Coordination Chemistry Reviews
172 (1998) 247–317

Tungsten 1996

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Contents

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0010-8545/98/$32.00
PII S0010-8545(98)00109-X

1. Introduction

This review covers the tungsten coordination chemistry literature published in the 1996 calendar year. As in previous reviews, organometallic compounds of tungsten will not be discussed unless they have features of particular interest to the coordination chemist. While not intended as a fully comprehensive compilation of tungsten coordination chemistry appearing in 1996, we aim to present here a representative survey of interesting new developments and important advances in the field.

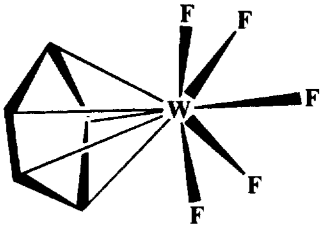
Complexes have been grouped in order of the tungsten centre's formal oxidation state while subsections have been arranged according to donor atom types. Where mixed-donor complexes occur, they have either been grouped in accord with the key ligands of interest or in the mixed-donor ligand subsection.

2. Tungsten(VI)

2.1. Complexes with halide ligands

Reaction of WF_6 with hexamethyldisilathiane, $S(SiMe_3)_2$, gave solid WSF_4 [1]. A solution EXAFS study of this and related halides confirmed their monomeric structures and yielded a W=S bond length of 2.026(8) Å and W–F of 1.863(3) Å. Addition of WF_6 to the cluster $Os_3(CO)_{12}$ in anhydrous HF gave $[HOs_3(CO)_{12}][W_2O_2F_9]$, presumably due to adventitious moisture [2]. A structural study confirmed formation of the fluoride-bridged dimeric anion.

The first chromium triad cyclopentadienylmetal(VI) halide complex, Cp^*WF_5, has been prepared from the air oxidation of Cp^*WF_4 [3]. This orange compound was found to be monomeric with a distorted octahedral environment around tungsten (1).

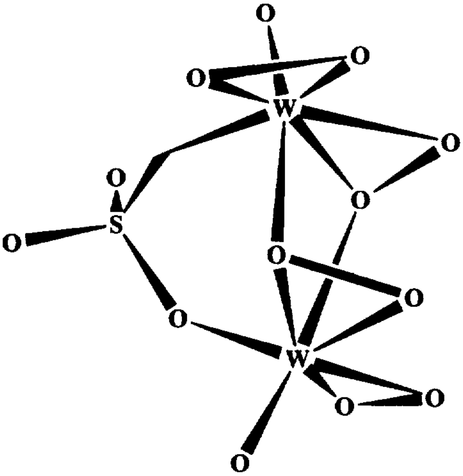


(1)

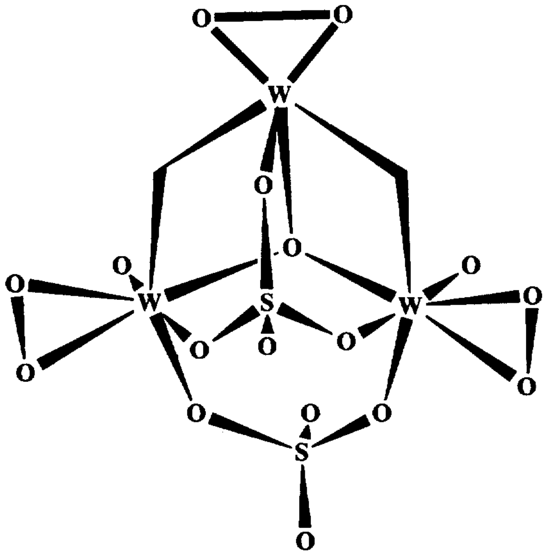
Chloride for oxide substitution in several polytungstates was accomplished using thionyl chloride to give the $[WOCl_5]^-$ anion in 75–100% yields [4]. A crystallographic study of $[^nBu_4N][W(O)Cl_5]$ revealed an O/Cl disorder at the pseudo-octahedral tungsten centre.

2.2. Complexes with oxygen and sulfur ligands

Novel oxoperoxosulfatotungsten(VI) species have been isolated and their structures determined [5]. These included the $[(SO_4)\{W_2O_2(\mu\text{-}O_2)_2(O_2)\}]^{2-}$ (**2**) and $[(HSO_4)(SO_4)\{W_3O_6(O_2)_3\}]^{3-}$ anions (**3**). The former was found to transfer oxygen efficiently to olefinic substrates at room temperature.

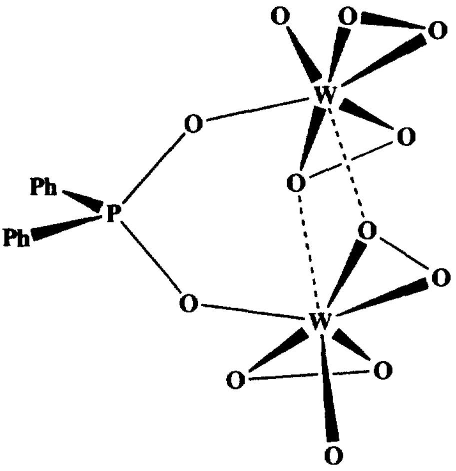


(2)



(3)

A dinuclear peroxo tungsten salt $[N^nBu_4][(Ph_2PO_2)\{WO(O_2)_2\}_2]$ has been isolated and structurally characterized [6]. The phosphato group was found to bridge the two tungsten centres with approximate pentagonal bipyramidal coordination geometries (**4**).



(4)

A report on the low pressure CVD of electrochromic tungsten glass using W(VI) oxo alkoxides and oxo/alkoxide/β-diketonate complexes has appeared [7]. Suitable thin films were obtained from $WO(OR)_4$, $WO(OR)_3$(acac), and $WO(OR)_3$(hfac) precursors.

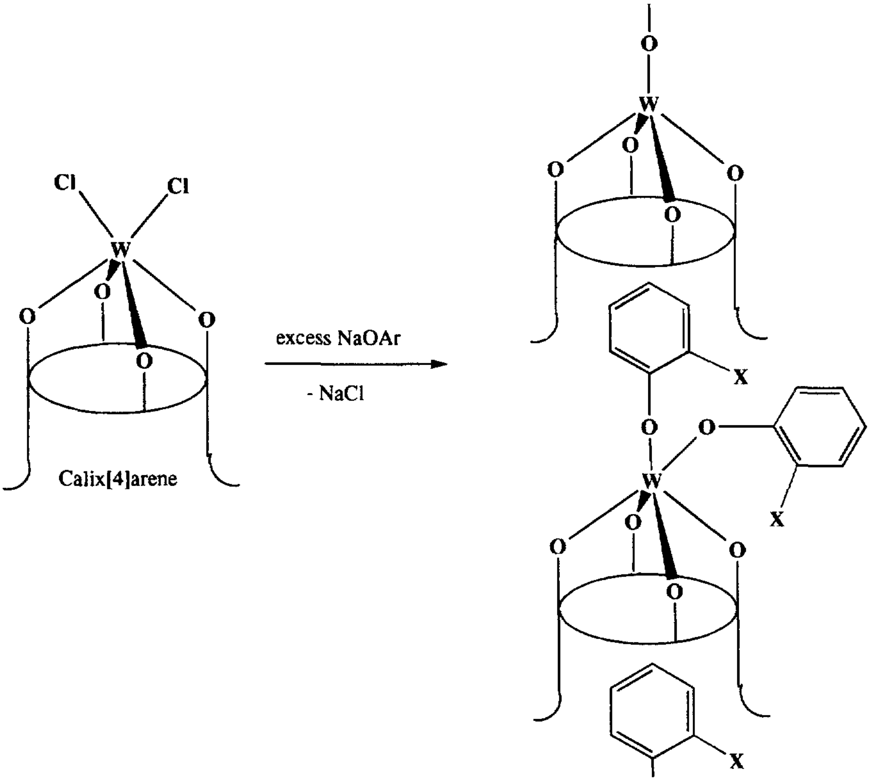
Tungsten(VI) oxo groups anchored on calix[4]arenes have yielded several interesting reports. The spectroscopic and photophysical properties of bowl-shaped tungsten oxo complexes of calix[4]arenes substituted at the *para* positions with phenyldiazenyl derivatives were investigated [8]. The presence of a pyridine guest molecule was found to decrease the emission lifetime of luminescent complexes.

Functionalization of a tungsten(VI) bonded over a calix[4]arene with phenoxy groups resulted in self-assembly into columnar structures (Scheme 1) [9].

In related work, exhaustive alkylation of Cl_2W-calix[4]arene led to novel electron-rich, anionic W-alkylidyne derivatives [10]. The reported chemistry is summarized in Scheme 2.

The first resolution of a chiral tungsten(VI) calix[4]arene has been accomplished by separation of the (*S*,*S*)-(−)-hydrobenzoin W(VI)-3,4-dimethylcalix[4]arene diastereomeric mixture using hplc or flash chromatography [11]. Decomposition of each enantiomer using $AlCl_3$ yielded the respective optically pure Cl_2W-3,4-dimethylcalix[4]arene.

Interest in modelling the enzymes tungsten oxidoreductases found in thermophilic and hyperthermophilic bacteria continued unabated. The dioxodithiolato–tungsten complex $[NEt_4]_2[W^{VI}O_2(ndt)_2]\cdot H_2O$ (ndt = 2,3-naphthalenedithiolate) (**5**) has been

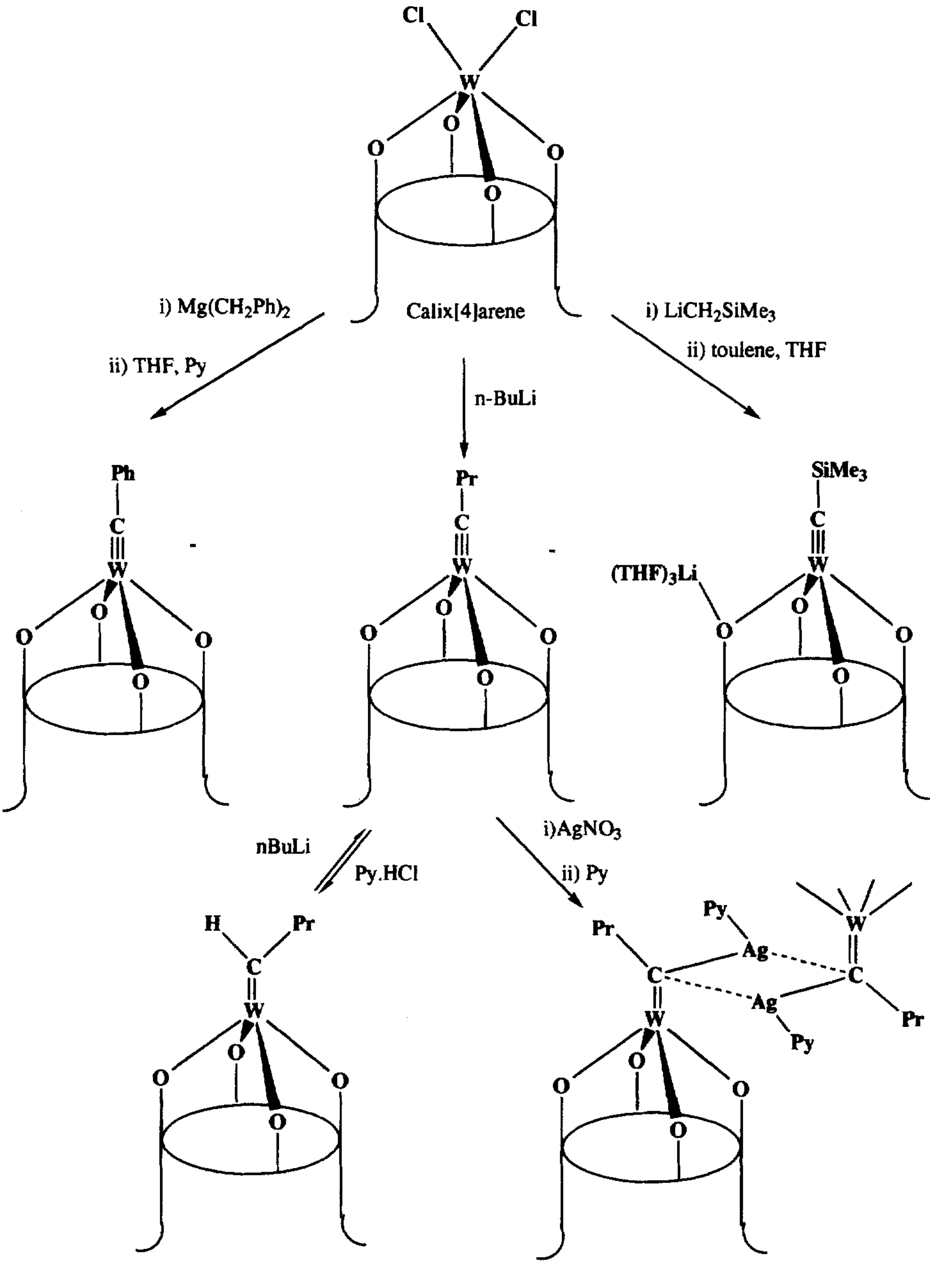


Scheme 1.

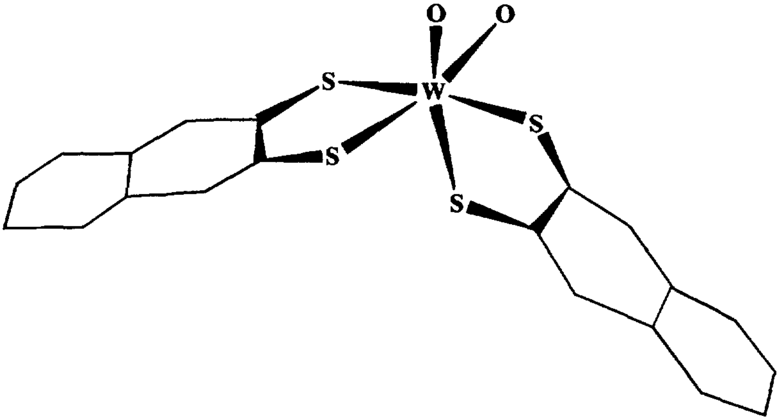
synthesized and structurally characterized [12,13]. The observed short C–S bonds *trans* to the W=O groups are suggestive of their partial thioketone nature, weakened W–S π-interactions, and indicate a stabilization of the $W^{VI}O_2$ moiety. It was proposed that this serves as a switching mechanism for the enzyme's oxo transfer chemistry. A related complex, $[NEt_4]_2[W^{VI}O_2(bdt)_2]$ (bdt = 1,2-benzendithiolate), was shown to oxidize benzoin via oxo transfer at above 100 °C [14].

Variable-temperature dynamic NMR spectroscopic studies of a series of tungsten *tris*(dithiolene) complexes $W(S_2C_2R^1R^2)_3$ revealed stereochemical nonrigidity of the trigonal prismatic structures at room temperature [15]. The *trans*/*cis* ratio was found to be three. The X-ray structure of a trimetallic complex $[NEt_4][Br_2Fe(\mu\text{-}S)_2W(\mu\text{-}S)_2Ag(PPh_3)_2]$ has been determined [16]. It contains a linear arrangement of the heterometals (**6**).

The known linear chain complex $[WS_4Ag]_n^{n-}$ can be converted to a new chain product $[W_4S_{16}Ag_4]_n^{4n-}$ by reaction with $Ca(NO_3)_2$ in DMSO [17]. X-ray structural determination showed the polymeric anion to have a repeating zig-zag pattern as shown in (**7**).


Cl
Cl
W
O
O
O
O
Calix[4]arene
i) Mg(CH2Ph)2
ii) THF, Py
n-BuLi
i) LiCH2SiMe3
ii) toulene, THF
Ph
C
W
Pr
C
W
SiMe3
C
W
(THF)3Li
nBuLi
Py.HCl
i)AgNO3
ii) Py
H
Pr
C
W
Pr
C
Py
Ag
Ag
Py
W
C
Pr

Scheme 2.



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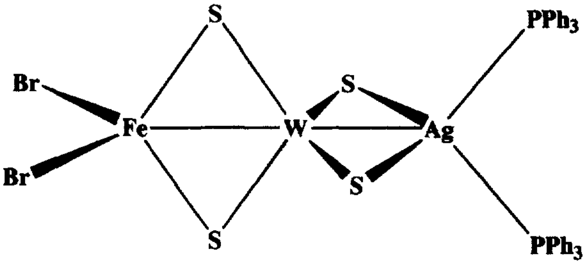

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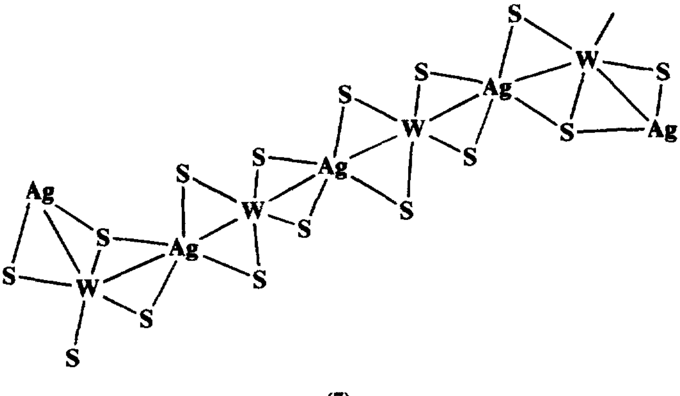
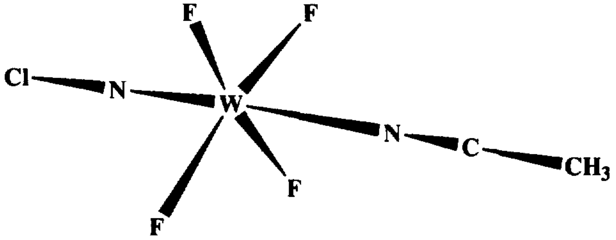


(7)

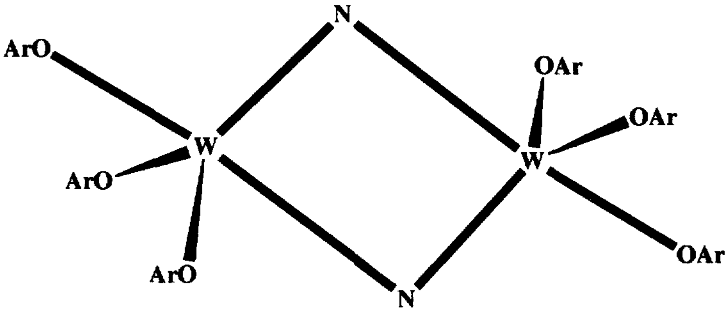
2.3. *Complexes with nitrogen and other pnictogen ligands*

Elemental fluorine was found to convert the nitrido chlorides $W(N)Cl_3$ and $WCl_4(NCl)$ to $WF_4(NCl)$ [18]. The structure of the latter as an acetonitrile adduct has been determined, yielding a W≡N distance of 172.2(8) pm and a W–N–Cl angle of 178.6(6)° (**8**).



(**8**)

Both solution NMR spectroscopic studies and single-crystal X-ray diffraction confirmed an asymmetric cyclic W_2N_2 core in the compound $[W(N)(O\text{-}2,6\text{-}C_6H_3{}^iPr_2)_3]_2$ [19]. The solid-state structure (**9**) revealed alternating short W≡N bonds of 1.77 Å and long W–N bonds of 2.02 Å. It was suggested that steric factors may favour this geometry.

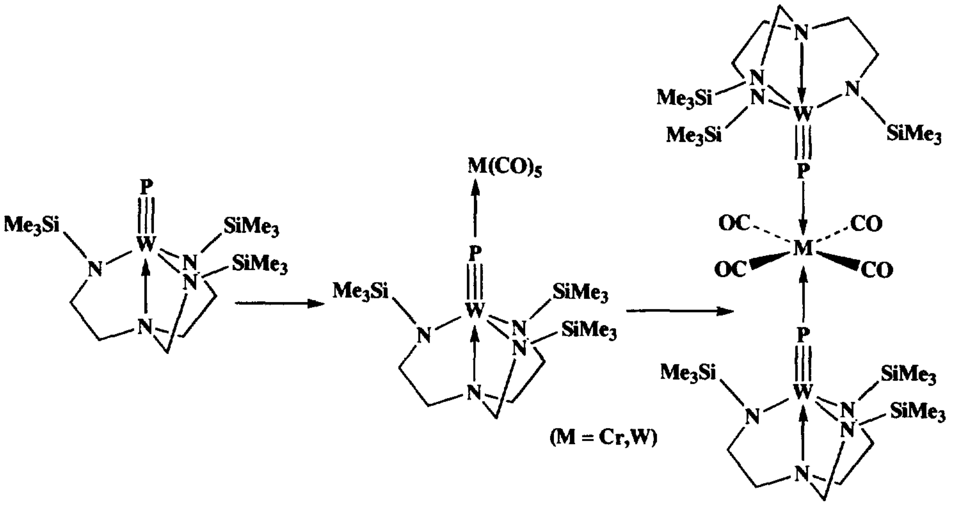


(**9**)

Tungsten complexes containing terminal W≡P and W≡As were prepared using lithium bis(trimethylsilyl)phosphide and arsenide respectively and structurally characterized [20]. Both the axial N–W–P and N–W–As angles were linear with the W–As triple bond 13 pm longer than the W≡P. Coordination of Group 6 metal carbonyls at the terminal phosphorus was demonstrated (Scheme 3). In closely related research, both terminal Mo≡As and W≡As complexes were also reported, which allowed the force constants of Mo and W pnictogen (N, P, As) triple bonds to be determined by Raman spectroscopy [21]. Observed reduction in W≡E force constants ($k_{W\equiv N} \gg k_{W\equiv P} > k_{W\equiv As}$) is consistent with the increasing W–E bond lengths. A second trend shows $k_{W\equiv E} > k_{Mo\equiv E}$. It was also suggested that the surprisingly low ${}^1J_{WP}$ is consistent with a low degree of *s*-character in the W≡P bond.

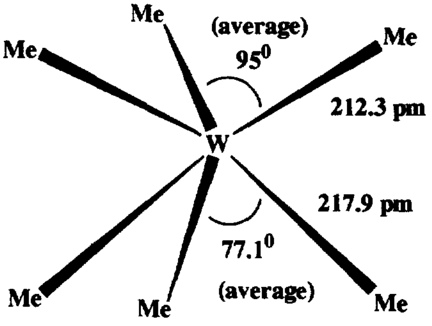
2.4. Complexes with hydride and selected organic ligands

A theoretical study of the hydrogen exchange coupling in $Cp_2WH_3^+$ gave results consistent with experimental observations [22]. The proposed transition state fea-



Scheme 3.

tures an η^2-H_2 ligand. The long-sought definitive molecular structure of hexamethyltungsten WMe_6, first prepared by Wilkinson in 1973, has finally been determined by X-ray diffraction at −163 °C [23,24]. It has a strongly distorted trigonal prismatic structure with C_{3v} symmetry (**10**). A qualitative molecular orbital model was proposed to account for this intriguing distortion from idealized D_{3h} geometry.

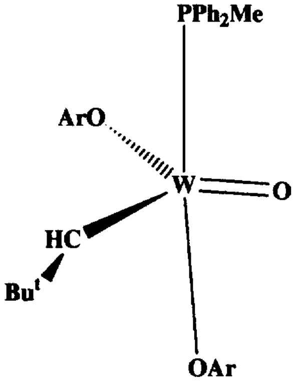


(10)

Dioxotungsten(VI) dichloride was found to coordinate to the carbenoid 1,3-dimethylimidazoline-2-ylidene (L) to give the green $W(O)_2Cl_2L_2$ complex [23,24]. The products from the reactions of W(η^2-diphenylacetylene)Cl_4 with substituted salicylic acid derivatives (H_2sal-R), W(η^2-diphenylacetylene)Cl_3(Hsal-R), were reported to form aggregates through hydrogen bonding interactions including a tetranuclear assembly around an 18-crown-6 template [25].

Structures of several tungsten-based olefin metathesis catalysts or catalyst precursors have been determined. These include W(CH-^{t}Bu)(O)(O-2,6-$Ph_2C_6H_3$)$_2$

(PPh_2Me) (**11**) and $WCl_2(O)(PPh_2Me)_2(\eta^2$-3,3-diphenylcyclopropene) (**12**), and $W(NPh)(CH_2SiMe_3)_2[OCMe(CF_3)_2]_2$ (**13**) [26–28].



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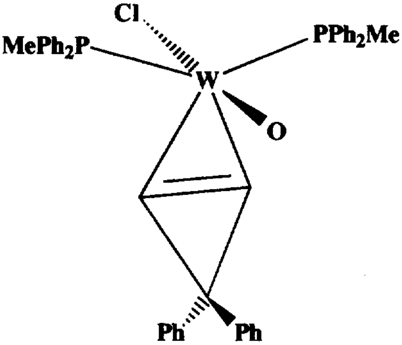

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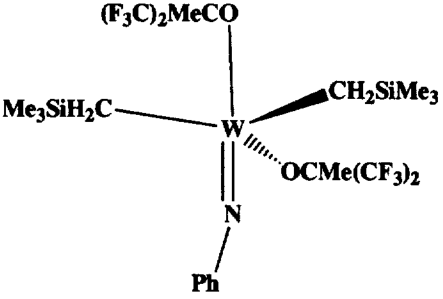
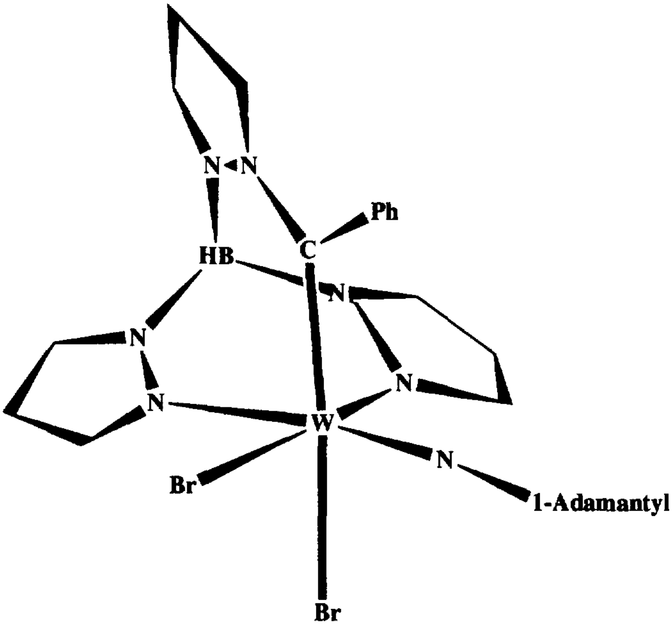


(13)

In an attempt to achieve alkylidene/imido coupling, a formal alkylidene insertion into a W–N bond was observed during the bromination of TpW(=CHPh)(=N-

1-adamantyl)Br [29]. The structure of the resulting cage-expanded complex is shown in (**14**).

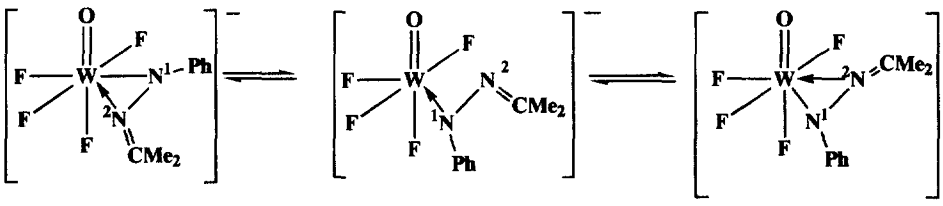


(14)

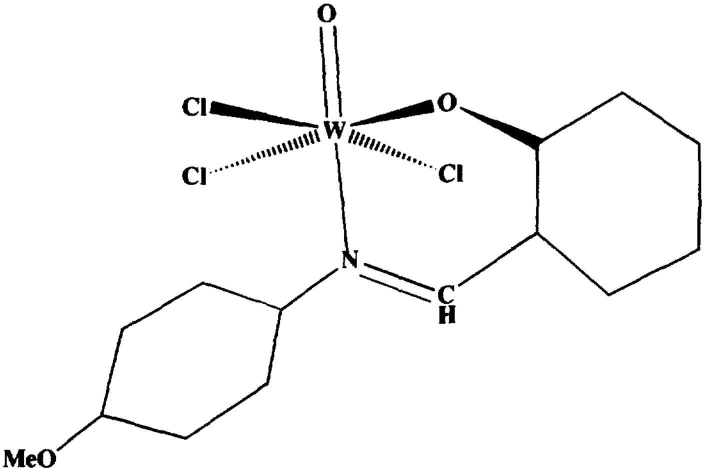
2.5. Complexes with mixed-donor ligands

A variable-temperature multinuclear NMR spectroscopic investigation has delineated the solution structure and intramolecular dynamics in the $W(O)F_4(\eta^2$-acetone phenylhydrazonato$)^-$ anionic complex [30]. Isomerization was believed to occur via breakage and reformation of the $W–N_2$ bond with simultaneous ligand rotation around the $W–N_1$ bond (Scheme 4).

The synthesis and structure of $W(O)Cl_3[N\{C_6H_4(OMe)\}=CH–C_6H_4O]$ (**15**) and related complexes were described [31]. An X-ray structural determination of *mer*-$W(O)Cl_3$[2-phenylaminopyridinato] revealed the geometry shown in (**16**) [32].



Scheme 4.



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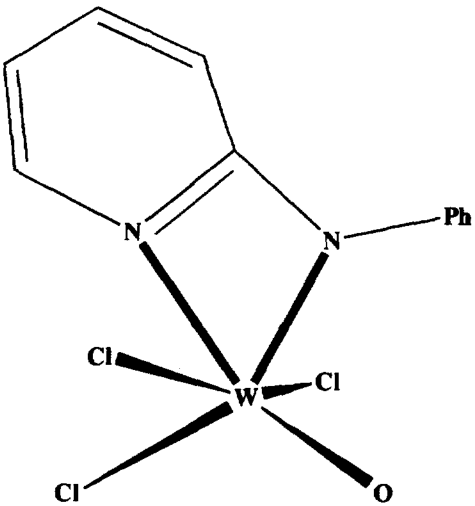
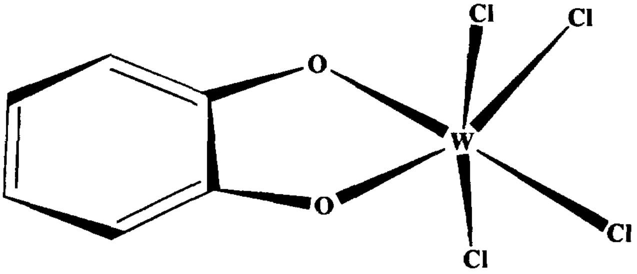


(16)

Reaction of WCl_6 with 1,2-bis(trimethylsiloxy)benzene and its derivatives gave selectively the monocatecholato–WCl_4 complexes, $WCl_4(O_2\text{-}1,2\text{-}C_6H_3R\text{-}4)$ [33]. Significant upfield ^1H NMR shifts of the aromatic protons due to the electron-deficient metal centre were observed. A distorted octahedral coordination geometry around W was found in the structure of $WCl_4(O_2\text{-}1,2\text{-}C_6H_4)$ (**17**).

A superoxo(oxo) tungsten(VI) complex with 2-(2-hydroxyphenyl)benzimidazole (L), $W(O)(O_2)L_2$ has been prepared [34]. This was found to readily transfer an oxo to PPh_3 and yield the peroxo complex $W^{IV}(O_2)L_2$.

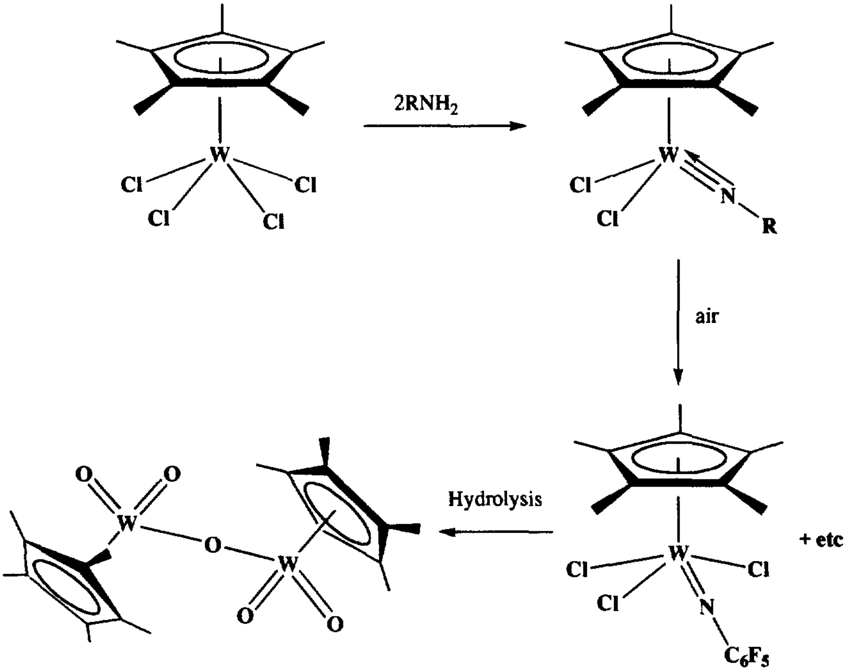


(17)

3. Tungsten(V)

Reaction of Cp*WCl$_4$ with primary amines RNH$_2$ (R = t-Bu, i-Pr, C$_6$F$_5$, and 2,6-(i-Pr)$_2$C$_6$H$_3$) led to the respective 17-electron imido complexes Cp*WCl$_2$(NR) [35]. X-ray structural determination of Cp*WCl$_2$(N^{t}Bu) confirmed a short W–N distance of 1.72(1) Å consistent with a triple bond. In air, Cp*WCl$_2$(NC$_6$F$_5$) was found to decompose to the W(VI) imido complex Cp*WCl$_3$(NC$_6$F$_5$) while further hydrolysis resulted in a dinuclear [Cp*WO$_2$]$_2$(μ-O) product (Scheme 5).

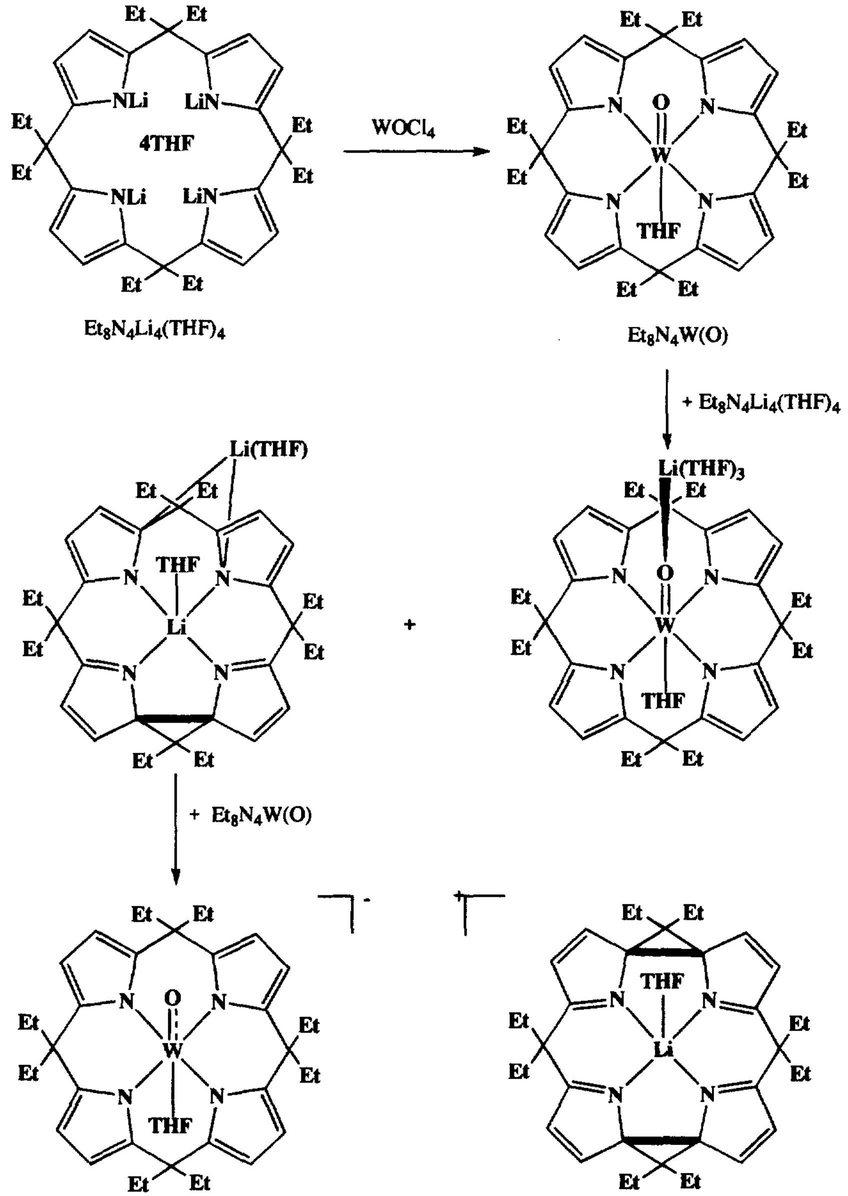
Interesting redox chemistry of *meso*-octaethylporphyrinogen followed the initial coordination of this ligand with WOCl$_4$ to give a 1:1 complex [36]. Depending on



Scheme 5.

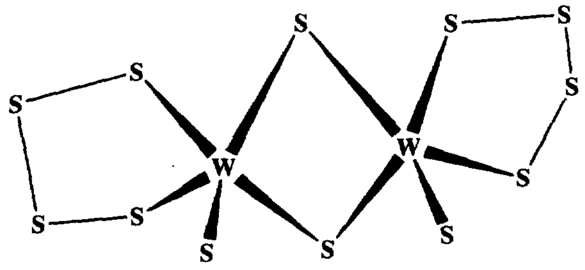
the stoichiometry, mono- and bis-cyclopropane forms of porphyrinogen can be obtained along with W(V) porphyrinogen anions (Scheme 6).

A new method of generating dinuclear sulfur-bridged oxo or sulfido complexes of W(V) in good yields has been reported [37]. Acidification of a mixture of



Scheme 6.

tungstate and aqueous ammonium polysulfide at pH 6 in the presence of H_2S gave red $[W_2S_2(\mu\text{-}S)_2(S_4)_2]^{2-}$. Its structure features the metal centres in distorted square pyramidal geometry (**18**).

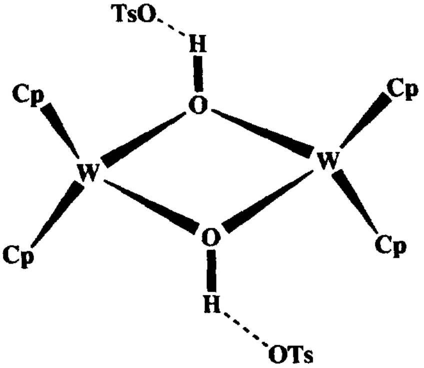


(18)

4. Tungsten(IV)

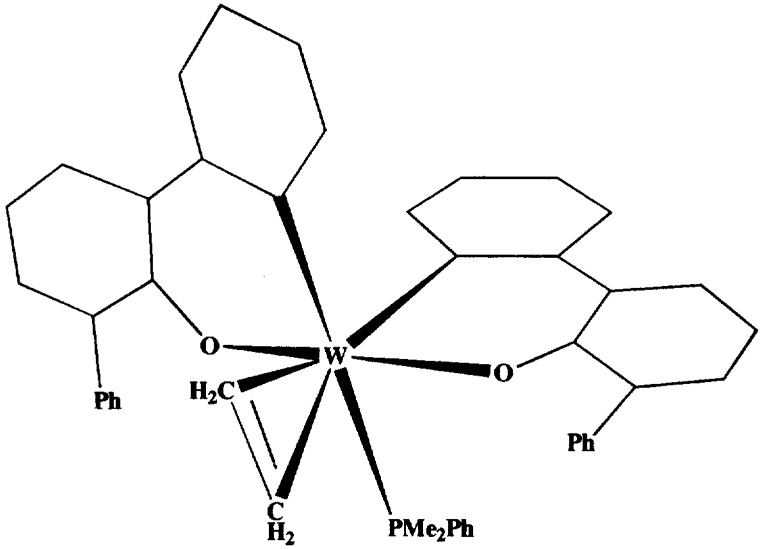
4.1. Complexes with oxygen and sulfur ligands

Hydroxy-bridged dinuclear tungsten(IV) complexes were prepared by the reaction of Cp_2WH_2 and $Cp_2W(OTs)_2$ and fully characterized [38]. A planar W_2O_2 core was found in $[Cp_2W(\mu\text{-}OH)_2WCp_2](OTs)_2$ (**19**). Displacement of the bridging OH groups with phosphines (PR_3) in alcohols (R'OH) gave novel cationic products $[Cp_2W(OR')(PR_3)]OTs$ ($R'=CH_2CF_3$, $R=n\text{-}Bu$).



(19)

An extension of previous work on bis(cyclometallated) W(IV) phenoxides reported on the coordination chemistry of $W(OC_6H_3Ph\text{–}C_6H_4)_2(\text{phosphine})_2$ with olefins [39]. The solid-state structure of the ethylene complex is shown in (**20**). Since the structural data indicate only weak π-backbonding towards the olefin, the observed barrier to olefin rotation of this complex in solution has been attributed to steric factors.



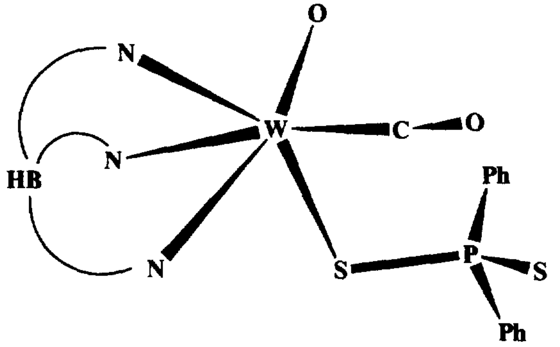
(20)

Tris(pyrazolyl)borate tungsten complexes containing both strong π-acid and strong π-donor ligands have been prepared and structurally characterized [40]. Two-electron oxidation of $Tp^{*}W(S_2PR_2)(CO)_2$ using pyridine N-oxide gave $Tp^{*}W^{IV}(O)(S_2PR_2)(CO)$ (**21**) with a nearly orthogonal O–W–C angle for maximum ligand–metal π-overlap. Prolonged thermal decomposition of $Tp^{*}WX(CO)_3$ (X = Cl, Br, I) in acetonitrile yielded novel four-electron donating η^2-MeCN complexes $Tp^{*}W^{II}X(\eta^2\text{-}MeCN)(CO)$ which, upon metathesis with $NH_4S_2PR_2$, afforded $Tp^{*}W^{II}(S_2PR_2)(\eta^2\text{-}MeCN)(CO)$ (**22**, R = (–)-mentholate). Further reaction with propylene sulfide yielded the corresponding $Tp^{*}W^{IV}(S)(S_2PR_2)(CO)$ products (**23**).

Tungsten(IV) thiolate complexes $CpW(SAr)_3(CO)$ were readily prepared from the corresponding TlSAr (Ar = C_6F_4H-4, Ph, C_6H_4Me-4) salt and $CpWX_3(CO)_2$ (X = Br, Cl) precursors [41]. The tetrathiolates were available from further reactions using five equivalents of MSAr salts (M = Tl, K, Rb, Cs; Ar = C_6F_4H-4) (Scheme 7). Multinuclear NMR spectroscopic studies revealed dynamic processes involving rotation/inversion of the SAr groups. Metal–F coupling provided evidence for reversible M^+ coordination to the organometallic anion.

4.2. Complexes with nitrogen and phosphorus ligands

Efforts continued in the syntheses of organonitrogen compounds from coordinated dinitrogen in tungsten complexes. Coordinated dinitrogen at tungsten was shown to transform to a novel (1-pyridinio)imido ligand which then formed a substituted pyridine after facile N–N cleavage [42]. This reaction scheme is shown in Scheme 8.



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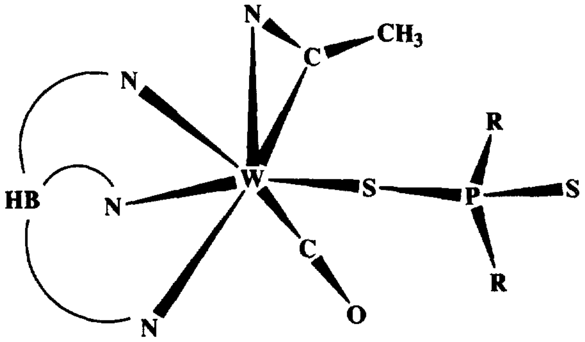

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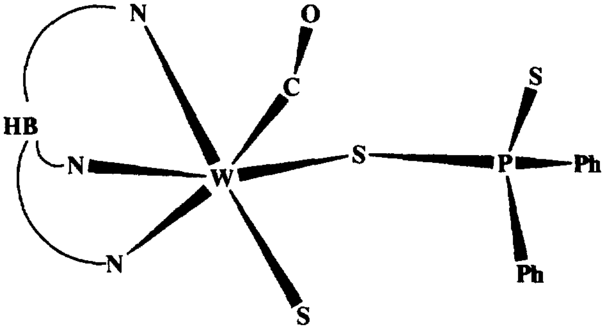
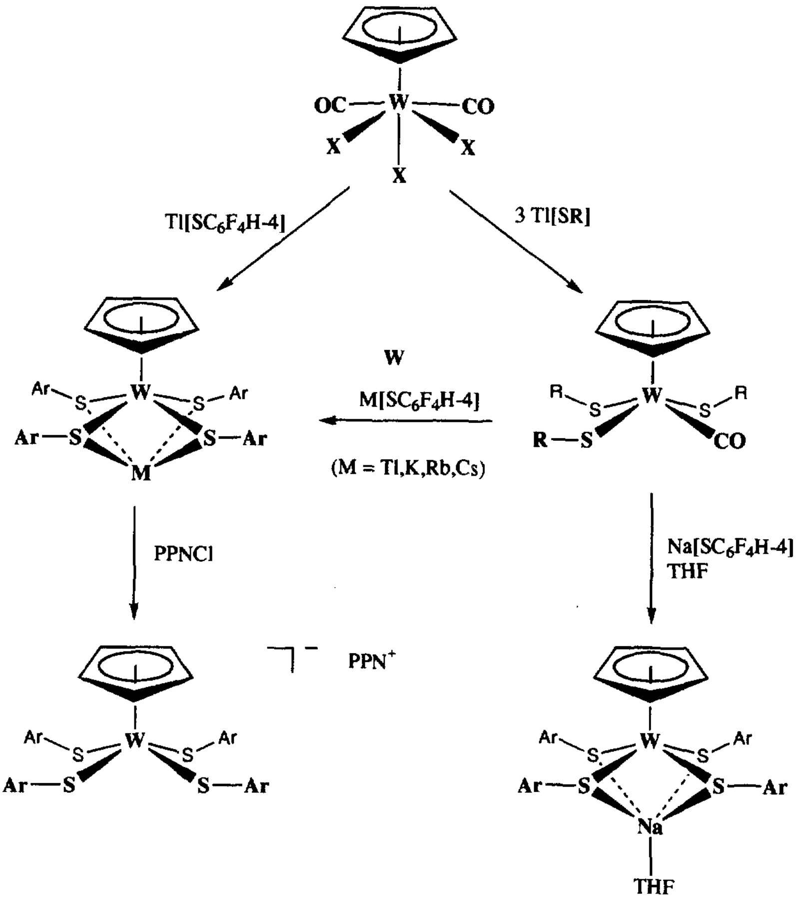


(23)

From WCl_6, a number of tungsten complexes featuring ligands with N–N bonds (phenyldiazendio, phenylhydrazido, diorganohydrazido) have been prepared and their reactions with acids studied [43]. In most cases, amines and smaller amounts of ammonia were produced. Comparisons with the acidification of unsubstituted hydrazido complexes were summarized. The solid-state structure of $WCl_2[NN(H)Ph](PMe_2Ph)_3$ has been determined (**24**) to reveal multiple bonding for both W–N (1.76(1) Å) and N–N (1.35(2) Å) bonds.

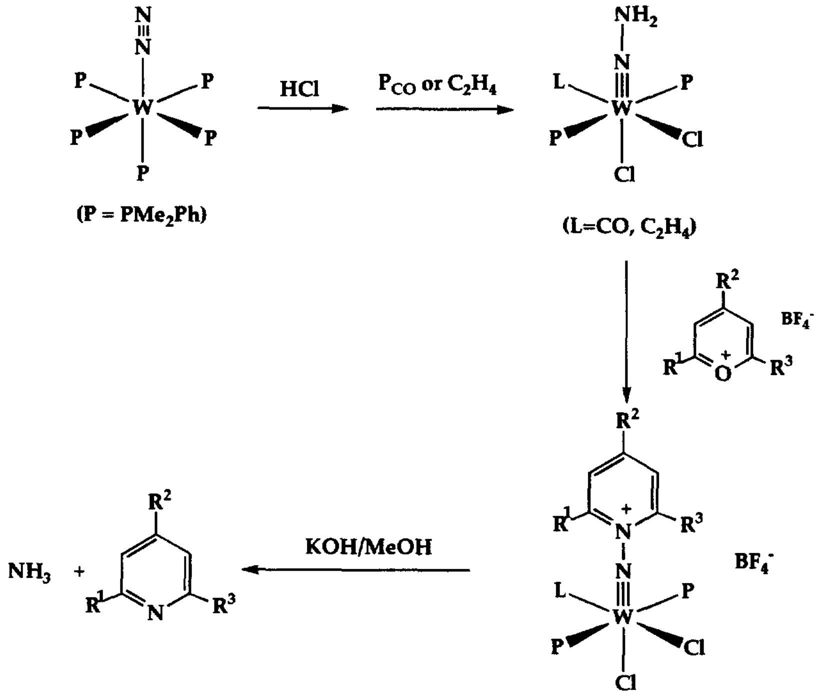


Scheme 7.

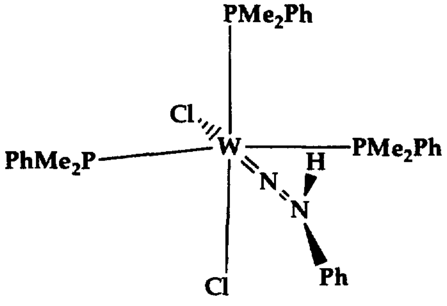
A phosphido-bridged ditungsten(IV) complex, $[(Cp_2WH)_2(\mu\text{-}PPh_2)]OTs$, was produced through the reaction of $Cp_2WH(OTs)$ with $Cp_2WH(PPh_2)$ [44]. Carbyne tungsten complexes of the type $CpW(CR)(CO)_2$ were readily converted to metallaphosphacyclopropene (η^2-phosphinocarbene) products by chlorophosphine addition in the presence of PF_6^- (Scheme 9) [45]. The reactivity of this cationic η^2-phosphinocarbene tungsten complex towards anionic nucleophiles was also reported [46]. Depending on the nucleophile, three types of pathways were observed as shown in Scheme 10.

4.3. Complexes with selected organic and heavier Group 14 ligands

A simplified approach to a single-component, well-defined metathesis catalyst based on oxo alkylidene tungsten complexes was sought [47]. Reactions of

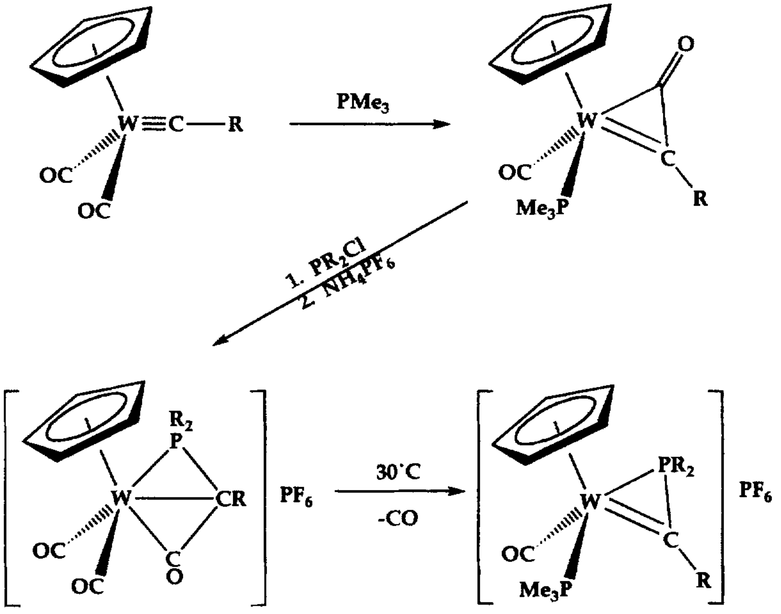


Scheme 8.



(24)

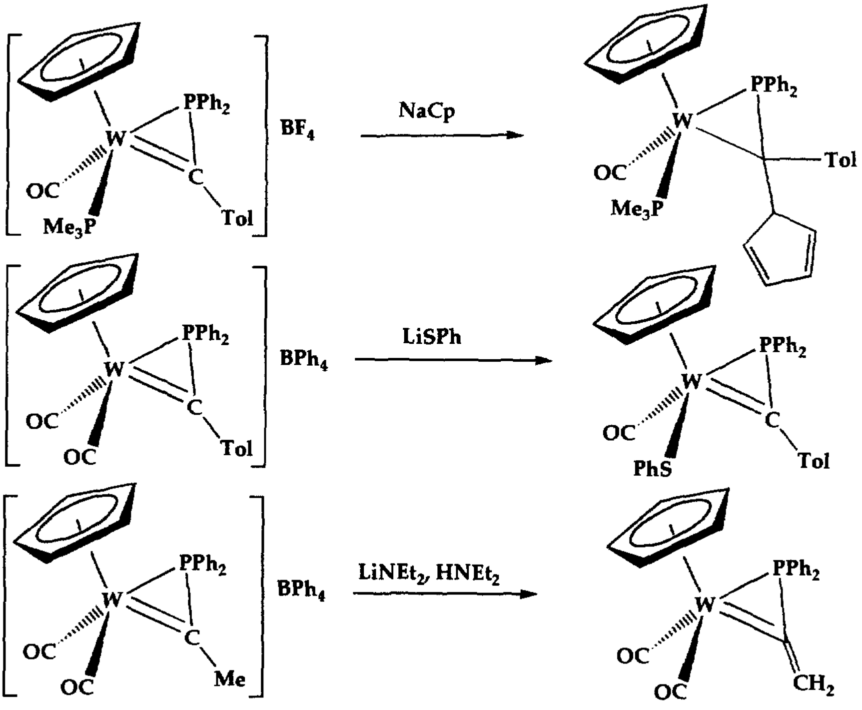
$WCl_2(O)(PR_3)_3$ ($R_3 = (OMe)_3$, $MePh_2$) with 3,3-diphenylcyclopropene afforded the respective W(η^2-diphenylcyclopropene)$Cl_2(PR_3)_2$ complexes which were proposed to have octahedral geometries with *trans*-PR_3 groups and equatorial cyclopropene *cis* to the oxo group. Their thermal decomposition led to *cis* and *trans* dimers of the cyclopropene while the first tungsten oxo vinylalkylidene complexes were prepared and shown to have catalytic metathesis activity (Scheme 11).



Scheme 9.

A three-carbon chain linking a tungsten and a molybdenum unit has been assembled from complementary carbyne fragments [48]. Reaction of $Tp^*(CO)_2W{=}C{=}CH_2^-$, from deprotonation of $Tp^*(CO)_2W{\equiv}C{-}CH_3$, with $Tp^*(CO)_2Mo{\equiv}C{-}Cl$ gave $Tp^*(CO)_2W{\equiv}C{-}CH_2{-}C{\equiv}Mo(CO)_2Tp^*$. This was further deprotonated to generate $[Tp^*(CO)_2W{\equiv}C{-}CH{-}C{\equiv}Mo(CO)_2Tp^*]^-$ and, ultimately, $[Tp^*(CO)_2W{=}C{=}C{=}C{=}Mo(CO)_2Tp^*]^{2-}$. Coupling of tungsten alkylidyne and a carbonyl ligand was observed in the treatment of *trans*-$W({\equiv}CR)Br(CO)_2(PPh_3)_2$ with $K^+[Tp]^-$ [49]. This $Tp(CO)(PPh_3)W(\eta^2\text{-}OCCR)$ complex was reacted with Cl_2PPh_3 to give a chloroalkyne product (Scheme 12). In follow-up research, was reacted with Lawesson's reagent to give a thioketenyl complex $Tp(CO)(PPh_3)W(\eta^2\text{-}SCCR)$ [50].

Germyl silyl complexes $Cp_2W(SiMe_3)(GeR_3)$ have been synthesized from the reaction of the silene complex $Cp_2W(\eta^2\text{-}Me_2Si{=}CH_2)$ and germanes $HGeR_3$ [51]. Treatment of $Cp_2W(SiMe_3)(GeR_2H)$ with CCl_4 generated the respective $Cp_2W(SiMe_3)(GeR_2Cl)$ derivatives. Thermolysis of these products led to both inter- and intramolecular germyl/silyl substituent redistribution. In related work, a base-free dimetallated germyl cation (germylium cation) has been synthesized and structurally characterized [52]. Thermolysis of $Cp_2W(SiMe_3)(GeMe_3OTf)$ gave Me_3SiOTf, $Cp_2W(SiMe_3)(GeMe_3)$, as well as dimeric (**25**). The geometry around the three-coordinate Ge is planar. Oxidative addition of Ph_3PbCl to $Li[Cp_2WSnPPh_3]$ was reported to yield $Cp_2W(PbPh_3)SnPh_3$ while use of Me_3PbCl



Scheme 10.

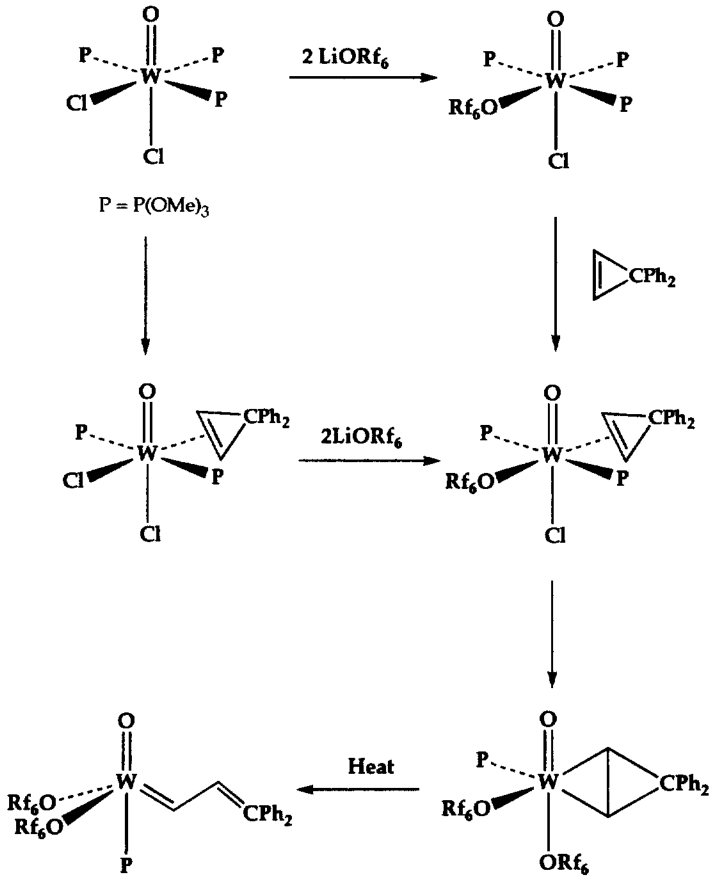
led to a mixture of $Cp_2W(PbMe_3)SnPh_3$ and $Cp_2W(PbMe_2Cl)SnPh_3$ due to redistribution reactions [53].

4.4. Complexes with mixed-donor ligands

The synthesis and structure of the ditungsten cyclooctatetraene/dimethylamido complex $W_2(\mu\text{-}\eta^5,\eta^5\text{-}C_8H_8)(NMe_2)_4$ have been described [54]. In the solid state, the structure was found to be derived from a $C_8H_8^{4-}$ anion coordinated to a W_2^{8+} template (**26**) but in solution the molecule was fluxional with the tub-shaped C_8H_8 ring moving around the W_2 centre.

Reaction of $Li[W(CO)_5PPh_2]$ with Cp_2WCl_2 was found to occur via a Cp ring substitution to yield the dinuclear $[\eta^5\text{-}C_5H_4PPh_2W(CO)_5]W(H)ClCp$ (**27**) [55]. Reduction with $LiAlH_4$ gave the dihydride product $[\eta^5\text{-}C_5H_4PPh_2W(CO)_5]W(H)_2$.

Tungstenocene was found to exclusively add the B–B bond of $B_2(cat')_4$ (cat′ = 4-^{t}Bu-catechol) in the presence of arene C–H bonds [56]. By contrast, $Cp_2W(H)(Bcat)$ eliminated catecholborane to form $Cp_2W(H)Ar$ under the same conditions. Both thermodynamic and kinetic factors are believed to favour B–B over C–H activation.

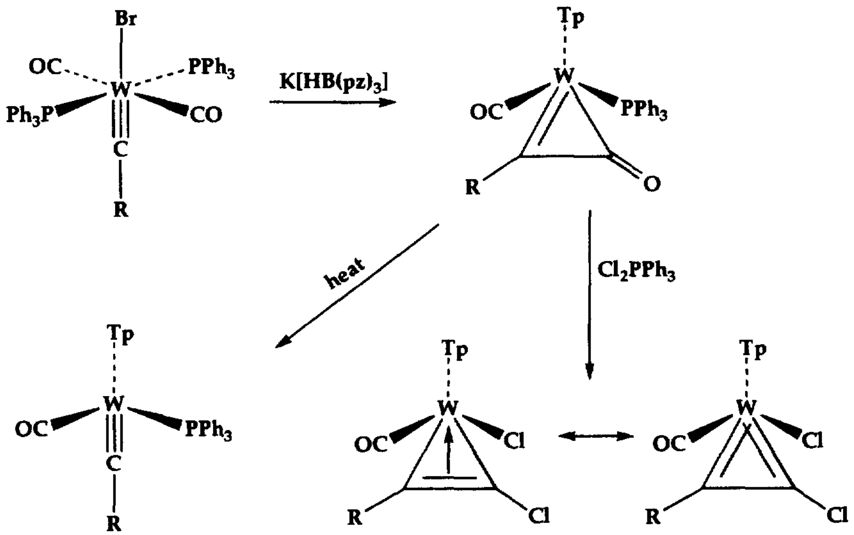


Scheme 11.

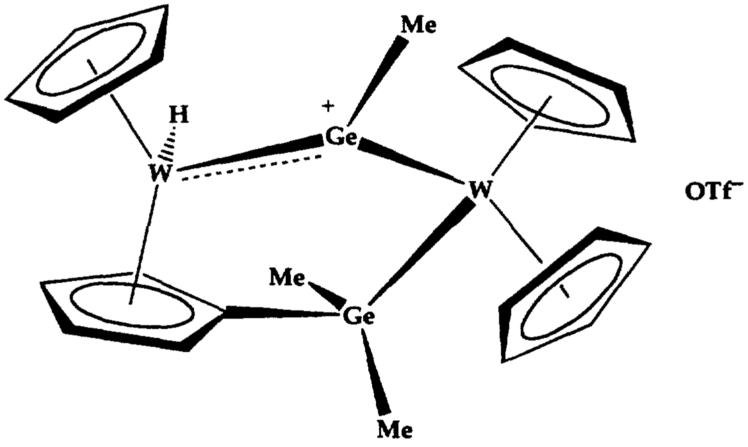
5. Tungsten(III) dimers

The optimized geometry and relative energies of ground and excited spin states of $[W_2Cl_9]^{3-}$ have been determined from density-functional calculations [57]. A dramatic increase in W–W distance as well as an increase in the W–Cl–W angle are predicted for an increase in dimeric spin state from 0 to 3. Use of broken-symmetry density functional calculation on the series $M_2Cl_9^{3-}$ (M = Cr, Mo, W) yielded metal–metal distances consistent with experimental data [58]. It is reasoned that the weaker magnetic orbital overlaps in the Cr–Cr and Mo–Mo chlorides rendered the full-symmetry calculations unrealistic while the stronger W–W interactions resulted in identical predictions.

The reaction of $W_2(\mu\text{-OOCPh})_4$, dppm, and Me_3SiBr was found to yield dimeric $W_2(\mu\text{-H})(\mu\text{-OOCPh})Br_4(\mu\text{-dppm})_2$ (**28**) [59]. An analogous reaction using Me_3SiI gave instead $W_2(\mu\text{-OOCPh})_2I_2(\mu\text{-dppm})_2$ (**29**).



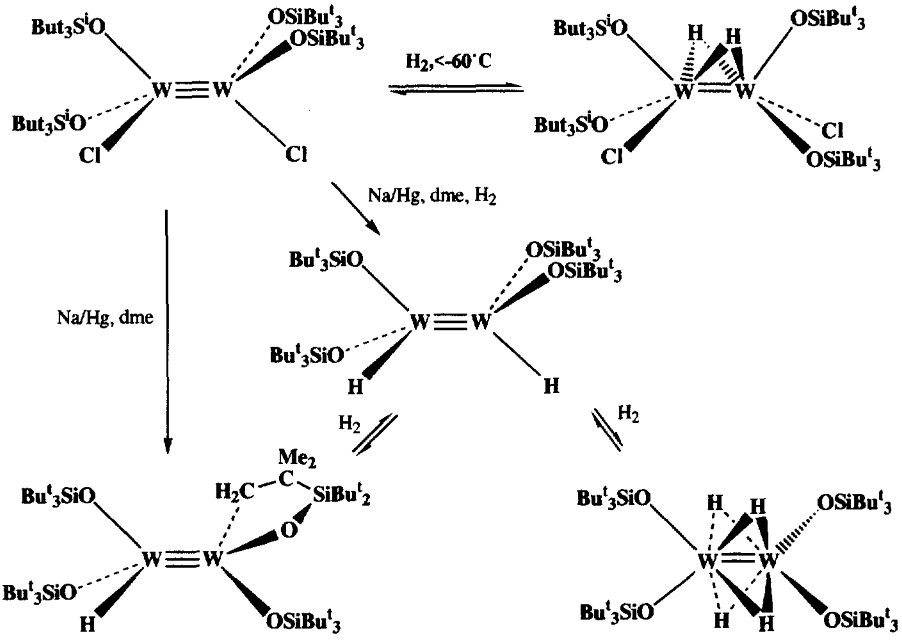
Scheme 12.



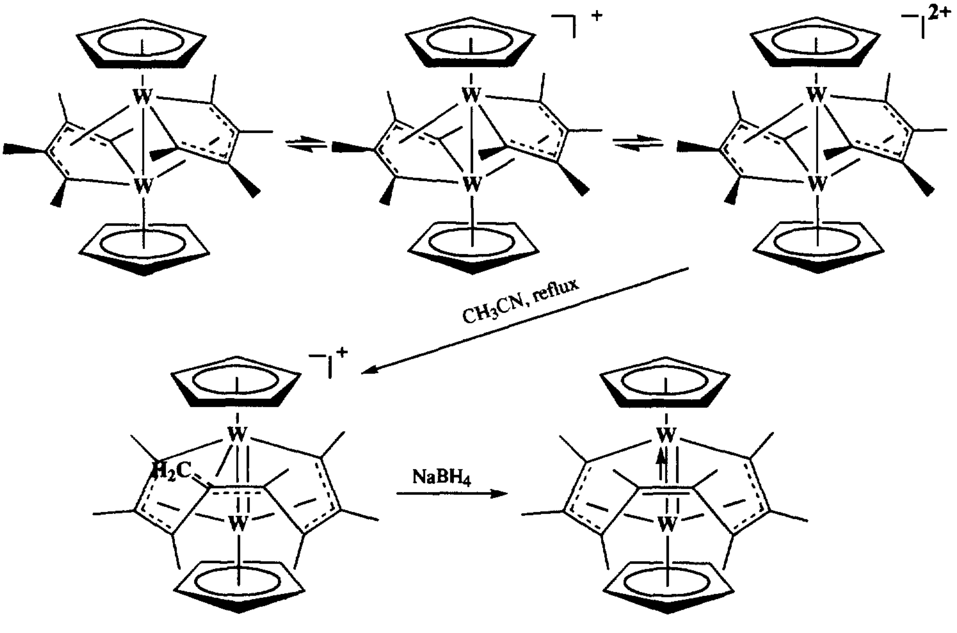
(25)

Addition of four equivalents of Na(silox) (silox = OSi^tBu_3) to $Na[W_2Cl_7(THF)_5]$ was reported to yield $(silox)_2ClW{\equiv}WCl(silox)_2$ [60]. The hydride derivative chemistry of this product was investigated in detail (Scheme 13).

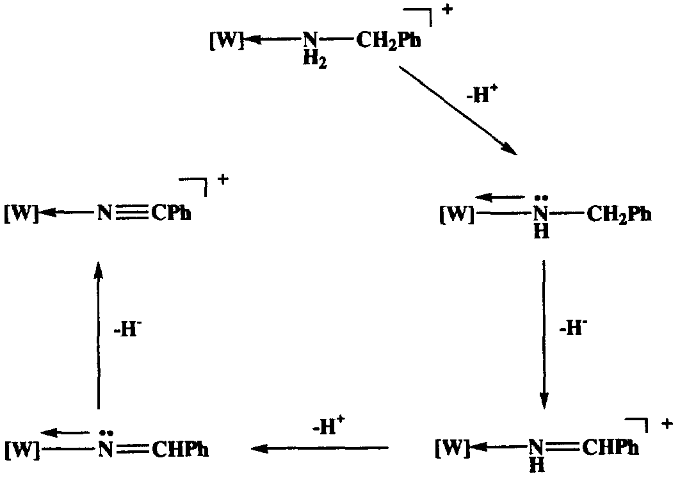
In acetonitrile, the bis(metallocyclopentadienyl) tungsten dimeric complex $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}Cp)_2]$ was sequentially oxidized to give the mono- and dication [61]. The dicationic $[W_2(\mu\text{-}C_4Me_4)_2(\eta\text{-}Cp)_2]^{2+}$ complex was found to undergo a C–C coupling and proton loss in boiling acetonitrile to give $[W_2(\mu\text{-}C_8Me_7CH_2)(\eta\text{-}Cp)_2]^+$ and then, with hydride addition, to form the metallocyclononatetraene product (Scheme 14).



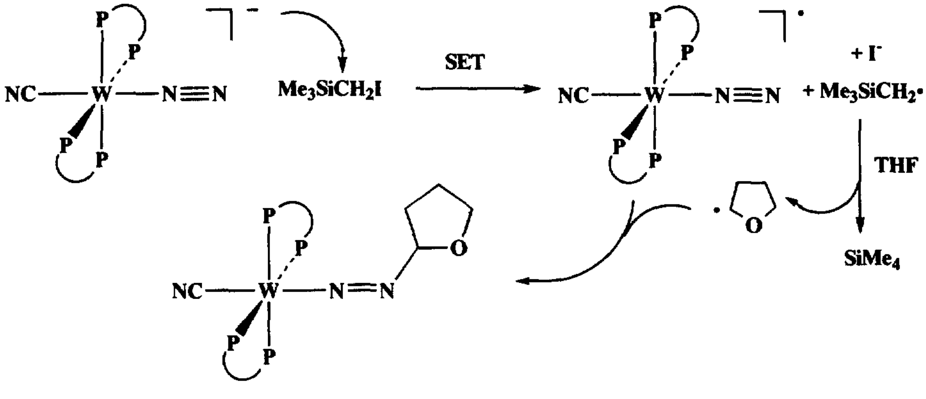
Scheme 13.



Scheme 14.



Scheme 15.



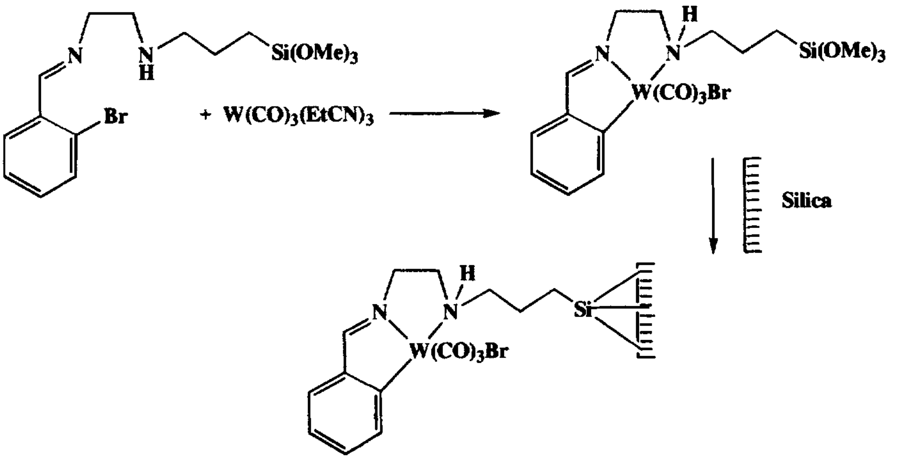
Scheme 16.

6. Tungsten(II)

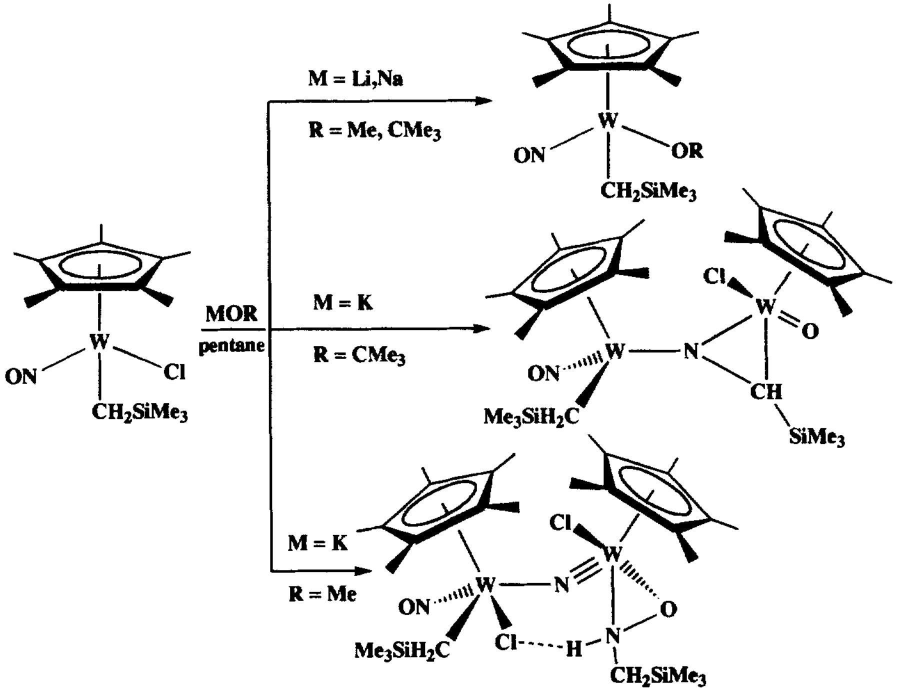
6.1. Complexes with nitrogen ligands

Treatment of the tungsten carbonyl fluoride complex (**30**) with either pentafluorobenzonitrile or tetrafluorophthalonitrile afforded η^2-nitrile complexes (**31**) in which the ligand functions as a four-electron donor [62].

Alkyne complexes of the Tp*W^{II}(CO) moiety have continued to produce interesting chemistry. Coordination of benzylamine to $[Tp^*W(CO)(PhC CMe)]^+$ was found to activate the amine towards stepwise oxidation by sequential hydride/proton removal steps to amido, imine, azavinylidene, and nitrile products (Scheme 15) [63]. Each intermediate complex was isolated and characterized.

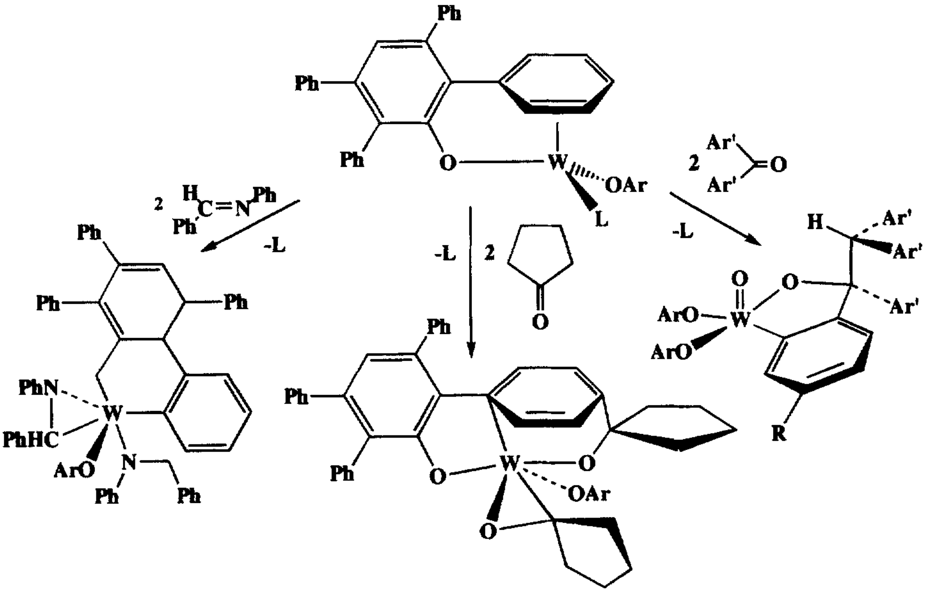


Scheme 17.

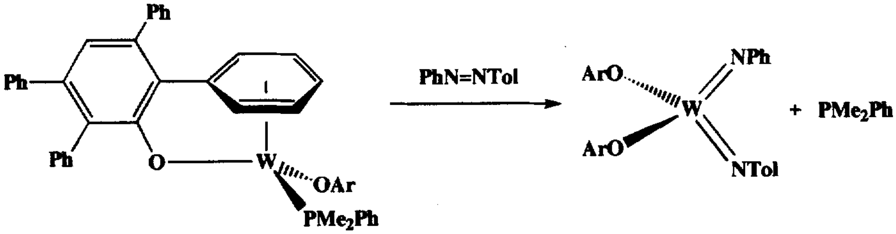


Scheme 18.

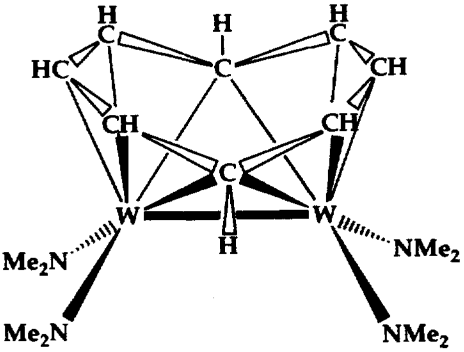
Coordination of *p*-anisaldehyde to [TpW(CO)(MeC$\equiv$CMe)]$^+$ has been shown to be π-bonding in nature (**32**), in contrast to the σ-bonding observed for the Mo analogue [64]. The different binding modes were also assessed in solution.



Scheme 19.



Scheme 20.



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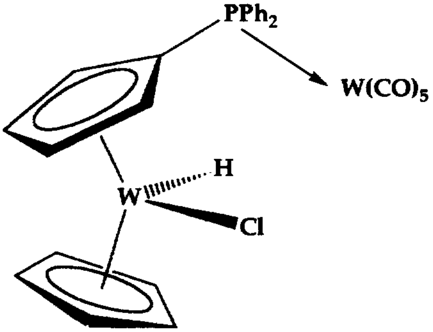
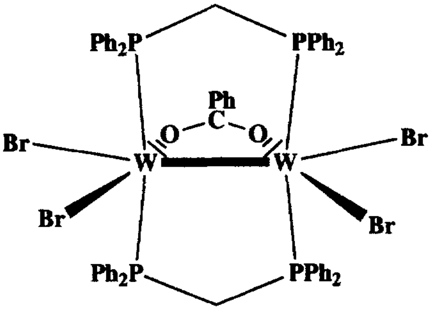
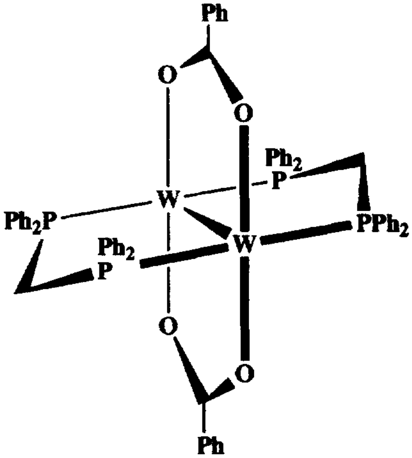

PPh2
W(CO)5
W
H
Cl

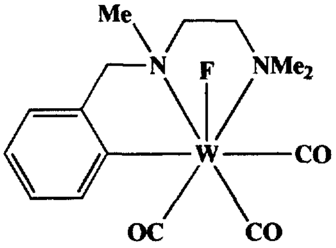
(27)


Ph2P
PPh2
Ph
C
O
O
Br
W
W
Br
Br
Br
Ph2P
PPh2

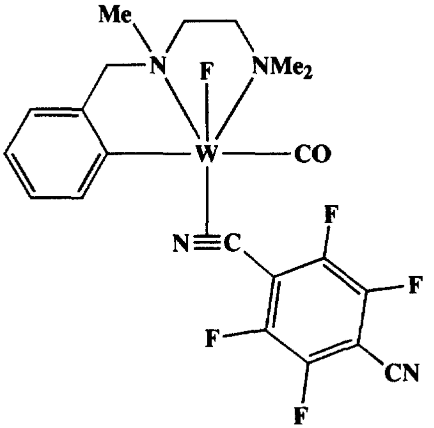
(28)


Ph
O
O
Ph2
P
W
Ph2P
PPh2
Ph2
P
W
O
O
Ph

(29)



(30)



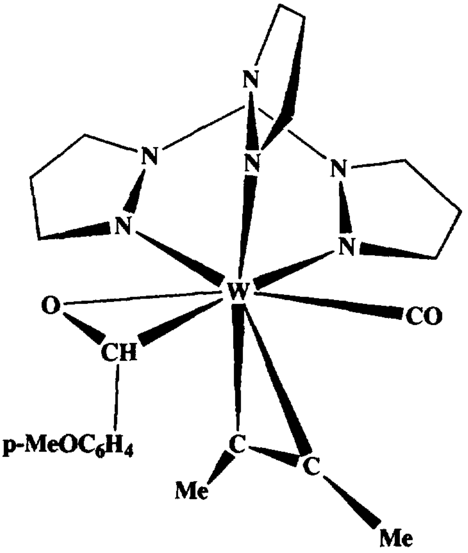
(31)

Reaction of *trans*-$[W(N_2)(CN)(dppe)_2]^-$ with Me_3SiCH_2I in THF afforded a tetrahydrofuranyldiazenide product [65]. A single-electron transfer/radical coupling mechanism was suggested for the C–N bond formation (Scheme 16).

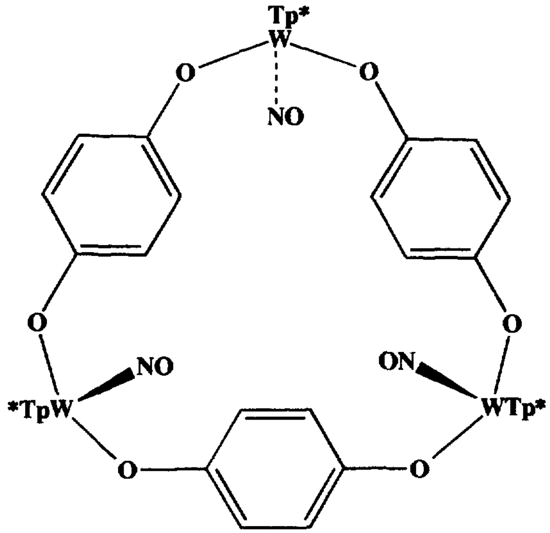
Two approaches were described for the derivatization of silica surfaces with tethered W(II) complexes [66]. The first relied on attachment of an aryl halide on the silica surface followed by oxidative addition using $W(CO)_3(RCN)_3$, while the second involved the synthesis of a W(II) complex with a pendant siloxane group which was then condensed onto silica (Scheme 17). Subsequent substitution and related reactions were also reported.

Different alkali metal alkoxides led to either simple metathesis or dimetallic products from $Cp^*W(NO)(CH_2SiMe_3)Cl$ in pentane (Scheme 18) [67]. Unlike the lithium or sodium salts, simple chloride metathesis was observed only with potassium alkoxide in THF or diethyl ether.

A trimeric metallocyclophane $[Tp^*W(NO)\text{–}O\text{–}C_6H_4\text{–}O]_3$ was prepared from $[Tp^*W(NO)I_2]$ and 1,4-dihydroxybenzene [68]. Its structure was determined and contains an *anti*, *syn* arrangement of nitrosyls (**33**). Three well-resolved reduction waves were observed in its cyclic voltammogram.



(32)

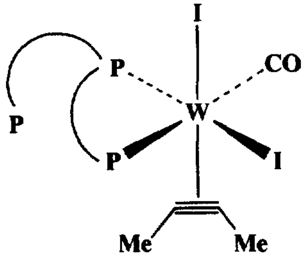


(33)

The 16-electron tungsten aryloxide complex [W(OC_6HPh_3-η^6-Ph)(OC_6HPh_4-2,3,5,6)(η^1-dppm)] was found to react with imines, ketones, and aldehydes (Scheme 19) [69]. A related aryloxide complex reacted with azobenzene to form a bis(phenylimido) complex in a facile four-electron reduction without overall metathesis of the azobenzenes (Scheme 20) [70].

6.2. Complexes with phosphine ligands

The polyphosphine $PhP(CH_2CH_2PPh_2)_2$ (L) and $[WI_2(CO)(NCMe)(\eta^2\text{-}RC{\equiv}CR')_2]$ were found to yield the monoalkyne product $[WI_2(L\text{-}P,P')(\eta^2\text{-}RC{\equiv}CR')]$ which existed as two diastereomeric forms in the solid state (**34**) and (**35**) [71]. The free phosphine sites in these products were used to prepare a variety of di- and trimetallic complexes.



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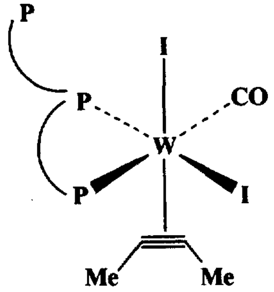


(35)

In contrast with its molybdenum analogue, reaction of the tungsten complex *trans*-W(CO)(DMF)(dppe)$_2$ with terminal acetylenes yielded only alkynyl/hydrido products of the type *trans*-W(C≡CR)H(CO)(dppe)$_2$ [72]. Alkylidyne and vinylidene derivatives were obtained by successive treatment with $HBF_4 \cdot Et_2O$ and NaOMe respectively. Metallophosphine complexes of the type $CpW(CO)_3\text{-}PR_2$ ($R_2 = {}^tBu_2$, (*o*-tolyl)$_2$, H(Mes), (Me)Mes) were oxygenated by dimethyldioxirane to give the corresponding metallophosphine oxides [73].

6.3. Complexes with cyclopentadienyl and carbonyl ligands

The new cationic complex $[Cp^*W(CO)_3(OEt_2)]^+$ was prepared from $Cp^*W(CO)_3Me$ and $[(Et_2O)_2H]BAr_4$ (Ar = 3,5-bis(trifluoromethyl)phenyl) [74]. Neutral donor ligands like MeCN, MeOH, and water readily replaced the diethylether. By contrast, tertiary phosphines PR_3 (R = Ph, Cy) yielded $Cp^*W(CO)_3H$ and novel phosphonium salts of the type EtOCH(Me)PR$_3^+$ via α-CH bond activation. A related cationic ether complex [CpW(CO)$_3$·O(Me)Bz]$^+$ was prepared from CpW(CO)$_3$H, PhCH(OMe)$_2$ and HOTf [75]. This was reported to decompose in solution with loss of BzOMe to form CpW(CO)$_3$OTf. The use of CpW(CO)$_3$–Co(CO)$_4$ as a single-source precursor for the MOCVD of a WCoO$_4$ film on silica was reported [76].

A variety of diynyl tungsten complexes were prepared by the CuI-catalyzed reactions of CpW(CO)$_3$–C≡C–C≡C–H with metal and nonmetal reagents [77]. A tetrayne complex was synthesized by the Hay coupling of this same precursor (Scheme 21).

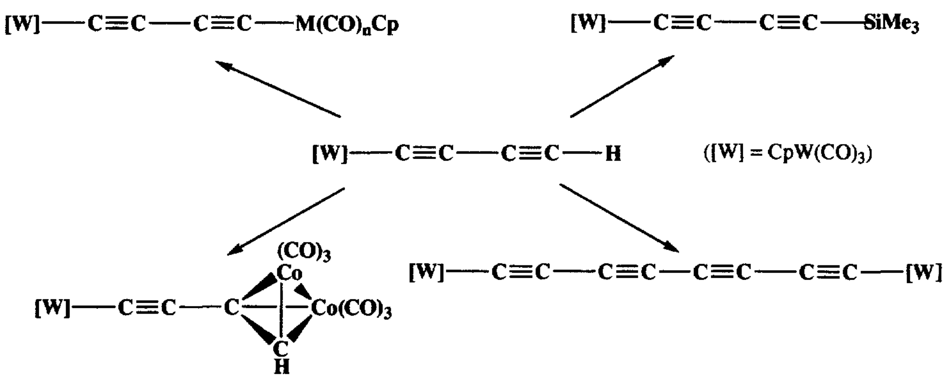
Preparation of new dinuclear CpW complexes singly- and doubly-bridged by SiMe$_2$ (Scheme 22) has been reported [78].

Lithium salts of ferrocenyl-substituted cyclopentadienes such as Li[C$_5$H$_2$Me$_2$C$_5$H$_4$FeCp] with WCl(NCMe)$_2$(CO)$_2$(η-C$_3$H$_5$) led to fulvalene-bridged heterodimetallic products (Scheme 23) [79]. Multiple palladium-catalyzed cyclopentadienylations led to tetra(cyclopentadienyl)Cp complexes of tungsten from (CO)$_3$W(η-C$_5$H$_4$I)Me (Scheme 24) [80]. No penta-Cp derivatives were obtained, probably due to severe sterical encumbrance.

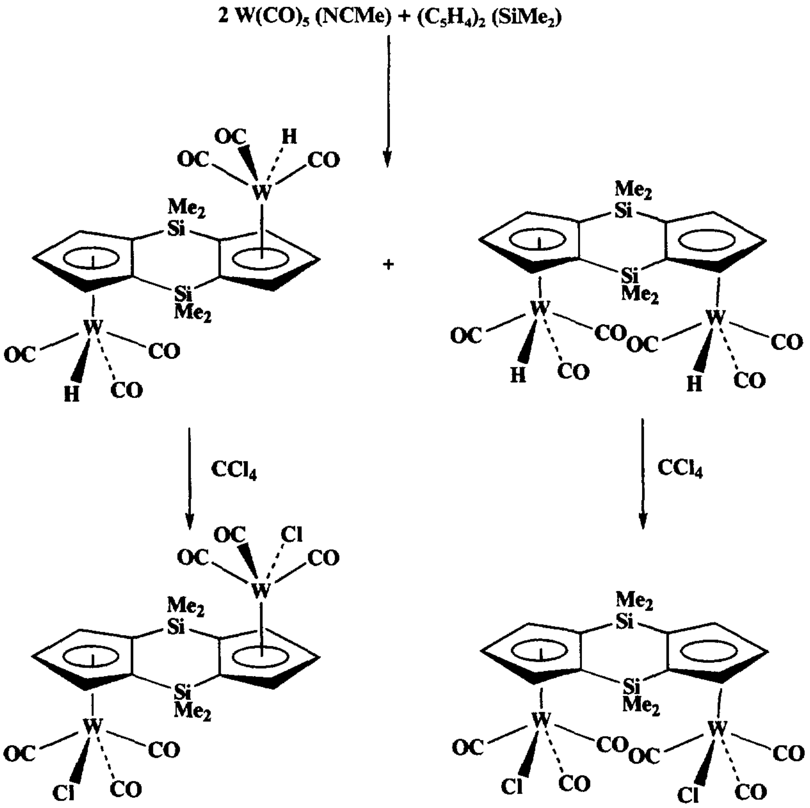
Labelling of biomolecules with tungsten may be realized with the new N-succinimidyl functionalized cyclopentadienyl complex (**36**) [81].

Electrophilic addition of CCl$_4$ to the cyclopentadienyl ring of Cp$_2$WCO gave CpW(CO)Cl(η^4-C$_5$H$_5$-*exo*-CCl$_3$) (**37**) [82]. Protonation of the respective cyclopentadienyl tungsten hydride complexes with triflic acid led to the dihydrides [CpW(CO)$_3$(H)$_2$]OTf and [CpW(CO)$_2$PMe$_3$(H)$_2$]OTf [83,84]. The solid-state structure of the latter (**38**) revealed weak hydrogen bonding between one W–H and two of the triflate fluorines.

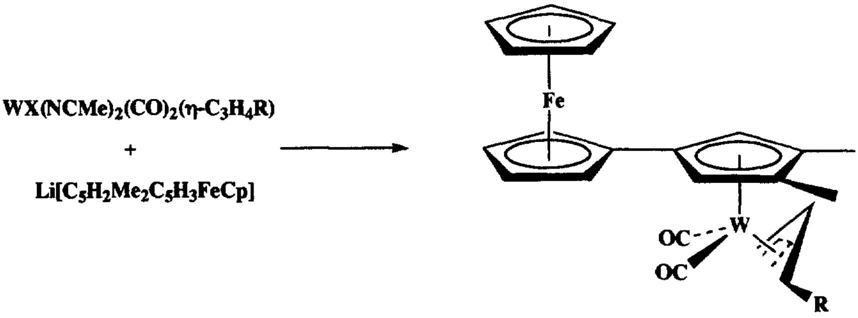
A 2-cyclopentenone and two cyclopentadienone tungsten carbonyl complexes have been prepared and structurally characterized [84]. These include W(η^3-C$_5$H$_5$O)(CO)$_2$(Tp), [W(η^4-C$_5$H$_4$O)(CO)$_2$(Tp)]$^+$, and [W(η^4-C$_5$H$_4$O)(CO)$_2$(dppm)Br]$^+$ (**38a**, **38b**, **38c**).



Scheme 21.



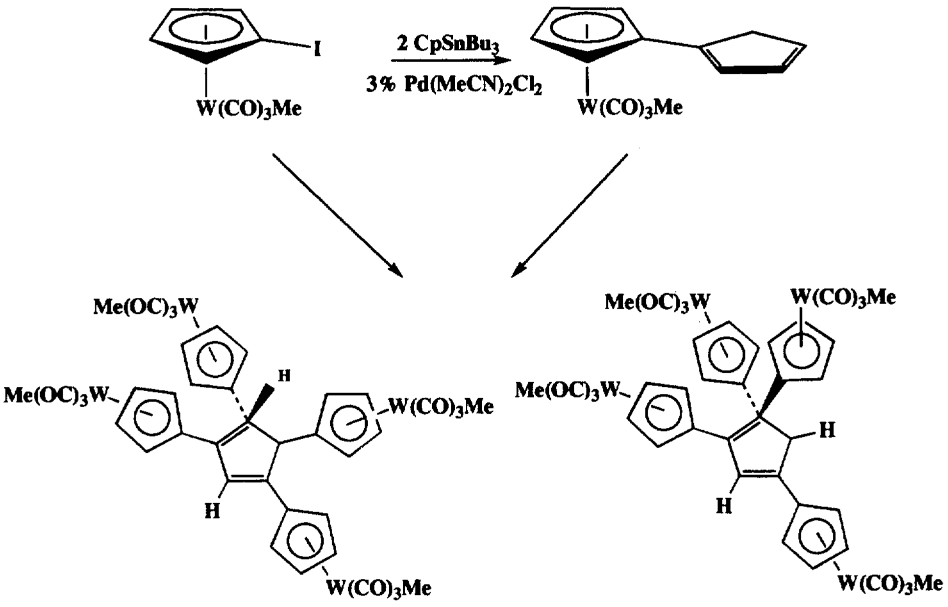
Scheme 22.



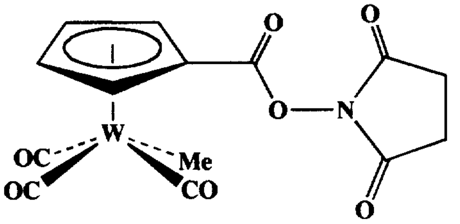
Scheme 23.

6.4. Complexes with tungsten–O, S, and Se bonds

N-acyl-α-aminocarboxylate complexes of tungsten (**39**) have been prepared from the respective N-acyl-α-aminoacidate and $WBr_2(CO)_2(PPh_3)_2$ [85]. Hydrido



Scheme 24.



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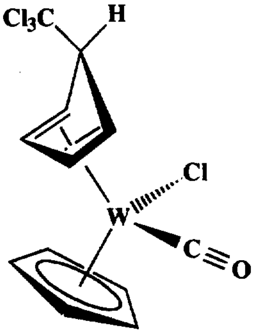

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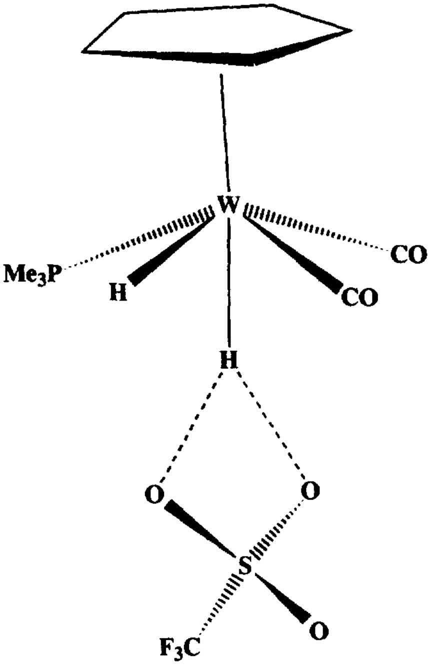

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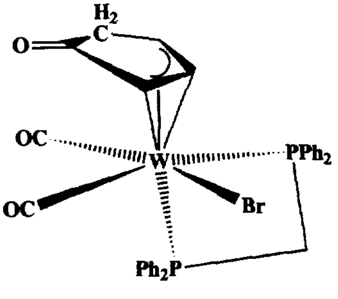
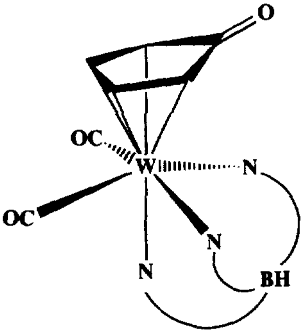
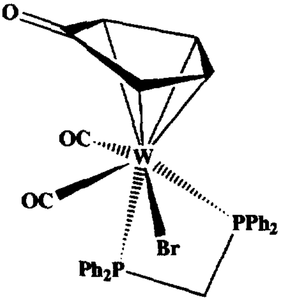


(38a)



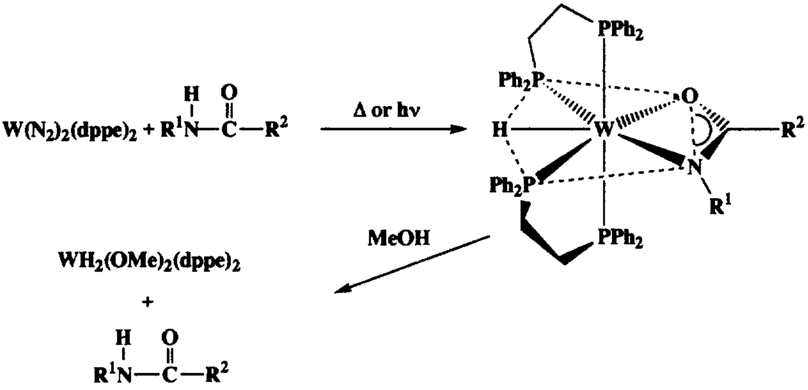
(38b)



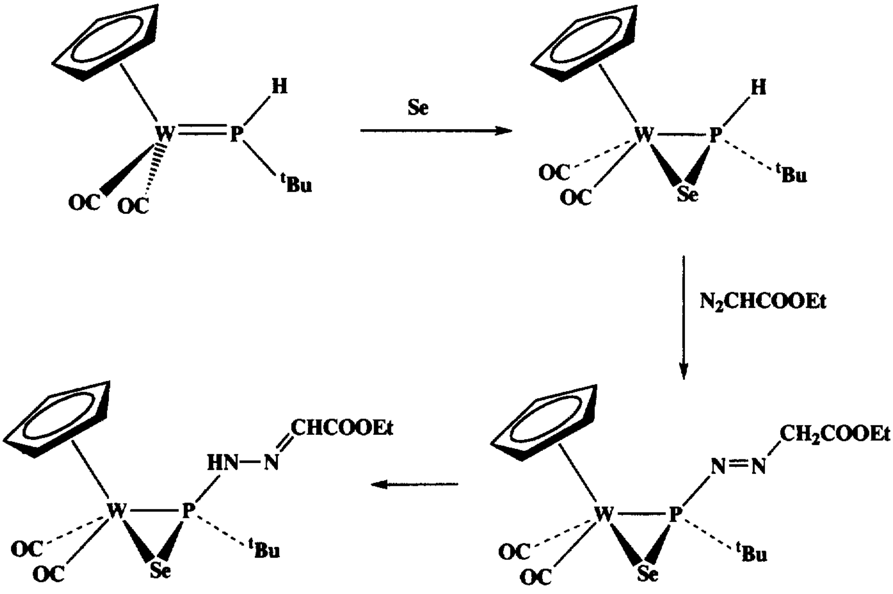
(38c)

tungsten(II) η^2-N-acylamido-N,O complexes were obtained from *trans*-$W(N_2)_2(dppe)_2$ and N-alkylamides [86]. The products $[WH\{NR^1COR^2\text{-N,O}\}(dppe)_2]$ were found to undergo methanolysis to yield the alkylamide and $WH_2(OMe)_2(dppe)_2$ (Scheme 25).

The dithio-chelating ligand $Ph_2P(S)CH_2P(S)Ph_2$ was reported to react with seven-coordinate $WI_2(CO)_3(NCMe)_2$ to give $WI_2(CO)_3\ \{Ph_2P(S)CH_2P(S)Ph_2\}$-*S*,*S′*. This



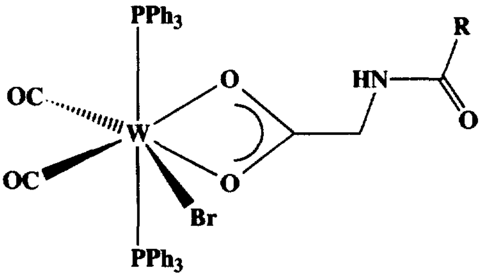
Scheme 25.



Scheme 26.

chelating ligand was readily displaced by dppm [87]. Reaction of the trithioether $MeS(CH_2)_2S(CH_2)_2SMe$ with $WI_2(CO)(NCMe)(PhC{\equiv}CPh)$ gave the product $WI_2(CO)((PhC{\equiv}CPh)(\eta^2\text{-}SMe(CH_2)_2S(CH_2)_2SMe\text{-}S,S')$ (**40**) [88].

The 1,4,9-trithiacyclononane ($[9]aneS_3$) ligand gave cationic $[WI(CO)_3([9]aneS_3)]I$ from $WI_2(CO)_3(NCMe)_2$ [89]. The solid state structure of this product as the tetraphenylborate salt revealed a CO-capped octahedral geometry (**41**). A related reaction using 2,5,8-trithia-[9]orthocyclophane (L) and $WI_2(CO)_3(NCMe)_2$ yielded the product $[WI(CO)_2L][WI_3(CO)_4]$.



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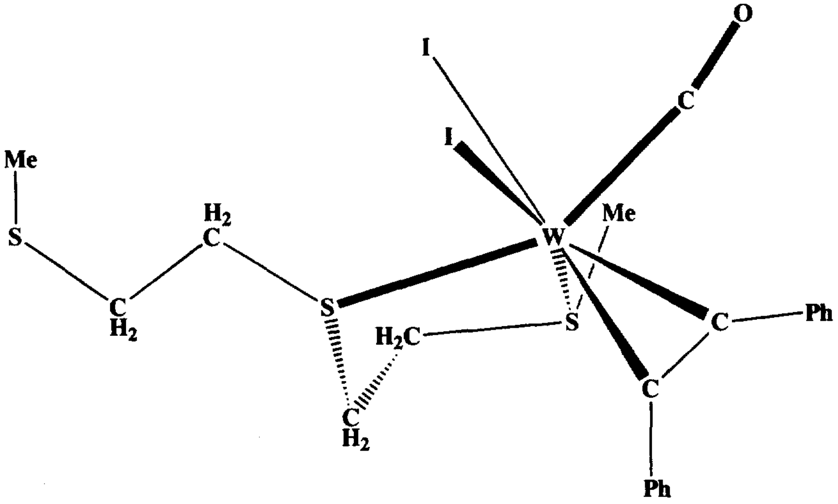


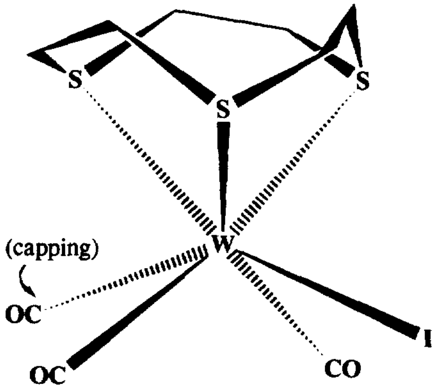
(40)

The X-ray structure of the selenophosphine tungsten cationic complex $[CpW(CO)_3(SePPh_3)]^+$ has been determined (**42**) [90]. It is noted that the long P–Se distance of 2.194(1) Å is more consistent with a selenophosphonium–W(I) formulation.

Three-membered phosphametallocycles were available from the [2+1] cycloadditions of S, Se, and Te to $Cp(CO)_2W{=}PH(^tBu)$ and $Cp^*(CO)_2W{=}PH(^tBu)$ [91]. These products were shown to undergo further reactions at their P–H functionality (Scheme 26).

6.5. Complexes with tungsten–tungsten bonds

The LMCT photochemistry of quadruply-bonded tungsten dimers $W_2Cl_4(PR_3)_2$ ($PR_3 = PMe_3$, PMe_2Ph, PBu_3) in dichloromethane has been examined



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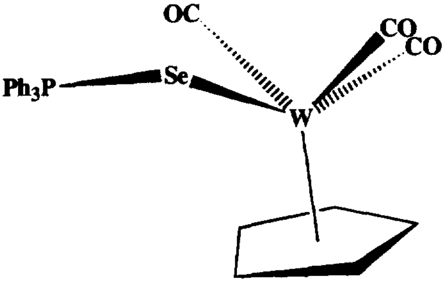
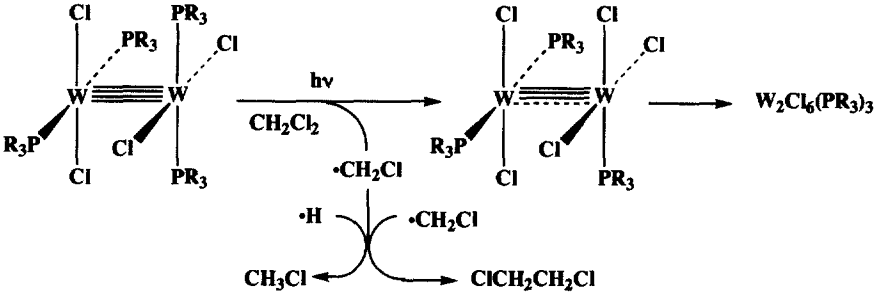


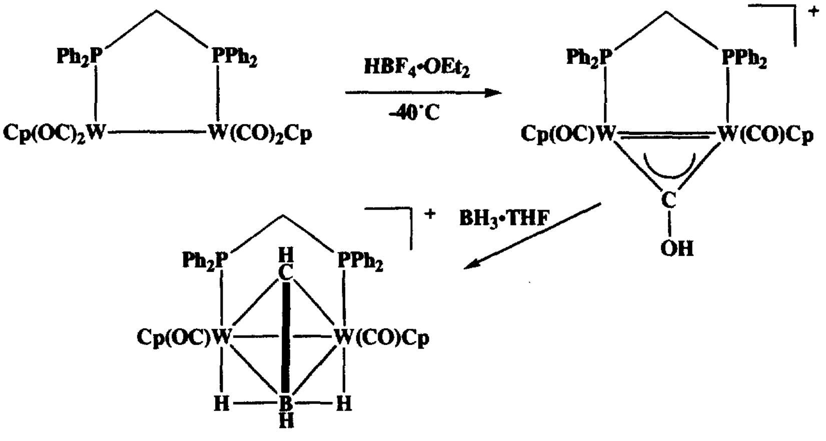
(42)

[92]. Only near-UV excitation produced a mixed-valent W_2(II,III) photoproduct and then confacial bioctahedral $W_2Cl_6(PR_3)_3$ (Scheme 27). This reduced the solvent to give chloromethane or dichloroethane at higher concentrations.

A stable hydroxycarbyne complex was obtained from the protonation of a tungsten carbonyl dimer (Scheme 28) in methylene chloride [93]. The carbonyl reduction to methylidyne was completed by using borane·THF. The tricobalt cluster

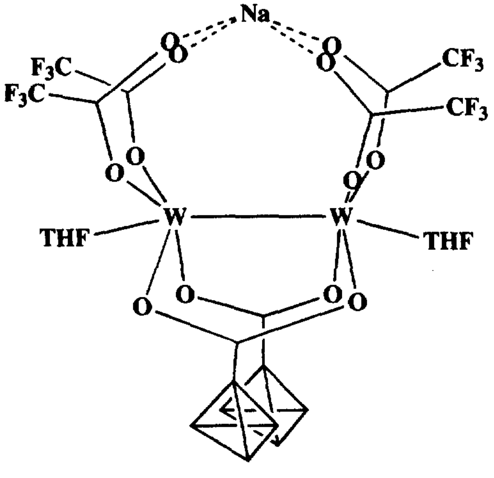


Scheme 27.



Scheme 28.

$Co_3(CO)_9COOH$ was used as a ligand to bridge the W–W bond in $W_2(OOCCF_3)_4$ [94]. In the presence of sodium triflate, the paramagnetic product $\{Na[W_2(OOCCF_3)_4(OOC\text{-}Co_3(CO)_9)_2(THF)_2]\}_2$ (**43**) formed.



(**43**)

7. Tungsten(I)

The gas phase reactions of the bare tungsten cation W^+ with silane have been investigated by FT-ion cyclotron resonance mass spectrometry [95]. The short-lived 17-electron radical complex $CpW(CO)_3^{\cdot}$ generated by the photolysis of

$Cp_2W_2(CO)_6$ has been studied by photomodulated voltammetry [96]. An oxidative shift of 115 mV from previous estimates was noted for the reduction potential. Acetic acid/Fe(III) oxidation of the dianionic product from the reaction of $W(CO)_3(MeCN)_3$ with $K_2[C_5H_4{-}CMe_2{-}C_5H_4]$ afforded the new ring-coupled dimetallic complex $W_2(CO)_6[\eta^5,\eta^5\text{-}C_5H_4{-}CMe_2{-}C_5H_4]$ [97].

8. Tungsten(0)

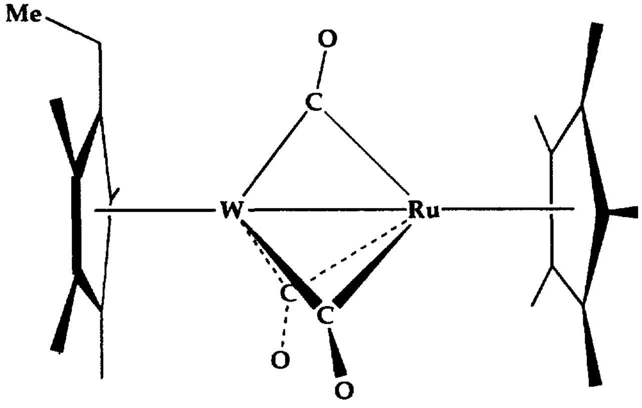
8.1. Complexes with carbon ligands

The cyanide-bridged complex $(CO)_5W{-}CN{-}Cu(PPh_3)_3$ has been prepared and its structure determined to reveal a C–N bond length of 1.15(2) Å [98]. The linkage isomer $(CO)_5W{-}NC{-}Cu(PPh_3)_3$ was also prepared and its dynamic NMR spectra studied.

All the iron vertices in the Fe_4S_4 cluster were bridged by cyanides to four $W(CO)_5$ moieties by the reaction of $[(CO)_5WCN]^-$ with the $[Fe_4S_4Cl_4]^{2-}$ cluster anion [99].

Carbon and oxygen NMR chemical shift tensors for hexacarbonyl Group 6 metal complexes have been calculated by ab initio metal effective core potential/density functional theory [100]. A time-resolved infrared and UV spectroscopic investigation of the photochemistry of Group 6 $M(CO)_6$ in supercritical noble gases as well as CO_2 solutions has been reported [101]. Detection of $W(CO)_5Ar$, $W(CO)_5Kr$, and $W(CO)_5Xe$ at room temperature has been realized. The xenon complex was found to have stability and reactivity comparable to $W(CO)_5(CO_2)$ and $W(CO)_5$(n-heptane) complexes.

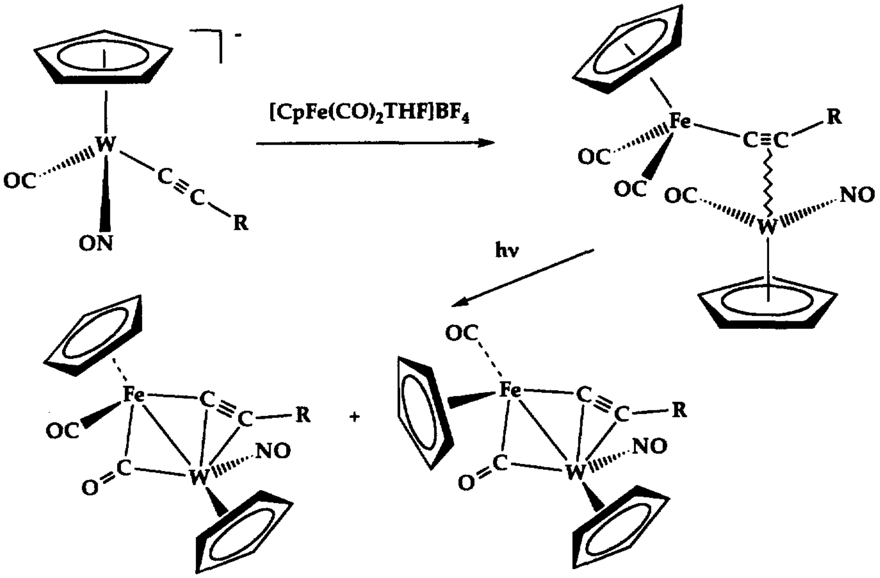
Reactions of $[C_5R_5W(CO)_3]^-$ and $[Cp^*Ru(MeCN)_3]^+$ yielded a series of unsymmetrically carbonyl-bridged heterodimetallic complexes $C_5R_5W(\mu\text{-}CO)_3RuCp^*$ (**44**) [102].



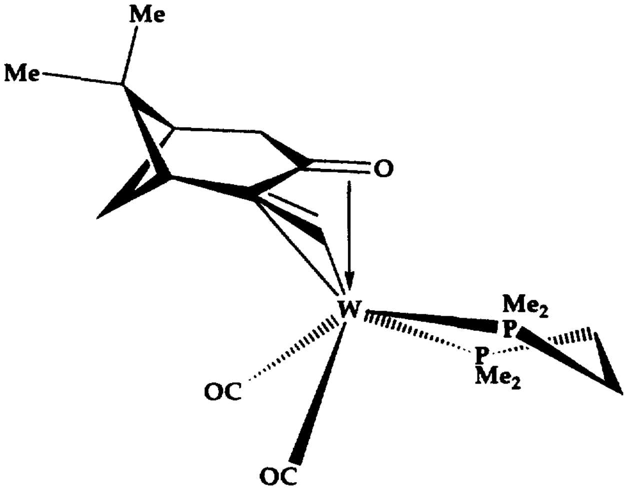
(44)

The anionic metallate [Cp(CO)(NO)W–C≡C–R)]$^-$ with [CpFe(CO)$_2$THF]BF$_4$ formed dimetallic η^2-alkyne complexes which were photodecarbonylated to give diastereomeric mixtures of bridged σ,π-acetylides (Scheme 29) [103].

Chelating ligands were found to displace one oxadiene ligand from W(CO)$_2$(η^4-1-oxa-1,3-diene)$_2$ to give complexes like (**45**) [104]. Decreased reactivity at the carbonyls allowed selective alkylations of their anionic derivatives.



Scheme 29.



(**45**)

Novel C–C double and triple bond cleavages and alkyne insertions were reported for the reactions of W(PhC≡CPh)$_3$(NCMe) with *o*-diphenylphosphinostyrene and allylbenzene (Scheme 30) [105]. It was suggested that three-electron η^2-vinyl intermediates were involved in these transformations.

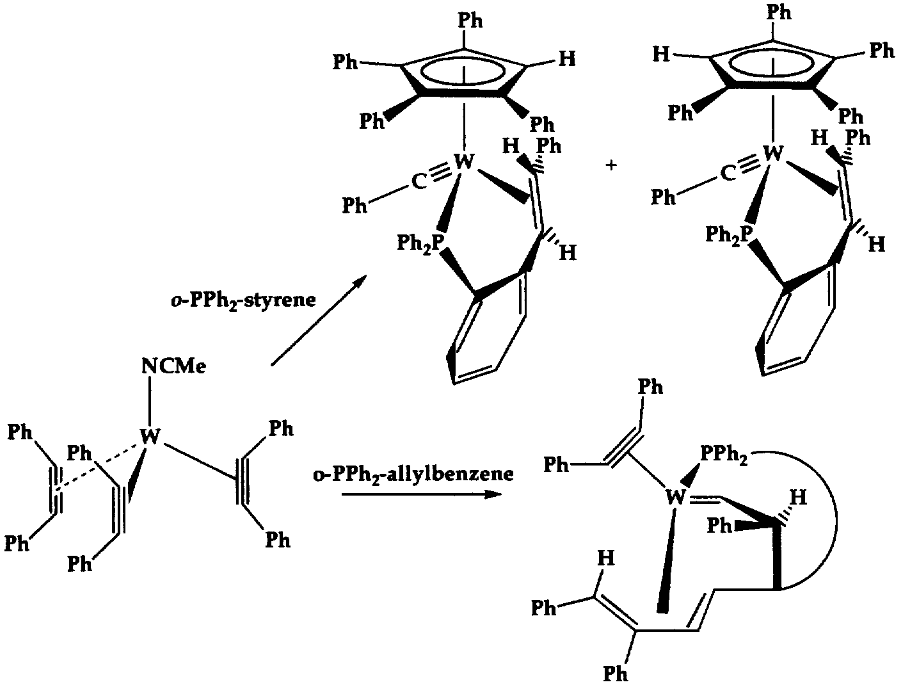
8.2. Complexes with nitrogen ligands

Interaction of ^{15}N-labelled *trans*-W(dppe)$_2$($^{15}N_2$)$_2$ with nitronium and nitrosonium salts was found to give up to 10–20 mol% labelled $^{15}N^{14}NO$, ^{15}NO, and $^{15}N^{14}N$ products [106]. The proposed mechanism involved initial protonation of the dinitrogen ligands followed by NO_2^+ and NO^+ attack.

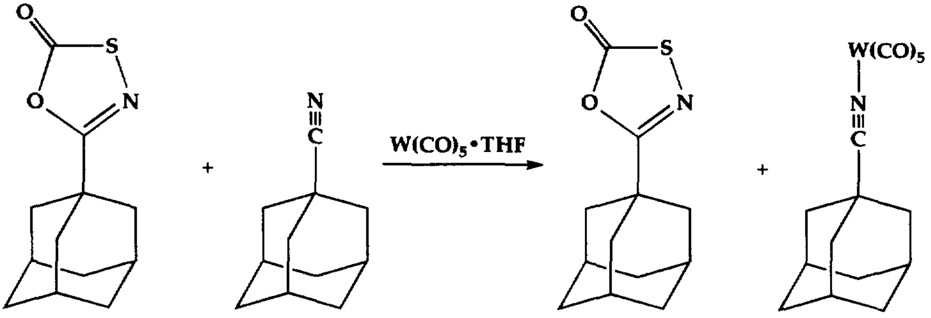
Selective complexation of the adamantane nitriles by W(CO)$_5$ allowed their easy separation from adamantyl-oxathiazol-2-ones (Scheme 31) [107].

The X-ray structure of *cis*-W(CO)$_4$(py)$_2$ has been determined [108]. The *trans,mer* tungsten complex [(PCy$_3$)$_2$(CO)$_3$W(N-alkylpyrazinium)]PF$_6$ was studied spectroelectrochemically [109]. It was found that oxidation yielded a labile 17-electron W(I) species while reduction was centred at the pyrazinium ligand resulting in reversible phosphine loss.

Iodine oxidation of the zwitterionic complex (CO)$_5$W–NPhNPhC(OMe)Ph in a 1:1 stoichiometry led to an iodo-bridged imido dimer while two equivalents of I$_2$



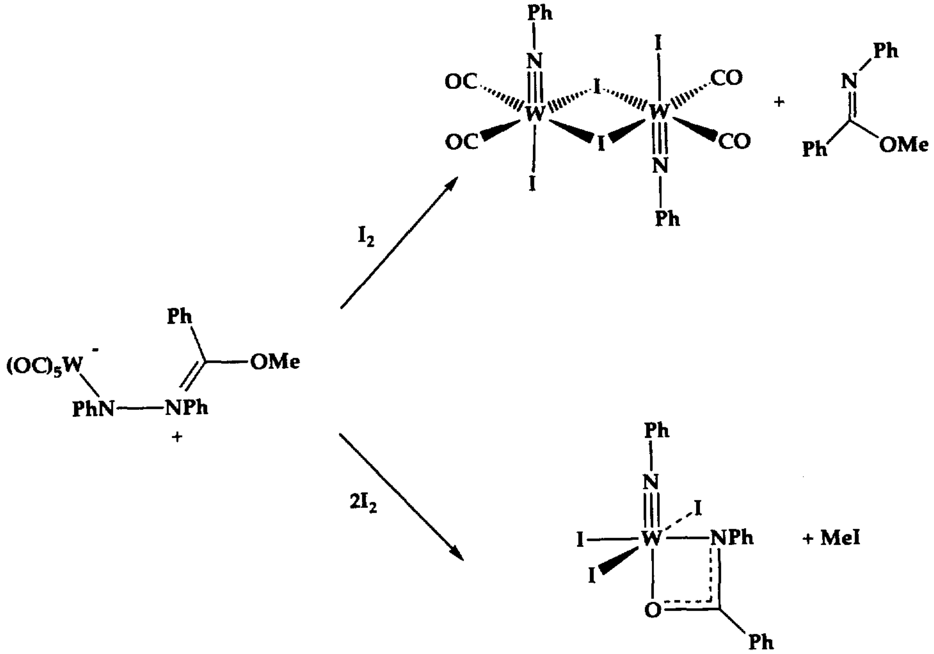
Scheme 30.



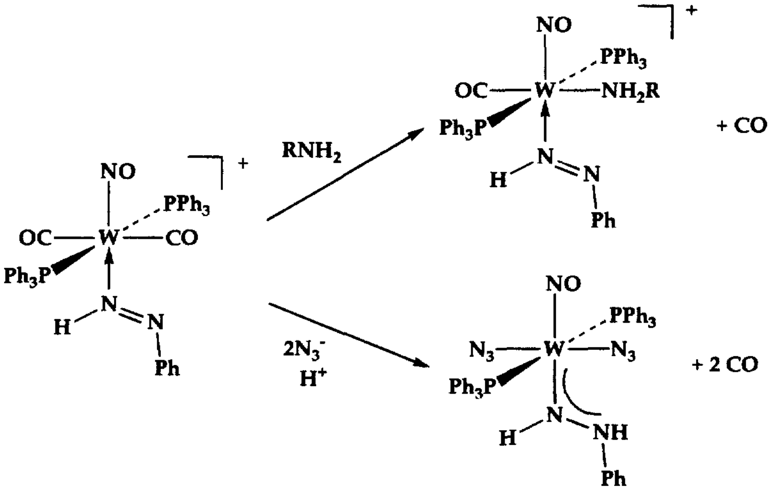
Scheme 31.

yielded an unusual 16-electron W(VI) metallocycle (Scheme 32) [110]. It was suggested that the common intermediate $(CO)_3W(NPh)I_2$ was involved in both processes.

Tungsten carbonyl complexes containing a variety of didentate nitrogen donor ligands have been prepared and studied by IR and multinuclear NMR spectroscopy [111]. Reactions of the tungsten phenyldiazene complex $[W(NH{=}NPh)(CO)_2(PPh_3)_2]PF_6$ with azide and amines were found to proceed without loss of the diazene ligand (Scheme 33) [112]. By contrast, bromide reactions led to facile displacement of the diazene ligand.



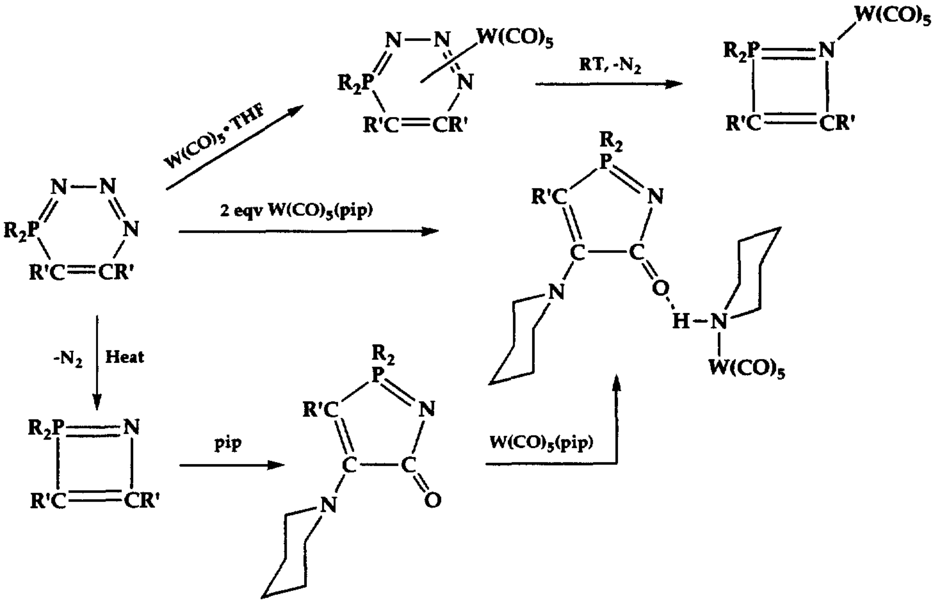
Scheme 32.



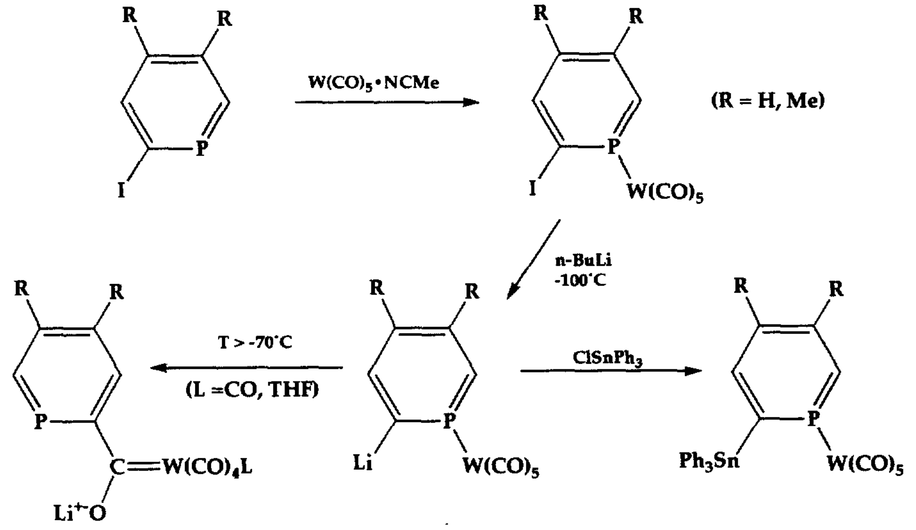
Scheme 33.

8.2.1. *Monometallic complexes with heterocyclic phosphorus ligands*

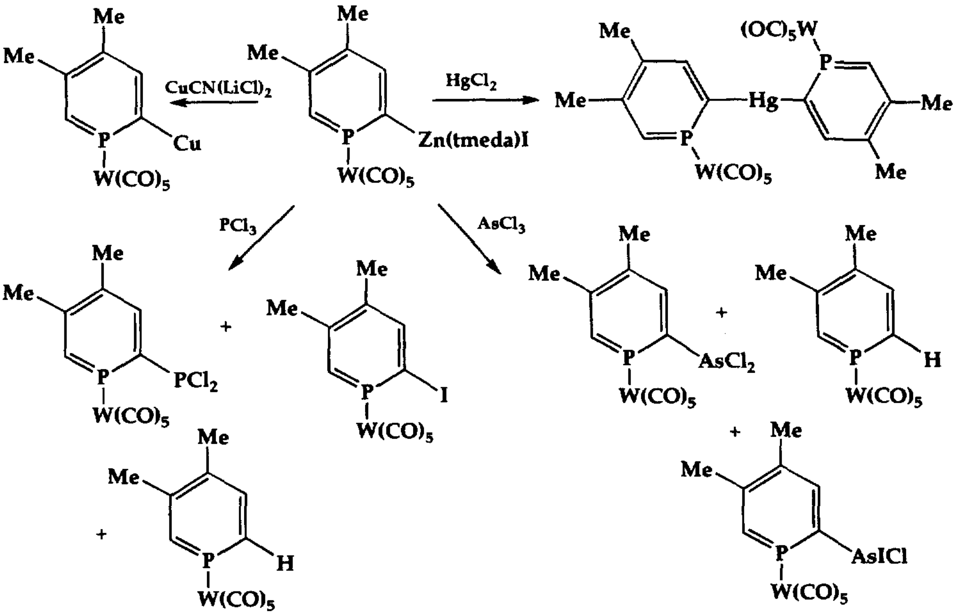
The triazaphosphinine (1,2,3,4λ^5-) was reported to react with $W(CO)_5 \cdot THF$ to give an intermediate which eliminated N_2 to afford an azaphosphete complex (Scheme 34) [113]. Reaction of the same ligand with two equivalents of $W(CO)_5(pip)$ led to a H-bonded phosphazene.



Scheme 34.



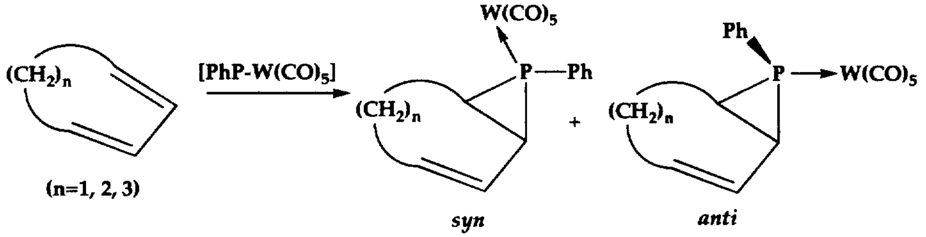
Scheme 35.



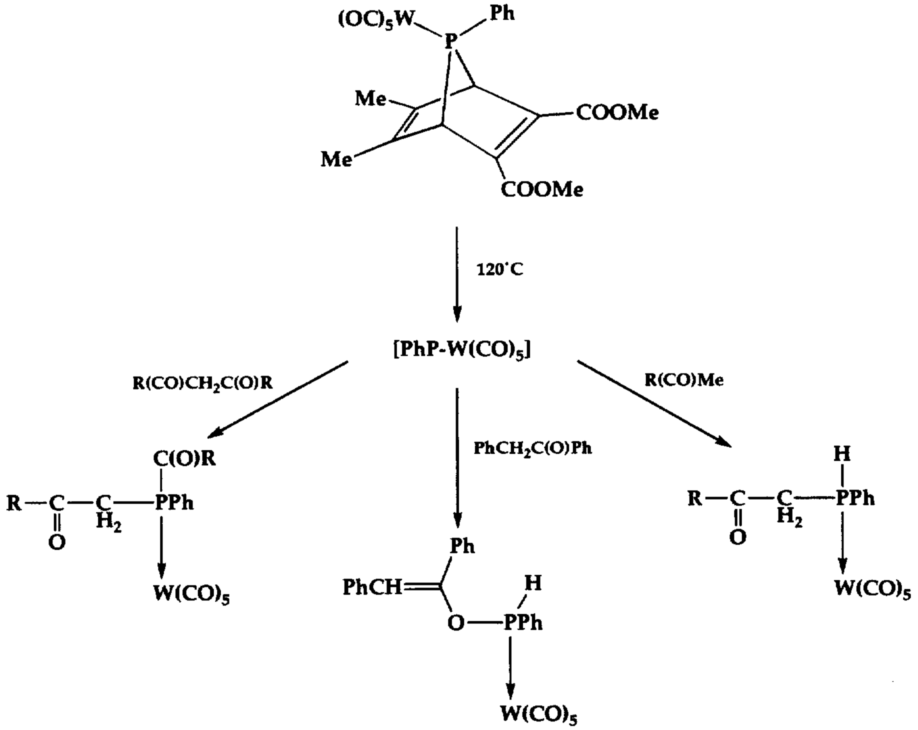
Scheme 36.

The synthesis and coordination of 2-iodophosphinines to pentacarbonyltungsten gave the corresponding 1:1 complexes [114]. These were lithiated to prepare 2-substituted derivatives (Scheme 35). The reactivity of an organozinc derivative of the same phosphinine with a variety of main group electrophiles was studied [115]. Both PCl_3 and $AsCl_3$ yielded several products (Scheme 36) while copper and mercury salts gave thermally unstable derivatives.

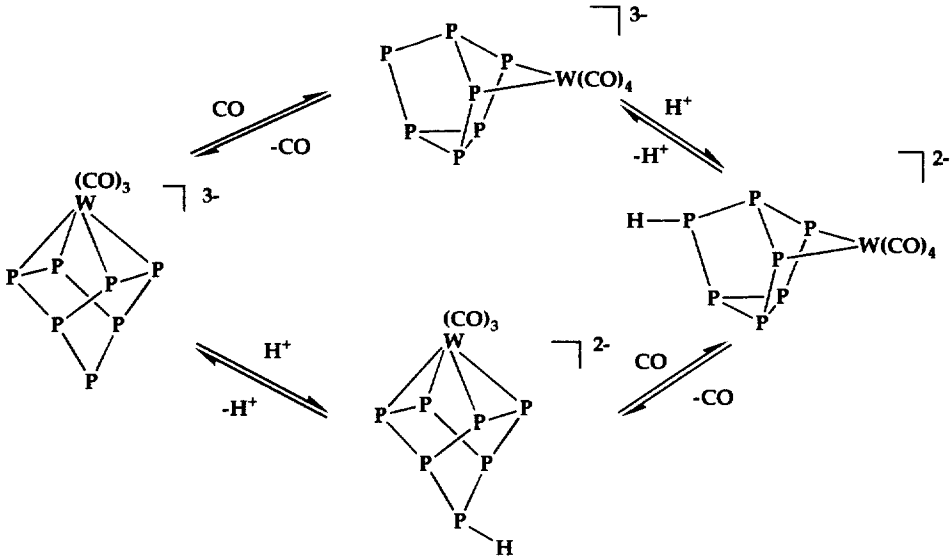
The transient phosphinidene complex PhP–W$(CO)_5$, generated in situ, was found to give isomeric mixtures of *syn*- and *anti*-vinylphosphiranes with a variety of cyclodienes (Scheme 37) [116]. Epimerization at the P centre was found to occur, converting *anti*- to *syn*-isomers. It was proposed that a biradical intermediate was involved except for the 1,3-cyclohexadiene adducts. The same transient phosphinidene tungsten complex was found to react with enolizable ketones to give products



Scheme 37.



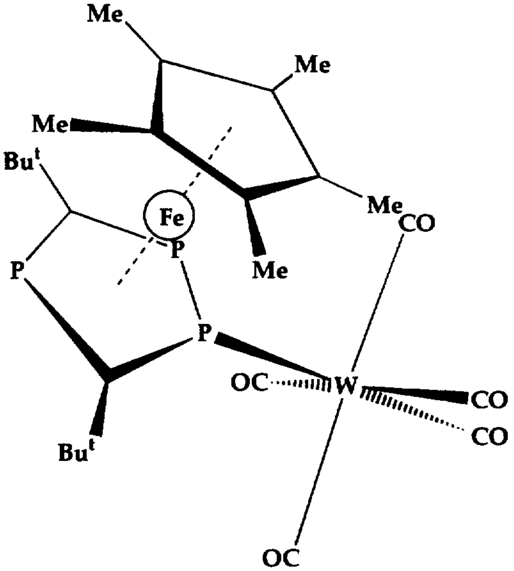
Scheme 38.



Scheme 39.

from P-insertion into either the α-C–H, the enol O–H, or the acyl CH_2 bonds (Scheme 38) [117].

Synthesis and structure of the $Cp^*Fe(C_3{}^tBu_3P_2)$ sandwich complex adduct with $W(CO)_5$ (**46**) have been described [118].

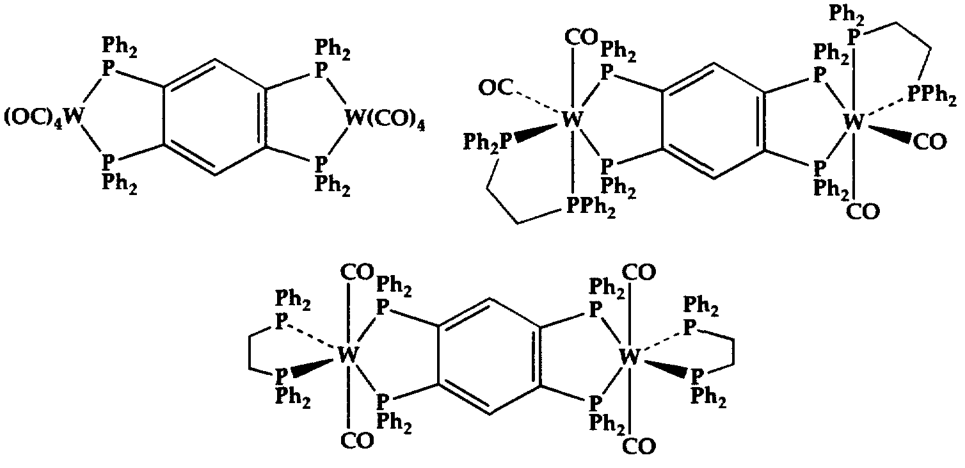


(46)

Reactions of the zintl ion complex $[\eta^4\text{-}P_7W(CO)_3]^{3-}$ with a variety of reagents were reported (Scheme 39) [119]. The P_7 core was conserved in all these transformations.

8.2.2. *Complexes with phosphines*

The tetradentate ligand, 1,2,4,5-*tetrakis*(diphenylphosphino)benzene, has been used to link Group 6 carbonyl complexes [120]. Examples of products are shown in (**47**). Tridentate phosphinothiolate tungsten complexes of the type $W(CO)_3[PhP(C_6H_4S\text{-}2)_2]^{2-}$ have been prepared [121]. New hybrid materials were prepared by intercalation of a bifunctional aminophosphine ($Ph_2PCH_2CH_2NMe_2$) inside solid α-zirconium phosphate [122].



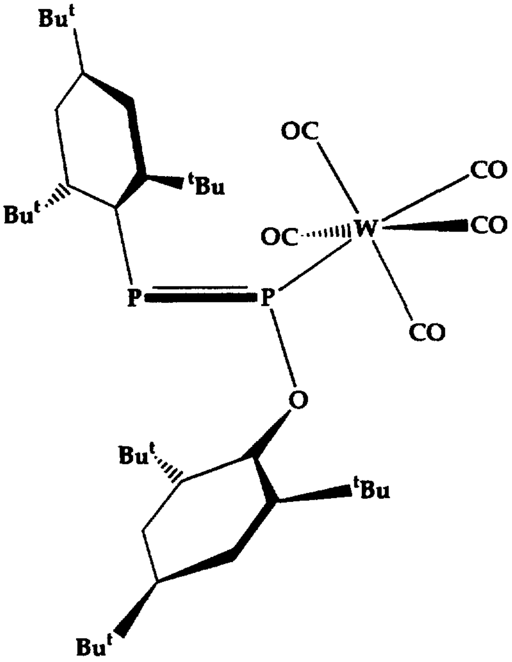
(**47**)

The kinetics of the *fac*/*mer* isomerization in $M(CO)_{6-x}[P(OMe)_3]_x$ (M = Cr, Mo, W) have been studied [123]. The rates increased in the order $x = 3 < 2$ and for M = Mo < Cr.

The asymmetric diphosphene bearing bulky aryl as well as aryloxy substituents was found to give as a major product the isomer with coordination at the less bulky aryloxy end (**48**) [124]. The ^{31}P chemical shift tensors for the complexes $M(CO)_5 \cdot PX_3$ (M = Cr, Mo, W; X = H, Me, F, Cl) have been studied by a combination of density functional theory and ab initio effective core potentials [125]. Optically active dimetallic complexes containing tungsten and featuring a chiral tantalum centre have been prepared [126]. Both diastereomers of $(1\text{-}^tBu\text{-}3,4\text{-}Me_2\text{-}C_5H_2)CpTa(CO)(\mu\text{-}PMe_2)W(CO)_4$ [(R)-(+)-phenyl (*o*-anisyl)-methylphosphine], differing only in the absolute configurations at Ta, were isolated and structurally characterized.

8.3. *Complexes with oxygen, sulfur and selenium ligands*

The $[W(CO)_5OH]^-$ anion was synthesized by the photolysis of $W(CO)_6$ in methanol, and its reversible reaction with carbon dioxide reported [127]. A monodentate



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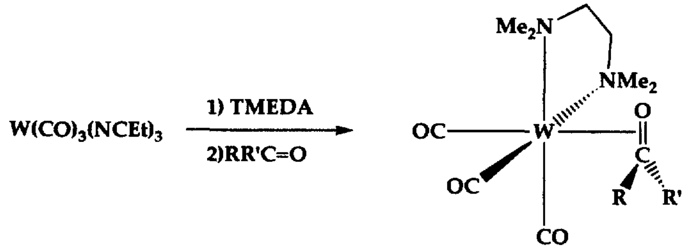
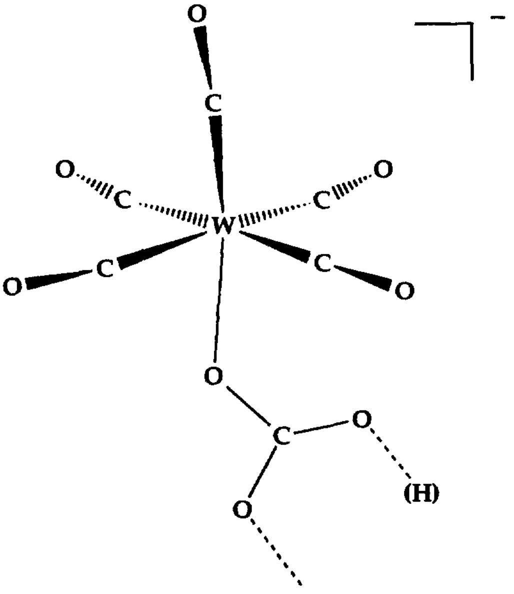


Scheme 40.

bicarbonate hydrogen-bonded to another identical anion was found in the product's structure (**49**). Additionally, kinetic studies revealed that the decarboxylation rate was faster than that of CO dissociation.

A first example of an η^2-bound aldehyde at tungsten(0) was reported [128]. These include the complexes $W(CO)_3$(tmeda)(η^2-RR′CO) (Scheme 40).

Unsaturated tungsten tricarbonyl dianions of 3,5-di-*tert*-butylcatechol, 2-aminophenol and 1,2-diaminobenzene have been prepared and characterized [129,130]. The formally 16 e^- metal centres are stabilized by π-donation from the oxygen and amido groups (**50**).



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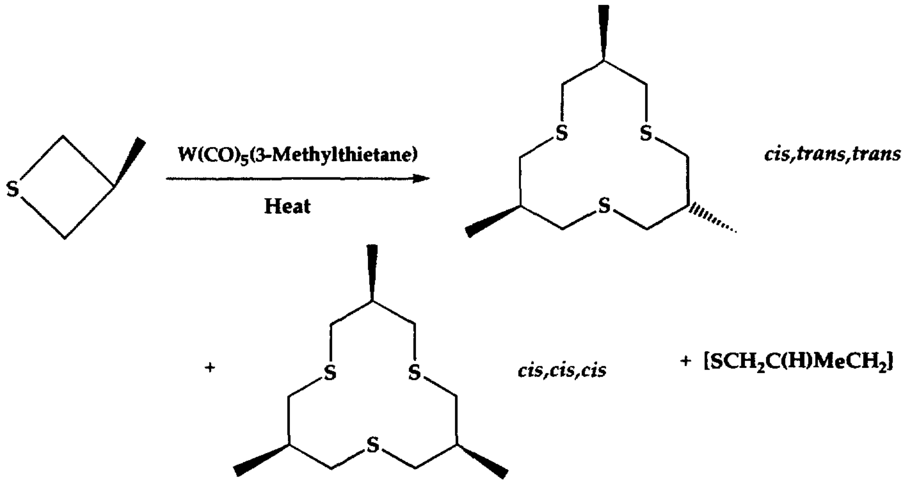
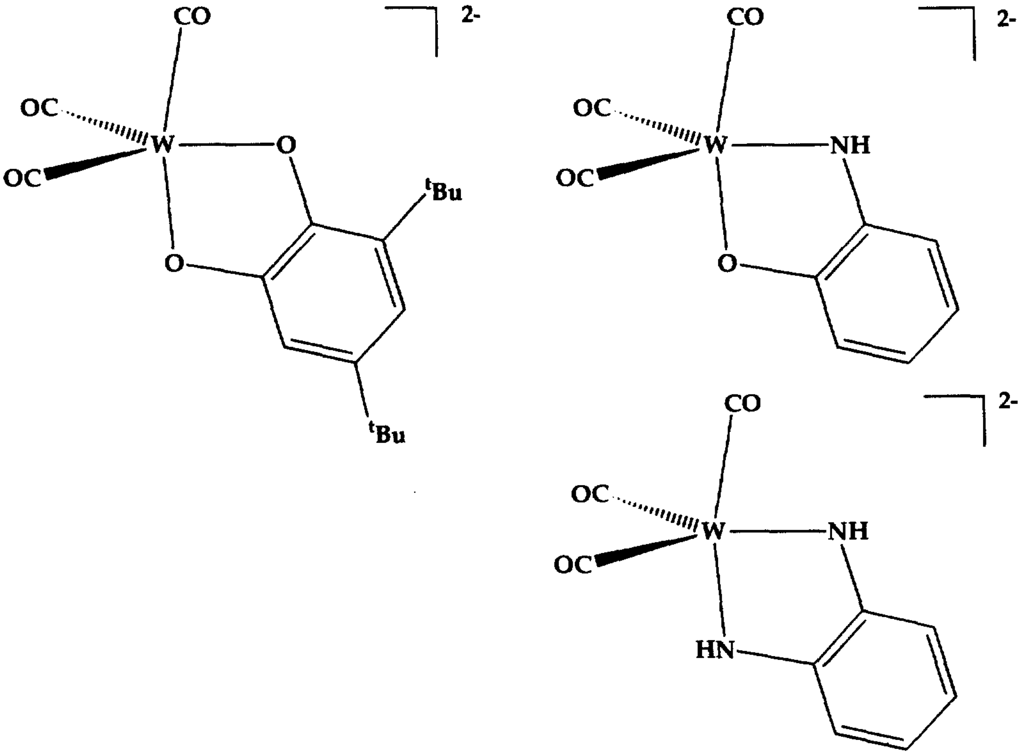


Scheme 41.

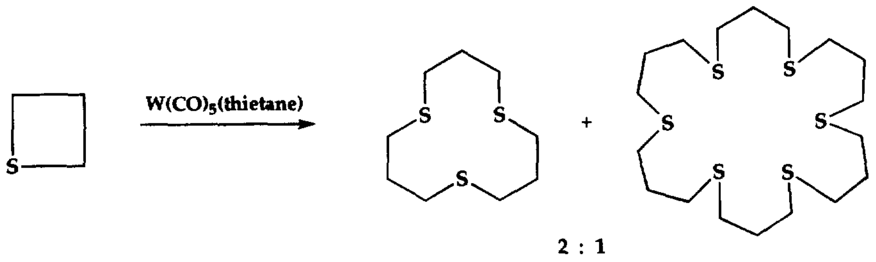
Catalytic macrocyclization of 3-methylthietane by W(CO)$_5$(3-methylthietane) yielded mainly trithiaether macrocycles (Scheme 41), though the activity and selectivity were less than that for the Re$_2$(CO)$_9$(3-methylthietane) catalyst [131]. In a related full paper [132], W(CO)$_6$ was found to form W(CO)$_5$(thietane), W(CO)$_5$(1,5,9-trithiacyclododecane), and [W(CO)$_5$]$_2$(1,5,9-trithiacyclododecane)



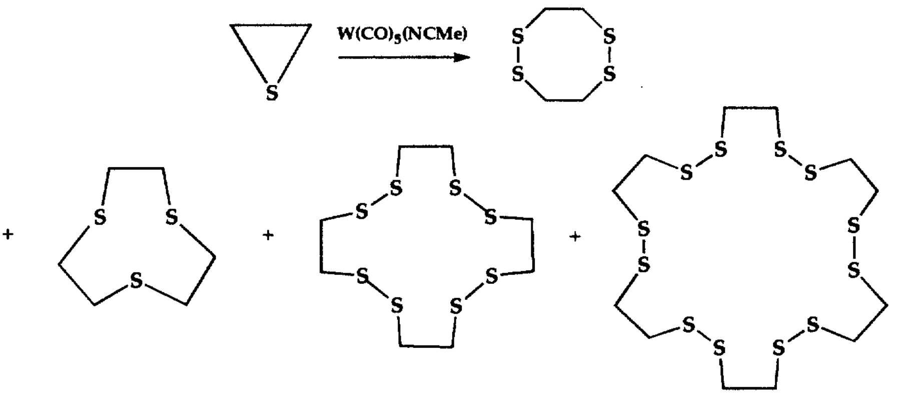
(50)

complexes. The latter two were active catalysts for the selective formation of the triathia macrocycle from thietane (Scheme 42).

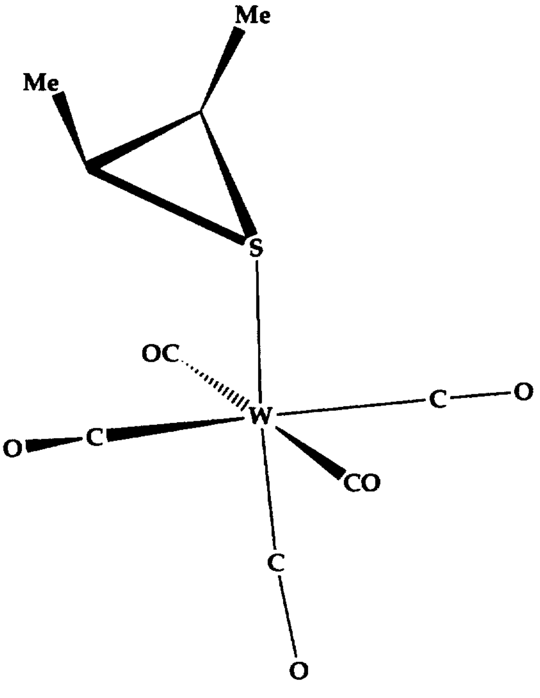
A subsequent communication reported the catalytic transformations of thiiranes by pentacarbonyltungsten(0) [133]. The major product was found to be $(CH_2CH_2SS)_2$ (Scheme 43). Structural characterization of a related intermediate (**51**) from 2(*R*),3(*S*)-dimethylthiirane was also achieved.



Scheme 42.



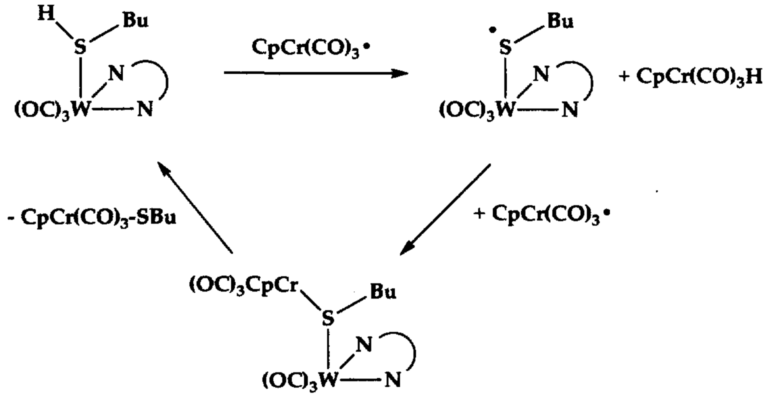
Scheme 43.



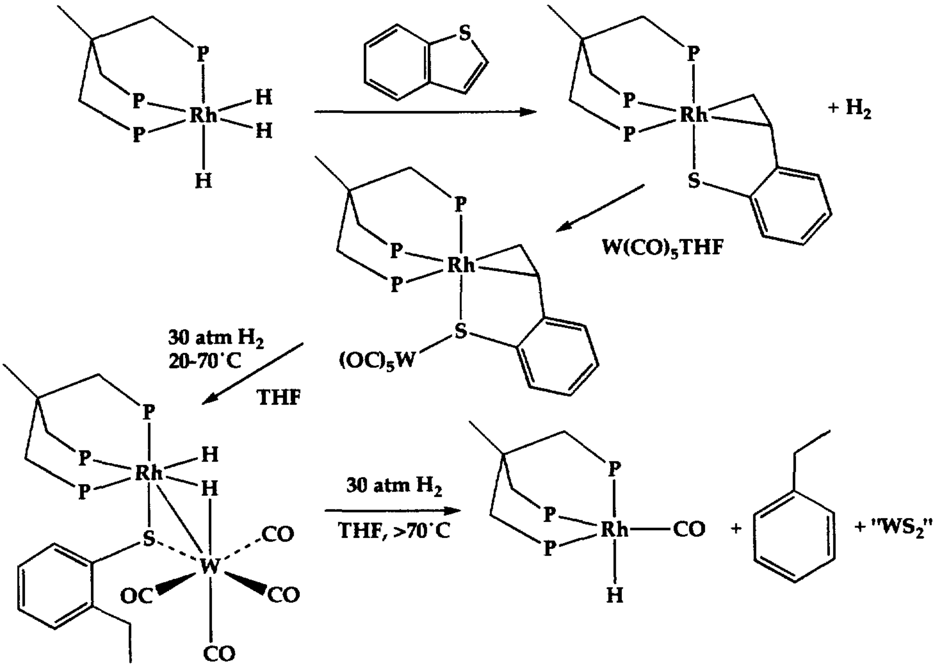
(51)

A third-order mechanism was proposed for the oxidative addition of thiols to the 17 e$^-$ Cr(CO)$_3$Cp* radical [134]. Dinuclear oxidative addition of thiols to two equivalents of the chromium radical was found to be catalyzed by W(CO)$_3$(phen)(NCEt) (Scheme 44).

An EHMO analysis of the fluxional behaviour of M(η^3-S$_2$CPMe$_3$)(CO)$_2$(PMe$_3$)$_2$ (M = Mo, W) complexes has been published [135]. A crystal structure



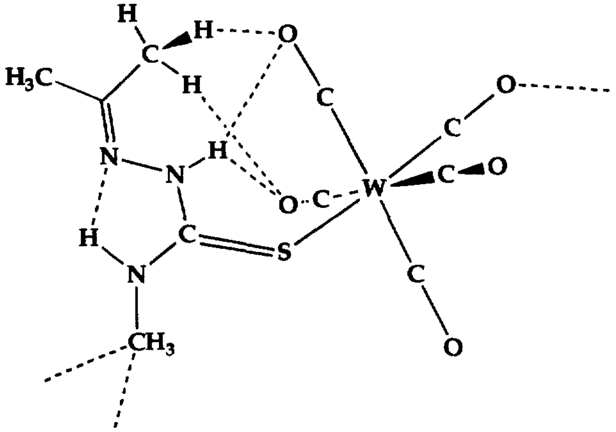
Scheme 44.



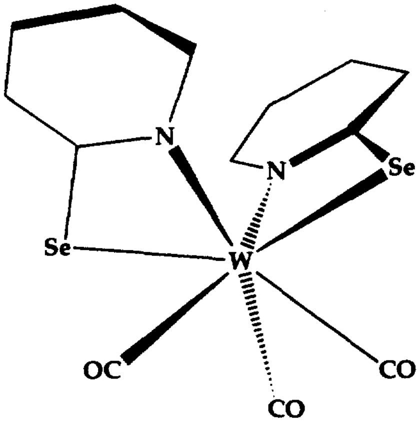
Scheme 45.

of W(CO)$_5$(acetone-4-methylthiosemicarbazone) revealed both intra- and intermolecular H-bonds (**52**) [136].

Insights into the commercially important heterogeneous hydrodesulfurization catalysts and their promoters have been obtained through the characterization of a Rh/W dimetallic intermediate (**53**) as shown in Scheme 45 [137].



(52)



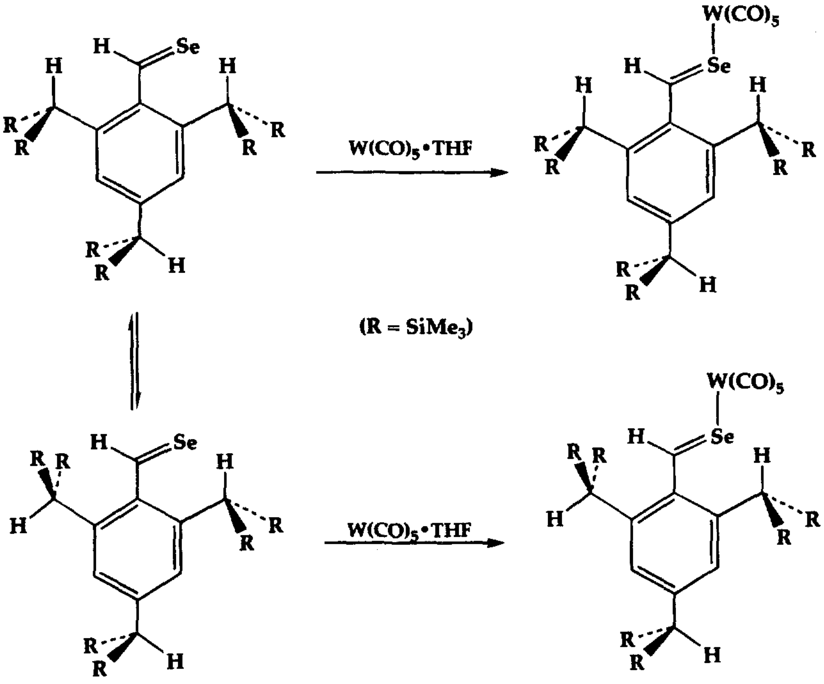
(54)

The reaction of 2,2′-dipyridyl diselenide with $W(CO)_4(nbd)$ led to cleavage of the Se–Se bond and metal oxidation to form the seven-coordinate $W(SePy)_2(CO)_3$ (**54**) [138]. Stable coordination complexes from the rotational isomers of selenaldehydes with pentacarbonyltungsten have been characterized (Scheme 46) [139].

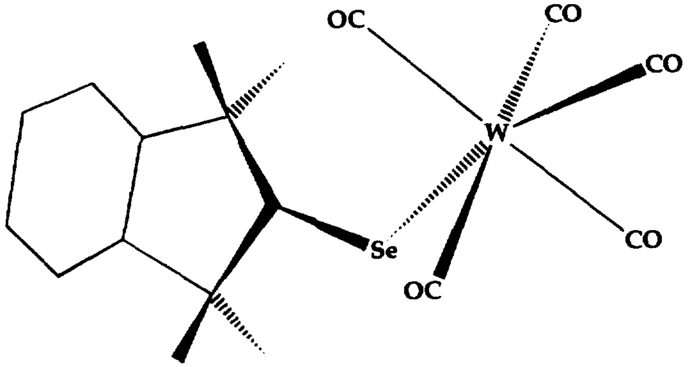
An η^1-σ-coordination of a telluroketone to pentacarbonyltungsten has been reported (**55**) [140]. The ligand can be released upon mild heating in acetonitrile.

8.4. Complexes with miscellaneous ligands

Intermolecular H-bonding between acidic alcohols and the hydride in $WH(CO)_2(NO)L_2$ (L = phosphines and phosphites) complexes have been observed spectroscopically [141]. The strongest bonding was found for the most basic

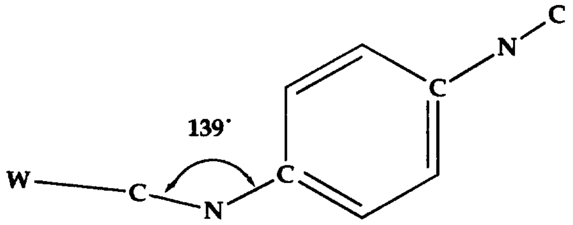


Scheme 46.



(55)

phosphine PMe_3. The hexahydrido rhenium complex $ReH_6(PPh_3)_2^-$ was found to coordinate $W(CO)_3$ via three bridging hydrido ligands [142]. Reaction of 1,4-diisocyanobenzene or 4-isocyanobenzonitrile (L) to *trans*-$W(N_2)_2(dppe)_2$ produced *cis*-$W(\eta^1\text{-}L)_2(dppe)_2$ complexes which were structurally characterized [143]. An interesting observation was the severe bending along the CNC axis (**56**) of



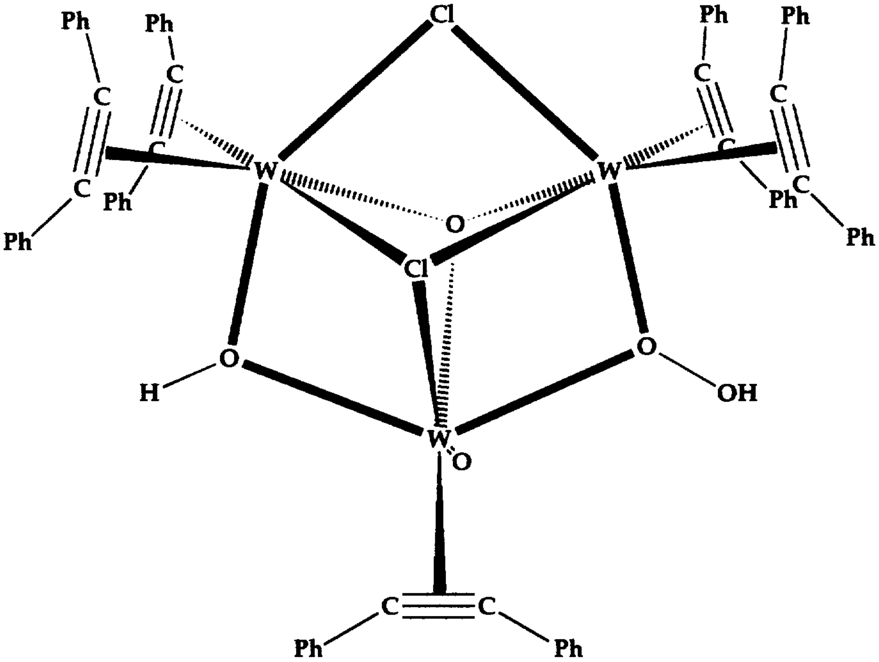
(56)

the coordinated isocyano group (average 139) which indicated substantial π-backdonation from the tungsten atom.

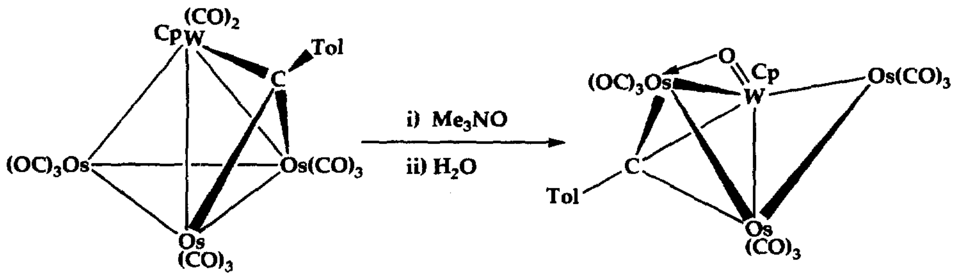
9. Selected tungsten clusters

9.1. Tungsten oxo clusters

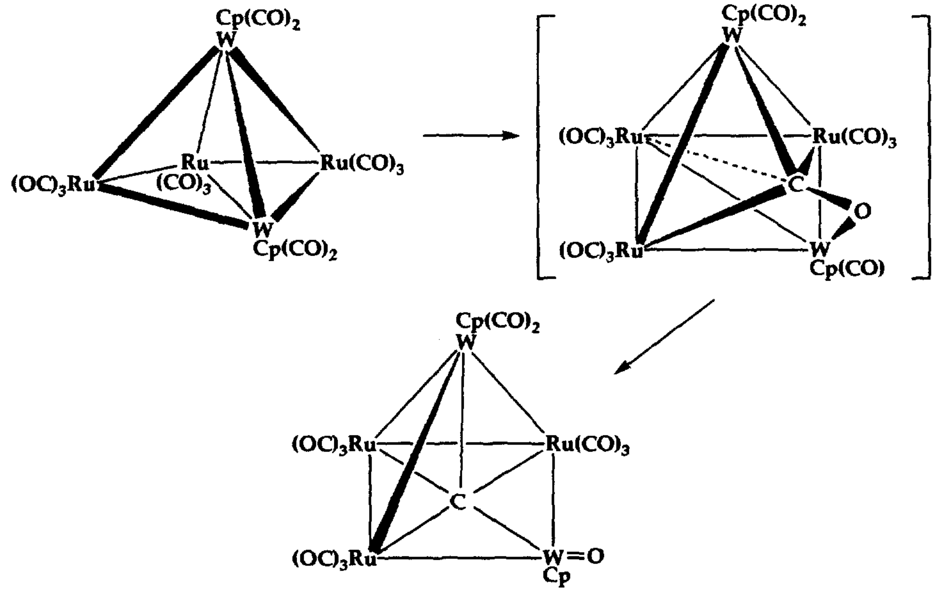
The synthesis and crystal structure of the $CpWOs_4(CO)_{10}(\mu\text{-}O)(\mu_3\text{-}C\text{-}Tol)$ cluster have been reported (Scheme 47) [144].



(57)

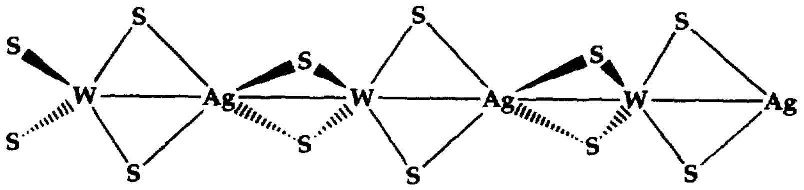


Scheme 47.



Scheme 48.

Reaction of the complex $(CO)_4W(\mu\text{-}Cl)_3W(SnCl_3)(CO)_3$ with alkynes such as diphenylacetylene gave a mixture of products converted by moist air into the $W_3(\mu_3\text{-}O)(\mu\text{-}OH)_2(\mu\text{-}Cl)_2(O)(\eta^2\text{-}PhC{\equiv}CPh)_5]$ cluster [145]. Its structure features both triply-bridging oxo and chloro ligands as well as a mixed-valent $W_2^{II}W^{IV}$ core (**57**).



(58)

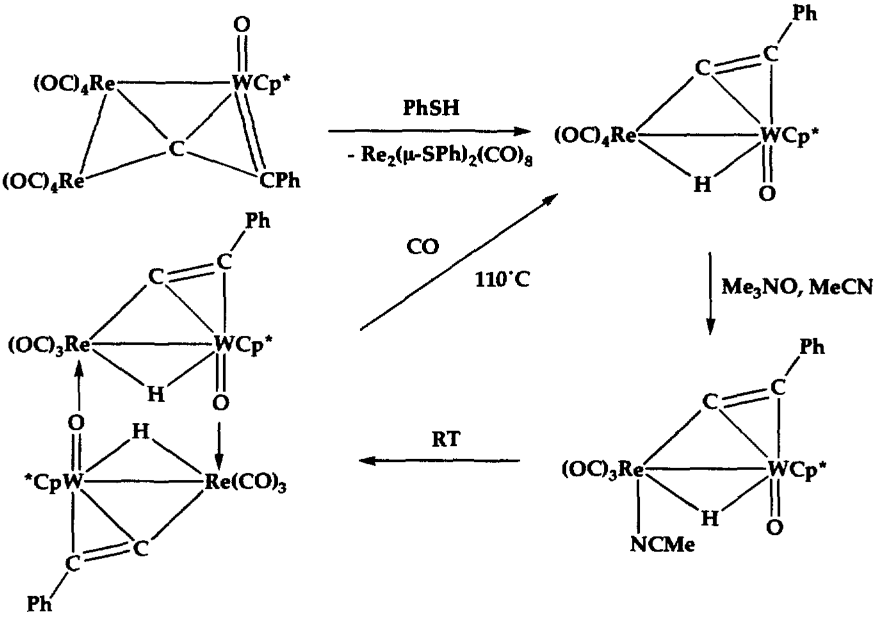
Direct scission of a coordinated carbonyl ligand in a W_2Ru_3 cluster led to generation of an oxo-carbide cluster [146]. Structural determinations of both precursor and product as well as ^{17}O NMR spectroscopic studies suggested a possible reaction path (Scheme 48).

The trinuclear oxo-acetylide cluster $Cp^*W(O)Re_2(CO)_8(\mu\text{-}C{\equiv}CPh)$ was found to react with thiophenol to give dinuclear $Cp^*W(O)Re(CO)_4(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$ which was treated with Me_3NO to give, ultimately, a head-to-tail dimer of $[Cp^*W(\mu\text{-}O)Re(CO)_3(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)]_2$ (Scheme 49) [147]. Characterization of intermediates in the reaction of the $CpWOs_3(CO)_{11}(\mu_3\text{-}C\text{-tolyl})$ cluster with hydrogen and water has been carried out [148]. The results are summarized in Scheme 50.

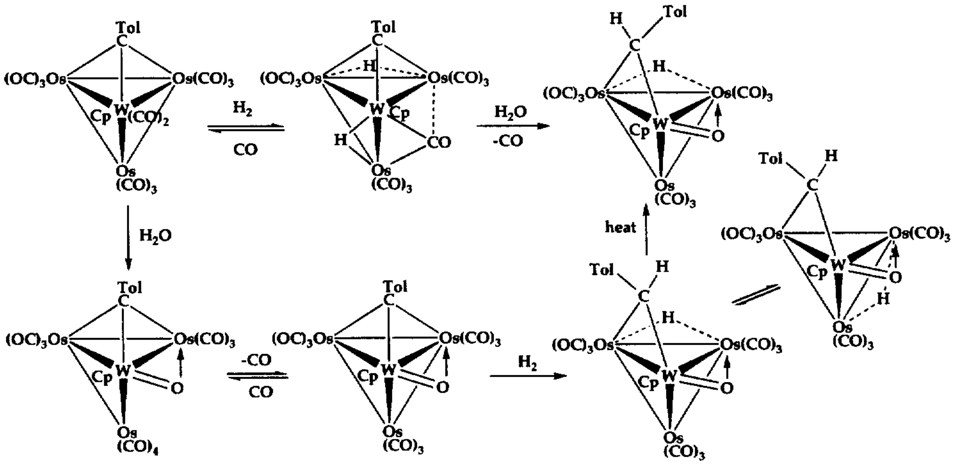
9.2. Sulfur and other chalcogen clusters

The crystal structure of a polymeric cluster complex $\{[Et_3NH][WAgS_4](DMF)\}_n$ has been reported [149]. It can be viewed as a polymeric chain of extended fragments of AgS_2W (**58**). In related work, lanthanoid cations Nd and La were encapsulated into a silver tetrathiotungstate polymeric chain [150]. The structure of $\{[W_4Ag_5S_{16}][Nd(DMF)_8]\}_n$ was found to consist of octanuclear cyclic $[W_4Ag_4S_{16}]^{4-}$ cluster fragments linked by Ag^+ cations (**59**). The $Nd(DMF)_8^{3+}$ ions were positioned linearly between the cluster anion chains but well separated from each other.

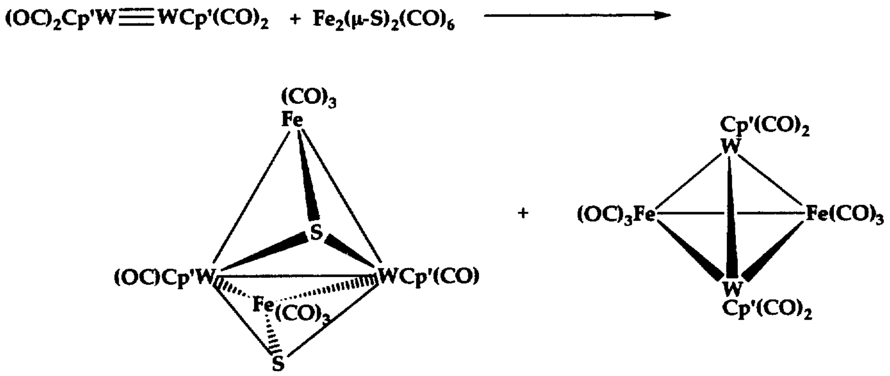
The W≡W dimers $[\eta^5\text{-}RC_5H_4W(CO)_2]_2$ (R=C(O)Me, COOMe) were found to react with $Fe_2(\mu\text{-}S)_2(CO)_6$ to yield clusters of the type $[(\eta^5\text{-}RC_5H_4)_2W_2(\mu_3\text{-}CO)_2Fe_2(\mu_3\text{-}S)_2(CO)_6]$ and $[\eta^5\text{-}RC_5H_4W(CO)_2]_2Fe(\mu_3\text{-}S)(CO)_3$ (Scheme 51)



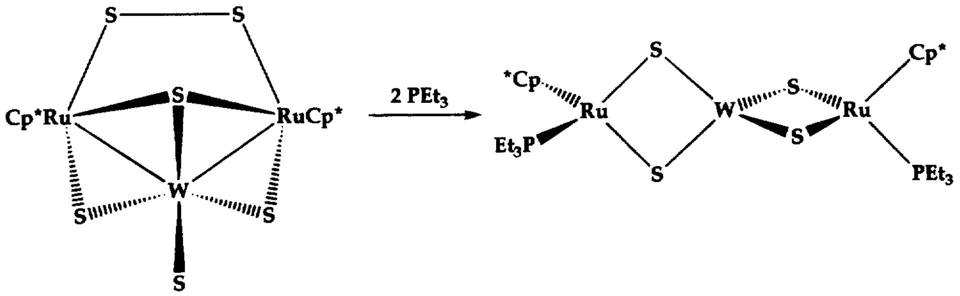
Scheme 49.



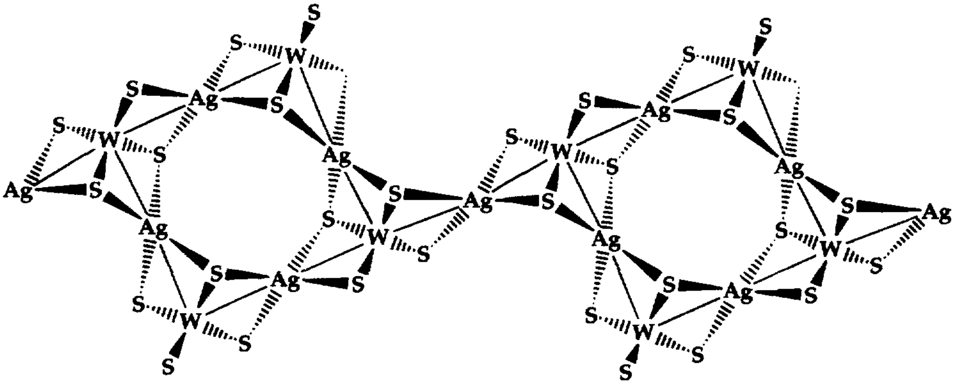
Scheme 50.



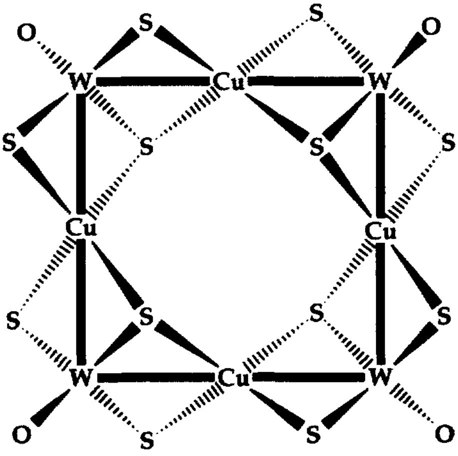
Scheme 51.



Scheme 52.



(59)



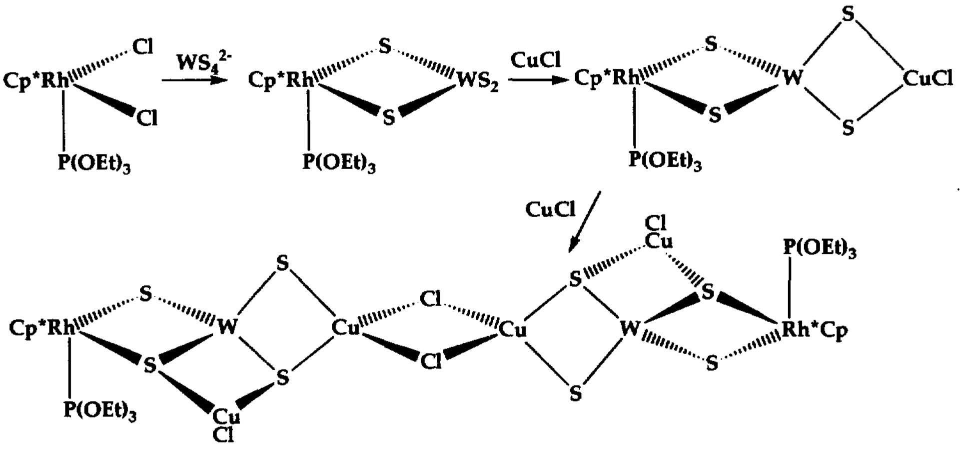
(60)

[151]. Unlike the molybdenum chemistry, similar reactions failed with the W–W precursors $[\eta^5\text{-}RC_5H_4W(CO)_3]_2$.

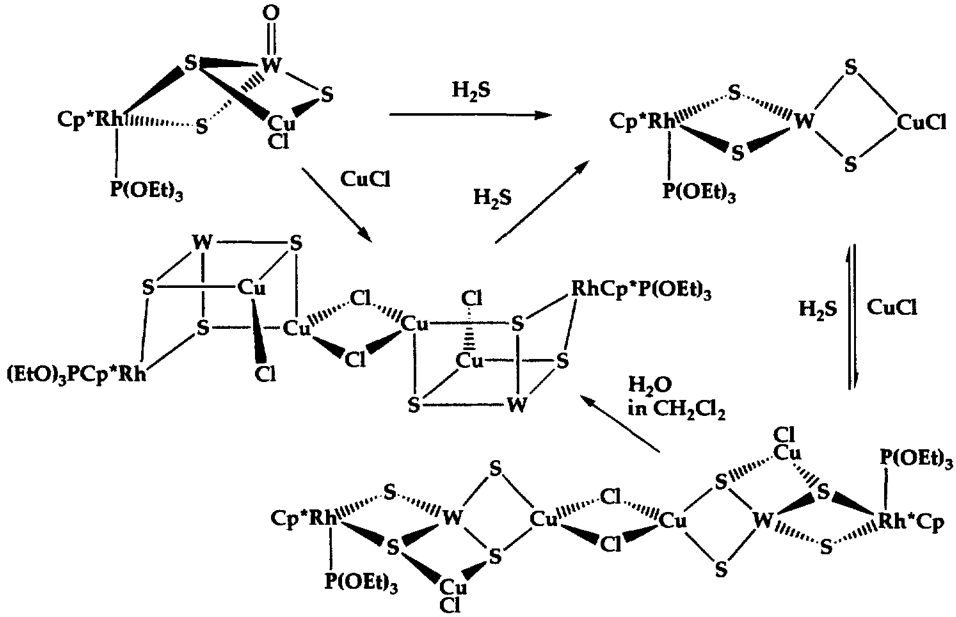
Heterometallic clusters of copper(I) with trithiotungstate have been prepared and structurally characterized [152]. The core structures of $[W_4Cu_4S_{12}O_4]^{4-}$ and $[W_4Cu_4S_{12}O_4(CuTMEN)_4]$ are shown in (**60**) and (**61**) respectively. The trinuclear heterometallic cluster $[Cp^*Ru(\mu_2\text{-}S)_2]_2(\mu_3\text{-}S)(\mu_2\text{-}S)_2WS$ has been prepared from WS_4^{2-} and $[Cp^*RuCl(\mu_2\text{-}Cl)]_2$ [153]. Its reaction with triethylphosphine resulted in formation of a linear trimetallic product (Scheme 52).

A full paper on the rationale synthesis of heterometallic sulfide clusters with M–S–M′ (M, M′ = Rh, W, and Cu) has appeared [154]. A summary of the synthetic, structural and reaction chemistry is shown in Schemes 53 and 54.

The incomplete cubane clusters $[M_3S_4(H_2O)_9]^{4+}$ ($M_3 = Mo_2W$, MoW_2, W_3) were reacted with metallic nickel to give the respective cubane clusters



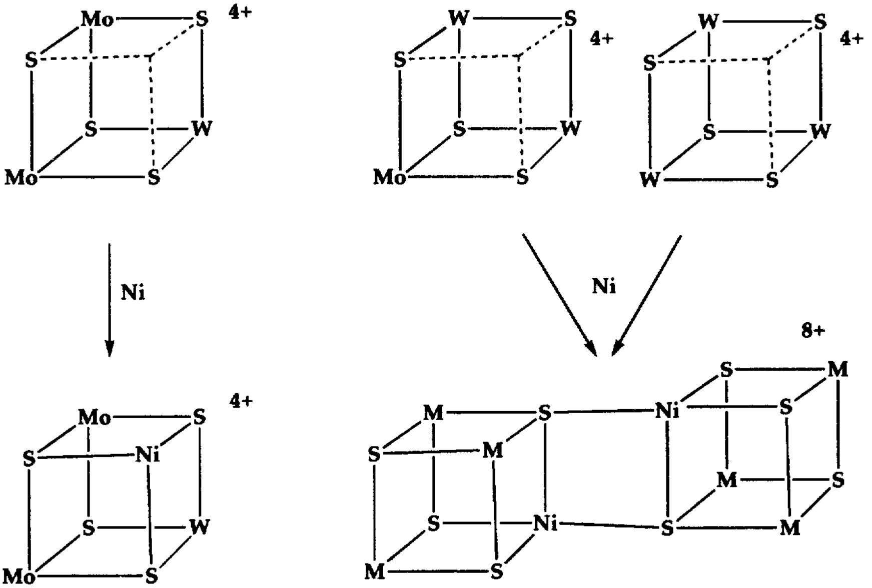
Scheme 53.



Scheme 54.

$[M_3NiS_4(H_2O)_{10}]^{4+}$. Their structural details (Scheme 55) and their olefin uptake were also studied [155]. Ethylene binding was found to occur exclusively at the Ni(II) vertex according to both structural and proton NMR spectroscopic data.

New heterometallic mixed-chalcogen clusters $[Fe_2W(CO)_{10}(\mu_3\text{-Se})(\mu_3\text{-E})]$ (E = Te or S) have been prepared from $W(CO)_5 \cdot THF$ and $Fe_2(CO)_6(\mu\text{-SeTe})$ and



Scheme 55.

$Fe_2(CO)_6(\mu\text{-SSe})$ [156]. Square pyramidal structures were suggested by both structural and ^{77}Se NMR spectroscopic data for both products (**62**).

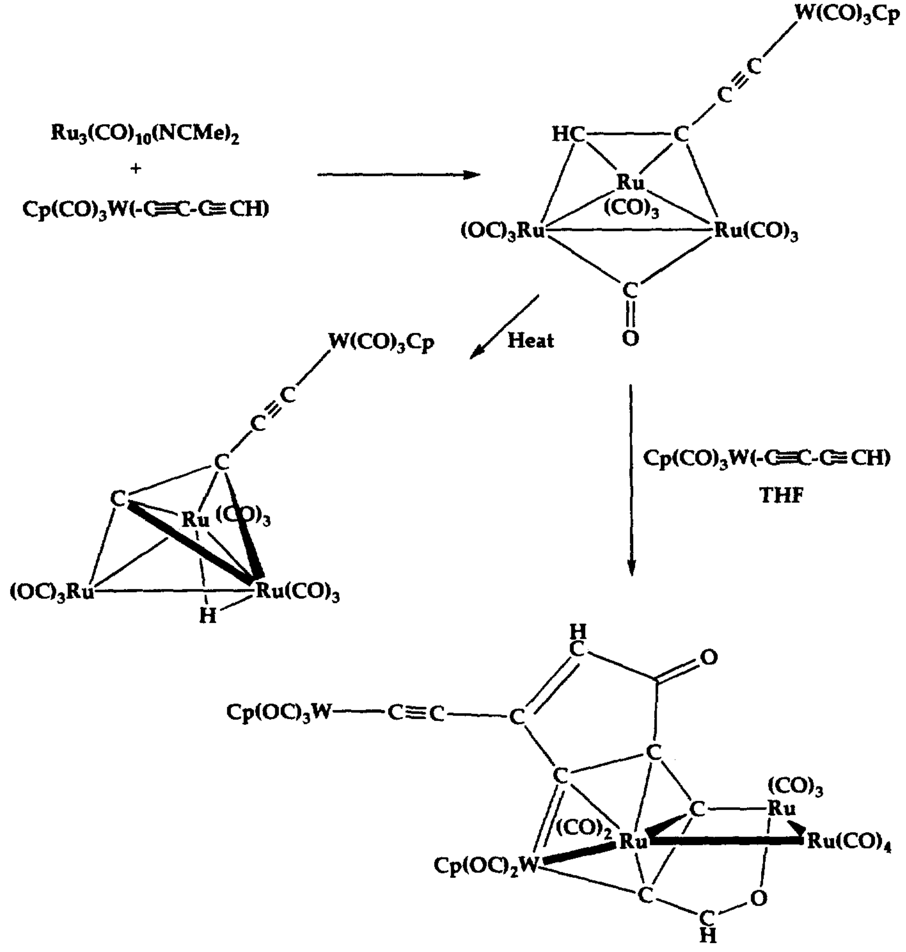
The first hexatungsten telluride clusters $[W_6Te_8(\text{piperidine})_6]$ and $[W_6Te_8(\text{pyridine})_6]^-$ have been prepared from W_6Cl_{12} and Na_2Te in the presence of the respective amine [157]. The structure of the latter anionic cluster revealed a Jahn–Teller distortion from octahedral symmetry.

9.3. *Miscellaneous clusters*

Site-specific reactivity was demonstrated in the octahedral W_6 cluster $[W_6(\mu\text{-H})_4H(\mu\text{-C}^iPr)(\mu\text{-O}^iPr)_7(O^iPr)_5]$ (**63**) which was found to react with deuterium and ethene using its terminal hydrides exclusively [158].

Tetranuclear phosphinidine, phosphide, arsenide, and oxide anionic clusters of tungsten were prepared [159]. Reaction of $W_2(OCH_2{}^tBu)_6$ with $NaP(SiMe_3)_2$ in the presence of 18-crown-6 yielded $[W_4(\mu_3\text{-PSiMe}_3)(OCH_2{}^tBu)_{11}]^-$ (**64**) which was identified as an intermediate for the formation of $[W_4(\mu_3\text{-P})(OCH_2{}^tBu)_{10}]^-$ (**65**). Reactions of the $CpWIr_3(CO)_{11}$ cluster with phosphines led to site-selective derivatives [160]. Structurally-characterized products are shown in (**66**). In related work, thermolysis of $CpWIr_3(\mu\text{-CO})_3(CO)_7PPh_3$ gave two cluster products, $CpWIr_3[\mu_3\text{-}\eta^2\text{-PPh}(C_6H_4)](\mu\text{-CO})_2(CO)_7$ and $CpWIr_3(CO)_{11}$ [161]. The structure of the former (**67**) confirmed orthometallation of a P–Ph group.

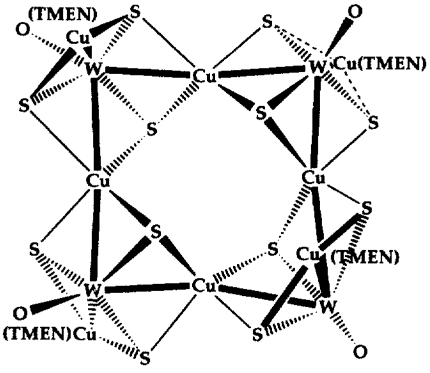
Codimerization of CO and the $Cp(CO)_3W(\text{–C}\equiv\text{C–C}\equiv\text{CH})$ diynyl complex at a Ru_3 cluster was reported (Scheme 56) [162].



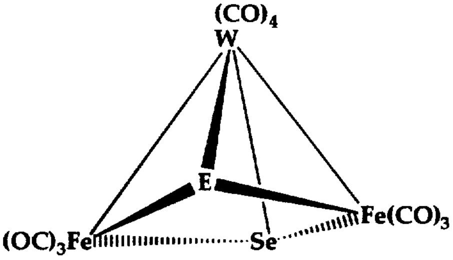
Scheme 56.

10. Reviews

A survey of the coordination chemistry of tungsten in 1994 appeared in this journal [163]. An account of the direct synthesis of organonitrogen compounds from dinitrogen complexes of tungsten and molybdenum has been published [164]. A review on metal–metal interactions in mixed-valent dinuclear complexes including tungsten nitrosyls has appeared [165]. Recent research into N–O cleavage in the chemistry of Group 6 nitrosyls was also updated [166]. A perspective on using the chemistry of ditungsten hexaalkoxides templates for organometallic chemistry and catalysis has appeared [167]. Group 6 metal chalcogenide clusters and their relationships to solid-state cluster chemistry were discussed [168]. Selected chalcogen clusters

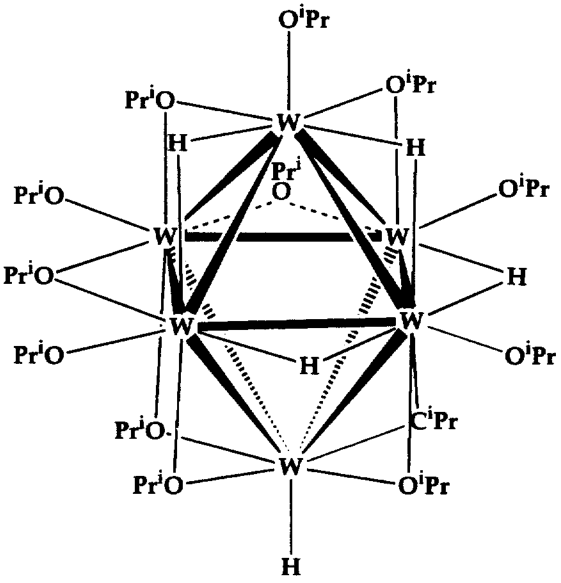


(61)

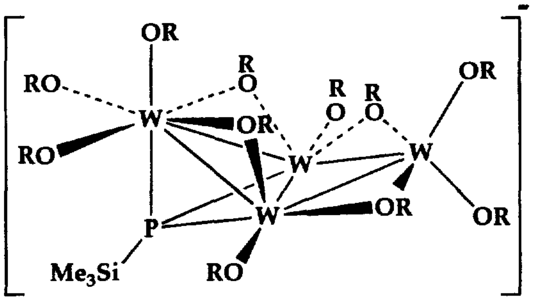


(E = Se, Te)

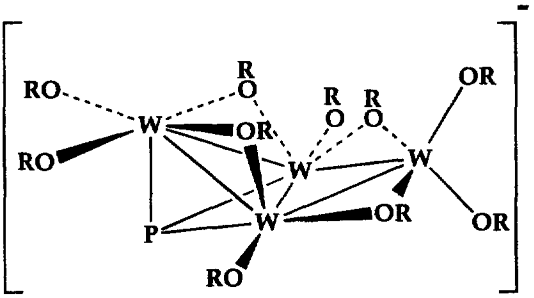
(62)



(63)


OR
RO
RO
R
O
OR
R R
O O
W
W
OR
W
OR
W
OR
P
Me3Si
RO
−

(64)


RO
RO
R
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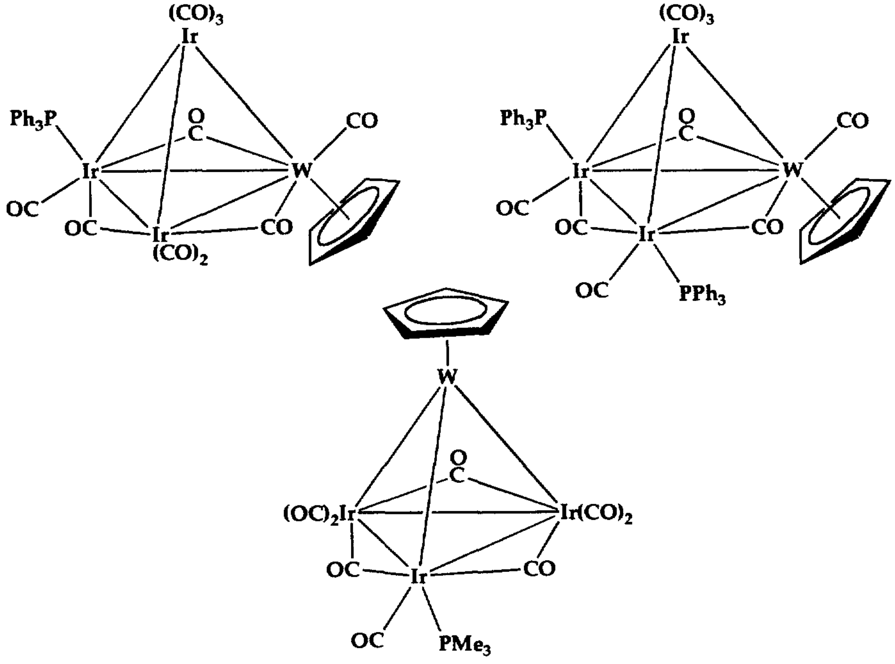
W
OR
R R
O O
W
W
OR
W
OR
OR
P
RO
−

(65)


(CO)3
Ir
Ph3P
O
C
CO
Ir
W
OC
OC
Ir
CO
(CO)2
(CO)3
Ir
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C
CO
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W
OC
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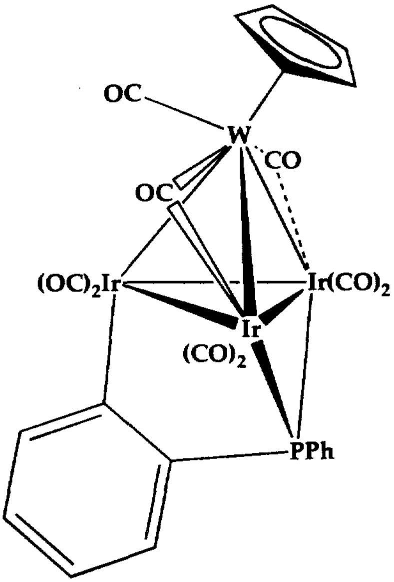
(OC)2Ir
Ir(CO)2
OC
Ir
CO
OC
PMe3

(66)



(67)

of chromium, molybdenum, tungsten, and rhenium were also described in another account [169]. The review on transition metal alkane complexes included a section on tungsten pentacarbonyl coordination chemistry [170]. The organometallic chemistry of halocarbonyl W(II) complexes was summarized [171].

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