$_3$WN] [33]. Addition of CO results in the reformation of the W-W bond and transformation of the polymethylene-bridged alkylidyne group into a μ-cycloalkyne ligand in

$[W_2(O^tBu)_6\{\mu\text{-}C_2(CH_2)_n\}(CO)]$ (n = 4,5). One of the alkoxy groups assumes a bridging position while the carbonyl remains terminal as shown by an X-ray structure analysis (n = 4, W-W = 2.637(2) Å; n = 5, W-W = 2.626(2) Å). There appears to be some degree of W-C π^* bonding with the μ-cycloalkyne group as evidenced by IR spectroscopy (n = 4, ν(CO) = 1960 cm^{-1}; n = 5, ν(CO) = 1933 cm^{-1}; μ-C_2Me_2 complex, ν(CO) = 1917 cm^{-1}). When n = 3 or 6, the complex is unreactive toward CO, presumably due to the steric requirements of the ring closure reaction.

The compound $[W_2(O^tBu)_6(py)(\mu\text{-}\eta^1\text{:}\eta^4\text{-}C_4H_6)]$ has been synthesized from $[W_2(O^tBu)_6(py)_2]$ and 1,3-butadiene by an organometallic Diels-Alder reaction [34]. The W-W bond order is reduced from three to two in the reaction. An X-ray crystallographic study indicates that one tungsten atom is in a pseudo-octahedral environment, bonded to three terminal and two bridging alkoxide ligands as well as to the terminal carbon of the bridging butadiene. The second tungsten is bonded to all four carbon atoms of the butadiene as well as to the two bridging alkoxide ligands, one terminal alkoxide, and the nitrogen of the pyridine ligand. In solution, the reaction appears to be reversible when excess butadiene is removed from the system.

3.4.2 Complexes with sulfur donor ligands

Reduction of WCl_4 with Na/Hg in refluxing thioethers (Me_2S, Et_2S, tht) produces $[Cl_3W(\mu\text{-}L)_3WCl_3]$ (L = Et_2S, tht) and $[SMe_3][Cl_3W(\mu\text{-}L)_2(\mu\text{-}Cl)WCl_3]$ (L = Me_2S) in *ca.* 80% yields [35]. The Et_2S and Me_2S molecules possess a confacial bioctahedral geometry with short W-S bonds (2.384(4) Å, W-Cl_{bridge} [Me_2S structure] 2.484(3) Å) as determined by X-ray crystallographic studies. IR and ^1H NMR data are also presented for the three complexes.

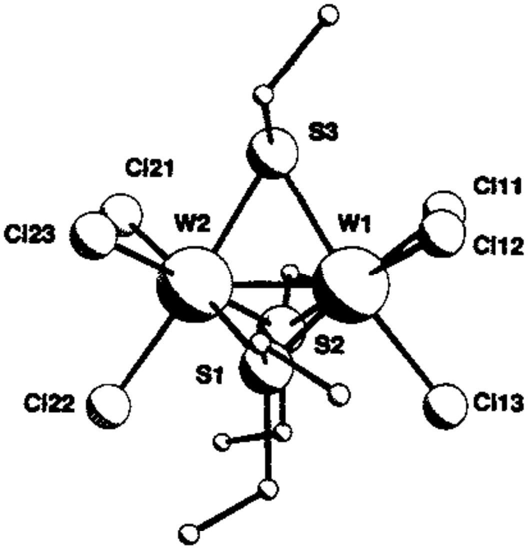
The thioether ligands in $[Cl_3W(\mu\text{-}SEt_2)_3WCl_3]$ and thiophene groups in $[Cl_3W(\mu\text{-}tht)_3WCl_3]$ are highly susceptible to nucleophilic attack by halides and pseudohalides X^- (X = SR, SeR, Cl, Br, H) resulting in C-S bond cleavage [36]. Attack on the thioether complex leads to formation of (**18**) and EtX, while attacks on the tht derivative result in ring-opening to give functionalized μ-thiolate anions of the form $[Cl_3W(\mu\text{-}tht)_2\{\mu\text{-}S(CH_2)_4X\}WCl_3]^-$. Loss of the ethyl group in (**18**) results in a decrease of the W-W bond distance from 2.499(1) Å to 2.474(1) Å. Bonds to the monoethylthiolate ligand from tungsten are longer than those to the thioether ligands. Both complex (**18**) and $[Cl_3W(\mu\text{-}tht)_2\{\mu\text{-}S(CH_2)_4X\}WCl_3]^-$ exhibit confacial bioctahedral bonding arrangements.

3.4.3 Complexes with mixed donor atom ligands

The reaction of $[W_2(NMe_2)_6]$ with cyclopentanol in hexane initially yields $[W_2(O\text{-}c\text{-}C_5H_9)_6(HNMe_2)_2]$ [37]. Further reaction with cyclopentanol and dimethylamine leads to the formation of $[W_2(\mu\text{-}H)(O\text{-}c\text{-}C_5H_9)_7(HNMe_2)]$. In a subsequent reaction, the coordinated dimethylamine has been replaced by PMe_3.

The reaction of $[W_2(NMe_2)_6]$ with bulky diols $Me_2C(OH)CH_2CH_2C(OH)Me_2$ and (**19**) leads to the isolation of ditungsten complexes containing eight- and nine-membered rings [38]. X-ray crystal analysis of (**20**) indicates that the W-W triple bond remains intact (W-W =

2.320(1) Å). The average W-O distance is 1.95(2) Å and the W-N distances are 2.29(1) Å. Reaction of **(19)** with $[W_2(NMe_2)_6]$ produces **(21)**, where one of the diol ligands is bonded in an η^3 fashion due to an insertion of the metal into the C-H bond. The W-W distance of 2.4946(6) Å in **(21)** is typical for a W-W double bond.



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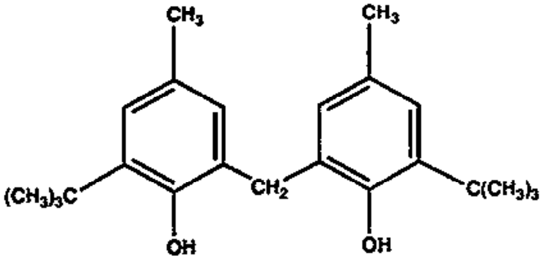
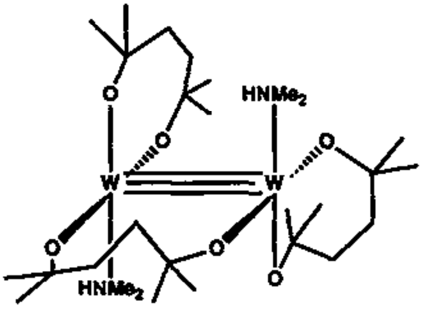


(19)

The reaction between $[W_2Cl_2(NMe_2)_4]$ and $LiGePh_3$ in toluene/thf readily produces $[W_2(GePh_3)_2(NMe_2)_4]$ in 69% yield [39]. An X-ray structure of the complex shows that the ligands in the molecule are arranged in an *anti* conformation **(22)**; the W-W bond distance is 2.2970(9) Å. This arrangement of the ligands is supported by the ^1H NMR spectrum, which lacks resonances attributable to a *gauche* conformer. The complex is air-stable and is inert to hydrolysis in either 6M HNO_3 or a 6M KOH/EtOH solution.

The reaction of $[W_2(O^tBu)_6]$ with aniline in diethyl ether/hexane solution produces the air-sensitive complex $[W_2(O^tBu)_4(HNPh)_2(H_2NPh)_2]$ in relatively high yield [40]. NMR spectroscopic studies of the compound indicate that the complex is in dynamic equilibrium, which could be due in part to the hydrogen bonding between the butoxy oxygen atoms and the hydrogens on the aniline and anilide groups. At temperatures above –30°C in solution, the aniline ligands are freely dissociating, yielding [$W_2(O^tBu)_4(HNPh)_2$]. Above room temperature, the latter species readily undergoes a conformational change from *anti* to *gauche*.



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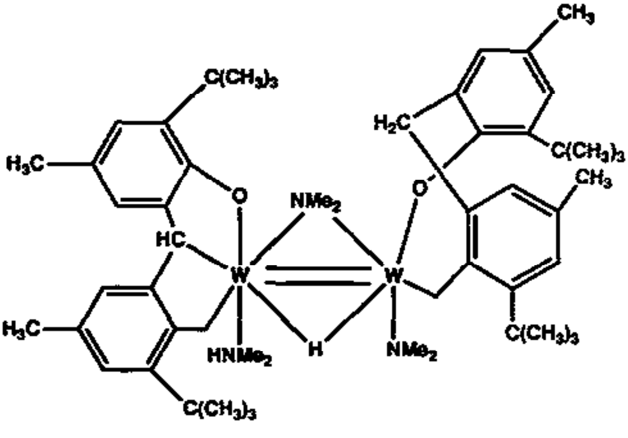
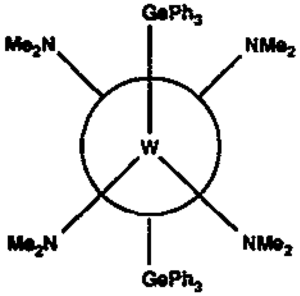


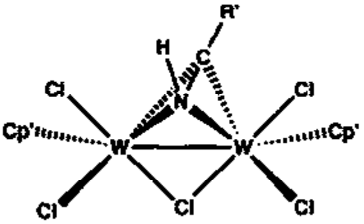
(21)

[$W_2(NMe_2)_6$] reacts with two equivalents of the tertiary alcohols Ph_3EOH (E = C, Si) to give [$W_2(OEPh_3)_2(NMe_2)_4$] [41]. The triphenylalkoxy derivative shows a temperature-dependent ^1H NMR spectrum, with a mixture of the *anti* and *gauche* conformers. An X-ray crystal structure of this complex, however, showed only the presence of the *gauche* conformer. Conversely, the triphenylsiloxy derivative exists only in the *anti* conformer, as evidenced by X-ray crystallography. Reaction of [$W_2(NMe_2)_6$] or [$W_2(O^tBu)_6$] with six or more equivalents of Ph_3SiOH results in formation of [$W_2(OSiPh_3)_4(NMe_2)_2$] and [$W_2(OSiPh_3)_4(O^tBu)_2$], respectively. The reaction does not occur with Ph_3COH, due to increased steric hindrance at the metal centre as a result of the shorter O-C bond versus that of O-Si.



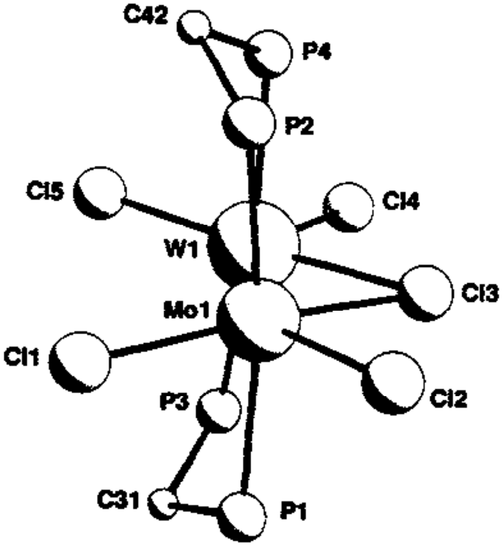
(22)

The compound $[W_2(\eta^5\text{-}C_5H_4R)_2Cl_4(\mu\text{-}Cl)(\mu\text{-}R'CNH)]$ (23) has been synthesized from the reaction of the triply bonded dinuclear species $[W_2(\eta^5\text{-}C_5H_4R)_2Cl_4]$ (R = Me, ^iPr) with R'CN (R' = Me, Et, Ph) followed by addition of HCl gas [42]. A crystallographic study (R = ^iPr, R' = Et) reveals a perpendicular bridging alkylidyne amide ligand, formed by the protonation of the organonitrile. The distances W-W = 2.3678(6) Å and C-N = 1.405(8) Å suggest that there is a significant amount of π^* back donation from the tungsten centres to the π^* orbitals of the C-N bond.



(23)

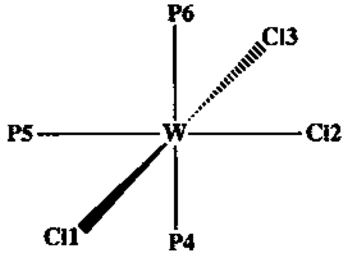
The reaction of $[MoWCl_4(PMe_2Ph)_4]$ with dppm in hydrocarbon solvents produces $[MoWCl_4(\mu\text{-}Cl)(\mu\text{-}H)(\mu\text{-}dppm)_2]$ (24) in 64% yield, the first example of a multiply bonded heteronuclear edge-sharing bioctahedral complex [43]. External sources of chloride ion used in the reaction increase the yield of (24) to 78%. The formation of $[MoWCl_4(\mu\text{-}Cl)(\mu\text{-}D)(\mu\text{-}dppm)_2]$ or the homologous ditungsten complex from deuterated solvents ($CDCl_3$ or CH_3OD) indicate that the solvent is the proton source in the reaction. The Mo and W atoms are disordered in the crystal structure (Site Mo1: 53.6% Mo, 46.4%W; Site W1: 53.6% W, 46.4% Mo). In contrast to expected trends, the Mo-W bond distance (2.4932(6)Å) is longer than the W-W distance in the homologous ditungsten complex (2.4830(9) Å). The lengthening is explained as a consequence of the 8.5° torsion angle about the M-M' vector.



(24)

The complex $[W_2(\eta^5\text{-}C_5H_4R)_2X_4]$ (X = Cl, R = Me, ^{i}Pr; X = Br, R = ^{i}Pr) undergoes oxidative addition reactions with HY (Y = H, Cl, SR'; R' = Me, Et, ^{i}Pr, Ph, ^{t}Bu) to produce $[W_2(\eta^5\text{-}C_5H_4R)_2X_4(\mu\text{-}H)(\mu\text{-}Y)]$ and with PHPhR'' (R'' = H, Ph) to yield $[W_2(\eta^5\text{-}C_5H_4R)_2X_4(\mu\text{-}H)(\mu\text{-}PPhR'')]$ [44]. A single crystal study of the bridging diphenylphosphide complex reveals a W-W distance of 2.6558(3) Å, which is typical of a W=W bond. The bridging thiolate complexes are fluxional in solution, undergoing inversion at the sulfur atom, while the bridging chloride complex is fluxional due to the apparent "rotation" of the chloride and hydride about the W=W bond. Reactions of $[W_2(\eta^5\text{-}C_5H_4{}^iPr)_2Cl_4(\mu\text{-}H)_2]$ or $[W_2(\eta^5\text{-}C_5H_4{}^iPr)_2Cl_4(\mu\text{-}H)(\mu\text{-}PPh_2)]$ with PMe_3 lead to adduct formation to give a product with a bridging chloride ligand. Metal-metal bond scission occurs in the analogous reaction of $[W_2(\eta^5\text{-}C_5H_4{}^iPr)_2Cl_4(\mu\text{-}H)(\mu\text{-}Cl)]$ or $[W_2(\eta^5\text{-}C_5H_4{}^iPr)_2Cl_4(\mu\text{-}H)(\mu\text{-}SR')]$ with PMe_3 to yield $[W(\eta^5\text{-}C_5H_4{}^iPr)Cl(PMe_3)_3]$. The products have been characterized by ^1H and ^{31}P NMR spectroscopies.

Reduction of $WCl_4(PMe_2Ph)_3$ with zinc metal produces $WCl_3(PMe_2Ph)_3$ (**25**), the first neutral mononuclear complex of W^{III} to be structurally characterized [45]. The geometry of the complex is *mer*, with all six W-L bonds exhibiting different lengths (W-Cl$_1$ 2.437(1) Å, W-Cl$_2$ 2.441(1) Å, W-Cl$_3$ 2.295(2) Å, W-P$_4$ 2.555(1) Å, W-P$_5$ 2.514(1) Å, W-P$_6$ 2.536(1) Å). Complex (**25**) was further used to synthesize $[WCl_3(PMe_2Ph)(dppe)]$, $[WCl_3(PMe_2Ph)_2(py)]$ and $[WCl_3(PMe_2Ph)(bipy)]$.



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3.5 TUNGSTEN (II)

The complex $[WI_2(CO)_3(NCMe)_2]$ has been shown to be a useful precursor for the syntheses of a large number of novel complexes. The acetonitrile ligands can be replaced by one or two equivalents of PPh_3 to yield $[WI_2(CO)_3(NCMe)(PPh_3)]$ and $[WI_2(CO)_3(PPh_3)_2]$ respectively [46]. Further reactions of these complexes with Na(acac), Na(hfacac) or Na(bzacac) yields seven-coordinate complexes of the form $[WI(CO)_3(PPh_3)(L\cap L)]$ or $[WI(CO)_2(PPh_3)_2(L\cap L)]$, which were characterized by low temperature ^{13}C NMR as well as by IR and ^1H NMR spectroscopies.

Reactions of $[WI_2(CO)_3(NCMe)(EPh_3)]$ (E=P, As, Sb) with dppm, dppe, dppb or the dangling diphosphine ligands in $[Fe(\eta^5-C_5H_4PPh_2)_2]$ result in the formation of dinuclear complexes of general formula $[W_2I_4(CO)_6(EPh_3)(L\cap L)]$ [47]. All of the products were determined to be diamagnetic and were characterized by IR and ^1H NMR spectroscopies as well as elemental analysis.

Diphosphazanes $RN[P(OPh)_2]_2$ (R=Me, Ph) react with $[WI_2(CO)_3(NCMe)_2]$ via substitution of the acetonitrile ligands to give $[WI_2(CO)_3\{P(OPh)_2\}_2NR]$ [48]. The phenyl derivative was subjected to a single crystal X-ray structure and exhibits a slightly distorted pentagonal bipyramidal structure, with two of the three carbonyls in apical positions. Unlike the complexes $[WI_2(CO)_3(L\cap L)]$ ($L\cap L$=dppe, dppm), these species do not undergo CO substitution even when heated in the presence of excess diphosphazane. Likewise, these complexes do not undergo decarbonylation to give six-coordinate complexes in contrast to the monophosphine complexes $[WI_2(CO)_3L_2]$ (L=PPh_3, PEt_3).

The dinuclear complex $[W(\mu\text{-}I)(CO)_3\{S_2CN(CH_2Ph)_2\}]_2$ has been reported from the reaction of $[WI_2(CO)_3(NCMe)_2]$ with $[S_2CN(CH_2Ph)_2]^-$ [49]. When one of the acetonitrile ligands in the starting material is replaced by PPh_3, $AsPh_3$ or $SbPh_3$, subsequent reaction with $[S_2CNR_2]^-$ (R=Me, Et) produces only the mononuclear species $[WI(CO)_3L(S_2CNR_2)]$. Further reaction with $[S_2CNR'_2]^-$ (R'=Et, CH_2Ph) produces $[W(CO)_3L(S_2CNR_2)(S_2CNR'_2)]$ for L=PPh_3 and $[W(CO)_3(S_2CNR_2)(S_2CNR'_2)]$ in low yield when L = $AsPh_3$ or $SbPh_3$.

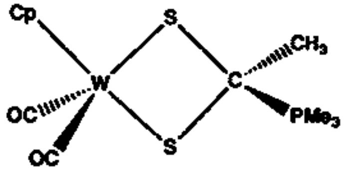
$[WCl_2(PMePh_2)_4]$ reacts with $Ph_2P(O)CH_2CH_2PPh_2$ to give $[WCl_2(Ph_2P\{O\}\text{-}CH_2CH_2PPh_2)(PMePh_2)_2]$. Upon heating at 80°C for 8 hours, the phosphoryl oxygen is transferred to the tungsten centre with formation of $[WOCl_2(diphos)(PMePh_2)]$,

$[WOCl_2(PMePh_2)_3]$ and $[WCl_2(diphos)(PMePh_2)_2]$ [50]. This reaction is one of the first documented examples of oxygen transfer from a ligand to a metal. $[WCl_2(PMe_3)_4]$ undergoes a similar reaction with the chelating phosphine oxide without observable intermediates. Non-chelating phosphine oxides have not been reported to undergo this type of oxygen-transfer reaction.

Oxidation of $[NEt_4][\{HB(Me_2pz)_3\}W(CO)_3]$ with Br_2 or I_2 in CH_2Cl_2 or CH_3CN yields $[\{HB(Me_2pz)_3\}W(CO)_3X]$. Further oxidation by O_2 in either refluxing toluene (X=I) or hot CH_3CN (X=Br) leads to the formation of $[\{HB(Me_2pz)_3\}WO(CO)X]$, where the oxo and carbonyl ligands are *cis* to each other [51]. This pyrazolylborate species is one of only a few known examples of a stable compound that contains both an oxo and a carbonyl ligand, since the two ligands will usually eliminate to form CO_2.

A chloride has been abstracted from $[W(bipy)(PMe_3)_2Cl_2]$ with $TlPF_6$ in acetonitrile to form the tungsten(II) cationic complex $[W(bipy)(PMe_3)_2Cl(MeCN)]^+$ [52]. An X-ray crystal structure reveals that the acetonitrile is in an η^2-coordination mode, donating four electrons to the tungsten centre. Bonds between the tungsten centre and the carbon and nitrogen atoms of the CH_3CN groups, respectively, are of nearly equal length, and the C-N bond distance is increased by 0.12 Å over that of the free ligand. Spectroscopic evidence for the η^2-coordination mode include IR and ^{13}C NMR spectroscopies; no CN triple bond stretch was observed in the IR spectrum and the nitrile carbon appeared as a triplet at a chemical shift of δ +235 versus δ +110 for the free ligand. A cyclic voltammogram of the complex consists of one reversible reduction (W^{II}/W^{I}) at −1.62V vs ferrocene/ferrocenium as well as an irreversible reduction (W^{I}/W^{0}) at −2.21V and an irreversible oxidation (W^{II}/W^{III}) at −0.08V.

Reactions of $[WCl_2(CO)_2(PMe_3)_3]$ with β-hydrogen stabilized Grignard reagents afford the acyl complexes $[W(\eta^2\text{-}C\{O\}R)Cl(CO)(PMe_3)_3]$ ($R=CH_2SiMe_3$, CH_2CMe_3, CH_2CMe_2Ph), while LiMe reacts with the tungsten starting material to give $[W(CH_3)Cl(CO)_2(PMe_3)_3]$ [53]. $[W(\eta^2\text{-}C\{O\}CH_2SiMe_3)Cl(CO)(PMe_3)_3]$ reacts via desilylation with two equivalents of dmpe to form $[W(CH_3)(CO)_2(dmpe)_2]Cl$. Reaction of the silyl starting material with CO also results in desilylation to form $[W(\eta^2\text{-}C\{O\}Me)Cl(CO)_2(PMe_3)_2]$. Similar reactions do not occur for the acyl derivatives, which merely substitute dmpe for PMe_3 with no attack on the ligand. Desilylation reactions have been observed for $[W(\eta^2\text{-}C\{O\}CH_2SiMe_3)Cl(CO)(PMe_3)_3]$ upon reaction with NaS_2CNMe_2. The product, $[W(CH_3)(S_2CNMe_2)(CO)_2(PMe_3)_2]$, undergoes a migratory insertion reaction upon addition of CO to produce the corresponding acyl complex.



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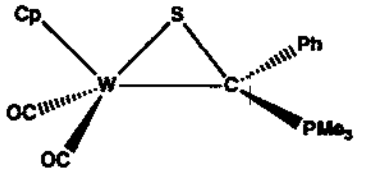
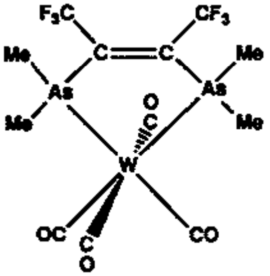


(27)

Chemistry of PMe_3 with tungsten η^2-dithiocarboxylate complexes has been found to be dependent on the alkyl substituents of the carboxylate carbon. Small alkyl groups (*e.g.* Me) allow for addition of PMe_3 to the carboxylate carbon to form tungstendithiacyclobutane ylides (**26**). Aryl substituents, however, promote the loss of sulfur to form tungstenthiacyclopropane ylides (**27**) and $Me_3P{=}S$ [54]. Compound (**26**) is unstable even at -50°C, whereas (**27**) forms only under conditions of boiling acetone. Infrared, ^1H, ^{13}C, and ^{31}P NMR spectroscopic data are presented as well as an X-ray crystal structure of (**27**). The reaction of $[Cp^*W(NO)I_2]$ with either methanol solutions of $(NH_4)_2S_x$ or hydrogen selenide solutions (generated by hydrolysis of Al_2Se_3) results in the formation of $[Cp^*W(NO)(S_5)]$ or $[Cp^*W(NO)(Se_5)]$ [55]. The products contain a cyclo-penta sulfido or selenido chelate in the chair conformation, as confirmed by an X-ray study. Also formed in the polyselenide reaction are the dinuclear tungsten species $[Cp^*{}_2W_2O_2(\mu\text{-}Se)_2]$ and $[Cp^*{}_2W_2(O)(Se)(\mu\text{-}Se)_2]$, as determined by IR, ^1H and ^{13}C NMR and mass spectroscopy.

The reaction of $W(CO)_6$ with *Z*-bis(dimethylarsenic)bis(trifluoromethyl)ethylene in the presence of mesitylene yields (**28**) [56]. This complex oxidatively adds Br_2 in CH_2Cl_2 with loss of one of the CO ligands to form the seven coordinate tungsten(II) complex $[W(L{\frown}L)(CO)_3Br_2]$. It was also reported that the complex can be decarbonylated with PPh_3 to form $[W(L{\frown}L)(CO)_2Br_2(PPh_3)]$.



(**28**)

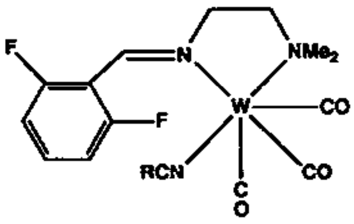
$[W_2Cl_4(PBu_3)_4]$ reacts with dmpm in a refluxing toluene/hexane mixture to produce green $[W_2Cl_4(dmpm)_2]$ and red $[Cl_2W(\mu\text{-}Cl)(\mu\text{-}PMe_2)(\mu\text{-}dmpm)_2WCl(\eta^2\text{-}CH_2PMe_2)]Cl$; the latter complex results from the oxidative addition of dmpm to the dinuclear complex with P-C bond cleavage [57]. The paramagnetic complex, which possesses a $W_2{}^{7+}$ core, is ESR active with a *g* value of 1.953 and a complicated superimposed hyperfine coupling pattern. X-ray crystal analysis shows that the complex exists as a distorted edge-sharing bioctahedral molecule with W-W = 2.7331 Å. The bond order of the W-W bond is either 2.5 or 1.5, depending on the population of the δ and δ^* orbitals.

3.6 *TUNGSTEN(0)*

3.6.1. *Complexes with hydride and halide ligands*

Reactions of the basic hydride complexes [*trans*, *trans*-$WH(CO)_2(NO)(PR_3)_2$] (R = Et, Me, Ph, O^iPr) with BH_3L (L = thf, SMe_2) yield [*trans*-$W(\eta^2\text{-}BH_4)(CO)(NO)(PR_3)_2$], which is unstable towards the elimination of $BH_3.PR_3$ [58]. The borohydride ligand occupies two coordination sites, placing the tungsten centre in a distorted octahedral geometry, as confirmed by X-ray crystallography.

Upon heating compound **(29)** in thf at 55°C for two hours, loss of the acetonitrile ligand occurs with insertion of the metal into the carbon-fluorine bond of the phenyl ring to form **(30)** [59]. A similar reaction occurs if the fluorine is replaced by chlorine. The chloro complex can be converted to **(30)** by addition of AgOTf and KF.



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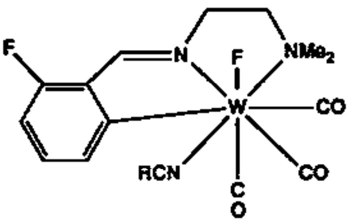


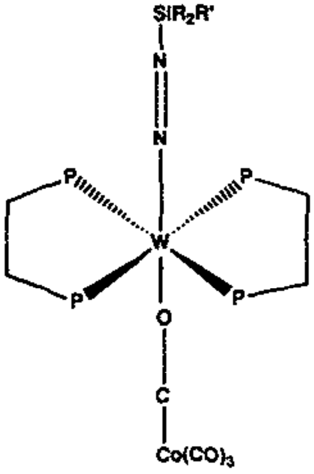
(30)

3.6.2 *Complexes with group 15 (N, P, As and Bi) donor ligands*

The photochemical reaction of tungsten(*p*-tolylphenylmethylidene)pentacarbonyl with $PhN{=}NNMe_2$ results in the formation of [$(CO)_5W{=}NNMe_2$] [60]. The complex is unstable but has a sufficient lifetime to allow for characterization by IR and multinuclear NMR spectroscopy [IR: ν(CO) 2069, 1932 cm^{-1}; ^1H NMR: δ 3.83(s); ^{13}C NMR: δ 197.4 (*cis*-CO), δ 213.2 (*trans*-CO)]. ^{15}N NMR spectroscopy has been used to support the conclusion that the N_2Me_2 ligand is a bent terminal group.

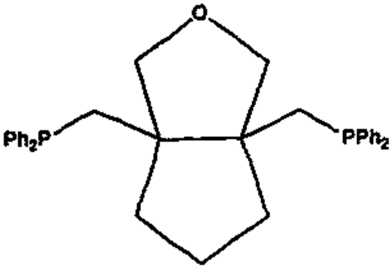
The pentacarbonyl imido complex [$(CO)_5W{=}NPh$] reacts with PPh_3 at the metal-nitrogen bond. Reaction of the complex with aldehydes, ketones, thioaldehydes or thioketones results in formation of imines (RR'C=NPh; R = aryl or alkyl; R' = aryl or H) via metathesis with the oxygen or sulfur atom [61].

Silyl transfer was found to occur in the reaction of [$W(N_2)_2(dppe)_2$] with [$R_2R'SiCo(CO)_4$], leading to **(31)**, a silyldiazenido complex of W^0 [62]. The β-nitrogen of the silyldiazenido group is protonated by H_2O, MeOH or HBr to form the corresponding silylhydrazido complex. The $[Co(CO)_4]^-$ group dissociates and the position *trans* to the silylhydrazido group is occupied by the conjugate base (OH^-, OMe^- or Br^-).



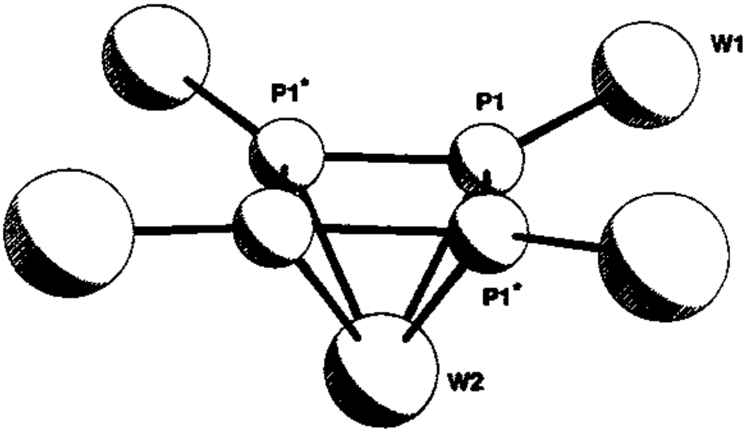
(31)

The synthesis of the novel phosphine ether ligand (32) has been described [63]. Reaction of this ligand with (cod)$W(CO)_4$ and (cht)$W(CO)_3$ produces [(P,P')$W(CO)_4$] and [(P,P',O)$W(CO)_3$], respectively. In the second product, the oxygen atom of the five-membered ring occupies the sixth coordination site of the tungsten centre. The products were characterized by ^1H, $^1H\{^{31}P\}$, ^{13}C and ^{31}P NMR spectroscopy.



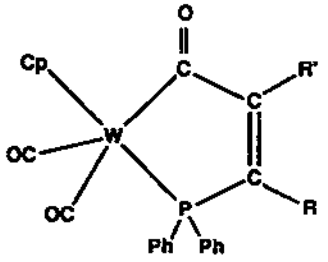
(32)

Two independent reports of the reaction of $W(CO)_6$ with white phosphorus (P_4) have been recently documented [64,65]. The product of this reaction, [$W(CO)_4${*cyclo*-[$PW(CO)_5]_4$}] (33), is only the second example of a metal complex containing a *cyclo*-P_4 ligand. The compound forms crystals of two different tetragonal symmetries; these are primitive tetragonal (P4nc) and body-centred tetragonal (I4) with nearly identical lattice parameters. The crystallographically imposed C_4 symmetry of the molecule is not preserved in solution, as the ^{31}P NMR spectrum exhibits three resonances in an AM_2X pattern at room temperature in highly polar solvents (acetone, CD_3CN or DMSO) and at low temperature in low polarity solvents (CD_2Cl_2, $CDCl_3$ or C_6D_6).



(33)

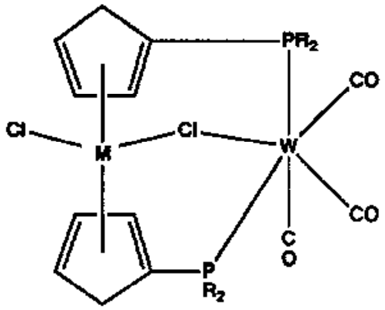
Reactions of [$CpW(CO)_3(PPh_2)$] with the electron-deficient alkynes methylpropiolate and dimethylacetylene dicarboxylate form the metallacyclic complexes (34) (R = H, CO_2Me; R' = CO_2Me) [66]. The mechanism of ring formation appears to involve initial nucleophilic attack of the alkyne on the coordinated phosphide followed by attack of a coordinated carbonyl on the other end of the alkyne, thereby giving rise to a five-membered ring.



(34)

The reaction of [$W(CO)_3(RCN)_3$] (R = Me, Et) with *cyclo*-P_5^- in DMF at 155°C proceeds with the formation of [$(\eta^5\text{-}P_5)W(CO)_3]^-$, one of only a few examples of a mixed carbonyl-pentaphosphacyclopentadienyl metal complex [67]. The species further reacts with Me_3SiCl to form the neutral species [$Me_3Si(\eta^5\text{-}P_5)W(CO)_3$] which was characterized by IR, ^{13}C and ^{31}P NMR spectroscopies.

Reactions of [$MCl_2(C_5H_4PR_2)_2$] (M = Ti, Zr; R = Ph, *p*-tol) with [(cht)$W(CO)_3$] give rise to heterodinuclear products (**35**) in which the two phosphines and one of the chlorine atoms bridge the two metal centres [68]. Addition of CO or $P(OMe)_3$ (irreversible) or MeCN (reversible) breaks the W-Cl interaction but leaves intact the two phosphine interactions. Reaction of (**35**) with KO^tBu leads to clean substitution of the non-bridging chloride. Reaction with two equivalents of $[SMe]^-$ replaces both chloride ligands.



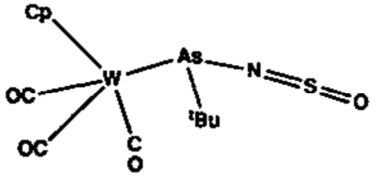
(35)

$W(CO)_6$ reacts with the chelating phosphine $PhP(C_2H_4PPh_2)_2$ in *n*-decane to yield the *mer* complex [(*P,P,P*)$W(CO)_3$] as determined by X-ray crystallography [69].

Thermal reaction of $Me_2Si[Cp'W(CO)_3]_2$ with P_2Me_4 and As_2Me_4 promotes oxidative coupling to give products with two bridging EMe_2 groups [70]. In addition, the P_2Me_4 reaction produces a by-product with one PMe_2 bridge and one hydride bridge, a molecule that is fluxional in solution due to exchange of the bridging groups via formation of the $HPMe_2$ ligand. Reaction of this by-product with additional P_2Me_4 yields the diphosphide-bridged complex along with free $HPMe_2$.

Chemistry of AsX_3, $^tBu_{3-n}AsCl_n$ and $Ph_{3-n}AsCl_n$ with thionylimides (NSO^-) has resulted in the synthesis of a series of arsenic thionylimides $R_{3-n}As(NSO)_n$ (n = 1, 2, 3) [71]. Reactions of these compounds, most of which are very moisture-sensitive oils, with [$CpW(CO)_3H$] produce species containing W-As bonds (**36**).

The trinuclear cluster $Bi[Cp'W(CO)_3]_3$ has been reported as the initial product in the reaction between $ClBi[Cp'W(CO)_3]_2$ and $Na[Cp'W(CO)_3]$. It was found, however, that exposure of this product to UV light yields (**37**), which has a butterfly arrangement of metal atoms, where the (μ-Bi_2) group is formally behaving as a four-electron donor [72]. This bonding description is supported by comparative extended Hückel calculations for (37) and the similar compound [$Mo_2(CO)_4Cp_2(\mu$-η^2-$P_2)$].



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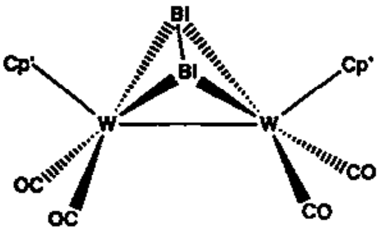


(37)

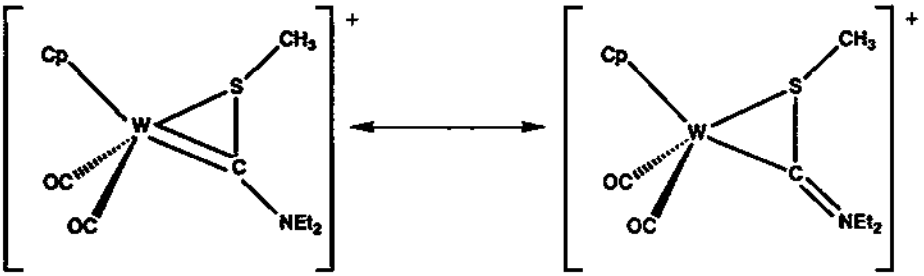
3.6.3 Complexes with group 16 (S and Te) donor ligands

Irradiation with UV light greatly accelerates the reaction between [$W(CO)_5(CH_3)$]$^-$ and CS_2 to yield [$W(CO)_4(\eta^2$-$S_2CCH_3)$]$^-$ [73]. The mechanism is thought to proceed by W-CH_3 homolysis and not by CO photodissociation, since an analogous reaction of [$W(CO)_5(CH_3)$]$^-$ with CH_2Cl_2 in thf quantitatively yields [$W(CO)_5Cl$]$^-$. The methyltungsten anion does not react photochemically with CO_2 to produce the tetracarbonylacetate complex as expected, but instead yields the tetracarbonylformate species, [$W(CO)_4(\eta^2$-$O_2CH)$], as indicated by NMR studies (^1H: δ +7.90; ^{13}C δ +168.8 [O_2CH], δ +201.4 [CO_{cis}], δ +206.5 [CO_{trans}]).

The reaction of [$CpW(CO)_2(CNEt_2)$) with dimethyl(methylthio)sulfonium tetrafluoroborate yields the tungstenthiacyclopropene cation (38) [74]. The presence of the two resonance forms of (38), one of which utilizes the nitrogen lone pair, reduces the carbene-like character of the carbon and hinders further nucleophilic attack.

Reaction of (38) with PMe_3 occurs with substitution of a carbonyl ligand. This product can also be formed in the reaction of [$CpW(CO)(PMe_3)(CR)$] with dimethyl(methylthio)sulfonium [75]. Additional PMe_3 causes attack at the carbene carbon to give a ylide.

Insertion of tellurium into a W-C bond to form [(CO)$_5$W(Te=CHPh)] results from the reaction of [(PhHC=)W(CO)$_5$] with tellurocyanate [TeCN]$^-$ [76]. Upon thermolysis, the Te=C bond further donates to a second W(CO)$_5$ unit. The compound [(CO)$_5$W(Te=CHPh)] also adds 2,3-dimethyl-1,3-butadiene or CpH to form tungsten complexes ligated by tellurium substituted rings that result from Diels-Alder reactions between the incoming diene and the Te=C bond.

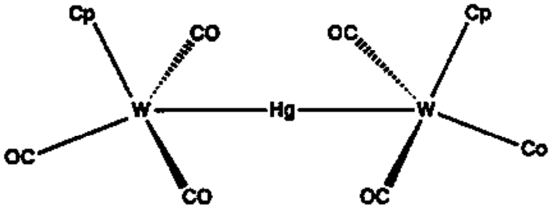


(38)

3.6.4 *Complexes with metallic (Sn and Hg) donor ligands*

The reagent BuSnCl$_3$ has been found to react with [W(CO)$_3$(EtCN)$_3$] to form [W(CO)$_3$(EtCN)$_2$(SnCl$_2$Bu)Cl] [77]. Further reaction with three equivalents of P(OR)$_3$ (R=Me, Et) leads to the formation of [W(CO)$_2${P(OR)$_3$}$_3$(SnCl$_2$Bu)Cl]. The complexes were characterized by IR, ^{1}H and ^{31}P NMR spectroscopy.

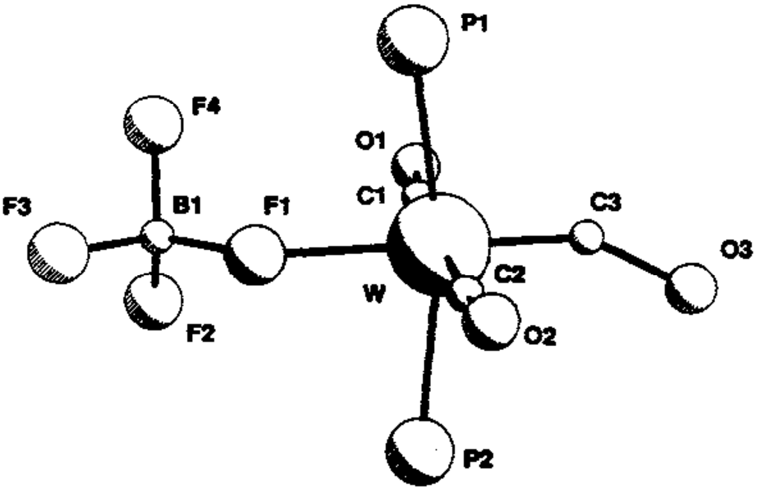
Chemistry of Na[CpW(CO)$_3$] and Na[(CH$_3$C{O}C$_5$H$_4$)W(CO)$_3$] with MeHgCl produces trimetallic clusters (39) [78]. An X-ray crystallographic analysis of (39) showed a nearly linear W-Hg-W angle (173.69(2)°) and a W-Hg bond distance of 2.7513(3) Å.



(39)

3.6.5. *Complexes with mixed donor atom ligands*

Protonation of $[W(CO)_3(PCy_3)_2]$ with $HBF_4{\cdot}Et_2O$ in toluene yields $[WH(BF_4)(CO)_3(PCy_3)_2]$ **(40)**, where the $[BF_4]^-$ anion assumes an η^1-coordination mode [79]. Other acids employed (e.g. HO_3SCF_3, $H_2C[SO_2CF_3]_2$, and $HCl{\cdot}Et_2O$) also lead to coordination of the conjugate base following protonation. The overall protonation reaction of the sixteen electron precursor appears to be initiated by proton transfer, and not by coordination of the lone pair of the conjugate base.

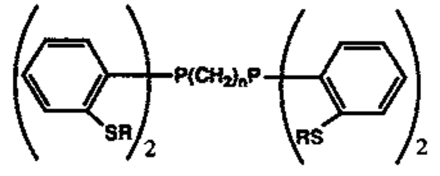


(40)

Dihydrogen can become an extremely strong acid upon coordination to certain transition metal centres. Reaction of $[W(N_2)_2(dppe)_2]$ with two equivalents of $[CpRu(\eta^2\text{-}H_2)(Ph_2PCH_2CH_2P\{p\text{-}CF_3C_6H_4\}_2]BF_4$ produces $[W(NNH_2)(F)(dppe)_2]^+$, which contains a fluoride ligand that was abstracted from $[BF_4]^-$ [80].

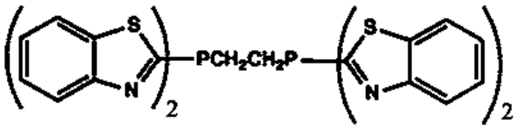
Reactions of $[W(CO)_3(py)_3]$ with a series of uninegative chelating donor ligands and PR_3 yield complexes of the form $[W(X, Y)(CO)_3(PR_3)]^-$ (X,Y=$S_2COC_2H_5$, 2-picolinate, 2-Spy, and 2-carboxynaphthalene; R=Ph, CH_2CH_2CN) [81]. The complexes were isolated only by adding a solution of the carbonyl complex in acetone or CH_2Cl_2 to a solution or suspension of the (X, Y) donor ligand and the phosphine in the same solvent. The complexes decompose gradually even at low temperature and in the absence of light. Characterization was afforded by IR as well as ^1H, ^{13}C and ^{31}P NMR studies.

Various functionalized diphosphines react with $[W(CO)_3(MeCN)_3]$ to produce dinuclear species wherein the functionalized side groups are coordinated to the metal centre [82]. The series of ligands and their abbreviations are given in (**41**). A crystallographic investigation of $[\{W(CO)_3\}_2(\mu\text{-mtppe})]$ indicates that each tungsten is coordinated to two sulfur atoms, one phosphorus atom and three carbonyls; the ethylene bridge of mtppe joins the two mononuclear centres. In addition to X-ray data, IR and ^1H and $^{31}P\{^1H\}$ NMR data are also presented.



n=1, R=Me; mtppm
n=2, R=Me; mtppe
n=2, R=^{i}Pr; iptppe

$(Ph_2PH_2C)_2PCH_2CH_2P(CH_2PPh_2)_2$ dppmpe



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(41)

3.7 SELECTED CLUSTERS

3.7.1 Polyoxotungstates

The anion $[W_{10}O_{32}]^{4-}$ is believed to effect the aerobic photooxidation of saturated hydrocarbons, notably branched hydrocarbons with tertiary carbon atoms [83}. *P*-xylene is oxidized to toluic acid in UV light in the presence of an acetonitrile solution of the polyoxoanion. It was found that $[W_6O_{19}]^{2-}$ and $[VW_5O_{19}]^{3-}$ are inactive under the same conditions.

Addition of vanadium to divalent γ-$[HSiW_{10}O_{36}]^{7-}$ produces γ-$[SiV_2W_{10}O_{40}]^{6-}$, which isomerizes in H_2O to produce three different isomers all having the β structure [84]. The two vanadium atoms are in positions (8,12), (3,12) and (3,8), respectively in the three isomers, as shown by IR and ^{183}W, ^{51}V and ^{29}Si NMR spectroscopies. The formation of the isomers is pH-dependent.

The cobalt-containing polyoxotungstate α-$[CoW_{12}O_{40}]^{6-}$ is reduced by two electrons to produce the "heteropoly blue" complex α-$[CoW_{12}O_{40}]^{8-}$, named for its intense blue color that arises from the delocalization of electrons in the reduced species [85]. Except for a slight shortening of the Co-O distances and lengthening of the corresponding W-O distances, there is very little change in the molecular parameters of the two complexes.

Polyoxotungstate anions have been synthesized with technetium incorporated into the structure. Reaction of $[TcOCl_4]^-$ with $[H_3PW_{11}O_{39}]^{4-}$ in acetonitrile results in the formation of $[PW_{11}TcO_{40}]^{4-}$ [86]. Reaction of $TcO(ethanediolate)_2^-$ with $[SiW_{11}O_{39}]^{8-}$ in buffered H_2O (pH 5.5) produces $[SiW_{11}TcO_{40}]^{5-}$. $TcNCl_4^-$ reacts with $[H_3PW_{11}O_{39}]^{4-}$ in acetonitrile to yield $[PW_{11}TcNO_{39}]^{4-}$. Characterization of the anions was based primarily on the results of negative ion FAB mass spectroscopy.

3.7.2 Complete and incomplete cubanes

Room temperature reaction of PEt_3 with $W_3S_7Br_4$ in thf produces $[W_3(\mu_3\text{-}S)(\mu\text{-}S)_3Br_4(PEt_3)_3(OPEt_2H)(H_2O)\cdot 2thf$ [87]. X-ray crystallographic analysis of the cluster reveals a $W\text{-}W_{ave}$ distance of 2.774(6)Å. The formation of the $OPEt_2H$ ligand is explained as follows: (a) PEt_3 is oxidized by adventitious oxygen to $OPEt_3$; (b) the phosphine oxide coordinates to one of the tungsten centres; (c) the tungsten centre inserts into a C-H bond of the β-carbon of one of the ethyl groups of the phosphine oxide, forming a five-membered ring and a hydride; and finally (d) ethylene is eliminated and the hydride ligand then adds to the phosphorus.

The reaction of arsenous anhydride and WO_3 leads to formation of $Na_3[As_3W_3O_{15}]\cdot 10H_2O$ [88]. The incomplete cubane contains a linear $As_3O_7^{5-}$ group, the first of its kind to be isolated.

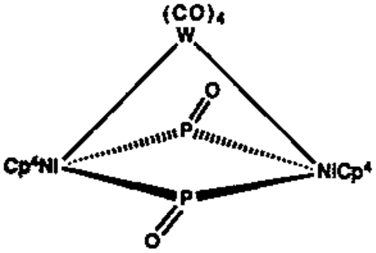
A large number of complete and incomplete cubanes are formed from the reactions of tungsten-containing complexes with group 11 metals (specifically copper and gold). The reader is referred to selected articles [89-93].

3.7.3 Other homo- and heteronuclear clusters

Tetranuclear clusters of tungsten have been prepared by the use of linking reagents to connect dinuclear clusters of tungsten in both a parallel and a perpendicular fashion [94]. By employing either dinuclear tetracarboxylate complexes with organic dicarboxylic acids or dinuclear tricarboxylate solvated complexes with bridging groups (*e.g.* oxalate), one can form not only tetranuclear clusters but polymeric chains of dinuclear species. The tetranuclear clusters are yellow to blue in color, whereas the polymer chains are much more intense in hue, with noticeable red-shifting of their electronic transitions as compared to the M_4 species. An MO consideration of the bonding in these clusters is presented.

The reaction of $[Cp^4{}_2Ni_2(\mu\text{-}\eta^{2:2}\text{-}P_2)]$ $(Cp^4{=}C_5H^iPr_4)$ with $W(CO)_5(thf)$ forms a trinuclear cluster of the type $[Cp^4{}_2Ni_2(\mu_3\text{-}\eta^{2:2:2}\text{-}P_2)W(CO)_4]$ [95]. Reaction of this complex with bis(trimethylsilyl)peroxide yields (**42**), the first complex reported which contains the PO group as a ligand. The complex was characterized by X-ray crystallography as well as by ^{31}P $\{^1H\}$ NMR and IR spectroscopies.

The reaction of $PbCl_2$ with $(NH_4)_2WSe_4$ in the presence of PPh_4Br yields the hexanuclear cluster $(PPh_4)_4[Pb_2(WSe_4)_4]$ (**43**) [95]. The complex can best be described as two octahedrally ligated Pb centres bonded to six selenium atoms, two of which bridge the two lead atoms and one tungsten, while the other four selenium atoms bridge the lead and one tungsten atom. The four tungsten centres are in tetrahedral geometries. Two of the tungsten atoms are bonded to one triply-bridging selenium, two doubly-bridging selenium atoms and one terminal selenium whereas the other two tungsten centres are bonded to two bridging selenium and two terminal selenium atoms.



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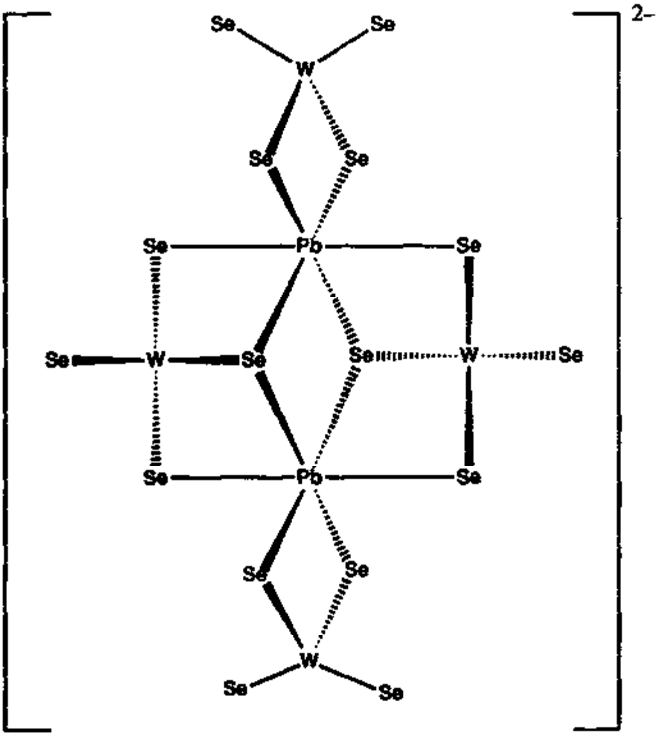

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