Coordination Chemistry Reviews, 80 (1987) 225–262
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

5 TUNGSTEN (1981)

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0010-8545/87/$13.30

INTRODUCTION

The material included in this review was obtained from reports published in primary research journals during 1981 and/or volumes 94 and 95 of Chemical Abstracts. The material follows on form the review [1] of the 1980 literature and is organised into sections following a similar scheme. The major classification is by oxidation state of tungsten, with additional sections dealing with specific areas which cut across several oxidation states.

A review has been published of the coordination chemistry of tungsten, with 346 references [2]. The 1976 annual survey of the organometallic chemistry of chromium, molybdenum and tungsten has been compiled [3].

Bond energy calculations have been made using thermodynamic data to establish relationships between bond energy and interatomic distance in complexes containing metal-halogen, metal-oxygen and metal-metal bonds, including WCl_4, WCl_5, WCl_6, W_2Cl_{10}, $(WSCl_4)_2$, W_3O_9, $WOCl_4$, WO_2Cl_2 and WO_3 [4].

5.1 TUNGSTEN(VI)

5.1.1 Tungsten Halides

The reaction between$[WF_6]$ and the azide ion N_3^- yields the adduct $[WF_6(N_3)]^-$, and exchange occurs *via* a displacement mechanism to give $[WF_7]^-$ and $[WF_5(N_3)]$ [5,6]. $[WF_6]$ reacts with PhOH to give $[WF_5(OPh)]$ and *cis*-$[WF_4(OPh)_2]$. In the presence of Et_2NH the reaction also produces *fac*-$[WF_3(OPh)_3]$, *cis*-$[WF_2(OPh)_4]$ and the cations *cis*-$[WF_4(OPh)(NHEt_2)]^+$ and *trans*-$[WF_2(OPh)_3(NHEt_2)]^+$. ^{19}F NMR spectroscopy was used to characterise the products [7]. The fluorides can be replaced in $[WF_6]$ by $(OTeF_5)^-$ by means of $B(OTeF_5)_3$ to yield complexes of general formula $[WF_n(OTeF_5)_{6-n}]$. The two compounds $[WF_5(OTeF_5)]$ and *cis*-$[WF_4(OTeF_5)_2]$ have been isolated and compounds with $n < 4$ identified by ^{19}F NMR spectroscopy [8].

Coordination compounds of $[WF_6]$ with benzhydroxamic acid of metal:ligand ratios 1 : 1.5 at pH 1 and 1 : 2 at pH 2.5-5 have been isolated and the formation of adducts between them and some organic compounds investigated [9]. $[WCl_6]$ reacts with $[MoO_2SO_4]$ to give $[WOCl_2]$, $[MoOCl_4]$ and SO_3. The reaction with $[WO_2SO_4]$ yields $[WOCl_4]$, $WO_2Cl_2]$ and SO_3 [10].

5.1.2 Oxo complexes

The infrared and electronic spectra of matrix-isolated [WOF_4], [$WOCl_4$] and [$WOBr_4$] have been recorded and interpretated [11]. The adduct $WOF_4.SbF_5$ has been obtained from the reaction of [WOF_4] with excess SbF_5, and characterised by Raman and mass spectra [12]. The reaction of [WOF_4] with KrF_2 at low temperatures yields the adduct $WOF_4.KrF_2$, shown by ^{19}F NMR and Raman spectra to contain Kr--F--W bridges [13].

The salt [NF_4][WOF_5] has been prepared from the reaction of [WOF_4] with [NF_4][HF_2] in anhydrous HF. It decomposes on heating to [WF_4][$W_2O_2F_9$], NF_3, OF_2 and [WF_6], and in dilute solutions of HF forms [$W_2O_2F_9$]$^-$. The syntheses and properties of $Cs_2[WO_2F_4]$ and $Cs[WF_6]$ were discussed [14]. ^{19}F NMR spectroscopy has been used to follow the reaction of imidazole (HL) with [WOF_4] to form [WOF_4(HL)] in which HL is *trans* to oxygen. In the presence of excess HL the product is converted to [H_2L][WOF_4L] with L *cis* to oxygen. Benzimidazole reacts in a similar manner [15]. The replacement of fluoride in [WOF_4(MeCN)] by oxygen-, sulfur- and nitrogen-containing ligands have been studied by ^{19}F NMR spectroscopy, and it was found that the ligands replace F^- *cis* to the W=O double bond [16].

New isomeric derivatives of [$WOCl_4$] and [WO_2Cl_2] have been prepared using K^+ and Ag^+ salts of ambidentate pseudohalides and nitriles. These were characterised by analyses and IR spectra, and a mechanism for the reaction proposed [17]. [$WOCl_4$] reacts on melting with MCl (M = K, Rb or Cs) to give free Cl_2 and $M_2[WOCl_5]$, characterised by IR spectra [18]. The thermal stabilities of $K_2[WO_2Cl_5]$ and $Cs_2[WO_2Cl_4]$ have been investigated and the heat and entropy of evaporation and sublimation of the caesium compound determined [19].

Two series of oxalate complexes containing $[WO_3(ox)]^{2-}$ and $[W_2O_5(ox)_3]^{4-}$ have been isolated and characterised by analyses, IR and thermogravimetric analyses [20]. The complex [WO_2L_2] (HL = propriohydroxamic acid) has been prepared in aqueous solution and characterised by spectrophotometry [21]. $K_2[WO_4]$ forms complexes with benzhydroxamic acid of metal:ligand ratios 1:1.5 and 1:2 in aqueous media of pH 1 and pH 2.5-5 respectively [9]. The ligand *N*-3-tolyl-4-methoxybenzohydroxamic acid extracts tungsten(VI) from the acidic aqueous media containing thiocyanate, forming a complex of composition 1:1:2 metal: thiocyanate:acid [22]. Complex formation between H_2WO_4 and tartaric acid was investigated to explain the optical activity of tartaric acid in the presence of constant amounts of tungstic acid. Three different complexes were postulated [23]. In solution of pH 8 chloranilic acid forms a complex with tungsten(VI) of stoichiometry 1:1 [24].

Two new tungsten(VI)-oxo complexes $[WO_2L_2]$ (HL = 8-hydroxquinoline and 8-mercaptoquinoline) have been synthesised, and electrochemical data collected for these compounds, and for $[WO_2X_2L]$ (X = Cl or Br; L = 2,2'-bipyridine or 1,10-phenanthroline) and $[WO_2(acac)_2]$ [25].

The alkylidene transfer reaction between $[WO(OCMe_2)_4]$ and $[Ta(CHCMe_3)(PR_3)_2Cl_3]$ (R = Me or Et) yields $[WO(CHCMe_3)(PR_3)_2Cl_2]$ and $[Ta(OCMe_3)_4Cl]$. A crystal structure determination of the PMe_3 tungsten complex revealed an octahedral molecule with the oxo- and alkylidene ligands mutually *cis*, the two chlorine groups *cis* and the phosphines *trans*. The PEt_3 analogue was found to be disordered [26]. Reaction of $[WO(CHCMe_3)(PEt_3)_2Cl_2]$ with $[Pd(PhCN)_2Cl_2]$ removed one phosphine ligand to yield $[WO(CHCMe_3)(PEt_3)Cl_2]$. The crystal structure showed the tungsten to have distorted trigonal-bipyramidal coordination the axial sites being occupied by the phosphine and one of the chloride ligands [27]. The reaction between $[(\eta^5\text{-}C_9H_7)_2WOCl_2]$ and $Na[S_2CNR_2]$ yields $[(\eta^5\text{-}C_9H_7)WO(S_2CNR_2)Cl]$ (R = Me, Et or $CHMe_2$). A similar reaction occurs with $Na[S_2CNRR']$ (R = Me, Et or $CHMe_2$; R' = cyclohexyl). Infrared spectra indicate the dithiocarbamate ligands to be bidentate, showing the tungsten atom to seven-coordinate [28].

5.1.3 Complexes with ligands derived from $[WO_4]^{2-}$

The mixed-valence compounds $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}O)_2WO_2]$, $[(\eta^5\text{-}C_5H_5)_2Mo(\mu\text{-}O)_2WO_2]$ and $[(\eta^5\text{-}C_5H_5)W(\mu\text{-}S)_2WS_2]$ have been made and their ^1H NMR and IR spectra reported [29]. Several complexes of the type $[M(WOS_3)_2]^{2-}$ and $[M(S_2CNEt_2)(WS_4)]^-$ (M = Ni, Pd or Pt) have been synthesised and characterised as tetraalkylammonium salts [30]. The preparation has been described of $[PPh_4]_2[M(WO_2S_2)_2]$ (M = Co or Ni) and their redox behaviour discussed in relation to their molecular and electronic structure [31]. The electrochemistry of $[Fe(WS_4)_2]^{2-}$ has been studied in solution, and a crystal structure obtained of the octahedral dimethylformamide adduct $[Ph_4P]_2[Fe(WS_4)_2(dmf)_2]$ [32].

5.1.4 Oxides, sulfides and homonuclear polyanions

A new tungsten trioxide hydrate, $WO_3.\frac{1}{4}H_2O$ has been prepared by hydrothermal treatment of tungstic acid gel or the crystallised hydrate, and crystallographically characterised [33]. A complex $WO_3.C_5H_6N$ has been reported which consists of layers of tungsten trioxide separated by layers of pyridine in which the nitrogen atoms are coordinated directly to the metal atoms [34]. The chemisorption and decomposition of substituted alcohols on tungsten trioxide has been investigated [35].

The existence of the heptatungstate ion $[W_7O_{24}]^{6-}$ has been established using infrared spectroscopy, and conditions for its production described [36]. The photochemistry and electrochemistry of some polyoxotungstates have been investigated and described [37]. A crystal structure determination of $[Bu_4N]_2[W_3OS_8]$ has shown it to contain two distorted WS_4 tetrahedra doubly bridged to a third tungsten(VI) atom in a square bipyramidal configuration with four sulfur atoms at the base and an apical oxygen atom [38]. The tetraalkylammonium salts $[R_4N]_2[WS_4]$ were found to decompose under variable conditions to give $[R_4N]_2[W_3S_9]$, characterised by chemical, thermoanalytical and spectroscopic techniques [39]. The reaction between $Na_2[WS_4]$ and H_2SO_4 has been investigated using pH and conductivity measurements. Three species $[W_4S_{15}]^{6-}$, $[W_2S_7]^{2-}$ and $[W_4S_{13}]^{2-}$ were formed at pH 6.2, 4.4, and 2.7 respectively. At pH $<$ 2.4 hydrated WS_3 was formed [40]. Structural determinations of two new complex polyanions have revealed unusual coordination geometry of the tungsten atoms. In $[Ph_4P]_2[W_4S_{12}]$ two atoms of tungsten(VI) are in tetrahedral sulfur environments, with two tungsten(V) atoms in trigonal bipyramidal sulfur environments. In $[Ph_4P]_2[W_2OS_8H_3]$ one tungsten atom is octahedrally coordinated to six sulfur atoms and the other is in a trigonal bipyramidal site. Both $[S]^{2-}$ and $[S_2]^{2-}$ ligands are present, the latter acting as a chelate and a bridge [41].

5.1.5 Heteronuclear polyanions and ternary phases

The photochemistry of some heteropolynuclear compounds of tungsten and molybdenum has shown that they can be reduced by multielectron excitation at the O-M charge transfer band followed by intermolecular electron or hydrogen transfer [42]. The Raman spectra of phases obtained by cooling molten mixtures of $Na_2[Mo_2O_7]$ and $Na_2[W_2O_7]$ are in agreement with expectations for formation substitutional phases $Na_2[Mo_{2-x}W_xO_7]$ with statistical distribution of tungsten and molybdenum atoms [43].

The preparations have been reported of $H_5[H_2W_{12}FO_{39}]$, $H_4[H_2W_{12}F_2O_{38}]$, $H_5[HW_{12}F_2O_{38}]$ and $H_4[HW_{12}F_3O_{37}]$. They all have a structure related to that of $[H_2W_{12}O_{40}]^{6-}$ [44]. In acidic aqueous media the fluorophosphates of the type $[HW_{12}F_nO_{40-n}]^{(7-n)-}$ (n = 1, 2 or 3), having one central proton, exhibit stabilities that evolve in a continuous manner as the number of fluorine atoms in the structure diminishes. The kinetics of protonation of these species has been studied [45]. In aqueous media at low pH $[H_2W_{12}F_2O_{38}]^{4-}$ and $[HW_{12}F_3O_{37}]^{4-}$ are hydrolysed to give $[HW_{12}F_2O_{38}]^{5-}$ and $[HW_{12}FO_{39}]^{5-}$. ^1H and ^{19}F NMR spectroscopy has been used to investigate how the F^- ions are lost [46]. The ^{183}W NMR spectra of $[H_2W_{12}FO_{39}]^{5-}$ and β-$[SiW_{12}O_{40}H_4]$ have been recorded, and $^2J_{W-W}$ coupling was detected between the inequivalent tungsten atoms [47].

The ^{17}O and ^{183}W NMR spectra of ethanenitrile solutions of salts containing $[(RPO_3)_2W_5O_{15}]^{4-}$ have shown this anion to exhibit intramolecular exchange behaviour [48]. Three new tungstophosphates $Cs_6[W_5P_2O_{36}]$, $Cs_7[W_{10}PO_{36}]$ and $Cs_7Na_2[W_{10}PO_{37}]$, have been prepared and the crystal structures obtained of the first two [49]. The anion $[W_{12}PO_{40}]^{3-}$ can be alkylated using $[Me_3O][BF_4]$ to yield $[(MeO)W_{12}PO_{39}]^{2-}$, in which a bridging oxygen atom is alkylated rather than a terminal oxygen [50]. The temperature dependance of the line widths in the ^1H and ^{31}P NMR spectra of $H_3[W_{12}PO_{40}]$ has been investigated. Analysis of the spectra showed the complex to exhibit reorientational mobility in its structure [51]. Several new mixed-metal phosphates of general formula $[W_{18-n}Mo_nP_2O_{62}]^{6-}$ (n = 2, 4 or 5) or $[W_{17-n}Mo_nP_2O_{61}]^{10-}$ (n = 1, 4 or 5) have been prepared and locations of the Mo atoms and vacant sites proposed [52].

^{183}W NMR and X-ray crystallography have been used to determine the structure of $H_2Rb_4[W_{21}As_2O_{69}(H_2O)].34H_2O$. The anion is made of two W_9AsO_{33} units joined asymmetrically by three tungsten atoms one of which is octahedrally coordinated and the other two are in a square-pyramidal environment [53]. Variable temperature EPR spectra of several polyanions of tungsten, including $[W_{18}As_2O_{62}]^{7-}$, $[H_2W_{18}AsO_{62}]^{5-}$ and $[W_5NbO_{19}]^{4-}$ have indicated that the unpaired electron is in an isolated metal site at temperatures below 30 K and delocalised at higher temperatures [54]. A semi-classical theoretical model has been developed to interpret the properties of mixed valence heteopolyanions containing an unpaired electron, such as $[W_9Mo_3SiO_{40}]^{5-}$ [55]. The thermal degradations of 12-tungstophosphoric acid, 12-tungstosilicic acid and 12-tungstaboric acid have been followed using IR spectroscopy and X-ray diffraction. The results indicate that WO_3 is formed at 620, 530, and 420 ˚C respectively [56].

The preparation of $[W_{12}AlO_{40}]^{5-}$ has been monitored by ^{27}Al NMR spectroscopy, which identified four different species in the reaction mixture [57]. The formation and reduction of tungsten heteropolycomplexes of indium have been studied photometrically [58].

A rational synthetic route to the anions $[P_2W_{18}M_4(H_2O)O_{68}]^{10-}$ (M = Co, Cu, Zn) has been devised, and the complexes characterised using ^{183}W NMR spectroscopy [59]. The conditions for the synthesis of isomers of cobalt and nickel tungstosilicates have been investigated, and their stabilities in acids and bases determined [60]. X-ray photoelectron spectroscopy has been used to determine electron bonding energies in complexes containing $[SiW_{11}MO_{39}]^{n-}$ and $[W_{12}MO_{40}]^{m-}$ (M = 3d element). The results were discussed and compared with magnetic data [61]. $[Bu_4N]^+$ salts of $[W_{12}MO_{40}]^{n-}$ anions (M = Fe, Co, Cu), with central transition metal ions in a tetrahedral oxygen environment, have been prepared, and their spectroscopic properties recorded [62]. Heteropolytungstates containing titanium and nickel in the ratios 1:1:11 and 1:1:5 (Ni:Ti:W) have been prepared from the reaction of $Na_2[WO_4].2H_2O$, $TiCl_4$ and $Ni(NO_3)_2$ in aqueous solution at controlled pH [63].

The vibrational spectra of Ln_2WO_6 (Ln = Sm, Eu, Tb, Dy, Ho, Er, Lu or Pr) have been recorded and interpreted [64]. The solid phase reaction between UO_3, WO_3 and MNO_3 (M = Na, K, Rb, Cs) was found to yield $M_2[UO_2(WO_4)_2]$, characterised by IR and luminescence spectroscopy, X-ray phase analysis and differental thermal analysis [65]. Stable heteropolyacids having ratios P:U:Mo:W of 1:1:3:8 and 2:1:6:16 have been identified in dilute solutions, and reduced complexes having ratios 2:1:6:16 and 2:1:10:12 have been produced. A new complex with a ratio 2:1:2:20 has been isolated and characterised by UV, IR and EPR spectroscopy [66].

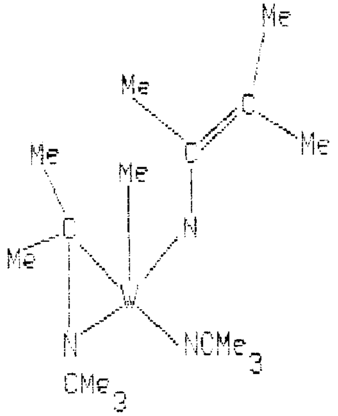
The properties have been investigated of phases in the mixed oxide systems WO_3-SrO-B_2O_3 [67], WO_3-BaO-Nb_2O_5 [68], WO_3-BaO-Sb_2O_5 [69], WO_3-BaO-Se_2O_5-Re_2O_5 [70], WO_3-BaO-Ln_2O_3-MgO, WO_3-BaO-Ln_2O_3-Y_2O_3 and WO_3-SrO-Ln_2O_3-Gd_2O_3 (Ln = Pr, Sm, Eu, Tb, Dy, Ho, Er or Tm) [71].

5.1.6 Complexes with sulfur or nitrogen bound ligands

A photometric method has been described for the determination of successive and stepwise formation constants in the 1:4 tungsten-maleonitrile dithiolate system [72]. ^{19}F NMR has been used to study the replacement of F^- in $[WOF_4.MeCN]$, $[W(NBu)F_5]^-$ and $[W(NCOCH_2)F_5]^-$ complexes by EtOH, ethyleneglycol, BuSH and Et_3N. It was found that the oyxgen-, sulfur-, and nitrogen-containing ligands replaced the F^- *cis* to the W–O or W–N multiple bond [16]. The complex $[WNCl_3(bipy)]$, containing a W–N triple bond, has been prepared and characterised [73]. The reaction of phenylimidotungsten tetrachloride with dimethylmagnesium in the presence of trimethylphosphine yields $[W(NPh)(\mu\text{-}O)Me_2(PMe_3)]_3$. A crystal structure determination revealed the complex to be an oxo-bridged trimer no metal-metal bonds [74].

5.1.7 Complexes with a tungsten-carbon bond (excluding carbonyls)

The reaction of $[WOCl_4]$ with excess $1,2\text{-}C_6H_4(CH_2MgCl)_2$ yielded $[W(CH_2\text{-}1\text{-}C_6H_4\text{-}2\text{-}CH_2)_3]$. A crystal structure determination showed the 1,2-xylidene ligand planes aligned parallel to the molecular axis [75]. $[WCl_6]$ reacts with $LiCH_2SiMe_3$ at - 78 °C to give $[(Me_3SiCH_2)_3W{\equiv}CSiMe_3]$ which has been characterised by analyses and by IR, ^1H and ^{13}C NMR, and mass spectroscopy [76]. $[WMe_6]$ reacts with Me_3CNC to yield $[W\text{-}N(CMe_3)CMe_2(Me)(NCMe_3)\{N(CMe_3)CMe{=}CMe_2\}]$. The structures of this complex, (1), and its hydrogen chloride adduct have been determined by X-ray crystallography [77].



(1)

5.2 TUNGSTEN(V)

5.2.1 Oxo complexes

The interaction of tungsten lower fluorides with water vapour has been studied by a thermogravimetric method, and the conditions for tha isolation of $[WOF_3].H_2O$ determined [78]. The complexes $[WOCl_3L]$ (L = 2,2'-bipyridine or 1,10-phenanthroline) and $[WOClL_2]$ (HL = 8-hydroxyquinoline or 8-mercaptoquinoline) have been prepared and their electrochemical properties, IR spectra and EPR parameters determined. Comparison with analogous molybdenum complexes showed that the tungsten compounds have a lower reduction potential, which was suggested as an explanation for the lack of activity of the enzyme sulfite oxidase when tungsten is substituted for molybdenum at the active site [25]. Complex formation in the systems $[WOCl_4]^-$-H_2L-Q (H_2L = quinoxaline-2,3-dithiol or toluene-3,4-dithiol; Q = solvent = dmf, $(Me_2N)_3PO$, MeCN or pyridine) has been investigated using EPR. In the oxygen-containing solvents $[WCl_5]$ is converted to $[WOCl_4Q]^-$, $[WOCl_3Q_2]$ and $[WOCl_2Q_3]^+$. Other species detected include $[WOCl_3(H_2L)]$, $[WOCl_3(HL)]^-$, $[WOCl_2LQ]^-$, $[WOClLQ_2]$, $[WOL_2Q]^-$, $[WOL(HL)_2]^-$ and $[WL_3]^-$ [79].

The series of mononuclear $B^+[WO(XR)_4]^-$ and triply bridged binuclear $B^+[W_2O_2(XR)_6(OMe)]^-$ (X = S or Se; R = aryl; B^+ = quaternary cation) salts have been isolated and their electronic properties investigated using EPR spectroscopy [80]. The electrochemistry of $[WO(XR)_4]^-$ and $[W_2O_2(XR)_6Z]^{n-}$ anions {X = S or Se; R = Ph, 4-MeC_6H_4 or CH_2Ph; Z = uninegative (n = 1) or neutral (n = 0) ligand} has been explored in MeCN and dmf solvents. Interconversion of the mononuclear and binuclear species occurs *via* reduction and oxidation processes involving the metal and ligand centres [81].

The reaction of $[WOCl_4]$ with 1,2-$C_6H_4(CH_2MgCl)_2$ or $Mg\{(CH_2)_2C_6H_4$-1,2$\}$(thf) yields $[W(CH_2\text{-}1\text{-}C_6H_4\text{-}2\text{-}CH_2)_2O\}_2Mg(thf)_4]$. The crystal structure of this complex has been determined, and shows some possible π-interaction between each tungsten atom and one of the chelating ligands [82].

5.2.2 Complexes with tungsten-carbon bonds

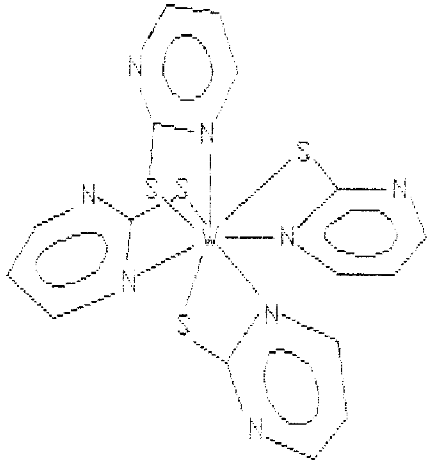
The reaction between $[W(\eta^5\text{-}C_5H_5)_2(Me)_2][PF_6]$ and $Ph_3C\cdot$ has been investigated. Initial hydrogen atom extraction leads to formation of $[W(\eta^5\text{-}C_5H_5)_2(Me)(CH_2)]^+$, which rearranges to give $[W(\eta^5\text{-}C_5H_5)_2(CH_2CH_3)]^+$, which can lose a proton in basic media to yield $[W(\eta^5\text{-}C_5H_5)_2(C_2H_4)]$ [83].

5.3 TUNGSTEN(V)/(IV)

The thermal decompositions of $[W_2O_4F]$.0.2(NOF) and $[W_2O_4F]$ have been studied by thermal, X-ray diffraction, chemical and mass spectroscopic analyses. The initial products are WO_2 (solid) and WO_2F_2 (gas) which condenses to form $[WOF_4]$ and $[WO_3]$ [84].

5.4 TUNGSTEN(IV)

The complex $[W(S_2C\text{-}SEt)_4]$ has been isolated and its crystal structure determined. The tungsten atom is bonded to eight sulfur atoms in a triangular dodecahedral geometry [85]. The ligand 2-mercaptopyrimidine (Hmpd) has been reacted with $[W(CO)_6]$ to yield $[W(mpd)_4]$. The crystal structure shows the ligand to act in a bidentate manner, giving a dodecahedrally octacoordinate tungsten atom, (2), [86].



(2)

The first oxotungsten(IV)-alkyne complexes, $[OW(R^1C{\equiv}CR^2)(S_2CNR_2)_2]$ have been synthesised by controlled oxidation of $[W(CO)(R^1C{\equiv}CR^2)(S_2CNR_2)_2]$ using $[Mo_2O_3\{S_2P(OEt)_2\}]$, and characterised by analysis, IR spectroscopy and variable temperature NMR techniques [87].

Several mixed valence tetraoxo- and tetrathio-molybdato and tungstato derivatives of cyclopentadienyl-tungsten complexes have been prepared and characterised. These include $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}O)_2WO_2]$ and $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}S)_2MS_2]$ (M = Mo or W) [29]. The standard enthalpies of formation of $[W(\eta^5\text{-}C_5H_5)_2(O_2CR)_2]$ (R = Ph or CF_3) have been determined by reaction solution calorimetry [88]. The reactions between $[W(\eta^5\text{-}C_5H_5)_2H_2]$ and MX_n (M = Fe, Al, Co, Cu or Zn; X = Cl, Br or I) yield complexes $[(\eta^5\text{-}C_5H_5)_2H_2WAlX_3]$, $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2MX_n]$ (M = Fe, Co, Cu or Zn), $[\{(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2\}_2Cu].Cl_2$ and $[(\eta^5\text{-}C_5H_5)_2W(\mu\text{-}H)_2MX_2].L$ (M = Fe or Zn; L = thf or dmf). IR and NMR spectroscopy were used to characterise the complexes and identify the hydride bridges [89]. $[W(\eta^5\text{-}C_5H_5)_2H_2]$ reacts with MX_2 (M =

Mg or Be; X = Cl, Br or I) to give $[(\eta^5\text{-}C_5H_5)_2H_2WMX_2]$ and with RMgX (X = Cl or Br) to give $[(\eta^5\text{-}C_5H_5)_2H_2W.MgX_2]$ or $[(\eta^5\text{-}C_5H_5)_2HW.RMgX.MgX.Et_2O]_2$, depending on conditions [90]. The reaction between $[W(\eta^5\text{-}C_5H_5)_2H_2]$ and $[IrH_2(PEt_3)_2(EtOH)]PF_6$ yields the W–Ir dinuclear complex $[(\eta^5\text{-}C_5H_5)W(\mu\text{-}C_5H_4)(\mu\text{-}H)_2IrH(PEt_3)_2]$, characterised by ^1H, ^{13}C and ^{31}P NMR [91]. The product of the reaction between $[W(\eta^5\text{-}C_5H_5)_2H_2]$ and $[(\eta^5\text{-}C_5H_5)_2Zr(Me)_2]$ in the presence of CO is $[(\eta^5\text{-}C_5H_5)_2WH\{CH(Me)OZr(Me)(\eta^5\text{-}C_5H_5)_2\}]$. This decomposes in solution to yield $[\{(\eta^5\text{-}C_5H_5)_2Zr(Me)\}_2O]$ and $[(\eta^5\text{-}C_5H_5)_2W(\eta^2\text{-}C_2H_4)]$. Use of ^{13}C labelled CO demonstrated the incorporation of one carbonyl carbon atom into the ethene ligand of the tungsten product [92].

Reaction of the alkylidyne complex $[W(CCH_2CMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ with 2,6-xylylisocyanide was found to give initially $[W(CCH_2CMe_3)(CN\text{-}2,6\text{-}Me_2C_6H_3)\{P(OMe)_3\}(\eta^5\text{-}C_5H_5)]$, then $[W\{\eta^3\text{-}RN{=}C\underline{\cdot\cdot}C(CH_2CMe_3)\underline{\cdot\cdot}C{=}NR(CNR_2)(\eta^5\text{-}C_5H_5)]$ (R = $2,6\text{-}Me_2C_6H_3$) [93]. Addition of BuLi to $[W(CCH_2CMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ affords the salt $Li[W(CCH_2CMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ which on quenching with D_2O affords a mixture of $[W(CCHDCMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ and $[W(CCD_2CMe_3)\{P(OMe)_3\}_2(\eta^5\text{-}C_5H_5)]$ [94]. The methylidyne complex $[W(CH)(PMe_3)_4Cl]$ has been prepared from the reaction between $[W(PMe)_4Cl_2]$ and $AlMe_3$. The complexes $[W(CH)(PMe_3)_3(AlMe_2R)Cl]$ (R = Cl or Me) have also been prepared and identified in solution using ^{31}P and ^{13}C NMR data [95]. X-ray diffraction studies on $[W(CH)(PMe_3)_4Cl]$ have shown the chloride and the methylidyne ligands *trans* to each other, but the structure is disordered. The structure of $[W(CH.AlMe_{2-x}Cl_{1+x})(PMe_3)_3Cl]$ (x = 0.18), a Lewis acid adduct of the $W{\equiv}C$ triple bond, demonstrated the interaction of the aluminium with the methylidyne carbon [96]. The reaction of $[W(CH.AlMe_2Cl)(PMe_3)_3Cl]$ with $AlMe_3$ and C_2H_4 yielded $[W(C.Al_2Me_4Cl)(Me)(PMe_3)_2(\eta^2\text{-}C_2H_4)]$. The crystal structure of this complex has been determined, and shows the phosphine ligands to occupy axial sites about a trigonal-bipyrimidal tungsten(IV) atom. The bonding of the $W\text{-}(C.Al_2Me_4Cl)$ fragment involves a $W{\equiv}C^-$ system linked by a three-centre two-electron bond to the two aluminium atoms of a $[Me_2Al(\mu\text{-}Cl)AlMe_2]$ moiety [97]. Protonation of $[W(CH)(PMe_4)_4Cl]$ with CF_3SO_3H yields the methylene complex $[W(CH_2)(PMe_3)_4Cl]^+[CF_3SO_3]^-$. A ^1H NMR study has indicated that the methylene ligand can distort towards giving a methylidyne hydride complex [98].

The kinetics of oxidation of $[W(CN)_8]^{4-}$ by periodate in neutral and weakly alkaline solution have been investigated [99]. The influence of acidity on the electron transfer reactions of diooxouranium(VI) octacyanotungstate(IV)-(V) has been determined electrochemically, using cerium(IV), chromium(VI) and manganese(VII) as oxidants [100].

5.5 TUNGSTEN(II)

The reactions of the quadruply bonded dimer $[W_2(mhp)_4]$ (Hmhp = 2-hydroxy-6-methylpyridine) with RNC (R = cyclohexyl or CMe_3) in the presence of $K[PF_6]$ lead to the formation of $[W(CNR)_7][PF_6]_2$. The Me_3CNC complex reacts with PR'_3 (R' = propyl or butyl) to give $[W(CNCMe_3)_6(PR'_3)][PF_6]_2$ and $[W(CNCMe_3)_5(PR'_3)_2][PF_6]_2$. The electrochemistry of these complexes has been investigated [101]. The crystal structure of $[W(CNCMe_3)_7][PF_6]_2$ has been determined. The geometry of the cation is distorted capped trigonal-prismatic, and by the comparison of structures of analogous tungsten and molybdenum complexes it was concluded that crystal packing forces are the dominant factor in determining the geometry adapted by $[M(\text{unidentate ligand})_7]^{n+}$ complexes in the solid state [102].

The reactions of Tl[LL] (LLH = pyridine-2-thiol, pyrimidine-2-thiol or thiazoline-2-thiol) with $[WCl(CF_3C{\equiv}CCF_3)_2(\eta^5\text{-}C_5H_5)]$ give products $[W\{(LL)C(CF_3)C(CF_3)\}(CF_3C{\equiv}CCF_3)(\eta^5\text{-}C_5H_5)]$ containing a novel η^2-vinyl ligand. With the thallium(I) salt of 2-mercaptopyridine *N*-oxide the reaction displaces the cyclopentadienyl group to give $[W(SC_5H_4NO)_2(CF_3C{\equiv}CCF_3)_2]$ and $[W(SC_5H_4N)(SC_5H_4NO)(CF_3C{\equiv}CCF_3)_2]$ [103].

5.6 TUNGSTEN(O)

A convenient synthesis of $[W(CNPh)_6]$ from $[W_2(dmhp)_4]$ (Hdmhp = 2,4-dimethyl-6-hydroxypyridine) has been devised, and its redox and substitution chemistry investigated [104]. The enthalpy of formation of $[W(PhMe)_2]$ has been calculated from microcalorimetric measurements of its heats of thermal decomposition and of iodination [105].

5.7 COMPOUNDS CONTAINING METAL-METAL BONDS

A book containing reviews on the reactivity of metal-metal bonds in various systems, including some tungsten complexes, has been published [106].

5.7.1 Higher oxidation state complexes

The oxidation of $[W_2Cl_4(\mu\text{-OEt})_2(OEt)_2(HOEt)_2]$ with $AgNO_3$ or molecular oxygen yields $[W_2Cl_4(\mu\text{-OEt})_2(OEt)_4]$. A crystal structure determination showed this to contain a central $Cl_2W(\mu\text{-OEt})_2WCl_2$ unit which is planer except for the ethyl groups. Two more ethyl groups around each tungsten atom complete the distorted octahedral coordination spheres, with a tungsten-tungsten single bond of 2.715 Å [107]. A crystal structure analysis of the product obtained from the reaction of $[W_2Cl_4(PBu_3)_4]$ with ethanoic acid has shown it to be $[W_3O_3Cl_5(O_2CMe)(PBu_3)_3]$. The tungsten atoms are in a equilateral triangle, capped on one side by a chloride ligand, with each edge bridged on the other side by oxygen atoms. The coordination sphere of each tungsten is completed by three other ligand atoms. The average tungsten-tungsten bond length is 2.609 Å [108]. A new bridging ligand, $H_3O_2^-$, has been identified in the complexes $[M_3O_2(O_2CEt)_6(H_2O)_2(\mu\text{-}H_3O_2)M_3O_2(O_2CEt)_6(H_2O)_2]Br_3.6H_2O$ (M = Mo or W). A crystal structure determination of the tungsten complex showed the triangular W_3 clusters (tungsten-tungsten bond average 2.756 Å) bridged by $H_3O_2^-$, which contains a short, symmetric hydrogen bond between the two oxygen atoms [109].

5.7.2 Complexes with a metal-metal double bond

Two complexes of formula $[W_2Cl_4(OR)_4(HOR)_2]$ (R = Me or Et) have been prepared from $[W_2(2,4\text{-dimethyl-6-oxopyrimidinate})_4]$. The crystal structures have been determined and found to contain a central $Cl_2W(\mu\text{-OR})_2WCl_2$ unit with distorted octahedral coordination around each of the tungsteen atoms completed by the two OR^- and two HOR ligands. The tungsten-tungsten distances are 2.481 Å (R = Me) and 2.483 Å (R = Et) [110].

5.7.3 Complexes with a metal-metal triple bond and their derivatives

The reaction of $[WCl_4(Me_2S)_2]$ with Et_3SiH yields $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_2(Me_2S)]$ from which the anion $[Cl_3W(\mu\text{-H})(\mu\text{-Me}_2S)_2WCl_3]^-$ can be prepared. A crystal structure determination of the $[HPPh_3]^+$ salt of this complex has shown it to possess a confacial bioctahedral framework with a tungsten-tungsten triple bond of length 2.410 Å [111].

1,2-$[W_2Cl_2(NMe_2)_4]$ compounds react with alkyllithium reagents to give 1,2-$[W_2R_2(NMe_2)_4]$ compounds (R = Et, CD_2CH_3, Bu, $CHMe_2$, CH_2CHMe_2, CH_2CMe_3, Ch_2SiMe_3, and CMe_3), which have been characterised by elemental analysis, and by IR, NMR and mass spectroscopy [112]. In hydrocarbon solvents $[W_2(NMe_2)_6]$

reacts with alcohols ROH to give $[W_4(OR)_{16}]$ (R = Me or Et). The crystal structure has been obtained for the ethoxide, and shows it to contain a W_4O_{16} skeleton akin to that of $[W_4O_{16}]^{8-}$, distorted by metal-metal bonds associated with the eight additional electrons [113,114]. The reaction between $[W_2(NMe_2)_6]$ and $CHMe_2OH$ yields a complex $[W_4(\mu\text{-H})_2(OCHMe_2)_{14}]$ which has been characterised by IR, NMR and mass spectroscopy, and a single crystal X-ray study. The molecule is centrosymmetric and has a chain of four tungsten atoms with two short (2.446 Å) and one long (3.407 Å) tungsten-tungsten distances. Each tungsten atom is coordinated to five oxygen atoms and a bridging hydride in a distorted octahedral geometry. The complex reacts with pyridine to form $[W_2(\mu\text{-H})(OCHMe_2)_7(py)_x]$ [115].

5.7.4 Complexes with a metal-metal quadruple bond and their derivatives

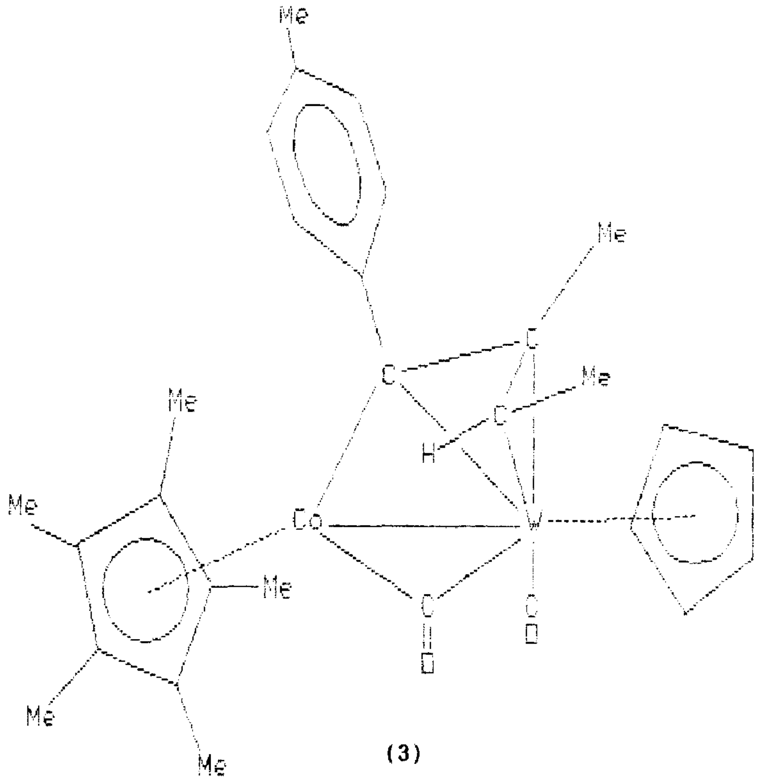
The structures have been determined of two isomers of the complex $[W_2Cl_4(dppe)_2]$ (dppe = 1,2-bis(diphenylphosphino)ethane). One isomer contains bridging dppe ligands with a tungsten-tungsten bond length of 2.314 Å, and with the rotational conformation twisted 31.1 ° from eclipsed. In the other isomer one dppe ligand is chelated to each tungsten, and the tungsten-tungsten distance is 2.281 Å with no net rotation from the eclipsed conformation [116]. The crystal structure of $[W_2Cl_4(dmpe)_2]$ (dmpe = 1,2-bis(dimethylphosphino)-ethane) shows one dmpe chelated to each tungsten, with a tungsten-tungsten bond length of 2.287 Å. In $[W_2Cl_4(PMe_3)_4]$ the sets of chlorine and phosphine ligands (two of each per tungsten) are staggered within themselves while the overall ligand arrangement about the dimetal unit is eclipsed. The metal-metal bond length is 2.130 Å [117]. The reaction of $[W_2Cl_4(PR_3)_4]$ (R = Et or Bu) with CO gives the monomeric complexes $[W(CO)_3(PR_3)_2Cl_2]$ and *trans*-$[W(CO)_4(PR_3)_2]$ [118]. The reduction of $[W_2Cl_4(PMe_3)_4]$ by sodium amalgam under hydrogen leads to the formation of $[W_2H_4(\mu\text{-H})(\mu\text{-PMe}_2)(PMe_3)_5]$. A crystal structure of this complex demonstrated it to contain a $(Me_3P)_2W(\mu\text{-PMe}_2)W(PMe_3)_3$ core, but could not locate the metal-bonded hydrogen atoms [119].

The reaction of CF_3CO_2H with $[W_2(mhp)_4]$ (Hmhp = 2-methyl-6-hydroxypyridine) at -78 °C yields the mixed ligand complex $[W_2(mhp)_2(CF_3CO_2)_2]$. The reduction of $[W_2Cl_6(thf)_4]$ using sodium amalgam gives a solution containing $[W_2Cl_4(thf)_4]$, which reacts with CF_3CO_2Na to yield $[W_2(CF_3CO_2)_4]$. This has been characterised by IR, Raman and ^{19}F NMR spectroscopy, and by a crystal structure determination of the diglyme adduct in which the diglyme acts as a tridentate axial bridging ligand [120].

5.7.5 Carbonyl and organometallic complexes

The product of the reaction between $[(\eta^5\text{-}C_5H_4R)_2Sn]$ (R = H, Me) and $[(\eta^5\text{-}C_5H_5)W(CO)_3H]$ had been reported to be $\{Sn[W(CO)_3(\eta^5\text{-}C_5H_5)]_2\}_n$. Further investigation has shown it actually to be $ClSn[W(CO)_3(\eta^5\text{-}C_5H_5)]_3$, formed from the reaction of the halogenated hydrocarbon solvent with $HSn[W(CO)_3(\eta^5\text{-}C_5H_5)]_3$, which is the initial product [121,122].

The reaction between $[(\eta^5\text{-}C_5H_5)(CO)_3W\text{-}SiH_2Me]$ and $[Co_2(CO)_8]$ yields the μ_3-SiMe bridged cluster $[(\eta^5\text{-}C_5H_5)(CO)_2W(\mu_3\text{-}SiMe)\{Co(CO)_3\}_2]$ [123]. The structures of the two complexes $[(\eta^5\text{-}C_5H_5)W\{\mu_2\text{-}C(C_6H_4Me\text{-}4)C(Me)\}Fe(CO)_5]$ and $[(\eta^5\text{-}C_5H_5)W(\mu_3\text{-}CC_6H_4Me\text{-}4)(\mu_2\text{-}Me_3SiC_2SiMe_3)(\mu_2\text{-}CO)Fe(CO)_6]$ have been determined by X-ray crystallography. The complexes are products of the reactions of alkynes with di- or tri-metal complexes with bridging alkylidyne ligands [124]. The reactions of polynuclear carbonyl complexes of iron, ruthenium or osmium with $[W{\equiv}CR(CO)_2(\eta^5\text{-}C_5H_5)]$ (R = C_6H_4-4-Me) yield several heteronuclear clusters. The crystal structures have been reported of $[\{(\eta^5\text{-}C_5H_5)W\}_2(\mu_3\text{-}C_2R_2)Fe(CO)_6]$, $[\{(\eta^5\text{-}C_5H_5)W\}_2(\mu_3\text{-}C_2R_2)Os(CO)_7]$, and $[(\eta^5\text{-}C_5H_5)W(\mu_3\text{-}CR)Os_3(CO)_{11}]$ [125]. The reaction between $[H_2Os_3(CO)_{10}]$ and $[W{\equiv}CR(CO)_2(\eta^5\text{-}C_5H_5)]$ (R = C_6H_4-4-Me) involves the cleavage of osmium-osmium bonds under very mild conditions. The crystal structures have been determined of $[(\eta^5\text{-}C_5H_5)WOs_3(CO)_{11}\{C(O)CH_2R\}]$ and $[\{(\eta^5\text{-}C_5H_5)W\}_2Os(CO)_7(C_2R_2)]$ [126]. The reaction of $[IrCl(CO)_2(NH_2C_6H_4\text{-}4\text{-}Me)]$ and $[(\eta^5\text{-}C_5H_5)W(CO)_3H]$ with CO in the presence of zinc yields $[(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}]$ and $[\{(\eta^5\text{-}C_5H_5)W\}_2Ir_2(CO)_{10}]$. The crystal structures of these complexes are related to that of $[Ir_4(CO)_{12}]$, with one or two $Ir(CO)_3$ vertices replaced by $(\eta^5\text{-}C_5H_5)W(CO)_2$ [127,128]. The tetrahydrothiophen group (tht) in $[Au(C_6F_5)_3(tht)]$ is readily displaced by $[(\eta^5\text{-}C_5H_5)W(CO)_3]^-$ to give $[(\eta^5\text{-}C_5H_5)(CO)_3W\text{-}Au(C_6H_5)_3]^-$ and $[\{(\eta^5\text{-}C_5H_5)(CO)_3W\}_2Au]^-$ which have tungsten-gold bonds [129]. The reactions and the syntheses of the complex salts $[L_nMW\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4Me\text{-}4)H\}(CO)_2(\eta^5\text{-}C_5H_5)][BF_4]$ (L_nM = $(\eta^5\text{-}C_5Me_5)(CO)Co$ or $(PMe_3)_2Pt$) have been described; the structures of the platinum-tungsten species and the compounds $[(PMe_3)_2PtW(\mu\text{-}H)\{\mu\text{-}CH(C_6H_4Me\text{-}4)\}(CO)_2(\eta^5\text{-}C_5H_5)]$ and $[(\eta^5\text{-}C_5Me_5)CoW\{\mu\text{-}\eta^1,\eta^3\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)H\}(\mu\text{-}CO)(CO)(\eta^5\text{-}C_5H_5)][BF_4]$, (3), have been determined [130].



(3)

The reaction of $[(\eta^7\text{-}C_7H_7)W(CO)_2I]$ with ER^- (E = S, Se or Te; R = alkyl or aryl) yields several types of complex, including $[(CO)_4W(\mu\text{-}ER)_2W(CO)_4]$, $[(\eta^7\text{-}C_7H_7)W(\mu\text{-}ER)_3W(CO)_3]$ and $[(\eta^7\text{-}C_7H_7)W(\mu\text{-}ER)_3W(CO)(\mu\text{-}ER)_2W(CO)_4]$, determined by analyses, IR, ^1H NMR, and mass spectroscopy, and by X-ray crystallography. The ER^- bases bridge across tungsten-tungsten single bonds [131,132]. The thermal reaction between $[W(CO)_6]$ and $Ph_2SbSbPh_2$ yields the bridged dimer $[(CO)_4W(\mu\text{-}SbPh_2)_2W(CO)_4]$, which contains a tungsten-tungsten single bond [133]. $[(\eta^5\text{-}C_5H_5)Co(cot)]$ (cot = cyclooctatetraene) reacts with $[(dmf)_3W(CO)_3]$ to give $[(\eta^5\text{-}C_5H_5)Co(\mu\text{-}cot)W(CO)_3]$, in which the cot ligand acts as a fluxional bridge across a cobalt-tungsten bond [134].

The vibrational spectra of the carbyne complexes $[(CO)_5Re\text{-}W(CO)_4(CR)]$ (R = Ph, Me) have been recorded and interpreted [135]. The reaction of $[(CO)_5Re\text{-}W(CO)_4(CR)]$ (R = Ph or C_6H_4-4-Me) with PMe_3 yields $[(CO)_4Re\{\mu\text{-}C(R)(PMe_3)\}Re(\mu\text{-}CO)W(CO)_4]$ with the ruthenium-tungsten bond bridged by an ylide and a carbonyl ligand. With excess PMe_3 the product is $[(CO)_3(PMe_3)Re\{\mu\text{-}C(R)(PMe_3)\}(\mu\text{-}CO)W(CO)_{4-n}(PMe_3)_n]$ (n = 0 or 1). The crystal structure of $[(CO)_3(PMe_3)Re\{\mu\text{-}C(C_6H_4Me)(PMe_3)\}(\mu\text{-}CO)W(CO)_4]$ has been determined [136]. Full synthetic procedures have been reported for a number of heteronuclear metal carbide clusters including $[Et_4N]_2[Fe_5WC(CO)_{16}]$ [137].

5.8 NITROGENASE RELATED CHEMISTRY

5.8.1 Tungsten-iron-sulfur clusters

A review has been published of Fe-M-S (M = Mo or W) complexes derived from $[MS_4]^-$ anions, and their relevance to the molybdenum enzyme nitrogenase [138]. The ground state electronic and magnetic properties of $[(FeCl_2)_2WS_4]^{2-}$ have been studied by Mössbauer spectroscopy and magnetic measurements. The results implied a high electron affinity of the $WS_4{}^{2-}$ group and intramolecular spin coupling [139]. The variation of the average magnetic moment, $\bar{\mu}_m$, in the temperature range 300-1.8 K, and how it changes with applied spin magnetic field of 0.125-2.0 T, has been reported for $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$. The results were interpreted in terms of antiferromagnetic spin coupling between iron atoms within the separate $\{Fe_3WS_4\}$ cubane-like clusters [140]. The electrochemical behaviour of $[Fe_6W_2S_8(SEt)_9]^{3-}$ in ethanenitrile has been reported. Both the 3-/4- and 4-/5- couples show good electrochemical reversibility, unlike the case in dimethylsulfoxide, due to the sensitivity of the tungsten atom in the reduced cluster to attack by oxygen-donor ligands [141].

5.8.2 Dinitrogenyl chemistry

Several reviews have been published dealing with the chemical reduction of dinitrogen bound to tungsten or molybdenum [142-144].

The formation of hydrazido(2-) complex intermediates in solution during the reaction of *cis*-$[W(N_2)_2(PMe_2Ph)_4]$ with H_2SO_4 in thf has been established by ^{15}N NMR spectroscopy, and $[W(NNH_2)(HSO_4)_2(PMe_2Ph)_3]$ has been isolated. When treated with H_2SO_4 in MeOH the complexes $[WX_2(NNH_2)(PMe_2Ph)_2]$, $[WX(NNH_2)(PMe_2)_3L]^+$ and $[W(NNH_2)(quinO)(PMe_2Ph)_3]X$ (X = Cl, Br or I; L = ternary phosphine or substituted pyridine; quinO = quinoline-8-olate) give ammonia or hydrazine. Ammonia was also produced on treatment of these hydrazido complexes with aqueous KOH, and from $[WX_2(NNH_2)(PMe_2Ph)_3]$ by reaction with $Na[BH_4]$ in thf or methanol. The preparation and characterisation of $[WBr(NNH_2)(NC_9H_7)(PMe_2Ph)_3]^+$ and $[W(NNH_2)L'(PMe_2Ph)_3]^+$ (L' = NC_5H_4-2-CO_2 or NC_9H_6-2-CO_2) were described [145]. X-ray diffraction studies of five complexes of formula $[M(NNH_2)(quinO)(PMe_2Ph)_3]X$ (quinO = quinolin-8-olate; M = Mo or W; X = Cl, Br or I) have shown almost identical octahedral coordination of the metal ion, with slight differences in the extended hydrogen-bonding schemes and orientations of the phosphines which may account for differences in protonation reaction products [146]. An investigation into the mechanism of the reaction of *cis*-$[W(N_2)_2)PMe_2Ph)_3]$ with HCl, HBr, and H_2SO_4 in MeOH to yield $[W(NNH_2)(OMe)_2(PMe_2Ph)_3]$ has shown that protic solvents play a unique role [147].

The complex *trans*-$[W(N_2)_2(dppe)_2]$ {dppe = 1,2-(diphenylphosphino)-ethane} may be acylated by trifluoroethanoic anhydride to give trifluoroethanoyldiazenide complexes in high yield. The reaction does not involve radicals and a mechanism analogous to protonation has been suggested. Other ligands can also be acylated, with methyldiazenido complexes yielding methyl(trifluoroethanoyl)hydrazido(2−), and ethanoyldiazenido complexes giving trifluoroethanoyldiazenido products [148]. The reaction of $[WBr(dppe)_2(NNH_2)]Br$ with PhI^+ in CH_2Cl_2 in the presence of $[CO_3]^{2-}$ yields $[WBr(dppe)_2(NNCHO)]$. A minor product of the reaction between $[WBr(dppe)_2(NNH_2)]Br$ and PhI^+ in $CHCl_3$/aqueous $[CO_3]^{2-}$ is the complex $[WBr(dppe)_2(NNCCl_2)]^+$. The reactions of this cation with various organic and inorganic bases have been investigated [150]. The reaction between PhI^+ and $[WBr(dppe)_2(NNH_2)]Br$ in $CHFBr_2$ in the presence of aqueous $[CO_3]^{2-}$ yields the binuclear cation $[W_2\{\mu\text{-}CH(N_2)_2\}(dppe)_4Br_2]^+$, which has been isolated as its Br^-, $[PF_6]^-$ and Reineckate salts. A crystal structure determination of $[W_2\{\mu\text{-}CH(N_2)_2\}(dppe)_4Br_2][Cr(NH_3)_2(NCS)_4].{}^1/_3CH_2Cl_2$ has shown that the cation contains a formazanido(3-) ligand, $[N_2CHN_2]^{3-}$, bridging two tungsten atoms in a seven atom chain [151,152].

Cyclic voltammetry has been used to investigate the electrochemistry of $[WF(dppe)_2(NNCRR')][BF_4]$ complexes. EPR spectra of species generated by controlled potential electrolysis have demonatrated that reduction occurs in these species on the two nitrogen atoms rather than the metal [153].

The reaction of *trans*-$[W(dppe)_2(N_2)_2]$ with $[HCo(CO)_4]$ or $[HFeCo_3(CO)_{12}]$ in the presence of alcohols yields $[W(OR)(NNH_2)(dppe)_2]^+[A]^-$ (A = $Co(CO)_4$, R = Me or Et; A = $Co_3(CO)_{12}$, R = Me; A = $FeCo_3(CO)_{12}$, R = Me, Et or Pr) [154].

5.9 TUNGSTEN CATALYSTS

The kinetics of the oxidation of dimethylsulfoxide by H_2O_2, catalysed by Na_2WO_4, have been investigated using iodometry. A mechanism was proposed involving formation of H_2WO_5 and H_2WO_8 [155]. The reaction of a mixture of α-hydroxodecyl hydroperoxide and epoxides is catalysed by tungstic anhydride and chlorosulfonic acid to give 1,2,4-trioxane in 7-63% yield [156]. The catalytic conversion of MeOH into hydrocarbons has been studied over a variety of metal and organic salts of $H_3PW_{12}O_{40}$. Pyrazinium salts exhibit remarkably high selectivity to ethene and propene [157]. A $PdSO_4$-$H_3PMo_6W_6O_{40}$ catalyst system has been used in the liquid phase oxidation of cyclo-alkenes to the corresponding ketones [158].

The photoelectrochemistry of alkylammonium tungstates has been studied as a route to the production of H_2 in a photogalvanic cell [159]. In strong acid solution *n*-type WS_2 can be used as a photoanode to effect the oxidation of SO_2 to $[SO_4]^{2-}$, driven with visible light. The presence of I^- as a mediator was found necessary for the oxidation to occur [160]. Specific chemical treatments of *n*-type WSe_2 photanodes have been developed which improves its conversion efficiency [161].

WCl_6 and $WOCl_4$ have been used as primary catalysts, with $SnMe_4$, $PbMe_4$, $(C_5H_5)TiCl_2$ and $(C_5H_5)ZrCl_2$ as co-catalysts, for the metathesis of methyl-10-undecenoate, methyloleate and olelylacetate. The $WOCl_4/(C_5H_5)_2TiCl_2$ system was found to be very active for the metathesis of unsaturated esters [162]. Unsaturated nitriles of general formula $CH_2{=}CH(CH_2)_nCN$, where $1 \leqslant n \leqslant 4$, undergo metathesis in the presence of a $WCl_6/SnMe_4$ catalyst system, with maximum reactivity for $n = 2$ [163]. Methyl dec-9-enoate has been obtained by cometathesis of ethene and methyloleate using a $WCl_6/SnMe_4$ catalyst system [164]. Very active, long-lived catalysts for alkene metathesis have been prepared from the reaction of the oxo complexes $[(RCH_2)_3W(O)X]$ (R = CMe_3; X = Cl, Br or OR) with $AlBr_3$, $AlCl_3$, $GaCl_3$ or BBr_3 to form 1:1 adducts with an oxo bridge [165]. The metathesis of alkynes by tungsten(VI)-alkylidyne complexes has been investigated [166].

Measurements have been carried out to determine the rate of H_2 production by the water gas shift reaction at temperatures of 200 °C and lower with $[M(CO)_6]$ (M = Cr, Mo or W) serving as catalyst precursors in basic methanol solutions. The overall kinetics were explained by a mechanism involving methanoate decomposition rather than activation of carbon monoxide [167]. Photogeneration of $[M(CO)_5]$ species from $[M(CO)_6]$ (M = Mo, Cr or W) has been shown to produce enhanced catalytic activity at low temperatures in the metal-carbonyl catalysed water gas shift reaction [168]. Although $[M(CO)_6]$ complexes (M = Cr, Mo or W) are non-catalysts in hydroformylation reactions $[M(CO)_5(SnCl_2)]$, $[M(CO)_5(SnO)]$ and $[M(CO)_6]/SnCl_2$ systems all show catalytic activity in hydroformylation and carboxylation of alkenes [169].

5.10 NITROSYL COMPLEXES

Thermogravimetric and gas chromatographic techniques have been used to study the pyrolysis of a series of complexes *cis*-$[W(NO)_2L_2]$ (L = neutral bidentate ligand). Mixtures of N_2, N_2O and NO gases were detected [170]. Gas-phase core electron binding energies have been determined using X-ray photoelectron spectroscopy of the series $[(\eta^5\text{-}C_5H_5)M(NO)_2Cl]$ (M = Cr, Mo or W). On going from chromium to tungsten, back-bonding to the nitrosyl group increases, and electron density is withdrawn from the chloride atoms [171]. The gas-phase ultraviolet photoelectron spectra of $[(\eta^5\text{-}C_5H_5)M(NO)_2X]$ (M = Cr or W; X = Cl, Br or I) have been reported. The interpretation of the spectra compared favourably with a Fenske-Hall molecular orbital calculation on the $[(\eta^5\text{-}C_5H_5)Cr(NO)_2Cl]$ complex, which suggested that the metal electrons are highly delocalised onto the nitrosyls [172]. The rate constant for the substitution reaction of PMe_3 with $[(\eta^5\text{-}C_5H_5)W(CO)_2(NO)]$ to give $[(\eta^5\text{-}C_5H_5)W(CO)(NO)(PMe_3)]$ has been measured at 25 °C in thf. At - 23 °C in pure PMe_3 the product of the reaction is $[(\eta^1\text{-}C_5H_5)W(CO)_2(NO)(PMe_3)_2]$ [173].

5.11 CARBONYL COMPLEXES

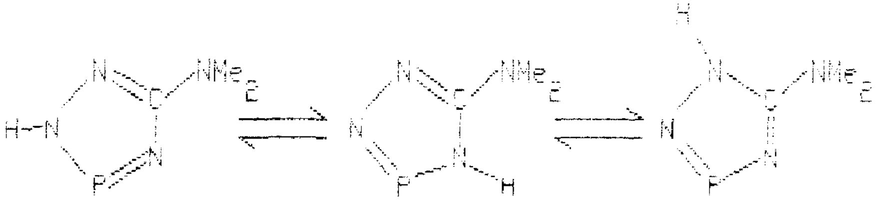
Vibrational spectra have been recorded for $[W(^{12}CO)_5(^{12}CS)]$ and *trans*-$[W(^{12}CO)_4(^{13}CO)(^{12}CS)]$, and for related chromium complexes. Definitive assignments have been proposed for most of the fundamental vibrations of these molecules on the basis of general quadratic valence potential fields employing both compliance and force constants [174]. Laser pulse photolysis of $[W(CO)_6]$ in methylcyclohexane (solv) produced an intermediate, thought to be $[W(CO)_5(solv)]$. In the presence of 4-ethanoylpyridine, L, the final product was $[W(CO)_5L]$. The reaction kinetics of these reactions were discussed [175]. The IR spectra of $[W(CO)_5(solv)]$ (solv = methylcyclohexane or CH_2Cl_2), formed by UV irradiation of $[W(CO)_6]$ in solvent at - 78 °C, have been reported and the photochemical reactions of $[W(CO)_6]$ with aromatic hydrocarbons studied [176].

^{13}C NMR has been used to investigate the site of W–CO bond breaking and fluxionality in ^{13}CO substituted $[W(CO)_4(phen)]$ (phen = 1,10-phenathroline), which is the first step in ligand substitution reactions of this type of complex. A mechanism was suggested involving loss of CO *cis* to the phen ligand, followed by complete scrambling of the five-coordinate intermediate

[177]. Redox reactions of *cis*-$[W(CO)_2(bipy)_2]$ (bipy = 2,2'-bipyridine) produce $[W(CO)_2(bipy)_2]^z$ ($z = \pm1, \pm2$). These species react with isocyanides to substitute CO or bipy, or both, depending on z [178]. The kinetics have been investigated for the reaction of $[W(CO)_4(bipy)]$ with cyanide in several non-aqueous solvents. Solvent effects have been dissected in to initial state and transition state components [179]. Stable anionic radical species $[(CO)_5W\text{-}L\text{-}W(CO)_5]^{\cdot-}$ (L = pyrazine or 4,4'-bipyridine) have been prepared by the reaction of $K^+L^{\cdot-}$ with $[W(CO)_6]$, and characterised by EPR spectroscopy [180]. The solution and solid IR spectra of $[W(CO)_4(dipyam)]$ (dipyam = di(2-pyridyl)amine) have been recorded and compared with those of the 2,2-bipyridine analogues. In solution the spectra are similar, but differences in the solid state spectra suggest that intermolecular interactions lead to an associated or polymeric structure in the dipyam complex [181]. The syntheses of $[W(CO)_5L]$ (L = 4-methyl- or 4-phenyl-1,2,4-triazole) have been reported. The IR and ^1H NMR spectra show the triazoles to be monodentate, and there is a strong solvent dependance in the ^1H NMR due to the solvent-solute interaction [182].

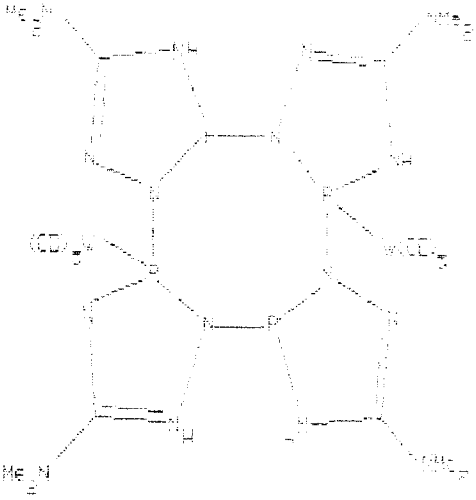
Luminescence spectra have been measured of matrix-isolated substituted tungsten and molybdenum carbonyls $[M(CO)_5L]$ (L = pyridine, 3-bromopyridine, pyridazine, piperidine, PMe_3 or PCl_3). The fluorescence band shifted to higher energy on going from *N*-donor to *P*-donor ligands corresponding to the shift of the lowest lying d-d transition in the UV/VIS absorption spectrum [183]. MCD spectra of $[M(CO)_5L]$ complexes (M = Cr, Mo or W; L = NMe_3, pyridine, pyrazine, pyridazine, piperidine, thiazole, PMe_3, PPh_3, or PCl_3) have been reported and discussed. The results were used to assign the absorption bands of the $[M(CO)_5L]$ complexes [184].

The reactions of diphenyl(3,5-dimethylpyrazolyl)phosphine, LL, with $[W(CO)_4L'_2]$ (L'_2 = norbornadiene or $(MeCN)_2$) proceed stepwise to give an equilibrium mixture of products $[(LL)W(CO)_4]$ and *cis*-$[(LL)_2W(CO)_4]$. The former product contains a four-membered *P,N*-bound metallocyle and the latter, favoured by excess ligand, contains *P*-bound ligands [185]. The coordinatively unsaturated species $[(LL)_2W(CO)_3]$ (LL = phenylbis(3,5-dimethylpyrazolyl)-phosphine) reacts reversibly with CO and irreversibly with H_2, C_2H_4, $P(OMe)_3$ and PF_3. The starting material has a pseudo C_{3v} structure in which the ligand is bound to the metal *via* two nitrogen atoms giving a six-membered boat metallocyle. The product of CO addition, $[(LL)W(CO)_4]$, contains a four-membered *P,N*-bound metallocycle [186]. The complex *trans*-$[(L)_2W(CO)_4]$ (L = *N*-(diphenylphosphino)-2,5-dimethylpyrrole) has been prepared and characterised using IR spectroscopy. The ligand is *P*-bound and has a poorer coordinating ability than PPh_3 [187]. The triazaphosphole ligand, (4),



(4)

forms a tetramer reaction with [(MeCN)M(CO)$_5$] (M = Cr or W) to give a product containing two W(CO)$_5$ fragments bridged by a bidentate *P*-donor macrocycle, (5), [188]. The two bicyclic aminophosphanes, (6), form stable adducts



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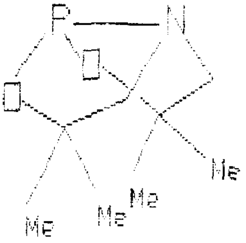
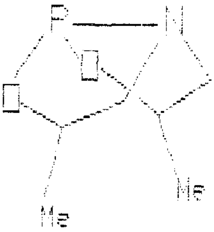


(6a)



(6b)

$[W(CO)_{6-n}L_n]$ (n = 1-3; L = **6a**, **6b**) in which the ligands are coordinated by the phosphorus atoms only, demonstrated using IR and ^{31}P NMR spectroscopy [189]. The monodentate *P*-bound ligand $Ph_2PCH_2CH_2NMe_2$, L, forms an adduct $[W(CO)_5L]$ which can be methylated using iodomethane to give $[W(CO)_5(Ph_2PCH_2CH_2NMe_3)]I$, which has been characterised by elemental analyses, conductivity measurements, ^1H and ^{31}P NMR, and IR spectroscopy [190].

The ^{13}C NMR spectrum of *cis*-$[W(CO)_4(^{13}CO)(PMe_2Ph)]$ shows a doublet due to ^{31}P coupling. After heating in heptane for twelve hours another doublet, due to *trans* ^{13}CO, was observed. The absence of ^{13}C–^{13}C coupling implies an intramolecular rrearrangement process, unlike the molybdenum complex which rearranges *via* an intermolecular exchange pathway [191]. The crystal structure of $[W(CO)_5(PMe_3)]$ has been determined to find the length of a tungsten-phosphine bond free of excess steric interactions [192]. The principal of electrochemical substitution of metal carbonyls has been applied to $[W(CO)_5(PR_3)]$ with the aim of selective preparation of di- and tri-substituted products $[W(CO)_4(PR_3)(PR_3')]$ and $[W(CO)_3(PR_3)(PR'_3)_2]$. As a result of simultaneous replacement of CO and PR_3 mixtures of products formed [193]. The crystal structure has been determined of the product of the reaction between *trans*-$[(CO)_4W(PPh_2CH{=}CH_2)_2]$ and PPh_2H. This confirmed the conclusions from the IR and NMR data, which had suggested that the product was $[(CO)_4W\{PPh_2CH(CH_2CH_2PPh_2)CH_2PPh_2\}]$, in which the ligand is coordinated *via* two phosphine atoms to form a six-membered metallocycle [194]. A series of complexes *cis*-$[W(CO)_4(PR_3)(alkene)]$ has been obtained from $[Et_4N][W(CO)_4(PR_3)Cl]$, either *via* $[W(CO)_4(PR_3)(solvent)]$ or directly in a two-phase system [195].

The mixed ligand seven coordinate tungsten(II) complexes $[W(CO)_2(PPh_3)L_2]$ (L^- = 8-quinolinato, picolinato or L_2^{2-} = anion of *N,N'*-disalicylidene-1,2-phenylenediamine) have been prepared and characterised [196]. The substituted xanthate complexes $[W(CO)_2(PPh_3)(Rxant)_2]$ (R = Et, CMe_3 or CH_2Ph) have been prepared and characterised by IR and UV/VIS spectroscopy. The xanthate acts as a bidentate ligand to give a seven-coordinate complex [197]. A series of compounds of the type $[W(CO)_2L(S_2CNR_2)_2]$ (L = phosphine or phosphite; R = alkyl) have been prepared and the crystal structure determined for the complex with L = PPh_3 and R = Et. The tungsten is seven-coordinate with a tetragonal base-trigonal base geometry [198].

A directed synthetic route has been described to the complexes $L_nM(EMe_2\text{-}E'Me_2)_2M'L_n$ (M,M' = Cr, Mo, W, Mn, Fe, Co, Ni; E,E' = P, As; L_n = $(CO)_4$ for W) which contain two bridging ligands forming a six-membered metallocycle. The IR and ^{31}P NMR spectra have been recorded and interpreted

[199]. The complex $[W(CO)_5(MeAsH_2)]$ has been prepared and isolated in a pure state [200]. The bulky arsine ligands $As(EMe_3)_3$ (E = Si, Ge, Sn) have been prepared and found to react with $[W(CO)_6]$ to give $[W(CO)_5\{As(EMe_3)_3\}]$. The NMR, IR, Raman and He(I)-PE data for the ligands and some complexes have been reported [201]. Pyridine analogues 4-R-λ^3-arsenines and 2-aryl-4-R-λ^3-arsenines react smoothly with $[W(CO)_3(MeCN)_3]$ to give stable $[\{\eta^6-(\lambda^3\text{-arsenine})\}W(CO)_3]$ complexes. IR, ^1H and ^{13}C NMR, UV and mass spectra have been obtained and discussed [202]. The adamantane structured $MeC(CH_2AsO)_3$ reacts with $[W(CO)_6]$ to give $[\{MeC(CH_2AsO)_3\}_2W(CO)_4]$ in which the ligand is coordinated *via* arsine atoms. IR, Raman, ^1H and ^{13}C NMR, and mass spectra have been recorded and the vibrational spectra discussed in detail [203].

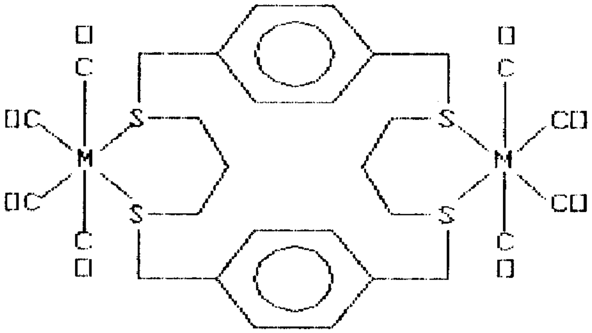
$[W(CO)_6]$ reacts with $Sb(SiMe_3)_3$ with substitution of one of the CO ligands to give $[W(CO)_5\{Sb(SiMe_3)_3\}]$. This complex can act as a initiator for the polymerisation of thf. The IR, ^1H NMR and mass spectra of this and related compounds have been measured and discussed [204]. The stibines dimethyl(α-picolyl)stibine, picstib, and dimethyl(8-quinolyl)stibine, quinstib, have been synthesised and used to prepare the complexes $[W(CO)_4(\text{picstib})]$ and $[W(CO)_4(\text{quinstib})]$ in which the stibines act as bidentate *Sb-,P-* chelating ligands [205].

The chelating ligands $Me_2XGeMe_2(CH_2)_2X'Me_2$ (X-X'; X = P or As; X' = P, As or N) replace norbornadiene (nbd) in $[W(CO)_4(nbd)]$ to give $[W(CO)_4\{Me_2XGeMe_2(CH_2)_2X'Me_2\}]$. In the reaction between $[W(CO)_4(\text{piperidine})_2]$ and the *As-,N-* ligand, the product is $[W(CO)_4(As\text{-}N)_2]$ with two monodentate *As*-bound ligands rather than the chelate [206,207].

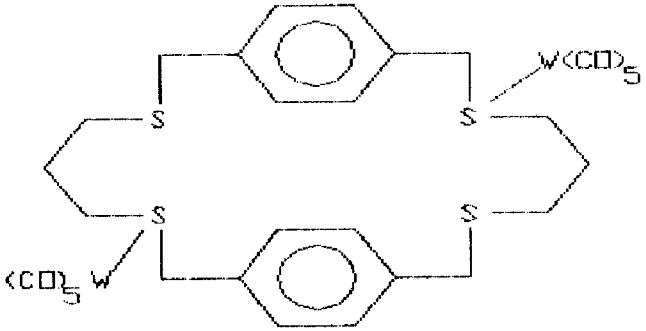
Photolysis of $[W(CO)_6]$ with phenanthroquinone in toluene yields a stable metal carbonyl quinone radical complex. This will undergo ligand exchange reactions between the carbonyl and the ER_3 ligands (E = P, As or N; R = Ph or Et). EPR spectroscopy has been used to follow these reactions and to indicate the probable exchange sites in thermal substitution reactions [208].

The photolysis reaction of $[W(CO)_6]$ with $Na_2S.9H_2O$ and 18-crown-6-ether yields $[W(CO)_5SH]^-$ and $[W_2(CO)_{10}(\mu\text{-}SH)]^-$ ions, isolated as $\{Na(\text{crown})\}^+$ salts. The structures have been determined of these two complexes, and show them to be polymeric in nature with Na-OC linkages between alternating cations and anions [209,210]. The photochemical or thermal reaction of $[W(CO)_6]$ with M_2X in alcohols (M = Li or Na; X = S, Se or Te) yields $[W(CO)_5(SH)]^-$, which have been isolated as $[(Ph_3P)_2N]^+$ or $[AsPh_4]^+$ salts [211]. The reactions of $Li[W(CO)_5(SH)]$ with $[Me_3O]^+$, Me_3SnCl, PPh_2Cl and $[(\eta^5\text{-}C_5H_5)Fe(CO)_2Cl]$ have been investigated and found to yield respectively $[W(CO)_5(SMe_2)]$, $[W(CO)_5\{S(SnMe_3)_2\}]$, $[W(CO)_5(SHPPh_2)]$, and $[(CO)_5W(\mu\text{-}SH)Fe(CO)_2(\eta^5\text{-}C_5H_5)]$

[212]. The macrocyclic ligand 2,6,15,19-tetrathia[7.7]paracyclophane reacts with $[W(CO)_6]$ to give $[(C_{22}H_{28}S_4)\{W(CO)_4\}_2]$ and $[(C_{22}H_{28}S_4)\{W(CO)_5\}_2]$, believed to be intermediate in the metal carbonyl catalysed elimination of 1,3-dithiapropane from the ligand. The structures have been determined by X-ray crystallography, and are illustrated as **(7a)** and **(7b)** [213]. The



(7a)



(7b)

crystal structures of $[\{(Me_3Y)_2S\}W(CO)_5]$ (Y = Ge or Pb) have been determined. The tungsten-sulfur bonds are single, with no evidence of significant π-bond contribution [214].

The ^{13}C NMR spectra of $[W(CO)_5L]$, where L is the sulfur-donor ligand ferrocenylphenylthioketone, have been studied. The carbon nuclei in the cyclopentadiene rings of the ligand are deshielded on coordination of the ligand to the $W(CO)_5$ fragment [215]. The chromium complex $[(\eta^5\text{-}C_5H_5)Cr(\mu\text{-}SCMe_3)(\mu\text{-}S)Cr(\eta^5\text{-}C_5H_5)]$ reacts with $[W(CO)_6]$ to substitute a carbonyl ligand. The chromium specoes acts as a sulfur-donor ligand *via* the bridging sulfide. The crystal structure of the product has been determined, and shows the geometry of the ligand to be almost unchanged on coordination to tungsten [216].

A series of stannylene complexes $[W(CO)_5L]$ {L = $SnCl_2$, $Sn(OCOMe)_2$, $Sn(OH)_2$, SnO, SnS or $Sn(NCS)_2$} has been prepared and characterised [217].

The mixed-metal dimer complex $[(CO)_5W(\mu\text{-}H)Cr(CO)_5]$ has been synthesised by the reaction of $[HCr(CO)_5]^-$ with the Lewis acid fragment $W(CO)_5$ [218]. A new synthetic route has been developed to the anions $[HM(CO)_5]^-$ (M = Cr, Mo or W) from the reduction of $[M(CO)_5(NMe_3)]$ to the dianion $[M(CO)_5]^{2-}$, followed by protonation [219].

The rate of hydogenation of α-methylstyrene by $[HW(CO)_3(\eta^5\text{-}C_5H_5)]$ has been investigated. The kinetics of the reaction suggest a mechanism involving transfer of a hydrogen atom to the β-carbon of the styrene as the rate limiting step [220].

The crystal structure has been determined of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ [221]. The reaction of $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ with $Ph_2P(O)C(S)N(H)R$ (R = Me, Ph) in the presence of Et_3N gives $[(\eta^5\text{-}C_5H_5)W(CO)_2\{Ph_2P(O)C(S)NR\}]$, in which the deprotonated ligand coordinates in a bidentate manner through nitrogen and sulfur to give a four-membered ring. $[W(CO)_3(PPh_3)_2Cl_2]$ reacts with the ligand in the presence of Et_3N to give complexes with seven-coordinate tungsten bound to two oxygen-, sulfur-bonded ligands forming five-membered rings, and to one PPh_3 and two CO ligands [222]. The ligands $Ph_2PC(X)N(H)R$, LH, (X = S, R = Ph or Me; X = O, R = Ph; X = *N*-4-tol, R = 4-tol) behave as nuetral monodentate ligands in substitution reactions with $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ to give $[(\eta^5\text{-}C_5H_5)W(CO)_2(LH)Cl]$, with the phosphorus bonded to the tungsten. Deprotonation using Et_3N occurs only when X = S to give phosphorus-, sulfur-bound chelate compounds $[(\eta^5\text{-}C_5H_5)W(CO)_2(L^-)]$. The reaction of $Me_2NC(S)N(H)R$, LH, (R = Me, Ph) with $[(\eta^5\text{-}C_5H_5)W(CO)_3Cl]$ in the presence of Et_3N yields the sulfur, nitrogen-bonded complexes $[(\eta^5\text{-}C_5H_5)W(CO)_2(L^-)]$ [223]. The reaction between $[(\eta^5\text{-}C_5H_5)W(CO)_3I]$ and RNC (R = $PhCH_2$, CMe_3 or 2,6-dimethylphenyl) is catalysed by the dimer $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ to yield

$[(\eta^5\text{-}C_5H_5)W(CO)_{3-n}(RNC)_nI]$. A reaction pathway involving a fast non-chain radical mecahnism and a slower chain radical reaction has been proposed [224]. Cycloelimination of $[(\eta^5\text{-}C_5H_5)(CO)_2W(X)\{PPh_2(CH_2)_3Cl\}]$ with sodium amalgam yields the complex $[(\eta^5\text{-}C_5H_5)(CO)_2WPPh_2(CH_2)_3]$, which contains a five-membered metallocycle [225].

$Na[(\eta^5\text{-}C_5H_5)W(CO)_3]$ and Ph_2PCl react to give $[(\eta^5\text{-}C_5H_5)(CO)_3WPPh_2]$, which can be converted to *trans*-$[(\eta^5\text{-}C_5H_5)(CO)_2(PMe_3)WPPh_2]$ *via* phosphine/CO exchange. These complexes react with HCl, MeI or Br_2 to give $[(\eta^5\text{-}C_5H_5)(CO)_2LWPPh_2R]Hal$ (L = CO or PMe_3; R = H, Me or Br) and with S or Se to give $[(\eta^5\text{-}C_5H_5)(CO)_2LWPPh_2E]$ (E = S or Se) [226]. The anionic thiocarbonyl complexes $[(\eta^5\text{-}C_5H_5)W(CO)_2(CS)]^-$ and $[\{HB(pz)_3\}W(CO)_2(CS)]^-$ (pz = 1-pyrazolyl) react with *N*-methyl-*N*-nitrosyl-4-toluensulfonamide and acid, or with $[NO][PF_6]$ to give $[LW(CO)(CS)(NO)]$ (L = $\eta^5\text{-}C_5H_5$ or $HB(pz)_3$). $[(\eta^5\text{-}C_5H_5)W(CO)_2(CS)]^-$ reacts with chloro-2,4-dinitrobenzene (DNP-Cl) to yield $[(\eta^5\text{-}C_5H_5)(CO)_2W{\equiv}C\text{–}S\text{–}DNP]$. $[\{HB(pz)_3\}W(CO)_2(CS)]^-$ reacts with MeI, EtI and DNP–Cl to give the stable mercaptocarbyne derivatives $[\{HB(pz)_3\}(CO)_2W(CS\text{–}R)]$. Reactions of $[(\eta^5\text{-}C_5H_5)\ W(CO)(CS)(NO)]$, $[\{HB(pz)_3W(CO)_2(CS)(NO)]$, *cis*-$[(\eta^5\text{-}C_5H_5)W(CO)_2(CS)(SnPh_3)]$ and *cis*-$[(\eta^5\text{-}C_5H_5)W(CO)_2(CS)(PbPh_3)]$ with H_2NMe smoothly transform the CS to the $C{\equiv}N\text{–}Me$ ligand [227].

The photochemistry of $[(\eta^5\text{-}C_5H_5)W(CO)_3Me]$ in solution has been investigated. The primary photoprocess was proposed to be W–CO bond dissociation, and a pathway was suggested for the formation of the dimer $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ [228]. The organic reactions of the side chain on the substituted cyclopentadienyl complexes $[(\eta^5\text{-}C_5H_4R)W(CO)_3Me]$ (R = CHO, $CH{=}CH_2$ or CH(OC)Me) have been reported, and the addition polymerisation of $[(\eta^5\text{-vinylcyclopentadienyl})W(CO)_3Me]$ and $[(\eta^5\text{-cyclopentadienylmethylacrylate})W(CO)_3Me]$ observed [229]. The kinetics of the reaction between $[(\eta^5\text{-}C_5H_5)W(CO)_3(SnMe_3)]$ and I_2 has been spectrophotometrically measured and used to illustrate the conditions necessary for a bimolecular reaction proceeding *via* an intermediate to appear to fit a rate equation for a simpler reaction [230]. The series of complexes $[(\eta^5\text{-}C_5H_5)M(CO)_3(PbR_3)]$ (M = Cr, Mo or W; R = Me or Et) has been synthesised. The methyl derivatives are photochemically and thermally unstable, decomposing to give $[(\eta^5\text{-}C_5H_5)M(CO)_3Me]$. The ethyl complexes exhibit the rearrangement reactions to give $\{(\eta^5\text{-}C_5H_5)W(CO)_2\}_2PbEt_2$ [231].

The ethene bridged complexes $[(\eta^5\text{-}C_5H_5)(CO)_3M(\mu\text{-}C_2H_4)M'(CO)_3(\eta^5\text{-}C_5H_5)]$ (M,M' = Mo,W), $[(\eta^5\text{-}C_5H_5)(PPh_3)(CO)_2W(\mu\text{-}C_2H_4)W(CO)_3(\eta^5\text{-}C_5H_5)]$, and $[(\eta^5\text{-}C_5H_5)(CO)_3W(\mu\text{-}C_2H_4)Re(CO)_5]$ have been obtained by nucleophilic addition of $[W(CO)_3(\eta^5\text{-}C_5H_5)]^-$, $[W(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)]^-$ and $[Re(CO)_5]^-$ to coordinated ethene in $[W(CO)_3(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)]^+$ and $[W(CO)_2(PPh_3)(\eta^5\text{-}C_5H_5)(\eta^2\text{-}C_2H_4)]$

[232]. The pseudo-tetragonal-bipyramidal complexes $[(\eta^5\text{-}C_5H_5)W(CO)_2(C_2H_4)Me]$ and $[(\eta^5\text{-indenyl})W(CO)_2(C_2H_4)Me]$ show hindered rotation of C_2H_4 around the $W\text{–}C_2H_4$ bonds, demonstrated by ^1H NMR spectroscopy. The $^1J(^{183}W\text{-}^{13}C)$ coupling in the ^{13}C NMR spectra of the ethene in the former complex, and the ethyne in $[(\eta^5\text{-}C_5H_5)W(CO)(C_2H_2)Me]$ indicate some s-character in the W–C bonds [233]. In $[(\eta^5\text{-}C_5H_5)W(CO)_3(C_2H_5)]$ the $W\text{–}C_2H_5$ bond is photolabile and irradiation of the complex in solution gives $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$, $[(\eta^5\text{-}C_5H_5)W(CO)_3H]$, C_2H_6 and C_2H_4. In the presence of PMe_3, UV irradiation of the solution gives $[(\eta^5\text{-}C_5H_5)(CO)(PMe_3)_2W\text{–}W(CO)_3(\eta^5\text{-}C_5H_5)]$, $[(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)(C_2H_5)]$ and $[(\eta^5\text{-}C_5H_5)W(CO)_2(PMe_3)H]$ [234]. Protonation of $[(\eta^5\text{-}C_5H_5)(CO)_3W\text{–}C{\equiv}CPh]$ gives $[(\eta^5\text{-}C_5H_5)(CO)_3W\{\mu\text{-}(\eta^1, \eta^2\text{-}C_2Ph)\}W\ (\eta^2\text{-}C_2PhH)(CO)(\eta^5\text{-}C_5H_5)]^+$, characterised as its $[BF_4]^-$ salt by X-ray crystallography. No tungsten-tungsten bond was found. In the presence of PPh_3, the protonation reaction gives $[(\eta^5\text{-}C_5H_5)(CO)_3W\{C(PPh_3)\text{=}CPhH\}][BF_4]$ [235].

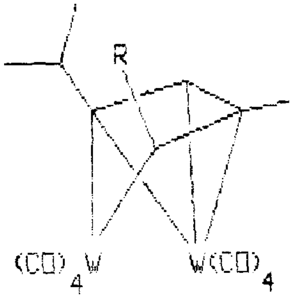
The ligand 6-dimethylaminofulvene acts as a zwitterionic η^5-donor in the complex $[(CO)_3W\{C_5H_4C(H)NMe_2\}]$. ^1H NMR has been used to determine the energy parameters for the barrier to rotation about the C–N bond [236]. The effect of protonation of the tungsten in $[(CO)_3W\{C_5H_4C(H)NMe_2\}]^+$ on the kinetic parameters of rotation about the C–N bond has been determined [237].

The electron impact mass spectra of a series of complexes $[(CO)_3M(\eta^6\text{-}PhX)]$ (M = Cr or W; X = OMe, OBu, CO_2Me or CO_2Bu) have been recorded. The fragmentation patterns of the tungsten complexes differ from those of the chromium complexes due to its stronger electrophilic character and the more pronounced tendency of tungsten to attain higher oxidation states [238].

The reaction of $[(\eta^7\text{-}C_7H_7)W(CO)_2I]$ with ER^- bases (E = O, S, Se, Te; R = alkyl, aryl) yields several types of compounds, including $[\eta^7\text{-}C_7H_7)W(CO)_2(ER)]$ and $[(\eta^3\text{-}C_7H_7)(CO)_2W(\mu\text{-}OR)_3W(CO)_2(\eta^4\text{-}C_7H_8)]$, characterised by analyses and by IR, ^1H NMR and mass spectroscopy [130]. The crystal structure of $[(\eta^7\text{-}C_7H_7)W(CO)_2(SePh)]$ has been determined [239].

Cyclic voltammetry has been used to investigate the electrochemical oxidation of the acyltungsten anions $[(RCO)W(CO)_5]^-$. Shifts in the peak potentials on changing cations demonstrated the influence of ion-pairing effects [240].

The μ-alkylidene comlex $[W_2(CO)_9(\mu\text{-}CHCHCMe_2)]$ reacts with but-2-yne to give an insertion product with a metal-metal bond, which rearranges to give the tungstole-tungsten derivative $[W_2(CO)_8(C_9H_{14})]$, (**8**), characterised by ^1H NMR spectroscopy and by an X-ray crystal structure determination [231,242].



(8)

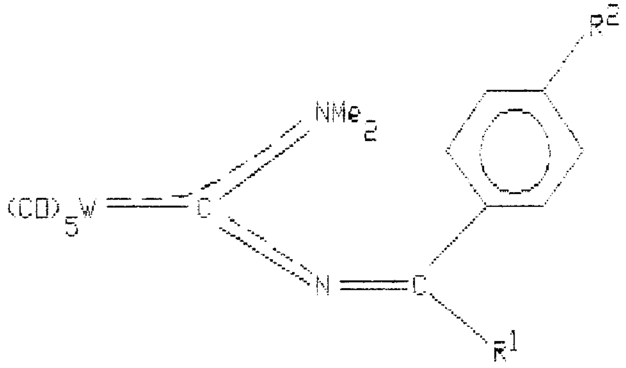
The tridentate *N-,O-,S*-donor ligand $\{Me_2Ga(N_2C_3HMe_2)(OCH_2CH_2SR)\}^-$, L^-, (R = Et or Ph) has been synthesised and used to prepare the tungsten derivatives $[W(CO)_2(\eta^3\text{-}C_7H_7)L]$ and $[W(CO)_2(NO)L]$ [243]. The complex $[Et_4N][W(CO)_3(N_2C_3H_4)\{Me_2Ga(N_2C_3H_3)_2\}]$, which contains both the pyrazole ligand and the bidentate dimethylbis(pyrazolyl)gallium anionic ligand, has been prepared and characterised [244].

The crystal structure of $[Et_4N][\{W(\eta^3\text{-}C_3H_5)(CO)_2\}_2(\mu\text{-}Cl)_3]$ has been determined. There is no metal-metal bond and the allyl groups are *trans* to each other [245]. The reactions of L (L = $PHPh_2$, $PMePh_2$) with $[WCl(CO)_2(\eta^3\text{-}C_3H_5)(MeCN)_2]$ in MeOH have been found to involve initial substitution to give $[WCl(CO)_2(\eta^3\text{-}C_3H_5)L_2]$. In MeCN, an excess of phosphine caused reductive elimination of allylchloride to give $[W(CO)_2(MeCN)L_3]$. During these reactions the anion $[WCl(CO)_2(\eta^3\text{-}C_3H_5)(PMePh_2)]^-$ was formed and isolated as a σ-allylphosphonium salt. The mechanism of reaction was discussed [246]. X-ray photoelectron spectroscopic measurements on complexes containing the $\{(\eta^3\text{-allyl})W(CO)_2\}$ moiety and neutral $[W(CO)_{6-x}L_x]$ complexes have been made to determine the W 4f binding energies. The results were discussed and compared with molybdenum analogues [247].

The reaction of $[WBr(\eta^3\text{-allyl})(CO)_2(bipy)]$ with sodium ethylxanthate (Na[Etxant]) yields $[W(Etxant)(\eta^3\text{-allyl})(CO)_2(bipy)]$. Monodentate coordination of the xanthate ligand was deduced from IR and NMR spectroscopic data [248]. The ligands 1-alkyl-3,5-diphenylthiabenzene-1-oxides, $C_5H_3Ph_2S(O)R$, form stable π-complexes $[W(CO)_3\{C_5H_3Ph_2S(O)R\}]$. These react with $[NO][PF_6]$ to give $[W(CO)_2\{C_3H_5Ph_2S(O)R\}][PF_6]$, which can be isolated if the R substituent is a bulky electron-releasing group such as $CH(CH_2Ph)_2$ or $CH(SiMe_3)_2$ [249].

The photoinduced degradation of the carbene complex $[(CO)_5W{=}CPh_2]$ in

C_6H_{14} gave $[W(CO)_6]$, $Ph_2C{=}CPh_2$, Ph_2CH_2 and $Ph_2HC{-}CHPh_2$. The dependence of the yields of the organic products on the concentration was investigated [250]. Insertion of dimethylcyanamide into the metal-carbene bond of complexes $[(CO)_5W\{R^1(C_6H_4\text{-}4\text{-}R^2)\}]$ (R^1 = OMe, R^2 = H, Me or CF_3; R^1 = Ph, R^2 = H, Me, CF_3 or Br) yields amino(alkylideneamino)carbene complexes , (9), characterised by

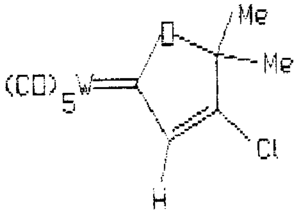


(9)

IR and ^1H NMR spectroscopy [251]. The complexes $[(CO)_5W\{CPh(C_6H_4\text{-}4\text{-}R)\}]$ (R = Me, OMe, H, Br or CF_3) react with elemental sulfur with insertion of one sulfur atom into the metal-carbene bond to give arylphenylthioketone complexes, characterised by analyses and by spectroscopic measurements [252]. The reaction of organoisocyanates R^1NCS (R^1 = Me, Et or Ph) with $[(CO)_5W\{CPh(C_6H_4\text{-}4\text{-}R)\}]$ (R = Me, OMe, H, Br or CF_3) results in insertion of the sulfur atom of the isocyanate into the metal-carbene bond, giving thioketone complexes. The kinetics of the insertion have been investigated and an associative mechanism proposed [253].

The reaction of $[W(CO)_5(CS)]$ with SR^- (R = alkyl) yields $[W(CO)_5\{C(S)SR\}]^-$ which can be alkylated using R^1I (R^1 = alkyl) to give $[W(CO)_5\{C(SR^1)SR\}]$. This reaction has been used as a general preparative route to substituted or cyclic dithiocarbene analogues and their reactions with amines and other nucleophiles have been investigated [254]. $[W(CO)_5\{C(SMe)_2\}]$ reacts with tertiary phosphines to give novel phosphorane products $[W(CO)_5\{(SMe)_2C{=}PR_3\}]$. The crystal structure of $[W(CO)_5\{(SMe)_2C{=}PMePh_2\}]$ has been determined, and shows the ligand to be bound *via* one of the sulfur atoms. PPh_2H reacts with $[W(CO)_5\{C(SMe)_2\}]$ to give the phosphine complex $[W(CO)_5(PPh_2\{CH(SMe)_2\})]$ [255]. An investigation of the reaction of $[W(CO)_5\{CMe(OCH_2)\}]^-$ with enol ethers $CH_2{=}C(OR)R'$, followed by protonation, led to new alkylidene complexes which result from pericyclic addition. Treatment with base gave after alcohol elimination new vinyl alkylidene complexes $[W(CO)_5\{C(OMe)(CH{=}CMeR')\}]$ [256].

The tungsten carbene complexes $[W(CO)_5\{CR(X)\}]$ (R = Me, X = NMe_2; R = Ph, X = NH_2, *E*-NHMe, *Z*-NHMe, NMe_2 or OMe) react with $HAuCl_4$ to give $[ClAu\{CR(X)\}]$ and $[W(CO)_4Cl_2]$. The reaction was found to proceed *via* a redox mechanism with retention of configuration of the carbene [257]. The reaction between $[Me_4N][W(CO)_5\{C(O)Me\}]$ and $[Cr(CO)_5(CNEt_2)][BF_4]$ at −78 °C yields $[(CO)_5Cr\{C(NEt_2)OC(Me)\}W(CO)_5]$, characterised by ^1H NMR [258]. $[W(CO)_5\{C(OLi)Me\}]$ reacts with $(Bu)_2BCl$ to give $[W(CO)_5\{C(CBBu_2)Me\}]$, which was isolated as a solvated solid and characterised by analyses and ^1H NMR [259]. $[W(CO)_6]$ and $LiC{\equiv}C{-}CMe_2OLi$ react to give the corresponding acylate complex, which on treatment with MeCOCl or HCl yields (2,2-dimethyl-3-chlorofuro-3-en-5-ylidene)-5-pentacarbonyltungsten(0), (10) [260].



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