CHROMIUM, MOLYBDENUM AND TUNGSTEN

ANNUAL SURVEY COVERING THE YEAR 1973

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CONTENTS

Introduction

The survey this year was done in much the same manner as those of previous years. We have covered the primary literature directly from the respective journals from January 1, 1973 to December 31, 1973. However some of the less available journals as well as all patents were covered from Chemical Abstracts over the same time period. Therefore, the survey contains some late 1972 papers obtained in this manner and similarly excludes until next year late 1973 papers.

Doctoral dissertations are listed separately in this survey and were reviewed by abstract only.

Dissertations

Doctoral dissertations which have dealt wholly or in part with topics falling within the scope of this review may be ordered from University Microfilms, 300 North Zeeb Road, Ann Arbor, Michigan, 48106; the microfilm order number for each dissertation is included in the bibliography.

Lewis acid-base reactions at the oxygen atom in Mo(I) and Mo(0) carbonyl complexes with a variety of Group III Lewis acids have been examined by Alich.[1] An investigation of organometallic carbonyl magnesium compounds has been carried out by Ulmer.[2] Included in this study was $Mg[Mo(CO)_3(\pi-C_5H_5)]_2(py)_4$ which was established by an X-ray structure study to contain Mo-C-O-Mg bonding. Compounds of the type $M[(\pi-C_5H_5)Mo(CO)_3]_3$

(where M = In and Tl) have been prepared and characterized in a thesis by Schussler,[3] whereas the synthesis of $M[(\pi-C_5H_5)Mo(CO)_3]_2$ (M = Zn and Cd) has been reported by Hayes.[4] Durney[5] has studied the preparation of erbium transition metal carbonyl complexes, e.g., $Er[(\pi-C_5H_5)Mo(CO)_3]_3$. Germanium dibromide was reported to undergo an insertion reaction with $[(\pi-C_5H_5)Mo(CO)_3]_2$ by Scibelli.[6] Jacobson[7] has carried out kinetic studies of SO_2 insertion into transition metal-carbon sigma bonds in such species as $\pi-C_5H_5Mo(CO)_3R$ (R = alkyl or aryl group), while Covey[8] has reported a kinetic study of amine substitution in $Mo(CO)_5$(amine) complexes. A study of the solvolytic reactivity of [π-(aryl)chromiumtricarbonyl]alkyl derivatives and related analogs has been carried out by Albert.[9]

Hoxmeier[10] has examined the reaction of $(\pi-C_5H_5)_2MH_2$ (M = W or Mo) with $CH_3Mn(CO)_5$ which lead to complexes of the type $(\pi-C_5H_5)(CO)M-^{\mu}-C_5H_4-Mn(CO)_4$ as indicated by X-ray structural studies on the species where M = Mo. Oxidation and photochemical reactions of $[(\pi-C_5H_5)Mo(CO)_3]_2$ have been examined by Burkett.[11] The synthesis and chemistry of the metallocarborane derivatives $[(\pi-B_{10}C_2H_{12})M(CO)_3]^{-2}$ (M = Mo and W) have been reported by Dustin.[12]

New dialkylaminodifluorophosphine and perfluoro-1-methylpropenyl complexes of chromium, molybdenum and tungsten have been prepared by Zipperer,[13] while Korenowski[14] has reported new metal carbonyl complexes of tris(dimethylamino)phosphine and tris(dimethylamino)arsine. The preparation and spectral characterization of complexes of eleven and twelve atom carboranes containing a phosphorus or arsenic atom in the cage and Group VIB metal carbonyls are reported by Beer.[15] A number of monosubstituted complexes of the types, $M(CO)_5L$ (M = Cr, Mo) and <u>trans</u>-

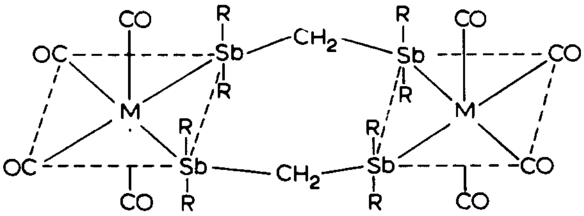
$M(CO)_4L_2$ (M = Cr, Mo, W) have been prepared by Kraus,[16] where L = tris(2-cyanoethyl)phosphine, bis(2-cyanoethyl)phenylphosphine, and 2-cyanoethyldiphenylphosphine. Reactions of $(CF_3P)_4$ with $M(CO)_6$ (M = Cr, W) in refluxing THF to form unstable species of the forms $(CF_3P)M(CO)_5(THF)$ and $(CF_3P)_2M(CO)_4(THF)$ are discussed in a thesis by Hill.[17] Coordination compounds of the unsymmetrical bidentate phosphine ligands $Ph_2PCH_2CH_2PPhR$ (R = Me, Et, i-Pr) of the Group VIB carbonyls have been prepared by Gaudio.[18] Seibold[19] has reported on the preparation and characterization of a large variety of dinitrogen complexes of molybdenum. Moser[20] has investigated the preparation of pentacarbonylmetal carbene complexes of chromium and tungsten employing pentachlorophenyllithium and ferrocenyllithium as well as other preparative reactions of chromium carbonyl derivatives. Reactions of phosphine ligands coordinated to molybdenum carbonyl derivatives have been studied by Bartish.[21] Conformational studies of some ditertiary arsine chelate complexes derived from the Group VIB hexacarbonyls have been reported by Ward.[22] White[23] has studied the use of Group VIB metal arene tricarbonyl derivatives as Friedel-Crafts catalysts. The reaction of SCN^- with $Cr(H_2O)_5R^{+2}$ ($R = CH_2Cl, CHCl_2$) to form $Cr(H_2O)_4R(NCS)^+$ has been investigated by Bushey.[24]

Mass spectral studies of the Group VIB hexacarbonyls as well as reactions of $Mo(CO)_6$ with substituted cyclopentadienes have been reported by Conville.[25] Bodner[26] has investigated the ^{13}C nmr spectra of a large variety of Group VIB transition metal organometallic compounds, while the ^{13}C nmr spectra of several series of ring-substituted phenyl amino and methoxy carbene complexes of Group VIB metal carbonyls have been observed by Kahl.[27]

Preparative

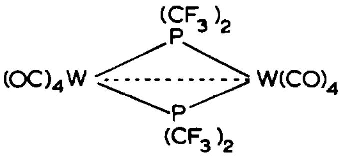
Lewis base derivatives of metal carbonyls. This year as in previous years the literature has many contributions dealing with the direct or indirect synthesis and characterization of substitution products of the Group VIB metal carbonyls. The synthesis and characterization of metal carbonyl complexes containing phosphorous-nitrogen donor bidentate ligands is described by Angelici.[28] Thus $M(CO)_4$ (M = Cr, Mo, W) derivatives of $Ph_2PCH_2CH_2NMe_2$, $Ph_2PCH_2CH_2NEt_2$, $Ph_2PCH_2C_5H_4N$, etc., were reported. A variety of Group VIB metal carbonyl derivatives of unsymmetrical bis tertiary phosphine ligands, $(C_6H_5)_2PCH_2CH_2P(C_6H_5)R$ (R = Me, Et, Pr^i), have been reported by Grim and coworkers.[29] The use of ^{31}P nmr was demonstrated to be extremely valuable in assigning structures to the possible species $[(C_6H_5)_2PCH_2CH_2P(C_6H_5)R]M(CO)_4$, $M(CO)_5[P(C_6H_5)_2CH_2CH_2\text{-}(C_6H_5)(R)P]M(CO)_5$, and $[P(C_6H_6)_2CH_2CH_2P(C_6H_5)R]M(CO)_5$. In the case of the latter species where a choice of ligands (diphenyl or (R)phenyl) might be attached to the metal it was concluded that the predominant factor, in determining which end was bound, is steric, e.g., for R = Me, the diphenyl end is free whereas for R = isopropyl, the isopropylphenyl end is free.

Complexes of ditertiary stibines of the types $M(CO)_5(Dpsm)$, $M(CO)_4(Dpsm)$, $[M(CO)_4(Dpsm)]_2$, and $Mo(CO)_3(Dpsm)_2$ (where M = Cr, Mo, W; Dpsm = $(C_6H_5)_2SbCH_2Sb(C_6H_5)_2$) have been prepared from thermal reactions of $M(CO)_6$, $M(CO)_4(NBD)$ and $Mo(CO)_3$(cycloheptatriene) with Dpsm, respectively.[30] These complexes were characterized by nmr and ir spectral measurements as well as molecular weight determinations. Similarly, tetracarbonyl complexes of bis(diarylstibino)alkane, $(R_2Sb)_2(CH_2)_n$ (n = 1; R = C_6H_5, p-$CH_3C_6H_4$ and n = 3; R = C_6H_5) in which the ligand acts as a bidentate ligand have been prepared.[31] Dimeric complexes of the form $\{M(CO)_4[(R_2Sb)_2CH_2]\}_2$ (I) (M = Cr, Mo; R = C_6H_5, p-$CH_3C_6H_4$) were obtained from substitution reactions of $M(CO)_4$(diene) (diene = 1,5-cyclooctadiene or 2,5-norbornadiene) with these ligands in chloroform. On the other hand, 1,3-bis(diphenylstibino)propane afforded the monomeric complexes $M(CO)_4$-$\{[(C_6H_5)_2Sb]_2(CH_2)_3\}$ (M = Cr, Mo, and W) in which $[(C_6H_5)_2Sb]_2(CH_2)_3$ binds to the metal as a chelating ligand.



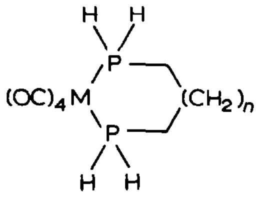
(I)

Formation of the fluorophosphine complexes, $W(CO)_5[P(CF_3)_2F]$ and $[W(CO)_4P(CF_3)_2]_2$ (II) was accomplished from a prolonged sealed tube reaction of $W(CO)_6$ and a equimolar quantity of $(CF_3)_4P_2$ at 175°.[32] Ir, ^{19}F nmr and mass spectral data for these complexes were reported and discussed.



(II)

The carbonyl-phosphine complexes of the Group VIB metal carbonyls, $Cr(CO)_5PH_2CRR^1OH$, (III) and (IV) have been prepared by treating mono- and diketones with $Cr(CO)_5PH_3$, $M(CO)_4(PH_3)_2$, and $Cr(CO)_{4-n}(PH_3)_{n+2}$, respectively in the presence of H_2O or base.[33]



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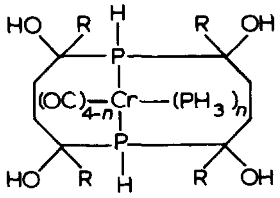
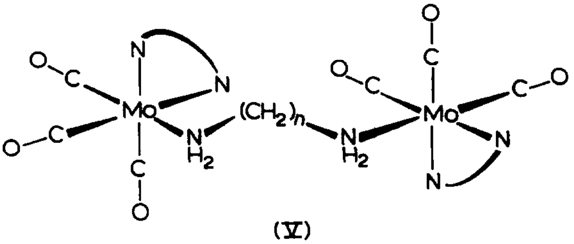


(IV)

(M = Cr, Mo, W)

The complexes cis-$(CO)_4M[As(CH_3)_2Cl]_2$ and cis-$(CO)_4M$-$[P(C_6H_5)_2Cl]_2$ (M = Cr, Mo) have been prepared from the corresponding Lewis bases and the $M(CO)_4(NBD)$ derivatives.[34] The arsine derivatives react with $NaMn(CO)_5$ to afford the cis-$M(CO)_4[As(CH_3)_2$-$Mn(CO)_5]_2$ complexes. Upon heating the chromium derivative to 110° in toluene the trans isomer was formed, whereas the molybdenum analog produced rearrangement products ($[(CO)_4Mn$-$As(CH_3)_2]_2$ and $(CO)_5Mo$-$As(CH_3)_2Mn(CO)_5$). Photolysis of $(CO)_4Fe$-$AsMe_2$-M' (M' = $Mo(CO)_3Cp$, $W(CO)_3Cp$, $Mn(CO)_5$, etc.) proceeds with loss of CO and formation of iron-metal bonds, e.g., $(CO)_4Fe[\mu$-$AsMe_2]Mo(CO)_2Cp$, etc.[35] The arsenic-bridged dinuclear starting complexes were prepared by reaction of $(CO)_4Fe\cdot AsMe_2Cl$ with the appropriate metalcarbonylates, NaM'.[36] Similar $(CO)_5Cr$-$AsMe_2$-M' complexes were also reported.[37]

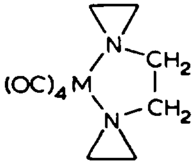
Reactions of the binuclear CO-bridged species $[Mo(CO)_3(bipy)]_2$ and $[Mo(CO)_3(phen)]_2$ with multidentate phosphorus ligands have been studied by Behrens and coworkers.[38] Reactions of these species in benzene solution with excess phosphorus ligands (L) (L = Ph_2PPPh_2, $Ph_2P(CH_2)_nPPh_2$ (n = 1-3), $Ph_2P(CH_2)_2$-$N(C_2H_5)_2$ and $CH_3C(CH_2PPh_2)_3$) form $Mo(CO)_3(bipy)L$ and $Mo(CO)_3(phen)L$ complexes. On the other hand reactions employing 1/1 stoichiometric quantities of L and the binuclear species led to production of complexes of the type $(bipy)(CO)_3MoLMo(CO)_3(bipy)$. Both the mononuclear and binuclear phosphorus substituted species were shown to exist as the facial isomers on the basis of ν(CO), ν(MoC) and δ(MoCO) spectral measurements. These workers have further studied the reactions of these binuclear CO-bridged molybdenum complexes with bidentate N-ligands, L.[39] For a reaction ratio of 1/1, where L = p-phenylenediamine and aliphatic diamines, binuclear complexes of the type $[Mo(CO)_3(bipy)]_2L$ (V) were produced; whereas, when L was employed in excess (reaction ratio of 1/2) facial mononuclear complexes of the type $Mo(CO)_3(bipy)L$ (L = o-, m-, p-phenylenediamine) were formed.



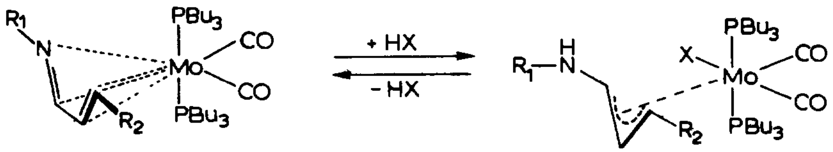
(V)

Complexes in which naphthyridine donors function as both mono- and bidentate ligands have been reported.[40] Complexes of the types $M(CO)_5(N\text{-}N)$, $M(CO)_4(N\text{-}N)$, and $M(CO)_3(N\text{-}N)_2$ (M = Cr, Mo, W and N-N = 1,8-naphthyridine(napy), 2-methyl-1,8-naphthyridine, or trans-decahydro-1,8-naphthyridine) were prepared and characterized by ir and ^1H nmr spectroscopy. In addition complexes of the type $Mo(CO)_3(N'\text{-}N')(napy)$ were prepared and characterized where N'-N' = 1,10-phenanthroline, 2,2'-bipyridine, 2,9-dimethyl-1,10-phenanthroline, or 2,7-dimethyl-1,8-naphthyridine.

When used as a simple ligand aziridine was found to form complexes of Cr, Mo, W of formula $M(CO)_{6-n}L_n$ (n = 1, 2, 3).[41] In the presence of aziridine and polar solvents such as THF/EtOH, <u>cis</u>-bis(aziridine)-tetracarbonylmetal compounds are found to undergo ligand rearrangement to produce a complex containing the chelate N-(2-aminoethyl)aziridine, (VI). In addition, cis-$(CH_3CN)_2Mo(PBu_3)_2(CO)_2$ has been observed to react with several 1-azabutadienes, $R_1N{=}CH{-}CH{=}CHR_2$, to yield 1-azabutadiene complexes of the form cis-$(R_1N{=}CH{-}CH{=}CHR_2)Mo(PBu_3)_2(CO)_2$ (VII).[42] These complexes were protonated by strong acids(HX) to yield the complexes (VIII). Ir and electronic spectra of these complexes and their butadiene analogs were reported and compared.



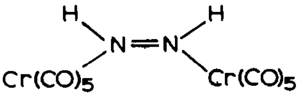
(VI)



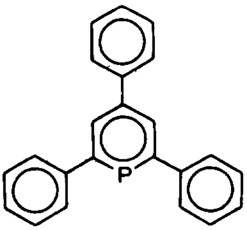
(VII)

(VIII)

The <u>cis</u> form of the diimine complex, $N_2H_2[Cr(CO)_5]_2$ (IX), has been prepared from the reaction of $N_2H_4[Cr(CO)_5]_2$ and $p\text{-}CH_3C_6H_4SO_2N_3$ in THF.[43] The complex was characterized by elemental analysis, molecular weight, ^1H nmr and ir spectra ($\nu(CO)$ occur at 2060 cm^{-1} ($A_1^{(2)}$) and 1905 cm^{-1} ($A_1^{(1)}$ + E)).



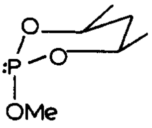
(IX)



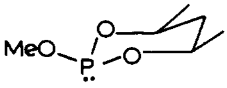
(X)

2,4,6-Triphenylphosphorine (X) Group VIB metal pentacarbonyl and tetracarbonyl complexes have been prepared from photochemical or ligand displacement (CH_3CN or C_7H_8) substitution reactions of $M(CO)_6$ or the corresponding substituted derivatives.[44] Ir, ^{31}P and ^{1}H nmr, electronic and mass spectral data are reported and compared with other mono- and disubstituted Group VIB carbonyl derivatives. It was concluded from these studies that coordination of phosphorine in these complexes occurs through the lone pair of electrons on the phosphorus atom and that the phosphorine system is best regarded as a weakly basic ligand.

Vande Griend and Verkade have prepared cis-$Mo(CO)_4L_2$ complexes, where L = the ring-locked isomeric phosphites (XI A and XI B), from stereospecific reactions of $Mo(CO)_4$(NBD) and L.[45] The ν(CO) values observed for the complex containing the phosphite (XI A) were higher than those of the corresponding complex of phosphite (XI B). This was ascribed to either the lower sigma basicity and/or better π acid properties of phosphite (XI A).



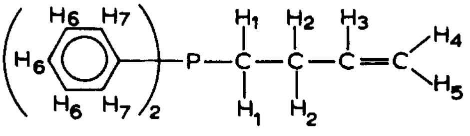
(XI A)



(XI B)

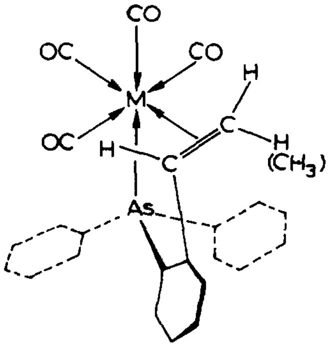
The preparation and properties of coordination complexes of ferrocenyldiphenylphosphine, diferrocenylphenylphosphine, and triferrocenylphosphine have been reported by Kotz and Nivert.[46] The ν(CO) $A_1^{(1)}$ and E vibrational frequencies were observed to decrease as the number of ferrocenyl groups increased in the $(Fc_xPh_{3-x}P)M(CO)_5$ series (M = Mo, W). This was interpreted as resulting from an increase in the σ donor ability of the ferrocenylphosphine ligands. ^{1}H nmr and preliminary cyclic voltametry studies on these complexes were also presented.

Unlike the reaction of Mvp(2-vinylphenyldiphenylphosphine) with $Mo(CO)_4(NBD)$ to yield $Mo(CO)_4(Mvp)$, the structurally similar ligand Mbp(3-butenyldiphenylphosphine) (XII) was found to react with $Mo(CO)_4(NBD)$ to give a mixture of cis and trans-$Mo(CO)_4(Mbp)_2$ where coordination is through the phosphorus atoms.[47] Further studies of the thermal and photochemical reactions involving Mbp, Dbp(di-3-butenylphenylphosphine) and Tbp(tri-3-butenylphosphine) with $Mo(CO)_6$, $Mo(CO)_4(NBD)$ and molybdenum tricarbonyl cycloheptatriene have been carried out. In contrast to the Mbp reaction, Dbp was observed to react with $Mo(CO)_4(NBD)$ to yield $Mo(CO)_4Dbp$ where coordination occurs through the phosphorus atom and a single olefin. Nmr and ir spectral measurements are reported for all complexes prepared in this study. In related work, Group VIB metal carbonyl derivatives of the analogous arsine ligands (o-vinylphenyl)diphenylarsine(SPA) and (o-vinylphenyl)dimethylarsine(SMA) were prepared of stoichiometry $M(CO)_4L$ and found to exist in isomeric forms such as XIII A and XIII B.[48]

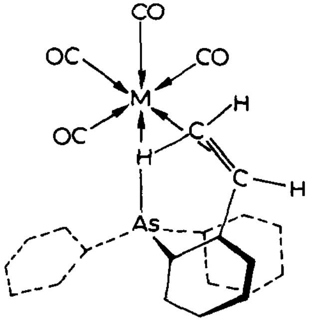


(XII)

$W(CO)_5(THF)$ has been observed to undergo THF displacement in the presence of hexaphenylcarbodiphosphorane ($[(C_6H_5)_3P]_2C$) to yield the complex $(CO)_5W\text{-}C[P(C_6H_5)_3]_2$.[49] In contrast, the in situ photolysis of $W(CO)_6$ and hexaphenylcarbodiphosphorane



(XIII A)



(XIII B)

M = Mo,W

resulted in formation of $(CO)_5W-C\equiv C-P(C_6H_5)_3$. The carbodiphosphorane ligand in $(CO)_5W-C[P(C_6H_5)_3]_2$ was readily displaced by triphenylphosphine to yield (triphenylphosphine)pentacarbonyltungsten. In the course of recrystallizing $W(CO)_5[C(PPh_3)_2]$, in an attempt to obtain crystals suitable for its structure determination, the hydrolysis product, $W(CO)_5(O{=}PPh_2CHPPh_3)$ was obtained.[50] Its structure indicated a bent (137°) W-O-P arrangement and three of the equatorial carbonyl ligands are slightly bent away from the phosphine oxide ligand.

Use of the $THF{\cdot}M(CO)_5$ (M = Cr, Mo, W) complex was also made in the preparation of derivatives of tellurides, $(OC)_5M-Te[M'Me_2]_2$, M' = Ge, Sn, and Pb.[51] Similarly an extensive list of selenide complexes, $(CO)_5MSe(M'Me_3)_2$ (M = Cr, Mo, W; M' = Ge, Sn, Pb), were prepared and characterized by ir, Raman, pmr, and chemical analysis.[52]

Tricarbonyl-tris(organometal phosphine)chromium and -molybdenum complexes have been prepared from the corresponding tris(acetonitrile)metaltricarbonyls (eq. 1).[53] Similarly tris(trimethyl-

$$(CH_3CN)_3M(CO)_3 + 3[(CH_3)_3E]_3P \rightarrow \{[(CH_3)_3E]_3P\}_3M(CO)_3 + 3CH_3CN \quad (1)$$

E = Ge, Sn; M = Cr, Mo

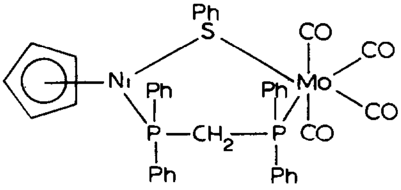
germyl)- and tris(trimethylstannyl)stibine pentacarbonyl Group VIB metal complexes have been prepared from photolysis of $M(CO)_6$ (M = Cr, Mo, W) in the presence of the free ligands.[54] Ir, Raman, and proton nmr spectra were presented and discussed.

Reactions of $M(CO)_6$ (M = Cr, Mo, and W) with di-tert-butyl sulfide, bis(trimethylgermyl)sulfide, bis(trimethylstannyl)sulfide, or bis(trimethylplumbyl)sulfide has led to the production of the corresponding pentacarbonyl(organometal sulfide)chromium(0), -molybdenum(0), or -tungsten(0) complexes.[55] The ir, Raman, and ^1H nmr spectra of these complexes were discussed.

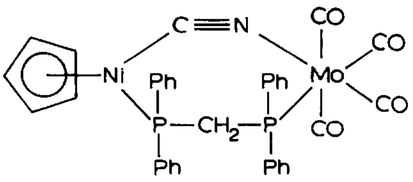
Ainscough and coworkers have reported the preparation of a series of complexes of the form $M(CO)_5L$ (where M = Cr, or W; L = Me_3PS, Me_2PhPS, $MePh_2PS$, Ph_3PS, Me_2PhPSe, Me_3AsS, or $Ph_2P(S)CH_2P(S)Ph_2$; M = Mo, L = Me_2PhPS; M = W, L = Ph_3AsO).[56] The chalcogenide ligands are readily displaced by CO and Ph_3P. Methylation reactions with methyl iodide resulted in formation of ionic species of the type, $[Me_2PhPSMe][M(CO)_5I]$. The infrared spectra in the $\nu(CO)$ region for these $M(CO)_5L$ complexes all showed a substantial splitting of the E mode vibration. Interaction between the substituted ligand (L) and the equatorial CO ligands was ruled out as a cause of this splitting on the basis of an X-ray crystal structure determination of the $Cr(CO)_5SPMe_3$ species.[57]

A further report on the preparation and infrared spectra of phosphine chalcogenide derivatives of chromium and tungsten carbonyls has appeared this year. Boorman and coworkers have studied compounds of the type $M(CO)_5L$, where M = Cr or W, and L = $Ph_3PS(Se)$, $Cy_3PS(Se)$, Me_3PS, and $(Me_2N)_3PS$.[58] From a comparison of the C-K force constants in these and related complexes (i.e., L = PPh_3 and $NH_2C_6H_{11}$) it was concluded that the chalcogenides do possess some π-acceptor character. However, the calculated force constants for these derivatives are clearly more similar to those of the non-π-acceptor ligand $NH_2C_6H_{11}$. In addition, phosphine sulfides (R_2HPS, R = Me, Et, Ph) were observed to react with photochemically prepared $LM(CO)_5$ (M = Cr, L = CH_3CN; M = Mo, L = THF) to yield the sulfur bound derivatives R_2HPS-$M(CO)_5$.[59] No hydrogen migration to yield the diorganylmercaptophosphine, phosphorous bound derivative (as is the case with M = Mn) was observed.

π-$C_5H_5NiPPh_2CH_2PPh_2(SC_6H_5)$ and π-$C_5H_5NiPPh_2CH_2PPh_2(CN)$ were found to react with $Mo(CO)_4(NBD)$ to afford the complexes π-C_5H_5Ni-μ-SPh-μ-$(PPh_2CH_2PPh_2)Mo(CO)_4$ and π-C_5H_5Ni-μ-CN-μ-$(PPh_2CH_2PPh_2)Mo(CO)_4$ (XIV A and XIV B), respectively.[60]



(XIV A)



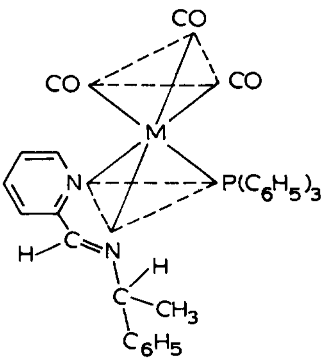
(XIV B)

The complexes $[M(CO)_4SCF_3]_2$ (M = Mo and W) have been prepared by photolysis of $M(CO)_6$ and CF_3SSCF_3 employing a filtered uv source.[61] The analogous chromium derivative was not obtainable either by photolysis or by thermal reaction at 370°K.

N,N-Dimethyldithiocarbamato(trimethyl)tin has been shown to be a useful reagent for the preparation of a variety of metal carbonyl complexes containing the dimethyldithiocarbamate ligand.[62] For example, the complex N,N-dimethyldithiocarbamato(π-cyclopentadienyl)dicarbonyltungsten, $(\pi$-$C_5H_5)W(CO)_2S_2CNMe_2$, has been prepared from 8 hrs of refluxing N,N-dimethyldithiocarbamato(trimethyl)tin and $(\pi$-$C_5H_5)W(CO)_3Cl$ in THF.

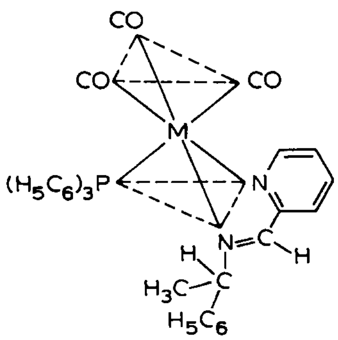
Reaction of $SnCl_2$ with $M(CO)_6$ (M = Cr, Mo, W) in a 1:2 molar ratio in THF has been reported to result in a loss of CO with concomitant formation of the complexes $Cl_2Sn[M(CO)_5]_2 \cdot nTHF$ complexes.[63] The ir spectra of these complexes were reported.

Brunner and Herrmann[64] have reported further studies on the preparation of optically active transition metal complexes. When $M(CO)_6$ (M = Cr, Mo, W) was reacted first with pyridine-2-carbaldehyde with (-)-α-phenylethylamine followed by additional CO substitution with $P(C_6H_5)_3$, the optically active complexes (XV A) and (XV B) were obtained upon fractional recrystallization.



(XV A)

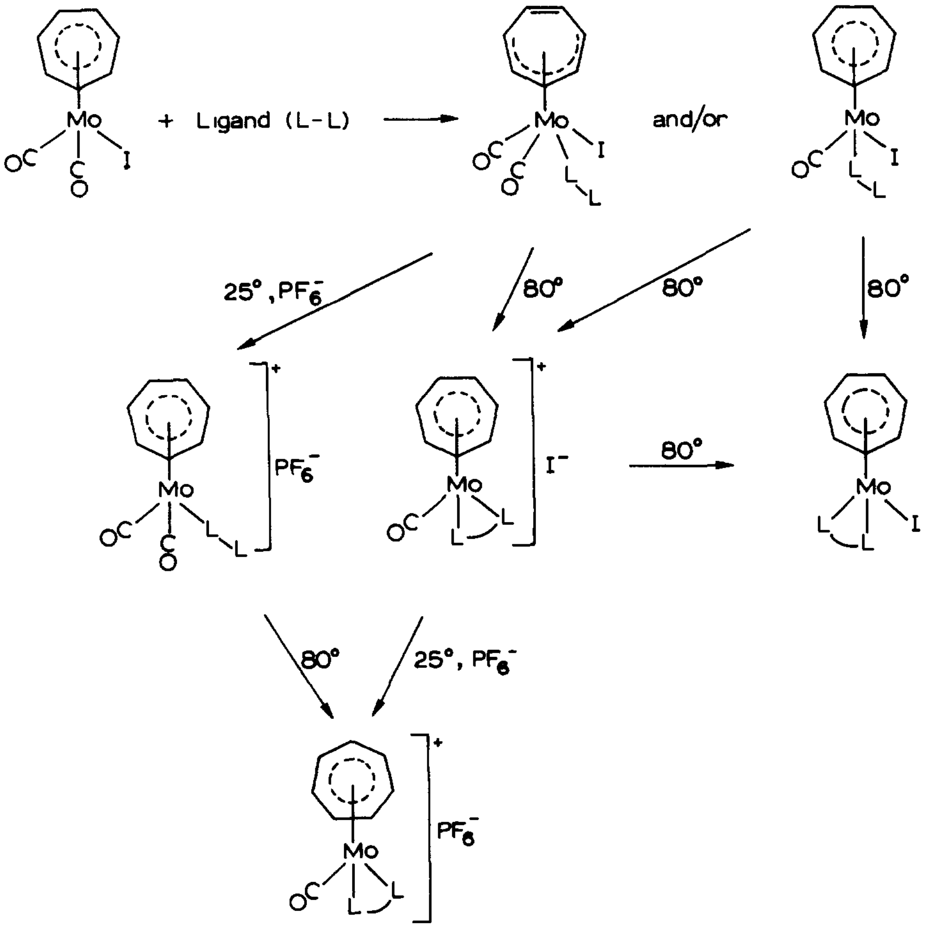
+



(XV B)

Stanclift and Hendricker have reported the synthesis of constrained phosphite esters of the type π-$C_5H_5Mo(CO)_2LX$ and π-$C_5H_5Mo(CO)L_2X$, where X = Cl, Br, or I and L = $P(OCH_2)_3CR$ (R = CH_3, C_2H_5, or C_3H_7).[65] Infrared and conductance data indicate that all compounds are covalent species in solution. The π-$C_5H_5Mo(CO)_2LCl$ complexes existed as inseparable mixtures of *cis* and *trans* isomers, whereas only the *trans* isomeric forms of the bromide and iodide were observed in solution. All of the π-$C_5H_5Mo(CO)L_2X$ complexes were shown by room temperature ^1H nmr studies to exist as the *trans* isomers in solution.

$PhW(CO)_3(\pi\text{-}C_5H_5)$ when photolyzed with PPh_3 or $P(OPh)_3$ in C_6H_6 has afforded the complexes $(\pi\text{-}C_5H_5)W(CO)_2Ph(PPh_3)$ and $(\pi\text{-}C_5H_5)W(CO)_2Ph[P(OPh)_3]$ in high yields.[66] In addition, treatment of $(\pi\text{-}C_5H_5)Mo(CO)_2Ph(PPh_3)$ with $P(OPh)_3$ gave a 40% yield of $(\pi\text{-}C_5H_5)Mo(CO)_2Ph[P(OPh)_3]$. Thermal reactions of $(\pi\text{-}C_5H_5)W(CO)_2PhL$ complexes ($L = PPh_3$, $P(OPh)_3$) with Ph_3P or $P(OPh)_3$, respectively were also reported.



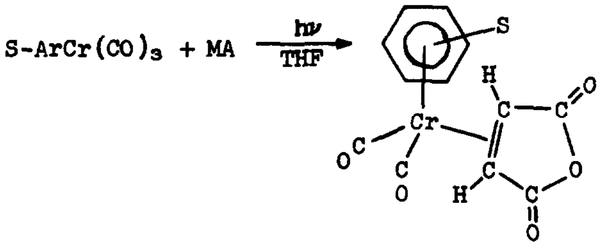
(XVI)

The effects of replacing one of the carbonyl ligands in $(PhCO_2CH_3)Cr(CO)_3$ and $(PhCO_2H)Cr(CO)_3$ with PPh_3, $P(OMe)_3$, or

$P(OEt)_3$ have been studied by Jaouen and Dabard.[67] $\nu(CO)$ vibrations in the ester derivatives were found to decrease in the order $CO > P(OMe)_3 > P(OEt)_3 > PPh_3$ as expected. The pK_a values of the acid derivatives were found to increase in the opposite order, $CO < P(OMe)_3 < P(OEt)_3 < PPh_3$. These effects were further studied in an additional publication by Jaouen and Simmoneaux.[68]

The reaction of cycloheptatrienylmolybdenum(I) dicarbonyl iodide with a variety of Group VA bidentate ligands yields various derivatives as shown in the Figure (XVI).[69] In addition, reaction of the parent molybdenum compound with the tritertiary chelating ligand $CH_3C[CH_2PPh_3]_3$ (triphos) was also investigated.

Various benzene substituted derivatives of arene chromium tricarbonyl have been prepared and photochemically reacted with maleic anhydride (MA), eq (2).[70] Ir spectra of the red,



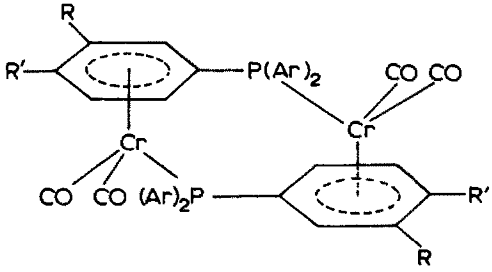
crystalline, thermally stable MA complexes characterize MA as a better electron-withdrawing ligand than CO.

Bowden, Colton, and Commons have shown that the discrepancies existing in the literature regarding solubility properties of $L_3M(CO)_3$ (M = Cr, Mo, W; L = PPh_3, $AsPh_3$) as prepared from reaction of (π-arene)$M(CO)_3$ complexes with L to be due to the formation of two different crystalline forms of $L_3M(CO)_3$.[71] It was also pointed out that $L_3M(CO)_3$ complexes readily disproportionate yielding $L_2M(CO)_4$ and non-carbonyl containing products; thus it is felt that $L_2M(CO)_4$ is not a primary product in the L/π-arene substitution reaction.

Cr is the more reactive member of the Group VIB family in reactions of $M(CO)_6$ with arylphosphines to yield complexes in which the phosphine is bonded to the metal through an arene ring rather than through phosphorus.[72] Ir was used to follow the course of reaction of $Cr(CO)_6$ with PPh_3, P(o-tolyl)$_3$ and P(p-tolyl)$_3$ in refluxing decalin, eq. 3.

$$L + Cr(CO)_6 \rightarrow Cr(CO)_5L \rightarrow \pi\text{-}LCr(CO)_3 \rightarrow [Cr(CO)_2L]_2 \qquad (3)$$

π-LCr(CO)$_3$ was not isolated; ir, nmr, and mass spectral data suggest the final product to be the dimer, (XVII).

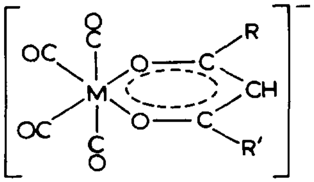


(XVII)

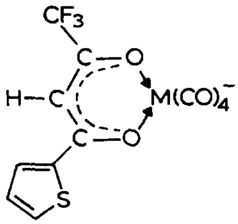
Use of (π-C_6H_5NHR)Cr(CO)$_3$ (R = H, Me) as an amine ligand towards $M(CO)_5$ moieties (M = Cr, Mo, W) has been reported.[73]

A large variety of new tetracarbonyl diketonate anions (XVIII) of chromium, molybdenum and tungsten have been synthesized by Doyle.[74] The most versatile preparative route involved refluxing a thallium(I) salt of the β-diketone with a metal pentacarbonyl halide [$M(CO)_5X^-$] in THF. ν(CO) values and C-K force constants were presented and discussed. The [$M(CO)_4$-(diket)]$^-$ anions were found to be very reactive and underwent oxidative elimination reactions with allyl chlorides and dimethyltin dichloride. Substitution reactions of the acetylacetonate derivatives (M = W, Mo) with Lewis bases (pyridine, P(OEt)$_3$, PPh_3 or P(n-Bu)$_3$) lead to the substitution products

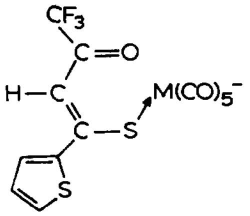
$[M(CO)_3L(acac)]^-$. The novel ligand β-diketone thenoyltrifluoroacetone (tta) and its monothio analogue (XIX and XX) have been characterized as to bonding properties towards zerovalent Cr, Mo, and W carbonyls.[75] Solutions of the S-bound pentacarbonyl evolve CO producing the bidentate ligand.



(XVIII)



(XIX)



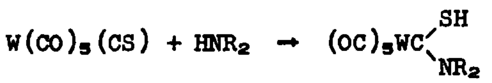
(XX)

Brown and coworkers have investigated preparations, magnetic properties, and ir and electronic spectra of a variety of Group VIB metal thiolates, $M(SR)_3$ [M = Mo or W; R = Me, Et, Bu, or Ph] and $W(\pi\text{-}C_6H_5Me)(CO)_2SMe$.[76] It was concluded that the $M(SR)_3$ compounds probably have polymeric chain structures with metal-metal interaction occurring between adjacent octahedra.

Complexes of the type $Mo(CO)_5L$ and $[\pi\text{-}C_5H_5Mo(CO)_2L]_2$ (L = aryl- or diarylthiourea) have been synthesized.[77] The infrared spectra of these species support the assumption that the aryl- or diarylthiourea ligands are bound to molybdenum via the sulfur atom. Frequencies in the ν(CO) region were reported.

The carboxylato compounds $(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)L$, where $L = O_2CH$, O_2CMe, O_2CPh, $O_2CCH_2Fe(CO)_2(\pi\text{-}C_5H_5)$, and related derivatives have been prepared starting from either $(\pi\text{-}C_6H_6)_2Mo$ or $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$.[78] The complexes where $L = NH_2CH_2CO_2$ or $NH_2[CH_2]_2S$ were prepared from the dimer and $NH_2CH_2CO_2K$ or $KS[CH_2]_2NH_2$, respectively. The latter complex was methylated by methyl iodide to give the cationic species $\{\pi\text{-}C_6H_6Mo(\pi\text{-}C_3H_5)\text{-}(MeS[CH_2]_2NH_2)\}^+$. β-Diketone derivatives where L = MeCOCHCOMe or MeCOCHCO(OEt) were also prepared from the reaction of the dimer, $[(\pi\text{-}C_6H_6)Mo(\pi\text{-}C_3H_5)Cl]_2$ and K(MeCOCHCOR), R = Me or OEt.

$M(CO)_5$ moieties have also proven useful in stabilizing the hitherto never isolated dimethylketimine, the imine analogue of acetone.[79] Thus reaction of $Na_2[M_2(CO)_{10}]$ (M = Cr, W) with $(CH_3)_2C(NO)Br$ yielded yellow crystalline $(CH_3)_2C{=}\underset{H}{N} \rightarrow M(CO)_5$. $M_2(CO)_{10}{}^{2-}$ (M = Cr, Mo, W) was also found by Angelici and Dombek to be an efficient reagent for reaction with thiophosgene, Cl_2CS, in the preparation of thiocarbonyl derivatives, $M(CO)_5CS$.[80] The yellow solids Cr- and $W(CO)_5CS$ are air, moisture, and thermally stable; the Mo derivative could not be isolated. Infrared ν(CO) values suggest the CS ligand to be a π-accepting ligand on the order of PF_3. Chemical reactivity studies indicate the CS ligand to be more labilizing than CO as well as more reactive towards nucleophilic addition (eq. 4).



$$W(CO)_5(CS) + HNR_2 \rightarrow (OC)_5WC\begin{smallmatrix} \diagup SH \\ \diagdown NR_2 \end{smallmatrix} \qquad (4)$$

The number of substituted halocarbonyls of Mo and W has been extended by Westland and Muriithi.[81] Thus $M(CO)_4X_2$ (X = Cl, Br) reacted with PEt_3, $P(OEt)_3$, $AsEt_3$, py and PhCN to form $M(CO)_xL_yX_2$. Fluoro derivatives of molybdenum and tungsten have been prepared by the metathetical displacement of Cl in $M(CO)_4Cl_2$

(M = Mo, W).[82] The yellow-orange $Mo(CO)_4F_2$ could be oxidized by XeF_2 to give the higher order derivatives $Mo(CO)_3F_3$, $Mo(CO)_4F_3$, and MoF_6. Similar treatment of $W(CO)_4F_2$ yields only WF_5 or WF_6.

The use of organometallics in the synthesis of strictly inorganic compounds continues to be explored.[83] Accordingly the reaction of $W(CO)_5Cl^-$ with WCl_6 in the presence of Cl^- was investigated in an attempt to prepare $W_2Cl_9^{3-}$. However, product mixtures were obtained, including, according to the stoichiometric conditions, $W_2Cl_9^{2-}$, $W_4Cl_{17}^{2-}$, $W(CO)_6$, $WCl_4(CO)_2$, $W(CO)_4Cl_3^-$, etc. On the other hand Delphin and Wentworth[84] were successful in the preparation of the dinuclear molybdenum halide anions according to a quite similar stratagem: (eqns. 5-7)

$$MoCl_6^{2-} + Mo(CO)_4Cl_3^- \rightarrow Mo_2Cl_9^{3-} + 4CO \qquad (5)$$

$$MoCl_5 + Cl^- \rightarrow MoCl_6^- \qquad (6)$$

$$MoCl_6^- + Mo(CO)_4Cl_3^- \rightarrow Mo_2Cl_9^{2-} + 4CO \qquad (7)$$

Another report along these lines indicates $W(CO)_6$ to be a uniquely suitable reducing agent for the preparation of WCl_4 from WCl_6 or WCl_5.[85] The WCl_4 was used in the subsequent preparation of WCl_4L_2, L = CH_3CN, C_2H_5CN, $(C_2H_5)_2S$, PPh_3.

Lee and Hester have reported an improved synthesis of $M(PF_3)_6$ derivatives (M = Cr, Mo, W) from $(PF_3)_3M(CO)_3$ and PF_3 photochemically.[86] The $(PF_3)_3M(CO)_3$ complexes were prepared from $C_7H_8M(CO)_3$ and PF_3 thermally. Raman and infrared spectral data were obtained throughout the 4000-50 cm^{-1} region which led to a complete vibrational mode assignment and normal coordinate analysis. In addition, a full analysis of the mass spectral fragmentation pattern was presented. An additional preparation of Group VIB hexakis(trifluorophosphine) complexes has been reported by Kruck and coworkers.[87] (π-allyl)$_3$Cr when reacted with PF$_3$ under pressure afforded Cr(PF$_3$)$_6$, whereas reaction of MoCl$_5$ or WCl$_6$ in the presence of copper and 200 atm. PF$_3$ gave Mo(PF$_3$)$_6$ and W(PF$_3$)$_6$, respectively.

Memering and Dobson have studied oxidative elimination reactions of Group VIB metal carbonyl derivatives with cyanogen iodide to form L$_2$M(CO)$_3$(CN)(I) (M = Mo, W; L = dipy, phen).[88] These complexes have been formulated as 7-coordinate molecular complexes on the basis of elemental analysis, infrared spectra in ν(CN) and ν(CO) regions, and conductivity measurements.

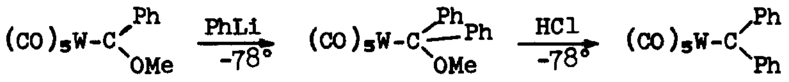
The reaction of Mo(CO)$_6$ with thiocyanogen, (SCN)$_2$, to yield a polymeric product, [Mo(CO)$_4$(SCN)$_2$]$_n$, has been investigated.[89] This material was found to be sensitive to moist air and to slowly decompose in the presence of water. It was assumed that the molybdenum is seven-coordinate in this species, analogous to the dimeric compound [Mo(CO)$_4$Cl$_2$]$_2$.

Rh[PPh$_3$]$_3$Cl abstracts CO from the acyl complexes π-C$_5$H$_5$M(CO)$_n$COR (M = Mo, n = 3, R = CF$_3$; M = Fe, n = 2, R = Me, Ph, etc.) and Mn(CO)$_5$COCH$_3$ at room temperature.[90] In the case of π-C$_5$H$_5$Mo(CO)$_3$COCF$_3$ the major Mo containing product was π-C$_5$H$_5$Mo(CO)$_2$[PPh$_3$]COCF$_3$; Rh[PPh$_3$]$_2$(CO)Cl was obtained in 100% yield.

Carbene and related complexes. Although some preparations of new carbene complexes have appeared, much literature in this area currently deals with compounds derived from reactions of carbene complexes.

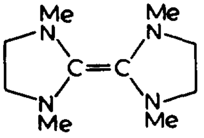
Significant in the synthesis of new carbene complexes was the first report by Casey and Burkhardt of a carbene ligand in which the carbene carbon atom is not attached to O, S, or N.[91]

The relatively thermally stable (diphenylcarbene)pentacarbonyltungsten(0) may be obtained as a black solid, mp 66°, according to the following reaction sequence (eq. 8):



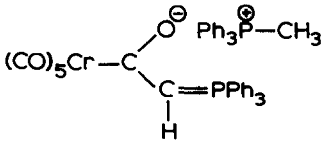
$$(CO)_5W{-}C\genfrac{}{}{0pt}{}{Ph}{OMe} \xrightarrow[-78^\circ]{PhLi} (CO)_5W{-}C\genfrac{}{}{0pt}{}{Ph}{OMe}{-}Ph \xrightarrow[-78^\circ]{HCl} (CO)_5W{-}C\genfrac{}{}{0pt}{}{Ph}{Ph} \qquad (8)$$

Lappert and coworkers have developed a general method of synthesis of transition-metal carbene complexes which involves displacement of a bound ligand by a nucleophilic carbene fragment produced from (XXI).[92] In this manner the Cr(0) dicarbene species, cis-$(OC)_4CrL_2$ (L_2 = (XXI)), was prepared.

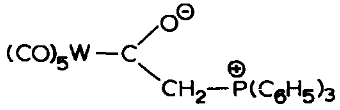


(XXI)

A 2/1 molar ratio of alkali halide free methylenetriphenylphosphorane and $Cr(CO)_6$ in THF has resulted in the formation of the addition product (XXII).[93] Complex (XXII) can be O-methylated in toluene using CH_3OSO_2F to give an ylide-carbene complex.



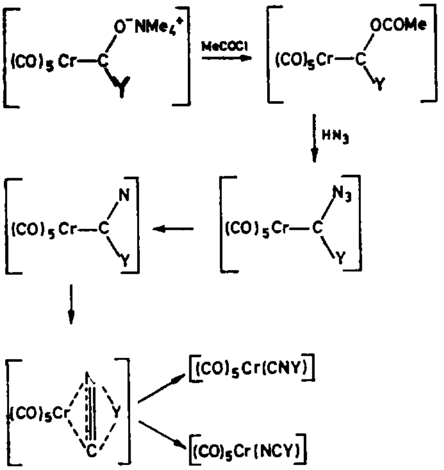
(XXII)



(XXIII)

Studies with a 1/1 molar ratio of alkali halide free methylenetriphenylphosphorane and $W(CO)_6$ show the initial product of the reaction to be (XXIII) which subsequently loses a proton to methylenetriphenylphosphorane to form the tungsten salt of (XXII).

Connor and Jones have reported the preparation and proton nmr studies of cyclopropylcarbene complexes $[(CO)_5CrC(X)C_3H_5]$ ($X = OH, OMe$, or NH_2).[94] Acetoxy-carbene complexes which would be anticipated from the reaction of $[(CO)_5CrC(O)Y]^-NMe_4^+$ ($Y = CH_2SiMe_3$ or C_3H_5) and acetyl chloride were inferred from their subsequent reaction with HN_3 to give $(YNC)Cr(CO)_5$ and $(YCN)Cr(CO)_5$ in a ratio 4:1, respectively. A mechanism (eq. 9)

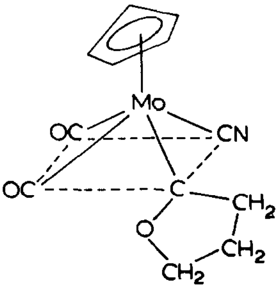


(9)

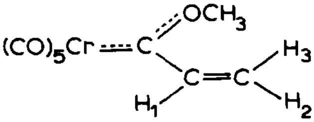
for this process was proposed. $(MeCONC)Cr(CO)_5$ was prepared in good yield (83%) from acetyl chloride and $Na[(CO)_5CrCN]$ in CH_2Cl_2. Reaction of the complex $[(Me_3CNC)Cr(CO)_5]$ with n-butyllithium followed by alkylation with Et_3OBF_4 gave the new carbene complex resulting from nucleophilic attack at a CO ligand rather than a isocyano-ligand, <u>cis</u>-$[(CO)_4(Me_3CNC)CrC(OEt)Bu]$, in high yield (87%).

Alkylation of $[Ph_4As][\pi\text{-}CpW(CO)_2(CN)(COR)]$ with Me_3OBF_4 yields 1:1 mixtures of the N-alkylated isonitrile complex, $\pi\text{-}CpW(CO)_2(CNMe)COR$, and the O-alkylated carbene complex, $\pi\text{-}CpW(CO)_2(CN)C(OMe)R$.[95] The starting acyltungstencarbonylates were prepared by reaction of $\pi\text{-}CpW(CO)_3R$ ($R = Me, Et$) with KCN in methanol. This latter nucleophilic reaction has been shown for Mo derivatives ($\pi\text{-}C_5H_5Mo(CO)_3R$, $R = CH_2Ph, Et, [CH_2]_3CN$)

to yield the *cis* cyanoacyl complexes stereospecifically.[96] This is followed by *cis*-*trans* isomerization of the thus formed $K[\pi\text{-}CpMo(CO)_2(CN)COR]$. Somewhat similar carbene complexes were formed in the reaction of (3-bromopropyl)tricarbonyl(π-cyclopentadienyl)molybdenum with KCN which was observed to yield the *trans*-isomer of dicarbonylcyano(π-cyclopentadienyl)(2-oxacyclopentylidene)molybdenum (XXIV).[97] This oxacarbene complex was shown to be formed *via* the intermediate $K[\pi\text{-}C_5H_5Mo(CO)_2(CN)\text{-}(COCH_2CH_2CH_2Br)]$, followed by an intramolecular O-alkylation. In addition, *cis* and *trans* isomers of $K[\pi\text{-}C_5H_5Mo(CO)_2(CN)\text{-}(CH_2CH_2CH_2CN)]$ were also prepared.



(XXIV)

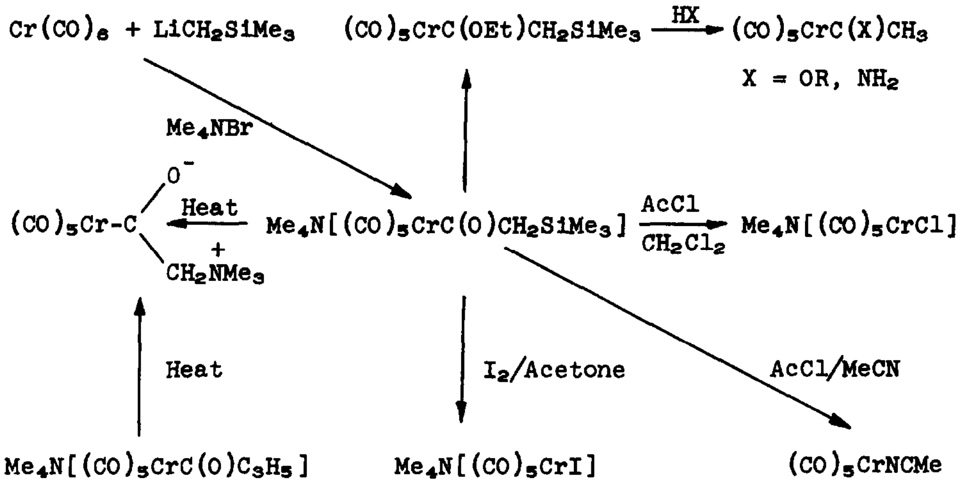


(XXV)

The preparation and complete characterization of vinylmethoxycarbene-pentacarbonylchromium (XXV) have been reported by Wilson and Fischer.[98] Mass spectral data indicated the presence of the $CrCH(CH{=}CH_2)$ grouping. ^1H and ^{13}C nmr studies indicated an increase in electron density at the carbene carbon atom, and therefore stabilization of the carbene carbon atom, as compared with the corresponding methylmethoxycarbene derivative. A warning as to the use of $Me_3O^+BF_4^-$ in CH_3CN as an alkylating agent was given, since such systems are known to form stable $[RC\equiv NR']BF_4$ salts.

Connor and Jones have reported the synthesis and characterization of the compounds $(CO)_5CrC(X)CH_2SiMe_3$ ($X = O^-NR_4^+$

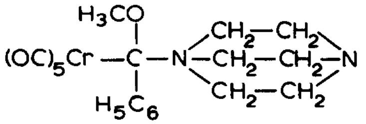
(R = Me, Et) and OEt).[99] The set of reactions of these complexes listed below were investigated and discussed.



The trimethylpropane phosphine ester (L) derivative of $M(CO)_4C(OEt)R$ (M = Cr, Mo, W; R = Me, Ph) have been prepared by reaction of $M(CO)_5L$ with the appropriate RLi and subsequent alkylation of the anion thus produced giving the air-stable yellow to orange solids.[100] The carbene ligand is found to be cis to the phosphine ester except for $Cr(CO)_4(P(OCH_2)_3CC_2H_5)$-C(OEt)Ph which is prepared as a mixture of cis and trans isomers. Aminolysis to yield $M(CO)_4[C(NHR')R]L$ ($R' = C_6H_{11}$, H) proceeds only at -78°; at room temperature there is no reaction.

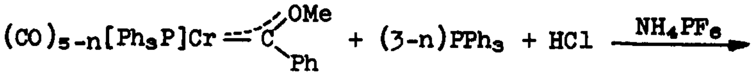
Hydroxymethyl- and hydroxyphenylcarbenepentacarbonyl complexes of chromium and tungsten have been prepared from reaction of HBr with $(OC)_5MC(OLi)R$ (M = Cr, Mo; R = CH_3, C_6H_5) in H_2O by Fischer and coworkers.[101] Ir, ^1H and ^{13}C nmr spectral data were presented for these complexes.

A large number of reactions investigated in carbene chemistry dealt with probing the electrophilicity of the metal bound carbene carbon atom. Thus, phenylmethoxycarbenepentacarbonylchromium(0) formed an adduct with 1,4-diazabicyclo[2.2.2]octane in Et_2O which was isolated as a yellow crystalline powder in 65% yield.[102] The adduct is regarded as a nitrogen ylide complex, (XXVI). Analogous phosphorus ylide



(XXVI)

complexes were prepared by reacting PX_3 (X_3 = Me_3, Et_3, Bu_3, Me_2H) with $(CO)_5M[C(Y)R]$ (M = Cr, Y = OMe, R = Ph; M = W, Y = OMe, R = Me; M = W, Y = SMe, R = Me) yielding $(CO)_5M\text{-}C(Y)(PX_3)R$.[103] In contrast triphenylphosphine reacts with phenylmethoxycarbenechromiumpentacarbonyl or its cis-triphenylphosphinechromiumtetracarbonyl analogue in the presence of HCl to produce phosphonium salts according to eq. 10.[104]

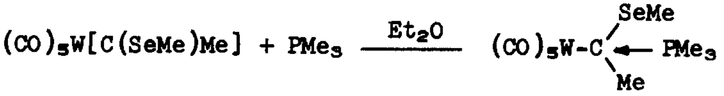


$$(CO)_{5-n}[Ph_3P]Cr{=}C{<}^{OMe}_{Ph} + (3-n)PPh_3 + HCl \xrightarrow{NH_4PF_6}$$

$$[Ph_3P\text{-}CH(OMe)Ph]^+PF_6^- + (CO)_4Cr(PPh_3)_2 + (1-n)CO \qquad (10)$$

The mechanism of this interesting reaction remains undefined.

Pentacarbonylchromium(0) and -tungsten(0) derivatives of (1-bromoethyl)methylsulfide resulted from addition of HBr to the appropriate thiocarbene complex, $M(CO)_5C(SMe)Me$ and subsequent rearrangement of the adduct thus formed.[105] This type of rearrangement had previously been noted from a somewhat similar reaction of $(CO)_5MC(OMe)Me$ with HSePh thus yielding the selenide, $(CO)_5MSe(Ph)[C(OMe)Me]$. On the other hand Fischer et al. were able to obtain the unrearranged selenocarbenes, pentacarbonyl[methyl(methylseleno)-carbene]chromium(0) and -tungsten(0) as air- and light-sensitive dark purple crystals, by reacting the corresponding methoxycarbene complex with methyl-selenol, $HSeCH_3$.[106] The W complex reacts with Me_3P at low temperatures according to eq. 11.

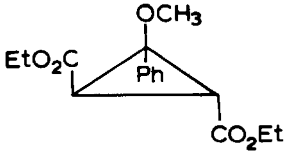


$$(CO)_5W[C(SeMe)Me] + PMe_3 \xrightarrow{Et_2O} (CO)_5W\text{-}\overset{SeMe}{\underset{Me}{C}} \leftarrow PMe_3 \qquad (11)$$

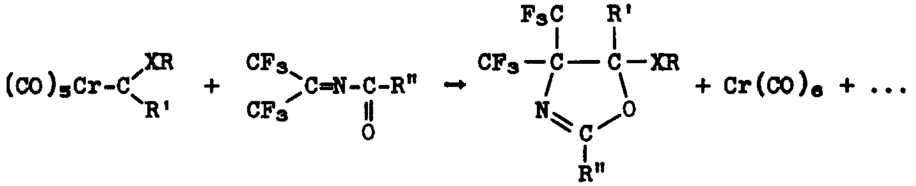
The reactions of the carbene Group VIB metal complexes, $(CO)_5MC(X)C_6H_4Y$ (X = OMe, NC_nH_{2n} (n = 2,4) and Y = p-OMe, p-Me, H, p-Cl) with R_3EH (R = alkyl, Ph and E = Si, Ge, Sn) in the presence of coordinating bases (pyridine, acetonitrile) to yield compounds of the type $R_3ECHXC_6H_4Y$ have been reported by Connor and coworkers.[107] A number of competition reactions involving $(CO)_5CrC(OMe)Ph$ and the various R_3EH species leading to the formation of $R_3SiCH(OMe)Ph$ were carried out, the order of reactivity being $Et_3SiH > Ph_3SiH < Ph_3GeH < Ph_3SnH$, Pr_3SnH (also see reference 244).

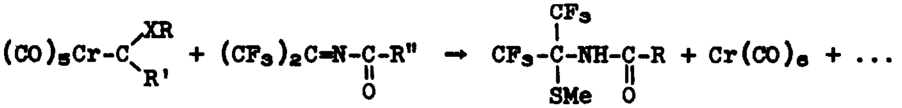
Crystalline HCl or HBr adducts of (aminocarbene)pentacarbonylchromium(0) or -tungsten(0) were formed at low temperatures and their various physical properties were studied.[108] These adducts were formulated as halometalcarbonyl salts of iminium cations, e.g., $[Me_2N{=}CHMe]^+[ClCr(CO)_5]^-$. A similar reaction of $(CO)_5Cr(OMe)Me$ with HI in Et_2O or hexane formed the dinuclear complex anion $Cr_2(CO)_{10}I^-$.[109] At higher temperatures and in the presence of an excess of triarylphosphine the reaction of methoxyphenylcarbene derivatives of Cr(0) with HCl yields phosphonium salts, $(R_3PCH(OMe)Ph)^+Cl^-$.[110] Fischer and Schubert assume α-chloroethers, ClCH(OMe)Ph, to be the primary reaction products.

The following reports illustrate investigations into the use of carbene complexes in organic and biochemical synthesis. Cooke and Fischer have shown through an elegant experiment employing the optically active metal-carbene complex [(-)(R)-methylphenylpropylphosphine]$Cr(CO)_4[C(OMe)Ph]$ that no free carbene is present in the synthesis of cyclopropanes from metal-carbene complexes.[111] A mixture of cis and trans-$Cr(CO)_4[P(CH_3)(Ph)(Pr)]C(OCH_3)Ph$ was found to react with diethyl fumarate at 40° for 6 hr to produce the optically active cyclopropane derivative (XXVII). Other reactions of the metal-bound carbene ligand RO(Ph)C:, RO(Me)C:, $Me_2N(Ph)C$:, and MeS(Me)C:, with N-acylimines of hexafluoroacetone were shown to proceed according to eqs. 12 and 13 yielding oxazoline derivatives for the oxa- and aminocarbene ligands and thioethers in the case of the thiocarbene ligand.[112]



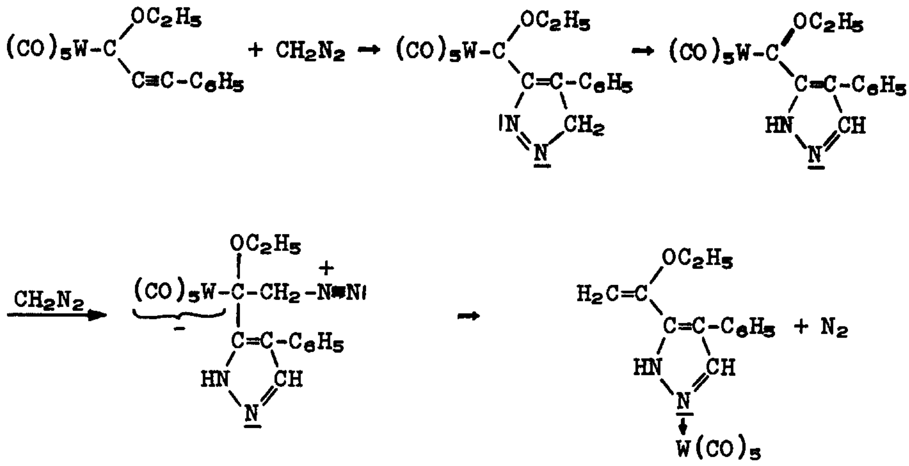
(XXVII)

 (12)

 (13)

$$(CO)_5Cr-C\begin{matrix}\nearrow XR\\ \searrow R'\end{matrix} + (CF_3)_2C{=}N-\underset{\underset{O}{\|}}{C}-R'' \rightarrow CF_3-\overset{\overset{CF_3}{|}}{\underset{\underset{SMe}{|}}{C}}-NH-\underset{\underset{O}{\|}}{C}-R + Cr(CO)_6 + \ldots \quad (13)$$

The reaction of phenylacetyleneethoxycarbene-pentacarbonyltungsten with diazomethane led to the formation of a pyrazole complex as end product (eq. 14).[113] ^{13}C and ^{1}H nmr spectra of the pyrazole complex were reported.

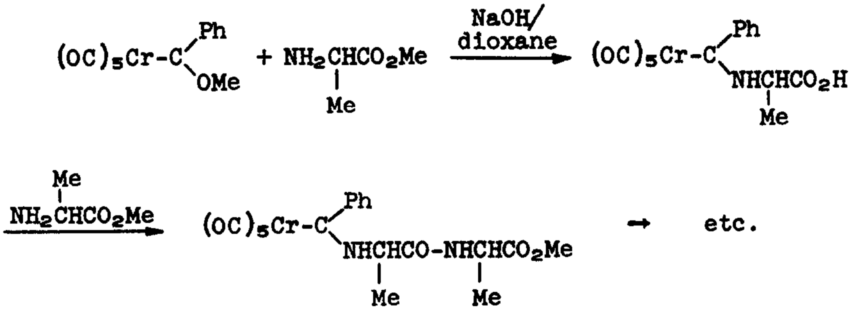


(14)

Connor and Lloyd have studied the reaction between mono-olefins and ferrocenylcarbene complexes of chromium.[114] $[(CO)_5CrC(X)Fc]$ (X = OMe, pyrrolidinyl; Fc = ferrocenyl) with dimethylfumarate afforded dimethyl, 3-ferrocenyl-3-methoxy-1, 2-cyclopropanedicarboxylate and dimethyl-5-[ferrocenyl(1-pyrrolidinyl)methyl]-3,4-bis(methoxycarboxyl)-2-hexenedioate, respectively. The carbene complex where X = pyrrolidinyl was found to react with $Ph_2C{:}CH_2$ to give 7% 3-ferrocenyl-1,1,5,5-tetraphenyl-3-(1-pyrrolidinyl)-1-pentene and 10% (3,3-diphenylpropionyl)ferrocene.

Fischer and Weiss have also investigated the possibility of using carbene complexes as amino protecting groups in peptide synthesis.[115] Eq. 15 illustrates the chemistry involved.

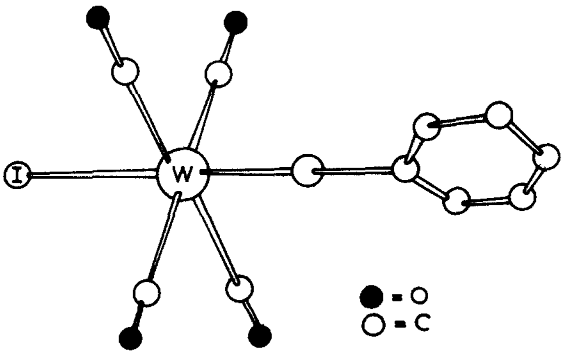
Several studies involving the carbene-like ligand, dicyanovinylidene were reported from the laboratories of R. B. King. Reaction of 2,2-cyanovinylchlorides $(NC)_2C{=}C(X)Cl$ (X = H, CN,



(15)

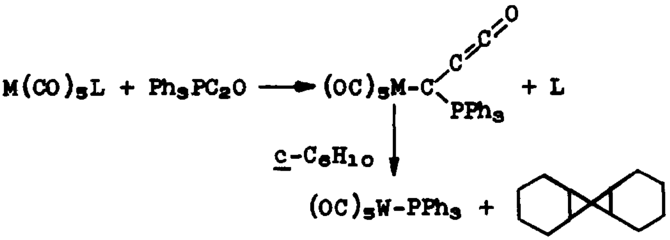
Cl) with sodium salts of metal carbonyl anions yields derivatives of the type $(NC)_2C{=}C(X)M(CO)_3(\pi\text{-}C_5H_5)$ (M = Mo, W), $(NC)_2C{=}C(X)Mn(CO)_5$, and $(NC)_2C{=}CHFe(CO)_2(\pi\text{-}C_5H_5)$.[116] Also obtained from the latter reaction mixture was $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ in which dicyanovinylidene (dicyanomethylenecarbene) acts as a bridging ligand. The preparations and characterization of these complexes are described. Further studies on the Mo and W complexes led to the preparation of $\pi\text{-}C_5H_5Mo(PPh_3)_2[C{=}C(CN)_2]Cl$ containing the $C{=}C(CN)_2$ moiety as a terminal ligand. Several other complexes containing various neutral L groups, $\pi\text{-}C_5H_5ML_2[C{=}C(CN)_2]Cl$ (M = Mo, W) as well as the cationic $\pi\text{-}C_5H_5Mo(triphos)[C{=}C(CN)_2]^+$ were also prepared.[117] No complex containing CO and $C{=}C(CN)_2$ simultaneously was prepared. This facet of the chemistry of complexes containing $C{=}C(CN)_2$ as well as the slight tendency for the group to bind terminally in the $(\pi\text{-}C_5H_5)_2Fe_2(CO)_3[C{=}C(CN)_2]$ complex has been discussed by King in terms of the expected superior π-acceptor ability and consequent labilizing ability of the ligand when bound terminally.[118]

An interesting new class of compounds containing a formal metal-carbon triple bond has been synthesized by Fischer, et al.[119] X-ray structure analysis of the product resulting from reaction of $W(CO)_5C(Ph)OMe$ with BI_3 confirmed the presence of the proposed "carbyne" ligand (XXVIII).



(XXVIII)

Finally, phosphorus ylide complexes of the type indicated in eq. 16 have been shown to readily decompose in the presence of cyclohexene to yield triphenylphosphinepentacarbonyltungsten(0) and 7,7'-spirobinorcarane via a carbene intermediate.[120]



(16)

M = Cr, W; L = CH_3CN. M = Mo; L = CO

<u>π-Cyclopentadienyl, π-arene, and other π-systems</u>. An extensive investigation of the generation and chemical reactivity of metallocene systems of the type $(\pi\text{-}C_5H_5)_2Mo$, $(\pi\text{-}C_5Me_5)_2Mo$ and $(\pi\text{-}C_5H_5)_2W$ has been presented by Thomas.[121]

The following are only a few of the reactions studied:

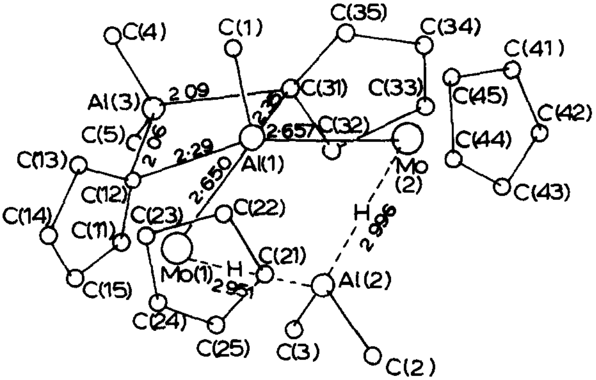
$$\begin{tikzcd}
 & MoCl_5 + 3NaC_5Me_5 + 2NaBH_4 \arrow[r] & (C_5Me_5)_2MoH_2 + \ldots \arrow[d, "CHCl_3"] \\
(C_5Me_5)_2MoH_2 & {[(C_5Me_5)_2Mo]_2} \arrow[l, "H_2"'] \arrow[dl, "CO"] \arrow[dr, "N_2"] & (C_5Me_5)_2MoCl_2 \arrow[l, "Na/Hg"'] \\
(C_5Me_5)_2Mo(CO) & & {[(C_5Me_5)_2Mo(N_2)]} \arrow[ll, "CO"']
\end{tikzcd}$$

Products of alkene and alkyne addition to the metallocenes were also investigated.

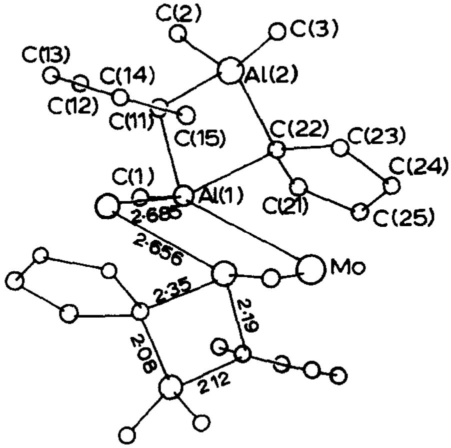
The composition of polynuclear π-cyclopentadienyl-sulfur-molybdenum complexes was shown to depend on the molar ratios of the starting reagents, $HMo(CO)_2(P(OPh)_3)(Cp)$ and propylene sulfide.[122] Thus $Cp_3Mo_3S_4$ and isomers of $Cp_2Mo_2S_4$ have been prepared. Mass spectrometry indicated the $Mo_3S_4^+$ unit of the former to be particularly stable.

Two novel compounds containing covalent molybdenum-aluminum bonds have been prepared from reaction of $(\pi\text{-}C_5H_5)_2MoH_2$ and trimethylaluminum dimer at 80° (XXIX and XXX).[123] Both compounds were characterized by single-crystal X-ray diffraction studies. They are pyrophoric in air, and readily hydrolyze to reform the parent dihydride species.

Other studies involving cyclopentadienyl hydrido complexes included those of Malisch of the reactions of ylides with $(\pi\text{-}C_5H_5)M(CO)_3H$, M = Cr, Mo, W.[124] The reactions may be regarded as acid-base interactions; for example, reaction with the ylide $Me_3P{=}CH_2$ produces the onium salt $Me_4P^+[(\pi\text{-}C_5H_5)\text{-}M(CO)_3]^-$. Similar reactions of $(\pi\text{-}C_5H_5)M(CO)_3E(CH_3)_3$ (M = Mo, W; E = Si, Sn) with ylides (e.g., $(CH_3)_3P{=}CH_2$) formed organosilicon or organotin substituted ylides (e.g., $(CH_3)_3P{=}CH\text{-}E(CH_3)_3$) as



(XXIX)



(XXX)

well as phosphonium-metal carbonyl salts (e.g., $[(CH_3)_4P]^+$-$[\pi\text{-}C_5H_5M(CO)_3]^-$).[125] A large variety of ylide species were studied.

The dimer, $[(\pi\text{-}C_5H_5)M(CO)_2Cl]_2$ (M = Mo and W), is the principal photochemical product obtained upon photolysis of $(\pi\text{-}C_5H_5)M(CO)_3Cl$ in dimethyl sulfoxide or pyridine solutions employing long wavelength irradiation ($\lambda > 400$ nm).[126] Further loss of CO from these dimers resulted upon irradiation with shorter wavelengths ($\lambda > 280$ nm) with concomitant incorporation of solvent. Photochemical reactions of $[(\pi\text{-}C_5H_5)M(CO)_2Cl]_2$ did not proceed in non-polar solvents. Under similar photolysis and solvent conditions the substituted complexes $[(\pi\text{-}C_5H_5)M(CO)_2LCl]$ (M = Mo or W; L = $P(OPh)_3$, PPh_3, or $P(C_6H_{11})_3$) were found to yield the dimer $[(\pi\text{-}C_5H_5)M(CO)_2Cl]_2$.[127] The mechanism for this process is proposed to involve loss of the ligand L in the primary photochemical process as shown in eqs. 17 and 18.

$$[(\pi\text{-}C_5H_5)M(CO)_2LCl] \xrightarrow{h\nu} [(\pi\text{-}C_5H_5)M(CO)_2Cl] + L \qquad (17)$$

$$2[(\pi\text{-}C_5H_5)M(CO)_2Cl] \longrightarrow [(\pi\text{-}C_5H_5)M(CO)_2Cl]_2 \quad \text{or} \qquad (18)$$

$$[(\pi\text{-}C_5H_5)M(CO)_2Cl] + [(\pi\text{-}C_5H_5)M(CO)_2LCl] \rightarrow$$

$$[(\pi\text{-}C_5H_5)M(CO)_2Cl]_2 + L$$

Eaborn and coworkers have reported the reactions of methyl fluorosulfonate and triethyloxonium tetrafluoroborate with a variety of transition-metal complexes.[128] Included in this study were the halogen abstraction reaction of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ with $MeOSO_2F$ to evolve MeCl and the oxidation reaction of $MoCl_2(diphos)_2$ with $MeOSO_2F$ to form $[MoCl_2(diphos)_2][SO_3F]$.

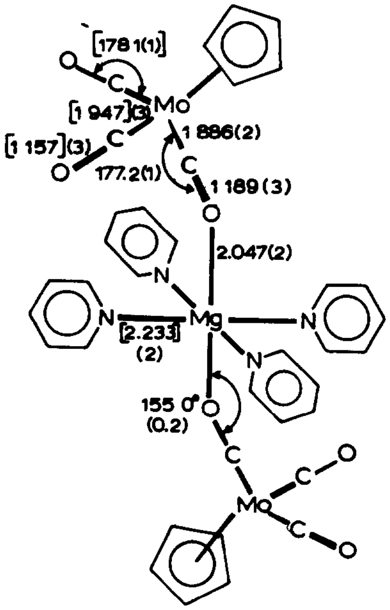
The preparation of some pentamethylcyclopentadienyl derivatives of chromium, molybdenum and tungsten has been described by King and coworkers.[129] Treatment of $[(CH_3)_5C_5M(CO)_3]_2$ (M = Cr, Mo) with sodium amalgam gave the anions $[(CH_3)_5C_5M(CO)_3]^-$ which further reacted with $(C_6H_5)_3SnCl$, $HgCl_2$ and $Hg(CN)_2$ to give the corresponding $(CH_3)_5C_5M(CO)_3R$ derivatives (R = $(C_6H_5)_3Sn$, ClHg, and 1/2 Hg). Reactions of $[(CH_3)_5C_5M(CO)_3]_2$ (M = Cr, Mo) with I_2 or NO gave $(CH_3)_5C_5M(CO)_3I$ and $(CH_3)_5C_5M(CO)_2(NO)$, respectively. $(CH_3)_5C_5M(CO)_3CH_3$ (M = Mo, W) was found to react with I_2 or SO_2 to give the complexes, $(CH_3)_5C_5M(CO)_3I$

and $(CH_3)_5C_5W(CO)_2I_3$, and $(CH_3)_5C_5M(CO)_3SO_2CH_3$, respectively. $(CH_3)_5C_5W(CO)_3(COCH_3)$ and its decarbonylated analog $(CH_3)_5C_5W(CO)_3CH_3$ were obtained from the reaction of acetylpentamethylcyclopentadiene and $(CH_3CN)_3W(CO)_3$ in boiling methylcyclohexane.

Finely divided lanthanide metals have been shown to react with a variety of transition-metal organometallic compounds resulting in cleavage of metal-metal or metal-halogen bonds.[130] For example, the metal-metal bond in $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ was found to be cleaved by Yb in refluxing THF, and Yb was found to instantly displace Hg from $\pi\text{-}C_5H_5Cr(CO)_3HgCl$ in THF at room temperature. Nesmeyanov and coworkers have studied symmetrization reactions of $(\pi\text{-}C_5H_5)M(CO)_nHgI$ to form $[(\pi\text{-}C_5H_5)M(CO)_n]_2Hg$ complexes.[131] This reaction was attained for M = Fe, n = 2 and for M = W, n = 3 by alkaline Na_2SnO_2; whereas, for M = Mo, n = 3 it was attained with either $Na_2S_2O_3$ or NaOH. $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$ was observed to react with Na_2SnO_2 to lose Hg and form $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$. In addition, these workers have shown that $(\pi\text{-}C_5H_5)M(CO)_3HgX$ complexes (M = Mo, W; X = halogen) react with Cl_2, Br_2, or I_2 to produce the complexes $(\pi\text{-}C_5H_5)M(CO)_3X$.[132] Halogenation reactions of $[(\pi\text{-}C_5H_5)M(CO)_3]_2Hg$ also afforded $(\pi\text{-}C_5H_5)M(CO)_3X$ complexes. A further report of the preparation of complexes of the type $(\pi\text{-}C_5H_5)M(CO)_3X$ has been published which involves heating of $(\pi\text{-}C_5H_5)M(CO)_3HgI$ with HCl in dioxane.[133]

$Me_4N[M^1\{M^2(CO)_3(\pi\text{-}C_5H_5)\}_2]$ salts (M^1 = Cu(I) and Ag(I), M^2 = Mo or W) have been obtained as stable solids from $Na[M^2(CO)_3(\pi\text{-}C_5H_5)]$ and copper(I) chloride or silver(I) nitrate.[134] The ir spectra of these complexes suggest linear $M^2\text{-}Ag\text{-}M^2$ bonding and that the $[(\pi\text{-}C_5H_5)M^2(CO)_3]^-$ ligands are poor π-acceptors.

Blackmore and Burlitch have prepared and characterized the first complexes of metal carbonyl O-coordinated to a transition metal.[135] In the presence of excess manganese metal $Hg[M(CO)_3C_5H_5]_2$ (M = Cr, Mo, W) in THF was found to react at room temperature to yield, upon recrystallization from pyridine, yellow crystals of $[C_5H_5Mo(CO)_3]_2Mn(py)_4$. The ir spectra of these new complexes contained three strong absorptions in the ν(CO) region (e.g., M = Mo, ν(CO) at 1905, 1808, and 1650). The presence of M-CO-Mn bonding was inferred from the one low ν(CO) vibration and the similarity of the ir spectra with that of $[C_5H_5Mo(CO)_3]_2Mg(py)_4$ (XXXI) which has been shown by X-ray crystallographic studies to contain Mo-CO-Mg bonding.[136] Both



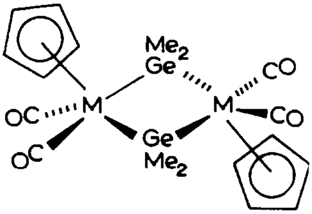
(XXXI)

in solution and in the solid state the Mg^{++} complexed CO experiences a ν(CO) shift to lower frequencies of ca. 60-90 cm^{-1} from the uncomplexed form. Similar derivatives of $[(\pi\text{-}C_5H_5)Fe(CO)_2]^-$, $Co(CO)_4^-$, and $Mn(CO)_5^-$ were also prepared.

Several Group IV derivatives of cyclopentadienyl complexes were prepared. The reaction of hexachlorodisilane with a variety of transition metal complexes has been investigated by Glockling and Houston.[137] Included in this study was the preparation of the known complex $Mo(CO)_3(\pi\text{-}C_5H_5)SiCl_3$ from $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and Si_2Cl_6. The preparation and photochemical reactivity of vinylsubstituted derivatives of metal carbonyls ($(CH_2{=}CHGeMe_2M(CO)_n$; $M = Mn(CO)_5$, $Mo(CO)_3(\pi\text{-}C_5H_5)$, $Co(CO)_4$, $Fe(CO)_3NO$, etc.) have also been reported.[138] The generally unstable σ-allylic complexes, isolated as oils or low-melting crystals, are quite photochemically active, however, no π-allylic complexes were produced upon irradiation. Instead scission of the Ge-M bond produced dimeric metal carbonyl species, for example, eq. (19).

$$CH_2{=}CHGeMe_2Mo(CO)_3(\pi\text{-}C_5H_5) \xrightarrow{h\nu} \pi\text{-}C_5H_5(CO)_2Mo{\equiv}Mo(CO)_2(\pi\text{-}C_5H_5) \quad (19)$$

Further photolysis studies of Me_2ClGeM complexes ($M = Mn(CO)_5$, $Co(CO)_4$, $Fe(CO)_2Cp$, $Mo(CO)_3Cp$, $Cr(CO)_3Cp$) produced more examples of complexes containing germanium bridged metal-metal bonds, (XXXII).[139]



(XXXII) M = Cr, Mo

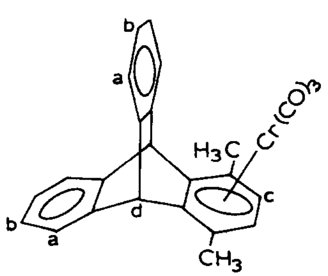
Abel and Dunster have studied the synthesis of organotin-transition metal carbonyl complexes from $(Me_3Sn)_2O$ and $(Me_3Sn)_3N$.[140] Employing this procedure the complex, $Me_3SnMo(CO)_3(\pi\text{-}C_5H_5)$, has been prepared from $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ and

$(Me_3Sn)_2O$ or $(Me_3Sn)_3N$ in 63 and 70% yields, respectively. Although the reaction of the tin acetylide, $Me_3SnC{\equiv}CPh$, with the Mo(0) species, $Mo(CO)_6$ and (norbornadiene)$Mo(CO)_4$, gave no reaction; the reaction of $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ with $Me_3SnC{\equiv}CPh$ in diglyme led to oxidative cleavage with the formation of $Mo(\pi\text{-}C_5H_5)(SnMe_3)(CO)_3$.[141]

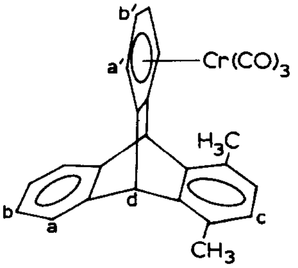
Several workers have utilized cocondensation techniques in the synthesis of bis(arene) derivatives. Thus the preparation and isolation of organochromium compounds such as bis-(cyclopentadienyl)-chromium and also bis(arene)chromium compounds in which the arenes contain highly electronegative substituents was reported.[142] Skell and coworkers also demonstrate the trimerization of alkynes and isomerization of alkenes by atomic chromium. Similarly, the synthesis of known bis-arenemolybdenum derivatives has been achieved in 10-20% yields from the cocondensation of molybdenum metal vapor with benzene, toluene, or mesitylene at 77°K.[143] Timms and coworkers also used this technique to prepare pure, solid bis(cumene)- and bis(m-di-isopropylbenzene)chromium by condensing chromium vapor with the arenes at -196°.[144] Similarly, stable complexes of the form $Cr(arene)(PF_3)_3$ (arene = benzene, hexafluorobenzene, cumene, or mesitylene) have been prepared from chromium vapor, PF_3 and the corresponding arene species. Relative intensities of some peaks in the mass spectra (obtained at 70 eV) for these complexes were reported. Timms has adapted the technique of the use of transition metal vapor in the chemical synthesis of organometallic compounds to an undergraduate laboratory experiment by describing the synthesis of dibenzenechromium.[145]

Several studies of substituted bis-arene complexes were reported. The behavior of microimpurities during the synthesis of organometallic compounds have been investigated. Included in this study was the preparation of $(EtPh)_2Cr$ from $CrCl_3$, Al, and EtPh in the presence of $AlCl_3$.[146] Infrared and proton nmr spectral studies on such $Mo(arene)_2$ complexes (arene = EtPh and $Et_2C_6H_4$) have indicated the presence of species of the types; $Mo(EtPh)(Et_2C_6H_4)$, $Mo(EtPh)_2$, and $Mo(Et_2C_6H_4)_2$. It was not possible to separate these various isomers by gas-liquid chromatography.[147] On the other hand separation of mixtures of bis arene π-complexes of molybdenum by distillation at reduced pressures has been achieved by Umilin and Tyutyaev.[148] In addition, autoxidation studies of bis(ethylbenzene)chromium to give 7% AcPh, 30% EtPh and an unstable solid described as $[(PhEt)_2Cr]_2CrO_4$ have been published.[149] Thermal decomposition reactions of $(arene)_2Cr$ phenolates have also been reported.[150] The pyrolysis probably occurs by disproportionation.

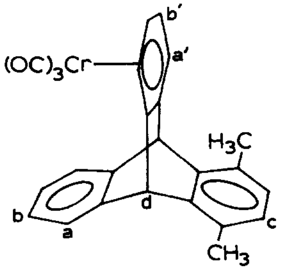
The following group of reports deal with π-arenes bound to $M(CO)_3$ groups. Tricarbonylchromium complexes of 9,10-dihydro-1,4-dimethoxy-9,10-o-benzenoanthracene and 9,10-dihydro-1,4-dimethyl-9,10-o-benzenoanthracene have been prepared.[151] The dimethoxy ligand forms two isomeric complexes, whereas the methyl substituted ligand forms three isomeric complexes (XXXIII A, B, C). The dimethoxy ligand complexes have been separated by both analytical and preparative scale



(XXXIII A)

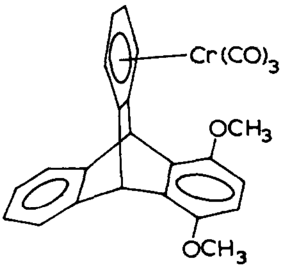


(XXXIII B)

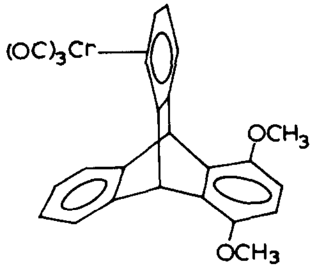


(XXXIII C)

liquid chromatography. Experiments with the nmr shift reagent $EuFod_3$ on these complexes indicate that structure XXXIV A is the predominant isomer, (65%) versus (35%) for isomer XXXIV B.

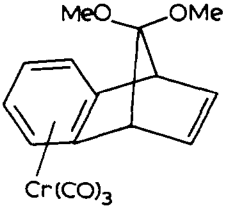


(XXXIV A)

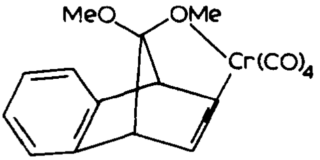


(XXXIV B)

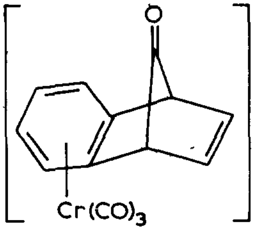
In attempts to synthesize benzonorbornadienone by acetal hydrolysis of 7,7-dimethoxybenzonorbornadiene, Wege and Wilkinson prepared tricarbonyl($\underline{h}^6$-7,7-dimethoxybenzonorbornadiene)chromium(0) (XXXV) in very low yield (1%) and ($\underline{h}^2$-7,7-dimethoxybenzonorbornadiene)$Cr(CO)_4$ (XXXVI) in 36% yield.[152] Hydrolysis of XXXV led only to (naphthalene)$Cr(CO)_3$ and naphthalene; the sought-after dienone (XXXVII) was not observed.



(XXXV)



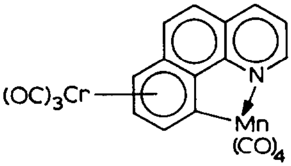
(XXXVI)



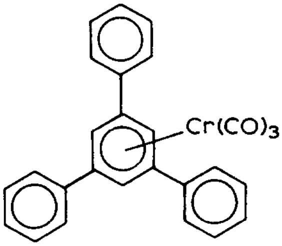
(XXXVII)

Reactions of benzo[h]quinoline (BqH) with a variety of transition metal carbonyl complexes have been investigated by Bruce, Goodall and Stone.[153] The reaction of BqH and $Mo(CO)_3(\pi\text{-}C_5H_5)Me$ led to the formation of a small quantity of an air-sensitive complex, which was thought to be $Mo(CO)_2Bq$-

(π-C_5H_5) on the basis of two strong ν(CO) bands, as well as a large quantity of $[Mo(CO)_3(\pi\text{-}C_5H_5)]_2$. Metallation of the $Cr(CO)_3$ π-complex of BqH was accomplished by heating this complex with $MeMn(CO)_5$, resulting in formation of complex XXXVIII. XXXVIII was isolated and fully characterized.



(XXXVIII)

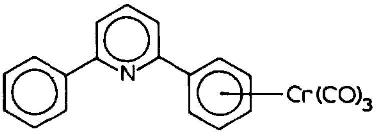


(XXXIX)

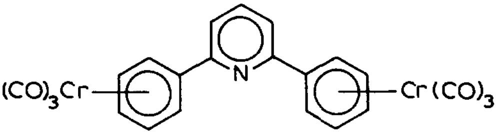
1,3,5-Triphenylbenzene (TPB) complexes of the form, $(TPB)[Cr(CO)_3]_n$ n = 1-3 , have been prepared from the reaction of 1,3,5-triphenylbenzene and $Cr(CO)_6$ in boiling dibutyl ether.[154] ^1H nmr studies were employed in establishing the mode of bonding of the $Cr(CO)_3$ group to the TPB ligand. In the $(TPB)Cr(CO)_3$ complex the $Cr(CO)_3$ group is bound to the central benzene ring (XXXIX), whereas, in the $(TPB)[Cr(CO)_3]_n$ (n = 2, 3) the $Cr(CO)_3$ groups are π-bonded to the phenyl rings. Further work by Nöth and Deberitz on the interaction of 2,4,6-triphenylphosphorine with derivatives of the Group VI metals led to the preparation of tricarbonyl(2,4,6-triphenyl-h^6-phosphorine)molybdenum(0).[155] An accompanying paper reported the crystal structure and nmr parameters of pentacarbonyl(2,4,6-triphenylphosphorine)chromium.[156]

(4-Phenylpyridine)$M(CO)_5$ (M = Cr, Mo, W) complexes have been prepared photochemically from 4-phenylpyridine and the corresponding $M(CO)_6$ compound.[157] Reaction of 2,6-diphenylpyridine with $Cr(CO)_6$ in refluxing dibutylether gave

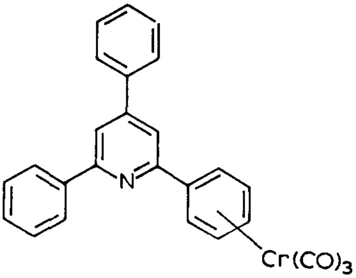
$C_{17}H_{13}N\cdot Cr(CO)_3$ (XL) and $C_{17}H_{13}N\cdot 2Cr(CO)_3$ (XLI). In an analogous manner 2,4,6-triphenylpyridine and $Cr(CO)_6$ gave $C_{23}H_{17}N\cdot Cr(CO)_3$, $C_{23}H_{17}N\cdot 2Cr(CO)_3$, and $C_{23}H_{17}N\cdot 3Cr(CO)_3$ (XLII A, B, and C). Ir, nmr, uv and mass spectral data were presented for these complexes. The bonding of the $Cr(CO)_3$ groups to the phenyl substituents was determined by nmr studies.



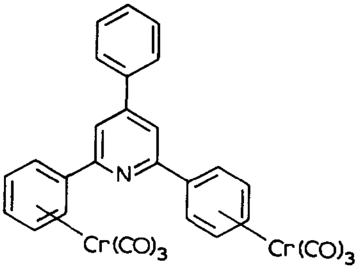
(XL)



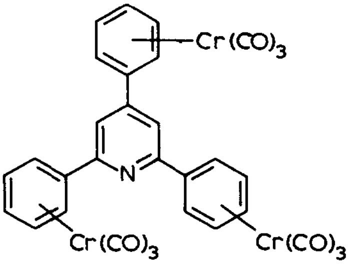
(XLI)



(XLII A)

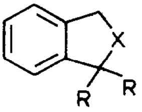


(XLII B)

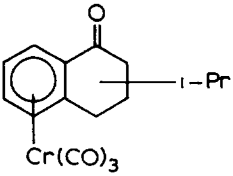


(XLII C)

The synthesis and ^1H nmr spectral properties of chromium tricarbonyl π-complexes of indan derivatives (XLIII) have been reported.[158] Transannular π-π-interactions in [2.2]metacyclophane, [2.2]paracyclophane, and 2,2'-spirobiindan have been investigated in the $-Cr(CO)_3$ derivatives of these π-ligands



(XLIII)



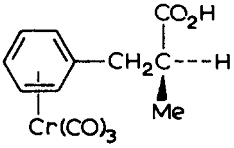
(XLIV)

R = H, Me; X = CH_2

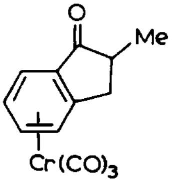
R = H; X = CMe_2, $SiMe_2$

by Langer and Lehner.[159] The exo- and endo-chromium tricarbonyl complexes (XLIV) (i-Pr at 2,3,4) have been prepared from the corresponding dihydroisopropylnaphthalenones with $Cr(CO)_6$.[160] When the isopropyl group was located at position 2 or 4 preferential formation of the endo form resulted, whereas when the isopropyl group was in position 3 the exo form was preferentially formed.

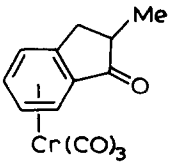
Studies involving mono-substituted π-arene complexes follow. Optically pure (S)-$PhCH_2CHMeCO_2Me$ when reacted with $Cr(CO)_6$ followed by saponification gave the optically pure acid (XLV).[161] Cyclization of this complex by polyphosphoric acid yielded two isomeric ketones (XLVI A and XLVI B) having an endo-exo ratio of 52:48. The absolute configuration of diastereoisomers (XLVI A and XLVI B) were determined.



(XLV)

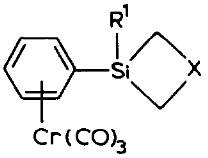


(XLVI A)



(XLVI B)

The synthesis of $Ph_3SnC_6H_5Cr(CO)_3$ from Ph_4Sn and $Cr(CO)_6$ in diglyme has been reported.[162] The Sn-Ph bond to the phenyl ring coordinated with $Cr(CO)_3$ was found to be more readily cleaved by acid or $HgCl_2$ than the uncoordinated phenyl groups. Similar organosilicon compounds of chromiumtricarbonyl have been prepared by reaction of Ph_nSiR_{4-n} (R = OH, halo, alkyl; n = 1-3) with $Cr(CO)_6$ in refluxing diglyme or in an autoclave at 160-70°.[163] The synthesis of π-arenetricarbonylchromium complexes containing silacyclobutane groups has also been reported.[164] These were prepared from $Cr(CO)_6$ and the corresponding silacyclobutane ligands (XLVII A and XLVII B) in dioxane-Bu_2O at 105° over a 40 hr period in the presence of $(C_8H_{17})_2NH$. Nmr spectral properties of these species were described.



(XLVII A) R' = Ph, X = CH_2

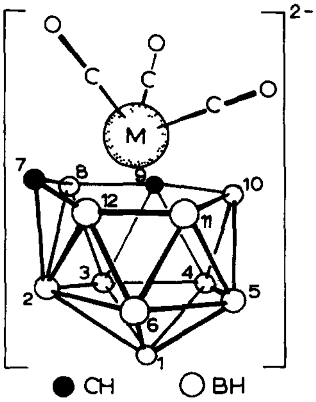
(XLVII B) R' = Me, X = $SiMe_2$

$(CO)_3CrC_6H_5HgCl$ was prepared in 43% yield from $C_6H_6Cr(CO)_3$ and $Hg(OAc)_2$ in refluxing ethanol followed by addition of $CaCl_2$.[165] The synthesis of $[(CO)_3Cr(XC_6H_4)]_2Hg$ complexes from $Cr(CO)_6$ and $(p\text{-}XC_6H_4)_2Hg$ (X = Me_2N, MeO, Me, H, F) has been described.[166] Spectral and reactivity studies of these species were discussed. A boron-substituted benzenechromiumtricarbonyl compound, $\underline{h}^6$-$(Ph_2B\text{-}C_6H_5)Cr(CO)_3$, was prepared by reaction of $Hg[(CO)_3CrC_6H_5]_2$ with Ph_2BBr.[167]

The chemistry of some less common π systems follows. Octamethylcyclotetraphosphazene molybdenumtricarbonyl has been synthesized and found by crystal structure analysis to be within bonding distance to 5-atoms (N-P-N-P-N) of the roughly planar P_4N_4 ring.[168] $B_{10}C_2H_{12}^{-2}$ is found to displace CO in $Mo(CO)_6$ and $W(CO)_6$ under photochemical conditions (eq. 20).[169] Details

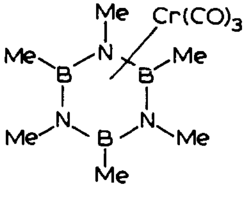
$$B_{10}C_2H_{12}^{2-} + M(CO)_6 \xrightarrow{h\nu} [(\pi\text{-}B_{10}C_2H_{12})M(CO)_3]^{=} + 3CO \qquad (20)$$

of the preparation and characterization of these as well as similar Fe, Co, and Ni derivatives are presented. The metallocarboranes are believed to assume "expanded" polyhedral structures containing 13 vertices. For example, the proposed structure of the extremely air-sensitive π-7,9-$B_{10}C_2H_{12}Mo(CO)_3$ and $W(CO)_3$ dianions is shown in Fig. XLVIII.

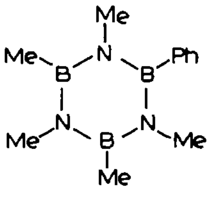


(XLVIII)

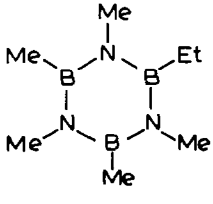
Adcock and Lagowski have extended the group of complexes containing a borazine bound to a $Cr(CO)_3$ moiety (XLIX A-D).[170]



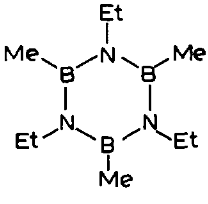
(XLIX A)



(XLIX B)



(XLIX C)

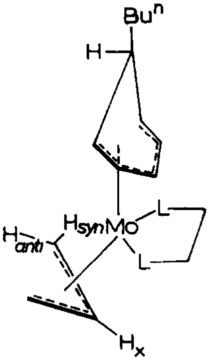


(XLIX D)

The borazine rings have a similar effect on $Cr(CO)_3$ $\nu(CO)$ values as does hexamethylbenzene and the effect is quite different from a purely σ-bound cyclic triammine. Based on analysis of vibrational spectra of the borazine rings as well as the electronic spectra of the complexes, the authors argue that the borazine ring is however puckered.

Several compounds of Mo and W containing π-allylic moieties have been studied. The dimers $[(arene)Mo(\pi\text{-}C_3H_5)Cl]_2$ have been prepared from the reaction of bis(arene)molybdenum (arene = benzene, toluene, and mesitylene) and allyl chloride.[171] Treatment of the π-allyl dimers with phosphines led to formation of the complexes $(arene)Mo(\pi\text{-}C_3H_5)(R_3P)Cl$. Reduction of these compounds with sodium borohydride in the absence of free, excess phosphine yielded the dihydride species, $(toluene)Mo(Ph_2MeP)_2H_2$ and $(arene)Mo(Ph_3P)_2H_2$. Treatment of these complexes with molecular nitrogen causes displacement of hydrogen and formation of dinitrogen derivatives $[(benzene)Mo(Ph_3P)_2]_2N_2$ or $(arene)Mo(PR_3)_2N_2$ (arene = MeC_6H_5 or sym-$Me_3C_6H_3$ and PR_3 = Ph_3P or Ph_2MeP). Solutions of either the dimeric or monomeric dinitrogen species react with CO to give the monomeric $(arene)Mo(PR_3)_2CO$ derivatives. Treatment of the compound $[(\pi\text{-}C_5H_5)Fe(dmpe)Me_2CO]^+BF_4^-$ in acetone with $(toluene)Mo(Ph_3P)_2N_2$ gave a brown solid which gave an elemental analysis consistent with the formation of the adduct $[(\pi\text{-}C_5H_5)Fe(dmpe)N_2(Ph_3P)_2Mo(MeC_6H_5)]^+BF_4^-$ (ν_{N_2} (Fe-N_2-Mo) = 1945 cm^{-1}).

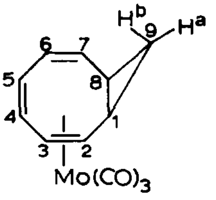
$[(RC_6H_5)Mo(\pi\text{-}C_3H_5)Cl]_2$ was observed to react in dry THF with excess allylmagnesium chloride to yield the bis-π-allyl derivatives $(C_6H_5R)Mo(\pi\text{-}C_3H_5)_2$ (R = H, Me); whereas reaction of the dimer with $C_4H_6/TlBF_4$ afforded the butadiene cation $[C_6H_6Mo(\pi\text{-}C_3H_5)C_4H_6]^+$.[172] Reaction of this cation with nucleophiles resulted in production of the neutral π-allylic derivatives $C_6H_6Mo(\pi-C_3H_5)(\pi-NuCH_2C_3H_4)$ (where Nu = CN, OMe, SMe, or H). Continuing these studies Green and coworkers found that the dimer $[C_6H_6Mo(\pi-C_3H_5)Cl]_2$ could be cleaved by chelating phosphorus or sulfur ligands (L_2) to afford the cations $[C_6H_6Mo(\pi-C_3H_5)L_2]^+$, where L_2 = $Ph_2PCH_2CH_2PPh_2$, $Me_2PCH_2CH_2PMe_2$, or $(MeSCH_2)_2$.[173] These cationic species were found to react with nucleophiles (CN^-, $LiAlH_4$, and n-BuLi) to give the neutral cyclohexadienyl derivatives $[(C_6H_6R)Mo(\pi-C_3H_5)L_2]$ (R = CN^-, H^-, and n-Bu^-). These species are shown by ^1H nmr spectra at 270 MHz and double-resonance experiments to possess asymmetric structures (e.g., L). The cations $[(C_6H_5R')Mo(\pi-C_3H_5)L_2']^+$ (R' = H or Me and L_2' = en, bipy, and o-phenylenediamine) were also reported.



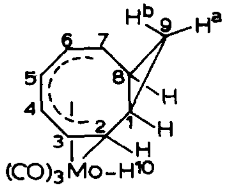
(L)

Organotin compounds such as allyltrimethyltin, cyclopentadienyltrimethyltin, and indenyltrimethyltin have been found to react with a variety of metal carbonyl compounds under very mild conditions to afford high yields of the corresponding π-enyl metal carbonyl derivatives.[174] Included in this study are the preparations of $(\pi-C_3H_5)(\pi-C_5H_5)M(CO)_2$ (M = Mo, W), $(\pi-C_7H_7)(\pi-C_5H_5)Mo(CO)_2$, and $(\pi-C_3H_5)(\pi-C_9H_7)Mo(CO)_2$.

Proton addition to bicyclo[6,1,0]nonatrienetricarbonylmolybdenum (LI) with HSO_3F-SO_2F_2 at -120° has been reported to result in a π to σ change in the nature of the bonding of the triene to the metal, producing species (LII).[175]

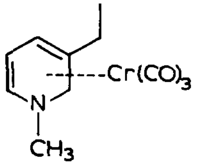


(LI)

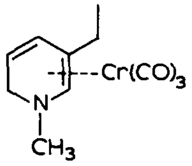


(LII)

The use of organometallic fragments to isolate an unstable π-electron system of biochemical significance has been reported.[176] Thus N-methyl-3-ethyl-1,2-dihydropyridinechromiumtricarbonyl as well as the 1,6-dihydropyridine derivative (LIII and LIV, respectively) have been synthesized and characterized by X-ray crystallography.



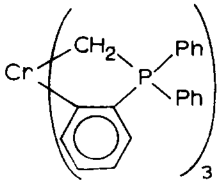
(LIII)



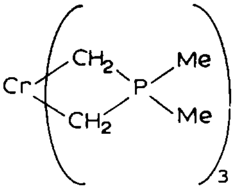
(LIV)

Metal-alkyl, -aryl, and -hydride complexes. The preparation and properties of hexamethyltungsten have been reported by Shortland and Wilkinson.[177] Hexamethyltungsten was isolated from the reaction of three equivalents of methyllithium with WCl_6 in diethylether. The very air-sensitive WMe_6 complex was characterized by elemental analysis, ir, nmr, and mass spectroscopy. Reaction of WMe_6 with nitric oxide gave tetramethyl<u>bis</u>(N-methyl-N-nitrosohydroxylaminato-)tungsten(VI) which was shown by nmr studies to be non-rigid at room temperature. Similarly, hexakis(neopentyl)dimolybdenum(III) was prepared from the reaction of neopentyllithium with $MoCl_5$ in ether.[178] A lower yield is observed when the complex was prepared from the corresponding Grignard reagent. This complex was observed to be rather inert.

Syntheses of several interesting chromium complexes involving metallation of phenyl or methyl groups were based on reactions of $R_3P{=}CH_2$ (R = Ph or Me) or $R_4\overset{+}{P}Cl^-$ with appropriate Cr-containing complexes ($Ph_3Cr(THF)_3$ or Li_3CrPh_6).[179] For example, complexes of the following types were prepared (LV and LVI):



(LV)



(LVI)

The direct synthesis of σ-bonded organochromium compounds of the type <u>cis</u>-bis(aryl)bis(2,2'-bipyridine)chromium(III) (aryl = 2-, 3-, and 4-methoxyphenyl, 4-methylphenyl and phenyl) from the appropriate arylmagnesium halide and $CrBr_2(THF)_2$ in the presence of bipyridine has been reported.[180] All the compounds were found to be paramagnetic to the extent of three unpaired electrons. In addition, bis(trimethylsilylmethyl)-bis-(2,2'-bipyridyl)chromium(III) iodide has been synthesized and its structure determined by X-ray analysis.[181] The Cr-C(sp^3) bond length was found to be 2.107(9) Å which is very similar to that observed in the aryl analog, $Ar_2Cr(bipy)_2^+$ (Ar = o-$MeOC_6H_4$ and Ph).

Distorted tetrahedral chromium(IV) alkyls, CrR_4 (R = CH_2CMe_3, CH_2CMe_2Ph, CH_2CPh_3, and CH_3), have been prepared and characterized by electronic, ir, and esr spectroscopy.[182]

Activation of a variety of transition metal-alkyl bonds by interaction with organoaluminum compounds has been demonstrated by Yamamoto and Yamamoto.[183] Included in this study was the activation of $Cr(C_2H_5)Cl_2Py_3$ by the addition of $Al(n\text{-}C_3H_7)_3$ to a THF solution of the complex to produce primarily ethane.

Studies of the formation of alkylchromium ions, $(H_2O)_5CrR^{2+}$, from $Cr(aq)^{2+}$ and organocobaloximes (Hdmg = dimethylglyoximate), indicate the rate of alkyl transfer to be highly dependent on the nature of R.[184] Mechanistic possibilities remain unresolved.

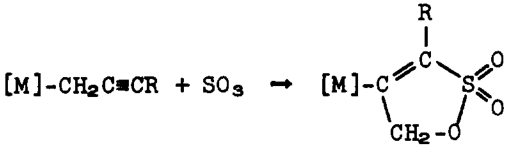
$$RCo(Hdmg)_2H_2O + Cr(aq)^{2+} + 2H^+ \rightarrow Co^{2+} + (H_2O)_5CrR^{2+} + 2H_2dmg \quad (21)$$

The preparation and characterization of cyclopentadienyl and indenyl complexes, R_4MoO (R = cyclopentadienyl, indenyl), from R_2MoOCl_2 or $MoOCl_4$ and RNa have been reported.[185] Reactions of R_2MoOCl_2 with phenols were discussed as well.

Several publications dealing with the preparations and reactions of metal carbonyl derivatives containing metal-alkyl bonds have appeared in the literature as well this year. King and Braitsch have reported the preparation of $ClCH_2M(CO)_3C_5H_5$ and $ICH_2M(CO)_3C_5H_5$ (M = Mo, W) from the corresponding sodium salts $Na[M(CO)_3C_5H_5]$ and $ClCH_2I$ or CH_2I_2, respectively.[186] These complexes were fairly inert to nucleophilic substitution reactions of the carbon-chlorine bonds. ν(CO) and proton nmr spectral data for these complexes were presented. Similarly, $\pi\text{-}C_5H_5Mo(CO)_3CH_2R$ (R = 1-naphthyl) has been prepared in 52% yield from $Na[(\pi\text{-}C_5H_5)Mo(CO)_3]$ and RCl in THF.[187] The complex was air-stable, however it was sensitive to light. Ir, uv, nmr, and mass spectral results were presented for this complex.

The first well defined example of a "carbon monoxide insertion" reaction of π-$C_5H_5Cr(CO)_3CH_3$ has been reported in the preparation of the yellow crystalline, stable π-$C_5H_5Cr(CO)_2(L)\overset{O}{\overset{\|}{C}}$-$CH_3$ derivatives from π-$C_5H_5Cr(CO)_3CH_3$ and L (where L = $P(C_6H_5)_3$, $P(p\text{-}CH_3OC_6H_4)_3$, and $P(C_6H_5)(CH_3)_2$).[188] The complexes were assigned a <u>trans</u> geometry on the basis of their proton nmr spectra.

Along with similar Fe and Mn derivatives, π-$C_5H_5Mo(CO)_3$-$\overline{C{=}C(Ph)C(O)N(SO_2Cl)CH_2}$ has been prepared <u>via</u> reaction of the metal 2-alkynyl, in this case, π-$C_5H_5Mo(CO)_3CH_2C\equiv CPh$, with $ClSO_2NCO$.[189] The more powerful electrophile SO_3 was also found to add to transition metal-2-alkynyl complexes yielding sultones:[190]


(22)

[M] = π-$C_5H_5Mo(CO)_3$, $Mn(CO)_5$, π-$C_5H_5Fe(CO)_2$

R = Ph, Me

Oxidation of the alkylmetal carbonyl derivatives, tricarbonyl-π-cyclopentadienyl-4-fluorobenzylmolybdenum, -tungsten, and tricarbonyl-π-cyclopentadienyl-3-pyridylmethylmolybdenum, by cerium(IV) ion in methanol has been found to occur rapidly with almost quantitative formation of methyl 4-fluorophenylacetate and methyl 3-pyridylacetate, respectively.[191] A mechanism was proposed involving the intermediacy of an acyl derivative.

The synthetic usefulness of methylfluorosulfonate has been illustrated for several preparations including the following involving molybdenum:[192]

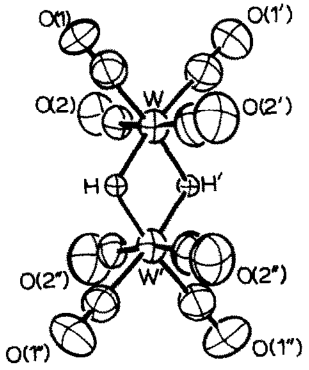
$$Mo(phen)(PR_3)_2(CO)_2 + CH_3SO_3F \rightarrow Mo(phen)(PR_3)_2(CO)_2 \cdot CH_3SO_3F \quad (23)$$

$$(\pi\text{-}C_5H_5)_2MoH_2 + CH_3SO_3F \rightarrow [(\pi\text{-}C_5H_5)_2MoH_2CH_3][SO_3F] \quad (24)$$

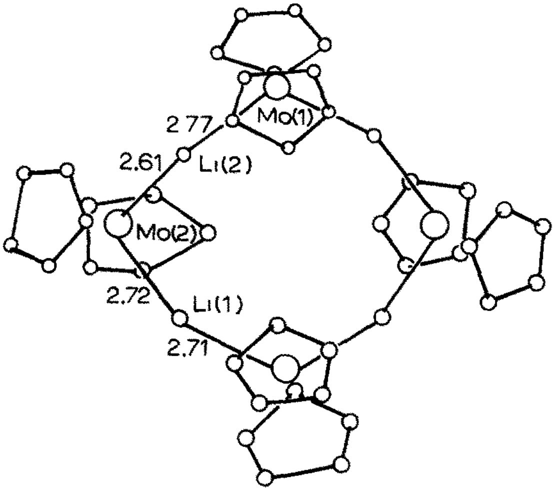
Both products are believed to contain a methyl group bound to molybdenum.

Several Group VIB metal hydride complexes have been prepared and characterized over the past year. These are reported in this section along with various reactions, involving metal-hydride bonds, which were employed in the preparation of new metal complexes. The dinuclear tungsten hydride complex, $HW_2(CO)_9NO$, has been prepared from the reaction of $[HW_2(CO)_{10}]^-$ with $NaNO_2$-acetic acid.[193] X-ray crystallography has shown the molecule to possess a distorted D_{4d} symmetry with a long W-W distance of 3.329 Å. This long W-W bond distance together with octahedral coordination about the tungsten atoms and Raman spectral data strongly support a bridging position for the hydrogen (W-H-W). In addition, new mixed-metal hydrogen bridged carbonyl complexes of the series $HM'M(CO)_{10}$ (M = Cr, Mo, W; M' = Mn, Re) have been synthesized.[194] For example, when $Et_4N^+[ReCr(CO)_{10}]^-$ was stirred in a pentane slurry with 85% H_3PO_4 for 2 days, crystals containing predominantly $HReCr(CO)_{10}$ were obtained upon cooling the pentane layer to -78°. Preliminary crystal structure data indicate an eclipsed metal pentacarbonyl conformation with a Re-Cr distance of 3.435(1) Å, however the bridging hydrogen position was not located crystallographically. $HReW(CO)_{10}$ was also prepared and characterized by infrared, nmr, and mass spectra.

The complex $[Et_4N]_2[W_2(CO)_8H_2]$ has been synthesized from the reaction of $[Et_4N][BH_4]$ and $W(CO)_6$ in THF under reflux conditions.[195] The molecular geometry of the $[W_2(CO)_8H_2]^{-2}$ ion has been demonstrated to be as that shown in Figure LVII by X-ray structural analysis. Most importantly, this structural analysis allowed for the direct location of the two μ_2-bridging hydride ligands.



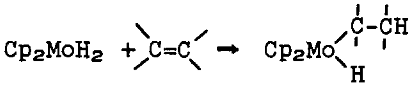
(LVII)



(LVIII)

The crystal structure of the complex prepared from treatment of $(\pi\text{-}C_5H_5)_2MoH_2$ with n-butyllithium, $[(\pi\text{-}C_5H_5)_2Mo(H)Li]_4$, has been described.[196] The molecule consists of eight-membered Mo-Li rings (LVIII). The presence of the hydrogen atom was inferred from several reactions of the tetrameric compound, but was not located by the X-ray structure analysis.

The preparation of a series of eight-coordinate Mo and W hydrides of the type H_4ML_4 (L = phosphines) have been reported.[197] Temperature dependent ^1H nmr studies established stereochemical non-rigidity with relatively high ($\Delta G^{\ddagger}$ = 12-16 kcal/mol) rearrangement barriers. The rearrangement process was discussed in terms of a "tetrahedral jump" mechanism which is based on a crystal structure determination of one of the complexes, $H_4Mo[PPh_2Me]_4$. Charge transfer interaction between olefins and metal orbital electrons of Cp_2MoH_2 prior to M-H bond insertion has been demonstrated for a number of olefins, eq. 25.[198] Further studies by Nakamura and Otsuka utilizing

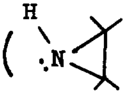


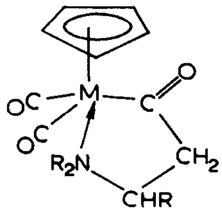
$$Cp_2MoH_2 + {>}C{=}C{<} \rightarrow Cp_2Mo\begin{matrix}\diagup \text{C-CH} \\ \diagdown \text{H}\end{matrix} \qquad (25)$$

$CpMoD_2$ and dimethyl fumarate or maleate established initial formation of $Cp_2MoD[CH(CO_2Me)CHD(CO_2Me)]$ followed by unimolecular elimination producing racemic or meso-dimethyl 1,2-dideuteriosuccinate with retention of configuration of the σ-bonded α-carbon atom.[199] This elimination reaction leads to the very reactive Cp_2Mo which reacts with any free olefin to yield $Cp_2Mo(\pi\text{-olefin})$. A study of factors influencing the kinetics of the insertion reaction included solvent effects on the observed induction period.

The selective reduction of haloalkanes, haloalkenes, and halobenzenes with $(\pi\text{-}C_5H_5)_2WH_2$ to give high yields of compounds resulting from replacement of one C-X bond (X = Cl, Br, I) by a C-H bond has been studied by Green and Knowles.[200]

Dichlorocarbene, produced by the thermal decomposition of sodium trichloroacetate, reacts with bis(π-cyclopentadienyl)tungstendihydride giving rise to the insertion product $Cp_2WH(CHCl_2)$.[201] Although the mechanism of this reaction was not elucidated, further investigations showed the difluorocarbene precursor, sodium chlorodifluoroacetate to react with the same hydride substrate to give the substitution product $Cp_2W(O_2C_2ClF_2)_2$.

1,3 insertion of aziridine () into the M-H bond of $(\pi\text{-}C_5H_5)M(CO)_3H$ (M = Mo, W) proceeds with ring-opening to form 3-aminopropionyl chelate complexes (LIX).[202]



(LIX)

Molecular nitrogen and nitrosyl complexes. The preparation and characterization of cis-$Mo(N_2)_2L_4$, cis-$Mo(CO)_2L_4$, MoH_4L_4 (L = $PhMe_2Ph$); trans-$Mo(N_2)_2L_4'$, trans- and cis-$Mo(CO)_2L_4'$, MoH_4L_4' (L' = $PhEt_2P$); trans-$Mo(CO)_2(diphos)_2$, cis- and trans-$MoH_2(diphos)_2$; and of trans-$Mo(N_2)_2(PMe_2Ph)_2(ds)$ (where ds = $PhSCH_2CH_2SPh$) have been reported by Aresta and Sacco.^{203} The reaction between $Mo(N_2)_2(diphos)_2$ with $FeH_4(PEtPh_2)_3$ in a 1:1 molar ratio gave $MoH_2(diphos)_2$, $FeH_2(N_2)(PEtPh_2)_3$ and N_2. These workers have further studied the reactions of some of these dinitrogen and carbonyl complexes with triethylaluminum.^{204} Two to one adducts of $AlEt_3$ with cis-$Mo(N_2)_2L_4$, cis-$Mo(CO)_2L_4$ (L = $PhMe_2P$); trans-$Mo(N_2)_2L_4'$ (L' = $PhEt_2P$); trans-$Mo(N_2)_2$-$(diphos)_2$; and cis- and trans-$Mo(CO)_2(diphos)_2$ were reported. The $AlEt_3$ was shown to be bound to the oxygen atom of the CO group or to the terminal nitrogen atom of the N_2 moiety. trans-$Mo(CO)_2(diphos)_2$ was also found to isomerize to the cis isomer in the presence of catalytic quantities of $AlEt_3$.

The base strengths of the terminal nitrogen atom in Mo(0) and W(0) dinitrogen complexes have been further investigated by Chatt and coworkers.^{205} The formation of adducts containing the $M-N\equiv N:AlR_3$ and $M-C\equiv O:AlR_3$ groupings (R = Me, Ph, or Cl) in a variety of molybdenum(0) and tungsten(0) complexes has been examined by ir and ^1H nmr spectroscopy. The relative order of base strengths observed were THF > trans-$[Mo(N_2)_2(diphos)_2]$

> <u>trans</u>-[$W(N_2)_2$(diphos)$_2$]. These were determined from ^1H nmr studies of the equilibrium reaction (26).

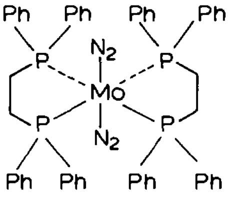
$$AlMe_3, Et_2O + [M\text{-}N{\equiv}N] \xrightarrow{benzene} Et_2O + [M\text{-}N{\equiv}N{:}AlMe_3] \qquad (26)$$

The reaction of Mo(N_2)$_2$(Dmtpe)$_2$ (Dmtpe = 1,2-bis(di-<u>m</u>-tolylphosphino)ethane) with H_2 to afford the tetrahydrido complex, MoH$_4$(Dmtpe)$_2$ has been reported by Archer and George.[206] In addition the complex was prepared from reduction of MoCl$_2$(Dmtpe)$_2$ with Na/Hg in the presence of H_2. The presence of four hydrogens was established by ^1H and ^{31}P nmr studies. This work suggests that the reaction of Mo(N_2)$_2$(diphos)$_2$ with H_2 produces MoH$_4$(diphos)$_2$ as well, rather than the dihydride previously reported by Hidai.[207] N_2 was found to react with MoH$_4$(Dmtpe)$_2$ to yield Mo(N_2)$_2$(Dmtpe)$_2$.

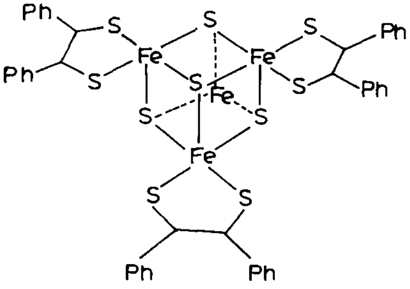
Carbon monoxide reacts with <u>trans</u>-Mo(N_2)$_2$(PPh$_2$Me)$_4$ at -78° and at ambient temperature to give the new complex <u>mer</u>-Mo(CO)$_3$(PPh$_2$Me)$_3$ and <u>cis</u>-Mo(CO)$_4$(PPh$_2$Me)$_2$, respectively; the <u>mer</u> isomer was also prepared by reduction of MoCl$_4$(PPh$_2$Me)$_2$ with Na/Hg in presence of excess phosphine and CO. <u>Fac</u>-Mo(CO)$_3$(PMe$_2$Ph)$_3$ was obtained from the reaction of CO with <u>cis</u>-Mo(N_2)$_2$(PMe$_2$Ph)$_4$ at room temperature.[208] The preparation of the starting dinitrogen complexes accompanied this report.[209]

On the other hand, trans-Mo(CO)$_2$(diphos)$_2$ has been observed as the initial product from the reaction of trans-Mo(N_2)$_2$(diphos)$_2$ and CO at 50 atm pressure in THF solution.[210] This complex was shown to rapidly isomerize to the <u>cis</u> isomer, cis-Mo(CO)$_2$(diphos)$_2$, under atmospheric pressure of carbon monoxide. However, trans-Mo(CO)$_2$(diphos)$_2$ was found to be stable in solution under large CO pressures. This result suggests that isomerization probably involves initial dissociation of CO to form a 5-coordinate intermediate, Mo(CO)(diphos)$_2$.

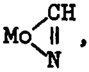
The mechanism of nitrogen fixation in the presence of *trans*-Mo(diphos)$_2$(N$_2$)$_2$ (LX), the diphenyldithiolene FeS cluster (LXI), and sodium naphthalenide has been investigated by van Tamelen, *et al.*[211] The facts that Mo(diphos)$_2$(N$_2$)$_2$ readily undergoes N$_2$ ligand exchange with CO and that the reduced form of the iron-dithiolene complex itself reduces N$_2$ to NH$_3$ suggests an initial release of N$_2$ by the Mo complex prior to reduction by the iron complex.



(LX)



(LXI)

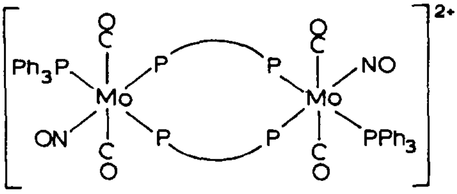
Schrauzer *et al.* propose a side-on bonded HCN,  $\mathrm{Mo}\overset{\mathrm{CH}}{\underset{\mathrm{N}}{\|}}$, in the reduction of CN$^-$ by nitrogenase model systems composed of molybdate and sulfur containing ligands such as L(+)-cysteine.[212]

A number of papers have dealt with the preparation and characterization of Group VIB metal complexes containing the metal-nitrosyl grouping. A second report of the preparation and characterization of tetranitrosylchromium which was mentioned in last year's survey has appeared in the literature.[213] Cr(NO)$_4$ was prepared as a red-black solid at room temperature from photolysis of Cr(CO)$_6$ in pentane solution with excess NO.[214] Raman and ir data of this elusive member of the isoelectronic series (Ni(CO)$_4$, Co(CO)$_3$(NO), Fe(NO)$_2$(CO)$_2$, and Mn(NO)$_3$(CO)) indicate T$_d$ molecular symmetry in solution and the solid state.

The interaction of cyclopentadienyl-lanthanides with some Group VIB metal carbonyl and nitrosyl complexes has been described by Crease and Legzdins.[215] The Lewis acids R_3Ln (R = C_6H_5 or MeC_5H_4; Ln = Nd, Sm, Gd, Dy, Ho, Er, or Yb) were found to undergo Lewis acid-base interactions with bridging and terminal carbonyl ligands, terminal nitrosyl ligands, and the metal atom in $(\pi\text{-}C_5H_5)_2WH_2$ as detected by ir and nmr spectroscopy. Some of the substrate molecules investigated were $(\pi\text{-}C_5H_5)Cr(NO)_2Cl$ and $(\pi\text{-}C_5H_5)M(CO)_2(NO)$ (M = Cr, Mo, W). These latter complexes were found to preferentially interact through the terminal NO ligand with lanthanide acids. The complexes, $(C_5H_5)_2LnM(\pi\text{-}C_5H_5)(CO)_3$ (Ln = Dy, Ho, Er, or Yb; M = Mo, W), were prepared and characterized.

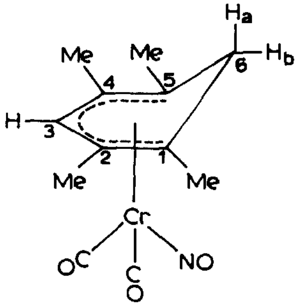
Cationic carbonylnitrosyl complexes of molybdenum and tungsten of the type $[M(CO)_3(NO)(diphos)]PF_6$ have been prepared from the reaction of $[M(CO)_4(diphos)]$ and $NOPF_6$ in methanol-toluene.[216] Reaction of these cations with halides or dithiocarbamate salts afforded the air-stable, crystalline complexes $[\overset{*}{M}(CO)_2(NO)(diphos)X]$ (X = Cl, Br, and I) and $[M(CO)(NO)(diphos)(S_2CNR_2)]$ (R = Me and Et), respectively. In addition, $[Mo(CO)_3(NO)(diphos)]PF_6$ was found to react with phosphine ligands L (where L = PPh_3, $P(OPh)_3$, $P(OMe)_3$, and diphos) in chloroform to yield $[Mo(CO)(NO)(diphos)(L)Cl]$; whereas, when the reaction was carried out in acetone $[Mo(CO)_2(NO)(diphos)(PPh_3)_2]_2[PF_6]_2 \cdot 2$ acetone (LXII) and $[Mo(CO)(NO)(diphos)_2]PF_6$ were formed. The $[Mo(CO)_3(NO)(diphos)]PF_6$ complex underwent as well decarbonylation in refluxing chloroform to yield $[Mo(NO)(diphos)Cl_2]_n$ and other polynuclear nitrosyl species.

Ball and Connelly have also reported the preparation of cationic arenechromium-nitrosyls and -hydrides.[217] $NOPF_6$ when



P⌒P = diphos

(LXII)



(LXIII)

reacted with $Cr(CO)_2L(C_6Me_{6-n}H_n)$ (n = 0-3, L = CO and PPh_3) afforded the complexes $[Cr(CO)L(NO)(C_6Me_{6-n}H_n)]PF_6$ (n = 0-3, L = CO; n = 0, L = PPh_3). For the complexes where L = CO, reactions with nucleophiles ($NaBH_4$ or methyllithium) gave neutral substituted cyclohexadienyl complexes of the form $Cr(CO)_2(NO)(C_6Me_{6-n}H_nX)$ (n = 2, X = H; n = 0, X = H; and n = 2, X = Me) (e.g., LXIII). The compounds $Cr(CO)_2(PhC{\equiv}CPh)$-$(C_6Me_{6-n}H_n)$ reacted with $NOPF_6$ to yield $[Cr(H)(CO)_2(PhC{\equiv}CPh)$-$(C_6Me_{6-n}H_n)]PF_6$, n = 0 and 1.

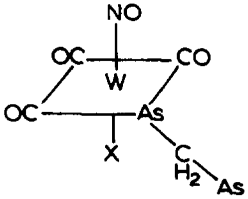
$[(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2$ (R = Me, Et, Pr^1, Pr^n, Bu^1, and CH_2Ph) complexes have been oxidized voltammetrically to produce monocationic species, $[(\pi\text{-}C_5H_5)Mo(NO)(SR)]_2^+$.[218] These complexes were all reduced at approximately +0.71 V ($E_{1/2}$ for the oxidation process) with the exception of the benzyl derivative which was 0.08 V more anodic.

The diamagnetic $[Cr(NO)(CNR)_5][PF_6]$ (R = Me, t-Bu or p-ClC_6H_4) complexes were prepared by denitrosylation of $[Cr(NO)_2(NCMe)_4][PF_6]_2$ by CNR.[219] These complexes could be oxidized chemically or voltammetrically to the paramagnetic $[Cr(NO)(CNR)_5][PF_6]_2$ (S = 1/2) complexes. Voltammetric evidence for $[Cr(NO)(CNR)_5]^{+3}$, and for $\{Cr[CN(p\text{-}MeC_6H_4)]_6\}^{+1,2}$ as oxidation products of $\{Cr[CN(p\text{-}MeC_6H_4)]_6\}^0$, was also obtained.

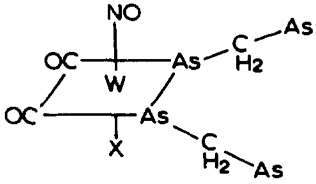
Reductive nitrosation of molybdenum and tungsten halides has been employed as a new route to complexes of the type $[M(NO)_2Cl_2]_n$ and $M(NO)_2Cl_2(PPh_3)_2$ (M = Mo or W).[220]

The molybdenum nitrosyl complexes, $[Mo(NO)_2Cl_2L]_n \cdot THF$ ($L = p\text{-}C_6H_4(NH_2)_2$; n = 1, 2, 3) and $Mo(NO)_2Cl_2L_2'$ (L' = m- and $p\text{-}C_6H_4(OMe)_2$, $p\text{-}C_6H_4(SMe)_2$) have been prepared and their uv and ir spectral properties were determined.[221]

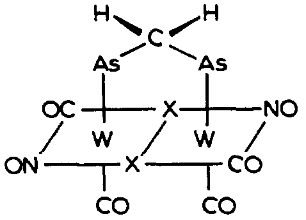
The carbonyl nitrosyl halide complexes, trans-$W(CO)_4(NO)X$ were obtained as stable yellow solids from reaction of NO^+ on $W(CO)_4X^-$, X = Cl, Br, I.[222] Small amounts of the analogous iodo- and bromo-molybdenum carbonyl nitrosyls were also prepared, however it was not possible to obtain the chloro-Mo derivative nor any analogous complexes of the Cr series. Thermal replacement of a CO group of $W(CO)_4(NO)X$ with PPh_3 and $AsPh_3$ yielded both mer and cis isomers of $W(CO)_3(L)(NO)X$ and, in the presence of excess L the disubstituted complexes $W(CO)_2(L)_2(NO)X$ were obtained.[223] The latter are suggested to have the CO groups and the L groups cis to each other; for PPh_3, thermal isomerization to the trans form is observed. Other studies of these carbonyl nitrosyl halides of W included reaction of $Ph_2AsCH_2AsPh_2$(dam) and $Ph_2PCH_2PPh_2$(dpm) with $W(CO)_4(NO)X$ yielding mono- and bidentate derivatives as well as a ligand-bridged binuclear species (LXIV A, B, C, D, E, and F).[224] The


$W(CO)_3(NO)(dam)X$

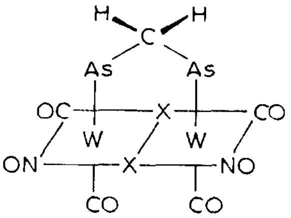
(LXIV A)


$W(CO)_2(NO)(dam)_2X$

(LXIV B)

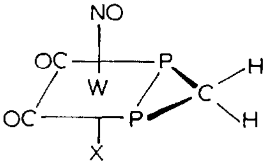

$\alpha\text{-}[W(CO)_2(NO)X]_2(dam)$

(LXIV C)



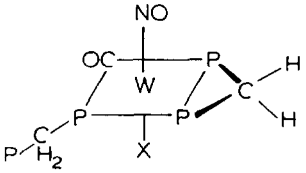
β-$[W(CO)_2(NO)X]_2$(dam)

(LXIV D)



$W(CO)_2(NO)(dpm)X$

(LXIV E)



$W(CO)(NO)(dpm)_2X$

(LXIV F)

reluctance of dam to act as a bidentate ligand was noted. ^{1}H nmr analyses of all these derivatives were given.

Stable arylazonitrosyl complexes of tungsten and molybdenum have been prepared from oxidative addition of nitrosyl chloride to arylazo complexes at -25°.[225] In this manner the complexes $LM(NO)(N_2Ph)Cl$ (M = Mo, W; L = tris-1-pyrazolylborate and C_5H_5) have been prepared and characterized.

A preparation of nitrosyl complexes of Re, Mo, Pd, Mn, U, and Co was reported which utilized gaseous NO and a suspension of the hydrated metal oxides in hot aqueous HCl.[226]

Replacement of a H_2O ligand by $AsPhR_2$ in complexes such as $Cr(NO)(H_2O)_3(S_2COEt)$ yields paramagnetic products which have been studied by esr.[227]

Miscellaneous complexes. The novel chromium(I) complex, $Cr(PhNC)_5{}^+BPh_4{}^-$ has been prepared in 90% yield from $Cr(PhNC)_6$ and I_2 in CH_2Cl_2.[228] Novotny and Lippard have described the synthesis of $[Mo(CNR)_7]X_2$ (R = Me, X = I^-; R = Bu^t, X = $PF_6{}^-$, $I_3{}^-$) compounds from $Mo(CO)_6$ and alkyl isocyanide in the presence of I_2 or from alkylation of $Ag_4Mo(CN)_8$.[229] Trends in the average ν(CN) for the series $Mo(CNR)_7{}^{+2} > Mo(CNR)_6I^+ > Mo(CNR)_5X_2$ were observed. Conductivity and electronic spectral data suggested the presence of seven-coordinate molybdenum(II) dications in solution.

Reactions of nitroxyl radicals with $Mo(CO)_6$ and $W(CO)_6$ have been reported by Alper.[230]

Oxidation and reduction reactions of some tungsten and molybdenum chlorides by chlorinated alkyl cyanides (e.g., Cl_3CCN) have been reported by Fowles and coworkers.[231]

Reactions of transition metal peroxides with n-BuLi have been investigated by Regen and Whitesides.[232] The ease with which lithium n-butoxide was formed from reaction of n-butyllithium with several peroxy metal compounds was found to decrease in the order $MoO(O_2)_2 \cdot HMPA$, $CrO(O_2)_2 \cdot Py > (Ph_3P)_3PtO_2$, $(Ph_3P)_2Ir(CO)(O_2)I \gg Na_2O_2$. In order to confirm that the reactivity of the molybdenum and chromium derivatives was indeed due to the peroxy moieties rather than to the isolated "oxo" oxygen atom, an experiment was carried out using $^{18}OMo(O_2)_2$. None of the ^{18}O label was incorporated in the lithium n-butoxide.

Kinetic and Mechanistic Studies

The volume of activation, ΔV^*, has been determined for reactions of $M(CO)_n$ ($n = 6$, M = Cr, Mo, W; $n = 4$, M = Ni) with phosphines or phosphites in low concentrations to yield the monosubstituted products.[233] Positive ΔV^* values were interpreted to signify a large degree of bond breakage in the transition state for the first order reactions of $Ni(CO)_4$ with $P(OEt)_3$ and $Cr(CO)_6$ or $Mo(CO)_6$ with PPh_3. On the other hand the second order reaction of $P(n\text{-}Bu)_3$ with $W(CO)_6$ showed a negative ΔV^* consistent with the associative mechanism hypothesis.

Kinetic studies of the competition of the intermediate $[Ph_3PMo(CO)_4]$, as derived from the thermal decomposition of cis-$Mo(CO)_4(PPh_3)$(amine), for entering ligands L thus forming cis-$Mo(CO)_4(PPh_3)(L)$ have been reported.[234] At low concentrations of L the reactions follow a simple first order expression, rate = k[$Mo(CO)_4(PPh_3)$(amine)]; at higher concentrations of a strongly nucleophilic L, rate = [k + k'[L]][$Mo(CO)_4(PPh_3)$(amine)]. The dependence of the rates of reaction and position of substitution equilibria on the steric and electronic nature of L is discussed. A similar study by Covey and Brown extended and corroborated these findings.[235] Near unity competition ratios for recombination of the intermediate $Mo(CO)_5$ with piperidine and L ($P(OMe)_3$, PPh_3, $AsPh_3$) suggests the $Mo(CO)_5$ moiety to be quite indiscriminate in reactivity. From the first order dissociative process ($Mo(CO)_5$amine $\xrightarrow{k_1}$ $Mo(CO)_5$ + amine) k_1 values are found to vary with amine, cyclohexylamine > piperidine > quinuclidine, and $\Delta H_1^{\ddagger}$ and $\Delta S_1^{\ddagger}$ are approximately 25 kcal/mole and +3 eu, respectively. Kinetic and activation parameters for the second order process ($Mo(CO)_5$amine + L $\xrightarrow{k_2}$ $Mo(CO)_5L$) are also presented and discussed.

A topological analysis of the stereochemical rearrangement aspects of any substitution or stereoisomerization reaction which proceeds via a five-coordinate intermediate produced from the dissociation of octahedral compounds has been presented by Springer.[236]

Dobson and Memering have discussed the mechanistic inferences derived from kinetic studies of the reaction of dipy$M(CO)_4$ (M = Mo, W) with phosphites, phosphines, and Ph_2SnCl_2.[237] They presented further kinetic data as well as convincing arguments for the possibility of three competing mechanisms in such reactions (eqns. 27-29). In addition, stopped-flow kinetic studies were performed on reactions of (dipyridyl)$W(CO)_4$ with a variety of Group IVA metal oxidants such as $SnCl_4$, $PhSnCl_3$, etc., also by Dobson and coworkers.[238] The mechanisms dis-

$$(\text{dipy})\text{M}(\text{CO})_4 \xrightarrow[-\text{CO}]{k_1} [(\text{dipy})\text{M}(\text{CO})_3] \xrightarrow[+\text{L}]{\text{fast}} \text{products} \qquad (27)$$

$$(\text{dipy})\text{M}(\text{CO})_4 + \text{L} \xrightarrow{k_2} [(\text{dipy})\text{M}(\text{CO})_4\text{L}] \xrightarrow{\text{fast}} \text{products} \qquad (28)$$

$$\begin{tikzcd} (\text{dipy})\text{M}(\text{CO})_4 \arrow[r, shift left, "k_3"] & {[\text{NN-M}(\text{CO})_4]} \arrow[l, shift left, "k_4"] \arrow[r, "k_5", "+\text{L}"'] & \text{NN-M}(\text{CO})_4\text{L} \arrow[d, "\text{fast}"] \\ & & \text{products} \end{tikzcd} \qquad (29)$$

cussed included rationale of the dependence of rate on the IVA metal substituents.

The kinetics of the reaction of acetonitrile with tricarbonyl(tropylium) cationic complexes of Group VIB metals have been studied.[239] The replacement of the tropylium ligand by three acetonitrile ligands obeys a rate law, rate = $k[M(CO)_3(C_7H_7)]^+[MeCN]$. This is interpreted in terms of an associative displacement of $C_7H_7^+$ by acetonitrile ligands to give the product $M(CO)_3(CH_3CN)_3$. The rates decrease drastically as the metal varies in the order Mo > W > Cr which is the same order of increasing enthalpy of activations ($\Delta H^{\ddagger} = 10.5$, 15.0, and 24.2 kcal/mole, respectively).

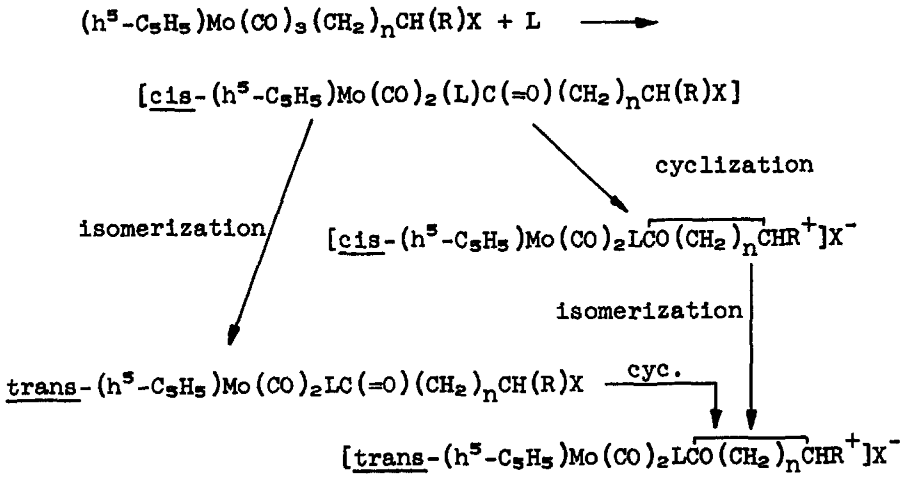
Connor and coworkers have prepared a series of complexes $LM(CO)_5$ (M = Cr, Mo, or W; L = dmpe, dpm, diphos, dpp, or arphos) which were characterized by elemental analysis, ir, mass, ^1H and ^{31}P nmr spectroscopy.[240] Methylation of the complexes with Me_3OBF_4 to give $[(MeL)M(CO)_5]BF_4$ complexes was achieved. Kinetic studies of the rate of the chelation reaction, $LM(CO)_5 \rightarrow LM(CO)_4 + CO$, show these reactions to follow first-order kinetics. The reaction proceeded faster the smaller the potential chelate ring was in the series $L = Ph_2P(CH_2)_nPPh_2$ ($n = 1, 2, 3$). This appeared to be largely an entropy effect.

Two kinetic investigations of reactions of main group organometallic reagents with tungsten-, molybdenum-, and chromium hexacarbonyls and substituted derivatives have appeared this year. Thus Darensbourg et al. studied the second order nucleophilic addition of benzylmagnesium chloride ($LM(CO)_x + PhCH_2MgCl \rightarrow LM(CO)_{x-1}C(CH_2Ph)O^-MgCl^+$; M = W, Mo, Cr, x = 5, product = cis; M = Fe, x = 4, product = trans; L = phosphines, phosphites), following this reaction via conventional ir techniques.[241] Kinetic parameters suggest nucleophilic addition to the C of CO groups cis to substituted ligands to be highly dependent on the steric properties of the ligand and relatively insensitive to the electronic character. However electronic properties of the CO ligand as indicated by the CO stretching force constant or frequency determine CO reactive sites within a molecule and also reaction rates for Grignard addition to CO ligands trans to a substituent. Dobson and Paxson utilized stopped flow kinetic techniques to study the methyllithium addition for which the rate law

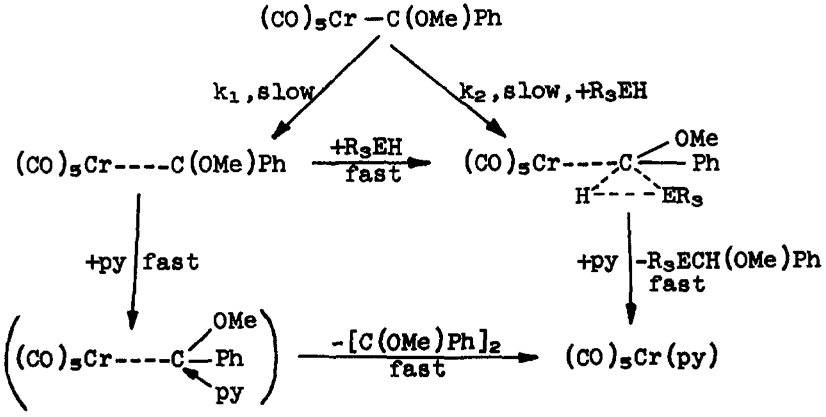
$$-d[MCO]/dt = k[MCO][CH_3Li]^{1/4}$$

was obtained where MCO = $M(CO)_6$ and $W(CO)_5L$.[242] The quarter order in CH_3Li is consistent with buildup of an equilibrium concentration of reactive monomer from Me_4Li_4. Dobson suggests an initial methyllithium-metal carbonyl adduct such as trans-$(CO)_4WL[COLiCH_3]$ followed by a rate-determining rearrangement to yield the observed cis products in this series.

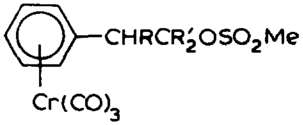
Cotton and Lukehart have presented an extensive kinetic and thermodynamic investigation of reactions leading to formation of cyclic 2-oxacarbene ligands from the cis acyl intermediate.[243] This work also contains a good review of related reactions of bound ligands.



The mechanism of methoxyphenylcarbene insertion into Group IV element-hydrogen bonds *via* $Cr(CO)_5[C(OMe)Ph]$ in the presence of pyridine was studied by Connor and coworkers.[244] Activation parameters indicate a reaction scheme involving incomplete dissociation of the carbene ligand as illustrated below.



π-Arenechromium tricarbonyl methanesulfonates (LXV) have been prepared and their rates of acetolysis and formolysis compared with those of the uncomplexed derivatives.[245] The rates were generally an order of magnitude greater for the complexed derivatives. Differences in product distribution resulting from acetolysis or formolysis of complexed versus uncomplexed derivatives were also discussed. Similar studies

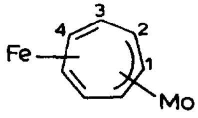


(LXV) $R = H, Me; R^1 = H, D$

on the steric and electronic effects on the rates of bimolecular substitution reactions of (benzylchlorides)- or (benzylbromides)-$Cr(CO)_3$ with sodium thiocyanate and the corresponding reactions with the uncomplexed benzylhalides in anhydrous acetone were also reported.[246] For the complexes $(p\text{-}XC_6H_4CH_2Cl)Cr(CO)_3$ ($X = H, Cl, OMe, Me$) a decrease in substitution rates was observed as compared with the corresponding uncomplexed species with the lone exception of the methoxy derivative. This decrease in reactivity was ascribed to steric effects. Activation parameters were determined as well for these reactions, e.g., for reactions employing $(C_6H_5CH_2Cl)Cr(CO)_3$ and uncomplexed $C_6H_5CH_2Cl$, $\Delta H^{\ddagger} = 19.3$ and 17.5 and $\Delta S^{\ddagger} = -18.5$ and -21.0, respectively.

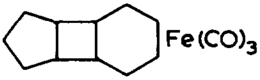
Fomin and coworkers have investigated the kinetics and the products of the autoxidation of chromium and molybdenum arene complexes in various hydrocarbon solvents.[247]

Complexes containing polypyrazolylborate ligands of the type $LMo(CO)_2C_7H_7$, where $L = B(C_3N_2H_3)_4$, $HB(C_3N_2H_3)_3$, $HB(3,5\text{-}Me_2C_3N_2H)_3$, $H_2B(3,5\text{-}Me_2C_3N_2H)_2$, and $Et_2B(C_3N_2H_3)_2$ have been shown to form adducts with $Fe(CO)_3$.[248] Both the starting materials and adduct molecules were found to be fluxional, exhibiting single proton nmr lines for the cycloheptatrienyl rings; however, coordination of $Fe(CO)_3$ substantially slowed down the rate of the C_7H_7 "ring whizzing." This is interpreted in terms of the starting compounds containing the trihapto-cycloheptatrienyl ring, and upon formation of adducts the $Fe(CO)_3$ group binds to the butadiene portions of the C_7H_7 rings (LXVI). These results are therefore very similar to those obtained for the π-$C_5H_5Mo(CO)_2C_7H_7$ analog and its behavior upon adduct formation with $Fe(CO)_3$.

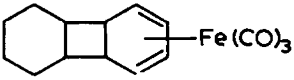


(LXVI)

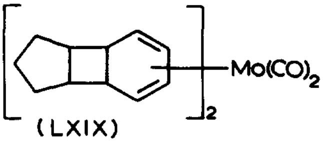
An impressive study of the effect of additional ring fusion and binding to $Mo(CO)_3$ or $Fe(CO)_3$ upon the cyclooctatriene-bicyclooctadiene equilibrium has been presented by Cotton and Deganello.[249] Qualitatively, fusion of a 5- or 6-membered ring to the cyclooctatriene system enhances the relative stability of the diene tautomers. Derivatives of $Fe(CO)_3$ and $Mo(CO)_3$ reflect the enhanced stability of the diene due to the ring fusion as well as the inherent dienophilic character of the former and trienophilic character of the latter metal carbonyl moiety. Some of the compounds thus prepared are LXVII-LXXII.



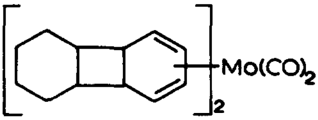
(LXVII)



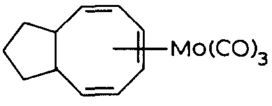
(LXVIII)



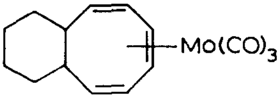
(LXIX)



(LXX)

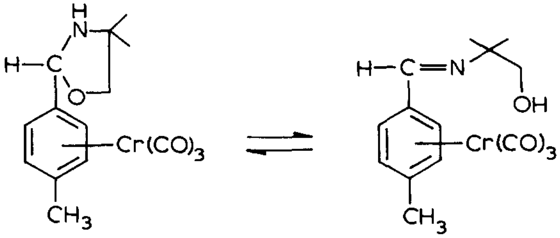


(LXXI)



(LXXII)

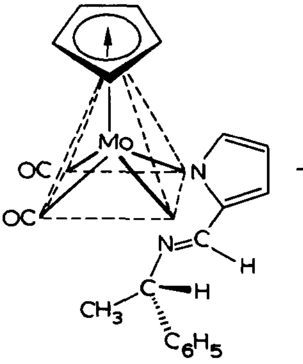
Similarly, the effect of complexation of $Cr(CO)_3$ on a dynamic ring-chain tautomerism reaction was reported by Alper and coworkers.[250] p-Tolualdehyde chromium tricarbonyl and 2-amino-2-methyl-1-propanol were found to react at room temperature to yield the yellow-orange complex (LXXIII A and LXXIV B). Nmr experiments indicated the presence of A and B in a ratio of 4.3:1.0. A similar ratio of 4.6:1.0 has been observed for uncomplexed A and B species where the p-methyl group was replaced by a p-nitro group, further substantiating the inductive similarity of $Cr(CO)_3$ and p-nitro substituents.



(LXXIII) (LXXIV)

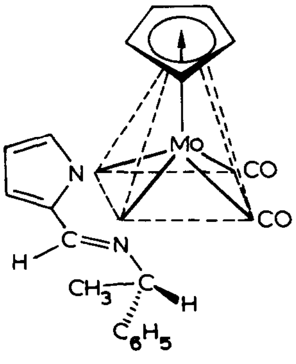
Solvent effects on the CO infrared spectrum of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ are pronounced and led to studies of the dynamic interconversion of the trans and gauche forms.[251] The trans form is purportedly the most stable tautomer with the gauche form becoming increasingly populated with increasing solvent dielectric constant. A substantial activation energy (15 kcal/mole) for rotation about the metal-metal bond is observed. Furthermore, temperature dependent pmr studies on the system $(h^5\text{-}C_5H_5)(CO)_3MoMo(CO)_2(CNCH_3)(h^5\text{-}C_5H_5)$ show rapid interconversion of non-bridged isomers and permutamers at room temperature and above.[252] The intramolecular ligand scrambling is proposed to proceed via doubly bridged species, $(h^5\text{-}C_5H_5)Mo(CO)_2(\mu\text{-}CO)_2Mo(CO)(CNCH_3)(h^5\text{-}C_5H_5)$ and $(h^5\text{-}C_5H_5)\text{-}Mo(CO)_2(\mu\text{-}CO)(\mu\text{-}CNCH_3)Mo(CO)_2(h^5\text{-}C_5H_5)$. In addition, the structural and dynamic properties of the isoelectronic series $[(h^5\text{-}C_5H_5)Cr(NO)_2]_2$, $[(h^5\text{-}C_5H_5)Mn(NO)(CO)]_2$, and $[(h^5\text{-}C_5H_5)\text{-}Fe(CO)_2]_2$ was examined by Ibers, Marks and others.[253] A comparison of crystal structures is given along with pmr studies of the cis and trans ligand-bridged isomers' interconversion along with the accompanying bridge-terminal ligand interchange. The activation energies for these processes vary in the order Cr > Mn > Fe.

Brunner and Herrmann have reported that $\pi\text{-}C_5H_5Mo(CO)_3Cl$ reacts with the sodium salt of the Schiff base derived from pyrrole carbaldehyde(2) and S-(-)-α-methylbenzylamine to afford the neutral diastereoisomeric complexes (LXXV A and B).[254] These diastereoisomers were separated by chromatography and fractional crystallization and were found to be configurationally stable at room temperature. Isomerization of LXXV A and B



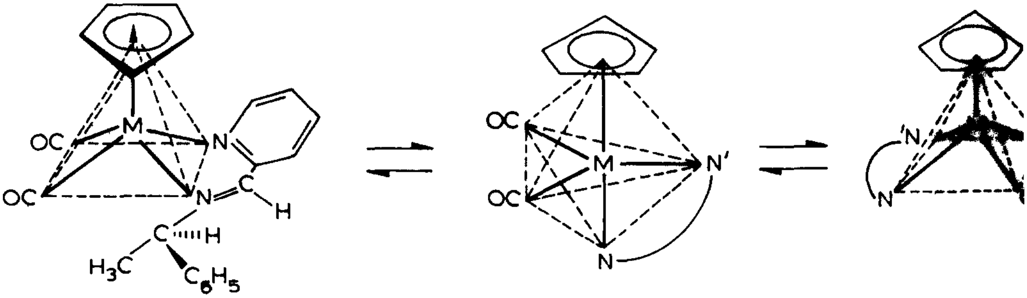
(LXXV A)

+



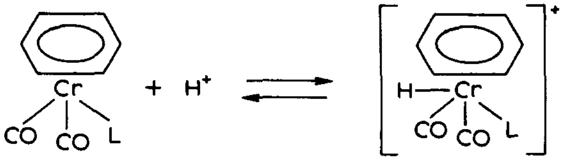
(LXXV B)

was measured between 85.0 and 95.0° and the process was found to obey a first order rate law ($\Delta H^{\ddagger} \approx 22$ kcal/mole and $\Delta S^{\ddagger} \approx -16$ e.u.). The epimerization of similar Mo and W compounds (LXXVI A and B) was also found to be first order in the complex.[255] Rate constants for interconversion were not dependent on addition of triphenylphosphine or Schiff bases, thus suggesting an intramolecular pseudorotation mechanism.



(LXXVI A) (LXXVI B)

The following studies involve H-exchange reactions of Group VIB organometallics. The effect of donor ligands (L) on the reactivity of the aromatic ring systems in π-$C_5H_5Mn(CO)_nL_{3-n}$ and π-$C_6H_5XCr(CO)_2PPh_3$ (L = phosphine, arsine, or stibine ligand) (LXXVII) during hydrogen isotopic exchange reactions with acids has been studied.[256] A reaction mechanism for this exchange process was proposed which involves a rapid equilibrium step in thich the H^+ ion reacts initially at the metal site (LXXVIII). Studies on the effect of PPh_3 on



(LXXVII) (LXXVIII)

the isotopic exchange of hydrogen of a π-aromatic ligand in (arene)$Cr(CO)_2PPh_3$ complexes have also been reported elsewhere.[257]

The kinetics of H exchange for triphenylphosphoniumcyclopentadienylide and its -$Mo(CO)_3$ derivative have been studied.[258] The hydrogen exchange involves only the hydrogen atoms of the cyclopentadiene ring. The rate constants were nearly the same for the complexed or uncomplexed ligand. In addition the rate constants for D exchange at the para position of the phenyl ring in σ-$PhCH_2M(CO)_3C_5H_5$ have been investigated for M = Mo and W.[259] The rate of exchange for M = Mo was observed to proceed at a faster rate than when M = W. The -$CH_2M(CO)_3(C_5H_5)$ groups were shown to be strong electron-donor substituents on a phenyl ring as indicated by isotopic-exchange and ^{13}C-nmr data.

Phosphine complexes of Cr, Mo, and W-carbonyls were investigated as to improved syntheses, ^{1}H-nmr, and crystal structure.[260] A qualitative ordering of the proton exchange rate as established in the presence of MeOH and $EtNH_2$ is as follows: $Cr(CO)_5PH_3$ > cis-$Cr(CO)_4(PH_3)_2$> fac-$Cr(CO)_3(PH_3)_3$> cis-$Mo(CO)_4(PH_3)_2$> cis-$W(CO)_4(PH_3)_2$. The intermediate $M(CO)_5PH_2^-$ was suggested.

Catalysis

The catalysis section will be presented in the following order: mechanistic studies, the efficacy of π-arene, π-cyclopentadienyl, π-allyl and metal carbonyl complexes as catalysts, new reports of the Ziegler-type multicomponent catalysts, and finally miscellaneous Group VIB metal-containing catalysts.

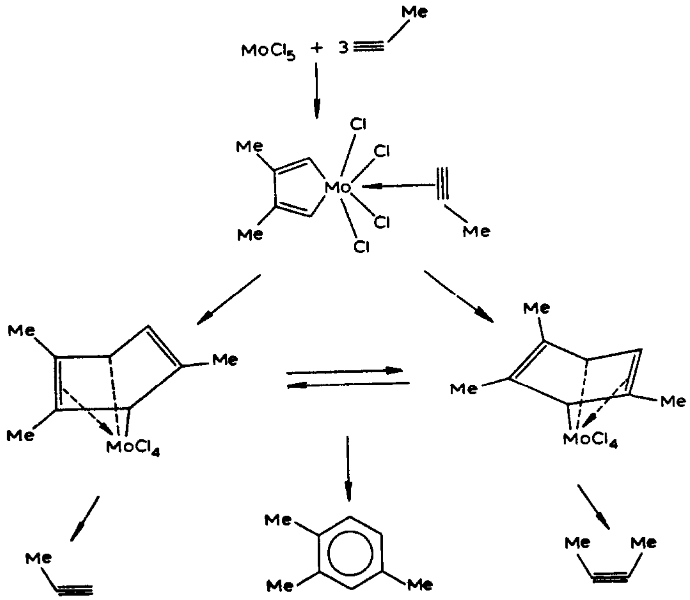
The Olives' have studied two factors which significantly increase the activity of the conventional heterogeneous molybdate/alumina catalyst system towards olefin metathesis.[261]

These are 1) impregnation of the alumina with ethanolic $Ti(O\text{-}Bu)_4$ and 2) activation (reduction) of the catalyst with CO. The more active reduced catalyst possesses paramagnetism due to Mo, possibly the Mo(V) species. This is viewed as catalyst "tailoring" of the Mo catalyst by introducing a Ti-containing ligand. Extending this approach, the SiO_2-supported chromium oxide (Phillips catalyst) system for the polymerization of ethylene was similarly ligand modified.[262] Inclusion of molybdate on the CrO_2 impregnated SiO_2 spheres prior to reduction by CO had the effect of drastically reducing polymer chain length and also of drastically increasing the amount of metathesis or disproportionation products.

Greco and coworkers have investigated reactions of molybdenum and tungsten halides with acetylenes which afforded a number of acetylene and mixed acetylene-nitrate complexes.[263] On the basis of the proposed structure of species involving more than one bound acetylenic ligand (i.e., a metal complex containing a conjugated nonaromatic double bond system) and on their pyrolysis products the decomposition scheme below was proposed. This scheme considers the formation of apparent metathesis products as side reactions of the cyclotrimerization of acetylenes to aromatic hydrocarbons.

The kinetics of epoxidation of 1-octene by cumene hydroperoxide catalyzed by powder molybdenum has been studied and was found to be determined by preferential formation of an olefin-Mo^{n+} complex.[264] The homogeneous catalytic decomposition reaction of cumene hydroperoxide in cumene or BuOH containing molybdenum was also studied by these workers.[265]

Infrared spectroscopy has been employed in the study of olefin disproportionation reactions using $Mo(CO)_6$ catalysts supported on silica, alumina, and magnesia.[266] Activation of



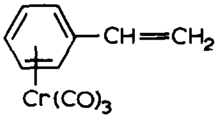
these catalysts was found to cause decomposition of the Mo(CO)$_6$. The intermediate sub-carbonyl species of the type Mo(CO)$_{6-x}$ observed on alumina and magnesia supports were shown not to be the active sites for olefin disproportionation. The active species was formed only upon complete loss of all six carbonyl ligands and is believed to consist of molybdenum in a higher oxidation state than Mo(0).

The Cr(acac)$_3$/Et$_3$Al catalyst formed in toluene at -78° produces an esr signal with g value of 1.9888, attributed to a Cr(III)-C bond most likely derived from alkyl-bridged organoaluminum components.[267] Upon warming to 25° a new signal develops with g of 1.986 corresponding to a di(arene)chromium(I) complex. The change in the esr spectrum is correlated with the change in catalyst activity towards butadiene polymerization upon aging.

Halogenated hydrocarbons were found to be reduced in the presence of (arene)$_2$Cr complexes as catalysts.[268] Dibenzenechromium has been found to polymerize acrylonitrile and its α-chloro and α-carbethoxy derivatives; it was inactive towards other derivatives such as methacrylonitrile, acrylamide, acrylic acid, etc.[269]

White and Farona have published a detailed report of their work involving the use of arenemolybdenum tricarbonyl compounds as active homogeneous catalysts in Friedel-Crafts reactions.[270] Reactions such as alkylation, acylation, sulfonylation of aromatic systems, dehydrohalogenation and polymerization were investigated. Evidence was presented for (arene)Mo(CO)$_3$ reacting with organic halides via a carbonium ion intermediate. The numerous advantages of these molybdenum catalysts over $AlCl_3$ in Friedel-Crafts reactions were discussed.

Copolymerization reactions of styrenetricarbonylchromium (LXXIX) as well as reactions of polystyrene with $Cr(CO)_6$ and $M(CO)_3(CH_3CN)_3$ (M = Mo, W) have been reported by Pittman and coworkers.[271]



(LXXIX)

Ethylene has been found to be polymerized in the presence of $(\pi\text{-}C_5H_5)_2Cr$ supported on activated SiO_2-Al_2O_3 to give low molecular weight, liquid polyethylenes.[272] An additional report on the use of aromatic complexes of transition metals in homogeneous catalysis has been published by Pavlik and Klikorka.[273] Included in their study was the use of $(C_6H_6)_2Cr$ in polymerization reactions of C_2H_4. $(C_6H_6)Cr(CO)_3$ and $(\pi\text{-}C_5H_5)_2Cr$ (in the presence of H_2 and CO, $C_5H_5Cr(CO)_3H$ being the effective catalyst) were also shown to be catalysts for selectively hydrogenating unsaturated molecules. Also, bis(cyclopentadienyl)chromium(II) supported on silica was treated with organometallic reducing agents (e.g., triethylaluminum and found to polymerize ethylene in high yields and at relatively low temperatures (85-90°).[274]

Tetra-π-allyldimolybdenum and tetra-π-crotyldimolybdenum complexes have been prepared from $(AcO)_4Mo_2$ and allylmagnesium chloride, allyllithium or crotylmagnesium bromide.[275] These complexes were then employed as catalysts in disproportionation reactions of 1-hexene to give ethylene and 5-decene at hexene conversions of 76% in 4 hr.

Copolymerization of butadiene and isoprene over tris(π-allyl)chromium-aluminosilicate catalyst yields a copolymer of predominantly 1,4-trans structure.[276] This system was further investigated using di-π-allylmonobutoxychromium or π-allyldibutoxychromium on aluminosilicate.[277] Again high molecular weight polybutadiene or polyisoprene of mainly 1,4-trans structure was obtained. It was noted that the unsupported catalyst gave lower molecular weight polymer and tributoxychromium is inactive as a catalyst. Tris(allyldimethylsilylmethyl)titanium is reported to polymerize ethylene in n-heptane at 60° with a catalyst activity of 0.07 g/mmole/atm/hr; aralkyl- or allylsilyl complexes of Cr, V, Zr, Ac also have this superior catalytic activity.[278]

Alkylation reactions of aromatics with alkyl halides in the presence of catalytic quantities of $Mo(CO)_6$ have been reported by Massie.[279] Similar reactions involving alkylation of aromatics with olefins have been reported as well by the same author.[280] Mixtures of 1,3 dienes have been subjected to photolysis in the presence of 1 atm H_2 and $Cr(CO)_6$ and their hydrogenated products analyzed by vpc.[281] ^{60}Co X-rays were found to affect the isomerization of 1-heptene in the presence of $Fe(CO)_5$ as catalyst; however $M(CO)_6$ molecules, M = Cr, Mo, W, were ineffective under these conditions.[282]

Ring-opening polymerization of cyclooctene was observed to give a 86% yield of polycyclooctene within 24 hr in the presence of $(o\text{-phen})W(CO)_4$ and $AlBr_3$ (benzene solution at room temperature).[283]

Catalytic polymerization of conjugated diolefins (e.g., butadiene) has been achieved employing dicarbonylhydrogenbis(tetrahydrofuran)(trifluoroacetato)molybdenum.[284]

The 4-component catalyst system (WCl_6, Et_3Al_2Cl, 1,3-dichloroisopropanol and thiophene) was used for diolefin metathesis with concurrent oligomerization.[285] The dienes studied were 1,4-pentadiene, 1,5-hexadiene, and 1,7-octadiene. Intramolecular disproportionation reactions of cis-1,4-polybutadiene have been studied using the complexes, WCl_6-$EtAlCl_2$, $(\pi\text{-}C_4H_7)_4W$-$EtAlCl_2$, and $(\pi\text{-}C_4H_7)_4Mo$-$EtAlCl_2$.[286] Matlin and Sammes have found $LiAlH_4$ to be an effective co-catalyst with WCl_6 for the homogeneous disproportionation of olefins.[287] In this manner the metathesis of hept-3-ene was studied and found to result in the formation of an equilibrium mixture of hex-3-ene, hept-3-ene, and oct-4-ene. The respective yields for a typical run were 18.5, 39, and 23%. Smaller quantities of nonene, pentene, and butene were formed as well.

$MoCl_5$ was found to be less effective than WCl_6 as the transition metal halide component in the $EtAlCl_2$ or Et_2AlCl catalyst system for the metathesis and ring-opening polymerization of cis, trans-1,5-cyclodecadiene.[288] The reaction of cis, cis-1,6-cyclodecadiene with the homogeneous catalyst of tungsten ($WCl_6/ROH/C_2H_5AlCl_2$) to yield cyclopentene in 1.9% (50°C) and 15.5% (80°C) has been communicated.[289]

A Ziegler-type catalyst system composed of WCl_6 and alkyl or aryl tin compounds was found to polymerize cyclopentene, norbornene, and other cyclic olefins to linear, unsaturated material *via* a ring-opening mechanism.[290] The catalyst systems $WCl_6/AlBu^{i}_{3}$, $WCl_6/AlBu^{i}_{2}Cl$ and $WCl_6/AlBr_3$-thiophene were used in the homopolymerization of 1,5-cyclooctadiene and norbornene in benzene at room temperature.[291] The effects on polymer type of ratio variation of catalyst were also studied. A German patent covering the preparation of copolyalkenomers from cycloolefins and polybutadienes in the presence of WCl_6 and $EtAlCl_2$ catalyst has been reported.[292] Polymerization reactions of the cycloolefins, cis,cis-1,5-cyclooctadiene, cis-cyclooctene, or cyclododecatriene, in the presence of WO_3 and $AlCl_3$, $EtAlCl_2$ or Et_3Al have as well been reported.[293] Cycloolefins such as cyclopentene have also been polymerized utilizing the tricomponent catalyst containing 1) alkyl Al, haloalkyl Al, or Al halide, 2) W or Mo halide and 3) trichloromelamine, N-bromosuccinimide, 2,4-dinitrophenylsulfenyl chloride, etc.[294] In order to S-vulcanize α-olefin polymers it was necessary to have a cyclic diene and WCl_6 or $VOCl_3$ in the complex catalytic system which also contained BuLi.[295]

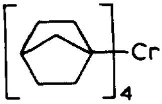
Butadiene and ethylene were copolymerized in the presence of chromic anhydride supported on silica-alumina and triethylaluminum to give ethylene-butadiene copolymers.[296] A study involving the alternating copolymerization of isoprene and butadiene with acrylonitrile in the presence of chromium tert-butoxide-dichloroethylaluminum catalyst has been reported by Koma and coworkers.[297] Formation of alternating structure was independent of the monomer feed ratio. Butadiene has been polymerized as well in the presence of $(EtO)_2MoCl_3$ and $(EtO)Et_2Al$ to give rubbery 1,2-polybutadiene.[298] An additional report employing (EtO)$_2$MoCl$_3$ and triisobutylaluminum for the polymerization of butadiene to rubbery 1,2-polybutadiene has appeared also.[299]

Low-molecular weight isobutylene-isoprene copolymer was obtained by mild catalytic degradation of high-molecular weight butyl rubbers using as catalyst MoCl$_5$/Et$_3$Al.[300] The WCl$_6$/Cl$_2$EtAl catalyst gave similar results in this system.[301]

Butadiene rubber, having 97% 1,2-configuration was obtained making use of the catalyst system dicyclopentadienylvanadium and molybdenum pentachloride.[302]

Dimerization, polymerization, and copolymerization of ethylene and propylene with the chromium complexes CrCl$_2$L$_2$, CrCl$_2$L$_2$(NO)$_2$, CrCl$_3$L$_3$, and [CrCl$_3$L$_2$]$_2$ (where L = pyridine, Bu$_3$P, Bu$_3$PO, Ph$_3$PO, and 4-ethylpyridine) have been reported.[303] The activating effect of NO on the olefin disproportionation catalyst MoOCl$_3$/Me$_3$Al$_2$Cl$_3$ has been further studied by Hughes and Zuech.[304] These investigations took the form of isolating the NO complexes of molybdenum halides resulting from reaction of NO with MoCl$_5$, MoOCl$_3$, etc., and the sequential reaction of MoCl$_5$ with NO and PPh$_3$. The catalytic ability of the complexes thus isolated was not reported. A catalytic system for epoxidation of olefinic compounds by molecular oxygen has been studied.[305] An epoxidation catalyst containing MoO$_2$Cl$_2$ or MoOCl$_4$, together with Al(OCHMe$_2$)$_3$, Me$_2$CHOH, or HOAc, and PPh$_3$ or (EtO)$_3$P showed 80-88% selectivity for epoxidation. The complex MoO$_2$(S$_2$CNR$_2$)$_2$ (R = Et, Pr, *iso*-Bu) and MoOCl$_4$ catalyze selective oxidation of PBu$_3$ to OPBu$_3$ supposedly through a molecular oxygen complex, e.g., Mo$_2$O$_3$(S$_2$CNR$_2$)$_4$, observed as a violet intermediate.[306]

Polymerization of 1-olefins using tetrakis(bicyclo[2·2·1]heptyl)chromium (LXXX) as catalyst was reported in a patent by



(LXXX)

Bower and Long.[307] Adsorption of chromium hydrocarbon complexes on the surface of γ-aluminum oxide afforded a material that catalyzed the polymerization of ethylene with propylene or dienes to give polymers of low crystallinity.[308] The intermediate chromium complexes, $Cr_2(C_2H_2)$ and $[Cr_2(C_2H_2)(NH_3)_8]Cl_4$, have been reported to be formed during chromium-catalyzed hydrogenation reactions of acetylene.[309]

Correlation between dehydration, oxidation and catalytic activity and selectivity was investigated for the ternary catalyst system containing MoO_3-P_2O_{10}-M_nO_m (M = metal).[310] Butadiene and 1-butene were used as standards for oxidation and polymerization, respectively. Air oxidation of dicyclopentadiene gave increased yields of maleic anhydride in the presence of a V-Mo-P catalyst.[311]

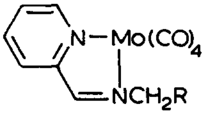
A nickel-chromium catalyst for hydrogenation of organic compounds was obtained by introducing $Al(OH)_3$ or Al_2O_3 into a Na_2CO_3 solution of Ni and Cr nitrates.[312] A similar catalyst system was reported for hydrogenation of piperylene to pentene.[313]

Trifluoroacetate compounds of Co, Ni, and Cr were investigated for their efficacy in polymerizing dienes or ethylene.[314] Chromium trifluoroacetate polymerized ethylene yielding essentially linear polyethylene.

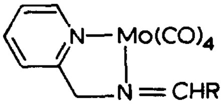
Spectroscopy

Electronic spectra and related photolysis studies. An interpretation of the electronic spectral changes upon variation of L in $Cr(CO)_5L$ complexes from the purely σ interaction of L = amine to the $(\sigma + \pi)$ interaction of L = phosphine has been put forth.[315]

Strong, negative solvatochromic effects of Group VIB metal complexes containing bidentate azomethine ligands have been reported by Walther.[316] The complexes $M(RCH{:}NR^1)(CO)_4$ (M = Mo, Cr; R = 2-pyridyl; R^1 = Et, cyclohexyl, $PhCH_2$, β-naphthyl, Ph, Me) and $(L(CO)_3MoRCH{:}N)_2Q$ (Q = p-phenylene, p,p'-biphenylene; L = CO, PPh_3) were prepared and their electronic spectra were determined in a variety of solvents. In addition the azomethine tetracarbonyl complexes of molybdenum (LXXXI A and LXXXI B) have been prepared and studied by ir and uv spectroscopy by Walther.[317]



(LXXXI A)



(LXXXI B)

Photochemical reactions of Group VIB hexacarbonyls and their derivatives continue to receive much deserved attention. Vacuum uv photolysis of $Cr(CO)_6$ in an argon matrix at 12°K has led to the production of the charged species $Cr(CO)_5^-$.[318] The $Cr(CO)_5^-$ anion was identified by ir spectral similarities with the previously reported species produced from co-condensation at 12°K of alkali-metal atoms and subsequent uv photolysis of $Cr(CO)_6$-Ar mixtures by Breeze and Turner.[319]

The flash photolysis of $Cr(CO)_6$ in highly purified cyclohexane solution has been examined using an apparatus with high resolution (flash half-width ≤ 3 μs).[320] A species with a lifetime of > 200 μs was immediately observed after the flash which had an absorption band of 503 ± 5 nm. This species reacted with impurities in the solvent to produce further species (λ_{max} 445 nm) which then decay (lifetime $<$ 1s) to reform the hexacarbonyl. If the solution were saturated with CO, the initially produced species reacted to reform $Cr(CO)_6$ with a half-life of 25 μs. These results are described below employing mechanisms (30), (31), and (32).

$$Cr(CO)_6 \xrightarrow{h\nu} Cr(CO)_5 + CO \tag{30}$$

$$Cr(CO)_5 + CO \rightarrow Cr(CO)_6 \quad (k = 3 \pm 1 \times 10^6 \ell\text{-mol}^{-1}\text{sec}^{-1}) \tag{31}$$

$$Cr(CO)_5 + X \rightarrow Cr(CO)_5X \quad (\lambda_{max}\ 445\ \text{nm}) \tag{32}$$

X was shown not to be $Cr(CO)_5$, $Cr(CO)_6$ or the solvent and was therefore proposed to be trace impurities in the solvent.

Photochemical reactions ($\lambda > 305$ nm) of $Mo(CO)_5P(C_6H_{11})_3$ in hydrocarbon glass were found to produce $[Mo(CO)_4P(C_6H_{11})_3]$ in two isomeric forms, with the phosphine and the vacancy in the coordination octahedron mutually <u>cis</u> and <u>trans</u>.[321] The <u>trans</u> isomer was found to convert into the <u>cis</u> isomer upon irradiation with visible light ($\lambda > 420$ nm). Additional photolysis of $Mo(CO)_5P(C_6H_{11})_3$ or the <u>cis</u> or <u>trans</u> form of $[Mo(CO)_4P(C_6H_{11})_3]$ was reported to produce the facial isomer of $[Mo(CO)_3P(C_6H_{11})_3]$. On the other hand photolysis of $Mo(CO)_5P(C_6H_{11})_3$ in MeTHF glass produced exclusively cis-$Mo(CO)_4[P(C_6H_{11})_3](MeTHF)$.

Further studies of this type have been carried out on bis(triisopropylphosphine)tetracarbonyltungsten in solution as well as in hydrocarbon or MeTHF glasses.[322] In solution photochemical loss of one phosphine ligand was observed, however in hydrocarbon or MeTHF glasses loss of a CO ligand only was observed. These contrasting results were explained as being due to a solvent cage effect in the matrix photolysis process. It was concluded that matrix isolation photolysis may be a poor test of photochemical mechanisms involving the displacement of relatively bulky ligands.

Photoprocesses in substituted tungsten carbonyl compounds have been investigated by Wrighton, Hammond, and Gray.[323] The excited state decay processes of chemical reaction, emission, and nonradiative transitions were discussed for $W(CO)_5(X)$ (X = pyridine, trans-2-styrylpyridine and trans-4-styrylpyridine) complexes. The lowest excited state ($^3E \rightarrow {}^1A_1$) was characterized by absorption and luminescence data. A decrease in photosubstitution yields of the styrylpyridines as compared with the pyridine complex was correlated with the lack of $^3E \rightarrow {}^1A_1$ emission and cis-trans photoisomerization of the coordinated styrylpyridine.

Infrared and Raman spectra. A thorough investigation of integrated infrared $\nu(CO)$ intensities of some 15 compounds of the type $L_2W(CO)_4$ and $LL'W(CO)_4$ has been carried out.[324] Overlapping bands were successfully separated by band shape analysis employing a Cauchy(Lorentz)-Gauss product function. The techniques presented should also prove useful for quantitative determination of mixtures of metal carbonyl species as well as for analysis of CO absorbed on metal surfaces. In addition, the effective atomic charges of $M(CO)_6$ (M = Cr, Mo, W) have been estimated by use of absolute integrated intensities for ir absorption bands of the molecules and the dipole moment derivatives subsequently calculated.[325]

A solution and single-crystal Raman study of the Group

VIB hexacarbonyls has been carried out by Adams and coworkers.[326] The previously unobserved $\nu_{10}(t_{2g})$ vibrational mode in the ν(M-CO) and δ(MCO) region for these three compounds are reported. Vibrations in ν(CO), ν(M-CO) and δ(MCO) regions were fairly insensitive to solvent effects. The single-crystal Raman studies led to results consistent with currently accepted assignments except for bands observed in $Mo(CO)_6$ below 120 cm^{-1} where many new lines were noted.

Force constants of metal-metal bonds in anions of the type $[MnM'(CO)_{10}]^-$, where M' = Cr, Mo, W, have been calculated through normal coordinate analyses based on assignment of the vibrational (both Raman and infrared) spectra and are in the order k(Mn-W) > k(Mn-Mo) > k(Mn-Cr).[327] For isoelectronic pairs k(Mn-Re) > k(Mn-W), and k(Mn-Mn) > k(Mn-Cr).

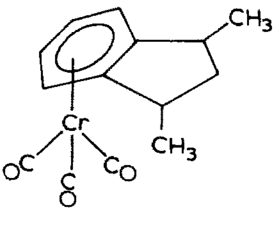
Vibrational studies, including Raman polarization data, are also reported for $Cr(CO)_4NBD$ (NBD = norbornadiene or 2:2:1-bicycloheptadiene) and PdX_2NBD (X = Cl, Br).[328] The authors have located and assigned the M-olefin stretching modes at <u>ca</u>. 250 cm^{-1}, the lowest known frequencies for such vibrations. Vibrational spectra (infrared and Raman) have also been obtained for h^5-$C_5H_5W(CO)_3CH_3$ and fully assigned based on the method of local symmetry.[329]

The 5K luminescence spectrum of $Cr(CN)_6^{-3}$ in $K_3Co(CN)_6$ has been used to determine infrared and Raman inactive fundamentals by Flint and Greenough.[330] In this manner the ir and Raman inactive T_{2u} Cr-C-N and C-Cr-C bending modes were located.

Ir frequency shifts of chromium- and iron-bonded nitrosyls have been correlated with epr spectral characteristics for a variety of these complexes which also contained diethyldithiocarbamate, butyl xanthate, thiourea, thiocyanate, etc., as ligands.[331]

Nuclear magnetic resonance and Mössbauer spectra. Carbon-13 nuclear magnetic resonance studies have been carried out on a large number of organometallic complexes during the past year.

The ^{13}C nmr spectra of tricarbonyl(trans-1,3-π-dimethylindane)chromium (LXXXII) and tricarbonyl(π-cyclo-octatetraene)-tungsten (LXXXIII) and their corresponding free ligands have been studied by Randall and coworkers.[332] Whereas the spectrum of LXXXII shows a separate resonance for every carbon atom in the ligand ring, the spectrum of LXXXIII indicates "fluxional" behavior. In a similar study the ^{13}C nmr spectra of $C_7H_8M(CO)_3$ (M = Cr, Mo) have been measured at room temperature and at -60°C.[333] At room temperature all three carbonyl C-atoms showed identical chemical shifts, however, at ~ -60°C distinct signals were observed for the chemically equivalent $C_{9,10}$ atoms and the C_8 atom (LXXXIV). However, the chemical shifts of the C-atoms of the ring system are essentially unaffected by temperature. These results were interpreted in terms of a spinning motion of the ring system at room temperature. An activation energy of ~ 12 kcal/mole was determined for this process.



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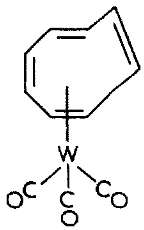
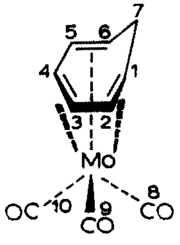


(LXXXIII)



(LXXXIV)

Mann has reported ^{13}C nmr spectral data for the complexes $M(CO)_6$, $W(CO)_nL_{6-n}$, $M'(CO)_4$(norbornadiene), and $M(CO)_3L'$ (where M = Cr, Mo, or W; M' = Cr or Mo; and n = 1, 2, or 3; L = PEt_3

and $P(OMe)_3$ and n = 1; L' = mesitylene, 1,2,4,5-tetramethylbenzene, hexamethylbenzene, or cyclohepta-1,3,5-triene).[334] In all cases replacement of CO ligands caused the ^{13}C (carbonyl) shift to move to lower field. Attempts to correlate ^{13}C (carbonyl) chemical shifts with Cotton-Kraihanzel force constants for complexes of varying geometry and oxidation state were unsuccessful. The first report of a $^{95}Mo-^{13}C$ coupling constant was included in this study, $^1J(^{95}Mo-^{13}C)$ being 68 Hz in $Mo(CO)_6$.

Carbon-13 nmr spectra have been reported for a series of substituted carbonyl complexes of tungsten and molybdenum of the form $(CO)_{6-n}ML_n$ (n = 1, L = tertiary phosphine, -phosphite, -arsine, amine, or carbene; n = 2, L = diphos and dpm) and for the corresponding free ligands.[335] The carbonyl ^{13}C chemical shifts were found to increase when CO was replaced by the ligands L. It was proposed that these chemical shifts reflect the charge donor ability of the ligands, L, as opposed to differences in π-bonding. The order of $\delta(CO)$ for the hexacarbonyl derivatives, Cr > Mo > W, was used as supportive evidence for this proposal. cis $^1J(^{183}W-^{13}CO)$ values were found to be insensitive to the nature of L in $W(CO)_5L$ species. This was attributed to a balancing of charges in $[\psi_m(0)]^2$, the s-electron density at the metal atom.

In addition to the report above several papers have appeared which probe the nature of the carbene ligand in carbene substituted metal carbonyl derivatives. The ^{13}C nmr spectra of a series of (carbene)$Cr(CO)_5$ derivatives have been recorded by Cotton and coworkers,[336] where carbene = $-C(OC_2H_5)Ph$, $-C(OC_2H_5)Me$, $-C(NHCH_3)Ph$, $-C(NHCH_3)Me$, $-C(NH(CHMe_2))Me$, and $-C(N(CH_3)_2)Me$. The chemical shifts of the carbene carbon atoms were observed to correlate with the ability of the attached substituents to engage in dative π bonding with the carbene carbon atom and were all found to be greatly deshielded (-271 to -360 vs TMS). The chemical shifts for the CO carbon atoms were found at higher fields (-218 (cis) and -224 (trans)) and were essentially unchanged with the nature of the carbene ligand. Short longitudinal relaxation times (T_1 = 1-2 sec) were observed for both carbene and carbonyl carbon atoms in the complex $(CO)_5Cr[C(CH_3)(OC_2H_5)]$.

Analysis of the ^{13}C nmr spectra of $M(CO)_5C(X)R'$ (M = Cr, W; X = NH_2, OR; R' = Me, Ph, and para- and meta-substituted phenyl) have been useful in further establishing the electronic nature of the carbene ligand.[337] For the compounds $(CO)_5MC(OMe)C_6H_4X'$ (X' = meta- or para-OCH_3, CH_3, Cl, CF_3, or Br) a general shift of $\delta(^{13}C)$ of the carbene carbon to higher fields with increasing π-donor ability of the substituent is observed. This work also presents a discussion of the apparent discrepancy between analysis of charge on carbonyl carbon atoms based on such factors as chemical reactivity and CO stretching force constant data as compared to $\delta(^{13}CO)$ data, i.e., evidently the most electron-deficient carbonyl carbon has the highest ^{13}C nmr chemical shift.

^{13}C nmr data for the bis carbene complex, cis-$(CO)_4Cr[C(SCH_3)_2]_2$ have been reported by Randall, et al.[338] Comparison of $\delta C_{carbene}$ (141.6 ppm in the above mentioned complex) with other carbene complexes of platinum and iron has been made.

^1H nmr studies have been used to show the interaction of orthophenyl hydrogen atoms of bis[1,2-bis(diphenylphosphine)-ethane] with cis CO ligands in cis-$[M(diphos)_2(CO)_2]$ (M = Cr, Mo, W) as well as similar Ir and Ru diphos complexes.[339] The authors suggest such an analysis of phenyl protons of complexed diphos to be diagnostic of cis or trans isomers.

Nmr techniques were used in an attempt to distinguish cis and trans isomers of h^5-$C_5H_5M(CO)L_2X$ (M = Mo, W; L = PRR'_2;

X = halogen).[340] The complicated low temperature ^{1}H nmr spectra were interpreted according to two possibilities: 1) restricted rotation of one or more L groups about the M-L bond at low temperatures, or 2) the slowing down of *cis-trans* isomerization and or *cis* $\rightleftharpoons$ *cis* interconversions at low temperatures. Room temperature spectra were indicative of either the *trans* isomeric form or an average spectrum due to rapidly interconverting isomers.

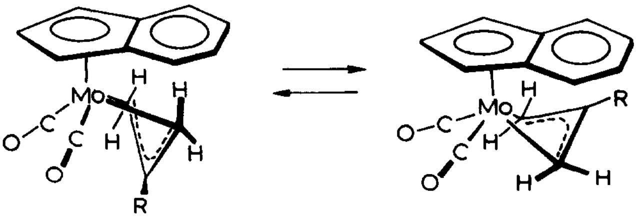
π-$C_5H_5W(CO)_2(L)SnMe_3$ has been synthesized by reaction of Me_3SnCl with $[\pi$-$C_5H_5W(CO)_2(L)^-]$ (L = phosphines or phosphites). Analysis of $\nu(CO)$ infrared as well as ^{1}H, ^{31}P and ^{13}C data lead the authors to propose a *trans* arrangement of the two CO groups in the square base formed by monodentate ligands. Values of $J_{^{31}P-^{117}Sn}$ or $_{^{119}Sn}$ correlate with the ligand basicities and are found to decrease as $J_{^{31}P-^{183}W}$ increase. The presence of ^{31}P-$^{1}H(C_5H_5)$ coupling concurrent with the absence of ^{31}P-$^{13}C(C_5H_5)$ coupling in the *trans* isomer led the authors to propose "through-space" ^{31}P-^{1}H coupling.[341] This suggestion was subsequently disputed by McFarlane, *et al*.[342]

The sign of ^{1}J (^{31}P-^{183}W) in the tungsten(0) octahedral complex, $Me_2PhPW(CO)_5$, has been determined to be positive (+ 230 ± 3 Hz) from heteronuclear double resonance experiments.[343] It therefore appears that theoretical treatments of these coupling constants which assume a dominance of the Fermi contact interaction and a mean excitation energy approximation are adequate.

A re-evaluation of the nmr spectrum of $(\pi$-$C_5H_5)W(CO)_3H$ in a nematic liquid crystal solvent has shown that three orientation parameters, rather than one as was previously reported, are required to specify the orientation of the molecule.[344]

Attempts to obtain additional dipolar couplings employing a 40% ^{13}CO enriched $(\pi\text{-}C_5H_5)W(CO)_3H$ sample failed to give a W-H bond length for a number of reasons which were discussed.

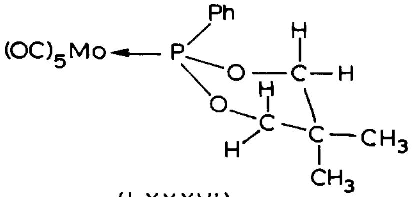
Faller and coworkers have further studied steric effects on π-allyl and π-indenyl orientation in molybdenum and tungsten complexes by nmr techniques in detail.[345] The two stable configurations of the allyl moiety (LXXXV A or LXXXV B) are found in approximately equal proportions in either the cyclopentadienyl or indenyl complex. However, large differences in the proton chemical shifts in the allyl resonances were observed for the indenyl species due to the magnetic anisotropy of the indenyl ring. This anisotropy was used to establish the stereochemistry of these type species in solution (A or B). Equilibrium constants for the reaction A $\rightleftharpoons$ B were determined as a function of the substituent on the allyl ligand, the metal (Mo or W), the temperature, and the solvent. Pronounced solvent effects were noted. Analysis of the magnitude of the magnetic anisotropy arising from the benzene ring has suggested that although there is relatively free rotation of the indenyl ligands, there is a preferred conformation where the benzene ring is oriented over the allyl group.



(LXXXV A) (LXXXV B)

The effect of a metal carbonyl moiety on the ring conformation of 2-substituted 5,5-dimethyl-1,3,2-dioxaphosphorinanes (2-X-DMP) has been investigated by Bartish and Kraihanzel.[346]

Analysis of nmr data of $M(CO)_5$ (M = Cr, Mo, W), $Fe(CO)_4$ and $Ni(CO)_3$ derivatives indicate the chair conformation to be the predominant form of the 1,3,2-dioxaphosphorinane ring. An abnormally large change in chemical shift of the axial methylene protons of 2-C_6H_5-DMP upon coordination to $Mo(CO)_5$ is attributed to the ring current of an axially oriented phenyl ring (LXXXVI).



(LXXXVI)

The base-coordinated "stannylene" complexes, $R_2SnCr(CO)_5 \cdot B$ (B = THF, DMSO, and py) and $R_2SnFe(CO)_4 \cdot B$ (B = DMSO and py) have been studied by ^{119m}Sn Mossbauer and photoelectron (ESCA) spectroscopy.[347] Both lines of evidence suggest the $R_2(B)Sn$ moiety is bonded to the metal as in conventional organotin-transition metal complexes, i.e., organic derivatives of tin(IV). Quadropole splitting values are abnormally large and increase in the order py > DMSO > THF.

Esr spectra. Few esr studies have been reported in organometallic reviews of Cr, Mo, and W. However an interesting study of the relatively stable radical anion of π-cyclopentadienyl-π-cycloheptatrienylchromium ($CpCrTr\cdot^-$) has been used to infer the LUMO of CpCrTr to be of predominantly π-ligand character.[348] This conclusion is substantiated by the general resistance of arene-chromium complexes towards forming radical anions. In addition, solution and frozen solution esr spectra as well as ^1H nmr spectra of polycrystalline samples of $(\pi\text{-}C_5H_5)(\pi\text{-}C_6H_6)Cr$,

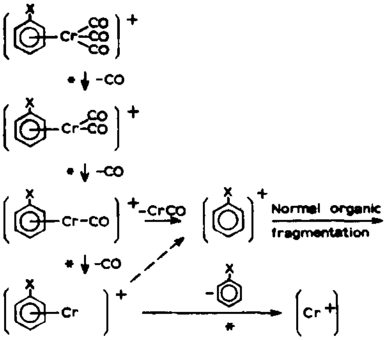
$(\pi\text{-}C_6H_6)_2Cr$, and $(\pi\text{-}C_5H_5)(\pi\text{-}C_7H_7)Cr^+$ have been reported.[349] An attempt was made to relate the magnetic parameters to the ring size of the aromatic ligands and the total charge of the complexes.

An esr study of chromium nitrosyl compounds with oxygen-containing ligands, as well as in one instance with molecular nitrogen, has been reported by Luchkina and Tokareva.[350] The g factors and the hyperfine parameters were given for the complexes, $[Cr(acac)_2(NO)(H_2O)]^{+2}$, $[CrL_2(NO)H_2O]^{+2}$, $[Cr(acac)(DDP)(NO)(H_2O)]^{+2}$, $[CrL_2(NO)H_2O]^{+2}$, and $[CrL_2(NO)N_2]^{+2}$ (HDDP = diethyldithiophosphate and L = pyrocatechol). In addition, esr spectral measurements of the chromium nitrosyl derivatives, $Cr(NO)(H_2O)_3L$ (HL = 2,4-dihydroxydithiobenzoic acid, 2,3,4-trihydroxydithiobenzoic acid, and 3-indolyldithiocarboxylic acid), have been reported at 77°K.[351]

<u>Mass spectra</u>. Bond and Duffy have reported the mass spectra of a variety of monosubstituted Group VIB carbonyl derivatives of the type $M(CO)_5L$ (where L = ligands of trivalent N, P, As, and Sb, or pyridine).[352] The mass spectral results were found to show no clear correlation with the Graham σ- and π-parameters. This was interpreted in terms of formation in the source of the mass spectrometer of $M(CO)_5L^+$ species, whose bonding properties should be considerably different from those of the neutral species $M(CO)_5L$.

Dissociation energies of M-L for bis(arene)molybdenum complexes such as $(\pi\text{-}C_6H_6)_2Mo$, $(\pi\text{-}C_6H_5Me)_2Mo$, and $(\pi\text{-}C_6H_4Me_2)Mo$ have been calculated from mass spectral studies.[353] The M-L bonds of the Mo series appear to be stronger than those of the analogous Cr series.

Ionization potentials and some appearance potentials of compounds of the type $ArCr(CO)_3$ have been measured by Gilbert, Leach, and Miller for a variety of substituted benzene derivatives.[354] The principal fragmentation patterns at 50 eV are shown in the scheme below. The values obtained for ionization and appearance potentials were found to correlate, for the loss of one and two carbonyl groups, with both the CO force constant and the Hammett σ_p function of the substituent on the benzene ring. The reactions of substituted arenechromium tricarbonyl derivatives in a mass spectrometer source have been studied



further by Gilbert, Leach, and Miller.[355] Ions of the types $[Ar_2Cr_2(CO)_3]^+$ and $[Ar_2Cr_3(CO)_6]^+$ have been observed which arise from ion-molecule reactions at pressures of 5×10^{-6} to 2×10^{-5} mm Hg. Fragmentation pathways of these secondary ions were investigated.

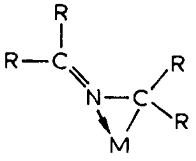
A study of gas-phase ion-molecule reactions of organometallics, including the reaction of $Cr(CO)_4^-$ and $Cr(CO)_3^-$ with $Cr(CO)_6$ to give $Cr_2(CO)_8^-$ and $Cr_2(CO)_6^-$, respectively has been carried out utilizing ion cyclotron resonance (icr) spectroscopy.[356] The icr technique is described.

Mass spectral studies show the pyrolysis of $Mo(CO)_6$ and

$W(CO)_6$ at 20-125° and 20-230° respectively yields $Mo(CO)_n$ and $W(CO)_n$ (n = 1-5) in a step-wise manner.[357]

Photoelectron spectra and molecular orbital calculations. The number of papers dealing with the measurement and interpretation of photoelectron spectra of organometallic complexes of the Group VIB metals has increased greatly. The photoelectron spectrum of $Cr(PF_3)_6$ has been determined.[358] Comparison of the vertical ionization potentials of the 3d orbitals in this and other PF_3 derivatives with those reported for the analogous metal carbonyls indicate a more positive charge on the metal in the PF_3 species. This is assumed to be due to a stronger electron-withdrawing property of PF_3 as compared with CO.

X-ray photoelectron spectral studies have been carried out on the complexes $(\pi\text{-}C_5H_5)M(CO)_2N{:}CR_2$ and $(\pi\text{-}C_5H_5)M(CO)_2R_2CNCR_2$ (where M = Mo or W; R = p-tolyl or p-$CF_3C_6H_4$).[359] These measurements support the structure of the latter complexes to be that of aza-allyl complexes (LXXXVII) as opposed to aza-allene complexes. Linear correlations were observed between the metal binding energies and the solid-state carbonyl stretching frequencies for both the molybdenum and the tungsten complexes. Increasing $\nu(CO)$ values (symmetric vibration used) were noted for increasing binding energies.



(LXXXVII)

He(I) radiation (58.4 nm), He(II) radiation (30.4 nm) and valence region X-ray photoelectron spectra of the Group VIB hexacarbonyls have been reported.[360] The assignments of these spectra have been made on the basis of relative band intensities and correlation with reliable molecular orbital calculations. The core electron ionization potential of carbon monoxide when complexed in $Cr(CO)_6$ has as well been reported by Hillier and coworkers.[361]

The He(I) photoelectron spectra of a variety of first row transition elements metallocene species, including $(\pi\text{-}C_5H_5)_2Cr$ and $(\pi\text{-}C_5H_4Me)_2Cr$, have been reported.[362] The metal 3d ionization structure was discussed in terms of ligand field theory, however no conclusive band assignments of the He(I) spectra for the chromium species were possible. In addition, the X-ray photoelectron spectra of the monomeric metallocenes of the first row transition metals (including $(\pi\text{-}C_5H_5)_2Cr$) have been reported and discussed in terms of molecular orbital calculations.[363] The metal was found to be positively charged in all cases studied.

The He(I) photoelectron spectra of some π-arene complexes, including $(\pi\text{-}C_6H_6)_2Cr$, $(\pi\text{-}C_6H_5CH_3)_2Cr$, and $(\pi\text{-}C_6H_6)(\pi\text{-}C_5H_5)Cr$ have been measured by Evans and coworkers.[364] The electronic structure of these species was discussed in terms of the obtained ionization energy data. X-ray photoelectron (ESCA) spectral measurements were performed which complemented previous He(I) photoelectron spectra for symmetrical and unsymmetrical bis-(arene)chromium complexes.[365] Additional ESCA studies of chromium complexes have as well been carried out by Pignataro and coworkers.[366] The chemical shifts of the core ionization energies of $(C_6H_6)_2Cr$, $(C_6H_6)Cr(CO)_3$, $CH_3COOC_6H_5Cr(CO)_3$, and $Cr(CO)_6$ were measured.

The He(I) photoelectron spectra of $[(CH_3)_3Si(CH_2)]_4M$ (where M = Cr, Sn, and Pb), $[(CH_3)_3CCH_2]_4Cr$, and $[(CH_3)_3SiCH_2Cl]$ have been examined.[367] The similarity in the first ionization potentials of $[(CH_3)_3SiCH_2]_4Cr$ (7.25 eV) and $[(CH_3)_3CCH_2]_4Cr$ (7.26 eV) suggest that these two ligands are very similar and therefore infers that d_π-d_π backbonding between chromium and silicon is not important in the silyl complex. The stabilities of the complexes were discussed in terms of their photoelectron spectra and it was concluded that these results substantiate the belief that the stability of these complexes is due to kinetic factors as opposed to unusually strong metal-carbon bonds.

Mason and Mingos have employed a molecular orbital approach to discuss the geometries of and bonding in a large variety of bi- and polynuclear transition and main group metal complexes containing bridging ligands.[368] Included in this study were the following Group VIB organometallic derivatives: $[Mo_2(CO)_4(\pi\text{-}C_5H_5)_2(PMe_2)H]$, $[(\pi\text{-}C_4H_4)MoBr(CO)_2]_2$, $Cr(NO)(\pi\text{-}C_5H_5)(SPh)]_2$, and $[Cr(NO)(\pi\text{-}C_5H_5)(NMe_2)]_2$.

Fitzpatrick and Mathews have carried out self-consistent charge and configuration molecular orbital (SCCC-MO) calculation on the complexes $\pi\text{-}C_5H_5Mn(CO)_2L$ and $\pi\text{-}C_6H_6Cr(CO)_2L$ (L = CO or N_2).[369] These calculations have shown that N_2 is a weaker π-acceptor ligand than CO in either the tricarbonyl or dicarbonyldinitrogen complexes, and a stronger $(\sigma + \pi)$ electron donor ligand than CO in the tricarbonyl complexes.

Miscellaneous studies, including measurements of thermodynamic quantities

The electric dipole moments of a variety of substituted benzene- and thiophene-chromium tricarbonyl compounds have been reported.[370] The arene-$Cr(CO)_3$ group moment was found to depend on the nature of the substituent on the arene ring and these values were correlated with ν(CO). The dipole moment of tricarbonylthiophenechromium was observed to be 0.95D larger than that of its benzene analog despite the lower π-bascity of thiophene. This result was explained by the relatively high S-Cr bond moment (e.g., 4.0D in(dimethylsulfoxide)$Cr(CO)_5$).

$^{99}Mo(CO)_6$, prepared by neutron irradiation of pure $Mo(CO)_6$, decays to produce 6 hr $^{99}Tc^m(CO)_x$ in extremely small quantities which were trapped in the solid molybdenum carbonyl matrix.[371] $IMn(CO)_5$ and photochemically produced $\cdot Mn(CO)_5$ were used to scavenge the technetium species, believed to be the $\cdot Tc(CO)_5$ radical. In a related study $^{99}Tc^m$ has been shown to be stabilized in 88% yield in the form of $(\pi\text{-}C_5H_5)_2{}^{99}Tc^mH$ following the β-decay of ^{99}Mo in $(\pi\text{-}C_5H_5)_2{}^{99}MoH_2$.[372]

A face-centered cubic metallic atoms carbide phase is formed during the thermal decomposition of $W(CO)_6$ at 400-800° with composition on the order of $WC_{0.59}$ at 400°.[373] At temperatures $>$ 700°, significant amounts of pure W are produced. Pyrolysis of $Mo(CO)_6$ yielding CO and Mo is reported to be complete in 10 min at 157° in hexylalcohol.[374]

DTA and X-ray diffraction measurements in $Mn_2(CO)_{10}$ and $Tc_2(CO)_{10}$ have shown a reversible structural change at 64-5°.[375] No such change was however observed in $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

The solubility as well as enthalpy and entropy of solution was determined for $Cr(CO)_6$ and $W(CO)_6$ in $Fe(CO)_5$ as solvent.[376] The vapor pressure of these binary systems was determined as well.

Trends in metal-carbon monoxide bond strengths have been noted in a recent communication.[377] It appears that $\bar{D}$(M-CO), the mean metal-carbon monoxide bond dissociation energy, increases across the latter half of the first row transition metal carbonyls and down the Group VIB hexacarbonyls.

A Calvet high temperature microcalorimeter has been used to measure the enthalpies of thermal decomposition of several metal carbonyls, including $Cr(CO)_6$ and $Mo(CO)_6$.[378] In addition, the enthalpy of reaction of $Cr(CO)_6$ with iodine vapor has been measured. The ΔH_f° for $Mo(CO)_6$ from thermal decomposition studies was measured as -229.5 kcal/mole, in good agreement with the literature value. However, the ΔH_f° values determined for $Cr(CO)_6$ from thermal decomposition studies (-229.9 kcal/mole) or from iodination reaction (-234.3 kcal/mole) were considerably less negative than the literature value of -257.4 kcal/mole. Similar studies have been carried out on $Cr(C_6H_6)_2I$, $(C_6H_6)_2Cr$, (arene)$Cr(CO)_3$ (where arene = C_6H_6, $C_6(CH_3)_6$ and $C_6H_5CH_3$), and (cyclo-C_7H_8)$Cr(CO)_3$.[379] Enthalpy of formation data for these compounds were combined with available enthalpy of sublimation data to calculate the total enthalpies of disruption of the chromium-ligand bonds. In the (arene)$Cr(CO)_3$ compounds, the ligand binding energy was found to be substantially increased on replacing arene = benzene by hexamethylbenzene.

Further electrochemical oxidation studies of organometallic complexes of $Cr(CO)_5L$ (L = Lewis base or carbene), $M(CO)_4L_2$ and $M(CO)_4LL$ (M = Cr, Mo, W), and $Mo(CO)_2(LL)_2$ have been carried out by McCleverty and coworkers.[380] The values of the oxidative one-electron transfer potential ($E_{1/2}$) were observed to be influenced by each of the variables M, L (or LL). The order of $E_{1/2}$ values appears to follow the apparent π-acceptor/σ-donor ratio of the ligands. In addition these workers have examined the voltammetric oxidation of substituted benzene, cycloheptatriene, and cycloheptatrienyl chromium tricarbonyl complexes.[381]

Bis(biphenyl)chromium and ferrocene were found to be suitable as reference redox systems for comparison of half-wave potentials in a number of non-aqueous solvents; i.e., the difference between their half-wave potentials is nearly equal in each non-aqueous solvent.[382]

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