MANGANESE, TECHNETIUM, AND RHENIUM

ANNUAL SURVEY COVERING THE YEAR 1977*

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CONTENTS

I. INTRODUCTION

The number of articles per year on manganese, technetium, and rhenium organo-
metallic chemistry has remained quite constant. For the third consecutive year over
180 articles were available to be abstracted for this review. A substantial number
of references are from the new Journal of Chemical Research. A marked increase in
the number of papers on derivatives of Groups IVA, VA, and VIA with manganese and
rhenium is noted. There has also been a continued and expanded interest in
mechanistic considerations in the descriptive chemistry of this group, particularly
when radical species are implicated as intermediates. Otherwise no substantial
trends are identified, with a balance among synthetic chemistry, studies on
physical properties and theory, and structural studies being little changed from

previous years.

The organization of this review generally follows that established in previous years. A minor change is noted wherein Section IV, a large section previously, is divided into two new sections. Section IV now covers hydrides only, and new Section V is on carbon ligands (other than CO and CS). Overall, the organization is based on compound type, with some effort being made to cross-reference articles following two or more classifications. A list of compounds which have been subject of structural studies is given at the end.

The reference to the ANNUAL SURVEY article for last year, 1976, is noted (ref. 1).

II. METAL CARBONYLS AND DERIVATIVES OBTAINED BY CARBONYL SUBSTITUTION

$$([M(CO)_{5-n}L_n]^-, M_2(CO)_{10-n}L_n, [M(CO)_{6-n}L_n]^+)$$
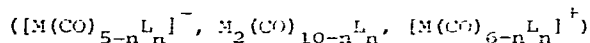
Work on reactions of the various metal carbonyls and their substituted derivatives has appeared from Poë and coworkers (refs. 2,3). This work further implicates radical intermediates formed by metal-metal bond dissociation. The rates of reactions of $[Mn(CO)_4P(OPh)_3]_2$ with O_2, CO, PPh_3, and $P(OPh)_3$ were measured in decalin. The rate of the reaction with oxygen as a function of concentration of the metal complex supports a mechanism in which the first step is metal-metal bond dissociation (ref. 2). Likewise the kinetics of $[Mn(CO)_4PPh_3]_2$ reactions with CO, O_2, and PPh_3 are in accord with this type of mechanism (ref. 3). In solutions of $[Mn(CO)_4PPh_3]_2$ and PPh_3 new carbonyl stretching frequencies at 1988w, 1938m, 1861s cm^{-1} are detected, as is an absorption in the visible region at 425 nm. It is suggested that these data relate to a 17e complex $Mn(CO)_3(PPh_3)_2$ which, however, could not be isolated from these solutions.

Electrochemical reduction potentials for six dinuclear metal carbonyls ($M_2(CO)_8L_2 + 2e \rightleftharpoons [M(CO)_4L]^-$; $M_2 = Mn_2$, Re_2, MnRe; L = CO, PPh_3) were recorded (ref. 4). Reduction potential values for the PPh_3 substituted complexes are more cathodic than the values for the unsubstituted species, and correlate with ultraviolet spectral data on $\sigma \rightarrow \sigma^*$ transitions. This observation is used to support the assertion that the metal-metal bond is weakened by phosphine substitution.

Two notes have appeared on the reactions of $Re_2(CO)_{10}$ with phosphorus ligands (refs. 5,6). Reaction with PPh_3 gives either $[Re(CO)_4(PPh_3)]_2$ or $Re(CO)_3(PPh_3)_2H$ depending on temperature and on the method of workup (ref. 5); the formation of products via a radical pathway is suggested. The same result is seen with $P(p-tol)_3$ reactions. However with $P(o-tol)_3$ the only product is an ortho-metallated species $\overline{Re(CO)_4P(o-tol)_2(o-C_6H_4CH_2)}$. Reactions with several phosphites (= L) were also run in refluxing xylene. The products include $Re_2(CO)_8L_2$, $Re_2(CO)_9L$ and $Re(CO)_3(L)(L-H)$, the last of the products (found with $P(OPh)_3$ only) also being an ortho-metallated compound (ref. 6).

Flash photolysis of $Mn_2(CO)_{10}$ in cyclohexane or THF gives as the dominant photoproduct $Mn(CO)_5$, vis:

$$Mn_2(CO)_{10} + h\nu \;\rightleftharpoons\; 2Mn(CO)_5$$
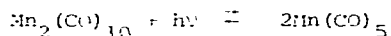
An input of 36 Kcal is required and the product dimerizes with a rate which is essentially diffusion controlled (ref. 7). A second long-lived intermediate is also detected but not identified. Irradiation of $Mn_2(CO)_{10}$ in the presence of a spin trapping nitroxyl reagent yields the stable $Mn(CO)_5NOR$ radical which can be characterized by its 18 line esr spectrum (ref. 8).

Reactions of $[Mn(CO)_4L]_2$ species (L = various phosphines and $PPh(OMe)_2$) with t-BuNO in the dark give $Mn(CO)_4LNOBu^t$ products, again detected by their esr signals. If these reactions are run in pyridine then $Mn(CO)_4(py)NOBu^t$ is the product (ref. 9) A radical species, $Mn(CO)_5$, is implicated in reactions of $[Mn(CO)_5]^-$ with $[CPh_3]BF_4$ and with $[C_7H_7]BF_4$, but not in reactions of $[Mn(CO)_5]^-$ with alkyl halides (ref. 10). This latter result contrasts with the similar reactions of the anion $[Fe(C_5H_5)(CO)_2]$ which are apparently radical processes. Reactions of $[M(CO)_5]^-$ with $M(CO)_5X$, $M(CO)_3(L\frown L)X$, and $Re(CO)_3(py)_2X$ (M = Mn, Re; $L\frown L$ = bipy, o-phen, dpe), to give the products $M_2(CO)_8L_2$, are suggested to proceed with prior electron transfer from $[M(CO)_5]^-$ to $M(CO)_3L_2X$ (Ref. 11). Finally, photolysis reactions of $Re_2(CO)_{10}$ and $Mn_2(CO)_{10}$ with hydrogen are believed to occur via $M(CO)_5$ radicals; in the former reaction a mixture of products arises including $Re(CO)_5H$, $Re_3(CO)_{14}H$, $Re_2(CO)_8H_2$, $Re_3(CO)_{12}H_3$; in the latter only $Mn(CO)_5H$ is a product (ref. 12).

The reactions of $Mn_2(CO)_5(dpm)_2$ with several isocyanides was studied (ref. 13). Initially a simple adduct is formed in a reversible reaction; vis:

$$Mn_2(CO)_5(dpm)_2 + L \;\rightleftharpoons\; Mn_2(CO)_5(L)(dpm)_2$$
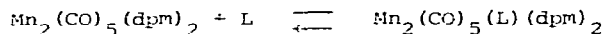
(L = MeNC, p-tolNC, benzylNC)

In the case of the p-tolNC carbon monoxide can be displaced upon heating; the product $Mn_2(CO)_4(CNtol)(dpm)_2$, I, has the isocyanide in an unsymmetric bridging position between the two metal atoms.

(I)
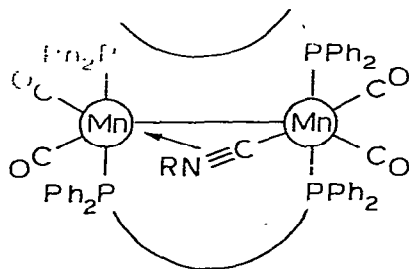
Manganese carbonyl is known to catalyze reactions of carbon monoxide and primary amines to give urea. In a study related to this reaction the equilibrium below was shown to exist:

$$Mn_2(CO)_{10} + 3RNH_2 \rightleftharpoons cis\text{-}Mn(CO)_4(RNH_2)(CONHR) + [RNH_3]^+[Mn(CO)_5]^-$$
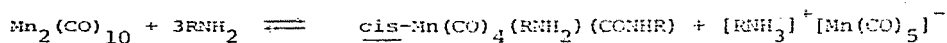
(R = Cyclohexyl, n-butyl)

Applying CO pressure to the system leads to the formation of urea (ref. 14).

Cobalt-60 gamma irradiation of $M_2(CO)_{10}$ (M = Mn, Re) at 77°K gives a substance which has an esr signal typical of two strongly coupled nuclei (ref. 15).

Little work on anionic metal carbonyl complexes has appeared. In addition to the paper referred to earlier on the electrochemical reductions of the dimeric carbonyls (ref. 4) there is another paper on electrochemical reductions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in a molten salt medium (ref. 16). These electrochemical processes could have some potential in the syntheses of metal carbonyl anions. More significant as a synthetic route to the metal carbonyl anions in the laboratory, however, is the procedure described by Gladysz and coworkers (ref. 17). In this work $LiBHEt_3$ and $Mn_2(CO)_{10}$ was found to generate a solution of $Li[Mn(CO)_5]$ in high yield. As a preparative method this route is notable for its lack of side products, and because the use of mercury can be avoided. An interesting mechanism for this reaction, via an intermediate formyl compound, $[(CO)_5MnMn(CO)_4CHO]^-$, is suggested.

It may be observed that reactions of metal carbonyls with $LiBHEt_3$ is a general route to formyl complexes; however this reagent does not react with $Mn(C_5H_4Me)(CO)_3$ (ref. 18).

A further paper has appeared on the highly reduced species $M(CO)_4^{3-}$ (M = Mn, Re), prepared from either $M_2(CO)_{10}$ or $M(CO)_5^-$ by reductions using sodium in HMPA (ref. 19). Reactions of these species with benzyl chloride gave $[M(CO)_4(COCH_2Ph)_2]^-$; organo-tin, -germanium, and -lead derivatives $[Mn(CO)_4(AR_3)_2]^-$ (AR_3 = Ph_3Sn, Ph_3Pb, Ph_3Ge, Me_3Ge, Me_3Sn) were also prepared as were gold complexes $M(CO)_4(AuPPh_3)_3$. These compounds contain a seven coordinate metal atom. The extensive chemistry of highly reduced metal carbonyls is described in a thesis (ref. 20).

The preparations of quite a large number of cationic carbonyl complexes have been reported. Edwards and Marshalsea (ref. 21) prepared over twenty fac-$[M(CO)_3L_3]^+$ complexes from $[M(CO)_3(NCMe)_3]^+$ (M = Mn, Re) by displacement of one or more of the coordinated acetonitrile ligands with nitrogen, phosphorus, and sulfur donors. They also compiled infrared ($\nu(CO)$), ^1H and ^{31}P nmr data on these compounds. Reported in another paper are reactions of $Mn(CO)_3(o\text{-phen})X$ with $AgClO_4$ in acetone, which give $[Mn(CO)_3(o\text{-phen})acet]ClO_4$ (ref. 22). In a different noncoordinating solvent, dichloromethane, the covalent perchlorate complex, $Mn(CO)_3(o\text{-phen})OClO_3$,

is obtained. The acetone complex can be used as a precursor to $[Mn(CO)_3(o\text{-phen})L]^+$, $[Mn(CO)_2(o\text{-phen})L_2]^+$ complexes may also be formed on occasion. Reaction of $Mn(CO)_5Br$ and the bidentate ligand $o\text{-}C_5H_4NNHPPh_2$ (an ortho substituted pyridine, abbreviated here as $N^\frown P$) gives both $Mn(CO)_3(N^\frown P)Br$ and $[Mn(CO)_2(N^\frown P)_2]Br$ (ref. 23). A full paper on isomeric cis and trans $[Mn(CO)_2(CNMe)_4]^+$ and mer and fac-$[Mn(CO)_3(CNMe)_3]^+$ complexes has appeared (ref. 24). The oxidation potentials ($E_{1/2}$ values) of these complexes were recorded and are correlated with calculated HOMO energies. The chemistry involved in formation of various $[Mn(CO)_{6-n}(CNMe)_n]^+$ complexes is described in a thesis (ref. 25).

An attempted oxidation reaction of $(Bu_4N)_2Re_4(CO)_{16}$ with $AgBF_4$ in acetonitrile gave an unexpected cationic complex fac-$[Re(CO)_3(NCMe)_3]BF_4$. A crystal structure study has been carried out on this complex (ref. 26). The preparation of several $[Re(CO)_{6-n}(L)_n]^+$ complexes (L = CNMe, CNtol) can be accomplished from reactions of $Re(CO)_{5-n}L_nBr$, a halide acceptor, and L or CO (ref. 27). This work is part of a general study on isocyanide-rhenium(I) complexes.

A series of cationic halide bridged complexes $[(CO)_5MXM'(CO)_5]AsF_6$ (M, M' = Mn, Re) is reported (ref. 28); they are prepared by three related methods. Reactions of $[M(CO)_5(SO_2)]AsF_6$ and $M'(CO)_5X$ give manganese and rhenium complexes with bridging chloride or bromide ions. The direct reaction of $M(CO)_5Br$ with $AgAsF_6$ can also be used to prepare the bromide bridged species. To prepare the iodide complex a route is used which involves addition of $[M(CO)_5(SO_2)]AsF_6$ to I^- in a stoichiometric (2:1) ratio.

There are three papers from Darensbourg and Froelich describing nucleophilic reactions at coordinated carbon monoxide in cationic carbonyl complexes. In the first (ref. 29) the reactions of $[Mn(CO)_5L]^+$ (L = PPh_3, PMe_2Ph, $Ptol_3$, $P(OCH_2)_3CEt$) and also of $[Re(CO)_5(PPh_3)]^+$ with NaSH are shown to give the metal hydrides, cis-$M(CO)_4(L)H$, by initial addition of SH^- to a coordinated carbonyl followed by β-hydrogen transfer to the metal. A second paper reports ^{18}O exchange between $[Mn(CO)_5L]^+$ (L = phos, py, MeCN) and $H_2{}^{18}O$ (ref. 30). This process is found to be slower than analogous exchange reactions with $[M(CO)_6]^+$, the non-carbonyl ligand hindering the β-hydrogen transfer step. Isotopic $^{16}O\text{-}^{18}O$ exchange reactions are shown (ref. 31) to occur preferentially with a carbonyl group cis to the substituent group L. These reactions are catalyzed by the base Et_3N.

Reaction of $[Re(CO)_4(dpe)]^+$ with Ph_3SiLi gave the first known silylacyl metal carbonyl complex, $Re(CO)_3(dpe)COSiPh_3$ (ref. 32). A structure for this compound was determined crystallographically.

The ^1H nmr spectra of several acetonitrile complexes including $[Mn(CO)_3(NCMe)_3]^+$ have been reported (ref. 33). An unusual chemical shift for the methyl protons of the coordinated acetonitrile is measured in these compounds.

There are two structural studies on rhenium-osmium mixed metal carbonyls. (ref. 34, 35). These are discussed in Section VI.

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

Technetium gets little emphasis in this review, so an article on the synthesis of various technetium carbonyl halides seems a good place to start. Mazzi et al. (ref. 36) have run carbonylation reactions with some phosphine complexes of technetium halides. Addition of carbon monoxide to several trans-TcX_4L_2 compounds (X = Cl, Br; L = PPh$_3$, PPhMe$_2$) in refluxing DMF gives trans-$Tc(CO)_3L_2X$. From mer-$TcX_3(PPhMe_2)_3$ and CO, one obtains either $Tc(CO)_3(PPhMe_2)_2X$ or $Tc(CO)_2(PPhMe_2)_3X$, the latter product is obtained exclusively if excess phosphine is present. Refluxing mer-$TcCl_3(PPhMe_2)_3$ in ethanol gives a technetium(III) carbonyl, $Tc(CO)$-$(PPhMe_2)_3Cl_3$.

Preparations of many substituted metal carbonyl halides, $M(CO)_{5-n}(L)_nX$ can be cited. Reactions of $Mn(CO)_5X$ compounds with various phosphorus ligands give trans-$Mn(CO)_3L_2X$ species; only with SbPh$_3$ is the fac isomer of this stoichiometry obtained (ref. 37). Vahrenkamp and coworkers have described compounds where a diphosphine P_2Me_4 bridges two metals. Compounds prepared include $(CO)_4FePMe_2PMe_2$-$Mn(CO)_4Br$ (ref. 38). Data on ^{31}P nmr spectra for these compounds are reported in a separate paper (ref. 39).

Lindner and Schilling (ref. 40) have carried out reactions of $Mn(CO)_5Br$ and $Re(CO)_5X$ (X = Cl, Br, I) with secondary phosphine oxides, $G = PHR_2$ (R = Me, Ph); very stable monosubstituted metal complexes, $M(CO)_4(PR_2OH)X$, containing a phosphorous acid ligand result. When $Mn(CO)_4(PPh_2OH)Br$ is treated with NH_3, elimination of HBr occurs with formation of the dimeric compound $[Mn(CO)_4(PPh_2)]_2$ (ref. 41). The crystal structure of this compound was determined to be II, below:

(II)
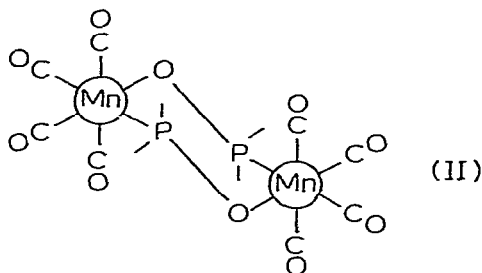
The structure of a similar complex of rhenium, $[Re(CO)_4(PMe_2O)]_2$, is also reported (ref. 42). Reactions of these metal carbonyl halides with secondary phosphine sulfides and selenides have been carried out by the same workers (ref. 43). These reactions, run at 60°-85°C, proceed differently; they give $M(CO)_4(A=PHR_2)X$ compounds, products where the substituting ligands have not rearranged. The ligand bonds to the metal through sulfur or selenium. If the sulfur complexes are heated to 120° they rearrange to $M(CO)_4(PR_2SH)X$; however the selenium compounds eliminate H_2Se when heated giving $M(CO)_4(PR_2H)X$. Both phosphine sulfide and phosphine selenide compounds when treated with base are found (ref. 44) to give

dimeric species $[M(CO)_4(PR_2X)]_2$ (X = S, Se), similar in structure to the dimeric phosphine oxide compound described above. A different route to these complexes from $[(CO)_4MXSnMe_3]_2$ and Me_2PCl is also noted (ref. 45).

Substitution products $Mn(CO)_3(P^\frown N)Br$ and $[Mn(CO)_2(N^\frown P)_2]^+$ derived from o-diphenylphosphinaminopyridine ($N^\frown P$) and $Mn(CO)_5Br$ were described earlier (ref. 23)

Reactions of NOCl with various metal carbonyls have been studied. With $Mn_2(CO)_{10}$ the product obtained is $Mn(CO)_5Cl$ (ref. 46).

The reactions of $Re(CO)_5Cl$ with both MeNC and tolNC using various conditions have been studied (ref. 27). Generally they are much slower than similar reactions of the manganese counterparts, and higher temperatures are required to achieve multiple carbonyl substitutions. Perhaps the most intriguing part of this work deals with various isomers which can be separated and characterized in these reaction systems. For example, fac-$Re(CO)_3L_2Cl$ is found to rearrange to the mer-trans isomer on heating. Also three isomers of the compounds $Re(CO)_2L_3Cl$ which arise under different circumstances were identified.

Reactions of α- and β-alanine (= al) with $Re(CO)_5Br$ were found to give fac-$Re(CO)_3(al)Br$ where the amino acid coordinates in a bidentate manner through nitrogen and one oxygen (ref. 47). The amino acid ligand is easily displaced by PPh_3 or $P(OPh)_3$. Addition of KOH to the α-alanine product gives a polymeric species $[Re(CO)_3(H_2NCHMeCO_2)]_x$ which with added ligands give monomeric $\overline{Re(CO)_2(L)_2H_2NCHMeCO}(=O)$; with KOH in THF the β-alanine product gives $\overline{Re(CO)_3(THF)H_2NCHMeCO}(=O)$.

The electrochemistry of fac-$Mn(CO)_3(dpm)X$ (X = Cl, Br) has been looked at in some detail (ref. 48). This complex undergoes a one-electron oxidation to give initially fac-$[Mn(CO)_3(dpm)X]^+$. This 17e complex is not stable however, rearranging to the mer- isomer which is stable and can be isolated. The mer- isomer had previously been mischaracterized as having fac- geometry. Reduction of mer-$[Mn(CO)_3(dpm)X]^+$ gives mer-$Mn(CO)_3(dpm)X$ which cannot be isolated; they decompose to non-organometallic compounds.

Mentioned earlier were reactions of $M(CO)_5^-$ (M = Mn, Re) with $M(CO)_5X$ and with various substituted derivatives $M(CO)_{5-n}L_nX$. These reactions probably occur with electron transfer to the metal carbonyl halide species (ref. 11). This means such reactions are presumably giving transient 19e $[M(CO)_{5-n}L_nX]^-$ complexes which lose X^- ions.

Several interesting rhenium(II) carbonyl halides, $Re(CO)_2(PR_3)_2Cl_2$ (R = n-propyl, ethyl) are formed on carbonylation of $Re_2X_4(PR_3)_4$ (ref. 49). Carbonylation is occurring here with concurrent cleavage of the metal-metal quadruple bond. Note that rhenium(II) organometallic compounds are relatively rare as yet.

The reactions of $Re(CO)_5Br$ and arenes give the ionic species $[Re(arene)(CO)_3]$ $[Re_2(CO)_6Br_3]$ as a byproduct (ref. 50), the main product being $[Re(arene)(CO)_3]Br$. A structure determination for the toluene compound showed that the anion contains two rhenium tricarbonyl groups bridged by three halide ions; no metal-metal bond is necessary and consequently the rhenium-rhenium distance in the anion is long.

When $Re(CO)_3(THF)_2Br$ is reacted with PhSSPh in THF the compound $Re_2(CO)_6Br_2^-$ (PhSSPh) is formed (ref. 51). Its structure was determined by X-ray diffraction techniques and is shown below. The structure determination of a similar compound derived from MeSSMe is also reported (ref. 52).

$$PhS \text{————} SPh$$

(III)
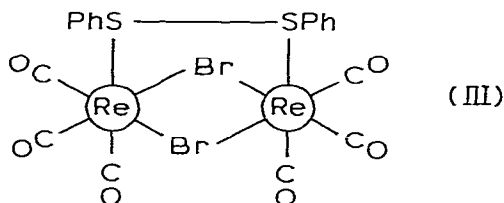
This latter compound exists in solution in equilibrium with its precursors; vis:

$$Re_2(CO)_6Br_2(MeSSMe) + 2HF \rightleftharpoons Re(CO)_3(THF)_2Br + MeSSMe$$
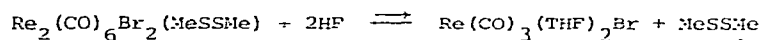
An equilibrium constant for this reaction was determined.

Two cyclopentadienyl-manganese halide compounds have been reported. When $Mn(C_5H_4Me)(CO)_2(PPhMe_2)$ is reacted with iodine the isolated product is $[Mn(C_5H_4Me)(CO)_2(PPhMe_2)I]I_9$ (ref. 53). Treatment of $[Mn(C_5H_4R)(NO)(CO)(CS)]^-$ (R = H, Me) compounds with KI gives $Mn(C_5H_4R)(NO)(CS)I$ (ref. 54); this product was also subjected to further reactions which are described later in this review.

The chemistry of $[Re(CO)_3]_2TTP$ (TTP = tetraphenylporphin) with $SbCl_5$ has been studied; this reaction gives $[\{Re(CO)_3Cl\}_2TTP]_2SbCl_6$. An X-ray diffraction study was used to determine the structure of this compound (ref. 55).

Carbon-13 nmr spectra were reported for $M(CO)_5X$ and $M(CO)_5H$ compounds (M = Mn, Re) (ref. 56). These compounds are stereochemically rigid on the nmr timescale. Manganese-55 nmr spectra were recorded for $Mn(CO)_5X$ (X = halide, SCN, H) (ref. 57). Photolyses of $M(CO)_5X$ (M = Mn, Re; X = Cl, Br) were carried out at 77°K in 2-methyltetrahydrofuran. The products arising from carbonyl loss were investigated by infrared spectroscopy (ref. 58).

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

Several papers on syntheses of metal carbonyl hydrides have already been cited in this review. These include: the preparation of cis-$Mn(CO)_4(L)H$ {L = several phosphines) and cis-$Re(CO)_4(PPh_3)H$ from the appropriate complexes $[M(CO)_5L]^+$ and NaSH (ref. 29); the preparation of mer-$Re(CO)_3(PPh_3)_2H$ and/or $Re_2(CO)_8(PPh_3)_2$ from $Re_2(CO)_{10}$ and PPh_3 (ref. 5), and a similar preparation of $Re(CO)_3[P(p-tol)_3]_2H$

using $P(p-tol)_3$ (ref. 6). A paper on the photolysis of $Re_2(CO)_{10}$ in the presence of hydrogen giving $Re(CO)_5H$, $Re_2(CO)_8H_2$, $Re_3(CO)_{12}H_3$ and $Re_3(CO)_{14}H$ and the photolysis of $Mn_2(CO)_{10}$ and hydrogen giving $Mn(CO)_5H$ was also referenced earlier (ref. 12). In the same paper, reactions of $Re(CO)_5H$ with PPh_3 and PBu_3 using 310 nm ultraviolet radiation were noted. The reactions, giving $Re(CO)_4(L)H$ and $Re(CO)_3(L)_2H$, are said to proceed via radical processes. On the other hand, the kinetics of thermal reactions of $Mn(CO)_5H$ with several ligands (L = PBu_3, PPh_3, $AsPh_3$, CO) in hexane, were found to be first order in each reagent. This information was used to suggest a mechanism involving hydrogen migration to an adjacent carbonyl to form an intermediate 16e formyl complex, $Mn(CO)_4(CHO)$. Relative rates of these reactions as a function of ligand decreased in the order given above (ref. 59). Mention was made of another formyl complex, $[(CO)_5Mn-Mn(CO)_4CHO]^-$, an intermediate in the $LiBHEt_3-Mn_2(CO)_{10}$ reaction. earlier in this review (17).

The reactions of $Re(CO)_5H$ and PF_3 were run. Compounds having all possible stoichiometries $Re(CO)_{5-n}(PF_3)_nH$ (n = 1-5) are found, all possible isomers being seen (ref. 60).

Manganese carbonyl hydride reduces α-methyl styrene to 2-phenylpropane. Manganese decacarbonyl is also formed (ref. 61).

An electron diffraction study on $Mn(CO)_5H$ is reported (ref. 62). The structure found is one previously determined by neutron diffraction; the value for d(Mn-H) is 1.576(18) Å. Carbon-13 nmr spectra for $M(CO)_5H$ (M = Mn, Re) are reported (ref. 56) as are PES data on the series of $Mn(CO)_{5-n}(PF_3)_nH$ complexes (ref. 63).

Much work has been carried out on polynuclear metal carbonyl hydrides. Facile deuterium-hydrogen exchange between D_2O and $Re_2(CO)_8H_2$ is observed (ref.64). This process was monitored by mass spectrometry, and a method of standardization of this data is provided. Refluxing $(NEt_4)_2[Re_4(CO)_{15}H_4]$ in ethanol gives the new anionic complexes $[Re_3(CO)_{10}H_4]^-$, $[Re_3(CO)_{10}H_3]^{2-}$, and $[Re_3O(CO)_9H_3]^{2-}$, along with $[Re_3(CO)_{12}H_2]^-$ and $[Re_4(CO)_{12}H_6]^{2-}$ which had been reported previously (ref. 65). The structure of the anion $[Re_3O(CO)_9H_3]^{2-}$, crystallized as the bis-NEt_4 salt, was determined by X-ray diffraction techniques; it was found that, its structure consists of a Re_3O tetrahedron, with the hydride ligands bridging the metal-metal edges (ref. 66). The structure of the anionic complex $[Re_4(CO)_{12}H_6]^{2-}$ was determined as the $[NMe_3(CH_2Ph)]^+$ salt (IV). The metal atoms are in a tetrahedral arrangement and the hydrides bridge the six edges; the mean Re-Re distance is 3.157 Å (ref. 67). The compound $NEt_4[Re_3(CO)_{10}H_4]$ was also studied intensively by a combination of spectroscopic techniques and X-ray crystallography (ref. 68). Its structure is drawn below. The rhenium atoms linked by two hydride bridges are found at a distance of 2.821(7) Å, suggesting double-bond character, whereas the average of the two remaining rhenium-rhenium distances is 3.18 Å, the predicted single bond length.

(IV)

(V)
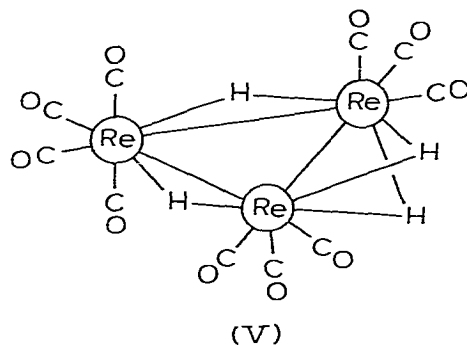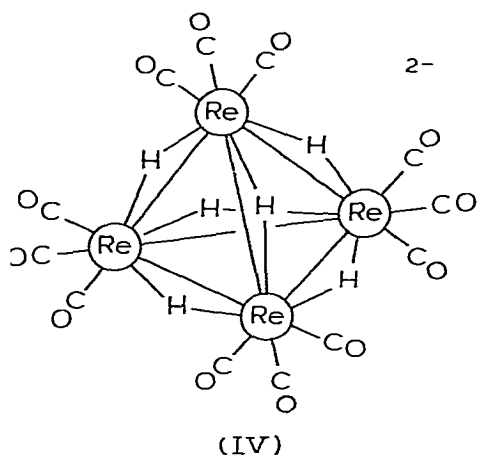
The structures of two compounds derived from $Re_2(CO)_{10}$ and Et_2SiH_2 are subjects for two papers (refs. 69, 70). These compounds have the formulas $Re_2(CO)_6(H)_4(SiEt_2)_2$ and $Re_2(CO)_7(H)_2(SiEt_3)_2$ (VI, VII) and the similarity of these compounds is clearly indicated by their structure.

(VI)

(VII)
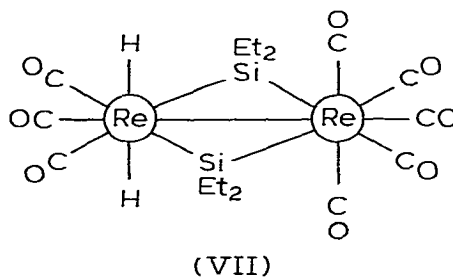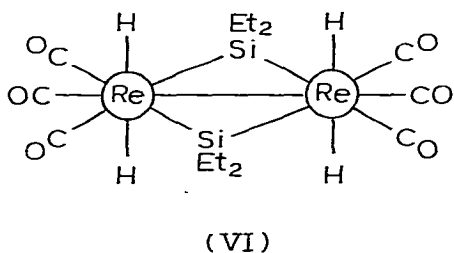
The compounds $Mn(C_5H_4R)(CO)_2(PPhMe_2)$ (R = H, Me) are quantitatively protonated in CF_3SO_3H to give $[Mn(C_5H_4R)(CO)_2(PPhMe)_2H]^+$ (ref. 71). Nmr spectra of these products show that two isomers are present in solution which undergo rapid, non-dissociative interconversion with a barrier, $\Delta G^{\ddagger}$, between 11 and 15 Kcal. The structure of cis-$Re(C_5H_5)(CO)_2(H)(Si\emptyset_3)$, (VIII), has been determined (ref. 72).

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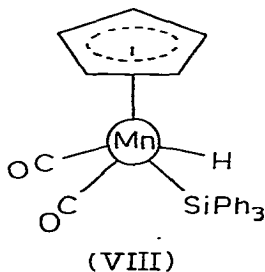
V. METAL COMPLEXES WITH CARBON GROUPS AS LIGANDS ($M(CO)_{5-n}(L)_n R$, $M(CO)_{5-n}(L)_n COR$, MR_n, Complexes with Carbene and Carbyne Ligands)

Several papers describe syntheses of alkyl-manganese and -rhenium complexes. Perhaps the most interesting paper is from Beck and Olgemoller (ref. 73) who reacted $[Re(CO)_5]^-$ with $[M(C_5H_5)(CO)_3(C_2H_4)]^+$ [M = Mo, W] to give $(OC)_5ReCH_2CH_2-M(C_5H_5)(CO)_3$; further reaction of the product with more $[Re(CO)_5]^-$ gave $(CO)_5Re-CH_2CH_2Re(CO)_5$. In both main group and transition metal chemistry, compounds having a $M-CH_2CH_2-M$ framework have been sought after but these syntheses have often proved difficult or impossible. This straightforward synthesis is impressive therefore.

Other interesting synthetic efforts deserve mention. Reactions of $[M(CO)_5]^-$ (ref. anions with $Mn(C_5H_4CH_2Cl)(CO)_3$ form $Mn[C_5H_4CH_2M(CO)_5](CO)_3$ (M = Mn, Re) derivatives 74). Reaction of $[Mn(CO)_5]^-$ with 1-bromopentacyanobutadiene gives $C_4(CN)_5Mn(CO)_5$ a σ-bonded percyanobutadienylmetal carbonyl complex (ref. 75). The compound $Mn(CO)_5CH_2R$ (R = o-phthalimidyl group) is made by reacting $[Mn(CO)_5]^-$ and RCl (ref. 76). From $Ag[C(CF_3)=C(CF_3)_2]$ and $Mn(C_5H_4R)(NO)(CS)I$ a perfluoroalkenyl derivative $Mn(C_5H_4R)(NO)(CS)[C(CF_3)=C(CF_3)_2]$ is obtained (ref. 54). Using $Li(C_6H_4CH_2NMe_2)$ in THF, MnI_2 is converted to the air sensitive, paramagnetic species $Li_2(THF)_2[MnI_2(C_6H_4CH_2NMe_2)_2]$; this in turn can be converted on heating to $Mn_2(C_6H_4CH_2NMe_2)_4$ (ref. 77). A crystal structure determination was carried out on this compound and the structure IX, below, was found.
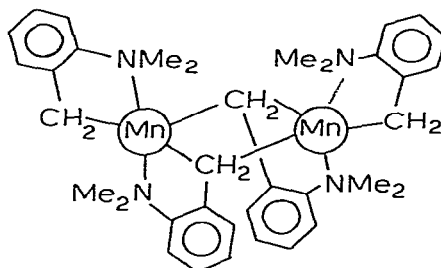

(IX)

Nucleophilic reactions of $[Mn(C_6H_{6-n}Me_n)(CO)_3]^+$ (n = 3, 5, 6) with $LiAlH_4$ and alkyllithium reagents have been carried out (ref. 78). The former are particularly interesting in that they proceed to $Mn(C_6H_{6-n}Me_n)(CO)_2CH_3$, with reduction of a coordinated carbonyl to a methyl group. This type of reaction has been seen previously in several instances and has obvious implications. With the latter reactions, addition of the alkyllithium to a coordinated CO gives acyl-metal compounds, $Mn(C_6H_{6-n}Me_n)(CO)_2COR$.

Cited earlier in this review are two references, one on the orthometallation that occurs when $Re_2(CO)_{10}$ is reacted with $P(o-tol)_3$ or $P(OPh)_3$ (ref. 6), the second on the failure to distinguish radical species when $[Mn(CO)_5]^-$ reacts with alkyl halides (ref. 10).

Kaesz and coworkers have followed up earlier studies which originated in the reactions of Mn(CO)$_5$Me and PPh$_3$. This area appears to provide a wealth of new compounds. In one paper (ref. 79) the reaction of $\overline{Mn(CO)_4PPh_2}C_6H_4$ and Mn(CO)$_4$(PPh$_3$)Me is reported to give several products, one of which was characterized by X-ray diffraction as (X). Second and third products of this reaction were identified by crystallography in a subsequent paper (ref. 80) as XI and XII.


(X)

(XI)

(XII)
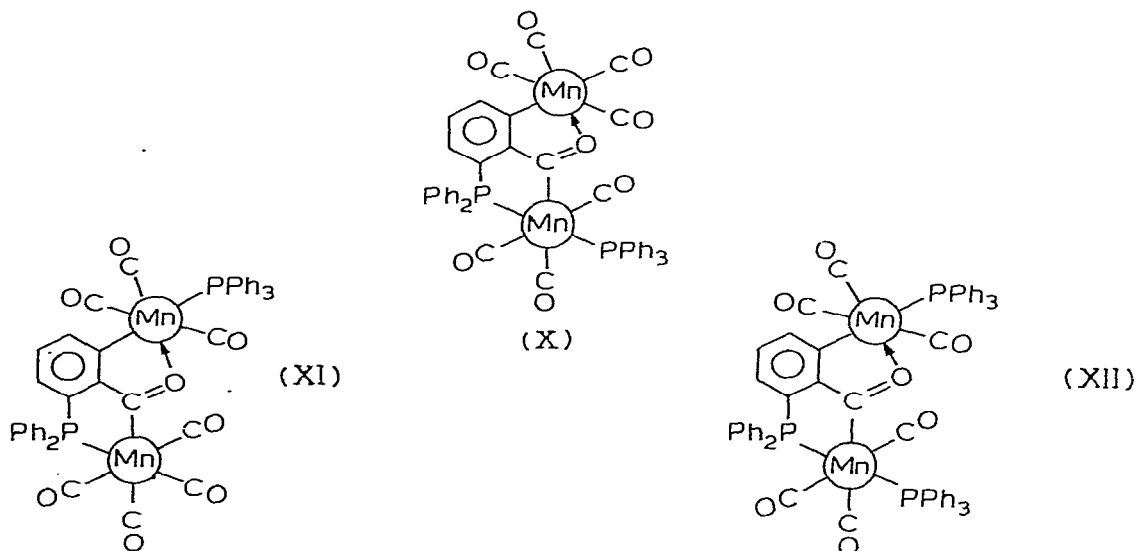
The reaction of $\overline{Re(CO)_4PPh_2C_6H_4}$ and Mn(CO)$_5$Me gives XIII whose structure was also identified (ref. 79). Huie's thesis also contains this work (ref. 81).

(XIII)
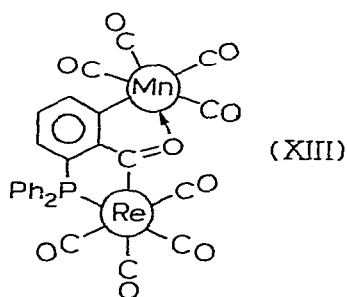
A crystal structure study on $\overline{Mn(CO)_4P(p-tol)_2C_6H_3}$Me is reported (ref. 82) Crawford and Kaesz also report the ortho-metallation reactions of Fe(C$_5$H$_5$)(C$_5$H$_4$COR) (R = Me, Ph) with M(CO)$_5$Me (M = Mn, Re) (ref. 83). The products react with CO or PPh$_3$ with addition or substitution at the metal.

Further work on $[Re(CO)_{6-n}(COR)_n]^{-(n-1)}$ complexes has been reported by two groups. Casey and Scheck (ref. 84) prepared $NMe_4[Re(CO)_4(COMe)(COPh)]$ and studied its thermal degradation. At a temperature of 70^c decarbonylation occurs to give $\underline{cis}$-$[Re(CO)_4(Ph)(COMe)]^-$ and $\underline{cis}$-$[Re(CO)_4(Me)(COPh)]^-$ in a ratio of 97:3. These two complexes are found to equilibrate at temperatures greater than $40°C$.

$$[Re(CO)_4(Ph)(COMe)]^- \; \rightleftharpoons \; [Re(CO)_4(Me)(COPh)]^-$$
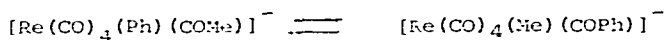
The compound $\underline{cis}$-$[Re(CO)_4(COMe)_2H]$ reacts with various hydrazines H_2NNHR (R = H, Me, Ph). Products from these reactions have the composition $\underline{cis}$-$Re(CO)_4$-$(NH_2R)COMe$ (ref. 85). A crystal structure was carried out on the aniline compound. The further use of $[Re(CO)_4(COMe)(COR)]^-$ (R = Me, i-Pr, CH_2Ph) (ref. 86) and $[Re(CO)_3(COMe)_3]^{2-}$ (ref. 87) as ligands to other metals is also reported. From AlX_3 and $[Re(CO)_4(COMe)(COCH_2Ph)]^-$, $Al[Re(CO)_4(COMe)(COCH_2Ph)]_3$ is obtained; from $[Re(CO)_3(COMe)_3]^{2-}$ hafnium and aluminum compounds, $Hf[Re(CO)_3(COMe)_3]_2$ and $NMe_4[Al\{Re(CO)_3(COMe)_3\}_2]$ respectively, are formed. Much of this coordination chemistry is contained in a Ph.D. thesis (ref. 88).

A review on carbon monoxide insertion reactions has appeared (ref. 89). Since a large amount of this work is on alkyl manganese carbonyls, citation of this review here is appropriate. The reaction of $Mn(CO)_5R$ compounds with isocyanides is the subject of a thesis (ref. 90). In this work the formal insertion of CO or CNR into a Mn-C bond is the topic of primary importance. The reaction of $Mn_2(CO)_{10}$ and primary amines to give $\underline{cis}$-$Mn(CO)_4(RNH_2)(CONHR)$ as one product was noted before (ref. 14).

Scattered reports of other reactions of alkyl metal compounds are reported. Reactions of $Re(CO)_5R$ (R = $C(=C(CF_3)_2)C(CF_3)=CF_2$) with $P(OPh)_3$ (= L) gives $Re(CO)_3L_2R$; no insertion of CO into the Re-C bond occurs (ref. 91). Treatment of $M(CO)_5COR$ (M = Mn, Re; R = Me, Ph) with P_4S_{10} or B_2S_3 gives $M(CO)_4S_2CR$ complexes; the acyl group is converted to chelating dithioacetate or -benzoate ligands (ref. 92). Thermolysis of the o-, m-, and p- isomers of $Mn(CO)_5CH_2C_6H_4CN$ was attempted, but no coordination of the CN group intra- or intermolecularly is seen to occur (ref. 93). Two papers on cyclization reactions of $M(CO)_5CH_2C\equiv CPh$ (M = Mn, Re) have appeared. With the electron-rich acetylene $MeO_2CC\equiv CCO_2Me$ and the manganese precursor, the product $Mn(C_5H_2-1,2-CO_2Me-3-Ph)(CO)_3$ is obtained; the acetylene and the organic group bonded to the metal add to give the substituted cyclopentadienyl group (ref. 94). With either $\underline{cis}$- or $\underline{trans}$- $CF_3C(CN)=C(CN)CF_3$ two isomers of the formula $M(CO)_5\overset{\cdot\cdot}{C}=CPhC(CN)(CF_3)C(CN)(CF_3)CH_2$ (XIV) are obtained (ref. 95). Similar mechanisms are involved in these cyclization reactions.
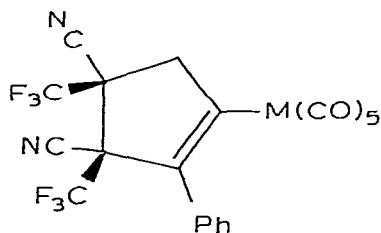
(XIV)   (cis isomer; trans also identified)

Oxygen 1s binding energies for the carbonyl oxygen atoms in Mn(CO)$_5$R compounds (R = Me, COMe, H, SiMe$_3$, Mn(CO)$_5$) are reported and this data is correlated to the degree of backbonding to the carbonyl groups (ref. 96). The electronic spectrum of [Re$_2$Me$_8$]$^{2-}$ is discussed (ref. 97).

Metal complexes with carbyne ligands have received much attention. The carbyne complex [Mn(C$_5$H$_5$)(CO)$_2$CPh]BCl$_4$ is formed from Mn(C$_5$H$_5$)(CO)$_2$(CPhOMe) and BCl$_3$ (ref. 98). This compound and similar species react with various nucleophiles :Nu$^-$, to reform the carbene complexes, Mn(C$_5$H$_5$)(CO)$_2$(CPhNu). Reactions of the above carbyne complexes with alkoxides give Mn(C$_5$H$_5$)(CO)$_2$(CPhOR) (ref. 98). Other reactions of both manganese and rhenium analogues with CN$^-$ and SCN$^-$ are noted in a separate paper (ref. 99). The dimethylcarbene complex, Mn(C$_5$H$_5$)(CO)$_2$(CMe$_2$), formed from [Mn(C$_5$H$_5$)(CO)$_2$CMe]BCl$_4$ and MeLi, was the subject of a crystal structure study (ref. 100). With Me$_3$P as a nucleophile either one or two phosphines add to [Mn(C$_5$H$_5$)(CO)$_2$CPh]BCl$_4$ giving [M(C$_5$H$_5$)(CO)$_2$(CPhPMe$_3$)]$^+$ (ref. 101) and [M(C$_5$H$_5$)(CO)$_2$(CPh(PMe$_3$)$_2$]$^+$ (ref. 102). A crystal structure study on [Re(C$_5$H$_5$)(CO)$_2$(CPhPMe$_3$)]BCl$_4$ shows that this compound has the structure XV below (ref. 103).
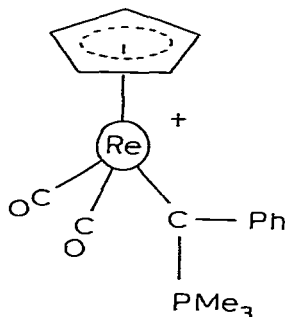

(XV)

A structural study on a compound having a CPh(PMe$_3$) bridging ligand is reported (ref. 104). The structure of this compound is shown below (XVI).
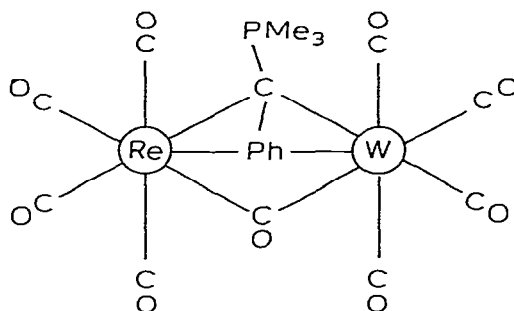
(XVI)

The carbene complex $Mn(C_5H_5)(CO)_2(\overline{CHMeCH_2CH_2NMe})$ is reported, formed from $\overline{Mn(C_5H_5)(CO)_2THF}$ and $Me\overline{NCH_2CH_2NMeC}=\overline{CNMeCH_2CH_2NMe}$ (ref. 105). Another carbene complex $\underline{fac}$-[Re(CO)$_3$(dpe)(C(OEt)SiPh$_3$)]$^+$ was mentioned earlier (ref. 32). Reacti of $Mn(C_5H_5)(CO)_2(CRR')$ (R = Me, Ph, R' = OR; R = R' = Ph) with $Et_2NC\equiv CMe$ occur with insertion of the acetylene into the metal-carbene bond to give the products XVII (ref. 106).
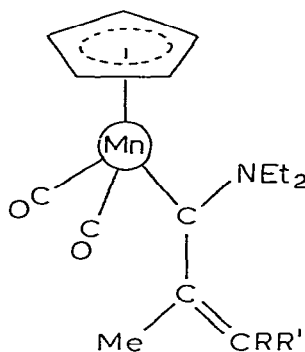
(XVII)

From reactions of Re(C$_5$H$_5$)(CO)$_3$ and PhC$\equiv$CH two products are obtained. The first is a monomer Re(C$_5$H$_5$)(CO)$_2$(C=CHPh). The second, a dimer, has the structure shown below (XVIII) according to a crystal structure study (ref. 107). Similar
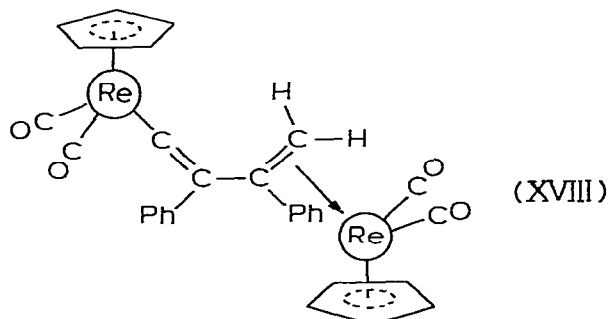

(XVIII)

chemistry with manganese is reported separately (ref. 108). The compound
Mn(C₅H₅)(CO)₂(C=CHPh) is formed from Mn(C₅H₅)(CO)₂(PhC CR) (R = GePh₃, SnPh₃ or H),
along with a second product [Mn(C₅H₅)(CO)₂]₂ (.-C=CHPh). The former compound can
be converted to the latter if Mn(C₅H₅)(CO)₂(THF) is added. Carbonyl
substitution reactions of Mn(C₅H₅)(CO)₂(C=CHPh) are also reported.

VI. METAL CARBONYL DERIVATIVES OF METALS AND METALLOIDS (DERIVATIVES OF ELECTRO-
POSITIVE METALS AND OF GROUP IIIA AND IVA)

Compounds containing either manganese or rhenium bonded to another transition
metal are grouped in three general categories. In the first category are compounds
with a simple M-M' bond. There is a reference to the compounds PhC M(CO)₄M'(CO)₅
(M = Cr, Mo, W; M' = Mn, Re). All six possible combinations of these metals are
described in this paper. These compounds are prepared from reactions of PhC M(CO)₄Br
and [M'(CO)₅]⁻ (ref. 109). Compounds with nickel-manganese bonds Mn(CO)₅Ni(PPh₃)NO
are assumed to be intermediates in the reactions of Ni(PPh₃)₂(NO)X with [Mn(CO)₅]⁻
(ref. 110). Not isolated, these compounds degrade to Ni(PPh₃)₂(CO)₂ and Mn(NO)₃L.

A second category includes polynuclear carbonyl species. Here there are two
references to compounds characterized by crystallographic studies. One is to the
substance HOs₃Re(CO)₁₅ (ref. 34) whose structure is drawn below (XIX). The second
compound has the formula H₂Re₂Os₃(CO)₂₀ (ref. 35), and is also shown (XX).
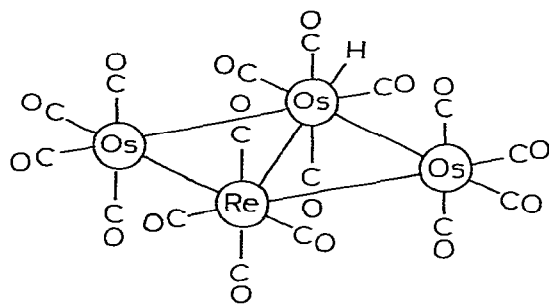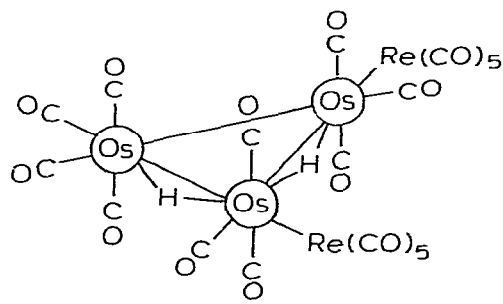

(XIX)   (XX)

In each instance the hydrogen atoms could not be located precisely and the positions
as drawn are those inferred to be correct.

There are three references to compounds which possess bridging ligands in
addition to a metal-metal bond. The first reference is to the compound
Mn(C₅H₄Me)(CO)(μ-CO)₂Co(PMe₃)(C₅H₅) which is formed from Mn(C₅H₄Me)(CO)₂(THF) and
Co(C₅H₅)(PMe₃)₂ (ref. 111). The structure for this species is assigned based on
infrared evidence for the bridging carbonyls. Reactions with added ligands
(L = PMe₃, PhC=CPh) cleave the species asymmetrically to give Mn(C₅H₄Me)(CO)₃ and
Co(C₅H₅)(PMe₃)(L). The other two reports concern species with AsMe₂ bridging
groups (ref. 112). The compounds Mn(C₅H₅)(CO)₂AsMe₂M(CO)₅ (M = Mn, Re) can be
obtained from Mn(C₅H₅)(CO)₂AsMe₂Cl and [M(CO)₅]⁻. On irradiation a carbonyl

is lost to give $(C_5H_5)(CO)_2MnAsMe_2M(CO)_4$ which has structure XXI. Similarly (ref. 113) photolyses of $(CO)_4FeAsMe_2M(CO)_5$ (M = Mn, Re) give the dimethylarsenic bridged products, $FeM(CO)_8(AsMe_2)$ (XXII).
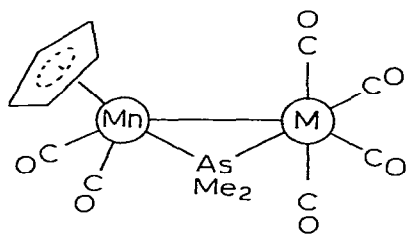

(XXI)
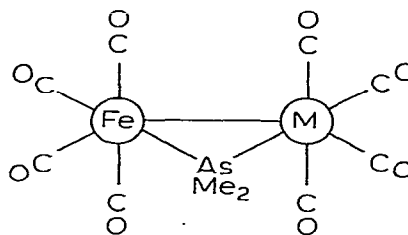
(XXII)

Reports of compounds in this group with boron containing ligands were common in the last few years but new work in this area is scarce. Herberich and Bauer (ref. 114) report manganese and rhenium complexes of 1-phenylborabenzene (XXIII) formed on heating $PhBCH=CHCH_2CH=CH$ with the metal carbonyls. In addition the work of Hildebrandt on manganese and rhenium carbonyl complexes of $[B_3H_8]^-$, reported in several papers during the last few years, has been written up in a Ph.D. thesis (ref. 115).
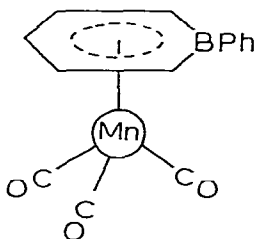
(XXIII)

In contrast to boron chemistry, work on Group IVA elements bonded to manganese and rhenium has continued unabated. There are a number of papers on synthesis including preparations of $Mn(CO)_4SiX_2CH_2CH_2PMe_2$ from $PMe_2CH_2CH_2SiX_3$ and $[Mn(CO)_5]^-$ (ref. 116), $Re(CO)_3(dpe)SiPh_2R$ from $Re(CO)_3(dpe)(COSiPh_2R)$ (R = Ph, Me) (ref. 32), and $[M(CO)_4(ER_3)_2]^-$ (M = Mn, Re); ER_3 = Ph_3Sn, Ph_3Ge, Ph_3Pb, Me_3Sn, Me_3Ge) from $M(CO)_4^{3-}$ and the appropriate R_3EX (ref. 19). The reaction of SiH_2I_2 with $[M(CO)_5]^-$ (M = Mn, Re) is reported, giving $SiH_2[M(CO)_5]_2$ and these compounds react with CBr_4, $CDCl_3$ or Ph_3CBF_4 to give the respective $SiX_2[M(CO)_5]_2$ species (ref. 117). Also the reactions of $Mn_2(CO)_{10}$ and SnX_2 (X = Br, I) giving $Mn_2(CO)_8[\mu-SnX(Mn(CO)_5)]_2$ are noted (ref. 118), as are the tin (ref. 117) Mossbauer spectra of these compounds (ref. 119).

Several cyclopentadienyl-metal carbonyls have been found to undergo oxidative addition reactions with group IV element halides or hydrides. The reaction of $SnCl_4$ with $Mn(C_5H_5)(CO)_2L \cdot$ (L = PR_3, $AsPh_3$, $SbPh_3$) gives a 2:1 adduct of these reagents. X-ray crystallography shows that the structure is ionic, vis, $[Mn(C_5H_5)(CO)_2(PPh_3)(SnCl_3)]SnCl_5$, with phosphine and $SnCl_3$ ligands trans to one another (ref. 120). The structure of an analogous rhenium complex cis-$Re(C_5H_5)(CO)_2(H)(SnPh_3)$ (ref. 72) has also been determined. Finally, the preparation and reactions of $Mn(C_5H_5)(CO)_2(H)(SiMePh-\alpha-Np)$ are reported. Interest in this compound focuses on the asymmetric silicon atom (ref. 121).

Structures of $Re_2(CO)_6H_4(SiEt_2)_2$ (ref. 69) and $Re_2(CO)_7H_2(SiEt_2)_2$ (ref. 70) were discussed earlier.

The kinetics of $Mn-MR_3$ (MR_3 = SnR_3, $SiMe_3$, $GeMe_3$) bond cleavage in $Mn(CO)_5MR_3$ by $HgBr_2$ have been studied (ref. 122). Also reported in a separate paper are similar studies using $M(CO)_5SnMe_3$ (M = Mn, Re) and HgX_2 (ref. 123). These reactions probably occur by initial adduct formation.

From appearance potential data, bond dissociation energies were calculated for Re-Si, Re-Ge and Re-Sn bonds in $Re(CO)_5EMe_3$. The values reported are, in order, 3.1, 3.2, and 3.7 ev. (ref. 124). The pyrolysis of $Mn(CO)_5SiH_3$ at 773°K in a flow system gives two solid phase materials identified as Mn_5Si_3 and MnSi (ref. 125).

VII. METAL COMPLEXES OF GROUPS VA AND VIA LIGANDS

Considered in this section are, in order, complexes of nitrogen ligands, complexes with phosphorus and arsenic ligands, and finally complexes with oxygen and sulfur ligand groups. Consistent with previous guidelines, complexes where compounds of these elements serve as simple electron pair donor ligands are excluded in this section.

Complexes that possess nitrogen containing ligands include $Mn(2-methylindolyl)-(CO)_3$ (ref. 126) and $Mn(CO)_4(\eta^2-CH_2=NCH_2C_5H_4FeC_5H_5)$ (ref. 127). Both compounds were subjects of crystallographic studies, the structures determined are sketched below (XXIV, XXV). The structure of the compound $[(Re(CO)_3Cl)_2TPP](SbCl_6)_2$ (TPP = tetraphenylporphyrin) was also reported (ref. 55).
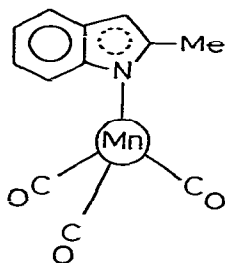
(XXIV)
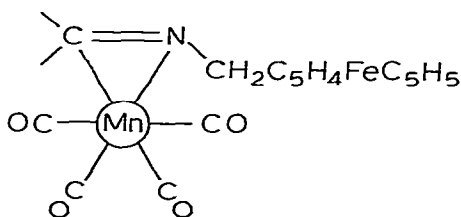
(XXV)

The chemistry of some bis(aryldiazo)manganese carbonyl complexes is reported in a communication (ref. 128). Treatment of Mn(CO)$_3$(PPh$_3$)$_2$H with [PhN$_2$]$^+$ followed by methoxide gives the starting complex Mn(CO)$_2$(PPh$_3$)$_2$N$_2$Ph. In turn this compound reacts further with [PhN$_2$]BF$_4$ to give either [Mn(CO)(PPh$_3$)$_2$(N$_2$Ph)$_2$]BF$_4$, or, if halide ion is present, Mn(PPh$_3$)$_2$(N$_2$Ph)$_2$X.
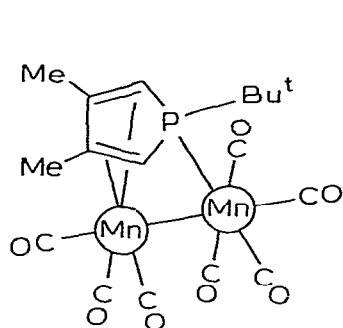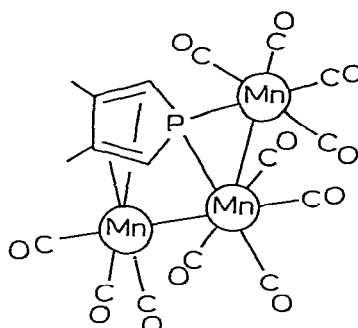
Two molecular structures that were determined for phosphole-manganese compounds (ref. 129) are shown below (XXVI, XXVII)

(XXVI)   (XXVII)

Vahrenkamp and several coworkers have published a large amount of work on compounds having AsMe$_2$ groups bridging two metals. Papers describing the syntheses of the following compounds are cited: Mn(C$_5$H$_5$)(CO)$_2$AsMe$_2$-m' (m' = Mo(C$_5$H$_5$)(CO)$_3$, W(C$_5$H$_5$)(CO)$_3$, Fe(C$_5$H$_5$)(CO)$_2$) (ref. 130); M(CO)$_4$(AsMe$_2$M'(CO)$_5$)$_2$ (M = Cr, Mo, W; M' = Mn, Re) (ref. 131, 132); (CO)$_5$ReAsMe$_2$M(CO)$_4$AsMe$_2$Cl and (CO)$_5$ReAsMe$_2$M(CO)$_4$AsMe$_2$M'(CO)$_5$ (M = Cr, Mo, W; M' = Mn, Re) (ref. 132); Fe$_2$(CO)$_5$(SMe)$_2$AsMe$_2$M(CO)$_5$ (M = Mn, Re) (ref. 133); Mn(C$_5$H$_5$)(CO)$_2$Me$_2$As-m (m = Mn(CO)$_5$, Re(CO)$_5$, Fe(C$_5$H$_5$)(CO)$_2$, Mo(C$_5$H$_5$)(CO)$_3$, W(C$_5$H$_5$)(CO)$_3$, Co(CO)$_4$) (ref. 112); and (CO)$_4$FeAsMe$_2$M(CO)$_5$ (M = Mn, Re) (ref. 113). A crystal structure study has been carried out on the compound cis-W(CO)$_4$(AsMe$_2$Mn(CO)$_5$)$_2$ (ref. 134). Ultraviolet irradiation of (CO)$_4$FeAsMe$_2$M(CO)$_5$ leads to carbonyl displacement and formation of the metal-metal bonded dimers, (CO)$_4$FeAsMe$_2$M(CO)$_4$ (M = Mn, Re) (ref. 113). Similarly, irradiation of Mn(C$_5$H$_5$)(CO)$_2$AsMe$_2$M(CO)$_5$ produces the metal-metal bonded compounds Mn(C$_5$H$_5$)(CO)$_2$AsMe$_2$M(CO)$_4$ (M = Mn, Re) (ref. 112).

Work on various dinuclear metal complexes, [M(CO)$_4$(PR$_2$X)]$_2$ with bridging R$_2$PX (X = S, O) groups was mentioned at an earlier time in this survey (refs. 41, 42, 43, 44, 45).

Several papers describing complexes with CS$_2$ as a ligand have been published. Addition of CS$_2$ followed by PPh$_3$ to Mn(C$_5$H$_4$R)(CO)$_2$THF (R = H, Me) gives a mixture of five products including Mn(C$_5$H$_4$R)(CO)$_2$L (L = CO, PPh$_3$, CS), [Mn(C$_5$H$_4$R)(CO)$_2$]$_2$CS, and [Mn(C$_5$H$_4$R)(CO)$_2$]$_2$CS$_2$. Addition of these reagents together gives only Mn(C$_5$H$_4$R)(CO)$_2$(CS). The chemistry involving the rhenium

analogue is similar (ref. 135). Infrared data suggests that an $\eta^2\text{-}CS_2$ ligand is
a stronger π acceptor than CO (ref. 136). It has been observed that the
carbon-13 nmr spectra of $Mn(C_5H_5)(CO)_2(CS_2)$ and $[Mn(C_5H_5)(CO)_2]_2CS_2$ are tempera-
ture dependent (ref. 137). The former complex is believed to undergo a flexional
process involving rotation of the ligand about the ligand-metal bond; this would
lead to equivalence of the carbonyl groups in the higher temperature spectrum. The
fluxional process for the second compound is more interesting since the one site
requires that the two metals exchange environments; vis:
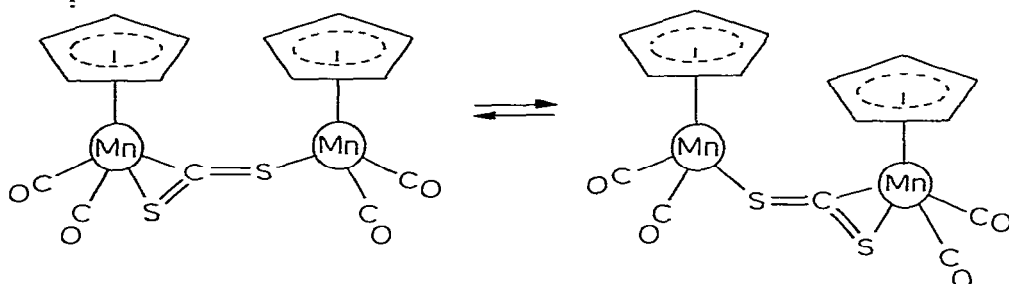
At the higher temperature limit the nmr pattern consists of single resonances
for the carbonyl and cyclopentadienyl carbon atoms.

Preparation of the anionic complex $[Mn(C_5H_4Me)(CO)_2SEt]^-$ is accomplished by
reaction of SEt^- with $Mn(C_5H_4Me)(CO)_2(THF)$ (ref. 138). This compound reacts with
perchloric acid to give a dinuclear compound having structure (XXVIII) according to
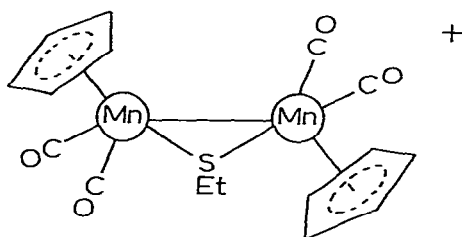
(XXVIII)

a crystallographic study. This compound is seen by electrochemistry to undergo two
reversible one electron oxidations but no products from these oxidations have yet
been isolated.

Reactions of $Mn(CO)_5Br$ or $Re(CO)_5Cl$ with $(Me_3Sn)_2E$ (E = Se, Te) give
$[Mn(CO)_4ESnMe_3]_2$. When heated the selenium compound loses carbon monoxide to form
the tetramer, $[M(CO)_3SeSnMe_3]_4$. With HCl the tin-selenium bond is cleaved and
compounds with bridging –SeH groups are formed (139).

Other papers from the same group describe further work in this area (refs. 140,
141, 142, 143). The sulfur bridged products $[M(CO)_4SR]_2$ (M = Mn, Re; R = H, Me,
$SnMe_3$) react with PMe_3 to form either $[M(CO)_3(PMe_3)SR]_2$ or $M(CO)_3(PMe_3)_2SR$ depending

on conditions (ref.140). From $M(CO)_3(PMe_3)_2SH$ and $M'(CO)_6$ ($M' = Cr$, Mo, W) the products $M(CO)_3(PMe_3)_2(\mu-SH)M'(CO)_5$ form (ref. 141). Also reported is the oxidation of $[Mn(CO)_4SSnMe_3]_2$ with iodine. A complicated polynuclear manganese carbonyl sulfide, $Mn_4(CO)_{15}S_4$, can be obtained. Its structure, XXIX, was determined by x-ray crystallography (ref. 142). Another structure determination was reported for a product $Re_3(CO)_{13}S_2SnMe_3$ (XXX), one of many complicated products from the reaction of $Re(CO)_5Cl$ and $(Me_3Sn)_2S$, obtained when the reaction is run in a 1:2 molar ratio (ref. 143).
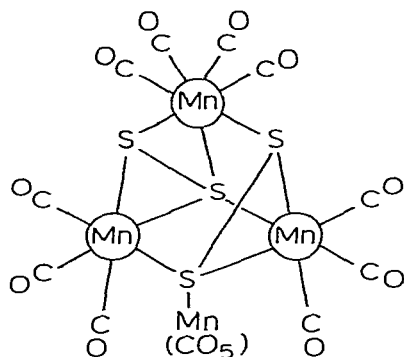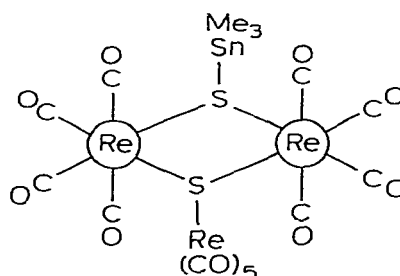
(XXIX)　　　　　　　　(XXX)

Concluding this section, mention is again made of the compounds $M(CO)_4S_2CR$ (M = Mn, Re) (ref. 92) and $Re_2(CO)_6(Br)_2RSSR$ (ref. 51, 52) cited earlier in this review.

IX.   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)

There are rather a large number of papers pertaining to $M(C_5H_5)(CO)_3$ or derivatives thereof; however many have been cited earlier.

Several papers report unusual syntheses of cyclopentadienyl metal carbonyl complexes. The preparation of a complex of the tricyanovinylcyclopentadienyl ligand is reported (ref. 144). This ligand is prepared from TlC_5H_5 and TCNE; its reaction with $Mn(CO)_5Br$ gives the product, $Mn(C_5H_4C(CN)=C(CN)_2)(CO)_3$. The preparations of various polyhalocyclopentadienyl complexes are noted; these are formed by degrading the polyhalodiazocyclopentadienylidene in the presence of $Mn(CO)_5X$ (ref. 145). A similar reaction with diazoindenylidene gives $Mn(1-haloindenyl)(CO)_3$ (ref. 146). In addition the reaction of $Mn(CO)_5CH_2C\equiv CPh$ and $MeO_2CC\equiv CCO_2Me$ to give $Mn(1,2-CO_2Me-3-Ph-C_5H_2)(CO)_3$ is noted (ref. 94), as is the reaction of $Ph_2P(=S)C_5H_5$ and $Mn_2(CO)_{10}$ to give $Mn(C_5H_4PPh_2)(CO)_3$ and $Mn(C_5H_4PSPh_2)(CO)_3$ (ref. 147).

Next, consideration will be given to carbonyl substitution reactions and the products derived from these reactions. A study recently carried out suggests

that $Mn(C_5H_5)(CO)_2$, the intermediate in substitution processes of $Mn(C_5H_5)(CO)_3$, has a trigonal configuration (counting a bond to the C_5H_5 centroid as one of three directed bonds from the metal). The dynamics of the inversion process are defined (ref. 148). This process involves a planar intermediate.

The use of Me_3NO to promote carbonyl substitution is becoming common in carbonyl chemistry. This reagent was used with $Mn(C_5H_4Me)(CO)_3$ to effect substitution and the compounds $Mn(C_5H_4Me)(CO)_2L$ (L = PPh_3, py, norbornadiene) were prepared (ref. 149).

Most other substituted compounds were made via the THF complex, formed in situ by irradiation of $Mn(C_5H_4R)(CO)_3$ compounds in this solvent. Prepared were $M(C_5H_4R)(CO)_2(CSe)$ (M = Mn, Re; R = H, Me), formed using CSe_2 and PPh_3 (ref. 150); the analogous thiocarbonyl complex was made by the same procedure (ref. 135). It is necessary to add the reagents CS_2 and PPh_3 together to maximize the yield; if added sequentially a mixture of products is obtained. Two olefin complexes were made from the THF complex. One is a complex of an enone, $Mn(C_5H_5)(CO)_2-$ ($CH_2=CHCHO$) (ref. 151), the second a complex of fulvenallene (ref. 152). The latter has the structure shown below (XXXI). Using ultraviolet irradiation it is
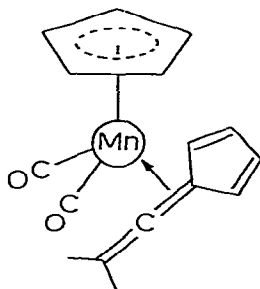
(XXXI)

possible to substitute all three carbonyls in $Mn(C_5H_5)(CO)_3$ by isocyanides, giving $Mn(C_5H_5)(CNR)_3$ (ref.153). Compounds were prepared from four ligands (CNR; R = Me.Ph, p-ClC_6H_4, C_6Cl_5). Similar complexes with phosphine and phosphite ligands are also reported, but these were prepared in a different manner displacing a hydrocarbon ligand from either $Mn(C_5H_5)_2$ or $Mn(C_5H_5)(C_7H_8)$ (ref. 154).

Syntheses of several compounds were referenced in earlier sections of this review. The preparation of $[Mn(C_5H_4Me)(CO)_2SEt]^-$, from SEt^- and the THF complex is noted. A dinuclear compound is derived from this species on protonation (ref. 138). Also mentioned was a carbene complex, $Mn(C_5H_5)(CO)_2(\overline{CNMeCH_2CH_2}NMe)$ (ref. 105), and a carboalkylidene species $Re(C_5H_5)(CO)_2(C=CHPh)$ (ref. 107). The latter compound is one of two products obtained from $Re(C_5H_5)(CO)_3$ and $PhC\equiv CH$; the second is a dimer of this formula. The use of several m-$AsMe_2$ compounds as ligands (m = $W(C_5H_5)(CO)_3$, $Mo(C_5H_5)(CO)_3$, $Fe(C_5H_5)(CO)_2$) to manganese was also mentioned earlier; the compounds $Mn(C_5H_5)(CO)_2AsMe_2-m$ were described (ref. 130).

A crystal structure study was carried out on the olefin compound $Mn(C_5H_5)$-$(CO)_2C_8H_8$ (C_8H_8 = cyclooctatetraene) (ref. 155). Electronic spectra of various $M(C_5H_5)(CO)_2L$ (M = Mn, Re; L = CO, amines, py, substituted py) are reported (ref.156). CNDO calculations were performed on a number of hydrocarbon complexes ($Cr(C_6H_6)(CO)_3$, $Mn(C_5H_5)(CO)_3$, $Fe(C_4H_4)(CO)_3...$) (ref. 157). Calculations of ^{13}C nmr paramagnetic shielding constants were also performed in several of these compounds (ref. 158).

Reference was made to the π acceptor character of CS_2 in the $Mn(C_5H_5)(CO)_2(CS_2)$ (ref. 136), and also to the fluxional characters of this compound and $[Mn(C_5H_5)(CO)_2]_2^-$ CS_2 (ref. 137).

A second general area of interest for compounds in this category involves reactions of coordinated ligands. Again much of this work has been cited earlier; note specifically the references to nucleophilic additions at the carbyne ligand in the carbyne complexes $[M(C_5H_5)(CO)_2CR]^+$ (refs. 98, 99, 100, 101, 102, 103), the insertion of $Et_2NC\equiv CMe$ into the manganese carbene bond of various $Mn(C_5H_5)(CO)_2$- (carbene) complexes (ref. 106), and the conversion of $Mn(C_5H_5)(CO)_2(PhC\equiv CGePh_3)$ to $Mn(C_5H_5)(CO)_2C=CHPh$ (ref. 108). Other work in this area is concerned with reactions at nitrogen, phosphorus, or arsenic ligands. It was shown that $Mn(C_5H_5)(CO)_2N_2H_4$ reacts with $Cr(CO)_5THF$ giving a product, $Mn(C_5H_5)(CO)_2HN=NHCr(CO)_5$, having a diimine ligand bridging the two metals (ref. 159). One P-H unit of $Mn(C_5H_5)(CO)_2$- $PPhH_2$ is capable of addition to acetylenes (C_2H_2, $PhC\equiv CH$, $PhC\equiv CPh$, $MeSi(C\equiv CH)_2$); the products are compounds having a phenylvinylphosphine ligand, $Mn(C_5H_5)(CO)_2$- (PPhH-CR=CHR). An x-ray structural study was performed on the product which was formed from $PhC\equiv CPh$ (ref. 160). In the presence of Et_3N, acetylacetone reacts with $Mn(C_5H_5)(CO)_2PPhCl_2$; the product is shown below XXXII (ref. 161). The reaction of
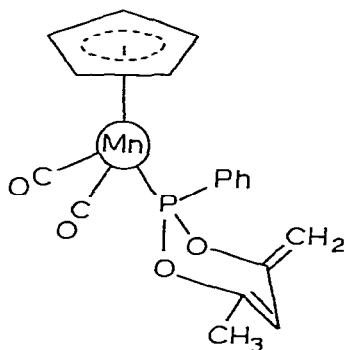
(XXXII)

$[Mn(C_5H_5)(CO)_2PMe_2S]^-$ with various silicon, germanium, or tin halides is shown to give $Mn(C_5H_5)(CO)_2PMe_2SER_3$ derivatives (ref. 162). Air oxidation of $Mn(C_5H_5)(CO)_2$- $AsMe_2H$ occurs in a unique fashion to give a species with As_2Me_4 bridging two $Mn(C_5H_5)(CO)_2$ groups (ref. 163). Reactions of $Mn(C_5H_5)(CO)_2AsMe_2Cl$ with several

metal carbonyl anions to give $Mn(C_5H_5)(CO)_2AsMe_2-M'$ species were cited earlier (ref. 112).

As usual, there is much work on reactions at the cyclopentadienyl ligand in $Mn(C_5H_5)(CO)_3$. Considerable emphasis during the last year has been directed to making compounds with metallic substituents on the cyclopentadienyl ring. The compounds $Mn(C_5H_4CH_2M(CO)_5)(CO)_3$ were cited earlier (ref. 74). As another example, compounds $M(C_5H_4R)(CO)_3$ (M = Mn, Re; R = $Pt(PPh_3)_2Cl$) are formed from $Mn(C_5H_4Li)(CO)_3$ and $Pt(PPh_3)_2Cl_2$ (ref. 164). Similar compounds $M(C_5H_4X)(CO)_2(PPh_3)$ are formed from $M(C_5H_4HgX)(CO)_2PPh_3$ and $Pt(Phos)_3$ (ref. 165). The compound $Mn(C_5H_4COfe)(CO)_2(PPh_3)$ (fe = $Fe(C_5H_5)(CO)_2$) is shown to decarbonylate (ref. 166), and this product $Mn(C_5H_4fe)(CO)_2(PPh_3)$ has been reacted with H^- or with I_2, producing ring-iron cleavage, and with PPh_3, causing CO insertion into the iron-ring unit (ref. 167).

Other examples of bimetallic systems include $Br(CO)_4W^-CC_5H_4Mn(CO)_3$ (ref. 168), and $(CO)_3MnC_5H_4C_6H_5XC_6H_5Cr(CO)_3$ (X = CO, CH_2, $-CH=CH-$) (ref. 169). The latter systems were studied to evaluate the transmission of electronic effects from one metal system to the other.

Borohydride reduction of an acyl substituted cyclopentadienyl compound, XXXIII is found to be stereospecific. The product has an _endo_ OH group, (ref. 170) so the hydride is attacking _exo_, on the side opposite the metal.
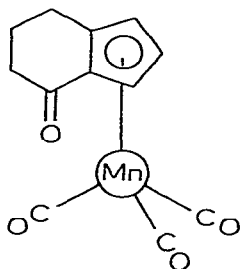
(XXXIII)

Electron-rich character is indicated for various phosphine substituted derivatives of $M(C_5H_5)(CO)_3$. The compound $Mn(C_5H_5)(CO)(dpe)$ is readily oxidized by one electron loss to the isolable 17e species $[Mn(C_5H_5)(CO)(dpe)]^+$ (refs. 53,171) Other complexes $Mn(C_5H_5)(CO)_{3-n}L_n$ (L = PEt_3, PPh_3, PPh_2Me, $P(OMe)_3$ n = 1,2) also oxidize. Esr can be used to detect the product, a 17e species, at lower temperatures, but the products cannot be isolated (ref. 53). An nmr study on $Mn(C_5H_4Me)(CO)_2(PPhMe_2)$ has shown that this compound is protonated quantitatively in CF_3SO_3H (ref. 71). Two isomers are detected. These isomers undergo rapid non-dissociative interconversion, with a ΔH^* between 11 and 15 Kcal.

The reaction of $Mn(C_5H_5)(CO)_2PPh_3$ with $SnCl_4$ to give $[Mn(C_5H_5)(CO)_2(PPh_3)-(SnCl_3)]SnCl_5$ is obviously related to the protonation work (ref. 120).

Various $Mn(C_5H_4R)(CO)LL'$ (R = COOH, Me, etc.) complexes have been synthesized. pKa and $\nu(CO)$ values were measured and correlated with the characters of the ligands L and L' (ref. 172).

Mentioned earlier in this survey were $Re(C_5H_5)(CO)_2(H)(SiPh_3)$ (ref. 72), $Mn(C_5H_5)(CO)_2(H)(SiMePh-\alpha-Np)$ (ref. 121), and $Mn(C_5H_5)(CO)-(\mu-CO)_2Co(PMe_3)(C_5H_5)$ (ref. 111).

Thermal decompositions of several metallocenes including $Mn(C_5H_5)_2$ have been reported (ref. 173). Also a Raman spectral study has been carried out on these compounds (ref. 174).

It is appropriate to turn next to complexes of hydrocarbons other than the cyclopentadienyl anion. There are, however, only a scattering of references to consider.

There are two papers on arene complexes. One reports a secondary product of arene-$Re(CO)_5Br$ reactions to be $[Re(arene)(CO)_3]Re_2(CO)_6Br_3$ (ref. 50). A crystal structure study was done on the toluene compound. The second reference is about reactions of $[Mn(C_6H_{6-n}Me_n)(CO)_3]^+$ reactions with $LiAlH_4$ and with RLi (ref. 78). The former reactions give $Mn(arene)(CO)_2CH_3$ while the latter gives $Mn(arene)(CO)_2COR$ complexes; both reactions occur with nucleophilic attack of coordinated carbonyl.

The reaction of $[Mn(fluorene)(CO)_3]^+$ with bases is reported in a paper and a thesis (refs. 175, 176). Bases as weak as Et_3N will remove a proton from the CH_2 group in the hydrocarbon to give a red crystalline species in which the metal remains bonded to one 6-membered ring on the hydrocarbon. This compound can be reprotonated or alkylated (exo) in the 9 position. It is also seen to rearrange slowly to give a new complex in which the metal coordination is now to the 5-membered ring of the ligand. This reaction is not reversible.
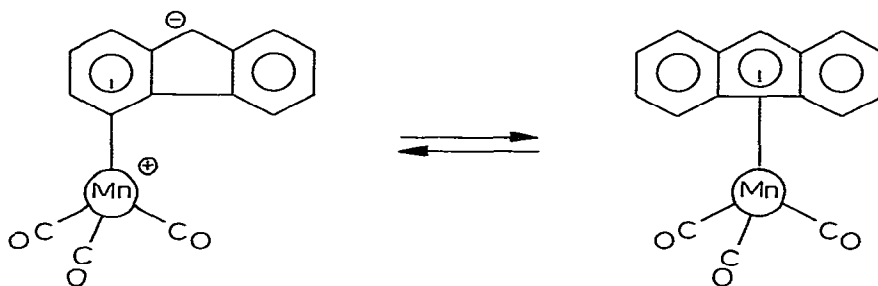
Addition of $Mn(CO)_5Ph$ to cycloheptatriene gives the product $Mn(CO)_3(C_7H_8Ph)$, shown below, XXXIV, along with small amounts of the cycloheptadienyl complex $Mn(C_7H_9)(CO)_3$ (ref. 177). The reaction with $Re(CO)_5Ph$ proceeds similarly. Hydride abstraction with $[Ph_3C]^+$ gives a 1-phenylcyclohexadienyl metal complex.
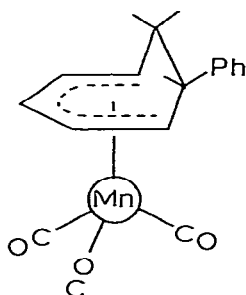
(XXXIV)

Crystal structure studies have been reported on $[Mn(azulene)(CO)_3]_2$ (ref. 178) and $C_{14}H_{10}Mn_2(CO)_6$ (XXXV) (ref. 179). The former compound contains $Mn(CO)_3$ groups bonded to the five membered ring of each azulene, with the azulenes linked by a bond between the 4-positions.
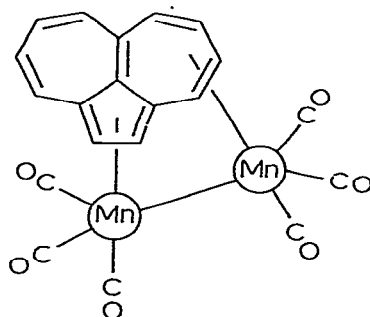
(XXXV)

There have been five papers concerned with hydrocarbons having heteroatoms (boron, phosphorus, nitrogen) as ligands. Four of these were referenced earlier $(C_5H_5BPhM(CO)_3,(M = Mn, Re)$ (ref. 114), $Mn(2-methylindolyl)(CO)_3$ (ref. 126), $Mn(CH_2=NCH_2fc)(CO)_3$ (ref. 127)), and two phosphole compounds $Mn_2(CO)_7(C_6H_8PBu^t)$ and $Mn_3(CO)_{11}(C_6H_8P)$ (ref. 129). In addition there is reported a compound from $Mn(pyrollyl)(CO)_3$ and acetic anhydride which has the structure XXXVI (ref. 180).
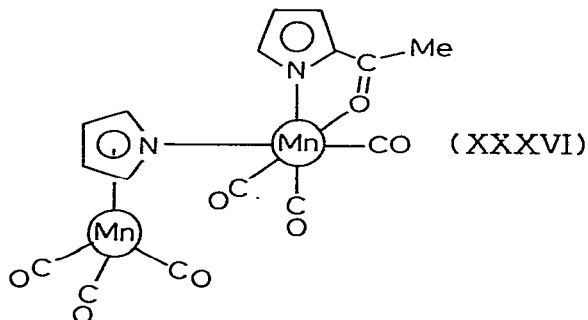
(XXXVI)

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 to be cited here, and these are primarily with isocyanide complexes.

Major work has appeared on $[Mn(CNR)_6]^+$ compounds. Electrochemical oxidations of 11 complexes were studied and correlations determined between $E_{1/2}$ and substituents on the aryl group (ref. 181). This work is also available in a thesis (ref. 25) along with other chemistry concerning $Mn(CNR)_5X$, $[Mn(CO)_{6-n}(CNR)_n]^+$ and $Mn(C_5H_5)(CNR)_3$ species. A paper on the $Mn(C_5H_5)(CNR)_3$ was cited earlier in the review (ref. 153). Also cited was work on reactions of $Mn(CO)_5R$ with isocyanides (ref. 90).

Similar chemistry on $Re(CO)_{5-n}(CNR)_nX$ and $[Re(CO)_{6-n}(CNR)_n]^+$ is noted (ref. 27).

An interesting theoretical paper on aryl isocyanides originates in the manganese isocyanide chemistry described above (ref. 182). It is noted that the interaction of the aryl π system with one of the π* (CN) orbitals causes a splitting degeneracy of π* levels, with one orbital stabilized. Interaction of this π* orbital with a filled metal d orbital allows aryl isocyanides to be quite good π acceptors relative to alkyl isocyanides.

The compound $Mn_2(CO)_5(dpm)_2$, it may be remembered, has a unique structure in which a CO bridges the two metals utilizing its π electrons. This compound can add CNR (R = tol, benzyl, Me) reversibly. In the case of the CNtol adduct, heating leads to CO loss to give $Mn_2(CO)_4(CNtol)(dpm)_2$, a compound in which the isocyanide has assumed the unique bridging role (ref. 13).

Several new rhenium isocyanide complexes are reported. From $KReI_6$ and cyclohexyl isocyanide (=L) a compound of the formula $Re_3L_6I_6$ is formed. Other reactions of ReI_3 give either $Re_3L_3I_6$ or $Re_3L_3I_9$. From K_2ReBr_6 and L one gets the rhenium(II) derivative ReL_4Br_2, an orange crystalline compound (ref. 183).

The three papers on nitrosyl complexes have been cited in earlier places in the review. These include: the use of NOCl as a nitrosating reagent with $Mn(C_5H_5)(CO)_3$ (ref. 46); the syntheses and reactions of $[M(C_5H_4R)(NO)(CO)(CS)]^+$ species (ref. 54); and the synthesis of $Mn(NO)_3(PPh_3)$ from $Ni(NO)(PPh_3)_2Cl$ and $[Mn(CO)_5]^-$ (ref. 110). Also cited was a paper on aryl-diazonium complexes of rhenium (ref. 128).

X. STRUCTURAL STUDIES

Compounds whose structures have been determined by x-ray crystallography or electron diffraction are listed: $fac-[Re(CO)_3(NCMe)_3]BF_4$ (ref. 26); $Re(CO)_3(dpe)-COSiPh_3$ (ref. 32); $HOs_3Re(CO)_{15}$ (ref. 34); $H_2Os_3Re_2(CO)_{20}$ (ref. 35); $[Mn(CO)_4PPh_2O]_2$ (ref. 41); $[Re(MeC_6H_5)(CO)_3][Re_2(CO)_6Br_3]$ (ref. 50); $Re_2(CO)_6Br_2(PhSSPh)$ (ref. 51);

$Re_2(CO)_6Br_2(MeSSMe)$ (ref. 52); $[Re(CO)_3Cl]_2TTF]_2SbCl_6$ (ref. 55); $Mn(CO)_5H$ (by electron diffraction (ref. 62)); $(Et_4N)_2[Re_3(CO)_4H_3]$ (ref. 66); $(NMe_3CH_2Ph)_2-[Re_4(CO)_{12}H_6]$ (ref. 67); $NEt_4[Re_3(CO)_{10}H_4]$ (ref. 68); $Re_2(CO)_6(H)_4(SiEt_2)_2$ (ref. 69) $Re_2(CO)_7(H)_2(SiEt_2)_2$ (ref. 70); $Re(C_5H_5)(CO)_2(H)SiPh_3$ (ref. 72); $Mn_2(C_6H_4CH_2NMe_2)_4$ (ref. 77); $Mn_2(CO)_8(PPh_3)(PPh_2C_6H_3)$, $MnRe(CO)_9(PPh_2C_6H_3)$ (ref. 79); $Mn_2(CO)_8(PPh_3)-(PPh_2C_6H_3)$ and $Mn_2(CO)_7(PPh_3)_2(PPh_2C_6H_3)$ (ref. 80); $Mn(CO)_4P(p\text{-tol})(C_6H_3Me)$ (ref. 82); $Re(CO)_4(CH_2Ph)COMe$ (ref. 85); $Mn(C_5H_5)(CO)_2(CMe_2)$ (ref. 100); $[Re(C_5H_5)(CO)_2(CPhPMe_3)]BCl_4$ (ref. 103); $(CO)_4Re(\mu\text{-CPhPMe}_3)(\mu\text{-CO})W(CO)_4$ (ref. 104); $Re(C_5H_5)(CO)_2C=CPhCPh=CH_2Re(C_5H_5)(CO)_2$ (ref. 107), $[Mn(C_5H_5)(CO)_2(PPh_3)SnCl_3]SnCl_5$ (ref. 119); $Mn(2\text{-Methylindolyl})(CO)_3$ (ref. 126); $Mn(CO)_4(\eta^2\text{-CH}_2\text{=N-CH}_2C_5H_4FeC_5H_5)$ (ref. 127); $Mn_2(CO)_7(C_6H_8P\text{-Bu}^t)$ and $Mn_3(CO)_{11}(C_6H_8P)$ (ref. 129); $\underline{cis}\text{-W(CO)}_4-(AsMe_2Mn(CO)_5)_2$ (ref. 134); $[Mn_2(C_5H_4Me)_2(CO)_4SEt]ClO_4$ (ref. 138); $Mn_4(CO)_{15}S_4$ (ref. 142); $Re_3(CO)_{13}S_2SnMe_3$ (ref. 143); $Mn(C_5H_5)(CO)_2(C_8H_8)$ (ref. 155); $Mn(C_5H_5)(CO)_2(PPhHCPh=CHPh)$ (ref. 160); $[Mn(azulene)(CO)_3]_2$ (ref. 178); $C_{14}H_{10}Mn_2(CO)_6$ (ref. 179); $Mn_2(CO)_6(pyrollyl)(C_4H_3NCOMe)$ (ref. 180).

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