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COORDINATION CHEMISTRY REVIEWS

7. Tungsten 1994

Edward H. Wong

CONTENTS

INTRODUCTION

This review covers the tungsten coordination literature published in the 1994 calendar year. *Current Contents* was searched as were the indices of the major journals. As in previous reviews,

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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 1994, we hope to present here a representative view of the field. Our sincere apologies to any author whose work we may have omitted.

Complexes have been grouped in order of the formal oxidation state of the tungsten centre 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.

7.1 TUNGSTEN(VI)

7.1.1 Complexes with halide ligands

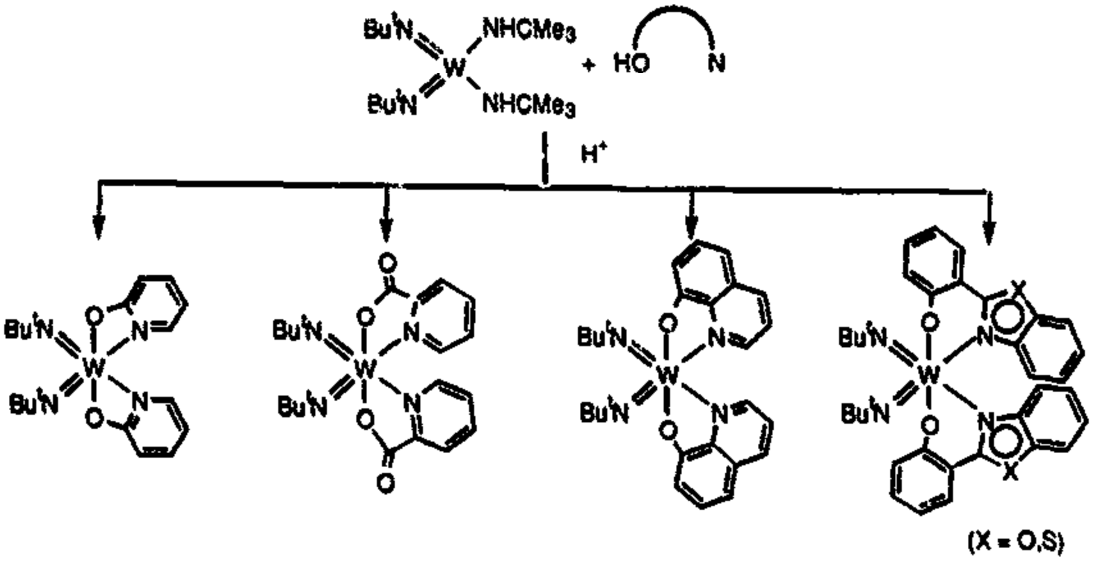
The gas-phase electron diffraction data of WCl_6 has been reinvestigated by adding three-atom scattering to the calculated intensities [1]. This increased the W-Cl distance by 0.008(2) Å and reduced the W-Cl vibrational amplitudes from 0.078(2) to 0.053(1) Å.

The oxidation of Cp_2WCl_2 with perfluorotriazinium tetrafluoroborate $[(FCN)_3F][BF_4]$ in liquid SO_2 in the presence of a fluoride acceptor yielded cationic $[Cp_2WCl_2][BF_4]_2$ [2].

The synthesis of $[WO_2F_4]^{2-}$ as the pyridinium salt has been reported to take place at room temperature by the reaction of tungstic acid with pyridinium poly(hydrogen fluoride) [3].

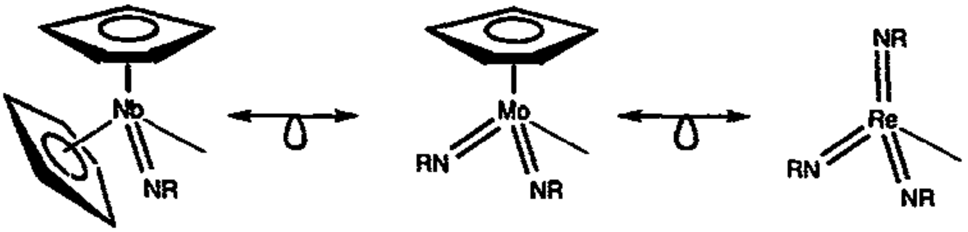
7.1.2 Complexes with nitrogen ligands

New d^0 tungsten imido complexes of the type $[W(NCMe_3)_2(O\text{-}N)_2]$ with bifunctional O-N chelating ligands have been prepared from $[W(NCMe_3)_2(NHCMe_3)_2]$ by protonation and substitution as shown in Scheme 1 [4].



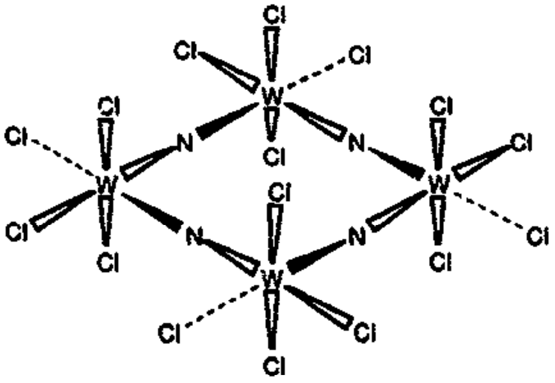
Scheme 1

The isolobal relationship of the metal-cyclopentadienyl fragments ($\eta 5$-C_5R_5M) to the imido complexes of the next higher group has been discussed (Scheme 2) [5]. Both Cp- and RN- are anionic ligands capable of donating up to 6 electrons in a σ/π manner.



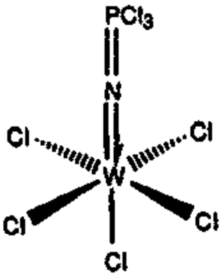
Scheme 2

A convenient synthesis of $WNCl_3$ from WCl_6 and Me_3SiN_3 in refluxing 1,2-dichloroethane was described [6]. The molecular structure of solvent-free $WNCl_3$ (**1**) featured planar $[WNCl_3]_4$ rings interconnected by bridging chlorine atoms.



(**1**)

The reaction of WCl_6 with phosphoranimines $Cl_2RP{=}NSiMe_3$ (R = Cl, Ph) afforded $WCl_5(N{=}PCl_3)$ (**2**) and $WCl_4(N{=}PCl_2Ph)_2$ (**3**) [7]. A weakly-coordinated $[GaCl_4]^-$ complex of $WCl_4\{N{=}PCl_3)^+$, compound (**4**), resulted from chloride abstraction from (**2**) using $GaCl_3$.



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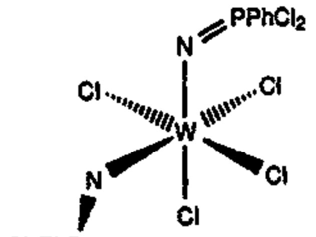

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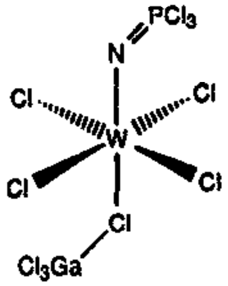
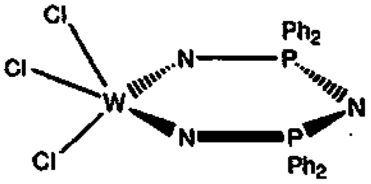


(**4**)

The metallacycle $[NPPh_2NPPh_2NWCl_3]$ (5) has been studied in methylene chloride using cyclic voltammetry [8]. Observed redox potentials indicated the cyclic π-ligand to be capable of stabilizing high-oxidation states in both W and Mo.



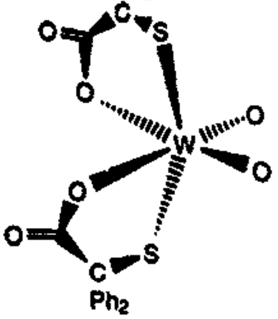
(5)

Tungsten-183 NMR spectra of a series of octahedral W(VI) imidophenyl and imidoethyl complexes were obtained using inverse detection based on nonspecific long-range interactions [9]. Both the metal coordination number and ligand type affected the chemical shift. Aqueous solutions of ditungstate complexes of the carbohydrates alditols have been studied by ^{183}W and ^{13}C NMR spectroscopic techniques [10]. Erythro and threo binding configurations could be distinguished in these mixtures.

7.1.3 Complexes with oxygen, sulfur, and selenium ligands

A review on the peroxo and superoxo complexes of Group 6 metals including tungsten was published [11].

The complex $[NH_4]_2[WO_2\{O_2CC(S)Ph_2\}_2]$ (6) has been shown to be the first example of a non-thiolene tungsten compound that can oxidize benzoin to benzil in methanol [12]. The reduced species was proposed to be a monomeric $W^{IV}O$ complex that can be reoxidized by nitrate to regenerate the starting $W^{VI}O_2$ catalyst.



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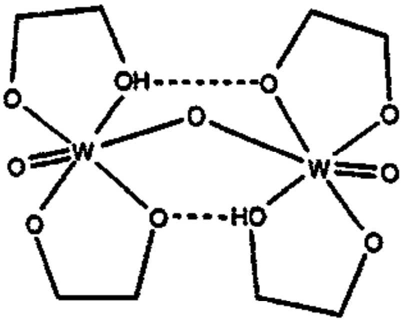


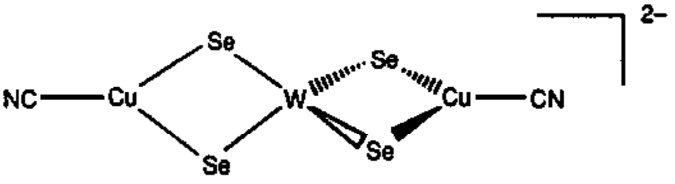
(7)

Ditungsten complexes $W_2O_3L_2(HL)_2$ (where H_2L = 2,3-dimethylbutane-2,3-diol, *trans*-cycloheptane-1,2-diol, or *trans*-cyclooctane-1,2-diol) were prepared in high yields by hydrolysis reactions [13]. The molecular structures of these revealed that each W centre was bonded to one diolate, one hydrogendiolate, one terminal, and one bridging oxide ligand. In addition, the two W moieties were also linked together by intramolecular O···H-O hydrogen bonding as shown in structure (7).

The diperoxo tungsten complex $[WO(O_2)(oxalato)]^{2-}$ is reported to react with bromide at a faster rate than its molybdenum counterpart though detailed kinetic studies were thwarted due to a tungsten-containing impurity [14].

Reductive desulfurization reactions of $[WS(S_2)(S_2CNR_2)_4](BF_4)_2$ [R = Et, Bu^i] with Me_3SiI in dichloromethane produced $[W_2(\mu\text{-}S_2)_2(S_2CNR_2)_4]I(I_3)$ [15]. An X-ray structural analysis revealed W(V) centres bridged by two $[S_2]^{2-}$ ligands as well as a metal-metal bond of 2.792(3) Å. Cyclo-octasulfur adducts of WCl_6 and $WCl_4(S)thf$ have been prepared and the molecular structure of $WCl_4(S)(thf)\cdot S_8$ has been determined [16]. A Cl-S contact of 3.491(3)Å was found indicating a weak interaction between the W-Cl and the S_8 rings.

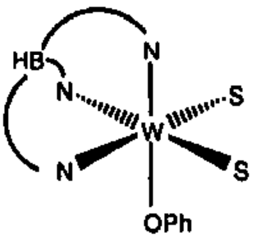
Two equivalents of CuCN reacted with $[PPh_4]_2[WSe_4]$ to give $[PPh_4]_2[(NC)Cu(\mu\text{-}Se)_2W(\mu\text{-}Se)_2CuCN]$ (8) [17]. Addition of excess PMe_2Ph ligand to this complex resulted in displacement of one CuCN unit as $[PMe_2Ph]_3CuCN$ and formation of $[PPh_4]_2[(NC)Cu(\mu\text{-}Se)_2WSe_2]$.



(8)

Neutral W(VI) complexes [W(1,2-ethanediolato)(2,3-dimethyl-2,3-butanediolato)$_2$] and [W(2,3-dimethyl-2,3-butanediolato)$_3$] were prepared from [W(1,2-ethanediolato)$_3$] by a diol exchange [18]. Structural characterization of both revealed an octahedral tungsten coordinated by six O atoms of the three diolato ligands.

Pterin-containing tungsten enzymes from thermophiles have been modelled by trispyrazolylborate tungsten complexes featuring S-donor ligands [19]. Thus LWS_2Cl (where L = hydrotris(3,5-dimethylpyrazol-1-yl)borate) reacted with HX (X = OPh [illegible], SePh) to give intensely-colored, air-stable complexes of the type LWS_2X (9). Solutions of these reacted with alkynes to form tungsten(IV)(ene-1,2-dithiolato) complexes (10) with short W-S distances which are almost identical to those observed from an EXAFS study for *Clostridium thermoaceticum*.



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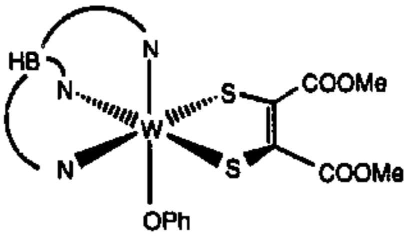
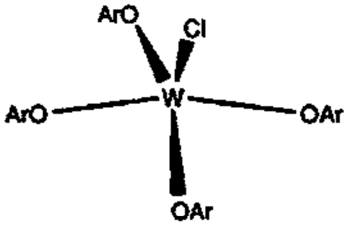


(10)

Reactions of WCl_6 with one or two equivalents of Me_3SiO-2,6-$Me_2C_6H_3$ yielded $WCl_5[O$-2,6-$Me_2C_6H_3]$ and both *cis*- and *trans* isomers of $WCl_4[O$-2,6-$Me_2C_6H_3]_2$ respectively [20]. A unique square pyramidal geometry was found for the related $WCl[O$-2,6-$Me_2C_6H_3]_4$ complex (**11**).

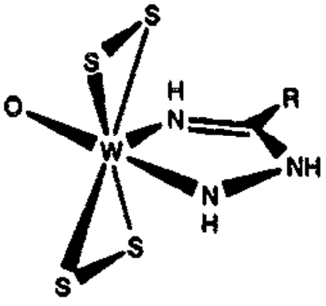


(**11**)

7.1.4 Complexes with mixed donor ligands

Quantum mechanical calculations at the Hartree-Fock and MP-2 levels using relativistic effective core potentials were reported for neutral and negatively charged oxo and nitrido complexes MEX_n (where M = Mo, W, Re, Os; E = O,N; X = F, Cl; and n = 3-5) [21]. It was found that calculated geometries and vibrational frequencies were in good agreement with experimental data. Analysis of electronic structure indicated strongly covalent M-O and M-N bonds while M-halide bonds were found to be mainly ionic.

A new reaction system of $WS_4^{2-}/P_2S_5/H_2NNH_2.2HCl$ in acetonitrile or ethyl nitrile at ambient temperature yielded the respective oxo-persulphido amidrazone tungstate complexes (**12**) [22]. A pentagonal bipyramidal coordination sphere around the tungsten was found with axial oxo and NH groups.

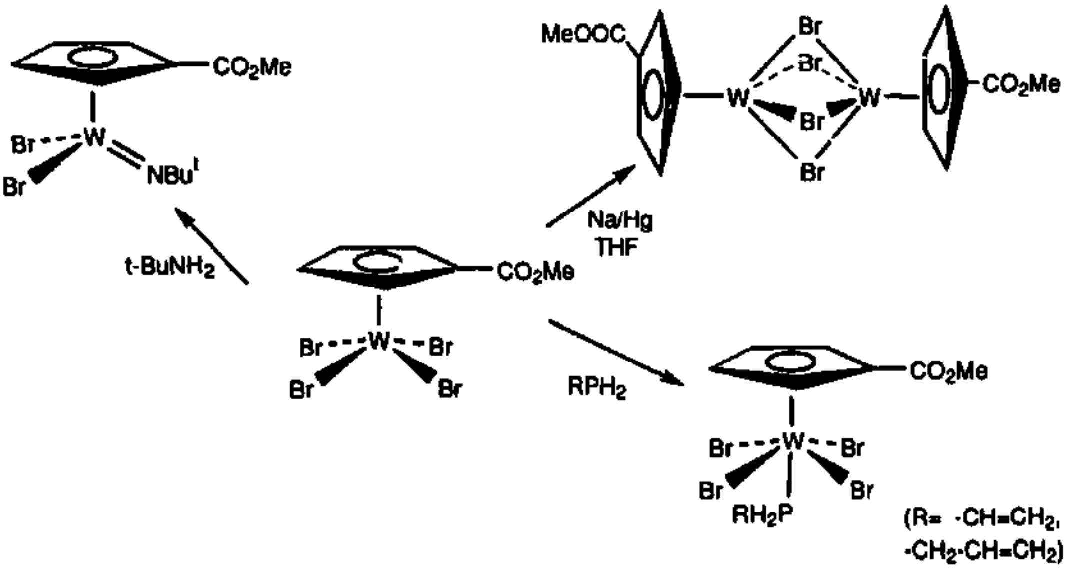


(**12**)

7.2 TUNGSTEN(V)

In a refutation of one of the most-cited examples of 'distortional isomerismd, it was found that the 'green' isomer of $[LWOCl_2]PF_6$ (where L = 1,4,7-trimethyl-1,4,7-triazacyclononane) was a ternary mixture of blue $[LWOCl_2]PF_6$, a tungsten(IV)-oxo species, and a tungsten(VI)-dioxo species [23]. The new paramagnetic complexes $[W(\eta\text{-}C_5H_4R)Cl_2(NBu^t)]$ (where R = H or Me) and their molybdenum analogues have been prepared from the respective $(C_5H_4R)MCl_4$ precursors [24] and primary amines.

Methylcarboxy-CpW(CO)$_3$Me was brominated with phosphorus pentabromide to give the tetrabromo derivative which served as a useful precursor to several new tungsten(V) and tungsten(III) complexes (Scheme 3) [25].



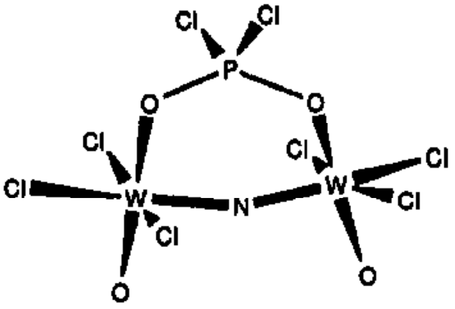
Scheme 3

Novel tungsten complexes [$W_2O_3Cl_4$(tmen)] and [$W_2O_3Cl_4$(*N,N'*-di-tert-butyl-1,4-diazabuta-1,3-diene)] were prepared from [$W_2O_3Cl_4(dme)_2$] [26]. From vibrational spectral data all were found to contain linear bridging oxo groups. Trends in M-O and M-Cl stretches were compared with Nb and Mo analogues.

7.3 TUNGSTEN(IV)

7.3.1 Complexes with halide ligands

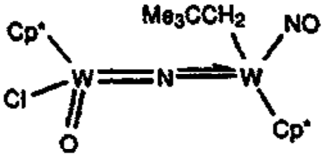
The structures of [$NMe_3Ph]_2[WCl_6$] and [$PPh_4]_2[W_2Cl_6O_2(\mu$-N)(μ-O_2PCl_2)] have been determined [27]. The former consisted of alternating layers of octahedral anions and cations parallel to the (100) plane. The structure of the anionic nitrido complex (13) contained two W atoms symmetrically linked by the μ-N (W=N=W angle 166.2°) and an additional bridging dichlorophosphate group.



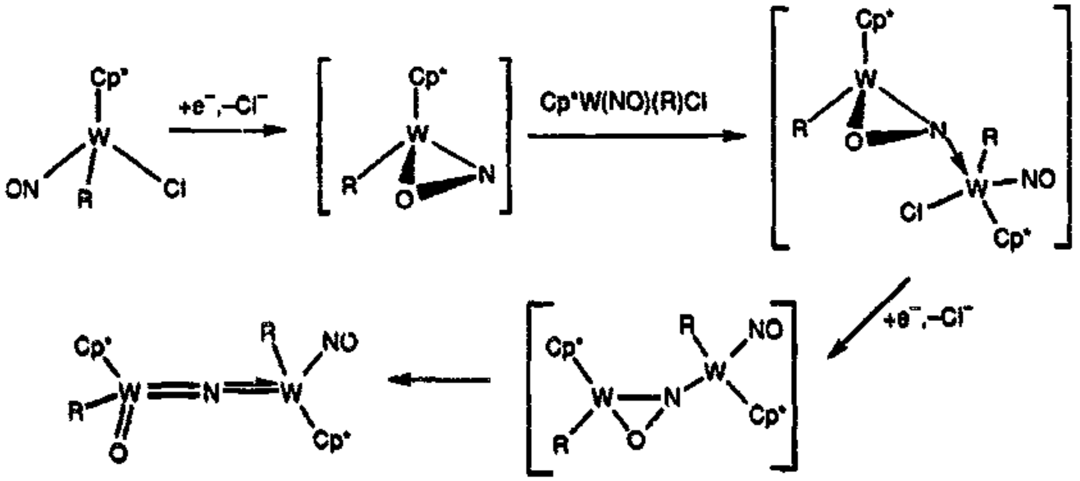
(13)

7.3.2 Complexes with nitrogen ligands

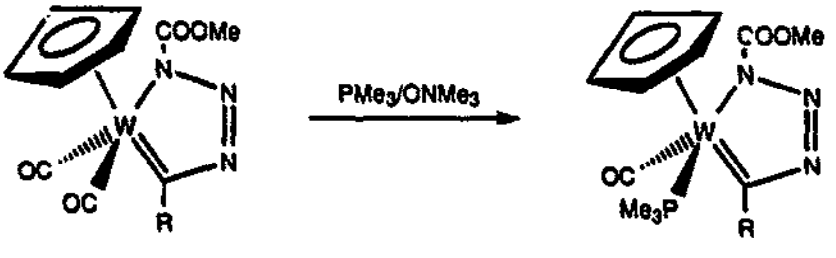
Reduction of $[Cp^*W(NO)(R)Cl]$ (where R = CH_2CMe_3, CH_2SiMe_3, Ph) with excess zinc dust in thf resulted in the formation of $[Cp^*W(NO)(R)](\mu\text{-}N)[Cp^*W(O)R]$ in good yields [28]. A related dimetallic complex $[Cp^*W(NO)(CH_2CMe_3)](\mu\text{-}N)[Cp^*W(O)Cl]$ (**14**) was prepared in low yield from treatment of a 2:1 mixture of $Cp^*W(NO)(CH_2CMe_3)Cl$ and $Cp^*W(NO)Cl_2$ with excess zinc dust. Consistent with multiple bonding, complex (**14**) was found to feature orthogonal orientations of the tungsten-containing moieties around an essentially planar W-N-W bridge. It was proposed that these dimetallics result from transient formation of a coordinatively-unsaturated $[Cp^*W(\eta^2\text{-}NO)X]$ (where X = R or Cl) species which then combined with the second tungsten unit (Scheme 4).



(**14**)



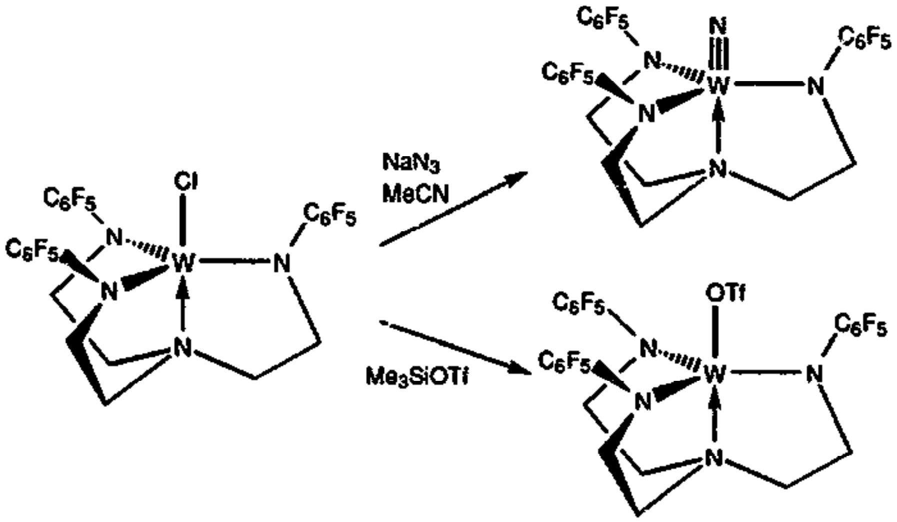
Scheme 4



Scheme 5

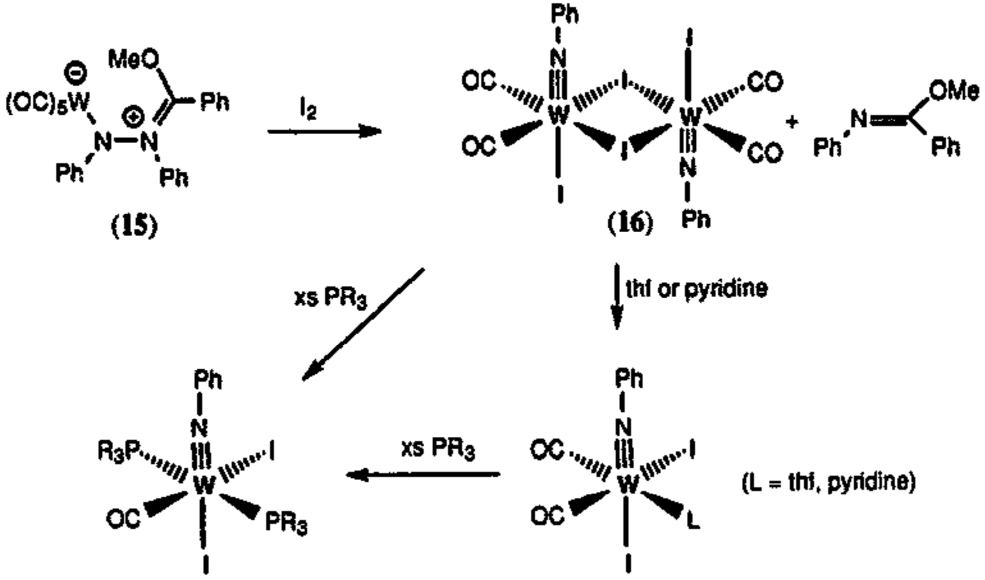
Tungsten triazametalole complexes were found to undergo high yield carbonyl substitution with PMe_3 in the presence of trimethylamine-N-oxide (Scheme 5) [29]. Stable tungsten complexes of the new ligand $(ArNHCH_2CH_2)_3N$ where (Ar = 3,5-bis-(trifluoromethyl)phenyl, 2-

(trifluoromethyl)phenyl, or pentafluorophenyl) have been prepared from $WCl_4(SEt_2)_2$ and the parent ligands in the presence of triethylamine [30]. The $[WCl\{N(C_6F_5)CH_2CH_2)_3N\}]$ product can be readily converted to the nitrido- and triflate derivatives (Scheme 6).



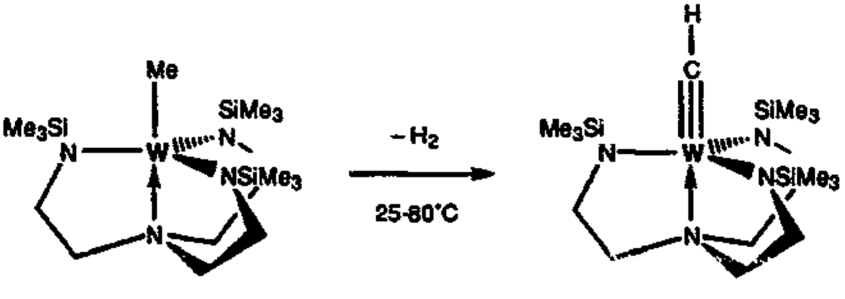
Scheme 6

Oxidation of a protected zero-valent tungsten nitrene precursor led to a W(IV) imido complex [31]. Specifically, the zwitterionic complex $[(CO)_5W\{NPhNPhC(OMe)Ph\}]$ (**15**) was reacted with 1 equivalent of iodine to give the unusual iodo-bridged dimer $[(CO)_2W(NPh)I_2]_2$ (**16**). Cleavage of the dimer with thf or pyridine led to the respective W(IV) imido complexes while excess PMe_3 or $P(OMe)_3$ led to $[W(NPh)I_2(CO)(PR_3)_2]$ in high yields (Scheme 7). It is believed that protection of the highly reactive zero-valent nitrene complex as the zwitterion allowed oxidation of the metal centre before cleavage of the N-N bond so that the imido ligand was generated and stabilized at a higher-valent site.



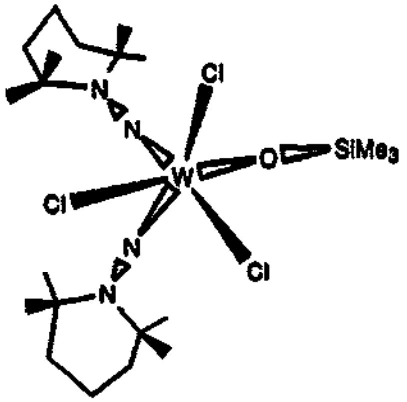
Scheme 7

It was found that attempted syntheses of triamidoamine complexes [{(R'NCH$_2$CH$_2$)$_3$N}W(alkyl)] led to alkylidyne complexes, even in the presence of β-hydrogens [32]. For example, the complex [Me$_3$SiCH$_2$CH$_2$)$_3$N]W(Me) (**17**) was converted in a first-order process to [Me$_3$SiCH$_2$CH$_2$)$_3$N]W(CH) (**18**) between 25-80°C by loss of molecular dihydrogen. It is believed that the steric protection of the trialkylsilyl groups as well as the low probability of ligand dissociation prevented intermolecular reactions.



(**17**) (**18**)

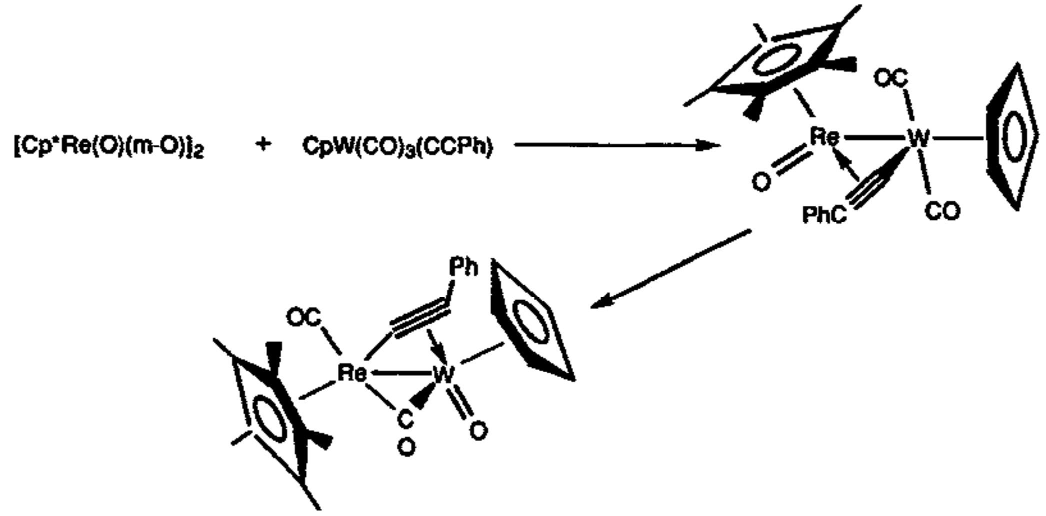
The tungsten precursor complex [WOCl$_2$(dme)] was found to react with 1-amino-2,2,6,6-tetramethylpiperidine in refluxing NEt$_3$/SiMe$_3$Cl to give [W(C$_9$H$_{18}$N$_2$)$_2$Cl$_3$(OSiMe$_3$)] (**19**) [33]. This octahedral complex has C$_s$ symmetry and has *fac*-chloro and *cis*-isodiazene ligands. The W-N distance at 1.841(5)Å was significantly longer than the typical W hydrazido bond of 1.75Å while the N-N distance of 1.248(7)Å was significantly shorter and closer to W-diazenido bond lengths.



(**19**)

7.3.3 Complexes with oxygen ligands

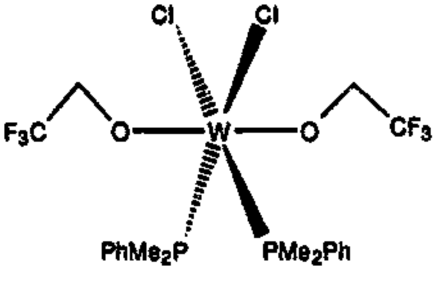
Treatment of the [Cp*Re(O)(μ-O)]$_2$ dimer with the tungsten-acetylide complex [CpW(CO)$_3$(CCPh)] in refluxing toluene yielded the oxo-acetylide heterodimetallic product [Cp*Re(O)(μ-CCPh)W(CO)$_2$Cp] [34]. Further thermolysis caused an intermetal oxo transfer from Re to W to give the isomeric product [Cp*Re(CO)$_2$(μ-CCPh)W(O)Cp] (Scheme 8).



Scheme 8

Hydridotosylate complexes $Cp_2WH(OTs)$ hasve been synthesized by the treatment of $Cp_2WH_3^+OTs^-$ with acetone [35]. This complex was characterized spectroscopically and was found to be stable to alcohols though alkoxides readily displaced the tosylate to form $Cp_2WH(OR)$ while phosphines yielded cationic $[Cp_2WH(PR_3)]^+[OTs]^-$.

The reaction of $[WCl_4(PMe_2Ph)_2]$ with two equivalents of $TlOCH_2CF_3$ yielded $[W(OCH_2CF_3)_2Cl_2(PMe_2Ph)_2]$ (**20**) which was shown to have a *trans,cis,cis*-stereochemistry by spectroscopy and X-ray diffraction [36]. The molecule was found to be surprisingly unreactive towards H_2O, PMe_2Ph, H_2, and even O_2 in spite of its formal 16-electron count. It was suggested that enhanced O-to-W π-donation resulted from the observed stereochemistry which left the two metal *d*-electrons spin-paired. Consistent with this are the long W-Cl bonds of 2.486(2) and 2.477(2) Å and short W-O distances of 1.844(5) and 1.852(5)Å.



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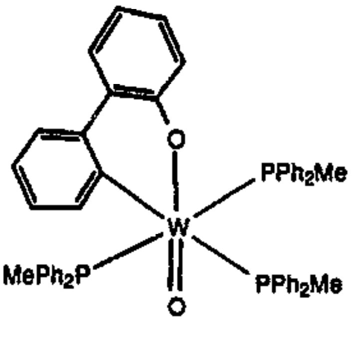
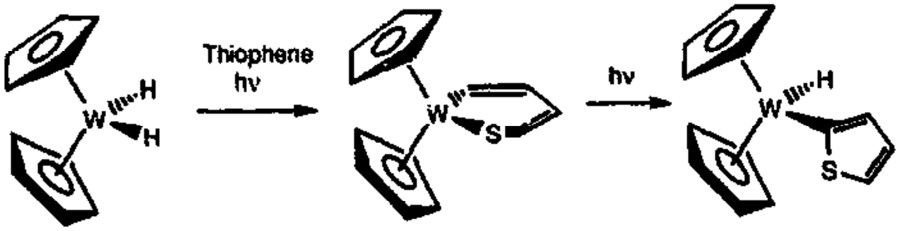


(21)

A pseudo-octahedral tungsten oxo compound $WO(OC_{18}H_{12})(PPh_2Me)_3$ containing a cyclometallated 2',6-di-phenylphenoxide ligand has been characterized by X-ray diffraction [37]. The WO_2CP_3 core (**21**) contained a terminal oxo (W-O 1.1717(3)Å) and an aryloxide (W-O 2.059(3)Å) *trans* to each other.

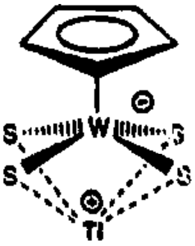
7.3.4 Complexes with sulfur and selenium ligands

Photolysis of Cp_2WH_2 in the presence of thiophene led to the initial formation of a C-S insertion product $Cp_2WSCH{=}CHCH{=}CH$ [38]. X-ray diffraction studies revealed that the W is 0.73Å out of the C_4S plane. Continued irradiation resulted in conversion into the C-H insertion product Cp_2W(2-thienyl)H (Scheme 9). Thermal reaction of $Cp_2W(Me)H$ with thiophene gave both C-S and C-H insertion products in an 11:1 kinetic ratio.



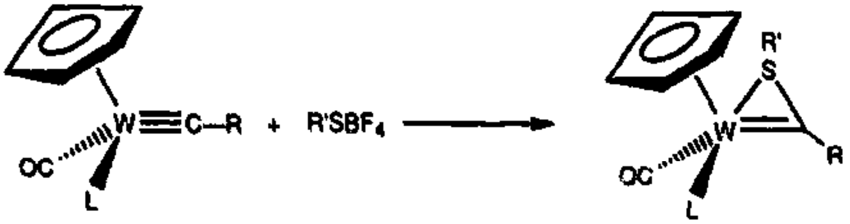
Scheme 9

The photochemical reaction of $[CpW(SC_6F_5)(CO)_3]$ with four equivalents of $TlSC_6F_5$ gave $Tl[CpW(SC_6F_5)_4]$ (**22**) only in low yields [39]. Reactions of the alkali metal salts $M[SC_6F_5]$ (M = Cs, Rb, or K) with $[CpW(SC_6F_5)_3(CO)]$ or $[CpW(CO)_2I_3]$ gave better yields of the ionic derivatives $M[CpW(SC_6F_5)_4]$. Dynamic ^{19}F and ^{133}Cs NMR spectroscopic studies revealed fluxional C_6F_5 groups and possible reversible coordination between Cs^+ and the organometallic anion.



(22)

Cationic η^2-thiocarbene complexes of tungsten were obtained from the reaction of cyclopentadienyl and hydrotrispyrazolylborato tungsten carbyne complexes with aryl and alkyl thiosulfonium tetrafluoroborate (Scheme **10**) [40].

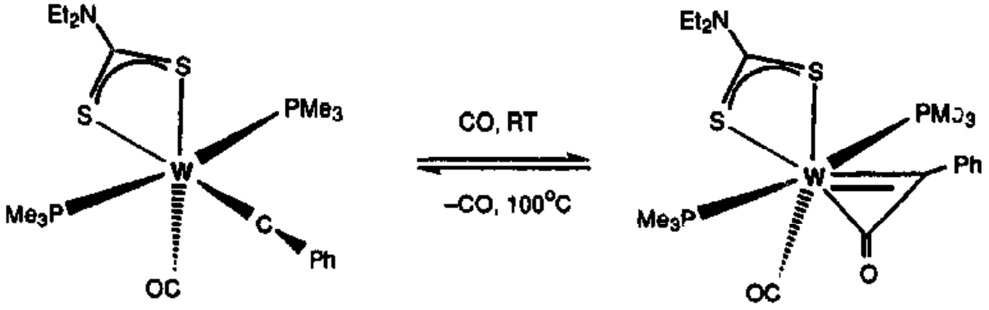


(L = CO, PMe_3; R = Me,Ph,Tol,; R' = alkyl, aryl)

Scheme 10

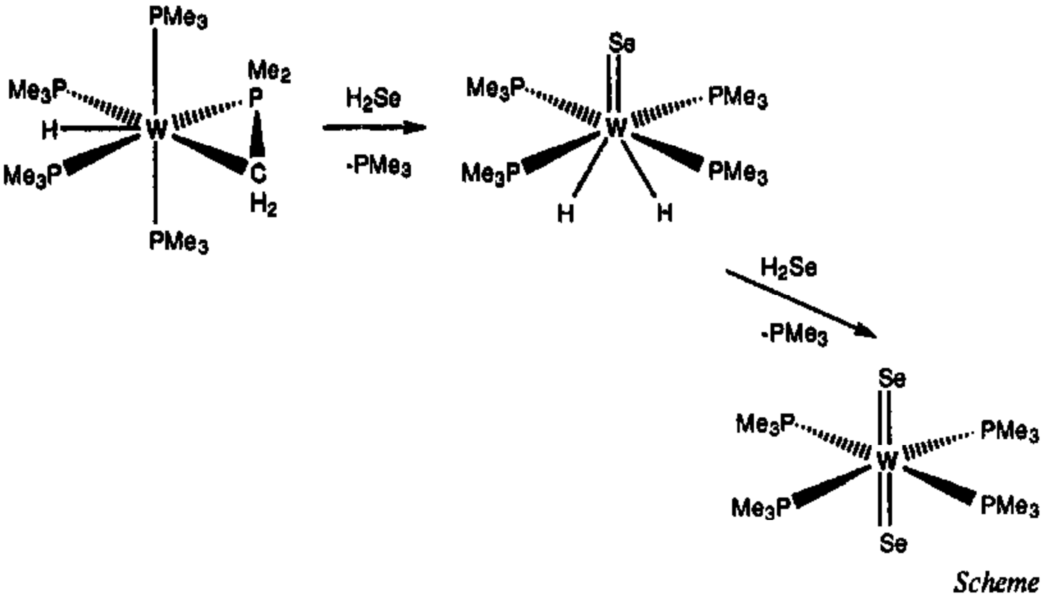
Pyramidal inversion at sulfur was observed by dynamic NMR spectroscopic studies of the thioether complexes $[Cp_2W(MeSCH_2CH_2SMe)][PF_6]_2$ and $[Cp_2W(SCH_2CH_2S)]$ [41]. An activation enrgy was determined from proton band shape analysis for the former to be 51.2±4.6 kJ mol^{-1}. EHMO calculations suggested local sulfur inversion rather than S-C-C-S chain inversion to be the fluxional process.

The alkylidyne tungsten complex *cis* or *trans*-$[W(CPh)Cl(CO)_2(PMe_3)_2]$ reacted with sodium diethyldithiocarbamate to give the ketenyl $[W(OCCPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ while $[W(CPh)Cl(CO)(PMe_3)_3]$ yielded a phosphine/chloride substitution product $[W(CPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ [42]. The latter can be reversibly carbonylated to the $[W(OCCPh)(S_2CNEt_2)(CO)(PMe_3)_2]$ product (Scheme **11**).



Scheme 11

Novel terminal selenido complexes of tungsten, $[W(PMe_3)_4(Se)H_2]$ and *trans*-$[W(PMe_3)_4(Se)_2]$, were formed sequentially by the reaction of $[W(PMe_3)_4(\eta^2\text{-}CH_2PMe_2)H]$ with H_2Se (Scheme **12**) [43]. These complexes and their derivatives have been studied by X-ray diffraction and ^{77}Se NMR spectroscopy.



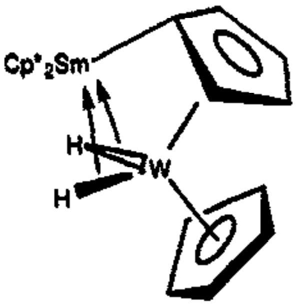
Scheme 12

7.3.5 *Complexes with hydride ligands*

Oxidative addition of dihydrogen to [$WCl_2(PMe_2Ph)_4$] yielded eight-coordinate [$WH_2Cl_2(PMe_2Ph)_4$] which was found to be stereochemically nonrigid [44]. This complex was a catalyst for the conversion of HD to H_2 and D_2. NMR spectroscopic evidence suggested a phosphine dissociation mechanism. Attempted nucleophilic substitution of the chlorides with $KN(SiMe_3)_2$ led instead to dehydrochlorination followed by orthometalation of the P-Ph group to give the complexes [$WH_2Cl(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$], [$WH_3Cl(PMe_2Ph)_4$], or [$WH_3(\eta^2\text{-}C_6H_4PMe_2)(PMe_2Ph)_3$].

Photochemical reaction of Cp_2WH_2 with hydrosilanes $HSiR_3$ at 350 nm produced good yields of the silyl hydride complex [$Cp_2W(H)SiR_3$] [45]. The stable silene complex [$Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$] with $HSiR_3$ gave excellent yields of bis(silyl) products [$Cp_2W(SiMe_3)(SiR_3)$] (where SiR_3 = $SiMe_3$, $SiMe_2Cl$, $SiPr^i_2Cl$, and $SiBu^t_2H$). Structural determinations revealed a general correlation of metal-silicon bond distance with steric congestion except for the chlorosilyl derivative which featured an unusually short W-Si distance. This was attributed to inductive as well as π-backbonding of the metal into the Si-Cl σ* orbital. Trends in the ^{29}Si NMR parameters such as $^{1}J_{WSi}$ provided further evidence for the partial silylene character in such species.

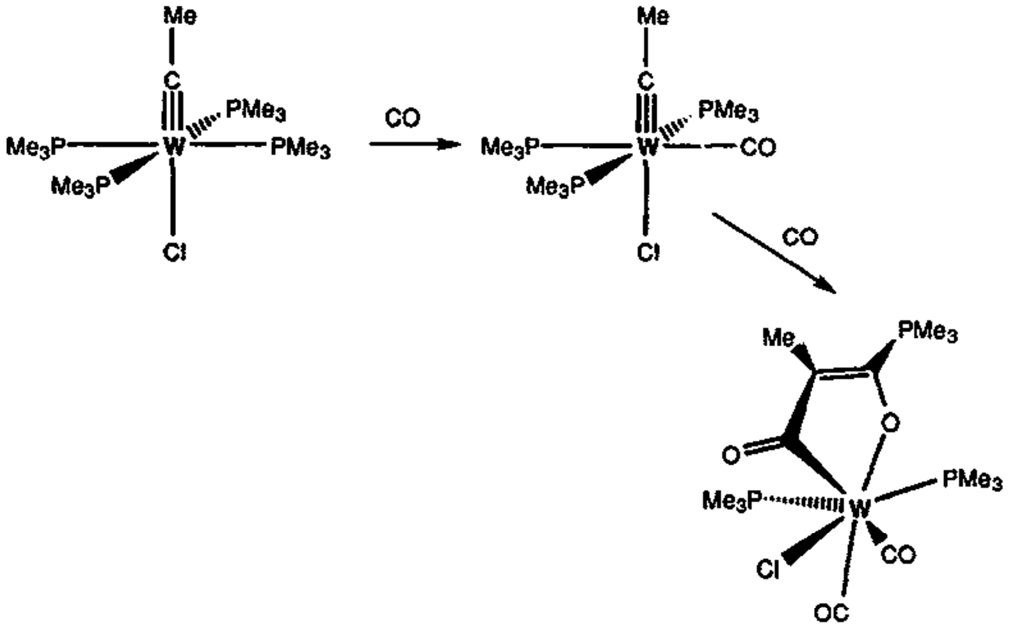
Reactions of the lanthanide [$Cp^*_2LnH]_2$ dimers (Ln = Y and Sm) with Cp_2WH_2 afforded the σ-bond metathesis product [$Cp^*_2Ln(\mu\text{-}\eta^1,\eta^5\text{-}C_5H_4)(\mu\text{-}H)_2WCp$] (**23**) via dehydrocoupling of the Ln-H and the C-H bond of the tungsten moiety despite the presence of the weaker W-H bonds [46,47]. The molecular structure of (**23**) failed to reveal the hydrides but proton NMR spectroscopic data were consistent with a depiction of the hydride bridges as coordination of W-H bonds to the lanthanide centre since Lewis bases like pyridine readily displaced them to give monometallic species.



(**23**)

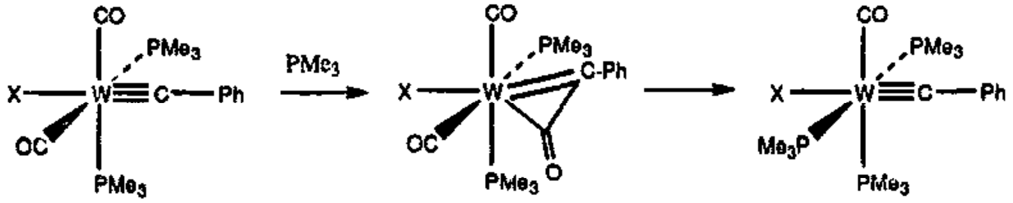
7.3.6 *Complexes with mixed donor ligands*

The tungsten carbyne complex [$W(CMe)(PMe_3)_4Cl$] was found to react with CO initially replacing one phosphine ligand [48]. Further carbonylation led to formation of an oxametallocyclopentenone complex [$W\{OC\{Me_3P{=}CMeC(O)\}\}Cl(CO)_2(PMe_3)_2$] (Scheme 13). The X-ray structure of this confirmed an unusual double carbonylation of the carbyne ligand.



Scheme 13

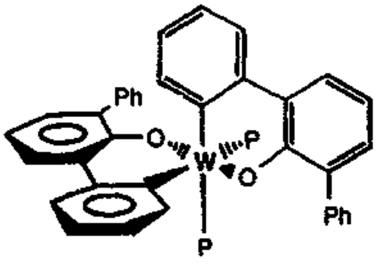
Reaction of the tungsten carbyne complex [W(CPh)X(CO)$_2$(PMe$_3$)$_2$] (X = Cl,Br) with neat PMe$_3$ gave [W(CPh)X(CO)(PMe$_3$)$_3$] via ketenyl intermediates (Scheme 14) [49]. Neat pyridine was found to replace a phosphine *trans* to the carbonyl ligand.



Scheme 14

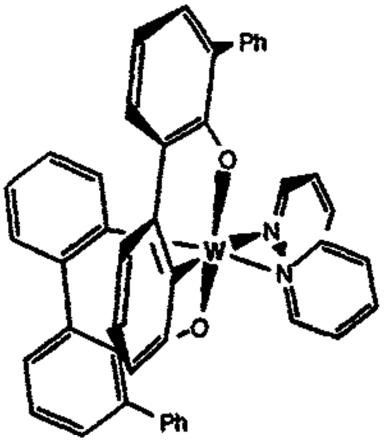
The bisphosphine tungsten complex (**24**) containing a cyclometallated 2,6-diphenylphenoxide was found to react rapidly with nitrogen heterocycles to yield [W(O-C$_6$H$_3$Ph-C$_6$H$_4$)$_2$L$_2$] (where L = substituted pyridines, and L$_2$ = substituted bipyridines and phenanthrolines) [50]. Variable-temperature proton NMR spectroscopic studies of these products revealed a thermal equilibrium between a singlet d^2-W(IV) ground state and triplet excited state. Calculations of the relative energy gaps led to the conclusion that stronger π-acidic pyridines stabilize the ground state d_{xy} HOMO while stronger π-acidic bipyridines and phenanthrolines stabilize the d_{xz}, d_{yz} LUMO's. The molecular structure of [W(O-C$_6$H$_3$Ph-C$_6$H$_4$)$_2$(py)$_2$] (**25**) has been determined which confirmed the nearly coplanar orientation of the *cis*-pyridines with the O-W-O axis.

Reduction of [W(NMes)$_2$Cl$_2$(dme)] or *trans*-[W(NMes)$_2$(PMe$_3$)$_2$Cl$_2$] with C$_8$K in the presence of PMe$_3$ gave the diamagnetic d^2 complex [W(NMes)$_2$(PMe$_3$)$_3$] [51]. π-Acidic ligands like ethylene, acetylene, and P(OMe)$_3$ readily replaced at least one PMe$_3$ (Scheme 15). The molecular structure of the ethylene adduct revealed a trigonal bipyramidal geometry about W with both arylamido groups in the equatorial plane and the C_2 vector of the alkene perpendicular to WN_2 plane.



(P = $PMePh_2$)

(24)



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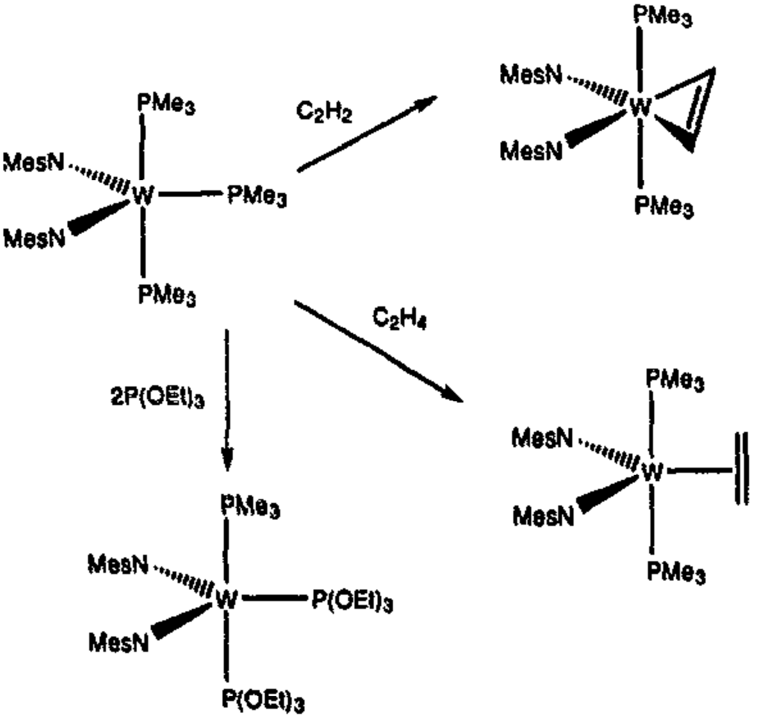
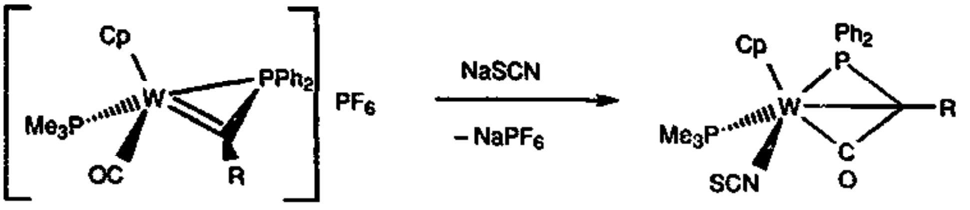
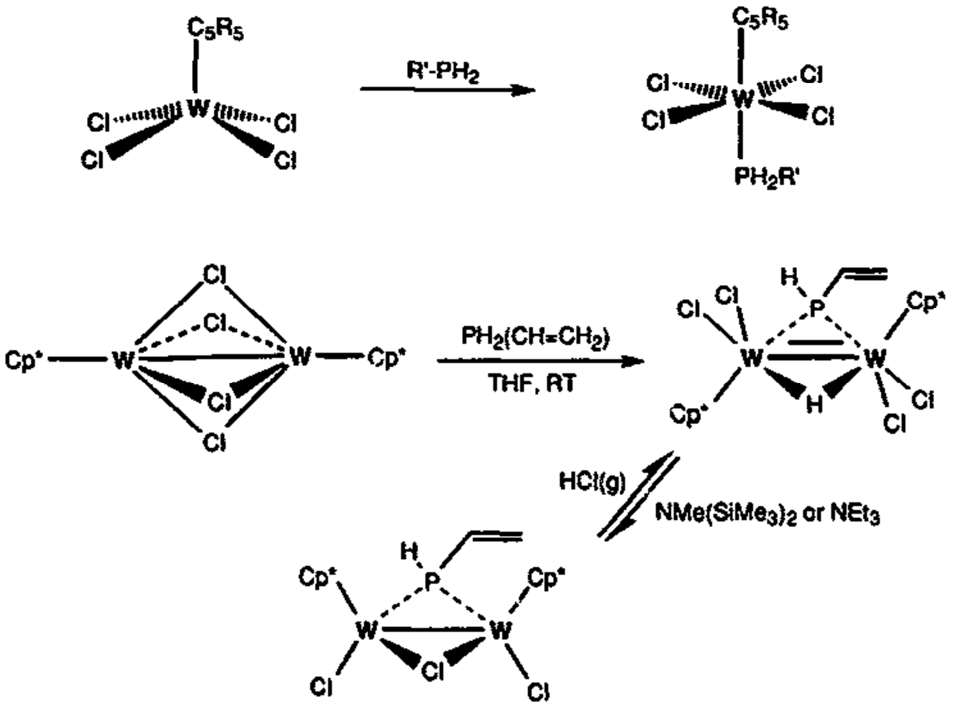


Scheme 15

Reaction of η^2-phosphino- or η^2-thiocarbene complexes of tungsten with sodium thiocyanate provided high yields of the respective metalla-(phospha/thia)bicyclo[1.1.0]butanone complexes (Scheme 16) [52]. New tungsten compounds of the type $[(C_5R_5)WCl_4(PH_2R')]$ featuring primary phosphine ligands have been prepared [53]. These were synthesized from $(C_5R_5)WCl_4$ ($R_5 = H_4Pr^i$, Me_4Et) or $[Cp^*W(\mu\text{-}Cl)_2]_2$ and the respective phosphines $R'PH_2$ (R' = CH=CH, CH_2CH=CH) according to Scheme 17.

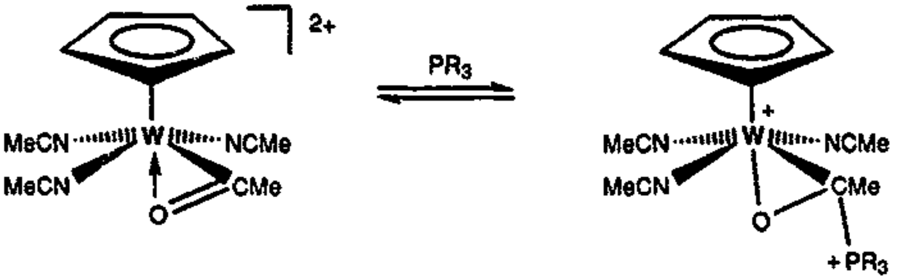


Scheme 16



Scheme 17

Nonrelativistic and relativistic discrete variational X_α–calculations have been performed on model complexes $W(PH_3)_4E_2$ (where E = O, S, Se, or Te) [54]. The results were found to be consistent with a formal description of these as 18-electron W(IV) d^2 systems. Increasingly covalent σ metal-chalcogen bonding was found down the group from O to Te while the tungsten-chalcogen contributions to π-bonding remained almost constant. The theroretical results were in good agreement with the experimental electronic spectra of $W(PMe_3)_4E_2$ (E = S, Se, or Te).



Scheme 18

Substitution chemistry of $[CpW(\eta^2\text{-acetyl})(NCMe)_3]^{2+}$ has been found to be catalysed by phosphines via phosphonium intermediates which are strongly *cis*-labilizing (Scheme 18) [55].

7.4 TUNGSTEN(III) AND TUNGSTEN(II) DIMERS

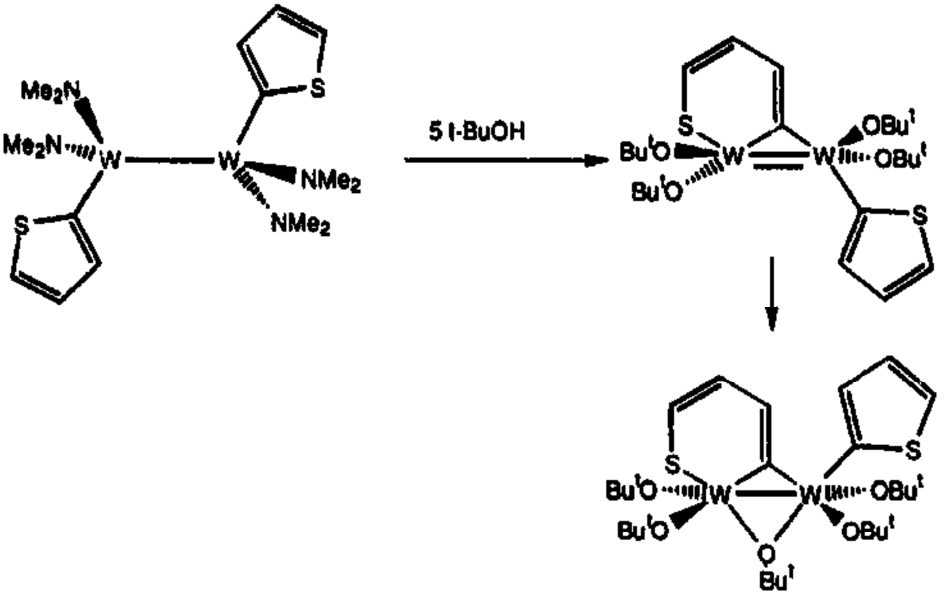
Reversible coordination of cyanide by the dimeric alkoxide complexes $[W_2(OBu^t)_6]$ and $[W_2(OCH_2Bu^t)_6]$ gave the respective $[W_2(OR)_6(CN)]^-$ species [56]. Spectroscopic data were consistent with either a bridging cyanide group or a fluxional bonding mode. Excess CN^- led to reversible formation of the 1,2-diadducts $[W_2(OR)_6(CN)_2]^{2-}$. Thermodynamic data for the equilibrium:

$$[W_2(OBu^t)_6] + CN^- \rightleftharpoons [W_2(OBu^t)_6(CN)]^-$$

were reported: $\Delta H^\circ = -11.2(1)$ kcal mol^{-1}, $\Delta S^\circ = -18.6(7)$ eu. The tungsten cyanide adducts were found to be more stable compared to the molybdenum analogues.

Tungsten complexes of the type $[W_2(carboxylate)_4]$ share a common ladder structure with their chromium and molybdenum analogues in the solid state [57]. X-ray data of $[W_2(OOCPr^n)_4]$ revealed weakly associated dimeric units through W···O bonds. Unlike their chromium and molybdenum analogues, these underwent simple crystal-to-isotropic liquid phase transition or decomposition due to the different strengths of their M···O intermolecular interactions.

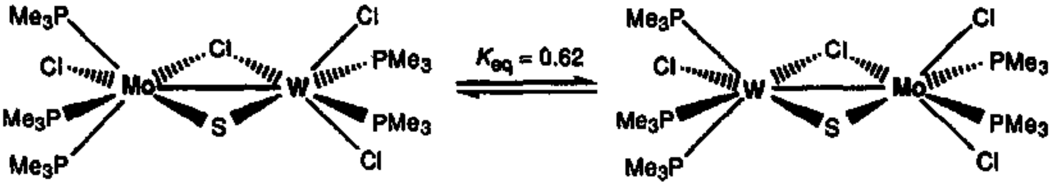
Proton and ^{31}P NMR spectroscopic studies of $[W_2Cl_4(NHCMe_3)_2(PR_3)_2]$ molecules (where $R_3 = Me_3$, Me_2Ph) have been used to study the *cis* ⇌ *trans* interconversions [58]. The *trans* ⇌ *cis* equilibrium constant at 50°C for PMe_2Ph was found to be 0.40±0.05. Presence of free phosphine greatly reduced the isomerization rate. Competing mechanisms including phosphine dissociation or internal flips were considered. A range of 25-30 kcal mol^{-1} for the flip barrier was proposed.



Scheme 19

Stepwise activation of σ-thienyl ligands at the ditungsten centres of [1,2-W$_2$(η^1-S$_4$C$_4$H$_3$)$_2$(NMe$_2$)$_4$] was reported [59]. This was achieved by reaction with excess t-butanol to give a novel thiolato-μ-alkylidyne metallacycle in [W$_2$(OBu^t)$_5$(μ-SC$_4$H$_4$)(η^1-2-SC$_4$H$_3$)] via an intermediate species identified by NMR spectroscopy as [W$_2$(OBu^t)$_4$(μ-SC$_4$H$_3$)(η^1-2-SC$_4$H$_3$)] with a bridging thiolato-vinylidene metallocycle (Scheme 19).

Reaction of either [Mo(S)Cl$_2$(PMe$_3$)$_3$] with [WCl$_2$(PMe$_3$)$_4$] or [MoCl$_2$(PMe$_3$)$_4$] with [W(S)Cl$_2$(PMe$_3$)$_3$] gave two isomeric mixed-metal dimers [MoW(μ-S)(μ-Cl)Cl$_3$(PMe$_3$)$_5$] differing only in the occupation of the two metal sites [60]. These isomers quickly re-established equilibrium in solution with $K_{eq} = 0.62$ at 24°C and were examples of incomplete S transfer:

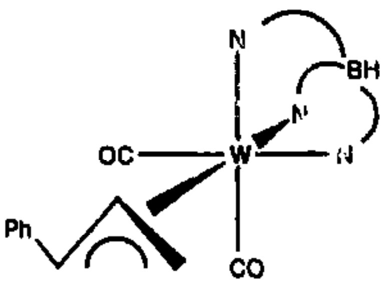


By contrast, the reaction of [Mo(O)Cl$_2$(PMe$_3$)$_3$] and [WCl$_2$(PMe$_3$)$_4$] led to complete O-transfer to yield [W(O)Cl$_2$(PMe$_3$)$_3$] and [MoCl$_2$(PMe$_3$)$_4$]. Conproportionation of [W(O)Cl$_3$(PMe$_3$)$_2$] with [WCl$_3$(PMe$_3$)$_3$] occurred by Cl atom transfer to give the monomers [W(O)Cl$_2$(PMe$_3$)$_3$] and [WCl$_4$(PMe$_3$)$_2$]. The mechanisms and extents of these atom transfer reactions were discussed.

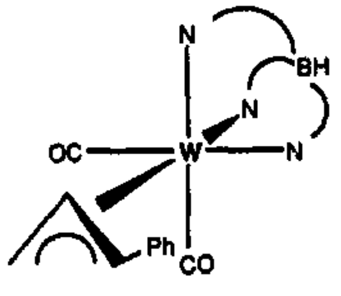
7.5 TUNGSTEN(II)

7.5.1 Complexes with nitrogen ligands

Pseudo-octahedral tungsten pyrazolylborate π-allyl complexes of the type [(HBpz*$_3$)W([illegible](η^3-CH$_2$CHCHPh)] and [(HBpz*$_3$)W(CO)$_2$(η^3-CH$_2$CHCHMe)] were studied by 2D ^{1}H-NOESY and inverse-detected ^{183}W NMR spectroscopic techniques [61]. Observed solution structure (26) was found to differ from the solid-state (27) due to allyl rotation and/or coordination of either allylic face.



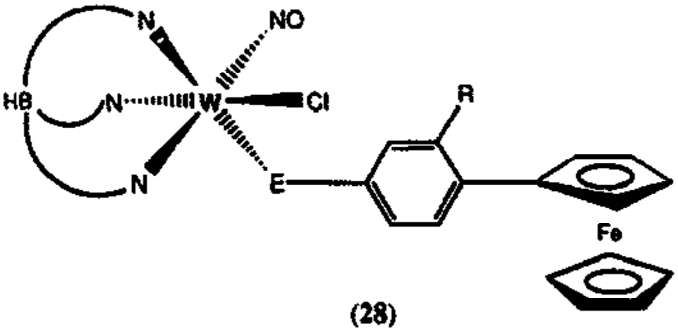
(26)



(27)

Net displacement of an iodide by a methyl group resulted from the reaction of lithium dimethylcuprate with [(HBpz*$_3$)W(CO)I(PhCCMe)] [62]. Protonation of this methyl complex in the presence of ketones or aldehydes afforded cationic η^1-ketone or η^1-aldehyde complexes $[(HBpz^*_3)W(CO)(PhCCMe)(\eta^1\text{-}O{=}CRR')]$. Variable-temperature NMR spectroscopic studies revealed equilibration between *E* and *Z* isomers about the C=O bond with a barrier of 11-15 kcal mol^{-1}.

Nonlinear optical materials containing tungsten mononitrosyl redox centres have been synthesized [63]. These included the $[(HBpz^*_3)W(NO)Cl]\text{-}EC_6H_3\text{-}(3\text{-}R)\text{-}[4\text{-}(\eta^5\text{-}C_5H_4)FeCp]$ (28) and $[(HBpz^*_3)W(NO)][\text{-}E\text{-}C_6H_4\text{-}4\text{-}(\eta^5\text{-}C_5H_4)FeCp]_2$ complexes (where E = NH, O and R = H, Me). Their second-order non-linear optical properties have been assessed. Related materials featuring diaromatic diazo derivatives have also been reported [64]. Frequency doubling at 1907 nm was found for several derivatives. A structural determination of the compound $[\{(HBpz^*_3)W(NO)Cl\}\{NHC_6H_3(Me\text{-}3)\}\{N{=}N\text{-}C_6H_4(\eta^5\text{-}C_5H_4FeCp\text{-}4)\}]$ (29) has been carried out and revealed crystal packing favouring phase matching.



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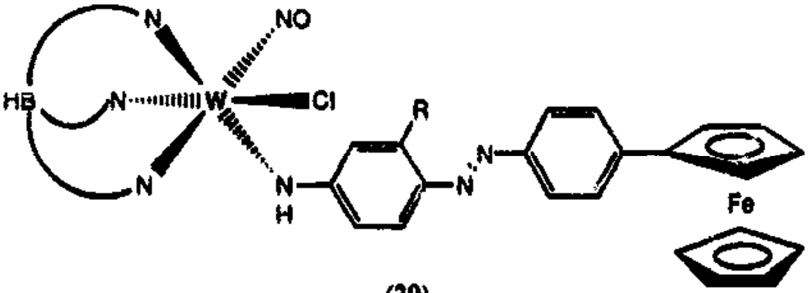

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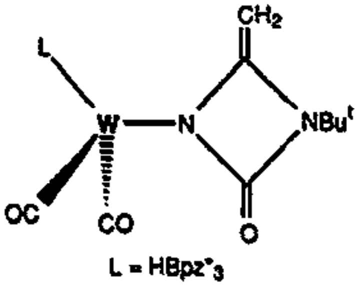
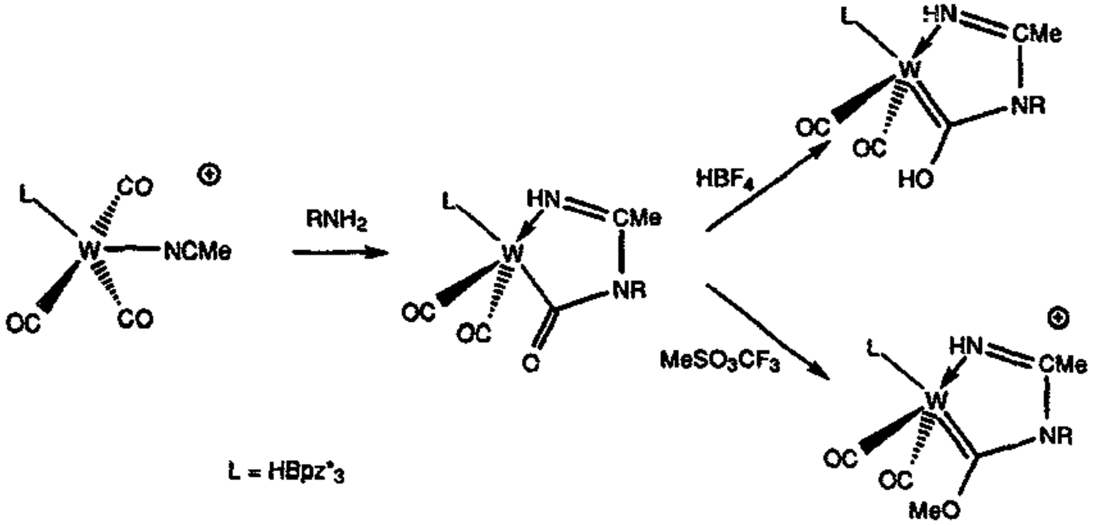


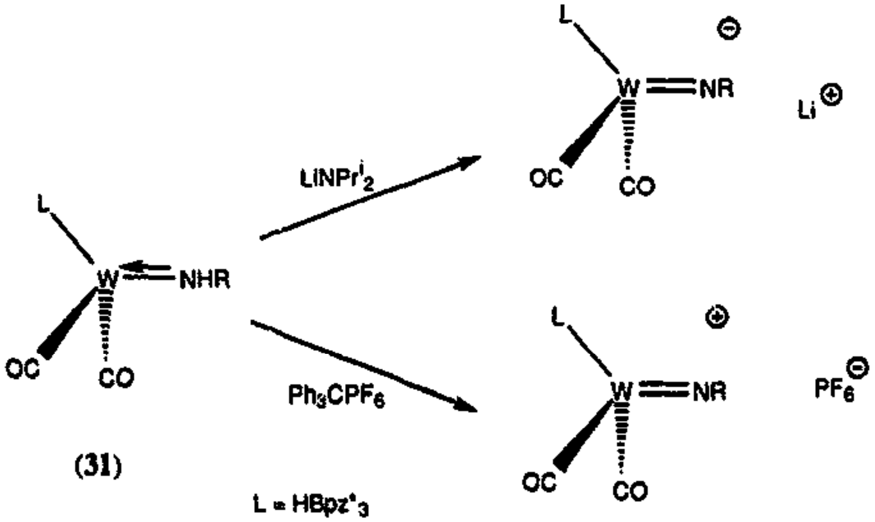
(30)

Amide-induced coupling of nitrile and carbonyl ligands at a tungsten(II) complex has been reported [65]. Reaction of $[(HBpz^*_3)W(CO)_3(NCMe)]BF_4$ with ammonia or n-butylamine generated neutral products $[(HBpz^*_3)W(CO)_2(C(O)NR\text{-}CMe{=}NH)]$ (where R = H or n-Bu).

Protonation or methylation led to cationic metallacyclic hydroxycarbene complexes (Scheme 20). By contrast, reaction of the tungsten precursor with t-BuNH$_2$ led to formation of an unusual amido complex (30) featuring a 3-coordinate nitrogen in a 4-membered ring.



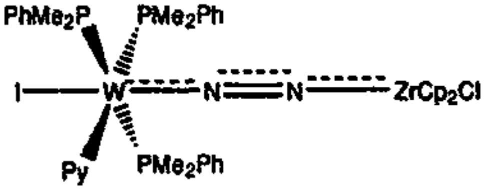
Scheme 20



Scheme 21

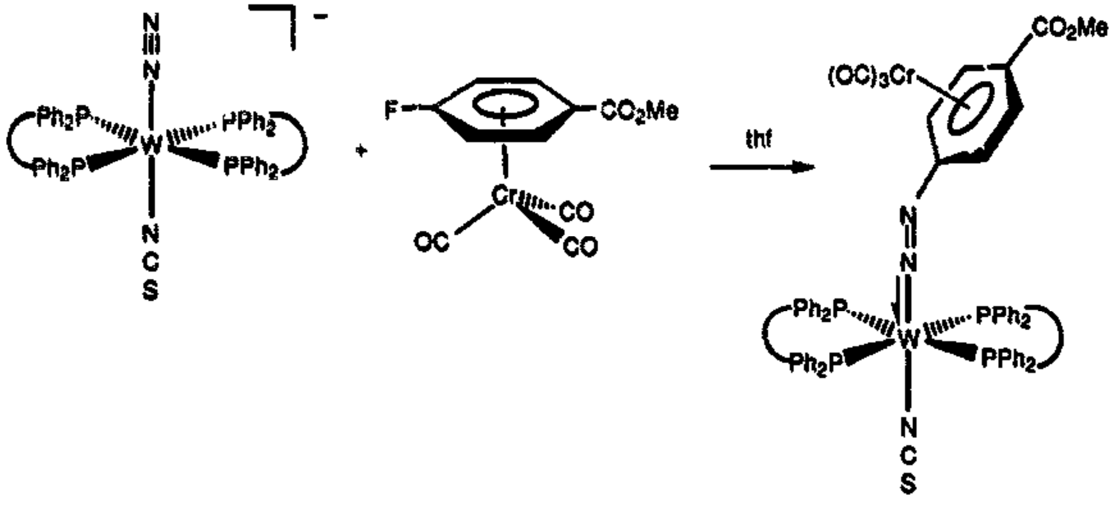
Syntheses and reactivity studies of tris(pyrazolyl)borate tungsten amido, imido, azavinylidene, and nitrido complexes have been reported [66]. Reaction of [(HBpz*$_3$)W(CO)$_3$I] with primary amines gave ambiphilic amido derivatives [(HBpz*$_3$)W(CO)$_2$(NHR)] (where R = Bu^t, Ph, CH$_2$Ph, Bu^n, and H) (31). Both anionic imido and cationic nitrene derivatives were accessible from this precursor (Scheme 21). The former can be alkylated with R'X to give [(HBpz*$_3$)W(CO)$_2$(NRR')] (where R' = Me, CH$_2$Ph). Molecular structures of these dialkylamido products have been determined. Cationic nitrene complexes were available by deprotonation of the amido precursors. The addition of LiBH$_4$ to [(HBpz*$_3$)W(CO)$_2$(=NPh)] yielded a formyl intermediate [(HBpz*$_3$)W(CO)(CHO)(=NPh)] which underwent hydride migration to regenerate the amido complex even at –70°C. X-ray structural studies of the nitrene complexes revealed linear imido ligands. The W-N bond length in [(HBpz*$_3$)W(CO)$_2$(=NPh)] was found to be 1.775(7) Å.

Reactions of *cis*-[W(N$_2$)$_2$(PMe$_2$Ph)$_4$] with either Cp$_2$TiCl$_2$ or a mixture of Cp$_2$MCl$_2$ (M = Zr, Hf) and excess NaI gave heterodimetallic products with bridging dinitrogen ligands [WX(PMe$_2$Ph)$_4$(μ-N$_2$)MCp$_2$Cl] (M = Ti, X = Cl; M = Zr, Hf, X = I) [67]. The W-Zr complex was further treated with excess pyridine to yield [WI(PMe$_2$Ph)$_3$(Py)(μ-N$_2$)ZrCp$_2$Cl] (32). This structure was confirmed by X-ray diffraction.



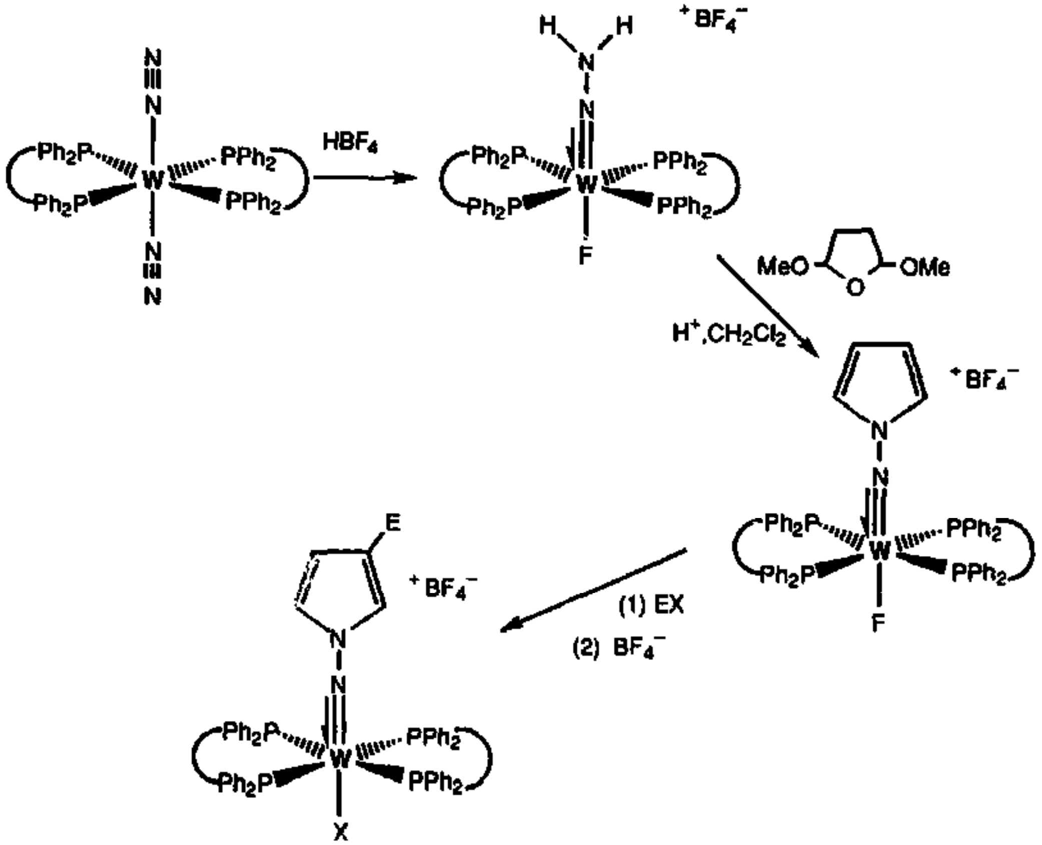
(32)

Dimetallic arylation of coordinated molecular nitrogen was accomplished in the reaction between [NBu$_4$][W(NCS)(N$_2$)(dppe)$_2$] and fluoroarene complexes [Cr(η^6-*p*-FC$_6$H$_4$COOMe)(CO)$_3$] or [CpRu(η^6-FC$_6$H$_4$R)] (where R = H, Me, OMe, COOMe) in thf at 0°C to ambient temperatures [68]. The reaction was suggested to proceed by direct nucleophilic substitution rather than a radical mechanism previously reported for dinitrogen alkylation (Scheme 22).



Scheme 22

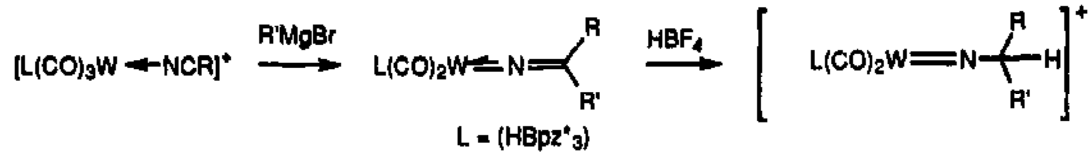
The conversion of molecular dinitrogen to pyrrole in a high-yield reaction was realized in a report on tungsten and molybdenum chemistry [69]. Protonation of [W(dppe)$_2$(N$_2$)$_2$] with fluoroboric acid yielded the hydrazido complex [W(dppe)$_2$(F)(NNH$_2$)] which reacted with 2,5-dimethyltetrahydrofuran under acidic conditions to give a 1-pyrrolylimido complex (Scheme 23).



Scheme 23

The pyrrole ring formed was found to undergo facile β-selective electrophilic substitution. Reduction with $LiAlH_4$ effectively liberated the pyrrole from the complex in over 80% yield.

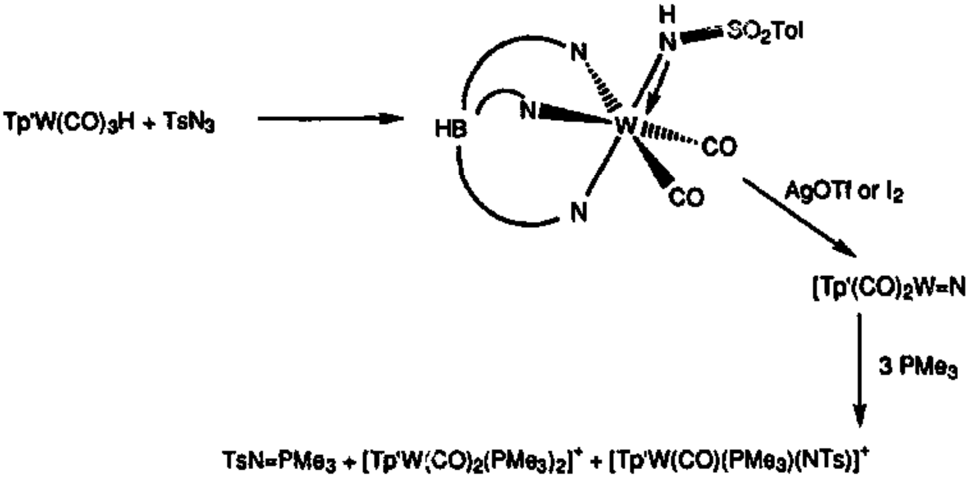
Nitriles can be converted to nitrenes via azavinylidenes in low-valent tungsten carbonyl complexes [70]. Reaction of $[(HBpz^*_3)W(CO)_3(NCR)]BF_4$ (R = Me, Ph) with nucleophiles NuH (Nu = H, Et, OMe) led to azavinylidene complexes $[(HBpz^*_3)W(CO)_2N{=}CR(Nu)]$. Alternatively photolytic insertion of nitrile into the W-H bond of $[(HBpz^*_3)W(CO)_3H]$ also led to $[(HBpz^*_3)W(CO)_2N{=}CR(H)]$ products. Structural and spectroscopic data were consistent with nitrogen lone pair donation to the metal centre in these complexes. Protonation of these products at the ligand carbon with HBF_4 effectively oxidized the metal to W(IV) and formed cationic nitrene complexes $[(HBpz^*_3)(CO)_2W{=}NCHRR']BF_4$ (Scheme 24).



Scheme 24

Nitrene transfer from a cationic tungsten tosylnitrene complex to trimethylphosphine has been reported [71]. Reaction of $[(HBpz^*_3)W(CO)_3H]$ with tosyl azide afforded the amido complex

[(HBpz*$_3$)W(CO)$_2$NHTs] which was oxidized by silver triflate or iodine to the imido complexes [(HBpz*$_3$)W(CO)$_2$(NTs)]X (X = OTf, I$_3$) (Scheme 25). These nitrene complexes were reacted with trimethylphosphine to give three species: the phosphinimine TsN=PMe$_3$, and the complexes [(HBpz*$_3$)W(CO)$_2$(PMe$_3$)$_2$]X and [(HBpz*$_3$)W(CO)PMe$_3$(NTs)]X.



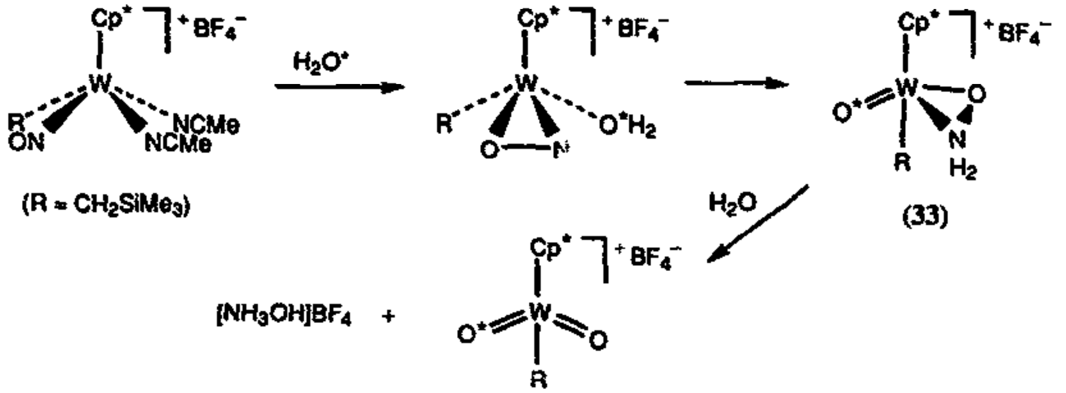
Scheme 25

The preparation of a series of dinuclear complexes featuring the Ru(bpy)$_3^{2+}$ moiety bearing a peripheral phenol group (at the 4-position of one bpy) which was O-linked to a [W(HBpz*$_3$)(NO)Cl] fragment was reported [72]. Only a small-to-moderate ground state interaction between the two metals was observed by electrochemical and UV-VIS spectroscopic studies. Luminescence studies at 77 and 298 K indicated quenching of the ruthenium centre via an energy transfer mechanism, leading to a non-luminescent W excited state.

Nitrite complexes of tungsten of the type [W(NO$_2$)$_2$(CO)$_2$(PPh$_3$)$_2$] were readily prepared by the reaction of NaNO$_2$ with [WBr$_2$(CO)$_2$(PPh$_3$)$_2$] [73]. Multinuclear NMR spectroscopic data suggested equivalent chelating nitrites ligands in these eight-coordinate products.

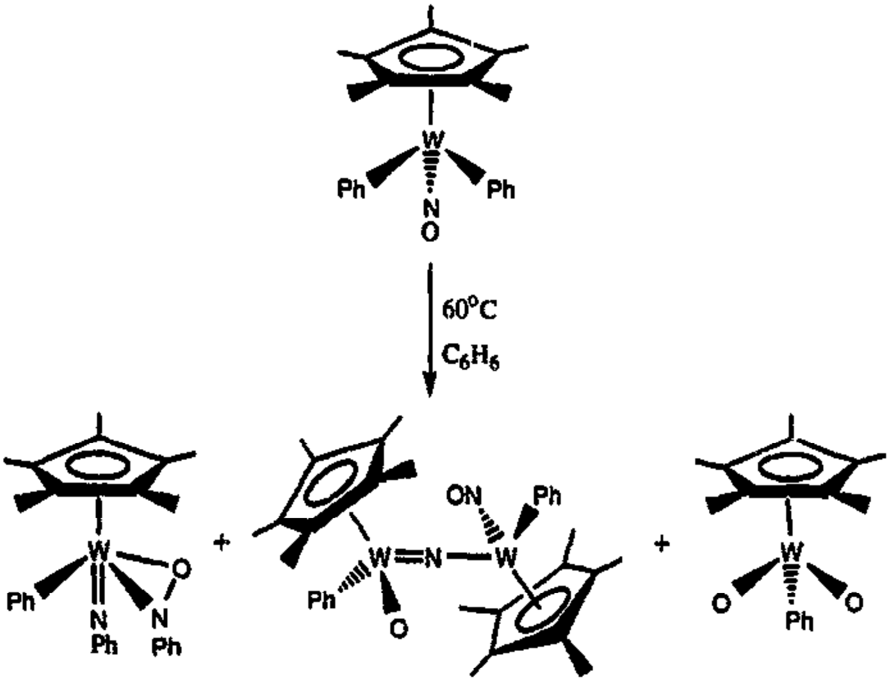
A potentially bridging ligand 4-(imidazol-1-yl)phenol was used to prepare mono- and dinuclear complexes of [(HBpz*$_3$)M(NO)X] (M= Mo,W; X= Cl,I) [74]. Electrochemical interaction between the two metal centres was found to be weak. The 17-electron (imidazolyl terminus) and 16-electron (phenolate end) centres were valence-trapped according to the EPR spectra. However, further reduction to the 17-e/17-e biradical led to a strong e$^-$/e$^-$ exchange interaction.

In an important discovery, the stepwise hydrolysis of a terminal nitrosyl ligand at tungsten was reported [75]. The [Cp*W(NCMe)$_2$(CH$_2$SiMe$_3$)(NO)]$^+$ complex was found to react with one equivalent of water to give an η^2-hydroxylamido product (33) whose structure was confirmed by X-ray crystallography. A second equivalent of water yielded the dioxo product [Cp*W(=O)$_2$(CH$_2$SiMe$_3$)]. A mechanistic study suggested the pathway shown in Scheme 26.



Scheme 26

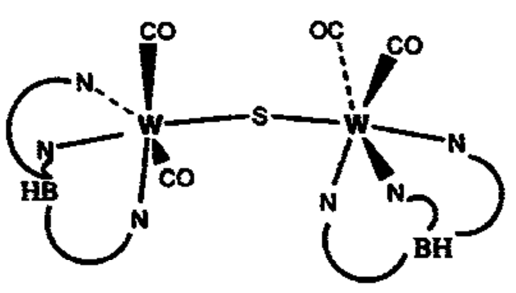
A parallel study of the thermolysis of [Cp*W(NO)Ph_2] revealed facile nitrosyl N-O cleavage [76]. Cleavage products included [Cp*W(η^2-ONPh)(NPh)Ph], [Cp*W(O)Ph](μ-N)[WCp*(NO)Ph], and [Cp*W$(O)_2$Ph] in isolated yields of 10, 9, and 30% respectively (Scheme 27). In the presence of PhSSPh, the thermolysis resulted in quantitative formation of [Cp*W(NO)(Ph)(SPh)].



Scheme 27

7.5.2 Complexes with sulfur ligands

Reaction of [LWBr$(CO)_2$] (L = HBpz$^*_3$) or [LWH$(CO)_3$] (where L = HBpz$^*_3$ or HB(Pr^i-pyrazolyl$)_3$) with propylene sulfide yielded blue, diamagnetic ditungsten complexes of the type $[LW(CO)_2]_2(\mu\text{-}S)$ [78]. These have been characterized spectrally and structurally and have distorted octahedral tungsten centres coordinated by *fac*-tris (pyrazolyl)borate, carbonyl, and bridging S ligands (34). The triatomic W_2S^{2+} cores were found to have short W-S distances of 2.17 to 2.18Å and nearly linear W-S-W units (angles 172-175°).



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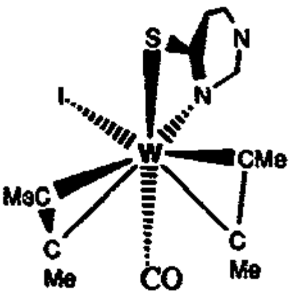
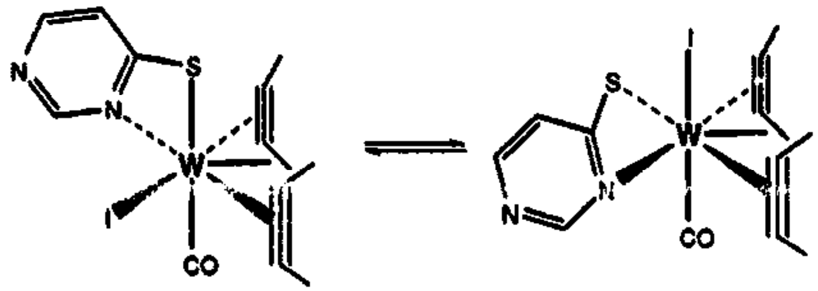


(35)

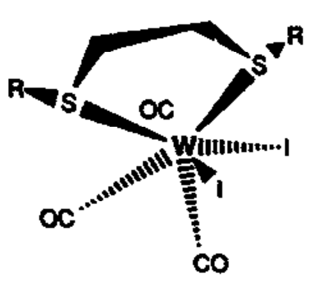
The synthesis of a pyrimidine-2-thionate tungsten complex from the reaction of $[WI_2(CO)(NCMe)(\eta^2\text{-}MeCCMe)_2]$ with the potassium salt of the $[C_4H_3N_2S]^-$ anion was described [79]. Its molecular structure has been determined to be distorted octahedral, with one butyne *trans*-to the iodide in an axial site while the other butyne, CO, and *S*,*N*-donors of the pyrimidine-2-thionate occupied equatorial positions as shown in structure (35). Variable-temperature ^1H NMR spectroscopy revealed fluxional behavior (Scheme 28).



Scheme 28

The same precursor reacted with one equivalent of potassium pyridine-2-thionate to give $[WI(CO)(SC_5H_4N)(\eta^2\text{-}MeCCMe)_2]$ [80], while two equivalents of the salt led to substitution of one butyne ligand to give $[W(CO)(SC_5H_4N)_2(\eta^2\text{-}MeCCMe)]$. The former complex reacted with $NaBPh_4$ to give product $[W(CO)(SC_5H_4N)(\eta^2\text{-}MeCCMe)_2]^+[BPh_4]^-$ which was structurally characterized by X-ray diffraction. Additionally, rotation barriers about the butyne ligand were studied by variable-temperature ^1H NMR spectroscopy.

Thioether tungsten complexes of the type $WI_2(CO)_3[RSCH_2CH_2SR]$ were prepared from $[WI_2(CO)_3(NCMe)_2]$ and $RSCH_2CH_2SR$ (where R = Ph, 4-MeC_6H_4, or 4-F-C_6H_4) [81]. X-ray crystallography revealed a CO-capped octahedral geometry at tungsten as structure (36) illustrates. Use of the trithio-ligand $MeSCH_2CH_2SCH_2CH_2SMe$ led to the compound $WI_2(CO)_3[MeSCH_2CH_2SCH_2CH_2SMe]$ (37) which was found to have a similar coordination geometry.



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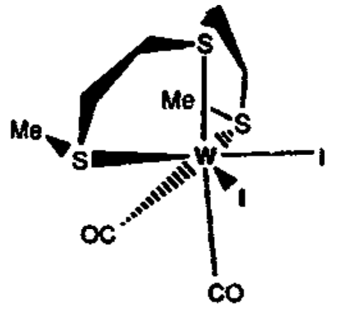
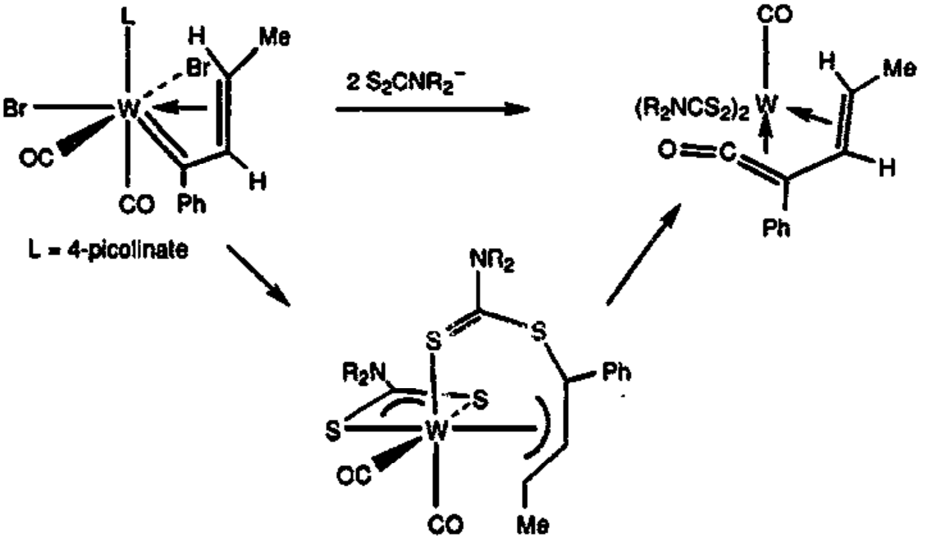


(37)

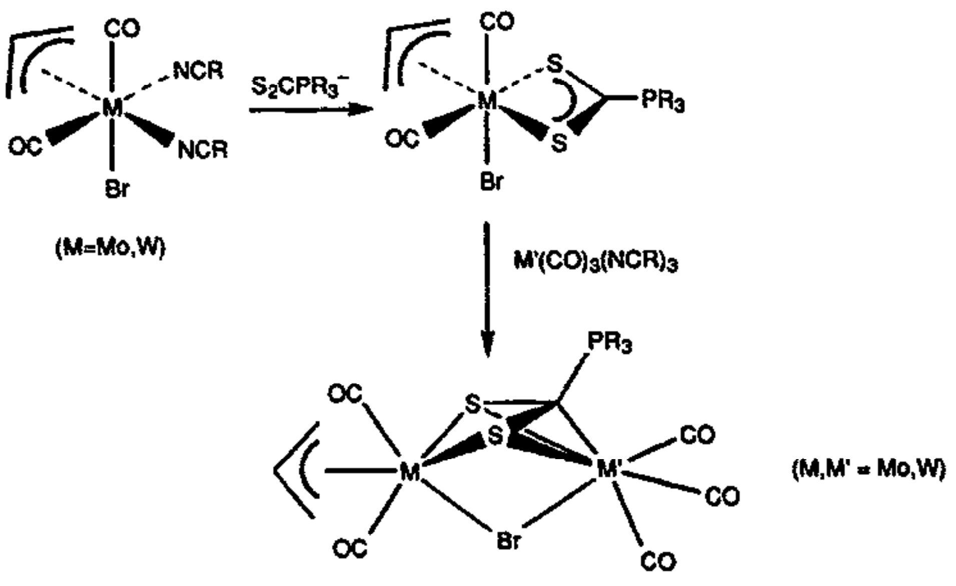
Dithiocarbamate was found to induce allylidene and carbonyl coupling at a tungsten centre [82]. Reaction of [W(CPhCHCHMe)$Br_2(CO)_2$(4-picoline)] with NaS_2CNR_2 (R= Et,Me) in thf led to vinylketene products [W$(S_2CNR_2)_2$(OCCPhCHCHMe)(CO)] via intermediates formed by addition of the dithiocarbamate across the W=C bond. One of these was isolated and identified as [W(η^4-Et_2NCS_2CPhCHCHMe)(S_2CNEt_2)$(CO)_2$], complex (38) in Scheme 29.



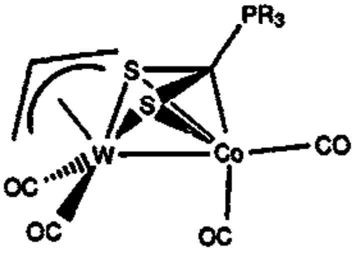
(38)

Scheme 29

Homo- and heterodimetallic M^{II}/M^0 complexes of Mo and W with S_2CPR_3 ligands have been prepared according to Scheme 30 [83]. Heterodimetallic complexes containing asymmetric S_2CPR_3 bridges between cobalt and tungsten have been reported [84]. Thus the reaction of $Co_2(CO)_8$ with [W(η^3-C_3H_5)$(CO)_2$(S_2CPR_3)] (R = Cy, Pr^i) gave [W(η^3-C_3H_5)$(CO)_2$(μ-S_2CPR_3)Co$(CO)_2$] in moderate yields. An X-ray structural determination of the molybdenum analogue confirmed the existence of a metal-metal bond as well as the η^2-(S,S') chelate to Mo (or W) and η^3-(S,C,S') pseudo-allyl ligand bonded to cobalt as shown in structure (39). An alternative way to view the bonding is to view the 5-electron donating MSCS-ring bonded to the Co$(CO)_2$ fragment as a Cp ligand-substitute.

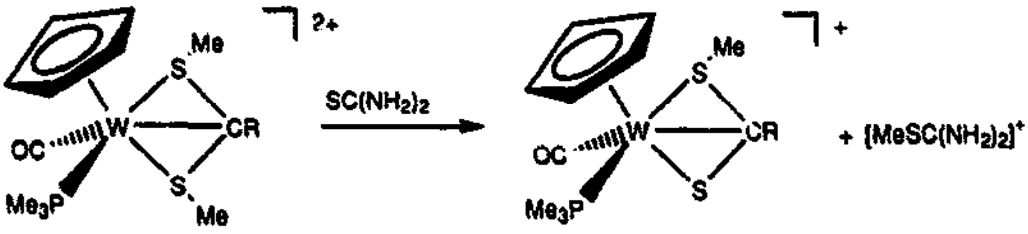


Scheme 30



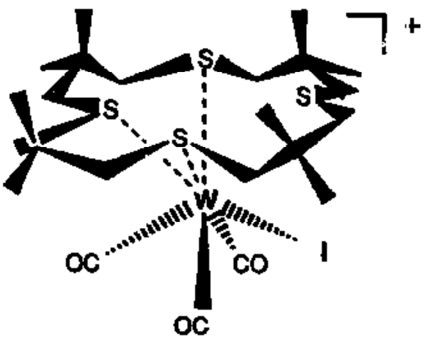
(39)

Thiourea was found to dealkylate 1-tungsta-2,4-dithiabicyclobutane complexes and give monocationic bicyclic products [85] (Scheme 31). Attempts to further dealkylate using strong bases were unsuccessful.



Scheme 31

Tetrathia-macrocycles were found to act as either tri- or tetra-dentate ligands to tungsten(II) [86]. Reaction of $[WI_2(CO)_3(NCMe)_2]$ with $Me_8[16]aneS_4$ gave the salts $[WI(CO)_3(\eta^3\text{-}Me_8[16]aneS_4)][WI_3(CO)_4]$ (40) in addition to $[WI(CO)_2(\eta^4\text{-}Me_8[16]aneS_4)][WI_3(CO)_4]$ (41) which was the major product. Both of the cations were found to adopt piano-stool structures. The Lewis acid $[CpW(CO)_3]^+$ was reacted with the sodium salt of acetate-protected thioglucose to give $CpW(CO)_3SR$ where R = 2,3,4,6-tetra-O-acetyl-1-thio-β-D-glucopyranosate-S [87].



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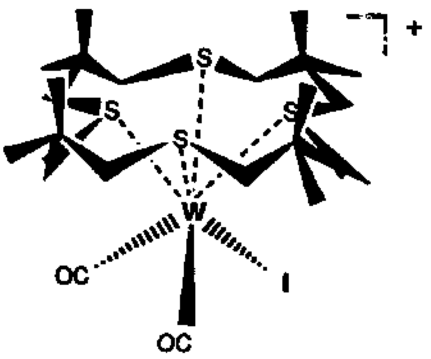
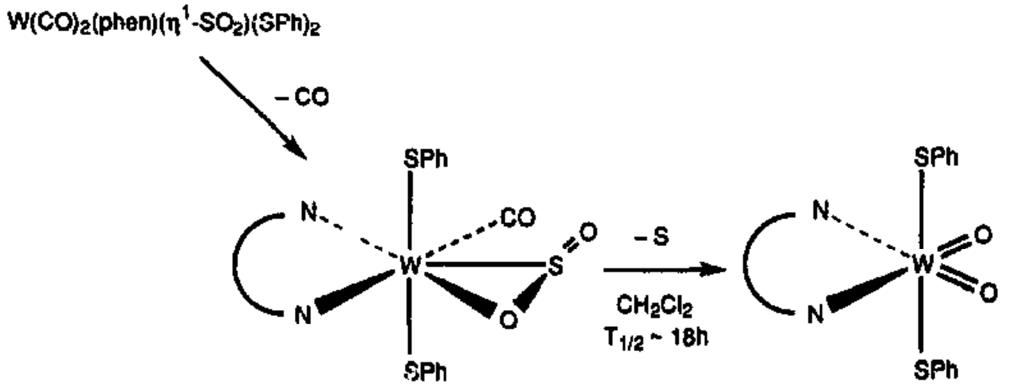


(41)

An interesting tungsten-induced elimination of S from coordinated sulfur dioxide was successfully carried out in a W(II)-SO_2 complex [88]. The compound [$W(CO)_2(phen)(\eta^1$-$SO_2)(SPh)_2$] was found to lose CO and give the η^2-SO_2 intermediate which in methylene chloride solution slowly extruded S to afford the tungsten(VI) dioxo complex (Scheme 32).

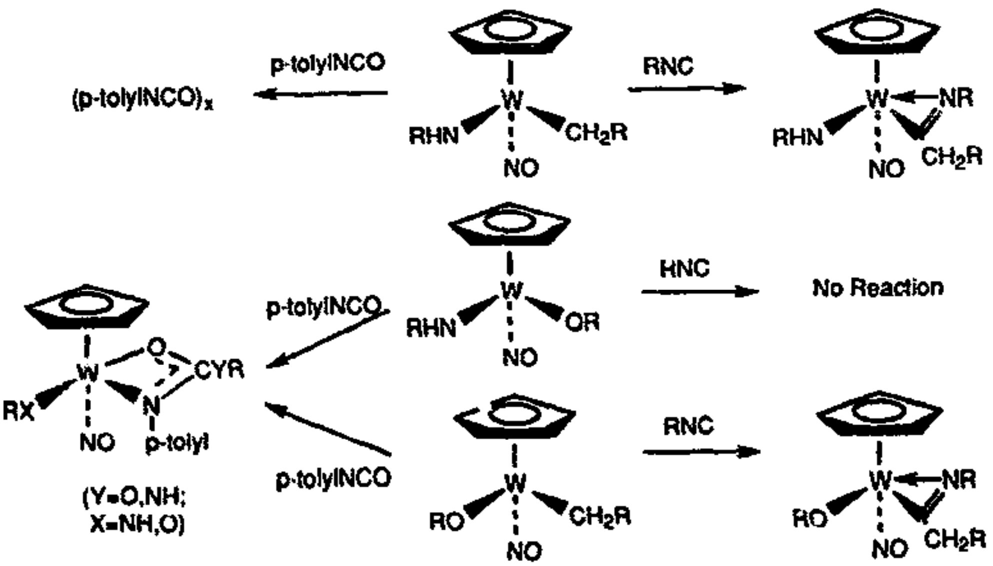


Scheme 32

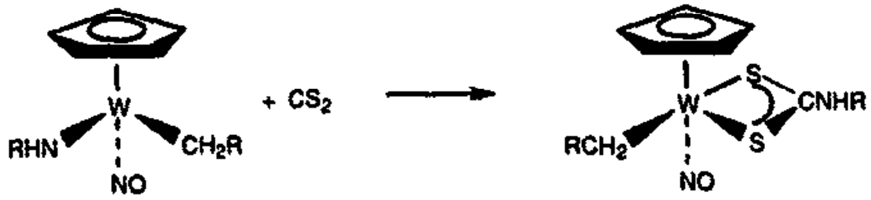
7.5.3 Complexes with mixed donor ligands

Polya's Theorem was used to enumerate the possible geometrical isomers of seven-coordinate complexes with capped octahedral geometry including those of W(II) [89]. These were compared with experimental data.

Three related complexes [$Cp^*W(NO)(CH_2CMe_3)(NHCMe_3)$], [$Cp^*W(NO)(OCMe_3)(NHCMe_3)$], and [$Cp^*W(NO)(OCMe_3)(CH_2CMe_3)$] were treated with ^{t}BuNC, *p*-tolyl isocyanate, and CS_2 in order to establish the relative tendencies of the W-C, W-N, and W-O bonds to undergo insertion reactions [90]. The isocyanide only reacted at the W-C bond while the isocyanate preferentially attacked at W-N >W-O >W-C linkages (Scheme 33). Carbon disulfide reacted at both W-N and W-C sites (Scheme 34). Mechanistic studies revealed that ^{t}BuNC attacked via initial adduct formation while p-tolyl isocyanate proceeded with direct attack at the W-element bond. Carbon dioxide also reacted with these precursors, leading to preferential CO_2 insertions.

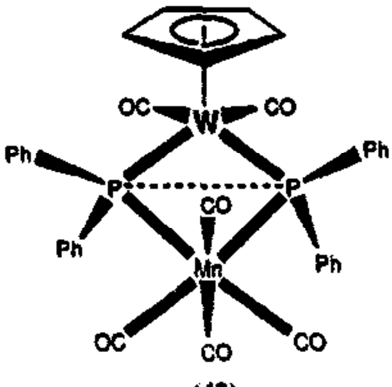


Scheme 33



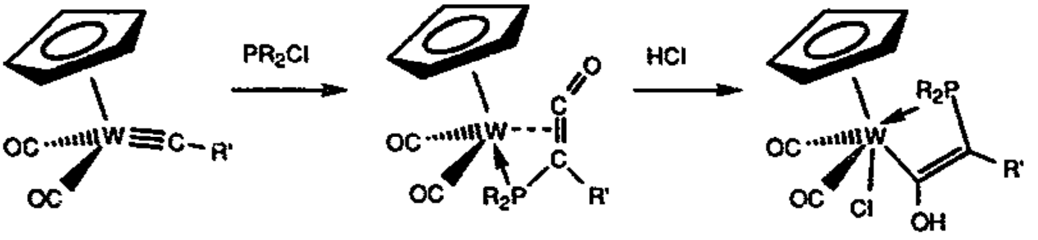
Scheme 34

Equimolar quantities of triphos ($Ph_2PCH_2CH_2P(Ph)CH_2CH_2PPh_2$) and $[WI_2(CO)_3(NCMe)_2]$ reacted in methylene chloride to give $[WI_2(CO)_3(\eta^2\text{-triphos})]$ [91]. Refluxing this product in CH_2Cl_2 led to loss of CO and formation of the η^3-complex. The X-ray structure of the heterodimetallic phosphido compound $[MnW(PPh_2)_2(Cp)(CO)_6]$ (42) has been determined and revealed an unusual folding in the $MnWP_2$ ring with a dihedral angle of 27.5(2)° [92].



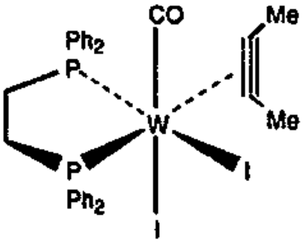
(42)

Phosphinoketene complexes of tungsten were protonated by HCl at the oxygen atom giving 1-tungsta-2-phospha-3-cyclobuten-4-ol complexes (Scheme 35) [93].

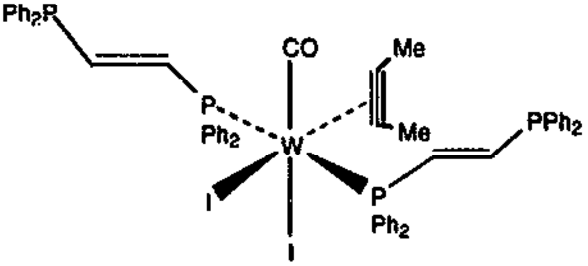


Scheme 35

Two equivalents of the phosphine ligands L (L=Ph_2P-napthyl, *trans*-$Ph_2PCH{=}CHPPh_2$) or one equivalent of LL (LL = *cis*-$Ph_2PCH{=}CHPPh_2$, *R*(+)-$Ph_2P\{CHMeCH_2\}PPh_2$ or $Me_2PCH_2CH_2PMe_2$) with the tungsten(II) complex [$WI_2(CO)(NCMe)(\eta^2$-MeCCMe$)_2$] gave [$WI_2(CO)(L_2$ or LL$)(\eta^2$-MeCCMe)] in high yields [94]. Proposed structures of two of these products are shown in (**43a**) and (**43b**). One iodide in [$WI_2(CO)(dmpe)(\eta^2$-MeCCMe)] was removed by $AgBF_4$ in acetonitrile to give the cationic complex [WI(CO)(NCMe)(dmpe)(η^2-MeCCMe)] which readily substituted urea and thiourea for the solvent molecule.

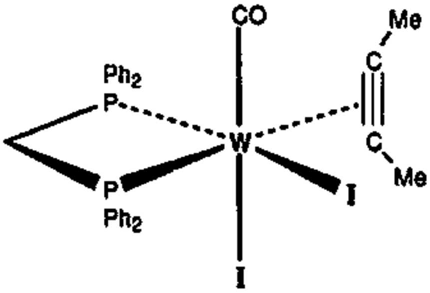


(43a)



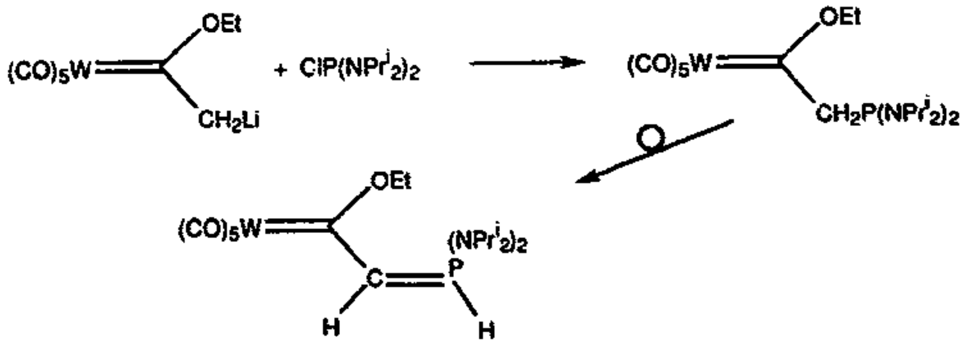
(43b)

The cationic complex [WI(NCMe)($Ph_2PCH_2PPh_2$)(η^2-MeCCMe)][BF_4] was found to react with an equimolar amount of alkali metal salts MX (MX = NaCl, NaBr, NaI, KNO_2, KNO_3, NaNCS, or KOH) in acetone to give neutral [WIX($Ph_2PCH_2PPh_2$)(η^2-MeCCMe)] (*e.g.* (**44**)) complexes in good yields [95]. These have been characterized by elemental analysis, IR, and ^1H NMR spectroscopy.



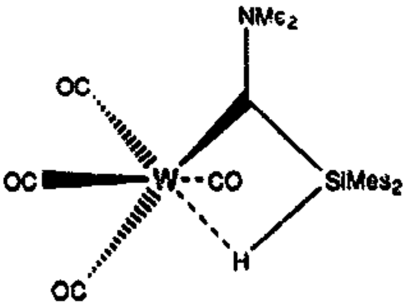
(44)

The synthesis of a PH-functionalized ylidic carbene complex of tungsten was reported [96]. This was formed from the reaction of [$(CO)_5W{=}C(OEt)CH_2Li$] with $ClP(NPr^i_2)_2$ to give the transient α-phosphinoalkylcarbene complex which then rearranged to the final product (Scheme 36). The structure of the chromium analogue has been determined by X-ray diffraction.



Scheme 36

A strong W---H---Si interaction was found in the 16-electron carbene complex $W(CO)_4[C(NMe_2)(SiHMes_2)]$ (45). This was the product of the photolysis of the carbene complex $W(CO)_5[C(NMe_2)(SiHMes_2)]$ which led to loss of one carbonyl ligand. The agostic interaction resulted in a very low J_{SiH} of 106 Hz and the location of the hydrogen in a bridging position between the Si and W atoms was confirmed in the X-ray structural analysis [97].

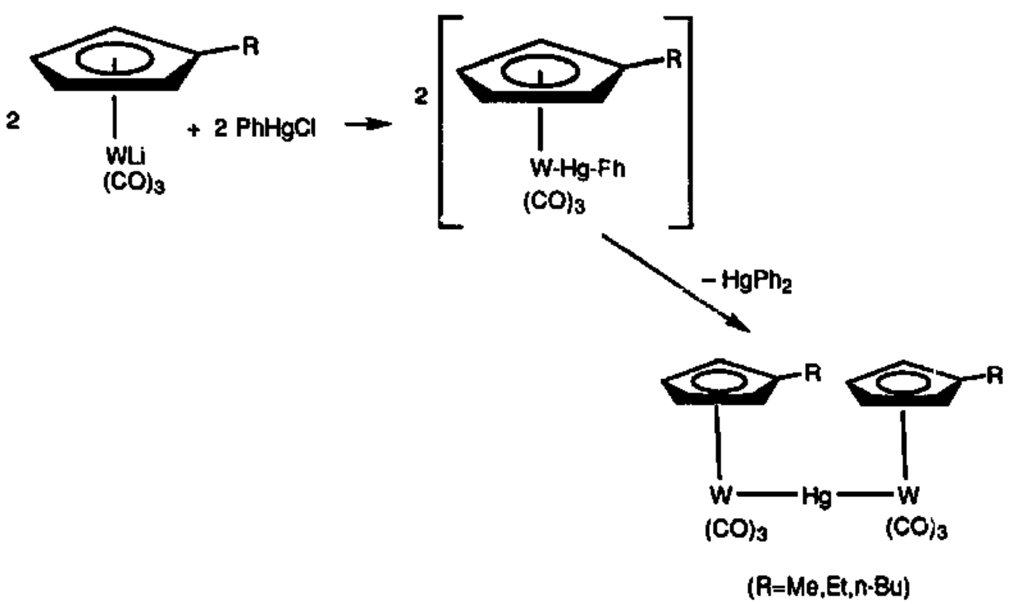


(45)

Imidazole and pyrazole tungsten complexes were obtained from the reactions of bis -alkyne complexes $[WI_2(CO)(NCMe)(\eta^2\text{-}RCCR)_2]$ (R=Me,Ph) with the respective ligand [98]. These were characterized by elemental analyses, and infrared and ^1H NMR spectroscopies. Picolinic acid, nicotinic acid, isonicotinic acid, and dipicolinic acid and $[WBr_2(NO)_2]_n$ in thf gave complexes of the type $[WBr_2(NO)_2{\cdot}2HL]_n$ [99]. Magnetic susceptibility measurements suggested diamagnetic behavior for these products.

A complex featuring a platinum-tungsten bond can be formed from the metathesis reaction of $[CpW(CO)_3]^-$ with $PtMe(dppe)NO_3$ in thf [100].

Linear trimetallic tungsten-mercury compounds were obtained from phenylmercuric chloride and $Li[R\text{-}C_5H_4W(CO)_3]$ (Scheme 37) [101]. The X-ray structure of the dichromium analogue has been determined.



Scheme 37

Geometrical features of d^4 tungsten dicarbonyl complexes containing π-donor ligands have been studied using extended Hückel molecular orbital calculations [102]. These include the $[H_3W(CO)_2(L)]^{2-}$ (where L = SH,OH,NH_2,NMe_2) and $[H_3W(CO)_2(HCCH)]^-$ species. Results revealed interplay between the OC-W-CO angle and orientation of the *cis*-π-donor ligand. Similar orientations of the π-donor ligand were observed whereby each encountered a rotation barrier around the W-ligand axis.

Reactions of $CpWI_3(CO)_2$ with thallium salts TlOAr in thf did not yield simple substitution products but led to the reduced species $[CpW(OC_6F_5)(CO)_3]$, oxidized species $[W(OC_6H_4Me)_6]$, or the thallium tritungsten derivative $Tl\{CpW(CO)_3\}_3$ [103]. Reaction of $[CpWBr_3(CO)_2]$ with $TlSeC_6F_5$ led to $[CpW(SeC_6F_5)_3(CO)]$ and $[CpW(SeC_6F_5)(CO)_3]$. Further reaction with excess thallium salt formed $TlCpW(SeC_6F_5)_4$. Dynamic ^{19}F NMR spectroscopic studies showed these to be fluxional.

7.6 TUNGSTEN(I) COMPLEXES

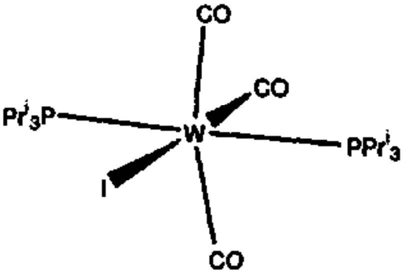
Stable and intensely coloured 17-electron radical complexes were obtained from the reaction of disulfides and iodine with $[W(CO)_3(PPr^i_3)_2]$ [104]. Specifically, the reaction in Scheme 38 was found to yield $[W(CO)_3(PPr^i_3)_2(SPh)]$ with a ΔH of −18.9(1.2) kcal mol^{-1}. Iodination led to $[W(CO)_3(PPr^i_3)_3I]$ (46) whose structure has been determined by X-ray diffraction to be near-octahedral and without any solid-state dinuclear interactions. Oxidative addition of thiols to the same precursor yielded the seven-coordinate complex $[W(CO)_3(PPr^i_3)_2(SR)H]$ with very weak W-H bonds. Hydrogen-transfer between this complex and the six-coordinate radical $[W(CO)_3(PPr^i_3)_2I]$ was facile at room temperature (Scheme 39).

$$W(CO)_3(PPr^i_3)_2 + 0.5\ PhSSPh \xrightarrow{\text{toluene}} W(CO)_3(PPr^i_3)_2SPh$$

Scheme 38

$$W(CO)_3(PPr^i_3)_2I + W(CO)_3(PPr^i_3)_2(SPh)(H) \longrightarrow W(CO)_3(PPr^i_3)_2(H)(I) + W(CO)_3(PPr^i_3)_2SPh$$

Scheme 39



(46)

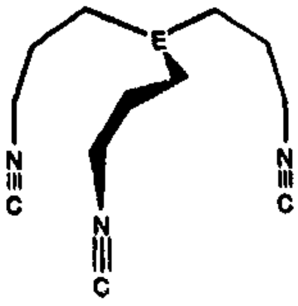
Thermolysis of the W-W bonded $[(\eta^5\text{-}C_5H_4\text{-}Bu^n)W(CO)_3]_2$ in toluene or diglyme yielded the triply-bonded dimer $[(\eta^5\text{-}C_5H_4\text{-}Bu^n)W(CO)_2]_2$ [105]. Further reaction with $Co_2(CO)_8$ led to $[(\eta^5\text{-}C_5H_4\text{-}Bu^n)W(CO)_3Co(CO)_4]$ presumably through a Co_2W_2 cluster intermediate.

7.7 *TUNGSTEN(0) COMPLEXES*

7.7.1 *Complexes with carbon ligands*

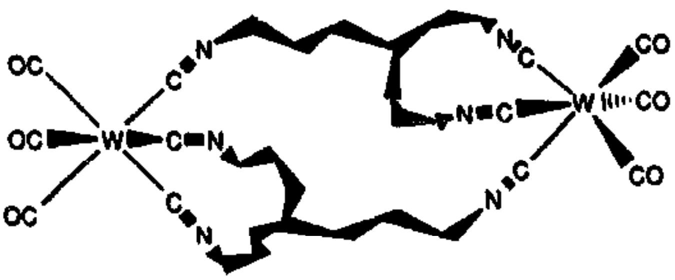
An annual survey on Cr, Mo, and W chemistry covering the year 1992 was published [106].

Photochemical carbonyl substitution at $W(CO)_6$ with tene in toluene afforded $W(CO)_4(\eta^2\text{-tene})$ [107]. Electronic, IR, and ^{13}C NMR spectra confirmed symmetrical binding of the alkene through its C=C bond with significant W→ligand π-interaction. The aliphatic tripodal triisocyanide ligands (47) reacted with [(cycloheptatriene)W(CO)$_3$] to give the respective *fac*-complexes [108]. Small amounts of a dimeric *fac,fac*-$[\{N(CH_2CH_2CH_2NC)_3\}W(CO)_3]_2$ complex (48) was also obtained for the nitrilo-ligand.



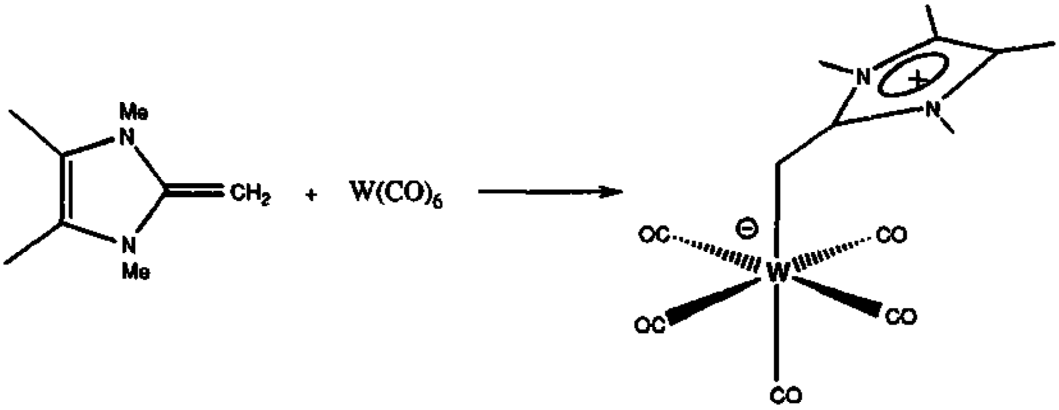
(E = CH,N)

(47)



(48)

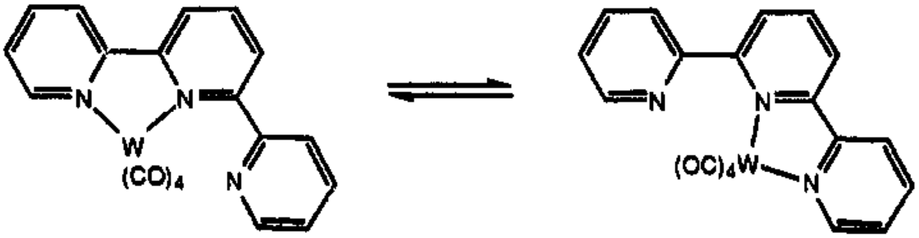
The complex $(C_8H_{14}N_2)W(CO)_5$ was obtained from $W(CO)_6$ and 1,3,4,5-tetramethyl-2-methyleneimidazoline (Scheme 40) [109]. X-ray structural determination of the molybdenum analogue revealed the ylidic end-on donation.



Scheme 40

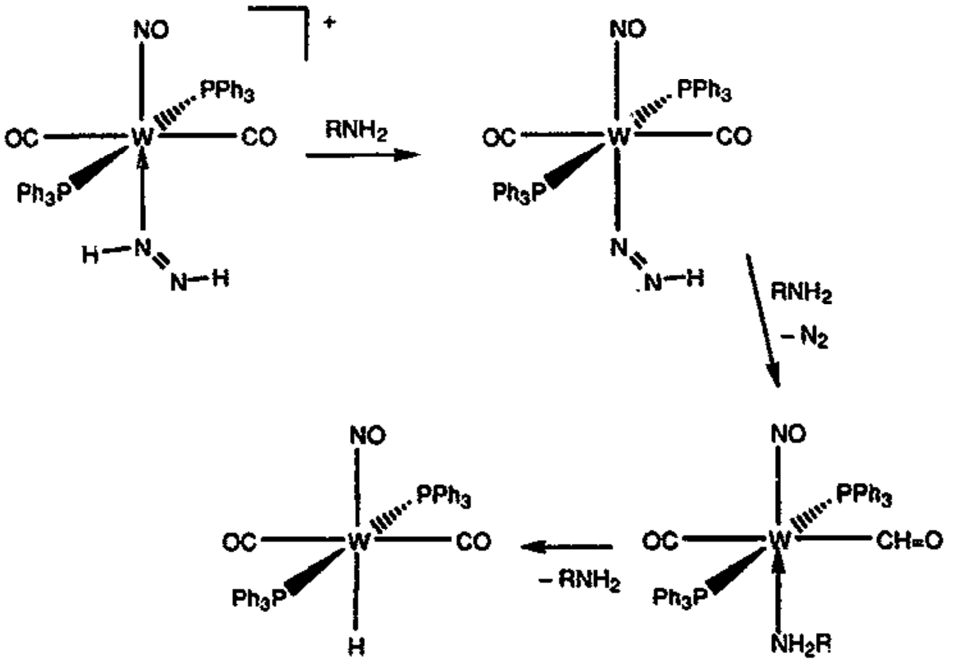
7.7.2 Complexes with nitrogen ligands

Under mild conditions, 2,2':6',2"-terpyridine (terpy) reacted with $[W(CO)_4(nbd)]$ to form octahedral *cis*-$[W(CO)_4(terpy)]$ [110]. The terpyridine was found to be didentate and, in solution, ^1H NMR spectroscopic studies revealed that this complex was fluxional with the ligand oscillating between equivalent didentate binding modes (Scheme 41).



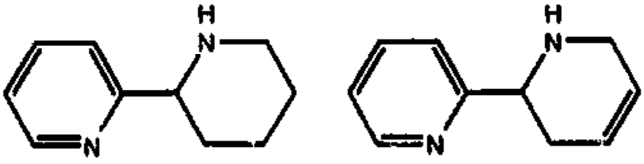
Scheme 41

Ammonia, methylamine, and hydrazine reacted with the tungsten diazene complex [*trans,trans*-$W(HN{=}NH)(CO)_2(NO)(PPh_3)_2][SO_3CF_3]$ to give *trans,trans*-$[W(\eta^1\text{-}OSO_2CF_3)(CO)_2(NO)(PPh_3)_2]$, [*trans,trans*-$W(H)(CO)_2(NO)(PPh_3)_2][SO_3CF_3]$, and [*trans, trans*-$W(NH_2NH_2)(CO)_2(NO)(PPh_3)_2][SO_3CF_3]$[111]. Interestingly, neutral formyl intermediates were characterized by multinuclear NMR spectroscopy and ^2H and ^{13}C-labelling experiments as [*trans*-$W(HC{=}O)(CO)(NO)(NH_2R)(PPh_3)_2][SO_3CF_3]$ (R=H, Me, NH_2). A reaction mechanism was proposed based on initial deprotonation of the diazene ligand followed by H-migration from nitrogen to carbonyl to give the formyl intermediate, and finally H-migration again to the metal to give the neutral hydride product (Scheme 42).



Scheme 42

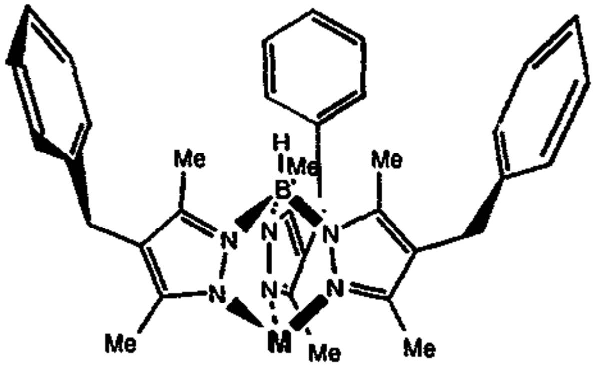
Two polyhydro derivatives of ligands (49) were used to form complexes with *cis*-[$W(CO)_4(piperidine)_2$] [112]. These were found to have solvatochromic properties.



(49)

A computational study of molybdenum and tungsten dinitrogen complexes of the type *trans*-[$M(A)_2(N_2)_2$] (M = Mo, A =PH_3,SH_2; M=W, A=PH_3) using local density functional theory discrete variational X_α calculations has been performed [113]. Reasonable qualitative correlation between theory and experimental data with respect to M-ligand bonding, N-N stretching frequencies, and the sites and relative rates of attacked on coordinated N_2 by protons and organic radicals was demonstrated. It was claimed that the DVX_α method gave a better description of the charge distribution compared to ab initio Hartree-Fock theory.

Benzyl-substituted pyrazolylborato Mo and W complexes with an inverted bowl-like structure were prepared and characterized [114]. Reaction of K[tris(4-benzyl-3,5-dimethylpyrazolyl)borate] (K[HB(bdmpz)$_3$]) with $M(CO)_6$ (M = Mo, W) and *p*-$MeC_6H_4SO_2N(NO)Me$ gave [$M(CO)_2(NO)$\{HB(bdmpz)$_3$\}]. Spectral and electrochemical studies showed no significant electronic effect from the benzyl substitution. A molecular structure determination of the molybdenum complex (50) revealed a geometry where the phenyl rings adopted an inverted bowl-like configuration with the BH group inside and the $Mo(CO)_2(NO)$ group (M) outside.



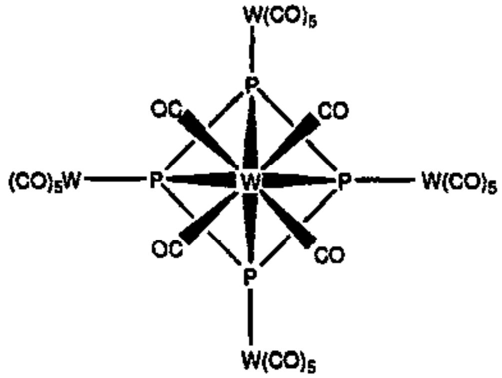
(50)

In an important study, time-resolved infrared spectroscopy was used to probe the electron distribution in the MLCT excited state of $[(CO)_5W(4,4'\text{-bpy})W(CO)_5]$ [115]. Shifts in the CO stretches were compared with the mononuclear $[(CO)_5W(4,4'\text{-bpy})]$ data to gauge the extent of valence delocalization in the dinuclear analogue. In a significant finding, it was concluded that the excited state can be characterized as a valence-localized $^*[W^I(4,4'\text{-bpy}^{-\cdot})W^0]$ species with spectroscopically distinct W^I and W^0 centres.

Reaction of spiro-(amino)cyclotriphosphazenes $N_3P_3(NMe_2)_4(NHCH_2CH_2NH)$ and $N_3P_3(NMe_2)_4(NHCH_2CH_2CH_2NH)$ with $W(CO)_6$ gave $W(CO)_4$(ligand) complexes featuring a chelating ligand using one phosphazene ring N and one of the NMe_2 groups [116].

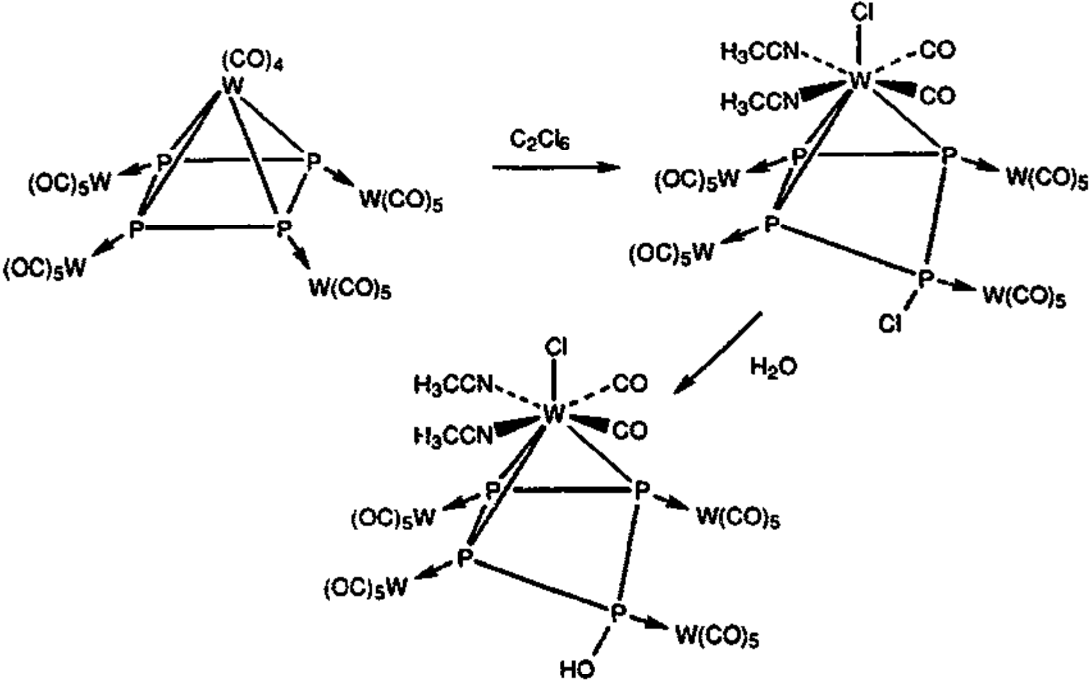
7.7.3 Complexes with phosphorus, arsenic or antimony ligands

The structure of homoleptic $W[PF_2Ph]_6$ has been determined [117]. The octahedral complex has significantly shortened W-P bonds of 2.375(2)Å compared to W-PMe_3, W-dmpe, and W-PF_2Bu^t analogues.



(51)

Reactions of white phosphorus with $W(CO)_5{\cdot}thf$ afforded a product $[(CO)_4W(\eta^4\text{-}P_4\{W(CO)_5\}_4]$ (**51**) containing square-planar cyclo-P_4 as a 12-electron donor with all P atoms coordinated [118]. Further reaction with hexachloroethane in acetonitrile gave first a dichloro derivative which was rapidly hydrolyzed by adventitious moisture to a phosphahydroxy product (Scheme 43).

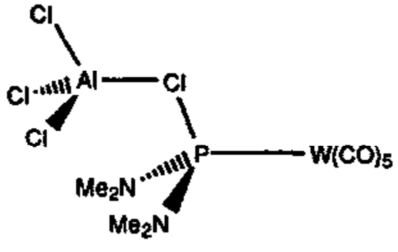


Scheme 43

Crystal structures of all nine [$M(CO)_5EPh_3$] (where M=Cr, Mo, or W and E = P, As, Sb) have now been determined in a systematic study [119]. Trends in bond lengths and angles were rationalized in terms of steric and electronic interactions between the $M(CO)_5$ and ligand fragments. Torsion angles defining the disposition of the EPh_3 ligands show little variation; all nine structures feature the propeller geometry with only small deviations from C_3 symmetry. Inclusion of other $M(CO)_5L$ structures gave a database of 29 compounds. It was shown that trends in structural parameters can be correlated to steric and the π–acceptor properties of a specific ligand L. In a related study, stereostructural preferences of the nine [$M(CO)_5EPh_3$] (M=Cr, Mo, W; E=P, As, Sb) complexes have been explored by investigating the electro-optical Kerr effect, electric dipole moments, IR carbonyl stretching frequencies, molecular mechanics calculations, as well as X-ray structural data [120]. It was found that in all gas, solution and solid states, phenyl ring dispositions of like helicity are favoured for the coordinated EPh_3 ligands.

Quantitative interpretation of A/D parameters for electronic excitations in *trans*-$M(CO)_4[P(n\text{-}Bu)_3]_2$ (where M=Cr, Mo, W) have been reported [121]. From deconvolution of electronic absorption (EA) spectra and circular dichroism spectra, the first EA band at about 27 x 10^3 cm^{-1} has been assigned to the $^1A_{1g}[e_g{}^4$ (approximately $d_{xz,yz}$)$] \rightarrow (x,y)^1E_{ua}[e_g{}^3a_{2u}{}^1$ (mainly π^*CO)] transition while the third band at around 39 x 10^3cm^{-1} was assigned to the $^1A_{1g}[b_{2g}{}^2$(mainly d_{xy})$] \rightarrow (x,y)^1E_{ub}[b_{2g}{}^1e_u{}^1$ (mainly π^*CO)] transition. The middle band at around 30 x 10^3 cm^{-1} was assigned to the z-polarized $^1A_{1g}[e_g{}^4$(mainly $d_{xz,yz}$)$] \rightarrow (z)^1A_{2u}[e_g{}^3e_u{}^1$(mainly π^*CO)] transition.

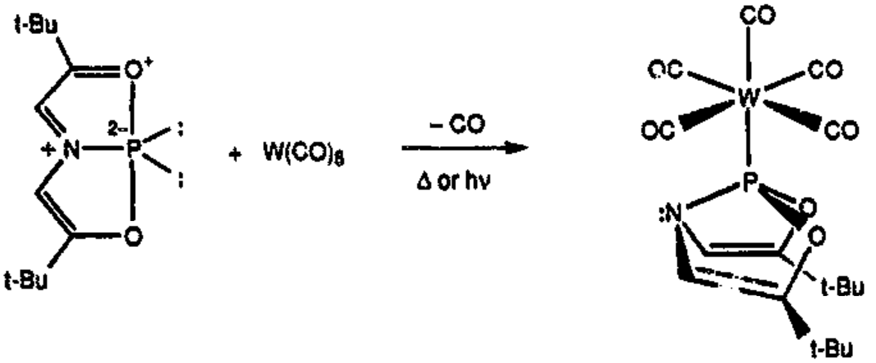
Reactions of haloamidophosphine ligands with $W(CO)_5$.thf afforded the complexes [$W(CO)_5P(NMe_2)_2Cl$] and [$W(CO)_5P(N(Me)CH_2CH_2NMe)Cl$] [122]. Spectral characterization by multinuclear NMR spectroscopy was used to gauge the σ-donor/π-acceptor ability of these ligands. An attempt to abstract a chloride from the complexes using $AlCl_3$ yielded unexpected adducts of the type [$W(CO)_5(PNMe_2)_2Cl \cdot AlCl_3$] (52).



(52)

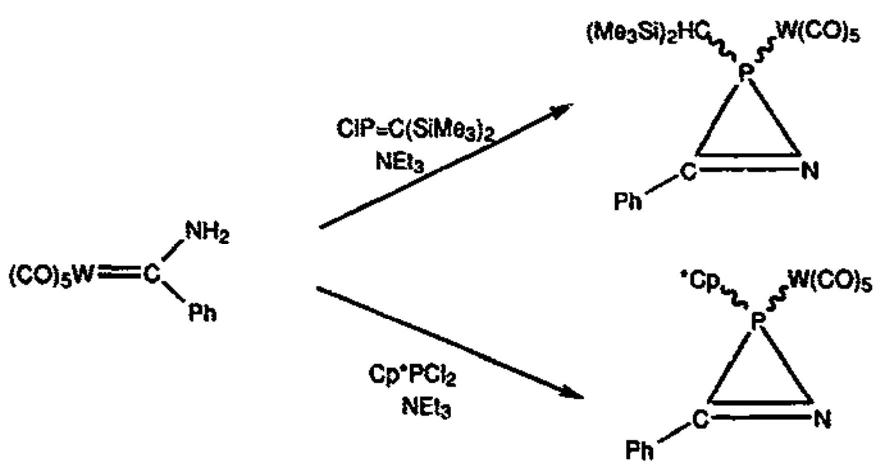
Pentacarbonylmetal complexes (M = Cr, Mo, W) of the bicyclic phosphite $P(OCH_2)_3CMe$ has been examined for their polarities, anisotropic polarizabilities, and carbonyl IR vibrational frequencies as well as bond distances to provide reinforcing evidence for π-acid behavior of the ligand [123]. Strong polarizability enhancement along the molecular axis and concurrent decrease of polarizability perpendicular to this axis was noted. The results were interpreted for a highly deformable π-component in P-M bonding and a π-delocalized *trans*-P-M-CO system.

The hypervalent phosphorus ligand ADPO (5-aza-2,8-dioxa-1-phosphabicyclo[3.3.0]octa-2,4,6-triene) was found to form an adduct with the tungsten pentacarbonyl fragment [124]. Folding of the bicyclic ligand led to a tetrahedral P centre in the complex (Scheme 44).

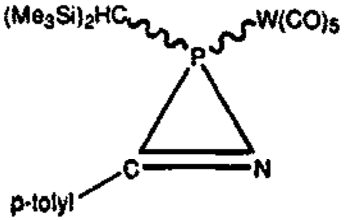


Scheme 44

Reactions of amino(aryl)carbene complexes of $W(CO)_5$ with chlorophosphine derivatives in the presence of triethylamine base led to 2H-1-aza-2-phosphirene complexes (Scheme 45) [125]. Investigations of thermally-induced ring opening reactions in the presence of trapping agents were also presented. A surprisingly low thermal stability was found for the 2H-1,2-azaphosphirene pentacarbonyltungsten complex (53) [126]. At 45°C in toluene, the complex reacted with excess benzaldehyde to give an oxaphosphirene complex (54) with diastereoselectivity, presumably via a phosphanediyl intermediate [$(Me_3Si)_2CHPW(CO)_5$].



Scheme 45



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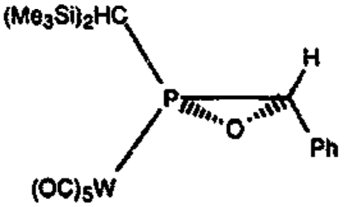
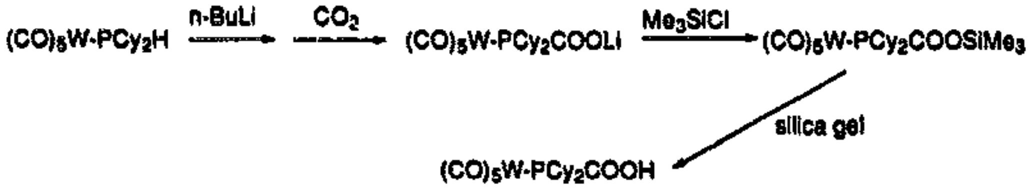


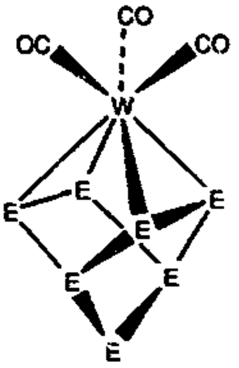
(54)

Previously unknown phosphorus analogs of carbamic acids have been stabilized as ligands in the complexes [$W(CO)_5(PRR'COOH)$] (R, R' = organic groups or H) [127]. This was accomplished by the typical reaction sequence shown in Scheme 46 from [$W(CO)_5(PCy_2H)$]. These products were characterized by IR, MS, ^1H, ^{13}C, and ^{31}P NMR spectroscopies.



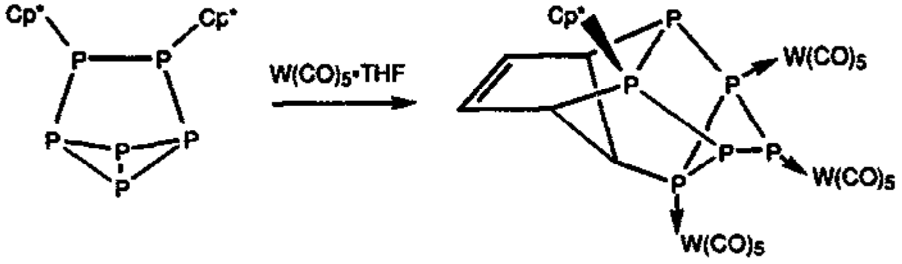
Scheme 46

Ethylendiamine solutions of K_3E_7 (E = P, As, Sb) were found to react with toluene solutions of [(η^6-Mes)$W(CO)_3$] in the presence of three equivalents of 2,2,2-crypt to give [K(2,2,2-crypt)]$_3$[$E_7W(CO)_3$] [128]. Structural and spectral characterization of these and their Cr and Mo analogues revealed distorted norbornadiene-like [η^4-E_7]$^{3-}$ clusters bound to $W(CO)_3$ moieties as shown in structure (55). Carbon-13 and ^{31}P NMR spectrocopic studies as well as IR and electronic spectral data were presented. The 3,4-bis [pentamethylcyclopentadienyl]-tricyclo[3.3.0(2,6)]hexaphosphane $Cp^*{}_2P_6$ was found to react with $W(CO)_5$•thf to give $Cp^*{}_2P_6[W(CO)_5]_3$ according to Scheme 47 [129].

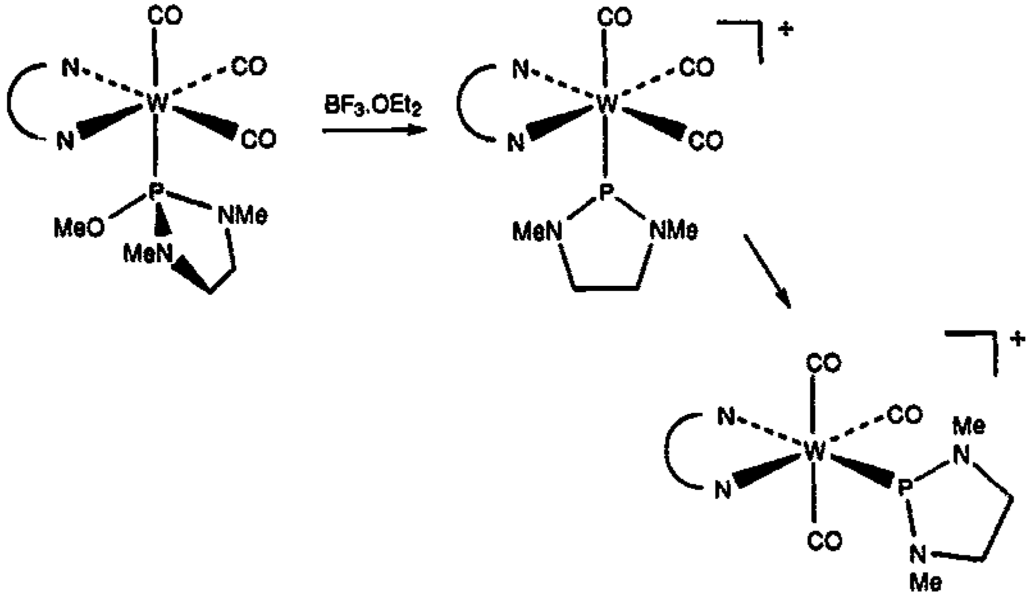


(E = P, As, Sb)

(55)

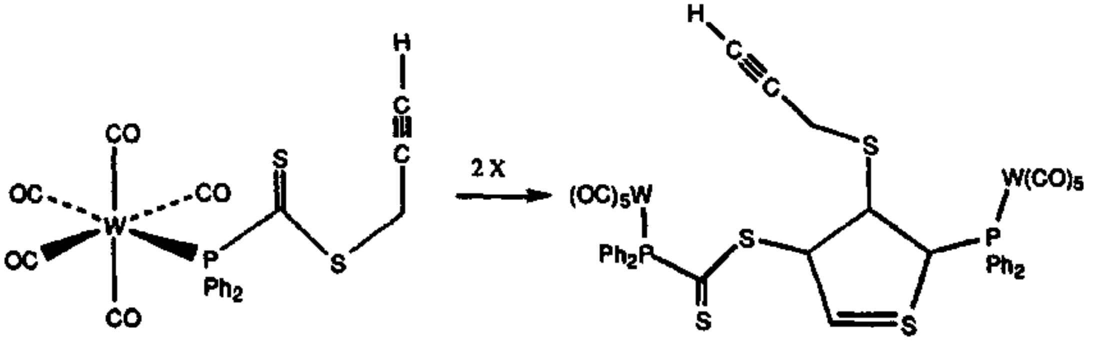


Scheme 47



Scheme 48

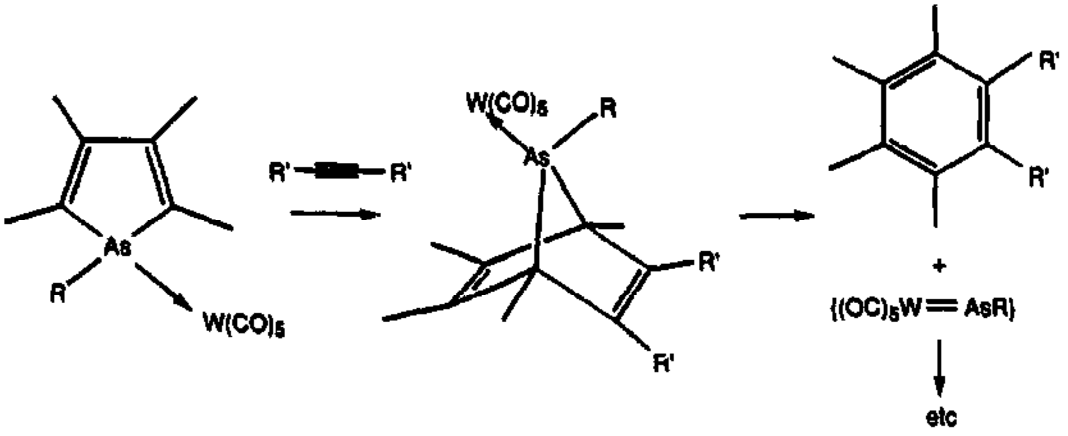
A *fac*-to-*mer* isomerization occurred spontaneously upon formation of the phosphenium *fac*-{W(bpy)(CO)$_3${PN(Me)CH$_2$CH$_2$N(Me)}]$^+$ complex [130]. This cation was formed by methoxy extraction from the precursor *fac*-[W(bpy)(CO)$_3${P(OMe)N(Me)CH$_2$CH$_2$N(Me)}] using BF$_3$•OEt$_2$ (Scheme 48). The isomerization rate was found to follow the order Cr>Mo>W. A slower isomerization was also observed for the related cationic complex *fac*-$[W(dppe)(CO)_3\{PN(Me)CH_2CH_2N(Me)\}]^+$.



Scheme 49

The propargylthio-tungsten complex $W(CO)_5[PPh_2(CS_2C_3H_3)]$ was found to undergo a dimerization reaction to give $W_2(CO)_{10}[P_2Ph_4(C_8H_6S_4)]$ (Scheme 49) [131]. An X-ray diffraction study confirmed the formation of this dimer. Deuterium labeling studies along with observed solvent effect suggested that this involved an unprecedented sulfur-assisted intermolecular cycloaddition of the propargyl and thiocarbonyl groups to give a 5-membered thiolene heterocycle. Protonation of the same precursor induced an intramolecular cyclization instead to give $W(CO)_5[PPh_2(CS_2C_3H_4)]BF_4$.

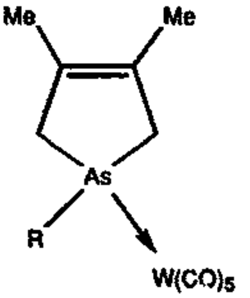
An unusually strong retardation of a bipyridyl chelate ring closure by a coordinated $P(OMe)_3$ ligand was observed in the complex *cis*-$[W(CO)_4P(OMe)_3(\eta^1\text{-bpy})]$ [132]. It neither underwent *cis*-to-*trans* isomerization nor chelation up to 150°C. Photolysis did effect this ring closure. This retardation was attributed to a reduced carbonyl lability.



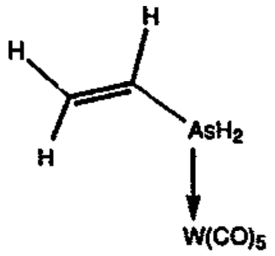
Scheme 50

Arsole complexes of tungsten were prepared from tetramethylarsoles with a variety of substituents at arsenic [133]. These included $[W(CO)_5(\text{arsole})]$, *cis*-$[W(CO)_4(\text{arsole})(\text{piperidine})]$ and *cis*-$[W(CO)_4(\text{arsole})(P^iPr_3)]$. Diels-Alder reactions with acetylenes led to unstable 7-arsanorbornadiene intermediates which decomposed to arene and arsinidene complexes (Scheme

50). Pentacarbonyl tungsten complexes (**56**) of 3-arsolenes have also been reported [134]. Primary unsaturated arsines including vinylarsine, isopropenylarsine, (*E*/*Z*)-prop-1-enylarsine, and secondary divinylarsine were prepared and found to be unstable at room temperature [135]. A pentacarbonyltungsten complex of vinylarsine has been prepared (**57**).



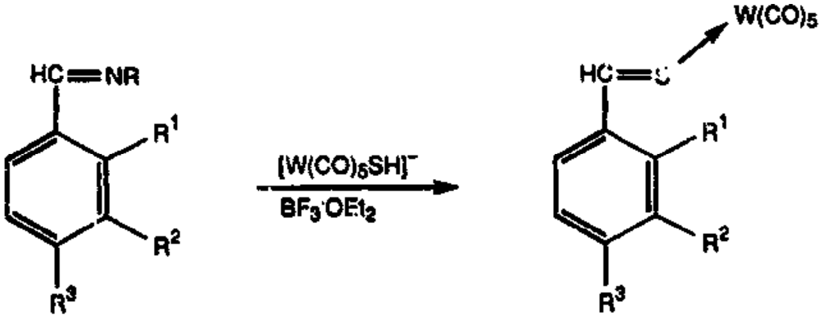
(**56**)



(**57**)

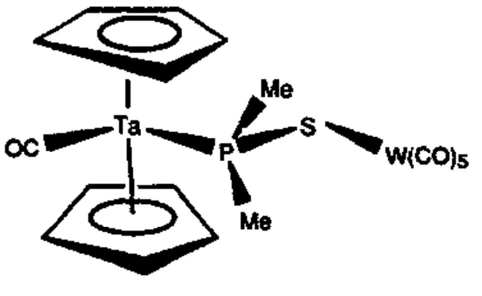
7.7.4 *Complexes with sulfur, selenium, germanium or tin ligands*

The reaction of [PPh$_4$][SH] and W(CO)$_5$•thf gave a new reagent [PPh$_4$][W(CO)$_5$SH] which was used to react with aldimines in the presence of an equimolar mixture of BF$_3$•Et$_2$O and acetic acid[136]. The products are complexes of aromatic thioaldehydes (Scheme **51**).



Scheme 51

Thiophosphoramides of niobocene and tantalocene were reported to form heterodimetallic complexes by donation from the thio group to W(CO)$_5$ (**58**) [137]. Reactions of the 1,2,3,4,5-tetrachalcogenastannolanes Tb(Tip)SnE$_4$ (where Tb = 2,4,6-tri(bis -trimethylsilylmethyl)phenyl, Tip =2,4,6-triisopropylphenyl, and E = S, Se) with W(CO)$_5$•thf yielded 1:1 complexes [138]. The sulfur complex (**59**) was found to have the sulfur β to the tin coordinated to W. The first base-free diarylgermylene mononuclear complex of a transition metal has been reported [139]. This was synthesized by using the kinetically-stabilized carbene analogue Tb(Tip)Ge: to react with W(CO)$_5$.thf. The resulting complex (**60**) has been characterized by a structural determination. Tin dichloride has been shown to act as a bridging ligand in the ditungsten complex obtained from the direct reaction of SnCl$_2$ with alkali metal salts of [W$_2$(CO)$_{10}$]$^{2-}$ in the presence of 12-crown-4 or [2,2,2]cryptands [140]. The resulting [W(CO)$_5$]$_2$(μ-SnCl$_2$)$^{2-}$ dianion has a W-Sn-W angle of about 130°.



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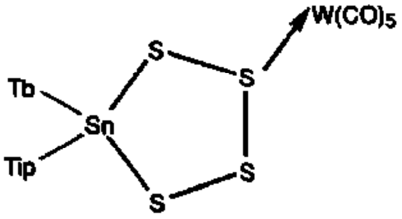

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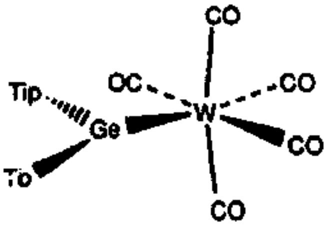

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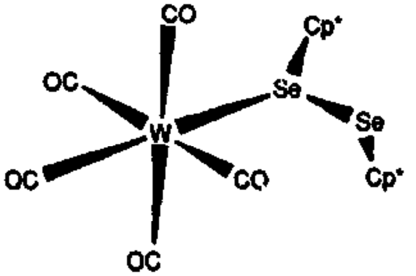
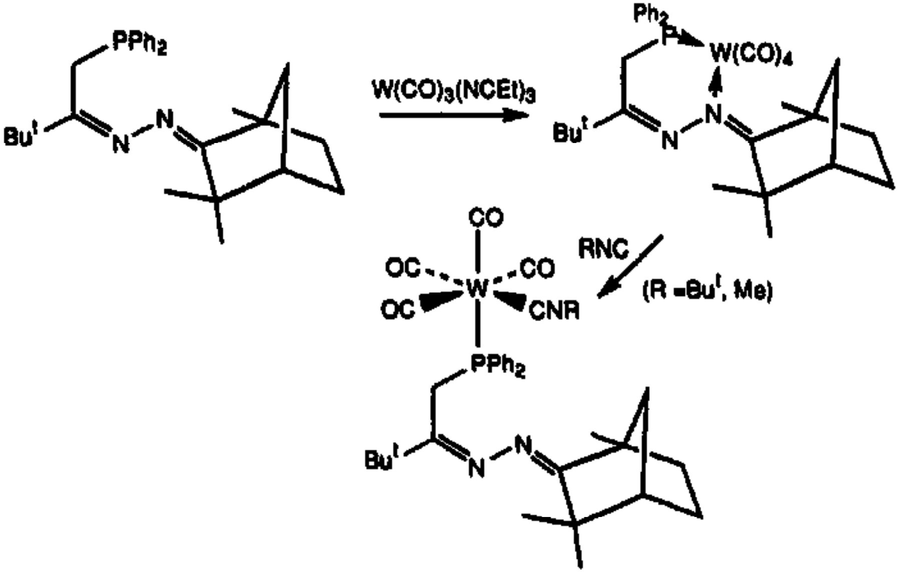


(61)

Complexes of the diselenide $Se_2Cp^*_2$ have been prepared from the reaction of $Se(Cp^*)_2$ with $M(CO)_5$ (M = Cr, W) sources [141]. These represent the first examples of selenide-to-diselenide reduction in the coordination sphere of a metal. The X-ray structure of the tungsten complex (61) was reported. The W-Se distance was 2.671(1)Å, Se-Se separation was 2.330(1)Å.

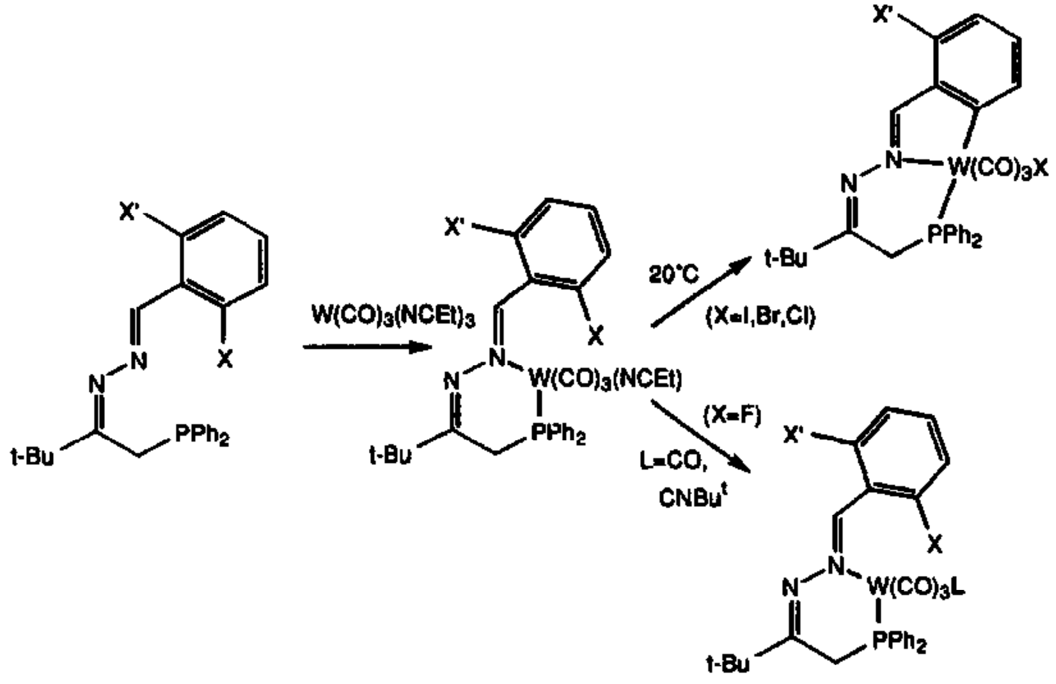
7.7.5 *Complexes with mixed donor ligands*

A fenchone-derived azine monophosphine was prepared and reacted with $[W(CO)_3(NCEt)_3]$ to give *cis*-$[W(CO)_4(\text{azinephosphine})]$ [142]. The P-N chelate ring can be partially substituted by organic isocyanides (Scheme 52).



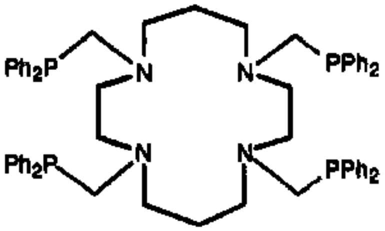
Scheme 52

Mixed azine phosphines of the type $PPh_2CH_2C(Bu^t)=N\text{-}N=CH(2\text{-halo-}C_6H_4)$ were reacted with $[W(CO)_3(NCEt)_3]$ to give *cis*-complexes with chelated P-N rings [143]. These readily underwent C-halogen cleavage to give seven-coordinate W(II) products (Scheme 53).



Scheme 53

A derivative of cyclam with four pendant diphenylphosphino arms (**61**) has been used to coordinate four separate $W(CO)_5$ units [144].



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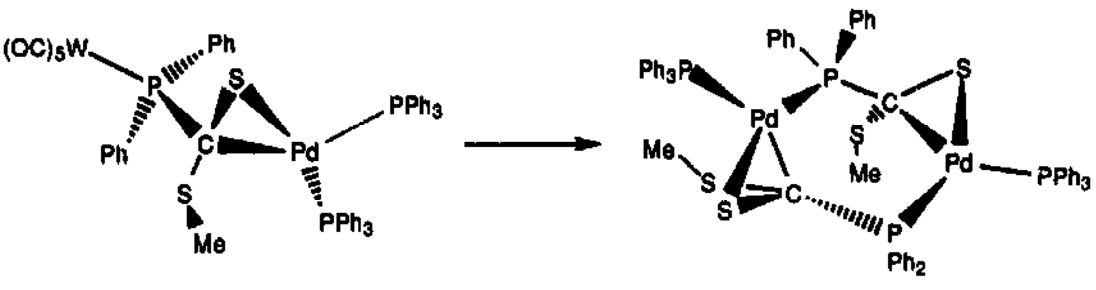
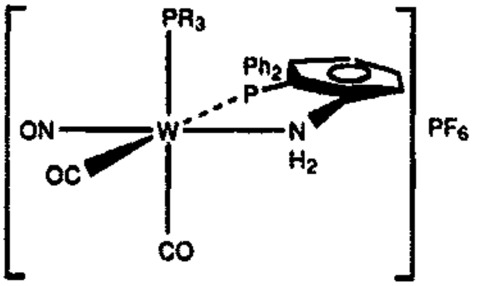


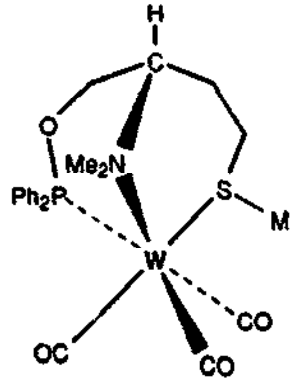
Scheme 54

Transfer of a phosphine ligand from tungsten to palladium has been observed in the reaction of $W(CO)_5[PPh_2(CS_2Me)]$ and $Pd(PPh_3)_4$ [145]. This was shown to occur via the η^2-bridging of the C=S group to Pd in the $[Pd(PPh_3)_2]$-μ,η^1,η^2-$MeS_2CPPh_2[W(CO)_5]$ intermediate to give $[Pd(PPh_3)$-μ,η^1,η^2-$MeS_2CPPh_2]_2$ (Scheme 54). The X-ray structures of the intermediate and product were both determined.

Mixed phosphine complexes of tungsten were prepared from the reaction of PR_3 with $[W(CO)_5Cl]^-$ followed by treatment of the resulting $[W(CO)_4(PR_3)Cl]^-$ with $PPh_2(2\text{-}C_6H_4X)$ (where X = NH_2, COOH) [146]. No well-defined nitrosyl derivatives were available from the reaction of these products with $NOPF_6$. However, preformed species like $[W(CO)(NO)(PR_3)FPF_5]$ and $[W(CO)_2(CO)(NCMe)_3]^+$ could be treated with the appropriate $PPh_2(2\text{-}C_6H_4X)$ ligand to give the desired products (*e.g.* (**62**)). Tungsten(0) complexes featuring chiral tridentate ligands derived from L-methionine and L-cysteine with *N*-, *P*-, and *S*-donors have been reported [147].These provided a chiral asymmetric environment at the metal as confirmed by an X-ray structural determination of (**63**).

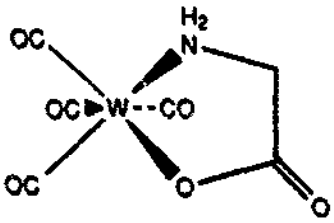


(**62**)



(**63**)

Aminoacid derivatives of tungsten(0) have been synthesized from $W(CO)_5$(thf) and the $[NEt_4]^+$ salt of the appropriate α-aminoacid in thf [148]. The glycine product was found to be highly water soluble and its structure was confirmed by X-ray diffraction. A slightly-distorted octahedral coordination geometry was found at W with a puckered five-membered glycinate chelate ring (**64**). Intermolecular H-bonding between N and H in the solid state and weaker interactions in solution were cited for the enhanced CO lability of this complex. Amine deprotonation and subsequent π-donation of the amide ligand in the transient species was believed to cause this labilization.



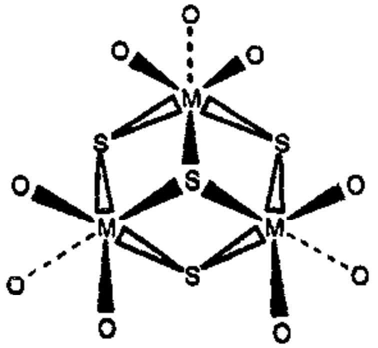
(**64**)

Air- and water-stable mixed-valent μ-cyano complexes of Cr, Mo, and W pentacarbonyls with Ru(III) and Os(III) have been prepared and characterized [149]. These have the general formula $[(CO)_5M^0(\mu\text{-}CN)(M')^{III}(NH_3)_5](CF_3COO)_2$. All were found to have Robin-Day Class II behaviour by spectroscopic and cyclic voltammetric studies. Moderately intense intervalence charge-transfer transitions were observed in the visible region while irreversible tungsten and molybdenum-centred oxidation waves were seen in their cyclic voltammograms.

7.8 CLUSTER COMPLEXES

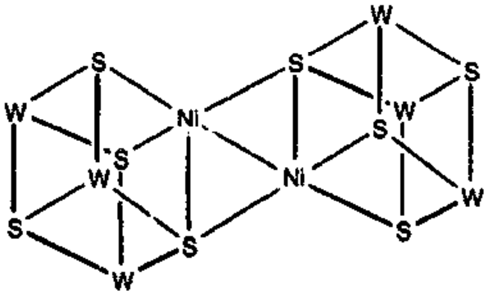
7.8.1 *Tungsten clusters*

Reduction of an equimolar amount of $(NH_4)_2[WS_4]$ and $Na_2[Mo_2O_2S_2(cys)_2]$ using $NaBH_4$ gave a mixture of S-bridged clusters including novel incomplete cubane Mo-W mixed-metal clusters $[MoW_2S_4(H_2O)_9]^{4+}$ and $[Mo_2WS_4(H_2O)_9]^{4+}$ [150]. Crystal structures of four derivatives of these have been determined. The core structure was as shown in (**65**). XPS spectra revealed only small changes as Mo and W vertices were replaced by each other due to the softness of the sulfur bridges which behaved as buffers. Electrochemical studies produced three consecutive one-electron reductions corresponding to (IV,IV,IV) → (IV,IV,III) → (IV,III,III) → (III,III,III) oxidation state changes. Half-wave potentials were dependent on the type of metals in the cluster.



M = Mo,W

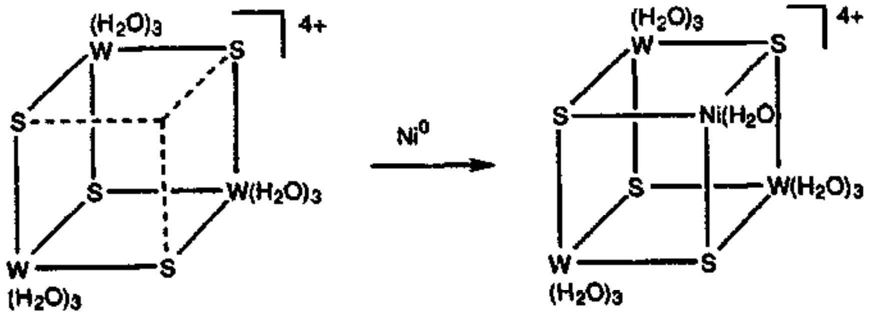
(65)



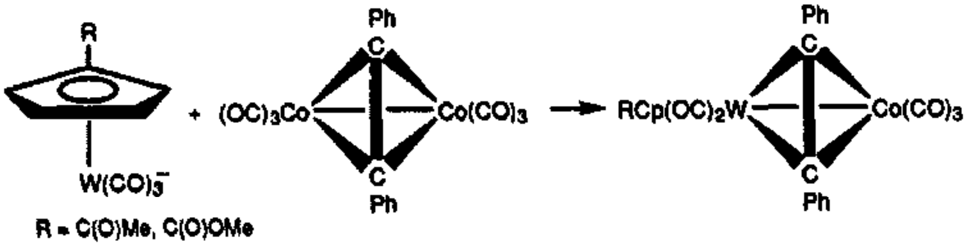
(66)

A related incomplete cubane cluster $[W_3S_4(H_2O)_9]^{4+}$ was reacted with nickel metal to give a mixed-metal cubane $[W_3NiS_4(H_2O)_{10}]^{4+}$ (Scheme 55) [151]. Toluenesulfonic acid and this cluster gave a product whose structure was determined by X-ray analysis and found to contain the double cubane core (**66**) with a formula of $\{[W_3NiS_4(H_2O)_9]_2\}(tosylate)_8$. Cubane-type heterometallic W_3Cu clusters were also prepared from the incomplete cuboidal $[W_3S_4(H_2O)_9]^{4+}$ precursor and copper metal or Cu(I) [152]. Both yielded the $[W_3CuS_4(H_2O)_{10}]^{5+}$ cluster, indicating that the 4+ cluster was less stable than in the Mo analogue. Oxidation with $[Co(pyridine\text{-}2,6\text{-}dicarboxylate)_2]^-$ and $[Fe(H_2O)_6]^{3+}$ regenerated $[W_3S_4(H_2O)_9]^{4+}$ and Cu(II). Kinetic studies revealed an outer-sphere redox mechanism and suggested involvement of the copper centre in the electron transfer process. Reactions of $Na[W(C_5H_4R)(CO)_3]$ with the $[Co_2(CO)_6(\mu\text{-}PhCCPh)]$

cluster yielded the respective mixed-metal clusters $[(C_5H_4R)W(CO)_2(\mu\text{-PhCCPh})Co(CO)_3]$ (Scheme 56) [153]. These were characterized by elemental analyses, IR and ^1H NMR spectroscopies and mass spectrometry. An X-ray structural determination of a Mo analogue was described.



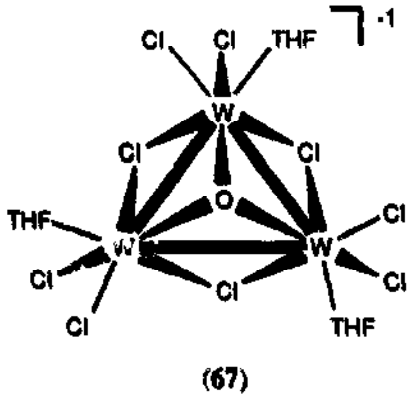
Scheme 55



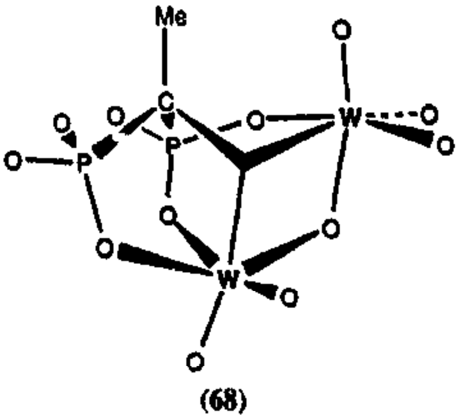
Scheme 56

Direct laser vaporization of mixtures of titanium carbide with tungsten was reported to produce metallocarbohedrene, with W substituting for Ti vertices in the parent Ti_8C_{12} cluster [154].

The first example of a triangular tritungsten cluster without acetate as a bridging ligand was obtained in low yield from the oxidation of $WCl_3(thf)_3$ with oxygen [155]. Structural analysis of this product revealed the $[W_3(\mu_3\text{-}O)(\mu\text{-}Cl)_3Cl_6(thf)_3]^-$ anion with a W-W distance of 2.605(2)Å (67).



(67)

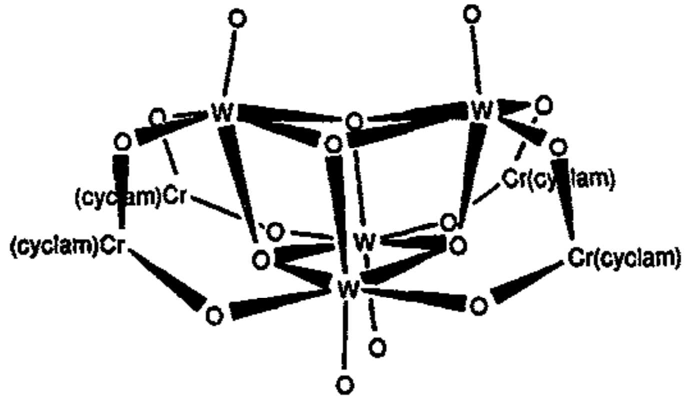


(68)

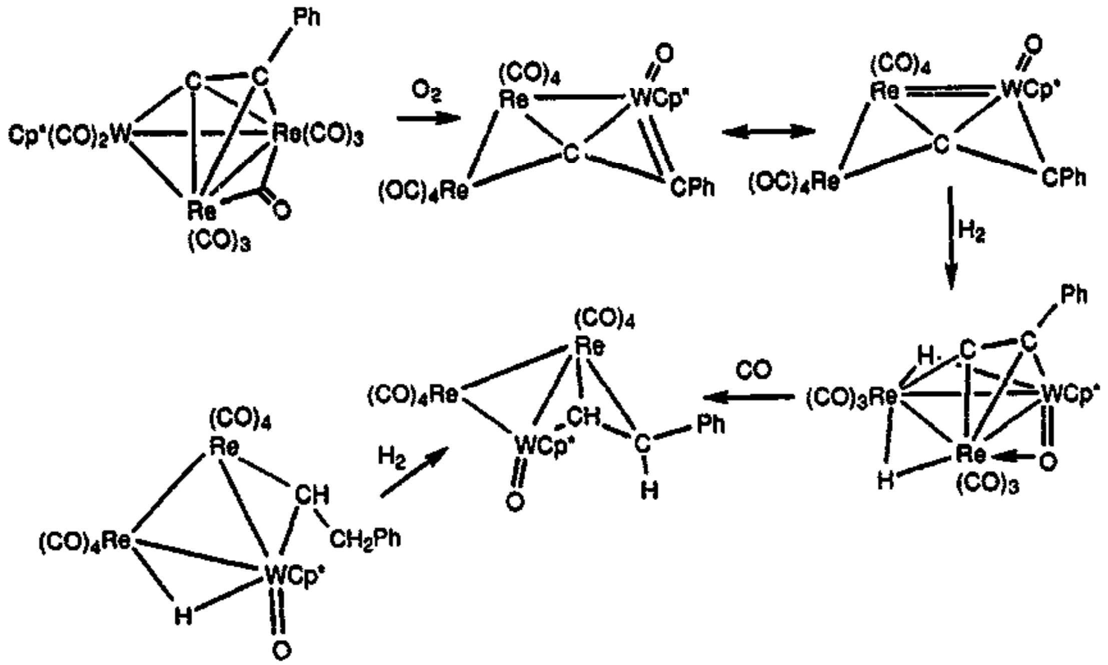
The reaction of $Na[W_3O_2(OOCEt)_9]$ with $Cr(CO)_6$ or alternately, $W(CO)_6$ with $CrCl_3 \cdot 6H_2O$ in propionic anhydride at 120°C gave an insoluble octametallic cluster $Na_2Cr_2[W_3O_4(OOCEt)_8]_2$ [156]. The skeletal conversion of $[W_3O_2(OOCEt)_9]^-$ into

$[W_3O_4(OOCEt)_8]^{4-}$ and the mode of formation were established. Use of $NaVO_3{\cdot}2H_2O$ and $W(CO)_6$ led to a vanadium analogue. These products were characterized by X-ray crystallography, IR spectra, and magnetic susceptibility measurements. The reaction of Na_2WO_4 with 1-hydroxyethylidenediphosphonic acid (H_5L^*) in the presence of guanidinium carbonate yielded $[C(NH_2)_3]_5[W_2O_6(L^*)]{\cdot}3H_2O$ which was structurally characterized [157]. The anionic core is shown in structure (68).

New di-, tetra-, and octametallic clusters containing W(VI) have been synthesized [158]. The crystal structure of $[WO_4Cr(cyclam)]_4(ClO_4)_4{\cdot}3H_2O$ was found to contain a distorted W_4O_4 cube as structure (69) illustrates. The cyclam ligands had the folded configuration in which alternate amine hydrogens were on opposite sides of the macrocycle. Magnetic susceptibility measurements revealed a *J* value of 8.41 cm^{-1}.



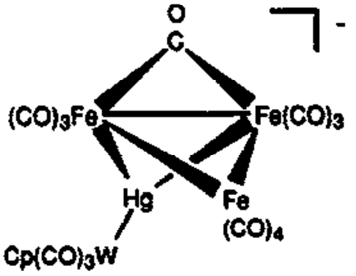
(69)



Scheme 57

Treatment of the acetylide cluster [$WRe_2Cp^*(CO)_9(CCPh)$] with O_2 or N_2O gave the new cluster [$WRe_2Cp^*(O)(CO)_8(CCPh)$] [159]. Hydrogenation of this yielded three isolable clusters, revealing an oxo-mediated sequential acetylide conversion to an alkenyl and then alkylidene group (Scheme 57).

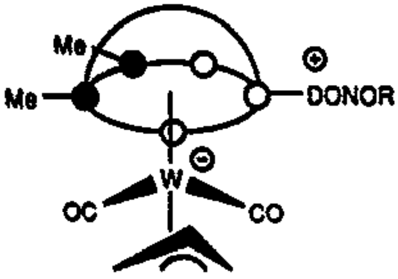
'Spiked butterfly' metal clusters including one with a Fe_3HgW core have been synthesized from the reaction of $[Fe_3(CO)_{11}]^{2-}$ with Cl-Hg-(metal) including $ClHg\text{-}W(CO)_3Cp$ [160]. Their IR FAB, and Mossbauer spectra were consistent with the spiked butterfly geometry (70). While these were stable towards metal/ligand redistribution processes, electrochemical oxidation led to paramagnetic species as identified by EPR spectroscopy which revealed the unpaired electron to be mostly localized in the Fe_3Hg core.



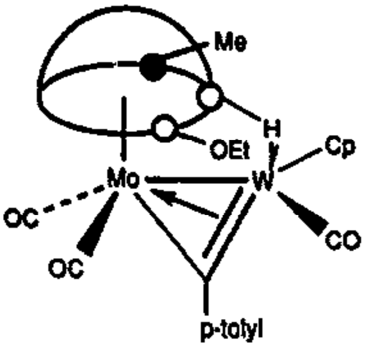
(70)

7.8.2 Boron clusters

Allylcarborane complexes of tungsten have been prepared by the hydride abstraction reaction of $NEt_4[W(CO)_2(allyl)(7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_9)]$ using CPh_3BF_4 in the presence of donor molecules like ether, pyridine, SMe_2, etc. [161]. The products were of the type [$W(CO)_2(allyl)(7,8,\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}donor)$] (71). The complex [$Mo(CO)_4(7,8\text{-}Me_2\text{-}7,8\text{-}C_2B_9H_8\text{-}10\text{-}OEt)$] reacted with the tungsten alkylidyne complex [$W(\equiv C\text{-}p\text{-}tolyl)(CO)_2Cp$] to give the Mo/W complex [$MoW(\mu\text{-}C\text{-}p\text{-}tolyl)(CO)_3Cp(2,8\text{-}Me_2\text{-}2,8\text{-}C_2B_9H_8\text{-}10\text{-}OEt)$ (72) whose structure has been confirmed by an X-ray study. The Mo–W bond was found to be 2.645(1)Å in length. Treatment of [$WBr(CO)_2(NCMe)_2(allyl)$] with $Na_2[7,9\text{-}C_2B_{10}H_{10}Me_2]$ gave the



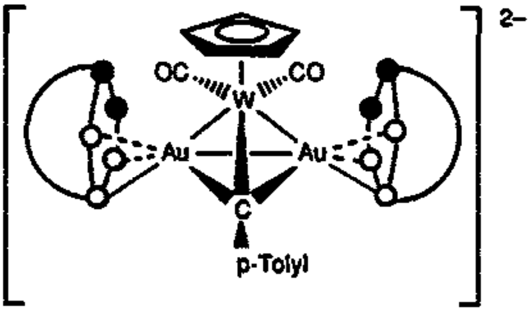
(71)



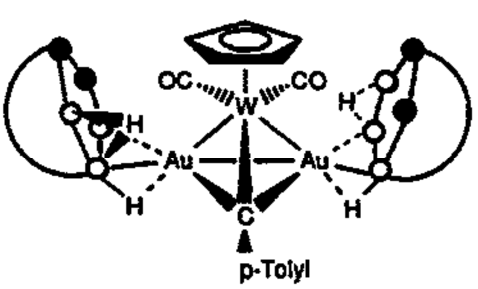
(72)

$[W(CO)_2(allyl)(7,9\text{-}Me_2C_2B_{10}H_{10}Me_2)]^-$ anion [162]. An excess of allyl bromide generated the $[WBr(CO)_3(7,9\text{-}C_2B_{10}Me_2)]$ anionic complex from $[W(CO)_3(7,9\text{-}C_2B_{10}H_{10}Me_2)]^-$ by an allyl-coupling reaction.

Gold-proton exchange was observed in a Au_2W carbaborane complex [163]. Reaction of $Tl[10\text{-}endo\text{-}\{Au(tht)\}\text{-}7,8\text{-}Me_2\text{-}nido\text{-}7,8\text{-}C_2B_9H_9]$ with $[CpW(C\text{-}tolyl)(CO)_2]$ followed by NEt_4Cl gave a deep-red Au_2W cluster $[NEt_4]_2[10,10'\text{-}endo\text{-}\{Au_2W(\mu_3\text{-}C\text{-}tolyl)(CO)_2Cp\}\text{-}nido\text{-}7,7',8,8'\text{-}(C_2B_9H_9)_2]$ (**73**). Reaction of this with $HBF_4{\cdot}Et_2O$ led to formation of $[9,9'\text{-}exo\text{-}\{Au_2W(\mu_3\text{-}C\text{-}tolyl)(CO)_2Cp\}\text{-}nido\text{-}7,7',8,8'\text{-}(C_2B_9H_{10})_2]$ (**74**) whose structure has been found to contain a tetrahedral CAu_2W core. Variable-temperature NMR spectroscopic studies revealed dynamic behaviour featuring exchange between gold and *endo*-hydrogens on the carborane cage open-faces (Scheme 58).



(73)



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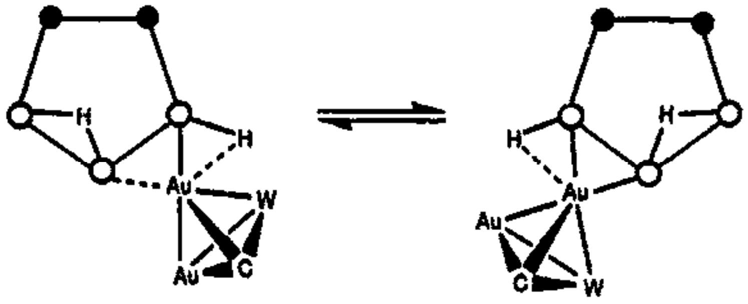
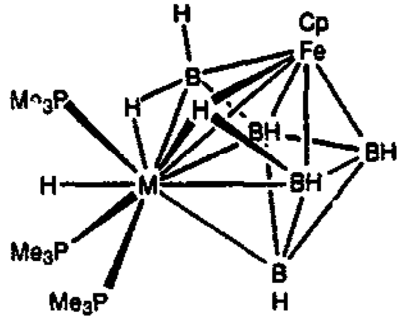


Scheme 58



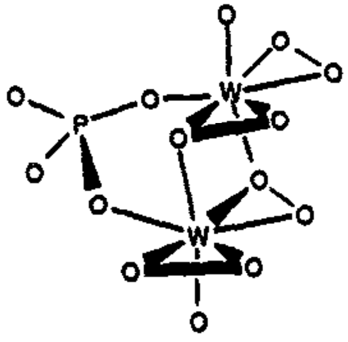
(75)

The reactivity of *nido*-[2-Fe(η-Cp)B_5H_{10}] with the tungsten (or molybdenum) polyhydride [$W(PMe_3)_3H_6$] was examined as was a Mo analogue [164]. Capped *closo*-geometries were obtained in the resulting [1-Fe(Cp)-2-{$M(PMe_3)_3H$}B_5H_7] (M = Mo, W) clusters (75).

7.8.3 *Polytungstate clusters*

Reaction of the lacunary $[PW_{11}O_{39}]^{7-}$ species with either of the compounds $(^nBu_4N)_2[Mo_5O_{13}(OMe)_4NO]\{Na(MeOH)\}\cdot 3MeOH$ or $[Mo(NO)(OMe)(Me_2CNO)_2]_2$ as a source of $\{Mo(NO)\}^{3+}$ led to diamagnetic $(n\text{-}Bu_4N)_4[PW_{11}O_{39}\{Mo(NO)\}]$ [165]. This has been characterized by elemental analysis, IR and ^{31}P and ^{183}W NMR spectroscopies, and electrochemistry. Comparison of the data obtained with the parent Keggin anions revealed the electron-withdrawing effect of the nitrosyl to be opposite to the overall charge increase. The ^{183}W NMR spectroscopic data further supported some delocalization of the Mo(II) *d*-electron density onto the polytungstate.

Multinuclear ^{31}P and ^{183}W NMR spectroscopic studies on the products of the $H_2WO_4/H_2O_2/H_3PO_4$ or $H_3[PW_{12}O_{40}]\cdot yH_2O/H_2O_2$ systems revealed new phosphato(oxo)-peroxotungstate species [166]. These included several salts of the $[HPO_4\{WO(O_2)_2\}_2]^{2-}$ anion (76) whose structure has been determined. The polyanion has one bridging and one nonbridging peroxo group at each W with slightly elongated peroxo bonds of 1.53(3) and 1.46(4) Å respectively. Spectral evidence confirmed retention of this structure in solution.



(76)

Preparation and characterization of three new fluorotungstates having the Dawson-Wells structure have been reported [167]. These included the $[Cu^IW_{17}O_{54}F_8NaH_4]^{8-}$, $[MgW_{17}O_{57}F_5NaH_6]^{8-}$, and $[Fe^{III}W^VW^{VI}_{16}O_{55}F_7NaH_4]^{8-}$ anions which were characterized by chemical analysis, FAB mass spectrometry, IR spectroscopy and X-ray powder patterns.

The crystal structure of $[py\text{-}H\text{-}py]_3[PW_{12}O_{40}]$ has been reported [168]. The cation has two pyridines linearly bridged by a proton while the trianion has T_d symmetry due to 3-fold disorder.

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