MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1978*

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CONTENTS

I. Introduction 129

II. Metal Carbonyls and Derivatives Obtained by Carbonyl Substitution ($[M(CO)_{5-n}L_n]^-$, $M_2(CO)_{10-n}L_n$, $[M(CO)_{6-n}L_n]^+$) 130

III. Metal Carbonyl Halides and Derivatives ($M(CO)_{5-n}L_nX$; $M(C_5H_5)(CO)_2X_2$) 134

IV. Metal Carbonyl Hydrides ($M(CO)_{5-n}L_nH$, polynuclear hydrides) 137

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) 139

VI. Metal Carbonyl Derivatives of Metals and Metalloids (Derivatives of electropositive metals, and of Group IIIA and IVA elements) 143

VII. Metal Complexes of Group VA and VIA Ligands 145

VIII. Hydrocarbon Metal Complexes ($M(C_5H_5)(CO)_3$, $[M(C_6H_6)(CO)_3]^+$, $M(C_6H_7)(CO)_3$, olefin, allyl complexes, others) 149

IX. Various Isocyanide and Nitrosyl Compounds ($[M(CNR)_6]^+$, $M(CO)_{4-n}L_nNO$, $M(NO)_3L$, $[M(C_5H_5)(CO)_2NO]^+$) 154

X. Structural Studies 154

I. INTRODUCTION

There are over 180 articles cited in this year's Annual Surveys article on Group VIIB organometallic compounds. This number is virtually the same as last year; see the 1977 Annual Surveys (ref. 1). Papers from J. Organometal. Chem. are still in much the largest number; in all, there are 57 references from this journal. Abstracted for the first time are a number of articles from Inorganic Syntheses. The appearance of some preparations of organometallic

*Manganese, Technetium and Rhenium; Annual Survey covering the year 1977 see J. Organometal. Chem., Vol. 176(1979)p. 307-338.

compounds of manganese and rhenium attests to their significance. Perhaps this also suggests a degree of maturity in this area of chemistry.

Some very good, substantial work is abstracted in this review. However there appears to be few developments that have opened up radically new areas of study; instead much of the published work seems, to this author, to serve to consolidate existing projects. In addition, many papers have appeared whose content has already been seen earlier in communication form.

The organization of this article follows previously established lines, with extensive cross-listing as necessary to provide easiest access to referenced material.

II. METAL CARBONYLS AND DERIVATIVES OBTAINED BY CARBONYL SUBSTITUTION ($[M(CO)_{5-n}L_n]^-$, $M_2(CO)_{10-n}L_n$, $[M(CO)_{6-n}L_n]^+$)

Further studies of reactions of the dinuclear carbonyls have appeared which implicate metal-metal bond cleavage as the first step in the reaction. This author is particularly impressed by the careful work of Kidd and Brown (ref. 2) on photolyses of $Mn_2(CO)_{10}$ in the presence of PBu_3 or $P(OEt)_3$ in heptane. The primary mechanistic scheme presented for this system is:

$$M_2(CO)_{10} \rightleftharpoons 2M(CO)_5$$

$$M(CO)_5 \rightleftharpoons M(CO)_4 + CO$$

$$M(CO)_4 + L \rightleftharpoons M(CO)_4L$$

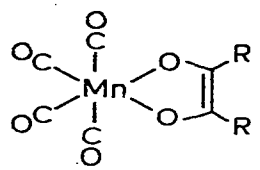
$$2M(CO)_4L \rightleftharpoons M_2(CO)_8L_2$$

Strong evidence is presented supporting the contention that a 17e species $Mn(CO)_5$ is very labile. The photosubstitution of L in $Mn_2(CO)_8L_2$ by CO was also studied. Kidd's thesis which contains this work, is noted (ref. 3).

Poë et al. report data on $\sigma \rightarrow \sigma^*$ transitions for twelve $Mn_2(CO)_8L_2$ compounds, the ligands including phosphines, phosphites, phosphinous, and phosphinic esters (ref. 4). Rates of decomposition of some of these compounds in decalin in the presence of molecular oxygen are measured; the activation enthalpies correlate with energies of the $\sigma \rightarrow \sigma^*$ transitions implying that metal-metal bond breaking is the rate controlling step. Metal-metal bond strengths increase with increasing σ donor character and π acidity of the ligands, but decrease with the ligand's steric bulk (ref. 5). The reaction of $Mn_2(CO)_8(PPh_3)_2$ with $P(OPh)_3$ to give $Mn_2(CO)_8(PPh_3)P(OPh)_3$ is also reported to occur via initial cleavage of the dimanganese species (ref. 6).

Photolysis of $Mn_2(CO)_{10}$ in the presence of 1,2-dicarbonyl compounds, Eq. 1, gives radical species $\overline{Mn(CO)_4OCR{=}CRO}$ characterized by their esr spectra

$$Mn_2(CO)_{10} + R\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}R \xrightarrow{h\nu}$$



EQ.1

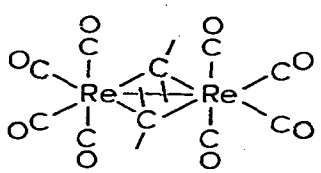
(ref. 7). The use of the spin-trap reagent t-BuNO to stabilize various $Mn(CO)_4L$ species and $Re(CO)_5$ as $Mn(CO)_4LNOR$ and $Re(CO)_5NOR$ is further reported in a thesis (ref. 8). Wojcicki et al. (ref. 9) report that pulsed radiolysis of $Mn_2(CO)_{10}$ and $Mn(CO)_5X$ (X = I, Br) compounds gives $Mn(CO)_5$ radicals. The photodissociation of $Re_2(CO)_{10}$ in a molecular beam experiment is described (ref. 10).

Photocalorimetry was used to study the energetics of the reaction of $Re_2(CO)_{10}$ and iodine. The value of ΔH°_{298} for this reaction is −52 Kcal (ref. 11).

The synthesis and characterization of several carbene derivatives $Re_2(CO)_9L$ (L = CROEt, R = Me, Ph) and $M_2(CO)_9(CMeNHMe)$ (M = Mn, Re) was accomplished by standard routes, Eq. 2, (ref. 12). When $Re_2(CO)_9(CROMe)$ (R = Ph, tol) is

$$Re_2(CO)_{10} \xrightarrow{LiR} Li[Re_2(CO)_9COR] \xrightarrow{Me_3O^+} Re_2(CO)_9CROMe \quad \text{EQ.2}$$

treated with additional LiAr followed by $[Me_3O]^+$ the products $Re_2(CO)_8(CArOMe)_2$ are formed (ref. 13). Interestingly, these compounds do not have the expected structures but are instead species in which the carbene ligands occupy bridging positions between the two metals. A structure was determined for the compound $Re_2(CO)_8(CtolOMe)_2$ by x-ray crystallography; this is shown below (I). The Re-Re distance in this compound is a short 2.810(3)Å.



(I)

A search for stable metal formyl complexes has intensified in the last few years due to the information such species might contribute toward understanding of the metal catalyzed reduction of CO by hydrogen. Two papers appeared back-to-back in J. Am. Chem. Soc. describing the synthesis and some chemistry of $[Re_2(CO)_9CHO]^-$. The first (ref. 14) describes the preparation of this anion in THF by a hydride transfer reaction between $[Fe(CO)_3(P(OPh)_3)CHO]^-$ and $Re_2(CO)_{10}$. The anion is isolated as a stable tetraethylammonium salt. Its geometry is cis according to ^{13}C nmr. Photolysis causes CO loss and formation

References p. 155

of $Et_4N[Re_2(CO)_9H]$ which can also be made from $Re_2(CO)_{10}$ and $K[HB(Oi\text{-}Pr)_3]$. The second paper (ref. 15) on $[Re_2(CO)_9CHO]^-$ describes its preparation from $Re_2(CO)_{10}$ and $Li[BHEt_3]$. Reactions of $[Re_2(CO)_9CHO]^-$ with acids (-50°, to give H_2, and $Re_2(CO)_{10}$) are noted. Also observed is a "transformylation" reaction with $Fe(CO)_5$, to give $Re_2(CO)_{10}$ and $[Fe(CO)_4CHO]^-$, and the use of this compound as a reducing agent to give $PhCH_2OH$ from PhCHO. Most intriguing is the further reaction of $[Re_2(CO)_9CHO]^-$ with $K[B(s\text{-}Bu)_3H]$ to give $[Re_2(CO)_9]^{2-}$ and formaldehyde. This result brings the research a step closer to its ultimate goal.

Several papers describe substitution reactions with the $M_2(CO)_{10}$ dimers. The use of a trialkylamine oxide facilitates substitution in manganese and rhenium decacarbonyls, and both mono- and disubstituted products are obtained using PPh_3, pyridine, and picoline (ref. 16). The preparation of $Mn_2(CO)_{10-x}(CNMe)_x$ (x = 1-4) from a direct reaction of $Mn_2(CO)_{10}$ and the ligand is reported in a thesis (ref. 17). A full paper on the crystal structure of $Mn_2(CO)_4(CN\text{-}p\text{-}tol)(dpm)_2$ (dpm = 1,2-bisdiphenylphosphinomethane) has appeared (ref. 18). The reactions of $Na[N(SiMe_3)_2]$ with $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ to give the anions $[M_2(CO)_9CN]^-$ (M = Mn, Re) are noted (ref. 19).

Photolysis of $Mn_2(CO)_{10}$ with NH_3 in pentane gives $[fac\text{-}Mn(CO)_3(NH_3)_3]Mn(CO)_5$; the reaction with MeCN gives an analogous product (ref. 20).

$$Mn_2(CO)_{10} + L \xrightarrow{h\nu} [Mn(CO)_3L_3]Mn(CO)_5 \qquad \text{EQ.3}$$

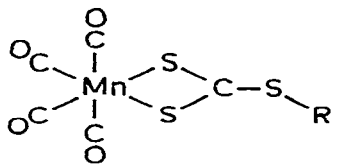
$(L = NH_3, MeCN)$

Addition of H_2O to the ammonia complex yields $[Mn(CO)_3OH]_4$. An x-ray diffraction study on the ammonia complex was carried out. Rhenium carbonyl or $Re(CO)_5Cl$ and water at 200° gives $[Re(CO)_3OH]_2$ (ref. 21). Both the reaction of $Mn_2(CO)_{10}$ and Mn metal in THF and the photolysis of $Mn_2(CO)_{10}$ in THF give $[MnL_{5-6}][Mn(CO)_5]_2$ (ref. 22). The reaction of $Mn_2(CO)_{10}$ and $GeBr_2$ gives $MnBr_2 + GeO_2$ (ref. 23). This is in contrast to reaction of $GeBr_2$ with several other dimetallic species for which insertion of $GeBr_2$ into the metal-metal bond is seen.

The reaction of $Re(CO)_5Me$ with CO under high pressure was followed using infrared spectroscopy. This gives $Re_2(CO)_{10}$, and not $Re(CO)_5COMe$. In contrast $Mn(CO)_5Me$ and CO gives only $Mn(CO)_5COMe$. When this manganese species is subjected to hydrogen gas under pressure, at 95°C, $Mn_2(CO)_{10}$ and MeCHO form (ref. 24).

A simple procedure for making $K[Mn(CO)_5]$ from $Mn_2(CO)_{10}$ and KH in THF is reported by Shore and coworkers (ref. 25). Photolysis of $PPN[Mn(CO)_5]$ ($PPN = Ph_3PNPPh_3^+$) in THF with added ligands gives $PPN[Mn(CO)_4L]$ L = PPh_3, $P(OMe)_3$, (ref. 26). Photolyses in the presence of Ph_3SiH or Ph_3SnH give $PPN[\underline{cis}\text{-}Mn(CO)_4(H)SiPh_3]$ and $PPN[(cis\text{-}Mn(CO)_4(SnPh_3)_2]$ respectively. Photolysis of pentacarbonylmanganate salts of PPh_4^+ and PPh_3Me^+ produce, respectively, $PhMn(CO)_4(PPh_3)$ and $PhMn(CO)_4(PPh_2Me)$.

When PPN[$Mn(CO)_5$] and CS_2 are reacted in THF for four days the product is PPN[$Mn(CO)_4S_2CS$]. This species can be alkylated with $MeOSO_2F$ or MeI giving $Mn(CO)_4S_2CSMe$ (IIa); with $[PhN_2]BF_4$ one gets the analogous phenyl compound $Mn(CO)_4S_2CSPh$ (IIb). The reaction of PPN[$Mn(CO)_5$] with a mixture of CS_2 and MeI also gives $Mn(CO)_4S_2CSMe$, but in lower yield; a second product of this reaction is $Mn(CO)_4S_2CSMn(CO)_5$ (IIc). A similar product is formed from CS_2, MeI, and PPN[$Re(CO)_5$]. This product can be made in better yield if $Re(CO)_5Br$ is added to a mixture of $[Re(CO)_5]^-$ and CS_2 (ref. 27).



(II)

a) R = Me
b) R = Ph
c) R = $Mn(CO)_5$

A reaction between Na[$M(CO)_5$] (M = Mn, Re) and CO_2 under pressure is said to give Na[$M(CO)_3CO_2$]. Treatment with acid leads to evolution of CO_2, while addition of MeI is said to give methyl acetate (ref. 28).

Cationic manganese carbonyl species, cis-$[Mn(CO)_4(L)(H_2O)]^+$, are reported to be formed from $Mn(CO)_4(L)Me$ (L = several phosphorus ligands) and Ph_3CBF_4 in wet CH_2Cl_2 (ref. 29). Water is rapidly displaced from its coordination to manganese by other ligands such as py, CNBu, CO, PPh_3, H_2S. If the reaction above is run in acetonitrile the product obtained is $[Mn(CO)_4(L)(MeCN)]BF_4$ (Eq. 4).

$$Mn(CO)_4(L)Me + Ph_3CBF_4 \xrightarrow{L'} [Mn(CO)_4(L)(L')]BF_4 \qquad \text{EQ.4}$$

(L = several phosphorus ligands, L' = H_2O, MeCN)

A study of the reaction of $Mn(CO)_5Cl$ and H_2O reports $[Mn(CO)_3(H_2O)_3]Cl$ as the initial product; however, this species could not be isolated. In reactions in benzene, with a low $[H_2O]$ concentration, evidence is seen for $Mn(CO)_4(H_2O)Cl$, $Mn(CO)_3(H_2O)_2Cl$ and $[Mn(CO)_3(H_2O)Cl]_2$ (ref. 30).

Two forms, green and yellow, of $[Re(CO)_6]Re_2F_{11}$ are obtained in the reaction of $Re_2(CO)_{10}$ and ReF_6. This reaction is run in HF at room temperature (ref. 33).

Darensbourg and Froelich report that $[Mn(CO)_4(dpe)]PF_6$ exchanges oxygen in labeled $H_2{}^{18}O$ (ref. 34). There is preferential enrichment in the axial position in this molecule. The reaction is quite slow in the absence of base.

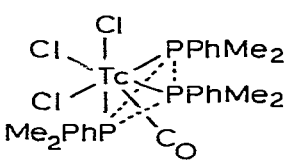
References p. 155

Behrens et al. have studied the solvolysis reactions of $[Re(CO)_6]^+$, $[M(CO)_5L]^+$, and $[M(CO)_4L_2]^+$ (M = Mn, Re; L = PPh_3, PEt_3, and o-phen, bipy for the L_2 complex) with liquid ammonia. These reactions yield the appropriate species $M(CO)_{5-n}(L)_nCONH_2$ (ref. 35). Reaction of $[Re(CO)_3(MeCN)_3]PF_6$ with $C_5H_4PPh_3$ and $C_5H_4SMe_2$ is said to give $[M(C_5H_4X)(CO)_3]^+$ complexes (X = PPh_3, SMe_2 (ref. 36).

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

A new class of rhenium(II) carbonyl halides has been reported by Walton et al. (ref. 37). These species, having the general formula trans-$ReX_2(CO)_2(PR_3)_2$ (X = Cl, Br; R = Et, Pr), are formed from $Re_2X_4(PR_3)_4$ and CO in refluxing EtOH, toluene, or MeCN. However there are complications in these syntheses, due to competing reactions that do not involve CO; for example, refluxing the starting material in ethanol without CO produces $Re_2Cl_5(PR_3)_3$ and $Re(CO)_3(PR_3)_2Cl$. Also the rhenium(II) species are prone to form $Re(CO)_3(PR_3)_2Cl$ and $ReCl_4(PR_3)_2$, in a valence disproportionation reaction.

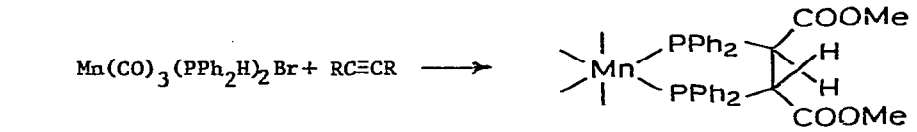
The preparation of $TcCl_3(CO)(PMe_2Ph)_3$ from mer-$TcCl_3(PMe_2Ph)_3$ in refluxing EtOH is reported. A molecular structure was determined by x-ray crystallography for this compound; the overall geometry, III, is that of a monocapped octahedron, with the CO ligand capping the face bounded by the three phosphines (ref. 38).



(III)

The syntheses of three rhenium carbonyl chloride compounds, $Re_2(CO)_8Cl_2$, $Re_2(CO)_5(NO)Cl_3$ and $[Re(CO)_2(NO)Cl_2]_2$, are given in Inorg. Syn. (ref. 39). Carbon tetrachloride reacts with $Mn(CO)_4(L)H$ (L = $P(CF_3)_2OCH_2CH_2Cl$) to give $Mn(CO)_4(L)Cl$ and $Mn_2(CO)_8Cl_2$ (ref. 40). Hydrogen iodide cleaves the ER_n group from $M(CO)_5ER_n$ (M = Mn, Re; ER_n = PR_2, AsR_2, SR, SeR) to yield $Mn(CO)_5I$ (ref. 41). The reaction of $Mn(CO)_5CCl{=}C(CN)_2$ with $Me_2PCH_2CH_2PMe_2$ gives, surprisingly, $Mn(CO)_3(Me_2PCH_2CH_2PMe_2)Cl$; in contrast other ligand reactions give the expected substituted vinylmanganese carbonyl products (ref. 42). The reaction of $Na[Mn(CO)_5]$ and $[Me_2N{=}CHCl]Cl$ produces $Mn(CO)_4(CHNMe_2)Cl$ (ref. 43).

A number of papers whose primary concern is the reactions of metal carbonyl halides can be cited. An interesting observation concerns the template addition of the P-H bonds to acetylenes using various cis-bis(secondary phosphine) metal complexes. Only one example involving a Group VIIA metal is given; this is the reaction of $Mn(CO)_3(PPh_2H)_2Br$ and $MeO_2CC{\equiv}CCO_2Me$, Eq. 5 (ref. 44). This work is also contained in a thesis (ref. 45).



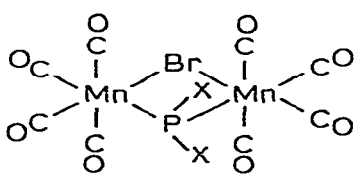
EQ.5

Studies on reactions of $Mn(CO)_5Cl$ and $Re(CO)_5Cl$ with water were cited earlier. With the latter system $[Re(CO)_3OH]_4$ was isolated (ref. 21). In the former reaction $[Mn(CO)_3(H_2O)_3]Cl$ was believed to be the product although this complex was not isolated. Under different conditions there was evidence for $Mn(CO)_4(H_2O)Cl$, $Mn(CO)_3(H_2O)_2Cl$, and $[Mn(CO)_3(H_2O)Cl]_2$ (ref. 30).

Various reactions of $Mn(CO)_3L_2Br$ (L = PPh_3, $P(OPh)_3$, 1/2 bipy) with $AgClO_4$ in CH_2Cl_2 have been carried out, yielding the σ-bonded perchlorate complexes $Mn(CO)_3L_2OClO_3$ (ref. 46). These complexes react readily, perchlorate being displaced by halide anions, phosphines, or even solvent (PhCN, MeOH, acetone, py). With F^- one can obtain $Mn(CO)_3F_3$. Using $AgPF_6$ instead of $AgClO_4$ in CH_2Cl_2 gives somewhat similar results. The product is $Mn(CO)_5OPOF_2$, partial hydrolysis of PF_6^- to $PO_2F_2^-$ having occurred to form the anionic ligand.

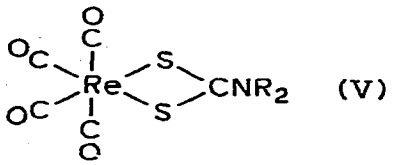
The reactions of $M(CO)_5X$ compounds (M = Mn, Re; X = Cl, Br) with triphenylphosphine, arsine, and stibine, and with $P(OPh)_3$ give cis-$M(CO)_4(L)X$ and then either mer-$Mn(CO)_3L_2X$ or fac-$Re(CO)_3L_2X$. An exception noted is that the $Mn(CO)_3(SbPh_3)_2X$ compounds have fac geometry. Cyclic voltammetry on the disubstituted species $M(CO)_3L_2X$ shows a one-electron oxidation process occurring at moderate voltages (ref. 47). There has also been an electrochemical study for the complexes fac-$Re(CO)_3(N\hat{}N)Cl$ (N^N = o-phen, and 4,7-diphenyl-1,10-phenanthroline), in MeCN using platinum electrodes (ref. 48). Nearly reversible oxidation and reduction processes (cyclic voltammetry) were seen for this compound at +1.3v and -1.3v respectively, vs. SCE, with chemiluminescence being observed if the voltage is varied in a stepwise fashion.

Among relatively unusual products of metal carbonyl halide reactions is the compound IVa, formed from $(Me_3Si)_3P$ and $Mn(CO)_5Br$ (ref. 49). This compound reacts with MeOH or CCl_4 to give IVb and IVc respectively.



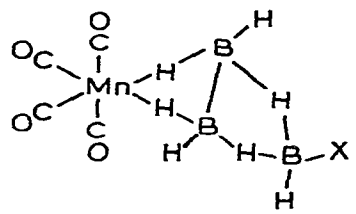
(IVa) X = $SiMe_3$
(IVb) X = H
(IVc) X = Cl

The reaction chemistry of $Re_2Br_2(CO)_6(THF)_2$ with nitrogen and phosphorus ligands is reported. Noteworthy are the reactions of the amines in the presence of CS_2, the dithiocarbamates, V, being isolated (ref. 50).



(V)

The reactions of $Mn(CO)_5X$ (M = Mn, Re) compounds and of several phosphine substituted manganese complexes, $Mn(CO)_4LX$, with $B_3H_8^-$ yield $M(CO)_4B_3H_8$, compound VIa. Halogenation, using either Cl_2 or Br_2, gives $Mn(CO)_4B_3H_7X$, VIb, and reactions with PF_3 and NH_3 give mer-$Mn(CO)_3(L)B_3H_8$ (ref. 51).



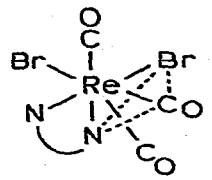
(VIa) X = H
(VIb) X = Cl, Br

Carbonyl replacement reactions in $Mn(CO)_5Br$ using Me_3NBH_2NC (ref. 52) and cis-1,2-difluorophosphinocyclohexane (ref. 53) are reported. Products are cis-$Mn(CO)_4(CNBH_2NMe_3)Br$ and $Mn(CO)_3(C_5H_{10}(PF_2)_2)Br$. Reactions of $Re(CO)_5Br$ with several α-amino acids have been reported in which CO is displaced by the amino group (ref. 54).

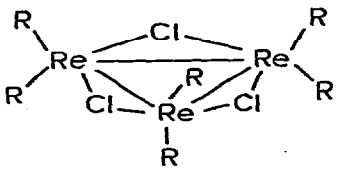
Reactions of $Mn(CO)_5X$ (X = Cl, Br) and $Re(CO)_5X$ (X = Cl, Br, I) with Et_4NX were carried out in refluxing $CHCl_3$. The products obtained have the stoichiometry $Et_4N[M_2(CO)_6X_3]$ (ref. 55). The anion $[Re_2(CO)_6Cl_3]^-$ is also encountered as a salt of protonated octaethylporphin $[OEPH_3]^+$, one of two products of the reaction of $OEPH_2$ with $Re(CO)_5Cl$. A crystal structure study on this salt reveals the structure of the anion to have two $Re(CO)_3$ groups linked by three bridging chloride ions (ref. 56).

The reaction of $[Cr(C_5H_5)(NO)_2]_2$ and $Mn(CO)_5Cl$ gives $Mn_2(CO)_{10}$ and $Cr(C_5H_5)(NO)_2Cl$; similar reactions of other metal carbonyl halides are noted (ref. 57). Treatment of $Mn(NO)_2L_2Cl$ (L = $PPhMe_2$, $PPh(OMe)_2$, $P(OMe)_3$) with $AgBF_4$ gives $[Mn(NO)_2L_3]BF_4$; from this one can obtain several derivatives by displacement of L (ref. 58).

The following structures were determined using x-ray crystallography: $Re_2Br_2(CO)_6(THF)_2$ (ref. 50); $Re(CO)_5$-F-ReF_5, a compound with a fluoride bridging rhenium atoms in two different oxidation states (ref. 59); $Re_2Br_2(CO)_6(Ph_2PPPh_2)$ (ref. 60); and $ReBr_3(CO)_2(bipy)$ (ref. 61). The last compound, a seven coordinate species, has a capped octahedral structure, VII, with CO on the face bounded by CO, Br, and one nitrogen of the bipy ligand. The structure of $Re_3Cl_3(CH_2SiMe_3)_6$ has also been determined; this is shown below (VIII) (ref. 62).



(VII)



(VIII)

R = CH_2SiMe_3

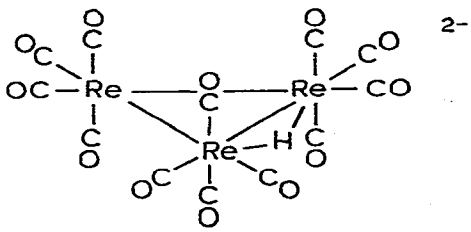
Reference was made earlier to the pulsed radiolysis experiments using $Mn(CO)_5X$ (X = Br, I) (ref. 9), and to a calorimetric study of the reaction of $Re_2(CO)_{10}$ and iodine (ref. 11). A study on the vis-uv spectrum of fac-$ReX(CO)_3$(3-benzoylpyridine)$_2$ is noted (ref. 63). Raman spectra have been run on mixed crystals of $Mn(CO)_5I$ and $Re(CO)_5I$ (ref. 64). There is a paper which attempts to understand various known metal carbonyl fluorides including $Re(CO)_5F$ (ref. 65).

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

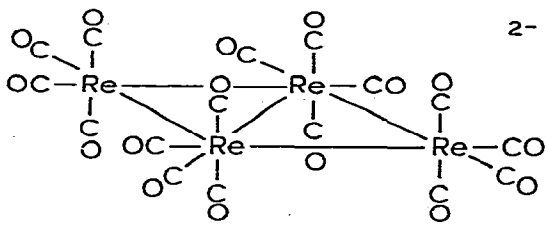
Various reports on synthesis of the metal carbonyl hydrides have appeared in the last year. This includes two articles in Inorg. Syn., describing preparations of $Re_3(CO)_{12}H_3$ (ref. 66) and $Re_4(CO)_{12}H_4$ (ref. 67). There is a reference to $Re(CO)(dpe)_2H$ (ref. 68); this compound is prepared from $Re(dpe)_2H$ and CO, the former reagent being obtained *in situ* from $Re(dpe)_2H_3$ by loss of H_2 upon photolysis. The formation of $Mn(CO)_3(dpe)H$ occurs from $[Mn(dpe)(CO)_4]^+$ and water when Et_3N is added (ref. 34); this synthesis presumably involves attack of OH^- on the cationic metal complex and elimination of CO_2. The preparation of $Mn(CO)_4(P(CF_3)_2OCH_2CH_2Cl)H$ was mentioned earlier in this review (ref. 40). Treatment of this compound with Me_3N leads to elimination of HCl and formation of $Mn(CO)_4P(CF_3)_2OCH_2CH_2$. Also mentioned earlier was the formation of PPN[cis-$Mn(CO)_4(H)(SiPh_3)$] from photolysis of PPN[$Mn(CO)_5$] and $HSiPh_3$ (ref. 26). Presumably the route to this product involves photolytic elimination of CO and oxidative addition of the silane to the 16e intermediate. The formation of $Et_4N[Re_2(CO)_9H]$ from $Et_4N[Re_2(CO)_9CHO]$ occurs when solutions of the latter compound are photolyzed (ref. 14). Finally the species $Mn(CO)_3L_2H$ are obtained from $[Mn(CO)_3L_2]^-$ and Me_3ACl (L = $P(OPh)_3$, A = C, Si, Ge). Using Ph_3SnCl one can obtain both this hydride and the triphenyltin derivative, $Mn(CO)_3L_2SnPh_3$ (ref. 69).

Extensive rhenium hydride chemistry has been developed by Ciani *et al.* (ref. 70, 71). Refluxing $Re_2(CO)_{10}$ in methanolic KOH gives the two anionic species $[Re_2(CO)_6(OMe)_3]^-$ and $[Re(CO)_4H_2]^-$. The latter is difficult to isolate, converting slowly to the former in methanol. Nonetheless, crystals of the Et_4N^+ salt have been obtained and a crystal structure determined, showing the anion to have a distorted octahedral geometry. Reactions of this anion were studied. Iodine gives $Et_4N[Re(CO)_4I_2]$, and strong protonic acids

like $HClO_4$ and HCl yield $Re_3(CO)_{12}H_3$. When $Et_4N[Re(CO)_4H_2]$ is boiled in EtOH the product is $(NEt_4)_2[Re_4(CO)_{15}H_4]$ (ref. 70). In boiling hydrocarbon solvents, $NEt_4[Re(CO)_4H_2]$ gives a mixture of polynuclear species including $[Re_4(CO)_{16}]^{2-}$, $[Re_3(CO)_{12}H_2]^-$, $[Re_3(CO)_{10}H_3]^{2-}$, $[Re_3O(CO)_9H_3]^{2-}$ and $[Re_4(CO)_{16}H_6]^{2-}$. Crystals of both $(NEt_4)_2[Re_3(CO)_{12}H]$ and $(NEt_4)_2[Re_4(CO)_{16}]$ were subjected to x-ray diffraction studies; the structure of each anion is sketched below (IX, X).



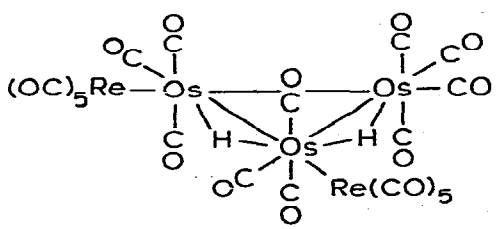
(IX)



(X)

In compound IX the hydrogen location is inferred to be bridging along the longer edge of an isosceles triangle of rhenium atoms; the three Re-Re distances are 3.014(3)Å, 3.018(3)Å and 3.125(3)Å (ref. 71).

Other crystal structure determinations have been carried out on $Mn(CO)_3(PPh_3)_2H$ (ref. 72) and $H_2Os_3Re_2(CO)_{20}$ (ref. 73). The latter compound, obtained from $Os_3(CO)_{10}(C_8H_{14})_2$ and $Re(CO)_5H$, has structure XI.



(XI)

The structures of $H_4Re_4(CO)_{12}$ and $Mn(NO)_3PPh_3$ are described in a thesis (ref. 74).

Special note must be made of the reaction of $Mn(allyl)(CO)L_3$ and H_2 to give $Mn(CO)L_4H$ (L = $P(OMe)_3$) (ref. 32). The compound $Mn(allyl)(CO)L_3$ was found to be a catalyst for the hydrogenation of olefins, but unfortunately this catalytic activity falls off rapidly with formation of this much less active hydride species.

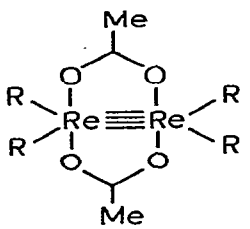
A communication reflects on the ability of various metal-hydride species,

including $Re(C_5H_5)_2H$, to behave as hydrides; this behavior was assessed based on the ability of each complex to reduce ketones. The hydridic character decreases from left to right in the periodic table (ref. 75).

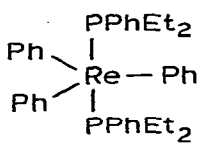
V. METAL COMPLEXES WITH CARBON GROUPS AS LIGANDS ($M(CO)_{5-n}(L)_nR$, $M(CO)_{5-n}(L)_nCOR$, MR_n, Complexes with Carbene and Carbyne Ligands)

Research on complexes in which alkyl or aryl groups are the only ligands or the primary ligand continues unabated. One paper (ref. 76) reports several new alkyl rhenium acetate species. When $Li_2Re_2Me_8(Et_2O)_2$ is reacted with acetic acid the compound $Re_2Me_2(acetate)_4$ is formed and may be isolated and characterized. Also described are the reactions of $Re_2(acetate)_4Cl_2$ with R_2Mg complexes (R = CH_2SiMe_3, t-Bu, CH_2Ph, etc.) in ether, which give products having the stoichiometry $Re_2R_4(acetate)_2$ (XII).

Crystal structures for two compounds $Re_3Cl_3(CH_2SiMe_3)_6$ (ref. 62) and $Re(PPhEt_2)_2Ph_3$ (ref. 77) are reported. The latter compound, whose structure is drawn below, XIII, was first reported in 1966. The photoelectron spectra



(XII)



(XIII)

for $ReMe_6$, $ReOMe_4$, and $ReO(CH_2SiMe_3)_4$ have been run and interpreted (ref. 78). Infrared data ($\nu(C\equiv C)$) on $Mn(C\equiv CR)_4^{2-}$ (R = H, Ph, Me) indicate that the acetylide ligands bond via primarily a electrostatic type of interaction (ref. 79).

It has been determined that the insertion of SO_2 into the carbon-manganese bond in cis-threo-$PhCHDCHDMn(CO)_4(PEt_3)$ occurs with inversion of carbon (ref. 80). However, cleavage reactions of the alkyl group using halogens give variable results, with both retention and inversion; the percent of each is dependent on solvent. Cleavage with $HgCl_2$ or $HgBr_2$ gives less than 10% retention (ref. 81).

The synthesis of $Mn(CO)_4P(CF_3)_2OCH_2\dot{C}H_2$ by dehydrohalogenation of $HMn(CO)_4P(CF_3)_2OCH_2CH_2Cl$ was discussed at an earlier point in this review (ref. 40).

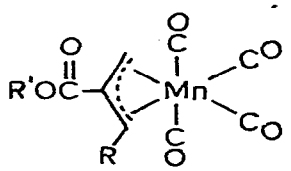
Various studies describing reactions of metal alkyl compounds can be identified here. Three references were cited earlier: the high pressure carbonylations of $Mn(CO)_5Me$ and $Re(CO)_5Me$ to give $Mn(CO)_5COMe$ and $Re_2(CO)_{10}$ respectively (ref. 24); carbonyl substitution in $Mn(CO)_5CCl{=}C(CN)_2$ to give fac-$Mn(CO)_3L_2CCl{=}C(CN)_2$ (L = tBuCN), $P(OMe)_3$, $P(OEt)_3$, and 1/2 L = $Ph_2PCH_2CH_2PR_2$ (ref. 42); and reactions of several $Mn(CO)_4(PR_3)Me$ compounds and $[Ph_3C]BF_4$ giving cationic species $[Mn(CO)_4(PR_3)(L)]^+$ (L = H_2O, MeCN) (ref. 29). Substitution of carbon monoxide in $Mn(CO)_5R$ (R = Me, $PhCH_2$, $ClC_6H_4CH_2$) by isocyanides

(t-BuNC, $C_6H_{11}NC$, n-BuNC) gives mixtures of cis and trans-$Mn(CO)_4(L)COR$. Thermal decarbonylation of $Mn(CO)_4(L)COCH_2C_6H_4Cl$ gives cis-$Mn(CO)_4(CNR)CH_2C_6H_4Cl$ which further reacts with $P(OCH_2CH_2)_3CEt$ to form fac- and mer-$Mn(CO)_3(CNR)(phos)$-$COCH_2C_6H_4Cl$ (ref. 82).

Studies on the ortho-metallation of azobenzenes $PhN{=}NC_6H_4R$ with $Mn(CO)_5Me$ are reported (ref. 83). Interest here is in the effect of R on the choice of the aryl ring to be metallated.

Water and alcohols add to the propynyl ligand in $Mn(CO)_5CH_2C{\equiv}CR$; the products are η^3 allyl complexes, Eq. 6 (ref. 84). Carbon monoxide may be seen to have inserted into a carbon-metal bond in this process.

$$Mn(CO)_5CH_2C{\equiv}CR + R'OH \longrightarrow$$



EQ. 6

Decarbonylation of $CH_3CH{=}CHCH_2Mn(CO)_5$ by $Ir(dpe)_2Cl$ gives the π-crotyl compound (ref. 85).

The isolation of cis-diacyl metal carbonyl anions and their use as chelating ligands to various other metals has been the subject of extensive study over several years. In 1978 eight additional references, all from Lukehart's group, have appeared. These include the synthesis of $[Mn(CO)_4(COMe)_2]_3Al$, reported in Inorg. Syn. (ref. 86), and the synthesis of $[Re(CO)_4(COMe)_2]_2Cu$ reported in a communication (ref. 87). This second compound was prepared from $Cu(OMe)_2$ and $[Re(CO)_4(COMe)_2]H$. The synthesis of $[Re(CO)_4(COMe)_2]_2BX_2$ species (X = F, Cl, Br, I) from $[Re(CO)_4(COMe)_2]H$ and BX_3 is also noted (ref. 88). In another paper (ref. 89) the following reaction sequence is presented, Eq. 7:

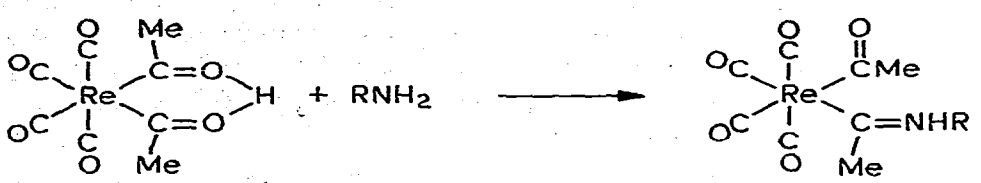
$$\text{cis-MeCOMn(CO)}_4\text{(CNR)} \xrightarrow{\text{MeLi}} \text{Li[cis-Mn(CO)}_4\text{(COMe)(CMeNMe)]}$$

$$\xrightarrow[-3\text{LiX}]{\text{AlX}_3} [Mn(CO)_4(COMe)(CMeNMe)]_3Al \qquad \text{EQ.7}$$

In this product the aluminum ion coordinates to both oxygen and nitrogen in the organometallic ligand. The protonated form of the free ligand (with rhenium rather than manganese, however) is obtained by the reaction given in Eq. 8 below (ref. 90).

It is interesting to compare the structures of $Re(CO)_4(COMe)_2H$ and $Re(CO)_4(COMe)$-$(CMe{=}NHR)$. In the latter the proton resides on the nitrogen which is a much more basic site.

Several papers relate studies on these molecules. Values of ν(CO) for

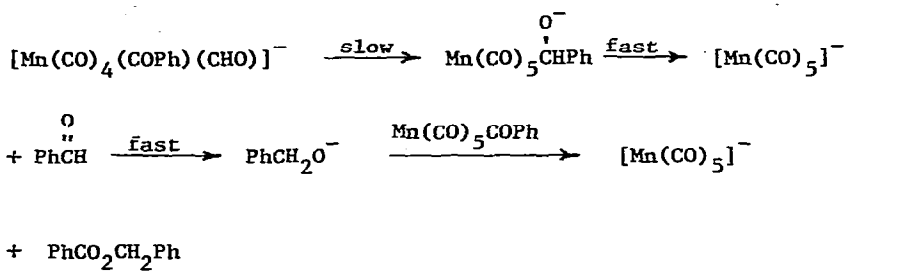


EQ.8

$[M(CO)_4(COMe)_2]_3Al$ and $Re(CO)_4(COMe)_2H$ were measured and carbonyl force constants calculated using the Cotton-Kraihanzel method (ref. 91). Carbon-13 nmr spectra for 12 compounds $[M(CO)_4(COR)_2]_nX$ (M = Mn, Re; X = H, BF_2, Al) have been recorded (ref. 92). The rate of mer-fac isomerization for $[Mn(CO)_4(COMe)$-$(COCH_2Ph)]_3Al$ was determined by nmr (ref. 93).

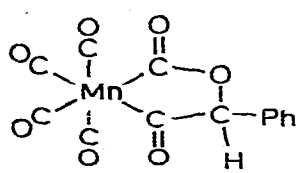
Two reports on formyl compounds of rhenium were cited earlier (ref. 14,15). Also cited was a paper describing carbamoyl derivatives of rhenium and manganese $M(CO)_{5-n}L_nCONH_2$, arising from reactions of cationic metal carbonyls with liquid ammonia (ref. 35).

Gladysz and Selover (ref. 94) have studied the decomposition of $[Mn(CO)_4$-$(COPh)CHO]^-$ which occurs to give $[Mn(CO)_5]^-$ and $PhCO_2CH_2Ph$. The following mechanism is suggested for this reaction (Eq. 9)



EQ.9

Also investigated by the same group is the reaction of $Mn(CO)_5COCOPh$ with $LiBHEt_3$ (ref. 95). A product of this reaction is isolated as a PPN^+ salt; its structure has been determined to be XIV.



(XIV)

Addition of Me_3SiCl to XIV leads to $Mn(CO)_5COCHPhOSiMe_3$ which can be decarbonylated to $Mn(CO)_5CHPhOSiMe_3$. Acid cleavage (HCl) of the $SiMe_3$ group then yields $Mn(CO)_5H$ and PhCHO, presumably via an unstable α-hydroxybenzyl compound $Mn(CO)_5CHPhOH$. A related sequence involves protonation of XIV to give $Mn(CO)_5COCHPhOH$, and its decarbonylation to give $Mn(CO)_5H$ and PhCHO, presumably via the same intermediate. All of this work is very significant in that it contributes to a mechanistic interpretation for metal catalyzed reductions of carbon monoxide by hydrogen.

Gladysz and Merrifield (ref. 96) also describe the results of a study to determine whether Et_3B mediates the hydride transfer from metal formyls. The latter species are generated in the presence of trialkylboron compounds in the reaction of metal carbonyls with $NaBHEt_3$.

A number of papers have appeared on carbene-metal complexes. Already identified in an earlier part of this review were the complexes $Re_2(CO)_9(CROMe)$ (ref. 12), $Re_2(CO)_8(CROMe)_2$, compounds with carbene groups bridging the two metals (ref. 13), $Mn(CO)_4(CHNMe_2)Cl$ (ref. 43), and $Re(CO)_4(CMeNHR)COMe$ (ref. 90). The compound $Mn(C_5H_5)(CO)_2CMenOMe$ can be prepared from $Mn(C_5H_5)(CO)_3$ by the reaction of menthyllithium followed by alkylation using the trimethyloxonium cation (ref. 97). It is reported that the choice of solvent and temperature determine the mode of reaction of organolithium compounds with $M(C_5H_5)(CO)_3$ (M = Mn, Re) (ref. 98). In THF, at -40°, butyllithium metallates the ring giving $M(C_5H_4Li)(CO)_3$ and butane, Eq. 10. On the other hand, reactions of MeLi and PhLi with $M(C_5H_5)(CO)_3$, run in ethyl ether at 20°, occur with addition of the carbon nucleophile to a carbonyl group (Eq. 11). Carbene complexes are then formed from these anion species in a reaction sequence involving protonation and then addition of diazomethane.

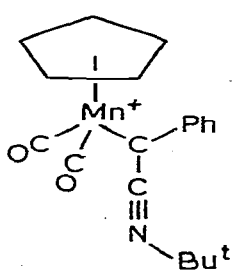
$$M(C_5H_5)(CO)_3 + RLi \xrightarrow[-40°]{THF} M(C_5H_4Li)(CO)_3 + RH \qquad EQ.10$$

$$M(C_5H_5)(CO)_3 + RLi \xrightarrow[20°]{Et_2O} Li[M(C_5H_5)(CO)_2COR] \qquad EQ.11$$

Substitution of the two carbonyls in $Mn(C_5H_4Me)(CO)_2(CMeOMe)$ using $MeN(PF_2)_2$ gives $Mn(C_5H_4Me)(MeN(PF_2)_2)(CMeOMe)$ (ref. 99). The electronic spectrum of $Mn(C_5H_5)(CO)_2CPh_2$ has been reported (ref. 100).

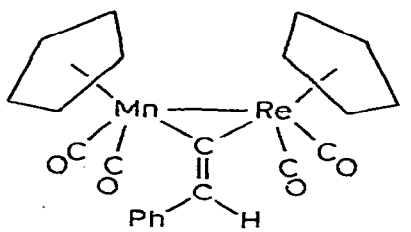
The reactions of the diphenylcarbene complexes, $Mn(C_5H_4R)(CO)_2(CPh_2)$ with carbon monoxide under pressure give complexes having an η^2 diphenylketene ligand. On treatment with hydrogen the organic products Ph_2CHCHO and Ph_2CHCH_2OH can be obtained (ref. 101).

Tert-butyl isocyanide adds to $[Mn(C_5H_5)(CO)_2CPh]BCl_4$ at -50° to give XV (ref. 102). Similar reactions with other bases were described last year.



(XV)

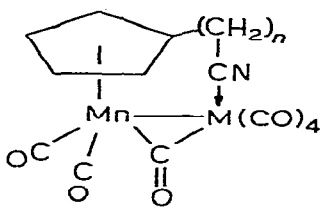
The mass spectra of phenylethylidene complexes, having formulas $M(C_5H_5)(CO)(L)(C{=}CHPh)$ (M = Mn, Re; L = CO, PPh_3, $P(OPh)_3$) have been recorded (ref. 103). A compound with a bridging phenylethylidene group, XVI, is formed when $Mn(C_5H_5)(CO)_2(C{=}CHPh)$ is reacted with $Re(C_5H_5)(CO)_2(THF)$ (ref. 104).



(XVI)

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

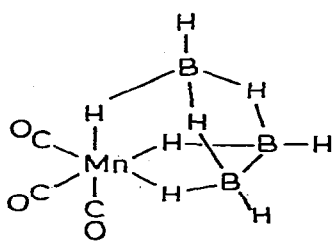
Syntheses of the following compounds, having a manganese or rhenium carbonyl group bonded to another transition metal, are reported: $Pt(CNR)_2(Mn(CO)_5)_2$ (R = C_6H_{11}, t-Bu) from $Pt(CNR)_2Cl_2$ and $Na[Mn(CO)_5]$ (ref. 105); $Mo(C_5H_5)(CO)_3Mn(CO)_5$ from $[Mo(C_5H_5)(CO)_2]_2$ and $Mn_2(CO)_{10}$ (ref. 106); $MenCW(CO)_4Re(CO)_5$ (Men is the optically active menthyl group) (ref. 107); and $Mn(C_5H_4(CH_2)_nCNM(CO)_7$ (M = Cr, W) compounds having structure XVII (ref. 108). The synthesis and structure for



(XVII)

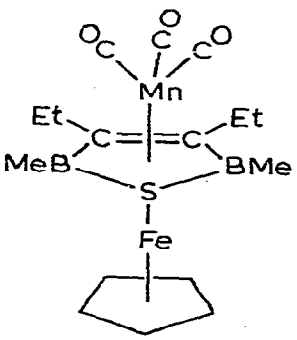
$H_2Os_3Re_2(CO)_{20}$ (ref. 73) are mentioned earlier in this review. A study of the electronic spectra of $M_2Fe(CO)_{14}$ (M = Mn, Re) and a discussion of bonding in these compounds are given in another paper (ref. 109)

The syntheses and characterization of $Mn(CO)_4B_3H_8$, $Mn(CO)_4B_3H_7X$ (X = Cl,Br) and $Mn(CO)_3(L)B_3H_8$ (L = PF_3, NH_3) are reported (ref. 51). A crystal structure study has defined the molecular geometry of $Mn(CO)_3B_3H_8$ (ref. 110), XVIII.

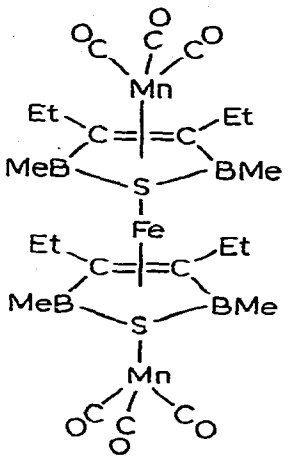


(XVIII)

Reaction of PhBCH=CHCH$_2$CH$_2$CH=CH (=L) and Mn(C_5H_5)(CO)$_3$ gives Mn(C_5H_5)(CO)(L) (ref. 111). In this compound, bonding to manganese by a delocalized C_4B unit is presumed to occur. The reaction of SBMeCEt=CEtBMe with a mixture of $Mn_2(CO)_{10}$ and [Fe(C_5H_5)(CO)$_2$]$_2$ gives XIX. When treated with aluminum metal and $AlCl_3$ in benzene a cationic species is obtained. Upon heating this at 140°/0.1 mm. compound XX is formed (ref. 112).

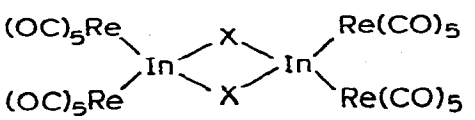


(XIX)



(XX)

X-ray diffraction studies have produced the molecular geometries of [((CO)$_5$Re)$_2$InX]$_2$ (X = Cl, Br, I). The general structure is sketched below XXI (ref. 113). An Inorg. Syn. article gives the preparation of



(XXI)

Tl[Mn(CO)$_5$]$_3$ (ref. 114).

The preparation of the compound Mn(CO)$_5$SiMeCH$_2$CH$_2$CH$_2$ from Na[Mn(CO)$_5$] and ClSiMeCH$_2$CH$_2$CH$_2$ has been carried out (ref. 115). Another organosilyl compound, PPN[Mn(CO)$_4$(H)SiPh$_3$], was referenced earlier along with PPN[Mn(CO)$_4$(SnPh$_3$)$_2$] (ref. 26). The compound Mn(CO)$_5$SnPh$_3$ is obtained in 60% yield upon photolysis of $Mn_2(CO)_{10}$ and Ph_3SiCl in THF (ref. 116). Carbonylation of Re_2O_7 in the presence of $SnCl_2$ gives [Re(CO)$_5$]$_2$SnCl$_2$ (ref. 117). Reaction of [Mn(CO)$_3$(P(OPh)$_3$)$_2$]$^-$ with Me_3SnCl gives Mn(CO)$_3$(P(OPh)$_3$)$_2$SnMe$_3$; preparations of other stannane derivatives are also reported in this paper (ref. 69). Cleavage of the RnE group in RnEMn(CO)$_5$ (RnE = R_2P, R_2As, RS, RSe; R = Me, CF_3) by Me_3SnH gives $Me_3SnMn(CO)_5$ (ref. 41).

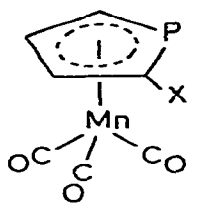
The preparation of $Re_2(CO)_8$[μ-SnXRe(CO)$_5$]$_2$ (X = Cl, Br, I) is accomplished from a reaction between $Re_2(CO)_{10}$ and SnX_2 (ref. 118). The molecular structure of the manganese analogue has been determined using X-ray diffraction methods

(ref. 119). The structure of $BrSn[Mn(CO)_5]_3$ was also determined; this is reported in the same paper.

Ionization potential and appearance potential data were accumulated for many compounds including $Mn(CO)_5SiMe_3$, $Mn(CO)_5SnX_3$ (X = Me, Ph, Cl), $Mn(CO)_5SnMe_2Cl$, and trans-$Mn(CO)_4(PPh_3)(SnPh_3)$ (ref. 120). A comparison between the Mn-Sn bond distance and dissociation energy is offered.

There are two papers describing reactions of $R_3SnM(CO)_5$ compounds. Dissolution in liquid SO_2 causes cleavage of tin-phenyl bonds, yielding species such as $Mn(CO)_5SnPh(OSOPh)_2$ (ref. 121). Another paper by the same authors discusses reactions of $R_3SnM(CO)_5$ complexes with various electrophilic reagents (ref. 122).

Pyrrollyl,phosphollyl, and arsollyl complexes of the Group VIIB metals represent a topic of further research. It has been shown that the pyrrollyl nitrogen in pyrrollylmanganese tricarbonyl can serve as a ligand (ref. 123), and a structural study of the compound $Mn(CO)_3(C_4H_4N\rightarrow Mn(CO)_2(C_5H_5))$ has been carried out. The reaction of 1-phenyl-3,4-dimethylphosphole and several other phospholes with $Mn_2(CO)_{10}$ at 150° gives the appropriate phosphollylmanganese tricarbonyl, XXIIa (ref. 124). These compounds undergo Friedel-Crafts acylations in the 2-position on the phosphollyl ring. An x-ray diffraction study was used to determine the structure of XXIIb.



(XXIIa) X = H
(XXIIb) X = PhCO

Compound XXIIa reacts with various organophosphorus ligands to give mono-substituted derivatives and, in one instance (L = $P(OMe)_3$), a disubstituted complex (ref. 125).

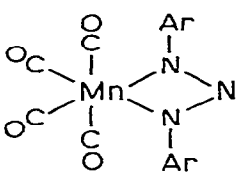
From 1-phenyl-2,5-dimethylarsole and $Mn_2(CO)_{10}$ at 150° the product 2,5-dimethylarsollylmanganese tricarbonyl forms. Under Friedel-Crafts conditions this compound acylates in the 3-position (ref. 126).

Extensive study by Sellmann et al. continues on the syntheses of metal complexes of dinitrogen, diimine, hydrazine, and ammonia and interconversions between members of this series. Two papers (ref. 127, 128) describe some reaction chemistry associated with the complex $Mn(C_5H_5)(CO)_2(N_2)$. With MeLi in THF (-30°C) one obtains a solution containing $Li[Mn(C_5H_5)(CO)_2NMe{=}N]$. Addition of H^+ to this solution regenerates the starting material and gives methane, while Me_3O^+ addition leads to formation of the dimethyldiimine complex, $Mn(C_5H_5)(CO)_2(MeN{=}NMe)$ (ref. 127). In turn, the dimethyldiimine ligand can be displaced with N_2. Related results arise using PhLi; one obtains initially $Li[Mn(C_5H_5)(CO)_2(NPh{=}N)]$ using PhLi. Protonation followed

by addition of $Mn(C_5H_5)(CO)_2(THF)$ gives $Mn(C_5H_5)(CO)_2PhN{=}NHMn(CO)_2(C_5H_5)$, a compound in which phenyldiimine PhN=NH bridges the two manganese groups (ref. 128).

Related chemistry is seen for rhenium (ref. 129). Photolysis of $Re(C_5H_5)(CO)_3$ in THF gives $Re(C_5H_5)(CO)_2(THF)$ and $Re_2(C_5H_5)_2(CO)_5$. The former compound reacts with either N_2 under pressure or with N_2O to give $Re(C_5H_5)(CO)_2N_2$. This species can also be obtained along with $Re(C_5H_5)(CO)_2NH{=}NHRe(CO)_2(C_5H_5)$ when $Re(C_5H_5)(CO)_2N_2H_4$ is oxidized. The disproportionation of $Re(C_5H_5)(CO)_2N_2H_4$ to $Re(C_5H_5)(CO)_2N_2$ and $Re(C_5H_5)(CO)_2NH_3$ is also described.

Other synthetic chemistry involving nitrogen ligands includes the synthesis of various nitroxide stabilized radical species $M(CO)_4(L)(t\text{-}BuNO)$ (M = Mn, Re, L = CO, phosphines) (ref. 8), and the synthesis of 1,3-trimethylsilyl- or -trimethylstannyltriazenido- complexes of manganese from the reaction of $Mn(CO)_5Br$ and $Me_3AN{=}N{-}NHAMe$ (ref. 130) (A = Si, Sn). Structure XXIII is proposed for these species.



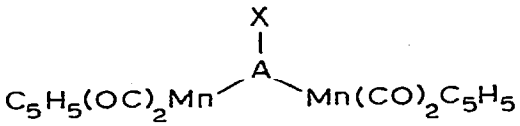
(XXIII)

The characterization of $[Mn(CO)_4NSOF_2]_2$ by x-ray crystallography has been accomplished (ref. 131). The $N{=}SOF_2$ groups bridge the metal atoms in this nuclear structure. A structure has been determined for $[OEPH_3][Re_2(CO)_6Cl_3]$ one of the two compounds obtained in the octaethylporphin-$Re(CO)_5Cl$ reaction (ref. 56).

Cyclic voltammetry on the tetraphenylporphyrin complexes $[Re(CO)_3]TPP$ and and $Re(CO)_3(TPP)H$ has been carried out (ref. 132). Similar first oxidation waves for both compounds are noted, but the potentials required for the second oxidation steps are different. The authors of this work suggest that oxidation of the second compound is accompanied by rearrangement to give a species with a rhenium-rhenium bond.

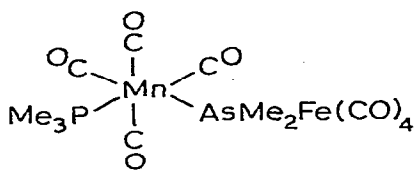
One of the more interesting developments in this area has been the synthesis and characterization by x-ray crystallography of arsinidine and stibinidine complexes of manganese. The compound $ClAs[Mn(C_5H_5)(CO)_2]_2$ arises in the reaction of $Mn(C_5H_5)(CO)_2(THF)$ with $AsCl_3$ (ref. 133) while the compound $PhSb[Mn(C_5H_5)(CO)_2]_2$ is formed in the reaction of $Mn(C_5H_5)(CO)_2(THF)$, $Mn(C_5H_5)(CO)_2SbPhI_2$, and potassium metal in THF with a crown ether present (ref. 134). Both compounds, XXIV, have a planar Mn_2AX framework with the Mn-A-Mn angle being about 140°. The overall structure and bond length argue for multiple bonding of the unique metalloidal ligand to the metal atoms.

Vahrenkamp and coworkers have described additional work which involves

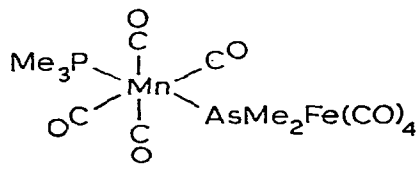


(XXIV) (AX = AsCl, SbPh)

$AsMe_2$ or PMe_2 groups bridging two dissimilar metals. Formation of $Mn(CO)_4(PR_3)(AsMe_2)$ from $[Mn(CO)_4(PR_3)]^-$ and $AsMe_2Cl$ is the first step in the formation of these species. This compound then reacts as a ligand displacing CO or other ligands in several metal carbonyl species to give the products $Mn(CO)_4(PR_3)AsMe_2M'$ (M' = $Fe(NO)_2(CO)$, $Co(CO)_2(NO)$, $Fe(CO)_4$, $W(CO)_5$) (ref. 135). In a second paper structures of cis- and trans-$Mn(CO)_4(PMe_3)AsMe_2Fe(CO)_4$, XXV and XXVI, are reported (ref. 136).



(XXV)



(XXVI)

Vahrenkamp has also reported structural data (ref. 137) for three $[M(CO)_4PMe_2]_2$ (M = V, Cr, Mn) species. The manganese compound has a long manganese-manganese distance, 3.675 Å, indicating that a metal-metal bond is lacking, whereas the progressively shorter chromium-chromium and vanadium-vanadium bond lengths correspond to single and double bonds respectively.

Earlier reference was made to $Mn_2(CO)_8(P(SiMe_3)_2)(Br)$, obtained from $Mn(CO)_5Br$ + $(Me_3Si)_3P$, and to two compounds derived from this species by cleavage of the Si-P bonds (ref. 49). Also identified earlier were cleavage reactions of the A-M bond in $R_2AM(CO)_5$ (R_2A = Me_2P, Me_2As, $(CF_3)_2P$, $(CF_3)_2As$; M = Mn, Re) by HI or $SnMe_3H$ (ref. 41). In addition this paper reports the dimerization of such species to $[M(CO)_4AR_2]_2$ and the formation of $M(CO)_4AR_2Mo(CO)_5$. Similar chemical behavior is accorded $RSM(CO)_5$ and $RSeM(CO)_5$ species.

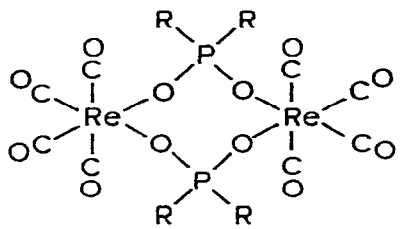
Reaction chemistry of the diorganophosphonic acid complexes $M(CO)_4(PR_2OH)Br$ (M = Mn, Re; R = Me, Ph) has been pursued (ref. 138). Treatment of this species with sodium amalgam gives initially $Na_2[M_2(CO)_8(POR_2)_2]$. For the manganese compound only, excess sodium yields another product $Na_2[Mn(CO)_4POR_2]$. This product gives $Mn(CO)_4(PR_2OMe)Me$ when treated with Me_2SO_4. Reaction of $M(CO)_4(PR_2OH)Br$ with Me_2SO_4 leads to the same product.

Rhenium carbonyl and the phosphinic acids R_2PO_2H (R = Me, Ph) react in THF or dioxane under photolytic conditions to give $[R_2PO_2Re(CO)_3(solv)]_x$ (ref. 139). Carbon monoxide addition displaces solvent giving $[R_2PO_2Re(CO)_4]_2$ which is also available from the reaction of $Re(CO)_5Br$ and $Ag[O_2PR_2]$. The compound

$[R_2PO_2Re(CO)_4]_2$ loses carbon monoxide readily, and there is evidence presented on the existence of the equilibrium given in Eq. 12.

$$[R_2PO_2Re(CO)_4]_2 \rightleftharpoons [R_2PO_2Re(CO)_3]_x + CO \qquad \text{EQ.12}$$

An x-ray diffraction study on $[Ph_2PO_2Re(CO)_4]_2$ shows that this compound has the structure below (XXVII).



(XXVII)

The compounds $[R_2PO_2Re(CO)_3(THF)]_x$ react with dpe giving $R_2PO_2Re(CO)_3(dpe)$ (ref. 140). At 110° carbon monoxide is lost from these compounds and a polymeric species $[R_2PO_2Re(CO)_2(dpe)]_x$ forms.

Other complexes having oxygen groups as ligands include the radical species $\overline{Mn(CO)_4(OCR{=}CRO)}$ (ref. 7), $Mn(CO)_3L_2OClO_3$ (L = PPh_3, $P(OPh)_3$, 1/2 bipy) and $Mn(CO)_5OPOF_2$ (ref. 46), $NEt_4[Re_2(CO)_6(OMe)_3]$ and (ref 70), $[Mn(CO)_3OH]_4$ (ref. 20). The compound $[Re(CO)_3OH]_4$, mentioned earlier (ref. 21), reacts with bases; when this is followed by alkyl halide addition the products $[Re(CO)_3OR]_4$ result. With weak bases such as THF, $OPPh_3$, and Br^- adducts of the form $[Re(CO)_3OH\cdots B]_4$ are formed.

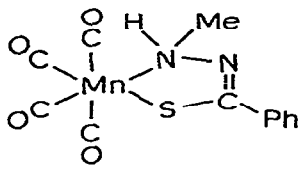
Reactions of $(allyl)Mn(CO)_2L_2$ (L = $P(OR)_3$) with sulfonic acids give $RSO_3Mn(CO)_2L_2$ (R = Me, CF_3) (ref. 32). This work is also reported in a thesis (ref. 141).

New chemistry has been developed using carbon disulfide as a ligand. Reaction of $Fe(CO)_2(L)_2CS_2$ (L = PMe_3) and $Mn(C_5H_5)(CO)_2(THF)$ gives $Fe(CO)_2(L)_2CS_2Mn(C_5H_5)(CO)_2$ (ref. 142). A similar compound $Co(C_5H_5)(PMe_3)$-$CS_2Mn(C_5H_5)(CO)_2$ is described in a separate paper (ref. 143). In both compounds one C=S unit is believed to bond sideways to one metal, while the other sulfur bonds to the $Mn(C_5H_5)(CO)_2$ group.

Earlier mention was made of the slow reaction of $PPN[Mn(CO)_5]$ with CS_2 to give $PPN[Mn(CO)_4S_2CS]$, and further reactions with MeI or PhN_2BF_4 to give $Mn(CO)_4S_2CSR$ (ref. 27). The compounds $M(CO)_4S_2CSM'(CO)_5$ (M, M' = Mn, Re) were also characterized in this work. Reaction of $PPN[Mn(CO)_5]$ with S_8 is said to give $[Mn(CO)_5S_n]_x$. The reaction of $Re_2Br_2(CO)_6(THF)_2$ with R_2NH and CS_2 gives $Re(CO)_3(R_2NH)S_2CNR_2$ (ref. 50).

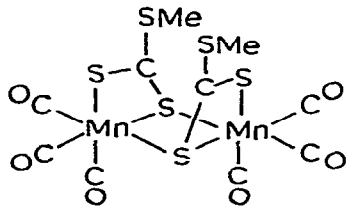
Several thiobenzoylhydrazides, PhCSNHNHR (R = H, Me, Ph) were reacted

with $Mn(CO)_5Cl$ (ref. 144). The products utilize the ligand in a chelating capacity as shown in Structure XXVIII sketched below.



(XXVIII)

Reactions of $Na[Mn(CO)_5]$ with PhNCS or MeNCS give after protonation both $Mn(CO)_4S_2CNHR$ and $Mn(CO)_3(CNR)S_2CNHR$ (ref. 145). If methyl iodide is used in the workup, however, compound XXIX, $Mn_2(CO)_6[SC(SMe)(NMe)]_2$, forms. An x-ray diffraction study assigns this structure.



(XXIX)

The structure of $[Re(CO)_3(PMe_3)_2]_2Se$ has also been determined (ref. 146). This compound is obtained from $[Re(CO)_4SeSnMe_3]_2$ with PMe_3. The trimethylphosphine ligands and the selenium atom occupy fac- positions in the octahedral environment of each rhenium.

Heating $Mn(CO)_5msc$ (msc = $-SeCONMe_2$) under CO pressure gives $[Mn(CO)_4msc]_2$ and not monomeric $Mn(CO)_4msc$ as had been previously reported. A small amount of $[Mn(CO)_3msc]_2$ also forms (ref. 147).

Compounds with sulfonium cations as ligands were first described in a communication last year. A full paper has now appeared on various $[Mn(C_5H_4R)(CO)_2SMe_2R']^+X^-$ species (R = H, Me; R' = Me, Et, Ph) (ref. 148). This paper also reports on the structure of the R = Et, X^- = PF_6^- compound, as determined by x-ray crystallography. This work is contained in a thesis (ref. 17).

VIII. HYDROCARBON METAL COMPLEXES ($M(C_5H_5)(CO)_3$, $[M(C_6H_6)(CO)_3]^+$, $M(C_6H_7)(CO)_3$, olefin, allyl complexes, others)

As usual, most organometallic chemistry dealing with hydrocarbon complexes of manganese, technetium, and rhenium involves the compounds $M(C_5H_5)(CO)_3$ and their derivatives. And, in many instances, the focal point is a unique ligand with the cyclopentadienyl unit being superfluous to the discussion. Many references to such species have already been made in the earlier portions of this review.

There are a few references to olefin and allyl complexes of these metals;

these are considered first. After consideration of C_5H_5-M complexes, this section concludes with references to arene- and cycloheptatrienyl complexes and to heterocyclic complexes.

The manganese(II) complexes of meso- tetraphenylporphin, Mn(TTP)(py) adds $C_2(CN)_4$ giving a stable olefinic complexes of this metal (ref. 149). Addition of C_2H_4 to $Re(dpe)_2H$ gives $Re(dpe)_2(C_2H_4)H$; a similar reaction with carbon monoxide was mentioned earlier (ref. 68).

The compounds $[M(CO)_4(COD)]^+$ (M = Mn, Re; COD = 1,5-cyclooctadiene) are formed from $M(CO)_5Cl$, $AlCl_3$, and COD. Various reactions of these species with nucleophiles are reported (ref. 31). With OMe^-, CN^-, or N_3^- the products are $Mn(CO)_4(2\text{-}X\text{-}1,5,6\text{-}\eta^3\text{-}C_8H_{12})$. Utilizing $NaBH_4$ one obtains a $1,4,5\text{-}\eta^3$-cyclooctenyl complex. This isomerizes on heating to $Mn(1,2,3\text{-}\eta^3\text{-}C_8H_{13})(CO)_4$, and also reacts with various ligands to give $Mn(CO)_3(L)_2(\eta^1\text{-}C_8H_{13})$.

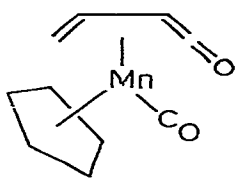
The synthesis of $Re_2(allyl)_4$ is reported in one paper (ref. 150). The molecular structure of this compound has been determined; it has overall D_{2h} symmetry; two $Re(allyl)_2$ groups are linked by a rhenium-rhenium triple bond (2.225(7) Å) (ref. 151).

The carbon-13 nmr spectrum of $Mn(CO)_4(allyl)$ has been recorded (ref. 152). Evidence on CO intramolecular exchange was being sought in this study, but results are inconclusive. Two papers from the same authors report synthesis of substituted m- and p- fluorophenyl substituted $Mn(allyl)(CO)_4$ species (ref. 153), and the ^{19}F nmr spectra of these species (ref. 154). The latter data are correlated with information on the electron density in the complexed allyl group. Vibrational spectra of various metal-allyl compounds including $Mn(CO)_4(allyl)$ are reported (ref. 155); data on skeletal vibrations of the allyl group is the primary concern here.

Reference to the synthesis of $Mn(CO)_4(CH_2C(COOR')CHR)$ by addition of R'OH to $Mn(CO)_5CH_2C{\equiv}CR$ (ref. 84), and to the synthesis of $Mn(CO)_4(C_4H_7)$ by decarbonylation of the σ- crotyl species (ref. 85) is made again. Also the formation of several substituted $Mn(CO)_{4-n}(L)_n(allyl)$ compounds (L = PEt_3, $P(OR)_3$, n = 2,3) is noted (ref. 32, 141). Reactions of these species with RSO_3H and with H_2 are reported, as is the use of $Mn(CO)(P(OMe)_3)_3(allyl)$ as a hydrogenation catalyst for alkenes.

Preparations of $[Re(C_5H_4PPh_3)(CO)_3]PF_6$ and $[Re(C_5H_4SMe_2)(CO)_3]PF_6$ are accomplished by reactions of substituted cyclopentadienyl ligand and $[Re(CO)_3(NCMe)_3]PF_6$ (ref. 36). Complexes of sulfonium ions, R_3S^+, were prepared by alkylation of disulfide complexes; these have the stoichiometry $[Mn(C_5H_5)(CO)_2SR_2R']PF_6$ (ref. 17, 148). An x-ray diffraction study yielded the molecular structure of $[Mn(C_5H_5)(CO)_2SMe_2Et]PF_6$. The preparation and study of $M(C_5H_4R)(CO)_2(CX)$ (M = Mn, Re; X = S, Se) compounds are described in a thesis (ref. 156); and the synthesis of $Mn(C_5H_5)(CO)_2(CS)$ appears in Inorg. Syn. (ref. 157). King and Gimeno have prepared $Mn(C_5H_5)(CO)(F_2PNMePF_2)$

and $Mn(C_5H_5)(F_2PNMePF_2)_2$ by photolyzing $F_2PNMePF_2$ and $Mn(C_5H_5)(CO)_3$ (ref. 158). Both compounds utilize one fluorophosphine as a bidentate ligand. In the second product the additional fluorophosphine ligand bonds in a monodentate fashion through phosphorus. Photolyses of $Mn(C_5H_5)(CO)_3$ with fulvenes give the products $Mn(C_5H_5)(CO)_2$(fulvene) and $[Mn(C_5H_5)(CO)_2]_2$ fulvene; the latter species has a structure in which each $Mn(C_5H_5)(CO)_2$- group is coordinated to one double bond in the five membered fulvene ring (ref. 159). Reaction of $Mn(C_5H_5)(CO)_2(THF)$ with 1,1-dimethylcyclopropene gives compound XXX (ref. 160).



(XXX)

Synthesis of $Mn(C_5H_5)(CO)(PhBCH{=}CHCH_2CH_2CH{=}CH)$ by a substitution reaction was mentioned earlier (ref. 111).

Photolysis of $Mn(C_5H_5)(CO)_3$ in an argon matrix at 20°K gives $Mn(C_5H_5)(CO)_2$ which is characterized by infrared spectroscopy. This primary photoreaction is not reversible (ref. 161).

Two papers report chemistry at a coordinated phosphorus ligand in $Mn(C_5H_5)(CO)_2L$ species. Consecutive treatment of $Mn(C_5H_5)(CO)_2PH_3$ with BuLi followed by either MeI or Me_3SiCl gave the products $Mn(C_5H_5)(CO)_2PMe_3$ and $Mn(C_5H_5)(CO)_2(P(SiMe_3)_3)$ (ref. 162). The compound $Mn(C_5H_5)(CO)_2(PMe_2SH)$, formed from $Mn(C_5H_5)(CO)_2(THF)$ and Me_2PSH, reacts with oxygen giving $[Mn(C_5H_5)(CO)_2PMe_2S]_2$. This compound also gives $[Mn(C_5H_5)(CO)_2(PMe_2S)]^-$, in situ, with either Et_3N or Na. This anionic species reacts with $Mn(C_5H_5)(CO)_2PMe_2Cl$ to give $Mn(C_5H_5)(CO)_2PMe_2SPMe_2Mn(CO)_2(C_5H_5)$ and with RCOCl to give $Mn(C_5H_5)(CO)_2(PMe_2SCOR)$. This latter compound decarbonylates on heating to form $Mn(C_5H_5)(CO)_2(PMe_2SR)$ (ref. 163).

Earlier mention was made of arsinidine and stibinidine complexes, $RA[Mn(C_5H_5)(CO)_2]$ (RA = ClAs, PhSb) (ref. 133, 134). Preparations of carbene complexes $M(C_5H_5)(CO)_2(COMeR)$ (R = menthyl, M = Mn (ref. 97); and M = Mn, Re; R = Bu, Ph (ref. 98) by standard routes are also given in the cited references. The preparation of $Mn(C_5H_4Me)(F_2PNMePF_2)(CMeOMe)$ by substitution of carbonyl groups in $Mn(C_5H_4Me)(CO)_2(CMeOMe)$ is noted (ref. 99).

Chemistry involving reactions at coordinated N_2 was covered earlier in this review, with diimine, hydrazine and ammonia complexes playing a significant role in reaction sequences (ref. 127, 128, 129). The formation of $[Mn(C_5H_5)(CO)_2CPh{=}CNBu^t]^+$ from $[Mn(C_5H_5)(CO)_2CPh]^+$ and t-BuNC (ref. 102) was also noted, as was the formation of a complex with a bridging phenylvinylidene ligand, $Mn(C_5H_5)(CO)_2(\mu\text{-}C{=}CHPh)Re(CO)_2(C_5H_5)$ (ref. 104). The carbonylation of $Mn(C_5H_4R)(CO)_2CPh_2$ gives $Mn(C_5H_4R)(CO)_2(Ph_2C{=}C{=}O)$ which

on treatment with hydrogen yields Ph_2CHCHO and Ph_2CHCH_2OH (ref. 101).

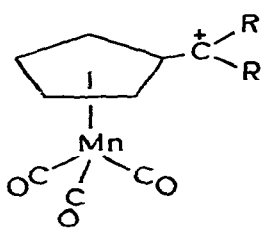
Papers on the electronic spectrum of $Mn(C_5H_5)(CO)_2(CPh_2)$ (ref. 100), and on the mass spectra for several vinylidene compounds , $M(C_5H_5)(CO)(C{=}CHPh)L$ have been published (ref. 103).

The gas phase proton affinity for $Mn(C_5H_4Me)(CO)_3$ has been found to be 825 ± 8 KJ/mol (ref. 164). Oxidation potential data for various $Mn(C_5H_5)$-$(CO)_{3-n}(L)_n$ compounds are reported (ref. 165).

INDO SCF molecular orbital calculations have been carried out on $Mn(C_5H_5)(CO)_3$ and on two other species, $Mn(C_5H_5)(C_6H_6)$ and $[Mn(C_6H_6)(CO)_3]^+$ (ref. 166). Correlations are offered between nucleophilic substitution reactions and frontier electron density parameters in a group of compounds which includes $Mn(C_5H_5)(CO)_3$ (ref. 167).

Various types of reaction chemistry involving either the cyclopentadienyl ring or a substituent group on the ring in $M(C_5H_4R)(CO)_3$ compounds have been reported mostly in Russian journals. One general interest seems to be complexes having two different metals. Thus one finds the syntheses of several $Mn(C_5H_4{-}X)(CO)_3$ compounds, X = $W(CO)_3C_5H_5$ and $COW(CO)_3C_5H_5$ (ref. 168); $Fe(CO)(PPh_3)(C_5H_5)$ and $COFe(CO)(PPh_3)(C_5H_5)$ (ref. 169). An anion radical derived from $Mn(C_5H_4COC_6H_5Cr(CO)_3)(CO)_3$ has been made and its esr spectrum recorded (ref. 170). Another reference describes the compound $Mn(C_5H_4X)(CO)_3$ (X = 2-Me_2NCH_2-1-$C_5H_3FeC_5H_5$) (ref. 171). Also of interest are the formation of $(CO)_3MnC_5H_4$-$C_5H_4Mn(CO)_3$ by two routes (ref. 172) and the formation of $Mn(C_5H_4CHO)(CO)_3$ from $Mn(C_5H_4Li)(CO)_3$ and DMF followed by hydrolysis (ref. 173).

The compounds $Mn(C_5H_4CO(CH_2)_nCN)(CO)_2$, XXX, in which the nitrile group coordinates in an intramolecular fashion to the metal, have been reported for n = 3, 4, 6 (ref. 174). Obviously, steric constraints pose some limitation to the compounds that can exist. The synthesis and structures of stabilized carbonium ions, $[Mn(C_5H_4CR_2)(CO)_2L]^+$ has been reported (ref. 175).



(XXXI)

Further structural studies on $Mn(C_5H_5)_2$ and $Mn(C_5H_4Me)_2$ have been published. Electron diffraction data on the latter species (ref. 176) indicates that two different forms of this compound are present in a gaseous sample. The more abundant species has a metal-carbon distance of 2.433(8) Å and is identified as a high spin complex while the less abundant of the two forms has a metal-carbon distance of 2.144(12) Å and is characterized as a low spin complex. The structure of $Mn(C_5H_5)_2$ has been determined crystallo-

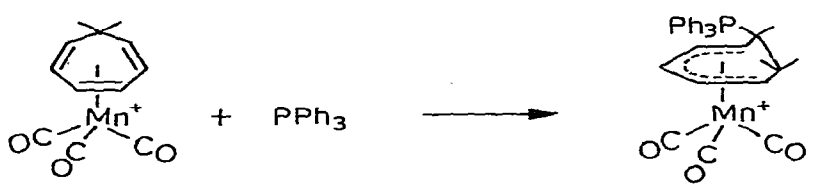
graphically (ref. 177). This compound has a polymeric structure. The long metal carbon bonds indicate a mode of bonding which is primarily ionic.

Cyclic voltammetry on $Mn(C_5Me_5)_2$ identifies both one-electron oxidation and a one electron reduction process (ref. 178). This compound, an air sensitive red-orange solid, is prepared from LiC_5Me_5 and $MnCl_2$ in THF and purified by sublimation and recrystallization. Magnetic studies indicate a low spin configuration (μ_B = 1.97 BM at 313°K). Chemical reduction with sodium naphthalide gives $Na[Mn(C_5Me_5)_2]$, a diamagnetic pyrophoric solid.

Referred to earlier in this review was a study of the reducing ability of various metal hydride species including $Re(C_5H_5)_2H$ (ref. 75). Discussion was also included earlier on heterocyclic systems complexed to these metals; included were complexes of the pyrollyl anion (ref. 123), several phosphollyl ligands (ref. 124, 125); and an arsollyl ligand (ref. 126).

The preparation of $[Mn(arene)(CO)_3]^+$ complexes can be accomplished from $Mn(C_5H_5)(CO)_3$, $AlBr_3$, and the arene (arenes = benzene, mesitylene, toluene). This type of reaction is similar to reactions which have been used to prepare $[Fe(C_5H_5)(arene)]^+$ complexes from ferrocene; the presence of $AlBr_3$ labilized the cyclopentadienyl ring in these precursors (ref. 179). Several reactions of $[Mn(ArN_3)(CO)_3]^+$ are reported (ref. 180). These include reduction by $LiAlH_4$ to give $[Mn(ArNH_2)(CO)_3]^+$, substitution of N_3^- by OMe^-, and pyrolysis at 130°C. This last reaction gives $Mn(C_5H_4CN)(CO)_3$.

Kinetics for the reaction of $[Mn(C_7H_8)(CO)_3]PF_6$ with PPh_3 have been measured (ref. 181). This reaction occurs with addition of the phosphine to the complexed hydrocarbon ring, as shown in Eq. 13.



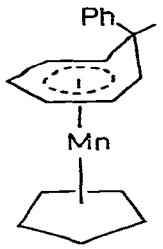
EQ. 13

Mass spectra of a series of $Mn(RC_7H_8)(CO)_3$ compounds indicate that two competing fragmentation processes are involved (ref. 182). These are the loss of CO, a typical process for metal carbonyls, and a loss of the R group. Compounds investigated included those with R = H, CN, OMe, OEt, OBu^t, NHMe, NHPh.

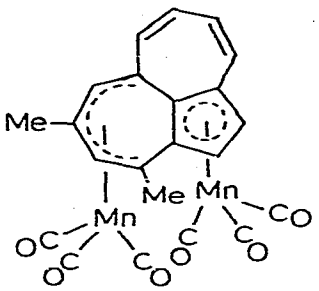
Structures have been determined by diffraction methods for $Mn(C_5H_4Me)$-(C_7H_7Ph), XXXII (ref. 183), and for $Mn_2(CO)_6$(3,5-dimethylheptylene), XXXIII (ref. 184).

INDO SCF molecular orbital calculations are reported for $Mn(C_5H_5)(CO)_3$ (ref. 166), $[Mn(C_6H_6)(CO)_3]^+$ (ref. 166), $Mn(C_5H_5)(C_6H_6)$ (ref. 166, 185), $[Mn(C_6H_6)_2]^+$ and $[Mn(C_5H_5)(C_7H_7)]^+$ (ref. 186).

References p. 155



(XXXII)



(XXXIII)

IX. VARIOUS ISOCYANIDE AND NITROSYL COMPOUNDS ($[M(CNR)_6]^+$, $Mn(CO)_{4-n}L_nNO$, $Mn(NO)_3L$, $[M(C_5H_5)(CO)_2NO]^+$)

Compounds in these categories are not being as actively investigated now as they were in the last few years. Consequently there are only a few references cited here.

The compound $Mn_2(CO)_4(dpm)_2(CNtol)$, having a CNR group bridging the two metals and serving as a four electron donor was described a year ago. The structure of this compound is reported in a full paper (ref. 18) and in a thesis (ref. 8). Reactions of cis-$Mn(CO)_4(CNR)COMe$ with MeLi followed by AlX_3 give chelating compounds $[Mn(CO)_4(COMe)(C{=}NR)]_3Al$ (ref. 89). The synthesis of $Mn(CO)_3(CNR)(S_2CNHR)$ as a by-product in the reaction of $Na[Mn(CO)_5]$ and RNCS is described (ref. 145). The product of the reaction of $Mn(CO)_5Br$ and Me_3NBH_2NC is cis-$Mn(CO)_4(CNBH_2NMe_3)Br$ (ref. 52). The reaction of $Mn(CO)_5CH_2Ph$ and several isocyanides gives $Mn(CO)_4(CNR)COCH_2Ph$ as a mixture of isomers. This compound decarbonylates to give cis-$Mn(CO)_4$-$(CNR)CH_2Ph$, which reacts with a constrained phosphite ligand (L) to give fac- and mer- $Mn(CO)_3(CNR)(L)COCH_2Ph$ (ref. 82).

The synthesis of $Mn(CO)(NO)_3$ is given in Inorg. Syn. (ref. 187). Photolysis of this compound in an argon matrix at 20°K gives $Mn(NO)_3$ which is identified spectroscopically (ref. 188). The structure of $Mn(NO)_3(PPh_3)$ is reported in a thesis (ref. 74).

Another Inorg. Syn. article describes the preparations of $Re_2(CO)_5(NO)Cl_3$ and $[Re(CO)_2(NO)Cl_2]_2$ (ref. 39). The compound $[Mn(C_5H_4Me)(CO)(NO)]_2$ is converted to $Mn(C_5H_4Me)(CO)_3$ and $Mn_3(C_5H_5)_3(NO)_4$ when refluxed in THF (ref. 57). The conversion of $Mn(NO)_2(L)_2Cl$ (L = $PPhMe_2$, $PPh(OMe)_2$, $P(OMe)_3$) to $[Mn(NO)_2L_3]PF_6$, and the reactions of this latter species with t-BuNC to give $[Mn(NO)_2(L)_2(CNBu^t)]PF_6$ are recorded (ref. 58).

X. STRUCTURAL STUDIES

Compounds whose structures have been determined by x-ray crystallography or electron diffraction are listed: $Re_2(CO)_8[C(p\text{-}tol)OMe]_2$ (ref. 13); $Mn_2(CO)_4(CN\text{-}p\text{-}tol)(dpm)$ (ref. 18); [fac-$Mn(CO)_3(NH_3)_3$]$Mn(CO)_5$ (ref. 20);

$TcCl_3(CO)(PPhMe_2)_3$ (ref. 38); $[OEPH_3][Re_2(CO)_6Cl_3]$ (ref. 56); $Re_2Br_2(CO)_6(THF)_2$ (ref. 50); $Re(CO)_5$-F-ReF_5 (ref. 59); $Re_2Br_2(CO)_6(Ph_2PPPh_2)$ (ref. 60); $ReBr_3(CO)_2(bipy)$ (ref. 61); $Re_3Cl_3(CH_2SiMe_3)_6$ (ref. 62); $Et_4N[Re(CO)_4H_2]$ (ref. 70); $(Et_4N)_2[Re_3(CO)_{12}H]$ and $(NEt_4)_2[Re_4(CO)_{16}]$(ref. 71); $Mn(CO)_3(PPh_3)_2H$ (ref. 72); $H_2Os_3Re_2(CO)_{20}$ (ref. 73); $H_4Re_4(CO)_{12}$ and $Mn(NO)_3(PPh_3)$ (ref. 72); $Re(PPhEt_2)_2Ph_3$(ref. 77); $PPN[\overline{Mn(CO)_4COCHPhOCO}]$ (ref. 95); $Mn(CO)_3B_3H_8$ (ref. 110); $[(CO)_5Re)_2InX]_2$ (three structures, X = Cl, Br, I) (ref. 113); $Mn_2(CO)_8$-$[\mu$-$SnClMn(CO)_5]_2$ and $BrSn[Mn(CO)_5]_3$ (ref. 119); $Mn(CO)_3C_4H_4N \rightarrow Mn(CO)_2(C_5H_5)$ (ref. 123); 2-PhCO-3,4-$Me_2C_4HPMn(CO)_3$ (ref. 124); $[Mn(CO)_4NSOF_2]_2$ (ref. 131); $ClAs[Mn(C_5H_5)(CO)_2]_2$ (ref. 133); $PhSb[Mn(C_5H_5)(CO)_2]_2$ (ref. 134); cis-$Mn(CO)_4$-$(PMe_3)AsMe_2Fe(CO)_4$ and trans-$Mn(CO)_4(PMe_3)AsMe_2Fe(CO)_4$ (ref. 136); $[Mn(CO)_4PMe_2]_2$ (ref. 137); $[Ph_2PO_2Re(CO)_4]_2$ (ref. 139); $Mn_2(CO)_6[SC(SMe)(NMe)]_2$ (ref. 145); $[Re(CO)_3(PMe_3)_2]_2Se$ (ref. 146); $[Mn(C_5H_5)(CO)_2SMe_2Et]PF_6$ (ref. 148); $Mn(C_5H_4Me)_2$, electron diffraction (ref. 176); $Mn(C_5H_5)_2$ (ref. 177); $Mn(C_5H_4Me)(C_7H_7Ph)$ (ref. 183); $Mn_2(CO)_6$(1,3-dimethylheptylene) (ref. 184).

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