MANGANESE, TECHNETIUM AND RHENIUM

ANNUAL SURVEY COVERING THE YEAR 1971

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Synthesis and Reactions

In general, the format of this section parallels that of the 1970 Survey. Briefly, papers concerned primarily with preparative aspects of organometallic chemistry of the Group VII elements are dealt with in the following order: metal carbonyls; carbonyl halides; carbonyls with N-donor, P- and As-donor, O-donor, and S-donor ligands; boron-containing metal carbonyls; N_2 complexes; metal-metal bonded compounds; hydrides; M-C σ-bonded complexes; compounds with fluorocarbon ligands; and π-complexes. The last part of this section does not include those reactions which lead to substitution on the π-C_5H_5 ring of π-$C_5H_5M(CO)_3$ without affecting the $M(CO)_3$ moiety. They are covered in the Chapter on ''Organic Reactions of Selected π-Complexes''.

Unless indicated otherwise, structures of the complexes referred to in this section were inferred with the aid of one or more of the following techniques: vibrational spectroscopy, proton (also, where applicable, ^{19}F, ^{11}B, etc.) resonance spectroscopy, and mass spectrometry.

A new synthetic procedure for $Mn_2(CO)_{10}$ has been patented which uses $(\pi\text{-}CH_3C_5H_4)Mn(CO)_3$, naphthalene, and sodium in diglyme at 80-150° and under 1 atm of CO [1]. High-pressure preparative methods for $Mn_2(CO)_{10}$ [2,3] and $Re_2(CO)_{10}$ [4] have been also reported, the first two in the patent literature.

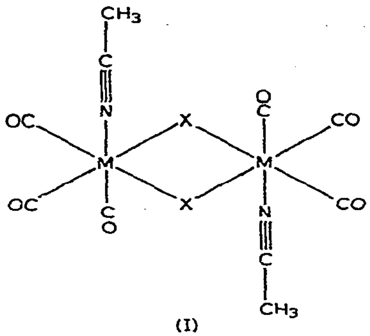
Photochemical reaction between $Re_2(CO)_{10}$ and I_2 yields either $Re(CO)_5I$ or $Re_2(CO)_8I_2$ depending on experimental conditions [5]. The use of Pyrex-filtered ultraviolet light at room temperature promotes the formation of $Re(CO)_5I$, whereas unfiltered ultraviolet light and higher temperatures (110°) favor $Re_2(CO)_8I_2$. Treatment of K_2ReI_6 in acetone with CO, followed by addition of R_4NI, affords the ionic R_4N[trans-$Re(CO)_2I_4$] [6]. However, if both KOH and R_4NI are introduced into K_2ReI_6 treated the same way with CO in acetone, then orange, paramagnetic $(R_4N)_2$[trans-$Re(CO)_2I_4$] becomes the product. A longer treatment of K_2ReI_6 with CO in acetone and subsequent addition of KOH and R_4NI yield the known $R_4N[Re(CO)_4I_2]$.

Reported in a doctoral dissertation are reactions of $Mn(CO)_4NO$ with halogens and pseudohalogens, as well as quantum yields for some photochemical substitution reactions of $Mn(CO)_4NO$ [7]. The latter vary with the ligand L and with the concentration of the better nucleophiles.

Several new halogenonitrosyl complexes of rhenium have been prepared by Zingales and coworkers [8]. Treatment of $[Re(CO)_4Cl]_2$ with NO and HCl affords chlorine-bridged $[Re(CO)_2(NO)Cl_2]_2$, from which the corresponding bromide and iodide can be synthesized by methatetical reactions. $[Re(CO)_2(NO)Cl_2]_2$ reacts with L ($L = P(C_4H_9)_3$, pyridines, and O-donor ligands) to give $Re(CO)_2(NO)LCl_2$. The bromo and iodo complexes react analogously with pyridine. The reaction of $Re(CO)_4LCl$ or $Re(CO)_3L_2Cl$ with NO and HCl also affords $Re(CO)_2(NO)LCl_2$.

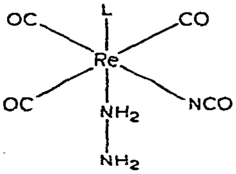
The complexes $[M(CO)_3(NCCH_3)X]_2$, of proposed structure (I), result when $M(CO)_5X$ (M = Mn or Re, X = Cl, Br, or I) reacts with CH_3CN in 2,2-dimethoxypropane [9]. One member of this series (M = Mn, X = Cl) was reported earlier (AS 9, 162).

Several isocyanatocarbonyls of rhenium have been prepared using anhydrous hydrazine as the source of nitrogen [10]. Reaction of trans-$Re(CO)_4LBr$ ($L = P(C_6H_5)_3$) or cis-$Re(CO)_4LBr$ ($L = P(C_6H_5)_3$, $P(CH_3)_2C_6H_5$,



(I)

or $As(CH_3)_2C_6H_5$) with hydrazine affords $Re(CO)_3L(NH_2NH_2)NCO$ (II), whereas that of mer(L's trans)-$Re(CO)_3L_2X$ (L = $P(C_6H_5)_3$, X = Br; L = $P(CH_3)_2C_6H_5$ or $P(CH_3)(C_6H_5)_2$, X = Cl) gives $Re(CO)_2L_2(NH_2NH_2)NCO$ (III). Substitution reactions of (II) and (III) furnish additional dicarbonyl and tricarbonyl isocyanato complexes. Some of these compounds were incorrectly reported earlier (AS 6, 1103) as containing molecular nitrogen. Treatment of $Re(CO)_3(PR_3)_2Cl$ with NaN_3 or $C_6H_5C(O)N_3$ affords $Re(CO)_3(PR_3)_2N_3$ (R = $P(CH_3)_2C_6H_5$ or $P(CH_3)(C_6H_5)_2$) rather than isocyanatocarbonyls.



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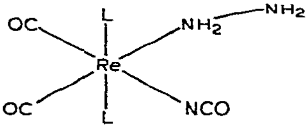
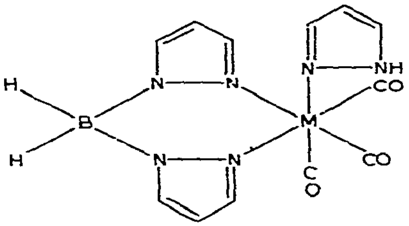


(III)

In a related study, mer(P's trans)-$Mn(CO)_3[P(CH_3)_2C_6H_5]_2Br$ was found to react with NH_2NH_2 to give $Mn(CO)_2[P(CH_3)_2C_6H_5]_2(NH_2NH_2)NCO$, which affords $Mn(CO)_3[P(CH_3)_2C_6H_5]_2NCO$ and $Mn(CO)_2[P(CH_3)_2C_6H_5]_3NCO$ upon reaction with CO and $P(CH_3)_2C_6H_5$, respectively [11]. The last dicarbonyl yields $Mn(CO)_2[P(CH_3)_2C_6H_5]_3Br$ when treated with bromide. The stereochemistries of these compounds are discussed.

Reaction of $M(CO)_5Br$ or $M_2(CO)_{10}$ (M = Mn or Re) with potassium dihydrobis(pyrazolyl)borate affords the crystalline complexes $[H_2B(N_2C_3H_3)_2]M(CO)_3$(pyrazole) (IV) [12]. Substitution reactions of (IV) have afforded *cis*-$[H_2B(N_2C_3H_3)_2]Mn(CO)_2L_2$ (L_2 = $(C_6H_5)_2P\ CH_2CH_2P(C_6H_5)_2$ or $2P(CH_3)_2C_6H_5$), *fac*-$[H_2B(N_2C_3H_3)_2]Mn(CO)_3X^-$ (X = Br or I), and $[H_2B(N_2C_3H_3)_2]M(CO)_2L_2$ (V: M = Mn, L = $P(OCH_3)_3$ or $C_2H_5C(CH_2O)_3P$; M = Re, L = $CH_3C(CH_2O)_3P$).



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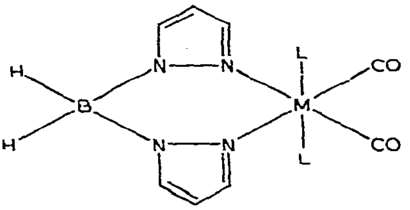


(V)

Chatt and associates [13] report reactions of some benzoylazo complexes of rhenium. $Re[P(C_6H_5)_3]_2(N_2COC_6H_5)Cl_2$ affords $Re(CO)_2[P(C_6H_5)_3]_2(N_2COC_6H_5)Cl_2$ when treated with CO. This unstable golden-yellow dicarbonyl reacts with Cl_2 to give $Re(CO)[P(C_6H_5)_3]_2(N_2COC_6H_5)Cl_3$ and decomposes upon chromatography on silica gel to furnish, among other products, $Re(CO)_2(N_2)[P(C_6H_5)_3]_2Cl_2$.

The complexes Ni(saen) and Ni(aben) (saen = N,N'-ethylenebis-(salicylideneiminato) and aben = N,N'-ethylenebis(*o*-aminobenzylideneiminato)) react with $Mn(CO)_5X$ (X = Cl or Br) to yield Ni(saen)$Mn(CO)_3X$ and Ni(aben)-$Mn(CO)_3X$, respectively [14]. The infrared spectra indicate C_{2v} local symmetry around manganese in both products.

Two metalloporphyrins have been isolated from the reaction of mesoporphyrin IX dimethyl ester with $Re_2(CO)_{10}$: μ-[mesophorphyrin IX dimethyl esterato]bis[tricarbonylrhenium(I)] and (monohydrogen mesoporphyrin IX dimethyl esterato)tricarbonylrhenium(I) [15].

Replacement of CO with PF_3 in $Mn(CO)_4NO$ [16], $HCF_2CF_2Mn(CO)_5$, and $HRe(CO)_5$ [17] has been the subject of doctoral dissertations. The use of

$Ni(PF_3)_4$ in synthesis of PF_3-containing metal complexes has been reported [18]. Prepared by this general procedure have been $Mn_2(CO)_{10-x}(PF_3)_x$ (x = 0, 1, or 2) or $Mn_2(CO)_8(PF_3)_2$, starting with $Mn(CO)_5Br$, and $Re(CO)_3(PF_3)_2Br$, from $Re(CO)_5Br$ and excess $Ni(PF_3)_4$.

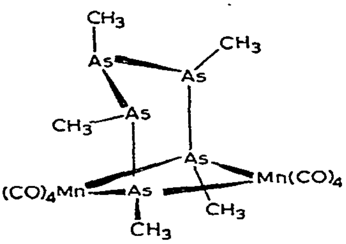
Reaction of $Mn_2(CO)_{10}$ with $P(C_6H_5)_3$ has been studied under various experimental conditions [19]. Two compounds analyzing for ''$Mn(CO)_4P(C_6H_5)_3$'' were obtained: dimeric $Mn_2(CO)_8[P(C_6H_5)_3]_2$ [20] and a monomeric, diamagnetic ''$Mn(CO)_4P(C_6H_5)_3$'', possibly trans-$HMn(CO)_4P(C_6H_5)_3$. The diamagnetic species had been isolated earlier from the interaction of $C_6H_5CH_2SO_2Mn(CO)_5$ with $P(C_6H_5)_3$ [21].

Dirhenium dodecacarbonyl reacts photochemically with 1 mole of $P(CH_3)(C_6H_5)_2$ (L) to give $Re_2(CO)_9L$, $Re_2(CO)_8L_2$, two isomers of $Re_2(CO)_7L_3$, and $Re_4(CO)_{10}L_6$ [22]. With 2 moles of L, $Re_2(CO)_{10}$ affords two isomers of $Re_2(CO)_7L_3$ and $Re(CO)_3L_2$. By way of contrast, thermal reaction between $Re_2(CO)_{10}$ and 1 mole of L yields $Re_2(CO)_8L_2$ as the only isolable product. The interaction between $Re_2(CO)_8L_2$, $Re_2(CO)_7L_3$, $Re_4(CO)_{10}L_6$, or $Re(CO)_3L_2$ and dry HCl leads to the formation of cis- and trans-$Re(CO)_4LCl$ and mer (L's trans)-$Re(CO)_3L_2Cl$. Reaction of mer-ReL_3Cl_3 with CO in ethanol furnishes mer(L's trans)-$Re(CO)_3L_2Cl$ and mer(CO's cis)-$Re(CO)_2L_3Cl$. The first product can be also obtained by treating mer-ReL_3Cl_3 with Na(Hg) and CO and by the reaction of ReL_2Cl_4 with CO in 2-methoxyethanol. An unusual paramagnetic $Re(CO)_5[P(CH_3)_2C_6H_5]$, obtained from $Re_2(CO)_{10}$ and $P(CH_3)_2C_6H_5$ (> 2 moles), is also mentioned.

In a series of papers King and coworkers report [23, 24, 25] on reactions between various manganese carbonyls and several polydentate phosphines. Treatment of $CH_3Mn(CO)_5$ and $Mn(CO)_5Br$ with $[(C_6H_5)_2PCH_2CH_2]_2PC_6H_5$ (Pf-Pf-Pf) yields $CH_3Mn(CO)_3$(Pf-Pf-Pf) and $Mn(CO)_2$(Pf-Pf-Pf)Br, respectively [23]. The tetradentate $(C_6H_5)_2PCH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)CH_2CH_2P(C_6H_5)_2$ (Pf-Pf-Pf-Pf) and $[(C_6H_5)_2PCH_2CH_2]_3P$ (P-(Pf)$_3$) furnish $CH_3Mn(CO)_3$(Pf-Pf-Pf-Pf),

$CH_3Mn(CO)_2[P\text{-}(Pf)_3]$, and $CH_3COMn(CO)_3[P\text{-}Pf)_3]$ upon reaction with $CH_3Mn(CO)_5$, and $Mn(CO)_2(Pf\text{-}Pf\text{-}Pf\text{-}Pf)Br$ and $Mn(CO)_2[P\text{-}(Pf)_3]Br$ with $Mn(CO)_5Br$ [24]. The hexatertiary phosphine $[(C_6H_5)_2PCH_2CH_2]_2PCH_2CH_2P[CH_2CH_2P(C_6H_5)_2]_2$ $(P_2\text{-}(Pf)_4)$ yields: (a) $[CH_3Mn(CO)_2]_2[P_2\text{-}(Pf)_4]$ and/or $CH_3Mn(CO)_2[P_2\text{-}(Pf)_4]$ upon reaction with $CH_3Mn(CO)_5$ in xylene or mesitylene at reflux, and $CH_3COMn(CO)_3[P_2\text{-}(Pf)_4]$ with $CH_3Mn(CO)_5$ in THF; (b) $(\pi\text{-}C_5H_5)_2Mn_2(CO)_3\text{-}[P_2\text{-}(Pf)_4]$ when treated with $\pi\text{-}C_5H_5Mn(CO)_3$; and (c) $\{(\pi\text{-}C_5H_5)_2Mn_2(CO)(NO)_2\text{-}[P_2\text{-}(Pf)_4]\}(PF_6)_2$ upon reaction with $[\pi\text{-}C_5H_5Mn(CO)_2NO]PF_6$ [25].

Dimanganese decacarbonyl and $(AsCH_3)_5$ react in the presence of light at room temperature to give $Mn_2(CO)_8(AsCH_3)_5$ (VI), whose proposed structure is based on the ^1H NMR and mass spectra [26]. The same reactants yield $[Mn(CO)_3(AsCH_3)_4]_2$, of possible structure (VII), when heated at 150°.



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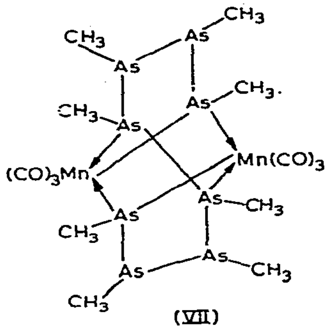
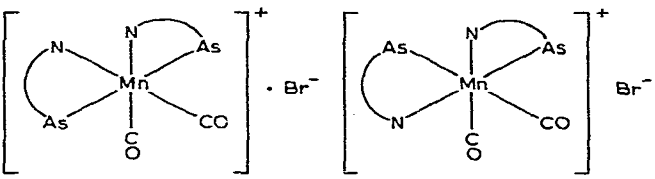


(VII)

The reaction between $Mn_2(CO)_{10}$ and $As(CH_3)_2I$ affords the unsymmetrically-bridged $Mn_2(CO)_8[As(CH_3)_2]I$, whereas that between $Mn_2(CO)_{10}$ and $As(CH_3)_2X$ ($X = Cl$ or Br) yields polymeric carbonyls of unknown structure [27]. A series of analogous complexes $Mn_2(CO)_8[As(CH_3)_2]X$ ($X = SCF_3$, SCH_3, Cl, $P(CH_3)_2$, and H) has been prepared starting with $Mn_2(CO)_8[As(CH_3)_2]I$. Both $Mn_2(CO)_8[E(CF_3)_2]_2$ and $Mn_2(CO)_8[E'(CH_3)_2][E(CF_3)_2]$ result upon treatment of $Mn_2(CO)_{10}$ with $(CH_3)_2E'\text{-}E(CF_3)_2$ ($E = P$, $E' = As$; $E = As$, $E' = P$). The infrared, ^1H NMR, and mass spectra of these dimanganese compounds are reported.

The photochemically generated complexes $M(CO)_5[E(CH_3)_2Cl]$ (M = Cr, Mo, and W, E = P and As) react with $NaM'(CO)_5$ (M' = Mn and Re) to produce $(CO)_5ME(CH_3)_2M'(CO)_5$ as yellow-to-orange, air-stable, crystalline solids [28]. On heating or photolysis, these products decompose to $M(CO)_6$ and $M'_2(CO)_8[E(CH_3)_2]_2$.

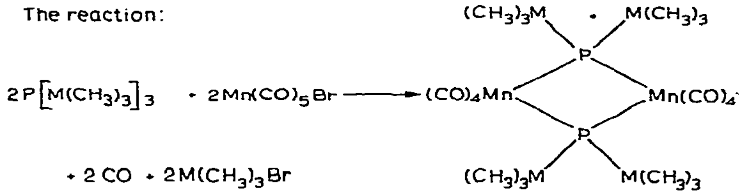
As part of a broader study, Chiswell, et al. [29] report on the reaction of $Mn(CO)_5Br$ with o-dimethylarsinoaniline (MAA) and 1-amino-2-(diphenylarsino)ethane (APE). Diamagnetic, insoluble complexes of formula $Mn(CO)_2(MAA)Br$ and $Mn(CO)_2(APE)Br$, tentatively assigned structure (VIII a or b: N-As = MAA or APE), were isolated.



(a) (b)

(VIII)

The reaction:



(1)

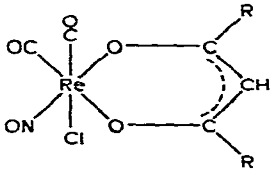
M = Ge or Sn, occurs at 60-70° and affords ca. 80% yields of the products [30]

The complexes mer(L's trans)-$Mn(CO)_3L_2Br$ (L = $P(CH_3)_2C_6H_5$ or $As(CH_3)_2C_6H_5$) and fac-$Mn(CO)_3L_2Br$ (L = $As(CH_3)_2C_6H_5$; L_2 = $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$ or $(C_6H_5)_2PCH_2P(C_6H_5)_2$) in benzene undergo rapid oxidation with $NOPF_6$ to give green crystalline [fac-$Mn(CO)_3L_2Br]PF_6$ [31]. These Mn(II) products can be reduced back to Mn(I) with $CHCl_3$, H_2, or alcohols.

The known anion $[Re_2(CO)_6(OH)_3]^-$ (AS 5, 630) has been synthesized via a different procedure which involves reaction of $Re_2(CO)_{10}$ or $Re(CO)_5Br$ with 0.1-0.3 M KOH [32].

Several carboxylatocarbonyl complexes of rhenium have been prepared by Lindner and Grimmer [33]. The reaction between RCO_2Na (R = CH_3 or C_6H_5) and $Re(CO)_5Br$ in THF at 60° affords the dinuclear $[RCO_2Re(CO)_3]_2$. These complexes can be carbonylated under 300 atm of CO at 50° to the corresponding $RCO_2Re(CO)_5$, in which the carboxylate is monodentate. The reaction can be reversed by heating the pentacarbonyls to 80°. Treatment of $[C_6H_5CO_2Re(CO)_3]_2$ with $P(C_6H_5)_3$ affords $C_6H_5CO_2Re(CO)_3[P(C_6H_5)_3]_2$.

New acetylacetonatonitrosyl complexes of rhenium, $Re(CO)_2(NO)(C_3HR_2O_2)Cl$ (IX), have been prepared by the reaction of $[Re(CO)_2(NO)Cl_2]_2$ with $RC(O)CH_2C(O)R$ (R = CH_3, CF_3, or C_6H_5) [34]. $[Re(CO)_2(NO)Cl_2]_2$ reacts also with cyclooctene to afford $[Re(CO)(NO)(cyclooctene)Cl_2]_2$, which upon treatment with N-, P-, and As-donor ligands (L) gives $Re(CO)(NO)L_2Cl_2$.



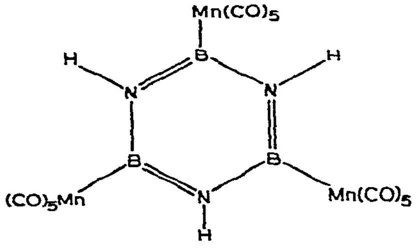
(IX)

A detailed account has appeared [35] of the preparation of $R_2PS_2M(CO)_4$ (M = Mn or Re, R = C_2H_5 or C_6H_5) via the reaction of R_2PS_2Na with $M(CO)_5Br$ (AS 9, 164-165). The complex with R = C_2H_5 and M = Re was also obtained photochemically from $(C_2H_5)_2P(S)S_2P(S)(C_2H_5)_2$ and $Re_2(CO)_{10}$. Upon heating under reduced pressure (10^{-2}mm) at 40° it forms $[(C_2H_5)_2PS_2Re(CO)_3]_2$, the reaction being reversed at high pressures of CO. Upon treatment with $P(C_6H_5)_3$ it affords $(C_2H_5)_2PS_2Re(CO)_3P(C_6H_5)_3$.

Preparation of new manganese complexes with boron-containing ligands has received some attention. The reaction:

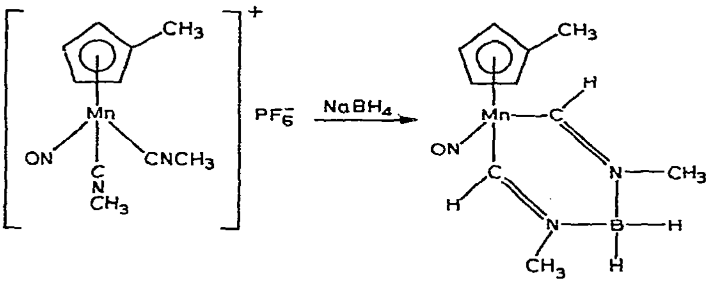
$$[(CO)_4MnSSn(CH_3)_3]_2 + 2(CH_3)_2BBr \longrightarrow [(CO)_4MnSB(CH_3)_2]_2 + 2(CH_3)_3SnBr \quad (2)$$

affords the first thermally stable transition metal complex of a B-S system [36]. Treatment of B-trichloroborazine with $NaMn(CO)_5$ yields $B_3[Mn(CO)_5]_3N_3H_3$ (X); $B_3Cl_3N_3(CH_3)_3$ and $NaMn(CO)_5$ gave an analogous, but rather unstable, compound [37].



(X)

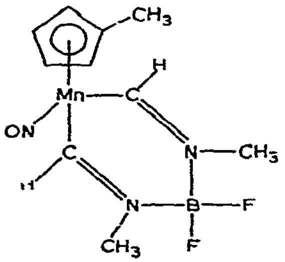
The reaction:



(XI)

(3)

affords a purple, crystalline product which is stable to air, and for which structure (XI) has been suggested [38]. Treatment of (XI) with $(C_6H_5)_3CBF_4$ yields the BF_2 analog (XII).



(XII)

The preparation and characterization of $[P(CH_3)_2C_6H_5]_4ClReN_2CrCl_3(THF)_2$ have been described [39]. The complex is obtained from trans-$Re[P(CH_3)_2C_6H_5]_4(N_2)Cl$ and $CrCl_3(THF)_3$; its magnetic moment indicates presence of Re(I) and Cr(III).

The synthesis of and studies on complexes containing Group VII metal-metal and metal-metalloid bonds continued to create interest during 1971. Displacement of the carbonyl anion with a more nucleophilic metal carbonylate from $(C_6H_5)_3SnM(CO)_x$ has been used in the synthesis of $(C_6H_5)_3SnRe(CO)_5$ and $(C_6H_5)_3SnMn(CO)_5$ from $(C_6H_5)_3SnCo(CO)_4$ and $NaRe(CO)_5$ or $NaMn(CO)_5$, respectively [40]. π-$C_5H_5Fe(CO)_2Sn(C_6H_5)_3$ was prepared similarly from $(C_6H_5)_3SnMn(CO)_5$ and $Na[\pi$-$C_5H_5Fe(CO)_2]$. The importance of the leaving group in the preparation of metal-metal bonded compounds by nucleophilic displacement reactions is further underscored by O'Brien, et al. [41]. For example, the reaction between $(C_6H_5)_2GeCl_2$ and $Mn(CO)_5^-$ gives $[(C_6H_5)_2ClGe]Mn(CO)_5$, whereas that between $(C_6H_5)_2GeBr_2$ and $Mn(CO)_5^-$ affords $(C_6H_5)_2Ge[Mn(CO)_5]_2$.

Treatment of $Mn_2(CO)_{10}$ with R_3SiH in a sealed tube at 130° yields (ca. 20%) the complexes $R_3SiMn(CO)_5$ (R_3SiH = $(CH_3)_3SiSi(CH_3)_2H$, $[(CH_3)_3Si]_2Si(CH_3)H$, or $[(CH_3)_3Si]_3SiH$) as white waxy crystals [42]. The reaction between $Mn_2(CO)_{10}$ and MCl_3^- (M = Sn or Ge) in the presence of ultraviolet light affords the axially-substituted $[Mn_2(CO)_9MCl_3]^-$ [43]. Similarly, $[\pi$-$C_5H_5Mn(CO)_2MCl_3]^-$ and $[(\pi$-$CH_3C_5H_4)Mn(CO)_2MCl_3]^-$ have been obtained from π-$C_5H_5Mn(CO)_3$ or $(\pi$-$CH_3C_5H_4)Mn(CO)_3$, respectively, and MCl_3^-.

Jetz and Graham [44] have obtained π-$C_5H_5Mn(CO)_2(H)SiCl_3$ photochemically from π-$C_5H_5Mn(CO)_3$ and $HSiCl_3$. Analogous oxidative addition reactions have been employed in the synthesis of $(\pi$-$CH_3C_5H_4)Mn(CO)_2(H)Si(C_6H_5)_3$ and $(\pi$-$CH_3C_5H_4)Mn(CO)_2(H)SiCl_3$, but the last complex was not fully characterized. π-$C_5H_5Mn(CO)_2(H)SiCl_3$ can be deprotonated with $(C_2H_5)_3N$ or $(C_2H_5)_4NCl$ to produce $[\pi$-$C_5H_5Mn(CO)_2SiCl_3]^-$ [45]. This anion reacts with $SnCl_4$ to afford

π-$C_5H_5Mn(CO)_2(SiCl_3)SnCl_3$. Several analogous compounds, viz., (π-$CH_3C_5H_4$)-$Mn(CO)_2(SiCl_3)SnCl_3$, [(π-$CH_3C_5H_4$)$Mn(CO)_2SiCl_3]_2SnCl_2$, (π-$CH_3C_5H_4$)$Mn(CO)_2$-$(SiCl_3)[Sn(C_6H_5)_2Cl]$, and (π-$CH_3C_5H_4$)$Mn(CO)_2(SiCl_3)[Sn(C_6H_5)Cl_2]$, have been also prepared.

Attempts to insert CF_2 into the Mn-M (M = Ge and Sn) bonds of $(CH_3)_3MMn(CO)_5$ using $(CH_3)_3MCF_3$ have led to the isolation of $[CF_3(CH_3)_2Sn]Mn(CO)_5$ and $M(CH_3)_4$ [46]. When M = Sn, the reaction:

$$[(CF_3)(CH_3)_2Sn]Mn(CO)_5 + (CH_3)_3SnMn(CO)_5 \longrightarrow (CH_3)_2Sn[Mn(CO)_5]_2 + (CH_3)_3SnCF_3 \qquad (4)$$

was also observed to occur.

Thermal reactions of $(C_6H_5)_3MMn(CO)_5$ (M = Si and Ge) with $P(C_6H_5)_3$ result in the formation of trans-$(C_6H_5)_3MMn(CO)_4P(C_6H_5)_3$ [47]. Similar substitution reactions were used in the synthesis of fac-$(C_6H_5)_3MMn(CO)_3$(dipy) and mer-$(C_6H_5)_3MMn(CO)_3[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]$ (M = Si, Ge, or Sn). In contrast, $(C_6H_5)_3SiMn(CO)_5$ reacts with $P(OR)_3$ (R = CH_3, i-C_3H_7, or C_6H_5) at 80° to give mer(P's trans)-$RCOMn(CO)_3[P(OR)_3]_2$ and $OP[OSi(C_6H_5)_3]_3$ (AS 6, 1105). Evidence is presented that this unusual process first involves formation of $RMn(CO)_5$ via a Michaelis-Arbuzov reaction.

In a preliminary communication, Marks [48] reports the formation of $[(C_6H_5)_2FGe]Mn(CO)_5$ from $[(C_6H_5)_2ClGe]Mn(CO)_5$ and $AgBF_4$.

Indium(I) chloride and bromide (X) undergo insertion into the Mn-Mn bond of $Mn_2(CO)_{10}$ when allowed to react in dioxane at reflux to afford, in good yield, $XIn[Mn(CO)_5]_2$ [49]. InX also insert into the Mn-Cl bond of $Mn(CO)_5Cl$. Infrared spectroscopic evidence is presented [50] for the ionization schemes (X = Cl or Br):

$$In[Mn(CO)_5]_3 \rightleftharpoons In[Mn(CO)_5]_2^+ + Mn(CO)_5^- \qquad (5)$$

$$XIn[Mn(CO)_5]_2 \rightleftharpoons In[Mn(CO)_5]_2^+ + X^- \qquad (6)$$

$$2X_2InMn(CO)_5 \rightleftharpoons In[Mn(CO)_5]_2^+ + InX_4^- \qquad (7)$$

in CH_3CN. Further support for the formation of such metal carbonyl cations is derived from the isolation of $(CH_3CN)_2In[Mn(CO)_5]_2^+ ClO_4^-$.

The previously reported (AS 2, 169-170) $Tl[Mn(CO)_5]_3$ has been also synthesized, virtually quantitatively, by the reaction [51]:

$$3TlCl + 3NaMn(CO)_5 \xrightarrow[25^\circ]{THF} Tl[Mn(CO)_5]_3 + 2Tl + 3NaCl \qquad (8)$$

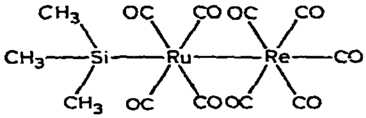
Reactions between $M[Mn(CO)_5]_2$ (M = Zn, Cd, or Hg) and Group IIB metal halides, Lewis bases, halogens, hydrogen halides, or organic halides have been investigated by Hsieh and Mays [52]. The prepared complexes include $(dipy)Zn[Mn(CO)_5]_2$, $(C_5H_5N)_2Zn[Mn(CO)_5]_2$, $(diglyme)Cd[Mn(CO)_5]_2$, and a number of related $M[Mn(CO)_5]_2$-Lewis base adducts.

The same authors have studied [53] various preparative routes to $M[Re(CO)_5]_2$ (M = Zn, Cd, or Hg). They include, *inter alia*, reactions of $Hg(CN)_2$ with $NaRe(CO)_5$ to give $Hg[Re(CO)_5]_2$, of $HRe(CO)_5$ with $Zn(C_2H_5)_2$ to yield $Zn[Re(CO)_5]_2$, of $HRe(CO)_5$ with $Cd(CH_3)_2$ to afford $Cd[Re(CO)_5]_2$, of $Re_2(CO)_{10}$ with Zn to give $Zn[Re(CO)_5]_2$, and of $Hg[Re(CO)_5]_2$ with Zn to yield $Zn[Re(CO)_5]_2$. The trimetallic $Hg[MnRe(CO)_{10}]$ was obtained from $Hg[Re(CO)_5]_2$ and $Hg[Mn(CO)_5]_2$ in THF at reflux, whereas $XHgRe(CO)_5$ (X = Cl, Br, or I) resulted upon heating $Hg[Re(CO)_5]_2$ with HgX_2 in acetone. Several Lewis base adducts of $M[Re(CO)_5]_2$ such as $(diglyme)Cd[Re(CO)_5]_2$, $(C_5H_5N)_2Cd[Re(CO)_5]_2$, and $(dipy)Cd[Re(CO)_5]_2$ were also prepared.

Treatment of C_6F_5HgBr with $Mn(CO)_5^-$ leads to the formation of $C_6F_5HgMn(CO)_5$, which is thermally stable to 100° [54].

A study of reactions between metal-metal bonded complexes and sulfur dioxide has revealed that $Mn_2(CO)_{10}$ is inert to SO_2 at 50° [55].

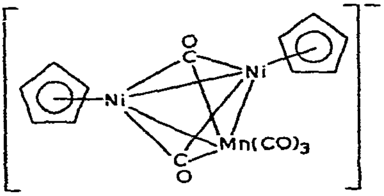
Several complexes containing Ru-Re bonds have been synthesized by Stone and associates [56, 57]. Treatment of $(CH_3)_3SiRu(CO)_4I$ with $Re(CO)_5^-$ or of $[(CH_3)_3SiRu(CO)_4]^-$ with $Re(CO)_5Br$ yields (6% and 23%, respectively) $(CH_3)_3SiRu(CO)_4Re(CO)_5$ (XIII) [56]. The synthesis of the analogous, known manganese complex (AS <u>6</u>, 1107) $(CH_3)_3SiRu(CO)_4Mn(CO)_5$ from $(CH_3)_3SiRu(CO)_4I$ and $Mn(CO)_5^-$ is also given. The germanium analog of (XIII), $(CH_3)_3GeRu(CO)_4Re(CO)_5$, also having a <u>trans</u> (D_{4d}) structure, was obtained <u>via</u> the reaction of $[(CH_3)_3GeRu(CO)_4]^-$ with $Re(CO)_5Br$ [57].



(XIII)

The complex $[P(C_6H_5)_3]_2Ni[Mn(CO)_5]_2$ undergoes a substitution reaction with $P(C_6H_5)_3$ to give $[P(C_6H_5)_3]_2Ni[Mn(CO)_4P(C_6H_5)_3]_2$ [58]. The same product is also obtainable from $[P(C_6H_5)_3]_2NiCl_2$ and $Na[Mn(CO)_4P(C_6H_5)_3]$.

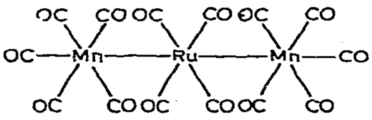
A new heteronuclear cluster, $[(\pi\text{-}C_5H_5)_2Ni_2Mn(CO)_5]^-$ of proposed structure (XIV), can be obtained when $(\pi\text{-}C_5H_5)_2Ni_2(CO)_2$ and $Mn(CO)_5^-$ are allowed to react in THF at reflux [59]. Its isolated, green $(CH_3)_4N^+$ salt is extremely air-sensitive.



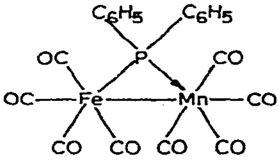
(XIV)

Treatment of $NaMn(CO)_5$ with UCl_4 produces orange, very air-sensitive $U[Mn(CO)_5]_4$, which reacts with Br_2 to yield UBr_4 and $Mn(CO)_5Br$ [60]. In contrast, only $Re(CO)_5Cl$ was obtained from reaction of $Re(CO)_5^-$ with UCl_4.

Thermally-induced reactions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with various metal carbonyls and other organometallics have furnished several new, as well as previously-synthesized polymetallic compounds [61]. Heating a mixture of $Mn_2(CO)_{10}$ and $Ru_3(CO)_{12}$ at 205° in an evacuated sealed tube affords $(CO)_5MnRu(CO)_4Mn(CO)_5$ (XV); prepared similarly were $(CO)_5MnOs(CO)_4$-$Mn(CO)_5$ and $(CO)_5ReOs(CO)_4Re(CO)_5$. The reaction between $Mn_2(CO)_{10}$ and $(\pi\text{-}C_5H_5)_2Fe_2(CO)_4$ or $(\pi\text{-}C_5H_5)_2Mo_2(CO)_6$ yields small quantities of $\pi\text{-}C_5H_5Fe(CO)_2Mn(CO)_5$ and $\pi\text{-}C_5H_5Mo(CO)_3Mn(CO)_5$, respectively, in addition to $\pi\text{-}C_5H_5Mn(CO)_3$. The last compound is obtained as the sole product of the reaction of $Mn_2(CO)_{10}$ with $(\pi\text{-}C_5H_5)_2Ni_2(CO)_2$ or $(\pi\text{-}C_5H_5)_2Fe$.



(XV)



(XVI)

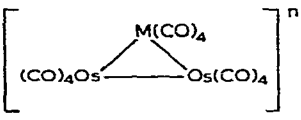
The known compound $(CO)_4FeP(C_6H_5)_2Mn(CO)_4$ (XVI) (AS 5, 636) was synthesized by an alternative route involving reaction of $Fe(CO)_4[P(C_6H_5)_2H]$ with $Mn(CO)_5Br$ in the presence of $(C_2H_5)_2NH$ [62].

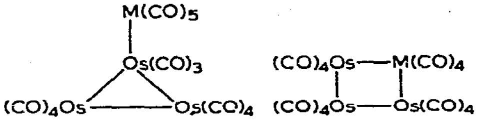
Metal carbonyl hydride clusters have continued to attract attention during 1971. A significant finding is that $Re_2(CO)_{10}$ reacts with hydrogen at atmospheric pressure at 90-170° in hydrocarbon solvents [63]. In this fashion $H_3Re_3(CO)_{12}$ and $H_4Re_4(CO)_{12}$ have been obtained in 50-60% yields.

Photolysis of $Mn_2(CO)_{10}$ in acetone under nitrogen, followed by addition of $(C_2H_5)_4NClO_4$, has afforded ionic $[(C_2H_5)_4N][H_2Mn_3(CO)_{12}]$, which is thought to possess a triangular arrangement of the manganese atoms [64].

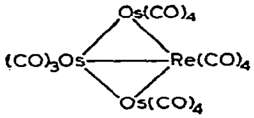
Acidification of the products of the reaction of $Os_3(CO)_{12}$ with $M(CO)_5^-$ (M = Mn or Re) under various conditions has afforded four new types of heterometallic polynuclear carbonyl hydrides [65]. They are: $HMOs_2(CO)_{12}$ (XVII: n = 0), $HMOs_3(CO)_{16}$ (XVIII a or b), $HReOs_3(CO)_{15}$ (XIX), and $H_3MOs_3(CO)_{13}$ (XX), the suggested possible structures not showing the positions of the hydrogens. In addition, the anions $[MOs_2(CO)_{12}]^-$ (XVII:

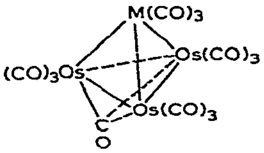
n = -1) were isolated, as the $(CH_3)_4N^+$ salts, from the reaction solution prior to acidification.


(XVII)


(a) (b)

(XVIII)

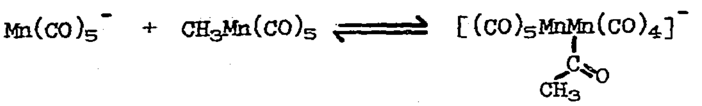

(XIX)


(XX)

Several new mononuclear hydridocarbonyls of rhenium were synthesized starting with H_3ReL_4 (L = $P(C_6H_5)_3$) [66]. Treatment of this hydride with CO affords $HRe(CO)_2L_3$ and $HRe(CO)_3L_2$. $HRe(CO)_2L_3$, of a probable mer (CO's cis) structure, reacts with CS_2 to give $Re(CO)_2L_2(S_2CH)$ (see structure LIII) and with HX (X = Cl, Br, and I) to furnish $Re(CO)_2L_2X$(solvent) (solvent = C_2H_5OH or acetone). $HRe(CO)_3L_2$ affords $Re(CO)_3L_2X$ with HX and $[Re(CO)_3L_2]_2$ with L.

Treatment of $HMn(CO)_5$ with $(CF_3)_2PX$ (L; X = Cl, Br, or I) leads to the formation of $Mn(CO)_5X$, $Mn_2(CO)_8X_2$, and $Mn_2(CO)_8[P(CF_3)_2]X$ [67]. In contrast, when X = F, CF_3, or CH_3, a cis-trans mixture of $HMn(CO)_4L$ results.

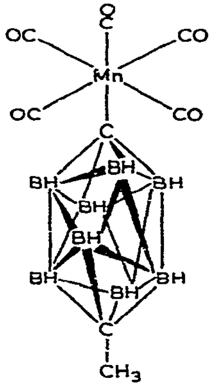
Several publications in 1971 were concerned with synthesis of compounds containing metal-carbon bonds and with investigation of their reactions. The preparation of $(CH_3)_3SiCH_2Mn(CO)_5$ from $Mn(CO)_5Br$ and $LiCH_2Si(CH_3)_3$ is described [68]. This alkyl undergoes carbon monoxide insertion upon treatment with CO. The observation that $CH_3Mn(CO)_5$ reacts with $Mn(CO)_5^-$ according to the equation [69]:



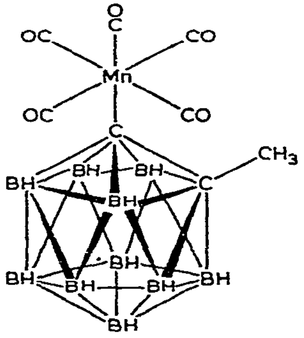
$$Mn(CO)_5^- + CH_3Mn(CO)_5 \rightleftharpoons [(CO)_5Mn\underset{\underset{CH_3}{\overset{|}{C}{=}O}}{Mn}(CO)_4]^- \qquad (9)$$

further attests to the generality of the CO insertion in reactions of metal alkyls with nucleophiles. Addition of $(CH_3)_3OBF_4$ to the above solution gives the known (AS 6, 1115) $(CO)_5MnMn(CO)_4[C(CH_3)OCH_3]$. It appears very likely that the carbene "$(CO)_5Mn(CH_2)_3Mn(CO)_5$" (AS 9, 173) is formed similarly.

When $Mn(CO)_5Br$ reacts with $1\text{-}Li\text{-}10\text{-}CH_3\text{-}1,10\text{-}B_8C_2H_8$, bright yellow $1\text{-}[Mn(CO)_5]\text{-}10\text{-}CH_3\text{-}1,10\text{-}(\sigma\text{-}B_8C_2H_8)$ (XXI) is obtained in 64% yield [70]. A related carborane complex, $1\text{-}[Mn(CO)_5]\text{-}2\text{-}CH_3\text{-}1,2\text{-}(\sigma\text{-}B_{10}C_2H_{10})$ (XXII), results (57%) from reaction of $Mn(CO)_5Br$ with $1\text{-}Li\text{-}2\text{-}CH_3\text{-}1,2\text{-}B_{10}C_2H_{10}$.

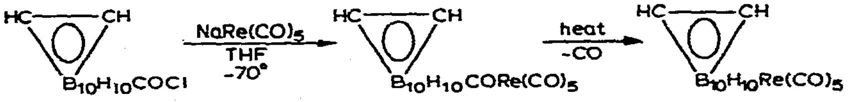


(XXI)



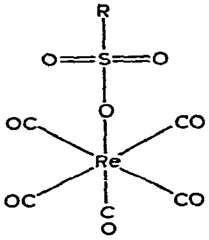
(XXII)

The first member of a new class of o-carborane derivatives of metal carbonyls containing a boron-metal σ-bond was obtained via the following sequence of reactions [71]:



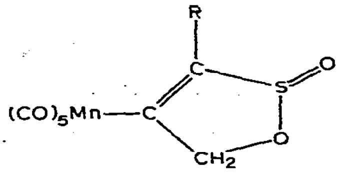
(10)

Insertion reactions of the oxides of sulfur into transition metal-carbon bonds were the subject of two papers. Spectroscopic evidence has been presented that $C_6H_5CH_2Mn(CO)_5$ reacts with SO_2 initially to form the O-sulfinate $C_6H_5CH_2S(O)OMn(CO)_5$, which then isomerizes to the isolable S-sulfinate [72]. Other transition metal-carbon compounds appear to exhibit similar behavior toward SO_2. The first example of insertion of SO_3 into a transition metal-carbon bond has been reported [73]. $RRe(CO)_5$ (R = CH_3, C_6H_5, and p-$C_6H_4CH_3$) react with SO_3 in CCl_4 at 0° to yield the sulfonato complexes $RSO_3Re(CO)_5$ (XXIII).

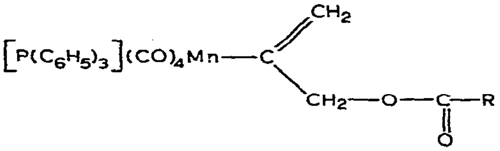


(XXIII)

Considerable interest has developed in reactions of transition metal propargyl complexes with electrophilic reagents. Wojcicki, et al. [74] describe the preparation of $RC{\equiv}CCH_2Mn(CO)_5$ (R = H and CH_3) from $Mn(CO)_5^-$ and $BrCH_2C{\equiv}CR$. These products react rapidly with SO_2 to yield $Mn(CO)_5(C_3H_2RSO_2)$ having a vinyl-sultine structure (XXIV) [75] rather than that proposed originally (AS 5, 623; structure IV with R = H). When the vinyl-sultine complex with R = H is heated in vacuo, it loses SO_2 and reverts to the parent 2-alkynyl. A similar reaction with SO_2 has been observed [76] for $HC{\equiv}CCH_2Mn(CO)_4P(C_6H_5)_3$, which also reacts with RCO_2H (R = CH_3, C_2H_5, or CH_2Cl) to yield $RCO_2CH_2(CH_2)CMn(CO)_4P(C_6H_5)_3$ (XXV). In contrast, treatment of $HC{\equiv}CCH_2Mn(CO)_4P(C_6H_5)_3$ with HX (X = Cl, Br, I, or CF_3CO_2) affords $Mn(CO)_4[P(C_6H_5)_3]X$. Unexpectedly, the disubstituted complex $HC{\equiv}CCH_2Mn(CO)_3[P(C_6H_5)_3]_2$ failed to react with SO_2 at -78°.

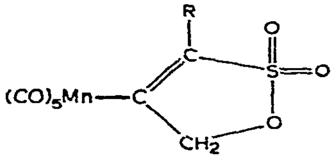


(XXIV)



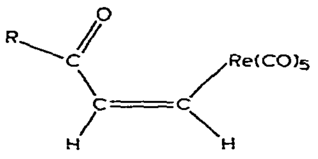
(XXV)

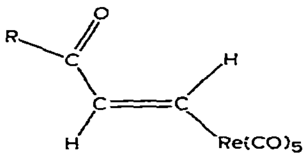
An extension of the foregoing cycloaddition reactions to SO_3 has led to the isolation of manganese vinyl-sultone complexes [77]. $RC{\equiv}CCH_2Mn(CO)_5$ (R = CH_3 and C_6H_5) react with $SO_3{\cdot}$dioxane in CH_2Cl_2 at 0° to produce $Mn(CO)_5(C_3H_2RSO_3)$ (XXVI). Oxidation of (XXIV: R = C_6H_5), obtained from the propargyl carbonyl and SO_2, with $KMnO_4$ in aqueous CH_3CO_2H yields (42%) (XXVI: R = C_6H_5).

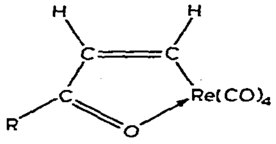


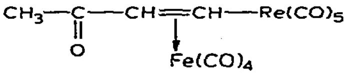
(XXVI)

Other vinyl derivatives of manganese and rhenium carbonyls have been reported during 1971. The reaction between $NaRe(CO)_5$ and trans-$RCOCH{=}CHCl$ (R = CH_3 or C_6H_5) furnishes three complexes: cis-$RCOCH{=}CHRe(CO)_5$ (XXVII), trans-$RCOCH{=}CHRe(CO)_5$ (XXVIII), and $RCOCH{=}CHRe(CO)_4$ (XXIX) [78]. (XXVII) readily loses CO yielding (XXIX) and isomerizes in the presence of HCl to (XXVIII). (XXVIII: R = CH_3) reacts with $Fe_2(CO)_9$ to give $CH_3COCH{=}CHRe(CO)_5Fe(CO)_4$ of proposed structure (XXX). The reaction between $NaRe(CO)_5$ and cis-$CH_3COCH{=}CHCl$ also yields (XXVII, XXVIII, and XXIX: R = CH_3), the last compound being the major product (65%) [79]. Vinyl ketone complexes of manganese of the type represented by (XXIX) can be prepared by the reaction of $RMn(CO)_5$ (R = CH_3 or C_6H_5) with the alkynes $HC{\equiv}CCH_2OH$, $HC{\equiv}CC(CH_3)_2OH$, and $HOCH_2C{\equiv}CCH_2OH$ [76].

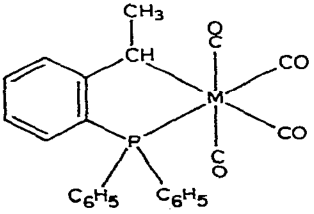

(XXVII)

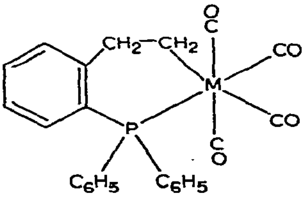

(XXVIII)

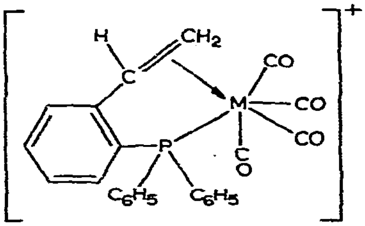

(XXIX)


$$CH_3-\underset{\underset{O}{\|}}{C}-\underset{\underset{Fe(CO)_4}{\downarrow}}{CH{=}CH}-Re(CO)_5$$
(XXX)

In two preliminary communications, Bennett and Watt report on reactions between the ligand o-styryldiphenylphosphine (SP) and $HM(CO)_5$ (M = Mn and Re) [80] or $CH_3Mn(CO)_5$ [81]. The reaction of $HMn(CO)_5$ at 35° gives initially $HMn(CO)_4(SP)$, which contains an uncoordinated vinyl group. On heating, two isomeric products $Mn(CO)_4[(C_6H_5)_2PC_6H_4C_2H_4]$ (XXXI and XXXII: M = Mn) are obtained. $HRe(CO)_5$ and SP afford initially $HRe(CO)_4(SP)$, which at higher temperatures isomerizes to (XXXII: M = Re). Treatment of (XXXI: M = Mn) or (XXXII: M = Mn or Re) with $(C_6H_5)_3CBF_4$ gives the cation (XXXIII: M = Mn or Re); reaction of (XXXIII: M = Re) with $NaBH_4$ furnishes (XXXI: M = Re). $CH_3Mn(CO)_5$ and SP afford two isomeric products $Mn(CO)_4[(C_6H_5)_2PC_6H_4C_2H_3CH_3]$ whose structures have been elucidated by X-ray crystallography (vide infra: LVII and LVIII).


(XXXI)

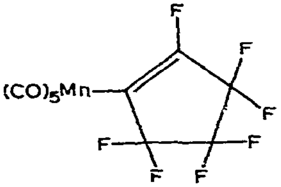

(XXXII)



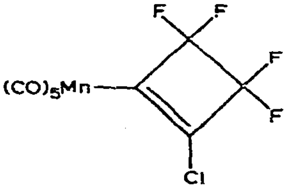
(XXXIII)

The stoichiometry and rate of decomposition of alkylmanganese species, R_2Mn, prepared in situ from $MnCl_2$ and RMgBr, have been examined [82]. The decomposition has been shown to proceed principally by α,β-elimination of a hydridomanganese species. Reactions have been also reported [83] of Mn(II) with <u>o</u>-diethynylbenzene to give polymeric, paramagnetic (5 unpaired electrons), and pyrophoric products.

Fluorocarbon derivatives of manganese carbonyl have been the subject of two papers during 1971. Treatment of $Mn(CO)_5^-$ with octafluorocyclopentene, C_5F_8, affords the perfluoro complex $(CO)_5MnC_5F_7$ (XXXIV), which reacts with $P(C_6H_5)_3$ to give the <u>cis</u> and <u>trans</u> isomers of $[P(C_6H_5)_3]$-$(CO)_4MnC_5F_7$ [84]. The <u>trans</u> isomer alone is obtainable from $[Mn(CO)_4P(C_6H_5)_3]^-$ and C_5F_8. The reaction between $NaMn(CO)_5$ and 3,3,4,4-tetrafluoro-1,2-dichlorocyclobutene has yielded $(CO)_5MnC_4F_4Cl$ (XXXV) [85].

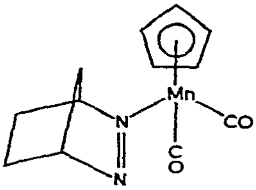


(XXXIV)



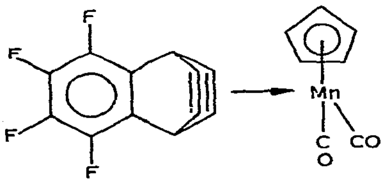
(XXXV)

Preparative investigations on π-complexes of the Group VII elements constituted the subject of a variety of papers during 1971. Several new $(\pi\text{-}XC_5H_4)Mn(CO)_2L$ derivatives have been reported. The photochemicallyinduced reaction between π-$C_5H_5Mn(CO)_3$ and 2,3-diazabicyclo[2.2.1]heptene-2 affords orange, sublimable π-$C_5H_5Mn(CO)_2(C_5H_8N_2)$ (XXXVI) [86]. Treatment of π-$C_5H_5Mn(CO)_2$(cycloheptene) with AsF_3 at 55° or a photochemical reaction between π-$C_5H_5Mn(CO)_3$ and AsF_3 affords yellow, sublimable π-$C_5H_5Mn(CO)_2AsF_3$ [87]. This product undergoes ethanolysis to yield the corresponding dicarbonyl complexes containing $AsF_2(OC_2H_5)$ and $AsF(OC_2H_5)_2$. The ionization potentials of π-$C_5H_5Mn(CO)_2EF_3$ (E = P and As) show that the electron density at manganese is lower in the AsF_3 than in the PF_3 derivative, and therefore AsF_3 is a better π-acceptor than PF_3.

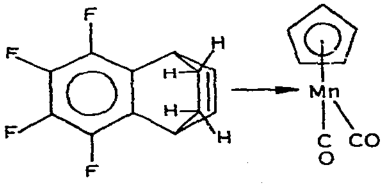


(XXXVI)

The complexes $(\pi$-$XC_5H_4)Mn(CO)_2L$ (X = H or CH_3, L = $P(\underline{t}$-$C_4H_9)_3$, $P[Si(CH_3)_3]_3$, $P[Ge(CH_3)_3]_3$, and $P[Sn(CH_3)_3]_3$) have been obtained photochemically from $(\pi$-$XC_5H_4)Mn(CO)_3$ and L [88]. Similarly, π-$C_5H_5Mn(CO)_2$-$[(CH_3O)_2C{=}C(OCH_3)_2]$ arises when π-$C_5H_5Mn(CO)_3$ undergoes a photochemical reaction with tetramethoxyethylene [89]. Also obtained photochemically has been π-$C_5H_5Mn(CO)_2(C_8H_6C_6F_4)$ (XXXVII), which can be hydrogenated to π-$C_5H_5Mn(CO)_2(C_8H_8C_6F_4)$ (XXXVIII) [90].

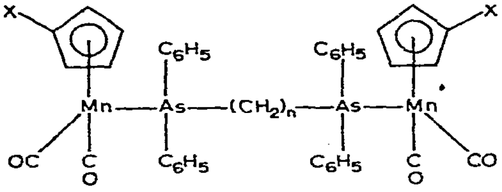


(XXXVII)



(XXXVIII)

Kursanov, et al. [91] have prepared a series of complexes (π-XC_5H_4)$Mn(CO)_2P(C_6H_5)_3$ (X = C_2H_5, $CH_2C_6H_5$, SCH_3, Cl, Br, I, $COCH_3$, CO_2H, and CO_2CH_3) via photochemical reaction of (π-XC_5H_4)$Mn(CO)_3$ with $P(C_6H_5)_3$. (π-XC_5H_4)$Mn(CO)_2P(C_6H_5)_3$ (X = Cl and Br) react with $BF_3 \cdot H_2O$ or CF_3CO_2H to give π-$C_5H_5Mn(CO)_2P(C_6H_5)_3$. A novel triferrocenylphosphine complex, π-$C_5H_5Mn(CO)_2P[\sigma$-(π-C_5H_4Fe-π-C_5H_5)$]_3$, was synthesized by a similar photochemical reaction [92]. Treatment of (π-XC_5H_4)$Mn(CO)_3$ (X = H or CH_3) with $(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2$, also under photochemical conditions, has afforded (π-XC_5H_4)$Mn(CO)[(C_6H_5)_2P(CH_2)_4P(C_6H_5)_2]$ [93]. In contrast, the diarsines $(C_6H_5)_2As(CH_2)_n As(C_6H_5)_2$ (n = 2 and 4) give $[(\pi$-$XC_5H_4)Mn(CO)_2]_2$-$[(C_6H_5)_2As(CH_2)_nAs(C_6H_5)_2]$ (XXXIX: X = H or CH_3, n = 2 or 4) under similar experimental conditions.

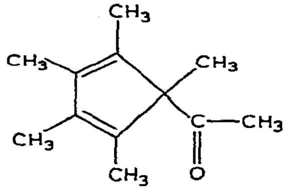


(XXXIX)

Two interesting ligand reactions have been effected using π-$C_5H_5Mn(CO)_2L$. Treatment of π-$C_5H_5Mn(CO)_2(N_2H_4)$ with H_2O_2 in the presence of Cu^{2+} at -40° in THF yields the reddish-brown, air-stable dinitrogen complex π-$C_5H_5Mn(CO)_2(N_2)$ [94]. The known (AS 6, 1119) π-$C_5H_5Mn(CO)_2PH_3$ and new π-$C_5H_5Mn(CO)_2$-$[P(C_6H_5)H_2]$ have been synthesized by the reaction of π-$C_5H_5Mn(CO)_2(PCl_2X)$ (X = Cl and C_6H_5, respectively) with $NaBH_4$ in THF [95].

The ligand $C_2H_5OC(O)CN$ (CFE) reacts under photochemical conditions with π-$C_5H_5Mn(CO)_3$ to yield a violet solid whose mass spectrum is consistent with the formula π-$C_5H_5Mn(CO)(CFE)$, yet whose infrared spectrum shows two $\nu(CO)$ bands [96]. Thermal reaction between $Mn_2(CO)_{10}$ and CFE affords $[Mn(CO)(CFE)_2]_2$.

New synthetic procedures have been reported for substituted π-cyclopentadienylmanganese and -rhenium tricarbonyls. Reaction of 5-acetyl-1,2,3,4,5-pentamethylcyclopentadiene (XL) with $Mn_2(CO)_{10}$ in boiling 2,2,5-trimethylhexane gives (12%) pale yellow, crystalline $[\pi\text{-}(CH_3)_5C_5]Mn(CO)_3$ [97]. The phosphine derivative $[\pi\text{-}(CH_3)_5C_5]Mn(CO)_2\text{-}P(C_6H_5)_3$ was also synthesized. The complexes $[\pi\text{-}(CH_3)_3SiC_5H_4]M(CO)_3$ arise when $M_2(CO)_{10}$ (M_2 = Mn_2 and Re_2) are heated with $(CH_3)_3SiC_5H_5$ [98]. The manganese reaction also affords $(CH_3)_3SiMn(CO)_5$ and $\pi\text{-}C_5H_5Mn(CO)_3$. Interaction of $[(CH_3)_3Sn](R)C_5H_4$ with $M(CO)_5Br$ (M = Mn or Re) has yielded the foregoing and other silyl-substituted π-cyclopentadienyl complexes [99]. Obtained in this fashion have been $(\pi\text{-}RC_5H_4)M(CO)_3$ (M = Mn or Re, R = $(CH_3)_3Si$, $(CH_3)_5Si_2$, and $(CH_3)_3SiCH_2$). The dinuclear $(CH_3)_2Si[\pi\text{-}C_5H_4M(CO)_3]_2$ and disubstituted $\{\pi\text{-}[(CH_3)_3Si]_2C_5H_3\}M(CO)_3$ (M = Mn or Re) derivatives result when $[(CH_3)_3SnC_5H_4]_2Si(CH_3)_2$ and $[(CH_3)_3Si]_2[(CH_3)_3Sn]C_5H_3$, respectively, are employed in conjunction with $M(CO)_5Br$.



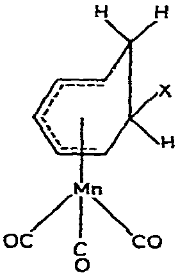
(XL)

A doctoral dissertation is concerned with the polymerization of vinylcymantrene, $(\pi\text{-}CH_2{=}CHC_5H_4)Mn(CO)_3$ [100], while a journal article deals with copolymerization of N-vinyl-2-pyrrolidone with vinylcymantrene in the presence of the initiator azobisisobutyronitrile [101].

Thioxanthate complexes of formula $\pi\text{-}C_5H_5Mn(NO)(S_2CSR)$, obtained from $[\pi\text{-}C_5H_5Mn(CO)_2(NO)]PF_6$ and NaS_2CSR (R = <u>t</u>-C_4H_9, <u>sec</u>-C_4H_9, <u>n</u>-C_4H_9, <u>i</u>-C_3H_7, and n-C_3H_7), have been shown by voltammetry to undergo a reversible one-electron oxidation [102]. The dinuclear mercaptide complexes [π-C_5H_5Mn(NO)SR$]_2$ (R = t-C_4H_9, sec-C_4H_9, and i-C_3H_7) can be oxidized in two one-electron steps. The cations [π-C_5H_5Mn(NO)LL'$]^+$ (L, L' = CO, $P(C_6H_5)_3$, $P(OC_6H_5)_3$, $P(CH_3)_2C_6H_5$, and 4-methylpyridine; LL' = dipy, o-phen, inter alia) also undergo a one-electron voltammetric oxidation process. Comparison of these voltammetric data and the ν(NO) values indicates that the π-C_5H_5Mn(NO) group is significantly responsible for the redox behavior of the complexes.

The reaction between $(CH_3)_3SnCH_2CH=CH_2$ and $M(CO)_5X$ (M = Mn and Re, X = Cl and Br) has been employed in the synthesis of π-$C_3H_5M(CO)_4$ in good yields [103]. Prepared similarly have been the substituted π-allyl, π-C_5H_5, π-$CH_3C_5H_4$, π-indenyl, and π-fluorenyl carbonyls of manganese and rhenium.

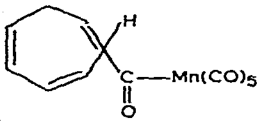
Nucleophilic attack of X^- (X = H, OCH_3, OC_2H_5, t-OC_4H_9, $N(CH_3)_2$, CN, CH_3, and C_6H_5) at the cycloheptatriene ring of [π-$C_7H_8Mn(CO)_3$]BF_4 has afforded the 6-exo isomers of (π-XC_7H_8)$Mn(CO)_3$ (XLI) [104]. When X = OCH_3, OC_2H_5, or t-OC_4H_9, treatment of (XLI) with HBF_4 reverses the above reaction. Interaction between (XLI: X = H) and $P(C_6H_5)_3$ under photochemical conditions has yielded the phosphine derivative π-$C_7H_9Mn(CO)_2P(C_6H_5)_3$.



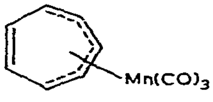
(XLI)

The reaction of C_7H_7COCl with $Mn(CO)_5^-$ affords the acyl $C_7H_7COMn(CO)_5$

(XLII), which can be converted photochemically at -68° to π-$C_7H_7Mn(CO)_3$ (XLIII) [105]. The orange, air-stable (XLIII) exhibits only one proton signal in its NMR spectrum at 88°; the limiting spectrum is obtained at -47°. The fluxional process in (XLIII) is slower than that in the isoelectronic iron + 1 ion, suggesting that the degree of backbonding is an important determinant of the rate of rotation.

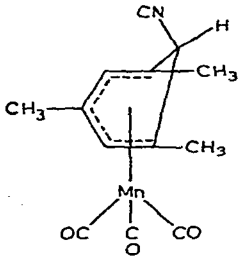


(XLII)

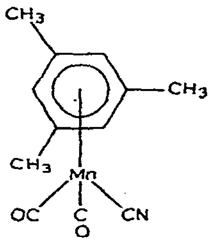


(XLIII)

A facile interconversion of arene- and cyanocyclohexadienylmanganese complexes has been reported by Mawby [106]. Treatment of $[\pi\text{-}(CH_3)_3C_6H_3]Mn(CO)_3^+I^-$ with NaCN in aqueous solution at 0° leads to the formation of $[\pi\text{-}(CH_3)_3(CN)C_6H_3]Mn(CO)_3$ (XLIV), which upon heating generates $[\pi\text{-}(CH_3)_3C_6H_3]Mn(CO)_2CN$ (XLV). The infrared spectrum of an aqueous solution of (XLV) is consistent with the presence of protonated $[\pi\text{-}(CH_3)_3C_6H_3]Mn(CO)_2CNH^+$ [107]. π-$C_6H_6Mn(CO)_2CN$ behaves similarly. Further evidence for the ability of (XLV) to act as a Lewis base is provided by its reactions with $(C_2H_5)_3O^+$ to yield $[\pi\text{-}(CH_3)_3C_6H_3]Mn(CO)_2CNC_2H_5{}^+$, with $(C_6H_5)_3C^+$ to give $[\pi\text{-}(CH_3)_3C_6H_3]Mn(CO)_2CNC(C_6H_5)_3{}^+$, and with HBF_4 to afford $[\pi\text{-}(CH_3)_3C_6H_3]Mn(CO)_2CNBF_3$. The two cations were isolated as their PF_6^- salts.



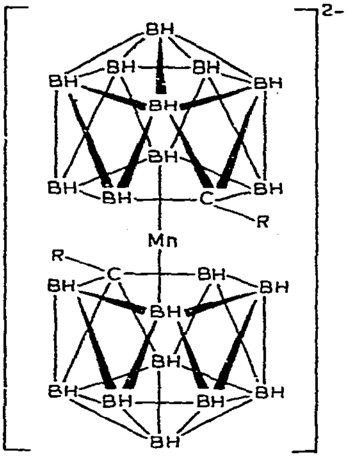
(XLIV)



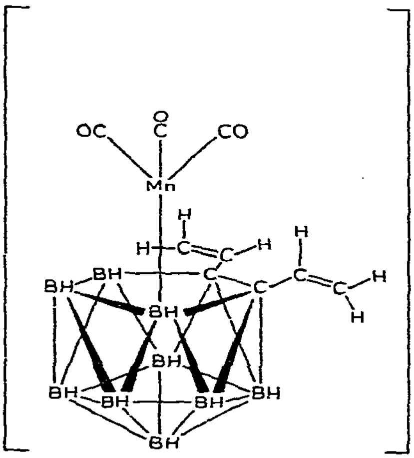
(XLV)

In a doctoral dissertation, Lewis [108] describes the reaction of $Re(CO)_5Br$ with methyl-substituted benzenes (Ar) to yield $[Re(CO)_3Br]_3Ar$. These compounds interact with C_5H_5N or $P(C_6H_5)_3$ (L) to give *fac*-$Re(CO)_3L_2Br$.

Several π-carborane and related derivatives of manganese and rhenium were reported during 1971. The preparation of $(\pi\text{-}CH_3C_3B_3H_5)Mn(CO)_3$, already published in 1969 (AS 6, 1116), is given in a Ph.D. thesis [109]. The metallomonocarborane complexes $[(CH_3)_3NH]_2[(\pi\text{-}B_{10}H_{10}CH)_2Mn]$ (anion XLVI: R = H) and $[(CH_3)_4N]_2[(\pi\text{-}B_{10}H_{10}CNH_2)_2Mn]$ (anion XLVI: R = NH_2) were prepared by the reaction of $(CH_3)_3NHB_{10}H_{12}CH$ or $B_{10}H_{12}CNH_3$, respectively, with *n*-C_4H_9Li and $MnCl_2$ [110]. π-(3)-1,2-Divinyl-1,2-dicarbollylmanganese tricarbonylate ion (XLVII) was obtained [111] by the application of the procedure analogous to that reported (AS 5, 630) for the unsubstituted analog. The polyhedral phosphaborane $B_{10}H_{12}PC_6H_5$ upon treatment with 2 equiv. of NaH and 1 equiv. of $Mn(CO)_5Br$ in THF yielded $[(\pi\text{-}B_{10}H_{10}PC_6H_5)Mn(CO)_3]^-$, which was isolated as the pale yellow, air-sensitive $(CH_3)_4N^+$ salt [112].



(XLVI)



(XLVII)

Kinetic and Stereochemical Studies

There was a significant increase in the number of mechanistic studies of reactions of organometallic compounds of manganese and rhenium during 1971. Particularly noticeable has been a marked growth of interest in stereochemical problems.

Substitution reactions of metal carbonyls have continued to attract attention. In a Ph.D. thesis, Spendjian [113] describes isotopic CO exchange reactions of cis-$Mn(CO)_4LBr$ (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$) and the kinetics of the thermal decomposition of mer(P's trans)-$Mn(CO)_3[P(C_6H_5)_3]_2X$ (X = Cl, Br, and I) to cis-$Mn(CO)_4[P(C_6H_5)_3]X$ (AS 9, 185-186).

The kinetics of the reaction:

$$Re(CO)_5X + P(C_6H_5)_3 \longrightarrow Re(CO)_4[P(C_6H_5)_3]X + CO \qquad (11)$$

$$(X = Cl, Br, \text{ or } I)$$

were studied in $CHCl_3$, CCl_4, and n-octane [114]. The substitution proceeds by a dissociative mechanism with the rate constants decreasing in the order: $Re(CO)_5Cl > Re(CO)_5Br > Re(CO)_5I$ and the activation energies increasing from the chloride to the iodide. These compounds react about 60 times more slowly than their manganese counterparts.

Angelici [115] has prepared $Re(CO)_5NCO$ via the reaction of $Re(CO)_6^+$ with N_3^- or NH_2NH_2. The pentacarbonyl reacts with L-L (L-L = o-phen, dipy, and $(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2$) to give fac-$Re(CO)_3(L\text{-}L)NCO$. Kinetic studies on this reaction in toluene have shown a dissociative mechanism, $\Delta H^{\ddagger}$ being 23.5 kcal/mole and $\Delta S^{\ddagger}$ 1.8 e.u. At 60°, $Re(CO)_5NCO$ undergoes substitution more rapidly than $Re(CO)_5Cl$.

The reaction:

$$(C_5H_5)_3MMn(CO)_5 + PR_3 \xrightarrow[150\text{-}190^\circ]{\text{decalin}} \underline{trans}\text{-}(C_6H_5)_3MMn(CO)_4PR_3 + CO \qquad (12)$$

$$(M = Ge \text{ or } Sn,\ R = C_6H_5 \text{ or } \underline{n}\text{-}C_4H_9)$$

follows a two-term rate law of the type $k_1[(C_6H_5)_3MMn(CO)_5]$ +

$k_2[(C_6H_5)_3MMn(CO)_5][PR_3]$ [116], suggesting two competing mechanisms in which the rate-determining steps involve slow fission of Mn-CO bonds and nucleophilic attack of L on the substrate.

The exchange of ^{13}CO with $HMn(CO)_5$ was followed by infrared spectroscopy [117] and, contrary to the previous report [118], found to proceed extremely slowly. At 40° in benzene, the radial: axial rate constant ratio is between 0.25 and 0.5.

The kinetics of the reaction:

$$[Re(CO)_2(NO)Cl_2]_2 + 2L \longrightarrow 2Re(CO)_2(NO)LCl_2 \qquad (13)$$

in CCl_4 and trichloroethylene were investigated by infrared spectroscopy [119]. The rates are first order both in complex and ligand concentrations, and $\Delta H^{\ddagger} = 11\text{-}15$ kcal/mole whereas $\Delta S^{\ddagger} = -16$ to -30 e.u. The rate constants decrease with decreasing polarizability of L in the order: $C_5H_5N > 3\text{-}ClC_5H_4N > 2\text{-}ClC_5H_4N \sim 4\text{-}ClC_5H_4N > 2\text{-}FC_5H_4N > 3\text{-}CNC_5H_4N$. A rate-determining attack of L upon the dibridged or Cl-monobridged dirhenium complex is proposed.

The red, sublimable $CH_3COCOMn(CO)_5$ was synthesized by the reaction of pyruvoyl chloride with $NaMn(CO)_5$ [120]. It decarbonylates on heating in benzene solution to an equilibrium mixture of $CH_3COMn(CO)_5$ and $CH_3Mn(CO)_5$. The rate of its decarbonylation at 75° is 21 times slower than that of $CH_3COMn(CO)_5$; therefore, pyruvoyl-type structures cannot be intermediates in the substitution reactions of $CH_3COMn(CO)_5$.

M-C bond cleavage in the compounds <u>trans</u>-$RCH{=}C(R)Mn(CO)_5$ ($R = CF_3$, CO_2CH_3, and CO_2H) with $HMn(CO)_5$ occurs with complete retention of configuration to yield the corresponding <u>trans</u>-olefins and $Mn_2(CO)_{10}$ [121]. Reaction of <u>trans</u>-$CF_3CH{=}C(CF_3)Mn(CO)_5$ with Br_2 occurs similarly with retention of configuration to give <u>trans</u>-$CF_3CH{=}C(CF_3)Br$, whereas cleavage of the compound <u>trans</u>-$(HO_2C)CH{=}C(CO_2H)Mn(CO)_5$ with Br_2 proceeds with complete inversion of configuration. <u>cis</u>-$(CH_3O_2C)CH{=}CHMn(CO)_5$ and <u>trans</u>-$(CH_3O_2C)CH{=}C(CO_2CH_3)Mn(CO)_5$

react with Br_2 to give mixtures of the corresponding cis- and trans-bromoolefins. Various possible mechanisms of these reactions are considered. The stereochemistry of the reactions of $HMn(CO)_5$ with substituted acetylenes to afford the corresponding olefins has also been studied and is discussed.

Lack of stereospecificity in the reactions of cis-$CH_3Mn(^{12}CO)_4(^{13}CO)$ with X_2 or HX (X = Br or I) to yield $Mn(^{12}CO)_4(^{13}CO)X$ has been communicated by Wojcicki, et al. [122]. These electrophilic cleavage reactions result in a statistical distribution of ^{13}CO among the five positions of the product molecule. The insertion of SO_2 into cis-$CH_3Mn(^{12}CO)_4(^{13}CO)$ gives a substantial amount of trans-$CH_3SO_2Mn(^{12}CO)_4(^{13}CO)$ in addition to the cis isomer.

By carrying out the following sequence of reactions:

$$\text{D-(-)-}C_6H_5CH(CH_3)Br \xrightarrow[P(C_6H_5)_3]{NaMn(CO)_5} C_6H_5CH(CH_3)COMn(CO)_4P(C_6H_5)_3$$

$$\xrightarrow[H_2O]{Br_2} \text{D-(-)-}C_6H_5CH(CH_3)CO_2H \qquad (14)$$

Johnson and Pearson [123] have been able to demonstrate inversion (> 80%) at α-carbon in nucleophilic attack of $Mn(CO)_5^-$ upon the alkyl bromide. Using this result in conjunction with the observation of inversion of configuration in the two-step process:

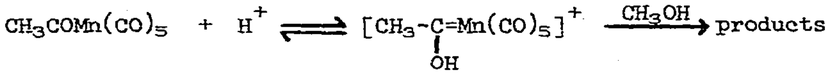
$$\text{(-)-}CH_3CH(CO_2C_2H_5)Br \xrightarrow{Mn(CO)_5^-} CH_3CH(CO_2C_2H_5)Mn(CO)_5$$

$$\xrightarrow{Br_2} \text{(+)-}CH_3CH(CO_2C_2H_5)Br \qquad (15)$$

they concluded that the Br_2 cleavage of the manganese alkyl proceeds with retention (> 60%) at α-carbon.

In another paper concerned with cleavage of manganese-carbon bonds, Johnson and Pearson [124] describe a kinetic study of reactions between $CH_3COMn(CO)_5$ and various nucleophiles. With methoxide in CH_3OH, the reaction is first order in each reagent. The corresponding reaction of $CF_3COMn(CO)_5$

is much faster. Cleavage of $CH_3COMn(CO)_5$ with NaOH and NH_2OH in H_2O also occurs and has been studied; in contrast, no Mn-C bond scission takes place with imidazole, C_5H_5N, $C_6H_{11}NH_2$, NH_3, HPO_4^{2-}, F^-, $CH_3CO_2^-$, or NO_3^-. The kinetics of the acid cleavage of $CH_3COMn(CO)_5$ with HCl in CH_3OH were found to be consistent with the mechanism:

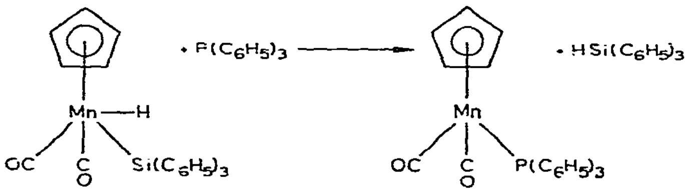


$$CH_3COMn(CO)_5 \;+\; H^+ \rightleftharpoons [CH_3\text{-}\underset{\displaystyle OH}{\underset{|}{C}}\text{=}Mn(CO)_5]^+ \xrightarrow{CH_3OH} \text{products} \qquad (16)$$

Overall, the behavior of $CH_3COMn(CO)_5$ toward the above reagents resembles that of the organic amides. The rate of the reaction of $CH_3Mn(CO)_5$ with HCl in CH_3OH to give $Mn(CO)_5Cl$ and CH_4 is dependent on the acid concentration and is significantly increased by additions of KCl. Mercury(II) chloride cleaves $CH_3Mn(CO)_5$ about 10 times as rapidly as HCl; $Hg(O_2CCH_3)_2$ is even more reactive. Johnson's doctoral dissertation [125] treats the subject of the foregoing reactions in considerable detail.

$Hg(ClO_4)_2$ and $Tl(ClO_4)_3$ readily displace $Mn(CO)_5^+$ from 3- and 4-pyridiniummethylmanganese pentacarbonyls in aqueous solution at 25° [126]. These reactions are believed to proceed by an S_E2 mechanism with an open, unbridged transition state. Added chloride slows down the rate of Mn-C bond scission. The reactivity of various Hg(II) and Tl(III) species in solution has been estimated.

An interesting reductive elimination reaction:

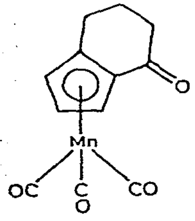


(17)

has been the subject of a kinetic study [127]. The rate-determining step is dissociation of the silane molecule; in hexane, $\Delta H^{\ddagger} = 29.2$ kcal/mole and $\Delta S^{\ddagger}$ = 16.3 e.u. The reaction is retarded by added $HSi(C_6H_5)_3$; competition experiments indicate that $P(C_6H_5)_3$ is 3.6 times as reactive as $HSi(C_6H_5)_3$ toward the intermediate π-$C_5H_5Mn(CO)_2$. The kinetic isotope effect is small for both forward and back reactions: $(\frac{k_H}{k_D})_f$ = 0.97 and $(\frac{k_H}{k_D})_b$ = 1.06. π-$C_5H_5Re(CO)_2(H)Si(C_6H_5)_3$ reacts with $P(C_6H_5)_3$ at least 10^6 more slowly than its manganese analog when allowance is made for a difference in temperature.

Kinetic studies of the racemization and epimerization of the optically-active π-$C_5H_5Mn(NO)[P(C_6H_5)_3](COOR)$ (R = CH_3 and $C_{10}H_{19}$) are the subject of two papers by Brunner [128, 129]. The enantiomeric π-$C_5H_5Mn(NO)$-$[P(C_6H_5)_3](COOCH_3)$ were prepared by a transesterification of the diastereomeric menthyl derivatives (+)- and (-)-π-$C_5H_5Mn(NO)[P(C_6H_5)_3](COOC_{10}H_{19})$ and by reaction of (+)- and (-)-$[\pi$-$C_5H_5Mn(CO)(NO)P(C_6H_5)_3]PF_6$ with CH_3O^- [128]. The rates of the racemization and epimerization were followed by polarimetry and found to be only slightly solvent dependent [129]. Moreover, the alkyl group R exerts little influence on the rate of scission of the Mn-$P(C_6H_5)_3$ bond, which is the slow step of this reaction. For the R = CH_3 complex in benzene, $t_{\frac{1}{2}}$ at 30° is 170 min and E_a = 31.1 kcal/mole. The rate of the exchange of π-$C_5H_5Mn(NO)[P(C_6H_5)_3](COOCH_3)$ with $P(C_6D_5)_3$ is equal to its rate of racemization [128].

The optically-active cymantrene $(\pi$-$C_4H_6OC_5H_3)Mn(CO)_3$ (XLVIII) does not undergo acid catalyzed racemization, in contrast to the behavior of optically-active acylferrocenes [130].



(XLVIII)

Hydrogen-deuterium exchange in $(\pi\text{-}RC_5H_4)Mn(CO)_2L$ has been investigated using CF_3CO_2D and D_2SO_4 [131, 132, 133]. For a series of R = H complexes, a correlation exists between the rate constant for the exchange and the Taft polar substituent constant of R in L = PR_3 [131]. At 27.7°, the exchange in $\pi\text{-}C_5H_5Mn(CO)_2L$ (L = $P(C_6H_5)_3$ and $P(OC_6H_5)_3$) is, respectively, 2000 and 70 times faster than that in $\pi\text{-}C_5H_5Mn(CO)_3$ [132]. Moreover, when L = CO, the R = $CH_2C_6H_5$ complex exchanges about 35 times faster than the R = H complex [133].

Miscellaneous Chemical Studies

Photopolymerization of a vinyl monomer initiated by $Mn_2(CO)_{10}$ in association with ethyl trichloroacetate is followed by a prolonged after-effect if acetylacetone or cyclohexanone is used as a solvent [134]. These observations are consistent with unsymmetrical fission of $Mn_2(CO)_{10}$ on photolysis and subsequent reaction of $Mn(CO)_6$ with solvent to give a species of relatively long life which generates radicals by reaction with the halide.

Nuclear recoil reactions in organomanganese compounds have been studied by Wiles and associates [135]. Manganese atoms in neutron-irradiated $\pi\text{-}C_5H_5Mn(CO)_3$ often form $HMn(CO)_5$, whereas in $(\pi\text{-}CH_3C_5H_4)Mn(CO)_3$ they form both $HMn(CO)_5$ and $CH_3Mn(CO)_5$. In $Mn(CO)_5I$ they primarily reform the original substance, whereas in $Mn_2(CO)_{10}$, a considerable proportion of them appear in the form of the $Mn(CO)_5\cdot$ radical. This radical was shown not to exchange with the $Mn_2(CO)_{10}$ matrix molecules and to decompose above 60°. Irradiation with neutrons of $HMn(CO)_5$, $DMn(CO)_5$, $CH_3Mn(CO)_5$, and $C_6H_5Mn(CO)_5$ leads to formation of $H^{56}Mn(CO)_5$ in all four cases, but in a much smaller quantity with the last two compounds [136].

A method is described [137] for the labelling of $^{*}Mn(CO)_5$ for use in exchange studies. Neutron-irradiated $HMn(CO)_5$ is treated with I_2 and $Mn_2(CO)_{10}$ in petroleum ether to give $Mn(CO)_5I$; the yield of ^{56}Mn in this form is 20% of the total ^{56}Mn. It has been shown that the exchange:

$$^{56}Mn(CO)_5I + HMn(CO)_5 \rightleftharpoons H^{56}Mn(CO)_5 + Mn(CO)_5I \qquad (18)$$

is complete in < 30 sec at room temperature. In contrast, $CH_3Mn(CO)_5$ and $C_6H_5Mn(CO)_5$ are relatively inert to such an exchange with $^{56}Mn(CO)_5I$. A method is also given for enrichment of ^{56}Mn by the Szilard-Chalmers reaction with neutron-irradiated $Mn_2(CO)_{10}$ [138].

Ion-molecule reactions have been described between π-$C_5H_5Mn(CO)_3$ and PF_3, AsF_3, SbF_3, or SF_4 (L) inserted into the ion source of a mass spectrometer [139]. They are of two types, depending on the excitation energy and the fluoride employed, and give the secondary ions $[\pi\text{-}C_5H_5Mn(CO)L]^+$ and $[\pi\text{-}C_5H_5MnL]^+$.

McCleverty, et al. [140] report on the voltammetric oxidation of $(\pi\text{-}CH_3C_5H_4)Mn(CO)_2[C(OCH_3)R]$ (R = 1-ferrocenyl and C_6H_5) and $[\pi\text{-}C_5H_5Mn(NO)LL']^+$ (L,L' = PR_3, pyridines, and RNC; LL' = dipy, etc.). By employing a rotating Pt electrode in CH_2Cl_2 solution, it was shown that the carbene complexes undergo two one-electron oxidations, whereas the nitrosyl cations are oxidized in a one-electron step.

Catalytic Studies

A paper by Andrianov [141] is concerned with the catalytic action of π-$C_5H_5Mn(CO)_3$ on the isomerization of 2-methyl-1-pentene to 2-methyl-2-pentene. π-$C_5H_5Mn(CO)_3$ also promotes addition of $HSiCl_3$ to isobutene.

The oligomerization of $C_6H_5C(CH_3)=CH_2$ in CCl_4 in the presence of $Mn_2(CO)_{10}$ has been studied at 95-150° [142].

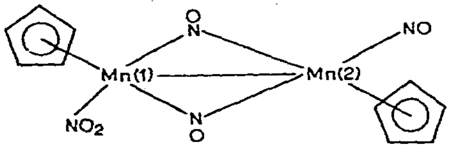
Polymeric catalysts containing phosphorus have been prepared by using $Re_2(CO)_{10}$ in conjunction with a polymer obtained from $C_6H_5PCl_2$ and poly(vinyl alcohol) [143].

X-Ray and Electron Diffraction Studies

The number of papers concerned with determination of structure of organometallic compounds of manganese and rhenium by diffraction methods has quintupled in 1971 compared to 1970. Many of the articles mentioned in this section deal with both preparation and structure.

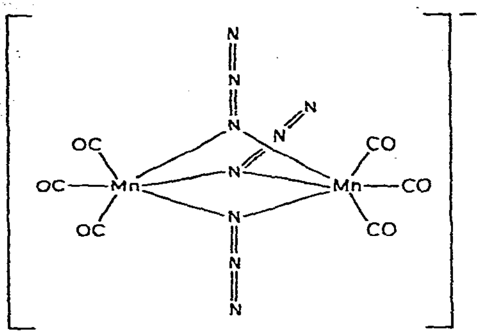
The molecules of $Mn(CO)_5Cl$ in the crystal exhibit small deviations from C_{4v} symmetry [144]. The Mn-C (ax) bond distance is 1.807 Å, whereas the Mn-C (eq) distance is 1.892-1.893 Å. In the substituted derivative cis-$Mn(CO)_4[P(C_6H_5)_3]Cl$, the Mn-C (trans to CO) distance is 1.84 Å, appreciably longer than the Mn-C (trans to Cl or $P(C_6H_5)_3$) distance, which is 1.75 Å [145]. This is consistent with the greater trans-effect of CO than Cl^- or $P(C_6H_5)_3$.

The complex $C_{10}H_{10}N_4O_5Mn_2$, prepared in the course of studies on $(C_5H_5)_3Mn_2(NO)_3$, was shown to possess structure (XLIX) [146]. The nitrosyl bridges are strikingly unsymmetrical (N-Mn(1) = 1.775 Å and N-Mn(2) = 1.943Å), suggesting that each NO donates two electrons to Mn(1) and one electron to Mn(2). The manganese-manganese distance of 2.526 Å is normal.



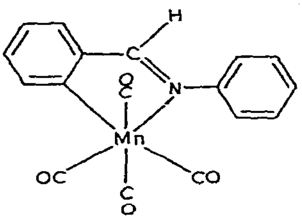
(XLIX)

The reaction between $Mn(CO)_5Br$ and NaN_3 in H_2O-C_2H_5OH at 20° affords $Na[Mn_2(CO)_6(N_3)_3]$ [147]. The structure of the corresponding $(CH_3)_4N^+$ salt was determined by X-ray crystallography. In the anion (L) each azide bridges through one nitrogen, the Mn-N-Mn separation is 2.893 Å, identical within experimental error to the Mn-Mn bond length in $Mn_2(CO)_{10}$ [148]. The synthesis of several other azido and isocyanato complexes of manganese and rhenium is also provided.



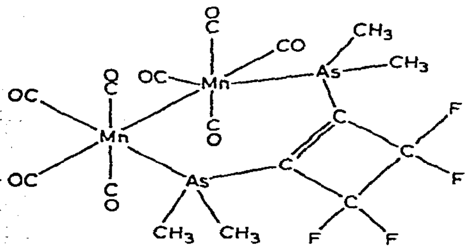
(L)

The complex $C_6H_5N{=}CHC_6H_4Mn(CO)_4$ (LI), prepared from $CH_3Mn(CO)_5$ and benzylideneaniline, has been the subject of a crystallographic study [149]. The Mn-C and Mn-N bond distances in the chelate ring are almost identical.



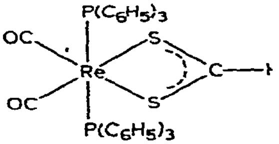
(LI)

Photochemical reaction between $Mn_2(CO)_{10}$ and $(CH_3)_2As\overline{C = CAs(CH_3)_2CF_2C}F_2$ (f_4fars) yields (f_4fars)$[Mn(CO)_4]_2$ (LII), whose structure has been elucidated by X-ray crystallography [150]. The reaction of (LII) with iodine affords (f_4fars)$[Mn(CO)_4I]_2$; preliminary structural results on this product are also reported.



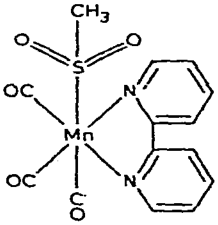
(LII)

Molecular structures have been determined of two dithiocarboxylato complexes of rhenium(I). In the compound $C_6H_5CS_2Re(CO)_4$, the Re-S distance is 2.49 Å [151], whereas in $HCS_2Re(CO)_2[P(C_6H_5)_3]_2$ (LIII), prepared from $HRe(CO)_2[P(C_6H_5)_3]_3$ and CS_2 [66], the Re-S distances are 2.500 and 2.532 Å [152].



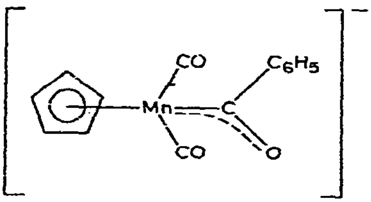
(LIII)

The sulfinate $CH_3SO_2Mn(CO)_3(dipy)$ has been shown [153] to adopt structure (LIV); this confirms the previously made assignment of molecular geometry and Mn-S bonding from infrared spectral data [154].



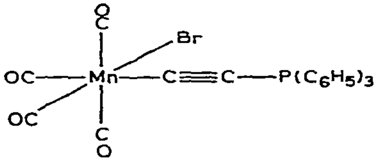
(LIV)

The crystal structure of $(CH_3)_4N[\pi\text{-}C_5H_5Mn(CO)_2COC_6H_5]$ (anion LV) shows the Mn-C (acyl or carbene) bond distance to be 1.96 Å [155], slightly shorter than that expected for an Mn-C single bond.



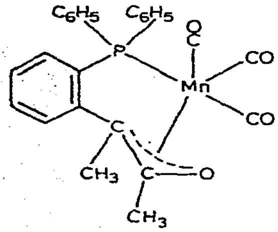
(LV)

The transition metal ylide $Mn(CO)_4[C_2P(C_6H_5)_3]Br$, whose preparation was reported last year (AS 9, 173-174), has been shown to possess structure (LVI) [156]. The C≡C bond distance of 1.20 Å, essentially acetylenic, prompts formulation of the $(C_6H_5)_3PC_2$ ligand as a phosphonium acetylide.

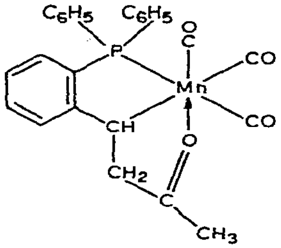


(LVI)

The structures of two previously-mentioned [81] isomeric complexes $Mn(CO)_4[(C_6H_5)_2PC_6H_4C_2H_3CH_3]$ (LVII and LVIII) have been elucidated by X-ray crystallography [157]. (LVII) contains a π-oxopropyl group which is essentially symmetrically bonded to the manganese.

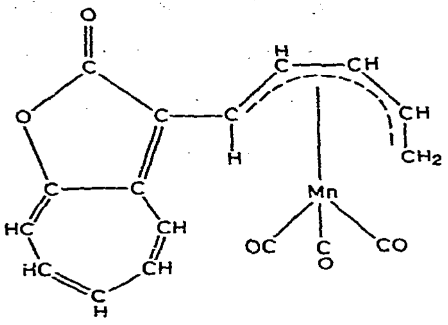


(LVII)



(LVIII)

The first recognized example of an open-chain π-pentadienyl complex of manganese, $C_{17}H_{11}MnO_5$ (LIX), results when $Mn_2(CO)_{10}$ reacts with tropone [158]. The molecular structure of this purple solid contains a nearly planar carbon framework with approximately equal C-C distances of the dienyl group.

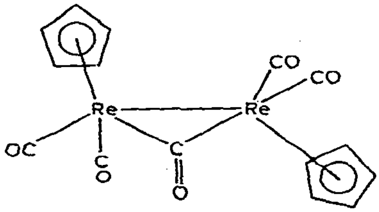


(LIX)

The structure of $Br_3GeMn(CO)_5$ (AS 9, 188) was determined by gas-phase electron diffraction [159]. The equatorial CO's are bent toward the germanium and the Mn-Ge distance is 2.43 Å.

Single-crystal X-ray diffraction studies have established that $Hg[Mn(CO)_5]_2$ is centrosymmetric and has approximate D_{4h} symmetry [160]. Again the equatorial CO's are bent inwards, toward the mercury by 5.3°.

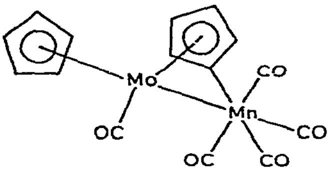
Ultraviolet irradiation of a hexane solution of π-$C_5H_5Re(CO)_3$ affords yellow $(\pi$-$C_5H_5)_2Re_2(CO)_5$ (LX), whose structure was elucidated by crystallography [161]. The rheniums are held together by a symmetrically bridging CO and by a long Re-Re bond of 2.957 Å.



(LX)

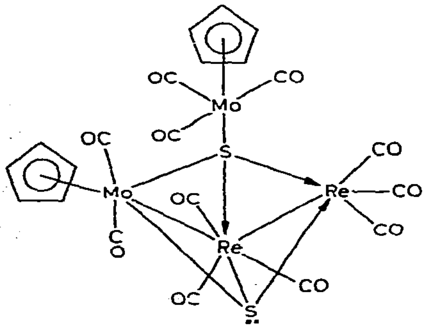
The reaction between $CH_3Mn(CO)_5$ and $(\pi$-$C_5H_5)_2MoH_2$ in warm benzene affords $C_{15}H_9O_5MoMn$ (LXI), which is moderately stable to air in the solid, and whose structure has been determined by X-ray methods [162]. An unusual feature of the molecule is a very short Mo-Mn bond distance of

2.961 Å. $CH_3Mn(CO)_5$ undergoes a similar reaction with $(\pi\text{-}C_5H_5)_2WH_2$ and $(\pi\text{-}C_5H_5)_2ReH$, the product of the latter interaction probably containing hydrogen instead of a CO group bonded to rhenium.



(LXI)

The air-stable, diamagnetic complex $(\pi\text{-}C_5H_5)_2Re_2Mo_2(CO)_{11}S_2$ (LXII), obtained from $\{Re(CO)_4[SSn(CH_3)_3]\}_2$ and $\pi\text{-}C_5H_5Mo(CO)_3Cl$ in benzene or 1,2-dimethoxyethane at 75°, has been investigated crystallographically [163]. A nonlinear trinuclear metal framework and presence of both triply-bridging, four-electron donating, and quadruply bridging, six-electron donating sulfurs are some of the salient features of this structure.



(LXII)

A doctoral dissertation is concerned with several structures; among them is that of $HRe_3(CO)_{14}$, in which the Re_3 fragment possesses a cis configuration [164].

In the molecular nitrogen complex trans-$Re[P(CH_3)_2C_6H_5]_4(N_2)Cl$, whose structure was examined by X-ray crystallography, the Re-N-N moiety is essentially linear [165].

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Electronic Spectra and Structures

The electronic spectra of $M(CO)_5X$ (M = Mn and Re, X = Cl, Br, I, H, CH_3, and CF_3) have been investigated in the range 5000-1900 Å [166]. Band assignments have been made and qualitative molecular orbital energy diagrams are given to account for charge-transfer bands. The electronic structures of $M(CO)_5X$ (M = Mn and Re, X = Cl, Br, and I) have been also discussed by application of the self-consistent charge and configuration molecular orbital method [167]. The relative reactivities of these pentacarbonyls to CO substitution were found to correlate with M-C overlap populations in a satisfactory manner.

Molecular orbital calculations have been made to determine the bonding characteristics of CO and CN^- in the isoelectronic series $Mn(CO)_6^+$, $Mn(CO)_5CN$, $[Mn(CN)_5CO]^{4-}$, and $Mn(CN)_6^{5-}$ [168]. Trends in carbonyl bonding can be attributed essentially to variations in π-acceptor ability, whereas the bonding of cyanide appears to be a function of both σ-donor and π-acceptor abilities which vary according to the total intramolecular environment.

The polarized electronic spectra of $Mn_2(CO)_{10}$ and $M_2Fe(CO)_{14}$ (M = Mn or Re) are reported in a Ph.D. thesis [169]. The nature of the metal-metal bond in $M_2(CO)_{10}$ (M_2 = Mn_2, Re_2, Tc_2, and MnRe) has been described by application of the self-consistent charge and configuration molecular orbital method [170]. An important contribution to the M-M bond energy is that from the cross-interaction between a metal atom and ligands directly bonded to the other metal atom.

Molecular core binding energies have been measured for some organometallic compounds, including π-$C_5H_5Mn(CO)_3$ [171]. Electron transfer from the ring to the CO groups <u>via</u> the metal orbitals is clearly discernible and the C_{1s} and O_{1s} levels for the CO groups are shifted considerably to lower binding energy compared with $Cr(CO)_6$, $Fe(CO)_5$, or $Ni(CO)_4$.

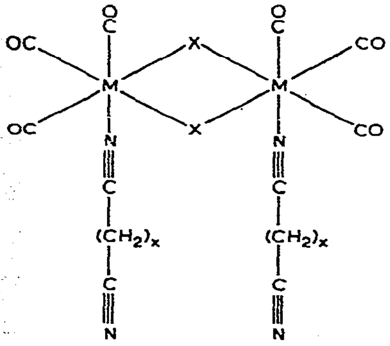
The ionization potentials of π-$C_5H_5Mn(CO)_2PX_3$ increase as a function of

X in the order X = H < Br < Cl < F, reflecting a decrease in the donor properties of PX_3 [172]. The compound $\pi\text{-}C_5H_5Mn(CO)_2PF_3$ was prepared for the first time, photochemically.

The complex $[Mn(CNCH_3)_6]I$ and the dipositive $[Mn(CNCH_3)_6]^{2+}$ have been investigated according to the self-consistent charge and configuration molecular orbital method with the aim of interpreting the electronic spectra [173].

Vibrational Spectra

Spectroscopic evidence has been presented [174] which casts doubt on the original formulation (AS 9, 162) of $M(CO)_3(dinitrile)X$ (M = Mn and Re, X = Cl and Br) as π-bonded dinitrile complexes. It appears now that the band at 2066 cm^{-1} in the infrared spectrum of $Mn(CO)_3[NC(CH_2)_2CN]Br$, assigned previously to ν(CN), is actually due to a CO stretching mode. The authors propose to reformulate these complexes as (LXIII).



(LXIII)

The previously reported [175] infrared spectra in the ν(CO) region of $\pi\text{-}C_5H_5W(CO)_3Mn(CO)_5$ and $MnRe(CO)_{10}$ have been found [176] to be in error. It appears that $\pi\text{-}C_5H_5W(CO)_3Mn(CO)_5$ had partially reacted with the solvent CCl_4, whereas ''$MnRe(CO)_{10}$'' was a mixture of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$.

The infrared spectrum of $\pi\text{-}C_5H_5Mn(CO)_2[C(OCH_3)C_6H_5]$ in hexane shows

4 ν(CO) bands indicating presence of isomers; in contrast, the spectrum of $(\pi\text{-}CH_3C_5H_4)Mn(CO)_2[C(OCH_3)CH_3]$ exhibits only 2 CO stretching absorptions [177].

There were many studies of the vibrational spectra of various types of carbonyl compounds of manganese and rhenium that dealt with the assignment of bands, calculation of force constants, and analysis of the absolute intensities. The infrared and Raman spectra of $Mn(CO)_5Br$ and $Mn_2(CO)_{10}$ have been recorded and assignments of bands made with the aid of isotopic substitution [178]. Another doctoral dissertation [179] is concerned with the Raman spectra, force constants from an approximate normal coordinate analysis, and Raman intensities of the complexes $(CH_3)_3M'M(CO)_5$ (M = Mn and Re, M' = Ge and Sn).

An assignment of bands has been made [180] in the vibrational spectra of $Re(CO)_5X$ (X = Cl and Br). By using an approach described earlier (AS 9, 190-191), Delbeke, et al. [181] have calculated CO stretching force constants for a variety of $Mn(CO)_5X$ complexes (X = SnR_3, SnR_2Cl, COR, etc.). These force constants were then used to obtain σ and π Graham parameters.

Available data on the absolute infrared intensities of ν(CO) of $M(CO)_5X$ (M = Mn and Re, X = Cl, Br, or I) have been analyzed [182].

The infrared spectra in the 2200-60 cm^{-1} region have been investigated for $X_3SnMn(CO)_5$ (X = Cl, Br, CH_3, or C_6H_5) [183]. Normal coordinate analyses of the first three complexes using a modified Urey-Bradley force-field showed that the force constants for the Mn-Sn stretch decrease with X as: $Cl > Br > CH_3$.

The Raman spectra and normal coordinate analyses are reported in a Ph.D. thesis [184] for $Mn_2(CO)_{10}$, $Tc_2(CO)_{10}$, $Re_2(CO)_{10}$, and $MnRe(CO)_{10}$. Also given are the absolute Raman intensities and molecular polarizability derivatives for the M-M stretching modes of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. Raman data are presented [185] for solutions, powders, and oriented single crystals of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ which allow a consistent assignment of the vibrational spectra.

The infrared and Raman spectra of the linear $Mn_2Fe(CO)_{14}$, $Re_2Fe(CO)_{14}$, and $MnFeRe(CO)_{14}$ have been examined in the 2200-1800 cm^{-1} region and a tentative assignment of the $\nu(CO)$ modes proposed [186].

Inelastic neutron scattering spectroscopy has been applied to assign molecular structures and force fields for $H_3M_3(CO)_{12}$ (M = Mn or Re) [187].

Three papers were concerned with vibrational spectra of π-$C_5H_5Mn(CO)_3$ and derivatives. The infrared spectra of $(\pi$-$CH_3C_5H_4)Mn(CO)_2L$ (L = $P(C_6H_5)_3$, $As(C_6H_5)_3$, and $Sb(C_6H_5)_3$) have been investigated in the regions 2100-1850 and 700-225 cm^{-1} [188]. Absorption bands due to vibrations of the $(\pi$-ring$)Mn(CO)_2$ moiety have been assigned. The infrared and Raman spectra of solid π-$C_5H_5Mn(CO)_3$ in the 3000 cm^{-1} region have been investigated [189]; factor-group splitting is observed and the correlation between this and the crystal structure has been considered. The relative Raman intensities and the depolarization behavior for the A_1 and E $\nu(CO)$ modes in π-$C_5H_5Mn(CO)_3$ differ considerably from those of π-$C_6H_6Cr(CO)_3$; this observation is interpreted in terms of a bond-derived polarizability model [190].

NMR, NQR, and Mössbauer Studies

The ^1H NMR spectra of π-cycloheptadienylmanganese tricarbonyl and its 6-exo-methoxy and 6-exo-methyl derivatives have been analyzed in some detail [191]. It appears that the skeleton of the ring carbons in the two derivatives lacks a plane of symmetry.

The ^1H NMR spectrum of π-$C_5H_5Mn(CO)_3$ oriented in the liquid crystalline nematic phase has been reported [192].

Presented by Stewart in his doctoral dissertation [193] are the ^{19}F NMR spectra of m- and p-fluorophenyl derivatives of manganese carbonyl. The CO stretching frequencies of these and related compounds are also given.

Onaka and coworkers [194,195] have investigated the electronic configuration around the tin atom in a series of $(R_{3-x}X_xSn)Mn(CO)_5$ complexes (R = CH_3 or C_6H_5, X = Cl or Br) by ^1H and ^{55}Mn NMR and ^{119}Sn Mössbauer spectroscopy. The results obtained indicate that the $Mn(CO)_5$ group is a stronger electron donor than CH_3, C_6H_5, or halogen [194]. The ^{55}Mn NMR data further show that in the series of $[(CH_3)_{3-x}Br_xSn]Mn(CO)_5$ pentacarbonyls, Mn $\rightarrow$ Sn π-interaction is most pronounced for $Br_3SnMn(CO)_5$ [195].

Single crystals of $Mn(CO)_5X$ (X = Cl, Br, and I) and π-$C_5H_5Mn(CO)_3$ were studied by broadline NMR spectroscopy at room temperature [196]. For $Mn(CO)_5X$, the ^{55}Mn quadrupole coupling constant increases in the order: X = Cl < Br < I. The anisotropic chemical shifts of ^{55}Mn in these four complexes were also determined.

The room temperature ^{55}Mn NQR spectra have been recorded [197] for 14 different ring-monosubstituted and one ring-disubstituted derivatives of π-$C_5H_5Mn(CO)_3$. An attempt was made to correlate the Mn resonance frequencies with infrared, NMR, and UV data which measure variations in the ring π-electron density.

Thermodynamic Studies

Temperature dependence of vapor pressures, heats and entropies of fusion and sublimation, melting points, and other thermodynamic data have been obtained for $Mn_2(CO)_{10}$ [198,199], $Re_2(CO)_{10}$, $MnRe(CO)_{10}$ [199], and π-$C_5H_5Mn(CO)_3$ [200].

Applications to Technology

A U.S. patent is concerned with the use of (π-$CH_3C_5H_4$)$Mn(CO)_3$ as an additive to natural gas fuel [201]. Another patent reports that addition of C_6H_5NSO to a π-cyclopentadienylmanganese tricarbonyl (used as a smoke-repressing agent) in jet fuel reduces manganese-containing deposits in the engine [202].

The use of (π-$CH_3C_5H_4$)$Mn(CO)_3$ as a photosensitizer for the light-induced cure of epoxy resins has been described [203].

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