CHROMIUM, MOLYBDENUM, AND TUNGSTEN
ANNUAL SURVEY COVERING THE YEAR 1981*

JIM D. ATWOOD

DEPARTMENT OF CHEMISTRY, STATE UNIVERSITY OF NEW YORK AT BUFFALO,
BUFFALO, NEW YORK 14214 (U.S.A.)

CONTENTS

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*Previous review see J. Organomet. Chem., 237 (1982) 95-160.

ABBREVIATIONS

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

This, my last Annual Survey, has been researched and placed into the same format as the preceding (1976, 1978, 1979, 1980) Annual Surveys of Chromium, Molybdenum and Tungsten. Professor William Jones (University of Rochester) will continue this survey in future years.

DISSERTATIONS

Dissertations covering the following areas were reported in 1981: reactions of isocyanides with quadruply bonded molybdenum and tungsten dimers;[1] chelated tungsten alkene complexes;[2] Group VI and Group VII mixed-metal clusters;[3] and the synthesis and characterization of polyoxomolybdate clusters containing organic and organometallic subunits.[4]

SYNTHESIS AND REACTIVITY

Metal Carbonyls and Derivatives

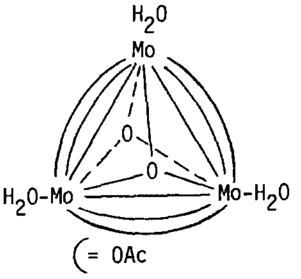
The use of $Bu_3P{=}O$ to facilitate isotopic labeling of the Group VI hexacarbonyls as previously described was extended to $K^+(\mu\text{-}H)Cr_2(CO)_{10}$.[5] In the presence of acid a 75% yield of $Cr(^{13}CO)_6$ was achieved.[5] The infrared spectra of $M(CO)_5(MCH)$ (MCH = methylcyclohexane; M = Cr, Mo, W), formed by 366 nm irradiation of $M(CO)_6$ at -78°C in rigorously purified methylcyclohexane, was reported.[6]

$$M(CO)_6 \xrightarrow[MCH]{h\nu} M(CO)_5MCH + CO \qquad (1)$$

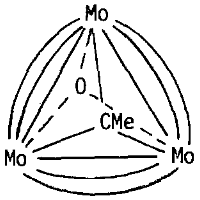
The previously reported spectrum of "$W(CO)_5$" at low temperature in methylcyclohexane/isopentane solution was attributed to $W(CO)_5$(impurity), where the impurity was probably an aromatic or olefinic hydrocarbon. The photochemical reactions of $W(CO)_6$ with aromatic hydrocarbon ligands in methylcyclohexane solution were also studied at -78°C in a low temperature infrared cell.[6] Irradiation (366 nm) of $W(CO)_6$ at -78°C in rigorously purified methylcyclohexane solution containing approximately 5% (v/v) toluene, benzene, mesitylene, biphenyl, or p-xylene initially produced the complex $W(CO)_5(MCH)$.[6] In the presence of the aromatic hydrocarbon, this complex was unstable and it decomposed in a dark reaction to give a complex with an infrared spectrum typical for a C_{4v} $M(CO)_5X$ molecule. It was proposed that the product of the dark reaction was $W(CO)_5$(aromatic), formed by reaction of $W(CO)_5(MCH)$ with the aromatic ligand in solution.[6] The infrared spectra of the $W(CO)_5$-(aromatic) complexes were different from the spectra previously reported for these complexes. It was shown that the spectra previously reported for $W(CO)_5$-(aromatic) are actually attributable to $W(CO)_5$(hexane) (hexane was the solvent used in the previous study); these spectra were probably obtained before $W(CO)_5$(hexane) had time to react with the aromatic hydrocarbon.[6] The species $Cr(CO)_5^-$ was prepared in inert-gas matrices at 10 K by three methods: (i) vacuum-UV irradiation, (ii) bombardment with electrons, and (iii) cocondensation with alkali-metal atoms and subsequent photolysis.[7] There was also evidence with the use of methods i and ii of carbonyl cations in the matrix. Analysis of the IR spectra obtained with the use of $^{13}C^{16}O/^{12}C^{16}O$ mixtures led to the determination of a square-pyramidal structure (C_{4v}) for $Cr(CO)_5^-$.[7] On photolysis of the anion with visible or UV radiation, photoionization occurred rather than loss of CO alone.[7] The reactions of Cp_2NbH_3 with metal carbonyls (metal = Cr, Mo, W) were studied in attempts to find a homogeneous catalytic system capable of activating CO towards reduction.[8]

$$Cr(CO)_6 + Cp_2NbH_3 \rightarrow C_2H_6 \qquad (2)$$

Only the reaction of Cp_2NbH_3 with $Cr(CO)_6$ gave a substantial yield (10%) of C_2H_6.[8] The reaction $Mo(CO)_6$ with acetic acid led to two trinuclear products which were characterized by X-ray crystallography in addition to $Mo_2(OAc)_4$.[9]



I

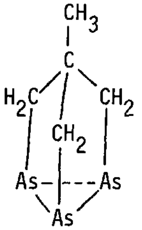


II

The adamantane-structured compound $CH_3C(CH_2AsO)_3$ reacted on ultraviolet irradiation with the hexacarbonyls of chromium, molybdenum and tungsten to give the complexes $CH_3C(CH_2AsO)_3Cr(CO)_5$, $CH_3C(CH_2AsO)_3[Cr(CO)_5]_2$, $CH_3C(CH_2AsO)_3[Cr(CO)_5]_3$, $[CH_3C(CH_2AsO)_3]_2Mo(CO)_4$ and $[CH_3C(CH_2AsO)_3]_2W(CO)_4$.[10] The following reactions illustrate the preparation and reactions.

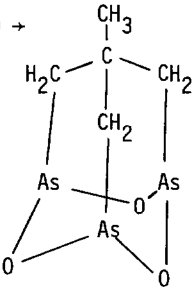
$$CH_3C[CH_2As(C_6H_5)_2]_3 + 6\ HI \rightarrow CH_3C(CH_2AsI_2)_3 + 6\ C_6H_6 \qquad (3)$$

$$CH_3C(CH_2AsI_2)_3 + 6Na \xrightarrow{THF} \qquad (4)$$



$+ 6\ NaI$

$CH_3C(CH_2AsI_2)_3 + 3\ H_2O \rightarrow$



$+ 6HI$ (5)

$$CH_3C(CH_2AsO)_3 + Cr(CO)_6 \xrightarrow{h\nu} CH_3C(CH_2AsO)_3Cr(CO)_5 + CO \qquad (6)$$

$$CH_3C(CH_2AsO)_3 + 2\ Cr(CO)_6 \xrightarrow{h\nu} CH_3C(CH_2AsO)_3[Cr(CO)_5]_2 + 2\ CO \qquad (7)$$

$$CH_3C(CH_2AsO)_3 + 3\ Cr(CO)_6 \xrightarrow{h\nu} CH_3C(CH_2AsO)_3[Cr(CO)_5]_3 + 3\ CO \qquad (8)$$

$CH_3C(CH_2AsO)_3$ can behave at most as tri-dentate ligand coordinating via arsenic atoms and being non-chelating.[10] Photochemical or thermal reaction of $Mo(CO)_6$ with 1,5-cyclooctadiene gave 1,3-$C_8H_{12}Mo(CO)_4$ which was treated with Ph_3P to give $(Ph_3P)_2Mo(CO)_4$.[11]

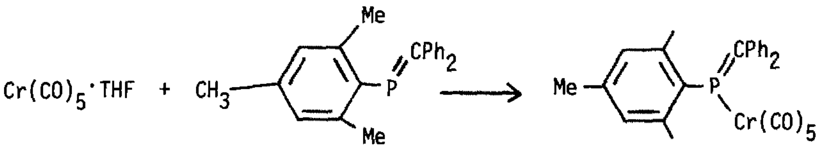
$$Mo(CO)_6 + COD \xrightarrow{-2CO} (COD)Mo(CO)_4 \xrightarrow{2PPh_3} cis\text{-}Mo(CO)_4(PPh_3)_2 \qquad (9)$$

$Me_2Si(N\text{-}t\text{-}Bu)_2Sn$ reacted under UV-irradiation with hexacarbonylchromium and -molybdenum to mono-stannylene complexes $Me_2Si(N\text{-}t\text{-}Bu)_2SnM(CO)_5$ (M = Cr, Mo) and in the case of molybdenum also to a bisstannylene-complex $[Me_2Si(N\text{-}t\text{-}Bu)_2Sn]_2\text{-}Mo(CO)_4$ presumably of cis structure.[12]

$$\begin{tikzcd}[column sep=small] M(CO)_6 \arrow[r, "h\nu\text{,}THF", "-CO"'] & (CO)_5M(THF) \arrow[dr] & \\ & & (CO)_5M\text{-}Sn(N\text{-}t\text{-}Bu)_2SiMe_2 \\ M(CO)_6 + Me_2Si(N\text{-}t\text{-}Bu)_2Sn \arrow[rru, "h\nu\text{,}C_6H_6", "-CO"'] & & \end{tikzcd} \qquad (10)$$

M = Cr, Mo

Alternatively the tin ligand displaced tetrahydrofuran in $(THF)M(CO)_5$ to yield the pentacarbonyl complexes.[12] Mesityldiphenylmethylenephosphine, a stable all-carbon substituted phosphaalkene, reacted with $Cr(CO)_5THF$ as shown below.[13]

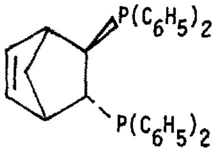


(11)

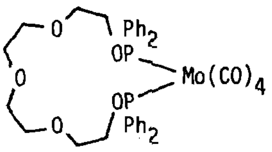
Spectral data suggested a close structural similarity between the free and the complexed ligand, with the ligand of moderate basicity towards chromium. X-ray crystal and molecular structure determination showed the phosphaalkene moiety to be nearly planar with a short P = C bond length of 1.679(4)Å.[13] Mo and W complexes with the water soluble ligand, (2-diphenylphosphinomethyl)trimethylammonium iodide, were prepared by treating $M(CO)_6$ with $Ph_2PCH_2CH_2NMe_2$ in the presence of Me_3NO, followed by methylation with MeI.[14]

$$M(CO)_6 + Ph_2PCH_2CH_2NMe_2 \xrightarrow{Me_3NO} \xrightarrow{MeI} M(CO)_5(Ph_2PCH_2CH_2NMe^+) \qquad (12)$$

Several new chelate complexes of the Group VI metals were prepared in 1981. The chelate complex of the rigid ligand Norphos, a bisphosphine ligand containing the norbornene skeleton, has been prepared, $Cr(CO)_4$(Norphos).



This optically active ligand offers considerable promise.[15] A series of complexes, cis-$M(CO)_4(Ph_2P(OCH_2CH_2)_nOPPh_2)$ (M = Cr, Mo, W; n = 2, 3, 4, 5), were prepared in 20-70% yield from reaction of the diphenylphosphonite ligand with (norbornadiene)$M(CO)_4$.[16] Several of the complexes are shown below for M = Mo.[16]



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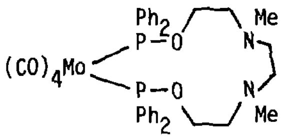
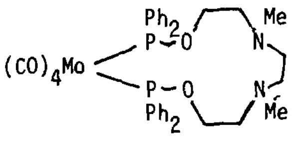
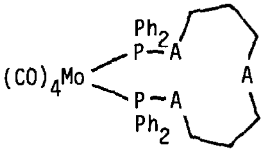


V

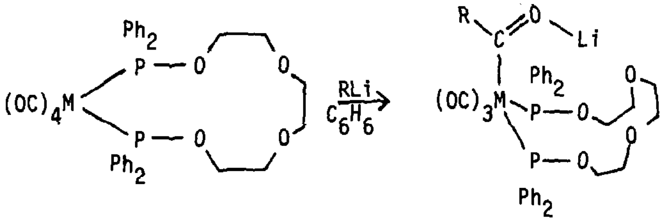


VI



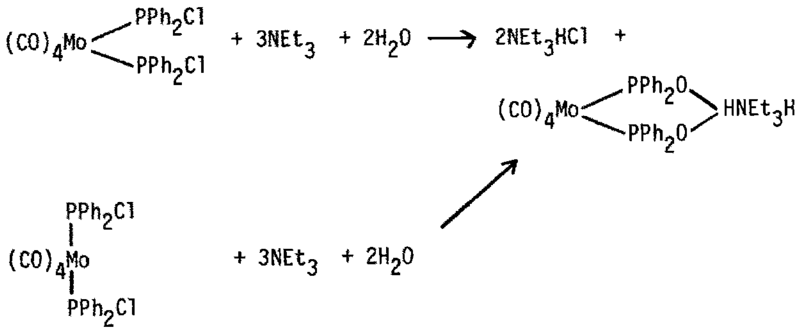
VII

While complexes such as cis-$Mo(CO)_4(PPh_2OMe)_2$ do not react with alkyllithium reagents, the phosphinite complexes reacted readily to give the following reaction,

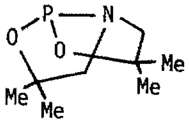


(13)

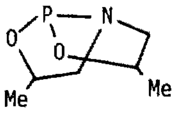
where the lithium is in a cavity created by five oxygen atoms. It was estimated that the binding of lithium within this cavity could contribute 9 kcal of stabilization.[16] The hydrolysis of cis- and trans-$Mo(CO)_4(PPh_2Cl)_2$ were reported to yield the same product,



with the P-O-H-O-P group chelating cis positions.[17] The coordination abilities of the bicyclic aminophosphanes, which have P-N bonds in a strained structure that maintains both phosphorus and nitrogen atoms in a pyramidal configuration, were evaluated with Mo(0) and W(0) carbonyls.[18]

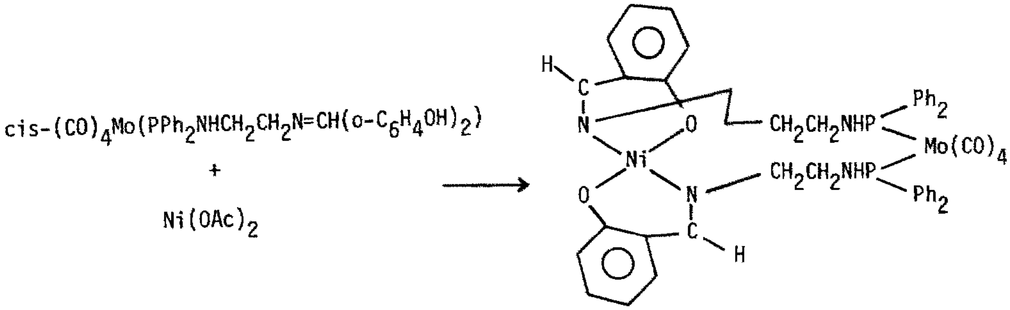


VIII



IX

A series of stable $M(CO)_{6-n}L_n$ adducts were synthesized with M = Mo or W, n = 1-3, from $M(CO)_5$(pyridine), $M(CO)_4$(norbornadiene), and $M(CO)_3$(mesitylene).[18] The ligands were coordinated through phosphorus only, as evidenced by the $\delta(^{31}P)$ displacements, the $J(31_P\text{-}95,97_{Mo}) = 210$ Hz or $J(31_P\text{-}183_W \simeq 370$ Hz couplings, and the $\nu(CO)$ vibration patterns. Low steric requirements (cis-$M(CO)_4(bcap)_2$ and fac-$M(CO)_3(bcap)_3$ isomers were formed readily and exclusively) and good π-accepting capabilities on the basis of the high $\nu(CO)$ absorption frequencies) were the outstanding characteristics of these constrained ligands.[18] The reactions of diphenyl(3,5-dimethylpyrazolyl)phosphine (L) with $[(nbd)M(CO)_4]$ (nbd = norbornadiene; M = Mo, W) and with $[(MeCN)_2W(CO)_4]$ under mild conditions proceed in a stepwise fashion to yield a mixture of products in equilibrium.[19] The four-membered metallocyclic species $LM(CO)_4$ and the P-coordinated cis-$[L_2M(CO)_4]$ were formed in competition, being favored by 1:1 and >2:1 reaction stoichiometries, respectively.[19] The unusual bimetallic complex containing a tetradentate Schiff base complex was prepared by the following reactions.[20]



The structure was determined showing a nearly octahedral geometry around molybdenum.[20] The reaction of $M(CO)_4(NBD)$ (NBD = norbornadiene; M = Cr, Mo, W) with the ligands $Me_2XGeMe_2(CH_2)_2X'Me_2$ yielded the chelate complexes $(CO)_4M[Me_2XGeMe_2(CH_2)_2X'Me_2]$ for X, X' = P, As, but not for X and/or X' = N.[21] The attempt to synthesize the compound $(CO)_4W[Me_2AsGeMe_2(CH_2)_2NMe_2]$ by replacement of two cis-coordinated piperidine ligands from cis-$W(CO)_4(pip)_2$, led to the formation of the cis-disubstituted product $W(CO)_4[Me_2AsGeMe_2(CH_2)_2NMe_2]_2$ with two As donor atoms. The reaction of $Cr(CO)_4(NBD)$ with $Me_2AsGeVi$ (Vi = vinyl) gave cis-$Cr(CO)_4(Me_2AsGeMe_2Vi)_2$ and not the possible σ/π-chelate $Cr(CO)_4(Me_2AsGeMe_2Vi)$.[21] For comparison of the monosubstituted derivatives $Cr(CO)_5L$ (L = $ClGeMe_2(CH_2)_2X'Me_2$ (X' = P, As); $Me_2AsGeMe_2Vi$) were prepared from $Cr(CO)_5THF$ or $Cr(CO)_5Py$ and the ligand. The complex $Cr(CO)_5(Me_2NGeMe_2Vi)$ was not formed by analogous reactions. The new compounds were characterized by analytical and spectroscopic (IR, NMR, mass spectral) methods.[21a] A subsequent publication summarized the spectroscopic data.[21b]

Complexes of other Group V donors with the Group VI metal carbonyls were also reported in 1981. The complexes $MeAsH_2 \cdot M(CO)_5$ with M = Cr, Mo and W, were so unstable that only $MeAsH_2 \cdot W(CO)_5$ would be isolated in a pure state.[22] They decomposed with loss of CO and H_2 to form oligomeric compounds of low solubility.[22] Di-t-butylchloroarsine reacted with t-butyllithium to give tri-t-butylarsine and with trimethylchlorosilane-magnesium-tetrahydrofuran with formation of di-t-butyl(trimethylsilyl)arsine.[23] Tris(trimethylsilyl)arsine was obtained in a similar way from arsenic trichloride with trimethylchlorosilane-magnesium-HMPA.[23]

$$AsCl_3 + 3\ Mg + 3\ (CH_3)_3SiCl \xrightarrow{HMPA} [(CH_3)_3Si]_3As + 3\ MgCl_2 \qquad (17)$$

$$[(CH_3)_3Si]_3As + 3\ (CH_3)_3ECl \rightarrow [(CH_3)_3E]_3As + 3\ (CH_3)_3SiCl \qquad (18)$$

Trimethylsilylarsines reacted with trimethylchloro-germane and -stannane to give the corresponding trimethyl-germyl- and -stannyl-arsines. Organometalarsines reacted with hexacarbonyl-chromium, -molybdenum, or -tungsten with formation of pentacarbonyl(organometalarsine)-chromium, -molybdenum, or -tungsten complexes.[23]

$$M(CO)_6 + As(t\text{-}C_4H_9)_3 \xrightarrow{h\nu} (CO)_5M\text{-}As(t\text{-}C_4H_9)_3 + CO \qquad (19)$$

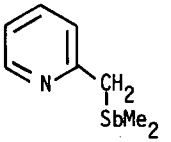
$$M(CO)_6 + As[E(CH_3)_3]_3 \xrightarrow{h\nu} (CO)_5M\text{-}As[E(CH_3)_3]_3 + CO \qquad (20)$$

NMR, IR, Raman, and He(I)-PE data of the new bulky arsine ligands and of some complexes were reported.[23] Hexacarbonyl-chromium, -molybdenum and -tungsten reacted with tris(trimethylsilyl)stibine with substitution of one CO ligand, yielding the corresponding pentacarbonyltris(trimethylsilyl)stibine-chromium, -molybdenum and -tungsten compounds.[24]

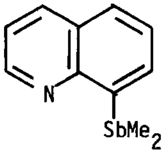
$$M(CO)_6 + (Me_3Si)_3Sb \xrightarrow{h\nu} (Me_3Si)_3SbM(CO)_5 + CO \qquad (21)$$

M = Cr, Mo, W

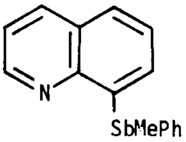
The complexes acted as initiators for the polymerization of tetrahydrofuran. The IR, ^1H NMR and mass spectra of these and some related compounds were discussed.[24] The unsymmetrical mono-tertiary stibines dimethyl(α-picolyl)stibine (picstib), dimethyl(8-quinolyl)stibine (quinstib), and (R;S)-methylphenyl(8-quinolyl)stibine (R;S-quinstib) were synthesized.[25]



X



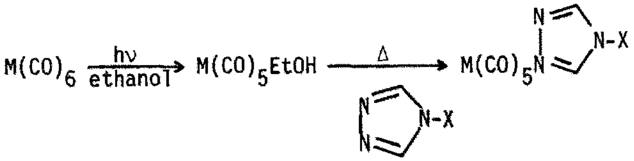
XI



XII

The octahedral complexes $[M(CO)_4(picstib)]$ and $[M(CO)_4(quinstib)]$ were prepared from the metal hexacarbonyls and the appropriate ligands by UV irradiation in tetrahydrofuran.[25]

Complexes of nitrogen donors were also reported in 1981. The synthesis of chromium and tungsten pentacarbonyl complexes with 4-methyl and 4-phenyl-1,2,4-triazole were reported.[26]

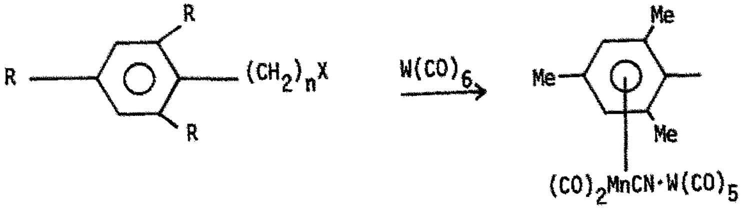


(22)

M = W or Cr

X = Ph, Me

The nature of the lowest energy absorption in the ultraviolet spectra of these complexes was examined and shown to be principally a ligand field band. The triazoles were shown to be acting as monodentate ligands by infrared and ^1H nuclear magnetic resonance spectroscopy. The compounds show strong solvent dependence in the ^1H NMR and these effects were explained by solvent-solute interaction.[26] The temperature dependence of the ^1H NMR spectrum of $W(CO)_5$(4-phenyl-1,2,4-triazole) was also examined.[26] Arenemanganesedicarbonyl cyanides (R = H,

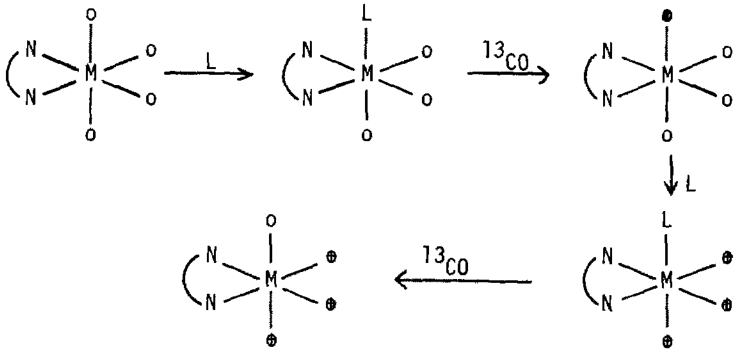


(23)

X = CH:CH_2, C:CH, n = 3; R = Me, X = CO_2Et, n = 3; R = H, Me, X = H, n = 0; R = H, X = CN, n = 1) were prepared by treatment of an appropriate arene with $BrMn(CO)_5$ in the presence of $AlCl_3$ followed by treatment with KCN.[27] Tungsten pentacarbonyl was complexed to the nitrogen of the cyanide.[27] In contrast to (phen)$Cr(CO)_4$, which undergoes ligand exchange exclusively via a unimolecular, ligand-dissociation path, both (phen)$Mo(CO)_4$ and (phen)$W(CO)_4$ react by way of a two-term rate law indicative of two competitive reaction paths.[28]

$$-d[(\mathrm{phen})M(CO)_4]/dt = k_1[(\mathrm{phen})M(CO)_4] + k_2[(\mathrm{phen})M(CO)_4][L] \qquad (24)$$

Displacement of acetonitrile from fac-(CH_3CN)(phen)$M(CO)_3$ (M = Mo, 0°C; M = W, 22°C) by ^{13}CO afforded stereospecifically labeled fac-(^{13}CO)(phen)$M(CO)_3$ products.

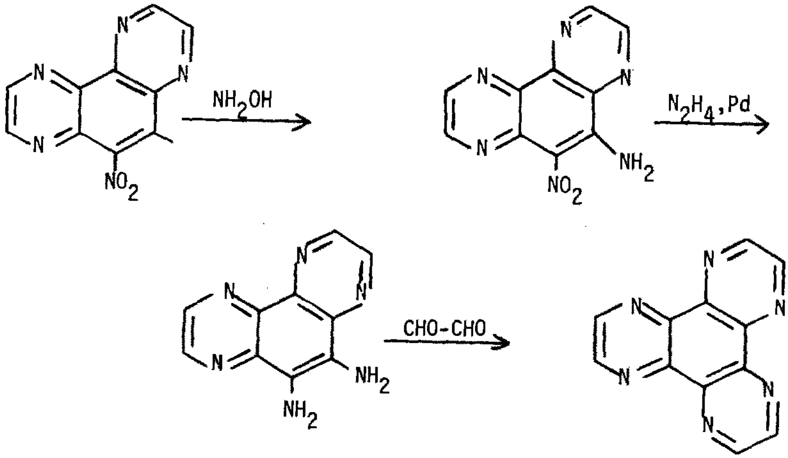


(25)

N N = O phen

● indicates partially enriched

Reaction of these species with acetonitrile and then with ^{12}CO afforded mixtures of products which, when assayed for ^{13}CO, demonstrated that reaction of (phen)M(CO)$_4$ with acetonitrile to afford fac-(CH$_3$CN)(phen)M(CO)$_3$ occurred exclusively via dissociation of an axial CO and that the carbonyls scramble statistically during the conversion.[28] The results for (phen)M(CO)$_4$ (M = Mo, W) were thus analogous to those for (phen)Cr(CO)$_4$, for which exclusive axial loss of CO and statistical scrambling of carbonyls in the resulting five-coordinate intermediate was also observed. Thus the identity of the metal atom appeared to exert little influence on these features of the ligand-exchange process in such group 6B metal carbonyl complexes.[28] A novel ligand, 1,4,5,8,9,12-hexaazatriphenylene, for low valent metal complexes was prepared and its chromium complexes described.[29]



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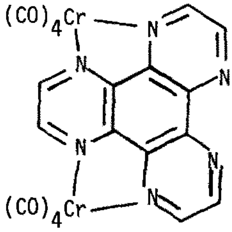
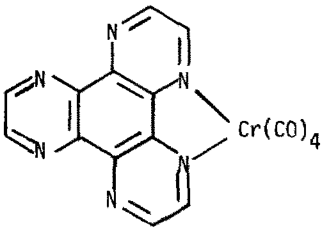
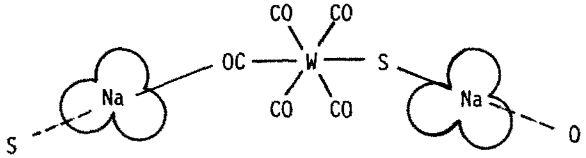




The CO stretching frequencies show that the ligand is a stronger electron acceptor than 1,10-phenanthroline.[29a] Redox reactions of cis-$[Mo(CO)_2(bpy)_2]$ (bpy is 2,2'-bipyridine) produced $[Mo(CO)_2(bpy)_2]^z$ ($z = \pm 1, +2$) which react with isocyanides to substitute CO or bpy or both of these, depending on the charge, z.[29b]

Ultraviolet irradiation has provided a convenient synthetic route to the anions $[M(CO)_5SH]^-$ and $[M_2(CO)_{10}(\mu\text{-}SH)]^-$ (M = Cr, Mo, and W) which were isolated as the sodium 18-crown-6-ether salts.[30]



XV

X-ray analysis has shown that the complexes [Na(18-crown-6)]$[W(CO)_5SH]$ and [Na(18-crown-6)]$[W_2(CO)_{10}(\mu\text{-}SH)]$ are chain polymeric in nature with sodium-carbonyl linkages between alternating cations and anions.[30] The reaction of $Li(CO)_5WSH$ with several complexes were reported.[31]

$$\mathrm{Li(CO)_5WSH} \xrightarrow{\mathrm{[Me_3O]BF_4}} \mathrm{(CO)_5WSMe_2} \tag{27}$$

$$\mathrm{Li(CO)_5WSH} \xrightarrow{\mathrm{Me_3SnCl}} \mathrm{(CO)_5WS(SnMe_3)_2} \tag{28}$$

$$\mathrm{Li(CO)_5WSH} \xrightarrow{\mathrm{PPh_2Cl}} \mathrm{(CO)_5WSPPh_2H} \tag{29}$$

The arene complexes, $(\eta^6\text{-}C_6H_6)Cr(CO)_2(CX)$ (X = S, Se), reacted with excess CO gas under pressure in tetrahydrofuran at about 60°C to produce the $Cr(CO)_5(CX)$ complexes in high yield.[32]

$$\begin{tikzcd}
\mathrm{Cr(CO)_6} \arrow[r, "\mathrm{Arene}", "h\nu"'] & (\eta^6\text{-}\mathrm{Arene})\mathrm{Cr(CO)_3} + 3\ \mathrm{CO} \arrow[d, "\mathrm{CX_2(X = S,\ Se)/PPh_3}"] \\
\mathrm{Cr(CO)_5(CX)} & (\eta^6\text{-}\mathrm{Arene})\mathrm{Cr(CO)_2(CX)} \arrow[l, "\mathrm{CO}"', "\mathrm{10\text{-}200\ atm}"]
\end{tikzcd} \tag{30}$$

The IR and NMR (^{13}C and ^{17}O) spectra of these complexes were in complete accord with the expected C_{4v} molecular symmetry. Like the analogous $W(CO)_5(CS)$ complex, both compounds reacted with cyclohexylamine to give $Cr(CO)_5(CNC_6H_{11})$. However, while $W(CO)_5(CS)$ underwent stereospecific CO substitution with halide ions (Y^-) to form trans$[W(CO)_4(CS)Y]^-$, the two chromium chalcocarbonyl complexes apparently yielded both CO and CX substitution to afford mixtures of $[Cr(CO)_5Y]^-$ and trans-$[Cr(CO)_4(CX)Y]^-$.[32] (1,1,4,4-Tetrafluoro-2-tert-butyl-1,4-disilabut-2-ene)-molybdenum(II) pentacarbonyl was prepared photochemically by reaction of 3-tert-butyl-1,1,2,2,-tetrafluoro-1,2-disilacyclobutene with molybdenum hexacarbonyl in pentane.[33] The crystal structure was determined by X-ray diffraction. The central molybdenum atom was seven-coordinated with a pentagonal-bipyramidal environment. The pentagonal base contained the disilabutene ligand and three carbonyl groups. The five-membered molybdodisilabutene ring was rather strained with endocyclic silicon and carbon valence angles substantially greater and smaller than their tetrahedral and trigonal ideal ones, respectively.[33] A five-membered disilametallacyclic complex was conveniently prepared by photochemical reactions between 1,1,2,2-tetrafluoro-1,2-disilacyclobutene and $Mo(CO)_6$.[34] The reaction mechanism can be rationalized as an initial dissociation of M-CO followed by oxidative addition of the Si-Si bonds to the coordinatively unsaturated metal carbonyl. The olefin complex could be isolated and converted to the disilametallacyclic compound by further irradiation.[34] The nitrido complexes $[MoN(S_2CNR_2)_3]$ ($R_2 = Me_2$, Et_2) reacted with halides R'X (R' = PhCO, $PhSO_2$, $2,4\text{-}(NO_2)_2C_6H_3$, $2,4\text{-}(NO_2)_2C_6H_3S$; X = Cl, R' = Me, X = I), $[R'_3O]BF_4$ (R' = Me, Et) or $[Ph_3C]BF_4$ to give the imido complexes $[Mo(NR')(S_2CNR_2)_3]^+$.[35]

$$\begin{tikzcd}[row sep=small]
 & {[Mo(NCOPh)(S_2CNMe_2)_3]} & (31) \\
 & {[Mo(NSO_2Ph)(S_2CNMe_2)_3]} & (32) \\
{[MoN(S_2CNR_2)_3]} \arrow[ruu] \arrow[ru] \arrow[r] \arrow[rd] \arrow[rdd] \arrow[rddd] & {[Mo(NSAr)(S_2CNR_2)_3]} & (33) \\
 & {[Mo(NAr)(S_2CNR_2)_3]} & (34) \\
 & {[Mo(NCPh_3)(S_2CNR_2)_3]} & (35) \\
 & {[Mo(NR')(S_2CNR_2)_3]} & (36)
\end{tikzcd}$$

$$Ar = 2,4\text{-}(O_2N)_2C_6H_3$$

The X-ray crystal structures of $[Mo(NCPh_3)(S_2CNMe_2)_3]BF_4$ and $[Mo(NSO_2Ph)(S_2CNMe_2)_3]PF_6$ were determined.[35] Both complexes have approximately pentagonal bipyramidal geometries although the NSO_2Ph complex was more distorted.[35] Cis-MoO_2L_2 and μ-$O[MoOL_2]_2$, complexes where HL = ferrocenedithiocarboxylic acid, were prepared and characterized by analysis and IR spectra.[36] In CH_2Br_2 the dimetallic complex disproportionated to cis-MoO_2L_2 and $MoOL_2$.[36]

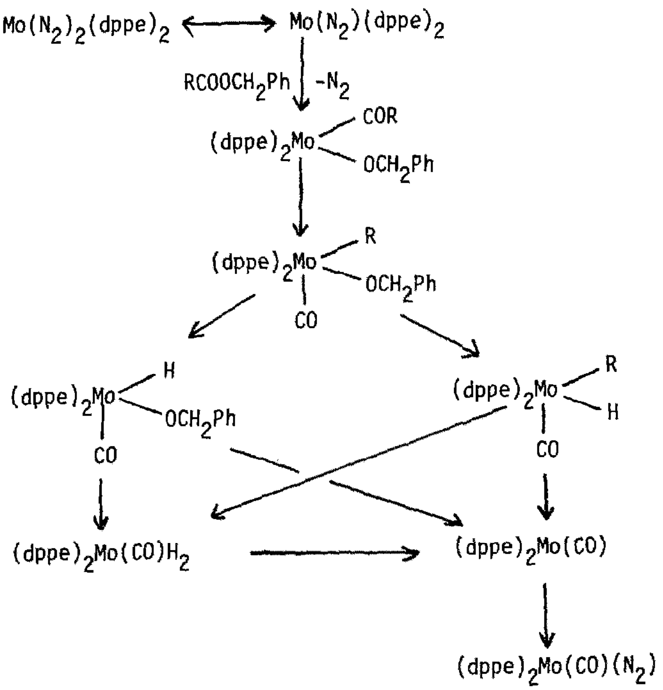
Dinitrogen complexes of the Group VI metals have remained an active research area in 1981. Two experiments were described in the J. of Chemical Education. Preparations were described for $Mo(N_2)_2(dppe)_2$, $MoH_4(dppe)_2$ and cis-$Mo(CO)_2(dppe)_2$.[37]

$$MoCl_5 + 2\ dppe \xrightarrow[THF]{Na/Hg} Mo(N_2)(dppe)_2 \qquad (37)$$

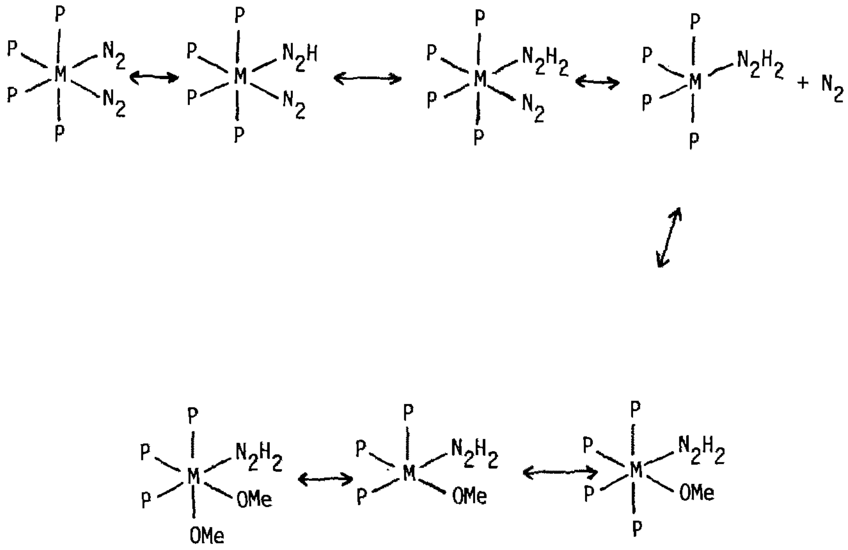
$$\begin{tikzcd}[row sep=small]
 & Mo(H_4)(dppe)_2 & \\
Mo(N_2)_2(dppe)_2 \arrow[ru, "H_2"] \arrow[rd, "CO"'] & & \\
 & cis\text{-}Mo(CO)_2(dppe)_2 & (38)
\end{tikzcd}$$

The formation of a C-N bond in reactions of dinitrogen complexes of Mo was also described.[38] Several reactions of trans-$Mo(N_2)_2(dppe)_2$ were reported. Reactions of formamides, formate esters and aldehydes with trans-$Mo(N_2)_2(dppe)_2$ yielded their respective decarbonylation products (amine, alcohol and alkane) and molybdenum carbonyl complexes.[39] The formation of the products was accounted for by assuming oxidative addition of the compounds to molybdenum, involving the cleavage of the formyl C-H bond followed by decarbonylation. Reactions of primary alcohols produced alkane and a mixture of molybdenum carbonyl complexes and molybdenum hydride.[39] Reactions of benzyl carboxylates, $RCOOCH_2C_6H_5$, (R = CH_3 or C_2H_5) with trans-$Mo(N_2)_2(dppe)_2$ gave RH, C_6H_6 and molybdenum carbonyl complex(es), whereas C_2H_4 and H_2 also were formed when the R group was C_2H_5.[40]

The formation of the product was accounted for by assuming oxidative addition of the ester to molybdenum followed by extrusion of CO.

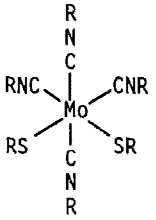


Reactions of phenyl carboxylates occur similarly by way of acyl-O bond cleavage.[40] In contrast, reaction of allyl acetate with trans-$Mo(N_2)_2(dppe)_2$ involved the cleavage of the allyl-O bond to give propylene and a molybdenum acetate complex containing orthometallated phosphine.[40] A postulated mechanism for the reaction between cis-$[M(N_2)_2(PMe_2Ph)_4]$ (M = Mo or W) and HCl, HBr and H_2SO_4 in methanol, to yield $[M(NNH_2)(OCH_3)_2(PMe_2Ph)_3]$, indicated that protic solvents play a role in this reaction.[41]



Diazoalkane complexes, $[MF(NN{=}CRR')(dppe)_2][BF_4]$ (M = Mo or W), derived from bis(dinitrogen) complexes $[M(N_2)_2(dppe)_2]$, underwent consecutive one- and two-electron oxidations and reductions under voltammetric conditions at a platinum electrode.[42] The ESR spectra of the species generated by the controlled potential electrolysis suggested that primary oxidation occurred on the metal atom and reduction on the two nitrogen atoms in the diazoalkane ligands.[42] Treatment of the complex $[WBr(dppe)_2L]Br$ ($L = NNH_2$) with Ph_2ICl in CH_2Cl_2/aq. Na_2CO_3 gave the formyldiazenido complex $[WBr(dppe)_2(N{=}NCHO)]Br$.[43] A mechanism was proposed involving free radical formation and addition to the complex, and this was tested by varying the solvent.[43] Similarly treatment of $[WBr(dppe)_2L]Br$ with Ph_2I^+ in aq $K_2CO_3/CBrCl_3$ gave >60% $WBr(dppe)_2NN{=}CCl_2$ which was stable to hydrolysis but underwent nucleophilic substitution reactions with a variety of compounds.[44] For example the complex reacted with NH_3 to give $WBr(dppe)_2(N{=}NCN)$ and with $(NC)_2CH_2$ to give $WBr(dppe)_2(N{=}NC(Cl)C(CN)_2$, a vinyldiazenido complex.[44]

Complexes of isocyanide ligands continue to be of interest, especially in seven-coordination. The synthesis of complexes of the type $Mo(CO)_2(CNR)_2(PR_3)_2$ ($R = CH_3$, CMe_3 or C_6H_{11} and $PR_3 = PEt_3$, PPr^n_3, $PMePh_2$ or $PEtPh_2$) was accomplished by the reaction of $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ with two equivalents of PR_3.[45] The stereochemistry of these complexes was deduced from IR and ^1H, ^{13}C and ^{31}P NMR measurements. When RNC was reacted with $(\eta^3\text{-}C_3H_5)Mo(CO)_2(CNR)_2Cl$ in the presence of a small amount of $PMePh_2$, the complexes cis-$Mo(CO)_2(CNR)_4$ were formed in 25% yield together with $[(\eta^3\text{-}C_3H_5)Mo(CO)(CNR)_4]^+$ ($R = CMe_3$ or C_6H_{11}).[45] The formation of cis-$Mo(CO)_2(CNR)_4$ under these conditions supported a phosphine-assisted allyl chloride elimination mechanism in the reactions of phosphines with derivatives of the type $(\eta^3\text{-}C_3H_5)Mo(CO)_2L_2Cl$.[45] The crystal structure of the coordinatively unsaturated molybdenum complex cis-$Mo(t\text{-}BuS)_2(t\text{-}BuNC)_4$ was determined by X-ray diffraction.[46] The six-coordinate molecule was substantially deformed from the ideal octahedral geometry, so that the S-Mo-S and C-Mo-C angles in the equatorial plane were 115.3(1) and 73.7(4)°.



R = t-Bu

XVI

A molecular orbital analysis of a model, $Mo(HS)_2(HNC)_4$, traced the deformation to the d^4 electron count.[46] The lowest lying unoccupied MO consisted of an S p-S p bonding combination and a Mo d orbital. The resulting imbalance in S-S bonding led to an opening up of the S-Mo-S angle.[46] The complex which had been formulated as $[Mo(CNCMe_3)_4Cl]_2$ was shown to be identical in properties with $[Mo(CNCMe_3)_6Cl]Cl$.[47] Electrochemical or chemical oxidations of $Mo(CNPh)_6$ and $W(CNPh)_6$ were shown to yield seven-coordinate $[M(CNPh)_7]^{2+}$ in yields of 80%.[48] The redox and substitution chemistry of these new complexes were explored. A synthesis of $W(CNPh)_6$ starting from $W_2(dmhp)_4$ was reported.[48] The structures of heptakis(cyclohexyl isocyanide)-molybdenum(II) hexafluorophosphate, $[Mo(CNC_6H_{11})_7](PF_6)_2$, cyanohexakis(tert-butyl isocyanide)molybdenum(II) hexafluorophosphate, $[Mo(CN\text{-}t\text{-}C_4H_9)_6(CN)](PF_6)$ and heptakis(tert-butyl isocyanide)tungsten(II) hexafluorophosphate, $[W(CN\text{-}t\text{-}C_4H_9)_7](PF_6)_2$, were reported.[49] The molybdenum atom of the cyclohexylisocyanide complex was situated on a crystallographic threefold axis, and the geometry that of a distorted capped octahedron. The Mo-C bond lengths were 2.145(8)Å for the uncapped face, 2.088 for the capping ligand.[49] The geometry of the cyano complexes was that of a capped trigonal prism with cyanide ion as the capping ligand. Seven coordinate geometries were discussed in general.[49] The reactions of the quadruply bonded tungsten dimer $W_2(mhp)_4$ (mhp is the anion of 2-hydroxy-6-methylpyridine) with cyclohexyl and tert-butyl isocyanides in the presence of KPF_6 led to the formation of the seven-coordinate isocyanide complexes $[W(CNR)_7](PF_6)_2$.[50] The tert-butyl isocyanide complex $[W(CNCMe_3)_7](PF_6)_2$ reacted with PR_3(R = Pr or Bu) and dppe to give the mixed-ligand complexes $[W(CNCMe_3)_6(PR_3)](PF_6)_2$ and $[W(CNCMe_3)_5(dppe)](PF_6)_2$.

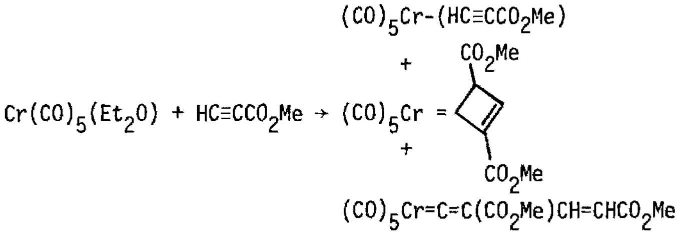
$$W(CNCMe_3)_7^+ + PR_3 \rightarrow W(CNCMe_3)_6PR_3^+ + CNCMe_3 \qquad (41)$$

$$W(CNCMe_3)_7^+ + dppe \rightarrow W(CNCMe_3)_5dppe^+ + 2CNCMe_3 \qquad (42)$$

Cyclic voltammetric studies on $[W(CNR)_7](PF_6)_2$ and the mixed-alkyl isocyanide-phosphine complexes show that they exhibit quasi-reversible one-electron oxidations ($E_{1/2}$ values in the range +1.07 to +0.96 V vs. SCE).[50] The reaction of hepta-coordinate $[Mo(CN\text{-}t\text{-}Bu)_7]^{2+}$ with zinc in refluxing ethanol was shown to produce the $[Mo(CN\text{-}t\text{-}Bu)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)(CN)]^+$ cation in 27% yield.[51] This complex contained the coupled ligand product (N,N'-di-tert-butyldiamino)acetylene and coordinated cyanide ion that arose from dealkylation of tert-butyl isocyanide. An X-ray study of cyanotetrakis(tert-butyl isocyanide)((N,N'-di-tert-butyldiamino)-acetylene)molybdenum(II) was performed.[51] The structure more closely resembled pentagonal-bipyramidal rather than capped trigonal-prismatic idealized geometry.[51] The HNCCNH unit was planar. Distortions of the cation were discussed in terms of hydrogen bonding and intramolecular steric interactions.[51] The syntheses of a series of compounds of the type $W(CO)_2L(S_2CNR_2)_2$ were reported for L = phosphine or phosphite.[52] The crystal and molecular structure of one of these complexes, dicarbonyl(triphenylphosphine)bis(N,N'-diethyldithiocarbamato)tungsten(II), was determined by a single-crystal X-ray diffraction study. Dynamic ^{13}C NMR studies of $W(CO)_2L(S_2CNEt_2)_2$ (L = PPh_3, PEt_3, $P(OEt)_3$) revealed an intramolecular rearrangement process which averaged the two distinct carbon monoxide resonances observed in the low-temperature limit for each of the three complexes investigated.[52] The tungsten ion was seven-coordinate with an inner coordination sphere which can be conveniently described as conforming to a tetragonal base-trigonal base geometry.[52] The structure and dynamic properties of $W(CO)_2L(S_2CNR_2)_2$ complexes were discussed with reference to previous studies characterizing related $W(CO)_3(S_2CNR_2)_2$ complexes. The predominant role of the d^4 configuration of the tungsten(II) ion present in $W(CO)_3(S_2CNR_2)_2$ complexes in labilizing one of the three π-acceptor carbonyl ligands to form dicarbonyl derivatives was discussed.[52]

Carbenes and Carbynes

Carbenes. Carbene complexes of the Group VI metals continue to be important although the emphasis has continued to shift from syntheses to reactions. Reaction of $Cr(CO)_5(Et_2O)$ with an acetylene led to carbene products.[53]



(43)

The products were formed in yields of 39, 43 and 9% respectively.[53] The reaction of $W(CO)_5CS$ with ^-SR (R = CH_3, C_2H_5, i-C_3H_7, n-C_4H_9, or t-C_4H_9) followed by alkylation of the resulting dithioester anion, $W(CO)_5[C(=S)SR]^-$ by R'I (R' = CH_3 or C_2H_5) produced [bis(alkylthio)carbene]tungsten complexes, $W(CO)_5[C(SR)(SR')]$, in good yield.[54] The substituted tetracarbonyl[bis(methylthio)carbene]tungsten complexes cis-W-$(CO)_4[P(OCH_3)_3][C(SCH_3)_2]$ and cis-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ were prepared by an analogous route using cis-W-$(CO)_4L(CS)$, where L = $P(OCH_3)_3$ or $P(OPh)_3$.[54] The carbene complex $W(CO)_5[C(SCH_3)[SFe(CO)_2Cp]]$ was prepared by the reaction of $W(CO)_5[C(=S)(SCH_3)]^-$ with $CpFe(CO)_2(THF)^+$. Isocyanide complexes, $W(CO)_5CN$-R, were formed when $W(CO)_5[C(SCH_3)_2]$ reacted with primary amines, RNH_2, where R = Me, Pr, etc.[54] When cis-$W(CO)_4[P(OPh)_3][C(SCH_3)_2]$ was reacted with NH_2CH_2Ph and $NH_2(CH_2)_3NH_2$, isocyanide complexes were also formed. The reaction of $W(CO)_5[C(SCH_3)_2]$ with secondary amines $NH(CH_3)_2$, $HN(CH_2)_2OCH_2CH_2$, or $HN(CH_2)_4CH_2$ produced (aminothiocarbene)tungsten complexes, $W(CO)_5[C(SCH_3)NR_2]$.[54] The synthesis of a pentacarbonyl(di-n-butylboroxy(methyl)carbene tungsten was reported.[55]

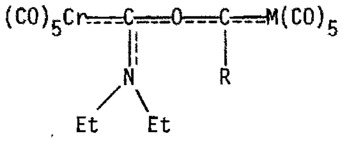
$$(CO)_5WC(OLi)CH_3 + (n\text{-}C_4H_9)_2BCl \xrightarrow{Et_2O} (CO)_5WC[OB(n\text{-}C_4H_9)_2]CH_3\cdot 1Et_2O + LiCl \quad (44)$$

The group 6 acylmetal(0) anions $RCOCr(CO)_5^-$ and $RCOW(CO)_5^-$ gave paramagnetic acylchromium(I) and tungsten(I) species upon anodic oxidation.[56] Ion-pairing effects with various cations were shown by the shifts of the cyclic voltammetric peak potentials and in the carbonyl IR frequencies of $PhCOCr(CO)_5^-$. The benzoylchromium(I) radical was sufficiently persistent at low temperatures to observe its well-resolved ESR spectrum, but it was readily converted to the hydroxycarbene complex $Ph(HO)C{=}Cr(CO)_5$ by hydrogen atom transfer.[56]

$$PhCOCr^{0}(CO)_5^- \rightleftarrows PhCOCr^{I}(CO)_5 + e^- \rightarrow Ph(HO)C{=}Cr(CO)_5 \quad (45)$$

The X-ray crystallographic determination of $Ph(HO)C{=}Cr(CO)_5$ indicated the structural consequences of strong hydrogen bonding to the hydroxy group in cyclic voltammetric studies of the carbene complex.[56] A communication describing the following reactions was reported.[57]

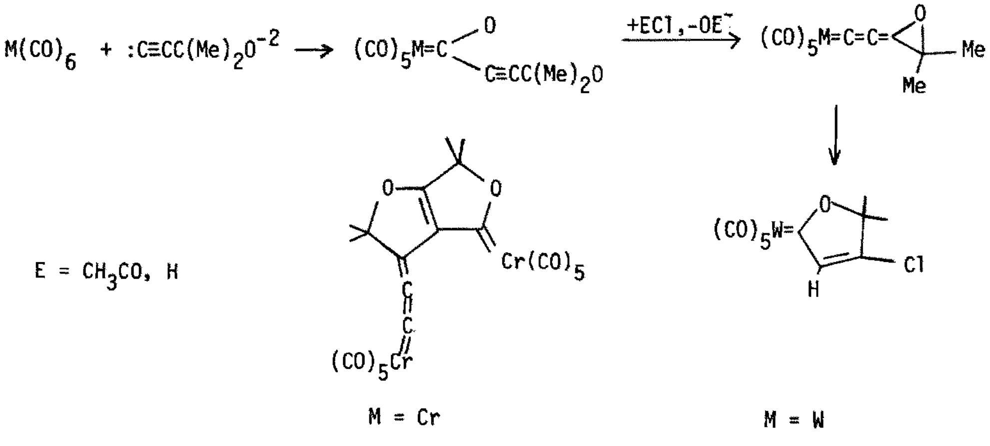
$$[(CO)_5CrCN(Et)_2]^+\ [BF_4]^- + [(CO)_5MC(O)R]^-\ [N(CH_3)_4]^+ \xrightarrow[-78°C]{CH_2Cl_2}$$



(46)

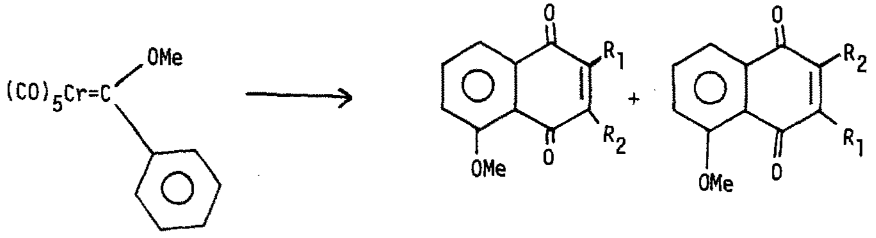
M = Cr, R = $p\text{-}C_6H_4CH_3$
M = W, R = CH_3

The reactions of $M(CO)_6$ (M = Cr, W) with $LiC{\equiv}C\text{-}C(Me)_2OLi$ leading to the corresponding acylate complexes were reported.[58] Treatment of these complexes with CH_3COCl or HCl led to cyclic carbene complexes.



The photolysis of the initially formed $(CO)_5CrC(O)C{\equiv}CC(CH_3)_2OLi_2$ and the subsequent reaction with CH_3COCl yielded the vinylidene complex $(CO)_5Cr{=}C{=}C(COCH_3)C(CH_3)_2\text{-}OCOCH_3$.[58]

A number of studies of reactions of carbene complexes were reported in 1981. The regiochemistry for reaction of chromium carbene complexes with unsymmetrical alkynes was investigated.[59]



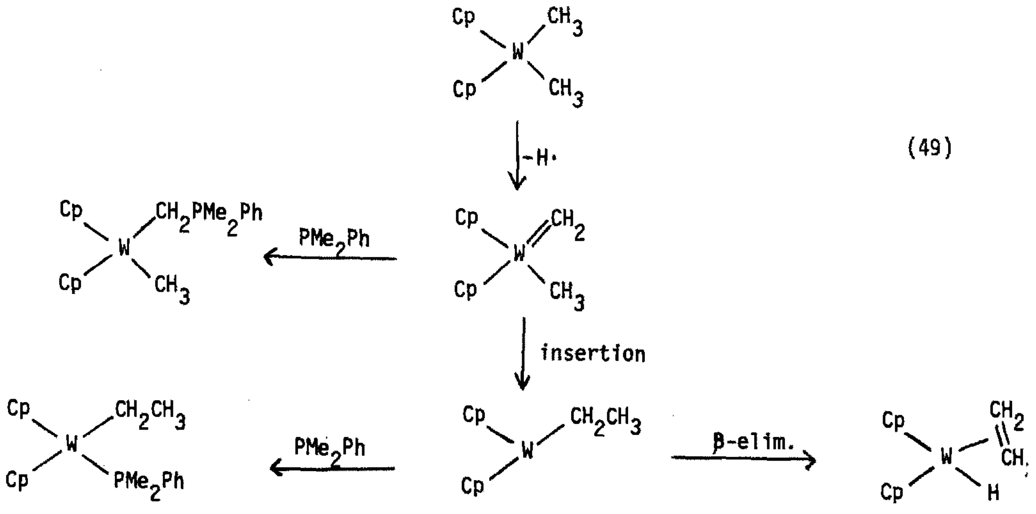
XVII XVIII XIX

(48)

Regioselectivity of Reaction

R_1	R_2	yield XVIII + XIX %	XVIII/XIX
Et	Me	81	1.5
n-Pr	Me	64	2.9
i-Pr	Me	61	4.8
Ph	Me	78	>100
n-Pr	H	74	>100
$(CH_2)_3CO_2$-t-Bu	H	66	>100
$(CH_2)_3$CONH-t-Bu	H	70	>100

The regioselectivity of meta substitution on the carbene complex was also investigated.[59] A number of reactions were examined which indicated insertion of a methylidene into a tungsten-methyl bond.[60]



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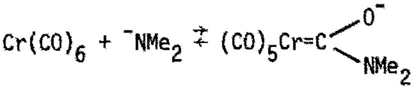
Isotopic labeling was used to confirm the suggested sequence.[60] The reaction of $M(CO)_6$ (M = Cr, Mo, W) with $LiNMe_2$ in HMPA yielding dimethyl formamide was investigated.[61] The scheme suggested



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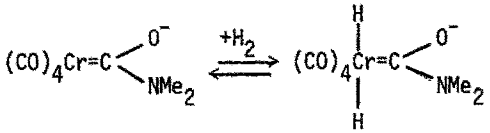
(51)



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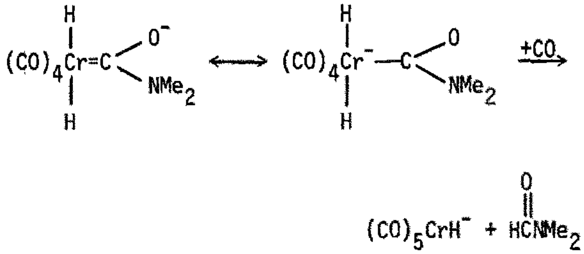
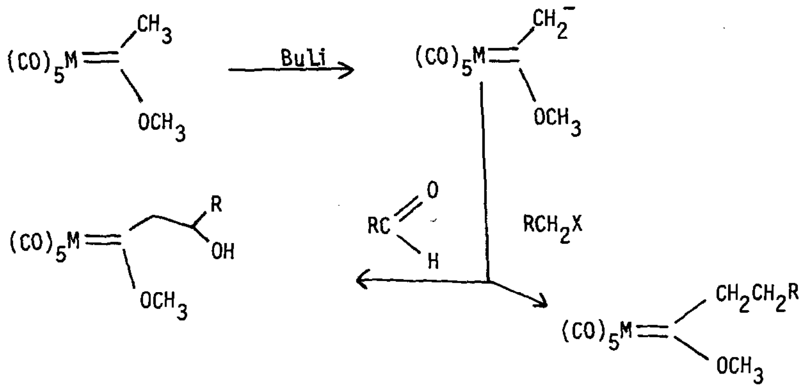


(53)

was offered as a model for the general case of nucleophilic activation of CO.[61] The photo-induced degradation of $Ph_2C{=}W(CO)_5$ in n-hexane solution was investigated, and found to produce tungsten hexacarbonyl and tetraphenylethylene, as well as products of hydrogen abstraction, diphenylmethane and 1,1,2,2-tetraphenylethane.[62] Yields of the organic products were dependent on the concentration of $Ph_2C{=}W(CO)_5$, the olefin being favored in more concentrated solution. Similar products and trends were found when $Ph_2C{=}W(CO)_5$ was thermally degraded in n-heptane.[62] Ligand transfer of the diphenylcarbene ligand was achieved by photolyzing $Ph_2C{=}W(CO)_5$ in diethyl fumarate, which produced diethyl 3,3-diphenyl-1,2-cyclopropanedicarboxylate, and via a thermal reaction of $Ph_2C{=}W(CO)_5$ with $CpMn(CO)_2(THF)$, which produced $Ph_2C{=}Mn(CO)_2Cp$.[62] Photolysis of the latter carbene complex in n-hexane produced the same organic products as those obtained from the photolysis of $Ph_2C{=}W(CO)_5$.[62] The reaction of the anion of methylmethoxycarbenetungsten with enol ethers gave, after protonation, new alkylidene complexes which result from pericyclic addition.[63]



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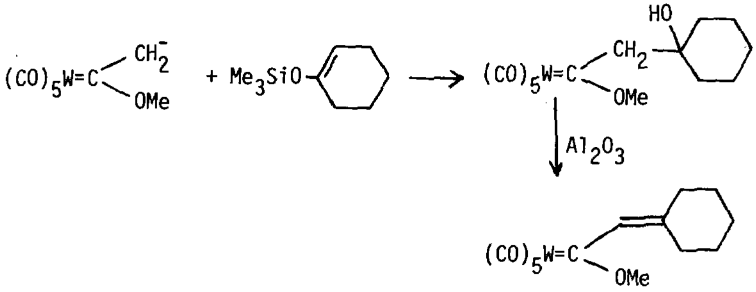
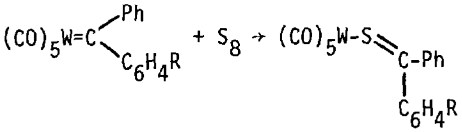


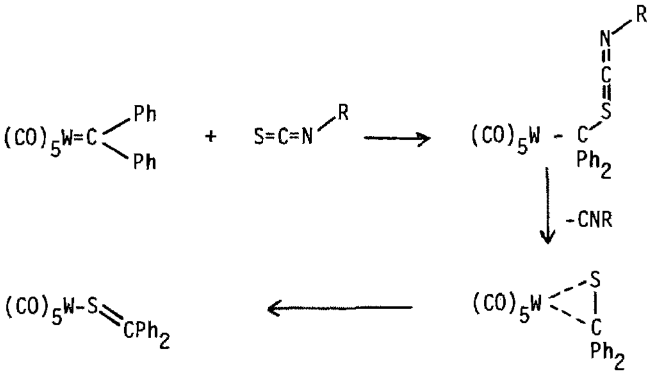
Treatment of these new complexes with base produced after alcohol elimination the new vinylalkylidene complexes of tungsten.[63] (Arylphenylcarbene)pentacarbonyltungsten complexes, $(CO)_5W[C(p-C_6H_4R)C_6H_5]$ reacted with elemental sulfur with insertion of one sulfur atom into the metal-carbene bond to give (arylphenylthioketone)pentacarbonyltungsten complexes.[64]



(56)

R = OMe, H, CF_3

(Arylphenylcarbene)pentacarbonyltungsten complexes, $(CO)_5W[C(p-C_6H_4R)C_6H_5]$ (R = OCH_3, H, Br, CF_3) reacted with organylisothiocyanates, R'NCS (R' = CH_3, C_2H_5, C_6H_5), via insertion of the sulfur atom from R'NCS into the metal-carbene bond to yield (arylphenylthioketone)pentacarbonyltungsten complexes, $(CO)_5W$-$[SC(p-C_6H_4R)C_6H_5]$.[65] The rate law was investigated and the following mechanism suggested.[65]



(57)

Replacement of R = H by electron-withdrawing substituents (Br, CF_3) resulted in an increase in rate while electron-donating groups (CH_3, OCH_3) resulted in a decrease of the reaction rate. The rate constant k increased in the series R' = C_6H_5, R' = CH_3, R' = C_2H_5.[65] Reaction conditions for the conversion into isocyanide complexes of the carbene $Cr(CO)_5[C(NHC_6H_5)_2]$ were established.[66] Isocyanide ligands could be transformed into each other at the complex without breaking the metal to carbon bond.[66]

Carbynes. From the reaction between $MoCl_5$ and $LiCH_2SiMe_3$ a purple distillate was obtained, in addition to $Mo_2(CH_2SiMe_3)_6$.[67] The purple distillate was shown to contain the carbene compound $(Me_3SiCH_2)_3Mo{=}CHSiMe_3$ and the carbyne compound $(Me_3SiCH_2)_3Mo{\equiv}CSiMe_3$ by analytical and spectroscopic studies.

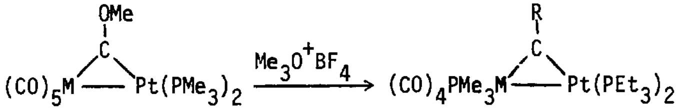
$$\begin{aligned}MoCl_5 + LiCH_2SiMe_3 \rightarrow Mo_2(CH_2SiMe_3)_6 + {} & (Me_3SiCH_2)_3Mo{\equiv}CSiMe_3 + \\ & (Me_3SiCH_2)_3Mo{=}CHSiMe_3\end{aligned} \qquad (58)$$

When reaction was carried out at -78°C, a yellow distillate was obtained, which was the pure carbyne compound.[67] Analogous reactions employing WCl_6 and $LiCH_2SiMe_3$ (6 equiv) at -78°C produced $(Me_3SiCH_2)_3W{\equiv}CSiMe_3$ as the sole volatile tungsten-containing product. The new compounds were characterized by elemental analyses and IR, NMR (^1H and ^{13}C), and mass spectroscopy.[67] Reaction of $MPt[\mu\text{-}C(OMe)Ph](CO)_5(PMe_3)_2$ with Me_3O^+ BF_4^- followed by addition of NaOEt gave $MPt(\mu\text{-}CPhR)(CO)_5(PMe_3)_2$ (M = Cr or W, R = OEt).[68]

$$\mathrm{MPt(\mu\text{-}C(OMe)Ph)(CO)_6(PMe_3)_2 \xrightarrow{Me_3O^+} \xrightarrow{NaOEt} MPt(\mu\text{-}C(OMe)(OEt))(CO)_5(PMe_3)_2} \quad (59)$$

M = Cr, W, R = OEt

Treating $MPt[\mu\text{-}C(OMe)R](CO)_4(PMe_3)_3$ (M = Cr, R = Ph; M = W, R = 4-tolyl) with Me_3O^+ BF_4- allowed isolation and characterization of $[CrPt(\mu\text{-}CPh)(CO)_4(PMe_3)_3][BF_4]$ and $[PtW(\mu\text{-}CC_6H_4Me\text{-}4)(CO)_4(PMe_3)_3][BF_4]$, respectively.[68]



(60)

$PtW[\mu\text{-}C(CO_2R)Ph](CO)_4(PMe_3)_3$ (R = Me, Et) were also prepared.[68] Pentacarbonyl(diethylaminocarbyne)chromium tetrafluoroborate, $[(CO)_5CrCNEt_2]BF_4$, reacted with PPh_3 with substitution of CO and formation of trans-tetracarbonyl(diethylaminocarbyne)triphenylphosphinechromium tetrafluoroborate, trans-$[PPh_3(CO)_4CrCNEt_2]BF_4$.[69]

$$\mathrm{(CO)_5Cr{\equiv}C\text{-}NEt_2^{\,+} + PPh_3 \rightarrow trans\text{-}PPh_3(CO)_4Cr{\equiv}C\text{-}NEt_2^{\,+} + CO} \quad (61)$$

Substitution of CO by PPh_3 in neutral trans-tetracarbonyl(halo)(diethylaminocarbyne)chromium complexes, trans-$X(CO)_4CrCNEt_2$ (X = Br, I), led in a reversible reaction to the corresponding tricarbonyl complexes, mer-$X(PPh_3)(CO)_3CrNEt_2$, PPh_3 occupying the cis-position to the carbyne ligand. With PPh_3 in large excess both reactions followed a first-order rate law. This as well as the activation parameters indicated a dissociative mechanism.[69] Carbyne complexes $[W(CNRMe)(CNMe)(dppe)_2]^+$ (R = H, Me) underwent protonation reactions at the isonitrile nitrogen yielding bridging carbyne complexes $[[W(CNRMe)(dppe)_2]_2(\mu\text{-}CNHMe)_2]^{4+}$ which underwent deprotonation and cleavage by solvents (pyridine, Me_2SO).[70] Deprotonation occurred in basic solvents yielding the parent species, but in F_3CCO_2H the carbyne ligand $CNMe_2$ gave protonation at nitrogen leading to the formation of trans-$[W(CNHMe_2)(CNHMe)(dppe)_2]^{3+}$. Dealkylation of the carbyne ligand $CNMe_2$ in trans-$[Mo(CNMe_2)(CNMe)(dppe)_2]^+$ resulted from reaction with LiMe yielding the bisisonitrile complex.[70]

Hydrides and Alkyls.

Hydrides. The interaction of Cr^+ with H_2, C_2H_6, C_2H_4 and O_2 have been used to evaluate bond energies of a Cr-H, Cr-CH_3, Cr=CH_2 and Cr=O.[71] The value of the bond dissociation energies of Cr-R were: R = H, 35 kcal/mol; R = CH_3, 37 kcal/mol; R = CH_2, 65 kcal/mol; and R = O, 77 kcal/mol.[71] $CpMo(CO)_3H$ reacted with metal alkyls such as $CH_3Mn(CO)_5$ and $CpMo(CO)_3R$ (R = CH_3, C_2H_5, $CH_2C_6H_5$) producing aldehydes and the dimers $[CpMo(CO)_3]_2$ and $[CpMo(CO)_2]_2$.[72] Reaction of

$CpMo(CO)_3H$ with ethylene produced ethane and diethyl ketone.

$$CpMo(CO)_3H + CpMo(CO)_3CH_3 \rightarrow CH_3CHO + [CpMo(CO)_3]_2 + [CpMo(CO)_2]_2 \tag{62}$$

$$CpV(CO)_3H^- + Cr(CO)_6 \rightarrow HCr(CO)_5^- + CpV(CO)_4 \tag{63}$$

The reaction of a vanadium hydride with $Cr(CO)_6$ effected a hydride transfer.[72] $CpV(CO)_3H^-$ was proposed to react by an electron-transfer mechanism, whereas $CpMo(CO)_3H$ was proposed to react by hydrogen transfer to a vacant coordination site. The relationship of the molybdenum hydride/alkyl reaction to the final step in hydroformylation was discussed.[72] The reaction of Cp_2Sn with $HW(CO)_3Cp$ in THF gave $HSn[W(CO)_2Cp]_3$ and not $[Cp(CO)_3W]_2Sn$ as previously reported.[73] $HSn[WCp(CO)_3]_3$ reacted with halogenated hydrocarbon solvents to give the corresponding Sn(IV) halides.[73] This result was also supported by work accomplished by Harrison.[74] New synthetic routes to $HM(CO)_5^-$, (M = Cr, Mo, W) complexes were reported.[75]

$$(K\text{-crypt } 222)OH + M(CO)_6 \rightarrow K\text{-crypt}^+\ HM(CO)_5^- + CO_2 \tag{64}$$

M = Cr, Mo, W

$$HVCp(CO)_3^- + Cr(CO)_6 \rightarrow HCr(CO)_5^- + CpV(CO)_4 \tag{65}$$

$$LiAlH_4 + Cr(CO)_5Cl^- \rightarrow HCr(CO)_5^- + LiCl + AlH_3 \tag{66}$$

$$M(CO)_5piper + BH_4^- \rightarrow HM(CO)_5^- + (piper)BH_3 \tag{67}$$

M = Cr, W

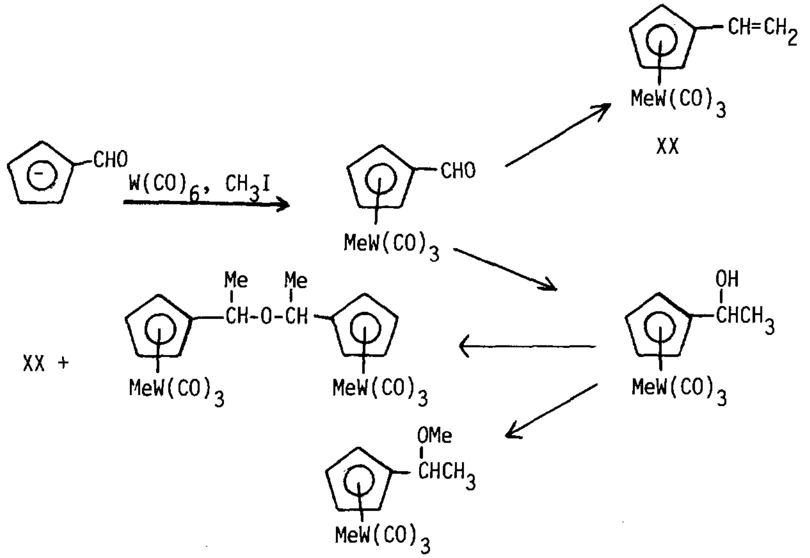
The preparation of pure complexes allowed spectral characterizations.[75] The hydridochromium pentacarbonyl anion, $HCr(CO)_5^-$, was shown to bind to transition-metal Lewis acids such as $[M(CO)_5{}^0]$ (M = Mo, W) and $[Mo(PPh_3)(CO)_4{}^0]$ which allowed for an efficient clean synthesis of heterobinuclear bridging hydride complexes.[76] The pentacarbonylmetalhydride anions were found to react with CO_2 or CS_2 yielding the corresponding pentacarbonylmetal formates or thioformates, respectively.[77]

$$HM(CO)_5^- + CX_2 \rightleftarrows HC(X)XM(CO)_5^- \tag{68}$$

M = Cr, Mo, W; X = O, S

The relation of this reaction to the water-gas shift reaction was discussed.[77]

Alkyls. The preparation, polymerization and copolymerization of two organotungsten vinyl monomers, (η^5-vinylcyclopentadienyl)tricarbonylmethyltungsten and (η^5-cyclopentadienylmethyl acrylate)tricarbonylmethyltungsten were described.[78] The vinyl complex was prepared from reaction between formylcyclopentadienylsodium and hexacarbonyltungsten, followed by methylation with methyl iodide to produce (η^5-formylcyclopentadienyl)tricarbonylmethyltungsten, and subsequent conversion of the latter into the product under phase transfer conditions employing triphenylmethylphosphonium iodide, 5 N sodium hydroxide and benzene.



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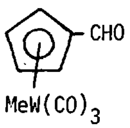
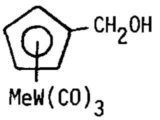
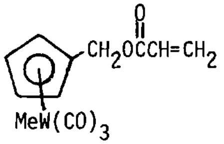
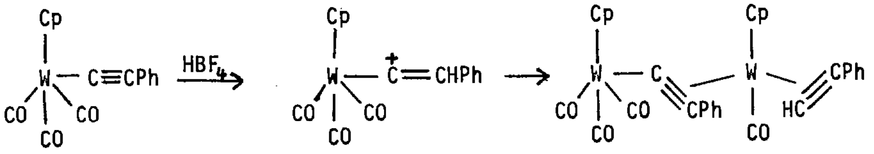






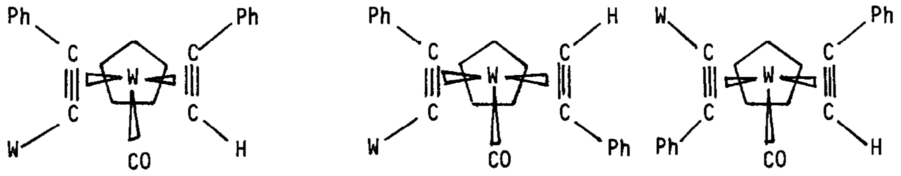
The acrylate complex was obtained by sodium borohydride reduction of the formyl, followed by treatment of the resulting carbinol with sodium hydride and subsequent reaction with acryloyl chloride.[78] The polymerization reactions of these species were explored.[78] A more extensive report of the polymerizations also appeared.[79] (η^5-Vinylcyclopentadienyl)tricarbonylmethyltungsten was radically homopolymerized and copolymerized with styrene, acrylonitile, Me methacrylate and N-vinyl-2-pyrrolidinone. No evidence of significant chain transfer in polymerization of styrene in the presence of (η^5-cyclopentadienyl)tricarbonylmethyltungsten, (η^5-cyclopentadienyl)tricarbonylmanganese, or poly[(η^5-vinylcyclopentadienyl)tricarbonylmanganese] was found, showing that hydrogen atom abstraction by the growing chain from the W-bound Me group was not an important process.[79] The photo-induced reaction between the complex $CpMo(CO)_3CH_3$ and the ligands o-$C_6H_4EPh_2(E'Ph_2)$ (E = E' = P; E = P; E' = As; E = E' = As; E = P; E' = Sb; E = P'; E' = Bi; E = As; E' = Sb;) and cis-$Ph_2PCH{:}CHPPh_2$, L, provided $CpMo(CO)CH_3(l)$.[80]

^{31}P NMR spectra of the molybdenum complexes suggested that the basic geometry for $Ph_2PCH{=}CHPPh_2$ was tetragonal pyramidal, while the preferred structure for $Ph_2PCH{=}CHPPh_2$ appeared to be trigonal bipyramidal with the ligand in equatorial positions.[80] The protonation of η^5-Cp(CO)$_3$WC≡CPh by HBF$_4$ in CH$_2$Cl$_2$ gave the stable cationic binuclear complex of tungsten $[(\eta^5\text{-Cp})(OC)_3W\{\mu\text{-}(\eta^1,\eta^2\text{-}C_2Ph)\}W(\eta^2\text{-}C_2PhH)(CO)(\eta^5\text{-Cp})]^+BF_4^-$.[81]

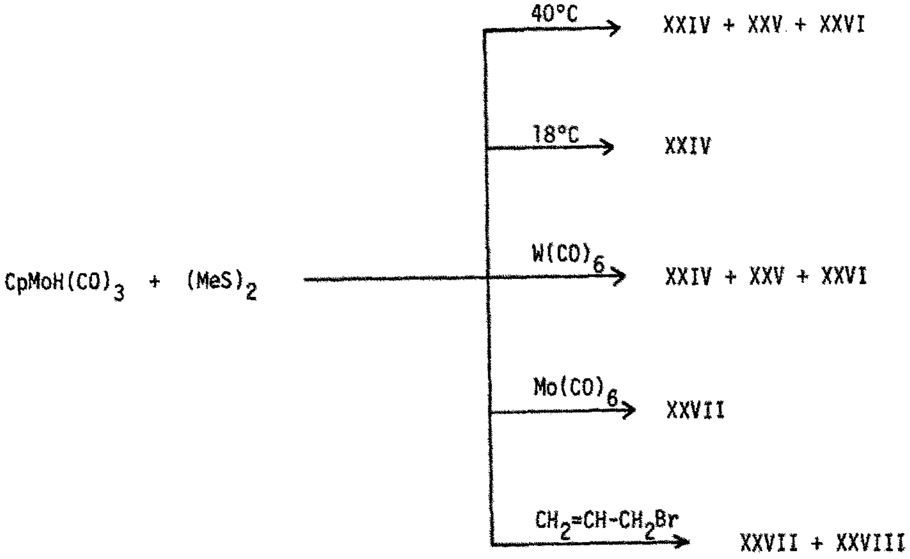


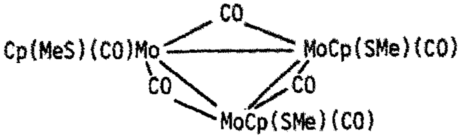
(70)

Rotamers were suggested to exist based on the ^{1}H NMR spectrum.[81]

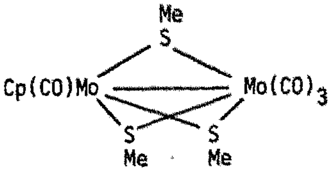


The structure of the binuclear complex was determined by X-ray diffraction methods.[81] The reaction between [CpMoH(CO)$_3$] and disulphides gave dimeric or trimeric complexes depending upon the conditions.[82] The syntheses of the novel trinuclear molybdenum carbonyl complex $[\{MoCp(SR)(\mu\text{-}CO)(CO)\}_3]$ (R = Me), and dinuclear compounds $[Mo_2Cp(\mu\text{-}SR)_3(CO)_4]$ (R = Me) and $[Mo_2Cp_2(SR)_2(CO)_2(\mu\text{-}SR)(\mu\text{-}Br)]$ (R = Me or Ph) were reported.[82]





XXV



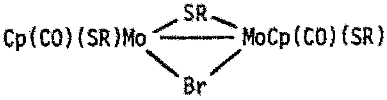
XXVII

$CpMo(CO)_2SMe_2$

XXIV

$(CpMo(CO)SMe_2)_2$

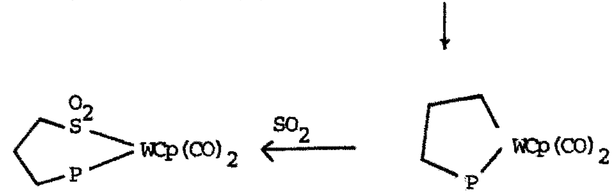
XXVI



XXVIII

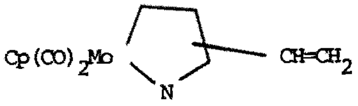
Ligand exchange reactions of $Cp(OC)_3WCl$ with $Ph_2P(CH_2)_3Cl$ gave $Cp(OC)_{m-1}W(X)PPh_2(CH_2)_3Cl$ which cyclized to give $Cp(CO)_2WCl(PPh_2CCH_2)_3Cl$.

$Cp(CO)_3WCl + Ph_2P(CH_2)_3Cl \rightarrow Cp(CO)_2WCl(PPh_2CCH_2)_3Cl$



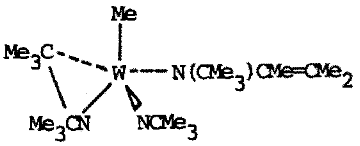
(76)

The cyclized complex inserted SO_2.[83] Tetrafluoroborate complexes $CpMo(CO)_2(PR_3)BF_4$ were prepared by hydride abstraction from the corresponding hydrido compounds[84] using Ph_3CBF_4. The tetrafluoroborate ligand in $(\eta^5\text{-}C_5H_5)Mo(CO)_2(L)$ (L = CO, PR_3) was easily substituted by phosphines, cis- and trans- 2-butene, α-acetamidocinnamic acid and butadiene. Nucleophilic addition of $HNMe_2$ to the butadiene complex $[(\eta^5\text{-}C_5H_5)Mo(CO)_3(H_2C{:}CHCH{:}CH_2)]^+BF_4^-$ gave the β-aminoacyl chelate compound.[84]

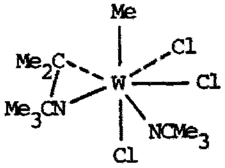


XXIX

Decomposition of $PhCH_2MgCl$ with WCl_6, yielded PhMe and $PhCH_2CH_2Ph$ as the principal products, in addition to minor amounts of stilbene and PhC⋮CPh, which suggested the formation of $(PhCH_2)_2WCl_m$ and $(PhCH_2)_3WCl_n$-type intermediates, followed by disproportionation.[85] Reaction of Me_3CNC with metallomethyl compounds gave insertion products in which Me groups were transferred to the NC ligand. With WMe_6, a transfer of 5 Me groups occurred to give XXX whose structure was determined by x-ray crystallographic analysis.[86] The W-C and W-N bond lengths in the azatungstacyclopropane moiety were 2.20 and 1.91 Å, respectively.



XXX



XXXI

Reaction of XXX with HCl gave XXXI, the structure of which was determined. Protonation of N in the azatungstacyclopropane ring of XXXI gave an increase in the W-N bond length in the ligand and shortening of the W-CMe_3 bond relative to XXX. $Mo(CNCMe_3)_6$ was also prepared. IR and ^{13}C, ^{31}P, and ^{1}H NMR spectra of the compounds were reported.[86]

Alkyne, Allyl and Nitrosyl Complexes

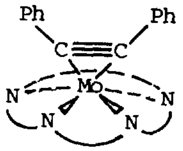
Alkynes. $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$ was prepared and characterized by spectroscopic and X-ray diffraction methods to examine the influence of the orbital occupancy of the HOMO upon the nature of the molybdenum-acetylene interaction.[87]

$$(\eta^5\text{-}C_5H_4Me)_2MoCl_2 + CF_3C{\equiv}CCF_3 \xrightarrow{Na/Hg} (\eta^5\text{-}C_5H_4CH_3)_2Mo(CF_3C{\equiv}CCF_3) \qquad (77)$$

The hexafluoro-2-butyne molecule was symmetrically coordinated to the Mo atom via two equivalent Mo-C bonds of 2.128(7) And 2.129(7)Å. This mode of coordination was accompanied by a ca. 0.08 Å lengthening of the carbon-carbon multiple bond with a concomitant decrease in its stretching frequency to 1778 cm^{-1}.[87] The nonbonding character of the HOMO was confirmed by a comparison of the corresponding structural parameters within the metallacyclopropene ring for $(\eta^5\text{-}C_5H_5)_2V(C_2(CO_2Me)_2)$ and $(\eta^5\text{-}C_5H_4CH_3)_2Mo(C_2(CF_3)_2)$.[87] The reaction of the tetrafluoroborato compounds $Cp(CO)_2(L)MoFBF_3$ with various alkynes gave mono- and bis-alkyne complexes $[CpMo(CO)(RCCR')_2]^+BF_4^-$ and $[CpMo(CO)(L)(RCCR')]^+BF_4^-$ (L = CO, $P(OPh)_3$, PEt_3, PPh_3; R = R' = H, Me, Ph; R = H, R' = Ph).[88]

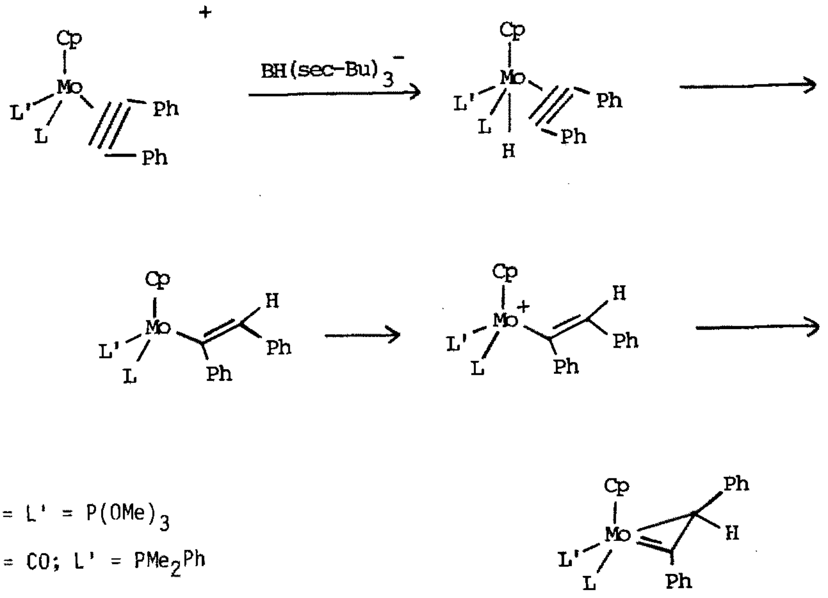
$$\begin{aligned}&Cp(CO)_2(L)MoFBF_3 + RCCR' \rightarrow \\ &[CpMo(CO)(RCCR')_2]^+BF_4^- + [CpMo(CO)L(RCCR')]^+BF_4^- + [CpMo(CO)_2LL']^+BF_4^-\end{aligned} \qquad (78)$$

The yields of the mono and bis alkyne complexes depend on the nature of L and that of the alkyne. The X-ray structure of $[CpMo(CO)(PPh_3)(PhCCPh)]^+BF_4^-$ was determined.[88] Reduction by lithium aluminum hydride of a toluene solution containing $Mo^{IV}(TTP)Cl_2$[4] (TTP = meso-tetra-p-tolylporphyrin, an excess of diphenylacetylene, and THF led to a green solution from which a violet compound $[MoTTP(PhC{\equiv}CPh)]\cdot C_6H_5CH_3$ was crystallized by addition of pentane.



XXXIII

The geometry about the metal was pseudo square pyramidal with the four porphynato nitrogens constituting the basal plane and the middle of the acetylenic carbon-carbon triple bond occupying the apical position. By comparison with the structure of $Cp_2Mo(PhC{\equiv}CPh)$ it was concluded that the $PhC{\equiv}CPh$ ligand in the porphyrin derivative was a four electron donor.[89] Reaction of a tetrahydrofuran solution of bis(trimethyl phosphite)diphenylacetylene(η^5-cyclopentadienyl)molybdenum tetrafluoroborate[3] with $KBH(sec\text{-}Bu)_3$ led to a rapid reaction and the formation of green crystalline complex.[90]



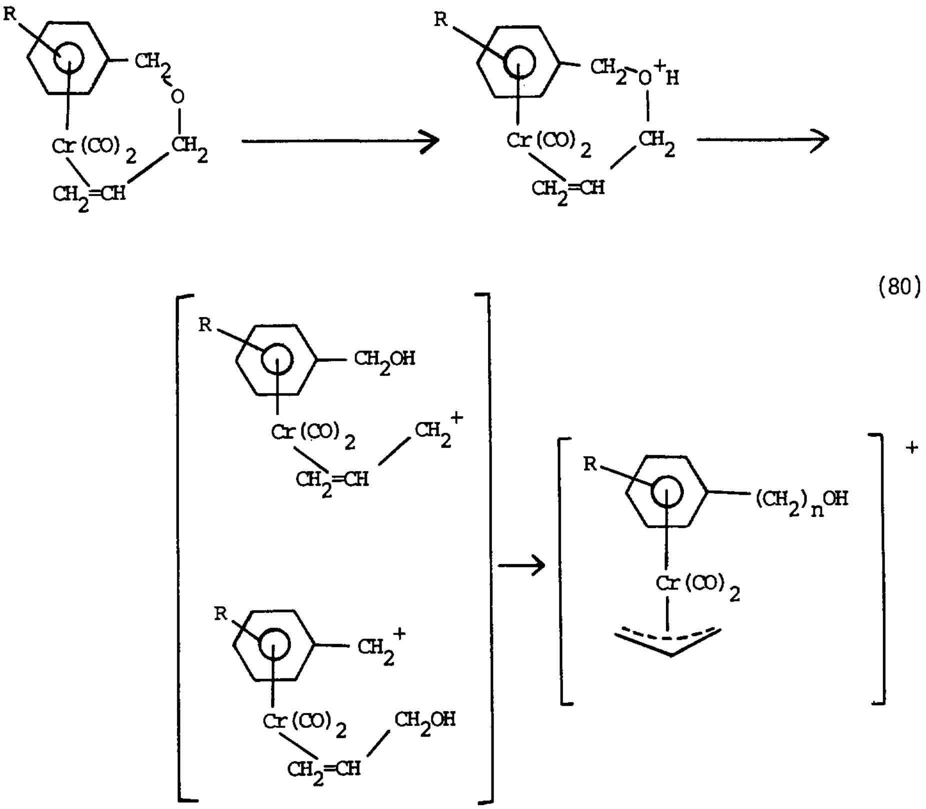
(79)

$L = L' = P(OMe)_3$

$L = CO;\ L' = PMe_2Ph$

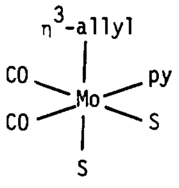
In order to confirm the indications from the NMR spectra that the complex was an alkylidene complex, a single-crystal X-ray diffraction study was undertaken.[90] The alkylidene complex contained the unusual three-electron η^2-bonded system Mo=CPhCHPh where the molybdenum was in a distorted square-pyramidal environment with angles P(1)-Mo-P(2) = 91.4(1) and C(4)-Mo-C(3) = 38.3(1)°.[90]

Allyls. The proton cleavage of chelate dicarbonylchromium complexes in the presence of benzyl and phenyl allyl ethers resulted in the formation of cationic areneallyldicarbonylchromium complexes.[91] A one step synthesis of these compounds upon ultra-violet irradiation of arenetricarbonylchromium compounds and allyl alcohol and its derivatives in the presence of hydrofluoroboric acid was described.[91] The following scheme was suggested.

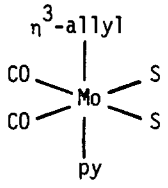


(80)

The substitution reactions of the $[MoBr(\pi\text{-allyl})(CO)_2(L)_2]$ complexes (L = acetonitrile, pyridine) with several xanthates and dithiocarbamates were studied.[92] The reaction led to the formation of $M^I[Mo(S,S)_2(\pi\text{-allyl})(CO)_2]$ complexes [(S,S) = methyl-, ethylxanthate or N-ethyl-, N-methyl- and N,N-diethyldithiocarbamate; M^I = Na or K] for L = acetonitrile and to $[Mo(S,S)(\pi\text{-allyl})(CO)_2(py)]$ complexes for L = pyridine. The solid state geometry was suggested as XXXIII while the solution structure was indicated by NMR as XXXIV.[92]

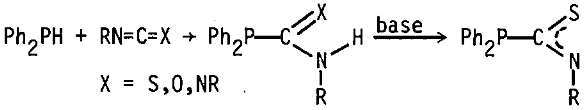


XXIII



XXXIV

The complexes [MBr(η^3-allyl)(CO)$_2$(bipy)] (M = Mo, W, reacted with alkylxanthates (M^{I}Rxant), and N-alkyldithiocarbamates (M^{I}RHdtc) (M^I = Na or K), yielding complexes of general formula [M(S,S)(η-allyl)(CO)$_2$(bipy)].[93] A monodentate coordination of the (S,S) ligand was deduced from spectral data. No reaction products were isolated from reaction of [MoBr(π-allyl)(CO)$_2$(dppe)] with xanthates or N-alkyldithiocarbamates.[93] The functionally substituted phosphines LH = Ph$_2$PC(X)N(H)R (X = S, R = Ph, Me; X = O, R = Ph; X = N-p-tol, R = p-tol) behaved an neutral monodentate (LH) ligands in substitution reactions with M(CO)$_3$CpCl (M = Mo, W), forming M(CO)$_2$CpCl(LH) with P bonded to the metal atom.[94] Deprotonation under the influence of the base Et$_3$N occurred only in the case of X = S and the chelate complexes M(CO)$_2$Cp(L$^-$) were formed with coordination via P and S.

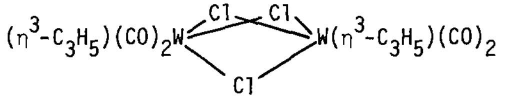

(81)

The related ligand Me$_2$NC(S)N(H)R (R = Me, Ph) reacted in the presence of Et$_3$N to form M(CO)$_2$(η^5-C$_5$H$_5$)(L$^-$) (M = Mo, W; L$^-$ = Me$_2$NC(S)NR$^-$; R Me, Ph) with coordination via S and N.[94] Tetramethyldithiobiuret (Me$_2$NC(S)N(H)C(S)NMe$_2$) reacted with Mo(CO)$_3$(η^5-C$_5$H$_5$)Cl only when Et$_3$N was present and a complex with a six-membered ring was formed. The molybdenum complexes were prepared by thermal reactions while the tungsten complexes were also prepared photochemically.[94] Ph$_2$P(O)C(S)N(H)R (R = Me, Ph) also reacted with M(CO)$_3$(η^5-C$_5$H$_5$)Cl (M = Mo, W) in the presence of Et$_3$N to give M(CO)$_2$(η^5-C$_5$H$_5$)(Ph$_2$P(O)C(S)NR).[95] The deprotonated ligand also coordinated in a bidentate manner through N and S to give a four-membered ring system.

$$\begin{array}{l} \mathrm{M(CO)_3(\eta^5\text{-}C_5H_5)Cl} + \mathrm{Ph_2P(O)C(S)N(H)R} \\ \qquad \mathrm{(M = Mo,\ W)} \qquad\qquad \mathrm{(R = Me,\ Ph)} \\ \xrightarrow{\mathrm{Et_3N}} \mathrm{M(CO)_2(\eta^5\text{-}C_5H_5)(Ph_2P(O)C(S)NR)} + \mathrm{CO} + \mathrm{Et_3NHCl} \end{array} \qquad (82)$$

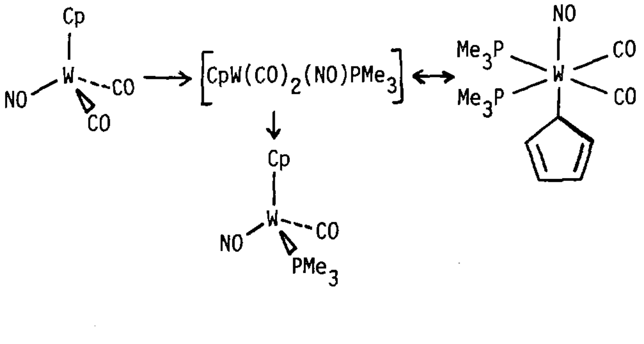
$$\begin{array}{l} \mathrm{Mo(CO)_4Cl_2} + 2\ \mathrm{Ph_2P(O)C(S)N(H)R} \\ \qquad\qquad\qquad \mathrm{(R = Me,\ Ph)} \\ \rightarrow \mathrm{Mo(CO)_3(Ph_2P(O)C(S)NR)_2} + \mathrm{CO} + 2\ \mathrm{Et_3NHCl} \\ \qquad\qquad \downarrow \mathrm{PPh_3} \\ \ \mathrm{Mo(CO_2(PPh_3)(Ph_2P(O)C(SN)NR)_2} + \mathrm{CO} \end{array} \qquad (83)$$

$M(CO)_3(PPh_3)_2Cl_2$ (M = Mo, W) reacted with $Ph_2P(O)C(S)N(H)R$ (R = Me, Ph) in the presence of Et_3N to give complexes in which the central metal atoms were seven coordinate through two ligands bonded via O and S to form five-membered ring systems, one PPh_3, and two CO groups.[95] A series of carboxylate complexes $[Mo(CO)_2(\eta^3\text{-}RC_3H_4)bipy(O_2CR')]$ (R = H, R' = Me, Ph, CF_3, C_2F_5 or C_3F_7; R = Me, R' = CF_3, C_2F_5 or C_3F_7 were prepared and the solution properties of the fluorinated derivatives examined.[96] Each β-methylallyl compound contained a symmetrical trihapto ligand and adopted a pseudooctahedral structure with approximate C_s symmetry over the temperture range -90 to +50°C. The allyl derivatives existed in two isomeric forms in solution at room temperature, one with local C_s symmetry and the other dynamic, assuming C_1 symmetry at low temperatures. The spectral observations on the dynamic species and high temperature interconversion of these two isomers were accounted for by an intramolecular trigonal twist rearrangement.[96] The complex $[Et_4N]W_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4$ was characterized by X-ray crystallography.[97] In the anion the two independent W atoms were each bonded to an allyl group and two carbonyl groups in a fac-arrangement. The two metal atoms were bridged by three Cl atoms.[97]



XXXV

Nitrosyls. The reaction of $CpW(CO)_2(NO)$ with $P(CH_3)_3$ proceeded rapidly at 25°C to give $CpW(CO)(NO)[P(CH_3)_3]$.[98] The rate of formation was found to be $4.48 \times 10^{-2}\ M^{-1}\ sec^{-1}\ [P(CH_3)_3]$ at 25.0°C in THF. In neat $P(CH_3)_3$ at -23°C, the product was $(\eta^1\text{-}C_5H_5)W(CO)_2(NO)[P(CH_3)_3]_2$.[98]

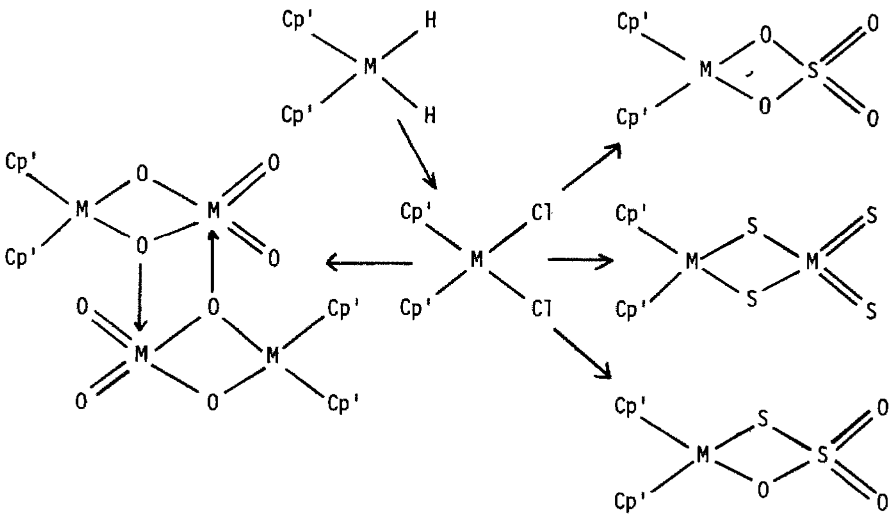


(84)

In dilute solution, the η^1-complex decomposed to initially give a 2:1 mixture of $CpW(CO)_2NO$ and $CpW(NO)(CO)(P(CH_3)_3)$. The mixture was then converted to $CpW(NO)(CO)(P(CH_3)_3)$. The reaction of $(\eta^5\text{-}C_5H_5)Mo(CO)_2(NO)$ with $P(CH_3)_3$ was 6.1 times faster than that of the tungsten analog.[98] The anionic thiocarbonyl complexes $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ reacted with N-methyl-N-nitroso-p-toluenesulfonamide and acid or with $NOPF_6$ to give $CpW(CO)(CS)NO$ and $HB(pz)_3W(CO)(CS)NO$.[99] The $CpW(CO)_2CS^-$ complex reacted with chloro-2,4-dinitrobenzene (DNP-Cl) to yield the mercaptocarbyne $Cp(CO)_2W{\equiv}C\text{-}S\text{-}DNP$. Analogous reactions of $CpW(CO)_2CS^-$ with MeI and EtI gave spectroscopic evidence for the formation of the less stable $CpW(CO)_2CS\text{-}R$ mercaptocarbyne complexes.[99] The hydrotris(1-pyrazolyl)borate complex $HB(pz)_3W(CO)_2CS^-$ reacted with MeI, EtI, and DNP-Cl to give the stable mercaptocarbyne derivatives $HB(pz)_3W(CO)_2CS\text{-}R$. These reactions of $CpW(CO)_2CS^-$ and $HB(pz)_3W(CO)_2CS^-$ with alkyl halides contrast with those of $CpW(CO)_3^-$ and $HB(pz)_3W(CO)_3^-$, which give σ-bonded W-R complexes.[99] Unexpectedly, $CpW(CO)(CS)(PPh_3)I$ reacted with LiPh to give the mercaptocarbyne $CpW(CO)(PPh_3)CS\text{-}Ph$, whose structure was established by an X-ray crystallographic determination. A stable mercaptocarbyne, $HB(pz)_3W(CO)_2CS\text{-}Me$, was isolated from the reaction of trans-$HB(pz)_3W(CO)_2(CS)I$ with LiMe. Possible mechanisms for the reactions of LiR with W(CS)I-containing complexes to give $W{\equiv}C\text{-}S\text{-}R$ and I^- were considered; a radical mechanism appeared most likely.[99] On the basis of the ESR spectra of nitrosyl diethyldithiophosphate complexes of Cr(I), which vary in relation to the concentration of PEt_3, the probable structural formulas of the compounds formed with 1 and 2 equivalents of PEt_3 were proposed.[100] With the introduction of 2 equivalents of PEt_3 a shift of the chelate ring occurred; PEt_3 ligands had cis configurations. As a result of hydrolysis, complexes with cis and trans configurations of the PEt_3 were obtained which suggests the dominating role of the organophosphorus ligands in the ligand field of the equatorial plane.[100] The series of nitrosyl Cr complexes of type $[CrNO(CN)_x(en)_y]^{n\pm}$ were prepared and studied: $K[CrNO(CN)_2(en)(OH)].4H_2O$; $[CrNO(CN)_2(en)(H_2O)]$; $Cr_2(NO)_2(CN)_4(en)_3]$; $[Cr_2(NO)_2(CN)_2(en)_4]Cl_2.2H_2O$; $[Cr_2(NO)_2(en)_5]Cl_4.6H_2O$.[101] The dimers contained bridged ethylenediamine with structure determined by the magnetic and spectroscopic (EPR, UV and IR) methods. The effect of the coordinated ligands upon the electronic structure of the molecular unit (CrNO) was determined.[101]

Cyclopentadienyl and Arene Complexes

Cyclopentadienyls. A number of high valent Group VI cyclopentadienyl complexes were reported in 1981. Cp_2Cr reacted with PX_3 (X = Cl, Br, I) to give $CpCrX_2$ (same X), whereas oxidative additions of IBr or ICl to Cp_2Cr gave the corresponding Cp_2CrIX (X = Cl, Br).[102] The compounds $[Mo(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}O)_2MoO_2]_2$, R = H, Me or Bu, $[Mo(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}S)_2MoS_2]_2$, R = H, Me or Bu, $[W(\eta^5\text{-}C_5H_5)_2(\mu\text{-}O)_2WO_2]_2$, $[WCp_2(\mu\text{-}S)_2MoS_2]$, $[MoCp_2(\mu\text{-}O)_2WO_2]_2$, $[WCp_2(\mu\text{-}S)_2WS_2]$, $[Mo(\eta^5\text{-}C_5H_4R)_2X_2]$, where R = Me or Bu and X = H or Cl, $[Mo(\eta^5\text{-}C_5H_4R)_2(\mu\text{-}O)(\mu\text{-}X)SO_2]$, where R = Me or Bu and X = O or S, were prepared and their properties described.[103]



The reaction of chromocene with trifluoroacetic acid gave the paramagnetic ionic complex $[Cp_2Cr]^+[CpCr(OOCCF_3)_3]^-$.[104] Upon recrystallizing from THF, the ionic complex gave the monomer $CpCr(OOCCF_3)_2\cdot THF$ which under treatment with an equimolar quantity of pyridine was transformed to violet needles of $CpCr(OOCCF_3)_2\cdot Py$.

$$\begin{tikzcd}
\mathrm{Cp_2Cr + CF_3C(O)OH} \arrow[r] & \mathrm{{[Cp_2Cr]^+[CpCr(O(O)CCF_3)_2]^-}} \arrow[d, "\mathrm{THF}"] \\
\mathrm{CpCr(O(O)CCF_3)_2\cdot Py} & \mathrm{CpCr(O(O)CCF_3)_2\cdot THF} \arrow[l, "\mathrm{Py}"'] \arrow[d, "\mathrm{CF_3C(O)OH,}"] \\
 & {} \arrow[d, "\mathrm{Py}"] \\
 & \mathrm{Cr(Py)_3(O(O)CCF_3)_3}
\end{tikzcd} \qquad (86)$$

The successive action of excess trifluoroacetic acid and pyridine on the THF adduct afforded the octahedral monomer $(C_5H_5N)_3Cr(OOCCF_3)_3$.[104] This complex was also obtained along with $[CpCrS]_4$ from the binuclear complex $(CpCrSCMe_3)_2S$.[104] Reaction of chromocene with acids of non-coordinating anions ($HClO_4$; HBF_4, etc.) provided spectral evidence for $CpCr(H_2O)_n{}^{+2}$.[105]

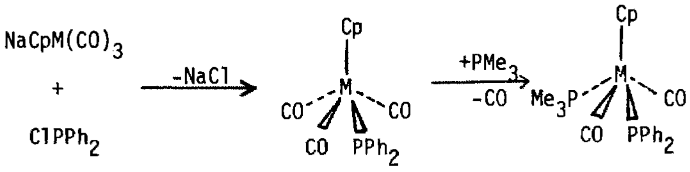
$$Cp_2Cr + 2H^+ \xrightarrow[H_2O]{HX} CpCr(H_2O)_n{}^{+2} + 1/2\ H_2 + C_5H_6 \qquad (87)$$

Since this represented an organometallic Cr(III) center, the rate of substitution reactions,

$$CpCr(H_2O)_3{}^{+2} + Cl^- \rightarrow CpCr(H_2O)_2Cl^+ + H_2O \qquad (88)$$

was of interest. The approximate second order rate constant of 10 $M^{-1}\ s^{-1}$ was considerably larger than rate constants for classic Cr(III) substitution reactions.[105] Refluxing bis(η^5-cyclopentadienyl)oxomolybdenum dichloride or its bis(η^5-indenyl)-analog with 8-quinolinol in THF gave complexes whose molecular formulas were $Cp_2MoOCl_2\cdot 2C_9H_7OH$ and $(C_9H_7)_2MoOCl_2$, respectively.[106] The reaction of elemental sulfur with $(CH_3)_5C_5Mo(CO)_3H$ produced $[(CH_3)_5C_5MoS_2]_2$ and $[(CH_3)_5C_5MoS_5]_2$ in 65% and 10% yields, respectively.[107] The tetrasulfide dimer contained a planar $Mo_2(\mu\text{-}S)_2$ unit with terminal sulfido ligands in the anti configuration. In the presence of oxygen, the complex was converted to $[(CH_3)_5C_5MoO(S)]_2$. The molecule is similar to the tetrasulfide with oxo ligands replacing the terminal sulfido ligands.[107] The metal ions in the decasulfide were each coordinated to a single sulfur atom of a bridging disulfide ligand. The coordination sphere of each molybdenum ion also included two η^2-S_2 ligands and the η^5-$(CH_3)_5C_5$ ligand. The reactions of $[CH_3C_5H_4Mo(CO)_3]_2$ and of $[C_5H_5Mo(CO)_3]_2$ with elemental sulfur resulted primarily in the formation of insoluble materials.[107] The dimer $[CH_3C_5H_4MoS_2]_2$ was isolated from the former reaction in very low yields. All complexes were characterized by X-ray crystallography. The reactions with H_2, ethylene and acetylene were also reported.[107]

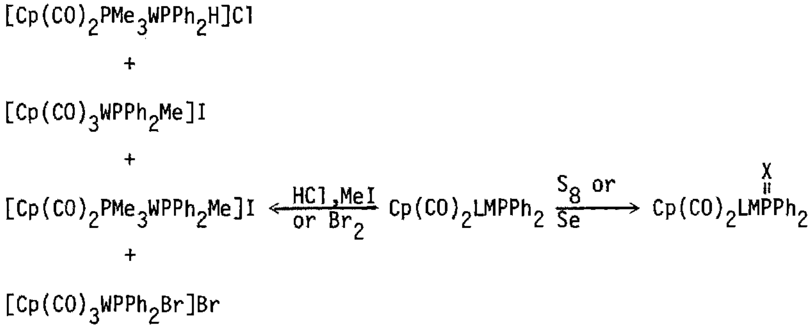
$Na[M(CO)_3Cp]$ (M = Mo, W) and Ph_2PCl reacted to give the transition metal substituted phosphines $Cp(CO)_3MPPh_2$ which were transformed to trans-$Cp(CO)_2$-PMe_3MPPh_2 via CO/PMe_3-exchange.[108]



(89)

M = Mo,W

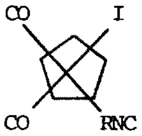
The high nucleophilicity of the phosphines was demonstrated by the spontaneous formation of $[Cp(CO)_2LMPPh_2R']Hal$ (L = CO, PMe_3; R' = H, Me, Br) with HCl, MeI, Br_2 or $Cp(CO)_2LMPPh_2S(Se)$ with elementary sulfur or selenium, respectively.[108]



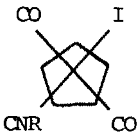
$$\begin{array}{l} [Cp(CO)_2PMe_3WPPh_2H]Cl \\ \quad + \\ [Cp(CO)_3WPPh_2Me]I \\ \quad + \\ [Cp(CO)_2PMe_3WPPh_2Me]I \xleftarrow[\text{or } Br_2]{HCl,MeI} Cp(CO)_2LMPPh_2 \xrightarrow[Se]{S_8 \text{ or}} Cp(CO)_2LM\overset{X}{\overset{\|}{P}}Ph_2 \\ \quad + \\ [Cp(CO)_3WPPh_2Br]Br \end{array} \qquad (90)$$

M = Mo or W
L = Co, PMe_3
X = S, Se

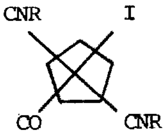
$Cp(CO)_3W\overset{X}{\overset{\|}{P}}Ph_2$ were easily converted to $Cp(CO)_2W[\eta^2\text{-}PPh_2X]$ with loss of CO on thermal treatment or photolysis.[108] The new compounds were characterized by IR spectroscopy, elementary analysis and detailed NMR spectroscopy.[108] The reaction between $CpM(CO)_3I$ (M = Mo, W) and isonitriles, RNC, (RNC = $PhCH_2NC$, t-BuNC and 2,6-dimethylphenylisocyanide (XyNC)) was catalyzed by the dimer $[CpM(CO)_3]_2$ to yield $CpM(CO)_{3-n}(RNC)_nI$ (n = 1-3) and $[CpMo(RNC)_4]I$.[109]



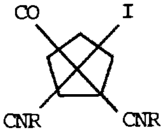
XXXVI



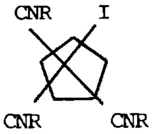
XXXVII



XXXVIII

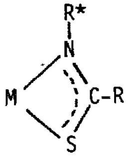


XXXIX



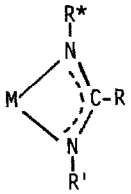
XL

The complexes $Cp_2Mo_2(CO)_{6-n}(RNC)_n$ (n = 1, 2) were prepared in moderate yield from the direct reaction between $[CpMo(CO)_3]_2$ and RNC, and also catalyzed the above reaction. A reaction pathway involving a fast non-chain radical mechanism and a slower chain radical mechanism was proposed to account for the catalyzed reaction.[109] $Cp(CO)_2$Mo-benzamidinato complexes with various N-substituents were investigated by ^1H NMR spectroscopy at 400 MHz.[110]

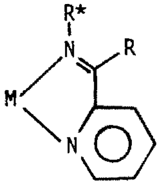


M = $CpMo(CO)_2$

XLI

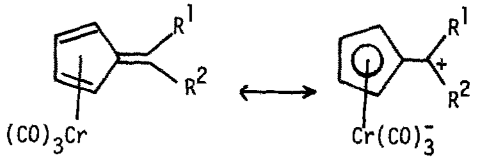


XLII

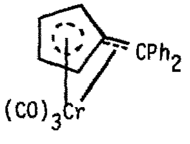


XLIII

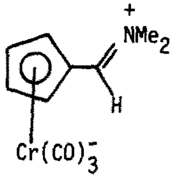
The preferred conformations of the thermodynamically more stable isomers were established by means of Nuclear-Overhauser-Effect Difference Spectroscopy.[110] The structures and properties of pentafulvenes π-complexed with $(OC)_3Cr$ were discussed and compared with those of the uncomplexed pentafulvenes.[111]



(91)



XLIV



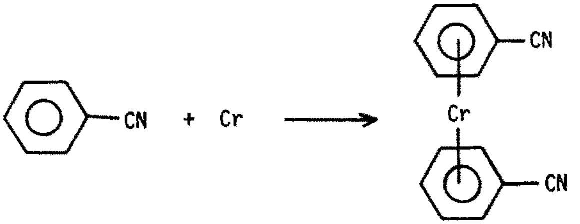
XLV

Rotational isomerization of 6-dimethylaminofulventungsten tricarbonyl in media of various acidities were studied by dynamic ^{1}H NMR spectroscopy, and the kinetic parameters of the rotation about the C(6)$\overset{\cdots}{-}$N bond determined.[112] The rate of rotation about this bond increased in weakly acidic media and decreased in strongly acidic solutions with respect to that in the parent complex. This dependence indicated that the complex has dual reactivity in protonation, i.e. in weakly acidic media the protonation involved the nitrogen atom, and in highly acidic solutions the tungsten atom.[112]

$$[C_5H_4CHN(CH_3)_2]W(CO)_3 \xrightarrow{H^+} \begin{cases} [C_5H_4CHN^{+}H(CH_3)_2]W(CO)_3 \\ [C_5H_5CHN(CH_3)_2]^{+}W(CO)_3 \\ [C_5H_{4-n}\overset{*}{H}_nCHN(CH_3)_2]W(CO)_3 \end{cases} \qquad (92)$$

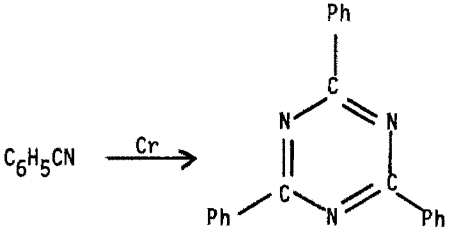
On increasing the acidity of the medium the ammonium form of the complex was converted into the W-protonated complex. A study of deuterium exchange in acidic media has shown that the H or D atom attached to the W atom may be readily exchanged for the deuteron (or the proton, respectively) of the acid, while the H atoms of the cyclopentadienyl ring do not undergo deuterium exchange under the conditions investigated.[112] Protonation involving the Cp ring of the complex was not observed.[112] The structures of $(C_5H_5)Mo(CO)_2(NHR)$-$[C(NC_5H_4)R']$ with R = $-CH(CH_3)(C_6H_5)$, R' = Me, and R = iso-Pr, R' = Ph were reported.[113] Both compounds were characterized by the existence of a 3-membered ring formed by a π-aminomethylene ligand bonded to the Mo through its C and N atoms.[113] The coordination polyhedron around the Mo was a distorted square pyramid. The orientation of the pyridine ring was determined by the formation of a strong intramolecular H-bond between N and the N(1)-H(6) H of the aminomethylene moiety.[113]

Arenes. Microcalorimetric measurements at 520-523 K of the heats of thermal decomposition and of iodination of bis-(benzene)molybdenum and of bis-(toluene)-tungsten led to the values (kJ mol^{-1}): $\Delta H_f^o[Mo(\eta^6\text{-}C_6H_6)_2]$ = (235.3 ± 8) and $\Delta H_f^o[W(\eta^6\text{-}C_7H_8)_2]$ = (242.2 ± 8) for the standard enthalpies of formation at 25°C.[114] The corresponding $\Delta H_f^o(g)$ values, using available and estimated enthalpies of sublimation, are (329.9 ± 11) and (352.2 ± 11) respectively, from which the metal-ligand mean bond-dissociation enthalpies, $\overline{D}$(Mo-benzene) = (247.0 ± 6) and $\overline{D}$(W-toluene) = (304.0 ± 6) kJ mol^{-1}, were derived.[114] Bis(benzonitrile)chromium was isolated from the reaction of benzonitrile with chromium vapor.[115]



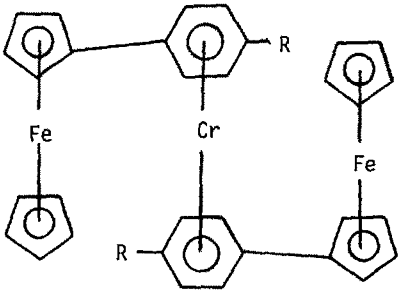
(93)

The major process was accompanied by cyclotrimerization of benzonitrile to form 2,4,6-triphenyltriazine.[115]



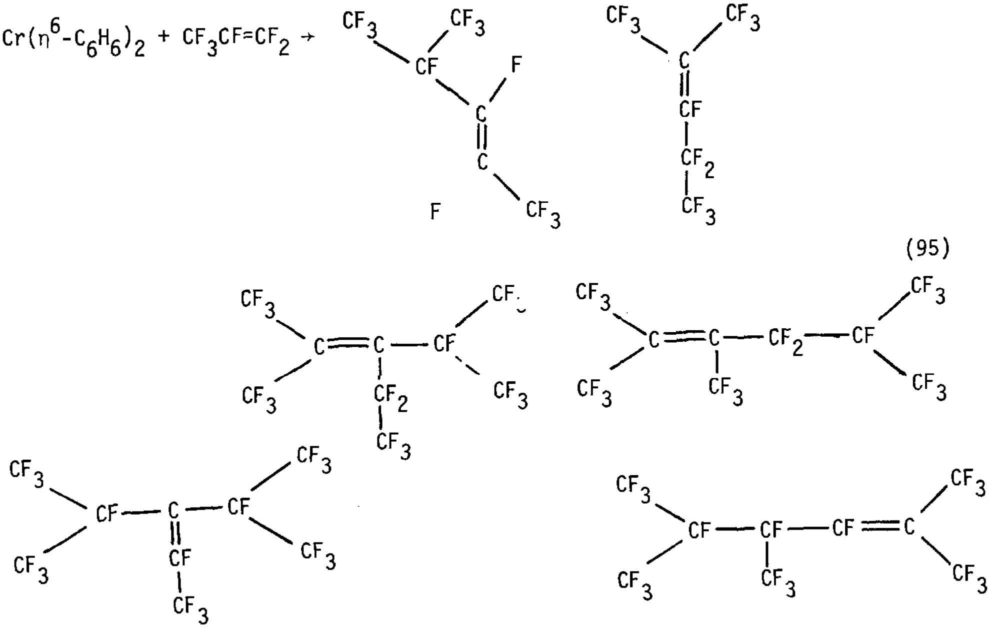
(94)

Phenyl bromide reacted with chromium to give insignificant amounts of cationic bis(arene)chromium compounds containing bromobenzene, diphenyl and benzene as ligands.[115] The crystal and molecular structures of hexaethylbenzene, tricarbonyl(hexaethylbenzene)chromium(0), tricarbonyl(hexaethylbenzene)molybdenum(0), and dicarbonyl(hexaethylbenzene)(triphenylphosphine)chromium(0) were determined.[116] The methyl groups in all except the PPh_3 complex projected alternately above and below the plane of the benzene ring. In the tricarbonyl complexes three of the ethyl groups were eclipsed by the carbonyl groups; the corresponding methyl groups projected toward the uncomplexes side of the ring.[116] The barrier to site exchange ($\Delta G^{\neq}$) of the ethyl groups was ca. 11.5 kcal mol^{-1}, as determined by dynamic NMR spectroscopy. The structure of the PPh_3 substituted complex differed markedly in that all six methyl groups projected toward the uncomplexed side of the ring, and the molecule assumed a staggered rather than an eclipsed conformation.[116] This conformational change has been ascribed to steric effects of the triphenylphosphine group.[116] Fluorinated complexes were also investigated crystallographically.[117] $[p\text{-}C_6H_4(CF_3)_2]_2Cr^0$, $[m\text{-}C_6H_4(CF_3)_2]_2Cr^0$, and $[m\text{-}C_6H_4\text{-}(CF_3)Cl]_2Cr^0$ crystallized as discrete sandwich complexes having C_2, C_1, and C_i symmetry, respectively.[117] Ring carbon atoms of the π-arene ligands were planar in each case, and opposite rings within the same complex were approximately parallel. A substantial rotation from the eclipsed orientation of ring carbon atoms, amounting to 17 and 10°, was observed for the two bis(trifluoromethyl)-benzene complexes.[117] These results suggested that the CF_3 group does not behave as a strongly σ-electron-withdrawing group such as fluorine, supporting the notion that the polar effect of CF_3 was a "through space" rather than a "through the bond" effect.[117] An investigation of hindered rotation about the metal-ligand bond in a bis(arene)-transition metal complex in solution, was accomplished by ^1H and ^{13}C NMR spectroscopy of the conformational interconversion of two rotamers of bis(1-methyl-4-t-butyl-η-benzene)chromium(0).[118] The activation parameters were determined as $\Delta G^{\neq} = 40.4 \pm 4$ kJ mol^{-1}, $\Delta H^{\neq} = 34.0 \pm 1.6$ kJ mol^{-1} and $\Delta S^{\neq} = -22 \pm 8$ JK^{-1} mol^{-1}.[118] Ferrocenyl-substituted bisarenechromium complexes



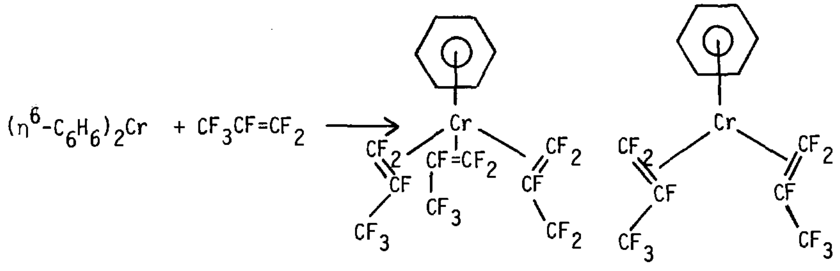
XLVI

were obtained by reacting Cr vapor with phenyl- or p-tolylferrocene in liquid nitrogen, followed by warming.[119] Oxidation of the neutral complexes gave cationic Cr^+ complexes, which were isolated as their iodides or tetraphenylborates.[119] In the presence of zerovalent η^6-bis(benzene)chromium(0), perfluoropropylene was found to undergo oligomerization under very mild conditions to dimers and trimers in the ratio of 2.5-3.0 to 1.[120]



(95)

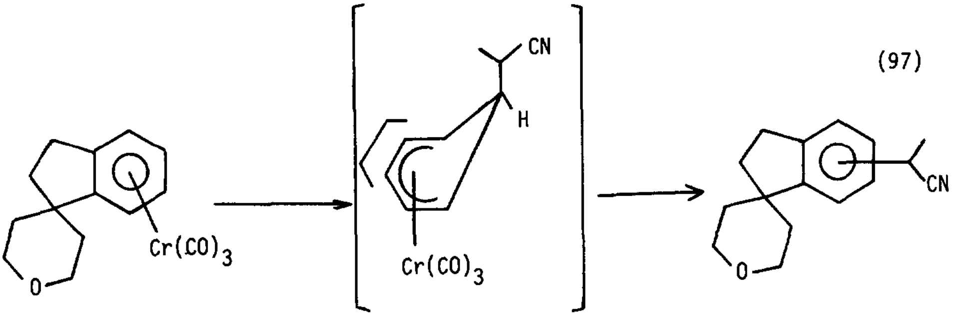
One mole of metal complex could catalyze the conversion of 50 mol of perfluoropropylene. On the basis of ^{19}F NMR, the structures of the dimers and the trimers were suggested.[120] In benzene solution, perfluoropropylene was shown not to be catalytically oligomerized by fluoride ion (KF, CrF_2 or $(CH_3)_4NF$) (nor by monovalent π-dibenzenechromium(I)). A possible mechanism of the reaction was proposed involving intermediates as shown below.[120]



(96)

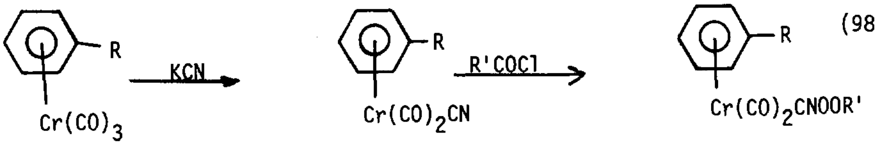
The effect of the metal catalyst was investigated by comparison of the oligomerization of perfluoropropylene catalyzed by four η^6-bis(arene)chromium(0) complexes (arene = benzene, diphenyl, 1,3,5-trimethylbenzene and hexamethylbenzene).[121] Besides dimers and trimers, two defluorotrimers were found to be present in the oligomer mixtures. The formation was shown to be derived from a trimer by hydrogenation followed by elimination of two moles of hydrogen fluoride.[121]

The product distribution obtained in addition reactions of $^{-}CH(CH_3)CN$ to an arenechromium tricarbonyl was studied.[122] The major product obtained after oxidative removal of the metal corresponded to nucleophilic addition on an arene carbon atom which is in an eclipsed position with respect to the carbonyl group of the $Cr(CO)_3$ unit of the most stable conformer.



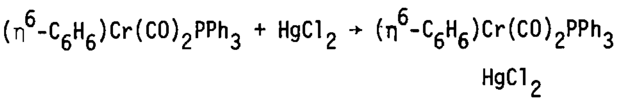
(97)

The synthesis of the corresponding acid represented an example of arenechromium tricarbonyl chemistry applied to synthesis of an organic compound having pharmaceutical properties which by classical methods could only be synthesized via a multi step process.[122] A series of various functionalized isocyanide ligands CNCOR (R = C_6H_5, $N(CH_3)_2$, OC_2H_5, SC_2H_5) were prepared as chromium complexes.[123] The IR and mass spectroscopic studies indicated that the presence of carbonyl function in the α position to the nitrogen resulted in the ligand being a better electron acceptor than CO.[123]



(98)

The strengthening of the metal-carbon bond, with respect to M-CO, allowed access to centro-chiral complexes, and also resulted in a more labile chromium-arene bond, giving a synthetic route to $Cr(CO)_5(CNCOC_6H_5)$.[123] $(\eta^6\text{-}C_6H_6)Cr(CO)_2(PPh_3)$ reacted with aprotic acids, $HgCl_2$ and $SnCl_4$, at the chromium atom.[124]

 (99)

$$(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3 + HgCl_2 \rightarrow \underset{HgCl_2}{(\eta^6\text{-}C_6H_6)Cr(CO)_2PPh_3} \qquad (99)$$

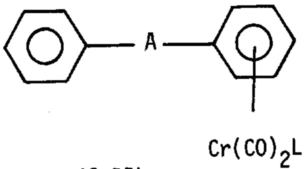
The formed complexes, $C_6H_6Cr(CO)_2(PPh_3)(HgCl_2)$ had higher carbonyl frequencies in addition to higher intensities.[124] The synthesis of the chromium tricarbonyl complex of 1,4-(dimethylsilyl)benzene was achieved by refluxing the latter compound with $Cr(CO)_6$.[125]

$$1,4\text{-}(HSiMe_2)_2C_6H_4 + Cr(CO)_6 \rightarrow \eta^6\text{-}[1,4\text{-}(HSiMe_2)_2C_6H_4]Cr(CO)_3 + 3CO \qquad (100)$$

The thermally stable complex was characterized by IR and NMR. The usefulness of $\eta^6\text{-}[1,4\text{-}HSiMe_2\text{-}C_6H_4\text{-}SiMe_2H]Cr(CO)_3$ as a synthetic precursor was demonstrated by the compound's reaction with $Co_2(CO)_8$.[125]

$$\eta^6\text{-}[1,4\text{-}HSiMe_2\text{-}C_6H_4\text{-}SiMe_2H]Cr(CO)_3 + Co_2(CO)_8 \rightarrow \qquad (101)$$
$$\eta^6\text{-}[1,4\text{-}(CO)_4CoSiMe_2\text{-}C_6H_4\text{-}SiMe_2Co(CO)_4]Cr(CO)_3 + H_2$$

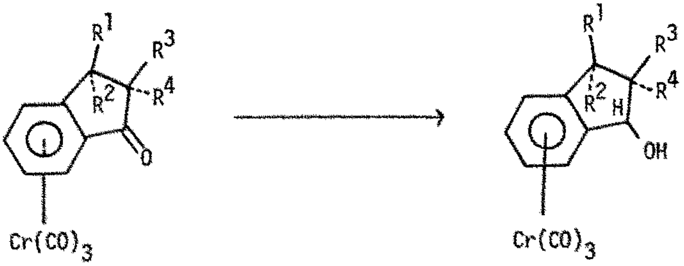
The identification of bis((tetracarbonylcobaltio)dimethylsilyl) containing a $Cr(CO)_3$-complexed bridging aromatic group was confirmed by infrared and NMR measurements.[125] Hydrogen isotopic exchange reactions of $ArCr(CO)_2L$ complexes ($L = CO$, PPh_3, and Ar = biphenyl, diphenylmethane, dibenzyl, diphenyloxide and benzophenone) in CF_3COOD was studied.[126]



L=CO,PPh_3

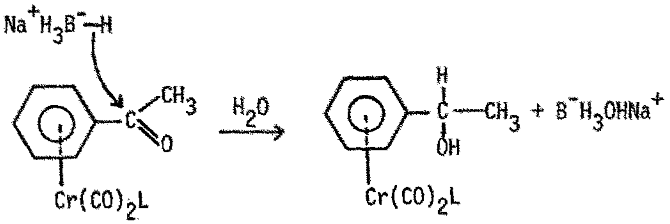
XLVII

The rate constants determined, show that in the series of complexes such ring substituents as Ph, $PhCH_2$, $PhCH_2CH_3$, PhO had no effect on the rate, in sharp contrast with the reaction of the corresponding free binuclear arenes. A quantitative estimation indicated that the o-, m- and p-positions in the π-coordinated ring of the complexes have almost the same reactivity. The effect of the π-coordination with the transition metal atom on the uncoordinated ring of the binuclear aromatic π-ligand was also discussed.[126] Tricarbonylchromium complexes of p-F-, p-Cl-, p-OCH_3, p-CH_3- and o-CH_3-monosubstituted benzophenones were prepared and characterized.[127] Included in the series were the coordination isomers of the p-CH_3 and o-CH_3 compounds. Changing the substituent on the uncomplexed ring caused only a small effect on the carbonyl stretching frequencies of the $Cr(CO)_3$ group. In the ^1H NMR spectra, the change in the upfield shift of the protons on the complexed ring was small but indicated some electron delocalization between the two rings.[127] Borohydride reduction of endo- and exo-α- and β-alkylindanonetricarbonylchromium in protic solvents was stereospecific leading solely to the endo-alcohol whose configuration was ascertained by IR and NMR.[128]



(102)

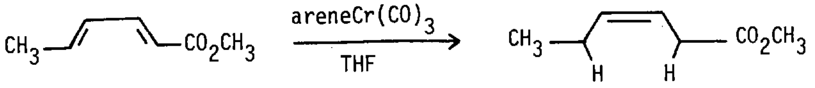
This stereospecificity together with an easy and quantitative decomplexation of the organometallic alcohols has allowed the liberation of cis- and trans-indanols.[128] The kinetic study of $NaBH_4$ reduction of acetophenones complexed by various $Cr(CO)_2L$ moieties showed electronic control of the arene ligand reactivity by the organometallic unit.[129]



(103)

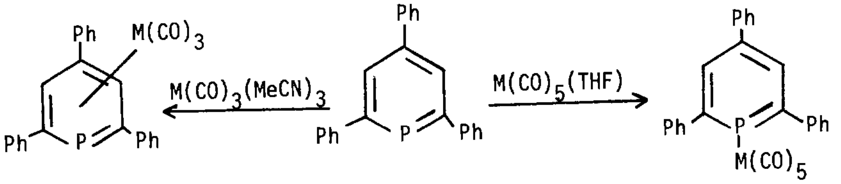
($L=CO, CS, P(OMe)_3, P(OPh)_3, PPh_3, PBu_3$)

The relative rates were: L = CS, 100; L = CO, 61; L = $P(OPh)_3$, 12; L = $P(OMe)_3$, 6; L = PPh_3, 3; L = PBu_3, 0.8.[129] Substituents bearing a heteroatom in the α position to an $Cr(CO)_3$-complexed arene group induced a strong perturbation in the six-electron ligand-metal bond allowing an increased catalytic efficiency of these derivatives under mild conditions.[130]



(104)

4-R-γ^3-arsenines and 2-aryl-4-R-λ^3-arsenines, reacted smoothly with tricarbonyltris(acetonitrile)chromium(-molybdenum, or -tungsten)(0) to give the stable η^6-(λ^3-arsenine)tricarbonylchromium(-molybdenum, or -tungsten)(0) complexes.[131]

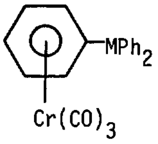


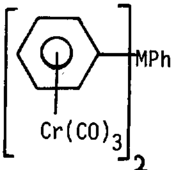
(105)

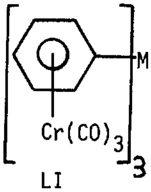
M = Cr, Mo

M = Cr, Mo, W

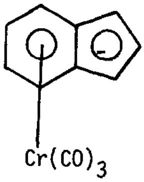
The IR, ^1H NMR, ^{13}C NMR, UV and mass spectra of these complexes were discussed.[131] The compounds $PhM_2(\eta^6\text{-}C_6H_5)Cr(CO)_3$, $PhM[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_2$ and $M[(\eta^6\text{-}C_6H_5)Cr(CO)_3]_3$ (M = Bi, Sb) were prepared by treating Ph_3Bi or Ph_3Sb with $(NH_3)_3Cr(CO)_3$.[132]


XLIX

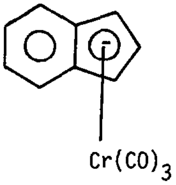

L


LI

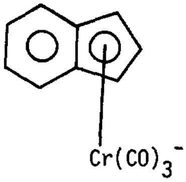
Reaction of Ph_3P gave 80% $(Ph_3P)Cr(CO)_5$ and 20% $(Ph_3P)_2Cr(CO)_4$.[132] Mass spectra of the negative ions η^6-$LCr(CO)_3$, where L = benzene, thiophene, indene, fluorene or azofluorene, were studied.[133] In the mass spectrum of thiophenechromium tricarbonyl, the $[SCr(CO)_3]^-$ ion was present, formed through a π-σ isomerization stage. For indenechromium tricarbonyl a process of re-coordination of the chromium atom from the benzene to the cyclopentadienyl ring was observed.[133]



LII

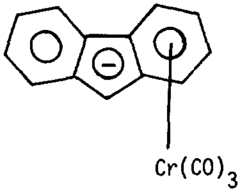


LIII

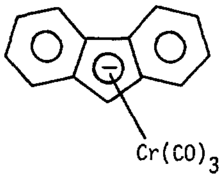


LIV

The rate of deprotonation of fluorene and of π-(tricarbonylchromium)fluorene by KH was measured by monitoring the hydrogen evolution.[134] The pseudo-first order rate constant for the complex was an order of magnitude higher than that for the free ligand. ^{1}H and ^{13}C NMR analysis showed that when the anion was produced at -20°C or below, the $Cr(CO)_3$ group was bonded to one of the phenyl rings (η^6-anion), whereas ionization at room temperature produced solutions containing mainly the anion with the $Cr(CO)_3$ bonded to the cyclopentadienyl ring (η^5-anion) in equilibrium with the η^6-isomer.

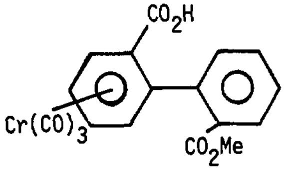


LV

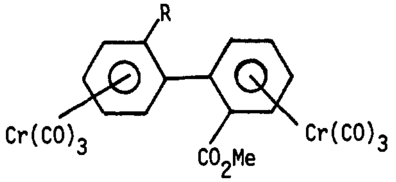


LVI

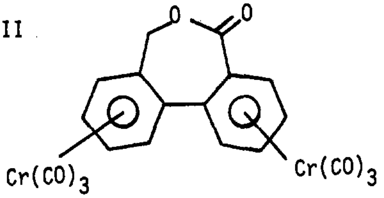
The effect of ionization on free and complexed systems, together with the effect of complexation of the free anion, was discussed on the basis of the NMR data.[134] The $\eta^6 \rightleftarrows \eta^5$ isomerization equilibrium was followed at various temperatures and different degrees of solvation were deduced for the two isomeric ion pairs from the kinetic and thermodynamic solvation parameters.[134] The complexes of diphenic acid and its mono-Me ester were prepared from their cinchonidinium salts, with enantiomeric purities $\leq 8\%$.[135]



LVII



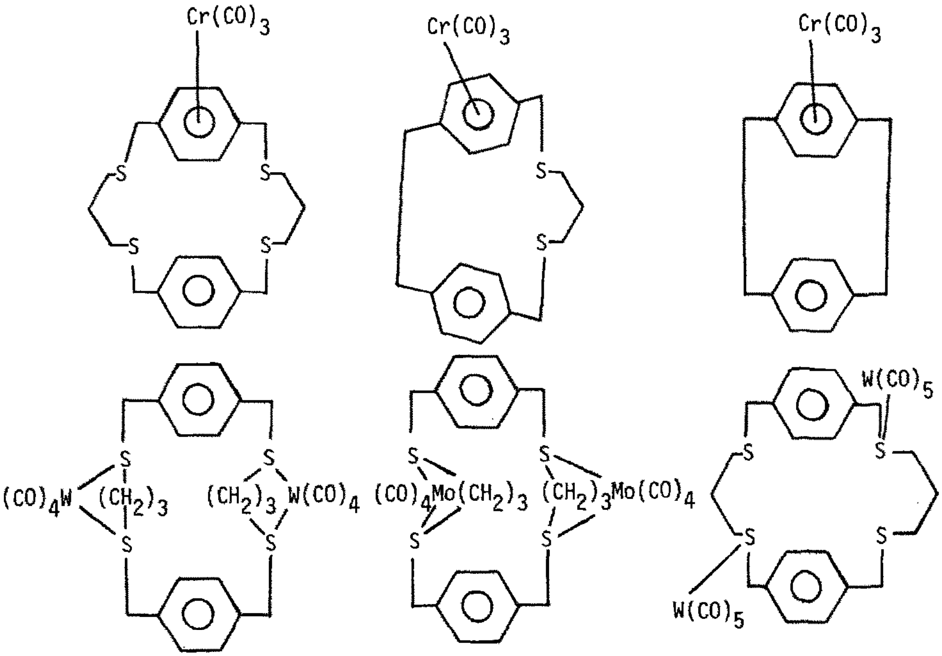
LVIII



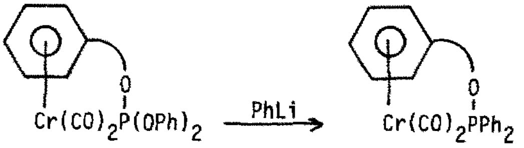
LIX

Reduction with a chiral $LiAlH_4$ complex was sometimes more successful. The chirality of the complexes was assigned by comparing their CD spectra with those of benchrotrenes of known absolute configuration.[135] The fragmentation of η^6-benzoic acid n-propyl ester tricarbonylchromium under electron impact was observed to be accompanied by several hvdrogen transfer processes which were studied by deuterium labeling of the propyl group in the 1-, 2- or 3-position.[136] Propylene elimination from the ester function was either specific or largely random, depending on the pressure of CO ligands. Another rearrangement involved transfer of hydrogen exclusively from the 1-position of the propyl group to the ester carbonyl carbon atom.[136]

Tricarbonyl(η^6-[2.2]paracyclophane)chromium formed a charge-transfer complex with 1,3,5-trinitrobenzene (1,3,5-TNB) in 1,2-dichloroethane.[137] The ionization potential of ([2.2]paracyclophane)$Cr(CO)_3$ was determined to be 7.2 eV from the observed intermolecular charge-transfer transition energy. The value was close to those obtained for the usual chromium tricarbonyl complexes with η^6-coordinated benzene derivatives.[137] In solution, the acceptor molecule was suggested to be more likely to interact directly with the chromium d orbital lobes by sitting beneath the base of the pyramid formed by three metal-carbonyl bonds rather than by stacking on the aromatic ring. This was also supported since other chromium-carbonyl complexes without an η^6-coordinated aromatic ring also exhibit spectral evidence of complex formation with 1,3,5-TNB.[137] The reaction of 2,6,15,19-tetrathia[7,7]paracyclophane with $Mo(CO)_6$ and $W(CO)_6$ was described.[138] The species $C_{22}H_{28}S_4[Mo(CO)_4]_2 \cdot 2C_6H_6$ and $C_{22}H_{28}S_4[W(CO)_4]_2$ and $C_{22}H_{28}S_4[W(CO)_5]_2$, respectively, could be isolated and characterized by X-ray structure analysis.

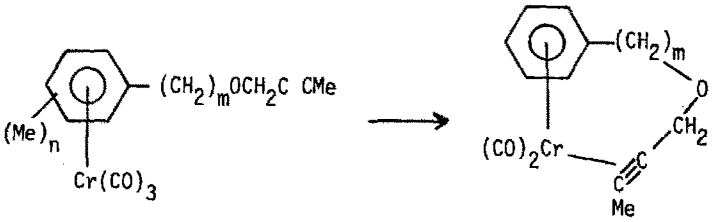


The species were believed to be intermediates in the 1,3-dithiapropane elimination from TTPH catalyzed by metal carbonyls.[138] Chromium chelates [R = Ph; n = 2 (3,5-Me$_2$), n = 3 (2,4,6-Me$_3$)] were obtained in 15 and 21% yield, respectively, by nucleophilic substitutions with PhLi.[139]



(106)

(Alkynyloxy)arenechromium tricarbonyls [n = m = 0; n = 2 (2,3-Me$_2$), m = 1, 2; n = 3 (2,4,6-Me$_3$), m = 2, 3], were prepared by treating the corresponding alcohol or phenol with BrCH$_2$C:CMe.[140]

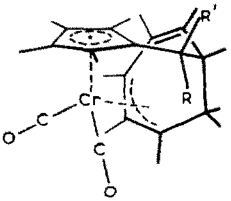


(107)

These complexes underwent intramolecular coordination in the presence of UV light to give the chelates in 52-70% yield.[140]

Larger rings. Crystal structure determinations of $(\eta^7\text{-}C_7H_7)Mo(CO)_2TePh$, $(\eta^7\text{-}C_7H_7)W(CO)_2SePh$ and $(CO)_3Mo(SePh)_3Mo(\eta^7\text{-}C_7H_7)$ were reported.[141] Tricarbonyl-η-1,3,5-cycloheptatrienechromium(0) reacted with 6-mono- and 6-disubstituted fulvenes under UV-irradiation in two different ways.[142] One was the formation of a C-C bond between C(1) of the cycloheptatriene ligand and C(6) of the fulvene yielding dicarbonylchromium complexes of substituted η^3-cyclohepta-2',4'-dien-1',6'-ylene-η^5-cyclopentadieneylidene-methanes.

$$Cr(CO)_3C_7H_8 + C_6H_4RR' \xrightarrow{h\nu}$$



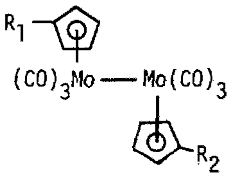
(108)

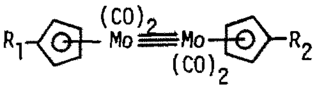
$R,R' = OCH_3, -SCH_2CH_2S-, CH_3C_6H_5$

Alternatively, hydride transfer from the cycloheptatriene to C(6) of the fulvene occurred and dicarbonyl-η^3-cycloheptatrienylchromium complexes with substituted η^5-cyclopentadienyl ligands were obtained. There was evidence for steric influence of the 6-substituents of the fulvenes in the mechanism of reaction.[142]

Metal-Metal Bonded Complexes.

Binuclear complexes. High performance liquid chromatography (HPLC) was used as an analytical and preparative tool for the characterization and isolation of six dinuclear molybdenum carbonyl complexes.[143]

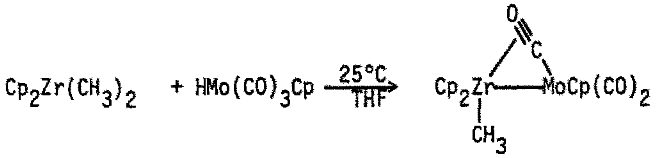




$R_1 = R_2 = H$
$R_1 = CH_3, R_2 = H$
$R_1 = R_2 = CH_3$

$R_1 = R_2 = H$
$R_1 = CH_3, R_2 = H$
$R_1 = R_2 = CH_3$

Reversed phase chromatography with octadecylsilyl-modified silica (ODS) as a stationary phase and polar mobile phases saturated with argon were employed in the separation of products.[143] The coordinatively unsaturated alkyl Cp_2ZrMe_2 and the hydride $HMo(CO)_3Cp$ eliminated methane as shown below.[144]

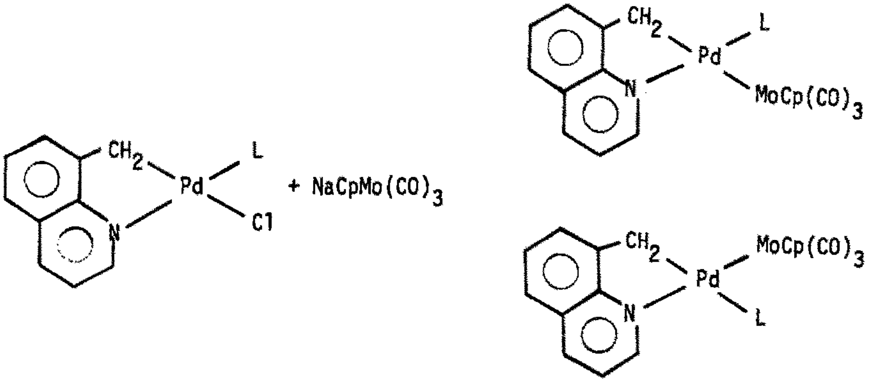


(110)

Carbonylation proceeded rapidly to give the η^2-acetyl dimer.[144]

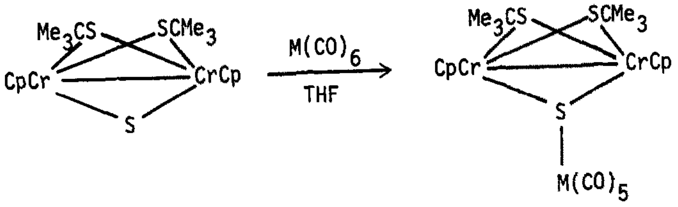
$$Cp_2ZrMe - MoCp(CO)_3 \xrightarrow{CO} Cp_2Zr(\eta^2\text{-}Ac)Mo(CO)_3Cp) \qquad (111)$$

Labeling experiments established unambiguously that the carbon in the acyl carbonyl came from the added carbon monoxide.[144] trans-Pentacarbonylrhenio-tetracarbonylcarbyne complexes of chromium and tungsten reacted with trimethylphosphine to give binuclear transition metalylid complexes containing one bridging ylid as well as a bridging carbonyl ligand in addition to a metal to metal bond.[145] Excess of trimethylphosphine led to substitution of carbonyl ligands.[145] Palladium molybdenum dimers were formed by the reaction shown below.[146]

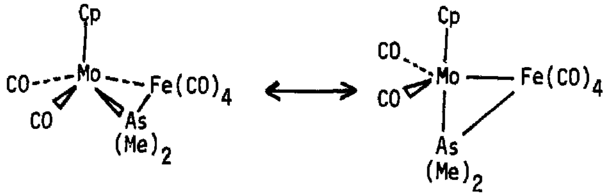


(112)

The crystal structure of the phosphine complex was determined.[146] Isostructural heterotrinuclear complexes $(C_5H_5CrSCMe_3)_2S \cdot M(CO)_5$ were isolated from photochemical reactions between the complex $(C_5H_5CrSCMe_3)_2S$ and metal hexacarbonyls, $M(CO)_6$, where M is Cr, Mo, or W.[147]


(113)

Structural data showed the geometry of the dimer remains practically unaffected by the complex formation with just a slight lengthening of the Cr-Cr bond.[147] A communication describing the ^1H and ^{13}C NMR spectra of the heterobimetallic compound $(CO)_4Fe\text{-}(\mu\text{-}AsMe_2)Mo(CO)_2Cp$ revealed three different fluxional processes.[148] One of the processes involved the rearrangement of the square pyramid to a trigonal bipyramid.[148]


(114)

Trimethyl- and triethyllead derivatives $CpM(CO)_3PbR_3$(M = Cr,Mo, and W) were synthesized.[149] The trimethyllead derivatives were photochemically, and thermally unstable with respect to methyl transfer reactions that yield the corresponding $CpM(CO)_3CH_3$ complex.

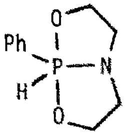
$$CpM(CO)_3PMe_3 \xrightarrow{h\nu} CpM(CO)_3Me \qquad (115)$$

The related triethyllead complexes behaved differently exhibiting rearrangements to $[CpM(CO)_3]_3PbEt_2$ (M = W, Mo). The reactions of the Cr, Mo, and W complexes with SO_2 yielded the corresponding alkyl sulphinato complexes.[149a]

$$CpM(CO)_3PbR_3 + SO_2 \rightarrow CpM(CO)_3(SO_2R) \qquad (116)$$

M = Cr,Mo,W
R = Me,Et

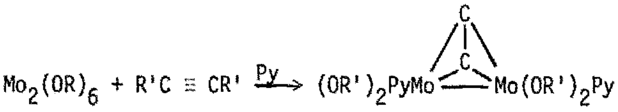
The reaction of the bicyclophosphorane with $Cp_2Mo_2(CO)_4$ gave several products.[149b]



(phoran)

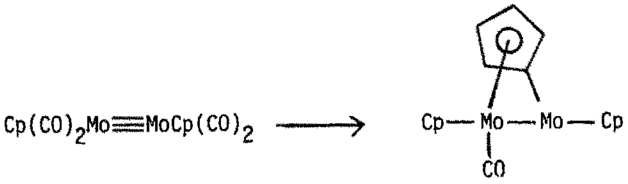
$$+\ Cp_2Mo_2(CO)_4 \rightarrow Cp_2Mo_2(CO)_2(phoran)_2 + Cp_2Mo_2(CO)_5(phoran) + Cp_2Mo_2(CO)_3(phoran) \qquad (117)$$

The structure of $Cp_2Mo_2(CO)_3(phoran)$ was determined showing that the Mo ≡ Mo remained intact.[149b] The compounds $Mo_2(OR)_6(py)_2(ac)$, where R = i-Pr, ac = HCCH, MeCCH, and MeCCMe and R = Ne (neopentyl), ac = HCCH, were precipitated as crystalline solids when the appropriate acetylene was added to a solution of $Mo_2(OR)_6$ dissolved in hexane-pyridine solvent mixtures.[150]



$$Mo_2(OR)_6 + R'C \equiv CR' \xrightarrow{Py} (OR')_2PyMo(\mu\text{-}C_2)Mo(OR')_2Py \qquad (118)$$

The crystal and molecular structure of the ethyne adduct, $Mo_2(O\text{-}i\text{-}Pr)_6(py)_2(HCCH)$, was determined showing acetylene bridging the two molybdenum atoms.[150] The reaction of $Cp_2Mo_2(CO)_4$ with diazocyclopentadiene was reported.[151]



(119)

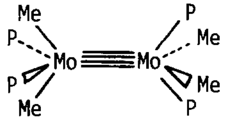
The product was characterized by x-ray diffraction.[151] $1,2\text{-}M_2Cl_2(NMe_2)_4$ compounds, where M = Mo and W, with alkyllithium reagents reacted in hydrocarbon solvents to give $1,2\text{-}M_2R_2(NMe_2)_4$ compounds where R = $-CH_2CH_3$, $-CH_2CD_3$, $-CD_2CH_3$, $-CH_2CH_2CH_2CH_3$, $-CH(CH_3)_2$, $-CH(CH_3)(C_2H_5)$, $-CH_2C(CH_3)_3$, $-CH_2Si(CH_3)_3$, $-CH_2Si(CH_3)_3$, and $-C(CH_3)_3$ retaining the M ≡ M[152].

$$(NMe_2)_2ClM \equiv MCl(NMe_2)_2 + RLi \rightarrow (NMe_2)_2RM \equiv MR(NMe_2)_2 + 2LiCl \quad (120)$$

These compounds were characterized by elemental analyses, mass spectroscopy, infrared spectroscopy, and NMR spectroscopy.[152] The molybdenum compounds where R = CH_2CH_3 and $-CH(CH_3)_2$ were examined by single-crystal X-ray diffraction studies. The characterization data established that all compounds have a staggered ethanelike $M_2N_4C_2$ core. In solution, NMR studies revealed the existence of a mixture of anti and gauche rotamers: as the bulkiness of the alkyl group increased, the gauche rotamer became increasingly favored.[152] In the crystalline state, a gauche $Mo_2(C_2H_5)_2(NMe_2)_4$ molecule was characterized by X-ray studies showing Mo-Mo = 2.203. The isolation of the isopropyl, sec- and tert-butyl, and labeled ethyl compounds (R = CD_2CH_3 and CH_2CD_3) demonstrated that β-hydrogen elimination did not occur readily in these compounds.[152] The methyl complex, 1,2-$Mo_2Me_2(NMe_2)_4$, reacted in hydrocarbon solvents with 1,3-di-p-tolyltriazine, $C_7H_7NNNHC_7H_7$, to give bis(1,3-di-p-tolyltriazenido)bis(dimethylamido)dimethyldimolybdenum as a red crystalline solid.[153]

$$(NMe_2)_2MeMo \equiv MoMe(NMe_2)_2 + C_7H_7NNNHC_7H_7 \rightarrow Mo_2Me_2(NMe_2)_2(C_7H_7N_3C_7H_7)_2 \quad (121)$$

The Mo ≡ Mo bond (2.174(1) Å) was bridged by a cis pair of triazenido ligands which afforded sufficient flexibility to allow a noneclipsed geometry. Each molybdenum atom was coordinated to three nitrogen atoms and one carbon atom which roughly lay in a plane.[153] Blue $Mo_2Me_4(PEt_3)_4$ was prepared from $Mo_2(O_2CCMe_3)_4$, MgMeCl, and PEt_3 in diethyl ether, followed by crystallization from diethyl ether at -10°C.[154] This complex underwent ligand exchange with excess PMe_2Ph or PMe_3 in toluene solution within minutes at room temperature to give the known $Mo_2Me_4(PMe_2Ph)_4$ or $Mo_2Me_4(PMe_3)_4$, respectively. An X-ray crystal structure analysis of $Mo_2Me_4(PMe_3)_4$ was performed.[154]



LXVI

The phosphine exchange process in these molecules was stepwise. At -50°C, the rate of disappearance of $Mo_2Me_4(PEt_3)_4$ was first order in $[Mo_2Me_4(PEt_3)_4]$ and zero order in $[PMe_2Ph]$, when the latter was in excess.[154]

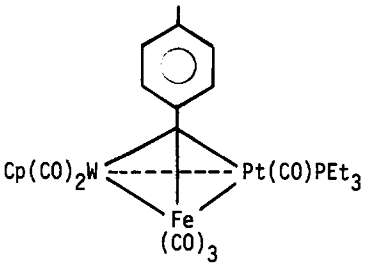
$$Mo_2Me_4(PEt_3)_4 + PMe_2Ph \rightarrow Mo_2Me_4(PEt_3)_{4-n}(PMe_2Ph)_n \qquad (122)$$

Further, the rate was invariant on $[PMe_2Ph]$, when the latter was varied over a 10- to 30-fold excess.[154] Under these conditions, the first-order rate constant was $k_{obs} = (5.5 \pm 0.1) \times 10^{-4}\ s^{-1}$ over three half-lives. The invariance of the reaction rates on the nature of the incoming group and the positive $\Delta S^{\ddagger}$ both indicated a dissociative mechanism.[154] t-Butyl isocyanide cleaved the quadruple metal-metal bonds in $Mo_2(O_2CMe)_4$, $Mo_2(O_2CCF_3)_4$, or $K_4Mo_2Cl_8$ to give the mononuclear, seven-coordinate species $Mo(t\text{-}BuNC)_5(O_2CMe)_2$ or $[Mo(t\text{-}BuNC)_6X][X]$, where X was O_2CCF_3 or Cl.[155] These diamagnetic, 18-electron complexes were converted into the known binary dication $[Mo(t\text{-}BuNC)_7][PF_6]_2$ by action of NH_4PF_6 and excess t-BuNC or into the polyoxoanion complex $[Mo(t\text{-}BuNC)_7][Mo_6O_{19}]\cdot 2Me_2CO$ by recrystallization from acetone in air.[155] The reactions of $M_2Cl_4(PR_3)_4$ derivatives (M = Mo, W and $PR_3 = PEt_3, PBu_3$) with CO at atmospheric pressure in toluene at 70°C afforded $M(CO)_3(PR_3)_2Cl_2$ and trans-$M(CO)_4(PR_3)_2$.[156]

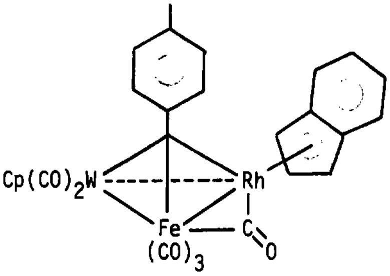
$$M_2Cl_4(PR_3)_4 + CO \rightarrow M(CO)_3(PR_3)_2Cl_2 + trans\text{-}M(CO)_4(PR_3)_2 \qquad (123)$$

M = Mo,W; R = Et,Bu

Metal clusters. Three compounds containing equilateral-triangular trimolybdenum clusters capped on both sides by ethylidyne (CCH_3) groups were described: $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3]SbF_6\cdot 3H_2O$, $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3](CF_3SO_3)_2$, and $[Mo_3(CCH_3)_2(O_2CCH_3)_6(H_2O)_3](p\text{-}CH_3C_6H_4SO_3)_2\cdot 10H_2O$.[157] All three were obtained by suitable workup of the reaction mixture after refluxing $Mo(CO)_6$ with a mixture of acetic acid and acetic annhydride. The crystal structures of the three compounds were solved.[157] The compound $[Mo_3(\mu_3\text{-}O)(\mu_3\text{-}CCH_3)(O_2CCH_3)_6(H_2O)_3]BF_4\cdot 9H_2O$ was also prepared and characterized by a variety of physical measurements, including an X-ray structure determination.[158] The compound was diamagnetic and exhibited well-resolved ^1H and ^{13}C NMR spectra. A ^{13}C tracer study showed that the ethylidyne group arose by reduction of the acetate group.[158] Cluster compounds containing triangles of 3 different metals capped by μ_3-CC_6H_4Me-p were prepared by treating $W(CC_6H_4Me\text{-}p)(CO)_2Cp$ with a Pt or Rh complex to give a W-Pt or W-Rh complex and treating this intermediate with $Fe(CO)_5$ or $Fe_2(CO)_9$.[159]



LXVII

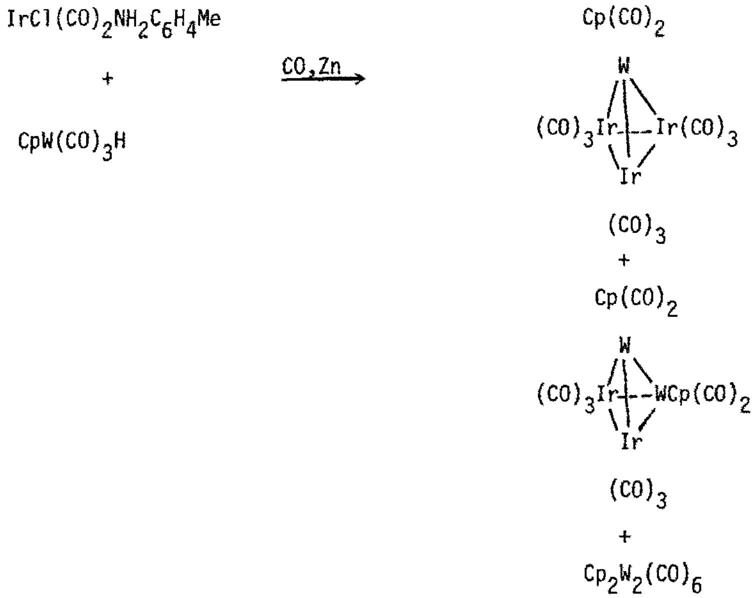


LXVIII

Similar complexes containing WCo_2 or WRh_2 moieties were obtained by treating the tungsten carbyne with a Co_2 or Rh_2 carbonyl complex.[159] For example, $Pt(C_2H_4)_3$ treated with PEt_3 reacted with the tungsten carbyne to give $PtW(\mu_2\text{-}CC_6H_4Me\text{-}p)(CO)_2(PEt_3)_2Cp$, which reacted with $Fe_2(CO)_9$ at room temperature to give $Fe(CO)_4PEt_3$ and the FePtW complex.[159]

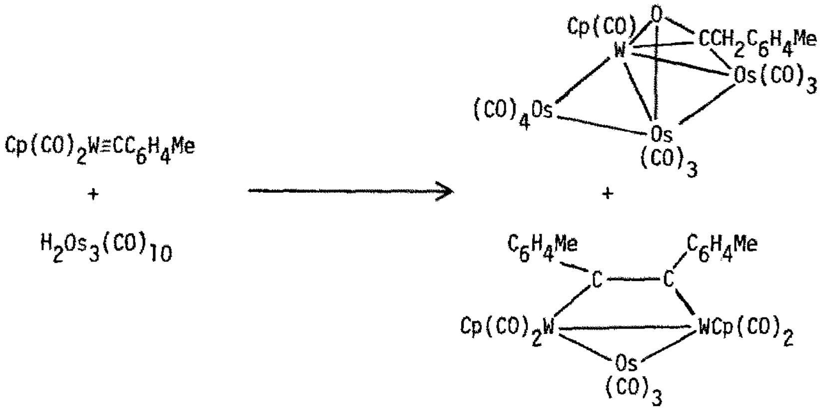
$$\begin{tikzcd}
Pt(C_2H_4)_3 + PR_3 \arrow[r, "CpW(CC_6H_4Me\text{-}p)(CO)_2"] & PtW(\mu^2\text{-}(C_6H_4Me\text{-}p))(CO)_2(PEt_3)_2Cp \arrow[d, "\begin{array}{l}+\,Fe_2(CO)_9\\ -Fe(CO)_4PE_3\end{array}"] \\
 & (LXVII)
\end{tikzcd} \qquad (124)$$

The tungsten carbyne similarly reacted successfully with dicarbonylindenylrhodium and $Fe_2(CO)_9$ to give the FeRhW complex which contained an Fe-Rh bond bridged by a CO. Crystal and molecular structures were determined.[159] The heteronuclear tungsten-iridium cluster complex $(\eta^5\text{-}C_5H_5)WIr_3(CO)_{11}$ crystallized and the structure was solved.[160] The molecule consisted of a tetrahedral cluster of metal atoms with the η^5-cyclopentadienyl ligand and two carbonyl groups bonded to the tungsten atom. This $(\eta^5\text{-}C_5H_5)W(CO)_2$ fragment was linked to three $Ir(CO)_3$ moieties with intermetallic distances of Ir-Ir = 2.699 [3] Å and Ir-W = 2.824 [37] Å.[160] The reaction of $IrCl(CO)_2NH_2C_6H_4Me$ with $CpW(CO)_3H$ under a CO atmosphere in the presence of zinc provided two tetrahedral mixed metal clusters.[161]



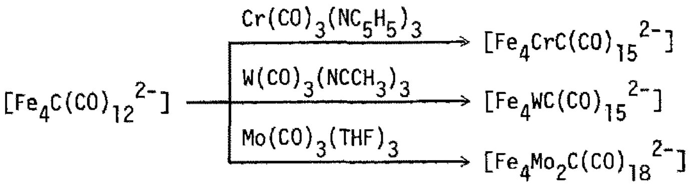
(125)

The structures of both tetrahedral clusters were reported. The clusters were deposited on alumina and their catalytic activity investigated.[161] The reaction of $Cp(CO)_2W{\equiv}CC_6H_4Me$ with $H_2Os_3(CO)_{10}$ produced $CpWOs_3(CO)_{12}(CH_2C_6H_4Me)$ and $Cp_2W_2Os(CO)_7(CC_6H_4Me)_2$.[162]



(126)

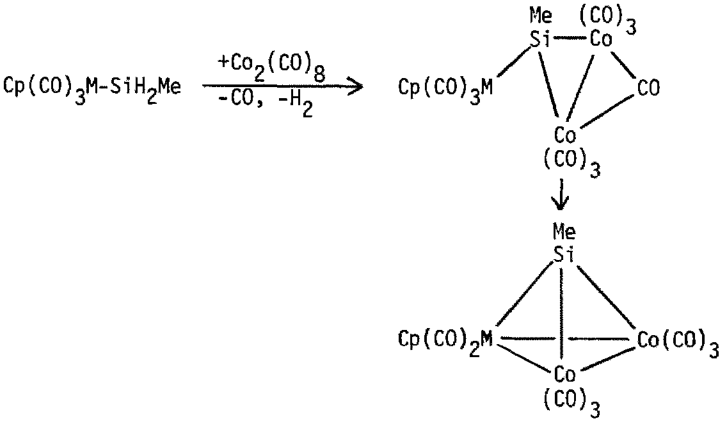
The structures of each were determined. The four metal cluster was nearly planar with an acyl group bridging a triangular face.[162] The trimetal cluster contained a triply-bridging acetylene.[162] The strategies in the synthesis of metal carbide clusters were examined and the full synthesis procedures for a number of heteronuclear metal carbide clusters were presented.[163]



$$[Fe_4C(CO)_{12}{}^{2-}] \xrightarrow{Cr(CO)_3(NC_5H_5)_3} [Fe_4CrC(CO)_{15}{}^{2-}]$$
$$[Fe_4C(CO)_{12}{}^{2-}] \xrightarrow{W(CO)_3(NCCH_3)_3} [Fe_4WC(CO)_{15}{}^{2-}]$$
$$[Fe_4C(CO)_{12}{}^{2-}] \xrightarrow{Mo(CO)_3(THF)_3} [Fe_4Mo_2C(CO)_{18}{}^{2-}]$$

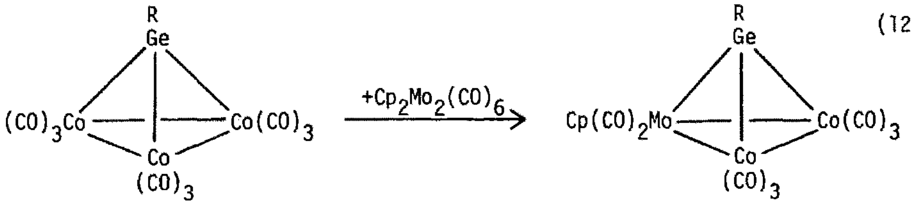
(127)

Two independent methods were used to prepare μ_3-RSi and μ_3-RGe bridged Co_2Mo and Co_2W clusters.[164] The construction method yielded the $RSiCo_2M$ (M = Mo,W) clusters from $Cp(CO)_3M\text{-}SiH_2Me$ and cobalt carbonyl.



(128)

The metal exchange method yielded two $RGeCo_2Mo$ clusters from $RGeCo_3(CO)_9$ and $[Cp(CO)_3Mo]_2$.[164]



(129)

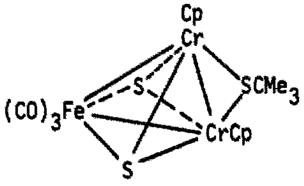
The reaction of $Fe_2(CO)_6S_2$ with $[CpCr(CO)_3]_2$ afforded the heterotetrametallic cluster $Cp_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6$.[165]

$$Fe_2(CO)_6S_2 + Cp_2Cr_2(CO)_6 \rightarrow Cp_2Cr_2Fe_2(\mu_3\text{-}CO)_2(\mu_3\text{-}S)_2(CO)_6 \tag{130}$$

Its X-ray analysis showed a butterfly arrangement for the Cr_2Fe_2 core; the two chromium atoms occupied the hinge, with a Cr-Cr bond distance of 2.775(4)Å, and the two iron atoms were on the tops of the wings, with average Cr-Fe bond distances of 2.762(3)Å. One Cp ring was bonded to each chromium atom, and three CO ligands were terminally bonded to each iron atom. Two carbonyls triply bridged very asymmetrically one Cr and two Fe atoms.[165] Two S atoms triply bridged the two triangular $FeCr_2$ faces with Cr-S and Fe-S average distances of 2.230(4) and 2.160(5) Å, respectively.[165] The photochemical reaction between $(C_5H_5CrSCMe_3)_2S$ and $Fe(CO)_5$ resulted in the elimination of two carbonyl groups and one tert-butyl radical to give $(C_5H_5Cr)_2(\mu^2\text{-}SCMe_3)(\mu^3\text{-}S)_2\cdot Fe(CO)_3$.[166]

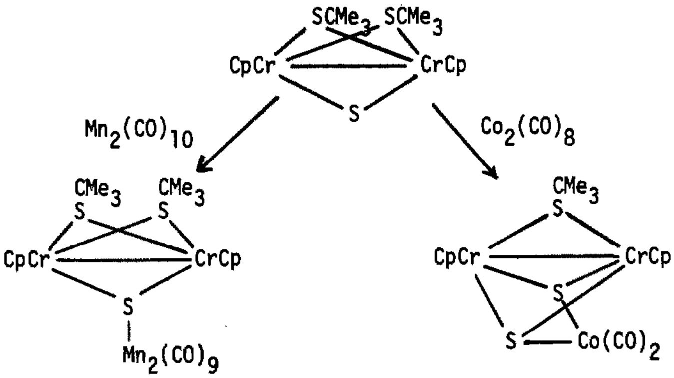
$$(CpCrSCMe_3)_2S + Fe(CO)_5 \rightarrow (CpCr)_2(\mu^2\text{-}SCMe_3)(\mu^3\text{-}S)_2Fe(CO)_3 \tag{131}$$

As determined by X-ray diffraction, this complex contained a Cr-Cr bond of 2.707 Å, together with one thiolate bridge.[166]



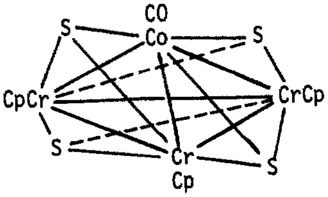
LXIX

The latter were also linked with the Fe atom of the $Fe(CO)_3$ moiety (average Fe-S bond length 2.300 Å). The Fe formed a bond, 2.726 Å long, with one of the Cr atoms, whereas its distance from the other Cr atom (3.110 Å) was attributed to non-bonded interactions.[166] Similar reactions with $Mn_2(CO)_{10}$ and $Co_2(CO)_8$ were also reported.[167]



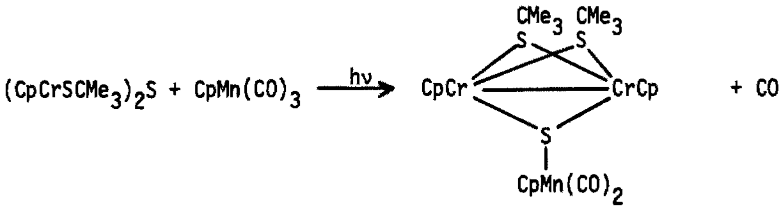
(132)

The structures were determined.[167] Heating the cobalt complex yielded a tetrahedral cluster whose structure was determined.[168]



LXX

The reaction of the chromium species with $CpMn(CO)_3$ and $CpV(CO)_4$ were also reported.[169]



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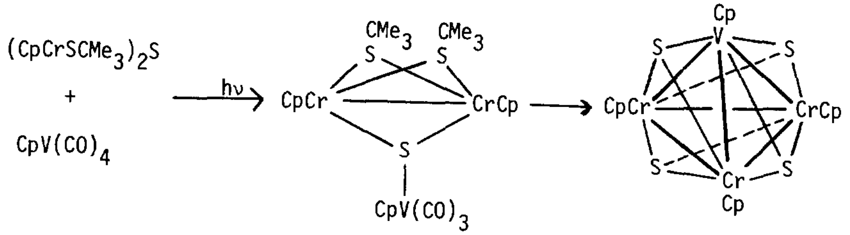


(134)

The structure of the tetranuclear complex was assigned by analogy with $Cp_4Cr_4S_4$.[169]

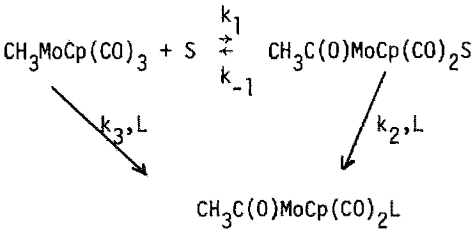
KINETICS

The decomposition and ligand substitution reactions of group 6B metal pentacarbonyl piperidine derivatives with phosphines were studied.[170] The reactions were catalyzed by the Lewis bases $OP(n\text{-}C_4H_9)_3$ and tetrahydrofuran (THF). It was concluded that the results were best accounted for in terms of hydrogen-bonded intermediates in the general-base catalysis with the mechanism for catalysis being closely analogous to a dissociative interchange (I_d) pathway. The intermediates were characterized by infrared spectroscopy.[170] Laser pulse photolysis at 353 nm of tungsten hexacarbonyl in room-temperature methylcyclohexane produced an intermediate, proposed to be $W(CO)_5S$, S denoting solvent.[171] In the presence of added L = 4-acetylpyridine, the intermediate reacted completely to form $W(CO)_5L$ as the final product.

$$W(CO)_6 \xrightarrow{h\nu,S} W(CO)_5S \xrightarrow{L} W(CO)_5L \qquad (135)$$

S = solvent, L = 4 acetylpyridine

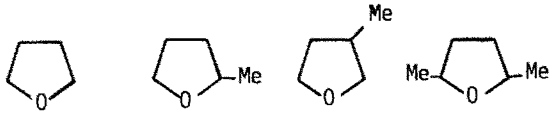
The rate of disappearance of the intermediate was pseudo first order, with k_{app} linear in L at low concentration but approaching a limiting value at higher concentrations.[171] The proposed mechanism was one of reversible dissociation of $W(CO)_5S$ to $W(CO)_5$ and S with rate constants k_1 and k_{-1}, followed by scavenging of the $W(CO)_5$ by L, with rate constant k_2. At 20°C $k_1 = 1.9 \times 10^6\ s^{-1}$ and $k_2/k_{-1} \sim 270$; the corresponding activation quantities were $E_1^* = 3.9$ kcal mol^{-1} and $E_{-1}^* - E_2^* = 2.6$ kcal mol^{-1}. The nature of the primary photolysis step was discussed.[171] The role of solvent in alkyl migration reactions was addressed for $CH_3MoCp(CO)_3$.[172]



(136)

L = $PMePh_2$

S =



The solvents were chosen for similar values of dielectric constants but quite different abilities to coordinate to the metal. The values of the rate constants as shown below indicate direct coordination of the solvent to the Mo in the 16-electron acyl transition state.[172]

solvent	$k_1(10^4 s^{-1})$	$k_3(10^4 M^{-1} s^{-1})$
THF	7.8	1.7
3-MeTHF	6.5	1.9
2-MeTHF	1.5	1.9
2,5-Me_2THF	0.2	1.7

The direct reaction of L with the methyl complex (k_3) showed very little effect on these solvents but the k_1 term showed a definite dependence on the ability of the solvent to directly coordinate.[172] Kinetic studies of reactions of the Mo-Mo bonded complex $Cp_2Mo_2(CO)_6$ in decalin showed that it reacted by reversible homolytic fission with an activation enthalpy required to break the Mo-Mo bond of 135.9 kJ mol^{-1}.[173] The scheme below was suggested.[173]

$$Cp_2Mo_2(CO)_6 \rightleftarrows 2\ CpMo(CO)_3\cdot \tag{137}$$

$$CpMo(CO)_3\cdot + O_2 \rightarrow \text{decomposition} \tag{138}$$

$$CpMo(CO)_3\cdot + RI \rightarrow CpMo(CO)_3I + R\cdot \tag{139}$$

$$R\cdot + O_2 \rightarrow RO_2\cdot \tag{140}$$

$$R\cdot + Cp_2Mo_2(CO)_6 \rightarrow \{R^-\ Cp_2Mo_2(CO)_6^{\dot{+}}\} \tag{141}$$

$$\{R^{-}\ Cp_2Mo_2(CO)_6^{\dot{+}}\} \rightarrow CpMo(CO)_3R + CpMo(CO)_3\cdot \tag{142}$$

$$CpMo(CO)_3R \rightarrow R\cdot + CpMo(CO)_3\cdot \tag{143}$$

Kinetic studies of the reaction of $Cp_2Mo_2(CO)_6$ with diphenylacetylene indicated successive dissociation of two CO ligands before reaction with C_2Ph_2 but this dissociative reaction was considerably slower than the completely reversible homolytic fission of the complex that occurred concurrently without leading to any product.[174]

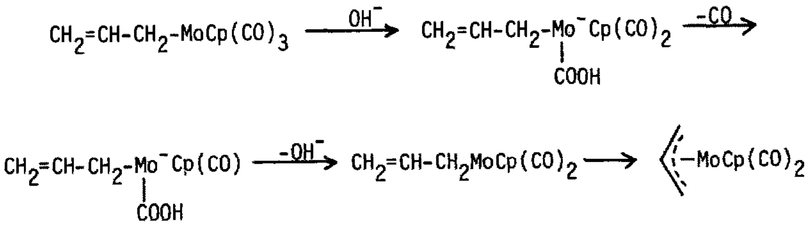
$$Cp_2Mo_2(CO)_6 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} Cp_2Mo_2(CO)_5 + CO \tag{144}$$

$$Cp_2Mo_2(CO)_5 \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} Cp_2Mo_2(CO)_4 + CO \tag{145}$$

$$Cp_2Mo_2(CO)_4 + C_2Ph_2 \xrightarrow{k_3} Cp_2Mo_2(CO)_4(C_2Ph_2) \tag{146}$$

The kinetics of reactions of $Cp_2Mo_2(CO)_6$ with I_2, ICl, Br_2, $CHBr_3$, and $C_2H_2Cl_4$ to form mononuclear halogen complexes were studied.[175] Reactions with halogens proceeded rapidly at 25°C and the kinetics suggested the involvement of intermediate adducts containing one or two molecules of halogen. It was suggested that the halogen molecules in the adducts were attached to the O atoms around the periphery of the complex. Reactions with $CHBr_3$ and $C_2H_2Cl_4$ proceeded cleanly to form $CpMo(CO)_3X$ at 72°C in decalin and a reaction path involving direct attack by two molecules of halocarbon competed with homolytic fission as the rate-determining step.[175]

Mechanisms were proposed for the hydroxide ion-initiated reactions of metal carbonyl halides leading to allyl-transition metal complexes under phase transfer conditions.[176] Evidence was presented for intermediate anionic metallocarboxylic acids in reactions leading to η^3-allyl products of molybdenum, whereas η^1 complexes were shown to result from halide displacement reactions in which simple metal carbonyl anions were generated.[176]



(148)

Kinetic data for $CpM(CO)_3SnMe_3$ reacting with I_2 were used to illustrate the simplification of consecutive rate laws.[177] Kinetic studies of exchange reactions at the bridging sulfur atoms in cyclopentadienylmolybdenum dimers were reported.[178] The kinetics of the reaction of $[CH_3C_5H_4Mo^{IV}(S)SH]_2$ with benzyl isocyanide resulting in the formation of H_2 and $[CH_3C_5H_4MoS_2CNCH_2C_6H_5]_2$ were studied by the method of initial rates. The reaction showed a first-order dependence on the molybdenum dimer and a first-order dependence on isocyanide. Activation parameters were derived with $\Delta H^{\neq} = 7.9$ kcal/mol and $\Delta S^{\neq} = -38$ cal K^{-1} mol^{-1}.[178] The reaction of $[CH_3C_5H_4Mo^{III}SC_2H_4S]_2$ with benzyl isocyanide resulted in the formation of the same dithiocarbonimidate complex, and ethylene. Studies of the latter reaction revealed a first-order dependence on the molybdenum complex, but a zero-order dependence on isocyanide with the activation parameters $\Delta H^{\neq} = 24.3$ kcal/mol and $\Delta S^{\neq} = 11$ cal K^{-1} mol^{-1}. The work suggested that the Mo(IV) dimer reacted by an associative mechanism, while the reaction of the Mo(III) derivative proceeded by a dissociative pathway. The different mechanisms of reaction for the Mo(IV) and -(III) dimers were discussed in terms of the molecular orbitals involved.[178] The kinetic study of the thermal and photochemical reaction,

$$[MoCp_2I(NCPh)][PF_6] + MeCN \rightleftarrows [Mo(\eta^5\text{-}C_5H_5)_2I(NCMe)][PF_6] + PhCN \qquad (149)$$

using excess MeCN and PhCN, was described.[179] The inverse of the pseudo first order constants for the forward and reverse reactions varied linearly with [PhCN]/[MeCN] and [MeCN]/[PhCN], respectively, while the inverse of the quantum yield for the disappearance of $[Mo(\eta^5\text{-}C_5H_5)_2I(NCPh)][PF_6]$ varied linearly with [PhCN]/[MeCN]. The results indicated a dissociative mechanism for both the thermal and photosubstitution reactions.[179] Copper(II) and iron(III) ions reacted with (α-hydroxyalkyl)chromium(2+) complexes (alkyl = methyl, ethyl, 2-propyl) in water or in aqueous alcohol solutions leading to the cleavage of the chromium-carbon bond.[180] The immediate products were Cr^{2+}, the reduced metal ion (Cu^+ or Fe^{2+}), and the corresponding aldehyde or ketone. The reactions obeyed the rate law

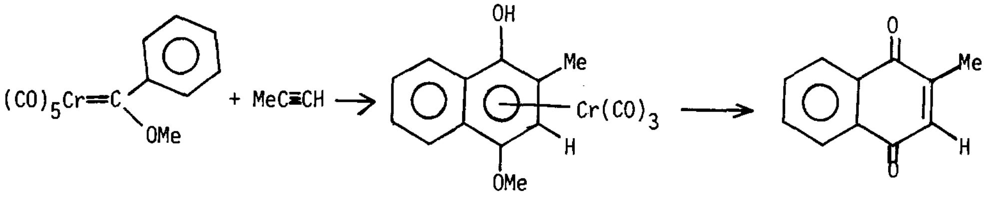
$$-d[CrROH^{2+}]/dt = (k + k'[H^+]^{-1})[CrROH^{2+}][M] \qquad (150)$$

where M = Cu^{2+} or Fe^{3+}. The reactivity toward Cu^{2+} and Fe^{3+} was significantly diminished upon substitution of the OH hydrogen by an alkyl group.[180] Copper(II) did not react with (α-alkoxyalkyl)chromium(2+) complexes at all, while iron(III) showed some reactivity. A mechanism proposed for the oxidation of (α-hydroxyalkyl)-chromium(2+) complexes by copper(II) and iron(III) consisted of the oxidant attack at the alcoholic OH group followed by a slow electron-transfer step.[180] The kinetics of oxygen transfer from $[MoO_2(Et\text{-}L\text{-}cys)_2]$ to PPh_3 and the reaction between $[Mo_2O_3(Et\text{-}L\text{-}cys)_4]$ and O_2 in C_6H_6 were studied at 25-40° using spectrophotometric techniques.[181] The results were interpreted in terms of a bimolecular mechanism with the interaction of $[MoO_2(Et\text{-}L\text{-}cys)_2]$ and PPh_3 in the activated complex.[181]

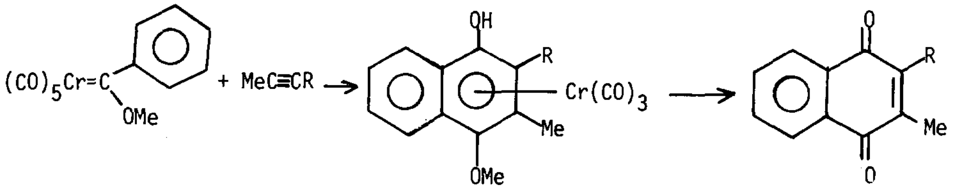
ORGANIC SYNTHESIS AND CATALYSIS

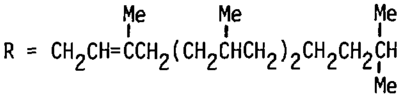
Organic Synthesis

Pentacarbonylchromium(methoxyphenylcarbene) was used in the synthesis of vitamins K_3 and $K_{1(20)}$ by the methodologies shown below.[182]



(152)

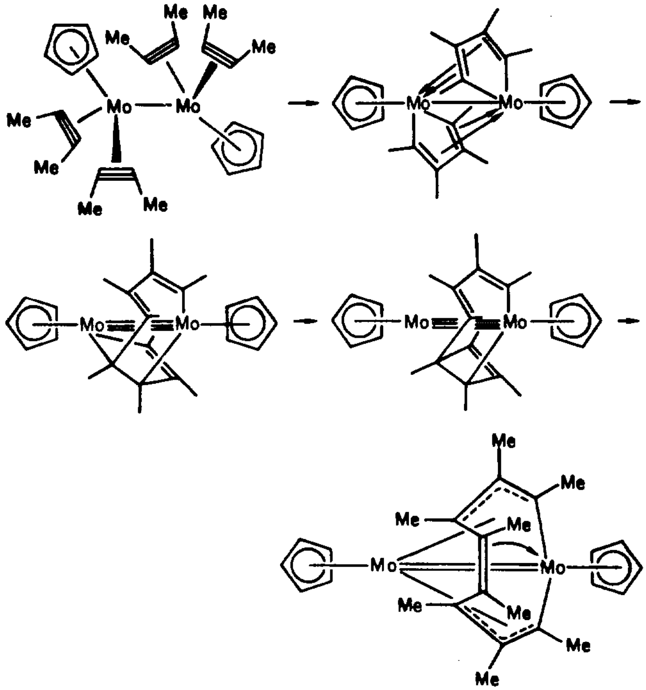




$$R = CH_2CH{=}\overset{Me}{C}CH_2(CH_2\overset{Me}{C}HCH_2)_2CH_2CH_2\underset{Me}{\overset{Me}{C}}H$$

(153)

Alkyne coupling was reported on a molybdenum complex leading to cyclotetramerization and dimer formation.[183]



(154)

In refluxing acetonitrile $[CpMo(CO)(MeC_2Me)_2][BF_4]$ lost CO to give $[CpMo(NCMe)(MeC_2Me)]BF_4$. Addition of $CpFe(CO)_2^-$ led to electron transfer with formation of the cyclotetramer and $Cp_2Fe_2(CO)_4$. The scheme above was suggested.[183]

Catalysis

Olefin metathesis. A theoretical study of olefin metathesis showed the following:[184] (1) There should be a dependence on electron count and the transition series arising from the orientation of the carbene and olefin. (2) For some electron counts the intermediate would be neither a metallocyclobutane or an olefin carbene but an intermediate between the two. (3) The role of the metal would be to hold the carbene and olefin in proper orientation for reaction while prohibiting cyclopropane elimination.[184]

A simple neopentylidyne complex was prepared by the route shown below.[185]

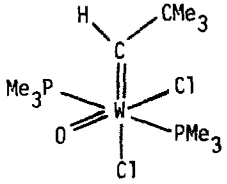
$$W(O)(CHCMe_3)(PEt_3)_2Cl_2 + C_2Cl_6 \xrightarrow{THF} C_2Cl_4 + Et_3P^+HCl^- + W(CCMe_3)(O{=}PEt_3)Cl_3 \qquad (155)$$

$W(CCMe_3)(O{=}PEt_3)Cl_3$ was characterized by NMR methods and its reaction with PEt_3 to give blue $W(CCMe_3)(O{=}PEt_3)(PEt_3)Cl_3$ and with excess PMe_3 to give rather insoluble, yellow $W(CCMe_3)(PMe_3)_3Cl_3$ and $Et_3P{=}O$ quantitatively. Other tungsten neopentylidyne complexes were also prepared.[185]

$$W(CCMe_3)(CH_2CMe_3)_3 + 3HCl + NEt_4{}^+Cl^- \xrightarrow{ether} [Et_4N]^+[W(CCMe_3)Cl_4]^- \qquad (156)$$

$$[Et_4N]^+[W(CCMe_3)Cl_4]^- + 3LiOCMe_3 \xrightarrow{THF} W(CCMe_3)(OCMe_3)_3 \qquad (157)$$

All of these tungsten(VI)-neopentylidyne complexes reacted with diphenylacetylene to give organic metathesis products and analogous benzylidyne complexes. For example, $W(CCMe_3)(O{=}PEt_3)Cl_3$ reacted with diphenylacetylene at 70°C in toluene in 1 h to give 95% of the expected $PhC{\equiv}CCMe_3$ and a green solution.[185] All the tungsten(VI)-alkylidyne complexes will catalytically metathesize acetylenes. The results suggested that the rate of productive metathesis depended on the steric and electronic properties of the acetylenes and the ligands on the catalyst.[185] The reaction of $Ta({=}CHCMe_3)(PR_3)_2Cl_3$ and $W({=}O)(OCMe_3)_4$ yielded mixed oxo-alkylidene complexes of tungsten(VI).[186] Two were subjected to single-crystal X-ray structural analysis. $W({=}O)({=}CHCMe_3)(PEt_3)_2Cl_2$ was disordered, but a full characterization of $W({=}O)({=}CHCMe_3)(PMe_3)_2Cl_2$ was completed.



LXXI

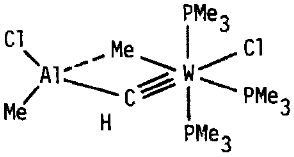
The oxo and alkylidene ligands occupied mutually cis locations.[186] The reaction between $WCl_2(PMe_3)_4$ and 2 equivalents of $AlMe_3$ in toluene gave an oil from which $W(CH)(Cl)(PMe_3)_4$ could be isolated.[187]

$$WCl_2(PMe_3)_4 \xrightarrow[\text{2. 2tmeda}]{\text{1. 2AlMe}_3\text{, toluene}} W(CH)(Cl)(PMe_3)_4 \qquad (158)$$

X-ray structural data suggested that the methylidyne and chloride ligands were trans to one another. The four PMe_3 ligands formed a flat tetrahedron. Reaction of this species with $AlMe_2Cl$ gave an adduct.[187]

$$W(CH)(Cl)(PMe_3)_4 \xrightarrow{AlMe_2Cl} W(CH)(Cl)(PMe_3)_3(AlMe_2Cl) \qquad (159)$$

LXXXII



LXXII

The metathesis reactions of methyl 10-undecenoate, methyl oleate and oleyl acetate were performed using WCl_6 and $WOCl_4$ as primary catalysts and $SnMe_4$, $PbMe_4$, Cp_2TiMe_2, and Cp_2ZrMe_2 as cocatalysts.[188] The catalyst system $WOCl_4/Cp_2TiMe_2$ was found to be very active for the metathesis of the unsaturated esters.

Catalyst[b]	Cocatalyst[c]	Time (h)	Yield (%)
$WOCl_4$	$SnMe_4$	18	54
$WOCl_4$	Cp_2TiMe_2	18	71
$WOCl_4$	$Cp_2TiClMe$	20	50.7
$WOCl_4$	Cp_2TiMe_2	20	60
WCl_6	$SnMe_4$	20	48.6
WCl_6	Cp_2TiMe_2	20	37.4

Diethyl 9-octadecene-1,18-dioate, obtained by the metathesis of ethyl oleate, was subjected to the Dieckmann cyclization.[188] The cyclized product was decarboxylated to give civetone as a mixture of the cis and trans isomers. Preliminary studies of macrolide synthesis by the intramolecular metathesis of oleyl oleate and 10-undecenyl 10-undecenoate to afford 9-octadecen-18-olide and 10-eicosen-20-olide, respectively, were also carried out.[188]

Other catalysts.

Measurements were carried out to determine the rate of hydrogen production by the water gas shift reaction operating at temperatures of 200°C with hexacarbonyls of chromium, molybdenum, and tungsten serving as catalyst precursors in basic methanol-water solutions.[189]

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (160)$$

The catalytic behavior of each of these systems was similar and turnover numbers as great as 12000 mol of H_2/mol of metal hexacarbonyl per day were achieved. The rate of hydrogen production was found to be (a) proportional to the amount of metal hexacarbonyl present in the system, (b) inversely proportional to carbon monoxide pressure; and (c) increasing with base concentration.[189] The overall kinetics of this reaction were explained by a mechanism involving formate decomposition rather than activation of carbon monoxide.[189] Rates of reaction of the hydrides of tungsten and molybdenum $HMCp(CO)_3$, with α-methylstyrene were determined. The rate law was first order in olefin and in hydride. A mechanism involving a rate limiting step of hydrogen atom transfer to the olefin was consistent with the rate law, isotope effect and the absence of CO inhibition.[190] The activation enthalpy for the reactions of $HW(\eta^5\text{-}C_5H_5)(CO)_3$ was approximately that of α-methylstyrene, while β-methylstyrene was not observed to react under similar conditions.[190] This suggested that attack by the hydride occurred at the β-carbon and this process was inhibited by substituents at that location.[190] A study of the reaction of CCl_4 with oct-1-ene in the presence of catalytic amounts of $[Mo_2(CO)_6(Cp)_2]$ demonstrated that in the early stages it proceeded by a redox-catalyzed mechanism.[191]

$$Cp_2Mo_2(CO)_6 + CCl_4 \rightarrow [MoCl(CO)_3(Cp)] + CCl_3\cdot + [Mo(CO)_3(Cp)\cdot] \tag{161}$$

$$CCl_3\cdot + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2CCl_3 \tag{162}$$

$$R\dot{C}HCH_2CCl_3 + [MoCl(CO)_3(Cp)] \rightarrow RCHClCH_2CCl_3 + [Mo(CO)_3(Cp)\cdot] \tag{163}$$

Gradual decomposition of the catalyst led to the intervention of a radical chain pathway.[191]

$$Cp_2Mo_2(CO)_6 + CCl_4 \rightarrow [MoCl(CO)_3(Cp)] + CCl_3\cdot \tag{164}$$

$$RCH{=}CH_2 + CCl_3\cdot \rightarrow R\dot{C}HCH_2CCl_3 \tag{165}$$

$$R\dot{C}HCH_2CCl_3 + CCl_4 \rightarrow RCHClCH_2CCl_3 + CCl_3\cdot \tag{166}$$

Furan reacted with t-butyl chloride at 130°C in the presence of $ArMo(CO)_3$ to yield 2-t-butylfuran and 2,5-di-t-butylfuran.[192] Up to 150 alkylation events occurred per Mo atom. At low conversions, the yields of 2-t-butylfuran were high while yields fell sharply with increasing catalyst concentration.[192] Butylation of 2-t-butylfuran occurred more readily than that of furan, and 2,5-di-t-butylfuran was formed in high yield. Both furan and 2-t-butylfuran reacted with t-butyl chloride more than 50 times as fast as toluene.[192] The utility of molybdenum porphyrin complexes in the epoxidation of alkenes was investigated.[193] The comparison of $Mo(CO)_6$ and 5,10,15,20-tetraphenylporphyrinato molybdenum(V) complexes, OMo(TPP)Cl, below was shown,

	relative rate	
alkene	$Mo(CO)_6$	OMo(TPP)Cl
trans-2-hexene	1.0	1.0
cis-2-hexene	2.0	3.5

indicating extra selectivity for the porphyrin complexes.[193]

PHYSICAL STUDIES

Vibrational Spectra

Vibrational spectra were recorded at ambient temperatures for the chalcocarbonyl complexes $Cr(^{12}CO)_5(^{12}CS)$, $Cr(^{12}CO)_5(^{13}CS)$, $Cr(^{13}CO)_5(^{12}CS)$, $Cr(^{12}CO)_5(^{12}CSe)$, and $Cr(^{13}CO)_5(^{12}CSe)$ as vapors and solids and in various solvents.[194] Definitive assignments were proposed for most of the fundamental vibrations of these molecules as well as for the related species $W(^{12}CO)_5(^{12}CS)$ and trans-$W(^{12}CO)_4(^{13}CO)(^{12}CS)$, on the basis of general quadratic valence potential fields employing both compliance and force constants. The sigma-donor/pi-acceptor capacities of the chalcocarbonyl ligands were discussed in terms of the interaction displacement coordinates which were derived from the MC and CX compliance constants.[194] The vibrational results reported provided further evidence for the transferability of compliance and force constants between species of closely related geometry and also for the similar bonding properties of the CS and CSe ligands.[194] The usefulness of high pressure infrared spectroscopic studies as a preliminary step in inorganic syntheses was illustrated in the reaction of $Mo_2Cl_4(PEt_3)_4$ with CO, N_2, and H_2.[195] The irreversible reaction of $Mo_2Cl_4(PEt_3)_4$ with CO under pressure was described.[195] Infrared spectroscopy of organometallic complexes in polymer films at 12-293 K was used to investigate reactive species.[196] In the photoreactions of $(\eta^5\text{-}C_5H_5)Mo(CO)_3(CH_3)$ both CO dissociation and Mo-CH_3 bond homolysis reactions were observed.[196]

$$\begin{tikzcd}
CpMo(CO)_3CH_3 \arrow[r, "h\nu"] \arrow[d, shift right, "h\nu"'] & CpMo(CO)_3^{\bullet} + CH_3^{\bullet} \arrow[d, "PVC"] \\
CpMo(CO)_2CH_3 + CO \arrow[u, shift right] & CpMo(CO)_3Cl
\end{tikzcd} \tag{167}$$

IR and Raman spectra of $(CO)_5ReM(CO)_4CC_6H_5$ (M = Cr, Mo, W) were recorded and interpreted.[197]

$(CO)_5ReM(CO)_4{\equiv}CPh$

LXXIII

Polarized Raman spectra obtained with single crystals of some of the compounds permitted the assignment of the vibrational bands for these molecules. The vibrational features of the phenyl group and the M≡C vibration were identical for this series and the $XM(CO)_4CPh$ series (X = Cl, Br, I). A comparison of the frequencies of the C-O groups of various compounds permitted a classification of the acceptor/donor behavior of other groups studied previously.[197]

Electronic Studies

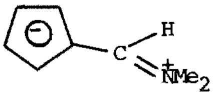
The energies of the low-lying unstable negative ion states of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ were obtained by electron transmission spectroscopy.[198] Calculations employing the SCF Xα method indicated that these compounds possessed a number of stable negative ion states and that the observed unstable states arose from electron capture into the antibonding ligand field orbitals and other empty orbitals correlating with the 2π and 6σ orbitals of free CO.[198] MCD spectra were reported and discussed for $M(CO)_5L$ complexes (M = Cr, Mo, W; L = PCl_3, PPh_3, PMe_3, thiazole, pyridine, pyrazine, pyridazine, piperidine, and NMe_3).[199] The results were used to assign the absorption bands of the $M(CO)_5L$ complexes. From the sign of the A term belonging to the lowest ligand field transition, it could be deduced that this transition was directed to the d_{z^2} orbital, a result of importance for the understanding of the photochemistry of these complexes.[199] Furthermore, the magnitude of this A term decreased going from piperidine to NMe_3, thiazole, pyridine, pyrazine, and pyridazine. The MCD spectrum of $Cr(CO)_5PCl_3$ closely resembled that of $Cr(CO)_6$, indicating that the electron distribution within the metal d orbitals of this pentacarbonyl complex was octahedral.[199] The problem of metal-ligand bonding in $Cr(CO)_5L$ compounds, where L was an aliphatic amine or an aromatic amine was addressed by X-ray work on a novel crystalline solid containing equimolar amounts of $Cr(CO)_5NHC_5H_{10}$ and $Cr(CO)_5NC_5H_5$ and on cis-$Cr(CO)_4(HNC_5H_{10})[P(OMe)_3]$ as well as by calculations on $Cr(CO)_5NH_3$.[200] The theoretical results showed that in the $Cr(CO)_5L$ compounds the $d_{x^2-y^2}$ orbital was above the d_{z^2} orbital. The structures showed that the replacement of an aliphatic by an aromatic amine has no significant effect on the structure of the $Cr(CO)_5$ group and that the two substituents $C_5H_{10}NH$ and $P(OMe)_3$ exert their structural effects on the $Cr(CO)_4$ residue essentially independently.[200] An XPS study yielded gas-phase core electron binding energies of η^6-$C_6H_6Cr(CO)_2CS$, $Cr(CO)_5CS$, $W(CO)_5CS$, $CpCr(CO)_2NS$, and the corresponding non-thio complexes.[201] The most significant feature of the data was the constancy of the binding energies of the metal atom and the carbonyl groups upon replacing the CO group by a CS group or replacing an NO group by an NS group. To account for the fact that replacement of CO by CS, or NO by NS, has little effect on the electron distribution of the remainder of the complex, it was concluded that increased back-bonding compensated for the greater donor character of the CS and NS groups.[201] The W 4f binding energies of various carbonyl-containing complexes of tungsten were reported.[202] Comparisons between W^{II} complexes containing the $[(\eta^3\text{-allyl})W(CO)_2]$ moiety and neutral derivatives of the type $W(CO)_{6-x}L_x$ were made. The absence of a clear-cut correlation between the W 4f binding energies and the value of x in $W(CO)_{6-x}L_x$ was discussed and the results compared with the analogous molybdenum complexes.[202]

An extension of the CNDO formalism was used for the donor/acceptor properties of the methylcarbyne ligand.[203] This ligand had electronic properties similar to the NO radical. The assumption of a carbon-metal triple bond as well as the possibility of a hyperconjugative coupling of the methyl group to the carbyne carbon atom was confirmed.[203] For trans-CO-substituted carbyne complexes a weak metal-CO bond was found. The electronic structure of $ClCr(CO)_4CCH_3$ was also compared with those of $Cr(CO)_6$, $Mn(CO)_5Cl$ and of a hypothetic $(CO)_5VCCH_3$.[203] The electronic structures and bonding capabilities of the carbyne ligands CMe^+, $CSiMe_3{}^+$, CPh^+, and $CNEt_2{}^+$ and $Cr(CO)_5$ were examined by a nonparametrized MO method.[204] The LUMO and the next lowest unoccupied MO in CPh^+ and $CNEt_2{}^+$ were different and not degenerate. Calculations were carried out on $(CO)_5CrCNEt_2{}^+$ which contained a triple metal-carbon bond.[204] Donation from the HOMO of the carbyne ligand into the LUMO of the metal fragment created a σ bond. Two π bonds were formed by back-donation from the two highest occupied orbitals of the metal fragment into the two lowest empty orbitals of the carbyne. The two lowest unoccupied molecular orbitals in each complex were pi antibonding between metal and carbon.[204] In frontier-controlled reactions, various nucleophiles added to the carbyne carbon atom, although it was invariably the most negative ligand site in the carbyne complex. An experiment was proposed to examine the relative importance of frontier and charge controls in these reactions.[204]

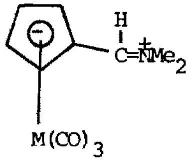
INDO SCF MO calculations were carried out for the species MCp_2 and $M(C_5H_5BH)_2$ ($M = Cr^-$, Mn, Fe^+) in order to make further comparison between the bonding characteristics of the cyclopentadienyl and borabenzene, C_5H_5BH, ligands in transition metal sandwich systems.[205] The calculations suggested differences in ground states would be observed. The findings were discussed in terms of the simple ligand field model.[205] The photoelectron spectra of $Cr(\eta^3\text{-}C_3H_5)_3$ were recorded.[206] The details observed were interpreted with reference to the intensity changes observed and to the results of ab initio molecular orbital calculations, which included consideration of configuration interaction to allow for the effects of orbital relaxation upon ionization. The two lowest spectral features were attributed to ionization from the metal localized levels. The latter ionization was considered to overlap with the ionization from the highest filled ligand level which correlated with the $1a_2$ π molecular orbital of the allyl group.[206] There was a significant amount of metal character in the orbitals arising from the interaction of the $1a_2$ ligand orbitals with empty chromium 3d and 4p orbitals; these overlaps are considered to be primarily responsible for the metal-ligand bonding interactions. The remaining peaks in the photoelectron spectra are attributed to ionizations from orbitals which are essentially localized on the ligands.[206] Gas-phase core electron binding energies of organometallic nitrosyl complexes of chromium, molybdenum, and tungsten were reported.[207] On going from Cr to W in the series $CpM(NO)_2Cl$, back-bonding to the NO groups increased and electron density was withdrawn from the Cl atoms. The data for $CpM(NO)_2Cl$ and $CpM(CO)_2NO$ (M = Cr, Mo, W) indicated that the back-bonding in the Mo and W compounds was different from that in first-row transition-metal nitrosyls. Electron density was transferred to the nitrosyl oxygen atom, while, in first-row nitrosyls, approximately equal amounts of electron density were transferred to the oxygen and nitrogen atoms.[207] The gas-phase ultraviolet photoelectron spectra were also reported for the compounds $CpM(NO)_2X$, where M = Cr, W and X = Cl, Br, I.[208] The observed spin-orbit splitting on the heavy atoms was used to assign and interpret the spectra. The results compared favorably with a molecular orbital calculation on the $CpCr(NO)_2Cl$ species. Although the complexes were formally M(0) d^6, the calculations suggested that the metal electrons were delocalized onto the nitrosyls.[208] This suggestion was supported by the similarity in the ionization energies of the chromium complexes to those of the isoelectronic $CpFe(CO)_2X$ systems. Comparison of the ionization energy of the metal-halogen sigma bonds suggested stronger W-X bonds than Cr-X bonds consistent with the reactivity of the complexes and with the relative metal-chloride bond lengths.[208]

Nuclear Magnetic Resonance

$(\eta^3\text{-allyl})_4M_2$ (M = Cr, Mo) existed in solution as two isomers with allyl groups which were trans and bridged the two metal atoms.[209] The other allyl groups were bonded to each one of the metals. In the major isomer these two allyl groups were cis, whereas in the minor isomer they were trans. The interconversion of the isomers were detected by magnetisation transfer difference spectroscopy (^1H NMR 400 MHz).[209] This interconversion proceeded by exchange of syn (anti) protons of the non-bridging allyl groups with syn (anti) protons of the non-bridging allyl groups. In addition, syn-syn (anti-anti) exchange of the protons of the bridging allyl groups was detected.[209] ^1H NMR spectroscopy was used in studying the rotational isomerism of 6-dimethylaminofulvene and its complexes with carbonyls of chromium, molybdenum and tungsten.[210] The energy for the barriers to rotation about the C-N bond were determined.



LXXIV

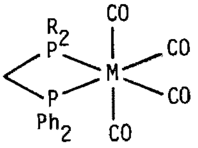


M = Cr, Mo, W

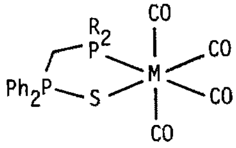
LXXV

It was shown that the coordination of 6-dimethylaminofulvene with Group VIB metal carbonyls increased the free energy for the barrier to rotation about the C-N bond, that is, it increased the degree of double-bond character between the C(6) and N atoms.[210] The free energy for the rotational barriers were strongly dependent on the nature of the central metal atom, increasing in the sequence W < Mo < Cr.[210]

Carbon-13 nuclear magnetic resonance data were reported for the compounds $[Ph_2PCH_2PR^1R^2]M(CO)_4$, where $R^1 = R^2$ = t-Bu or i-Pr and R^1 = Ph and R^2 = i-Pr and M = Cr, Mo, or W, and $[Ph_2P(S)CH_2PR^1R^2]M(CO)_4$ where $R^1 = R^2$ = i-Pr or Ph and R^1 = i-Pr and R^2 = Ph and M = Cr, Mo, or W.[211]



LXXVI



LXXVII

Multiple resonance selective decoupling and spin-tickling experiments were used to determine the signs of the carbonyl carbon-13 to phosphorus-31, phosphorus-31 to phosphorus-31, and phosphorus-31 to tungsten-183 coupling constants and also used to aid the chemical shift assignments of the carbonyl carbon-13 resonances. Carbon-13 data were also reported for many of the ligand carbons in these complexes.[211] The ^{13}C NMR spectra of binuclear Group VI metal carbonyl complexes with ferrocenylphenylthioketone as a ligand were reported.[212] These complexes had an octahedral structure with the metallocenyl thioketone in the axial position.

It was found that the carbon nuclei in the cyclopentadienyl rings of the thioketone were deshielded upon coordination to the $M(CO)_5$ group; the degree of deshielding depended on the central metal atom and decreased in the series W ⩾ Mo > Cr.[212] ^{13}C-^{13}C spin-spin coupling between axial and equatorial CO ligands in $M(CO)_5L$ (M = Group VIB metal) derivatives was employed in establishing intramolecular versus intermolecular axial-equatorial carbon monoxide ligand exchange pathways.[213]

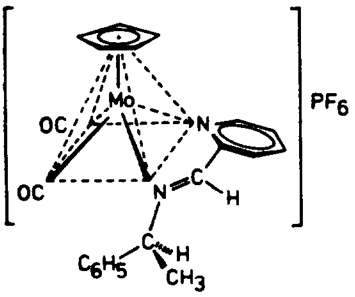
A number of studies of organomolybdenum complexes by molybdenum-95 NMR were reported in 1981. Molybdenum-95 NMR spectra were measured for a selection of molybdenum carbonyl compounds and $Mo(\sigma\text{-}C_5H_5)(\eta\text{-}C_5H_5)(NO)(S_2CNMe_2)$.[214] A chemical shift range of more than 1500 ppm was found.

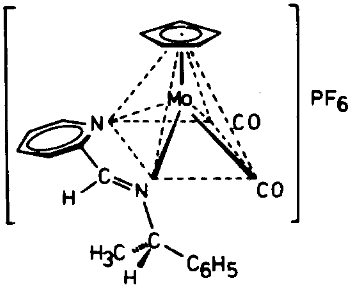
Compound	$\delta(^{95}Mo)$(ppm)	$\Delta\nu_{1/2}$(Hz)
$Mo(CO)_6$	-1857.2	3
$Mo(CO)_5PPh_3$	-1740.1	40
$Mo(CO)_5AsPh_3$	-1752.6	145
$Mo(CO)_5SbPh_3$	-1861.8	240
$Mo(CO)_5py$	-1387.4	68
$[Mo(CO)_5Br][NEt_4]$	-1540.0	125
$Mo(CO)_5CNCMe_2Ph$	-1752.2	130
$Mo(CO)_4$(norbornadiene)	-1590.7	25
$Mo(CO)_3$(cycloheptatriene)	-1675.3	18.5
$[Mo(CO)_3Cp]_2$	-1855.7	180
fac-$Mo(CO)_3(py)_3$	-1033.1	85
fac-$Mo(CO)_3(PCl_3)_3$	-1884.7	3
fac-$Mo(CO)_3(AsPh_3)_3$	-1548.9	350
fac-$Mo(CO)_3(SbPh_3)_3$	-1668.8	49
$Mo(CO)_2(C_7H_7)I$	-1348.2	107
$[Mo(CO)_2(C_7H_7)(dppe)][PF_6]$	-1083.0	250
$Mo(\eta C_5H_5)(\sigma\text{-}C_5H_5)(NO)(S_2CNMe_2)$	- 369.0	390

The chemical shifts and linewidths were discussed.[214] Molybdenum-95 NMR spectra of a variety of cyclopentadienylmolybdenum(II) carbonyl species were also reported.[215] Shielding of the ^{95}Mo nucleus increased in the sequence $(\eta^5\text{-}C_5H_5)(CO)_3MoCl < (\eta^5\text{-}C_5H_5)(CO)_3MoBr < (\eta^5\text{-}C_5H_5)(OC)_3MoI$.

Compound	δ(Mo)(ppm)	$\Delta\nu_{1/2}$(Hz)
$[Cp(OC)_3MoCl]$	-836	120
$[Cp(OC)_3MoBr]$	-956	115
$[Cp(OC)_3MoI]$	-1248	105
$[Cp(OC)_3Mo(CH_3)]$	-1736	40
$[\{Cp(OC)_3Mo\}_2Hg]$	-1834	160
$[Cp(OC)_3MoH]$	-2047	25

The results were discussed in terms of general applications of the technique to organomolybdenum chemistry. The direct observation of the naturally abundant ^{95}Mo NMR spectra of $[LMo(CO)_3]$ (L = cycloheptatriene, mesitylene, o-, m-, and p-xylene, toluene, cyclopentadienyl anion) compounds were reported and discussed.[216] Narrow resonances ($\Delta\nu_{1/2} \simeq 6$ Hz) were observed, and the signals quite shielded. The ^{95}Mo NMR chemical shift was related to the molybdenum-arene bond strength for L = arene. Arene exchange between $[LMo(CO)_3]$ derivatives was not detected.[216] Molybdenum-95 NMR was used to directly detect the two diastereomers differing only in the Mo configuration in the square pyramidal molybdenum(II) complex $[CpMo(CO)_2NN]PF_6$, where NN was the chiral pyridine-2-carbaldimine ligand derived from pyridine-2-carbaldehyde and (S)(-)-1-phenylethylamine.[217]

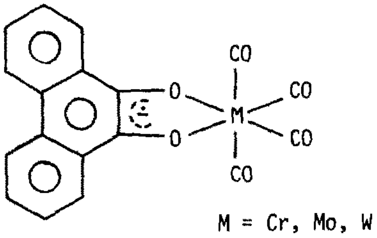




The simplicity of the spectra clearly revealed the optical purity of the complex with respect to the metal center.[217]

Electron Spin Resonance

Photolyses of Group VIB metal hexacarbonyls with phenanthroquinone in toluene solution led to the formation of some stable metal carbonyl-quinone radical complexes.[218]

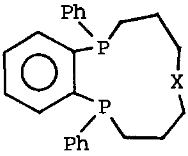


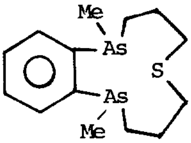
LXXX

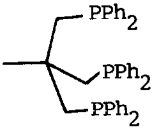
These parent radical complexes underwent further ligand exchange reactions between the carbonyl and Group VA organometals. The ESR observations provided some insight into the reaction mechanism.[218] An ESR study showed that a paramagnetic η^5-cyclopentadienylchromium dioxygen complex was generated in the thermal reaction of $Cr_2Cp_2(CO)_6$ in oxygenated solution and by photolysis and oxygenation of $[CpCr(CO)_3Cu(o\text{-}phen)]_n$ and of $Hg[CrCp(CO)_3]_2$.[219] The radical anions $RC_6H_4COC_6H_4R^1$-$Cr(CO)_3^-$ (R = H, o-CH_3, p-CH_3, p-OCH_3, p-Cl, p-F and R^1 = H; R = H, R^1 = o-CH_3, p-CH_3) were prepared by potassium reduction in 1,2-dimethoxyethane and their ESR spectra measured.[220] Both coordination isomers of the o-CH_3 complexes and the ligand had spectra consisting of four lines assigned to splittings from the para- and ortho-protons of the unsubstituted ring. The p-CH_3 complexes both had 7-line spectra assigned to splittings from the two sets of o-protons one set having half the hyperfine splitting of the other.[220] The reduction in hyperfine splitting of the uncomplexed as well as the complexed ring protons was an indication that the unpaired electron density was delocalized throughout the ligand system.[220] The self-exchange rates and activation parameters in the $(\eta^6\text{-arene})_2Cr^0/(\eta^6\text{-arene})_2Cr^I$ systems (where arene = toluene, benzene, methoxylbenzene, biphenyl, ethylbenzoate and chlorobenzene) were measured by ESR line broadening.[221] The one-electron reduction was investigated by cyclic voltammetry for the series of substituted complexes of $(\eta^6\text{-arene})_2Cr^I$. A linear correlation was obtained between the measured $E_{1/2}$ values and the sum of Hammett parameters.[221] A correlation of the oxidation stability of sandwich compounds with their gas-phase ionization potentials was evident from a linear relationship between the oxidation half-potentials $E_{1/2}$ and the gas-phase ionization potentials.[221]

Electrochemical Investigations

The difficulty of interpreting the electrochemistry of compounds which have isomers with similar standard redox potentials was illustrated with data for $Mo(CO)_4L_2$ (L = PBu_3, PEt_3, PPh_3) complexes.[222] A series of fac group 6 metal tricarbonyl complexes of 11-membered tridentate macrocycles (ligating sites P_2N, P_2S, P_3, and As_2S) were studied by cyclic voltammetry.[223]







These complexes underwent quasi-reversible single-electron oxidations with redox potentials dependent on the nature of X in the 11-P_2X series. The range of oxidation potentials was 0.42-0.47 V for a series X = N, S, P with a particular metal, with ease of oxidation decreasing as X is varied from N to S to P.[223] The electrochemical oxidation of the mono- and bis- (tricarbonylchromium) complexes of dimethyldiphenyltin provided stable cations on the cyclic voltammetric time scale in contrast to arenetricarbonylchromium complexes.[224] Oxidation of the mono-complex was a one-electron process yielding a stable cation while oxidation of the bis-complex was a two-electron process yielding a stable dication. The stability of the cations was increased by substitution of electron donating groups in the 2, 4, and 6 positions of the phenyl rings.[224] Similarly, the electrochemical oxidation of the tris-(tricarbonylchromium) complex of methyltriphenyltin was a three-electron process yielding a stable trication. All of the electrochemical data on the bis- and tris-complexes indicate that the arenetricarbonylchromium groups within each molecule were noninteracting.[224] The redox properties of a number of bisarenechromium complexes were studied by the rotating disk electrode technique in DMSO.[225] The half-wave potentials were found to correlate with the meta-substituent constants. It was concluded that the electronic effects of substituents were transferred to the metal atom by an inductive mechanism. The conjugation of substituents with the coordinated ring was weaker in bisarenechromium complexes than in ferrocene derivatives.[225] The rhena-acetylacetonate complexes, $[cis\text{-}(OC)_4Re(CH_3CO)_2]_3Cr$, and the corresponding acac-complexes were examined by cyclic voltammetry in methylene chloride solutions.[226] Redox potentials of the central coordinating chromium for the metalla- and the analogous non-metalla-acetylacetonate complexes were determined.

Miscellaneous Physical Techniques

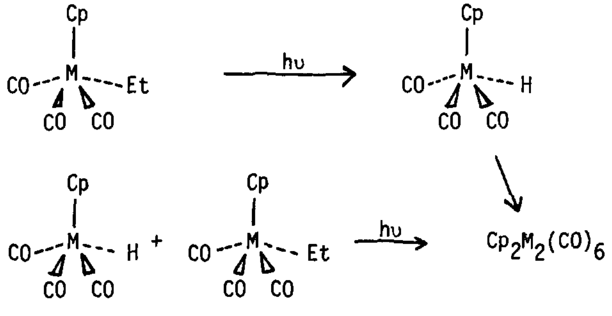
Irradiation of $CpW(CO)_3CH_3$ in a variety of solvents produced $Cp_2W_2(CO)_6$ and methane.[227] In CH_2Cl_2 and $CHCl_3$ solutions, $CpW(CO)_3Cl$ and $CpW(CO)_2Cl_3$ were secondary and tertiary photoproducts, respectively. The disappearance quantum yield for $CpW(CO)_3CH_3$ in CH_2Cl_2 solution was 0.08; this value dropped to 0.04 when excess CO was present. Irradiation of $CpW(CO)_3CH_3$ in the presence of PPh_3, $AsPh_3$, or Ch_3CN gave the substituted products $CpW(CO)_2(L)CH_3$.[227] The quantum yield of disappearance for $CpW(CO)_3CH_3$ in these photosubstitution reactions was about 0.4. $CpW(CO)_3CH_3$ reacted photochemically with THF at -78°C to give $CpW(CO)_2(THF)CH_3$.[227] Solutions of this product were stable at -78°C, but the complex decomposed to $Cp_2W_2(CO)_6$ and $CpW(CO)_3CH_3$ upon warming to room temperature. Irradiation of $CpW(CO)_2(PPh_3)(COCH_3)$ at room temperature in CH_2Cl_2 or THF solution produced $CpW(CO)_3CH_3$. The primary photoprocess of the $CpW(CO)_3CH_3$ complex was proposed to be W-CO bond dissociation, and the following pathway was suggested for the formation of $Cp_2W_2(CO)_6$.[227]

$$CpW(CO)_3CH_3 \xrightarrow{h\nu} CpW(CO)_2CH_3 + CO \tag{168}$$

$$CpW(CO)_2CH_3 + CpW(CO)_3CH_3 \rightarrow Cp_2W_2(CO)_5 + 2\ CH_3 \tag{169}$$

$$Cp_2W_2(CO)_5 + CO \rightarrow Cp_2W_2(CO)_6 \tag{170}$$

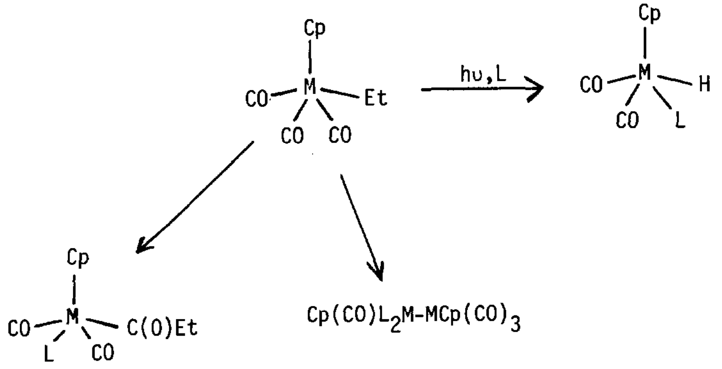
The source of the extra hydrogen for the methyl radical to form methane was proposed to be the solvent since in benzene-d_6 CH_3D was formed. In the compounds $CpM(CO)_3Et$(M = Mo, W) the metal-ethyl σ-bond was shown to be photolabile.[228] Upon irradiation of a solution of $CpM(CO)_3Et$ with UV light mainly $[CpM(CO)_3]_2$, $CpM(CO)_3H$, ethane, and ethylene were produced.



(171)

M = Mo, W

Formation of $CpM(CO)_3H$ indicated a β-elimination pathway for the photo-induced degradation. In the presence of trimethylphosphine UV-irradiation of a solution of $CpM(CO)_3Et$ led to the products $Cp(CO)(L)_2M - M(CO)_3Cp$, $CpM(CO)_2(L)Et$ and $CpM(CO)_2(L)H$ while the thermal reaction produced the propionyl complexes $CpM(CO)_2$-(L)(COEt).[228]

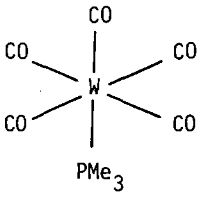


(172)

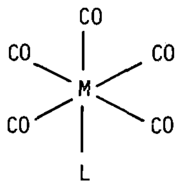
The electron impact mass spectra of $(CO)_3MC_6H_5$-X complexes (M = Cr, W; X = OCH_3, OC_4H_9, CO_2CH_3, $CO_2C_4H_9$) were recorded.[229] From metastable transitions and by high-resolution measurements complete fragmentation diagrams were obtained. The fragmentation of the tungsten complexes differed from that of the chromium compounds. The differences were attributed to the stronger electrophilic character as well as to the tendency of tungsten for higher oxidation states.[229]

Structural Determinations

The structure of $W(CO)_5PMe_3$ was determined to evaluate the length of a tungsten-phosphine bond with minimal steric interactions.[230] The geometry was octahedral with a W-P bond of 2.516(2).[230]



LXXXIV



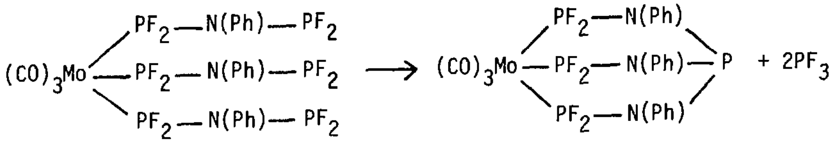
LXXXV

M = Cr, Mo

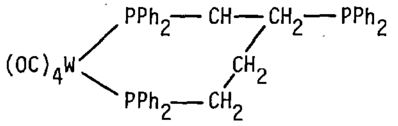
L = $P(CH_2CH_2CN)_3$

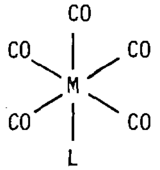
PPh_3

The X-ray crystal structures of the compounds $M(CO)_5P(CH_2CH_2CN)_3$, M = Cr and Mo and $Mo(CO)_5P(C_6H_5)_3$ were reported.[231] The M-P distances are 2.364 (1) and 2.506 (1) Å for the Cr and Mo compounds for L = $P(CH_2CH_2CN)_3$. The Mo-P distance was 2.560 (1) Å for $Mo(CO)_5PPh_3$. On the basis of these structural data tris(2-cyanoethyl)-phosphine was described as a good π-acceptor ligand.[231] A solution of fac-$(CH_3CN)_3Mo(CO)_3$ was stirred with $C_6H_5N(PF_2)_2$ for 2 days at 40-45°C.[232]


(173)

The structure of the chelate was that of an octahedral fac-$L_3Mo(CO)_3$ complex. The tridentate ligand, $P[N(C_6H_5)PF_2]_3$, had its three PF_2 groups linked to the Mo atom so as to form a cage molecule.[232] The structure of the product from the reaction of trans-$(CO)_4W(PPh_2CH{=}CH_2)_2$ with PPh_2H was reported showing cis octahedral geometry with a bidentate phosphorus ligand.[233] The P-W-P angle of 87.58(6)° was relatively unstrained.[233]

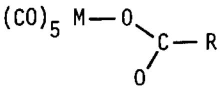

LXXXVI


LXXXVII

M = Cr, W

L = $S(SnMe_3)_2$, $Se(SnMe_3)_2$, $S(GeMe_3)_2$, $S(PbMe_3)_2$

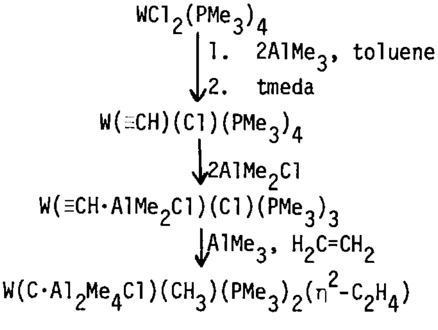
The structures of the isostructural compounds $[(CH_3)_3Sn]_2SCr(CO)_5$, $[(CH_3)_3Sn]_2SeW(CO)_5$, $[(CH_3)_3Ge]_2SW(CO)_5$ and $[(CH_3)_3Pb]_2SW(CO)_5$ were determined by single crystal X-ray analyses.[234] The substitution of one carbonyl group of the corresponding metal hexacarbonyls by the organometal chalcogenide caused a distortion of the $M(CO)_5$ group. The metal-chalcogen bonds were single without significant π-bond contributions. The coordination around the chalcogen atoms was nearly tetrahedral.[234] The reaction of $[PNP][Mo(CO)_5Cl]$, PNP = $[Ph_3PNPPh_3]^+$, with AgO_2CCH_3 and AgO_2CCF_3 afforded the complexes $[PNP][Mo(CO)_5(O_2CCH_3)]$ and $[PNP][Mo(CO)_5(O_2CCF_3)]$.[235] The trifluoroacetate derivative of chromium was conveniently prepared in a similar manner. The most significant structural aspects were equivalent (M)O-C and C=O bond lengths and short trans M-C(O) bond distances. Ligand substitutional processes involving displacement of either the acetate or carbonyl ligands in [PNP][$Mo(CO)_5(O_2CCH_3)$] were very facile.[235]



M = Cr, Mo
R = CH_3CF_3

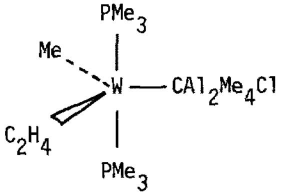
LXXXVIII

The reductive coupling of adjacent isocyanide ligands in the heptacoordinate $[Mo(t\text{-}BuNC)_6X]^+$ complexes produced $[Mo(t\text{-}BuNC)_4(t\text{-}BuHNCCNH\text{-}t\text{-}Bu)X]^+$ cations that contain the novel (N,N'-dialkyldiamino)acetylene molecule coordinated to molybdenum(II).[236] The structures of three compounds containing these cations, with X = Br or I, were determined in single-crystal X-ray diffraction studies. The geometries of the halotetrakis(tert-butyl isocyanide)((N,N'-di-tert-butyldiamino)-acetylene)molybdenum(II) cations were similar and resembled those of the starting, capped trigonal-prismatic complexes. In these compounds the coupled ligand was considered as a four-electron-donating (dialkyldiamino)acetylene.[236] The dialuminamethylidyne complex $W(CAl_2Me_4Cl)(CH_3)(PMe_3)_2(\eta^2\text{-}C_2H_4)$ was investigated by a single-crystal X-ray diffraction study.[237]

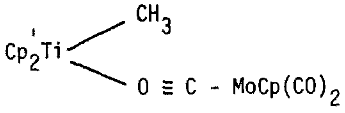


(174)

The trimethylphosphine ligands occupy axial sites about a distorted trigonal-bipyramidal W(IV) atom with the equatorial sites occupied by a methyl group, an η^2-ethylene ligand, which lay perpendicular to the equatorial coordination plane, and a CAl_2Me_4Cl ligand. The W-(CAl_2Me_4Cl) fragment was described as a $W{\equiv}C{:}^-$ system linked by a three-center, two-electron bond to the two aluminum atoms of a $[Me_2Al(\mu\text{-}Cl)AlMe_2^{\ +}]$ moiety.[237]



LXXXIX

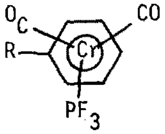


Cp' = η^5 - C_5Me_5

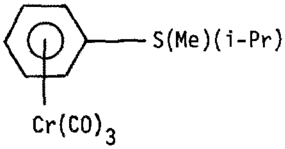
XC

The addition of $CpMo(CO)_3H$ to (η^5 - C_5Me_5)(C_5Me_4 = CH_2)TiMe resulted in formation of a Lewis-acid carbonyl adduct.[238] Molecular orbital calculations supported the description.[238]

The crystal effect on the molecular geometry of substituted derivatives of benzenechromium tricarbonyl was evaluated by determining favoured conformations of several complexes (substituted at the arene ring or the metallic moiety) in the gaseous state.[239] The conformation was compared to the solid state conformation showing that the two conformations were similar in most cases.[239] The crystal and molecular structure of dicarbonyltrifluorophosphine chromium methylbenzoate was determined.[240] The molecular structure, compared with those of some derivatives of the type $CH_3CO_2(C_6H_5)Cr(CO)_2L$, was intermediate between those corresponding to L = PPh_3 and L = CO. The Cr-P distance (2.132(3) Å) was very short, suggesting that the PF_3 ligand was a good pi-electron acceptor.[240]

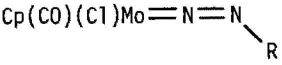


XCI

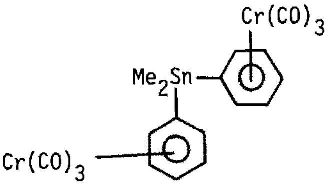


XCII

The structure of tricarbonylchromium phenylisopropylmethyl sulfonium tetrafluoborate was determined by a three-dimensional X-ray analysis.[241] A tentative interpretation of the diastereotopic NMR shifts was given on the basis of the preferred conformations. The difference in chemical shifts between the two geminal methyl protons of the isopropyl groups of three sulfonium tetrafluoborates free and complexed with $Cr(CO)_3$, was also reported.[241] (η^5-methylcyclopentadienyl)-bis(p-fluorophenyldiazenido)chloromolybdenum(0) was isolated as a byproduct of the reaction of (p-FC_6H_4N)(BF_4) with Na(η^5-$CH_3C_5H_4Mo(CO)_3$) and characterized crystallographically.[242] The molybdenum coordination was distorted octahedral with three facial sites occupied by the η^5-$CH_3C_5H_4$ ligand and the remaining three sites by the chlorine and two arenediazo ligands.



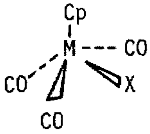
XCIII



XCIV

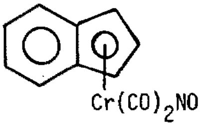
The structure of η^6,η^6-Dimethyldiphenylstannane-bis-tricarbonylchromium, $(CH_3)_2Sn[C_6H_5\text{-}Cr(CO)_3]_2$ was reported.[243] The geometry of the four groups around the tin atom was tetrahedral. The spectral properties of this compound could not be attributed to molecular distortions of the normal tin geometry.[243]

Single-crystal X-ray diffraction studies were accomplished on three simple $CpM(CO)_3X$ derivatives, X = Cl, HgCl; M = Mo, W.[244] The $CpM(CO)_3Cl$ complexes were isostructural with W-Cl = 2.490 (2) Å and Mo-Cl = 2.498 (1) Å.[244]



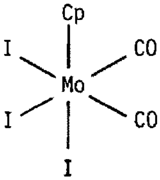
M = Mo, W
X = Cl, HgCl

XCV



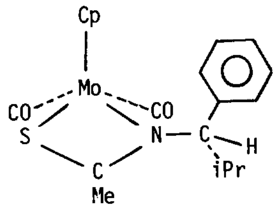
XCVI

The structure of (η^5-indenyl)$Cr(CO)_2NO$ was reported with the indenyl ligand tilted.[245] The structure of the Mo(IV) complex, $(MeCp)Mo(CO)_2I_3$ was accomplished showing the eight-coordinate complex to be a distorted octahedron (if the MeCp occupied one site).[246]

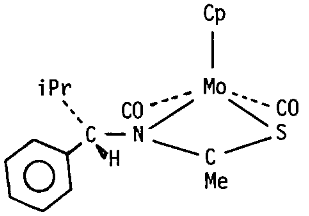


XCVII

The crystal structures of one of the diastereoisomers and of the racemic pairs having composition $(\eta^5\text{-}C_5H_5)Mo(CO)_2SC(CH_3)NR$ with R = $CH[CH(CH_3)_2](C_6H_5)$ were determined from single crystal X-ray diffraction data.[247] The Bijvoet test was applied to the enantiomorphic crystal and the configuration assigned was (S) for both the optically active carbon and the Mo site. Both compounds had an approximately square-pyramidal configuration around the Mo atom in which the thioamide ligand was bound through the S and N atoms.[247]

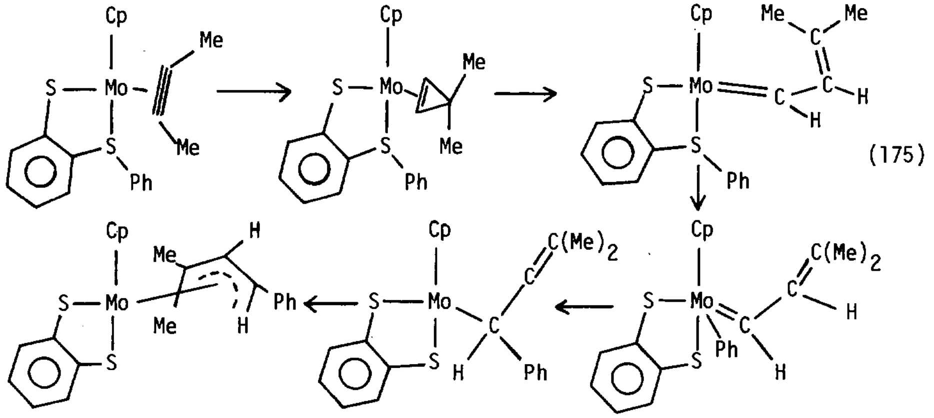


XCVIII



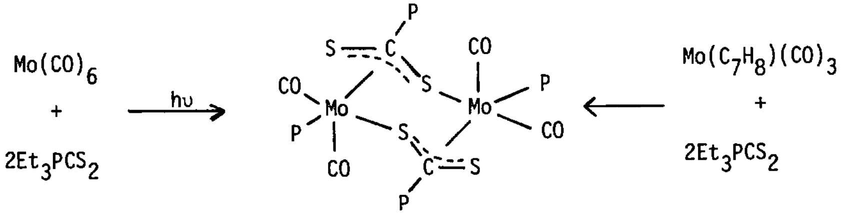
XCIX

Reaction of $[Mo(\eta\text{-}MeC_2Me)(SC_6H_4\text{-}o\text{-}SC_6H_5)Cp]$ with 3,3-dimethylcyclopropene led to displacement of the acetylene and a migration of the phenyl group from sulphur to a carbon atom of the ring-opened cyclopropene with formation of the η^3-allylic complex $[Mo(\eta^3\text{-}syn\text{-}1\text{-}Ph\text{-}3,3\text{-}Me_2\text{-}C_3H_2)(1,2\text{-}C_6H_4S_2)Cp]$, which was identified by X-ray crystallography.[248] The following scheme was suggested.[248]



(175)

The zwitterion Et_3PCS_2 reacted with $Mo(CO)_6$ or $Mo(C_7H_8)(CO)_3$ to give the dinuclear complex $[Mo(CO)_2(PEt_3)(\mu\text{-}S_2CPEt_3)]_2$.[249]

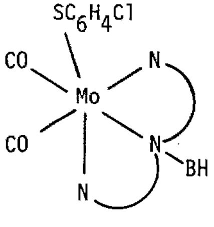


(176)

An X-ray crystal structure determination has showed that both zwitterions coordinate one metal through an η^3-S_2C linkage and the second metal through a single sulphur atom.[249] $Cp_2Mo(HgSC_2H_5)_2$ crystallized in two different forms which were determined by X-ray diffraction.[250] The electronic structure of the $Cp_2Mo(HgSR)_2$ compounds was discussed on the basis of ^1H, ^{13}C, ^{199}Hg and ^{95}Mo NMR results and compared with the geometrical parameters. A relation between the nature of the X-ligands in the Cp_2MoX_2 complexes (X = O, Cl, S, H, Hg), the Cp-Mo-Cp angle and the $^1H(C_5H_5)$ chemical shifts was evident.[250] The reaction between $CHFBr_2$ and the dinitrogen-derived hydrazido complex $[WBr(dppe)_2N_2H_2]^+Br^-$, in the presence of $[Ph_2I]^+Br^-$ and aqueous base, gave a cationic, binuclear complex $[W_2(\mu\text{-}N_2CHN_2)(dppe)_4Br_2]^+$.[251] This complex was investigated by single-crystal X-ray study. The cation contained a formazanido ligand, $[N_2CHN_2]^{3-}$, bridging two tungsten atoms in a seven-atom chain.[251]

$(dppe)_2BrW\text{-}N = N\text{-}CH\text{-}N = N\text{-}WBr(dppe)_2$

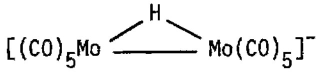
C



CI

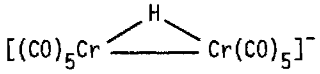
Crystals of $HB(Me_2pz)_3Mo(CO)_2SC_6H_4Cl$, a formally 16-electron Mo(II) complex, were investigated.[252] The molybdenum atom had slightly distorted octahedral coordination with the pyrazolylborate ligand occupying three facial sites. The Mo-S distance indicated considerable double-bound character.[252]

The structures of the $[M_2(CO)_{10}H]^-$ species continued to attract interest. X-ray diffraction studies of several salts of the $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ monoanion were undertaken to examine the influence of lattice effects upon the anion's solid-state geometry.[253] These studies indicated that the $[Mo_2(CO)_{10}(\mu\text{-}H)]^-$ anion can adopt either a linear, eclipsed ($[Et_4N]^+$ salt) or an appreciably bent, staggered ($[(Ph_3P)_2N]^+$ and $[K(crypt\text{-}222)]^+$ salts) configuration with the degree of bending dictated by the choice of the cation. This greater bending of the Mo-H-Mo bond and the metal carbonyl framework for the latter sales was accompanied by a reduction of the Mo···Mo separation in the three-center, two-electron bond from 3.4219(9) to 3.4056(5) Å.[253]



$$[(CO)_5Mo \overset{H}{\text{———}} Mo(CO)_5]^-$$

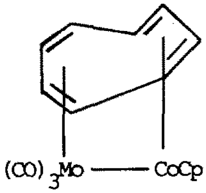
CII



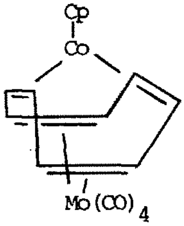
$$[(CO)_5Cr \overset{H}{\text{———}} Cr(CO)_5]^-$$

CIII

A combination room-temperature X-ray and low-temperature (20 ± 1 K) neutron diffraction study of $[K\text{-}C_{18}H_{36}N_2O_6]^+[Cr_2(CO)_{10}(\mu\text{-}H)]^-$ was performed to determine the anion's configuration in the absence of crystallographic site symmetry constraints.[254] The two independent $Cr(CO)_5$ groups of the anion were rotated 19° with respect to each other about the Cr-Cr line. This configurational change in the metal carbonyl framework was accompanied by a reduction of the Cr···Cr separation to 3.300 (4) Å and the Cr-H-Cr bond angle to 145.2 (3)°, which indicated an increase in the metal-metal bonding component of the closed three-center, two-electron Cr-H-Cr bond.[254] The bridging hydrogen atom resided in a symmetrical electronic environment as suggested by the two independent, but equivalent, Cr-H separations of 1.735 (5) and 1.723 (5) Å.[254] The reaction of $CpCoC_8H_8$ with $(diglyme)Mo(CO)_3$, $(CH_3CN)_3Cr(CO)_3$ and $(DMF)_3W(CO)_3$ provided dimetallic complexes $CpCoC_8H_8M(CO)_3$ which contained bridging fluctional cyclooctatetraene.[255] The electron deficiency of the $Mo(CO)_3$ groups relative to CpCo was suggested to be balanced by a π-donor metal-metal bond. This was indicated by an unusually low absorption band in the IR spectrum, and by the X-ray structure of the Co-Mo dimer, which showed a shortened Mo-CO bond trans to the metal-metal bond.[255]

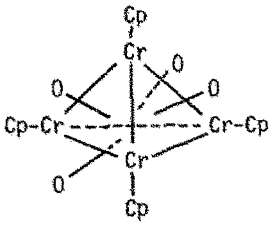


CIV



CV

A further product was the dimer $CpCoC_8H_8Mo(CO)_4$, in which cyclooctatetraene retained a rigid tub conformation. Reaction of $C_8H_8Fe(CO)_3$ with $(diglyme)Mo(CO)_3$ also gave a dimeric product $(CO)_3FeC_8H_8Mo(CO)_3$ with a fluctional bridge ligand.[255] Treatment of a toluene solution of Cp_2Cr with N_2O followed by sublimation at 275-300°C and recrystallization of the sublimate from hexane gave deep blue, very air- and water-sensitive crystals of $Cp_4Cr_4O_4$ in 8% yield.[256] The chromium atoms formed an approximate tetrahedron, capped by the Cp rings and with the oxygen atoms above each face.[256]



CVI

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