CHROMIUM, MOLYBDENUM AND TUNGSTEN
ANNUAL SURVEY COVERING THE YEAR 1972

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CONTENTS

ABBREVIATIONS

Ph--phenyl

Vy--vinyl

TCNE--tetracyanoethylene

Me--methyl

THF--tetrahydrofuran

Et--ethyl

triphos--bis(2-diphenylphosphinoethyl)phenylphosphine

^{i}Pr--isopropyl

^{t}Bu--tertiary butyl

^{n}Bu--normal butyl

Ac--acyl

Cp--π-C_5H_5

py--pyridine

bipy--2,2'-bipyridine

diphos--1,2-bis(diphenylphosphino)ethane

diars--1,2-bis(diphenylarsino)ethane

phen--1,10-phenanthroline

pz--pyrazolyl

Ar--aryl

Introduction

The increasing volume of work in organometallic chemistry has necessitated the reduction of overlap in coverage in Annual Surveys. Accordingly, as has been the case in the past few years, structural determinations for Group VIB organometallic compounds will not be dealt with in this review. In addition, duplication of material covered in the section, "Organic Reactions of Selected π-Complexes" will be minimized. The reader is referred to the review, "Organometallic Structure-Transition Metals" elsewhere in Annual Surveys for structural determinations of Group VIB organometallic compounds.

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

Dissertations

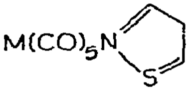
Doctoral dissertations which have dealt wholly or in part with topics falling within the scope of this review may be ordered from University Microfilms, 300 North Zeeb Road, Ann Arbor, Michigan, 48106; the microfilm order number for each dissertation is included in the bibliography.

Bond[1] has investigated the mass spectra and bonding in Group VIB metal pentacarbonyl compounds of the form $M(CO)_5L$ (where M = Cr, Mo, W and L = trivalent compounds of N, P, As and Sb, or pyridine). Approximate molecular orbital calculations on large, low symmetry transition metal complexes of the type $M(CO)_{6-x}L_x$ (where M = Cr, L = Cl, Br, I and x = 1 and 2) were carried out by Hall[2]. The electrochemical reduction of $Cr(CO)_6$ to produce the $Cr_2(CO)_9^{-4}$ anion has been studied by Halm[3], while Schlientz[4] has investigated reactions of Group VI metal dinuclear carbonyl dianions, $M_2(CO)_{10}^{=}$ (M = Cr, Mo, W) with mercury and silver salts. Myrott[5] has examined the ^{31}P nmr spectrum of $W(CO)_3(QP)$, where QP = $(o\text{-}C_6H_4\text{-}PPh_2)_3P$. Infrared studies of Group VI metal carbonyl derivatives of the type $LM(CO)_5$ and $(L\text{-}L)M(CO)_4$ have been investigated in both the CO and metal-carbon stretching regions by Brown.[6] Kinetic and vibrational spectral measurements have been carried out on a variety of Group VIB metal carbonyls by Jernigan.[7] The reactions of electrophiles with $M(CO)_4L_2$ (M = Mo, W; L_2 = 2,2'-bipyridine, 1,10-phenanthroline) and $Mo(CO)_2(diphos)_2$ (diphos = 1,2-bis(diphenylphosphino)ethane) have been reported by McDonald.[8] Benedict[9] has reported the synthesis and characterization for a number of new cyclopentadienylmetal cations, including π-$C_5H_5M(CO)_2(L)(L')^+$, (M = Mo, W; L and L' = CO, $CNCH_3$, $P(C_6H_5)_3$ and $P(OCH_3)_3$). The results of the reactions of these cations with the nucleophiles C_6F_5Li and $NaBH_4$ were also reported. Transition metal complexes of heptafulvene, including attempts at the preparation of a heptafulvenechrominum tricarbonyl complex, are described by Ehntholt.[10] Adcock[11] has reported the preparation and characterization by i.r., nmr and uv-visible spectra of tricarbonylchromium(0) complexes of hexamethylborazine, B-monophenylpentamethylborazine, B-monoethylpentamethylborazine, and N-triethyl-B-trimethylborazine. The chemistry and ligative capacities of a number of inorganic cage molecules [P_4S_3, $P_4S_3I_2$, As_4S_3, $As_4(NCH_3)_6$, $P_4(NCH_3)_6$ and $P_4Se_3I_2$] with Group VIB metal carbonyls have been investigated by Willingham.[12] MacInnes[13] has reported reactions of a new compound 1,2,3,4,5,6-hexaphenyl-1,4-diphosphacyclohexa-2,5-diene (L) (prepared from $(PhPLi)_x$ and <u>cis</u>-1,2-dichloroethylene) with $Cr(CO)_6$ to yield $Cr(CO)_5L$. Reactions of derivatives of phenarsazine chloride with $Cr(CO)_6$ and $Mo(CO)_6$ have been examined by Hunt.[14] Sigma-allyl analogs of transition metal carbonyls, including $Me_2VyEM(CO)_x$ (E = Sn, Ge and $M(CO)_x$ = $(\pi$-$C_5H_5)Mo(CO)_3$, $(\pi$-$C_5H_5)Mo(CO)_2$-(PPh_3), and others), were synthesized and investigated by

Job.[15] Su[16] has reported reactions of TCNE with several alkyl, alkenyl, and alkynyl complexes of substituted molybdenum carbonyls to form addition products. Stanclift[17] has described the preparation and spectral properties of transition metal carbonyl complexes of constrained bicyclic phosphite esters, including $M(CO)_{6-x}L_x$ (x = 1-3, M = Cr, Mo, W, and L = $P(OCH_2)_3CR$ where R = CH_3, C_2H_5, or C_3H_7), π-C_5H_5-$Mo(CO)_2LX$ and π-$C_5H_5Mo(CO)L_2X$ (X = Cl, Br, I). The synthesis and structural characterization of some novel organomolybdenum sulfur cluster complexes have been reported by Vergamini.[18] Chan[19] has studied the crystal and molecular structure of $(\pi\text{-}C_5H_5)_2Cr_2(NO)_3(NH_2)$ in which the two chromium atoms are linked by a Cr-Cr bond and bridging nitrosyl and amido groups. The crystal structure of benzocyclobutadiene chromium tricarbonyl triphenylphosphine has been determined by single crystal x-ray diffraction techniques by Oliver.[20] The crystal and molecular structure of π-allyl-dihydrobis-(3,5-dimethyl-1-pyrazolyl)boratodicarbonylmolybdenum has been reported by Kosby.[21] The crystal structure of $MoHB(pz)_3(CO)_2$-N_2Ph has been solved by Nemiroff.[22] The x-ray structure determination of metal-cage complexes, including ,$[(C_4H_9)_4N^+]_2$-$[Fe(1,7\text{-}B_9H_9CHPCr(CO)_5)_2^{-2}]$, is contained in a thesis by Reis.[23] Plastas[24] has reported the crystal and molecular structures of pentacarbonyl(triphenylphosphite)chromium(0) and pentacarbonyl(triphenylphosphine)chromium(0).

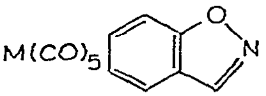
Preparative

Lewis base and related derivatives. Again this year the literature contains numerous papers which have dealt with the direct or indirect synthesis and subsequent characterization of simple substitution products of the Group VIB metal carbonyls. A specific synthesis of monosubstituted derivatives of the Group VI metal carbonyls ($LM(CO)_5$, L = NH_3, NCMe, PH_3, PMe_3, $Me_2NCH_2CH_2NMe_2$ (monodentate) and $Me_2PCH_2CH_2PMe_2$ (monodentate); M = Cr, Mo, W) has been reported.[25] The high yield (~ 80 %) synthesis consists of reaction of halopentacarbonylmetallates with L in CH_2Cl_2 and in the presence of a Lewis acid such as Et_3OBF_4. The photochemical preparation and ^{14}N, ^{1}H-NMR and IR spectra of the pentacarbonyl complexes of Cr, Mo and W with isothiazole (I), 1,2-benzisoxazole (II) and 2-methylbenzoxazoles, -thiazoles and -selenazoles (III) have been reported.[26] Linkage isomers of 2-methylbenzthiazole with chromium, 2-methylbenzselenazole with tungsten, and isothiazole with molybdenum were observed.



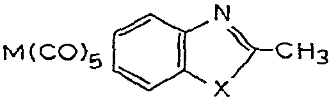
I

(M = Cr, Mo, W)



II

(M = W)



III

(M = Cr, W and X = O, S, Se; M = Mo and X = O)

The thermal and photochemical preparation of several Group VIB penta- and tetracarbonyl complexes of simple and conjugated P-triphenylphosphorus ylides have been reported by tom Dieck and co-workers (eqns. 1-3).[27]

$$Ph_3P{=}CHR + M(CO)_6 \rightarrow M(CO)_5(Ph_3P{=}CHR) + CO \qquad (1)$$

(M = Cr, Mo, W, R = Ph; M = Cr, R = $CH{=}CHCH_3$;
M = Mo, R = $CH{=}CH_2$, $CH{=}CHCH_3$, $CH{=}CHPh$)

$$2Ph_3P{=}CHPh + M(CO)_6 \rightarrow \underline{cis}\text{-}M(CO)_4(Ph_3P{=}CHPh)_2 + 2CO \quad (2)$$

(M = Mo, W)

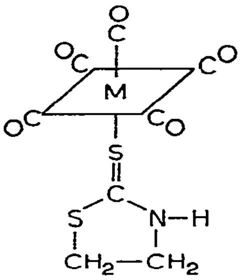
$$Ph_3P{=}CH\text{-}CR{=}CH_2 + Mo(CO)_6 \rightarrow (Ph_3P{=}CH\text{-}CR{=}CH_2)Mo(CO)_4 + 2CO \quad (3)$$

(R = H, CH_3)

A variety of organometalarsine Group VIB metal pentacarbonyl complexes have been prepared photochemically in THF at room temperature from the organometalarsine and the hexacarbonyls.[28] Prepared in this manner were the complexes $[(CH_3)_3M]_3AsM'(CO)_5$, where M' = Cr, Mo, W and M = C, Si, Ge, and Sn. Monosubstituted derivatives of $M(CO)_6$ containing the novel ligand $[Ph_2P]_3P$ are obtained either by irradiating THF solutions of $M(CO)_6$ in presence of the ligand or according to eq. 4.[29]

$$[Me_3Sn]_3P\text{-}M(CO)_5 + 3Ph_2PCl \rightarrow [Ph_2P]_3P\text{-}M(CO)_5 + 3Me_3SnCl \quad (4)$$

The yellow, crystalline complexes $M(CO)_5ttz$ (where M = Cr, Mo, W, and ttz = thiazolidine-2-thione) (IV) have been prepared by u.v. irradiation of toluene solutions of $M(CO)_6$ and ttz.[30] These complexes were characterized by mass-spectra, i.r. and nmr which indicated that the metal-ligand bond takes place through the sulfur atom of the thioketonic group. Quantum yield studies carried out on these systems indicated a S_N1-type mechanism for these processes, first-order in $M(CO)_6$ and zero-order in thiazolidine-2-thione.



IV

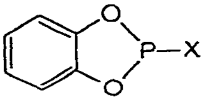
Mathieu and Poilblanc[31] have reported the preparation of penta- and hexasubstituted derivatives of Group VIB metal hexacarbonyls. The following complexes were prepared by extensive irradiation of pentane solutions of the carbonyls with excess of ligand; ML_6 (M = Cr, Mo, W and L = $\underline{n}$-$C_3H_7OPF_2$ and $P(OCH_3)_2F$), $Mo[P(OCH_3)_3]_6$, $M(CO)L_5$ (M = Cr, Mo, W and L = $P(OCH_3)_3$ and $CH_3P(OCH_3)_2$, and $Cr(CO)[CH_3OP(CH_3)_2]_5$. Infrared and nmr data were reported for these complexes. The degree of substitution was discussed in terms of the electronic and steric properties of the phosphine ligands.

Photochemical substitution reaction of $M(CO)_5L$ compounds with Lewis bases (eq. 5) (where M = Cr, Mo, W; L = an amine or phosphine; L' = an amine, phosphine, or ^{13}CO) have been studied by Schwenzer, Darensbourg and Darensbourg.[32] The preparation of new mixed phosphine-amine ligand compounds of molybdenum and tungsten was achieved in good yield by this procedure.

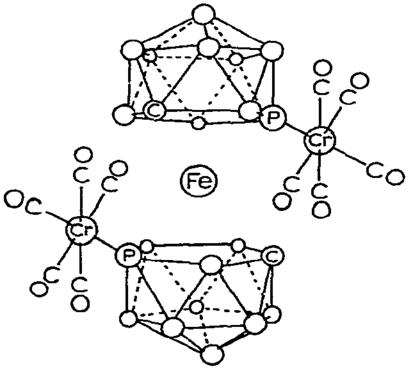
$$M(CO)_5L + L' \xrightarrow{h\nu} M(CO)_4LL' + CO \qquad (5)$$

The $\underline{\text{cis}}$-disubstituted products obtained from irradiation of the pentacarbonyl phosphine complexes, based on ^{13}CO substitution and $\underline{\text{trans}} \rightarrow \underline{\text{cis}}$ studies, were proposed to result from initial formation of the trans isomer followed by a trans → cis photochemical isomerization.

2-Substituted 1,3,2-benzodioxaphosphole derivatives of $W(CO)_6$ have been prepared from reactions of the appropriate ligands (V) with the $W(CO)_5THF$ complex.[33] Attempts to prepare other derivatives (e. g. X = NCO, NSC, SC_6H_5, SCH_3, and OCH_3) of $C_6H_4O_2P(X)$ led to unstable compounds.



V



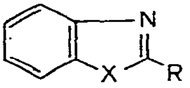
VI

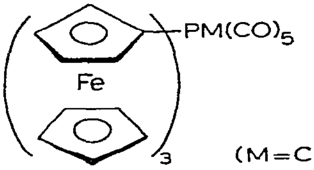
Todd and Beer[34] have reported the preparation of novel Group VI metal carbonyl derivatives of substituted phospha- and arsacarboranes π-bonded to iron. The stoichiometry of the complexes of proposed structure (VI) is $[1,7\text{-}B_9H_9CHE\text{-}M(CO)_5]_2Fe^{=}$ where E = P or As and M = Cr, Mo, W. In addition neutral complexes such as $7,8\text{-}B_9H_9(3\text{-bromopyridine})CHP\cdot Cr(CO)_5$ have been prepared.

Bowden and Colton[35] have investigated reactions of o-, m- and p-tritolylphosphine with $M(CO)_6$ (M = Cr, Mo, W) under a variety of conditions of temperature, u.v. irradiation, and molar ratio. Products of the general formulae $M(CO)_5L$ and cis- and trans-$M(CO)_4L_2$ were prepared. A novel series of derivatives with tri(o-tolyl)phosphine (L') were isolated which on the basis of i.r., nmr, and mass spectral data were formulated as π-L'M$(CO)_3$ derivatives. The nature of the reactions and the properties of the products obtained were explained in terms of steric effects. In addition, reactions of $M(CO)_4X_2$ (M = Mo, W; X = Cl, Br, I) with o-, m- and p-tritolylphosphine have led to formation of products of the types $M(CO)_3L_2X_2$, $M(CO)_2L_2X_2$, $[LH][M(CO)_3LI_3]$.[36] The oxidation of trans-$M(CO)_4(PPh_3)_2$ with halogens and the reaction of PPh_3 with $M(CO)_4I_2$ have been reinvestigated along with a study of the corresponding reactions with tritolylphosphines.

Reactions of the potentially bidentate ditertiaryarsine ligand, $(Ph_2As)_2CH_2$ (dam) with $M(CO)_6$ (M = Cr, Mo, W) have been studied.[37] The complexes where dam is acting as a monodertate ligand $M(CO)_5$(dam), $M(CO)_4(dam)_2$, and $M(CO)_3(dam)_3$ and a bidentate ligand, $M(CO)_4$(dam) have been prepared. Another complex of the formula $M(CO)_2$(dam) (M = Cr, Mo) has been prepared. The results of i.r., nmr and mass spectra could only be explained on the assumption that dam was bound to the metal by an arene π linkage and by one As atom. This novel structure was confirmed by single crystal x-ray diffraction studies on the chromium compound.

$W(CO)_6$ has been found to react with azoles to form $LW(CO)_5$ and $L_2W(CO)_4$ complexes, where L = benzoxazole, benzothiazole, 2-methylbenzothiazoles, 1-phenyltetrazole, 1-methyl-, 1-ethyl-, 1,2-dimethyl- or 3,5-dimethylimidazole.[38] The complexes were prepared by u.v. irradiation of $W(CO)_6$ in the presence of L. Dipole moments of the 3,5-dimethylpyrazole derivatives were determined to be 6.8-9.3 D for $LW(CO)_5$ and >10 D for $L_2W(CO)_4$. A cis geometry was therefore assigned to the $L_2W(CO)_4$ species. Similarly, $LM(CO)_5$ and $L_2M(CO)_4$ (M = Cr, W; L = 1-methylimidazole, 3,5-dimethylpyrazole, 1-phenyltetrazole or (VII) where R = Me or H; X = EtN, MeN, $PhCH_2N$, S, or O) were prepared from $M(CO)_6$ and L.[38] The complexes were characterized by dipole moment measurements and infrared spectra. The ligands L were bonded to the metal via σ-N bonds.


VII


(M=Cr,Mo,W)

VIII

The monosubstituted products (VIII) of the Group VIB metal hexacarbonyl with triferrocenylphosphine (TFP) have been prepared from $M(CO)_6$ (M = Cr, Mo, W) and TFP in refluxing diglyme.[40] From the calculated Cotton-Kraihanzel CO stretching force constants, TFP was concluded to be a better donor ligand than triphenylphosphine.

The displacement of THF from the photochemically generated $M(CO)_5THF$ moiety (M = Cr, Mo, W) by Et_2NPF_2 has afforded $M(CO)_5PF_2NEt_2$ complexes.[41] The oxidation of $Cr_2(CO)_{10}^{-2}$ with $HgCl_2$ in THF has also afforded $Cr(CO)_5PF_2NEt_2$. The $M(CO)_5PF_2NEt_2$ derivatives were found to react with HBr to give the $M(CO)_5PF_2Br$ derivatives.

The reaction of mercuric mercaptides with $M_2(CO)_{10}^{-2}$ (where M = Cr, Mo, and W) has been shown to be the best method for the preparation of derivatives of the type $M(CO)_5SR^-$.[42] Complexes prepared in this manner were: $M(CO)_5SCF_3^-$ (M = Cr, Mo, W), and $W(CO)_5SR^-$ (R = CH_3, C_6H_5, and $(CH_3)Sn(CH_3)_3$). All the monoculear mercaptide derivatives were isolated using the bis(triphenylphosphiniminium) cation. Cis bis-substituted products were obtained from irradiation of $W(CO)_5SR^-$ salts in THF with Ph_3P (R = CH_3 or CF_3). Infrared, nmr and conductance measurements were carried out on all complexes.

Perfluoropropenyl anionic derivatives of Group VI metal carbonyls were prepared by utilizing the following redox reaction:

$$M_2(CO)_{10}^{-2} + 2\ \underline{trans}\text{-}AgC_4F_7 \rightarrow 2M(CO)_5C_4F_7^- + 2\ Ag^{\circ} \qquad (6)$$

(M = Cr, Mo, W)

^{19}F nmr spectra of the three complex anions were nearly identical to that for trans-AgC_4F_7 indicating retention of the trans configuration of the propenyl group.[43] The utility of eq. 6 is further illustrated by preparations of bis(triphenylphosphine)iminium salts of metal carbonyl carbonylates, $[RCO_2M(CO)_5]^-$ (M = Cr, Mo, W; R = H, CH_3, CF_3, C_2F_5, C_6F_5) under similar mild conditions (-10°).[44] Silver(I) or mercury(II) carboxylates were used as oxidants. Physical and chemical properties of the carboxylate complexes are discussed.

The reactions of $Mo(CO)_6$ and $W(CO)_6$ with 1,4-cyclooctadiene (1,4-COD) to yield $Mo(CO)_4$(1,5-COD) and an unidentifiable yellow oil respectively have been reported.[45]

Several deprotonation and subsequent alkylation reactions of phosphine-metal carbonyl complexes have been reported.[46] $M(CO)_5L$ ($M = Cr, Mo, W$ and $L = P(C_6H_5)_2H$) and cis-$Mo(CO)_4L_2$ were found to react with n-butyllithium to form the lithio compounds which further reacted in situ with methyl iodide to yield the appropriate methylphenylphosphine metal carbonyl complexes.

The trivalent tautomer of dimethyl- and diphenylphosphinous acids may be stabilized by molybdenum pentacarbonyl.[47] The new compounds may be prepared by either route 7 or 8. Carbonyl complexes containing the unique bridging ligand systems, diphosphoxanes, were prepared by reaction of the amine salt of IX with the chlorophosphine complex thus yielding complexes of the type $(CO)_5Mo\text{-}\mu\text{-}[PR_2OPR_2]Mo(CO)_5$. The compounds $(ClR_2P)(CO)_5Mo$ ($R = CH_3$ or C_6H_5) were also found to react with a variety of nucleophilic reagents leading to the formation of new $(R_2PX)(CO)_5Mo$ complexes.[48] $(R_2POR')(CO)_5Mo$, $[R_2P(NR''R''')](CO)_5Mo$ and $(R_2PSC_2H_5)(CO)_5Mo$ were obtained in good yields from the reaction with $R'OH$ ($R' = CH_3$, C_2H_5, n-C_3H_7, i-C_3H_7), $R''R'''NH$ ($R'' = H$, $R'' = R''' = CH_3$, and $R'' = H$ with $R''' = CH_3$), and C_2H_5SH, respectively. H_2S and $(C_2H_5)_3N$ were observed to react with the chlorophosphine complexes to give $[(CH_3)_2PSH]Mo(CO)_5$ and $(C_2H_5)_3NH^+[(C_6H_5)_2$-

$$\left.\begin{array}{l} [ClR_2P]Mo(CO)_5 + H_2O \\ \\ R_2P(O)H + Mo(CO)_6 \end{array}\right\} \rightarrow Mo(CO)_5PR_2(OH) \qquad \begin{array}{r}(7)\\ \\ (8)\end{array}$$

$(R = Ph, Me)$ (IX)

PO](CO)$_5$Mo$^-$. In addition the latter complex reacted with (CH$_3$)$_3$SiCl to give [(C$_6$H$_5$)$_2$P(OSi(CH$_3$)$_3$)](CO)$_5$Mo. ^{1}H nmr and infrared spectral properties of all new complexes were reported.

The stannylphosphine-metal pentacarbonyls (CO)$_5$MPPh$_2$-SnMe$_3$ (M = Cr, Mo, W) have been found to methylate BCl$_3$ to yield the monochloro compounds (CO)$_5$MPPh$_2$SnMe$_2$Cl.[49] However, up to two of the methyl groups were replaced during the methylation of BBr$_3$, yielding (CO)$_5$MPPh$_2$SnMe$_2$Br and (CO)$_5$-MPPh$_2$SnMeBr$_2$. The complexes were characterized by elemental analysis and infrared, ^{1}H and ^{31}P nmr spectral measurements.

The Group VIB metal hexacarbonyls have been found to react with tri-_tert_-butylphosphine, tris(trimethylgermyl)-phosphine and tris(trimethylstannyl)phosphine in THF at room temperature with uv-irradiation to yield the monosubstituted derivatives, (CO)$_5$MP[M'(CH$_3$)$_3$]$_3$ (where M = Cr, Mo, W and M' = C, Ge, Sn).[50] At higher reaction temperature (60°) with irradiation the _bis_-phosphine tetracarbonyl derivatives were obtained, (CO)$_4$M$\left[P[M'(CH_3)_3]_3\right]_2$ (where M = Cr, Mo, W, and M' = C, Ge, Sn).

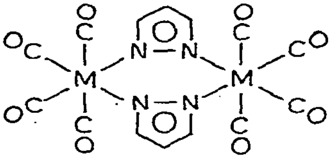
The reactions of _bis_(diarylstibino)methane, (R$_2$Sb)$_2$CH$_2$, with M(CO)$_6$ has led to the formation of the monosubstituted complexes, M(CO)$_5$(R$_2$Sb)$_2$CH$_2$ (M = Cr, Mo, W; R = C$_6$H$_5$, _p_-CH$_3$-C$_6$H$_4$), whereas _bis_(dimethylstibino)methane gave the complexes [M(CO)$_5$]$_2$[(CH$_3$)$_2$Sb]$_2$CH$_2$ (M = Mo, W).[51] From molecular weight, ^{1}H nmr and infrared data, it was concluded that _bis_(diarylstibino)methane behaves as a monodentate ligand and _bis_(dimethylstibino)methane as a bridging ligand in these complexes.

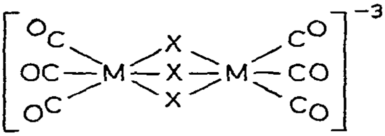
Photochemical reactions of $M(CO)_6$ (M = Cr, Mo, W) in THF with $(CH_3)_2P\text{-}P(CH_3)_2$ were found to afford $(CO)_5M\text{-}P(CH_3)_2\text{-}P(CH_3)_2$ complexes. These reacted with another mole of $M'(CO)_6$ (M' = Cr, Mo, W) to produce the dinuclear complexes $(CO)_5M\text{-}P(CH_3)_2\text{-}P(CH_3)_2\text{-}M'(CO)_5$.[52] Pyrolysis of these dinuclear species in benzene at 250° resulted in loss of CO and cleavage of the P-P bond with formation of complexes of the types $(CO)_4M[P(CH_3)_2]_2M'(CO)_4$ which are proposed to contain Cr-Mo, Cr-W, and Mo-W bonds.

The air-stable complexes $(CO)_5W\text{-}E(CH_3)_2\text{-}X\text{-}E(CH_3)_2\text{-}W(CO)_5$ (E = P, As; X = O, S, NCH_3, PC_6H_5) have been prepared from $(CO)_5W\text{-}E(CH_3)_2Cl$ and H_2X or from $(CH_3)_2E\text{-}X\text{-}E(CH_3)_2$ or $(CO)_5WPC_6H_5[E(CH_3)_2]_2$ and $W(CO)_5THF$.[53] The products where X = O or S were observed to be thermally fairly stable, whereas when X = NCH_3 or PC_6H_5 disproportionation into simpler carbonyl complexes resulting upon heating, e. g. $(CO)_5W\text{-}P(CH_3)_2\text{-}NCH_3\text{-}P(CH_3)_2\text{-}W(CO)_5 \rightarrow W(CO)_6 + CH_3N[P(CH_3)_2]W(CO)_4$.

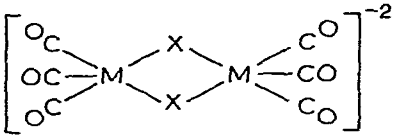
$M(CO)_6$ (M = Mo and W) were found to react with sodium pyrazolate in diglyme to yield the pyrazolate bridged tetracarbonyl species $[(CO)_4ML_2M(CO)_4]^{-2}$ (X).[54] In addition the 5-substituted tetrazolate ions $(RCN_4)^-$, where R = CF_3 and CH_3S, yield the monomeric anionic pentacarbonyl metalates $[M(CO)_5L]^-$ (M = Cr, Mo, W). The i.r. and nmr spectra of these complexes were discussed.

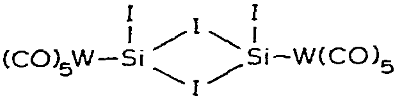
A variety of compounds of the general formula $(R_4N)_3[(CO)_3MX_3M(CO)_3]$ (M = Cr, Mo, W; X = F, Cl, Br, I, OH, SCN, N_3, OC_2H_5) (XI) have been prepared from arene$M(CO)_3$ and tetraalkylammoniumhalides and pseudohalides.[55] Two-member bridged complexes with the formula $(R_4N)_2[(CO)_3MX_2M(CO)_3]$ ($R = C_2H_5$, M = Mo, X = I and Cl) (XII) were also prepared. The structures indicated were primarily suggested from conductivity measurements. These reactions were taken to demonstrate the strong Lewis acid properties of arene-$M(CO)_3$ and provide further support for the contention that arene$M(CO)_3$ complexes serve as effective catalysts in Friedel-Crafts reactions by promoting ionic type reactions.


X


XI

U.v. irradiation of $W(CO)_6$ and Si_2I_6 in pentane has afforded the dimeric pentacarbonyl(diiodosilylene)tungsten(0) complex, $[(CO)_5WSiI_2]_2$. Infrared and mass spectra results are consistent with a structure (XIII) in which the iodine atoms serve as bridging ligands between the Si atoms.[56]


XII


XIII

Tetrahydrofuran opens the halogen bridges by coordination to the Si atoms (eq. 9).

$$[(CO)_5WSiI_2]_2 + 2OC_4H_8 \rightleftarrows 2(CO)_5WSiI_2\cdot OC_4H_8 \qquad (9)$$

Bencze[57] has synthesized halo-metal carbonyls by reductive carbonylation of halides and oxyhalides of Mo and W. Reaction of $WOCl_4$ with $EtAlCl_2$ in chlorobenzene under 1 atm of CO resulted in the formation of $W(CO)_6$ in 30 % yield. Halo carbonyl complexes were also formed which reacted with Ph_3P to give $W(CO)_3(PPh_3)_2Cl_2$. The corresponding $AsPh_3$ derivative was also prepared by this manner. The method was employed as well in the preparation of the molybdenum analogs. $M(CO)_4Cl_2$ (M = Mo, W) complexes are presumed to be the initially formed species which react with L to form $ML_2(CO)_3Cl_2$ complexes.

Special fluorinated, silanated, chlorinated, etc., diarsine ligands have been synthesized in order to study conformational preferences of chelate rings in solution.[58] Compounds of the type $Cr(CO)_4(AsMe_2CHX\text{-}CF_2AsMe_2)$ where X = H, F, $SiMe_3$, $SiCl_3$, Cl or CN, have been prepared and their nmr spectra analysed in detail with particular emphasis on vicinal $^1H-^1H$ and $^{19}F-^1H$ coupling.

cis-bis(Trifluoromethylphosphine) complexes of the Group VIB metal carbonyls have been prepared by reaction of the respective metal tetracarbonyl norbornadiene complexes with excess of the phosphine ligand (eqns. 10 and 11) at room temperature.[59]

$$2(CF_3)_2PR + (C_7H_8)Mo(CO)_4 \rightarrow \textit{cis}\text{-}[(CF_3)_2PR]_2Mo(CO)_4 + C_7H_8 \qquad (10)$$

(R = Cl, Br, I, NMe_2, NCS and H).

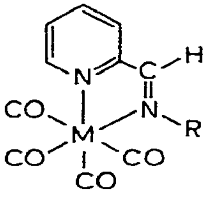
$$CF_3PQ_2 + (C_7H_8)M(CO)_4 \rightarrow \textit{cis}\text{-}[CF_3PQ_2]_2M(CO)_4 + C_7H_8 \qquad (11)$$

(M = Mo, Q = Cl, Br, H; M = Cr, Q = H).

^{19}F and ^{1}H nmr data are presented and discussed.

$M(CO)_6$ (M = Cr, Mo, W) have been reported to react with the terdentate nitrogen donor ligands, T, to give fac-$M(CO)_3T$ derivatives (where T = bis(2-pyridylmethyl)amine, bis(2-pyridylmethyl)methylamine and bis(2-pyridylethyl)amine).[60] $Mo(CO)_3$(cycloheptatriene) and $W(CO)_3$(acetonitrile)$_3$ have also been used to prepare the molybdenum and tungsten derivatives where T = bis(2-pyridylmethyl)methylamine. The fac-$Mo(CO)_3T$ and fac-$W(CO)_3T$ derivatives were shown to react with iodine to form seven coordinate divalent compounds of the type $[M(CO)_3(T)I]^+I^-$.

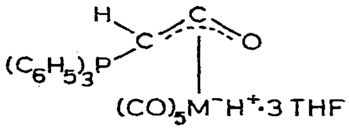
The methods of preparation, properties, infrared, electronic and mass spectra of tetracarbonyl(pyridine-2-carbaldehydeimine)M complexes (M = Cr, Mo, W) have been reported (XIV).[61] These complexes react with PPh_3 in refluxing toluene to form the tricarbonyltriphenylphosphine(pyridine-2-carbaldehydeimine) complexes in which the PPh_3 ligand has been shown by nmr to be cis to the azomethine-chelate ligand.



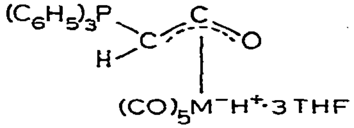
XIV

($R=CH_3, i\text{-}C_3H_7, C_6H_{11}, C_6H_5$, and OH)

$M(CO)_6$ (M = Mo and W) when reacted with methylenetriphenylphosphorane in THF resulted in the formation of 1:1 metal carbonyl-phosphorus ylide adducts (XV) and (XVI), with structure XV being the minor isomer.[62]

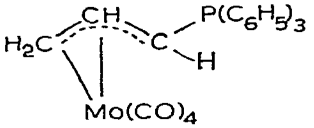


XV



XVI

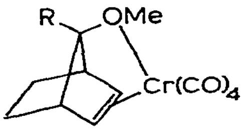
The structures were assumed to be that of an oxonium salt, formed by the shift of one proton from the ylide group to tetrahydrofuran. In addition allylidenetriphenylphosphorane reacted with Mo(CO)$_6$ and W(CO)$_6$ to yield (CO)$_4$M[(C$_6$H$_5$)$_3$P=CH-CH=CH$_2$]$_6$. Preliminary x-ray analysis of the molybdenum complex revealed the complex to have structure XVII.



XVII

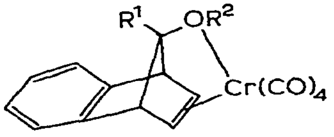
It was possible to replace one of the CO ligands in this complex with Ph$_3$P in hot benzene yielding (CO)$_3$Mo[P(C$_6$H$_5$)$_3$]-[(C$_6$H$_5$)$_3$P=CHCH=CH$_2$].

syn-7-Alkoxynorborn-2-enes were found to react with Cr(CO)$_6$ in di-*n*-butyl ether-cyclohexane at 140° to afford complexes of the type (alkoxynorbornene)Cr(CO)$_4$ (XVIII, XIX, and XX).[63] Similarly, M(CO)$_4$ (M = Mo, Cr) and Fe(CO)$_3$



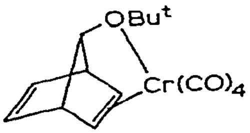
(R=H,OMe)

XVIII



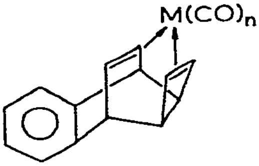
(R^1=H, R^2=Bu^t)
(R^1=OMe, R^2=Me)

XIX



XX

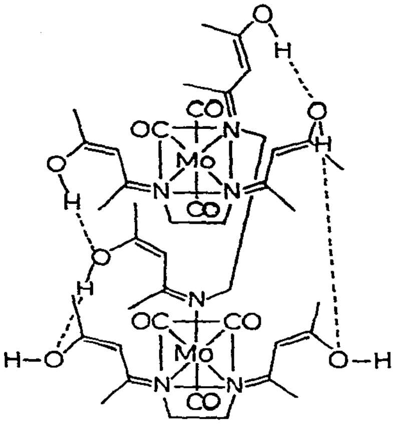
derivatives of anti-7,8-benzotricyclo [4.2.0.0^{2,5}]deca-3,7,9-triene (XXI) have been prepared in good yields and characterized.[64] The metal is simultaneously bound to the two double bonds in all cases.



XXI

(Butadiene)Cr(CO)$_4$ has been prepared by co-condensation of metal atoms evaporated by CO$_2$ laser with $CH_2=CHCH=CH_2$ at liquid nitrogen temperatures and subsequent treatment with CO.[65] This complex decomposes above 0°. Complexes such as this have been postulated as intermediates in the photochemical hydrogenation of 1,3-dienes with Cr(CO)$_6$ and H$_2$ but could not be isolated for reasons which can now be appreciated.

Reaction of molybdenum hexacarbonyl with potentially tetradentate Schiff's bases gave the complexes dicarbonyl-NN'-ethylenebis(salicylylaminato)molybdenum(II) (from NN'-ethylenebis(salicylideneimine) and also NN'-ethylene-bis-(salicylylamine)), dicarbonylaminobis-N-ethylenesalicylylaminato)molybdenum(II)hydrochloride (from aminobis(N-ethylenesalicylideneimine)hydrochloride), and hexacarbonyltris[bis-(acetylacetone)ethylenediimine]dimolybdenum(0) (from bis-(acetylacetone)ethylenediimine).[66] The latter complex was shown to be binuclear with cis-(CO)$_3$ groups (XXII) whereas the other two complexes were mononuclear, distorted octahedral with cis-(CO)$_2$ groups. Attempts to use these complexes as catalysts for the fixation of N$_2$ (at atmospheric pressure and 1500 p.s.i.) failed.



XXII

Tellurophene chromiumtricarbonyl has been prepared from reaction of $(CH_3CN)_3Cr(CO)_3$ and tellurophene in dibutyl ether at 50 - 60°.[87] The infrared spectrum shows three $\nu(CO)$ absorptions at 1967 (A_1) and 1895, 1872 cm^{-1} (E mode split). The i.r., u.v., and nmr spectral properties, as well as the dipole moment of this new complex were compared with those of the thiophene-, selenophene- and pyrrolechromium tricarbonyl derivatives.

Octamethylcyclotetraphosphonitrile and decamethylcyclopentaphosphonitrile were found to react with $M(CO)_6$ (M = Mo or W) to give $LM(CO)_3$ complexes.[88] The coordination was postulated as occurring through the nitrogen atoms. The octadimethylamido-derivative, $N_4P_4(NMe_2)_8$, was shown to form a tetracarbonyl complex. $[N_4P_4Me_9]^+I^-$ reacted with $M(CO)_6$ (M = Cr, Mo) to give the salts $[N_4P_4Me_9]^+[M(CO)_5I]^-$. In the compound $N_4P_4(NMe_2)_8W(CO)_4$ the phosphonitrile ligand was shown by x-ray diffraction studies to be acting as a bidentate σ-ligand, through one ring nitrogen atom and one exocyclic nitrogen group.[89]

Tricarbonylhexachlorocyclotriphosphazenechromium, $(PNCl_2)_3Cr(CO)_3$, has been obtained as a bright yellow, sublimable crystalline solid from hexachlorocyclotriphosphazene and $(MeCN)_3Cr(CO)_3$ in THF or Et_2O.[70] The composition of the new complex was established by elemental analysis and mass spectrometry.

Two isomeric forms of a novel hetero-bimetallic species, $Br(CO)_3Mn(triphos)Cr(CO)_5$, have been prepared from $Mn(CO)_3$-(triphos)Br and $Cr(CO)_5THF$ in THF.[71] The three-dimensional crystal structure of one of the isomeric forms was determined by x-ray diffraction methods and shown to exist as a facial arrangement of carbonyl ligands with two of the phosphorus atoms of triphos coordinated to Mn and the third attached to $Cr(CO)_5$.

The photochemical preparations of $C_7H_8Cr(CO)_2P(C_6H_5)_3$ and $C_7H_8Cr(CO)_2P(OC_6H_5)_3$ from the corresponding tricarbonyl derivative with $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ have been reported by Anderson and co-workers.[72] The mass spectra of these complexes were observed and compared with those of $C_7H_8Cr(CO)_3$ and $C_6H_6Cr(CO)_2P(C_6H_5)_3$.

Reactions of π-$C_7H_7Mo(CO)_2I$ (M = Mo, W) with phosphines and phosphites have afforded complexes of the type π-$C_7H_7M(CO)LI$, where L = $P(OC_6H_5)_3$, $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(\underline{i}\text{-}OC_3H_7)_3$, $P(C_6H_5)_3$, $P(\underline{n}\text{-}C_4H_9)_3$, M = Mo; and L = $P(OC_2H_5)_3$ and $P(\underline{i}\text{-}OC_3H_7)_3$, and M = W.[73] Infrared and nmr spectral data were reported for these new π-complexes.

The preparation of a series of isonitrile complexes $[(CO)_{6-x}M(CNR)_x]$ (x = 1-3; M = Cr, Mo; R = Me, Et, i-Pr, hexyl, t-Bu, p-tolyl, Ph, p-ClC_6H_4) has been reported.[74]

Extensive spectroscopic data (i.r., u.v., mass, and nmr) and electrochemical measurements are reported and discussed. The data are interpreted as indicating that (d-π^*) back bonding is negligible in these type complexes. Reactions of the weak nucleophiles (amines, alcohols) with the (RNC)Cr-$(CO)_5$ complexes were not observed.

$Mn(CNCH_3)_6^+$ is found to be substantially easier to oxidize than analogous manganese aryl isocyanide complexes. Unlike the manganese systems which exhibit two one-electron oxidation processes (+1 → +2 and +2 → +3, the latter at considerally higher potential), similar aryl isocyanide complexes of Cr undergo only one oxidation process (0 → +1) however a reduction process (0 → -1) is observed at small negative potentials.[75]

The compound $Mo(CNR)_6I_2$, R = t-butyl, has been prepared from the reaction of $Ag_4Mo(CN)_8$ and t-butyliodide.[76] A single-crystal x-ray diffraction study on this red-orange product has shown the correct structure to be $[Mo(CNR)_6I]I$.

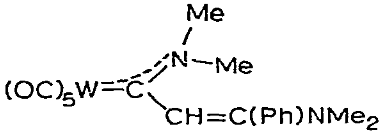
Carbene and related complexes. Several new carbene complexes have been prepared from the reaction of metal carbonyls or substituted metal carbonyls with organolithium reagents followed by alkylation with various alkylating agents. The preparation of a series of carbene complexes $[(CO)_5MC(Fc)X]$ (M = Cr, W; Fc = ferrocenyl; X = $O^-NMe_4^+$, OMe, OEt, NH_2, NMe_2, NC_4H_8) has been reported.[77] The ferrocenyl group was shown to be a strong electron donor on the basis of i.r., nmr and electronic spectral measurements. The preparation of phenylphenoxycarbenepentacarbonylchromium(0) from $(CO)_5CrC(OLi)C_6H_5$

and $[C_6H_5N_2]BF_4$ in benzene/water has been reported by Fischer and Kalbfus.[78] Infrared and mass spectral results were obtained on this new carbene complex. Other new carbene complexes have been formed by employing dicyclopentadienyltitaniumdichloride as alkylating agent.[79] Thus $(CO)_5CrC(OLi)Me$ reacts with $(\underline{h}^1\text{-}C_5H_5)_2TiCl_2$ yielding $(CO)_5CrC(OTi(\underline{h}^1\text{-}C_5H_5)_2Cl)Me$ (47 %) and $(CO)_5CrC(CH_3)OTi(C_5H_5)_2O(CH_3)CCr(CO)_5$ (28 %).

Fischer and co-workers[80] have reported the preparation of two new bis carbene complexes of chromium and tungsten carbonyls, $(CO)_4M[C(OC_2H_5)P(CH_3)_2]_2$ (M = Cr and W), from the reactions of $M(CO)_6$ with lithium dimethylphosphide in ether followed by successive ethylation with $Et_3O^+BF_4^-$ in CH_2Cl_2. The cis structures of these complexes were ascertained by means of infrared and nmr spectral measurements.

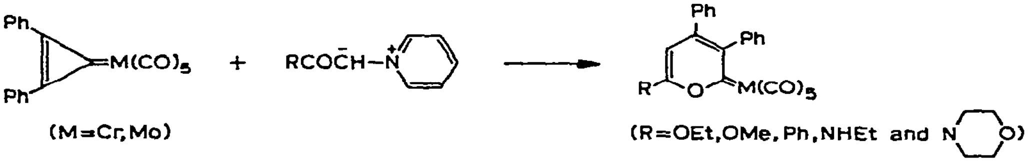
Ultraviolet irradiation of cyclopentadienylmolybdenumcarbonylnitrosyl carbene complexes of the type $\pi\text{-}C_5H_5Mo(CO)(NO)C(R)C_6H_5$ ($R = OCH_3, OC_2H_5, N(CH_3)_2$) in benzene in the presence of $Fe(CO)_5$ has been shown to yield carbene complexes of the form $(CO)_4FeC(R)C_6H_5$.[81]

Phenylacetyleneethoxycarbene ($PhC{\equiv}C\text{-}\ddot{C}(OEt)$) derivatives of tungsten- and chromiumpentacarbonyl have been prepared by Fischer's in situ reaction of $Et_3O^+BF_4^-$ with the corresponding lithium metalcarbonylacylate.[82] The enthalpy of activation, determined from low temperature ^1H nmr studies, for the rotation process about the carbene carbon-oxygen bond was found to be <8 kcal/mole, a value less than that for phenyl- or alkylalkoxycarbene complexes. $PhC{\equiv}C(EtO)CW(CO)_5$ reacts with 2 moles of Me_2NH to give compound XXIII.



XXIII

A new type of carbene complex stabilized by 6π-electron delocalization has resulted from reaction of the cyclopropenylidene complexes of chromium and molybdenum with pyridinum ylides (eq. 12).[83]



(12)

Some reactions of these complexes were also discussed.

$[Me_2NCHCl]^+Cl^-$ has been found to oxidatively add to $Na_2[Cr(CO)_5]$ to produce the carbene complex $(CO)_5CrC(H)NMe_2$ in which the hydrogen atom attached to C(carbene) is deshielded (τ = -0.86), characteristic of an electrophilic C(carbene).[84]

Fischer, Leupold, Kreiter and Muller[85] have found that (methylmethoxycarbene)pentacarbonylchromium(0), (phenylmethoxycarbene)pentacarbonylchromium(0), and (methylmethoxycarbene)pentacarbonyltungsten(0) react with thiols (HSR') at room temperature to form thiocarbenepentacarbonyl complexes of the form $(CO)_5MC(SR')R$ (where M = Cr, W; R = CH_3, C_6H_5; R' = CH_3, C_2H_5, C_6H_5). From the CO stretching frequencies, the energy barrier for rotation about the carbene carbon-sulfur bond, the ionization potentials, and the dipole moments of the thiocarbene complexes it was concluded that the thiocarbene ligands are intermediate between the alkoxy- and aminocarbene ligands in their electron donating ability towards the $M(CO)_5$ moieties.

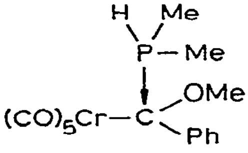
The reaction of $(CO)_5CrC(OCH_3)C_6H_5$ with ammonia and the amines HNRR' (CH_3NH_2, $(CH_3)_2NH$, $C_2H_5NH_2$, pyrrolidine, C_6H_5-NH_2, p-$CH_3OC_6H_4NH_2$) has been used to prepare the corresponding [amino(phenyl)carbene]pentacarbonylchromium complexes $(CO)_5CrC(NRR')C_6H_5$.[86] The i.r., ^1H nmr, and u.v. spectra of these amino carbene complexes were discussed. Treatment of $(CO)_5CrC(NH_2)C_6H_5$ with carbon monoxide (100 atm) in benzene at 155° resulted in formation of $Cr(CO)_6$, C_6H_5CN and $C_6H_5CH_2$-NH_2, whereas, similar treatment of $(CO)_5CrC(NHCH_3)C_6H_5$ resulted in formation of $Cr(CO)_6$ and $C_6H_5CH{=}NCH_3$ by hydrogen migration.

The reactions of amines with alkoxycarbene complexes yielding aminocarbene complexes have been extended to aliphatic and aromatic diamines.[87] Aliphatic diamines react with $(CO)_5CrC(OMe)Me$ to give the bridged diaminocarbene complexes, $(CO)_5CrC(Me)NHRN(CH_3)CCr(CO)_5$ whereas the aromatic diamines, benzidine and o-tolidine give the mononuclear aminocarbene complexes only.

Connor and Rose[88] have shown that the displacement of the aminocarbene ligand from complexes of the type $[(CO)_5$-$CrC(R)NHR']$ (R = Ph; R' = Ph, NHPh; R = Me, R' = 2-(3-indolyl)ethyl) with pyridine yields the corresponding imine, RCH=NR', and $(C_5H_5N)_3Cr(CO)_3$ as a result of intramolecular hydrogen transfer. The reaction of $Cr(CO)_5C(OEt)Ph$ with hydrazine to form $(CO)_5CrNCPh$ was shown to proceed via the hydrazine-carbene complex, $[(CO)_5CrC(Ph)NHNHPh]$.

Reactions similar to those reported by Connor (J. A. Connor and P. D. Rose, J. Organometal. Chem., 24 (1970) C45) in which metal carbonyl carbene complexes are used as a source of carbene fragments for insertion into Si-H bonds have been reported. Thus $(CO)_5CrC(OMe)Ph$ reacts thermally with diphenylsilane yielding $Ph_2SiHCH(OMe)Ph$ and $Cr(CO)_6$.[89] Thermal reactions of the carbene complex in diphenyl-methane or cyclohexane do not yield insertion products however; decomposition of the carbene complex yields $Cr(CO)_6$ and cis- and trans-α,α'-dimethoxystilbene.

Addition of Me_2PH to $(CO)_5CrC(OMe)Ph$ in pentane at -50° forms a phosphorus ylide complex, $Me_2HPC(OMe)(Ph)Cr(CO)_5$ (XXIV).[90] The nmr spectra of this complex are consistent with a phosphorus-carbene carbon bond and two magnetically non-equivalent P-methyl groups. Whereas, $(CO)_5CrC(OMe)Me$ was found to react with PR_3 (R = Et, i-Pr, n-Bu, C_6H_{11}, n-C_8H_{17}) in hexane, benzene, or THF solvent at 60° to afford mixtures of cis- and trans-$Cr(CO)_4(PR_3)C(OMe)Me$.[91] Rate constants were measured for the isomerization of $Cr(CO)_4(PEt_3)C(OMe)Me$ and the conversion of geometrical isomers was observed to occur according to a first-order rate law. Activation parameters were determined for both cis → trans and trans → cis reactions. The isomerization was concluded to occur via intramolecular rearrangement without bond fission.

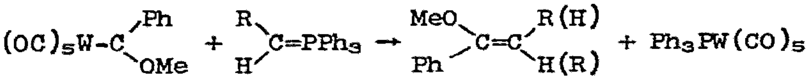


XXIV

Transition metal carbene complex anions have been generated at low temperatures by the deprotonation of a carbon α to the carbene carbon atom in $(OC)_5Mn\text{-}Mn(CO)_4\text{-}\overline{COCH_2CH_2CH_2}$ and $W(CO)_5C(OMe)Me$.[92] Thus treatment of either carbene complex produces anions α to the carbene carbon which have been deuterated by DBr and alkylated by methyl fluorosulfonate. Products due to addition of RLi to a carbonyl group are not observed. Other reactions of the anions are discussed.

The thermal decomposition of Cl_3CCO_2Na in diglyme in the presence of $(\pi\text{-}C_5H_5)_2WH_2$ has been shown to yield $(\pi\text{-}C_5H_5)_2WHCHCl_2$.[93] This complex results from insertion of the carbene $:CCl_2$ into a tungsten-hydrogen bond. The new complex was characterized by elemental analysis, nmr, infrared and mass spectral data.

The use of metal carbene complexes as carbene precursors in organic synthesis has met with limited success. Casey[94] has however reported facile reactions of phenylmethoxycarbenepentacarbonyltungsten(0) with Wittig reagents in ether at room temperature to give enol ethers in high yields (eq. 13). A 1:1 mixture of methyl cis- and trans-1-

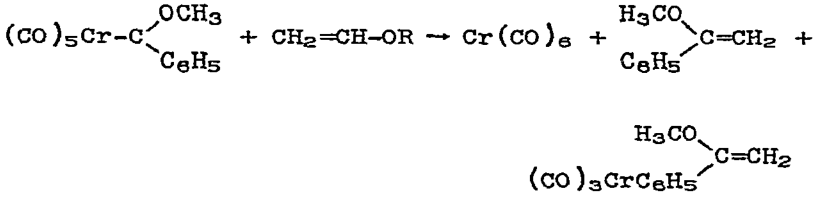


$$(OC)_5W\text{-}C\begin{smallmatrix}\diagup Ph\\ \diagdown OMe\end{smallmatrix} + \begin{smallmatrix}R\diagdown\\ H\diagup\end{smallmatrix}C{=}PPh_3 \rightarrow \begin{smallmatrix}MeO\diagdown\\ Ph\diagup\end{smallmatrix}C{=}C\begin{smallmatrix}\diagup R(H)\\ \diagdown H(R)\end{smallmatrix} + Ph_3PW(CO)_5 \qquad (13)$$

phenylpropenyl ether was obtained for R = Me. Production of $W(CO)_5$ during the course of the reaction was verified by addition of tri-p-tolylphosphine to the reaction mixture with subsequent isolation of $(p\text{-}CH_3C_6H_4)_3PW(CO)_5$.

The synthesis of cyclopropane derivatives from α,β-unsaturated alkyl carboxylates with the aid of transition metal carbene complexes has been accomplished by Dotz and Fischer.[95] Thus, $(CO)_5CrC(OMe)Ph$ reacts stereospecifically with <u>trans</u>-methyl cinnamate, diethyl fumarate and diethylmaleate to give the corresponding methyl- and diethyl[methoxy(phenyl)cyclopropane]carboxylates resulting from the transfer of the carbene ligand. A dependence of the ratio of the cyclopropane isomers on the nature of the metal atom was noted going from Cr to Mo to W.

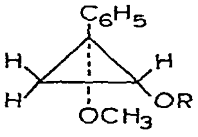
In related experiments, $(CO)_5CrC(OMe)Ph$ was found to react with ethylvinyl ether and isobutylvinyl ether to give mainly α-methoxystyrene (eq. 14).[96] In contrast, under a



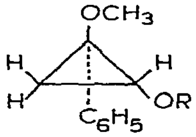
$$(CO)_5Cr{-}C\begin{matrix}OCH_3\\C_6H_5\end{matrix} + CH_2{=}CH{-}OR \rightarrow Cr(CO)_6 + \begin{matrix}H_3CO\\C_6H_5\end{matrix}C{=}CH_2 + \begin{matrix}H_3CO\\(CO)_3CrC_6H_5\end{matrix}C{=}CH_2 \qquad (14)$$

(R = Et and <u>i</u>-butyl)

pressure of CO, reaction 14 results in <u>syn</u> and <u>anti</u> dialkoxycyclopropane derivatives (XXV A) and (XXV B).



XXV A
(anti)



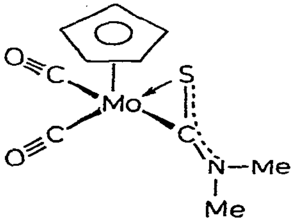
XXV B
(syn)

As observed before, the distribution of isomers were dependent on the particular metal derivative (Cr, Mo, W) of $(CO)_5MC(OMe)Ph$.

<u>π-Cyclopentadienyl complexes</u>. The compounds π-C_5H_5-$Mo(CO)_2(L)Sn(CH_3)_3$ ($L = P(C_6H_5)_3$, $P(C_6H_5)(CH_3)_2$, $P(OCH_2)_3$-CCH_3, $As(C_6H_5)_3$, $Sb(C_6H_5)_3$) have been prepared from [π-C_5H_5-$Mo(CO)_2L]^-$ with $(CH_3)_3SnCl$.[97] The triphenylphosphine derivative was also prepared by direct reaction of π-$C_5H_5Mo(CO)_3$-$Sn(CH_3)_3$ and $P(C_6H_5)_3$. All of these derivatives were found to liberate $Sn(CH_3)_4$ at 200° and the other product was characterized to be $[\pi$-$C_5H_5Mo(CO)_2L]_2Sn(CH_3)_2$ for $L = P(C_6H_5)_3$ and $P(OCH_2)CCH_3$. The <u>trans</u> configuration was suggested for all new compounds by way of infrared and proton nmr studies.

Davidson and Sharp[98] have reported the synthesis of trifluoromethylthio-metal derivatives from the photochemical reaction of bis(trifluoromethyl)disulfide and low oxidation state transition metal complexes. New complexes prepared by this route include $(\pi$-$C_5H_5)Mo(CO)_3SCF_3$ and $(\pi$-$C_5H_5)W(CO)_3$-SCF_3. The dimer $[(\pi$-$C_5H_5)Mo(CO)_2SCF_3]_2$ was readily formed by decarbonylation of $(\pi$-$C_5H_5)Mo(CO)_3SCF_3$, however, it was not possible to prepare the corresponding tungsten dimer in a similar manner.

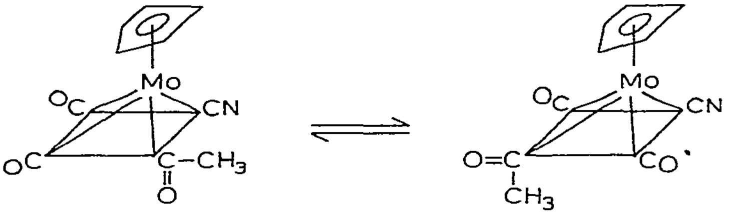
Treichel and Dean[99] have reported that reaction of either $(\pi$-$C_5H_5)Mo(CO)_3^-$ or $(\pi$-$C_5H_5)Mo(CO)_2PPh_3^-$ with $ClCSNMe_2$ in THF gives a red-brown crystalline dicarbonyl complex (XXVI), $(\pi$-$C_5H_5)Mo(CO)_2CSNMe_2$.



XXVI

$(\pi\text{-}C_5H_5)Mo(CO)_2CSNMe_2$ was found to react with $[Me_3O]BF_4$ to give $[(\pi\text{-}C_5H_5)Mo(CO)_2C(SMe)NMe_2]^+$ which was isolated as the PF_6^- salt.

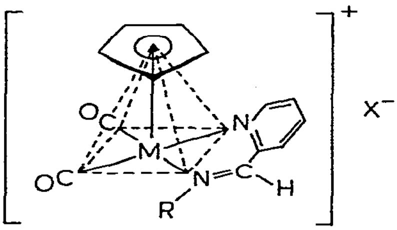
The reaction of $\pi\text{-}C_5H_5M(CO)_3CH_3$ (M = Mo, W) with KCN in methanol has afforded the corresponding cyano anions $[(\pi\text{-}C_5H_5)M(CO)_2(COCH_3)CN]^-$.[100] Methylation of $(\pi\text{-}C_5H_5)$-$Mo(CO)_2(COCH_3)CN$ with MeI resulted in information of the neutral isonitrile complex $(\pi\text{-}C_5H_5)Mo(CO)_2(COCH_3)(CNCH_3)$. It was shown that the carbonyl insertion reaction of $\pi\text{-}C_5H_5$-$Mo(CO)_3CH_3$ with KCN proceeded stereospecifically to the cis-complex which then isomerized to the trans-isomer (eq. 15).



(15)

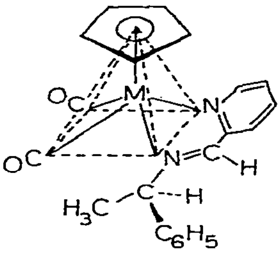
The reaction of Schiff bases of pyridine-2-carbaldehyde with $(\pi\text{-}C_5H_5)M(CO)_3Cl$ (M = Mo, W) has been found to yield cationic complexes with asymmetric metal atoms (XXVII).[101,102]

(M = Mo, W; X^- = Cl^- or PF_6^-; R = CH_3, i-C_3H_7, C_6H_{11}, C_6H_5, $CH_3CH(C_6H_5)$).

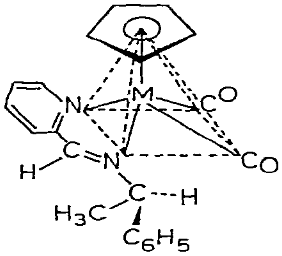


XXVII

Highly stable optically active complexes (XXVIII A and B) have been obtained by fractional crystallization of the diastereoisomers obtained with (-)-1-phenylethylamine as the amine component in the azomethine complexes.



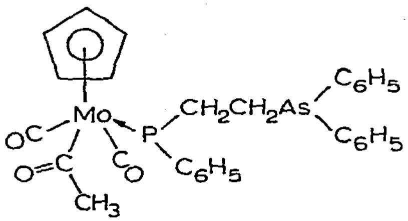
XXVIII A



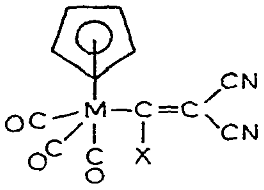
XXVIII B

King and Kapoor[103] have reported the preparations of a large variety of metal complexes of the phosphine-diarsine $[(C_6H_5)_2AsCH_2CH_2]_2P(C_6H_5)$ (abbreviated as Asf-Pf-Asf). Included in this study were the preparations of biligate monometallic complexes of the form (Asf-Pf-Asf)$M(CO)_4$ (M = Cr and Mo) and $[\pi\text{-}C_5H_5Mo(CO)_2$Asf-Pf-Asf)]$[PF_6]$ and triligate monometallic complexes of the form (Asf-Pf-Asf)$Mo(CO)_3$ (M = Cr and Mo). The reaction of $CH_3Mo(CO)_3C_5H_5$ with Asf-Pf-Asf or $(C_6H_5)_2AsCH_2CH_2P(C_6H_5)_2$ (Asf-Pf) in acetonitrile at room temperature led to the formation of the monoligate monometallic complexes (Asf-Pf-Asf)$Mo(CO)_2(COCH_3)(C_5H_5)$ (XXIX) and (Asf-Pf)$Mo(CO)_2(COCH_3)(C_5H_5)$, respectively.

Polycyanovinyl transition metal derivatives of structural type XXX have been produced by reaction of the metal carbonyl anions $(C_5H_5)M(CO)_3^-$ (M = Mo and W) with dicyanovinyl chorides such as $(NC)_2C{=}CHCl$, $(NC)_2C{=}CCl_2$ and $(NC)_2C{=}C(CN)Cl$.[104]



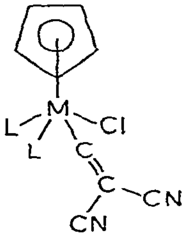
XXIX



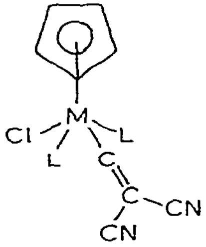
XXX

(M = Mo, W; X = H, CN, Cl).

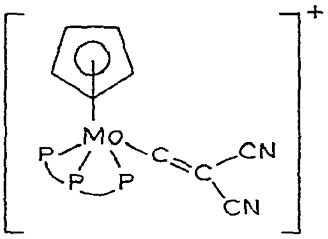
Reactions of the 1-chloro-2,2-dicyanovinyl derivatives $(NC)_2C{=}C(Cl)M(CO)_3C_5H_5$ (M = Mo, W) with phosphines and related ligands were found to result in migration of the chlorine from carbon to the transition metal with concomitant formation of products of the type π-$C_5H_5ML_2[C{=}C(CN)_2]Cl$ (M = Mo, W; L = Ph_3P, Ph_3As, Ph_3Sb, $(MeO)_3P$, $(EtO)_3P$, and $(PhO)_3P$) which contain a terminal dicyanomethylene carbene ligand.[105] These products are formulated as mixtures of the two isomers XXXI and XXXII. On the other hand, reaction of $PhP(CH_2CH_2PPh_2)_2$ with $(NC)_2C{=}C(Cl)Mo(CO)_3C_5H_5$ resulted in formation of the salt XXXIII in which all CO groups are replaced.



XXXI



XXXII

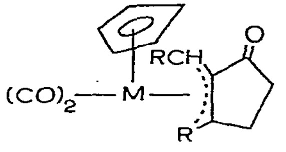


XXXIII

The synthesis, i.r., pmr, and ^{19}F nmr spectra of *m*- and *p*-fluorophenyl complexes of Mo and W have been reported.[106] σ°_R and σ_I Taft constants for the compounds, $\underline{h}^5$-$C_5H_5M(CO)_2$-

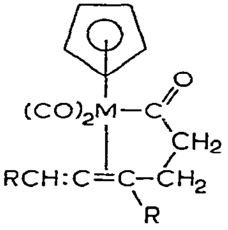
$L(C_6H_4F$-m- or -p), had negative values and were interpreted as follows: increase in electron density at the metal atom, caused by changing L from CO to PPh_3 is transferred to the phenyl ring via inductive σ-bond polarization of the $W-C_6H_4F$ bond and π-interaction with the phenyl ring is unchanged.

The synthesis of cyclopentenone π-complexes by cyclization of σ-π allenic intermediates has been achieved.[107] $(\pi-C_5H_5)M(CO)_3(CH_2)_2CR{:}C{:}CHR$, prepared from $(\pi-C_5H_5)M(CO)_3^-$-Na^+ and $Br(CH_2)_2CR{:}C{:}CHR$, when heated at 50° for 48hrs gave the cyclopentenone complexes (XXXIV) via the intermediate (XXXV) which was produced by heating $(\pi-C_5H_5)M(CO)_3(CH_2)_2$-$CR{:}C{:}CHR$ at 30° for 2 hrs. The structure of XXXIV was confirmed by i.r. and nmr.



(M=Mo; R=H,Me; M=W,R=H)

XXXIV



XXXV

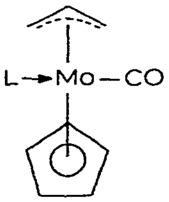
The synthesis and acylation of σ-benzyl-π-$(C_5H_5)(CO)_3W$ have been reported.[108] $(\pi-C_5H_5)W(CO)_3Na$ reacted with $PhCH_2Cl$ in THF at 20° to give $(\pi-C_5H_5)W(CO)_3CH_2Ph$ which reacts with AcCl and $AlCl_3$ in CH_2Cl_2 to give $(\pi-C_5H_5)W(CO)_3CH_2C_6H_4Ac$-p and $(\pi-C_5H_5)W(CO)_3Cl$.

The synthesis of the benzoyl derivatives, $\pi-C_5H_5M(CO)_3$-COC_6H_5 (M = Mo and W), and the investigation of their decarbonylation to the respective phenyl compounds have been carried out by Nesmeyanov and co-workers.[109] The decarbonylation reaction proceeds easily to the product $[(C_6H_5)C_5H_4Mo(CO)_3]_2$ in quantitative yield in which the phenyl group has migrated to the C_5H_5 ring. The reaction of π-$C_5H_5W(CO)_3COC_6H_5$ with $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ was found to yield π-$C_5H_5W(CO)_2$-$[P(C_6H_5)_3]COC_6H_5$ and π-$C_5H_5W(CO)_2[P(OC_6H_5)_3]COC_6H_5$ complexes, however, π-$C_5H_5Mo(CO)_3COC_6H_5$ reacted with $P(C_6H_5)_3$ and $P(OC_6H_5)_3$ to yield $[P(C_6H_5)_3]_2Mo(CO)_4$ and $[P(OC_6H_5)_3]_3Mo(CO)_3$, respectively.

Treichel, Dean and Douglas[110] have studied reactions of various metal carbonyl derivatives with diphenylphosphine(L) or phenylphosphine(L'). The reaction of π-C_5H_5-$Mo(CO)_3X$ ($X = Cl$ or Br) and L led to the formation of π-C_5H_5-$Mo(CO)_2(L)X$; but in the presence of aluminum chloride the cationic species $[\pi$-$C_5H_5Mo(CO)_3L]AlX_4$ was formed. Reactions of L' with $Cr(CO)_3(NCCH_3)_3$ and with (norbornadiene)$Mo(CO)_4$ gave *cis*-$Cr(CO)_4L'_2$ and *fac*-$Mo(CO)_3L'_3$, respectively. $[\pi$-C_5H_5-$Mo(CO)_3L]PF_6$ was deprotonated with methoxide ion to give π-$C_5H_5Mo(CO)_3P(C_6H_5)_2$ which then decomposed with no dinuclear complex, $[\pi$-$C_5H_5Mo(CO)_2P(C_6H_5)_2]_2$, being formed. Deprotonation of the complex, π-$C_5H_5Mo(CO)_2[P(C_6H_5)_2H]Br$, with *n*-BuLi led to the hydride bridged species $(C_5H_5Mo)_2(CO)_4$-$[P(C_6H_5)_2]H$. Irradiation of $M(CO)_5PR_2H$ and $M(CO)_5PR_2Li$ species ($M = Cr$, Mo, W; $R = C_6H_5$) led to dimerization with accompanying oxidation to give $M_2(CO)_8(PR_2)_2$ and $M(CO)_4$-$(PR_2H)_2$.

King and co-workers[111] have described several reactions of dialkylaminodifluorophosphines with cyclopentadienylmetal carbonyl derivatives. $(\pi$-$C_5H_5)Mo(CO)_3CH_3$ was found to react with $(CH_3)_2NPF_2$ in acetonitrile to give $(\pi$-$C_5H_5)Mo(CO)_2$-

$(COCH_3)[PF_2N(CH_3)_2]$, whereas, reaction with $C_5H_{10}NPF_2$ gave cis-$(C_5H_{10}NPF_2)_4Mo(CO)_2$. U.v. irradiation of $(\pi\text{-}C_5H_5)Mo(CO)_2(C_3H_5)$ with $(C_2H_5)_2NPF_2$ gave the yellow derivative $(\pi\text{-}C_5H_5)Mo(CO)(C_3H_5)[PF_2N(C_2H_5)_2]$ which was assigned structure XXXVI on the basis of ^1H nmr spectral data. Reactions of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ with R_2NPF_2 in boiling benzene gave $(\pi\text{-}C_5H_5)Mo(CO)_2(PF_2NR_2)Cl$ and/or $(\pi\text{-}C_5H_5)Mo(CO)(PF_2NR_2)_2Cl$ depending on the mole ratio of reactants. The seven coordinate product, $(\pi\text{-}C_5H_5)Mo(CO)[PF_2N(CH_3)_2][P(C_6H_5)_3]Cl$, was obtained from $(\pi\text{-}C_5H_5)Mo(CO)[PF_2N(CH_3)_2]_2Cl$ with $P(C_6H_5)_3$ in boiling benzene. The tungsten derivative, $(\pi\text{-}C_5H_5)W(CO)_2(PF_2NC_5H_{10})I$, was also reported.



XXXVI

Nesmeyanov and co-workers[112] have reported upon the insertion of Hg at the metal-halogen bond in $(\pi\text{-}C_5H_5)M(CO)_3X$ (M = Mo, W and X = I, Br) to yield the complexes $(\pi\text{-}C_5H_5)M(CO)_3HgI$ (M = Mo, W) and $(\pi\text{-}C_5H_5)Mo(CO)_3HgBr$ and $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2Hg$. In addition insertion of Hg at the M-Cl or metal-metal bonds in $[(\pi\text{-}C_5H_5)M(CO)_3Cl]$ or $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ afforded $[(\pi\text{-}C_5H_5)M(CO)_3]_2Hg$ complexes. $(\pi\text{-}C_5H_5)W(CO)_3Br$ and $(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)I$ were found not to undergo insertion reactions with mercury.

Complexes containing mercury-transition metal bonds have also been prepared by the reaction of C_6F_5HgBr with the sodium salts of organometallic transition metal anions in THF.[113] Thus $C_6F_5HgMo(CO)_2L(\underline{h}^5-C_5H_5)$ (L = CO, PPh_3, $P(OPh)_3$), $C_6F_5HgFe(CO)_2(\underline{h}^5-C_5H_5)$, and $C_6F_5HgMn(CO)_5$ are reported to be thermally stable to 100°.

Nesmeyanov and co-workers[114] have reported the reaction of GeI_2 in refluxing C_6H_6 with $[(\pi-C_5H_5)M(CO)_3]_2Hg$ (M = Mo, W) to give the corresponding $[(\pi-C_5H_5)M(CO)_3GeI_2]_2$ complexes in 10 and 22 % yields respectively.

Diphenylmercury has been shown to react with $Cr(CO)_6$ in a boiling diglyme/octane mixture to result in formation of bis(phenyltricarbonylchromium)Hg in 70 % yield.[115] $[(CO)_3CrC_6H_5]_2Hg$ was found to react with mercuric chloride, iodine, HCl and $LiAlH_4$ to produce (phenyltricarbonylchromium)-mercury chloride, iodobenzenechromium tricarbonyl and benzenechromium tricarbonyl, respectively.

Cleavage reactions of compounds of the type $R_3SnM(\underline{h}^5-C_5H_5)(CO)_3$, M = W and Mo; R = Me, $CH_2{=}CHCH_2$, have been studied.[116] Thus I_2 and $HgBr_2$ cleave the metal-metal bond of the trimethyltin derivatives; $HgBr_2$ on the other hand reacts with the triallyltin derivatives cleaving the tin-carbon bond. MeHgCl reacts with the trimethyltin compound to give the products, Me_2Hg and $Hg[Mo(\underline{h}^5-C_5H_5)(CO)_3]_2$.

$[(\pi-C_5H_5)M(CO)_3]_2Hg$ (M = Cr, Mo, W) react with $R_2NC(S)S-S(S)CNR_2$ to yield metal-mercury bonded dithiocarbamate complexes of the type $(\pi-C_5H_5)(CO)_3M-Hg(S_2CNR_2)$ (R = Me, Et).[117] I.r. and nmr sprectral data were presented for these complexes. The Hg-metal bond in these type species was thought to be stronger than that in the $[(\pi-C_5H_5)M(CO)_3]_2Hg$ compounds.

Conder and Robinson[118] have studied the reaction of $Hg[Co(CO)_4]_2$ and neutral organometallic Lewis bases. Included in this study was (mesitylene)$Mo(CO)_3$ which was not observed to undergo reaction with $Hg[Co(CO)_4]_2$. Amines, halides, $Co(CO)_4^-$, or $Hg[Mn(CO)_5]_2$ were also found not to react with $Hg[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$.

The synthesis of air- and moisture-sensitive transition-metal carbonyl derivatives of magnesium, including $B_xMg[(\pi\text{-}C_5H_5)Mo(CO)_2L]$ (where L = CO, alkyl or aryl phosphines, and B = THF or py), has been achieved by the reductive cleavage of dimeric transition metal carbonyl complexes with magnesium amalagam in the presence of a Lewis base.[119]

Hackett and Manning have studied the insertion of tin(II) halides, SnX_2 (X = F, Cl, Br, or I), into the metal-metal bonds of the dimers $[(\pi\text{-}C_5H_5)M(CO)_3]_2$ (M = Cr, Mo, W).[120] The products obtained were $[(\pi\text{-}C_5H_5)M(CO)_3]_2SnX_2$ derivatives as well as $(\pi\text{-}C_5H_5)M(CO)_3X$ and $(\pi\text{-}C_5H_5)M(CO)_3SnX_3$ compounds. The results were thought to be consistent with two reaction pathways; "direct" and "indirect" insertion, the latter proceeding via the $(\pi\text{-}C_5H_5)M(CO)_3SnX_3$ compounds. The importance of the "indirect" route increases along the series $Cr < Mo \sim W$ and $F < Cl < Br < I$. The reactions between $[(\pi\text{-}C_5H_5)Mo(CO)_3SnX_3]$ and $[(\pi\text{-}C_5H_5)M'(CO)_3]_2$ (X = Cl, Br, or I, and M, M' = Cr, Mo, W) were used to prepare $[(\pi\text{-}C_5H_5)M(CO)_3][(\pi\text{-}C_5H_5)M'(CO)_3]SnX_2$. $[(\pi\text{-}C_5H_5)Fe(CO)_2][(\pi\text{-}C_5H_5)M(CO)_3]SnX_2$ was prepared in a similar manner.

Reaction of the trialkylacetylides ($Me_3Sn(C{\equiv}CPh)$) with $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ in refluxing diglyme has led to the production of $\pi\text{-}C_5H_5Mo(CO)_3SnMe_3$ plus unidentified products.[121]

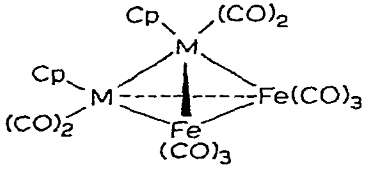
Tetrameric transition metal carbonyl zinc alkoxides have been reported from the alcoholysis reactions of transition metal carbonyl derivatives of zinc.[122] In this manner, $[CH_3OZnMo(CO)_3C_5H_5]_4$ and $[C_2H_5OZnMo(CO)_3C_5H_5]$, were prepared from $Zn[Mo(CO)_3C_5H_5]$ with methanol and ethanol, respectively. Methanol was found to be more reactive than ethanol in the alcoholysis process. The observed order of reactivity for various transition metal species with a given alcohol was found to parallel the pK_a values of the corresponding metal carbonyl hydrides.

Several new complexes containing Mo-In and W-In bonds have been reported.[123] These include $[\pi\text{-}C_5H_5(CO)_3M]_3In$ (M = Mo, W), $[\pi\text{-}C_5H_5(CO)_3Mo]_2InX$ (X = Cl, Br), $[\pi\text{-}C_5H_5(CO)_3W]_2InCl$ and $\pi\text{-}C_5H_5(CO)_3MoInCl_2$. A comparative study of the relative utility of the various methods available for the preparation of such complexes was carried out.

$Me_2Tl[Mo(\pi\text{-}C_5H_5)(CO)_3]$ has been prepared from Me_3Tl and $(\pi\text{-}C_5H_5)Mo(CO)_3H$ in CH_2Cl_2 at -78°.[124] The complex was characterized by infrared, nmr, and mass spectral analyses. The analogous tungsten derivative was prepared but was not fully characterized.

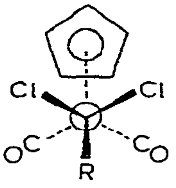
Mono- and di-halogen disilanyl compounds react with transition metal complex anions to give the disilanyl derivatives.[125] Included in the list of new complexes are the following: $Cp(CO)_3MoSiMe_2SiMe_3$, $Cp(CO)_3WSiMe_2SiMe_2Cl$, and $Cp(CO)_2FeSiMe_2SiMe_2Br$. No disilanyl bridge complexes were reported.

Reactions of $CpMo(CO)_2PPh_3^-$ and $CpMo(CO)_2(PPh_3)H$ towards fluorocarbon substrates have been described.[126] New mixed metal cluster anions have been prepared by reaction of $CpMo(CO)_3^-$ or $CpW(CO)_3^-$ with $Fe_2(CO)_9$.[127] Thus air-sensitive tetramethylammonium salts of stoichiometry $[Me_4N]_2$-$[Cp_2M_2Fe_2(CO)_{10}]$ were isolated. On the basis of the observed infrared spectra the authors suggest a tetrahedral arrangement of metal atoms as shown below (XXXVII).

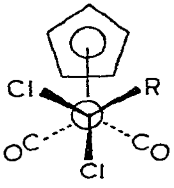


XXXVII

Complexes of formula $\underline{h}^5$-$C_5H_5(CO)_3M$-$SnCl_2R$, where M = Mo, W and R = S_2CNMe_2, S_2CNEt_2 have been prepared by reacting the corresponding trichlorotincyclopentadienyl metal carbonyl derivative with sodium dithiocarbamate.[128] Complicated i.r. spectra in the CO stretching region lead Glass and Shiels to suggest the presence of rotamers XXXVIII A and B due to hindered rotation about the metal-tin bond. ^1H nmr spectra show no evidence for this isomerism.



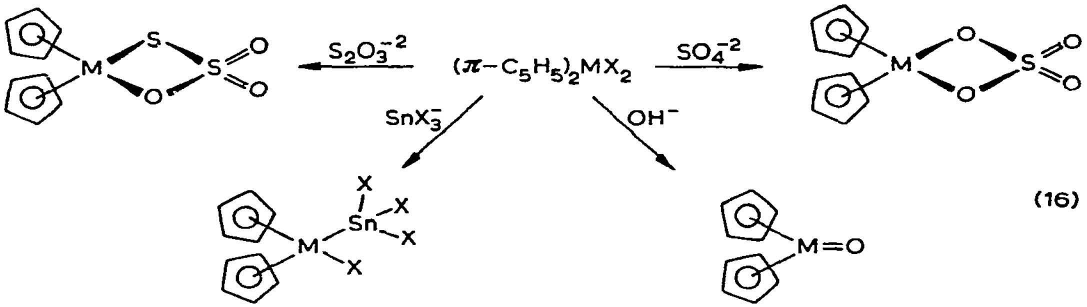
XXXVIII A



XXXVIII B

The preparation of $(\pi$-$C_5H_5)_2M(SnX_3)X$, where M = Mo or W and X = Cl or Br, has been reported.[129] These were found to react with Cl_2 or Br_2 to yield the salts $[(\pi$-$C_5H_5)_2$-

$MX_2]^+SnX_3^-$. Analogous metathetic reactions of $(\pi\text{-}C_5H_5)_2MX_2$ with $SO_4^=$, $S_2O_3^{-2}$ and OH^- were found to produce the complexes shown in the scheme below (eq. 16).



(16)

$(\pi\text{-}C_5H_5)M(CO)_3Cl$ (M = Mo or W) complexes were found to react with $(\underline{p}\text{-tolyl})_2C{=}NLi$ to yield three types of complexes, $[(\pi\text{-}C_5H_5)M(CO)_2NC(\underline{p}\text{-tolyl})_2]$ ($\underline{A}$), $[(\pi\text{-}C_5H_5)M(CO)_2\{(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2\}]$ ($\underline{B}$), and $[(\pi\text{-}C_5H_5)M(CO)_2\{(\underline{p}\text{-tolyl})_2CNC(\underline{p}\text{-tolyl})_2\}(\underline{p}\text{-tolyl})_2CO]$ ($\underline{C}$).[130] Complex $\underline{B}$ apparently can exist in two isomeric forms in the solid state which become interconverted in solution. $\underline{C}$ dissociates in solution to form $\underline{B}$ and free $(\underline{p}\text{-tolyl})_2CO$. The complexes failed to undergo substitution reactions with Ph_3P. I.r. and nmr data are reported for the respective complexes.

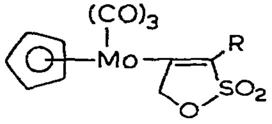
The carboxamido complexes $(CpM(CO)_3C(O)NR_2$, M = Mo or W) formed from reaction of cationic complexes $CpM(CO)_4^+$ with secondary amines are converted into $CpM(CO)_3^-$ and urea upon further reaction with excess amine.[131] This latter reaction is proposed to go through a deprotonation of the carboxamido NH proton by the excess amine leaving a complex which decomposes to the metal carbonyl anion and the corresponding isocyanate. Further reaction of the RNCO with amine yields the observed urea. Evidence of this mechanism is based on the fact that a carboxamido derivative may be formed on reaction of $CpW(CO)_3H$ with MeNCO, i. e., the MeNCO inserts into the W-H bond.

The silyl metal complexes $(\pi\text{-}C_5H_5)(CO)_3MSiRR^1R^2$ (M = Mo, W; R = H, Me, halogen; R^1 = Me, halogen; R^2 = Me, halogen) have been prepared by reaction of $[(\pi\text{-}C_5H_5)(CO)_3M]Na$ with excess halosilanes.[132] These complexes decompose in solution with M-Si bond cleavage to yield $[(\pi\text{-}C_5H_5)(CO)_3M]_2$ complexes. Replacement of the trimethylsilyl group in $(\pi\text{-}C_5H_5)(CO)_3M\text{-}SiMe_3$ (M = Mo, W) with heterosiloxanes occurred (eq. 17).

$$(\pi\text{-}C_5H_5)(CO)_3M\text{-}SiMe_3 + Me_3XOSiMe_3 \rightarrow (\pi\text{-}C_5H_5)(CO)_3M\text{-}XMe_3 + Me_3SiOSiMe_3 \qquad (17)$$

(X = Ge, Sn)

Formation of γ-sultones of iron and molybdenum using SO_3 has been observed.[133] $(\pi\text{-}C_5H_5)Mo(CO)_3CH_2C{\equiv}CR$ (R = H, Me, Ph) when treated with SO_3 in dioxane gave the sultones XXXIX. In addition, sulfur trioxide is found to react with transition metal-2-alkynyls to yield vinyl-sultone complexes,



XXXIX

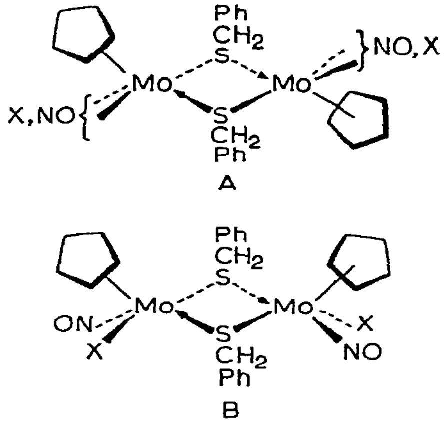
$\overline{M\text{-}C{=}C(R)\text{-}S(O)_2\text{-}CH_2}$ (M = $h^5\text{-}C_5H_5Fe(CO)_2$, R = Me and Ph; M = $h^5\text{-}C_5H_5Mo(CO)_3$, R = Ph; M = $Mn(CO)_5$, R = Me and Ph).[134]

The green, paramagnetic complex $(\pi\text{-}C_5H_5)_2Nb(SMe)_2\text{-}Mo(CO)_4$ has been prepared from $(\pi\text{-}C_5H_5)_2Nb(SMe)_2$ and C_7H_8-

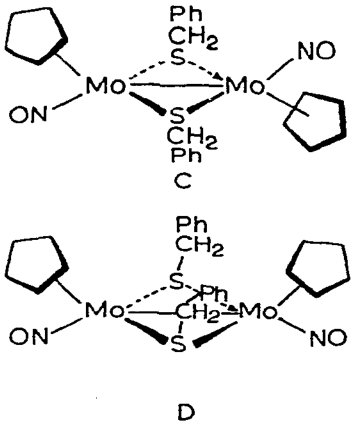
$Mo(CO)_4$ in toluene.[135] The e.s.r. spectrum of this complex showed the ten expected lines arising from coupling with the ^{93}Nb nucleus, I=9/2.

Dinuclear metal carbonyl complexes containing a single methylthiobridge, π-$C_5H_5(CO)_2Fe$-SCH_3-$M(CO)_5$, π-$C_5H_5(CO)_3$-Mo-SCH_3-$M(CO)_5$, π-$C_5H_5(CO)_3W$-SCH_3-$M(CO)_5$, $(C_6H_5)_3PAu$-SCH_3-$M(CO)_5$ (M = Cr, W) and π-$C_5H_5(CO)_3M'Mn(CO)_2(\pi$-$C_5H_5)$ (M' = Mo, W), were prepared: (a) from the π-$C_5H_5(CO)_nM$-SCH_3 complexes and $(THF)M'(CO)_5$ or (b) from the methylthiostannane derivatives $(CH_3)_3Sn$-SCH_3-$M'(CO)_5$ and $(\pi$-$C_5H_5)(CO)_nM$-Cl.[136] The complexes are all highly colored, air stable, crystalline solids. Infrared and nmr spectral results were reported.

Reaction of $[(\pi$-$C_5H_5)Mo(NO)X_2]$ (X = Br or I) with RSH (R = Me, Et, Pr, Bu^t, Bu or CH_2Ph) gave $[(\pi$-$C_5H_5)Mo(NO)X$-$(SR)_2]$.[137] The ^{1}H nmr spectra of the complexes where R = CH_2Ph or Pr^i (X = Br or I) could not distinguish between the two isomers XL A and B. Reduction of $[(\pi$-$C_5H_5)Mo(NO)Br(SR)]_2$ with zinc dust afforded $[(\pi$-$C_5H_5)Mo(NO)SR]_2$ which appears to exist as a mixture of isomers XL C and D, whereas treatment



XL A and B



XL C and D

of $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ with $NaSBu^n$ (X = Br) gave $[(\pi\text{-}C_5H_5)\text{-}Mo(NO)(SPr^n)_2]_2$ and with $NaSPr^i$ (X = I) gave both $[(\pi\text{-}C_5H_5)\text{-}Mo(NO)(SPr^i)]_2$ and $[(\pi\text{-}C_5H_5)Mo(NO)(SPr^i)_2]_2$. The mass, nmr, i.r., and electronic spectra of these compounds are described.

The reactions of $[(\pi\text{-}C_5H_5)Mo(NO)(CO)_2]$ with Cl_2 or Br_2 have afforded $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$ (X = Cl or Br).[138] These species react with Lewis bases L (L = PPh_3, $AsPh_3$, PMe_2Ph, py or bipy) or halide ion (X = Cl or Br) to give $[(\pi\text{-}C_5H_5)\text{-}Mo(NO)X_2L]$, $[(\pi\text{-}C_5H_5)Mo(NO)Br(PMe_2Ph)_2]Br$, $[(\pi\text{-}C_5H_5)Mo(NO)Cl\text{-}(bipy)]Cl$ and $[(\pi\text{-}C_5H_5)Mo(NO)X_3]^-$. Nmr and infrared spectral properties of these complexes are discussed.

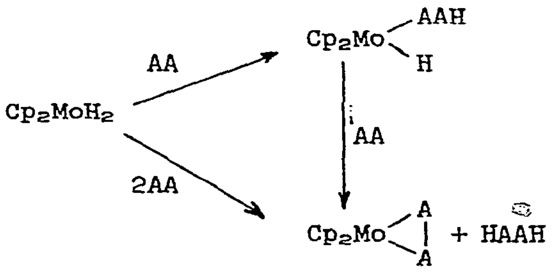
Several perfluoro-1-methylpropenyl derivatives of metal carbonyls and metal cyclopentadienyls have been reported.[139] The reaction of $(\pi\text{-}C_5H_5)Cr(NO)_2Cl$ with C_4F_7Ag to give $(\pi\text{-}C_5H_5)Cr(NO)_2C_4F_7$ was included in this study.

Photolysis of $\pi\text{-}C_5H_5Cr(CO)_2NO$ in cyclooctene has been shown to eliminate CO and result in the formation of the cyclooctene complex, $\pi\text{-}C_5H_5Cr(CO)(NO)(C_8H_{14})$.[140] The π-bonded cycloolefin complex, $\pi\text{-}C_5H_5Cr(CO)(NO)(C_8H_{14})$, was found to react <u>via</u> replacement of cyclooctene with various monoolefins and alkynes in benzene to form the complexes, $\pi\text{-}C_5H_5Cr(CO)(NO)L$ (where L = ethylene, acetylene, acetylenedicarboxylic dimethylester, acenaphthylene, norbornene, and malic anhydride).

Attempts at preparing molybdenocene have resulted in the isolation of $[(C_5H_5)_2Mo]_x$, x = 2 or greater, from the reaction of $(C_5H_5)_2MoCl_2$ with sodium amalgam in THF.[141] Also isolated from the reaction mixture was $(C_5H_5)_2MoH_2$. During the course of studying reactions of the coordinatively unsaturated molybdenocene believed to be present initially, the novel compounds $(C_5H_5)_2Mo(CO)$ and $(C_5H_5)_2Mo(N_2)$ were also prepared.

Giannotti and Green have observed that irradiation of $(\pi\text{-}C_5H_5)_2WH_2$ in benzene solutions results in formation of the phenyl hydride complex $(\pi\text{-}C_5H_5)_2WHPh$ in high yield.[142] When deuteriobenzene was used $(\pi\text{-}C_5H_5)_2WD(C_6D_5)$ was obtained. On the basis of this result, in conjunction with a lack of exchange observed between $(\pi\text{-}C_5H_5)_2WHPh$ and C_6D_6, it was proposed that irradiation causes loss of hydrogen from the dihydride followed by insertion of the "carbene-like" species $W(\pi\text{-}C_5H_5)_2$ into the aromatic C-H bond.

In an effort to more clearly describe correlations between heterogeneous and homogeneous catalysis a comprehensive study of the reactions of dihydridobis(cyclopentadienyl)molybdenum with olefins and acetylenes has been done.[143] In particular the conditions necessary for reaction *via* route 18 or 19 were under investigation. Electron-poor acetylenes such as hexafluoro-2-butyne and acetylenedicarboxylate follow eq. 18; diphenylacetylene follows eq. 19



(18)

(19)

(20)

yielding exclusively the <u>cis</u> isomer of stilbene at 25°. Structure and chemical properties of the reaction products are discussed. The third pathway, eq. 20, for formation of an olefin complex was observed in the thermal decomposition of the hydrido-σ-alkenyl complex $Cp_2MoH[\sigma\text{-}C(CO_2CH_3){=}CHCO_2CH_3]$. This latter reaction exhibited geometrical isomerization of the alkene.

Deprotonation of the cations $[(\pi\text{-}C_5H_5)_2MH(C_2H_3R)]^+$ (M = Mo, R = H; M = W, R = H and CH_3) formed from reaction of $(\pi\text{-}C_5H_5)_2MCl_2$ with excess ethylaluminum dichloride or isopropylmagnesium bromide has provided a convenient route to divalent complexes of the type $(\pi\text{-}C_5H_5)_2M(C_2H_3R)$ in near quantitative yields.[144] This procedure was extended to the preparation of $(\pi\text{-}C_5H_5)_2Mo(CO)$ from the corresponding cation, $[(\pi\text{-}C_5H_5)_2MoH(CO)]^+$. Further reactions of these divalent complexes are discussed.

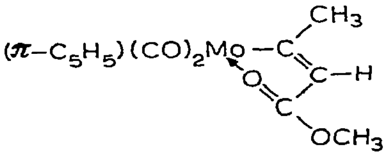
Ring exchange reactions involving $Li(C_5D_5)$ with $Cr(\pi\text{-}C_5H_5)_2$ in THF and $Ni(\pi\text{-}C_5H_5)_2$ with $Cr(\pi\text{-}C_5H_5)_2$ in heptane have been reported by Switzer and Rettig.[145] The half-life for this exchange process was observed to be considerably faster for $Cr(\pi\text{-}C_5H_5)_2$ with $Li(C_5D_5)$ as compared with $Ni(\pi\text{-}C_5D_5)_2$.

An interesting use of organometallic reagents as an aid to equilibrium studies in organic chemistry has been presented by Cotton and Deganello.[146] Metal carbonyl moieties ($Mo(CO)_3$ and $Fe(CO)_3$) have been used to influence the position of equilibrium of derivatives of mono- and bicyclic tautomers of C_8H_{10} and to allow isolation of isomeric olefins.

In further evidence of the similarity of the CO and PF_3 ligands, $Ni(PF_3)_4$ has been used as a source of PF_3, i.e., a trifluorophosphinating agent, in the preparation of metal-trifluorophosphine complexes.[147] Among the complexes prepared were $CpMo_2(CO)_5PF_3$, $[CpMo(CO)_2PF_3]_2$, $MeMo(CO)_2(PF_3)Cp$, and $MeW(CO)_2(PF_3)Cp$.

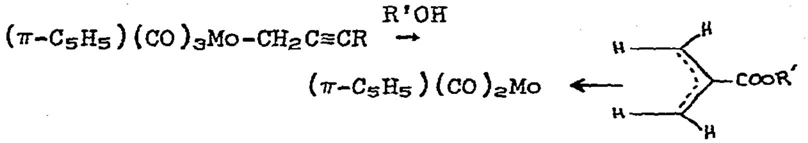
Further details of the reaction between acetylpentamethylcyclopentadiene and various metal carbonyls have been presented by King and Efraty.[148] Based on observed products such as $[\underline{h}^5\text{-}Me_5C_5M(CO)_2]_2$ (M = Cr, Mo, W), $MeM(CO)_3(\underline{h}^5\text{-}Me_5C_5)$ (M = W, Mo), and $(\underline{h}^4\text{-}Me_5C_5C(O)Me)Fe(CO)_3$ a four-step scheme is proposed for the reaction. This scheme would include an acetyl migration from the initially metal-bound pentadiene ring onto the metal with subsequent decarbonylation of the monohaptoacetylderivative. Subsequent homolytic clevage of the metal-methyl σ bond would lead to the dimer products of the type observed. M-M triple bonds are proposed for the Group VI dimers.

The reaction of $(\pi\text{-}C_5H_5)(CO)_3Mo\text{-}CH_2C{\equiv}CH$ with methanol has been shown to yield the vinyl carbonyl complex XLI, whereas reactions of $(\pi\text{-}C_5H_5)(CO)_3Mo\text{-}CH_2C{\equiv}CR$ with a variety of



XLI

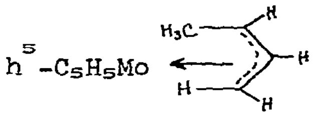
alcohols have resulted in formation of π-allylic complexes according to eq. 21.[149]



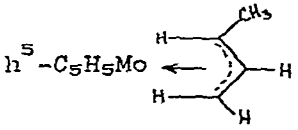
(21)

($R = CH_3$, $R' = H$; $R = CH_3$, $R' = CH_3$; $R = CH_3$, $R' = C_2H_5$; and $R = C_6H_5$, $R' = CH_3$).

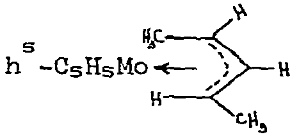
Substituted allyl bromides react with (π-cyclopentadienylmolybdenumtricarbonyl)sodium to yield anti- and <u>syn</u>-forms of π-allyl complexes (XLIIA through XLIIIB).[150] Reaction of the molybdenum anion with 1-bromo-4-methylpent-3-ene results in the σ-bonded organometallic, XLIV.



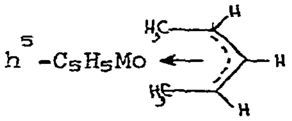
(XLII A) (<u>anti</u>)



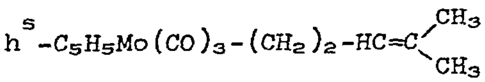
(XLII B) (<u>syn</u>)



(XLIII A) (<u>syn-anti</u>)



(XLIII B) (<u>anti-anti</u>)



$$h^5\text{-}C_5H_5Mo(CO)_3\text{-}(CH_2)_2\text{-}HC{=}C\begin{matrix} CH_3 \\ CH_3 \end{matrix}$$

(XLIV)

The effect of a metal carbonyl moiety $[Cr(CO)_3]$ on the chemistry of the olefinic and acetylenic groups in $(CO)_3Cr(C_6H_5CH{=}CH_2)$ and $(CO)_3Cr(C_6H_5C{\equiv}CH)$ has been studied.[151] Cationic, anionic and free radical agents were ineffective as polymerization initiators towards the styrene complexes. Phenyllithium added to the β-carbon of the styrene complex and yielded, after hydrolysis, the tricarbonyl complex of bibenzyl. Other reactions are presented.

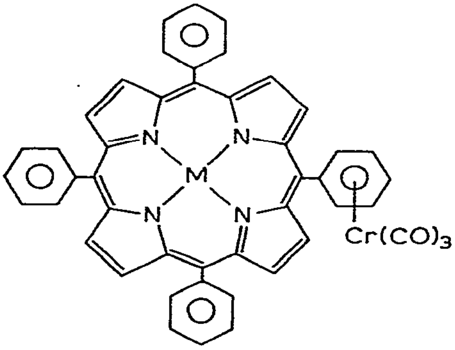
Through the use of infrared spectroscopy, protonation of the arenechromium dicarbonyl triphenylphosphine complexes, $XC_6H_5Cr(CO)_2PPh_3$ ($X = CH_3OOC$, H, CH_3, CH_3O and $(CH_3)_2N$) and $(CH_3)_3C_6H_3Cr(CO)_2PPh_3$, in trifluoroacetic acid has been shown to occur at the metal atom.[152] The ease of protonation appeared to increase with the introduction of increasing electron-releasing substituents into the π-bonded aromatic ring. Similarly, from ^1H nmr studies, it has been shown that C_6H_6-$Cr(CO)_3$, $CH_3C_6H_5Cr(CO)_3$, $CH_3OC_6H_5Cr(CO)_3$ and 1,3,5-$(CH_3)_3$-$C_6H_3Cr(CO)_3$ protonate at the chromium atom in a mixture of $BF_3 \cdot H_2O$ and CF_3COOH.[153] The arene-$Cr(CO)_3$ complexes were however found to be less basic than their monosubstituted PPh_3 analogs.

The mechanism for the proton exchange in cations of the type $(C_6H_5R)Cr(H)(CO)_3^+$ has also been investigated by Lillya and Sahatjian.[154]

The reactions of $(C_6H_6)_2Cr^+$ with strong bases yield, in addition to diamagnetic products, a paramagnetic species for which the structure $(\pi\text{-}C_6H_6)Cr^+(\pi\text{-}C_6H_6)^-$ was suggested on the basis of e.s.r. spectroscopic evidence.[155]

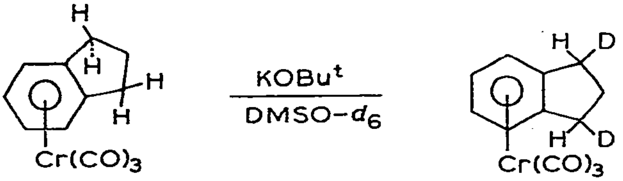
The base catalyzed deuteration of $(arene)Cr(CO)_3$ (arene = anisole, ethylbenzoate, N,N-dimethylaniline) has been studied by Ashraf.[156] Ortho-substitution was found to be predominate in the anisole complex whereas random substitution was observed for ethylbenzoate. No exchange was observed for the N,N-dimethylaniline derivative.

Tricarbonylchromium π-complexes of β-tetraphenylporphin (TPP), where M = Co(II), Ni(II), Cu(II) and Mn(III)Cl, have been reported (XLV).[157] Zn(TPP)[$Cr(CO)_3]_2$ was also reported. From a study of the CO stretching vibrations it was concluded that there was no appreciable interactions between the two metals.



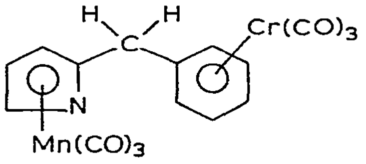
XLV

The effects of organometallic fragments on organic reactions are further demonstrated in the increased facility of base-catalysed hydrogen-deuterium exchange of benzylic protons upon complexation of alkylbenzenes to tricarbonylchromium(O).[158] In addition, exclusive exchange of protons <u>anti</u> to the $Cr(CO)_3$ moiety in indane complexes such as XLVI has been observed.



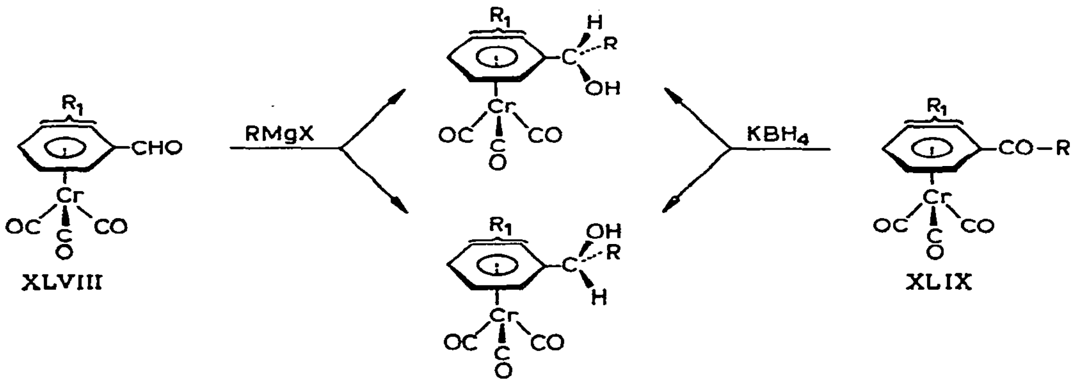
XLVI

Gogan and Davies[159] report the synthesis of $Cr(CO)_3$ and $Mn(CO)_3$ complexes of 2-benzylpyrrole and 2-phenylpyrrole. The $Cr(CO)_3$ moiety is in both cases bound to the phenyl ring and the $Mn(CO)_3$ to the pyrrolyl ring. The mixed metal complex, (XLVII), has also been prepared and isolated.



XLVII

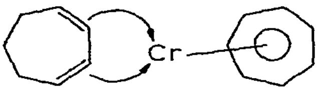
The reaction of aldehyde (XLVIII) and ketone (XLIX) derivatives of ortho- and meta-substituted benzenechromium tricarbonyls with RMgX or KBH_4 respectively to form asymmetric alcohol derivatives have been studied by Meyer and Dabard.[160] In general the two different routes to the synthesis of assymmetric alcohols led to different mixtures of diastereomers with the Grignard reagent procedure being somewhat more stereospecific.



XLVIII XLIX

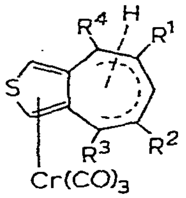
(R_1 = *o*, *m*-CH_3, $-OCH_3$, $-OC_2H_5$, $-Cl$). (R_1 = *o*, *m*-CH_3, $-OCH_3$, $-OC_2H_5$ and R = CH_3).

Cycloheptatrienyl(1,3-cycloheptadiene)chromium (L) has been obtained from the reaction of $CrCl_3$, cycloheptatriene, 1,3-cycloheptadiene and isopropyl Grigand in ether.[161] The e.s.r. spectrum of this complex in *n*-hexane shows one signal with a g value of 1.998. Mass spectral data are also presented for this complex.

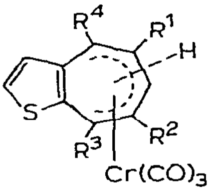


L

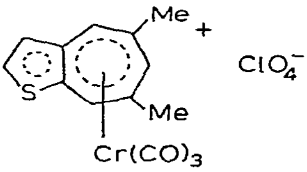
Thermal reactions of $Cr(CO)_6$ with cycloheptathiophenes yield the tricarbonyl thiophene chromium(0) derivatives.[162] Compounds LI A and LI B in which the $Cr(CO)_3$ moiety is attached *via* the thiophene ring or the cycloheptatriene ring were obtained from the respective thiophene derivatives. The salt LI C was obtained by reaction of the corresponding complex LI B with tropylium perchlorate.



LI A

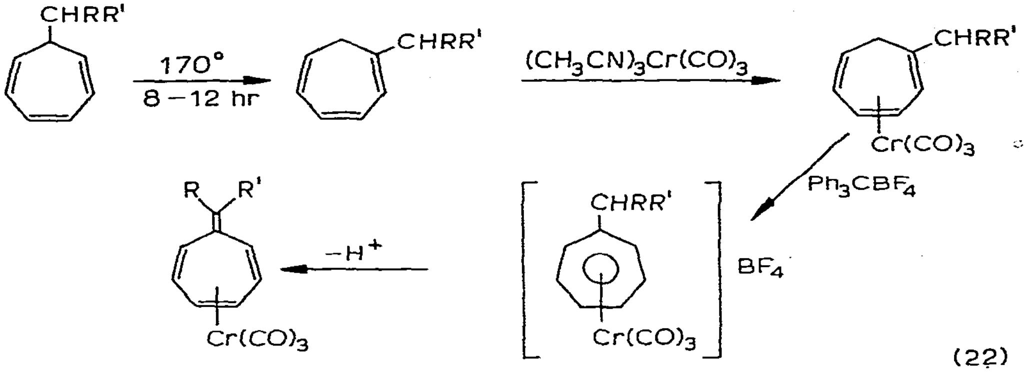


LI B



LI C

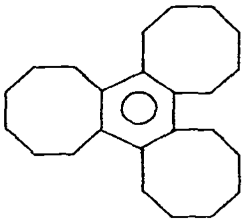
Several new heptafulvene complexes have been prepared by the route shown in reaction 22.[163] Unlike the tricarbonyliron analogs, which coordinate through the butadiene unit, the chromium complexes resemble free heptafulvenes, showing a greater reactivity to electrophiles at the exocyclic double bond.

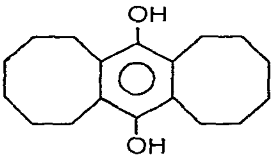


(22)

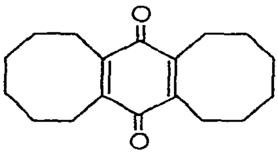
(R = R' = Me; R = R' = Ph; R = R' = H; R = H, R' = Ph; R = H, R' = Me).

Cyclooctyne was observed to react with $Mo(CO)_6$ in the dark at room temperature to give ∽ 100 % of triscyclooctenobenzene (LII).[164] In the presence of u.v. irradiation, the reaction gave 13 % biscyclooctanohydroquinone (LIII), 1 % biscyclooctanoquinone (LIV), 3 % carbonyltris(cyclooctyne)-molybdenum and 20 % LII.


LII

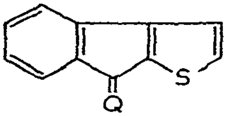


LIII

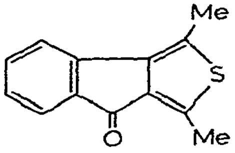


LIV

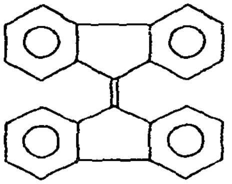
$Cr(CO)_6$ was shown to condense with the benzene ring of indenothiophene (LV) and indenothiophenones (LVI) and (LVII) to give the corresponding indenothiophene and indenothiophenone chromium tricarbonyl complexes.[165] Fluorenone was found to react with $Cr(CO)_6$ to give the $Cr(CO)_3$ complex as well as dimer LVIII. However, LVI and $W(CO)_6$ gave the dimer LIX but no $W(CO)_3$ complex.



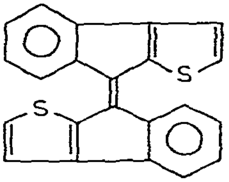
LV $Q=H_2$
LVI $Q=O$



LVII



LVIII



LIX

1,2-dicarba-<u>closo</u>-dodecaborane has been reported to undergo a 2-electron reduction with Na-THF to form $(B_{10}C_2H_{12})^{-2}$ which serves as a ligand in the formation of transition metal complexes.[186] Included in the list of compounds prepared are $(\pi\text{-}B_{10}C_2H_{12})M(CO)_3^{-2}$ (M = Mo, W). A <u>closo</u>-polyhedral structure is proposed for these complexes with the metal atom located at one of the three vertexes.

A modified Unterzaucher procedure for the determination of the total oxygen in organometallic compounds, including several Group VIB arenemetaltricarbonyl derivatives, has been reported.[187]

High speed column liquid chromatography has been used to separate organometallic complexes of very similar physical properties.[188] Isomers of (2,3-dimethylnaphthalene)tricarbonylchromium in which the $Cr(CO)_3$ moiety is bound to the methylated or to the unmethylated ring have been effectively separated and quantitatively analysed by this method.

Metal-alkyl and -aryl complexes. An increasing number of papers have dealt with the preparation and properties of metal-alkyl or metal-aryl complexes of the Group VIB metals. The red solid, $W(CH_3)_6$, was obtained by interaction of tungsten hexachloride with methyllithium in ether.[169] It was found to be extremely volatile and to sublime in vacuum at room temperature. The mass spectrum did not show the parent ion; the highest abundant species seen was $W(CH_3)_5^+$. The ^1H nmr spectrum had a single resonance at $\tau = 8.18$ with $J(W^{183}-H) = 3.0$ Hz. $LiW(C_6F_5)_5 \cdot 2Et_2O$ may be prepared by reaction of (pentafluorophenyl)lithium with WCl_6 in ether at -10°.[170] The bright green crystalline compound may be stored under an inert atmosphere for months at -10°. Thermal decomposition of the etherate gives low yields of the sublimable $W(C_6F_5)_5$.

Reactions of various chlorides of Cr, Mo, and W with lithium or Grignard reagents derived from $(CH_3)_3SiCH_2Cl$ produce thermally stable alkyls of the formula $Cr(CH_2SiMe_3)_4$ and $M_2(CH_2SiMe_3)_6$ (M = Mo or W).[171] I.r., Raman, electronic, e.s.r. and nmr spectral data are presented and discussed.

$Ph_2CHCrCl_2 \cdot 2THF$ reacts with two moles of PhLi to give $Ph_2CHCrPh_2$.[172] From a solution of $Ph_2CHCrPh_2$ the new Cr(II) compounds $CrPh_2 \cdot 2bipy$ and $Li_2CrPh_4 \cdot 4THF$ were prepared by addition of 2,2'-bipyridyl or 2 moles of PhLi respectively.

A series of monoalkylchromium complexes, $RCrCl_2(THF)_3$ where R = Me, Et, n-Pr and i-Bu, have been prepared by the reactions of $CrCl_3$ and the corresponding organoaluminum compounds.[173] The thermal stabilities of the complexes were found to decrease in the order $CH_3 > C_2H_5 > C_3H_7 > C_4H_9$, with alkanes, alkenes, dimeric alkanes and THF being released during the thermal decomposition process. Stable pyridine alkylchromium complexes were prepared by ligand exchange reactions of $RCrCl_2(THF)_3$ with pyridine. The alkylchromium complexes were found to catalyze the polymerization of ethylene under mild conditions with catalytic activity decreasing in the order: Me > Et > i-Bu.

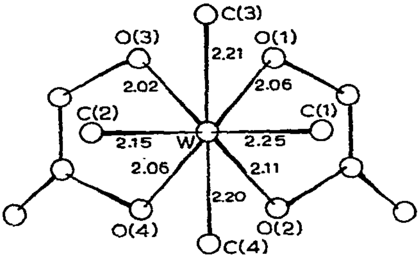
Kruse has prepared tetra-t-butylchromium from t-butyllithium and $CrCl_3 \cdot 3THF$ or $Cr(OR)_4$ (R = t-butyl).[174] This complex was isolated by sublimation and characterized by epr, u.v., visible and i.r. spectral measurements. The following compounds were not isolated in this study but were characterized in solution by their epr spectra: tetramethylchromium, tetraisopropylchromium, tetra-sec-butylchromium, tetra-n-butylchromium, tetra-3-pentylchromium, and tetrakis(cyclohexylmethyl)chromium.

Tetrahedral chromium(IV) compounds containing carbon as ligand in the form of alkyl groups chosen to avoid hydride transfer and alkene elimination have been prepared.[175] $Cr(CH_2CMe_3)_4$, $Cr(CH_2CMe_2Ph)_4$, and $Cr(CH_2CPh_3)_4$ are intensely colored crystalline solids with melting points > 110°.

(Diphenylmethyl)chromium dichloride, $Ph_2CHCrCl_2 \cdot 2THF$, has been prepared by the reaction of $CrCl_3$ with $Ph_2CHLi \cdot 2$-(dioxane) in THF at -50°.[176] The observed magnetic moment of this complex was 3.92 μB. $Ph_2CHCrCl_2 \cdot 2THF$ reacted in the presence of hexane, benzene, or Et_2O to afford $2CrCl_2 \cdot 2THF$ and $Ph_2CHCHPh_2$ and with donors $MeOCH_2CH_2OMe$, pyridine and 2,2'-dipyridyl to give $2CrCl_2 \cdot$donor and $Ph_2CHCHPh_2$.

Nitric oxide was found to insert into WMe_6 to yield yellow elongated prisms of the air-sensitive complex, WMe_4-

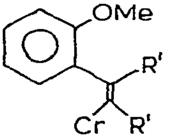
$[ON(Me)NO]_2$. Structure LX was established by x-ray structural analysis.[177]



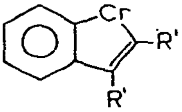
LX

The phosphine adducts, $Ph_3Cr{\cdot}2PPhR_2$ (R =Et, Bu), have been prepared in 60 - 65 % yield from the reaction of $Ph_3Cr{\cdot}3THF$ and R_2PPh in THF.[178] The complex was purified by recrystallization from hexane at -70°.

Reactions of tris(2-,3-, or 4-methoxyphenyl)chromium(III) with 2-butyne have been investigated.[179] Major products of the $(o\text{-}MeOC_6H_4)_3Cr$ reaction with 2-butyne were MeOPh, $o\text{-}MeOC_6H_4$ substituted butenes, hexamethylbenzene and methoxyl-free 1,2,3,4-tetramethylnaphthalene. The methoxyl-free naphthalene formation is particular to the ortho-anisylchromium compound. Postulated mechanisms for the naphthalene formation involve a cis-vinylchromium intermediate (LXI) and/or a chromocycle (LXII).



LXI



LXII

Cohen and Meyerstein have determined the specific rates of reactions of the radicals ($\dot{C}H_2CO_2H$, $\dot{C}H_2OH$, $CH_3\dot{C}HOH$, $(CH_3)_2\dot{C}OH$, and $CH_3\dot{C}HOCH_2CH_3$) with $Cr(H_2O)_6^{+2}$ to form chromium-carbon bonds.[180] The order of reactants was found to be: $\dot{C}H_2CO_2H > \dot{C}H_2OH > CH_3\dot{C}HOH > (CH_3)_2\dot{C}OH > CH_3\dot{C}HOCH_2CH_3$ which correlates with the unpaired electron density on the reacting carbon atom as determined by e.s.r. measurements.

The epr spectra of Cr(IV) in the tetrakis-alkylchromium compounds CrR_4 ($R = CH_2CH_2CH_2CH_3$, $C(CH_3)_3$, $CH_2C(CH_3)_3$, norbornyl, $CH_2C(C_2H_5)_3$, and $CH_2C(CH_3)_2(C_6H_5)$) have been observed at +25° and -196°.[181] In general, the +25° spectra of these compounds consists of a single intense peak (~3270 gauss) for which the calibrated area was consistent with a d^2 Cr(IV) species. At -196° a second weak absorption peak was observed at 1500 - 1650 gauss and was assigned to the "forbidden" $\Delta m = 2$ transition in Cr(IV).

Molecular nitrogen and nitrosyl complexes. Dinitrogen complexes of molybdenum containing arsine ligands have been reported by George and Seibold.[182] $Mo(N_2)_2L_2$ (L = 1-diphenylarsino-2-diphenylphosphinoethane or bis(1,2-diphenylarsino)ethane) were prepared by reduction of $MoCl_3(THF)_3$ with Na amalgam in THF in the presence of 2 equivalents of the appropriate ligand (L) under N_2. The trans configuration for these complexes was established via infrared spectroscopy.

Dinitrogen complexes of molybdenum have been prepared according to eq. 23.[183] The yield of the most likely polynuclear dinitrogen complex is decidedly influenced by both

$$Mo(acac)_3 + PPh_3 + AlR_3 + N_2 \xrightarrow{\text{toluene}} Mo(N_2)(PPh_3)_2 \cdot C_6H_5CH_3 \qquad (23)$$

the nature of R in AlR_3 and the ratio of PPh_3 to the parent molybdenum complex. Other monodentate ligands such as $P(\underline{n}\text{-}Bu)_3$, $P(C_6H_4\text{-}\underline{p}\text{-}CH_3)_3$ or $PEtPh_2$ do not yield a N_2 complex. Chelating diphosphine ligands such as $Ph_2P(CH_2)_nPPh_2$, $n = 1$, 2, or 3, yielded a new series of complexes, *trans*-$Mo(N_2)_2$-$PPh_2(CH_2)_nPPh_2$. Structure and chemical properties of the complexes are discussed. No reduction of coordinated N_2 to NH_3 was observed upon treatment of the complexes with $NaBH_4$.

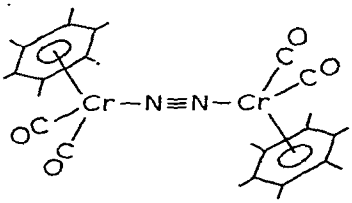
George has reported the preparation of a dinitrogen complex of molybdenum(I).[184] Addition of $Mo(N_2)_2(diphos)_2$ to a methanolic solution of I_2 produces the red, air-stable $[Mo(N_2)_2(diphos)_2]^+I_3^-$.

The reaction of *trans*-$Mo(N_2)_2(diphos)_2$ with carbon monoxide under photochemical conditions gave 50 % conversion to *cis*-$Mo(CO)_2(diphos)_2$ in 15 min. of reaction time.[185] Thermally this reaction has been reported to occur during a 4 day reaction period.[183]

The reduction of *trans*-$[WCl_4(PR_3)_2]$ by sodium amalgam in THF under N_2, H_2 and CO to yield hydrido, dinitrogen, and carbonyl complexes has been reported by Chatt and co-workers.[186] $WCl_4(PMe_2Ph)_2$ and $WCl_4(diphos)_2$ reacted with N_2 in the presence of excess phosphines under these conditions to form *cis*-$W(N_2)_2(PMe_2Ph)_4$ and *trans*-$W(N_2)_2(diphos)_2$. The reduction of $WCl_4(PMe_2Ph)_2$ with H_2 yielded $[WH_6(PMe_2Ph)_3]$. In the presence of CO the reduction of $WCl_4(PR_3)_2$ resulted in the formation of a variety of polycarbonyls, including fac- and mer-tricarbonyl derivatives.

The species CrN_2 has been identified in a low-temperature matrix by infrared spectroscopy.[187] The i.r. spectra of N_2 chemisorbed on metal clusters of chromium have also been obtained. The relative lowering of the CO stretching force constant in CrCO versus free CO was shown to be larger than the comparable lowering in going from N_2 to CrN_2. It was suggested that the lack of observation of metal-N_2 complexes beyond the bis-adduct is due to the large positive charge created on the metal atom when bound to the N_2 ligand.

Synthesis of the dinitrogen complex, $(\pi\text{-}C_6H_6)Cr(CO)_2N_2$, has been achieved by treatment of the hydrazine complex $(\pi\text{-}C_6H_6)Cr(CO)_2N_2H_4$ with H_2O_2/Cu^{+2} in THF at -10°.[188] Alternatively, the complex results from the elimination of $2H_2$ from $(\pi\text{-}C_6H_6)Cr(CO)_2N_2H_4$ at 20° under high vacuum conditions. In addition (hexamethylbenzene)$Cr(CO)_2$THF reacts with N_2 to form (HMB)$Cr(CO)_2N_2$ or (HMB)$Cr(CO)_2N{\equiv}N(CO)_2Cr$(HMB) (LXIII). (Mesitylene)$Cr(CO)_2N_2$ has also been prepared from (mesitylene)$Cr(CO)_2N_2H_4$ with H_2O_2/Cu^{+2} in THF at -78° or from (mesitylene)$Cr(CO)_2$THF and N_2.[189]

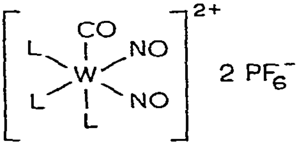


LXIII

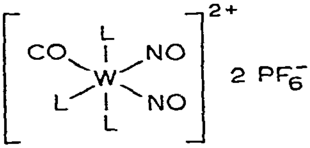
The crystal and molecular structure of di-μ-thio-n-butyl(bis-π-cyclopentadienylmolybdenum)irondichloride, a model compound of the nitrogenase system, has been determined by Cameron and Prout.[190] The Fe-Mo separation in the bent S bridge was found to be 3.660 Å and there was no metal-metal bond observed.

Nitrosyl halides of molybdenum(II) and tungsten(II) of the form $M(NO)_2LX_2$ and $M(NO)_2L_2X_2$, where X = Cl, Br, I and L = $CH_2(AsPh_3)_2$ (dam) and $CH_2(PPh_3)_2$ (dpm), have been prepared from $[M(NO)_2X_2]_n$ (obtained from $M(CO)_4X_2$ and NO) and dam or dpm respectively.[191] The differences between nitrosyl halide derivatives and the corresponding carbonyl halide complexes were interpreted on the basis of steric effects.

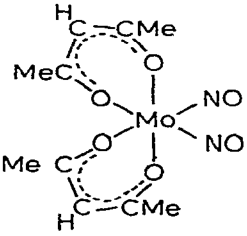
Treatment of $Mo(MeCN)_3(CO)_3$ with $NOPF_6$ in acetonitrile affords the complex cis-$[Mo(NO)_2(MeCN)_4]^{+2}[PF_6]^-_2$, whereas, the corresponding tungsten complex affords cis-$[W(NO)_2(CO)(MeCN)_3]^{+2}[PF_6]^-_2$ (LXIV A and B).[192] Reactions of these derivatives with sodium diethyldithiocarbamate gave the known complexes cis-$[M(NO)_2(S_2CNEt_2)_2]$ (M = Mo or W), whereas, reaction with acetylacetone-Na_2CO_3 gave the new compounds cis-$[M(NO)_2(acac)_2]$ (M = Mo or W) (LXV).



LXIV A



LXIV B



LXV

Nitrosylchloride adds to $(CO)_3M(CH_3CN)_3$ (M = Mo or W) in THF in the presence of Lewis base to give non-ionic compounds of the type $M(CO)_2(NO)(L)Cl$ where L is a bidentate ligand such as diphos, bipyridyl, or phenanthroline.[193] Further reaction of $W(CO)_2(NO)(bipy)Cl$ with NOCl gives $W(NO)_2Cl_2(bipy)$. NOCl was also observed to react with $M_2(CO)_8Cl_4$ (M = Mo or W) at -40° to yield the green-black complexes $[M(NO)_2Cl_2]_m$ and $[M(NO)Cl_3]_n$.[194] The mononitrosyl polymeric complexes react with Ph_3P, Ph_3PO, 2,2'-dipyridyl, or sodium N,N'-dialkyldithiocarbamates to yield the derivatives, $M(NO)Cl_3(Ph_3PO)_2$, $M(NO)Cl_3(dipy)$, or $M(NO)(S_2CNR_2)_3$ which have all been fully characterized. In contrast NOBr reacts with the $M_2(CO)_8Br_4$ complexes to yield only the $[M(NO)_2Br_2]_m$ complexes. Infrared spectral data on the new complexes are reported.

Organolanthanides have been used as Lewis acids towards π-$C_5H_5Cr(NO)_2Cl$ in which the lanthanide element interacts with the oxygen atom of the nitrosyl ligands to form isonitrosyl linkages.[195] Upon complex formation both NO stretching frequencies were lowered (e. g. 1818 to 1786 and 1712 to 1686 cm^{-1} for Cp_3Yb). The extent of complexation was found to be dependent upon the metal. The organolanthanides employed in this study were: $(MeCp)_3Sm$, Cp_3Er, Cp_3Yb, Cp_2YbCl and $(MeCp)_2YbCl$.

A number of new cationic nitrosyl complexes which are isoelectronic with known neutral species have been isolated.[196] Included in the series are $[W(NO)(CO)_3diphos]PF_6$, $[Mo(NO)(CO)_3diphos]PF_6$, $[Ni(NO)(PPh_3)_3]PF_6$, and $[Co(NO)_2(PPh_3)_2]PF_6$.

$Cr(NO)_4$ (T_d structure) has been synthesized by the irradiation of hydrocarbon solutions (pentane, hexadecane or benzene) of $Cr(CO)_6$ while a slow stream of NO is drawn through the solution.[197] Recarbonylation of $Cr(NO)_4$ by CO gas was not achieved in this study.

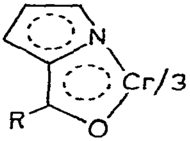
The effect of substituents on phosphorus in phosphines and phosphites contained in low spin nitrosyl complexes of Cr(I) has been studied using e.s.r. spectroscopy.[198] The phosphorus derivatives investigated were PR_3 (R = MeO, EtO, i-PrO, n-PrO, n-BuO, and EtS). Changes in substituents were found to affect the hyperfine structure of the e.s.r. spectra. This phenomena was discussed in light of the structure and bonding in these complexes.

Miscellaneous studies. Cotton and Jeremic have reported the preparation and properties of some tungsten carboxylates from $W(CO)_6$.[199] $W(CO)_6$ and benzyl alcohol were found to react in an evacuated tube at 130-5° or 185-9° to give $[W(OBz)_2]_x$. $[W(O_2CR)_2]_x$ (R = p-MeC_6H_4, C_6H_5, Pr, C_3F_7) were also prepared. $W(CO)_6$ was also found to react with a $HOAc$-Ac_2O mixture in an evacuated tube at 150-5° to give $W_3(OAc)_9O$. The complexes were characterized by their i.r. and nmr spectra.

$Mo(CO)_6$ has been observed to react with $PhCSCH_2COPh$ (HL) and the disulfide derivative of HL in refluxing anhydrous pyridine to give MoL_4.[200]

The reaction of EtO_2CCN (CFE) with carbonyl derivatives of Mo, W, Mn, and Fe gives complexes in which the C:N linkage is coordinated laterally with the metal.[201] $Mo(CO)_6$ in refluxing heptane solution with a slight excess of CFE results in liberation of 6 moles of CO and precipitation of $[Mo(CFE)_3]_n$. Other complexes which were formed similarly include; $Mo(CFE)_3$, $W(CFE)_3$, $W(CO)_3(CFE)_3$ among others of Mn and Fe.

Cr(III) chelates of 2-acylpyrroles have been prepared from $Cr(CO)_6$ and $RCOC_4H_3NH$ ($R = H, CH_3, C_6H_5$). U.v., i.r., and mass spectral data were interpreted in terms of a structure in which both pyrrolato N and the oxygen carbonyl group are complexed to the metal to form a 5-membered chelate ring (LXVI).[202]



LXVI

(R = H, Me, Ph)

The thermodynamic analysis of the decomposition of $W(CO)_6$ has been carried out.[203] In order to prepare pure W coatings, films or powders, temperatures > 900°K and pressures < 1 torr were necessary to avoid carbide and oxide formation.

The ΔH°_f for $Cr(CO)_6$ and $Mo(CO)_6$ have been determined to be -223.5 ± 3 and -229.5 ± 3 kcal/mole respectively via high temperature microcalorimetry studies.[204] The ΔH°_f values were not corrected for thermal effects due to CO adsorption on metal surfaces. In addition, the behavior of the Group VIB hexacarbonyls under polythermal conditions have been studied and the order of thermal stability was found to be $Cr(CO)_6 < Mo(CO)_6 < W(CO)_6$.[205]

$B_3N_3Me_6$-$M(CO)_6$ (M = Cr, Mo, W) systems have been studied by differential thermal analysis.[206] Compounds of the composition $3B_3N_3Me_6$-$M(CO)_6$ (m.p. 121, 120, 124° for Cr, Mo, and W respectively) were found in the system.

Tensimetric studies in binary systems of $M(CO)_6$ (M = Cr, Mo, W) with $Ni(CO)_4$ have been carried out.[207] The vapor pressures of $Ni(CO)_4$ mixtures in the presence of the solid carbonyls were determined experimentally and calculated by the graphic relation, $\log P = f\ (1/T°K)$ in which the temperature T was increased in small intervals from 1.70 to 43.96°.

A gas generator that could be restored after the bed had cooled to ∽ room temperature was achieved by contacting a hydrazine or methylhydrazine monopropellant with a mixture of an oxidizer (HIO_3, $KMnO_4$ or I_2O_5) and a metal carbonyl (e. g. $Cr(CO)_6$) on an inert support to simultaneously ignite and combust the propellant.[208]

The production of $Cr(CO)_6$ electrolytically using Cr(III) complexes at moderate CO pressures (80 - 180 atm) has been studied.[209] Yields up to 85 % of $Cr(CO)_6$ can be obtained by carbonylation of $CrCl_3(py)_3$ in pyridine at 85° and 60 atm of CO pressure.

Bombardment of $Cr(CO)_6$ with 4 keV $^{56}Mn^+$ ions has led to the formation of $-Mn(CO)_5$ and $-Mn(CO)_4$ in small yields (< 1 %).[210]

Kinetics and catalysis. Dobson and Rettenmaier have examined the kinetics of the reactions of $(P\text{-}en)Mo(CO)_4$

(P-en = ethylenediphosphine, $H_2PC_2H_4PH_2$) with phosphines and phosphites(L) in mesitylene at 108 - 135°.[211] Three competing mechanisms were proposed for these substitution processes which are dependent upon the particular Lewis base employed. These were: (a) rate-determining dissociation of CO; (b) nucleophilic attack of L on (P-en)$Mo(CO)_4$; and (c) reversible dissociation of one end of the P-en ligand, followed by attack of L on the resulting five-coordinate intermediate. When L = $P(OC_6H_5)_3$ mechanisms (a) and (c) were operative, whereas, $P(OC_2H_5)$ and $P(\underline{n}\text{-}C_4H_9)_3$ were observed to react principally <u>via</u> paths (c) and (b) respectively. The rate of reaction <u>via</u> path (b) was examined in terms of the nature of the interaction in the activated complex for these processes. Further discussions of the ligand-dependent mechanism (b) in terms of electrophilic attack of the incoming ligand (L) at the metal site in substitution reactions of this type have been put forth by Dobson.[212]

Oxidative elimination reactions of (5-X-phen)$Mo(CO)_4$ complexes (X = H, CH_3, Cl, and NO_2) with $HgCl_2$ in acetone to give (X-phen)$Mo(CO)_3(Cl)HgCl$ have been investigated employing stopped-flow techniques.[213] The kinetic data determined support a mechanism as shown in eqns. 24 - 26. The rate con-

$$(5\text{-X-phen})Mo(CO)_4 + HgCl_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (5\text{-X-phen})Mo(CO)_4\cdot HgCl_2 \tag{24}$$

$$(5\text{-X-phen})Mo(CO)_4\cdot HgCl_2 + HgCl_2 \xrightarrow{k_2} (5\text{-X-phen})Mo(CO)_4\cdot 2HgCl_2 \tag{25}$$

$$(5\text{-X-phen})Mo(CO)_4\cdot 2HgCl_2 \xrightarrow{\text{fast}} (5\text{-X-phen})Mo(CO)_3\text{-}(Cl)HgCl + CO + HgCl_2 \tag{26}$$

stants, k_1, were observed to increase as the charge-releasing abilities of the X-substituents increased. This trend is opposite to that observed for reactions of (X-phen)$Mo(CO)_4$ complexes with $P(OCH_2)_3CCH_3$.[214] These latter reactions are therefore suggested to proceed with some interaction of the filled metallic d_π orbitals with the vacant d_π orbitals on phosphorus (i. e. the $P(OCH_2)_3CCH_3$ ligand is behaving more as an electrophilic than as a nucleophilic reagent).

The kinetics of the thermal decomposition reactions of $M(CO)_5$amine compounds (where M = Cr, Mo, and W) to form $M(CO)_6$ products have been investigated for a variety of amines.[215] The rate of reaction was shown to follow the first-order rate law: rate = $k_1[M(CO)_5\text{amine}]$. The rate constant k_1, for a particular metal, was found to decrease as the pKa of the amine increased. This is consistent with the proposed dissociative mechanism which involves the cleavage of the metal-nitrogen bond in the rate-determining step. Compounds containing unsaturated amines, such as pyridines, were observed to be more stable than their pKa values would indicate. This was interpreted as resulting from a small amount of metal-nitrogen "back-bonding". No correlation was observed between the nature of the metal-nitrogen bond, as indicated by the rate constant (k_1) or pKa for the amine group, and the calculated CO stretching force constants.

The kinetics of the reaction of acetonitrile with Group VIB metal hexacarbonyls to form <u>cis</u>-$M(CO)_3(CH_3CN)_3$ has been studied.[216] The rate law observed for M = Cr and Mo was: rate = $k_1[M(CO)_6] + k_2[M(CO)_6][CH_3CN]$. The reaction was shown by infrared spectral changes to occur <u>via</u> a stepwise process (eqns. 27 - 29), where $k_b \gg k_a$ and $k_c > k_a$. Similar conclusions appear to hold for $W(CO)_6$.

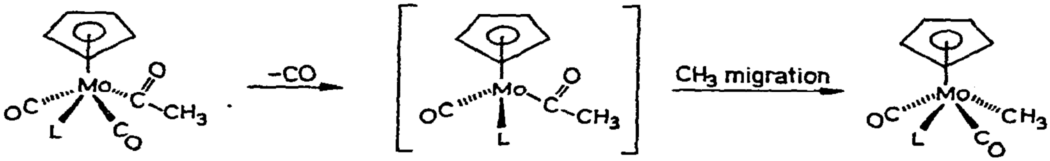
$$M(CO)_6 + CH_3CN \xrightarrow{k_a} M(CO)_5(CH_3CN) + CO \qquad (27)$$

$$M(CO)_5(CH_3CN) + CH_3CN \xrightarrow{k_b} M(CO)_4(CH_3CN)_2 + CO \qquad (28)$$

$$M(CO)_4(CH_3CN)_2 + CH_3CN \xrightarrow{k_c} M(CO)_3(CH_3CN)_3 + CO \qquad (29)$$

Paxson and Dobson have investigated the kinetics of the reaction of methyllithium with Group VIB carbonyls by stopped-flow techniques.[217] The complexes studied included $M(CO)_6$ (M = Cr, Mo, W) and $LW(CO)_5$ (L = Ph_3P, Ph_3As, and $(PhO)_3P$). The rate expression observed was: rate = k[substrate]-$[CH_3Li]^{1/4}$. The rates for the hexacarbonyls varied W > Mo > Cr and for $W(CO)_5L$, CO ≫ $P(OPh)_3$ > $AsPh_3$ > PPh_3. The rates for the hexacarbonyls were approximately two orders of magnitude greater than those for $W(CO)_5L$.

Decarbonylation of $\underline{h}^5$-$C_5H_5Mo(CO)_2(L)COCH_3$ is first order in acetyl complex concentration and unaffected by ligand concentration or $\underline{h}^5$-$C_5H_5Mo(CO)_3Me$ thus suggesting the mechanism in eq. 30.[218]



(30)

The reaction is found to depend on steric factors with rates decreasing in the order $P(\underline{c}\text{-}C_6H_{11})_3 > PPh_2(\underline{i}\text{-}C_3H_7) > PPh_3 > PPh_2Me > P(\underline{n}\text{-}Bu)_3 > PPhMe_2$, as well as electronic factors as is demonstrated by the series $PPh_3 > P(\underline{p}\text{-}MeC_6H_4)_3 > P(\underline{p}\text{-}OMeC_6H_4)_3$. Values of K_{eq} for eq. 31 exhibit the same ligand dependence as k_{decarb}.

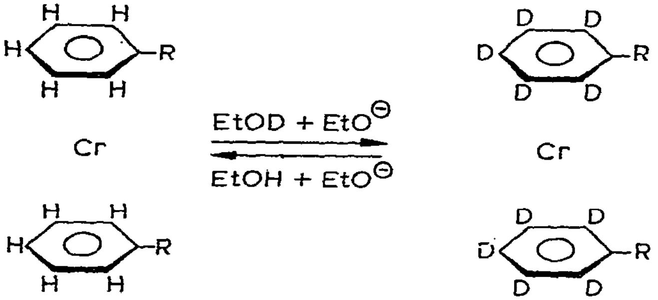
$$\underline{h}^5\text{-}C_5H_5Mo(CO)_2(L)COCH_3 \rightleftarrows \underline{h}^5\text{-}C_5H_5Mo(CO)_3CH_3 + L \qquad (31)$$

The very interesting olefin complex, tungstenpentacarbonylsemibullvalene has been synthesized by Moriarty and co-workers.[219] Low temperature nmr studies indicate the activation energy for the Cope rearrangement of semibullvalene bound to $W(CO)_5$ to be 12 ± 1 kcal/mole. The $\Delta F^{\ddagger}$ for semibullvalene itself has not been experimentally measured but is calculated to be 3.6 kcal/moles by the MINDO/2 method.

The $Cr(CO)_3$ moiety is found to strongly enhance the rate of HY elimination from $\underline{p}\text{-}X\text{-}C_6H_4CH_2CH_2Y$, X = Br or OTs, over that of the uncomplexed form.[220] The $\underline{p}\text{-}NO_2$ uncomplexed compounds however eliminate much more readily than the $Cr(CO)_3$ derivatives. The increase in rate of the $\underline{p}\text{-}NO_2$ derivatives are shown to be due to a lower $\Delta H^{\ddagger}$ while the increase in rate of the $Cr(CO)_3$ derivatives are due to a less negative $\Delta S^{\ddagger}$, $\Delta H^{\ddagger}$ being very similar to that of the unsubstituted compounds.

Kursanov and co-workers[221] have shown that hydrogen atoms will readily undergo isotopic exchange under conditions of protophilic substitution in the presence of bases (eq. 32).

The first-order rate constant for $(C_6H_6)_2Cr$ was found to be $8.35\ (\pm\ 0.14) \times 10^{-5}\ sec^{-1}$ at 45°. When R = Me and Et,



(R = H, Me, Et) (32)

both π-aromatic ring hydrogens and side chain hydrogen entered into exchange reactions. Under the conditions employed in this study the aromatic hydrocarbons do not undergo exchange reactions of this type. The $[Ar_2Cr]^+I^-$ species were found to also exchange hydrogens under even milder conditions than neutral species.

Organometallic molybdenum and tungsten compounds have been used as catalyst for the stereospecific polymerization and copolymerization of unsaturated hydrocarbons.[222] The complexes used especially for the preparation of polybutadiene were of the general structure $[(H_{3-n}X_n)CCO_2M(CO)_m(R)_p(L)_q]_r$ (where X = halogen, containing at least one F, n = 1, 2, or 3; M = Mo or W; R = H or alkyl, alkenyl, etc.; L = Lewis base, containing at least 1 ether and/or alcohol and/or ketone group; m = 1, 2, 3, or 4; p and q = 1 or 2 and r = 1 or 2).

Organometallic catalysts containing metal-metal bonds, $R_2Al\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ (R = Me, Et, i-Bu; M = Mo, W) or their complexes with dioxane, PPh_3 or Et_3N, which are useful for hydrogenation, dimerization, polymerization and oxo type reactions have been prepared from the Group VIB transition metal complexes and organoaluminum compounds.[223] For example, 2 mmoles of i-Bu_2AlH and 2 mmoles of $HMo(CO)_3(\pi\text{-}C_5H_5)$ react in C_6H_6 to give i-$Bu_2Al\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ which polymerized propylene at 80°.

The reactions of methyl trichloroacetate with olefins were found to be catalyzed by metal carbonyl derivatives.[224] The $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ complex was observed to be an active catalyst for this process.

Metal-metal bond complexes have been investigated and found to be useful as liquid-phase olefin disproportionation catalysts operating at ambient temperatures.[225] These include $A_n^+[(CO)_5M\text{-}M'(CO)_5]^{n-}$ with $MeAlCl_2$ as activator and Bu_4NCl as cocatalyst for M-M' = Mo-Mo with n = 2 and A = Bu_4N or Na; W-W with n = 2 and A = Bu_4N; Mo-Re with n = 1 and A = Na or Et_4N; and Mo-Mn with n = 1 and A = Bu_4N. Mo-Mo system showed the highest catalytic activity.

$[(\pi\text{-}C_5H_5)Mo(\pi\text{-}C_3H_5)Cl]_2$ in the presence of $EtAlCl_2$ has been shown to be an effective catalyst for the conversion of mono-olefins into diene complexes and paraffins.[226]

Transalkylation of aromatic hydrocarbons by a metathesis catalyst ($WCl_6\text{-}C_2H_5AlCl_2$) has been studied by Hocks and coworkers.[227] Whereas $AlCl_2(C_2H_5)$ gives mixtures of mono-, di- and higher alkylated products, $WCl_6/AlCl_2(C_2H_5)$ promotes formation of mono-alkylated derivatives. When mixtures of mono- and polyalkylated benzenes were treated with $WCl_6/AlCl_2(C_2H_5)$, the di- and polyalkylated products disappeared to give exclusively mono-alkylated products.

Supporting evidence for a metallocyclic intermediate in the tungsten-catalysed olefin metathesis reaction is based on the reaction of 1,4-dilithiobutane or 1,4-dilithio-2,3-dideuteriobutane with WCl_6 in benzene.[228] Production of ethylene occurred immediately upon mixing either of the dilithio reagents with WCl_6. Furthermore, 12 % of the ethylene obtained from the deuterated reagent resulted from a rearranged intermediate, i. e., 88 % was D_1 ethylene, 6 % D_0 and 6 % D_2.

Organolithium reduced tungsten hexachloride reagents have been very effective for deoxygenation of aldehydes, ketones, and epoxides yielding olefins.[229] While a mixture of WCl_6-BuMgI has been found to be an active homogeneous catalyst for converting hept-2-ene into butene and dec-5-ene into benzene at room temperature.[230] The catalytic activity was effectively destroyed by the addition of ether or THF.

The hydridic reagents $LiAlH_4$ and $NaBH_4$ have been found to form active catalysts for metathesis of olefins with WCl_6 and comparable in activity with those derived from alkyllithium or Grignard reagents.[231] For example, pent-2-ene was converted into its equilibrium mixture of but-2-ene in hex-2-ene in less than 3 hours employing WCl_6 and an excess of $LiAlH_4$ (W : olefin = 1 : 100).

Metathesis reactions of methyl oleate and methyl elaidate with $WCl_6/(CH_3)_4Sn$ under mild conditions were found to give as products octadec-9-ene and the dimethyl ester of octadec-9-enedioic acid.[232] Other metathesis reaction observations, primarily of the high ratio of C_4 to C_2 found in the metathesis of propylene on $Mo(CO)_6/Al_2O_3$ catalyst, have led workers to suggest the possibility of π-allylic complex formation and/or metal methylene intermediates as was formerly proposed by Pettit.[233] (G. S. Lewandos and R. Pettit, Tetrahedron Lett., 789 (1971)).

A new synthesis of olefins by the reductive deoxygenation of vicinal dialkoxyalkanes with W^{IV} halide derivatives has been reported.[234]

Activities of the commercial cobalt molybdate catalyst for disproportionation of propene have been observed to parallel the activities of this catalyst for converting diazomethane into N_2 and ethylene.[235] These results suggest that the sites on molybdate catalysts which disproportionate olefins also selectively convert adsorbed methylenes into ethylene.

1,5-Octadiene and 1,6-octadiene have been prepared by selective hydrogenation of 1,3,7-octatriene over a chromium carbonyl catalyst, (methylbenzoate)chromium tricarbonyl.[236]

$Mo(CO)_6$ has been employed as a catalyst for the preparation of amine oxides from tertiary amines by treatment with ozonides.[237] For example, pyridine in pentane was treated with 3-methyl-5-ethyl-1,2,4-trioxolane and $Mo(CO)_6$ to give 50 % pyridine 1-oxide. Triethylamine oxide and C_{10}-C_{14}-alkyldimethylamine oxides were also prepared.

A patent for the hydroformylation of 1-hexene with $M(CO)_5PBu_3$ (M = Cr, Mo, W) as a catalyst and $HCo(CO)_4$ as a cocatalyst has been obtained which gives conversion to linear alcohols and aldehydes.[238]

The kinetics and mechanism of the disproportionation of 2-pentene to C_4H_8 and C_6H_{12} in the presence of $W(CO)_5$-PPh_3 and alkylaluminum has been investigated.[239]

A patent has been obtained for the use of (1,5-cyclooctadiene)tungsten tetracarbonyl as a catalyst for the isomerization of alkenes.[240]

A variety of metal halide complexes, including MCl_6 (M = Mo, W), have been shown to rapidly catalyze at room temperature exchange of the aromatic hydrogens between two molecules such as perdeuteriobenzene and toluene.[241]

The chemistry of initiation reactions between $Mo(CO)_6$ and CCl_4 in methyl methacrylate and $Mo(CO)_6$ and CBr_4 in ethyl acetate have been studied by e.s.r.[242]

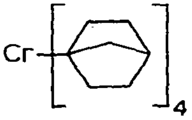
Carbene metal complexes of the types, $R(R')C{:}M(CO)_5$ (M = W, Mo; R = EtO, MeO; R' = Me, Ph) or $Cl_2(Ph_3P)Pd{:}C(OMe)$-NHPh, and a Lewis acid (e. g. $EtAlCl_2$ or $AlCl_3$) have been found to be useful compounds for polymerization, disproportionation or tetramerization of olefins.[243]

Catalysts for the polymerization of cycloalkenes have been based on transition metal π-allyl complexes, e. g. tetrakis(π-crotyl)W.[244] Polymerization by either ring or double bonding opening were found to be dependent on the nature of the transition metal and number and type of ligands. For example, Mo and W catalysts were found to suppress double bond opening, while Zr and Cr catalysts allowed both types of polymerization to occurr. In addition, the polymerization kinetics of 1,1,3,3-tetramethyl-1,3-disilacyclobutane catalyzed by di-π-crotyldichlorodinickel has been studied, as well as the activity of other π-complexes of Ni and Cr.[245] Tri-π-crotylchromium was found to be inactive.

Polymers for general use in the rubber industry have been prepared using organometallic compounds of Group IA, II, IIIA and π-allyl complexes of tungsten or molybdenum as a catalyst mixture.[246]

Tetraallyldichromium has been used as a catalyst for the polymerization of ethylene.[247]

The tetrakis(bicycloheptyl)Cr complex (LXVII) has been used as a catalyst for polymerization of 1-olefins.[248] Tetrakis(1-camphyl)Cr was also employed as a catalyst in place of LXVII.



LXVII

A mixture of a turpentine solution of chromium octanoate, Et_3Al in benzene when heated under argon for 1 hr at 60° and then shaken for 10 hrs at 60° with epichlorohydrin produces poly(epichlorohydrin).[249]

Polybutadiene of controlled molecular weight and vinyl configuration have been prepared in the presence of hydrogen and catalysts containing chromium phosphine complexes, tributylaluminium and HCO_2H, H_3PO_4 or water.[250]

The molecular weight distribution and impact resistance of polyethylene prepared with an oxide-supported bis(cyclopentadienyl)chromium(II) catalyst were found to be increased when the catalyst was pretreated with an ether or disiloxane.[251]

Polyalkenamer graft copolymers have been prepared by the ring opening polymerization of a cycloolefin on a diene polymer in the presence of a catalyst containing a W, Ta, or Mo halide and an aluminum alkyl derivative.[252]

Vinyl compounds have been polymerized by interaction with a transition metal carbonyl ($Cr(CO)_6$) and an activator containing covalently bound halogen (CCl_4).[253] The molecular weight of the polymer obtained could be controlled by the proportion of activator.

Tetra-tert-butylchromium or tetraneopentylchromium, organic aluminum compounds, and light or triethylborane were employed as a polymerization catalyst in the preparation of polyethylene and polypropylene.[254]

Cyclopentene was polymerized in the liquid phase over 1 - 100 hrs at -50 - 150° in the presence of an oxygen-containing Mo or W halide, an organic Group I, II, or IIIA metal halide and a C_{1-30}amine ternary catalyst.[255]

Linear polymers of alicyclic polyolefins (e. g. poly-trans, trans, cis-1,5,9-cyclododecatriene) which are useful as rubber compounds have been prepared by polymerization without induction periods in organic solvents over the catalyst tetra-π-crotyl-tungsten and aluminum bromide.[256]

Elastomeric copolymers of cyclic monoolefins and cyclic polyolefins have been prepared by polymerization of a C_{5-10} cyclic monoolefin with a non-conjugated cyclic polyene or ω-alkenyl cycloolefin in the presence of an alkylaluminum halide and a Group VIB metal compound.[257] Thus polymerization of a mixture of cyclopentene, cyclopentadiene, molybdenum trichloride dilaurate, $Al(Et)_2Cl$, and PhMe for 4 hrs at 5° gave 47 % cyclopentadiene-cyclopentene copolymer.

Spectroscopy and Theory

Vibrational and electronic spectra. Brown and Dobson have observed the infrared spectra of a large variety of

$LM(CO)_5$ (L = Lewis base; M = Cr, Mo, W) compounds in the regions 2100 - 1800 and 700 - 300 cm^{-1}.[258] These workers found that the $\nu(MC)$ vibration were lowest for the "hard" bases (oxygen and nitrogen) and highest for the "soft" bases (phosphorus, arsenic, antimony and bismuth) with sulfur being intermediate between these two extremes. Although the above results are contrary to inferences made employing $\nu(CO)$, i. e. lower $\nu(CO)$ results infer higher $\nu(MC)$, within a series of derivatives of ligands containing the same donor atom however, the "reciprocal relationship" between $\nu(CO)$ and $\nu(MC)$ was observed. These results were discussed with respect to reactivity via rate-determining dissociation of CO and current bonding theories. These workers have also observed the M-C stretching vibrations in CH_2Cl_2 solution in cis-$M(CO)_4$(bidentate) complexes (M = Cr, Mo, W; bidentate = bidentate chelating through N, P, As, or S donor atoms).[259] The positions of the bands were considered with respect to observed reactivities of cis-(bidentate)$M(CO)_4$ complexes via a path involving rate determining dissociation of CO and with respect to positions of other assigned M-C stretches in $M(CO)_5L$ and trans-$M(CO)_4L_2$ complexes. The B_1 $\nu(M-C)$ mode for a given metal was strongly dependent on the donor atoms and was observed to decrease along the series $P \sim As > N$.

The carbonyl stretching spectra of a large number of cis-$L_2M(CO)_4$ complexes (L_2 = bidentate chelating ligand bonding through N, P, As or S donor atoms; M = Cr, Mo, W) have been observed.[260] The two carbonyl stretching force constants (k_1 and k_2) and the three CO-CO interaction constants were determined from the four observable $\nu(CO)$ using an iterative procedure which a priori assumed no relationship between the interaction constants. The results were shown to be in good agreement with force constants calculated employing ^{13}CO enrichment data. An approach was presented to separate the σ-donor and π-acceptor properties of the substituted chelating ligands which related charges in the CO stretching force constants to the direct ligand (N, P, As, S) interaction with the π^* orbitals of the adjacent CO groups and the metal-to-CO π bonding.

CO stretching frequencies and force constants for the complexes $(CO)_5WP(C_6H_5)_2CH_2CH_2P(C_6H_5)_2$, $(CO)_5WP(C_6H_5)_2CH_2$-$P(C_6H_5)_2$, $[(CO)_5WP(C_6H_5)_2CH_2CH_2P^+(C_6H_5)_2CH_2C_6H_5][PF_6^-]$, and $[(CO)_5WP(C_6H_5)_2CH_2P^+(C_6H_5)_2CH_3][I^-]$ have been determined in order to test the effect of a positive charge on a non metal-bound phosphorus atom on ν_{CO} and F_{CO}.[261] The ν_{CO} or F_{CO} values (Cotton-Kraihanzel) obtained in these complexes were all very similar indicating little, if any, effect of the remote positive charge on ν_{CO} or F_{CO}.

I.r., nmr and mass spectral data are reported for the phosphorus coordinated $(R_2NPPh_2)Mo(CO)_5$ (R = Et, Pr, Bu) and cis- and trans-$(R_2NPPh_2)_2Mo(CO)_4$ (R = Me, Et, Pr, Bu).[262] CO stretching frequencies of these new complexes are substantially the same as analogous PPh_3 complexes, indicating the P to be little affected by bonding to N.

Metal-metal stretching frequencies have been reported for the complexes trans-$PtL_2[Mo(CO)_3(\pi-C_5H_5)]$ (L = py and 3-Mepy), trans-$Pdpy_2[Mo(CO)_3(\pi-C_5H_5)]_2$ and trans-$Ptpy_2Cl$-$[Mo(CO)_3(\pi-C_5H_5)]$.[263] The asymmetric metal-metal vibrations were observed to occur between 144 - 134 cm^{-1}. Force constants for the metal-metal bond were estimated on the basis of a linear triatomic model and were compared with the corresponding force constant in $Hg[Mo(CO)_3(\pi\text{-}C_5H_5)]_2$.

Further experiments investigating the nature of $Cr(CO)_5$, the coordinately unsaturated intermediate photochemically produced in solid matrices, have been carried out.[264] Photolysis of $Cr(CO)_6$ in methane at 20°K produces a species with u.v.-vis bands at 237 nm (the same as in Ar at 20°K) and at 492 nm (542 nm in Ar and approximately the same as in hydrocarbon glasses at 77°K). Turner, et al., suggest the discrepancy of the latter bands is due to the presence of C_{4v} $Cr(CO)_5S$ (S = methane or in other experiments, hydrocarbon solvent). Weak bands formerly assigned to small concentrations of D_{3h} $M(CO)_5$ structures are found to be dilution dependent and thought to be due to polymer formation of $M(CO)_5$ and $M(CO)_6$.

Breeze and Turner have presented infrared spectroscopic evidence for the presence of $Cr(CO)_5^-$ anion obtained by cocondensation at 20°K of sodium atoms with $Cr(CO)_6$ in an argon matrix.[265] The observed band pattern (1855 (E mode) and 1838 cm^{-1} ($A_1^{(1)}$ mode)) are believed to be consistent with a C_{4v} $Cr(CO)_5^-$ structure although the low intensity high frequency $A_1^{(2)}$ band was not observed. Only small frequency shifts were noted (~ 2 cm^{-1}) in changing the alkali metal from sodium to potassium. Similar results were obtained for cocondensation of sodium and $W(CO)_6/Ar$.

Darling and Ogden have discussed a general method for characterizing simple binary carbonyls produced under matrix isolation techniques by i.r. spectroscopy.[266] In particular it was shown that when $C^{16}O$ and $C^{18}O$ are used in the synthesis of carbonyl compounds, the species $M(CO)$, $M(CO)_2$, $M(CO)_3$ (D_3h), $M(CO)_4$ (D_{4h} or T_d) and $M(CO)_6$ (O_h) would each give rise to a characteristic frequency and intensity patterns. The appropriate Cotton-Kraihanzel force constants were determined for these species.

A linear correlation was established between the ν_{N_2} and the absolute infrared intensity of the dinitrogen ligand in isoelectronic transition metal compounds.[267] The complexes involved in this study include Os(II), Re(I) and W(0) dinitrogen species. The infrared intensities were shown to increase as the nuclear charge decreased with a concomitant decrease in the N_2 stretching frequencies.

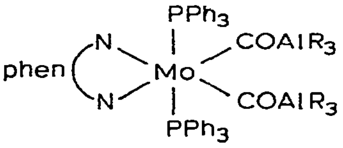
Kettle and co-workers[268] have applied a Wolkenstein bond polarizability approach (relates molecular properties to bond properties) to Raman intensities of the terminal CO stretching vibrations in metal carbonyl complexes, including $M(CO)_6$ (M = Cr, Mo, W) and arene$Cr(CO)_3$. The reversal of intensity of the totally symmetric and non-totally symmetric modes in the Raman effect, the latter being more intense, was presumed to be associated with the M-C-O bonding.

The diamagnetic, nonelectrolytic complexes $M(CN)_4(CNR)_4$ (M = Mo, W; R = Me, Et, n-Pr, i-Pr, t-Bu, or CPh_3) gave remarkably simple infrared spectra which consisted of a single band attributable to C-N stretching and a more intense band at higher frequency assigned to the C-NR stretching modes.[269] On the basis of x-ray data for $Mo(CN)_4(CNMe)_4$, all the complexes were presumed to have dodecahedral configurations.

A complete set of symmetry coordinates based on conventional valence coordinates of a C_{3v} model of $(C_6H_6)Cr(CO)_3$ has been presented by Brunvoll and co-workers.[270] Another set of symmetry coordinates are described which preserves the identity of the benzene ligand. This set of symmetry coordinates were then used in a normal coordinate analysis of $(C_6H_6)Cr(CO)_3$.[271]

The Raman spectrum of $(C_6H_6)Cr(CO)_3$ in both the solid state and in solution (CS_2 and C_6H_6) has been reported.[272] The vibrational spectra of $(C_6D_6)Cr(CO)_3$ and $(C_6H_6)Cr(CO)_3$ (infrared and Raman) have also been recorded at low temperature by Hyams and Lippincott.[273]

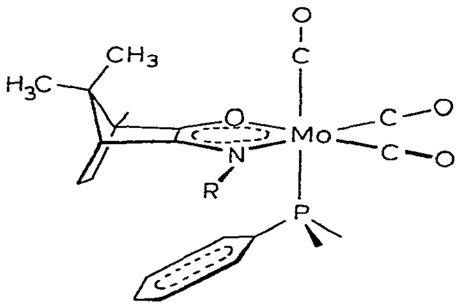
Shriver and Alich[274] have observed that $Mo(L\text{-}L)[P(C_6H_5)_3]_2(CO)_2$ (L-L = phen, and 5-6-dimethylphen) and $Mo(phen)_2(CO)_2$ interact with 2 moles of trialkylaluminum to form complexes containing Mo-CO-Al bridges (LXVIII). The assigned $Mo(CO)_2 \rightarrow$ phen charge-transfer transition was found to undergo a large blue shift upon adduct formation. Changes in this transitional energy upon adduct formation were discussed in terms of a molecular orbital treatment. It was concluded that these blue shifts were due to an increase in Mo-CO π backbonding upon adduct formation. These shifts were employed to infer the electron-pair acceptor strength: $Al(C_2H_5)_3 > Al(\underline{i}\text{-}C_4H_9)_3 > Ga(CH_3)_3$.



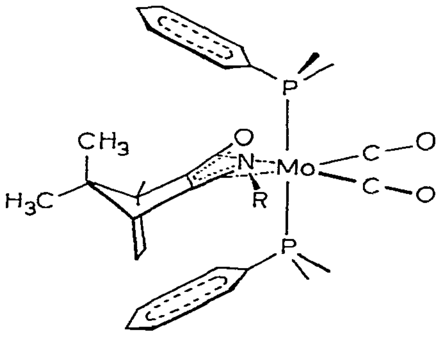
LXVIII

The emission lifetimes of tungsten carbonyl complexes of the type $W(CO)_5X$, where X is a Lewis base containing nitrogen or oxygen donor atoms, have been investigated by Wrighton, Hammond and Gray.[275]

Stable complexes of molybdenum carbonyls and substituted carbonyl derivatives with 1,4-diheterobutadienes (DHB) such as glyoxal or biacetyl diimines and camphorquinone monoimines of the type $(DHB)Mo(CO)_4$, fac-$(DHB)(Ph_3P)Mo(CO)_3$, and cis-$(DHB)(PPh_3)_2Mo(CO)_2$ have been prepared.[276] The solvent dependence of the electronic spectra of a large variety of these complexes has provided information concerning the oxidation state of the metal and ligand, the direction of the low energy electronic transition, and the importance of π-backbonding. Irregularities in the camphorquinone derivatives were understood in term of changes in the coordination geometry as shown below (LXIX A and B). In order to further study the extent of π-backbonding in these complexes, polarographic reduction potentials of $(DHB)(PPh_3)Mo(CO)_3$ and $(DHB)(PPh_3)_2Mo(CO)_2$ have been measured and compared with that of free DHB and $(DHB)Mo(CO)_4$.[277]



LXIX A



LXIX B

The luminescence spectra of (2,2'-bipyridyl)$M(CO)_4$ (M = Cr, Mo, W) and the related methyl substituted complexes have been measured.[278] The luminescence arises from the lowest "metal-to-bipyridine" charge transfer triplet excited without dissociation of CO.

The solvent variation of the maximum absorption for intramolecular charge-transfer spectra of $M(LL)(CO)_4$ (M = Mo, W; LL = phen, bipy) in mixed solvents has also been reported.[279]

(2,2'-Bipyridyl)$M(CO)_4$ (M = Cr, Mo, W) anions, formed by reduction of (2,2'-bipyridyl)$M(CO)_4$ with sodium in THF, have been studied by electronic and e.s.r. spectroscopy.[280] These complexes were concluded to involve the coordination of a mononegative ion of bipyridine in which the electron was trapped in a π^* orbital of bipyridine.

Mass spectra. The mass spectra of metal carbonyl complexes of tris(dimethylamino)phosphine (TDP), including $(TDP)M(CO)_5$ and $(TDP)_2M(CO)_4$ (M = Cr, Mo, W) have been obtained.[281] The data reported included fragmentation patterns as well as ionization and appearance potential measurements. The average bond dissociation energies of the metal-carbonyl bond in these complexes were obtained from the ionization and appearance potential measurements.

Methane chemical ionization mass spectra of chromium, molybdenum, and tungsten hexacarbonyls have been reported by Hunt and co-workers.[282] These spectra were relatively uninformative when compared with conventional electron impact mass spectra. The M + 1 ion (M = Cr, Mo, W) was observed to be the base peak in each case and was accompanied by a relatively low abundance of M^+ (10 - 40 %) and (M + 1 - CO) (4 - 20 %) ions. Dimeric ions corresponding to $M_2(CO)_{12}H^+$ and $M_2(CO)_{11}H^+$ were also observed (< 2 %).

Hsieh has reported the mass spectra of some halomercury derivatives of transition metal carbonyls.[283] Included in this study was the report of the mass spectrum of $(\pi\text{-}C_5H_5)(CO)_3MoHgI$. The observed meta-stable transitions indicate fragmentation of the molecular ion occurs by loss of CO groups, Hg atom, halogen atom or halomercury group (HgX).

Ionization potentials of $W(CO)_5L$ (L = 2,6-dimethylpyridine, 4-methylpyridine, pyridine, and 2-cyanopyridine) and $Cr(CO)_5L$ ($L = S(CH_2)_4$, $SOMe_2$, $SO(OCH_2)_2$) and the corresponding free ligands have been measured.[284] A good linear correlation was found between the complex and ligand (L) ionization potentials. The results were discussed in terms of dative σ and π back bonding.

Substituent effects in bimolecular ion-molecule reactions (eq. 33) involving arenechromium tricarbonyls which occur in a mass spectrometer have been studied by Gilbert, Leach and Miller.[285] The composite rate constant (k') was

$$[ArCr(CO)_3]^+ + ArCr(CO)_3 \rightarrow [Ar_2Cr_2(CO)_3]^+ + 3CO \qquad (33)$$

obtained from plots of concentration of $[Ar_2Cr_2(CO)_3]^+$ vs. concentration of $\{[ArCr(CO)_3]^+\}^2$. An excellent correlation was observed by applying the Hammett treatment to these data, i. e., $\log(k'/k'_0)$ vs. σ_p values for the ring substituent yielded a straight-line with a large negative slope.

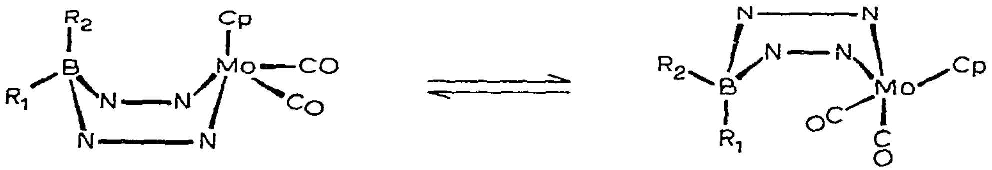
The decomposition of organometallic complexes in a mass spectrometer has been discussed by Mueller.[286] This report covers a number of general rules for decomposition of organometallic complexes upon electron impact. The classification into decomposition types which were presented and illustrated includes (1) cleavage of M-L bonds, (2) simple cleavage of bonds within the ligands, and (3) fragmentation reactions with rearrangement.

<u>Nuclear magnetic resonance, photoelectron spectra and theory</u>. Carbon-13 nuclear magnetic resonance studies have been applied to organometallic complexes. The effect of changes in the electronic environment of the sp^2 hybridized carbene carbon atom in complexes of the type $(CO)_5MCXY$ (M = Cr or W; X = OR or NR^1R^2, and Y is an organic group) have been discussed with the aid of ^{13}C nmr data.[287] Changing the nature of the heteroatom X was shown to have the most important influence on the chemical shift of the carbene carbon atom. The low-field chemical shift was thought to result from the electron-deficient character of the carbene carbon together with paramagnetic shielding and/or ΔE. The data were taken to suggest that the carbene complexes of transition metals can best be thought of as metal-stabilized carbonium ions. The ^{13}C nmr chemical shifts in $(CO)_5MC(X)Y$ (M = Cr, X = OMe, Y = Me, Ph; M = W, X = OMe, SMe, and NHMe, Y = Me) carbene complexes have also been reported.[288] ^{13}C nmr shows the carbene carbon atom to be extremely deshielded.

A discussion of the utility of ^{13}C-H satellite PMR spectral analysis as a criterion for distinguishing π- and σ-structures of metal cyclopentadienyls has been presented.[289]

Unequivocal assignment from nmr data as to π- or σ-bound cyclopentadienyl is not possible for bent sandwich structures or for compounds whose symmetry is distorted by ligand interaction or by substituents in the cyclopentadienyl ring. Among the compounds discussed are the following: π-$C_5H_5Fe(CO)_2$-σ-C_5H_5; $C_5H_5Mo(CO)_3C_2H_5$; $(C_5H_5)_2Sn$, $(C_5H_5)_2TiCl_2$ and C_5H_5Au-$P(C_6H_5)_3$.

Two new compounds containing the novel polypyrazolylborate ligand have been structurally investigated.[290] Infrared and ^{1}H nmr data are consistent with the conformational isomers A and B existing for the complexes $[HB(pz)_3](C_5H_5)$-$(CO)_2Mo$ and $[Et_2B(pz)_2](C_5H_5)(CO)_2Mo$ (eq. 34).

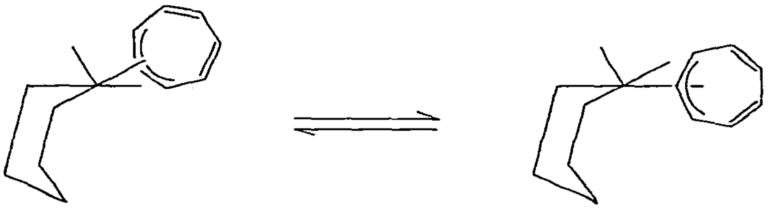


(34)

Studies on the structure of $[B(pz)_4](C_5H_5)(CO)_2Mo$ have shown that the $B(pz)_4$ ligand is bidentate, while the cyclopentadienyl ligand is pentahapto.[291] The BN_4Mo ring was shown by infrared and temperature dependent ^{1}H nmr to exist in two conformers (LXX A and B) in solution which interconvert with an activation energy of approximately 10 kcal/mole.

LXX A LXX B

Calderon, Cotton and Shaver[292,293] have studied solution structure of $[H_2B(3,5\text{-}Me_2pz)_2](C_7H_7)(CO)_2Mo$ (A) and $[Et_2B(pz)_2](C_7H_7)(CO)_2Mo$ (B) by infrared and ^{1}H nmr spectral measurement. The presence of two sites in these molecules for fluxionality can led to a variety of possible structures for these compounds. Compound A shows only one doublet in the ν(CO) region whereas compound B shows a set of 4 doublets. In compound A the BN_4Mo ring and the h^3-C_7H_7 ring do not combine their two conformations each in solution to generate a set of 4 conformers. Instead one conformer was observed to be highly favored due to a stabilized Mo...H-B interaction and restrictive motion of h^3-C_7H_7 caused by the bulkiness of the $H_2B(Me_2pz)_2$ ligand. However, A does exist as enantiomers (LXXI and LXXII) which were found to interconvert at 120° by an intramolecular motion. In compound B however four conformers were observed in solution in varying ratios.

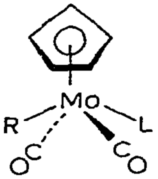


LXXI LXXII

^{183}W-^{31}P spin-spin coupling interactions in $(PX_3)W(CO)_5$ complexes have been determined for X = Cl, Br and I.[284] A good correlation between J(W-P) and the electronegativity of the X atom bound to phosphorus was observed which differed from the correlation between J(W-P) and aryl- and alkyl-phosphines and phosphite substituents electronegativities.

Tungsten-183-phosphorus-31 coupling constants have also been measured in order to determine the effect of a positive charge on a trivalent phosphorus ligand.[295] This data would suggest that the $-CH_2CH_2P^+(\underline{n}\text{-Bu})Ph_2$ group is only slightly more electronegative than the $-CH_2CH_2PPh_2$ group in compounds of the type $(OC)_5WPPh_2CH_2CH_2PPh_2$ and its n-Bu cationic derivative. W-P coupling through three bonds is observed in the former complex, however such coupling is eliminated in its n-Bu cationic derivative.

NMR spectroscopy has been employed to demonstrate that the acyl complexes, $RCOMo(CO)_2[C_6H_5P(CH_3)_2](\pi\text{-}C_5H_5)$ (R = CH_3 and C_2H_5), exist in solution exclusively in the trans form (LXXIII).[296] The lack of interconversion between cis and trans acyl complexes as compared with the cis-trans interconversion of alkyl derivatives was taken to further substantiate bond breaking of the alkyl-metal bond in this isomerization process.



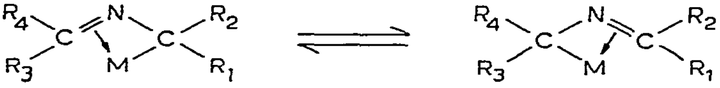
LXXIII

The temperature-dependent ^1H nmr of $\pi\text{-}C_5H_5Cr(CO)(NO)(C_2H_2)$ has been shown to indicate intramolecular rotation of the π-bonded acetylene ligand in solution.[297] While the acetylene ligand appears to assume a favored rotameric position in the complex at low temperature (-50°), at room temperature rotation about the metal-C_2H_2 bond takes place. The free energy of activation ($\Delta G^{\neq}$) for the rotation of acetylene was found to be slightly solvent dependent, ranging from 13.8 kcal/mole in hexane to 12.1 kcal/mole in tetradeuterofuran.

Temperature-dependent ^{1}H nmr for π-allylmolybdenum pyrazolylborates of the type $R_1B(pz)_3Mo(CO)_2$-π-$CH_2C(R_2)CH_2$ have been quantitatively analysed according to an intramolecular fluxional model.[298] The equilibration of the pyrazolyl protons is attributed to a rotation of the tridentate ligand about a Mo-B axis, a process analogous to the Bailar twist. Activation parameters for the process were calculated.

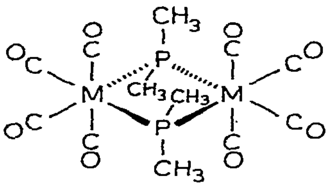
The isonitrile complex $[(h^5\text{-}C_5H_5)Mo(CO)_3\text{-}Mo(CO)_2\text{-}(CNCH_3)(h^5\text{-}C_5H_5)]$ exhibits a single C_5H_5 and a single CH_3 ^{1}H nmr resonance at +60°.[299] Upon cooling to -43° both resonances are resolved. Rapid isomerization of the isonitrile ligand at the higher temperature is believed to occur via an isonitrile bridging group.

Variable-temperature ^{1}H nmr studies of the complexes $[(\pi\text{-}C_5H_5)M(CO)_2\{(p\text{-tolyl})_2CNC(p\text{-tolyl})_2\}]$ (M = Mo or W) have shown the molecules to be fluxional.[300] Further nmr studies on $[(\pi\text{-}C_5H_5)M(CO)_2\{(p\text{-}CF_3C_6H_4)_2CNC(p\text{-}CF_3C_6H_4)_2\}]$ (M = Mo, W) gave values for the energy of activation of 11.6 and 6.8 kcal respectively for this process (eq. 35).

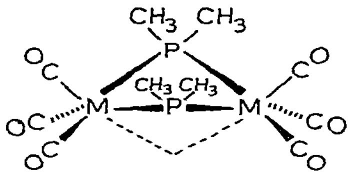


(35)

Dessy and co-workers report nmr studies of neutral bi-µ-phosphido-dimetallic species of types LXXIV and LXXV and their electrochemically reduced dianions.[301] Arguments for an increase of the M-P-M bond angle and a concurrent decrease of the C-P-C bond angle upon reduction to the dianion are presented. Activation parameters for the conformationally fluxional iron containing neutral and dianion systems have also been determined.

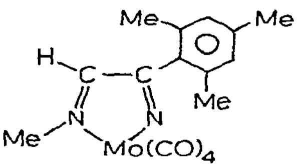


LXXIV (M=Cr,Mo,W)



LXXV (M=Fe,Ru)

The mesityl group has been used as a probe for ring current in transition metal 1,2-diimine chelates.[302] Chelates with mesityl substituents were synthesized in which deviations between chemical shifts of two equivalent *o*-methyl groups above and below the plane of the chelate ring and the *p*-methyl group which acts as an internal standard afford a means of detecting ring currents. The molybdenum derivative (LXXVI) was prepared and studied. Studies of this type indicate that the mesityl group represents a probe for ring current effects and also for varying the electron densities in ring systems.

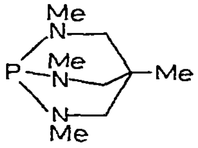


LXXVI

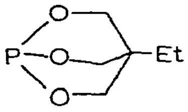
Rare earth shift reagents are shown to interact with basic sites in transition metal organometallic complexes such as *h*^{5}-$(C_5H_5)_2WH_2$, $(phen)(PPh_3)_2Mo(CO)_2$, *h*^{5}-$C_5H_5Mo(CO)_3GePh_2Cl$ and several of the more basic *h*^{5}-C_5H_5 iron carbonyl derivatives.[303] PMR chemical shifts are considerably expanded permitting detection of spin-spin coupling hitherto not observed.

NMR spectral studies show the amine proton of *meta*- and *para*-substituted anilinetricarbonylchromium(0) to be less sensitive to electronic changes in the aromatic ring induced by the substituents than of uncomplexed substituted anilines.[304] Plots of chemical shifts *vs* Hammett substituent constants are linear, however the slope of the plot of the uncomplexed compounds is greater than that of the complexed compounds.

Aromatic solvent-induced shift effects of polar metal complexes of the type $(CO)_5CrL^1$, *cis*-$(CO)_4MoL^1_2$, $(CO)_5MoL^1$ and $(CO)_4FeL^2$; nonpolar *trans* complexes of the type $(CO)_4ML^1_2$ (M = Cr, Mo, W), $(CO)_3FeL^1_2$, $(CO)_3FeL^2_2$, $(CO)_4CrL^2_2$ and NiL^3_4 in benzene and hexafluorobenzene have been studied by Verkade and co-workers.[305] The ligands involved were: L^1 = (LXXVII), L^2 = $P(OMe)_3$ and L^3 = (LXXVIII). The ASIS effects



LXVII



LXVIII

at the protons in the waist of ligand dipoles (NCH_2 in LXXVII and OCH_2 in LXXVIII) were consistent with ligand dipole enhancement upon complexing which alternates in the trans complexes.

Meakin, Muetterties and Jesson have made another contribution to the topic of intramolecular rearrangement mechanism.[306] Specifically, the pseudotetrahedral form of HML_4 complexes (H on a T_d face of ML_4) is recognized as a regular 5-coordinate polytopal form and a new intramolecular rearrangement mechanism is proposed which recognizes this ground state geometry. Although the complexes studied are all 5-coordinate the topic is pertinent to this review in view of the 5-coordinate intermediates present in many reaction processes of organometallic Group VI complexes.

Several tungsten tetrahydrides, $WH_4(PR_3)_4$ (PR_3 = PMe_2Ph, $PMePh_2$) and $WH_4(Ph_2PCH_2CH_2PPh_2)_2$, have been prepared by the reduction of the corresponding $WCl_4(PR_3)_2$ complexes with $NaBH_4$ in alcoholic solution in the presence of excess phosphine.[307] In contrast to the $MoH_4(PR_3)_4$ derivatives which have non-rigid structures at room temperature, the tungsten tetrahydride complexes were found to exhibit a rigid structure. In addition, $[WH_6(PMe_2Ph)_3]$ was prepared from reduction of trans-$[WCl_4(PMe_2Ph)_2]$, trans-$[WBr_4(PMe_2Ph)_2]$ or $[WCl_4(PMe_2Ph)_3]$ with sodium borohydride and was shown by nmr to be fluxional.[308] Impure $[WH_6(PEt_2Ph)_3]$ was prepared in a similar manner.

The nitrogen 1s binding energies for a variety of transition metal nitrosyl complexes, including $MoCl_2(NO)_2$(diars), trans-$[CrCl(NO)(diars)_2]^+$, $K_3[Cr(NO)(CN)_5]$ and

$[\pi\text{-}C_5H_5Cr(NO)_2]_2$, have been determined by Finn and Jolly.[309] It was concluded that a definite correlation exists between the nitrogen 1s binding energy of NO and the electron density on that group. Bent nitrosyls have low binding energies and linear nitrosyls have either low or high binding energies, depending on the extent of π back bonding from the metal.

Measurements of the core binding energies and calculations of the charge distributions in CO, $Cr(CO)_6$ and $Cr(CO)_5NH_3$ have shown that the σ framework of the CO ligand, which is drastically altered on formation of $Cr(CO)_6$, remains unaltered essentially upon substitution of NH_3 for CO.[310] An increase in the CO ligand electron density and an associated decrease in C and O 1s binding energies are a result of an increase in population of C and O 2pπ orbitals. The formal charge distribution on Cr was essentially unchanged by substitution of NH_3 for CO.

The photoelectron spectrum of WMe_6 exhibits narrow bands at 10.00 (intermediate intensity), 10.35 (strongest) and 10.8 (weakest) eV which were assigned to the e_g, t_{1u}, and a_{1g} W-C σ bonding levels, respectively and a broad band (11.5 - 16 eV) with a maximum at 12.8 eV which was assigned to C-H bonding levels derived from C 2p orbitals.[311] Assignment of the narrow bands was based on the premise that the intensity of the bands are related to the electron content of the corresponding orbital. The electron transition responsible for the red color of this compound is attributed to the symmetry allowed (T_{1u}) transition, $(t_{1u})^6 \rightarrow (t_{1u})^5(t_{2g})^1$. The binding energy of the vacant t_{2g} W 5d level was estimated to be 7.4 eV.

X-ray photoelectron spectra for an olefin disproportionation catalyst prepared by condensing molybdenum hexacarbonyl on to γ-alumina indicate that the molybdenum in an activated disproportionation catalyst does not exist as hexacarbonyl but is displaced to higher binding energies, i. e. molybdenum entities have an oxidation number greater than zero.[312] The loss of activity of these catalysts on exposure to air was shown to be due to oxidation of the molybdenum.

A molecular orbital bonding model for bent bis-(π-cyclopentadienyl)metal compounds of the type $(\pi\text{-}C_5H_5)_2MoH_2$ has been discussed by Prout and co-workers.[313]

An approximate molecular orbital approach (effects of all overlap terms and of the charge distribution on all neighboring atoms included) has been carried out on several metal carbonyls, including $Cr(CO)_5Cl^-$ and $Cr(CO)_5Br^-$.[314] From the derived electronic structure of these molecules the CO stretching force constants have been correlated with the calculated occupancies of the σ-donor and π-acceptor orbitals on the carbonyl ligands. The result indicate the both d_π-p_π backbonding and σ donor bonding have important effects on the carbonyl's force constant. In addition the calculations point out the importance of direct donation of electron density from the halogen's σ orbital to the cis carbonyl's 2π orbital.

Skeletal electron counting in clusters has been generalized by Wade.[315,316] Bonding electrons contributed by various units were discussed, including $M(CO)$, $M(CO)_2$, $M(\pi\text{-}C_5H_5)$ (M = Cr, Mo, W) and several metal-hydrocarbon π-complexes.

The application of orbital symmetry rules for unimolecular reaction to the olefin disproportionation reaction catalysed by transition metal complexes has been discussed by Pearson.[317]

Mingos[318] has discussed symmetry arguments which suggest that metal electronic configuration can influence the activation energy for metal-carbon homolytic bond dissociation, while Braterman[319] has recently critically discussed this theoretical explanation.

Braterman and Cross[320] have discussed the stability of transition metal-carbon bonds in terms of possible pathways for metal-carbon bond cleavage, both concerted and non-concerted pathways. The decomposition of $(CD_3)_3Cr(THF)_3$ to give CD_3H was suggested to be an example of non-concerted promotional bond cleavage, i. e. to involve an oxidation of the ligand from formally R^- to $\dot{R}$ with concomitant reduction of the metal. S_n1 substitution reactions of $M(CO)_6$ (M = Cr, Mo, W) were discussed as examples of non-concerted non-promotional bond cleavage, i. e., the excited states of the products correlate with the excited states of the reactions.

A discussion of [1,3] vs [1,2] sigmatropic shifts in the 5-membered ring of indenyl organometallic complexes has been presented by Dalton and McAuliffe.[321]

A topological treatment of polyhedral metal clusters and boron hydrides has been presented by King.[322] Summarization and comparisons of actual structures of transition metal clusters with the generated polyhedral possibilities indicate that transition metal clusters avoid using polyhedra with vertices of order five or higher. Such high order polyhedra would lead to excessive angular strain or a very high coordination number. In contrast, polyhedra with vertices of order four or five are the preferred structures for closed boron hydride or carborane cages. This paper presents a good summary of known types of metal atom clusters.

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References

1. S. T. Bond, Diss. Abstr. Int. B 32 (1972), 5080; No. 72-9247.
2. M. B. Hall, Diss. Abstr. Int. B 32 (1972), 4469; No. 72-1031.
3. J. M. Halm, Diss. Abstr. Int. B 33 (1972), 1045; No. 72-23,835.
4. W. J. Schlientz, Diss. Abstr. Int. B 32 (1972), 5678; No. 72-11,035.
5. R. J. Mynott, Diss. Abstr. Int. B 33 (1972), 2517; No. 72-31,792.
6. R. A. Brown, Diss. Abstr. Int. B 32 (1972), 3829; No. 72-4066.
7. R. J. Jernigan, Diss. Abstr. Int. B 33 (1972), 1046; No. 72-24,190.
8. J. W. McDonald, Diss. Abstr. Int. B 33 (1972), 2517; No. 72-32,510.
9. J. J. Benedict, Diss. Abstr. Int. B 32 (1972), 3828; No. 71-28,977.
10. D. J. Ehntholt, Diss. Abstr. Int. B 32 (1972), 4486; No. 72-6412.
11. J. L. Adcock, Diss. Abstr. Int. B 32 (1972), 5669; No. 72-11,295.
12. W. M. Willingham, Diss. Abstr. Int. B 32 (1972), 5090; No. 72-10,196.

13. D. F. MacInnes, Jr., Diss. Abstr. Int. B 33 (1972), 100; No. 72-18,778.

14. A. L. L. Hunt, Diss. Abstr. Int. B 32 (1972), 5086; No. 72-10,186.

15. R. C. Job, Diss. Abstr. Int. B 32 (1972), 6274; No. 72-14,904.

16. S. R. Su, Diss. Abstr. Int. B 32 (1972), 6283; No. 72-15,304.

17. W. E. Stanclift, Diss. Abstr. Int. B 33 (1972), 620; No. 72-22,069.

18. P. J. Vergamini, Diss. Abstr. Int. B 32 (1972), 6283; No. 72-11,267.

19. L. Y. Y. Chan, Diss. Abstr. Int. B 33 (1972), 98; (order directly from the National Library of Canada at Ottawa).

20. J. D. Oliver, Diss. Abstr. Int. B 32 (1972), 6280; No. 72-15,808.

21. C. A. Kosky, Diss. Abstr. Int. B 33 (1972), 1977; No. 72-28,253.

22. M. H. Nemiroff, Diss. Abstr. Int. B 33 (1972),1980; No. 72-28,266.

23. A. H. Reis, Jr., Diss. Abstr. Int. B 33 (1972), 1049; No. 72-24,652.

24. H. J. Plastas, Diss. Abstr. Int. B 33 (1972), 1980; No. 72-29,415.

25. J. A. Connor, E. M. Jones, and G. K. McEwen, J. Organometal. Chem., 43, 357 (1972).

26. J. Chr. Weis and W. Beck, J. Organometal. Chem., 44, 325 (1972).

27. K. A. Ostoja Starzewski, H. tom Dieck, K. D. Franz, and F. Hohmann, J. Organometal. Chem., 42, C35 (1972).

28. H. Schumann, G. Pfeifer and H. Roser, J. Organometal. Chem., 44, C10 (1972).

29. H. Schumann and E. von Deuster, J. Organometal. Chem., 40, C27 (1972).

30. D. DeFilippo, F. Devillanova, C. Preti, E. F. Trogu, and P. Viglino, Inorg. Chim. Acta, 6, 23 (1972).

31. R. Mathieu and R. Poilblanc, Inorg. Chem., 11, 1858 (1972).

32. G. Schwenzer, M. Y. Darensbourg and D. J. Darensbourg, Inorg. Chem., 11, 1967 (1972).

33. A. D. George and T. A. George, Inorg. Chem., 11, 892 (1972).

34. D. C. Beer and L. J. Todd, J. Organometal. Chem., 36, 77 (1972).

35. J. Bowden and R. Colton, Aust. J. Chem. 24, 2471 (1971).

36. J. Bowden and R. Colton, Aust. J. Chem. 25, 17 (1972).

37. R. Colton and C. J. Rix, Aust. J. Chem. 24, 2461 (1971).

38. A. D. Garnovskii, N. E. Kolobova, I. B. Zlotina, G. K. Mitina, K. N. Anisimov and O. A. Osipov, Izv. Akad. Nauk SSSR, Ser. Khim., 629 (1972); Chem. Abstr., 77, (1972) 55790c.

39. A. D. Garnovskii, N. E. Kolobova, O. A. Osipov, K. N. Anisimov, I. B. Zlotina, G. K. Mitina and Y. V. Kolodyazhnyi, Zh. Obshch. Khim., 42, 929 (1972); Chem. Abstr., 77, (1972) 96372m.

40. C. V. Pittman, Jr., and G. O. Evans, J. Organometal. Chem., 43, 361 (1972).

41. W. M. Douglas and J. K. Ruff, Syn. Inorg. Metal-Org. Chem., 2, 151 (1972).

42. W. J. Schlientz and J. K. Ruff, Inorg. Chem., 11, 2265 (1972).

43. W. J. Schlientz and J. K. Ruff, J. Organometal. Chem., 33, C64 (1971).

44. W. J. Schlientz, Y. Lavender, N. Welcman, R. B. King, and J. K. Ruff, J. Organometal. Chem., 33, 357 (1971).

45. H. A. Tayim, A. Bouldoukian and M. Kharboush, Inorg. Nucl. Chem. Lett., 8, 231 (1972).

46. P. M. Treichel, W. M. Douglas, and W. K. Dean, Inorg. Chem., 11, 1615 (1972).

47. C. S. Kraihanzel and C. M. Bartish, J. Am. Chem. Soc., 94, 3572 (1972).

48. C. S. Kraihanzel and C. M. Bartish, J. Organometal. Chem., 43, 343 (1972).

49. H. Noth and S. N. Sze, J. Organometal. Chem., 43, 249 (1972).

50. H. Schumann and J. Kuhlmey, J. Organometal. Chem., 42, C57 (1972).

51. T. Fukumoto, Y. Matsumura and R. Okawara, J. Organometal. Chem., 37, 113 (1972).

52. M. Brockhaus, F. Staudacher and H. Vahrenkamp, Chem. Ber., 105, 3716 (1972).

53. H. Vahrenkamp, Chem. Ber., 105, 3574 (1972).

54. J. C. Weis and W. Beck, Chem. Ber., 105, 3203 (1972).

55. J. F. White and M. F. Farona, J. Organometal. Chem., 37, 119 (1972).

56. G. Schmid and R. Boese, Chem. Ber., 105, 3306 (1972).

57. L. Bencze, J. Organometal. Chem., 37, C37 (1972).

58. W. R. Cullen, L. D. Hall, and J. E. H. Ward, J. Am. Chem. Soc., 94, 5702 (1972).

59. J. F. Nixon and J. R. Swain, J. Chem. Soc. Dalton, 1038 (1972).

60. J. G. Dunn and D. A. Edwards, J. Organometal. Chem., 36, 153 (1972).

61. H. Brunner and W. A. Herrmann, Chem. Ber., 105, 770 (1972).

62. A. Greco, J. Organometal. Chem., 43, 351 (1972).

63. D. Wege and S. P. Wilkinson, J. Chem. Soc. Chem. Comm., 1335 (1972).

64. Y. Menachem and A. Eisenstadt, J. Organometal. Chem., 33, C29 (1971).

65. E. Koerner von Gustorf, A. Jaenicke and O. E. Polansky, Angew. Chem. Int. Ed. Engl., 11, 532 (1972).

66. P. C. H. Mitchell and D. A. Parker, J. Chem. Soc. Dalton, 1828 (1972).

67. K. Öfele and E. Dotzauer, J. Organometal. Chem., 42, C87 (1972).

68. N. L. Paddock, T. N. Ranganathan, and J. N. Wingfield, J. Chem. Soc. Dalton, 1578 (1972).

69. H. P. Calhoun, N. L. Paddock, J. Trotter and J. N. Wingfield, J. Chem. Soc. Chem. Comm., 875 (1972).

70. N. K. Hota and R. O. Harris, J. Chem. Soc. Chem. Comm., 407 (1972).

71. M. L. Schneider, N. J. Coville and I. S. Butler, J. Chem. Soc. Chem. Comm., 799 (1972).

72. W. P. Anderson, W. G. Blenderman, and K. A. Drews, J. Organometal. Chem., 42, 139 (1972).

73. T. W. Beall and L. W. Houk, Inorg. Chem., 11, 915 (1972).

74. J. A. Connor, E. M. Jones, G. K. McEwen, M. K. Lloyd, and J. A. McCleverty, J. Chem. Soc. Dalton, 1246 (1972).

75. P. M. Treichel and G. E. Direen, J. Organometal. Chem., 39, C20 (1972).

76. D. F. Lewis and S. J. Lippard, Inorg. Chem., 11, 621 (1972).

77. J. A. Connor and J. P. Lloyd, J. Chem. Soc. Dalton, 1470 (1972).

78. E. O. Fischer and W. Kalbfus, J. Organometal. Chem., 46, C15 (1972).

79. E. O. Fischer and S. Fontana, J. Organometal. Chem., 40, 159 (1972).

80. E. O. Fischer, F. R. Kreissl, C. G. Kreiter and E. W. Meineke, Chem. Ber., 105, 2558 (1972).

81. E. O. Fischer, H. J. Beck, C. G. Kreiter, J. Lynch, J. Muller and E. Winkler, Chem. Ber., 105, 162 (1972).

82. E. O. Fischer and F. R. Kreissl, J. Organometal. Chem., 35, C47 (1972).

83. C. W. Rees and E. von Angerer, J. Chem. Soc. Chem. Comm., 420 (1972).

84. B. Cetinkaya, M. F. Lappert, and K. Turner, J. Chem. Soc. Chem. Comm., 851 (1972).

85. E. O. Fischer, M. Leupold, C. G. Kreiter, and J. Müller, Chem. Ber., 105, 150 (1972).

86. E. O. Fischer and M. Leupold, Chem. Ber., 105, 599 (1972).

87. E. O. Fischer and S. Fontana, J. Organometal. Chem., 40, 367 (1972).

88. J. A. Connor and P. D. Rose, J. Organometal. Chem., 46, 329 (1972).

89. E. O. Fischer and K. H. Dötz, J. Organometal. Chem., 36, C4 (1972).

90. F. R. Kreissel, C. G. Kreiter and E. O. Fischer, Angew. Chem. Int. Ed. Engl., 11, 643 (1972).

91. E. O. Fischer, H. Fischer and H. Werner, Angew. Chem. Int. Ed. Engl., 11, 644 (1972).

92. C. P. Casey, R. A. Boggs, and R. L. Anderson, J. Am. Chem. Soc., 94, 8947 (1972).

93. K. S. Chen, J. Kleinberg and J. A. Landgrebe, J. Chem. Soc. Chem. Comm., 295 (1972).

94. C. P. Casey and T. J. Burkhardt, J. Am. Chem. Soc., 94, 6543 (1972).

95. K. H. Dötz and E. O. Fischer, Chem. Ber., 105, 1356 (1972).

96. E. O. Fischer and K. H. Dötz, Chem. Ber., 105, 3966 (1972).

97. T. A. George, Inorg. Chem., 11, 77 (1972).

98. J. L. Davidson and D. W. A. Sharp, J. Chem. Soc. Dalton A, 107 (1972).

99. P. M. Treichel and W. K. Dean, J. Chem. Soc. Chem. Comm., 804 (1972).

100. T. Kruck, M. Hofler and L. Liebig, Chem. Ber., 105, 1174 (1972).

101. H. Brunner and W. A. Herrmann, Angew. Chem. Int. Ed. Engl., 11, 418 (1972).

102. H. Brunner and W. A. Herrmann, Chem. Ber., 105, 3600 (1972).

103. R. B. King and P. N. Kapoor, Inorg. Chim. Acta, 6, 391 (1972).

104. R. B. King and M. S. Saran, J. Am. Chem. Soc., 94, 1784 (1972).

105. R. B. King and M. S. Saran, J. Chem. Soc. Chem. Commun., 1053 (1972).

106. A. N. Nesmeyanov, L. G. Makarova, N. A. Ustynyuk, B. A. Kvasov and L. V. Bogatyreva, J. Organometal. Chem. 34, 185 (1972).

107. J. L. Roustan, J. Benaim, C. Charrier and J. Y. Merour, Tetrahedron Lett., 1953 (1972).

108. E. G. Perevalova, A. I. Shakhnovich and S. S. Churanov, Zh. Obshch. Khim., 42, 1171 (1972); Chem. Abstr., 77, (1972) 101838z.

109. A. N. Nesmeyanov, L. G. Makarova, N. A. Ustynyuk and L. V. Bogatyreva, J. Organometal. Chem., 46, 105 (1972).

110. P. M. Treichel, W. K. Dean, and W. M. Douglas, J. Organometal. Chem. 42, 145 (1972).

111. R. B. King, W. C. Zipperer, and M. Ishaq, Inorg. Chem., 11, 1361 (1972).

112. A. N. Nesmeyanov, L. G. Makarova and V. N. Vinogradova, Izv. Akad. Nauk SSSR, Ser. Khim., 122 (1972); Chem. Abstr., 77, (1972) 19773r.

113. T. A. George, J. Organometal. Chem., 33, C13 (1971).

114. A. N. Nesmeyanov, L. G. Makarova, V. N. Vinogradova, Izd. Akad. Nauk SSSR, Ser. Khim., 1449 (1972); Chem. Abstr., 77, (1972) 114539c.

115. G. A. Razuvaev, G. G. Petuchov, A. N. Artemov and N. I. Sirotkin, J. Organometal. Chem., 37, 313 (1972).

116. R. M. G. Roberts, J. Organometal. Chem., 40, 359 (1972).

117. W. K. Glass and T. Shiels, Inorg. Nucl. Chem. Lett., 8, 257 (1972).

118. H. L. Conder and W. R. Robinson, Inorg. Chem., 11, 1527 (1972).

119. G. B. McVicker and R. S. Matyas, J. Chem. Soc. Chem. Comm., 972 (1972).

120. P. Hachett and A. R. Manning, J. Chem. Soc. Dalton, 2434 (1972).

121. B. Cetinkaya, M. F. Lappert, J. McMeeking, and D. Palmer, J. Organometal. Chem., 34, C37 (1972).

122. J. M. Burlitch and S. E. Hayes, J. Organometal. Chem., 42, C13 (1972).

123. A. T. T. Hsieh and M. J. Mays, J. Organometal. Chem., 37, 9 (1972).

124. B. Walther and C. Rockstroh, J. Organometal. Chem., 44, C4 (1972).

125. W. Malisch, J. Organometal. Chem., 39, C28 (1972).

126. M. I. Bruce, B. L. Goodsall, D. N. Sharrocks and F. G. A. Stone, J. Organometal. Chem., 39, 139 (1972).

127. A. T. T. Hsieh and M. J. Mays, J. Organometal. Chem., 39, 157 (1972).

128. W. K. Glass and T. Shiels, J. Organometal. Chem., 35, C64 (1972).

129. M. L. H. Green, A. H. Lynch, and M. G. Swanwick, J. Chem. Soc. Dalton, 1445 (1972).

130. H. R. Keable and M. Kilner, J. Chem. Soc. Dalton, 153 (1972).

131. W. Jetz and R. J. Angelici, J. Am. Chem. Soc., 94, 3799 (1972).

132. W. Malisch, H. Schmidbauer, and M. Kuhn, Angew. Chem. Int. Ed. Engl., 11, 516 (1972).

133. J. L. Rouston, J. Y. Merour, J. Benaim and C. Charrier, C. R. Acad. Sci., Ser. C, 274, 537 (1972).

134. D. W. Lichtenberg and Andrew Wojcicki, J. Organometal. Chem., 33, C77 (1971).

135. W. E. Douglas and M. L. H. Green, J. Chem. Soc. Dalton, 1796 (1972).

136. W. Ehrl and H. Vahrenkamp, Chem. Ber., 105, 1471 (1972).

137. J. A. McCleverty and D. Seddon, J. Chem. Soc. Dalton, 2588 (1972).

138. J. A. McCleverty and D. Seddon, J. Chem. Soc. Dalton, 2526 (1972).

139. R. B. King and W. C. Zipperer, Inorg. Chem., 11, 2119 (1972).

140. M. Herberhold and H. Alt, J. Organometal. Chem., 42, 407 (1972).

141. J. L. Thomas and H. H. Brintzinger, J. Am. Chem. Soc., 94, 1387 (1972).

142. G. Giannotti and M. L. H. Green, J. Chem. Soc., Chem. Commun., 1114 (1972).

143. A. Nakamura and S. Otsuka, J. Am. Chem. Soc., 94, 1886 (1972).

144. F. W. S. Benfield, B. R. Francis, and M. L. H. Green, J. Organometal. Chem., 44, C13 (1972).

145. M. E. Switzer and M. F. Rettig, J. Chem. Soc., Chem. Comm., 687 (1972).

146. F. A. Cotton and G. Deganello, J. Am. Chem. Soc., 94, 2142 (1972).

147. R. B. King and A. Efraty, J. Am. Chem. Soc., 94, 3768 (1972).

148. R. B. King and A. Efraty, J. Am. Chem. Soc., 94, 3773 (1972).

149. J. L. Roustan, C. Charrier, J. Y. Merour, J. Benaim, and C. Giannotti, J. Organometal. Chem., 38, C37 (1972).

150. J. Y. Merour, C. Charrier, J. Benaim, J. L. Roustan, and D. Commereuc, J. Organometal. Chem., 39, 321 (1972).

151. G. R. Knox, D. G. Leppard, P. L. Pauson, and W. E. Watts, J. Organometal. Chem., 34, 347 (1972).

152. B. V. Lokshin, V. I. Zdanovich, N. K. Baranetskaya, V. N. Setkina and D. N. Kursanov, J. Organometal. Chem., 37, 331 (1972).

153. D. N. Kursanov, V. N. Setkina, P. V. Petrovskii, V. I. Zdanovich, N. K. Baranetskaya and I. D. Rubin, J. Organometal. Chem., 37, 339 (1972).

154. C. P. Lillya and R. A. Sahatjian, Inorg. Chem., 11, 889 (1972).

155. C. Elschenbroich, F. Gerson, and J. Hernzer, Z. Naturforsch. B, 27, 312 (1972).

156. M. Ashraf, Can. J. Chem., 50, 118 (1972).

157. N. J. Gogan and Z. V. Siddiqui, Can. J. Chem., 50, 720 (1972).

158. W. S. Trahanovsky and R. J. Card, J. Am. Chem. Soc., 94, 2897 (1972).

159. N. J. Gogan and C. S. Davies, J. Organometal. Chem., 39, 129 (1972).

160. A. Meyer and R. Dabard, J. Organometal. Chem., 36, C38 (1972).

161. J. Müller and B. Mertschenk, Chem. Ber., 105, 3346 (1972).

162. R. Guilard, J. Tirouflet, and P. Fournari, J. Organometal. Chem., 33, 195 (1971).

163. J. A. S. Howell, B. F. G. Johnson, and J. Lewis, J. Organometal. Chem., 42, C54 (1972).

164. H. Kolshorn, H. Meier, and E. Mueller, Tetrahedron Lett., 1589 (1972).

165. G. Brule and J. Y. LeBihan, C. R. Acad. Sci., Ser. C., 274, 1218 (1972).

166. D. F. Dustin, G. B. Dunks and M. F. Hawthorne, U.S. Nat. Tech. Inform. Serv. AD Rep. No. 743492 (1972); Chem. Abstr., 77, (1972) 152339v.

167. C. F. Meade, G. A. Moser, and M. D. Rausch, Inorg. Chem., 11, 217 (1972).

168. J. M. Greenwood, H. Veening, and B. R. Willeford, J. Organometal. Chem., 38, 345 (1972).

169. A. Shortland and G. Wilkinson, J. Chem. Soc. Chem. Comm., 318 (1972).

170. E. Kinsella, V. B. Smith and A. G. Massey, J. Organometal. Chem. 34, 181 (1972).

171. W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, J. Chem. Soc. Dalton, 533 (1972).

172. W. Seidel, K. Fischer and K. Schmiedeknecht, Z. Anorg. Allg. Chem., 390, 273 (1972).

173. K. Nishimura, H. Kuribayashi, A. Yamamoto and S. Ikeda, J. Organometal. Chem., 37, 317 (1972).

174. W. Kruse, J. Organometal. Chem., 42, C39 (1972).

175. W. Mowat and G. Wilkinson, J. Organometal. Chem., 38, C35 (1972).

176. W. Seidel and K. Fischer, Z. Chem., 12, 147 (1972).

177. S. R. Fletcher, A. Shortland, A. C. Skapski, and G. Wilkinson, J. Chem. Soc. Chem. Comm., 922 (1972).

178. K. Schmiedeknecht, W. Reichardt and W. Seidel, Z. Chem., 11, 432 (1971).

179. R. P. A. Sneeden and H. H. Zeiss, J. Organometal. Chem., 40, 163 (1972).

180. H. Cohen and D. Meyerstein, J. Chem. Soc. Chem. Comm., 320 (1972).

181. G. A. Ward, W. Kruse, B. K. Bower, J. C. W. Chien, J. Organometal Chem. 42, C43 (1972).

182. T. A. George and C. D. Seibold, Inorg. Nucl. Chem. Lett., 8, 465 (1972).

183. M. Hidai, K. Tominari, and Y. Uchida, J. Am. Chem. Soc., 94, 110 (1972).

184. T. A. George and C. D. Seibold, J. Am. Chem. Soc., 94, 6539 (1972).

185. D. J. Darensbourg, Inorg. Nucl. Chem. Lett., 8, 529 (1972).

186. B. Bell, J. Chatt, G. J. Leigh, J. Chem. Soc. Dalton, 2492 (1972).

187. J. K. Burdett, M. A. Graham, J. J. Turner, J. Chem. Soc. Dalton, 1620 (1972).

188. D. Sellmann and G. Maisel, Z. Naturforsch. B, 27, 465 (1972).

189. D. Sellmann and G. Maisel, Z. Naturforsch. B, 27, 718 (1972).

190. T. S. Cameron and C. K. Prout, Acta Crystallogr., B, 28, 453 (1972).

191. J. A. Bowden, R. Colton, and C. J. Commons, Aust. J. Chem., 25, 1393 (1972).

192. M. Green and S. H. Taylor, J. Chem. Soc. Dalton, 2629 (1972).

193. W. R. Robinson and M. E. Swanson, J. Organometal. Chem. 35, 315 (1972).

194. R. Davis, B. F. G. Johnson, and K. H. Al-Obaidi, J. Chem. Soc. Dalton, 508 (1972).

195. A. E. Crease and P. Legzdins, J. Chem. Soc. Chem. Comm., 268 (1972).

196. B. F. G. Johnson, S. Bhaduri and N. G. Connelly, J. Organometal. Chem., 40, C36 (1972).

197. M. Herberhold and A. Razaui, Angew. Chem. Int. Ed. Engl., 11, 1092 (1972).

198. N. S. Garif'yanov, A. D. Troitskaya, A. T. Razumov, I. V. Ovchinnikov, P. A. Gurevick, and O. I. Kondrat'eva, Zh. Neorg. Khim., 17, 1346 (1972); Chem. Abstr., 77 (1972) 80198y.

199. F. A. Cotton and M. Jeremic, Syn. Inorg. Metal-Org. Chem., 1, 265 (1971).

200. E. Uhlemann and U. Eckelmann, Z. Chem., 12, 298 (1972).

201. J. Y. Chenard, C. R. Acad. Sci., Ser. C, 273, 1469 (1971).

202. C. S. Davies and N. J. Gogan, J. Inorg. Nucl. Chem., 34, 2791 (1972).

203. V. G. Syrkin and A. A. Vel'skii, Zh. Fiz. Khim., 46, 2229 (1972); Chem. Abstr., 77 (1972) 169529e.

204. H. A. Skinner and Y. Virmani, Rev. Roum. Chim., 17, 467 (1972); Chem. Abstr., 77 (1972) 10458j.

205. I. V. Kryukova and E. M. Fedneva, Sb. Nauch. Fr. Chelyabinsk. Politekh. Inst., No. 91, 108 (1971); Chem. Abstr. 77 (1972) 108941m.

206. I. V. Kryukova and E. M. Fedneva, Sb. Nauch. Fr. Chelyabinsk. Politekh. Inst., No. 91, 112 (1971); Chem. Abstr. 77 (1972) 152319p.

207. U. K. Baev, Obshch. Prikl. Khim., 9 (1972); Chem. Abstr., 77 (1972) 130929k.

208. W. A. Duncan and J. A. Murfree, U.S. Patent No. 3,665,708 (1972); Chem. Abstr., 77 (1972) 90793c.

209. M. Guainazzi, G. Silvestri, S. Gambino, and G. Filardo, J. Chem. Soc. Dalton, 927 (1972).

210. G. M. Jenkins and D. R. Wiles, J. Chem. Soc. Chem. Comm., 1177 (1972).

211. G. R. Dobson and A. J. Rettenmaier, Inorg. Chim. Acta, 6, 507 (1972).

212. G. R. Dobson, Proc. South Dakota Acad. Sci., 50, 244 (1971).

213. R. J. Jernigan and G. R. Dobson, Inorg. Chem., 11, 81 (1972).

214. J. R. Graham and R. J. Angelici, Inorg. Chem., 6, 992 (1967).

215. R. J. Dennenberg and D. J. Darensbourg, Inorg. Chem., 11, 72 (1972).

216. K. M. Al-Kathumi and L. A. P. Kane-Maguire, J. Inorg. Nucl. Chem., 34, 3759 (1972).

217. J. R. Paxson and G. R. Dobson, J. Coord. Chem., 1, 321 (1972).

218. K. W. Barnett, T. G. Pollman, and T. W. Solomon, J. Organometal.Chem., 36, C23 (1972).

219. R. M. Moriarty, Chin-Lung Yeh, Ei-Lan Yeh, and K. C. Ramey, J. Am. Chem. Soc., 94, 9229 (1972).

220. A. Ceccon and G. S. Biserni, J. Organometal. Chem., 39, 313 (1972).

221. D. N. Kursanov, V. N. Setkina and B. G. Gribov, J. Organometal. Chem., 37, C35 (1972).

222. F. Dewans and E. Goldenberg, Ger. Offen. 2,200,405 (1972); Chem. Abstr., 77 (1972) 141188u.

223. W. R. Kroll, U.S. Patent No. 3,644,445 (1972); Chem. Abstr., 76 (1972) 154452e.

224. Y. Mori and J. Tsuji, Tetrahedron, 28, 29 (1972).

225. W. R. Kroll and G. Doyle, J. Catal., 24, 356 (1972).

226. M. L. H. Green, J. Knight, L. C. Mitchard, G. G. Roberts, W. E. Silverthorn, J. Chem. Soc. Chem. Comm., 987 (1972).

227. L. Hocks, A. J. Hubert and P. Teyssie, Tetrahedron Lett., 3687 (1972).

228. R. H. Grubbs and T. K. Brunck, J. Am. Chem. Soc., 94, 2540 (1972).

229. K. B. Sharpless, M. A. Umbreit, M. T. Nieh, and T. C. Flood, J. Am. Chem. Soc., 94, 6539 (1972).

230. T. Takagi, T. Hamaguchi, K. Fukuzumi, and M. Aoyama, J. Chem. Soc. Chem. Comm., 838 (1972).

231. J. Chatt, R. J. Haines, and G. J. Leigh, J. Chem. Soc. Chem. Comm., 1202 (1972).

232. P. B. van Dam, M. C. Mittelmeijer, and C. Boelhouwer, J. Chem. Soc. Chem. Comm., 1221 (1972).

233. P. P. O'Neil and J. J. Rooney, J. Am. Chem. Soc., 94, 4383 (1972).

234. K. B. Sharpless and T. C. Flood, J. Chem. Soc. Chem. Comm., 370 (1972).

235. P. P. O'Neill and J. J. Rooney, J. Chem. Soc. Chem. Comm., 104 (1972).

236. L. W. Gosser, U.S. Patent No. 3,673,270 (1972); Chem. Abstr., 77 (1972) 89083q.

237. R. D. Smetana, U.S. Patent No. 3,657,251 (1972); Chem. Abstr., 77 (1972) 5355u.

238. E. R. Tucci, U.S. Patent No. 3,631,111 (1971); Chem. Abstr., 76, (1972) 58983h

239. L. Ramain and Y. Trambouze, C. R. Acad. Sci., Ser. C., 273, 1409 (1971).

240. J. Wang, U.S. Patent No. 3,634,540 (1972); Chem. Abstr., 76 (1972) 71975b.

241. J. L. Garnett, M. A. Long, R. F. W. Vining, and T. Mole, J. Chem. Soc. Chem. Comm., 1172 (1972).

242. C. H. Bamford and F. J. T. Fildes, Polym. Prepr., Amer. Chem. Soc., Div. Polym. Chem., 11, 927 (1970); Chem. Abstr., 77 (1972) 5873m.

243. Y. Chauvin, J. P. Soufflet, D. Commereuc and P. N. Hung, Ger. Offen., 2,151,662 (1972); Chem. Abstr., 77 (1972) 25343s.

244. V. A. Kormer, I. A. Poletaeva and T. L. Yufa, J. Polym. Sci., Part A-1, 10, 251 (1972); Chem. Abstr., 76 (1972) 127550d.

245. V. A. Polataev, V. M. Vdovin and N. S. Nametkin, Dokl. Akad. Nauk SSSR, 203, 1324 (1972); Chem. Abstr., 77 (1972) 75561g.

246. T. L. Yufa, I. A. Poletaeva, V. A. Kormer, B. D. Babitskii, M. I. Loback, U. V. Markova and L. A. Churlyaeva, Belg. Patent No. 770,823 (1972); Chem. Abstr., 77 (1972) 76407v.

247. K. Tanaka, K. Ono and H. Tachibana, Japan Patent No. 72 10,850 (1972); Chem. Abstr., 77 (1972) 89127g.

248. B. K. Bower and W. P. Long, U.S. Patent No. 3,666,743; Chem. Abstr., 77 (1972) 62538e.

249. K. Hashimoto, N. Mogi, M. Shido, U.S. Patent No. 3,644,223; Chem. Abstr., 77 (1972) 89139n.

250. M. Ichikawa, Y. Takeuchi, N. Yamaguchi, M. Endo and A. Kihi, Japan Patent No. 72 08,211 (1972); Chem. Abstr., 77 (1972) 36002f.

251. K. J. Karol and C. S. Wu, Ger. Offen. 2,147,793 (1972); Chem. Abstr., 77 (1972) 35272g.

252. G. Pampus, J. Witte and M. Hoffmann, Ger. Offen., 2,016,471 (1971); Chem. Abstr., 76 (1972) 60711m.

253. C. Bamford and C. A. Finch, Brit. Patent No. 1,033,161 (1966); Chem. Abstr., 76 (1972) 25832e.

254. W. M. Kruse and W. P. Long, Ger. Offen., 2,204,902 (1972); Chem. Abstr., 77 (1972) 165305f.

255. J. E. Burleigh and C. A. Uroneck, U.S. Patent No. 3,640,986 (1972); Chem. Abstr., 76 (1972) 141537m.

256. T. L. Yufa, I. A. Poletaeva, V. A. Kormer, B. D. Babitskii, M. I. Lobach, V. V. Markova, and L. A. Churlyaeva, Ger. Offen., 2,133,905 (1972); Chem. Abstr., 76 (1972) 142093a.

257. J. D. Brown, C. A. Uraneck and J. E. Burleigh, Ger. Offen., 2,137,524 (1972); Chem. Abstr., 76 (1972) 142106g.

258. R. A. Brown and G. R. Dobson, Inorg. Chim. Acta, 6, 65 (1972).

259. G. R. Dobson and R. A. Brown, J. Inorg. Nucl. Chem., 34, 2785 (1972).

260. R. T. Jernigan, R. A. Brown, and G. R. Dobson, J. Coord. Chem., 2, 47 (1972).

261. R. L. Keiter and D. P. Shah, Inorg. Chem., 11, 191 (1972).

262. L. K. Atkinson and D. C. Smith, J. Organometal. Chem., 33, 189 (1971).

263. P. Braunstein and J. Dehand, J. Chem. Soc. Chem. Comm., 164 (1972).

264. M. A. Graham, R. N. Perutz, M. Poliakoff, and J. J. Turner, J. Organometal. Chem., 34, C34 (1972).

265. P. A. Breeze and J. J. Turner, J. Organometal. Chem., 44, C7 (1972).

266. J. H. Darling and J. S. Ogden, J. Chem. Soc. Dalton, 2496 (1972).

267. D. J. Darensbourg, Inorg. Chem., 11, 1436 (1972).

268. S. F. A. Kettle, I. Paul, and P. J. Stamper, J. Chem. Soc. Dalton, 2413 (1972).

269. R. V. Parish and P. G. Simms, J. Chem. Soc. Dalton, 2389 (1972).

270. S. Kyelstrup, S. J. Cyvin, J. Brunvoll and L. Schafer, J. Organometal. Chem., 36, 137 (1972).

271. J. Brunvoll, S. J. Cyvin and L. Schafer, J. Organometal. Chem., 36, 143 (1972).

272. L. Schafer, G. M. Begun and S. J. Cyvin, Spectrochim. Acta, 28A, 803 (1972).

273. I. J. Hyams and E. R. Lippincott, Spectrochim. Acta, 28A, 1741 (1972).

274. D. F. Shriver and A. Alich, Inorg. Chem., 11, 2984 (1972).

275. M. Wrighton, G. S. Hammond and H. B. Gray, Inorg. Chem., 11, 3122 (1972).

276. I. W. Renk and H. tom Dieck, Chem. Ber., 105, 1403 (1972).

277. H. tom Dieck and I. W. Renk, Chem. Ber., 105, 1419 (1972).

278. Y. Kaizu, I. Fujita, and H. Kobayashi, Z. Phys. Chem. (Frankfurt/Main), 79, 298 (1972).

279. J. Burgess and S. F. N. Morton, J. Chem. Soc. Dalton, 1712 (1972).

280. Y. Kaizu and H. Kobayashi, Bull. Chem. Soc. Jap., 45, 470 (1972); Chem. Abstr., 76 (1972) 106055f.

281. F. E. Saalfeld, J. J. DeCorpo and M. V. McDowell, J. Organometal. Chem., 44, 333 (1972).

282. D. F. Hunt, J. W. Russell, R. L. Torian, J. Organometal. Chem., 43, 175 (1972).

283. A. T. T. Hsieh, Int. J. Mass Spectrom. Ion Phys., 7, 297 (1971); Chem. Abstr., 76 (1972) 7928m.

284. G. Distefano, A. Foffani, G. Innorta, and S. Pignataro, Int. J. Mass Spectrom. Ion Phys., 7, 383 (1971); Chem. Abstr., 76 (1972) 51396k.

285. J. R. Gilbert, W. P. Leach, and J. R. Miller, J. Organometal. Chem., 42, C51 (1972).

286. J. Mueller, Angew. Chem. Int. Ed. Engl., 11, 653 (1972).

287. J. A. Connor, E. M. Jones, E. W. Randall and E. Rosenberg, J. Chem. Soc. Dalton, 2419 (1972).

288. C. G. Kreiter and V. Formacek, Angew. Chem. Int. Ed. Engl., 11, 141 (1972).

289. Yu. K. Grishin, N. M. Sergeyev, and Yu. A. Ustynyuk, J. Organometal. Chem. 34, 105 (1972).

290. J. L. Calderon, F. A. Cotton, and A. Shaver, J. Organometal. Chem., 38, 105 (1972).

291. J. L. Calderon, F. A. Cotton,and A. Shaver, J. Organometal. Chem., 37, 127 (1972).

292. F. A. Cotton, J. L. Calderon, M. Jeremic, and A. Shaver, J. Chem. Soc. Chem. Comm., 777 (1972).

293. J. L. Calderon, F. A. Cotton and A. Shaver, J. Organometal. Chem., 42, 419 (1972).

294. E. O. Fischer, L. Knauss, R. L. Keiter, and J. G. Verkade, J. Organometal. Chem., 37, C7 (1972).

295. R. L. Keiter and L. W. Cary, J. Am. Chem. Soc., 94, 9232 (1972).

296. P. J. Craig and J. Edwards, J. Organometal. Chem., 46, 335 (1972).

297. M. Herberhold, H. Alt, C. G. Kreiter, J. Organometal. Chem., 42, 413 (1972).

298. P. Meakin, S. Trofimenko, and J. P. Jesson, J. Am. Chem. Soc., 94, 5677 (1972).

299. R. D. Adams and F. A. Cotton, J. Am. Chem. Soc., 94, 6193 (1972).

300. H. R. Keable and M. Kilner, J. Chem. Soc. Dalton, 1535 (1972).

301. R. E. Dessy, A. L. Rheingold, and G. D. Howard, J. Am. Chem. Soc., 94, 746 (1972).

302. G. Haefelinger, R. G. Weissenhorn, F. Hack, and G. Westermayer, Angew. Chem. Int. Ed. Engl., 11, 725 (1972).

303. T. J. Marks, J. S. Kristoff, A. Alich, and D. F. Shriver, J. Organometal. Chem., 33, C35 (1971).

304. A. Wu, E. R. Biehl, and P. C. Reeves, J. Organometal. Chem., 33, 53 (1971).

305. J. A. Mosbo, J. R. Pipal, and J. G. Verkade, J. Magn. Resonance, 8, 243 (1972).

306. P. Meakin, E. L. Muetterties and J. P. Jesson, J. Am. Chem. Soc., 94, 5271 (1972).

307. B. Bell, J. Chatt, G. J. Leigh and T. Ito, J. Chem. Soc. Chem. Comm., 34 (1972).

308. J. R. Moss and B. L. Shaw, J. Chem. Soc. Dalton, 1910 (1972).

309. P. Finn and W. L. Jolly, Inorg. Chem., 11, 893 (1972).

310. M. Barber, J. A. Conner, I. H. Hillier and W. N. E. Meredith, J. Electron Spectrosc. Relat. Phenomena, 1, 110 (1972).

311. S. Craddock and W. Savage, Inorg. Nucl. Chem. Lett., 8, 753 (1972).

312. D. A. Whan, M. Barber and P. Swift, J. Chem. Soc. Chem. Comm., 198 (1972).

313. J. C. Green, M. L. H. Green and C. K. Prout, J. Chem. Soc. Chem. Comm., 421 (1972).

314. M. B. Hall and R. F. Fenske, Inorg. Chem., 11, 1619 (1972).

315. K. Wade, Inorg. Nucl. Chem. Lett., 8, 559 (1972).

316. K. Wade, Inorg. Nucl. Chem. Lett., 8, 563 (1972).

317. R. G. Pearson, J. Am. Chem. Soc., 94, 8287 (1972).

318. D. M. P. Mingos, J. Chem. Soc. Chem. Comm., 165 (1972).

319. P. S. Braterman, J. Chem. Soc. Chem. Comm., 761 (1972).

320. P. S. Braterman and R. J. Cross, J. Chem. Soc. Dalton, 657 (1972).

321. J. Dalton and C. A. McAuliffe, J. Organometal. Chem., 39, 251 (1972).

322. R. B. King, J. Am. Chem. Soc., 94, 95 (1972).