ELSEVIER

Coordination Chemistry Reviews
164 (1997) 345–413

COORDINATION CHEMISTRY REVIEWS

Tungsten 1995

Edward H. Wong *

University of New Hampshire, Dept. of Chemistry, Parsons Hall, Durham, U.S.A.

Contents

1. Introduction . . . 346
2. Tungsten(VI) . . . 346
   2.1. Complexes with halide ligands . . . 346
   2.2. Complexes with nitrogen and phosphorus ligands . . . 347
   2.3. Complexes with oxygen and sulfur ligands . . . 350
   2.4. Complexes with hydride and alkyl ligands . . . 351
   2.5. Complexes with mixed donor ligands . . . 352
3. Tungsten(V) . . . 353
4. Tungsten(IV) . . . 356
   4.1. Complexes with halide ligands . . . 356
   4.2. Complexes with nitrogen ligands . . . 356
   4.3. Complexes with oxygen, sulfur, selenium, or tellurium ligands . . . 357
   4.4. Complexes with hydride ligands . . . 358
   4.5. Complexes with mixed donor ligands . . . 360
5. Tungsten(III) and (II) dimers . . . 363
6. Tungsten (II) . . . 367
   6.1. Complexes with nitrosyl ligands . . . 367
   6.2. Complexes with phosphine ligands . . . 369
   6.3. Complexes with cyclopentadienyl and carbonyl ligands . . . 372
   6.4. Complexes with tungsten–silicon bonds . . . 373
   6.5. Complexes with tungsten–metal bonds . . . 375
   6.6. Complexes with mixed donor ligands . . . 380
7. Tungsten(0) . . . 382
   7.1. Complexes with carbon ligands . . . 382
   7.2. Complexes with nitrogen ligands . . . 384
   7.3. Complexes with phosphorus ligands . . . 386
      7.3.1. Monometallic complexes with phosphorus ligands . . . 386
      7.3.2. Polymetallic complexes with phosphorus ligands . . . 390
   7.4. Complexes with sulfur and selenium ligands . . . 395
   7.5. Complexes with miscellaneous ligands . . . 397

* Corresponding author. E-mail: ehw@ghrista.unh.edu

0010-8545/97/$32.00
PII S0010-8545(97)00034-9

8. Selected tungsten clusters 400
8.1. Sulfur and other chalcogenide clusters 400
8.2. Miscellaneous clusters 405
References 409

1. Introduction

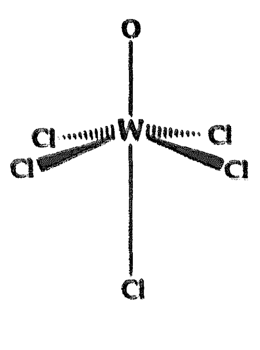
This review covers the tungsten coordination chemistry literature published in the 1995 calendar year. *Current Contents* as well as the indices of the major journals were searched. As in previous reviews, organometallic compounds of tungsten will not be discussed unless they have features of particular interest to the coordination chemist. While not intended as a fully comprehensive compilation of tungsten coordination chemistry in 1995, we hope to present here a representative survey of new developments and advances in the field.

Complexes have been grouped in order of the tungsten centre's formal oxidation state while subsections have been arranged according to donor atom types. Where mixed-donor complexes occur, they have either been grouped in accord with the key ligands of interest or in the mixed-donor ligand subsection.

2. Tungsten(VI)

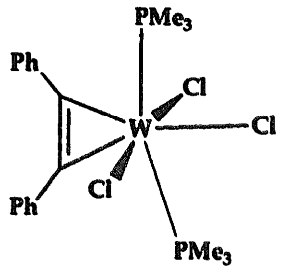
2.1. *Complexes with halide ligands*

The reaction of $W(CO)_6$ with 21-crown-7, water, and HCl(g) in toluene under UV irradiation gave a moderate yield of $[H_5O_2^+ \cdot 21\text{-crown-7}][WOCl_5^-]$ [1]. X-Ray structural determination revealed that the $[H_5O_2]^+$ cation fits snugly inside the macrocycle which adopts a shallow bowl-like conformation. The $[WOCl_5]^-$ ion (**1**) has a highly-distorted octahedral geometry with the axial W–Cl *trans* to the oxo group lengthened to 2.666(5) Å compared to the average of 2.366(7) Å for the other four equatorial W–Cl distances. The average oxo–W–Cl_{eq} angle of 96.5(6)° indicates a bending away from the oxo group.

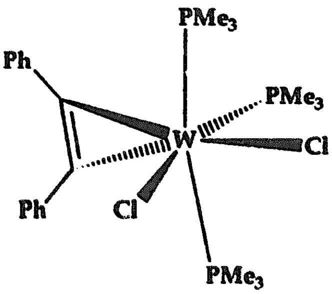


(**1**)

X-Ray photoelectron spectroscopy of $[WCl_4(PhC_2Ph)]_2$ gave a $W(4f_{7/2})$ binding energy consistent with a d^0 tungsten(VI) formulation [2]. In accord with this, its reaction with NaOH-EtOH gave *cis*-stilbene while reduction with Na/Hg in the presence of PMe_3 gave the d^1-complex $WCl_3(PhC_2Ph)(PMe_3)_2$ (**2a**). Reduction with four equivalents of Na/Hg gave $WCl_2(PhC_2Ph)(PMe_3)_3$ (**2b**).



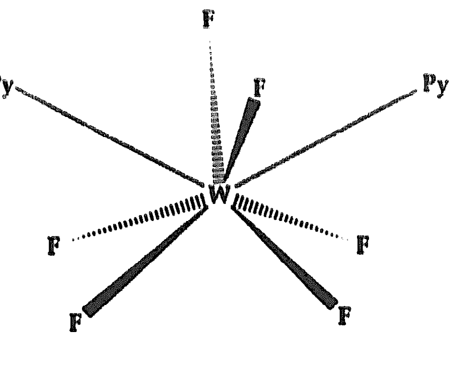
(2a)



(2b)

The structure of WO_2Br_2 has been determined by electron diffraction [3]. The molecule has C_{2v} symmetry with W=O at 1.710(6) Å, W–Br at 2.398(5) Å, and nearly tetrahedral angles of OWO at 111(2)° and BrWBr at 114(1)°.

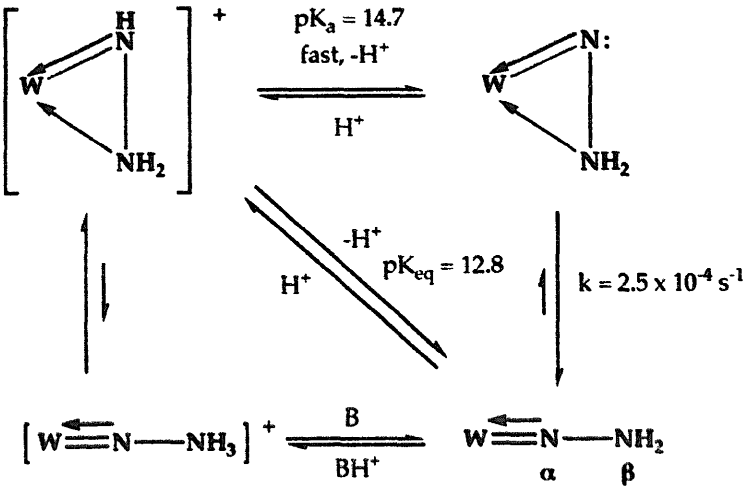
Characterization of the adducts $WF_6 \cdot py$ and $WF_6 \cdot 2py$ have been reported together with the crystal structure of the latter [3a]. The tungsten atom is in a bicapped trigonal prism environment with the pyridyl nitrogens capping two square faces of a WF_6 prism (3). Solution ^{19}F, ^1H, and ^{13}C NMR spectral studies support a monocapped trigonal prismatic geometry for the $WF_6 \cdot py$ structure.



(3)

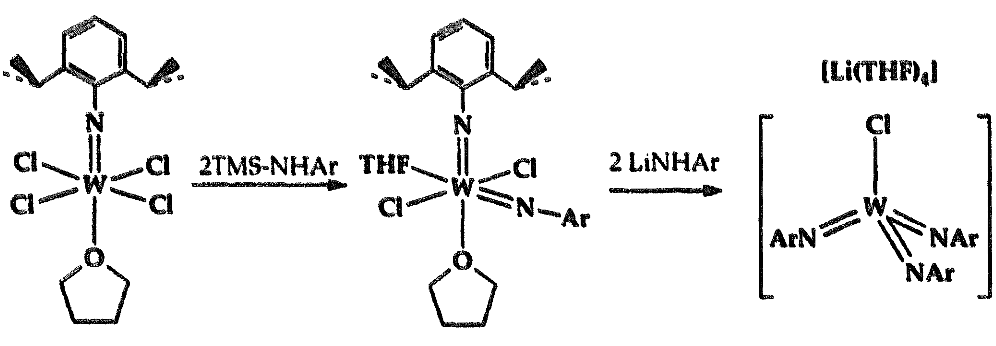
2.2. *Complexes with nitrogen and phosphorus ligands*

Relevant to transition metal-mediated nitrogen fixation, the kinetic protonation site of the complex $Cp^*WMe_3(NNH_2)$ was studied [4]. Scheme 1 details the observed interconversions which clearly established the protonation site to be the β-nitrogen.



Scheme 1.

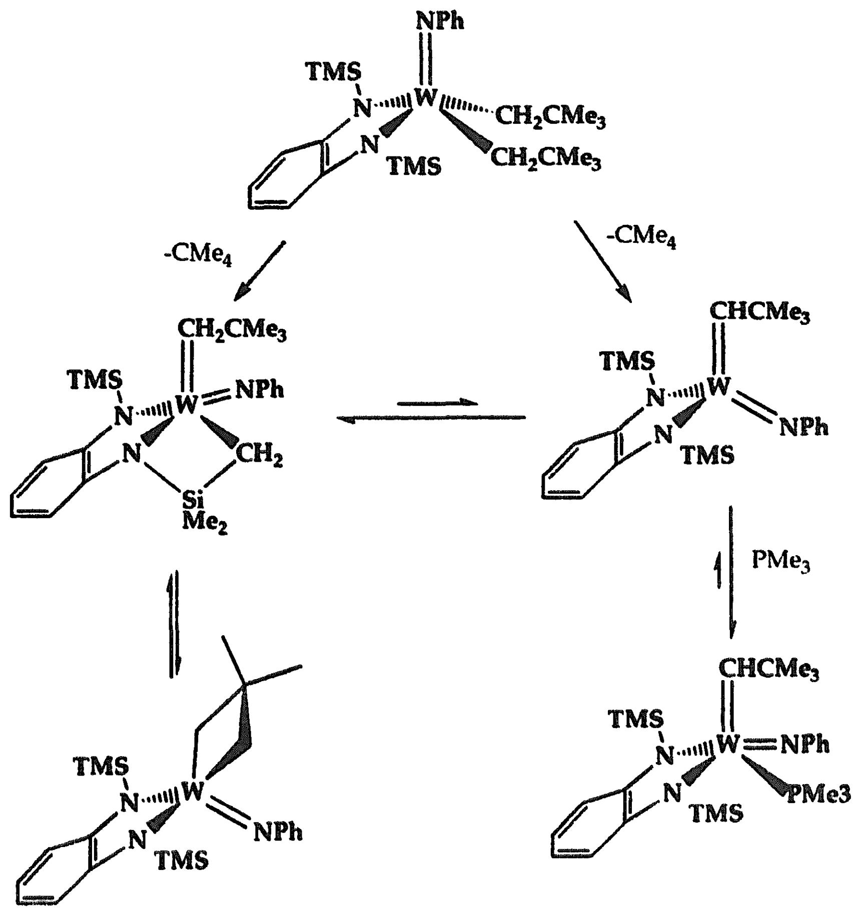
The synthesis, reactivity, and structure of the d^0-tris(imido) complex $[Li(THF)_4][W(NAr)_3Cl]$ ($Ar=2,6-C_6H_3^iPr_2$) have been reported [5]. Experiments support intermolecular deprotonation of the $W(NAr)_2(NHAr)Cl$ intermediate by the $[NHAr]^-$ anion. A kinetic product $W(NAr)_2Cl_2(THF)_2$ was isolated and found to form via intramolecular α-H abstraction in $W(NAr)(NHAr)_2Cl_2(THF)_2$ (Scheme 2). Nucleophilic substitution of the chloride at $[W(NAr)_3Cl]^-$ gave products like $W(NAr)_3PMe_3$ and $[W(NAr)_3Me]^-$. The molecular structures of both $[W(NAr)_3Cl]^-$ and $W(NAr)_3PMe_3$ were found to be nearly tetrahedral. In accord with MO calculations of C_{3v} $Mo(NAr)_3L$ which revealed the HOMO to be imido-based, protonation of $[W(NAr)_3Me]^-$ occurred at the imido nitrogen and not the W–Me bond.



Scheme 2.

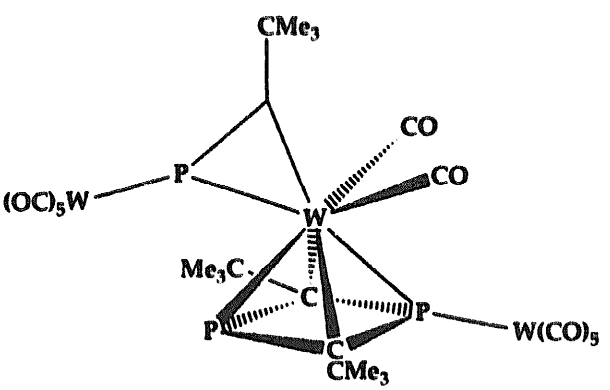
Depending on the presence or absence of PMe_3, thermolysis of $LW(NPh)(CH_2CMe_3)_2$ (L = *N,N'*-bis(trimethylsilyl)-o-phenylenediamido) can lead to α- or γ-H abstraction products respectively (Scheme 3) [6].

The three-component reaction of $W_2(OBu^t)_6$ with the phosphaalkyne $Bu^tC{\equiv}P$ and $M(CO)_5 \cdot THF$ (M = Cr, W) led to interesting products [7]. The molecular structure of the formally trimeric, major tungsten product is shown in structure (4). At lower reaction temperatures, spectral evidence (^{31}P NMR δ 595, 545, $^1J_{WP}=536, 554$ Hz))



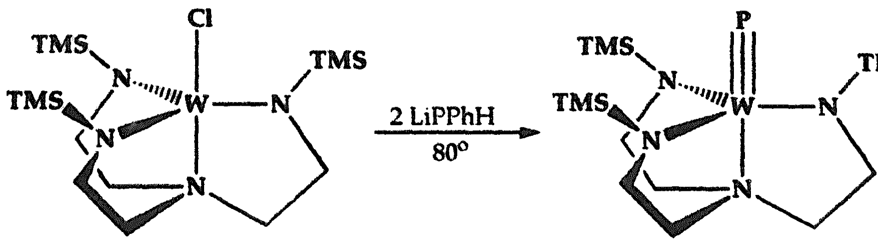
Scheme 3.

was presented for the formation of $(Bu^tO)_3WP{\rightarrow}M(CO)_5$ intermediates featuring stabilized WP triple bonds.



(4)

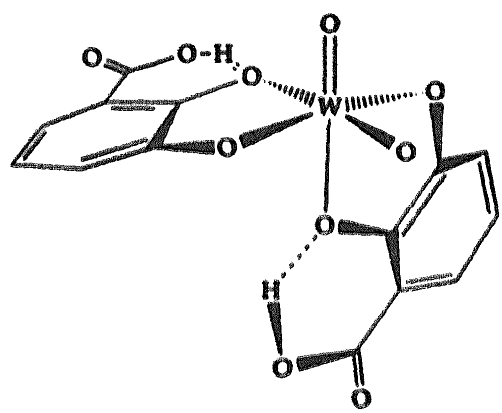
Unequivocal evidence for a terminal tungsten-phosphorus triple bond was reported in the fully-characterized complex $(N_3N)WP$ where N_3N is the $[(Me_3SiNCH_2CH_2)_3N]^{3-}$ ligand (Scheme 4) [8]. An intermediate, $(N_3N)W\text{-}PPhH$, was proposed based on spectral data. The triply-bonded WP distance was found to be 2.162(4) Å while the ^{31}P NMR spectroscopic shift was δ 1080 with a low $^{1}J_{WP}$ of only 138 Hz.



Scheme 4.

2.3. Complexes with oxygen and sulfur ligands

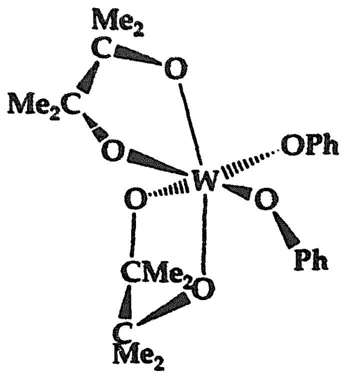
New complexes $[WO_2L_2]^{2-}$ (H_2L=2,3- or 3,4-dihydroxybenzoic acid) have been prepared and characterized [9]. A molecular structure determination of the molybdenum congener revealed catecholato rather than salicylato coordination as shown in (5). Other spectral data were presented.



(5)

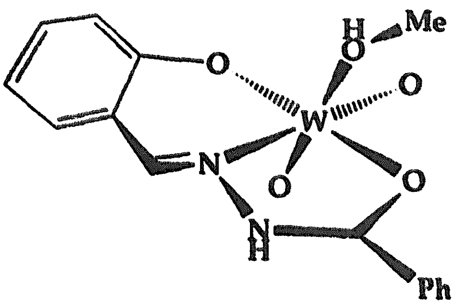
A tungsten(VI) complex $[WCl_2(\text{pinacolate})_2]$ was found to react with water and form dimeric $[W_2O_3(\text{pinacolate})_2]$ [10]. In the presence of tripropylamine, the hexatungstate $[W_6O_{19}]^{2-}$ was formed instead. Reaction of $[WCl_2(\text{pinacolate})_2]$ with pinacol led to $W(\text{pinacolate})_3$ while phenol gave $W(\text{pinacolate})_2(OPh)_2$. The structure of the latter product has been determined to contain an octahedral WO_6 core (6).

The complex formation of tungstate with mandelate $[PhCH(OH)COO^-]$ has been investigated by potentiometric and enthalpimetric titrations [11]. It was proposed that the major complex is the *cis*- $WO_2(\text{mandelate})_2^{2-}$ species.A general method for the preparation of dioxotungsten(VI) complexes of the type $[WO_2L(MeOH)]$ (where H_2L is a Schiff base) from $WO_2(acac)_2$ has been described [12]. The crystal structure o: $[WO_2(o\text{-}C_6H_4CH{=}NN{=}C(O)C_6H_5)(MeOH)]$ (7) has been determined. A convenient synthesis of dioxotungsten(VI) from the $W(O)(O_2)$ *N*-isonicoti-



(6)

namidosalicylaldimine complex via oxygen abstraction with PPh_3 has been reported [12a].



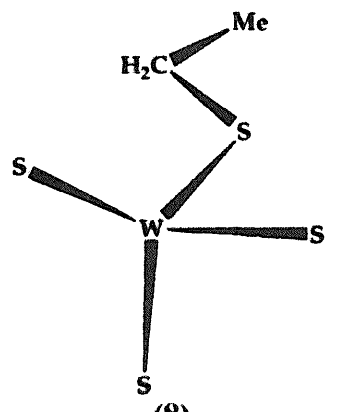
(7)

Mixed-metal complexes of W and Sm were prepared by the reaction of $Cp^{\ddagger}_2Sm(THF)_2$ with $[PPh_4]_2WS_4$ [13]. The dimetallic product $[PPh_4]_2[Cp^{\ddagger}_2Sm(\mu\text{-}S)_2WS_2]$ contains a tetrahedral WS_4 unit bridged by two sulfides to the Sm centre. Reaction of $[PPh_4]_2WS_4$ with ethyl bromide yielded the $[WS_3(SEt)]^-$ anion [14]. The solid-state molecular structure (8) revealed no intramolecular redox in its formation but concentrated solutions underwent rapid reactions to give $[W_3S_9]^{2-}$ and Et_2S_n (n = 1–3).

A 2.3 Å resolution crystal structure of the hyperthermophilic tungstopterin enzyme, aldehyde ferredoxin oxidoreductase, has been completed [14a]. Each of the two subunits contains two molybdopterin molecules that coordinate a single tungsten with four sulfur ligands. Resonance Raman spectra of $[NEt_4]_2[M^{VI}O_2(1,2\text{-benzenedithiolato})_2]$, $[NEt_4]_2[M^{IV}(O)(1,2\text{-benzenedithiolato})_2]$, (M = Mo, W) and related model species of the oxo-metal bonds in molybdenum and tungsten oxidoreductases have been reported [14b].

2.4. *Complexes with hydride and alkyl ligands*

The non-octahedral geometries of WH_6 and WMe_6 are predictable by a simple localized bonding scheme derived from Pauling's valence bond theory using only s

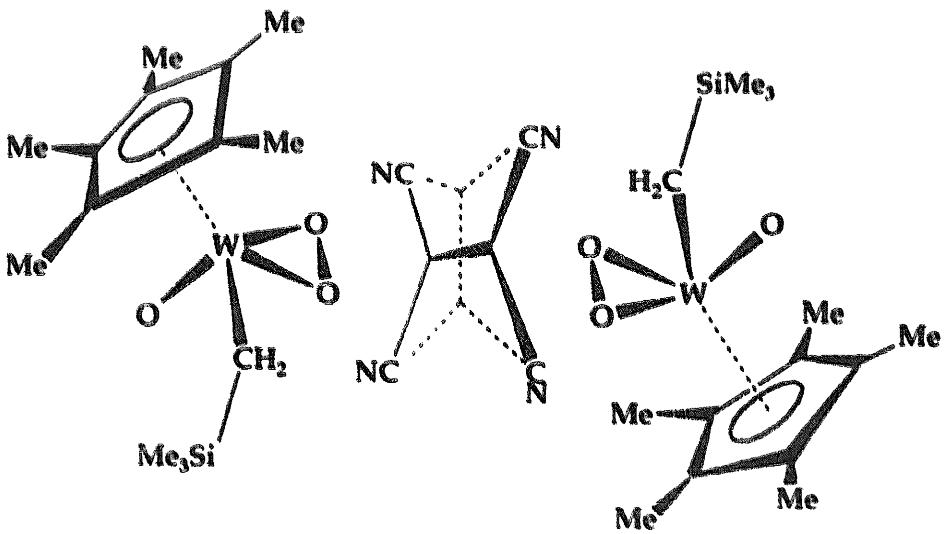


(8)

and d atomic orbitals [15]. For both molecules, six localized sd^5 hybrids favour arrangements with C_{3v} and C_{5v} structures including bond angles of 63° and 117° respectively rather than an O_h geometry.

2.5. Complexes with mixed donor ligands

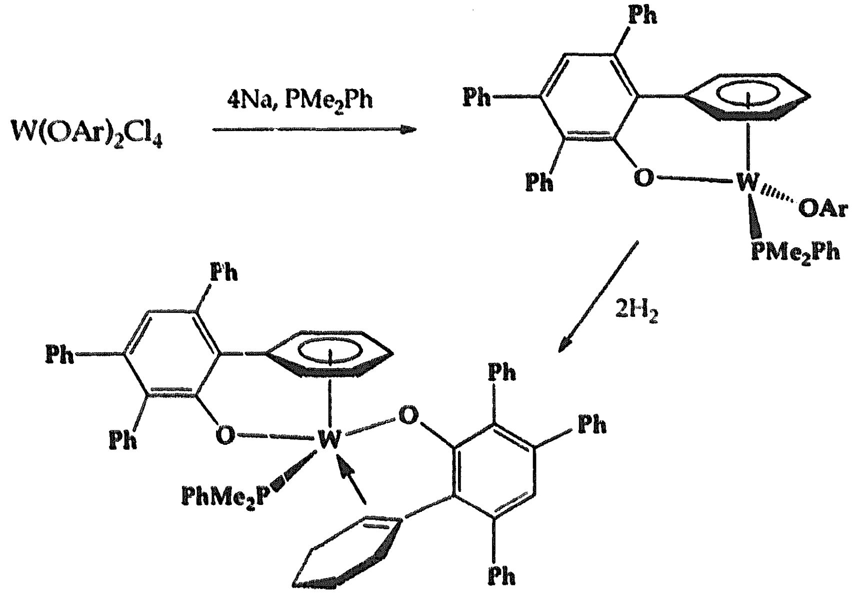
The crystal structures of $CpW(O)(O_2)(CH_2SiMe_3)$ and $[Cp^*W(O)$-$(O_2)CH_2SiMe_3]_2[TCNE]$ have similar piano-stool geometries around the W centres [16]. The W-oxo distances are 1.69(3) and 1.727(7) Å respectively while the W-peroxo distances average to 1.91 Å. The latter 2:1 complex has a disordered TCNE molecule sandwiched between the two organometallic molecules as shown in structure (9).



(9)

The synthesis and organometallic chemistry of aryloxy tungsten complexes $W(OAr)_xCl_{6-x}$ are described [17]. Applications of these compounds in olefin metathesis are reviewed. The role of bisphenol ligands in the stereocontrol of organic transformations catalysed by tungsten complexes has been reviewed [18].

Sodium amalgam reduction of $W(OAr)_2Cl_4$ (Ar = 2,3,5,6-C_6HPh_4) in the presence of PMe_2Ph and $PMePh_2$ led to deep-green [W(OAr)(O-C_6HPh_3-η^6-Ph)(phosphine)] [19]. Hydrogenation of this arene complex resulted in formation of an η^2-cyclohexene ring from one of the *o*-phenyl groups (Scheme 5).



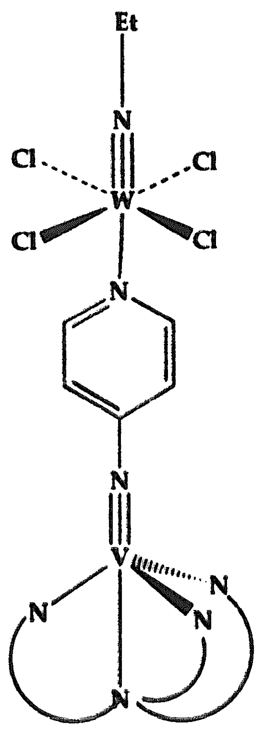
Scheme 5.

A tungsten(VI) complex, WOL_4, of the carbohydrate derivative diacetoneglucose (HL) was derived from the reaction of its lithium salt with $WOCl_4$ [20]. This product can add a pyridine to form WOL_4(py). Reaction of LiL with W{N(*p*-tolyl}Cl_4 gave the imido derivative W{N(*p*-tolyl}L_4.

The exposed N atom of the *p*-pyridylimido ligand in the vanadium(V) complex [$(TMS\text{-}NCH_2CH_2)_3N$]VN-$C_5H_4N$ was found to complex the imido-tungsten complex $EtNWCl_4$ and give a novel heterodimetallic product (**10a**) [20a].

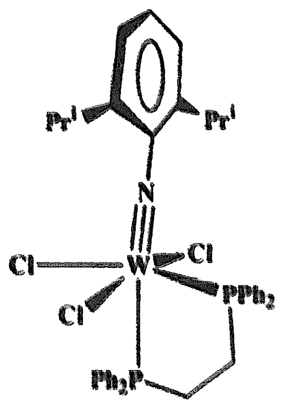
3. Tungsten(V)

Sodium amalgam reduction of $[WCl_4(NAr)]_2$ (Ar = 2,6 – $C_6H_3Pr^i_2$) in the presence of 4,4′-dimethyl-2,2′-bipyridyl (dmbpy) or dppe gave the d^1 complexes WCl_3(NAr)(dmbpy) and WCl_3(NAr)(dppe) respectively [21]. A crystal structure of the latter complex (**10**) revealed a *mer* arrangement of the chlorides. Similar reductions of $[WCl_4(PhCCPh)]_2$ yielded WCl_3(PhCCPh)(dmbpy) and WCl_3(PhCCPh)(dppe) respectively. In a related work, sodium amalgam (2 equivalents) reduction of $[WCl_4(NAr)]_2$ (Ar = 2,6-$C_6H_3Pr^i_2$) in the presence of monophosphines led to d^1 complexes $WCl_3(NAr)L_2$ (L = PMe_3, PMe_2Ph, $PMePh_2$) [22]. The

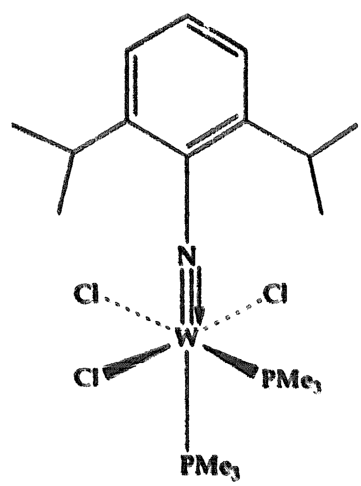


(10a)

crystal structure of the trimethylphosphine complex (11) shows that the 2,6-diisopropylphenylimido ligand exerts a greater *trans* influence than the phenylimido even though its steric pressure is only slightly larger. Air oxidation of this complex afforded the phosphoryl complex $[WCl_3(NAr)(PMe_3)(OPMe_3)]_2$ with the $OPMe_3$ ligand trans to the imido group. Use of 4 equivalents of Na/Hg in the reduction of $[WCl_4(NAr)]_2$ in the presence of phosphines led to the d^2 complexes $WCl_2(NAr)L_3$ (L = PMe_3, PMe_2Ph).

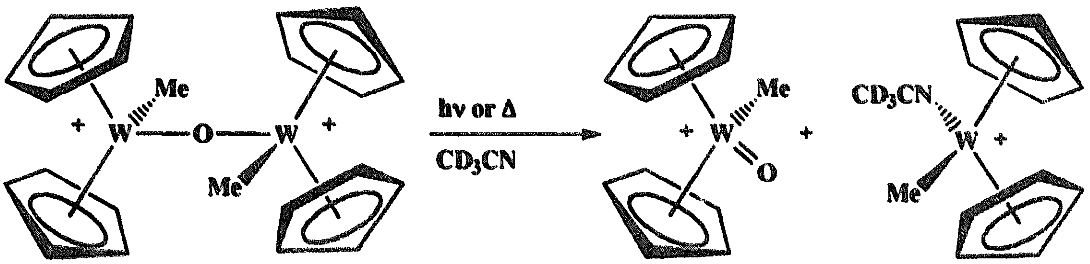


(10)



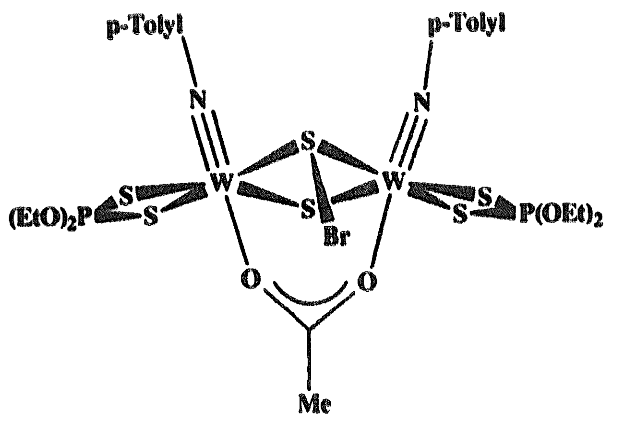
(11)

The oxo-bridged tungsten(V) dimer $[\{Cp_2WMe\}_2O]^{2+}$ was obtained by oxidation of $Cp_2W(OMe)Me$ with the ferrocenium cation [23a]. Structural characterization of the dimer revealed a linear W–O–W bridge with the methyl groups *anti*. Photolysis of this in MeCN resulted in disproportionation to the d^0 $[Cp_2W^{VI}(=O)Me]^+$ and d^2 $[Cp_2W^{IV}Me(NCMe)]^+$ products. Ferrocenium oxidation of the dimer in CH_2Cl_2 gave the radical cation $[Cp_2W(Me)Cl]^+$. The diamagnetic dimer $[\{Cp_2WMe\}_2O]^{2+}$ was also found to undergo a thermal disproportionation in CD_3CN to give the d^0 $[Cp_2W^{VI}(O)Me]^+$ and d^2 $[Cp_2W^{IV}Me(CD_3CN)]^+$ monomers (Scheme 6) [23]. Kinetic studies revealed a first-order reaction with a large enthalpic barrier of 33.7(1.7) kcal mol^{-1} and positive entropy of activation of 25.1(5.2) e.u. at 25°C. Photodissociation of the dimer in the UV(310 nm) and VIS(530 nm) regions was found to have quantum yields of 0.082 and 0.014, respectively.

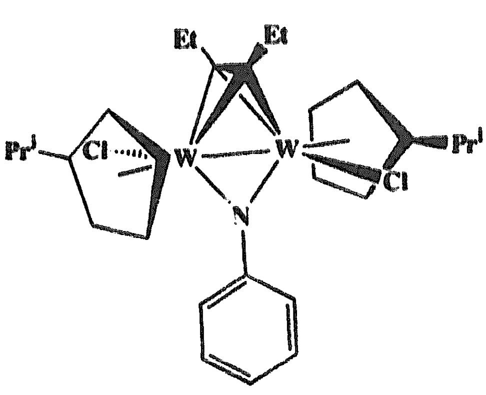


Scheme 6.

Halogenation reactions at various dimeric $W_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CMe)$ precursors yielded covalent halosulfide complexes [24]. For example, elemental bromine gave $W_2\{N(p\text{-tolyl}\}_2(S_2P(OEt)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CMe)(\mu\text{-}SBr)$ (**12**), the molecular structure of which has been determined. Trihalo polymers of the type $[W_2\{N(p\text{-tolyl}\}_2(S_2P(OEt)_2)_2(\mu\text{-}S)(\mu\text{-}O_2CMe)(\mu\text{-}SX_3)]_n$ were also obtained for X = Br or I. The crystal structure of a $Mo_2S_2I_3$ polymer revealed bent I_3 units linking Mo_2S_2 moieties.



(12)



(13)

Treatment of the alkyne-bridged $W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_4(\mu\text{-}C_2Et_2)$ complex with amines including $HN(SiMe_3)_2$, $MeN(SiMe_3)_2$, or aniline yielded imido-bridged dimers [25]. The X-ray structure of $W_2(\eta\text{-}C_5H_4Pr^i)_2Cl_2(\mu\text{-}C_2Et_2)(\mu\text{-}NPh)$ (**13**) revealed an sp^2-N, suggesting a three-centre, two-electron W–N–W banana bond.

A model for tungsten oxireductases, $NEt_4[W^V(O)L_2]$ has been synthesized from $[NEt_4][W(O)(SPh)_4]$ and the bulky dithiol $Ph_3SiC_6H_3(SH)_2$ (H_2L = 3-triphenylsilyl-1,2-benzenedithiol) [26]. The blue molybdenum congener reacted with oxygen in DMF solution to give the pale yellow oxo-bridged dimer $[Mo^{VI}O_2L]_2(\mu\text{-}O)$ which, in turn, reacted with excess oxygen to give polymolybdates.

Oxidation of elemental selenium with WCl_6 in a sealed ampoule afforded a novel selenium polycation in the product $[Se_{17}][WCl_6]_2$ [27]. The $[Se_{17}]^{2+}$ cation consists of two 7-membered Se_7 rings in the chair conformation connected by a Se_3 chain while the $[WCl_6]^-$ anion is distorted from O_h symmetry with an average W–Cl distance of 2.32 Å. This type of chemistry is related to that of tellurium but contrasts to sulfur which yielded $WSCl_4$ and S_2Cl_2 [28].

4. Tungsten(IV)

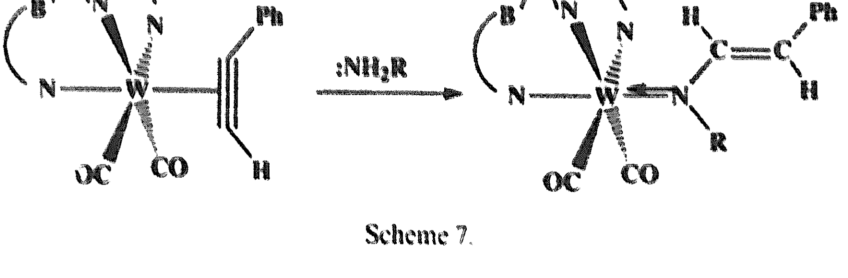
4.1. Complexes with halide ligands

The photochemical reaction of $W(CO)_6$ with $SnCl_4$ in the presence of triphenylphosphine gave $WCl_4(OPPh_3)_2$ which has been characterized by X-ray diffraction [29]. The molecule has C_2 symmetry and a *cis*-arrangement of the phosphine oxides. A slight lengthening of W–Cl bonds *trans* to these is noted.

Reaction between $WCl_4(dme)$ and the bis-cyclopentadienyl salt $Li_2[C_5H_4\text{-}CMe_2\text{-}C_5H_4]$ gave the *ansa*-bridged metallocene dichloride $[W(\eta\text{-}C_5H_4\text{-}CMe_2\text{-}\eta\text{-}C_5H_4)Cl_2]$ [30]. This can be converted to the dihydride and dimethyl derivatives by treatment with $LiAlH_4$ and $ZnMe_2$ respectively. The *ansa*-bridging is proposed to result in substantial electronic modifications compared to normal $Cp_2W(IV)$ chemistry.

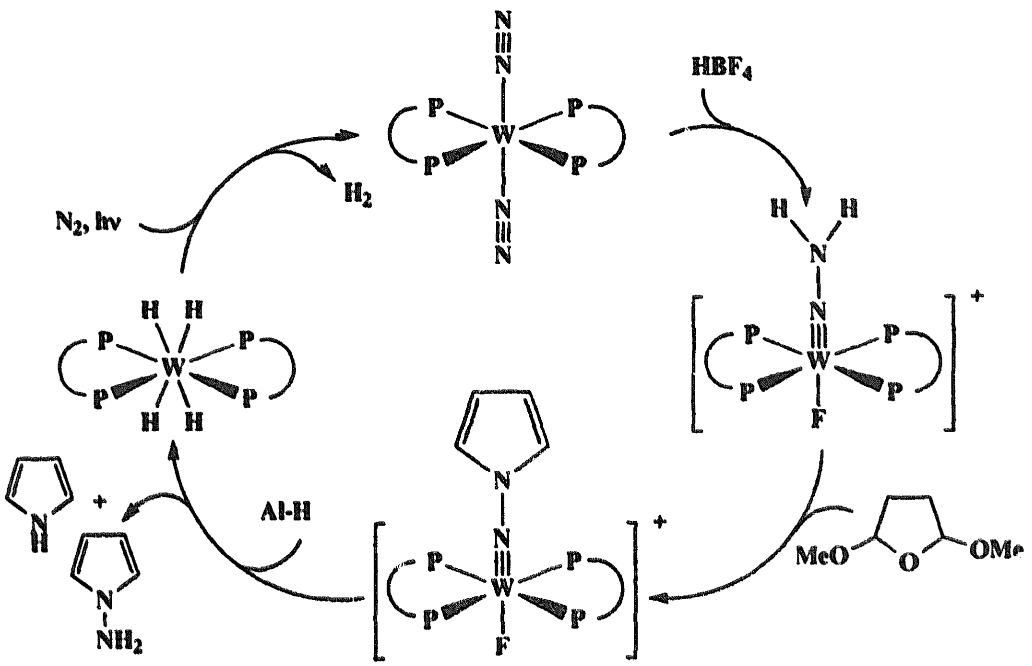
4.2. Complexes with nitrogen ligands

Reactions of the alkyne complex $[Tp'(CO)_2W(RC{\equiv}CH)][BF_4]$ with primary amines $R'NH_2$ afforded vinyl amido complexes $[Tp'(CO)_2W(N(R')(CH{=}CHR)]$ (R = Ph, R′ = Ph, Bu^t, CH_2Ph, Bu^n; R = Bu^t, Bu^n, R′ = CH_2Ph) (Scheme 7) [31]. Spectral and structural data support a W=N double bond.

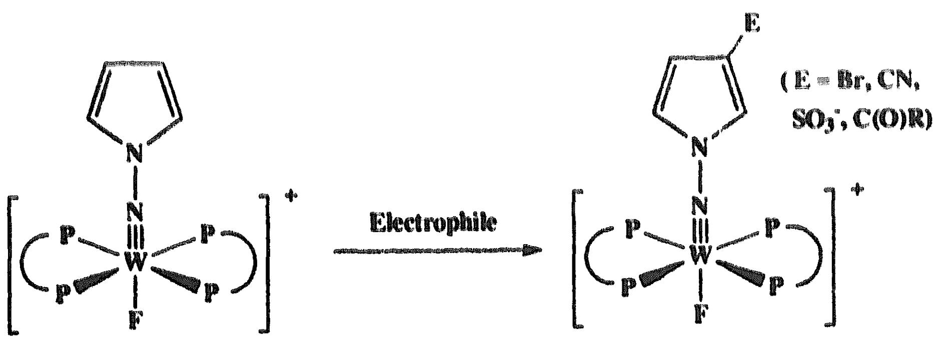


Scheme 7.

A synthetic cycle for β-substituted pyrroles has been accomplished via the hydrazido tungsten complexes *trans*-$[WX(=NNH_2)P_4]^+$ (where $P_4=2$ dppe or 4 PMe_2Ph) [32]. This is shown in Scheme 8 for the dppe complex. The pyrrolimido complex underwent electrophilic substitutions to give predominately β-substitution (Scheme 9).



Scheme 8.

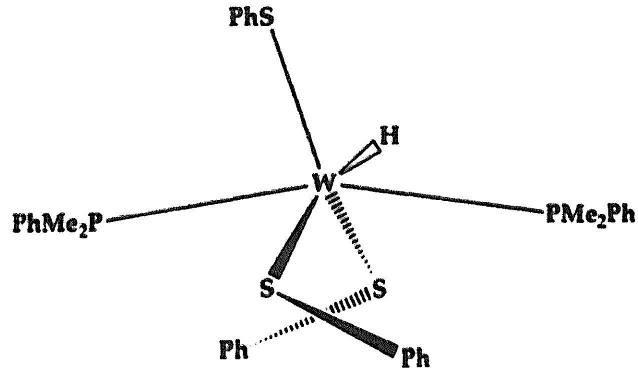


Scheme 9.

4.3. Complexes with sulfur, selenium, or tellurium ligands

The thermal reactivity of hydride-thiolate complex $[WH(SC_6H_2Me_3\text{-}2,4,6)_3(PMe_2Ph)_2]$ was studied by combined TGA-mass spectrometry [33]. Three events were observed with mesitylene, the hydrodesulfurization product, detected in each case.

The structures of the related hydride-thiolate complexes $[WH(SC_6H_2Pr^i_3\text{-}2,4,6)_3(PMe_2Ph)L]$ ($L=py$, PMe_2Ph) have been elucidated by a combination of ^1H and ^{31}P NMR spectroscopies as well as X-ray techniques [34]. The WS_3NP core consists of a distorted trigonal bipyramid with the phosphine(s) and(or) py axial and the thiolates equatorial while the hydride was proposed to be at the S_2P face as shown in structure (**13a**).



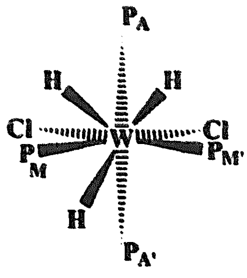
(**13a**)

An ionic product was obtained from the reaction of [$TlCpW(SC_6F_5)_4$] and $AuCl(PR_3)$ in the presence of PR_3 [35]. Variable temperature ^{19}F NMR spectroscopic studies of these [AuL][$CpW(SC_6F_5)_4$] (L = 3 PPh_3, 3PEt_3, 2 dppe, 2 dppp) complexes revealed rotation/inversion activation free energies at the SC_6F_5 groups to be 43-44 kJ mol^{-1} and to be essentially solvent independent.

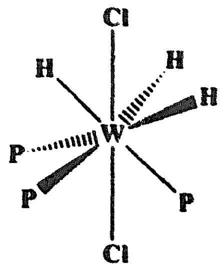
Novel terminal chalcogenido complexes of tungsten have been prepared and characterized [36,36a]. Reaction of $W(PMe_3)_5(H)_2$ with elemental Te gave $W(PMe_3)_4(H)_2(\eta^2\text{-}Te_2)$ which lost hydrogen to give an unprecedented oxidative cleavage and form the terminal Te complex *trans*-$W(PMe_3)_4(Te)_2$ (Scheme 10). The reaction of $W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H$ with H_2E (E = S,Se; Scheme 11) or elemental Te yielded the respective *trans*-$W(PMe_3)_4(E)_2$ (E = S, Se, Te) complex. Structural and bonding aspects of these were probed by X-ray diffraction, ^{77}Se and ^{125}Te NMR spectroscopic techniques. All three reacted reversibly with aldehydes to give η^2-$W(PMe_3)_2(E)_2(OCHR)$ products (Scheme 12). Unlike its S and Te congeners, the reaction of *trans*-$W(PMe_3)_4(Te)_2$ with Bu^tNC did not give simple substitution products. Instead, an unusual coupling of the terminal tellurides occurred (Scheme 13).

4.4. Complexes with hydride ligands

Interactions of tungsten(IV) hydrides of the type $WH_4(dppe)_2$ with proton donors led first to a molecular hydrogen-bonded complex followed by a proton transfer to give $[WH_5(dppe)_2]^+$ [37]. Deprotonation of this product was found to proceed through similar intermediates. Low temperature multinuclear NMR spectroscopic studies of the protonation of $WH_2Cl_2(PMe_3)_4$ has revealed two intermediate products [38]. In CD_2Cl_2, at −85°, a kinetic product with inequivalent hydrides was observed. This transformed to a fluxional tungsten(VI) $[W(H)_3Cl_2(PMe_3)_4]^+$ species (**14**) at −70° with equivalent hydrides. Finally, at −30°, a rigid C_3-symmetry complex $W(H)_3Cl_2(PMe_3)_3^+$ (**15**) was formed.

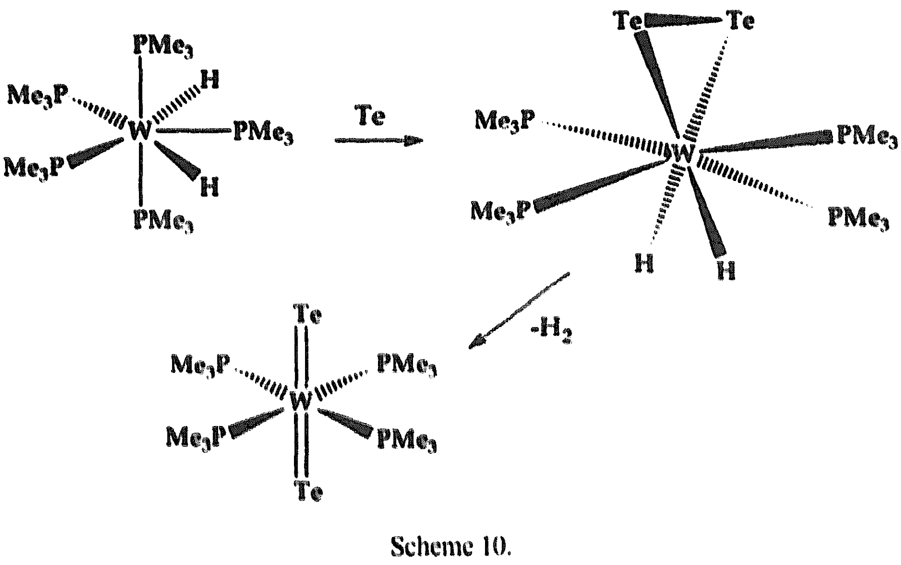


(14)

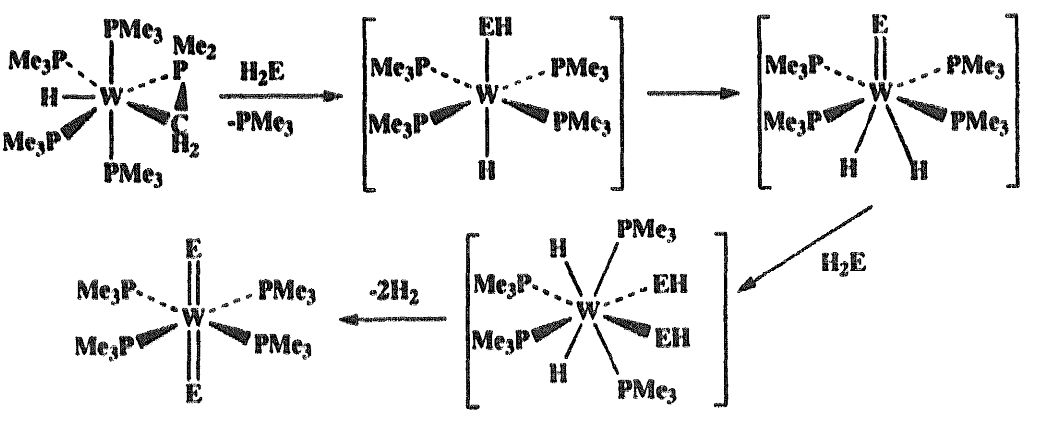


(15)

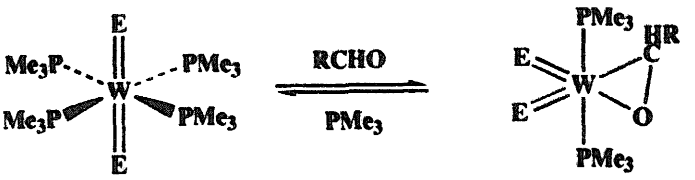
Similar to several rhenium polyhydrides, $WH_4(PMePh_2)_4$ was found to form intermolecular hydrogen bonds of the type MH···HX to weak proton acids like indole and 2,4,6-$Me_3C_6H_2OH$ [39]. The crystallographic structure of $WH_3(\eta^1$-OOCMe)$(dppe)_2$ (**15a**), a product of the electrochemical reduction of $[WH_2(\eta^1\text{-OOCMe})(dppe)_2]^+$ in the presence of protons, revealed a novel intramolecular W-H···O=C hydrogen bond with an O···H distance of 2.33(6) Å [39a]. Reaction of excess anhydrous DX (X=Cl,Br) with the same tungsten trihydride



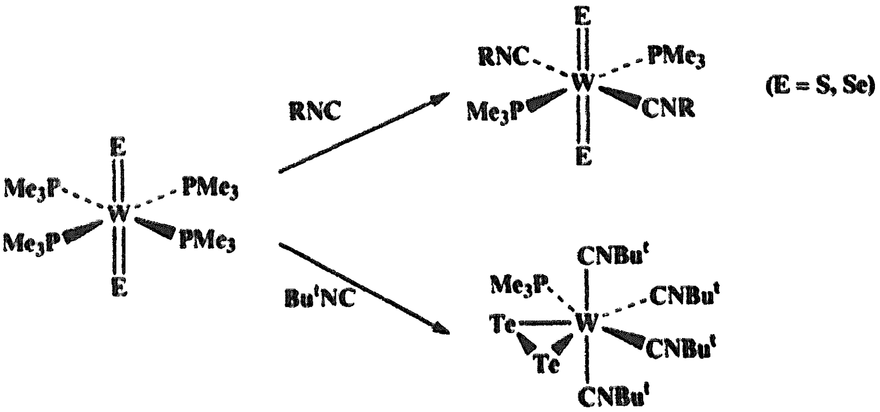
Scheme 10.



Scheme 11.

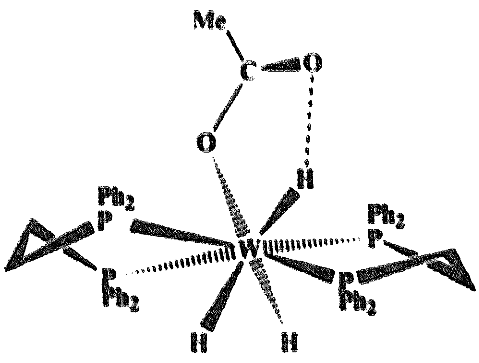


Scheme 12.



Scheme 13.

selectively produced H_2 and $[WHD(\eta^1\text{-OOCMe})(dppe)_2]^+$ [39b]. It is postulated that deuteration occurred at the pendant acetate while H_2-evolution proceeded at the metal.

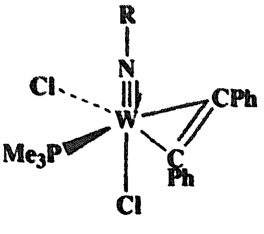


(15a)

4.5. Complexes with mixed donor ligands

The d^0 tungsten(VI) complex $[WCl_4(PhC\ CPh)]_2$ has been reacted with silylamines Me_3SiNHR ($R = CMe_3$, $CHMe_2$, 2,6-$CHMe_2Ph$) to generate d^2 imido complexes [40]. Disruption of the perpendicular bonding component of the acetylene is supported by spectroscopic and structural studies (**16**).

The structural, spectral, and magnetic behaviour of $WCl_4(SEt_2)_2$ has been reported



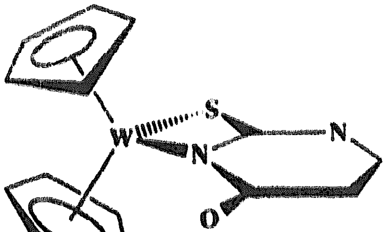
(16)

[41]. An octahedrally-coordinated metal atom was found with *trans*-thioethers and average W–Cl and W–S distances of 2.331 and 2.517 Å, respectively.

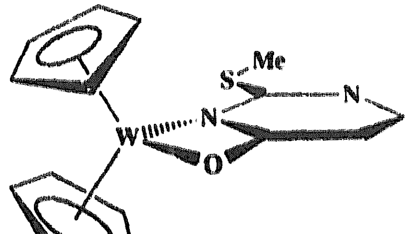
An update on cyclopentadienyl-imido molybdenum(IV) and tungsten(IV) complexes and their chemistry has appeared [42]. *Ansa*-bridged sandwich complexes were found to be much more resistant to reductive elimination reactions than their parent compounds.

Terminal phosphido complexes $Cp_2M(H)PPh_2$ (M = Mo, W) were found to react with $M'(CO)_5 \cdot THF$ (M = Cr, Mo, W) to give phosphido-bridged products $Cp_2M(H)(\mu\text{-}PPh_2)M'(CO)_5$ and $Cp_2M((\mu\text{-}PPh_2,H)M'(CO)_4$ in high yields [43]. These were examined by IR and NMR spectroscopies and EHMO studies for fluctuation of electron density between the metal fragments. A crystal structure of $Cp_2W((\mu\text{-}PPh_2H)W'(CO)_4$ revealed a W–W separation of 3.271(1) Å.

Uracil and thiouracil were found to react with Cp_2WCl_2 in the presence of triethylamine to give the respective 1:1 complexes (**17**) and (**18**) [44]. Spectral and X-ray data supported the metal binding preference of N(3) > N(1),S > O.



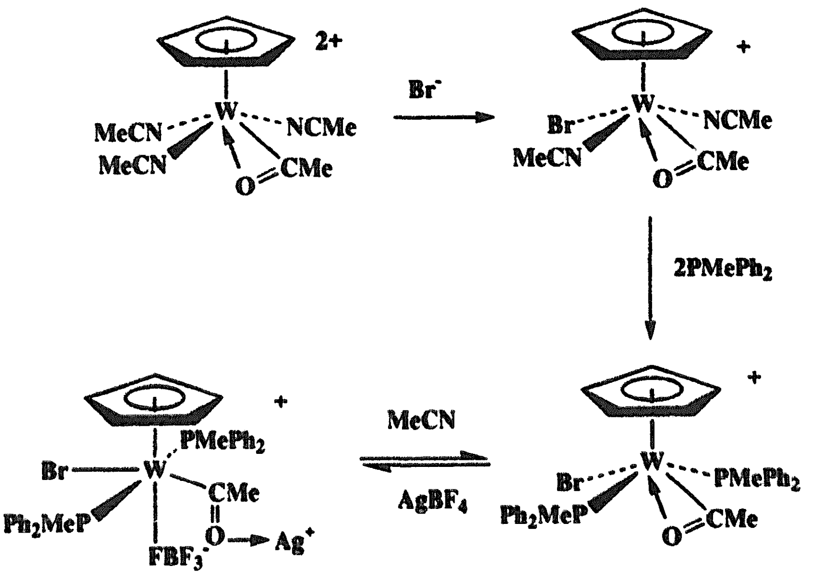
(17)



(18)

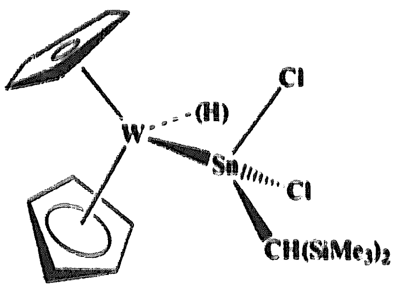
New tungsten(IV) acetyl complexes can be formed from $[CpW(NCMe)_3(\eta^2\text{-}COMe)]^{2+}$ and halides [45]. These retained the didentate acetyl ligand and can be further substituted by phosphines to give, for example, $[CpW(Br)(PMePh_2)_2(\eta^2\text{-}COMe)]^+$ (Scheme 14). Reaction with $AgBF_4$ resulted in reversible attachment of Ag^+ at the acetyl oxygen and $[BF_4]^-$ coordination to W.

Reaction of $[Cp_2W(H)(\mu\text{-}Li)]_4$ with tin halides SnX_2R_2 and $SnCl_3R$ (X = F, Cl; R = $CH(SiMe_3)_2$) yielded the corresponding tungsten(IV)-Sn complexes [46]. The crystal structure of $Cp_2W(H)\text{-}SnCl_2[CH(SiMe_3)_2]$ has been determined (**19**) and a W–Sn distance of 2.706(1) Å found. Cationic complexes $[Cp_2W(R)(NCMe)][PF_6]$ (R = Et, H) have been prepared and characterized structurally (**20**) and spectrally [47]. The complex $[Cp_2W(H)(NCMe)][PF_6]$ was found to be unstable in solution

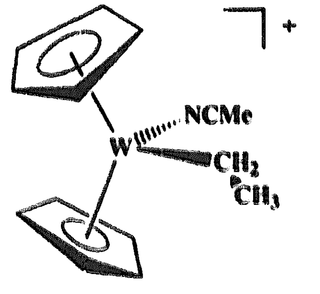


Scheme 14.

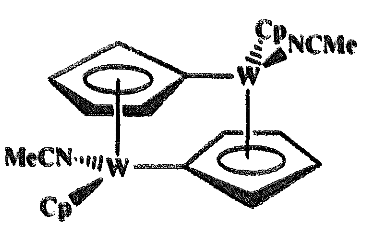
at room temperature, decomposing by C–H activation to the dinuclear product $[\{CpW(\mu\text{-}\eta^1:\eta^5\text{-}C_5H_4)(NCMe)\}_2][PF_6]_2$ (**21**).



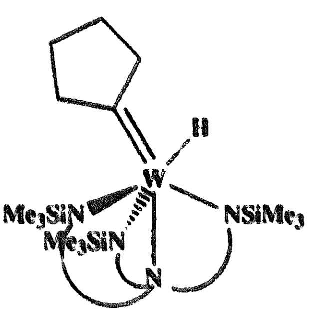
(19)



(20)



(21)



(22)

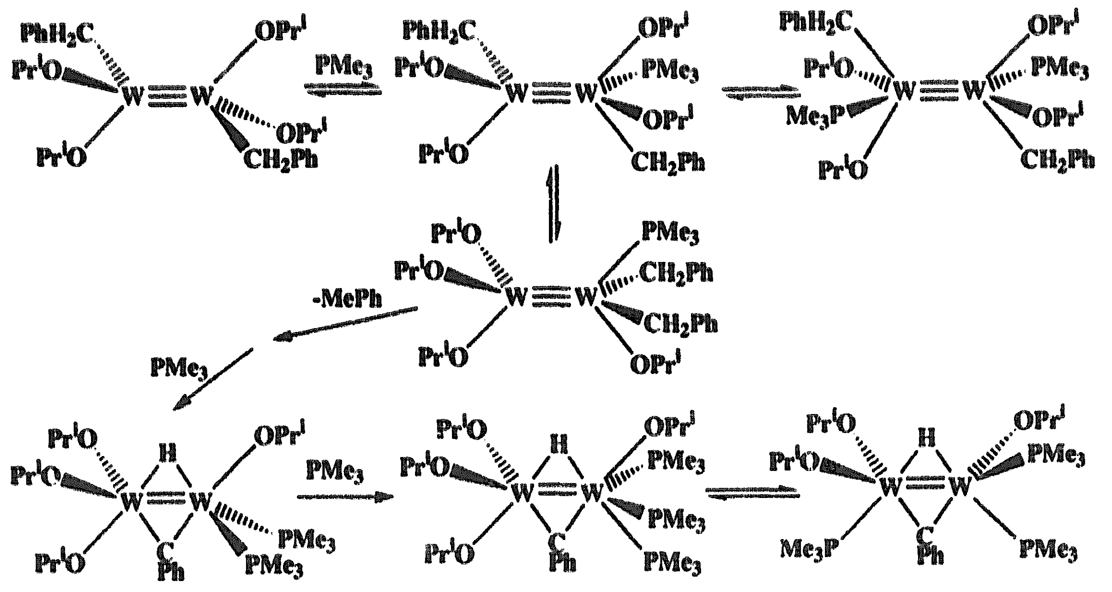
A rare case of faster α- over β-elimination was noted in the triamido tungsten complex $[(Me_3SiNCH_2CH_2)_3N]W(cyclopentylidene)H$ (**22**) [48]. Specifically, above 0°, the deuterium scrambling of the α-D labelled complex was found to be statistical, indicating favoured α-elimination (Scheme 15).

Scheme 15.

The kinetics of the substitution reactions between CN^-, HCN, F^- and the tungsten(IV) complex $[WO(OH_2)(CN)_4]^{2-}$ have been reported [49]. A dissociative mechanism was found in the replacement of the aqua ligand by cyanide while a negative volume of activation was found for the fluoride substitution. Acidic photolysis of $[W(CN)_8]^{4-}$ in the presence of bpy or phen has been investigated [50]. Formation of $[W(CN)_6L]^{2-}$ (L = bpy, phen), postulated in the literature, has been definitively excluded. Instead, the main species formed was found to be $[W(O)(CN)_3L]^-$ which underwent further reactions.

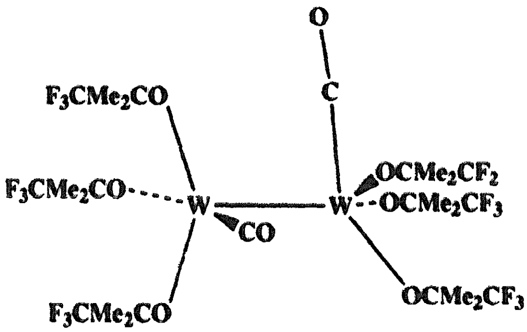
5. Tungsten(III) and (II) dimers

Trimethylphosphine and quinuclidene promoted double α-CH activation and toluene elimination in the dimeric 1,2-$W_2(CH_2Ph)_2(OPr^i)_4$ complex [51]. Kinetic studies revealed reversible ligand uptake to give an intermediate 1,2-$W_2(CH_2Ph)_2(OPr^i)_4PMe_3$ which induced a benzyl migration across the W W triple bond. Subsequent toluene elimination from a single W site gave 1,2-$W_2(\mu$-H)(μ-CPh)$(OPr^i)_4L_x$ (Lx = quin, x = 2; L = PMe_3, X = 2,3) (Scheme 16). By contrast, the chelating diphosphine dmpm yielded the stable adduct 1,2-$W_2(CH_2Ph)_2(O$-$Pr^i)_4$(dmpm).



Scheme 16.

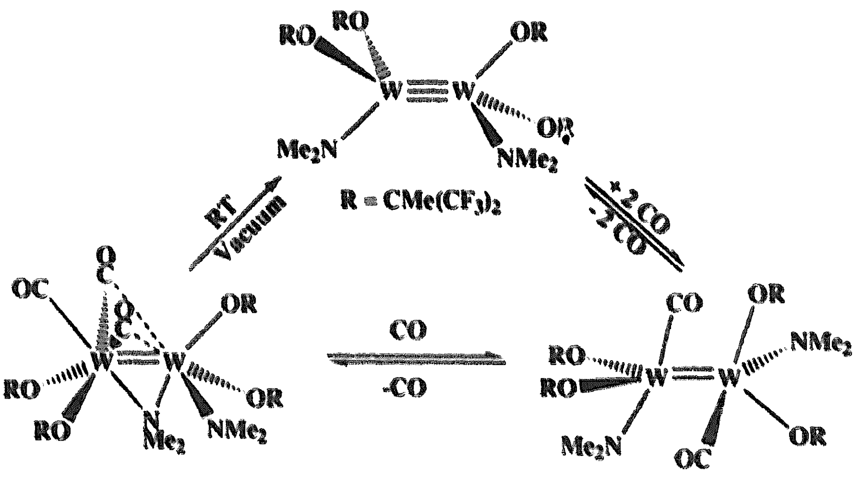
Dicarbonyl adducts of W_2^{6+} complexes were formed reversibly from $W_2(OR)_6$ (R = SiBu^{t}Me$_2$, CMe$_2$CF$_3$, 2,6-Me$_2$C$_6$H$_3$) and CO [52]. The CO ligands were added in a manner that allowed mixing of W-W π and W dπ* to CO π* orbitals as is shown for $W_2(CMe_2CF_3)_6(CO)_2$ (**22a**). By contrast, the mixed-ligand dimer $W_2(OCMe(CF_3)_2)_2(NMe_2)_2$ formed both di- and tri-carbonyl adducts (Scheme 17).



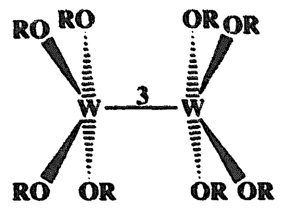
(22a)

The reaction of $W_2(OR)_6$ with KOR (R = Bu^t, Pr^i, CH$_2$Bu^t) in the presence of 18-crown-6 led to the reversible formation of the anions $M_2(OR)_7^-$ (R = Bu^t, Pr^i) and $W_2(OR)_8^{2-}$ (R = CH$_2$Bu^t only) [53]. By analogy to their molybdenum congeners, the bridging alkoxide ligand in both monoanions are postulated to have an unusual pyramidalized oxygen probably to avoid unfavourable oxygen pπ and W–W π interactions. These monoanions are thermally labile, yielding $W_2(\mu-H)(\mu-O)(OR)_6^-$ and the corresponding alkene. A crystal structure determination of a salt of $[W_2(OCH_2Bu^t)_8]^{2-}$ (**23**) revealed a triply-bonded W_2^{6+} unit symmetrically enclosed in an O_8 cube.

In an interesting development, a symmetrical W W triple bond was converted to an asymmetric W–W bond by the hydrogenation of $W_2(Bu^t)_2(OPr^i)_4$ in the presence of dmpe [54]. This dark brown $W_2(\mu\text{-}H)_2(OPr^i)_4(dmpe)_2$ product (**24**) was found

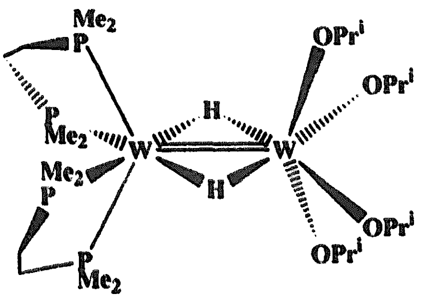


Scheme 17.



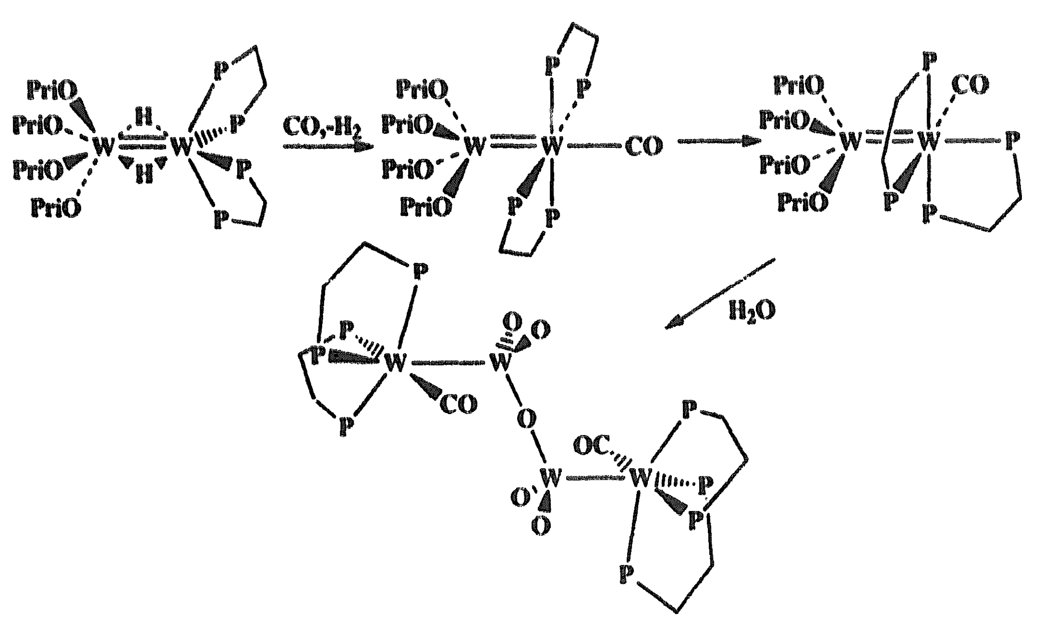
(23)

to contain a polar W=W double bond connecting a soft to a hard metal centre. Reaction of this asymmetric complex with CO afforded $W_2(CO)(OPr^i)_4(dmpe)_2$ which further reacted with water to give a novel, water-soluble tetra-tungsten complex $W_2O_4(\mu\text{-}O)[W(CO)(OPr^i)_4(dmpe)_2]_2$ (Scheme 18).



(24)

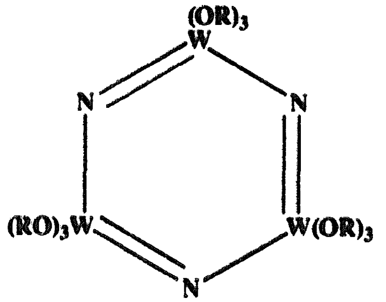
The quadruple tungsten–tungsten bond in $W_2Cl_4(dppm)_2$ was found to photoreact with PhSSPh to give $W_2Cl_4(dppm)_2(SPh)_2$ [55], while the thermal reaction was much slower. Wavelength dependence of the photochemistry suggested metal-localized excited states lying to higher energy of the $\delta\delta^*$ excited state. A homoleptic diacetone-



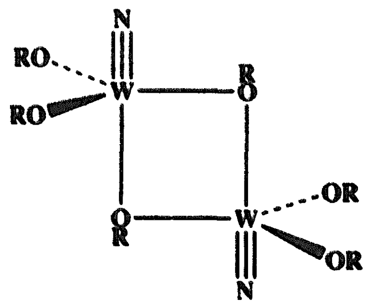
Scheme 18.

glucose complex of a W≡W triple bond was obtained from the reaction of 1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (HL) with $W_2(NMe_2)_6$ in toluene [56]. The structure of W_2L_6 was determined. The W–W distance is 2.335(1) Å with the sugar substituents in a staggered conformation.

Reactions involving $W_2(OR)_6$ and organic nitriles and factors favouring W≡W and C≡N triple bond metathesis were discussed [57]. The solid-state structure of $[(N)W(OCMe_2CF_3)_3]_3$ (**25a**) was reported to feature alternating W–N bond lengths. By contrast, the solution structure of $[NW(OSiBu^tMe_2)_3]$ was postulated to be dimeric as shown in (**25b**).



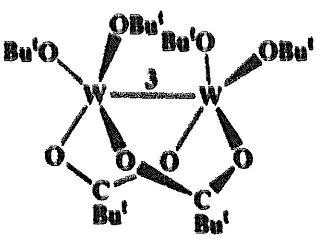
(**25a**)



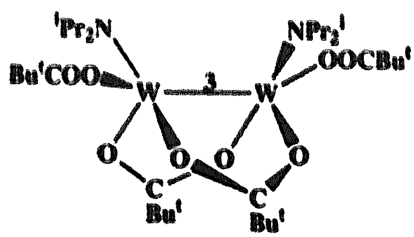
(**25b**)

Metathetic reactions of ditungsten hexapivalate, $W_2(O_2CBu^t)_6$, with $[OBu^t]^-$, $[NPr^i_2]^-$, and Cp^- were reported [58]. Among the isolated and structurally characterized products were $W_2(O_2CBu^t)_2(OBu^t)_4$ (**26**), $W_2(O_2CBu^t)_4(NPr^i_2)_2$ (**27**), $W_2(O_2CBu^t)_2(OBu^t)_2(NPr^i_2)_2$ (**28**), and $Na_2W_4O_4(O_2CBu^t)_6Cp_2$ (**29**).

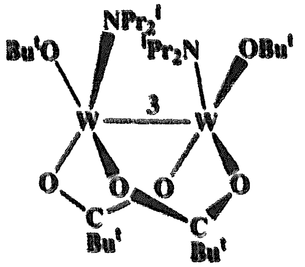
A tungsten dimer with a W–W bond order of 3.5 was reported [59]. This paramag-



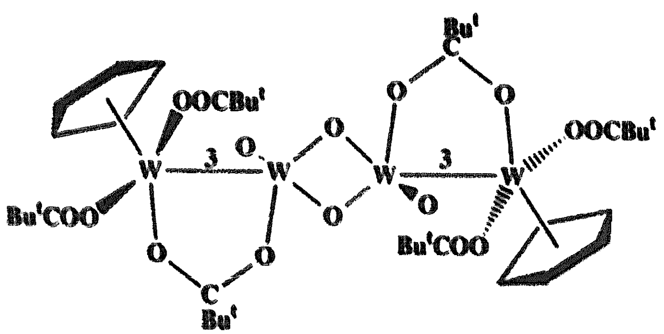
(**26**)



(**27**)

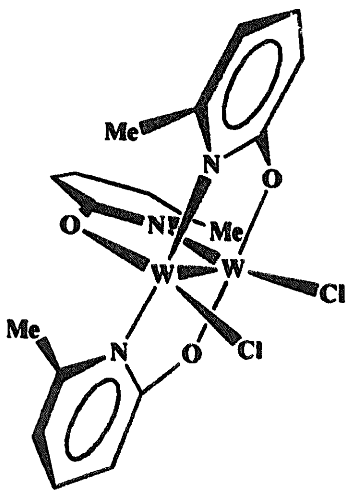


(**28**)



(**29**)

netic compound, $W_2Cl_2(mph)_3$ (**30**), was obtained from the reaction of $W_2(mhp)_4$ (where mhp = anion of 2-hydroxy-6-methylpyridine) with $AlCl_3$. Its crystal structure, spectral and electrochemical properties are consistent with a reduced bond order of 3.5.



(30)

Quantum mechanical calculations of the dinitrogen cleavage reaction:

$$2ML_3 + N_2 \rightarrow 2NML_3 \quad (L = H, Cl, NH_2;\ M = Mo, W)$$

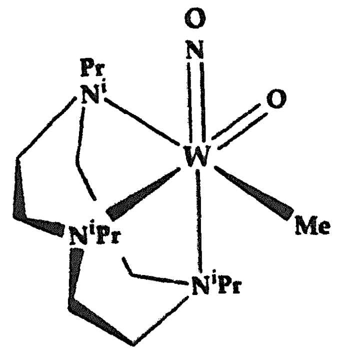
have been completed [60]. It was postulated that the smaller energy gap between tungsten's ground state s^1d^5 and excited s^2d^4 state should enable the $W(NH_2)_3$ complex to cleave dinitrogen more efficiently than $Mo(NH_2)_3$.

6. Tungsten(II)

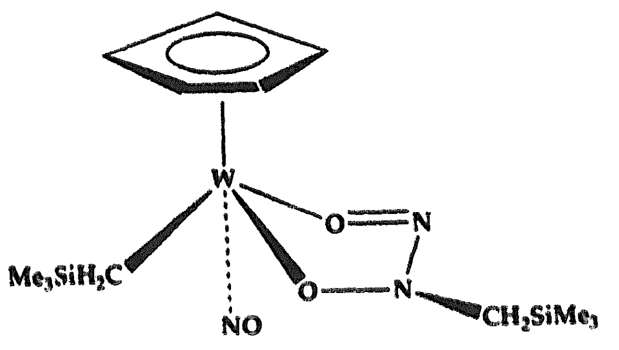
6.1. Complexes with nitrosyl ligands

An unusual nitrosyltungsten complex featuring both strong π-acid and π-donor ligands was found in LW(NO)(O)Me (**31**) (where L = *N,N',N''*-triisopropyl-1,4,7-triazacyclononane) [61]. This was obtained from the reaction of dioxygen with LW(NO)(CO)Me. Its NO infrared stretching frequency was observed at a very low value of 1433 cm^{-1}.

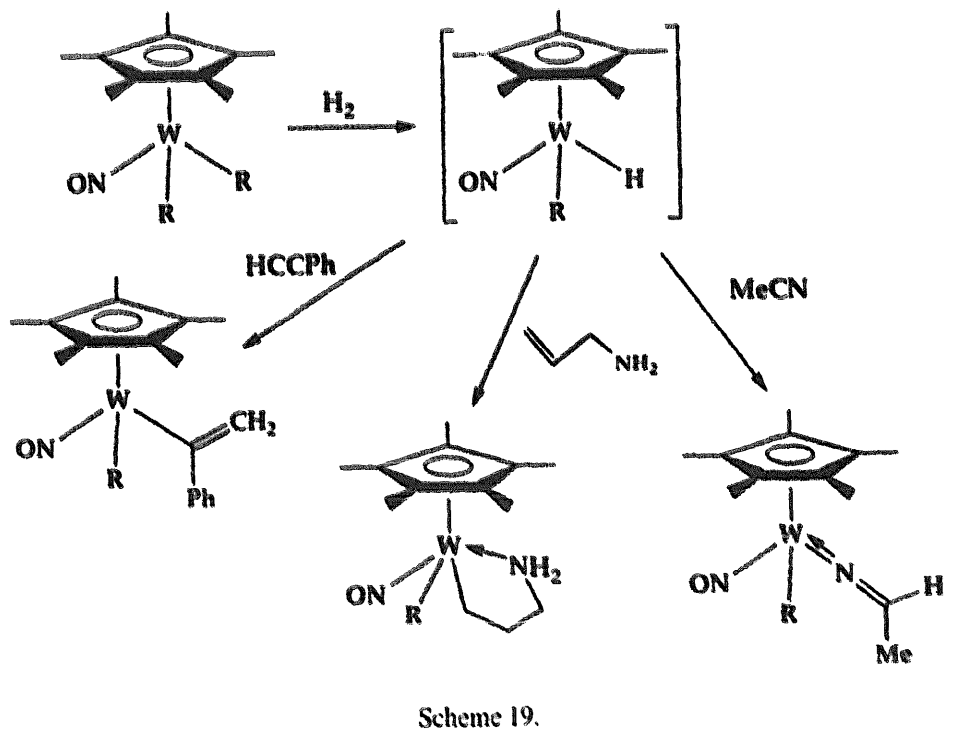
Insertion of nitric oxide into one W-C bond of $CpW(CH_2SiMe_3)_2$ yielded $CpW(CH_2SiMe_3)(ON(NO)CH_2SiMe_3)$ [62]. Its crystal structure revealed a four-legged piano-stool geometry as shown in structure (**32**). Hydrogenation of solutions of $Cp^*W(NO)(CH_2SiMe_3)_2$ generated the reactive 16-electron alkyl hydride $Cp^*W(NO)(CH_2SiMe_3)H$ [63]. When this intermediate was treated with PPh_3, it gave the orthometallated complex $Cp^*W(NO)(H)(PPh_2C_6H_4)$. The W–H bond in $Cp^*W(NO)(CH_2SiMe_3)H$ was found to insert into various unsaturated linkages including olefins, acetylenes, and nitriles (Scheme 19).



(31)

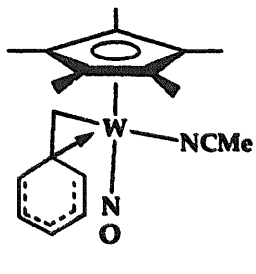


(32)



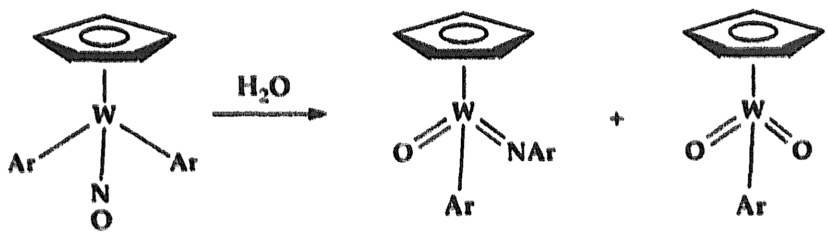
Scheme 19.

Treatment of $Cp^*W(NO)(\eta^2\text{-}CH_2Ph)Cl$ with $AgBF_4$ afforded the salt $[Cp^*W(NO)(\eta^2\text{-}CH_2Ph)(NCMe)]BF_4$ (33) which was shown by X-ray crystallography to be contain discrete cations and anions [64]. This electrophilic cation reacted only with bases stronger than the chloride anion. Reaction of $Cp^*W(NO)(\eta^2\text{-}CH_2Ph)Cl$ with silver carboxylate gave $Cp^*W(NO)(\eta^1\text{-}CH_2Ph)(\eta^2\text{-}OOCR)$ complexes.



(33)

Hydrolysis of $CpW(NO)(o\text{-tolyl})_2$ led to a mixture of the expected product $CpW(O)_2(o\text{-tolyl})$ and an interesting structural isomer $CpW(O)\{N(o\text{-tolyl}\}(o\text{-tolyl})$ (Scheme 20) [65]. Labelling studies confirmed the intramolecular nature of this unique water-catalysed transformation. The general reactivity of the starting complex was also investigated.

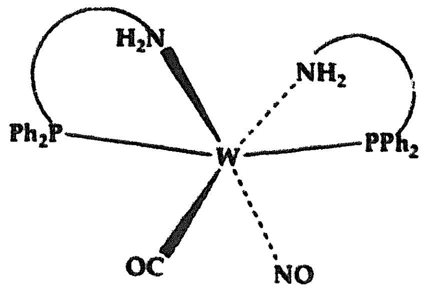


Scheme 20.

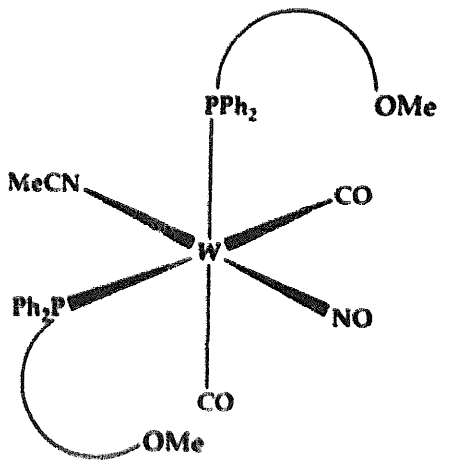
6.2. Complexes with phosphine ligands

The tungsten complexes $[W(CO)_3(NO)(PR_3)F\text{-}PF_5]$ and $[W(CO)_2(NO)\text{-}(NCMe)_3]^+$ are convenient precursors to a variety of phosphine complexes containing the $Ph_2P(2\text{-}X\text{-}C_6H_4)$ (X=OMe, OH, or COOH) ligands [66]. The crystal structures of several of these have been determined including $[W(CO)(NO)(\eta^2\text{-}PPh_2(2\text{-}C_6H_4\text{-}NH_2))_2]BF_4$ (34), $[W(CO)_2(NO)(NCMe)(PPh_2\text{-}(2\text{-}C_6H_4\text{-}OMe))_2][SbF_6]$ (35), and *cis*-$[W(CO)_2(NO)(PMe_3)(\eta^2\text{-}PPh_2(2\text{-}C_6H_4\text{-}NH)]$ (36).

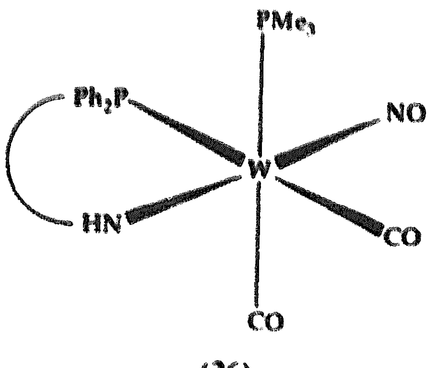
Reaction of PMe_2Cl or PPh_2Cl and the tungsten carbyne complex $CpW(CR)(CO)_2$ in the presence of $NaBPh_4$ effected the direct conversion of the W C into an η^2-phosphinocarbene moiety [67]. In the absence of $NaBPh_4$, a base-induced CO carbene coupling occurred to give an η^3-phosphinoketene complex (Scheme 21).



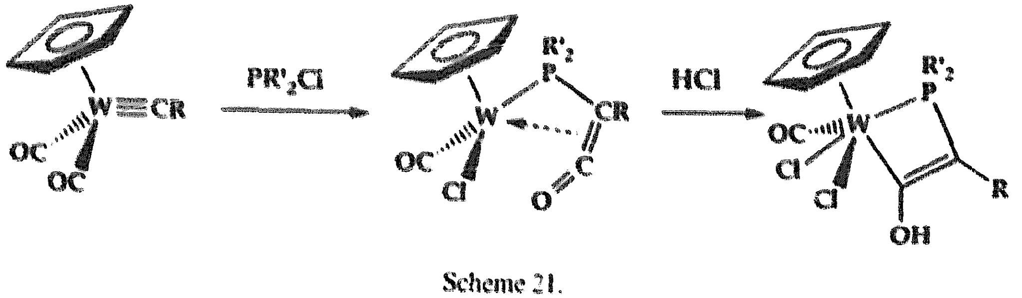
(34)



(35)

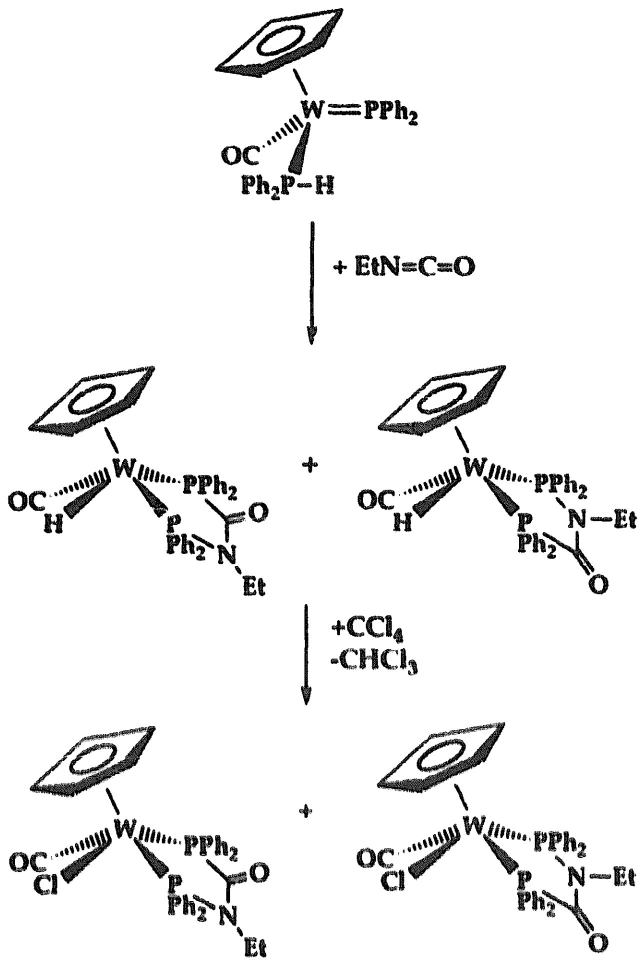


(36)



Scheme 21.

A communication concerning the formation of a chelating bis-phosphine $Ph_2PN(Et)C(O)PPh_2$ via a novel [3+2] cycloaddition between $CpW(=PPh_2)(CO)(PPh_2H)$ and ethyl isocyanate has appeared [68]. Two isomers were obtained which can both be converted to the chloro derivatives by treatment with CCl_4 (Scheme 22).

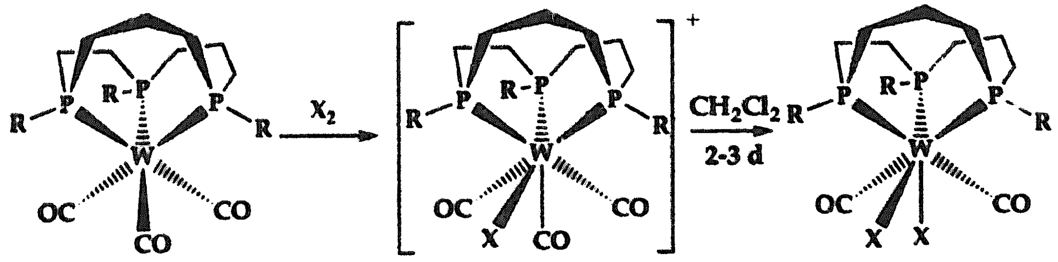


Scheme 22.

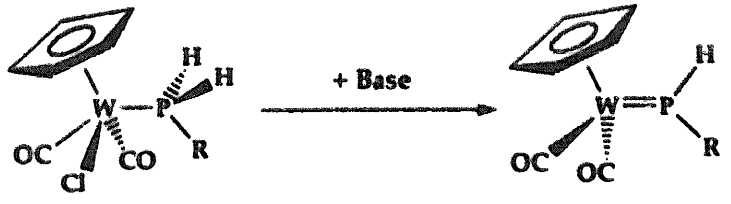
Halogenation of the triphospha-macrocyclic complex $LW(CO)_3$ (where L = 1,5,9-tris(isopropyl)-1,5,9-triphosphacyclododecane) afforded the corresponding W(II) complexes [69]. Fluxional ionic intermediates of the type $[LW(CO)_3X]^+X^-$ were observed. These slowly converted to the neutral 7-coordinate $[LW(CO)_2X_2]$ products (Scheme 23).

P–H-Functionalized phosphenium complexes of the type $Cp^*W(=P(H)R)(CO)_2$ (where R = Bu^t, supermesityl) are accessible from the dehydrochlorination of the appropriate primary phosphine complex (Scheme 24) [70]. The curtailed reactivity of the W=P bond allowed the reactive P–H group to undergo various reactions.

Related tungsten phosphido complexes $CpW(CO)_3$-$P(X)Bu^t$ (X = Cl, H) were



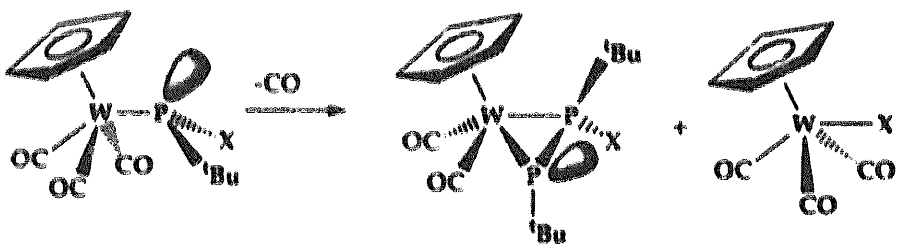
Scheme 23.



(Base = DBU, KO^{t}Bu, NEt$_3$)

Scheme 24.

slowly converted in benzene solution to two products including a cyclic phosphinidene-metallaphosphorane $CpW(CO)_2[P(X)Bu^t\text{-}PBu^t]$ (Scheme 25) [71].



Scheme 25.

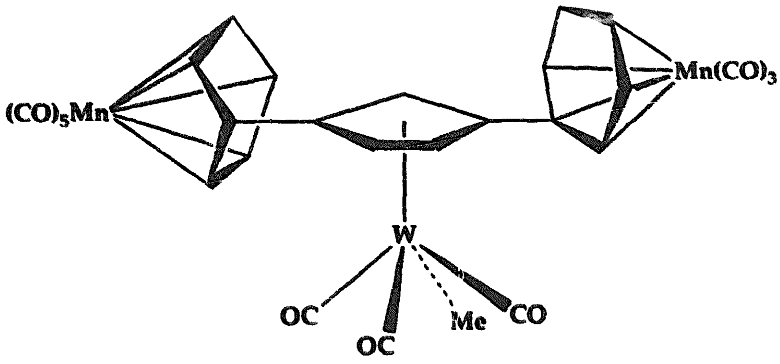
6.3. *Complexes with cyclopentadienyl and carbonyl ligands*

The pentabenzylated cyclopentadienyl complex $[(C_5Bz_5)W(CO)_3]^-$ can be halogenated with PCl_3, PBr_3, or I_2 to give the corresponding $(C_5Bz_5)W(CO)_3X$ derivatives [72].

Photolysis of $Cp^*W(CO)_3Me$ in acetonitrile yielded *cis*-$[Cp^*W(CO)_2(NCMe)Me]$ which can be stereospecifically substituted by tertiary phosphines [73]. Time-resolved infrared spectroscopy revealed that the photolysis of $CpW(CO)_3Me$ in n-heptane was produced the solvated $CpW(CO)_2Me\cdots$n-heptane intermediate. Appropriate second-order rate constants were found for the reactions of this with CO, PPh_3, and N_2. A small amount of the radical $CpW(CO)_3$ which dimerized was also formed in the photolysis [74].

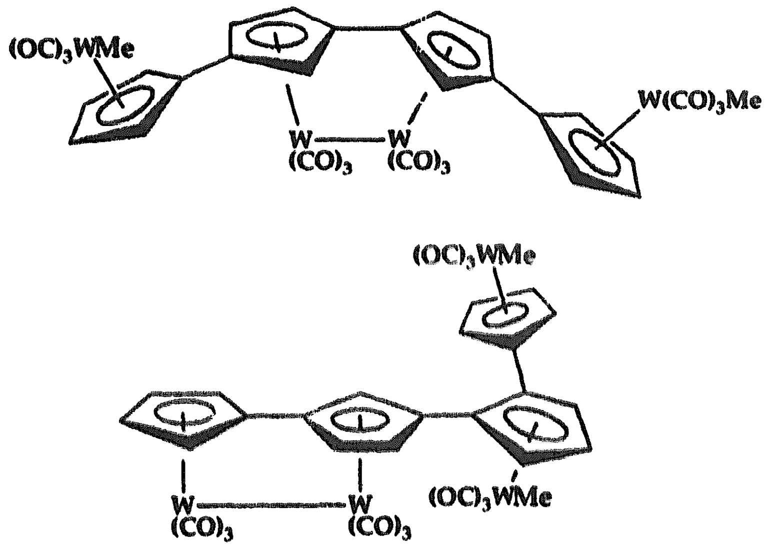
The molecular structure of the trimetallic product from the reaction of

$W(CO)_3(MeCN)_3$ with 1,3-[(η-C_6H_6)$Mn(CO)_3$]$_2C_5H_4$ has been determined (**37a**) [75a].



(**37a**)

The synthesis of a quaterocyclopentadienyl ligand featuring four linked Cp groups as a tetra-tungsten complex has also been described [75]. Two of the eight isomers are shown in diagram (**37**).

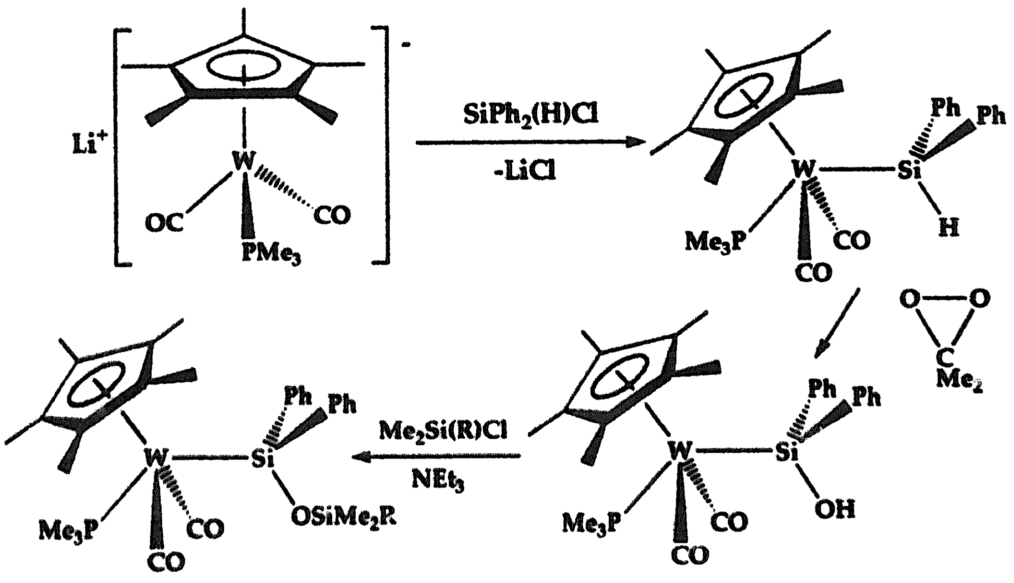


(**37**)

6.4. Complexes with tungsten–silicon bonds

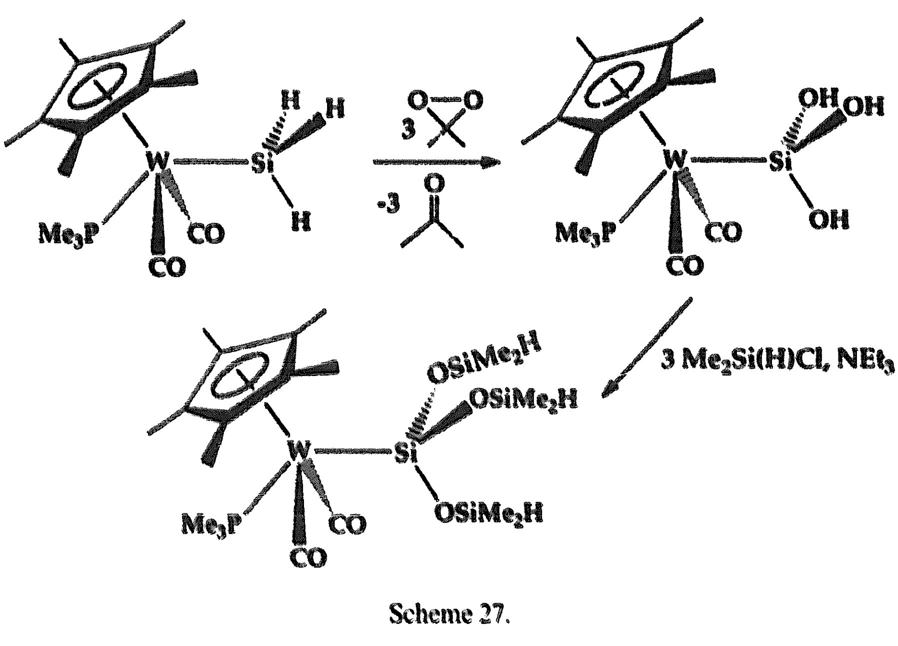
The tungsten silane complex $CpW(CO)_2(PMe_3)$-$SiPh_2H$ was converted to the W-silanol by functionalization with dimethyldioxirane [76]. Further treatment with chlorosilanes in the presence of triethylamine led to the disiloxane complexes $CpW(CO)_2(PMe_3)$-$SiPh_2OSiMe_2R$ (Scheme 26).

In a related work, $Cp'W(CO)_2(PMe_3)SiHCl_2$ (Cp' = Cp, Cp*) were prepared from $Li[Cp'W(CO)_2(PMe_3)]$ and $HSiCl_3$ [77]. Lithium aluminium hydride reduction of

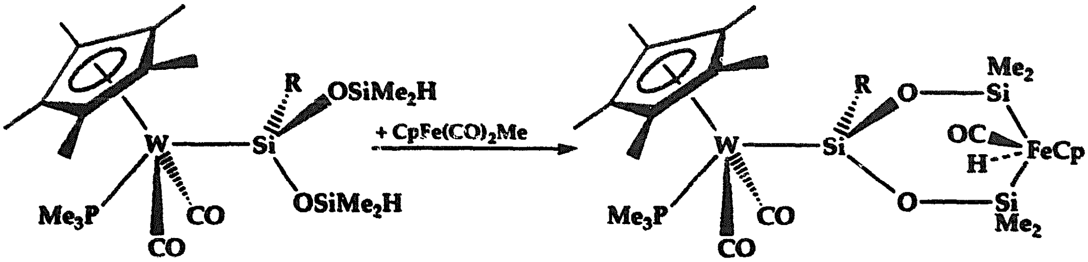


Scheme 26.

these yielded the W-silane complexes $Cp'W(CO)_2(PMe_3)SiH_3$ whose vibrational spectra have been reported in detail. The reaction of $Cp^*W(CO)_2(PMe_3)SiHCl_2$ with dimethyldioxirane led to the silanetriol complex $Cp^*W(CO)_2(PMe_3)Si(OH)_3$ which was in turn transformed into the metallatetrasiloxane complex $Cp^*W(CO)_2(PMe_3)Si(OSiMe_2H)_3$ (Scheme 27) [78]. The related complexes $Cp^*W(CO)_2(PMe_3)SiR(OSiMe_2H)_2$ (R = Me, Ph) were treated with $CpFe(CO)_2Me$ to give the respective disiloxane-bridged W/Fe complexes (Scheme 28) [79].



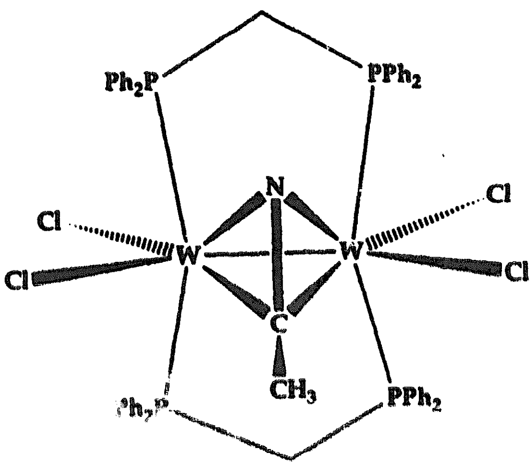
Scheme 27.



Scheme 28.

6.5. Complexes with tungsten-metal bonds

A new ditungsten complex with a bridging acetonitrile ligand, $W_2Cl_4(dppm)_2(\eta^2\text{-}\mu\text{-}NCMe)$ (**38**) has been prepared [80]. The ligand's CN axis was found to be perpendicular to the W–W bond axis with a C–C–N angle of 116.3(7)° while the metal-metal bond was lengthened to 2.498(1) Å.



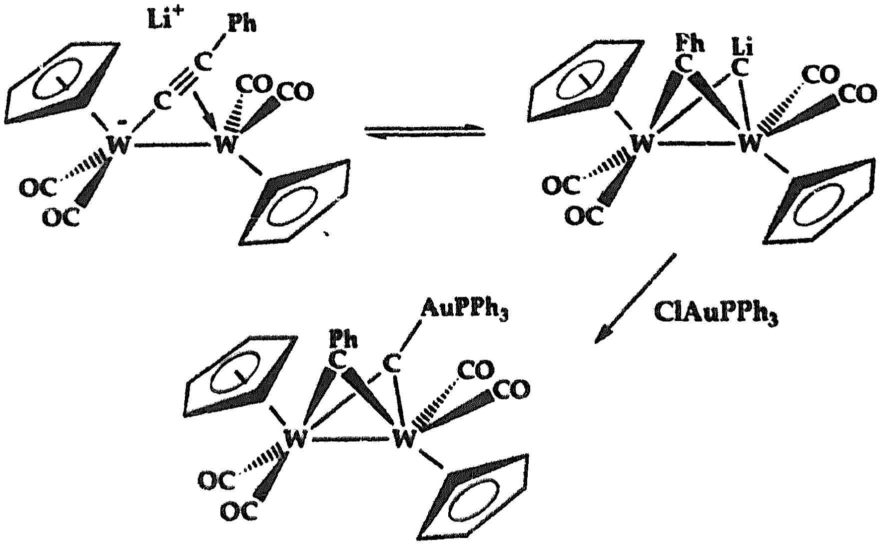
(38)

The dinuclear anion $[Cp_2W_2(\mu\text{-}\sigma\text{:C CPh})(CO)_4]^-$ was found to react with the gold halide complexes $ClAu(PR_3)$ (R = Me, Ph) to give the trimetallic alkyne-bridged products $[Cp_2W_2(\mu\text{-}C(AuPR_3)CPh)(CO)_4]$ (Scheme 29) [81]. Similar reaction with half-an-equivalent of $HgCl_2$ led to a Hg-bridged pentametallic analogue.

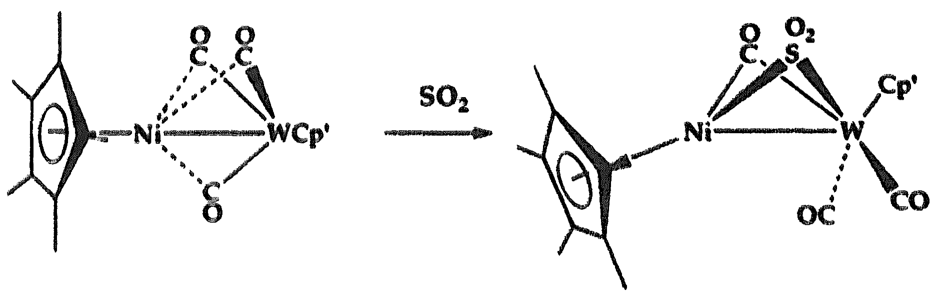
The unsaturated complex $Cp^*NiW(CO)_3Cp'$ was treated with SO_2 to form an SO_2-bridged product $Cp^*Ni(\mu\text{-}CO)(\mu\text{-}SO_2)W(CO)_2Cp'$ (Scheme 30) with a NiWCS butterfly core [82].

Dimetallic phosphido-bridged $CpW(CO)_3(\mu\text{-}PPh_2)W(CO)_5$ and $W(CO)_2(\mu\text{-}\eta^5\text{-}C_5H_4PPh_2)W(CO)_5$ were prepared from $(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3$ and $W(CO)_5\cdot THF$ [83]. The long W–W bond of 4.510(1) Å in the former indicated lack of a metal-metal bond. By contrast the shorter W–W distance of 3.194(1) Å in the latter is consistent with such a bond. Ligand substitution reactions of the latter with phosphines and phosphite at $W(CO)_5$ were found to occur *trans* to the PPh_2 bridge.

A related reaction of $(\eta^5\text{-}C_5H_4PPh_2)W(CO)_3$ with $Fe_2(CO)_9$ gave similar hetero-

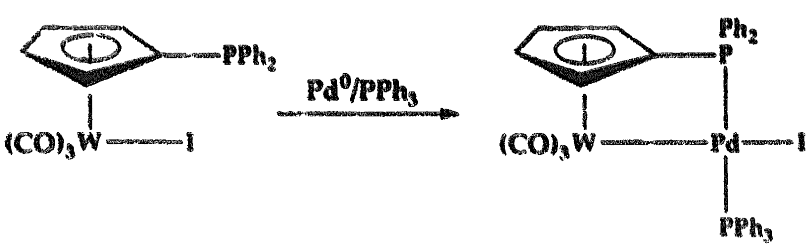


Scheme 29.



Scheme 30.

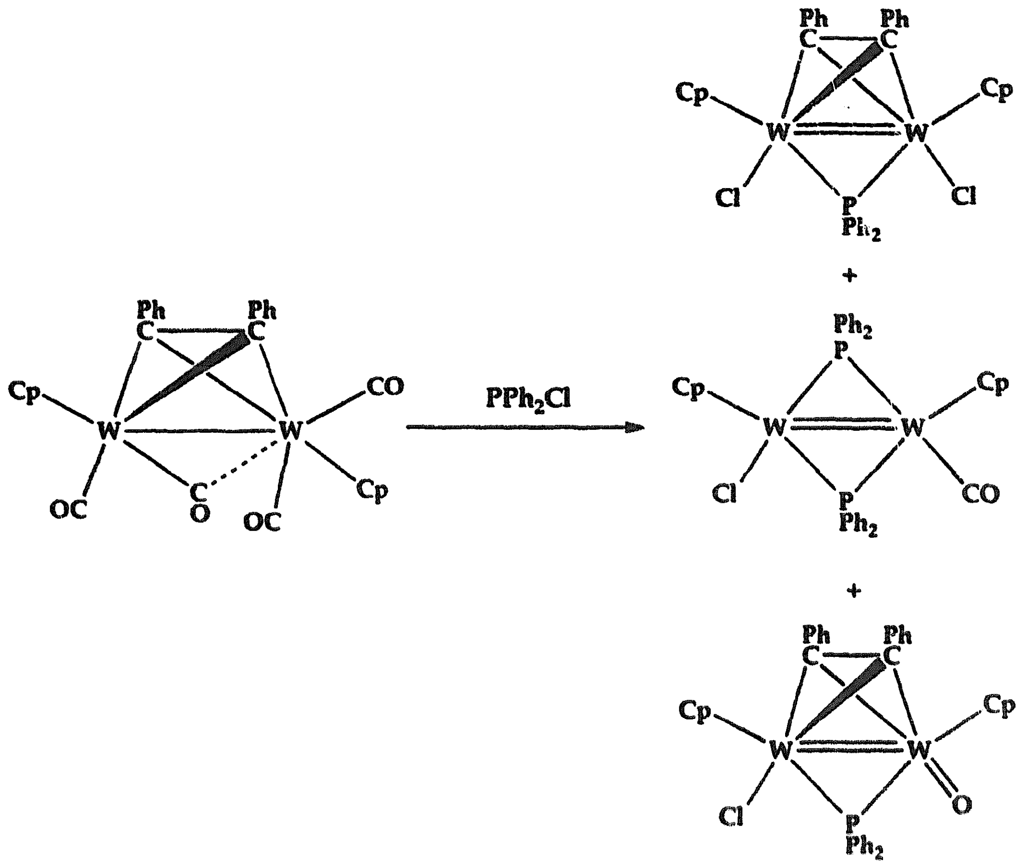
dimetallic phosphido-bridged complex $W(CO)_3(\mu$-η^5-$C_5H_4PPh_2)Fe(CO)_4$ and $W(CO)_2(\mu$-η^5-$C_5H_4PPh_2)Fe(CO)_3$ [84]. Again, structural data were consistent with a W–Fe bond only in the latter product. This also reacted with Lewis bases, substituting regiospecifically at the iron site. The oxidative addition of W-I of the complex $(\eta^5$-$C_5H_4PPh_2)W(CO)_3I$ at Pd^0 was studied to elucidate the mechanism of palladium-catalysed metal-carbon bond formation (Scheme 31) [85].



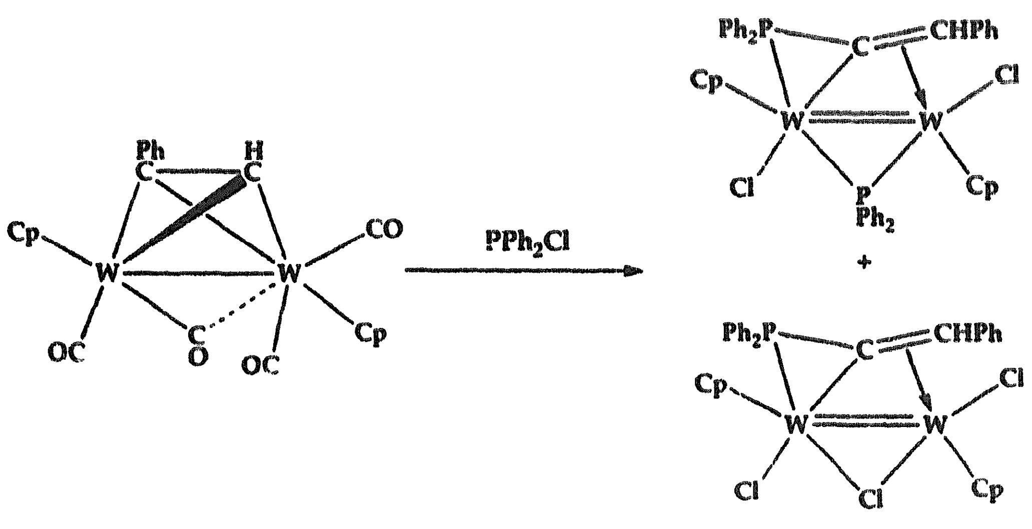
Scheme 31.

Alkyne-bridged ditungsten complexes $Cp_2W_2(\mu$-RC CR')$(CO)_4$ have been prepared [86]. Reaction of $Cp_2W_2(\mu$-PhC CPh)$(CO)_4$ with PPh_2Cl gave three products all featuring bridging PPh_2 groups (Scheme 32). By contrast, reaction of

$Cp_2W_2(\mu\text{-PhC CH})(CO)_4$ with PPh_2Cl led to P-alkyne coupling products (Scheme 33).



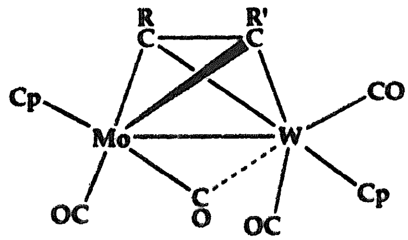
Scheme 32.



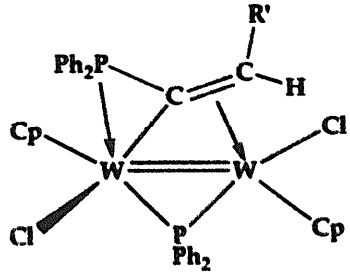
Scheme 33.

In related chemistry, reaction of a mixture of $Cp_2Mo_2(CO)_6$ and $Cp_2W_2(CO)_6$ with alkynes RCCR′ yielded heterodimetallic complexes $Cp_2MoW(\mu\text{-RC}$

CR')(CO)$_4$ (**39**) [87]. Thermolysis of these with PPh$_2$Cl led to P–Cl cleavage and alkyne/PPh$_2$ coupling in four ways. The structure of one product is shown in (**40**).



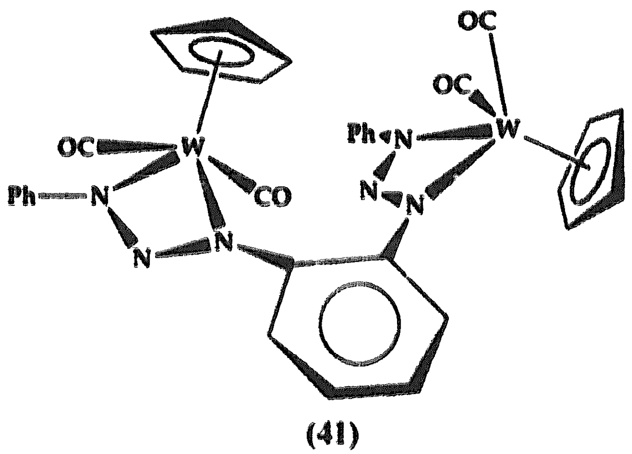
(**39**)



(**40**)

Reactions of the alkyne-bridged dimer (C$_5$H$_4$Pr^i)$_2$W$_2$Cl$_4$(μ-EtC CEt) gave imido-bridged derivatives (C$_5$H$_4$Pr^i)$_2$W$_2$Cl$_2$(μ-NR)(μ-EtC CEt) containing three-centre, two-electron W–N–W banana π-bonds [88].

Phenylenebistriazenide, PhN$_3$(H)C$_6$H$_4$N$_3$(H)Ph and sodium ethoxide reacted with CpW(CO)$_3$Cl to yield dimetallic [CpW(CO)$_2$]$_2$(1,2-PhN$_3$C$_6$H$_4$N$_3$Ph) (**41**) [89]. This product has a crystal structure in which the [PhN$_3$C$_6$H$_4$N$_3$Ph]$^{2-}$ ligand is nonplanar due to the chelation of two bulky CpW(CO)$_2$ moieties.

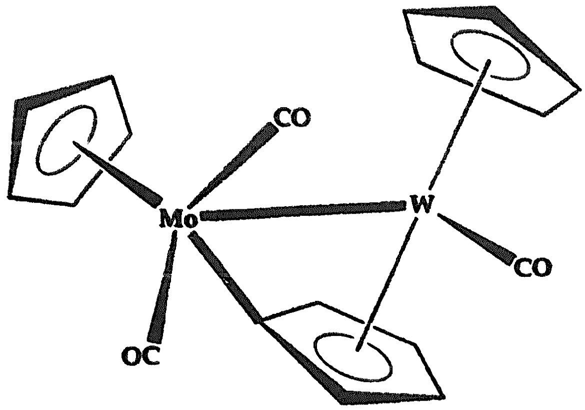


(**41**)

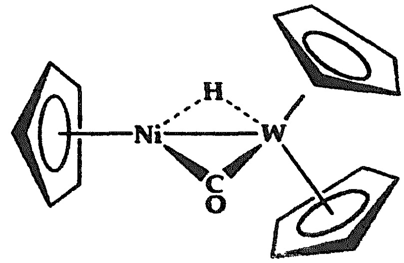
Irradiation of Cp$_2$WH$_2$ with a variety of dimetallic precursors has been found to be a convenient source of di- and tri-nuclear complexes [90]. Specifically, Cp$_2$WH$_2$ and Cp$_2$MoH$_2$ afforded CpW(CO)(μ,σ-η^5-C$_5$H$_4$)Mo(CO)$_2$Cp (**42**), Cp$_2$WH$_2$ with [CpNi(CO)$_2$]$_2$ gave Cp$_2$W(μ-H)(μ-CO)NiCp (**43**), and Cp$_2$WH$_2$ and [CpRu(CO)$_2$]$_2$ yielded CpW(μ,σ-η^5-C$_5$H$_4$)(μ-CO)$_2$RuCpRuCp(CO)H and (μ,σ-η^5-C$_5$H$_4$)$_2$WH$_2$[Ru(CO)Cp]$_2$ (**44**) and (**45**).

Unlike the iron analogues, treatment of [CpW(CO)$_3$]$_2$GeMe$_2$ with lithium diisopropylamide (LDA) base followed by MeI quenching led to cleavage of the Ge–W bonds and formation of CpW(CO)$_3$Me [91]. The related [CpW(CO)$_3$]$_2$SnMe$_2$ complex did undergo base-induced double migration (Scheme 34).

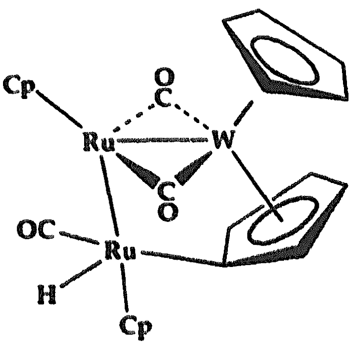
Reaction of the metalla-acid Cp*Re(CO)(NO)-COOH with CpW(CO)$_3$F-BF$_3$ first yielded the μ_2-η^2-CO$_2$ intermediate which readily converted to the Cp*Re(CO)(NO)(μ_2-η^3-CO$_2$)W(CO)$_2$Cp product (**46**) [92]. The coordination



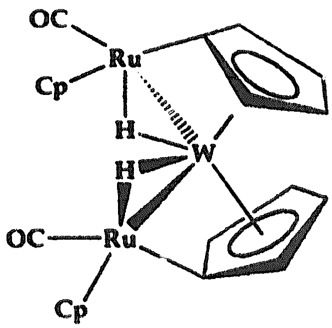
(42)



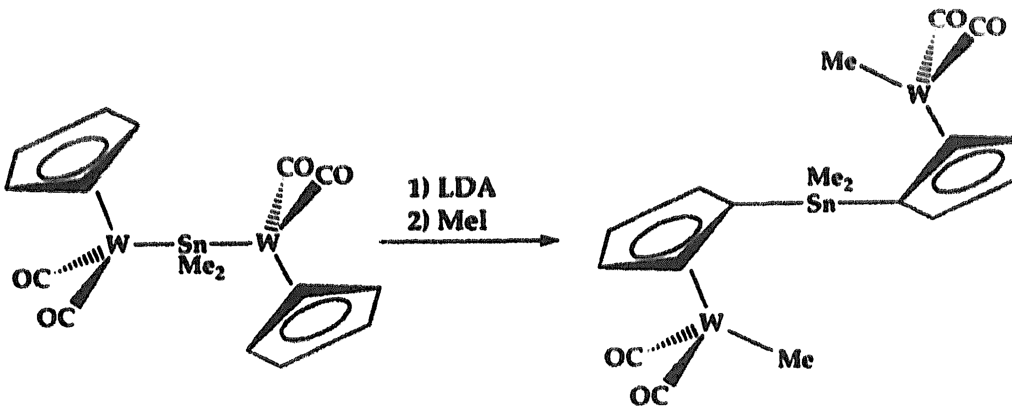
(43)



(44)

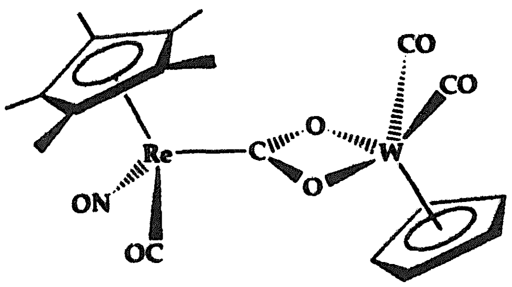


(45)

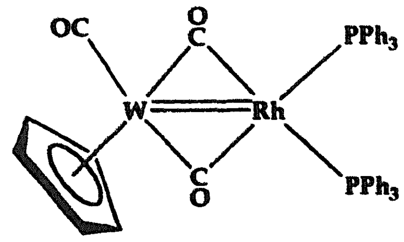


Scheme 34.

geometry and bonding details were supported by diffuse reflectance IR FT-spectroscopy. The hydroxy-bridged rhodium dimer $[Rh_2(PPh_3)_4(\mu\text{-}OH)_2]$ when treated with $CpW(CO)_3H$ gave the heterodimetallic complex $[(PPh_3)_2Rh(\mu\text{-}CO)_2W(CO)Cp]$ (47) [93].



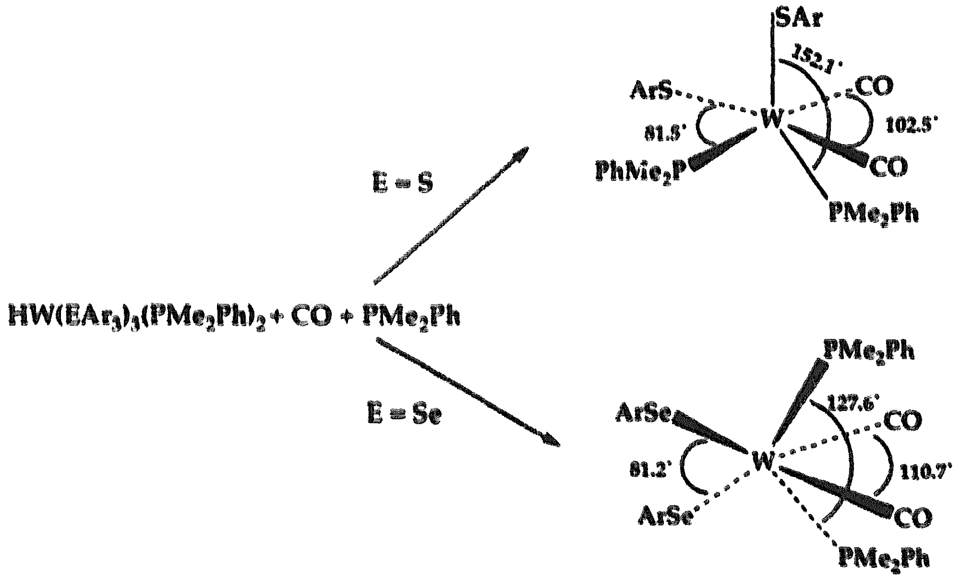
(46)



(47)

6.6. Complexes with mixed donor ligands

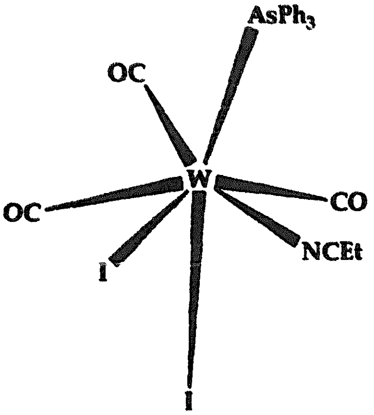
Reaction of carbon monoxide with $[W(H)(2,4,6\text{-}SC_6H_2Me_3)_3(PMe_2Ph)_2]$ produced green *cis,cis,cis*-$[W(2,4,6\text{-}SC_6H_2Me_3)_2(PMe_2Ph)_2(CO)_2]$ with a distorted octahedral geometry (Scheme 35) [94], while reaction of CO with $[W(H)(2,6\text{-}SeC_6H_2Pr^i_2)_3(PMe_2Ph)]$ afforded burgundy, trigonal prismatic $[W(2,6\text{-}SeC_6H_2Pr^i_2)_2(PMe_2Ph)_2(CO)_2]$. A classification of these and related molybdenum complexes into three general types was proposed.



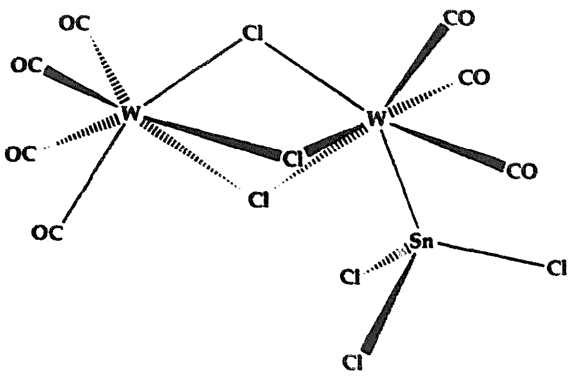
Scheme 35.

Nitrile exchange reactions of seven-coordinate $[WI_2(CO)_3(NCMe)_2]$ led to mixed-ligand complexes $[WI_2(CO)_3(NCR)_2]$ (where R = Bz, Ph, Et, Bu^t) [95]. These, in turn, were substituted by one equivalent of EPh_3 (E = P, As, Sb) to give $[WI_2(CO)_3(NCR)(EPh_3)]$. Crystal structures of the $AsPh_3$ derivative (**48**) revealed distorted monocapped trigonal prismatic coordination geometries.

A water-soluble seven-coordinate tungsten(II) complex $[WI_2(CO)_2(4\text{-}NaOOC\text{-}Py)_2]$ has been prepared [96]. This underwent ligand substitution with $3\text{-}NaO_3S$-pyridine in water. Photolysis of $W(CO)_6$ with $SnCl_4$ led to a novel seven-coordinate tungsten(II) complex $[(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3]$ (**49**)



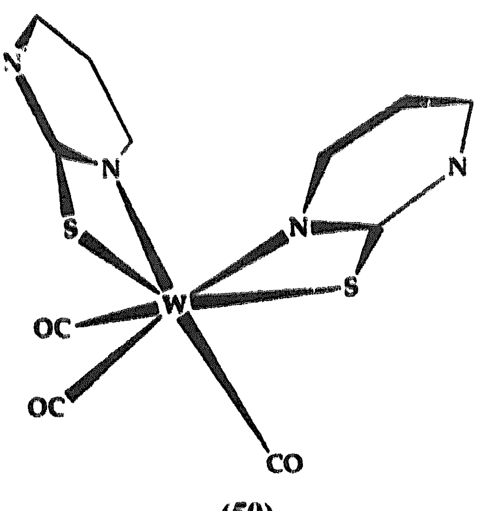
(48)



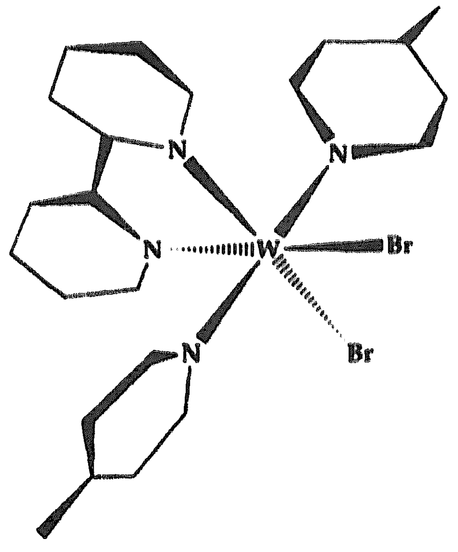
(49)

whose crystal structure has been determined [97]. The formation of Lewis base derivatives $[WCl(SnCl_3)(CO)_3L_2]$ (L = N and P donors) was also described [98].

The synthesis and crystal structure of seven-coordinate $[W(CO)_3$-(η^2-pyrimidine-2-thionate)$_2]$ (**50**) were reported [99]. The molecular structure of a tungsten(II) complex *cis,trans*-(2,2′-bpy)WBr_2(4-Me-py)$_2$ (**51**) has been determined [100].



(50)

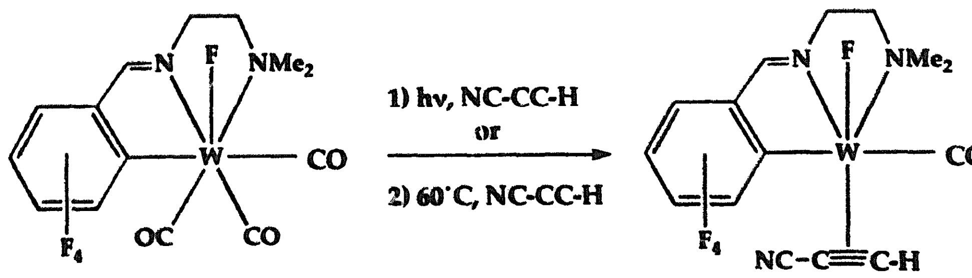


(51)

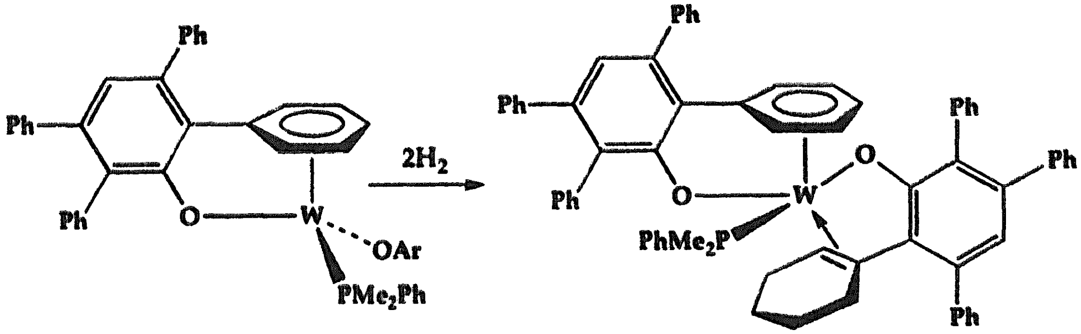
Upon photolysis with cyanoacetylene, the tungsten(II) fluoride carbonyl complex (Scheme 36) gave a product containing the alkyne as a four-electron donor [101].

Sodium amalgam reduction of $W(OAr)_2Cl_4$ (Ar = 2,3,5,6-tetraphenylphenoxide) in the presence of phosphines led to a product featuring an η^6-phenyl group [102]. This reacted slowly with H_2 to give an η^2-cyclohexene product which retained the η^6-phenyl group (Scheme 37).

The redox chemistry of carbonyl hydride tungsten complexes



Scheme 36.



Scheme 37.

$[W(CO)_2(PP)_2H]SO_3CF_3$ (PP = dmpm, dppe) has been studied by voltammetry to establish kinetic and thermodynamic properties [103a].

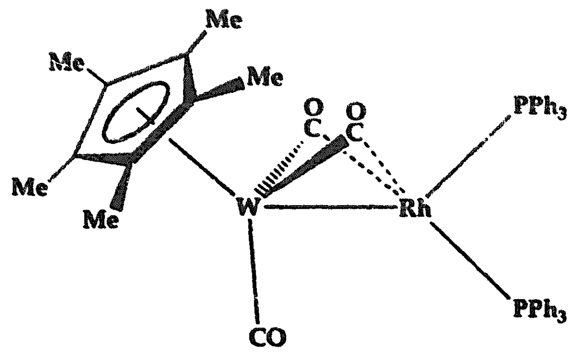
7. Tungsten(0) complexes

7.1. Complexes with carbon ligands

The novel ligand isocyanoacetonitrile $CH_2(CN)(NC)$ has been prepared and its complexes with chromium and tungsten carbonyls isolated [103]. Exclusive coordination of these soft metals through the isocyano group was observed. The structure and dynamic behaviour of *cis*-dicarbonyl-bis(η^4-1,3-butadiene)tungsten(0) and *cis*-dicarbonyl-bis(η^4-1,3-cyclohexadiene)tungsten(0) revealed hindered ligand movements [104]. Coordination of the unsaturated tetracarbonyltungsten fragment in the gas phase with ethylene was probed by time-resolved IR absorption spectroscopy [105]. A nascent $W(CO)_4(\eta^2\text{-}C_2H_4)$ with C_s symmetry featuring a square-pyramid geometry with a basal alkene was observed. This subsequently converted to the C_{2v} trigonal bipyramidal structure.

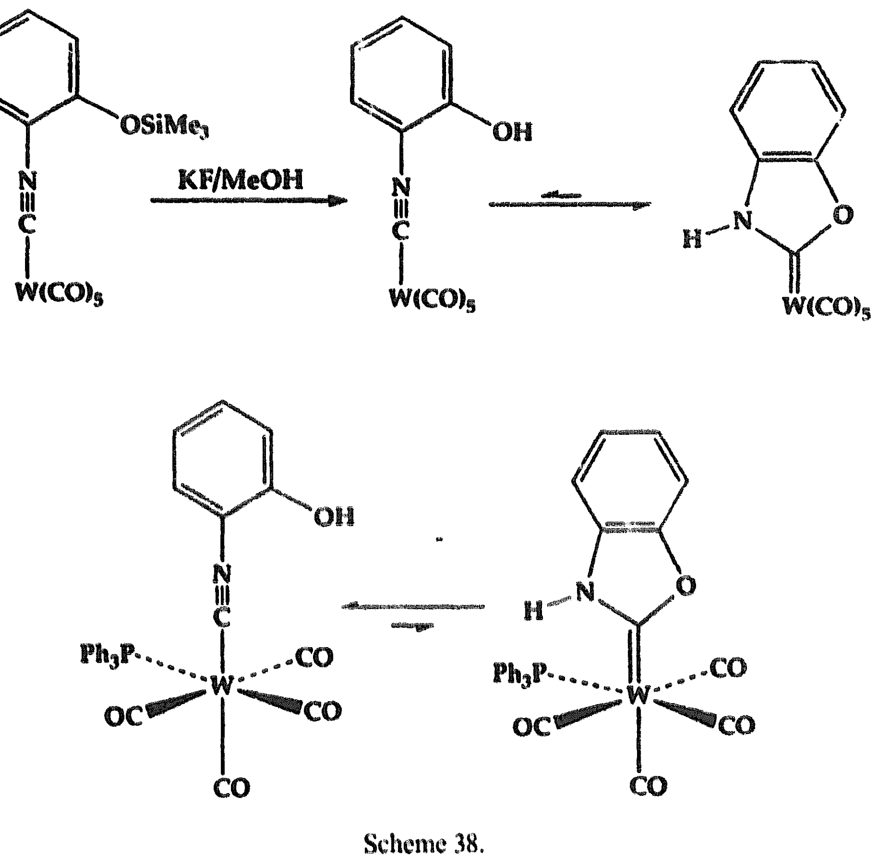
Dimetallic tungsten/rhodium and tungsten/copper complexes were prepared from $Li[Cp^*W(CO)_3]$ with the respective $MCl(PPh_3)_3$ complexes [106]. An X-ray structural determination of $Cp^*W(CO)(\mu\text{-}CO)_2Rh(PPh_3)_2$ (**52**) revealed a short W–Rh bond of 2.5820(6) Å while the W/Cu product was identified as $Cp^*W(CO)_3CuPPh_3$.

An equilibrium between the isocyanide and ylidene forms was observed for the



(52)

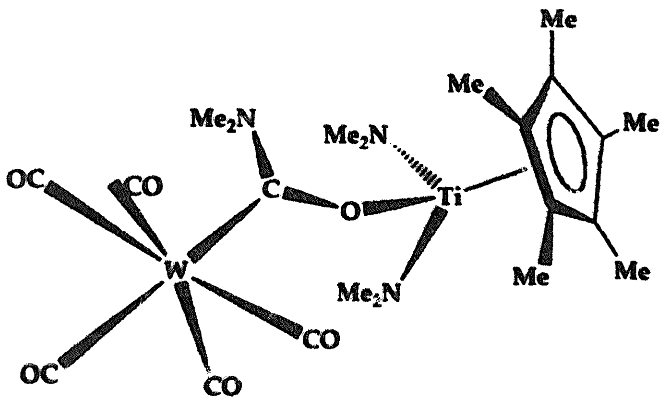
2-hydroxyphenyl isocyanide (Scheme 38) in its $W(CO)_5$ complex [107]. Interestingly substitution of a carbonyl by PPh_3 was found to favour the ylidene structure.



Scheme 38.

Hexacarbonyltungsten was found to insert into $Cp^*M(NMe_2)_3$ (M = Ti, Zr) to give $Cp^*M(NMe_2)_2[OC(NMe_2)]W(CO)_5$ in good yields [108]. The structure of the Ti/W complex (**53**) revealed metal bridging by the $OC(NMe_2)$ unit with a Fischer carbene at W and oxygen bound to Ti.

Ab initio calculations comparing $W(CO)_5(L)$ and $WCl_4(L)$ (L = HCCH, C_2H_4, CO_2, CS_2, CH_2O) complexes have been carried out [109]. The strongest W–L interaction was predicted for L = C_2H_4 in the former and L = HCCH for the latter



(53)

family of complexes. It was concluded that the Dewar–Chatt–Duncanson model is inappropriate for $W(CO)_5(L)$ complexes due to their highly covalent bonding.

The syntheses and characterization of tris(1-oxa-1,3-diene)tungsten complexes were described [110]. Structural determinations indicated significant contribution from the σ^2,η^2-ligand binding mode in these homoleptic species. Interestingly, platinum-catalysed hydrogenation converted phenyl substituents to cyclohexyls without affecting the oxadiene ligands.

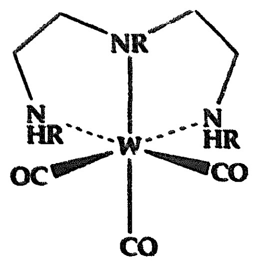
A donor-free stannylene complex of pentacarbonyltungsten has been reported [111]. In solution the alkylarylstannylene RR'Sn (R = 2,4,6-tri-*tert*-butylphenyl; R' = $-CH_2C(Me_2)$-3,5-$^tBu_2C_6H_3$) gave the product $(CO)_5W=SnRR'$ whose molecular structure revealed a strictly planar three-coordinate tin environment with an acute C–Sn–C angle of 91.5°.

A quasi-relativistic density function calculation of metal carbonyls $M(CO)_n$ gave satisfactory M–CO bond lengths, first bond dissociation energies, as well as CO association energies [112]. Relativistic effects were found to contract the W–CO bond and increase its bond dissociation energy compared to Mo–CO.

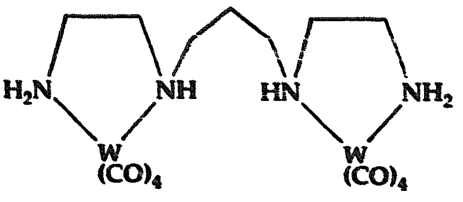
7.2. *Complexes with nitrogen ligands*

Lowest ligand-field excited state frequencies of the ν_{CO} bands of $W(CO)_5L$ (L = pyridine or piperidine) have been obtained by fast time-resolved IR spectroscopy in low-temperature glasses [113]. Shifts from ground state values indicate lengthening of the C–O bond upon excitation. Pentacarbonyltungsten amine complexes $W(CO)_5L$ (L = py, pyrazine, quinuclidine, trimethylamine) have been studied by ^{13}C and ^{17}O NMR spectroscopic spin-lattice relaxation time measurements [114]. Results indicate that enhancement of W–CO π bond is strongly *trans*-directed and independent of amine basicity. Further, no evidence for π-acceptor behaviour of the π^* orbitals in aromatic amines was found. Linear tri- and tetraamines were found to act as di- or tridentate ligands towards $W(CO)_6$, giving rise to $LW(CO)_4$, $L[W(CO)_4]_2$, and $LW(CO)_3$ complexes (54) and (55) [115].

The kinetics and mechanism of piperidine displacement from tungsten(0)phosphine carbonyl complexes were reported by several groups [116,117]. The reactions

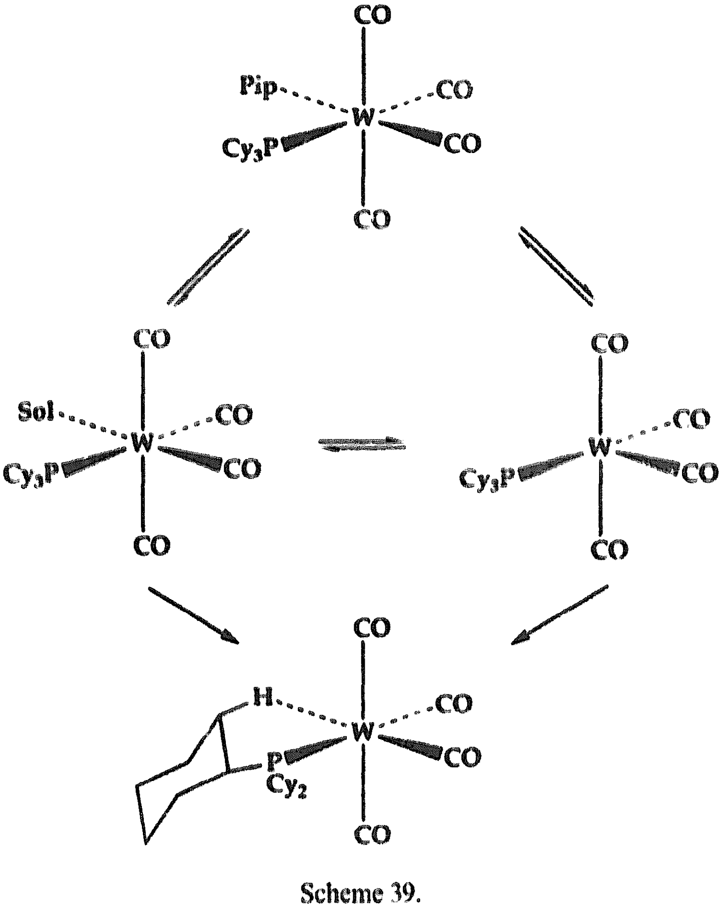


(54)



(55)

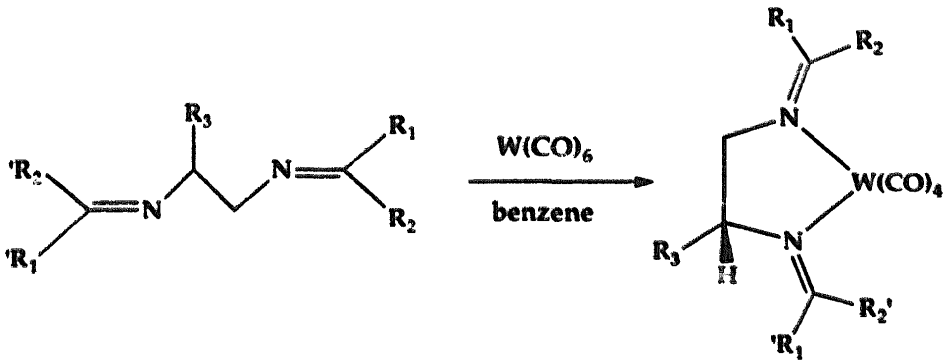
of *fac*-(pip)(diphos)W$(CO)_3$ with phosphines and phosphites were found to proceed by reversible piperidine dissociation followed by ligand attack. Significant steric or electronic dependence on the nucleophile was not observed [116]. Two consecutive first-order reactions were found for the displacement of piperidine by a cyclohexyl oxidative addition from *cis*-η^1-(PCy_3)(pip)W$(CO)_4$ [117]. Initial loss of piperidine was stabilized by an agostic interaction from a cyclohexyl C–H (Scheme 39). Subsequent oxidative addition of this C–H gave the cyclometallated product [η^2-$PCy_2(C_6H_{10})$]W(H)$(CO)_4$.



Scheme 39.

Potential liquid crystals based on pentacarbonyltungsten derivatives of stibazole-type ligands have been reported [118].

Solvatochromism in substituted (2,2′-bpy)W$(CO)_4$ complexes and related species has been examined [119]. Fast time-resolved infrared spectroscopy has been used to probe the lowest MLCT excited states of $(CO)_5W(L)W(CO)_5$ (L = pyrazine, 4,4′-bpy) [120]. Evidence was presented for a localized excited state (W^+L^-W) with little coupling between the metal centres. The carbonyl nitro monoanion $[W(CO)_5NO_2]^-$ has been isolated from the reaction of $W(CO)_6$ with trimethylamine oxide in the presence of $[PPN][NO_2]$ [121]. The X-ray structure of the $[PPh_4]^+$ salt revealed coordination of the nitrite ligand in the nitro form. Synthesis and characterization of *cis*-$W(CO)_4$ complexes of functionalized imines have been reported (Scheme 40) [122].



Scheme 40.

The reduction of coordinated acetonitrile in the tungsten complex $W(PhC\equiv CPh)_3(NCMe)$ with MeLi or PhLi followed by water led to imine derivatives $W(PhC\equiv CPh)_3(NH{=}CMe_2)$ and $W(PhC\equiv CPh)_3(NH{=}CPhMe)$ respectively [123].

7.3. *Complexes with phosphorus ligands*

7.3.1. *Monometallic complexes with phosphorus ligands*

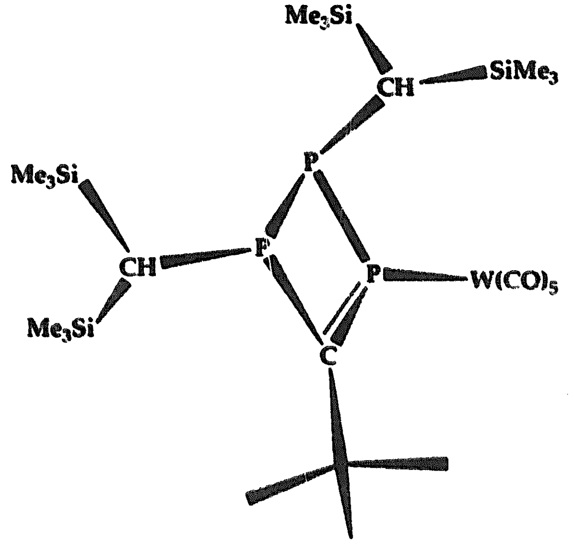
Hydrogenolysis of tetra(allyl)tungsten in the presence of tertiary $PPhMe_2$ resulted in the loss of all allylic groups and formation of $WH_4(PPhMe_2)_4$ [124]. Interestingly, use of chelating dmpm resulted in formation of homoleptic $W(dmpm)_3$.

Reaction of $^tBu_2Si(OLi)_2$ with PPh_2Cl yielded the chelating ligand $^tBu_2Si(OPPh_2)_2$ which was shown to chelate a *cis*-$W(CO)_4$ moiety [125]. Selective mono- and di-alkylation of the backbone of $W(CO)_3[PPh_2CH_2C(^tBu){=}N\text{-}N{=}C(^tBu)CH_2PPh_2]$ was achieved via ^nBuLi followed by alkylation [126].

X-ray crystallographic studies of the series of complexes $M(CO)_5PY_3$, revealed that $W(CO)_5PCl_3$, $W(CO)_5PBr_3$, and $Cr(CO)_5PCl_3$ are isomorphous [127]. Analysis of observed bond distances showed no convincing evidence for involvement of the P–Y σ^* orbital in metal π-back donation. Correlations between ^{31}P NMR spectroscopic chemical shifts and Hammett σ-substituent constants have been reported for both *syn* and *anti*-phosphiranes complexed to $W(CO)_5$ [128]. The data strongly suggest conjugation between the remote *p*-X-phenyl and *trans*-P-phenyl groups in the *syn*-1 substituted styrenes.

A new class of chelating phosphines with hydrazine backbones have been reported with their tungsten complexes [129]. Thus *cis*-$W(CO)_4[PR_2N(Me)N(Me)PR_2]$ (R = OPh, OC_6H_4Br-*p*) have been prepared and characterized.

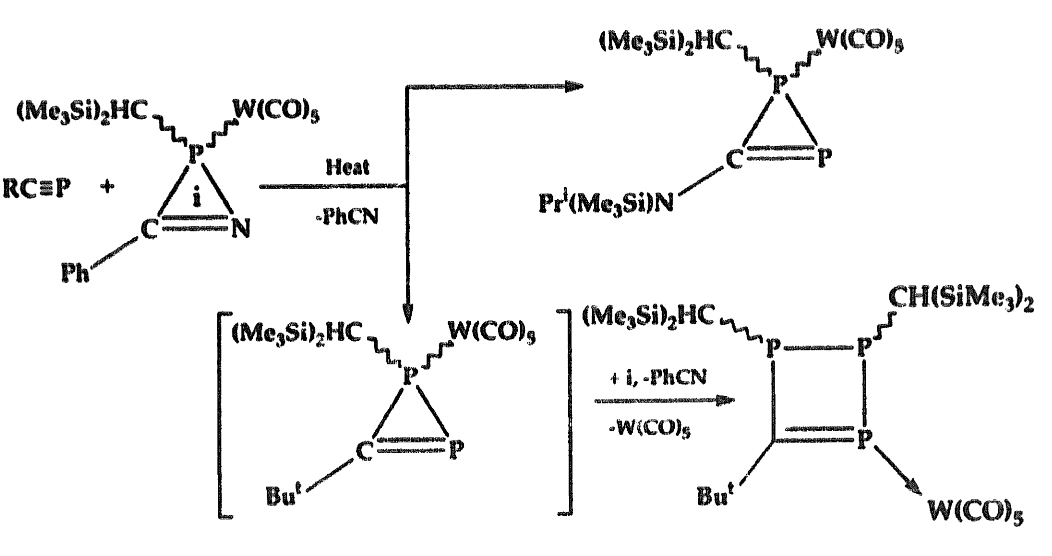
The first *trans*-1,2-dihydro-1,2,3-triphosphete tungsten complex has been prepared and characterized [130]. Thermal decomposition of the $W(CO)_5$ complex of 2*H*-azaphosphirene (Scheme 41) in the presence of a phosphalkyne gave the 1*H*-phosphirene complex as well as the novel product (**56**) whose molecular structure has been determined.



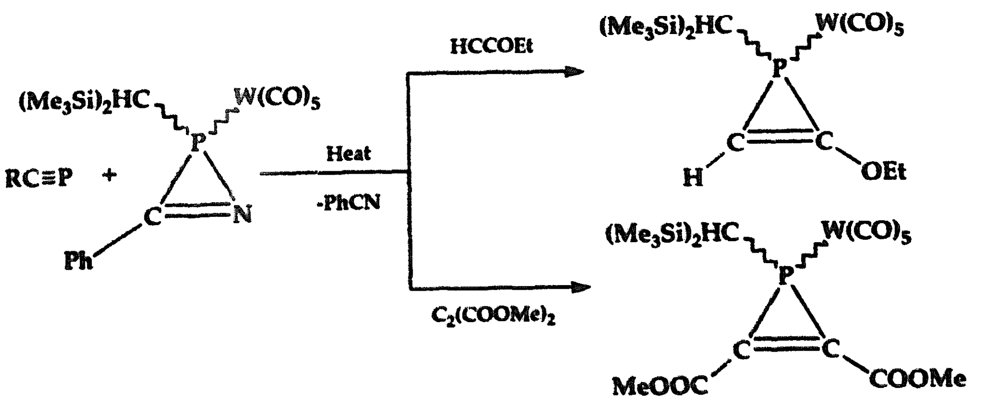
(**56**)

Reaction of the same 2*H*-azaphosphirene · $W(CO)_5$ precursor with acetylenes yielded *C*,*C*′-difunctionalized 1*H*-phosphirene-tungsten complexes (Scheme 42) [131].

Tungsten carbonyl complexes of α-functionalized 2-methylphenylphosphine have

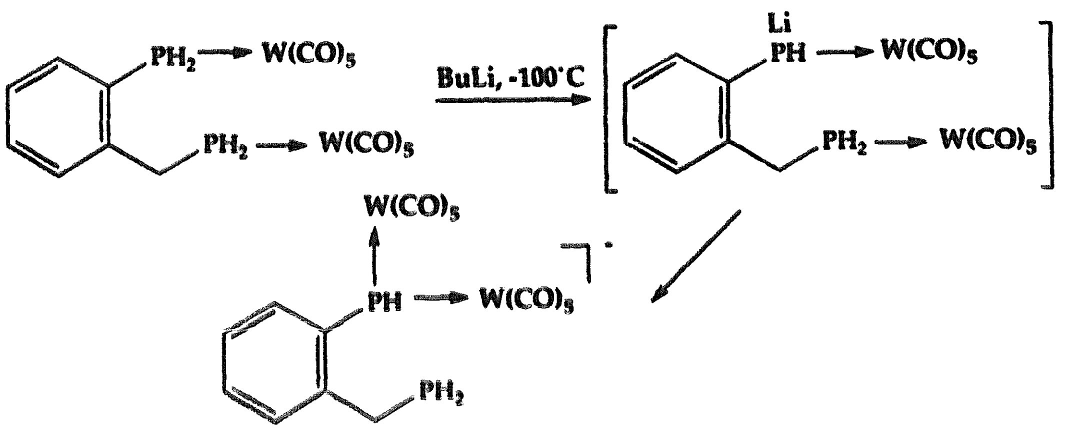


Scheme 41.



Scheme 42.

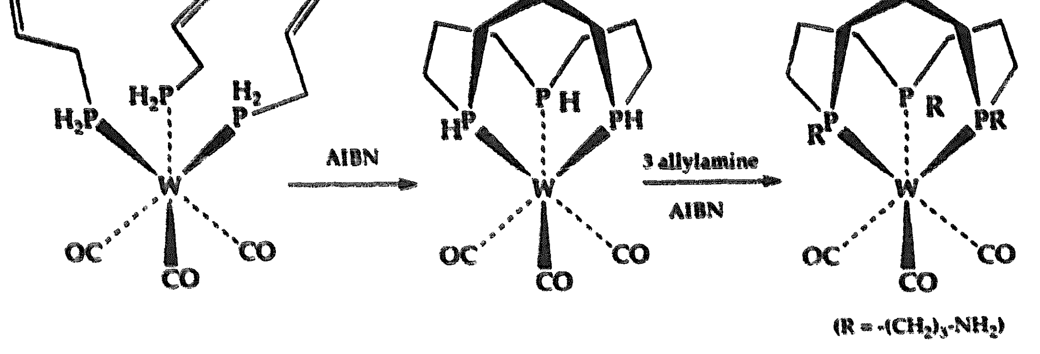
been described [132]. An interesting $W(CO)_5$ migration was observed upon deprotonation of a coordinated PH_2 unit (Scheme 43).



Scheme 43.

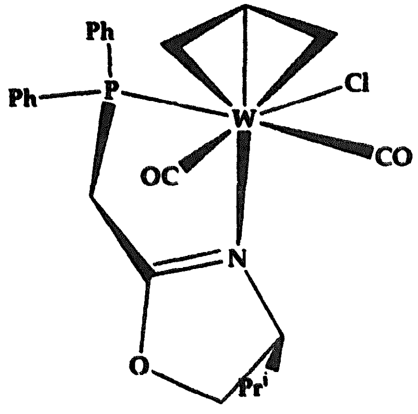
The first tungsten complexes of the tritertiary phosphine macrocycle 1,5,9-triphosphacyclododecane have been prepared from the tris-secondary 1,5,9-triphosphacyclododecane precursor (Scheme 44) [133].

Tungsten nitrosyl carbonyl complexes with 2-phenylphosphino-anisole, -anilide,

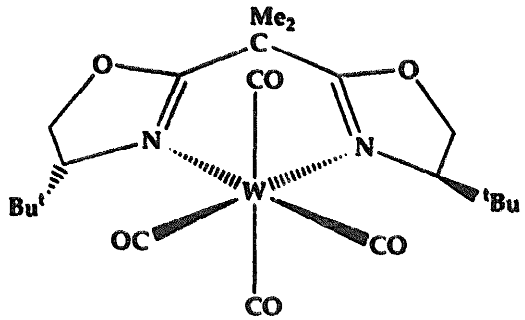


Scheme 44.

-benzoate, and -phenolate ligands have been described [134]. Pentacarbonyltungsten complexes of other functionalized phosphines including 3-aminophenyl-PPh_2, phenyl-2-carbaldehyde-PPh_2, phenyl-4-carbaldehyde-PPh_2 have also been reported [135]. Chiral didentate oxazoline–phosphine and bis-oxazoline ligands have been prepared and their tungsten carbonyl complexes synthesized [136]. The structures of several of these products, (**57**) and (**58**), have been determined. These were found to be effective enantioselective catalysts in allylic substitution reactions.



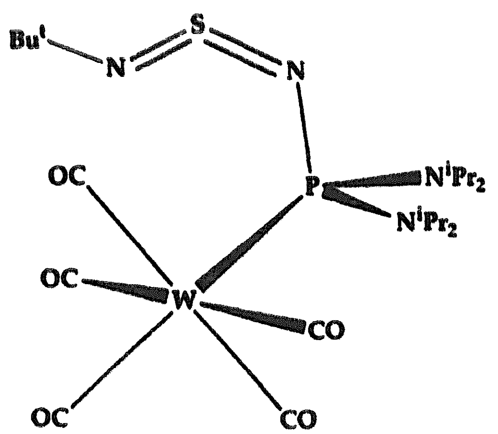
(**57**)



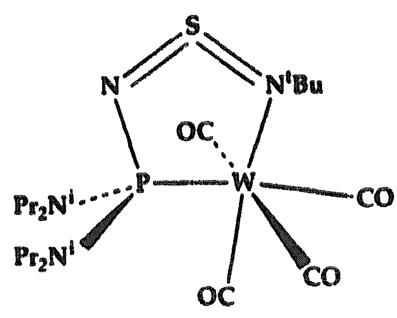
(**58**)

Tungsten carbonyl complexes featuring the dithioformato-PPh_2 ligand have been prepared from CS_2 and $NEt_4[W(CO)_5PPh_2]$ or $W(CO)_5MeCN$ with $NEt_4[PPh_2CS_2]$ [137]. Both alkylation and acylation reactions were found to occur only at the sulfur atom of this complex. Several dimetallic products were also obtained in its reactions (Scheme 45).

A sulfur diimide was found to react with $W(CO)_5 \cdot THF$ to give an adduct which adopted the Z/E configuration in the solid state (**59**) and at low temperature in solution [138]. Photo-induced CO loss gave the novel metallacycle containing a WPNSN ring (**60**).

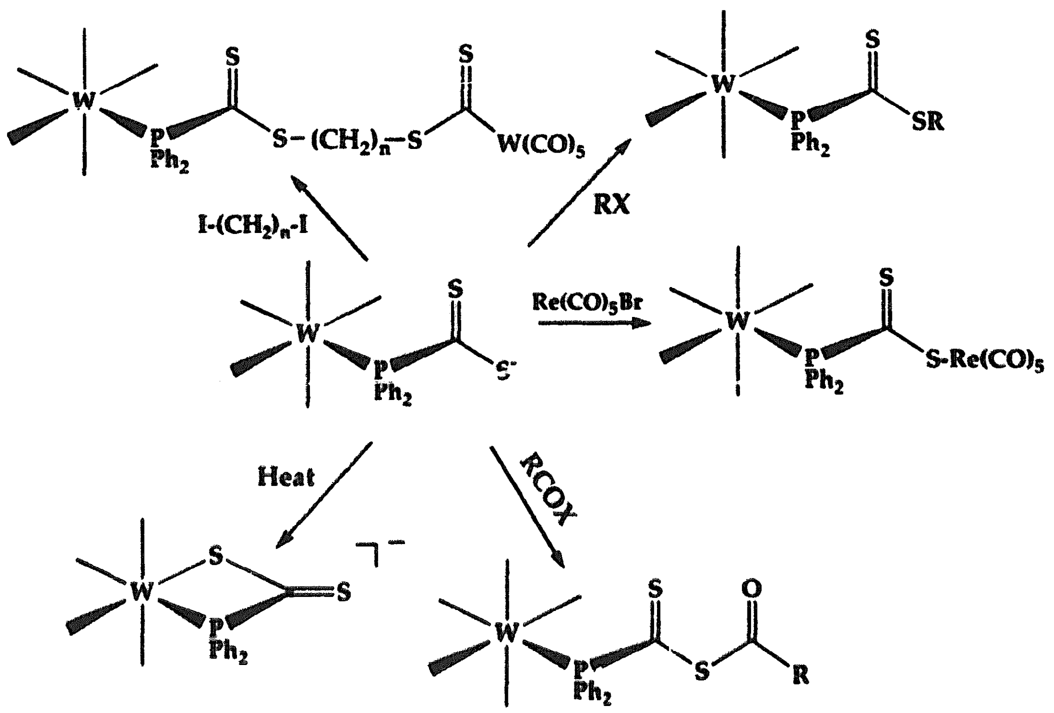


(**59**)



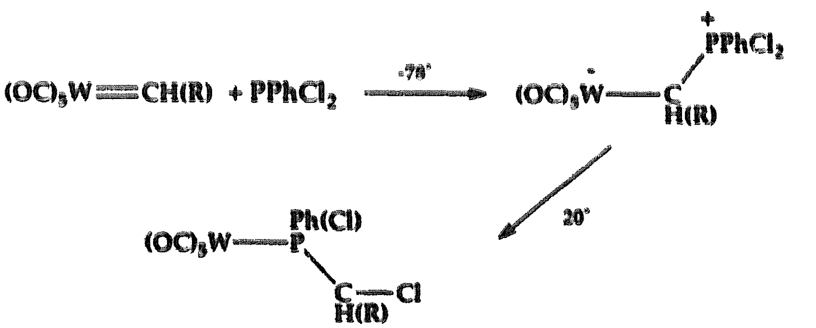
(**60**)

The tungsten benzylidene complex $(CO)_5W{=}C(Ph)H$ was reacted with $PhPCl_2$ at low temperature to give a ylide complex $(CO)_5W$-C(Ph)H-PPhCl which isomerized



Scheme 45.

at room temperature to the phosphine complex (Scheme 46) [139]. The initial stereospecific rearrangement was found to be followed by epimerization at the P.

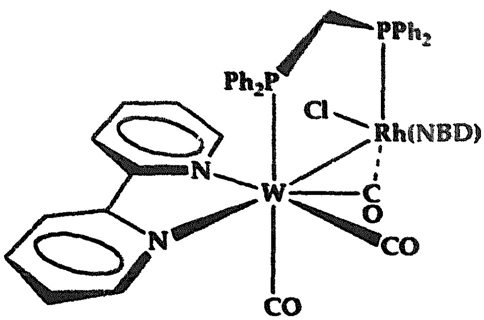


Scheme 46.

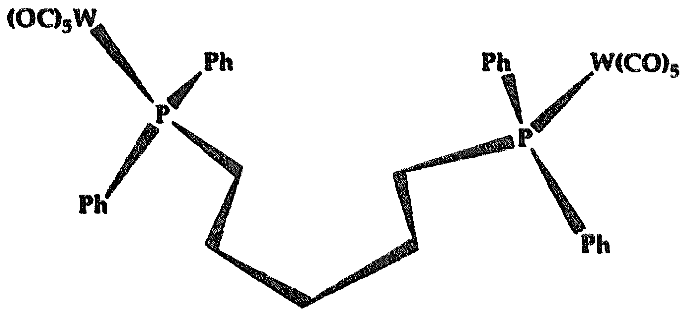
7.3.2. Polymetallic complexes with phosphorus ligands

Either a 2:1 mixture of $W(CO)_5 \cdot NCMe$ with $(CO)_5W$-η^1-dppm or a 3:1 mixture of $W(CO)_5 \cdot NCMe$ and dppm resulted in the dimetallic complex $W(CO)_5(\mu$-dppm$)W(CO)_5$ [140]. A new synthetic route to a W–Rh complex has been reported [141]. Reaction of dimeric [(diolefin)RhCl]$_2$ with $W(CO)_3(NN)(\eta^1$-dppm) led to a diphosphine-bridged Rh–W product (**61**).

Organomercuration of the carbanion derived from $W(CO)_4$[dppm] with RHgCl afforded neutral dimetallics of the type $W(CO)_4[\eta^2$-$PPh_2CH(HgR)PPh_2]$ where R can be Me, Et, Ph, or C_5H_4FeCp [142]. The X-ray structure of the ditungsten complex $W_2(CO)_{10}[(\mu$-$PPh_2(CH_2)_5PPh_2]$ (**62**) has been determined [143]. Niobium-



(61)



(62)

and tantalum-tungsten complexes bridged by both dppm (or dppe) and a hydride were obtained from the reactions of $Cp_2MH[\eta^1$-diphosphine] and $W(CO)_4$ fragments [144]. Ditungsten complexes containing polydentate phosphines have been reported [[145]. These included $W(CO)_4[\mu\text{-}PPh(CH_2CH_2PPh_2)_2]W(CO)_5$ and $W(CO)_4$-$[\mu\text{-}P(CH_2CH_2PPh_2)_3]W(CO)_4$.

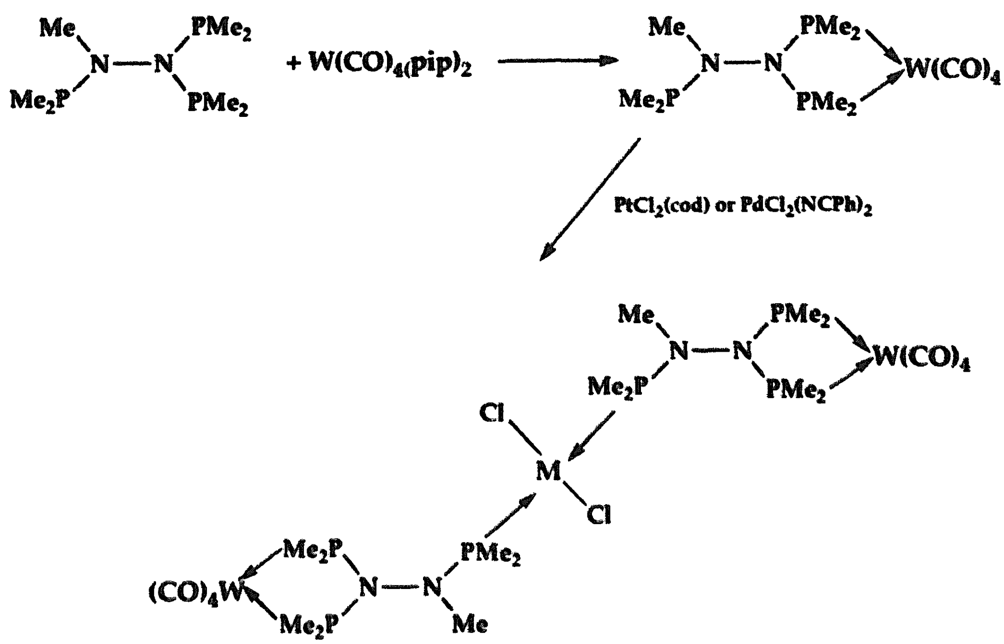
Reactions of the cyclodiphosphazane complex *cis*-$W(CO)_4$(pip)[*cis*-{PhNP{O(*p*-tolyl)}}$_2$] with (cod)MCl_2 (M = Pd, Pt) yielded the trimetallic complexes *cis*-MCl_2{*cis*-$W(CO)_4$(pip)[*cis*-{PhNP{O(*p*-tolyl)}}$_2$]}$_2$ [146]. Related heterotrimetallic complexes have also been made from the new hydrazide-based triphosphine $(Me_2P)_2N\text{-}NMe(PMe_2)$ (Scheme 47) [147].

Treatment of $W(CO)_3(NCMe)_3$ with dppf was found to give $W(CO)_3(NCMe)(\eta^2$-dppf) which was iodinated to form the seven-coordinate complex $W(CO)_3I_2(\eta^2$-dppf) (Scheme 48) [148]. Further oxidation with hydrogen peroxide yielded the phosphine oxide-coordinated product $W(CO)_2I_2[\eta^2$-dppf(=O)].

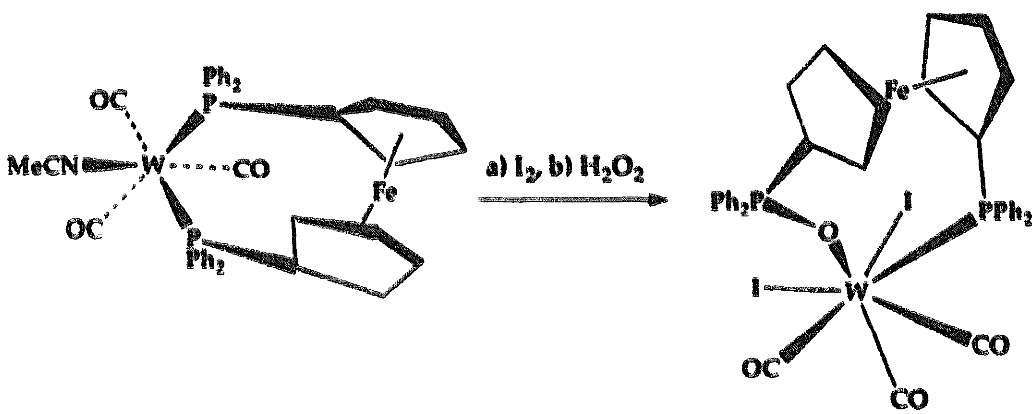
Thermal reaction of the *cyclo*-triphosphoxane $[Cy_2N\text{-}PO]_3$ with $W(CO)_6$ was reported to give two ditungsten *cyclo*-tetraphosphoxane products $W_2(CO)_7[Cy_2NPO]_4$ (63) and $W_2(CO)_6[Cy_2NPO]_4$ (64) [149].

Metalation of a 2-vinylphosphirane tungsten complex was found to lead to a 1-phospha-pentadienide product which was treated with $CpFe(CO)_2I$ to give a heterodimetallic product (Scheme 49) [150]. An *E*-stereochemistry was observed at the P–C=C–C=C chain.

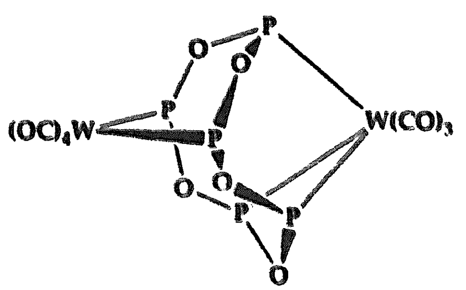
A mono-phosphido-bridged Nb/W complex $Cp_2Nb(\mu\text{-}PMe_2)[(cis\text{-}W(CO)_4$-



Scheme 47.

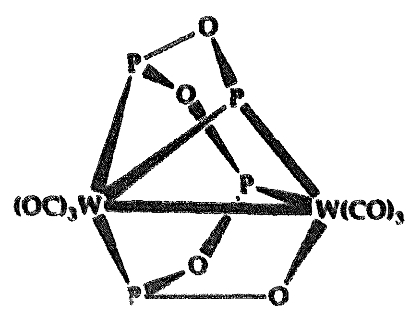


Scheme 48.



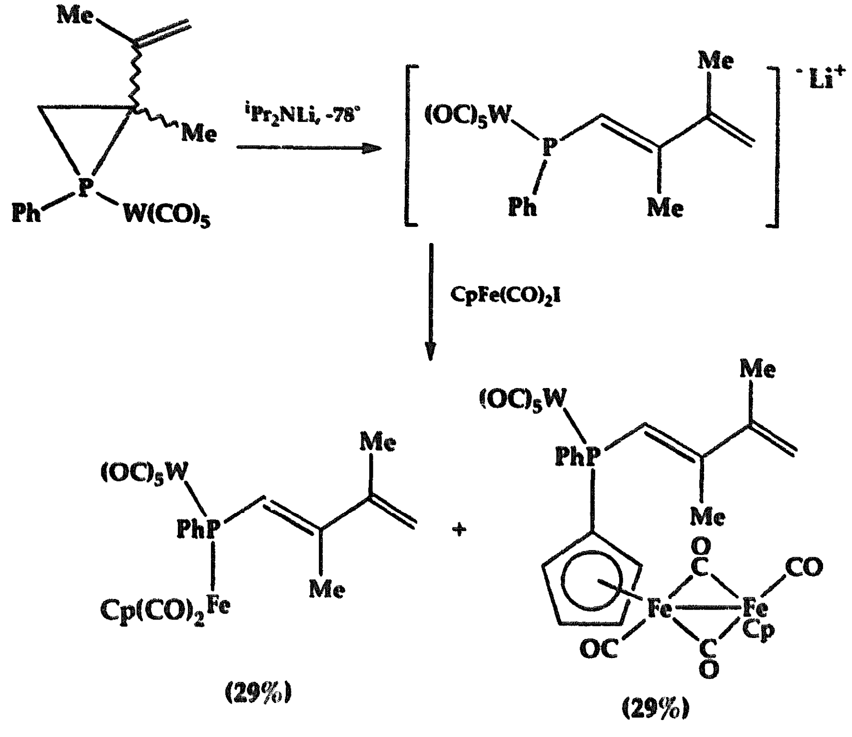
(P = P-NCy$_2$)

(63)



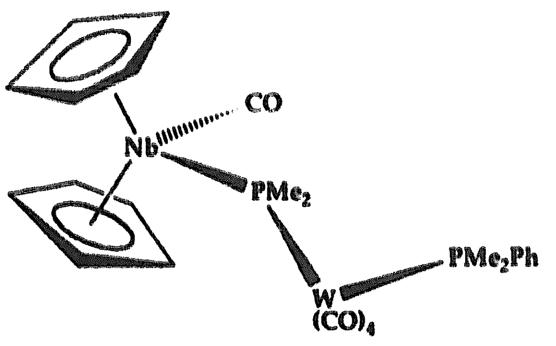
(P = P-NCy$_2$)

(64)



Scheme 49.

(PMe_2Ph)] has been reported to have the structure shown (**65**) [151]. A Nb–P–W angle of 124.9(2)° and non-bonded Nb–W separation were found.

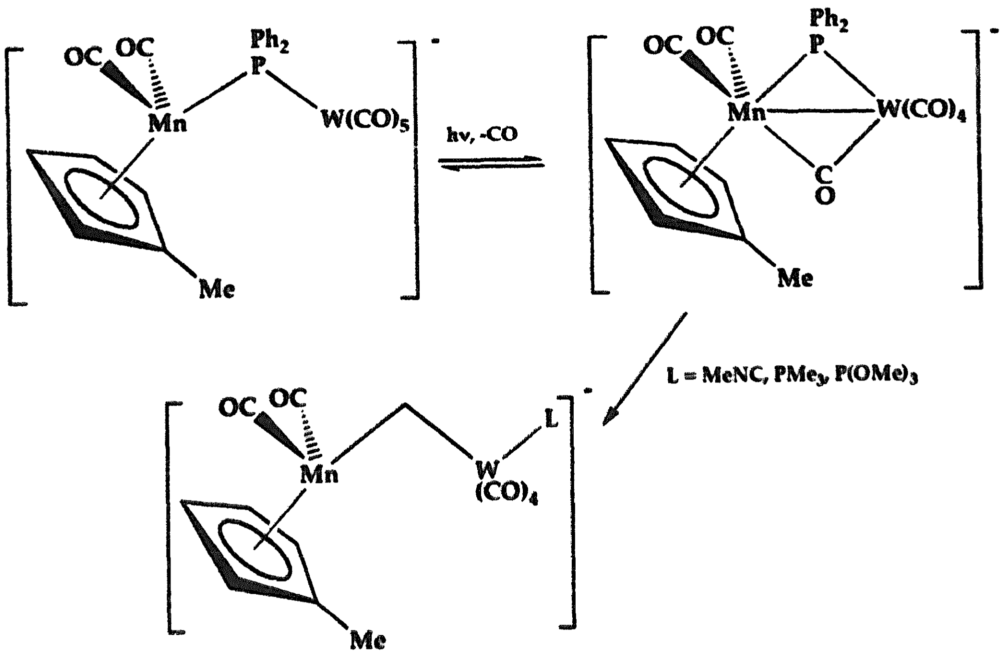


(**65**)

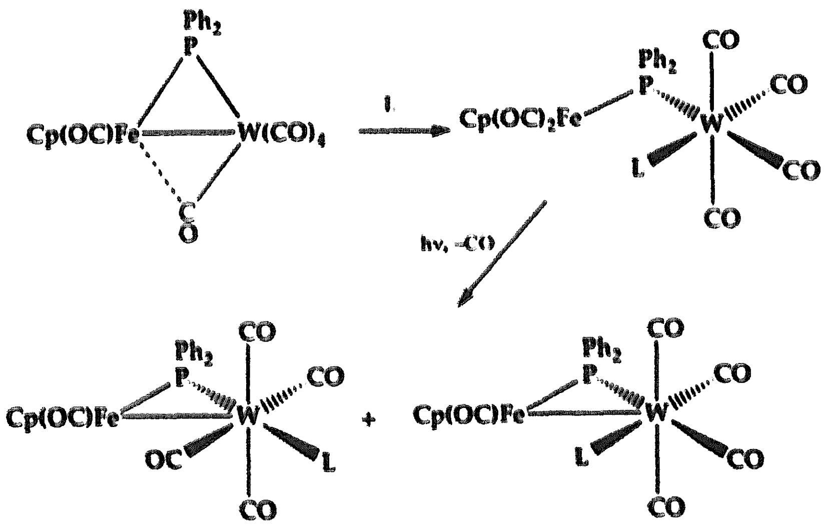
Treatment of $MeCpMn(CO)_2PPh_2Li$ with $W(CO)_5 \cdot THF$ gave $[MeCpMn(CO)_2(\mu\text{-}PPh_2)W(CO)_5]^-$ which was photolysed to yield a Mn–W bonded product, $[MeCpMn(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}CO)W(CO)_4]^-$ [152]. Lewis bases like MeNC and $P(OMe)_3$ were found to cleave the Mn–W bond and give the corresponding $[MeCpMn(CO)_2(\mu\text{-}PPh_2)(\mu\text{-}CO)W(CO)_4L]^-$ complex (Scheme 50).

Similarly, the metal–metal bond in phosphido-bridged CpFe(CO)-(μ-PPh_2)(μ-CO)$W(CO)_4$ can be cleaved by a variety of Lewis bases (L) to give $CpFe(CO)_2(\mu\text{-}PPh_2)[cis\text{-}W(CO)_4L]$ [153]. Additional reported reactions of these adducts are shown in Scheme 51.

Another phosphido-bridged tungsten complex, $Cp_2Ta(CO)(\mu\text{-}PMe_2)W(CO)_5$, was



Scheme 50.

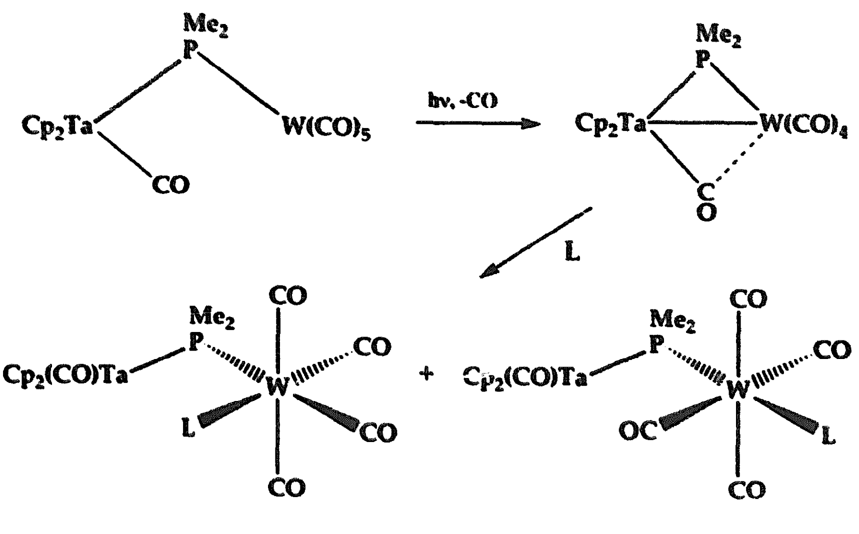


Scheme 51.

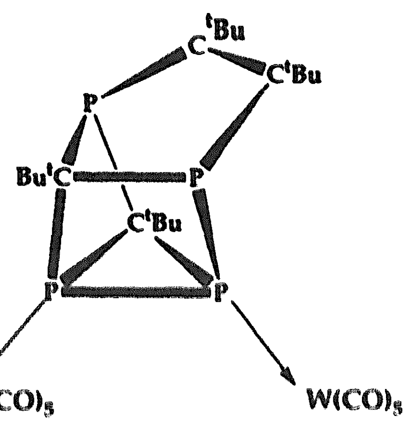
prepared from $Cp_2Ta(CO)PMe_2$ and $W(CO)_5 \cdot THF$ [154]. Photolytic elimination of CO from tungsten yielded a dibridged product whose metal-metal bond was also cleaved with a variety of Lewis bases (Scheme 52).

The interesting tetramerization of a phosphaalkyne to form a tetraphospha-bis-homoprismane has been confirmed by the full structural characterization of its tungsten complex, $W_2(CO)_{10}[P_4C_4Bu^t_4]$ (66) [155].

Further coordination of the Co_2P_4 cluster to $W(CO)_5$ moieties has been reported [156]. Structural and spectral studies revealed the formation of an acyclic, trapezoidally arranged P_4 chain in the products (Scheme 53).



Scheme 52.



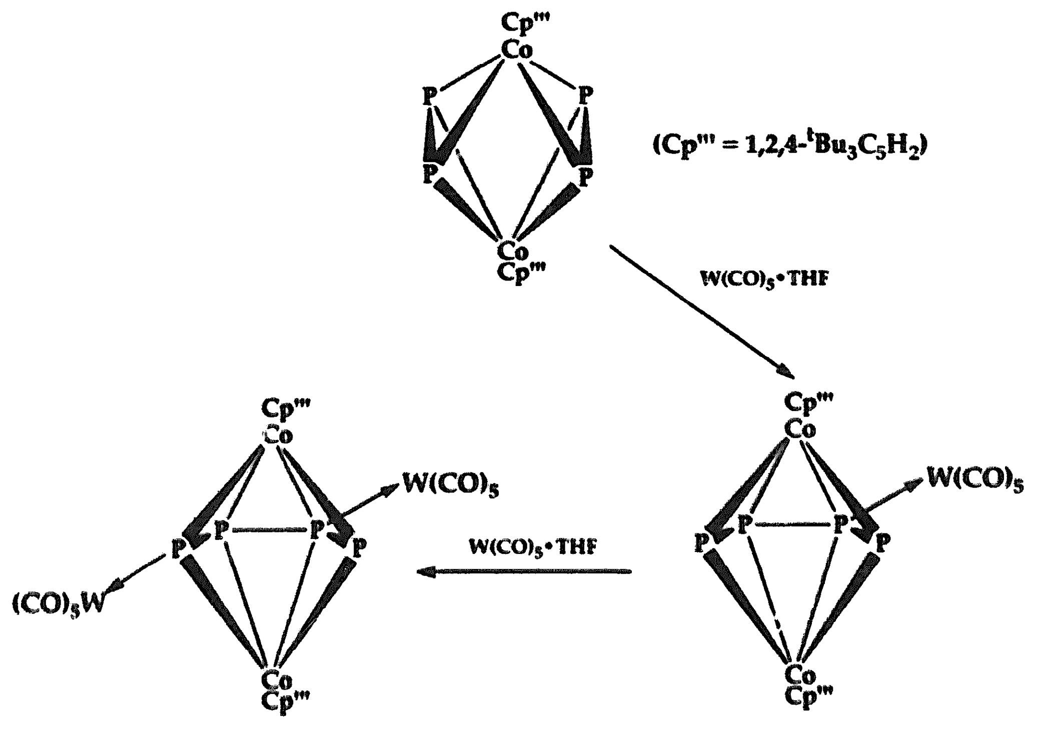
(66)

The novel tetra-armed porphyrin *meso-tetrakis*[4-(diphenylphosphino)-phenyl]porphyrin has been shown to react with $W(CO)_5 \cdot THF$ to form the tetra-tungsten complexes (**67**) [157].

7.4. Complexes with sulfur and selenium ligands

Insertion of carbon disulfide into a W–N bond has been used to prepare dithiocarbamate tungsten complexes [158]. Deprotonation of the N–H proton in $W(CO)_4(pip)_2$ by n-BuLi followed by reaction with CS_2 in the presence of NEt_4Br gave the complex $[NEt_4][(C_5H_{10}NCS_2)W(CO)_4]$ whose structure has been determined (Scheme 54).

Both the hybrid S/N/S ligands 2,6-bis(methylthiomethyl)pyridine and 2,6-bis(*p*-tolylthiomethyl)pyridine were found to chelate $W(CO)_4$ in a S/N fashion [159]. NMR spectral studies revealed three fluxional processes (Scheme 55). Tungsten carbonyl complexes of the mesocyclic 1,5-dithiacyclooctane have been reported



Scheme 53.

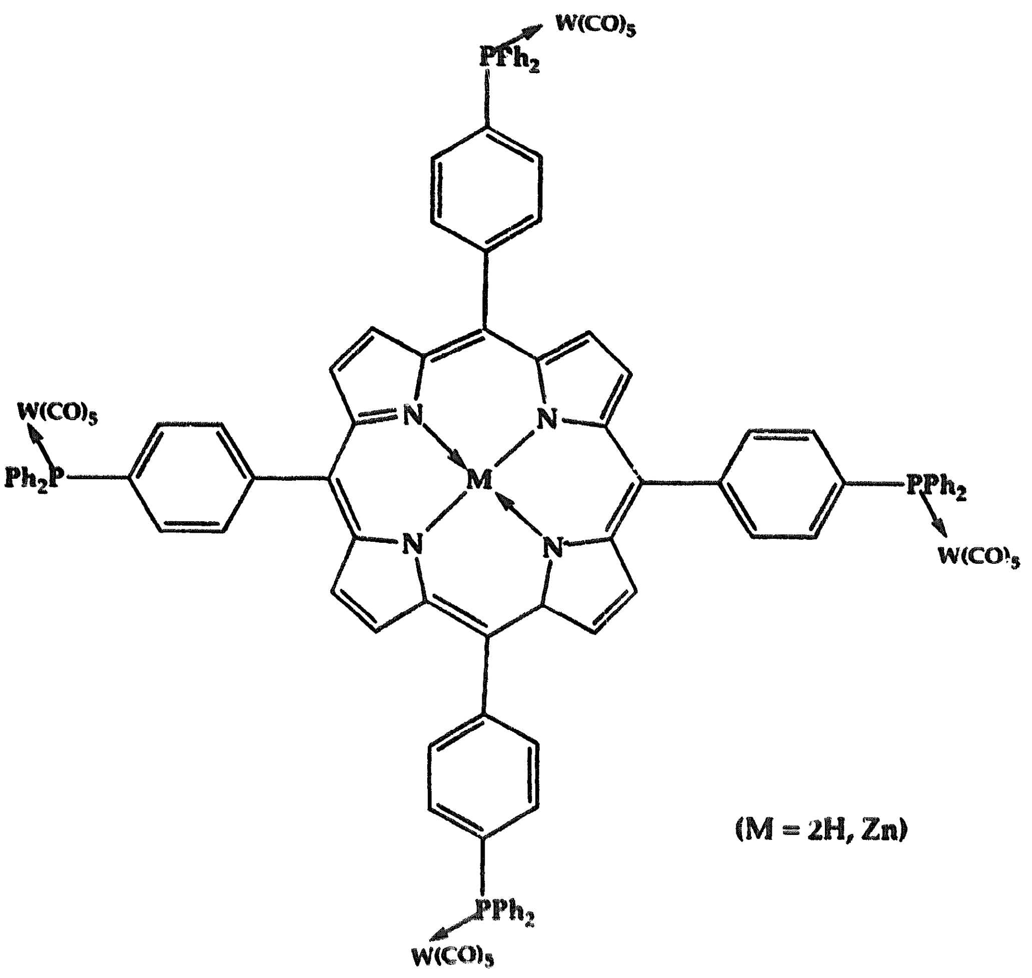
[160]. Spectral data supported facile *boat-chair* to *chair-boat* interconversions. Sequential treatment of $NEt_4[W(CO)_5Cl]$ with 4-methylthiazol-2-yllithium or isothiazol-5-yllithium and CF_3SO_3Me or CF_3SO_3H yielded the 2,3-dihydro-1,3-thiazol-2-ylidene and 2,5-dihydroisothiazol-5-ylidene tungsten complexes respectively (Scheme 56) [161].

Application of the hydrothermal technique using $W(CO)_6$ and Na_2S_2 resulted in the isolation of two mixed-valent tungsten complexes $[(W(CO)_4)_nWS_4]^{2-}$ (n = 1,2) (Scheme 57) [162].

The dihydroxy-bridged $[NBu_4][MR_2(\mu\text{-OH})]_2$ (M = Pd,Pt; R = Ph, C_6F_5) was reacted with $[WS_4]^{2-}$ to yield trinuclear $(MR_2)_2(\mu\text{-}WS_4)$ [162a].

The syntheses and reactivities of tungsten complexes containing the diphenylphosphinodithioformato ligand have been described in detail [163]. Treatment of $NEt_4[W(CO)_5PPh_2]$ with CS_2 afforded $NEt_4[W(CO)_5PPh_2CS_2]$ which was found to react with a variety of organic electrophiles with alkylation and acylation occurring exclusively at the sulfur sites (Scheme 58).

Addition of $W(CO)_5$ to the Ta=S bond in $Cp'_2Ta(=S)H$ resulted in a red, sulfur-bridged complex $Cp'_2Ta(=S\text{-}W(CO)_5)H$ where the sulfur atom behaved as a 4-electron donor [164]. Spectroscopic and electrical properties of the $[W(C_3Se_5)_3]$ dianion have been reported [165]. The tungsten selenobenzaldehyde complex $(CO)_5W\cdot Se=C(Ph)H$ was found to react with ^{t}Bu-C C-SMe with insertion of the C≡C triple bond into the Se=C bond to give the α,β-unsaturated thioselenocarboxylic ester complex (**68**) [166]. By contrast, three products were produced in the analogous reaction with Me-C CSMe (Scheme 59).



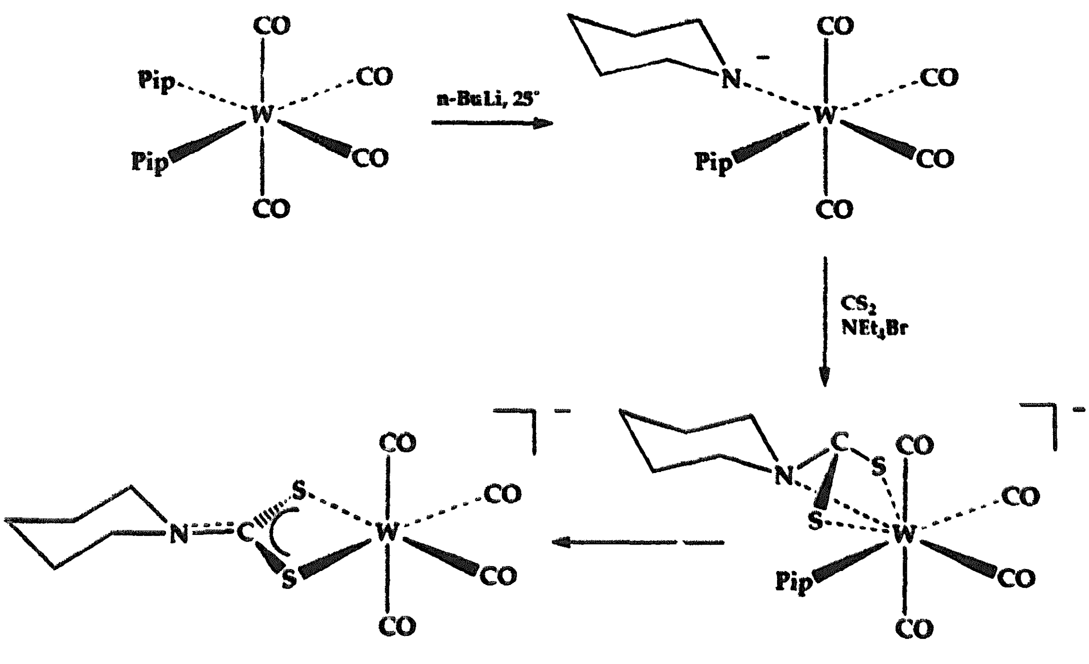
(67)

In a related study, ^{t}BuS-C C-S^{t}Bu inserted into the Se=C bond of tungsten selenobenzaldehdye complexes to give 2H-selenete products [167]. These were found to exist in solution in rapid equilibrium with the thioselenocarboxylic ester forms. Uncoordinated 2H-selenete and 3,4-dihydro-1,2-diselenine were liberated by treatment with NEt_4Br (Scheme 60).

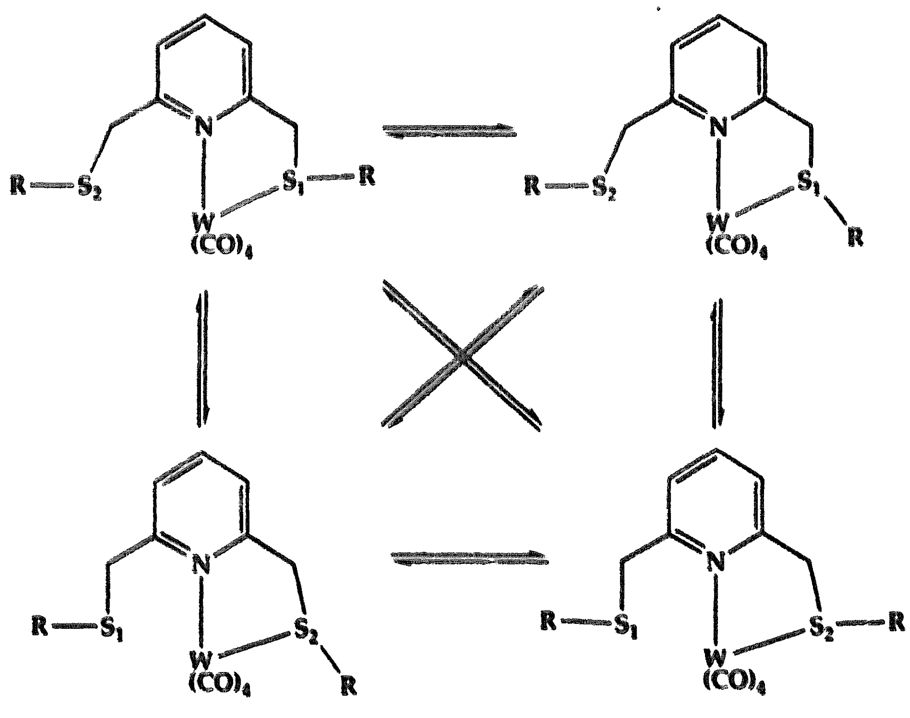
7.5. Complexes with miscellaneous ligands

The syntheses of ditungsten complexes $W_2(CO)_{10}[^tBuSb]_4$ and $W_2(CO)_{10}[Ph_4Sb_2]$ have been described along with their structures (**69**) and (**70**) [168].

The polyhydrido rhenium complex $[ReH_6(PPh_3)_2]^-$ has been shown to act as a ligand towards $(PrCN)_3W(CO)_3$ to give a hydride-bridged product $(PPh_3)_2ReH_6W(CO)_3^-$ [169]. The structure and bonding in $W(CO)_5(H_2)$ and related group 6 metal dihydrogen complexes have been studied [170]. Dihydrogen binding enthalpies were reported as 15.9 kcal mol^{-1} (Cr), 12.8 kcal mol^{-1} (Mo), and



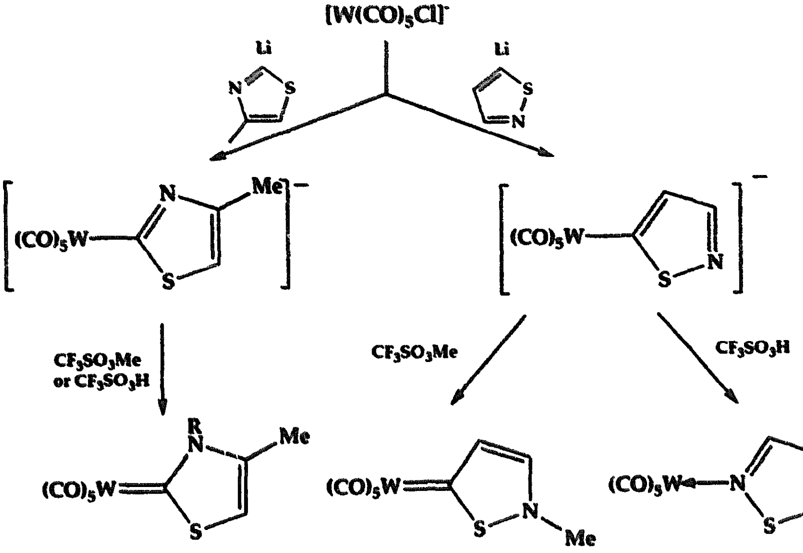
Scheme 54.



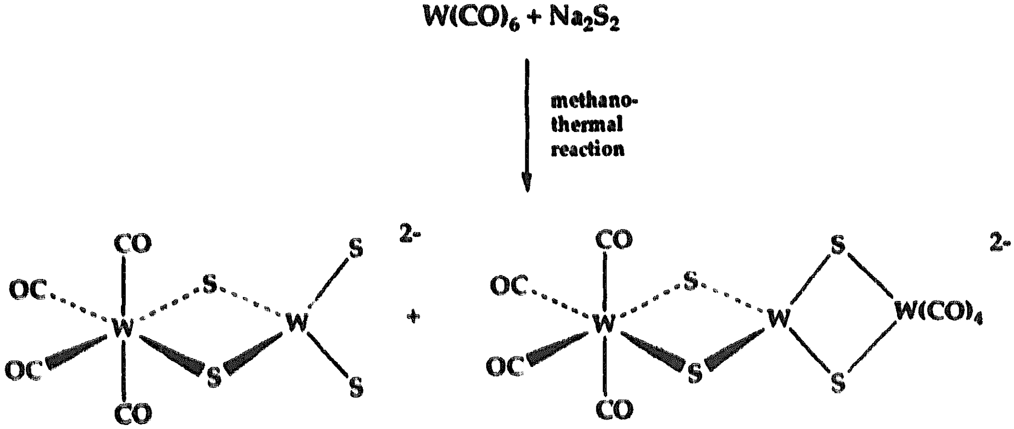
Scheme 55.

16.3 kcal mol^{-1} (W). Charge analyses showed that the H_2 ligand is a significant σ-donor and moderate π-acceptor.

Addition of $W(CO)_5 \cdot THF$ to anhydrous $[NEt_4]F$ in THF gave $[NEt_4]_3[W_2(CO)_6F_3]$ whose structure has been determined and found to contain three bridging fluorides (71) [171]. Excess CO converted this rapidly to



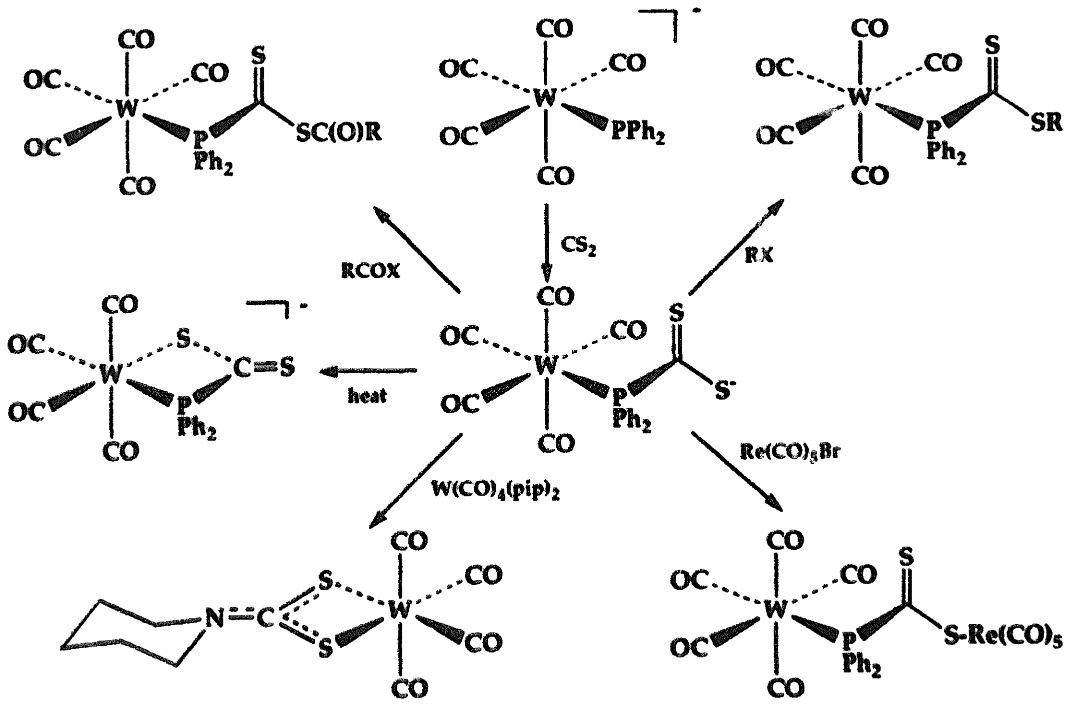
Scheme 56.



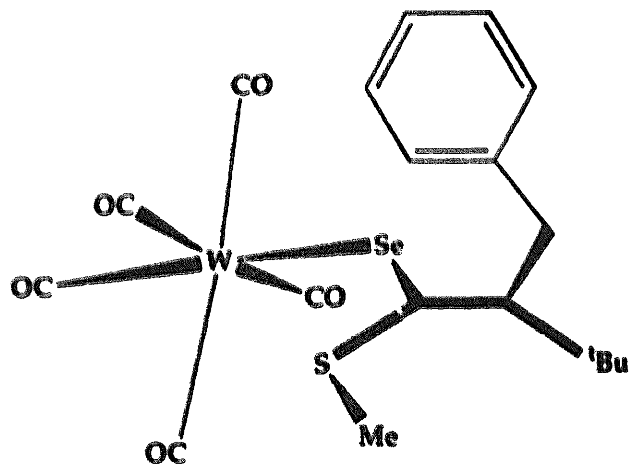
Scheme 57.

$[W(CO)_5F]^-$. The CO-labilizing ability of a fluoride has been estimated to be at least as potent as that of phenoxide.

Three symmetrical π-conjugated dinucleating aromatic amines (pyrazine, 4,4′-bpy, and 3,6-bis(4-py)-1,2,4,5-tetrazine (4,4′-bptz)) as their *trans,mer*-$(PR_3)_2W(CO)_3$ and related group 6 complexes were systematically studied for their spectroscopic and electrochemical behaviour [172]. A stable mixed-valent W(I)(μ-pyrazine)W(0) complex was found to exhibit complete delocalization on the vibrational timescale. No mixed-valency was observed for the other bridging ligands. Similar studies of the series of mononuclear complexes *trans,mer*-$W(PR_3)(CO)_3L$ revealed that the tungsten-centred oxidations were facilitated in the order L = pyrazine, η^2-H_2, 4,4′-bptz, bp, and THF. This confirms the ability of the $W(CO)_3(PR_3)_2$ fragments to bind molecular hydrogen due to their unique combination of σ-acceptor and fairly strong π-donor characteristics.



Scheme 58.



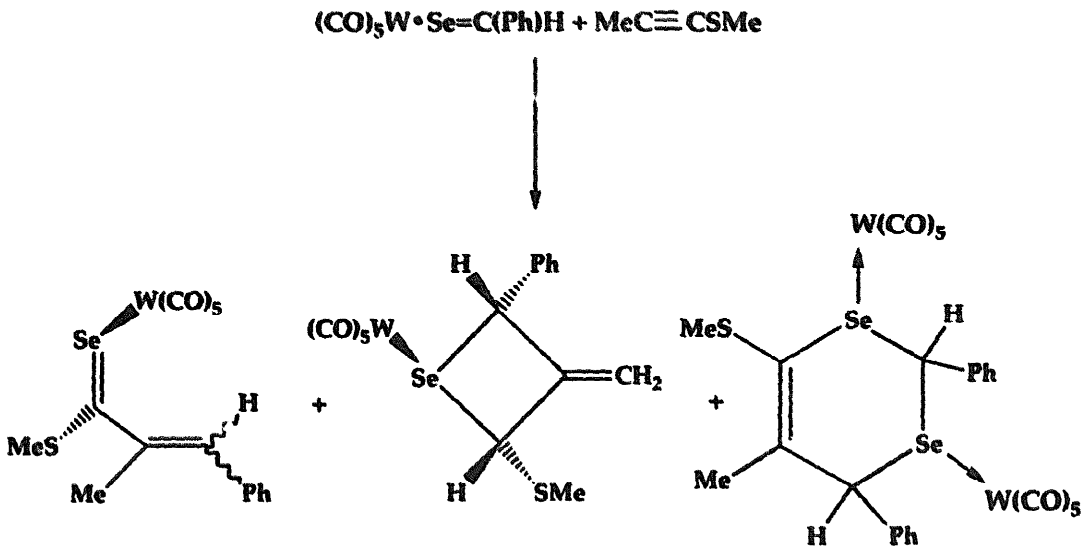
(68)

8. Selected tungsten clusters

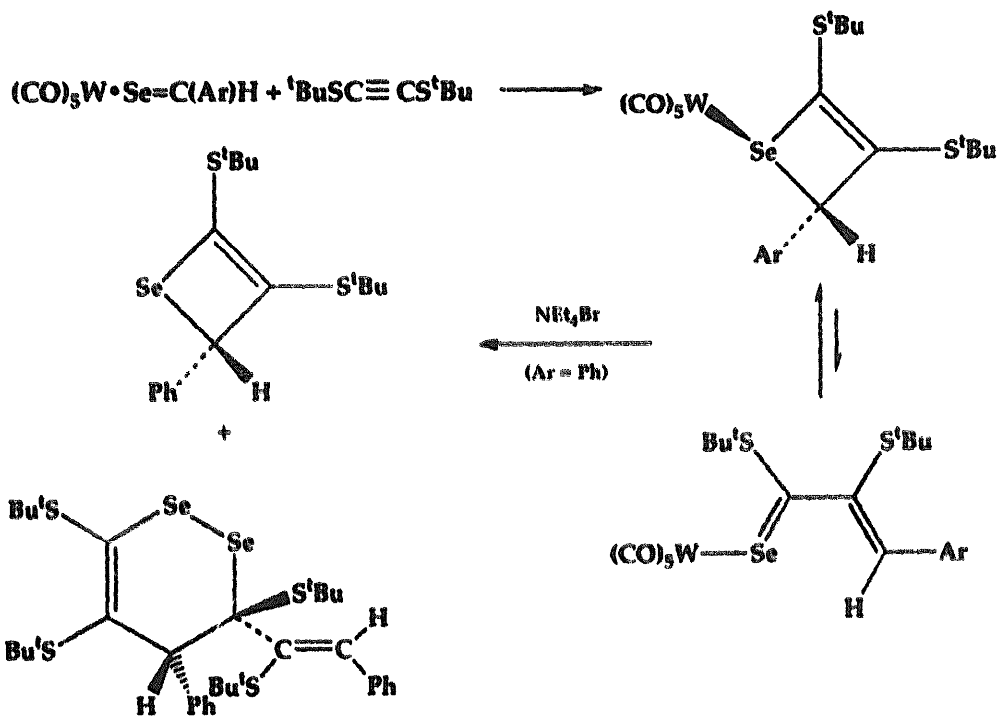
8.1. Sulfur and other chalcogenide clusters

Tetranuclear tungsten sulfide clusters with both raft-type and tetrahedral cores have been prepared [173]. Reaction of $W(N_2)_2(PMe_2Ph)_4$ with $(Me_3Si)_2S\cdot MeOH$ gave a raft-type $[W_4(\mu_3\text{-}S)_2(\mu\text{-}S)_4(SH)_2(PMe_2Ph)_6]$ cluster (**72**) which was converted to a tetrahedral $[W_4(\mu\text{-}S)_6(SH)(PMe_2Ph)_4]$ structure (**73**).

The antiferromagnetic complex $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)$ was found to react with



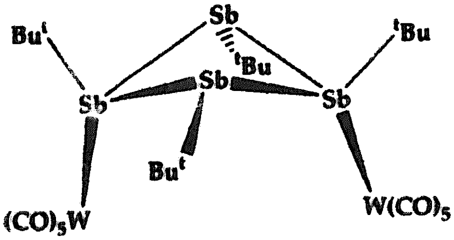
Scheme 59.



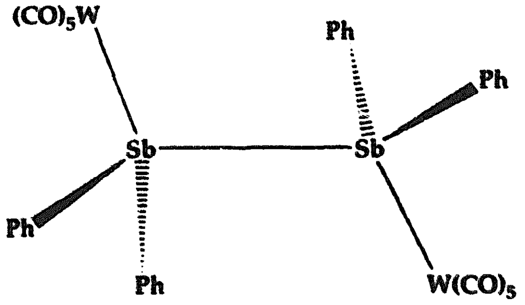
Scheme 60.

polymeric $[W(NO)_2Cl_2]_n$ to form an adduct $[Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)]W(NO)_2Cl_2$ [174]. Thermolysis of this product yielded the triangular clusters $Cp_2Cr_2(\mu\text{-}SCMe_3)_2(\mu\text{-}S)_2W(NO)_2$ (**74**) and $Cp_2Cr_2(\mu\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)Cl$ (**75**), $Cp_2Cr_2(\mu\text{-}S)_2(\mu\text{-}SCMe_3)_2W(NO)CMe_3$ as well as $Cp_2Cr_2(\mu\text{-}SCMe_3)(\mu\text{-}Cl)\text{-}(NO)_2$.

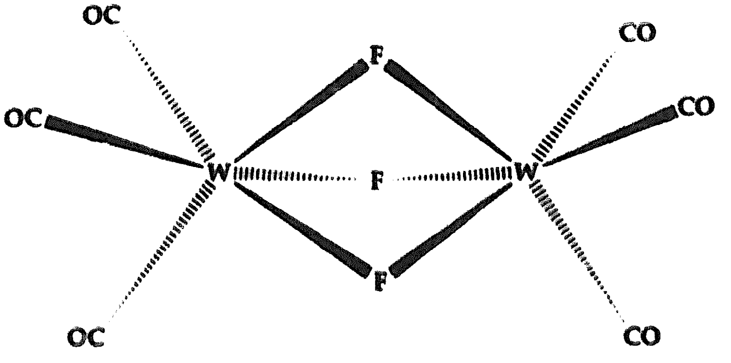
Reaction of $[Cu_2(dppm)_2(MeCN)_4]^{2+}$ with $[WS_4]^{2-}$ yielded the cationic d^0/d^{10} complex $[Cu_3(dppm)_3WS_4]^+$ which has a core structure of a distorted flywheel (**76**)



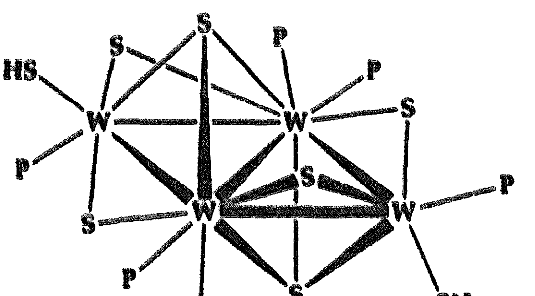
(69)



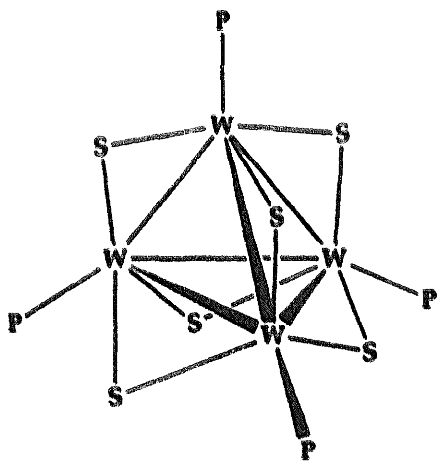
(70)



(71)



(72)

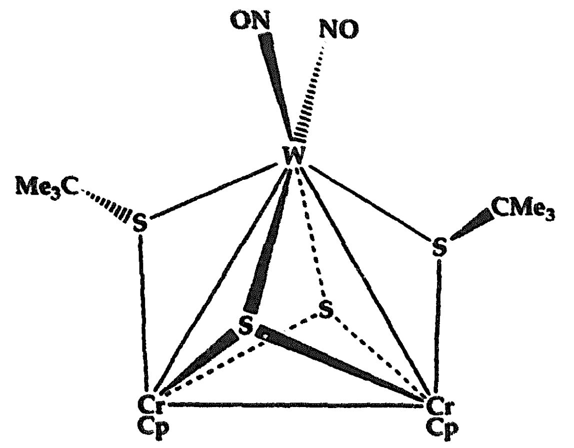


(P = PMe$_2$Ph)

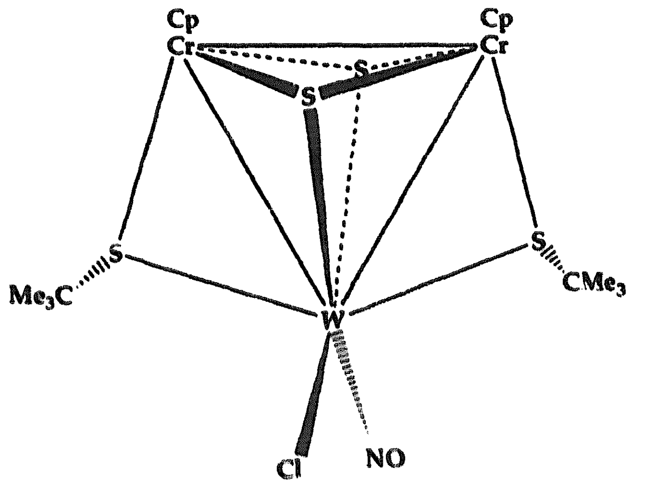
(73)

[175]. It was suggested that the intense emission spectrum observed may be the result of a Cu–P to tungsten CT transition.

Syntheses and structures of two silver/tungsten polymeric clusters have been reported [176]. In, DMF, ammonium tetrathiotungstate, silver nitrate, tris(hydroxymethyl)aminomethane (1:2:1) gave orange (77) with polymeric single chains of



(74)

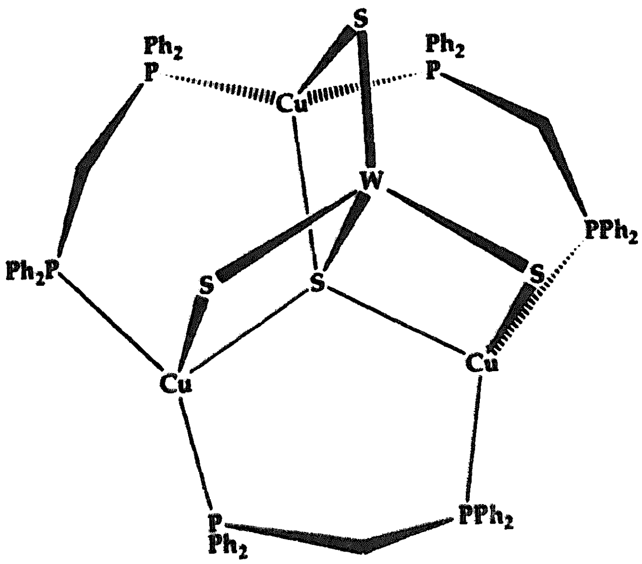


(75)

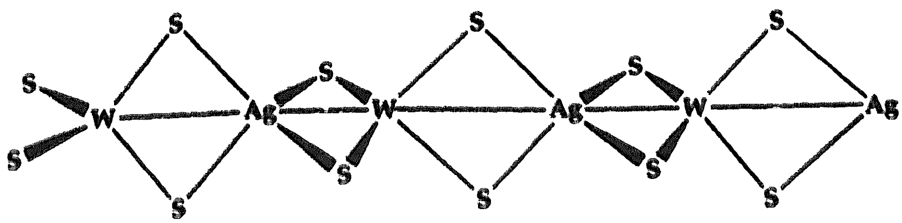
$[S_2WS_2Ag]^-$ units. Recrystallization of this product from ethanol containing a trace of moisture yielded instead (**78**) with the same cluster units in double-chains instead.

Reactions of $[(CpR)W(CO)_3]^-$ with $FeCo_2(CO)_9(\mu_3\text{-}S)$ gave the functionalized clusters $(CpR)W(CO)_2FeCo(CO)_8(\mu_3\text{-}S)$ where R = COOMe, COOEt, and C(O)Me (Scheme 61) [177]. The third product was further functionalized at the acyl group.

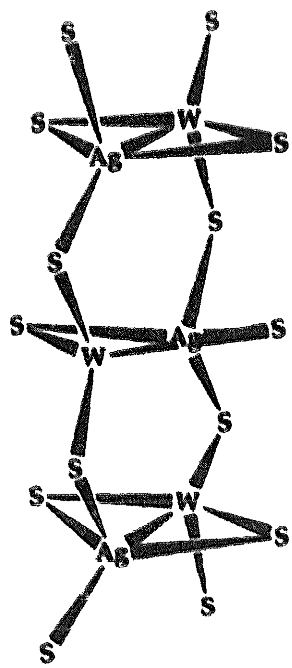
A high-yield synthesis of the W_6S_8 cluster unit as $W_6S_8py_6$ has been accomplished by reacting W_6Cl_{12} with NaSH and $NaOBu^n$ in pyridine [178]. Attempts at pyridine removal to generate the Chevrel phases were unsuccessful. Similarly, syntheses and characterization of N-ligated $W_6S_8L_6$ (L = py, 4-t-Bu-py) clusters from W_6Cl_{12}, SH^-, OBu^-, and pyridines have been reported [179]. Both clusters have the neutral, substitution-resistant W_6S_8 cores (**79**) with one additional pyridine at each tungsten vertex. Two new W_6Se_8 clusters have been prepared from the reaction of W_6Cl_{12} with Na_2Se in refluxing pyridine or piperidine [180]. Both were found to have the basic $W_6Se_8L_6$ structure (**80**).


S
Ph2
P
Cu
Ph2
P
W
PPh2
Ph2P
S
S
S
Cu
Cu
P
Ph2
PPh2

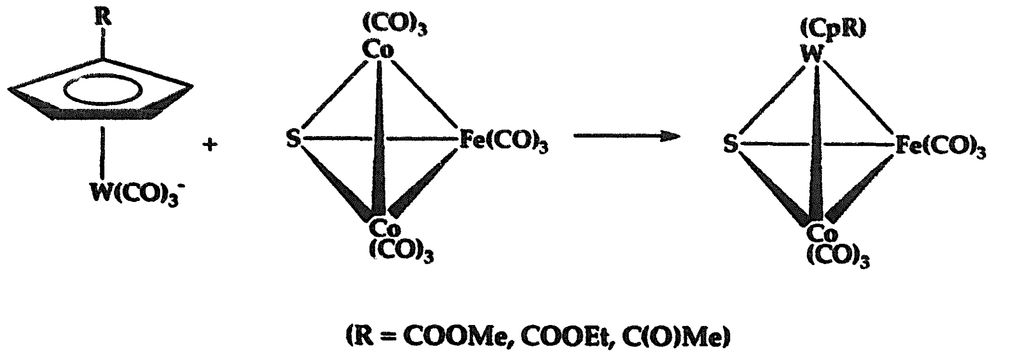
(76)


S
W
Ag
W
Ag
W
Ag

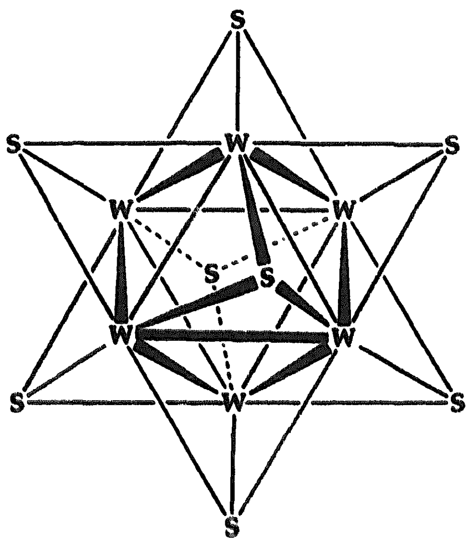
(77)


S
W
Ag
S
W
Ag
S
W
Ag

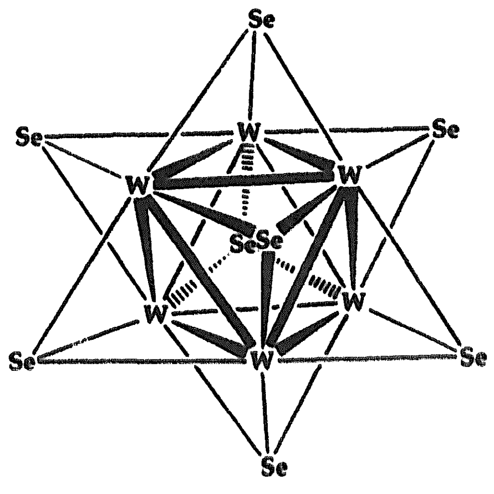
(78)



Scheme 61.



(79)



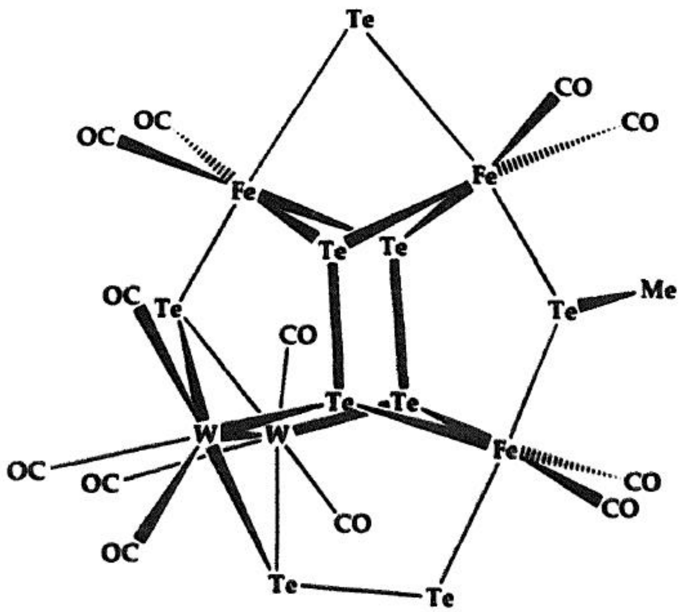
(80)

Methanothermal synthesis from $Fe_3(CO)_{12}$ and $W(CO)_6$ of the mixed-metal telluride cluster $[Fe_3W_2Te_8(TeMe)(CO)_{12}]^{3-}$ (**81**) has been accomplished [181].

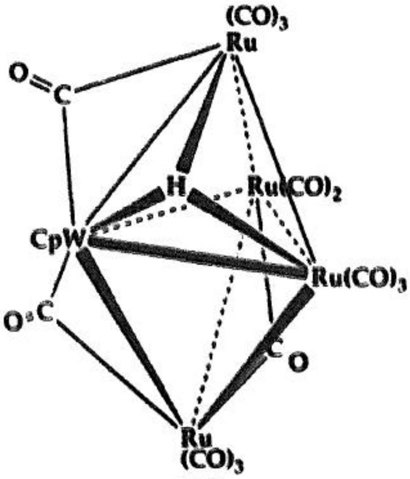
8.2. *Miscellaneous clusters*

The pentametal clusters $CpWRu_4(CO)_{14}(\mu_3\text{-}H)$ (**82**) and $Cp^*WRu_4(CO)_{14}(\mu_3\text{-}H)$ were obtained by the condensation of $Ru_3(CO)_{12}$ with the corresponding [PPN][$CpW(CO)_3$] reagents, followed by triflic acid treatment [182]. Their solution dynamics were monitored spectroscopically.

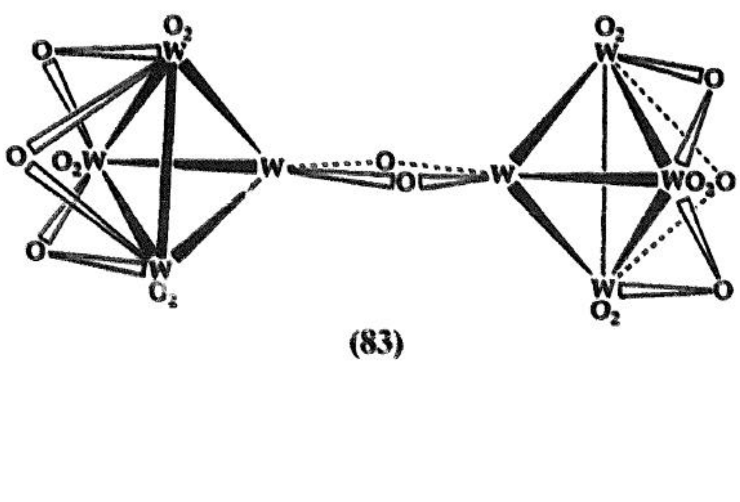
The hydrogenation of $W_4(p\text{-tolyl})_2(O^iPr)_{10}$ afforded an unusual octanuclear oxo-alkoxide cluster $[W_4(O)_2(O^iPr)_8]_2$ [183]. Details of the formation of this cluster as well as its structure were reported (**83**). The oxidation kinetics of the trinuclear $[W_3(\mu_3\text{-}O)_2(\mu\text{-}OAc)_6(H_2O)_3]^{2+}$ and $[W_3(\mu_3\text{-}O)(\mu\text{-}OAc)_6(H_2O)_3]^{2+}$ have been reported [184]. New trinuclear peroxo clusters $[NMe_4]_2[(PhPO_3)\{WO(O_2)_2\}_2\{WO(O_2)_2(H_2O)\}]$ (**84**) and $[NBu_4]_2[W_4O_6(O_2)_6(OH)_2(H_2O)_2]$ (**85**) have been isolated and their use as oxidation catalysts for organics examined [185].


Te
OC
OC
CO
CO
Fe
Fe
Te
Te
OC
Te
Te
Me
CO
Te
Te
W
W
Fe
OC
OC
CO
CO
CO
OC
Te
Te

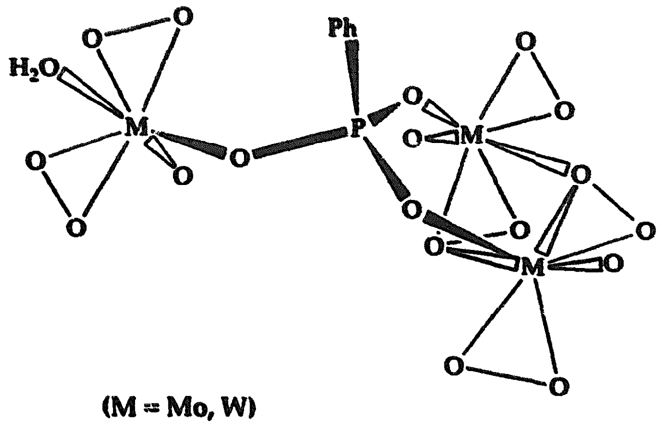
(81)


(CO)3
Ru
O=C
H
Ru(CO)2
CpW
Ru(CO)3
O=C
C
O
Ru
(CO)3

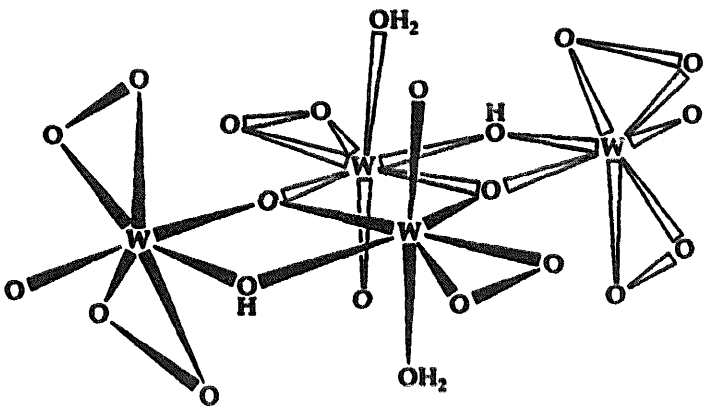
(82)


O2
O
W
O
O2W
W
O
O
W
O
O
W
O2
O2
W
O
W
WO2O
O
W
O2

(83)



(84)



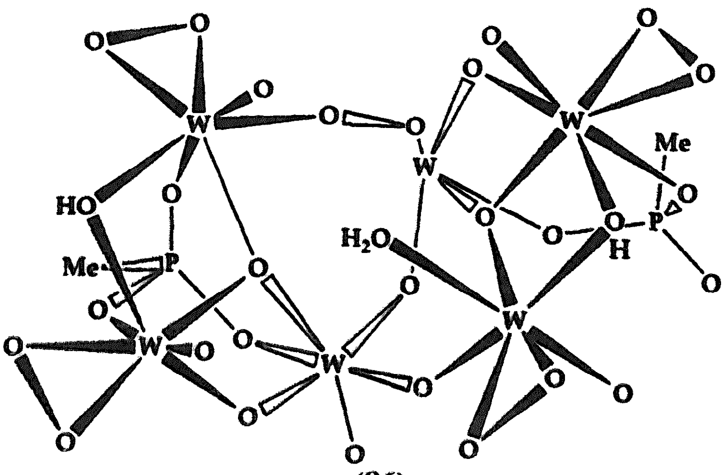
(85)

A novel hexanuclear peroxo cluster $[NMe_4]_3[(MePO)\{MePO_2(OH)\}W_6O_{13}(O_2)_4(OH)_2(H_2O)] \cdot 4H_2O$ containing anion (**86**) has been characterized [186]. Two distinct tungsten centres were found, four distorted pentagonal-bipyramidal sites bearing the peroxo groups and two octahedral sites. This has been shown to be an effective catalyst for the oxidation of alcohols with hydrogen peroxide. The structure of $[NBu_4]_4[Ag_2I_4][W_6O_{19}]$ has been determined [187]. It contains the hexatungstate cage anion (**87**) and planar Ag_2I_4 units.

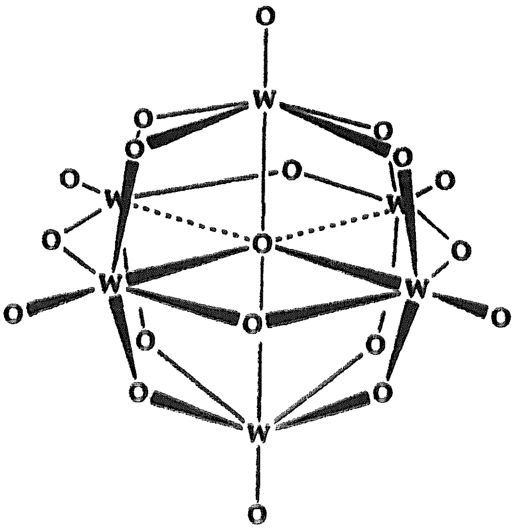
A detailed investigation into the realm of tungsten–iodide cluster chemistry through the reaction of $W(CO)_6$ with elemental iodine revealed details of the nucleation process leading to the formation of the $[W_6I_{14}]^{2-}$ cluster [188]. Temperature-dependent isolation of intermediate binary tungsten iodides suggested a reaction sequence of $[W_3I_9]^- \rightarrow [W_4I_{11}]^- \rightarrow [W_5I_{13}]^- \rightarrow [W_6I_{14}]^{2-}$. Octahedral tungsten bromide clusters MW_6Br_{14} and $M_2W_6Br_{14}$ have also been prepared and characterized [189].

The reaction of $LiBH_4$ with $W(CpR)Cl_4$ gave *closo*-$[(CpR)WH_2]_2B_3H_7$ for R = Me, and for R = ^{i}Pr, both *closo*-$[(CpR)WH_2]_2B_3H_7$ and *nido*-$[(CpR)WH_3]B_4H_8$ [190]. The corresponding reaction with $W(PMe_3)_3Cl_4$ gave a mixture of *nido*-$[W(PMe_3)_2H_4]B_4H_8$ as well as *arachno*-$[W(PMe_3)_3H_3]B_3H_8$.

Tetrahedral cluster $[CpW(CO)_2]_3P$ and its derivative $[CpW(CO)_2]_3P \cdot W(CO)_5$ (**88**)

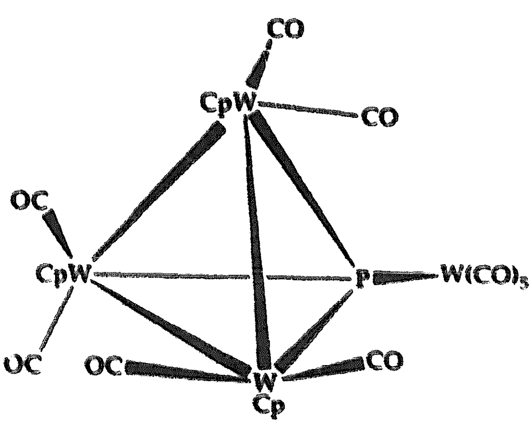


(86)



(87)

have been prepared and characterized from the reaction of $NaCpW(CO)_3$ with PCl_3 [191].



(88)

References

[1] P.C. Junk, J.L. Atwood, J. Chem. Soc., Chem. Commun., (1995) 1551.
[2] A. J. Nielson, P.D.W. Boyd, G.R. Clark, P.A. Hunt, M.B. Hursthouse, J.B. Metson, C.E.F. Rickard, P.A. Schwerdtfeger, J. Chem. Soc., Dalton Trans., (1995) 1153.
[3] N.I. Giricheva, G.V. Girichev, V.M. Petrov, V.N. Petrova, V.A. Totiv, T.P. Chusova, J. Struct. Chem. 36 (1995) 606.
[3a] L. Arnaudet, R. Bougon, B. Buu, M. Lance, M. Nierlich, P. Thuery, J. Vigner, J. Fluorine Chem. 71 (1995) 123.
[4] P.S. Wagenknecht, J.R. Norton, J. Am. Chem. Soc. 117 (1995) 1841.
[5] D.L. Morrison, P.M. Rodgers, Y.-W. Chao, M.A. Bruck, C. Grittini, T.L. Tajima, S.J. Alexander, A.L. Rheingold, D.E. Wigley, Organometallics 14 (1995) 2435.
[6] W.M. Vaughan, K.A. Abboud, J.M. Boncella, J. Am. Chem. Soc. 117 (1995) 11015.
[7] M. Scheer, K. Schuster, T.A. Budzichowski, M.H. Chisholm, W.E. Streib, J. Chem. Soc., Chem. Commun., (1995) 1671.
[8] N.C. Zanetti, R.R. Schrock, W.M. Davis, Angew. Chem. Int. Ed. Engl. 34 (1995) 2044.
[9] W.P. Griffith, H.I.S. Nogueira, B.C. Parkin, R.N. Sheppard, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans., (1995) 1775.
[10] A. Lehtonen, R. Sillanpaa, J. Chem. Soc., Dalton Trans., (1995) 2701.
[11] J.J. Cruywagen, E. A. Rohwer, J. Chem. Soc., Dalton Trans., (1995) 3433.
[12] M.R. Maurya, D.C. Antony, S. Gopinathan, V.G. Puranik, S.S. Tavale, C. Gopinathan, Bull. Chem. Soc. Jpn. 68 (1995) 2847.
[12a] M.R. Maurya, J. Chem. Res.-S (1995) 248.
[13] W.J. Evans, M.A. Ansari, J.W. Ziller, S.I. Khan, Organometallics 14 (1995) 3.
[14] P.M. Boorman, M.P. Wang, M. Parvez, J. Chem. Soc., Chem. Commun., (1995) 999.
[14a] M.K. Chan, S. Mukund, A. Kletzin, M.W.W. Adams, D.C. Reese, Science 267 (1995) 1463.
[14b] H. Oku, N. Ueyama, A. Nakamura, Inorg. Chem. 34 (1995) 3667.
[15] C.R. Landis, T. Cleveland, T.K. Firman, J. Am. Chem. Soc. 117 (1995) 1859.
[16] P. Legzdins, E.C. Phillips, J. Trotter, V.C. Yee, Acta Crystallogr., Sect. C 51 (1995) 2498.
[17] F. Lefebvre, M. Leconte, S. Pagano, A. Mutch, J.-M. Basset, Polyhedron 14 (1995) 3209.
[18] N.W. Eilerts, J.A. Heppert, Polyhedron 14 (1995) 3255.
[19] M.A. Lockwood, P.E. Fanwick, I.P. Rothwell, Polyhedron 14 (1995) 3363.
[20] U. Pirulli, D.N. Williams, C. Floriani, G. Gervasio, D. Viterbo, J. Chem. Soc. Dalton Trans., (1995) 3329.
[20a] P.L. Hill, G.P.A. Yap, A.L. Rheingold, E.A.Maatta, J. Chem. Soc., Chem. Commun., (1995) 737.
[21] G.R. Clark, M.W. Glenny, A.J. Nielson, C.E.F. Rickard, J. Chem. Soc., Dalton Trans., (1995) 1147.
[22] G.R. Clark, A. J. Nielson, C.E.F. Rickard, J. Chem. Soc., Dalton Trans., (1995) 1907.
[23] R.L. Thompson, M.D. Hopkins, N.J. Cooper, S. Lee, Organometallics 14 (1995) 1969.
[23a] P. Jernakoff, J.R. Fox, J.C. Hayes, S. Lee, B.M. Foxman, N.J. Cooper, Organometallics 14 (1995) 4493.
[24] J.Q. Lee, M.L. Sampson, J.F. Richardson, M.E. Noble, Inorg. Chem. 34 (1995) 5055.
[25] M.L.H. Green, P.C. McGowan, P. Mountford, J. Chem. Soc., Dalton Trans., (1995) 1207.
[26] K. Oku, N. Ueyama, A. Nakamura, Chem. Lett., (1995) 621.
[27] J. Beck, J. Wetterau, Inorg. Chem. 34 (1995) 2.
[28] J. Beck, Chem. Ber. 128 (1995) 23.
[29] T. Szymanskabuzar, T. Glowiak, J. Organometal. Chem. 490 (1995) 203.
[30] L. Labella, A. Chemega, M.L.H. Green, J. Chem. Soc., Dalton Trans. (1995) 395.
[31] S.G. Feng, P.S. White, J.L. Templeton, Organometallics 14 (1995) 5184.
[32] H. Seino, Y. Ishii, T. Sasagawa, M. Hidai, J. Am. Chem. Soc. 117 (1995) 12181.
[33] T.E. Burrow, D.L. Hughes, A.J. Lough, M.J. Maguire, R.H. Morris, R.L. Richards, J. Chem. Soc., Dalton Trans., (1995) 2583.
[34] T.E. Burrow, A.J. Lough, R.H. Morris, R.L. Richards, Can. J. Chem. 73 (1995) 1092.
[35] J.L. Davidson, W.E. Lindsell, K.J. McCullough, C.H. McIntosh, Organometallics 14 (1995) 3497.

[36a] V.J. Murphy, D. Rabinovich, S. Halkyard, G. Parkin, J. Chem. Soc., Chem. Commun., (1995) 1099.
[36] D. Rabinovich, G. Parkin, Inorg. Chem. 34 (1995) 6341.
[37] E.S. Shubina, A.N. Krylov, N.V. Belkova, L.M. Epstein, A.P. Borisov, V.D. Mahaev, J. Organomet. Chem. 493 (1995) 275.
[38] H. Rothfuss, D.G. Gusev, K.G. Caulton, Inorg. Chem. 34 (1995) 2894.
[39] E. Peris, J. Wessel, B.P. Patel, R.H. Crabtree, J. Chem. Soc., Chem. Commun., (1995) 2175.
[39a] S.A. Fairhurst, R.A. Henderson, D.L. Hughes, S.K. Ibrahim, C.J. Pickett, J. Chem. Soc., Chem. Commun., (1995) 1569.
[39b] R.A. Henderson, S.K. Ibrahim, K.E. Oglieve, C.J. Pickett, J. Chem. Soc., Chem. Commun., (1995) 1571.
[40] A.J. Nielson, P.D.W. Boyd, G.R. Clark, P.A. Hunt, J.B. Metson, C.E.F. Rickard, P. Schwerdtfeger, Polyhedron 14 (1995) 1255.
[41] P. Dierkes, G. Frenzen, S. Wocadlo, W. Massa, S. Berger, J. Pebler, K. Dehnicke, Z. Naturforch., Teil B 50 (1995) 159.
[42] M.L.H. Green, Pure Appl. Chem. 67 (1995) 249.
[43] C. Barre, P. Boudot, M.M. Kubicki, C. Moise, Inorg. Chem. 34 (1995) 284.
[44] A.R. Dias, M.T. Duarte, A.M. Galvao, M.H. Garcia, M.M. Marques, M.S. Salema, D. Masi, C. Mealli, Polyhedron 14 (1995) 675.
[45] V. Skagestad, C. Romming, M. Tilset, Inorg. Chem. 34 (1995) 3194.
[46] R. Bohra, P.B. Hitchcock, M.F. Lappert, S.C.F. Au-Yeung, W.-P. Leung, J. Chem. Soc., Dalton Trans., (1995) 2999.
[47] A.J. Carmichael, A. McCamley, J. Chem. Soc., Dalton Trans., (1995) 3125.
[48] R.R. Schrock, K.Y. Shih, D.A. Dobbs, W.M. Davis, J. Am. Chem. Soc. 117 (1995) 6609.
[49] J.P. Smit, W. Purcell, A. Roodt, J.G. Leipoldt, J. Chem. Soc., Dalton Trans., (1995) 1201.
[50] J. Szklarzewicz, A. Samotus, Transition Met. Chem. (London) 20 (1995) 174.
[51] R.J. Blau, M.H. Chisholm, B.W. Eichhorn, J.C. Huffman, K.S. Kramer, E.B. Lobkovsky, W.E. Streib, Organometallics 14 (1995) 1855.
[52] T.A. Budzichowski, M.H. Chisholm, D.B. Tiedtke, J.C. Huffman, W.E. Streib, Organometallics 14 (1995) 2318.
[53] T.A. Budzichowski, M.H. Chisholm, K. Folting, J.C. Huffman, W.E. Streib, J. Am. Chem. Soc. 117 (1995) 7428.
[54] M.H. Chisholm, K.S. Kramer, W.E. Streib, Angew. Chem. Int. Ed. Engl. 34 (1995) 891.
[55] T.-L.C. Hsu, S.A. Helvoigt, C.M. Partigianoni, C. Turro, D.G. Norcera, Inorg. Chem. 34 (1995) 6186.
[56] U. Piarulli, D.N. Williams, C. Floriani, G. Gervasio, D. Viterbo, J. Organomet. Chem. 503 (1995) 185.
[57] M.H. Chisholm, K. Folting, D.B. Tiedtke, F. Lemoigno, O. Eisenstein, Angew. Chem., Int. Ed. Engl. 34 (1995) 110.
[58] T.A. Budzichowski, M.H. Chisholm, K. Folting, M.G. Fromhold, W.E. Streib, Inorg. Chim. Acta 235 (1995) 339.
[59] T.R. Ryan, R.E. McCarley, Croatia Chem. Acta 68 (1995) 769.
[60] Q. Cui, D.G. Musaev, M. Svensson, S. Sieber, K. Morokuma, J. Am. Chem. Soc. 117 (1995) 12366.
[61] J. Bohmer, K. Wieghardt, B. Nuber, Angew. Chem., Int. Ed. Engl. 34 (1995) 1435.
[62] S.V. Evans, P. Legzdins, S.J. Rettig, L. Sanchez, J. Trotter, Acta Crystallogr., Sect. C 51 (1995) 584.
[63] J.D. Debad, P. Legzdins, S.A. Lumb, R.J. Batchelor, F.W.B. Einstein, Organometallics 14 (1995) 2543.
[64] N.H. Dryden, P. Legzdins, S.F. Sayers, J. Trotter, V.C. Yee, Can. J. Chem. 73 (1995) 1035.
[65] P. Legzdins, S.J. Rettig, K.J. Ross, R.J. Batchelor, F.W.B. Einstein, Organometallics 14 (1995) 5579.
[66] J. Pietsch, L. Dahlenburg, A. Wolski, H. Berke, I.L. Eremenko, J. Organomet. Chem. 495 (1995) 113.
[67] F.R. Kreissl, J. Ostermeier, C. Ogric, Chem. Ber. 128 (1995) 289.
[68] W. Malisch, H. Pfister, Organometallics 14 (1995) 4443.
[69] S.J. Coles, P.G. Edwards, J.S. Fleming, M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1995) 4091.

[70] W. Malisch, U.-A. Hirth, K. Grun, M. Schmeusser, O. Fey, U. Weis, Angew. Chem., Int. Ed. Engl. 34 (1995) 2500.
[71] B.K. Schmiedeskamp, J.G. Reising, W. Malisch, K. Hindahl, R. Schemm, W.S. Sheldrick, Organometallics 14 (1995) 4446.
[72] L.C. Song, L.Y. Zhang, Q.M. Hu, X.Y. Huang, Inorg. Chim. Acta 230 (1995) 127.
[73] H. Sakaba, K. Ishida, H. Horino, Chem. Lett., (1995) 1145
[74] I.V. Virrels, M.W. George, F.P.A. Johnson, J.J. Turner, J.R. Westwell, Organometallics 14 (1995) 5203.
[75] C.G. de Azevedo, R. Boese, D.A. Newman, K.P.C. Vollhardt, Organometallics 14 (1995) 4980.
[75a] J.A. Kim, T.M. Chung, Y.K. Chung, J.H. Jung, S.W. Lee, J. Organomet. Chem. 486 (1995) 211.
[76] W. Malisch, S. Schmitzer, R. Lankat, M. Neumayer, F. Prechtl, W. Adam, Chem. Ber. 128 (1995) 1251.
[77] W. Malisch, R. Lankat, S. Schmitzer, R. Pikl, U. Posset, W. Kiefer, Organometallics 14 (1995) 5622.
[78] W. Malisch, R. Lankat, S. Schmitzer, J. Reising, Inorg. Chem. 34 (1995) 5701.
[79] W. Malisch, R. Lankat, O. Fey, J. Reising, S. Schmitzer, J. Chem. Soc., Chem. Commun., (1995) 1917.
[80] J.L. Eglin, E.M. Hines, E.J. Valente, J.D. Zubkowski, J. Inorg. Chim. Acta 229 (1995) 113.
[81] M. Ferrer, O. Rossell, M. Seco, M.A. Pellinghelli, A. Tiripicchio, Organometallics 14 (1995) 57.
[82] A.F. Bartlone, M.J. Checuti, R. Navarro, M.Y. Shang, Inorg. Chem. 34 (1995) 980.
[83] S.G. Shyu, W.J. Wu, Y.S. Wen, S.M. Peng, G.H. Lee, J. Organomet. Chem. 489 (1995) 113.
[84] S.-G. Shyu, S.-M. Hsiao, K.-J. Lin, H.-M. Gau, Organometallics 14 (1995) 4300.
[85] L. Spadoni, C.L. Sterzo, R. Crescenzi, G. Frachey, Organometallics 14 (1995) 3149.
[86] M.J. Mays, P.F. Reinisch, G.A. Solan, M. MacPartlin, H.R. Powell, J. Chem. Soc., Dalton Trans., (1995) 1597.
[87] G.A. Acum, M.J. Mays, P.R. Raithby, G.A. Solan, J. Chem Soc., Dalton Trans., (1995) 3049.
[88] M.L.H. Green, P.C. McGowan, P. Mountford, J. Chem. Soc., Dalton Trans., (1995) 1207.
[89] M. Horner, J.M. Galvan, J. Beck, Z. Anorg. Allg. Chem. 621 (1995) 1755.
[90] T. Nakajima, T. Mise, I. Shimizu, Y. Wakatsuki, Organometallics 14 (1995) 5598.
[91] S. Sharma, J. Cervantes, J.L. Mata-Mata, M.-C. Brun, F. Cervantes-Lee, K.H. Pannell, Organometallics 14 (1995) 4269.
[92] D.H. Gibson, J.O. Franco, J.M. Mehta, M.S. Mashuta, J.F. Richardson, Organometallics 14 (1995) 5068.
[93] V.V. Grushin, V.F. Kuznetsov, C. Bensimon, H. Alper, Organometallics 14 (1995) 3927.
[94] T.E. Burrow, D.L. Hughes, A.J. Lough, M.J. Maguire, R.H. Morris, R.L. Richards, J. Chem. Soc., Dalton Trans., (1995) 1315.
[95] P.K. Baker, M.E. Harman, M.B. Hursthouse, A.I. Karaulov, A.J. Lavery, K.M.A. Malik, D.J. Muldoon, A. Shawcross, J. Organomet. Chem. 494 (1995) 205.
[96] P.K. Baker, A.E. Jenkins, A.J. Lavery, D.J. Muldoon, A. Shawcross, J. Chem. Soc., Dalton Trans., (1995) 1525.
[97] T. Szymanskabuzar, T. Glowiak, J. Organomet. Chem. 489 (1995) 207.
[98] T. Szymanskabuzar, J. Organomet. Chem. 492 (1995) 241.
[99] P.K. Baker, M.E. Harman, S. Hughes, M.B. Hursthouse, K.M.A. Malik, J. Organomet. Chem. 498 (1995) 257.
[100] I. Leban, J.V. Brencic, B. Ceh, Acta Crystallogr., Sect. C 51 (1995) 817.
[101] J.L. Kiplinger, A.M. Arif, T.G. Richmond, Inorg. Chem. 34 (1995) 399.
[102] M.A. Lockwood, P.E. Fanwick, I.P. Rothwell, Polyhedron 14 (1995) 3363.
[103a] F. Marken, A.M. Bond, R. Colton, Inorg. Chem. 34 (1995) 1705.
[103] S. Willemsen, Angew. Chem. Int. Ed. Engl. 34 (1995) 914.
[104] S. Ozkar, C.G. Kreiter, M. Kotzian, J. Organomet. Chem. 494 (1995) 115.
[105] H. Takeda, M. Jyoo, Y. Ishikawa, S. Arai, J. Phys. Chem. 99 (1995) 4558.
[106] W.E. Lindsell, K.J. McCullough, S. Plancq, J. Organomet. Chem. 491 (1995) 275.
[107] F.E. Hahn, M. Tamm, Organometallics 14 (1995) 2597.
[108] M. Galakhov, A. Martin, M. Mena, F. Palacios, C. Yelamos, P.R. Raithby, Organometallics 14 (1995) 131.

[109] U. Pidun, G. Frenking, Organometallics 14 (1995) 5325.
[110] T. Schmidt, S. Neis, R. Goddard, Z. Naturforsch., Teil B 50 (1995) 315.
[111] M. Weidenbruch, A. Stilter, J. Schlaefke, K. Peters, H.G. von Schnering, J. Organomet. Chem. Soc. 501 (1995) 67.
[112] J. Li, G. Schreckenbach, T. Ziegler, J. Am. Chem. Soc. 117 (1995) 486.
[113] F.P.A. Johnson, M.W. George, S.L. Morrison, J.J. Turner, J. Chem. Soc., Chem. Commun., (1995) 391.
[114] K.S. Wang, D. Wang, K. Yang, M.G. Richmond, M. Schwartz, Inorg. Chem. 34 (1995) 3241.
[115] N. Lebris, J.J. Yaouanc, J.C. Clement, H. Handel, H. Desabbayes, J. Organomet. Chem. 487 (1995) 131.
[116] A.M.A. Morsi, A.G.K. Gamal, J. Indian Chem. 72 (1995) 5.
[117] O. Laboy, E.I. Pares-Matos, J.E. Cortes-Figueroa, J. Coord. Chem. 36 (1995) 273.
[118] D.W. Bruce, J.R. Rourke, Polyhedron 14 (1995) 1915.
[119] P.N.W. Baxter, J.A. Connor, J. Organomet. Chem. 486 (1995) 115.
[120] M.W. George, F.P.A. Johnson, J.J. Turner, J.R. Westwell, J. Chem Soc., Dalton Trans., (1995) 2711.
[121] A. Sieker, A.J. Blake, S. Parsons, B.F.G. Johnson, J. Chem. Soc., Dalton Trans., (1995) 1391.
[122] M.A. Paz-Sandoval, M.E. Dominguez-Duran, C. Pazos-Mayen, A. Ariza-Castolo, M. de J. Rosales-Hoz, R. Contreras, J. Organomet. Chem. 492 (1995) 1.
[123] W.-Y. Yeh, C.-S. Ting, S.-M. Peng, G.-H. Lee, Organometallics 14 (1995) 1417.
[124] R.U. Kirss, J. Organomet. Chem. 498 (1995) 171.
[125] H. Voelker, S. Freitag, U. Pieper, H.W. Roesky, Z. Anorg. Allg. Chem. 621 (1995) 694.
[126] U.U. Ike, S.D. Perera, B.L. Shaw, M. Thornton-Pett, J. Chem. Soc., Dalton Trans., (1995) 2057.
[127] M.S. Davies, M.J. Aroney, I.E. Buys, T. W Hambley, J.L. Calvert, Inorg. Chem. 34 (1995) 330.
[128] V.S. Reddy, K.V. Katti, C.L. Barnes, Inorg. Chem. 34 (1995) 5483.
[129] J.T. Hung, K. Lammertsma, J. Organometal. Chem. 489 (1995) 1.
[130] R. Streubel, L. Ernst, J. Jeske, P.G. Jones, J. Chem. Soc., Chem. Commun., (1995) 2113.
[131] A. Ostrowski, J. Jeske, P.G. Jones, R. Streubel, J. Chem. Soc., Chem. Commun., (1995) 2507.
[132] J. Kalbitz, E. Leissring, H. Schmidt, Z. Anorg. Allg. Chem. 621 (1995) 1605.
[133] S.J. Coles, P.G. Edwards, J.S. Fleming, M.B. Hursthouse, J. Chem. Soc., Dalton Trans., (1995) 1139.
[134] J. Pietsch, L. Dahlenburg, A. Wolski, H. Berke, I.L. Eremenko, J. Organometal. Chem. 495 (1995) 113.
[135] E.W. Ainscough, A.M. Brodie, S.L. Ingham, J.M. Waters, Inorg. Chimica Acta 234 (1995) 163.
[136] G.C. Lloyd-Jones, A. Pfaltz, Z. Naturforsch., Teil B 50 (1995) 361.
[137] K.H. Yih, Y.C. Lin, M.C. Cheng, Y. Wang, J. Chem. Soc., Dalton Trans., (1995) 1305.
[138] M. Heberhold, C. Kohler, W. Milius, B. Wrackmeyer, Inorg. Chim. Acta 231 (1995) 249.
[139] H. Fischer, J. Schmid, J. Riede, J. Organomet. Chem. 491 (1995) 71.
[140] J.W. Benson, E.A. Keiter, R.L. Keiter, J. Organomet. Chem. 495 (1995) 77.
[141] M. Cano, P. Ovejero, J.V. Heras, J. Organomet. Chem. 486 (1995) 63.
[142] A.T. Hutton, F.P. Wewers, J. Organomet. Chem. 492 (1995) C14.
[143] C.-H. Ueng, G.-Y. Shih, Acta Crystallogr., Sect. C 51 (1995) 1524.
[144] G. Boni, P. Oudet, C. Moise, J. Organometal. Chem. 487 (1995) 105.
[145] D.-N. Horng, C.-H. Ueng, J. Organometal. Chem. 505 (1995) 53.
[146] V.S. Reddy, S.S. Krishnamurthy, M. Nethaji, J. Chem. Soc., Dalton Trans., (1995) 1933.
[147] V.S. Reddy, K.V. Katti, Z. Anorg. Allg. Chem. 621 (1995) 1939.
[148] S.C.N. Hsu, W.Y. Yeh, M.Y. Chiang, J. Organomet. Chem. 492 (1995) 121.
[149] X. Sun, E.H. Wong, M.M. Turnbull, A.L. Rheingold, B.E. Waltermire, R.L. Ostrander, Organometallics 14 (1995) 83.
[150] N.H.T. Huy, L. Ricard, F. Mathey, Organometallics 14 (1995) 4048.
[151] P. Odet, M.M. Kubicki, C. Moise, Acta Crystallogr., Sect. C 51 (1995) 811.
[152] J.A.T. Lin, A.C. Yeh, Y.C. Chou, T.Y.R. Tsai, Y.S. Wen, J. Organomet. Chem. 486 (1995) 147.
[153] S.-G. Shyu, P.-J. Lin, K.-J. Lin, M.-C. Chang, Y.-S. Wen, Organometallics 14 (1995) 2253.
[154] G. Boni, P. Sauvageot, E. Marpeaux, C. Moise, Organometallics 14 (1995) 5652.
[155] P.B. Hitchcock, C. Jones, J.F. Nixon, J. Chem. Soc., Chem. Commun., (1995) 2167.

[156] O.J. Scherer, G. Berg, G. Wolmershauser, Chem. Ber. 128 (1995) 635.
[157] G. Markl, M. Reiss, P. Kreitmeier, H. Noth, Angew. Chem. Intl. Ed. Engl. 34 (1995) 2230.
[158] K.H. Yih, S.C. Chen, Y.C. Lin, G.H. Lee, Y. Wang, J. Organomet. Chem. 494 (1995) 149.
[159] E.W. Abel, E.S. Blackwall, M.L. Creber, P.J. Heard, K.G. Orrell, J. Organomet. Chem. 490 (1995) 83.
[160] E.W. Abel, K.G. Orrell, M.C. Poole, V. Sik, M.B. Hursthouse, M.A. Mazid, Polyhedron 14 (1995) 585.
[161] H.G. Raubenheimer, M. Desmet, J. Chem. Res.-S (1995) 30.
[162] S.P. Huang, M.G. Kanatzidis, Inorg. Chim. Acta 230 (1995) 9.
[162a] J. Ruiz, V. Rodriguez, G. Lopez, P.A. Chaloner, P.B. Hitchcock, J. Organomet. Chem. 493 (1995) 77.
[163] K.-H. Yih, Y.-C. Lin, M.-C. Cheng, Y. Wang, J. Chem. Soc., Dalton Trans., (1995) 1306.
[164] H. Brunner, S. Challet, M.M. Kubicki, J.-C. Leblanc, C. Moise, F. Volpato, J. Wachter, Organometallics 14 (1995) 3623.
[165] K. Douki, G. Matsubayashi, Inorg. Chim. Acta 230 (1995) 235.
[166] H. Fischer, K. Trieier, C. Troll, Chem. Ber. 128 (1995) 1149.
[167] H. Fischer, K. Treier, C. Troll, R. Stumpf, J. Chem. Soc., Chem. Commun., (1995) 2461.
[168] H.J. Breunig, J. Pawlik, Z. Anorg. Allg. Chem. 621 (1995) 817.
[169] J.W. Freeman, A.M. Arif, R.D. Ernst, Inorg. Chim. Acta 240 (1995) 33.
[170] S. Dapprich, G. Frenking, Angew. Chem. Int. Ed. Engl. 34 (1995) 354.
[171] D.J. Darensbourg, K.K. Klausmeyer, J.H. Reibenspies, Inorg. Chem. 34 (1995) 4933.
[172] W. Bruns, W. Kaim, E. Waldhor, M. Krejcik, Inorg. Chem. 34 (1995) 663.
[173] S. Kuwata, Y. Mizobe, M. Hidai, J. Chem. Soc., Chem. Commun., (1995) 1057.
[174] I.L. Eremenko, S. Rosenberger, S.E. Nefedov, H. Berke, V.M. Novotortsev, Inorg. Chem. 34 (1995) 830.
[175] C.-K. Chan, C.-X. Guo, R.-J. Wang, T.C.W. Mak, C.-M. Che, J. Chem. Soc., Dalton Trans., (1995) 753.
[176] Q. Huang, X. Wu, T. Sheng, Q. Wang, Inorg. Chem. 34 (1995) 4931.
[177] L.-C. Song, J.-Y. Shen, Q.-M. Hu, X.-Y. Huang, Organometallics 14 (1995) 98.
[178] X. Zhang, R.E. McCarley, Inorg. Chem. 34 (1995) 2678.
[179] G.M. Erlich, C.J. Warren, D.A. Vennos, D.M. Ho, R.C. Haushalter, F.J. DiSalvo, Inorg. Chem. 34 (1995) 4454.
[180] X. Xie, R.E. McCarley, Inorg. Chem. 34 (1995) 6124.
[181] B.K. Das, M.G. Kanatzidis, Inorg. Chem. 34 (1995) 5721.
[182] C.-J. Su, Y. Chi, S.-M. Peng, G.-H. Lee, Organometallics 14 (1995) 4286.
[183] M.H. Chisholm, K.S. Kramer, W.E. Streib, J. Cluster Science 6 (1995) 135.
[184] M.C. Ghosh, S. Mandal, S.K. Chandra, E.S. Gould, Inorg. Chem. 34 (1995) 509.
[185] W.P. Griffith, B.C. Parkin, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans., (1995) 3131.
[186] W.P. Griffith, B.C. Parkin, A.J.P. White, D.J. Williams, J. Chem. Soc., Dalton Trans., (1995) 2183.
[187] H.-W. Hou, X. Ye, X. Xin, Z. Wang, S. Liu, J. Huang, Acta Crystallogr., Sect. C 51 (1995) 2013.
[188] J.D. Franolic, J.R. Long, R.H. Holm, J. Am. Chem. Soc. 117 (1995) 8139.
[189] S. Ihmaine, C. Perrin, M. Sergent, Croatica Chim. Acta 68 (1995) 877.
[190] H.J. Bullick, P.D. Grebenik, M.L.H. Green, A.K. Hughes, J.B. Leach, P.C. McGowan, J. Chem. Soc., Dalton Trans., (1995) 67.
[191] T. Kilthau, B. Nuber, M.L. Ziegler, Chem. Ber. 128 (1995) 197.