Journal of Organometallic Chemistry. 180 (1979) 205—299

CHROMIUM, MOLYBDENUM, AND TUNGSTEN

ANNUAL SURVEY COVERING THE YEAR 1978

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ABBREVIATIONS

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

INTRODUCTION

This survey covers the 1978 literature and is the first year for my participation. The coverage and format are very similar to those used by M. Darensbourg, D. Darensbourg, and G. Dobson, although some differences in interpretation naturally occur. The main journals were covered directly and a computer search was accomplished to insured a comprehensive review of the literature. This search used the same key word index that was used in previous years to ensure comparable coverage.

Since this is my first year for the survey, I will explain the method used to place papers in one section or another. A general division was made into papers that dealt primarily with Synthesis and Reactivity or with Physical Studies. The Synthesis and Reactivity Section is divided according to the groups coordinated to the metal with aromatics, cyclopentadienyls, and carbonyls having the lowest priority (i.e. $CH_3Mo(Cp)(CO)_3$ is in alkyls). The Physical Studies Section is divided very similar to previous years although the growth of photochemistry had led to a separate section on Photochemistry.

DISSERTATIONS

Several dissertations appeared in 1978 dealing with Group VI organometallic compounds. Alkyl and arylpentacarbonyltungsten anions were prepared and their reactivity investigated;[1] the photochemistry and spectroscopy of $W(CO)_5L$ was reported;[2] the deposition of Cr vapor and aminodifluorophosphines was examined;[3] reactions of phosphorus ligands coordinated to Group VI metals were observed;[4] organophosphines of Mo and Cr were described;[5] carbanions were observed to add to η^6-arenetricarbonylchromium complexes;[6] and the Freidel-Crafts acylation of η^5-$C_5H_5Cr(CO)_2NO$ was reported.[7]

REVIEWS

Reviews of the following areas of Group VI organometallic chemistry were published: matrix isolation of the Group VI metal carbonyls;[8] reviews of the photochemistry of isocyanides, $M(CN\phi)_6$, M = Cr, Mo, W,[9] and of the photoreactions of alkyl halides with $Mo(N_2)_2(diphos)_2$;[10] tungsten cyclopentadienyl and tungsten and molybdenum cyclobutanes;[11] three reviews of the utility of arenetricarbonylchromium in organic synthesis;[12-14] stereoselective preparations and reactions of cationic η^4-diene and η^3-allyl complexes of molybdenum.[15]

SYNTHESIS AND REACTIVITY

Metal carbonyls

A new synthesis of $W(CO)_6$ and $Mo(CO)_6$ has been reported.[16] The reaction of the metal oxides with CO at 300°C and 2000 atm is reported to give the hexacarbonyls in near quantitative yield.[16] The use of $W(CO)_6$ in liquid allylglycolcarbonates led to plastic lenses with photochromic and IR-absorbing capabilities.[17]

The reaction of the hexacarbonyls with different species continues to provide new complexes. A specific route to cis-substituted complexes of molybdenum hexacarbonyl has been observed.[18] The reaction of piperidine with $Mo(CO)_6$ in refluxing heptane led to cis-$Mo(CO)_4(C_5H_{10}NH)_2$. This complex reacts at moderate conditions (40°C) with L to give cis-$Mo(CO)_4L_2$ ($L{=}P\phi_3$, PBu_3, $P(O\phi)_3$, etc.).[18]

$$Mo(CO)_6 + C_5H_{10}NH \rightarrow cis\text{-}Mo(CO)_4(C_5H_{10}NH)_2 \xrightarrow{L} cis\text{-}Mo(CO)_4L_2 \qquad (1)$$

These cis-complexes are apparently sterically crowded as qualitative observation of the dissociations are explainable in terms of the ligand "cone angle".[18] Darensbourg has also reported a route to $Mo(CO)_5L$ ($L{=}CO$, $P(C_6H_5)_3$, and $P(C_4H_9)_3$) species specifically labeled with oxygen-18 in the equatorial position.[19] The metal carbonyl complex, $\mathrm{Mo(CO)_5L}$, dissolved in dry benzene is added to 11 M $\mathrm{Na^{18}OH}$ in the presence of a phase transfer catalyst, $\mathrm{N\text{-}C_4H_9NI}$.

$$\mathrm{Mo(CO)_5L + Na^{18}OH \xrightarrow[75^\circ]{n\text{-}C_4H_9NI} Mo(C{*}O)_5L} \qquad (2)$$

For ligands which are poorer electron-withdrawing than CO, the equatorial CO's exchange much faster than the axial.[19] Reaction of the hexacarbonyls with the new bidentate ligand, $\mathrm{(CH_3O)_2PCH_2CH_2P(OCH_3)_2}$ (pompom), led to both the mono- and bis-substituted complexes. $\mathrm{M(pom\text{-}pom)(CO)_4}$ (M=Cr, Mo) and $\mathrm{M(pom\text{-}pom)_2(CO)_2}$ (M = Cr, Mo, W).[20] The infrared frequencies indicate that pom-pom is a very strong π-accepting ligand.[20] Another strong π-accepting ligand, 1,2-bis-(difluorophosphino) ethane has been observed in complexes with Mo by replacement of norbornadiene in $\mathrm{(C_7H_8)Mo(CO)_4}$.[21]

$$\mathrm{(C_7H_8)Mo(CO)_4 + PF_2C_2H_4PF_2 \rightarrow Mo(CO)_4(PF_2C_2H_4PF_2) + C_7H_8} \qquad (3)$$

This ligand is a very strong π-acceptor as shown by infrared frequencies of the carbonyls at 2074, 2005, 1991 and 1973 $\mathrm{cm^{-1}}$.[21] A similar ligand, 1,2-bis(difluorophosphine) cyclohexane

$$\mathrm{(C_7H_8)_2Mo + PF_2C_6H_{10}PF_2 \rightarrow Mo(PF_2C_6H_{10}PF_2)_3} \qquad (4)$$

This complex was characterized by IR, NMR (^{1}H, ^{19}F, ^{31}P, and ^{13}C), and mass spectroscopy. This ligand is also a strong pi-acceptor, bidentate ligand.[22] The photolytic reaction of pyrazine (pz) with $\mathrm{Mo(CO)_6}$ has been observed.[23]

$$\mathrm{Mo(CO)_6 + pz \xrightarrow{h\nu} Mo(CO)_5pz + (Mo(CO)_5)_2pz} \qquad (5)$$

$\mathrm{Mo(CO)_5pz}$ was detected in solution (absorption at 387 nm).[23] Removal of the solvent led to formation of $\mathrm{(Mo(CO)_5)_2pz}$, although addition of pyrazine reverses the reaction. The kinetics were studied and the UV-visible spectra interpreted in terms of pi-bonding.[23] Reactions of $\mathrm{L\text{-}O^-K^+}$ (L= anion of succinimide, phthalimide, and benztriazole) with the hexacarbonyls have been reported with the

$$\mathrm{M(CO)_6 + L\text{-}O^-K^+ \xrightarrow{100^\circ} ((CO)_5ML)\text{-}K^+ + CO_2} \qquad (6)$$

product indicating a deoxygenation of the N-O bond.[24] Reaction also occurs with $\mathrm{CpW(CO)_3Cl}$ by replacement of the chloride leading to $\mathrm{CpW(CO)_3L}$.[24] Reaction with complete replacement of the CO's was observed with picoline acid and peroxydisulfuryldifluoride. The products observed were an eight-coordinate complex $\mathrm{Mo(Pic)_4}$, and $\mathrm{M(SO_3F)_3}$ (M = Cr, Mo, W), respectively.[25,26] Attachment of the metal carbonyls to a polymer was accomplished by reacting poly(styryl)bipyridine with $M(CO)_6$ (M=Cr, Mo, W) in THF reflux.[27] Infrared characterization indicated a cis structure, polymer-Ph-bipy-$M(CO)_4$.[27] Ellis extended his research on super-reduced metal carbonyl anions by synthesizing $Na_4M(CO)_4$ (M=Cr, Mo, W).[28]

$$(TMEDA)M(CO)_4 \xrightarrow[NH_3]{Na} Na_4M(CO)_4 + TMEDA \qquad (7)$$

The reaction of (tetramethylethylenediamine)-TMEDA $M(CO)_4$ with sodium in liquid ammonia gave $M(CO)_4^{-4}$ in near quantitative yield.[28] The product was not isolated but characterized by infrared bands centered at 1500 cm^{-1} and by reactions such as the following.

$$Na_4M(CO)_4 + (C_6H_5)_3SnCl \rightarrow Na_2((C_6H_5)_3Sn)_2M(CO)_4 \qquad (8)$$

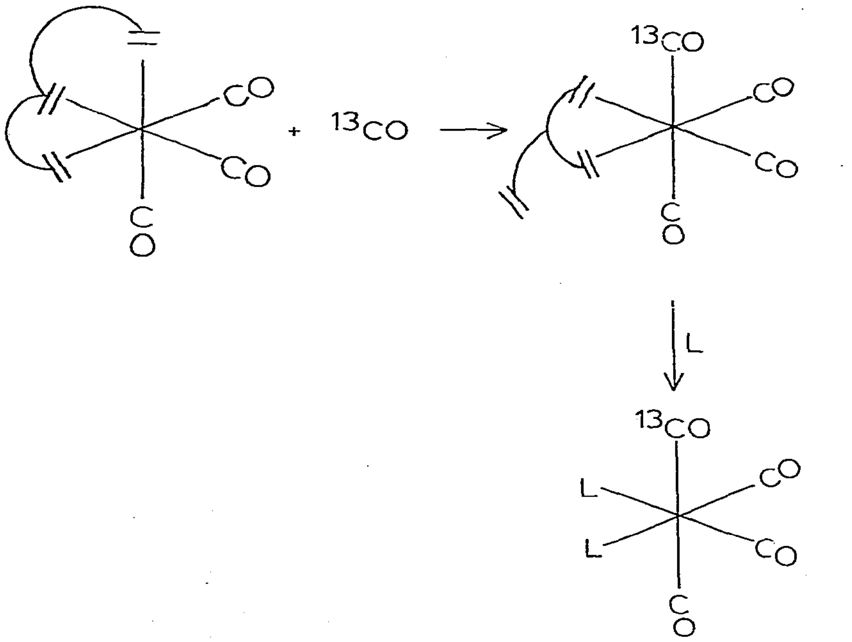
The bis substituted complex was the only product observed.[28]

Reactions of several more highly substituted derivatives of the hexacarbonyls were reported in the past year. Darensbourg and Salzer have reported a series of reactions of $Mo(CO)_3$(triene) (triene=bicyclo[6.1.0]nona-2,4,6-triene).[29]

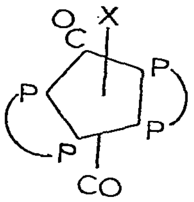
$$Mo(CO)_3(triene) + L \rightarrow Mo(CO)_3L(triene) \qquad (9)$$

$$L = {}^{13}CO,\ P\O_3,\ P(O\O)_3$$

They observe only cis products for all L except $P(OCH_3)_3$ which further substitutes.[29]

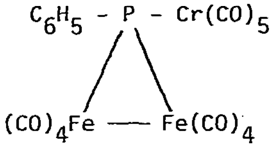


This sequence provides a route to stereospecifically labelled $Mo(CO)_3{}^{13}COL_2$, L= phosphites and phosphines. The observation of stereospecifically labeled product suggests that the intermediates, Mo(CO)$_4$ and $Mo(CO)_4L$, are non-fluxional.[29] Interconversion of cis-trans isomers in seven coordinate $MoX(CO)_2(L\text{-}L')_2$ (L-L' = unsymmetric, bidentate phosphines such as 1-dimethylphosphine-2-diethylphosphinoethane) complexes has been studied by ^{31}P NMR.[30] They suggest a monocapped trigonal prismatic structure with equal amounts of cis and trans isomers giving an AA'BB' spectrum. Interconversion of cis and trans isomers is postulated to occur through the pentagonal bipyramidal intermediate.[30]



(I)

Reactions at phosphorus ligands coordinated to Group VI carbonyls have been observed. Reaction of $Cr(CO)_5PRCl_2$ with $Fe_2(CO)_9$ leads to an interesting phosphorus metallocycle.[31]



(II)

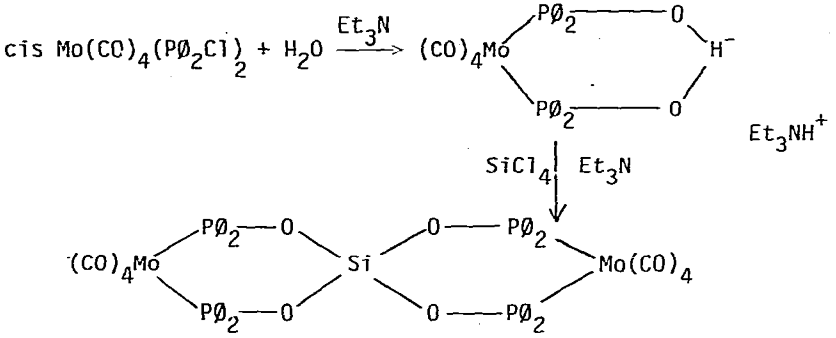
The crystal structure was reported.[31] The synthesis of 1-diphenylphosphinylalkylidenetriphenylphosphoranepentacarbonylchromium was reported from $(CO)_5Cr(P\phi_2Cl)$.[32]

$$(CO)_5CrP\phi_2Cl + Et_3P{:}CHR \rightarrow (CO)_5Cr[P\phi_2CR{:}PEt_3] \qquad (11)$$
$$R = H,\ Me$$

The normally unstable tris(amino)-phosphine ligand has been prepared in a complex with $M(CO)_5$ (M=Cr,Mo,W).[33]

$$(CO)_5MPCl_3 + 6NH_3 \rightarrow (CO)_5MP(NH_2)_3 + 3NH_4Cl \qquad (12)$$

Characterization by IR, NMR, and mass spectra indicate the same binding properties as $P(NMe_2)_3$.[33] In complexes of molybdenum, $Mo(CO)_4(P\phi_2Cl)_2$, the coordinated chlorodiphenylphosphine ligand was shown to react with alcohols, amines, and thiols, leaving monodentate P-donor ligands, $P\phi_2X$.[34] A series of reactions of these complexes were carried out, the most interesting is below.[34]



(13)

Complexes with metal-nitrogen coordination have been observed in several classes of nitrogen ligands. Diazene, hydrazine, and ammonia complexes with $W(CO)_5$ were prepared by reactions of $W(CO)_5THF$.[35]

$$\begin{array}{l} W(CO)_5THF + N_2H_4 \rightarrow [(CO)_5W]_2N_2H_4 + (CO)_5WN_2H_4 \qquad (14) \\ \qquad\qquad\qquad\qquad\quad \downarrow \text{oxidation} \\ \qquad\qquad\qquad\qquad [(CO)_5W]_2N_2H_2 \end{array}$$

The reactions were also accomplished with substituted derivatives ($P\phi_3$ and PMe_3) although the product stability was reduced.[35] All of the complexes undergo base catalyzed H-D exchange yielding N-D species. The reaction of diazene was much more rapid than the hydrazine or ammonia complexes. The diazene complex disproportionated to hydrazine and free N_2.[35] The reaction of a thiocyanate complex with methyl fluorosulphonate produced coordinated methylthiocyanate.[36]

$$[N(P\phi_3)_2][M(NCS)(CO)_5] + SFO_2(OMe) \rightarrow M(CO)_5(NCSMe) \qquad (15)$$

$$M = Cr, W$$

X-Ray crystallography confirmed the sequence Cr-N-C-S-Me. The Cr is octahedral with the trans CO having a shorter Cr-C bond and longer C-O bond than the cis CO's, consistent with the lower π-acceptor capability for MeSCN. The C-S-C angle is 98.7° very similar to the free ligand.[36] Reaction of the nitrile ligand in $Cr(CO)_5NCR$ with $\emptyset_3P{=}CH_2$ has been reported.[37]

$$(CO)_5CrNCR + \emptyset_3P = CH_2 \rightarrow (CO)_5CrNH{=}CH{-}CH{=}P\emptyset_3 \qquad (16)$$

The reaction of mixed amine tricarbonyls of molybdenum with Br_2 and I_2 has been observed.[38,39]

$$\begin{aligned} &Mo(CO)_3LL' + Br_2 \rightarrow [Mo(CO)_3LL'Br]Br_3 \\ &Mo(CO)_3LL' + I_2 \rightarrow Mo(CO)_3LL'I_2 \end{aligned} \qquad (17)$$

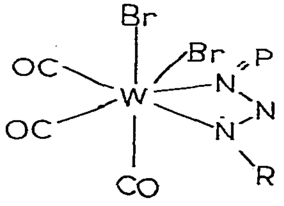
L = o-phenanthroline (o-phen) and bipyridine (bipy)

L' = butylamine, piperidine, etc.

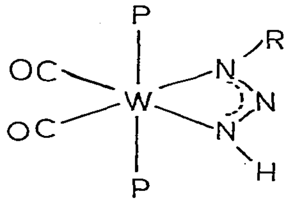
The complexes were characterized by IR and NMR.[38,39] Nitrene ligands have been synthesized by the interaction of aryl azides with tungsten complexes.[40] The aryl azides insert into W-P and W-H bonds.

$$\begin{aligned} &WBr_2(CO)_3(P\emptyset_3)_2 + \emptyset N_3 \rightarrow WBr_2(CO)_3(\emptyset N_3P\emptyset_3) \\ &WH(CO)_2(NO)(P\emptyset_3)_2 + \emptyset N_3 \rightarrow W(\emptyset N_3H)(CO)(NO)(P\emptyset_3)_2 \end{aligned} \qquad (18)$$

On the basis of IR and ^1H NMR, the following structures were predicted.



III



IV

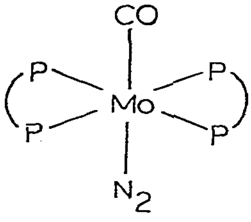
Several dinitrogen compounds have been prepared, primarily with molybdenum. George has reported a direct one-step synthesis of bis-(dinitrogen) complexes of Mo(0) from $MoCl_5$.[41]

$$MoCl_5 + N_2 + PR_3 \xrightarrow{Na/Hg} Mo(N_2)_2(PR_3)_4 \qquad (19)$$

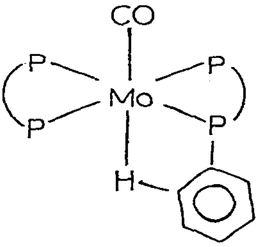
The yield is up to 72% and is most effective for bisphosphino ligands.[41] The reactions of bis(dinitrogen)bis(diphenylphosphinoethane) molybdenum with ethyl chloroformate and benzylpropionate have been reported.[42,43] The reaction with benzylpropionate causes decarbonylation to $Mo(N_2)(CO)(diphos)_2$. Treatment of this complex with argon leads to a five coordinate complex.[42]

$$Mo(N_2)(CO)(diphos)_2 \xrightarrow{Ar} Mo(CO)(diphos)_2 \qquad (20)$$

The structures of both complexes have been determined. There is a very short Mo-H interaction in the position trans to CO in the five-coordinate complex.[43]

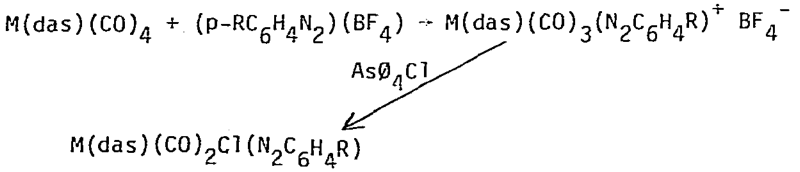


V



VI

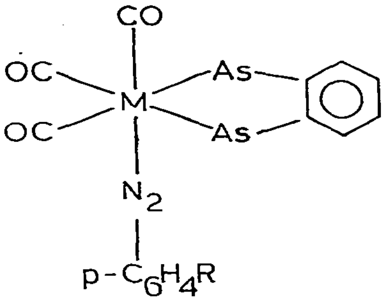
Reaction of trans-$Mo(N_2)(RCN)(dppe)_2$ and ØCOCl was reported to give $MoCl(N_2CO\text{Ø})(dppe)_2$.[44] A crystal structure showed the Mo-N-N to be linear and less than a double bond.[44] Arenediazo derivatives of o-phenylenebis(dimethylarsine)-tetracarbonylmolybdenum and tungsten were synthesized by reaction with $(p\text{-}RC_6H_4N_2)(BF_4)$.[45]



$$M(das)(CO)_4 + (p\text{-}RC_6H_4N_2)(BF_4) \rightarrow M(das)(CO)_3(N_2C_6H_4R)^+ BF_4^- \qquad (21)$$

$$M(das)(CO)_3(N_2C_6H_4R)^+ BF_4^- \xrightarrow{As\text{Ø}_4Cl} M(das)(CO)_2Cl(N_2C_6H_4R)$$

The tricarbonyl compound was postulated to be the facial isomer on the basis of IR data.[45]



VII

Several routes to isocyanide complexes of Cr, Mo, and W were reported last year. By substitution of the CO from the hexacarbonyl, King and Heckley prepared a series of α-methylbenzylisocyanide complexes.[46] They prepared $LM(CO)_5$, cis-$L_2M(CO)_4$, and fac-$L_3M(CO)_3$ for M=Cr, Mo, W. Use of pure enantiomers led to optically active complexes; rotation by the bis-substituted complex is twice that of the mono-substituted suggesting that the metal has no effect on the asymmetric carbon.[46] Seven-coordinate complexes with t-butylisocyanide have been prepared by oxidative-addition to the hexacarbonyl ($Mo(CO)_6$ and $W(CO)_6$) resulting in complete replacement of the CO's.[47]

$$Mo(CO)_6 + I_2 + 7\,RNC \rightarrow [(RNC)_7Mo]I_2 + 6CO \qquad (22)$$

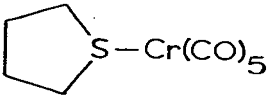
A crystal structure of $[Mo(t\text{-}C_4H_9NC)_6Br]^+$ showed a capped trigonal prism with the bromide capping. NMR (^1H and ^{13}C) indicates fluxional behavior.[47] Replacement of the dinitrogen in bis(dinitrogen)bis(diphenylphosphinoethane) molybdenum and tungsten gave a series of bis-substituted isocyanide complexes.[48]

$$M(N_2)_2(diphos)_2 + 2RCN \rightarrow M(RCN)_2(diphos)_2 \qquad (23)$$

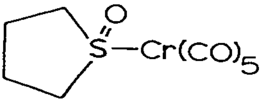
$$M = Mo, W \qquad R = Me, t\text{-}Bu, \phi, etc.$$

The isocyanides are trans in the product. The infrared frequency, 1800-1850 cm^{-1}, is very low, approaching that of bridging isocyanides.[48]

Organometallic complexes containing metal-sulfur bonds have been reported for Cr, Mo, and W. A number of sulfide and sulfoxide complexes of dihydro- and tetrahydro-thiophene with chromium pentacarbonyl were prepared and characterized.[49] IR and NMR suggest binding of the sulfide to chromium but the results were ambiguous for sulfoxides. The crystal structure of 2,5-dihydrothiophene-1-oxide chromium pentacarbonyl was determined.[49]

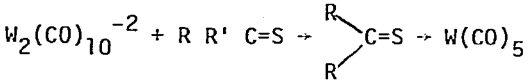


VIII



IX

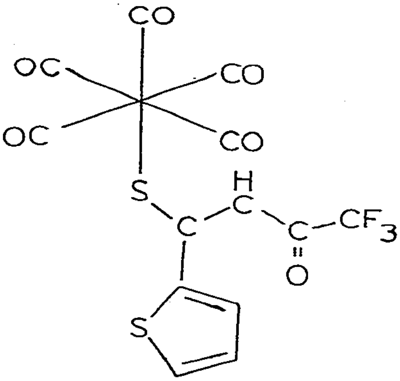
The reaction of thioketones with ditungsten dianions has led to sulfur coordination.[50]



$$W_2(CO)_{10}^{-2} + R\ R'\ C{=}S \rightarrow \overset{R}{\underset{R'}{>}}C{=}S \rightarrow W(CO)_5$$

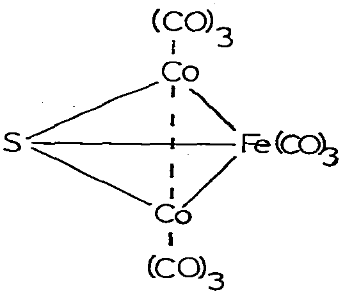
$$R,\ R' = \text{Ø},\ p\text{-}CH_3OC_6H_4,\ p\text{-}CH_3C_6H_4,\ C_{10}H_{14},\ C_{10}H_{16} \qquad (24)$$

These compounds were prepared in good yield and characterized by IR and NMR.[50] Sulfur bonded monothio-β-diketone complexes, RCSCHOCR, have been studied (R = CH_3) in the complex $M(CO)_5L^-$.[51] L is monodentate, and coordinated through the sulfur as indicated by ^1H NMR and IR. A crystal structure was done on tetraethylammonium pentacarbonyl-[1,1,1-trifluoro-4-(2-thienyl)-4-thioxobutan-2-onato-S]tungstate (0).[51]



X

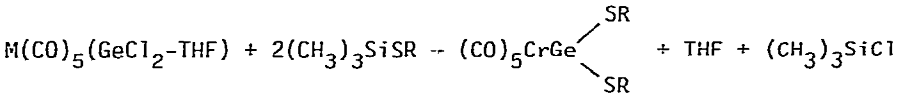
There is very little distortion of the metal carbonyl framework.[51] A rather unusual sulfur ligand displaces THF in $Cr(CO)_5THF$.[52-53] The crystal structure



XI

shows a quite short Cr-S bond suggesting that $SFeCo_2(CO)_9$ is a strong sigma donor and pi acceptor ligand. Pentacarbonyl complexes of Mo and W with another unusual sulfur ligand $[C_5H_5Cr(SCMe)_3]_2S$, were also reported.[54]

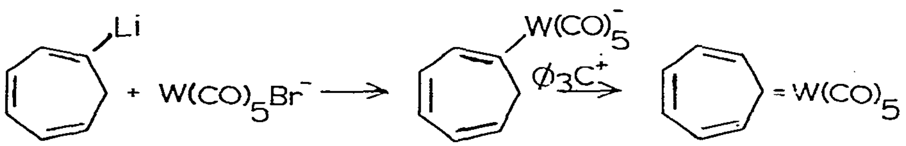
Complexes of stannyl and germyl ylide complexes of the metal carbonyls were reported. DuMont has reported reactions of $W(CO)_5(SnCl_2\text{-}THF)$ with $P(t\text{-}Bu)_3$ leading to $W(CO)_5(SnCl_2\text{-}P(CMe_3)_3)$ which was characterized by ^{31}P and ^{119}Sn NMR[55] and reaction with $(CH_3)_3Si\text{-}P(t\text{-}Bu)_2$ leading to $W(CO)_5(SiCl\text{-}(P(t\text{-}Bu)_2))$ which was studied by IR.[56] The reaction of $M(CO)_5(GeCl_2\text{-}THF)$ (M = Cr, W) with two equivalents of $(CH_3)_3SiSR$ (R = methyl, mesitylene) was also reported.[57]



$$M(CO)_5(GeCl_2\text{-}THF) + 2(CH_3)_3SiSR \rightarrow (CO)_5CrGe\begin{matrix}\diagup SR\\ \diagdown SR\end{matrix} + THF + (CH_3)_3SiCl \qquad (25)$$

Carbenes and carbynes

Carbenes. Several interesting carbenes were synthesized in 1978. The synthesis of cycloheptatrienylidene tunsten pentacarbonyl was reported.[58]



(26)

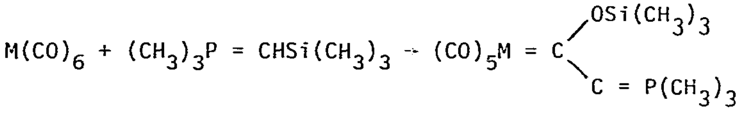
Very low IR stretching frequencies for the CO's indicate a negative charge on the W and thus a positive charge on the ring.[58] The synthesis of carbenes by reactions of pentacarbonyl metal dianions and cyclopentadienyl tricarbonyl anions with dichloro compounds (chloromethylene)dimethylammonium chloride was described.[59]

$$Na_2M(CO)_5 + [N(Me)_2(CHCl)]Cl \rightarrow (CO)_5MCH(NMe_2) + 2NaCl \qquad (27)$$

$$2Na[C_5H_5M(CO)_3] + [N(Me)_2(CHCl)]Cl \rightarrow [Cp(CO)_3MCH(NMe_2)][CpM(CO)_3]$$

$$M = Cr, Mo, W$$

The first reaction is simple salt elimination while the second is salt elimination with oxidative addition giving a cationic carbene complex.[59] The quantitative addition of $(CH_3)_3P = CHSi(CH_3)_3$ to coordinated carbon monoxide on the hexacarbonyls led to trimethylphosphoranediyl(trimethylsiloxy)carbene complexes.[60]



(28)

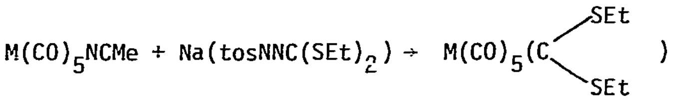
$$M(CO)_6 + (CH_3)_3P = CHSi(CH_3)_3 \rightarrow (CO)_5M = C\begin{cases} OSi(CH_3)_3 \\ C = P(CH_3)_3 \end{cases}$$

$$M = Cr, Mo, W$$

These complexes were characterized by IR and NMR spectroscopy.[60] Fluoride abstraction by SbF_5 from $CpMo(CO)_3CF_3$ has led to the first fluorocarbene complex.[61]

$$CpMo(CO)_3CF_3 + SbF_5 \rightarrow [CpMo(CO)_3CF_2]SbF_6 \qquad (29)$$

Although this complex could not be isolated it was identified by spectroscopic techniques including ^{19}F and ^{13}C NMR.[61] Lappert and Shaw synthesized bis-(ethylthio)-carbene complexes of chromium and tungsten.[62]

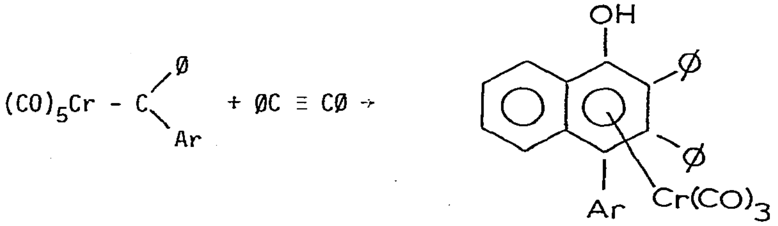


$$M(CO)_5NCMe + Na(tosNNC(SEt)_2) \rightarrow M(CO)_5(C\begin{smallmatrix}SEt\\SEt\end{smallmatrix}) \qquad (30)$$

tos = MeC_6H_4-p-SO_2, M = Cr, W

The complex, $(CO)_5CrNCN(C_2H_5)_2$, was prepared by a reaction that probably proceeded through a carbene intermediate, $(CO)_5CrC\begin{smallmatrix}N\colon\\N(C_2H_5)_2\end{smallmatrix}$, before rearranging to the nitrogen coordinated ligand.[63] A crystal structure was reported showing the linear Cr-N-C-N linkage.[63]

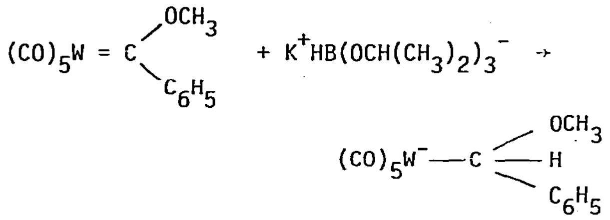
Reactions of Group VI metal carbenes have led to a variety of complexes. Treatment of $(CO)_5W=C\phi(\phi)$ with cyclopentanone in n-hexane led to the ring-opened product $(CO)_5W = C(OEt)[(CH_2)_3CH=C\phi(\phi)$, which was isolated and characterized.[64] Stereoselective synthesis of condensed aromatic ligands from reactions of pentacarbonyl(carbene)chromium complexes with alkynes was reported.[65]



(31)

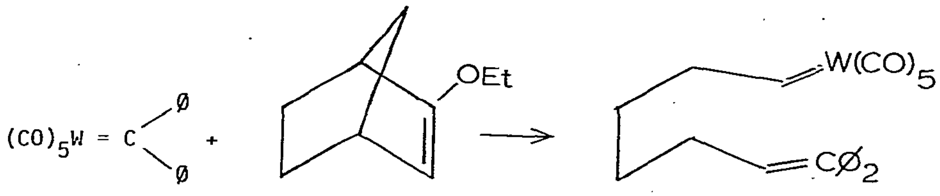
Ar = $2\text{-}C_4H_3O$
$2\text{-}C_{10}H_7$

Pentacarbonylchromium complexes with substituted phenyl, naphthyl-, furyl, thienyl, and cyclopentenylcarbene ligands reacted with alkynes (tolan and 1-pentyne) in a strongly stereoselective way to give substituted naphthol, phenanthrene, benzofuran, benzothiophene, and indan ligands coordinated to a tricarbonyl chromium fragment.[65] The reaction of (2-furyl)phenyl carbene complexes with tolan led exclusively to naphthol complexes showing that the phenyl ring is preferrably annellated with respect to the furyl and naphthyl rings.[65] Casey et al. have reported the addition of hydride to pentacarbonyltungstenmethoxyphenylcarbene.[66a]



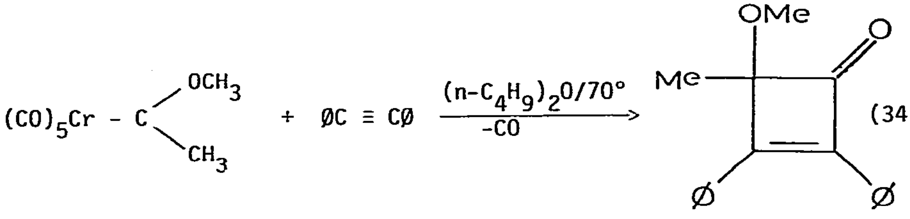
$$(CO)_5W{=}C(OCH_3)(C_6H_5) + K^+HB(OCH(CH_3)_2)_3^- \rightarrow (CO)_5W^-{-}C(OCH_3)(H)(C_6H_5) \qquad (32)$$

A crystal structure determination of the product, tetraethylammonium (α-methoxybenzyl)pentacarbonyltungstate, showed the W-C bond to be 2.34 Å, somewhat longer than a normal W-C bond.[66a] The barrier to rotation about the phenyl ring - benzylic carbon single bond was evaluated from temperature dependent NMR spectra. The value of 8.7 kcal/mole was attributed to a destabilization of the transition state both sterically and electronically.[66a] Diphenylcarbene tungstenpentacarbonyl was reported to react with cyclic enolethers cleaving the olefinic bond in a possible model for olefin metathesis.[66b]



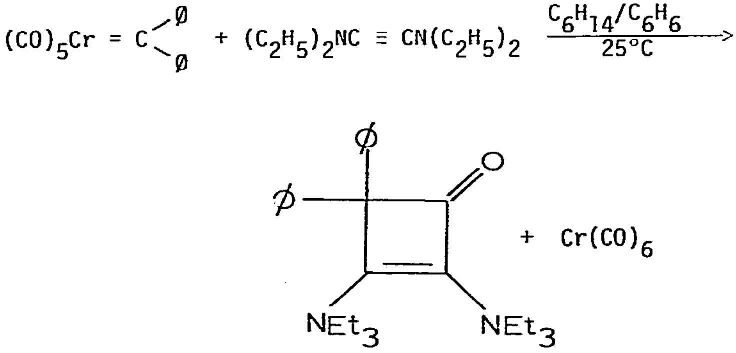
(33)

A crystal structure of the product shows no coordination from the double bond to the tungsten.[66b] Cyclobutenone compounds have been synthesized by reaction of alkynes with chromiumpentacarbonyl carbene.[67]



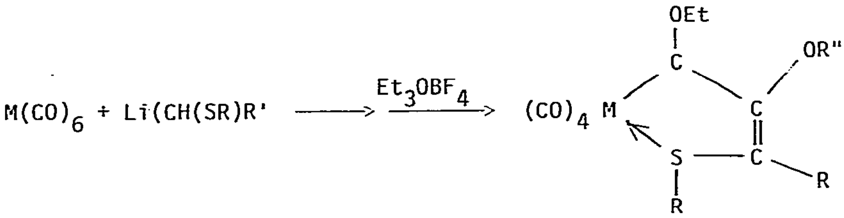
(34)

The $Cr(CO)_3$ was interpreted as coordinated to the phenyl ring by the shift in the NMR.[67] A similar reaction gives $Cr(CO)_6$ and another cyclobuteneone compound.[67]



(35)

Carbonyl insertion into a metal carbene bond has been suggested in the reaction converting the hexacarbonyls of chromium and tungsten into tetracarbonyl-(carbene-thio) complexes.[68]



(36)

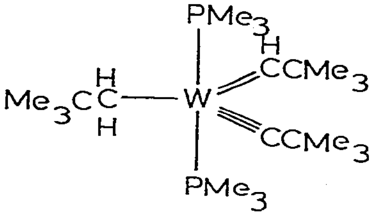
M = Cr, W, R = Me, Ø, R' = Ø, R" = H, Et

These complexes were studied by IR, electronic spectra, NMR (^1H and ^{13}C), and mass spectra.[68]

Carbynes. Reports of syntheses and reactions of group VI carbynes have greatly increased in 1978. Clark and Schrock reported the reaction of neopentyllithium with tungstenhexachloride.[69]

$$WCl_6 + 6\ LiCH_2CMe_3 \longrightarrow W(CH_2CMe_3)_3(\equiv CCMe_3) \qquad (37)$$

A similar product was observed in the corresponding reaction of $MoCl_5$. Both products are apparently dimers. The reaction of the tungsten neopentylcarbyne with two moles of $P(Me)_3$ led to an unusual alkyl, carbene, and carbyne complex (alkyl, alkylidene, and alkylidyne in Schrock's nomenclature), $W(CCMe_3)(CHCMe_3)(CH_2CMe_3)(PMe_3)_2$.[69]

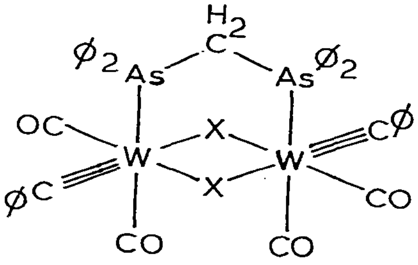


XII

Fischer has continued his excellent work on carbynes, primarily tungsten carbynes. The structures of the complexes $X(CO)_4W(CCH_3)$, X = Cl, Br, I, were reported.[70] Normal octahedral coordination was observed with X trans to the carbyne carbon. The W-C distances were 1.77 Å and 1.82 Å for the iodide and bromide respectively.[70] Reaction of the phenylcarbyne analogue, $Br(CO)_4W(CC_6H_5)$, with bis(diphenylarsino)methane (dam) proceeded as follows:[71]

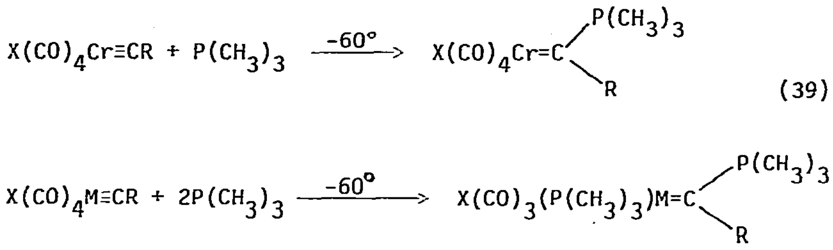
$$\begin{tikzcd}
Br(CO)_4W\equiv CC_6H_5 + dam \arrow[r, "-20^\circ C"] & Br(CO)_3(dam)W\equiv CC_6H_5 + CO \arrow[d, "40^\circ", "-CO"'] \\
& Br(CO)_2(dam)_2W\equiv CC_6H_5
\end{tikzcd}$$

In these complexes dam is a monodentate ligand. The substitution is quite facile suggesting that the carbyne accelerates the reaction. A dimer was also isolated and assigned the following structure based on IR and NMR data.[71]



XIII

The reactions of trans-$X(CO)_4M(CR)$ with $P(CH_3)_3$ suggest the route of accelerated substitution is through an ylide complex.[72]

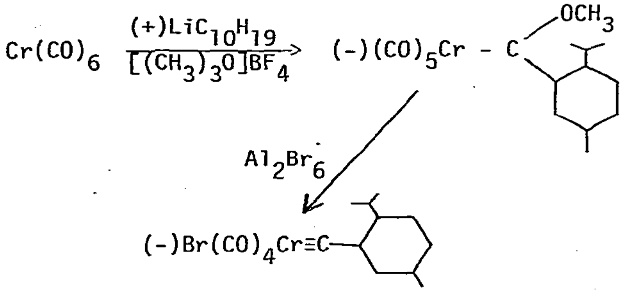


$$X(CO)_4Cr{\equiv}CR + P(CH_3)_3 \xrightarrow{-60°} X(CO)_4Cr{=}C\begin{matrix}P(CH_3)_3\\R\end{matrix} \qquad (39)$$

$$X(CO)_4M{\equiv}CR + 2P(CH_3)_3 \xrightarrow{-60°} X(CO)_3(P(CH_3)_3)M{=}C\begin{matrix}P(CH_3)_3\\R\end{matrix}$$

M=Mo, W, X=Cl, Br, I, R=CH_3, $CH_2C_6H_5$, C_6H_5, etc.

At higher temperatures two CO's are substituted by $P(CH_3)_3$ in the tungsten complex.[72] An optically active carbyne complex, $(-)Br(CO)_4Cr(C_{11}H_{19})$ was prepared by the following series of reactions.[73]



(40)

The crystal structure was reported with the absolute configuration; the Cr–C bond length was 1.49 Å.[73] Nucleophilic substitutions on trans-tetracarbonyl-(organylcarbyne)tetrafluoroborato complexes of Cr and W with PØ_3, CN^-, and SCN^- have been reported to give displacement of BF_4^- leading to the following complexes.[74]

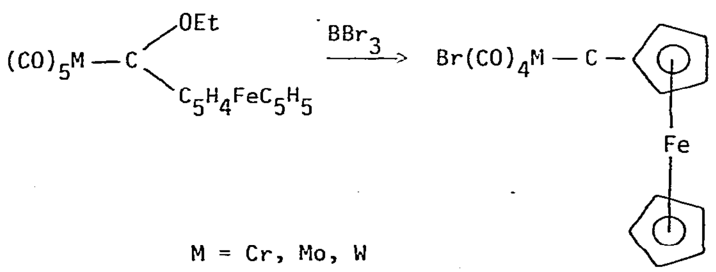
trans-$SCN(CO)_4MCR$ M = Cr, W, R=CH_3, Ø

trans-$NC(CO)_4MCR$ M = Cr, W, R=CH_3, Ø

[trans-$(\text{Ø}_3P)(CO)_4W\text{CØ}]^+\ BF_4^-$

[trans-$(\text{Ø}_3P)(CO)_4CrCCH_3]^+\ BF_4^-$

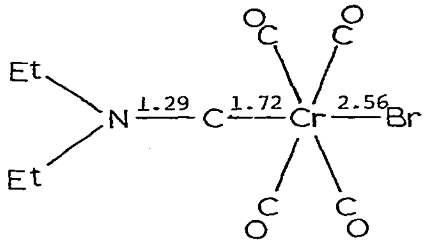
The first product was assigned as an isothiocyanate by IR.[74] Fischer and coworkers synthesized interesting ferrocenylcarbyne complexes from the analogous carbenes.[75]



(41)

M = Cr, Mo, W

The structure of $Br(CO)_4CrC\text{-}C_5H_4FeC_5H_5$ was determined giving a Cr–C bond length of 1.71 Å, normal octahedral coordination around Cr, and normal geometry for ferrocene.[75] Trans-halogeno-tetracarbonyl-dialkylaminocarbyne complexes were synthesized from the alkoxy-carbene by reaction with boron halides.[76] The crystal structure of the diethylamino complex was determined by X-ray diffraction.[76]



Distances are in Å

XIV

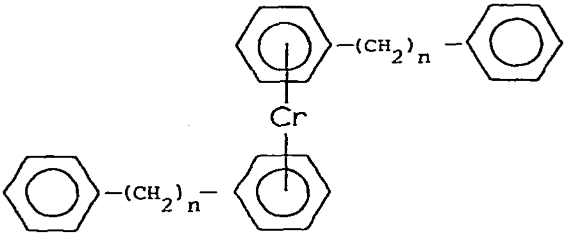
The cationic carbyne complex, $[(CO)_5Cr(CNEt_2)][BF_4]$ was shown to react with PMe_3 followed by cleavage of the metal carbon bond leading to the cationic half-ylide $[Et_2N\text{-}C(PMe_3)_2][BF_4]$.[77a] A mechanism was proposed for this reaction.[77a]

Aromatics and cyclopentadienyls

Aromatics. Metal atom vaporizations have been the primary new means for synthesis of arene complexes. A new technique for the synthesis of bisarenes was reported involving vaporization of K atoms into a stirred solution of $MoCl_5$ in THF in the presence of an arene (toluene or methylnaphthalene).[77b]

$$MoCl_5 + \text{Arene} + K \xrightarrow[-100°]{THF} Mo(\text{Arene})_2 \qquad (42)$$

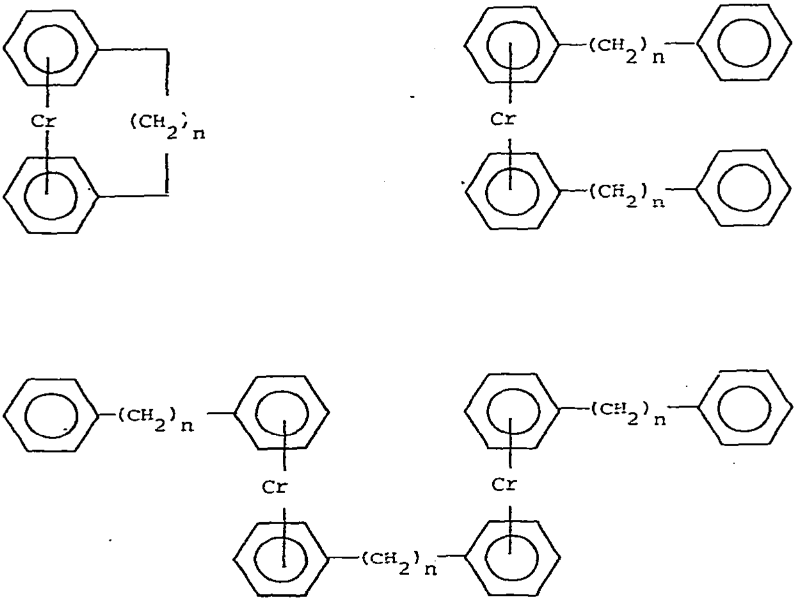
The more normal cocondensation of Cr atoms with arenes led to only the bisarene, $Cr(arene)_2$, with no indication of any other product at 77°K or 10°K.[78] Two studies of the condensation of α,ω-diphenyl alkanes and Cr atoms were reported.[79,80] Gladysz and coworkers observed only one product[79] while Nesmeyanov and coworkers obtained mixtures which were separated by preparative thin



n = 1,4

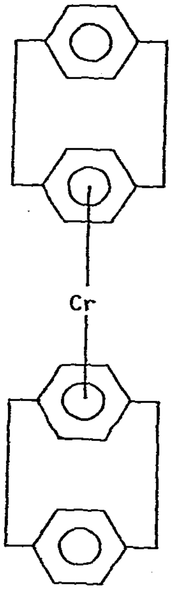
XV

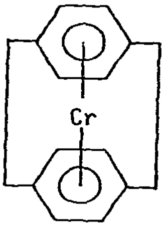
layer chromatography.[80]

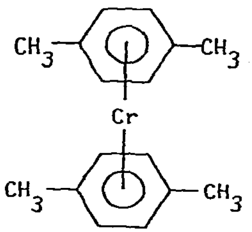


XVI

These products were characterized by elemental analyses, mass spectra, and EPR of the iodides.[80] The condensation of Cr and [2.2] paracyclophane produced several compounds as shown below.[81]



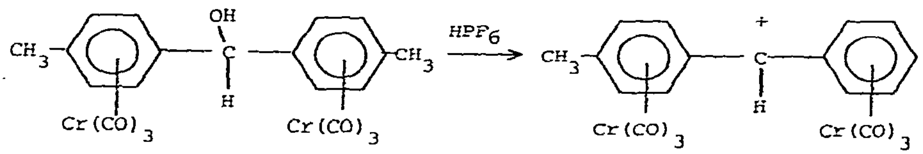




The first bis arene tunsten hydride was synthesized by cocondensation of benzene and tungsten followed by protonation with dilute HCl solutions.[82] Addition of PF_6^- causes precipitation of the hydride as a salt.[82]

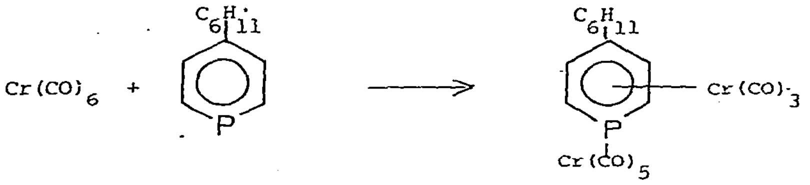
$$W(g) + C_6H_6 \longrightarrow (C_6H_6)_2W \xrightarrow{H^+} (C_6H_6)_2WH^+ \qquad (43)$$

Two novel arene complexes of chromium have been synthesized by reaction with $Cr(CO)_6$. The reaction of diarylmethanes with two equivalents of $Cr(CO)_6$ gave products with both arene rings π-coordinated.[83] Protonation leads to



(44)

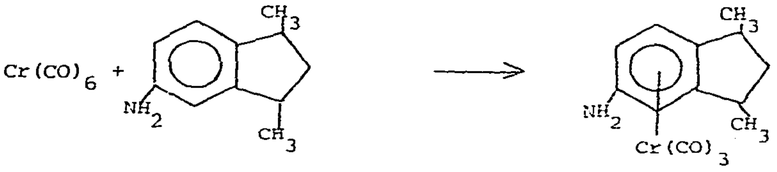
carbonium ions stabilized by coordination to the Cr. The blue carbonium salts are carbon electrophiles. ^{13}C NMR and IR indicate delocalization of the positive charge onto the Cr atoms.[83] Reaction of 4-cyclohexylphosphorin with $Cr(CO)_6$ results in coordination through both the heterocyclic aromatic ring and through the phosphorus.[84] The structure was deduced by IR, NMR, and mass



(45)

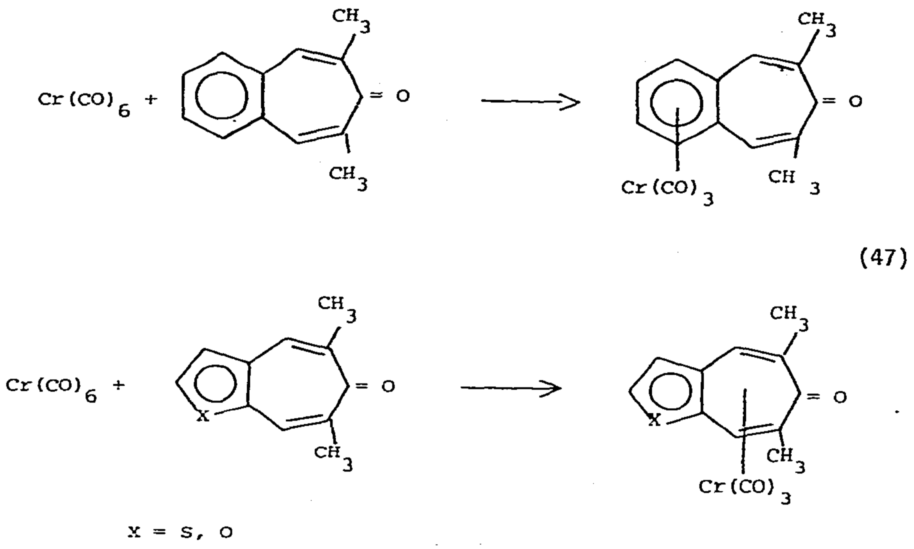
spectra. The composition of organic impurities present in $(EtØ)_2M$ (M = Cr,Mo), prepared by Friedel-Crafts reaction was determined by GC, IR, and mass spectrometry. The impurities arise in the transalkylation stage with EtØ under the reaction of $AlCl_3$.[85]

A number of complexes of bicyclic species have been reported. The reaction of $Cr(CO)_6$ with cis- and trans-1,3-dimethylindan-5-amine produced the tricarbonylchromium complex.[86]



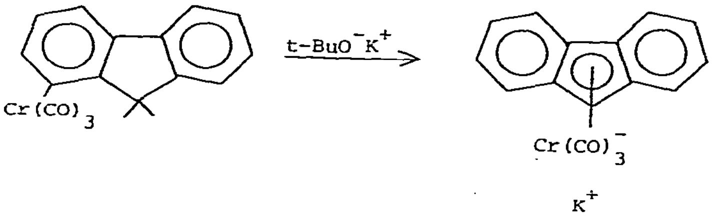
(46)

The trans isomer formed two diastereomers in equal amounts indicating no preference by interaction with the amine.[86] The reaction of $Cr(CO)_6$ with arenotropones has also been observed.[87]



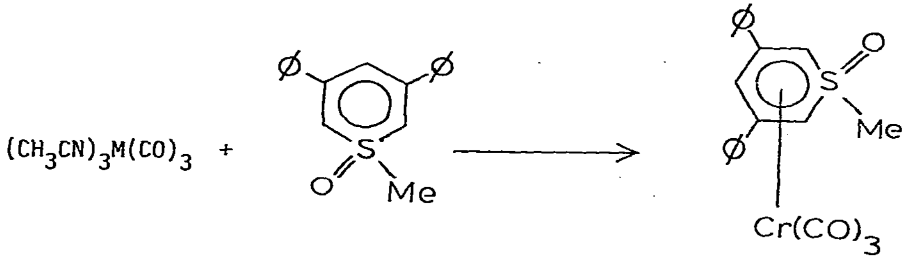
(47)

The coordination of the chromium tricarbonyl varies with the arenotropone used.[87] The conversion from η^6 - to η^5-coordinated indenyl and fluorenyl complexes were studied by Nesmeyanov and coworkers.[88]



(48)

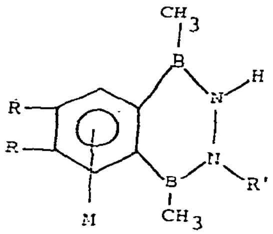
They prepared η^5-$C_{13}H_9(CO)_3Cr^-$ and η^5-$C_9H_7(CO)_3M^-$, M = Cr, Mo, W, by deprotonation. Methylation and protonation led to $\eta^5 \rightarrow \eta^6$ although for Mo and W stable methyl complexes are formed and for W a stable hydride was formed. Mechanisms were postulated for each reaction.[88] The structure of 1-methyl-3,5-diphenylthiabenzene 1-oxide tricarbonylchromium, -molybdenum, and -tungsten have been elucidated.[89]



(49)

M = Cr, Mo, W

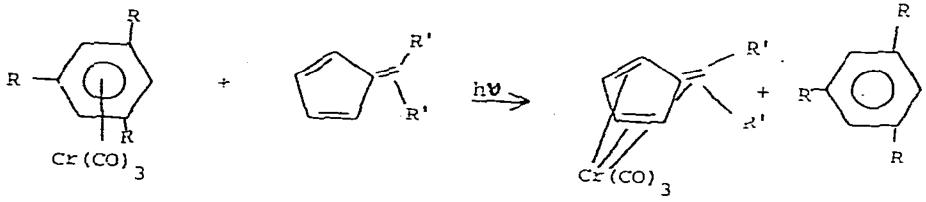
The ring was non-planar, but there was no evidence of sulfur coordination.[89] Benzo-1,2,3,6-diazadiborines were shown to react with $Cr(CO)_6$ giving exclusive coordination through the benzo ring.[90]



XVII

These complexes were studied by NMR (^{1}H, ^{13}C, and ^{11}B) indicating that this ligand has better donor properties than benzene.[90] A large series of complexes with possible competition between benzo groups and heterocycles show exclusive coordination through the benzo ring, by NMR (^{1}H and ^{11}B), IR and mass spectra.[91]

Reactions. Photochemical reaction of (arene)$Cr(CO)_3$ with fulvenes resulted in quantitative displacement of the arene by the fulvene.[92]



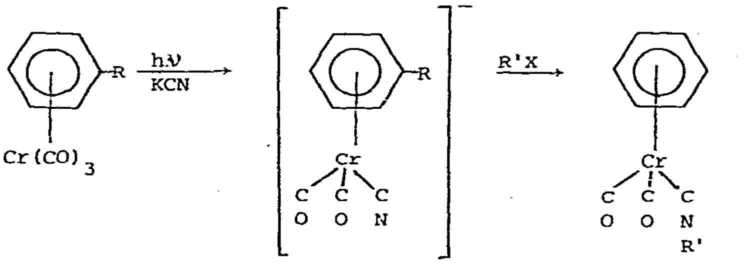
(50)

Photochemical reaction of (arene)$Cr(CO)_3$ with CS_2 resulted in CO displacement and formation of a carbon disulfide complex.[93]

$$ArCr(CO)_3 + CS_2 \xrightarrow{h\nu} ArCr(CO)_2CS_2 \xrightarrow{PMe_3} ArCr(CO)_2CS \quad (51)$$

Ar = hexamethylbenzene, mesitylene, and benzene

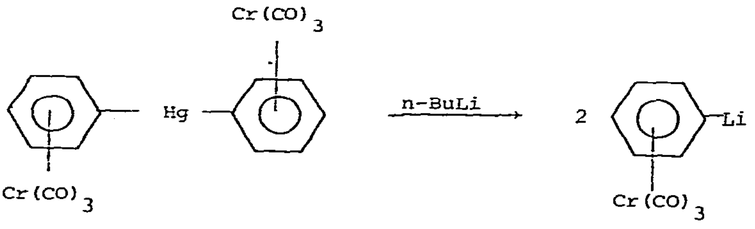
Further reaction with PMe_3 produce a thiocarbonyl, $ArCr(CO)_2CS$. The infrared spectrum shows very little difference in $ArCr(CO)_2CS$ and $ArCr(CO)_3$ in the carbonyl stretching region; The CS stretch occurred at 1190 cm^{-1}.[93] Another photochemical reaction of $ArCr(CO)_3$ was reported which resulted in displacement of CO by CN^-.[94]



(52)

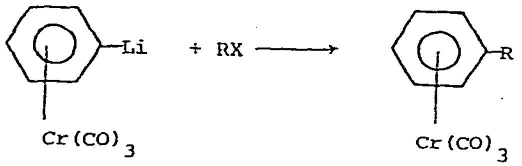
A crystal structure determination showed the final product to be a coordinated isocyanide formed by reaction of R'X with coordinated cyanide.[94] Reaction of $(C_6H_6)Cr(CO)_2S(CH_3)_2$ with CH_3SO_3F formed a cationic complex with a sulfonium cation coordinated, $[(C_6H_6)Cr(CO)_2S(CH_3)_3]^+ SO_3F^-$.[95]

Reactions of the coordinated arenes on Groups VI metals were observed in a few cases. Rausch and Gloth reported the preparation of (n^6-phenyllithium)-tricarbonylchromium and reactions of this complex.[96]



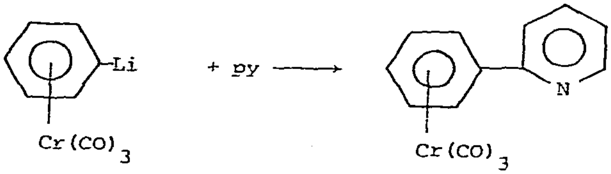
(53)

Reaction of the phenyllithiumchromiumtricarbonyl and organic halides, RX (R = COOH, $Si(CH_3)_3$, $C(O)CH_3$, $P(C_6H_5)_2$) leads to substitution on the benzene.[96]



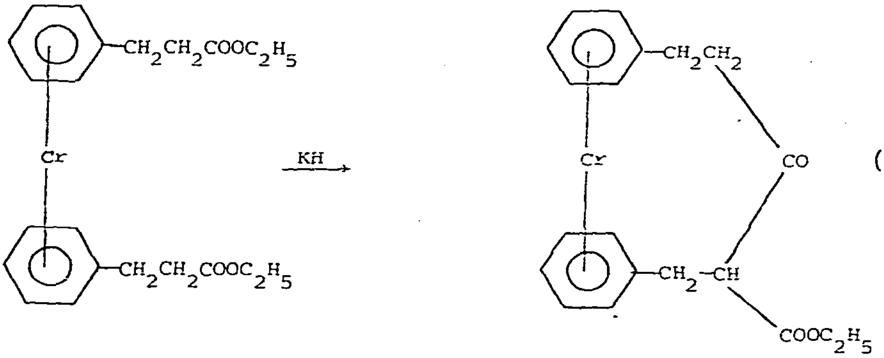
(54)

Coupling reactions were also observed as shown below with pyridine.[96]



(55)

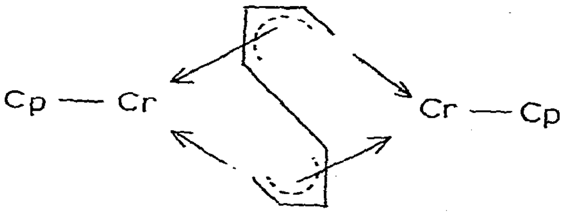
Dieckman condensation of bis(ethyl-β-phenylpropionate) chromium led to [5] dibenzenechromocenophane-2-carbethoxy-3-one.[97] Condensation of bis(benzaldehyde)chromium with ethylacetate produced bis(ethylcinnamate)chromium which was hydrogenated to bis(ethyl-β-propionate). This reacts with KH to cyclize.[97]



(56)

The product was characterized by mass spectroscopy.[97] Stereospecific ring expansion of arenechromium tricarbonyl complexes with $\phi CH_2Cl-Li(N(Me_2CH)_2)$ gave 2- or 3-substituted cycloheptatriene derivatives still coordinated to the chromium tricarbonyl group.[98]

Cyclopentadienyls. The reaction of chromocene with cyclooctatriene (COT) produced a dichromium complex, $(CpCr)_2C_8H_8$.[99] It was postulated that the COT opened to an eight carbon chain and coordinated to each Cr with both sigma and π bonds.



XVIII

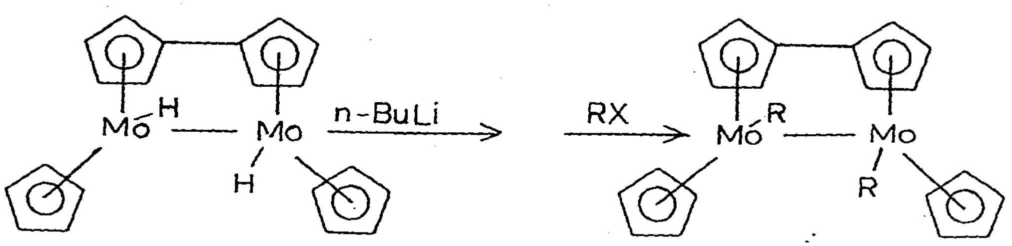
Reaction of this complex with CO gave $(CpCr)_2(CO)_5$ and cyclooctatriene.[99] Photolyses of Cp_2MH_2 (M= Mo, W) caused rearrangements leading to several products.[100]

$$(Cp)_2MoH_2 \xrightarrow[\text{benzene}]{h\nu} [(\eta^5C_3H_5)(\mu-(\eta^1:\eta^5-C_5H_4))Mo]_2$$

$$(Cp)_2WH_2 \xrightarrow[Et_2O]{h\nu} [(Cp)_2W(H)(C_2H_4)]PF_6 \qquad (57)$$

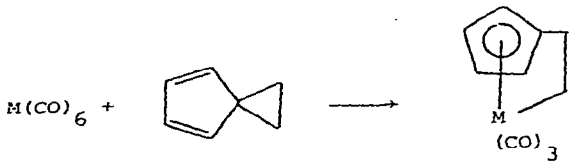
$$+ \text{ cis and trans } [(\eta^5-C_5H_5)(\mu-(\eta^1:\eta^5-C_5H_4))WH]_2$$

The complexes are catalysts for the deoxygenation of epoxides.[100] Green and Simpson reported several reactions of bicyclopentadienylmolybdenum.[101]



(58)

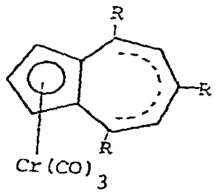
Also reported were reactions with 1,2 dibromoethane, and I_2. The iodide complex reacted with NaSR to give sulfur derivatives.[101] Photolysis gave a complex of the formula $C_{20}H_{18}Mo_2$.[101] The formation of σ-alkyl-π cyclopentadienyl complexes with the tricarbonyls was observed.[102]



(59)

From ^{13}C NMR it was concluded that the three-membered ring was completely opened.[102] The decomposition of $Cp(CO)_3W(\eta^1\text{-}(CpMn(CO)_3))$ has been observed to produce $CpMn(CO)_3$, $(CpW(CO)_3)_2$, and a product with two $Cp(CO)_3W$ groups coordinated to the Cp ring of a single $CpMn(CO)_3$.[103] Reaction of $(CH_3CN)_3Cr(CO)_3$ with azulene afforded the first azulene derivative of chromiumhexacarbonyl.[104]

$(CH_3CN)_3Cr(CO)_3$ + Azulene ⟶



(60)

R = H, CH_3

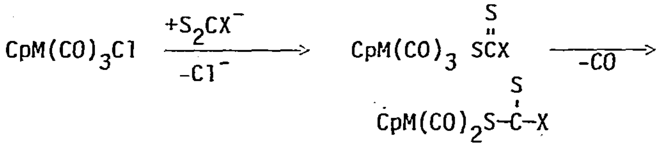
The $Cr(CO)_3$ is coordinated only to the five-membered ring.[104] The methyl substituted complex reacts with CH_3Li to give tricarbonyl(1,7-10-η-2,4,6,6 tetramethylbicyclo[5.3.0]deca-2,4,7,9 tetraen-1, yl)-chromate ion.[104]

Reactions of the cyclopentadienyltricarbonyl metal halides have yielded several new cyclopentadienyl complexes. King and Gimeno prepared complexes of the strong pi-accepting ligand, methylaminobis(difluorophosphine), with the ligand replacing either one or two CO's.[105] The reaction of $CpMo(CO)_3Cl$ wth pyridine-(2)-carboxylic acid thioamides gave the optically active neutral complexes $CpMo(CO)_2LL^*$ with LL^* coordinated by pyridine-N and thioamide-S.[106] The diastereomers can be separated by chromatography and characterized by NMR.

$$CpMo(CO)_3Cl + CH_3N(PF_2)_2 \longrightarrow CpMo(CO)_2((PF_2)_2NCH_3)Cl + CpMo((PF_2)_2NCH_3)_2Cl \qquad (61)$$

$$CpMo(CO)_2NO + CH_3N(PF_2) \longrightarrow CpMo(NO)((PF_2)_2NCH_3)$$

Racemization of the isomers occurred at 90°C.[106] Complexes of the type $[M(Cp)\{HC(N\text{-}P\text{-}tolyl)_2\}(CO)L]$, (M = Mo, W) (L = $PØ_3$, $AsØ_3$, $SbØ_3$, $P(OØ)_3$, $P(OCH_3)_3$) were prepared by reaction of $[M(Cp)(CO)L_2Cl]$ with potassium N,N'-di-p-tolyformamidine.[107] These complexes were characterized by NMR (^1H, ^{13}C, ^{31}P) and IR and the bonding of metal-to-formamidine was discussed.[107] Reaction of $CpM(CO)_3Cl$ with xanthate and thioxanthate ions leads to either dicarbonyl or tricarbonyl products depending on the time of reaction.[108]



$$CpM(CO)_3Cl \xrightarrow[-Cl^-]{+S_2CX^-} CpM(CO)_3\,S\overset{S}{\overset{\|}{C}}X \xrightarrow{-CO} CpM(CO)_2S\underset{}{\overset{S}{\overset{|}{C}}}\!-\!X \qquad (62)$$

X = OR, SR

Possible mechanisms are discussed with two paths probably involved, one with Cl^- displacement by xanthate (thioxanthate) and the second with CO displacement.[108] Chloride abstraction by trimethylsilicon (tin) led to 1,3 diaryltriazenido-cyclopentadienyl-molybdenum dicarbonyl.[109]

$$CpMo(CO)_3Cl + (p\text{-}XC_6H_4)_2N_3Sn(CH_3)_3 \longrightarrow (p\text{-}XC_6H_4)_2N_3Mo(CO)_2(Cp) + Me_3SnCl + CO \qquad (63)$$

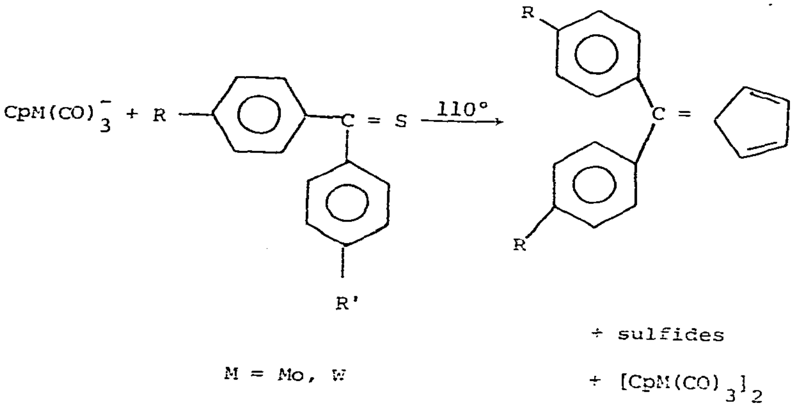
The triazene is apparently a three-electron donor.[109] Octahydrotriborate complexes of molybdenum and tungsten were prepared by reaction of $CpM(CO)_3X$ with tetramethylammoniumoctahydrotriborate.[110]

$$CpM(CO)_3X + (CH_3)_4NB_3H_8 \longrightarrow CpM(CO)_2B_3H_8 \qquad (64)$$

M = Mo, W

The compounds were investigated by proton and ^{11}B NMR.[110]

Reaction of cyclopentadienyltricarbonyl molybdenum hydride with biscyclopentadienyltin produced $HSn[Mo(Cp)(CO)_3]_3$.[111] Reactions at the tin center were investigated. Synthesis and stereochemistry of σ-propargylic molybdenum complexes coordinated by a phosphine or a phosphite ligand were described.[112] The complexes, $CpMo(CO)_2L(CH_2C{\equiv}C\text{-}R)$ ($L=PØ_3$, $P(OØ)_3$, $P(OMe)_3$) (R = H, Me, Ø), react to give π-allyl complexes. An acid catalysis was observed and a reaction scheme proposed.[112] Reaction of the cyclopentadienylcarbonyl anions with thiobenzophenones under phase transfer conditions produced fulvenes and the cyclopentadienyl tricarbonyl dimer.[113]



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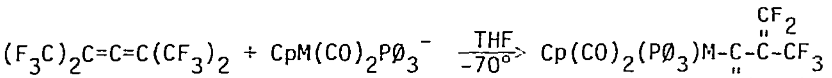
Triphenylphosphine substituted anions, $CpM(CO)_2PØ_3^-$, reacted with tetrakis-(trifluoromethyl)allene leading to the sigma-bonded complex.[114]



$$(F_3C)_2C{=}C{=}C(CF_3)_2 + CpM(CO)_2PØ_3^- \xrightarrow[-70°]{THF} Cp(CO)_2(PØ_3)M\text{-}\underset{\underset{C(CH_3)_2}{\|}}{C}\text{-}\overset{\overset{CF_2}{\|}}{C}\text{-}CF_3 \qquad (66)$$

M = Mo, W

The alkyl complex produced an allyl complex in refluxing pentane.[114] A Mo formyl was prepared by reaction of $LiEt_3BH$ with $Cp(CO)_3Mo(CO_2Me)$ in THF at -50°C.[115]

$$Cp(CO)_3Mo(CO_2Me) + LiEt_3BH \xrightarrow[-70°]{THF} CpMo(CO)_2(CHO)(CO_2Me) \qquad (67)$$

Abstraction of CH_3 from $P(OCH_3)_3$ was observed by the complex $CpMo(CO)_3(EMe_2)$.[116]

$$\mathrm{CpMo(CO)_3(EMe_2) + P(OMe)_3 \longrightarrow \begin{array}{l} \mathrm{CpMo(CO)_2(EMe_2)P(OMe)_3} \\ \\ \mathrm{CpMo(CO)_2(EMe_3)P(O)(OMe)_2} \end{array}} \qquad (68)$$

$$E = \mathrm{As,\ Sb}$$

Cyclopentadienyl complexes coordinated to nitrogen have been prepared including some new bis(arenediazo) complexes of Mo and W.[117] The compound $[CpMo(N_2Ar)(N_2Ar')P\phi_3]PF_6$ reacts with bidentate ligands such as 2,2' bipyridyl and o-phenanthroline yielding cis, bis diarylazo ligands.[117] A study of amine reactions with $CpW(CO)_3(CH_2COCH_3)$ showed that the amine attacked the coordinated CO in preference to the organic carbonyl producing $CpW(CO)_2(NH_2CH_3)$-$(CONHCH_3)$.[118] A crystal structure determination was done on this compound.[118] The reaction of Mo and W hydrazine complexes was studied this past year.[119]

$$[\mathrm{CpMo(CO)_3(N_2H_4)]Cl} + L \longrightarrow [\mathrm{CpMo(CO)_3L}]^+\ \mathrm{Cl^-} \qquad (69)$$

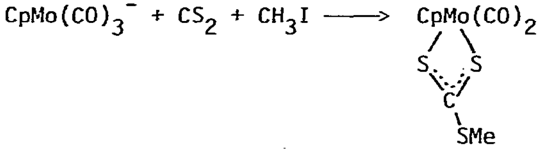
$$L = P\phi_3,\ PMe\phi_2$$

$$[\mathrm{CpM(CO)_3(N_2H_4)]Cl} + \mathrm{acetone} \longrightarrow [\mathrm{CpM(CO)_3(NH_2NCMe_2)}]^+\ \mathrm{Cl^-}$$

$$M = \mathrm{Mo,\ W}$$

These reactions provide a convenient high yield synthesis of the cations. These compounds were characterized by NMR, IR, and conductivity.[119] In addition the structure of the PF_6^- salt of the tungsten compound was determined. The hydrazone was coordinated through the amino-nitrogen rather than the expected imino-nitrogen.[119]

A trithiocarbonato complex of molybdenum was prepared by reaction of $CpMo(CO)_3^-$ with CS_2 and CH_3I.[120]



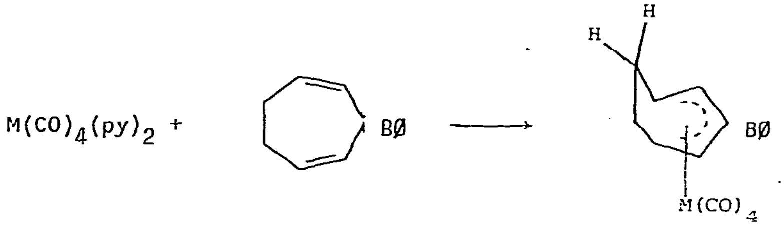
(70)

The fluxional behavior of bis(cyclopentadienyl)dithiocarbamatomolybdenum complexes has been investigated.[121] The compound, $[Mo(Cp)(\eta^1\text{-}C_5H_5)(NO)(S_2CNR_2)]^+$, ($R = CH_3$, Bu), was observed to undergo three independent fluxional processes, (1) 1,2 shifts of the η^1-C_5H_5 ring, (2) η^1-η^5 ring interchange, and (3) CN rotation of the S_2C-NH_2 group.[121] Possible mechanisms are discussed. The rotation of the aryl group in thiamidato complexes, $Cp(CO)_2Mo$-$SC(R)NR'CR$ is ortho substituted aryl and R' = CH_3, C_6H_5, etc.), has been studied by ^1H NMR.[122] The barrier to rotation was determined from the two isomers which differ in the relationship of C_5H_5 and the ortho substituent.[122]

Larger Rings. A few complexes of larger rings were prepared this past year. A paramagnetic, 17-electron species, η^7-$(C_7H_7)Mo(acac)(NCS)$, was prepared by reaction of the cationic aquo complex, $[Mo(acac)(H_2O)(\eta^7-C_7H_7)]^+$ with the thiocyanate anion.[123] The crystal structure was determined. The reaction between tricarbonyl(tropylium)tungsten(0) and molybdenum(0) cations and iodide was studied by stopped-flow techniques to determine whether initial attack occurs at the metal, at CO, or at tropylium ion.[124] From stopped-flow spectroscopy and stopped-flow NMR data it was postulated that initial coordination of iodide to the metal occurs, iodide is transferred to C_7H_7, acetone displaces CO, and finally I^- displaces acetone.[124] Cycloheptatriene $W(CO)_3$ has been reduced with Na.[125]

$$C_7H_8W(CO)_3 \xrightarrow{Na} C_7H_9W(CO)_3^- \xrightarrow{CH_3I} CH_3W(C_7H_9)(CO)_3 \qquad (71)$$

This compound is analogous to $C_5H_5W(CO)_3CH_3$ and was prepared electrochemically in 80% yield.[125] Complexes with 1-phenyl-4,5-dihydroborepin were prepared by reaction with $M(CO)_4(py)_2$ (M = Cr, Mo, W).[126]



(72)

Olefins, acetylenes, dienes, and allyls. Only a few olefin complexes have been synthesized this year. Cis-$W(CO)_4AsMe_3$(olefin) complexes were prepared photochemically from $W(CO)_5AsMe_3$ and olefin in THF.[127] The olefins used are ethylene, dimethylmethylenemalonate, dimethylmaleate, and dimethylfumarate.[127] Olefin complexes were also prepared from PMe_3 and bisarsine complexes. These complexes were investigated by IR and NMR with the NMR data indicating hindered rotation of the olefin.[127] The barrier to rotation of ethylene in $CpW(CO)_2CH_3(C_2H_4)$ was measured by ^1H NMR.[128] This compound was prepared by photochemical substitution of C_2H_4 for CO in $CpW(CO)_3CH_3$.

$$CpW(CO)_3CH_3 \xrightarrow[-CO]{h\nu, C_2H_4} CpW(CO)_2(C_2H_4)CH_3 \qquad (73)$$

The barrier to rotation about the metal-olefin bond was reported as 59 kJ/mole.[128]

Biscyclopentadienylmolybdenum (methylacetylene) was prepared by the reaction of biscyclopentadienylmolybdenumdichloride with sodium amalgam in the presence of methylacetylene.[129]

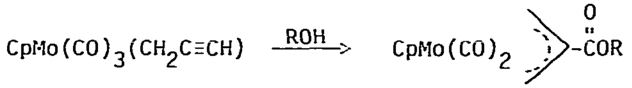
$$(C_5H_5)_2MoCl_2 \ + \ CH_3C{\equiv}CH \xrightarrow[1\ atm]{Na/Hg} (C_5H_5)_2Mo(CH_3C{\equiv}CH) \qquad (74)$$

The structure was postulated as a metallocycle from ^1H and ^{13}C NMR.[129] Dithioalkyne complexes of molybdenum and tungsten were synthesized by the reaction of $M(CO)_3(NCMe)_3$ with $CH_3SC{\equiv}CSCH_3$.[130]

$$M(CO)_3(NCMe)_3 \ + \ CH_3SC{\equiv}CSCH_3 \longrightarrow M(CO)(CH_3SC{\equiv}CSCH_3)_3 \qquad (75)$$

M = Mo, W

Also prepared was $CpMCl(CH_3SC{\equiv}CSCH_3)_2$. These species are bonded through the triple bond with no evidence of coordination to the sulfur.[130] σ-Propargylic molybdenum and tungsten complexes were alkoxycarbonylated by alcohols, water, and thiols yielding pi-allyl complexes in most cases.[131]



(76)

The reaction of the σ-2-propynylmolybdenum complex with alcohols yielded carbenoid complexes instead of the pi-allyl.[131]

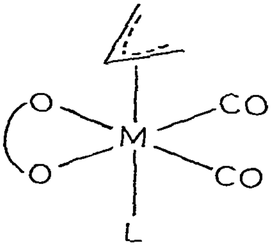
Synthesis and reactions of a few allyl complexes have been reported. The reaction of substituted anionic carbonyls of Mo and W with allyl halides produced a series of allyl complexes.[132]

$$fac\text{-}[MX(CO)_3L_2] + (allyl)X \longrightarrow MX(CO)_2(\eta^3\text{-}RC_3H_4)L_2 \qquad (77)$$

M = Mo, W L_2 = 1,10 phenanthroline, 2,2' bipyridine

X = Cl, Br, I

These complexes were investigated by IR with force constant calculations on several complexes.[132] Similar allyl complexes were prepared containing β-diketonate substituents, $M(CO)_2(\eta^3\text{-allyl})(\text{diket})L$ (M = Mo, W, L = py, THF, CH_3CN, diket = acetylacetonate, etc.), for different allyls, diketones, and L's.[133] The molecule is fluxional at -60°C for acetylacetonate complexes, with the postulated structure as shown below.[133]



XIX

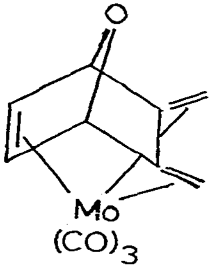
Attack on the coordinated allyl by pyridine and phosphines in the complex $[CpMo(\eta^3\text{-}C_3H_5)(CO)(NO)][PF_6]$ led to the following reaction.[134]

$$[CpMo(C_3H_5)(CO)(NO)]^+[PF_6]^- + L \longrightarrow [CpMo(C_3H_5L)(CO)(NO)]^+PF_6^- \qquad (78)$$

$$L = PR_3,\ NC_5H_5$$

On the basis of IR and NMR evidence coordination through the olefin was postulated with the ligand attached to the carbon as a pyridinium or phosphonium center instead of the often postulated $\eta^3 \rightarrow \eta^1$ complex with L attached to the metal.[134] The reaction of bidentate arsine ligands ($\phi_2AsCH_2As\phi_2$ and $\phi_2AsCH_2CH_2As\phi_2$) with $MoX(CO)_2(\eta^3\text{-}C_3H_5)(CH_3CN)_2$ leads to replacement of acetonitrile instead of X and allyl as observed for monodentate ligands.[135]

Only a very few papers on group VI metal polyene complexes have appeared. A complex of 5,6-dimethylene-7-oxabicyclo[2.2.1]hept-2-ene has been prepared from $Mo(CO)_3(CH_3CN)_3$.[136]



XX

All three of the olefin groups are apparently coordinated.[136] Detailed investigation of the IR and NMR of (diene)M$(CO)_4$ (M = Cr, Mo, diene = 1,3-butadiene, 1,5-cyclooctadiene, and substituted derivatives) showed the dynamic behavior proceeds through a trigonal prismatic transition state.[137] The reaction of the diene, $C_7H_8Mo(CO)_4$, with Me_3CPF_2 was observed.[138]

$$C_7H_8Mo(CO)_4 + Me_3CPF_2 \longrightarrow \text{cis } (Me_3CPF_2)_2Mo(CO)_4$$

$$C_7H_8 = \text{bicyclo[2.2.1]hepta-2,5-diene} \qquad (79)$$

The product was isolated in greater than 90% yield.[138]

Alkyls and hydrides

The synthesis of tetrakis (2,2'-dimethyl-1-phenylethenyl)chromium (IV) was reported this year.[139]

$$CrCl_3.3THF + 4LiC\phi = CMe_2 \xrightarrow[Et_2O]{-78°} Cr(C\phi = CMe_2)_4 \qquad (80)$$

Green crystals were isolated and characterized by IR, NMR, ESR, and X-ray crystallography. The carbons were tetrahedrally arranged around Cr with no distortions. There was no evidence of multiple character to the Cr-C bonds.[139] Casey and Polichnowski prepared several tungsten alkyls by decarbonylation of the acyls or by reaction of the carbonyl halide anions with alkyl lithium species.[140]

$$(CO)_5WCOR^- \xrightarrow[-CO]{h\nu} (CO)_5WR^-$$

$$W(CO)_5Br^- + RLi \longrightarrow (CO)_5WR^- \qquad (81)$$

$$R = CH_3,\ C_6H_5,\ CH_2C_6H_5,\ \text{etc.}$$

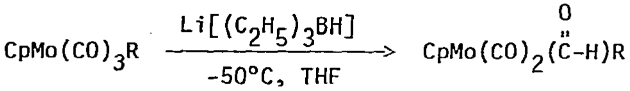
Reaction of these pentacarbonyltungstenalkyls with HCl gave RH and $W(CO)_5Cl^-$.

Reaction with CO and $P\emptyset_3$ at room temperature produced acyls for all alkyls except benzyl.[140] Bis(methyl)molybdenum complexes were prepared by reaction of $MoCl_3 \cdot 3THF$ with dimethylmagnesium in the presence of an arene and a phosphine.[141]

$$MoCl_3 \cdot 3THF + PR_3 + Mg(CH_3)_2 + \text{arene} \longrightarrow (CH_3)_2\ Mo(\eta^6\text{-arene})(PR_3)_2 \qquad (82)$$

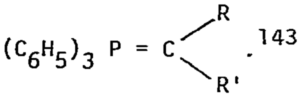
Arene = benzene, toluene, or xylene

On the basis of IR and NMR (^1H, ^{13}C, and ^{31}P) a trans structure was assigned to these complexes. Reaction with CO produced $(CH_3)_2Mo(\text{arene})(PR_3)(CO)$ which forms acetone on sitting; $(\text{arene})Mo(PR_3)_3$ is the Mo product.[141] Reaction of the molybdenum acyl, $CpMo(CO)_3(\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3)$, with $Li[(C_2H_5)_3BH]$ at -50° in THF resulted in formation of the formyl, $Cp(CO)_2Mo(CHO)(\overset{O}{\overset{\|}{C}}\text{-}\overset{O}{\overset{\|}{C}}\text{-}OCH_3)$.[142]

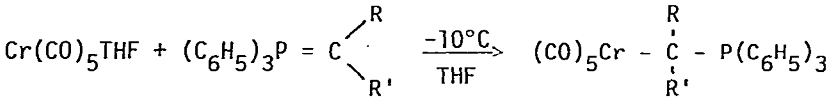


$$CpMo(CO)_3R \xrightarrow[-50°C,\ THF]{Li[(C_2H_5)_3BH]} CpMo(CO)_2(\overset{O}{\overset{\|}{C}}\text{-}H)R \qquad (83)$$

This formyl complex which could not be isolated but was characterized by NMR (12.9 δ), was formed in 17% yield.[142] Syntheses of chromium pentacarbonylylid complexes have been accomplished by reaction of $Cr(CO)_5THF$ with



$(C_6H_5)_3\ P = C(R)(R')$.[143]



$$Cr(CO)_5THF + (C_6H_5)_3P = C(R)(R') \xrightarrow[THF]{-10°C} (CO)_5Cr - \underset{R'}{\overset{R}{C}} - P(C_6H_5)_3 \qquad (84)$$

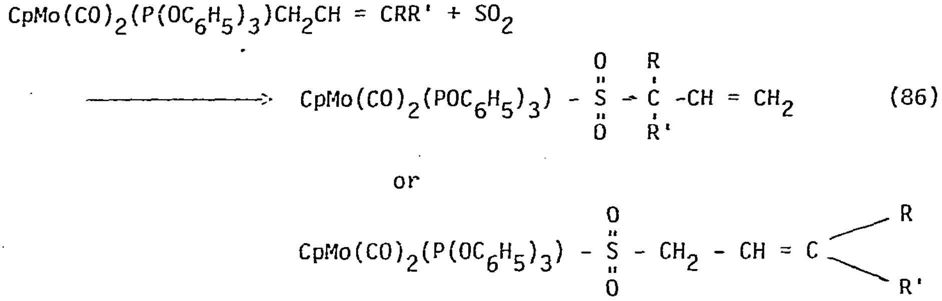
R = R' = H; R = H, R' = C_6H_5; R = R' = CH_3

The phosphorylide complex, $(C_6H_5)Cr[CH_2P(CH_3)_3][(CH_2)_2P(CH_3)_2]_2$, was isolated in low yield as an intermediate in the reaction of tetramethyl phosphonium choride and tris(lithium)hexaphenyl chromate(III).[144] The reaction of the tris lithium compound with phenylacetylene yields the onium-stabilized complex tris(phenylethynyl) tris(trimethylphosphonium methylide) chromium(III), $(C_6H_5C_2)_3Cr[CH_2P(CH_3)_3]_3$.[144]

The reaction of $CpM(CO)_3CH_3$ with CO at high temperature and pressure gave $M(CO)_6$ with no evidence of acyls when studied in a high pressure IR cell.[145] The reaction of this complex, $CpM(CO)_3CH_3$ with $P(CH_3)_3$ gave the mono- and disubstituted products, $CpM(CO)_2(P(CH_3)_3)CH_3$ and $CpM(CO)(P(CH_3)_3)_2CH_3$ upon irradiation.[146]

$$CpM(CO)_3CH_3 \xrightarrow[h\nu]{P(CH_3)_3} CpM(CO)_2(P(CH_3)_3)CH_3,\ CpM(CO)(P(CH_3)_3)_2CH_3 \qquad (85)$$

A side reaction leads to the dimer, $Cp(CO)(P(CH_3)_3)_2M\text{-}M(CO)_3Cp$. The indenyl complex of chromium reacts to give cis-$Cr(CO)_2L_4$ exclusively. The Mo and W indenyl compounds give photosubstitution of 1 or 2 carbonyls.[146] Schrauzer and coworkers have shown the R group (R = CH_3 and C_2H_5) in $RMo(O)_2Br(bipy)$ to have carbanionic reactivity.[147] Formation of hydrocarbons upon hydrolysis is accelerated by the presence of thiol ligands.[147] Insertions of SO_2 into M-C bonds have been studied. The stereochemistry of the insertion of SO_2 into threo-1,2-dideuterophenethyl compounds of tungsten (trans-(threo-ϕCHDCHD)$W(CO)_2$-$(P(CH_3)_3)(Cp)$ was shown to yield the sulfinate with inversion of configuration.[148] In a series of papers on SO_2 insertions into Mo alkenyl complexes, Wojcicki and coworkers investigated the alkene-sulfinato products.[149-151]



$$CpMo(CO)_2(P(OC_6H_5)_3)CH_2CH = CRR' + SO_2$$
$$\longrightarrow CpMo(CO)_2(POC_6H_5)_3) - \overset{O}{\underset{O}{S}} - \overset{R}{\underset{R'}{C}} -CH = CH_2 \qquad (86)$$

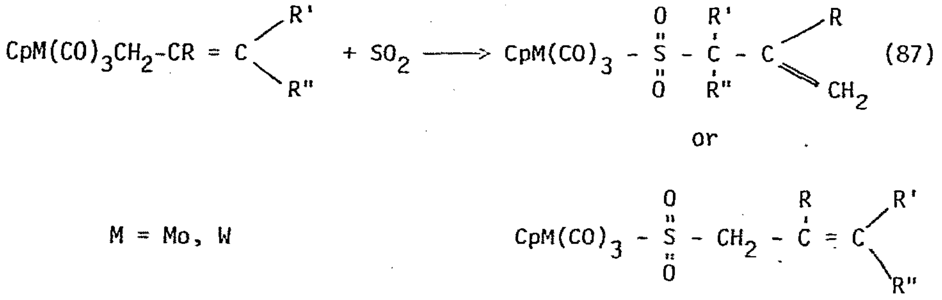
or

$$CpMo(CO)_2(P(OC_6H_5)_3) - \overset{O}{\underset{O}{S}} - CH_2 - CH = C\begin{matrix} R \\ R' \end{matrix}$$

R = H, CH_3

R' = CH_3, C_6H_5

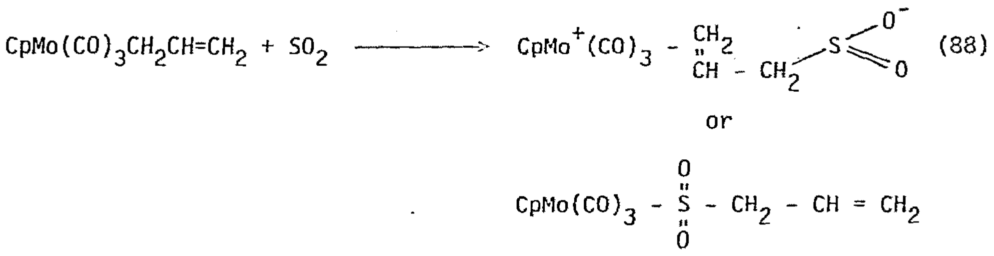
The stable product depends on R and R'.[149] Similar products are observed for insertions into $CpM(CO)_3CH_2CR = CR'R''$[150]



(87)

M = Mo, W

with the product depending on R, R', R" and the metal.[150]



(88)

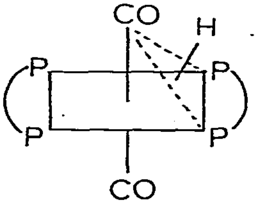
The structures were assigned by IR and the conversion from the alkene-coordinated product to the sulfinato was observed.[151]

The preparation of phosphine tetrahydrides of molybdenum were reported this year.[152]

$$MoCl_5 + L + KBH_4 \longrightarrow H_4MoL_4 \qquad (89)$$

$$L = P\phi Et_2,\ P\phi_2Me$$

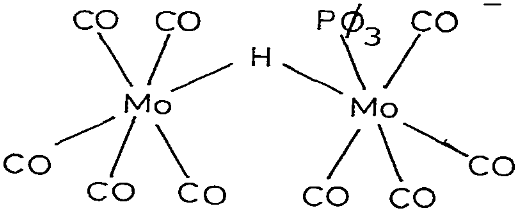
Protonation of the tetrahydride of W, H_4WL_4, was observed with $HClO_4$ and CF_3CO_2H producing $[H_5WL_4]X$, with the product characterized by IR and NMR.[153] Further evidence for radical mechanisms was obtained by Hoffman and Brown in a study of the thermal and photochemical substitution reactions of the tricarbonyl(cyclopentadienyl)hydrido compounds of tungsten and molybdenum.[154] The reaction of $HW(CO)_3Cp$ with PBu_3 led to cis and trans products at non-reproducible rates in the dark. Photolysis of the dimer, $[W(CO)_3Cp]_2$, with $HW(CO)_3Cp$ in the presence of ligand gave quantum yields of 1000 with the more nucleophilic ligand reacting much faster.[154] Irradiation of Cp_2WH_2 in thiophene or furan caused insertion of the Cp_2W unit into the heterocyclic C-H bond to give the 2-thienyl or 2-furyl complex.[155] A study of the dynamics of monocapped octahedral $[MoH(CO)_2(P\text{-}P)_2]^+$ (P-P = dmpe, diphos, etc.) showed two exchange mechanisms when investigated by ^1H, ^{31}P, and ^{13}C NMR.[156] The pairwise mechanism (observed for diphos), corresponds to rotation of H about the CO-Mo-CO axis and would constitute detection of a mono-capped octahedron $\rightleftarrows$ pentagonal bipyramid interconversion.



XXI

The non-pairwise does not involve dissociation, but the steps could not be determined.[156] Reaction of Et_4N^+ μ-$H(M(CO)_5)_2^-$ (formed by the reaction of $M(CO)_6$ with $NaBH_4$ in EtOH reflux) with a ligand L produces $M(CO)_4L_2$, M = Cr, Mo, W, suggesting that μ-$H(M(CO)_5)_2^-$ is an intermediate in the reaction of $NaBH_4$, $M(CO)_6$, and 2L.[157] Initial substitution occurs on the binuclear complex in a first order, CO dissociative process, then break-up and further substitution. No definitive evidence for the later steps were obtained although a formyl was postulated.[157] The reaction of the μ-hydrido bridged molybdenum species with $P\phi_3$ was shown to produce stereospecifically the cis species.[158]

$$\mu\text{-}H(M(CO)_5)_2^- + P\phi_3 \xrightarrow{-CO}$$



(90).

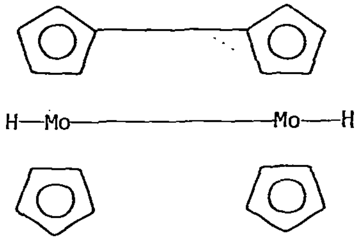
The reaction of the triphenylphosphine complex with ^{13}CO produced stereospecifically ^{13}CO labelled $[(\mu\text{-}H)(Mo(CO)_5)_2]^-$.[58] Detailed analysis of the IR spectrum of this compound required coupling of the CO's on the two metals. Using Cotton-Kraihanzel analysis, the interaction constants were calculated for the equatorial CO's on both metals.[158]

Metal-Metal bonded systems. A new high yield synthesis of the dimers, $(\eta^5\text{-}RC_5H_4)_2M_2(CO)_6$, (M = Cr, Mo, W), was reported from the reaction of $(\eta^5\text{-}RC_5H_4)M(CO)_3^-$ with $Fe_2(SO_4)_3$.

$$(\eta^5\text{-}RC_5H_4)M(CO)_3^- \xrightarrow[Fe_2(SO_4)_3/H_2O]{diglyme} (\eta^5\text{-}RC_5H_4)_2M_2(CO)_6 \qquad (91)$$

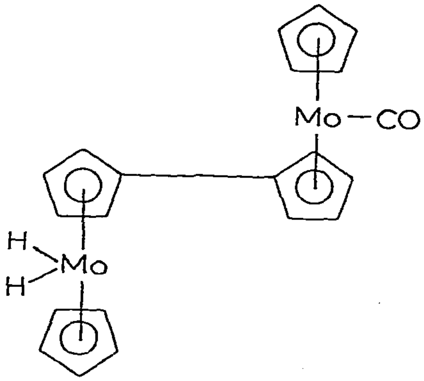
A molybdenum hydride dimer was synthesized and characterized from reaction of Mo acetate with sodium cyclopentadienide in THF.[160]

$$Mo(II) + NaCp \xrightarrow{THF}$$



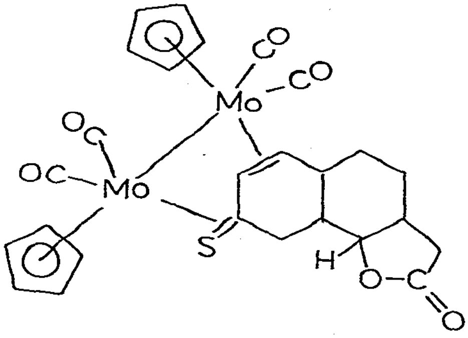
(92)

This product was characterized by IR and NMR. Reaction with CO leads to cleavage of the Mo-Mo bond and formation of the following product.[160]



XXII

This product was also characterized by IR and NMR. Complexation of diene thiones to both Mo atoms has been observed by reaction with $Cp_2Mo_2(CO)_6$.[161]

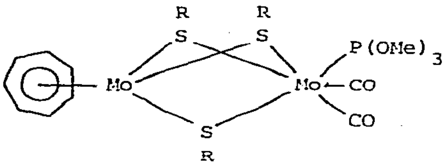


XXIII

The coordination was through the pi electron of the less substituted double bond and the thiocarbonyl.[101] Rearrangements of the complex $(CO)_4M[As(CH_3)_2\text{-}M'(CO)_3Cp]_2$ (M, M' = Cr, Mo, W) have led to a metal-metal bonded system with bridging $As(CH_3)_2$.[162]

$$(CO)_4M[(As(CH_3)_2\text{-}M'(CO)_3Cp]_2 \longrightarrow (CO)_5M[\mu\text{-}As(CH_3)_2]M'(CO)_2Cp \quad \text{and} \quad (CO)_5M\text{-}As(CH_3)_2\text{-}M'(CO)_3Cp \qquad (93)$$

The first product has a metal-metal bond but the second does not. The metal-metal bonded species are active for the catalytic polymerization of norbornadiene.[162] Complexes with three sulfur atoms bridging two molybdenums have been prepared and studied.[163] Low energy barriers were observed for sulfur inversion in the complexes, $Mo_2(CO)_2L(\mu\text{-}SR)_3(\eta^7\text{-}C_7H_7)$, (R = CH_3, C_2H_5, etc., L = CO, $P(OCH_3)_3$, etc.). Complete averaging of the R group environments was observed by ^1H NMR when L = CO, but only limited averaging for other L.[163] To further investigate this process, a crystal structure determination of $Mo_2(CO)_2(P(OMe)_3)\ (\mu_2\text{-}S(t\text{-}Bu))_3\ (\eta^7\text{-}C_7H_7)$ was accomplished.[163]



R = t-Bu

XIV

The sulfurs are bridging asymmetrically, favoring the molybdenum bound to CO and L. It was postulated that the phosphorus ligand has a dramatic effect on the SR trans, affecting the inversion process.[163]

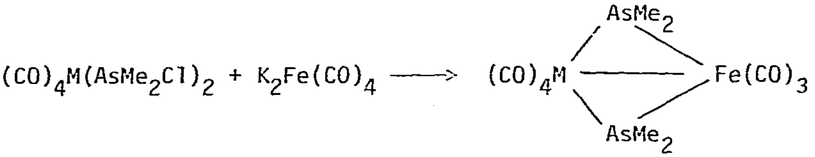
Several heterometal dimers have been synthesized this year. Methane elimination in the reaction of $(Cp)_2Zr(CH_3)_2$ and $CpMo(CO)_3H$ resulted in formation of a Zr-Mo bonded species, $(Cp)_2(CH_3)ZrMo(Cp)(CO)_3$.[164]

$$(Cp)_2Zr(CH_3)_2 + CpMo(CO)_3H \longrightarrow (Cp)_2(CH_3)ZrMo(Cp)(CO)_3 \qquad (94)$$

This compound was characterized by NMR, microanalysis, and reactions with CCl_4 and dibromoethane.[164] A similar reaction led to $(Cp)_2NbMo(CO)_3Cp$.[165]

$$(Cp)_2NbBH_4 + Cp(CO)_3Mo(Me) \xrightarrow[Et_3N]{benzene} (Cp)_2NbMo(CO)_3(Cp)$$

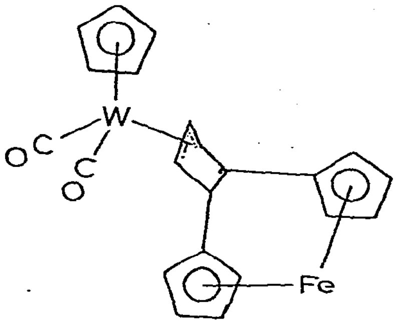
Reaction of $(CO)_4M(AsMe_2Cl)_2$ (M = Cr, Mo, W) with $K_2Fe(CO)_4$ produced complexes containing M-Fe bonds.[166]



(95)

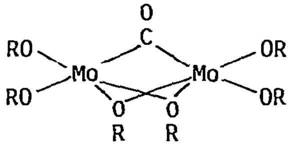
M = Cr, Mo, W

The compounds were characterized by IR and NMR.[166] An unusual bimetallic complex containing Fe and W, $(Cp)(CO)_2W(\eta^3\text{-}C_5H_5)(\eta^5\text{-}C_5H_4)_2Fe)$, was prepared by the reduction of $[Cp(CO)_2W(\eta^3\text{-}C_5H_5(C_5H_5)_2)]I$ with sodium followed by addition of $FeCl_2$.[167] The complex was characterized by IR, ^1H NMR and mass spectrometry. The suggested structure is shown below.[167]



XXV

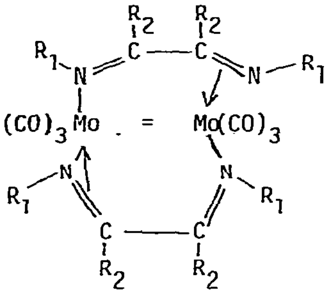
Reports on two complexes containing Mo = Mo double bonds have appeared. Synthesis of $Mo_2(OR)_6CO$ by reaction of CO with the triply bonded species, $Mo_2(OR)_6$, was reported.[168] The crystal structure determination showed the carbonyl to occupy a bridging position.



XXVI

R = t-Bu

Further reaction with CO gives $Mo_4(OR)_{12}(CO)_4$.[168] Mild oxidation of the diazabutadiene complex, $Mo(CO)_4DAB^-$(DAB = diazabutadiene), resulted in a species postulated to have the following structure.[169]

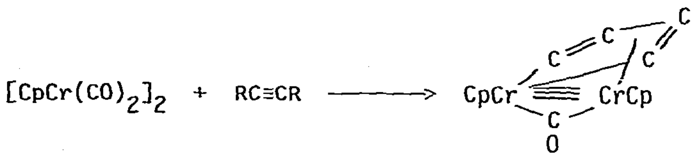


XXVII

R_1, R_2 = t-Bu or i-Pr

This complex showed 5 or 6 bands in the carbonyl stretching region indicating an asymmetry to the binding.[169]

Several reports on complexes with triple bonds between the metals, $(CpM(CO)_2)_2$, have appeared. The reaction of $[CpCr(CO)_2]_2$ with acetylenes did not produce an addition product, but rather gave substitution for CO.[170]



(96)

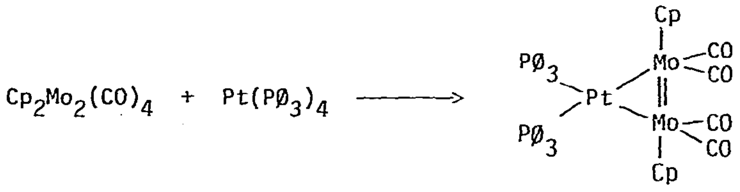
The product was characterized by IR, NMR (^1H and ^{13}C), and an X-ray crystal structure.[170] Curtis and Klinger reported reaction of bis(cyclopentadienyldicarbonylmolybdenum) with a number of species.[171]

$$Cp_2Mo_2(CO)_4 + L \longrightarrow \text{trans } (CpMo(CO)_2L)_2 \qquad (97)$$

$$L = P\phi_3,\ P(OMe)_3$$

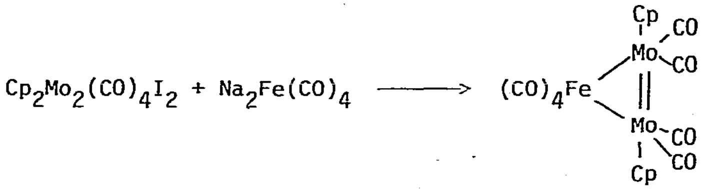
$$Cp_2Mo_2(CO)_4 + I_2 \longrightarrow Cp_2Mo_2(CO)_4I_2 \qquad (98)$$

$$Cp_2Mo_2(CO)_4 + RC_2R \longrightarrow (\mu\text{-}RC_2R)\ (Cp_2Mo_2(CO)_4) \qquad (99)$$



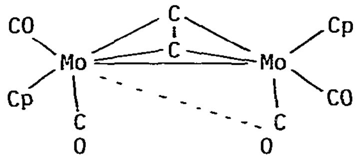
(100)

The latter complex contains both bridging and terminal CO's. Reaction of the diiodide complex, $Cp_2Mo_2(CO)_4I_2$, with $Na_2Fe(CO)_4$ led to μ-$Fe(CO)_4$-$(Cp_2Mo_2(CO)_4)$.[171]



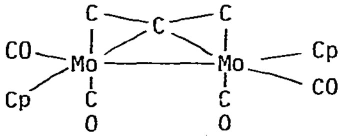
(102)

This compound has no bridging CO's.[171] The reaction of $Cp_2Mo_2(CO)_4$ with acetylene was the subject of another study which led to a crystal structure.[172]



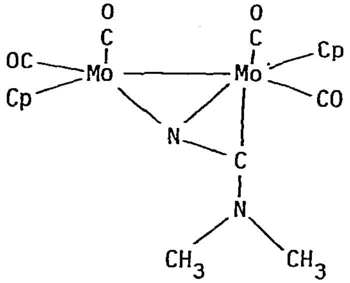
XXVIII

The bridging acetylene and two Mo atoms are almost tetrahedral. One CO is in a semi-bridging position. The two molybdenum atoms are different probably due to steric crowding.[172] The dynamics of these complexes were studied by ^{13}C and ^{1}H NMR.[172] The addition of allene to $Cp_2Mo_2(CO)_4$ has also been studied.[173] The product, µ-allene-bis(cyclopentadienyl)tetracarbonyldimolybdenum, was characterized by X-ray crystallography; the structure is shown below.[173]



XXIX

The NMR was invariant with temperature. The allene was strongly coordinated and could not be replaced by CO or $PØ_3$.[173] The reaction of $Cp_2Mo_2(CO)_4$ with a number of small molecules (CO_2, NO_2, CS_2, CH_3CN, 1,3 butadiene, and cyanamides) has been reported.[174] Only the cyanamides, H_2NCN and Me_2NCN, gave a reaction; the product was characterized by an X-ray structure.[174]



XXX

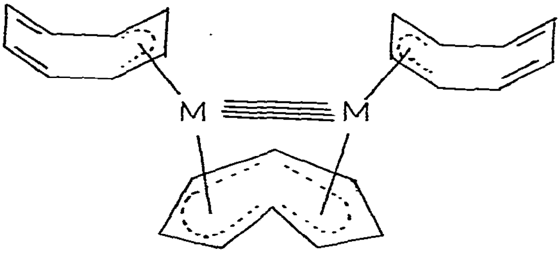
A number of other multiply bonded metal-metal systems have been studied. Possible metal-metal metatheses of the triple-bonded species, $Mo_2(CH_2SiMe_3)_6$ and $W_2(CH_2SiMe_3)_6$, were explored but no mixed product was observed.[175] Mixed compounds were observed in the mass spectrum for reaction of $Cp_2M_2(CO)_4$ at 80°C or photochemically at 25°C.[175] Preparation of an ethyl molybdenum complex with a Mo≡Mo bond by reaction of LiEt with the chloromolybdenum compound[176] was demonstrated.

$$Mo_2Cl_2(NMe_2)_4 + 2LiEt \longrightarrow Mo_2Et_2(NMe_2)_4 + LiCl \qquad (103)$$

Reaction of the ethyl complex with CO_2 led to reductive elimination with formation of a Mo≡Mo bond.[176]

$$Mo_2Et_2(NMe_2)_4 + CO_2 \longrightarrow Mo_2(O_2CNMe_2)_4 + C_2H_4 + C_2H_6 \qquad (104)$$

X-ray and neutron diffraction of tris(cyclooctatetraene)dimolybdenum and the tungsten analogue, $M_2(C_8H_8)_3$, indicate a quadruple bond between the metals, as shown below.[177]



XXXI

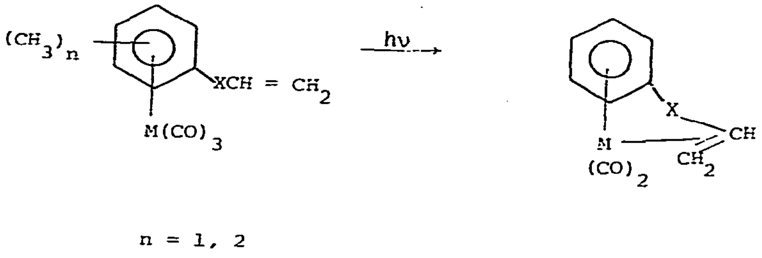
Preparation of a Cr≡Cr species by reaction of tetra-μ-acetato-dichromium with bis(trimethylsilylmethyl)magnesium in the presence of $P(CH_3)_3$ was accomplished.[178]

$$Cr_2(O_2CMe)_4 + MgR_2 + P(CH_3)_3 \longrightarrow Cr_2R_4(PMe_3)_2 \qquad (105)$$
$$R = CH_2Si(CH_3)_3$$

Reaction of the molybdenum-acetato complex with dimethylmagnesium produced $Mo_2(Me)_4(PMe_3)_4$. Both of these compounds were studied by IR, NMR (^1H, ^{31}P, ^{13}C), and X-ray crystallography and apparently have metal-metal quadruple bonds.[178] Acidification of $Cr(C_5H_5)_2$ with $HC_2H_3O_2$ led to bis(cyclopentadienyl)-hexakis(trifluoro-acetato)trichromium.[172] This compound is linear with bridging trifluoro acetate groups and cyclopentadienyl groups on each terminal chromium atom.[179]

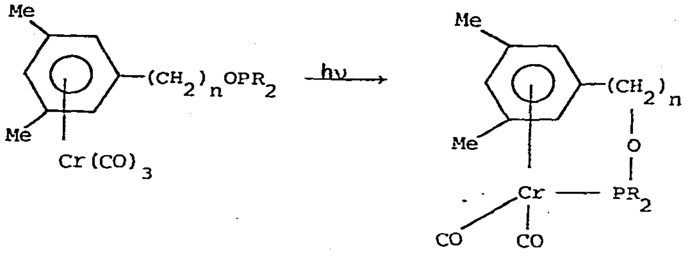
Chelates

Reports of chelate complexes of the Group VI metals have continued to grow this year. The work of Nesmeyanov and co-workers has provided many of the new complexes as derivatives of $ArM(CO)_3$. Photolysis of alkenylarene metal tricarbonyls for Cr, Mo, and W compounds in which the double bond is separated from the arene moiety by a two-or three-atom chain results in CO dissociation and intramolecular cyclization to give stable alkenylarenedicarbonylmetal complexes.[180]



(106)

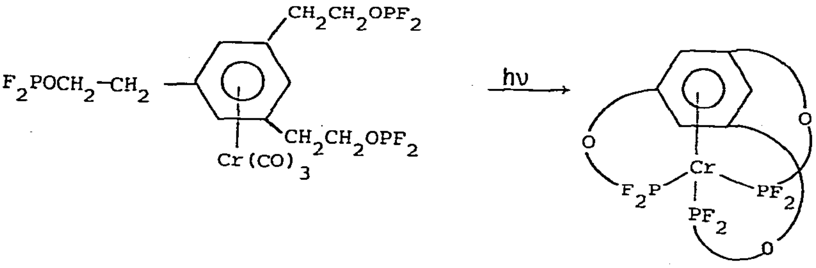
Irradiation of styrenetricarbonyl-chromium and molybdenum leads to dinuclear complexes. All of the complexes were studied by IR and NMR (^1H and ^{13}C).[180] The same type of reaction was effected with an arenephosphite chromium tricarbonyl.[181]



(107)

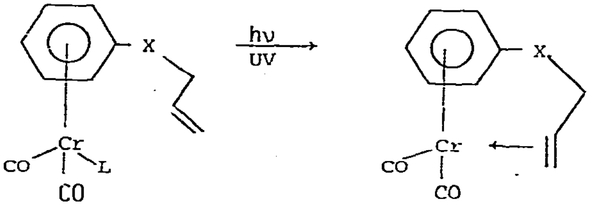
R = Oϕ, ϕ n = 4,5

By using an arene triply substituted with difluorophosphite they effected complete replacement of the CO's.[182]



(108)

This complex was isolated in 50% yield.[182] A similar synthetic technique was studied by Donnini and Shaver for alkenylarene chromium complexes.[183]



(109)

X = O, CH_2

For the complexes $(\eta^6\text{-}C_6H_5XCH_2CH{=}CH_2)Cr(CO)_2L$ for L = $P\phi_3$, $P(O\phi)_3$, $P(OC_2H_5)_3$, and $P(CH_3)_2\phi$, photolysis always leads to replacement of the ligand L by the olefin, indicating that the Cr-L bond is photolabile for UV irradiation.[183]

Several bidentate ligands based on phosphorus have been synthesized. Methylaminobis(difluorophosphine) complexes with Cr, Mo, and W have been prepared by King and Gimeno.[184]

$$M(CO)_6 + CH_3N(PF_2)_2 \xrightarrow{h\nu} M(CH_3N(PF_2)_2)_3 + 6\ CO \qquad (110)$$

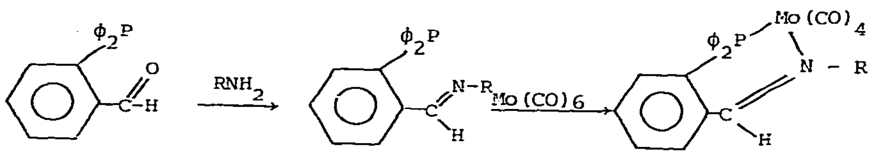
$$M = Cr,\ Mo,\ W$$

The volatile and air-stable complex was determined as the tris(bidentate) by IR and NMR (^1H, ^{13}C, and ^{31}P).[184] Reaction of the similar ligand, 1,2 bis-(difluorophosphino)cyclohexane with the hexacarbonyls produced a different product.[185]

$$M(CO)_6 + P_2F_4C_6H_{10} \longrightarrow [M(CO)_4P_2F_4C_6H_{10}]_X \qquad (111)$$

$$X = 1\text{-}3$$

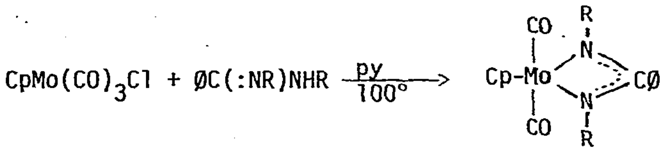
The bidentate ligands bridge instead of chelating. It was suggested that the product selection is kinetically controlled rather than thermodynamically.[185] Rauchfuss has synthesized new amino-phosphine chelating agents and prepared molybdenum complexes of them.[186]



(112)

The primary product was the disubstituted species although dinuclear complexes were also obtained.[186] The chelate ligands, $Me_2XM'Me_2CH_2X'Me_2$ (X, X' = N, P, As, M' = Si, Ge), were prepared and reacted with the hexacarbonyls, forming $M(CO)_4L$ (M = Cr, Mo, W).[187] The chemical and spectroscopic properties of this bidentate ligand were discussed in terms of bonding models.[187]

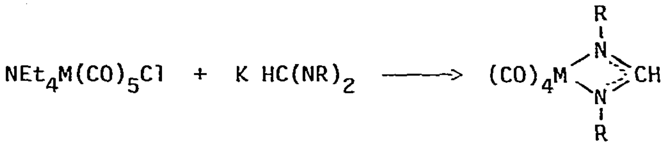
Nitrogen base chelates were prepared by several techniques, including the reaction of amidines with tricarbonyl(chloro)cyclopentadienylmolybdenum.[188]



(113)

R = Me, Ø, etc.

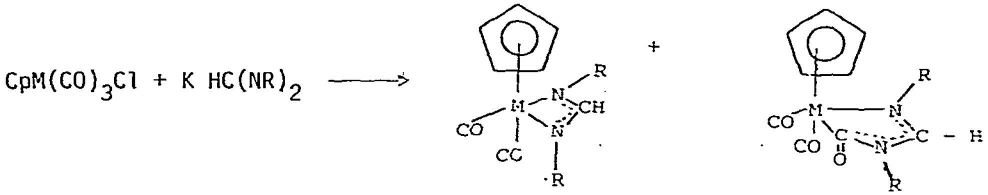
A similar complex has been prepared by reaction of $NEt_4M(CO)_5Cl$ and $KHC(NR)_2$.[189]



(114)

M = Cr, Mo, W
R = aryl, t-butyl

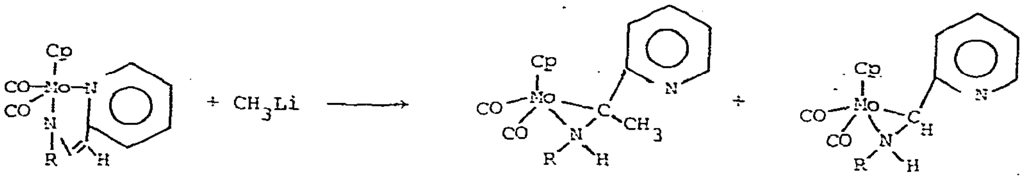
The anionic formamidino complexes were investigated by IR and NMR (^1H and ^{13}C). Reaction with $PØ_3$ or py led to the facial substituted product.[189] The reaction of potassium N,N'-diphenylformamidine with $CpM(CO)_3Cl$ led to two products in equal yield.[190]



R = Ø, M = Cr, Mo, W

(115)

The reactions and products were studied by IR and ^{13}C NMR and a mechanism proposed for the reaction.[190] A ring contraction was observed in the reaction of cationic $CpMo(CO)_2$(chelate) complexes with methyllithium.[191] The reaction of cationic pyridinecarbaldimine complexes with CH_3Li gave two products.[191]

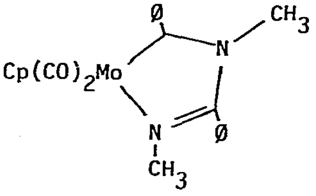


(116)

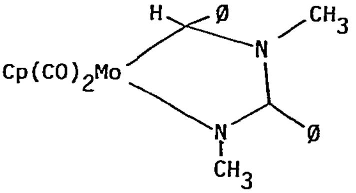
The structure of the second product with R = $CH(CH_3)C_6H_5$ was determined crystallographically. Both products were characterized by IR and NMR.[191] New $Cp(CO)_2Mo$ chelate complexes were prepared with 2-imidoyl fragments by reaction of the sodium salt with N-methylbenzimidechloride.[192]

$$NaCpMo(CO)_3 + CH_3N{=}C(Cl)\emptyset \rightarrow CpMo(CO)_2[C(\emptyset)N(CH_3)C(\emptyset)N(CH_3)]^+\ Cl \qquad (117)$$

which was assigned the following structure (XXXII) based on IR and NMR data.

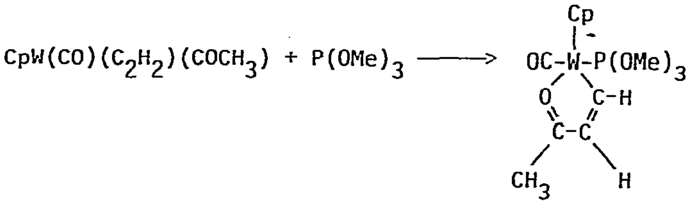


XXXII

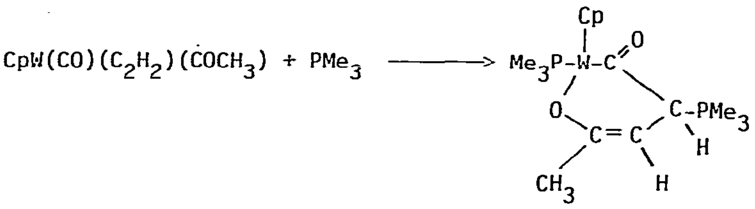


XXXIII

Protonation led to the second product (XXXIII).[192] The reaction of $P(OCH_3)_3$ and $P(CH_3)_3$ with tungsten cyclopentadienyl carbonyl acetyl acetylenes led to chelate complexes.[193]

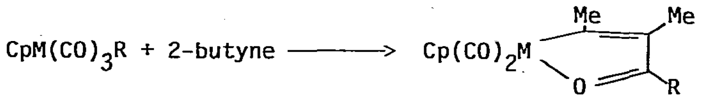


(118)



(119)

Insertion of acetylene into carbon-Mo and W bonds has also led to chelate complexes.[194]

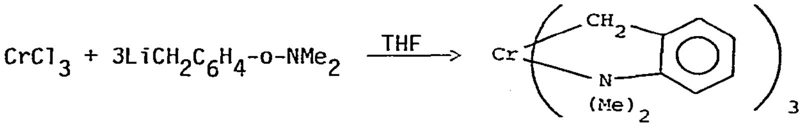


(120)

M = Mo, R = CH_3, $CH_2Ø$, $COCF_3$

M = W, R = CH_3, $COCF_3$

The structure was assigned from elemental analysis, mass spectra, IR and NMR. Reaction of this species with L (L = CO, CNt-Bu, CNC_6H_{11}) led to η^3-allylic lactone complexes.[194] A crystal structure was done for R = CH_3, M = Mo, L = t-butylisocyanide. In the reaction of 2-butyne with the Mo($COCF_3$) complex formation of an eight-membered ring containing an η^2-ketenic group was observed and a crystal structure was accomplished.[194] A paramagnetic, tris-chelate complex was prepared by reaction of $CrCl_3$ with $LiCH_2C_6H_4$-o-NMe_2.[195]

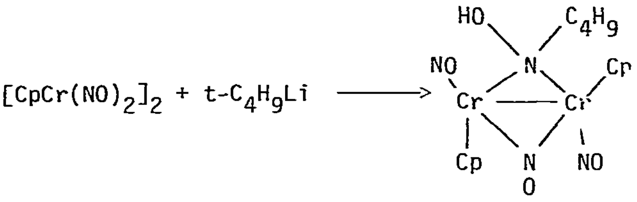


(121)

The compound is pyrophoric and soluble in CH_2Cl_2, toluene, and THF. The structure was suggested on the basis of analytical data, magnetic moment, (3.6 μ_B), and mass spectra.[195]

Nitrosyls

Several reactions of bis(cyclopentadienyl dinitrosylchromium), $[CpCr(NO)_2]_2$, have been studied. Reactions with carbanions occur by attack at the nitrogen atom of one bridging nitrosyl ligand.[196] t-Butyl gave, after hydrolysis, dicyclopentadienyl-μ-(N-t-butylhydroxylamido)-dinitrosyl-μ-nitrosyldichromium.



(122)

Methyl- or n-butyl-lithium gave dicyclopentadienyl-μ-nitrosyldichromium with methyleneamido-dinitrosyl-μ-nitrosyldichromium with elimination of water by abstraction of an α-hydrogen.[196] The dimer, $[CpCr(NO)_2]_2$, was cleaved to the halide by I_2, HCl, NOCl, $SnCl_4$, $SnCl_2$, $Mn(CO)_5Cl$, and $CpFe(CO)_2Cl$.[197] Reaction of $(Cp)_2Mo(NO)I$ with carboxylic acid caused replacement of one cyclopentadienyl.[198]

$$(Cp)_2Mo(NO)I + RCO_2H \longrightarrow CpMo(NO)(O_2CR)I \qquad (123)$$

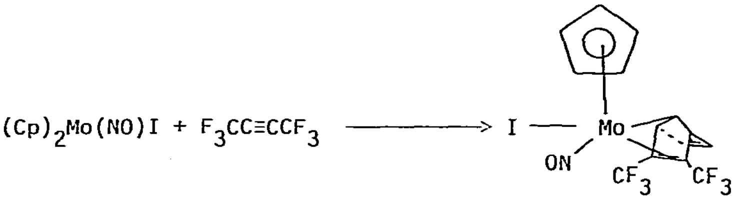
$$R = CH_3,\ C_2H_5,\ \text{etc.}$$

The carboxylate group is bidentate. This reaction with acid is characteristic of σ-C_5H_5. A number of reactions of cyclopentadienyl nitrosyl molybdenum were reported.[198]

The formation of $[C_5H_5Cr(NO)_2]_2$ was observed in the reaction of $CpCr(CO)_2NO$ with NO under photolysis, although the primary product was a nitrite.[199]

$$CpCr(CO)_2NO \xrightarrow[NO]{h\nu} [CpCr(NO)_2]_2 + CpCr(NO)_2NO_2 \qquad (124)$$

Ready displacement of both CO's producing a seventeen-electron species $CpCr(NO)_2$, which can dimerize or react with more NO to give the nitrite compound was postulated.[199] An optically active nitrosyl complex, CpM(CO)(NO)L was prepared for M = Cr, Mo, and W with L = chiral phosphorus ligands by replacement of CO in $CpM(CO)_2NO$.[200] Reaction of bis-(cyclopentadienyl)nitrosylmolybdenum iodide with $F_3CC{\equiv}CCF_3$ led to $CpMo(C_7H_5(CF_3)_2)(I)(NO)$.[201]



(125)

Nitrosylchloride was shown to oxidize $Cr(CO)_6$ and $C_6H_6Cr(CO)_3$ to a polymeric species, $[CrCl_2(NO)_2]_n$.[202] At low temperature evidence was obtained for a solvated $CrCl(CO)_2(NO)$.[202] Reaction of Mo and W pentacarbonyl amines with NO in benzene produced $[M(NO)_3(Am)]_2$.[203]

$$M(CO)_5Am + NO \xrightarrow{\text{benzene}} [M(NO)_3(Am)]_2 \qquad (126)$$

M = Mo, W

Am = $BuNH_2$, py, piper, etc.

These dimers were characterized by NMR and IR with IR showing both bridging and terminal NO ligands.[203] $CpM(CO)_2(NO)$ was synthesized in 60-93% yield by $CpM(CO)_3^-$.[204]

$$\begin{tikzcd} NaCpM(CO)_3 + p\text{-}C_6H_4SO_2N(NO)Me \arrow[r, "THF"] & CpM(CO)_2NO \arrow[d, "CH_2Cl_2"', "NOCl"] \\ & CpM(NO)_2Cl \end{tikzcd} \qquad (127)$$

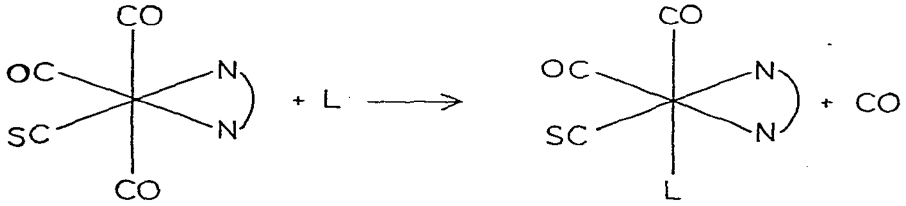
The second reaction occurred in 80% yield. The first organometallic thionitrosyl complex, $CpCr(CO)_2NS$ was prepared.[205]

$$Na[CpCr(CO)_3] + 1/3\ (S_3N_3Cl_3) \xrightarrow[-78°]{THF} CpCr(CO)_2(NS) + CO + NaCl \qquad (128)$$

The NS ligand was more effective in removing electron density from the Cr center than NO as indicated by the IR of the carbonyl stretches.[205]

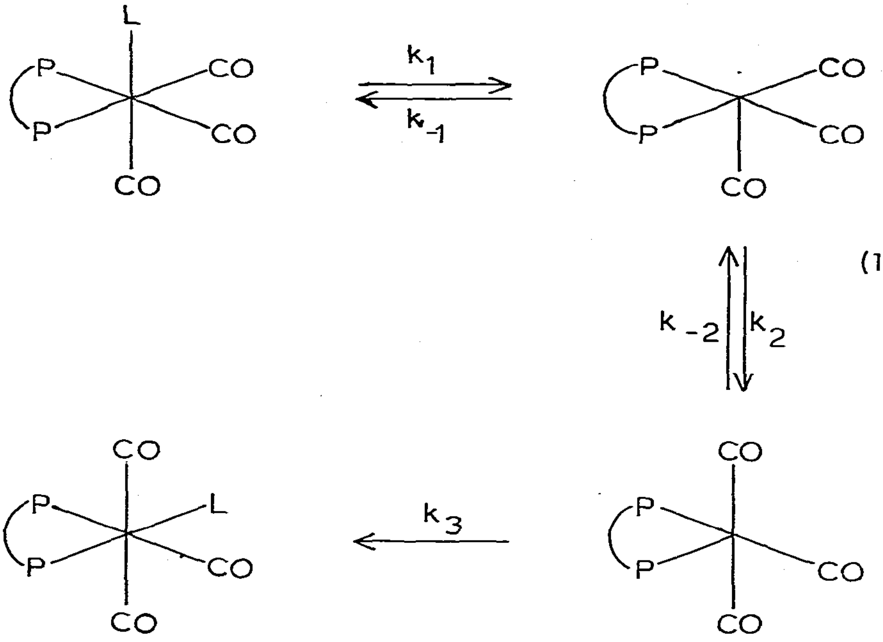
KINETICS AND MECHANISMS

Pickering and Angelici studied the substitution reactions of $W(CO)_3(CS)$-(o-phen).[206]



(129)

The rate law showed both ligand independent and ligand dependent terms with the independent predominating, especially at higher temperatures. The complex, $W(CO)_3(CS)$(o-phen), is labilized compared to $W(CO)_4$(o-phen) by 140 times.[206] It was postulated that the strong-pi bonding of CS weakens all CO bonds.[206] The rate and mechanism of facial-meridional isomerization were reported for fac 1,2-bis(diphenylphosphinoethane) (triisopropylphosphite) tricarbonylmolybdenum(0).[207] The reaction showed a first order rate law with the following mechanism proposed.



(130)

It was suggested that $k_{-2} >> k_2$ indicating the greater stability of the intermediate with the substituted ligand in the equatorial plane.[207] A study of the reaction of $P(O\text{-}i\text{-}C_3H_7)_3$ with (2,5 dithiahexane)tetracarbonyltungsten(0) showed non-linear plots of k_{obs} vs [L] and a highly negative entropy of activation.[208] A predominantly associative mechanism was suggested.[208] The kinetics and mechanism of the substitution reaction of $(tmen)W(CO)_4$, (tmen = N,N,N'N'-tetramethyl-ethylenediamine) were investigated.[209]

$$(tmen)W(CO)_4 + 2L \longrightarrow L_2W(CO)_4 \qquad (131)$$

$$L = P(OC_6H_5)_3,\ P(OCH_3)_2CCH_3,\ P\phi_3,\ etc.$$

For the different substrates the rate data supported a mechanism involving two competing pathways, one involving unimolecular, reversible ring opening and the other a concerted process involving an interchange of L and one end of the bidentate, chelating ligand.[209] The ring opening process predominates.[209] The rate constants for the cis-trans isomerization of cis-$M(CO)_2(P\text{-}P)_2$ and cis-$[Mo(CO)_2(P\text{-}P)_2]^+$ were evaluated.[210]

$$\text{cis-}M(CO)_2(P\text{-}P)_2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \text{cis-}[M(CO)_2(P\text{-}P)_2]^+ \qquad (132)$$

$$\text{trans-}M(CO)_2(P\text{-}P)_2 \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} \text{trans}[M(CO)_2(P\text{-}P)_2]^+$$

(P-P) = dpm, diphos, dmpe

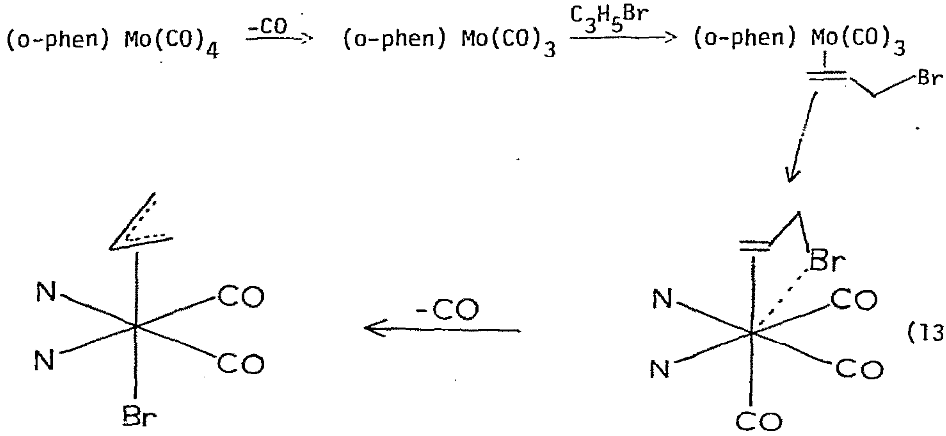
Rates of isomerization were independent of the bidentate ligand and [CO], $\Delta S^{\ddagger}$ values were similar and negative, and there was no solvent dependence. It was suggested that both the 17- and 18-electron complexes underwent a twist mechanism for the cis-trans isomerization.[210] The reaction of allyl bromide with (o-phen)$Mo(CO)_4$ was shown to proceed by a two term rate law in CH_2Cl_2 and THF.[211]

$$Mo(o\text{-phen})(CO)_4 + C_3H_5Br \longrightarrow (o\text{-phen})Mo(CO)_2(\eta^3\text{-}C_3H_5)Br \qquad (133)$$

rate $k_1\,[M] + k_2\,[M]\,[L]$

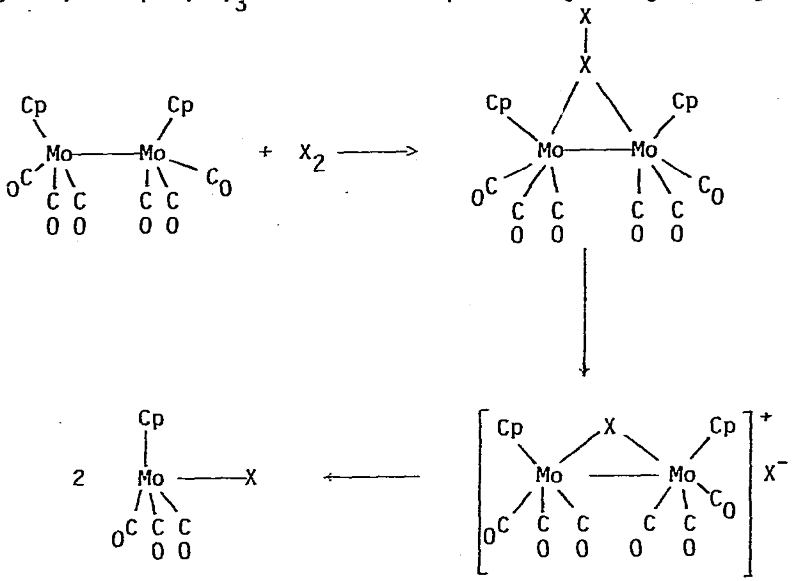
$M = (o\text{-phen})Mo(CO)_4$, $L = C_3H_5Br$

In 1,2-dichloroethane only the first order step was observed. The suggested mechanism is as follows.[211]



(134)

The reaction of halogens with bis(cyclopentadienyltricarbonyl-molybdenum and -tungsten) to $CpMo(CO)_3X$ was shown to proceed by halogen bridged intermediates.[212]



(135)

The iodide bridged complex, $[(CpMo(CO)_3)_2I]\ B(C_6H_5)_4$ was isolated as confirmation of the mechanism.[212] The reaction with bromine proceeded to $CpMo(CO)_2Br_3$.[212] The kinetics and mechanism of the inversion at sulfur were studied for $M(CO)_5S$ (S = 2,5-dihydrothiophene sulfide or β-phenethylmethylsulfide).[213] The β-phenethyl complex was shown by ^{13}C and ^1H NMR to exist as diastereomers at -100°C. The inversion barrier, calculated from line broadening, was shown to be $\Delta H^{\ddagger}$ = 10.0 kcal/mole and $\Delta S^{\ddagger}$ = 2.4 e.u. Ligand exchange occurs at higher temperature with rate-determining dissociation of the sulfide.[213]

CATALYSIS AND ORGANIC SYNTHESIS

Olefin metathesis

The interaction of $AlBr_3$ with $W(CO)_5L$ ($L = P\O_3$ and PBu_3) was studied by IR and ^{31}P NMR.[214,215] The presence of an IR absorption at 1665 was interpreted as an interaction of the aluminum with a carbonyl, $L(CO)_4W\text{-}CO\text{-}AlBr_3$. It was suggested that the interaction was trans to the ligand L and that the decreased electron density caused ready dissociation of the ligand.[214] The products were $W(CO)_6$ and $W(CO)_4Br_2$. An analogy between the reaction with $AlBr_3$ and olefin metathesis by complexes ($W(CO)_5L$) supported on alumina was drawn.[216] It was suggested that the interaction to the alumina is $Al\text{-}O{\equiv}C\text{-}W$ and that this leads to facile dissociation of the ligand L.[216] The metathesis of propylene by $Mo(CO)_6$ supported on alumina was reported to occur with 99% selectivity to ethylene and 2-butene.[217] The degenerate metathesis of $CD_2 = CHC_6H_{13}$ and

(Z)-CDH = CHC_8H_{17} with $MoCl_2(NO)_2(P\phi_3)_2$ and $(CH_3)_3Al_2Cl_3$ was studied by Casey and Fuinstra.[218] The stereochemistry of this reaction provided further evidence for a carbene intermediate, M = CHR.[218] Polymer supported tungsten compounds

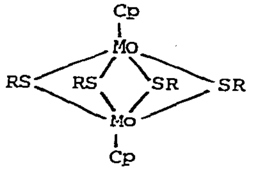
$$\wr\!-\ P\phi_2 - W(CO)_5$$

$$\wr\!-\ CH_2 - W(CO)_3(Cp)$$

were active for the metathesis of trans-3-heptene to 3-hexene and 4-octene.[219] These complexes had activity and selectivity under mild conditions, ease of separation, regenerability and reuse.[219] The activity profile corresponded to that of heterogeneous catalyses i.e.,low initial activity, rising to a maximum, and then leveling off.[219] The reaction of polystyrylbipyridine with $W(CO)_6$ led to binding of $W(CO)_4$ groups to the polymer.[220] As a cocatalyst with $C_2H_5AlCl_2$ this species was active for the metathesis of 2-pentene to a 1:2:1 ratio of 2-butene, 2-pentene, and 3-hexene in 40 min. at room temperature. The presence of oxygen increased the rate.[220] Irradiation (λ = 350 mm) of $W(CO)_6$, CCl_4, and an olefin led to metathesis.[221] Use of trans-2-pentene produced 2-butene and 3-hexene with a 50% conversion ratio. The trans to cis ratio was 4.1, and only 1% byproducts were observed. The intermediates were believed to be $W(CO)_5$ and $W(CO)_5Cl$ by IR and ESR.[221] The irradiation of $W(CO)_6$ with $TiCl_4$ also gave an active metathesis catalyst.[222] It was suggested that the key step in formation of the catalyst was the reaction of sixteen-electron species, $W(CO)_5$, with $TiCl_4$.[222] The metathesis of 2-pentene and 3-heptene has been studied in the presence of $WCl_6/AlEtCl_2/EtOH$, WCl_6/BuLi, and $WCl_6/LiAlH_4$.[223] Percents of metathesis as a function of time were reported.[223]

Other catalytic reactions

A number of reactions were reported to be catalyzed by Group VI compounds last year. King and co-workers have shown that hexacarbonyls ($Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$) were active homogeneous catalysts for the water-gas shift reaction.[224] These carbonyls were active in the presence of base (KOH, KBH_4) in alcoholic solution at temperatures in excess of 100°C.[224] Treatment of the paramagnetic cation $[(\eta^6\text{-}C_7H_8)Mo(py)_3]^+$ with methanethiol yields the diamagnetic cation $[(\eta^6\text{-}C_7H_8)Mo\text{-}(\mu\text{-}SMe)_4Mo(\eta^6\text{-}C_7H_8)]^{+2}$, which undergoes complete deuterium exchange of the toluene methyl hydrogens in $D_2O\text{-}Na_3PO_4$ buffer (pD = 11) at 25°.[225] The crystal structure was done showing four symmetrically centered methanethiolate ligands.



$R = CH_3$

XXXIV

The Mo-Mo distance is 2.614 Å suggesting a direct metal-metal bond.[225] Arenetricarbonylmolybdenum (arene = toluene and mesitylene) was an active catalyst for the isomerization of olefins.[226] The molybdenum compound was more active at 100-120°C for olefin isomerization than the chromium analogue with slightly different activities. Mixtures were obtained where more than one product was possible.[226]

$$\text{1-hexene} \longrightarrow \text{2-hexene (26\%)} + \text{3-hexene (74\%)} \qquad (136)$$

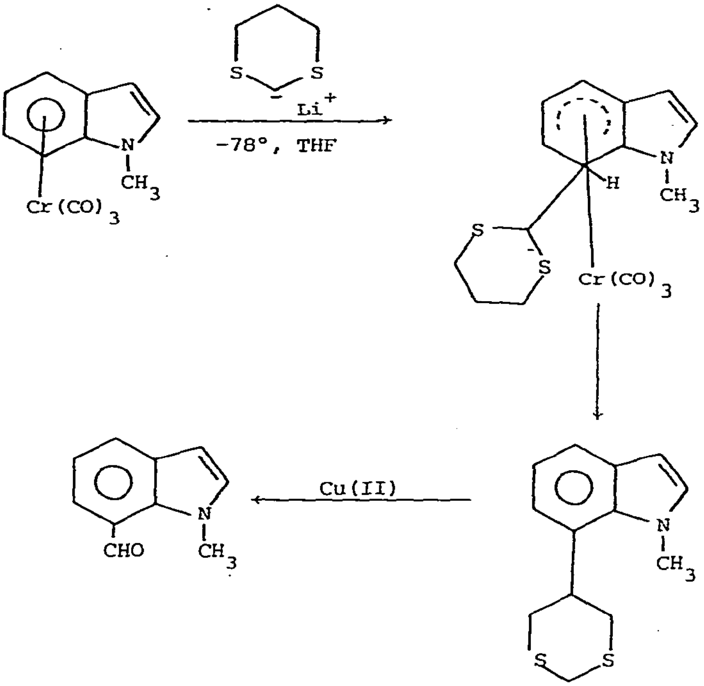
The reaction of styrene-divinylbenzene copolymers with $Cr(CO)_6$ gave polymer - $Cr(CO)_3$ complexes which were active for hydrogenation of methylsorbate.[227] The complex lost activity after 2 cycles.[227] A mixture of tris(η^3-allyl)chromium and titanium tetrachloride was active for isoprene polymerization.[228] It was postulated that a bimetallic compound was the active species with bridged M-C bonds which are sites for stereospecific chain propagation.[228]

Organic synthesis

A technique for the removal of organic ligands from $\text{Arene}Cr(CO)_3$ allowing recovery of the $Cr(CO)_3$ unit was reported.[229]

$$\begin{tikzcd}
(\eta^6\text{-Arene})\,Cr(CO)_3 \arrow[r, "\text{py, reflux}", "\text{-arene}"'] & Cr(CO)_3(py)_3 \arrow[d, "{BF_3,\ Et_2O\ \text{(reflux)}}", "\text{arene}"'] \\
 & (\eta^6\text{-Arene})Cr(CO)_3
\end{tikzcd} \qquad (137)$$

This reaction sequence was suggested as a method for decomplexation of an arene after reaction on $Cr(CO)_3$. A high yield of arene and $Cr(CO)_3(py)_3$ was obtained and the $Cr(CO)_3(py)_3$ could be recomplexed with a new arene and used again.[229] The chromium tricarbonyl complex of N-methylindole underwent nucleophilic substitution with generation of 7-substituted indoles.[230]

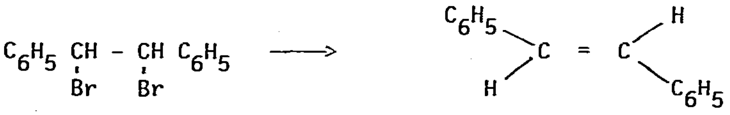


(138)

The 7-substituted indole was isolated in 41% yield.[230] Selective removal of halogen from organic halides was accomplished using $[(Cp)Cr(NO)_2]_2$.[231]

$$[CpCr(NO)_2]_2 + RX \longrightarrow 2\ CpCr(NO)_2X + R\text{-}R \qquad (139)$$

This reaction couples diarylhaloalkanes to ethanes, but does not couple allyl or methylallylhalides and does not react with alkyl halides. The complex reacts with vic-dihaloalkanes to give alkenes.[231]



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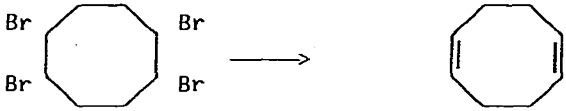
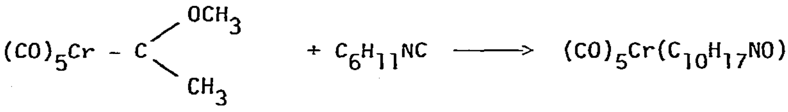


(141)

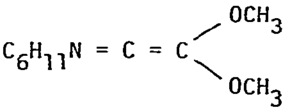
$C_6H_5CHBrCHBr_2 \longrightarrow C_6H_5CH = CHBr$ (142)

The last reaction proceeded in 73% yield. Coupling was also effected by $W(CO)_6$ and $Mo(CO)_6$ for carbonyl compounds (ØCHO, EtCHO, and cyclohexanone) to give olefins (stilbene, etc.).[232] Methyl(methoxy)carbene chromium pentacarbonyl was used in the synthesis of ketenimines.[233]

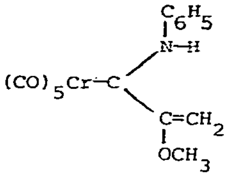


(143)

The latter compound reacted with excess isocyanide to give



and $Cr(CO)_5NC_6H_{11}$.[233] Reaction with a protonic source gives carbenes as below.[233]



XXXV

PHOTOCHEMISTRY

A detailed study of photochemical substitutions of the hexacarbonyls was reported.[234] In cyclohexane the quantum yield was 0.67 for substitution of $Cr(CO)_6$.

$$M(CO)_6 + L \xrightarrow{h\nu} M(CO)_5L + CO \qquad (144)$$

To determine whether concentration effects had led to non-unity quantum yields the reaction of $Cr(CO)_6$ with CH_3CN (neat) was investigated.[234] The quantum yield was 0.7 indicating that concentration effects were not significant. A plot of solvent viscosity with extrapolation to zero viscosity gave a quantum yield of 0.68.[234] The reaction of $W(CO)_6$ with ligands was also quantum deficient (quantum yield = 0.72). Only a very small wavelength dependence of the quantum yield was noted.[234] The data was interpreted as indicating the presence of an excited singlet which does not lead to dissociation but could cross very efficiently to a triplet which was dissociative.[234] Photosubstitution of the amine pentacarbonyl complexes of the Group VI metals was observed with ^{13}CO.[235] Two processes were observed - replacement of amine by ^{13}CO and incorporation of ^{13}CO into $M(CO)_5$ amine exclusively in the cis position.[235]

$$M(CO)_5\text{amine} \xrightarrow[^{13}CO]{h\nu} M(CO)_6^* + M(CO)_5\ \text{amine}^* \qquad (145)$$

amine = py, piper

The relative ease of the two reactions is dependent on the metal. With light of 313 or 366 nm the amine is dissociated preferentially for Mo and W.[235] For Cr the quantum yield for CO dissociation is comparable to that of amine dissociation. The photoreactivity for CO dissociation was summarized as Cr > Mo > W; for amine dissociation, Cr ∿ Mo > W.[235] Darensbourg and Murphy also studied the photosubstitution of $Mo(CO)_5P\phi_3$ and $Mo(CO)_4(P\phi_3)_2$.[236] The reactions of $Mo(CO)_5P\phi_3$ are summarized below.

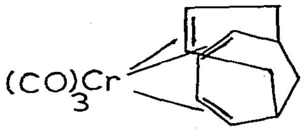
$$\begin{array}{lll}
Mo(CO)_5P\phi_3 + P\phi_3 \xrightarrow{h\nu\ (366,\ 313\ nm)} & \text{cis } Mo(CO)_4(P\phi_3)_2 & 86\% \\
 & \text{trans } Mo(CO)_4(P\phi_3)_2 & 14\% \\
Mo(CO)_5P\phi_3 + {}^{13}CO \xrightarrow{h\nu} & \text{cis labeled } Mo(CO)_5P\phi_3 & \\
 & \text{trans labeled } Mo(CO)_5P\phi_3 & \\
Mo(CO)_5P\phi_3 + CO \xrightarrow{h\nu} & Mo(CO)_6 \quad \text{Low Quantum Yield} &
\end{array} \qquad (146)$$

The reactions are consistent with loss of both cis and trans CO with the C_s form of the intermediate the most stable.[236] Dissociation of $P\O_3$ from $Mo(CO)_4(P\O_3)_2$ was also consistent with this.[236] The photosubstitution reactivity of a series of bis(substituted pyridine) tungsten tetracarbonyls was reported by Abrahamson and Wrighton.[237] The complexes studied were cis-$W(CO)_4X_2$ (X = 3,4-dimethylpyridine, 4-ethylpyridine, 3-benzoylpyridine, etc.). Spectral data showed that the tungsten → pyridine charge-transfer state moves to lower energy with more electron-withdrawing substituents on the pyridine while the ligand field states are insensitive to these changes.[237] Photosubstitution occurred in all cases upon irradiation into the lowest energy absorption system, but the quantum efficiency was very dependent on whether the lowest energy excited state was ligand field or W → pyridine charge-transfer in character.[237] W-pyridine charge transfer was unreactive (quantum yield = 0.001). Complexes with ligand field lowest excited states are photosubstitution labile (quantum yield = 0.4).[237]

Geoffroy and Bradley have described the photoinduced elimination of H_2 from $(Cp)_2MoH_2$.[238]

$$(Cp)_2MoH_2 \xrightarrow{h\nu} (Cp)_2Mo + H_2 \qquad (147)$$

The intermediate was trapped by reaction with CO, C_2H_2, $P(Et)_3$ and $P\O_3$. The quantum yield was 0.1 with 366 nm irradiation.[238] From deuterium labeling they suggested a direct concerted elimination of H_2 and not H·, H^+, or H^-.[238] The photoreaction of methyl- or η^1-benzyl-$CpW(CO)_3$ were reported to depend on the reaction conditions.[239] Both compounds produce the dimer, $[CpW(CO)_3]_2$, by W-R bond scission but the η^1-benzyl complex also produces $(\eta^3\text{-}CH_2C_6H_5)\text{-}W(Cp)(CO)_2$ by CO dissociation.[239] Photolysis (310-490 nm) in the presence of $P\O_3$ led to $CpW(CO)_2(P\O_3)(CH_3)$ and a dependence on the cation for the reaction pathway and quantum efficiency in reactions of $W(CO)_5X^-$, X = Br, NCO, N_3.[240] For the cations, Li^+, $As\O_4^+$, PPN^+ (μ-nitrido-bis triphenylphosphorus), and NEt_4^+, the efficiency of the photochemical transformation and the nature of the photoproducts depend on the cation. The quantum efficiency varied by > 300% when Li^+, NEt_4^+, and $As\O_4^+$ salts of $W(CO)_5Br^-$ were irradiated at 436 nm.[240] Irradiation of $W(CO)_5N_3^-$ led to $W(CO)_5NCO^-$ and $W(CO)_6$ when PPN^+ was the cation; the quantum yield for production of these products using the $As\O_4^+$ salt of the azide was zero.[240] Conjugated dienes, e.g. 1,3-butadiene or trans, trans-2,4-hexadiene, underwent [4S + 6S] cycloaddition with tricarbonyl-1,3,5-cycloheptatrienechromium(0) on irradiation with UV light.[241] Tricarbonyl-bicyclo[4.4.1]undeca-1,3,7-trienechromium(0) complexes, $Cr(CO)_3C_{11}H_{17}$ and $Cr(CO)_3C_{13}H_{18}$, were isolated. The latter complex had a crystal structure done and both were characterized by IR, NMR, and mass spectra.[241]



XXXVI

Flash photolysis of the tungsten-dinitrogen complex, $W(N_2)_2(diphos)_2$, in the presence of an alkyl halide produced either $WX(N_2R)(diphos)_2$ or $[WX(N_2RH)(diphos)_2]X$.[242]

$$W(N_2)_2(diphos)_2 \xrightarrow{RX} WX(N_2R)(diphos)_2 + [WX(N_2RH)(diphos)_2]X \qquad (148)$$

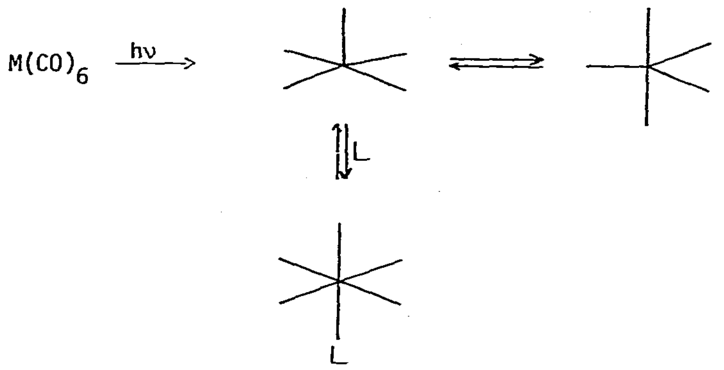
$$RX = CH_3COCl,\ t\text{-}BuBr$$

The reaction was assumed to involve a free radical mechanism, with initial cleavage of the R-X bond.[242] Abrahamson and Wrighton prepared mixed metal dimers such as $Cp(CO)_3MCo(CO)_4$ and $Cp(CO)_3MFe(CO)_2Cp$, (M = Mo, W) by photolysis of the dimers $[Cp(CO)_3M]_2$ with $Co_2(CO)_8$ and $[CpFe(CO)_2]_2$.[243]

$$Co_2(CO)_8 + Cp_2M_2(CO)_6 \xrightarrow{h\nu} 2Cp(CO)_3MCo(CO)_4 \qquad (149)$$
$$Cp_2Fe_2(CO)_4 + Cp_2M_2(CO)_6 \xrightarrow{h\nu} 2Cp(CO)_3MFe(CO)_2Cp$$

The electronic spectra were reported and assigned. Flash photolysis of the mixed metal dimers, M-M', $(Cp)(CO)_3MCo(CO)_4$ and $Cp(CO)_3MFe(CO)_2Cp$ (M = Mo, W), resulted in formation of the homonuclear dimers, M-M and M'-M', consistent with homolytic fission of metal-metal bond.[243] Photoreaction of the mixed dimers was observed with CCl_4, RX, and I_2 leading to cleavage of the metal-metal bond.[243]

A substantial body of research was published on photolyses of the carbonyls isolated in matrices at low temperature. Use of polarized photolysis and spectroscopy on matrix isolated $M(CO)_6$ provided data that led to a proposed mechanism for the photochemical reaction.[244] The first step was postulated to be photoinduced dissociation of CO forming $M(CO)_5$. Internal rearrangement of $M(CO)_5$ from the square pyramidal to trigonal bipyramidal and back to square pyramidal was followed by recombination with a ligand.[244]



(150)

The intermediate $M(CO)_5$ generated by photolysis of $M(CO)_6$, M = Cr, Mo, W, with 314 nm radiation, was shown to react with N_2 when isolated in a N_2 matrix forming $Cr(CO)_5N_2$.[245] The complex was characterized by infrared and Raman spectroscopy.[245] Evidence for $Cr(CO)_3(NO)_2$ was obtained in frozen gas matrices from photolytic reaction of $Cr(CO)_6$ with NO and $Cr(NO)_4$ with CO.[246]

$$Cr(CO)_6 \xrightarrow[h\nu]{NO} Cr(CO)_3(NO)_2 \xleftarrow[h\nu]{CO} Cr(NO)_4 \qquad (151)$$

Isotopic labeling studies indicated D_{3h} geometry for the five-coordinate species.[246] Photolysis of $Cr(CO)_5PCl_3$ in an argon matrix produced only $Cr(CO)_5$ by PCl_3 dissociation while photolysis of $Cr(CO)_5$(pyrazine) caused CO dissociation producing only $Cr(CO)_4$(pyrazine).[247] Similar results were also obtained on photolysis (λ = 229, 254, 280, 313, and 366) of $W(CO)_5PCl_3$.[248] Only $W(CO)_5$ was observed, with no evidence for $W(CO)_4PCl_3$. Prolonged irradiation produced $W(CO)_4$.[248] The reasons for the selective dissociation of PCl_3 were discussed.[248] Ultraviolet photolysis of benzenechromium-tricarbonyl gave $C_6H_6Cr(CO)_2$ by CO dissociation.[249] The reaction could be reversed by irradiation with visible light.[249] Although not strictly organometallic, Klotzbucher and Ozin reported the photoaggregation of Cr and Mo atoms to clusters of known size, Cr_nMo_m, n = 0-3, m = 0-3.[250]

SPECTROSCOPIC STUDIES

Infrared and Raman

Infrared and Raman spectroscopic studies were greatly reduced in number from preceding years. A Raman investigation of the hexacarbonyls, $M(CO)_6$ (M = Cr, Mo, W) was reported with the relative intensities of the ν(CO) and ν(M-C).[251] The relative intensities of the A_{1g} and E_g stretching modes of C-O and M-C for the hexacarbonyls were interpreted in terms of exact and approximate derived bond polarizability models. The results were in good agreement for the ν(CO) but not for the low frequency ν(M-C) bands.[251] For all cases the transverse and the corresponding longitudinal derivatives were of opposite sign.[251] Infrared investigations of $M(CO)_4((C_6H_5)_2P(CH_2)_3P(C_6H_5)_2)$ led to the assignment of ν(M-C) and ν(M-P) modes.[252] Fischer and coworkers investigated the infrared and Raman spectra of trans-$X(CO)_4W{\equiv}CCH_3$.[253,254] Use of trans $X(CO)_4WCCH_3$ (X = Br, Cl), and trans $Br(CO)_4WCCD_3$ and polarized Raman spectroscopy allowed assignment of the W≡C stretching mode.[253,254] In the undeuterated complex this mode is coupled to the symmetric deformation. The force constant is 7.4 mdynes/Å confirming the triple bond.[253,254] Raman spectra of mixed crystals of $Cr(CO)_6$ and $Mo(CO)_6$ were reported.[255] Intermolecular coupling of modes occurred leading to a spectrum that is not just a mixture of the two spectra.[255] The vibrational spectra of mixed crystals of chromium-, molybdenum-, and tungsten-tricarbonyl mesitylene complexes were also reported.[256] Although the Cr structure was not isomorphous with that of Mo and W, it still forms mixed crystals with Mo and W species. The carbon monoxide stretches showed one mode behavior.[256] The Raman spectrum of solid $Cr(C_5H_5)_2$ was recorded from 10-1200 cm^{-1} at ambient and low temperatures.[257] This data was used to calculate distortions from D_{5d} symmetry.[257]

Magnetic Studies. From NMR(^1H and ^{13}C) studies of $(Arene)_2Cr$ it was found that the chemistry and stability of these complexes can be correlated with the sum of the Hammett σ_n parameters of the substituents.[258] It was proposed that unsymmetrical chromarenes exhibit an internally compensating stabilization effect analogous to that of the chromiumtricarbonyl moiety.[258] NMR (^1H, ^{31}P, and ^{13}C) was also used to investigate allyl rotations about the bond in the pseudooctahedral molybdenum and tungsten complexes $(\eta^3\text{-}C_3H_5)M(CO)_3(L\text{-}L)^+PF_6^-$ where L-L is a bidentate phosphorus.[259] A ^{13}C NMR study of the metal carbonyls, $CpM(CO)_3X$ (M = Mo and W, X = Cl, Br, I, CH_3, and CH_3CO_2), showed two carbonyl resonances in a 1:2 ratio.[260] This is consistent with the "piano stool" structure and suggests that structures of substituted complexes can be assigned as cis or trans based on the number of resonances observed.[260] The barrier to rotation about the Mo-C bond in $CH_3Mo(CO)_3Cp$ was measured by ^{13}C relaxation techniques.[261] The barrier was rather large, greater than 6 kcal/mole.[261] The ^{13}C chemical shift upon complexation for $ArCr(CO)_3$, Ar = benzene, hexamethylbenzene, and hexaethylbenzene, was studied by solid state NMR.[262] The upfield change in ^{13}C chemical shift was assigned to a very large (> 50 ppm) specific increase in screening when the external magnetic field lies in the plane of the aromatic ring along the bonds to the substituents.[262] The NMR (H) of

$C_6H_6Cr(CO)_3$ was recorded in a nematic solvent and natural abundance ^{13}C satellites due to ring and carbonyl carbons were observed.[263] The structural data were in agreement with previous structural work and indirect proton-proton coupling constants were determined.[263]

Chromium tricarbonyl complexes with α-substituted trans-4,4'-dimethylstilbenes were also studied by NMR.[264] The coordination site of $Cr(CO)_3$ in diarylimines derived from aromatic aldehydes or ketones and aromatic amines has been studied.[265] Electron density was not the only factor involved; the energy, symmetry, and representativity must also be considered.[265]

Electron transfer in the system $(Arene)_2Cr/(Arene)_2Cr^+$ was studied by ESR and ^1H NMR line broadening.[266] The rate constants for electron exchange between bis-(η^6-arene)chromium(0) complexes of toluene, p-xylene, mesitylene, and durene and the corresponding radical cation showed no dependence on the degree of methylation. The rate constant, $k_{ex} = 3 \times 10^8$ ℓ $mole^{-1}s^{-1}$, approaches the diffusion controlled limit.[266] The ESR spectrum of aromatic ketals complexed with $Cr(CO)_3$ was measured.[267] A strong decrease of the hyperfine coupling constant in comparison to the uncomplexed ketone was observed. This decrease was explained as a result of the sigma-electron density of $Cr(CO)_3$.[267] The combination of magnetic circular dichroism and resonance Raman were used to show that four different electronic transitions make up one charge-transfer band of $Mo(CO)_4$(2-imino-methyl-pyridine).[268] The magnetic susceptibility of chromocene, $(C_5H_5)_2Cr$, was studied between 0.90 and 300°K.[269] This data was interpreted by employing complete ligand field theory in a slightly distorted $C_{\infty v}$ symmetry.[269]

Photoelectron spectra, electronic spectra, and calculations

A number of photoelectron spectral studies, primarily on the metal carbonyls were reported this year. Satellites were observed in the X-ray photoelectron spectra (ESCA) of the metal hexacarbonyls in the gas phase.[270] The satellites were assigned to a shake-up process, simultaneous excitation of core and valence electrons. The spectra were tentatively assigned to specific transitions.[270] The photoelectron spectra of pentacarbonyl-chromium, -molybdenum, and -tungsten complexes with ligands having pi-acceptor and sigma-donor capabilities were recorded.[271] For the complexes, $LM(CO)_5$ (M = Cr, Mo, W; L = PEt_3, PMe_3 $P(NMe_2)_3$, $P(OEt)_3$, $P(OMe)_3$, and PF_3), the pi-acceptor capabilities were reflected in the splitting of the t_{2g}, while sigma-donor property was reflected by the ionization potential of M-P.[271] The orders observed are as follows:

$$\text{pi-acceptor } PR_3 < P(NR_2)_3 < P(OR)_3 < PF_3$$

$$\text{sigma-donor } PR_3 > P(OR)_3 > P(NR_2)_3 > PF_3$$

A similar study using u.v. photoelectron spectroscopy was accomplished on $M(CO)_5PX_3$, (M = Cr, Mo, W; X = F, Cl, Br).[272] It was found that pi-backbonding more than compensates for the poor sigma donating ability. The electron density on the metal gave the following order for the ligands.

$$PF_3 < CO < PCl_3 \sim PBr_3$$

and for the metals.[272]

$$W < Mo < Cr$$

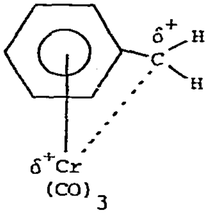
X-ray photoelectron studies were also reported on $M(CO)_5L$, L = N_2H_2, N_2H_4, and NH_3.[273] The results, primarily satellite lines from shake-up processes, were discussed in terms of sigma-donor and pi-acceptor bonding.[273] A study was also done on $Cr(CO)_5L$ complexes where L = organosulfide and organophosphine ligands.[274] The photoelectron spectrum of WMe_6 was reported and discussed.[275]

A few reports of electronic absorption studies appeared in 1978. Absorption spectra of the pyridazine, pyrazine, and pyrimidine tungstenpentacarbonyl complexes were recorded.[276] The data was interpreted with HOMO primarily localized on the metal and with LUMO of considerable ligand character.[276] The spectra of (diazene)pentacarbonyl metal complexes (M = Cr, Mo, W, diazene = cyclohexyldiazene, 2,3-diazanorbornene, and 4-R-3,3-bis(methoxycarbonyl-1-pyrazoline)) were assigned with the lowest band a metal charge transfer.[277] A 1,2 shift of the $M(CO)_5$ group along the N=N linkage is observed in ^{13}C and ^{1}H NMR.[277] The electronic absorption spectra of $(C_6H_6)M(CO)_3$ (M = Cr, Mo, W) contained 4, 6, and 7 bands respectively.[278] The effects of electron-donating and electron-accepting substituents were examined.[278] The electronic spectra of chromocene, $(Cp)_2Cr$, was also recorded and assigned.[279] One broad band at 21.97 $cm^{-1} \times 10^3$ was assigned to $^{3}\Delta \rightarrow 2^{3}\pi$, $^{3}\Phi$, ^{3}H, and $^{3}\pi$.[279]

Several molecular orbital calculations primarily on aromatic and cyclopentadienyl complexes were reported. INDO SCF calculations on $(C_5H_5)Cr(C_6H_6)$ showed the predominantly metal α-levels have $e_2 < a_1 < e_1$, with the e_1 interacting primarily with the pi orbitals on C_5H_5 and the metal e_2 primarily interacting with the C_6H_6 pi-orbitals.[280] Calculations on $(C_6H_6)_2Cr$ gave the following electronic structure:[281]

$$e_{1u}(\pi\text{-}C_6H_6) < e_{1g}(\pi(C_6H_6)) < e_{2g}(3d) < a_{1g}(3d) < e^*_{1g}(3d)$$

INDO calculations on benzyl$Cr(CO)_3^+$ showed a strong back donation from $Cr(d_{x^2-y^2})$ to the non-bonding π- orbital of benzyl.[282] The CH_2 group is bent 40° towards the Cr. The suggested structure is shown below.[282]



XXXVII

Calculations have also been reported on $Cr(CO)_5$ where the C_{4v} was found to be the lowest electronic state;[283] on $Mo(PH_3)_4(C_2H_4)_2$ for different conformations of the trans ethylenes;[284] on (cycloheptatriene)$Cr(CO)_3$ and (fulvene)-$Cr(CO)_3$ where barriers to rotation were discussed;[285] on the conformational preferences of substituted cyclopentadienyl and heterocyclopentadienyl complexes, such as diazaboralene;[286] and on the metal-metal interaction in $Cr_2(CH_3)_8^{-2}$.[287]

<u>Miscellaneous physical studies</u>

Photoelectron spectroscopy, UV, and ^{13}C NMR were used to study the bonding properties of $M(CO)_5L$ (M = Cr, W, L = amine, pyridine, or azine).[288] No correlation was observed between the sigma-donating ability (pK_a value), ionization potential of the lone pair in the free ligand, and the stabilization energy upon complexation. The orbital energies of the d-orbitals were assigned with the e lower than b_2 by 0.2-0.3 eV for the full range of compounds. There was evidence for pi-interactions between imines and $M(CO)_5$.[288] The complex, $W(CO)_4(CS)L$, was studied by IR and ^{13}C NMR.[289]

$$\text{trans-}W(CO)_4(CS)I + Ag^+ + L \rightarrow \text{trans-}W(CO)_4(CS)L \rightleftarrows \text{cis-}W(CO)_4(CS)L \quad (152)$$

$$L = P(O\emptyset)_3,\ P(OCH_3)_3,\ P\emptyset_3,\ \text{etc.}$$

Cis-trans equilibrium constants were correlated with Graham π-acceptor values for the ligand L.[289] The CS ligand seemed to offer a buffering effect as witnessed by ^{13}C NMR of the CS and trans CO.[289] On the basis of electronic absorption, Raman, IR, and NMR (^{13}C and ^{15}N) spectra, it was concluded that

$M(CO)_4DAB$ complexes have C_{2v} symmetry.[290] Similar studies of $Mo(CO)_{4-X}L(PR_3)_X$ (X = 0, 1, 2; L = DAB, pyridine-2-carbaldehydeimine, and bipy) showed the DAB ligand to be a much better pi-acceptor than the other two ligands.[291] Darensbourg and Davis reported a mass spectral study of cis-$M(CO)_4(^{13}CO)$(piperidine) (M = Cr, W).[292] Low voltage mass spectra of cis $M(CO)_4(^{13}CO)$ piperidine showed loss of CO to occur statistically. It was suggested that the seventeen-electron, six coordinate species, $M(CO)_4(^{13}CO)\text{-(piperidine)}^+$ is fluxional prior to CO dissociation.[292] Mass spectra of $(Cp)_2MoH_2$, $(Cp)_2WH_2$, $(Me_2CHC_5H_4)_2MoH_2$, $(Me_2CHC_5H_4)_2WH_2$ were also reported this year.[293]

Only two electrochemical studies were reported in 1978. The electrochemical reduction of arylmethoxycarbene complexes of Cr, Mo, and W was accompanied by a change in the conformation of the aryl ring from a perpendicular to a coplanar geometry relative to the M-C(carbene)-O plane.[294] The reaction was studied by cyclic voltammetry of carbenes which are constrained to the planar or perpendicular geometry.[294] Reduction of seven-coordinate, substituted Mo(II) and W(II) complexes, $M(CO)_3(P\O_3)_2X_2$, has been reported.[295] When the reduction was done under CO for M = Mo the product observed was $Mo(CO)_5Cl^-$. Under argon $Mo(CO)_4(P\O_3)_2$ was observed in the expected yield for disproportionation of $Mo(CO)_3(P\O_3)_2Cl_2$.[295] In all other cases $M(CO)_5X^-$ was the only product observed.[295]

The heats of formation of $(Cp)_2W(CH_3)_2$ and $(Cp)_2Mo(CH_3)_2$ were evaluated from the following reaction.

$$(Cp)_2M(CH_3)_2 + HCl \longrightarrow (Cp)_2MCl_2 + CH_4 \qquad (153)$$

$$M = Mo,\ W$$

The reaction was studied by calorimetry giving the standard heats of formation.

$$\Delta H^\circ_f\ [(Cp)_2Mo(Me)_2] = 283.8 \pm 3.8\ \text{kJ/mole}$$

$$\Delta H^\circ_f[(Cp)_2W(Me)_2] = 295.6 \pm 3.5\ \text{kJ/mole}$$

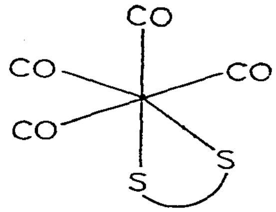
These values allowed derivation of the bond-enthalpy values, D(Mo-Me) = 149.5 kJ/mole and D(W-Me) = 197.8 kJ/mole.[296] Microcalorimetric measurements were also made on the decomposition reactions of pyridine and acetonitrile complexes with Cr, Mo, and W carbonyl complexes.[297] The bond enthalpies evaluated from these calculations are below.[297]

Cr-py	(102 kJ/mole)		
Mo-py	(146 kJ/mole)	$Mo-NCCH_3$	(135 kJ/mole)
M-py	(173 kJ/mole)	$W-NCCH_3$	(169 kJ/mole)

The order for the bonds is D(M-CO) > D(M-py) > $D(M-NCCH_3)$.[297] The effect of complexation by tricarbonylchromium on the thermodynamic stability of stable carbocations was evaluated as the pK_R+'s for the ionization equilibria between a number of p,p' substituted diphenylmethanols.[298] The $Cr(CO)_3$ group can make the complexed cation either more or less stable than the free ion depending on the structure. The effect of complexation was explained in terms of electronic and conformational effects.[298] A phase transition was observed at 185°K for $C_4H_4SCr(CO)_3$, which was assigned to a monoclinic → triclinic transition.[299]

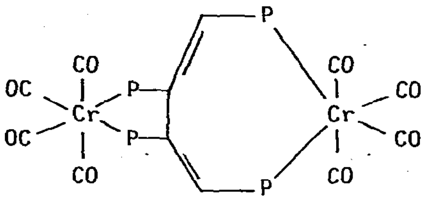
STRUCTURE DETERMINATIONS

The structures of $Cr(CO)_5 \cdot THF$[300] and diethylaminonitrile chromium pentacarbonyl[301] were determined by X-ray crystallography. The Cr-N≡C-N was linear with a Cr-N bond length of 2.063.[301] The carbonyls were normal.[300,301] The structure of $(CO)_4W(t-BuS(CH_2)_nS-t-Bu$ (n=2,3) showed a distorted octahedron.[302]

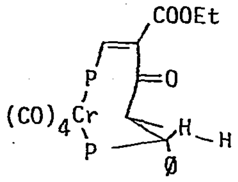


XXXIX

The smaller ring was more highly strained (S-W-S angle is 80°) as shown by the structure. Release of the ring strain was believed to be the driving force for reactions of this complex.[302] The reaction of $Cr(CO)_4(P\O_2H)_2$ and $CF_3C{\equiv}CCF_3$ led to a product with the ligand 1,2,3,4-tetrakis (diphenylphosphino)-1,4-difluorobutadiene chelating to two $Cr(CO)_4$ groups by the 1,4 and 2,3 phosphine groups.[303] Reaction with ØC≡CCOOEt gave a different product, as shown below, also characterized by crystallography.[303]

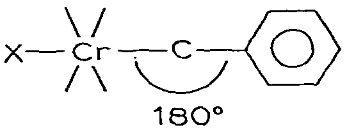


XL



XLI

Crystal structures of trans-chloro-and trans-bromo-phenyl-carbyne chromium tetracarbonyl were reported.[304]

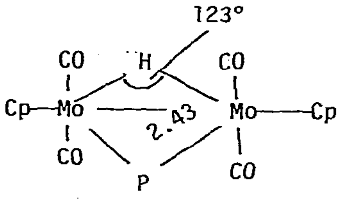


XLII

	Distances X=Cl	X=Br
Cr-X	2.40	2.57
Cr-C	1.68	1.68
C-Ø	1.46	1.48

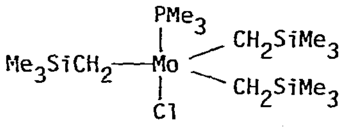
The halogen chromium bond was shortened and the Cr-C bond was typical for Cr≡C-R.[304] Reaction of $W(CO)_6$ with N,N'-di-3,5-xylylformamidine produced $[W_2(CO)_2$-{μ-HC(N-3,5-xylyl)$_2$}$_2$ {HC(N-3,5-xylyl)$_2$} {(N-3,5-xylyl)CH_2}] which has the two tungstens bridged by 2 CO and two formamidino groups.[305,306] This reaction and the structure was reported by two groups.[305,306] The tungstens were pentagonal bipyramidal with a W-W distance of 2.464Å which was ascribed to a double bond.[306] The structure of hexakis(phenylisocyanide)chromium(0), $Cr(CNC_6H_5)_6$, showed the isocyanide groups to have an almost octahedral arrangement around chromium with Cr-C and C-N bond lengths of 1.938 and 1.1776Å, respectively.[307] The ligands were nearly linear with Cr-C-N, 174°, and C-N-C, 173°.[307] Codeposition of Cr atoms with $(CH_3)_2NPF_2$ and $CH_3N(PF_2)_2$ produced $CH_3N(PF_2)_2Cr(PF_2N(CH_3)_2)_4$ which was characterized by a crystal structure determination.[308]

Both single-crystal neutron and X-ray diffraction techniques were used to elucidate the structure of the bis(triphenylphosphine)iminium salt of $Cr_2(CO)_{10}(\mu\text{-}H)^-$.[309] The bridging hydrogen is displaced symmetrically between two chromiums with the two chromiums eclipsed giving overall pseudo-D_{4h} geometry. The anisotropic character of the thermal ellipsoid of the bridging hydrogen indicated a slightly bent $(Cr_2(CO)_{10}H)^-$ anion of C_{2v}-2mm geometry as observed for the Et_4N^+ salt.[309] The location of the bridging hydrogen in $Mo_2(Cp)_2(CO)_4$-$(\mu\text{-}P(CH_3)_2)$ was the subject of another study.[310]

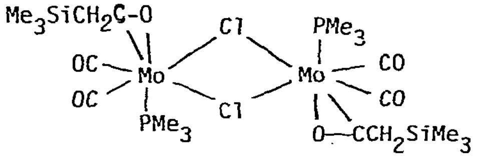


XLIII

The X-ray location of the hydrogen is displaced toward the metal-metal bond from the neutron-diffraction position. In both cases the Mo-H-Mo bond was bent.[310] Churchill, et.al. have determined the crystal structure of the mixed-metal clusters $(\mu_2\text{-}H)Os_3W(CO)_{12}(Cp)$ and $(\mu_2\text{-}H)_3Os_3W(CO)_{11}(Cp)$.[311] The metals form a tetrahedral array with the tungsten coordinated to Cp and two terminal carbonyls and another CO asymmetrically coupling W to one Os. For the trihydride the bridging CO was replaced by two H's bridging the W to Os.[311] The structures of two molybdenum-methyltrimethylsilyl complexes (XLIV and XLV) have been determined.[312]

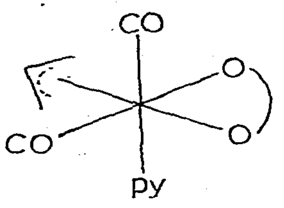


XLIV

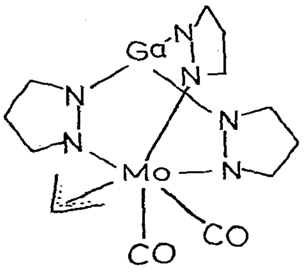


XLV

Both solution and solid state structure determinations (XLVI) were done on Ø(η^3-C_3H_5)(dicarbonyl)(pentane-2,4-dionato)-pyridine molybdenum(II).[313]



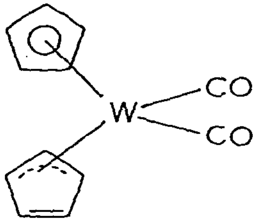
XLVI



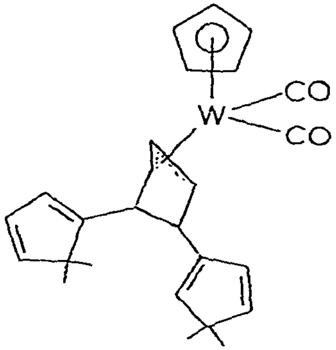
XLVII

The molecule was fluxional at room temperature and a second isomer was detected at low temperature. The fluxionality arose by rotation of one trigonal face with respect to the second and the second isomer came by dissociation of a ligand.[313] The structure (XLVII) of an unusual gallium-molybdenum allyl was also determined.[314]

The structure of $NMe_4(Cp)Cr(CO)_3$ was determined showing the expected configuration.[315] One of the cyclopendienyls in $(Cp)_2W(CO)_2$ (XLVIII) has been shown to be nonplanar (20° deviation from planarity).[316]



XLVIII

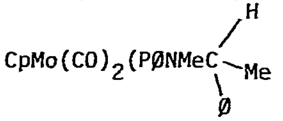


XLIX

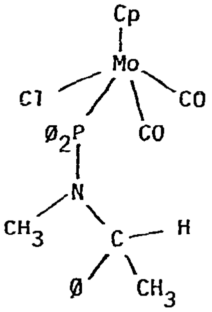
The nonplanar Cp was considered as an allyl + an olefin, thus maintaining 18 electrons around the tungsten.[316] Atwood and coworkers have reported the synthesis and structure of a closely related compound by reaction of $CpW(CO)_2Cl_3$ and NaC_5H_5.[317]

$$CpW(CO)_2Cl_3 + NaC_5H_5 \longrightarrow C_{20}H_{20}W(CO)_2 \tag{154}$$

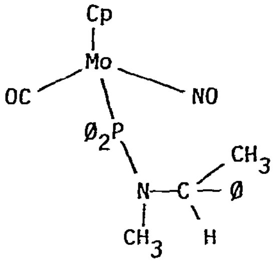
The structure (L) of the optically active, square-pyramidal molybdenum complex,



$CpMo(CO)_2(PØNMeC(H)(Me)(Ø))Cl$ was reported.[318]

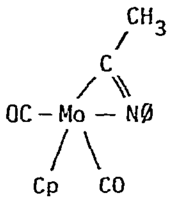


L

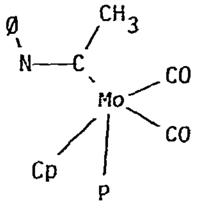


LI

The complex interconverts rapidly in solution. Replacement of one CO and a Cl with NO produced the optically active complex, CpMo(CO)(NO)L (L = $PØ_2N(CH_3)$-(CMeHØ), which was also characterized by X-ray crystallography (LI).[319] A structure determination of $Cp(CO)_3MoHgCl$ showed the Mo-Hg-Cl angle to be 160° and Mo-Hg = 2.673 Å.[320] The non-linearity was attributed to secondary halogen interactions of the Hg with two chlorides 3.075 Å away (the primary Hg-Cl was 2.437 Å).[320] The structures (LII and LIII) of two molybdenum complexes containing η^1- and η^2- iminoacyl ligands were reported by Adams and Chodosh.[321]

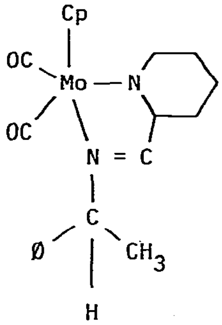


LII

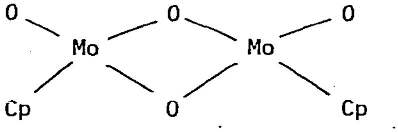


LIII

The C and N bonded iminoacyl was considered a three-electron donor. The Mo-N bond length was 2.143 Å in the first complex and 3.062 Å in the second.[321] Bernal and coworkers determined the structure and absolute configuration (LIV) of a square pyramidal molybdenum complex.[322]



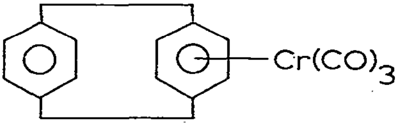
LIV



LV

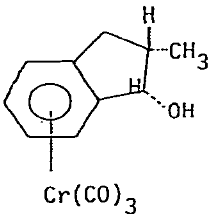
The structure of an oxo bridged cyclopentadiene molybdenum dimer (LV) is shown above.[323]

The distance between the two benzene rings was shown to be shorter than usual in 3-8-η-[2.2.] paracyclophane chromium tricarbonyl (LVI).[324]

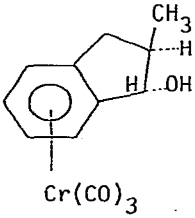


LVI

The crystal structure of exo (LVIII) and endo (LVII) 2-methyl-1-indanol-chromium tricarbonyl was reported.[325]

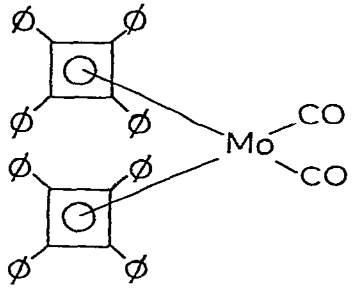


LVII



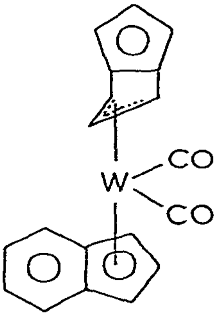
LVIII

In both structures the five-membered ring was bent towards the chromium; the two structures differed in whether the methyl group was on the same side as OH or up in the "equatorial" position.[325] It was suggested that these structures aid in the interpretation of reductions of cyclic ethers to alcohols.[325] The structure of dicarbonyl bis(tetraphenylcyclobutadiene) molybdenum (LIX) was sterically crowded as shown by the OC-M-CO angle of 83.6°.[326]



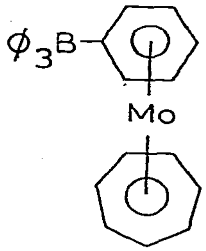
LIX

The contacts between CO's and $Ø_4C_4$ groups led to asymmetry in the bonding of the cyclobutadienes.[326] Reaction of $W(CO)_6$ with indene led to $(C_9H_7)_2W(CO)_2$ and $[(\eta^5\text{-}C_9H_7)W(CO)_3]_2$ and the structure of the first (LX) was determined.[327]

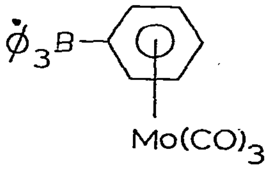


LX

The complex contains a planar $\eta^5\text{-}C_9H_7$ ring and a π-allyl, η^3-ligand, which is bent back by 26° with the distance to non-bonding carbons, 3.2 Å. It was suggested that η^3-indenyl species are likely intermediates in reactions.[327] Structures of two tetraphenylborate complexes of molybdenum (LXI and LXII) with coordination to a phenyl ring were studied.[328]

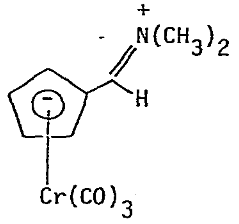


LXI

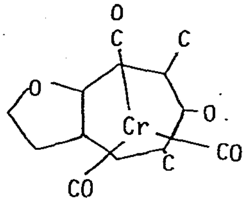


LXII

In cycloheptatrienyl(tetraphenylborato)molybdenum, the Mo was sandwiched between the cycloheptatriene and one phenyl ring from $B\phi_4^-$. In the tetraethylammonium salt of tricarbonyl(tetraphenylborato)molybdate there were three carbonyls and one phenyl ring bound to Mo. In both complexes the distance to the carbon bound to B was considerably longer than the other five Mo-C distances.[328] The crystal structure (LXIII) of $(C_8H_{11}N)Cr(CO)_3$ which contains 6-dimethylaminofulvene coordinated to Cr was reported.[329]



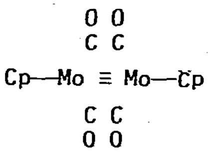
LXIII



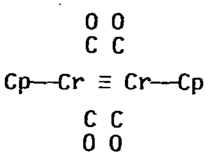
LXIV

The structure of 3a-4:8-8a-η-(dimethyl-5,7 cyclohepta[b]furan-one-6) chromium tricarbonyl (LXIV) showed that the heterocycle-ortho-fused to the tropone does not modify the structure of the complex obtained when Cr condenses on arenotropones.[330]

Structures of several metal-metal bonded complexes were reported in 1978. Curtis and coworkers reported the structures of the complexes $(CpM(CO)_2)_2$ for M = Cr, Mo where a M≡M exists.[331,332]



$\mathrm{Cp{-}\overset{CO\,CO}{\underset{CO\,CO}{Mo \equiv Mo}}{-}Cp}$

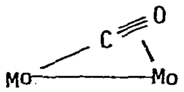


$\mathrm{Cp{-}\overset{CO\,CO}{\underset{CO\,CO}{Cr \equiv Cr}}{-}Cp}$

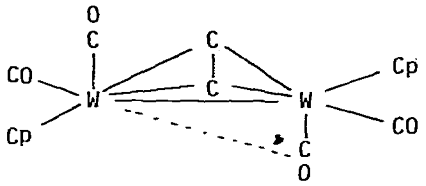
LXV

LXVI

In the molybdenum complex (LXV) the carbonyls are bent over the triple bond, Mo-Mo-C angle was 67°, and the M-C-O angle is 176°, very unusual for bridging CO.[331] They suggested

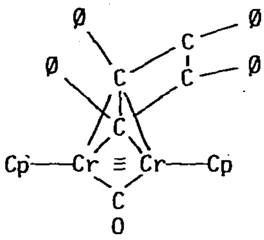


with CO as a four-electron donor. The Cp-Mo-Mo-Cp was very nearly linear.[331] The chromium complex (LXVI) was similar in the semi-bridging CO's (Cr-Cr-CO angle was 74°) but the Cr-Cr-Cp angle was 160°.[332] The bonding in these complexes was discussed from the molecular orbitals.[331,332] Reaction of the tungsten analogue, $Cp_2W_2(CO)_4$, with C_2H_2 produced $Cp_2W_2(CO)_4(C_2H_2)$ (LXVII) which was characterized by X-ray crystallography.[333]



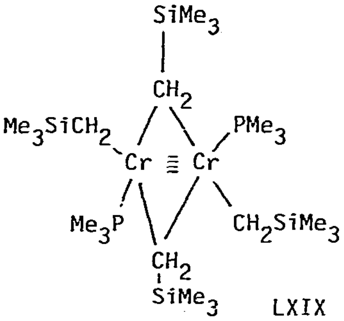
LXVII

The W_2C_2 core is pseudotetrahedral with a single semi-bridging CO.[333] Acetylene complexes with Cr and Mo were also reported, $Cr_2(CO)(Cp)_2(\phi C_2\phi)_2$ and $Mo_2(Cp)_2\{(MeO_2CC_2CO_2Me)(HC_2H)(MeO_2CC_2CO_2Me)_2\}$.[334]

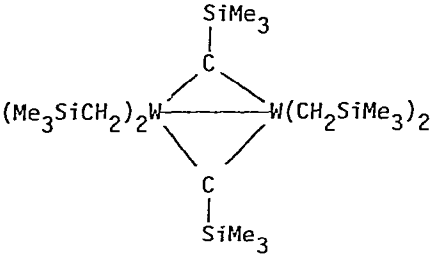


LXVIII

The acetylenes were linked by C-C bonds. In the molybdenum complex four acetylenes were linked to an eight carbon chain. It was suggested that these bimetallic centers are intermediates in cyclizations catalyzed by transition metals.[334] A very long Cr-Cr bond, 3.19 Å, was observed in the structure of $Cr_2(CO)_7(Cp)As(CH_3)_2$, probably from the steric crowding around the chromiums.[335] The X-ray analysis of di-μ-(phenylthio)bis {dicarbonyl(Cp)Mo(II)} showed the Mo atoms to be joined by two symmetrical thiophenyl bridges with a Mo-Mo distance of 3.916 Å.[336] The coordination around each Mo was pseudo-square pyramidal.[336] Chromium atoms bridged by trimethylsilylmethyl were shown in the crystal structure (LXIX) of di-μ-trimethylsilylmethyl-bis[(trimethylphosphine)(trimethylsilylmethyl)chromium(II)].[337]



LXIX



LXX

The structure and bonding were discussed; the Cr-Cr distance of 2.1007 Å was consistent with a quadruple bond.[337] A tungsten complex (LXX) with bridging alkylidyne groups, bis(μ-trimethylsilylmethyl)ditungsten, was also reported.[338] The alkylidyne groups and W atoms were coplanar; the W-W distance was typical for single bonded tungstens.[338]

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