

# Chromium, molybdenum, and tungsten. Annual survey covering the year 1992

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*Key words:* Chromium; Molybdenum; Tungsten; Group 6; Review; 1992

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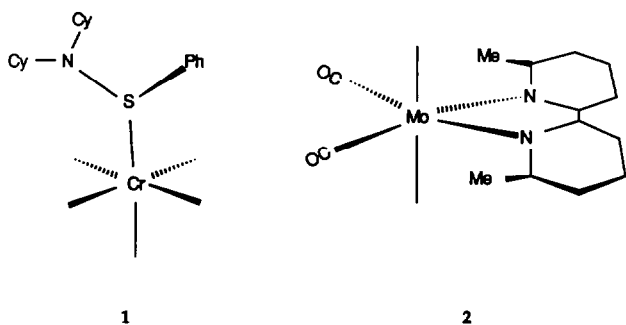
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The organometallic literature of the chromium triad has not been surveyed in this journal since 1982. This compilation covers the literature published during the 1992 calendar year pertinent to the subject area. Only compounds containing at least one metal-carbon bond have been included. Metal carborane derivatives are not covered nor are polyoxometallates and metal sulfido or other clusters without metal-carbon bonds.

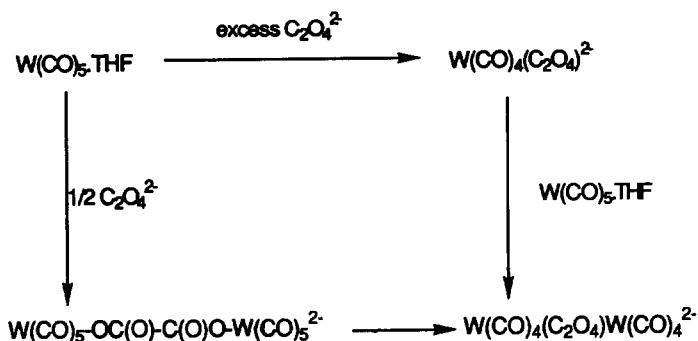
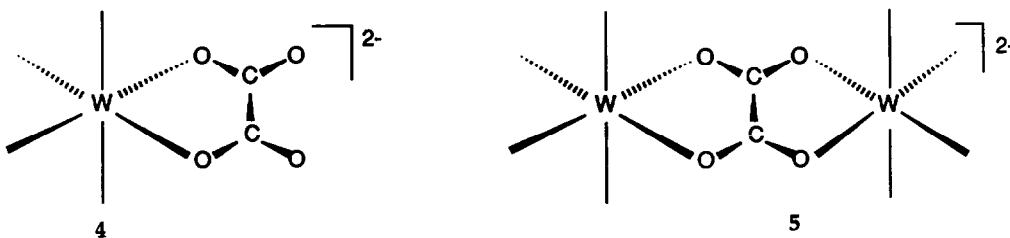
## 1. Carbonyl complexes

### 1.1. Structure, synthesis, and reactivity

The crystal structure of  $\text{Cr}(\text{CO})_5\text{-}N,N\text{-dicyclohexylbenzenesulfenamide}$  (**1**) confirmed coordination through the S atom with an average Cr-S distance of 2.443(2) Å for the two independent molecules [1].



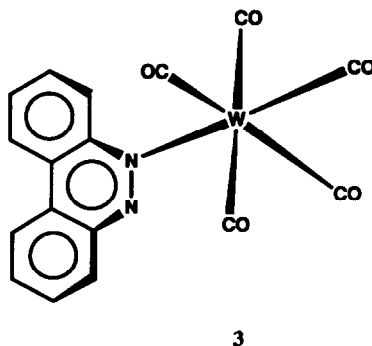
The structure of  $\text{cis-Mo}(\text{CO})_4(3,3'\text{-dimethyl-2,2'-bipyridine})$  (**2**) revealed that repulsion between the methyl groups and equatorial COs caused most of the structural distortions [2]. Both methyl groups were found to be out of the equatorial coordination plane (0.39 and 0.63 Å). Similar distortions were also found for the Cr and W analogues [3].



Scheme 1.

Five Schiff bases (SB) containing aromatic moieties were complexed with  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ). Mo and W gave  $\text{cis-SB}(\text{CO})_4$  exclusively while Cr yielded a mixture of  $\text{cis-SB}(\text{CO})_4$  and  $(\text{arenc})\text{Cr}(\text{CO})_3$  complexes [4]. Use of  $\text{M}(\text{CO})_5\text{PPh}_3$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) led to bimetallic  $\text{M}(\text{CO})_4(\text{PPh}_3)(\mu\text{-SB})\text{M}(\text{CO})_4\text{-PPh}_3$ .

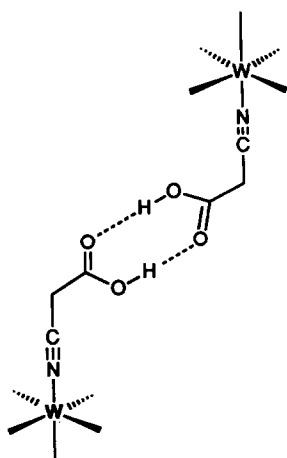
The structure of  $\text{W}(\text{CO})_5\text{-}(\text{benzo}[c]\text{cinoline-N}')$  (**3**) featured W-N1 coordination with the N1-N2 partial double bond at a distance of 1.31(1) Å [5].



The intermediate  $\text{W}(\text{CO})_5(\eta^1\text{-C}_2\text{O}_4)^{2-}$  from the reaction of  $\text{W}(\text{CO})_5 \cdot \text{solvent}$  and the oxalate anion has a labile  $\text{cis-CO}$  and readily formed  $\text{W}(\text{CO})_4(\eta^2\text{-C}_2\text{O}_4)^{2-}$  (**4**) [6]. The latter also reacted with more  $\text{W}(\text{CO})_5 \cdot (\text{solvent})$  to give a stable dimer  $\text{W}_2(\text{CO})_8(\eta^4\text{-C}_2\text{O}_4)^{2-}$  (**5**) (Scheme 1).

Both solid-state X-ray and solution spectral data confirm strong intermolecular H-bonding between carboxyl groups in  $\text{W}(\text{CO})_5\text{NCCH}_2\text{COOH}$  (**6**) [7]. CO displacement of the cyanoacetic acid ligand proceeded by a solvent-assisted  $I_d$  pathway in THF and a  $D$  mechanism in  $\text{CH}_2\text{Cl}_2$ . The relevance of this study to

the catalytic decarboxylation of cyanoacetic acid by  $W(CO)_5-O_2CCH_2CN^-$  is discussed.



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Refluxing  $Mo(CO)_6$  in DMF afforded *fac*- $Mo(CO)_3(DMF)_3$  in high yields [8]. Substitution of the DMF ligands typically occurred under mild conditions, or can be facilitated by addition of  $BF_3 \cdot Et_2O$ .

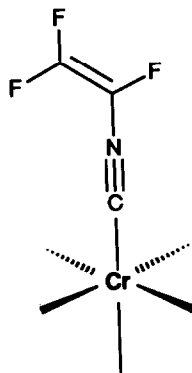
The complex *fac*- $Mo(CO)_3(MeCN)_3$  reacted with ICl to give  $MoICl(CO)_3(MeCN)_2$  [9]. This product with one equivalent of ligand L afforded iodo-bridged dimers  $[MoCl(\mu-I)(CO)_3L]_2$  (L =  $PPh_3$ ,  $AsPh_3$ ,  $SbPh_3$ ). Two equivalents of L or one of chelating diphosphines yielded  $MoICl(CO)_3L_2$ .

Photolysis of  $W(CO)_5(1\text{-ethoxy-2-methyl-2-propenylidene})$  with  $Re_2(CO)_{10}$  yielded two bimetallics and one trimetallic product (Scheme 2) [10]. All of these products featured the 1-ethoxy-2-methyl-2-propenylidene bridging ligand.

The complexes  $W(CO)_5(CNR)$  (R =  $CF_2H$  and  $CFH_2$ ) were prepared and their vibrational spectra

indicate that these ligands have a lower  $\pi$ -acceptor/ $\sigma$ -donor ratio than  $CF_3NC$  [11].

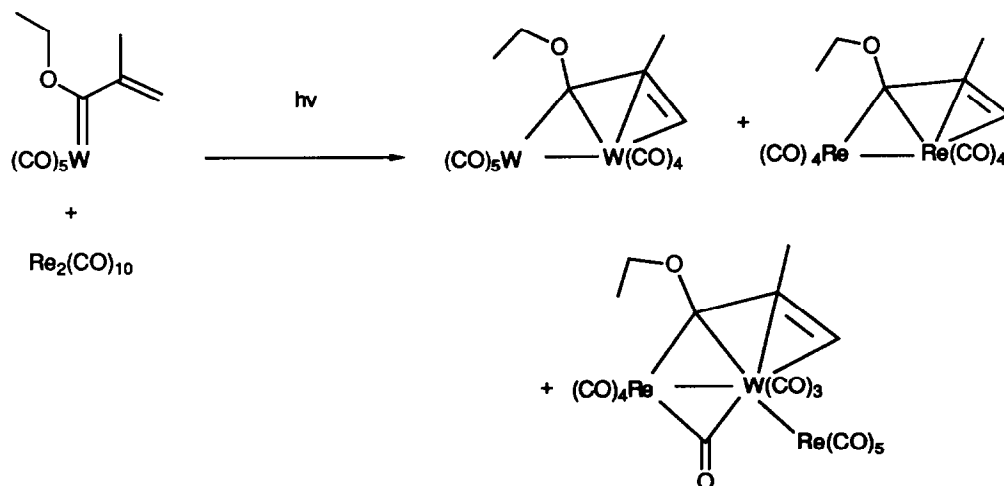
Reaction of  $Cr(CO)_5CN^-$  with phenyldiazonium tetrafluoroborate in  $HClFC-CF_2Cl$  yielded the complex  $Cr(CO)_5(CN-CF(Cl)-CF_2Cl)$  which was dechlorinated with zinc in ether-acetic acid to give  $Cr(CO)_5(CN-CF=CF_2)$  (7) [12]. Vacuum pyrolysis of the trifluorovinyl isocyanide complex at  $240^\circ C$  afforded the first fluorinated alkenyl isocyanide,  $F_2C=CF-NC$ .



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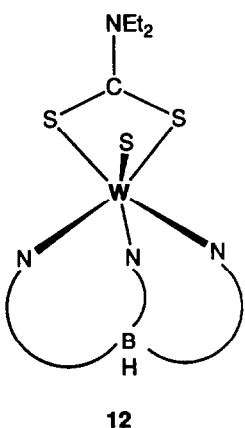
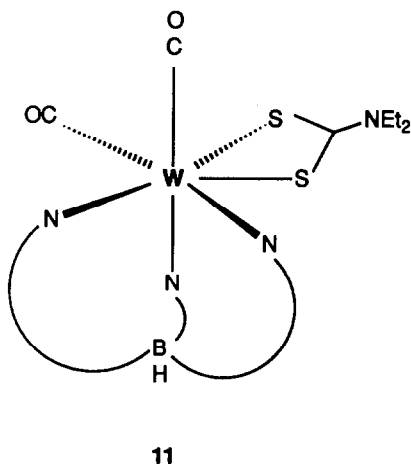
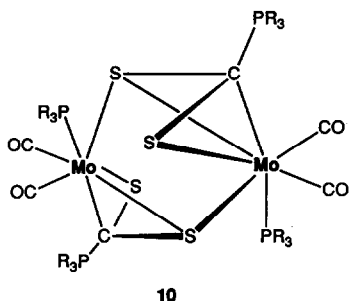
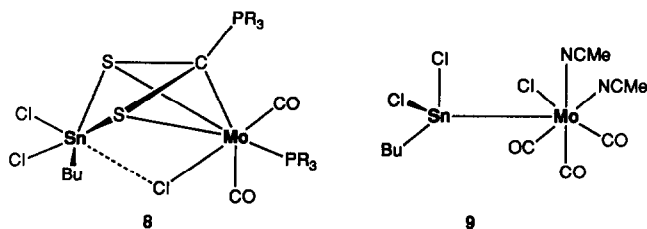
The S-bridged complex **8** was formed from the reaction of  $Mo(CO)_3Cl(MeCN)_2-SnBuCl_2$  (9) with  $PR_3$  and  $CS_2$ . It can also be prepared from the reaction of **10** with  $BuSnCl_3$  [13].

Reactions of  $NEt_4[HB(Me_2pz)_3]W(CO)_3$  ( $Me_2pz = 3,5\text{-dimethyl-1-pyrazolyl}$ ) with  $[S_2CNet_2]_2$  in MeCN at  $80^\circ C$  afforded  $[HB(Me_2pz)_3]W(CO)_2(S_2CNet_2)$  and mixed-valence  $[HB(Me_2pz)_3]W^{II}(CO)_2(\mu-S)W^{IV}(S_2CNet_2)_2(SCNet_2)$  [14]. The structure of the former was found to be a distorted pentagonal bipyramid (**11**). These complexes are intermediates to the ultimate

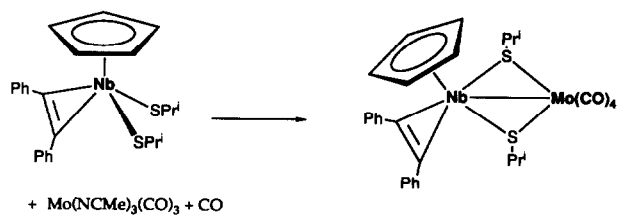


Scheme 2.

products  $[\text{HB}(\text{Me}_2\text{pz})_3]\text{WS}(\text{S}_2\text{CNEt}_2)$ ,  $\text{W}_2(\mu\text{-S})_2(\text{S}_2\text{CNEt}_2)_4$ , and  $[\text{W}(\text{S}_2\text{CNEt}_2)_4]^+$ .



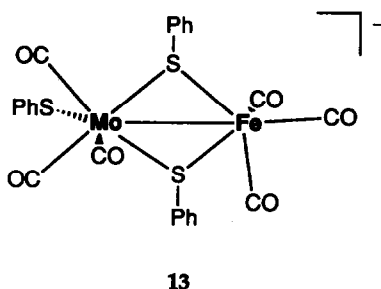
The final products of the reaction between  $\text{NEt}_4[\text{Tp}'\text{W}(\text{CO})_3]$  and tetraethylthiuram disulfide in refluxing MeCN include the red, diamagnetic



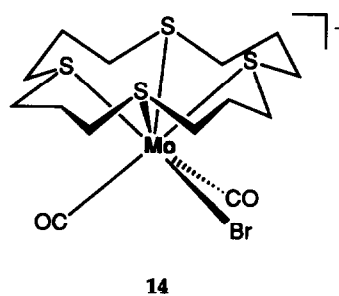
Scheme 3.

$\text{Tp}'\text{WS}(\text{S}_2\text{CNEt}_2)$  whose structure contains a distorted octahedral *fac*- $\text{N}_3$ -*fac*- $\text{S}_3$  coordination sphere (**12**) [15].

Reaction of  $\text{CpNb}(\text{S}^i\text{Pr})_2(\text{PhCCPh})$  with  $\text{Mo}(\text{MeCN})_3(\text{CO})_3$  and CO afforded  $\text{CpNb}(\text{PhCCPh})(\mu\text{-S}^i\text{Pr})_2\text{Mo}(\text{CO})_4$  (Scheme 3) [16]. Another thiolate bridge heterobimetallic was formed in the reaction of  $\text{Fe}(\text{CO})_4\text{Br}_2$  with  $\text{NEt}_4[\text{SPh}]$  and  $\text{Mo}(\text{CO})_3(\text{MeCN})_3$  to give  $[\text{NEt}_4]\text{Fe}(\text{CO})_3(\mu\text{-SPh})_2\text{Mo}(\text{CO})_3\text{SPh}$  (**13**) [17].

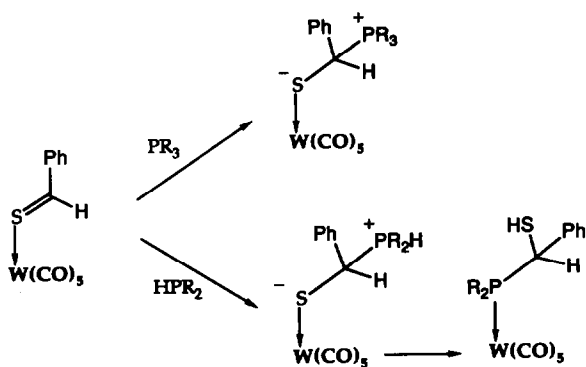


$[\text{MoBr}(\mu\text{-Br})(\text{CO})_4]_2$  with the tetrathio crown ether  $\text{Me}_8[16]\text{aneS}_4$  yielded a novel seven-coordinate ionic complex  $[\text{MoBr}(\text{CO})_2(\text{Me}_8[16]\text{aneS}_4)][\text{MoBr}_3(\text{CO})_4]$  [18]. The cationic complex features a 4:3 piano-stool geometry with the Mo atom 1.488(2) Å off the  $\text{S}_4$  plane (**14**).



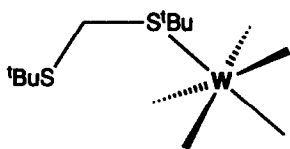
Reaction of  $\text{W}(\text{CO})_5\text{-SC}(\text{H})\text{Ph}$  with phosphines gave phosphonothiolate complexes of the type  $(\text{CO})_5\text{W}[\text{SC}(\text{H})\text{Ph}(\text{PR}_3)]$  ( $\text{R} = \text{Me}, \text{Et}, \text{Ph}, 4\text{-MeC}_6\text{H}_4$ ) whereas  $\text{PPh}_2\text{H}$  yielded a product that rapidly rearranged by  $\text{S},\text{P}$  migration of W and  $\text{P},\text{S}$  migration of H to form the phosphine complex  $(\text{CO})_5\text{W}[\text{PPh}_2\{\text{C}(\text{Ph})\text{HSH}\}]$  (Scheme 4) [19]. The thiobenzophenone complex gave  $(\text{CO})_5\text{W}[\text{SC}(\text{Ph})_2\text{PMe}_3]$ .

The thioether complexes  $\text{M}(\text{CO})_5(\text{RSCH}_2\text{SR})$  ( $\text{M} = \text{Cr}, \text{W}$ ;  $\text{R} = \text{Et}, ^i\text{Pr}, ^t\text{Bu}$ ) were synthesized and the



Scheme 4.

molecular structure of  $\text{W}(\text{CO})_5(\text{}^t\text{BuCH}_2\text{}^t\text{Bu})$  determined (**15**) [20]. Their sulfur inversion barriers were measured by NMR and found to be in the range

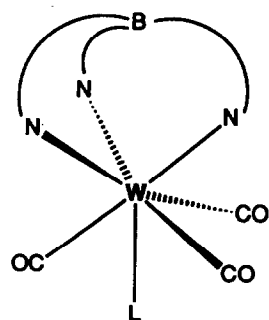


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34–42  $\text{kJ mol}^{-1}$ . In a subsequent study, the complexes  $\text{M}(\text{CO})_5(\text{MeSCH}_2\text{SR})$  ( $\text{M} = \text{Cr}, \text{W}; \text{R} = \text{}^i\text{Pr}, \text{}^t\text{Bu}, \text{Ph}$ ) were found to exist as equilibrium mixtures of MeS- and RS-bonded isomers in  $\text{CDCl}_3$  or  $\text{CD}_2\text{Cl}_2$  solvents [21]. The sulfur inversion barriers were found



to vary with the S-alkyl substituent from 38–44  $\text{kJ mol}^{-1}$  ( $\text{Me} > \text{}^i\text{Pr} \approx \text{}^t\text{Bu}$ ). Analogously, the complexes  $\text{W}(\text{CO})_5(\text{RSCH}_2\text{SR}')$  ( $\text{R} = \text{R}' = \text{Et}, \text{}^i\text{Pr}, \text{}^t\text{Bu}; \text{R} = \text{Me}, \text{R}' = \text{}^i\text{Pr}, \text{}^t\text{Bu}$ ) also exhibited 1,3-metallotropic shifts of S-coordination sites above ambient temperature [22]. Activation energies for the symmetrical lig-



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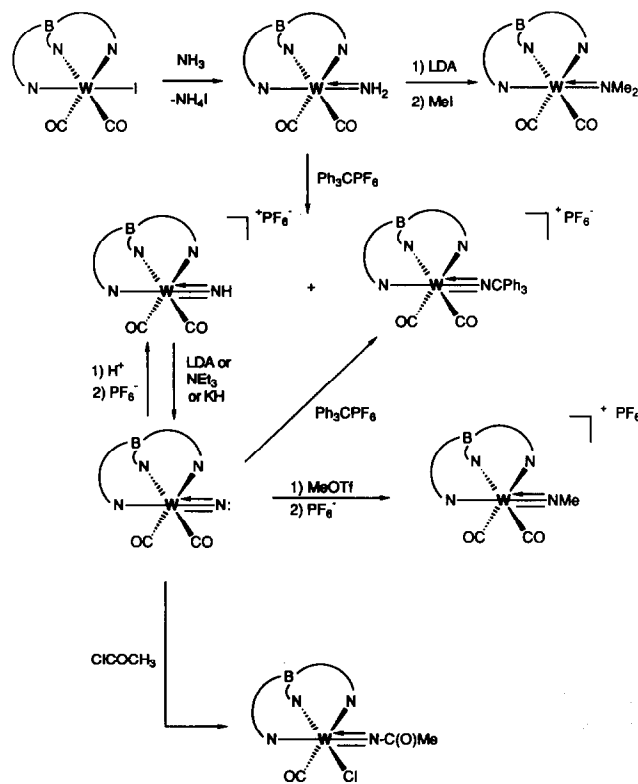
and complexes were in the range 74–84  $\text{kJ mol}^{-1}$  ( $\text{Me} > \text{Et} > \text{}^i\text{Pr} > \text{}^t\text{Bu}$ ).

Novel 17-electron  $\text{TpCr}(\text{CO})_3$ ,  $\text{Tp}^*\text{Cr}(\text{CO})_3$ ,  $\text{Tp}''\text{Cr}(\text{CO})_3$ , and  $\text{TpCr}(\text{CO})_2\text{PMe}_3$  ( $\text{Tp}^* = \text{hydrido}(3,5\text{-dimethylpyrazolyl})\text{borate}$ ,  $\text{Tp}'' = \text{tetra}(\text{pyrazolyl})\text{borate}$ ) have been prepared and characterized [23]. Their EPR spectra were used to gain information about their electronic structures.

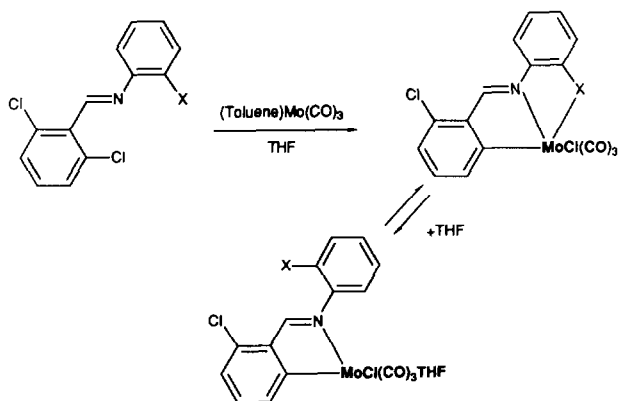
Oxidation of the  $\text{Tp}'\text{W}(\text{CO})_3$  ( $\text{Tp}' = \text{hydridotris}(3,5\text{-dimethylpyrazolyl})\text{borate}$ ) radical with ferrocenium followed by addition of phosphine afforded cationic  $\text{Tp}'\text{W}(\text{CO})_3\text{L}^+$  ( $\text{L} = \text{PMe}_3, \text{PET}_3, \text{PPh}_3, \text{PMe}_2\text{Ph}$ ) [24]. These seven-coordinate  $\text{W}^{\text{II}}$  complexes were found to have a capped octahedral geometry (**16**).

Treatment of  $\text{Tp}'\text{W}^*(\text{CO})_2\text{I}$  ( $\text{Tp}' = \text{hydridotri}(3,5\text{-dimethyl-1-pyrazolyl})\text{borate}$ ) with ammonia afforded the green amido complex  $\text{Tp}'\text{W}(\text{CO})_2(\text{NH}_2)$  [25]. This amphiphilic complex produced two nitrene products with  $[\text{CPh}_3]\text{PF}_6$ ,  $[\text{Tp}'\text{W}(\text{CO})_2(\text{NR})]\text{PF}_6$  ( $\text{R} = \text{H}, \text{CPh}_3$ ), in a 4:1 ratio. It can also be methylated ( $\text{Li}^i\text{Pr}_2\text{N}, \text{MeI}$ ) to give  $\text{Tp}'\text{W}(\text{CO})_2\text{NMe}_2$ . The cationic nitrene complex  $\text{Tp}'\text{W}(\text{CO})_2\text{NH}$  can also be reversibly deprotonated to give a nitrido species,  $\text{Tp}'\text{W}(\text{CO})_2(\text{N})$  (Scheme 5).

Schiff base chelate-assisted oxidative additions of a series of aryl halides to  $\text{Mo}(\text{CO})_3(\text{THF})_3$  were studied



Scheme 5.



Scheme 6.

quantitatively by spectroscopic techniques (Scheme 6) [26].

It was found that the structure of the chelate ring rather than the type of halide controlled the strength of the aryl halide coordination to the Mo center.

### 1.2. Oxidation and decomposition

Oxidation of  $M(\text{CO})_5^-$  ( $M = \text{Cr}, \text{Mo}, \text{W}$ ) was examined with a FT-ion cyclotron resonance spectrometer [27]. Generation of  $\text{MO}_5^-$  was not observed under low pressure conditions and may require termolecular reactions.

Photooxidation of  $\text{Mo}(\text{CO})_6$  in sodium zeolite Y resulted in clean formation of  $\text{MoO}_3$  and  $\text{CO}_2$  [28]. Vacuum, thermally-induced reductive  $\text{O}_2$  elimination yielded  $\text{MoO}_2$  quantitatively.

Thermal decomposition studies of  $\text{Mo}(\text{CO})_6$  on Co or Fe catalysts gave activation energies of 59.8(1.4) and 59.2(1.4)  $\text{kJ mol}^{-1}$  respectively [29]. Thermal decomposition of  $\text{Cr}(\text{CO})_6$  on iron has been found to have an activation energy of 21.3(1.1)  $\text{kJ mol}^{-1}$  [30]. Chemisorbed  $\text{W}(\text{CO})_6$  on Ni(100) surfaces decomposed at 250 K to W atoms and CO [31]. Surface W was then partially oxidized to  $\text{W}^{\text{II}}$  and  $\text{W}^{\text{VI}}$  species.

Photooxidation of encapsulated  $\text{W}(\text{CO})_6$  in  $\text{Na}_{56}\text{Y}$ , sodium zeolite Y, produced  $\text{WO}_3$  while thermal vacuum treatment yielded encapsulated  $\text{WO}_2$  instead [32].

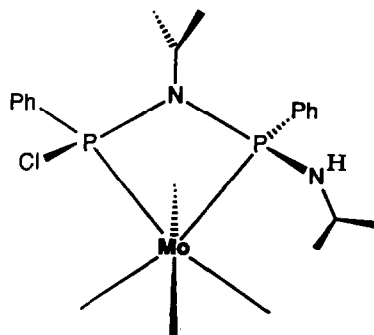
## 2. Phosphine complexes

### 2.1. Structure and synthesis

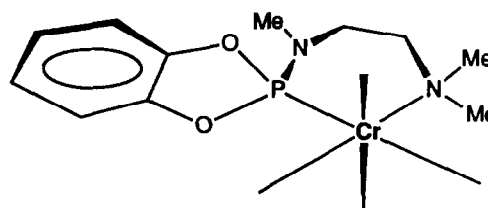
A new bis(phosphino)amine has been prepared diastereoselectively and used to form the *erythro*- $\text{RN}[\text{PhP}(\text{RNH})]\text{PhPCl}]\text{Mo}(\text{CO})_4$  complex which has been structurally characterized (17) [33].

2-[[2-(Dimethylamino)ethyl]methylamino]-1,3,2-benzodioxaphosphole (L) reacted with  $M(\text{CO})_4(\text{NBD})$  ( $M = \text{Cr}, \text{Mo}$ ) to give  $M(\text{CO})_4(\text{L-N,P})$  (18) and *trans*-

$\text{Mo}(\text{CO})_4(\text{L-P})_2$  complexes [34]. L also reacted with  $\text{Mo}(\text{CO})_3(\text{CHT})$  to give *fac*- $\text{Mo}(\text{CO})_3(\text{L-P})_3$ .

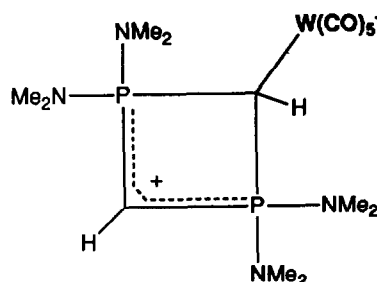


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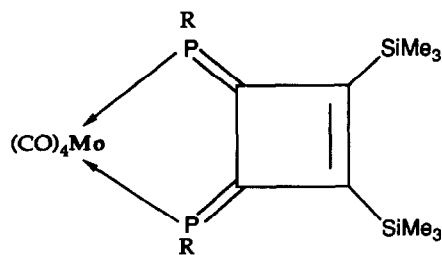


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1,1,3,3-Tetrakis(dimethylamino)-diphosphete was reported to react with  $\text{W}(\text{CO})_5(\text{Z-cyclooctene})$  to give the X-ray characterized complex  $[\text{HCP}(\text{NMe}_2)_2]_2\text{W-}$



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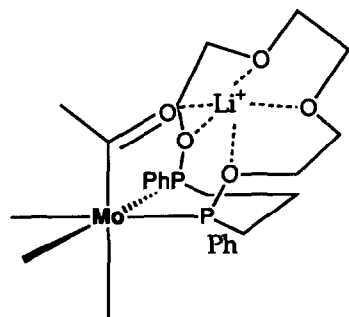
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(CO)<sub>5</sub> (19) [35]. Structures of both [(*E,E*)-3,4-bis(2,4,6-tri-*tert*-butylphenylphosphinidene)-1,2-bis(trimethylsilyl)cyclobutene] and its Mo(CO)<sub>4</sub> complex were determined (20) [36].

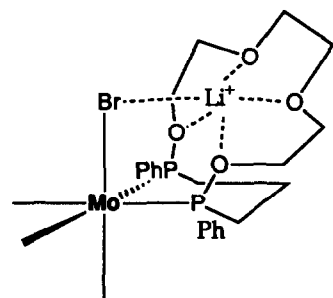
Reactions of cyclo-diphosphazanes [PhNP(OR)]<sub>2</sub> (R = CH<sub>2</sub>CF<sub>3</sub>, *p*-tol) with group 6 M(CO)<sub>6</sub> were investigated [37]. The *trans*-diphosphazane afforded a ligand-bridged dinuclear product while the *cis*-isomer led to η<sup>1</sup>-bonded mononuclear species.

Bicyclic diazadiphosphetidines (PhNP)<sub>2</sub>(XC<sub>2</sub>H<sub>4</sub>Y) (X = Y = O; X = O, Y = NMe<sub>2</sub>) gave M(CO)<sub>4</sub>L<sub>2</sub> and M(CO)<sub>3</sub>L<sub>3</sub> complexes with M(CO)<sub>6</sub> in which the ligands exhibited the η<sup>1</sup>-coordination mode [38].

A hybrid phosphinite macrocycle [15]P<sub>2</sub>O<sub>4</sub> has been complexed to Mo(CO)<sub>4</sub> [39]. Addition of RLi reagents gave *fac*-Mo(CO)<sub>3</sub>(RCOLi){[15]P<sub>2</sub>O<sub>4</sub>} in which the Li<sup>+</sup> was encapsulated by the five O's from the acyl and macrocycle (21). The structure of the *fac*-[Mo(CO)<sub>3</sub>-Br]{[15]P<sub>2</sub>O<sub>4</sub>} Li complex has also been determined (22).



21

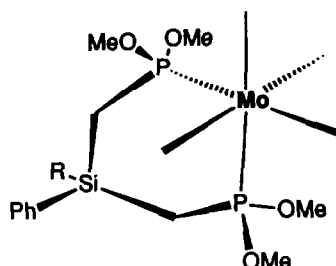


22

Structures of two silylated diphosphite complexes Mo(CO)<sub>4</sub>[P(OMe)<sub>2</sub>O]<sub>2</sub>SiPh<sub>2</sub> and Mo(CO)<sub>4</sub>[P(OMe)<sub>2</sub>O]<sub>2</sub>SiMePh were determined (23) [40]. Their six-membered chelate rings were found to adopt unusual twist-boat conformations.

Reactions of P<sub>7</sub>(SiMe<sub>3</sub>)<sub>3</sub> with increasing equivalents of Cr(CO)<sub>5</sub>·THF yielded first the 1:1 adduct with coordination to a P(equatorial) atom [41]. A second

Cr(CO)<sub>5</sub> moiety bonded to a P(bridge). The 1:3 adduct was found to have two Cr's on P(bridge) and a third on

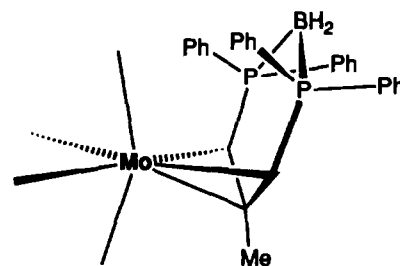


R = Ph, Me

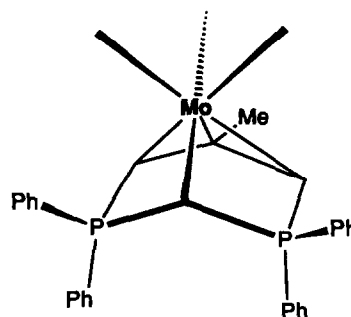
23

either P(eq) or P(ax). Mixtures of (SiMe<sub>3</sub>)<sub>3</sub>P<sub>7</sub>[Cr(CO)<sub>5</sub>]<sub>n</sub>Cr(CO)<sub>4</sub> (n = 1, 2, 3) were also obtained.

Heterophosphabenzenes were complexed to Mo(CO)<sub>4</sub> and Mo(CO)<sub>3</sub> [42]. In the 5-methyl-1,1,3,3-tetra-phenyl-1-phospha-3-phosphonia-2-boratabenzene complex, four-electrons were donated from the methallylic function. For the related diphosphabenzene complex, an additional pair of electrons was available from the semiylidic PCHP group (24, 25).



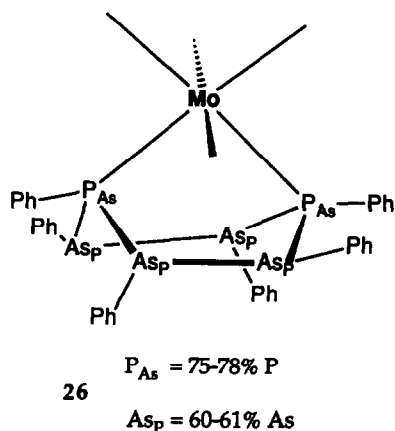
24



25

*Cyclo*-(Ph<sub>6</sub>As<sub>3</sub>P<sub>3</sub>) with alternating As and P atoms in the heterocycle reacted with Mo(CO)<sub>6</sub> to give Mo(CO)<sub>3</sub>[Ph<sub>6</sub>As<sub>3</sub>P<sub>3</sub>] containing completely scrambled phenyl-pnictidene units (26) [43]. The original chair conformation has also been converted to a twist-boat.

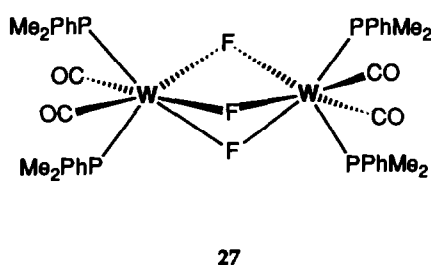
It was postulated that ring opening and scrambling occurred before complex formation.



Substituted phosphole (1-phenyl-3,4-dimethyl, 1-phenyl-3-methyl, 1-phenyl) complexes of  $M(CO)_4$  and  $M(CO)_5$  ( $M = Cr, Mo, W$ ) were prepared and found to contain only phosphorus rather than the diene coordination [44]. C-13 NMR data revealed drastically reduced P-participation in the ring  $\pi$ -delocalization.

The competitive formation of  $Cr(CO)_5$  complexes with  $P(SiMe_3)_3$  and  $P(^tBu)_3$  were found to be clearly favored over  $(^tBu)_2P-P(SiMe_3)_2$  and  $(SiMe_3)_2P-PMe_2$  [45]. At  $-18^\circ C$ ,  $Cr(CO)_5 \cdot THF$  reacted with  $^tBu-(SiMe_3)P-P(SiMe_3)_2$  (L) to give both  $(\eta^1-L)Cr(CO)_5$  and  $(\eta^2-L)Cr(CO)_4$  products.

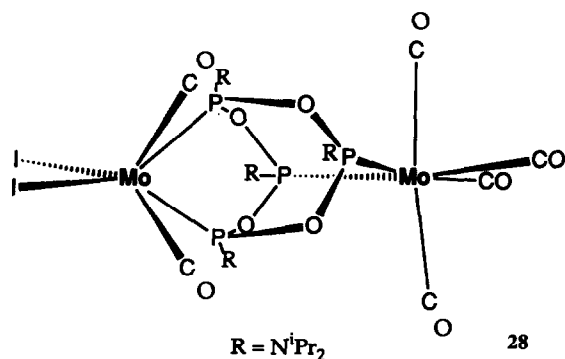
Protonation of  $WH_6(PMe_2Ph)_3$  with  $HBF_4 \cdot Et_2O$  under CO generated  $\{[W(CO)_2(PMe_2Ph)_2]_2(\mu-F)_3\}BF_4$  which was found to have a coordination geometry at each W featuring three basal F's. The other four ligands formed a second, parallel plane with the phosphines mutually *trans* (27) [46].



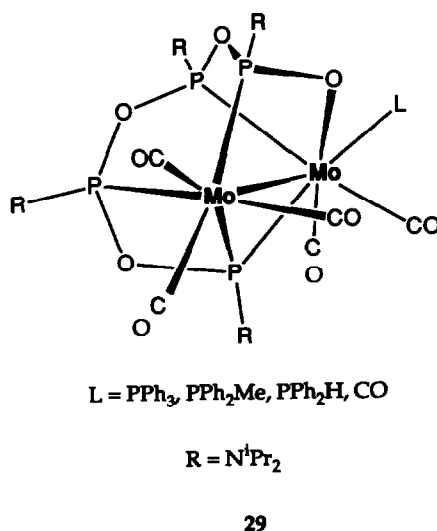
## 2.2. Reactions

Iodination and chlorination of the  $Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4$  cage complex afforded first the mixed-valent  $Mo(CO)_2X_2[{}^iPr_2NPO]_4Mo(CO)_4$  and then the  $Mo(CO)_2I_2[{}^iPr_2NPO]_4Mo(CO)_2I_2$  complexes (Scheme 7) [47]. The tetrabromo complex was similarly prepared but the dibromo mixed-valent species could only be synthesized indirectly from metathesis of the diiodo complex. X-ray structural determination of the

diiodo complex confirmed a trigonal prismatic coordination geometry at the  $Mo^{II}$  center (28). By contrast to these products, the P-Ph cage complex,  $Mo(CO)_4[PhPO]_4Mo(CO)_4$  gave unstable and poorly characterized halogenation derivatives.

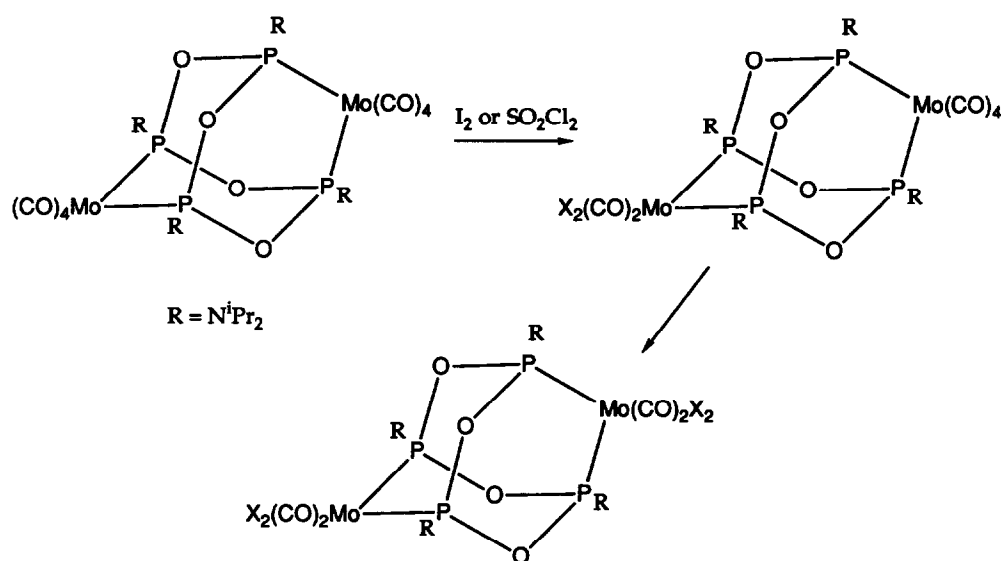


Reactions of phosphine nucleophiles  $PPh_2R$  ( $R = Ph, Me, H$ ) on the above  $Mo(CO)_4[{}^iPr_2NPO]_4Mo(CO)_4$  cage complex led to the incorporation of one phosphine and loss of three CO's to form orange-red  $Mo(CO)_3[{}^iPr_2NPO]_4Mo(CO)_2PPh_2R$  [48]. 2-D P-31 NMR spectroscopy and X-ray structural studies confirmed the cleavage of a P-O-P bond and formation of a phosphido-bridged Mo-Mo bond across the original cage structure (29). By contrast, phosphites like  $P(OMe)_3$  gave isolable substitution products like  $Mo(CO)_3P(OMe)_3[{}^iPr_2NPO]_4Mo(CO)_4$  and  $Mo(CO)_3-P(OMe)_3[{}^iPr_2NPO]_4Mo(CO)_3P(OMe)_3$  which underwent similar P-O-P cleavages only upon further activation.



Complexes of the bicyclic ditertiary phosphine ether ligand *cis*-1,5-bis(diphenyl(phosphino)methyl)-3-oxabicyclo[3.3.0]octane (L) of the type *fac*-(L-P,P,O) $M(CO)_3$  ( $M = Mo, W$ ) reacted with nucleophiles  $L' = MeCN$ , piperidine, pyridine, and  $P(OCH_2)_3CMe$  to give two





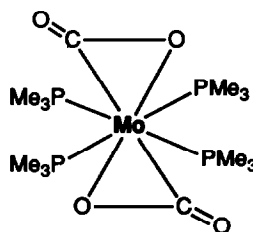
Scheme 7.

diastereomers of *fac*-(L-P,P')M(CO)<sub>3</sub>L' (Scheme 8) [49]. NMR spectroscopic evidence confirmed substitution of the ether O site in the major isomers. Carbonylation of these products with <sup>13</sup>CO gave 2 diastereomers of *fac*-(L-P,P')M(CO)<sub>3</sub>(<sup>13</sup>CO) in ratios of 5:1 and 7:1 for M = Mo and W respectively. A scheme involving isomerization of the diastereomeric 5-coordinate square-pyramidal intermediate was suggested (Scheme 9). For L' = MeCN, piperidine, and pyridine, solution NMR data revealed partial dissociation to regenerate free L' and the starting complex.

Irradiation of Mo(PMe<sub>3</sub>)<sub>4</sub>(η<sup>2</sup>-CO<sub>2</sub>)<sub>2</sub> (30) in toluene at -20°C produced *cis*-Mo(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>4</sub> and OPMe<sub>3</sub> along with smaller amounts of *mer*- and *fac*-Mo(CO)<sub>3</sub>(PMe<sub>3</sub>)<sub>3</sub> [50].

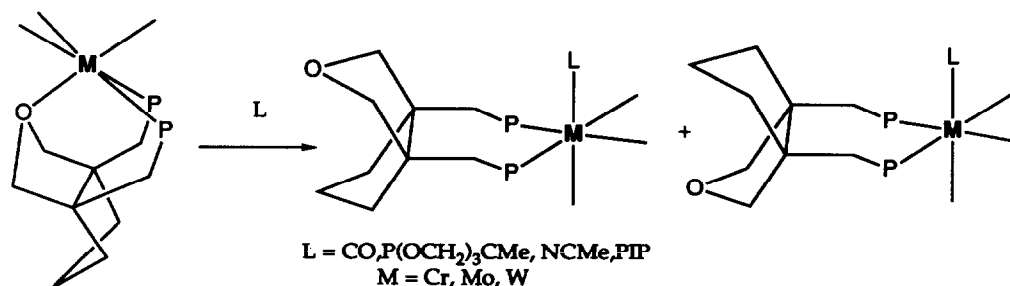
The azine diphosphine Z,Z-[Ph<sub>2</sub>PCH<sub>2</sub>C('Bu)=N-]<sub>2</sub> (L) was prepared and found to react with M(CO)<sub>3</sub>-(CHT) to give the *fac*-M(CO)<sub>3</sub>(η<sup>3</sup>-L) (M = Cr, Mo, W) complexes [51]. Use of M(CO)<sub>4</sub>(NBD) led to M(CO)<sub>4</sub>(η<sup>2</sup>-L) products which could be converted to the tricarbonyl complexes. Neutral Mo<sup>II</sup> complexes Mo(CO)<sub>2</sub>Br<sub>2</sub>(η<sup>3</sup>-L) could be obtained by bromination

of these Mo<sup>0</sup> products. The tungsten analogues gave instead cationic W(CO)<sub>3</sub>Br(η<sup>3</sup>-L)<sup>+</sup>.

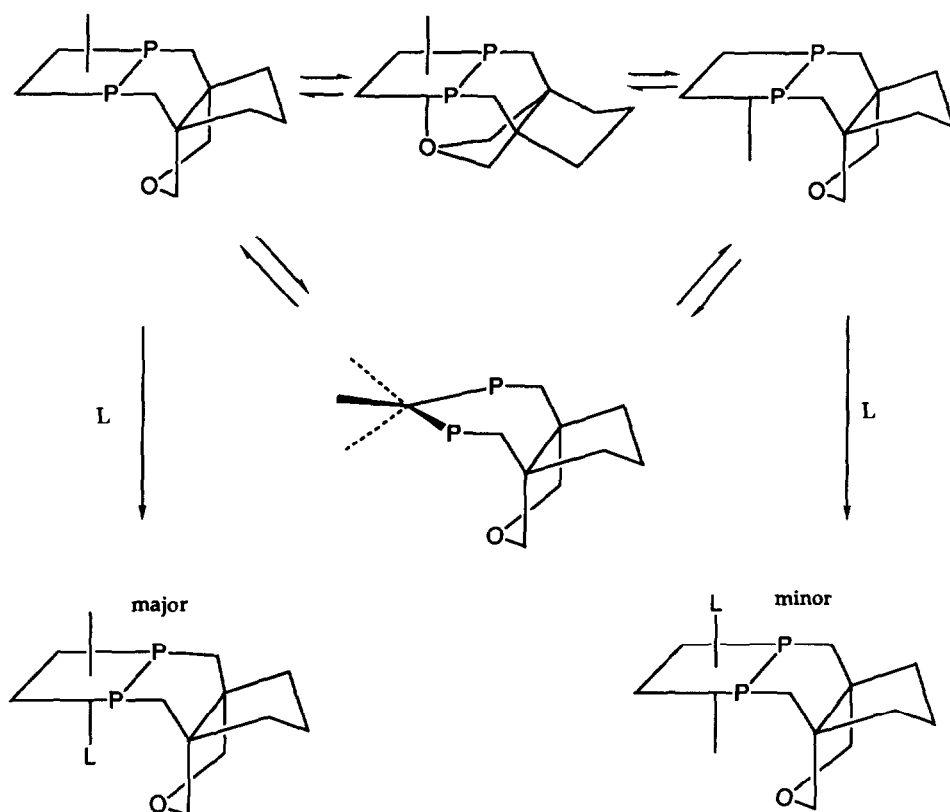


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The phosphino dimethylhydrazone Z-PPh<sub>2</sub>CH<sub>2</sub>C('Bu)=NNMe<sub>2</sub> reacted with Mo(CO)<sub>4</sub>(NBD) to give the Mo(CO)<sub>4</sub>{η<sup>2</sup>-PPh<sub>2</sub>CH<sub>2</sub>C('Bu)=NNMe<sub>2</sub>} complex featuring a six-membered chelate ring (31) [52]. In addition to this product, an isomeric complex with a five-membered chelate ring was formed in the thermal reaction of the ligand with Mo(CO)<sub>6</sub>. Heating of the former product in diglyme to 150°C gave the imine complex Mo(CO)<sub>4</sub>{PPh<sub>2</sub>CH<sub>2</sub>C('Bu)=NH} (Scheme 10).

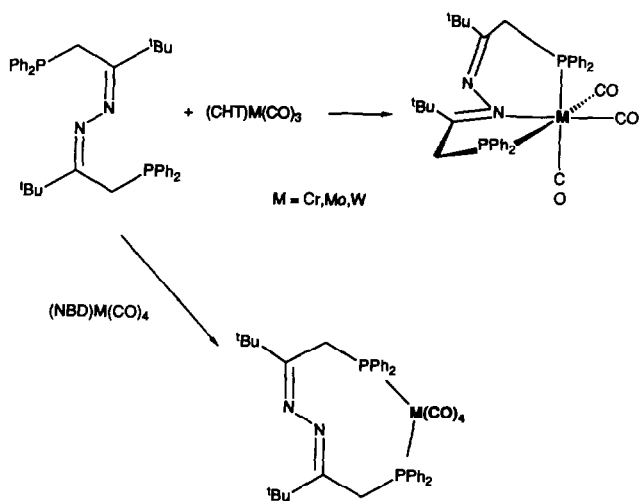


Scheme 8.



Scheme 9.

Treatment of the (1*R*)-(+)-camphor dimethylhydrazone complex  $\text{Mo}(\text{CO})_4(\eta^2\text{-PPh}_2\text{-C}_{10}\text{H}_{15}\text{NNMe}_2)$  with



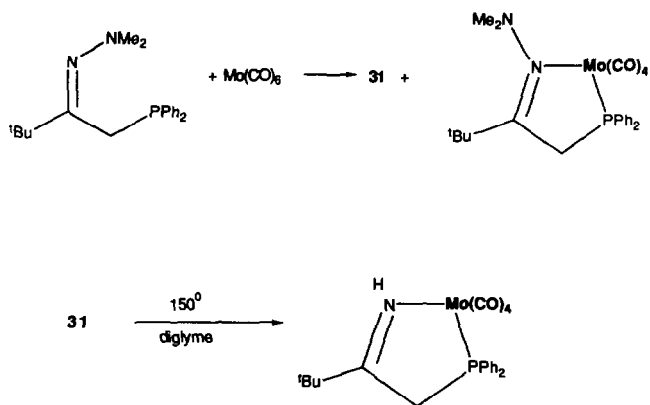
HCl resulted in a rapid redox/fission reaction and formation of a  $\text{Mo}^{\text{II}}$  imine  $\text{Mo}(\text{CO})_3\text{Cl}_2(\text{PPh}_2\text{-C}_{10}\text{H}_{15}\text{NH})$  [53]. Reaction of this imine with  $\text{NaBH}_4$  under CO yielded  $\text{Mo}(\text{CO})_4(\text{PPh}_2\text{-C}_{10}\text{H}_{15}\text{NH})$  which was methylated with MeI at N after deprotonation (Scheme 11).

A study of nucleophilic attacks at coordinated P-X

(X = Cl, Br) by HER (E = NH, O, S; R = H, alkyl, aryl) on  $\text{cis-Mo}(\text{CO})_4[\text{XP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})_2]$  was reported (Scheme 12) was reported [54]. Multinuclear NMR studies of the products were presented as well as X-ray structures of  $\text{cis-Mo}(\text{CO})_4[\text{RP}(\text{OCH}_2\text{CMe}_2\text{CH}_2\text{O})_2]$  (R =  $^i\text{PrO}$ ,  $^i\text{PrNH}$ ) which had the  $^i\text{Pr}$  group axial but the  $^i\text{PrNH}$  group equatorial (32, 33).

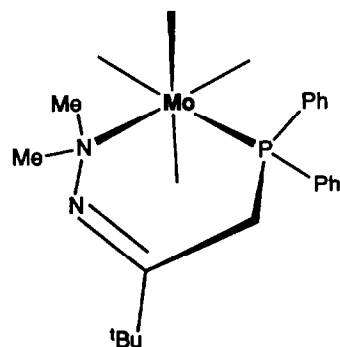
### 2.3. Phosphine-polymetallics

Reactions of alkyne-coordinated  $\text{W}(\text{CO})(\text{PPh}_2\text{-C}\equiv\text{C}(\text{PPh}_2)(\text{S}_2\text{CNEt}_2)_2)$  with  $\text{M}(\text{CO})_4(\text{pip})_2$  (M = Cr,

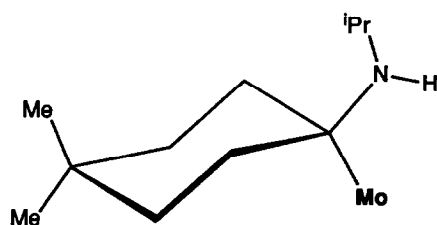


Scheme 10.

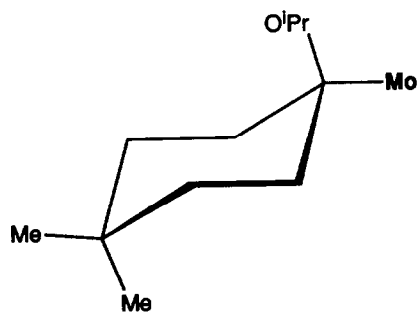
Mo, W) afforded  $W(CO)[(Ph_2PC\equiv CPh_2)M(CO)_4](S_2CNEt_2)_2$  whose structures have been determined (34)



31

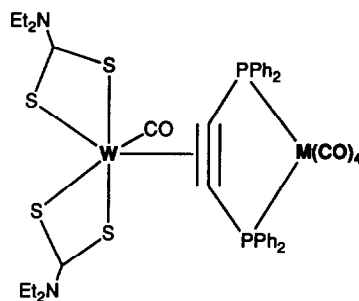


32

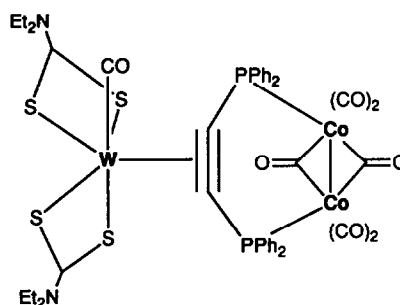


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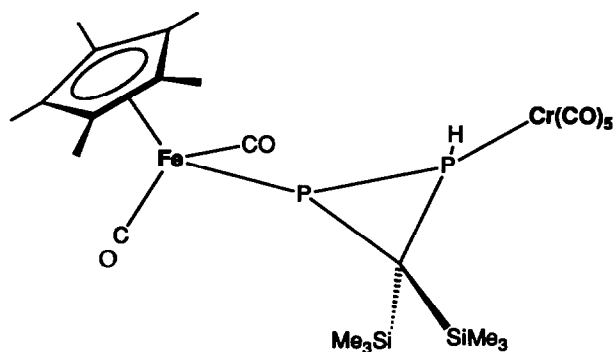
Reactions of  $Mo(CO)_3(\mu-C_5H_4PPh_2)Mn(CO)_4$  with phosphines and isonitriles were studied. Less bulky



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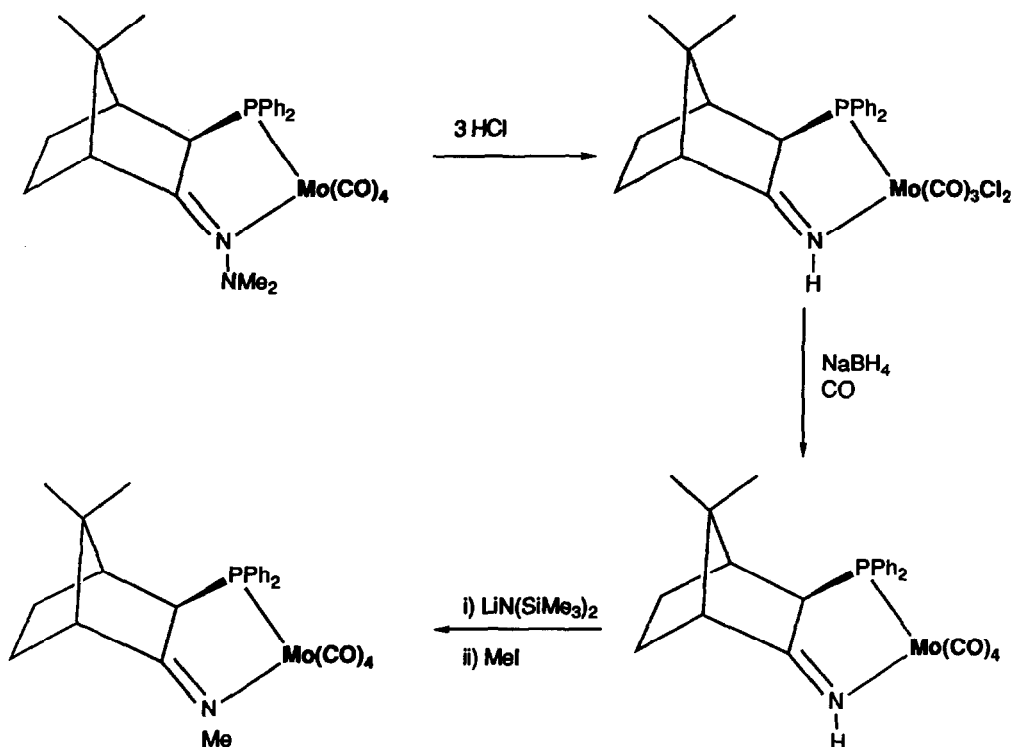
[55]. In all cases  $W^{II}$  was coordinated to the alkyne and the group VI metal chelated by the diphosphine (34). Trimetallics were formed from  $Fe_2(CO)_9$  and  $Co_2(CO)_8$  (35) using the same  $W^{II}$  precursor.

Ethanol and  $Cp^*Fe(CO)_2P(SiMe_3)_2$  gave  $Cp^*Fe(CO)_2PH_2$  which was coupled with  $Cl-P=C(SiMe_3)_2$  to give the diphosphirane  $Cp^*Fe(CO)_2-PC(SiMe_3)_2PH$  [56]. The free PH site was shown to complex  $Cr(CO)_5$  (36).

Reaction of  $Mo(CO)_4[PPh_2CH_2OH]_2$  and  $Mo(CO)_4[PPh_2(CH_2CH_2OH)]_2$  with  $TiCl_4$  and  $KTp^*$  produced heterobimetallics of the type  $Tp^*TiCl[OCH_2PPh_2]_2Mo(CO)_4$  and  $Tp^*TiCl[OCH_2CH_2PPh_2]_2Mo(CO)_4$  respectively [57].

phosphines ( $PPh_2H$ ,  $PPh_2Me$ ,  $PPhMe_2$ ,  $P(OMe)_3$ ) gave products of monosubstitution at Mn while  $PPh_3$  substituted only at Mo. Phosphines of intermediate bulk yielded both types of products [58]. Thermolysis of the  $PPh_2H$  complex afforded  $Mo(CO)_2(\mu-C_5H_4PPh_2)(\mu-PPh_2)(\mu-H)Mn(CO)_3$ . Thermolysis of a vinylphosphine derivative produced  $Mo(CO)_2(\mu-C_5H_4PPh_2)(\mu-PPh_2CH=CH_2)Mn(CO)_3$  wherein the vinyl group was found to be bonded to Mo. Hydrogenation of this complex resulted in vinylphosphine transfer to the Mo center (Scheme 13).

A reinvestigation of the reaction of  $PPh_3AuCl$  with *mer*- $2-Mo(\eta^2-dppm)(\eta^1-dppm)(CO)_3$  has shown it to be solvent dependent [59]. In benzene, the reaction pro-



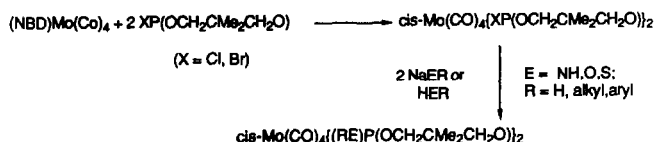
Scheme 11.

duced orange  $\text{Mo(CO)}_3\text{Cl}(\mu\text{-dppm})_2\text{Au}$  containing *trans*- $\text{P}_2\text{Mo}$  and *trans*- $\text{P}_2\text{Au}$  centers with a nonbonded Mo...Au separation. In dichloromethane, yellow  $[(\text{dppm(O)})_2\text{Mo(CO)}_2\text{AuPPh}_3]\text{PF}_6$  was obtained. This contained a seven-coordinate Mo with two chelating dppm-O ligands, two CO's and a Mo-AuPPh<sub>3</sub> bond (Scheme 14).

#### 2.4. Phosphine-sulfur complexes

Room-temperature decomposition of  $\text{Mo}^{\text{II}}$  complexes  $\text{Mo(CO)}_2(\text{PPh}_3)(\text{L})$  ( $\text{L} = 1,2\text{-bis(2-mercapto-3,5-di-t-butylphenylthio)ethane(2-)}$ ) led to CO and ethylene loss by thioether-S-dealkylation to give a  $\text{Mo}^{\text{IV}}$  complex  $\text{Mo(CO)(PPh}_3)(3,5\text{-di-t-butyl-1,2-benzene-dithiolate(2-})$  (Scheme 15) [60]. The product has a pseudo-trigonal bipyramidal  $\text{S}_4\text{CP}$  coordination geometry in the solid-state but *trans*-octahedral geometry in solution.

Treatment of  $\text{Mo(S}_2\text{CPMe}_3)(\text{CO})_2(\text{PMe}_3)_2$  with



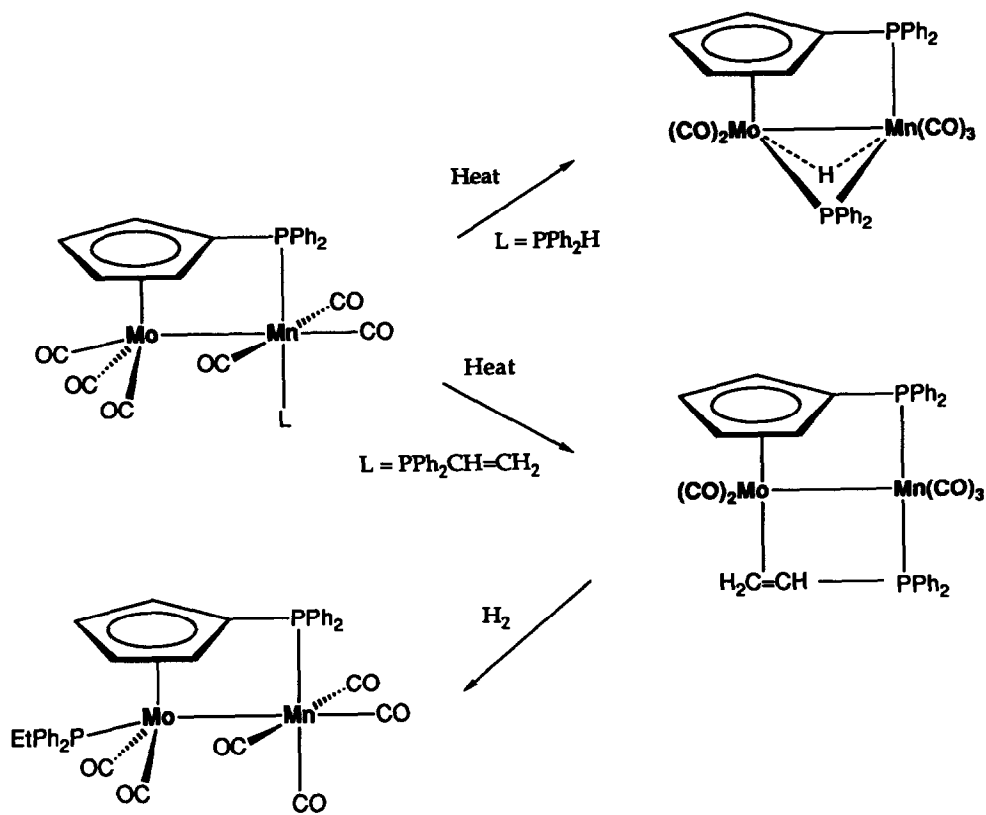
Scheme 12.

$\text{HBF}_4$  or  $\text{RI}$  gave  $[\text{Mo(S}_2\text{C(H)PMe}_3)(\text{CO})_2(\text{PMe}_3)_2]\text{[BF}_4\text{]}$  and  $[\text{Mo}(\eta^2\text{-SC(SR)PMe}_3)(\text{CO})_2(\text{PMe}_3)_2]\text{I}$  respectively (Scheme 16) [61]. The latter's structure indicated S-alkylation and a trihapto bonding by the resulting phosphoniodithioester ligand.

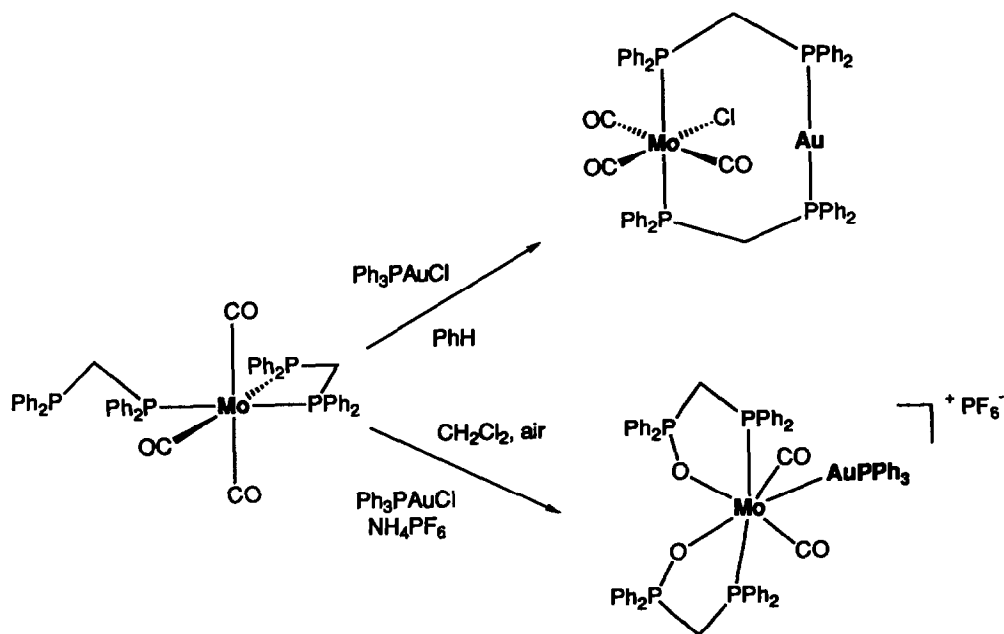
Molybdenum acetyl complexes of the type  $\text{Mo(COCH}_3)(\text{L-L})\text{CO(PMe}_3)_2$  ( $\text{L-L} = \text{S}_2\text{CNCR}_2$ ) have been prepared [62]. These contain the agostic acetyl unit  $\text{Mo(COME)}$  both in solution and in the solid state. The related xanthate complexes were also found to be agostic in the solid state but existed in equilibrium mixtures of the agostic acetyl, bidentate acyl, and methyldicarbonyl derivatives (Scheme 17).

The donor/acceptor properties of the complex *trans*- $\text{W(CO)}_4(\text{dppe})$  were investigated with the stereoinicator (*cis*-4,4'-dimethoxystilbene and *cis*- $\alpha, \beta$ -dinitrostilbene) [63]. A *cis-trans* conversion of the latter was observed due to charge transfer from the tungsten complex.

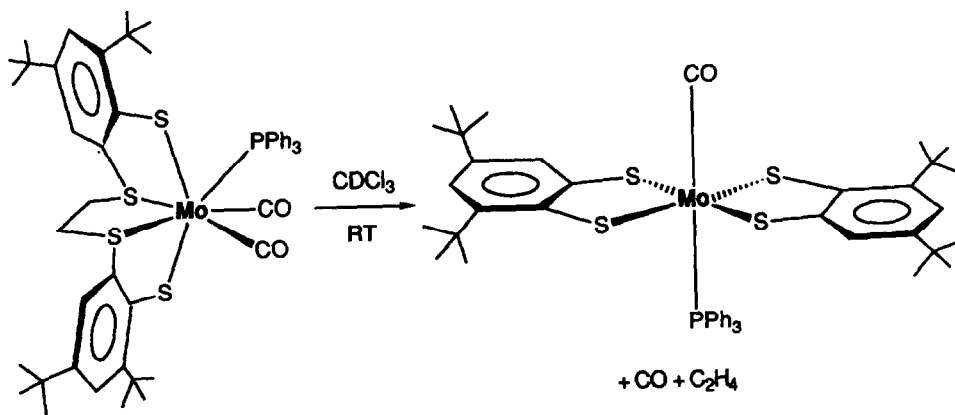
Reaction of *trans*- $[\text{W(CO)}(\text{N}_2)(\text{dppe})_2]$  with excess MeOH or  $\text{HNR}_2$  under  $\text{CO}_2$  led to a hydrido-carbonato complex  $\text{WH}(\eta^1\text{-OCO}_2\text{Me})(\text{CO})(\text{dppe})_2$  and hydrido-carbamato  $\text{WH}(\eta^2\text{-O}_2\text{CNR}_2)(\text{CO})(\eta^1\text{-dppe})(\eta^2\text{-dppe})$  respectively (Scheme 18) [64]. The latter reacted with  $\text{AlEt}_3$  under  $\text{CO}_2$  to give the  $\text{CO}_2$  complex *trans*- $\text{W(CO)}(\eta^2\text{-CO}_2)(\text{dppe})_2$ .



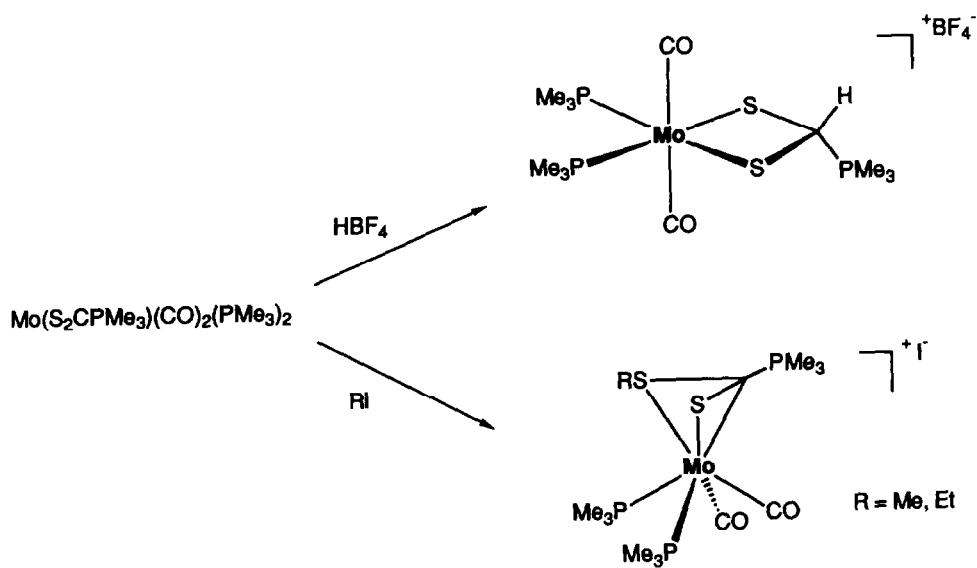
Scheme 13.



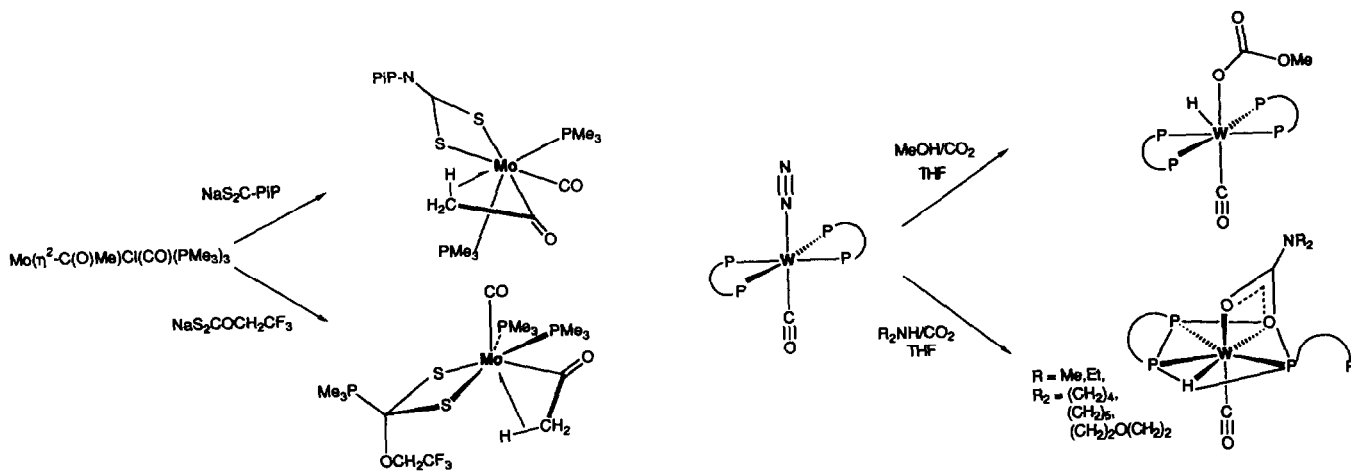
Scheme 14.



Scheme 15.



Scheme 16.



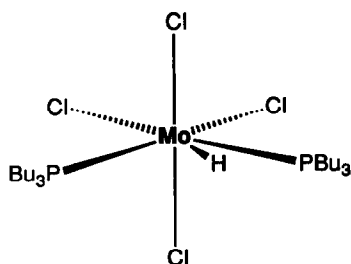
Scheme 17.

Scheme 18.

### 3. Hydrogen and hydride complexes

The reaction of water with  $M(\text{CO})_3(\text{PR}_3)_2$  and  $M(\text{CO})_3(\text{PR}_3)_2(\eta^2\text{-H}_2)$  ( $M = \text{Mo}, \text{W}$ ;  $R = \text{Cy}, \text{Pr}$ ) complexes has been studied in a variety of organic solvents. In THF, molecular hydrogen was instantly displaced by a water molecule to give  $M(\text{CO})_3(\text{PR}_3)_2\text{OH}_2$ . The coordinated water was found to be reversibly bound [65].

Reactions of anhydrous hydrogen halides with  $\text{MoH}_4(\text{PR}_3)_4$  afforded anionic paramagnetic, hydrido complexes  $[\text{PHR}_3]_2[\text{MoHCl}_4(\text{PR}_3)_2]$  ( $R = \text{Et}, X = \text{Cl}, \text{Br}$ ;  $R = \text{Bu}, X = \text{Cl}$ ;  $R_3 = \text{Me}_2\text{Ph}, X = \text{Br}$ ) [66]. The structure of  $\text{MoHCl}_4(\text{PBU}_3)_2$  revealed a distorted pentagonal bipyramidal coordination geometry with apical Cl's (37).



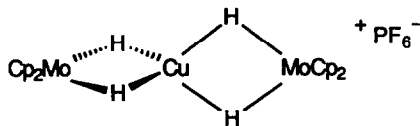
37

The nitrosyl complexes  $\text{trans-Mo}(\text{Cl}(\text{AlCl}_3)(\text{NO})(\text{CO})_4)$  reacted with three equivalents of  $\text{PR}_3$  ( $R = \text{Ph}, \text{Cy}$ ) to give  $\text{trans,trans-Mo}(\text{Cl})(\text{CO})_2(\text{NO})(\text{PR}_3)_2$  which was reduced by  $\text{LiBH}_4$  to  $\text{trans,trans-Mo}(\text{H})(\text{CO})_2(\text{NO})(\text{PR}_3)_2$  [67]. Phenyl diazonium cation underwent a 1,1-insertion with the hydride complex to form *trans*,

*trans*- $\text{Mo}(\text{NH}=\text{NPh})(\text{CO})_2(\text{NO})(\text{PPh}_3)_2^+$ . The coordinated phenyldiazene was removable by treatment with bromide at  $-40^\circ\text{C}$ .

The electrochemical oxidation of  $\text{CpMo}(\text{CO})_2(\text{PPh}_3)\text{H}$  in acetonitrile formed *cis*- $\text{CpMo}(\text{CO})_2(\text{PPh}_3)(\text{MeCN})^+$  [68]. Hydride abstraction with a trityl reagent produced the *trans*-isomer instead. This isomerized in MeCN solution to the *cis*-isomer in an intramolecular, nondissociative process with an activation enthalpy of  $24.2(4) \text{ kcal mol}^{-1}$ .

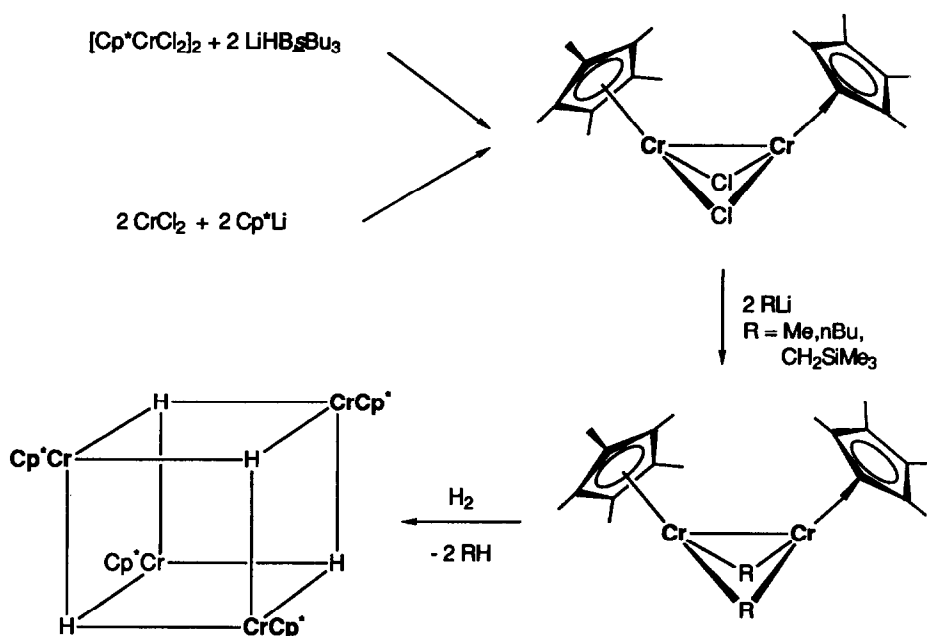
Reaction of  $\text{Cu}(\text{NCMe})_4^+$  with 2 equivalents of  $\text{Cp}_2\text{MH}_2$  ( $M = \text{Mo}, \text{W}$ ) afforded  $(\text{Cp}_2\text{MH}_2)_2\text{Cu}^+$  in which all hydrides were found to bridge the M's to Cu (38) [69]. Reaction of  $\text{AgBF}_4$  with  $\text{Cp}_2\text{WH}_2$  yielded first  $(\text{Cp}_2\text{WH}_2)_2\text{Ag}^+$  which can be oxidized by more  $\text{Ag}^+$  to give the adduct  $(\text{Cp}_2\text{WH}_2\text{Ag})_2^{2+}$  and eventually  $\text{Cp}_2\text{WH}_3^+$  and  $\text{Cp}_2\text{WH}(\text{NCMe})^+$ .



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Addition of 2 equivalents of  $\text{Li}[\text{HB}^s\text{Bu}_3]$  to a solution of  $[\text{Cp}^*\text{CrCl}_2]_2$  in THF yielded the reduced product  $[\text{Cp}^*\text{Cr}(\mu\text{-Cl})_2]_2$  which was also synthesized directly from  $\text{CrCl}_2$  and  $\text{LiCp}^*$  [70]. This was easily alkylated with organolithium reagents to give  $[\text{Cp}^*\text{Cr}(\mu\text{-R})_2]_2$  ( $R = \text{Me}, \text{Bu}, \text{CH}_2\text{SiMe}_3$ ). The methyl complex was hydrogenated to give the tetrachromium cubane complex  $[\text{Cp}^*\text{Cr}(\mu_3\text{-H})_4]_4$  (Scheme 19).

Upon gamma-irradiation, the polyhydrido com-



Scheme 19.



Scheme 20.

plexes  $\text{WH}_4(\text{dppe})$  and  $\text{WH}_5(\text{dppe})_2^+$  were reported to fix and reduce  $\text{N}_2$  to amines [71]. Analogous tetrahydride complexes of W with diphenylethylphosphine and diphenylmethylphosphine also reacted under gamma-irradiation with  $\text{N}_2 + 3\text{H}_2$  in THF/hexane solution to give hydrazine, ammonia, and amines [72].

Tungstenocene hydrides with ester or nitrile functionalized alkyls reacted with  $\text{LiAlH}_4$  to give olefin complexes [73]. For example,  $\text{Cp}_2\text{WH}(\text{CH}(\text{COOMe})\text{Me})$  yielded  $\text{Cp}_2\text{WH}(\text{CH}_2=\text{CHMe})$ . Similarly, functionalized olefin complexes were reduced to alkyls. Thus  $\text{Cp}_2\text{W}(\text{CH}_2=\text{CHCOOMe})$  afforded the metallacyclobutane  $\text{Cp}_2\text{W}(\text{CH}_2)_3$  (Scheme 20).

Activated acetylenes of the type  $\text{R}-\text{C}\equiv\text{C}-\text{COOR}'$  ( $\text{R} = \text{H}, \text{Me}, \text{COOR}'$ ) inserted into *trans,trans*- $\text{WH}(\text{CO})_2(\text{NO})(\text{PMe}_3)_2$  to give tungsten vinyl complexes,  $\text{W}[(Z)-\text{C}(\text{COOR}')=\text{CHR}](\text{CO})_2(\text{NO})(\text{PMe}_3)_2$ , by selective  $\alpha$ -methylation [74]. For  $\text{R} = \text{Ph}$ , both *Z* and *E* products were obtained with the latter being the

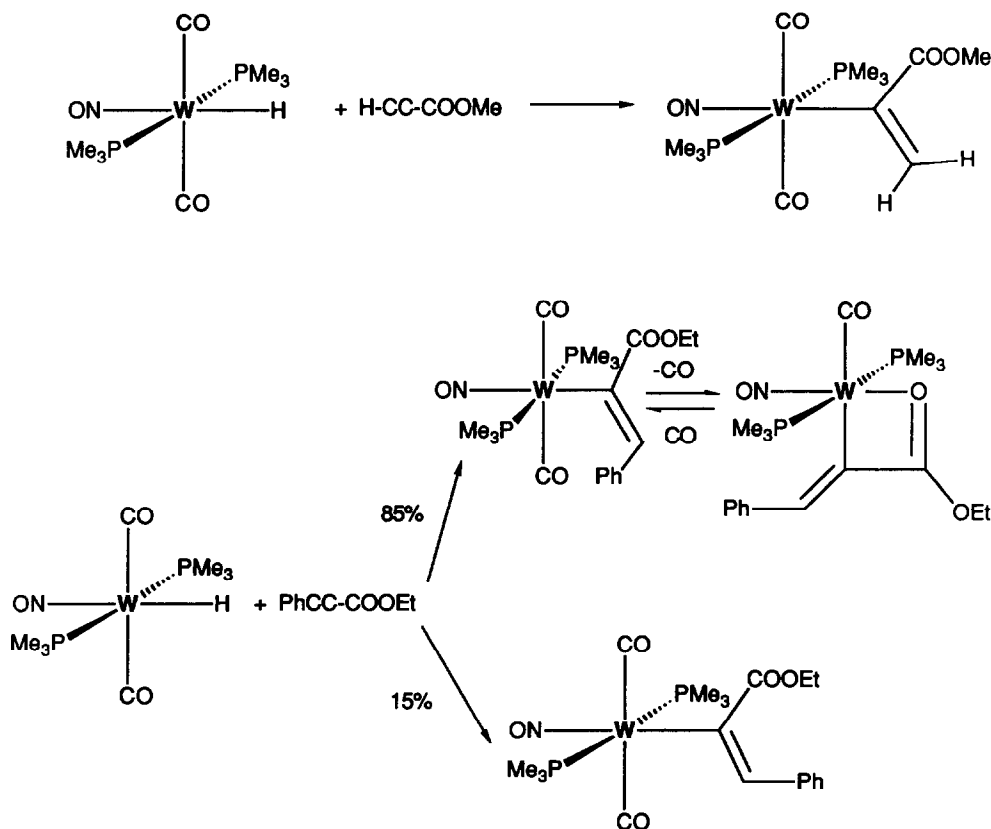
thermodynamic product. The former reversibly lost CO to give a WOCC-metallacycle (Scheme 21).

The tungsten hydride complex *trans-trans*- $\text{WH}(\text{CO})_2(\text{NO})(\text{PMe}_3)_2$  reduced a wide variety of  $\beta$ -diketones to  $\beta$ -hydroxy ketones, resulting in formation of *trans*- $\text{W}(\beta\text{-diketone})(\text{CO})(\text{NO})(\text{PMe}_3)_2$  [75]. Different  $\beta$ -substituents yielded isomeric mixtures in slow equilibrium.

#### 4. Nitrosyl complexes

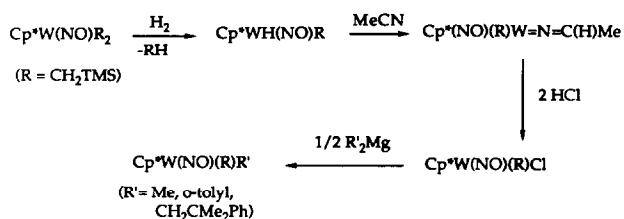
A three-step synthesis of new asymmetric  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)\text{R}$  ( $\text{R} = \text{alkyl, aryl}$ ) complexes was described [76]. The  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$  precursor was hydrogenated in acetonitrile to give the 18-electron ethylideneamido  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)(\text{N}=\text{C}(\text{H})\text{Me})$  complex. This was treated with two equivalents of HCl in ether to give deep blue 16-electron  $\text{Cp}^*\text{W}(\text{NO})(\text{CH}_2\text{SiMe}_3)\text{Cl}$ . Metathesis with  $\text{MgR}_2$  produced the desired 16-electron asymmetric complexes (Scheme 22).

A series of new diamagnetic nitrosyl cationic complexes  $\text{Cp}^*\text{Mo}(\text{NO})(\text{MeCN})_3^+$  and  $\text{Cp}^*\text{M}(\text{NO})\text{X}(\text{MeCN})_2^+$  ( $\text{M} = \text{Mo, W}$ ;  $\text{X} = \text{Cl, Br, I}$ ) were prepared from the respective  $\text{Cp}^*\text{M}(\text{NO})\text{X}_2$  precursors by treatment



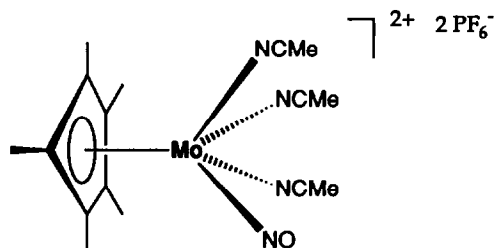
Scheme 21.





Scheme 22.

with  $\text{NO}^+$  or  $\text{Ag}^+$  salts in MeCN [77]. These were found to have the expected four-legged piano stool geometry (39). The MeCN ligands were found to exchange readily with MeCN solvent. Treatment of  $[\text{CpCr}(\text{NO})\text{I}_2]$  with  $\text{AgPF}_6$  in MeCN led to formation of the paramagnetic 17-electron  $[\text{CpCr}(\text{NO})(\text{MeCN})_2]\text{PF}_6$ . Its ESR spectrum indicated delocalization of the unpaired electron onto the NO ligand.

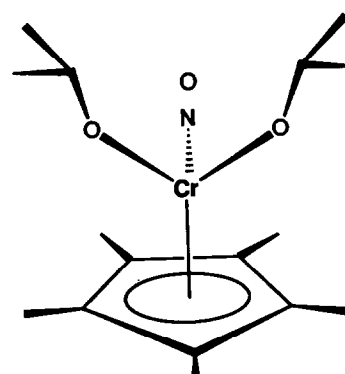


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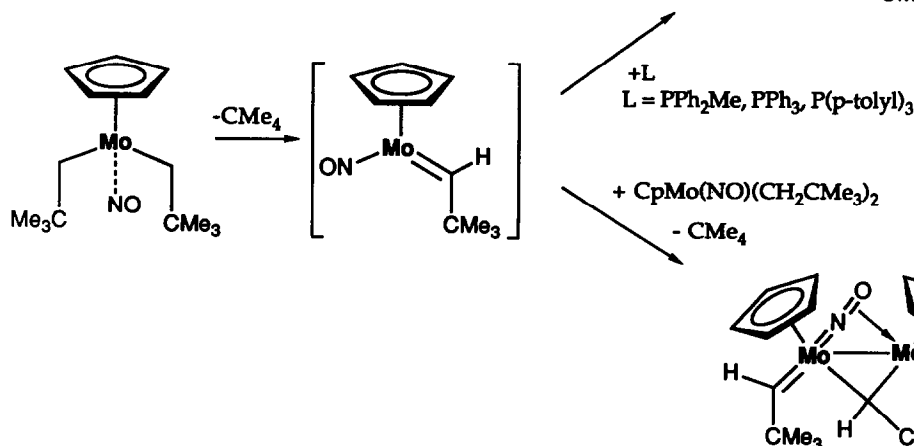
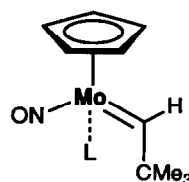
Thermally unstable  $\text{CpMo}(\text{NO})(\text{CH}_2^t\text{Bu})_2$  transformed at room temperature to a novel dimer  $[\text{CpMo}(\text{NO})](\mu\text{-}\eta^1:\eta^2\text{-NO})(\mu\text{-CH}^t\text{Bu})\text{CpMo}=\text{C}(\text{H})^t\text{Bu}]$  [78]. The bridging nitrosyl was found to act as an

unprecedented 3-electron donor to one Mo and a 2-electron donor to the other. Kinetic studies into the mechanism of this transformation suggested formation of the alkylidene complex  $\text{CpMo}(\text{NO})=\text{C}(\text{H})^t\text{Bu}$  after neopentane elimination and subsequent coupling with a second  $\text{CpMo}(\text{NO})(\text{CH}_2^t\text{Bu})_2$  (Scheme 23).

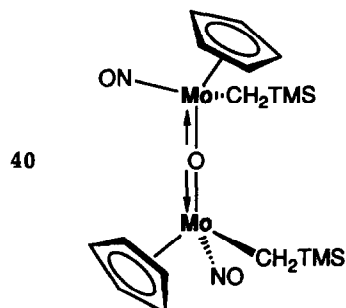
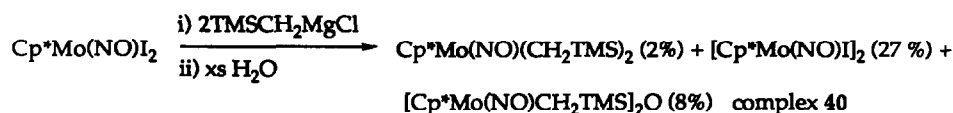
Treatment of  $\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2$  with 2 equivalents of  $\text{Me}_3\text{SiCH}_2\text{MgCl}$  led to three products upon workup: the desired 16-electron dialkyl complex  $\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2$ , its hydrolysis product  $[\text{Cp}^*\text{Mo}(\text{NO})(\text{CH}_2\text{SiMe}_3)_2(\text{O})]$ , and a reduction product  $[\text{Cp}^*\text{Mo}(\text{NO})\text{I}_2]$  (Scheme 24) [79]. The Mo moieties bonded to the bridging oxygen atom were found to be orthogonal, suggesting multiple Mo-O bonding (40). Although this hydrolysis was general for  $\text{Cp}^*\text{Mo}(\text{NO})(\text{alkyl})_2$ , no reaction was observed for tungsten analogues. The  $\text{Cp}^*\text{W}(\text{NO})(\text{aryl})_2$  complexes were hydrolyzed to  $\text{Cp}^*\text{W}(\text{O})_2(\text{aryl})$ .



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Scheme 23.

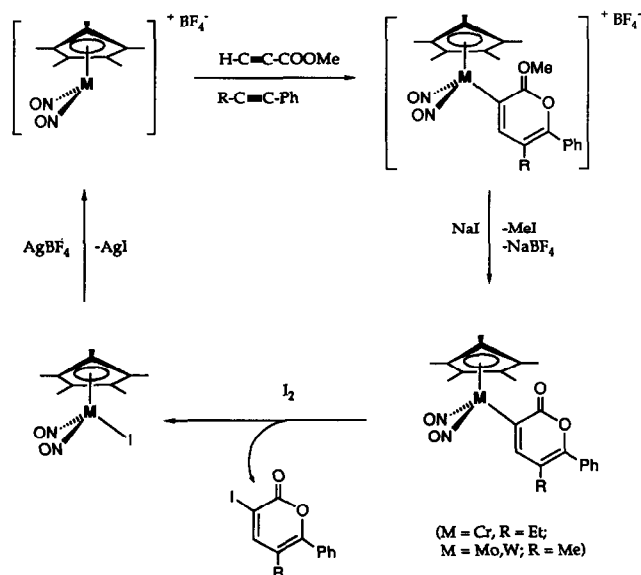


Scheme 24.

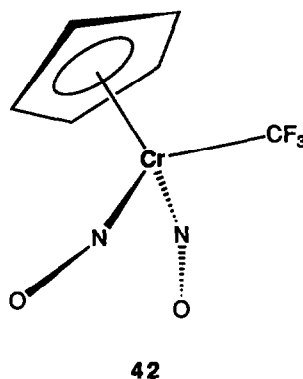
The formally 16-electron cations  $[\text{Cp}^*\text{M}(\text{NO})_2]^+$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) were found to mediate the regioselective assembly of iodopyrones,  $\text{IC}=\text{C}(\text{H})\text{C}(\text{R})=\text{C}(\text{Ph})\text{OC}=\text{O}$  ( $\text{R} = \text{Me}, \text{Et}$ ), from methyl propiolate,  $\text{HC}\equiv\text{CCOOMe}$ , phenylacetylenes, and iodine (Scheme 25) [80].

Treatment of  $\text{Cp}^*\text{Cr}(\text{NO})_2\text{CH}_2\text{Cl}$  or  $\text{Cp}^*\text{Cr}(\text{NO})_2\text{Cl}$  with excess  $\text{NaO}^i\text{Pr}$  in iso-propanol gave the blue-green mononuclear diamagnetic  $\text{Cr}^{\text{II}}$  complex  $\text{Cp}^*\text{Cr}(\text{NO})(\text{O}^i\text{Pr})_2$  [81]. Its X-ray indicated a terminal  $\text{NO}^+$  as well as significant  $\text{Cr}-\text{O}$   $\pi$ -bonding which rendered the formally 16-electron complex coordinately saturated (41).

Complexes of the type  $\text{CpMo}(\text{CO})_2[\eta^2\text{-anti-1-CH}_2\text{CH}(\text{OH})\text{R-syn-3-R}'\text{CH}_2-\text{C}_3\text{H}_3]$  have been prepared [82]. These reacted with excess  $\text{NOBF}_4$  to give 3-(1'- $\text{R}'\text{CH}_2\text{CH}=\text{CH}$ )-5-R-isoxazole *via* a novel  $\text{NO}$  insertion into the  $\pi$ -allyl ligand (Scheme 26). Chromium(I) complexes of the type *cis,cis*- $\text{Cr}(\text{NO})$ -

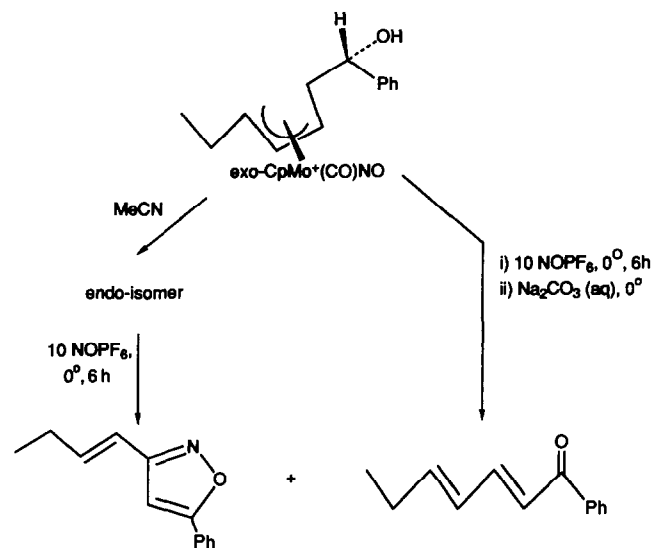


Scheme 25.

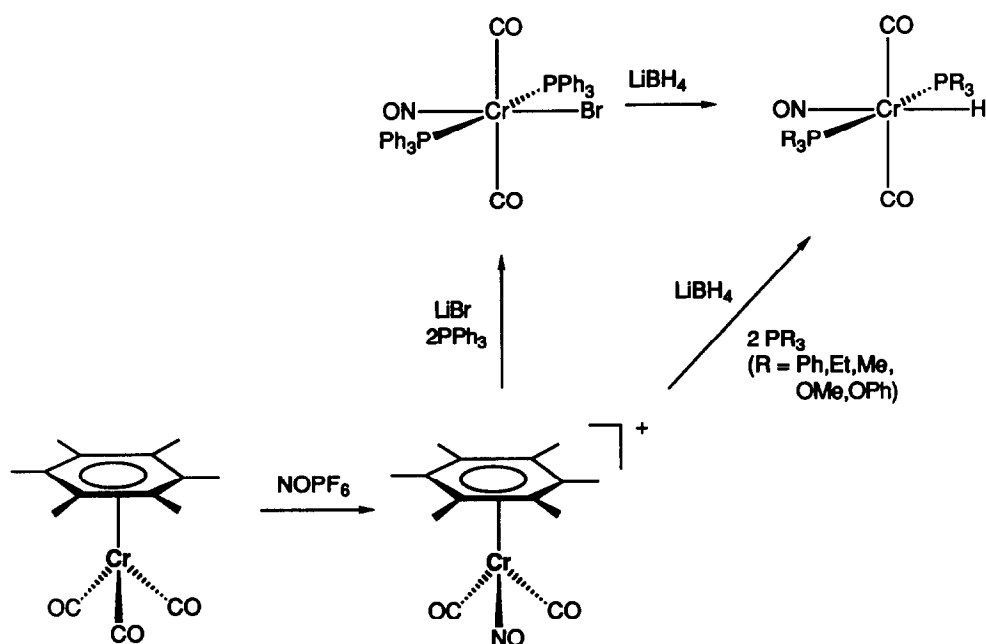


$(\text{CN})_2\text{L}_2(\text{H}_2\text{O})$  ( $\text{L} = \text{aromatic aldehyde oxime or Mannich base}$ ) have been prepared [83]. Their ir data suggested aromatic N-coordination in all cases.

Reactions of  $(\text{arene})\text{Cr}(\text{CO})_3$  with  $\text{NOPF}_6$  gave  $(\text{arene})\text{Cr}(\text{CO})_2\text{NO}^+$  which were converted to the novel hydrides *trans,trans*- $\text{CrH}(\text{CO})_2(\text{NO})(\text{PR}_3)_2$  with  $\text{LiBH}_4$  in the presence of phosphines (Scheme 27) [84].



Scheme 26.



Scheme 27.

Interaction of  $\text{Cd}(\text{CF}_3)_2 \cdot \text{glyme}$  with  $\text{CpM}(\text{NO})_2\text{Cl}$  ( $\text{M} = \text{Cr}, \text{Mo}$ ) yielded the corresponding  $\text{CpM}(\text{NO})_2(\text{CF}_3)$  complexes which were fully characterized (**42**) [85]. The Cr complex was found to be exceptionally thermally and oxidatively inert while the Mo complex was quite air-sensitive.

## 5. Carbene complexes

### 5.1. Structure, synthesis and reactivity

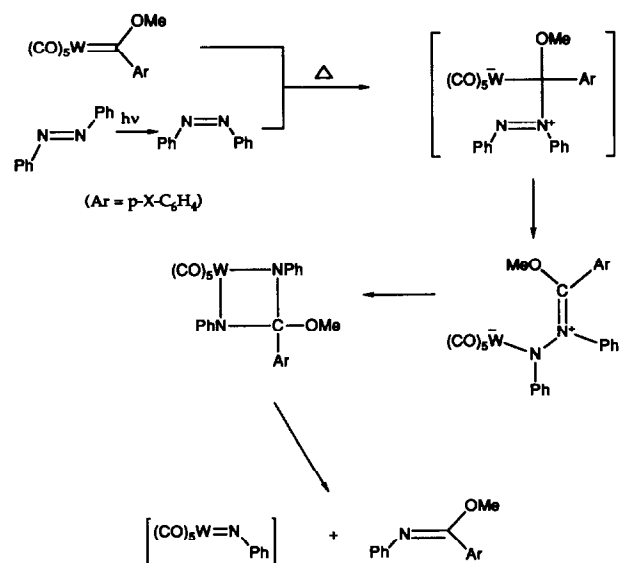
The reaction of *cis*-azobenzene with a series of *p*-phenyl carbenes  $\text{W}(\text{CO})_5=\text{C}(\text{OMe})\text{-}p\text{-XC}_6\text{H}_4$  ( $\text{X} = \text{H}, \text{OMe}, \text{CF}_3$ ) was studied [86]. Initially the zwitterion  $\text{W}(\text{CO})_5\text{NPhNPhC}(\text{OMe})(\text{-}p\text{-XC}_6\text{H}_4)$  formed. In non-coordinating solvents the  $\text{X} = \text{H}$  zwitterionic species was converted to an isomeric intermediate as well as a 2,4-diazametallacyclic complex. Ultimately both decomposed to the metathesis product  $\text{PhN}=\text{C}(\text{OMe})\text{Ph}$  (Scheme 28). In acetonitrile, the coordinated diaziridine was displaced by solvent without leading to the metallacycle.

Reactions of 1,4-dihydropyridines  $\text{R}'\text{C}_5\text{H}_5\text{NR}$  with the carbenes  $\text{M}(\text{CO})_5=\text{C}(\text{OEt})\text{Me}$  ( $\text{M} = \text{Cr}, \text{W}$ ) gave either the ylides  $\text{M}(\text{CO})_5\text{CH}(\text{Me})(\text{R})\text{NC}_5\text{H}_5\text{R}'$  or the pyridinium tungstates or chromates  $\text{M}(\text{CO})_5\text{CH}(\text{Me})(\text{OEt})^-\text{RNC}_5\text{H}_5\text{R}'^+$  via hydride transfer (Scheme 29) [87].

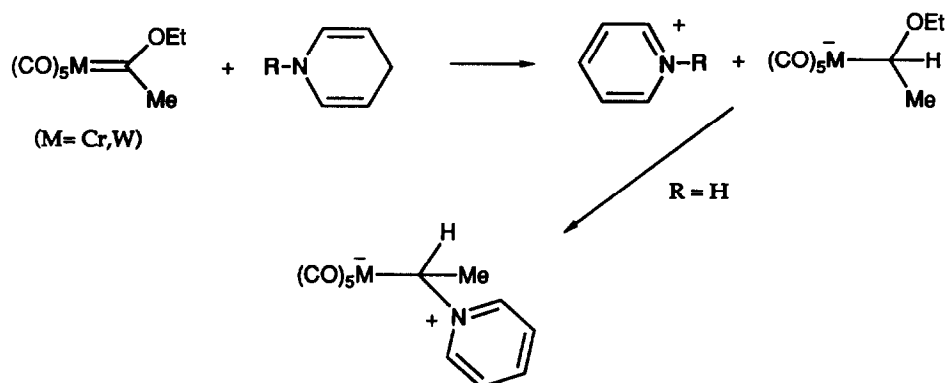
The anionic chromium carbene  $\text{Cr}(\text{CO})_5=\text{C}(\text{OMe})\text{-CH}_2^-$  added to olefins in  $\text{CpFe}(\text{CO})_2(\text{olefin})^+$  to form bimetallic complexes of the type  $\text{Cr}(\text{CO})_5=\text{C}(\text{OMe})\text{-CH}_2\text{-CHR-CHR'-Fe}(\text{CO})_2\text{Cp}$  [88]. The carbene also added to  $[(\eta^5\text{-cyclohexadienyl})\text{Fe}(\text{CO})_3]^+$  to give a

bimetallic product. In addition, trimetallic  $\text{Fe}_2\text{Cr}$  stereoisomers with two  $(\eta^4\text{-cyclohexadiene})\text{Fe}(\text{CO})_3$  moieties attached to the  $\beta\text{-C}$  of the chromium carbene were also prepared and characterized (Scheme 30).

Treatment of  $\text{W}(\text{CO})_5=\text{C}(\text{NMe}_2)\text{Me}$  with  $^n\text{BuLi}$  followed by excess diiodoalkanes afforded the corresponding iodoalkylaminocarbene complexes  $\text{W}(\text{CO})_5=\text{C}(\text{NMe}_2)\text{CH}_2(\text{CH}_2)_n\text{I}$  ( $n = 1\text{-}5$ ) [89]. Low yields for  $n = 1$  and no yield for  $n = 2$  were found. Subsequent reaction of these products with more  $\alpha$ -lithio(amino)carbene yielded ditungsten complexes  $\text{W}(\text{CO})_5=\text{C}(\text{NMe}_2)\text{CH}_2(\text{CH}_2)_n\text{CH}_2\text{C}(\text{NMe}_2)=\text{W}(\text{CO})_5$  (Scheme 31).



Scheme 28.



Scheme 29.

Reaction of the carbenes  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\sigma\text{:}\eta^2\text{-}(4\text{e})\text{-C}=\text{CR}_2)]$  with  ${}^1\text{BuNC}$ ,  $\text{PMe}_3$ , or  $\text{P}(\text{OMe})_3$  led to unexpected attack on the carbenoid  $\alpha\text{-C}$  of the vinylidene (Scheme 32) [90]. Cyclohexenesulfide transferred a S atom to the  $\alpha\text{-C}$  and formed a bimetallic thioketene complex which upon successive protonation and hydride addition yielded a  $\mu$ -thioacetaldehyde complex.

The carbene  $[\text{CpW}(\text{CO})(\text{PMe}_3)=\text{C}(\text{Tol})\text{PR}_2]\text{PF}_6$  reacted with  $[\text{Me}_2(\text{MeS})\text{S}]\text{BF}_4$  to give the dicationic tungstaphosphathiabicyclo[1.1.0]butane (Scheme 33) [91].

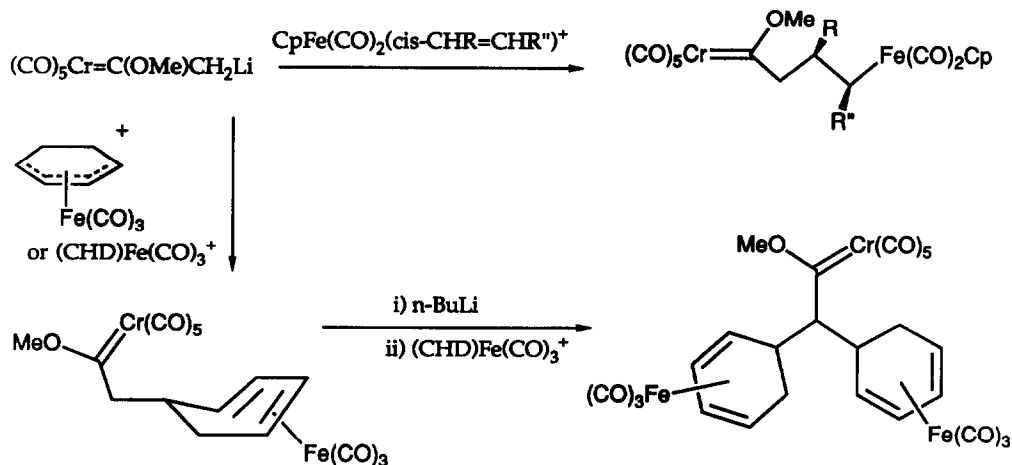
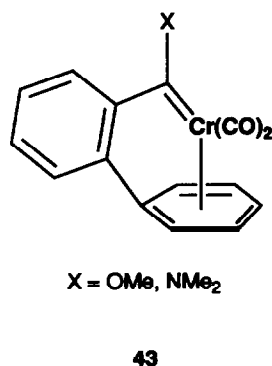
Condensation of ( $\beta$ -aminovinyl)carbene complexes of Cr and W with alkynes afforded pyridines and pyridinium salts in good yields [92].

Aminocarbene complexes of Cr, Mo, and W underwent N-acylation with DMAP catalysis followed by decarbonylation to give (acylamino)carbene chelates [93]. Reactions of these with alkynes resulted in stereoselective insertions (Scheme 34).  $\text{Cr}(\text{CO})_5=\text{C}(\text{tol})\text{NR}\text{-COCMe}_3$  favored *E* insertion and subsequent carbene annulation or double alkyne insertion products. The Mo analogues most likely led to *Z*-alkenylcarbene pre-

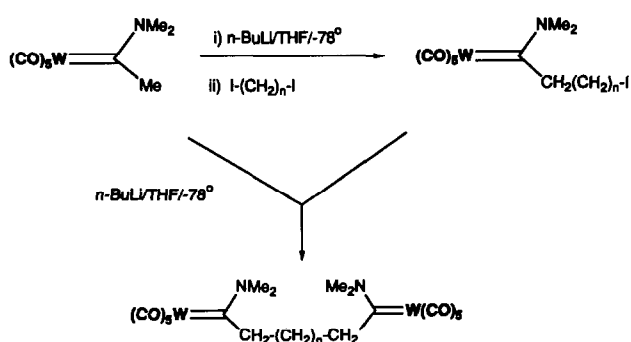
cursors to isolated pyrrole and pyrrolone cycloaddition products.

Thermolysis of chromium carbene complexes  $\text{Cr}(\text{CO})_5=\text{CX}(1,1'\text{-biphenyl-2-yl})$  ( $\text{X} = \text{OMe}, \text{NMe}_2$ ) provided the new cyclic arene carbene complexes shown (43) [94]. These were found to be remarkably stable and did not exhibit the electrophilic Fischer carbene chemistry.

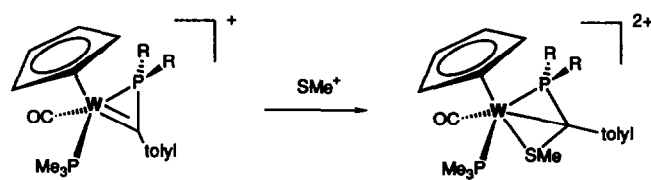
New (hydroxyalkyl)pyrrolidiniocarbene chromium complexes were prepared from the ring-opening reac-



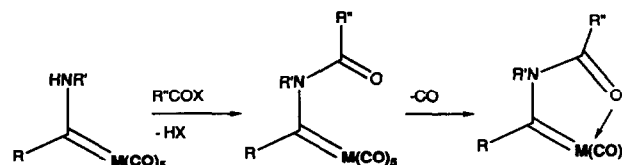
Scheme 30.



Scheme 31.



Scheme 33.

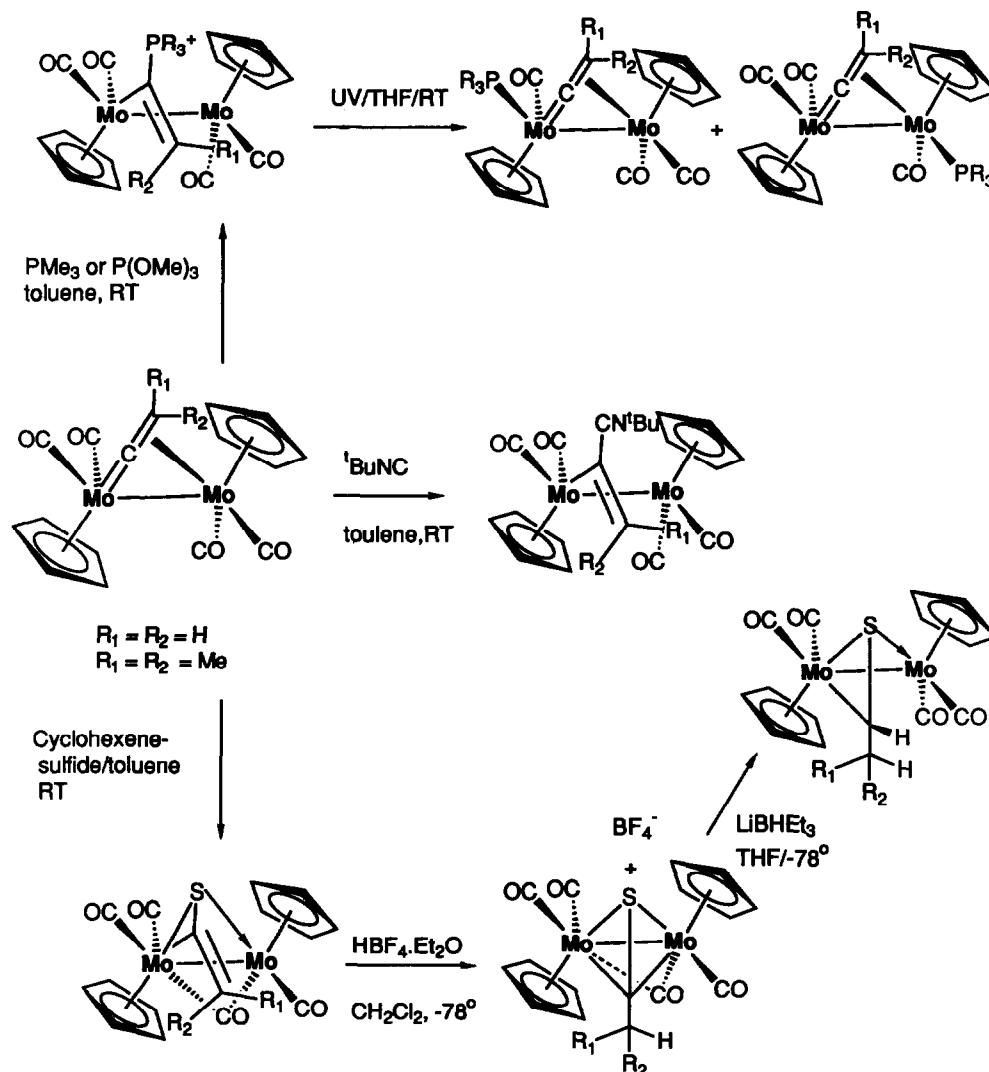


Scheme 34.

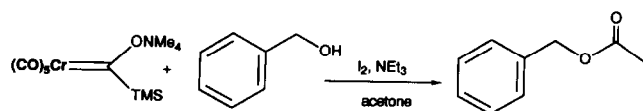
tion of epoxides promoted by the conjugate base of  $\text{Cr}(\text{CO})_5=\text{C}(\text{pyrrolidino})\text{Me}$  in the presence of  $\text{BF}_3 \cdot \text{ether}$  [95].

Reaction of  $\text{Cr}(\text{CO})_5=\text{C}(\text{SiMe}_3)\text{O}[\text{NMe}_4]$  with  $\text{I}_2$  in the presence of a base and alcohol afforded carboxylic

acid esters (Scheme 35) [96]. Substituting an amine or water for the alcohol yielded an amide or a carboxylic acid, respectively.



Scheme 32.



Scheme 35.

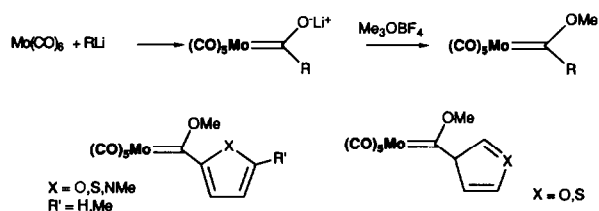
Tandem nucleophilic addition/electrophilic alkylation on  $\text{Mo}(\text{CO})_6$  gave phenyl-, pyrrol-, furyl-, and thienyl-carbene complexes (Scheme 36) [97].

Thioketones  $\text{S}=\text{CR}_2$  reacted with  $\text{W}(\text{CO})_5=\text{C}(\text{Ph})\text{H}$  by formal addition to the carbene C and cyclization to give thiirane complexes  $\text{W}(\text{CO})_5[\text{SC}(\text{Ph})\text{HCR}_2]$  [98]. Demetallation with  $\text{NEt}_4\text{Br}/\text{CH}_2\text{Cl}_2$  or pyridine/THF yielded the free thiirane (Scheme 37).

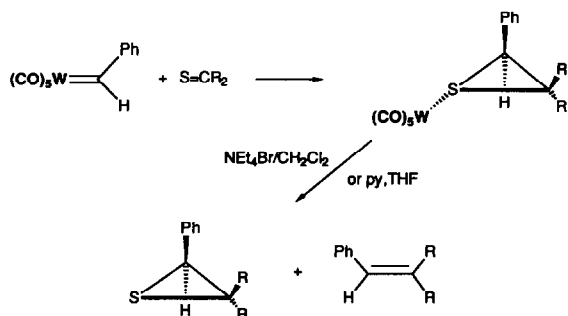
Hydride abstraction by tropylium cation from cycloheptatrienyl complexes  $\text{M}(\text{CO})_5=\text{C}(\text{OEt})(\text{CH}_2-\text{C}_7\text{H}_7)$  ( $\text{M} = \text{Cr}, \text{W}$ ) followed by deprotonation with  $\text{NEt}_3$  yielded heptafulvenyl carbene complexes  $\text{M}(\text{CO})_5=\text{C}(\text{OEt})(\text{CH}=\text{C}_7\text{H}_7)$  (Scheme 38) [99]. Further reaction of these with cyclohexyl isocyanide led to a ketenimine intermediate which cyclized to form the azaspiro [4.6]undecatetraene complexes. Pyridine demetallation of the latter afforded the pyrrole while thermolysis gave an azulene.

These same heptafulvenyl carbene complexes  $\text{M}(\text{CO})_5=\text{C}(\text{OEt})(\text{CH}_2-\text{C}_7\text{H}_7)$  ( $\text{M} = \text{Cr}, \text{W}$ ) added isocyanides  $\text{RNC}$  to form intermediate ketenimine species  $\text{M}(\text{CO})_5[\text{RN}=\text{C}=\text{C}(\text{OEt})\text{CH}_2\text{C}_7\text{H}_7]$  [100]. These isomerized *via* an intramolecular [2s + 2a] reaction to give cyclobutanimes which reacted with pyridine to yield a tetrahydroazulene-1-imine (Scheme 39).

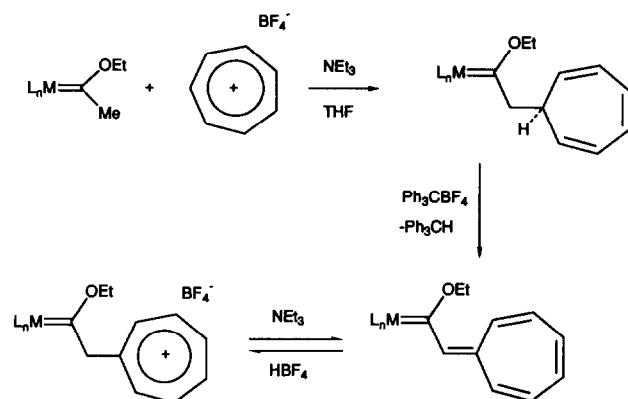
Reactions of the above  $\text{M}(\text{CO})_5=\text{C}(\text{OEt})(\text{CH}_2-\text{C}_7\text{H}_7)$  complexes with the alkyne  $\text{Et}_2\text{N}-\text{C}\equiv\text{C}-\text{Me}$  gave



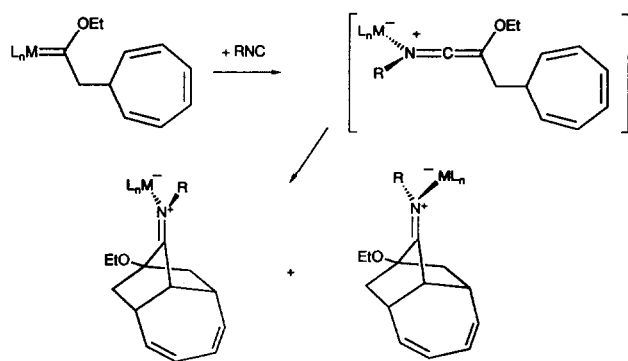
Scheme 36.



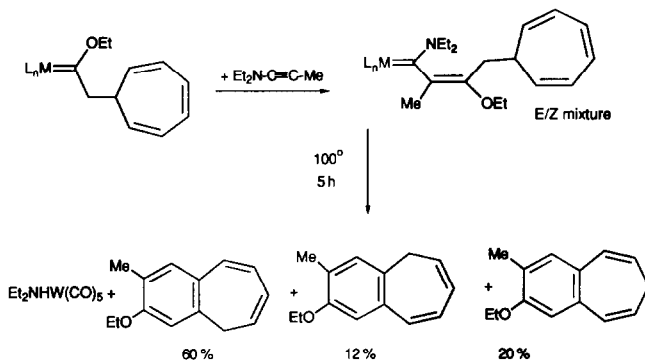
Scheme 37.



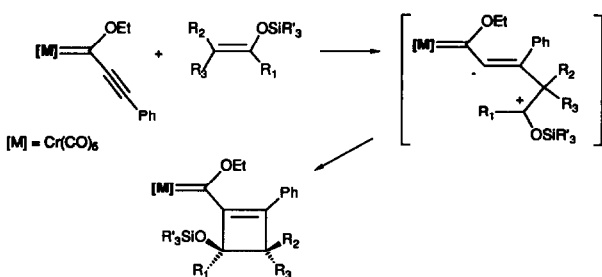
Scheme 38



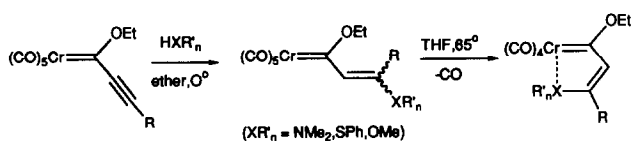
Scheme 39.



Scheme 40.



Scheme 41.



Scheme 42.

*E/Z*-1-amino(1-alkenyl)carbene complexes M(CO)<sub>5</sub>-[C(NEt<sub>2</sub>)-C(Me)=CH<sub>2</sub>-C<sub>7</sub>H<sub>7</sub>] [101]. Thermolysis of the W product led to elimination of W(CO)<sub>5</sub>NEt<sub>2</sub>H and regiospecific formation of three isomeric ethoxycycloheptatrienes (Scheme 40).

The reaction of Cr(CO)<sub>5</sub>=C(OEt)-C≡CPh with silyl enol ethers yielded cyclobutenyl carbene complexes *via* a Michael-type addition of the enol ether to the carbene (Scheme 41) [101a].

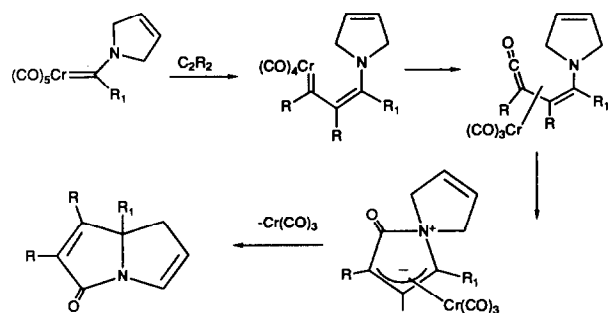
Michael addition of amines, alcohols, and thiols to alkynylcarbene complexes Cr(CO)<sub>5</sub>=C(OEt)-C≡CR yielded η-donor substituted α,β-unsaturated carbene complexes [102]. These vinyl carbenes decarbonylated in refluxing THF to give Cr(CO)<sub>4</sub>=C(OEt)C=CR(XR'<sub>n</sub>) (X = N, O, S) (Scheme 42).

Reactions of amino carbenes bearing alkyl groups of low migratory tendency: Cr(CO)<sub>5</sub>=C(R<sup>1</sup>)NR<sup>2</sup>R<sup>3</sup> (R<sup>1</sup> = H, Me, Ph; R<sup>2</sup> = Me; R<sup>3</sup> = Me, C<sub>3</sub>H<sub>5</sub>, CH<sub>2</sub>C<sub>3</sub>H<sub>5</sub>; R<sup>2</sup>R<sup>3</sup> = (CH<sub>2</sub>)<sub>5</sub>) and Cr(CO)<sub>5</sub>=C[(CH<sub>2</sub>)<sub>3</sub>C≡CPh]NR<sup>1</sup>R<sup>2</sup> (R<sup>1</sup> = R<sup>2</sup> = Me, R<sup>1</sup>R<sup>2</sup> = (CH<sub>2</sub>)<sub>4,5</sub>) with alkynes led to stable nitrogen ylides *via* ketene precursors (Scheme 43) [103]. These underwent Stevens-type rearrangements upon heating to give the expected heterocycles.

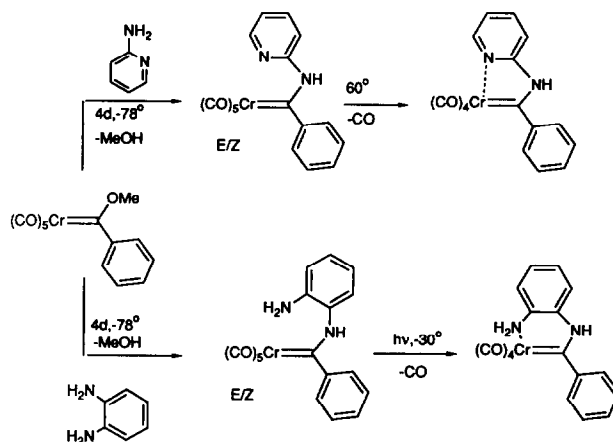
Aminolysis of Cr(CO)<sub>5</sub>=C(OMe)Ph with cyclic aromatic diamines afforded aminocarbene complexes which underwent thermal or photochemical CO-loss to give chelate complexes (Scheme 44) [104].

Mild decarbonylation of Mo(CO)<sub>5</sub>=C(OMe)(*o*-C<sub>6</sub>H<sub>4</sub>X) (X = OMe, SMe, NMe<sub>2</sub>) led to chelated carbene complexes of Mo(CO)<sub>4</sub> [105]. In contrast to the C, N and C, S chelates, the C, O complex underwent ready ring opening with PPh<sub>3</sub> even at -40°C.

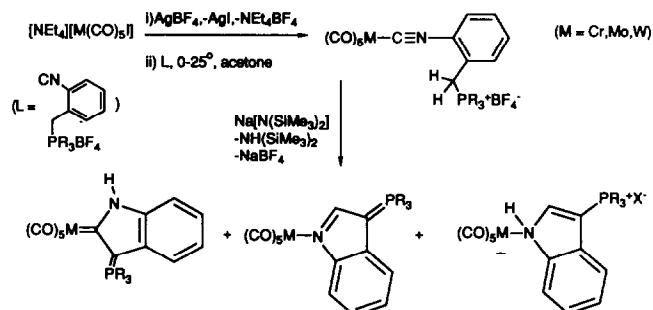
Reaction of NEt<sub>4</sub>[M(CO)<sub>5</sub>I] (M = Cr, Mo, W) with phosphonium-substituted phenyl isocyanides in the presence of AgBF<sub>4</sub> gave M(CO)<sub>5</sub>[*o*-CNC<sub>6</sub>H<sub>4</sub>H<sub>2</sub>PR<sub>3</sub>][BF<sub>4</sub>] [106]. The coordinated ligands reacted with



Scheme 43.



Scheme 44.



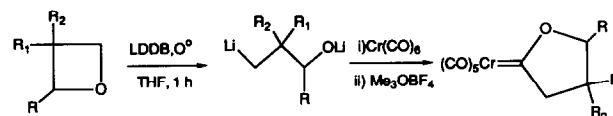
Scheme 45.

NaN(SiMe<sub>3</sub>)<sub>2</sub> to give mixtures of cyclization products of the carbene type M(CO)<sub>5</sub>[*o*-CNHC<sub>6</sub>H<sub>4</sub>PR<sub>3</sub>], indole type M(CO)<sub>5</sub>[*o*-NCHCPR<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>)], or M(CO)<sub>5</sub>-[NHCHCPR<sub>3</sub>(C<sub>6</sub>H<sub>4</sub>)] (Scheme 45). Cyclic voltammetry of these complexes indicated electron-donor ability of the ligands to follow the trend indole > carbene > protonated carbenes or indoles > isocyanides.

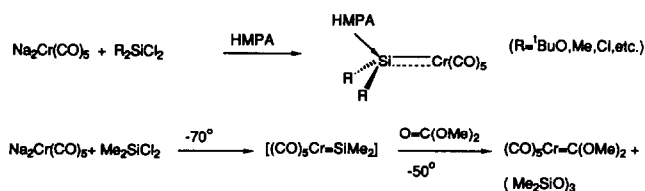
Reductive lithiation of oxetanes was employed in the synthesis of pentacarbonyl(2-oxacyclopentilidene) chromium complexes (Scheme 46) [107].

Reaction of (NBD)M(CO)<sub>4</sub> (M = Cr, W) with ArLi and subsequent alkylation with Et<sub>3</sub>OBF<sub>4</sub> gave C<sub>7</sub>H<sub>8</sub>M(CO)<sub>3</sub>=C(OEt)Ar complexes [108]. (COD)W(CO)<sub>4</sub> reacted similarly to give C<sub>8</sub>H<sub>12</sub>W(CO)<sub>3</sub>=C(OEt)Ar.

Reaction of R<sub>2</sub>SiCl<sub>2</sub> [R = <sup>t</sup>BuO-, <sup>t</sup>BuS-, MesO-, 1-Ada-O-, 2-Ada-O-, Nep-O-, Trit-O-, Me, Cl) with M(CO)<sub>5</sub><sup>2-</sup> (M = Cr, W) in the presence of HMPA yielded the base-stabilized silylene complexes (HMPA)<sub>2</sub>R<sub>2</sub>Si=M(CO)<sub>5</sub> [109]. Coordination geometry at silicon was found to be severely distorted from tetrahedral, dependent on the free silylene frontier



Scheme 46.



Scheme 47.

orbital energy and electron density. At  $-50^\circ\text{C}$ ,  $\text{Na}_2\text{Cr}(\text{CO})_5$  and  $\text{Me}_2\text{SiCl}_2$  gave base-free  $\text{Me}_2\text{Si}=\text{Cr}(\text{CO})_5$  which could be trapped with dimethylcarbonate to give hexamethyltrisiloxane and  $(\text{MeO})_2\text{C}=\text{Cr}(\text{CO})_5$  in a sila-Wittig reaction (Scheme 47).

### 5.2. Carbenes in organic synthesis

The photochemical reaction of  $\text{Cr}(\text{CO})_5(\text{C}=\text{CRR}')$  (R = OMe, R' = Me, Ph; R = OBz,  $\text{CHMe}_2$ , R' = Me; R = NBz<sub>2</sub>, R' = H) with  $\text{R}^2\text{N}=\text{C}(\text{SMe})_2$  produced 4,4-bis(methylthio)  $\beta$ -lactams in good to excellent yields [110]. Upon NBS oxidation, these afforded 4-oxo  $\beta$ -lactams (malonamides).

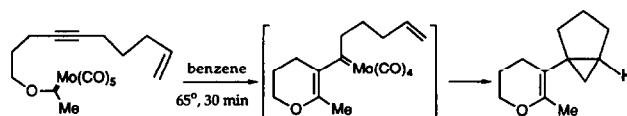
Photolytic reaction of  $\text{Cr}(\text{CO})_5=\text{CR}(\text{OR}')$  (R = Me, Bu, Ph, tol, cyclopropyl, 2-furyl; R' = Bz; RR' =  $(\text{CH}_2)_3$ ) with valine-derived optically active thiazolines produced optically active  $\beta$ -lactam penams in fair to good yields and with high stereoselectivity [111]. For most of these alcoholysis followed by solvolysis of the thiazolidine ring produced optically active formylalkanoates.

(Cycloheptatrienylmethyl)carbene complexes  $\text{M}(\text{CO})_5=\text{C}(\text{OEt})\text{CH}_2\text{C}_7\text{H}_7$  (M = Cr, W) were obtained from  $\text{M}(\text{CO})_5=\text{C}(\text{OEt})\text{Me}$  and  $[\text{C}_7\text{H}_7]\text{BF}_4$  [112]. Thermolysis of these led to equilibrium mixtures of 4,5-homotropilidenes.

Photochemical reactions of chromium carbenes with electron-rich olefins were compared to [2 + 2] cycloadditions of ketenes to olefins (Scheme 48) [113].

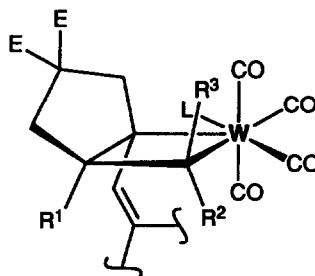
The benzylidene complexes  $\text{W}(\text{CO})_5=\text{C}(\text{C}_6\text{H}_4\text{R-}p)\text{H}$  (R = OMe, Me, H) were found to transfer the benzylidene ligand to olefins generating cyclopropanes [114].

Reactions of  $\text{M}(\text{CO})_5=\text{C}(\text{OMe})\text{Me}$  (M = Mo, W) with  $\alpha,\omega$ -enynes gave higher selectivities for the formation of cyclopropanes than the chromium analogues [115]. It was proposed that seven-coordination accessible to tungsten only (44) may account for the formation



Scheme 49.

of unusual Pauson-Khand cyclization to give cyclopentenone products.



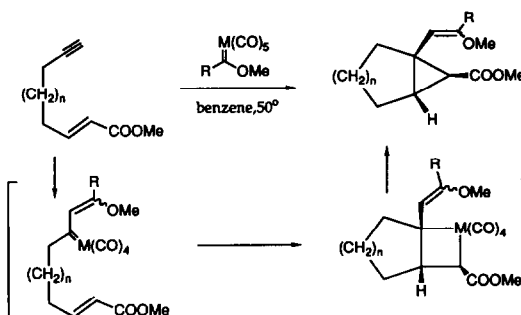
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Thermolysis of enyne and diene tethered molybdenum carbene complexes led to intramolecular formation of a variety of tricyclic ring systems (Scheme 49) [116].

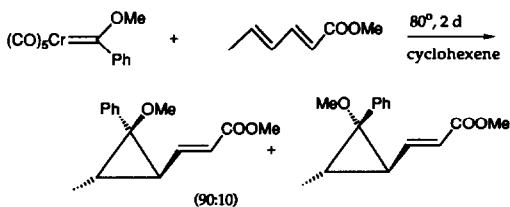
Reaction of  $\text{Mo}(\text{CO})_5=\text{C}(\text{Bu})\text{OMe}$  with 1,6- and 1,7-enynes produced vinylcyclopropanes in good to excellent yields (Scheme 50) [117]. Chromium analogues gave significantly poorer yields.

Thermal reactions of Fischer carbene complexes with electron-deficient 1,3-dienes provided functionalized vinylcyclopropanes in good yields (Scheme 51) [118]. The diastereomer with *cis*-OMe group to the olefin was favored.

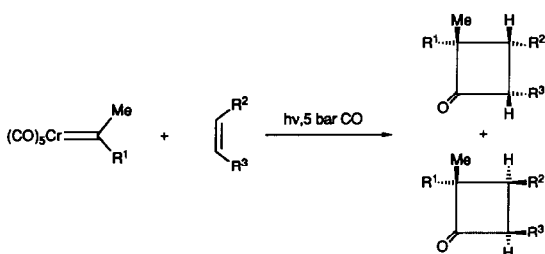
Photochemical or thermal reaction of chromium alkoxy carbene complexes with stabilized sulfur ylides



Scheme 50.

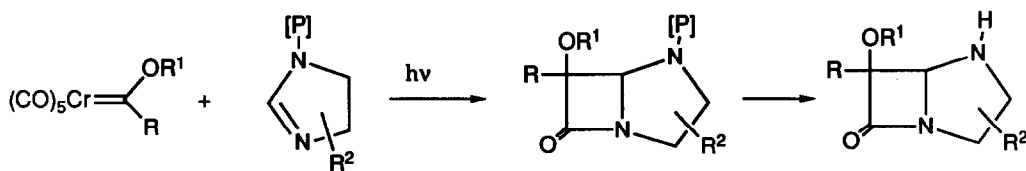


Scheme 51.



Scheme 48.





Scheme 52.

afforded vinyl ethers with differing yields and stereoselectivity [119].

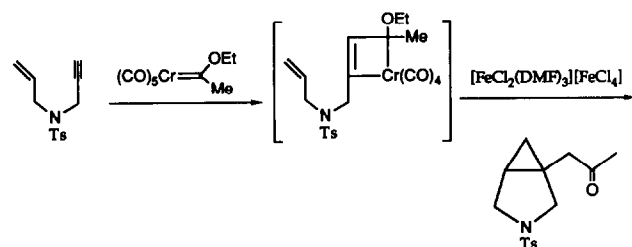
Photolysis of optically active chromium-aminocarbenes with optically active  $\alpha$ -amino acids produced dipeptides in excellent yields with high diastereoselectivity [120]. Both the (*S,S*) and (*R,S*) diastereomers can be synthesized with high selectivity.

Photolysis of chromium alkoxy-carbenes with *N*-(benzyloxycarbonyl)imidazolines produced protected azapenamams [121]. Hydrogenolysis yielded stable free azapenamams (Scheme 52). Treatment of these with camphorsulfonic acid produced unsaturated 14-membered tetraazamacrocycles which can be reduced to dioxocyclams.

Pyrrolidine derivatives have been synthesized *via* chromacyclobutanes upon treatment with  $[\text{FeCl}_2(\text{DMF})_3][\text{FeCl}_4]$  [122]. These metallacyclobutanes were formed from the Fischer carbene complex  $\text{Cr}(\text{CO})_5=\text{C}(\text{OEt})\text{Me}$  and aza-enynes (Scheme 53). The photochemical reaction of optically active chromium aminocarbenes with functionalized imines provided precursors to optically active 1-carbacephalothin (Scheme 54) [123].

Chromium carbene dienyl complexes reacted with isonitriles to yield aminobenzannulation products (Scheme 55) [124]. It is believed that metathesis of the carbene with isonitrile first generated a dienylketenimine which then underwent electrocycloolization and tautomerization.

Low-temperature photochemical decarbonylation of  $\text{M}(\text{CO})_5(o\text{-alkynylarylcarbene})$  ( $\text{M} = \text{Cr}, \text{W}$ ) afforded for the first time the  $\text{M}(\text{CO})_4(\text{alkynecarbene})$  complexes which were stabilized towards intramolecular carbene annelation [125]. By contrast, thermal decarbonylation of the precursor at  $55^\circ\text{C}$  yielded after oxida-



Scheme 53.

tive demetallation a chrysenes derivative, a product of an intermolecular process (Scheme 56).

Tandem benzannulation/aromatic nucleophilic addition was achieved by generating the  $(\text{phenol})\text{Cr}(\text{CO})_3$  intermediates from the respective chromiumcarbenes in the presence of silyl triflate and 2,6-lutidine [126]. These silylated phenol complexes were isolable and subsequent nucleophilic aromatic substitution led to spirocyclic and fused bicyclic products.

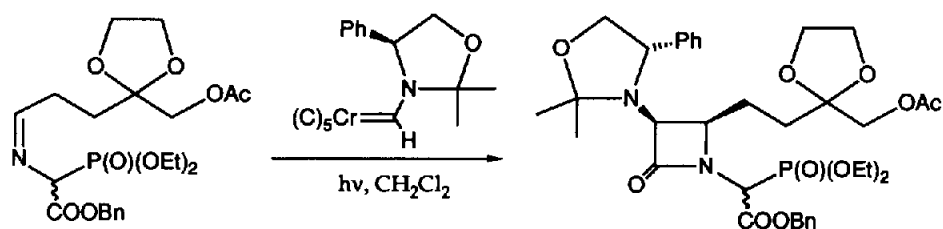
A variety of cyclopropylcarbene-chromium complexes have been examined for their reactivity with alkynes in  $[4 + 2 + 1 - 2]$  cycloadditions [127]. It was found that the reaction was general for simple alkynes to yield cyclopentenones. The proposed mechanism involved metallacyclobutene formation, electrocyclic ring opening and closure, CO insertion, alkene insertion, metallacyclopentene fragmentation, and cyclopentadienone reduction (Scheme 57).

The first intermolecular Diels-Alder reactions of tungsten aminocarbene complexes were achieved [128]. For example, only the *E* isomer of [*trans*-propenyl-(methylamino)methylene] $\text{W}(\text{CO})_5$  will react with 1-methoxy-1,3-butadiene or Danishefsky's diene. All reactions were selective for the *exo*-cycloadduct (Scheme 58). An even more reactive complex was obtained by CO extrusion from [*trans*-propenyl(*N*-methyl-*N*-benzoylamino)methylene] $\text{W}(\text{CO})_5$ .

Addition of nucleophiles (alcohols, thiols, phosphines) to Cr or W alkynylalkoxy carbene complexes was studied [129]. Smaller nucleophiles were found to attack regioselectively at the  $\beta$ -carbene position. Bulkier ones reacted much more slowly although catalytic amounts of DBU speeded up the reaction and improved the *E/Z* ratio.

Photoinduced CO loss from  $[(2\text{-}N,N'\text{-dimethylamino)anilino}(4\text{-methylphenyl)carbene}]\text{Cr}(\text{CO})_5$  led to complexes with 6-membered chelate rings [130]. These reacted with internal alkynes to yield either (iminoindane-*N,N*) $\text{Cr}(\text{CO})_4$  or (iminoindane) and (aminoindane) $\text{Cr}(\text{CO})_3$  complexes, depending on the solvents used. Demetallation under CO yielded iminoindanes and aminoindanes (Scheme 59). By contrast, terminal alkynes afforded [azabutadiene(*N,N*)] $\text{Cr}(\text{CO})_4$  chelate complexes.

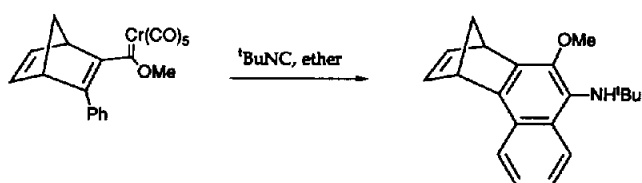
Photolysis of Cr amino(aryl)carbene complexes with the optically active (1*R*,2*S*)-(–)- or (1*S*,2*R*)-(+)–2-



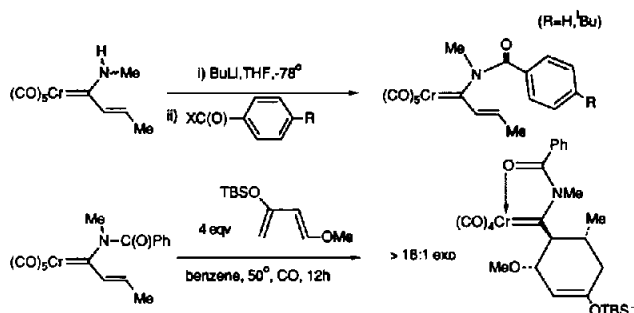
Scheme 54.

amino-1,2-diphenylethanol as the amino group produced aryl-substituted oxazinones with good diastereoselectivity (Scheme 60) [131]. Optically active arylglycines were accessible from these products.

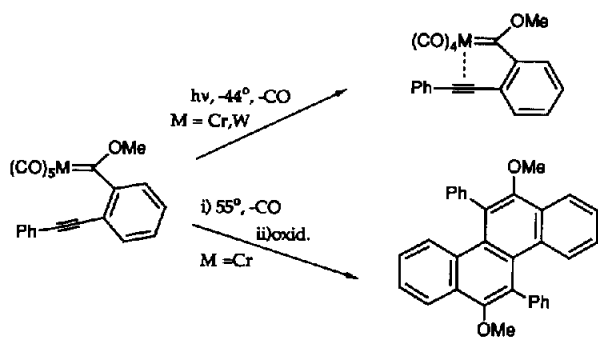
The first metal carbene complexes of carbohydrate derivatives were prepared by addition of the sugars regioselectively at C-3 of the alkynylcarbene complexes  $M(CO)_5=C(OEt)-CCPh$  ( $M = Cr, W$ ) to give



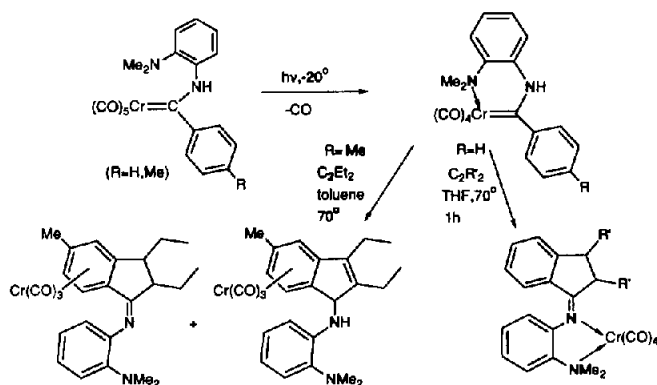
Scheme 55.



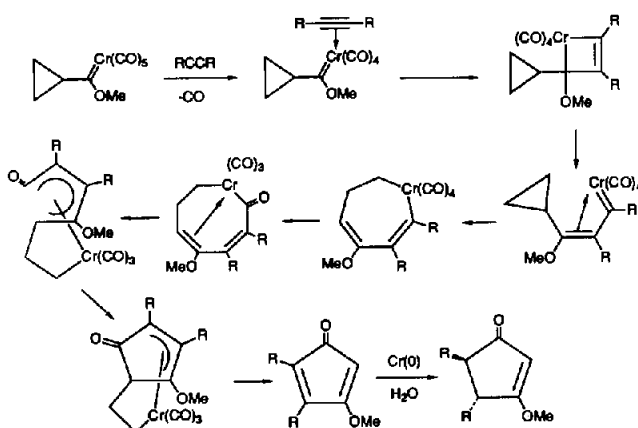
Scheme 58.



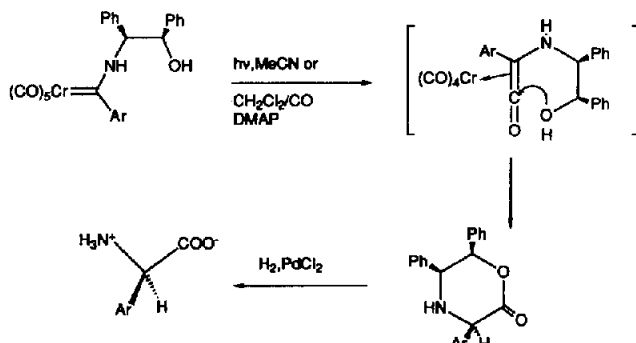
Scheme 56.



Scheme 59.



Scheme 57.

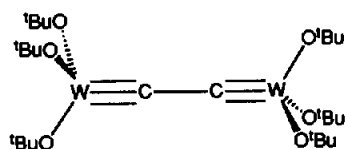


Scheme 60.

vinylcarbene products of the type  $M(\text{CO})_5=\text{C}(\text{OEt})-\text{CH}=\text{C}(\text{Ph})-\text{O}-(\text{sugar})$  [132].

## 6. Alkylidyne and alkyne complexes

The molecular structure of  $(^t\text{BuO})_3\text{W}\equiv\text{C}-\text{C}\equiv\text{W}(\text{O}^t\text{Bu})_3$  revealed that the two W moieties were arranged in the staggered conformation with a C-C distance of 1.34(3) Å and  $\text{W}\equiv\text{C}$  of 1.819(16) Å (45) [133]. Cyclic voltammetry showed two irreversible oxidations. Fenske-Hall calculations indicated that the C-C ligand was simultaneously a strong  $\pi$ -donor and acceptor.

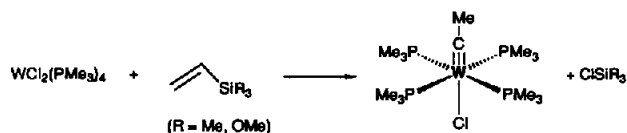


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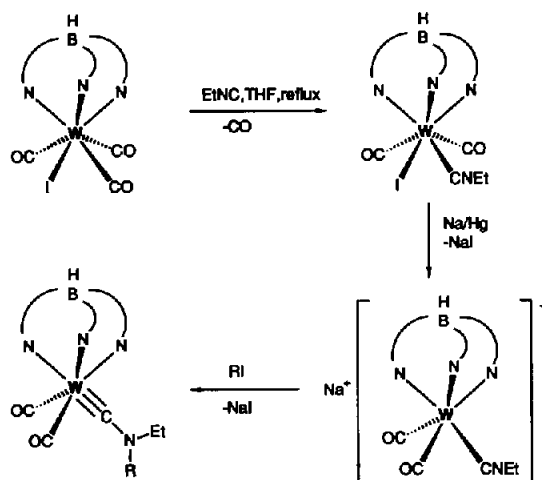
The vinylsilanes  $\text{CH}_2=\text{CHSi}(\text{OMe})_3$  or  $\text{CH}_2=\text{CHSiMe}_3$  reacted with  $\text{WCl}_2(\text{PMe}_3)_4$  to give the methylcarbyne complex  $\text{W}(\equiv\text{CMe})(\text{PMe}_3)_4\text{Cl}$  with the formal transformation of a  $\text{CH}_2=\text{CH}-$  group into a  $\text{MeC}\equiv$  group (Scheme 61) [134]. Labeling studies revealed that the reaction occurred by transfer of the methyne H to the methylene. The driving force was thought to be the formation of a very strong  $\text{W}\equiv\text{C}$  bond.

Starting from  $\text{Tp}'\text{W}(\text{CO})_3$ , thermal substitution of CO by EtNC gave  $\text{Tp}'\text{W}(\text{CO})_2(\text{CNEt})$ . This was reduced with Na(Hg) to give  $\text{Na}[\text{Tp}'\text{W}(\text{CO})_2(\text{CNEt})]$  which could be alkylated with RI (R = Me, Et) exclusively at the isocyanide N to give aminocarbyne complexes  $\text{Tp}'(\text{CO})_2\text{W}\equiv\text{CN}(\text{R})\text{Et}$  (Scheme 62) [135]. By contrast, alkylation of  $\text{Na}[\text{CpW}(\text{CO})_2(\text{CNEt})]$  occurred at the metal center to give *cis/trans*- $\text{CpW}(\text{CO})_2\text{R}(\text{CNEt})$ . This different reactivity was ascribed to the steric demands of the  $\text{Tp}'$  ligand which shielded the metal from electrophiles.

A successful optical resolution of a chiral tungsten alkyne complex was reported [136]. First, displacement of CO from  $[\text{Tp}'\text{W}(\text{CO})_2(\text{PhC}\equiv\text{CMe})]\text{X}$  (X =  $\text{PF}_6$ ,  $\text{BF}_4$ , OTf) by the counterion was effected by refluxing in THF. Substitution of the triflate by (*S*)-(-)- $\alpha$ -methylbenzylamine yielded a pair of amido diastereomers which were separable by recrystallization to (*RS*) and (*SS*)- $\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CMe})\text{NHR}^*$ . Protonation of these afforded optically pure (*RS*)- and (*SS*)-cationic



Scheme 61.

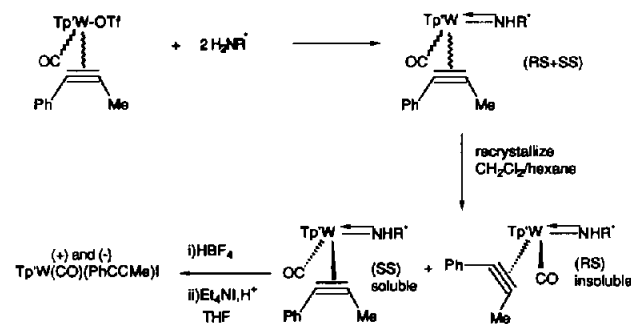


Scheme 62.

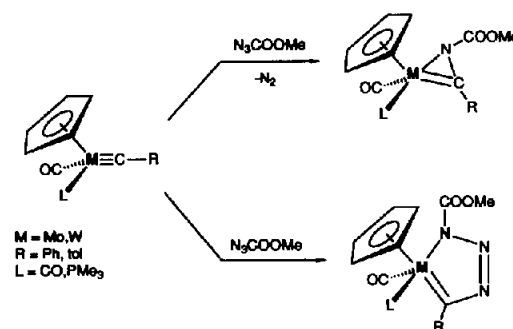
amine complexes respectively. Substitution of the chiral amine by iodide yielded optically pure (+) and (-)- $\text{Tp}'\text{W}(\text{CO})(\text{PhC}\equiv\text{CMe})\text{I}$  (Scheme 63).

The electron-rich  $\text{M}\equiv\text{C}$  in  $\text{CpM}(\text{CO})_{2-n}(\text{PMe}_3)_n(\text{CR})$  (M = Mo, W; R = Ph, tol; n = 0, 1) was attacked by  $\text{N}_3\text{COOMe}$  to give neutral 3*H*-1,2,3,4-triazametallolene complexes (Scheme 64) [137].

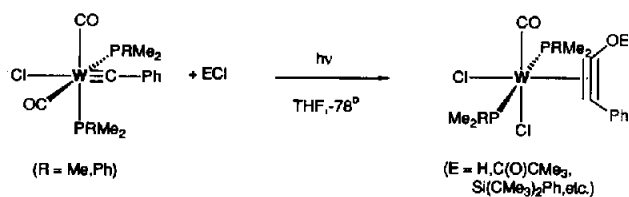
Irradiation of the alkylidyne complex  $\text{W}(\equiv\text{CPh})(\text{CO})_2\text{Cl}(\text{PMe}_2\text{R})_2$  (R = Me, Ph) in the presence of electrophiles ECl (E = H,  $^t\text{BuCO}$ , *p*-tol-CO,  $\text{Si}(^t\text{Bu})_2-$



Scheme 63.



Scheme 64.



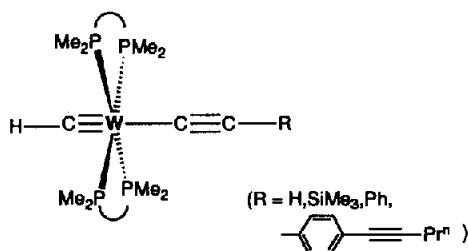
Scheme 65.

Ph) led to alkylidyne-carbonyl coupling to form *trans*-W(CO)Cl<sub>2</sub>(EOC≡CPh)(PMe<sub>2</sub>R)<sub>2</sub> (Scheme 65) [138].

Reaction of the alkylidyne complexes [W(CR)Br(CO)<sub>3</sub>L] (L = CO, phosphine; R = *p*-C<sub>6</sub>H<sub>4</sub>OMe, *p*-C<sub>6</sub>H<sub>4</sub>NMe<sub>2</sub>) with MeLi in THF at -78°C yielded alkylidyne acyl complexes Li[W(CR)(COMe)Br(CO)<sub>2</sub>L] which further reacted with (COBr)<sub>2</sub> and PPh<sub>3</sub> to give WBr<sub>2</sub>(CO)(MeC≡CR)(PPh<sub>3</sub>)<sub>2</sub> in a formal alkylidene coupling (Scheme 66) [139].

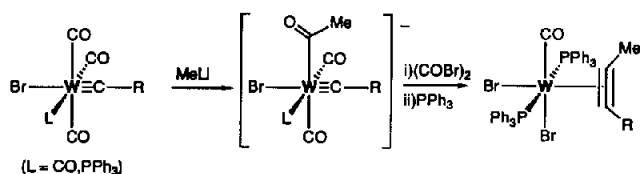
Treatment of MoH<sub>3</sub>(C≡C<sup>t</sup>Bu)(dppe)<sub>2</sub> with [Et<sub>2</sub>OH]BF<sub>4</sub> afforded *trans*-MoF(≡CCH<sub>2</sub><sup>t</sup>Bu)(dppe)<sub>2</sub>, the first example of a stable paramagnetic alkylidyne complex [140].

Alkynyl-methylidyne tungsten complexes were accessible from the reaction of alkynyllithiums with W(CH)(dmpe)<sub>2</sub>(O<sub>3</sub>SCF<sub>3</sub>) to give W(≡CH)(dmpe)<sub>2</sub>(C≡CR) (R = H, SiMe<sub>3</sub>, Ph, *p*-C<sub>6</sub>H<sub>4</sub>CCPr) [141]. Both structural and NMR data were consistent with the formulation of these as π-conjugated metallabutadiynes (46).



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The tungsten carbyne W(≡CMe)Cl(PMe<sub>3</sub>)<sub>4</sub> was carbonylated to give W(≡CMe)Cl(PMe<sub>3</sub>)<sub>3</sub>CO first and then W[OC(PMe<sub>3</sub>)=CMeC(O)]Cl(CO)<sub>2</sub>(PMe<sub>3</sub>)<sub>2</sub> which was shown to contain a 7-coordinate W<sup>II</sup> center bonded to in an unusual metallacyclopentene ring *via* an enolate oxygen and an acyl carbon (Scheme 67) [142]. The carbyne starting complex also displayed acetylene



Scheme 66.

metathesis activity in its reaction with C<sub>2</sub>Ph<sub>2</sub> to give W(CPh)Cl(PhC≡CMe)(PMe<sub>3</sub>)<sub>2</sub>.

Deprotonation of CpMo≡CR(CO)P(OMe)<sub>3</sub> (R = Me, cyclopropyl) with BuLi generated anionic vinylidene species that underwent electrophilic attack at the β-C [143]. Quenching of the cyclopropylidene complexes with acid chlorides yielded acylcyclopropyl carbyne complexes CpMo(CO)P(OMe)<sub>3</sub>≡C{C(O)RCH<sub>2</sub>CH<sub>2</sub>}. Nucleophilic ring opening of these by chloride yielded oxymetallacycles Cp(CO)P(OMe)<sub>3</sub>Mo{CH=C(CH<sub>2</sub>CH<sub>2</sub>Cl)C(O)R} (Scheme 68) while photooxidation of the cyclopropyl carbynes led to ring expansion and carbonylation to give 3-acylcyclopentenones.

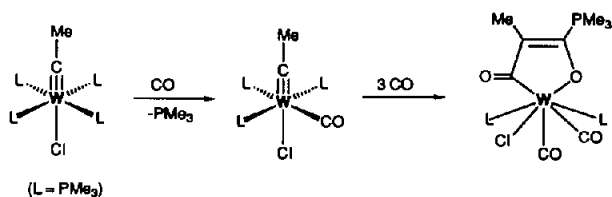
Reaction of W(≡CPh)Cl(CO)<sub>2</sub>py<sub>2</sub> with CN<sup>t</sup>Bu gave W(≡CPh)Cl(CN<sup>t</sup>Bu)<sub>2</sub>(CO)<sub>2</sub> [144]. Subsequent reaction with pyrrole-2-carboxaldehyde methylimine in the presence of KOH gave the ketenyl complex K[W(C<sub>6</sub>H<sub>7</sub>N<sub>2</sub>)<sub>2</sub>(PhCCO)(CO)] (Scheme 69). A similar preference for nucleophile-induced carbonyl/alkylidyne over isocyanide/alkylidyne coupling was observed in the reaction of NaS<sub>2</sub>CNEt<sub>2</sub> with W(CPh)I(CN<sup>t</sup>Bu)<sub>2</sub>(CO)<sub>2</sub> to give Na[W(PhCCO)(S<sub>2</sub>CNEt<sub>2</sub>)<sub>2</sub>(CO)].

Analysis of the C-13 NMR data of (arene)Cr(CO)<sub>3</sub> complexes of phenylacetylene and phenyl(trimethylsilyl)acetylene suggested a direct interaction between the metal and the ethynyl π-system [145]. NMR and IR spectral data confirmed the overall electron withdrawing effect of metal complexation.

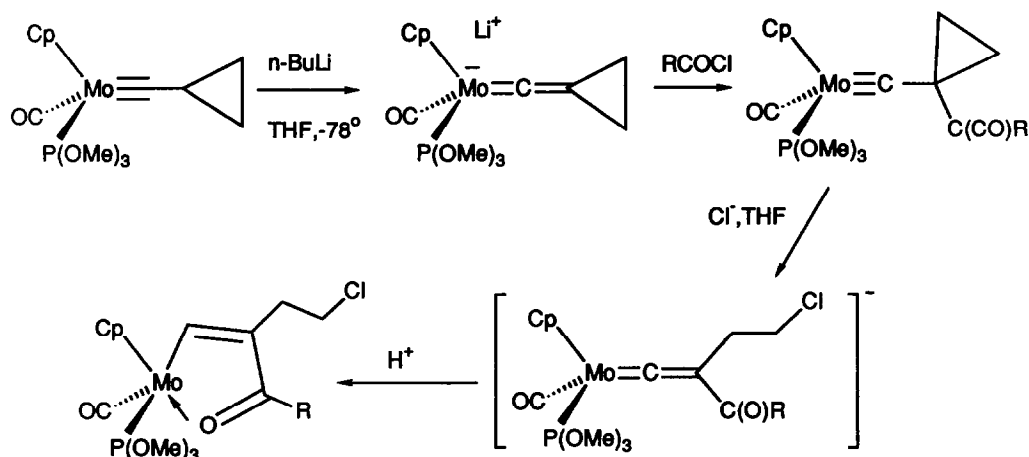
Reactions of RC≡CH (R = Ph, COOMe, COOEt) with *trans*-M(N<sub>2</sub>)<sub>2</sub>(dppe)<sub>2</sub> (M = Mo, W) and *trans*-Mo(N<sub>2</sub>)<sub>2</sub>(depe)<sub>2</sub> gave products including Mo(HC≡CPh)<sub>2</sub>(dppe)<sub>2</sub>, MH<sub>2</sub>(-C≡CR)<sub>2</sub>(diphosphine), and *trans*-M(-C≡CR)<sub>2</sub>(dppe)<sub>2</sub>, depending on the reaction conditions [146].

The alkyne complexes [WCl<sub>4</sub>(PhC≡CPh)]<sub>2</sub>, WCl<sub>3</sub>(PhC≡CPh)(L)<sub>2</sub>, and WCl<sub>2</sub>(PhC≡CPh)(L)<sub>3</sub> (L = phosphine) were related by their synthetic, structural, and spectroscopic properties as well as theoretical calculations to the organoimido complexes as *d*<sup>0</sup>, *d*<sup>1</sup>, and *d*<sup>2</sup> tungsten complexes respectively [147].

High yield syntheses of Mo<sup>II</sup> and W<sup>II</sup> bis(diethylamino)acetylene complexes have been reported [148]. Conversion of M(CO)<sub>6</sub> to M(CO)<sub>2</sub>(CNR)<sub>3</sub>Br<sub>2</sub> (R = Et, <sup>t</sup>Bu) followed by reaction with Et<sub>2</sub>NC≡CNEt<sub>2</sub> gave the ionic *mer*-[M(CO)Br(CNR)<sub>3</sub>(Et<sub>2</sub>NCCNEt<sub>2</sub>)]Br. This was thermally decarbonylated in the presence of RNC



Scheme 67.



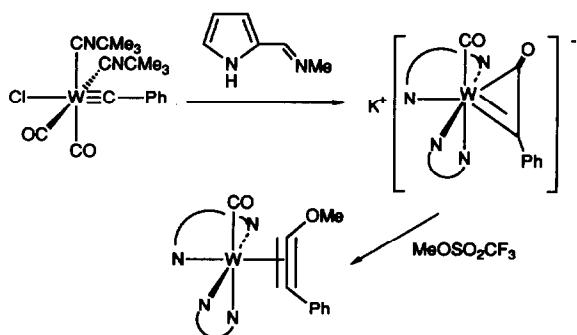
Scheme 68.

to *trans*-[MBr(CNR)<sub>4</sub>(Et<sub>2</sub>NCCNEt<sub>2</sub>)]Br. The same product was prepared *via* an alkyldiene-alkyldiene coupling reaction: diethylation of M(CNEt)<sub>6</sub> with [Et<sub>3</sub>O]BF<sub>4</sub> gave [(EtNC)<sub>4</sub>M(≡CNEt<sub>2</sub>)<sub>2</sub>](BF<sub>4</sub>)<sub>2</sub> which upon treatment with bromide underwent a carbyne-carbyne coupling to give the acetylene complex.

Gas phase electron-impact-induced loss of CO's from (1,2-dioxocyclobutabenzene)Cr(CO)<sub>3</sub> in the gas phase generated the benzyne complex C<sub>6</sub>H<sub>4</sub>-Cr<sup>+</sup> [149]. Its reactions with various species including MeOH, ammonia, alkanes, aromatics, etc. were studied using FT-ICR spectrometry. Results indicated release of Cr<sup>+</sup> in most cases due to the highly exothermic reactions exclusively at benzyne.

Treatment of diynes like *E*-1,6-bis(trimethylsilyl)hexa-1,5-diyne-3-ene with [CpMo(CO)<sub>2</sub>]<sub>2</sub> yielded mono and bis-Cp<sub>2</sub>Mo(CO)<sub>4</sub> complexes of the linear conjugated diynes [150].

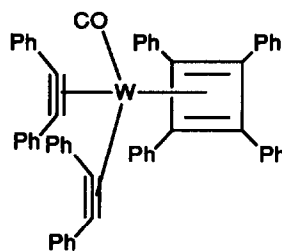
Active magnesium and Cp\*CrCl<sub>2</sub> and 2-butyne afforded Cr<sub>2</sub>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>4</sub>Me<sub>4</sub>) and Cr<sub>2</sub>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>6</sub>Me<sub>6</sub>) whose structures featured fly-over ligands; a chromacyclopentadiene and a cycloheptatriene respectively [151]. Use of MgH<sub>2</sub> instead of active magnesium gave related Cr(C<sub>5</sub>Me<sub>5</sub>)(C<sub>6</sub>Me<sub>6</sub>)H and Cr<sub>2</sub>(C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>(C<sub>4</sub>Me<sub>4</sub>)H species (Scheme 70). These results verified the



Scheme 69.

stepwise cyclotrimerization of an alkyne within metal coordination spheres.

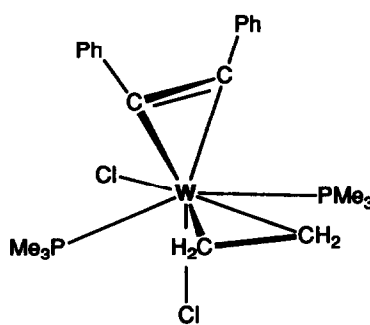
Reaction of molten diphenylacetylene with W(C<sub>2</sub>Ph<sub>2</sub>)<sub>3</sub>CO resulted in alkyne-alkyne coupling and the formation of W(η<sup>4</sup>-C<sub>4</sub>Ph<sub>4</sub>)(C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>(CO) (47) [152]. This was also formed by carbonylation of the product of the reaction between W(C<sub>2</sub>Ph<sub>2</sub>)(MeCN) with diphenylacetylene, W(η<sup>4</sup>-C<sub>4</sub>Ph<sub>4</sub>)(C<sub>2</sub>Ph<sub>2</sub>)(MeCN).



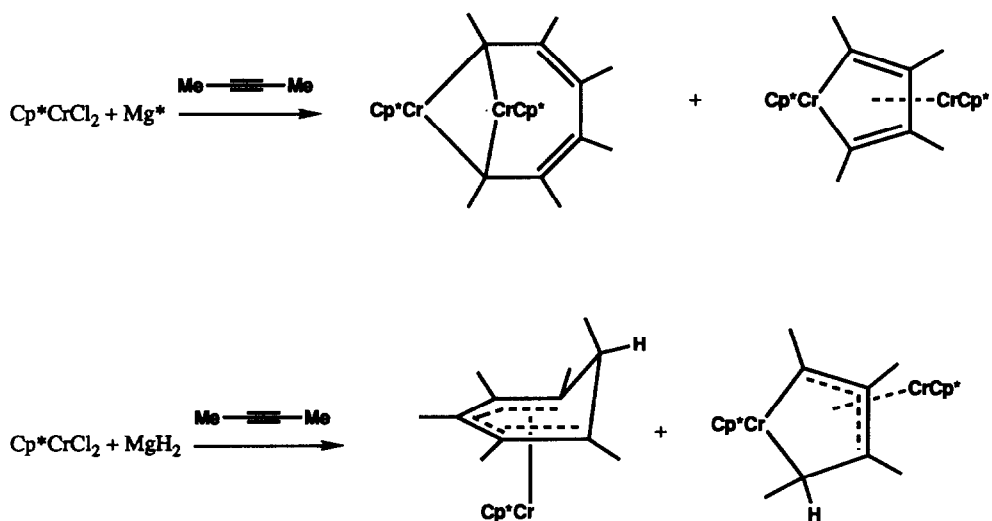
47

Treatment of W(C<sub>2</sub>Ph<sub>2</sub>)<sub>2</sub>CO with Me<sub>3</sub>NO in acetonitrile gave W(C<sub>2</sub>Ph<sub>2</sub>)MeCN from which the MeCN was readily substituted by phosphines [153].

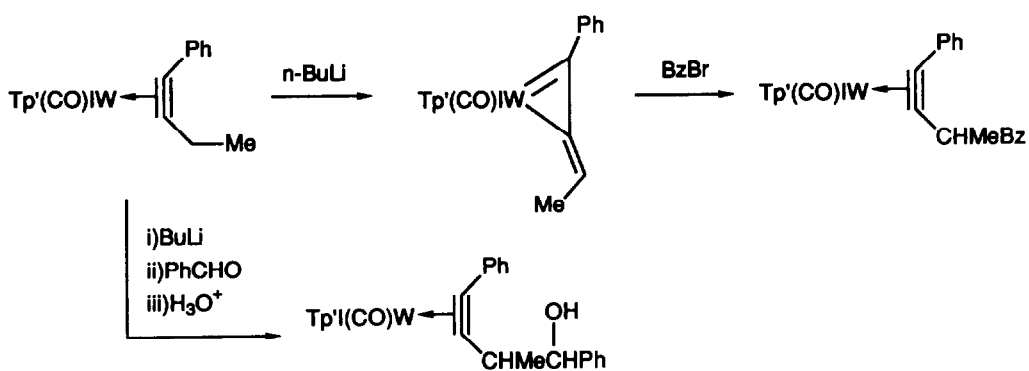
Deprotonation of the alkyne methyl group in Tp'W(CO)I(PhC≡CCH<sub>2</sub>Me) (Tp'=hydridotris(3,5-dimethylpyrazolyl)borate) produced a nucleophilic



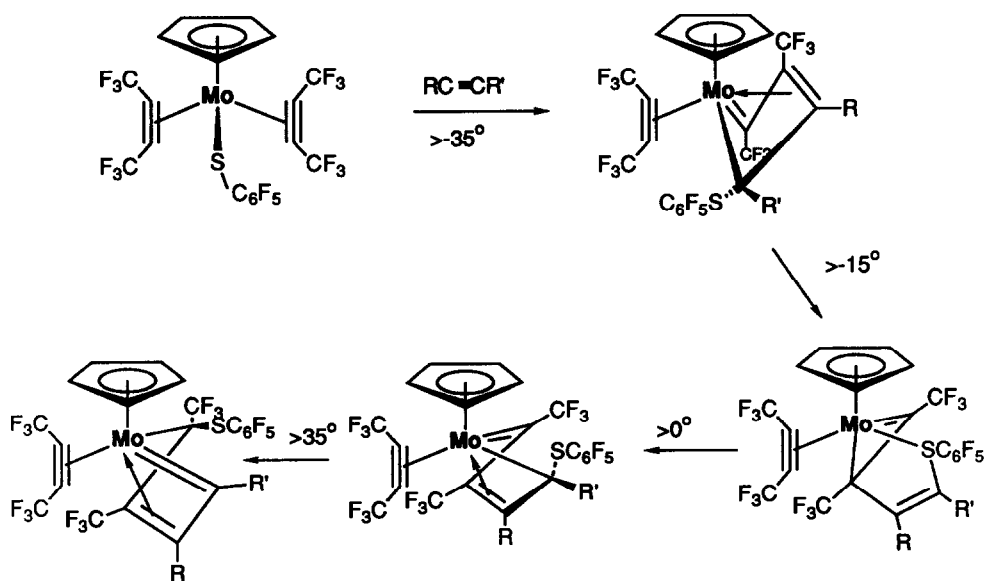
48



Scheme 70



Scheme 71.



Scheme 72.

propargyl synthon (Scheme 71) [154]. With MeI or PhCH<sub>2</sub>Br this yielded an elaborated alkyne without the propargyl/allenyl regiochemical control problem. The two diastereomers of Tp\*W(CO)I[PhC≡CCH(Me)-Bz] were also selectively prepared. Pivaldehyde or benzaldehyde added to Li[Tp\*W(CO)I(PhC≡CCHMe)] to give alcohol products.

Phosphine substitution at WCl<sub>2</sub>(PhC≡CPh)(PMe<sub>3</sub>)<sub>3</sub> by alkynes or reduction of WCl<sub>3</sub>(PhC≡CPh)(PMe<sub>3</sub>)<sub>2</sub> in the presence of alkynes yielded mixed bis-alkyne complexes which could also be reduced by ethylene or propene to give mixed alkyne-alkene complexes (48) [155].

The complexes WI<sub>2</sub>(CO)(MeCN)(RC≡CR)<sub>2</sub> (R = Me, Ph) reacted with 1 to 5 equivalents of <sup>t</sup>BuNC to give WI<sub>2</sub>(CO)(CN<sup>t</sup>Bu)(RC≡CR), WI<sub>2</sub>(CO)(CN<sup>t</sup>Bu)<sub>2</sub>(RC≡CR), WI<sub>2</sub>(CN<sup>t</sup>Bu)<sub>3</sub>(RC≡CR), [WI(CN<sup>t</sup>Bu)<sub>4</sub>(RC≡CR)]I, and [W(CN<sup>t</sup>Bu)<sub>5</sub>(RC≡CR)]I<sub>2</sub> respectively [156].

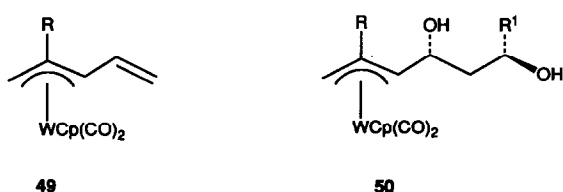
Treatment of CpMo(CO)<sub>2</sub>(μ-HOCH<sub>2</sub>C≡CCH<sub>2</sub>OH)-Co(CO)<sub>3</sub> and Cp<sub>2</sub>Mo<sub>2</sub>(CO)<sub>4</sub>(μ-HOCH<sub>2</sub>C≡CCH<sub>2</sub>OH) with EtSH gave the corresponding dimetallic thioalkyne complexes [157].

Reactions of CpMo(SC<sub>6</sub>F<sub>5</sub>)(F<sub>3</sub>CC≡CCF<sub>3</sub>)<sub>2</sub> with alkynes RC≡CR' (R = R' = Me; R = H, R' = Me, Ph; R = Me, R' = COOMe) gave novel η<sup>4</sup>-butadienyl complexes CpMo{η<sup>4</sup>-C(CF<sub>3</sub>)C(CF<sub>3</sub>)=CRCR'}(SC<sub>6</sub>F<sub>5</sub>)(F<sub>3</sub>CC≡CCF<sub>3</sub>) [158]. These isomerized *via* η<sup>2</sup>-C,C vinyl intermediates to the supine isomer followed by a 1,4-thiolate migration to give supine-CpMo{η<sup>4</sup>-CR'CR=C(CF<sub>3</sub>)C(CF<sub>3</sub>)(SC<sub>6</sub>F<sub>5</sub>)}(CF<sub>3</sub>C≡CCF<sub>3</sub>) (Scheme 72). NMR studies revealed fast exchange between these species for the alkyne PhC≡CMe.

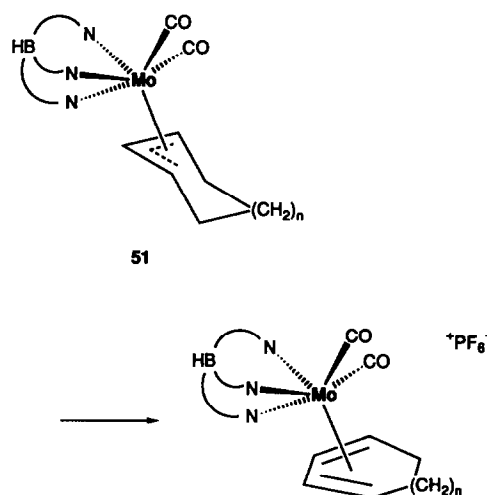
## 7. Allyl and polyene complexes

### 7.1. Allyl complexes

The CpW(CO)<sub>2</sub>(η<sup>3</sup>-2-R pentadienyl) complexes (49) were shown to undergo BF<sub>3</sub>-catalyzed stereoselective C-C bond formation with RCHO to give *s-trans*-diene complexes [159]. These hydrolyzed to CpW(CO)<sub>2</sub>η<sup>3</sup>-allyl-1,3-diols (50).



The molybdenum allyl complexes Tp\*Mo(CO)<sub>2</sub>(η<sup>3</sup>-crotyl), TpMo(CO)<sub>2</sub>(η<sup>3</sup>-cyclohexenyl), Tp\*Mo(CO)<sub>2</sub>(η<sup>3</sup>-cyclohexenyl), and TpMo(CO)<sub>2</sub>(η<sup>3</sup>-cycloheptenyl) were synthesized (51) [160]. The cyclic allyl complexes were treated with CPh<sub>3</sub>PF<sub>6</sub> to give cationic TpMo(CO)<sub>2</sub>(η<sup>4</sup>-cyclodiene)<sup>+</sup> products (Scheme 73). Nucle-



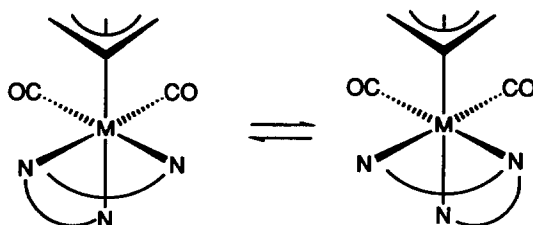
Scheme 73.

ophilic attacks on these were found to occur from the non-metal coordinated side.

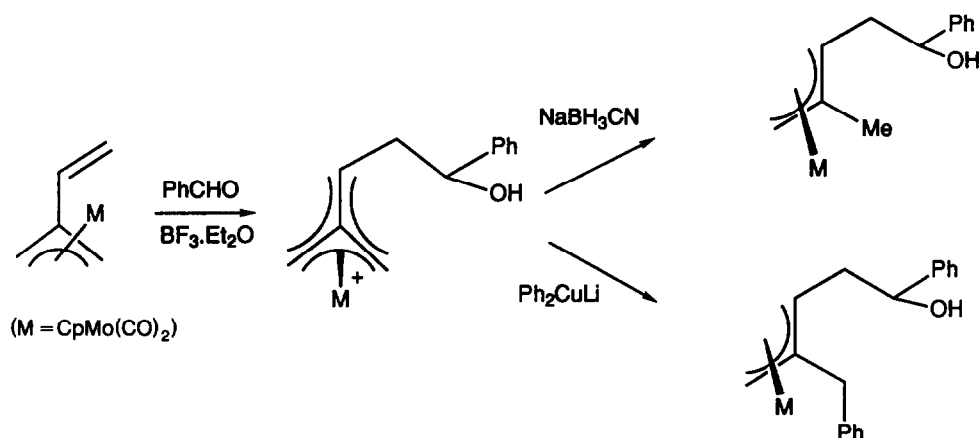
Cationic allyl complexes of the type W(CO)<sub>2</sub>(allyl)(L<sub>3</sub>)<sup>+</sup> (allyl = C<sub>3</sub>H<sub>5</sub> or 2-MeC<sub>3</sub>H<sub>4</sub>, L<sub>3</sub> = bis(2-pyridylmethyl)amine, bpma) and M(CO)<sub>2</sub>(allyl)(L<sub>4</sub>)<sup>+</sup> (M = Mo, W, allyl = C<sub>3</sub>H<sub>5</sub>, 2-MeC<sub>3</sub>H<sub>4</sub>, L<sub>4</sub> = tris(2-pyridylmethyl)amine, tpma) were prepared and their isomerism and dynamic behavior examined (Scheme 74) [161]. The Mo(CO)<sub>2</sub>(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(tpma)<sup>+</sup> complex underwent rapid exchange of the three N-donors at high temperatures in solution.

A novel cyclization was observed from the reaction of CpMo(CO)<sub>2</sub>(η<sup>3</sup>-vinylallyl) with TCNE to give a 6-membered ring [162]. A similar reaction with PhCHO/BF<sub>3</sub>·Et<sub>2</sub>O in benzene led to electrophilic addition of PhCHO to the vinyl group and the η<sup>4</sup>-trimethylenemethane Mo salt. This was subsequently reacted with NaBH<sub>3</sub>CN and R<sub>2</sub>CuLi (Scheme 75).

New η<sup>3</sup>-cyclooctenyl-Mo(CO)<sub>2</sub>Cp complexes were prepared and found to undergo clean hydroborations to give the endo-hydroxycyclooctenyl complex [163]. This was oxidized with H<sub>2</sub>O<sub>2</sub> under basic conditions to the oxocyclooctenyl complex. Subsequent nucleophilic attack proceeded anti to the Mo moiety and led to stereodefined tetrasubstituted cyclooctenes (Scheme 76).



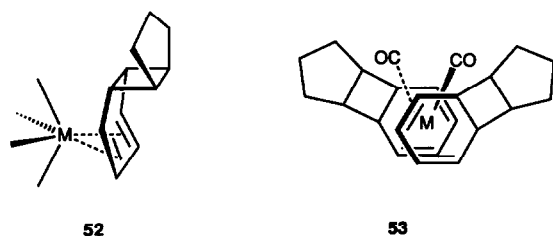
Scheme 74.



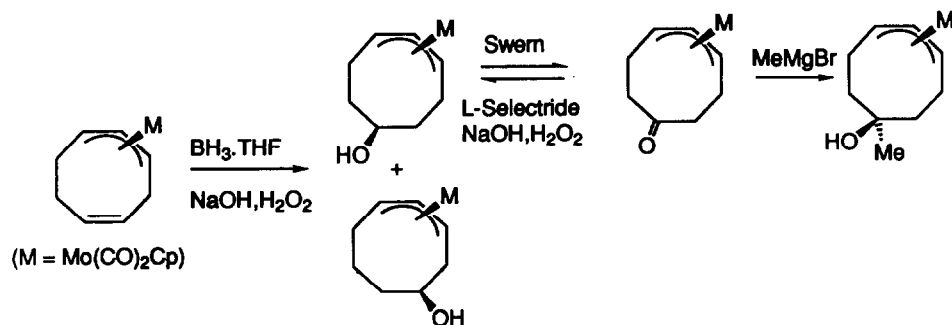
Scheme 75.

### 7.2. Dienyl complexes

Photolysis of M(CO)<sub>6</sub> (M = Cr, Mo, W) with tricyclo[6.3.0.0<sup>2,7</sup>]undeca-3,5-diene led initially to η<sup>4</sup>-tetracarbonyl complexes (52) [164,165]. The Mo and W complexes reacted further to give dicarbonyl complexes (53). The NMR spectra of both types of products were temperature-dependent, suggestive of hindered ligand movements.

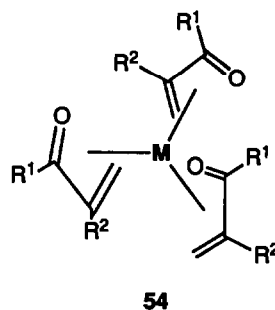


Highly functionalized zinc-copper reagents RCu(CN)ZnI were found to add to (η<sup>4</sup>-cyclohexadiene)Mo(CO)<sub>2</sub>Cp<sup>+</sup> at the terminus of the diene to give (π-allyl)Mo(CO)<sub>2</sub>Cp complexes [166]. Intramolecular cyclization of a pendant propanoic acid unit (R = (CH<sub>2</sub>)<sub>2</sub>COOH) generated the δ-lactone derivative (Scheme 77). Homoleptic tris(η<sup>4</sup>-1-oxa-1,3-diene) complexes of W and Mo were synthesized in 57–80% yield from α,β-unsaturated ketones and W(CO)<sub>3</sub>(pro-



Scheme 76.

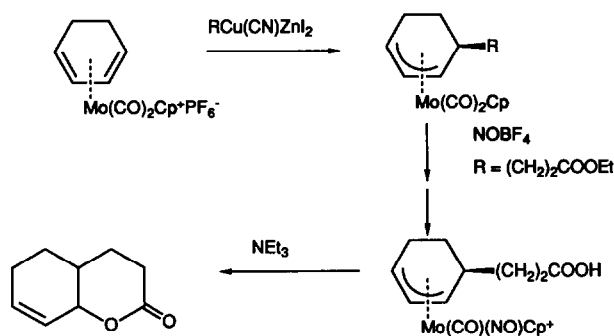
pionitrile)<sub>3</sub> (54) [167]. The products were shown by NMR to have C<sub>3</sub> symmetry.



Reaction of the anionic complexes (η<sup>4</sup>-C<sub>7</sub>H<sub>8</sub>)Mn(CO)<sub>3</sub><sup>-</sup>, (η<sup>4</sup>-C<sub>8</sub>H<sub>10</sub>)Mn(CO)<sub>3</sub><sup>-</sup>, and (η<sup>4</sup>-C<sub>8</sub>H<sub>8</sub>)Mn(CO)<sub>3</sub><sup>-</sup> with (η<sup>7</sup>-C<sub>7</sub>H<sub>7</sub>)M(CO)<sub>3</sub><sup>+</sup> (M = Cr, Mo, W) afforded hydrocarbon-bridged bimetallics of the types shown (Scheme 78) [168].

Treatment of the cationic Mo-diene complex TpMo(CO)<sub>2</sub>(η<sup>4</sup>-1,3-cyclohexadiene)<sup>+</sup> with single-electron donors like cobaltocene or Li naphthalenide led to the allylic complex TpMo(CO)<sub>2</sub>(η<sup>3</sup>-cyclohexenyl) [169]. By contrast, TpMo(CO)<sub>2</sub>(η<sup>4</sup>-cycloheptadiene)<sup>+</sup> gave both the allylic and 4,5-didehydro-η<sup>3</sup>-cycloheptenyl complexes. Tertiary amines or LDA gave similar reactions (Scheme 79).



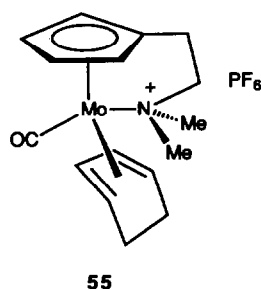


Scheme 77.

The reaction of  $\text{Li}[(\text{exo-C}_5\text{H}_4\text{-}\eta^5\text{-cyclohexadienyl)-Mn(CO)}_3]$  with  $\text{M(CO)}_3(\text{NCMe})_3$  ( $\text{M} = \text{Cr, Mo, W}$ ) and then  $\text{MeI}$  yielded  $(\text{CH}_3)\text{M(CO)}_3[\eta^5\text{-C}_5\text{H}_4\text{-(}\eta^5\text{-C}_6\text{H}_6\text{)Mn(CO)}_3]$  (Scheme 80) [170].

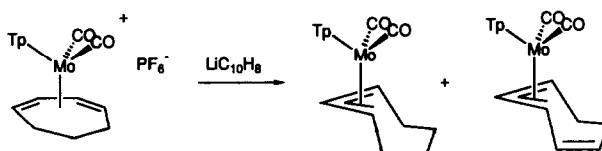
Tungsten diene complexes of the type  $\text{W(CO)}_2\text{-(dmpe)(}\eta^4\text{-diene)}$  where diene = 1,3-butadiene, *E*-1,3-pentadiene, *E,E*-2,4-hexadiene, and *E*-2-methyl-1,3-pentadiene were prepared and hindered ligand movements were demonstrated by NMR spectroscopy for the first and third diene complexes [171].

Hydride abstraction from  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{-NMe}_2)\text{Mo(CO)}_2(\eta^3\text{-C}_6\text{H}_9)$  followed by CO loss afforded a cationic dienyl complex whose structure contained the cyclohexadienyl ligand in a boat form (**55**) [172]. A demethylated product  $(\eta^5\text{-C}_5\text{H}_4\text{CH}_2\text{CH}_2\text{-N(H)Me})\text{Mo(CO)}_2(\eta^3\text{-C}_6\text{H}_9)^+$  was also isolated.



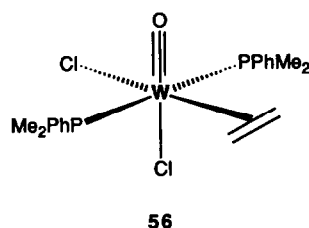
55

The tungsten(II) complex  $\text{WCl}_2(\text{PMe}_2\text{Ph})_4$  reacted with acetone and ethylene to yield a  $\text{W}^{\text{IV}}$ -oxo complex  $\text{W(O)(CH}_2=\text{CH}_2\text{)Cl}_2(\text{PMe}_2\text{Ph})_2$  and 3-methyl-1-butene (**56**) [173]. Similar reactions with other ketones



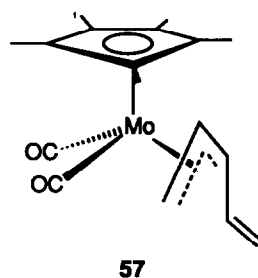
Scheme 79.

also yielded the same  $\text{W}^{\text{IV}}$ -oxo product. The suggested mechanism involved the coordination of both ketone and ethylene followed by coupling to form a 2-oxametallacyclopentane,  $\beta$ -H elimination to an allyloxy hydride, C-O cleavage to an oxo allyl hydride complex and reductive elimination of alkene.

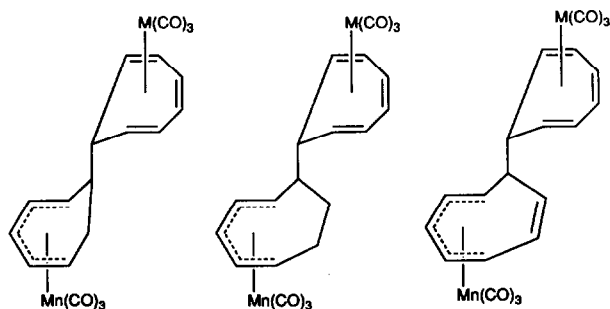


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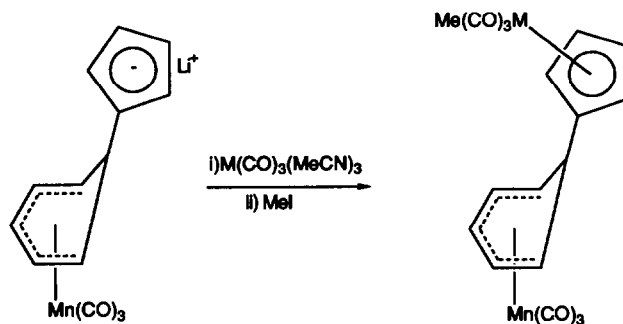
Deprotonation of  $\text{Cp}^*\text{Mo(CO)}_2(\eta^4\text{-butadiene})^+$  yielded the  $\text{Cp}^*\text{Mo(CO)}_2(\text{exo-2-1,2,3-}\eta\text{-trans-CH}_2\text{-CHC=CH}_2\text{)}$  complex with the adjacent allyl and  $\text{C=CH}_2$  groups orthogonal (**57**) [174]. The same product was obtained from the desilylation of  $\text{Cp}^*\text{Mo(CO)}_2(\eta^4\text{-CH}_2=\text{CH(SiEt}_3\text{)=CH}_2)^+$  by  $[\text{NBu}_4]\text{F}$ . Reaction of  $\text{Li}[\text{Cp}^*\text{Mo(CO)}_3]$  with  $\text{CH}_2=\text{C=C(Me)CH}_2\text{Cl}$  gave instead an unusual cyclized product  $\text{Cp}^*\text{Mo(CO)}_2(\eta^3\text{-CH}_2\text{CC(Me)CH}_2\text{CO})$  (Scheme 81). Protonation of complex **57** with  $\text{CF}_3\text{SO}_3\text{H}$  produced a vinylketene complex  $[\text{Cp}^*\text{Mo(CO)}_2(\eta^4\text{-CH}_2=\text{CHC(Me)=C=O})\text{]}\text{[SO}_3\text{CF}_3\text{]}$ .



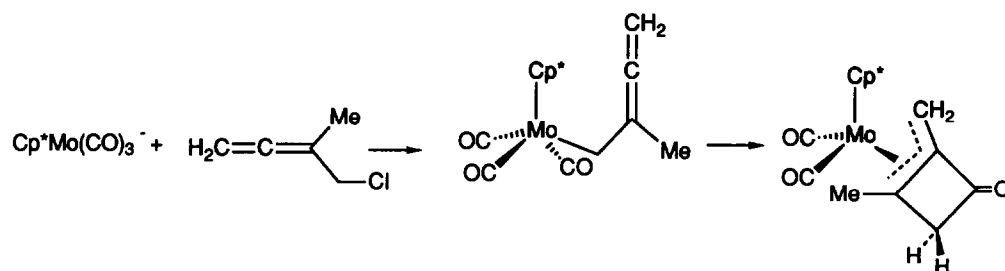
57



Scheme 78.



Scheme 80.

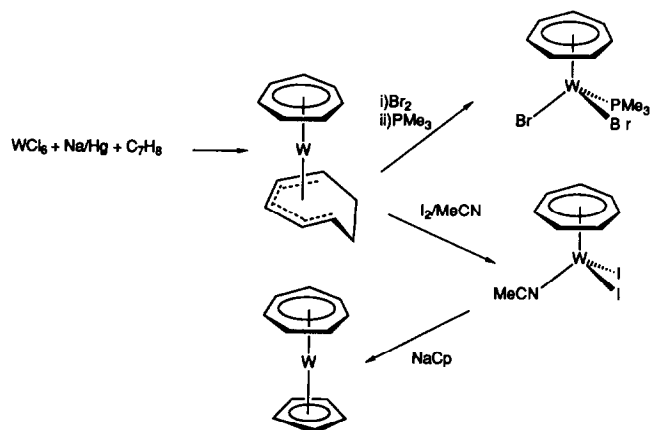


Scheme 81.

### 7.3. Trienyl complexes

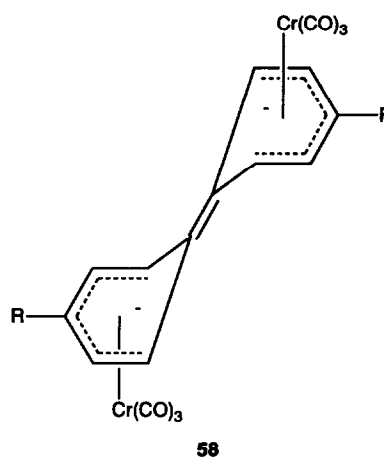
Reduction of  $\text{WCl}_6$  with  $\text{Na}/\text{Hg}$  in the presence of cycloheptatriene afforded  $(\eta\text{-C}_7\text{H}_7)\text{W}(\eta\text{-C}_7\text{H}_9)$  which was a convenient precursor to  $(\eta^5\text{-C}_7\text{H}_7)\text{W}$  complexes of phosphines, halides, hydride, and methyl (Scheme 82) [175].

Similarly, a one-pot reaction of  $\text{MoCl}_5$  with  $\text{Na}/\text{Hg}$  and cycloheptatriene afforded a 55% yield of the



Scheme 82.

$\text{Mo}(\eta^5\text{-C}_7\text{H}_7)(\eta\text{-C}_7\text{H}_9)$  complex [176]. This was shown to be an excellent precursor to half-sandwich complexes of the  $\text{Mo}(\eta\text{-C}_7\text{H}_7)$  type (Scheme 83).



Reaction of the  $(\eta^6:\eta^6\text{-biphenyl})\text{bis}(\text{tricarbonylchromium})$  dianion with primary electrophiles resulted exclusively in ipso additions (**58**) [177]. Results suggested an inner-sphere polar  $\text{S}_{\text{N}}2$  mechanism for most primary electrophiles but easily reduced or bulky halides may also involve electron-transfer pathways. Subsequent iodine oxidation of these 4,4'-substituted biphenyls provided entry into 2-alkyl-5,4'-disubstituted biphenyls.

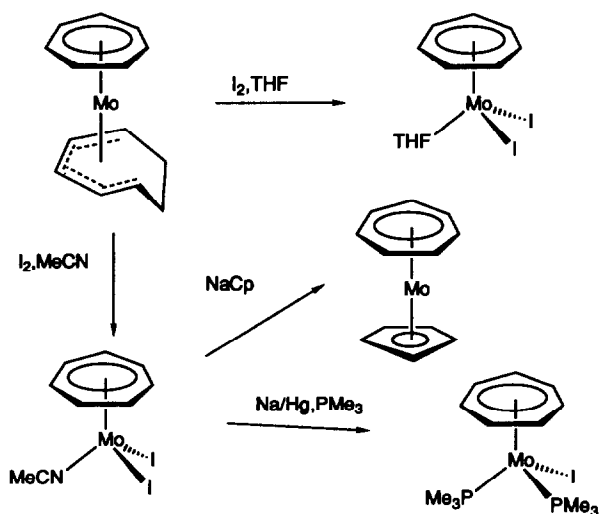
Chemical or electrochemical reduction of  $(\text{Cycloheptatrienyl})\text{Mo}(\text{C}_6\text{F}_5)(\text{CO})_2$  yielded an orange intermediate which reacted further with trimethylphosphite to displace the cycloheptatrienyl ligand to yield *cis-mer*- $\text{Mo}(\text{C}_6\text{F}_5)(\text{CO})_2[\text{P}(\text{OMe})_3]_3$  [178].

## 8. Cyclopentadienyl complexes

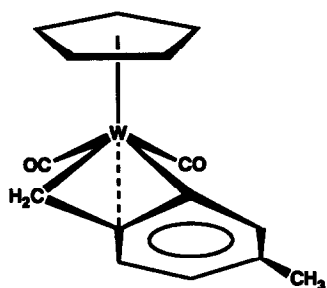
### 8.1. Structural chemistry

The structure of  $(p\text{-methylbenzyl})\text{WCp}$  contained an unusual  $\alpha, 1,2\text{-}\eta$  coordination mode for the *p*-methylbenzyl ligand (**59**) [179].

The structure of  $\text{CpMo}(\text{CO})_2\text{P}(\text{OPh})_3(\text{CH}_2\text{-PPh}_3)$  contained a piano-stool arrangement with apical cyclopentadienyl, two *trans* CO's, one basal phosphite

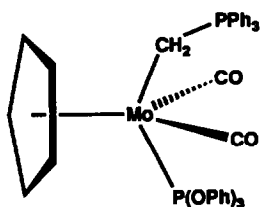


Scheme 83.



59

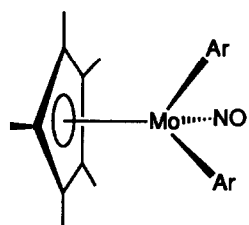
and a methylene phosphorane ligand (**60**) [180]. The Mo–C–P angle is 126.4(1)°.



60

Benzoylformyl complex of CpMo(CO)<sub>3</sub>(COCOPh) was prepared from CpMo(CO)<sub>3</sub><sup>-</sup> and PhCOCOCI [181]. Its structure contained a near perpendicular *s-trans* oxalyl moiety with the O–C–O torsional angle of 104(1)°.

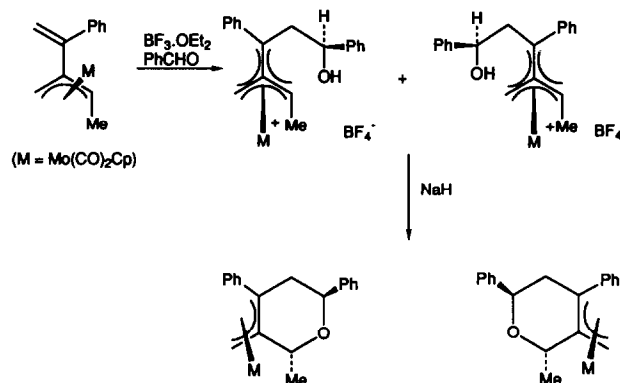
Treatment of Cp<sup>\*</sup>M(NO)Cl<sub>2</sub> (M = Mo, W) with diarylmagnesium yielded Cp<sup>\*</sup>M(NO)Ar<sub>2</sub> (Ar = Ph, *o*-tolyl, *p*-tolyl) [182]. These were found to have the three-legged piano-stool structure though the Ar–M–Ar angles were significantly larger than the ones found in dialkyl analogs (**61**). Electrochemistry, IR data and stable Lewis base adducts all provided evidence for their more electron-deficient metal centers.



61

### 8.2. Reaction chemistry

The strong base DBU deprotonated Cp(CO)(CF<sub>3</sub>COO)<sub>2</sub>W(η<sup>2</sup>-methylbenzylacyl) to give the anionic ketenyl complex Cp(CO)(CF<sub>3</sub>COO)<sub>2</sub>W(O=C=C(H)C<sub>6</sub>H<sub>4</sub>Me)<sup>-</sup> [183].



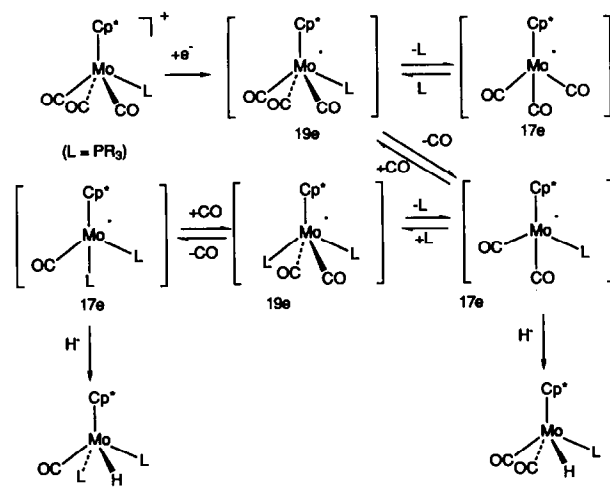
Scheme 84.

In the presence of BF<sub>3</sub>·Et<sub>2</sub>O, the allyl complex CpMo(CO)<sub>2</sub>(η<sup>3</sup>-*anti*-1-Me,2-(CH<sub>2</sub>=CPh)C<sub>3</sub>H<sub>3</sub>) reacted with benzaldehyde, Me vinyl ketone, and acetone to give the respective η<sup>4</sup>-trimethylenemethane cations. The crystal structure of a derived pyran complex is also reported (Scheme 84) [184].

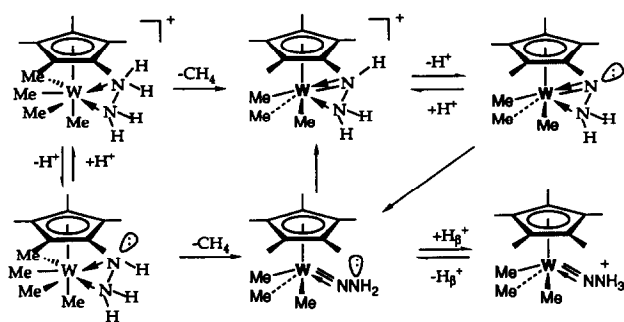
Thermal reactions of Cp<sup>\*</sup>Mo(CO)<sub>3</sub>H with phosphines and phosphites yielded Cp<sup>\*</sup>Mo(CO)<sub>2</sub>(PR<sub>3</sub>)H (R<sub>3</sub> = Me<sub>3</sub>, MePh<sub>2</sub>, Ph<sub>3</sub>, (OMe)<sub>3</sub>, (OPh)<sub>3</sub>) [185]. Reduction of [Cp<sup>\*</sup>Mo(CO)<sub>3</sub>PR<sub>3</sub>]PF<sub>6</sub> with LiAlH<sub>4</sub> in the presence of PR<sub>3</sub> gave Cp<sup>\*</sup>Mo(CO)(PR<sub>3</sub>)<sub>2</sub>H via electron transfer and subsequent CO exchange of a 17-electron species (Scheme 85).

The complexes CpW(CO)<sub>3</sub>(η<sup>1</sup>-C=CR–CHR'–O–CH<sub>2</sub>) were prepared and their acid-catalyzed rearrangements and demetallation reported [186].

The aryl bromides 1,4-C<sub>6</sub>H<sub>4</sub>Br<sub>2</sub>, 2,6-C<sub>5</sub>NH<sub>3</sub>Br<sub>2</sub>, and 1,3,5-C<sub>6</sub>H<sub>3</sub>Br<sub>3</sub> were treated with Mg/SiMe<sub>2</sub>HCl to give their respective aryldimethylsilanes [187]. Halogenation of these with Cl<sub>2</sub> or Br<sub>2</sub> afforded the aryldimethylsilyl halides 1,4-C<sub>6</sub>H<sub>4</sub>(SiMe<sub>2</sub>Br)<sub>2</sub>, 2,6-C<sub>5</sub>NH<sub>3</sub>(SiMe<sub>2</sub>Br)<sub>2</sub>, 1,3,5-C<sub>6</sub>H<sub>3</sub>(SiMe<sub>2</sub>X)<sub>3</sub> in excellent



Scheme 85.



Scheme 86.

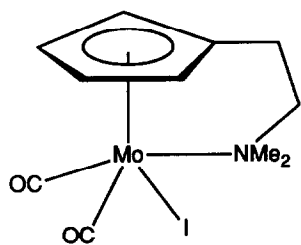
yields. These halides were then substituted by a variety of cyclopentadienides. Deprotonation with NaH and complexation with  $W(CO)_3(MeCN)_3$  and MeI led to the  $\eta^6$ -complexes  $1,4-C_6H_4(SiMe_2CpW(CO)_3Me)_2$  and  $1,3,5-C_6H_3(SiMe_2CpW(CO)_3Me)_3$ , for example.

Reaction of bistriflates  $(CH_2)_n(CF_3SO_3)_2$  ( $n = 5, 10$ ) with the metallate  $[CpM(CO)_3]^-$  ( $M = Mo, W$ ) led to the hydrocarbon-bridged  $M-(CH_2)_n-M$  complexes [188]. The action of  $SO_2$  resulted in the formation of  $CpMo(CO)_3SO_2(CH_2)_nO_2SMo(CO)_3Cp$ .

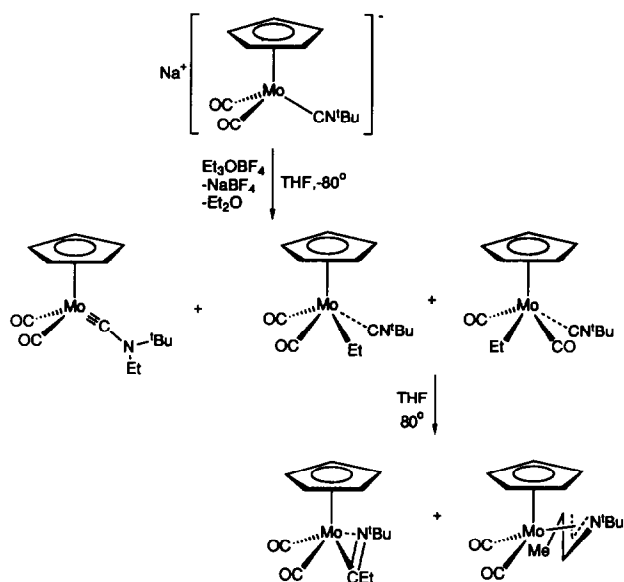
Addition of hydrazine derivatives to  $[Cp^*WMe_4]PF_6$  yielded 1:1 adducts which either decomposed to  $[Cp^*WMe_3(\eta^2\text{-hydrazido})]^+$  via methane loss or were readily deprotonated to give hydrazido(1-) complexes  $Cp^*WMe_4(\eta^2\text{-hydrazido})$  (Scheme 86) [189]. The conversion of these to  $Cp^*WMe_3(\eta^1\text{-hydrazido}(2-))$  derivatives was discussed as well as the proposal of the need for an  $\eta^2-N_2H_x$  intermediate towards ammonia synthesis.

Reactions of monosubstituted  $Cp^*Mo(CO)_3I$  ( $Cp^* = C_5H_4Me, C_5H_4CMe_3$ ) and (Indenyl) $Mo(CO)_3I$  with nucleophiles L ( $L = tBuNC, PPh_3, P(OPh)_3$ , etc.) resulted in substitution of a single CO in each case [190]. Their proton NMR spectra were discussed in terms of the L and  $Cp^*$  steric factors. The ratio of *cis/trans* isomers also increased with these factors.

Irradiation of  $(\eta^5-C_5H_4CH_2CH_2NMe_2)Mo(CO)_3I$  resulted in an intramolecular amino displacement of a CO ligand [191]. The resulting pseudo-square pyramidal structure was found to have the remaining CO's *cis* to each other (62).



62

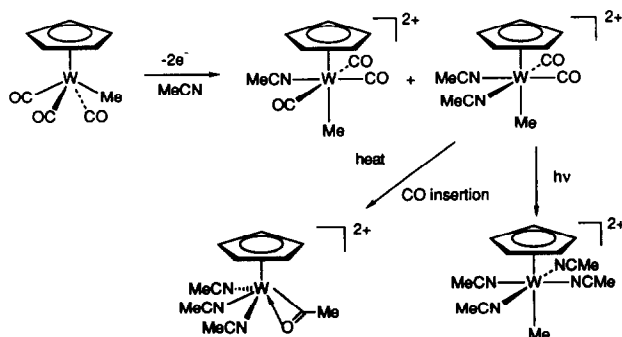


Scheme 87.

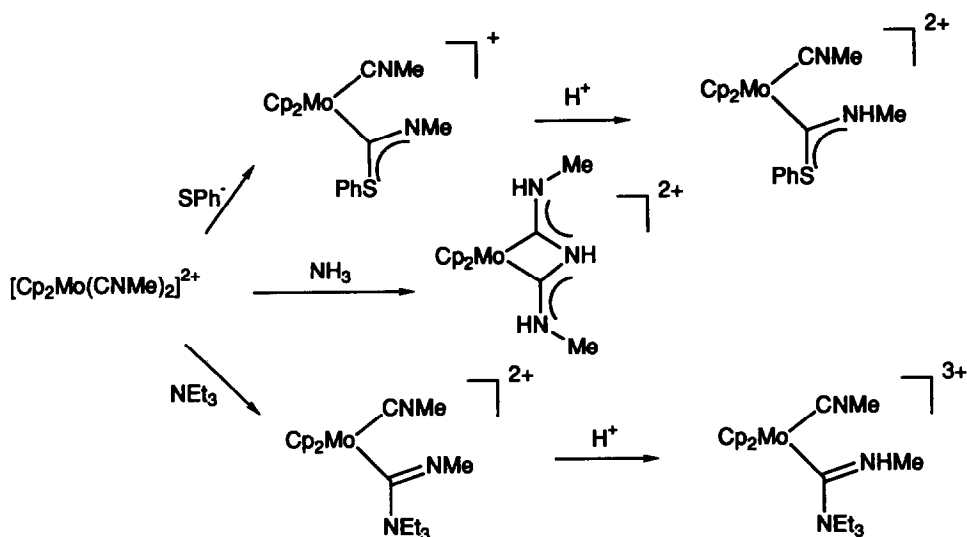
Reaction of *cis/trans*- $CpMo(CO)_2(CN^tBu)I$  with Na gave  $Na[CpMo(CO)_2(CN^tBu)]$  which can be alkylated by  $Et_3OBF_4$  at the metal center to yield two isomers of  $CpMo(CO)_2(CN^tBu)Et$  as well as at the isocyanide N to yield  $CpMo(CO)_2[=CN(Et)^tBu]$  [192]. Upon heating in THF, the former isomerized to a mixture of the iminoacyl complex  $CpMo(CO)_2(\eta^2\text{-EtC=N}^tBu)$  and 1-azaallyl complex  $CpMo(CO)_2(\eta^3\text{-CH(Me)CHN}^tBu)$  (Scheme 87).

Two-electron oxidation of  $CpW(CO)_3Me$  yielded a  $W^{IV}$  dication  $CpW(CO)_2(MeCN)_2Me^{2+}$  which can serve as a precursor to CO insertion and photolytic substitution reactions [193]. Thus  $CpW(MeCN)_3(\eta^2\text{-COMe})^{2+}$  and  $CpW(MeCN)_4Me^{2+}$  were obtained in acetonitrile (Scheme 88). Analogous CO insertion reactions were not observed for  $CpW(CO)_3(MeCN)Me^{2+}$  and  $CpW(CO)_3(MeCN)Et^{2+}$ .

In an unusual oxygen insertion into a  $C_5$  ring, air-oxidation of  $[Cp^*Mo(CO)_2]_2$  in chloroform gave  $[Cp^*O][Cp^*Mo_6O_{18}]$  (63) as well as other products [194]. The polymetallic anion has been shown to be a deriva-

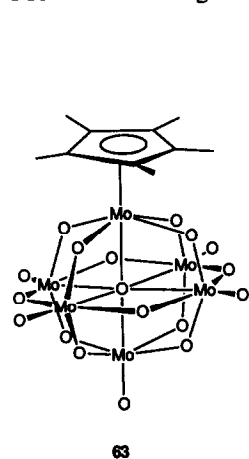


Scheme 88.

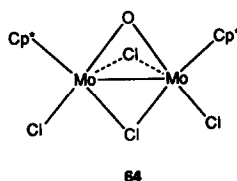


Scheme 89.

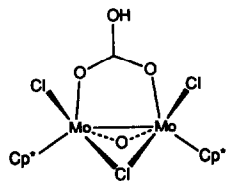
tive of the well-known  $[\text{Mo}(\text{O}(\mu\text{-O})_2)_6(\mu_6\text{-O})]^{2-}$ . By contrast, irradiation of  $[\text{Cp}^*\text{Mo}(\text{CO})_2]_2$  in air gave *syn*- $[\text{Cp}^*\text{MoCl}_2(\mu\text{-Cl})_2(\mu\text{-O})]$  and *syn*- $[\text{Cp}^*\text{MoCl}_2(\mu\text{-Cl})(\mu\text{-CO}_3\text{H})(\mu\text{-O})]$ . Though the structures of these two complexes contained Mo–Mo distances of 2.72 and 2.80 Å respectively (**64**, **65**), EHMO indicated little Mo–Mo bonding.



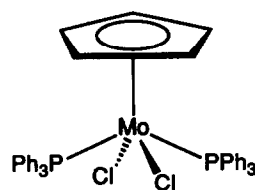
63



64

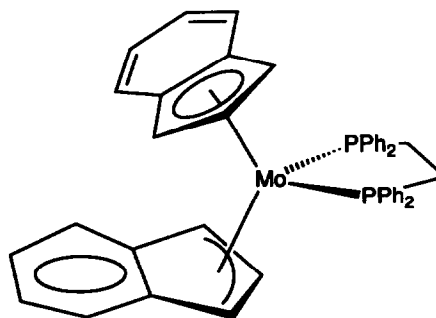


65



66

Interaction between  $\text{MoI}_3(\text{THF})(\text{dppe})$  and excess  $\text{Na}(\text{indenyl})$  produced  $(\eta\text{-C}_9\text{H}_7)_2\text{Mo}(\text{dppe})$  which was shown to have both  $\eta^5\text{-}$  and  $\eta^3\text{-indenyl}$  bonding (**67**) [197]. These rings were found to undergo rapid exchange in solution on the NMR timescale down to  $-90^\circ\text{C}$ .

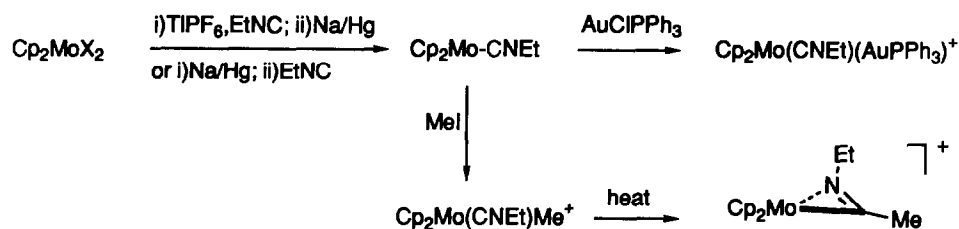


67

Low-temperature (12 K) photolysis of *cis* or *trans*- $\text{CpW}(\text{CO})_2(\text{L})\text{I}$  ( $\text{L} = \text{P}(\text{OMe})_3, \text{PPh}_3, \text{P}^n\text{Bu}_3$ ) resulted in CO loss and formation of distinctive intermediates which were solvated [195]. At 77 K, however, these isomerized and generated a mixture of the *cis* and *trans* precursors upon a thermal back reaction with CO.

Either the reaction of  $\text{CpMoCl}_2$  with phosphine or that of  $\text{MoCl}_3(\text{THF})_3$  with phosphine/ $\text{TiCp}$  led to the same 17-electron  $\text{CpMoCl}_2\text{L}_2$  ( $\text{L} = \text{PPh}_3, \text{PMePh}_2$ ) complexes [196]. Their four-legged piano stool structure was confirmed by X-ray studies (**66**). The complexes were also investigated by both X- and Q-band EPR spectroscopy.

Reaction of  $\text{Cp}_2\text{MoHI}$  with  $\text{Cp}_2\text{MX}_2$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ) led to cationic complexes  $[\text{Cp}_2\text{MoH}(\text{CNMe})\text{I}]$ ,  $[\text{Cp}_2\text{MoI}(\text{CNMe})\text{I}]$ ,  $[\text{Cp}_2\text{Mo}(\text{CNMe})_2]\text{X}_2$ , and  $[\text{Cp}_2\text{WBr}(\text{CNMe})]\text{Br}$  [198]. Borohydride attack on  $[\text{Cp}_2\text{Mo}(\text{CNMe})_2][\text{PF}_6]_2$  yielded  $[\text{CpMo}(\eta^4\text{-C}_5\text{H}_6)(\text{CNMe})_2][\text{PF}_6]$  while other nucleophiles ( $\text{OMe}^-$ ,  $\text{SPh}^-$ ,  $\text{NEt}_3$ ,  $\text{NH}_3$ ) added to the methylisocyanide to form Fischer carbene complexes such as  $[\text{Cp}_2\text{Mo}=\text{C}(\text{SPh})\text{N}(\text{H})\text{Me}(\text{CNMe})][\text{PF}_6]_2$  (Scheme 89).



Scheme 90.

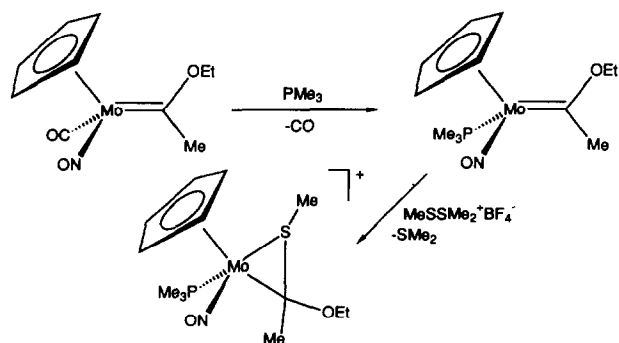
Reaction of EtNC with  $\text{Cp}_2\text{Mo}(\text{H})\text{I}$  produced  $[\text{Cp}_2\text{Mo}(\text{H})\text{CNEt}]\text{I}$  which can be converted to  $[\text{Cp}_2\text{Mo}(\text{CNEt})\text{I}]$  by MeI [199]. Treatment of  $\text{Cp}_2\text{MoX}_2$  ( $\text{X} = \text{Cl}, \text{I}$ ) with  $\text{TlPF}_6$  and  $\text{RNC}$  ( $\text{R} = \text{Et}, \text{tBu}$ ) gave the related  $[\text{CpMoX}(\text{CNR})]\text{PF}_6$  which can be reduced with  $\text{Na}(\text{Hg})$  to  $\text{Cp}_2\text{MoCNR}$ . These species behaved like analogs of ketene imines. The  $\text{Mo}^{\text{II}}$  ethylisocyanide product can be alkylated exclusively at the metal to form  $[\text{Cp}_2\text{Mo}(\text{R}')\text{CNR}]^+$  ( $\text{R}' = \text{Me}, \text{Et}$ ). It also reacted with  $\text{PPh}_3\text{AuCl}$  to give the bimetallic  $[\text{Cp}_2\text{Mo}(\text{AuPPh}_3)\text{CNEt}]\text{Cl}$  (Scheme 90). Heating of  $[\text{Cp}_2\text{Mo}(\text{R}')\text{CNR}]^+$  caused a clean isocyanide insertion to yield iminoacyl products; for example,  $[\text{Cp}_2\text{Mo}(\text{Et})\text{CNEt}]\text{BF}_4$  gave  $\text{Cp}_2\text{Mo}[\eta^2\text{-C}(\text{NEt})\text{Et}]\text{BF}_4$ .

Methoxyethyl complex  $\text{CpM}(\text{CO})_3(\text{CH}_2\text{CHR}\text{OMe})$  ( $\text{M} = \text{Mo}, \text{W}; \text{R} = \text{H}, \text{Me}$ ) readily inserted  $\text{SO}_2$  into their C–O bonds to form metallated sulfonic acid esters  $\text{CpM}(\text{CO})_3(\text{CH}_2\text{CHR}\text{SO}_2\text{OMe})$  [200]. Triphenylphosphine converted the Mo complex into an acyl derivative which was oxidized by  $\text{Ce}^{\text{IV}}$  to the diester  $\text{MeOC}(\text{O})\text{CH}_2\text{CHR}\text{SO}_2\text{OMe}$ .

### 8.3. Complexes with metal–C, N, O, and P multiple bonds

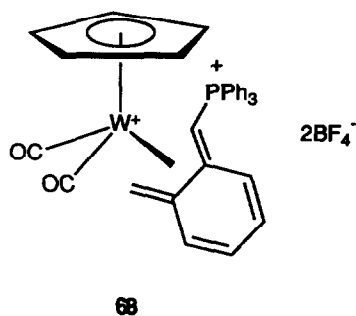
Trimethyl phosphine was found to substitute the CO in  $\text{CpNO}(\text{CO})\text{Mo}=\text{C}(\text{OEt})\text{Me}$  [201]. Subsequent electrophilic attack by  $\text{SMe}^+$  at the carbene C led to a cationic molybdathia–cyclopropane complex (Scheme 91).

Protonation with 2 equivalents of  $\text{CF}_3\text{COOH}$  on  $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CR}$  gave  $\text{Cp}(\text{CO})(\text{CF}_3\text{COO})_2\text{W}(\eta^2\text{-CO-CH}_2\text{R})$  while  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  afforded  $\text{Cp}(\text{CO})\text{W}(\text{Me-CN})_2(\eta^2\text{-COCH}_2\text{R})[\text{BF}_4]_2$  [202].



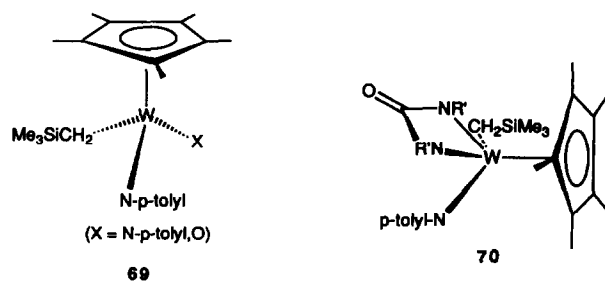
Scheme 91.

The complex  $\text{Cp}(\text{CO})_2\text{W}\equiv\text{CC}_6\text{H}_4\text{CH}_2\text{OMe}$  has been prepared and its protonation investigated [203]. In  $\text{CH}_2\text{Cl}_2$  at  $-78^\circ\text{C}$  treatment with  $\text{HBF}_4 \cdot \text{Et}_2\text{O}$  in the presence of  $\text{PPh}_3$  led to  $\text{Cp}(\text{CO})_2\text{W}(\eta^4\text{-C}_6\text{H}_4(\text{CH}_2)\text{-CHPPH}_3)[\text{BF}_4]_2$  (**68**). With aq HI the alkylidene complex  $[\text{Cp}(\text{CO})_2\text{W}=\text{CHC}_6\text{H}_4\text{CH}_2\text{OMe}]\text{I}$  was first formed followed by  $\text{Cp}(\text{CO})\text{WI}_2(\eta^2\text{-COCH}_2\text{C}_6\text{H}_4\text{CH}_2\text{OMe})$ .

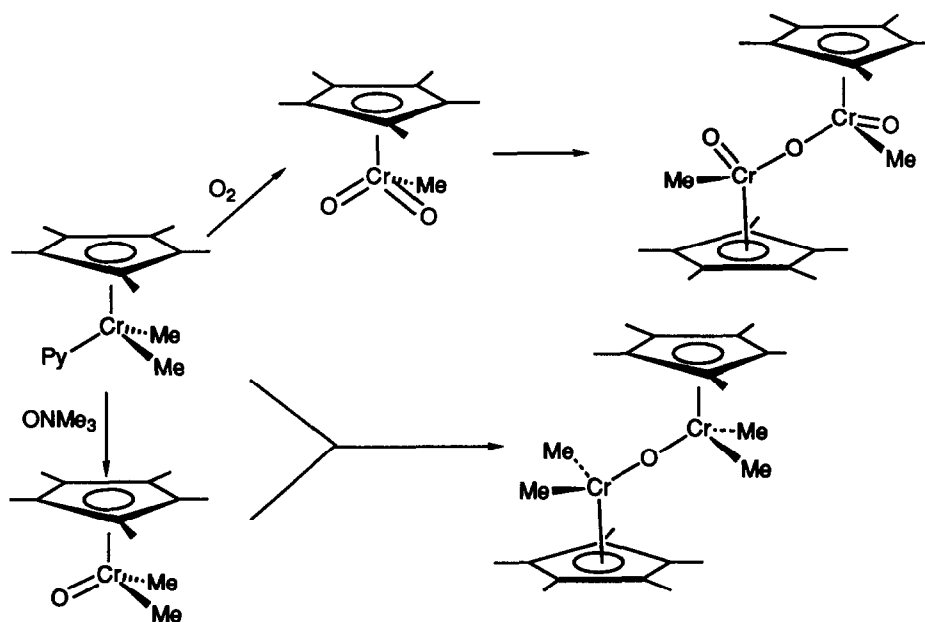


Reaction of  $\text{Cp}^*\text{Cr}(\text{Me})_2\text{Py}$  with  $\text{O}_2$  and  $\text{Me}_3\text{NO}$  at low-temperature yielded the novel oxo–alkyl complexes  $\text{Cp}^*\text{Cr}(\text{O})_2\text{Me}$  and  $\text{Cp}^*\text{Cr}(\text{O})\text{Me}_2$  which were completely characterized (Scheme 92) [204].

Treatment of  $\text{Cp}^*\text{W}(\text{O})_2(\text{CH}_2\text{SiMe}_3)$  with *p*-tolyl isocyanate led sequentially to  $\text{Cp}^*\text{W}(\text{O})(=\text{N-}p\text{-tol})(\text{CH}_2\text{SiMe}_3)$ ,  $\text{Cp}^*\text{W}(=\text{N-}p\text{-tol})_2(\text{CH}_2\text{SiMe}_3)$ , and  $\text{Cp}^*\text{W}(=\text{N-}p\text{-tol})\{\text{N}(p\text{-tol})\text{C}(\text{O})\text{N}(p\text{-tol})\}(\text{CH}_2\text{SiMe}_3)$  [205]. The first two products have three-legged piano-stool structures while the third has a four-legged piano stool structure (**69**, **70**).



The syntheses and structures of new imido complexes  $(\text{C}_5\text{H}_4\text{R})\text{MCl}_2(\text{NR}')$  ( $\text{M} = \text{Mo}, \text{R} = \text{H}, \text{R}' = \text{tBu}, \text{Pr}, \text{Ph}; \text{R} = \text{Me}, \text{R}' = \text{tBu}, \text{Ph}; \text{M} = \text{W}, \text{R} = \text{H}, \text{R}' = \text{tBu}$ ),  $(\text{C}_5\text{H}_4\text{R})\text{MoCl}(\text{L})(\text{NR}')$  ( $\text{R} = \text{H}, \text{R}' = \text{tBu}, \text{L} = \text{C}_2\text{H}_4, \text{C}_2\text{Me}_2$ ),  $[(\text{C}_5\text{H}_4\text{R})\text{Mo}(\text{C}_2\text{H}_4)(\text{N}^{\text{tBu}})]_2\text{Hg}$ ,  $\text{Mo}(\text{N}^{\text{tBu}})\text{Cl}_2(\text{PMe}_3)_3$ ,  $\text{CpMoCl}_3(\text{N}^{\text{tBu}})$ , and  $(\text{C}_5\text{H}_4\text{Me})$ -

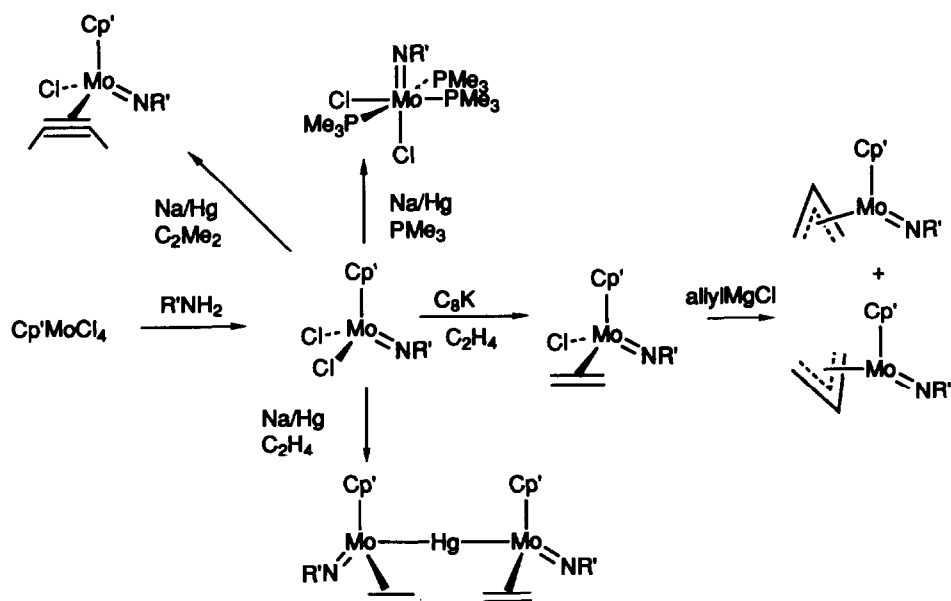
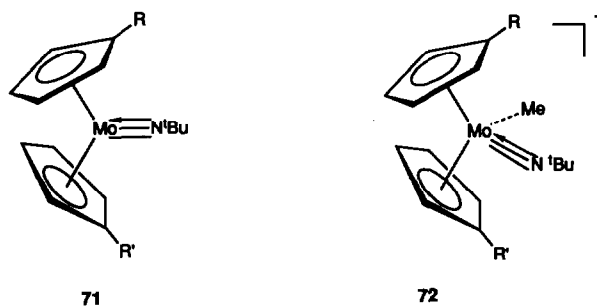


Scheme 92.

$\text{Mo}(\pi\text{-allyl})(\text{N}^t\text{Bu})$  have been reported (Scheme 93) [206].

Photolysis of imido complexes  $\text{CpM}(\text{=N}^t\text{Bu})(\text{C}_2\text{H}_4)\text{-Cl}$  ( $\text{M} = \text{Mo}, \text{W}$ ) with  $\text{NaCp}'$  afforded red, air-sensitive bis(cyclopentadienyl) imido complexes  $\text{CpCp}'\text{M}=\text{N}^t\text{Bu}$  [207]. X-ray structures of  $\text{Cp}_2\text{Mo}=\text{N}^t\text{Bu}$  and a MeI methylation product  $[(\text{C}_5\text{H}_4\text{Me})_2\text{Mo}(\text{N}^t\text{Bu})\text{Me}]\text{I}$  suggested that the imido ligand behaved as a strong  $\pi$ -donor in these complexes (71, 72).

Organolithiums reacted with  $\text{CpMo}(\text{N}^t\text{Bu})_2\text{Cl}$  and  $\text{CpW}(\text{N}^t\text{Bu})_2\text{Cl}$  to give the respective volatile



Scheme 93.

$\text{CpM}(\text{N}^t\text{Bu})_2\text{R}$  ( $\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3, \text{Ph}$ ) complexes (Scheme 94) [208]. Protolysis of the precursors with HCl yielded the monoimido complexes  $\text{CpM}(\text{N}^t\text{Bu})\text{Cl}_3$ .

A convenient entry into high-valent  $\text{Cp}^*\text{Mo}$  and  $\text{W}$  chemistry was from the  $\text{LiCp}^*$  reaction with  $\text{Mo}(\text{N}^t\text{Bu})_2\text{Cl}_2$  or  $\text{W}(\text{N}^t\text{Bu})_2\text{Cl}_2\text{Py}_2$  to yield  $\text{Cp}^*\text{M}(\text{N}^t\text{Bu})_2\text{Cl}$  (Scheme 95) [209]. These were converted to a variety of diimido, monoimido, and oxo derivatives. Treatment with  $\text{MeLi}$  gave volatile  $\text{Cp}^*\text{M}(\text{N}^t\text{Bu})_2\text{Me}$ . Protolysis with HCl gas led to  $\text{Cp}^*\text{M}(\text{N}^t\text{Bu})\text{Cl}_3$  while aq HCl produced the known  $[\text{Cp}^*\text{MO}_2]_2(\mu\text{-O})$  species. The  $\text{M}-\text{O}-\text{M}$  bridges in the latter were readily cleaved by hydroxide to form  $[\text{Cp}^*\text{MO}_3]^-$ .

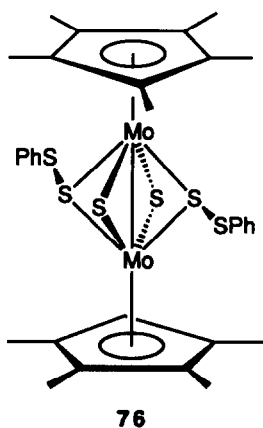
Cyclopentaphosphide  $(\text{MeP})_5$  reacted with  $\text{CpW}(\text{CO})_2=\text{ER}_2$  ( $\text{E} = \text{P}, \text{As}; \text{R} = ^t\text{Bu}, o\text{-tol}$ ) to give cyclized phosphinidine(metalla)phosphoranes  $\text{CpW}(\text{CO})_2\text{-ER}_2\text{-PMe}$  (**74**) [210]. This product was alkylated by  $\text{MeI}$  to the cationic  $[\text{CpW}(\text{CO})_2\text{P}^t\text{Bu}_2\text{-PMe}_2]^+$ . Four-membered



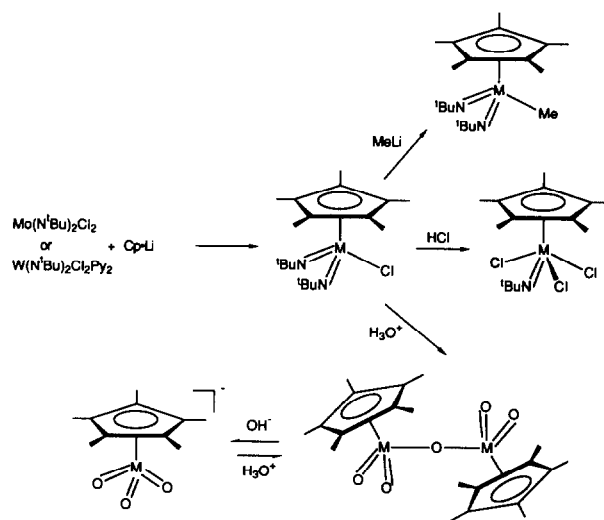
bered metallacycles of the type  $\text{CpW}(\text{CO})_2\text{-P}(o\text{-tol})_2\text{-X-P}(=\text{X})\text{Me}$  ( $\text{X} = \text{S}, \text{Se}$ ) were formed from reactions with elemental S or selenium (**75**).

#### 8.4. Complexes with metal-sulfur bonds

Thermal reaction of  $\text{Cp}'_2\text{Mo}_2(\text{CO})_4$  ( $\text{Cp}' = \text{C}_5\text{Et}_4\text{Me}$ ) with  $\text{As}_4\text{S}_4$  yielded the tetrahedranes  $\text{As}_3\text{MoCp}'(\text{CO})_2$ ,



Scheme 94.



Scheme 95.

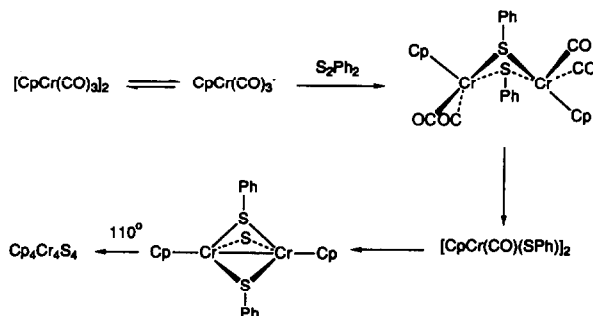
$\text{As}_2[\text{MoCp}'(\text{CO})_2]_2$ , as well as *trans*- $\text{Cp}'\text{Mo}_2\text{S}_4$ , *trans*- $\text{Cp}'_2\text{Mo}_2\text{O}_2\text{S}_2$ , and *cis/trans*- $\text{Cp}'_2\text{Mo}_2\text{OS}_3$  [211].

Reaction of  $\text{Cp}'_2\text{Mo}_2\text{S}_4\text{I}_2$  with two equivalents of  $\text{NaSR}$  gave the products  $\text{Cp}'_2\text{Mo}_2(\mu, \eta^1\text{-SSR})_2(\mu\text{-S})_2$  [212]. X-ray data for the  $\text{R} = \text{Ph}$  product showed the presence of two  $\eta^1\text{-PhSS}$ -bridges (**76**).

Reaction products of  $[\text{CpCr}(\text{CO})_3]_2$  with  $\text{S}_2\text{Ph}_2$  were temperature dependent [213]. Major species were  $[\text{CpCr}(\text{CO})_2\text{SPh}]_2$  at room temperature,  $[\text{CpCr}(\text{CO})\text{SPh}]_2$  at  $60^\circ\text{C}$ , and  $[\text{CpCr}(\text{SPh})]_2\text{S}$  at  $80^\circ\text{C}$ . Thermolysis studies showed the degradation of the first two products to the third and ultimate formation of  $\text{Cp}_4\text{Cr}_4\text{S}_4$  (Scheme 96).

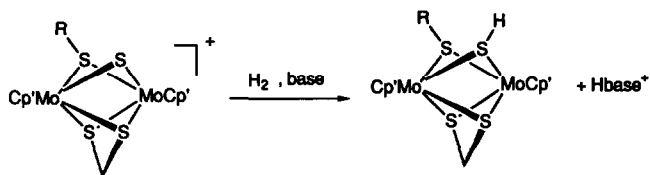
Cationic  $[(\text{MeCpMo})_2(\text{S}_2\text{CH}_2)(\mu\text{-S})(\mu\text{-SR})]\text{X}$  ( $\text{R} = \text{C}_4\text{H}_8\text{S}, \text{CH}_2\text{COOMe}; \text{X} = \text{Br}, \text{SO}_3\text{CF}_3$ ) have been synthesized and structurally characterized (**77**) [214]. The bromide salts reacted with dihydrogen to form  $\text{RH}$ ,  $\text{HBr}$ , and  $(\text{MeCpMoS})_2\text{S}_2\text{CH}_2$ . In the presence of a nitrogen base, neutral  $(\text{MeCpMo})_2(\text{S}_2\text{CH}_2)(\mu\text{-SR})(\mu\text{-SH})$  formed (Scheme 97). The kinetics of this reaction indicated first-order behavior in  $\text{H}_2$  as well as cationic complex. Activation parameters were consistent with a heterolytic activation of hydrogen.

Triflic acid with  $[\text{CpMoS}_2\text{CH}_2]_2$  at  $-70^\circ\text{C}$  resulted in diamagnetic  $[\text{CpMo}(\text{H})(\text{S}_2\text{CH}_2)_2\text{MoCp}]\text{SO}_3\text{CF}_3$



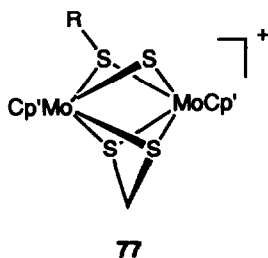
Scheme 96.





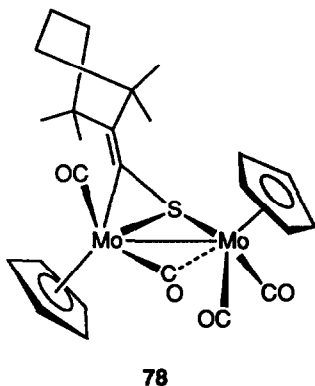
Scheme 97.

[215]. Above  $-50^{\circ}\text{C}$ , an intermolecular redox occurred to form  $[\text{CpMoS}_2\text{CH}_2]\text{SO}_3\text{CF}_3$  and 0.5 mol  $\text{H}_2$ . Reaction of the starting Mo dimer with methyl triflate gave

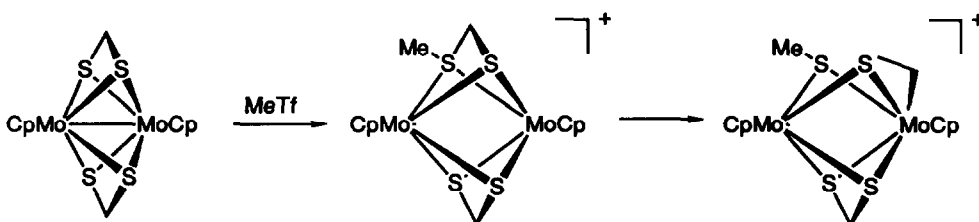


an unstable product  $[(\text{CpMo})_2(\text{S}_2\text{CH}_2)(\text{SCH}_2\text{SMe})]\text{SO}_3\text{CF}_3$ . This readily rearranged in solution to  $[\text{CpMo}(\text{S}_2\text{CH}_2)(\mu\text{-SMe})(\mu\text{-SCH}_2)\text{MoCp}]\text{SO}_3\text{CF}_3$  with a bridging thioformaldehyde (Scheme 98).

The thioketene  $\text{C}_{11}\text{H}_{18}\text{S}$  reacted with  $[\text{CpMo}(\text{CO})_2]_2$  to give  $\text{Cp}_2\text{Mo}_2(\text{C}_{11}\text{H}_{18}\text{S})$  whose structure was determined (78) [216]. This thioketene also reacted with a ketenimine complex to form  $\text{Cp}_2\text{Mo}_2(\text{CO})_2(\text{C}_{11}\text{H}_{18}\text{S})[\text{N}(\text{tol})\text{C}=\text{CPh}_2]$  (Scheme 99).

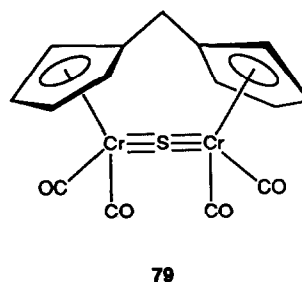


Reaction of the dicyclopentadienylmethane (L) complex  $\text{LCr}_2(\text{CO})_6$  with sulfur produced  $\text{LCr}_2(\text{CO})_4\text{S}$  (79) and  $\text{L}_2\text{Cr}_2\text{S}_4$  [217]. Low-temperature NMR revealed that the former displayed a topomerization in

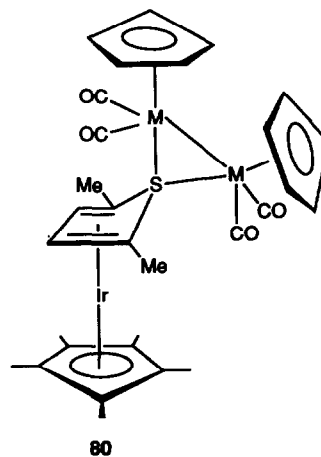


Scheme 98.

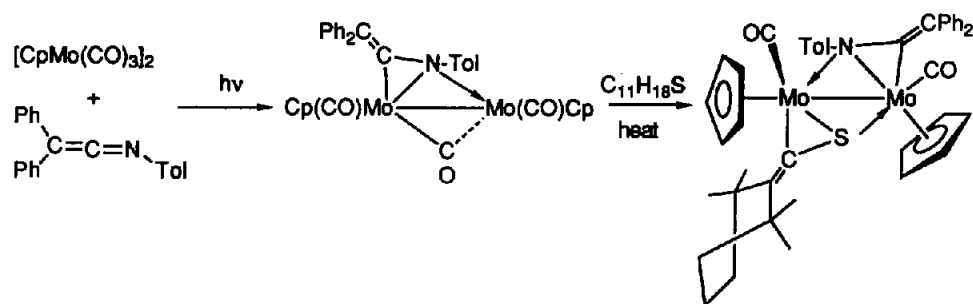
the ligand bridge. The latter was found to be a heterocubane with magnetic behavior between the antiferromagnetic  $\text{Cp}_4\text{Cr}_4\text{O}_4$  and diamagnetic  $\text{Cp}_4\text{Cr}_4\text{S}_4$  cubanes.



The 2,5-dimethylthiophene ligand (L) in the isomers  $\text{Cp}^*\text{Ir}(\eta^4\text{-L})$  and  $\text{Cp}^*\text{Ir}(\text{C}, \text{S-L})$  was sufficiently activated to react with the dimers  $[\text{CpM}(\text{CO})_2]_2$  ( $\text{M} = \text{Mo}, \text{W}$ ) giving the complexes  $\text{Cp}^*\text{Ir}(\text{L})(\text{Cp}_2\text{M}(\text{CO})_2)_2$  in which the thiophene bridges all three metals (80) [218]. Despite this novel coordination mode, no fresh insights into hydrodesulfurization of thiophenes were revealed in its reactivity.



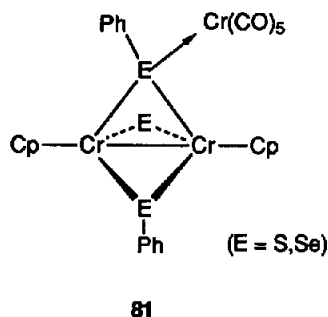
Various substituted cyclopentadienyl complexes  $\text{L}_2\text{M}_2(\text{CO})_4$  ( $\text{L} = \text{C}_5\text{EtMe}_4, \text{C}_5^t\text{BuH}_4, \text{C}_5^i\text{PrH}_4$ ;  $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) were examined for their reactions with sulfur [219]. For  $\text{M} = \text{Cr}$ , only  $(\text{C}_5\text{EtMe}_4)_2\text{Cr}_2\text{S}_5$  was isolated. For  $\text{M} = \text{Mo}$ , three isomers of  $\text{L}_2\text{Mo}_2\text{S}_4$  ( $\text{L} = \text{C}_5\text{EtMe}_4, \text{C}_5^i\text{PrH}_4$ ) were obtained but only two for  $\text{L} = \text{C}_5^t\text{BuH}_4$ . For  $\text{M} = \text{W}$ , only two isomers of  $\text{L}_2\text{W}_2\text{S}_4$



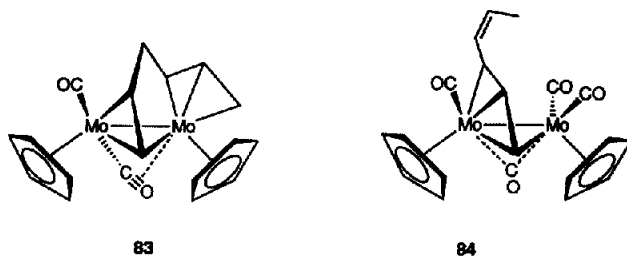
Scheme 99.

were isolated along with  $\text{L}_2\text{W}_2(\text{CO})_2\text{S}_3$ . The structures of the *syn*- $(\text{C}_5\text{EtMe}_4)_2\text{M}_2(\mu\text{-S})_2\text{S}_2$  isomers ( $\text{M} = \text{Mo}, \text{W}$ ) were determined and a thermal equilibrium was found between  $\text{L}_2\text{Mo}_2(\mu, \eta^2\text{-S}_2)(\mu\text{-S})_2$  and *syn*- $\text{L}_2\text{Mo}_2(\mu\text{-S})_2\text{S}_2$  (Scheme 100).

The complexes  $[\text{CpCr}(\text{EPh})_2]\text{E}$  ( $\text{E} = \text{S}, \text{Se}$ ) reacted with  $\text{Cr}(\text{CO})_5 \cdot \text{THF}$  to give adducts  $[\text{CpCr}(\text{EPh})_2]\text{E} \cdot \text{Cr}(\text{CO})_5$  (**81**) [220]. The  $\text{Cr}(\text{CO})_5$  moiety was removable using  $\text{PPh}_3$ .

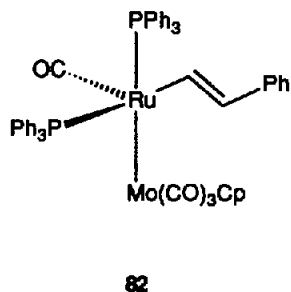


Photochemical reactions of  $[\text{Cp}_2\text{M}_2(\text{CO})_4(\mu\text{-}\eta^{2:2}\text{-C}_2\text{H}_2)]$  ( $\text{M} = \text{Mo}, \text{W}$ ) with acetylene, 1,3-butadiene, and isoprene were studied [222]. Acetylene led to fly-over  $[\text{Cp}_2\text{M}_2(\text{CO})_2(\mu\text{-}\eta^{1:3:3:1}\text{-1,3,5-hexatriene-1,6-diyl})]$  as well as  $[\text{Cp}_3\text{Mo}_3(\text{CO})_6(\mu\text{-}\eta^{1:2}\text{-ethynyl})]$ . 1,3-Butadiene afforded  $[\text{Cp}_2\text{Mo}_2(\text{CO})(\mu\text{-}\eta^{1:2}\text{-CO})(\mu\text{-}\eta^{1:2:3}\text{-1,5-hexadiene-1,4-diyl})]$  and  $[\text{Cp}_2\text{Mo}(\text{CO})_4(\mu\text{-}\eta^{1:3}\text{-E,Z-2,4-hexadien-1-ylidene})]$  (**83**, **84**). Isoprene gave  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}\eta^{1:3}\text{-E,Z-5-methyl-2,4-hexadien-1-ylidene})]$ . Analogous reactions with tungsten were also described.



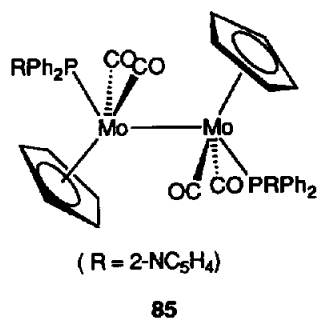
### 8.5. Complexes with metal-metal bonds

Metathesis of  $\text{Na}[\text{CpM}(\text{CO})_3]$  ( $\text{M} = \text{Mo}, \text{W}$ ) with  $\text{Ru}(\textit{trans-styryl})\text{Cl}(\text{CO})(\text{PPh}_3)_2$  yielded heterodinuclear complexes of the type  $\text{CpM}(\text{CO})_3\text{-Ru}(\textit{trans-styryl})(\text{CO})(\text{PPh}_3)_2$  (**82**) [221].



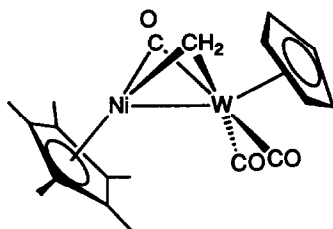
Scheme 100.

Addition of 2 equivalents of 2-(diphenylphosphino)pyridine ( $\text{py-PPh}_2$ ) to  $\text{Cp}_2\text{Mo}_2(\text{CO})_4$  gave  $\text{Cp}_2\text{Mo}_2(\text{CO})_4(\text{py-PPh}_2)_2$  [223]. The X-ray structure revealed a piano-stool dimer with a very long Mo-Mo bond  $3.276(3) \text{ \AA}$  which was thought to be the result of a compromise between M-M bonding and lone pair repulsion forces (**85**). Oxidation with  $\text{Ag}^{\text{I}}$  and reduction with  $\text{Na}(\text{Hg})$  gave the expected monometallic cation and anion complexes respectively.



Unsaturated  $\text{Cp}^*\text{Ni-W}(\text{CO})_3\text{Cp}$  reacted with two-electron donors to yield  $\text{Cp}^*\text{Ni}(\mu\text{-CO})(\mu\text{-L})\text{W}(\text{CO})_3$

$L'Cp$  ( $L = CO$ ,  $L' = CO$ ,  $PMe_3$ ,  $PMe_2Ph$ ,  $P(OMe)_3$ ,  $PPh_2Cl$ ,  $PPh_2H$ ;  $L = 'BuNC$ ,  $CH_2$ ,  $L' = CO$ ) (**86**). All complexes exhibited dynamic NMR behavior [224]. Several Ni–Mo analogs were also prepared.

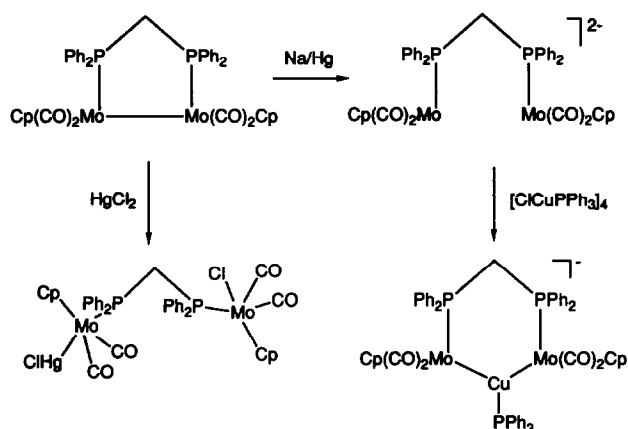


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The complexes  $Cp_2Mo_2(CO)_4(L)$  ( $L =$  bridging  $Ph_2PCH_2PPh_2$ ,  $dppm$ , or  $(EtO)_2POP(OEt)_2$ ,  $tedip$ ) were prepared from  $Cp_2Mo_2(CO)_4$  and the respective ligands [225]. Treatment of the  $dppm$  complex with  $HBF_4$  or  $[IPy_2]BF_4$  yielded  $[(\mu-X)(\mu-dppm)Cp_2Mo_2(CO)_4]BF_4$  ( $X = H, I$ ), whereas  $I_2$  and  $HgCl_2$  gave  $(X)(CO)_2CpMo(dppm)MoCp(CO)_2(Y)$  ( $X = Y = I$ ;  $X = HgCl$ ,  $Y = Cl$ ). Reduction with  $Na/Hg$  led to  $Na_2Cp_2Mo_2(CO)_4(dppm)$  which can be protonated to yield  $Cp_2Mo_2(CO)_4(dppm)H_2$ . Treatment of the dianion with  $CH_2I_2$  formed  $(ICH_2)CpMo(CO)_2^-(dppm)Mo(CO)_2Cp(I)$  while  $(CuClPPh_3)_4/Ph_4AsCl$  gave the trinuclear  $Ph_4As[(\mu-CuPPh_3)(\mu-dppm)Cp_2Mo_2(CO)_4]$  (Scheme 101).

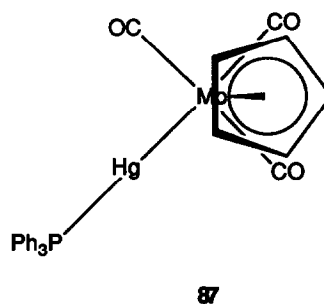
Reactions of trimetallic complexes  $[CpMo(CO)_2L]_2-Hg$  ( $L = CO, PPh_3, PMePh_2, PPh_2Me$ ) with  $Hg(BF_4)_2$  in the presence of phosphines led to cationic bimetallics of the type  $[L'Hg-Mo(CO)_2LCp]BF_4$  ( $L' = PPh_3, PCy_3$ ) [226]. Structure of the  $[PPh_3HgMo(CO)_3Cp]BF_4$  has been found to be of the usual four-legged piano stool type (**87**).

Oxidation of the trimetallic complex  $[CpMo(CO)_2(PPh_3)_2Hg]$  occurred in two one-electron steps [227]. The first generated a transient cation which underwent  $Mo-Hg$  bond cleavage to give  $[CpMo(CO)_2PPh_3]^+$  and the mercury-centered radical  $CpMo(CO)_2PPh_3Hg^+$ . It



Scheme 101.

was proposed that the latter dimerized and reacted with the transient cationic complex to produce an

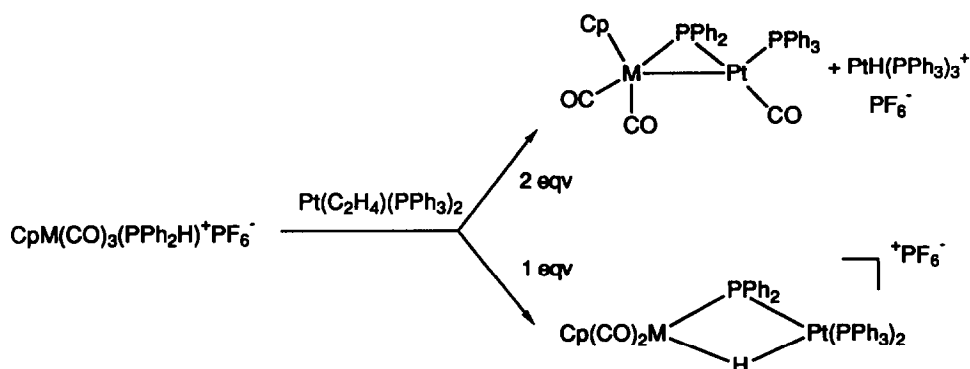


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observable pentametallic intermediate. The second electron transfer then generated  $[CpMo(CO)_2PPh_3-Hg]^+$  which eliminated  $Hg$  to give  $[CpMo(CO)_2PPh_3]^+$  which coordinated available solvent or other ligands.

Reaction of  $[CpM(CO)_3PPh_2H]PF_6$  ( $M = Mo, W$ ) with two equivalents of  $Pt(C_2H_4)(PPh_3)_2$  readily yielded  $Cp(CO)_2M(\mu-PPh_2)Pt(CO)(PPh_3)$  and  $[PtH(PPh_3)_3]PF_6$  [228]. A 1:1 stoichiometry resulted instead in  $[Cp(CO)_2M(\mu-H)(\mu-PPh_2)Pt(PPh_3)_2]PF_6$  (Scheme 102).

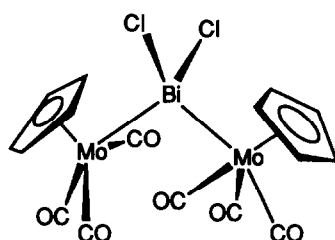
A water-soluble dicyclopentadienyl Mo dimer ( $\eta^5-C_5H_4CH_2CH_2NH_3^+$ ) $_2Mo_2(CO)_6$  was synthesized [229].



Scheme 102.

Its photochemistry was found to be similar to the parent dimer, as low-energy irradiation homolytically cleaved the Mo–Mo bond to form 17-electron radicals. In the presence of ligands, 19-electron adduct intermediates formed which were good reductants. The earlier suggestion that 19-electron intermediates from the irradiation of  $(\text{CpCOOH})_2\text{W}_2(\text{CO})_6$  in basic aqueous solution reduced water to  $\text{H}_2$  has been modified in that a water–gas shift reaction may be the actual  $\text{H}_2$  source.

The reaction of  $[\text{BiCl}(\text{Mo}(\text{CO})_3\text{Cp})_2]$  with PPNCl afforded the complex  $\text{PPN}[\text{BiCl}_2(\text{Mo}(\text{CO})_3\text{Cp})_2]$  [230]. The bromide as well as W analogues were similarly prepared. Structural studies showed an interesting variation of coordination geometries at Bi ranging from disphenoidal (trigonal bipyramid with axial Cl's) to near tetrahedral (**88**).

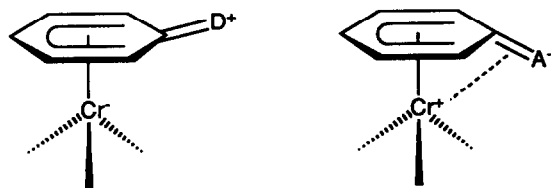


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## 9. Arene complexes

### 9.1. Structure and dynamical behavior

X-ray structures of five arene- $\text{Cr}(\text{CO})_3$  complexes having  $\pi$ -donor/acceptor substituents on the benzene rings have been determined (**89**) [231]. It was found that  $\pi$ -donor groups and their *ipso*-C's are bent away from the  $\text{Cr}(\text{CO})_3$  fragments while  $\pi$ -acceptors and their *ipso*-C's are bent slightly towards the metal. These distortions have been found to be mainly due to electronic and not steric effects.

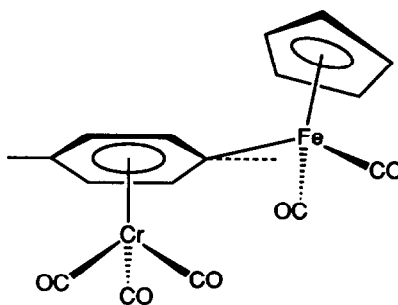


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Crystal structures of hexakis(dimethylsilyl)benzene and  $\text{M}(\text{CO})_3$  complexes ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) have been determined [232]. All exhibited orientational disorder. The  $\text{M}(\text{CO})_3$  units adopt a staggered conformation with respect to the side-chains with arene bond alter-

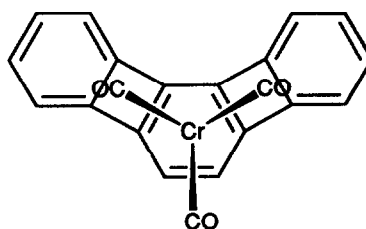
ations and substantial out-of-plane deviations of the dimethylsilyl groups.

The structures of several heterobimetallic arene  $\text{Cr}(\text{CO})_3$  complexes with  $\sigma$ -bonded organometallic groups have been determined [233]. These included  $[\text{C}_6\text{H}_5(\text{C}_5\text{H}_4\text{Me})\text{Fe}(\text{CO})_2]\text{Cr}(\text{CO})_3$ ,  $[\text{C}_6\text{H}_5(\text{indenyl})\text{Fe}(\text{CO})_2]\text{Cr}(\text{CO})_3$ , and  $[1,4\text{-C}_6\text{H}_4\text{Me}(\text{Cp})\text{Fe}(\text{CO})_2]\text{Cr}(\text{CO})_3$ . Each displayed nonplanar benzene rings with the Fe atoms and *ipso* C's bent substantially away from the  $\text{Cr}(\text{CO})_3$  centers (**90**). It was again suggested that these distortions arose primarily from the  $\pi$ -donor nature of the Fe moieties.



90

The structure of a centrally bound angular- $(\eta^6\text{-terphenylene})\text{Cr}(\text{CO})_3$  has been determined (**91**) [234]. Empirical, semi-empirical, as well as *ab initio* MO calculations of this have been performed to be compared to NMR data on the rotation barrier (9.4 kcal  $\text{mol}^{-1}$ ) about the Cr–arene bond.



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Stereodynamics of several persubstituted arenes ( $1,4\text{-R}_2\text{-C}_6\text{Et}_4$ ;  $\text{R} = \text{OMe}, \text{MeOCH}_2, \text{neohexyl}$ ) and their  $\text{Cr}(\text{CO})_3$  complexes have been studied by variable-temperature NMR techniques [235]. Results indicated that rotation barriers about the  $\text{sp}^2\text{-sp}^3$  bonds did not change significantly after metal complexation. The possibility of correlated dynamics between the metal tripodal and ethyl group rotations was discussed.

Variable-temperature C-13 NMR studies of the barrier to metal-arene rotation in  $[1,4\text{-bis}(4,4\text{-dimethyl-3-oxopentyl})\text{-2,3,5,6-tetraethylbenzene}]\text{Mo}(\text{CO})_3$  was found to be mainly steric in nature. [236].

Extended Huckel MO was used to calculate the

rotational barrier in benzocyclobutane–Cr(CO)<sub>3</sub> [237]. The distorted arene ring population differences between the long and short C–C bonds correlated well with the barrier since it directly measured the diminished Cr-binding ability during the rotation. Its magnitude also depended on the strength of the antiaromatic effect from the  $\pi$  bond of the annelated cyclobutane ring.

### 9.2. Electrochemistry

Electrochemical one-electron oxidation of (arene)M(CO)<sub>3</sub> and (thiophene)M(CO)<sub>3</sub> (M = Cr, Mo, W) in acetonitrile were reported to produce 17-electron [(MeCN)<sub>n</sub>M(CO)<sub>6-n</sub>]<sup>+</sup> cations [238].

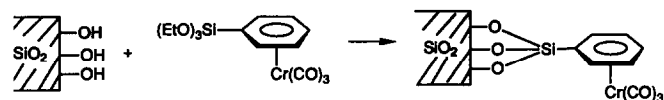
Electrochemical and electrical properties of soluble poly(*n*-hexylphenylene) Mo(CO)<sub>3</sub> were studied [239]. It was found that oxidation occurred at  $E^\circ = 0.51$  V *vs.* Ag/Ag<sup>+</sup> which was less positive than that of the free polymer by 0.3 V. The band gap, however, was not significantly changed.

Iodine oxidation of (benzene)<sub>2</sub>Mo yielded [(benzene)<sub>2</sub>Mo]<sup>+</sup> whose cyclic voltammogram showed a reversible redox at 730 mV *vs.* SCE [240]. The radical cation has been assigned a 2A<sub>1g</sub> ground state according to its isotropic EPR spectrum. Solid-state EPR of the [(benzene)<sub>2</sub>Mo][FeBr<sub>4</sub>] salt exhibited two resonances assignable to the ions. Magnetic susceptibility data suggested antiferromagnetic coupling of the anions below 15 K.

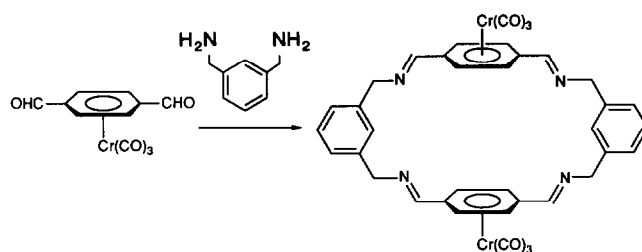
Electrochemical oxidation of sterically congested (C<sub>6</sub>Et<sub>6</sub>)M(CO)<sub>3</sub> (M = Cr, Mo, W) reversibly generated 17-electron cationic radicals which were stabilized towards ligand association to form 19-electron species [241]. These were shown to undergo clean CO substitution by P(OBu)<sub>3</sub> with relative rates of Mo > W  $\gg$  Cr.

### 9.3. Synthesis

Direct reactions of mono- and di-substituted organosilylarenes with Cr(CO)<sub>6</sub> or (MeCN)<sub>3</sub>Cr(CO)<sub>3</sub> yielded a variety of (organosilylarene)Cr(CO)<sub>3</sub> complexes [242]. Electrochemical oxidation of these were found to be very dependent on solvent and ring substituents. The alkoxy-silyl derivatives were covalently linked to silica supports (Scheme 103) while complexes with Si(NMe<sub>2</sub>)<sub>2</sub>, SiCH=CH<sub>2</sub>, and Si–H groups were used to form new siloxanyl polymers. (Arene)Cr(CO)<sub>3</sub> complexes were prepared from cone (92), 1,2-alternate (93), and 1,3-alternate (94) conformers of 25,26,27,28-tetrapropoxycalix[4]arene [243].

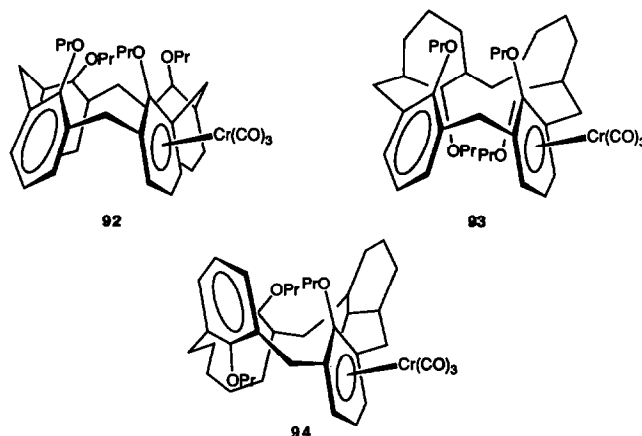


Scheme 103.



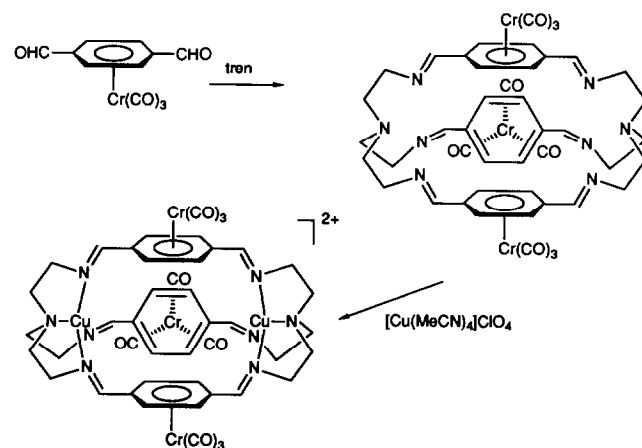
Scheme 104.

Condensation reaction of 1,3-bis(aminomethyl)benzene with the appropriate chromium complex gave a

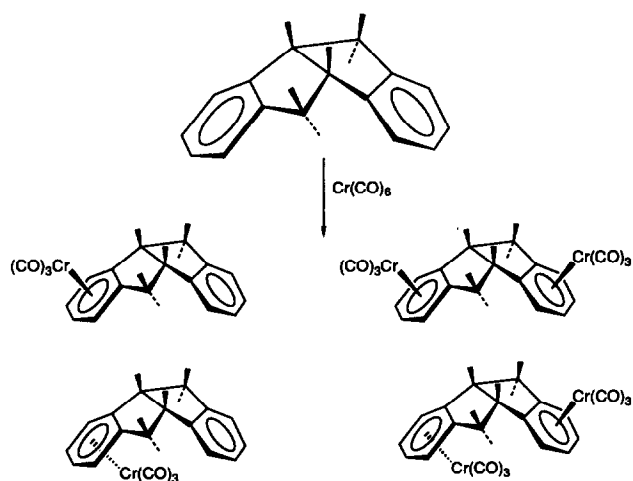


macrocyclic in good yield (Scheme 104) [244]. Proton NMR studies revealed presence of two weakly bound water molecules in D<sub>2</sub>O. An analogous macrocycle was also prepared using 1,6-diaminohexane. The dialdehyde chromium complex reacted with tren to give a cryptand which was able to encapsulate two cuprous cations to give a tetrametallic (Scheme 105).

HPLC separations of three racemic cyclophanes led to pure enantiomers which were complexed with Cr(CO)<sub>3</sub> [245]. These chiral complexes were lithiated and derivatized with electrophiles. (Arene)Cr(CO)<sub>3</sub>

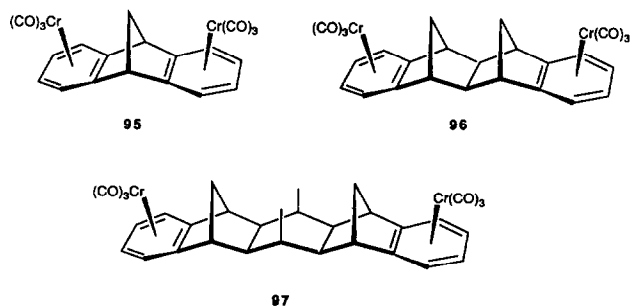


Scheme 105.

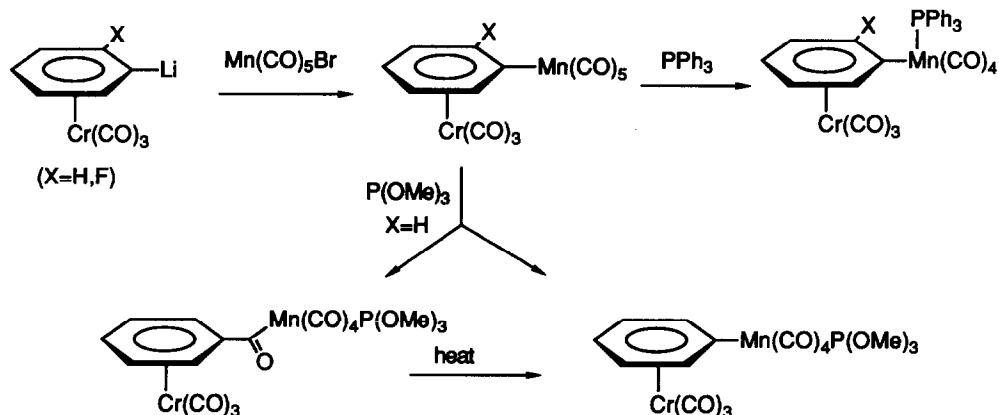


Scheme 106.

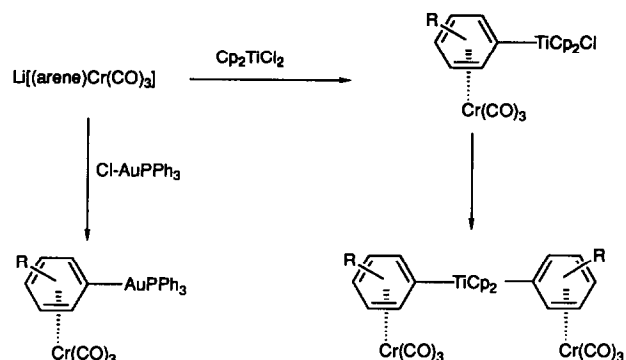
moieties linked by rigid polynorbornyl-type spacers have been prepared and shown to adopt exo, exo configurations (**95**, **96**, **97**) [246]. Electrochemical studies of these binuclear complexes showed two-electron oxidations to form dications. Despite the M–M separation of 6.48 Å two resolved one-electron steps were observed in complex (**95**) with a 140 mV difference due probably to efficient through-bond coupling through the bicyclic spacer.



Reactions of a centro-polyindan, 4b,5,9b,10-tetrahydroindeno[2,1-a]indene, with  $\text{Cr}(\text{CO})_6$  produced two 1:1 complexes with the  $\text{Cr}(\text{CO})_3$  moieties bonded to



Scheme 107.

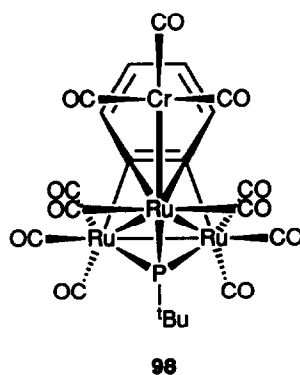


Scheme 108.

either the concave or convex side of the ligand [247]. Prolonged reaction times led to formation of two isomers; one with two  $\text{Cr}(\text{CO})_3$  units on the convex side and the other on both sides (Scheme 106).

#### 9.4. Formation of polymetallics

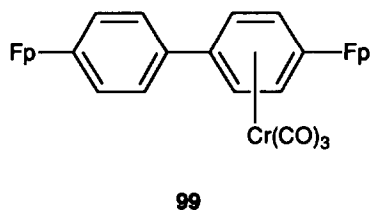
Reaction of  $\text{Ru}_3(\text{CO})_{12}$  with  $\text{P}[\text{C}_6\text{H}_5\text{Cr}(\text{CO})_3]_2^t\text{Bu}$  afforded the novel benzyne complex  $\text{Ru}_3(\text{CO})_8[\mu_3\text{-C}_6\text{H}_4\text{Cr}(\text{CO})_3][\mu_3\text{-P}^t\text{Bu}]$  wherein the aryne was bound symmetrically to the  $\text{Ru}_3$  cluster with the  $\eta^2\text{-C}$ 's four-electron donors (**98**) [248]. A Cr–Ru bond was also formed.



The complexes  $(\text{C}_6\text{H}_4\text{XLi})\text{Cr}(\text{CO})_3$  ( $\text{X} = \text{H}, \text{F}$ ) reacted with  $\text{Mn}(\text{CO})_5\text{Br}$  to give novel heterobimetallics

$(\text{CO})_5\text{Mn}[\text{C}(\text{O})\text{C}_6\text{H}_4\text{X}]\text{Cr}(\text{CO})_3$  with bridging  $\sigma, \pi$ -benzoyl ligands [249]. In the presence of  $\text{P}(\text{OMe})_3$ , both  $(\text{CO})_4\text{P}(\text{OMe})_3\text{Mn}[\text{C}(\text{O})\text{C}_6\text{H}_4\text{X}]\text{Cr}(\text{CO})_3$  and  $(\text{CO})_4\text{P}(\text{OMe})_3\text{Mn}(\mu\text{-Ph})\text{Cr}(\text{CO})_3$  were obtained. The former converted to the latter upon refluxing in hexane. In the presence of  $\text{PPh}_3$ , the unusual  $(\text{CO})_4\text{-PPh}_3\text{Mn}[\text{C}_6\text{H}_4\text{X}]\text{Cr}(\text{CO})_3$  complex was formed (Scheme 107).

Bimetallic acyl-bridged iron complexes like 1,4- $\text{C}_{10}\text{H}_8(\text{COFp})_2$  ( $\text{Fp} = \text{CpFe}(\text{CO})_2$ ) were heated with excess  $\text{Cr}(\text{CO})_6$  to give heterometallic (arene-Fp) $\text{Cr}(\text{CO})_3$  complexes containing  $\pi$ -arene-Fe and  $\eta$ -arene-Cr bonds (**99**) [250]. These complexes displayed the expected transfer of electron density from Fe to Cr. The  $\text{Cr}(\text{CO})_3$  fragment preferentially coordinated to the more electron-rich, though sterically crowded arene ring in  $(\eta^6\text{-1,4-C}_6\text{H}_4\text{PhFp})\text{Cr}(\text{CO})_3$ .



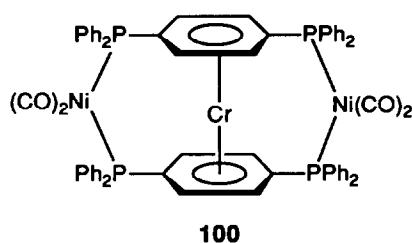
New heterobi- and tri-metallics of the types  $\text{Cp}_2\text{Ti}(\text{Cl})\text{-}(\text{arene})\text{Cr}(\text{CO})_3$  and  $\text{Cp}_2\text{Ti}[(\pi\text{-arene})\text{Cr}(\text{CO})_3]_2$  were prepared from the respective lithiated (arene) $\text{Cr}(\text{CO})_3$  and  $\text{Cp}_2\text{TiCl}_2$  (Scheme 108) [251]. From  $\text{PPh}_3\text{AuCl}$ ,  $\text{PPh}_3\text{Au}\text{-}(\text{arene})\text{Cr}(\text{CO})_3$  was similarly prepared. As expected, the  $\text{Cr}(\text{CO})_3$  fragments were  $\pi$ -bonded and the Ti/Au were  $\sigma$ -bonded to the arenes.

Reaction of  $(\text{HOCH}_2\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3$  with  $\text{Cp}_2\text{MX}_2$  ( $\text{M} = \text{Ti}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ;  $\text{M} = \text{Zr}$ ,  $\text{X} = \text{Bz}$ ) led to  $\text{Cp}_2\text{-MX}[(\mu\text{-OCH}_2\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3]$  complexes while a 2:1 reagent ratio gave  $\text{Cp}_2\text{M}[(\mu\text{-OCH}_2\text{C}_6\text{H}_5)\text{Cr}(\text{CO})_3]_2$  [251a].

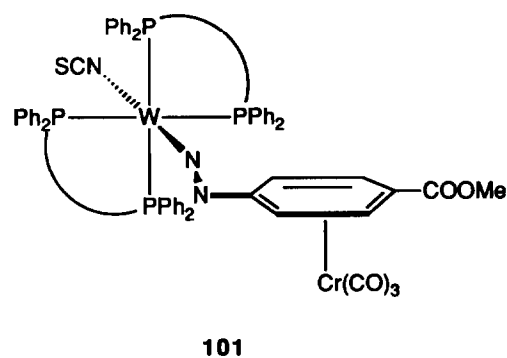
Nucleophilic substitution at bis(1,4-dichlorobenzene)Cr by  $\text{LiPPh}_2$  afforded di[1,4-bis(diphenylphosphino)benzene]Cr [252]. This bifunctional chelating complex was exploited for the synthesis of heterometallacyclophane by complexation with two  $\text{Ni}(\text{CO})_2$  moieties (**100**). Variable temperature NMR spectroscopy showed dynamics at the P-Ni-P bridges while electrochemical studies indicated rich redox chemistry. EPR studies of the radical monocation indicated spin delocalization into the ligand periphery.

The reaction of  $[\text{W}(\text{NCS})(\text{N}_2)(\text{dppe})_2]^-$  with  $(p\text{-FC}_6\text{H}_4\text{COOMe})\text{Cr}(\text{CO})_3$  in THF at room temperature led to a novel arylation of the coordinated  $\text{N}_2$  to give dark-red  $[\text{W}(\text{NCS})(\text{N}=\text{N}\text{-}p\text{-C}_6\text{H}_4\text{COOMe})]\text{Cr}(\text{CO})_3$  [253]. Structural determination showed a long N=N bond (1.314(5) Å) and suggested significant contribu-

tions from the zwitterionic form by  $\text{Cr}(\text{CO})_3$  electron withdrawal (**101**).



Lithiation of  $(\text{benzene})_2\text{Cr}$  and reaction with  $\text{Se}_2\text{Ph}_2$  or  $\text{Se}/\text{MeI}$  gave the complexes  $(\text{PhSe-C}_6\text{H}_5)_2\text{Cr}$  and  $(\text{MeSe-C}_6\text{H}_5)_2\text{Cr}$  respectively [254]. The latter could be converted to the interannularly-bridged  $(\text{MeSe-C}_6\text{H}_5)_2\text{Cr}[\text{M}(\text{CO})_4]$  ( $\text{M} = \text{Cr}$ ,  $\text{Mo}$ ,  $\text{W}$ ). Dynamic NMR studies of the  $\text{M} = \text{Cr}$  complex indicated a bridge reversal as well as a higher energy bridge inversion process. Electrochemical studies were also reported.



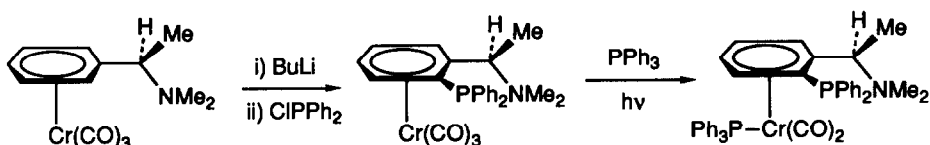
### 9.5. Derivatization of the arene ring

New chiral monophosphine ligands containing (arene)Cr were prepared from the stereoselective ortho-lithiation of  $[(R)\text{-}N,N\text{-dimethyl-1-phenylethylamine}]\text{Cr}(\text{CO})_3$  (Scheme 109). Asymmetric cross-coupling of 1-phenylethylmagnesium or zinc reagents with vinyl bromides in the presence of Ni or Pd catalysts using these ligands gave up to 61% ee [255].

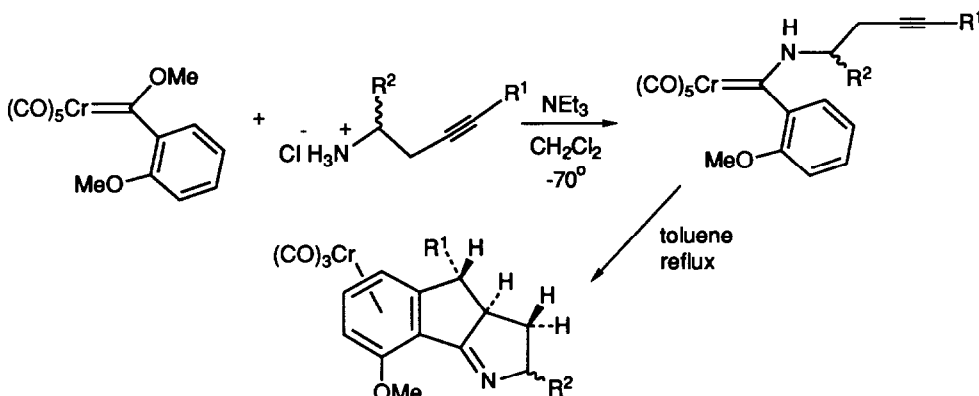
Cyclization of alkynylamino carbene complexes of Cr provided one-step regio- and diastereoselective routes to tetrahydroindenopyrroles *via* intramolecular annulation (Scheme 110) [256].

Alkoxycarbonylation was found to compete with nucleophilic substitution and palladium-catalyzed reduction during the reaction of  $(\text{chloroarene})\text{Cr}(\text{CO})_3$  with  $\text{HCOOR}/\text{MOR}/\text{PdCl}_2(\text{PPh}_3)_2$  ( $\text{R} = \text{alkyl}$ ,  $\text{M} = \text{Na}$ ,  $\text{K}$ ) (Scheme 111) [257].

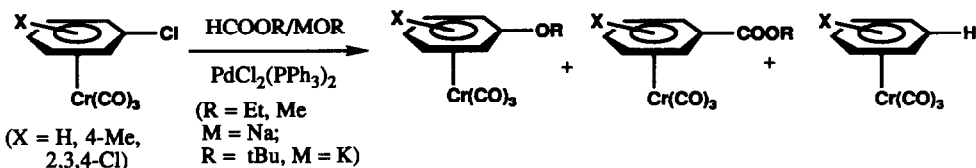
The pig-liver esterase catalyzed hydrolysis of  $[o\text{-C}_6\text{H}_4(\text{CH}_2\text{COOR})_2]\text{Cr}(\text{CO})_3$  was found to yield the half ester in good yield and with high enantiomeric excess [258].



Scheme 109.



Scheme 110.

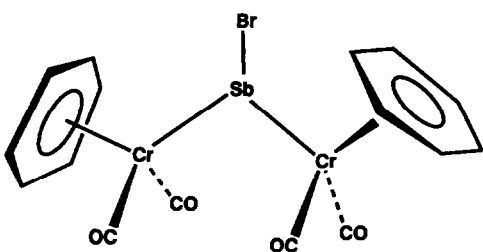


Scheme 111.

### 9.6. Reactions at the metal

Photolysis of (arene)Cr(CO)<sub>3</sub> in the presence of trichlorosilane resulted first in CO loss followed by oxidative addition to give (arene)Cr(CO)<sub>2</sub>H(SiCl<sub>3</sub>) [259]. Further photolysis caused H<sub>2</sub> elimination and formation of (arene)Cr(CO)<sub>2</sub>(SiCl<sub>3</sub>)<sub>2</sub>. Presence of the trichlorosilyl groups labilized the arene to exchange reactions (Scheme 112).

The half-sandwich complexes (C<sub>6</sub>MeH<sub>5</sub>)W(PMe<sub>3</sub>)<sub>3</sub> and (C<sub>6</sub>MeH<sub>5</sub>)W{SiMe(CH<sub>2</sub>PMe<sub>2</sub>)<sub>2</sub>} were monoprotonated by NH<sub>4</sub>BF<sub>4</sub> whereas the former was diprotonated by HCl(g) [260]. Treatment of [(C<sub>6</sub>H<sub>5</sub>Me)W(η-



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C<sub>3</sub>H<sub>5</sub>)dmpe]<sup>+</sup> with LiAlH<sub>4</sub> led to an inseparable mixture of (η<sup>5</sup>-C<sub>6</sub>H<sub>6</sub>Me)W(C<sub>3</sub>H<sub>5</sub>)dmpe isomers (Scheme 113).

Photochemically induced reductive dehalogenation of SbX<sub>3</sub> yielded doubly-bridged Sb ligands in [(arene)Cr(CO)<sub>2</sub>]<sub>2</sub>SbX (X = Cl, Br, I) [261]. Structural studies confirmed trigonal planar coordination at Sb (**102**). The stability of these products decreases with the number of + I substituents at the arene.

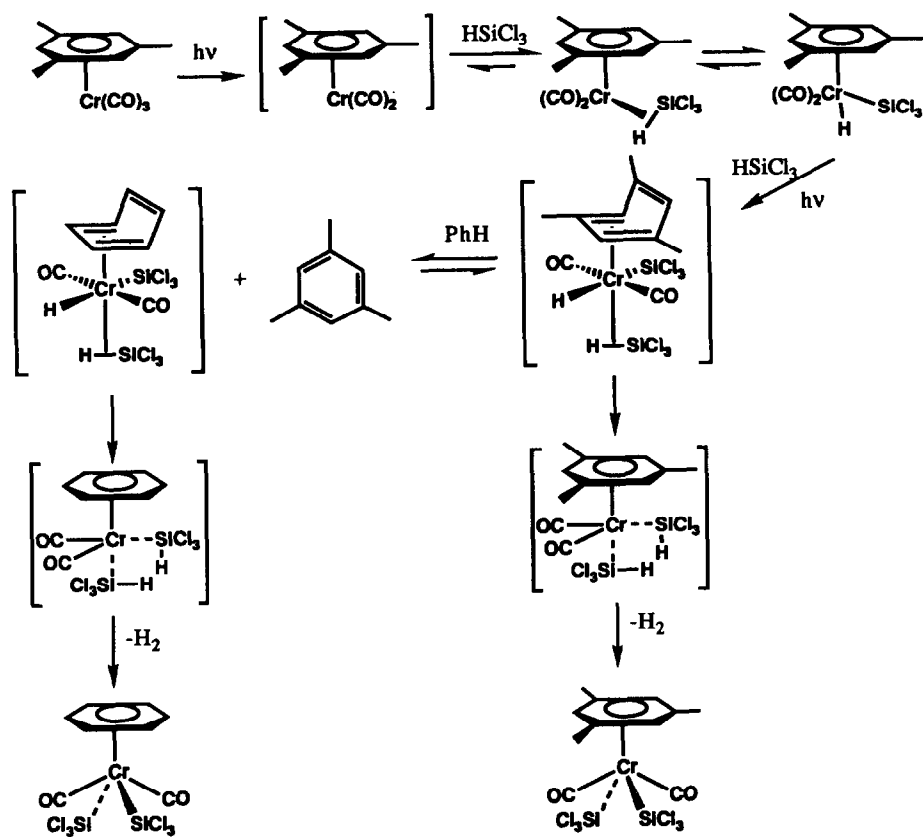
### 9.7. Organic chemistry

Reactions of haloarene-Cr(CO)<sub>3</sub> complexes with sodium trifluoroacetamide and sodium dibenzyl phosphoramidate led to substituted aniline complexes in good yields (Scheme 114) [262].

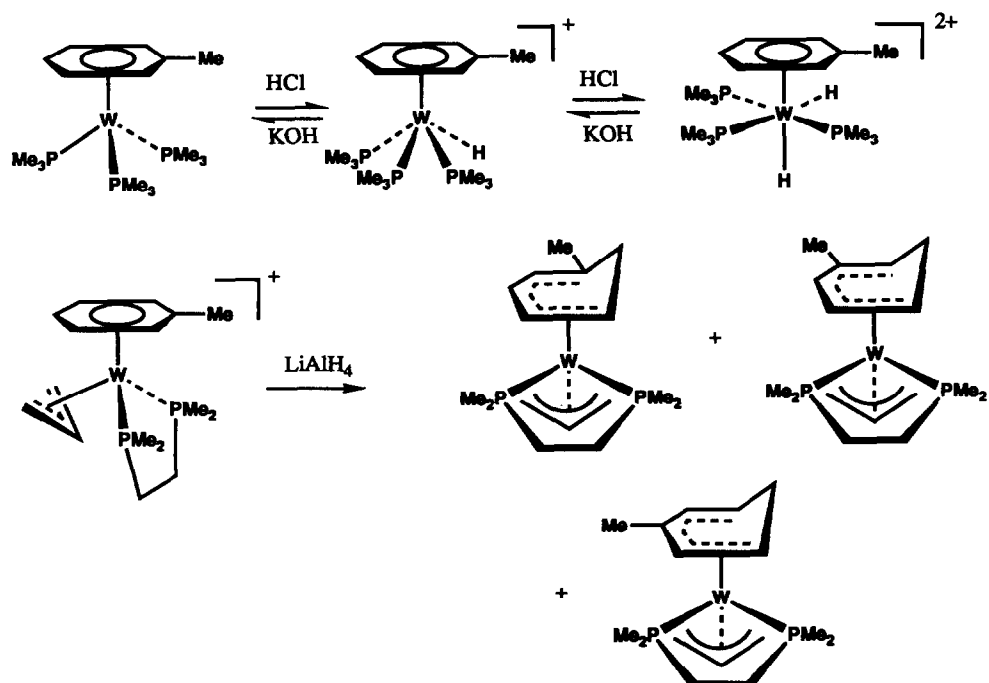
Reaction of lithiated alkylarene-Cr(CO)<sub>3</sub> derivatives with carbon dioxide in THF resulted in regioselective carboxylations at the benzylic position [263].

Deprotonation of polycyclic aromatic hydrocarbon (naphthalene, anthracene, phenanthrene, pyrene, fluoroanthrene) complexes of Cr(CO)<sub>3</sub> and treatment with an electrophile (trialkyl borate, trimethylsilyl chloride, ethyl chloroformate) resulted in hydroxylation, trimeth-

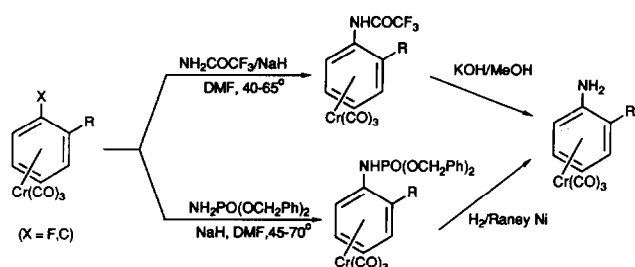




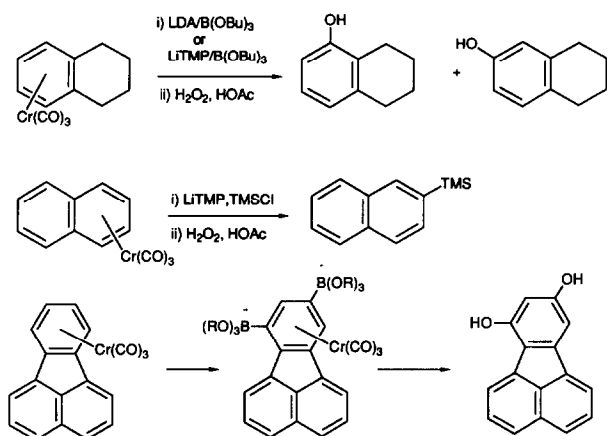
Scheme 112.



Scheme 113.



Scheme 114.



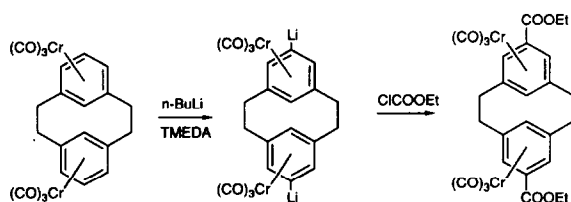
Scheme 115.

ylsilylation, carbethoxylation respectively after oxidative workup (Scheme 115) [264]. Sterical factors were found to control the site of substitution.

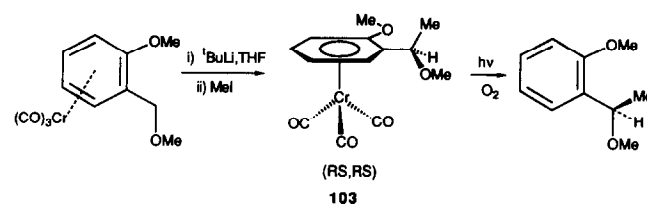
Complexation of both benzene rings of [2.2]-metacyclophane was achieved [265]. Its reaction with six equivalents of BuLi/TMEDA yielded the bis(aryl-lithium)Cr(CO)<sub>3</sub> complex which was quenched with ethyl chloroformate to give the 5,13-disubstituted complex (Scheme 116). Decomplexation led to the free disubstituted cyclophane.

Treatment of (*o*-methoxybenzyl methyl ether)Cr(CO)<sub>3</sub> with <sup>t</sup>BuLi followed by an electrophile gave a single diastereomer of the  $\alpha$ -substituted complex (Scheme 117) [266]. A structural determination of the  $\alpha$ -methyl complex established a (*RS,RS*) relative configuration (**103**).

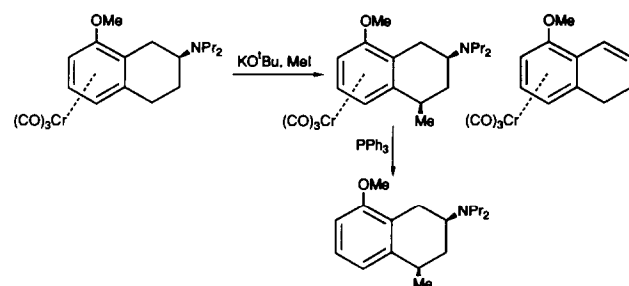
Methyl and trimethylsilyl groups were introduced regioselectively at the C-6 and C-7 positions of Cr(CO)<sub>3</sub> complexes of C-8-oxygenated 2-(dipropylamino)tetralin



Scheme 116.



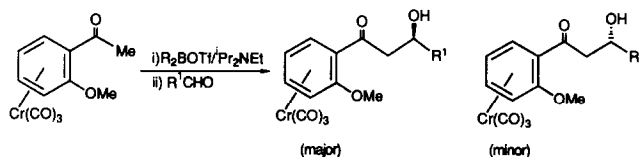
Scheme 117.



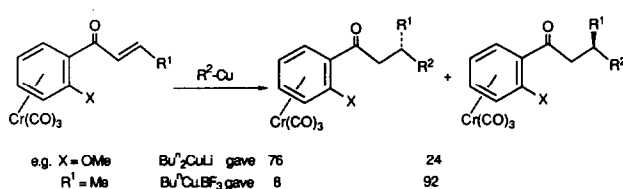
Scheme 118.

derivatives [267]. The C-6 regioisomer was produced using a bulky triisopropylsilyloxy C-8 substituent while the C-7 isomer was from the C-8 methoxy arene complex. Treatment of *endo*-[2-(dipropylamino)-8-methoxy-tetralin]Cr(CO)<sub>3</sub> with <sup>t</sup>BuOK and MeI placed a methyl group at C-1 *trans* to the C-2 amino group and *anti* to the Cr moiety. By contrast, the *exo* complex was methylated at the C-4 position *cis* to the amino group and *anti* to the Cr(CO)<sub>3</sub> moiety (Scheme 118).

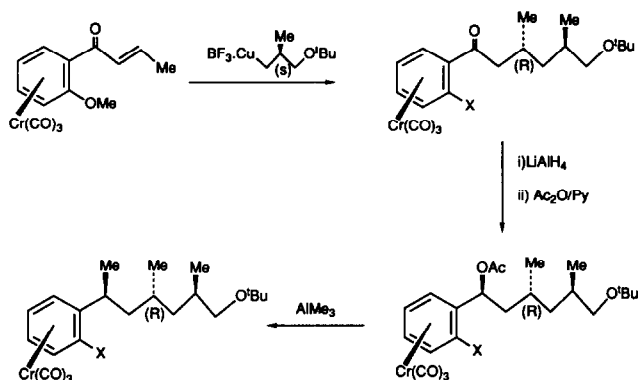
Aldol reactions of (*o*-alkoxyacetophenone)Cr(CO)<sub>2</sub>L (L = CO, PR<sub>3</sub>) complexes with boron enolates gave mainly one diastereomer from attack at the re-face of the aldehydes (Scheme 119) [268]. The *o*-substituent and the Cr-ligands were found to exert major influences on the selectivity. For (*o*-methoxyacetophenone)Cr(CO)<sub>2</sub>L, *anti* boron enolate was formed *via* coordination with the benzylic carbonyl oxygen. Attack at the re-face of the aldehyde through a six-membered cyclic twist-boat transition state led to diastereoselective aldol condensations.



Scheme 119.



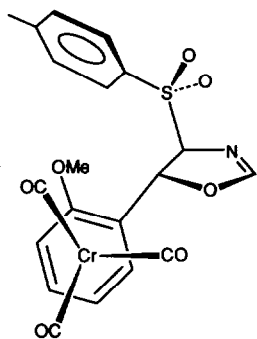
Scheme 120.



Scheme 121.

Conjugate addition of organocopper reagents to *o*-alkenylphenyl (*E*)- $\alpha,\beta$ -unsaturated enone) $\text{Cr}(\text{CO})_3$  complexes caused a dramatic reversal of diastereofacial selectivity [269]. Gilman reagents attacked at the *si*-face at the  $\beta$ -position of the enone double bond while  $\text{RCu}.\text{BF}_3$  attacked at a *re*-face of the  $\beta$ -C of the enone (Scheme 120). This diastereoselective 1,4-conjugate addition provided a new method for remote stereocontrol at the 1,3,5-positions of the side chain (Scheme 121).

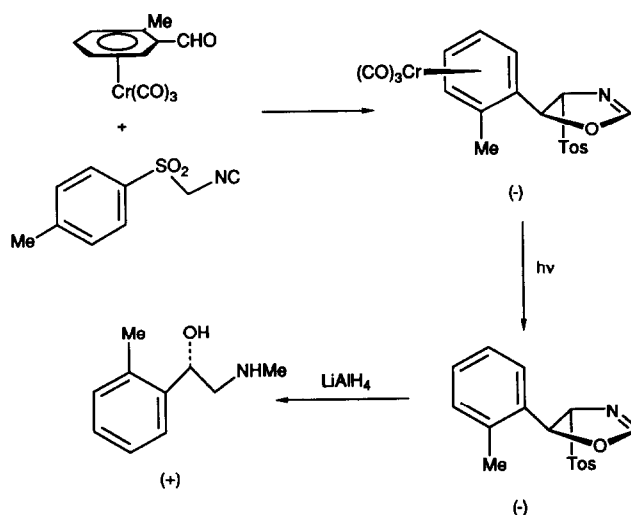
An optically pure (+)-*S*-halostachine analog was prepared in 57% yield in three steps from optically pure (–)-*aR*-[*o*-tolualdehyde] $\text{Cr}(\text{CO})_3$  (Scheme 122) [270]. The X-ray structure of the intermediate oxazoline complex confirmed the proposed approach of the nucleophile (103).



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(1*R*,2*S*) Norephedrine was bisalkylated to give *N,N*-dialkyl precursors which were complexed to  $\text{Cr}(\text{CO})_3$  [271]. These catalysts were found to mediate the addition of diethylzinc to a variety of aldehyde with very high enantioselectivity (Scheme 123).

Nucleophile addition and acylation of (benzene) $\text{Cr}(\text{CO})_2\text{L}$  (L =  $\text{PPh}_3$ ,  $\text{P}(\text{OMe})_3$ ,  $\text{PPh}_2$ -(–)-menthyl,  $\text{P}(\text{OPh})_2$ -(–)-menthyloxy,  $\text{P}(-)$ -menthyloxy) $_3$  gave *trans*-5,6-disubstituted cyclohexadienes [272]. The chiral phosphines led to low-to-moderate asymmetric induction. Evidence for alkylation at Cr *trans* to the phosphine was presented.



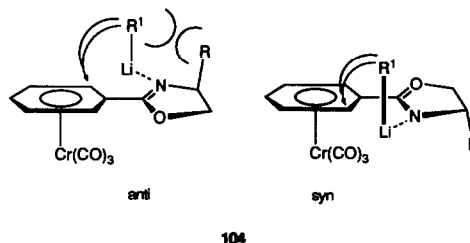
Scheme 122.

Diastereoselective complexation of  $\text{Cr}(\text{CO})_3$  by tetralol derivatives was the key step in the efficient enantioselective preparation of the valuable 1-tetralone derivative of  $\text{Cr}(\text{CO})_3$  (Scheme 124) [273].

Chiral 1,2-disubstituted arene complexes of  $\text{Cr}(\text{CO})_3$  with  $\text{Ni}(\text{acac})_2$  catalyzed the enantioselective (up to 78% ee) conjugate addition of diethylzinc to chalcone (Scheme 125) [274].

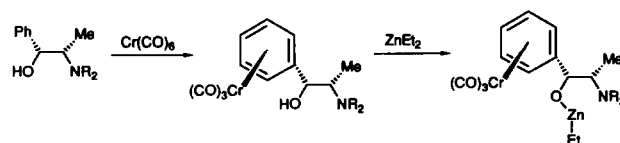
An asymmetric aldol reaction of (+)- $\text{Cr}(\text{CO})_3$  complexed *o*-substituted benzaldehyde with the titanium enolate from the ethanethiolate yielded the anti-aldol product stereoselectively (Scheme 126) [275].

Enantiomerically pure (2-phenyl-4,5-dihydrooxazole) $\text{Cr}(\text{CO})_3$  complexes were subjected to low-temperature sequential additions of  $\text{LiR}$  and allyl bromide to give cyclohexadiene derivatives with high diastereoselectivity (Scheme 127) [276]. This selectivity is suggested to originate from the favored Li coordination by the *syn* rotamer (104).

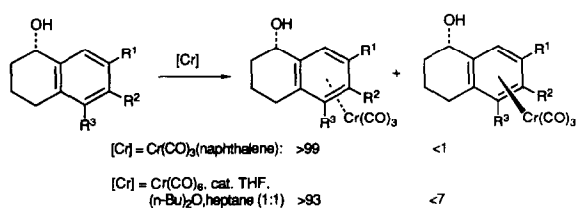


104

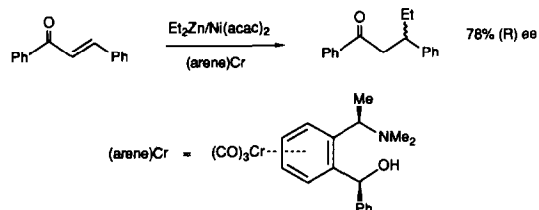
Chiral *o*-substituted benzaldehyde complexes of  $\text{Cr}(\text{CO})_3$  were obtained by the resolution of their di-



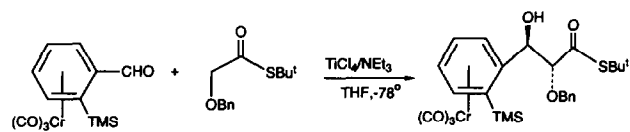
Scheme 123.



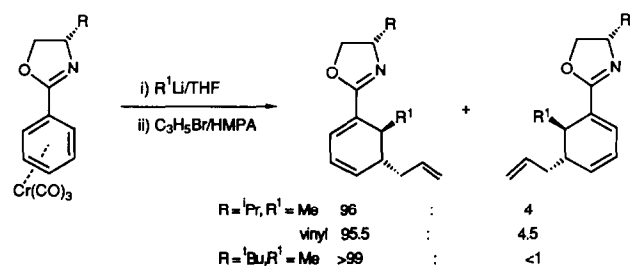
Scheme 124.



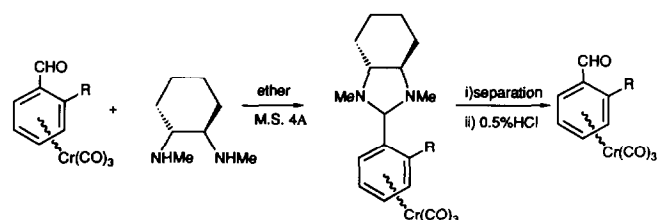
Scheme 125.



Scheme 126.



Scheme 127.



Scheme 128.

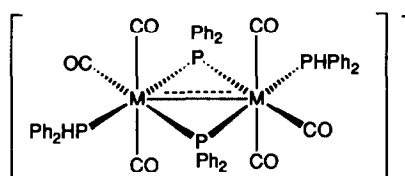
astereomeric aminals with (*R,R*)-1,2-bis(*N*-methylamino)cyclohexane [277]. Subsequent acid-hydrolysis yielded the homochiral aldehyde complexes readily (Scheme 128).

## 10. Binuclear complexes

### 10.1. Redox chemistry

Oxidation of (HPh<sub>2</sub>P)(CO)<sub>3</sub>M(PPh<sub>2</sub>)<sub>2</sub>M(CO)<sub>3</sub><sup>-</sup> (PPh<sub>2</sub>H) (M = Mo, W) with AgPF<sub>6</sub> produced the 33-electron phosphido-bridged bimetallic cations which

were much more stable than the corresponding [(CO)<sub>4</sub>M(PPh<sub>2</sub>)<sub>2</sub>M(CO)<sub>4</sub>]<sup>+</sup> species (**105**) [278].

**105**

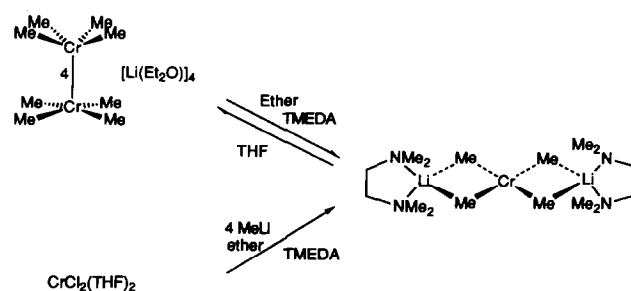
Photochemistry of [CpW(CO)<sub>2</sub>]<sub>2</sub> in the presence of *o*-quinones or *p*-benzoquinones were studied by EPR [279]. With *o*-quinones, two successive paramagnetic species CpW(CO)<sub>3</sub>(*o*-quinone) and CpW(CO)<sub>2</sub>(η<sup>2</sup>-*o*-quinone) were produced. With *p*-benzoquinones in THF, paramagnetic carbonyl-bonded complexes of CpW(CO)<sub>3</sub>(*p*-benzoquinone) were observed while in toluene, a C-bonded complex was formed instead.

The reversible two-electron oxidation of the anionic dimer [W<sub>2</sub>(SBz)<sub>2</sub>(CO)<sub>8</sub>]<sup>2-</sup> was studied [280]. At 25°C, the homogeneous disproportionation constant of the 1-radical was equal to 7500 ± 4000. The electronic destabilization of this relative to the dianion and W<sub>2</sub>(SBz)<sub>2</sub>(CO)<sub>8</sub> was proposed to explain the reversal of the individual 1-electron redox potentials.

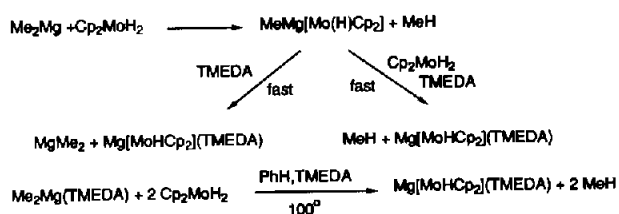
### 10.2. Synthesis and substitution chemistry

The formally Cr–Cr quadruply-bonded complex [Li(Et<sub>2</sub>O)]<sub>4</sub>[Cr<sub>2</sub>Me<sub>8</sub>] was reversibly cleaved to the monomer by TMEDA in an unprecedented reaction [281]. The resulting [Li(TMEDA)]<sub>2</sub>[CrMe<sub>4</sub>] structure consisted of a paramagnetic square-planar Cr<sup>II</sup> center. This same product was also formed directly from CrCl<sub>2</sub>(THF)<sub>2</sub> by reaction with four equivalents of methyl lithium (Scheme 129). The importance of the Cr–Me–Li–Me–Cr bridge in the dimeric precursor was pointed out since the analogous molybdenum dimer was resistant to such cleavages.

Neither MgCp<sub>2</sub> nor MgCp<sub>2</sub><sup>\*</sup> reacted with Cp<sub>2</sub>MH<sub>2</sub> (M = Mo, W) while MgMe<sub>2</sub>/TMEDA produced Mg[Cp<sub>2</sub>Mo(H)]<sub>2</sub>(TMEDA) (Scheme 130) [282]. The tungsten analogue was unreactive.

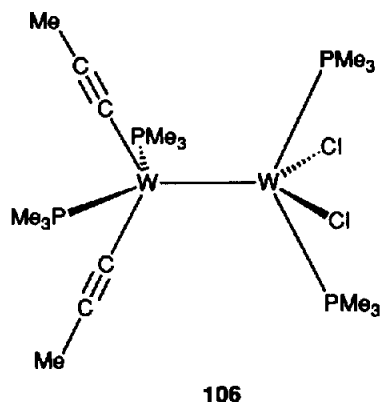


Scheme 129.

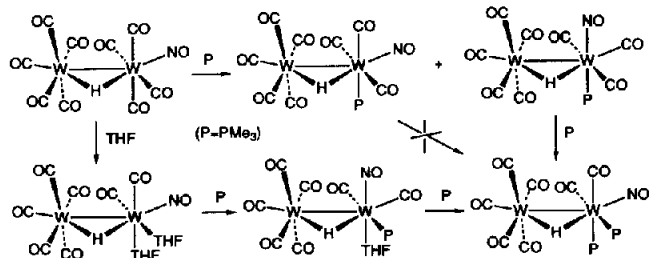


Scheme 130.

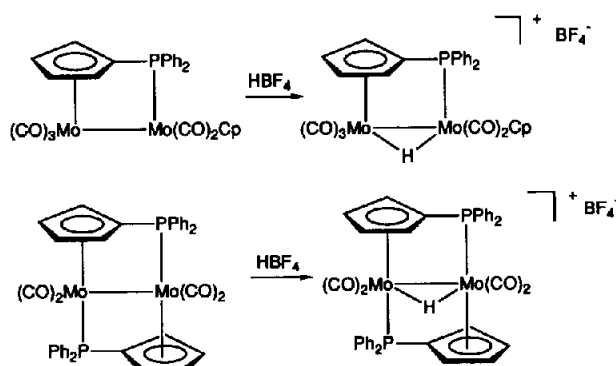
In an attempt to prepare conjugated bimetallic polyynes, two equivalents of  $\text{LiC}\equiv\text{CMe}$  were reacted with  $\text{W}_2\text{Cl}_4(\text{PMe}_3)_4$  yielding  $\text{W}_2$ -1,1-( $\text{C}\equiv\text{CMe}$ )<sub>2</sub>-2,2- $\text{Cl}_2(\text{PMe}_3)_4$  [283]. The asymmetric substitution was confirmed by X-ray crystallography (**106**). The short W-C (2.13 Å) distances were proposed to suggest strong  $\delta(\text{MM})-\pi(\text{CC})$  conjugation. Both long-range proton NMR coupling, the band red shifts and band intensity of the  $\delta \rightarrow \delta^*$  electronic absorption spectrum of the complex were also consistent with  $\delta-\pi$  conjugation, indicating strong similarities to conjugated organic molecules.



Carbonyl substitution of  $\text{W}_2(\text{CO})_7(\text{NO})(\mu\text{-H})(\mu\text{-Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2)$  ( $n = 1-3$ ) gave the corresponding monosubstituted complexes with  $\text{L} = \text{PhPH}_2$ ,  $\text{PrNC}$  [284]. Deprotonation of the  $\text{PhPH}_2$  complex followed by Michael addition onto several olefin derivatives yielded, for example,  $\text{W}_2(\text{CO})_6(\text{NO})(\text{H})(\text{DPPM})(\text{PhPCH}_2\text{CH}_2\text{X})$  ( $\text{X} = \text{CN}, \text{C}(\text{O})\text{H}, \text{C}(\text{O})\text{Me}$ ). Interconversion of these diastereomers were thought to involve dissociation of the  $\text{PhPCH}_2\text{CH}_2\text{X}$  ligand.



Scheme 131.



Scheme 132.

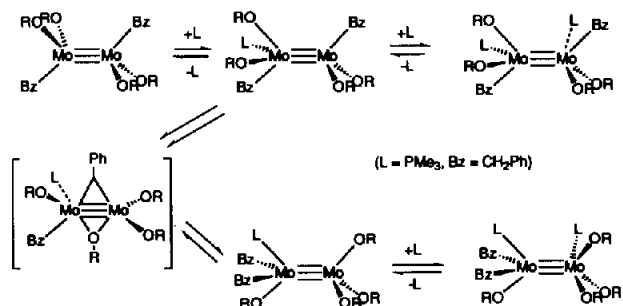
Ligand substitution of  $\text{HW}_2(\text{CO})_9(\text{NO})$  and  $\text{HW}_2(\text{CO})_7(\text{THF})_2(\text{NO})$  had been investigated using multinuclear NMR and IR spectroscopy [285]. Both were found to follow dissociative pathways with subsequent rearrangement of the nitrosyl ligand in the product (Scheme 131). Isolated products included  $\text{HW}_2(\text{CO})_8\text{-}[\text{P}(p\text{-C}_6\text{H}_4\text{X})_2(\text{NO})]$  ( $\text{X} = \text{Me}, \text{OMe}, \text{F}$ ),  $\text{NMe}_4[\text{HW}_2(\text{CO})_7(\text{S}_2\text{CNR}_2)(\text{NO})]$ , and  $\text{HW}_2(\text{CO})_7(\text{py})_2(\text{NO})$ .

New complexes of the heterodifunctional ligand  $\text{Cp-PPh}_2$  ( $\text{L}$ ) of Mo and W have been reported [286]. These included  $\text{CpMoM}(\mu\text{-L})(\text{CO})_5$  ( $\text{M} = \text{Mo}, \text{W}$ ),  $\text{Mo}_2(\mu\text{-L})(\eta^5\text{-L})(\text{CO})_5$ ,  $\text{Mo}_2(\mu\text{-L})_2(\text{CO})_4$ , and  $\text{Mo}_2(\mu\text{-L})(\eta^5\text{-L})(\text{CO})_4\text{P}(\text{OMe})_3$ . Protonation of these resulted in  $\mu\text{-H}$  cationic complexes (Scheme 132).

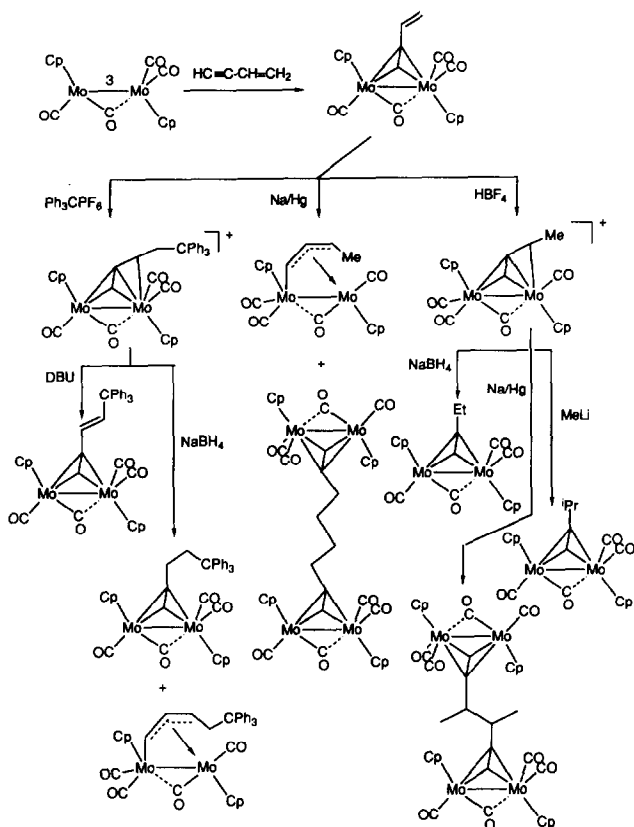
Addition of 1-2 equivalents of trimethylphosphine to 1,2- $\text{Mo}_2(\text{Bz})_2(\text{O}^i\text{Pr})_4$  led to an equilibrium mixture of the two reagents and  $\text{PMe}_3(\text{Bz})_2(\text{O}^i\text{Pr})\text{Mo}\equiv\text{Mo}(\text{O}^i\text{Pr})_3$  (Scheme 133) [287]. The new adduct lost  $\text{PMe}_3$  in the solid state upon warming in vacuum. In solution, it reversibly added a second phosphine to give an unsymmetrical adduct  $\text{PMe}_3(\text{Bz})_2(\text{O}^i\text{Pr})\text{Mo}\equiv\text{Mo}(\text{O}^i\text{Pr})_3\text{PMe}_3$ . Bridging and monodentate isomeric forms of the bis(dimethylphosphino)methane adduct were also detected in solution.

### 10.3. Organic chemistry

Reaction of vinylacetylene with  $[\text{CpMo}(\text{CO})_2]_2$  afforded the adduct  $[\text{CpMo}(\text{CO})_2]_2(\mu\text{-HC}\equiv\text{CCH}=\text{CH}_2)$  [288]. Protonation by  $\text{HBF}_4$  yielded the allylic cation



Scheme 133.

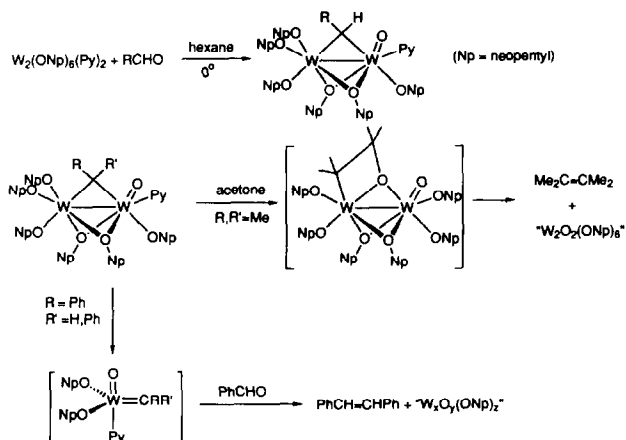


Scheme 134.

$[\{\text{CpMo}(\text{CO})_2\}_2(\mu-\eta^2, \eta^3-\text{HC}\equiv\text{CC}(\text{H})\text{Me})]^+$ . Nucleophilic attacks using  $\text{NaBH}_4$  or  $\text{MeLi}$  occurred exclusively at the C bearing the Me group to give  $\mu$ -alkyne complexes  $[\{\text{CpMo}(\text{CO})_2\}_2(\mu-\text{HC}\equiv\text{CCH}_2\text{Me})]$  and  $[\{\text{CpMo}(\text{CO})_2\}_2(\mu-\text{HC}\equiv\text{CCHMe}_2)]$  respectively. Reaction of  $\text{Ph}_3\text{CPF}_6$  with the vinylacetylene adduct led instead to  $[\{\text{CpMo}(\text{CO})_2\}_2(\mu-\eta^2, \eta^3-\text{HC}\equiv\text{CHCH}_2\text{-CPh}_3)]^+$ . Delocalization of the positive charge produced two attack sites for  $\text{NaBH}_4$  to form, in addition to the  $\mu$ -alkyne complex, also the allylic  $[\{\text{CpMo}(\text{CO})_2\}_2(\mu-\sigma, \eta^3-\text{HCCHCH}_2\text{CPh}_3)]$ . Reduction of the vinylacetylene adduct with  $\text{Na}(\text{Hg})$  produced the allylic  $[\{\text{CpMo}(\text{CO})_2\}_2(\mu-\sigma, \mu^3-\text{HCCHCHMe})]$  and tetrametallic  $[\{\text{CpMo}(\text{CO})_2\}_2]_2 \mu-(\mu-\text{HC}\equiv\text{CCH}_2\text{CH}_2)_2$  (Scheme 134).

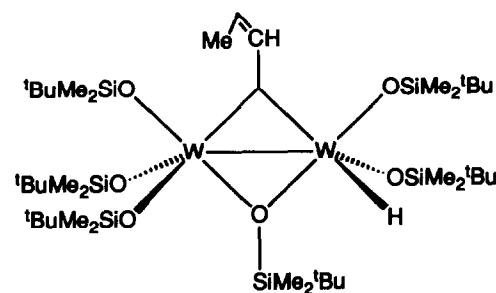
Studies on the olefination reactions of  $\text{W}_2(\text{OCH}_2\text{-}^t\text{Bu})_6\text{Py}_2$  with aldehydes or ketones revealed two stages [289]. Initial reductive cleavage of the carbonyl group gave a bridging alkylideneoxo complex. Cyclopropanecarboxyaldehyde and  $\text{W}_2(\text{OCH}_2\text{-}^t\text{Bu})_6\text{py}_2$  yielded  $\text{W}_2(\text{O})(\mu-\text{CH}-c-\text{C}_3\text{H}_5)(\text{OCH}_2\text{-}^t\text{Bu})_6\text{py}$  with retention of the cyclopropyl ring, suggesting a concerted process. The second stage involved formation of the olefin  $\text{C}=\text{C}$  bond *via* a proposed dimetallaoxacyclopentane complex (Scheme 135).

Reaction between  $1,2\text{-W}_2\text{Cl}_2(\text{NMe}_2)_4$  and  $1,4\text{-}$



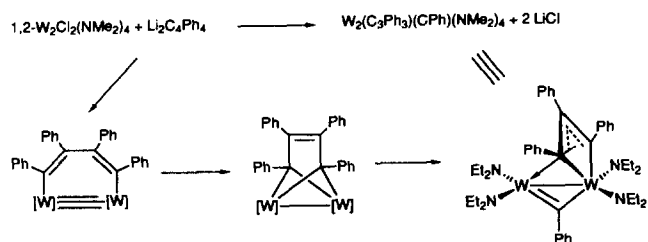
Scheme 135.

$\text{Li}_2\text{C}_4\text{Ph}_4$  yielded black  $\text{W}_2(\mu-\text{C}_3\text{Ph}_3)(\mu-\text{CPh})(\text{NMe}_2)_4$  which contained a  $\text{W}-\text{W}$  bond bridged by a benzyldiynide group and a metallacyclobutadiene ligand (Scheme 136) [290]. Reaction of ethylene with the ditungsten complex  $\text{W}_2(\text{C}_2\text{H}_2)(\text{OSi}^t\text{BuMe}_2)_6\text{Py}$  at  $-20^\circ\text{C}$  gave blue, crystalline alkylidene-bridged  $\text{W}_2\text{H}(\mu-\text{CCH}=\text{CHMe})(\text{OSi}^t\text{BuMe}_2)_6$  (107) [291]. Alcoholysis of  $\text{W}_2(\text{OCH}_2\text{-}^t\text{Bu})_6(\text{C}_2\text{H}_4)_2$  with  $^t\text{BuOH}$  formed  $\text{W}_2(\mu-\text{CMe})(\text{OCH}_2\text{-}^t\text{Bu})_6(\text{O}^t\text{Bu})$ .

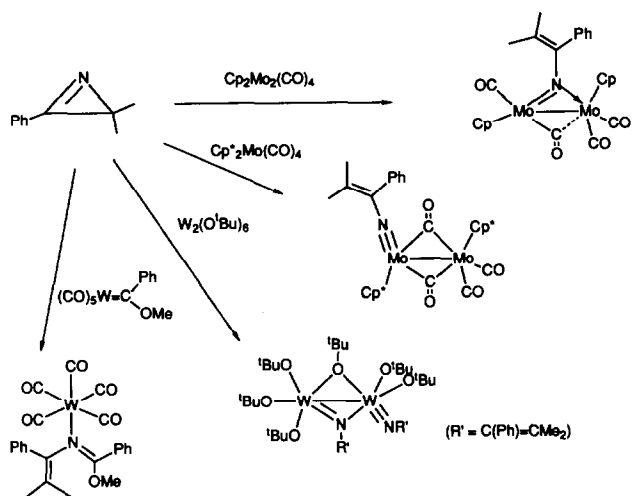


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Reaction of  $\text{Cp}'_2\text{M}_2(\text{CO})_4$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{Cp}' = \text{Cp}, \text{Cp}^*$ ) and  $\text{W}_2(\text{O}^t\text{Bu})_6$  with  $2,2\text{-dimethyl-3-aryl-2H-aziridines}$  led to the vinylimido adducts  $\text{Cp}'_2\text{M}_2(\text{CO})_4[\text{NC}(\text{Ar})=\text{CMe}_2]$ ,  $\text{Cp}_2\text{Mo}_2(\text{CO})_4[\text{NC}(\text{Ph})=\text{CMe}_2]$ , and  $\text{W}_2(\text{O}^t\text{Bu})_6[\text{NC}(\text{Ar})=\text{CMe}_2]$  [292]. Reaction of the aziridines with carbene complex  $\text{W}(\text{CO})_5=\text{C}(\text{OMe})\text{Ph}$  led to vinylimido  $\text{W}(\text{CO})_5\text{N}[\text{C}(\text{OMe})\text{Ph}][\text{CPh}=\text{CMe}_2]$



Scheme 136.



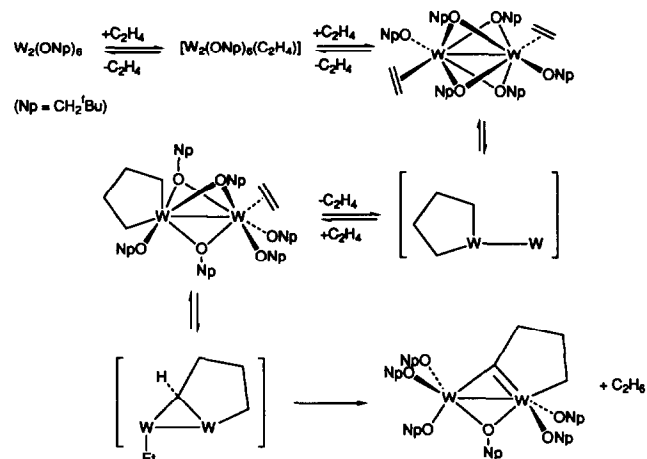
Scheme 137.

(Scheme 137). Air-oxidation of this released the free imidate ligand.

Excess ethylene reacted with  $W_2(OCH_2^tBu)_6$  at  $0^\circ C$  in hydrocarbon solution to give  $W_2(OCH_2^tBu)_6(C_2H_4)_2$  [293]. This molecule was found to have near  $C_2$  symmetry with four unsymmetrically bridging alkoxide ligands spanning the W–W bond. Due to W  $d\pi$ -olefin  $\pi^*$  bonding, the two olefin  $C_2$  axes were found to be mutually orthogonal as well as perpendicular to the W–W axis. Solution dynamical behavior has been delineated by labeling and NMR techniques. Above  $0^\circ C$ , this complex reacted further with ethylene to afford  $W_2(OCH_2^tBu)_6(\mu-CCH_2CH_2CH_2)$  and ethane *via* a metallacyclopentane–ethylene intermediate  $W_2(OCH_2^tBu)_6(CH_2)_4(C_2H_4)$  (Scheme 138).

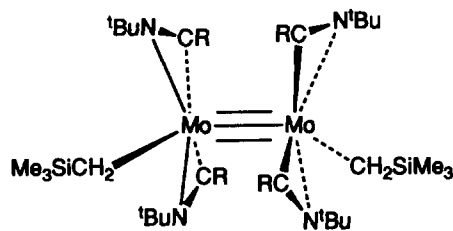
The dimer  $Mo_2(CH_2SiMe_3)_6$  reacted readily with four or more equivalents of  $^tBuNC$  to form the  $\mu^2$ -iminoacyl product 1,2- $Mo_2(CH_2SiMe_3)_2(CN^tBu)_4$  [294]. Its solid-state structure consisted of an unbridged  $Mo\equiv Mo$  with each metal further  $\pi$ -bonded to two iminoacyl groups as well as the alkyl group (108). The formally five-coordinate metals were found to have near pentagonal planar geometries. Facile rotation around the metal–metal bond was detected by dynamic NMR.

The  $\alpha$ -substituted alkyne complex  $Cp_2Mo_2(CO)_4-(CHCH_2OMe)$  was deprotonated with sodium amide in the presence of 15-crown-5 to give the  $\sigma,\pi$ -acetylide

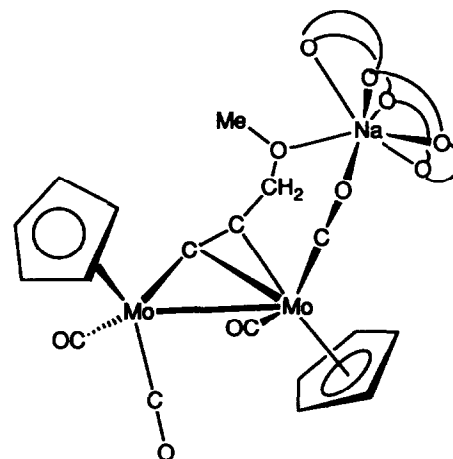


Scheme 138.

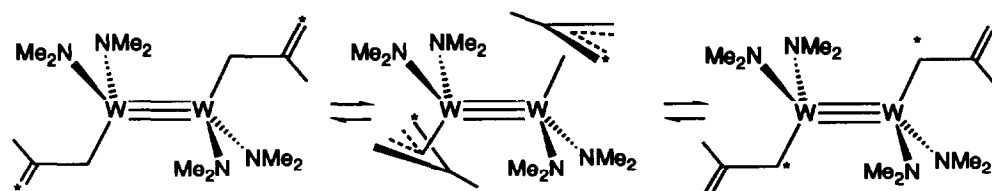
complex  $[Na(15\text{-crown-}5)[Cp_2Mo_2(CO)_4(\mu-\eta^1:\eta^2-C\eta-CCH_2OMe)]$  (109) [295].



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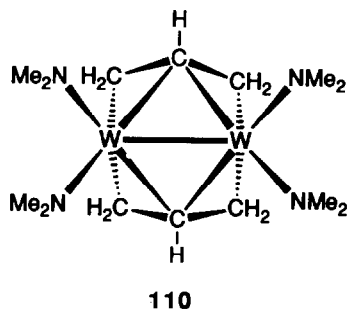


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Scheme 139.

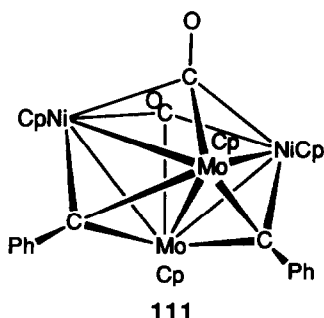
Reaction between two equivalents of  $\text{RMgCl}$  and  $1,2\text{-W}_2\text{Cl}_2(\text{NMe}_2)_4$  produced  $\text{W}_2\text{R}_2(\text{NMe}_2)_4$  ( $\text{R} = \text{allyl}, 2\text{-Me-allyl}$ ) [296]. Solid-state structure of the allyl complex was found to have  $\text{C}_2$  symmetry with bridging allyl groups and terminal amido ligands (**110**). Both bonding details and Fenske–Hall MO calculations suggested donation from the  $\text{W}\equiv\text{W}^{6+}$  core to the  $\pi^*$ -MO of the allylic ligands. In solution, a second isomer with two  $\eta^3$ -allylic ligands was observed. For the methylallyl complex, solution dynamic NMR data revealed *anti*- and *gauche*-rotamers as well as a facile process equilibrating both ends of the 2-Me-allyl ligand *via* an  $\eta^3$ -bound intermediate (Scheme 139).



## 11. Metal clusters

Reaction of  $\text{Hg}[(\text{arene})\text{Cr}(\text{CO})_3]_2$  with  $\text{HCCO}_3(\text{CO})_9$  yielded mixed metal clusters  $(\text{arene})\text{Cr}(\text{CO})_3\text{CCO}_3(\text{CO})_9$  [297]. At  $-25^\circ\text{C}$ , a chemically-reversible one-electron oxidation was observed for these complexes.

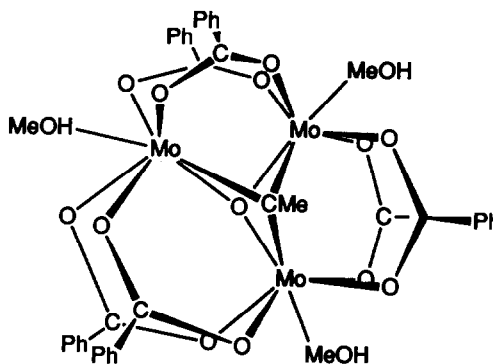
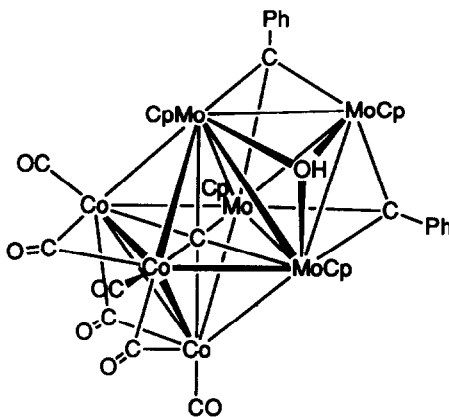
Refluxing of  $\text{Cp}_2\text{Ni}_2(\text{C}_2\text{Ph}_2)$  with  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  in *o*-xylene afforded a mixed-metal cluster  $\text{Cp}_4\text{Ni}_2\text{Mo}_2(\mu_3\text{-CPh})_2(\mu_3\text{-CO})_2$  with carbyne bridges under the  $\text{Mo}_2\text{Ni}_2$  butterfly cluster wings (**111**) [298]. Reaction



of  $\text{Co}_2(\text{CO})_6(\text{C}_2\text{Ph}_2)$  with  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  under similar conditions yielded an unusual heptanuclear cluster  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-OH})(\mu_3\text{-CPh})_2(\mu_6\text{-C})\text{Co}_3(\mu\text{-CO})_3(\text{CO})_3$  (**112**). This structure resulted from  $\text{C}\equiv\text{O}$  as well as  $\text{C}\equiv\text{C}$  bond rupture and featured  $\mu_6$ -carbide bridging of the distorted tetrahedral  $\text{Cp}_4\text{Mo}_4(\mu_3\text{-OH})(\mu_3\text{-CPh})_2$  fragment with the triangular  $\text{Co}_3(\text{CO})_6$  fragment.

Acetate replacement by benzoates in  $[\text{Mo}_3(\mu_3\text{-CMe})(\mu_3\text{-O})(\text{OAc})_6(\text{H}_2\text{O})_3]^+$  in  $\text{MeOH}/\text{MeCN}$  gave

$[\text{Mo}_3(\mu_3\text{-CMe})(\mu_3\text{-O})(\mu\text{-PhCOO})_6(\text{MeOH})_3]^+$  which could not be directly synthesized (**113**) [299].

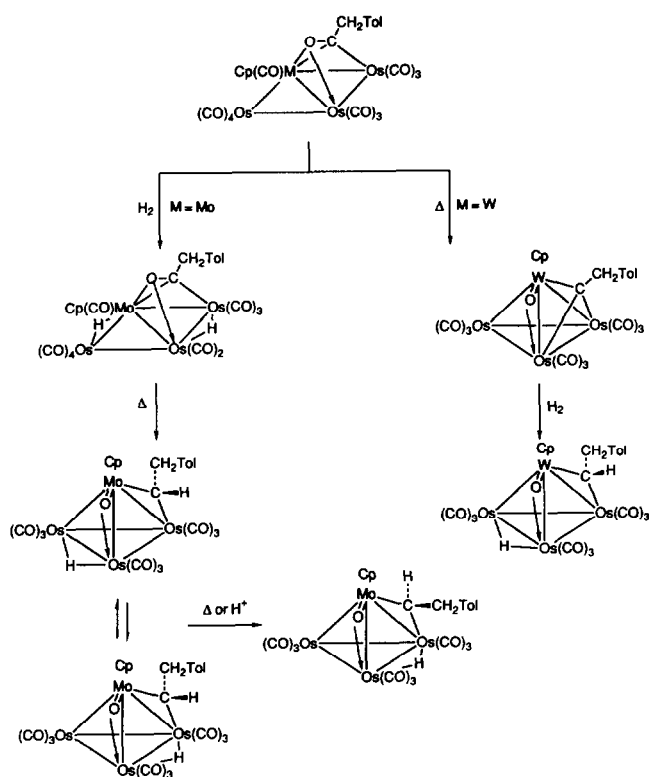


Treatment of  $\text{CpMo}(\equiv\text{CTol})(\text{CO})_2$  with  $\text{H}_2\text{Os}_3(\text{CO})_{10}$  produced three mixed-metal clusters:  $\text{CpMoOs}_3(\text{CO})_{11}\{\mu_3\text{-C(O)CH}_2\text{Tol}\}$  (65%),  $\text{CpMoOs}_3(\text{CO})_{10}(\mu_3\text{-CTol})(\mu\text{-H})$  (10%), and  $\text{CpMoOs}_3(\text{CO})_{10}(\mu_3\text{-}\eta^2\text{-C}_2\text{Tol}_2)(\mu\text{-H})$  (6%) (**114**, **115**, **116**) [300]. The minor products have been examined by dynamic  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.

Decarbonylation of  $\text{CpMoOs}_3(\text{CO})_{11}\{\mu_3\text{-}\eta^2\text{-C(O)CH}_2\text{Tol}\}$  with  $\text{Me}_3\text{NO}$  followed by hydrogenation led to  $\text{CpMoOs}_3(\text{CO})_{10}(\text{H})_2(\text{C(O)CH}_2\text{Tol})$  [301]. Thermolysis of this dihydride cluster induced scission of the acyl C–O to give three isomeric oxo-alkylidene compounds  $\text{CpMoOs}_3(\text{CO})_9(\text{H})(\text{O})(\text{CHCH}_2\text{Tol})$ . Heating the isomeric mixture to  $100^\circ\text{C}$  resulted in conversion to a single species (Scheme 140). Its structure revealed a tetrahedral  $\text{MoOs}_3$  core with oxo, alkylidene, and hydride bridging each edge of one of the Os–Os–Mo faces. These results were discussed in comparison to previous tungsten analogues.

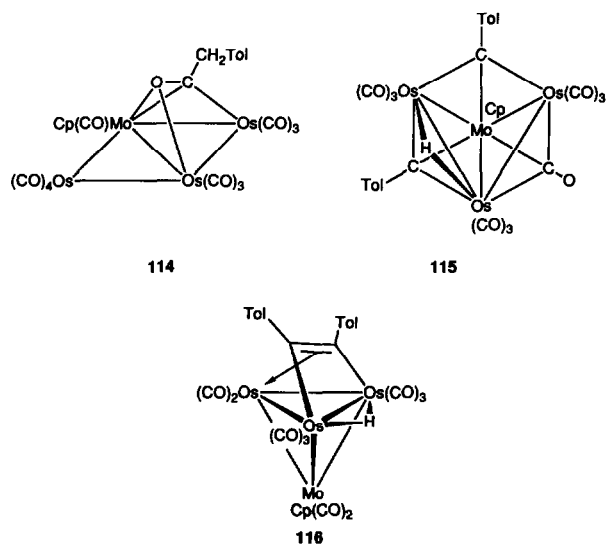
Reaction of the carbyne complex  $\text{Mo}(\equiv\text{CPh})(\text{CO})_2\text{-Br}(\text{py})_2$  with  $\text{Co}_2(\text{CO})_8$ ,  $\text{Fe}_2(\text{CO})_9$ , and  $\text{Mn}_2(\text{CO})_{10}$  gave tetrahedral trimetallic clusters  $\text{Co}_2\text{Mo}(\mu_3\text{-CPh})(\text{CO})_8\text{-}$





Scheme 140.

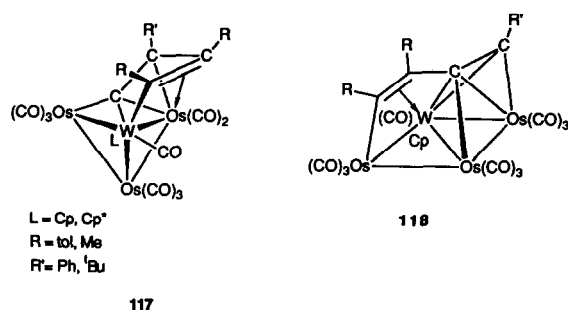
$\text{Br}(\text{py})_2$ ,  $\text{Fe}_2\text{Mo}(\mu_3\text{-CPh})(\text{CO})_9\text{Br}(\text{py})_2$ , and  $\text{Mn}_2\text{-Mo}(\mu_3\text{-CPh})(\text{CO})_{10}\text{Br}(\text{py})_2$  respectively (Scheme 141)



[302]. The structure of the  $\text{Co}_2\text{Mo}$  cluster with bipyridine was found to contain an isosceles metal triangle capped by the triply-bridging CPh group.

Condensation of 1:1 combinations of triosmium alkyne complexes  $\text{Os}_3(\text{CO})_{10}(\text{RC}\equiv\text{CR})$  ( $\text{R} = \text{Tol}, \text{Ph}$ ) with the acetylide  $\text{LW}(\text{CO})_3\text{C}\equiv\text{CR}'$  ( $\text{L} = \text{Cp}, \text{Cp}'$ ;  $\text{R}' = \text{Ph}, \text{tBu}$ ) produced six  $\text{WO}_3$  clusters [303]. Tetrahedral  $\text{LWOs}_3(\text{CO})_{10}[\text{CC}(\text{R}')\text{C}(\text{R})\text{C}(\text{R})]$  complexes formed

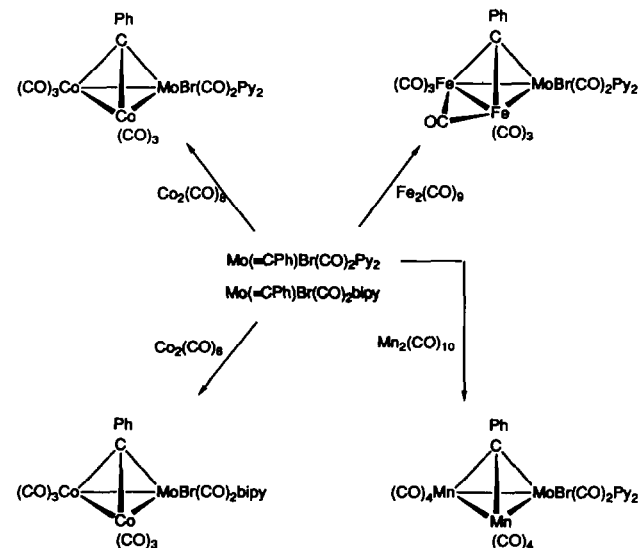
from the coupling of the ligated alkyne with the  $\beta\text{-C}$  of the acetylide were isolated in all cases (117). The only planar rhomboidal  $\text{CpWOs}_3(\text{CO})_{10}[\text{C}(\text{Me})\text{C}(\text{Me})\text{CC}(\text{Ph})]$  (118) originated from coupling to the  $\alpha\text{-acetylide}$



carbon. On heating, this lost CO to produce  $\text{CpWOs}_3(\text{CO})_9((\mu\text{-H})(\text{CCMeCMe})(\text{C}-\mu_2\text{-}\eta^2\text{-C}_6\text{H}_4))$  (119) via cleavage of the C-C bond of the  $\text{C}_4$  ligand. Three additional clusters were also isolated from the  $\text{Cp}^*\text{W}(\text{CO})_3(\text{CCPh})/\text{Os}_3(\text{CO})_{10}(\text{MeCCMe})$  reaction: butterfly complexes  $\text{Cp}^*\text{WOs}_3(\text{CO})_9(\text{MeCCMe})(\mu_3\text{-CCPh})$  and  $\text{Cp}^*\text{WOs}_3(\text{CO})_9(\text{MeCCMe})(\mu_4\text{-CCPh})$ , as well as tetrahedral  $\text{Cp}^*\text{WOs}_3(\text{CO})_9(\mu_3\text{-CPh})[\text{CC}(\text{Me})\text{C}(\text{Me})\text{CO}]$  (120, 121, 122).

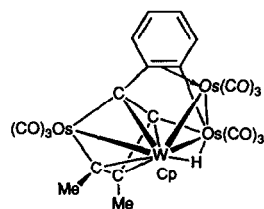
Treatment of the phenylimido cluster  $[\text{Cp}^*\text{WRu}_2(\text{CO})_7(\mu_3\text{-NPh})(\text{CF}_3\text{CCHCF}_3)]$  with hex-3-yne generated  $[\text{Cp}^*\text{WRu}_2(\text{CO})_6(\text{NPh})(\text{C}(\text{Et})\text{C}(\text{Et})\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3))]$ , a cluster with a novel terminal phenylimido ligand (123) [304]. By contrast, reaction with dimethylacetylenedicarboxylate afforded  $[\text{Cp}^*\text{WRu}_2(\text{CO})_6(\mu_3\text{-NPh})(\text{C}(\text{COOMe})\text{C}(\text{COOMe})\text{C}(\text{CF}_3)\text{CH}(\text{CF}_3))]$  (124), a cluster with a regular face-bridging imido group.

Reaction of  $\text{PPh}_3\text{AuCl}$  with  $\text{K}[\text{Cp}_2\text{Mo}_2(\text{H})(\text{PPh}_2)]$  gave  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-PPh}_2)(\mu\text{-AuPPh}_3)]$  (125) [305].

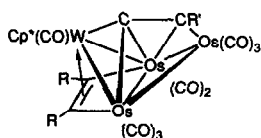


Scheme 141.

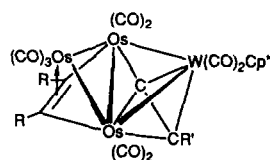
The structure of this and related complexes  $[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-H})(\mu\text{-PPh}_2)]$  (**126**) and  $\text{PPN}[\text{Cp}_2\text{Mo}_2(\text{CO})_4(\mu\text{-}$



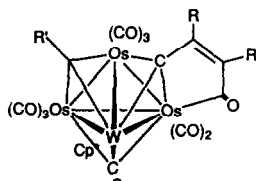
119



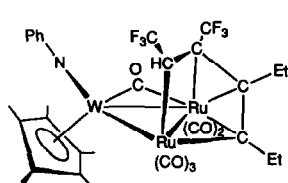
120



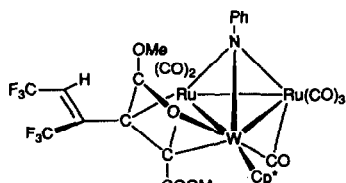
121



122

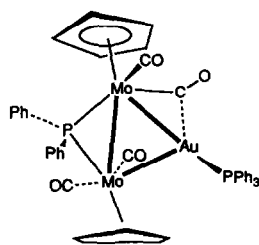


123

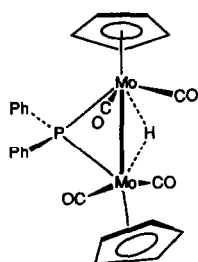


124

$\text{PPh}_2)_2]$  all contained  $\text{CpMo}(\text{CO})_2$  fragments bridged by  $\text{PPh}_2$  plus another  $\text{AuPPh}_3$ , H, or  $\text{PPh}_2$  bridge respectively.



125

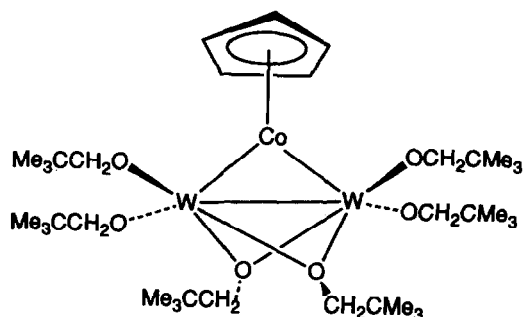


126

Reaction of  $[\text{W}_2(\text{OCH}_2^t\text{Bu})_6\text{py}_2]$  with  $\text{CpCo}(\text{ethylene})_2$  gave  $\text{CpCoW}_2(\text{OCH}_2^t\text{Bu})_6$  whose structure was compared to that of  $\text{W}_2(\text{OCH}_2^t\text{Bu})_6(\mu\text{-CO})$  by X-ray and by Fenske–Hall MO calculations (**127**) [306].

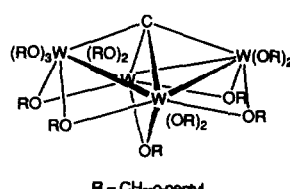
Two paths for the reductive cleavage of CO were explored [307]. Addition of CO to  $\text{W}_4(\text{OR})_{12}$  ( $\text{R} = \text{CH}_2\text{-}i\text{-pentyl}$ ) led to three products:  $\text{W}_4(\mu_4\text{-C}(\text{OR})_{14})$  (**128**),  $\text{W}_4(\mu_4\text{-CO})(\text{CO})_2(\text{OR})_{12}$  (**129**), and an oxotungsten alkoxide. The second product was favored by excess CO and was shown not to be an intermediate

for the CO cleavage. A second path used the reaction between  $\text{W}_2(\mu\text{-CO})(\text{O}^t\text{Bu})_6$  and  $\text{W}_2(\text{O}^t\text{Bu})_6$  in the

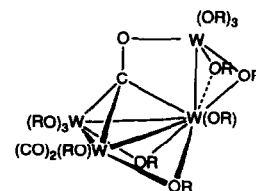


127

presence of excess ROH ( $\text{R} = \text{CH}_2^i\text{Bu}$ ,  $^i\text{Pr}$ ) to produce  $\text{W}_4(\mu_4\text{-C}(\text{OR})_{12})$  (**130**). The cores of **128** and **130** differ only in the position of the  $\mu_2$ -oxo group and its replacement by a pair of alkoxide ligands. These results represent the first successful cleavage of a CO to give carbide and oxide ligands in a molecular system. Competing reactions led to  $\text{W}_4(\text{CO})_2(\text{O}^t\text{Bu})_{12}$  and  $\text{W}_4(\text{OR})_{12}$ . Relevance to CO cleavage on a metal surface is also discussed.



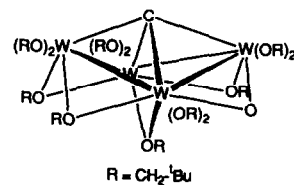
128



129

$\text{R} = \text{CH}_2\text{-}i\text{-pentyl}$

$\text{R} = \text{CH}_2\text{-}i\text{-pentyl}$



130

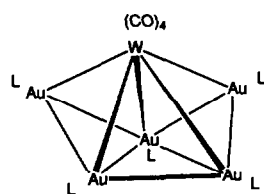
$\text{R} = \text{CH}_2^i\text{Bu}$

Reaction of  $[\text{AuPPh}_3\text{-}(\text{AuPPh}_3)_3]^{2+}$  with  $\text{W}(\text{CO})_3\text{-}(\text{MeCN})_3$  or  $\text{W}(\text{CO})_6$  gave  $[\text{W}(\text{CO})_4(\text{AuPPh}_3)_5]^+$  (**131**) and  $[\text{W}(\text{CO})_3(\text{AuPPh}_3)_7]^+$  (**132**) [308]. Additionally, electrophilic addition of  $\text{AuPPh}_3^+$  to the former gave  $[\text{W}(\text{CO})_4(\text{AuPPh}_3)_6]^{2+}$ .

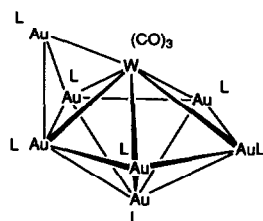
Photolysis of  $\text{Mo}(\text{CO})_6$  and  $\text{PPh}_3\text{AuN}_3$  in THF yielded cationic  $[(\text{PPh}_3\text{Au})_5\text{Mo}(\text{CO})_4]^+$  whose structure was determined to contain a capped trigonal bipyramidal  $\text{Au}_5\text{Mo}$  cluster with the Mo vertex equatorial [309].

Clusters of the type  $\text{M}(\text{CO})_5[\text{Os}(\text{CO})_3\text{PR}_3]_2$  ( $\text{M} =$

Cr, Mo, W; R = Me, OMe;  $R_3 = (\text{OCH}_2)_2\text{CMe}$  have been obtained from the uv-photolysis of  $(\text{PR}_3)(\text{CO})_4$ -



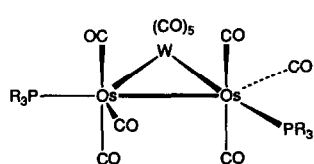
131



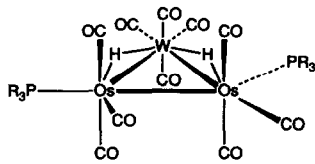
132

L =  $\text{PPh}_3$ 

Os- $\text{M}(\text{CO})_5$  in perfluorobenzene [310]. Their solid-state structures have been determined (133). C-13 NMR spectra of these clusters indicated presence of an additional isomer with both phosphorus ligands *trans* to the Os-Os bond. The hydride cluster  $(\text{CO})_4\text{W}[(\mu\text{-H})\text{Os}(\text{CO})_3\text{PMe}_3]_2$  (134) was synthesized from hydrogen and  $(\text{CO})_5\text{W}[\text{Os}(\text{CO})_3\text{PMe}_3]_2$ . Spectral data suggested bridging H's at each Os-W bond.

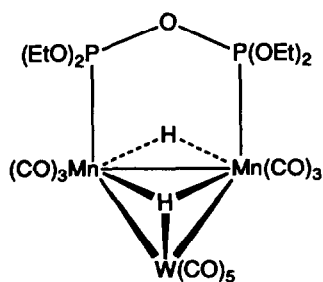


133



134

Low-temperature photolysis of the dihydride complex  $\text{Mn}_2(\text{H})_2(\text{L})(\text{CO})_6$  ( $\text{L} = (\text{EtO})_2\text{POP}(\text{OEt})_2$ ) with  $\text{W}(\text{CO})_6$  led to the thermally unstable cluster  $\text{Mn}_2\text{W}(\mu_2\text{-H})(\mu_3\text{-H})(\text{L})(\text{CO})_{11}$  (135) [311].

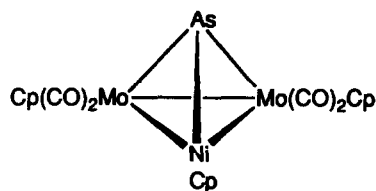


135

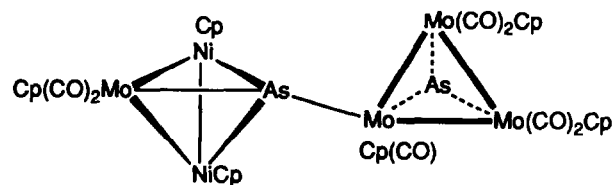
Photolysis of  $\text{AsCp}_3\text{Mo}_3(\text{CO})_6$  with  $\text{Cp}_2\text{Ni}_2(\text{CO})_2$  yielded the clusters  $\text{AsCp}_3\text{Mo}_2\text{Ni}(\text{CO})_4$  and  $\text{As}_2\text{Cp}_6\text{Mo}_4\text{Ni}_2(\text{CO})_7$  (136, 137) [312]. Similar photolysis of  $\text{AsCp}_3\text{Mo}_3(\text{CO})_6$  with  $\text{Pt}(\text{ethylene})(\text{PPh}_3)_2$  led to the butterfly cluster  $\text{AsCpMoPt}_2(\text{CO})_4(\text{PPh}_3)_2$ .

Reaction of  $\text{Na}[\text{CpMo}(\text{CO})_3]$  with  $\text{SbCl}_3$  in diglyme gave  $\text{Cp}_2\text{Mo}_2(\text{CO})_6$  and  $\text{Cp}_4\text{Mo}_5(\text{CO})_{14}(\mu_4\text{-Sb})_2$ , the structure of which consisted of a  $\text{Mo}_2\text{Sb}_2$  butterfly cluster bridged by a  $\text{CpMo}(\text{CO})_2$  fragment, one  $\text{CpMo}$ -

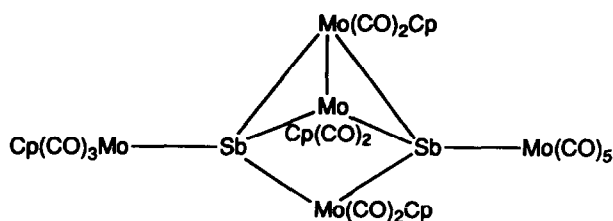
$(\text{CO})_3$  coordinated to an antimony atom, and a  $\text{Mo}(\text{CO})_5$  fragment coordinated to the other Sb atom (138) [313].



136

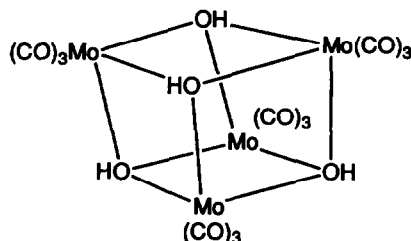


137



138

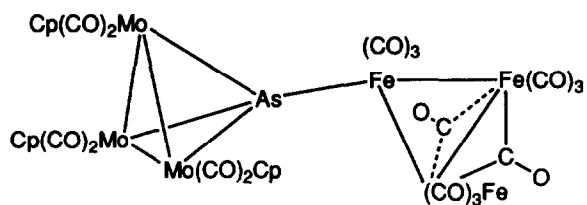
Synthesis of  $\text{Cs}_4[\text{Mo}_4(\mu_3\text{-OH})_4(\text{CO})_{12}]\cdot n\text{H}_2\text{O}$  (139) from  $\text{KOH}$  and  $\text{Mo}(\text{CO})_6$  in hot ethanol was described [313a]. Mo-95 NMR data of this and related clusters in polar solvents were also reported. The results raised some doubt on the identity of the  $\mu$ -triol complex  $\text{K}_3[\text{Mo}_2(\mu\text{-OH})_3(\text{CO})_6]$  previously described by Hieber.



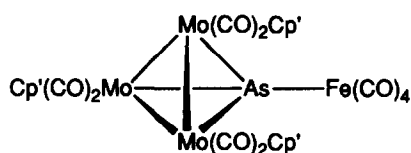
139

Photolysis of  $(\mu_3\text{-As})(\text{C}_5\text{H}_4\text{R})_3\text{Mo}_3(\text{CO})_3$  ( $\text{R} = \text{H}, \text{Me}$ ) with  $\text{Fe}_3(\text{CO})_{12}$  afforded the  $\mu_4$ -As clusters  $\text{As}(\text{C}_5\text{H}_4\text{R})_3\text{Fe}_3\text{Mo}_3(\text{CO})_{17}$  (140),  $\text{As}(\text{C}_5\text{H}_4\text{R})_3\text{FeMo}_3(\text{CO})_{10}$  (141), and  $\text{As}(\text{C}_5\text{H}_4\text{R})_3\text{Fe}_2\text{Mo}_3(\text{CO})_{12}$  (142) [314]. Similar reaction of  $\text{As}_2\text{Cp}'_2\text{Mo}_2(\text{CO})_4$  with  $\text{Fe}_3(\text{CO})_{12}$  led to  $\text{As}_2\text{Cp}'_2\text{Mo}_2\text{Fe}_4(\text{CO})_{17}$  (143) with a

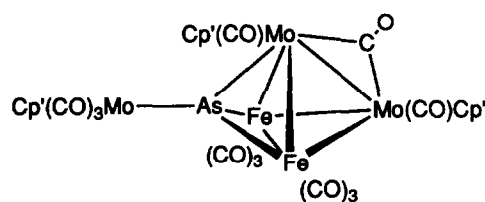
$\mu_5$ -As moiety. By comparison, thermal reaction of  $\text{As}_2\text{Cp}_2\text{Mo}(\text{CO})_4$  with  $\text{Fe}_3(\text{CO})_{12}$  yielded the square-pyramidal  $(\mu_4\text{-As})_2\text{Cp}_2\text{Mo}_2\text{Fe}_3(\text{CO})_{15}$  (**144**).



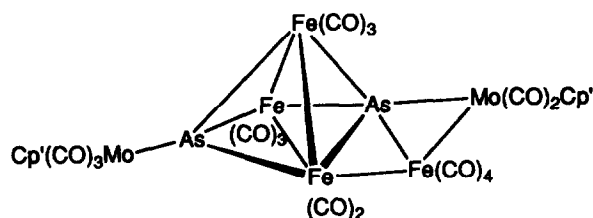
140



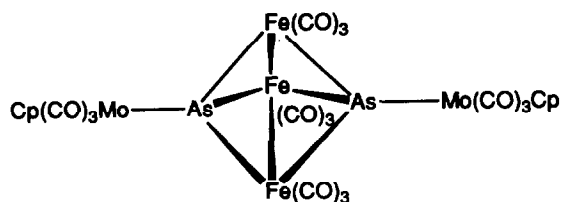
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142



143

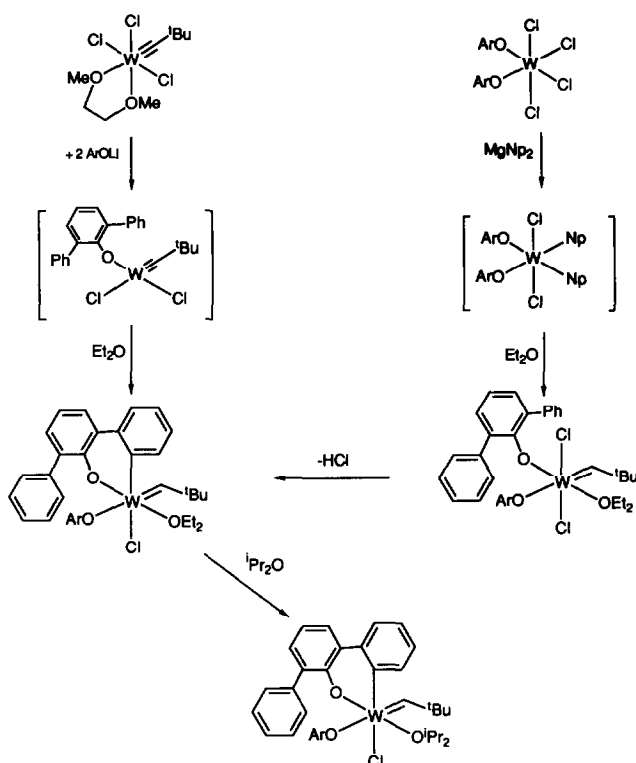


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## 12. Catalysis

### 12.1. Olefin metathesis

Reaction of  $\text{EtAlCl}_2$  with  $\text{Mo}(\text{OOCR})_2(\text{NO})_2$  yielded new complexes  $[(\text{AlCl}_2)_2(\text{OOCR})_2\text{Mo}(\text{NO})_2]$ .



Scheme 142.

$(\text{CHMe})_n$  and  $[(\text{EtAlCl}_2)_2(\text{AlCl}_2)_2(\text{OOCR})_2\text{Mo}(\text{NO})_2(\text{CHMe})]$  [315]. The latter were found to be active catalysts for olefin metathesis.

The syntheses of two cyclometallated aryloxy (chloro)neopentylidene-tungsten catalysts were described [316]. Either  $\text{WCl}_3(\text{C}^t\text{Bu})\text{DME}$  or  $\text{WCl}_4(\text{O}-2,6\text{-C}_6\text{H}_3\text{Ph}_2)$  led to these products (Scheme 142). Both were found to be excellent stereoselective metathesis catalysts for *cis/trans*-2-pentene, norbornene, 1-methylnorbornene, and ethyl oleate with retention of starting olefin configurations.

Several types of activated carbon were used as supports for  $\text{Mo}(\text{CO})_6/\text{C}$  homologation of ethylene to produce propene as well as metathesis of propene [317]. Pretreatment of the carbon surface with acids like  $\text{HCl}$ ,  $\text{HNO}_3$  or air oxidation resulted in enhanced activity. It was also found that the supported  $\text{Mo}(\text{CO})_6$  decomposed thermally by rapid loss of all  $\text{CO}$ 's.

The catalyst precursors  $\text{W}(\text{XO})_3(\text{allyl})\text{X}$  ( $\text{X} = \text{Cl}, \text{I}$ ) have been characterized by UV-Vis, IR, and ESCA spectroscopy [318]. In combination with  $\text{R}_n\text{SnCl}_{4-n}$  and activated  ${}^t\text{BuAlCl}_2/\text{O}_2$ , they had high activity for 2-pentene metathesis.

Solvent-free metathesis of difunctionalized linear olefins led to cyclized 5- and 7-membered ring products instead of linear polymer in the presence of the  $\text{Mo}(\text{=CHCMe}_2\text{Ph})(\text{NAr})(\text{OCMe}(\text{CF}_3)_2)_2$  catalyst [319].

### 12.2. Olefin polymerization

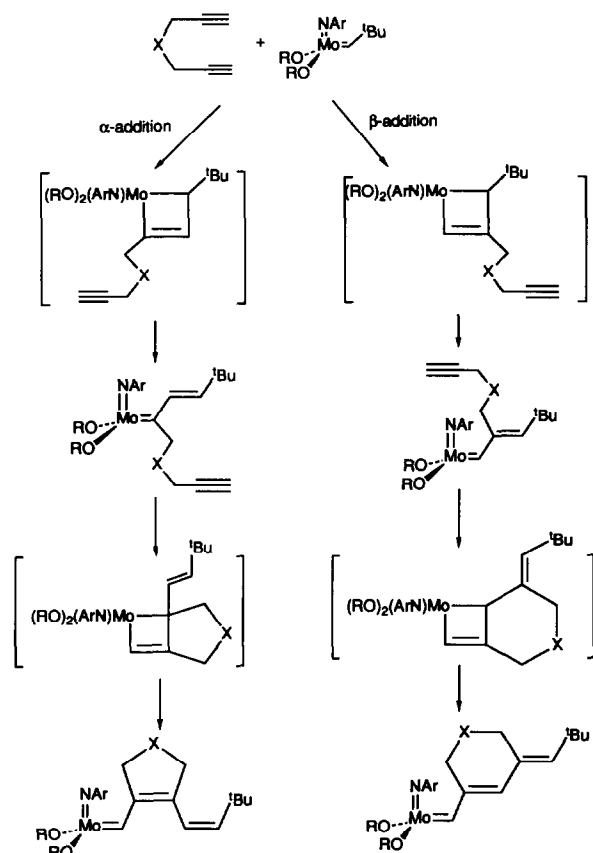
Living copolymerization of diethyl dipropargylmalonate by the catalyst  $\text{Mo}(=\text{CH}^t\text{Bu})(\text{NAr})[\text{OCMe}(\text{CF}_3)_2]_2$  in DME was observed to give a conjugated polyene containing both 5- and 6-membered rings in the backbone (Scheme 143) [320].

Mixtures of reducing agents like trialkylaluminum or Grignards with 2,6-dimethylphenoxo- $\text{W}^{\text{VI}}$  were found to be catalyst precursors for the polymerization of alk-1-yne [323]. The activity appeared to depend on the number of aryloxo ligands.

The ROMP of [*o*-(trifluoromethyl)phenyl]acetylene and a phenylacetylene with an electron-withdrawing group was achieved using the three-component catalytic system:  $\text{MoOCl}_4/\text{Bu}_4\text{Sn}/\text{EtOH}$  (1:1:0.5) to give a polymer with a narrow MW range [324].

ROMP of 5[[*n*-[(4'-methoxy-4-biphenyl)oxy]alkyl]-carbonyl]bicyclo[2.2.1]hept-2-ene ( $n = 2-8$ ) (**144**) by  $\text{Mo}(=\text{CH}^t\text{Bu})(\text{NAr})(\text{O}^t\text{Bu})_2$  has been described [325]. Polymers with narrow MW distributions were obtained in high yield.

Equimolar amounts of  $\text{WCl}_6$  or  $\text{WOCl}_4$  and mono-substituted acetylenes  $\text{RC}\equiv\text{CH}$  produced catalytic systems for the ring-opening polymerization of cyclic olefins [325]. Addition of small amounts of oxygenated



Scheme 143.

substances enhanced this activity. It was postulated that initial insertion of acetylene into the  $\text{W}-\text{Cl}$  bond occurred which led to metal carbene active centers.

Molecular mechanics MM2 calculations were used for studying the stereoselectivity of the  $\text{WCl}_4\text{CH}_2$  catalyst believed to be generated in the  $\text{WCl}_6 \cdot \text{SnMe}_4$  system for ring-opening polymerization of norbornene [326]. It was found that the structures of the  $\pi$ -complexes were favorable for a  $[2s + 2a]$  cycloaddition that was suprafacial to the olefin and antarafacial with respect to the carbene.

Bimetalliccyclobutadiene complexes of the type  $\text{W}_2(\text{Me}_3\text{SiCH}_2)_2(\mu\text{-CSiMe}_3)_2$  induced the ring-opening metathesis polymerization (ROMP) of norbornene [327]. Kinetic studies revealed a first-order dependence on both catalyst and monomer.

Reaction of  $\text{WOCl}_4$  with stoichiometric amounts of substituted phenol or lithium aryloxo produced pure  $\text{WOCl}_{4-x}(\text{OAr})_x$  [328]. Structural studies of  $\text{WOCl}_2(\text{OC}_6\text{H}_3\text{-2,6-}^i\text{Pr}_2)_2$  and  $\text{WO}(\text{O}-\text{C}_6\text{H}_3\text{-2,6-Me}_2)_4$  revealed pseudo-square-pyramidal geometries at the W centers. The high-yield ring-opening metathesis polymerization of dicyclopentadiene with these complexes in the presence of  $\text{R}_3\text{SnH}$  or  $\text{Ar}_3\text{SnH}$  was studied. It was found that the activity correlated with the  $\text{W}^{\text{VI}} \rightarrow \text{W}^{\text{V}}$  redox potential of the complex as well as the charge on the phenoxide oxygen.

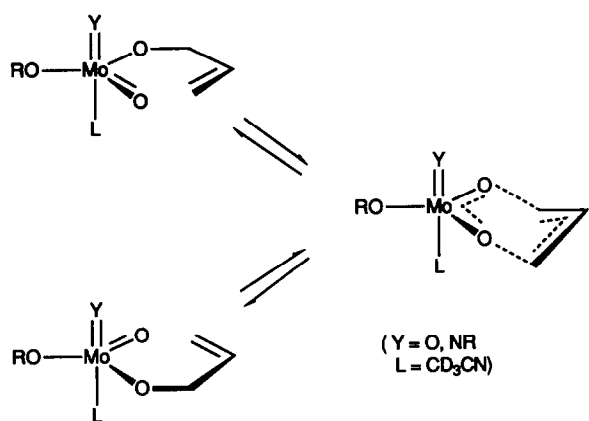
The catalytic system  $\text{Mo}(\text{CO})_5 \cdot \text{py}/\text{EtAlCl}_2/\text{Bu}_4\text{NCl}$  was studied for activity in the polymerization of cyclic olefins (cyclopentene, dicyclopentadiene, norbornadiene, indene) [329]. Both ring opening and ring retention polymers were found, depending on the temperature. C-13 NMR investigation of the norbornene polymerization suggested a combination of both insertion and olefin metathesis processes.

Reaction of  $\text{Tp}'\text{W}(\equiv\text{CR})\text{X}_2$  ( $\text{R} = ^t\text{Bu}$ ,  $\text{X} = \text{Cl}$ ;  $\text{R} = \text{Ph}$ ,  $\text{X} = \text{Cl}$ ,  $\text{Br}$ ) and neutral alumina or aniline gave  $\text{Tp}'\text{W}(\equiv\text{CHR})(\text{E})\text{X}$  ( $\text{E} = \text{O}$ ,  $\text{NPh}$ ) [330]. When combined with  $\text{AlCl}_3$ , the aniline derivative was active for the oligomerization of 1,9-decadiene while the oxo complex was an efficient catalyst for the ROMP of cyclooctene.

### 12.3. Miscellaneous

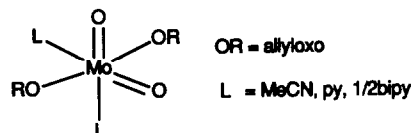
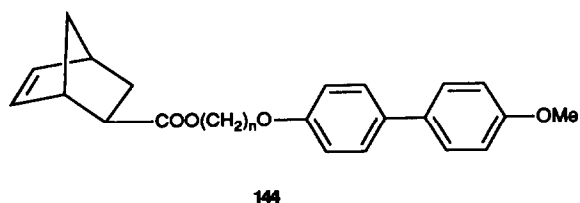
The metal oxo complex  $\text{MoO}_2(\text{OR})_2(\text{MeCN})_2$  ( $\text{RO} = \text{H}_2\text{C}=\text{CHCMe}_2\text{O}$ ) (**145**) was synthesized and shown by proton NMR to undergo allyloxo rearrangement at room temperature [331]. An intramolecular  $[3,3]$  sigmatropic shift of the allyl group was suggested and might be rate-determining in the catalytic isomerization of allylic alcohols (Scheme 144).

Dioxomolybdenum(VI) complexes including  $\text{MoO}_2(\text{L})(\text{HMPA})$  and  $\text{MoO}_2(\text{L}')_2$  ( $\text{L} = 2,6\text{-pyridinecarboxylate}$ ,  $\text{L}' = N,N\text{-diethyldithiocarbamate}$ ) were found to



Scheme 144.

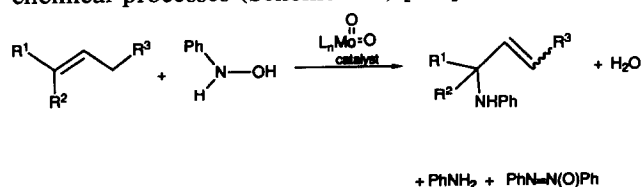
catalyze regioselectively the allylic amination of alkenes by phenyl hydroxyamine (Scheme 145) [332].



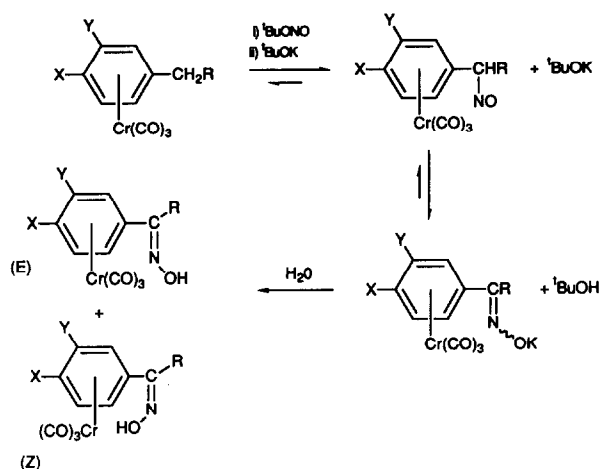
The new complex [Cr<sub>2</sub>Cl<sub>4</sub>L]Cl where L was 1,3-bis[1-(pyridin-2-yl)ethylideneamino]propan-2-ol was examined as a catalyst for alkene epoxidation with iodosylbenzene [333]. It was found to be less effective than the manganese analogue.

In basic media, aromatic hydrocarbons and benzylmethylethers complexed by Cr(CO)<sub>3</sub> units were found to be easily nitrosated at the benzylic position by <sup>t</sup>BuONO to give *E/Z* oximes and hydroximates (Scheme 146) [334]. Dinitrosation was observed for *m*-xylene and isochromane complexes.

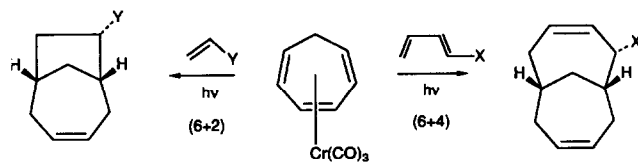
A chromium catalyst, (CHT)Cr(CO)<sub>3</sub>, was found to catalyze the thermal [6π + 4π] and [6π + 2π] higher-order cycloadditions giving identical products to photochemical processes (Scheme 147) [335].



Scheme 145.



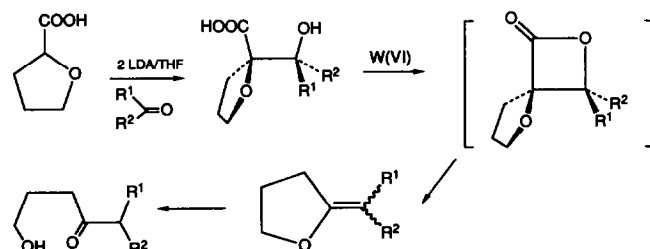
Scheme 146.



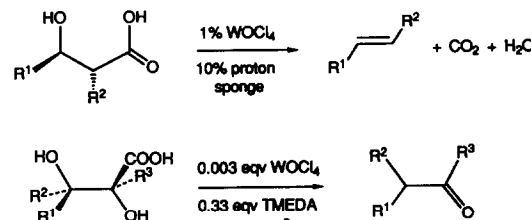
Scheme 147.

Catalytic amounts of chromium-pillared montmorillonite were found to provide an efficient method for the benzylic oxidation of arylmethylenes by <sup>t</sup>BuOOH to carbonyl derivatives [336]. Monocarbonyls were selectively formed.

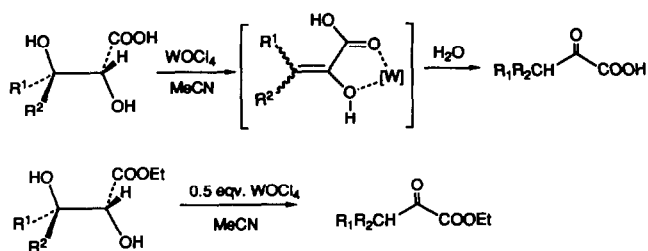
Substituted ( $\alpha$ -alkylidene)tetrahydrofurans were prepared by the tungsten-catalyzed reaction of substituted hydrofuroic acids [337]. It was suggested that  $\beta$ -lactone intermediates were first formed which then decarboxylated (Scheme 148).



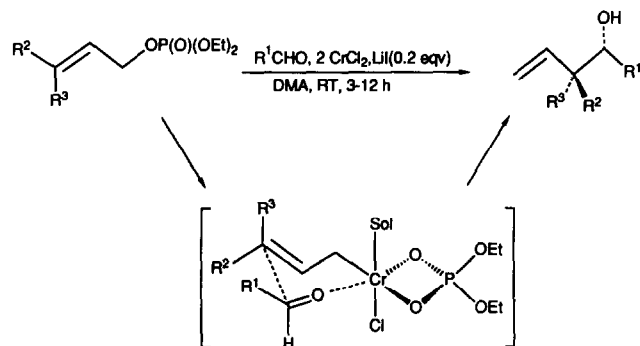
Scheme 148.



Scheme 149.



Scheme 150.



Scheme 151.

Dehydrative decarboxylation of 2,3-dihydroxycarboxylic acids were catalyzed by  $\text{WOCl}_4$  to form enols *via*  $\beta$ -lactone intermediates (Scheme 149) [338].

Rapid dehydration of 2,3-dihydroxycarboxylic acids to  $\alpha$ -keto acids were catalyzed by  $\text{WOCl}_4$  [339]. This rapid dehydration also worked for esters derivatives. It was postulated that a chelated intermediate was involved (Scheme 150).

In the presence of fluoride, alkyl iodides  $\text{RI}$  were carbonylated by  $\text{Mo}(\text{CO})_6$  to esters  $\text{RCOOR}$  while diiodides led to good yields of lactones [340]. Methyl formate was used as a CO source for ester formation.

In contrast to  $\gamma$ -monosubstituted allylic chromium reagents,  $\gamma$ -disubstituted allylic  $\text{Cr}^{\text{III}}$  organometallics were found to undergo highly stereoselective stereodivergent additions to aldehydes (Scheme 151) [341].

Mixtures of reducing agents and 2,6-dimethylphenoxy-tungsten(VI) are catalyst precursors for the polymerization of terminal alkynes. The activity was controlled by the number of aryloxy groups at the metal center to give high MW polymers [342].

### 13. Physical studies

#### 13.1. Energetics

$\text{CO-CO}$  interactions in  $\text{M}(\text{CO})_6$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ) were studied using Penning ionization electron spectroscopy [343]. It was found that through-space  $\text{CO } 5\sigma$  interactions stabilize the totally-symmetrical MO and give rise to a diffuse electron distribution.

MO SCF calculations were used to study  $\text{Cr}(\text{CO})_6$

[344]. Charge transfer from the chromium  $t_{2g}$  to the empty  $2\pi^*$   $t_{2g}$  of the  $(\text{CO})_6$  cage was found.

Thermocycles were used to estimate the solution acidities and bond dissociation energies of the radical cations from  $\text{CpCr}(\text{CO})_2(\text{PR}_3)\text{H}$  and  $\text{Cp}^*\text{Cr}(\text{CO})_3\text{H}$  [345]. In accord with 17-electron metal hydride cation reactivities, the 1-electron oxidation of these hydrides increased their acidities by 23–26 pKa units in MeCN, corresponding to an activation of the  $\text{Cr-H}$  bonds towards heterolytic cleavage of 32–35  $\text{kcal mol}^{-1}$  while the bond dissociation energies were only lowered by 8–11  $\text{kcal mol}^{-1}$ .

Heats of formation for (naphthalene) $\text{Cr}(\text{CO})_3$ , (cycloheptatriene) $\text{Cr}(\text{CO})_3$ , (cycloheptatriene) $\text{W}(\text{CO})_3$ , and  $(\text{EtCN})_3\text{W}(\text{CO})_3$  with pyridine, phosphines, phosphites were determined [346].

Spectroscopic studies showed that triflic acid protonation of *cis*- $\text{M}(\text{CO})_2(\text{LL})_2$  ( $\text{M} = \text{Cr}, \text{Mo}, \text{W}$ ;  $\text{LL} =$  bidentate phosphine) occurred at the metal centers to form  $[\text{M}(\text{H})(\text{CO})_2(\text{LL})_2]\text{CF}_3\text{SO}_3$  with *trans*- $\text{CO}$ 's [347]. For  $\text{LL} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ , the enthalpies of protonation are less exothermic as the ring size increases from  $n = 1-3$ . For Mo, the basicity increases from arphos to dppe to dmpe. Within the metal triad, the basicities of dmpe complexes increase as  $\text{Cr} \gg \text{Mo} > \text{W}$ .

#### 13.2. NMR spectroscopy

Molybdenum-95 NMR spectroscopy was used to probe the nature of phosphorus(III) ligands in a series of *fac*- $\text{Mo}(\text{CO})_3(\text{PY}_3)_3$  ( $\text{Y} = \text{halide}, \text{R}, \text{Ar}, \text{OR}, \text{NR}_2$ ) complexes [348]. It was found that the Mo-95 chemical shifts varied from  $-1860$  ppm for the  $\text{PF}_3$  complex to the surprising  $-910$  ppm for the  $\text{PCl}_3$  derivative. Correlation of shifts with the Kabachnik  $\Sigma\sigma^{\text{ph}}$  electronic parameters were superior. It was concluded that  $\pi$ -acceptor strengths were weak for chlorophosphines, reversing the commonly accepted trend of  $\text{PPh}_3 < \text{PClPh}_2 < \text{PCl}_2\text{Ph} < \text{PCl}_3$ .

In order to explain the well-known ring-contribution to the P-31 chemical shifts, chem. shift tensors of  $\text{M}(\text{CO})_4\text{L}$  ( $\text{L} = \text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2$ ;  $n = 1, 5$ ;  $\text{M} = \text{Mo}, \text{W}$ ) and *fac*- $\text{Mo}(\text{CO})_3\text{PhP}(\text{CH}_2\text{CH}_2\text{PPh}_2)_2$  were determined by solid-state NMR spectroscopy [349]. It was found that the isotropic shifts are dominated by the tensor component perpendicular to the chelate ring plane which in turn depends on the ring size.

Mo-95 NMR chem. shifts of a series of  $\text{Mo}(\text{CO})_4(\text{pip})_{2-n}\text{L}_n$  ( $n = 1, 2$ ;  $\text{L} =$  substituted pyridines) correlate well with pKa's of the pyridines [350].

Mo-95 NMR spectra of 28 carbonyl, isonitrile, and amine complexes were obtained and compared [351]. Within each structural class, excellent correlation between the chemical shift and ligand  $\pi$ -acceptor strength

was found. Analysis of the linewidths and relaxation behavior of isonitrile complexes indicated that scalar coupling to N-14 was responsible for the Mo-95 line width.

The spectroscopic and electrochemical behavior of 63 (arene)Cr(CO)<sub>3</sub> complexes with between zero to six ring substituents were studied [352]. A nonlinear incremental effect was found for the oxidation potential, the IR carbonyl stretching frequency and force constant, as well as the C-13 carbonyl shift. It was proposed that  $\pi$ -donor/ $\pi$ -acceptor interactions between each of the ring substituents and with the chromium center gave rise to this effect.

The chirotopicity of the Me group in ( $\alpha$ -D-*o*-chlorotoulene)Cr(CO)<sub>3</sub> has been demonstrated through the diastereotopicity of the benzylic protons using NMR spectroscopy (4 Hz at 500 MHz) [353]. The second-order three-line AB pattern has been successfully simulated.

Several fluorobenzene-Cr(CO)<sub>3</sub> complexes were studied by NMR to determine *syn*-eclipsed and *anti*-eclipsed conformer populations using scalar C-13/F-19 spin coupling constants [354].

The C-13 NMR spectra of fluorinated biphenyl complexes of Cr(CO)<sub>3</sub> have been examined and C-13/F-19 couplings used for structural determination [355].

Tricarbonyl chromium complexes of several fluorobenzene derivatives were prepared and their spectral data analyzed [356]. Predictions of F-19 NMR data for mono- as well as difluoro complexes have been achieved.

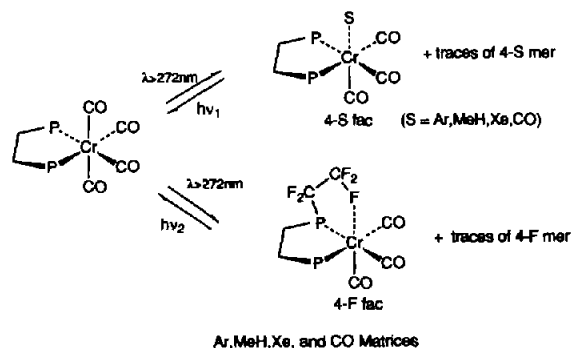
Predictions of F-19 NMR spectra of fluoroarene complexes of Cr(CO)<sub>3</sub> have been reanalyzed using the field, resonance and Charlton steric parameters and molecular refractivity to give improved correlations [357].

### 13.3. Vibrational spectroscopy and PES

Time-resolved IR spectra of the coordinatively unsaturated (Benzene)Cr(CO)<sub>x</sub> ( $x = 1, 2$ ) intermediates generated by laser photolysis from (benzene)Cr(CO)<sub>3</sub> were presented [358]. Photolysis at 355 nm produced mainly the dicarbonyl while at 266 nm the monocarbonyl was also observed (2:5 ratio).

Gas phase high-resolution X-ray photoelectron spectra of the valence and core level for Cr(CO)<sub>6</sub> were obtained and support a close to complete charge transfer screening accompanying ligand core ionization of Cr(CO)<sub>6</sub> [359].

The high resolution W 4f photoelectron spectrum of W(CO)<sub>6</sub> was found to be analogous to the 5d valence-level spectrum, both showing vibrational structure from W-C and C-O vibrations [360].

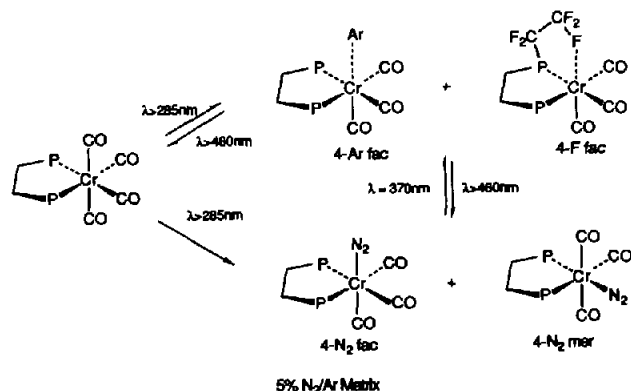


Scheme 152.

Photoelectron spectroscopy was used to study molybdenum carbonyl with monodentate diphosphine complexes [361]. Results indicated that the phosphine  $\pi$ -accepting abilities were all about 25% of a CO's. The  $\sigma$ -donor strength followed the trend  $\text{PMe}_3 > \text{dmpe} > \text{dmpm}$ . The difference between the ionization energy of the coordinated lone pair and the free one indicated an opposite trend with  $\text{PMe}_3 > \text{dmpe} > \text{dmpm}$ . Transfer of negative charge from the free phosphine end *via* the alkyl backbone to the coordinated end was significant. Overall, dmpm and dmpe were found to be very similar in  $\sigma$ -donor and  $\pi$ -acceptor strengths to  $\text{PMe}_3$ .

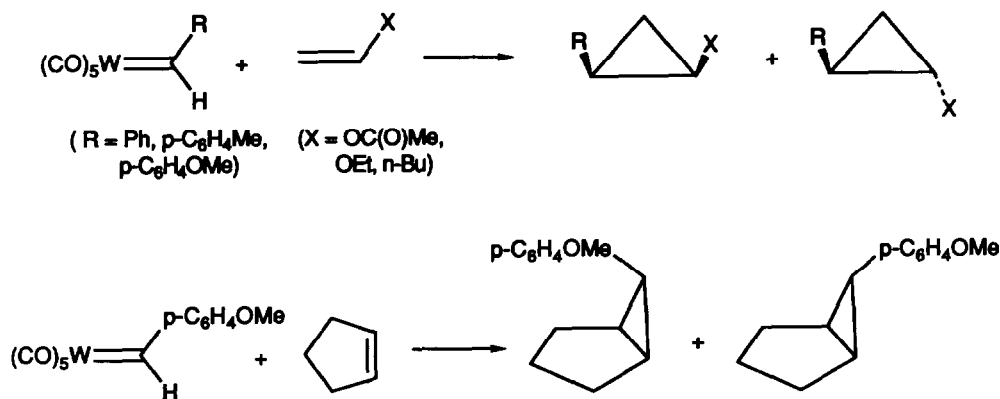
Energy-factored force constants and CO stretches were calculated from the ligand effect constants for Cr(CO)<sub>3</sub>(NO)<sub>2</sub> and suggest a  $C_{2v}$  structure with an equatorial NO of a trigonal-bipyramid [362]. The new complex Cr(CO)<sub>4</sub>NO appears to have a  $C_{4v}$  structure.

Metal-metal communication in ditungsten complexes of 1,4-diisocyanobenzene, CN-C<sub>6</sub>H<sub>4</sub>-NC, containing W<sup>0</sup>-W<sup>0</sup>, W<sup>0</sup>-W<sup>II</sup>, and W<sup>II</sup>-W<sup>II</sup> centers was studied [363]. Vibrational and NMR data indicated that the mixed-valent metal centers were effectively hybrids of the W<sup>0</sup>-W<sup>0</sup> and W<sup>II</sup>-W<sup>II</sup> species. However, the binuclear MLCT bands were red-shifted by 1221 cm<sup>-1</sup> from the mononuclear values, indicative of ligand  $\pi$ -participation. This apparent contradiction was resolved by X-ray PES which showed nearly identical



Scheme 153.





Scheme 154.

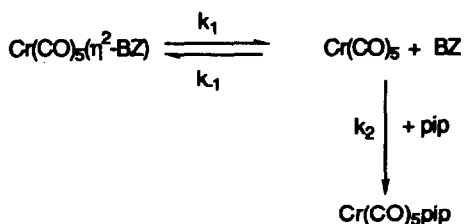
$\text{W}^{4f}$  shifts for both  $\text{W}^0$  and  $\text{W}^{\text{II}}$ , suggesting very similar electronic environments.

Matrix isolation and transient absorption studies of  $[\eta^2\text{-(dfepe)Cr(CO)}_4]$  (dfepe =  $(\text{C}_2\text{F}_5)_2\text{PCH}_2\text{CH}_2\text{P}(\text{C}_2\text{F}_5)_2$ ) complexes have been carried out [364]. In Ar, methane, and Xe matrices, it was found that photodissociation of a *cis*-CO generated almost exclusively *fac*-(dfepe)Cr(CO)<sub>3</sub>L where L was the matrix host or an intramolecularly coordinated F on one of the phosphine pendant groups (Scheme 152). In nitrogen matrix, however, both *fac*- and *mer* isomers were observed (Scheme 153). In hydrocarbon solutions, it was found that both Cr-C and Cr-P bonds were photolabile to give the respective alkane complexes.

### 13.4. Kinetic studies

The benzylidene complex  $\text{W(CO)}_5=\text{C}(\text{p-C}_6\text{H}_4\text{R})\text{H}$  (R = OMe, Me, H) reacted with vinylacetate, ethylvinylether, 1-hexene, and cyclopentene by transfer of the benzylidene to the olefinic C=C bond to give cyclopropanes (Scheme 154) [365]. The kinetics and mechanisms of these cyclopropanations were investigated.

The kinetics of the ring closure of the  $\text{Mo(CO)}_5 \cdot \text{L}$  intermediate supported an associative interchange mechanism for L = bipy and 4,4'-dimethyl-bipy for CO extrusion [366]. For the bulkier L = 4,4'-diphenyl-bipy, a changeover to a dissociative interchange pathway was suggested by the volume of activation data.

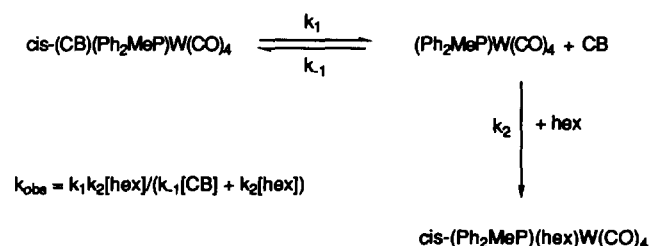


$$k_{\text{obs}} = k_1 k_2 [\text{pip}] / (k_{-1} [\text{BZ}] + k_2 [\text{pip}])$$

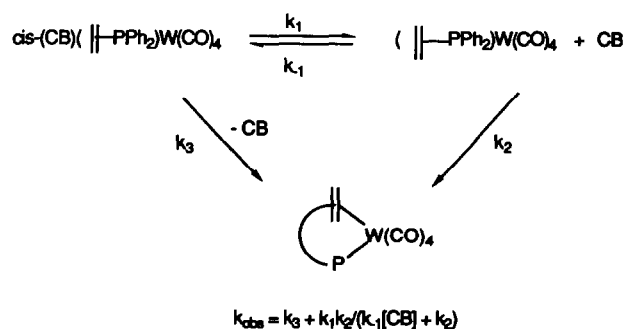
Scheme 155.

Conductance studies of the substitution reaction of  $\text{M}(\text{tBuNC})_7^{2+}$  with halides indicated a dissociative process with participation of both ion-paired and non-ion-paired complexes [367].

Substitution of chlorobenzene (CB) in *cis*- $\text{W(CO)}_4(\text{CB})(\text{PPh}_2\text{Me})$  by 1-hexene and chelate ring closure in *cis*- $\text{W(CO)}_4(\text{CB})(\text{PPh}_2(\text{CH}_2)_n\text{CH}=\text{CH}_2)$  were studied by volume of activation measurements in CB/hexane solvent mixtures [368]. For the former reaction, a dissociative mechanism was operative as found for the piperidine substitution of  $\text{Cr(CO)}_5(\eta^2\text{-BZ})$ , (Schemes 155, 156). By contrast, the chelate ring closure for  $n = 1, 2$  involved an interchange ( $I_d$ ) mechanism (Scheme 157). Agostically H-bonded intermediates were postulated.



Scheme 156.



Scheme 157.

The kinetics of chelate ring closure in a series of *cis*-(CB)( $\eta^1$ -P-ol)W(CO)<sub>4</sub> transients from the laser flash photolysis of *cis*-(pip)( $\eta^1$ -P-ol)W(CO)<sub>4</sub> in CB solution (CB = chlorobenzene, pip = piperidine, P-ol = Ph<sub>2</sub>P-(CH<sub>2</sub>)<sub>n</sub>CH=CH<sub>2</sub>, *n* = 1–4) have been investigated [369]. It was found that competitive solvent displacement *via* ring closure and pip attack occurred. For reactions of the transient *cis*-(CB)(Ph<sub>2</sub>MeP)W(CO)<sub>4</sub> with 1-hexene, a single solvent displacement was observed. These data and activation parameters supported the intermediacy of species with agostic Ph<sub>2</sub>MeP or P-ol bonding to the W center.

The solvent displacement reactions of Cr(CO)<sub>5</sub>·S (S = fluorobenzene and *n*-heptane) with piperidine was studied as a function of pressure [370]. The former was found to be dissociative in nature while the latter took place *via* competitive dissociative and interchange pathways.

Laser photolysis studies of the ring closure of Mo(CO)<sub>5</sub>-(1,10-phenanthroline) demonstrated an interchange mechanism [371].

The influence of pressure on [2 + 2] cycloaddition reactions of  $\alpha,\beta$ -unsaturated Fischer carbene complexes (CO)<sub>5</sub>M=C(OR')C≡CR (M = Cr, W; R = R' = Me; M = W, R = Ph, R' = Et) with 3,4-dihydro-2H-pyran was studied. These were found to be pressure sensitive and showed remarkable rate acceleration independent of the metal center. Activation parameters were obtained which suggested a one-step, concerted, synchronous mechanism [371a].

The acetate-catalyzed heterolysis of chromium(III) complexes like LCr-CH<sub>2</sub>OH<sup>2+</sup> and LCr-CMe<sub>2</sub>OH<sup>2+</sup> (L = (H<sub>2</sub>O)<sub>5</sub>, [15]aneN<sub>4</sub>, NTA) have been studied as a function of concentration, temperature and pressure [372]. The data supported catalysis due to *trans*-labilization of coordinated acetate and solvent attack on the coordinated Cr-C bond.

High pressure kinetic evidence for a dissociative interchange (*I<sub>d</sub>*) substitution mechanism in the reaction of Cr(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> with organic radicals (R·) to give water and (H<sub>2</sub>O)<sub>5</sub>CrR<sup>2+</sup> was provided by volume of activation studies [372a].

#### 14. Reviews

A review of transition metals in organic synthesis covering the year 1990 with 1048 references including C-C bond formation and functional group synthesis has appeared [373].

A review of chromium-catalyzed oxidations in organic synthesis leading to new C-O or C=O bonds with 296 references has been published [374].

A review of the mechanism of alkene epoxidation by higher-valent chromiumporphyrins has appeared [375].

There was a review on the chemistry of CpMX<sub>2</sub> (M = Mo, W) with 37 references [376].

A review of the chemistry of organochromium(III) complexes has been published [377].

A review of some unconventional uses of transition metal coordination (especially W) in the syntheses of organophosphorus compounds has also appeared [378].

Coordination chemistry of soluble metal oxides (polyoxymolybdates) of molybdenum has been reviewed [379].

A report on cyclopentadienyl metal oxide chemistry has appeared [380].

A review of transition metal complexes of silylenes, silenes, disilenes, and related species has been published [381].

The reactions of transition metal dihydrogen complexes have been reviewed [382].

A review with 75 references on framework solids based on reduced molybdenum phosphates has appeared [383].

High-surface area WC and W<sub>2</sub>C powder catalysts have been reviewed [384].

A review of H-insertion compounds, especially H-W and H-Mo bronzes has been published [385].

#### 15. Miscellaneous

Reaction of Cr(mes)<sub>3</sub>(THF)<sub>3</sub> with <sup>t</sup>BuNCO gave Cr[OC(mes)N<sup>t</sup>Bu]<sub>3</sub> while <sup>t</sup>BuNC afforded Cr[(mes)C=N<sup>t</sup>Bu]<sub>3</sub> [383].

Mo<sub>2</sub>Cl<sub>10</sub> reacted with 4 equivalents of MeLi at -70°C to give a thermally unstable methylated species which transformed to Cl<sub>3</sub>Mo( $\mu$ -CH<sub>2</sub>)<sub>2</sub>MoCl<sub>3</sub> at higher temperatures according to NMR data [384]. This carbonyl olefination reagent reacted with aldehydes, ketones, azomethines and epoxides.

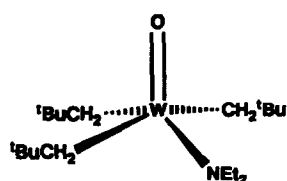
Ketones with a basic group (e.g. OH, OMe, NMe<sub>2</sub>) in the  $\alpha$  or  $\beta$  position are selectively methylated by MeCrCl<sub>2</sub>(THF)<sub>3</sub> in preference to normal ketones [385].

Irradiation of solutions of Cr<sup>II</sup> and RX (R = primary, secondary, or tertiary alkyl; X = Br, Cl) at 254 nm and pH 3 yielded organochromium cations RCr-(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup> including the novel <sup>t</sup>Bu-Cr(H<sub>2</sub>O)<sub>5</sub><sup>2+</sup> species [386].

Proton NMR of tungsten(IV) complexes WO(CH<sub>2</sub>-Bu<sup>t</sup>)<sub>2</sub>(NR<sub>2</sub>)Cl and WO(CH<sub>2</sub>Bu<sup>t</sup>)<sub>3</sub>(NR<sub>2</sub>) suggested and X-ray studies of the latter confirmed distinct stereochemistries due to competing  $\eta$ -donor demands of the amido and oxo ligands (146) [387].

Reactions of Cr<sup>II</sup> and Cr<sup>III</sup> mesoporphyrin-IX ((MSP) with methyl and other alkyl radicals were studied using radiolysis techniques [388]. Both reacted rapidly to produce relatively stable Cr-R bonds. The R-Cr<sup>IV</sup>-MSP was air-oxidized only very slowly.

Studies of the acetate-catalyzed heterolysis of  $\text{Cr}^{\text{III}}-\text{CH}_2\text{OH}$  and  $\text{Cr}^{\text{III}}-\text{CMe}_2\text{OH}$  with different spectator



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ligands demonstrated that the catalytic effect arose from a *trans*-labilization by the coordinated acetate ion [389].

The organochromium compound  $\text{Cr}(\text{tBu})_4$  was found to have sufficient volatility for use as a chromium source in chemical vapor deposition [390]. Chromium carbide films were formed at 100–150°C.

## 16. List of abbreviations

Bipy	2,2'-Bipyridyl
Bu	n-Butyl
<sup>t</sup> Bu	t-Butyl
CHT	Cycloheptatriene
COD	Cyclooctadiene
Cp	Cyclopentadienyl
Cp'	Methylcyclopentadienyl
Cp*	Pentamethylcyclopentadienyl
Dme	Dimethoxyethane
Dmpe	1,2-Bis(dimethylphosphino)ethane
Dppm	Bis(diphenylphosphino)methane
Dppe	1,2-Bis(diphenylphosphino)ethane
Et	Ethyl
Et <sub>2</sub> O	Diethylether
Me	Methyl
Mes	Mesityl
NBD	Norbornadiene
Neo/Np	Neopentyl
NTA	Nitrilotriacetic acid
Ph	Phenyl
Pr	n-Propyl
<sup>i</sup> Pr	iso-Propyl
Py	Pyridine
Pz	Pyrazolyl
THF	Tetrahydrofuran
TMEDA	Tetramethylethylenediamine
TMS	Trimethylsilyl
Tp	Hydrido-tris(pyrazolyl)borate
Tp'	Hydrido-tris(4-methylpyrazolyl)borate
Trityl	Triphenylmethyl

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