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TUNGSTEN

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CONTENTS

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INTRODUCTION

This article is a review of the tungsten chemistry published in primary research journals during 1982 and/or volumes 96 and 97 of Chemical Abstracts. Previous articles in the series covered the years 1980 and 1981 [1,2]. In general, the material is classified according to oxidation state, however, additional sections dealing with specific areas which overlap several oxidation states are also included.

A review of the chemistry of Mo and W, with 607 references has been published [3]. Molecular orbital calculations, which analyse various interactions in reactions, have been presented. This method is especially suitable for large and strongly interacting systems, where other methods are not practical, since it is able to isolate the particular interaction of interest, from the whole system by a procedure termed the partial diagonalisation of the bond order matrix. The method is exemplified by the adsorption of CO onto Pt and W surfaces [4].

2.1 TUNGSTEN(VI)

2.1.1 *Halides*

$[WF_6]$ reacts with $[B(OTeF_5)_3]$ at 120°C to give $[WF_n(OTeF_5)_{6-n}]$; $[WF_5(OTeF_5)]$ and *cis*-$[WF_4(OTeF_5)_2]$ were isolated and characterised using IR, Raman, and NMR spectroscopy [5]. Reaction of $[WF_6]$ with $NH_4HF_2.nHF$ yields $[NF_4][WF_7]$, which is a crystalline hygroscopic solid, stable in a dynamic vacuum at 125°C [6]. $[WF_6]$ has been used as a fluorinating agent with aliphatic carbonyl or carboxyl derivatives, forming the corresponding difluorides or carbonic acid difluorides [7].

$[WCl_6]$ can be obtained as the final product, when WO_3 is heated with PCl_5 at 122°C [8]. Treatment of $[WCl_6]$ with Cl_3CNO_2 gives $[WOCl_4]$ and $[WO_2Cl_2]$ in practically quantitative yields [9]. The preparation of the complexes $[WCl_6L_4]$ (L = 2 or 4-chlorophenylhydrazine) has been reported and their characterisation by IR, electrical conductiometric, and magnetic moment measurements reported [10].

2.1.2 *Oxocomplexes*

According to ^{19}F NMR data, [WOF_4] reacts with hydroxyacids to form [$WOF_3(HL)$]] (HL = lactic, malic, 2-,3-, 4-hydroxybenzoic, citric or gallic acid). Addition of Et_2NH to these solutions produces [Et_2NH_2][WOF_3L] for most of the hydroxyacids [11]. A new phase with the composition $Na_2[WO_2F_4]$ has been prepared in the Na-W(VI)-O-F system. The lattice is built up by parallel sheets of corner-sharing NaX_6 and WX_6 octahedra (X = O or F) tied together by common edges [12]. New oxo-complexes of W(VI) have been obtained, for example, when W(VI) salts were reacted with $(CF_3SO_2)_2O$ to give $Na_2[WO_2(CF_3SO_3)_4]$ [13]. The prominent IR and UV/visible bands of the complexes [WO_2Cl_2] and [WO_2Br_2], isolated as monomers in low temperature matrices, have been reported and assigned; relative band intensities predict OWO = 107 ± 2° for both molecules [14]. The IR and Raman spectra of a series of salts containing the anion, $[WYCl_5]^-$ (Y = O or S) have been reported and an assignment of the a_1, stretching modes made [15]. [$WOSCl_2$] and [WS_2Cl_2] have been prepared and, on the basis of the IR spectral data and lack of reactivity towards various ligands, it has been suggested that these complexes are polymeric with chlorobridges [16]. The structure of [$W(O)(CHCMe_3)(PMe_3)_2Cl_2$] has been published; the W atom is in a distorted octahedral environment with the PMe_3 ligands *trans* to each other, while the Cl ligands are mutually *cis*. The neopentylidene ligand (W=C = 1.986Å) and the oxo ligand (W=O = 1.697Å) are mutually *cis* with $O\hat{W}C$ = 102.0° [17].

The results of a ^{13}C NMR study of oxotungsten(VI) complexes with aminocarboxylic ligands have suggested that complex formation requires facial, tridentate orientation of the ligand dentates; coordination *via* an hydroxyl group resulted in the loss of the OH proton and the formation of a W_2O_5 core structure [18]. Complexes of tungsten(VI) with aminopropanols have been prepared and characterised by IR and thermal decomposition studies; the complexes identified include: $[W_2O_4(OH)_2L].4H_2O$, $[WO_2L].H_2O$ (L = $BuN(CH_2CH_2OH)_2$), $[W_2O_4(OH)Q].3H_2O$ ($H_3Q = NH_2C(CH_2OH)_3$) and $[WO_2L'].BuOH$ (L' = $NH_2CH_2CH(OH)CH_2OH$) [19]. The stoichiometry of W(VI) tartrates has been investigated by measuring, at constant pH, the variation of optical rotations with concentration. No complexes were formed at pH > 6; at pH < 3 only 1:1 complexes were found and at pH = 6-8 only 1:2 W(VI)-*l*(+)-tataric acid compounds. Between pH 3 to 6 mixtures were obtained. UV spectroscopy and electrophoresis have been used to examine complex formation between W(VI) and chloranilic acid: stoichiometries, formation constants, and spectral properties were determined [21]. Tungstic acid has been reacted with ethanolamines to produce complexes like $[WO_2L].H_2O$ (H_2L = diethanolamine), $[WO_2(HL')]$ (H_3L' = triethanolamine), and $[HQ][WO_3(HQ)]$ (HQ = ethanolamine) [22,23].

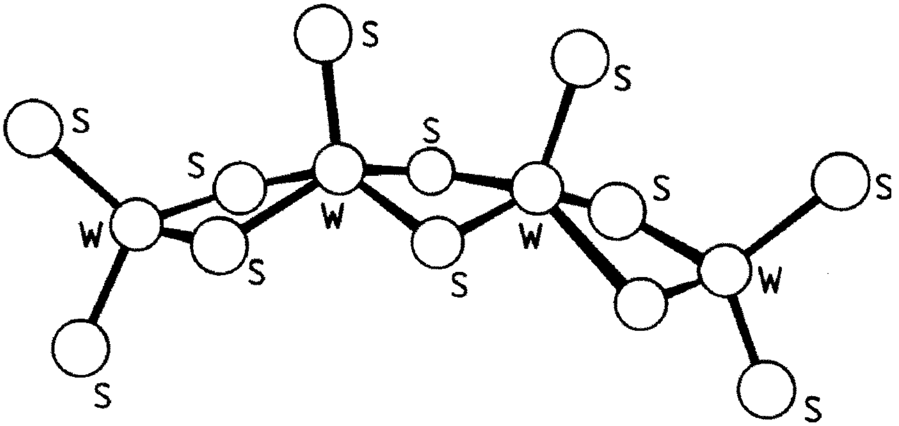
2.1.3 *Oxides, sulphides, and homonuclear polyanions*

A review, with 11 references, dealing with the chemical structure of tungsten oxides has appeared [24].

Irradiation, with visible light, of aqueous dispersions of WO_3 in NaCl generates Cl_2 [25]. Similar illumination of polycrystalline WO_3 electrodes in acid hydrogen sulphate solution has produced peroxodisulphate with 85% current efficiency [26]. Heating $K_2[WO_4]$ *in vacuo* and condensation of the product in a low temperature matrix produces a molecular species and IR studies, including ^{18}O enrichment, have shown possesses D_{2d} symmetry [27]. The structure of indium tungstate, In_6WO_{12} has been reported; it is a fluorite superstructure in which the oxygen vacancies are paired around the W atoms [28]. The polymorphism of $Ag_2[WO_4]$ has been described [29]. Formation of the compounds $[RNH_3]_2[WO_4]$, by the reaction of alcoholic RNH_2 (R = dodecyl, tetradecyl, or octadecyl) with aqueous $Na_2[WO_4]$ has been reported, supported by IR spectral, conductiometric, and thermal analytical data [30]. Several new forms of tungstic acid have been described; these include a highly photochromic form, $WO_3.0.75H_2O$ [31] and a white form. $WO_3.nH_2O$ ($2.42<n<2.78$) [32].

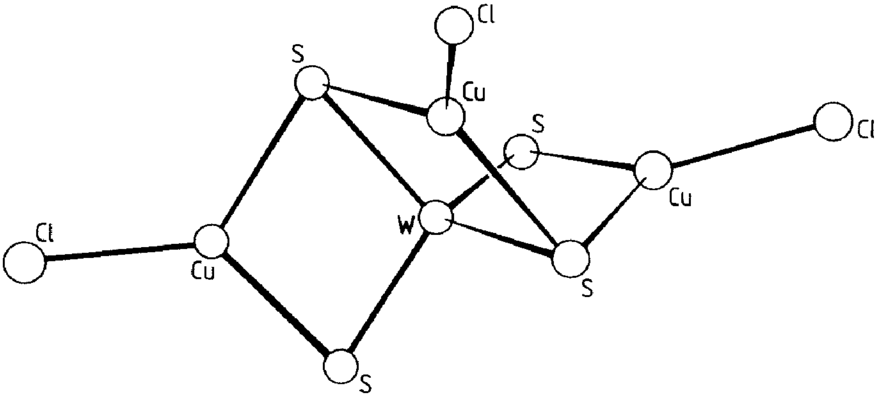
The reaction between Hg^{2+} and $[WS_4]^{2-}$ ions has been studied by means of direct and reverse pH and conductiometric titrations in aqueous and aqueous-alcoholic solutions. These studies have shown that, at pH 4.5, $Hg[WS_4]$ is precipitated almost quantitatively [33]. $[Bu_4N]_2[NiL(WS_4)]$ (H_2L =

$(CN)_2C{:}C(SH)_2$) has been prepared by heating $[Bu_4N][NiL_2]$ and $[NH_4]_2[WS_4]$ under reflux and characterised using IR and UV/visible spectroscopy and electrical conductance measurements [34]. $[NH_4]_2[WS_4]$ has been reacted with $CuSO_4.5H_2O$ to give $[Cu(WS_4)_2]^{3-}$ which was isolated as its $[Et_4N][PNP]_2$ salt (PNP = $Ph_3P{=}\overset{+}{N}{=}PPh_3$) and a similar cobalt compound, $[Et_4N][PNP]_2[Co(WS_4)_2].2MeCN$, has been obtained by the reduction of $[PNP]_2[Co(WS_4)_2]$ with $[BH_4]^-$ in acetonitrile in the presence of $[Et_4N]Cl$ [35]. The crystal and molecular structures $[Ph_4P]_2[(WS_4)WS(WS_4)]$ and $Cs_4[(WS_4)WS(WS_4)].2H_2O$ have been reported. These anions may be regarded as coordination compounds of WS^{2+} containing two $WS_4{}^{2-}$ ligands [36]. $[Ph_4As]_2[(W_2S_4)(WS_4)_2]$, the first tungsten compound containing a $W_2S_4{}^{2+}$ core has been prepared by acidification of $[WS_4]^{2-}$ with acetic acid in an anhydrous medium. Each W atom in the central $W_2S_4{}^{2+}$ core has a tetragonal sulphur environment, the apex of each pyramid being occupied by a sulphido group and the equatorial planes being formed by bridging sulphido groups and S atoms of a $WS_4{}^{2-}$ ligand (1) [37].



(1)

IR, electronic, and ESR spectroscopy and cyclic voltammetry have been used to identify the products of the reaction between $[Et_4N]_2[FeL_2]$ (H_2L = *o*-xylyl-α,α'-dithiol) and $[Et_4N]_2[WS_4]$ in CH_2Cl_2. The products, $[Et_4N]_2[L_2(\mu\text{-}S)_2WS_2]$ undergo pseudo-reversible reductions [38]. Reaction of $[Ph_4P]_2[WS_4]$ with CuCl in acetonitrile gives $[Ph_4P]_2[Cu_3WS_4Cl_3]$, which has been shown by X-ray analysis to contain a new type of cluster compound involving one W atom and 3 Cu atoms bridged by sulphido ligands (2) [39].



(2)

IR and UV/visible spectroscopy, cyclic voltammetry, and magnetic moment measurements have been used to characterise the products of the reaction between $Ni(NO_3)_2.6H_2O$ or $CoSO_4.7H_2O$, $[Ph_4P]Cl$ and $[NH_4]_2[WO_2S_2]$ in aqueous solution. The products identified were $[Ph_4P]_2[M'(WO_2S_2)_2]$ (M'=Ni or Co) [40]. In the anion of the compound $[Ph_4P][W_2S_8(OH)_3]$, one W atom has a very distorted octahedral coordination to 6 S atoms and the other W atom is in a very distorted tetragonal pyramid with 4 S atoms forming the base and the apex occupied by an oxo ligand. Both S^{2-} and S_2^{2-} ligands are present, one of the S_2^{2-} ligands acts as a bridging and chelate ligand [41].

The preparation of the isopolytungstate $[LH_4][W_{12}O_{40}].H_2O$ from the reaction of ethylenedibiguamide dihydrogensulphate ($L.2H_2SO_4$) with W ions in acid solution has been described [42]. The crystal structure of $Na_2Zr[W_3O_{12}]$ has been determined and it consists of zig-zag ribbons of edge-linked WO_6 octahedrons joined to NaO_6 and ZrO_6 octahedra with a WO_4 tetrahedron and a 7-coordinate Na polyhedra. Thus, the structure has the actual formula $Na_2Zr[W_2O_8(WO_4)]$ [43].

2.1.4 *Heteropolyanions and ternary phases*

^{183}W NMR studies of heteropoly- and isopolytungstates have sought to explain the observed chemical shifts in terms of: (1) the availability of paramagnetic contributions from low lying excited states and (2) the degree of electronic anisotropy at the sites of respective W atoms. Inductive charge variation on the W atoms was found to be an insignificant factor [44]. The preparation and characterisation, by electronic adsorption spectra and chemical analysis, of the compounds $Q_6[H_4W_{12}O_{41}]$ (QCl = parafuschine), $Q'_{10}[W_{12}O_{41}]$ (Q'Cl = crystal violet) and $Q''[W_{12}O_{41}]$ (Q"Cl = malachite green) has been reported [45]. The conditions for obtaining paratungstates formulated as $[(Ln_2OH)_2[W_{12}O_{40}(OH)_2(H_2O)_8](H_2O)_{16}](H_2O)_{10}.(H_2O)$ (Ln = La or Nd) have been published and the materials characterised using IR and ^1H NMR spectroscopy, X-ray diffraction, crystal optical methods, and thermal analysis [46]. The heteropolytungstate $[LH_2]_3[H_2W_{12}O_{40}]$ (L = phenylbiguanide) has been precipitated, from acid solutions containing phenylbiguanide hydrochloride, and identified by chemical analysis, IR spectroscopy, X-ray diffraction, and thermogravimetry, [47]. Several papers have been published concerning 12-tungstophosphates, these include the preparation and properties of neodynium 12-tungstophosphate, $NaH_3[PW_{12}O_{40}]_2.47.5H_2O$ [48], and a pulse radiolysis study of the reaction of one-electron reducing radicals ($\cdot CH_2OH$, $MeC\cdot HOH$ or $Me_2C\cdot OH$) with $[PW_{12}O_{40}]^{3-}$. The relative reaction rates increase in the order $\cdot CH_2OH < MeC\cdot HOH < Me_2C\cdot OH$, which is the same order as that of their electron donating abilities [49]. Precipitation of tungstophosphoric acid by addition of $[Bu_4N]Br$

to an aqueous solution has produced $[Bu_4N]_3[\alpha\text{-}PW_{12}O_{40}]$. However, an aqueous solution of $Na_2[WO_4]$ and $Na_2[HPO_4]$ (mole ratio = 3:1), after acidification with acetic acid and addition of $[Bu_4N]Br$, precipitated $[Bu_4N]_4[H_3PW_{11}O_{39}]$; this compound, on recrystallisation from an ethanol-acetone mixture, gave $[Bu_4N]_3[\gamma\text{-}PW_{12}O_{40}]$ [50]. The thermal stability of the salts, $M_6[P_2W_{18}O_{62}]\cdot H_2O$ (M = Rb, Li, or K) have been studied and the products of the thermal decomposition monitored by IR spectroscopy [51]. $H_6[P_2W_{18}O_{62}].33H_2O$ has been prepared from $[NH_4]_6[P_2W_{18}O_{22}]$ in aqueous solution and the non-isothermal dehydration of $H_6[P_2W_{18}O_{62}].33H_2O$ studied using IR and ^1H NMR spectroscopy and thermal analysis [52]. Two mixed-valence phosphorus-tungsten oxides have been reported; $[P_8W_{12}O_{52}]$ and $[P_4W_8O_{32}]$. The latter structure consists of WO_6 octahedra and PO_4 tetrahedra and can be described as ReO_3-type slabs connected *via* PO_4 tetrahedra; this type of connection creates pentagonal tunnels in the [100] direction [53]. $[P_8W_{12}O_{52}]$ is built up from WO_6 octahedra in ReO_3-type slabs connected by P_2O_7 groups, creating pseudo-pentagonal and distorted hexagonal tunnels [54]. A pulse radiolysis study of 18-tungstodiphosphate ions in aqueous solution has been reported [53]. Heating $Pb(PO_3)_2$ with Pb_2WO_5 in 1:1 and 1:3 molar ratio has produced $Pb_3[P_2WO_{11}]$ and $Pb_7[P_2W_3O_{21}]$, respectively; when $Pb_2P_2O_7$ and Pb_2WO_5 were used as starting materials, $Pb_4[P_2WO_{12}]$ was formed. These reactions were monitored using DTA and X-ray phase analysis [56].

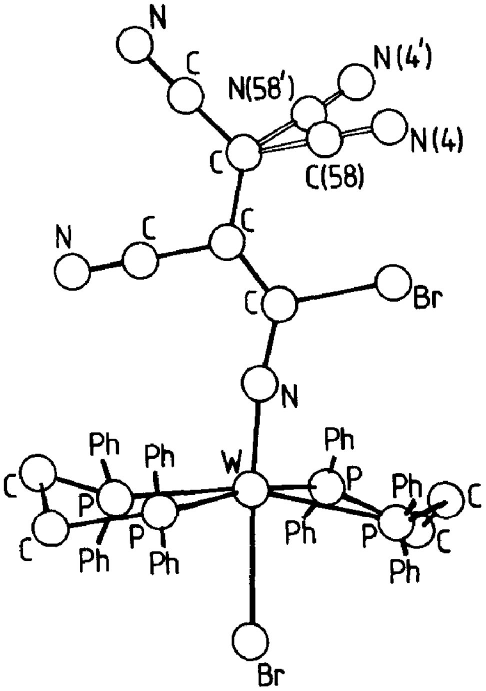
A new series of fluoropolytungstates has been obtained, these are $[HW_{12}F_3O_{37}]^{5-}$, $[H_2W_{12}F_2O_{38}]^{5-}$, $[HW_{12}F_2O_{38}]^{6-}$, $[H_2W_{12}FO_{39}]^{6-}$, $[HW_{12}FO_{39}]^{7-}$, and $[H_2W_{18}F_6O_{56}]^{9-}$ and they were produced electrochemically [57]. Two new material series of formula $Na_{5-x}A_x[W_3O_9F_5]$ ($0 \leqslant x \leqslant 0.75$; A = Li, or K) have been obtained by substituting Na in $Na_5[W_3O_9F_5]$ with either Li or K; these materials all have ferroelectric and ferroelastic properties [58]. The polytungstate ions $[\alpha\text{-}XM(III)(OH_2)W_{11}O_{39}]^{n-}$ (X = B, Si, Ge, P or As; M(III) = Al, Ga, In, or Tl) and $[X_2M(III)(OH_2)W_{17}O_{61}]^{7-}$ (X = P or As) have been reported. Their stability in acidic to slightly basic aqueous solution, both with and without support electrolyte, is classified in terms of the nature of X and M(III). The sensitivity of the P-O antisymmetric stretching vibration splitting to charges in M(III) has been described [59]. A similar series of heteropolytungstates containing M(III)=Fe and, for the first time, M(III)=Rh have been reported. These materials have been studied using electronic and IR spectroscopy and their redox properties described. The aquo ligand of the M(III) element can be completely or partially deprotonated. In approximately neutral aqueous solution the Fe(III)-containing anions form dimers, $[XW_{11}O_{39}Fe\text{-}O\text{-}FeO_{39}W_{11}X]^{q-}$, which can be isolated as solid salts [60]. The structure of potassium lead tungstogallate hydrate, $K_7[GaPbW_{11}O_{39}].16H_2O$, has been determined. The anion is related to the Keggin structure; the Ga is in the tetrahedral site and the Pb located in the vacant site of the $GaW_{11}O_{39}$ anion strongly linked to 4 oxygen atoms with a pyramidal arrangement like that for Pb in the oxide PbO [61]. New mixed heteropolyanions $[XPb(II)W_{11}O_{39}]^{n-}$ (X = Si, Ge, B, or Ga), $[XPb(II)W_{11}O_{40}]^{7-}$ (X = As(V) or P(V)) and $[X_2'Pb(II)W_{17}O_{61}]^{8-}$ (X' = As(V) or P(V)) have been prepared and the results of conductiometric, polarographic, spectrophotometric, and crystallographic studies described. The peculiar structure of these mixed heteropolyanions may be due to the large radius of Pb(II) [62]. The reduction of $[GaMoW_{11}O_{40}]^{5-}$ and $[GaMo_2W_{10}O_{40}]^{5-}$ by $Ti_2(SO_4)_3$ has been studied and shown to involve one and two electrons, respectively with the formation of the blues $[GaMoW_{11}O_{40}]^{6-}$ and $[GaMoW_{10}O_{40}]^{7-}$. The absorption spectra of these blues show a hypochromic shift of the fundamental charge-transfer band, $Mo(V) \rightarrow W(VI)$, to 500-510nm. X-ray diffraction indicated that all the above complexes were isostructural [63]. In aqueous DMSO solution, the following reaction has been observed: $H_4W_{10}O_{22} + VO^{2+} \rightleftharpoons H_2W_{10}VO_{33} + 2H^+$; in the presence of excess VO^{2+}, $[VO(W_{10}O_{33})]$ crystallises [64]. The basicity of the salts of $[NiTiW_{11}O_{39}(H_2O)]^{6-}$ and their preparation have been described [65]. The rate constants have been measured for the reaction of I^- with $[CoW_{12}O_{40}]^{5-}$ in both aqueous and in binary aqueous/solvent mixtures containing up to 40% MeOH, 40% MeCN, or 60% DMSO. From these kinetic results, solubility measurements on $K_5[CoW_{12}O_{40}]$, and published data on Gibbs free energy of transfer of appropriate ions, the dominant factor in determining the marked decrease in rate observed on going from water to binary aqueous solvent mixtures appears to be destabilisation of the transition state for the electron-transfer reaction [66]. Tetrabutylammonium salts of 12-heteropolytungstates with central transition metal ions in a tetrahedral environment, $[MW_{12}O_{40}]^{n-}$ (M = Cu(II), Fe(III), or Co(II)) have been prepared and spectroscopic data presented [67]. The structure of $K_{12}[As_2W_{18}O_{66}Cu_3(H_2O)_2].11H_2O$ has been determined and consists of two $\alpha.BAsWO_{33}$ subunits joined by three Cu atoms, the coordination shells of which are different [68]. In the anion $[\{(C_7H_8)Rh\}_5(Nb_2W_4O_{19})_2]^{3-}$ the two *cis*-$Nb_2W_4O_{19}{}^{4-}$ ions, using both terminal and bridging oxygen atoms, behave as pentadentate bridging ligands [69] $K_4[Th(BW_{11}O_{39})_2].38H_2O$ has been prepared by heating together $Na_2WO_4.2H_2O$, H_3BO_3, and $Th(NO_3)_4.4H_2O$ in acetic acid at 80-90°C and characterised using IR and UV spectroscopy, DTA, and X-ray diffraction. A variety of other M^+ salts can be obtained from the K^+ salt [70].

2.1.5 *Complexes with sulphur and nitrogen bond ligands*

Gas phase electron diffraction measurements at average nozzle temperatures of 200 and 220°C for $[WSCl_4]$ or $[WSeCl_4]$, respectively, have been made and have shown that both molecules are square pyramidal with C_{4v} symmetry [71]. Infrared spectra were used to characterise $[Ph_4As]_2[WNCl_3(PO_2Cl_2)]$, obtained by the reaction of $[Ph_4As][PO_2Cl_2]$ with $NNCl_3$ [72]. Ordinary diazoalkanes, N_2CHR' and $N_2C(Me)R'$ (R' = Ph or 4-tolyl) have been reacted with $[W(CO)_5(S_2CNR_2)_2]$ (R = Me, Et; $R_2 = (CH_2)_4$) at room temperature to form stable complexes of the type $[W(CO)(N_2CHR')(S_2CNR_2)]$. Oxidation of this compound with one equivalent of Cl or Br gave $[WX_2(N_2CHR')(S_2CNR_2)_2]$ (X = Cl or Br) and addition of excess of HBr to $[W(CO)(N_2CHR')(S_2CNMe_2)_2]$ produced the red solid $[WBr_2(N_2CHR')(S_2CNMe_2)_2]$. Physical and spectroscopic data have indicated that in these complexes, the diazoalkane ligands behave as terminal, singly-bent 4-electron donor ligands. The preparation of the new complexes, $[W(CO)_3(S_2CNR_2)_2]$, $[W(CO)_2(S_2CNR_2)_2]$, $[W(CO)_2(L)(S_2CWR_2)_2]$ (L = $4\text{-}MeC_6H_4NH.NH_2$, 4-Mepyridine), $[WBr_2(S_2CNR_2)_2]$, $[W(S_2CNR_2)_2]$, $[W(S_2CNR_2)_4]$, and $[WBr_3(S_2CNR_2)_2]$

have been reported [73].

The crystal structure of $[Ph_4As]_2[W_2NCl_{10}]$ has been determined and the atomic parameters, bond angles and lengths given; the $[W_2NCl_{10}]^{2-}$ anion consists of W(VI) and W(V) linked by a linear asymmetric nitride bridge. The *trans* effect of the W-N multiple bonding causes a significant difference in the axial and equatorial W-Cl bond lengths [74]. The reaction of WCl_6 with IN_3 in CH_2Cl_2 has yielded $[WNCl_3.0.5NH_3]_4$, which has been characterised by IR spectroscopy and X-ray diffraction and has shown that the four tungsten atoms are arranged in a square, the edges being formed by almost linear W≡N-W bridge bonds of alternating lengths (1.68 and 2.10Å). The two opposite tungsten atoms are coordinated by a NH_3 molecule and three terminal chloride ligands. The other two tungsten atoms attain six-fold coordination by two terminal and two bridging chloride ligands linking the tetrameric units to form bands along [101] directions [75]. The X-ray structure of $[WBr(dppe)_2\{NC(Br)C(CN)C(CN)_2\}]$ (3) has been reported and shown to contain a W≡N bond distance of 1.777Å [76].



(3)

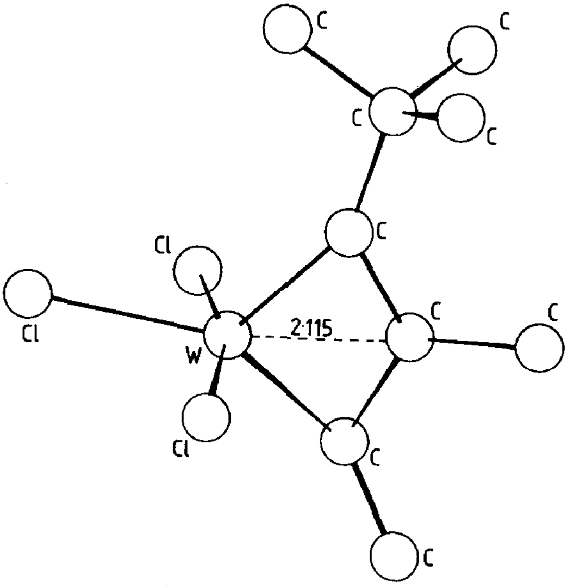
The complexes $[W(NH_3)_2L_4]Cl_2$ (HL = 3-(4-pyridyl)triazoline-5-thione) have been prepared and shown to have *trans*-octahedral structures [77].

2.1.6 Tungsten hydride complexes

The preparation of several tungsten(VI) hydride complexes have been reported. $[WH_5L_4]Cl.HCl$ (L = $PMePh_2$, $P(OPr\text{-}i)_3$, PEt_2Ph, $PBuPh_2$, $PEtPh_2$, or 0.5 dppe) complexes have been prepared by reacting $[WH_4L_4]$ with dry HCl, while $[WH_5Q][ClO_4]$ (Q = $PMePh_2$ or 0.5 dppe) were obtained from $[WH_4Q_4]$ and $HClO_4$ in methanol. Treatment of $[WH_5L_4]Cl.HCl$ (L = $PMePh_2$ or $PBuPh_2$) with $Na[BH_4]$ gave the corresponding $[WH_5L_4][BPh_4]$ salt. Other complexes obtained include $[WH_5(PMePh_2)_4]Br$ and $[WH_5(dppe)_2][CLO_4]$. These complexes were characterised using IR and NMR spectroscopy [78].

2.2 TUNGSTEN(V)

The reaction of $[MOCl_3(THF)_2]$ (M = Mo or W) with a series of Schiff base ligands (L) containing phenolic imine and various side chain donors has been described. The products $[WOCL_3L_2]$, in which the ligand generally binds as a neutral monodentate imine donor, have been shown by ESR measurements to have a *cis-mer* structure [79]. The magnetic properties of $[WOF_3.3H_2O]$ have been studied between 77 and 298K and the compound reported to have a polymeric structure with fluoride bridges and metal-metal bonds [80]. Yellow $[W(CCMe_3)Cl_3(PMe_3)_2]$ has been reacted with molecular H_2 (30psi, 12h, CH_2Cl_2) to give the pale yellow complex, $[W(CCMe_3)(H)Cl_3(PMe_3)_2]$, which has a pentagonal-bipyramidal structure with the neopentylidene ligand and a chloride ligand occupying the axial positions. The W-alkylidene (W=C) distance is 1.859Å [81]. The preparation and structure of a stable tungsten cyclobutadiene complex, $[W(C\text{-}Bu^tCMeCMe)Cl_3]$ has been reported **(4)** [82].



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2.3 TUNGSTEN(IV)

The structures of MCl_4 (M = Nb, Ta, Mo, W, or Re) have been studied by X-ray diffraction and IR spectroscopy [83]. In the cation of $[W(NH)Br(dppe)_2]Br$ the tungsten is six coordinate with approximate C_{4v} symmetry. The equatorial plane is defined by the phosphorus atoms of the two dppe ligands, with an average W-P bond distance of 2.55Å and the tungsten displaced 0.25Å from the plane towards the axial imido group [84].

The tetrahydrides of tungsten(IV) have been the subject of several papers dealing with improvements in their synthesis and their photochemical properties. WCl_6 has been reacted with $PMePh_2$ or $PEtPh_2$ in THF in the presence of $LiEt_3BH$ to give $[WH_4(PMePh_2)_4]$ or $[WH_4(PEtPh_2)_4]$, respectively [85]. These two complexes have also been obtained using $Li[BH_4]$ and Et_2O [86]. Photophysical and photochemical investigations have shown that $[WH_4(dppe)_4]$

exhibits emission of visible light at 77K in 2-methyltetrahydrofuran and irradiation in the presence of an alkene results in stoichiometric reduction to the alkane [87].

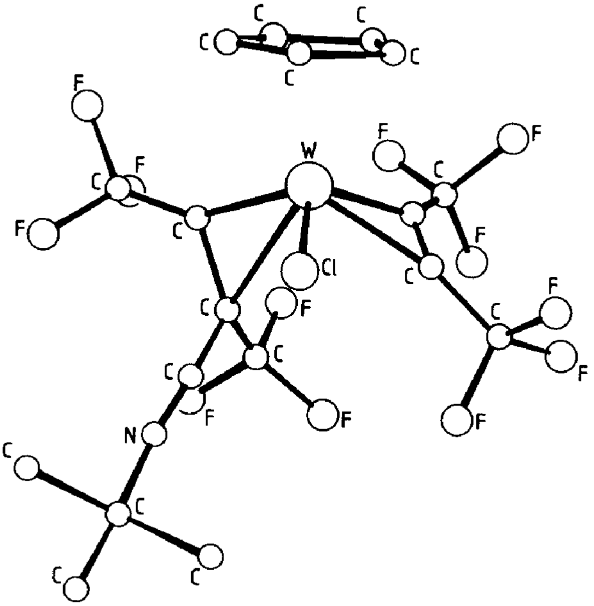
The preparation of several tungsten(IV) alkylidene complexes of the type $[W(CR)L_4Cl]$ (R = H or CMe_3; L = PMe_3 or 0.5 $Me_2P.CH_2CH_2OMe_2$) has been reported, together with the results of protonation of these complexes [88]. Tungsten(IV) carbenes, such as $[W(CHBu^t)(OCH_2Bu^t)_2X_2]$, in the presence of aluminium halides are highly active catalysts for olefine metathesis and the nature of the initiating and propagating species has been studied by NMR spectroscopy [89]. *Insitu*, photolysis of $[W(cp)_2H_2]$, $[W(cp)_2D_2]$, $[W(cp)_2(Me)H]$ and $[W(cp)_2(C_2H_4)]$ and $[W(cp)_2(CO)]$ in Argon has been shown to lead to a common product, $[W(cp)_2]$ which has been identified by matrix isolation methods with IR and UV/visible detection [90]. The structure of $[W(cp)_2(Me)(C_2H_4)]$ contains disorderd methyl and ethylene groups [91]. Reaction of this compound with PMe_3 produces $[W(cp)_2Me(CH_2CH_2PMe_3)][PF_6]$ [92].

2.4 TUNGSTEN(III)

The reactions of WCl_3 with a number of other tungsten and molybdenum halides have been reported. WCl_3 reacts with WCl_6 at 316°C to give WCl_4 and WCl_5, while its reaction with WCl_5 at 300°C gives WCl_4. WCl_3 reacts with $MoCl_4$ or MoO_2Cl_2 at 150°C to give $WOCl_4$ or WO_2Cl_2, respectively. $WOCl_3$ is produced when WCl_3 reacts with $MoOCl_3$, while WCl_5 is obtained upon reaction with $MoCl_5$ [93]. Coordination of hydrotris(1-pyrazolyl)borate (HBP^-) and hydrotris(3,5-dimethyl-1-pyrazolyl)borate ($HBMP^-$) to tungsten(III) centres has been shown to stabilise these with respect to oxidation. This has been achieved by reacting $[NR_4][M(CO)_5L]$ with $SOCl_2$ to produce $[WCl_3L]$ (L = HBP, HBMP), which on reduction yielded $[NH_4]_{0.5}[Et_4N]_{0.5}[WCl_3L]$. X-ray diffraction has shown the W anions to be monomeric with facial (C_{3v}) geometries and near octahedral coordination [94].

2.5 TUNGSTEN(II)

The synthesis, characterisation, and novel reactions of seven-coordinate complexes of Mo(II) and W(II) have been described [95]. Other reports on seven-coordinate complexes of W(II) have included the preparation of $[W(CNR)_4(CNHR_2)X]^+$ ($R = Bu^t$), in which the ligand RHNCCNHR is formally regarded as an (*N*,*N*'-dialkyldiamino)acetylene [96], and a description of the redox properties of the cations $[W(CNR)_7X]^+$ and $[W(CNR)_7]^{2+}$ (R=alkyl, X=Cl, Br, I, CN, or $SnCl_3$). All the alkyl isocyanide complexes exhibit a quasi reversible, one-electron oxidation to form seven-coordinate W(III) cations and also show an irreversible reduction [97]. The structures of the $[W(SC_6H_4Me\text{-}4)\{\eta^2\text{-}C(CF_3).C(CF_3)PEt_3\}\{\eta^2\text{-}CF_3C{\equiv}CCF_3\}Cp$ and $[WCl\{\eta^2\text{-}C(CF_3).C(CF_3)CNBu^t\}(\eta^2\text{-}CF_3C{\equiv}CCF_3)cp]$ (5) have been described and shown to contain a metal-stabilised 1,3-dipolar vinyl ligand coordinated in a η^3



(5)

manner about the metal centre [98]. The mono- and bis-arenetungsten(II) complexes $[WH(\eta^6-C_6H_5Me)_2][PF_6]$, $[WH(\eta^6-C_6H_5F)_2][PF_6]$ and $[WH(\eta^6-C_6H_5Me)(MeCN)(\eta^3-CH_2CHCH_2)][PF_6]$ have had their structures determined, also reported were the structures of $[W(\eta^6-C_6H_5Me)_2]$ and $[WH(\eta^6-C_6H_5Me)(PMe_3)_2Cl_2][PF_6]$. There was no evidence that the arene ligands act as dienes [99].

One electron reduction of *trans*-$[WF(N_2CH_2CH_2)L_2]^+$ (L_2 = dppe) in acetonitrile electrolyte at a mercury pool cathode has produced $[L_2FW(N_2CH_2CH_2N_2)WFL_2]$ in moderate yields [100].

2.6 TUNGSTEN(0)

$[W(bipy)_3]$ and $[W(phen)_3]$ have been synthesised by the reduction of the corresponding $[WCl_4L]$ compound in THF by a sodium amalgam [101]. The chemistry and synthesis of phosphite complexes of tungsten(0) have been described. Thus, reduction of tungsten chlorocomplexes with $P(OMe)_3$ produces $[W(P(OMe)_3)_6]$. These phosphite complexes react with protic acids to give complexes such as $[HW(P(OMe)_3)_5P(OMe)_2]^+$ and $[HW(P(OMe)_3)_4(O_2CCF_3)]$. The photoreactions of the phosphite complexes with H_2, CO, $(CN)_2$, and NO have been described [102].

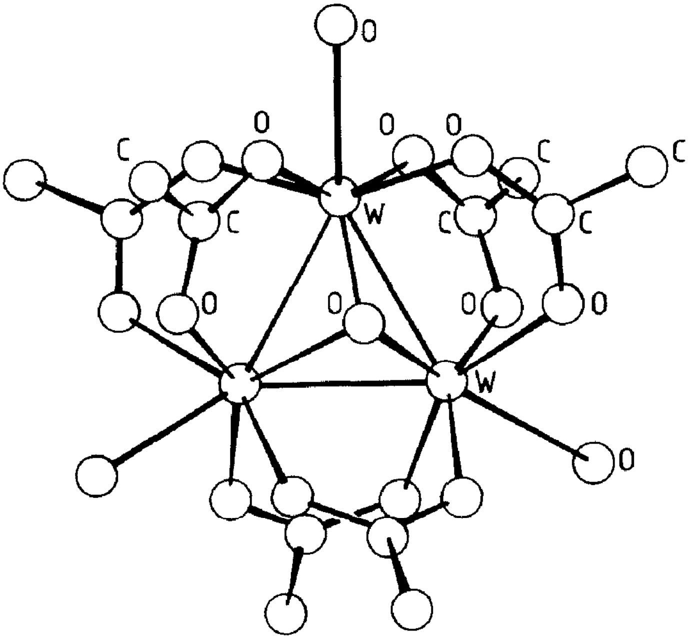
2.7 COMPOUNDS CONTAINING METAL-METAL BONDS

Heterobinuclear complexes, where there is NO metal-metal bond or single atom bridge have been reviewed [103]. Also, there have been two reviews of compounds containing metal-metal bonds; one dealing with the alkoxides of molybdenum and tungsten [104], the other with binuclear complexes containing the ligands $RN(PF_2)_2$ (R = Me or Ph) [105].

2.7.1 Higher oxidation states

Reaction of $[WCl_4(Me_2S)_2]$ with one mole-equivalent of $SiMe_3(SEt)$ in CH_2Cl_2 produces $[(Me_2S)Cl_2W(\mu-S)(\mu-SEt)_2WCl_2(Me_2S)]$. A crystal structure determination has shown this compound to have a confacial bioctahedral structure with a W-W bond length of 2.526A. Reaction of this compound with two mole-equivalents of $[Ph_4P]Cl$ in CH_2Cl_2 gives $[Ph_4P]_2[Cl_3W(\mu\text{-}S)(\mu\text{-}SEt)WCl_3]$ which has a similar structure to the starting material and a W-W bond length of 2.522Å [106]. Other similar complexes, of general formula $[W_2Cl_4(\mu\text{-}SR)_2(\mu\text{-}S)L_2]$, have been prepared in a metathetical reactions between $[WCl_4L_2]$ and one mole-equivalent of $Me_3Si(SR)$ (L = Me_2S or tetrahydrothiophene, R = Me, Et, Bu^i, CH_2Ph). These compounds react with stronger nucleophiles (Ph_3P, MeCN, pyridine, or chloride) under ambient conditions giving simple disubstituted products. This series of homologous complexes was studied by ^1H and ^{13}C NMR spectroscopy and trends in the ^1H NMR chemical shifts of the methylene and Me protons of the SEt groups in the complexes $[W_2Cl_4(\mu\text{-}SEt)(\mu\text{-}S)L_2]$ allowed the absolute assignment of the resonance of the two magnetically inequivalent thiolato groups [107]. Reduction of $[W_2Cl_4(PMe_3)_4]$ by a sodium amalgam in the presence of excess PMe_3 in THF under H_2(3 atm.) has produced $[W_2H_4(\mu\text{-}H)(\mu\text{-}PMe_2)(PMe_3)_5]$ in 40% yield. Its structure consists of a pentahydride of the binuclear unit, although it was not possible to locate the metal-bonded hydrogen atoms [108].

$[\{W_3O_2(O_2CEt)_6(H_2O)_2\}_2(H_3O_2)]Br_3.6H_2O$ contains the $H_3O_2^-$ ligand bridging between 2 metal atoms of adjacent cluster ions. The $H_3O_2^-$ unit is symmetrical with an O-O separation of 2.50Å. Characterisation of four similar complexes with a variety of counterions was also reported [109]. Small amounts of a new, dark blue, tritungsten cluster cation has been obtained as a byproduct in the preparation of the well known $[W_3O_2(OAc)_6(H_2O)_3]^{2+}$ ion. This new species has been isolated in the form of the isomorphous, $[W_3O(OAc)_6(H_2O)_3][MBr_4].8H_2O$ (M = Fe or Zn) compounds. The trinuclear cation has approximate C_{3v} symmetry with a W-W distance of 2.710Å. The electronic structure of the hemicapped cluster can be considered similar to that of the bicapped species, except that in place of the three bonds to a second capping oxygen atom there is an empty *e* orbital and a filled a_1 orbital that has a moderate bonding character with respect to the W_3 triangle (6) [110].



(6)

The preparations and characterisation by chemical analysis and IR spectroscopy of some diamagnetic binuclear tungsten(VI) complexes of nicotinic and isonicotinic acids, $[W_2O_4L(OH)_3.H_2O].nH_2O$ (HL = nicotinic, isonicotinic acid, n = 1,3) in acidic medium (pH = 2.5-3.0) has been reported [111]. $[Ph_4As]_2[Cl_2OW(\mu\text{-}Cl)(\mu\text{-}SBu^i)WOCl_2]$ has been structurally characterised and shown to have a confacial bioctahedral configuration with oxo ligands *cis* to one another [112].

2.7.2 Complexes with a metal-metal double bond

The ditungsten(IV) alkoxides, $[W_2Cl_4(\mu\text{-}OR)_2(OR)_2(ROH)_2]$, which posses a W=W bond, have been used as reagents for C-C bond formation *via* the reductive coupling of ketones [113]. Addition of CO(1 atm., 25°C) to hydrocarbon solutions of $[W_2(OR)_6]$ (R = i-Pr or CH_2CMe_3) in the presence of donor ligands (L) has led to the isolation of $[W_2(OR)_6L_2(\mu\text{-}CO)]$ (L = pyridine), in which in the formal sense, there exists a W=W bond of length 2.429Å. The central $W_2O_6N_2C$ skeleton has a confacial bioctahedral structure with the CO ligand and a pair of OR groups making up the bridging face [114].

2.7.3 Complexes with a metal-metal triple bond

Metathesis of W≡W bonds with alkynes and nitriles has produced alkylidene and nitride complexes; for example $[W_2(OCMe_3)_6]$ reacts under mild conditions (25°, C_6H_6) with RC≡CR (R = Me, Et, or Pr) or RCN (R = Me or Bz) to give $[(Me_3OC)_3W{\equiv}CR]$ or $[(Me_3OC)_3W{\equiv}N]$, respectively. This is the first example of a metathesis reaction of a metal-metal multiple bond [115]. Treatment of $[W_2(CH_2Ph)_2(NMe_2)_4]$ with excess CO_2 has produced the compound $[W_2(CH_2Ph)_2(O_2C\text{-}NMe_2)_4]$ in which the $(W{\equiv}W)^{6+}$ moiety is retained [116]. Characterisation by a single-crystal X-ray crystallographic study and NMR spectroscopy of $[W_2(\mu\text{-}H)(\mu\text{-}Cl)Cl_2(PBu_3)_2(OBz)_2]$ has shown that the lattice contains two crystallographically independent molecules which are essentially identical, and consist of two distorted octahedra sharing an edge. There is a central $W(OBz)_2W$ unit that is planar, except for the phenyl groups, and the H and Cl atoms are placed above and below this plane forming a $W(\mu\text{-}H)(\mu\text{-}Cl)W$ plane approximately perpendicular to the former plane. The W-W distances are 2.423Å and 2.435Å and the metal-metal bond is of formal order 3 [117].

2.7.4 Complexes with a metal-metal quadruple bond

The homologous compounds $[M_2Cl_4(PR_3)_4]$ (M = Mo or W) have been used in a combined theoretical and experimental study to compare the electronic structures of quadruple bonds between a pair of Mo and a pair of W atoms. The theoretical work was carried out by the SCF-Xα-SW method on the model system with R = H, but using in all other respects the experimentally measured bond lengths and angles for the compounds R = Me. The W-W bonding appears to be weaker than that of Mo-Mo, and in general, the results are consistent with the greater reactivity of the W-W quadruple bond [118]. Reduction of WCl_4 by sodium amalgam in THF produces the blue $[W_2Cl_8]^{4-}$ ion; addition of tetramethylethylenediamine (TMEDA) to the Na salt in cold THF gave $[Na(TMEDA)]_4[W_2Cl_8]$. The W-W distance in this anion is 2.257Å and each

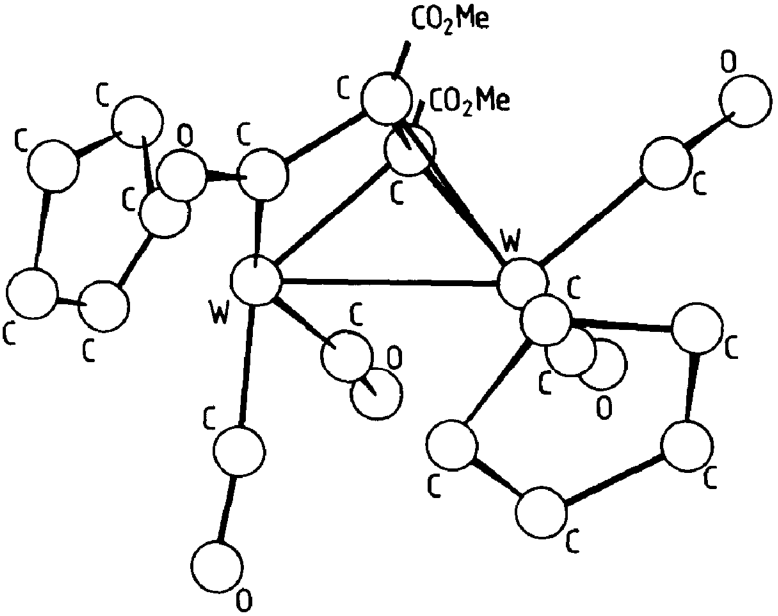
$[W_2Cl_8]^{4-}$ anion is surrounded by 4 $[Na(TMEDA)]^+$ ions [119]. $[W_2(OBz)_4(THF)_2]$ has been prepared, by the reaction of WCl_4 and sodium amalgam in THF with NaOBz, and its structure determined; the W-W distance is 2.196Å [120]. The three metal-metal molecular orbitals $[b_{2g}(\delta), e_u\ (\pi)$, and $a_{1g}(\sigma)]$ that form the W-W quadruple bond are resolved in the photoelectron spectrum of $[W_2(O_2CCF_3)_4]$ [121].

The attempted synthesis of tetrameric cluster compounds $[W_4Cl_8(mhp)_4]$ (mhpH=2-methyl-6-hydroxypyridine), led to the formation of $[W_2Cl_2(mhp)_3]$ with a metal bond order of 3.5. Cyclic voltammetry showed that the compound could be reversibly reduced to the W_2^{4+} dimer containing a W-W quadruple bond. The X-ray crystal structure of $[W_2Cl_2(mhp)_3]$ showed that the Cl ligands were situated *cis* with one bound to each tungsten atom. The isolation of $[W_4Cl_8(PR_3)_4]$ was also reported in this study [122].

2.7.5 Carbonyl and organometallic complexes

$[Cl(CO)_4OsOs(CO)_4Os(CO)_4SnCl_3]$ reacts with nucleophilic reagents such as $[W(CO)_3cp]$ to give $[Cl(CO)_4OsOs(CO)_4Os(CO)_4SnCl_2W(CO)_3cp]$ which contains a Os-Sn-W bond [123]. $[W_2(CO)_{10}]^{2-}$ has been obtained by the reaction of WCl_6 with metallic magnesium or sodium amalgam under an atmosphere of CO and the chemical properties and IR characteristics of the $[Mg(THF)_2]^{2+}$ salt have been discussed [124]. The action of heat on $[cp(OC)_3M(\mu\text{-}SR)M'(CO)_3]$ **(1)** (M = Mo, W or Cr; R = Me or Ph) gave $[cp(OC)_2M(\mu\text{-}SR)M'(CO)_5]$ **(2)** containing a metal-metal bond; photolysis of **(2)** in the presence of CO regenerates **(1)**. The spectroscopic parameters and the crystal structure of (**1a**: M = M' = W; R = Me), (**2b**: M = Mo,M' = W; R = Me) and $[cp(OC)W(\mu\text{-}SMe)W(CO)_5]$ have been reported and discussed in terms of the electronic properties of the bridging thiolate ligands [125]. New, unsaturated, heterobimetallic complexes $[WRh(\mu\text{-}CO)_2(CO)(PPH_3)_2cp)]$ have been reported and their chemical properties examined [126]. $[WM(\mu\text{-}H)(CO)_2(PR_3)]$ complexes (M = Au, R = Ph; M = Ag, R = Me) have been prepared by the reaction of $[AuCl(PPh_3)]$ or $[AgI(PMe_3)]$ with

$[(Ph_3P)_2N]$ $[W(CO)_5H]$ in THF containing $Tl[PF_6]$ [127]. Complexes of the type *trans*-$[Pt(C{\equiv}CR)_2(dppm)_2]$ (R = Me, Ph or 4-tolyl) have been used to effect systematic, high yielding, syntheses of heterobimetallic complexes with, amongst other metals, W(0). For example, refluxing *trans*-$[Pt(C{\equiv}CR)_2(dppm)_2]$ with *fac*-$[W(CO)_3(NCMe)_3]$ in benzene for 2 hours gives the dark red binuclear Pt-W complex, $[(R_2C{\equiv}C)_2Pt(\mu\text{-dppm})_2W(CO)_3]$ [128]. The X-ray structure of $[N(PPh_3)_3][W_2(\mu\text{-CHR})(CO)_7cp]$ and $[AuW(\mu\text{-CHR})(CO)_2(PPh_3)cp]$ (R = 4-tolyl) have been reported, together with that of $[W(=CHR)(SnPH_3)(CO)_2(\eta\text{-}C_5H_5)]$ [129]. UV irradiation of a mixture of $[W_2(CO)_6(cp)_2]$ and dimethylacetylene-dicarboxylate has produced the complex $[W_2(CO)_4\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}C(O)C_2(CO_2Me)_2\}(cp)_2]$, which has been shown by X-ray diffraction to contain an unusual bridging ligand composed of a linked alkyne and CO. The molecule has a ditungsten unit, one atom of which is part of a metallobutenone ring, whose ethylenic bond is η^2-coordinated to the tungsten atom (7) [130].



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An X-ray crystallographic study of the complex, [PtW(μ-C.C_6H_4OMe-4)$(CO)_5$-(η-C_8H_{12})] has been published [131].

Several papers dealt with the synthesis and characterisation of heterotrinuclear metallic species, in which, at least, one of the atoms is tungsten. These MM'M" units are usually triangular. [W(≡C.C_6H_4Me-4)$(CO)_2$cp] reacts with [$Co_2(CO)_8$] in pentane at room temperature to give the dicobalt-tungsten complex, [Co_2W(μ-C.C_6H_4Me-4)$(CO)_8$cp]. The molecule contains a Co_2W isosceles triangle (W-CO = 2.672Å) capped by a triply bridging tolylidene (W-C = 2.103Å) group. These were common structural features of this series of heterotrinuclear complexes. In the corresponding Rh_2W complex, [Rh_2W(μ_3-C.C_6H_4Me-4)$(acac)_2$(μ-CO)$(CO)_2$cp], as well as the triply bridging ligand, there is a bridging carbonyl ligand associated with Rh-Rh [132]. Other trinuclear complexes in the series that have been reported are: [Pt_2W(μ_3-C.C_6H_4Me-4)$(CO)_4$$(PMePh_2)_2$cp] [133], [FePtW($\mu_3$-CR)$(CO)_5$$(PMePh_2)_2$cp], [FePtW($\mu_3$-CR)$(CO)_6$$(PEt_3)$cp] [134], and [RhFeW($\mu_3$-C.$C_6H_4$Me-4)($\mu$-CO)$(CO)_5$(η-$C_5H_5$)(η-$C_9H_7$)] [135]. The structure of the related complex [(η-C_5H_5)$_2$$W_2Os(CO)_7${$\mu_3$-Me$C_6H_4$C≡C$C_6H_4$Me}] is unusual, in that it contains two isomers of the complex in the same ordered single crystal. There are two distinct molecules in the crystallographic asymmetric unit and they have different connectives, in particular, they are related by a $^{2\pi}/_3$ rotation of a triply bridging di-4-tolylalkyne ligand above the triangular W_2Os face. Molecule **A** (the "*sym isomer*") has η^2-alkyne-Os linkage in conjunction with two η'-alkyne-W linkages. Molecule **B** (the "*unsymm isomer*") has a η^2-alkyne-W linkage along with η^1-alkyne-Os and η^1-alkyne-W linkage [136].

[As_2{W$(CO)_5$}$_3$] has been obtained from $AsCl_3$ and $Na_2[W_2(CO)_{10}]$ or [$(CO)_5$W(THF)]. Its wheel type molecular framework, as determined by X-ray crystallography, has D_{3h} symmetry with three W$(CO)_5$ groups surrounding the axial As_2 ligand, which acts as a six-electron donor. This unusual bonding situation has been analysed by extended Huckel methods [137]. A similar complex, in which the As_2 ligand has been replaced by the Bi_2 ligand, has been reported. This was obtained by reductive dehalogenation of $BiCl_3$ with

$Na_2[W_2(CO)_{10}]$ [138].

Compounds with general formula $[NR_4]_n[W(CO)_8(XR)]$ (n = 3 or 4; XR = OMe, OEt, or SPh) have been prepared by refluxing the corresponding $[M(CO)_3(PMTA)]$ (PMTA = 1,1,4,7,7-pentamethyldiethylenetriamine) with the appropriate NaXR compound in tetrahydrofuran, followed by metathesis with tetramethyl- or tetraethylammonium halides. One of the complexes, $[Me_4N]_2[W_3(CO)_9(\mu\text{-OEt})(\mu\text{-OEt})_2]$ has been characterised by X-ray crystallography; the anion contains a highly unsymmetrical metal triangle, which is best considered as containing one W-W bond [139]. The structure of $[cpW_2Ir_2(CO)_{10}]$ is based on a closed tetrahedral W_2Ir_2 core, with each Ir atom linked to three terminal CO ligands, while the two tungsten atoms are each associated with a cp ligand and two CO ligands [140]. Heating together $[M(CO)_2(NO)cp]$ and $[M_2(CO)_6cp]$ at 200°C gives the metal cluster nitrides $[M_3(N)(O)(CO)_4(cp)_3]$ (M_3 = Mo_3, Mo_2W, MoW_2, or W_3); isotropic labelling has shown that the coordinated oxygen does not come from NO, whose O appears in CO_2 [141].

2.8 NITROGENASE RELATED CHEMISTRY

2.8.1 Tungsten-iron-sulphur clusters

The variation of the effective magnetic moment with temperature in the range 1.9-300K, and with the applied magnetic field in the range 1.25-20.0 kG of $[Et_4N]_3[Fe_6M_2S_8(SPh)_6(OMe)_3]$ (M = Mo(1) or W(2)), $[Bu^n{}_4N]_3[Fe_6Mo_2S_8(SPh)_9]$ **(3)**, and $[Et_4N]_3[Fe_6W_2S_8(SEt)_9]$ **(4)** has been investigated. The ESR spectra for the powders **(2)**, **(3)** and **(4)** at 4.2K and for a frozen glass of **(2)** in MeCN have also been reported. An interpretation of these data, in terms of a model involving antiferromagnetic spin coupling between the two Fe(II) atoms and an Fe(III) atom within a Fe_3MS_4 subunit with additional much weaker coupling between the subunits [142]. Reaction of the Fe(III)-bridged double cubane clusters $[M_2Fe_7(SEt)_{12}]^{3-}$ (M = Mo or W) with 3,6-disubstituted catechols $R_2'catH_2$ (R' = Pr or $CH_2CH{=}CH_2$) in MeCN solution at ambient temperature causes bridge cleavage and has produced the new clusters $[M_2Fe_6S_8(SEt)_6(R_2'cat)_2]^{4-}$

which have been isolated as the $[Et_4N]^+$ salts. In solution, these clusters undergo complete thiolate ligand substitution with arylthiols (RSH) to afford $[M_2Fe_6S_8(SR)_6(R_2'cat)_2]^{4-}$ (R = Ph, 4-tolyl, 4-C_6H_4Cl). In coordinating solvents such as DMSO, MeCN, and DMF, the double cubanes are cleaved to the single cluster solvates $[MFe_3S_4(SR)_3(R_2'cat)(solv)]^{2-}$. Magnetic susceptibility and ESR spectral properties confirmed a $S = {}^3/_2$ ground state. These solvated clusters undergo a single one-electron reduction at ~ 1.1 to 1.5V (vs. SCE) this, together with the lability of coordinated solvent molecules, suggests the possibility that (reducible) nitrogenase substrates may be bound and activated at the M atom site [143,144].

Reactions of the double cubane cluster $[W_2Fe_7S_8(SEt)_{12}]^{3-}$ with PhSH and CH_3COCl have been studied to ascertain ligand substitution propensities of the thiolate ligands. The results suggest that the two electrophilic reagents effect only terminal ligand substitution under the given reaction conditions (Me_2SO and MeCN solution, ambient temperature, stoichiometric or (specified) excess of reagents) that leave intact the individual cluster structures [145].

2.8.2 *Dinitrogenyl chemistry*

Reduction of $[WCl_4(PEt_2Ph)_2]$ with magnesium (and PEt_2Ph) in THF under N_2 at 20°C has produced the complex $[\{W(N_2)_2(PEt_2Ph)_3\}_2(\mu\text{-}N_2)]$ that contains both bridging and terminal N_2 ligands [146]. It has been shown that the structure of $[(cp)_2WH(p\text{-}NNHC_6H_4F)][PF_6].Me_2CO$ contains a cation, in which the environment of the tungsten atom is that of a very flattened tetrahedron; the 4-fluorophenylhydrazido(2-) ligand is bound to the metal with a distinctly non-linear W-N(1)-N(2) skeleton (W-N(1)-N(2) = 146.4°) [147]. The preparation of the compounds $[WX_2H(NNH_2)(PMe_2Ph)_3]X$ (X = Cl or Br), $[WCl_3H(NNH_2)(PMe_2Ph)_2]$ and $[WCl_3H(NNHPh)(PPhRR')_2]$ (R = R' = Me or Ph; R = Me, R' = Ph) has been described. The structure of the complex *cis*-$[WCl_3(NNH_2)(PMe_2Ph)_2]$ was included in this paper [148]. Reaction of $[MCl_4(PR_3)_2]$ (M = Mo or W: PR_3 = PPh_3, PPh_2Me_2 PMe_2Ph) with $Me_3SiNHNMe_2$ in MeCN has led to the formation of the complexes $[MCl(NNMe_2)_2(PR_3)_2]Cl$ [149].

The chemistry of dinitrogen complexes has been the subject of a number of reports. Treatment of $[W(N_2)_2L_2]$ (L = dppe) with Me_3SiN_3 in refluxing toluene or THF for 3 and 4 hours, respectively, gives $[WN(N_3)L_2]$ in a 40% yield *via* a free radical mechanism [150]. The kinetics of the reaction between *trans*-$[M(N_2)_2\{(R_2PCH_2)_2\}_2]$ (1) (M = Mo or W; R = Ph or Et) and HX(X = Br or HSO_4) in THF giving *trans*-$[M(NNH_2)_X\{(R_2PCH_2)_2\}_2]$ (2) has been studied. The formation of (2) involves rapid adduct formation between HX and (1), protonation of a coordinated N by a second molecule of HX and the rate determining dissociation of nitrogen [151]. The reaction of *trans*-$[W(N_2)_2(dppe)(PPh_2Me)_2]$ with HBr in THF has been described and compared with that of the analogous molybdenum complex [152]. Treatment of *trans*-$[W(N_2)_2(PMe_2Ph)_4]$ with alcohol/ketone systems (e.g. $MeOH/Me_2CO$) at 50°, followed by base distillation gives N_2H_4 as the main nitrogen hydride. Addition of KOH to the systems results in an increase of free N_2H_4 formation [153]. Photoirradiation of $[M(N_2)_2L_2]$ (M = Mo or W; L = dppe) in the presence of $P(OR)_3$ (R = Ph or 4-ClC_6H_4) gives $[M(P(OR)_3)_2L_2]$ [154]. NH_3 and N_2H_4 can be produced in moderate yields by the treatment of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with an acidic hydridometal carbonyl, e.g. $[HCo(CO)_4]$ in MeOH, followed by KOH distillation. Reactions of *trans*-$[W(N_2)_2(dppe)_2]$ with the hydride complexes in an alcohol giving alkoxide hydrazido(2-) compounds of the type *trans* -$[W(OR)(NNH_2)(dppe)_2]^+$ A^- (A = $FeCo_3(CO)_{12}$; R = Me, Et, Pr, *i* -Pr, Bu, *s* = Bu, cyclohexyl, hexyl, or CH_2Ph : A = $Co(CO)_4$; R = Me or Et : A = $Co_3(CO)_{10}$; R = Me). The crystal structure of one of these compounds, $[W(OMe)(NNH_2)(dppe)_2]^+$ $[FeCo_3(CO)_{12}]^-$, has been described [155].

2.9 TUNGSTEN CATALYSTS

Catalysts containing a variety of metal oxides, including molybdenum and tungsten oxides, have been prepared and used for the ammonoxidation of propene to acrolein and for the oxidation of olefins to aldehydes [156]. A detailed account of the preparation of these catalysts has appeared elsewhere [157]. A systematic study has been carried out to relate alkene metathesis activity and the structure of γ-alumina supported molybdenum and tungsten oxides. It would appear that the catalytic behaviour of the catalysts correlates with this reducibility; the more easily they are reduced, the higher is the catalytic activity [158]. The activity of Ag_2WO_4-MgO catalysts; which are used for microanalysis of hydrocarbons by oxidation has been studied by XPS/ESCA methods. The binding energies of Ag, W, and Mg in the catalyst were determined and the results used to estimate the activities of the catalysts [159]. The use of WCl_6-Ph_4Sn based catalysts for metathesis has been studied in two papers which looked at the reaction of WCl_6 with Ph_4Sn, Ph_3SnCl, and Ph_2SnCl_2 and the kinetics of the reaction between WCl_6 and Ph_4Sn in benzene; the reactions were monitored using UV/visible spectroscopy [160,161]. The fundamental properties of 12-heteropolyacids of molybdenum and tungsten, (such as structure, the surface area, the acidity and the redox mechanism) have been studied in the solid state in relation to heterogeneous catalysis. The primary structure of the heteropolyanion was considered to be rather stable, but the secondary structure appears to be variable, according to the interaction with various molecules like water, alcohols, ketones, and pyridine. This structural characteristic is important for the understanding of the catalysis of these compounds. Multistep thermal analysis of alumina supported $[M(CO)_3X_2L_2]$ (M = Mo or W; X = Cl or Br; L = PPh_3 or $AsPh_3$) complexes has been attempted. Thermolysis products of molybdenum chlorides were inactive for propene metathesis, while tungsten complexes gave active catalysts, when heated at 70-120°C in a vacuum. Based on IR, DTA, kinetic and stereochemical considerations, two isomers of the $[W(CO)X_2L_2]$ species, having no direct link with the alumina, are assumed to be the active species [163]. A spectroscopic study of $[W(CO)_6]$ absorbed MgO has been published. The $[W(CO)_6]$ attaches itself to the surface as $Mg[(CO)_5W(CO_2)]$. Progressive decarboxylation of the anchored metal carbonyls produces low nuclearity carbonyl clusters and metal particles [164].

2.10 NITROSYL COMPLEXES

Passage of a slow stream of NO through a C_6H_6 solution containing $[W(CO)_5L]$ (L = triazoline-5-thiones) gives dimeric $[W(NO)_3L]_2$ complexes, which contain four terminal and two bridging nitrosyl ligands and their IR spectra have been reported [165]. On reaction with alkoxides, hydrazine, or zinc, the 18-electron nitrosyl complexes $[(cp)W(NO)_2L]^+$ (L = $P(OPh)_3$, PPh_3, or $P(OMe)_3$) undergo a one-electron reduction giving the purple air-sensitive, 19-electron neutral compound, $[(cp)W(NO)_2L]$. The ESR spectra of these neutral compounds contain a 10 line pattern resulting from hyperfine coupling of the unpaired electron with ^{31}P and the two inequivalent ^{14}N nuclei. The ν(N-O) frequencies decrease by 160-175cm^{-1}, on going from the cationic to the neutral complexes, suggesting that the extra electron is added, primarily, to the NO groups [166]. WCl_6 reacts with NO in the presence of CH_2Cl_2 and MeCN to give $[W(NO)Cl_3(MeCN)_2]$ which, when treated with L(=PPh_3, tricylcohexylphosphine, $AsPh_3$, or $OPPh_3$) in CH_2Cl_2 gives $[W(NO)Cl_3L_2]$ [167]. The series of complexes *trans* -$[WX(NO)(dppe)_2]$ (X = NCO, OH, or H) have been obtained by the reaction of *trans*-$[W(N_2)(dppe)_2]$ with $MeN(NO)CONH_2$ in THF (X = NCO), or THF/MeOH (X = H), or Et_2NNO in THF/K_2CO_3 (X = OH). The related complexes (where X = N_3, Cl, Br, I, or NCS) can be obtained by metathesis, while oxidation gives $[WI(NO)(dppe)_2]I_3$ (from I_2) or $[WX(NO)(dppe)_2]Y$ (Y = $FeCl_4$, $CuCl_2$, or BF_4] [168]. A description of the preparation of the complexes, $[W(HBL_2L')(NO)BrL'']$ (L = 3,5-dimethylpyrazolyl, L' = 4-bromo-3,5-dimethylpyrazolyl, L" = H_2, NHCHMe, $NHCH_2Ph$) has appeared in a paper describing the preparation of many similar molybdenum complexes [169]. The preparation of other complexes of the same type, $[W\{HB(Me_2pz)_2(Me_2Brpz)\}(NO)LL']$ (Me_2pz = 3,5-dimethylpyrazolyl, Me_2Brpz = 3,5-dimethyl-4-bromopyrazolyl; L = Br; L' = OMe or OEt, $OCHMe_2$; L = L' = OEt) has also been published [170] *cis*-$[M(R_2dtc)_2(NO)_2]$ complexes (M = Mo or W; R = Me or Et, *i*-Pr, *n*-Bu, Bz, or pyridine) undergo a reversible one-electron reduction to give the radical anion $[M(R_2dtc)_2(NO)_2]^-$. ESR studies have shown that the unpaired electron is delocalised over both nitrosyl groups, but no metal hyperfine couplings were observed [171].

2.11 CARBONYL COMPLEXES

The chemistry of carbonyl fluoro complexes of several transition metals, including molybdenum and tungsten, has been reviewed [172].

Refluxing Ph_3P, $[BH_4]^-$ and $[(Ph_3P)_2N]$ $[W(CO)_5I]$ in THF has produced $[(Ph_3P)_2N]_2$ $[H_2W_2(CO)_{10}]$ in 65% yield and reaction of the dianion with BH_3. THF in THF gave approximate D_{2h} symmetry and contains a planar $W(\mu\text{-}H)_2W$ bridge (W...W = 3.010Å). The two bridging hydrogen atoms are displaced slightly from the intersections of the *trans* CO-metal vectors in the direction of the metal-metal axis [173].

The dinuclear pentacarbonyl complexes with paramagnetic bridging ligands $[L\{M(CO)_5\}_2]^-$ have been prepared and the metal carbonyl coordination established using high resolution ESR spectroscopy, which also provided data on the spin distribution and on the conformation of the radical complexes [174]. The photochemical disproportionation of $[(cp)_2W_2(CO)_6]$ has been studied and it is suggested that the reaction proceeds neither by homolytic nor heterolytic cleaveage of the metal-metal bond but *via* the formation of a carbonyl bridged intermediate [175].

^{13}C NMR and IR spectroscopy have been used to establish that in the complex $Li_2[W(CO)_5(CO_2)]$ contains an η^1-CO_2 ligand. When the CO_2 complex was formed, from a 1:1 mixture of $^{13}CO_2$ and $C^{18}O_2$, subsequent conversion to $[W(CO)_6]$ by reaction with CO demonstrated that there was extensive intermolecular exchange of O atoms after a few hours in solution at 0°C, suggesting that transfer of the nucleophilic oxide ions from coordinated CO_2 to coordinated CO is facile in anionic CO_2 complexes [176].

Variable temperature ^1H NMR spectroscopy of the mononuclear complexes $[M(CO)_5(Me_3SiCH_2EECH_2SiMe_3)]$ (M = Cr, Mo or W; E = S or Se) has established the occurrence of two distinct fluxional phenomena; the first in the not unexpected-pyramidal inversion about the coordinated S or Se atoms but, at higher temperatures, a novel 1,2-metal shift between the two ligand atoms of the disulphide or diselenide occurs [177]. A variable temperature ^1H NMR study on the complexes $[M(CO)_5L]$ (M = Mo or W; L = 1,8-naphthyridine or phthalzine) has shown low temperature structures involving strong metal coordination to only one of the *N* donor sites on the L ligand but, at higher temperatures, rapid exchange of the $M(CO)_5$ group between the two *N* sites occurs [178]. $S_4N_4H_4$ reacts with $[(THF)M(CO)_5]$ (M = Cr, W) giving isolable complexes of the type $[(S_4N_4H_4)M(CO)_5]$ and $[(S_4N_4H_4)\{M(CO)_5\}_2]$. ^1H NMR spectroscopy and X-ray studies have shown that the metal is coordinated to a S atom [179].

^{95}Mo and ^{183}W NMR spectra have been measured by direct observation and by multiple resonance methods for 65 related derivatives of $[W(CO)_6]$ with (mainly) phosphorus donor ligands. The chemical shifts are temperature dependent and trends in these can be largely accounted for by variations in mean electronic excitation energy [180]. Exposure of tetraalkylammonium salts of $[M(CO)_5I]^-$ (M = Cr, Mo, W) in methyltetrahydrofuran to ^{60}Co γ-rays at 77K gives electron addition products, which have been characterised by ESR spectroscopy. These products exhibit large hyperfine coupling to the halogen and metal nuclei. In all cases, the extra electron appears to be in the metal-halogen σ^*-orbital. For the tungsten complex, a species exhibiting additional hyperfine coupling to a single proton was detected [181] $[Hg\{PPh_2(M(CO)_5)_2\}]$ (M = Cr, Mo or W), prepared by mercuration of $[M(CO)_5(PPh_2H)]$ with $Hg[N(SiMe)_2]$, has been characterised, using ^{31}P and ^{199}Hg NMR and mass spectroscopy [182].

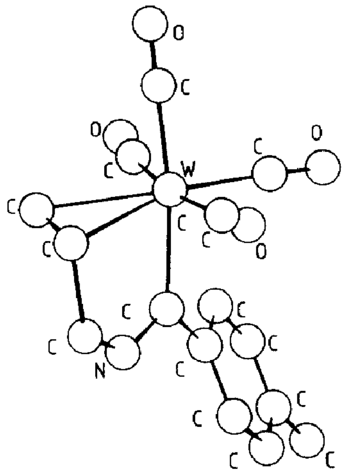
The luminescence spectrum of $[W(CO)_5py]$ is associated with the ground state normal mode having a frequency of 550cm^{-1}; surprisingly there are no totally symmetric infrared or Raman bands at or near 550cm^{-1}. An explanation of the missing mode effect (MIME) has been given [183]. Luminescence data have been recorded for the complexes, $[W(CO)_5L]$ (L = 4-acetylpyridine, 4-benzolypyridine, 4-cyanopyridine, or 4-formylpyridine) as solids and in fluid solution. From the temperature dependence of the emission and photoreactivity processes, the apparent activation energies of $[W(CO)_5L]$ complexes in several solvents have ben estimated. Excited state absorption and primary photoproduct spectra have been recorded for the $[W(CO)_5L]$ complexes in methylcyclohexane and benzene. A common photoproduct is inferred, its spectrum being close to that of $[W(CO)_5S]$ (S = solvent) [184].

The structure of $[(CO)_5WP\{P(O)(OC_2H_5)_2\}_2SnCl]$ has been published; the W-P bond distance is 2.573A [185]. Tetraphenyldiphosphine monoxide forms complexes of the type $[M(CO)_5(Ph_2P.P(O).Ph_2)]$ (M = Cr, Mo or W) which, on heating in diglyme, loss of CO and the diphosphine oxide ligand tautomerises into the chelating diphosphoxane ligand, the product being identified as *cis*-$[M(CO)_4(PPh_2OPPh_2)]$. Reaction of excess OP_2Ph_4 with *cis*-$[M(CO)_4L_2]$ (L = piperidine) gives H-bonded heterocycles of the type *cis*-$[M(CO)_4(PPh_2P(Ph_2)O...L)]$ [186]. The central P atom of the anion in piperidinium bis(diethoxyphosphinoyl)phosphide acts as an electron donor towards one or two $W(CO)_5$ groups, forming $[W(CO)_5\{(EtO)_2P(O)PP(O)(OEt)_2\}]^{2-}$; NMR and IR spectroscopy, as well as X-ray diffraction data, have been presented [187]. Vinyl addition reactions have been used to control ligand coordination and an outline of five possible nonchelated triphosphine $(Ph_2PCH_2CH_2PPhCH_2CH_2PPh_2)$ complexes of pentacarbonyltungsten given [188]. The structure of $[(CO)_5W(PhP.CPh:CPh)]$ has been reported as an example of a stable phosphinee complex [189]. Several $(CO)_5W$-sulphur derivatives have been described, including the structure of $[Na(18\text{-crown-}6)][W(CO)_5SH]$ obtained by UV-irradiation of $W(CO)_6$, $Na_2S.9H_2O$ and 18-crown-6 in absolute ethanol [190]. The preparation and characterisation by IR, UV/Vis., NMR and mass spectra of thioketone complexes $[(CO)_5W\{S:C(C_6H_4R4)Ph]$ (R = H, OMe, Me, Br, or CF_3) [191] and a dynamic NMR study of the mononuclear complexes $[W(CO)_5L]$ (L = $MeSCH_2SMe$, $MeSeCH_2SeMe$, or $MeSCH_2SeMe$) have been reported. These mononuclear complexes possess a novel fluxional character which, from the dynamic NMR study, has been interpreted as intramolecular 1,3-metal jump between ligand atoms. This study also provided an indication of the relative strengths of $S \rightarrow W$ and $Se \rightarrow W$ bonds [192].

$[M(CO)_5SC(O)H]^-$ (M = Mo, Cr, or W) complexes have been prepared *via* COS insertion reactions into M-H bonds. Unlike their formate analogues, these derivatives show no tendency to extrude COS with concomitant $[HM(CO)_5]^-$ formation [193]. K_2SN_2 reacts with $W(CO)_6$ producing $K[W(CO)_5(NCO)]$ [194].

Monomeric and dimeric derivatives of the type $[W(CO)_5L]$ and $[\{W(CO)_5\}_2L]$ (L = bipy) have been synthesised by a method involving the photochemical generation of the intermediate solvent adduct $[W(CO)_5THF]$. The monomers and dimers were characterised by HPLC, ^1H NMR, ^{13}C NMR, elemental analysis, and electronic spectroscopy. The metal-to-ligand charge-transfer absorption band in the electronic spectrum occurs at a much lower energy than the ligand field band at 405nm for the dimers $[\{W(CO)_5\}_2L]$ (L = bipy or 1,2-bis(4-pyridyl)ethglene) [195]. The structures of $[PNP][W(CO)_5O_2CCH_3]$ **(1)** and [PNP] $[W(CO)_4(PEt_3)(O_2CCH_3)]$ **(2)** have been determined by X-ray crystallography. The anion in **(2)** is a distorted octahedron with a arrangement of the PEt_3 and acetate ligands. $[W(CO)_5(O_2CCH_3)]$, in solution, loses equatorial CO readily and stereoselectively, at ambient temperature; this is in contrast to $[W(CO)_4(PEt_3)(O_2CCH_3)]$ which does not [196].

Allylamine and 1-amino-3-butene reacts with $[(CO)_5WC(OMe).C_6H_4CH_3\text{-}4]$ to produce $[(CO)_5WC(NHCH_2CH{=}CH_2)C_6H_4.Me\text{-}4]$ ((Z)-**3** and (E)-**3**) and $[(CO)_5WC(NHCH_2CH_2CH{=}CH_2)C_6H_4Mo\text{-}4]$ ((Z)-**4** and **(E)-4**) as mixtures of isomers about the carbene carbon-nitrogen partial double bond. The alkene units in **(3)** and **(4)** are not coordinated to the W atom. Thermolysis or photolysis of a mixture of **(Z)-3** and **(E)-3** led to the formation of $[(CO)_4WC(NHCH_2CH{=}CH_2)(C_6H_4Me\text{-}4]$ a stable tungsten-carbene-alkene complex, in which the alkene and carbene ligands are perpendicular to each other **(8)** [197]. A variety of tetraazaadamantane (taad) derivatives of Group(VI) metal hexacarbonyls have been prepared, including $[(taad)N(CO)_5]$. The complexes were indentified by elemental analysis, IR spectroscopy, conductivity, and magnetic measurements [198]. $[M(CO)_5(THF)]$ (M = Cr or W), $[M(CO)_4L]$ (L = norbornadiene), $[Cr(CO)_6]$, and $[W(CO)_3(MeCN)_3]$ have been reacted with 3,3,4,4-tetramethyl-1,2-diazetine (Q) or its mono-*N*-oxide (Q') to produce $[QM(CO)_5]$, $[Q_2M(CO)_4]$, $[QM_2(CO)_{10}]$, $[Q_2M_2(CO)_8]$ or $[Q'M(CO)_5]$, and $[Q_2'M(CO)_4]$. The stability of these complexes and others of the N=N group is resulted to the ring size of the cyclic diazene ligand [199]. ^1H NMR and IR spectroscopy have



8)

indicated that triazole acts a monodentate ligand in the complexes [W(CO)$_5$L] (L = 4-Me- or 4-phenyl-1,2,4-triazole), whose synthesis was reported. The ^{1}H NMR spectra showed strong solvent dependence and the temperature dependence of [W(CO)$_5$L] (L = 4-phenyl-1,2,4-triazole) was also examined [200]. Stable crystalline salts of the dianions [M(CO)$_5$]$^{2-}$ (M = Mo or W) have been prepared by complexing the Na$^+$ counterion with a cryptand [201]. IR spectroscopy has been used to characterise the newly synthesised carbonyl clusters [M(CO)$_5$Sn{M(CO)$_4$}$_2$] (M = Cr or W; M' = Mn, or Re) clusters [W(CO)$_5$Sn{Co(CO)$_4$}$_2$] [202].

The tetracarbonyl tungsten complexes, [WI$_2$(CO)$_4$L] (L = PMe$_3$, AsMe$_3$, or SbMe$_3$) and [WBr$_2$(CO)$_4$L] (L = PMe$_3$, or AsMe$_3$) have been isolated by oxidative addition of Br$_2$ and I$_2$ to [W(CO)$_5$L], while the complexes [WI$_2$(CO)$_4$L] (L = PBu$_3$, NMe$_3$, NEt$_3$, or SMe$_2$) have been identified spectroscopically. The bromo complexes are reversibly converted to [WBr$_2$(CO)$_3$L]$_2$ by CO elmination and the coordination geometry of [WI$_2$(CO)$_4$(PMe$_3$)] in the crystal is that of a capped octahedron with a CO ligand in the capping position and *facile* arrangement of I and PMe_3 ligands [203]. IR and ^{13}C studies have confirmed a *cis* arrangement of the hydride and *P*-donor ligand in the complexes $[PPN][HW(CO)_4(PR_3)]$ (R = Me, OMe, or Ph), which are obtained by careful protonation of $[W(CO)_4(PR_3)]^-$. Their reactions with CO_2 and protic, main-group and transiton-metal Lewis acids have also been described [204]. A number of tetracarbonyl tungsten complexes with SO_2 have been described; *cis*-$[W(CO)_4L(SO_2)]$ (L = PPh_2Me, PMe_3, or $P(OMe)_3$) in which the SO_2 is η^1-planar coordinated and *fac*-$[(\eta^2\text{-}SO_2)M(CO)_3(Ph_2PCH_2CH_2PPh_2)]$ [205]. Further comments have appeared concerning one-electron oxidation versus nitrosyl complex formation during the reactions of the nitrosyl cation with metal carbonyl derivatives such as $[W(CO)_4L]$ (L = $(Ph_2P)_2CH_2$ or $(Ph_2PCH_2)_2$). Indirect evidence has been obtained for the formation of a seven-coordinate intermediate $[W(CO)_4(NO)L]^+$ [206].

Heating $[W(CO)_4\{Ph_2PCH(COPh)PPh_2\}]$ with H_2NNH_2 in ethanol for a few hours causes the four-membered chelate ligand to expand to a seven-membered chelate ligand $[W(CO)_4\{Ph_2PNHN{:}C(Ph_2)CH_2PPh_2\}]$ (1). The structure of (1) has been determined by X-ray crystallography and the mechanism of ring expansion discussed in terms of an enolate intermediate [207]. Deprotonation of $[M(CO)_4(Ph_2PCHRPPh_2]$ (R = H; M = Cr, Mo, or W) with LiBu in the presence of $(Me_2NCH_2)_2$, followed by treatment with MeI, EtI, $CH_2{=}CHCH_2Cl$, $PhCH_2Cl$, Me_3SiCl, Ph_2PCl, or BzCl gives the corresponding C-substituted complexes $[M(CO)_4(Ph_2PCHRPPH_2)]$ (R = Me, Et, $H_2C{=}CHCH_2$, $PhCH_2$, Me_3Si, Ph_2P, or PhCO) [208].

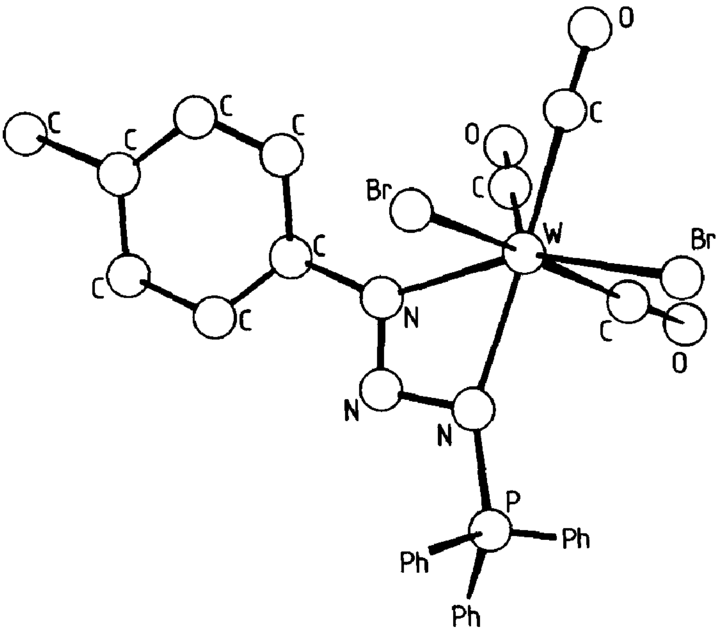
The chelating and monodentate coordination modes of the tetraphenyldiphosphoxane (Ph_2POPPh_2) ligand in complexes such as *cis*-$[W(CO)_4(Ph_2POPPh_2)]$ have been discussed [209]. ^1H and ^{13}C NMR spectroscopy has been used to study the metal complexes of the ligand L-L (= $Ph_2ECH_2CMe_2CH_2EPh_2$; E = P or As) such as $[W(CO)_4(L\text{-}L)]$ and $[Mo(CO)_4(L\text{-}L)]$. This study has shown that a rapid chair-chair interconversion of the six-membered metal chelate ring system results in the apparent equivalence of the phenyl groups, this methyl groups and the methylene proton [210].

The light intensity normally found in a laboratory was sufficient to transform the four-membered ring chelate [$W(CO)_4\{PH_2CH(COPh)PPh_4\}$] into the six-membered ring chelate [$W(CO)_4\{Ph_2P(O)C(Ph)=CH.PPH_2\}$] which, on hydrolysis, gave [$W(CO)_4(PPh_2OH)(PPH_2CH_2COPh)$]. Neither reaction proceeded in the absence of light [211]. The ligand $(Et_2N)_2P(CH_2)_4P(NEt)_2$ (= L) has been used to prepare several tungsten(0) complexes such as *cis*-[$W(CO)_4L$], [$(CO)_5W.L.W(CO)_5$] and *cis*-[$(CO)_4W\{Et_2N(Br)P(CH_2)_4P(Br)NEt_2\}$]. The NMR, IR, and mass spectra of these complexes have been discussed [212].

The resonance Raman spectra of [$W(CO)_5L$] (L = 1,2-bis(arylamino)ethane or 1,2-bis(propylamino)ethane), obtained by excitation of the lowest absorption band, have been reported. It would appear that an increase in the π-back bonding from the metal to the di-imine ligand is accompanied by a decrease of the resonance Raman effect for the symmetrical stretching modes of the ligand with respect to the metal-ligand stretching modes [213]. Rapid scan FT IR spectroscopy has shown that the photochemical formation of [$W(CO)_4(4,4'\text{-}R_2\text{-bipy})$] (R = Me or *n*-$C_{19}H_{39}$) from [$W(CO)_6$] occurs *via* [$W(CO)_5(4,4'\text{-}R_2\text{-bipy})$], where the normally bidentate ligand is coordinated in a monodentate fashion [214]. Microanalysis and IR, ^1H and ^{13}C NMR and UV/visible spectroscopy have been used to characterise a series of 2,2'-byrimidine (bpym) complexes [$MoM(CO)_8(bpym)$] (M = Cr, Mo or W) [215]. A study of the donor properties of [$W(CO)_4(py)_2$] has been reported, in particular, its reaction with *cis*-α-nitrostilbene [216].

A variety of complexes of the type [$W(CO)_4L$] and [$\{W(CO)_4\}_2L$] have been prepared and characterised, where the ligand (L) is a series of aromatic 2-bis(methylthio)ethers (e.g. $C_6(SMe)_6$) [2.7]. [$W(CO)_6$] reacts with potassium ethylxanthate (KL) or sodium diethylcarbamate (NaQ) in deoxygenated DMSO at 60-65°C to give *cis*-[$W(CO)_4L]^-$ and *cis*-[$W(CO)_4Q]^-$, respectively. These complexes have been characterised using IR spectroscopy [218]. Several mononuclear and binuclear tungsten carbonyl derivatives of (alkylamino)bis(difluorophosphines), $RN(PF_2)_2$ (R = Me or Ph) have been reported and studied using infrared, and ^{31}P and ^{19}F NMR spectroscopy. ^1H and ^{13}C NMR spectroscopy was used to distinguish between monodentate and bidentate $MeN(PF_2)_2$ ligands [219].

The structures of the compounds $[cpFe(C_5H_4COCH_2)W(CO)_3cp]$ and $[(CO)_3Mn(\mu\text{-}C_5H_4COCH_2)W(CO)_3cp]$ have been reported [220]. Orange, seven-coordinate complexes $[W(S_2CNR_2)_2(CO)_3]$ (R = Me or Et) have been prepared by the reaction of $[W(CO)_4Br_2]$ with $Na[S_2CNR]$. On refluxing, the tricarbonyl complexes are converted to the coordinatively unsaturated complexes $[W(S_2CNR_2)_2(CO)_2]$, which can be used to produce new carbonyl dithiocarbamate complexes of tungsten such as $[W(S_2CNR_2)_2(CO)_2L]$ (L = NH_2NHMe, NH_2NMe_2, NH_3, $NH_2NHCOPh$, py, $NH_2NHSO_2C_6H_4Me$, or PPh_3). ^1H NMR and IR spectra of the complexes have been presented [221] $[WBr_2(CO)_3(RN_3{=}PPh_3)]$ (R = 4-tolyl) has been obtained by reacting RN_3 with $[WBr_2(CO)_3(PPh_3)]$ in dry CH_2Cl_2 at 20°C and its structure determined. It is monomeric and seven-coordinate, with the phosphazide ligand bound to the W atom *via* the α- and γ-nitrogen atoms (**9**) [222].



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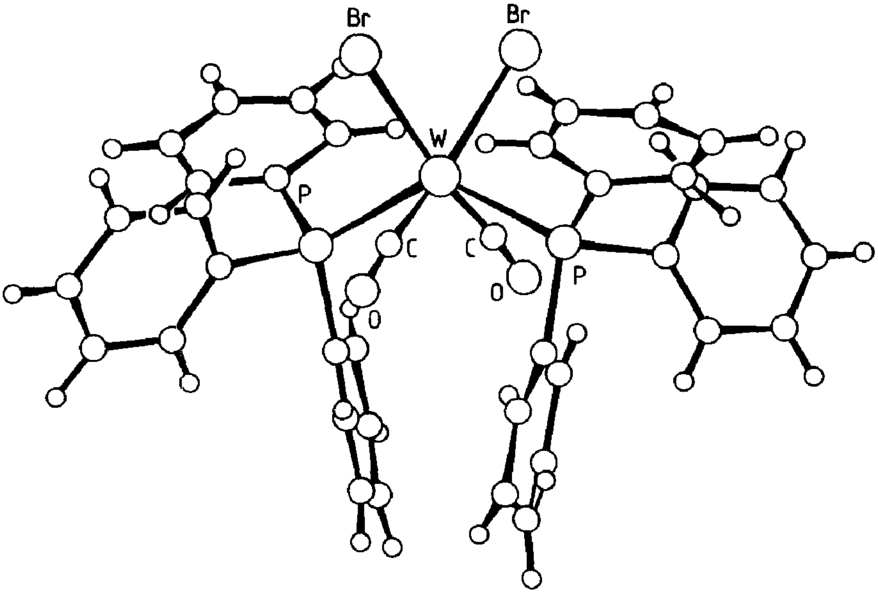
The preparation of a number of seven-coordinate tungsten complexes has been described; these are of the type $[WX_2(CO)_3LL']$ (X = I, Br, or Cl, L =

PMe_3, $AsMe_3$, or $SbMe_3$; L' = L, $AsMe_2H$, $P(OMe)_3$ PPh_3, py, or I) [223]. The decarbonylation of $[W(CO)_6]$ by $[RhCl(PPh_3)_3]$ in MeCN at 80°C has been achieved, giving complexes formulated as $[W(PPh_3)_x(MeCN)_{3-x}(CO)_3]_x$ $(x = 1,2)$. A mechanism for the decarbonylation was proposed [224].

Bulk and transient electrochemical methods have revealed a novel chain process for the ligand substitution of metal complexes. The large turnover numbers that obtained for the ligand substitution of $[W(CO)_3(MeCN)_3]$ with phosphines and isocyanides underscore an electrocatalytic phenomenon. The efficient chain process derives from the substitution lability of the cation radicals, which are formed by the one-electron oxidation of metal carbonyls and subsequently undergo rapid electron transfer [225]. It has been reported that cationic coordinatively unsaturated complexes such as $[cpW(CO)_3]^+$ induce methyl-CO insertion on a second metal centre and form an acetyl ligand bridging two centres [226]. The reactivity of several transition metal complexes towards liquid CO_2 has been studied, as a means of screening such complexes for their ability to bind CO_2. $[W(CO)_3(PCy_3)_2]$ reacts with wet $CO_2(l)$ to give $[WH(O_2COH)(CO)_3$ [227].

The photochemical transformation of $[W(CO)_2(S_2C_2Me_2)_2]$ to $[W(S_2C_2Me_2)_3]$ as a function of wavelength, solvent, and concentration has been described and a mechanism for the reaction was proposed [228]. Reaction of $[W(=CH_2)(PMe_3)_4Cl][CF_3SO_3]$ with CO gives the seven-coordinate cation $[W(CH_2PMe_3)(CO)_2Cl(PMe_3)_3]^+$, in which the stereochemistry around the tungsten atom approximates to a monocapped trigonal-prismatic geometry. One triangular face is occupied by a CO ligand and by the phosphorus atoms (P(1) and P(2)) of two PMe_3 ligands while the other face contains the phosphorus atom of the third PMe_3 ligand and disordered CO and Cl ligands. The CH_2PMe_3 ligand is linked to the tungsten atom (W-C = 2.305A) and occupies the capping position on the square face defined by P(1), P(2), and the disordered CO and Cl ligand [229]. The structure of $[W(CO)_2Br_2(PPh_3)_2]$ contains six-coordinate tungsten atoms, whose geometry is not octahedral or trigonal-prismatic (10) [230].



(10)

$[W(CO)_2(PPh_3)_2L_2]$ (LH = 8-quinolinol or picolinic acid) and $[W(CO)_2(PPh_3)_2L']$ ($L'H_2$ = *N*,*N*'-disalicylidene-1,2-phenylenediamine) have been prepared and characterised by IR and electronic spectroscopy [231]. The preparation and chemistry of the complexes $[cpW(SH)(PMe_3)(CO)_2]$ has been described [232]. Nucleophilic substitution reactions of *cis*-$[W(CO)_2(bipy)_2]$ by various unidentate (PR_3; R = OMe, Ph, or Bu^t) and bidentate (dppe) phosphorus and carbon (CNR; R = Et or 4-tolyl) donor ligands (L) have been investigated. The bipy ligand was displaced giving *cis*, *cis*-$[W(CO)_2L_2(bipy)]$ (L = CNEt) and *cis*-$[W(CO)_2L_4]$ (L = 4-tolyl), depending on the ligand, temperature, and solvent. The products were characterised by microanalysis, IR, ^1H, and ^{31}P NMR, electronic, and mass spectroscopy [233]. $[HB(pz)_3M(CO)_2N_2R]$ complexes react with PPh_3 in boiling xylene giving $[HB(pz)_3M(CO)(PPh_3)(N_2R)]$ (M = Mo or W; pz = 1-pyrazolyl; R = 4-tolyl or C_6H_4F-4) [234].

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