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# 8. TUNGSTEN

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CONTENTS

The period of this review coincides with the coverage of Vols. 90 and 91 of Chemical Abstracts. Thus the majority of the papers cited were published in 1979, although some from 1978 are included. The review concentrates upon aspects which are normally associated with the coordination chemistry of tungsten, and papers dealing primarily with organometallic aspects have not been included. Most of the work reported concerns tungsten(VI), metal—metal bonded systems, and tungsten in oxidation states less than two. There are relatively few reports concerning the chemistry of the oxidation states two to five inclusive.

## 8.1 TUNGSTEN(VI)

### *8.1.1 Tungstates(VI), iso- and hetero-polytungstates(VI) and tungsten bronzes*

The reaction between tungsten(VI) oxide and certain bases has been reported; with liquid ammonia the previously unreported $[NH_4]_2[W_2O_7]$ was formed, whilst with piperidine five different compounds were isolated. Two of these latter compounds were shown to contain the heptatungstate anion, $[W_7O_{24}]^{6-}$ and the isolation of $[Bu_3NH]_5[H_3W_{12}O_{40}]$ was also reported [1]. The interactions between aqueous cadmium nitrate and sodium tungstate(VI) solutions, with different acidities and cadmium concentrations ($X = [H^+]/$

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$[Cd^{2+}]$ = 0.1—1.6) and with 0.1 M < $[Cd^{2+}]$ < 0.4 M, have been reported. At low $[Cd^{2+}]$ and $X < 1$, mixtures of ortho- and para-tungstates were formed; with $[Cd^{2+}] \geqslant 0.3$ M, and $X \leqslant 1$, $Cd(WO_4) \cdot 6\ H_2O$ formed, but with $X = 1.17$ the paratungstate $Cd_5[W_{12}O_{38}(HO_2)_2] \cdot 5\ H_2O$ was produced and the metatungstate $Cd_3[W_{12}O_{36}(HO_2)_2] \cdot 3\ H_2O$ was obtained when $X \geqslant 1.5$ [2]. The single crystal unit cell parameters have been reported for the thermally unstable compounds $K_4Mg(WO_4)_3$, $K_2Mg(WO_4)_2$ and $K_2Mg_2(WO_4)_3$ [3]. Powder X-ray diffraction and IR techniques have been used to demonstrate the formation of α- and β-phases of both $Ag_2WO_4$ and $Ag_2W_2O_7$, but only a single phase for $Ag_2W_4O_{13}$ [4].

The oxidation of an aqueous solution of sodium tungstate(VI) and manganese(II) sulphate with $K_2[S_2O_8]$ leads to the isolation of $Na_2K_6[MnW_6O_{24}] \cdot 12\ H_2O$, the crystal structure of which has been determined [5]. The reaction of $Na_2GeO_3$, $Na_2WO_4 \cdot 2\ H_2O$, $WO_3$ and $NaVO_3$, in aqueous solution in the ratios 1 : 5 : 5 : 3.5, in the presence of sulphuric acid, has resulted in the formation of the heteropoly acid $GeV_2W_{10}O_{37} \cdot n\ H_2O$ [6]. Based on IR and Raman spectra, the structures of the anions $[MW_{10}O_{36}]^{n-}$ (where $n = 8$ or 9; M = a tri- or tetra-positive lanthanide or actinide ion) have been shown to be the same in both solution and solid states [7]. In aqueous solution at pH 7, sodium silicate and sodium tungstate(VI) react to form both the α- and β-isomers of the anion $[SiW_{11}O_{39}]^{8-}$ [8]. These anions react further with chromium(III) in aqueous solution at pH 5.5 to give the α- and β-isomers of $[SiCrW_{11}O_{39}(H_2O)]^{5-}$. Each of these anions was characterised by IR and visible absorption spectroscopy. The behaviour of $K_{10}[U(PW_{11}O_{39})_2] \cdot 22\ H_2O$ between 20 and 800°C has been studied by thermogravimetric analysis, differential thermal analysis, and X-ray and IR analyses of the products. Between 45 and 165°C seventeen zeolitic water molecules were lost, followed by four further similar water molecules in the range 165—325°C. The loss of the final non-zeolitic water molecule, in the temperature range 325—480°C, was accompanied by the formation of a new crystalline phase [9].

Several members of the new classes of substituted polytungstate(VI) anions of the general formulae $[X(RM)W_{11}O_{39}]^{n-}$ (where X = P, Si, Ge or B; RM = MeSn, BuSn, PhGe or PhPb) and $[X_2(RM)W_{17}O_{61}]^{6-}$ (where X = P or As) have been reported. The anion closely resembles the related trivalent metal ion containing heteropolytungstates [10]. The $^{31}P$ NMR spectra of the anions $[P_2W_{17}O_{61}]^{10-}$, $[M(P_2W_{17}O_{61})_2]^{16-}$ (where M = Th, U or Ce) and of $[Ce(P_2W_{17}O_{61})_2]^{17-}$ indicate that these latter types of anion exist in aqueous solution in only one isomeric form [11]. The preparation and crystal structure of the compound $[NH_4]_7[H_2AsW_{18}O_{60}] \cdot 16\ H_2O$ has been reported. The anion consists of two $\{XW_9O_{33}\}$ units which share six oxygen atoms; one such unit contained an arsenic(III) atom with its lone pair directed towards the other unit. $^1H$ NMR studies have shown that the second unit contained two non-titratable protons within the structure [12]. A new hexagonal form of tungsten(VI) oxide has been identified in which slightly distorted $WO_6$ octahedra share corners. This results in six-membered rings stacked in layers normal to the hexagonal axis giving large hexagonal tunnels [13].

From single-crystal X-ray diffraction studies of crystals of ten different compositions in the $In_xWO_3$ bronze series (where $0.12 < x < 0.33$), it has been concluded that the off-centre tungsten atoms tend towards regular octahedral geometry as the amount of indium increases [14]. New phases $(Li_2O)_{1-x}U_{1.4}W_{4.6}O_{18}$ and $(Cu_2O)_{1-x}U_{1.4}M_{4.6}O_{18}$ (where $0 < x < 0.4$; M = Mo or W) have been identified [15]; by comparison with $K_{0.33}WO_3$, it was shown that they possessed an ordered hexagonal bronze-type structure [15]. Reviews of the structural background to non-stoicheiometry in tungsten-containing oxides and bronzes [16] and of alkali—metal tungsten bronzes [17] have appeared.

### *8.1.2 Monomeric compounds*

The reaction of $WOF_4$ with acetoxime yields the anions $[WOF(ON{=}CMe_2)_2]^-$ and $[W_2O_2F_7(ON{=}CMe_2)_2]^-$, in which the acetoxime acts as a bidentate ligand [18]. The compounds $[Et_4N][WO_2F_3L]$ (where L is a phosphine oxide or pyridine-*N*-oxide) have been isolated and characterised. Variable temperature $^1H$, $^{19}F$ and $^{31}P$ NMR studies in $ClCH_2CN$ solution show that ligands *trans* to the oxo-group dissociate rapidly on the NMR time scale; new species form on ageing the solutions at 80°C, $[WO_2F_2L_2]$ being predominant [19]. The exchange of halide ligands between $WSF_4$ and $WXCl_4$ (where X = O or S) in ethanenitrile solution has been studied using $^{19}F$ NMR spectroscopy. When X = O, there is an almost equal distribution of fluoride between the oxo and sulphido species, but for X = S the formation of $WSF_{4-n}Cl_n$ is unfavourable [20]. Electron impact excitation spectra of $WF_6$ have been obtained in the impact energy range 30—75 eV and at scattering angles from 5 to 80°. Four transitions were found at 7.25, 7.90, 8.50 and 9.85 eV, in agreement with optical spectroscopy, plus three previously unreported features at 11.75, 12.60 and 13.50 eV. All the transitions were assigned to fluorine to tungsten-5*d* orbital charge transfer excitations [21].

Reactions between tungsten(VI) oxide and tungsten(V) chloride have been studied; below 200°C, the equilibrium (1) was observed, whilst above 350°C the equilibrium (2) was established [22].

$$WO_3 + 2\ WCl_5 \rightleftharpoons 2\ WOCl_3 + WOCl_4 \qquad (1)$$

$$WO_3 + 2\ WCl_5 \rightleftharpoons 2\ WOCl_4 + WOCl_2 \qquad (2)$$

Reaction between tungsten(VI) chloride and phenol at 180—200°C, for 10—12 h has resulted in the formation of $[W(OPh)_6]$ [23]. The reduction of tungsten(VI) by bromide ions, to give tungsten(V) and eventually tungsten(III), has been studied polarographically, coulometrically and spectrophotometrically; the results of this study have been used as the basis of a method of quantitative analysis [24]. The formation of complexes between tungsten(VI) and tartaric or malic acids has been studied polarimetrically [25]. The kinetics of the decomplexation reaction (3) (where M = Mo or W, and L = iminodiacetate, ethylenediamine-*N,N'*-diacetate, nitrilotriacetate or ethylenediamine-*N,N,N',N'*-tetracetate) have been interpreted in terms of the rate of cleavage of the metal—nitrogen bond being the key process [26].

$$[MO_3L]^{n-} + 2[OH]^- \rightarrow [MO_4]^{2-} + L^{n-} + H_2O \qquad (3)$$

### *8.1.3 Tungsten—metal—sulphur cluster compounds*

Thiotungstate anions have been used in the preparation of interesting cluster compounds. Thus, $[WS_4]^{2-}$ was used as a reagent in the preparation of $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$, in which two $\{Fe_3WS_4\}$ cubane-like entities are bridged by three methoxy groups between the tungsten atoms [27]. The reaction of $Cs_2[WOS_3]$ with $CuCl_2 \cdot 2\ H_2O$ and $PPh_3$ has resulted in the isolation of $[(WOS_3)(CuPPh_3)_3Cl]$; a crystal structure determination of this compound has shown it to consist of an approximate tetrahedral $\{WOS_3\}$ unit with $\{CuPPh_3\}$ groups bridging each of the sulphur—sulphur edges and with chloride bridges between all three copper atoms [28]. In a similar preparation using $[PPh_3Me]_2[WO_2S_2]$, CuCl and P(4-tolyl)$_3$, two compounds, $[\{(C_7H_7)_3P\}_4Cu_4W_2S_8]$ and $[\{(C_7H_7)_3P\}_4Cu_4W_2O_2S_6]$ were isolated [29]. An X-ray crystal structure of the second of these compounds showed that it involved two approximately tetrahedral $\{WOS_3\}$ units bridged on adjacent edges by $\{(C_7H_7)_3PCu\}$ groups.

## 8.2 TUNGSTEN(V)

The isolation of paramagnetic and monomeric complexes of the type [WOXL] (where $H_2L$ = a substituted porphyrin; X = OH, OMe or $H_2O$) has been accomplished by reacting a slight stoicheiometric excess of $[W(CO)_6]$ with $H_2L$ in refluxing dimethylmethanamide [30,31]; the compounds were characterised using magnetic susceptibility, IR, EPR and electronic absorption spectral measurements. Stable dimeric alkoxides, $[\{Cl_2W(OR)_3\}_2]$, have been produced by the reaction of $WCl_6$ and $R'CH{=}CH_2CH_2OR$ in monochlorobenzene solution, in the presence of tetramethyltin [32].

An X-ray crystal structure of the paramagnetic mono-adduct of 1,2-bis(methylthio)ethane and $WCl_3S$ has shown that it consists of six coordinate monomers, with a terminal sulphido-group [33]. The W—S (terminal) separation of 2.146(11) Å is reported to be longer than that in $WSCl_4$, and reflects an increase in the ionic radius of tungsten(V) as compared to tungsten(VI). The terminal sulphido-group also exerts a significant *trans* effect, which is reflected in the longer W—S (ligand) distance (2.668 Å) *trans* to this group as compared to the corresponding distance (2.560 Å) to the *cis* ligand. The product of the reaction between $WCl_3Se$ and $[AsPh_4]Cl$ has been shown by X-ray crystallography to be $[AsPh_4]_2[W_2Cl_8Se_3]$; the anion consists of two $WCl_4$ units bridged by three selenium atoms. The tungsten—tungsten separation of 2.862(3) Å is considered to be representative of a single bond distance. In addition to this, two of the bridging selenium atoms are closer together (2.255(8) Å) than they are in $Na_2Se_2$ (2.38(5) Å), indicating that they should probably be regarded as an $[Se_2]^{2-}$ group [34].

## 8.3 TUNGSTEN(IV)

The structure of $WO_2$ has been reported to consist of a monoclinically distorted rutile structure, with alternate tungsten—tungsten separations of 2.475 and 3.095 Å, along the rutile chain [35]. The preparation of the compounds $[WX_4L_2]$ (where X = Cl or Br; L = py or 4-Mepy) has been reported; an X-ray crystal structure determination showed $[WCl_4(py)_2]$ to have a *trans* octahedral structure, with *r*(W—Cl) = 2.347(1) Å and *r*(W—N) = 2.181(4) Å. $[WBr_4(py)_2]$ was reported to be isostructural with the chloro-analogue [36]. The reaction of HX and $[W(NNH_2)X_2(PMe_2Ph)_3]$ (where X = Cl or Br) in tetrahydrofuran, has resulted in the formation of the hydride $[WX_3H(NNH_2)(PMe_2Ph)_3]$. Slow recrystallisation of the chloro-analogue gave $[WCl_3(NNH_2)(PMe_2Ph)_2]$. Crystal structure determinations of this compound and of $[WCl_3(NNHPh)(PMe_2Ph)_2]$, showed that, in both, the hydrazide ligands are essentially planar. This observation is indicative of strong conjugation within the W—N—N moiety [37].

Ligand exchange between $K_4[W(CN)_8]$ and HCN in aqueous sulphuric acid, and between $H_4[W(CN)_8]$ and HCN in aqueous solution, has been studied using radioactively labelled cyanide. The observed enhancement of the rate of ligand exchange in acidic media was explained in terms of a reversible decomposition of the octacyano-complex at low pH but an irreversible decomposition at high pH [38]. The enthalpies of formation of the compounds $K_2[WCl_6]$ and $M_2[WBr_6]$ (where M = K, Rb or Cs) have been determined from their enthalpies of hydrolysis and oxidative hydrolysis. These data were also used to estimate the halide ion affinities of $WX_4$ and the two electron affinities of $WX_6$ (where X = Cl or Br) [39].

The possibility of tungsten(IV) chelate complexes acting as energy transfer agents has been reviewed [40].

## 8.4 TUNGSTEN(III)

The reaction between $[W_2(OCMe_3)_6]$ and two equivalents of nitric oxide in hydrocarbon solvents has resulted in the formation of an insoluble product with the empirical formula $[W(OCMe_3)_3NO]$. From this material the addition compounds $[W(OCMe_3)_3(NO)L]$ (where L = $NH_3$, $NMe_3$ or py) were obtained; an X-ray crystal structure of the compound with L = py showed that these molecules have a distorted trigonal bipyramidal structure, with a linear W—N—O arrangement [41]. The isolation of the compounds $[W\{HB(3,5\text{-}Me_2C_3HN_2)_2(3,5\text{-}Me_2\text{-}4\text{-}BrC_3N_2)\}(NO)XY]$ (where X = Br or σ-alkyl; Y = NHR′; R′ = H, alkyl, $NH_2$, NMe, $NMe_2$, NHPh, $CH_2CH_2NH_2$ or $Me_2CN$) has been reported [42].

## 8.5 TUNGSTEN(II)

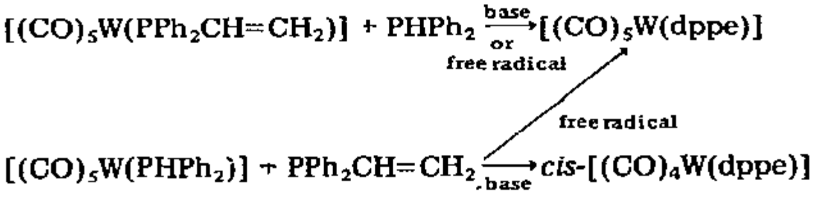
The crystal structure of $[(cp)W\{(CO_2Me)C{=}C(CO_2Me)(\underline{C}O \cdot SMe)\}(CO)_2]$, which was prepared by the reaction between $[(cp)W(SMe)(CO)_3]$ and dimethylacetylene dicarboxylate, showed the tungsten to have square pyramidal coordination with the cp group occupying the apex. The basal coordination consisted of two carbon monoxides, the sulphur atom, and a $\sigma$-bond to the carbon atom $\underline{C}$ [43]. A single crystal structure determination at −140° C of the methyldiazo compound, $[(cp)W(CO)_2(N_2CH_3)]$, showed it to have the expected three-legged stool geometry about the metal atom. Compared to the carbon monoxide group, the $(N_2CH_3)$ group causes a shortening of the essentially *trans* W—C(cp) distance [44].

The geometry about the tungsten atom in the compound $[(Me_3CNC)_3W(CO)_2I_2]$ has been described as a 4 : 3 square-based trigonal-capped piano stool, similar to that found in polyhedral $ZrO_2$ and $YbCl_2$ [45]. Three monomeric diamagnetic seven-coordinate compounds, $[W(CO)_2(PPh_3)(dcq)_2]$, $[W(CO)_3(PPh_3)(dcq)Cl]$, and $[W(CO)_2(PPh_3)_2(dcq)Cl]$ (where dcq = 5,7-dichloro-8-quinolinato) have been isolated from reactions between dcqH and $[W(CO)_3(PPh_3)Cl_2]$ in $CHCl_2/MeOH$ solution under varying conditions [46]. The preparation of $[W(CO)_3(S_2CNMe_2)_2]$ and its intramolecular dynamics, as studied by $^{13}C$ NMR spectroscopy, have been reported. On heating, $[W(CO)_3(S_2CNMe_2)_2]$ undergoes a reversible loss of one CO ligand to give the insoluble blue product $[W(CO)_2(S_2CNMe_2)_2]$ [47].

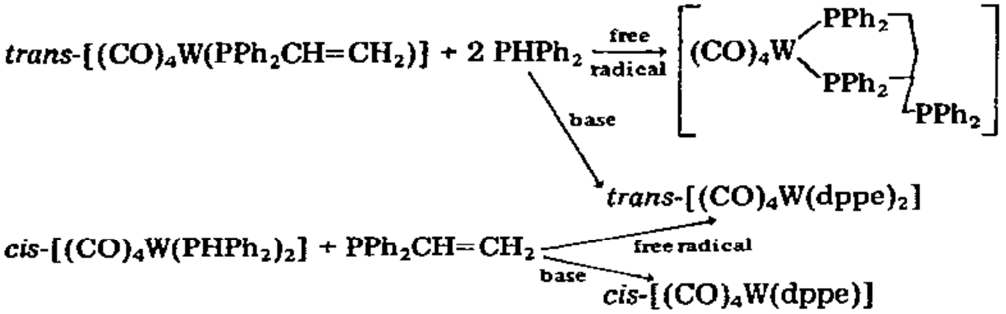
## 8.6 LOW OXIDATION STATE COMPOUNDS

The IR and Raman spectra of *trans*-$[X(CO)_4W{\equiv}C{-}CH_3]$ (where X = Cl, Br or I) and of *trans*-$[Br(CO)_4W{\equiv}C{-}CD_3]$ have been measured; band assignments were made and confirmed by normal coordinate analyses [48].

The conditions under which control may be exercised over the number of phosphorus atoms, of bi- and tri-dentate phosphines, which will coordinate to a metal atom have been investigated. The reactions between $[(CO)_5W(PPh_2CH{=}CH_2)]$ and $[PHPh_2]$, and between $[(CO)_5W(PHPh_2)]$ and $[PPhCH{=}CH_2]$, under both basic and free radical conditions may be summarised in Scheme 1 [49].



$$\begin{tikzcd}
{[(CO)_5W(PPh_2CH{=}CH_2)] + PHPh_2} \arrow[r, "\text{base}", "\text{or free radical}"'] & {[(CO)_5W(dppe)]} \\
{[(CO)_5W(PHPh_2)] + PPh_2CH{=}CH_2} \arrow[r, "\text{base}"'] \arrow[ur, "\text{free radical}"'] & {cis\text{-}[(CO)_4W(dppe)]}
\end{tikzcd}$$



Scheme 1

The preparation of $[(OC)_4M\{MeC(CH_2AsPh_2)_3\}]$ (where M = Mo or W), in which the arsine acts as a bidentate ligand, has been reported to occur in 65—70% yield upon the UV irradiation of $[M(CO)_6]$ and $[MeC(CH_2AsPh_2)_3]$ in ethanenitrile [50]. Tungsten(0) hexacarbonyl has been used in model studies of the metal binding sites of nucleic acid components. Thus, 6-mercaptopurine (L) forms $[W(CO)_5L]$ and $[W(CO)_4L]$ {where L is, respectively, monodentate through sulphur (6) or bidentate through sulphur (6) and nitrogen(7)}. In contrast, 2′,3′-*O*-isopropylideneguanosine (L′) forms only $[W(CO)_5L']$, in which L′ acts as a monodentate ligand [51].

In a $^{13}C$ NMR spectroscopic study of $^{18}O$ enriched $[W(CO)_6]$, an upfield shift of the resonance by 0.04 ppm was observed for $^{18}O$, as compared with $^{16}O$, bound to $^{13}C$ [52]. The electronic absorption and emission spectra of $[L_2W(dppe)_2]$ (where L = $N_2$ or CO) in 2-methyltetrahydrofuran have been reported. The former compound is claimed the first photoluminescent dinitrogen complex; at 77 K excitation at 26 000 $cm^{-1}$ gave an emission spectrum with $\lambda_{max}$ = 17 700 $cm^{-1}$, halfwidth 1500 $cm^{-1}$, and lifetime 19 $\mu s$ [53]. The UV photolysis of $[W(CO)_5L]$ (where L = py, 3-Brpy or $H_2S$) at high dilution in a methane or argon matrix at 10 K resulted in the photo-detachment of L to give $[W(CO)_5]$ and L; subsequent irradiation with visible light regenerated $[W(CO)_5L]$. In a carbon monoxide or a dinitrogen matrix, UV photolysis led to the formation of $[W(CO)_6]$ and $[W(CO)_5(N_2)]$, respectively [54]. Irradiation of the lowest energy electronic transition of $[(\mu\text{-}H)W_2(CO)_{10}]^-$ alone has led to disruption of the dimer whilst in the presence of carbon monoxide, photosubstitution of CO occurred. The quantum efficiencies and probable mechanisms of the processes were reported [55].

The preparation of $[H_4W\{P(OCHMe_2)_3\}]$ from $[H_4W(PPh_2R)_4]$ (where R = Bu or Et) [56], and the X-ray photoelectron spectra [57,58] of $[H_4ML_4]$ (where M = Mo or W; L = $PHPh_2$, $PMePh_2$, $PEtPh_2$, $PBuPh_2$, $PEt_2Ph$, $P(OCHMe_2)_3$ or $\frac{1}{2}$ dppe) complexes have been reported. These photoelectron spectral results were taken to indicate that the tungsten atom has an increased electron density, corresponding to a formal charge of minus two, whereas for molybdenum the formal charge was considered to be zero.

## 8.7 METAL—METAL BONDED COMPOUNDS

### *8.7.1 Homonuclear metal—metal bonds*

At room temperature, in hydrocarbon solvents, $[W_2(NMe_2)_6]$ reacts with $Me_3COH$ or $Me_3SiOH$ to give $[W_2(OCMe_3)_6]$ or $[W_2(OSiMe_3)_6(NHMe_2)_2]$, respectively [59]. Similar reactions involving isopropanol and neopentanol have given products which are thought to be tetrameric in solution. In pyridine solution, the reaction between $[W_2(NMe_2)_6]$ and $Me_2CHOH$ gives $[W_2(OCMe_2H)_6(py)_2]$, the crystal structure of which has revealed a binuclear molecule with a conformation intermediate between staggered and eclipsed, and with a tungsten—tungsten triple bond of length 2.332(1) Å. The reaction of $[W_2(NMe_2)_6]$ and $Me_2CHOH$ has been reported to give the crystallographically characterised tetramer $[W_4H_2(OCMe_2H)_{14}]$ [60]. This tetramer consists of $[W_2(OCMe_2H)_7(\mu\text{-}H)]$ units, associated via $OCMe_2H$ bridges; within these dimer units the tungsten—tungsten separation is 2.446(1) Å. Also, in hydrocarbon solvents, $[W_2(NMe_2)_6]$ has been shown to react with 1,3-diphenyltriazine to yield $[W_2(NMe_2)_4(PhN_3Ph)_2]$. A crystal structure determination showed this dimer to consist of two $[W(NMe_2)_2(PhN_3Ph)]$ units, joined by a tungsten—tungsten triple bond of length 2.314(1) Å, with overall $C_2$ molecular symmetry [61]. The tungsten—tungsten quadruply bonded compound $[W_2(dmhp)_2\{(PhN)_2CCH_3\}_2]$ (where dmhpH = 2,4-dimethyl-6-hydroxypyrimidine) has been obtained from the reaction between $[W_2(dmph)_4]$ and $Li[(PhN)_2CCH_3]$; the W≡W distance is 2.174(1) Å [62].

### *8.7.2 Heteronuclear metal—metal bonds*

IR spectroscopy has been used to confirm the presence of a tungsten to metal bond in the compounds $[NBu_4][(CO)_3(cp)W\text{-}MPh_3]$ (where M = Al or In) [63]. The addition of the nucleophilic compounds $[Pt(C_2H_4)(PMe_2R)_2]$ to mononuclear $[W(CC_6H_4Me\text{-}4)(CO)_2(cp)]$, has resulted in the formation of the tungsten—platinum bonded species $[PtW(\mu CC_6H_4Me\text{-}4)(CO)_2(PMe_2R)_2(cp)]$ [64]. The carbon monoxide bridged dimers $[(cp)_2NbM(CO)_3(cp)]$ (where M = Mo or W) have been formed by the reaction of $[(cp)_2Nb][BH_4]$ and $[(cp)M(CO)_3Me]$ in toluene solution, in the presence of triethylamine [65]. The crystal structure of the molybdenum analogue has been determined, and an Nb—Mo distance of 3.073 Å obtained. A tetrahedral heterometallic core of $\{Os_3W\}$ has been shown to occur in each of the compounds $[(\mu\text{-}H)Os_3W(CO)_{12}(cp)]$ [66] and $[(\mu\text{-}H)_3Os_3W(CO)_{11}(cp)]$ [67] and the locations of the bridging hydrogen atom have been considered.

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