CHROMIUM, MOLYBDENUM, AND TUNGSTEN

ANNUAL SURVEY COVERING THE YEAR 1979

JIM D. ATWOOD

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

CONTENTS

ABBREVIATIONS

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

INTRODUCTION

This survey covers the 1979 literature with the coverage and format indentical to that of the 1978 survey. The main journals were covered directly and a computer search was accomplished to insure a comprehensive review of the literature.

DISSERTATIONS

Several dissertations on Group VI organometallic compounds appeared in 1979. Metal vaporization techniques were used to prepare molybdenum complexes of trifluorophosphine and chromium complexes of aminodifluorophosphines;[1,2] thiocarbonyl complexes of tungsten were prepared and studied;[3] chromium tri-carbonyl complexes of phenylsilanes were synthesized and characterized;[4] supported molybdenum catalysts were used in hydrogenations and to catalyze reactions of alkynes;[5,6] the synthesis and characterization of substituted and unsubstituted alkyldiazenido complexes were reported;[7] photochemistry of nitrogen exchange, substitution kinetics and electronic absorption spectra of dinitrogen complexes of molybdenum and tungsten were studied;[8,9] and a new series of chelated organochromium(III) complexes were reported.[10]

SYNTHESIS AND REACTIVITY

Metal Carbonyls

The reaction of $M(CO)_6$ (M = Cr, Mo, W) with AlH_3 in THF solution at 22°C resulted in selective formation of ethylene by reduction of coordinated carbon monoxide.[11] The maximum yield was 17% for a $Cr(CO)_6:AlH_3$ molar ratio

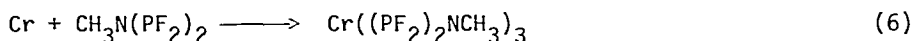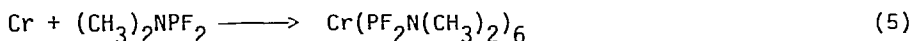$$Cr(CO)_6 + AlH_3 \longrightarrow C_2H_4 \qquad\qquad (1)$$

of 1:6. Acidification resulted in formation of methane and ethane.[11] Use of $LiAlH_4$ also gave reduction of coordinated CO, although conversion was reduced. It was suggested that the reaction proceeded through a carbene intermediate.[11] Hexakis(phosphite ester) chromium compounds, $Cr[P(OR)_3]_6$, were prepared by Cr atom vaporization and cocondensation with a phosphite.[12]

$$Cr + P(OR)_3 \longrightarrow Cr[P(OR)_3]_6 \qquad\qquad (2)$$

$$Cr[P(OR)_3]_6 + H_2 \longrightarrow H_2Cr[P(OR)_3]_5 \qquad\qquad (3)$$
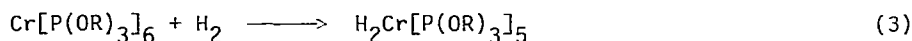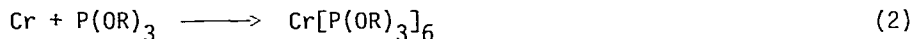
Dihydridopentakis(phosphite ester) compounds were prepared by hydrogenation of the corresponding hexakis compound. Both the hexakis- and the dihydrido-pentakis(phosphite ester) chromium compounds were reported to be active hydrogenation catalysts.[12] Reduction of $W(CO)_6$ with Na amalgam and reaction with Cl_2CS gave ~ 70% $W(CO)_5CS$.[13]

$$W(CO)_6 + Na + Cl_2CS \longrightarrow W(CO)_5CS \qquad\qquad (4)$$
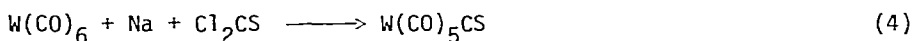
Purification was effected by reduction and subsequent re-oxidation.[13] Reaction of $Cr(CO)_6$ and $Cr(CNC_6H_5)_6$ led to cis-$Cr(CO)_2(CNC_6H_5)_4$ and $Cr(CO)(CNC_6H_5)_5$. Electrochemical data was collected on $Cr(CNC_6H_5)_6$ and suggested three sequential one-electron oxidation processes.[14] The cocondensation of Cr vapor with (dimethylamino)-difluorophosphine and (methylamino)bis(difluorophosphine) was reported.[15]

$$Cr + (CH_3)_2NPF_2 \longrightarrow Cr(PF_2N(CH_3)_2)_6 \qquad\qquad (5)$$

$$Cr + CH_3N(PF_2)_2 \longrightarrow Cr((PF_2)_2NCH_3)_3 \qquad\qquad (6)$$

The product, $Cr(PF_2N(CH_3)_2)_6$, was not very stable; this was attributed to the

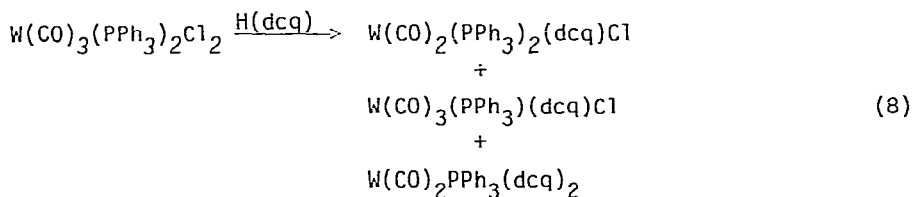bulkiness of the ligand. Using a 4:1 mixture of $PF_2N(CH_3)_2$ to $(PF_2)_2NCH_3$ they obtained $Cr(PF_2N(CH_3)_2)_4(PF_2)_2NCH_3$. Examination of the mass spectrum of fac-(nbd)-$Mo(^{13}CO)(CO)_3$ (nbd = norbornadiene) showed that CO loss occurred with complete scrambling.[16] In contrast the mass spectrum of fac-(bcnt)-$Mo(^{13}CO)(CO)_3$ (bcnt = bicyclo[6.1.0]nona-2,4,6-triene) showed that loss of CO occurred almost exclusively through the labeled group. This was interpreted in terms of accompanying formation of a new metal-olefin bond on loss of CO from (bcnt)-$Mo(CO)_4$.[16]


$$\tag{7}$$
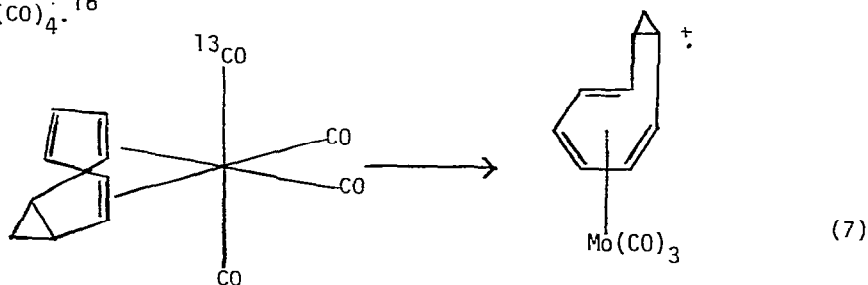
The interaction of cations with transition metal carbonylates and cyanocarbonylates was reported by Darensbourg and Barros.[17] The cation was always associated with the cyanide ligand in preference to the carbonyl in the mixed complexes. They presented a general discussion of the site and infrared spectral changes.[17]

Several seven coordinate complexes have been studied this year. The reaction of $W(CO)_3(PPh_3)_2Cl_2$ with H(dcq)(dcq = 5,7-dichloro-8-quinolinato) led to several new seven-coordinate tungsten(II) complexes.[18]

$$W(CO)_3(PPh_3)_2Cl_2 \xrightarrow{H(dcq)} W(CO)_2(PPh_3)_2(dcq)Cl$$
$$+$$
$$W(CO)_3(PPh_3)(dcq)Cl \tag{8}$$
$$+$$
$$W(CO)_2PPh_3(dcq)_2$$

The two mono dcq species were always formed in mixture; the bis dcq complex could only be formed in the presence of added strong base. The dcq ligand was coordinated through phenolato oxygen and heterocyclic nitrogen leading to the seven-coordinate structures.[18] The synthesis of diiododicarbonyltris(t-butyl-isocyanide)-tungsten(II) from $(t-C_4H_9NC)_3W(CO)_3$ and I_2 was described.[19]

$$(t-C_4H_9NC)_3W(CO)_3 + I_2 \longrightarrow W(t-C_4H_9NC)_3(CO)_2I_2 + CO \tag{9}$$
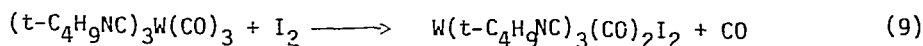
Analysis of the geometry revealed the coordination polyhedron of the tungsten to be that of a 4:3 square based-trigonal capped piano stool with 2 I's and one CO making up the trigonal cap and three isocyanides and one CO making up the base.[19] Addition of an excess of t-BuNC to $Mo_2(O_2CCF_3)_4$ or $Mo_2(O_2CMe)_4$ gave $(t-BuNC)_5Mo(O_2CCF_3)$ or $(t-BuNC)_4Mo(O_2CMe)_2$, respectively, by cleavage of the molybdenum-molybdenum quadruple bonds.[20]

$W(CO)_3(dmtc)_2$ (Hdmtc = dimethyldithiocarbamic acid) was prepared and two distinct intramolecular dynamic processes were identified by variable-temperature ^{13}C NMR studies of this 7-coordinate molecule.[21]

$$W(CO)_4L_2 + Na(dmtc) \longrightarrow W(CO)_3(dmtc)_2 \qquad (10)$$
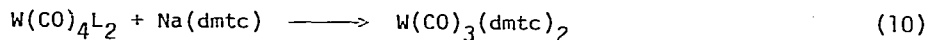
The reactions of this seven-coordinate complex were investigated.[21]

The intramolecular isomerization of bis(tri-n-butylphosphine)molybdenum tetracarbonyl was investigated from both directions with K_{eq} equal to 5.3 for cis → trans.[22]

$$cis-Mo(CO)_4(PBu_3)_2 \longleftrightarrow trans-Mo(CO)_4(PBu_3)_2 \qquad (11)$$
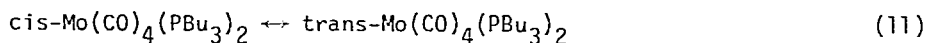
The trans isomer was more stable by 1 kcal/mol.[22] The reaction did not proceed by a dissociative process, as the isomerization was observed in the presence of ^{13}CO and $P(OC_6H_5)_3$ with no detectable incorporation. They suggested an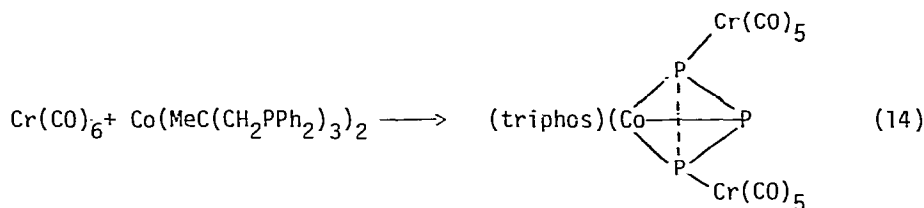 intramolecular, trigonal-twist to account for the observations.[22] Photochemical reaction of $Cr(CO)_6$ with MePPh$_2$ produced trans-bis(methyldiphenylphosphine)tetracarbonylchromium.[23]

$$Cr(CO)_6 + PMePh_2 \xrightarrow{h\nu} trans-Cr(CO)_4(PMePh_2)_2 \qquad (12)$$
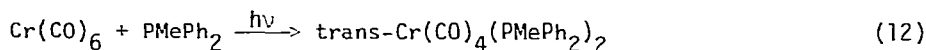
This reaction occurred in 69% yield and the properties of the compound were determined.[23] The pentacarbonyl complexes $M(CO)_5L$ were prepared by the following reaction.[24]

$$M(CO)_6 + L \longrightarrow M(CO)_5L + CO \qquad (13)$$

$$L = \underset{(CF_2)_n}{\overset{PR_3}{\diagup\diagdown}} \qquad R = Ph, cyclohexyl; n = 2-4$$

The ligand was only bound through the phosphorus.[24] $Co(triphos)_2$ (triphos = $MeC(CH_2PPh_2)_3$) reacted with $Cr(CO)_6$ under UV irradiation to give (triphos)-$Co(\eta^3-P_3)[Cr(CO)_5]_2$ or $(triphos)Co(\eta^3-P_3)Cr(CO)_5$ depending on the molar ratio of reactants.[25]

$$Cr(CO)_6 + Co(MeC(CH_2PPh_2)_3)_2 \longrightarrow (triphos)(Co \overset{\displaystyle Cr(CO)_5}{\underset{\displaystyle Cr(CO)_5}{\cdots P \cdots P}}) \qquad (14)$$

The donor character of the $AsCo_3(CO)_9$ cluster was tested by reacting it with the hexacarbonyls.[26]

$$M(CO)_6 + AsCo_3(CO)_9 \longrightarrow (CO)_5M\text{——}AsCo_3(CO)_9 \qquad (15)$$
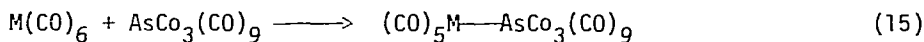
M = Cr, Mo, W

Complexes of the ligand, $Me_nP(CF_3)_{3-n}$ (n = 0-3), were prepared by reacting $M(CO)_5THF$ or $M(CO)_4(nbd)$ with L at room temperature.[27]

$$M(CO)_5THF + L \longrightarrow M(CO)_5L \qquad (16)$$

$$M(CO)_4(nbd) + 2L \longrightarrow cis\text{-}M(CO)_4L_2 \qquad (17)$$
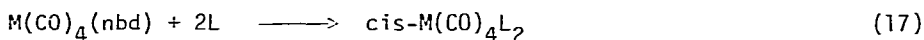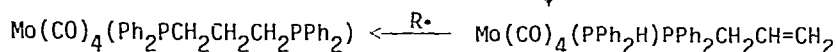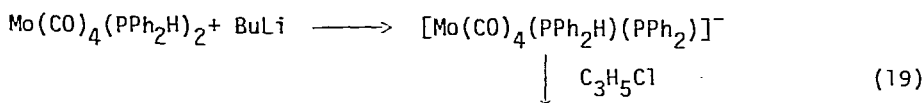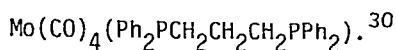
M = Cr, Mo, W; L = $Me_nP(CF_3)_{3-n}$

The $cis\text{-}M(CO)_4L_2$ complexes isomerize at >50° to the trans complexes; the rate of isomerization increased with increasing number of CF_3 groups. The thermal reaction of $M(CO)_6$ with $P(CF_3)_3$ gave $M(CO)_5P(CF_3)_3$ and $trans\text{-}M(CO)_4(P(CF_3)_3)_2$.[27] Phosphanes were prepared as ligands in the complexes $(CO)_5MoP(NHX)_3$ (X = H, Me, i-Pr, Ph, PhNH) by reaction of $(CO)_5MoPCl_3$ with NH_3, RNH_2, and phenyl-hydrazine.[28]

$$Mo(CO)_5PCl_3 + RNH_2 \longrightarrow (CO)_5MoP(NHR)_3 \qquad (18)$$
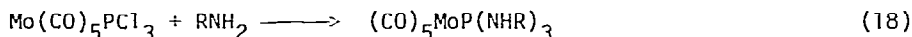
R = H, Me, i-Pr, Ph

Attempts to prepare $(CO)_5MoP(NH\text{-}t\text{-}Bu)_3$ were unsuccessful; however $(CO)_5MoPCl_3$ reacted with an excess of $t\text{-}BuNH_2$ to give $(CO)_5Mo(NH_2\text{-}t\text{-}Bu)$.[28] The preparation of mono- and di-substituted mononuclear carbonyls of Cr, Mo, and W with the cage ligand $P(NMeCH_2)_3CMe$(L) were reported.[29] Complexes of the similar arsenic ligand were also prepared.[29]

Synthesis of the compounds $M(CO)_4(PPh_2H)(PPh_2R)$ (M = Cr, Mo; R = $CH_2CH=CH_2$, $CH_2(CH_3)=CH_2$, etc.) was accomplished from the reaction of the appropriate allyl or substituted allyl chloride with $[M(CO)_4(PPh_2H)PPh_2]^-$.[30] This latter reagent was generated in situ from $M(CO)_4(PPh_2H)_2$ and one equivalent of BuLi in THF. Addition of a free radical catalyst to $Mo(CO)_4(PPh_2H)(PPh_2CH_2CH = CH_2)$ caused the P-H unit to add to the allylic double bond, giving

$Mo(CO)_4(Ph_2PCH_2CH_2CH_2PPh_2).^{30}$

$$Mo(CO)_4(PPh_2H)_2 + BuLi \longrightarrow [Mo(CO)_4(PPh_2H)(PPh_2)]^-$$

$$\downarrow C_3H_5Cl \qquad\qquad (19)$$

$$Mo(CO)_4(Ph_2PCH_2CH_2CH_2PPh_2) \xleftarrow{R\cdot} Mo(CO)_4(PPh_2H)PPh_2CH_2CH=CH_2$$

The compounds $M(CO)_4(PPh_2H)PPh_2CH=CH_2$ were prepared by reaction of $M(CO)_4(PPh_2H)Cl^-$ and $PPh_2CH=CH_2$ in the presence of $AgNO_3$.[30] Cyclization of this compound was effected by PhLi.[30] Similar products were observed in reactions of $(CO)_5WPPh_2CH=CH_2$ with PPh_2H under free radical or base catalyzed conditions which yielded $(CO)_5WPPh_2CH_2CH_2PPh_2$.[31]

$$(CO)_5WPPh_2CH=CH_2 + PPh_2H \xrightarrow{R\cdot} (CO)_5WPPh_2CH_2CH_2PPh_2 \qquad (20)$$
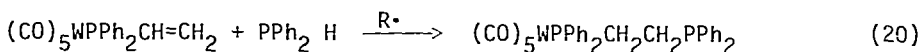
The reaction of $(CO)_5WPPh_2H$ with $PPh_2CH=CH_2$ produced the same product under free-radical conditions, but only the chelated product, $(CO)_4W(PPh_2CH_2CH_2PPh_2)$ in the presence of base. Similar reactions on the bis-substituted complexes, $trans$-$(CO)_4W(PPh_2CH=CH_2)_2$ and cis-$(CO)_4W(PPh_2H)_2$, led to more highly substituted species in which di- and tri-(tertiary phosphines) were not fully coordinated.[31] All complexes were characterized by ^{31}P NMR.[31] Reaction on the coordinated phosphorus was also effected on complexes of the type $(CO)_5CrPRCl_2$, which on treatment with $CpCo(CO)_2$ underwent dehalogenation giving mixed metal compounds, $(CO)_5CrPR[CoCp(CO)]_2$.[32]

$$(CO)_5CrPRCl_2 + C_5H_5Co(CO)_2 \longrightarrow (CO)_5CrPR[CoCp(CO)]_2 \qquad (21)$$
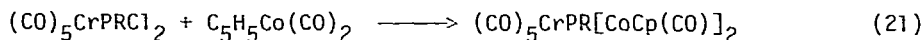
These complexes were investigated by IR, ^{31}P NMR, and microanalysis.[32]

Connor and Riley reported several reactions of $M(CO)_2(dmpe)_2$.[33] The complexes cis-$M(CO)_2(dmpe)_2$ (M = Cr, Mo) underwent one-electron oxidation by $AgBF_4$ in solution to give paramagnetic complexes, $trans$-$[M(CO)_2(dmpe)_2]$ $[BF_4]$.

$$cis\text{-}M(CO)_2(dmpe)_2 \xrightarrow{AgBF_4} trans\text{-}[M(CO)_2(dmpe)_2][BF_4] \qquad (22)$$

$$cis\text{-}M(CO)_2(dmpe)_2 \xrightarrow{AgX} cis\text{-}[MoX(CO)_2(dmpe)_2]X \qquad (23)$$
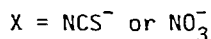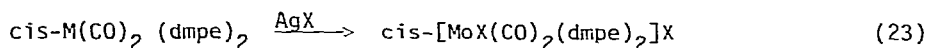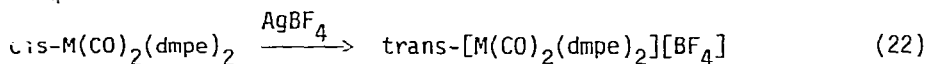
$X = NCS^-$ or NO_3^-

Oxidation of the Mo complex with silver(I) salts of coordinating anions (NCS^-, NO_3^-, NO_2^-, CO_3^{-2}, or SO_4^{-2}) produced seven-coordinate Mo complexes cis-$[MoX(CO)_2(dmpe)_2]X$ (X = NCS^- or NO_3^-), $MoX(CO)(NO)(dmpe)_2$ (X = NO_2^-) and cis-$MoX(CO)_2(dmpe)_2$ (X = SO_4^{-2}, CO_3^{-2}) which were characterized by microanalysis,

infrared and visible spectroscopy.[33] Reaction between cis-Mo(CO)$_2$(dmpe)$_2$ and organic pi-acids tetracyanoethene (TCNE), 1,2,4,5-tetracyanobenzene (TCNB) and 1,3,5-trinitrobenzene proceeded by electron transfer from the metal complex, which was oxidized to the 17-electron trans-[Mo(CO)$_2$(dmpe)$_2$]$^+$ ion, to the organic acceptor which was reduced to the radical anion.[34] The final products of the reactions were characterized as cis-[Mo(C$_2$(CN)$_3$)(CO)$_2$(dmpe)$_2$] [CN], cis-[Mo(C$_6$H$_2$(CN)$_4$)(CO)$_2$(dmpe)$_2$] [C$_6$H$_2$(CN)$_4$]$_8$ and [Mo(CO)$_2$(dmpe)$_2\cdot$2C$_6$H$_3$(NO$_2$)$_3$] by analysis and spectroscopic analysis.[34] The complexes cis-[M(CO)$_2$(dmpe)$_2$] (M = Cr, Mo) were also shown to react with a number of alkyl halides to form trans-[M(CO)$_2$(dmpe)$_2$]X and subsequently either cis-[Mo(CO)$_2$(dmpe)$_2$]X or trans-[MoH(CO)$_2$(dmpe)$_2$]X.[35] The reaction was studied by IR, ESR and electronic spectroscopy with rate data collected in certain cases. The ESR experiments indicated the presence of free radical species. A mechanism was suggested with initial electron transfer in an outer sphere process from the metal complex to RX producing the metal cation.[35]

$$\text{cis-Mo(CO)}_2\text{(dmpe)}_2 + RX \rightarrow \text{cis-Mo(CO)}_2\text{(dmpe)}_2^+ + RX^{-\cdot} \qquad (24)$$

$$\downarrow$$

$$\text{trans-Mo(CO)}_2\text{(dmpe)}_2^+ + X^- + R^\cdot$$

$$\text{trans-[Mo(CO)}_2\text{(dmpe)}_2]X + RX \rightarrow \text{cis-[Mo(CO)}_2\text{(dmpe)}_2X]X + R^\cdot \qquad (25)$$

$$R^\cdot + R^\cdot \rightarrow R\text{-}R$$
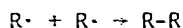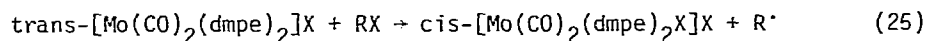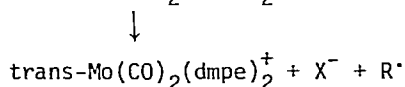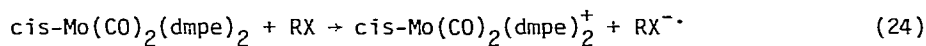
For Mo a second electron transfer (inner sphere) occurred to the final Mo(II) complex.[35]

UV irradiation of M(CO)$_6$ (M = Cr, Mo, W) with the potentially tridentate chelating ligand MeC(CH$_2$AsPh$_2$)$_3$ in MeCN gave 70% yield of cis-M(CO)$_4$[MeC(CH$_2$AsPh$_2$)$_3$] (I) in which one As donor of the ligand was uncoordinated.[36]
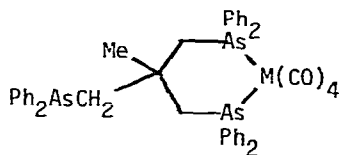
Complexes of the chelating diphosphine, [2-(di-m-tolylphosphino)ethyl]diphenyl-phosphine (pmtpf) of general formula [(pmtpf)M(CO)$_4$] (M = Cr, Mo, W) were prepared.[37] These complexes were characterized on the basis of elemental analysis, electronic, IR and ^{1}H NMR spectral measurements, magnetic suscepti-bilities and electrical conductance data.[37] The 1:1 reaction of photo-

chemically generated solutions of pentacarbonyl(tetrahydrofuran)chromium and tungsten with R_2SbSbR_2 gave a 40% yield of $R_2SbSbR_2M(CO)_5$ (M = Cr, R = Et; M = W, R = Me, Et, Ph) and the 2:1 reaction gave $(CO)_5MR_2SbSbR_2M(CO)_5$ (M = Cr, W; R = Ph, CMe_3).[38]

$$M(CO)_5THF + R_2SbSbR_2 \longrightarrow M(CO)_5R_2SbSbR_2$$
$$+$$
$$(CO)_5MR_2SbSbR_2M(CO)_5$$

(26)
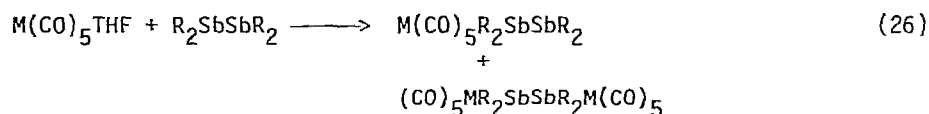
M = Cr, W; R = Me, Et, etc.

Reactions of Group VIB metal carbonyls with cis- and trans-3,4-dihydro-2,3,4,5-tetraphenyl-2H-1,2,3-diazaphosphole (DAP) yielded $(CO)_5M(DAP)$ in which the ligand is bonded through the phosphorus atom.[39]

cis-DAP
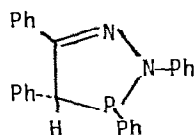
trans-DAP

The reaction of $[NEt_4][Cr(CO)_5Br]$ with methylene- and benzylidene-phosphoranes yielded stable yellow complexes of the type $(CO)_5CrCHR\text{-}P(Ph)_{3-x}(CH_3)_x$ (R = H, C_6H_5; x = 0-3).[40] Reaction with phosphines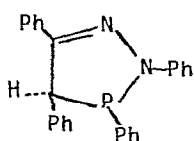 caused replacement of CO leading to the cis complex.[40] Bis(acetonitrile)dicarbonyl-diphosphine-molybdenum(0) and a corresponding monoacetonitrile-triphosphine complex reacted with α,β-unsaturated nitriles to give substitution products.[41] In the case of tributylphosphine complexes a rapid subsequent reaction gave dimers with a pi-olefin-sigma-nitrile bridging functions (II).[41]

II
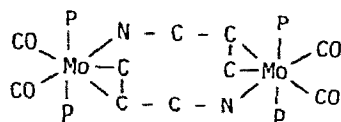
The crystal structure of the acrylonitrile complex was determined by X-ray diffraction[41].

Nitrogen bases of the Group VI carbonyls continued to be important in 1979. Darensbourg studied the effect of intramolecular hydrogen-bonding interactions between -P-O⁻···H-N- grouping in $cis\text{-}Mo(CO)_4(P(OMe)_3)\text{-}NHC_5H_{10}$ on the solution dynamics of this species toward amine displacement reactions.[42] The hydrogen-bonding interaction resulted in an enhanced stabilization of the piperidine ligand toward dissociative loss with $\Delta H^{\ddagger}$ for NC_5H_{10} dissociation 3.5 kcal/mol higher for loss from $Mo(CO)_4P(OMe)_3(NHC_5H_{10})$ than from $Mo(CO)_5(piper)$. Reaction of $cis\text{-}Mo(CO)_4P(OMe)_3(piper)$ with ^{13}CO afforded stereospecifically the equatorially labeled $Mo(CO)_4(^{13}CO)P(OMe)_3$; $fac\text{-}Mo(CO)_3(^{13}CO)(P(OMe)_3)\text{-}(piper)$ reacted with ^{13}CO to yield exclusively the equatorially substituted complex.[42]

$$cis\text{-}Mo(CO)_4P(OMe)_3(piper) + {}^{13}CO \rightarrow cis\text{-}Mo(CO)_4({}^{13}CO)piper \qquad (27)$$
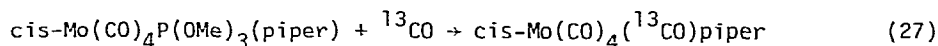
The intermediates involved were indicated to be nonfluxional.[42] Reaction of $Cr(CO)_5THF$ with nitriles yielded stable $(CO)_5CrNCR$ complexes.[43]

$$Cr(CO)_5THF + NCR \rightarrow (CO)_5CrNCR + THF \qquad (28)$$

Depending on the substituent R the reactions with $Ph_3P=CH_2$ led to substitution of the nitrile with formation of the complex $(CO)_5Cr\text{-}CH_2\text{-}PPh_3$ or to nucleophilic attack on the nitrile carbon to yield ketimine complexes $(CO)_5CrNH=CR\text{-}CH=PPh_3$ as cis- and trans- isomers. The complexes were characterized by their IR and NMR spectra.[43] The 1,4,5,8-tetraazaphenanthrenemetaltetracarbonyl complexes (M=Cr, Mo, W) were synthesized.[44]
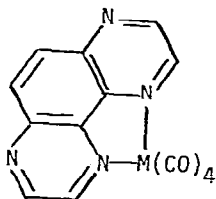
The CO force constants showed that there was more backbonding in these complexes than in the analogous 1,10-phenanthroline complexes. It was suggested that the presence of the two additional electron-withdrawing nitrogen atoms were responsible.[44] Treatment of transition metal-ammonia complexes with ketones yielded complexes with a RR'C=NH ligand in a condensation reaction.[45]

$$(CO)_5MNH_3 + (CH_3)_2C=O \longrightarrow M(CO)_5NH=C(CH_3)_2 + H_2O \qquad (29)$$
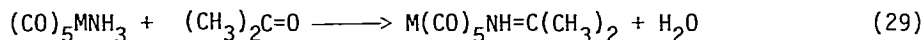
M = Cr, Mo, W

Complexation with the pentacarbonyls, $M(CO)_5(NH=C(CH_3)_2)$, caused stabilization of the dialkylketimines. Disubstituted complexes $M(CO)_4(NH=C(CH_3)_2)_2$ were also obtained.[45] Reduction and subsequent oxidation of $Mo(CO)_4DAB$ (DAB = 1,4-diazabutadiene) yielded complexes of formula, $Mo_2(CO)_6(IAE)$ IAE = μ-(1-isopropylamino)-2-(isopropylimino)ethane.[46] Several methods were developed for the preparation of $Mo_2(CO)_6(IAE)$ all of which have in common the oxidative elimination of CO from $[Mo(CO)_4DAB]^-$ resulting in formation of $Mo(CO)_3DAB$ which had DAB both sigma and pi coordinated. Dimerization resulted in $Mo_2(CO)_6(IAE)$.[46] The X-ray structure showed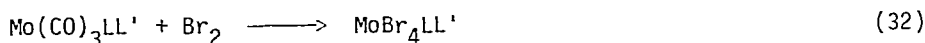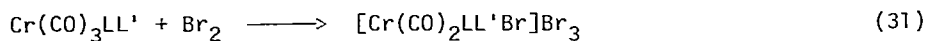 the formation of a carbon-carbon bond between two DAB ligands and a relatively short Mo-Mo bond (2.813Å).[46] Reactions of 2-(alkenyl) pyridines with $M(CO)_6$ or $M(CO)_4(nbd)$ (M = Cr, Mo, W; nbd = norbornadiene) were described.[47] Isomerization of the alkenyl side chain occurred with 2-(CR'Me=CR"- and 2-CH_2=CR'CH_2CH_2-) etc. giving $M(CO)_4L$ (L = 2-prop-2'enyl) complexes. Related reactions with $Ph_2PCH_2CH_2CH=CH_2$ and $PhPCH_2CH_2CH_2CH=CH_2$ gave $Mo(CO)_4(Ph_2P(CH_2)_nCH=CH_2)$ complexes.[47] Reactions of NO with $M(CO)_3Lpy$ (M = Mo, W; L = o-phen or bipy) at ambient temperature yielded dimeric complexes of the type $[M(CO)_2(NO)L]_2$[48]

$$M(CO)_3Lpy + NO \longrightarrow [M(CO)_2(NO)L]_2 \qquad (30)$$
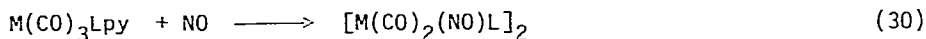
L = o-phen, bipy; M = Mo, W

These compounds were characterized on the basis of microanalysis, conductance data, magnetic measurements and IR spectra.[48] Oxidation of similar complexes, $Cr(CO)_3LL'$ and $Mo(CO)_3LL'$, with Br_2 or I_2 (L = o-phen, bipy; L' = cyclohexylamine, piper, $BuNH_2$) led to the following reactions.[49,50]

$$Cr(CO)_3LL' + Br_2 \longrightarrow [Cr(CO)_2LL'Br]Br_3 \qquad (31)$$

$$Mo(CO)_3LL' + Br_2 \longrightarrow MoBr_4LL' \qquad (32)$$

These complexes were characterized by magnetic measurements, IR spectra, etc.[49,50]

Studies of dinitrogen, diazene and hydrazine complexes of the Group VI metals continued in 1979. The preparation of dinitrogen complexes of Mo and W were reported.[51]

$$WCl_6 + Mg + dppe \xrightarrow{N_2} trans-W(N_2)_2(dppe)_2 \qquad (33)$$
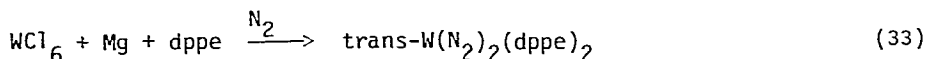
Similar reactions produced $Mo(N_2)_2(dppe)_2$, $Mo(N_2)_2(PMePh_2)_4$ and $W(N_2)_2(PMePh_2)_4$.[51] Archer and George reported the reaction of bis(dinitrogen) complexes of molybdenum, $Mo(N_2)_2L_2$, where L is a bidentate tertiary phosphine ligand with hydrogen in solution to form H_4MoL_2.[52]

$$Mo(N_2)_2L_2 + 2H_2 \longrightarrow MoH_4L_2 + 2N_2 \qquad (34)$$
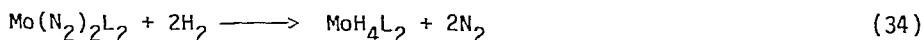
L = bidentate tertiary phosphine

Confirmation of a tetrahydride rather than a dihyride came from both ^{1}H and ^{31}P NMR studies using the bidentate phosphines $(tol)_2PCH_2CH_2P(tol)_2$ where tol = m-tolyl or p-tolyl.[52] Ligating dinitrogen was converted into hydrazine with a hydrazido complex as an intermediate when cis-$Mo(N_2)_2(PMe_2Ph)_4$ was treated with HCl.[53] Synthesis and properties of $Cp(CO)_2Mn-N_2H_4-Cr(CO)_5$, $Cp(CO)_2Mn-N_2H_2-Cr(CO)_5$ and $Cp(CO)_2Mn-N_2-Cr(CO)_5$ were reported, giving the first series of heteronuclear complexes in which N_2, N_2H_2 and N_2H_4 were bound to identical metal centers.[54] The hydrazine and dinitrogen complexes were obtained by reacting $CpMn(CO)_2N_2H_4$ and $CpMn(CO)_2N_2$, respectively, with $Cr(CO)_5THF$.[54]

$$Cr(CO)_5THF + CpMn(CO)_2L \rightarrow (CO)_5Cr-L-Mn(Cp)(CO)_2 \qquad (35)$$

$$L = N_2, N_2H_4$$

The diazene complex, which disproportionated to the N_2 complex and H_2 on addition of base, was obtained by oxidation of the hydrazine complex.[54] The G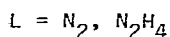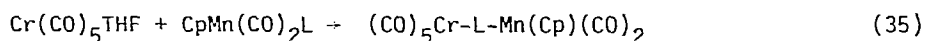roup VIB complexes $M(CO)_5L$ were synthesized for L = cis-1,2-diisopropyldiazene (c-dipd) with M = Cr, Mo, W; L = trans-1,2-diisopropyldiazene(t-dipd) with M = Cr, W; and L = 1,2-diisopropylhydrazine (diph) with M = Cr, W.[55] The available evidence indicated that cis diazenes were better ligands than their trans isomers. Complex stability decreased in the order W > Cr >> Mo and c-dipd > t-dipd.[55] The complexes $W(CO)_5L$ (L = $CH_3NHNHCH_3$, cis-$CH_3N=NCH_3$, and trans-$CH_3N=NCH_3$) and $[W(CO)_5]_2(trans-CH_3N=NCH_3)$ were obtained by reaction of $W(CO)_5THF$ with the corresponding ligand.[56]

$$W(CO)_5THF + L \rightarrow W(CO)_5L + THF \qquad (36)$$

L = $CH_3NHNHCH_3$, cis-$CH_3N=NCH_3$ and trans-$CH_3N=NCH_3$
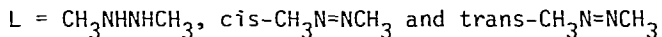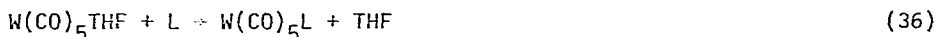
$W(CO)_5(cis-CH_3N=NCH_3)$ underwent exchange between the two nitrogens with a $\Delta G^{\ddagger}$ of 16.0 kcal/mol as shown by NMR investigations. The hydrazine complex $W(CO)_5(CH_3NHNHCH_3)$ was oxidized in high yield to a 5:1 mixture of $W(CO)_5(cis-CH_3N=NCH_3)$ and $W(CO)_5(trans-CH_3N=NCH_3)$.[56] The complexes $[WX_2(NNH_2)(PMe_2Ph)_3]$ (X = Cl, Br) reacted with HX in THF to give hydride complexes $WX_3H(NNH_2)(PMe_2Ph)_3$.[5]

$$WX_2(NNH_2)(PMe_2Ph)_3 + HX \rightarrow WX_3H(NNH_2)(PMe_2Ph)_3 \qquad (37)$$
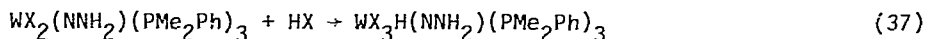
This complex lost PMe_2Ph upon addition of more HCl to give $HWCl_3(NNH_2)(PMe_2Ph)_2$ which slowly crystallized to $WCl_3(NNH_2)(PMe_2Ph)_2$ which was characterized by X-ray crystallography.[57]

   A number of sulfur-based ligand complexes of the carbonyls have been prepared and studied. Gingerich and Angelici prepared mononuclear $W(CO)_5SH^-$ and binuclear bridged $\mu-HS[W(CO)_5]_2^{-2}$ complexes by reaction of SH^- with $W(CO)_6$.[58]

$$W(CO)_6 + SH^- \rightarrow W(CO)_5SH^- + \mu-HS[W(CO)_5]_2^{-2} \qquad (38)$$
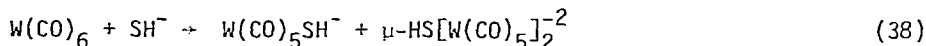
The reactivity of the SH^- group was shown by reaction of $W(CO)_5SH^-$ with acetic anhydride and 2,4-dinitrophenyl acetate to give the thioacetate complex, $MeC(=O)SW(CO)_5^-$; and by reactions with aliphatic ketones and aromatic aldehydes to yield thioketones, $W(CO)_5(S=CR_2)$, and thioaldehydes $(ArCHS)W(CO)_5$.[58]

$$W(CO)_5SH^- + R_2C=O \rightarrow W(CO)_5(S=CR_2) \qquad (39)$$
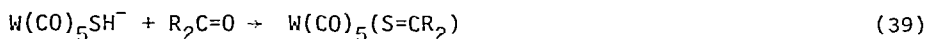
The SH^- group in $\mu-HS[W(CO)_5]_2^{-2}$ was less reactive but deprotonation with a strong base gave sulfur-bridged complexes which readily reacted with halogenated complexes.[58] Treatment of $Cr(CO)_6$ with $C_2(SR)_4$ ($L^{SR}2$) under photolysis in THF afforded cis-$Cr(CO)_4(L^{SR}2)$ (R = Me).[59]

$$Cr(CO)_6 + L^{SR}2 \xrightarrow[THF]{h\nu} Cr(CO)_4L^{SR}2 + 2CO \qquad (40)$$
$$L^{SR}2 = C_2(SR)_4$$
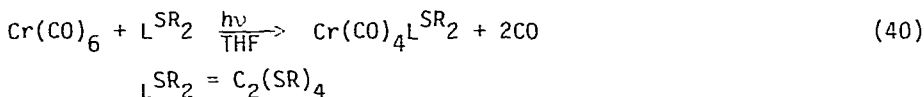
Complexes of this type were also obtained by reaction of $M(CO)_6$ with $L^{SR}2$ in EtOH in the presence of $NaBH_4$.[59] The complex, $Cr(CO)_5(L^{SR}2)$ (R = Et), was obtained by reaction of $[NEt_4][Cr(CO)_5Cl]$ and the olefin in the presence of $[OEt_3][BF_4]$.[59] Infrared and ^{13}C NMR spectra were used to suggest structures and indicated some M-S pi interaction. The X-ray crystal structure was accomplished for M = Cr, R = Me.[59] The reaction of thioketones with $Mo(CO)_6$ was reported to give the thioketone molybdenum pentacarbonyl complex in good yield.[60]

$$Mo(CO)_6 + S=CRR' \rightarrow (CO)_5Mo-S=CRR' \qquad (41)$$

Geometrical isomers were isolated for thiocamphor.[60] Purine-substituted tungsten carbonyls were shown to be useful model compounds for studying metal

binding sites of nucleic acid components.[61] Elemental analysis, molecular weight determinations, ^{1}H NMR and IR data revealed that 6-mercaptopurine was capable of acting as a monodentate S(6)-bonded and bidentate S(6)-N(7) bonded ligand to give $W(CO)_5L$ and $W(CO)_4L$. 2',3'-O-isopropylideneguanosine behaved as a monodentate ligand yielding $W(CO)_5L$.[61]

Carbenes and Carbynes

Investigations of carbenes and carbynes of Cr, Mo and W have shifted from primarily synthesis and structural studies to reactions and reactivity studies. Casey and co-workers investigated the reactions of the carbene, $(CO)_5WC(H)C_6H_5$, with alkenes.[62] Addition of CF_3CO_2H to a CH_2Cl_2 solution of $N(Et)_4^+(CO)_5$-$WCH(OCH_3)C_6H_5^-$ at -78°C produced a red solution of $(CO)_5WCHC_6H_5$ which was characterized by ^{1}H NMR and by reaction with PBu_3.[62]

$$(CO)_5WCH(OCH_3)C_6H_5 \xrightarrow{CF_3CO_2H} (CO)_5WCHC_6H_5 \qquad (42)$$
$$\downarrow \text{alkene}$$
$$\text{phenylcyclopropane}$$
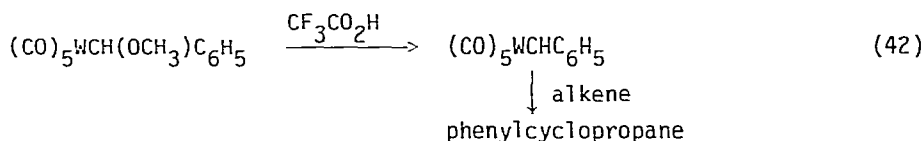
Reaction of the carbene with alkenes occurred at -78°C to give phenylcyclopropanes; no metathesis products were observed.[62] The relative reactivity of alkenes toward $(CO)_5WCHC_6H_5$ was in the order $CH_2=C(CH_3)_2 > CH_2=CHCH_3 >> CH_2=CH_2$, indicating that the reaction involved electrophilic attack of the carbene complex on the alkene.[62] The stereochemistry of cyclopropane formation was explained in terms of formation of a bond from the carbene carbon atom to the less substituted end of an alkene and interaction of the positively polarized, more substituted end of the alkene with the ipso carbon atom of the phenyl group.[62] The reaction of pentacarbonyl-(arylmethoxycarbene)tungsten $(CO)_5W[C(OCH_3)(p-C_6H_4R)]$ (R = OCH_3, CH_3, H, Br, CF_3) with tributylphosphine at low temperature resulted in reversible addition of PBu_3 to the carbene carbon atom.[63]

$$(CO)_5W=C(OCH_3)(C_6H_4R) + PBu_3 \rightleftharpoons (CO)_5W-C(OCH_3)(C_6H_4R) \qquad (43)$$
$$\underset{\displaystyle PBu_3}{|}$$

$$R = OCH_3, CH_3, H, Br, CF_3$$
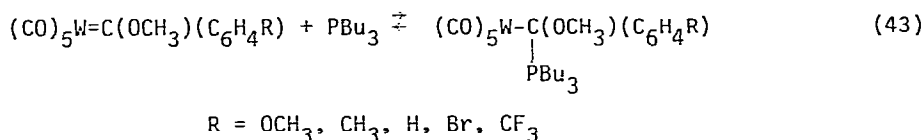
The equilibrium was dependent on the temperature and the substituent R. $\Delta G, \Delta H$ and the equilibrium constants were evaluated.[63] For all substituents a linear dependence from Jaffe's σ constants was observed for ΔH. A correlation was also observed between log K and the CO force constants.[63] Treating

$(CO)_5WC(OMe)Ph$ with PhLi gave $(CO)_5WLiCPh_2OMe$, which reacted with HCl to produce a 75% yield of $(CO)_5W=CPh_2$.[64]

$$(CO)_5WC\begin{array}{c} OMe \\ \diagdown \\ Ph \end{array} + PhLi \longrightarrow (CO)_5WCPh_2(OMe)Li \xrightarrow{HCl} (CO)_5W=C\begin{array}{c} Ph \\ \diagup \\ \diagdown \\ Ph \end{array} \qquad (44)$$
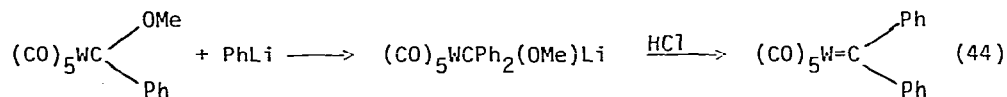
Pentacarbonyl(dihydro-2(3H)-furanylidene)chromium(0) (III) was prepared by lithiation of $(CO)_5CrC(OMe)Me$ with BuLi followed by treatment with ethylene oxide.[65]
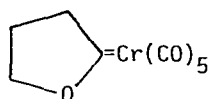
III

Nucleophilic substitution of $(CO)_5WC(OMe)Ph$ with Me_2NH gave an 88% yield of $(CO)_5WC(NMe_2)Ph$.[66] Reaction of $W(CO)_6$ with PhLi gave $Li[W(CO)_5C(0)Ph]$ which with $[Me_3O][BF_4]$ gave 90% yield of $(CO)_5WC(OMe)Ph$.[67]

$$W(CO)_6 + PhLi \longrightarrow (CO)_5W-C\begin{array}{c} OLi \\ \diagup \\ \diagdown \\ Ph \end{array} \xrightarrow{[Me_3O][BF_4]} (CO)_5WC(OMe)Ph \qquad (45)$$
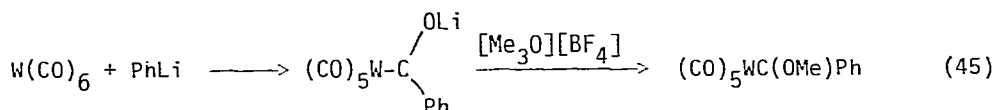
Reactions of carbenes with alkynes have been reported. 1-Diethylamino-propyne reacted with pentacarbonyl[methoxy(2,2-diphenylethenyl)carbene]-chromium via insertion of the alkyne into the metal-carbene bond to give pentacarbonyl-[diethylamino-E-(2-methoxy-1-methyl-4,4-diphenyl-1,3-butadienyl)-carbene]chromium.[68] A similar type reaction was observed between pentacarbonyl[ferrocenyl(methoxy)carbene] chromium with diphenylacetylene.[69] On warming tricarbonyl-[(5-ferrocenyl-2-methoxy-3-η^6-phenyl-4-phenyl)furan]-chromium(0) was formed.[69]

$$(46)$$
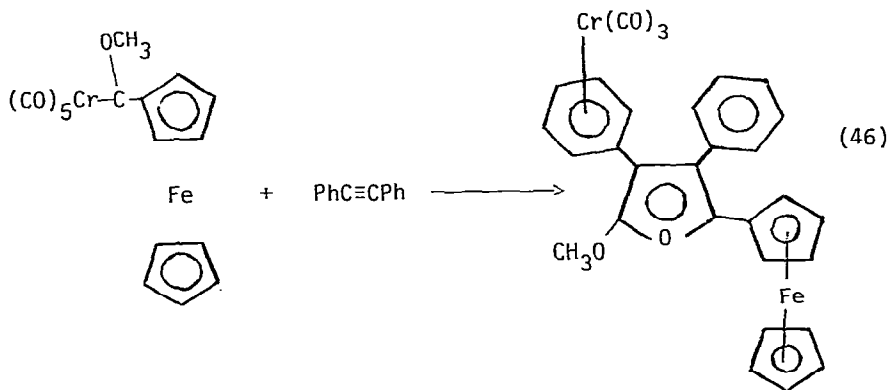
The product was characterized by X-ray crystallography.[69] Treatment of $(CO)_5WC(OEt)Me$ with MeLi followed by acidification with CF_3CO_2H afforded a red crystalline compound which was found to be the binuclear complex, $(CO)_4W-W(CO)_4CHCH=CMe_2$.[70]

IV
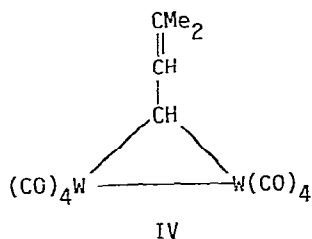
The X-ray analysis showed a W-W distance of $3.15\overset{\circ}{A}$ and a W-C(bridging) distance of $2.32\overset{\circ}{A}$. The following scheme was suggested.[70]

$$(47)$$
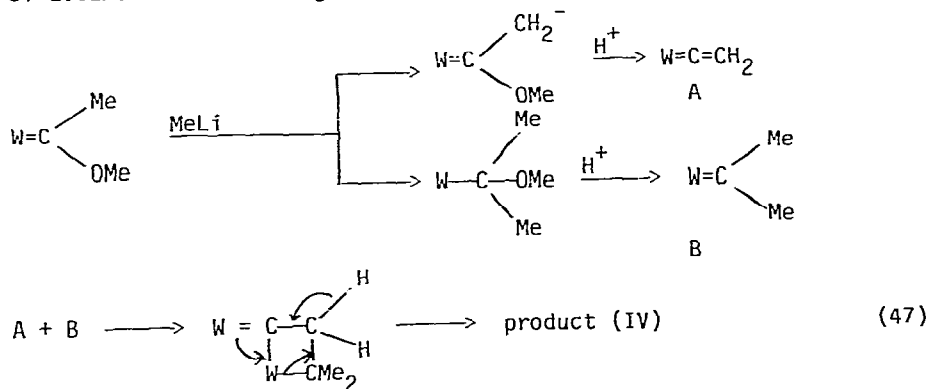
The synthesis and structure of $CpWPPh_3(CO)(CSPh)$, by transformation of a thiocarbonyl ligand into a carbyne ligand, was reported.[71] The complex was prepared by the following sequence of reactions.

$$W(CO)_4(CS)I^- + C_5H_5^- \rightarrow CpW(CO)_2CS^- + I^- + 2CO$$

$$CpW(CO)_2CS^- + I_2 \rightarrow CpW(CO)_2(CS)I + I^- \tag{48}$$

$$CpW(CO)_2(CS)I + PPh_3 \rightarrow CpW(CO)(PPh_3)(CS)I$$

$$CpW(PPh_3)(CO)(CS)I + LiPh \rightarrow CpW(PPh_3)(CO)(CSPh) + LiI$$
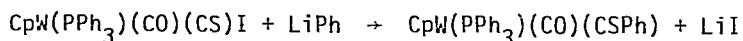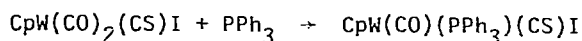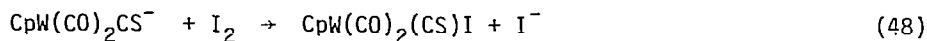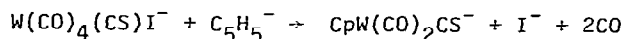
The structure was determined showing a W-C bond length of 1.807Å, which was attributed to a carbyne bonding mode.[71]
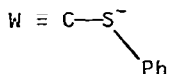
Reaction of cyclopentenyllithium with $M(CO)_6$ (M = Cr and W) led to cyclopentylcarbene and carbyne complexes by the following reactions.[72]

$$M(CO)_6 + LiC_5H_7 \longrightarrow \left[(CO)_5M\!=\!\!\!=\!\!\!=C \begin{matrix} {}^{O} \\ {}_{C_5H_7} \end{matrix} \right]^- Li^+ \tag{49}$$

$$\downarrow [(C_2H_5)_3O]BF_4$$

$$trans\text{-}X(CO)_4M\!\equiv\!C\!-\!\!\bigcirc \xrightarrow{BX_3} (CO)_5M\!=\!\!\!=C \begin{matrix} {}^{OC_2H_5} \\ {}_{C_5H_7} \end{matrix}$$

M = Cr, W   X = Cl, Br, I
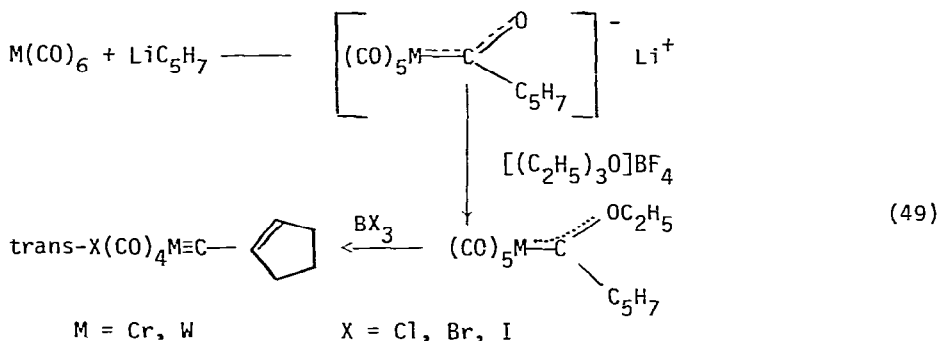
These compounds were characterized by IR and NMR and an X-ray structural determination of $I(CO)_4Cr\equiv C\text{-}C_5H_7$.[72] The Cr≡C bond distance was 1.65Å.[72] A series of reactions on silyl-carbene and -carbyne complexes were reported.[73] The reaction of $(CO)_5MC(OCH_3)SiPh_3$ (M = Cr, W) with Al_2Br_6 at low temperatures produced $trans\text{-}Br(CO)_4M\equiv C\text{-}SiPh_3$. The halogen exchanged rapidly and allowed formation of $(CO)_5Re\text{-}(CO)_4W\equiv CSiPh_3$ by reaction with $NaRe(CO)_5$.[73]

$$(CO)_5M=C(OCH_3)SiPh_3 + Al_2Br_6 \rightarrow Br(CO)_4M\equiv CSiPh_3$$

$$\downarrow NaRe(CO)_5 \qquad\qquad (50)$$

$$(CO)_5Re-(CO)_4W\equiv CSiPh_3$$
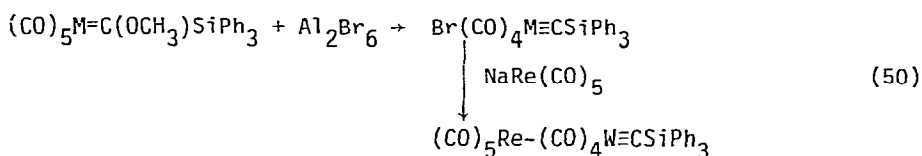
Sodium cyclopentadienide reacted with these halogenocarbynes to form $Cp(CO)_2$-$WCSiPh_3$ complexes.[73] The photochemical interaction of trans-chlorotetracarbonyl-(p-tolylcarbyne)-tungsten with acetylacetone led to a crystalline compound whose structure was determined.[74]

$$t-Cl(CO)_4W\equiv C-C_7H_7 + Hacac \xrightarrow[Et_2O, -60°]{h\upsilon} t-Cl(CO)_2(acac)W + \begin{matrix} C-OH \\ \parallel \\ C-C_7H_7 \end{matrix} \qquad (51)$$
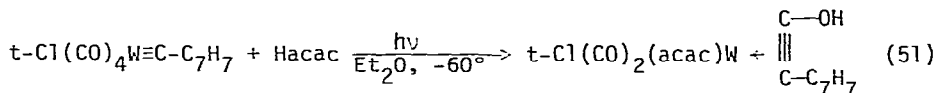
Two cis carbonyl ligands were replaced by acac. One CO was evolved as carbon monoxide while the second combined with the carbyne to give a new ligand, hydroxy(p-tolyl)-acetylene.[74] Metal-substituted ketenes of Mo and W, $Cp(CO)(PMe_3)_2MC(CO)R$ were formed on treatment of dicarbonyl $Cp(CO)_2M\equiv CR$ with trimethylphosphine.[75]

$$Cp(CO)_2M\equiv C-R + 2PMe_3 \rightarrow Cp(CO)(PMe_3)_2M-C\begin{matrix}\diagup C\!\!=\!\!O \\ \diagdown R\end{matrix} \qquad (52)$$
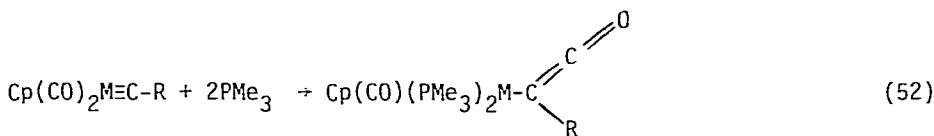
$$M = Mo, W; R = CH_3, C_6H_5, etc.$$

The cleavage of one phosphine ligand led in a reversible reaction to η^2-ketenyl compounds, $Cp(CO)(PMe_3)M-(O\cdots C\cdots C-R)$ or reaction with CO to give dicarbonyl substituted η^1-ketenes, $Cp(CO)_2(PMe_3)M-C(CO)R$.[75] The reaction of $(CO)_5WC(OMe)Ph$ with BBr_3 was reported to give trans-$Br(CO)_4W\equiv CPh$ in 82% yield.[76]

$$(CO)_5WC(OMe)Ph + BBr_3 \rightarrow trans-Br(CO)_4W\equiv CPh \qquad (53)$$
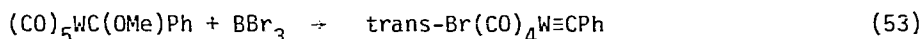
Irradiation of trans-$Cl(CO)_4W\equiv CC_6H_4Me-P$ with acetylacetone (Hacac) in Et_2O at -60° gave trans-$Cl(CO)_2$ (acac)-$W(HOC\equiv CC_6H_4Me-P)$.[77]

Aromatics and Cyclopentadienyls

Aromatics. Direct reaction of an arene with $Cr(CO)_6$ gave $ArCr(CO)_3$ (Ar = anisole, benzene, fluorobenzene, chlorobenzene, N,N-dimethylaniline, C_6H_4OMe) in up to 90% yield.[78]

$$Ar + Cr(CO)_6 \rightarrow ArCr(CO)_3 + 3CO \hspace{2cm} (54)$$
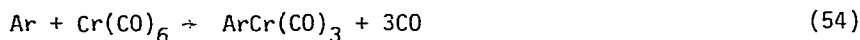
Ar = anisole, benzene, etc.

The reaction of 9-fluorenone ethylene ketal diphenic anhydride with $Cr(CO)_6$ produced xylenetricarbonylchromium (V) (ortho, meta and para) which was also formed by refluxing pure Bu_2O with $Cr(CO)_6$.[79]

V
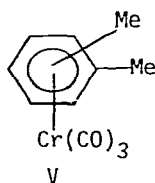
Similarly dipentylether and $Cr(CO)_6$ produced isobutyl-and 1-methyl-3-propyl-benchrotrene.[79] Complexation of Me-2-amino-2-(o-tolyl)-benzoate with $Cr(CO)_6$ gave the isomeric complexes VI and VII both existing as two torsional isomers as seen by NMR.[80]

VI

VII
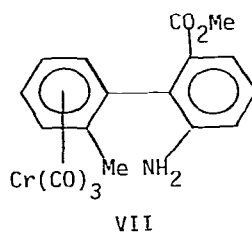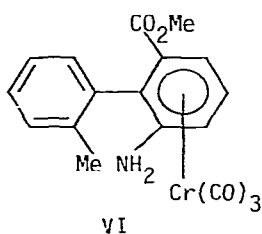
For the main product, VI, the preferrred conformations of the two torsional isomers were deduced by the lanthanide shift technique. The activation energy for the interconversion process (91 kJ/mol) was determined from variable temperature NMR data.[80] Chromium complexes of heterocyclic ligands (VIII and IX) were prepared by treating $RFe(CO)_2Cp$ (R = 2-thienyl, 2-benzofuryl) with

VIII

IX
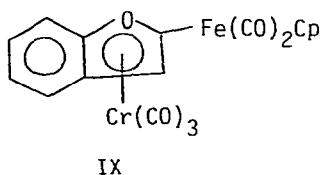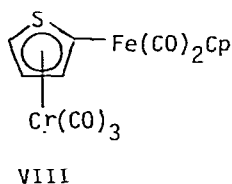
$Cr(CO)_6$.[81] The reaction of pentacarbonyl[ferrocenyl(methoxy)-carbene]chromium with tolan in Bu_2O gave X in 35% yield.[82]
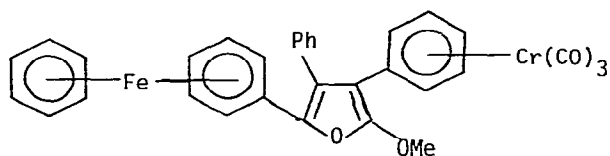
X

Cyclophanes reacted with $Cr(CO)_6$ in diglyme at 140°C under nitrogen to give the complexes XI in 40% yield.[83]

XI

$R = R_3 = R_4 = H$, $R_1 = R_2 = Me$; $R = R_1 = R_2 = R_3 = Me$, $R_4 = H$;

$RR_4 = CH_2CH_2$, $R_1 = R_2 = R_3 = H$
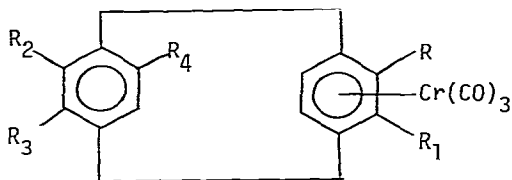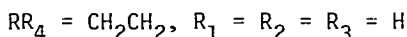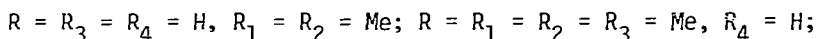
Photolysis of $ArCr(CO)_3$ with cis-cyclooctene gave $ArCr(CO)_2(C_8H_{14})$.[84]

$$ArCr(CO)_3 + C_8H_{14} \longrightarrow ArCr(CO)_2(C_8H_{14}) \qquad (55)$$
$$\downarrow CS_2,\ PPh_3$$
$$ArCr(CO)_2(CS)$$

$Ar = o\text{-}Me_2C_6H_4$, $C_6H_5CO_2Me$, $m\text{-}MeC_6H_4CO_2Me$
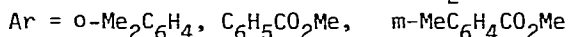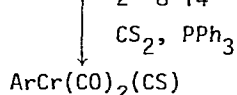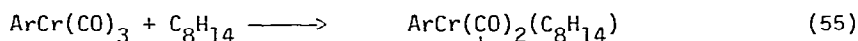
Further reaction with CS_2 and PPh_3 gave a high yield of $ArCr(CO)_2(CS)$.[84] Reaction of $[PhCr(CO)_3]_2$ with $CuCl_2$ gave a mixture of $PhCr(CO)_3$ and $PhClCr(CO)_3$, with the ratio of products highly dependent on the temperature.[85] A new preparation of arenebischromium tricarbonyl was reported. Heating of $Cr(CO)_6$ and a polyaromatic compound in a mixture of dibutylether and THF (90/10) under reflux allowed the direct dicomplexation of the polyaromatic in good yield.[86] The exchange of arenes in $(\eta^6\text{-arene})Mo(CO)_3$ was investigated by Muetterties and co-workers.[87] Exchange of arene' for $(\eta^6\text{-arene})Mo(CO)_3$ occurred in the absence of a catalyst at 60°C.

$$(\eta^6\text{-arene})Mo(CO)_3 + arene' \;\rightleftharpoons\; (\eta^6\text{-arene'})Mo(CO)_3 + arene \quad (56)$$
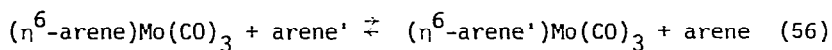
arene = mesitylene, toluene, hexamethylbenzene

arene' = benzene, toluene, xylenes, tetramethylbenzenes

Acetone or THF catalyzed exchange at 20°C to an equilibrium in 8 hrs.[87] They believed that exchange occurred by an associative process. Equilibrium constants established that arene complex stability increased with the degree of methyl substitution.[87] Arene exchanges on $(arene)Cr(CO)_3$ complexes were studied under stoichiometric equilibrium conditions and were shown to be facilitated by nitrogen and oxygen donors as substituents on the arene.[88] The more firmly bonding arenes tended to displace the more weakly held in the following order.

$C_6Me_6 > C_6H_2Me_4 > C_6H_3Me_3 > PhNMe_2 \gg C_6H_4Me_2 > PhMe \sim C_6H_6 > PhC(O)Me$

$\sim PhOMe > BzOMe \sim PhF > C_{10}H_8$
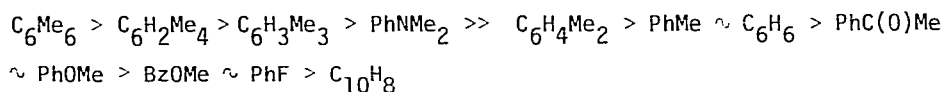
Mechanisms for the exchange reactions were discussed.[88] The attempted hydrogenation of $H_2Mo(\eta^6\text{-}C_6H_5CH_3)(PPh_3)_2$ showed no evidence of hydrogen transfer to toluene or benzene solvent up to 85°C where decomposition occurred.[89] The complex, $(\eta^6\text{-}CH_3C_6H_5)Mo(P(OMe)_3)_3$, didn't react with H_2 at 125°C.[89]

Reactions on arenes coordinated to chromium tricarbonyl complexes have continued to be studied, primarily by Rausch's and Semmelhack's groups. Both groups reported the metallation of arenechromiumtricarbonyl with n-butyl lithium.[90]
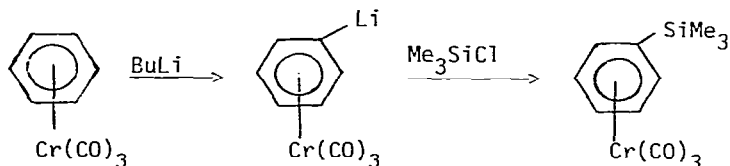
A study of the interaction of η^6-benzenetricarbonylchromium and n-butyllithium to form $(\eta^6$-phenyllithium)tricarbonylchromium was conducted under a variety of reaction conditions.[90] The complex was generated in 60% yield at -40°C. The synthetic utility was shown by reactions with I_2 and $SiMe_3Cl$, which produced the corresponding arene-chromium complexes in yields of 30% and 45%, respectively.[90] Coordination to the chromiumtricarbonyl unit enhanced the acidity of the ring protons more than the benzylic protons.[91] Treatment of $(\eta^6$-toluene)chromiumtricarbonyl with n-BuLi (-78°C, ether) followed by reaction with CO_2, methylation with diazomethane, and decomplexation with Ce(IV) led to

methyl toluates (ortho:meta:para, 10:45:45) in 53% yield and methylphenyl-acetate in 13% yield.[91] The addition of carbanions to coordinated arene was the subject of two reports. The position of nucleophilic attack on coordinated arenes was investigated for both mono- and di-substituted arene complexes.[92]

$$X \overset{\text{Li Y}}{\longrightarrow} \quad Y \; H$$

$$Cr(CO)_3 \qquad\qquad Cr(CO)_3 \tag{57}$$
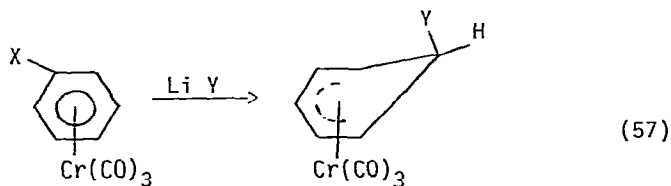
The attacking species was a lithium carbanion, the substituent on the ring was Cl, $SiMe_3$, CF_3, NMe_2, CMe_3, C_2H_5, and OCH_3. A useful correlation was found between the regioselectivity and the LUMO coefficients estimated for the free arene ligand ignoring any contribution from the $Cr(CO)_3$ group.[92] The addition of reactive carbanions to $\eta^6\text{-}C_6H_6Cr(CO)_3$ produced η^4-(6-alkylcyclohexadienyl)-tricarbonylchromium(0) anion complexes, as the lithium salts.[93] Reaction with a variety of oxidizing agents (iodine, Ce(IV), O_2) removed the hydrogen from C-6 and detached the $Cr(CO)_3$ unit producing a substituted arene. Reaction with electrophiles led to cleavage of the carbon-carbon bond at C-6 with regeneration of $\eta^6\text{-}C_6H_6Cr(CO)_3$.[93] Spectral data were consistent with the η^5-cyclohexadienyl structure and an X-ray structure was accomplished on the product of $C_6H_6Cr(CO)_3$ and 2-lithio-1,3-dithiane.[93]

Metal atom vaporization was used for the synthesis of three aromatic complexes.[94,95] Codeposition of Cr vapor and $m\text{-}(F_3C)_2C_6H_4$ gave bis[1,3-bis(trifluoromethyl)benzene]chromium(0).[94]

$$Cr + 2\ m\text{-}(F_3C)_2C_6H_4 \rightarrow [1,3\text{-}(CF_3)_2C_6H_4]_2Cr \tag{58}$$
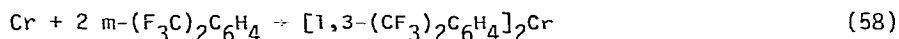
Complexation of Mo with PhX (X = Cl, NMe_2) gave $Mo(C_6H_5X)_2$.[95]

$$Mo + 2PhX \rightarrow Mo(PhX)_2 \tag{59}$$
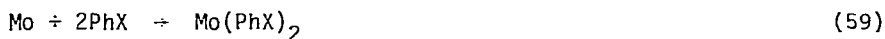
Reaction of chromium atoms with PPh_3 produced $Cr(\eta^6\text{-}C_6H_5PPh_2)_2$.[96]

$$Cr + PPh_3 \longrightarrow Cr \xrightarrow{(PhCN)_2PdCl_2} Cr \tag{60}$$
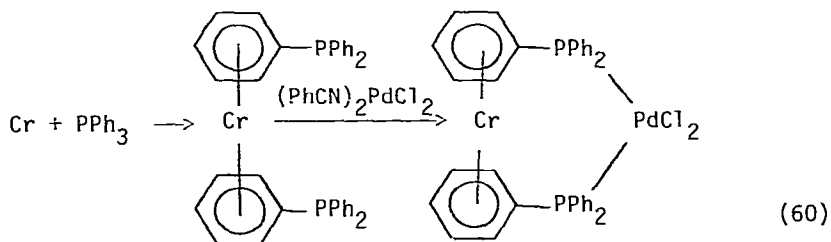
The kinetics of thermal decomposition of bis(ethylbenzene)chromium was studied.[97] The activation energies were comparable to metal-ligand bond energies.[97]

Highly reactive, paramagnetic compounds, $[(\eta^6\text{-areneMo(py)}_3]PF_6$ (arene = benzene or toluene), were prepared by the reaction of pyridine with $[(\eta^6\text{-arene})_2Mo]PF_6$.[98] The pyridine ligands were readily replaced by 1-methyl-imidazole (1-Me-Im) yielding $[(\eta^6\text{-}C_6H_6)Mo(1\text{-Me-Im})_3]PF_6$.

$$(\eta^6\text{-}C_6H_6)_2Mo^+ \ + \ py \ \longrightarrow \ [(\eta^6\text{-}C_6H_6)Mo(py)_3]^+ \ \xrightarrow{\text{1-Me Im}}$$

$$[(\eta^6\text{-}C_6H_6)Mo(1\text{-Me-Im})_3]^+$$
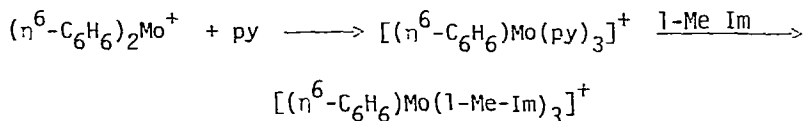
1-Me-Im = 1-methylimidazole

The pyridine complexes also reacted with CO yielding $trans\text{-}[Mo(CO)_2py_4]PF_6$ which readily and reversibly lost one molecule of CO under N_2 and afforded the compound $[Mo(CO)py_4]_n^{+n} [PF_6]_n$ ($n \geq 2$).[98] A number of reactions of $(\eta^6\text{-}C_6F_5Li)Cr(\eta^6\text{-}C_6H_6)$ were reported.[99]
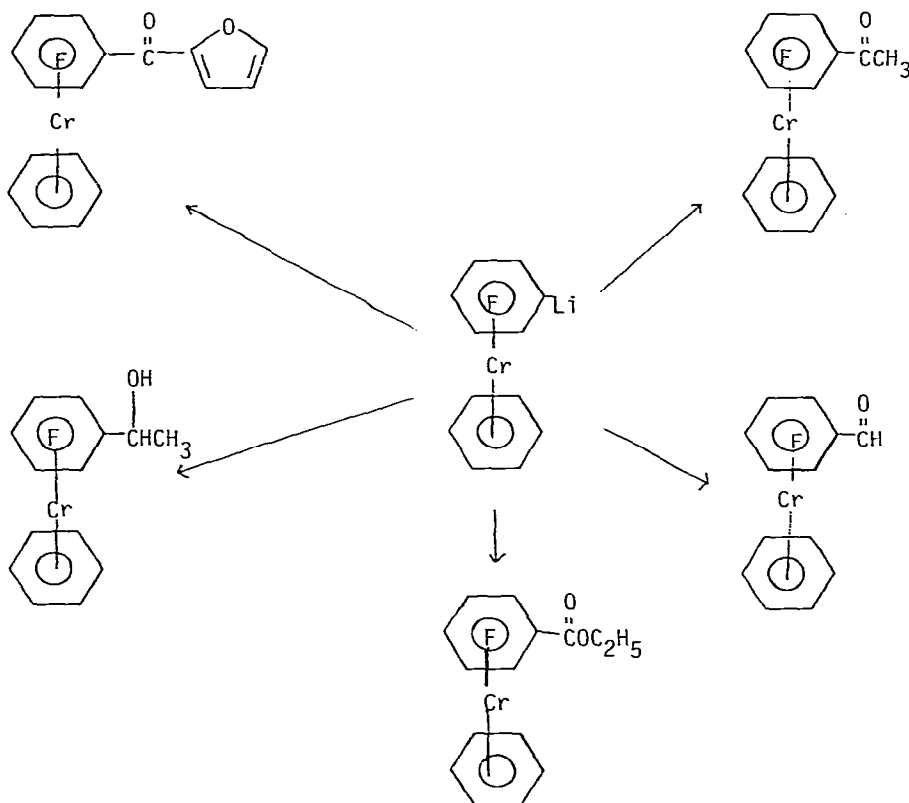
The dilithio complex, $(\eta^6\text{-}C_6F_4Li_2)Cr(\eta^6\text{-}C_6H_6)$ formed a stable diester, but the bis(trimethylsilyl) derivative was labile. The structure and reactivity of the $(\eta^6\text{-mesitylene})(\eta^2\text{-maleic anhydride})$chromium dicarbonyl complex was investigated.[100] The structure established that the olefin ligand was symmetrically bonded with the double bond parallel to the benzene ring.[100] Alkylation at the nitrogen of nitriles with tricarbonylchromium complexes of benzyl and related alcohols was effected.[101] The in situ generation of various carbenium ions, temporarily stabilized by an organometallic unit situated in the α-position, in the presence of nitriles allowed the readily preparation of amines in high yield from primary alcohol **precursors**, extending the scope of the Ritter reaction.[101]

$$(\eta^{6'}\text{-}R'C_6H_4CR^2R^3OH)Cr(CO)_3 + R^4CN$$
$$\downarrow \; H_2SO_4, \; -15°C \qquad\qquad (61)$$
$$(\eta^6\text{-}R'C_6H_4CR^2R^3NHCOR^4)Cr(CO)_3$$
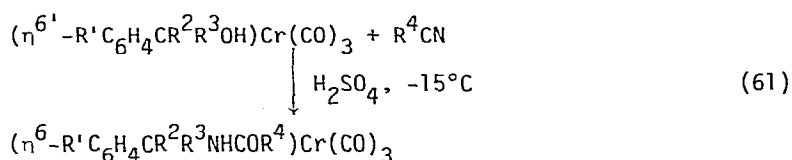
A series of N-functionalized isocyanide ligands (amide, ketone, ester, thioester) were prepared by the reactions shown below for $C_6H_6Cr(CO)_3$.[102]

$$C_6H_6Cr(CO)_3 \xrightarrow[h\upsilon]{KCN} \quad [C_6H_6Cr(CO)_2(CN)]^-K^+$$
$$\downarrow \quad RC(O)Cl \qquad (62)$$
$$C_6H_6Cr(CO)(P(OC_6H_5)_3)(CNC(O)R) \xrightarrow[h\upsilon]{P(OC_6H_5)_3} C_6H_6Cr(CO)_2CNC(O)R$$
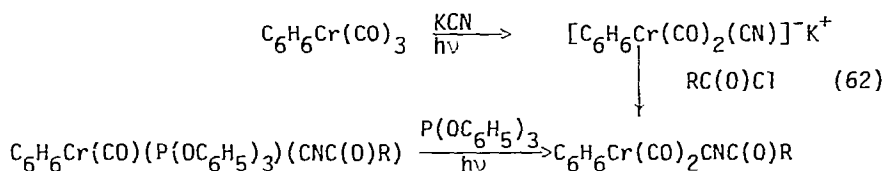
The carbonyl function α to the nitrogen strengthened the Cr–C bond such that further reaction caused replacement of CO leading to a chiral metal atom.[102] A high degree of asymmetric induction was obtained in reactions of Grignard reagents with chiral chromiumtricarbonyl complexes of diarylimines.[103]

PhC = N
R$_1$
R$_2$
Cr(CO)$_3$
+ RMgX ⟶
R(Ph)CH - NH
R$_1$
R$_2$
Cr(CO)$_3$
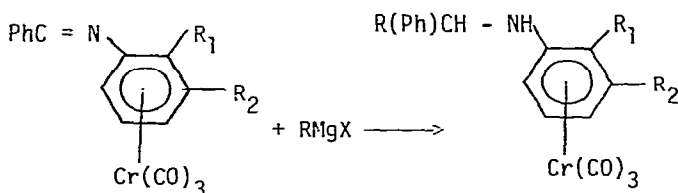
The extent of induction depended strongly on the substituent present in the ortho position; meta substitution led to less asymmetric induction than ortho substitution. This was discussed mechanistically.[103]

Cyclopentadienyls.   A new preparation of chromocene from $CrCl_3$ was·reported.[104]

$$CrCl_3 \cdot THF + LiAlH_4 \rightarrow CrCl_2 \cdot THF$$

$$\downarrow Na, \ C_5H_6 \qquad\qquad\qquad (63)$$

$$Cp_2Cr$$
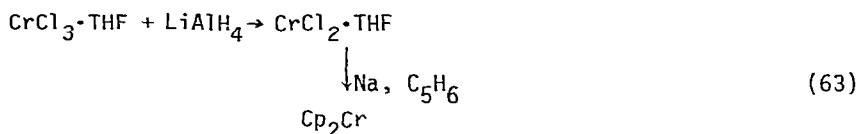
The reaction proceeded in 75% yield.[104]   To determine the validity of his suggestion that $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ reacted with $(\eta^5\text{-}C_5Me_5)_2Zr(CO)_2$ by attack on the carbonyl, Bercaw and co-workers reacted $(\eta^5\text{-}C_5Me_5)_2ZrH_2$ with $Cp_2W(CO)$.[105]

$$Cp_2W(CO) + (\eta^5\text{-}C_5Me_5)_2ZrH_2 \rightarrow Cp_2W=C(H)OZr(H)(\eta^5\text{-}C_5Me_5)_2 \qquad (64)$$
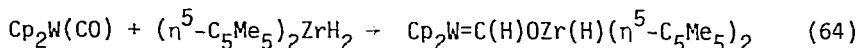
The structure of the product was confirmed by X-ray diffraction.   Reaction of $Cp_2W=C(H)OZr(H)(\eta^5\text{-}C_5Me_5)_2$ with H_2 at 170° for 48 hrs gave Cp_2WH_2 and $(\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3)$.[105]

$$Cp_2W=C(H)OZr(H)(\eta^5\text{-}C_5Me_5)_2 \xrightarrow[170°]{H_2} Cp_2WH_2 + (\eta^5\text{-}C_5Me_5)_2Zr(H)(OCH_3) \quad (65)$$
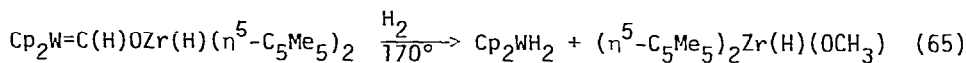
Similar reactions were observed for $Cp_2Mo(CO)$ and $Cp_2Cr(CO)$ although the chromium product was unstable in solution.[105]   Blumer, Barnett and Brown investigated the substitution reactions of $CpM(CO)_3X$ complexes (M = Mo or W, X = halide) with phosphines and arsines which proceeded rapidly at room temperature in the presence of $(CH_3)_3NO$ to give $cis\text{-}CpM(CO)_2(L)X$.[106]

$$CpM(CO)_3X + L \xrightarrow{Me_3NO} cis\text{-}CpM(CO)_2LX + Me_3N + CO_2 \qquad (66)$$
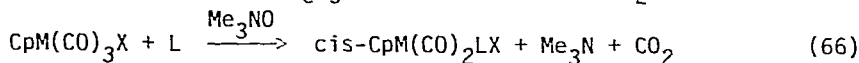
$$M = Mo, \ W; \ X = halide$$

Stereoselectivity, product yields, and reaction rates were dramatically enhanced by use of the amine oxide reagent.[106]   Reactions of $Cp_2Cr_2(CO)_6$ with $P(OMe)_3$ were explored.[107]   Reaction with 2 moles of $P(OMe)_3$ at 25°C gave the disubstituted dimer and the structure was determined.[107]

$$Cp_2Cr_2(CO)_6 + 2P(OMe)_3 \rightarrow Cp_2Cr_2(CO)_4(P(OMe)_3)_2$$

$$CpCr(CH_3)(CO)_2P(OMe)_3 \xleftarrow{\quad P(OMe)_3 \quad} \quad \text{polar} \quad \Big| H_2 \downarrow \quad CpCr(CO)_2(P(OMe)_3)H \quad (67)$$

$$+$$

$$CpCr(PO(OMe)_2)(CO)_2P(OMe)_3 \qquad \text{solvent} \quad \Big|$$

$$\downarrow$$

$$CpCr(CO)_2(P(OMe)_3)_2^+$$

$$+$$

$$CpCr(CO)_3^-$$
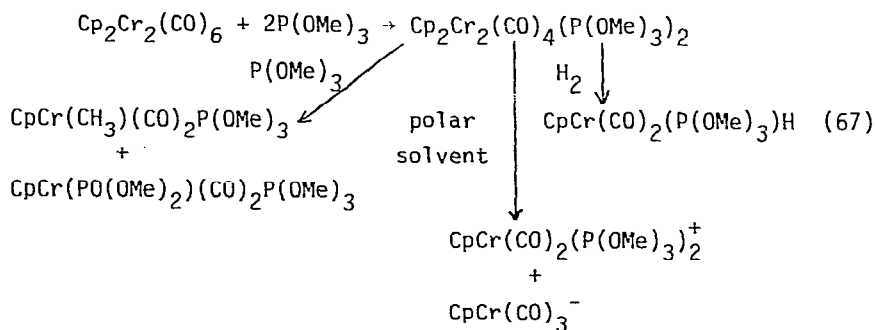
The long Cr-Cr bond (3.343Å) was very reactive. Reaction with H_2 occurred giving a hydride; reaction with $P(OCH_3)_3$ caused decomposition of the ligand; and disproportionation occurred in polar solvents.[107]

The mechanism of halogenation of the derivatives $[CpM(CO)_2L]_2$ (M = Mo, W; L = CO, $P(OMe)_3$) was investigated.[108] Treatment of $[CpM(CO)_3]_2$ with I_2 in ethanol at 0°C in the presence of $Na[B(Ph)_4]$ produced the iodine-bridged derivative $[(CpM(CO)_3)_2(\mu-I)][BPh_4]$ which was an intermediate in the formation of $CpM(CO)_3I$ from $[CpM(CO)_3]_2$ and I_2.[108] Bromination and chlorination of $[CpM(CO)_3]_2$ and $[CpM(CO)_2P(OMe)_3]_2$ always gave M(IV) derivatives $CpM(CO)_2X_3$ and $CpMo(CO)(P(OMe)_3)X_3$ as products. The following mechanism was proposed.[168]
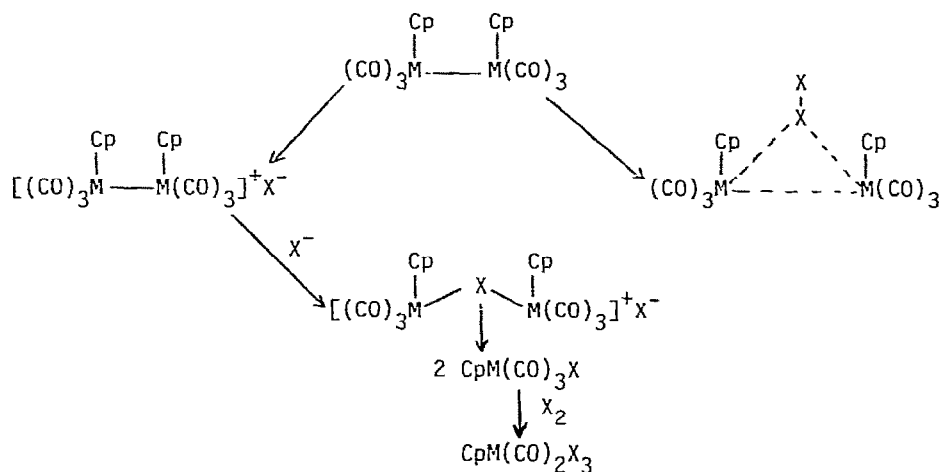
The mutual interconversions of the species $Cp(CO)_3M^-$, $Cp(CO)_3MM'(CO)_3Cp$ and $Cp(CO)_3M$ (M, M' = Cr, Mo, W) were investigated.[109] The mixed dimers $Cp(CO)_3CrMo(CO)_3Cp$ and $Cp(CO)_3CrW(CO)_3Cp$ were prepared for the first time; the Mo-W compound could not be purified.[109] The Mo and W radicals, $Cp(CO)_3M$ in contrast to the Cr radical, were not stable in solution. Electrochemical measurements and redox and redistribution reactions indicated their formation and existence under normal conditions.[109] The reaction of $ClMPh_3$ (M = Ge, Sn, Pb) with $[Cp_2WHLi]_4$ gave a good yield of $Cp_2WH(MPh_3)$.[110]

$$[Cp_2WHLi]_4 + ClMPh_3 \rightarrow Cp_2WH(MPh_3)$$
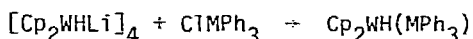
$$M = Ge, Sn, Pb$$

Gladysz and co-workers reported a near quantitative preparation of the metal carbonyl monoanion, $CpMo(CO)_3^-$, by trialkylborohydride cleavage of metal carbonyl dimers.[111]

$$[CpMo(CO)_3]_2 + LiBR_3H \rightarrow CpMo(CO)_3^- + BR_3 + Li^+ \qquad (68)$$
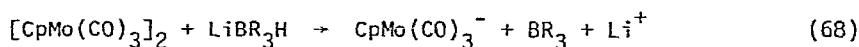
$$R = Et \text{ and } s\text{-Bu}$$

This procedure was reported to be safer and better than mercury amalgam.[111]
The coordination of $CpW(CO)_3^-$ to triphenylaluminum, triphenylgallium, and
triphenylindium was investigated.[112] By infrared analysis of $[Bu_4N]^+[CpW(CO)_3]^-$
stirred with Ph_3Al showed the oxygen atom of a carbonyl to be the site of
ligand basicity. Dichloromethane solutions of $[Bu_4N]^+[(Ph_3Ga)CpW(CO)_3]^-$
contained a metal-metal bonded species and a C- and O-coordinated complex.[112]
The corresponding indium complex was only metal-metal bonded. Tetraphenyl-
phosphole, -arsole and -stibole complexes containing phosphorus-, arsenic-,
and antimony-metal bonds respectively were prepared for Mo and W by the follow-
ing reactions.[113]

$$CpM(CO)_3^+ \ + \ \text{[ring]}E\text{-Cl} \ \longrightarrow \ Cp(CO)_3M\text{-E[ring]} \tag{69}$$

$$(\eta^7\text{-}C_7H_7)Mo(CO)_2 \ + \ \text{[ring]}As^- \ \longrightarrow \ (\eta^7\text{-}C_7H_7)(CO)_2Mo\text{-As[ring]} \ + \ I^- \tag{70}$$

M = Mo, W, E = P, As, Sb
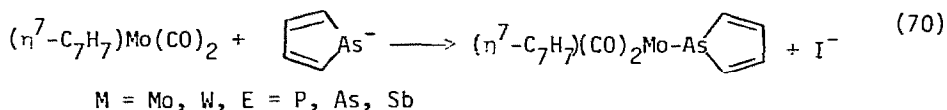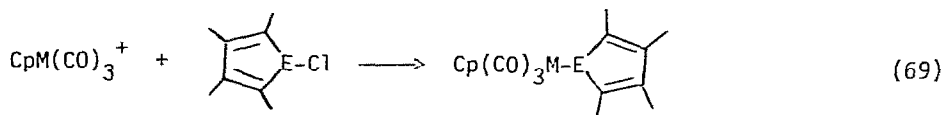
Complexes of the type $RCOCH_2M(CO)_3Cp$ (R = ferrocenyl, cymantrenyl; M = Mo, W)
were prepared in good yield by treating $NaM(CO)_3Cp$ with $RCOCH_2Cl$ in THF.[114]

$$NaM(CO)_3Cp \ + \ RCOCH_2Cl \ \longrightarrow \ RCOCH_2M(CO)_3Cp \tag{71}$$

R = ferrocenyl, cymantrenyl; M = Mo, W
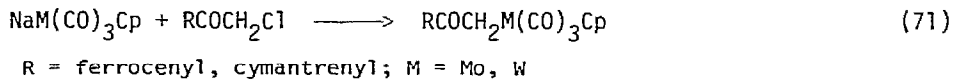
The transition metal arsines $Cp(CO)_2LMAs(Me)_2$ (M = Mo, W; L = CO, PMe_3) reacted
with elemental sulfur (selenium) in CS_2 to give the transition metal sub-
stituted arsine chalcogenides $CpM(CO)_2As(CH_3)_2$-S or -Se.[115] Due to the pro-
nounced basicity of the chalcogen center, they were readily converted into
cationic mononuclear complexes $[trans\text{-}Cp(CO)_2(PMe_3)MoAsMe_2SR]^+X^-$ by alkyl
halides and into bridged dinuclear complexes $trans\text{-}Cp(CO)_2(PMe_3)MoAs(Me)_2SCr(CO)_5$
on treatment with $Cr(CO)_5THF$.[115] Reaction of $TlCr(CO)_3Cp$ with $Cl_3SnMn(CO)_4L$ (L
= CO, PEt_2Ph) and $Cl_3SnFe(CO)_2Cp$ gave the products $Cl_2Sn[Mn(CO)_4L][Cr(CO)_3Cp]$
and $Cl_2Sn[CpFe(CO)_2][Cr(CO)_3Cp]$, respectively.[116]

$$TlCr(CO)_3Cp \ + \ Cl_3SnMn(CO)_4L \ \longrightarrow \ Cl_2Sn[Mn(CO)_4L][CpCr(CO)_3] \tag{72}$$
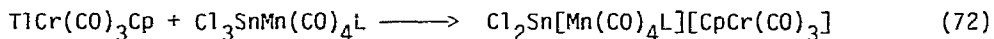
L = CO, PEt_2Ph

The complexes were characterized by IR, Raman and mass spectra.[116]

New cyclopentadienyl complexes of molybdenum with dppe as a ligand were
reported.[117]

$$\left[\begin{array}{c} Cp \\ \quad MoH_3 \\ Cp \end{array}\right]^+ \xrightarrow{\text{dppe}} \left[\begin{array}{c} Cp \quad P \\ \quad Mo \\ Cp \quad P \end{array}\right]^+$$
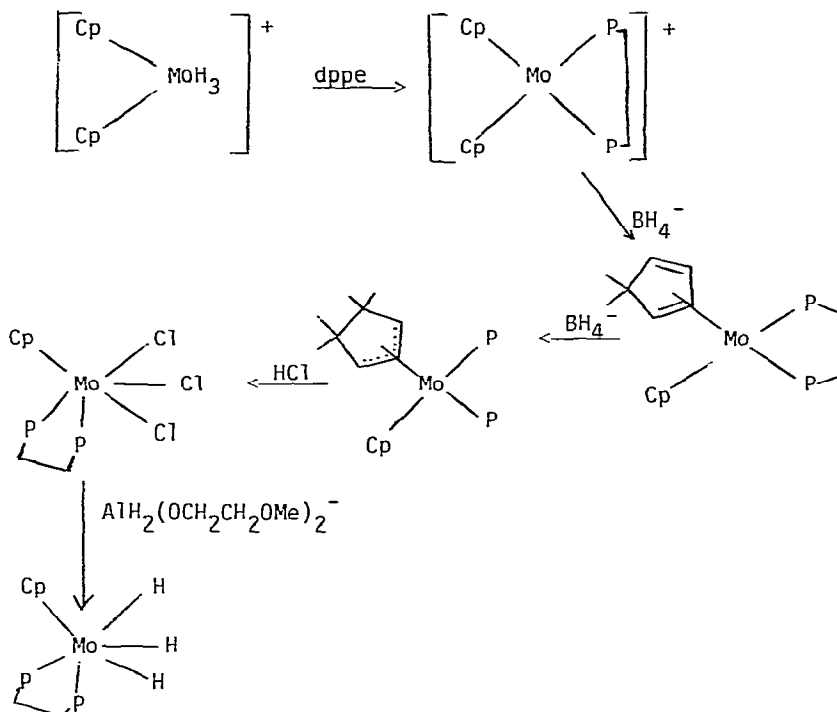
The trihydride, CpMo(dppe)H$_3$ reacted with butadiene giving [Mo(Cp)(dppe)(η^3-C$_3$H$_4$CH$_3$).[117] The synthesis of α,α'-dicyclopentadienyl-m-xylene and its ligand chemistry were investigated.[118] Reaction of this ligand with NaH gave the dianion, disodium (m-phenylenedimethylene)dicyclopentadienide. Thermolysis of Mo(CO)$_6$ and photolysis of W(CO)$_6$ with the dianion in THF gave m-C$_6$H$_4$(CH$_2$C$_5$H$_4$M(CO)$_3$)$_2^{-2}$ (M = Mo, W).[118] Reaction with alkyl halides gave m-C$_6$H$_4$(CH$_2$C$_5$H$_4$M(CO)$_3$R)$_2$ (R=CH$_3$,C$_2$H$_5$).

M(CO)$_3$R   M(CO)$_3$R

XII
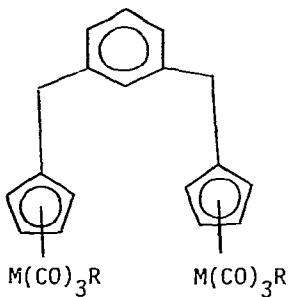
They were also able to prepare the hydride and the metal-metal bonded compound $C_6H_4(CH_2C_5H_4Mo(CO)_3)_2$.[118] The synthesis of mixed cyanothiocyanate and cyano-selenocyanate complexes of cyclopentadienylchromium was reported.[119]

$$Cp_2Cr + (SeCN)_2 \rightarrow Cp_2Cr(NCSe)_2 \qquad (73)$$

$$Cp_2Cr + Se(CN)_2 \rightarrow Cp_2Cr(CN)(NCSe)$$
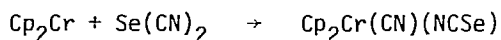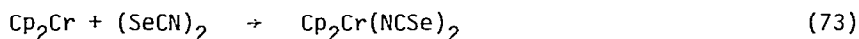
These complexes were characterized by IR, EPR and magnetic moments.[119] Reactions of lithium salts of amidines with CS_2 led to complexation by $CpMo(CO)_2$ of N-alkyl-N-iminoacyl-dithiocarbamates.[120] A number of different bonding modes were observed.[120] The reaction of ethylene sulfide or propylene sulfide with $CpMo(CO)_3H$ or $Cp_2Mo_2(CO)_6$ gave $[CpMoSC_nH_{2n}S]_2 (n = 2,3)$.[121] Cyclic voltammetry showed that each complex underwent two reversible oxidations at 0.13 and 0.79 V vs. SCE. Both the one-electron and two-electron oxidation products were synthesized and characterized by spectral and magnetic data.[121] The electrochemical data for the oxidized complexes supported the conclusion that the complexes had the same gross structural features in all three oxidation states. The structure of $[CpMoSC_3H_6S]_2BF_4$ was determined.[121]
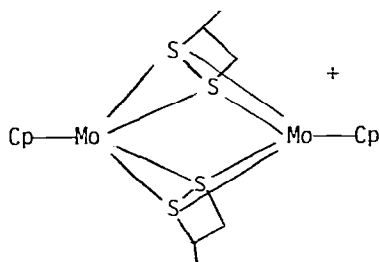
The metal ions were bridged by two 1,2-propanedithiolate ligands. The four sulfur atoms of these ligands formed a plane which bisected the metal-metal distance.[121] Reaction of $(CpMoSC_2H_4S)_2$ with acetylene at 25°C gave ethylene and the complex $[CpMoSC_2H_2S]_2$, which could be hydrogenated at 60° back to the starting complex.[121] The complexes $CpMo(NO)X(p-MeC_6H_4-p-Me)$ (X = Cl, Br, I), $CpMo(CO)_2(p-MeC_6H_4N_3(R)O)$ (R = Me, i-Pr) and $CpMo(CO)_2(MeC(O)CHC(O)R)$ (β-diketonate, R = CF_3, Ph) were prepared and characterized.[122] The fluxional behavior of cyclopentadienyl molybdenum complexes with a piano-stool configuration and a cis-chelating ligand were discussed.[122] The bite of the chelating ligand was important. Electronegative donating atoms (halogens or oxygens) or very strongly electron-withdrawing ligands (NO) inhibited the

fluxional process.[122]

There was a substantial body of research reported in 1979 on cyclopentadienyl complexes of sulfur ligands. Reaction of $[CpMo(CO)_3]_2$ with dimethyl disulfide and hexafluorobut-2-yne under irradiation gave an orange-red product which was shown by X-ray analysis to have the structure below.[123]
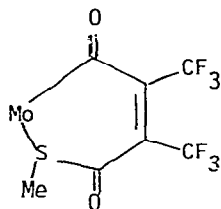
XIV

The metal atom was incorporated into a six-membered ring, formed by linking a methylthio group through a carbonyl to the alkyne which was in turn attached to a second carbonyl group. An 18-electron configuration was completed by donation of a lone pair of electrons from sulfur and of three electrons from an η^3-C_3 unit.[123] Further study of this type insertion showed that reaction between $CpW(CO)_3(SR)$ (R = Me, Et, i-Pr) and hexafluorobut-2-yne involved initial attack at sulfur and carbonyl ligands to give coordinatively unsaturated acetylene complexes.[124]

(74)
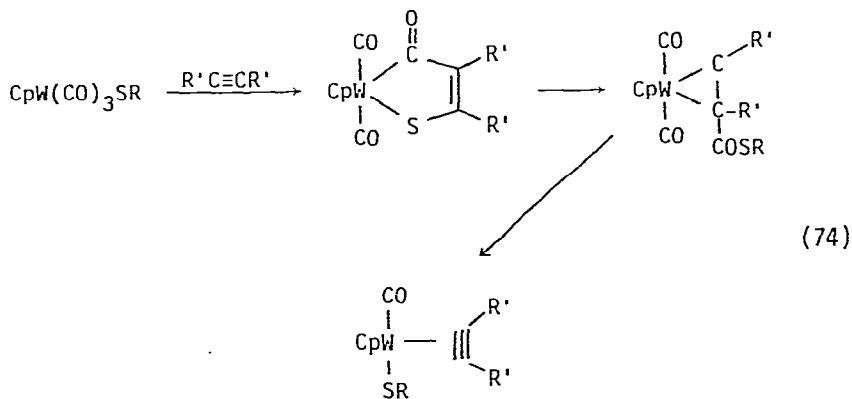
The remaining carbonyl could be displaced by phosphines or phosphites.[124] Tricarbonylcyclopentadienyl(triphenylstannyl)-molybdenum and tungsten reacted with SO_2 at 25°C primarily by insertion into Sn-C bonds although a second mole could be absorbed, cleaving the tin-metal bond.[125]

$$Cp(CO)_3MSnPh_3 \xrightarrow{SO_2} Cp(CO)_3MSnPh_2\text{-}SO_2\text{-}C_6H_5 \xrightarrow{SO_2}$$

$$Cp(CO)_3M\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}SnPh_2—SO_2—C_6H_5 \qquad (75)$$
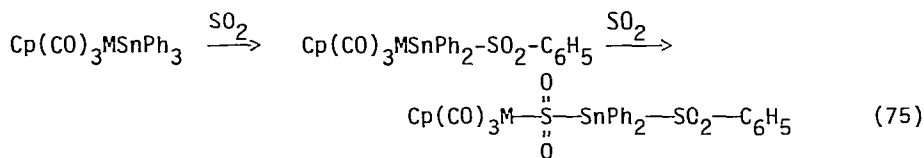
The reaction between dimethylacetylene dicarboxylate and $CpW(CO)_3SMe$ led to $CpW\{C(CO_2Me){=}C(CO_2Me)C(O)SMe\}_2$ and the structure was determined.[126] The tungsten co-ordination was square pyramidal, the apical site occupied by the cyclopentadienyl ring. The basal coordination sites contained two carbonyls and also the sulfur and sigma-bonded carbon atoms of a chelating carbothiolic methyl ester ligand derived from the incoming alkyne and CO and the SMe groups of the original complex.[126] The reaction of $CpMo(CO)_3Cl$ with pyridine-2-carboxylic acid [(S)-1-phenylethylthioamide] yielded two diastereomers of composition $CpMo(CO)_2(\text{thioamide})$.[127]

$$CpMo(CO)_3Cl + \text{thioamide} \longrightarrow CpMo(CO)_2(\text{thioamide}) \quad (76)$$
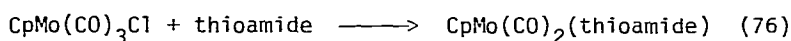
The crystal structure of one diastereomer was obtained. The molecules consisted of a central Mo surrounded by an approximately square-pyramidal array with the thioamide bidentate through the nitrogen of the pyridine and the sulfur. The absolute configuration at the Mo site was established as (S).[127] The synthesis, spectroscopic and stereochemical properties of $Cp(CO)_2Mo\text{-}NH_2CH(COOCH_3)CH_2S$ with a cysteine methylester acting as a bidentate ligand through nitrogen and sulfur were reported.[128] Several molybdenum complexes $Cp(CO)_2MoN(R')C(R)S$ derived from thioacetamide and thiobenzamide with chiral C atoms at the amide nitrogen atom were prepared.[129] The asymmetric induction at the Mo atom in the equilibrium of the diastereomers was determined by ^{1}H NMR to be 48 and 98% for $CH(Ph)R'$, $R' = C_2H_5$ and $CH(CH_3)_2$, respectively.[129] The reaction of $Na[CpCr(CO)_3]$ with $S_3N_3Cl_3$ in THF afforded the bimetallic complex $[CpCr(CO)_2]_2S$.[130]

$$CpCr(CO)_3^- + S_3N_3Cl_3 \rightarrow [CpCr(CO)_2]_2S \qquad (77)$$
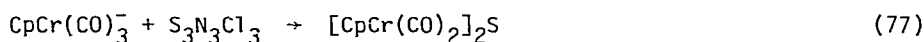
The CrSCr linkage was essentially linear with very short Cr-S bonds (2.074Å).[130] This was interpreted as $Cr{\equiv}S{\equiv}Cr$ bonding, consistent with the chemical inertness.[130]

Larger rings. There were only a few reports of Group VI complexes with larger rings in 1979. The reaction of $(\eta^7\text{-}C_7H_7)Mo(CO)(PPh_3)I$ with NaCN yielded

$(\eta^7-C_7H_7)Mo(CO)(PPh_3)(CN)$ which was ethylated by $[Et_3O]BF_4$ to yield $[(\eta^7-C_7H_7)Mo(CO)(PPh_3)(CNC_2H_5)]^+$.[131]

$$\eta^7-C_7H_7Mo(CO)(PPh_3)I + NaCN \rightarrow (\eta^7-C_7H_7)Mo(CO)(PPh_3)(CN) \xrightarrow{[Et_3O]BF_4}$$

$$(\eta^7-C_7H_7)Mo(CO)(PPh_3)(CNC_2H_5)^+ \qquad\qquad (78)$$
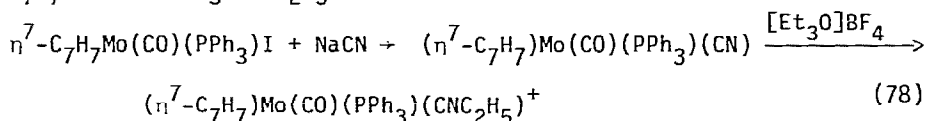
The interaction of the iodide complex with $AgBF_4$ in acetonitrile and pyridine yielded $[(\eta^7-C_7H_7)Mo(CO)(PPh_3)(NCCH_3)]^+$ and $[(\eta^7-C_7H_7)Mo(CO)(PPh_3)(py)]^+$, respectively.[131] A kinetics study of the displacement of cycloheptatriene from $(\eta^6-C_7H_8)M(CO)_3$ (M = Cr, Mo, W) by benzonitrile showed unusual changes in rate law as the metal was varied.[132] While the chromium complex obeyed the second-order rate law,

$$rate = k[complex][RCN]$$

the molybdenum species followed the third-order rate law,

$$rate = k[complex][RCN]^2$$

and the tungsten complex was intermediate between the second and third order.[132] These results were rationalized by a mechanism involving attack by two benzonitrile nucleophiles via the steadystate intermediate $[(\eta^4-C_7H_8)M(CO)_3RCN]$. Attack of a third benzonitrile rapidly led to products.[132] The reaction of $(\eta^3-C_7H_7)W(CO)_2$ with sodium alkoxides yielded unsymmetrical binuclear complexes of tungsten with three OR bridges, $(\eta^3-C_7H_7)(CO)_2W(OR)_3W(CO)_2(\eta^4-C_7H_8)$.[133-13] These complexes were characterized by IR, NMR, mass spectroscopy and for R = CH_3 by X-ray crystallography (XV).[133-134].

XV
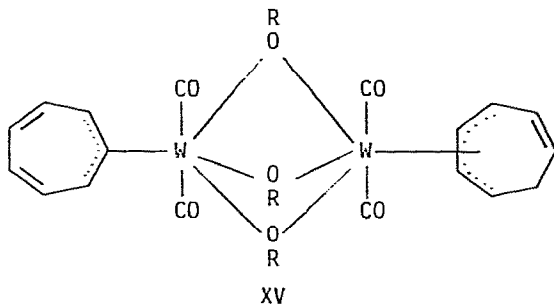
The crystal structures of a similar complex $(\eta^3-C_7H_7)(CO)_2Mo(\mu-OCH_3)_3Mo(\eta^7-C_7H_7)$ was also reported.[135]
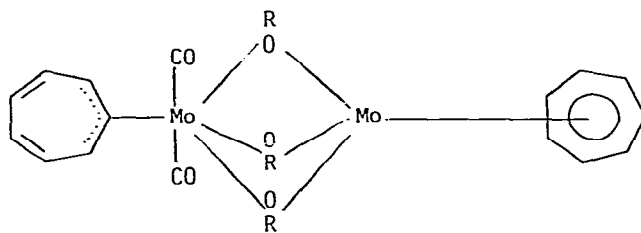
XVI

The Mo-Mo distance was in the single-bond length range, but the Mo-O-Mo angle did not reflect a metal-metal interaction.[135]

Olefins, Acetylenes, Dienes and Allyls

Olefins. The reaction of PMe_2Ph with $[Cp_2W(C_2H_4)Me]PF_6$ led to a series of reactions.[136]

$$XVII$$

$$[Cp_2W(C_2H_4)Me]^+ + PMe_2Ph \rightarrow [Cp_2W(CH_2CH_2PMe_2Ph)Me]^+$$

$$\Delta \downarrow -C_2H_4 \qquad\qquad (79)$$

$$[Cp_2W(Me)PMe_2Ph]^+ \xleftarrow{\;\Delta\;} [Cp_2W(CH_2PMe_2Ph)H]^+$$
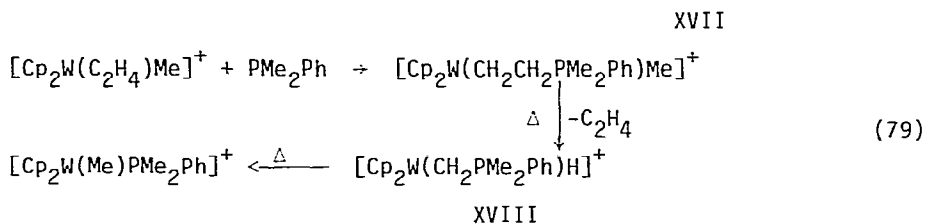
$$XVIII$$

Repeating the reaction with the deuterio-methyl analogues showed that the CD_3 in XVII was reformed quantitatively in XVIII supporting the proposal that the mechanism involved a reversible 1,2-hydrogen shift equilibrium between Cp_2WMe^+ and $Cp_2W(CH_2)H^+$.[136] The implications of 1,2-hydrogen shifts (α-elimination) were discussed.[136] Tricyanoethylene metal complexes were formed by reaction of 1-chloro-2,2'dicyanovinylmolybdenum with t-BuNC.[137]

$$Cp(CO)_3Mo-C(Cl)=C(CN)_2 + \text{t-BuNC} \rightarrow \text{cis and trans-}CpMo(\text{t-BuNC})_2(C_2(CN)_3H)Cl \quad (80)$$
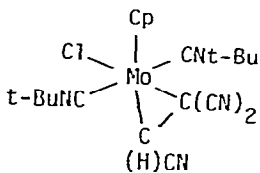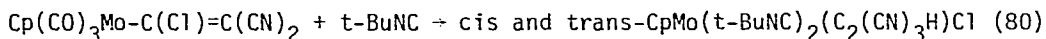
XIX
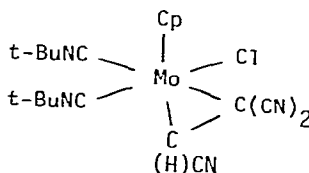
XX

Similar complexes of fumaronitrile were obtained by UV-irradiation of CpMo(CO)(t-BuNC)$_2$Cl and fumaronitrile in THF. The structures were assigned from ^{13}C NMR.[137] Reaction of CpM(CO)$_3$CH$_2$CH=CHMe (M=Mo, W) with Ph$_3$CBF$_4$ yielded, instead of the expected cationic butadiene complexes [CpM(CO)$_2$(η^4-C$_4$H$_6$)][BF$_4$], which would have been formed in the case of hydride cleavage, [CpM(CO)$_3$(η^2-C$_4$H$_8$)][BF$_4$], which would have been formed by protonation of the single C$_4$H$_7$ ligand.[138]

Acetylenes. The propeller-like rotations of each of the coordinated acetylenes in the 16-electron complex CpMo(PhC≡CMe)$_2$Cl were found to not be independent and the barrier to rotation of one of the acetylenes was influenced by the orientation of the other.[139]

The barrier in the neutral complex, CpMo(PhC≡CMe)$_2$Cl, was found to be ∿ 5 kcal/mole lower than the cationic complex, [CpMo(HOH$_2$CC≡CCH$_2$OH)$_2$(CO)]Cl.[139] Cyclic 1,3-dienes were found to react with Cp$_2$Mo$_2$(CO)$_4$(μ-C$_2$H$_2$) to give products arising from formal Diels-Alder addition to the bridging ethyne.[140] The structure of the bicyclo[4.2.2] deca-2,4,7,9-tetraene complex, Cp$_2$Mo$_2$(CO)$_2$(C$_{10}$H$_{10}$), derived from cyclooctatetraene addition was determined by X-ray diffraction.[140]

XXI
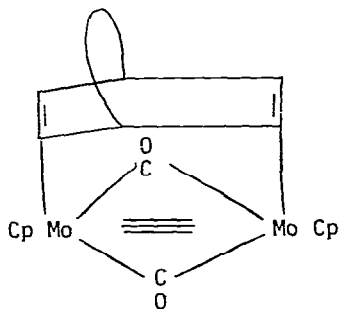
Dienes. Bicyclo[4.2.1]nona-2,4,7-triene-9-one reacted smoothly to form tricarbonylmetal complexes with M = Mo and Cr.[141] 9-Methylene-bicyclo[4.2.1] nona-2,4,7-triene complexes coordinated in the exo fashion rather than the expected endo mode. [13]C chemical shift data supported the structural and stereochemical assignments.[141]

Allyls. Reaction of [CpW(NO)I$_2$]$_2$ with Sn(C$_3$H$_5$)$_4$ led to CpW(NO)(η^3-C$_3$H$_5$)I in high yield.[142] A crystal structure determination showed a marked asymmetry of the allyl ligand with the best representation of the allyl-W bonding as below.[142]
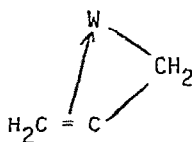
Treatment of Mo(Cp)(η^3-C$_3$H$_5$)I(NO) with NaS$_2$CNR$_2$ afforded CpMo(η^1-C$_3$H$_5$)(NO)-(S$_2$CNR$_2$) (R = Me or Et).[143]

CpMo(η^3-C$_3$H$_5$)I(NO) + NaS$_2$CNR$_2$ →

$$\text{CpMo}(\eta^1\text{-C}_3\text{H}_5)(\text{NO})\text{S}_2\text{CNR}_2$$

$$\downarrow \text{E}$$

$$\overline{\text{CpMo}(\text{CHCH}_2\text{ECH}_2)(\text{NO})(\text{S}_2\text{CNR}_2)}$$

or

$$\text{CpMo}(\text{ECH}_2\text{CHCH}_2)(\text{NO})\text{S}_2\text{CNR}_2$$

E = C$_2$(CN)$_4$, (CF$_3$)$_2$CO, CF$_3$C$_2$CF$_3$ or SO$_2$
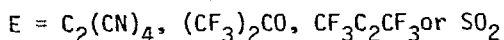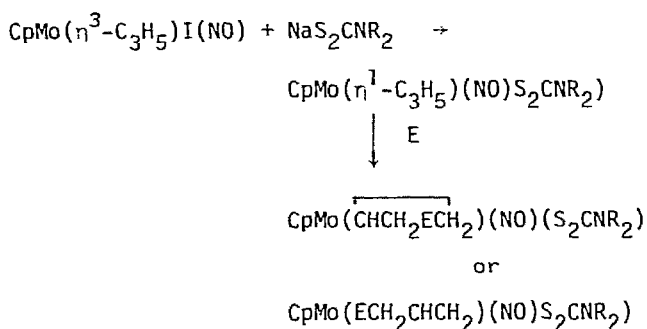
Treatment with electrophiles, E, gave cyclization products, [CpMo(CHCH$_2$ECH$_2$(NO)(S$_2$CNR$_2$) (E = C$_2$(CN)$_4$ or (CF$_3$)$_2$CO) or insertion products CpMo(ECH$_2$CHCH$_2$)(NO)(S$_2$CNMe$_2$) (E = CF$_3$C$_2$CF$_3$ or SO$_2$). The structures of the compounds were discussed and properties of the η^1- and η^3-allyls were compared to other allyls.[143] The synthesis and stereochemical and dynamical studies of phosphine and phosphite η^3-allylcyclopentenone complexes were described.[144] An interaction of cyclopentenone and the phosphine or phosphite ligands led to only one conformation of the diastereomer.[144] Unsubstituted complexes of η^3-allylcyclopentenone with Mo and W were obtained by treating homoallenic bromides with CpMo(CO)$_3^-$ and CpW(CO)$_3^-$.[145] Conformational equilibria were

observed and interpreted by assuming that the dominant factor was a steric inter-
action between the Cp ring and the substituents on the allyl ligand.[145] The
complex, $(\eta^3\text{-}C_3H_5)\text{-Mo(CO)}_2(dppe)Cl$, was investigated by X-ray crystallography
and NMR.[146]
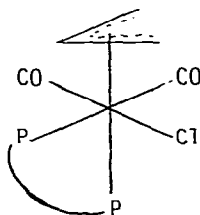
$$P\char"5E P = dppe \qquad XXII$$

Analysis of variable temperature ^1H, ^{13}C and ^{31}P NMR allowed study of the
dynamics of this complex. A trigonal twist rearrangement was proposed for the
dynamical behavior in these complexes in which a rotation of the triangular
face formed by the halogen and two phosphorus atoms relative to the face
formed by the allyl and two carbonyl groups were involved.[146] The barrier to
rotation for the iodo-complex was 10-12 kcal/mole.[146] Diastereomers and
conformers of η^3-allyl molybdenum phosphine or phosphite complexes were
identified by NMR spectroscopy.[147] The most stable conformations were those
which minimized the steric interaction between the allyl substituents and the
phosphorus-containing ligand. The largest coupling constants were between the
phosphorus and hydrogen in the cis position.[147] Equilibrium studies were
accomplished on $MoCl(\eta^3\text{-}C_3H_5)(CO)_2(RCN)_2$ complexes.[148]

$$MoCl(\eta^3\text{-}C_3H_5)(CO)_2(RCN)_2 \rightarrow [Mo(\eta^3\text{-}C_3H_5)(CO)_2(RCN)_3]^+ + [Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$$

$$R = Me, Ph \qquad\qquad (81)$$
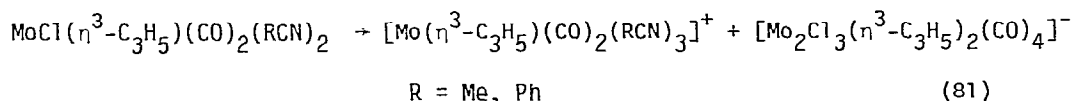
The chloride complexes ionized extensively in polar and non-polar solvents to
$[Mo(\eta^3\text{-}C_3H_5)(CO)_2(RCN)_3]^+$ $[Mo_2Cl_3(\eta^3\text{-}C_3H_5)_2(CO)_4]^-$ with the liberation of free
nitrile.[148] Equilibrium constants were evaluated by IR and NMR. Similar
bromo complexes ionized to a lesser extent and the iodo-complexes were not
ionized at all.[148]

Nucleophilic attacks on endo- and exo- η^3-allyl complexes, such as CpMo(CO)-
(NO)(1,3-dimethylallyl)$^+$ cation occurred stereospecifically.[149] The struc-
tures determined of the olefinic derivatives formed by addition of the nucleo-
phile, were consistent with nucleophilic attack trans to NO in the endo
isomer and cis to NO in the exo isomer. The configuration of the chiral
center implied that attack occurred on the face of the allyl opposite to the

metal and not directly at the metal center.[149] In the structures of the olefin derivatives, $CpMo(CO)(NO)(\eta^2-C_8H_{14}O)$ and $CpMo(CO)(NO)(\eta^2-C_9H_{16}O)$, formed by addition of the enamine of isobutyraldehyde, the olefinic bond tended to be aligned parallel to the molybdenum-carbonyl vector rather than parallel to the Cp plane. The orientational preference had a profound effect on the selectivity of the reaction.[149] Synthetic methods were described for the preparation of sigma- and pi- allyl complexes of molybdenum from $CpMo(CO)_3Cl$ and C_3H_5Br in phase transfer catalyzed reactions.[150] The synthesis of η^3-bonded α-methylene lactone complexes of molybdenum was reported from hydroxy-6-alkynyl-molybdenum complexes.[151]

$$CpMo(CO)_3^- + ClCH_2C\equiv C(CH_2)_nCRR'OH \rightarrow Cp(CO)_3Mo-CH_2C\equiv C(CH_2)_n-CRR'OH$$

$$\Delta \downarrow Al_2O_3 \qquad\qquad (82)$$
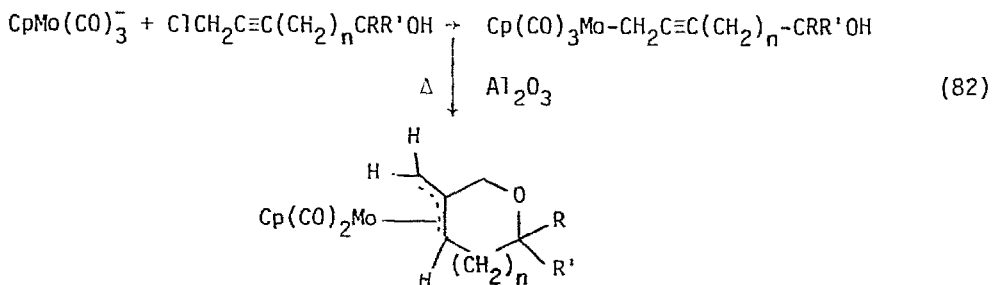
Alkyls and Hydrides

Alkyls. A large number of studies of alkyl complexes were reported in 1979. The reaction of 1,3-diphenyltriazine with the $M_2(CH_3)_8^{-4}$ anions (M = Cr or Mo) were employed to obtain triazino-bridged Cr-Cr and Mo-Mo quadruple bonds.[152]

$$M_2(CH_3)_8^{-4} + PhN_3Ph \rightarrow M_2(PhN_3Ph)_4 \qquad\qquad (83)$$

M = Cr, Mo
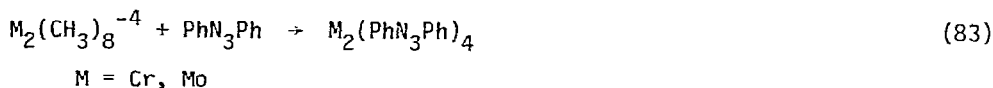
Reaction gave $Cr_2(PhN_3Ph)_4$, $Cr(PhN_3Ph)_3$ and $Mo_2(PhN_3Ph)_4$. All three products were characterized by X-ray crystallography.[152] The reaction of WCl_4Y with Me_2Mg led to formation of $WMeCl_3Y$.[153]

$$WCl_4Y + Me_2Mg \rightarrow W(Me)Cl_3Y \qquad\qquad (84)$$

Y = O, S, Se

The compounds were very reactive and could not be isolated. A number of complexes with nitrogen and oxygen donors were isolated and characterized.[153] Reaction of $Cr(acac)_3$ with $(PhCH_2)_2Mg$, $(PhCH_2)_3Al$, and $PhCH_2MgCl$ led to $PhCH_2Cr(acac)_2$.[154]

$$Cr(acac)_3 + (PhCH_2)_2Mg \rightarrow PhCH_2Cr(acac)_2 \tag{85}$$
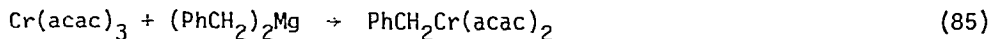
When tris(N,N-dimethyl-o-toluidyl)chromium was treated with metalla-β-diketones, a ligand exchange reaction occurred affording mixed-ligand transition metal complexes containing metalla-β-diketonate ligands.[155] All of these complexes were polynuclear, paramagnetic molecules, and the chromium complexes possessed either one or two chromium-carbon bonds.[155] 3,3'-Oxybis-[(chromiomethyl) benzene] (4$^+$) was prepared from bis[m-(bromomethyl)phenyl] ether and excess Cr(II) in aqueous acetone.[156] This compound was characterized by its spectrum and from products obtained on base hydrolysis and on reaction with Hg(II) and mild oxidants.
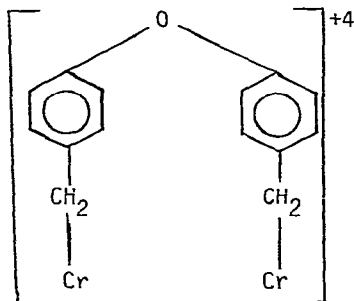
XXIII

Reaction of the dibromide with limiting quantities of Cr(III) produced the complex [CrCH$_2$C$_6$H$_4$OC$_6$H$_4$CH$_2$Br]$^{+2}$ which was similarly characterized.[156] Kinetic data was obtained on the formation of these species and on the reactions with Hg(II).[156] Chromium(II) chloride formed a complex with a water soluble 15-membered macrocyclic [15]aneN$_4$ which reacted with organic halides producing the monoalkyl complexes, trans-RCr([15]aneN$_4$)H$_2$O^{+2}.[157] The kinetics of this reaction showed a second order rate law. A two step mechanism was suggested with the Cr(II) complex reacting with alkyl halide by rate-limiting halogen atom abstraction generating a carbon-centered free radical which couples with a second Cr(II) center.[157]

Several sigma mesitylene complexes were prepared in the past year. Reaction of mesityllithium with molybdenum trichloride in THF produced LiMo(C$_9$H$_{11}$)$_4$-(THF)$_4$.[158]

$$MoCl_3 + LiC_9H_{11} \rightarrow LiMo(C_9H_{11})_4(THF)_4$$
$$\downarrow \text{oxidant} \tag{86}$$
$$Mo(C_9H_{11})_4I_2 \xleftarrow{\ I_2\ } Mo(C_9H_{11})_4$$
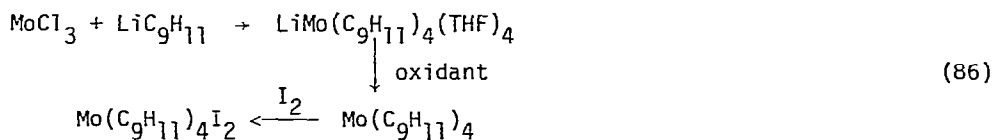
This compound was readily oxidized to $Mo(C_9H_{11})_4$.[158] The molybdenum(IV) complex was very stable and paramagnetic. Addition of iodine or bromine produced $Mo(C_9H_{11})_4X_2$ compounds, maintaining the carbon-metal bonds.[159] These compounds were salt like with the homoleptic cation, $Mo(C_9H_{11})_4^+$.[159] Air oxidation of the tetramesitylene complex, $Li_2Cr(C_9H_{11})_4(THF)_4$, gave $LiCr(O_2)(C_9H_{11})_3(THF)_3$ in 35% yield.[160] Reaction of this tris-mesityl complex with LiR under argon produced the $Cr(C_9H_{11})_4$ complex.[160]

$$Li_2CrR_4(THF)_4 \xrightarrow{O_2} LiCr(O_2)R_3(THF)_3$$

$$\downarrow LiR$$

$$CrR_4$$

$$\text{(87)}$$

$$R = 2,4,6\text{-}Me_3C_6H_2$$
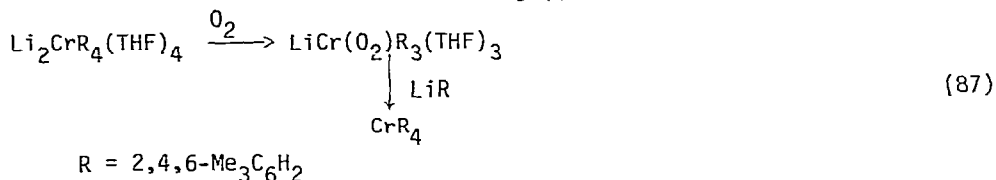
Air oxidation of $LiCr(C_9H_{11})_3(OEt)_2(dioxane)$ produced $CrR_3(THF)$ in low yield.[160]

Jones and Bergman studied the reaction between organotransition metal alkyls and hydrides.[161] The methyl and ethyl complexes were converted to aldehydes at temperatures between 25 and 50°C.[161]

$$CpMo(CO)_3H + CpMo(CO)_3R \rightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-H + Cp_2Mo_2(CO)_4 + Cp_2Mo_2(CO)_6 \quad \text{(88)}$$

$$R = CH_3,\ C_2H_5,\ CH_2C_6H_5,\ CD_3,\ CD_2C_6H_5$$
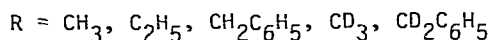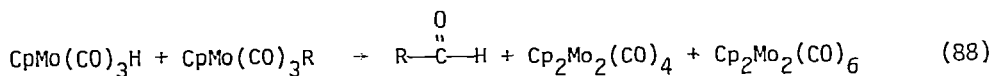
The yields for methyl and ethyl were quantitative with no trace of alkanes. The following scheme was suggested.[161]
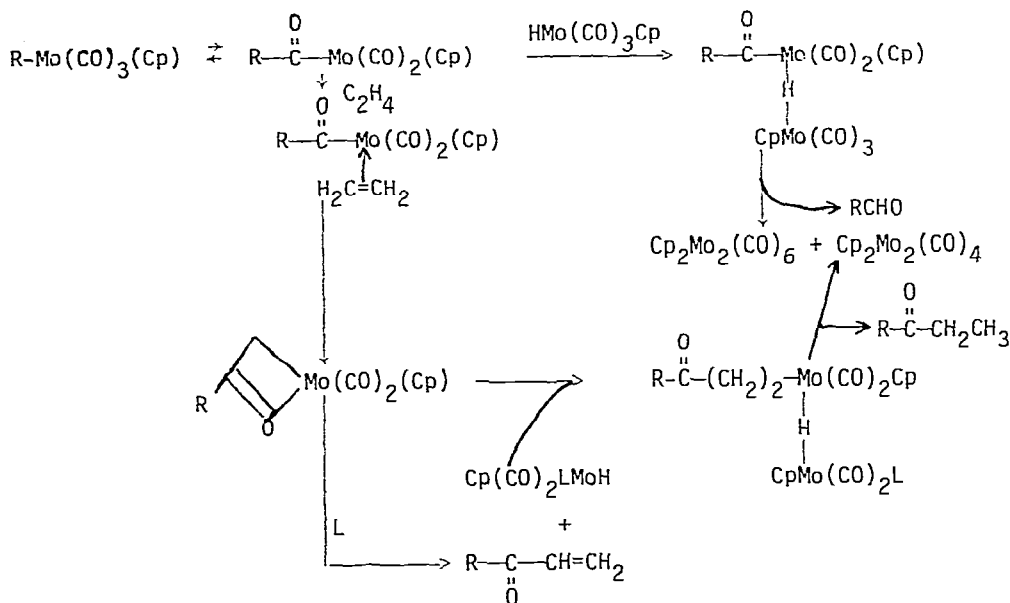
This Mo system mimicked the oxo reaction except that reaction of $Cp_2Mo_2(CO)_6$ with H_2 was slow.[161] The behavior of the benzyl complex was more complicated than that of the methyl and ethyl complexes. The reaction was slower, as expected for initial alkyl migration. Toluene was formed with the aldehyde and the ratio RCHO:RH was dependent on initial hydride concentrations (more hydride produced a higher yield of aldehyde).[161] Reaction of metal carbonyl anions with haloacetylenes or ethynylphosphonium salts produced sigma-ethynyl metal carbonyl complexes, $Cp(CO)_3M-C\equiv C_6H_5$.[162]

$$CpCr(CO)_3^- + C_6H_5C\equiv CBr \rightarrow Cp(CO)_3Cr-C\equiv CC_6H_5 \qquad (89)$$

$$CpM(CO)_3^- + [C_6H_5C\equiv CPPh_3]Br \rightarrow CpM(CO)_3-C\equiv CC_6H_5$$
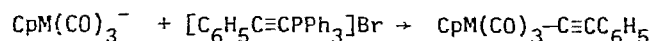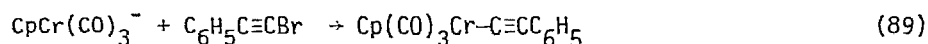
$$M=Mo, W$$

Watson and Bergman reported the synthesis and cyclization of alkynyl-$CpM(CO)_3$ complexes (M = Mo, W).[163] Cyclization of the complexes, $CH_3C\equiv C(CH_2)_nM(Cp)(CO)_3$ (n = 3,4,5; M = Mo, W) occurred under mild conditions to give cyclized products, $Cp(CO)_2M[C(CH_3)=C(O)(CH_2)_n]$, derived from intramolecular insertion of the acetylenic function into a metal-acyl bond.[163]

$$Cp(CO)_3M-(CH_2)_nC\equiv CCH_3 \rightarrow Cp(CO)_2M \underset{O=}{\overset{\wedge}{\diagdown}} (CH_2)_n \qquad (90)$$
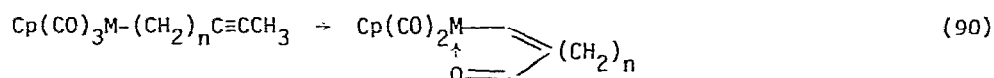
$$n = 3,4,5; M = Mo, W$$

Yields depended on the value for n, n = 3, > 70%; n = 4, 50%; n = 5, < 15%. Hydrogenation of the cyclized Mo species produced 2-ethylcyclohexanone and $Cp_2M_2(CO)_4$ in high yield.[163]

Insertion of molecules into alkyl-Group VI complexes continued to be reported. Reaction of $(\eta^5-C_9H_7)(CO)_3MoMe$ with but-2-yne afforded the vinyl ketone complex, $(\eta^5-C_9H_7)(CO)_2Mo\{C(Me)=C(Me)C(Me)O\}$.[164]

$$(\eta^5-C_9H_7)(CO)_3MoMe + but-2-yne \rightarrow (\eta^5-C_9H_7)(CO)_2Mo\{C(Me)C(Me)=C(Me)O\} \quad (91)$$

$$(\eta^5-C_9H_7)(CO)_3MoMe + 3,3'-dimethylbut-1-yne \rightarrow$$

$$(\eta^5-C_9H_7)(CO)_2Mo\{CH=C(t-Bu)C(Me)O\} \qquad (91)$$

$$\downarrow$$

$$(\eta^5-C_9H_7)(CO)_2Mo\{\eta^3-C(Me)C(t-Bu)CHCH=C(t-Bu)O\}$$
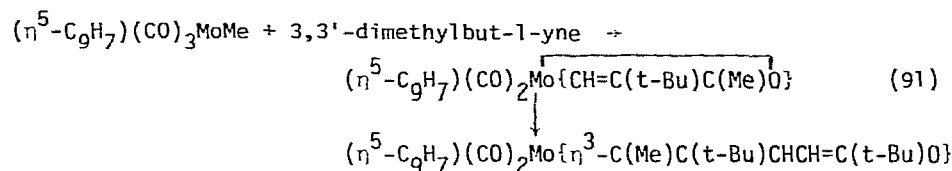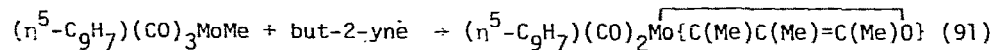
In contrast 3,3-dimethylbut-1-yne reacted under similar conditions to give consecutively $(\eta^5-C_9H_7)(CO)_2Mo\{CHC(t-Bu)C(Me)O\}$ and the η^3-pyranyl complex, $(\eta^5-C_9H_7)(CO)_2Mo\{\eta^3-C(Me)C(t-Bu)CHCH=C(t-Bu)O\}$.[164] Methylencyclopropane

reacted slowly with $(\eta^5\text{-}C_9H_7)(CO)_3MoMe$ to give the ring-opened complex, $\eta^5\text{-}$ $C_9H_7(CO)_2Mo\{\eta^3\text{-anti-}CH(Me)C(C(O)Me)CH_2\}$ and 1,3-butadiene to afford $(\eta^5\text{-}$ $C_9H_7)(CO)_2Mo\{\eta^3\text{-}CH_2CHCHCH_2C(O)Me\}$. The mechanism of formation of these products was discussed.[164] Reaction of CS_2 with $Cp(CO)_2MoR$ (R = Me, Et) yielded the $\eta^2\text{-}CS_2$ complexes, $Cp(CO)_2Mo(\eta^2\text{-}CS_2)(C(O)R)$ which reversibly lost CS_2 in reflux-ing benzene to regenerate the starting material.[165] Reaction of $Cp(CO)_2Mo(\eta^2\text{-}CS_2)(C(O)Me)$ with PPh_3 yielded $Cp(CO)(PPh_3)Mo(\eta^2\text{-}CS_2)(C(O)Me)$.[165] Sulfur dioxide insertion into alkyl-W bonds was shown by Severson and Wojcicki to be accelerated by BF_3 and SbF_5.[166]

$$R\text{-}W(Cp(CO)_3 \ + \ SO_2 \ \xrightarrow{\ BF_3\ } \ R\text{-}\underset{\underset{\underset{BF_3}{|}}{\overset{\|}{O}}}{S}{=}O\text{-}W(Cp)(CO)_3 \tag{93}$$
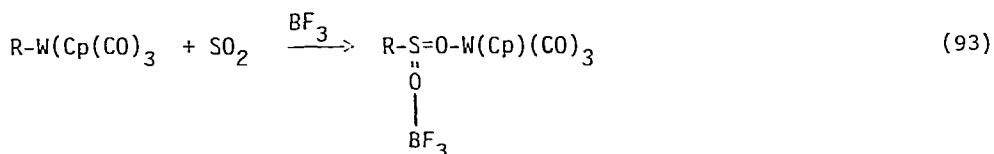
BF_3 accelerated the rate by a factor of 20,000, leading to $Cp(CO)_3W[OS(OBF_3)R]$ (the O-sulfinato complex) instead of the S-sulfinato complex observed in unassisted insertions.[166]

Green and co-workers continued their studies of bis-cyclopentadienyl alkyl complexes.[167-169] The methyl hydride complex, $Cp_2W(Me)H$, was prepared by treatment of Cp_2WMeX (X = I or OCOPh) with $Na[AlH_2(OCH_2CH_2OMe)_2]$.

$$Cp_2W(Me)X \ \xrightarrow{\ Na[AlH_2(OCH_2CH_2OMe)_2]\ } \ Cp_2W(Me)H$$
$$\Big\downarrow \Delta$$
$$Cp_2W(R)H \ \xleftarrow{\ RH\ } \ [Cp_2W] + CH_4 \tag{94}$$
$$R = Ph,\ C_6H_4F,\ OMe,\ etc.$$
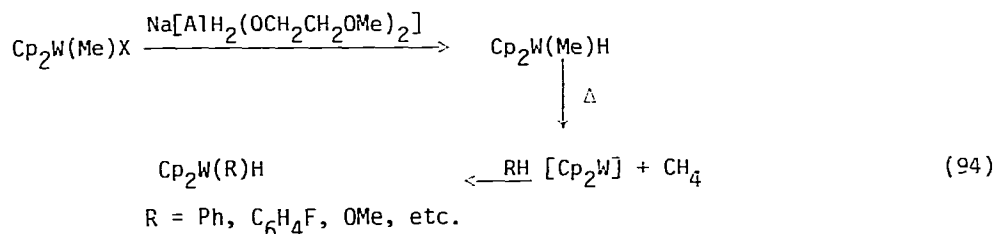
Thermal decomposition of $Cp_2W(Me)H$ in benzene, fluorobenzene, methanol, etc., evolved methane and the compounds $Cp_2W(R)H$, R = Ph, C_6H_4F, OMe, etc.[167] The oxidation of Cp_2WMe_2 with I_2 yielded paramagnetic $Cp_2WMe_2^+$ which could be reduced to the parent dimethyl compound.[167] The compounds $[Cp_2MoR(CO)]PF_6$ (R = Me, $\eta^1\text{-}C_3H_5$, etc.) and $[Cp_2WMe(CO)]PF_6$ were prepared by addition of RX to $Cp_2M(CO)$.[168]

$$Cp_2M(CO) + RPF_6 \ \longrightarrow \ [Cp_2MR(CO)]PF_6 \ \xrightarrow{\ PMe_2Ph\ } \ Cp_2M(C(O)R)PMe_2Ph \tag{95}$$
$$M = Mo,\ W$$
$$R = Me,\ etc.$$
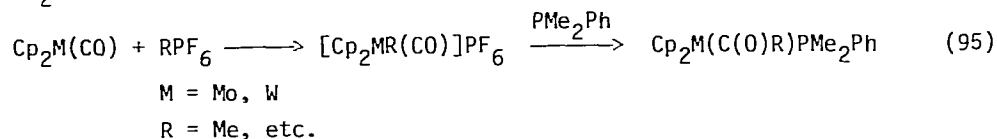
Reaction of the alkyl carbonyl complexes ($[Cp_2MoMe(CO)]PF_6$) with PMe_2Ph produced $[Cp_2Mo(C(O)Me)(PMe_2Ph)]PF_6$. The olefin complex, $[Cp_2W(C_2H_4)R]PF_6$, could be prepared similarly; no insertion of the ethylene was observed.[168] The rate of the thermal rearrangement of the compounds $[Cp_2WH(CH_2PR_3)]PF_6$ to $[Cp_2W(Me)(PR_3)]PF_6$ increased in the order R_3 = Ph_2Me > $PhMe_2$ > Me_3, and when R_3 = Me_3 the two compounds were found to be in equilibrium in solution.[169]

$$Cp_2WH(CH_2PR_3) \rightleftarrows Cp_2W(Me)PR_3 \tag{96}$$

$$R_3 = Ph_2Me, \ PhMe_2, \ Me_3$$

When R_3 = Ph_2Me, the $PMePh_2$ group exchanged with added PMe_3 producing $[Cp_2WH(CH_2PMe_3)]PF_6$.[169]

Hydride. Borisov and co-workers reported the synthesis and reactions of H_4WL_4 (L = $PPhMe_2$, $PPhEt_2$, PPh_2H, $P(OEt)_3$, etc.).[170] Solutions of WCl_6 in dimethoxyethane or THF were treated with KBH_4 and then phosphites or phosphines to give H_4WL_4.

$$WCl_6 + KBH_4 \xrightarrow{L} H_4WL_4 \tag{97}$$
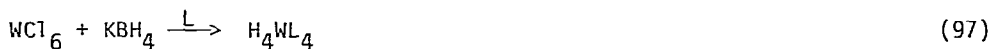
L = phosphines and phosphites

These W hydride complexes were characterized by IR and ^1H NMR.[170] When toluene solutions containing H_4WL_4 (L =$PMePh_2$, $PBuPh_2$) in a CO_2 atmosphere were refluxed 2 hr a mixture of fac- and mer-$W(CO)_3L_3$ was obtained.[171] The carbonylation of H_4WL_4 did not require the presence of a reducing agent as in the case of $Rh(PPh_3)_3Cl$. CO_2 reacted with WH_4 at 20° to give a complex containing coordinated CO_2 or a product of its reaction.[171] For the ligands PPh_2Et and $PPhEt_2$, the hydride complexes, H_6WL_3, were prepared and identified by ^1H NMR spectra.[170] Addition of acids, HX (X = BF_4, HSO_4, Cl, etc.) under controlled conditions gave the hydride complexes $[MH(CNR)_2(dppe)_2][X]$ and the hydrido-carbyne complexes $[MH\{CN(H)R\}(CNR)(dppe)_2][X]_2$.[172]

$$trans\text{-}[M(CNR)_2(dppe)_2] \xrightarrow{HX} [MH(CNR)_2(dppe)_2][X] \tag{98}$$
$$+$$
$$[MH\{CN(H)R\}(CNR)(dppe)_2][X]_2$$
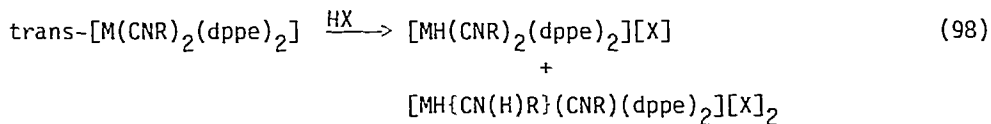
The IR and NMR spectra of the complexes were discussed in terms of their structures.[172] The chloro compounds, $CpM(NO)_2Cl$ (M = Mo, W) reacted with $Na[AlH_2(OCH_2CH_2OCH_3)_2]$ in toluene to form the hydrido complexes $CpM(NO)_2H$.[173]

$$CpM(NO)_2Cl \xrightarrow{H^-} CpM(NO)_2H \tag{99}$$

M = Mo, W.

The hydridomolybdenum complex slowly decomposed at ambient temperatures, but the thermally stable tungsten analogue could be isolated and fully characterized. $CpW(NO)_2H$ exhibited a ν_{M-H} at 1900 cm^{-1} in its IR and a low field hydride resonance at δ 2.27.[173] Its chemistry was characterized by its tendency to function as a source of H$^-$.[173] Darensbourg and Incorvia studied the substitution and dimer disruption chemistry of μ-H[Cr(CO)$_5$]$_2^-$.[174]

$$\mu\text{-H[Cr(CO)}_5]_2^- \quad \overset{\nearrow \quad \text{substituted dimer}}{\underset{\searrow \quad M(CO)_5L}{}} \qquad\qquad (100)$$
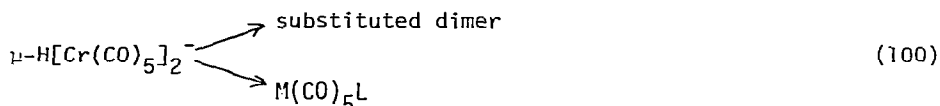
Photolysis to the substituted dimer occurred with a higher quantum yield than break up of the dimer.[174] The ligands used were PPh$_3$ and ^{13}CO. ^{13}CO substitution was equatorial on the dimer.[174] The complex, Bu$_4$N[μ-H(Cr(CO)$_5$)$_2$], reacted with HCl in MeOH to give Bu$_4$N[Cr(CO)$_5$Cl].[175] Analogous reactions of K(phen)$_3$ Cr$_2$H(CO)$_{10}$ gave (phen)$_2$H[μ-H(Cr(CO)$_5$)$_2$].[175] Cp$_2$MH$_2$ complexes have continued to be investigated. The mechanism of carbonylation of Cp$_2$MoH$_2$ was reported.[176]

$$Cp_2MoH_2 + CO \rightarrow Cp_2Mo_2(CO)_6 + CpMo(\eta^3\text{-}C_5H_7)(CO)_2 \qquad\qquad (101)$$
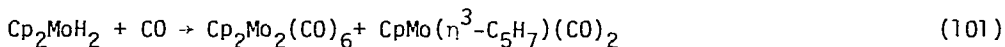
The final products were Cp$_2$Mo$_2$(CO)$_6$ and CpMo(η^3-C$_5$H$_7$)(CO)$_2$. The intermediates, Cp$_2$Mo(CO), [Cp$_2$Mo(H)CO]$^+$, [CpMo(CO)$_3$]$^-$ and CpMo(CO)$_3$H, were believed to be important and the following scheme was suggested.[176]
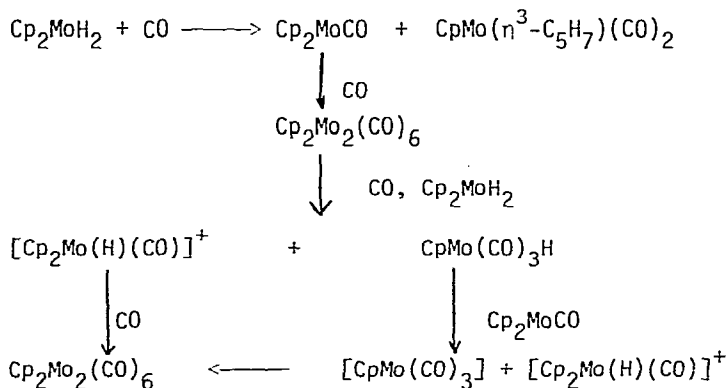
It was suggested that the hydrogen transfer took place by a radical process.[176] Catalysis of the exchange of D$_2$ with Cp$_2$WH$_2$ was effected by Mn$_2$(CO)$_{10}$.[177] Treatment of Cp$_2$WH$_2$ with D$_2$ at 80°C in the presence of Mn$_2$(CO)$_{10}$ indicated that deuterium had equilibrated throughout the metallocene, but not with the solvent.[177] It was suggested that binuclear intermediates were involved in

this reaction.[177] The treatment of Cp_2MH_2 (M = Mo, W) with $CH_3Mn(CO)_5$ gave the binuclear complexes, $Cp(CO)M(\mu-(\eta^5:\eta^1-C_5H_4))Mn(CO)_4$, accompanied by evolution of CH_4 and H_2[178]

$$Cp_2MH_2 + CH_3Mn(CO)_5 \rightarrow Cp(CO)M(\mu-(\eta^5:\eta^1-C_5H_4))Mn(CO)_4 + CH_4 + H_2 \quad (102)$$
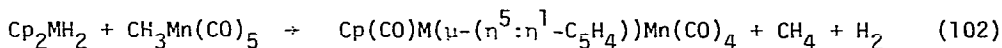
M = Mo, W.

Methane was formed from a hydrogen of a cyclopentadienyl ring of the metallocene hydride and the methyl group of $CH_3Mn(CO)_5$.[178] The preparation of mixed organotransition metal complexes $[Cp_2M(\mu-H_2)-Rh(PPh_3)_2]PF_6$ (M = Mo, W), was achieved by reaction of Cp_2MH_2 with $H_2Rh(PPh_3)_2 \cdot 2$ acetone at room temperature.[179]

$$Cp_2MH_2 + H_2Rh(PPh_3)_2^{\overset{\text{\tiny +}}{}} \rightarrow Cp_2W(\mu-H_2)Rh(PPh_3)_2^+ \quad (103)$$
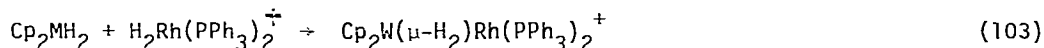
The X-ray structure of the tungsten compound showed the dinuclear, hydride-bridged nature of this complex.[179] The reaction of Cp_2WH_2 with $[RN_2][X]$ at low temperature led to $[Cp_2WH(NN(H)R)][X]$ (R = aryl; X = BF_4 or PF_6), which rearranged in solution above -20°C to yield $[Cp_2W(H_2NNR)][X]$ in which the arylhydrazido ligand was bound to W in a "side-on" or η^2-manner.[180]

$$Cp_2WH_2 + [RN_2][X] \xrightarrow{\text{low temperature}} [Cp_2WH(NN(H)R)][X]$$
$$\downarrow \text{0°C} \quad (104)$$
$$[Cp_2W(H_2NNR)][X]$$

R = aryl; X = BF_4, PF_6
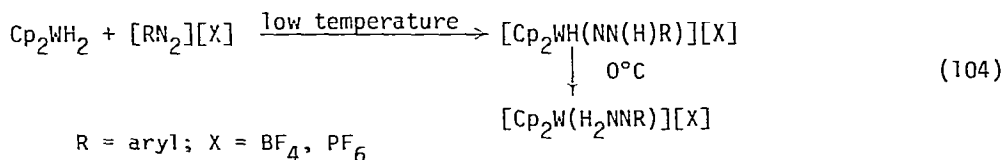
The X-ray structure was reported for $[Cp_2W(H_2NNR)][BF_4]$.[180]

Metal-Metal Bonded Systems.

A large number of studies of multiple metal-metal bonded systems were reported in 1979. Reactions of appropriate metal carbonyl derivatives with pentamethylcyclopentadiene in boiling n-decane provided routes to $[Me_5C_5M(CO)_2]_2$ (M = Cr, Mo, W).[181] Infrared spectroscopic studies at elevated pressure indicated that the ease of CO addition to the triple bond increased in the sequence Cr < W < Mo.[181]

$$[(Me_5C_5)M(CO)_2]_2 + CO \rightarrow [(Me_5C_5)M(CO)_3]_2 \quad (105)$$
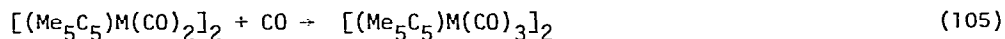
M = Cr, Mo, W.

Carbonylation was also used to prepare $[(Me_5C_5)M(CO)_3]_2$. The chromium dimer was least stable.[181] The reaction of dinuclear acetates of molybdenum with di-arylmagnesiums in the presence of PMe_3 led to sigma-aryl molybdenum complexes

containing a Mo-Mo quadruple bond.[182]

$$Mo_2(O_2CMe)_4 + PMe_3 + MgAr_2 \longrightarrow$$
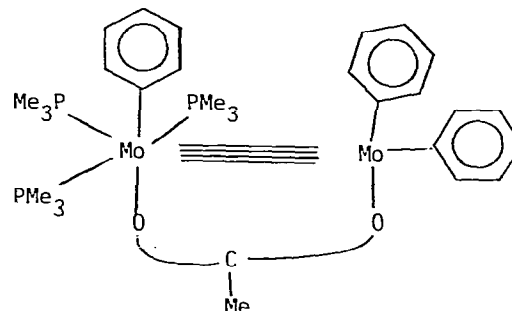
Ar = aryl

In the absence of PMe_3 only decomposition occurred. The compounds were characterized by microanalysis, IR and NMR (^{13}C, ^{1}H, ^{31}P).[182] A similar reaction with 2-methoxyphenyl led to a product with no acetato groups (XXIV).[182]
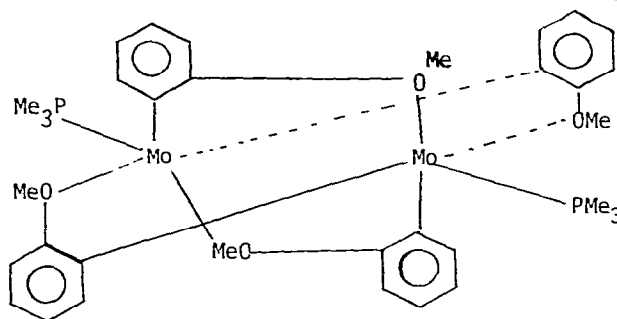
XXIV

Dicyclopentadienyl di-tert-butoxydichromium was prepared.[183]
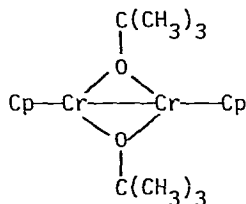
XXV

The structure was determined (XXV) with a Cr-Cr bond length of 2.65Å which indicated a strong bond, but the bond order wasn't suggested. The Cp-Cr-Cr-Cp was linear.[183] Reactions were studied with acetylenes, CO, CO_2, NO_2 and NO.

The compounds $Cp_2Cr_2(O\text{-}t\text{-}Bu_4)_2(NO)_2$ and $Cp_2Cr_2(O\text{-}t\text{-}Bu)_2\text{-}(CF_3C\equiv CCF_3)$ were prepared and characterized.[183] Dialkyl dimolybdenum and ditungsten (M≡M) complexes were prepared by the following reaction.[184]

$$M_2Cl_2(NMe_2)_4 + 2LiR \rightarrow M_2R_2(NMe_2)_4 + 2LiCl \qquad (106)$$
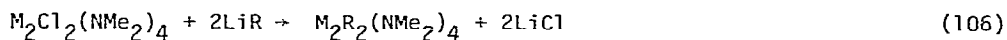
$$R = CH_3, \ C_2H_5, \ CH_2CD_3, \ C_4H_9, \ etc.$$

These alkyls were reported to be remarkably stable with no evidence of β-elimination. Reaction with CO_2 led to insertion into the M-N bond.[184] Retention of the M-M triple bond was observed for β-elimination stabilized alkyls, while the following reaction was observed for non-β-elimination stabilized alkyls.[184]

$$Mo_2R_2(NMe_2)_4 + CO_2 \rightarrow M_2(O_2CNMe_2)_4 + R\text{-}H + 1\text{-}alkene \qquad (107)$$
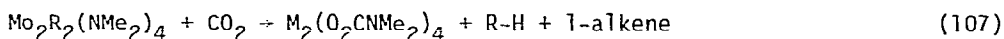
Deuterium labeling experiments indicated that CO_2 insertion caused β-elimination to occur followed by reductive elimination of RH.[184] Hydrocarbon solutions of $Mo_2(O\text{-}t\text{-}Bu)_6$ (Mo≡Mo) reacted with CO at room temperature and 1 atmosphere through the monocarbonyl, $Mo_2(O\text{-}t\text{-}Bu)_6(\mu\text{-}CO)$, to $Mo(CO)_6$ and $Mo(O\text{-}t\text{-}Bu)_4$.[185] A crystal structure was accomplished. Diaryl, aralkyl and cycloalkyl thioketones reacted with dicyclopentadienylhexacarbonyldimolybdenum or -ditungsten to give a new class of thione complexes of formula $(R_2CS)M_2(CO)_4(\eta^5\text{-}C_5H_4R')_2$ (M = Mo, W).[186] The structures were elucidated by elemental analysis, IR, and NMR (^1H and ^{13}C) as well as X-ray analysis of the thiocamphor molybdenum complex. The thioketone was bonded in an unusual fashion and one semi-bridging CO was observed.[186] The complex, $K_3[Mo_2(CO)_6(OMe)_3]$, was prepared by treating the hydroxide precipitate formed during addition of MeOH solutions of alkali to solutions of $TiCl_3$, $MoCl_5$ and $MgCl_2$, with CO for 10 min. at 50°C.[187] For aqueous solutions the methoxy groups were substituted by μ^2-OH bridges. During crystallization in H_2O the dimer was converted to the tetramer, $K_4[Mo(OH)(CO)_3]_4 \cdot H_2O$.[187] Both the tetramer and dimer were characterized by IR and X-ray photoelectron spectra.[187] Reaction of $M(CO)_6$ (M = Cr, Mo, W) with Me_2SO in H_2O gave $[Me_2SO](H_2O)(CO)Cr(O)OCr(O)(H_2O)(Me_2SO)$, $[(Me_2SO)_3Mo(O)]_2O$, and $(H_2O)_2(CO)W(O)OW(O)(H_2O)_2(Me_2SO)$.[188]

The number of preparations and structural analyses of mixed-metal complexes containing Group VI metals has grown in 1979. The reaction of Cp_2NbBH_4 and $CpM(CO)_3Me$ in toluene in the presence of Et_3N gave binuclear complexes, $Cp_2Nb\text{-}M(CO)_3(Cp)$.[189]

$$Cp_2NbBH_4 + MeM(CO)_3(Cp) \rightarrow Cp_2NbM(CO)_3Cp \qquad (108)$$
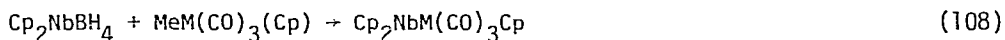
$$M = Mo, \ W$$

The structure of the Mo complex was determined (XXVI) showing the structure below with a Nb-Mo bond length of 3.073Å.[189]

$$(Cp)_2Nb \overset{\overset{\displaystyle O \atop \displaystyle C}{\diagdown}}{\underset{\underset{\displaystyle O \atop \displaystyle C}{\diagup}}{\text{—————}}} Mo(Cp)(CO)$$
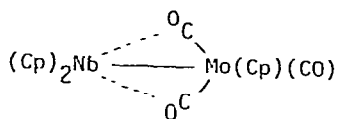
<div align="center">XXVI</div>

The infrared absorption frequencies showed evidence for the interaction (1870, 1700, and 1560 cm^{-1}) in a semi-bridging position.[189] The preparation of carbonyl-free mixed organotransitionmetal complexes, $[Cp_2M(\mu-H)_2Rh(PPh_3)_2][PF_6]$ (M = Mo, W) was described.[190] The X-ray structure of the tungsten compound was done showing square planar coordination at rhodium (2P and 2H) and normal geometry at the tungsten. Rapid H + D exchange of the hydrides and the Cp rings was observed under mild conditions. This was ascribed to an oxidative-addition of a Cp C-H bond onto the rhodium.[190] The new heteroclusters, $PhPFeMoCo-Cp(CO)_8$ (XXVII) and $PhPMoCo_2Cp(CO)_6$ (XXVIII) (μ-AsMe$_2$) were prepared and studied.[191]
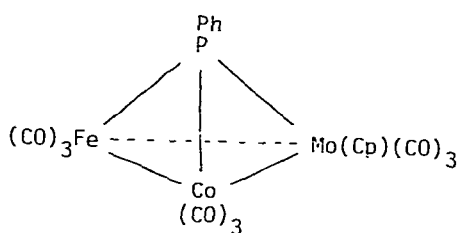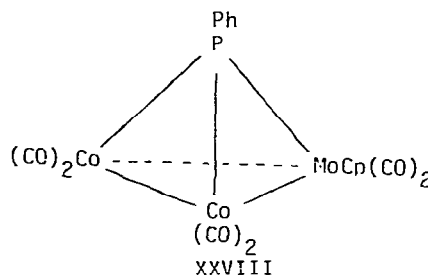
<div align="center">XXVII   XXVIII</div>

These compounds were characterized by IR and NMR; the iron complex (XXVII) was chiral.[191] Reaction of $Cp(CO)_3W-AsMe_2$ with the μ_3-sulfido-bridged trimer, μ_3-$S-MoFeCo-Cp(CO)_8$ led to the first cluster with four different metals.[192,193]
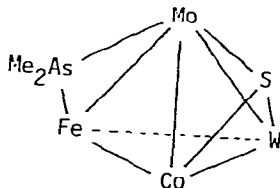
Reaction of $NaCpMo(CO)_3$ with $cis\text{-}Cl_2Pt(CNC_6H_{11})(C(OC_2H_5)NC_6H_{11})$ led to a trimetallic carbene complex with Mo-Pt-Mo bonds.[194]

$cis\text{-}Cl_2Pt(CNC_6H_{11})(C(OEt)NHC_6H_{11})$
  +
$NaMo(Cp)(CO)_3$

$$\text{(Cp)(CO)}_3\text{Mo}\text{———}\overset{\displaystyle \overset{NC_6H_{11}}{\diagdown}C\overset{OEt}{\diagup}}{\underset{\displaystyle \underset{N}{\overset{|}{C}}}{Pt}}\text{———}\text{Mo(CO)}_3\text{Cp} \qquad (109)$$

$$\underset{C_6H_{11}}{|}$$
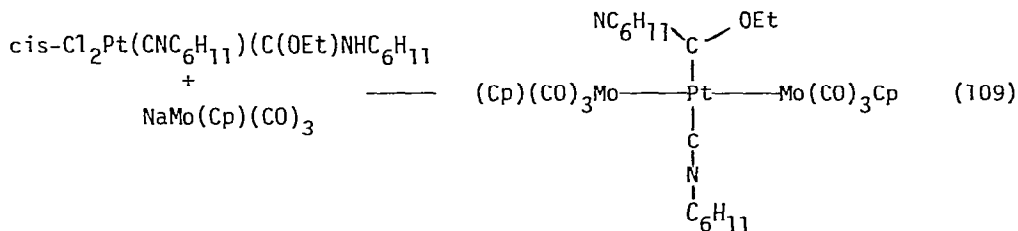
The crystal structure determination showed a Mo-Pt distance of 2.889Å, indicating strong bonding. The Pt geometry was square planar and the geometry was near normal although one CO was semi-bridging.[194] The compounds $Pt(C_2H_4)_2(PR_3)$, $(PR_3 = P(t\text{-}Bu)_2Me$ or $P(C_6H_{11})_3)$, reacted with carbene complexes $M\{C(OMe)Ph\}(CO)_5$, (M = Cr, W) to give trimetallic molecules $MPt_2\{\mu\text{-}C(OMe)Ph\}(CO)_6(PR_3)_2$, with the structure of the tungsten compound (XXIX) established by X-ray crystallography.[195]
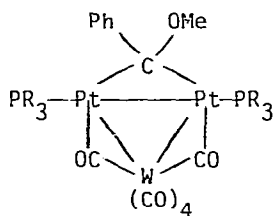
XXIX

The W-Pt distance was 2.83Å and the Pt-Pt distance was 2.63Å.[195]

Chelates

Electrochemical oxidation of the complexes, $M(CO)_2(dam)$ (M = Cr, Mo; dam = bis(diphenylarsino)methane) which have the structure (XXX) shown below showed unusual reaction pathways.[196]
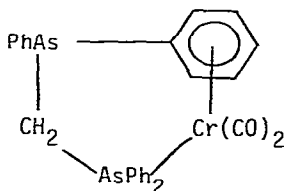
XXX

At mercury electrodes the following reactions were observed.[196]

$$2M(CO)_2(dam) + 2Hg \rightleftharpoons 2[HgM(CO)_2dam]^+ + 2e^- \tag{110}$$

$$2[HgM(CO)_2(dam)]^+ \rightleftharpoons [Hg(M(CO)_2(dam))_2]^{+2} + Hg \tag{111}$$
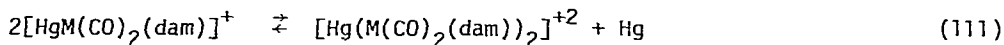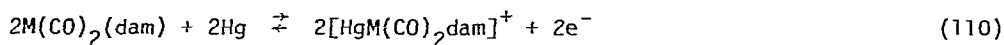
Under voltametric conditions at a platinum electrode the reversible one-electron oxidation was observed.[196]

$$Cr(CO)_2(dam) \rightleftharpoons [Cr(CO)_2(dam)]^+ + e^- \tag{112}$$
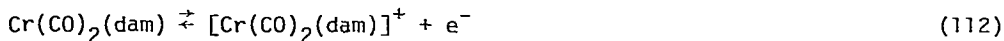
A further irreversible oxidation was also observed.

$$[Cr(CO)_2(dam)]^+ \rightarrow [Cr(CO)_2(dam)]^{+2} \tag{113}$$

The $Mo(CO)_2(dam)^+$ underwent irreversible oxidation at platinum under all conditions.[196] Chemical oxidation with Hg(II), Ag(I), I_2 and $POPF_6$ were also investigated.[196] Nesmeyanov and coworkers continued their study of arene-chelate complexes. UV irradiation of arene-tricarbonylchromium complexes containing $-OP(OR)_2$ phosphorus atoms in the δ- or ε-positions of two side chains caused displacement of two CO ligands to give two-bridged chelate arenebisphosphite carbonyl chromium complexes.[197]

$$\xrightarrow{h\nu} \text{ substituted species} \tag{114}$$
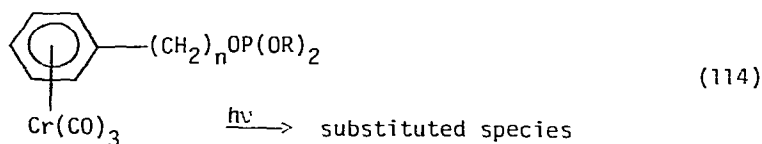
With phosphorus in the γ position only singly bridged chelate complexes were formed. Structures were assigned by IR and NMR(^{31}P, ^{1}H).[197] A crystal structure of (3,5-dimethylbenzyl)diphenylphosphitodicarbonyl chromium (XXXI) was accomplished.
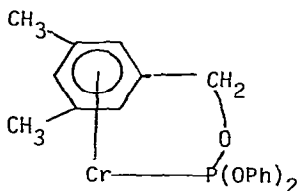
XXXI

The chromium geometry was a distorted octahedron with an extremely short Cr-P

bond (2.201Å). This was ascribed to a chelate effect.[198] UV irradiation of arenedifluorophosphite complexes resulted in replacement of all the CO groups.[199] Complexes with one, two or three chelate cycles were prepared. The structure of the tris-substituted complex (XXXII) was determined.[199-200]
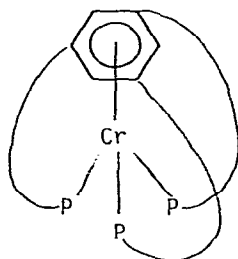
XXXII

The aromatic ring maintained its planarity; the chromium was octahedral with the P-Cr-P angle 91.9°.[200] The reaction of LiBu with pentacarbonyl(thioether) complexes of chromium and tungsten $[M(CO)_5S(CH_2R)R']$ in the presence of a pi-acid ligand (phosphine, phosphite or isocyanide), followed by alkylation produced a series of trisubstituted carbonyl complexes of the type fac-$[M(CO)_3L\{C(OEt)C-OEt)=C(SR')R\}]$.[201] A proposed mechanism involving a double consecutive carbonylation was substantiated by the formation of a cis-tetra-carbonyl(aminocarbenethio)-chelate as a by-product during one reaction with L = CNBu^t.[201] The complexes $[CpM(CO)_2(NN')]Cl$ (M = Mo, W; NN' = five-membered chelate rings, Schiff-base derived from 2-pyridinecarbaldehyde and various amines) reacted with lithium- and magnesium-reagents to form neutral metalla-aziridines.[202] NMR (^1H and ^{13}C) indicated a stereospecific course for the ring contraction.[202]

Nitrosyls

Treatment of $Bu_4N[W(CO)_5I]$ in CH_2Cl_2 with $(NO)HSO_4$ led to $W(CO)_4(NO)(I)$.[203] Refluxing the nitrosyl complex in MeCN produced $(MeCN)_2W(CO)_2(NO)I$ which reacted with PPh_3 in THF or $CHCl_3$ to give cis- and trans-$(Ph_3P)_2W(CO)_2(NO)I$; in C_6H_6 or MeCN one acetonitrile and one CO were replaced leading to $(PPh_3)_2W(CO)(NO)(MeCN)I$.[203]

$$(MeCN)_2W(CO)_2(NO)I + 2\ PPh_3 \xrightarrow{\text{THF or CHCl}_3} (PPh_3)_2W(CO)_2(NO)I \qquad (115)$$

$$(MeCN)_2W(CO)_2(NO)I + 2\ PPh_3 \xrightarrow{\text{C}_6\text{H}_6 \text{ or MeCN}} (PPh_3)_2W(CO)(NO)(MeCN)I \quad (116)$$
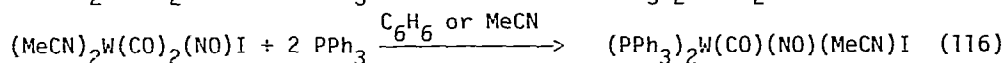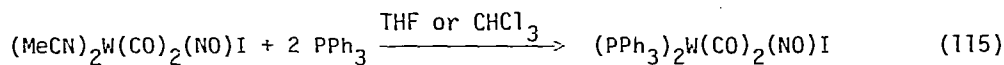
The bis-acetonitrile complex also reacted with CpTl to give $CpW(CO)_2NO$.[203]

$(MeCN)_2W(CO)_2(NO)I + CpTl \rightarrow CpW(CO)_2NO$ (117)
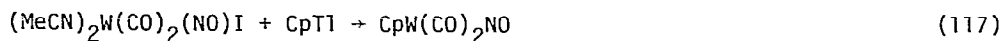
The complexes were characterized by IR and Raman spectra.[203] The preparation of nitrosyl complexes of molybdenum and tungsten was effected by reactions on tetracarbonyl-[o-phenylenebis(dimethylarsine)]-molybdenum and tungsten.[204]

$$M(dma)(CO)_4 + NOPF_6 \rightarrow [mer-M(dma)(CO)_3NO][PF_6]$$
$$\downarrow X$$
$$M(dma)(CO)_2(NO)X$$
(118)
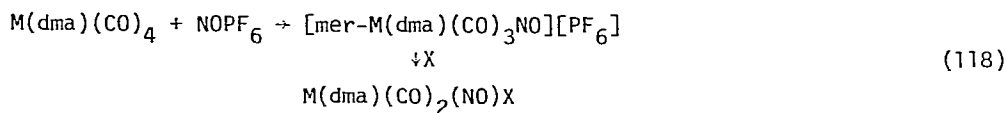
dma = o-phenylenebis(dimethylarsine)

$X = Cl^-, Br^-, I^-, S_2CNMe_2^-$

The determination of stereochemistry by IR and NMR spectroscopy and the detection or isolation of reaction intermediates, allowed comments to be made on the mechanism of the formation and substitution reactions of $[M(dma)(CO)_3-NO][PF_6]$.[204]

The aprotic acids $HgCl_2$ and $SnCl_4$ reacted with the complexes $CpM(CO)(NO)-(PPh_3)$ (M = Mo, W) by electrophilic attack at the metal.[205] This reaction did not occur for $CpMo(CO)_2NO$ indicating that substitution of PPh_3 for CO increased the basicity of the metal.[205] Complexes with both NO and CS ligands, $CpCr(CO)(NO)(CS)$, $CpCr(NO)(CS)(PMe_3)$ and $CpCr(NO)_2CS^+$, were prepared by the following reactions.[206]

$$CpCr(CO)_2NO \xrightarrow[-CO]{h\nu} \xrightarrow[-SPPh_3]{+CS_2,\ PPh_3} CpCr(CO)(CS)(NO)$$
(119)
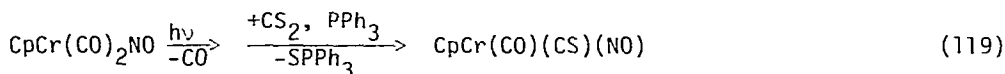
The CS ligand was shown by NMR and IR to be a much more effective acceptor ligand than CO.[206] Reaction of $[CpMo(NO)X_2]_2$ (X = Cl, Br, I), $CpMo(NO)(O_2CMe)$, or $CpMo(NO)I$ with alkyl- or aryl-hydrazines afforded simple hydrazine adducts, $CpMo(NHRNR'R'')(NO)X_2$, $CpMo(NRNR'R'')(NO)I$ and $[CpMo(NO)X]_2NNR'R''$ complexes.[207] The species, $CpMo(NHRNR'R'')(NO)X_2$, were shown by spectral data to contain either a unidentate or a chelating hydrazine. The $CpMo(NRNR'R'')(NO)I$ complex had a known structure with a bidentate hydrazine bound to only one metal atom.[207] The organometallic thionitrosyl complex, $CpCr(CO)_2(NS)$, was isolated from the reaction of $CpCr(CO)_3^-$ and $S_3N_3Cl_3$ at -78°C.[208]

$$CpCr(CO)_3^- + S_3N_3Cl_3 \xrightarrow{-78°C} CpCr(CO)_2NS$$
(120)
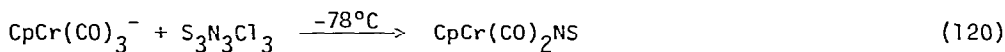
The structure was done showing the geometry to be the expected "piano stool" with a linear NS ligand coordinated to the metal via the nitrogen atom.[208]

KINETICS AND MECHANISMS

Darensbourg and Graves studied the kinetics and mechanisms of the reaction of cis-$Mo(CO)_4L_2$ (L = phosphine or phosphite) with carbon monoxide which led to removal of one of the ligands.[209]

$$\text{cis-}Mo(CO)_4L_2 + CO \rightarrow Mo(CO)_5L + L \tag{120}$$

These processes were observed to proceed by a dissociative mechanism with the rate of substitution being greatly enhanced as the size of the phosphorus ligand increased within a series of phosphine or phosphite derivatives. The cis-$Mo(CO)_4L_2$ species were found to react stereospecifically with ^{13}CO to afford cis-$Mo(CO)_4(^{13}CO)L$ derivatives.[209]

$$\text{cis-}Mo(CO)_4L_2 + {}^{13}CO \rightarrow \text{cis-}Mo(CO)_4(^{13}CO)L + L \tag{122}$$

$$\text{trans-}Mo(CO)_4(PPh_3)_2 + {}^{13}CO \rightarrow \text{cis-}Mo(CO)_4(^{13}CO)PPh_3 \tag{123}$$
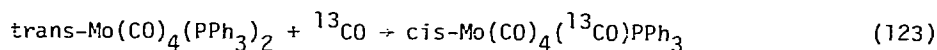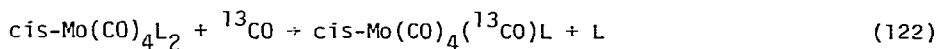
L = phosphine or phosphites

The intermediate ($Mo(CO)_4L$) was shown to be nonfluxional during its solution lifetime although the trans-$Mo(CO)_4(PPh_3)_2$ species reacted with ^{13}CO to give stereospecifically the cis-$Mo(CO)_4(^{13}CO)L$ complex.[209] Nucleophilic attack of OH^- at the carbon atom of a chromium-bound CO was observed with a subsequent process leading to the extrusion of CO_2.[210] These two processes were studied for the reaction of ^{18}O-enriched NaOH with $Cr(CO)_6$ in a biphasic medium in the presence of a phase-transfer catalyst. Oxygen exchange was faster than

$$Cr(CO)_6 + {}^{18}OH^- \longrightarrow Cr(C^{18}O)_6$$
$$\longrightarrow \mu\text{-H}[Cr(CO)_5]_2^- + CO_2$$
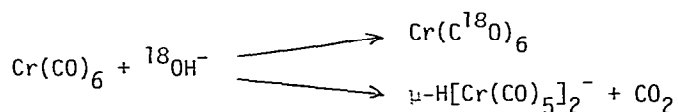
metal hydride (μ-H$[Cr(CO)_5]_2^-$) formation with concomitant production of CO_2.[210] The kinetic parameters for the reaction of μ-H$[Cr(CO)_5]_2^-$ with CO in alcohol solvents to afford $Cr(CO)_6$ and H_2 were determined.[210] In a very nice piece of work Shriver and coworkers showed that the presence of a Lewis acid assisted the methyl migration reaction.[211] The addition of $AlBr_3$ to $CpMo(CO)_3CH_3$ in toluene led to Lewis acid coordinated metal acetyls.[211]

$CpMo(CO)_3CH_3$ + $AlBr_3$ →

$$CpMo(CO)_2 \overset{Br}{\underset{Al}{\diagdown}} \overset{C-CH_3}{\underset{Br_2}{\diagup}}$$

(124)

$\downarrow$ CO

$CpMo(CO)_3$—$C(OAlBr_3)CH_3$
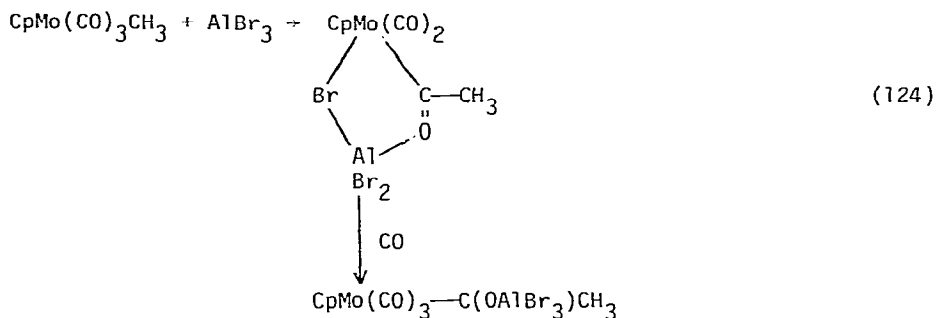
Reaction with CO was facile and hydrolysis of $AlBr_3$ led to simple metal acyls.[211] The halopentacarbonyl compounds of molybdenum and tungsten reacted with phosphines in polar aprotic solvents with CO substitution to give the ionic derivatives $[LM(CO)_4X]^-$ (X = Cl, Br; M = Mo, W; L = PEt_3, $P(OPh)_3$, PPh_3, etc.).[212]

$$M(CO)_5X^- + L \rightarrow M(CO)_4LX^- + CO \qquad (125)$$

M = Mo, W; X = Cl, Br; L = PEt_3, $P(OPh)_3$, PPh_3

The substitution of the halide ligand which was catalyzed by protic solvents, provided a convenient route to the neutral complexes $LM(CO)_5$ and $LL'M(CO)_4$ (L = phosphines; L' = NH_3, py, piper, etc.).[212]

The rates of combination of pyridine with five-coordinate species formed via laser flash photolytic M-CO bond scission in $Mo(CO)_4(dppe)$ and $W(CO)_4(P-en)$ (P-en = ethylenediphosphine) in cyclohexane was determined at room temperature.[213]

$$Mo(CO)_4(dppe) \xrightarrow{flash\ photolysis} Mo(CO)_3(dppe) \xrightarrow{py} Mo(CO)_3(dppe)py \quad (126)$$
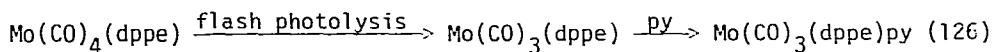
Free energies of activation for these reactions were 2-5 kcal/mole. These results indicated that transition states leading to formation of combination products closely resemble the intermediates.[213] Hexacarbonyltungsten(0) reacted with $(Ph_3P)_2NX$ salts (X = CN^-, OCN^-, SCN^-) in chlorobenzene at 90°-120°C to afford $[PPN]^+[W(CO)_5X]^-$ (X = OCN^-, SCN^-) and $[PPN]_2^+[W(CO)_4(CN)_2]^{-2}$.[214] Rate data showed the following rate law.[214]

$$rate = k_2[W(CO)_6][PPN^+X^-]$$

This was interpreted in terms of a mechanism involving initial attack of the anionic nucleophiles at a carbonyl carbon of the substrate. The following scheme was suggested.[214]

$(CO)_5W-CO + [PPN]^+[X] \rightarrow (CO)_5W-CO$
$\qquad\qquad\qquad\qquad\qquad\qquad \vdots$
$\qquad\qquad\qquad\qquad\qquad\qquad X \cdots PPN$

$\qquad\qquad\qquad\qquad\qquad \downarrow$

$CO + [(CO)_5WX][PPN]^+ \leftarrow (CO)_5W \cdots CO \, [PPN]^+$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \vdots \quad \vdots$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad X$

$X = OCN^-, SCN^-$
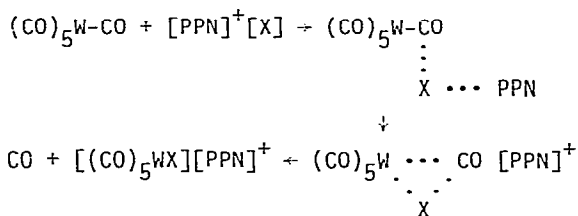
The data suggested that no coordinatively unsaturated species formed during the substitution process.[214] Asali and Dobson suggested that most reactions of anionic nucleophiles involve interaction at the carbon of a bound CO in a bimolecular path.[214] Kinetic data were obtained on the substitution reaction of $[(Me_3CSCH_2)_2]W(CO)_4$ with PBu_3 showing the existence of two competing reaction paths, one of unimolecular ring opening and the second of displacement of one end of the chelating ligand by PBu_3.[215]

The kinetics of the reaction of trans-bromo(tetracarbonyl)-phenylcarbyne-tungsten with L (L = PPh_3, $AsPh_3$, $P(OPh)_3$, etc.) were studied in a variety of solvents.[216]

$$\text{trans-}Br(CO)_4W \equiv C-Ph + L \rightarrow \text{mer-}Br(CO)_3LW\equiv C-Ph \qquad\qquad (126)$$

L = PPh_3, $AsPh_3$, $P(OPh)_3$, etc.
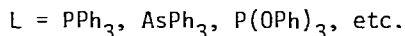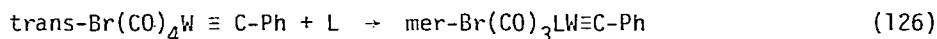
The formation of the monosubstituted carbyne complex followed a 1st order rate law with the rate dependent on neither the nature of the substituent nucleophile nor on its concentration.[216] The rate decreased with increasing polarity of the solvent. The activation parameters found were $\Delta H^{\ddagger}$ = 98-108 kJ/mole and $\Delta S^{\ddagger}$ = 26-53 eu.[216] The data were interpreted on the basis of a CO dissociative mechanism.[216] The stereochemistry and mechanisms of the $HgCl_2$ cleavage of threo-1,2-dideuteriophenmethyl compounds of tungsten were studied.[217]

$$PhCHDCHDW(CO)_2(PEt_3)(Cp) + HgCl_2 \rightarrow PhCHDCHDHgCl$$
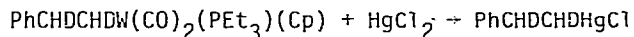
The reaction occurred with retention of configuration. It was suggested that this proceeds by an oxidative (S_E) process.[217]

CATALYSIS AND ORGANIC SYNTHESIS

Olefin Metathesis

Studies of Group VI catalysts for olefin metathesis have continued in 1979. A series of catalytic systems for olefin metathesis $M(NO)_2X_2(PPh_3)_2$ + $EtAlCl_2$ (M = Mo, W; X = Cl, Br, I), $M(CO)_5PPh_3$ + $EtAlCl_2$ + O_2 (M = Mo, W), (arene)$M(CO)_3$ + $EtAlCl_2$ (arene = benzene, mesitylene; M = Cr, Mo, W) were

examined for their stereoselectivity.[218] The stereoselectivity was determined for cis- and trans- $RCH=CHCH_3$ by the trans/cis ratios of 2-butenes. The variations in stereoselectivity observed (Cr > Mo >> W) was explained as a result of the 1,3-diaxial interaction.[218] Grubbs and Happin examined the metathesis of cis-cis-2,8-decadiene with $Mo(NO)_2(Cl)_2(PPh_3)_2$ and WCl_6 + $SnMe_4$.[219] The metathesis was studied for those catalysts with cis,cis-2,8-decadiene and cis,cis,-2,8-decadiene-1,1,1,10,10,10-d_6. The isotopic labeling in the 2-butene product provided further evidence for a carbene mechanism in the metathesis reaction.[219] Metathesis of acetylenes was observed with $Mo(CO)_3(PhOH)$ as a catalyst.[220] p-TolylC≡CPh was converted into PhC≡CPh and p-tolylC≡C-(p-tolyl) in n-octane at the reflux temperature.

$$p-CH_3C_6H_4C≡CC_6H_5 \xrightarrow{\quad Mo(CO)_3(PhOH) \quad} C_6H_5C≡CC_6H_5$$

$$+$$

$$p-CH_3C_6H_4C≡C(p-C_6H_4CH_3) \qquad (127)$$
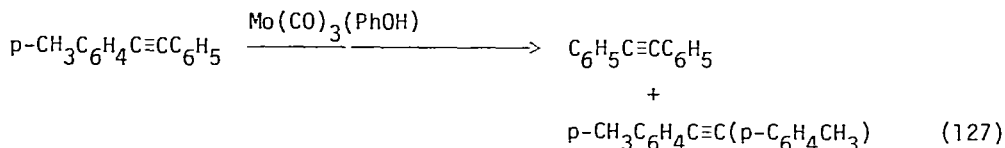
Other molybdenum complexes, such as $Mo(CO)_3(NH_3)_3$, $Mo(CO)_3(MeCN)_3$, trans-Mo $(CO)_4(PPh_3)_2$ and cis-$Mo(CO)_2(dppm)_2$, also catalyzed metathesis, the first two in the absence of phenol.[220] Coordinatively unsaturated species such as "$Mo(CO)_3$" were considered to be active in promoting metathesis with the phenol a good leaving group instead of assisting in removal of complexed acetylene from molybdenum.[220] The temperature-programmed decomposition of the hexacarbonyls ($Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$) supported on SiO_2 gave rise to a single, narrow peak which was uncharacteristic of high surface area supports.[221] The hexacarbonyls provided a route to low-valent, supported Cr, Mo, W which could not be achieved by the traditional methods of catalyst synthesis. The nature of the active sites for the metathesis of propylene was suggested to be due to both a subcarbonyl species which was formed near 100°C and mildly oxidized and decarbonylated species which were formed at higher temperatures.[221] These materials were slightly active for propylene hydrogenation and the chemistry of these catalysts was compared to the hexacarbonyls supported on Al_2O_3.[221]

The photo-induced metathesis [$W(CO)_6$-CCl_4-hν] of cis- and trans-RCH=CHMe gave 2-butene in a very high yield trans but low cis stereoselectivity.[222]

$$RCH=CHMe \xrightarrow[W(CO)_6 + CCl_4]{hν} RCH=CHR + MeCH=CHMe \qquad (128)$$
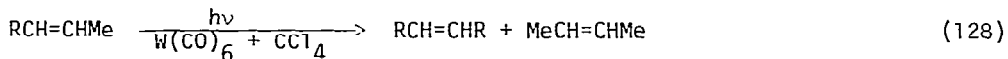
Propene behaved like a cis olefin. The results were interpreted in terms of a dinuclear tungsten intermediate, which required high steric constraints in the trans-alkylidenation step.[222]

XXXIII

At ambient temperature an active species generated by the electroreduction of WCl_6 with an aluminum anode catalyzed the metathesis of internal olefins (2-pentene) with good activity and selectivity.[223] A terminal olefin such as 1-octene, in the presence of a WCl_6-$EtAlCl_2$ catalytic system with PhCl as solvent underwent polymerization and the solvent underwent concomitant alkylation.[224] Addition of $Ni(P(OPh)_3)_4$ to this system caused the formation of internal olefins. Through cross-and homometathesis, a series of olefinic products was formed.[224] The reaction of CD_3Li with WCl_6 and $MoCl_5$ was studied at various Li-Mo and Li-W ratios.[225] The decomposition of the W or Mo organometallic intermediate gave CD_4, C_2D_6 and C_2D_4. The formation of CD_4 was ascribed to CD_2: which by recombination of CD_2: fragments gave C_2D_4.[225]

Other Catalytic Reactions

Considerably more reports of catalytic reactions by Group VI compounds appeared in 1979, especially polymerizations. A review of the use of the metal carbonyls as initiators of radical reactions of organic halogen compounds was published.[226] The catalytic alkylation of benzene with CO and H_2 was reported.[227] Alkylbenzenes, $C_6H_5(CH_2)_nH$ with n = 1-5, were formed in the reaction of $W(CO)_6$ and $AlCl_3$ in benzene treated with CO and H_2 under pressure at 200°C. The chain length was maximized at n = 2.[227]

$$C_6H_6 + CO + H_2 \xrightarrow[200°C]{W(CO)_6/AlCl_3} C_6H_5(CH_2)_nH \qquad (129)$$
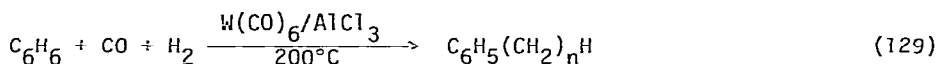
n = 1-5

$W(CO)_6$ was reported to be completely recovered, although activity decreased during reaction, probably because $AlCl_3$ was used up.[227] $Mo(CO)_6$ absorbed on Al_2O_3 was shown to be highly active for propene hydrogenation.[228] The hydrogenation of norbornadiene was catalyzed by $Cr(CO)_6$.[229]

norbornadiene $\longrightarrow$ norbornene   tricyclene
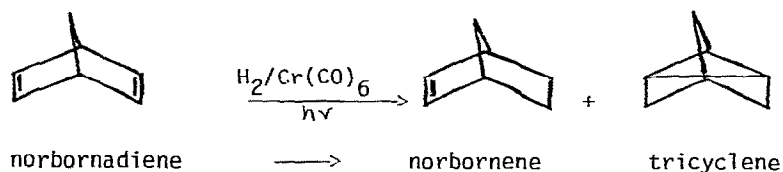
The hydrogenation was studied at pressures up to 80 Bar. The norbornene/-tricyclene ratio increased considerably with increasing pressure and above 40 Bar both double bonds were hydrogenated to give norbornane.[229] Active Mo catalysts prepared by H_2 and O_2 treatment of the product of SiO_2 or Al_2O_3 with $Mo(C_3H_5)_4$ were examined by XPS, UV reflectance, IR, Raman, ESR and luminescence spectroscopy.[230] The fixed catalyst active centers had the tetrahedral dioxo structure of 6-valent Mo with coordinative unsaturation. These properties were essential for abstraction of H from C-H bonds of a substrate.[230] Molybdenum hexacarbonyl was shown to be active for electron transfer reactions.[231] The dehydration of dimethylphenylcarbinol by $Mo(CO)_6$ in CCl_4 was characterized by an induction period during which Cl_2 was generated; Cl_2 activated the dehydration.[231] Cl_2 or Br_2 activated $Mo(CO)_6$ in the reactions of hydroperoxide epoxidation of 1-hexene and dehydration of $PhCMe_2OH$.[232] Under the reaction conditions the Mo did not change its zero valency, while in the absence of olefin or $PhCMe_2OH$ it underwent oxidative destruction with irreversible loss of CO groups.[23]

The activity of a series of arenetricarbonyl complexes of Cr, Mo and W for the polymerization of phenylacetylenes was investigated.[233] The relative reactivities of the compounds varied as below.

$$Me_3C_6H_3Mo(CO)_3 \;>\; Me_3C_6H_3Cr(CO)_3$$

The tungsten analogue ($Me_3C_6H_3W(CO)_3$) didn't initiate the polymerization of $PhC\equiv CH$.[233] The polymerization was first order in acetylene and in metal complex. The activity for chromium complexes changes as follows.[233]

$$MeOC_6H_5Cr(CO)_3 \;<\; EtC_6H_5Cr(CO)_3 \;<\; MeC_6H_5Cr(CO)_3 \;<\; ClC_6H_5Cr(CO)_3$$
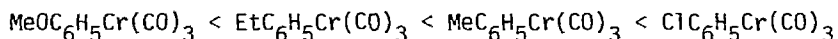
A linear structure was suggested for poly(phenylacetylene) on the basis of IR spectra.[233] In a series of patents Goodyear workers reported a series of polymerizations.[234-237] A solution of WCl_6 and $Et_3Al_2Cl_3$ was found to be active for ring-opening solution polymerization of cyclopentene and dicyclopentadiene leading to gel-free rubber-like polymers.[234] The same catalyst solution was also active for the co-polymerization of cyclopentadiene and

bicycloheptane mixture to give polymers with high impact strength which could be oil extended and used as general purpose rubbers.[235] Conjugated diolefins (isoprene, 1,3-butadiene, etc.) were polymerized to rubbers by catalysts containing alkyls of Al, Mg or Zn, Cr alkonoates and phosphite esters.[236-237] A chromium-dad (dad = 1,4 diaza-1,3-diene) system was able to transform isoprene in a highly specific manner to 2,7-dimethyl-2, trans-4,6-octatriene which involved tail-to-tail linkage with a double hydrogen shift.[238]
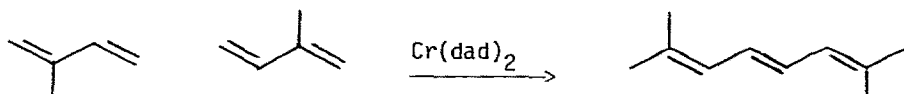
It was suggested that the specificity arose from steric interactions.[238] Pi-alkenyl compounds of chromium were used to polymerize dienes.[239] The cyclode-gradation of polydienes was reported for a molybdenum-trichlorodistearate-organoaluminum catalyst.[240]

Organic Synthesis

Thermal decomposition of dicyclopentadienone in the presence of M(CO)$_6$ (M = Cr, Mo, W) yielded indanone.[241]

(130)
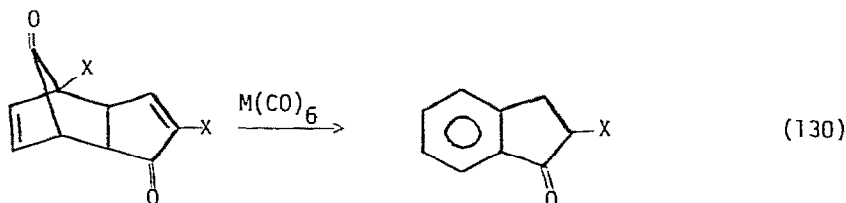
2-Bromocyclopentadienone dimer, on the other hand, afforded 4-bromoindanone under the same conditions. The reactions provided a 50% yield of the indan-one.[241] No corresponding organometallic complexes were isolated, although the mechanism was discussed.[241] Isomerization of ergosterol acetate with Cr(CO)$_6$ in octane gave 81% of ergosterol B$_2$ acetate.[242] Similar isomerization of ergosterol B$_3$ acetate gave 78% ergosterol B$_1$ acetate.[242]
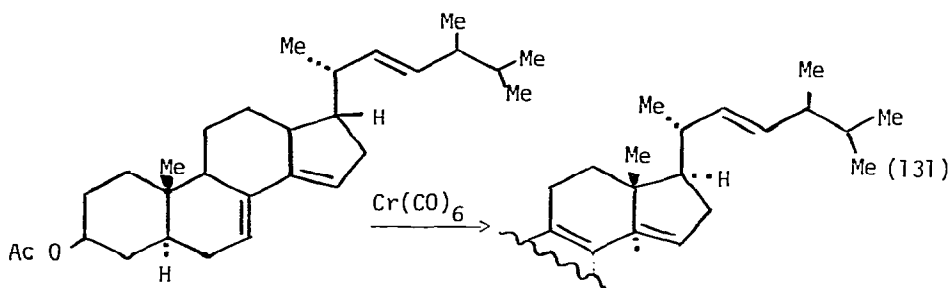
Molybdenum hexacarbonyl on alumina was shown to be effective in dehalogenation reactions.[243] The compounds, $RC(O)CH_2Br$ (R = $4\text{-}MeOC_6H_4$, $4\text{-}ClC_6H_4$, $4\text{-}BrC_6H_4$, $4\text{-}PhC_6H_4$, 1-adamantyl, 2-naphthyl), and $Mo(CO)_6$ on alumina produced dehalogenated monoketones in 60-88% yield after 18 hours at room temperature. This heterogeneous method was reported to be superior to the homogeneous reaction in terms of simplicity, mildness, speed and yield.[243] It was found that Cp_2MoH_2 was a mild reducing agent in selective reductions of organic halides and α-diketones.[244] Among many organic halides $Ph\text{-}CH_2\text{-}CBr_2\text{-}CH_3$ was reduced stereoselectively to the monobromo stage.

$$Ph\text{-}CH_2\text{-}CBr_2\text{-}CH_3 \xrightarrow{\ Cp_2MoH_2\ } Ph\text{-}CH_2\text{-}CHBr\text{-}CH_3 \qquad (132)$$

$$Ph\text{-}CHCl\text{-}CO_2Et \xrightarrow{\ Cp_2MoD_2\ } Ph\text{-}CHD\text{-}CO_2Et \qquad (133)$$
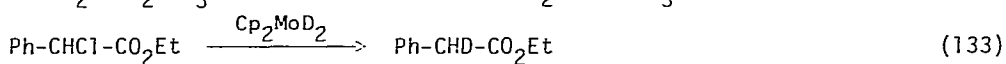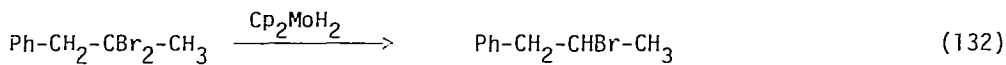
The reaction mechanism was studied with optically active $Ph\text{-}CHCl\text{-}CO_2Et$ and Cp_2MoD_2 giving $Ph\text{-}CHD\text{-}CO_2Et$ with no optical activity.[244] Use of radical agents confirmed a radical-chain mechanism. Selective reduction of α-ketyl was also effected with Cp_2MoH_2. A radical mechanism was suggested for this reduction also.[244] Oxiranes and olefins were obtained from the reactions of free and complexed phenylmethylsulfonium methylides with tricarbonylchromium with benzophenone, benzaldehyde and cyclohexanone.[245] Good yields were obtained from benzophenone, but only low yields from the other two.[245]

PHOTOCHEMISTRY

The photochemical decomposition of $M(CO)_6$ (M = Cr, Mo, W) was studied in polychlorinated solvents by ESR using spin traps.[246] Decomposition of $M(CO)_6$ by UV light in CCl_4 solution in the presence of $PhCHN(O)CMe_3$ gave $PhCH(CCl_3)\text{-}N(O\cdot)CMe_3$, in the presence of nitrosodurene, $Cr(CO)_6$ and $W(CO)_6$ gave $2,3,5,3\text{-}Cl_3CN(O\cdot)C_6HMe_4$.[246] The partial photoionization cross sections of the valence levels of $Cr(CO)_6$ were reported in the photon energy range of 30 to 100 eV.[247]

The 4σ derived level showed a resonance at ∿ 18 eV kinetic energy. This resonance was seen in gas phase CO at 12 eV and in CO absorbed on Ni(100) at 20 eV.[247] The $Cr(CO)_6$ data showed that the large shift in kinetic energy of the resonance in absorbed CO was due to potential changes upon bonding, not changes in the C-O distance.[247] The following reaction yielded the new complex, $W(P(OMe)_3)_6$.[248]

$$WCl_4(py)_2 \cdot 2py + K + KI \xrightarrow[80°, \ 2h]{benzene} \xrightarrow[-benzene, \ 112°]{+P(OMe)_3} W(P(OMe)_3)_6 \qquad (134)$$

$$\downarrow h\nu,$$

$$H_2W(P(OMe)_3)_5$$

$$+$$
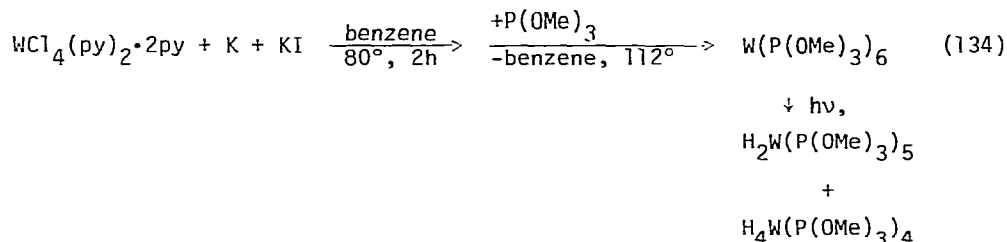
$$H_4W(P(OMe)_3)_4$$

The complex, $W(P(OMe)_3)_6$, was shown to be photochemically very reactive by the synthesis of seven- and eight-coordinate tungsten hydrides, $H_2W(P(OMe)_3)_5$ and $H_4W(P(OMe)_3)_4$.[248] Photolysis of $Mo(CO)_6$ in the presence of cyclopentadiene produced initially $Mo(CO)_5(\eta^2-C_5H_6)$.[249] Continued irradiation led to several products which were described by the following reactions.[249]

$$Mo(CO)_6 \underset{\Delta}{\overset{h\nu}{\rightleftharpoons}} Mo(CO)_5 + CO \xrightarrow{C_5H_6} Mo(CO)_5(\eta^2-C_5H_6) \qquad (135)$$

$$Mo(CO)_5(\eta^2-C_5H_6) \xrightarrow{h\nu} Mo(CO)_4(\eta^4-C_5H_6) + CO \qquad (136)$$

$$Mo(CO)_4(\eta^4-C_5H_6) \xrightarrow{h\nu} (\eta^5-C_5H_5)Mo(CO)_3H + CO \qquad (137)$$

$$CpMo(CO)_3H \xrightarrow{h\nu}{C_5H_6} Mo(CO)_2(Cp)(\eta^3-C_5H_7) + CO \qquad (138)$$
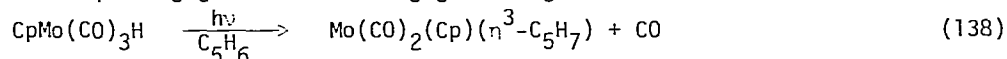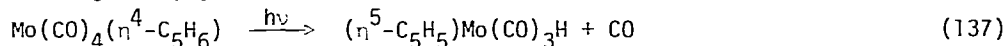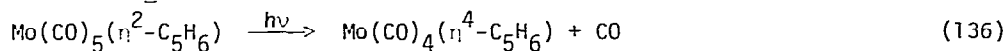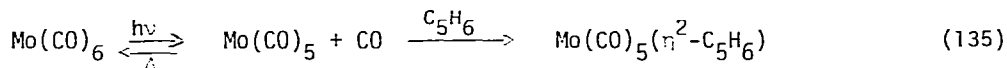
Upon reacting cis-$W(CO)_4P(OMe)_3(NHC_5H_{10})$ with ^{13}CO in octane at 78° for a prolonged period, a statistical mixture of cis- and $trans$-$W(CO)_4(^{13}CO)P(OMe)_3$ was obtained.[250]

$$cis\text{-}W(CO)_4(P(OMe)_3)(NHC_5H_{10}) + {}^{13}CO \rightarrow cis\text{-}W(CO)_4(^{13}CO)(P(OMe)_3) \qquad (139)$$

$$\downarrow$$

$$\text{statistical mixture}$$
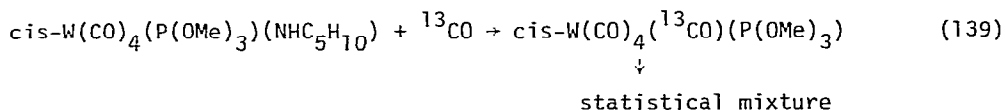
If the reaction was stopped earlier in the substitution process, the $W(CO)_4(^{13}CO)(P(OMe)_3)$ product was enriched more in the equatorial position. It was determined that a non-dissociative intramolecular path was involved by preparing cis-^{18}O labeled $W(CO)_5P(OMe)_3$ and following the equilibrium in the presence of $^{12}C^{16}O$.[250] The equilibration occurred with no loss in ^{18}O labeled material.[250] The photochemistry of the complexes, $W(CO)_5L$ (L = py, 3-bromopyridine, H_2S), in frozen gas matrices was investigated.[251] IR spectro-

scopic evidence was presented to show that photodetachment of bulky ligands with relatively high molecular weights took place in gas matrices at 10°K. UV photolysis of $W(CO)_5L$ isolated at high dilution in methane or argon matrices produced IR absorptions for $W(CO)_5$ and free L.[251]

$$W(CO)_5L \xrightarrow{h\upsilon} W(CO)_5 + L \qquad\qquad (140)$$

The reaction was shown to be photochromic since irradiation with visible light regenerated $W(CO)_5L$. Photodetachment of L in CO and N_2 matrices led to $W(CO)_6$ and $W(CO)_5N_2$, respectively.[251] The photochemistry of $Cr(CO)_5L$ (L = PCl_3, py, pyrazine) was also investigated in argon matrices.[252] Photolysis of $Cr(CO)_5PCl_3$ in an Ar matrix at 10°K with different wavelengths (λ = 229, 254, 280, 313 and 366 nm) resulted in formation of $Cr(CO)_5$. Photolysis of $Cr(CO)_5py$ and $Cr(CO)_5(pyrazine)$ in an Ar matrix caused dissociation of CO or the unique ligand depending on the wavelength or irradiating light.[252]

$$Cr(CO)_5L \rightarrow cis\text{-}Cr(CO)_4L + Cr(CO)_5 \qquad\qquad (141)$$

L = PCl_3, py, pyrazine

The five-coordinate species $cis\text{-}Cr(CO)_4py$ and $cis\text{-}Cr(CO)_4(pyrazine)$ were formed. Regeneration of the octahedral complexes was not quantitative because of rearrangement to the trans complexes, $Cr(CO)_4L$.[252] Dahlgren and Zink reported the photochemistry of several derivatives of tungstenhexacarbonyl.[253] The photochemistry and electronic and infrared spectroscopy of $W(CO)_5X$ (X = Cl^-, Br^-, I^-, NCO^- and CS) were reported. The lowest excited state of $W(CO)_5CS$ was metal to ligand charge transfer as shown by magnetic circular dichroism spectroscopy.[253] The lowest excited state of the anions was primarily ligand field. The low photoreactivity (ϕ < 0.1) of all of these compounds was interpreted in terms of excited state bonding properties.[253] The photochemistry of azidopentacarbonyltungsten(0) was very dependent on the cation.[254]

$$PPN^+W(CO)_5N_3^- + CO \xrightarrow{h\upsilon} W(CO)_5NCO^- \quad \phi = 0.06 \qquad (142)$$

$$As(Ph)_4^+W(CO)_5N_3^- \xrightarrow{h\upsilon} noncarbonyl \quad \phi = 0.07 \qquad (143)$$
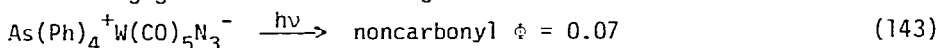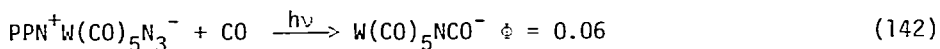
CO dissociation also occurred and was studied by ^{13}CO labeling.[254] The photoactive excited state was assigned to an admixture of both azide to metal charge transfer and ligand field character on the basis of electronic, magnetic circular dichroism, vibrational and emission spectra. A model of the excited-state potential surfaces was proposed.[254]

Organocyclotriarsine, $CH_3C(CH_2As)_3$, reacted with the Group VI metal hexa-

carbonyls under ultraviolet irradiation to give the complexes $CH_3C(CH_2As)_3$-$M(CO)_5$ (M = Mo, W), $[CH_3C(CH_2As)_3]_2M(CO)_4$ (M = Cr, W), and $[CH_3C(CH_2As)_3Mo$-$(CO)_4]_n$ (n $\geq$ 2).[255]

$$M(CO)_6 + CH_3C(CH_2As)_3 \xrightarrow{h\nu} CH_3C(CH_2As)_3M(CO)_5 \qquad (144)$$

$$+$$
$$[CH_3C(CH_2As)_3]_2M(CO)_4$$
$$+$$
$$[CH_3C(CH_2As)_3Mo(CO)_4]_n$$
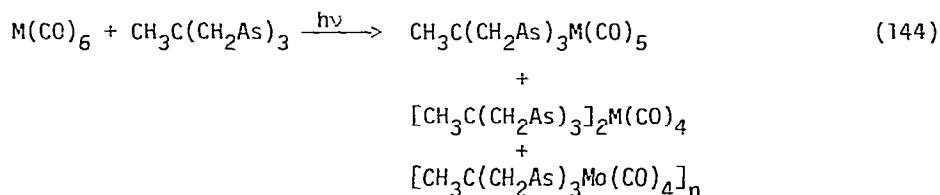
The reactions depended on the solvent employed and the molar ratios of the reagents. Starting with $C_7H_8Mo(CO)_3$ yielded the polymeric complex $[CH_3C(CH_2As)_3Mo(CO)_3]_n$.[255] The structures of the compounds were discussed on the basis of their mass, infrared, far infrared and Raman spectra.[255] The resonance Raman effect was used to explain differences in the photochemical reactivity of $M(CO)_4(\alpha$-di-imine) (di-imine = 2,iminomethylpyridine) compounds which were irradiated within the metal to α-di-imine charge transfer band.[256] Group VIB carbonyl complexes of pyrazino[2.3-f] quinoxaline or 1,4,5,8 tetra-azaphenanthrene were synthesized photochemically.[257]
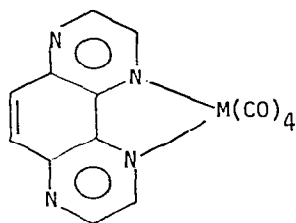
XXXIV

These complexes were studied by IR and electronic spectra.[257] The CO force constants showed that there was more backbonding in these complexes than in the analogous 1,10-phenanthroline complexes. This was ascribed to the two additional electron-withdrawing nitrogen atoms.[257]

Photolysis of Cp_2WH_2 was studied in low temperature matrices and in solution.[258,259] U.V. photolysis of Cp_2WH_2, Cp_2WD_2, $Cp_2W(CO)$ and $Cp_2W(CH_3)H$ in an argon matrix at 10°K led to a common product believed to be Cp_2W.[258] Similar experiments with Mo gave similar results.[258] Photolysis of solutions of Cp_2WH_2 produced H_2 and led to insertions into C-H bonds of both aliphatic and aromatic compounds.[259]

$$\text{Cp}_2\text{W(H)(p-C}_6\text{H}_4\text{F)} + \text{Cp}_2\text{W(H)(m-C}_6\text{H}_4\text{F)}$$

$$h\nu \uparrow \quad C_6H_5F$$

$$\text{Cp}_2\text{W(H)(p-C}_6\text{H}_4\text{OMe)} \xleftarrow[\text{MeOC}_6\text{H}_5]{h\nu} \text{Cp}_2\text{WH}_2 \xrightarrow[\text{C}_6\text{H}_6]{h\nu} \text{Cp}_2\text{W(H)(C}_6\text{H}_5)$$

$$h\nu \downarrow \quad 1,2\text{-Me}_2\text{C}_6\text{H}_4$$

$$\text{Cp}_2\text{W(H)} \text{---}\langle \bigcirc \rangle\text{---Me}$$
$$\text{Me}$$
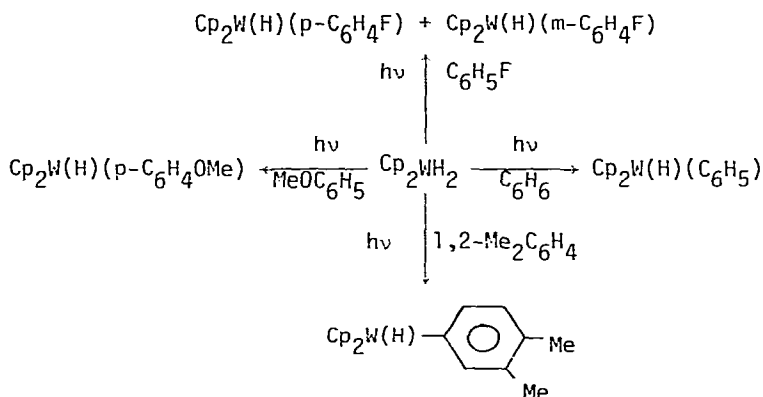
Insertion into fluorobenzene gave $\text{Cp}_2\text{WH(C}_6\text{H}_4\text{F-3)}$ while insertion into mesityl-ene gave $\text{Cp}_2\text{WH(CH}_2\text{C}_6\text{H}_3\text{Me}_2\text{-3,5)}$. The mechanism was discussed.[259] Irradiation of di-η^5-cyclopentadienyl-molybdenum and tungsten complexes led to photo-induced substitution by pyridine, acetonitrile, or dimethylphenylphosphine.[260]

$$\text{Cp}_2\text{MX}_2 \xrightarrow[h\nu]{S} \text{Cp}_2\text{MXS or Cp}_2\text{MS}_2 \qquad (145)$$

M = Mo, W; X = CH_3, Br; S = py, CH_3CN, PMe_2Ph

Monosubstituted product was formed by irradiation of the d-d transition (390-450 nm) while disubstituted product was formed by irradiation of the charge transition (390 > λ > 220 nm).[260] The photo-induced methyl-metal bond cleavage in $\text{CpM(CO)}_3\text{CH}_3$ compounds (M = Cr, Mo, W) was studied by ESR.[261] The Cr and Mo compounds exhibited signals due to paramagnetic species in which the methyl-metal bond was preserved; no such signals were observed for the W analogue. The formation of these paramagnetic species was believed to proceed by both electron and methyl transfer. A mechanism was postulated for these reactions.[261]

Photo-induced reactions of tetraneopentylchromium ($\text{Cr(CH}_2\text{CMe}_3)_4$) and trimesitylchromium tetrahydrofuranate ($\text{Cr(2,4,6-Me}_3\text{C}_6\text{H}_2)_3\text{THF}$) were investi-gated.[262] Upon photolysis, both function as active catalysts for the poly-merization of vinyl monomers such as styrene and for the polymerization of ethylene under mild conditions.[262] The photochemical synthesis of [(arene)-

$Cr(CO)_2CN]^-$ derivatives in the presence of KCN, followed by electrophilic attack of benzoyl chloride on the cyanide ligand, afforded benzoyl isocyanide complexes of the type $(arene)Cr(CO)_2(CNCOPh)$.[262]

$$(arene)Cr(CO)_3 \xrightarrow[h\upsilon]{KCN} (arene)Cr(CO)_2CN^- \xrightarrow{PhCOCl} (arene)Cr(CO)_2(CNCOPh)$$

$$\downarrow h\upsilon \quad (146)$$

$$(arene)Cr(CO)P(OPh)_3^-(CNCOPh)$$
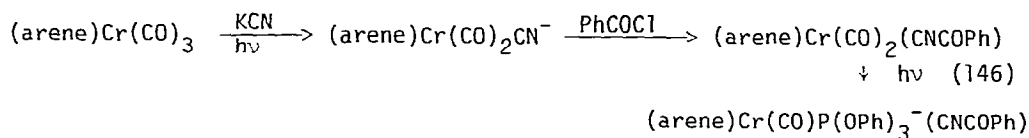
Spectroscopic properties of these complexes suggested that N-acyl isocyanides have electronic properties close to those of carbon monoxide. Specific photochemical substitution of CO by $P(OPh)_3$ in $(arene)Cr(CO)_2(CNCOPh)$ confirmed the strength of the Cr-CNCOPh bond and provided a new route to chiral complexes.[263] Photosubstitution of PPh_3 for CO on XXXV was reported.[264]

$$(147)$$

XXXV
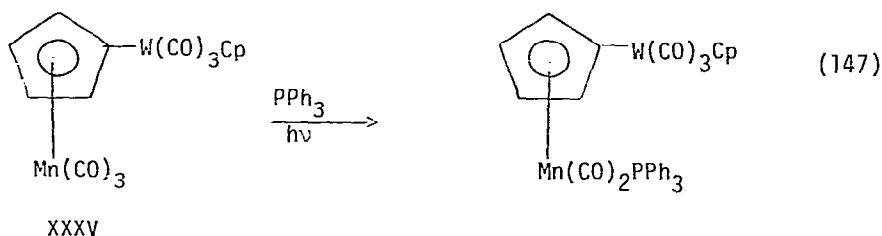
SPECTROSCOPIC STUDIES

Infrared and Raman

Studies of infrared and Raman spectra continued to decline in 1979. The IR and Raman spectra in the CO stretching region of $Cr(CO)_6$ were recorded in n-hexane, CCl_4, $CHCl_3$ and benzene.[265] The half-band widths were different, showing different sensitivities to solvent effects and were dominated by vibrational relaxation.[265] Isotopic infrared data were obtained for $HW_2(CO)_{10}$ using $C^{18}O$.[266] There was very little shift observed from the $C^{16}O$ complex in the 900 cm^{-1} region. This data ruled out Fermi resonance for the extra bands seen.[266] The resonance Raman and electronic absorption spectra of $M(CO)_4(DAB)$ (DAB = diazabutadiene) in alkane solutions or glasses below 200°C indicated the existence of a second isomer in which the $M(CO)_4$ moiety had pseudo C_{4v} symmetry.[267] Infrared spectra in the range from 2200 to 300 cm^{-1} and Raman spectra in the range of 220 to 50 cm^{-1} of the carbyne complexes trans-$Cl(CO)_4W\equiv C-CH_3$, trans-$Br(CO)_4W\equiv C-CH_3$, trans-$I(CO)_4W\equiv C-CH_3$ and of the deuterated compound trans-$Br(CO)_4W\equiv C-CD_3$ were investigated and the bands assigned.[268] A preliminary normal coordinate analysis was accomplished.[268] The vibrational spectra and valence force field were determined for methyl benzoatodicarbonyl-

selenocarbonylchromium, $(\eta^6-C_6H_5CO_2CH_3)Cr(CO)_2CSe$.[269] The stretching frequency for the CSe ligand, $\nu(CSe)$, was 1055 cm^{-1}. The effects of the ligands on the CO stretches were discussed.[269] The IR and Raman spectra of $(\eta^6$-naphthalene)-chromium tricarbonyl were obtained and band assignments made.[270] On coordination, several C-C vibrational frequencies of the naphthalene ring increased, whereas several C-H nonplanar frequencies decreased.[270]

Nuclear Magnetic Resonance

The use of NMR to study Group VI metal organometallics has grown with the continued use of ^{13}C NMR and with the growth of other types, especially ^{17}O NMR. The ^{13}C NMR spectra of η^6-arene chromium complexes $XC_6H_5Cr(CO)_2L$ (L = CO, PPh_3; X = aliphatic and aromatic substituents) were investigated.[271] The effect of the nature of the substituent X on the chemical shifts of the carbons in the aromatic ring was analyzed showing a correlation between $\delta(^{13}C)$ and σ_R (Taft's constant) for both the C(4) nuclei and for C(3) (meta) atoms.[271] The ^{13}C NMR spectra of arenechromiumtricarbonyl complexes were also recorded in trifluoroacetic acid.[272] The complexes $C_6H_6Cr(CO)_3$, $C_6H_5XCr(CO)_2PPh_3$ (X = H, Me, OMe, Ph, CO_2Me), etc. were studied. In CF_3CO_2H, the signals of all the C nuclei in the benzene ring were shifted to weaker field in comparison to their position in neutral media. This shift to weaker field (10-12 ppm) arose from protonation inducing de-screening of the C nuclei of the η^6-arene ligand.[272] The ^{13}C NMR spectra of chalcocarbonyl complexes $(\eta^6-C_6H_6)Cr(CO)_2CX$ and $(\eta^6-C_6H_5CO_2Me)Cr(CO)_2CX$ (X = O, S, Se) were recorded between -30° and -50°C. The chemical shift data suggested that the pi-acceptor/sigma-donor capacity of these ligands increased in the order.[273]

$$CO < CS < CSe$$
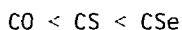
^{13}C NMR and SCCC MO studies were reported on substituted benzophenonetri-carbonylchromium complexes.[274] ^{13}C NMR on the unsubstituted and p-F, p-Cl and p-OCH_3 derivatives with the substituents on the uncomplexed ring, showed a small substituent effect on the complexed ring and on the carbons of the $Cr(CO)_3$ group. The SCCC MO calculations showed the ring to be more negatively charged than before complexation.[274] ^{13}C NMR relaxation mechanisms were studied in a series of methyl compounds, including $CpMo(CO)_3CH_3$.[275]

NMR spectra of ^{17}O in natural abundance were obtained for $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$ with line widths of less than 10 Hz.[276] The natural abundance ^{17}O NMR shielding values observed by FTNMR on Group VI carbonyl complexes were shown to range 300-400 ppm downfield from $^{17}OH_2$.[277] The carbonyl ^{17}O shift trends were generally opposite to those for the carbonyl ^{13}C chemical shifts as expected by metal pi-backbonding to the carbonyl antibonding orbitals.

There was an upfield shift in the carbonyl oxygen shielding values from Cr to Mo to W.[277] Natural abundance ^{17}O NMR shifts were determined for tungsten carbonyl compounds, $L_nW(CO)_{6-n}$, and shown to vary depending on the sigma-donor/pi-acceptor ratios for the ligands.[278] The ^{13}C and ^{17}O NMR spectra of a series of arenechromium(0) complexes, $(\eta-C_6H_{6-n}R_n)Cr(CO)_2(CX)$ (R = H, Cl, Me, OMe, etc.; X = O, S; n = 0-3), were measured at 30°C in CH_2Cl_2 solution.[279] Linear regression analyses relating the observed ^{13}C and ^{17}O chemical shifts of the CO and CS ligands with the primary CX stretching force constants, k_{CX}, indicated a definite correlation only for $\delta(^{13}CO)$ vs. k_{CO}. The much poorer correlations for $\delta(^{13}CS)$ and $\delta(C^{17}O)$ suggested that these chemical shifts were not influenced by the same factors as $\delta(^{13}CO)$.[279] In contrast to ^{13}C and ^{17}O NMR studies on other substituted metal carbonyls, replacement of a CO group by CS in $(\eta^6-C_6H_{6-n}R_n)Cr(CO)_3$ produced an upfield shift in $\delta(^{13}CO)$ and a down-field shift in $\delta(C^{17}O)$. This difference was attributed to a greater net electron-withdrawing capacity of CS compared to CO in the $Cr(CO)_2(CS)$ moiety. The ^{13}C and ^{17}O carbonyl shielding values exhibited opposite trends on going from O to S in CS and on changing the electronegativity of R in $C_6H_{6-n}R_n$ ring.[279]

^{15}N NMR was also used to investigate Group VI organometallics. ^{15}N NMR signals at the natural abundance level were detected for eight nitrosyl complexes, $CpM(CO)_2NO$, $CpM(NO)_2Cl$, etc. (M = Cr, Mo, W).[280] In all cases the ^{15}N resonance was a single sharp line. Comparisons were made to the ^{13}C NMR spectra.[280] ^{29}Si NMR of carbenes, $(CO)_5MC(Y)SiR_3$ (M = Cr, Mo, W; Y = OCH_3, NMe_2) and carbynes, $XM \equiv C-SiR_3$ (M = Cr, Mo, W; X = $Br(CO)_4$, $Cp(CO)_2$; R = Ph) were reported.[281] The chemical shift data were used to distinguish whether SiR_3 was bound to carbene or via a heteroatom. By varying R it was shown that carbenes and carbynes behaved as vinyl groups (for δ ^{29}Si).[281] The electron-releasing effect of the substituent Y was also investigated. The shift was smallest for Mo; this was attributed to a pi-interaction between transition metals and silicon transmitted by hyperconjugation or silicon d-orbitals.[281] An investigation of the ring current contribution to the ^1H NMR chemical shifts of benzenetricarbonylchromium complexes ([2.2]-metacyclophanes or [2.2]-metaparacyclophane) was presented.[282] The evidence indicated that the ring current shielding in benzenetricarbonylchromium complexes was considerably reduced above the ring plane. The observations were suggested to strongly favor the ring current disrupture hypothesis.[282] The ^{13}C Forsen-Hoffman spin-saturation method was used to evaluate the fluxionality of tricarbonyl(η^6-cyclooctatetraene)-chromium and -tungsten.[283] It was shown that the mechanism of metal migration in $M(CO)_3(\eta^6-C_8H_8)$ was a combination of 1,2- and 1,3-shifts. The mechanism was discussed.[283]

Photoelectron Spectra, Electronic Spectra, and Calculations

Photoelectron spectra. Parameter-free MO calculations on various hole states and calculated intensities of the satellites in the X-ray photoelectron spectrum of $Cr(CO)_6$.[284] The electronic absorption, photoelectron, ^{13}C NMR and vibrational spectra of a series of $M(CO)_5L$ complexes (M = Cr, W and L = imidazole, pyrazole, isoxazole, thiazole and isothazole) were reported and assigned.[285]
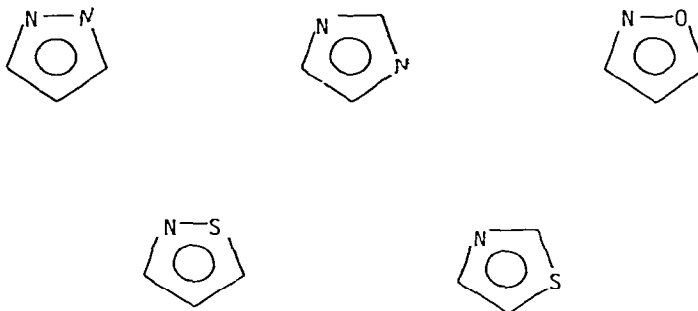
The results were used to interpret the sigma- and pi- bonding between the metal and the nitrogen donor ligand.[285] The He(I) photoelectron spectrum of $Cr(CO)_5CSe$ was measured and all ionization potentials were slightly lower than those of the related thiocarbonyl.[286] The PES spectrum of $C_6H_6Cr(CO)_2CSe$ was also reported and indicated a significant transfer of electron density from the benzene ring to the chromium atom.[286] The satellite structure in the XPES of $[Mo(CNR)_7][PF_6]_2$ (R = CH_3, $C(CH_3)_3$ or C_6H_{11}) was recorded and assigned by comparison to $Mo(CO)_6$. Gas phase UV photoelectron spectra were reported for methylaminobis(difluorophosphine) and its tris complexes, ML_3 (M = Cr, Mo, W).[288] Ionization occurred at relatively low ionization energy (7.7-7.9 eV). An assignment was proposed for the ionization processes.[288] X-ray photoelectron spectra of polyhydride complexes of tungsten and molybdenum, H_4ML_4 (M = Mo, W; L = $PHPh_2$, $PMePh_2$, $PEtPh_2$, PEt_2Ph, and $P(O-i-Pr)_3$) showed the tungsten to have a negative charge while the charge on molybdenum was 0.[289] Photoelectron spectra of Group VI metal complexes, $M(CO)_3(\eta^6-C_7H_8)$, were assigned using experimental criteria and quantum mechanical calculations.[290] Agreement between computed and measured ionization energies was found for molecular orbitals mainly ligand in character although for the mainly d-orbitals on the metal correlations did not hold. Relaxation terms dominated the energy associated with ionization processes in this case.[290]

Electronic Spectra

The electronic structure of $Cr(CO)_6$ was studied by X-ray fluorescence spectroscopy.[291] The order of succession of the MOs was established with the MOs associated with the 3d orbitals as the upper occupied orbitals. The experimental results were compared with nonempirical calculations.[291] Optical spectra of $Mo(CO)_6$ were measured in Ar matrices at 10°K, focusing on the intense $^1A_{1g} \rightarrow ^1T_{1u}$ transitions at 286 and 230 nm.[292] A detailed band shape analysis was performed on both absorption bands and excited state electronic parameters were obtained. The distortion of the CO moiety was found to be small for both transitions.[292] Transition-state X_α calculations were performed for the low-lying allowed metal-to-ligand and metal charge-transfer transitions as well as for the metal-localized $d(t_{2g}) \rightarrow p(t_{1u})$ excitation. The results confirmed assignment of the electronic absorption bands to $d(t_{2g})$ $\rightarrow CO(\pi^*)(t_{1u}$ and $t_{2u})$; however the π^* levels of CO in $Mo(CO)_6$ and $W(CO)_6$ differed considerably from the π^* level in free CO.[292] Luminescence spectra were also obtained for $M(CO)_6$ (M = Cr, Mo, W) and $M(CO)_5py$ (M = Mo, W) complexes in argon and methane matrices at 12°K for the first time.[293] The new emissions at 340-360 nm were assigned $^1T_{1g} \rightarrow ^1A_{1g}$ or $^1T_{2g} \rightarrow ^1A_{1g}$ because of their positions relative to the absorption bands and the observation of a triplet sensitized emission at 400 nm.[293] The energy diagram of the metal d-orbitals in $M(CO)_5L$ (L = piper, py, SEt_2, PCl_3, $P(C_6H_{11})_3$) complexes was described taking into account mutual electron replusion and ligand field effects.[294] The parameters governing the diagram were estimated from absorption and photoelectron spectra. The ligand field transitions were assigned in detail and the shifts by replacement of L were discussed.[294] It was stated that in general the lowest LF transition shifted to higher energy when sigma-donor and pi-acceptor properties increased. The lowest excited state was shown to have mainly σ_z^* character.[294] With the use of M.C.D. spectra, the nature of the lowest field excited state of $Cr(CO)_5L$ complexes (L = piper, py, NMe_3 or pyrazine) was characterized.[295] This data was used to explain the photochemical behavior of these complexes.[295] The electronic emission and absorption spectra were reported for trans-$W(dppe)_2(N_2)_2$ and trans-$W(dppe)_2(CO)_2$.[296] Different electronic transitions within the first CT band of $M(CO)_4L$ (M = Cr, Mo, W; L = 1,4 diazabutadiene and pyridine-2-carbaldehydeimine) were detected and assigned.[297] The MCD and electronic absorption spectra of $Mo(CO)_4$(pyridine-2-carbaldehyde-(N-phenyl)-imine) revealed that the first Mo to L charge transfer band consisted of different electronic transitions which were assigned with the help of resonance Raman spectra. The resonance Raman gave detailed information about the properties of the excited states.[297] Oxidation of the complexes trans-$[M(CNR)_2(dppe)_2]$ (M = Mo, W; R = Me, t-Bu or

4-$CH_3C_6H_4$) with diiodine or silver salts gave the paramagnetic cations, trans-$[M(CNR)_2(dppe)_2]^+$.[298]

$$[M(CNR)_2(dppe)_2] \xrightarrow{\text{oxidant}} [M(CNR)_2(dppe)_2]^+ \qquad (148)$$
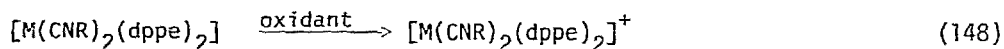
Mixtures of products were produced when Cl_2 or Br_2 were the oxidizing agents with the seven-coordinate cations $[MX(CNR)_2(dppe)_2]^+$ also formed. The oxidation and electronic spectra were explained by a simple MO scheme.[298]

Calculations. Extended Hückel MO calculations on $Mo(CO)_2(PH_3)_4$, $Mo(CO)_3(PH_3)_3$, $Mo(O_2)(PH_3)_4$, and the related cationic species showed that the relative stabilities of the geometric isomers containing strong pi-acid or pi-donor ligands depend on the number of valence electrons and in a complimentary fashion on whether the ligands were pi-donors or pi-acceptors.[299] INDO SCF MO calculations were carried out for the formally d^6 system bis(η^6-pyridine) chromium, $Cr(C_5H_5N)_2$, and the corresponding cation.[300] For the neutral molecule the results indicated that the nitrogen heteroatom should lead to an ionization potential about 1.5 eV greater than for the bis-benzene complex.[300] Extended CNDO/2 calculations of $(\eta^6$-PhX)Cr(CO)$_3$ (X = H, Me, NH_2, OH, F) were used to rationalize the substituent effects on the dipole moment and IR.[301] The Wiberg indices and bonding in $(\eta^6$-PhX)Cr(CO)$_3$ were discussed.[301] CNDO/2 calculations were also reported for $C_6H_6Cr(CO)_3$ and $C_6H_6Cr(CO)_2N_2$.[302] The electronic structures were investigated with trends in bond strength correlated with infrared frequency.[302] Calculations of the observed regioselectivity in nucleophilic attack on the complexes CpMLL'(allyl) and -(ethylene) (L=CO, L'=NO), were attempted.[303]

Thermochemistry. The vapor pressures and heats of sublimation of a number of $M(CO)_5L$ complexes (M=Cr, Mo, W; L=piper, py, pyrazine, pyrazole, thiazole) were determined by the Knudsen effusion method.[304] The results were compared with similar complexes and dipole moment measurements from the literature.[304] These complexes underwent both disproportionation and substitution in a CO atmosphere, when heated on a thermobalance.[305] Heats of reaction were determined and heats of formation were calculated. Combined with heats of sublimation of these complexes, individual metal-ligand bond energies were evaluated.[305] The thermochemistry of bis-arene and arenetricarbonyl-chromium compounds containing hexamethylbenzene, 1,3,5-trimethylbenzene and naphthalene were reported.[306] Microcalorimetric measurements at elevated temperatures of the heats of thermal decomposition and iodination have led to values of the standard enthalpies of formation of the following compounds.[306]
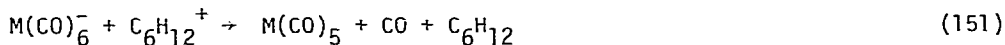
	ΔH_f° (kJ/mole)	ΔH sublimation (kJ/mole
$(\eta^6\text{-}1,3,5\text{-}C_6H_3Me_3)_2Cr$	63	104
$(\eta^6\text{-}C_6Me_6)_2Cr$	-88	119
$(naph)_2Cr$	407	
$(naph)Cr(CO)_3$	-258	107

Measurements by the vacuum sublimation microcalorimetric technique gave the values above. These data allowed evaluation of the bond enthalpy contributions of the metal-ligand bonds in the gaseous metal complexes, $[\eta^6\text{-}C_6H_3Me_3\text{-}Cr]$ (151), $[\eta^6\text{-}C_6Me_6\text{-}Cr]$ (155), [naph-Cr] (145) kJ/mole.[306] Bond enthalpy contributions in Cp_2ML_2 complexes (M = Mo, W; L = H, CH_3, Cl) were evaluated by the solution calorimetric measurements of the reaction with CCl_4.[307]

$$Cp_2MH_2 + 2CCl_4 \rightarrow Cp_2MCl_2 + CHCl_3 \tag{149}$$
$$M = Mo, W$$
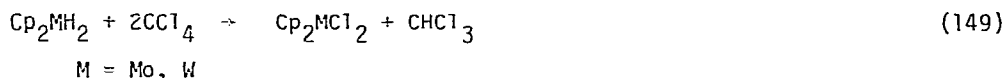
The values $\bar{D}$ (Mo-H) 251.4 kJ/mole and $\bar{D}$ (W-H) 305.2 kJ/mole were determined.[307]

Miscellaneous Physical Studies. The nature of the quenching of the luminescent state of uranyl ion by $M(CO)_6$ (M = Cr, Mo, W) was studied in aprotic solvents.[308] Flash photolysis and ESR and IR spectroscopy showed that the quenching process takes place with formation of the reactive intermediate, $M(CO)_6^+$.[308] A method for determining Ag, Cr, Co, Cu, Fe, Mn, Ni, V, Ti and Zn in $W(CO)_6$ was described.[309] Powdered samples were applied as mixtures with carbon powder to an interrupted a.c. arc and the spectra were photographed in the range of 270-350 nm. The method could be used to determine metals down to $5 \times 10^{-3}\%$ with a relative precision of $\pm$ 15%.[309] Pulse radiolysis of cyclohexane solutions of the hexacarbonyls of Cr, Mo, and W yielded transient visible absorptions with λ_{max} at 505 nm, 410 nm and 415 nm, respectively, assigned by comparison with photochemical data to the related pentacarbonyls.[310] The following reactions were responsible for the pentacarbonyl formation by pulse radiolysis.[310]

$$M(CO)_6 + e^- \text{ (solvated)} \rightarrow M(CO)_6^- \tag{150}$$

$$M(CO)_6^- + C_6H_{12}^+ \rightarrow M(CO)_5 + CO + C_6H_{12} \tag{151}$$

In argon saturated solutions the pentacarbonyls decayed by 1st order kinetics. Reaction of the pentacarbonyls with cyclohexane, H_2, N_2 and CO were detected and the reaction rates measured.[310] Spectra of transient $M(CO)_5C_6H_{10}$ and $M(CO)_5N_2$ were reported.[310] X-ray analysis of the reaction of $W(CO)_6$ and

$Mo(CO)_6$ with atomic hydrogen in a glow-discharge plasma indicated the absence of known oxide and carbide phases in the product and indicated the formation of compounds of the formula $WC_{0.9}O_{1.3}H_{1.4}$ and $Mo_{0.4}O_{0.8}H_{0.9}$.[311] An examination was reported of the first field free region metastable fragmentations of $(\eta^6\text{-PhMe})Cr(CO)_3$ using the linked scan technique.[312] The molecular ion fragmented exclusively by single and multiple CO loss. The ion $[C_7H_8Cr(CO)_2]^{\cdot+}$ fragmented directly to $[C_7H_8Cr]^{\cdot+}$.[312] The low and high resolution mass spectra of $CpCr(NO)_2Cl$ and of $Cp_2Cr_2(NO)_2(\mu\text{-NO})(\mu\text{-X})$ compounds with X = NO, NH_2, etc. were measured and interpreted.[313] The degradation of the dinuclear complexes was determined by the group X.[313] A report of the gas phase molecular anion formation by η^6-cycloheptatriene derivatives of zerovalent chromium, molybdenum and tungsten appeared.[314] These compounds formed molecular anions in high abundance in their negative ion mass spectra.[314]

Olefinic and aromatic sandwich complexes of Cr were oxidized and reduced electrochemically.[315] Oxidation at a Pt electrode was in most cases chemically reversible. The oxidation of complexes with an 18-electron configuration was observed in a potential range of $E_{1/2} \approx -0.65$ to -0.8 V whereas oxidation of complexes with a 17-electron configuration occurred between $E_{1/2} \approx -0.2$ and -0.4 V.[315] Only one 18-electron complex, but all 17-electron complexes were reduced in THF. Most of these electron transitions were chemically reversible.[315]

STRUCTURAL DETERMINATIONS

Accurate X-ray data for $Cr(CO)_5(XPh_3)$ (X = As,Sb,Bi) (XXXVI) when compared with data for $Cr(CO)_5PPh_3$ showed significant variations in C-X-C and Cr-X-C bond angles as well as in Cr-X distances consistent with increasing s-orbital participation in Cr-X bonding down the series $P \le As < Sb < Bi$.[316]
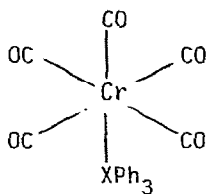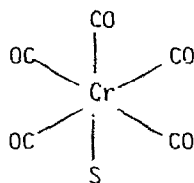
CO	CO
OC — Cr — CO	OC — Cr — CO
OC — Cr — CO	OC — Cr — CO
XPh_3	S
X = As, Sb, Bi	S = 2,2,4,4-tetramethyl-3-thietanone
XXXVI	XXXVII

The crystal and molecular structure of pentacarbonyl(2,2,4,4-tetramethyl-3-thietanone) chromium(0) (XXXVII) was reported.[317] The thietanone ligand, coordinated to the Cr through the S, displayed similarities with the bonding geometry of cyclobutanone but the endocyclic bond angle about the carbonyl C

was ~10° larger and that about the S was 11° smaller than their analogs in cyclobutanone.[317] The crystal structure of (triphos)Co(μ-CS$_2$)-Cr(CO)$_5$ (XXXVIII) was determined.[318] The CS$_2$ group was found to hold together the triphos Co and Cr(CO)$_5$ fragments. The cobalt atom was coordinated to the three phosphorus atoms of triphos and by the C=S linkage, through pi-bonding. The other sulfur atom of the CS$_2$ group was sigma bonded to the chromium atom.[318]
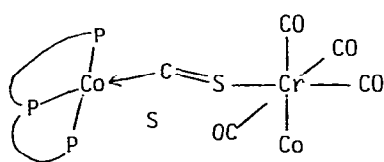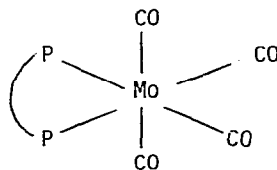

p^p^p = triphos

XXXVIII

XXXIX

The crystal structure of 1,4-diphenyl-2,2'-3,3',5,5',6,6'-octamethylcyclo-1,4-diphospha-2,3,5,6-tetrasilahexane, (PhPSi$_2$Me$_4$)$_2$Mo(CO)$_4$ (XXXIX) was determined by X-ray diffraction.[319] The coordination of boat-shaped (PhPSi$_2$Me$_4$) ligand to Mo(CO)$_4$ produced a distorted octahedral environment about the Mo. The Si-Si (2.358Å) and P-Si (2.275Å) distances were not altered from the free ligand. The relatively long Mo-P (2.592Å) distances were interpreted in terms of reduced pi-bonding from the metal caused the presence of silyl groups.[319] In the crystal structure of W(CO)$_3$(P(Me$_2$pz)$_2$(Ph)), the COs occupied fac positions in an irregular octahedron about the metal.[320] The phenylbis(3,5-dimethyl-pyrazolyl)phosphine ligand was coordinated to the tungsten atom through the two nitrogen atoms of the pyrazolyl rings and to two carbon atoms of the phenyl ring as a tridentate ligand.[320] Reactions of hexamethyltungsten, WMe$_6$, led to WMe$_6$·PMe$_3$, trans-WMe$_2$(PMe$_3$)$_4$ and WN$_2$(PMe$_3$)$_5$. The crystal structure of trans-WMe$_2$(PMe$_3$)$_4$ (XL) was determined showing distorted octahedral geometry.[321]
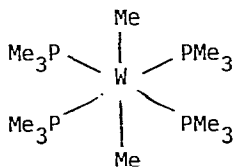
XL
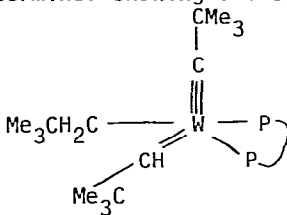
XLI

Churchill and Youngs reported the crystal structure of W($\equiv$CCMe$_3$)(=CHCMe$_3$)-(CH$_2$CMe$_3$)(dmpe).[322,323] This complex contained metal-alkylidyne, metal-alkylidene, and metal-alkyl linkages in a distorted square pyramidal environ-

ment around tungsten with the neopentylidyne in the special site and with neopentylidene and neopentyl ligands in adjacent basal sites. The bond lengths confirmed the formulation, $W \equiv C$ (1.785Å), $W = C$ (1.942Å), and $W-C$ (2.258Å).[322,323] NMR (^{13}C and [29]Si) and X-ray structure determination of pentacarbonyl{furyl[tris(trimethylsilyl)]siloxycarbene}chromium (XLII) showed the central Si atom to have a distorted trigonal-bipyramidal configuration by interaction with the oxygen of the furyl moiety both in solution and solid state.[324] The Si-O bond within the carbene ligand was lengthened and could be cleaved in ether solution by LiBr.[324]
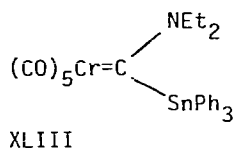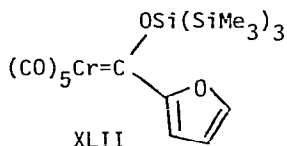
XLII

XLIII

Pentacarbonyl(diethylamino-(triphenylstannyl)carbene)chromium(0) (XLIII) was prepared by reaction of the cationic carbyne complex $[(CO)_5Cr \equiv CNEt_2]BF_4$ with Ph_3SnK.[325]

$$[(CO)_5Cr \equiv CNEt_2]^+ + Ph_3SnK \longrightarrow (CO)_5Cr = C(NEt_2)SnPh_3 \qquad (152)$$
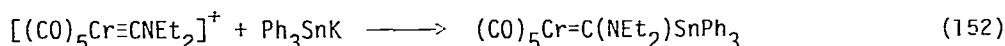
A structure determination showed a Cr-C distance of 2.11Å and a Sn-C(carbene) distance of 2.24Å.[325]

The structures of cis-bromodicarbonyl(Cp)(PPh$_3$)molybdenum (XLIV) and trans-dicarbonylcyclopentadienyliodo(phenylisocyanide)molybdenum (XLV) were
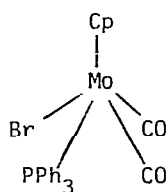
XLIV
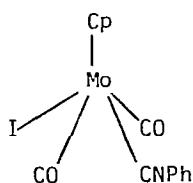
XLV

reported.[326,327] The crystal structure of carbonylcyclopentadienyl-1,5-η-[(η-methylene-1)cyclopentenonato-2] triphenylphosphinemolybdenum(II) was (XLVI) reported showing a pseudo tetrahedral environment around the molybdenum with the phosphine, the carbonyl groups, the cyclopentadienyl group and the allylic ketone occupying the four vertices.[328]

152
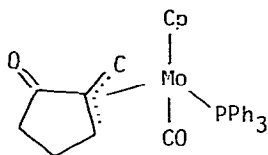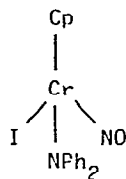
XLVI

XLVII

The crystal structure of (η^5-cyclopentadienyl)(diphenyl amido)iodonitrosyl-chromium (XLVII) also showed a pseudotetrahedral arrangement around chromium.[329] The migration of an alkylthio group across an enone ligand coordinated to tungsten was demonstrated from reaction CpW(SR)(CO)$_3$ with acetylenes, with X-ray structures of the two products (XLVIII and XLIX), one of which contained an alkyl-carbene ligand which functions as a three-electron donor.[330]

R' = Me, R" = CF$_3$

XLVII

R' = Me, R" = CO$_2$Me
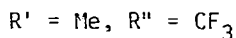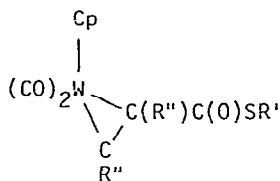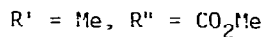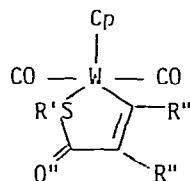
XLIX

The synthesis and X-ray structural analysis of a molybdenum complex with η^2-coordinated benzaldehyde were reported from the following reaction.[331]

+ P-RC$_6$H$_4$MgBr $\longrightarrow$
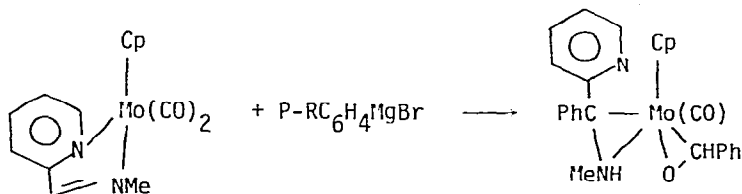
The structure of the methyldiazo complex $CpW(CO)_2(N_2CH_3)$ (L) was determined at $-140°C$ by X-ray diffraction techniques.[332] The complex, prepared by reaction of CH_2N_2 with $CpW(CO)_3H$, contained a normal methyl group attached in a singly bent fashion to the W-N-N linkage. The W-N bond length was 1.856Å.[332]
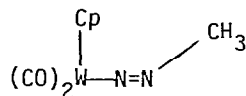
L
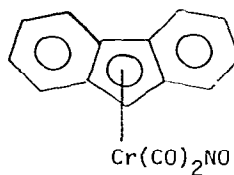
LI

The preparation and crystal structure of dicarbonylcyclopentadienyl-nitro-sylchromium and dicarbonylfluorenylnitrosylchromium (LI) were reported.[333] The cyclopentadienyl complex was disordered such that the nitrosyl couldn't be distinguished from carbonyls.[333] The structure of tricarbonyl(4,6,8-trimethyl-azulene)chromium (LII) was determined by ^{13}C NMR and X-ray analysis.[334] The analysis showed the azulene ligand was coordinated to the $Cr(CO)_3$ group only via the five membered ring.[334]
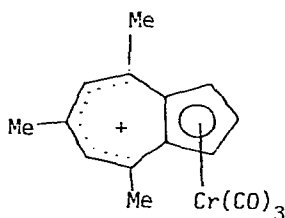
LII
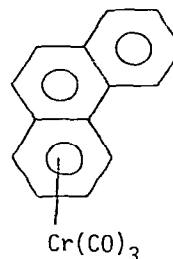
LIII

Arenetricarbonylchromium compounds formed 1:1 charge transfer adducts with 1,3,5-trinitrobenzene in solution, but only a few were stable in the crystal-line form.[335] The structure of a 1:1 adduct of phenanthrenetricarbonylchromium with 1,3,5-trinitrobenzene (LIII) was reported. The structure was composed of stacks of alternating donor and acceptor molecules.[335] The structure of tricarbonyl(1,1-dimethoxy-2,4,6-triphenyl-λ^5-phosphorin)chromium (LIV) was determined.[336]

LIV

LV
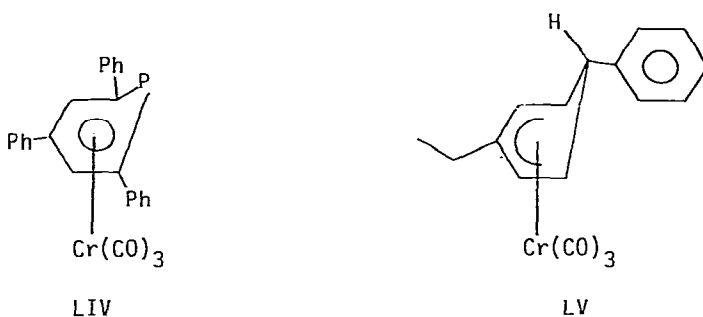
The structure of tricarbonyl(1,2,3,4,5,6-η-3-ethylendo-7-phenyl-1,3,5-cyclo-heptatriene)chromium (LV) was described.[337] The structure orientation of the aromatic was endo.[337]

J. L. Atwood and co-workers reported the crystal structure of $(\eta^6\text{-}C_6H_6)$-Mo$(CH_3)_2$(PPhMe$_2$) (LVI) and $(\eta^6\text{-}C_6H_5CH_3)Mo(CH_3)_2$(PPhMe$_2$).[338] The presence of the methyl group on the toluene did not alter the electronic environment of the molybdenum.[338]

LVI
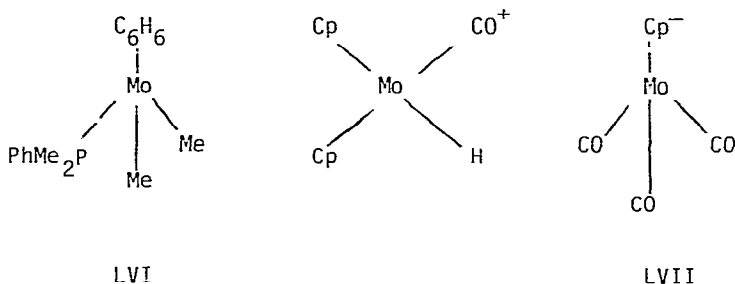
LVII

The structure of $[Cp_2Mo(H)(CO)]^+[CpMo(CO)_3]^-$ (LVII) was determined at -125°C.[339] The anion, $CpMo(CO)_3^-$, suffered only minor distortion from a symmetric "piano stool" configuration. In the cation, $Cp_2Mo(CO)H^+$, the Mo-CO distance was longer than in the anion while the M-C(Cp) distance was shorter than in the anion, suggesting as expected that the lower oxidation state has enhanced pi-bonding.[339] The geometry of MoCl(CO)$_2$(η^3-C$_3$H$_5$)(P(OCH$_3$)$_3$)$_2$ (LVIII) was described as pentagonal bipyramidal with Cl and one CO occupying axial sites, and the allyl occupying two adjacent sites of the equatorial plane and the two P(OCH$_3$)$_3$ groups trans.[340] The plane was rather distorted.[340]

P = P(OCH$_3$)$_3$

$\bigcap$ = [Me$_2$Ga(NH$_2$C$_5$H$_7$)(OCH$_2$CH$_2$NH$_2$)
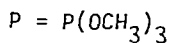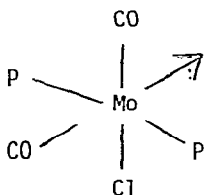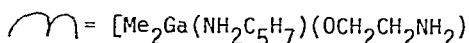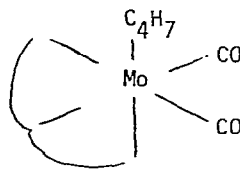
LVIII   LIX

In the structure of [Me$_2$Ga(NH$_2$C$_5$H$_7$)(OCH$_2$CH$_2$NH$_2$)]Mo(CO)$_2$(η^3-C$_4$H$_7$) (LIX), the Mo atom had a distorted octahedral environment with η^3-C$_4$H$_7$ occupying one of the six coordination sites, the gallate ligand a tridentate chelating ligand in the facial arrangement with two carbonyls completing the coordination.[341]

The crystal and molecular structure of tricarbonyl-1,6-bis(diphenylphosphino)-trans-hex-3-ene molybdeum was reported.[342]
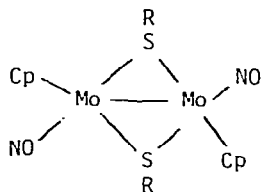
trans   cis
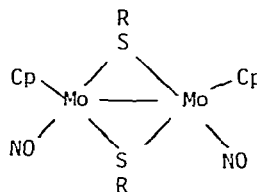
LX   LXI

The preparation and crystal structures of trans-[CpMo(NO)(SC$_2$H$_5$)]$_2$ (LX) and cis-[CpMo(NO)(SCH(CH$_3$)$_2$)]$_2$ (LXI) were reported.[343] The following reaction produced an antiferromagnetic dimer.[344]

Cp$_2$Cr + HSCMe$_3$ $\longrightarrow$ Cp$_2$Cr$_2$(S)(SCMe$_3$)$_2$ (153)
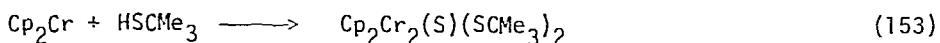
The structure was determined (LXII) showing a Cr-Cr distance of 2.689.[344]

P = PPh$_3$
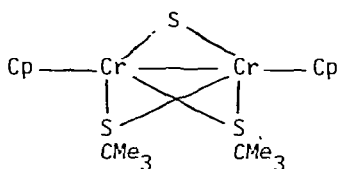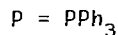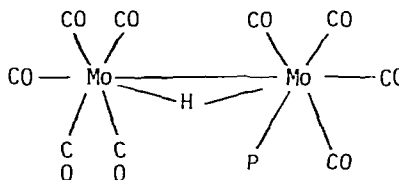
LXII   LXIII

A low-temperature (17°K) neutron diffraction study of $[(Ph_3P)_2N]^+[Cr(CO)_{10}(\mu-D)]^-$ was carried out to examine the nature of the Cr-D-Cr bond.[345] The deuterium atom was located at the midpoint of Cr-Cr line on a crystallographic center of symmetry, but was believed to be the result of a four-fold disorder.[345] An x-ray structure determination of Et_4N^+ $(\mu-H)[Mo_2(CO)_9PPh_3]^-$ (LXIII) affirmed the positioning of PPh_3 as cis to the bridging hydride in a (bent, staggered) molecular anion framework.[346] The Mo-Mo separation was 3.4736Å, the bend of the molecular anion framework was 162.7°, the Mo-H-Mo angle was 127° and the hydride was located asymmetrically between the Mo atoms, with the shorter Mo-H distance being to the $Mo(CO)_5$ moiety.[346] The Mo-P bond was quite long (2.565Å) corroborating the solution chemistry.[346] The molecular structures of $Cr_2(CO)_8(AsMe_2)_2$ (LXIV) and $CrFe(CO)_7(AsMe_2)_2$ were determined and compared to that of $Fe_2(CO)_6(AsMe_2)_2$.[347] The metal-metal bond lengths were 2.994Å for the dichromium complex and 2.829Å for the iron-chromium species. The fact that the M_2As_2 core was planar for $Cr_2(CO)_8(AsMe_2)_2$ and folded (pseudotetrahedral) for the other two complexes was explained by the steric demands of the ligands.[347]

LXIV   LXV
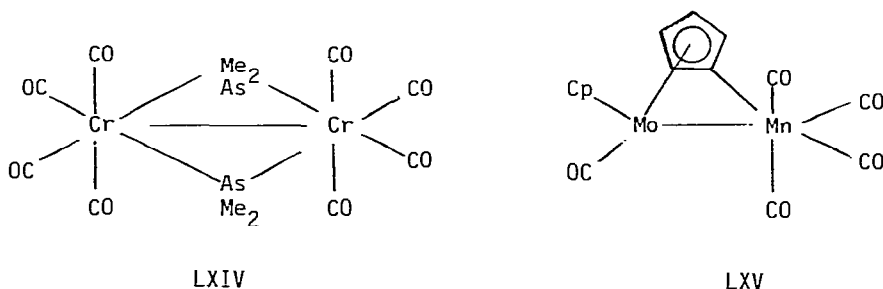
The structure of the compound $Cp(CO)Mo(\mu-(\eta^5:\eta^1-C_5H_4))Mn(CO)_4$ (LXV) was determined by X-ray diffraction.[348] The configuration around Mn was approximately octahedral; the configuration around Mo was very similar to Cp_2MoH_2. The C_5H_4 ring was described as a cyclopentadienyl ring rather than a diene-carbenoid ring. The Mn-C bond was 2.005Å and the Mo-Mn distance was 2.961Å.[348] The crystal structures of trans-Cp(H)W$[\mu-(\eta^1:\eta^5-C_5H_4)]_2$WH(Cp), and cis- and trans-Cp(CH_2SiMe_3)W$[\mu-(\eta^1:\eta^5-C_5H_4)]_2$ WH(Cp) (LXVI) were determined.[349] The tungsten atoms were separated by about 3.8Å in all three compounds and were bridged by cyclopentadienyl ligands.[349]

R = H, CH$_2$SiMe$_3$

LXVI

Cr(CO)$_3$
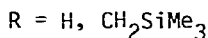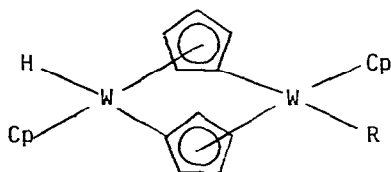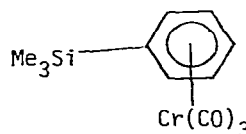
LXVII

The crystal structure of tricarbonyl[trimethyl(η^6-phenyl)silane]chromium was determined and shown to have the configuration as shown in LXVII.[350]

The mild carbonylation (room temperature, 1 atmosphere pressure) of Mo$_2$(O-t-Bu)$_6$ in hexane-pyridine solvent mixtures yielded a green crystalline compound, Mo(O-t-Bu)$_2$(py)$_2$(CO)$_2$.[351] The structure was solved by X-ray diffraction showing normal values for M-CO bond lengths although the frequencies were very low (1908 and 1768 cm^{-1}). The pi-donor properties of the alkoxy ligands were thought to be involved.[351] The crystal structure of di-μ-acetato-bis[(trimethylphosphine)(trimethylsilylmethyl)molybdenum(II)] showed a very short Mo-Mo distance (2.0984Å), consistent with the presence of a quadruple bond.[352] The compounds, [Me$_2$P(CH$_2$)$_2$]$_4$Cr$_2$ and [Me$_2$P(CH$_2$)$_2$]$_4$Mo$_2$, were investigated crystallographically and shown to be isomorphous with extremely short metal-metal bonds (1.895 and 2.082Å, respectively).[353]

Churchill and Hollander reported the crystal structure of the mixed metal cluster, (μ-H)$_3$Os$_3$W(CO)$_{11}$Cp (LXVIII).[354]

LXVIII

P = PEt$_3$
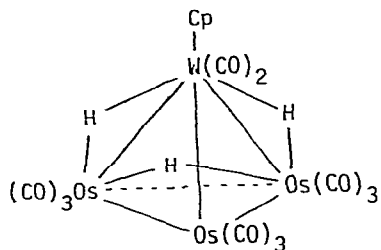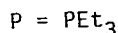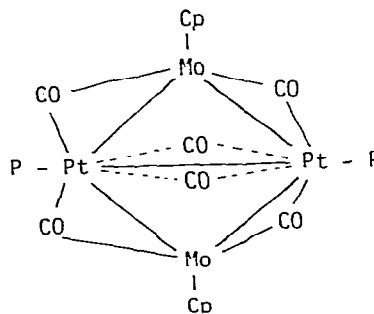
LXIX

The cluster compounds Pt$_2$M$_2$Cp$_2$(CO)$_6$L$_2$ (M = Mo, W; L = PEt$_3$, PPh$_3$) were prepared from cis-PtCl$_2$L$_2$ and NaM(CO)$_3$Cp.[355]

$$\text{cis } PtCl_2L_2 + NaCpM(CO)_3 \longrightarrow Pt_2M_2Cp_2(CO)_6L_2 \qquad (154)$$

$$M = Mo, W; L = PEt_3, PPh_3$$
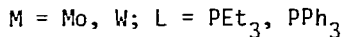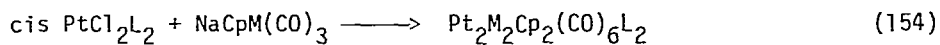
The compounds were characterized by a planar, triangular centrosymmetric arrangement of the metal atoms and by strongly asymmetric carbonyl bridges, which was shown by the crystal structure determination of $Pt_2Mo_2Cp_2(CO)_6(PEt_3)_2$ (LXIV).[355] The compound $[CpMo(CO)_3HgMo]_4$ was isolated as an additional product of the reaction between $Cp_2Mo_2(CO)_6$, 2-butenyl chloride and sodium amalgam.[356] The X-ray structure revealed that the compound had a slightly distorted cubane structure with the cubane unit built up by two different metal atoms (Mo and Hg).[356]

References

1. T. E. Gedris, Diss. Abstr. 40 (1979) 2685 B.

2. M. Chang, Diss. Abstr. 39 (1979) 3318 B.

3. W. W. Greaves, Diss. Abstr. 40 (1979) 234 B.

4. A. M. Mance, Diss. Abstr. 40 (1979) 2183 B.

5. R. G. Bowman, Diss. Abstr. 40 (1979) 2685 B.

6. S. Vastanathan, Diss. Abstr. 39 (1979) 5915 B.

7. C. D. Busley, Diss. Abstr. 39 (1979) 3318 B.

8. L. J. Archer, Diss. Abstr. 40 (1979) 738 B.

9. B. J. Carter, Diss. Abstr. 39 (1979) 5370.

10. G. J. Samuels, Diss. Abstr. Int. B 40 (1979) 235.

11. C. Masters, C. VanderWoude, and J. A. VanDoorn, J. Am. Chem. Soc., 101, (1979) 1633.

12. S. D. Ittel and C. A. Tolman, U.S. 4,155,925 May 22, 1979, Appl. 878,652 February 16, 1978.

13. B. D. Dombek, and R. J. Angelici, Inorg. Synth. 19 (1979) 183.

14. P. M. Treichel, D. W. Firsich, and G. P. Essenmacher, Inorg. Chem. 18 (1979) 2405.

15. R. B. King and M. Chang, Inorg. Chem. 18 (1979) 364.

16. R. Davis, M. L. Webb, and D. J. Darensbourg, J.C.S. Chem. Comm. (1979) 409.

17. M. Y. Darensbourg and H.L.C. Barros, Inorg. Chem. 18 (1979) 3286.

18. W. H. Batschelet, R. D. Archer, and D. R. Whitcomb, Inorg. Chem. 18 (1979) 48.

19. E. B. Dreyer, C. T. Lam, and S. J. Lippard, Inorg. Chem. 18 (1979) 1904.

20. G. S. Girolami and R. A. Andersen, J. Organomet. Chem. 182 (1979) C43.

21. J. L. Templeton, Adv. Chem. Ser. 173 (1979) 263.

22. D. J. Darensbourg, Inorg. Chem. 18 (1979) 14.

23. J. Ellermann, and H. Gaebelein, Z. Anorg. Allg. Chem. 449 (1979) 61.

24. W. R. Cullen, and M. Williams, J. Fluorine Chem. 14 (1979) 273.

25. S. Midollini, A. Orlandini, and L. Sacconi, Angew. Chem. 91 (1979) 93.

26. A. Vizi-Orosz, V. Galamb, I. Otvos, G. Palyi, and L. Marko, Transition Met. Chem. 4 (1979) 294.

27. J. Apel, R. Bacher, J. Grobe, and D. LeVan, Z. Anorg. Allg. Chem. 453 (1979) 39.

28. H. Maisch, Z. Naturforsch., B: Anorg. Chem. Org. Chem. 34B (1979) 784.

29. R. D. Kroshefsky, J. G. Verkade, and J. R. Pipal, Phosphorus Sulfur 6 (1979) 377.

30. P. M. Treichel and W. K. Wong, Inorg. Chim. Acta. 33 (1979) 171.

31. R. L. Keiter, Y. Y. Sun, J. W. Brodack, and L. W. Cary, J. Amer. Chem. Soc. 101, (1979) 2638.

32. R. L. De, J. V. Seyerl, and G. Huttner, J. Organomet. Chem. 178 (1979) 319.

33. J. A. Connor and P. I. Riley, J.C.S. Dalton (1979) 1231.

34. J. A. Connor and P. I. Riley, J. Organomet. Chem. 174 (1979) 173.

35. J. A. Connor and P. I. Riley, J.C.S. Dalton (1979) 1318.

36. J. Ellermann, and H. Gaebelein, Z. Anorg. Allg. Chem. 449 (1979) 52.

37. N. D. Sadanani, A. Walia, P. N. Kapoor, and R. N. Kapoor, Aus. J. Chem. 32 (1979) 1143.

38. H. J. Breunig, and W. Fichtner, Z. Anorg. Allg. Chem. 454 (1979) 167.

39. G. Baccolini and L. Busetto, Synth. React. Inorg. Met.-Org. Chem. 9 (1979) 263.

40. L. Knell, J. Organomet. Chem. 183 (1979) 77.

41. F. Hohmann and H. T. Dieck, J. Organomet. Chem. 171 (1979) 353.

42. D. J. Darensbourg, Inorg. Chem. 18 (1979) 2821.

43. L. Knoll and H. Wolff, Chem. Ber. 112 (1979) 2709.

44. D. Martens, J. Nasielski and R. Nasielski-Hinkens, J. Organomet. Chem. 168 (1979) 177.

45. D. Sellmann and E. Thallmar, J. Organomet. Chem. 164 (1979) 337.

46. L. H. Staal, A. Oskam, K. Vrieze, E. Roosendaal, and H. Schenk, Inorg. Chem. 18 (1979) 1634.

47. B. T. Heaton and D.J.A. McCaffrey, J.C.S. Dalton (1979) 1078.

48. D. N. Pathak, Indian J. Chem. Sect. A. 17A (1979) 310.

49. S. C. Tripathi, S. C. Srivastava, and C. P. Singh, Transition Met. Chem. 4 (1979) 53.

50. D. N. Pathak, Indian J. Chem. Sect. A. 16A (1978) 986.

51. A. P. Borisov, V. D. Makhaev, amd K. N. Semenenko, Koord. Khim. 5 (1979) 948.

52. L. J. Archer and T. A. George, Inorg. Chem. _18_ (1979) 2079.

53. T. Takahashi, Y. Mizobe, M. Sato, Y. Uchida, and M. Hidai, J. Am. Chem. Soc. _101_ (1979) 3405.

54. D. Sellman, R. Gerlach, and K. Jödden, J. Organomet. Chem. _178_ (1979) 433.

55. M. N. Ackermann, R. M. Willett, M. H. Englert, C. R. Barton, and D. B. Schewitz, J. Organomet. Chem. _175_ (1979) 205.

56. M. N. Ackermann, D. J. Dobmeyer and L. C. Hardy, J. Organomet. Chem. _182_ (1979) 561.

57. J. Chatt, M. E. Fakley, P. B. Hitchcock, R. L. Richards, N. T. Luong-Thi and D. L. Hughes, J. Organomet. Chem. _172_ (1979) C55.

58. R.G.W. Gingerich and R. J. Angelici, J. Am. Chem. Soc. _101_ (1979) 5604.

59. M. F. Lappert, D. B. Shaw, and G. M. McLaughlin, J.C.S. Dalton (1979) 427.

60. H. Alper and R. Sachdeva, J. Organometal. Chem. _169_ (1979) 63.

61. N. Kottmair and W. Beck, Inorg. Chim. Acta _34_ (1979) 137.

62. C. P. Casey, S. W. Polichnowski, A. J. Shusterman, and C. P. Jones, J. Am. Chem. Soc. _101_ (1979) 7282.

63. H. Fischer, J. Organomet. Chem. _170_ (1979) 309.

64. C. P. Casey, T. J. Burkhardt, S. M. Neumann, D. M. Scheck, and H. E. Tuinstra, Inorg. Synth. _19_ (1979) 180.

65. C. P. Casey, R. L. Anderson, S. M. Neumann, and D. M. Scheck, Inorg. Synth. _19_ (1979) 178.

66. E. O. Fischer, U. Schubert, and H. Fischer, Inorg. Synth. _19_ (1979) 169.

67. E. O. Fischer, U. Schubert, W. Kleine, and H. Fischer, Inorg. Synth. _19_ (1979) 164.

68. K. H. Dötz, B. Fügen-Köster and D. Neugebauer, J. Organomet. Chem. _182_ (1979) 489.

69. K. H. Dötz, R. Dietz, and D. Neugebauer, Chem. Ber. _112_ (1979) 1486.

70. J. Levisalles, H. Rudler, Y. Jeannin, and F. Dahan, J. Organometal. Chem. _178_ (1979) C8.

71. W. W. Greaves, R. J. Angelici, B. J. Helland, R. Klima, and R. A. Jacobson, J. Am. Chem. Soc. _101_ (1979) 7618.

72. E. O. Fischer, W. R. Wagner, F. R. Kreissl and D. Neugebauer, Chem. Ber. _112_ (1979) 1320.

73. E. O. Fischer, H. Hollfelder, and F. R. Kreissl, Chem. Ber. _112_ (1979) 2177.

74. E. O. Fischer and P. Friedrich, Angew Chem. Int. Ed. _18_ (1979) 327.

75. W. Vedelhoven, K. Eberl, and F. R. Kreissl, Chem. Ber. 112 (1979) 3376.

76. E. O. Fischer, U. Schubert, and H. Fischer, Inorg. Synth., 19 (1979) 172.

77. E. O. Fischer, and P. Friedrich, Angew. Chem., 91 (1979) 345.

78. C.A.L. Mahaffy, and P. L. Pauson, Inorg. Synth. 19 (1979) 154.

79. K. Schloegl, and R. Schoelm, Monatsh. Chem., 110 (1979) 1067.

80. O. Hofer, K. Schloegl, and R. Schoelm, Monatsh. Chem., 110 (1979) 437.

81. N. E. Kolobova, and L. V. Goncharenko, Izv. Akad. Nauk SSSR, Ser. Khim. (1979) 900.

82. K. H. Doetz, R. Dietz, and D. Neugebauer, Chem. Ber., 112 (1979) 1486.

83. A. F. Mourad, and H. Hopf, Tett. Lett. (1979) 1209.

84. G. Jaouen, and G. Simonneaux, Inorg. Synth. 19 (1979) 197.

85. G. A. Razuvaev, N. I. Sirotkin, and A. N. Artemov, Izv. Akad. Nauk SSSR Ser. Khim. (1979) 1379.

86. S. Top and G. Jaouen, J. Organomet. Chem. 182 (1979) 381.

87. E. L. Muetterties, J. R. Bleeke, and A. C. Sievert, J. Organometal. Chem. 178 (1979) 197.

88. C.A.L. Mahaffy, and P. L. Pauson, J. Chem. Res. Synop. (1979) 126.

89. E. L. Muetterties, H. Schaeffer, R. I. Mink, M. Y. Darensbourg, M. Millar, T. Groshens, and K. J. Klabunde, Inorg. Chem. 18 (1979) 883.

90. M. D. Rausch, G. A. Moser and W. A. Lee, Synth. React. Inorg. Met.-Org. Chem., 9 (1979) 357.

91. M. F. Semmelhack, J. Bisaha, and M. Czarny, J. Am. Chem. Soc., 101, (1979) 768.

92. M. F. Semmelhack, G. R. Clark, R. Farina, and M. Saeman, J. Am. Chem. Soc. 101 (1979) 217.

93. M. F. Semmelhack, N. T. Hall, Jr., R. Farina, M. Yoshifuji, G. Clark, T. Bargar, K. Hirotsu, and J. Clardy, J. Am. Chem. Soc. 101 (1979) 3535.

94. K. J. Klabunde, H. F. Efner, and T. O. Murdock, Inorg. Synth. 19 (1979) 70.

95. J. E. Dobson, R. J. Remick, B. E. Wilburn, and P. S. Skell, Inorg. Synth. 19 (1979) 80.

96. A. N. Nesmeyanov, L. P. Yur'eva, N. N. Zaitseva, G. A. Domrachev, V. D. Zinov'ev, Y. A. Shevelev, and N. I. Vasyukova, Koord. Khim. 5 (1979) 673.

97. A. D. Zorin, V. A. Umilin, E. N. Karataev, and T. A. Sorokoumova, Zh. Fiz. Khim. 53 (1979) 302.

98. W. E. Silverthorn, Inorg. Chem. 18 (1979) 1835.

99. N. Hao, and M. J. McGlinchey, J. Organomet. Chem. <u>165</u> (1979) 225.

100. Yu. T. Struchkov, V. G. Andrianov, V. N. Setkina, N. K. Baranetskaya, V. I. Losilkina, and D. N. Mursanov J. Organomet. Chem. <u>182</u> (1979) 213.

101. S. Top and G. Jaouen, J.S.C. Chem. Comm. (1979) 224.

102. P. LeMaux, G. Simmoneaux, P. Caillet, and G. Jaouen, J. Organomet. Chem. <u>177</u> (1979) C1.

103. A. Solladie-Cavallo and E. Tsamo, J. Organomet. Chem. <u>172</u> (1979) 165.

104. K. Handlir, J. Holecek, and J. Klikorka, Z. Chem. <u>19</u> (1979) 265.

105. P. T. Wolczanski, R. S. Threlkel, and J. E. Bercaw, J. Am. Chem. Soc., <u>101</u> (1979) 219.

106. D. J. Blumer, K. W. Barnett, and T. L. Brown, J. Organomet. Chem. <u>173</u> (1979) 71.

107. L. Goh, M. J. D'Aniello, Jr., S. Slater, E. L. Muetterties, I. Tavanaiepour, M. I. Chang, M. F. Fredrich, and V. W. Day, Inorg. Chem. <u>18</u> (1979) 192.

108. J.C.T.R. Burckett-St. Laurent, J. S. Field, R. J. Haines, and M. McMahon J. Organomet. Chem. <u>181</u> (1979) 117.

109. T. Madach, and H. Vahrenkamp, Z. Naturforsch. B: Anorg. Chem. Org. Chem. <u>34B</u> (1979) 573.

110. N. V. Perevozchikova, A. S. Smirnov, Yu. A. Sorokin, R. V. Kaplina, and V. A. Dodonov, Zh. Obshch. Khim. <u>49</u> (1979) 945.

111. J. A. Gladysz, G. M. Williams, W. Tam, D. L. Johnson, D. W. Parker, and J. C. Selover, Inorg. Chem. <u>18</u> (1979) 553.

112. J. M. Burlitch, M. E. Leonowicz, R. B. Petersen, and R. E. Hughes, Inorg. Chem. <u>18</u> (1979) 1097.

113. E. W. Abel and C. Towers, J.C.S. Dalton (1979) 814.

114. A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva, and S. A. Eremin, Dokl. Akad. Nauk SSSR <u>243</u> (1978) 1208.

115. W. Malisch, R. Janta, and G. Kuenzel, Z. Naturforsch. B: Anorg. Chem. Org. Chem. <u>34B</u> (1979) 599.

116. H. Behrens, K. Goerting, P. Merbach, and M. Moll, Z. Anorg. Allg. Chem., <u>454</u> (1979) 67.

117. T. Aviles, M.L.H. Green, A. R. Dias, and C. Romao, J.C.S. Dalton (1979) 1367.

118. P. A. Wegner and V. A. Uski, Inorg. Chem., <u>18</u> (1979) 646.

119. M. Moran and V. Fernández, J. Organomet. Chem. <u>165</u> (1979) 215.

120. H. Brunner and J. Wachter, J. Organomet. Chem. <u>175</u> (1979) 285.

164

121. M. R. Dubois, R. C. Haltiwanger, D. J. Miller, and G. Glatzmaier, J. Am. Chem. Soc. _101_ (1979) 5245.

122. E. Pfeiffer, K. Vrieze, and J. A. McCleverty, J. Organomet. Chem. _174_ (1979) 183.

123. J. E. Guerchais, F. LeFloch-Perennou, F. Y. Petillon, A. N. Keith, L. Manojlović-Muir, K. W. Muir, and D.W.A. Sharp, J.C.S. Chem. Comm. (1979) 410.

124. J. L. Davidson, J.C.S. Chem. Comm. (1979) 597.

125. U. Kunse and S. B. Sastrawan, Chem. Ber. _112_ (1979) 3149.

126. L. Manojlović-Muir and K. W. Muir, J. Organomet. Chem. _168_ (1979) 403.

127. G. M. Reisner and I. Bernal, J. Organomet. Chem. _173_ (1979) 53.

128. H. Brunner, W. Nowak, and D. K. Rastogi, Inorg. Chim. Acta. _33_ (1979) L115.

129. H. Brunner and R. Lukas, Chem. Ber., _112_ (1979) 2528.

130. T. J. Greenhough, B.W.S. Kolthammer, P. Legzdins, and J. Trotter, Inorg. Chem. _18_ (1979) 3543.

131. D. L. Reger, D. J. Fauth, and M. D. Dukes, J. Organomet. Chem. _170_ (1979) 217.

132. M. Gower and L.A.P. Kane-Maguire, Inorg. Chim. Acta. _37_ (1979) 79.

133. W. Schulze, K. Weidenhammer, and M. L. Ziegler, Angew. Chem. Int. Ed. _18_ (1979) 404.

134. W. Schulze, K. Weidenhammer, and M. L. Ziegler, Angew. Chem. _91_ (1979) 432.

135. K. Weidenhammer, and M. L. Ziegler, Z. Anorg. Allg. Chem., _455_ (1979) 43.

136. N. J. Cooper and M.L.H. Green, J.C.S. Dalton (1979) 1121.

137. R. B. King, M. S. Saran, D. P. McDonald, and S. P. Diefenbach, J. Am. Chem. Soc. _101_ 1138.

138. S. Fadel, K. Weidenhammer, and M. L. Ziegler, Z. Anorg. Allg. Chem. _453_ (1979) 98.

139. J. W. Faller and H. H. Murray, J. Organomet. Chem. _172_ (1979) 171.

140. S.A.R. Knox, R.F.D. Stansfield, F.G.A. Stone, M. J. Winter, and P. Woodward, J.C.S. Chem. Comm. (1979) 934.

141. A. Salzer and W. vonPhilipsborn, J. Organomet. Chem. _170_ (1979) 63.

142. T. J. Greenhough, P. Legzdins, D. T. Martin, and J. Trotter, Inorg. Chem. _18_ (1979) 3268.

143. J. A. McCleverty and A. J. Murray, J.C.S. Dalton (1979) 1424.

144. J. Collin, J. L. Roustan and P. Cadiot, J. Organomet. Chem. _169_ (1979) 53.

145. J. L. Roustan, J. Y. Merour, C. Charrier, J. Benaim, and P. Cadiot, J. Organomet. Chem. 169 (1979) 39.

146. J. W. Faller, D. A. Haitko, R. D. Adams, and D. F. Chodosh, J. Am. Chem. Soc. 101 (1979) 865.

147. J. Collin, Cl. Charrier, M. J. Pouet, P. Cadiot, and J. L. Roustan, J. Organomet. Chem. 168(1979) 321.

148. B. J. Brisdon and M. Cartwright, J. Organomet. Chem. 164 (1979) 83.

149. R. D. Adams, D. F. Chodosh, J. W. Faller, and A. M. Rosan, J. Am. Chem. Soc. 101 (1979) 2570.

150. D. H. Gibson, W. L. Hsu, and D. S. Lin, J. Organomet. Chem. 172 (1979) C7.

151. J. Benaim and F. Giulieri, J. Organomet. Chem. 165 (1979) C28.

152. F. A. Cotton, G. W. Rice, and J. C. Sekutowski, Inorg. Chem. 18 (1979) 1143.

153. G.W.A. Fowles, W. M. wanMohamed, and D. A. Rice, J. Organomet. Chem. 170 (1979) 203.

154. K. Jacob, K. H. Thiele, and V. Dimitrov, Z. Anorg. Allg. Chem. 447 (1978) 136.

155. K. P. Darst, D. T. Hobbs and C. M. Lukehart, J. Organomet. Chem. 179 (1979) C9.

156. W. Marty and J. H. Espenson, Inorg. Chem. 18 (1979) 1246.

157. G. J. Samuels and J. H. Espenson, Inorg. Chem. 18 (1979) 2587.

158. W. Seidel and L. Bürger, J. Organomet. Chem. 171 (1979) C45.

159. W. Seidel and I. Bürger, J. Organomet. Chem. 177 (1979) C19.

160. K. Schmiedeknecht, Z. Chem. 19 (1979) 29.

161. W. D. Jones and R. G. Bergman, J. Am. Chem. Soc. 101 (1979) 5447.

162. A. N. Nesmeyanov, L. G. Makarova, V. N. Vinogradova, V. N. Korneva, and N. A. Ustynyuk, J. Organomet. Chem. 166 (1979) 217.

163. P. L. Watson and R. G.Bergman, J. Am. Chem. Soc. 101 (1979) 2055.

164. M. Bottrill and M. Green,   J.C.S. Dalton (1979) 820.

165. N. J. Coville and M. O. Albers, J. Organomet. Chem. 172 (1979) C1.

166. R. G. Severson and A. Wojcicki, J. Am. Chem. Soc. 101 (1979) 877.

167. N. J. Cooper, M.L.H. Green, and R. Mahtab, J.C.S. Dalton (1979) 1557.

168. M.L.H. Green and R. Mahtab, J.C.S. Dalton (1979) 262.

169. M. Canestrari and M.L.H. Green, J.C.S. Chem. Comm. (1979) 913.

170. A. P. Borisov, Deposited Doc. (1979) 1805.

166

171. A. P. Borisov, V. D. Makhaev, and K. N. Semenenko, Izv. Akad. Nauk SSSR, Ser. Khim. (1979) 1914.

172. J. Chatt, A.J.L. Pombeiro, and R. L. Richards, J.C.S. Dalton (1979) 1585.

173. P. Legzdins and D. T. Martin, Inorg. Chem. 18 (1979) 1250.

174. D. J. Darensbourg and M. J. Incorvia, Inorg. Chem., 18 (1979) 18.

175. M. D. Grillone, and B. B. Kedzia, Transition Met. Chem. 4 (1979) 256.

176. M. A. Adams, K. Folting, J. C. Huffman, and K. G. Caulton, J. Organomet. Chem. 164 (1979) C29.

177. J. R. Blickensderfer, R. J. Hoxmeier, and H. D. Kaesz, Inorg. Chem. 18 (1979) 3606.

178. R. J. Hoxmeier, J. R. Blickensderfer, and H. D. Kaesz, Inorg. Chem. 18 (1979) 3453.

179. N. A. Alcock, O. W. Howarth, P. Moore, and G. E. Morris, J.C.S. Chem. Comm. (1979) 1160.

180. J. A. Carroll, D. Sutton, M. Cowie, and M. D. Gauthier, J.C.S. Chem. Comm. (1979) 1058.

181. R. B. King, M. Z. Iqbal, and A. D. King, Jr., J. Organomet. Chem. 171 (1979) 53.

182. R. A. Jones and G. Wilkinson, J.C.S. Dalton (1979) 472.

183. M. H. Chisholm, F. A. Cotton, M. W. Extine, and D. C. Rideout, Inorg. Chem. 18 (1979) 120.

184. M. H. Chisholm and D. A. Haitko, J. Am. Chem. Soc. 101 (1979) 6784.

185. M. H. Chisholm, F. A. Cotton, M. W. Extine, and R. L. Kelley, J. Am. Chem. Soc. 101 (1979) 7645.

186. H. A. Alper, N. D. Silavwe, G. I. Birnbaum, and F. R. Ahmed, J. Am. Chem. Soc. 101(1979) 6582.

187. T. A. Bazhenova, M. S. Ioffe, L. M. Kachapina, R. M. Lobkovskaya, R. P. Shibaeva, A. E. Shilov, and A. K. Shilova, Zh. Strukt. Khim. 19 (1978) 1047.

188. V. I. Spitsyn, N. A. Subbotina, M. G. Felin, S. I. Pakhomov, and A. I. Zhirov, Dokl. Akad. Nauk SSSR 245 (1979) 1130.

189. A. A. Pasynskii, Yu. V. Skripkin, I. L. Eremenka, V. T. Kalinnikov, G. G. Aleksandrov, V. G. Andrianov, and Yu. T. Sturchkov, J. Organomet. Chem. 165 (1979) 49.

190. N. W. Alcock, O. W. Howarth, P. Moore and G. E. Morris, J.C.S. Chem. Comm. (1979) 1160.

191. F. Richter, H. Beurich, and H. Vahrenkamp, J. Organomet. Chem. 166 (1979) C5.

192. F. Richter and H. Vahrenkamp, Angew. Chem. Int. Ed. 18 (1979) 531.

193. F. Richter and H. Vahrenkamp, Angew. Chem. 91 (1979) 566.

194. P. Braunstein, E. Keller, and H. Vahrenkamp, J. Organomet. Chem. 165 (1979) 233.

195. T. V. Ashworth, M. Berry, J. A. Howard, M. Laguna, and F.G.A. Stone, J.C.S. Chem. Comm. (1979) 45.

196. A. M. Bond, R. Colton, and J. J. Jackowski, Inorg. Chem., 18 (1979) 1977.

197. A. N. Nesmeyanov, V. V. Krivykh, and M. I. Rybinskaya, J. Organomet. Chem. 164 (1979) 159.

198. A. N. Nesmeyanov, Yu. T. Struchkov, V. G. Andrianov, V. V. Krivykh, and M. I. Rybinskaya, J. Organomet. Chem. 164 (1979) 51.

199. A. N. Nesmeyanov, V. V. Krivykh, G. A. Panosyan, P. V. Petrovskii, and M. I. Rybinskaya, J. Organomet. Chem. 164 (1979) 167.

200. A. N. Nesmeyanov, Yu. T. Struchkov, V. G. Andrianov, V. V. Krivykh, and M. I. Rybinskaya, J. Organomet. Chem. 166 (1979) 211.

201. H. G. Raubenheimer, S. Lotz, H. E. Swarepoel, H. W. Viljoen and J. C. Rautenbach, J.C.S. Dalton (1979) 1701.

202. H. Brunner, H. Schwägerl, and J. Wachter, Chem. Ber. 112 (1979) 2079.

203. N. E. Kolbova, V. I. Zdanovich and I. A. Lobanova, Koord. Khim. 5 (1979) 86.

204. N. G. Connelly and C. Gardner, J.C.S. Dalton (1979) 609.

205. A. G. Ginsburg, V. N. Satkina, and D. N. Kursanov, J. Organomet. Chem. 182 (1979) C1.

206. M. Herberhold and P. D. Smith, Angew. Chem. Int. Ed. 18 (1979) 631.

207. P. D. Frisch, M. M. Hunt, W. G. Kita, J. A. McCleverty, A. E. Rae, D. Seddon, D. Swann, and J. Williams, J.C.S. Dalton (1979) 1819.

208. T. J. Greenhough, B.W.S. Kolthammer, P. Legzdins, and J. Trotter, Inorg. Chem. 18 (1979) 3548.

209. D. J. Darensbourg and A. H. Graves, Inorg. Chem. 18 (1979) 1257.

210. D. J. Darensbourg, M. Y. Darensbourg, R. R. Burch, Jr., J. A. Froelich, and M. J. Incorvia, Adv. Chem. Ser. 173 (1979) 106.

211. S. B. Butts, E. M. Holt, S. H. Strauss, N. W. Alcock, R. E. Stimson and D. F. Shriver, J. Am. Chem. Soc. 101 (1979) 5864.

212. W. A. Schenk, J. Organomet. Chem. 179 (1979) 253.

213. G. R. Dobson and J. C. Rousche, J. Organomet. Chem. 179 (1979) C42.

214. K. J. Asali and G. R. Dobson, J. Organomet. Chem. 179 (1979) 169.

215. G. R. Dobson, L. D. Schultz, B. E. Jones, and M. Schwartz, J. Inorg. Nucl. Chem. 41 (1979) 119.

216. H. Fischer and A. Ruhs, J. Organomet. Chem. <u>170</u> (1979) 181.

217. D. Dong, D. A. Slack, and M. C. Baird, Inorg. Chem. <u>18</u> (1979) 188.

218. M. Leconte and J. M. Basset, J. Am. Chem. Soc. <u>101</u> (1979) 7296.

219. R. H. Grubbs and C. R. Hoppin, J. Am. Chem. Soc. <u>101</u> (1979) 1499.

220. S. Devarajan, D.R.M. Walton, and G. J. Leigh, J. Organomet. Chem. <u>181</u> (1979) 99.

221. A. Brenner, D. A. Hucul, and S. J. Hardwick, Inorg. Chem. <u>18</u> (1979) 1478.

222. F. Grarnier, P. Krausz, and J. E. Dubois, J. Organomet. Chem. <u>170</u> (1979) 195.

223. M. Gilet, A. Mortreux, J. Nicole, and F. Petit, J.C.S. Chem. Comm. (1979) 521.

224. J.A.K. DuPlessis, and P. J. Heenop, S. Afr. J. Chem. <u>32</u> (1979) 1.

225. B. A. Dolgoplosk, I. A. Oreshkin, S. A. Smirnov, I. A. Kop'eva, and E. I. Tinyakova, Eur. Polym. J. <u>15</u> (1979) 237.

226. E. Ts. Chukovskaya, R. G. Gasanov, I. I. Kandror, and R. Kh. Freidlina, Zh. Vses. Khim. O-va. <u>24</u> (1979) 161.

227. G. Henrici-Olivé and S. Olivé, Angew. Chem. <u>18</u> (1979) 77.

228. A. Brenner, J. Mol. Catalysis <u>5</u> (1979) 157.

229. M. J. Mirbach, D. Steinmetz, and A. Saus, J. Organomet. Chem. <u>168</u> (1979) C13.

230. Y. Iwasawa, and S. Ogasawara, J. Chem. Soc., Faraday Trans. I <u>75</u> (1979) 1465.

231. V. S. Markevich and N. Kh. Shtivel, Kinet. Katal. <u>20</u> (1979) 345.

232. V. S. Markevich, N. Kh. Shtivel, S. Yu. Gurileva, and L. K. Goryunova, Kinet. Katal. <u>20</u> (1979) 504.

233. L. M. Svanidze, T. G. Samedova, E. A. Mushina, I. R. Gol'ding, B. A. Krentsel, N. M. Sirotkin, A. K. Artemov, G. N. Bondarenko, A. M. Sladkov, and B. E. Davydov, Vysokomol. Soedin., Ser. B <u>21</u> (1979) 455.

234. E. A. Ofstead, and M. L. Senyek, Ger. Offen. 2,838,302 (1977).

235. R. J. Minchak, U.S. 4,138,448 (Cl. 260-879; C08F4/60) Feb. 6 1979, Appl. 857,547, Dec. 5, 1977, pp. 6.

236. M. C. Throckmorton, and C. J. Suchma, Belg. 875,324 (Cl.Co8FO July 31, 1979. US Appl. 893,724, April 5, 1978, pp. 24

237. M. C. Throckmorton, U.S. 4,148,983 (Cl. 526-139; C08F4/50), April 10 1979, Appl. 893,725, April 5, 1978, pp. 6.

238. H. tomDieck and A. Kinzel, Angew. Chem. Int. Ed., <u>18</u> (1979) 324.

239. I. F. Gavrilenko, V. L. Sokolova, N. N. Stefanovskaya, E. I. Tinyakova, and B. A. Dolgoplosk, Zh. Khim. (1979) Abstr. No. 18S206.

240. N. I. Pakuro, A. R. Gantmakher, and B. A. Dolgoplosk, Zh. Khim. (1979) Abstr. No. 18S205.

241. T. Lau, J. Organometal. Chem. 174 (1979) 169.

242. D.H.R. Barton, S. G. Davies, and W. B. Motherwell, Synthesis, (1979) 265.

243. H. Alper, and L. Pattee, J. Org. Chem. 44 (1979) 2568.

244. A. Nakamura, J. Organomet. Chem. 164 (1979) 183.

245. A. Ceccon, F. Miconi, and A. Venzo, J. Organomet. Chem. 181 (1979) C4.

246. R. G. Gasanov, and R. Kh. Freidlina, Dokl. Akad. Nauk SSSR 246 (1979) 111.

247. G. Loubriel, and E. W. Plummer, Chem. Phys. Lett. 64 (1979) 2348.

248. H. W. Choi, R. M. Gavin, and E. L.Muetterties, J.C.S. Chem. Comm. (1979) 1087.

249. W. C. Mills, III and M. S. Wrighton, J. Am. Chem. Soc. 101 (1979) 5830.

250. D. J. Darensbourg and B. J. Baldwin, J. Am. Chem. Soc. 101 (1979) 6447.

251. T. M. McHugh, A. J. Rest, and J. R. Sodeau, J.C.S. Dalton (1979) 184.

252. G. Boxhoorn, D. J. Stufkens, and A. Oskam, Inorg. Chim. Acta 33 (1979) 215.

253. R. M. Dahlgren and J. I. Zink, J. Am. Chem. Soc. 101 (1979) 1448.

254. R. M. Dahlgren and J. I. Zink, Inorg. Chem. 18 (1979) 597.

255. J. Ellermann, H. A. Lindner, and H. Gäbelein, J. Organomet. Chem. 172 (1979) 39.

256. R. W. Balk, D. J. Stufkins and A. Oskam, J.C.S. Chem. Comm. (1979) 604.

257. D. Martins, J. Nasielski, and R. Nasielski-Hinkins, J. Organomet. Chem. 168 (1979) 177.

258. P. Grebenik, A. J. Downs, M.L.H. Green, and R. N. Perutz, J.C.S. Chem. Comm. (1979) 742.

259. M. Berry, K. Elmitt and M.L.H. Green, J.C.S. Dalton (1979) 1950.

260. S.M.B. Costa, A. R. Dias, and F.J.S. Pina, J. Organomet. Chem. 175 (1979) 193.

261. E. Samuel, M. D. Rausch, T. E. Gismondi, E. A. Mintz, and C. Giannotti, J. Organomet. Chem. 172 (1979) 309.

262. E. A. Mintz and M. D. Rausch, J. Organomet. Chem. 171 (1979) 345.

263. G. Simmoneaux, P. LeMaux, G. Jaouen, and R. Dabard, Inorg. Chem. 18 (1979) 3167.

264. A. N. Nesmeyanov, E. G. Perevalova, L. I. Leont'eva and E. V. Shumilina, Izv. Akad. Nauk SSSR, Ser. Khim. (1979) 683.

265. M. Vermeulen, G. Michel, and J. Nasielski, Spectrochim. Acta, 35A(2) (1979) 147.

266. C. B. Cooper, III, D. F. Shriver, D. J. Darensbourg, and J. A. Froelich, Inorg. Chem. 18 (1979) 1407.

267. L. H. Staal, A. Tempstra, and D. J. Stufkens, Inorg. Chim. Acta. 34 (1979) 97.

268. N. Q. Dao, E. O. Fischer, W. R. Wagner and D. Neugebauer, Chem. Ber. 112 (1979) 2552.

269. P. Caillet and G. Jaouen, J. Organomet. Chem. 164 (1979) 329.

270. E. B. Nazarova, B. V. Lokshin, A. N. Artemov, and N. I. Sirotkin, Izv. Akad. Nauk SSSR, Ser. Khim. (1979) 58.

271. L. A. Fedorov, P. V. Petrovskii, E. I. Fedin, G. A. Panosyan, A. A. Tsoi, N. K. Baranetskaya, and V. N. Setkina, J. Organomet. Chem. 182 (1979) 499.

272. L. A. Fedorov, P. V. Petrovskii, E. I. Fedin, N. K. Baranetskaya, V. I. Zdanovich, A. A. Tsoi, V. N. Setkina, and D. N. Kursanov, Koord. Khim. 5 (1979) 1339.

273. D. Cozak, I. S. Butler, and I. M. Baibich, J. Organomet. Chem. 169 (1979) 381.

274. N. J. Fitzpatrick, N. J. Gogan, and I. J. King, J. Organomet. Chem. 166 (1979) 45.

275. R. F. Jordan and J. R. Norton, J. Am. Chem. Soc. 101 (1979) 4853.

276. S. Aime, L. Milone, D. Oseila, G. E. Hawkes, and E. W. Randall, J. Organomet. Chem. 178 (1979) 171.

277. J. P. Hickey, J. R. Wilkinson and L. J. Todd, J. Organomet. Chem. 179 (1979) 159.

278. V. Kawada, T. Sugawara, and H. Iwamura, J.C.S. Chem. Comm. (1979) 291.

279. D. Cozak, I. S. Butler, J. P. Hickey, and L. Todd, J. Magn. Reson. 33 (1979) 149.

280. R. E. Botto, B.W.S. Kolthammer, P. Legzdins, and J. D. Roberts, Inorg. Chem. 18 (1979) 2049.

281. F. H. Köhler, H. Hollfelder, and E. O. Fischer, J. Organomet. Chem. 168 (1979) 53.

282. E. Langer and H. Lehner, J. Organomet. Chem. 173 (1979) 47.

283. J. A. Gibson and B. E. Mann, J.C.S. Dalton (1979) 1021.

284. M. B. Hall and D. E. Sherwood, Jr., Inorg. Chem. 18 (1979) 2323.

285. H. Daamen, A. Oskam, D. J. Stufkens, and H. W. Waaijers, Inorg. Chim. Acta. 34 (1979) 253.

286. A. M. English, K. R. Plowman, I. S. Butler, E. Diemann, and A. Müller, Inorg. Chim. Acta 32 (1979) 113.

287. P. Brant, W. S. Mialki, and R. A. Walton, J. Am. Chem. Soc. 101 (1979) 5453.

288. M. V. Andreocci. C. Cauletti. C. Furlani, and R. B. King, Inorg. Chem. 18 (1979) 954.

289. Yu. M. Shulga, A. P. Pivovarov, V. D. Makhaev, and A. P. Borisov, J. Organomet. Chem. 164 (1979) 47.

290. I. Fragala, E. Ciliberto, G. Granozzi, and G. Deganello, J. Organomet. Chem. 182 (1979) 511.

291. A. P. Sadovskii, and E. A. Kravtsova, Koord. Khim. 5 (1979) 197.

292. W. C. Trogler, S. R. Desjardins, and E. I. Solomon, J. Am. Chem. Soc. 101 (1979) 2131.

293. T. M. McHugh, R. Narayanaswamy, A. J. Rest and K. Salisbury, J.C.S. Chem. Comm. (1979) 208.

294. H. Daamen, A. Oskam, and D. J. Stufkens, Inorg. Chim. Acta 32 (1979) 249.

295. G. Boxhoorn, D. J. Stufkens, P. Coolwijk, and A.M.F. Hezemans, J.C.S. Chem. Comm. (1979) 1075.

296. A. Caruanda and H. Kisch, Angew. Chem. Int. Ed. 18 (1979) 328.

297. R. W. Balk, D. J. Stufkens, and A. Oskam, Inorg. Chim. Acta 34 (1979) 267.

298. A.J.L. Pombeiro and R. L. Richards, J. Organomet. Chem. 174 (1979) 459.

299. D.M.P. Mingos, J. Organomet. Chem. 179 (1979) C29.

300. D. W. Clack and K. D. Warren, Inorg. Chim. Acta. 33 (1979) 35.

301. N. J. Fitzpatrick, and H. Nakasone, Rev. Latinoam. Quim. 10 (1979) 59.

302. N. J. Fitzpatrick, A. J. Rest, and D. J. Taylor, J.C.S. Dalton (1979) 351.

303. B.E.R. Schilling, R. Hoffmann, and J. W. Faller J. Am. Chem. Soc. 101 (1979) 592.

304. H. Daamen, J. M. Ernsting, and A. Oskam, Thermochim. Acta 33 (1979) 217.

305. H. Daamen, H. Van der Poel, D. J. Stufkens, and A. Oskam, Thermochim. Acta 34 (1979) 693.

306. J. A. Connor, J. A. Martinho-Simoes, H. A. Skinner and M. T. Zafarani-Moattar, J. Organomet. Chem. 179 (1979) 331.

307. J.C.G. Calado, A. R. Dias, and J.A.M. Simoes, J. Organomet. Chem. 174 (1979) 77.

172

308. S. Sostero, O. Traverso, P. DiBernardo, and T. J. Kemp. J.C.S. Dalton (1979) 658.

309. M. Czajlik and K. Florian, Zb. Ved. Pr. Vys. Sk. Tech. Kosiciach (1979) 249.

310. L. Flamigni, Radiat. Phys. Chem. 13 (1979) 133.

311. M. G. Felin, S. V. Mitrokhin, and A. F. Aerov, Khim. Tekhnol. Kozh. Mekhovogo Proizvod (1979) 88.

312. R. Davis, M. L. Webb, D. S. Millington, and V. Parr, Org. Mass Spectrom. 14 (1979) 289.

313. J. Müller, F. Lüdemann and S. Schmitt, J. Organomet. Chem. 169 (1979) 25.

314. M. R. Blake, J. L. Garnett, I. K. Gregor, and S. B. Wild, J. Organomet. Chem. 178 (1979) C37.

315. U. Koelle, W. Holzinger, and J. Mueller, Z. Naturforsch., B: Anorg. Chem. Org. Chem. 34B (1979) 759.

316. A. J. Carty, N. J. Taylor, A. W. Coleman, and M. F. Lappert, J.C.S. Chem. Comm. (1979) 639.

317. K. H. Jogun and J. J. Stezowski, Acta Crystallogr., Sect. B, B35 (1979) 2310.

318. C. Bianchini, A. Meli, A. Orlandini, and L. Sacconi, Inorg. Chim. Acta. 35 (1979) L375.

319. J. C. Calabrese, R. T. Oakley, and R. West, Can. J. Chem. 57 (1979) 1909.

320. R. E. Cobbledick, L.R.J. Dowdell, F.W.B. Einstein, J. K. Hoyano, and L. K. Peterson, Can. J. Chem. 57 (1979) 2285.

321. R. A. Jones, G. Wilkinson, A.M.R. Galas, and M. B. Hursthouse, J.C.S. Chem. Comm. (1979) 926.

322. M. R. Churchill and W. J. Youngs, J.C.S. Chem. Comm. (1979) 321.

323. M. R. Churchill and W. J. Youngs, Inorg. Chem. 18 (1979) 2454.

324. U. Schubert, M. Wiener, and F. H. Köhler, Chem. Ber. 112 (1979) 708.

325. E. O. Fischer, R.B.A. Pardy and U. Schubert, J. Organomet. Chem. 181 (1979) 37.

326. G. A. Sim, J. G. Sime, D. I. Woodhouse, and G. R. Knox, Acta Crystallogr., Sect. B35 (1979) 2403.

327. G. A. Sim, J. G. Sime, D. I. Woodhouse, and G. R. Knox, Acta Crystallogr., Sect. B35 (1979) 2406.

328. S. Jeannin and Y. Jeannin, J. Organomet. Chem. 178 (1979) 309.

329. G. A. Sim., D. I. Woodhouse, and G. R. Knox, J.C.S. Dalton (1979) 83.

330. J. L. Davidson, M. Shiralian, L. Manojlović-Muir, and K. W. Muir, J.C.S. Chem. Comm. (1979) 30.

331. H. Brunner, J. Wachter, and I. Bernal, Angew. Chem. 91 (1979) 920.

332. G. L. Hillhouse, B. L. Haymore, and W. A. Herrmann, Inorg. Chem. 18 (1979) 2423.

333. J. L. Atwood, R. Shakir, J. T. Malito, M. Herberhold, W. Kremnitz, W.P.E. Bernhagen, and H. G. Alt, J. Organomet. Chem. 165 (1979) 65.

334. O. Koch, F. Edelmann, and U. Behrens, J. Organomet. Chem. 168 (1979) 167.

335. R. L. De, J. V. Seyerl, L. I. Zsolnai, and G. Huttner, J. Organomet. Chem. 175 (1979) 185.

336. T. Debaerdemaeker, Acta Crystallogr., B35 (1979) 1686.

337. M. Louër, G. Simmoneaux, and G. Jaouen, J. Organomet. Chem. 164 (1979) 235.

338. J. L. Atwood, W. E. Hunter, R. D. Rogers, E. Carmona-Guzman and G. Wilkinson, J.C.S. Dalton (1979).

339. M. A. Adams, K. Folting, J. C. Huffman, and K. G. Caulton, Inorg. Chem. 18 (1979) 3020.

340. M.G.B. Drew, B. J. Brisdon, D. A. Edwards, and K. E. Paddick, Inorg. Chim. Acta 35 (1979) L381.

341. K. S. Chong, S. J. Rettig, A. Storr, and J. Trotter, Can. J. Chem. 57 (1979) 1335.

342. G. R. Clark, C. M. Cochrane, P. W. Clark, A. J. Jones, and P. Hanisch, J. Organomet. Chem. 182 (1979) C5.

343. G. R. Clarke, D. Hall and K. Marsden, J. Organomet. Chem. 177 (1979) 411.

344. A. A. Pasynskii, I. L. Eremenko, Yu. V. Rakitin, V. M. Novotortseri, V. T. Kalinnikov, G. G. Aleksandrov, and Yu. T. Struchkov, J. Organomet. Chem. 165 (1979) 57.

345. J. L. Petersen, R. K. Brown, J. M. Williams, and R. K. McMullan, Inorg. Chem. 18 (1979) 3493.

346. M. Y. Darensbourg, J. L. Atwood, R. R. Burch, Jr., W. E. Hunter, and N. Walker, J. Am. Chem. Soc. 101 (1979) 2631.

347. H. Vahrenkamp and E. Keller, Chem. Ber. 112 (1979) 1991.

348. R. J. Hoxmeier, C. B. Knobler, and H. D. Kaesz, Inorg. Chem. 18 (1979) 3462.

349. C. Couldwell, and K. Prout, Acta Crystallogr., B35 (1979) 335.

350. D. Van der Helm, R. A. Loghry, D. J. Hanlon, and A. P. Hagen, Cryst. Struct. Commun. 8 (1979) 889.

351. M. H. Chisholm, J. C. Huffman, and R. L. Kelley, J. Am. Chem. Soc. 101 (1979) 7615.

174

352. M. B. Hursthouse and K. M. A. Malik, Acta Crystallogr., <u>B35</u> (1979) 2709.

353. F. A. Cotton, B. E. Hanson, W. H. Ilsley, and G. W. Rice, Inorg. Chem. <u>18</u> (1979) 2713.

354. M. R. Churchill and F. J. Hollander, Inorg. Chem. <u>18</u> (1979) 161.

355. R. Bender, P. Braunstein, Y. Dusausoy, and J. Protas, J. Organomet. Chem. <u>172</u> (1979) C51.

356. J. Deutscher, S. Fadel and M. L. Ziegler, Chem. Ber. <u>112</u> (1979) 2413.