CHROMIUM, MOLYBDENUM AND TUNGSTEN

ANNUAL SURVEY COVERING THE YEAR 1971

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ABBREVIATIONS

en--ethylenediamine

Ph--phenyl

Me--methyl

Bu^t--tertiary butyl

Et--ethyl

THF--tetrahydrofuran

Ar--aryl

pz--pyrazolyl

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

^nBu--normal butyl

^iPr--isopropyl

bipy--2,2'-bipyridine

o-phen--1,10-phenanthroline

py--pyridine

TCNE--tetracyanoethylene

Bz--benzoyl

Pr--propyl

CONTENTS

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 by Dr. M. I. Bruce, "Organic Reactions of Selected π-Complexes" will be minimized. The reader is referred to the review, "Organometallic Structures-Transition Metals" elsewhere in Annual Surveys for structural determinations of Group VIB organometallic compounds, again reviewed by Dr. M. I. Bruce.

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.

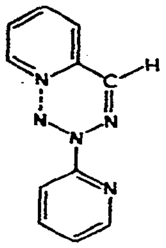
Charkoudian[1] has investigated the electric charge distribution in diacetylanil derivatives of the Group VIB tetracarbonyls by a novel method coupling various electrochemical and spectroscopic (ir, nmr, and esr) techniques. Configurational equilibria studies were carried out by Mattina[2] using the technique of variable temperature proton magnetic resonance spectroscopy on allylic complexes of molybdenum and tungsten. Anderson[3] has examined in detail the barriers to intramolecular interconversions in π-$C_5H_5M(CO)_3H$ (M = Mo, W), π-$C_5H_5Mo(CO)_2LR$ (L = phosphines, R = alkyl groups or halides), π-$C_9H_7Mo(CO)_2LI$, and cycloheptatrienylmolybdenum complexes. The reactions of sulfur dioxide with allylic complexes of π-$C_5H_5Mo(CO)_2P(OC_6H_5)_3$ have been examined by Ross.[4] Painter[5] has investigated the reactions of bis-(π-arene)chromium(0) compounds with boron halides. Gloth[6] has studied the synthesis and chemistry of arene tricarbonyl complexes of chromium and tungsten and Strickland[7], the solvolytic reactivity of π-tricarbonylchromium complexes. Lofquist[8] has studied the kinetics and mechanism of the reaction of $W(CO)_6$ with azide ion to form $W(CO)_5NCO^-$ and N_2, as well as, reactions of halide ions with $Mo(CO)_6$ to form $Mo(CO)_5X^-$ and $Mo(CO)_6$ with amines and phosphines to form the $Mo(CO)_5L$ complexes. The infrared, Raman, and electronic spectra for a variety of phosphine and aliphatic amine derivatives of the Group VIB metal carbonyls have been investigated by Wensky.[9] Terzis[10] has analyzed the Raman intensity data of the two A_{1g} modes in $M(CO)_6$ (M = Cr, Mo, W) which supports the well-accepted notion that π-backbonding is significant in these compounds and increases in the order Mo<Cr<W. Lauver[11] has evaluated correlation functions and spectral moments for the carbonyl stretching vibrations of several metal carbonyls in the condensed phase. Metal carbonyl complexes of a novel bifunctional non-chelating phosphite-phosphine ligand, $P(OCH_2)_3P$ have been synthesized and characterized (ir, nmr, and mass spectrometry) by Allison.[12] The reactions of diphenyl dichalcogenides with several π-cyclopentadienylmetal carbonyls, including those of molybdenum and tungsten, have been investigated by Schermer.[13] Jones[14] has synthesized and characterized Group VIB metal carbonyl complexes of dimethyl methylphosphonite and bis (dimethylamino)methylphosphine, and several cyanophosphine complexes of chromium and molybdenum; while Parrott[15] has studied chromium, molybdenum, and tungsten complexes of 5,5-dimethyl-1,3,2-dioxaphosphorinanes. The preparation and characterization of 1, 8-naphthyridine complexes of Group VIB metal carbonyls and subsequent reactions of these complexes with halide- and alkyl-tin compounds have been described by Reed.[16] The synthesis and attempted deprotonation of the compounds $C_5H_5M(CO)_2(en)^+PF_6^-$ (M = Mo, W) are presented in a dissertation by Stenson.[17] The crystal structure of $(Me_2AsCF(CF_3)CF_2AsMe_2)Mo(CO)_4$ is included in a dissertation by Roberts.[18]

Preparative

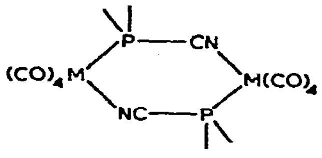
Lewis base and related derivatives. Again this year a large number of papers have dealt with the direct or indirect synthesis and subsequent characterization of simple substitution products of the

Group VIB metal carbonyls. A large variety of substituted Group VIB metal carbonyl compounds of the type cis- and trans-$M(CO)_4L_2$ and fac-$M(CO)_3L_3$ (where M = Cr, Mo, W and L = amine, phosphine, arsine, or stibene) have been prepared from the sodium borohydride catalyzed reaction of the corresponding Lewis base and the hexacarbonyls in boiling ethanol.[19] Brown and Dobson[20] have prepared $M(CO)_5BiPh_3$ (M = Cr, Mo, W) complexes by ultraviolet irradiation of the hexacarbonyls in benzene with triphenylbismuth. These derivatives were found to be much more thermally and solution unstable than the corresponding PPh_3, $AsPh_3$ and $SbPh_3$ complexes. Cotton-Kraihanzel force constants and Graham parameters were reported for these complexes. The addition of tertiary phosphine and arsine chalcogenide derivatives to ultraviolet irradiated THF solutions of $M(CO)_6$ (M = Cr, W) has produced the yellow air-stable crystalline compounds, $M(CO)_5L$ (L = Me_3PS, Me_2PhPS, Ph_3PS, Me_3AsS, and Me_2PhSe). The infrared and nmr spectra of these complexes were discussed.[21] A series of transition-metal carbonyl derivatives of the types $M(CO)_5L$, cis-$Mo(CO)_4L_2$, and cis-$Mo(CO)_3L_3$ (L = Bu^tPF_2 and $Bu^t{}_2PF$; M = Cr, Mo, W) have been prepared.[22] Using infrared and nmr data (^1H, ^{19}F, ^{31}P) the relative π-acceptor ability of the phosphines in the series $PF_{3-n}Bu^t{}_n$ (n = 0-3) was assessed to be $PF_3 > Bu^tPF_2 > Bu^t{}_2PF > Bu^t{}_3P$.

Compounds of the types $M(CO)_4L_2$ and $Mo(CO)_3L_2Y$ have been prepared where M = Cr, Mo, and W, L_2 = Z-pyridine-2-aldehyde, 2'-pyridylhydrazone (I) and Y = PPh_3, $AsPh_3$, $SbPh_3$, Ph_3PSe and SO_2. The E-isomer (180° rotation of $C_5H_5N_2$ about the bridging C=N bond of the Z-isomer) of the hydrazone was stabilized by molybdenum in the complexes $Mo(CO)_4L_2$, $Mo(CO)_3L_2(PPh_3)$ and $Mo(CO)_2L_2I_2$. Compounds such as $Mo(CO)_3(L_2)X_2$, where L_2 = Z-hydrazone and X = Br, I, and $[L_2H_2]Mo(O)X_5$, where X = Cl, Br have been obtained from halogen oxidations of either the E- or Z-isomers of $Mo(CO)_4L_2$.[23] $[M(CO)_4L]_2$ complexes (II), where M = Cr or Mo and L = Ph_2PCN, $PhP(CN)_2$, Me_2PCN, $(EtO)_2PCN$, or $(Me_2N)_2PCN$ have been prepared from reactions of L with $M(CO)_4C_7H_8$ (C_7H_8=norbornadiene). These bridged complexes were found to react further with another molar equivalent of L or L' to give complexes of the type $M(CO)_4L_2$ and $M(CO)_4LL'$. ^1H nmr, infrared, and mass spectral data of the bridged complexes were reported and discussed.[24]



(I)

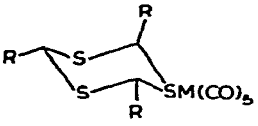


(II)

The synthesis of substituted metal carbonyls of the types $M(CO)_{6-x}L_x$, where M = Cr, Mo, or W and X = 1, 2, or 3 for L = $CH_3P(OCH_3)_2$, and where x = 1 or 2 for L = $CH_3P(N(CH_3)_2)_2$ has been described by Jones and Coskran.[25] An order was proposed for the π-acceptor strength of the ligands: $P(OCH_3)_3 > CH_3P(OCH_3)_2 > (CH_3)_3P$ $CH_3P(N(CH_3)_2)_2 > P(N(CH_3)_2)_3$ which was based on CO stretching frequencies and force constants. P-H and P-P coupling constants observed in the proton nmr spectra of several of these complexes were used to interpret the nature of the metal-phosphorous bond.

Ultraviolet irradiation of $M(CO)_6$ (M = Cr and Mo) in THF with s-trithiane (trimer RCHS) gave the complexes $(RCHS)_3M(CO)_5$ (where M = Cr, R = H and Me; M = Mo, R = Me) (III). The compounds were characterized by their ir spectra.[26] $M(CO)_5(C_7H_5NX)$ (X= NH, O, S, Se) (IV) complexes have been prepared from $M(CO)_5THF$ or by photochemical reactions of $M(CO)_6$ with the benzazole ligands in

THF. In addition, $Mo(CO)_4(C_7H_5NX)_2$ (X = O, S, Se) complexes have been obtained from bicycloheptadienemolybdenum tetracarbonyl and the appropriate benzazole. ^{14}N, ^{1}H nmr and infrared spectral studies indicated the potentially ambidentate ligands to be always coordinated through the nitrogen atom.[27]



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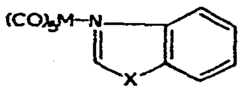
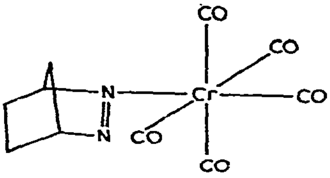


(IV)

2,3-Diazabicyclo[2.2.1]-hept-2-ene was found to displace one CO group from $Cr(CO)_6$ in THF on irradiation to form $(C_5H_8N_2)Cr(CO)_5$ (V). An analogous reaction was observed with $(1,3,5\text{-}Me_3C_6H_3)Cr(CO)_3$. When $Cr(CO)_5(C_5H_8N_2)$ was heated at 80° $Cr_2(CO)_6(C_5H_8N_2)_3$ (three bridging N=N groups), $Cr(CO)_6$, and CO were formed.[28]

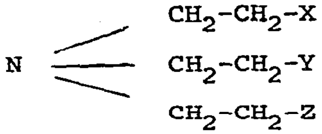


(V)

$(Me_3M)_3Sb$ (M = Ge, Sn) reacted with $M'(CO)_6$ (M' = Cr, Mo, W) in THF under irradiation to afford $(Me_3M)_3SbM'(CO)_5$ complexes in 90-95% yields. NMR and infrared spectral data were presented for these new complexes.[29] Similarly, $(Me_3M)_3PM'(CO)_5$ (M = C, Si, Ge, Sn for M' = Cr; M = C, Ge, Sn for M' = Mo, W), as well as (Me_3Si)-$Ph_2PCr(CO)_5$ and $(Me_3M)_2PhPCr(CO)_5$ (M = Si, Sn) have been prepared by ultraviolet irradiation of the metal hexacarbonyl with the corresponding phosphine in THF solution. The i.r., u.v., ^{1}H nmr, and ^{31}P nmr spectra were reported and discussed.[30]

New anionic metal carbonyl complexes, $M(CO)_5C{\equiv}CR^-$ (M = Cr, Mo, W; R = Me or Ph), were obtained from the photochemical reactions of the metal hexacarbonyls and the acetylide anions in THF. In the case of M = Mo or W, photochemical substitution of a CO ligand in these complexes by PPh_3 occurred. The infrared spectra of these species were consistent with a cis-disubstituted product.[31]

The reactions of the "tripod-like" ligands of the type (VI) containing different combinations of peripheral donor atoms with $M(CO)_6$ (M = Cr, Mo, and W) have been investigated by Bacci and Midollini. The ligands N_2P_2, NOP_2, N_2S_2, and NS_3 behave as tridentate ligands to yield complexes of the form $M(CO)_3L$ which are monomeric and soluble in organic solvents. NP_3 provided insoluble complexes of empirical formula $M(CO)_3NP_3$, one of which was converted at 280° into the complex $M(CO)_2NP_3$ (for M = Mo) where NP_3 acts as a quadridentate ligand. No compounds have been isolated with the N_4 and N_3P ligands.[32]



X = Y = Z = PPh_2 (NP_3)
X = Y = PPh_2, Z = NEt_2 (N_2P_2)
X = Y = PPh_2, Z = OMe (NOP_2)
X = Y = Z = $S[CH(CH_3)_2]$ (NS_3)
X = Y = SMe, Z = NEt_2 (N_2S_2)
X = Y = Z = NEt_2 (N_4)
X = Y = NEt_2, Z = PPh_2 (N_3P)

(VI)

The complexes $M(CO)_5SbH_3$ (M = Cr, Mo, or W) have been prepared in 4-10% yield by reaction of $M(CO)_5L$ (L = fumaronitrile) and SbH_3 in C_6H_6 at 25°. The ir, ^1H nmr, and mass spectra of these complexes are reported. The ligand properties of SbH_3 are discussed in terms of the $\nu(CO)$ force constants and the relative ion intensities in the mass spectra and are compared with those of $M(CO)_5EX_3$ compounds (E = N, P, As; X = H, Ph).[33]

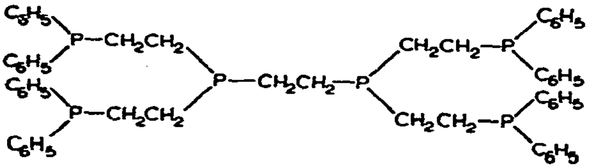
The crystalline, air-stable compounds $(CO)_5M-E(CH_3)_2-M'(CO)_5$ (M = Cr, Mo, W; E = P, As; M' = Mn, Re) were obtained from reaction of the photochemically prepared $(CO)_5ME(CH_3)_2Cl$ complexes and the corresponding $NaM'(CO)_5$ species. Thermal and photochemical decomposition of these complexes resulted in disproportionation into $M(CO)_6$ and $[M'(CO)_4E(CH_3)_2]_2$.[34] In addition, the complexes $(CO)_5M-E(CH_3)-Sn(CH_3)_3$ (M = Cr, W; E = P, As) have been observed to react with the halides $(CH_3)_2E'Cl$ (E' = P, As) to give the complexes $(CO)_5M-E(CH_3)_2E'(CH_3)_2$. These complexes were also formed from reactions of $(CO)_5M-E(CH_3)_2Cl$ with $(CH_3)_2E'-Sn(CH_3)_3$. Photochemical reactions of the $(CO)_5M-E(CH_3)_2-E'-(CH_3)_2$ complexes with $M'(CO)_6$ in THF afforded the dinuclear species $(CO)_5M-E(CH_3)_2-E'(CH_3)_2M'(CO)_5$ (M,M' = Cr, W; E,E' = P, As). Each one of the ten conceivable complexes were prepared and characterized by ^1H nmr spectral measurements. It was also possible to introduce other metal atoms, e.g., $(CO)_5Cr-P(CH_3)_2-P(CH_3)_2$ and $Fe_2(CO)_9$ gave a good yield of $(CO)_5Cr-P(CH_3)_2-P(CH_3)_2-Fe(CO)_4$. Thermolysis of $(CO)_5CrP(CH_3)_2-P(CH_3)_2W(CO)_5$ in benzene led to the production of the diamagnetic complex $(CO)_4Cr[P(CH_3)_2]_2W(CO)_4$, which is proposed to contain two bridging $-P(CH_3)_2-$ units and a Cr-W bond.[35]

A comparative study of the ligands $[(CH_3)_2N]_3E$ (E = P and As) bonded to Group VIB metal carbonyls has been carried out by King and Korenowski. $(tdas)M(CO)_5$ (M = Cr, Mo; tdas=tris(dimethylamino) arsine) were prepared thermally from the hexacarbonyl and tdas; whereas, $LW(CO)_5$ (L = tris(dimethylamino)phosphine(tdp) and (tdas)) were prepared photochemically from $W(CO)_6$ and tdp or tdas. Reactions of <u>trans</u>-$L_2Cr(CO)_4$ (L = tdp and tdas) with carbon monoxide gave

$LCr(CO)_5$. The reactions of tdp and tdas with $C_7H_8M(CO)_4$ (M = Cr, Mo, W; C_7H_8 = norbornadiene), $C_7H_8M(CO)_3$ (M = Cr, Mo, W; C_7H_8= cycloheptatriene), and cis-$(C_6H_8)_2M(CO)_2$ (M = Mo, W; C_6H_8 = 1,3-cyclohexadiene) in hydrocarbon solvents were shown in all cases to involve complete displacement of the coordinated olefin(s) with formation of the cis tdp or tdas complexes. These products were found to be unstable and to undergo further isomerization and decomposition reactions.[36]

The reaction of $M(CO)_6$ (M = Cr, Mo, and W) with molar equivalents of the arsines, ferrocene-1,1'-bis(dimethylarsine) (fdma) and ferrocene-1,1'-bis(diphenylarsine) (fdpa) afforded the complexes $(fdma)M(CO)_4$ and $(fdpa)M(CO)_4$. Prolonged reaction of excess fdma with $Mo(CO)_6$ led to the formation of μ-fdma-$[fdmaMo(CO)_3]_2$ and $(fdma)_2Mo(CO)_3$. The structure of μ-fdma-$[fdmaMo(CO)_3]_2$ is proposed to contain a bridging diarsine and a facial arrangement of donor arsenic atoms, while $(fdma)_2Mo(CO)_3$ is proposed to have one unidentate and one bidentate diarsine with a meridional arrangement of the donor arsenic atoms. The complexes were studied by infrared and ^1H nmr spectroscopy.[37]

Group VIB metal carbonyl complexes of polytertiary phosphines have received much attention. Reactions of the metal hexacarbonyls or their norbornadiene or cycloheptatriene derivatives with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (P_f-P_f-P_f) afforded either (P_f-P_f-P_f)$M(CO)_4$ (M = Cr and Mo) or (P_f-P_f-P_f)$M(CO)_3$ (M = Cr, Mo and W) depending on the reaction conditions. Reaction of $CH_3Mo(CO)_3C_5H_5$ with P_f-P_f-P_f in acetonitrile gave (P_f-P_f-P_f)$[Mo(CO)_2(COCH_3)(C_5H_5)]_3$. Thermal reaction (room temp.) of $C_5H_5Mo(CO)_3Cl$ with P_f-P_f-P_f in benzene gave the cation $C_5H_5Mo(CO)_2(P_f\text{-}P_f\text{-}P_f)^+$; whereas, the reaction in the presence of ultraviolet irradiation provided the carbonyl-free tridentate complex $C_5H_5Mo(P_f{-}P_f{-}P_f)Cl$.[38] Reactions of the metal hexacarbonyls with the tetrateriary phosphines $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ $(P_f{-}P_f{-}P_f{-}P_f)$ and $[(C_6H_5)_2PCH_2CH_2]_3P$ $(P(-P_f)_3)$ in boiling xylene gave (tetraphos)$M(CO)_3$ (M = Cr and Mo) complexes. Reactions of $C_7H_8M(CO)_4$ (C_7H_8 = norbornadiene; M = Cr and Mo), $C_7H_8Mo(CO)_3$ (C_7H_8 = cycloheptatriene), and $(1,3\text{-}C_6H_8)_2M(CO)_2$ (M = Mo and W) with the tetratertiary phosphines afforded (tetraphos)$M(CO)_4$ (M = Cr and Mo), (tetraphos)$Mo(CO)_3$, and $P(-P_f)_3M(CO)_2$ (M = Mo and W), respectively. $CH_3Mo(CO)_3C_5H_5$ was found to react with the tetratertiary phosphines in acetonitrile to give (tetraphos)$[Mo(CO)_2(COCH_3)(C_5H_5)]_4$ derivatives.[39] Reactions of the metal hexacarbonyls $M(CO)_6$ M = Cr, Mo, and W) with $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ $(P_2(-P_f)_4)$ (VII) in boiling toluene or xylene led to the formation of the derivatives $P_2(-P_f)_4[M(CO)_3]_2$ (M = Cr, Mo, and W). $C_7H_8M(CO)_4$ (M = Cr and Mo) was found to react with $P_2(-P_f)_4$ in benzene at room temperature to give $P_2(-P_f)_4M(CO)_4$ (M = Cr and Mo). Analogous to the reactions of the other polytertiary phosphines, $P_2(-P_f)_4$ reacted with $CH_3Mo(CO)_3C_5H_5$ in acetonitrile at room temperature to give $P_2(-P_f)_4[Mo(CO)_2(COCH_3)(C_5H_5)]_6$.[40]



(VII)

$Ni(saen)M'(CO)_4$ adducts {where M' = Mo, W and saen = N,N'-ethylenebis(salicylideneiminato)} were obtained from the reaction of the Schiff-base complex, Ni(saen), and the metal hexacarbonyls. The structure of these was proposed to be of approximately C_{2v}

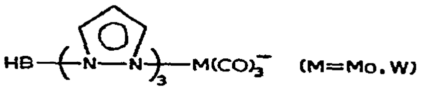
symmetry as indicated by four ir-active absorptions assigned to the terminal CO stretching vibrations. These absorptions were, however, observed at unusually low frequencies, as low as 1630 cm^{-1} in the tungsten derivative.[41] Similarly, novel heteronuclear transition metal complexes having the general formula $(L\text{-}L)M'(SR)_2M(CO)_4$ [L-L = 1,2-bis-(diphenylphosphine)ethane, o-phenylenebis(diethylarsine); M' = Pd, Pt; R = Me, Ph; M = Cr, Mo, W] have been prepared from the corresponding $L\text{-}LM'(SR)_2$ and (norbornadiene)$M(CO)_4$ compounds. Infrared and diffuse reflectance electronic spectral studies indicate the $L\text{-}LM'(SR)_2$ complexes to be acting as chelating disulfide ligands. There was no evidence for metal-metal bonding in these complexes.[42]

$M(CO)_6$, where M = Cr, Mo, and W, was found to react with cis-1,2-bis(dimethylarsino)ethylene (cis-edas) to afford the complexes $M(CO)_4$(cis-edas). The complexes were characterized by means of infrared, nmr, and mass spectroscopy. An improved method for the preparation of $M(CO)_4$(das) [M = Cr, Mo, W; das = o-phenylenebis(dimethylarsine)] was also reported.[42] However, when $Cr(CO)_5$(dam) [dam = $Ph_2AsCH_2AsPh_2$] or stoicheiometric amounts of $Cr(CO)_6$ and (dam) were heated in decane the orange diamagnetic complex, $Cr(CO)_2$(dam), was obtained.[44] A crystal structure analysis of this complex indicated the two carbonyl groups and one arsenic of the (dam) ligand to occupy three mutually cis octahedral coordination sites with the remaining sites being occupied by one phenyl group attached to the second arsenic of the (dam) ligand.

Jetz and Graham have irradiated benzenechromium tricarbonyl in the presence of Cl_3SiH to form the moderately air-stable hydridotrichlorosilyl(π-benzene)-dicarbonylchromium. The structure of the complex was inferred from the relative intensities of the CO stretching bands to be a distorted square-pyramidal structure with the benzene in the apical position and the carbonyl groups mutually cis to one another.[45] Nesmeyanov and coworkers[46] have found that triferrocenyl phosphine reacts with $C_6H_6Cr(CO)_3$ in C_6H_6-hexane under ultraviolet irradiation to afford $C_6H_6Cr(CO)_2$-$[P(C_5H_4FeC_5H_5)_3]$.

Treatment of bis(benzene)molybdenum with tertiary-phosphines or -phosphites afforded the compounds $(C_6H_6)MoL_3$ (where L = $PPhMe_2$, PPh_2Me, $P(OMe)_3$, $PPh_2(OMe)$, $P(OPh)_3$).[47] When L = PPh_2Me or $PPhMe_2$ the compounds are basic and were readily protonated to afford the hydrides $[(C_6H_6)MoL_3H]^+$.

Trofimenko[48] has studied reactions of $HB(3,5-(CH_3)_2Pz)_3M(CO)_3^-$ (VIII) with either $ArSO_2Cl$ or ArSCl to yield the stable monomeric derivatives $HB(3,5-(CH_3)_2pz)_3M(CO)_2SAr$ (where M = Mo, Ar = $p-CH_3C_6H_4$, $p-BrC_6H_4$, $p-ClC_6H_4$, and C_6H_5; and M = W, Ar = $p-ClC_6H_4$). The selenium analog was prepared from reaction with $(C_6H_5Se)_2$ and bromine. $HB(3,5-(CH_3)_2pz)_3Mo(CO)_3^-$ was reacted with aryldiazonium salts to form $HB(3,5-(CH_3)_2pz)_3Mo(CO)_3Ar$ compounds; while thionyl chloride was found to produce $HB(3,5-(CH_3)_2pz)_3MoCl_2O$. Nitrosation of $HB(3-5(C_2H_5)_2pz)_3Mo(CO)_3^-$ gave $HB(3,5-(C_2H_5)_2pz)_3Mo(CO)_2NO$.



(VIII)

B,B,B-Trimethyl-N,N,N-triethylborazene- and B,B,B-triethyl-N,N,N-trimethylborazene-molybdenumtricarbonyl have been prepared in low yields starting with the borazene derivatives and either cis-$(CH_3CN)_3Mo(CO)_3$ or $Mo(CO)_6$ in the presence of ultraviolet irradiation. The molybdenum complexes are generally less stable than the previously prepared chromium derivatives and react with

Lewis bases by cleavage of the borazene-metal bond. The infrared spectra illustrate a strong similarity of the borazene-metal bonds in the molybdenum and chromium derivatives.[49] A crystal-structure analysis of (hexaethylborazene)$Cr(CO)_3$[50] indicates a similar donor/acceptor behavior of benzene and borazene on the basis of the Cr-C distances.

Group VIB halogenmetalpentacarbonyl complexes have been employed as reagents in several preparations. Reaction of the thallium(I) complex of ttas (monothiothenoyltrifluoroacetone) with $M(CO)_5Cl^-$ (M = Cr, Mo, W) anions in diglyme at room temperature has afforded diamagnetic $M(CO)_5ttas^-$ complexes in which the ttas acts as a monodentate sulfur donor. At higher temperatures the $M(CO)_5ttas$ species eliminate another CO to form the highly unstable $M(CO)_4ttas^-$ complexes in which the ligand acts as a bidentate sulfur-oxygen donor $Et_4N[MoCl(CO)_2(maleimide)_3]$ has been prepared from maleimide and $Et_4N[Mo(CO)_5Cl]$ in refluxing THF. The Li salt was similarly produced using diglyme in place of THF. Reaction of $Et_4N[Mo(CO)_5Cl]$ with p-benzoquinone for 16 hr at 20° in THF yielded $Et_4N[MoCl(C_6H_4O_2)$ Similar complexes of tungsten with maleic anhydride were produced.[52] Mono- and bis-isonitrile metal complexes have been found to be useful as fuel additives and in the production of metallic films. Complexes of these types were prepared from $[Et_4N][M(CO)_5I]$ (M = Cr, Mo, W) and isonitriles in THF at room temp. (Cr, Mo) or at 45° (W).[53] Alper[54] has investigated the reactions of molybdenum and tungsten hexacarbonyl with diphenyliodonium chloride, bromide, and iodide which gave the air-stable halopentacarbonylmetal anions, $(C_6H_5)_2I^+[M(CO)_5X]^-$(X = Cl, Br, I; M = Mo, W).

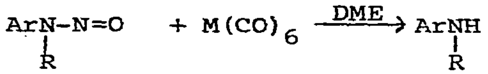
Treatment of the N-methylpyridinium salt of $[Mo(CO)_5I]^-$ with $(CH_2)_2PH$ in CH_2Cl_2 has resulted in formation of $[(CH_2)_2PH]Mo(CO)_5$.

$[(CH_2)_2PH]_2Mo(CO)_4$ and $[(CH_2)_2PH]_3Mo(CO)_3$ have also been prepared from $(CH_2)_2PH$ and (norbornadiene)$Mo(CO)_4$ and (cycloheptatriene)$Mo(CO)_3$, respectively. The complexes were characterized by analysis and ^1H and ^{31}P nmr spectra. $[(CH_2)_2PH]Mo(CO)_5$ reacted with KPH_2 to form $[(CH_2)_2PMo(CO)_5]^-$ and phosphine. The $[(CH_2)_2PMo(CO)_5]^-$ anion afforded $[(CH_2)_2PSiMe_3]Mo(CO)_5$ when reacted with Me_3SiCl.[55] Similarly, $PH_3Mo(CO)_5$ was deprotonated by KPH_2 in dimethyl ether to yield the yellow salt $K[PH_2Mo(CO)_5]$. This salt reacted with excess $PH_3Mo(CO)_5$ to yield the binuclear anion, $[(CO)_5MoPH_2Mo(CO)_5]^-$; with CH_3Cl to give $CH_3PH_2Mo(CO)_5$; and with Me_3SiCl or acetylchloride to afford a mixture of products $R_nPH_{3-n}Mo(CO)_5[R = (CH_3)_3Si$ or $CH_3CO]$. $CH_3PH_2Mo(CO)_5$ was also deprotonated by KPH_2 to yield the anion $[CH_3PHMo(CO)_5]^-$ which formed the bridged anion, $[(CO)_5MoPH(CH_3)Mo(CO)_5]^-$, in excess $CH_3PH_2Mo(CO)_5$.[56]

Cis-$[Mo(CO)_2(diphos)_2]$ has been found to react with $NOPF_6$ in CH_2Cl_2 to afford trans-$[Mo(CO)_2(diphos)_2]PF_6$ initially, followed by isomerization to the cis-$[Mo(CO)_2(diphos)_2]PF_6$ isomer. Treatment of cis- or trans-$[Mo(CO)_2(diphos)_2]PF_6$ with $NOPF_6$ in nitromethane led to the formation of the stable dipositive cationic salt cis-$[Mo(CO)_2(diphos)_2](PF_6)_2$.[57] Alternatively, the cation trans-$[Mo(CO)_2(diphos)_2]^+$ has been prepared by aerial oxidation of cis-$[Mo(CO)_2(diphos)_2]$ in dilute perchloric acid in THF. In contrast with the molybdenum derivative, the neutral trans species of chromium was shown to exist, $[Cr(CO)_2(diphos)_2]$, and to be in equilibrium with the trans chromium(I) cation in solution. $[Cr(CO)_2(diphos)_2]ClO_4$ was isolated upon addition of sodium perchlorate to the equilibrium mixture in dichloromethane.[58]

P-N bond cleavage in $Mo(CO)_5P(NMe_3)_3$ and trans-$Mo(CO)_4[P(NMe_3)_3]_2$ with HX acids (X = Cl, Br, I) has been employed to prepare $Mo(CO)_5PX_3$ (X = Cl, Br, I) and trans-$Mo(CO)_4(PCl_3)_2$ complexes. The reactivity of the halogen hydracid HX increased in the series HCl < HBr < HI.[59]

Alper[60] has studied the reactions of the Group VI metal carbonyls with nitrosamines. $M(CO)_6$ (M = Cr, Mo, W) were found to be useful reagents for converting aromatic nitrosamines into secondary amines (eq. 1). $Mo(CO)_6$ was found to be more effective

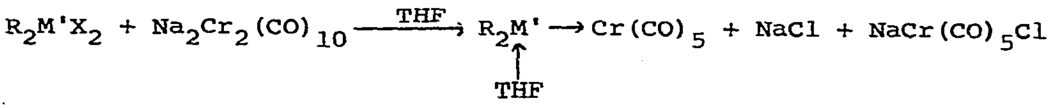


$$\underset{\displaystyle R}{ArN}\text{-}N{=}O + M(CO)_6 \xrightarrow{DME} \underset{\displaystyle R}{ArNH} \qquad (1)$$

(M = Cr, Mo, W), DME = 1,2-dimethoxyethane.

in this process than $Cr(CO)_6$ or $W(CO)_6$. Treatment of non-aromatic nitrosamines with $M(CO)_6$ gave mono- and di-substituted amine metal carbonyl complexes. A mechanism involving attack of the oxygen atom of the nitrosamine on the metal atom has been proposed for these reactions.

Dinuclear Group VIB carbonyl anions have been used in the preparation of several novel complexes. Marks has reported synthetic results on pentacarbonylchromium complexes of dialkylgermylenes and -stannylenes from the low temperature (-78°) reaction of $Na_2Cr_2(CO)_{10}$ (eq. 2). These complexes were isolated as extremely air-sensitive, pale-yellow, tetrahydrofuran adducts. The structural



$$R_2M'X_2 + Na_2Cr_2(CO)_{10} \xrightarrow{THF} \underset{\displaystyle \uparrow \atop THF}{R_2M'} \rightarrow Cr(CO)_5 + NaCl + NaCr(CO)_5Cl$$

M' = Ge, R = CH_3
M' = Sn, R = CH_3 or t-C_4H_9.

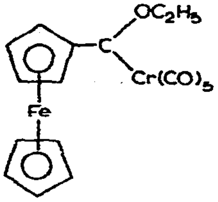
formulation was supported by infrared and nmr spectral data.[61] The preparation, structure, and bonding of a new type of metal cluster system, $[M_2Ni_3(CO)_{16}]^{-2}$ (M = Cr, Mo, and W), obtained from the reaction of $Ni(CO)_4$ and $M_2(CO)_{10}^{-2}$ have been reported by Ruff, White and Dahl.[62] These relatively air-stable, diamagnetic complexes are shown to be nonconformist to the noble gas rule and to all be of the same basic geometry. The detailed atomic parameters of these anions have been unambiguously established from three-dimensional X-ray diffraction studies of $[(C_2H_5)_4N]_2[W_2Ni_3(CO)_{16}]$ and $[PPN]_2$ $[M_2Ni_3(CO)_{16}]$ (where M = Mo, W; and PPN = bis (triphenylphosphine) iminium cation).

Reaction of π-allyldicarbonylmolybdenum complexes with PPh_3 and P^nBu_3 was found to produce, along with the corresponding phosphonium salts, tetrasubstituted molybdenum carbonyls cis-$(PR_3)_2L_2$-$Mo(CO)_2$ (L = MeCN; R = Ph, ^{n}Bu). Ligand substitution yielded the unstable dicarbonyls, cis-$(PR_3)_2(R^1N{:}CRCR{:}NR^1)(CO)_2Mo$ (R = H; Me; R^1 = Me, cyclohexyl, p-HOC_6H_4, ^{n}Bu, ^{i}Pr, p-$CH_3OC_6H_4$, NH_2, Me_2N). Disproportionation reactions of the cis-$(Ph_3P)_2(MeCN)_2$-$Mo(CO)_2$ complex led to the formation of cis- and trans-$(Ph_3P)_2$-$(MeCN)Mo(CO)_3$ and cis-(L-L)$(PPh_3)Mo(CO)_3$ (L-L = bipy, o-phen). The CO stretching frequencies, as well as, the mechanism of allyl elimination were discussed.[63]

Tetraphenylporphines(TPP) complexes of chromium and molybdenum have been prepared from thermal reactions of TPP and $Cr(CO)_6$ or $Mo(CO)_6$ by Fleischer and Srivastava.[64] These metalloporphines were characterized by magnetic susceptibility measurements and their esr, infrared, and visible absorption spectra.

The binuclear complexes $[(PhR)Mo(\pi\text{-}C_3H_5)Cl]_2$ (R = H or Me) have been isolated from treatment of bis-arene molybdenum with allyl chloride. Treatment of $[(PhR)Mo(\pi\text{-}C_3H_5)Cl]_2$ with tertiary phosphines resulted in cleavage of the chloro-bridge with formation of the complexes $(PhR)Mo(\pi\text{-}C_3H_5)$ $(PR^1_3)Cl$ (R^1_3 = Me_2Ph, $MePh_2$, or Ph_3). Treatment of the new compound $C_6H_6Mo(\pi\text{-}C_3H_5)(PPh_3)Cl$ with $NaBH_4$ led to the formation of $C_6H_6Mo(PPh_3)_2H_2$ which reacted with nitrogen gas to give the binuclear dinitrogen complex $[C_6H_6Mo(PPh_3)_2]_2N_2$.[65] Further reactions of the arene-molybdenum-π-allyl complex, $[PhRMo(\pi\text{-}C_3H_5)Cl]_2$, with a variety of reagents have been described.[6

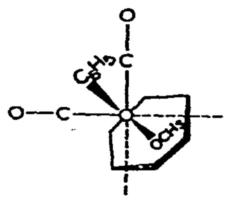
Carbene and related complexes. Several new carbene complexes have been prepared from the reaction of metal carbonyls or substituted metal carbonyls with organolithium reagents followed by alkylation. Moser, Fischer and Rausch have prepared the complexes $Cr(CO)_5C(OR)C_6Cl_5$ (R = Et, Me) and $Cr(CO)_5C(OEt)(ferrocenyl)$ (IX) from the corresponding reactions of pentachlorophenyllithium and ferrocenyllithium with chromium hexacarbonyl followed by alkylation with trialkyl oxonium tetrafluoroborates. Infrared spectral studies of the carbonyl stretching frequencies in these new carbene complexes were in agreement with the known electron-withdrawing and electron-releasing nature of the pentachlorophenyl and ferrocenyl groups, respectively. A small quantity of the bridging dicarbene species $(CO)_5Cr(OEt)C(C_6Cl_4)\text{-}C(OEt)Cr(CO)_5$ was obtained in the reaction of $Cr(CO)_6$ and (pentachlorophenyl)lithium; presumably from the impurity, $C_6Cl_4Li_2$.[67]



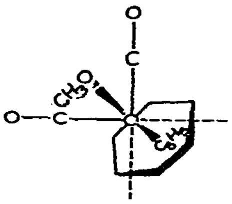
(IX)

The preparation of a series of ring-substituted complexes $(CO)_5CrC(OCH_3)R$ (R = $p\text{-}(CH_3)_2NC_6H_4$, $p\text{-}CH_3OC_6H_4$, $p\text{-}CH_3C_6H_4$, $p\text{-}FC_6H_4$, $p\text{-}ClC_6H_4$, $p\text{-}BrC_6H_4$, $p\text{-}CF_3C_6H_4$, $m\text{-}(CH_3)_2NC_6H_4$, $m\text{-}CH_3OC_6H_4$, $m\text{-}ClC_6H_4$, $m\text{-}CF_3C_6H_4$, $o\text{-}CH_3OC_6H_4$, $o\text{-}CF_3C_6H_4$, $2,4,6\text{-}(CH_3)_3C_6H_2$, 2,6-$(CH_3O)_2C_6H_3$) and also (methoxy-1-naphthylcarbene)-,and (methoxybenzylcarbene)pentacarbonylchromium has been described by Fischer and coworkers.[68] The effect of the substituent on the ring has been studied through carbonyl stretching frequencies (and force constants), proton nmr, electronic spectra and ionization potentials. The rotational energy of activation about the $C_{carbene}$ $-OCH_3$ bond in these complexes has been determined by temperature dependent proton nmr, with E_a ranging between 11.5 - 13.8 Kcal/mole depending on the ring-substituent. Further details of these studies, including solvent effects on the <u>cis</u>-<u>trans</u> equilibriumprocess has appeared in a subsequent publication by Kreiter and Fischer.[69]

The complexes π-Ar$(CO)_2CrC(OCH_3)C_6H_5$ (Ar = C_6H_6, $CH_3C_6H_5$ 1,4-$(CH_3)_2C_6H_4$, and 1,3,5-$(CH_3)_3C_6H_3$) have been synthesized and are shown by their infrared spectra in the carbonyl stretching region to exist in two isomeric forms due to hindered rotation about the metal-carbene bond. These isomeric forms are believed to be structures (X <u>A</u> and <u>B</u>).[70]



(X)A



(X)B

Phenyllithium has been shown to add to one of the two carbonyl groups in $(\pi-C_5H_5)M(CO)_2NO$ (M = Cr, Mo, W) to form acylmetallates which upon alkylation result in the formation of stable, volatile, diamagnetic carbene complexes, $(\pi-C_5H_5)M(CO)(NO)[C(OCH_3)C_6H_5]$. $(\pi-C_5H_5)Mo(CO)(NO)[C(OCH_3)C_6H_5]$ reacts with $HN(CH_3)_2$ to afford $(\pi-C_5H_5Mo(CO)(NO)[C(N(CH_3)_2)C_6H_5]$. When the $(\pi-C_5H_5)Mo(CO)(NO)$-$[C(R')C_6H_5]$ (R' = OCH_3, OC_2H_5, $N(CH_3)_2$) complexes were irradiated in the presence of iron pentacarbonyl the carbene ligands were found to transfer to the iron atom to give the corresponding $(CO)_4Fe$-carbene complexes and $(\pi\text{-}C_5H_5)Mo(CO)_2NO$.[71]

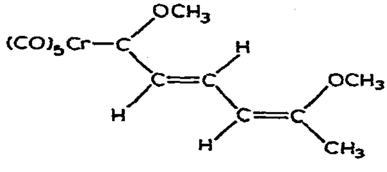
The acyloxy-carbene complex, $MeOC{\cdot}O{\cdot}(Fu)CCr(CO)_5$, has been prepared from the reaction of acetylchloride with $Me_4N[(Fu){\cdot}CO{\cdot}Cr(CO)_5]$ (Fu = 2-furyl).[72,73] Reactions of the <u>carbene</u> complex with a variety of reagents have been examined, including: (i) ROH, (ii) PhONa, (iii) RSH, (iv) RR'NH, (v) $PhC{\equiv}CLi$, and (vi) HN_3 resulting in formation of $(CO)_5CrC(Fu)OR$ (R = Me, Et); $(CO)_5CrC(Fu)OPh$; $(CO)_5CrC(Fu)SR$ (R = Et, Ph, COMe); $(CO)_5CrC(Fu)NRR'$ (R = R' = H; RR' = $(CH_2)_4$; R = Me, R' = Ph; R = H, $o\text{-}ClC_6H_4$; and R = R' = Ph); $(CO)_5CrC(Fu)C{\equiv}CPh$; and $(CO)_5CrNCFu$ respectively.

Chromium carbonyl derivatives containing Lewis Bases, including several of the carbene complexes prepared above, have been oxidized in dichloromethane by one-electron transfer reactions employing a rotating platinum electrode. The half-wave potentials, $E_{1/2}$, for the oxidation of $Cr(CO)_5L$ complexes (L = Lewis bases) were observed to be dependent on the π-acceptor/σ-donor abilities of L. In the carbene complexes, $Cr(CO)_5C(X)Y$, the oxidation potentials were significantly dependent upon the nature of X and Y. For Y = 2-furyl, the $E_{1/2}$ values decreased in the order X = OR > SR > NR_2 > O^-, which was taken as being indicative of a decrease in π-acceptor ability of the carbene ligands.[74]

The aminophenylcarbene complexes $Cr(CO)_5C(NHR)C_6H_5$ have been prepared from nearly quantitative reactions of $Cr(CO)_5C(OCH_3)C_6H_5$ with the primary amines RNH_2 (R = $n\text{-}C_4H_9$, C_6H_{11}, $CH_2C_6H_5$, C_6H_5). The reaction of $Cr(CO)_5C(OCH_3)C_6H_5$ with pyridine led to the formation of $Cr(CO)_5py$ and <u>cis</u>-$Cr(CO)_4(py)_2$ which is proposed to occur <u>via</u> a mechanism involving initial cleavage in two parallel reactions of either a metal-carbene or metal-carbonyl bond.[75] Similarly, the preparation of the yellow diamagnetic (aminoarylcarbene)-pentacarbonylchromium(O) complexes, $(CO)_5CrC(NH_2)R$ (R = p-$(CH_3)_2NC_6H_4$, p-$CH_3OC_6H_4$, p-$CH_3C_6H_4$, p-ClC_6H_4, p-BrC_6H_4, m-$CH_3OC_6H_4$, and m-ClC_6H_4) from $(CO)_5CrC(OCH_3)R$ and NH_3 has been reported by Fischer and Kollmeier. A linear-relationship between the CO stretching force constants in these complexes and the Jaffe σ-substituent constants was observed.[76]

The reaction of (methoxyphenylcarbene)pentacarbonylchromium(O) with 1-aminoethanol to yield $(CO)_5CrC(N{:}CHCH_3)C_6H_5$ and $(CO)_5CrC(NH_2)$-C_6H_5 has been studied by Knauss and Fischer.[77] The reaction proceeds via interaction of the carbene complex with the two alternative dissociation products of 1-aminoethanol, [$NH{=}CHCH_3$] and NH_3 in a manner analogous to other reactions of amine ligands with the bound methoxyphenylcarbene ligand.

(Methoxymethylcarbene)pentacarbonylchromium(O) has been found to react with the reducing agent $LiAlH[OC(CH_3)_3]_3$ in tetrahydrofuran at room temperature to afford [(4-methoxy-4-methylbutadienyl-1,3)methoxycarbene]pentacarbonylchromium(O) (XI). The structure of this complex was assessed by infrared, nmr, and mass spectral analyses.[78]



(XI)

Cotton and Lukehart[79] have reported the preparation of a cyclic 2-oxocarbene cation, cis and trans-(pentahaptocyclopentadienyl)(dicarbonyl)(triphenylphosphine)(2-oxacyclopentylidene) molybdenum, from (pentahaptocyclopentadienyl)(tricarbonyl)(3-bromon-propyl)molybdenum and triphenylphosphine. It appears that the reaction involves the initial attack of $P(C_6H_5)_3$ on molybdenum to form the acyl derivative $BrCH_2CH_2CH_2C(O)Mo(h^5-C_5H_5)(PPh_3)(CO)_2$ in the *cis* configuration, which spontaneously undergoes internal nucleophilic attack of the acyl oxygen atom on the γ-carbon atom to displace Br^- and generate the *cis* form of the cation. This *cis* isomer was shown to rearrange unimolecularly to afford an equilibrium mixture (Keq = 42 ± 5, [trans]/[cis] at 27°) with the *trans* isomer, with a rate constant of 1.3×10^{-5} sec^{-1} at 27°. The presence of the coordinated carbene, $:\overline{COCH_2CH_2CH_2}$, was demonstrated by infrared and proton nmr and by formation of γ-butyrolactone when the complex was treated with pyridine N-oxide.

The molybdenum-carbene complex, $[(\pi-C_5H_5)Mo(CO)_2\{P(C_6H_{11})\}-\{C(OEt)Me\}]^+BF_4^-$, has been prepared by treatment of the molybdenum-acyl complex, $(\pi-C_5H_5)Mo(CO)_2\{P(C_6H_{11})_3\}C(O)Me$, with triethyloxonium tetrafluoroborate.[80]

In an unsuccessful attempt to insert difluorocarbene into the tin-tungsten bond, $(CH_3)_3SnCF_3$ and $(CH_3)_3SnW(CO)_3(\pi-C_5H_5)$ were heated at 115° for 17 hours leading to the production of $CF_3(CH_3)_2Sn$ $(CO)_3(\pi-C_5H_5)$.[81]

π-Cyclopentadienyl complexes. - The preparation and properties of the complexes $(\pi-C_5H_5)_2Ti(SR)_2M(CO)_4$ (R = Me or Ph; M = Cr, Mo or W) have been reported by Braterman and coworkers.[82] These heterodinuclear transition-metal complexes containing bridging organothioligands were prepared according to reaction (3) at room temperature in toluene.

$$(\pi-C_5H_5)_2Ti(SR)_2 + (norbornadiene)M(CO)_4 \rightarrow (\pi-C_5H_5)_2Ti(SR)_2M(CO)_4 + norbornadiene \qquad (3)$$

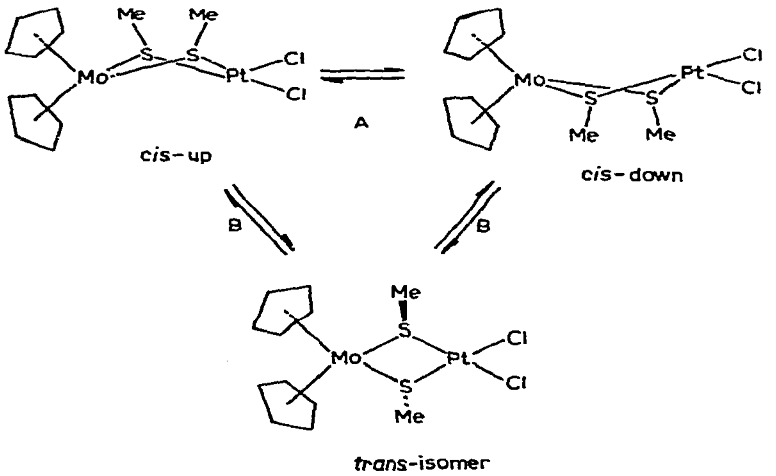
A crystallographic study has been carried out on the $(\pi-C_5H_5)_2-$

$Ti(SMe)_2Mo(CO)_4$ derivative which indicates the TiSMoS ring to be planar (XII).[83] However, nmr data indicate that a small quantity of the transoid isomer is also present in solution. The i.r., ^1H nmr, and electronic spectra of these compounds provide evidence for metal-metal interaction. The interaction may be regarded as partial σ-donation of electrons in the appropriate $d(t_{2g})$ orbital of M to a vacant orbital of titanium.

Similar dithiol derivatives, $(\pi-C_5H_5)_2M(SR)_2$, have also been shown to react with cobalt(II) halides or $Co(SCN)_2$ to yield green, crystalline, air-and thermally stable products of the form $(\pi-C_5H_5)_2M-(SR)_2CoX_2$ (M = Mo, W; R = Me, Et. Bu^n; X = Cl, Br, I, SCN). Infrared and electronic properties of these complexes have been determined. In addition, treatment of anhydrous ferrous chloride in dry tetrahydrofuran with $(\pi-C_5H_5)_2M(SR)_2$ (M = Mo, W; R = Me, Bu^n) affords $(\pi-C_5H_5)_2M(SR)_2FeCl_2$ complexes. Mössbauer spectra of these iron complexes were determined at 77°K yielding values for the isomer shift ($mm\text{-}s^{-1}$) and quadrupole splitting ($mm\text{-}s^{-1}$) of 0.91 and 3.56 (R = Me) and 0.81 and 2.77 (R = Bu^n), respectively. These values are of the order of magnitude generally found for tetrahedral ferrous complexes.[84] The crystal and molecular structure of $(\pi-C_5H_5)_2Mo(SBu^n)_2FeCl_2$ has been determined. The molybdenum and iron atoms are shown to be linked by a double sulfide bridge with a Mo-Fe distance of 3.66Å. The iron is indeed in a tetrahedral environment.[85]

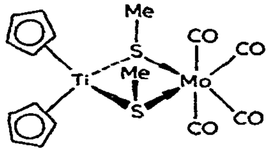
In addition, the complexes $(\pi-C_5H_5)_2M(SMe)_2$ (M = Mo, W) were observed to act as bidentate, four-electron ligands and to form diamagnetic complexes of stoicheiometries $[\{(\pi-C_5H_5)_2M(SMe)_2\}_2M']^{+2}X^{-2}$ (M' = Ni, Pd, Pt), $(\pi-C_5H_5)_2M(SMe)_2M''Cl_2$ (M" = Pd, Pt), and $[(\pi-C_5H_5)_2M(SMe)_2RhL_2]^+PF_6^-$ [L_2 = $(CO)_2$, cyclo-octa-1,5-diene or

$(\pi\text{-allyl})_2]$. The low-temperature ^1H nmr spectra of $(\pi\text{-}C_5H_5)_2M(SMe)_2M'Cl_2$ (M = W, M' = Pt and M = Mo, M' = Pd) in liquid SO_2 suggest that there is an overall cis-up to cis-down equilibrium (eq. 4). This equilibrium may be achieved either by a symmetrical, concerted inversion (route A) or via an intermediate trans-methyl isomer (route B). If route B is correct then the equilibrium concentration of the trans-methyl intermediate must be very small since no nmr evidence for this species in solution at any temperature was observed.[85]

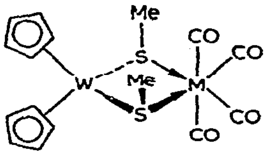


(4)

Crystal structure data have been obtained for $(\pi\text{-}C_5H_5)_2W(SPh)M(CO)_4$ (M = Cr, Mo, and W) complexes indicating all of these to have similar geometries, with a planar $W(S)_2M$ ring system(XIII) analogous to that found in $(\pi\text{-}C_5H_5)_2Ti(SR)_2M(CO)_4$ compounds.[87]



(XII)



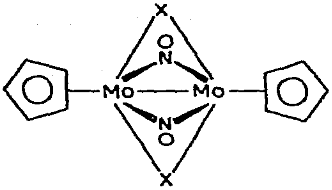
(XIII) (M = Cr, Mo, W)

The syntheses and X-ray structural analyses of the mixed metal-sulfur complexes, $[Re_2Mo(h^5\text{-}C_5H_5)(CO)_8](S)[SMo(h^5\text{-}C_5H_5)(CO)_3]$[88] and $[Mo_3(h^5\text{-}C_5H_5)_3S_4]^+[Sn(CH_3)_3Cl_2]^-$,[89] have been reported by Dahl and coworkers. Both compounds are air-stable and diamagnetic.

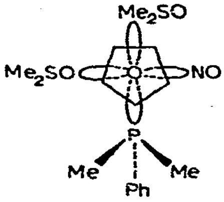
James and McCleverty[90] have reported the syntheses and chemistry of the related binuclear complexes, $[(\pi\text{-}C_5H_5)Mo(NO)X_2]_2$, $[(\pi\text{-}C_5H_5)Mo(NO)X]_2$, and $[(\pi\text{-}C_5H_5)Mo(NO)(I)(SCH_2Ph)]_2$ (X = I, SCH_2Ph or SPh). The structures of $[(\pi\text{-}C_5H_5Mo(NO)X_2]_2$ and $[(\pi\text{-}C_5H_5Mo(NO)(I)(SCH_2Ph)]_2$ have been shown by i.r. and mass spectral studies to be similar, and probably to contain two bridging groups X and two terminal X and NO groups. On the other hand the structure of $[(\pi\text{-}C_5H_5)Mo(NO)X]_2$ may contain only bridging groups, X and NO, and a Mo-Mo bond (XIV). The mixed ligand species, $[(\pi\text{-}C_5H_5)Mo(NO)(I)(SCH_2Ph)]_2$, was shown spectrally to exist as two isomers, one of which contains bridging SCH_2Ph groups and terminal I atoms.

Treatment of $[\{(\pi\text{-}C_5H_5)Mo(NO)I_2\}_2]$ with L, where L = PMe_2Ph, $AsMe_2Ph$, $AsPh_3$, or p-$MeOC_6H_4NC$, in acetone has been shown to readily afford $[(\pi\text{-}C_5H_5)Mo(NO)I_2L]$. $[(\pi\text{-}C_5H_5)Mo(NO)IL(S)]^+$ (S = Me_2CO, Me_2SO) and $[(\pi\text{-}C_5H_5)Mo(NO)L(Me_2SO)_2]^{+2}$ were formed when $[(\pi\text{-}C_5H_5)Mo(NO)I_2L]$ complexes were dissolved in acetone or dimethyl sulfoxide solvents as indicated by conductance measurements. ^1H nmr spectra support this interpretation of solvated species. $[(\pi\text{-}C_5H_5)Mo(NO)L(Me_2SO)_2]^{+2}$ (L = PMe_2Ph and $AsMe_2Ph$) were shown to exist as <u>cis</u> and <u>trans</u> isomers from the form of their methyl proton resonances (XV A, B).[91]

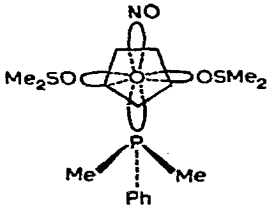
The complexes $[(\pi\text{-}C_5H_5)_2Mo(SRMe)X]^+PF_6^-$ (R = Me, X = Cl or Br; and R = allyl, X = Cl) have been prepared (eq. 5). These complexes react with ligands L, forming the complexes $[(\pi\text{-}C_5H_5)_2$-



(XIV)



(XV) A



(XV) B

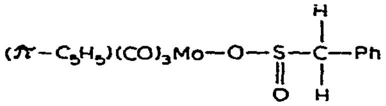
MoLX]$^+$PF$_6^-$ (L = PPh$_3$, P(OPh)$_3$, PPh$_2$H, diphos, P(Bu^n)$_3$ or pyridine, X = Br; and L = PPh$_3$ or P(OPh)$_3$, X = Cl or I) (eq. 6). Several tungsten analogs of these complexes were similarly prepared. The complexes [(π-C$_5$H$_5$)$_2$M(PR$_3$)Br]$^+$PF$_6^-$ (M = Mo, R = Ph; and M = W, R = OMe or Ph) when treated with sodium borohydride afford the air-sensitive hydrides [(π-C$_5$H$_5$)$_2$Mo(PR$_3$)H]$^+$PF$_6^-$ in good yields.[92]

$$\begin{tikzcd}
(\pi\text{-}C_5H_5)_2Mo(SMe)_2 + RX \arrow[r] & {[(\pi\text{-}C_5H_5)_2Mo(SRMe)X]^+X^-} \arrow[d, "NH_4PF_6"] \\
 & {[(\pi\text{-}C_5H_5)_2Mo(SRMe)X]^+PF_6^-} \qquad (5)
\end{tikzcd}$$

$$[(\pi\text{-}C_5H_5)_2Mo(SRMe)X]^+PF_6^- \xrightarrow[-SRMe]{+L} [(\pi\text{-}C_5H_5)_2Mo(L)X]^+PF_6^- \qquad (6)$$

Treatment of the complex [(π-C$_5$H$_5$)$_2$Mo(SMe$_2$)Br]$^+$PF$_6^-$ with amines R^{1}R^{2}CHNH$_2$ (R^{1}R^{2}CH = Me, Et, Pr^i, Bu^t, Ph, and PhCH$_2$) in water afford the amine-hydrides cations [(π-C$_5$H$_5$)$_2$Mo(NH$_2$CHR^{1}R^2)H]$^+$ together with aldehydes or ketones, R^{1}R^{2}CO (R^2 = H or alkyl group).[93]

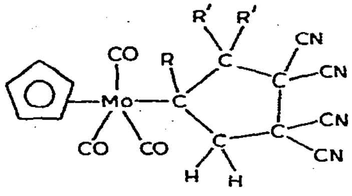
π-C$_5$H$_5$Mo(CO)$_3$CH$_2$C≡CR (R = H, CH$_3$, C$_6$H$_5$), π-C$_5$H$_5$Mo(CO)$_2$-[P(OC$_6$H$_5$)$_3$]CH$_2$C≡CCH$_3$, and (π-C$_5$H$_5$)Mo(CO)$_3$CH$_2$C≡CCH$_2$Mo(CO)$_3$(π-C$_5$H$_5$) have been observed to undergo facile reactions with liquid sulfur dioxide or with SO$_2$ in solution to form the corresponding vinyl derivatives containing a sultine ring, $\mathrm{Mo\overline{C{=}C(R)S(O)OC}H_2}$; namely, π-C$_5H_5$Mo(CO)$_3$(C$_3H_2RSO_2$), π-C$_5H_5$Mo(CO)$_2$[P(OC$_6H_5$)$_3$](C$_4H_5SO_2$), and π-C$_5H_5$Mo(CO)$_3$(C$_3H_2SO_2$)CH$_2$Mo(CO)$_3$(π-C$_5H_5$).[94] The SO stretching vibrations in the infrared spectra of these complexes occur at 1115-1094 and 915-893 cm^{-1}, which are comparable to the corresponding vibrations in organic sultines. In addition, magnetic nonequivalence of the $-OCH_2-$ protons is observed in these complexes as is also found in organic sultines. The most reasonable mechanism for the formation of these metal-sultine complexes is proposed to involve initial attack by the electrophilic SO_2 at the electron-rich C≡C bond. In related studies Wojcicki and coworkers[95] have observed that oxygen-bonded sulfinates are the initial products in some reactions of SO_2 with transition-metal alkyls and aryls. ^1H nmr spectral evidence is found for an intermediate (XVI) in the insertion reaction between $(\pi\text{-}C_5H_5)Mo(CO)_3CH_2Ph$ and SO_2 to form the thermodynamically stable and isolable $(\pi\text{-}C_5H_5)(CO)_3Mo\text{-}SO_2CH_2Ph$ complex.



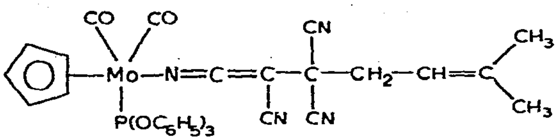
$$(\pi\text{-}C_5H_5)(CO)_3Mo\text{—}O\text{—}\underset{\underset{O}{\|}}{S}\text{—}\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\text{—}Ph$$

(XVI)

$\pi\text{-}C_5H_5Mo(CO)_3CH_2C(R){=}CR'_2$ ($R = CH_3$, $R' = H$; $R = H$, $R' = CH_3$) were found to react with TCNE in THF or CH_2Cl_2 within 30 minutes to form products which analyze as 1:1 adducts of the two reactants. Primarily on the basis of the proton NMR spectra these adducts are proposed to be 1,3-addition products of TCNE to C-C bonds (XVII). However, $\pi\text{-}C_5H_5Mo(CO)_2[P(OC_6H_5)_3]CH_2CH{=}C(CH_3)_2$ and TCNE were found to react very slowly (~ 50h) to give the 1,4-insertion product (XVIII). It appears that the pronounced inhibition and a different course for this reaction are due to the steric properties of the bulky phosphite ligand.[96]

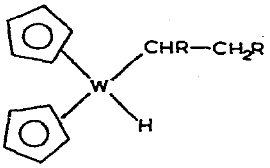


(XVII)

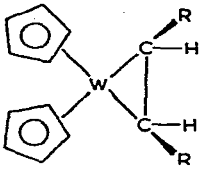


(XVIII)

Treatment of solutions of $(\pi\text{-}C_5H_5)_2WH_2$ in C_6H_6, C_6D_6, or toluene with isoprene (or penta-1,3-diene) at 120° for 3-4 days has been found to produce hydride(aryl)tungsten compounds of the type $(\pi\text{-}C_5H_5)_2WH(R)$ (R = Ph, C_6D_5, or p-C_6H_4Me). The aryl hydrides $(\pi\text{-}C_5H_5)_2WH(R)$ (R = Ph or p-C_6H_4Me) reacted with halocarbons to give the compounds $(\pi\text{-}C_5H_5)_2WX(Ph)$ (X = Cl, Br, I) or $(\pi\text{-}C_5H_5)_2$-WCl(p-C_6H_4Me).[97] Further studies of the reactions of $(\pi\text{-}C_5H_5)_2WH_2$ have shown that this dihydride complex readily adds to the maleic acid ester RCH=CHR (R = CO_2Et), giving the succinyl derivative (XIX). A tungstenacyclopropane derivative (XX) is also formed in comparable yield in this reaction which is assigned the trans-configuration from its ^{1}H nmr spectrum. In addition, the preparation and properties of other complexes of the type $(\pi\text{-}C_5H_5)_2$WHR (R = COPh, COMe, p-C_6H_4COPh), and of some molybdenum analogs have been described.[98] In addition, the Lewis bases $(\pi\text{-}C_5H_5)_2MH_2$ (M=Mo and W) have been shown to combine with the Group III Lewis acids AlR_3 (R=Me, Et, or Ph) and $AlMe_2H$ to result in formation of a series of 1:1 complexes of the type $(\pi\text{-}C_5H_5)_2MH_2 \cdot AlR_3$. Infrared evidence suggest that the bonding in these adducts consists of a direct metal-metal interaction with no bridging hydride bonds. Several of the complexes were found to undergo a slow elimination of H_2 or alkane in benzene solution. Attempts to isolate AlH_3 and GaH_3 metal adducts were unsuccessful.[99]



(XIX)



(XX)

A new type of intramolecular aromatic substitution product for transition metal complexes has been observed by Kaesz and coworkers.[100] When $CH_3Mn(CO)_5$ was combined with the Lewis bases $(C_5H_5)_2MH_2$ (M=Mo, W) at room temperature in tetrahydrofuran, H_2 and CH_4 were evolved after two days. Adduct formation (eq. 7), although not favored by the equilibrium, is proposed to initiate the reaction, followed by a loss of H_2 and a shift of CO into the coordination site on Mo (or W) (eq. 8). Finally, a novel intramolecular aromatic substitution of Mn on the adjacent cyclopentadienyl ring of molybdenum produces $(C_5H_5)(CO)\overline{Mo\text{-}\mu\text{-}C_5H_4\text{-}Mn}(CO)_4$ whose structure has been confirmed by X-ray determination.

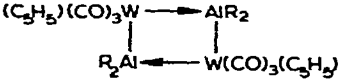
$$(C_5H_5)_2MoH_2 + CH_3Mn(CO)_5 \rightleftharpoons [(C_5H_5)_2MoH_2 \cdot Mn(CO)_4(COCH_3)] \qquad (7)$$

$$[(C_5H_5)_2MoH_2 \cdot Mn(CO)_4(COCH_3)] \xrightarrow[\text{CO shift}]{-H_2} [(C_5H_5)_2(CO)Mo \cdot Mn(CO)_4(CH_3)] \qquad (8)$$

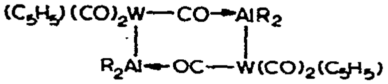
Protolysis of trialkylaluminum or dialkylaluminum hydrides with hydridocyclopentadienylmolybdenum carbonyls at ambient temperature affords the novel complexes $R_2Al\text{-}Mo(\pi\text{-}C_5H_5)(CO)_2L$ (L = CO or phosphine) (eq. 9).

$$R_2AlR' + H\text{-}Mo(\pi\text{-}C_5H_5)(CO)_2L \longrightarrow R_2Al\text{-}Mo(\pi\text{-}C_5H_5)(CO)_2L + R'H \qquad (9)$$

This reaction was also observed with the tungsten analogs. The following order of reactivity was noted: $Bu^t_2AlH > AlEt_3 > AlMe_3$. Reaction of the $R_2Al\text{-}Mo(\pi\text{-}C_5H_5)(CO)_2L$ complexes with stoichiometric quantities of weak organic acids (phenol, acetylacetone) results in a facile, quantitative cleavage of the aluminum-molybdenum bond indicating that the reactivity of the mixed metal-metal bond is greater than that of the Al-C bond towards protolytic attack.[101] $R_2AlW(CO)_3(\pi-C_5H_5)$ (R = Me or Et) have similarly been prepared from R_2AlH and $HW(CO)_3(\pi-C_5H_5)$.[102] Cryoscopic measurements on these complexes indicate these species to exist as dimeric molecules in benzene solution. Structures (XXI) and (XXII) are tentatively favored for the Me and Et derivatives, respectively.



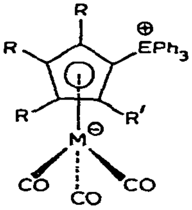
(XXI)



(XXII)

The complex $Al[W(CO)_3(C_5H_5)]_3(C_4H_8O)_3$ has been prepared by Burlitch and coworkers[103] from $Hg[W(CO)_3(C_5H_5)]_2$ and excess powdered aluminum metal or powdered aluminum amalgam in THF. A crystal structure analysis on this molecule indicated a nearly regular octahedral stereochemistry around the aluminum atom involving three W-C-O-Al linkages through one of the carbonyls on each of the three $[W(CO)_3(C_5H_5)]$ groups. The remaining three coordination sites about the aluminum atom are occupied by three THF molecules. The W-C-O-Al linkages readily explain the unusually low carbonyl stretching absorptions observed in both the solution and solid state infrared spectra of this species.

Several Group VIB metal carbonyl complexes of triphenylphosphonium cyclopentadienylide and related ligands have been prepared.[104] These compounds (XXIII) were prepared either from the appropriate metal hexacarbonyl or tris(acetonitrile)metaltricarbonyl and the triphenylphosphonium cyclopentadienide ligands, where (M = Cr, Mo, and W; R = R' = H; E = P), (M = Mo; R = H, R' = -N-Aryl; E = P), (M = Mo; E = P, As; R = R' = Ph). Several of these complexes were shown to be capable of coupling with p-anisyldiazonium ions, of being oxidatively halogenated, and of forming stable adducts with Lewis acids such as HgX_2 (X = Cl, Br, I), CdI_2, InBr, and $GaBr_3$. In each case the site of reaction was the metal atom. Reaction of $[Ph_3PC_5H_4Mo(CO)_3]$ with amminium perchlorate salt causes oxidative dimerization with formation of a Mo-Mo bond.



(XXIII)

$[(\pi-C_5H_5)Cr(CO)_3]_2Hg$ has been observed to react with HgX_2 (X=Cl, Br, or I), bromine, iodine, and various phosphorous ligands L (L=Ph_3P, $(PhO)_3P$, and $(MeO)_3P$) to afford $(\pi-C_5H_5)$-$Cr(CO)_3HgX$, $(\pi-C_5H_5)Cr(CO)_3X$ (X=Br, I), and $[(\pi-C_5H_5)Cr(CO)_2L]_2Hg$, respectively. These chromium derivatives are considerably less stable than their molybdenum and tungsten analogs. The reaction of $[(\pi-C_5H_5)W(CO)_3]_2Hg$ with one mole of halogen splits one on the W-Hg bonds to yield a mixture of $(\pi-C_5H_5)W(CO)_3X$ and $(\pi-C_5H_5)W$-$(CO)_3HgX$ (X=Br or I); whereas, reaction with excess halogen affords $(\pi-C_5H_5)W(CO)_3I$ and $(\pi-C_5H_5)W(CO)_2Br_3$.[105]

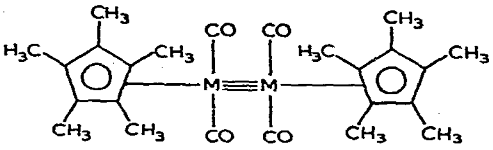
$[\pi-C_5H_5M(CO)_3]_2$ (M=Mo, W) has been observed to react with InX (X=Cl, Br) to give $[\pi-C_5H_5(CO)_3M]_2InX$ and with excess InX to give $\pi-C_5H_5(CO)_3MInX_2$. InX was found also to react with symmetrical mercurials such as $[\pi-C_5H_5(CO)_3Mo]_2Hg$ to afford $[\pi-C_5H_5(CO)_3Mo]_2$-InX.[106]

$[\pi-C_5H_5Mo(CO)_3]_2$ has also been found to react with the ligands L = $P(OC_3H_5)_3$, $P(OC_3H_5)_2C_6H_5$, and $P(OC_3H_5)(C_6H_5)_2$ (where C_3H_5 = allyl) to yield the products $[\pi-C_5H_5Mo(CO)_2L_2][\pi-C_5H_5Mo(CO)_3]$,

$[\pi\text{-}C_5H_5Mo(CO)_2L]_2$, and $[\pi\text{-}C_5H_5Mo(CO)_2LL']$ $[L'{=}P(O)(OC_3H_5)_2$, $P(O)(OC_3H_5)(C_6H_5)$ or $P(O)(C_6H_5)_2)$ depending on the reaction conditions.[107] By monitoring the reactions of $[\pi\text{-}C_5H_5Mo(CO)_3]_2$ with the L ligands in benzene it was observed that the ionic derivatives $[\pi\text{-}C_5H_5Mo(CO)_2\text{-}L_2][\pi\text{-}C_5H_5Mo(CO)_3]$ are intermediates in the formation of $\pi\text{-}C_5H_5Mo(CO)_2LL'$ complexes.

Thermally induced reactions of manganese and rhenium decacarbonyls have been observed to occur with a large number of metal carbonyls and organometallic compounds.[108] Included in this study was the reaction of $Mn_2(CO)_{10}$ with $[(\pi\text{-}C_5H_5)Mo(CO)_3]_2$ to produce small quantities of $(\pi\text{-}C_5H_5)Mo(CO)_3Mn(CO)_5$, with extensive formation of $(\pi\text{-}C_5H_5)Mn(CO)_3$.

King and Efraty[109] have reported a general synthesis of pentamethylcyclopentadienylmetal carbonyls which utilizes the readily available 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene as a starting reagent. Reaction of $Cr(CO)_6$ with the acetyl derivative in boiling 2,2,5-trimethylhexane yielded green crystalline $[(CH_3)_5C_5Cr(CO)_2]_2$, the chromium analog of $[(CH_3)_5C_5Mo(CO)_2]_2$ (XXIV) previously reported by King.[110] $Mo(CO)_6$ reacts under similar conditions to give $[(CH_3)_5C_5Mo(CO)_2]_2$ and $CH_3Mo(CO)_3C_5(CH_3)_5$. $(CH_3CN)_3W(CO)_3$ gives the analogous σ-methyl tungsten complex, $CH_3W(CO)_3C_5(CH_3)_5$. Since $CH_3M(CO)_3C_5(CH_3)_5$ (M = Mo and W) are the expected thermal decomposition products of the σ-acetyl derivatives, $CH_3COM(CO)_3C_5(CH_3)_5$, it is proposed that the acetyl-pentamethylcyclopentadiene first transfers the acetyl group to the metal atom i these reactions. The orange $(CH_3)_5C_5Cr(CO)_2NO$ complex has also been prepared employing the acetyl-pentamethylcyclopentadiene reagent.



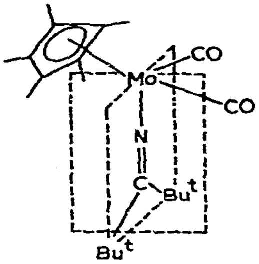
(XXIV)

The reactions of (trimethylsilyl)cyclopentadiene with a variety of metal carbonyls have afforded several π-[(trimethylsilyl)cyclopentadienyl] metal carbonyl derivatives.[111] Included in these are $[(\pi\text{-}Me_3SiC_5H_4)M(CO)_3]_2$ (M=Mo and W) which were formed from (trimethylsilyl)cyclopentadiene and the corresponding $M(CO)_6$ compounds.

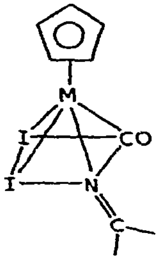
U.V. irradiation of a benzene solution of triphenylphosphine and dicarbonyl-π-cyclopentadienylnitrosylmolybdenum affords approximately equal quantities of $[(\pi\text{-}C_5H_5)Mo(CO)(NO)(PPh_3)]$ and a complex shown to be $[(\pi\text{-}C_5H_5)Mo(CO)(PPh_3)_2(NCO)]$ (A) by a three-dimensional X-ray crystal-structure analysis. Irradiation of $[(\pi\text{-}C_5H_5)Mo(CO)(PPh_3)_2N_3]$ under an atmosphere of carbon monoxide and of $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)N_3]$ in the presence of triphenylphosphine gives mixtures of $[(\pi\text{-}C_5H_5)Mo(CO)(PPh_3)_2(NCO)]$ and $[(\pi\text{-}C_5H_5)Mo(CO)_2(PPh_3)(NCO)]$. These reactions are consistent with the formation of organometallic nitrenes which capture carbon monoxide to produce the isocyanate ligand. The X-ray structure analysis of (A) indicates the phosphine ligands to be in the trans positions. However, ^1H nmr measurements indicate that the bulk sample of the photochemically generated complex consists of a mixture of the cis- and trans-isomers.[112]

King and Efraty[113] have shown $Ni(PF_3)_4$ to be a convenient source of PF_3 in the synthesis of metal-trifluorophosphine complexes. Reaction of $(C_5H_5)Mo(CO)_3Cl$ with $Ni(PF_3)_4$ results in formation of $(C_5H_5)_2Mo_2(CO)_5PF_3$ or $[(C_5H_5)Mo(CO)_2PF_3]_2$, depending upon the reaction conditions. $CH_3M(CO)_3(C_5H_5)$ (M = Mo and W) also were found to react with $Ni(PF_3)_4$ in boiling toluene to afford derivatives $CH_3M(CO)_2(PF_3)(C_5H_5)$.

Reactions between $[(\pi\text{-}C_5H_5)M(CO)_3Cl]$ (M=Mo,W) and $Bu^t{}_2C{:}NLi$ or $Bu^t{}_2C{:}NSiMe_3$ have resulted in formation of blue complexes of the type $[(\pi\text{-}C_5H_5)M(CO)_2N{:}CBu_2{}^t]$. I.r. and nmr spectral changes in solution with changes in temperature are observed in the molybdenum complex. The structural changes are consistent with rotational changes about the metal-nitrogen bond of a complex having structure (XXV). Iodine displaces CO in $[(\pi\text{-}C_5H_5)M(CO)_2N{:}\text{-}CBu^t{}_2]$ to produce $[(\pi\text{-}C_5H_5)M(CO)I_2(N{:}CBu_2{}^t)]$ which is tentatively assigned the structure (XXVI). $[(\pi\text{-}C_5H_5)Mo(CO)_2N{:}CBu_2{}^t]$ reacts with PPh_3 in monoglyme and CCl_4 to give $[(\pi\text{-}C_5H_5)Mo(CO)(PPh_3)_2H]$ and $[Ph_3PBu^t][(\pi\text{-}C_5H_5)MoCl_4]$ respectively.[114] Analogous reactions of $(\pi\text{-}C_5H_5)M(CO)_3Cl$ (M=Mo, W) with $PhBu^tC{:}NLi$, and the reaction of $(\pi\text{-}C_5H_5)W(CO)_3Cl$ with Ph $Bu^tC{:}NSiMe_3$ produced compounds of the type $[(\pi\text{-}C_5H_5)M(CO)_2N{:}CBu^tPh]$. The molybdenum complex reacts with triphenylphosphine to form the substitution product $[(\pi\text{-}C_5H_5)Mo(CO)\text{-}(PPh_3)N{:}CBu^t{\cdot}Ph]$, in contrast to all other methylene-amino complexes investigated. With iodine, substitution analogous to that of the di-t-butyl complex,[115] led to the formation of $[(\pi\text{-}C_5H_5)M(CO)I_2N{:}CBu^tPh]$



(XXV)



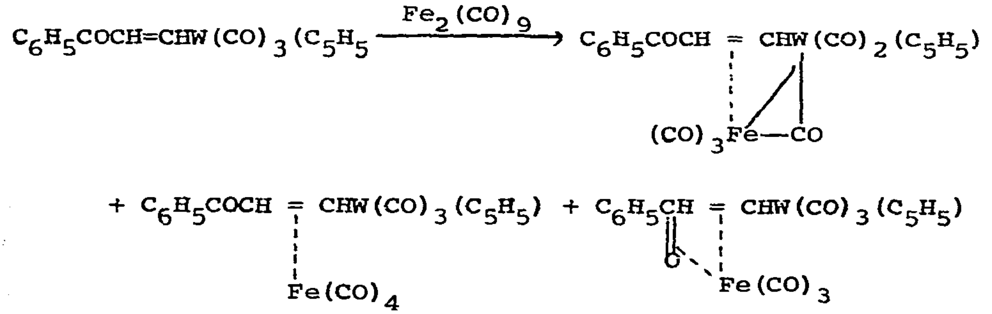
(XXVI)

Green and Sanders[116] have observed that treatment of the complexes $Na^+[(\pi\text{-}C_5H_5)M(CO)_3]^-$ (M = Mo and W) with ethyl diazoacetate followed by hydrolysis givesthe neutral complexes $(\pi\text{-}C_5H_5)(CO)_2\overline{M{:}NNHC(CO_2Et)C}OH$ (XXVII). These complexes are monobasic and protonate to form the cations $[(\pi\text{-}C_5H_5)(CO)_2\overline{M{:}NHNHC(CO_2Et)C}\text{-}OH]^+$. The neutral complex react with strong bases to form anionic $[(\pi\text{-}C_5H_5)(CO)_2\overline{M{:}NNC(CO_2Et)C}OH]^-$ complexes which were isolated as tetra-n-butylammonium salts. The anions reacts with methyl iodide to afford the neutral methyl derivative $(\pi\text{-}C_5H_5)(CO)_2\overline{M{:}NNMeC(CO_2Et)C}OH$ which are also monobasic and protonate to form the corresponding cations.

σ-2-Acylvinyl derivatives of iron and tungsten have been synthesized by the reaction (eq. 10).

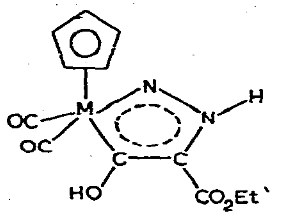
$$RCOCH{=}CHCl + NaM(CO)_n(C_5H_5) \longrightarrow RCOCH{=}CHMn(CO)_n(C_5H_5) \qquad (10)$$

where (M=Fe, n=2, R=Me and Ph) and (M=W, n=3, R=Me, Ph, and $p\text{-}BrC_6H_4$). Reaction of the $C_6H_5COCH{=}CHW(CO)_3(C_5H_5)$ complex with $Fe_2(CO)_9$ in benzene at 40° afforded three binuclear complexes (eq. 11).



(11)

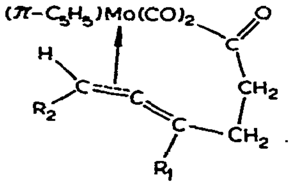
Attempted reactions of σ-(2-acylvinyl)-π-cyclopentadienylirondicarbonyls with $M(CO)_6$, $(CH_3CN)_3M(CO)_3$, and $(CH_3CN)M(CO)_5$, where M=Mo and W were unsuccessful.[117] Similarly, $NaW(CO)_3(\pi\text{-}C_5H_5)$ was found to react with RCOCH:CHCl (R = Ph or $p\text{-}BrC_6H_4$) in THF to give RCOCH:-$CHW(CO)_3C_5H_5$ when reacted with $Fe_2(CO)_9$ gave a variety of compounds, namely, $BzCH{:}CH[Fe(CO)_3]W(CO)_3C_5H_5$, $BzCH{:}CH[Fe(CO)_3](CO)W(CO)_2C_5H_5$ and $BzCH{:}CH[Fe(CO)_4]W(CO)_3C_5H_5$.[118]



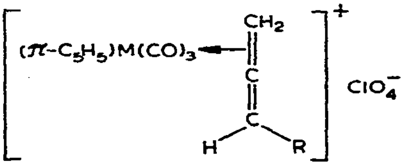
(XXVII)

A novel type of molybdenum compound has been prepared by reaction of β-bromoallene derivatives with $NaMo(CO)_3(C_5H_5)$ in THF solvent. Compounds containing an allene ligand attached to the metal by both a σ and π bond of the form (XXVIII) were obtained, where ($R_1 = H$, $R_2 = H$; $R_1 = H$, $R_2 = CH_3$; $R_1 = CH_3$, $R_2 = H$).[119]

$(\pi\text{-}C_5H_5)Mo(CO)_3CH_2C{\vdots}CR$ has been shown to undergone protonation with $HClO_4$ in benzene to give the cation $(\pi\text{-}C_5H_5)Mo(CO)_3R\text{-}CH{:}C{:}CH_2^+$ (R = Me, Ph) (XXIX).[120]



(XXVIII)

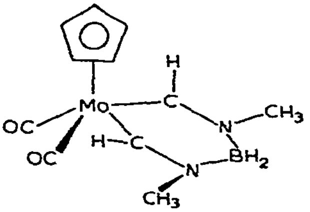


(XXIX)

Oxidation addition-elimination reactions of $Me_3M(C_5H_5)$ (M = Ge, Sn) with $M'(MeCN)_3(CO)_3$ (M' = Cr, Mo and W) to yield $M'(\pi\text{-}C_5H_5)\text{-}(Me_3M)(CO)_3$ have been reported by Keppie and Lappert. For a given M, reactivity decreased in the order Cr > Mo ≈ W, and Sn > Ge >> Si (unreactive) for a given M'. $M'(MeCN)_3(CO)_3$ complexes were also observed to react with C_5H_6 to afford the thermally unstable hydrides, $M'H(\pi\text{-}C_5H_5)(CO)_3$.[121] The related silicon compounds, $H_3SiM(CO)_3\text{-}(\pi\text{-}C_5H_5)$, (where M=Cr, Mo, W) were synthesized by the reaction of

H_3SiBr with $KM(CO)_3(\pi-C_2H_5)$. The silicon-transition metal bond was cleaved by water and hydrogen chloride at room temperature and by dimethylamine at slightly higher temperatures. Trimethylamine and dimethylamine formed in most cases 1:1 adducts with these complexes at room temperature. However, $H_3SiW(CO)_3(\pi-C_5H_5)$ formed a 1:2 adduct with dimethylamine.[122]

The borohydride ion has been found to react with several cyclopentadienyl metal carbonyl isocyanide complexes, including $\pi-C_5H_5Mo(CO)_2(CNCH_3)_2{}^+$, resulting in addition of BH units across the two C≡N bonds in the coordinated isocyanide ligands. Structure (XXX) is strongly favored for these type species.[123]



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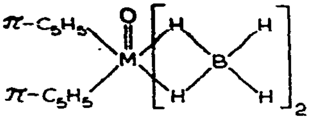


(XXXI)

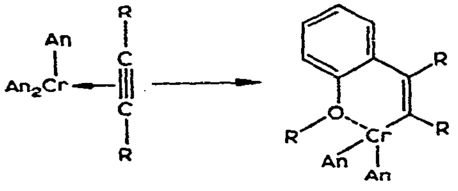
The interactions of di-π-cyclopentadienyl M(VI) oxide dichloride (M=Mo and W) with sodium borohydride in tetrahdrofuran have led to bis(borohydride) derivatives of the type $(\pi-C_5H_5)_2MO(BH_4)_2$. The presence of a M=O group is indicated by infrared absorptions at approximately 950 cm^{-1}. The proposed structures for these species involve bridging metal-H-B bonds (XXXI).[124] In addition, the reaction between di-π-cyclopentadienyl M(VI) oxide dichloride (M=Mo and W) with various bidentate ligands has also been investigated affording chelated complexes of the type, $[(\pi-C_5H_5)_2MOL]^+ClO_4{}^-$ (L=acetylacetonate, benzoylacetonate, ethylacetonate, benzoylacetoacetate, and dibenzoylmethane).[125] The formation of $(\pi-C_5H_5)_2MOCl$ on treatment of the complexes with dry hydrogen chloride (eq. 12) confirms that these complexes contain the $(\pi-C_5H_5)_2M{=}O$ unit, as inferred from their infrared spectra.

$$[(\pi\text{-}C_5H_5)_2\mathrm{MOL}]^+ClO_4^- + 2HCl \rightarrow (\pi\text{-}C_5H_5)_2\mathrm{MOCl}_2 + HL + HClO_4 \qquad (12)$$

π-$C_5H_5Mo(CO)_3Cl$ was observed to react with $(C_2H_5)_2PS_2Na$ in THF at 65° to form the complex π-$C_5H_5Mo(CO)_2S_2P(C_2H_5)_2$ in which the dithiophosphinate ligand acts as a bidentate ligand.[126]

Solid KOH in contact with weakly acidic cyclopentadiene dissolved in the nonhydroxylic solvents $MeOCH_2CH_2OMe$ or Me_2SO was found to provide a solution of the deprotonated anion which when treated with $Mo(CO)_6$ and MeI gave $MeMo(CO)_3C_5H_5$.[127]

Miscellaneous Complexes. Several papers have appeared this year dealing with the preparations and reactions of organochromium compou Tris(2-methoxyphenyl)chromium(III) and 2-butyne have been observed to interact to give the bis(-2 methoxyphenyl)chromium(II) species. Treatment of the reaction mixture with D_2O gave, along with several non-enriched deuterium products, monodeutericanisole and $(2\text{-}CH_3OC_6H_4)\cdot C(CH_3){=}C(CH_3)D$. The formation of the latter deuteriospecies was interpreted in terms of the rearrangement of an organochromium-acetylene complex (XXXII A) to a σ-bonded vinylchromium species (XXXII B). A scheme was presented for formation of other products from this reaction.[128] Both triallylchromium(III) and tetraallyldichromium(II) were found to react with 2-butyne in THF to give the same overall mixture of products. Three of the four major component have been isolated and identified as 1,2,3,4-tetramethyl-benzene,



(XXXII) A (XXXII) B

(An= 2-methoxyphenyl and R=CH_3)

pentamethylbenzene and hexamethylbenzene. The presence of 1,2,3,5-tetramethylbenzene as a minor constituent was detected by gas-chromatographic analysis.[129]

The air-stable σ-bonded organochromium compound cis-bis-(2-methoxyphenyl)bis-(2,2'-bipyridyl)-chromium(III) iodide has been synthesized by the Grignard method and the structure of its monohydrate has been determined by X-ray analysis. A chromium-carbon bond length of 2.10Å was observed.[130]

The tri-tert-alkylchromium system has been shown to thermally undergo stepwise fragmentation. At low temperatures a homolytic process takes place leading to the exclusive formation of alkane and 1-alkene (eq. 13).

$$3PhCH_2CH_2C(CH_3)_2MgCl + CrCl_3(THF)_3 \xrightarrow[2.\ H_2O]{1.\ -70\ to\ -15°} PhCH_2CH_2CH(CH_3)_2 + PhCH_2CH_2C(CH_3)=CH_2 \qquad (13)$$

At higher temperatures the products consisted of alkane, 1- and 2-alkene and hydridochromium species. From these studies the catalytic activity of organochromium systems is shown to be associated with chromium(II) or lower valence chromium species.[131] Further studies of alkylchromium species involve the interaction of tris(2,2-dideutero-4-phenylbutyl)chromium with 1,7-octadiene which affords as hydrogenation products deutero-2-octene and isomerization products. These results prove the intermolecular transfer of hydrogen (deuterium) from the β-position of an alkyl group bound to the metal to the diene substrate.[132]

The preparation of tetraallyldichromium has been reported in a Japanese patent from $CrCl_2$ and $CH_2{:}CHCH_2MgCl$ in THF.[133] Complex formation between Cr^{+2} and C_2H_2 in ethanol has been studied at 0-50°. The temperature dependent equilibrium constants for this reaction were determined and the enthalpies and entropies calculated. $CrCl_2$ and C_2H_2 in ethanol containing NH_3 gave the complex $[Cr_2(C_2H_2)(NH_3)_8]Cl_4$ at -50° which had a magnetic moment of 1.98μB. The structure of this complex was discussed.[134]

Schmidt, Swinehart, and Taube[135] have investigated the formation and kinetic stability of complexes containing chromium-carbon bonds in aqueous medium. The complexes, pentaaquochromium(III) ions bonded to small acyclic anions, were formed by reduction of organic radicals (derived from isopropyl alcohol and diethylether) with Cr(II Rate laws for these processes are described and a mechanism was proposed.

Several pyrrole complexes of Cr(II) and Cr(III) have been prepared from alkali- or Grignard-pyrrolyl reagents and the corresponding chromium halides. Cyclopentadienyl(pyrrolyl)chromium derivatives were also synthesized and characterized. The pyrrolylchromium complexes were shown to bond <u>via</u> a metal-to-nitrogen linkage.[136] On the other hand, $Cr(CO)_3$ π-complexes of pyrrole and phenyl N-substituted pyrrole have been prepared from the reactions of $Cr(CO)_6$ and $(CH_3CN)_3Cr(CO)_3$ and the corresponding pyrrole ligand. In the case of 1-phenylpyrroles, the $Cr(CO)_3$ group was found to coordinate with either the pyrrole or phenyl ring. Ir. and nmr measurements indicate the pyrrole ligands to be behaving as strong donor groups in these complexes. At the same time, they were observed to be less stable than arenechromiumtricarbonyls.[137]

Dicyclooctatetraenylmolybdenum oxide dichloride, $(C_8H_7)_2MoOCl_2$, has been reported to undergo reactions with mono-,di-, and trihydroxy phenols and with mono- and dicarboxylic acids to afford phenoxide and carboxylate derivatives of the types, $(C_8H_7)_2MoO(OC_6H_4CH_3)_2$ and $(C_8H_7)_2MoO(O_2CC_2H_3)_2$, respectively.[138] Complexes of the type $K_3[M_2(CO)_6(OH)_3]$ (M = Mo, W) have been prepared and their reactions investigated.[133] Reaction of these complexes with acid (HCl) affords the hydride species $[(HO)M(CO)_3H]_4$ which readily form 1:4 adducts with tertiary phosphine oxides. The nitrosyl derivatives have been shown to contain a similar tetrameric unit, $[(HO)M(CO)_2(NO)]_4$, and to form analogous 1:4 adducts with OPR_3. The structures of all these species have been confirmed by X-ray structural analyses. The results from this study are discussed with respect to earlier work reported by Hieber and coworkers.[140]

WCl_6 was found to react with dimethyl zinc or diphenyl zinc to form the green complexes $RWCl_5$ (R = Me or Ph). Longer chain dialkyl zinc compounds caused WCl_6 to be reduced to WCl_4. In addition, $RWCl_5$ complexes were readily prepared from WCl_6 and R_4Sn or R_3B reagents.[141]

Kinetic and Catalysis

Bowden and Colton[142] have observed that substitution reactions of halopentacarbonylchromium,-molybdenum, and-tungsten(O) anions with carbon monoxide proceed smoothly at room temperature and pressure.

$$[M(CO)_5X]^- + CO \rightarrow M(CO)_6 + X^- \quad (M = Cr, Mo, W) \qquad (14)$$

A first-order rate law was found, where the rate of reaction = k $([M(CO)_5X]^-)$. The rate constant (k) varied in the following order for a given anion or metal, respectively: Mo > Cr > W and Cl > Br > I. The order of reactivity of the anions of a particular metal containing different halogens was observed to be consistent with the known order of their *trans* effect: CO > PR_3 > I > Br > I.

Wrighton, Hammond and Gray found that ligand substitution reactions between $W(CO)_5$(acetone) and alkenes occur to give the products $W(CO)_5$(alkene) and uncomplexed acetone *via* a rate-determining dissociative process. The structure of the alkene was observed to be an important factor in the rate of substitution and in the equilibrium ratio of $W(CO)_5$(acetone) and $W(CO)_5$(alkene). cis alkenes were found to react faster and form more stable metal complexes than tran alkenes.[143]

The kinetics of the reaction of (methoxyphenylcarbene)pentacarbonylchromium(O), $Cr(CO)_5C(OCH_3)C_6H_5$ (A), with primary amines RNH_2 (R = n-C_4H_9, C_6H_{11}, $CH_2C_6H_5$) have been studied in a variety of solvents.[144] The formation of the aminophenylcarbene complexes $Cr(CO)_5C(NHR)C_6H_5$ (B) follows a complex fourth-order rate law $d[(B)]/dt = k_A \cdot [(A)][RNH_2][HX][Y]$ where HX represents a proton donating and Y a proton accepting agent. The results of the kinetic studies are consistent with a consecutive step mechanism which starts with the formation of a one-to-one adduct of (A) and the proton donor HX and includes the activation of the attacking amine by the proton acceptor Y. The existence of hydrogen bonds between (A) and HX, and between RNH_2 and Y was illustrated using nmr. This mechanism explains the decrease in rate of formation of (B) with increasing temperature, i.e., a negative Arrhenius activation energy was observed.

Darensbourg and Darensbourg[145] have investigated the reaction of organomagnesium halide reagents with metal carbonyls. Organomagnesium halides were observed to react with metal carbonyls apparently by a similar process as organolithium reagents to form addition products which upon alkylation give carbene compounds. The addition reactions employing Grignard reagents are however, considerably slower than the organolithium reactions and are amenable to kinetic studies by conventional techniques. Initial kinetic results are consistent with the earlier proposal that the relative rates of nucleophilic attack on the carbon of the carbonyl group are related to the CO stretching force constant.[146]

Kinetic data have been obtained in both acetone and 1,2-dichloroethane solvents for the oxidative elimination reactions of $M(CO)_4L_2$ (M = Mo, W; L_2 = 2,2'-bipyridine, 1,10-phenanthroline) with mercuric halides which yield $M(CO)_3L_2(HgX)(X)$ and CO. In acetone the reaction involves the initial rapid formation of $M(CO)_4L_2 \cdot 2HgX_2$ which decomposes in the rate-determining step to yield the final product. Equilibrium constants for the formation of the intermediate for the tungsten systems have been calculated with the equilibrium constant for $HgBr_2$ found to be greater than that for $HgCl_2$. No intermediate was observed for the reactions of the molybdenum compounds, but the kinetic data were consistent with the mechanism proposed for the tungsten systems. In 1,2-dichloroethane the kinetic data indicate the presence of both $M(CO)_4L_2 \cdot HgX_2$ and $M(CO)_4L_2 \cdot 2HgX_2$ as intermediates.[147]

Kinetic data for the reactions (eq. 15) of chloro-tricarbonyl-(π-tetrahydroindenyl)molybdenum with phosphorus ligands in a variety of solvents have been collected,

$$(\pi\text{-}C_9H_{11})Mo(CO)_3Cl + L \rightarrow (\pi\text{-}C_9H_{11})Mo(CO)_2LCl + CO \qquad (15)$$

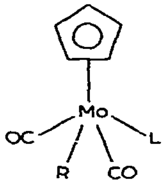
where L = PPh_3, $P(OPh)_3$, and $P(OMe)_3$.[148] The rate of the reaction was observed to be essentially independent of the nature and concentration of the incoming ligand, and was not markedly sensitive to the solvent used. An S_N1 mechanism in which the rate-determining step involves loss of carbon monoxide was proposed (eq. 16).

$$(\pi\text{-}C_9H_{11})Mo(CO)_3Cl \xrightarrow[-CO]{k_{obs}} (\pi\text{-}C_9H_{11})Mo(CO)_2Cl \xrightarrow[+L]{fast} (\pi\text{-}C_9H_{11})Mo(CO)_2LCl \qquad (16)$$

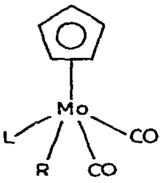
The rate of reaction and activation parameters for $(\pi\text{-}C_9H_{11})Mo(CO)_3Cl$ and $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ were quite similar. However, these were in noticable contrast with kinetic data for $(\pi\text{-indenyl})Mo(CO)_3Cl$ which was observed to be much more reactive. These differences are attributed to a "long-range effect" of the aromatic ring in π-indenyl.

Racemization processes in $\pi\text{-}C_5H_5Mo(CO)_2LR$ and π-indenyl $Mo(CO)_2LR$ (L = phosphine, R = halide) have been investigated by Faller and coworkers.[149] The coordination geometry about the molybdenum atom is described as a square pyramid with the cyclopentadienyl or indenyl moiety at the apex and the remaining ligands at the corners of the square base. This arrangement allows for one trans and two enantiomeric cis isomers (XXXIII A, B, C). On the nmr time scale two distinct processes, cis-trans isomerization and cis-cis racemization wereobserved. The most likely intermediate for these arrangements would resemble a trigonal bipyramid with one axial position occupied by the π-indenyl or $\pi\text{-}C_5H_5$ moiety and the other axial position occupied by one of the other ligands. If the axial position is occupied by CO the intermediate is chiral. If, however, either an R or L group occupies such a position, the intermediate is achiral. The type of intermediate involved in the rearrangement may be determined, therefore, from a study of the racemization pathway of the cis enantiomer. It was observed in this study that the cis→cis enantiomic interconversion truly occurred without intermediate formation of the trans isomer. Thermodynamic data indicate that the cis isomer is generally more favored in the indenyl compounc than in the corresponding cyclopentadienyl analog.

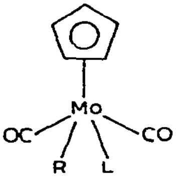
The cis-trans isomerism of $\pi\text{-}C_5H_5Mo(CO)L_2Cl$ (L = $PMePh_2$, PMe_2Ph) has been studied by low-temperature nmr. At 25° the complex (L = $PMePh_2$) exhibits only one resonance for the cyclopentadienyl protons.



(XXXIII) A



(XXXIII)B

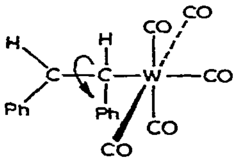


(XXXIII) C

However, at -62° two distinct cyclopentadienyl resonances are observed corresponding to the cis and trans isomers. The isomerization is shown not to involve dissociation of a phosphorus ligand.[150]

The isomerization of (benzylthiocyanate)chromium-tricarbonyl to the iso-thiocyanate derivative has been carried out in acetone at 65-85°.[151] (Benzylthiocyanate)chromiumtricarbonyl isomerizes in acetone at a rate comparable with that of benzhydrylthiocyanates. The data were observed to be sensitive to the addition of salts such as $NaClO_4$. The π-complexed benzylthiocyanate is proposed to isomerize by way of a rate-determining ionization.

Wrighton, Hammond, and Gray[152] have reported the $M(CO)_6$-photo-assisted cis-trans isomerization of stilbene, where M = Mo and W. $Cr(CO)_6$ was found to be ineffective in photoassisting the isomerization of stilbene. An interemediate (XXXIV) which is characterized by a metal-carbon σ bond with free rotation about the olefinic bond was proposed for the excited-state isomerization.



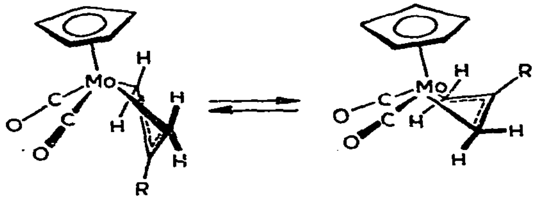
(XXXIV)

The synthesis and spectral characteristics of the complexes $(PR_3)_4MoH_4$ (PR_3 = tertiary phosphine) have been described.[153] Jesson, Muetterties, and Meakin[154] have reported data for the limiting fast-and slow-exchange ^{1}H and ^{31}P nmr spectra for complexes of this type. These workers proposed that the H_4MoL_4 phosphine complexes have a D_{2d} tetrahedral or near regular tetrahedral MoP_4 substructure and that intramolecular rearrangement comprises a concerted hydrogen atom traverse of the tetrahedral faces.

The 220 MHz nmr spectrum of π-cyclopentadienyltungsten hydride has been studied in a partially oriented state by dissolving the complex in the liquid crystal N-(-methoxybenzylidene)-p-n-butylaniline.[155] The W-H bond was shown to be inclined towards the cyclopentadienyl ring. It was concluded from this study that pseudo-rotation is rapid compared with the time for molecular orientation in the nematogen.

The fluxional character of the cyclopentadienyl group in transition-metal complexes has been discussed in several studies. Su has employed a combination of energy level correlation diagrams and a simple perturbation method to show that the rearrangement pathways (under thermal conditions) of fluxional organometallics with metal-carbon σ bonds are governed by the highest occupied molecular orbitals of the organic portion of the transition state. Comparisons between predicted and observed fluxional shifts in organometallic derivative of the type, $(h^5\text{-}C_5H_5)(NO)_2M(h^1\text{-}C_5H_5)$ (M = Cr, Mo) were good.[156] Chemical shifts in the ^{1}H nmr spectra due to magnetic anisotropy of the indenyl or cyclopentadienyl ring systems have been employed to elucidate rapid conformational equilibria in π-cyclopentadienylmolybdenumdicarbonyl-π-alkyl and π-indenylmolybdenumdicarbonyl-π-allyl complexes (XXXV).[157]

The PMR spectra of $(C_5H_5)_2Mo(NO)I$ and $(C_5H_5)_2Mo(NO)CH_3$ have been examined to temperatures as low as -120°.[158] Neither compounds shows any broadening of the resonance due to all ten protons. These

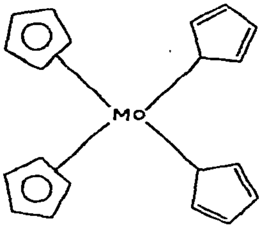


(XXXV)

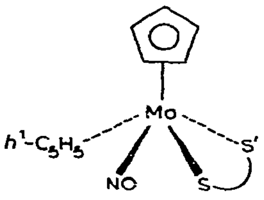
results support the previous view held by the authors[159] concerning the structural and dynamical nature of $(C_5H_5)_3Mo(NO)$ (A). (A) shows 15 equivalent protons at room temperature. Upon lowering the temperature to -80°, the PMR spectrum shows one h^1-C_5H_5 group and two magnetically nonequivalent h^5-C_5H_5 rings. This is attributed to very slow hindered rotation about the Mo-C bond to the h^1-C_5H_5 ring, whereby the highly anisotropic π system of the h^1-C_5H_5 group causes the two otherwise equivalent C_5H_5 rings to experience different magnetic environments. Tetracyclopentadienylmolybdenum has been prepared in a pure form by the reaction of C_5H_5Tl with $(C_5H_5)_2MoI_2$. Its PMR spectrum implies the structure $(h^5\text{-}C_5H_5)_2$ $(h^1\text{-}C_5H_5)_2Mo$ (XXXVI), with the h^1-C_5H_5 rings fluxional at 25°.

The ^1H n.m.r. spectra of $[Mo(C_5H_5)_2(NO)(S_2CNMe_2)]$ (XXXVII) and of $[Ph_4P][Mo(C_5H_5)_2(NO)\{S_2C_2(CN)_2\}]$ have been studied over the temperature range -80 to +130°.[160] The limiting low-temperature spectra are consistent with the structure $[Mo(h^5\text{-}C_5H_5)(h^1\text{-}C_5H_5)(NO)(S\text{-}S)]$ (S-S = sulfur ligand). At intermediate temperatures, the monohapto-ring is fluxional, and at high temperatures the rings in (XXXVII) undergo site exchange, and the methyl groups become equivalent. A pseudo-rotational mechanism is used to explain the high-temperature spectral behavior of (XXXVII).

The disproportionation reaction of olefins effected by various transition metal catalysts has received considerable interest over the past year. In particular, the role played by the metal atom has

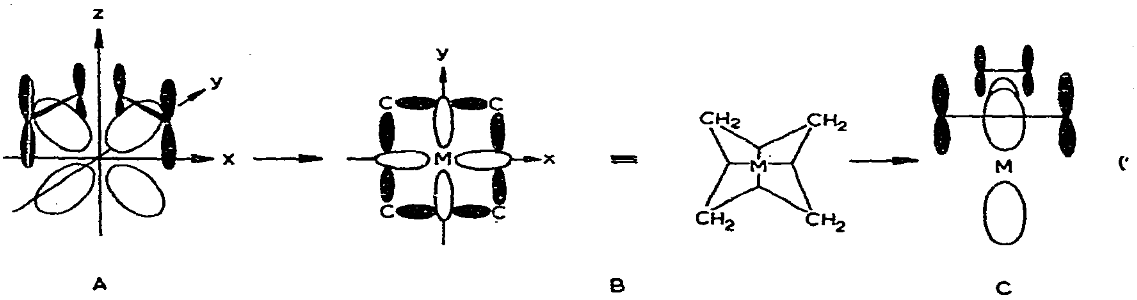


(XXXVI)



(XXXVII)

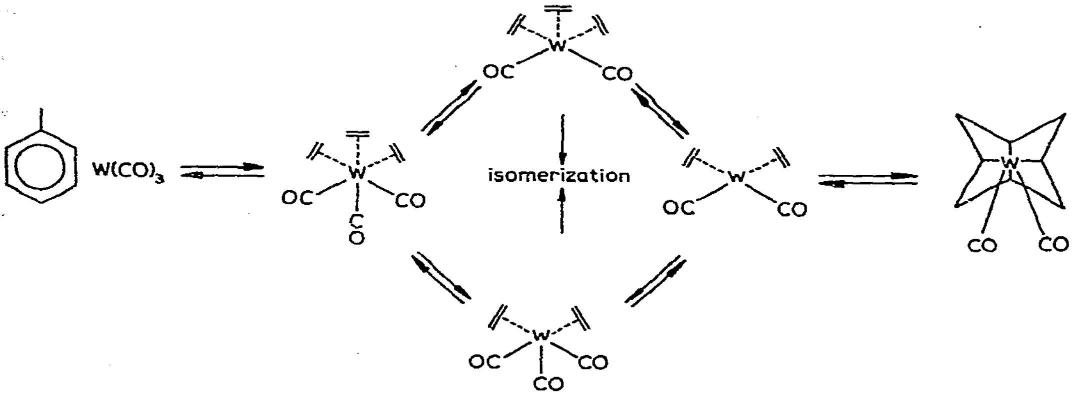
stimulated discussion. Lewandos and Pettit[161] have proposed that the reaction proceeds via reversible transformation of two coordinated olefinic bonds into a multi-three-centered species B which contains four CH_2 groups of sp^3-hybridized carbon atoms (eq. 17).



The two virtues of this mechanistic scheme are that it avoids invoking a cyclobutane ring structure as an intermediate and that it offers an explanation of the role played by the metal atom in removing the "forbiddenness", according to the Woodward-Hoffman rules of orbital symmetry, of this reaction.

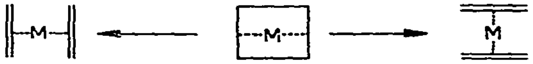
Data consistent with this mechanistic scheme have been presented by Lewandos and Pettit[162] employing $W(CO)_6$, $Mo(CO)_6$ and (arene) $W(CO)_3$ complexes as homogeneous catalyst precursors for the disproportionation of olefins. The detailed scheme (eq. 18) makes use of the effective atomic number rule (EAN).

Mango and Schachtschneider[163] have also discussed symmetry-forbidden valence isomerizations processes in which a transition metal totally removes the symmetry restrictions to reaction through



(18)

metal-ligand orbital interaction. The importance of the coordinate bonding in the catalysis of these systems and its inseparability from orbital symmetry conservation have been reiterated.[164] These authors proposed a coordinated cyclobutane ring intermediate which can open to a bis-olefin system in two directions (eq. 19).



(19)

There has been an increasing interest among organometallic chemists in the identification and structure determination of unstable molecular species. A convenient method for observing these short-lived species is to trap them in an inert solid by a technique known as matrix isolation followed by use of conventional spectroscopic methods. Ogden and Turner[165] have outlined the basic technique and recent developments in this area. Photolysis of metal carbonyls at low temperatures along with observation of the species produced by ir and uv spectroscopic methods have led to many interesting results. In addition to the experiments discussed below, active metal carbonyl fragments produced by photolysis have been shown to react with molecular nitrogen to give $M(CO)_5N_2$ (M = Cr, Mo, W).[166]

Infrared and ultraviolet spectral data have been reported for the C_{4v} pentacarbonyl fragments produced by photolysis of chromium, molybdenum, and tungsten hexacarbonyls in inert-gas matrices at 20°K by Turner and coworkers.[167] The C_{4v} structures were deduced from accurate infrared intensity data. These workers found it readily possible to regenerate the hexacarbonyls at 20°K by irradiation with light corresponding to the u.v. absorptions of the pentacarbonyls. For example, for $Cr(CO)_5(C_{4v})$ generated by photolysis of $Cr(CO)_6$ in an argon matrix, the visible absorption band occurs at 542 nm. In the absence of irradiation the reverse reaction was just detectable at 42-45°K but only in the presence of an excess of carbon monoxide. This reverse process has been shown with reasonable certainty to be thermally controlled.

These studies may be compared with the work of Nasielski and coworkers[168] who have studied the flash photolysis of $Cr(CO)_6$ in cyclohexane at room temperature. This process yields a transient species whose half-life at room temperature is approximately 6msec. The transient species (A) was assumed to be $Cr(CO)_5(C_{4v})$ with an absorption at 483 nm and was found to convert to a second species (B) which recombines with carbon monoxide to yield chromium hexacarbonyl. A and B were thought to be isomeric chromium pentacarbonyls which exhibit quite different reactivities towards various ligands. This scheme is illustrated below:

$$Cr(CO)_6 \xrightarrow{h\nu} \underset{\substack{\underline{A} \\ (\lambda_{max}\ 483nm)}}{Cr(CO)_5(C_{4v})} \xrightarrow[\text{unimolecular}]{k \sim 10^2 sec^{-1}} \underset{\substack{\underline{B} \\ (\lambda_{max}\ 440nm)}}{Cr(CO)_5(D_{3h})} \xrightarrow{CO} Cr(CO)_6$$

Boylan, Braterman and Fullarton[169] however, have rejected the assignment of the species (B) to the D_{3h} structure on the basis of their results from u.v. photolysis of $Cr(CO)_6$, $Mo(CO)_6$ and $W(CO)_6$. These workers conclude, that since the species (B) is formed neither in primary photolysis nor under photoreversal conditions, that this species is most likely polynuclear and that the D_{3h} species does not exist as a stable species.

Because of the discrepancy between the absorption data of Turner[167] in an argon matrix and that of Nasielski[168] in a hydrocarbon environment, Turner, et.al.[170] have investigated the behavior of $Cr(CO)_6$ in a solid methane matrix at 20°K. These authors propose the following scheme which is relevant to the solution photochemistry of $Cr(CO)_6$:

$$\begin{tikzcd}
Cr(CO)_6 \arrow[r, "h\nu"] & Cr(CO)_5(C_{4v}) \arrow[r, "\text{hydrocarbon}", "\text{solvent (S)}"'] \arrow[d, shift right, "\lambda_{max}\ 542nm)"'] \arrow[rd, "\text{``strong''}", "\text{ligand}"'] & Cr(CO)_5S \arrow[r] \arrow[d, phantom, "(\lambda_{max}\ 483nm)\ \underline{A}"] & \underline{B}? \arrow[d, "CO"] \\
 & Cr(CO)_5(D_{3h}) \arrow[u, shift right] & Cr(CO)_5L & Cr(CO)_6
\end{tikzcd} \qquad (21)$$

This scheme is consistent with Braterman's[169] suggestion that B is polymeric and not the D_{3h} structure. In addition, the rapid $C_{4v} \rightarrow D_{3h}$ equilibrium lying towards C_{4v} is consistent with Darensbourg, et.al.[171] observations on ^{13}CO exchange.

Darensbourg, Darensbourg and Dennenberg[171] have studied the nature of the intermediate, $[Mo(CO)_5]$, produced in the thermal decomposition or substitution reactions of $Mo(CO)_5$(amine) complexes (reaction 22).

$$\begin{tikzcd}
Mo(CO)_5(\text{amine}) \arrow[r, shift left, "k_1"] \arrow[rd, "k_2", "L"'] & {[Mo(CO)_5]} \arrow[l, shift left, "k_{-1}"] \arrow[d, "\text{fast}"', "L"] & + \ \text{amine}\ (k_1 \gg k_{-1}) \\
 & Mo(CO)_5L &
\end{tikzcd} \qquad (22)$$

This same intermediate is believed to be present in both the photochemical and thermal substitution reactions of the Group VIB hexacarbonyls. It was possible to substitute with ^{13}CO equatorial carbonyl groups in $Mo(CO)_5NHC_5H_{10}$ to a greater extent than the axial carbonyl group by using uv irradiation (40.5% vs. 3.7% resp.). The specifically labeled $Mo(CO)_5NHC_5H_{10}$ when reacted with $As(C_6H_5)_3$ *via* a S_N1 process produced $Mo(CO)_5As(C_6H_5)_3$ in which there was a redistribution of equatorial and axial carbonyl groups during the substitution process. This was suggested to occur by way of a highly distorted square pyramid or trigonal bipyramid intermediate. The labeled species were identified by ir techniques.

In a related photolysis process Nasielski and coworkers[172] have found chromium hexacarbonyl to be a good catalyst for the light-induced hydrogenation of 2,3-dimethylbutadiene and 1,3-cyclohexadiene, yielding respectively 2,3-dimethyl-2-butene and cyclohexene. The hydrogenation occurred exclusively on the 1-4 positions, isomer-free 2,3-dimethyl-2-butene being obtained.

Several Group VIB metal complexes have been reported to be effective as catalysts for disproportionation reactions of olefins. Group VI metal carbene complexes of the type $NR_4[M(CO)_5COR']$ have been shown to catalyze the disproportionation of both terminal and non-terminal olefins in the presence of alkylaluminum halides. The order of reactivity for the disproportionation of pent-1-ene was Mo $>$ W and Ph $>$ Me. The use of neutral carbene species of the type $W(CO)_5(COMe)Et$ and $W(CO)_5[CNMe_2]Me$ was investigated and these were found not to be effective disproportionation catalysts.[173] Bencze and Marko have found that carbon monoxide increases the catalytic activity of mixtures of tungsten halide complexes with $EtAlCl_2$ towards disproportionation of olefins, presumably through formation of tungsten carbonyl derivatives.[174]

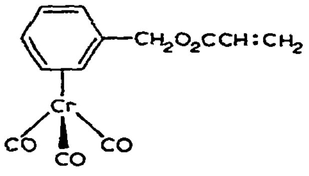
Doyle has also observed olefins to disproportionate at room temperature over $Bu_4N^+[M(CO)_5X]$ (M = Mo, Cr, W; X = Br, Cl) in the presence of $MeAlCl_2$ as activator. Thus, 10 ml of 1-pentene in 10 ml of PhCl reacts with 5 x 10^{-5} moles of $Mo(CO)_5Cl^-$ and 4 x 10^{-4} moles of $MeAlCl_2$ for 24 hr. to give 54% 4-octene and 46% 1-pentene.[175] Whereas, Khidekel and coworkers[176] have studied the disproportionation of olefins in a homogeneous system catalyzed by WCl_6-RMgX (R = Bu or pentyl, X = Cl or Br). Thus, these workers found that 3.4 ml of 2-pentene, 11.5 ml of 0.04M WCl_6 in C_6H_6 and 0.4 ml of 0.61M BuMgCl in 2:1 iso-octane-C_6H_6 attained equilibrium in 1 hr and gave 31% 2-butenes, 65% 2-pentenes, and 4% 3-hexenes.

Davie, Kemball, and Whan observed that treatment of $Mo(CO)_6$ on γ-alumina catalyst with halogenated olefins (e.g. $Cl_2C{:}CH_2$, trans-ClHC:CHCl, $Cl_2C{:}CClH$, $F_3CCH{:}CH_2$) prior to propene disproportionation increased the catalyst activity by 22-155 times.[177] In addition $M(CO)_6$ (M = Cr, Mo, W) on Al_2O_3, SiO_2-Al_2O_3, or charcoal supports were found to catalyze double bond isomerization, polymerization, cyclization, and disproportionation of alkenes and the conversion of C_2H_2 to C_6H_6.[178]

Olefins have been treated with catalysts comprising Et-$AlCl_2$ or $AlCl_3$ and $M(CO)_{6-n}R_n$ (M = W or Mo, n = 1-6, R = electron donating group) to give oligomers and (or) polymers. $W(CO)_5PPh_3$, $W(CO)_3(MeCN)_3$, $[W(CO)_5I][C_5H_5NMe]$, and $Mo(CO)_6$ were used to treat 2-pentene, cyclopentane, 2-hexene, and cyclooctene.[179] A mixture of an alkylaluminum halide, tungsten tetracarbonyl (1,5-cyclooctadiene) or molybdenum tetracarbonyl (norbornadiene) and oxygen, chlorine, bromine, iodine or cyanogen halides were shown to catalyze the ring-opening polymerization of unsaturated alicyclic compounds to give elastomers.[180]

Wang and Menapace[181] have found 1,5-cyclooctadienetungsten-tetracarbonyl to catalyze the isomerization of terminal to internal olefins with no undesirable side effects, such as polymerization or degradation of reactants or products. For example, 2-methyl-1-butene and 1-pentene were isomerized by this catalyst to 2-methyl-2-butene and 2-pentene, respectively, in high conversion. Selectivities to the internal olefins varied from 90 to 100% in the temperature range 115-265°C at olefin/W ratio of 50.

(π-Benzylacrylate)chromiumtricarbonyl (XXXVIII) has been prepared by treating $Cr(CO)_6$ with $PhCH_2OH$ to yield (π-benzylalcohol)-chromiumtricarbonyl followed by esterification with $H_2C{:}CHCOCl$ and Et_2O-pyridine. (XXXVIII) was homopolymerized in the presence of azobis (isobutyronitrile) to yield solid homopolymers with $M_n \leq$ 60,000 and was copolymerized with styrene, methylacrylate, or 2-ferrocenylethyl acrytate.[182] The synthesis of coordination polymers of Ph_2PO_2H with $M(CO)_6$ (M = Cr, W) in organic solvents (oxidation decarbonylation) gave insoluble crosslinked polymers. On the other hand, the polycoordination of Ph_2AsO_2H with $W(CO)_6$ gave a soluble polymer (XXXIX) of mol wt. 3,000.[183]



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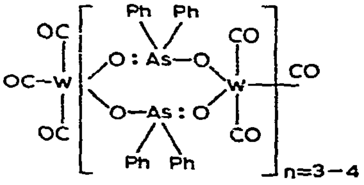


(XXXIX)

Cyclopentene, norbornene and cyclooctene were found to be homopolymerized at -30° to +50° to polyalkenylenes in 60-94% yield in solvents such as benzene, CCl_4, or Et_2O in the presence of the π-complexes, tetra-π-crotyltungsten, tri-π-allylchromium and metal-halides.[184] Several other π-complexes were also reported to be effective. These catalysts are more efficient than known cyclo-olefin polymerization catalysts.

$Mo(CO)_6$ has been shown to have catalytic properties in the desulfurization of hydrocarbon oils in the presence of 90% tert-BuO_2H in benzene solvent.[185] The $W(CO)_6$ could be replaced by V(acetylacetonate), Mo(oxide)/Al_2O_3, V(oxide)/clay, Pt/Al_2O_3, or Co(octanoate).

Soybean methyl esters have been homogenously, selectively hydrogenated in the presence of a variety of catalysts, including $[MoCl_2(CO)_3(PPh_3)_2]$ plus $SnCl_2 \cdot 2H_2O$.[186] Many variations were made in these catalysts without destroying their selectivity. All of the catalysts have been shown to bring about isomerization of the substrate molecules. Studies on the mechanism of stereoselectivity of chromium tricarbonyl catalysts with model compounds have provided the basis for the preparation of simulated fats.[187] These synthetic fats were prepared by taking advantage of the unique property of chromium tricarbonyl to catalyze hydrogenation of polyunsaturates to cis-monounsaturates.

Matsuda and Gutman[188] have studied the acceleration of the shock-tube initiated reaction of C_2H_2-O_2 in the presence of trace amounts of $Cr(CO)_6$. An activated complex of the type $Cr(CO)_5(C_2H_2)$ as suggested in flash photolysis studies was thought not to be probable under the experimental conditions of this study. A more likely pathway appears to be that Cr atoms formed by the decomposition of $Cr(CO)_6$ are oxidized to CrO, CrO_2, and CrO_3 and the CrO_3 (or CrO_2) reacts with C_2H_2 to form chain carriers.

The removal of Fe, Al, Si, and other metal compounds in trace amounts of 10^{-3}-10^{-1}% in $Mo(CO)_6$ and $W(CO)_6$ has been studied by treatment with NaOH solutions, by extraction with organic solvents, and by distillation. The best method found was to distill the hexacarbonyls in pure nitrogen at 70-120mm Hg at 60-100°. The impurities were thereby reduced by 1-2 orders of magnitude and the loss of hexacarbonyls was approximately 2%.[189]

Thermodynamic studies have been carried out on the Group VIB hexacarbonyls. At 43-150° the temperature dependence of the vapor pressure of $Mo(CO)_6$ has been described by the equation: $\log P = (3607.93/T) + 11.2939$. At 118-137.5°, the partial pressures in the gaseous phase were found to change according to the equations: $Mo(CO)_6$, $\log P = -(3497.2/T) + 10.9900$; $[Mo(CO)_6]_2$, $\log P = -(4924.8/T + 13.4381$; and the change in the equilibrium constant of $[Mo(CO)_6] \rightleftarrows 2\ Mo(CO)_6$ was described by $\log K_p = -(2513.6/T) + 6.7759$.[190] Similarly, in the temperature range 42-154° and 60-160°, the dependence of the vapor pressure of $Cr(CO)_6$ and $W(CO)_6$ were described by the equations: $\log P = -(3575.9/T)-11.349$ and $\log P = -(3886.394/T) + 11.538$, respectively. Monomers and dimers of both compounds were indicated by molecular weight measurements in the gaseous phase.[191]

The thermal decompositions of Cr and Mo carbonyls have in addition been investigated employing a hot-zone reaction calorimeter and the enthalpy changes for these reactions were determined.[192]

Target elements ranging from Mo to In have been irradiated in close contact with $Cr(CO)_6$ with 600 Mev p. ^{90}Mo and $^{93}Mo^m$ recoil atoms reacted with the $Cr(CO)_6$ to form $Mo(CO)_6$. The yield of this reaction was determined for the individual isotopes and thei recoil energy. $Mo(CO)_6$ was also irradiated with 600 Mev p, fast n, and thermal n. The percentage of ^{90}Mo, $^{93}Mo^m$, and ^{99}Mo having the configuration of the target was measured for the individual isotopes and the irradiation conditions. In all cases, the retention of $^{93}Mo^m$ was higher than that of ^{90}Mo and ^{99}Mo. The existence or nonexistence of nuclear levels having sufficient lifetime ($<10^{-12}$sec) in the deexcitation cascade of the excited recoiling isotopes was cited as a cause for the difference in chemical behavior for the different isotopes recoiling from nuclear reactions.[193]

Spectroscopy and Theory

Vibrational and electronic spectra. The origin of an extra band in the CO stretching region in the complex $(C_5H_5)(CO)_3WMn(CO)_5$ when the spectrum was observed in CCl_4 as compared with cyclohexane has been discussed by Kaesz and coworkers. This additional band at 2055 cm^{-1} was attributed to the decomposition product $Mn(CO)_5Cl$ formed in carbon tetrachloride solution. No attempt was made to determine the fate of the tungsten and no $(C_5H_5)(CO)_3WCl$ was observed. The rhenium analog was observed to be more stable in CCl_4 solution.[194]

Miller has developed relationships between the non-rigorous Cotton-Kraihanzel C-O force constants and those of a quadratic general valence force field for symmetrical metal carbonyls. These relationships were tested for the Group VIB hexacarbonyls and the non-rigorous force constants are concluded to be valid and realistic quantities when the co-ordinate system is properly defined.[195]

Refined CO stretching force constants were calculated by direct methods for $M(CO)_5L$ complexes.[196] Included in this study were Group VIB pentacarbonyl species of the types; halogenmetal-pentacarbonyls, aminocarbene complexes $[RHN(Me)C]Cr(CO)_5$, carbene complexes $[R(OC_2H_5)C]M(CO)_5$ ($R = CH_3$, $n\text{-}C_4H_9$ and M = Cr, W), phosphacarborane complexes $(CH_3)_4N[B_9H_{10}CHEM(CO)_5]$ (with E = P, As and M = Cr, Mo, and W), and arsine pentacarbonyl complexes of Cr, Mo, and W. These CO stretching and interaction constants were not significantly different from those calculated by the Cotton-Kraihanzel procedure.

The infrared and Raman spectra of cis-diethylenetriamine $M(CO)_3$ (M = Cr, Mo, W) and 1,2,3-, 1,2,4,5-, and 1,3,5-methylbenzene $Cr(CO)_3$ have been studied in the 2000 cm^{-1} region. The spectra for the latter complexes could be interpreted on the basis of a standard factor analysis, however, a derived vibrational factor group analysis was necessary for the triamine complexes. It was observed that the vibrations of these molecules in dilute solutions essentially retain their identities in the solid-state.[197]

Pince and Poilblanc[198] have calculated the force constants for C-O, Mo-C, Mo-C-O, and C-Mo-C vibrations in liquid $Mo(CO)_6$ to be 16.44, 1.937, 0.573, and 0.335 mdynes/Å from fundamental frequencies (3-4000 cm^{-1}) determined by analysis of the Raman spectrum at 170°. Force constants of $Mo(CO)_6$ in the liquid phase were found to be similar to those in CCl_4 solution.

Inelastic neutron scattering spectra have been measured for the complexes $(\pi\text{-}C_5H_5)_2MH_2$ and $(\pi\text{-}C_5H_5)MH_3PF_6$ (where M = Mo and W). Frequencies in the region 400-0 cm^{-1} were assigned to the various deformation and lattice vibrations in these molecules.[199]

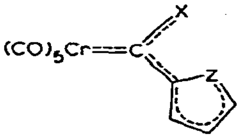
Metal-metal bond dissociation energies have been obtained for the series $(\pi\text{-}C_5H_5)(CO)_3M^1M^2Me_3$ (where M^1 = Cr, Mo, or W; M^2 = Ge or Sn) by measuring the appearance potentials for the ions $M^2Me_3{}^+$ in the mass spectra. The following order of metal-metal bond dissociation energies was observed: $D(W\text{-}M^2) > D(Mo\text{-}M^2) > D(Cr\text{-}M^2)$ (M^2 = Ge or Sn); and $D(M^1\text{-}Sn) > S(M^1\text{-}Ge) > D(M^1\text{-}Si)$. D(ev) ranged from 2.03 to 3.28 depending on M^1 and M^2. The metal-metal stretching modes (165-195 cm^{-1}) were assigned from the observed Raman and infrared spectra. These frequencies (after considering mass effects) did not correlate well with changes in D as determined by the appearance potential measurements.[200]

Anderson and Brown[201] have employed a simple molecular orbital model to calculate the infrared intensities of the CO stretching modes in model $M(CO)_5L$ and <u>fac</u>-$M(CO)_3L_3$ compounds. The intensity of the E species mode was found to be dependent on the net charge residing on L, regardless of the σ and π bonding distribution, whereas, the A_1 mode intensities increased with increasing π acceptor ability of L. The intensity ratio, $I(E)/I(A_1)$, in $M(CO)_3L_3$ compounds was suggested to be a sensitive measure of the importance of π-bonding in the M-L bond in these species.

Kettle and coworkers[202] have examined some of the factors influencing the absolute infrared intensity of the CO stretching modes in the complexes $XM(CO)_5^-$ (X = Cl, Br, I; M = Cr, W), as well as in the Mn and Re analogs. Their treatment involve a determination of the extent of the contribution of a transverse component (non-colinear with the carbonyl bond) to the dipole moment derivative in these complexes. This component was observed to be as large as 17% of the corresponding longitudinal bond moment derivative. The existence of an asymmetry in either the X-M or X-(CO) equatorial interactions was proposed to account for the transverse component.

Terzis and Spiro have measured the Raman intensities of the two A_{1g} modes in $M(CO)_6$ (M = Cr, Mo, W) corresponding to the M-C and C-O vibrations. The M-C data support the well-accepted notion that π-backbonding is important in the Group VIB hexacarbonyls and decreases in the order W $>$ Cr $>$ Mo. However, the results for C-O vibrations were unsatisfactory giving rise to C-O bond orders between 4.2 and 4.4. This inflated bond order for CO was ascribed to synergistic effects which are neglected in bond polarizability theory.[203]

Infrared, electronic, and nmr spectral studies have been carried out on a series of chromium carbene complexes of the types $(CO)_5CrC(X)CH{:}CH_2$ ($X = O^-NMe_4^+$, OMe) and $(CO)_5CrC(X)C_4H_3Z$ ($X = O^-NMe_4^+$, OMe and Z = O, S, NMe). Spectroscopic evidence for extensive stabilization of the empty carbene carbon p_z orbital by donation from the C_4H_3Z groups was obtained but no definite evidence for this stabilization was found for the vinyl carbene complexes. The electron withdrawing power of the carbene ligands in the complexes, $(OC)_5CrC(X)C_4H_3Z$, was observed to increase in the order $X = O^-NMe_4^+ < NH_2 <$ OEt for a constant Z and Z = O > S > NMe for a given X. This stabilization was ascribed primarily to a conjugative release mechanism (XL) as opposed to π→p interaction.[204]



(XL)

Dieck and Renk[205] have investigated the electronic spectra of a large variety of diazabutadiene complexes of the type $(RN{:}CR'CR'{:}NR)Mo(CO)_4$. These complexes show an intense low-energy electronic transition antiparallel to the ground state dipole moment. The solvent dependence of this transition was measured and taken to indicate the degree of metal-ligand π interaction. The π-delocalization of metal <u>d</u>-electrons was observed to strongly depend on the nature of R and R'. Polarographic reduction potentials for these complexes were determined in order to separate competing mesomeric, inductive and steric effects of the diazabutadiene ligands.

Wrighton, Hammond and Gray[206] have reported the emission spectra for $W(CO)_5L$ compounds where L = ketone, ether, amine, or pyridine. An emission maximum was observed at 77°K between 510 and 545 nm for all the complexes, which was taken to strongly suggest that the axial ligand field is dominated by the CO group. However, it was obvious from differences in the intensity of the emission spectra that the L ligand can provide nonradiative decay pathways.

Mass spectra. The mass spectra and ionization potentials of compounds of the type $M(CO)_5L$, where M = Cr, Mo, and W and L = $P(OMe)_3$, $P(OEt)_3$, PCl_3, CNPh, CNBu, and CNC_6H_{11} have been reported.[207] Variations in the donor-acceptor ability of these ligands were found to be the main factor influencing both molecular ionization potentials and cracking patterns. All the compounds showed very low relative abundance of the $M(CO)_5L^+$ and M^+ ions and high intensity of the $M(CO)_xL^+$ and ML^+ ions. The overall intensity of the chromium complexes differed significantly from those of Mo and W. The molecular ionization potentials were shown to depend both on M and L, increasing in the order $Cr < Mo < W$.

Mass spectral studies of a series of carbene complexes $(CO)_5CrC(X)C_4H_3Z$ (Z = S, NMe; X = OEt, NH_2), $(CO)_5CrC(X)C_4H_3O$ (X = $OCOCH_3$, OPh, OEt, SEt, SPh, NH_2, NC_6H_8) and $(CO)_5CrC(OMe)C_2H_3$ have shown that the abundance ratio parameter, R_I, cannot necessarily be used as an index for the ionization potentials. The mass spectrum of the vinyl complex, $(CO)_5CrC(OMe)C_2H_3$, indicates formation of a π-allyl complex, $[C_3H_5Cr(CO)_4]^+$. The influence of the heteroatom, Z, upon the fragmentation of the ligand, $(X)CC_4H_3Z$ was discussed.[208]

Secondary ions, $M_m(CO)_n^+$, have also been observed by Kraihanzel and coworkers[209] in the mass spectra of $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ at 10^{-5}-10^{-6} torr at 35-100°, a temperature where thermal decomposition should not have occurred. The value of n was 0-14 depending upon m (1-3 for Cr, 1-2 for Mo, and 1-4 for W). Simultaneous introduction into the ion source of $Me_3NW(CO)_5$ and $Cr(CO)_6$ produced a number of ions, including $Me_3NWCr(CO)_n^+$ (where n = 3-6). The formation of the $Me_3NWCr(CO)_n^+$ ions were thought most likely to occur via ion-molecule reactions, as were the formation of the various $M_m(CO)_n^+$ $(m > 1)$ species. In addition it was shown that the relative intensities of the various $W_2(CO)_n^+$ are directly proportional to the square of the relative intensity of $W(CO)_6^+$.

Muller and Fenderl[210] have studied the behavior of the complexes $Cr(CO)_6$, $Cr(C_6H_5)_2$, $C_5H_6Cr(CO)_3$, $C_5H_5Cr(NO)(CO)_2$, and $Cr(C_5H_5)_2$ under slightly increased pressure in the ion source of a mass spectrometer. Ion-molecular reactions were found to occur which led to the formation of bi- and in few cases trinuclear secondary ions, e.g. the secondary ions observed for $Cr(CO)_6$ were $Cr_m(CO)_n^+$ (m = 2, n = 2-11; m = 3, n = 12-14). The short-life primary collision complexes were found to be stabilized by loss of the most loosely bound ligands.

Mass-spectrometric studies of the effect of alkyl substituents in benzene rings on the metal-ligand bond strength in a series of substituted $(C_6H_6)_2Cr$ derivatives with PrPh, MePh, EtPh, $Et_2C_6H_4$, $Me_2C_6H_4$, $Me_3C_6H_3$, and Me_6C_6 groups. The bond between Cr and the ligands was observed to be strengthened by increased donor ability of the alkyl substituents in the rings.[211] In a related study, mass spectra and ionization potentials for a series of benzene chromium tricarbonyl derivatives have been determined.[212] The complexes containing the Me, Et, Pr, or Bu ester of benzoic acid, phenylacetic acid or cinnamic acid showed a series of general fragmentation reactions.

The influence of the complexed metal ion on the mass spectra of organometallic complexes, e.g. (benzene)Cr(CO)$_3$, has been investigated by Budzikiewicz.[213] It was concluded that the mode of fragmentation of aromatic π-ligands is retained with metals of different valency. Hence, the radical site in the molecular ion is stabilized by the aromatic π-system and not by the complexed metal so that possible changes of valency are of no major importance.

Nuclear magnetic resonance, photoelectron spectra and theory.

Carbon-13 nuclear magnetic resonance studies have been applied to a variety of carbonyl containing organometallic complexes. Gansow and collaborators[214] have measured the spectra of the three Group VIB metal carbonyls M(CO)$_6$ (M = Cr, Mo, W) and monosubstituted complexes LW(CO)$_5$ [L = P(OC$_6$H$_5$)$_3$, P(O-n-C$_4$H$_9$)$_3$, P(O-n-C$_4$H$_9$)$_2$C$_6$H$_5$, P(O-n-C$_4$H$_9$)(C$_6$H$_5$)$_2$, P(C$_6$H$_5$)$_3$, As(C$_6$H$_5$)$_3$, Sb(C$_6$H$_5$)$_3$, Bi(C$_6$H$_5$)$_3$, and NH$_2$(C$_6$H$_{11}$)]. A linear-relationship between the Cotton-Kraihanzel carbonyl stretching force constants _versus_ the carbon-13 carbonyl chemical shifts for tungsten complexes was illustrated. This was taken to strongly suggest that for a given metal, changes in M-C-O π bonding exert a dominant influence on ^{13}C chemical shifts. ^{183}W-^{13}C, ^{183}W-^{31}P, and ^{31}P-^{13}C coupling constants were reported for the complexes studied. Mann[215] has reported the ^{13}C nmr spectra for the complexes [LM(CO)$_3$], (L = mesitylene, durene or cycloheptatriene; M = Cr, Mo, W), and the ^{183}W-^{13}CO coupling constant for (durene)W(CO)$_3$. The average coordination chemical shift in the cycloheptatriene complexes was observed to be considerably greater than the corresponding shift in arene complexes, implying stronger metal-triene bonding. In addition, Randall and coworkers[216] have reported ^{13}C chemical shift data for the Group VIB metal complexes: $(OC)_5CrC(OMe)Me$, $(OC)_3(\pi-C_5H_5)WMe$, $(OC)_5MoP(OPr^i)_3$, $(\pi-C_6H_6)Cr(CO)_3$, and $(m\text{-xylene})Mo(CO)_3$ along with several other transition metal organometallic species.

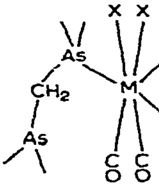
The magnitude and signs of phosphorus-phosphorus coupling constants, $^2J_{PMP'}$, in transition metal-phosphine complexes have been the subject of discussion. Heteronuclear "tickling" experiments on cis-$(PH_3)_2Mo(CO)_4$ were carried out and $^2J_{PMP'}$ was observed to be negative. These results together with other available data on cis-$L_2M(CO)_4$ complexes ($L = (CH_3)_3P$; M = Cr, Mo, W and $L = (CH_3O)_3P$; M = Mo) suggest that $^2J_{PMP'}$ is likely to be negative in all such cis-disubstituted complexes of Group VIB metals. However, heteronuclear "tickling" experiments on cis-$EtN(PF_2)_2Mo(CO)_4$ indicated a positive value of $^2J_{PMP'}$ in this case. The magnitude of $|^2J_{PMP'}|$ was observed to decrease in the order Cr > Mo > W.[217]

Shaw and coworkers[218] have observed a linear correlation between the ^{31}P chemical shift of the free phosphine, δ, and the change in chemical shift upon coordination with a metal atom, Δ ($\Delta = A\cdot\delta + B$). ^{31}P data for a number of complexes, including previously published data for $M(CO)_5L$ (M = Cr, Mo, W) species[219], are reported to observe this relationship. A and B values found for the $M(CO)_5L$ complexes were: A = -0.132, -0.069, +0.001; B = -58.99, -42.01, and 25.25 for the chromium, molybdenum, and tungsten derivatives, respectively. As of yet this relationship between δ and Δ is not understood theoretically.

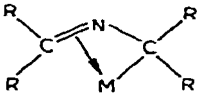
Green and Brown[220] have investigated ^{183}W chemical shifts in cis- and trans- bis(tributylphosphine)tetracarbonyltungsten. The ^{183}W chemical shifts were observed at +1965 and +2021 ppm (relative to WF_6) for the two isomers, respectively. These higher field resonances as compared with WF_6 parallel the trend previously noted for the variation in chemical shifts between the different oxidation states in transition metal compounds.[221]

Temperature dependent nmr studies of π-$C_5H_5M(CO)_2[(p\text{-}MeC_6H_4)_2$-$CNC$-$(p\text{-}MeC_6H_4)_2]$ (M = Mo, W) in the range -20 to 70° have shown the bonding of the aza-allyl group to the metals to be of σ-π type (XLI). At 70°, interchange of σ-π bonding and rotation about the C-N bonds is thought to occur producing four equivalent p-MeC_6H_4-groups.[222]

The proton nmr spectra of the complexes $M(CO)_2(dam)_2X_2$ (M = Mo, W; X = Cl, Br, I; dam = bis(diphenylarsino)methane) (XLII) have been examined over a temperature range between 60° and -60°. Exchange was observed between the non-equivalent dam molecules near room temperature. however, at lower temperatures the exchange was quenched with further fine structure in the spectra appearing due to the freezing-in of certain molecular conformations. Rate constants for the various exchange processes were determined by line shape analyses employing the density matrix method.[223]



(XLI)



(XLII)

(R=p-MeC_6H_4)

The ^1H nmr spectrum of $[M(NO)_2(S_2CNMe_2)_2]$ (M = Mo or W) was found to be consistent with a rigid cis-octahedral structure at room temp. and to undergo rapid interconversion of the two types of N-methyl groups at higher temperatures (80-140°). The mononitrosyl complex $[Mo(NO)(S_2CNMe_2)_3]$ exhibited a room temp. ^1H nmr spectrum which was interpreted in terms of a pentagonal bipyramidal structure. At higher temperatures (60-128°) interconversion of both the N-methyl groups and the two types of dithiocarbamato-ligands was observed. The most favorable mechanism for interconversions in both these compounds was proposed to involve partial dissociation of a dithiocarbamato-ligand with a concomitant rotation of the N-methyl groups about the C-N bond. ΔG^* values of 21 and 18 kcal-mole^{-1} were determined for the dinitrosyl and mononitrosyl complexes, respectively.[224]

The ^{182}W Mossbauer spectra of $W(CO)_6$ utilizing the 100 keV transition of ^{182}W has been reported.[225] A single line spectrum with a chemical isomer shift value of -0.1 ± .2 mm/sec was observed. This is consistent for a W(O) species with a d^6 configuration and a symmetric arrangement of six carbonyl ligands.

The high energy photoelectron spectra of several transition metal carbonyls, including $M(CO)_6$ (M = Cr, and W), have been measured by Hillier and coworkers.[226] In all cases, both the carbon and oxygen 1s electrons are less tightly bound than in free CO by ca. 2.5 and 1.5 ev, respectively. These results are taken to indicate that there is an increase in electron density on the bound CO in the complexes as compared with free carbon monoxide. Similarly, molecular core binding energies have been measured by X-ray photoelectron spectroscopy in a variety of transition metal carbonyls and π-cyclopentadienyls by Clark and Adams.[227] $Cr(CO)_6$ and $(\pi\text{-}C_5H_5)_2Cr$ core binding energies were determined in this study. The C_{1s} binding energies of the cyclopentadienyl ligands as compared with that for the neutral free ligand indicate a small positive charge in the rings.

Ionization potentials, photoelectron spectra, and mass spectra of a series of trifluorophosphine metal complexes, including $Cr(CO)_6$

$(PF_3)_n$ (where n = 1,2,and 3), have been investigated by Müller, et.al.[228] This study indicates PF_3 to be a very good π acceptor ligand, possibly better than carbon monoxide.

Pierpont and Eisenberg[229] have presented an orbital correlation diagram for the two bonding modes in transition metal nitrosyls, linear NO^+ or bent NO^-, which allows for the prediction of the preferred arrangement in these complexes. $Cr(CN)_5NO^{-3}$ was predicted to have a linear structure in agreement with crystal structure data.

Employing a semiempirical and self-consistent charge and configuration (SCCC) molecular orbital method the electronic configurations of $Cr(CO)_6$ and $Cr(CO)_5N_2$ have been compared.[230] This method interprets the replacing of a CO in $Cr(CO)_6$ with N_2 as resulting in a decrease in σ donation and π back donation. The final charge calculated for chromium in $Cr(CO)_6$ was 0.2753 compared to 0.2859 in $Cr(CO)_5N_2$, thus the decrease in charge due to decreased back donation in the nitrogen complex is more than compensated for by the decrease in σ donation. However, the results indicate that the $Cr(CO)_5N_2$ complex should be thermodynamically stable with an approximated enthalpy of formation calculated to be -233 kcals/mole. It is interesting at this point to recall an earlier reference[166] in this survey of possible spectroscopic evidence for the existence of $M(CO)_5N_2$ (M = Cr, Mo, W) complexes.

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