MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1979 *

P. M. TREICHEL
Department of Chemistry, University of Wisconsin-Madison,
Madison, Wisconsin 53706 (U.S.A.)

CONTENTS

I. INTRODUCTION

The 1978 Manganese, Technetium, and Rhenium Annual Surveys article has appeared (ref. 1). This article follows the format in that survey and in preceding surveys in this area by this author.

Work on a number of interesting and significant projects were abstracted for the 1979 Annual Surveys. Some of the most interesting work, in the opinion of this author, is concerned with the syntheses and reactions of metal-formyl compounds. Quite a number of interesting papers have appeared, especially from the Casey and Gladysz research groups. This work is discussed in Section V.

Once again, over 180 articles in this area were abstracted. The number of articles has been virtually constant over the last five years.

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* Manganese, technetium and rhenium; Annual Survey covering the year 1978 see J. Organometal. Chem., 189(1980)129-161.

II. METAL CARBONYLS AND DERIVATIVES OBTAINED BY CARBONYL SUBSTITUTION ($[Mn(CO)_{5-n}L_n]^-$, $Mn_2(CO)_{10-n}L_n$, $[Mn(CO)_{6-n}L_n]^+$)

Two papers have investigated the basicity at manganese in $[Mn(CO)_5]^-$. Onaka and Furuichi (ref. 2) studied the interaction of this species with $SmCp_3$. Interaction of $SmCp_3$ at the metal site in this anion contrasts with adduct formation of $SmCp_3$ with a carbonyl oxygen in various $Mn(CO)_{5-n}L_nBr$ complexes. Burlitch and several coworkers (ref. 3) investigated the acid-base interactions between $AlPh_3$, $GaPh_3$ and $InPh_3$ and various metal carbonyl anions including $[Mn(CO)_5]^-$ (as the NPr_4 salt). The complexes formed were generally less thermally stable and more air sensitive than some of the complexes of other metal carbonyl anions that were investigated. Only $NPr_4[Ph_3InMn(CO)_5]$ could be isolated and fully characterized among the manganese carbonyl species; the gallium analogue was unstable above 0°C and the triphenylaluminum complex was not obtained pure even at -20°C. The structures of the adducts were deduced from infrared ($\nu(CO)$) data to be similar to that of $Ph_3SnMn(CO)_5$.

Useful preparations of $Li[Mn(CO)_5]$ and $K[Mn(CO)_5]$ in THF were reported (ref. 4); these utilize the borohydride reducing agents $LiBHEt_3$ or $KBHBu^s_3$ with $Mn_2(CO)_{10}$ at room temperature. It is also possible to reduce $Mn(CO)_5Br$ to $[Mn(CO)_5]^-$ with $LiBHEt_3$. The reactions are homogeneous and proceed in high yield. The yield of these anions was assessed by their subsequent reactions with Ph_3SnCl, Me_3SiBr, and MeOCOCOCl; and in addition the salt $PPN[Mn(CO)_5]$ ($PPN^+ = Ph_3PNPPh_3{}^+$) was isolated from one experiment when [PPN]Cl was added. In a subsequent paper the use of this manganese carbonyl anion to prepare anhydrous $Mn(CO)_5H$ was described (ref. 5).

A paper by Darensbourg and Barros reports infrared data on several anionic transition metal carbonyls and cyanocarbonyls, investigating the alkali metal cation-anion site interaction (ref. 6). Reference data are presented on $Na[Mn(CO)_5]$ and $Na[Mn(CO)_4PPh_3]$ in the presence and absence of a crown ether, to indicate the sort of effect encountered when Na^+ interacts with a carbonyl oxygen.

Extended Hückel calculations have been used for a variety of metal carbonyl species including $[Mn(CO)_5]^-$ and the unstable 17e complex $Mn(CO)_5$ (ref. 7). This work is alleged to reproduce and predict optimum geometries including bond lengths for these species and for other first row transition metal carbonyls.

When $PPN[Mn(CO)_5]$ is dissolved in CF_3SO_3H one equivalent of H_2 is evolved and a yellow solution is obtained (ref. 8). This solution is believed to contain a compound $[Mn(CO)_5]OSO_2CF_3$, having $\nu(CO)$ 2164w, 2117w, 2083s, 2042m cm^{-1}. It is thought that there is an ion-pair association between cation and anion in this complex, based upon a well resolved absorption at ~400 nm (ε_{max} ~1400). The same complex forms when $[Mn(CO)_5py]^+$ is dissolved in this solvent. The yellow trifluoromethylsulfonate complex is readily converted into cationic complexes having the formula $[Mn(CO)_5L]^+$ (L = CO, MeCN) upon addition of L (Eq. 1). The formation of $[Mn(CO)_5]OSO_2CF_3$ in the reaction of $[Mn(CO)_5]^-$ with CF_3SO_3H

presumably goes via $Mn(CO)_5H$ with this species, known to be a protonic acid under other circumstances, acting as a hydride donor toward the highly protonic solvent.

$$\begin{array}{c}[Mn(CO)_5]^-\\ \text{or}\\ [Mn(CO)_5py]^+\end{array} \xrightarrow{CF_3SO_3H} [Mn(CO)_5H] \xrightarrow[-H_2]{CF_3SO_3H} [Mn(CO)_5]OSO_2CF_3$$

$$\xrightarrow{+L} [Mn(CO)_5L]OSO_2CF_3 \qquad \text{Eq. 1}$$

Syntheses of the cationic complexes, $[Mn(CO)_{6-n}(CNPh)_n]PF_6$ (n = 2 → 6), has been reported (ref. 9). These complexes were obtained from reactions of known $Mn(CO)_{5-n}(CNPh)_nBr$ with a halide acceptor, $AlCl_3$ or $AgPF_6$, and CO or CNPh. Both the <u>fac</u>- and <u>mer</u>- isomers of $[Mn(CO)_3(CNPh)_3]PF_6$ and the <u>cis</u> and <u>trans</u> isomers of $[Mn(CO)_2(CNPh)_4]PF_6$ were characterized as the only products in stereospecific reactions (Eq. 2-5):

$$\underline{cis}\text{-}Mn(CO)_3(CNPh)_2Br + CNPh + AgPF_6 \rightarrow \underline{fac}\text{-}[Mn(CO)_3(CNPh)_3]PF_6 + AgBr \qquad \text{Eq. 2}$$

$$\underline{mer},\underline{cis}\text{-}Mn(CO)_2(CNPh)_3Br + CO + AlCl_3 \xrightarrow{2)PF_6^-} \underline{mer}\text{-}[Mn(CO)_3(CNPh)_3]PF_6 + AlX_4^- \qquad \text{Eq. 3}$$

$$\underline{mer},\underline{cis}\text{-}Mn(CO)_2(CNPh)_3Br + CNPh + AgPF_6 \rightarrow \underline{cis}\text{-}[Mn(CO)_2(CNPh)_4]PF_6 \qquad \text{Eq. 4}$$

$$\underline{trans}\text{-}Mn(CO)(CNPh)_4Br + CO + AlCl_3 \xrightarrow{2)PF_6^-} \underline{trans}\text{-}[Mn(CO)_2(CNPh)_4]PF_6 + AlX_4^- \qquad \text{Eq. 5}$$

Isomer identification was based on ν(CO) and ν(CN) data. In each instance the incoming ligand takes the specific site occupied by the halide ion. A cyclic voltammogram on each complex was recorded. The ease of oxidation ($E_{1/2}$ for the one electron oxidation, $[Mn(CO)_{6-n}(CNPh)_n]^+ \rightleftharpoons [Mn(CO)_{6-n}(CNPh)_n]^{2+} + e$) varies depending on n, with complexes having more isocyanides being easier to oxidize. There is a smaller but significant difference between the isomeric complexes which is rationalized based on how the relative π bonding ability of CO and CNPh affects the HOMO in each system.

Also characterized (ref. 10) were a group of mixed ligand complexes, $[Mn(CO)_{5-n}(CNMe)_n(CNPh)]PF_6$ (n = 1 → 4), $[Mn(CO)_{5-n}(CNPh)_n(CNMe)]PF_6$ (n = 1 → 4). Syntheses of these complexes were carried out in the general manner described in the previous reference from a substituted derivative of $Mn(CO)_5Br$, L, and $AgPF_6$. Again stereospecific replacement of halide ion by L was encountered; the specific isomers formed were identified based on infrared spectral data.

The reaction of $Mn(CO)_5Br$ with $AgClO_4$ in CH_2Cl_2 is reported to give $Mn(CO)_5OClO_3$, from which the perchlorate ligand may be easily displaced (ref. 11). Many complexes of phosphorus ligands $[Mn(CO)_5L]ClO_4$ were prepared from this intermediate species. If the $Mn(CO)_5Br-AgClO_4$ reaction is carried out in the presence of acetone then fac-$[Mn(CO)_3(acetone)_3]ClO_4$ forms; added ligands readily displace the acetone to give fac-$[Mn(CO)_3L_3]ClO_4$. Heating (reflux in this solvent) converts the fac-isomers to the second isomers, mer-$[Mn(CO)_3(L)_3]ClO_4$.

There are two other brief references to syntheses of cationic carbonyl complexes. Solvolysis of a number of complexes $[\eta-R_2PO_2Re(CO)_3L]_n$ (R = Me, Ph; L = py, NH_3, PPh_3, PCy_3, $AsPh_3$, OEt_2) in liquid NH_3 at 20°C gives $[Re(CO)_3(NH_3)_3]O_2PR_2$ (ref. 12). In addition the complex $(\eta^5-C_6H_6PBu_3)Mn(CO)_3$ reacts when dissolved in acetonitrile to give $[Mn(CO)_3(MeCN)_3]^+$ (ref. 13). Reactions of a complex of a tridentate phosphine, $[Mn(CO)_3\{(Ph_2PCH_2)_3CMe\}]^+$ are given in two papers. The ClO_4^- salt of this complex with $NaBH_4$ gives $Mn(CO)_2\{(Ph_2PCH_2)_3CMe\}H$, while boiling the BPh_4^- salt in aqueous acetone with NaOH gives $Mn(CO)_3\{(Ph_2PCH_2)_3CMe\}H$; in the latter complex the phosphine ligand acts in a bidentate manner (ref. 14). The complex $[Mn(CO)_3\{(Ph_2PCH_2)_3CMe\}]-Mn(CO)_5$ undergoes metathetical reactions with halide ions to give halide salts which can be converted photolytically to covalent species $Mn(CO)_3\{(Ph_2PCH_2)_3CMe\}X$ (X = Cl, Br, I) in which the phosphine ligand is also bidentate. Refluxing these compounds in acetone converts them to the dicarbonyl complexes (ref. 15), which are more easily obtained by photolysis of $[Mn(CO)_3\{(Ph_2PCH_2)_3CMe\}]ClO_4$ and an alkali metal halide in methanol; in these complexes the polyphosphine is tridentate.

The syntheses of a series of complexes $[Re(CO)_3(N\frown N)(S)]^+$ from $Re(CO)_3(N\frown N)Cl$, $AgOSO_2CF_3$, and S in THF or MeCN ($N\frown N$ = 2,2'-biquinoline, 1,10-phenanthroline; S = MeCN, PhCN, py, pip) are reported (ref. 16). These complexes were isolated as trifluoromethylsulfonate salts. They are of particular interest because they exhibit two optically excited emissions. It was found that systematic variation of charge density on rhenium(I) resulted in systematic variation in the energy of the rhenium-ligand charge transfer emissive state.

Studies during the past several years on the photolyses of dinuclear metal carbonyls have clearly identified metal-metal bond cleavage as a primary photoprocess. Further studies have continued along these lines, involving $Mn_2(CO)_{10}$ and derivatives of this species. Hallock and Wojcicki (ref. 17) report photolysis of $Mn_2(CO)_{10}$ in the presence of I_2, MeI, SnI_4, $CuCl_2 \cdot 2H_2O$, HgX_2, PhHgI, and other organometallic complexes. Long-lived adducts of the $Mn(CO)_5$ radical with o-quinones, $[Mn(CO)_4(RCOCOR)]$ have been studied by esr (ref. 18). Esr studies on $Mn(CO)_5O_2$ and $Mn(CO)_4LO_2$ (L = PBu_3, $P(OEt)_3$) are also mentioned (ref. 19). Photolyses of $Mn_2(CO)_{10}$ in the presence of polyvinylpyridine and in the presence of 4-picoline are noted; in the latter system the use of a spin trap reagent leads to $Mn(CO)_4(pic)NOBu^t$ which is identified by esr (ref. 20). Photolysis of hexachlorocyclopentadiene and $Mn_2(CO)_{10}$ gives two products, $C_5Cl_5Mn(CO)_5$ and $Mn(CO)_5Cl$. It is proposed that this reaction involves intermediate generation of $Mn(CO)_5\cdot$, C_5Cl_5 and $Cl\cdot$; products then evolve by appropriate combination of these radicals (ref. 21).

Poë and coworkers have published three papers concerned with the kinetics of various reactions of dimanganese and dirhenium carbonyls. Activation enthalpies for the thermal decomposition reactions of various $Mn_2(CO)_8L_2$ complexes, in decalin under 1.0 atm O_2, show an interesting variation relative to the cone angle of L (L = phosphines, and other phosphorus ligands). Except for complexes of a few ligands having low steric requirements (CO, $P(OMe)_3$) the values of $\Delta H^{\ddagger}$ decrease regularly with increasing cone angle. The rate determining step for these reactions is assumed to involve manganese-manganese bond fission (ref. 22).

The kinetics of the thermal decomposition of $Re_2(CO)_{10}$ with O_2 in decalin and the substitution of CO by PPh_3 in this molecule are consistent with initial homolytic fission of the rhenium-rhenium bond (ref. 23). The $Re(CO)_5$ radical is believed to be more stable than the $Mn(CO)_5$ radical. Evidence is presented which suggests that the PPh_3 substitution reaction is an associative process; this would contrast with earlier work on the manganese system.

In contrast to the above described work are results of a kinetic study on bromine reactions with $M_2(CO)_{10-n}L_n$ (various examples from M_2 = Mn_2, Re_2, MnRe; L = phosphorus ligands; n = 1,2) in cyclohexane or decalin (ref. 24). Reactions were found fast and reaction orders in $[Br_2]$ as high as three were observed. Evidence is presented for a preassociation of Br_2 with the metal carbonyl species, believed to be via the carbonyl oxygen, followed by a slower oxidation step. Rates of reaction generally increase with ligand basicity, although the PPh_3 and PCy_3 complexes show some steric retardation of rates. The rates were found to be inversely related to the ease of polarographic reduction.

Syntheses of $(CO)_5MnM(CO)_3(DAB)$ (M = Mn, Re; DAB = 1,4-diazobutadienes, RN=CH-CH=NR) have been accomplished from reactions of $[Mn(CO)_5]^-$ and $M(CO)_3(DAB)Cl$ (ref. 25). A number of complexes having isocyanide ligands, $Mn_2(CO)_9CNR$, (R = Et, Me_3Si, Me_3Ge, Me_3Sn, Ph_2P, CH_3CO) were prepared by reactions of $[Mn_2(CO)_9CN]^-$ with the appropriate RX compound (ref. 26). Photolysis of $Mn_2(CO)_9(CNEt)$ produces $Mn_2(CO)_8(CNEt)_2$ along with $Mn_2(CO)_{10}$.

A very interesting paper by Kaesz and coworkers (ref. 27) describes the catalysis by $Mn_2(CO)_{10}$ of deuterium-hydrogen exchange in $W(C_5H_5)_2H_2$ using D_2. The mechanism of this process is believed to involve initial formation of $Mn(CO)_5D$. This reaction is discussed further in Section IV.

Modified Huckel theory has been used to calculate molecular energies of various metal carbonyl species, and from this enthalpies of activation for various dissociative processes were determined. The Mn-Mn dissociation enthalpy is calculated to be 39.6 Kcal/mole, comparable to the experimental value of 37 Kcal/mole (ref. 28).

A note has appeared in which the authors state that crystallographic manganese-manganese distances vary widely from 2.50-3.23Å; they caution against drawing conclusions concerning bond orders from bond length data (ref. 29).

An x-ray PES study on $Mn_2(CO)_{10}$ and $Mn(CO)_5H$, and on several other metal carbonyl hydrides has appeared (ref. 30). Formal atomic charges were calculated based on these data. A single crystal Raman study on $Re_2(CO)_{10}$ was reported (ref. 31). Two papers have appeared reporting ^{17}O nmr data on $Mn_2(CO)_{10}$ and various other compounds (ref. 32, 33).

III. METAL CARBONYL HALIDES AND DERIVATIVES ($M(CO)_{5-n}L_nS$; $M(C_5H_5)(CO)_2X_2$)

Synthesis of three $Mn(CO)_5X$ complexes (X = Cl, Br, I) are given in Volume 19 of Inorganic Syntheses (ref. 34). A number of syntheses of other manganese complexes ($Mn(C_5H_5)(CO)(PPh_3)(CS)$, $Mn(C_5H_5)(dppe)(CS)$, $Mn(C_5H_5)(CO)_2(CSe)$, and $Mn(CO)_4B_3H_8$ are also included in that volume.

Carbonyl substitution reactions were used to produce $Mn(CO)_4LBr$ ($L = P(CH_2SiMe_3)_3$ and $As(CH_2SiMe_3)_3$) and $Mn(CO)_3L_2Br$ ($L = PPh_2CH_2SiMe_3$) from $Mn(CO)_5Br$ (ref. 35). The reactions of $Mn(CO)_5X$ and $Re(CO)_5X$ (X = Cl, Br, I) with various 1,4-diazabutadienes (DAB = RN=CH=CH=NR; R = t-Bu, i=Pr, aryl) gave $M(CO)_3(DAB)X$ (ref. 36); cationic manganese complexes could then be prepared from these precursors by addition of $AgBF_4$ and CO (eq. 6)

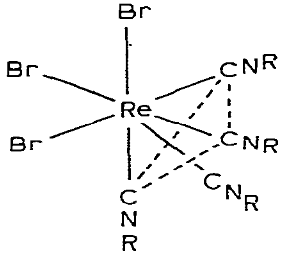
$$Mn(CO)_3(DAB)X + AgBF_4 + CO \rightarrow cis\text{-}[Mn(CO)_4(DAB)]BF_4 + AgX \qquad \text{Eq. 6}$$

Addition of the potassium salt of tris-3,5-dimethylpyrazolylborate to $Re_2(CO)_8Cl_2$ gave two products, $Re[(3,5\text{-}Me_2C_3N_2H)_3BH](CO)_3$ and $Re(3,5\text{-}Me_2C_3N_2H)_2\text{-}(CO)_3Br$; in the latter compound the pyrazolylborate ligand is bidentate (ref. 37). A reference was made earlier to the compounds $Mn[(Ph_2PCH_2)_3CMe](CO)_3X$ and $Mn[(Ph_2PCH_2)_3CMe](CO)_2X$ (X = Cl, Br, I); the former was prepared by photolysis of $[Mn\{(Ph_2PCH_2)_3CMe\}(CO)_3]X$, while the latter was prepared from the former by refluxing in acetone (ref. 15). An extensive paper concerned with photolysis of $Mn_2(CO)_{10}$ with various halo-compounds giving $Mn(CO)_5X$ products was also cited earlier (ref. 17).

Kinetics for the reaction of $Mn(CO)_5Br$ and β-alanine to give $Mn(CO)_3(\beta\text{-al})Br$ were determined (ref. 38). Also the reaction kinetics for the $Mn(CO)_5X$ (X = Cl, Br, I) with CN^- were measured (ref. 39). The two species, $Mn(CO)_5CN$ and $[Mn(CO)_4(CN)X]^-$, are suggested as intermediates in the latter reaction system. The eventual product under the designated reaction conditions is $[Mn(CO)_4(CN)_2]^-$.

The reaction between $PPN[Mn(CO)_5]$ and Me_3SiCl gave $[Mn(CO)_4Cl_2]^-$ (ref. 40). In contrast, other reactions with $PhCH_2Cl$, Ph_3SnCl, and Me_3GeCl produced $Mn(CO)_5R$ compounds. At several previous times it has been reported that the reaction of $[Mn(CO)_5]^-$ with Me_3SiCl gave unexpected or uncharacterized products.

Several seven-coordinate rhenium(III) halide complexes have been characterized. Reactions of $Re(CO)(L)_4Br$ (L = MeNC, tolNC) with bromine were used to obtain ReL_4Br_3 complexes. An X-ray diffraction study was carried out for the compound $Re(CNtol^P)_4Br_3$; it defined a monocapped octahedral structure, with one isocyanide bridging the face of the octahedron bounded by the other three isocyanides (ref. 41); see Fig. I.



(I)

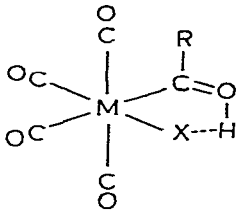
A similar reaction between $Re(CO)_3(dpm)X$ and X_2 (X = Cl, Br) gave $Re(CO)_2(dpm)X_3$. Longer reaction times produced some $Re(dpm)Br_4$ (ref. 42). The reaction of $Re(CO)_3(bipy)X$ with Cl_2 in $CHCl_3$ at room temperature gave $ReCl_3(CO)_2(bipy)$, while the same reagents at reflux gave $ReCl_3(CO)(bipy)$.

The quadruple bond in $Re_2(OAc)_4Cl_2$ does not survive reaction with t-BuNC. These precursors have been shown to give $Re(CNBu^t)_5Cl$ (ref. 43).

The unstable compound $Mn(C_5H_5)(CO)(NO)I$ was prepared from two different reactions. The first route is the cleavage of $[Mn(C_5H_5)(CO)(NO)]_2$ by iodine in CH_2Cl_2. If run in benzene, this reaction gives $Mn_2(C_5H_5)_3(NO)_3I$. This compound was also formed from $[Mn(C_5H_5)(CO)_2(NO)]^+$ and I^-. Treating $Mn(C_5H_5)(NO)(CO)I$ with PPh_3 gives stable $Mn(C_5H_5)(NO)(PPh_3)I$ (ref. 44). Similar chemical reactions were reported by Reger and coworkers (ref. 45), except that in that work the C_5H_4Me ligand replaced the unsubstituted cyclopentadienyl group. Additionally Reger et al. reported conversion of $Mn(MeC_5H_4)(NO)(PPh_3)I$ to $[Mn(MeC_5H_4)(NO)(PPh_3)(MeCN)]^+$ using $AgBF_4$ in MeCN, and the formation of $Mn(MeC_5H_4)(NO)(PPh_3)CN$ and $[Mn(MeC_5H_4)(NO)(PPh_3)(CNEt)]^+$. The complex $Mn(MeC_5H_4)(NO)(PPh_3)I$ is also found to be oxidized by NO^+ at -78°C to a 17e complex; however this species reverts back to the 18e complex on warming to room temperature.

A significant omission in the 1978 Annual Surveys article was made. An article by Bond and coworkers on oxidative chemistry of $Mn(dpm)(CO)_3X$ (ref. 46) was not abstracted in that survey; consequently this is now included here. It was shown that several fac-$Mn(CO)_3(L^\frown L)X$ complexes undergo electrochemical oxidation reactions to give the manganese(II) derivatives fac-$[Mn(CO)_3(L^\frown L)X]^+$ which readily convert to the more stable mer- isomers. The kinetics for the isomerization step were measured and a twist mechanism suggested. The mer-isomers of $[Mn(CO)_3(L^\frown L)X]^+$ are found to be quite reactive toward solvolysis with ligand loss and toward reduction.

Reactions of $Mn(CO)_5Br$ and $Re(CO)_5X$ (X = Cl, Br, I) with MeLi produced anionic acyl complexes, cis-$[M(CO)_4(COMe)X]^-$. Protonation then yielded carbenoid complexes, for which the hydrogen bonded structure II was suggested (ref. 47):

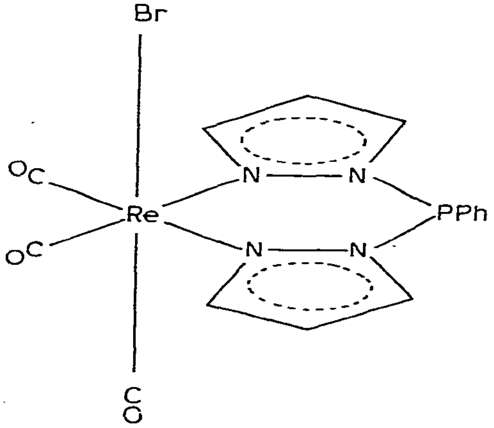


(II)

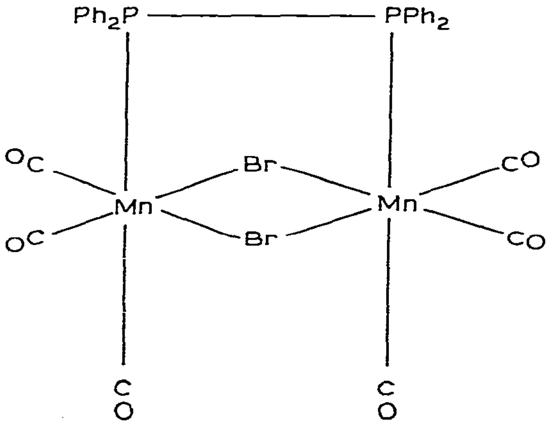
Analogous rhenium formyl complexes were obtained in a $Re(CO)_5X$–$LiBHEt_3$ reaction. The acid-base interactions between $Mn(CO)_{5-n}L_nBr$ and $Sm(C_5H_5)_3$ was mentioned earlier (ref. 2). Interaction is believed to occur between the samarium compound and a carbonyl oxygen.

Earlier in this review, reference was made to extended Hückel calculations of total energies of reactions. Included in these calculations were data pertaining to the cis labelization in $Mn(CO)_5X$ compounds (ref. 28). A study on the electronic spectra of $Re(CO)_3L_2X$ (X = Cl,Br, I; L = 4-PhC_5H_4N, 4,4' bipy) was published (ref. 48). Oxygen-17 nmr spectra of $Mn(CO)_5Br$ were run (ref. 33).

Five papers report crystal structure studies on different manganese and rhenium carbonyl halide species. Simple compounds studied include: fac-$Re(CO)_3$-($Me_2NCH_2CH_2NMe_2$)Br (ref. 49) and fac-$Re(CO)_3[(3,5\text{-}Me_2C_3N_2H)_2PPh]Br$ (ref. 50). In the latter compound the coordination to rhenium is via the two pyrazolyl nitrogens while the phosphorus atom is not coordinated to the metal (III). Structures of $Mn_2(CO)_6Br_2(Ph_2PPPh_2)$ IV, (ref. 51) and $Re_2(CO)_6Br_2(PhSeSePh)$ (ref. 52) have also been reported.

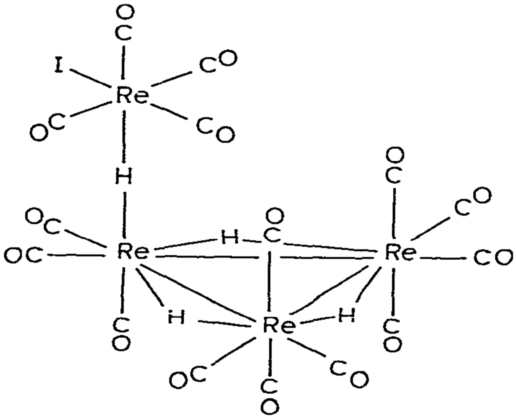


(III)



(IV)

Finally the polynuclear rhenium carbonyl iodide anion, $[H_4Re_4(CO)_{15}I]^-$, was synthesized from $[H_4Re_4(CO)_{15}]^{2-}$, and I_2 (ref. 53). The anion structure (NEt_4^+ salt) is shown below, V.



(V)

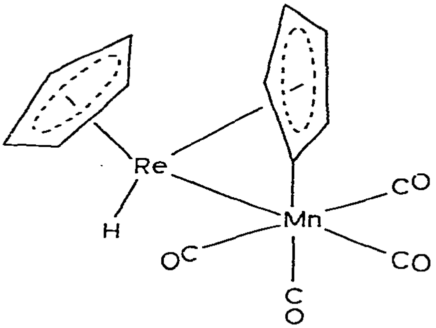
Infrared and Raman data on $Mn(CO)_5Br$ were obtained in several solvents. Half widths of these absorptions were primarily due to vibrational relaxation (ref. 54).

IV. METAL CARBONYL HYDRIDES ($M(CO)_{5-n}L_nH$, polynuclear hydrides)

Earlier in this review, several synthetic procedures were cited which involved metal carbonyl hydrides. These include a simple synthetic procedure to obtain anhydrous $Mn(CO)_5H$ by protonation of $[Mn(CO)_5]^-$ in THF with CF_3SO_3H (ref. 5). This compound was also formed from $Mn(CO)_5SiMe_3$ and methanol. The deprotonation of $Mn(CO)_5H$ by $LiBHEt_3$ and the preparation of fac-$Mn(CO)_3(dppe)H$ are mentioned in this paper. Another paper on the formation of $[Mn(CO)_5]OSO_2CF_3$ from $[Mn(CO)_5]^-$ and CF_3SO_3H (as solvent) was cited earlier (ref. 8), as was a reference to $Mn(CO)_3[(Ph_2PCH_2)_3CMe]H$ and $Mn(CO)_2[(Ph_2PCH_2)_3CMe]_3H$ (ref. 14). The synthesis of $NEt_4[H_4Re_4(CO)_{15}I]$ and the structure of the anionic complex have also been published (ref. 53).

Ultraviolet irradiation of $Re_3(CO)_{12}H_3$ in a degassed system has been shown to produce $Re_2(CO)_8H_2$ quantitatively (ref. 55). Various mechanisms for this conversion were considered. In the presence of CO, the products of photolysis of $Re_3(CO)_{12}H_3$ were $HRe(CO)_5$ and $Re_2(CO)_8H_2$. However the latter species reacted further with CO to give $Re(CO)_5H$ and $Re_2(CO)_{10}$. The photolysis of $Mn_3(CO)_{12}H_3$ gave $Mn(CO)_5H$ and $Mn_2(CO)_{10}$ and an unidentifiable brown powder.

In a reaction of $Re(C_5H_5)_2H$ and $Mn(CO)_5Me$ a product was formed having the formula $(C_5H_5)(H)Re(\mu-(\eta^5:\eta^1-C_5H_4))Mn(CO)_4$, and carbon monoxide and hydrogen were evolved (ref. 56). The presumed structure of the organometallic product is sketched below (VI). This structure is similar to the structure of $(C_5H_5)(CO)Mo(\mu$-$(\eta^1{:}\eta^5$-$C_5H_4))Mn(CO)_4$ which was determined by crystallography (ref. 57); this

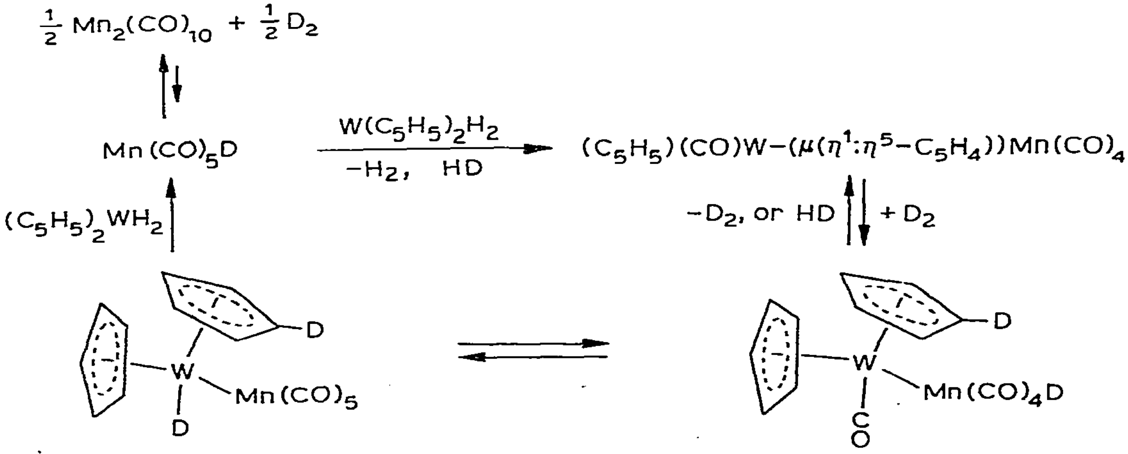


(VI)

latter compound was formed in a reaction between $Mo(C_5H_5)_2H_2$ and $Mn(CO)_5Me$. A similar tungsten derivative was formed from $W(C_5H_5)_2H_2$ and $Mn(CO)_5Me$ (ref. 56).

When $Re(C_5H_5)_2D$ and $Mn(CO)_5CD_3$ were reacted D_2 was evolved. The remaining deuterium atoms were randomly distributed in the ligands in the complex. The compound $(C_5H_5)(H)Re$-$\mu(\eta^1{:}\eta^5$-$C_5H_4)Mn(CO)_4$ was stable to H_2 at 80° but at this temperature the hydrogens in this molecule slowly exchanged with deuterium in D_2. In a similar reaction the tungsten carbonyl species added H_2 at ambient temperature to give unstable $(C_5H_5)_2WHMn(CO)_5$; at 80° conversion to $Mn_2(CO)_{10}$ and $W(C_5H_5)_2H_2$ was noted. Deuterium, replacing hydrogen in this reaction sequence, gave d^n-$W(C_5H_5)_2H_2$ in which the deuterium content was high.

Earlier in this review the $Mn_2(CO)_{10}$ catalysis of H/D exchange between $W(C_5H_5)_2H_2$ and D_2 was noted (ref. 27). Based on the chemistry discussed above (ref. 56, 57) and the fact that $Mn_2(CO)_{10}$ and H_2 (or D_2) give $Mn(CO)_5H$ (or $Mn(CO)_5D$), the following reaction scheme was proposed:



Reactions of $Mn(CO)_5H$ and $Mn(CO)_4(PPh_3)H$ with $CH_2{=}SO_2$ gave $Mn(CO)_4(L)$-SO_2CH_3 (ref. 58). Reaction of $[Mn(CO)_5]^-$ and $MeCO_2{}^{13}CHO$ gave carbon-13 labeled $Mn(CO)_5H$ (ref. 59). This reaction was presumed to proceed via the unstable formyl complex, $Mn(CO)_5{}^{13}CHO$.

It is possible to deprotonate $Re(C_5H_5)_2H$ using butyllithium in the solvent PMDT (pentamethyldiethylenetriamine, $Me_2NCH_2CH_2NMeCH_2CH_2NMe_2$). The product formed, $Re(C_5H_5)_2Li{\cdot}PMDT$, was used in subsequent reactions (ref. 60). This deprotonation was also reported in another paper (ref. 61), along with other reactions of $Re(C_5H_5)_2H$. This includes the formation of $[Re(C_5H_5)_2Me_2]^+$. When MeI was added to $Re(C_5H_5)_2H$, and the formation of $[Re(C_5H_5)_2(\eta^2\text{-}C_3H_6)]Br$ from $Re(C_5H_5)_2H$ and $CH_2{=}CHCH_2Br$. Also $[Re(C_5H_5)_2H_2]^+$ was reacted with diazomethane and a nitrile, RCN, to form $Re(C_5H_5)_2(CRNHMe)$.

The compounds $Mn(MeC_5H_4)(CO)_2(H)Si(Ph)(Np)X$ (Np = 1-naphthyl, X = H, OMe, Cl, F) were prepared from $Mn(MeC_5H_4)(CO)_3$ and the silane SiHX(Ph)(Np) upon irradiation (ref. 62). Various reactions of these complexes were studied, including deprotonation with bases of substantial strength to give anionic complexes which are isolable.

Hückel theory calculations of total energies were applied to the energetics of deprotonation of $Mn(CO)_5H$ (ref. 28). An X-ray PES study on $Mn(CO)_5H$ identified moderate hydridic character for the hydrogen in this compound; a -0.8 e charge on the hydrogen was calculated (ref. 30).

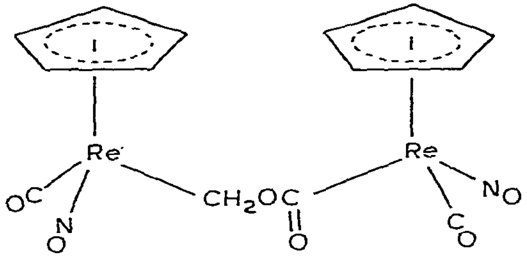
V. METAL COMPLEXES WITH CARBON GROUPS AS LIGANDS ($M(CO)_{5-n}L_nR$, $M(CO)_{5-n}L_nCOR$, MR_n, complexes with carbene and carbyne ligands)

Research on the reduction of carbon monoxide to hydrocarbons using homogeneous catalysts has taken major steps forward in the past year. Most of the activity in this area has centered in organorhenium chemistry, and in particular on reactions originating with $[Re(C_5H_5)(NO)(CO)_2]^+$.

Casey, Andrews and Rinz (ref. 63) published a communication in early 1979 which reported the synthesis and characterization of the formyl-rhenium complex $Re(C_5H_5)(NO)(CO)CHO$. This compound, an orange oil, was obtained by reduction of $[Re(C_5H_5)(NO)(CO)_2]^+$ by either $KBH(OPr^i)_3$ or $LiBHEt_3$ in THF. It shows the appropriate $\nu(CO)$, $\nu(NO)$ and $\nu(CHO)$ infrared absorptions at 1991s, 1723s, and 1619m cm^{-1}. This compound is moderately air sensitive and somewhat unstable in dilute solution, decomposing to $Re(C_5H_5)(NO)(CO)H$; $\tau_{1/2}$ for this process was about 10 hr. Decomposition of the pure compound was more rapid, and was reported in another communication (ref. 64, vide infra). When treated with $BH_3{\cdot}THF$ the formyl compound was reduced to $Re(C_5H_5)(NO)(CO)Me$ in 56% yield.

Also reported in this communication was the reaction of $[Re(C_5H_5)(NO)(CO)_2]^+$ and NaOH in aqueous ether giving $Re(C_5H_5)(NO)(CO)COOH$. Acid regenerates the starting material while base converts this product to $Re(C_5H_5)(NO)(CO)H$. The reaction of $[Re(C_5H_5)(NO)(CO)_2]^+$ with $LiBHEt_3$ gave the first diformyl metal complex reported, $[Re(C_5H_5)(NO)(CHO)_2]^-$, which was not isolated but characterized spectroscopically.

The decomposition of neat $Re(C_5H_5)(NO)(CO)CHO$ was particularly interesting (ref. 64). This compound reacted with itself in a Cannizaro-like condensation to give $Re(C_5H_5)(NO)(CO)CH_2OCORe(C_5H_5)(NO)(CO)$, compound VII. This compound reacted readily with methanol giving $Re(C_5H_5)(NO)(CO)COOMe$ and $Re(C_5H_5)(NO)(CO)CH_2OH$; the latter product is the first hydroxymethyl metal complex to be reported.



(VII)

The hydroxymethyl compound continued to react slowly with methanol to give $Re(C_5H_5)(NO)(CO)CH_2OMe$. This ether could be converted back to the hydroxymethyl species by an acid catalyzed hydrolysis followed by quenching with NEt_3 prior to workup.

Some of the same chemistry was carried out concurrently by Gladysz and coworkers, and published in three papers (ref. 65, 66, 67). Specifically the synthesis of $Re(C_5H_5)(NO)(CO)CHO$ and its further conversion to $Re(C_5H_5)(NO)(CO)Me$ and $[Re(C_5H_5)(NO)(CHO)_2]^-$ are noted. In addition, these workers reported the reduction of $[Re(C_5H_5)(NO)(PPh_3)(CO)]^+$ by $LiBHEt_3$ to give the more stable, crystalline product $Re(C_5H_5)(NO)(PPh_3)CHO$ (ref. 65) on which a crystal structure study has been performed (ref. 66). It is noted that the electrophiles CF_3COOH, $MeOSO_2F$ or Me_3SiCl will convert this rhenium formyl compound back to its precursor, $[Re(C_5H_5)(NO)(PPh_3)(CO)]^+$, and to $Re(C_5H_5)(NO)(PPh_3)Me$ (ref. 67). The following mechanism is proposed:

$$1.\quad \underset{\underline{a}}{ReCp(NO)(PPh_3)CHO} \xrightarrow{MeOSO_2F} \underset{\underline{b}}{[ReCp(NO)(PPh_3)(CHOMe)]^+}$$

$$2.\quad \underline{b} + \underline{a} \longrightarrow \underset{\underline{c}}{ReCp(NO)(PPh_3)CH_2OMe} + \underset{\underline{d}}{[ReCp(NO)(PPh_3)(CO)]^+}$$

$$3.\quad \underline{c} \xrightarrow{MeOSO_2F} \underset{\underline{d}}{[ReCp(NO)(PPh_3)CH_2OMe_2]^+} + \underset{\underline{e}}{[ReCp(NO)(PPh_3)CH_2]^+} + OMe_2$$

$$4.\quad \underline{d} \text{ and/or } \underline{e} + \underline{a} \text{ or } \underline{b} \longrightarrow ReCp(NO)(PPh_3)Me + \underline{d} \text{ or } \underline{b}$$

Additional chemical reactivity along a different line was also reported in this paper. When the methyl compound $Re(C_5H_5)(NO)(PPh_3)Me$ was reacted with a hydride acceptor, Ph_3CBF_4, in CD_2Cl_2 at -70° the methylene complex $[Re(C_5H_5)(NO)(PPh_3)CH_2]^+$ was formed in 88-100% yield. Although unstable, this compound could be trapped by addition of various bases (B = PPh_3, PBu_3, py) giving isolable $[Re(C_5H_5)(NO)(PPh_3)CH_2B]^+$ complexes; also the carbene complex reacted with PhLi to give $Re(C_5H_5)(NO)(PPh_3)CH_2Ph$. Reaction of $[Re(C_5H_5)(NO)(PPh_3)CH_2py]^+$ with NaOMe then gave $Re(C_5H_5)(NO)(PPh_3)CH_2OMe$, which reacted with $MeOSO_2F$ in turn giving $[Re(C_5H_5)(NO)(PPh_3)(CHOMe)]^+$.

A final paper in this area, a comunication from Graham and Sweet (ref. 68), should be given some emphasis. Graham's group had been the first to establish that it was possible to reduce the coordinated CO in $[Re(C_5H_5)(NO)(CO)_2]^+$ to a methyl group by $NaBH_4$. In this paper Graham and Sweet were able to trace this reduction through its intermediates, the formyl and hydroxymethyl compound, isolating these species. The presence of H_2O in the solvent system (1:1 THF/H_2O) was the key factor in obtaining these species.

There has been an earlier mention of two other formyl species in this review. The decomposition of $Mn(CO)_5COCHO$ to $Mn(CO)_5H$ was shown to occur via the unstable species, $Mn(CO)_5CHO$, by a carbon-13 labeling experiment (ref. 59). Also the reduction of $Re(CO)_5X$ (X = Cl, Br, I, H) with $LiBHEt_3$ to give $[Re(CO)_4(X)(CHO)]^-$ was reported (ref. 47).

A review on the use of various borohydride reagents in organometallic syntheses has been written by Gladysz (ref. 69). This reference contains extensive discussion on organo-rhenium formyl complexes and related products.

The synthesis of $Mn(CO)_5CH_2OCOBu^t$ from $[Mn(CO)_5]^-$ and $ClCH_2OCOBu^t$ was carried out (ref. 70), and this compound was then subjected to hydrogen gas (100 psi, 75°, 1 hr). The product of this reduction was determined to be $HOCH_2CH_2OCOBu^t$. This was assumed to be formed by initial carbonyl insertion into the manganese alkyl bond followed by cleavage to give an aldehyde and reduction of this compound to the product, Eq. 7:

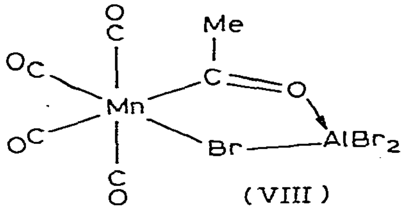
$$Mn(CO)_5CH_2OCOBu^t \rightleftharpoons Mn(CO)_4COCH_2OCOBu^t \xrightarrow{+H_2} [Mn(CO)_4H]$$

$$+ \ HCOCH_2OCOBu^t \xrightarrow{H_2} HOCH_2CH_2OCOBu^t \qquad \text{Eq. 7}$$

At lower hydrogen pressure a slower reaction gave primarily CH_3OCOBu^t; this was also the product when Me_3NO was added. It may be assumed that under these conditions the insertion step was bypassed. When CO was added to the reaction system, another organic product, $HCOCH_2OCOBu^t$, was formed.

Other experiments on hydrogenation of $Mn(CO)_5Me$ and $Mn(CO)_5CH_2OEt$ were run, and EtOH and $EtOCH_2CH_2OH$ were isolated. Thus it appears that this type of reaction is quite general, not requiring an α-oxygen atom for its occurrence.

Methylmanganese pentacarbonyl reacts rapidly with $AlBr_3$ to give a 1:1 adduct whose structure is VIII, according to a single crystal x-ray diffraction study. Carbonylation of VIII gives $Mn(CO)_5COMe$. It is noted that the presence of



(VIII)

Lewis acids greatly facilitates the CO insertion reaction with alkylmetal carbonyls (ref. 71).

The compounds $M(CO)_5COCH_2Cl$ (M = Mn, Re) were prepared and thermal and photolytic decomposition reactions giving $M(CO)_5Cl$, CH_4, and CO were studied (ref. 72). This decomposition pathway contrasts with the reactions of other metal complexes having this acyl group which gave $CH_2{=}C{=}O$ by a β-halide elimination route. Presumably, in the manganese system decarbonylation occurred rapidly and took precedence to this halide migration.

Synthesis of $Mn(CO)_5COCOOMe$ from $[Mn(CO)_5]^-$ was reported (ref. 4). Ammonolysis of $[Mn(C_5H_5)(NO)(CO)_2]^+$ gave $Mn(C_5H_5)(NO)(CO)CONH_2$; a structural study was performed on this product (ref. 73). *Fac*-$[Re(CO)_3(COR)(COMe)_2]^{2-}$ (R - Me, iPr, Bz) complexes were synthesized from MeLi and $Re(CO)_5COR$ (ref. 74). These anionic complexes could be isolated as PPN salts; in addition they were used as tridentate ligands with Al(III), Ga(III), Hf(IV) and Zr(IV).

Ligand exchange reactions between $Re(CO)_4(COMe)(COR)H$ (R = Me, Bz, iPr) and $Cr(CH_2C_6H_4NMe_2)_3$ gave various $Cr(CH_2C_6H_4NMe_2)_{3-n}(Re(CO)_4(COMe)(COR))_n$ complexes. Complete exchange of the $[acac]^-$ ligands in $Cu(acac)_2$ by this rhenium carbonyl species occurred in a similar reaction (ref. 75).

Various $(CO)_5M(COC_5H_4)M'(CO)_3$ species (M,M' = Mn, Re) were prepared from $[M(CO)_5]^-$ and $ClCOC_5H_4M'(CO)_3$ (ref. 76). Decarbonylation occurred using photolytic conditions giving compounds with $M(CO)_5$ groups substituted on the cyclopentadienyl group in cyclopentadienylmanganese and -rhenium tricarbonyl.

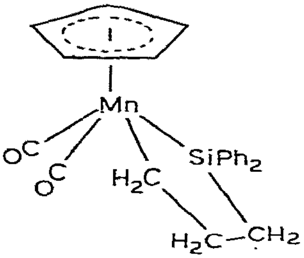
The rate of carbonylation of $Mn(CO)_5CH_2R$, and the rate of decarbonylation of $Mn(CO)_5COCH_2R$ (R = Cy, H, Ph, OMe, COOOEt, COMe, CF_3, $COCH_2Ph$) were measured (ref. 77). Linear free energy relationships between these rates and substituent parameters were developed.

The syntheses of $Mn(CO)_5C_5Cl_5$ from the $Mn_2(CO)_{10}$–C_5Cl_6 photolysis (ref. 21) and $Mn(CO)_5CH_2Ph$ from $PhCH_2X$ and $PPN[Mn(CO)_5]$ were reported (ref. 40). The reaction of 1,1'-dichloro-2-lithioferrocene with $Mn(CO)_5Br$ gave 1,1-dichloro-2-pentacarbonylmanganatoferrocene (ref. 78). The Grignard reagent $PPh_2(CH_2)_3MgCl$ was reacted with $M(CO)_5Br$ (M = Mn, Re) to give $\overline{M(CO)_4(CH_2)_3P}Ph_2$ (ref. 79); a crystal structure study was carried out on the manganese compound.

The preparation of $Re(CO)_5CH_2CH=CH_2$ and its conversion to $Re(CO)_4(\eta^3-C_3H_5)$ is noted (ref. 80). The first η^1-cycloheptatrienyl-metal complex was prepared by two routes, by photolytic decarbonylation of $Re(CO)_5COC_7H_7$ in acetone at -78°, and by reaction of $[C_7H_7]BF_4$ with $[Re(CO)_5]^-$. An nmr study on this compound showed that migration of the metal around the cycloheptatrienyl ring occurs only by 1,2-shifts. This was determined by the spin saturation transfer technique in dioxane-d_8, irradiation of the H_7 resonance causing a decrease in the intensity of the proton resonances for the hydrogens in the one and six positions (ref. 81).

It was found that $Mn(CO)_5SiMe_3$ added to benzaldehyde (5°, 2 wks) to give $Mn(CO)_5CHPhOSiMe_3$ in ~90% yield. No reaction occurred between benzaldehyde and $Mn(CO)_5H$ or $[Mn(CO)_5]^-$. The driving force of this reaction was suggested to be the oxophilicity of the $SiMe_3$ group. Pyrolysis of the product at 80° gave $Mn_2(CO)_{10}$ and the two diastereomers of $SiMe_3OCHPhCHPhOSiMe_3$ (ref. 82).

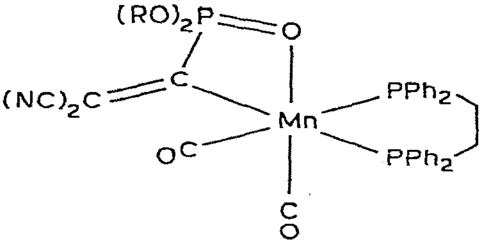
Generation of $Ph_2Si=CH_2$ by photolysis of $\overline{SiPh_2CH_2CH_2CH_2}$ is known to occur. However when photolysis is carried out in the presence of $Mn(C_5H_5)(CO)_3$ the product, IX, is formed (ref. 83).



(IX)

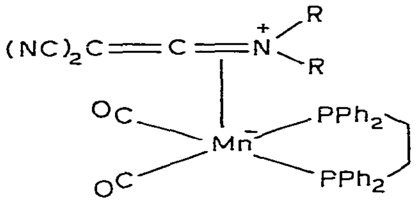
Mentioned earlier in this review was the synthesis of various $Re(C_5H_5)_2R$ compounds (R = Et, Me, Pr, allyl) (ref. 60, 61). The ethyl compound gave $[Re(C_5H_5)_2(C_2H_4)]^+$ when treated with a hydride abstracting agent, $[Ph_3C]BF_4$ (ref. 60). Reaction of $Re(C_5H_5)_2H$ with MeI gave $[Re(C_5H_5)_2Me_2]^+$; which when treated with MeLi produced $Re(C_5H_5)(C_5H_5Me)Me_2$ (ref. 61).

Photolysis of $Mn(CO)_3(dpe)-CCl=C(CN)_2$ with triisopropyl phosphite gave a complex having structure (X) shown below (ref. 84), along with CO and iPrCl.



(X)

An x-ray diffraction study identified this structure. With $P(OMe)_3$ or $P(OEt)_3$(=L) related compounds $Mn(CO)(dpe)(L)C(PO(OR)_2)=C(CN)_2$ were obtained; these have the same structure except that $P(OR)_3$ has been substituted for one carbonyl group. It was also possible to prepare $Mn(CO)_2(dpe)C(PO(OR)_2)=C(CN)_2$ by irradiation of a THF solution of $Li[PO(OR)_2]$ and $Mn(CO)_3(dpe)CCl=C(CN)_2$ (ref. 85). Photolysis of $Mn(CO)_3(dpe)CCl=C(CN)_2$ with various amino phosphines or Et_2NH gave manganese complexes with the 1,1-dicyanoketenimmonium ligand, XI. However reactions using similar conditions with a number of other secondary amines resulted in formation of carbamoyl derivatives, $Mn(CO)_2(dpe)(CONR_2)(C(NHR_2)=C(CN)_2)$ (R_2 = Me_2, $(CH_2)_4$ or 5, $O(CH_2CH_2)_2$), XII, (ref. 86).



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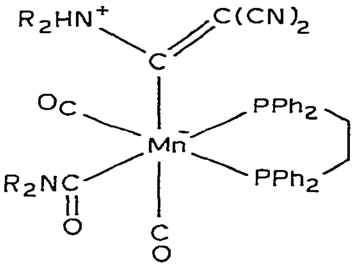
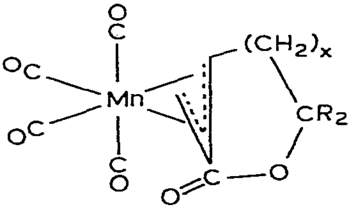


(XII)

Carbonyl substitution reactions were enhanced by addition of Me_3NO. Improvements in yields, increased rates and higher stereoselectivity (to the cis isomer of $Mn(CO)_4(L)Ph$) were noted (ref. 87). The compound $Mn(CO)_4$-$(P(OPh)_3)Ph$, exists as a cis-trans isomer mixture. The kinetics of the cis-trans isomerization process were measured in heptane, at 30-55°C. These reactions were first order in the manganese complex concentration, and independent of CO and $P(OPh)_3$ concentrations. There was no exchange between the complex and a deuterated $P(OPh)_3$ (ref. 88).

Cleavage of the alkyl-manganese bond in threo-$PhCHDCHDMn(CO)_4PEt_3$ using $HgCl_2$ occurs with inversion of configuration at carbon (ref. 89). Cleavage by halogens was also studied, with the stereochemistry of carbon dependent upon reaction conditions. Possible mechanisms for the halogen cleavage reactions include S_E2 (with retention or inversion) or an S_E oxidative mechanism (ref. 90).

The complexes $Mn(CO)_5CH_2C{\equiv}C(CH_2)_nCRR'OH$ rearranged when heated or when contacted with alumina. The structure of the products was identified as XIII (ref. 91).



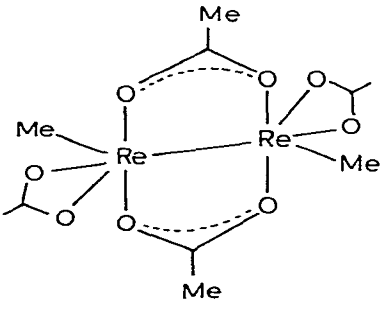
(XIII)

Synthesis of $MeReO_3$ was accomplished inadvertently when Me_4ReO or Me_3ReO_2 were contacted with air. The crystalline compound is air stable (ref. 92).

The reaction of $Mn(acac)_3$, $AlPh_3 \cdot Et_2O$, and PCy_3 gives $MnPh_2(PCy_3)$. Reactions of this compound with CO_2 and with ketones have been studied (ref. 93). The compound $Mn(CH_2Ph)_2 \cdot 2diox$ was prepared from $MnCl_2 \cdot 1.5THF$ and either $PhCH_2MgCl$ or $(PhCH_2)_2Mg$. Reactions of this species with CO_2 or CS_2 gave $PhCO_2H$ or $PhCS_2H$. The benzyl groups were cleaved by I_2 or by $HgCl_2$. Also a 1:1 adduct between $(PhCH_2)_2Mn$ and $Mg(acac)_2$ and a 3:1 adduct between $(PhCH_2)_2Mn$ and $Al(acac)_3$ were reported (ref. 94).

The reactions of $Re_3Cl_3(CH_2SiMe_3)_6$ or Re_3Me_9 with carboxylic acids, β-diketones, and PhN=N-NHPh were investigated. The former species lost $SiMe_4$ while the latter lost CH_4 from terminal alkyl groups; the resulting products still had the Re_3 groups intact (ref. 95).

Molecular structures were determined for $Re_2Me_2(O_2CMe)_4$ (XIV) and $Re_2Me_2(O_2CMe)_2Cl_2(DMSO)$ (XV) (ref. 96) by x-ray diffraction techniques.



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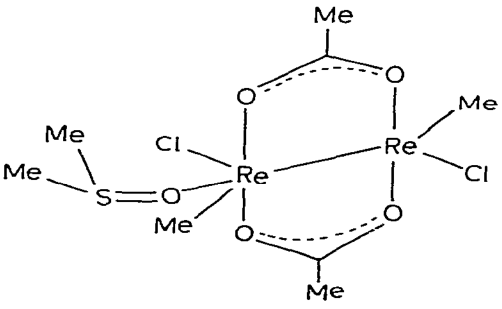
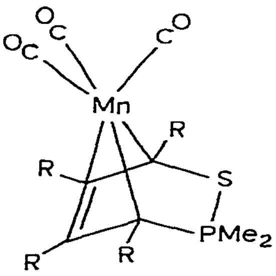


(XV)

Crystal structure studies were also carried out on $Mn(CO)_3[Me_2PS(RC{\equiv}CR)_2]$ (ref. 97) XVI and trans-$Mn(CO)_4(PPh_3)C(CF_3)=C=C(CF_3)_2$ (ref. 98). The former product was obtained in the reaction of $[Mn(CO)_4(PMe_2S)]_2$ with $RC{\equiv}CR$ (R = COOMe).



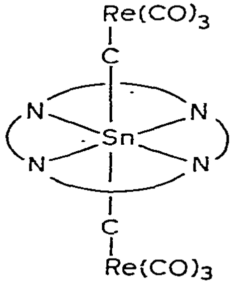
(XVI)

Two papers reported ion cyclotron resonance studies of manganese carbonyl compounds. The first was a study of the gas phase reactions of $Mn(CO)_5Me$ with proton donors (ref. 99). The reaction of $Mn(CO)_5CH_2F$ with proton donors was found to give $[Mn(CO)_5CH_2]^+$ (ref. 100). A ^{13}C nmr study on various methyl-metal compounds, including $Re(CO)_5Me$, was carried out with the intention of defining the possible relaxation mechanisms available (ref. 101).

Complexes with carbene, carbyne, and other carbon containing ligands are considered next in this review. Mononuclear species are covered first and dinuclear species second.

The carbene complexes, $Mn(C_5H_4R)(CO)_2CR'OMe$ (R = H, Me; R' = Me, Ph) reacted with BCl_3 to give $[Mn(C_5H_4R)(CO)_2CR']BCl_4$ (ref. 102). Reactions of these carbyne complexes with X^- (X^- = SCN^-, $C_5H_5^-$) gave $Mn(C_5H_4R)(CO)_2CR'X$. Reactions of $Re(dpe)_2(CNR)Cl$ (R = Me, Bu^t) with HBF_4 gave $[Re(dpe)_2(CNHR)Cl]BF_4$ (ref. 103).

The tetraphenylporphyrin (TPP) complex, $Sn(TPP)Cl_2$, and $Re_2(CO)_{10}$ reacted at 180° to give $Sn(TPP)[Re(CO)_3]_2$. At 160° a different complex, $Sn(TPP)[Re(CO)_3C]_2$ was obtained. This latter compound, a carbide complex, was identified by a crystal structure study; see structure XVII below (ref. 104).



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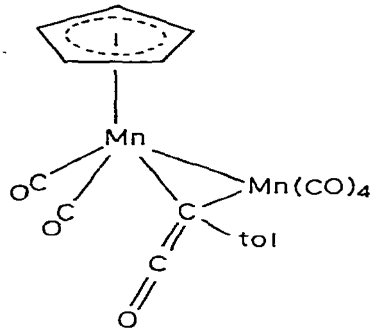
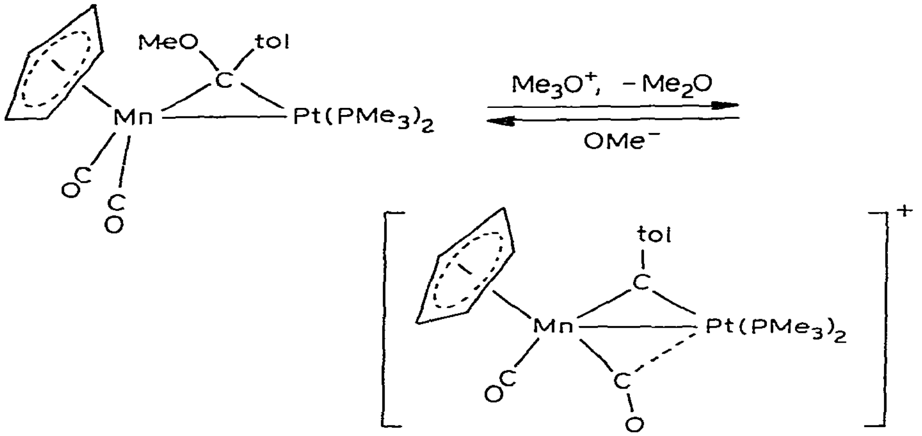
Silicon-29 nmr data were reported on thirteen carbene complexes including $Mn(C_5H_5)(CO)_2C(OMe)SiPh_3$ (ref. 105). Carbon-13 data were obtained for the compounds $Re(C_5H_5)(CO)_2CX$ (X = O, S, Se) compounds (ref. 106). A paper has appeared describing the influence of the CS ligand on H^+/D^+ exchange in $Mn(C_5H_5)(CO)_2(CS)$ (ref. 107).

Unexpected and unusual products were obtained in reactions between $[M(C_5H_5)(CO)_2Ctol]^+$ (M = Mn, Re) and $PPN[Mn(CO)_5]$. The molecular structure of the dimanganese compound, $Mn_2(C_5H_5)(CO)_6(CtolCO)$ (crystallized with 0.5 equivalents of Et_2O) is shown below in XVIII; this structure was obtained from our x-ray crystallographic study (ref. 108). Another unusual reaction sequence



(XVIII)

is portrayed below (eq. 8). Methylation of the OMe group in the reactant species and loss of Me_2O gave the product, XIX; methoxide ion converted this product back to starting material. An x-ray diffraction study identified the product, which was crystallized as the BF_4^- salt. It contains a semi-bridging carbonyl group. A similar reaction sequence was reported with $Re(C_5H_5)(CO)_2(\mu\text{-CtolOMe})Pt(PPhMe_2)_2$ (ref. 109).



Eq. 8

The syntheses of starting materials for this previously described reaction were carried out by the reaction shown below, Eq. 9:

$$Mn(C_5H_5)(CO)_2(CPhOMe) + Pt(C_2H_4)_3 \xrightarrow{2)\,PMe_3} Mn(C_5H_5)(CO)_2(\mu\text{-CPhOMe})Pt(PMe_3)_2$$

Eq. 9

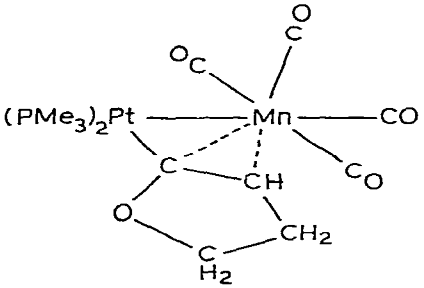
Analogous palladium and nickel compounds were obtained when $Pd(dba)_2$ or $Ni(COD)_2$ were substituted for $Pt(C_2H_4)_3$ (ref. 110).

A reaction between $Mn(C_5H_5)(CO)_2(THF)$ and $HC{\equiv}CCOPh$ at 20°C gave $Mn(C_5H_5)(CO)_2(HC{\equiv}CCOPh)$ and $Mn_2(C_5H_5)_2(CO)_4(\mu\text{-C=CHCOPh})$. Hydrogen chloride or acetic acid (HX) converted the former material to $Mn(C_5H_5)(CO)_2(HCX{=}CHCOPh)$; i.e., the molecule HX added across the coordinated triple bond in this compound (ref. 111).

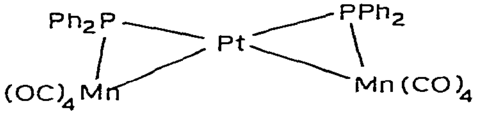
The synthesis of $Mn(C_5H_5)_2(CO)_4(\mu\text{-}C{=}CH_2)$ occurred upon photolysis of $Mn(C_5H_5)(CO)_2THF$ and C_2H_2. A crystal structure study on this compound was reported (ref. 112). Another paper reported the electronic structures of several μ-alkylidene complexes including $Mn_2(C_5H_5)_2(CO)_4(\mu\text{-}C{=}CHPh)$ (ref. 113). A crystal structure determination was carried out on $Mn_2(C_5H_4Me)_2(CO)_4(\mu\text{-}CH_2)$ (ref. 114) and mass spectrometric data on $Mn_2(C_5H_5)_2(CO)_4(\mu\text{-}CH_2)$ were recorded (ref. 115).

VI. METAL CARBONYL DERIVATIVES OF METALS AND METALLOIDS (Derivatives of Electropositive metals, of Group IIIA, and IVA elements)

Some of the work in this area has already been cited earlier in this survey and as a consequence will only be identified here. This includes the three papers by Kaesz and coworkers (ref. 27, 56, 57) on dinuclear complexes which arose in reactions between $Mn(CO)_5Me$ and $M(C_5H_5)_2H_2$ (M = Mo, W). The structure of one of these compounds was sketched earlier (structure VI). Also, the three papers by Stone and coworkers, just cited in the previous section should be mentioned here (ref. 108, 109, 110). There is additional work reported in ref. 110 on two products, red and yellow crystalline species, obtained in the reaction of $Mn_2(CO)_9(\overline{C(CH_2)_3O})$ with $Pt(C_2H_4)_3$ followed by PMe_3 addition. These products, both having the formula $Mn(CO)_4(\mu\text{-}\overline{C{=}CHCH_2CH_2O})Pt(PMe_3)_2$ were each subjects of crystal structure determinations. They have basically the same structure, but differ with respect to the orientation of the $Mn(CO)_4$ group. The structure of the red isomer is drawn below, XX.



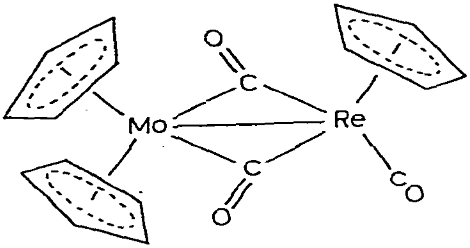
(XX)



(XXI)

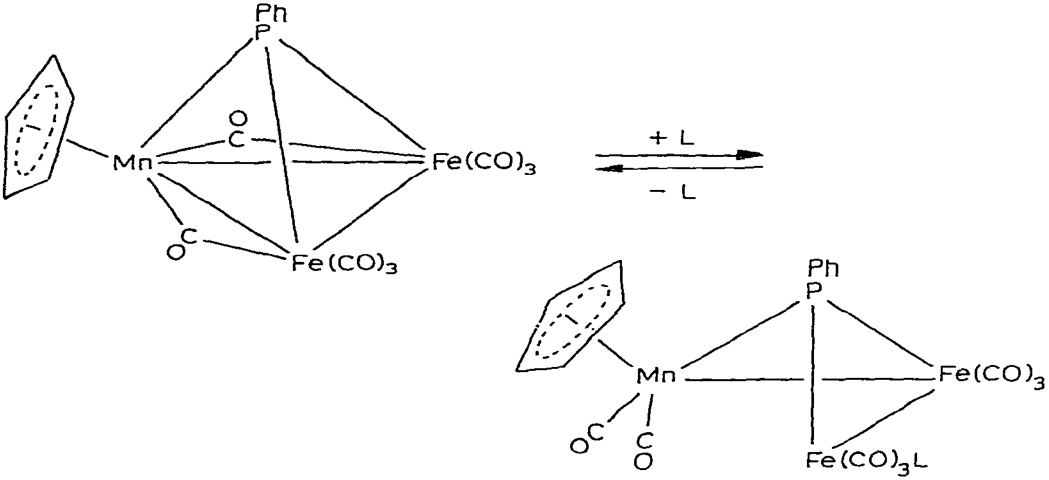
Another new platinum-manganese complex was formed when $[Mn(CO)_5]^-$ reacted with $PtCl_2(PPh_2Cl)_2$ (ref. 116). This product, XXI, was accompanied by trans-$Pt(CO)_2$-$[Mn(CO)_5]_2$ in this reaction. A crystal structure study on XXI was carried out. The crystal structure of $Re(C_5H_5)(CO)(\mu\text{-}(CO)_2)Mo(C_5H_5)_2$, XXII, was also determined (ref. 60); this compound was obtained in a reaction of $Re(C_5H_5)_2Li{\cdot}PMDT$ with

$Mo(C_5H_5)(CO)_3Cl$. A tungsten analogue was also prepared.



(XII)

The reversible ring opening reaction of a trimetallic cluster compound was the subject of a paper by Huttner et al. (ref. 117). The equation below (Eq. 10) identifies this reaction system:



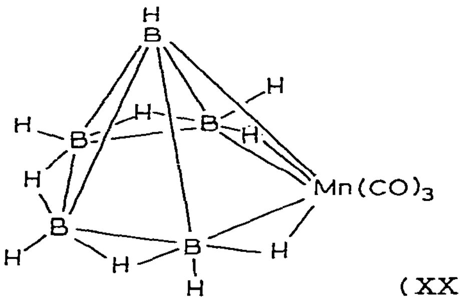
Four papers on $AsMe_2$ bridged bimetallic complexes having metal-metal bonds have been published from Vahrenkamp's group (ref. 118-121). Other related work from Grobe's laboratory is also noted (ref. 122). Discussion on these papers will be deferred until Section VII.

Electrochemical oxidations of zinc, cadmium, and indium in organic solvents in the presence of $Mn_2(CO)_{10}$ and 2,2'-bipyridine have been carried out. The isolated products were $Zn(bipy)_2[Mn(CO)_5]_2$, $Cd(bipy)_2[Mn(CO)_5]_2$, and $In(bipy)_3$-$[Mn(CO)_5]_3$ (ref. 123).

Treatment of THF solutions of $Na[Mn(CO)_5]$, formed from Na/Hg and $Mn_2(CO)_{10}$, with $AlEt_2Cl{\cdot}THF$ produced $Hg[Mn(CO)_5]_2{\cdot}THF$ (ref. 124). Other mercury containing organometallic compounds were formed from $M(C_5H_4HgCl)(CO)_3$ and $Na[M'(CO)_5]$ (M,M' = Mn, Re) (ref. 125). Mercuric chloride acts as a Lewis acid, forming 1:1 adducts with $Mn(C_5H_5)(CO)_2L$ ($L = PPh_3$, $AsPh_3$, $SbPh_3$) and with $Re(C_5H_5)(CO)_2(PPh_3)$ (ref. 126).

Adducts between $[Mn(CO)_5]^-$ and Ph_3A (A = Al, Ga, In) were mentioned earlier in this review (ref. 3). Crystal structure determinations were carried out on the two compounds $[Re(CO)_5]_4In_2(\mu\text{-}X)_2$ (X = Cl, Br) (ref. 127).

A preparation of $Mn(CO)_4B_3H_8$ is given in Inorganic Syntheses, Vol. 19 (ref. 34). The reaction between B_5H_9 and $Mn(CO)_5H$ (or $Mn_2(CO)_{10}$ + H_2) produced $B_5H_{10}Mn(CO)_3$ (XXIII). This product could be deprotonated in base to give $[B_5H_9Mn(CO)_3]^-$; also it reacted with Br_2 to give apically substituted $1\text{-}BrB_5H_9Mn(CO)_3$ (ref. 128).



(XXIII)

INDO-SCF molecular orbital calculations on $Mn(C_5H_5BH)_2$ and other borabenzene compounds were reported (ref. 129). It is noted parenthetically that the manganese compound is as yet unknown.

The preparations of $Mn(CO)_5SiMe_3$ and $Mn(CO)_5SnPh_3$ from $[Mn(CO)_5]^-$ and either $SiMe_3Cl$ or $SnPh_3Cl$ were carried out (ref. 4). The synthesis of $Mn(CO)_5SnPh_3$ and $Mn(CO)_5GeMe_3$ from PPN$[Mn(CO)_5]$ was mentioned earlier (ref. 40). The same article describes the reaction of this pentacarbonylmanganate salt with Me_3SiCl, the product being $[Mn(CO)_4Cl_2]^-$ and not $Mn(CO)_5SiMe_3$. Also reviewed earlier were: a) a study of reactions of the compounds $\overset{*}{Mn}(C_5H_4Me)(CO)_2(H)Si(Ph)(Np)X$ (X = H, Cl, F, OMe) (ref. 62); b) the synthesis of $\overline{Mn(C_5H_5)(CO)_2SiPh_2CH_2CH_2CH_2}$ (ref. 83); c) the reaction of $Mn(CO)_5SiMe_3$ with benzaldehyde (ref. 82); and d) the reaction of $Mn(CO)_5SiMe_3$ and methanol (ref. 5). The complexes $Sn(TPP)[Re(CO)_3]_3$ and $Sn(TPP)[Re(CO)_3C]_2$ were mentioned as products of the reaction of $Sn(TPP)Cl_2$ and $Re_2(CO)_{10}$, the product of choice depending on temperature (ref. 104). The former product was also identified in a communication along with a related species Sn(phthalocyaninato)$[Re(CO)_3]_2$ (ref. 130).

The synthesis of $Mn(CO)_5Ge_2H_5$ from $[Mn(CO)_5]^-$ and $Fe(CO)_4(Ge_2H_5)_2$ has been reported (ref. 131). Photolysis of $Mn(C_5H_5)(CO)_3$ and $SnCl_2$ in THF produced $Mn(C_5H_5)(CO)_2SnCl_2\cdot THF$; hydrolysis of this compound gave $Mn(C_5H_5)(CO)_2Sn(OH)_2$ which is presumed to be polymeric (ref. 132). The structure of the 1:2 adduct of $Re(C_5H_5)(CO)_2(PPh_3)$ and $SnCl_4$ is a salt, $[Re(C_5H_5)(CO)_2(PPh_3)SnCl_3]SnCl_5$ (ref. 133).

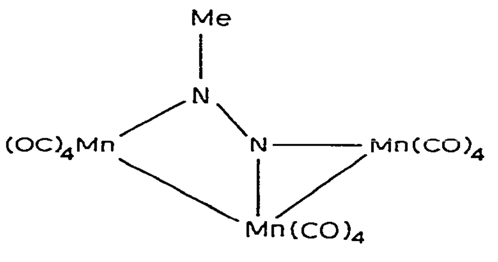
When $Re_2(CO)_{10}$ and SnX_2 (X = Cl, Br, I) were reacted together the product $Re_2(CO)_8[\mu\text{-}Sn(X)Re(CO)_5]_2$ was obtained only if CO was allowed to vent from the system. If CO was retained, or if the compound $Re_2(CO)_8[\mu\text{-}Sn(X)Re(CO)_5]_2$ was subjected to CO pressure, a different species, $SnX_2[Re(CO)_5]_2$, was formed instead (ref. 134). Also reported in this paper were the compounds $Re_2(CO)_8[\mu\text{-}Ge(X)M(CO)_5]_2$ (M = Mn, X = Br, I, and M = Re, X = I).

Photolysis of $Re(CO)_3$(o-phen)$SnPh_3$ or $Re(CO)_3$(o-phen)$GePh_3$ can proceed with either Re-M cleavage or radiative decay (ref. 135). Silicon-29 nmr spectra for $Mn(CO)_5SiMe_3$, $Re(CO)_5SiMe_3$, and trimethylsilyl derivatives of other metals were reported (ref. 136).

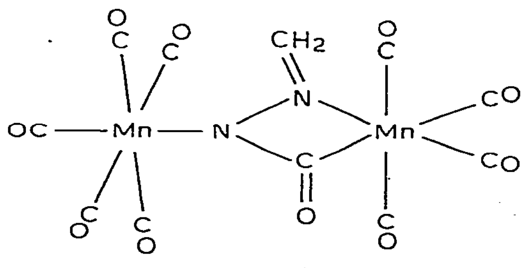
VII. METAL COMPLEXES WITH GROUP VA AND VIA LIGANDS

The general order of coverage in this section is to be nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium ligands. Most complexes with ligands serving simply as two electron donors (phosphine complexes, etc.) are not included, having been covered in other sections as derivatives of metal carbonyl species.

The three compounds $Mn(C_5H_5)(CO)_2(\mu\text{-}N_2)Cr(CO)_5$, $Mn(C_5H_5)(CO)_2(\mu\text{-}N_2H_2)Cr(CO)_5$ and $Mn(C_5H_5)(CO)_2(\mu\text{-}N_2H_4)Cr(CO)_5$ were prepared. The first and third compounds were made from $Mn(C_5H_5)(CO)_2L$ (L = N_2, N_2H_4) and $Cr(CO)_5THF$; the diimine compound was formed upon oxidation of the dinitrogen complex (ref. 137). A crystal structure study was carried out on the N_2 bridged compound $[Mn(C_5H_4Me)(CO)_2]_2N_2$. A very short N-N bond length was noted (ref. 138). Other x-ray crystallographic studies on the compounds $Mn_3(CO)_{12}(CH_3N_2)$ (XXIV) and $Mn_2(CO)_{10}(CH_2N_2)$ (XXV) were reported (ref. 139). Manganese pentacarbonyl bromide reacted with $PhN{=}NSiMe_3$ to form $Mn_2(CO)_8(\mu\text{-}N_2Ph)_2$; this dinuclear complex was cleaved in a a reaction with triphenylphosphine to give $Mn(CO)_3(PPh_3)N_2Ph$ and $Mn(CO)_2(PPh_3)_2$-N_2Ph; in these complexes the phenyldiazonium ligand functions as a three electron donor (ref. 140).



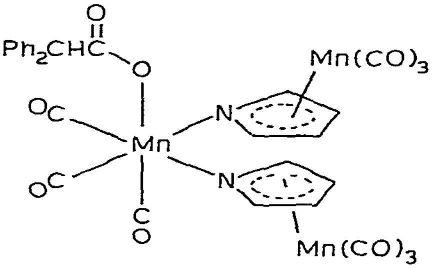
(XXIV)



(XXV)

Various pyrazolyl containing compounds have been studied as ligands. The formation of $Re(CO)_3[(3,5\text{-}Me_2C_3N_2H)_3BH]$ and $Re(CO)_3[(3,5\text{-}Me_2C_3N_2H)_3BH]Cl$ from $[Re(CO)_4Cl]_2$ and $K[BH(3,5\text{-}Me_2C_3N_2H)_3]$ was noted earlier (ref. 37), as was a crystal structure study on $Re(CO)_3[(3,5\text{-}Me_2C_3N_2H)_2PPh]Br$ (ref. 50). The use of $[GaMe_2(pz)OCH_2CH_2NMe_2]^-$ (pz = various 3,5-substituted pyrazolyl groups) as a ligand (=L) was reported, and various compounds $Mn(CO)_3(L)$ were prepared (ref. 141).

Sellmann and Thallmair have described reactions of ammonia complexes with acetone. The compound $Mn(C_5H_5)(CO)_2(NH{=}CMe_2)$ was among the products of one such reaction (ref. 142). A complicated reaction occurred between $Mn(C_4H_4N)(CO)_3$ and diphenylketene, giving the product XXVI, characterized by an x-ray crystallographic study (ref. 143). A compound $(Bu_4N)_3[Re_2(NCS)_{10}]$ was identified in another crystal structure study; this compound had been incorrectly characterized previously as a carbonyl containing compound (ref. 144).

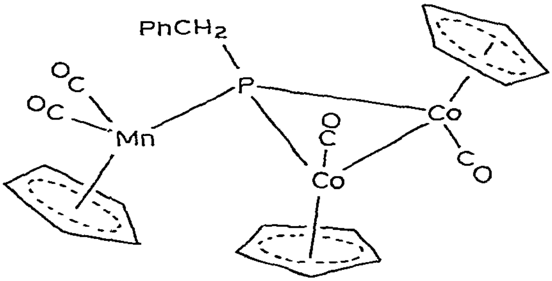


(XXVI)

Mentioned earlier in this review were complexes of the η^2-dicyanoketenimine ligand (ref. 86) and complexes involving the $NOBu^t$ spin trap reagent (ref. 20). Also covered earlier was a paper describing the complexes $Mn(CO)_n[(Ph_2PCH_2)_3CMe]X$ (n = 2, 3) in which X is a halide ion or a pseudohalide, NCO^- or N_3^- (ref. 15).

Various studies on phospholyl complexes were found in this year's literature. Reactions of C_4Ph_4PCl with $Na[Mn(CO)_5]$ or $Na[Re(CO)_5]$ produced $M(CO)_5PC_4Ph_4$ in poor yield, along with $M_2(CO)_{10}$ and $(C_4Ph_4P)_2$; analogous arsenic and antimony derivatives were also prepared. Heating the phosphido and arsenido complexes at 70°C gave dimeric bridged species $M_2(CO)_8(\mu\text{-}PC_4Ph_4)_2$ (ref. 145). Higher temperature (140°C) converted these dimers to the tricarbonyl complexes, $Mn(C_4Ph_4X)(CO)_3$ (X = P, As). The arsolyl compound and NO^+ gave $[Mn(C_4Ph_4As)(NO)(CO)_2]^+$ (ref. 146). Acylation of $Mn(3,4\text{-}R_2C_4H_2P)(CO)_3$ has been shown to occur at the 2-position of the coordinated phospholyl ligand (ref. 147). An ^1H nmr study of $Mn(C_4H_4P)(CO)_3$ oriented in the nematic phase of a liquid crystal was published (ref. 148).

Dehalogenation of $Mn(C_5H_5)(CO)_2(PhCH_2PCl_2)$ occurred when this compound was reacted with $Co(C_5H_5)(CO)_2$. The product of this reaction, XXVII, was characterized in a crystal structure study (ref. 149). Other polynuclear metal systems include $Pt[PPh_2Mn(CO)_4]_2$ (ref. 116), $Mn(C_5H_5)(CO)_2Fe_2(CO)_6PPh$ and $Mn(C_5H_5)(CO)_2Fe_2(CO)_5(L)PPh$ (ref. 117). The reaction of $[Mn(CO)_4(R_2PS)]_2$ (R = Me, Ph) with $R'C{\equiv}CR'$ (R = COOMe, COOEt) (ref. 97), and the reactions of various $[Re(CO)_3(L)(R_2PO_2)]_2$ compounds with liquid ammonia (ref. 12) are noted. In the latter paper there is included a crystal structure study on $[Re(CO)_3(THF)(Me_2PO_2)]_2$.



(XXVII)

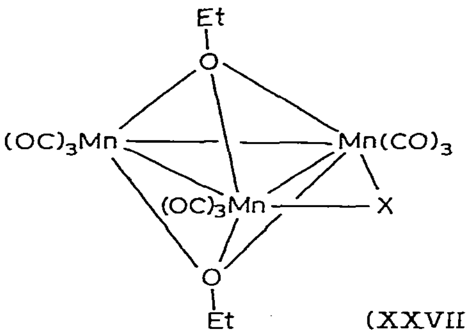
Vahrenkamp and Langenbach described the results of an extensive study on Me_2As bridged iron-manganese complexes. The precursor for this work was $(CO)_4FeAsMe_2Mn(CO)_5$ which lost CO to give the metal-metal bonded species $(CO)_4FeAsMe_2Mn(CO)_4$. Then, upon addition of a ligand (PMe_3 or $P(OMe)_3$) the metal-metal bond was cleaved and $(CO)_4FeAsMe_2Mn(CO)_4L$ formed as the cis and/or trans isomer. This process could be repeated twice again, so that up to three ligands L may be added and four carbonyls displaced. In all, 41 new compounds were described in this study (ref. 118).

The redox chemistry of $Mn(C_5H_5)(CO)_2AsMe_2M(CO)_4$ (M = Mn, Re) and other dimethylarsino-bridged species has been studied (ref. 119, 120). The use of $Mn(C_5H_5)(CO)_2AsMe_2Co(CO)_3$ as a catalyst for norbornadiene dimerization was noted (ref. 121).

The reaction of $MnRe(CO)_{10}$ and $As_2(CF_3)_4$ gave $MnRe(CO)_8(As(CF_3)_2)_2$. Similar reactions between $MnCo(CO)_9$ and this compound, and between $MnCo(CO)_9$ and $P_2(CF_3)_4$, $S_2(CF_3)_2$, $Se_2(CF_3)_2$, and with several other reactants are noted; products include $MnCo(CO)_7(X(CF_3)_2)_2$ (X = P, As) (ref. 122).

Complexes with oxygen ligands included $Mn(CO)_5OClO_3$ (ref. 11), $Mn(CO)_5OSO_2CF_3$ (ref. 8); $\overline{Mn(CO)_4OCRCRO}$ (ref. 18), $Mn(CO)_4(L)O_2$ (L = CO, PBu_3, $P(OEt)_3$) (ref. 19) and a number of complexes derived from $Mn(CO)_3(dpe)CCl{=}C(CN)_2$ and phosphites (ref. 84, 85). Various reactions of $[Mn(CO)_3OEt]_3$ have been described including: 1) the reaction with OPh^- to give $Mn_3(CO)_9(OEt)_2(OPh)$; 2) reaction with SPh^-

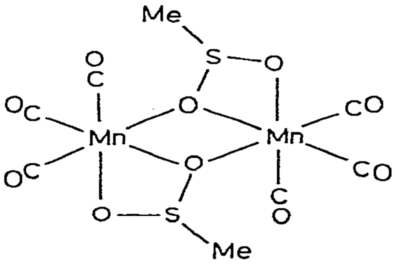
to give $[Mn(CO)_3SPh]_4$; and 3) the substitution of one CO by $PPhMe_2$ (ref. 150). Reactions of $[Mn(CO)_3OEt]_3$ with BX_3 (X = F, Cl, Br, I) or with HCl or HF gave $Mn_3(CO)_9(OEt)_2X$. A crystal structure study on the compounds with X = F and I showed the following structure, XXVIII (ref. 151).



(XXVIII)

The product of the reaction between cesium dithiooxalate and $Mn(CO)_5Br$ was characterized crystallographically as $(CO)_5MnSCOCOSMn(CO)_5$ (ref. 152). Preliminary x-ray data identified the structure of the compound, $Re_2(CO)_8$-$[\mu\text{-}SPMe_2Mn(CO)_2C_5H_5]_2$, obtained from $Na[Mn(C_5H_5)(CO)_2PMe_2S]$ and $Re(CO)_5Cl$ (ref. 153). Another crystal structure study was directed to the anionic complex $[(CO)_3Re(\mu\text{-}SCOPh)_3Re(CO)_3]^-$ isolated as the Cs^+ salt. This compound and the analogous manganese species were prepared in a reaction of $M(CO)_5Br$ and Cs(SCOPh) (ref. 154).

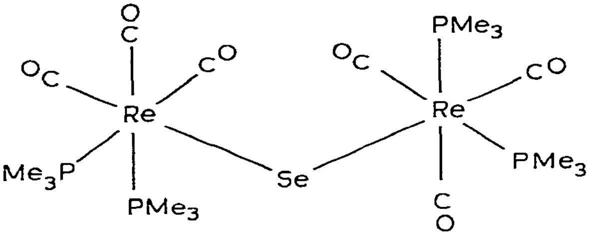
The reaction of $Mn_2(CO)_5(PMe_3)_2(SSnMe_3)_2$ with iodine gave $Mn_2(CO)_5(PMe_3)_2S_2$. Oxidation of $Mn_2(CO)_8(SSnMe_3)_2$ gave $Mn_4(CO)_{15}S_4$; the structure of this compound was identified by x-ray crystallography (ref. 155). The product of the reaction of $Mn(CO)_4(L)H$ (L = CO, PPh_3) and $CH_2{=}SO_2$ is $Mn(CO)_4(L)SO_2CH_3$. This compound was decarbonylated to give XXIX (ref. 58).



(XXIX)

Decarbonylation of $Re(CO)_4X_2CNMe_2$ (X = S, Se) compounds gave $[Re(CO)_3X_2CNMe_2]_2$, whereas the same reaction of $Re(CO)_5XCONMe_2$ gave a mixture of $[Re(CO)_4XCONMe_2]_2$ and $[Re(CO)_3XCONMe_2]_2$ (ref. 156).

The reaction of Me_3P with $[M(CO)_4SeX]_2$ (M = Mn, Re; X = H, $SnMe_3$) gave $[M(CO)_3(L)SeX]_2$ and/or $M(CO)_3(L)_2SeX$. The latter product degrades to $(Me_3Sn)_2Se$ and $[Re(CO)_3L_2]_2Se$, whose structure, XXX, was determined by x-ray diffraction methods (ref. 157).



(XXX)

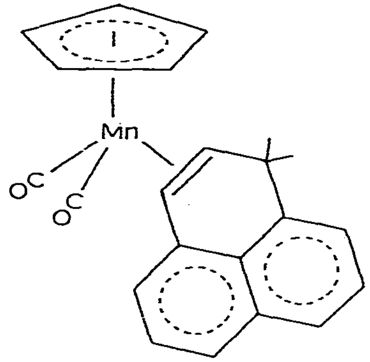
VIII. HYDROCARBON METAL COMPLEXES $(M(C_5H_5)(CO)_{3-n}L_n$, $[M(C_6H_6)(CO)_3]^+$, olefin, allyl complexes, and others)

Further interest in manganocene chemistry could be identified during the last year. Perhaps the most significant work, in the opinion of this author, is a study on the redox chemistry of $Mn(C_5Me_5)_2$. This compound was shown to be oxidized to a low spin 16e complex $[Mn(C_5Me_5)_2]^+$, by ferrocenium salts. Isolation of the PF_6^- salt was accomplished. Sodium naphthalenide reduced $Mn(C_5Me_5)_2$ to $Na[Mn(C_5Me_5)_2]$ an 18e anion which is isoelectronic with $Fe(C_5Me_5)_2$ (ref. 158).

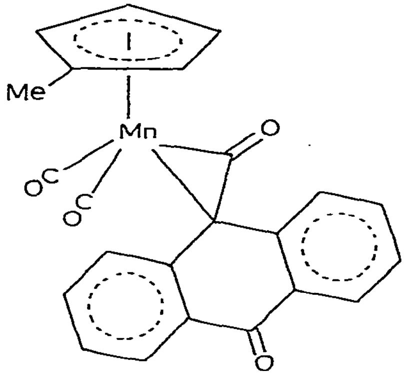
An x-ray diffraction study was used to establish the structure of $Mn(C_5Me_5)_2$, a low spin complex (ref. 159). An electron diffraction study was carried out on $Mn(C_5H_5)_2$ (ref. 160). The manganese carbon distance in this high spin complex was found to be 2.380(6)Å, less than the value previously found for $Mn(C_5H_4Me)_2$. A report on the thermal decomposition of the first row metallocenes established an order of stability $Mn(C_5H_5)_2 > Cr(C_5H_5)_2 > V(C_5H_5)_2$ (ref. 161). Bomb calorimetry was used to determine ΔH°_f for $Mn(C_5H_5)_2$; a value of -198 ± 2 kJ/mole was measured (ref. 162).

The first example of a complex of the hydrocarbon phenalene was reported (ref. 163). This is the compound $Mn(C_5H_4Me)(CO)_2(C_{13}H_{10})$, essentially an olefin complex XXXI. This compound was prepared by irradiation of $Mn(C_5H_4Me)(CO)_3$ and the hydrocarbon in hexane.

Compound XXXII was the product obtained when the diazoanthrone was photolyzed in the presence of a mixture $Mn(C_5H_4Me)(CO)_3$ and $Mn(C_5H_5)(CO)_2(THF)$. Its structure was determined crystallographically. Apparently the diazo compound loses its nitrogen to give a carbene which added to a coordinated carbonyl in the manganese containing precursor (ref. 164).

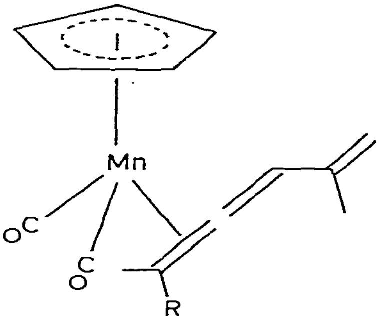


(XXXI)



(XXXII)

Protonation of the acetylene complex $Mn(C_5H_4Me)(CO)_2(MeOCOC{\equiv}CCH{=}CMe_2)$ occurred at the acetylenic ligand with a concurrent rearrangement generating an allene complex, XXXIII. The allene can be released intact by Ce^{4+} oxidation; alternatively, photolysis of the complex caused rearrangement and release of cis-$MeOCOCH_2CH{=}CH$-$CMe{=}CH_2$ (ref. 165).



(XXXIII)

The preparation and characterization of $[Mn(C_5H_4Me)(CO)_2]_2(\mu\text{-}MeC{\equiv}C\text{-}C{\equiv}CMe)$ has been reported (ref. 166). Discussed earlier in this review was the conversion of $Mn(C_5H_5)(CO)_2(HC{\equiv}CCOPh)$ to $Mn(C_5H_5)(CO)_2$(cis-$CHX{=}CHCOPh$), (X = Cl, OCOMe) (ref. 111). Also mentioned in an earlier part of this article were the olefin complex $[Re(C_5H_5)_2(C_2H_4)]^+$ (ref. 60) and the methylcyclopentadiene (diolefin) complex $Re(C_5H_5)(C_5H_5Me)Me_2$ (ref. 61).

The synthesis of various allylmanganese carbonyls by phase transfer catalysis methods was a significant new development (ref. 167). Synthesis of $Re(\eta^3\text{-}C_3H_5)(CO)_4$ and study of its infrared and nmr spectra and its mass spectrum are noted (ref. 80). Rearrangement of $Mn(CO)_5CH_2C{\equiv}C(CH_2)_nCRR'OH$ occurred on alumina to give an allyl compound (ref. 91).

Rate studies on the reaction of $[Mn(C_6H_5X)(CO)_3]^+$ with excess OMe^- showed a pseudo-first order kinetics. The rates were greater for X = F^- than for X = Cl^-, and were accelerated by THF and dioxane. It was possible to detect an intermediate in this reaction, in which OMe^- had added to the carbon containing the X^- group (ref. 168).

An improved preparation of $[Mn(C_6H_6)(CO)_3]^+$ was described. Reactions with RLi to give Mn(exo-RC_6H_6)$(CO)_3$ and the thermal rearrangement of these compounds have been studied (ref. 169).

Rate constants and the equilibrium constant for the reactions shown below (Eq. 11) were measured (M = Mn, Re):

$$[M(C_6H_6)(CO)_3]^+ + Bu_3P \underset{k-1}{\overset{k_1}{\rightleftarrows}} M(\underline{exo}\text{-}Bu_3PC_6H_6)(CO)_3 \qquad \text{Eq. 11}$$

Photolysis of this mixture caused CO loss and formation of $[Mn(C_6H_6)(CO)_2(PBu_3)]^+$ (ref. 13).

Almost all of the work pertaining to derivatives of $Mn(C_5H_5)(CO)_3$ has been cited earlier in this review since the significant chemistry dealt with the substituted ligands. Because of this a detailed review of this area is not warranted; it should be sufficient to merely indicate the general coverage and assign pertinent references. The following references are noted: (ref. 44, 45, 73) on various nitrosyl complexes; derivatives of $Re(C_5H_5)_2$ (ref. 60, 61); work on the formyl-rhenium complexes and related areas involving reduction of coordinated CO (ref. 63-68); silyl manganese species (ref. 62, 83); carbene and carbyne complexes including bridging carbene and alkylidene species (ref. 102, 105, 108-110, 112-115); Lewis acid-base adducts of $HgCl_2$ and SnX_4 (ref. 126, 132, 133); complexes with unusual nitrogen, phosphorus and sulfur ligands (ref. 137, 138, 142, 149, 153); and complexes with hydrocarbon ligands (ref. 163-166). In addition, there were papers dealing with the ^{13}C nmr spectra of $Re(C_5H_5)(CO)_2CX$ (X = O, S, Se) (ref. 106) and on H^+/D^+ exchange in $Mn(C_5H_5)(CO)_2(CS)$ (ref. 107), and ^{17} oxygen nmr spectra on $Mn(C_5H_5)(CO)_2(L)$, for L = CO, CS, and PPh_3 (ref. 32, 33).

Specific mention should be made at this point to Inorganic Syntheses preparations of $Mn(C_5H_5)(CO)_2(CSe)$, $Mn(C_5H_5)(dpe)(CS)$ and $Mn(C_5H_5)(CO)(PPh_3)(CS)$ (ref. 34). The preparation of $Mn(C_5Me_5)(CO)_3$ was accomplished from C_5Me_5H and $Mn_2(CO)_{10}$ (ref. 170). A crystal structure study was carried out on $Mn(1\text{-}BrC_9H_6)(CO)_3$ (ref. 171).

Isocyanide derivatives, $Mn(C_5H_5)(CO)_2CNR$, for R = COPh (ref. 172) and for R = PEt_2, PPh_2, $P(OEt)_2$ and $AsPh_2$ (ref. 173) were prepared by reactions of $K[Mn(C_5H_5)(CO)_2(CN)]$ and RX. The isocyanophosphane compound was reacted further with $Mn(C_5H_5)(CO)_2(THF)$ to give $Mn(C_5H_5)(CO)_2(CNPR_2)Mn(C_5H_5)(CO)_2$, in which the $CNPR_2$ bridged the two metal groups. A reaction of $Mn(CO)_5Br$ and $Me_3SnC_5H_4CH_2CH_2PPh_2$ gave $Mn(C_5H_4CH_2CH_2PPh_2)(CO)_3$. Photolysis at 20° for 10 min converted this to

$Mn(C_5H_4CH_2CH_2PPh_2)(CO)_2$; in this compound the phosphine group on the side chain of the cyclopentadienyl ligand is coordinated to the metal (ref. 174).

Formation of α-carbonium ion complexes, $Mn(C_5H_4CRR^+)(CO)(dpe)$ occurred when the corresponding alcohol was dissolved in CF_3COOH (ref. 175). The phosphine ligands, being good donors, promote this reaction. A crystal structure study was carried out on $[(CO)_3MnC_5H_4]_2SnCl_2$ (ref. 176). Molecular orbital calculations on various N_2 complexes including $Mn(C_5H_5)(CO)_2(N_2)$ were reported (ref. 177). Mass spectral data for $(CO)_3MnC_5H_4COCH{=}CHR$ ($R = C_5H_4Mn(CO)_3$, Ph) were published (ref. 178).

No effort was made in this review to abstract all the references for the organic chemistry at the cyclopentadienyl group in $Mn(C_5H_5)(CO)_3$. However a few significant references were picked up while surveying this area. This includes the syntheses of the mixed metal complexes $M(C_5H_4COM'(CO)_5)(CO)_3$ (M = Mn, Re) and $M(C_5H_4M'(CO)_5)(CO)_3$ (ref. 76) and the formation of $(CO)_3MnC_5H_4HgPt(PPh_3)_2C_5H_4Mn(CO)_3$ from $[(CO)_3MnC_5H_4]_2Hg$ and $Pt(PPh_3)_3$ (ref. 179). The product in this second reaction lost mercury at 20° to give $[(CO)_3MnC_5H_4]_2Pt(PPh_3)_2$. Lithiation (butyllithium) of $Mn(C_5H_4CH_2NMe_2)(CO)_3$ was shown to occur specifically at the 2-position; deuteration of the lithio compound gave $Mn(1\text{-}CH_2NMe_2\text{-}2\text{-}DC_5H_3)(CO)_3$. The sequence could be repeated to obtain the dideuterio compound, labeled only at the 2 and 5 positions. Lithiation adjacent to the CH_2NMe_2 group only occurred because of the ability to stabilize the product by intramolecular coordination of the nitrogen group (ref. 180).

The compound $Mn(1\text{-}CH_2NMe_2\text{-}2\text{-}CHOC_5H_3)(CO)_3$ was resolved into enantiomers. This species and glycylglycine gave copper(II) complexes which were alkylated with CH_3CHO; hydrolysis then gave threonine in 92-98% optical purity (ref. 181).

IX. VARIOUS ISOCYANIDE AND NITROSYL COMPLEXES ($[M(CNR)_6]^+$, $[M(C_5H_5)(NO)(CO)_2]^+$, others)

The only reference in this area which was not abstracted earlier is to the compound $NBu_4[Re(CNMe)Cl_5]$ (ref. 182). This green crystalline compound was prepared from $(NBu_4)_2Re_2Cl_8$ and MeNC, and its structure was determined by x-ray methods. Other references to isocyanide complexes of metals in this group include: a) synthesis of $Re(CNBu\}_5Cl$ (ref.43); b) synthesis and structural study on $Re(CNtol)_4Br_2$ (ref. 41); c) synthesis of $Mn_2(CO)_9CNR$ (R = Et,MeSi, Me_3Sn, Ph_2P, MeCO) and $Mn_2(CO)_8(CNEt)_2$ (ref. 28); d) syntheses of $Mn(C_5H_5)(CO)_2(CNR)$ ($R = PEt_2$, PPh_2, $P(OEt)_2$, $AsPh_2$ COPh) (ref. 172, 173), e) synthesis of $[Mn(C_5H_4Me)(NO)(CNEt)(L)]^+$ (L = CNEt, PPh_3) (ref. 45); and f) the synthesis of $Re(dpe)_2(CNR)Cl$ (R = Me, Bu^t) and its reaction with acid (ref. 103). In addition the preparations of $[Mn(CO)_{6-n}(CNPh)_n]^+$ were reported; included were specific syntheses of the *mer* and *fac* isomers for n = 3 and the *cis* and *trans* isomers for n = 4 (ref. 9). The related complexes $[Mn(CO)_{5-n}(CNPh)_n(CNMe)]PF_6$ and $Mn(dpe)(CO)_{4-n}(CNMe)_n]PF_6$ were prepared also (ref. 10). Electrochemical oxidations of these series of compounds were reported.

Extensive chemistry originating with $[Re(C_5H_5)(NO)(CO)_2]^+$ was discussed in detail earlier in Section V (ref. 63-69). Other nitrosyl compounds mentioned were $Mn(C_5H_5)(NO)(CO)(CONH_2)$ (ref. 73) and $Mn(C_5H_5)(NO)(CO)I$ and products derived from this species (ref. 44-45).

X. STRUCTURAL STUDIES

Compounds whose structures have been determined by x-ray crystallography or by other methods are listed: $[Re(CO)_3(THF)(Me_2PO)]_2$ (ref. 12); $Re(CNtol^P)_4Br_3$ (ref. 41); *fac*-$Re(CO)_3(Me_2NCH_2CH_2NMe_2)Br$ (ref. 49); *fac*-$Re(CO)_3[PPh(3,5\text{-}Me_2C_3N_2H)_2]Br$ (ref. 50); $Mn_2(CO)_6Br_2(Ph_2PPPh_2)$ (ref. 51); $Re_2(CO)_6Br_2(PhSeSePh)$ (ref. 52); $NEt_4[H_4Re_4(CO)_{15}I]$ (ref. 53), $(C_5H_5)(CO)Mo(\mu\text{-}(\eta^1\!:\!\eta^5\text{-}C_5H_4))Mn(CO)_4$ (ref. 56); $Re(C_5H_5)(NO)(PPh_3)CHO$ (ref. 66); $Mn(CO)_4(COMe)AlBr_3$ (ref. 71); $Mn(C_5H_5)(NO)(CO)CONH_2$ (ref. 73); $\overline{Mn(CO)_4(CH_2)_3P}Ph_2$ (ref. 79) $Re_2Me_2(O_2CMe)_4$ and $Re_2Me_2(O_2CMe)_2Cl_2\cdot dmso$ (ref. 96); $Mn(CO)_3[Me_2PS(RC{\equiv}CR)_2]$, R = COOMe (ref. 97); *trans*-$Mn(CO)_4(PPh_3)C(CF_3){=}C{=}C(CF_3)_2$ (ref. 98); $Sn(TPP)[Re(CO)_3C]_2$ (ref. 104); $Mn_2(C_5H_5)(CO)_6CtolCO\cdot 0.5\ Et_2O$ (ref. 108); $[Mn(C_5H_5)(CO)_2\text{-}\mu\text{-}Ctol\text{-}Pt(PMe_3)_2]BF_4$ (ref. 109); $Mn_2(C_5H_5)_2(CO)_4(\mu\text{-}C{=}CH_2)$ (ref. 112); $Mn_2(C_5H_4Me)_2(CO)_4(\mu\text{-}CH_2)$ (ref. 114); red and yellow isomers of $Mn(CO)_4(\mu\text{-}\overline{C{=}CHCH_2CH_2O})Pt(PMe_3)_2$ (ref. 110); $Pt[(\mu\text{-}PPh_2)Mn(CO)_4]_2$ (ref. 116); $Re(C_5H_5)(CO)(\mu\text{-}(CO)_2)Mo(C_5H_5)_2$ (ref. 60); $[Re(CO)_5]_4In_2(\mu\text{-}X)_2$ (X = Cl, Br) (ref. 127); $[Mn(C_5H_4Me)(CO)_2]_2N_2$ (ref.138); $Mn_3(CO)_{12}(CH_3N_2)$ and $Mn_2(CO)_{10}(CH_2N_2)$ (ref. 139); $Mn(CO)_3[(NC_4H_4)Mn(CO)_3]_2OCOCHPh_2$ (ref. 143); $(Bu_4N)_3[Re_2(NCS)_{10}]$ (ref. 144); $Mn(C_5H_5)(CO)_2(Co(C_5H_5)CO)_2PCH_2Ph$ (ref. 149); $Mn_3(CO)_9(OEt)_2I$ and $Mn_3(CO)_9(OEt)_2F$ (ref. 151); $Mn(CO)_5SCOCOSMn(CO)_5$ (ref. 152); $Re_2(CO)_8[\mu\text{-}SPMe_2\text{-}Mn(CO)_2C_5H_5]_2$ (ref. 153); $Cs[(CO)_3Re(\mu\text{-}SCOPh)Re(CO)_3]$ (ref. 154); $Mn_4(CO)_{15}S_4$ (ref. 155); $[Re(CO)_3(PMe_3)_2]_2Se$ (ref. 157); $Mn(C_5Me_5)_2$ (ref. 159); $Mn(C_5H_5)_2$ electron diffraction (ref. 160); $Mn(C_5H_4Me)(CO)_2(C_{15}H_8O_2)$ (ref. 164); $Mn(1\text{-}BrC_9H_6)(CO)_3$ (ref. 171); $[(CO)_3MnC_5H_4]_2SnCl_2$ (ref. 176).

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