CHROMIUM, MOLYBDENUM AND TUNGSTEN

ANNUAL SURVEY COVERING THE YEAR 1980 *

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* Previous review see J. Organometal. Chem., 196(1980) 79-174.

ABBREVIATIONS

acac - acetylacetonate
bipy - bipyridine
Bu - n-butyl
t-Bu - t-butyl
COT - cyclooctatriene
Cp - cyclopentadienyl
dam - bis(diphenylarsino)methane
das - o-phenylenebis(dimethylarsine)
dppe - 1,2-bis(diphenylphosphino)ethane
dmpe - 1,2-bis(dimethylphosphino)ethane
dpm - bis(diphenylphosphino)methane
Et - ethyl
Me - methyl
o-phen - o-phenanthroline
piper - piperidine
Pr - propyl
i-Pr - isopropyl
Pz - pyrazine
TMEDA (tmen) - tetramethylethylenediamine

This 1980 Annual Survey of the Organometallic Chemistry of Chromium, Molybdenum and Tungsten was constructed and organized like those of 1978 and 1979. The primary literature was covered directly and a computer literature search was accomplished to insure a comprehensive review.

SYNTHESIS AND REACTIVITY

Metal Carbonyls

An inexpensive catalyst for substitution reactions on the hexacarbonyls was reported.[1] $CoCl_2 \cdot 2H_2O$ was found to catalyze the substitution of CO on Group VI metal carbonyl by isonitriles to yield $M(CO)_{6-n}(RNC)_n$ [M=Cr, Mo, W; n=1-3; RNC=t-BuNC, MeNC]. The reactions occurred by stepwise replacement of the CO groups and mixed isonitrile derivatives could be obtained ($Mo(CO)_4(MeNC)$-(t-BuNC)).[1] The following steps were suggested (M=Mo).[1]

$$\begin{tikzcd}
\mathrm{Mo(CO)_6} \arrow[r, "\mathrm{CoCl_2(RNC)_n}"] & \mathrm{(CO)_5Mo\text{-}CO\text{-}CoCl_2(RNC)_n} \arrow[d, "\substack{+\mathrm{R'NC} \\ -\mathrm{CoCl_2(RCN)_n} \\ -\mathrm{CO}}"] \\
 & \mathrm{(CO)_5Mo(R'NC)}
\end{tikzcd} \qquad (1)$$

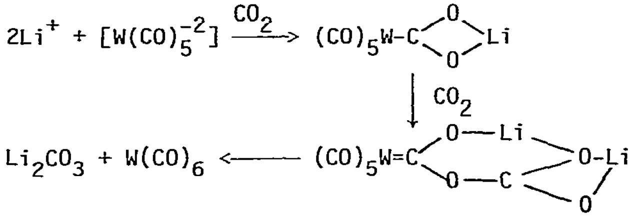
Wong and Labinger reported the reduction of CO on $Cr(CO)_6$ by Cp_2NbH_3.[2] Reaction of Cp_2NbH_3 with $Cr(CO)_6$ led initially to C_2H_4, which was subsequently hydrogenated to ethane.[2]

$$Cr(CO)_6 \xrightarrow{Cp_2NbH_3} C_2H_4 \tag{2}$$

An unusual CO_2 reduction using electron transfer from Group VI dianions in which the oxygen sink was an alkali metal carbonate was reported.[3]

$$Li_2W(CO)_5 + 2CO_2 \longrightarrow Li_2CO_3 + W(CO)_6 \tag{3}$$

Treatment of $Li_2W(CO)_5$ in THF with gaseous CO_2 at -78°C resulted in loss of color from $W(CO)_5^{-2}$ and formation of Li_2CO_3. $W(CO)_6$ was the only carbonyl containing product after warming to room temperature.[3] The suggested scheme was as follows:



(4)

Tungsten or molybdenum atoms were incorporated into thermoplastic or thermosetting polymers by treating a monomer or prepolymer containing at least one free CO_2H group with a reaction product of $M(CO)_6$, (M=Mo or W) with pyrrolidine.[4] As an example $W(CO)_6$ was treated with excess pyrrolidine to form a metal complex which was mixed with maleic anhydride-ethylene glycol prepolymer and heated above 200°C to give a thermoplastic polyester containing chemically bonded tungsten atoms.[4] Chromium carbonate was prepared by reaction of $Cr(CO)_6$ with 3000 bar CO_2 at 280°C.[5]

Dissociation of L from $Cr(CO)_5L$ and trans-$Cr(CO)_4L_2$ was studied for L=PPh_3, $P(OPh)_3$, $P(OMe)_3$, PBu_3 and $AsPh_3$.[6,7]

$$Cr(CO)_5L + CO \longrightarrow Cr(CO)_6 + L \tag{5}$$

$$t\text{-}Cr(CO)_4L_2 + CO \longrightarrow Cr(CO)_5L + L \tag{6}$$

For the monosubstituted complexes, $Cr(CO)_5L$, the rates spanned several orders of magnitude with the order[6]

$$AsPh_3 > PPh_3 > P(OPh)_3 > P(OMe)_3 > PBu_3$$

This order doesn't correspond to pi- or sigma-bond changes or steric size but represents bonding strength.[6] The ligands dissociated more rapidly from bis-substituted complexes, $Cr(CO)_4L_2$, than from the mono-substituted complexes.[7] For phosphines the bis complexes reacted 10^5 more rapidly than the mono complexes; for phosphites dissociation from the bis complex occurred only a factor of 10 more rapidly than from the mono-substituted complex. This suggested that pi-bonding of the trans ligand was important.[7] Phase-transfer-catalyzed nucleophilic reactions of hydroxide ions with Group 6B metal carbonyls ($M(CO)_{6-n}L_n$, n=0 or 1; L = phosphine or phosphite ligands) were reported by Darensbourg and coworkers.[8] In the presence of $H_2{}^{18}O$, oxygen-18 enriched $M(CO)_{6-n}L_n$ species were afforded. During the reaction of OH^- with $M(CO)_6$ slow formation of highly oxygen-18 labeled-μ-$H[M(CO)_2]_2^-$ derivatives were observed.[8] Under CO, hydrogen gas was produced catalytically. The metal dependence of the oxygen-exchange process was found to be W > Mo > Cr, with phosphite-substituted derivatives being more reactive than their phosphine analogues.[8] Reaction of substituted derivatives occurred exclusively cis.[8] Schenk has reported the synthesis of cis- and trans-tetracarbonyltungsten complexes $(R_3P)(R'_3E)W(CO)_4$ (R_3P, R'_3E = i-Pr_3P, Ph_3P, $(Me_2N)_3P$, (i-$PrO)_3P$, $(PhO)_3P$, etc.) from reaction of chlorotetracarbonyltungstates ($R_3PW(CO)_4Cl^-$).[9] A cis-trans equilibrium was attained at 20°-80°C with the trans isomers thermodynamically more stable in nearly all cases. The isomerization of the phosphine-arsine and phosphine-stibine complexes occurred by dissociation of the arsine and stibine, respectively.[9] The bis (phosphine) complexes isomerized intramolecularly without bond cleavage.[9] New complexes of molybdenum and tungsten with dinitrogen and other small molecules, trans-$[M(CO)_3(PCy_3)_2L]$ (L = N_2, H_2, C_2H_4 or SO_2; M = Mo or W) were synthesized by the reaction of $M(CO)_3(C_7H_8)$ with 2 PCy_3 in the presence of L.[10]

$$\begin{tikzcd}(C_7H_8)M(CO)_3 + 2\ PCy_3 \arrow[r, "L"] & M(CO)_3(PCy_3)_2L \arrow[d, "-L"] \\ & M(CO)_3(PCy_3)_2\end{tikzcd} \tag{7}$$

L = N_2, H_2, C_2H_4 or SO_2
M = Mo or W

Removal of L led to the five-coordinate species, $M(CO)_3(PCy_3)_2$.[10] The molybdenum complexes, $Mo(CO)_3(PCy_3)_2L$, partially dissociated in solution, even in the presence of excess L. The tungsten adducts were more stable.[10]

A number of Group VI chelate complexes were prepared in 1980. N,N-Dimethylethanolamine reacted with $(CO)_5Mo(PPh_2Cl)$ to give $(CO)_5Mo(PPh_2OCH_2CH_2NMe_2)$ which was characterized by heating to form the mixed donor (P,N) chelate complex, $(CO)_4Mo(PPh_2OCH_2CH_2NMe_2)$.[11] The chromium and tungsten analogs

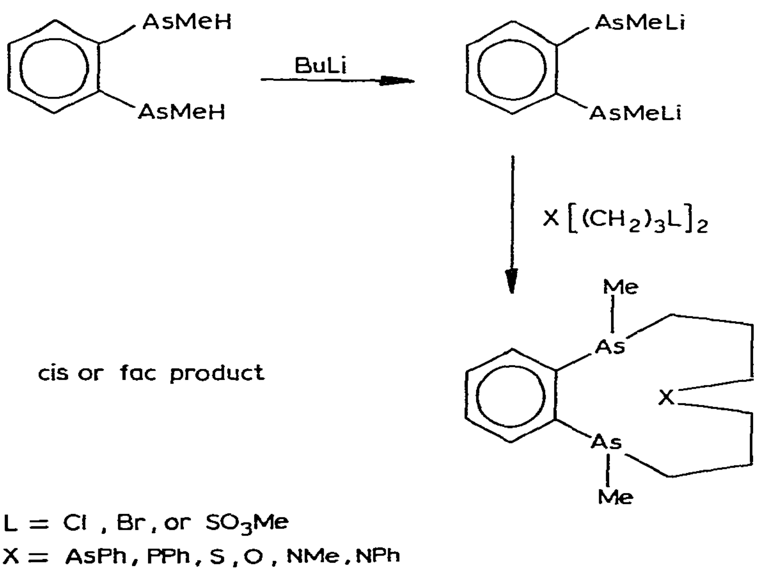
$$\begin{tikzcd}
(CO)_5MoPPh_2Cl + HOCH_2CH_2NMe_2 \arrow[r] & (CO)_5MoPPh_2OCH_2CH_2NMe_2 \arrow[d, "\Delta,\ -CO"] \\
 & (CO)_4Mo(PPh_2OCH_2CH_2NMe_2)
\end{tikzcd} \qquad (8)$$

were prepared by photochemical reactions between the hexacarbonyls and the uncomplexed ligand. Ethylenediamine, N-methylethylenediamine, and N,N-dimethylethylenediamine reacted with cis-$Mo(CO)_4(PPh_2Cl)_2$ to yield cis-$Mo(CO)_4(PPh_2NHCH_2CH_2NR_2)_2$ ($R_2 = H_2$, HMe, Me_2).[11] N,N'-dimethylethylenediamine

$$(CO)_4Mo(PPh_2Cl)_2 + 2H_2NCH_2CH_2NR_2 \longrightarrow (CO)_4Mo(PPh_2NHCH_2CH_2NR_2)_2 + 2HCl \qquad (9)$$

$$R_2 = H_2,\ HMe,\ Me_2$$

yielded only the chelate complex $(CO)_4Mo(PPh_2NMeCH_2CH_2NMePPh_2)$.[11] New tertiary-arsine containing macrocycles were synthesized and the molybdenum carbonyl complexes prepared.[12] Cis-$LM(CO)_4$ (L = bicyclo[2.2.1]hepta-2,5-diene;

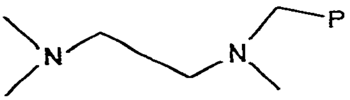


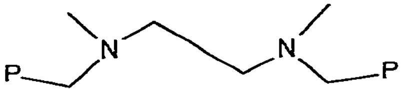
M=Cr, Mo, W) complexes reacted with $R_2PCH_2PR_2$ (R=Me_2CHO, Me_2N) to yield cis substituted $[R_2PCH_2PR_2]M(CO)_4$ derivatives.[13] The crystal structure was determined for R=Me_2CHO, M=Mo. Diphosphorus ligands, $R_2P(S)CH_2PR_2$ (R=F, Me_2CHO) were monodentate while the compound $(Me_2N)_2P(S)CH_2P(NMe_2)_2$ acted as a bidentate ligand.[13] Reactions of the four-membered ring chelate complex, $CH_3N(PF_2)_2Cr(CO)_4$, with trivalent phosphorus ligands (L) at 80°C led to facile opening of the chelate ring to give the mixed ligand complexes trans-$CH_3N(PF_2)_2Cr(CO)_4L$ (L=PPh_3 or $PhN(PF_2)_2$ containing a monodentate $CH_3N(PF_2)_2$ ligand.[14]

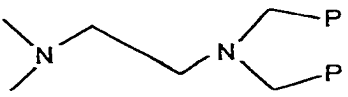
$$CH_3N(PF_2)_2Cr(CO)_4 + L \longrightarrow t\text{-}CH_3N(PF_2)_2Cr(CO)_4L \qquad (11)$$

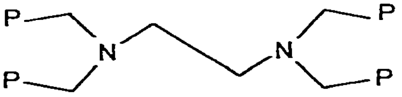
L=PPh_3, $CH_3N(PF_2)_2$

Group VI carbonyl complexes of the following ligands were reported.[15]


I L^1


II L^2


III L^3


IV L^4

The following complexes were synthesized and characterized: $L^4M(CO)_5$, $L^3M(CO)_4$, $L^2[M(CO)_5]$, $L^3[W(CO)_5]_2$, $L^4M(CO)_4$, $L^4[M(CO)_4]_2$, $L^4[Cr(CO)_4]$-$[Mo(CO)_4]$ and $L^4[W(CO)_5]_4$.[15] Stibine complexes were prepared from $Cr(CO)_5THF$ and $(Ph_2Sb)_2SNMe_2$.[16]

$$Cr(CO)_5THF + (Ph_2Sb)_2SNMe_2 \longrightarrow Me_2SN[SbPh_2Cr(CO)_5]_2 \qquad (12)$$

Polymeric $[Me_2SbSbMe_2Cr(CO)_4]_n$ was obtained from $Cr(CO)_4LL$ (LL = bicyclo-[2.2.1.]heptadiene).[16]

Several studies of dinitrogen complexes were reported. Isonitriles, RNC (R=Me, t-Bu or C_6H_4Me-4), displaced dinitrogen quantitatively from cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M=Mo or W) and trans-$[Mo(N_2)_2(PMePh_2)_4]$ in benzene under irradiation.[17]

$$M(N_2)_2L_4 \xrightarrow[RNC]{h\nu} M(RNC)_nL_{6-n} + 2N_2 \tag{13}$$

L = PMe_2Ph; R = Me, t-Bu or C_6H_4Me-4

For the cis complexes, the stepwise formation of the complexes trans-$M(CNR)_2L_4$, cis-$M(CNR)_2L_4$, mer-$M(CNR)_3L_3$ and cis-$M(CNR)_4L_2$ was established using NMR of reaction solutions. For trans-$Mo(N_2)_2(PMePh_2)_4$ the only products characterized by NMR spectroscopy were mer-$Mo(CNR)_3L_3$ and trans-$Mo(CNR)_4L_2$.[17] Chatt and coworkers also reported the preparation of some new anionic dinitrogen complexes of the type trans-$[M(N_2)_2X(dppe)_2]^-$ (M=Mo, W; X=SCN, CN or N_3).[18] Comparison of the properties of these complexes with those of $M(N_2)(NCR)(dppe)_2$ aided in the identification of a labile ammine complex $[Mo(N_2)(NH_3)(dppe)_2$. Aspects of the reactivity of coordinated dinitrogen ligand were correlated with the electron-richness of the complex.[18] George and coworkers reported the reaction of $Mo(N_2)_2(dppe)_2$ with RBr to form the 2-alkyldiazenido-N derivative, $MoBr(N_2R)(dppe)_2$, with loss of one mole of N_2, probably by a radical path.[19]

$$Mo(N_2)_2(dppe)_2 + RBr \longrightarrow Mo(N_2R)Br(dppe)_2 + N_2 \tag{14}$$

The reaction of $Mo(N_2)_2(triphos)L$ with HBr in THF resulted in NH_4Br, $MoBr_3(triphos)$ and N_2.[20]

$$2Mo(N_2)_2(triphos)L + 8HBr \longrightarrow 2NH_4Br + 2MoBr_3(triphos) + 3N_2 + 2L \tag{15}$$

The six electrons required for the reduction came from 2Mo(0) → 2Mo(III) transitions instead of one Mo(0) → Mo(VI). No trace of hydrazine was seen.[20] The complexes, $Mo(CO)L(dppe)_2$ (L = amides, imidazoles, amines, nitriles, pyridines and olefins) were obtained by the reaction of trans-$Mo(CO)(N_2)(dppe)_2 \cdot 1/2\, C_6H_6$ or $Mo(CO)(dppe)_2$ with the corresponding ligand.[21]

$$trans\text{-}Mo(CO)(N_2)(dppe)_2 + L \longrightarrow trans\text{-}Mo(CO)L(dppe)_2 + N_2 \tag{16}$$

The CO stretching vibrations in the IR spectra of the complexes were quite low (1680-1880 cm^{-1}) and related to the donor, acceptor properties of the ligands. The coordination ability of the ligands was dependent on steric size.[21]

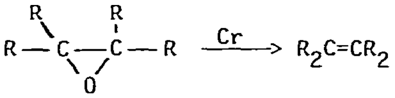
RSH (R = Ph_3C, β-naphthyl, 9-phenanthryl, etc.) underwent desulfurization with $Mo(CO)_6$ in AcOH at 120°C to give high yields of RH with thioacetates sometimes obtained as by-products.[22]

$$RSH \xrightarrow{Mo(CO)_6} RH \qquad (17)$$

Desulfurization was also observed when $Mo(CO)_6$ was adsorbed onto SiO_2.[22] The hexacarbonyls, $M(CO)_6$ (M=Cr, Mo, W) were mixed with Bu_2O and $(i\text{-}PrO)_2MeP{=}O$ and refluxed for two days to give CrL_3 (HL=(i-PrO)MeP(O)OH), $MoOL_3$, and WO_2L.[23] Reaction of di-imidosulfur compounds, $S(NR)_2$ (R=t-Bu, Ph, etc.), with a potassium mirror in vacuo gave solutions of anion radicals.[24] Potassium-metal reduction of $[M(CO)_4\{S(N(t\text{-}Bu))_2\}]$ (M=Cr, Mo, or W) produced the corresponding anions with well defined e.s.r. spectra.

$$[M(CO)_4\{S(NtBu)_2\}] \xrightarrow{K} [M(CO)_4\{S(Nt\text{-}Bu)_2\}] \qquad (18)$$

The results suggested that the unpaired electron is located mainly in the $S(N(t\text{-}Bu)_2)$ ligand.[24] Attempts to produce $[M(CO)_4\{S(NPh)_2\}]^-$ were unsuccessful except for M=Cr, when an unstable species was formed.[24] In reaction of metal atoms with various oxygen- and sulfur-containing organic compounds, several reactions of Cr atoms were investigated.[25]



(19)

$$Me_2SO \xrightarrow{Cr} Me_2S \qquad (20)$$

$$(C_6H_5CH_2)_2O \xrightarrow{Cr} (\eta^6\text{-}(C_6H_5CH_2)_2O)_2Cr \qquad (21)$$

$$(C_6H_5CH_2)_2S \xrightarrow{Cr} C_6H_5CH_2CH_2C_6H_5 \qquad (22)$$

Heating $Mo(CO)_6$ and $CH_2{=}CHCH_2Cl$ in MeCN at 50°C gave $(\eta^3\text{-}C_3H_5)(MeCN)_2\text{-}Mo(CO)_2Cl$.[26] Scrubbing a kerosine solution of this complex with a mixture of H_2, CH_4, C_2H_6, C_3H_8, C_4H_{10} and N_2 containing .090043% mercaptan sulfur lowered the mercaptan S content to 0.0003%, showing an ability to oxidize mercaptans.[26]

New germylene complexes of chromium and tungsten were prepared by reaction of $M(CO)_5[GeCl_2(THF)]$ (M=Cr,W) with Me_3SnNPh_2 to give $M(CO)_5\text{-}[Ge(NPh_2)_2]$ and Me_3SnCl.[27]

$$M(CO)_5[GeCl_2(THF)] + Me_3SnNPh_2 \longrightarrow M(CO)_5[Ge(NPh_2)_2] + Me_3SnCl \qquad (23)$$

A similar reaction led to $M(CO)_5[Ge(OR)_2]$, which was unstable. The complexes $Cr(CO)_5GeX_2L$ (X=Cl, Br; L=Py, Me_3N, etc.), $W(CO)_5[Ge(NPh_2)_2]L$ (L=py, Ph_2NH) and $W(CO)_5[GeCl(py)N(i\text{-}Pr)_2]$ were also prepared and characterized by chemical analysis and IR and ^1H NMR spectra.[27] The pi-acceptor capability of the germylenes was discussed from the IR spectra.[27] The methanediazo complexes $CpM(CO)_2(N_2Me)$ (M=Mo,W) reacted with $Cr(CO)_5(THF)$ and $CpMn(CO)_2(THF)$ via metal coordination of the basic nitrogen function to yield the thermally stable heterodinuclear complexes.[28]

$$CpM(CO)_2(N_2Me) + Cr(CO)_5(THF) \longrightarrow \mu\text{-}(N_2Me)[CpM(CO)_2][Cr(CO)_5] \qquad (24)$$

Oxidative pyrolysis of the hexacarbonyls, $M(CO)_6$ (M=Cr, Mo, W), was used to obtain films of Cr, Mo and W oxides.[29]

The prepation of the alkyl isocyanides, $[Cr(CNR)_6][PF_6]_2$, was reported ($R=C_6H_{11}$, CMe_3), allowing comparison with the previously characterized aryl analogues.[30] Addition of neat CNR to $[Cr(CNR)_6][PF_6]_2$ produced the seven-coordinate alkyl isocyanide complexes, $[Cr(CNR)_7][PF_6]_2$ in quantitative yield.[30]

$$[Cr(CNR)_6][PF_6]_2 + CNR \longrightarrow [Cr(CNR)_7][PF_6]_2 \qquad (25)$$

$R = C_6H_{11}$, CMe_3

The reactions of $Mo_2Cl_4(dppm)_2$, $Mo_2Cl_4(dppe)$ and $Mo_2Cl_4(PR_3)_4$ with alkyl isocyanides RNC ($R=CH_3$, CMe_3 or C_6H_{11}) led to cleavage of the Mo-Mo quadruple bond and formation of the seven-coordinate cations, $[Mo(CNR)_5dppm]^{+2}$, $[Mo(CNR)_4dppe]^{+2}$, $[Mo(CNR)_5(PR_3)_2]^{+2}$ and $[Mo(CNR)_6\text{-}PR_3]^{+2}$.[31]

$$Mo_2Cl_4(dppm)_2 + RNC \longrightarrow Mo(CNR)_5(dppm)^{+2} \qquad (26)$$

These complexes were isolated as the PF_6^- salts.[31] The same compounds were formed by substitutions of $[Mo(CNR)_7]^{+2}$[26] with the appropriate phosphine. The compounds were characterized by various spectroscopic techniques.[31] Several $Mo(CO)_5L$ complexes were prepared by reaction of $Mo(CO)_5THF$ with L at room temperature ($L = R_2EER'_2$, $R_2EE'R$; R,R'=Me, CF_3; E = P, As; E' = S, Se, Te).[32]

$$Mo(CO)_5THF + L \longrightarrow Mo(CO)_5L + THF \qquad (27)$$

$L = R_2EER'_2$ or $R_2EE'R$

Several complexes of $CNN{=}PPh_3$ which was prepared from $HCONHNH_2$ and PPh_3 were prepared from $W(CO)_6$.[33]

$$W(CO)_6 + CNN{=}PPh_3 \longrightarrow W(CO)_5CNNPPh_3 \qquad (28)$$

Further reactions of this complex were also observed.[33]

$$\begin{tikzcd}
(CO)_5WC\equiv NNH_2 & W(CO)_5CNNPPh_3 \arrow[l, "H_2O"'] \arrow[r, "RR'C(O)"] \arrow[d, "H^+"] & (CO)_5WC\equiv NN=CRR' \\
 & (CO)_5WN\equiv CNPPh_3 &
\end{tikzcd}$$

(29)

The Mo and Cr complexes were prepared similarly.[33] Heterobimetal complexes with bridging diazenes were prepared.[34] The complexes $(CO)_5CrZMo(CO)_5$, $(CO)_5CrZFe(CO)_4$, $(CO)_5WZFe(CO)_4$ and $(CO)_5CrZMn(CO)_2(\eta^5\text{-}C_5H_4Me)$ ($Z=\eta^2$-pentamethylenediazirine) were prepared. The structure of the Cr and Mo complex was determined by X-ray analysis.[34] All complexes were characterized by IR and UV-vis spectroscopy.[34] The treatment of the complexes, trans-$[M(CNMe)_2(dppe)_2]$ (M=Mo or W) with $MeFSO_3$, Me_2SO_4 or $[Et_3O]BF_4$ in benzene gave complexes trans-$[M(CNRMe)_2(dppe)_2]X$ Cr=Me or Et; $X=FSO_3$, $MeSO_4$ or BF_4).[35] The compounds isomerize in CH_2Cl_2 solution to give the cis isomer.

$$\begin{tikzcd}
t\text{-}[M(CNMe)_2(dppe)_2] + [Et_3O]BF_4 \arrow[r] & trans\text{-}[M(CNEtMe)_2(dppe)_2]BF_4 \arrow[d] \\
M = Mo,\ W & cis\text{-}[M(CNEtMe)_2(dppe)_2]BF_4
\end{tikzcd}$$

(30)

Spectroscopic data indicated alkylation of the nitrogen atom of the ligating isonitrile.[35] The alkylation was only accomplished on one nitrogen although protonation occurred at both nitrogens and on W. The reasons for the difference was suggested as steric although more data were necessary.[35] Propadienone ylide was stabilized by complexation with pentacarbonylchromium.[36]

$$[Bu_4N][(CO)_5CrI] + AgC\equiv CCO_2Na \longrightarrow (CO)_5Cr=C=C=CO \qquad (31)$$

The reaction occurred in 36% yield.[36]

Carbenes and Carbynes

Reports of Group VI carbenes and carbynes have dramatically decreased in 1980. $W(CO)_6$ in CCl_4 reacted under illumination with olefins RCH=CHR' to give the products $RCH=CCl_2$ and $R'CH=CCl_2$.[37] Photochemical reaction of $W(CO)_6$ in CCl_4 with cyclic enol ethers gave products resulting from the insertion of metalladichlorocarbene moieties into the carbon-carbon double bond. Possible mechanisms were discussed.[37] Stabilized metal carbenes reacted much faster with acetylenes than with alkenes, while unstabilized metal carbenes show opposite selectivity.[38] The rearrangement of pentacarbonyl[diethylamino(triphenylstannyl)carbene]chromium(0) with CO elimination to trans-tetracarbonyl(diethylaminocarbyne)(triphenylstannyl)-chromium followed a first order rate law.[39]

$$(CO)_5Cr{=}C(NEt_2)(SnPh_3) \longrightarrow t\text{-}(CO)_4(SnPh_3)Cr{\equiv}CNEt_2 + CO \qquad (32)$$

Carbon monoxide had no effect and the solvent had little effect on the rate. The results were discussed on the basis of an intramolecular C,Cr migration of the triphenylstannyl group.[39] The insertion reaction of complexes $(CO)_5M{=}C(OMe)C_6H_4R$ (M=Cr, R=H, CF_3; M=W, R=CF_3, Br, H, Me, OMe) with $MeC{\equiv}CNEt_2$ to give $(CO)_5M{=}C(NEt_2)CMe{=}C(OMe)C_6H_4R$ followed second order kinetics in octane.[40]

$$(CO)_5M{=}C(Me)C_6H_4R + MeC{\equiv}CNEt_2 \longrightarrow (CO)_5M{=}C(NEt_2)CMe{=}C(OMe)C_6H_4R \qquad (33)$$

The tungsten complexes reacted faster than the chromium complexes. The reaction was accelerated by electron withdrawing substituents (CF_3,Br) and slowed by electron-donating groups (Me,OMe).[40] Negative entropies and low activation enthalpies suggested a stepwise mechanism in which the ynamine attacked the carbene carbon in the first step.[40] Carbenemetal complexes having bulky alkyl substituents at the carbene carbon, $[(CO)_5MC(OR')R$ (M=Cr,Mo,W; R = CH_2CMe_3, CH_2SiMe_3, or $CH(SiMe_3)_2$; R'=Me,Et, or $SiMe_3$) were reported by Lappert and coworkers.[41] The Mo complexes showed good thermal stability. Photolysis of $Cr(CO)_5L$ (L=$C(OEt)CH(SiMe_3)_2$) in the presence of $P(OPh)_3$ yielded fac-$Cr(CO)_3L(P(OPh)_3)_2$.[41]

$$Cr(CO)_5L + 2P(OPh)_3 \longrightarrow fac\text{-}Cr(CO)_3L(P(OPh)_3)_2 \qquad (34)$$

The complexes were characterized by IR, ^1H and ^{13}C NMR, photoelectron spectroscopy and mass spectrometry.[41] Treatment of the complexes, trans-$[M(CNR)_2(dppe)_2]$ (M=Mo or W; R=Me, t-Bu, or 4-MeC_6H_4), with mineral acids caused protonation at one or both nitrogen atoms to give the compounds trans-$[M(CNHR)(CNR)(dppe)_2]$ X (X=BF_4, HSO_4, SFO_3).[42]

$$t\text{-}[M(CNR)_2(dppe)_2 + HX \longrightarrow t\text{-}[M(CNHR)(CNR)(dppe)_2X \qquad (35)$$

With HX (X=BF_4 or HSO_4), cis-$[Mo(CO)_2(dppe)_2]$ gave trans-$[M(CO)_2(dppe)_2]X$. The structures were discussed from spectroscopic data.[42] The reaction of $Br(CO)_4Cr{\equiv}CPh$ with PhSLi gave PhCH(SPh)C(O)SPh.[43]

Alkyls and Hydrides

Alkyls. Espenson and coworkers continued their mechanistic investigations of alkyl complexes of chromium. The chromium(III) cations, $(H_2O)_5CrCH_2OH^{+2}$ and $(H_2O)_5CrCR(R'')OH^{+2}$, were found to be stable towards unimolecular decomposition.[44] These complexes were very powerful, selective reducing agents.

They reacted with the mild oxidants Fe^{+3} and Cu^{+2} as in the following reaction.[44]

$$CrCRR'OH^{+2} + Cu^{+2} \longrightarrow Cr^{+2} + Cu^{+} + RR'C(O) + H^{+} \qquad (36)$$

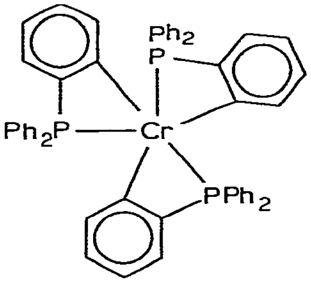
The following mechanism was suggested.[44]

$$Fe^{+3} + H_2O \rightleftarrows FeOH^{+2} + H^{+} \qquad (37)$$

$$(H_2O)_5CrCH_2OH^{+2} + FeOH^{+2} \rightleftarrows [(H_2O)_5CRCH_2OFe]^{+4} \qquad (38)$$

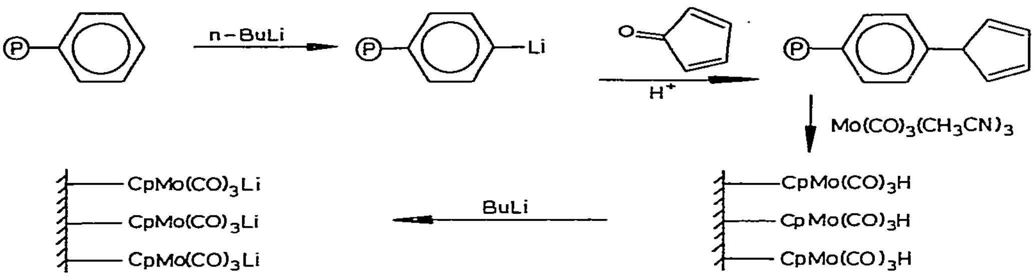
$$[(H_2O)_5CrCH_2OFe]^{+4} \longrightarrow Cr^{+2} + Fe^{+2} + H_2CO \qquad (39)$$

Kinetic data were also obtained on the reactions of $R\text{-}Cr([15]ane\text{-}N_4)(H_2O)^{+2}$ complexes R=Me,Et, etc. with mercury(II) and methyl-mercury(II) ions in aqueous perchloric acid.[45] The reactions followed a second order rate expression, first order with respect to organochromium concentration and first order in Hg(II) electrophile. The rates decreased sharply with increased steric bulk of R.[45] Complexation of $O\text{-}LiC_6H_4CH_2PPh_2$ with $CrCl_3(THF)_3$ gave an 85% yield of the chelated complex shown below.[46]



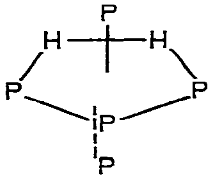
The reaction of $CrCl_2$, $CrCl_3$, $MoCl_3$ or WCl_6 with Mg and THF yield organometallic clusters which produced hydrocarbons and H_2 upon hydrolysis.[47] The composition of the gas suggested that metallocyclic compounds were involved.[47]

Hydrides. Frommer and Bergman reported the preparation of a polystyrene attached $CpMo(CO)_3H$ and its reactions with several bases.[48]

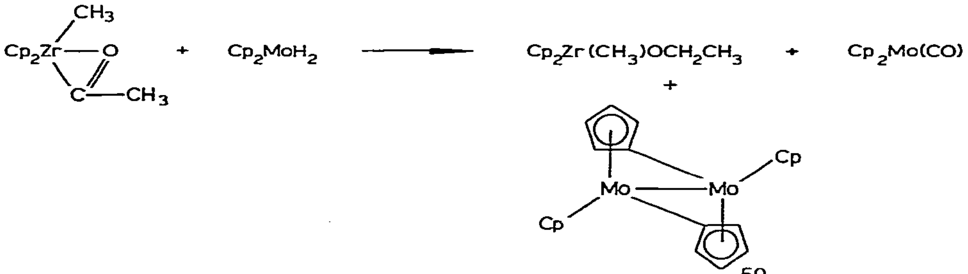


(40)

Enolates of β-dicarbonyl compounds quantitatively deprotonated the polymer bound hydride, giving polymer bound anions. Binding to the polymer was shown to have little effect on the pKa.[48] $Cr(P(OMe)_3)_5H_2$ was reported to be fluxional on the NMR time scale allowing the first detailed mechanistic analysis of intramolecular exchange in a seven-coordinate complex having all monodentate ligands.[49] The geometry based on NMR specta is that shown below.[49]



Reduction of the acyl in $Cp_2Zr(CH_3)C(O)CH_3$ was effected by Cp_2MoH_2.[50]



(41)

The same reaction with Cp_2WH_2 produced an intermediate.[50]

(42)

Both reactions occur rapidly at room temperature.[50] The hydride, Cp_2WH_2, in toluene reacted with equimolar $[ArN_2][X]$ below -20°C to give yellow salts of composition $[Cp_2WH(NNHAr)]X$.[51]

$$Cp_2WH_2 + [ArN_2]X \xrightarrow{20°C} [Cp_2WH(NNHAr)]X \qquad (43)$$

Spectroscopic determinations showed the formally arylhydrido ligand coordinated to W through N(1). The stereochemistry of the arylhydrazido ligand and its orientation were examined.[51] Repeating the synthesis at 0°C led to an isomer $[Cp_2W(H_2NNAr)]X$, which was an arylhydrazido complex in which the ligand was bound to W through both nitrogen atoms.[51] $Cp_2MoH_2AlX_{3-n}H_n$ (X=Cl, Br; n=0, 1) complexes were prepared by treating Cp_2MoH_2 with $AlX_{3-n}H_n \cdot Et_2O$.[52]

$$Cp_2MoH_2 + AlX_3 \longrightarrow Cp_2MoH_2AlX_3 \qquad (44)$$
$$X = Cl, Br$$

Pierantozzi and Geoffroy reported the photoinduced elimination of H_2 from $MoH_4(dppe)_2$ and $MoH_4(PPh_2Me)_4$.[53] Irradiation under an N_2 atmosphere produced a high yield of trans-$Mo(N_2)_2(dppe)_2$ and trans-$Mo(N_2)_2(PPh_2Me)_4$. Photolysis under CO led to cis and trans $Mo(CO)_2(dppe)_2$.[53]

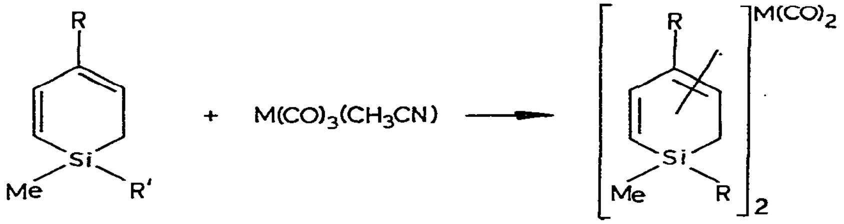
$$MoH_4L_4 \xrightarrow{h\nu, N_2} \text{trans-}Mo(N_2)_2L_4 + 2H_2 \qquad (45)$$

$$MoH_4(dppe)_2 \xrightarrow{h\nu, CO} \text{cis-and trans-}Mo(CO)_2(dppe)_2 + 2H_2 \qquad (46)$$

Reaction in the absence of a substrate led to elimination of 1.9 moles of H_2 and a product which could not be characterized.[53]

Alkene and Alkyne Complexes.

Alkenes. The results of kinetic studies on the ligand-exchange and substitution reactions of (buta-1,3-diene)tetracarbonylchromium and tetracarbonyl-(trans, trans-hexa-2,4-diene)chromium with cod, nbd, $P(OMe)_3$, and $P(OPh)_3$ to yield $Cr(CO)_4(cod)$, $Cr(CO)_4(nbd)$, and $Cr(CO)_4L_2$ were consistent with a mechanism involving a stepwise displacement of the diene ligand.[54] For diene exchange the reaction was S_N1 in nature; for substitution by phosphites the reaction had an S_N2 component.[54] 1,1-Dialkyl(aryl)-1-silacyclohexa-2,4-diene reacted with tris(acetonitrile) molybdenumtricarbonyl and -tungstentricarbonyl to give the corresponding dicarbonyl complexes with two silacyclohexadiene ligands.[55]

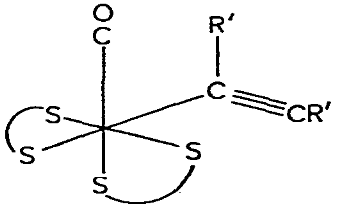


(47)

Complexes with functional groups at the silicon (chlorine, alkoxy) were also prepared. 1,6-Dichloro-1-methyl-4-cyclohexyl-1-silacyclohexa-2,4-diene reacted with $Mo(CO)_3(CH_3CN)_3$ by dehalogenation and dimerization at C(6) to give a pi-allyl dimer.[55]

Alkynes. Watson and Bergman reported a preparative method for $[CpM(CO)(2\text{-butyne})]PF_6$ complexes for M = Mo and W.[56] The alkyne ligands were shown to be labile at temperatures above 100°C. Several reactions of these alkyne complexes were reported.[56] The alkyne complexes were active (with NEt_3 as a cocatalyst) for hydrogen exchange between 2-butyne and acetonitrile or acetone.[56] Ward and Templeton prepared tungsten alkyne complexes of the type $W(CO)(RC{\equiv}CR')(S_2CNR_2)_2$ for R=R'=H, Me, Et, Ph and R=H, R'=Ph by allowing tricarbonylbis(dithiocarbamato)tungsten(II) to react with the appropriate alkyne.[57]

$$W(CO)_3S_2CNR_2)_2 + R'C{\equiv}CR' \longrightarrow W(CO)(R'C{\equiv}CR')(S_2CNR_2)_2 \qquad (48)$$



Ethylene did not react with $W(CO)_3(S_2CNR_2)_2$ under the same conditions. In contrast to the alkynes, phosphorus ligands displaced only one CO.[57] The symmetrically substituted alkyne ligands underwent a fluxional process which averaged the two ends of the alkyne at room temperature while the four independent alkyl groups of the two dithiocarbamate ligands remained distinct.[57] Activation energies of 11-12 kcal/mole were typical for the alkyne rotations investigated. The low field ^{13}C chemical shifts of acetylenic carbons in these complexes (200-210 ppm below TMS) suggested that the mode of alkyne-metal bonding could be correlated with ^{13}C NMR data.[57] Ward and Templeton concluded that the chemical reactivity patterns and spectroscopic data supported a four-electron donor role of alkynes in these tungsten (II) complexes.[57] The bis-alkyne complex, $CpWCl(CF_3C{\equiv}CCF_3)$, underwent metathetical reactions with TlSR (R=Ph, R-MeC_6H_4, Et, etc.) to give complexes of stoichiometry $CpWSR(CF_3C{\equiv}CCF_3)_2$ which, with the more electron donating groups, existed as sulfur-bridged dimers.[58]

$$CpWCl(CF_3C{\equiv}CCF_3)_2 + TlSR \longrightarrow [CpWSR(CF_3C{\equiv}CCF_3)_2]_n \quad n=1 \text{ or } 2 \tag{49}$$

$CpW(S\text{-}4\text{-}MeC_6H_4)(CF_3C{\equiv}CCF_3)_2$ gave 1/1 adducts in reactions with PEt_3, PMe_2Ph and $P(OMe)_3$. Acetylene propeller rotation was observed in some derivatives.[58] The alkyne complexes, $W(CO)(RC{\equiv}CR)_3$ (R=Ph,SMe) reacted with the ditertiary alkylphosphine, dmpe, at ambient conditions.[59] $W(CO)(MeSC{\equiv}CSMe)_3$ produced $W(CO)dmpe(MeSC{\equiv}CSMe)_2$ and $W(dmpe)(MeSC{\equiv}CSMe)_2$. All of the alkyne ligands were displaced from $W(CO)(PhC{\equiv}CPh)_3$ to give cis-$W(CO)_2(dmpe)_2$ as the primary product.[59]

$$W(CO)(MeSC{\equiv}CSMe)_3 + dmpe \longrightarrow W(CO)dmpe(MeSC{\equiv}CSMe)_2 + W(dmpe)(MeSC{\equiv}CSMe)_2 \tag{50}$$

$$W(CO)(PhC{\equiv}CPh)_3 + dmpe \longrightarrow cis\text{-}W(CO)_2(dmpe)_2 \tag{51}$$

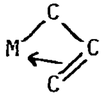
Other ligands such as PPh_3, dppe, and $PhSCH_2CH_2SPh$ gave no detectable reaction with these alkyne complexes.[59]

Allyl Complexes

Reactions of the allyl and 2-methylallyl complexes, $Mo(CO)_2Cl(n^3\text{-}C_3H_4R)(NCMe)_2$ (R=H or Me) with ligands L=PMe_2Ph or $PMePh_2$ involved initial substitution to give $Mo(CO)_2Cl(n^3\text{-}C_3H_4R)L_2$ followed by reduction to cis-$[Mo(CO)_2L_4]$ or $Mo(CO)_2(NCMe)(PMePh_2)_3$.[60]

$$\begin{tikzcd} Mo(CO)_2Cl(n^3\text{-}C_3H_4R)(NCMe)_2 + L \arrow[r] & Mo(CO)_2Cl(n^3\text{-}C_3H_4R)L_2 \arrow[d] \\ & cis\text{-}Mo(CO)_2L_4 \text{ or } Mo(CO)_2(NCMe)(PMePh_2)_3 \end{tikzcd} \tag{52}$$

The reduction, which was first order in the concentrations of molybdenum complex and L, was thought to involve nucleophilic attack on the allyl ligand. The allyl intermediate, $Mo(CO)_2X(n^3\text{-}C_3H_4R)L_2$ (X=Cl, Br, I; R=H, Me; L=py, NC_5H_4Me-4 or NC_5H_3Me-3,5), existed in solution at low temperatures in a single isomeric form in which the two carbonyl ligands, the two amine ligands and the two ends of the allyl group are inequivalent.[60,61] At higher temperatures intramolecular rearrangements remove the inequivalencies from the ^1H and ^{13}C NMR spectra of the complexes. The rearrangement rate was independent of the nature of L, decreased with increasing size of X and was greater for the 2-methyl allyl than for the allyl complexes.[60,61] Two structures were suggested for the complexes in solution: (1) a trigonal twist of the halogen and the amine ligands or (2) an oscillation of the allyl ligand about the metal-allyl axis.[61] The nature of the allyl ligand was investigated in the complexes $CpMo(CO)_2(\eta^3\text{-}C_3H_5)$ and $CpMo(NO)(I)(\eta^3\text{-}C_3H_5)$.[62] The electronic asymmetry induced by replacing two carbonyl ligands by a nitrosyl and iodide caused severe distortions in the allyl moiety. The allyl group in the nitrosyl complex was bound in a sigma pi mode rather than the symmetrical mode found in the dicarbonyl.[62]



VIII

This change in ground state structure altered the endo-exo conformer interconversion mechanism from a rotation of the allyl in the dicarbonyl to a sigma-pi interconversion in the nitrosyl iodide.[62] Reactions of $(\eta^3\text{-}C_3H_5)WX(CO)_2(MeCN)_2$ with arsines $Ph_2AsCH_2CH_2AsPh_2$(dae) and $Ph_2AsCH_2AsPh_2$ (dam) yielded complexes $WX(\eta^3\text{-}C_3H_5)(CO)_2$(dae) (X=Cl, Br, I) and $W_2X_2(\eta^3\text{-}C_3H_5)_2(CO)_4$(dam) (X=Cl, Br).[63] The former series of complexes contained chelating dae; the latter contained dam bridges which were readily cleaved by nucleophiles. Under forcing conditions the nitrile complexes reacted with ditertiary phosphines to give low yields of cis-$W(CO)_2(L_2)_2$.[63]

Metal Cyclopentadienyls and Aromatics

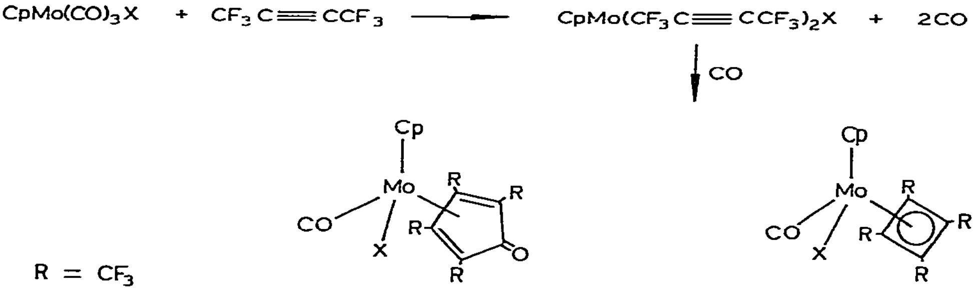
Cyclopentadienyls. Substitution reactions of $CpMo(CO)_3X$ (X=H, Cl) have been investigated with a new bidentate ligand, $PhHP(OCH_2CH_2)_2N$.[64] Reaction of the hydride with the phosphorane at room temperature resulted in substitution of one CO.

$$CpMo(CO)_3H + PhHP(OCH_2CH_2)_2N \longrightarrow CpMo(CO)_2H(PhP(OCH_2CH_2)_2NH \qquad (53)$$

The ligand was coordinated through the phosphorus.[64] The chloride complex led initially to the complex ligated through phosphorus in a unidentate mode, but refluxing in benzene produced the chelate complex.[64]

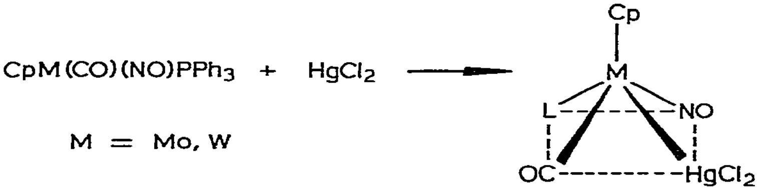
$$\begin{tikzcd} CpMo(CO)_3Cl + PhHP(OCH_2CH_2)_2N \arrow[r] & CpMo(CO)_2Cl(PhP(OCH_2CH_2)_2NH \arrow[d, "\Delta"] \\ & CpMo(CO)Cl(PhP(OCH_2CH_2)_2NH \end{tikzcd} \qquad (54)$$

Reaction of the molybdenum chloride, $CpMo(CO)_3Cl$, with amidines resulted in asymmetric molybdenum amidinato chelate complexes.[65] Use of optically active amidines yielded pairs of diastereomers which could be separated. The compounds epimerized at 70° and the ratios at equilibrium could be calculated.[65] Reactions of $CpMo(CO)_3X$ (X=Cl, Br, I) with hexafluorobut-2-yne led initially to the bishexafluorobut-2-yne which reacted with CO to give cyclobutadiene and cyclobutadienone complexes.[66]



(55)

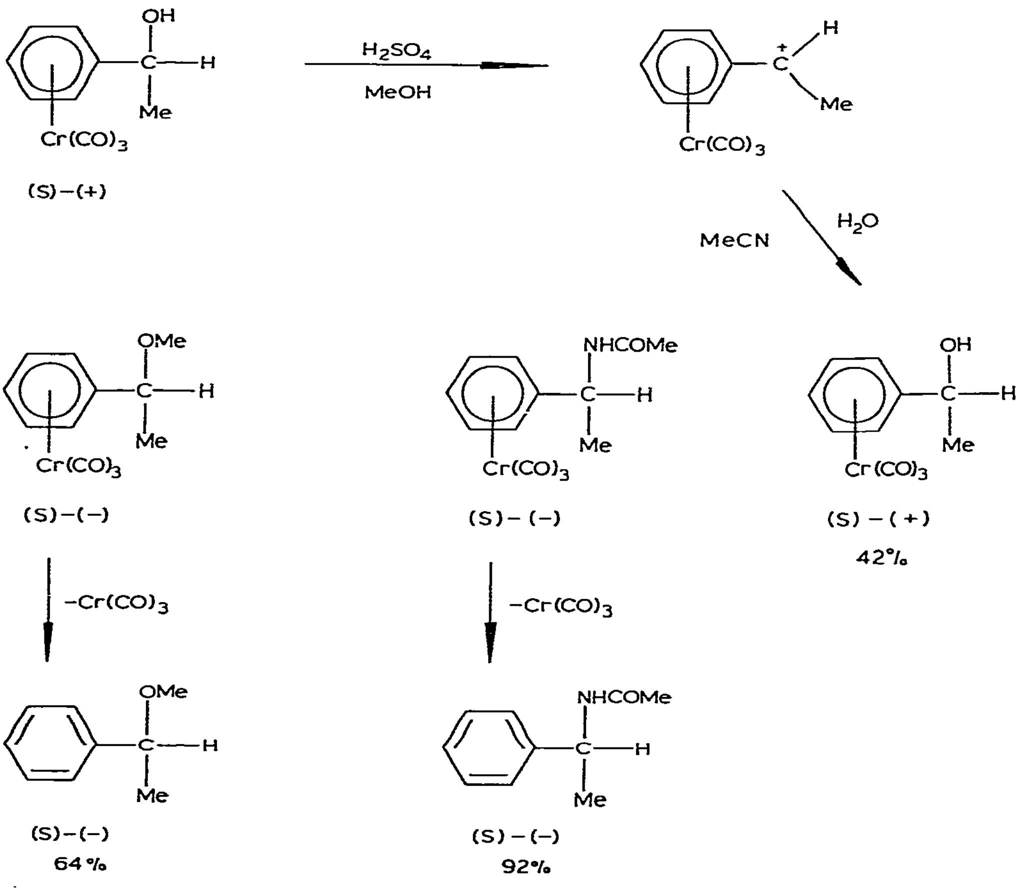
The aprotic acids $HgCl_2$ and SnX_4 (X=Cl, Br) were reported to react with $CpM(CO)(NO)L$ (M=Mo, W; L=PPh_3) by attack at the metal center.[67] With $HgCl_2$ stable 1:1 adducts $CpM(CO)(NO)L\cdot HgCl_2$ were formed.



(56)

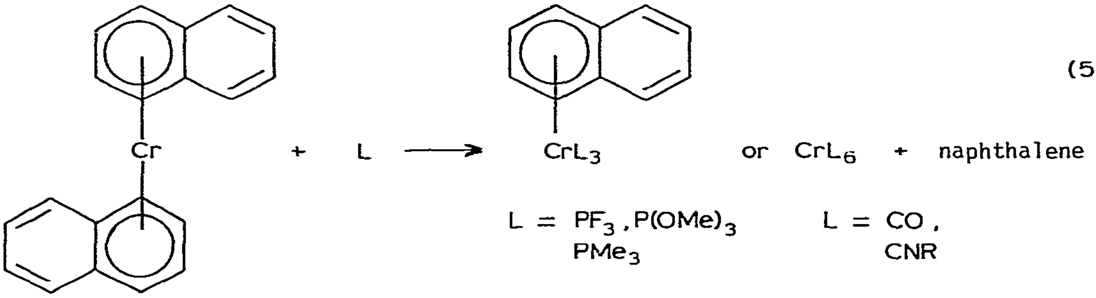
In the case of $SnCl_4$ the initial complex was the 1:2 ionic adduct, $[CpM(CO)(NO)(PPh_3)(SnCl_3)Cl]$.[67] Reaction of $[(\eta^5\text{-}C_5Me_5)Mo(CO)_3]BF_4$ with methylene cyclopropanes afforded dicarbonyl (η^4-trimethylenemethane)(η^5-pentamethylcyclopentadienyl)molybdenum cationic complexes.[68] The stereochemistry indicated a disrotatory ring opening.[68] Pyridine-2-carbalidimines (NN^*) were prepared and complexed to molybdenum, $[CpMo(CO)_2NN^*]PF_6$, giving complexes which were chiral at Mo.[69] Two diastereisomeric pairs of enantiomers were obtained and separated by fractional crystallization. Equilibration occurred at 80° and the asymmetric induction in the equilibrium was obtained by NMR integration.[69] New biscyclopentadienyl complexes were prepared by reactions of Cp_2MBr_2 (M=Mo, W) with imidazole ligands.[70]

Aromatics. Nucleophilic and electrophilic substitution in (arene)-chromium tricarbonyl complexes were investigated by extended Hückel molecular orbital calculations.[71] It was found that regioselectivity of attack on the arene could be controlled by the substituent on the ring and by the conformation of the $Cr(CO)_3$ unit. Arene carbons which are eclipsed with respect to the carbonyl groups are preferentially attacked by nucleophiles and staggered carbons are preferentially attacked by electrophiles.[71] Complexation of (S)-(-)-1-phenylethanol by $Cr(CO)_3$ allowed the use of carbenium ions to accomplish asymmetric transformations with a high degree of retention of configuration.[72]



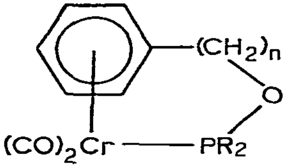
(57)

The optical purities are given as per cents under the complex.[72] Bis(η^6-naphthalene)chromium(0) was formed in high yield from chromium atoms and naphthalene in solution at -80°C.[73] This complex was a thermally stable, but very reactive compound. Two electron donor ligands displaced one naphthalene ring (L=PF_3, $P(OMe)_3$ or PMe_3) or both naphthalene rings (L=CO, $CNBu^t$, CNC_6H_{11}).[11]



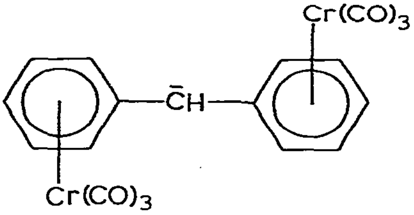
(58)

Reaction of chromium atoms with 1,4-dimethylnaphthalene is stereospecific with 95% as the isomer with chromium bound to the unsubstituted ring.[73] Reaction with 1-methylnaphthalene led to 10 isomers.[73] The mass spectra of one-, two- or three-bridge arene-chelate complexes of chromium were investigated.[74]



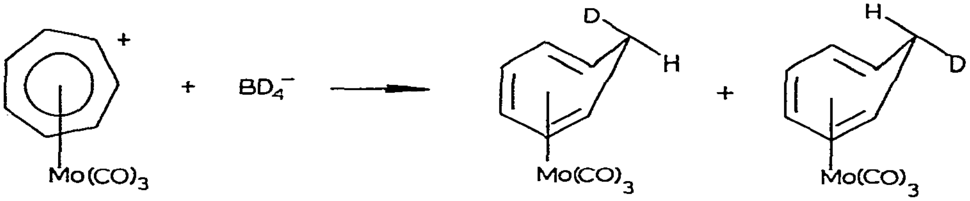
IX

Arenechromium tricarbonyl complexes with phosphorus-containing groups in the side chain were converted to the corresponding arene-chelate complexes.[74] A stabilization of the bis(tricarbonylchromium)diphenylmethyl carbanion by delocalization of negative charge onto the carbonyl moieties was indicated by ^{13}C and ^{1}H NMR chemical shift and coupling constant data.[75]



X

There did not appear to be an interaction between the alpha-carbon and the chromium.[75] The addition of borodeuteride to (tropylium) molybdenum tricarbonyl cation led to a 28:72 mixture of endo to exo cycloheptatriene product.[76] Since intermolecular exchange is extremely slow this was evidence for the initial site of attack, contrary to previous suggestions of specific exo attack. When cyanoborodeuteride was used an even lower specificity was found.[76]

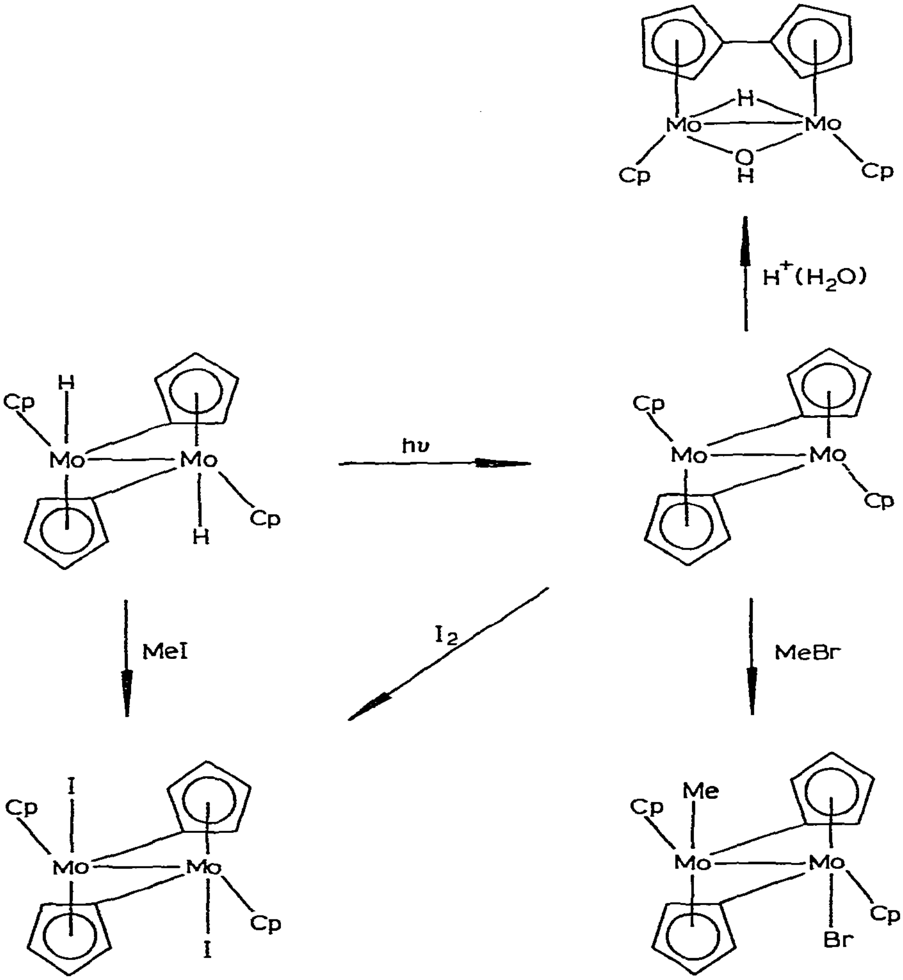


(59)

Thus an alternative to direct attack on the ring must be available, probably attack at the metal or on a carbonyl.[76]

Metal-Metal Bonded Complexes

By combination of the seventeen-electron carbonyl metal units (generated photochemically), $Cp(CO)_3Cr$, $Cp(CO)_3W$, $(CO)_5Mn$, $Cp(CO)_2Fe$, $(CO)_4Co$ and $Cp(CO)Ni$, the seven homonuclear as well as twenty-one heteronuclear dimetal complexes were prepared and investigated.[77] All of the heterodinuclear complexes were formed in benzene from mixtures of the homodinuclear compounds. The reactions led to equilibrium mixtures which resulted equally from the two homodinuclear as well as from the heterodinuclear complexes.[77] When $Cp(CO)_3Cr$, $Co(CO)_4$ and $Cp(CO)Ni$ are participants the equilibrium lay on the side of the mixed compounds.[77] The tetramer, $[Cp_2MoHLi]_4$, reacted with N_2O giving the yellow dimers cis- and trans-$[CpMoH(\mu\text{-}\sigma{:}\eta^5\text{-}C_5H_4)]_2$.[78] These thermally rearranged to the green dimer $[\{CpMoH\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$. Protonation of the latter gave $[\{CpMoH\}_2(\mu\text{-}H)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][PF_6]$. Further reactions of these complexes are outlined below.[78]



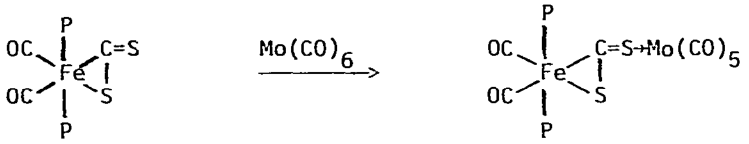
(60)

Addition of HBr to a saturated solution of $Mo_2(CH_2SiMe_3)_6$ led to $Mo_2Br_2(CH_2SiMe_3)_4$ in greater than 60% yield.[79] The bromide could be readily replaced leading to a variety of compounds.[79]

$$\begin{tikzcd}
 & \mathrm{Mo_2Me_2R_4} & \\
\mathrm{Mo_2R_6} \arrow[r, "2HBr"] & \mathrm{Mo_2R_4Br_2} \arrow[u, "2MeLi"'] \arrow[r, "2Li(O\text{-}i\text{-}Pr)"] \arrow[d, "2LiNMe_2"] & \mathrm{Mo_2(O\text{-}i\text{-}Pr)_2R_4} \\
 & \mathrm{Mo_2(NMe_2)_2R_4} &
\end{tikzcd} \qquad (61)$$

$R=CH_2SiMe_3$

New dimetallic organochromium cations, each containing two benzylchromium-like units per molecule were prepared by Pohl and Espenson.[80] These tetrapositive complexes were isolated and purified by ion-exchange chromatography in aqueous solution. The complexes were characterized by their UV-visible absorption spectra and by reactions with the chloropentaaminecobalt(III) ion, with sodium carbonate, and with mercury(II) chloride.[80] Binuclear organosulfur molybdenum complexes of formula $Cp_2Mo_2(CO)_4(R_2CS)$ which contain a metallathiacyclopropane unit and a semibridging carbonyl group reacted with phosphites and alkoxyphosphines giving alkyl migration and ligand substitution products.[81] Mechanisms were proposed for these reactions.[81] The heterodinuclear complex $(Me_3P)_2(CO)_2FeCS_2Mo(CO)_5$ containing CS_2 as a bridging group was synthesized.[82]



(62)

$P=PMe_3$

PHOTOLYSIS

Several photolyses of the hexacarbonyls were reported in 1980. The flash photolysis at 353 nm of $Cr(CO)_6$ in perfluoromethylcyclohexane revealed that the $Cr(CO)_5$ produced was extremely reactive, combining with CO, N_2, C_6H_{12} and $Cr(CO)_6$ with rate constants approaching those of diffusion control.[83]

$$Cr(CO)_6 \xrightarrow[-CO]{h\nu(353\ nm)} Cr(CO)_5 \xrightarrow{Cr(CO)_6} Cr_2(CO)_{11} \qquad (63)$$

The coordination of $Cr(CO)_5$ to $Cr(CO)_6$ was presumed to be through the carbonyl oxygen.[83] MoL_3 (HL=1,1,1,5,5,5-hexafluoro-2,4-pentanedione) was prepared in 75% yield by UV irradiation of $Mo(CO)_6$ and HL in benzene solution.[84] The photodissociation of $M(CO)_6$ (M=Cr or W) and the multiphoton ionization spectra of the resulting atoms were studied using a tunable visible dye laser.[85] Fine powders of Cr, Mo and W were prepared in milligram quantities by induced dielectric breakdown of the carbonyl compounds irradiated with a CO_2 transversely excited laser with a maximum focused power of 10 GW/cm^2.[86] The chromium deposit consisted of a polymeric chain-like agglomeration of particles with an average size of 75 Å.[86] Laser irradiation of a heated mixture of hydrogen, $Mo(CO)_6$ and 1-hexene, did not produce the expected Mo particles with catalytic hydrogenation of hexene.[87] Molybdenum cobwebs did form over periods of time when mixtures of 1-hexene and $Mo(CO)_6$ were irradiated with a single CO_2 laser pulse.[87]

Photolysis of $W(CO)_6$ in the presence of cyclooctatetraene in hexane led to sequential displacement of CO resulting in formation of dihapto, tetrahapto and hexahapto complexes of cyclooctatetraene with tungsten.[88]

$$\begin{tikzcd}
W(CO)_6 + C_8H_8 \arrow[r, "h\nu"] & W(CO)_5(\eta^2\text{-}C_8H_8) \arrow[d, "h\nu"] \\
W(CO)_3(\eta^6\text{-}C_8H_8) & W(CO)_4(\eta^4\text{-}C_8H_8) \arrow[l, "h\nu"']
\end{tikzcd} \qquad (64)$$

This led to a simple preparation of η^4-cyclooctatetraenetetracarbonyltungsten.[88] Schenk described the photochemistry of $W(CO)_4LL'$ complexes.[89] The complexes fall into two categories with respect to their photochemistry. Compounds which contained at least one strongly donating phosphine ligand, lost one of the axial phosphines upon irradiation.[89] One phosphine was always lost preferentially, with the photochemical lability increasing in the series below.

$$(Me_2N)_3P < (i\text{-}PrO)_3P < (PhO)_3P < Ph_3P$$

Compounds which contained only weakly donating phosphine ligands lost CO upon irradiation.[89] Emission from a $W(CO)_5L$ complex in room temperature solution was observed.[90] $W(CO)_5(4\text{-}CNC_5H_4N)$ excited by 353 or 530 nm irradiation, produced a relatively weak emission with a decay time of 360 ns at 630 nm. The emission could be quenched by 9-methylanthracene and by 1,2 benzanthracene, but not by 1,2,5,6-dibenzanthracene or ferrocene.[90]

Irradiation of $CpW(CO)_3$(n-pentyl) in isoctane solution at 25°C resulted in formation of $CpW(CO)_2$(pentene)(H) and eventually $CpW(CO)_3H$ and $Cp_2W_2(CO)_6$.[91] Flash photolysis gave $CpW(CO)_2$(1-pentene)H in near quantitative yield. Low temperature irradiation in hydrocarbon matrices provided direct evidence for the following steps.[91]

$$CpW(CO)_3(n\text{-}pentyl) \xrightarrow{h\nu} CpW(CO)_2(n\text{-}pentyl) + CO \qquad (65)$$

$$CpW(CO)_2(n\text{-}pentyl) + CO \xrightarrow{\Delta} CpW(CO)_3(n\text{-}pentyl) \qquad (66)$$

$$CpW(CO)_2(n\text{-}pentyl) + PPh_3 \xrightarrow{\Delta} CpW(CO)_2(PPh_3)(n\text{-}pentyl) \qquad (67)$$

$$CpW(CO)_2(n\text{-}pentyl) \xrightarrow{\Delta} CpW(CO)_2(1\text{-}pentene)H \qquad (68)$$

Irradiation resulted in loss of CO as the primary photoprocess followed by β-hydride transfer to yield an alkene-hydride complex.[91] The primary photochemical process for $CpM(CO)_3X$ (M=Mo, X=Br, I; M=W, X=Cl, Br, I) at 366 or 436 nm was also dissociation of a CO.[92] Irradiation of benzene solutions containing PPh_3 led stereospecifically to cis-$CpM(CO)_2PPh_3X$.[92]

$$CpM(CO)_3X + PPh_3 \xrightarrow{h\nu} cis\text{-}CpM(CO)_2PPh_3X \qquad (69)$$

M=Mo,W; X=Cl,Br,I

Quantum yields varied as a function of irradiation wavelength ($\Phi_{366} > \Phi_{436}$), central metal ($\Phi_{Mo} > \Phi_W$) and halogen ($\Phi_{Cl} > \Phi_{Br} > \Phi_I$) but were relatively insensitive to PPh_3 concentration. The substituted complexes, $CpMo(CO)_2PPh_3X$, underwent cis $\rightleftarrows$ trans isomerization and ligand-exchange reactions leading to $CpMo(CO)(PPh_3)_2X$ and $CpMo(CO)_3X$.[92]

$$cis\text{-}CpMo(CO)_2PPh_3X \rightarrow trans\text{-}CpMo(CO)_2(PPh_3)X + CpMo(CO)(PPh_3)_2X + CpMo(CO)_3X \qquad (70)$$

Near UV irradiation of tetrakis(1-norbornyl)chromium yielded homolytic cleavage of the metal-alkyl bond as a result of a ligand-to-metal charge transfer transition.[93] Ligand field excited states were apparently not involved.[93] Flash photolysis of trans-$(N_2)_2W(dppe)_2$ at -60, -30, or -10°C indicated that loss of dinitrogen occurred stepwise through several intermediates, one of which was the doubly coordinatively unsaturated species, $W(dppe)_2$.[94]

$$W(N_2)(dppe)_2 \xrightarrow{h\nu} W(dppe)_2 \qquad (71)$$

A foil containing benzenetricarbonylchromium was shown to be photosensitive with a spectral sensitization to 570 nm.[95]

Several reports of photochemistry of complexes in matrices were reported in 1980. Photolysis (229-366 nm) of $Cr(CO)_5PMe_3$ in argon and methane matrices at 10°K resulted in the formation of $Cr(CO)_4PMe_3$ and CO.[96] The reaction was only partly reversed by irradiation above 400 nm because of isomerization of $Cr(CO)_4PMe_3$.

$$\begin{tikzcd} \mathrm{Cr(CO)_5PMe_3} \arrow[r, "h\nu"] & \mathrm{Cr(CO)_4PMe_3} \arrow[d] \\ & \text{isomerization} \end{tikzcd} \qquad (72)$$

This behavior was explained by means of a one electron d-orbital energy diagram.[96] Short wavelength photolysis (229, 254 nm) of $M(CO)_5(piper)$ (M=Cr, Mo, W) in argon matrices at 10°K resulted in the formation of $M(CO)_4L$ species of C_s symmetry.[97] Photolysis with longer wavelengths (366, 405 nm) caused M-L bond breaking and formation of $M(CO)_5$.

$$M(CO)_5(piper) \xrightarrow{h\nu} M(CO)_4(piper) + CO \qquad (73)$$
$$\lambda = 229,\ 254\ nm$$

$$M(CO)_5(piper) \xrightarrow{h\nu} M(CO)_5 + piper \qquad (74)$$
$$\lambda = 366,\ 405\ nm$$

M=Cr,Mo,W

The structures of the photoproducts were determined by ^{13}CO labeling and force field calculations.[97] These authors also studied the photolysis of $Cr(CO)_5NMe_3$ in inert matrices.[98] The results were very similar.[98]

$$Cr(CO)_5NMe_3 \xrightarrow{h\nu} Cr(CO)_4NMe_3 + CO \qquad (75)$$
$$\lambda = 229,\ 254$$

$$Cr(CO)_5NMe_3 \xrightarrow{h\nu} Cr(CO)_5 + NMe_3 \qquad (76)$$
$$\lambda = 366,\ 405,\ 436\ nm$$

Photolysis of the hexacarbonyls in hydrocarbon glasses at 80°K produced $M(CO)_n$ (n=3-5) by successive CO loss.[99] Slow warming led to recombination, hexacarbonyl precipitation, polymeric species and $M(CO)_5(H_2O)$. The species $Cr(CO)_5(H_2O)$ was photolabile in solution but not in the glass.[99] Photolyses were also investigated in glasses containing oxygen donors with evidence for complex formation.[100]

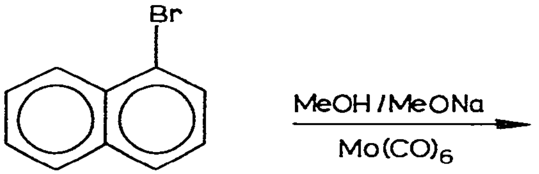
ORGANIC SYNTHESIS AND CATALYSIS

Organic Synthesis

Thiols or mercaptans in acetic acid solution could be desulfurized at 120°C by $Mo(CO)_6$.[101] Good yields of hydrocarbons were obtained for aromatic, benzylic and aliphatic thiols.[101] A patent described the carbonylation of alkyl esters at CO partial pressures $\geq$ 1 bar.[102] Thus, carbonylating MeOAc over $RhCl_3$, PBu_3 and $Cr(CO)_6$ in the presence of MeI gave Ac_2O with 98% selectivity.[102] The hexacarbonyls, $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$, initiated the selective reduction of $HOCMe_2CCl_3$ with Me_2CHOH.[103]

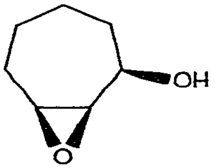
$$HOCMe_2CCl_3 + Me_2CHOH \rightarrow Me_2C{=}CCl_2 + HOCMe_2CHCl_2 \qquad (77)$$

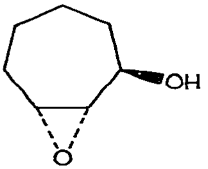
$Me_2C{=}CCl_2$ was only formed in the presence of the hexacarbonyls. The yield of $HOCMe_2CHCl_2$ was higher for $Mo(CO)_6$ and $W(CO)_6$.[103] Chromium hexacarbonyl initiated the telomerization of propylene with CCl_4.[104] The similarity to initiation by $(C_6H_5)_2O_2$ suggested a radical mechanism.[104] Reaction of 1-bromonaphthalene with MeOH-MeONa in the presence of $Mo(CO)_6$ gave the ester product.[105]



(78)

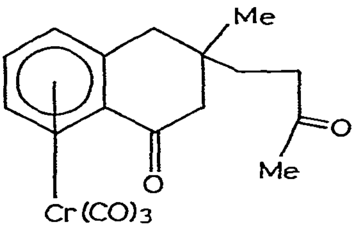
Hydrolysis of 3-bromocycloheptene gave cyclohept-2-en-1-ol in 91% yield. Oxidation by Me_3COOH in the presence of $Mo(CO)_6$ gave 80% of the epoxide, XI,

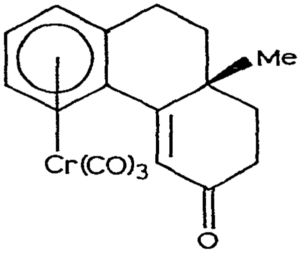




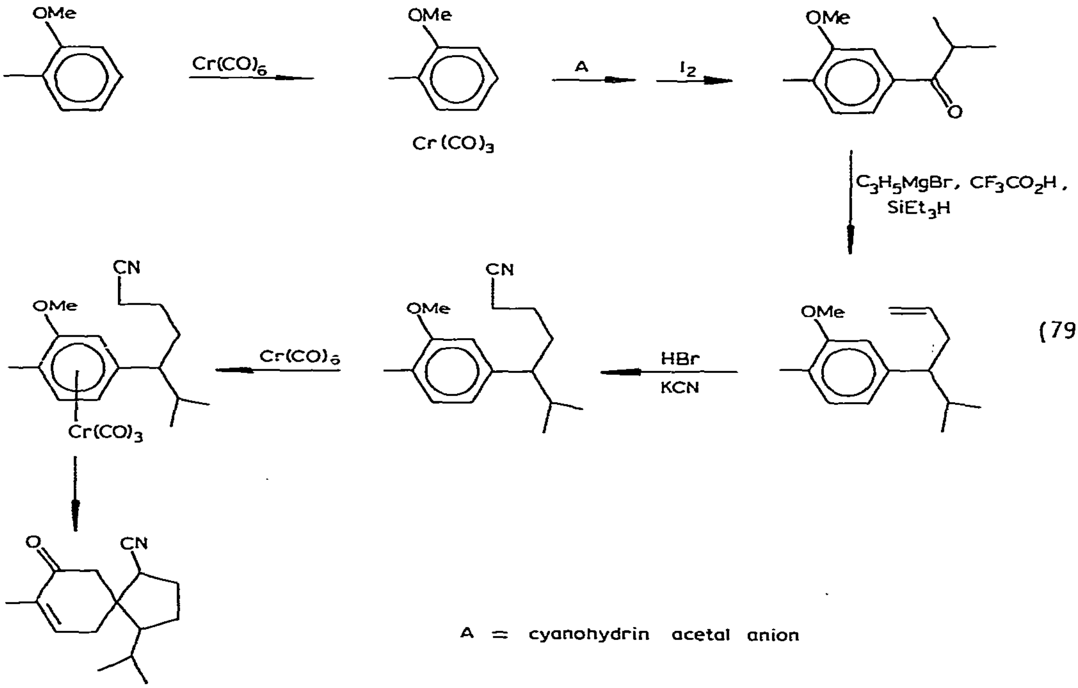
which could be rearranged to epoxide, XII.[106] Epoxidation of cycloolefins (cyclopentene, cyclohexene, and their methyl derivatives) was first order in olefin, $Mo(CO)_6$ and $Me_2CPhOOH$.[107] The methylcyclopentenes were epoxidized at a lower rate than the methylcyclohexenes.[107]

A new synthetic scheme for the preparation of families of optically active benzobicylic systems was developed, a key step in the synthesis involved the use of arenetricarbonylchromium derivatives.[108] Stereospecific base-catalyzed ring closure of 2-methyl 2-(3-oxobutyl)-1-indanone and 1-tetralonetricarbonylchromium led to optically active α-enones via classical annulation and to optically active benzobicyclic keto alcohols by an unusual cyclization at benzylic carbons.[108]





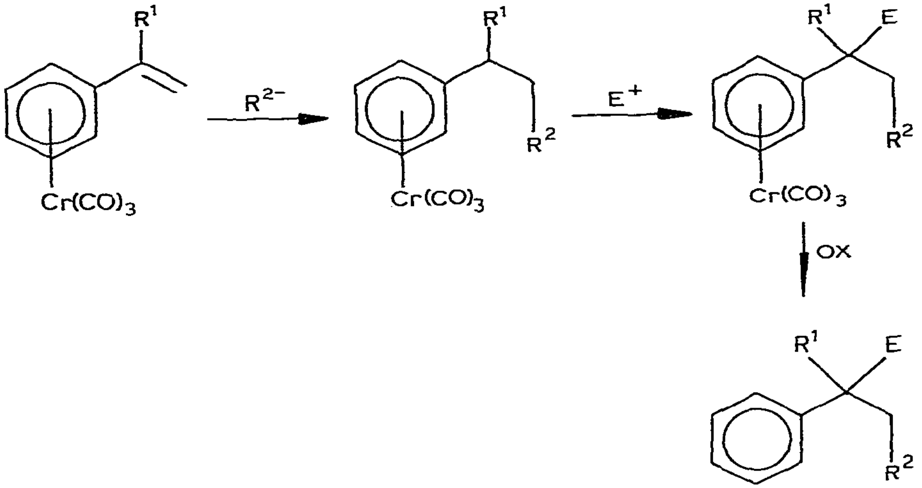
The assignment of the endo/exo stereochemistry was solved by a combination of ^1H NMR methods. The complexed arenes, with a fully determined absolute configuration at every step of the reaction, were good precursors to known or previously inaccessible optically active benzobicyclic derivatives.[108] The synthesis of acorenone and acorenone B were reported by utilizing the activating and meta-directing effects of the chromium tricarbonyl group and specific exo addition to coordinated arenes.[109]



(79)

A = cyanohydrin acetal anion

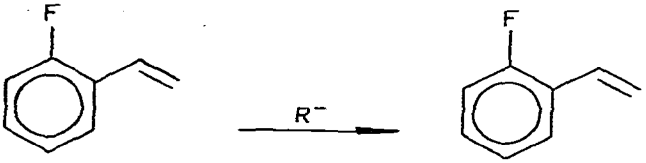
The synthesis was completed by non-organometallic reactions.[109] Nucleophilic addition to several styrene complexes of $Cr(CO)_3$ were reported.[110]



(80)

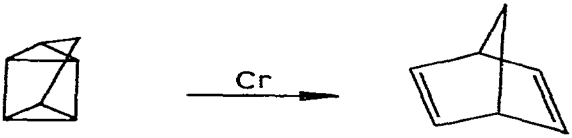
R_1=H, CH_3, SEt; R_2=$C(CH_3)_2CN$, C_4H_9, Ph, Me, etc.
E=H^+, CH_3I, etc.

The nucleophile was added at -78°C and the solution warmed to room temperature; addition of the electrophile led to a stable complex from which the aromatic could be freed by oxidation.[110] Use of fluorobenzene led to replacement of the fluorine instead of addition to the olefin.[110]



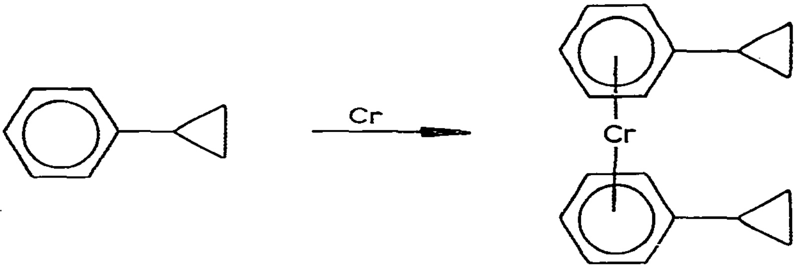
The complexation of a $Cr(CO)_3$ group to certain aromatic hydrocarbons enhanced the benzylic position towards attack by superoxide (KO_2) in DMSO.[111] The ketones produced could also be prepared by treatment of the corresponding benzylic anion complex with molecular oxygen.[111] A naturally occurring methoxyphthalide derivative was synthesized by employing stereoselective carbonyl reduction of (η^6-arene)tricarbonylchromium and regioselective lithiation of 7-methoxy-2-(1-hydroxyethyl)-1-tetralol.[112]

The reaction of various metal atoms with organocyclopropanes were studied.[113] Quadricyclane was isomerized to norbornadiene.[113]



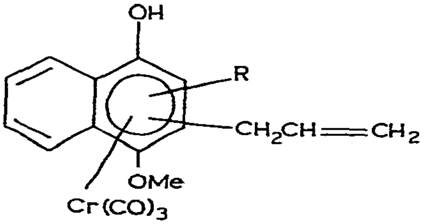
(81)

When cyclopropylbenzene was cocondensed with chromium, only bis(cyclopropylbenzene)chromium(0) was formed.[113]



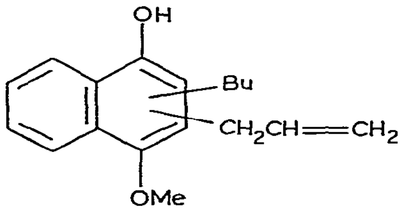
(82)

The epoxidation of 1-octene catalyzed by molybdenum naphthenate using cumene hydroperoxide stabilized by BaO was reported.[114] The selectivity for 1-octene oxide was 95% versus 9% in the absence of BaO.[114] Pentacarbonyl-(methoxyphenylcarbene)chromium(0) and $RC{\equiv}CCH_2CH{=}CH_2$ (R=Me,Et,Pr,Bu) reacted on warming in Bu_2O to give the aromatic complexes.[115]

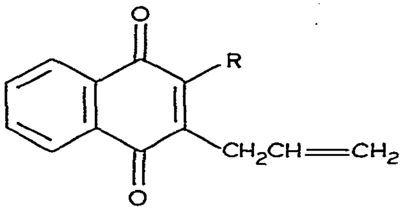


XV

Chromatography of these complexes on silica gel led to decomplexation to give naphthols or naphthoquinones.[115]

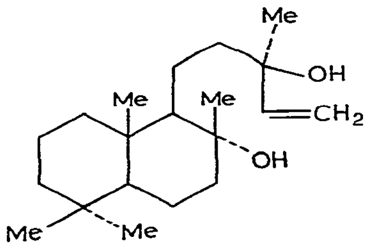


XVI

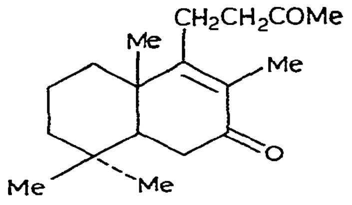


XVII

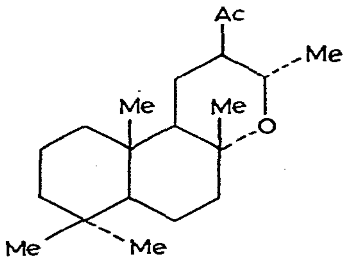
Oxidation with Ag_2O gave only the quinones or their tricarbonylchromium complexes.[115] Oxidation of sclareol by chromium mixtures gave a number of products including derivatives of 15,14-bisnorlabdane, epoxyketones and norsesquiterpeneketones.[116-118]



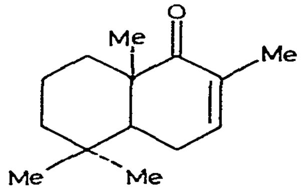
XVIII



XIX



XX



XXI

Homogeneous Catalysis

Olefin metathesis. Two studies explored the possible intermediates in catalysis of olefin metathesis by $M(O)Cl_4$ complexes.[119,120] The complexes, $M(O)Cl(neopentyl)_3$ (M=Mo,W), were isolated from solutions which were active in olefin metathesis.[119] Although inactive for metathesis alone these complexes were very active upon treatment with $W(O)Cl_4$. The synthesis of $M(O)(neopentyl)_4$ was also reported.[119] The reaction between $WOCl_4$ and $MgMe_2$, which produced an active olefin metathesis catalyst was studied.[120]

$$WOCl_4 + MgMe_2 \rightarrow CH_3WOCl_3 \cdot Et_2O \qquad (83)$$

A methyl-tungsten complex, $CH_3WOCl_3 \cdot Et_2O$, was isolated in low yield and investigated spectroscopically and by its reactions.[120] The studies established $CH_3WOCl_3 \cdot Et_2O$ as a catalyst precursor and incorporation of a CH_2 fragment from the CH_3 into the olefin metathesis products.[120] The product distributions from metathesis, degenerate metathesis and cis-trans isomerization were determined by the type of alkene coordination to the metallocarbene.[121] The steric course was reported to depend on a compromise of various types of repulsive interactions in the transition state metallocyclobutene. These interactions decreased in the order Cr > Mo > W.[121] The minor products from the cross-metathesis of norbornadiene with 1-hexene and of cyclopentene with 1,7 octadiene using $W(AsPh_3)_2(CO)_3Cl_2$ or WCl_6 and $SnMe_4$ as catalyst, were reported to show that the complexed alkylidenes, RCH=M (M-catalyst) were much preferred to complexed methylene, CH_2-M as chain carriers.[122] However CH_2=M, when formed, was highly reactive with the strongly electrophilic methylene ligand selectively adding to terminal olefins at the C-1 position.[122] The addition of cycloalkenes to $(CO)_5W{=}C(OMe)Ph$ produced no polyalkenamers; in the presence of phenylacetylene they were produced although no metathesis of cis-2-pentene was observed.[123] The yields were inversely related to the concentration of PhC≡CH. The stereoselectivity was good - for cycloheptene the product was 97% cis.[123] This study supported the idea that acetylene polymerization, like olefin metathesis involved the addition of metal carbenes to carbon-carbon multiple bonds.[123] Using ab initio methods, the bond energies and reaction enthalpies for several processes involved in olefin metathesis and epoxidation were calculated.[124] The results suggested that to activate metal chlorides it was essential to have spectator metal oxo bonds.[124] Supported molybdenum catalysts (on Al_2O_3 and SiO_2) were shown to be active for the metathesis of propene.[125]

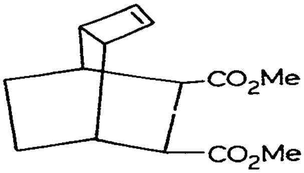
Other catalytic systems. At temperatures above 100°C hydrogen reacted with $Cp_2Mo_2(CO)_4(RC_2R)$ to form cis-RCH=CHR and $Cp_2Mo_2(CO)_4$.[126]

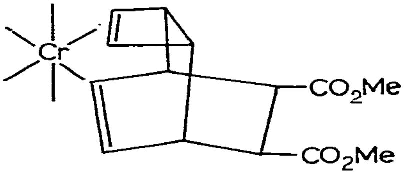
$$Cp_2Mo_2(CO)_4(RC_2R) + H_2 \rightarrow Cp_2Mo_2(CO)_4 + RCH{=}CHR \qquad (84)$$

In the presence of excess alkyne, the reaction was catalytic with turnover rates of 0.031/min. at 150°C. The complex $Cp_2Mo_2(CO)_3P(OMe)_3(RC_2R)$ was prepared and shown to be a catalyst precursor that was at least an order of magnitude more active, although disproportionation was observed.[126] These catalysts were specific to cis olefins. Possible fragmentation was checked by using a mixture of $Cp_2Mo_2(CO)_4(RC_2R)$ and $(\eta^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4(RC_2R)$.[126] No mixed products were obtained.

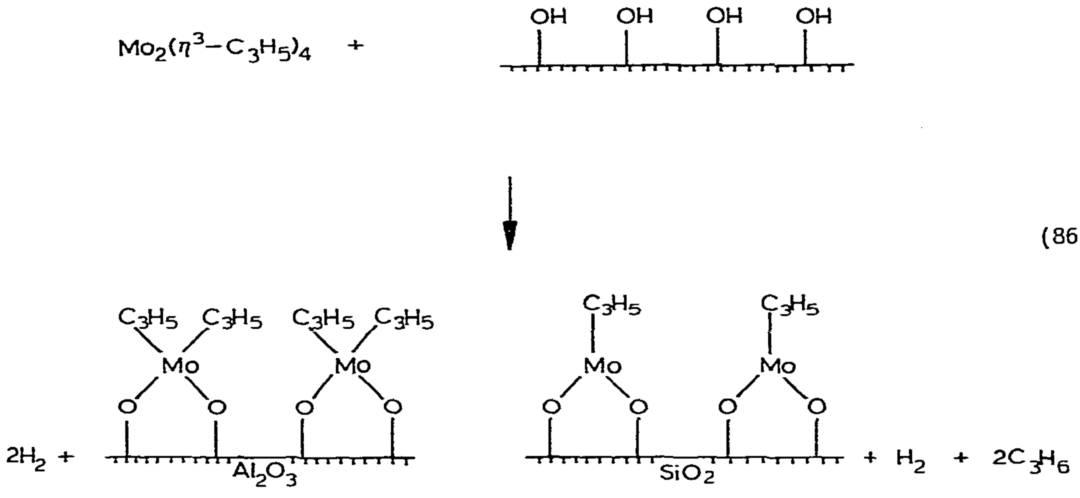
$$Cp_2Mo_2(CO)_4(RC_2R) + (\eta^5\text{-}C_5H_4CH_3)_2Mo_2(CO)_4(RC_2R) \not\longrightarrow (Cp)(\eta^5\text{-}C_5H_4CH_3)Mo_2(CO)_4(RC_2R) \qquad (85)$$

Kinetic studies of the acetylene-exchange reaction established the rate law to be of the form $k_1[Cp_2Mo_2(CO)_4(RC_2R)]$.[126] For both the hydrogenation reaction and the alkyne-exchange reaction, the first step was thought to be CO dissociation.[126] Stereospecific and regioselective hydrogenation of tricyclo[4.2.2.0]deca-3,9-diene was reported to be catalyzed by phenanthrene-chromium tricarbonyl.[127]





The addition of hydrogenation was cis-endo. The mechanism involved ligand exchange of the diene with chromium carbonyl.[127] Hydroformylation of internal olefins in the presence of $RhH(CO)(PPh_3)_3$ and a Group VI cocatalyst gave straight chain aldehydes.[128] The use of the Rh(I) catalyst, an excess of PPh_3 and a mixture of 2- and 3-hexenes with $Mo(CO)_6$ cocatalyst (Rh/Mo = 1/1) gave a ratio of normal to isoheptanals of two.[128] The surface species which were chemically well-defined, acted as catalysts for ethene hydrogenation at room temperature or below.[129]



(86)

When $Mo(CO)_3$-(dehydroxylated alumina, γ^- + δ-Al_2O_3) was activated in He to 500°C, clusters of Mo about 4 nm in diameter were formed.[130] The clusters consisted of Mo^{+2} plus Mo(0) in which the charge was delocalized and balanced by Al-O^- groups at the surface. Materials so prepared exhibited a turnover frequency for formation of methane at 300°C of 0.04 s^{-1} per surface Mo atom in flowing H_2 and CO.[130]

Polymerization of terminal olefins with ethene was accomplished by an oxide-supported CrO_3 catalyst and an aluminum catalyst activator.[131] The polymerization of acetylenes was accomplished by (phenylmethoxycarbene)-pentacarbonyltungsten in much better yields than previously.[132] The ability of several olefin metathesis catalysts to polymerize acetylenes paralleled their ability to induce olefin metathesis.[132] Polymerization of acetylenes was also effected by photolysis of the carbonyls.[133] The polymerization of PhC≡CH induced by photolysis of $W(CO)_6/CCl_4$ gave a polymer of molecular weight $\leq$80,000 in high yield.[133] No polymerization occurred in the absence of UV irradiation or halogen compounds. The polymerization of PhC≡CCl was best effected by $Mo(CO)_6$ giving a polymer with molecular weight 400,000.[133]

Temperature-programmed decomposition was used to study the nature of the bonding to Al_2O_3 of the zero-valent catalyst precursor $W(CO)_6$.[134] The pretreatment conditions and activation temperatures which led to the formation of supported, low-valent tungsten were identified. At temperatures of less than 200°C, highly dispersed, zero-valent, subcarbonyl species were formed.[134] W(CO)ads was identified.[134] A catalyst for preparing polyalkenes was prepared by impregnating silicon supports with $(i\text{-PrO})_4Ti$ and a pi-bonded organochromium compound (dibenzenechromium or dicumenechromium).[135] Molybdenum hexacarbonyl catalyzed the cyclopropanation of acrylonitrile, methacrylonitrile, or ethylacrylate by ethyldiazoacetate or alpha-diazoacetophenone at 25-65°C.[136] Product ratios of geometrical isomers formed were relatively insensitive to temperature. $Cr(CO)_6$ was also catalytically active, but $W(CO)_6$ was inactive.[136] The results suggested the intermediacy of molybdenum carbene species in the formation of the cyclopropane derivatives.[136] The addition of CCl_4 to 1-octene was catalyzed by $Cr(CO)_6$ in DMF at 120°C, giving $n\text{-}C_6H_{13}CHClCH_2CCl_3$.[137]

$$\text{1-octene} + CCl_4 \xrightarrow{Cr(CO)_6} C_6H_{13}CHClCH_2CCl_3 \tag{87}$$

The addition of $CHCl_3$ to 1-heptene was unsuccessful at 140°C in the presence of $Cr(CO)_6$ or $W(CO)_6$.[137] $Mo(CO)_6$ was used in the epoxidation and allylic oxidation of cholesteryl acetate by ROOH (R=H, Et, etc.).[138] Several organometallic complexes were prepared of heterododecatungstate and heterododecamolybdate.[139]

PHYSICAL STUDIES

Infrared and Raman

Semiempirical calculations were performed on $Cr(CO)_6$ with the aim of resolving the sign ambiguities in the polar tensors.[140] A test of the usefulness of these polar tensor values, obtained from intensities measured in solution, for the prediction of the IR intensities of $Mo(CO)_6$ and $W(CO)_6$ was reported.[140] The infrared spectra of $Mo(CO)_6$ adsorbed on two types of $\gamma\text{-}Al_2O_3$ were determined after initial absorption at 25°C and after activation in flowing He at 100°C to produce $Mo(CO)_3$(ads).[141] The amount of hydroxylation was varied. Reaction between $Mo(CO)_6$ and the surface occurred at 25°C by attack of surface O^{-2} or OH^- on the carbon of one CO ligand with consequent labilization of the other CO ligands.[141] On fully hydroxylated alumina the primary species was $(\text{-OH})_3Mo(CO)_3$ while on dehydroxylated it was $(\text{-O})_3Mo(CO)_3$.[141] An empirical linear relationship between the ratio of cis interaction constants and the ratio of stretching force constants was derived and a method for determining the ratio of cis interaction constants for ligand substituted metal carbonyls was proposed.[142] The results allowed an assessment of the validity of the Cotton-Kraihanzel approximation.[142] The binuclear complexes $[\{M(CO)_5\}_2\text{-}\mu\text{-pyrazine}]$ (M=Cr,W) were prepared by heating mononuclear $M(CO)_5$(pyrazine) in an inert atmosphere.[143]

$$2M(CO)_5(\text{pyrazine}) \xrightarrow{\Delta} [\{M(CO)_5\}_2\text{-}\mu\text{-pyrazine}] \quad (88)$$

Spectroscopic data deomonstrated that the $M(CO)_5$ moieties in these complexes retained C_{4v} symmetry. The allowed metal-to-pyrazine charge-transfer transitions were detected and assigned by the resonance Raman effect.[143] An explanation was given for the enhancement of the Raman intensity of the symmetrical stretching mode of the carbonyls cis with respect to L when the complexes, $M(CO)_{4-x}L(P(OMe)_3)_x$ (M=Cr,Mo,W; x=0,1; L=1,4 diazabutadiene, bipy, o-phen, etc.) were excited within the lowest M-L CT band.[144] Irradiation within this band also caused photosubstitution of a cis carbonyl ligand with quantum yields varying from 10^{-5} to 10^{-2}. A relationship apparently existed between the photosubstitution quantum yields and the resonance enhancement of the carbonyl stretching mode.[144] The infrared and Raman spectra of a series of carbynes, $Br(CO)_4CrCPh$, $Br(CO)_4WCPh$, $I(CO)_4WCPh$ and their deuterated analogues were discussed.[145] Polarized Raman spectra in CH_2Cl_2 and of single crystals of $Br(CO)_4WCPh$ permitted the assignment of all the vibrational bands for these carbyne complexes. The metal-carbon (carbyne) stretching vibration was found at 1250-1380 cm^{-1} and was strongly coupled to the C-Ph and the skeletal ring deformation modes.[145] A new valence force field was derived to explain the neutron scattering spectrum of $(\eta^6\text{-}C_6H_6)Cr(CO)_3$ from 10-2000 cm^{-1}.[146] The infrared and Raman spectra of $(\eta^6\text{-}C_6H_6)Cr(\eta^6\text{-}C_6F_6)$ and $(\eta^6\text{-}C_6D_6)Cr(\eta^6\text{-}C_6F_6)$ were analyzed, resulting in assignment of half of the 46 normal modes in each molecule.[147] The assignments fit with a model of pi-electron migration from the C_6H_6 ring to the C_6F_6 ring.[147]

Nuclear Magnetic Resonance Studies

A series of $Cr(CO)_5L$ ($L=PPh_{3-n}R_n$, n=0-3, R=H, Me, etc.) complexes were studied by ^1H, ^{13}C and ^{31}P NMR.[148] The ^{31}P chemical shifts were dominated by steric effects with a small inductive effect and very little pi-back bonding. The ^{13}C results for the carbonyl carbons confirmed that there are no important changes in the Cr-P pi-bonding in this series of compounds.[148] Bodner and coworkers reported the ^{13}C NMR spectra of a series of $LCr(CO)_5$, $LMo(CO)_5$ and $(\eta^6\text{-}C_6H_6)Cr(CO)_2L$ derivatives.[149] Analysis of the carbonyl chemical shift data allowed estimation of the ratio of sigma-basicity to pi-acidity of the ligands. The donor/acceptor ratio for phosphorus ligands increased in the order below.[149]

$$PCl_3 < P(OPh)_3 < P(SR)_3 < P(OR)_3 < PPh_3 < P(NR_2)_3 \leq PR_3$$

The donor/acceptor ratio for phosphite ligands increased (1) with the replacement of aryl by alkyl substituents, (2) with the replacement of caged phosphites by open-chained analogues and (3) with increasing chain length for alkyl substituents.[149] The donor/acceptor ratio for phosphines increased (1) with decreasing unsaturation of the alkyl substituents, (2) with increasing chain length, and with increasing substitution at the α carbon.[149] The ^{13}C-^{1}H spin-spin coupling constants for deuterated η^6-benzenechromiumtricarbonyl and η^7-tropyliumchromiumtricarbonyl cation were determined using the $^{13}C\{^{2}H\}$ double resonance technique.[150] The complexation effects on $^{1}J(CH)$ correlated to the C-H overlap population and hybridization changes, $^{2}J(CH)$ depended on C-C bond lengths and the C-C-H bond angle, and $^{3}J(CH)$ correlated to the C-C bond lengths and the pi-bond orders.[150] Templeton and Ward reported that the number of electrons donated per alkyne ligand on molybdenum and tungsten complexes correlated with the chemical shift of the bound alkyne carbon nuclei.[151] Treatment of $Mo(CO)_6$ with $H_2{}^{17}O$, L (L=PPh_3, $AsPh_3$, $SbPh_3$ and $PPhMe_2$), and a catalytic amount of NaOH formed cis-$Mo(C^{17}O)_4L_2$.[152] The ^{17}O data are shown below.

L	δ (^{17}O ppm from $H_2{}^{17}O$)	
PPh_3	359.9	357.2
$AsPh_3$	362.4	358.8
$SbPh_3$	365.3	362.6
$PPhMe_2$	358.3	356.6

These bands could not be resolved with natural abundance samples.[152]

Molybdenum-95 NMR spectra of a variety of substituted molybdenum carbonyl species were reported. The large chemical shift range permitted resolution of substituent effects. Some data is shown below.

Compound	δ (Mo)(ppm)	
$Mo(CO)_6$	-1856.7	
$Mo(CO)_5P(OMe)_3$	-1863.8	J(Mo-P) = 219 Hz
$Mo(CO)_5P(OEt)_3$	-1853.5	J(Mo-P) = 215 Hz
$Mo(CO)_3(P(OEt)_3)_3$	-1721.1	J(Mo-P) = 210 Hz
$CpMo(CO)_3(CH_2Ph)$	-1598.8	
(toluene)$Mo(CO)_3$	-2034.0	
$Mo(CO)_4$(bipy)	-1189.6	

The results were discussed in terms of general applications to molybdenum organometallic chemistry.

Electronic Spectra

The charge-transfer complexes of arenetricarbonylchromium, -molybdenum and -tungsten with various pi-acceptors (tetracyanoethylene, trinitrobenzene, chloranil, bromanil, and trinitrophenol) were investigated by electronic absorption spectroscopy.[154] It was shown that (1) molecular arenetricarbonylchromium complexes with tetracyanoethylene were of the pi, pi-type; (2) the character of the donor-acceptor interaction of the tricarbonylchromium group with arene depended on the positive charge on the ring.[154] In particular for the relatively strong pi-acceptor tetracyanoethylene, the group $Cr(CO)_3$ was an electron-donor with respect to the benzene ring and was an electron acceptor for trinitrobenzene.[154] Electronic absorption spectral parameters and photolysis rate constants were determined for $ArCr(CO)_3$ (Ar=C_6H_5OR (R=Me,Et), biphenyl, trans-stilbene, etc.).[155] A photodecomposition mechanism involving loss of a CO ligand, followed by loss of the aromatic ligand and formation of $Cr(CO)_6$ was proposed.[155] The magnetic circular dichroism spectra of $M(CO)_6$ (M=Cr,Mo,W) were measured.[156] The A terms for the two low-lying charge-transfer transitions in these compounds were calculated using the irreducible tensor method.[156] The direct band identification for the molecules, $M(CO)_5A$ (M=Cr, A=piper, cyclohexylamine; M=Mo, A=cyclohexylamine; M=W, A=NH_3, piper, cyclohexylamine) was accomplished by using magnetic circular dichroism spectroscopy.[157] The dominant optical band at ∿400 nm was assigned to an $^1A_1 \rightarrow {}^1E_1$ transition.[157] Cyclohexane solutions of $Cp_2W_2(CO)_6$ and $Cp_2Mo_2(CO)_6$ exhibited weak bimodal emission spectra when excited with 354 nm picosecond pulses, but did not luminesce when pumped at 530 nm.[158] Picosecond lifetimes characterized the short wavelength emission bands which were suggested to originate from metal-cyclopentadienyl charge transfer excited states.[158] Intense metal-ligand charge-transfer transitions in the visible region were observed for $M(CO)_4L$ complexes (M=Cr, Mo, W; L=α-diimine).[159] With the use of resonance Raman excitation profiles the three allowed transitions could be detected and assigned. A close relationship was suggested between the photosubstitution reactivity upon irradiation within the metal-ligand charge-transfer band and the resonance enhancement of Raman intensity observed for $\nu(CO_{cis})$.[159]

Mass Spectrometry

Mass spectra, ionization energies, fragmentation energies, ionic and neutral dissociation energies, and heats of formation for the hexacarbonyls and pentacarbonyl thiocarbonyls were measured and compared.[160] Substitution of CS for CO resulted in (1) a slight modification of the mass spectra, (2) a lowering of the ionization energies by 0.1-0.4 eV, a reduction by 0.1 eV in the average M-CO bond energies in the molecule and molecular ion, and

(4) a reduction of 3. eV in the heats of formation.[160] Within each molecule or molecular ion the M-CS bond was stronger than the M-CO bond by 1.5-2.0 eV. Both M-CS and M-CO bonds were reported to increase in strength in going from Cr to Mo to W.[160] The mass spectrometric behavior of arenetricarbonylchromium complexes under electron impact and chemical ionization conditions were reported.[161] The pseudomolecular ion (MH^+, protonation of complex) was the base peak for all simple complexes using chemical ionization, whereas $areneCr^+$ or Cr^+ dominated the spectra with electron impact ionization.[161] Ion-molecule reactions occurred in the ionization chamber of a mass spectrometer during vaporization of arenechromium tricarbonyls, $ArCr(CO)_3$ ($Ar=C_6H_6$, C_6H_5Cl, etc.) and various aromatic compounds.[162] In each case sandwich complexes $ArCrL^+$ were formed.[162] The Fourier transform ion-cyclotron-resonance mass spectra were determined for $CpCr(CO)_2NO$ and $CpCr(CO)_2NS$.[163] Condensation reactions were observed for the ions with elimination of NO and CO for $CpCr(CO)_2NO$ and elimination of N_2 and CO for $CpCr(CO)_2NS$. Possible mechanisms were discussed.[163]

Thermochemistry and Electrochemistry

Vapor pressure determinations of the metal carbonyls indicated heats and entropies of dissociation, of formation, and of phase transitions.[164] Investigation of the binary system containing $Mo(CO)_6$ and $W(CO)_6$ showed that it did not obey Raoult's law.[165] An explanation was offered.[165] A scale of liquid constants, P_L, was defined according to the equation below.[166]

$$P_L = E^{ox}_{1/2}[Cr(CO)_5L] - E^{ox}_{1/2}[Cr(CO)_6]$$

This scale was used to analyze the $E^{ox}_{1/2}$ of various closed shell octahedral complexes in terms of the equation below,

$$E^{ox}_{1/2} = E_a + \beta \cdot P_L$$

where E_a is a measure of the electron-richness of the metal site and β is a measure of its polarizability.[166] Some of the desired parameters are shown in the table below.[166]

Ligand	Ligand constant (P_L/V)
NO^+	1.40
CO	0.00
N_2	-0.07
$P(OPh)_3$	-0.18
PPh_3	-0.35
CNPh	-0.38

NCPh	-0.40
Py	-0.59
NH_3	-0.77
CN^-	-1.00
Cl^-	-1.19
H^-	-1.22
OH^-	-1.55

Reaction solution calorimetric measurements of reactions of Cp_2MH_2 (M = Mo, W) with CBr_4 in toluene led to bond-enthalpy contributions, $\bar{D}$(Mo-Br) = 242 kJ/mole and $\bar{D}$(W-Br) = 299 kJ/mole.[167] Variable temperature ^{31}P and ^{13}C NMR spectra were obtained to evaluate equilibrium thermodynamic and activation parameters for isomer exchange in $[MoI(CO)_2(Me_2PCH_2CH_2PEt_2)_2]I$.[168] These data established that carbonyl-edge rotation was slower than the process responsible for cis-trans exchange. It was suggested that the simplest nondissociative mechanism capable of accounting for cis-trans exchange was a ligand twist of the bidentate phosphine.[168]

A cathodic needle growth from $Mo(CO)_6$ and $Cr(CO)_6$ which was possibly associated with temperature-field electron emission was described.[169] Densely populated needle crystals grew at the tip area of a pointed cathode when it was operated in a $Mo(CO)_6$ or $Cr(CO)_6$ atmosphere at 600-700°K at a field strength just insufficient to draw field electrons.[169] The electrochemical synthesis of Group VI metal carbonyls and their phosphine derivatives from suitable metal complexes in the +3 oxidation state was described.[170] The ions $(C_5H_4R)^-$ (R=COMe, CO_2Me) generated by electroreduction of $(\eta^5\text{-}C_5H_4R)_2Fe$ in THF, reacted with $M(CO)_3L_3$ (M=Mo or W, L=THF or DMF), giving $(\eta^5\text{-}C_5H_4R)M(CO)_3^-$.[171]

$$(\eta^5\text{-}C_5H_4R)_2Fe + M(CO)_3(THF)_3 \xrightarrow{e^-} (\eta^5\text{-}C_5H_4R)M(CO)_3^- \qquad (89)$$

Treatment of these M=Mo,W carbonylate ions with MeI afforded $CH_3M(\eta^5\text{-}C_5H_4R)(CO)_3$, and their electrooxidation gave either $(\eta^5\text{-}C_5H_4R)_2M_2(CO)_6$ or $[(\eta^5\text{-}C_5H_4R)_2M_2(CO)_6]Hg$ depending on the working electrode employed.[171] The new complexes were characterized by spectroscopic and electroanalytical methods, and it was suggested that the bulky nature of the R substituent inhibited free rotation about the ring-metal bond.[171] Cathodic reduction of $(Cp(CO)_3M)_2PtL_2$ (Cr, Mo, W; L=t-BuNC) on platinum and gold electrodes in aprotic media led to paramagnetic Pt(I) species.[172]

$$(Cp(CO)_3M)_2PtL_2 \xrightarrow{e^-} CpM(CO)_3^- + Cp(CO)_3MPtL_2^{\cdot} \qquad (90)$$

Calculations and Photoelectron Spectroscopy

Two groups reported calculations on $Cr(CO)_6$ which showed a substantial pi-donation component to the bonding of CO and that interaction coordinates could be interpreted without invoking a sigma-only-bonding model.[173,174] Molecular orbital calculations on Mo_2, which can be prepared by flash photolysis of $Mo(CO)_6$, were conducted to describe the nature of the sextuple bond.[175] The UV photoelectron spectra (PES) and ^{13}C NMR spectra of $M(CO)_5PR_3$ (M=Cr, W; $R=C_6H_{11}$, Ph, OPh) were presented and assigned by comparison with the spectra of free PR_3 and $M(CO)_6$.[176] From the PES data it was concluded that the sigma-donor properties increased in the following order.[176]

$$PX_3 < P(O\text{-}i\text{-}Pr)_3 < PPh_3 < P(C_6H_{11})_3$$

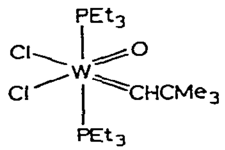
Backbonding to a P-donor ligand was found to be stronger than to a pyridene-like ligand![176] Calculations were also reported on $Cp_2M_2(CO)_4$.[177] The Mo 3d binding energies of complexes of Mo(II) containing the $[(\eta^3\text{-allyl})Mo(CO)_2]$ moiety were recorded.[178] These data were compared to that for Mo(0) complexes. The work showed that Mo 3d energies were not dependent in any simple way on the number of carbonyls bound to Mo.[178] The valence PES of $CpCr(CO)_2NO$ and $CpCr(CO)_2NS$ were recorded and assigned.[179] The comparison of NO and NS orbital interactions with the metal was done with MO calculations. The differences in electronic structure between the two complexes were influenced more substantially by the ligand orbital energies than by orbital overlaps.[179] The π^* orbital of NS was lower in energy and accepted more electron density from the metal than NO.[179] Shifts in the K-absorption edges, ΔE, of a series of Cr and Mo compounds were investigated.[180] The ΔE values in a given series vary in the same direction as the metal-core-level binding energies obtained from XPS.[180] Two studies were reported on the PES of $Cr(NO)_4$.[181,182]

Crystal Structures

An oxo alkylidene complex of tungsten was prepared by an alkylidene exchange reaction.[183]

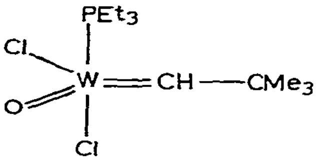
$$Ta(CHCMe_3)_2(PEt_3)_2Cl_3 + W(O)(OCMe_3)_4 \longrightarrow \qquad (91)$$

$$Ta(OCMe_3)_4Cl \quad +$$



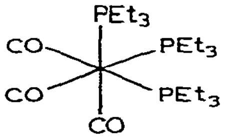
XXII

Other alkylidene complexes could be prepared by exchange of the alkylidene units between (XXII) and alkenes. The alkylidenes functioned as catalysts for metathesis of terminal and internal alkenes.[183] The reaction proceeded by PEt_3 dissociation and the active five coordinate catalyst (XXIII) was separated and identified by X-ray crystallography.[183]

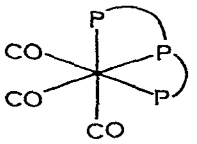


XXIII

The molecule was a distorted trigonal bipyramid with the oxo, neopentylidene and chloride describing the plane.[183] The structure of fac-$Cr(CO)_3(PEt_3)_3$ (XXIV) was reported.[184] The complex was sterically crowded with very long Cr-PEt_3 bonds and large angles.[184]

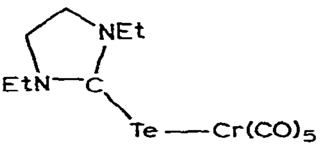


XXIV

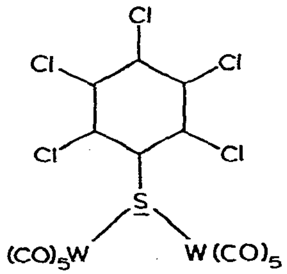


XXV

The structure of another facial isomer, fac-bis(2-diphenylphosphinoethyl)-phenylphosphine tricarbonyl chromium and molybdenum (XXV) was reported.[185] The central metal phosphorus bond distance was shorter than the terminal metal phosphorus bond distances.[185] Reaction of the electron-rich olefin $[EtN(CH_2)_2N(Et)C=]_2$ with tellurium afforded the labile complex $EtN(CH_2)_2N(Et)C=Te$ which reacted with $M(CO)_5(NCMe)$ (M=Cr, Mo or W) to yield $M(CO)_5[TeCN(Et)(CH_2)_2NEt]$.[1 This chromium compound (XXVI) could be detellurated to yield the carbenemetal complex, $Cr(CO)_5(CN(Et)(CH_2)_2NEt$.[186]

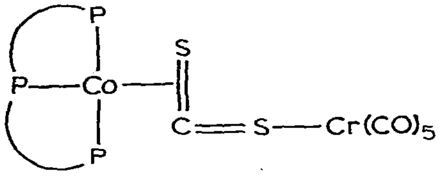


XXVI

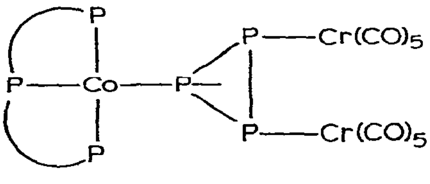


XXVII

The reaction of $[NEt_4]W(CO)_5Cl$ with $Tl(SC_6Cl_5)$ and $AgBF_4$ yielded the complex $[NEt_4][(CO)_5W\text{-}SC_6Cl_5\text{-}W(CO)_5]$ (XXVII).[187] The crystal structure showed the W-S-W angle to be 132°.[187] A triphos cobalt complex with CS_2 bridging to $Cr(CO)_5$ was prepared and studied crystallographically, XXVIII.[188] The cobalt atom was bonded to the three phosphorus atoms of the triphos ligand and pi-bonded to a C=S linkage. The other sulfur atom was sigma bonded to the chromium atom which was six-coordinate in a distorted octahedron.[188]

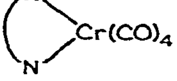


XXVIII

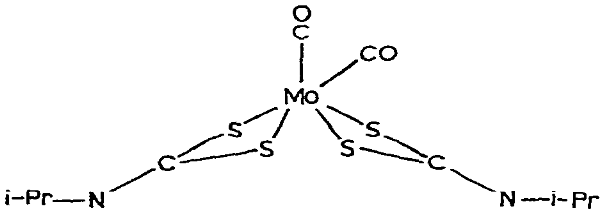


XXIX

Cobalt(II) reacted with white phosphorus in the presence of triphos to yield $(triphos)Co(\eta^3\text{-}P_3)$, XXIX.[189] The P_3 group could be complexed with $Cr(CO)_5$ units, $(triphos)Co(\mu\text{-}(\eta^3P_3))Cr(CO)_5$ and $(triphos)Co(\mu\text{-}(\eta^3\text{-}P_3))[Cr_2(CO)_{10}]$.[189] The crystal structure of tetracarbonyl (S,S-dimethylsulfonium 2-picolinyl-methylide)tungsten(0) was reported.[190] The ylide ligand coordinated to tungsten through the pyridine nitrogen and carbonyl oxygen atom forming a distorted octahedral geometry around the metal atom.[190] The crystal and molecular structures of tetracarbonyl [N,N,N',N'-tetramethyl-ethylenediamine-N,N']chromium(0) and tetracarbonyl-cis-[ethyl-α-ethoxy-α-(1,3-dithian-2-ylidene)acetimidate-N,S]chromium, XXX, were interpreted in terms of hybridization and steric effects on the chromium-nitrogen bond strength.[191] The Cr-N (amine) bond lengths average 2.217 Å and the Cr-N(azomethine) distance was 2.095 Å.[191]

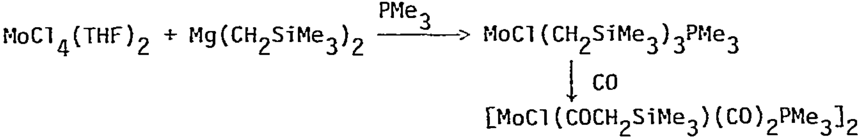


XXX



XXXI

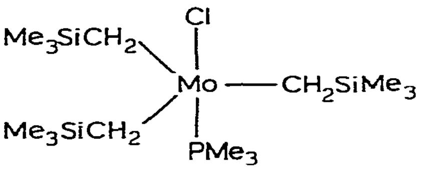
A trigonal-prismatic molybdenum complex, $Mo(CO)_2[S_2CN\text{-}i\text{-}Pr]_2$, was investigated crystallographically by Templeton and Ward.[192] It was suggested that the trigonal prismatic geometry allowed a maximization of the pi-back bonding to CO.[192] Tetrachlorobis(THF) molybdenum and bis(trimethylsilylmethyl)magnesium reacted in the presence of trimethylphosphine to give a five-coordinate molybdenum alkyl.[193]



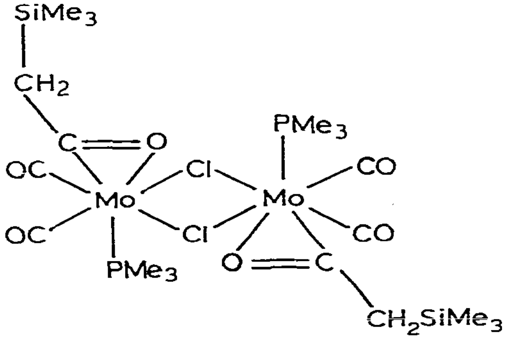
(92)

$$\begin{array}{l} \mathrm{MoCl_4(THF)_2 + Mg(CH_2SiMe_3)_2 \xrightarrow{PMe_3} MoCl(CH_2SiMe_3)_3PMe_3} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \downarrow \mathrm{CO} \\ \qquad\qquad\qquad\qquad\qquad\qquad\quad \mathrm{[MoCl(COCH_2SiMe_3)(CO)_2PMe_3]_2} \end{array} \qquad (92)$$

The crystal structures of both products were obtained.

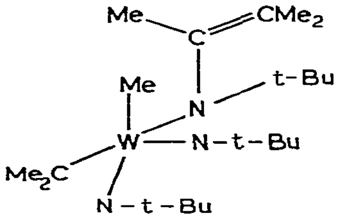


XXXIII

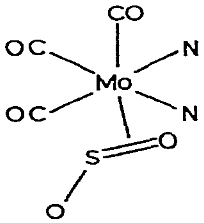


XXXIV

The geometry of XXXIII around Mo is nearly trigonal bipyramidal while the geometry of XXXIV around each Mo can be approximated as an octahedron with a side-bonding acyl occupying one coordination position.[193] The reaction of t-butylisocyanide with hexamethyltungsten led to $WN(t\text{-}Bu)CMe_2(Me)(N\text{-}t\text{-}Bu)\text{-}[N\text{-}t\text{-}Bu(CMe{=}CMe_2]$, XXXV, which was characterized by X-ray crystallography.[194]



XXXV

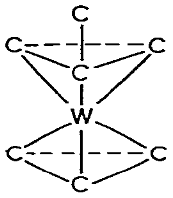


XXXVI

The structure of tricarbonyl(1,10 phenanthroline)(η^2 sulfur dioxide)molybdenum-(0), XXXVI, has been determined.[195] The sulfur dioxide was side-bonded with Mo-S distance of 2.532(3)Å and Mo-O distance of 2.223(7) Å.[195] The reaction of tripotassium enneachloroditungstate, $K_3W_2Cl_9$, with excess t-butylisocyanide produced heptakis(t-butyl isocyanide)tungsten(II) hexatungstate, XXXVII.[196]

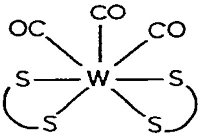
$$K_3W_2Cl_9 + t\text{-}BuNC \longrightarrow [W(CN\text{-}t\text{-}Bu)_7][W_6O_{19}] \qquad (93)$$

The molybdenum complex could be prepared by similar reactions. The crystal structure of the tungsten compound could be best described as a distorted monocapped trigonal prism.[196]



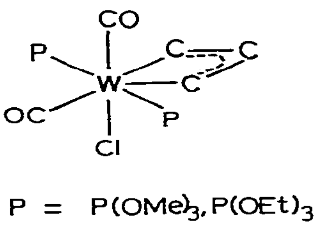
C = CN-t-Bu

XXXVII

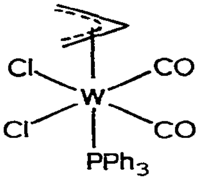


XXXVIII

The crystal and molecular structure of tricarbonylbis(N,N-dimethyldithiocarbanato)tungsten(II) was determined showing a polyhedron best described as a 4:3 tetragonal base-trigonal base geometry.[197] The fluxional properties exhibited by $W(CO)_3(S_2CNR_2)_2$ complexes were studied by ^{13}C NMR which revealed two distinct intramolecular rearrangement processes for both R=Me and Et.[197] The structures of seven-coordinate chelates with hard and soft donors were studied for tricarbonylchloro[5,7-dichloro-8-quinolinolato-N,O(1-)triphenylphosphine-tungsten(II), $W(CO)_3Cl(deq)PPh_3(PPh_3)$.[198] Compounds of the type $[MX(CO)_2(\eta^3\text{-}C_3H_4R)L_2]$ (M=Mo, W; X=Cl, Br, I; L=$P(OMe)_3$ or $P(OEt)_3$), XXXIX, gave a structure which could be best described as a distorted pentagonalbipyramidal structure with a chlorine atom and a carbonyl occupying axial sites and the two phosphites, a carbonyl and the allyl spanning the equatorial positions.[199]



XXXIX



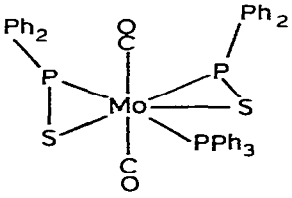
XL

The preparation, chemical and structural studies of (η^3-allyl)dichlorodicarbonyltriphenylphosphinetungsten (XL) were reported.[200] The structure was described as an octahedron with the allyl occupying one coordination site.[200] The reaction of $CpM(CO)_3Cl$ or $M(CO)_3(PPh_3)_2Cl_2$ (M=Mo, W) with $SPPh_2H$ and Et_3N led to $CpM(CO)_2(\eta^2\text{-}SPPh_2)$ and $M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2$, respectively[201]

$$CpM(CO)_3Cl + SPPh_2H \xrightarrow{NEt_3} CpM(CO)_2(\eta^2\text{-}SPPh_2) \tag{94}$$

$$M(CO)_3(PPh_3)_2Cl_2 + SPPh_2H \xrightarrow{NEt_3} M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2 \tag{95}$$

An X-ray crystal structure of $Mo(CO)_2PPh_3(\eta^2\text{-}SPPh_2)_2$, XLI, revealed a seven-coordinate, pseudo-pentagonalbipyramidal geometry for the molybdenum.[201]

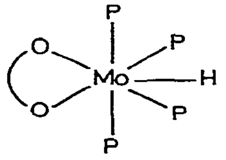


XLI

Several structural studies on Group 6 hydrides were reported in 1980. Hydrogenolysis of hexamethyltungsten in the presence of $PPh(i\text{-}Pr)_2$ afforded $WH_6(PPh(i\text{-}Pr)_2)_3$.[202]

$$WMe_6 + 6H_2 + 3PPh(i\text{-}Pr)_2 \longrightarrow WH_6(PPh(i\text{-}Pr)_2)_3 + 6CH_4 \tag{96}$$

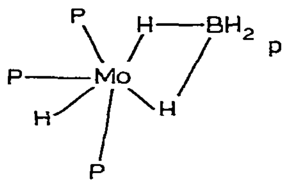
^{31}P NMR and X-ray diffraction showed the complex to have C_{2v} symmetry in both solution and solid state. The structure of the complex was described as a tricapped trigonal prism with one phosphorus in a capping position and the other two phsophorus ligands in eclipsed positions on opposite axial prism faces.[202] The crystal structure of $HMo(P(OMe)_3)_4(O_2CCF_3)$, XLII, showed pentagonal bipyramidal geometry.[203] Two phosphites occupied axial sites and the other two were separated by the hydride in the plane. The complex was stereochemically non-rigid.[203]



P = $P(OMe)_3$

O⌒O = O_2CCF_3

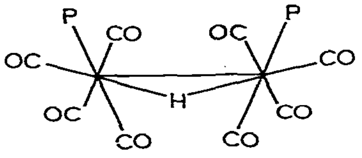
XLII



P = PMe_3

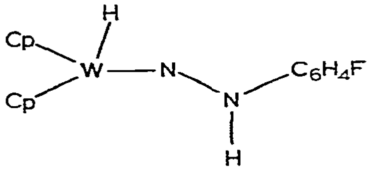
XLIII

The interaction of trichlorotris(tetrahydrofuran)molybdenum(III) with PMe_3 gave trichlorotris(trimethylphosphine)molybdenum(III) which reacts further with $NaBH_4$ to give $MoH(BH_4)(PMe_3)_4$, XLIII.[204] The crystal structure of this compound showed the BH_4^- to be bidentate.[204] The reaction of $Et_4N[HMo_2(CO)_{10}]$ with an excess of $PMePh_2$ led to $Et_4N[HMo_2(CO)_8(PMePh_2)_2]$, XLIV.[205] Crystals of this compound were used to determine the structure.[205]



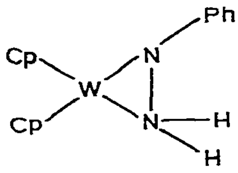
P = $PMePh_2$

XLIV



XLV

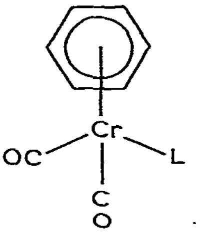
An arylhydrazido complex of tungsten was prepared by insertion of the p-fluorobenzenediazonium ion into one W-H bond in Cp_2WH_2.[206] This complex showed a bent W-N-N skeleton.[206] The geometry of $[Cp_2W(H_2NNPh)][BF_4]$ was determined by X-ray crystallography.[207]



XLVI

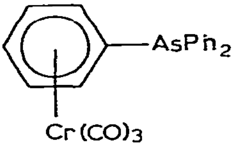
The compound was prepared by insertion of PhN_2^+ into the W-H bonds of Cp_2WH_2.[207]

The crystal structures of hexaethylbenzenechromiumtricarbonyl and hexaethylbenzenechromiumdicarbonyltriphenylphosphine were reported.[208] For L=CO the conformation of the aromatic ring was similar to the free ligand. For $L=PPh_3$ all the ethyl groups were on the side away from the metal.[208] NMR spectra confirmed that this conformation persisted in solution.[208]



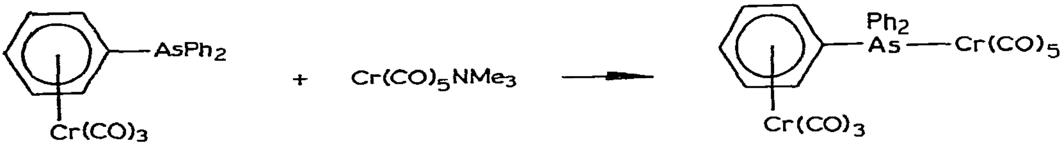
L = CO, PPh_3

XLVII

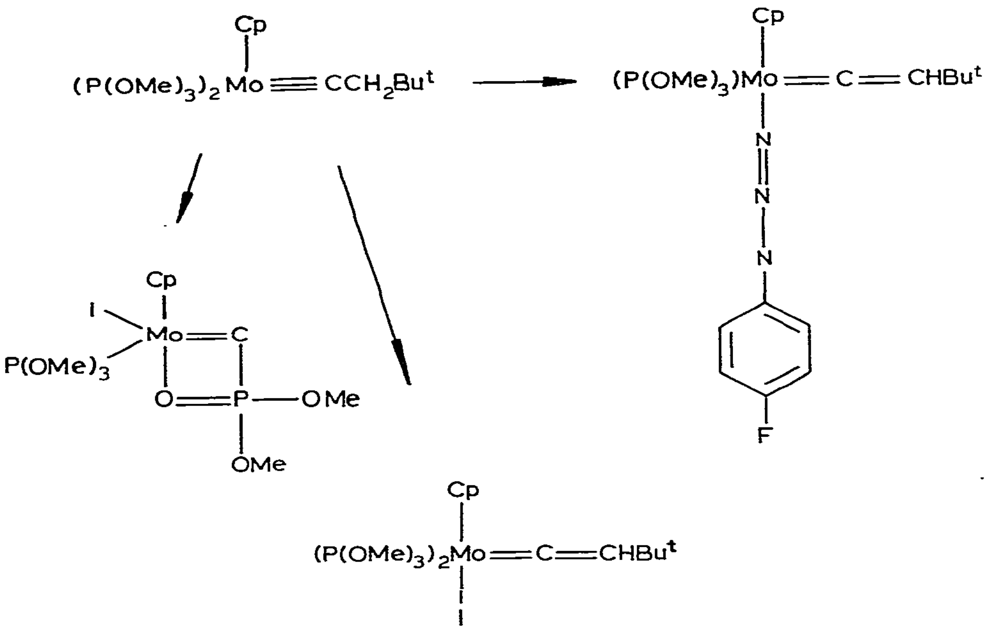


XLVIII

The high temperature reaction between $Cr(CO)_6$ and $AsPh_3$ led to the preparation of $((\eta^6-C_6H_5)AsPh_2)Cr(CO)_3$, XLVIII.[209] The structure showed normal arene coordination to the $Cr(CO)_3$ moiety. The arsine retained its basicity as shown by the reaction with $Cr(CO)_5NMe_3$.[209]

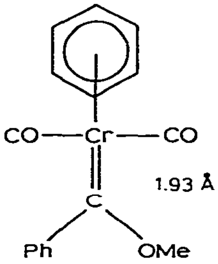


Several reactions of a molybdenum-alkylidyne complex were reported.[210]

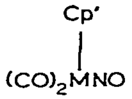


XLIX

The structure of XLIX was accomplished showing the geometry.[210] The crystal structure of benzenedicarbonylmethoxyphenylcarbenechromium(L) was reported to show the shortest Cr=C distance yet observed.[211]



L

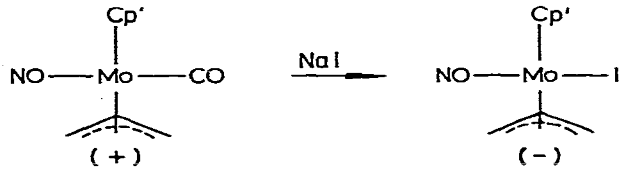


$\mathrm{(CO)_2}\overset{\mathrm{Cp'}}{\mathrm{M}}\mathrm{NO}$

M = Cr, Mo, W, Cp' = C_5Me_5

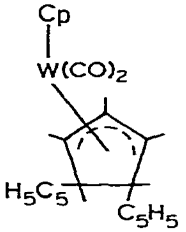
LI

The structures of the complexes, (η^5-C_5Me_5)M$(CO)_2$(NO) (M=Cr, Mo, W) were determined showing the methyl groups to be bent away from the metals.[212] The structures of the resolved neomenthylcyclopentadienyl complexes allowed the stereochemistry of carbonyl displacement to be determined with retention of configuration at molybdenum.[213]

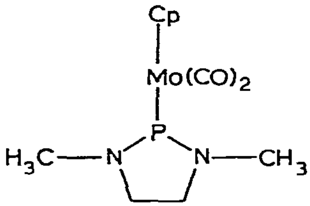


LII LIII

The crystal structure of $W(CO)_2(\eta^5\text{-}C_5H_5)(\eta^3\text{-}C_{15}H_{15})$, LIV, was reported.[214]



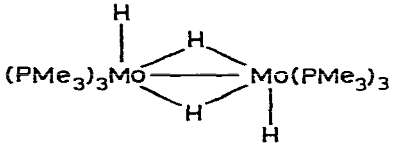
LIV



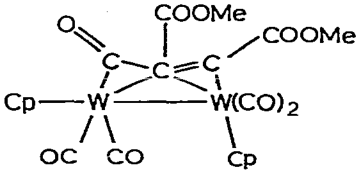
LV

The structure of the phosphenium-molybdenum complex, $CH_3NCH_2CH_2N(CH_3)P$ $MoCp(CO)_2$ (LV) showed Mo-P bond length of 2.213 Å which suggested multiple bond character.[215]

A number of metal dimers were characterized crystallographically in 1980. The interaction of dimolybdenum tetraacetate, $Mo_2(O_2CMe)_4$ with sodium amalgam in THF in the presence of an excess of PMe_3 under hydrogen yielded the dimeric phosphine hydride, $(PMe_3)_3HMo(\mu\text{-}H)_2MoH(PMe_3)_3$, LVI, whose structure was determined by X-ray diffraction methods.[216]

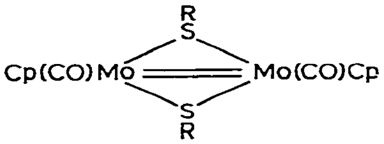


LVI



LVII

Dimethylacetylenedicarboxylate reacted with $Cp_2W_2(CO)_4$ under photolysis to yield the dimetallocycle, $Cp_2W_2(CO)_4(\mu\text{-}\eta^2\text{-}\eta^2\text{-}C(O)C_2(CO_2Me)$, LVII, and the structure was determined.[217] Further reaction led to CO loss and the acetylene bridged dimer, $Cp_2W_2(CO)_4(\mu\text{-}C_2CO_2Me)$.[217] The thiolato-bridged dimolybdenum complexes, $Cp_2Mo_2(CO)_4(\mu\text{-}SR)_2$, thermally decarbonylated to $CpMo_2(CO)_2(\mu\text{-}SR)_2$ which contained a Mo-Mo double bond.[218]



R = Me, t-Bu, Ph, p-tolyl

LVIII

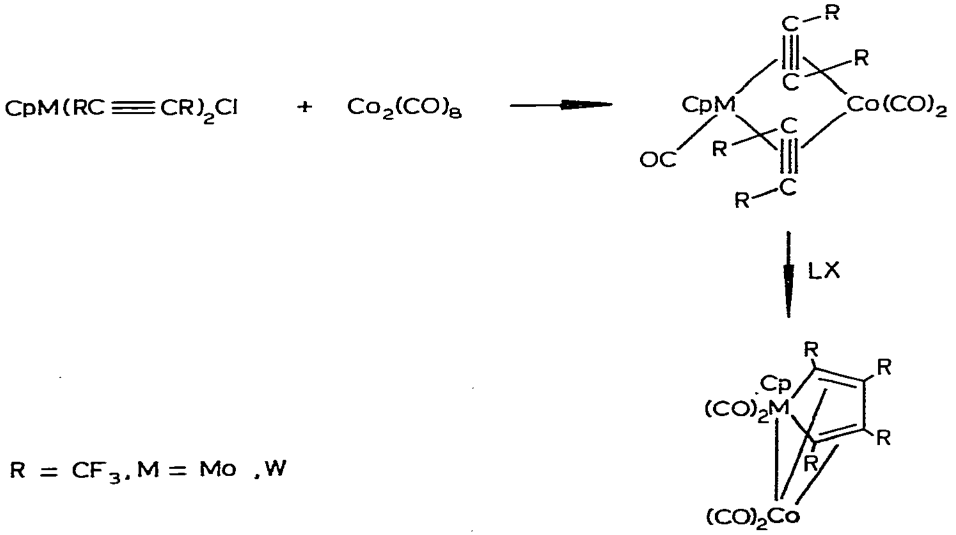
$(Me_3SiCH_2)(NMe_2)_2Mo\equiv Mo(CH_2SiMe_3)_3$

or

$(NMe_2)(Me_3SiCH_2)_2Mo\equiv Mo(CH_2SiMe_3)_2(NMe_2)$

LIX

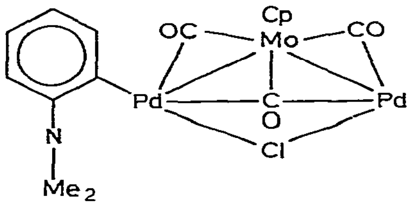
Reaction of 1,2 $Mo_2Br_2(CH_2SiMe_3)_4$ with $LiNMe_2$ and $HNMe_2$ gave 1,1 and 1,2-$Mo_2(NMe_2)_2(CH_2SiMe_3)_4$ in 95% and 5% yield respectively.[219] Isomerization was not observed after formation.[219] Reaction of bis(hexafluorobut-2-yne) complexes, $Cp(CO)M(CF_3C{\equiv}CCF_3)_2Cl$ (M=Mo, W), with $Co_2(CO)_8$ led to acetylene bridged derivatives, $Cp(CO)M(\mu\text{-}CF_3C{\equiv}CCF_3)_2Co(CO)_2$, LX.[220]



R = CF_3, M = Mo, W

LXI

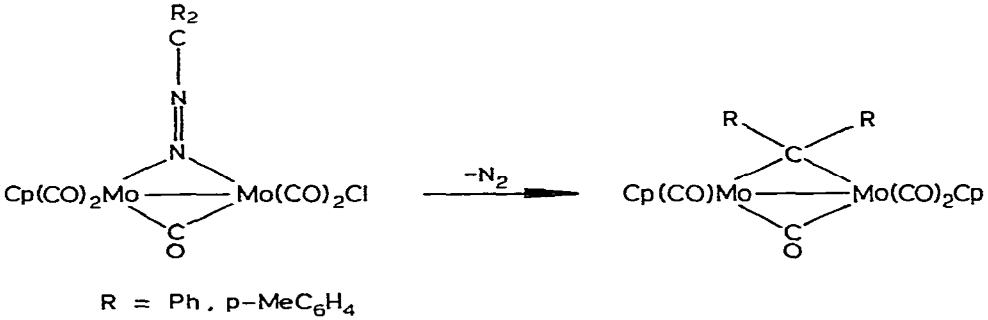
Further reaction led to metallocyclopentadiene complexes, LXI.[220] Use of molybdenum carbonylate anions to bridge two palladium atoms was reported. The replacement of a chloride bridge with $CpMo(CO)_3^-$ resulted in the structure shown below (LXII).[221]



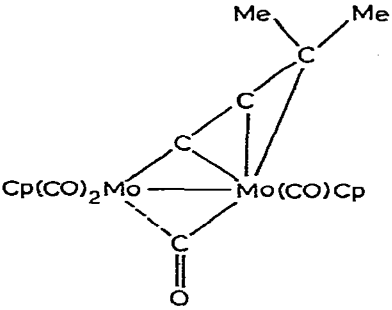
LXII

Other carbonylates could also be used.[221]

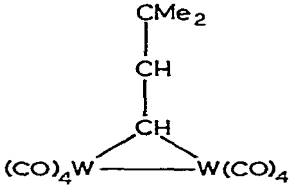
Reaction of $Cp_2Mo_2(CO)_4$ with diaryldiazomethanes led to a bridging diazoalkane which eliminated N_2 to give the bridging alkylidene complexes.[222]



The structures of both complexes were determined.[222] The molybdenum-molybdenum triple bond complex was also utilized to open the ring of 3,3-dimethylcyclopropene to give an allyl bridged dimolybdenum complex, LXIII.[223]

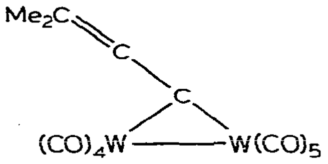


LXIII

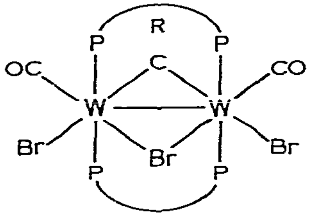


LXIV

A number of alkylidene bridged tungsten dimers have been studied. The reaction of MeLi with $W(CO)_5CMe(OMe)$ gave the binuclear complex $[(CO)_4W]_2$-(μ-$CHCH{=}CMe_2$), LXIV.[224] This complex rearranged to $CHCHCMe_2[W_2(CO)_9]$ (LXV) with the double bond coordinated to tungsten.[225]



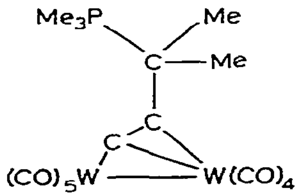
LXV



P⌒P = $F_2PN(CH_3)PF_2$
R = C_6H_4Me

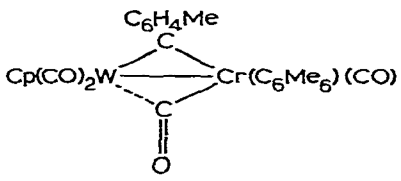
LXVI

Reaction of the tungsten carbyne, $Br(CO)_4W{\equiv}CC_6H_4CH_3$, with $F_2PN(CH_3)PF_3$ under photolysis led to the dimer LXVI.[226] The reaction of phosphine with the bimetallic unsaturated μ-alkylidene tungsten complex proceeded by either substitution of one CO group or by nucleophilic attack on the carbon chain.[227] The X-ray structure of the PMe_3 complex was obtained.[227]

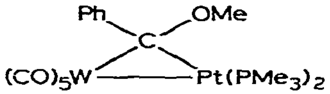


LXVII

The Bristol group reported a number of preparations of heterobimetallic carbene and carbyne bridged complexes in 1980.[228-231] Reaction of the tungsten alkylidyne complex $Cp(CO)_2W{\equiv}CC_6H_4Me$ with a number of low-valent metal complexes led to heterobimetallic complexes with the carbyne bridging and the structure was determined for the chromium complex, LXVIII.[228]

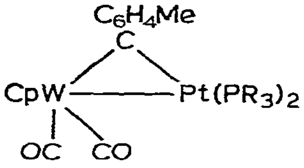


LXVIII

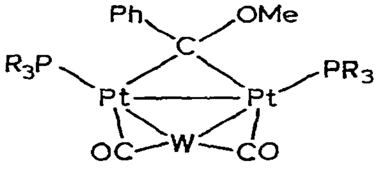


LXIX

The reaction of chromium and tungsten carbene complexes with $Pt(cod)_2$ in the presence of a phosphine led to a series of carbene bridged complexes which were fully characterized.[229] The reaction of the tungsten carbyne complex, $Cp(CO)_2W{\equiv}CC_6H_4Me$, with $Pt(C_2H_4)(PR_3)_2$ gave the dimetallic species $PtW(\mu\text{-}CC_6H_4Me)(CO)_2(PR_3)_2Cp$.[230] The structure was determined for $R_3{=}Me_2Ph$, LXX.[230]



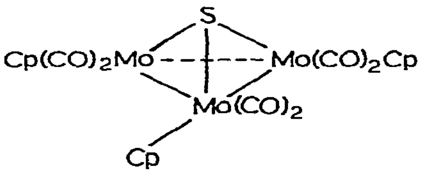
LXX



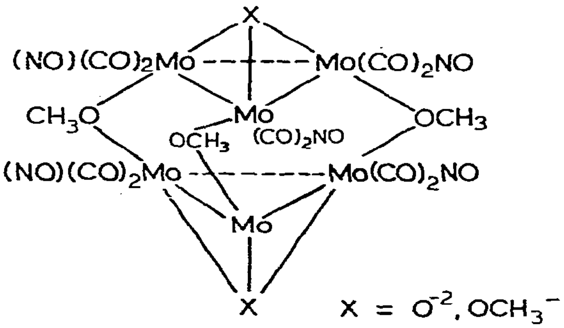
LXXI

The reaction of chromium and tungsten carbenes with $Pt(C_2H_4)_2PR_3$ produced trimetal compounds.[231] The crystal structure was determined for the tungsten derivative, LXXI.[231]

Only a few structures of Group VI clusters appeared in 1980. Reaction of elemental sulfur with $Cp_2Mo_2(CO)_4$ led to the salt, $[Cp_3Mo_3(CO)_6S]$-$[CpMo(CO)_3]$.[232] The structure was determined and the cation is shown below, LXXII.[232]

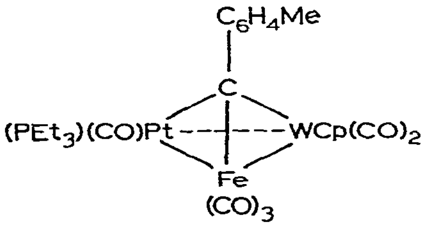


LXXII



LXXIII

The compounds $[(Ph_3P)_2N]_3\{Na[Mo_3(CO)_6(NO)_3(\mu_2\text{-}OCH_3)_3(\mu_3\text{-}O)]_2\}$ and $[Me_4N]$-$[Mo_3(CO)_6(NO)_3(\mu_2\text{-}OCH_3)_3(\mu_3\text{-}OCH_3)]$ were synthesized by refluxing $Mo(CO)_6$, $NaNO_2$ and NaOH in methanol.[233] Reactions of $PtW(\mu_2\text{-}CC_6H_4Me)(CO)_2(PEt_3)_2(Cp)$ with $Fe_2(CO)_9$ led to $Fe(CO)_4PEt_3$ and the μ_3-alkylidyne complex shown below.[234]



LXXIV

The addition of a photogenerated fragment from $(\eta^6\text{-}C_6H_5Me)Cr(CO)_6$ to $Cp_2Co_2(CO)_2$ produced the trinuclear mixed metal cluster $(\eta^6\text{-}C_6H_5Me)CrCo_2$-$(\mu\text{-}CO)_3(\mu_3\text{-}CO)$.[235]

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