MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1973

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CONTENTS

I INTRODUCTION

This 1973 Annual Survey on the organometallic chemistry of manganese, technetium, and rhenium, is again organized based on compound type. The order for consideration is generally the same as was used in the previous article for 1972.

A few citations will be made within this article to papers published in

1972; these are references in Journals not available in our library immediately after their publication, which eliminated their consideration in the 1972 Annual Survey.

From among the extensive studies in manganese, technetium, and rhenium organometallic chemistry, three studies particularly attracted my attention. Notwithstanding the obvious limitations offered in a subjective selection and judgment of this type, I would like to emphasize them here in the Introduction. The first general subject deals with the one electron oxidation of a number of complexes having the general formulas $Mn(CO)_{5-n}L_nX$ and $Mn(CO)_{6-n}L_n^+$ to give stable and isolable 17e species $Mn(CO)_{5-n}L_nX^+$ and $Mn(CO)_{6-n}L_n^{2+}$; this work was carried out primarily by Reimann and Singleton (1,2). In addition to the isolation of these novel product species, there was considerable effort directed to elucidation of the stereochemistry of these complexes. Second, some elaborate work from three groups has appeared on ortho-metallation reactions occurring when $Mn(CO)_5Me$ or $Re(CO)_5Me$ was treated with various organic aryl species (3-8). Finally, in conjunction with an extensive program to study stereochemically non-rigid molecules, Marks and Ibers along with their coworkers (9) have investigated the compound $[C_5H_5Mn(CO)(NO)]_2$ by nmr and infrared spectroscopy and have concluded that both carbonyl and nitrosyl groups undergo facile bridge-terminal exchange while in solution.

Further discussion on each of these topics will appear at the appropriate places in this survey.

II THE METAL CARBONYLS AND DERIVATIVES OBTAINED BY SIMPLE LIGAND SUBSTITUTION

There are two intriguing reports concerning photochemical dissociation of the dimetal dodecacarbonyls. Wojcicki and Hallock (10) observed that when a yellow tetrahydrofuran solution of $Mn_2(CO)_{10}$ was subjected to 350 nm irradiation the color changed to orange; on standing for about an hour the solution reverted back to the original color. An esr signal for the orange solution was noted.

Also when the orange solution was treated with iodine, there was rapid formation of $Mn(CO)_5I$. On the basis of these data, it was proposed that an unstable radical species, $Mn(CO)_5$, had been formed by photolytic dissociation of $Mn_2(CO)_{10}$.

$$Mn_2(CO)_{10} \xrightarrow{h\nu} 2Mn(CO)_5$$

Wrighton and Bredeson (11) report that 313 or 366 nm irradiation of a solution of $Re_2(CO)_{10}$ in carbon tetrachloride generates $Re(CO)_5Cl$. They propose a mechanism whereby $Re_2(CO)_{10}$ dissociates photochemically into $Re(CO)_5$ radicals, which react with the solvent to give the observed product.

Nuclear decomposition by β decay of ^{99}Mo in $Mo(CO)_6$ is reported to give $^{99}Tc(CO)_5$ in high yield (12). The $Tc(CO)_5$ radical species trapped in the $Mo(CO)_6$ lattice is quite stable, surviving to 110°. It is shown to react with $Mn(CO)_5I$ to generate $Tc(CO)_5I$ and with photochemically generated $Mn(CO)_5$ giving $MnTc(CO)_{10}$.

Other studies appear to indicate that dissociation of the metal-metal bond in $M_2(CO)_{10}$ is a viable pathway in reactions of these species. Activation enthalpies for a number of reactions (of $M_2(CO)_{10}$ (M = Mn, Tc, Re), $MnRe(CO)_{10}$, and of $[Mn(CO)_4L]_2$ (L = PPh_3, $P(OPh)_3$) with O_2 in decalin) show a direct correlation with calculated force constants for the metal-metal bond (when available) and with electronic spectral absorptions assigned as $\sigma \rightarrow \sigma^*$ transitions associated with the metal-metal bond (13). Since these latter parameters are obviously related to metal-metal bond strengths, the observed correlation supports the idea that these reactions occur via initial homolytic cleavage of the metal-metal bond.

The same authors (14) also describe kinetic studies on the reactions of $[Mn(CO)_4L]_2$ (L = PPh_3, $P(OPh)_3$) and of $[Re(CO)_4(PPh_3)]_2$ with additional phosphine or phosphite ligand. The reaction is believed to generate cis-$M(CO)_3L_2$ species. (The characterization of $Mn(CO)_3(PPh_3)_2$ is described as tentative; no mention of characterization of the other reaction products is given). These reactions show a rate dependence on complex concentration of order one-half; this is in accord with a mechanism involving initial homolytic fission of the metal-metal bond.

Although reactions of various phosphines with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ have been known for some time, analogous reactions of the mixed metal carbonyl species $MnRe(CO)_{10}$ have only just been reported (15). The product of reaction of this carbonyl with triphenylphosphine is characterized as ax-$(CO)_5MnRe(CO)_4P$ with the phosphine attached to rhenium according to ^{31}P nmr and vibrational spectral studies. The second isomer, ax-$PPh_3(CO)_4MnRe(CO)_5$ with phosphine attached to manganese is not seen in this direct substitution reaction; however it is formed, in conjunction with the first isomer, in the 1.0 atm carbonylation of $MnRe(CO)_8(PPh_3)_2$ in decalin at 90-120°.

Carbene complexes formally derived from $MnRe(CO)_{10}$, have been reported (16), formed by the following route:

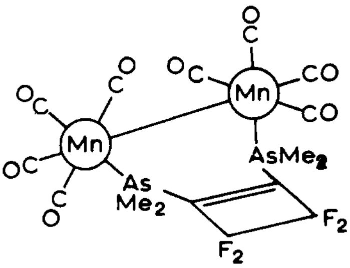
$$\begin{tikzcd}
Mn(CO)_5R \arrow[r, "NaRe(CO)_5"] & Na[(CO)_5ReMn(CO)_4COR] \arrow[d, "MeOSO_2F"] \\
(R = Me, Ph) & \underline{eq} - (CO)_5ReMn(CO)_4C(OMe)R
\end{tikzcd}$$

The geometry around manganese involves cis-$Re(CO)_5$ and C(OMe)R groups. The use of methylfluorosulfonate as a methyl donor appears to be favorable, both here, and in other situations; its use in the synthesis of $Mn_2(CO)_9C(OMe)Me$ results in an improved yield of this product (17).

Other derivatives of the general formula $Mn_2(CO)_9L$ (L = various carbene ligands), formed from $NaMn(CO)_5$ and various α,ω-dihalogen compounds, are described in two theses (18, 19).

A structural study on the compound ax-$Mn_2(CO)_9PPhMe_2$ has been carried out (20); the metal-metal bond length in this compound is 2.904Å, not particularly dissimilar to manganese-manganese bond lengths in other compounds.

The structure of $Mn_2(CO)_8\ Me_2As\overline{C{=}C(AsMe_2)CF_2C}F_2$ has also been determined (21). The structure is derived from that for $Mn_2(CO)_{10}$ with the arsenic atoms coordinated to different manganese atoms. The Mn_2As_2 unit is not planar allowing the manganese carbonyl groups to twist with respect to one another and to assume a staggered configuration (I). The metal-metal bond length is 2.971(2)Å in this compound.



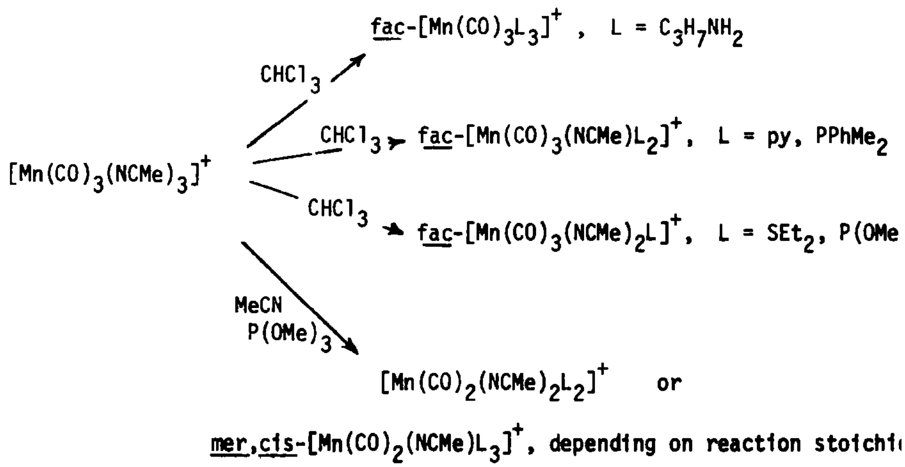
(I)

Complexes derived from $Mn_2(CO)_{10}$ and tris(dimethylamino)phosphine are described in a thesis (22) along with a method for preparing $Mn_2(CO)_{10}$ from $MeC_5H_4Mn(CO)_3$ at low pressures.

There are a series of references to vibrational spectroscopy of mixed metal carbonyls including $MnCo(CO)_9$ and $ReCo(CO)_9$ (23), $TcCo(CO)_9$ (a new compound prepared from $NaCo(CO)_4$ and $Tc(CO)_5Br$) (24), and the anionic $[MnM(CO)_{10}]^-$ (M = Cr, Mo, W) (25).

There are few references to anionic metal carbonyls of this group of metals, excepting of course the references to the use of these species as synthetic intermediates. There is one interesting paper, citing the isolation of the salt $[C_3Bu_3^t][Mn(CO)_5]$ from the reaction of the cation and anion (26). Ordinarily oxidation of the metal carbonyl anion to $Mn_2(CO)_{10}$ occurs in this type of reaction with the cyclopropenium cation being reduced in the process.

A number of studies involving derivatives of the cationic hexacarbonyl species, $[M(CO)_6]^+$, have been reported. Reimann and Singleton (2) have reacted $Mn(CO)_5Br$ in refluxing acetonitrile to prepare the cationic complex fac-$[Mn(CO)_3(CH_3CN)_3]^+$ isolable as the hexafluorophosphate salt. The acetonitrile ligands are quite labile as expected, and can then be replaced by other ligands; several different products may be formed depending on the nature of the incoming ligand. Information on these reactions is summarized in the equations below:



Cationic species from these reactions were isolated as hexafluorophosphate salt: Several were also prepared by other routes. For example, the preparation of mer,cis-$[Mn(CO)_2(NCMe)L_3]PF_6$ from $Mn(CO)_2L_3Br$ and $AgPF_6$ in acetonitrile is mentioned, as is the preparation of $[Mn(CO)_3(CH_3CN)L_2]PF_6$ from $Mn(CO)_3L_2Br$ and $AgPF_6$, in the same sôlvent (L = $P(OMe)_3$).

The analogous reaction of $Re(CO)_5Br$ in acetonitrile gave only $Re(CO)_3$-$(NCMe)_2Br$ (2). When $AgPF_6$ was added however , $[Re(CO)_5(NCMe)]PF_6$ is initiall obtained; this in turn loses two additional carbonyls on refluxing in acetonitr to form $[Re(CO)_3(NCMe)_3]PF_6$.

Several other acetonitrile derivatives of manganese have also been described by these workers (27). Treatment of $Mn(CO)_5Br$ with $NOPF_6$ in acetonitrile gives $[Mn(CO)_5(NCMe)]PF_6$; the same reaction with cis-$Mn(CO)_4(PPhMe$ leads to $[Mn(CO)_4(PPhMe_2)(NCMe)]PF_6$. Oxidation of $[Mn(CO)_4PPh_3]_2$ with NO_2 is al reported, giving cis-$[Mn(CO)_4(PPh_3)(NCMe)]^+$ isolated as hexafluorophosphate salt

It is found that the 17e species mer,trans-$[Mn(CO)_2L_3Br]PF_6$, obtained from one electron oxidation of the uncharged precursor with $NOPF_6$, reacts further with the ligand L to form cis-$[Mn(CO)_2L_4]PF_6$ (L = $P(OMe)_3$, $P(OEt)_3$, $PPh(OMe)_2$). The substitution reaction is followed by reduction (1, 27), in a manner unspecified. The monocation $[Mn(CO)_2\{PPh(OMe)_2\}_4]PF_6$ can be oxidized by $NOPF_6$ or NO_2 to the paramagnetic, 17e species $[Mn(CO)_2\{PPh(OMe)_2\}_4](PF_6)_2$, and in turn this product may be reduced by hydrazine to the starting material (27).

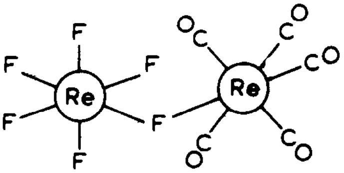
Discussion of the synthesis (28) and the infrared spectra (29) of the methyl isocyanide complexes $[Mn(CO)_{6-x}(CNMe)_x]PF_6$ are found in two theses. Reactions of various $[M(CO)_{6-x}L_x]^+$ compounds with secondary amines to give carboxamido complexes (30, 31) are discussed further in a later section of this review, as is the characterization of a complex $[Re(CO)_6]Re_2F_{11}$ (32).

III METAL CARBONYL HALIDE COMPLEXES AND DERIVATIVES

Earlier mention was made of the photochemical preparation of $Re(CO)_5Cl$ (11) and $Mn(CO)_5I$ (10).

Metal carbonyl fluorides are rare, so reports of these species are quite noteworthy. Two research groups are looking at reactions of rhenium carbonyls which appear to be directed to the synthesis of such compounds. O'Donnell et al. (33) report that the reaction of $Re(CO)_5Cl$ with anhydrous HF at room temperature for three days gives a brown solution, from which a brown, non-crystalline compound identified as $Re(CO)_5F$ can be obtained. The same product is obtained from $Re_2(CO)_{10}$ and XeF_2. Characterization was made from analyses and molecular weight; the solid was diamagnetic and non-conducting. The infrared spectrum (Nujol mull) showed ν(CO) at 2160, 2050, 1970, 1955 cm^{-1}, and ν(M-C) at 350 cm^{-1}; a band at 475 cm^{-1} was assigned to ν(Re-F). Regretably mass spectrometric data could not be obtained.

The same paper reports the reaction of $Re_2(CO)_{10}$ with ReF_6 to give a mixture of $Re(CO)_5F$ and $Re(CO)_3F_3$ along with ReF_5 and CO; identifications of the carbonyl species were made spectroscopically. The compound $Re(CO)_3F_3$, a brown solid with ν(CO) at 2120 cm^{-1}, was also obtained from $Re(CO)_5F$ and XeF_2, but characterization appears to be lacking. It is of interest that a second report (32) appears to contradict some of this work. The reaction of ReF_6 and $Re_2(CO)_{10}$ in HF is said to give a green solution from which two compounds can be obtained. One, in the form of orange prisms, has the stoichiometry $Re(CO)_5F \cdot ReF_5$, and was the subject of an x-ray crystallographic study. Its structure, which has a fluorine atom bridging $Re(CO)_5$ and ReF_5 groups is shown below (II):



(II)

The second compound, a green crystalline species, was also the subject of a crystallographic study. It was found to be made up of discrete $[Re(CO)_6]^+$ cations and $[Re_2F_{11}]^-$ anions. The point is made, however, that the infrared and x-ray powder pattern data for this compound resemble the data presented for the presumed $Re(CO)_3F_3$. Further confirmation of the supposed similarity of these compounds is awaited.

There have been quite a number of references to studies of reactions of various donor molecules with manganese and rhenium pentacarbonyl halides. One of the more extensive studies (34) presents $Mn(CO)_5Br$ reactions with a series of phosphites, phosphines and phosphinic esters. These reactions in refluxing benzene proceed rapidly with the displacement of two carbonyls to give initially _fac_-$Mn(CO)_3L_2Br$ (L = $P(OMe)_3$, $P(OEt)_3$, $PPh(OMe)_2$, PMe_3, $PPhMe_2$); however isomerization to _mer_-$Mn(CO)_3L_2Br$ (_trans_ L groups) is rapid, so that isolation of the pure _fac_- isomer is usually impossible in these reactions. The _fac_-isomers could be isolated from reactions in a lower boiling solvent such as acetone. Among the examples studied, only with the complex formed from $AsPhMe_2$ was the _fac_ isomer more stable than the _mer_ isomer.

Refluxing of benzene solutions of $Mn(CO)_5Br$ with excess phosphorus ligands eventually yield the trisubstituted species *mer*-$Mn(CO)_2L_3Br$; however the $AsPhMe_2$ complex could only be prepared in refluxing n-hexane. No further substitution was then observed in these systems. However, *mer*- $Mn(CO)_2[P(OMe)_3]_3Br$ in $P(OMe)_3$ at reflux did give some $[Mn(CO)_2\{P(OMe)_3\}_4]^+$ in solution, identified by infrared spectrum. Further substitution could be effected only by the circuitous route via *trans*-$Mn(CO)_2\{P(OMe)_3\}_3Br$ shown below.

$$\textit{mer}\text{-Mn(CO)}_2\text{L}_3\text{Br} \xrightarrow{\text{NOPF}_6} \textit{trans}\text{-[Mn(CO)}_2\text{L}_3\text{Br]PF}_6$$

$$\xrightarrow{\text{N}_2\text{H}_4} \textit{trans}\text{-Mn(CO)}_2\text{L}_3\text{Br} \xrightarrow[80^\circ]{\text{L}} \textit{trans}\text{-Mn(CO)L}_4\text{Br}$$

$L = P(OMe)_3$

As stated in the introduction the stable existence of 17e species is noteworthy. The equation above provides an indication of the potential usefulness of such species as intermediates to products not accessible by usual routes. Several examples of 17e complexes, of the formula $Mn(CO)_2L_4{}^{2+}$ were noted earlier in this review. In addition a whole series of $[Mn(CO)_2L_3Br]PF_6$ species which are derived from the one electron oxidation by $NOPF_6$ of the neutral 18e compounds, $Mn(CO)_2L_3Br$ are reported (27). These include *mer,cis*-$[Mn(CO)_2(PMe_3)_3Br]PF_6$, and *mer,trans*-$[Mn(CO)_2L_3Br]PF_6$ ($L = P(OMe)_3$, $P(OEt)_3$, $PPh(OMe)_2$, $PPhMe_2$). The use of NO_2 as an oxidant with $Mn(CO)_2\{P(OPh)_3\}_3Br$, to give $[Mn(CO)_2\{P(OPh)_3\}_3Br]^+$ is also mentioned (1). See also the comments on nitrosyl complexes found in Section VIII, later in this survey, concerning this reaction of NO_2.

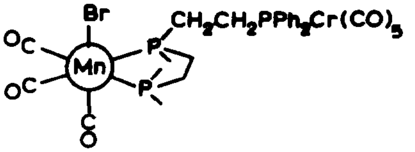
There is also a reference to the one-electron oxidation of $Re(CO)_3(PPh_3)_2Cl$ to $[Re(CO)_3(PPh_3)_2Cl]BF_4$ by $[Et_3O]BF_4$ (35).

Other derivatives of $Mn(CO)_5Br$ to be reported in the last year include $Mn(CO)_3(PH_3)_2Br$ (36) and $Mn(CO)_4(PR_2SH)Br$ (R = Me, Et, Ph) (37). The latter, prepared from the phosphine sulfide, SPR_2H, and $Mn(CO)_5Br$ in cyclohexane (55°),

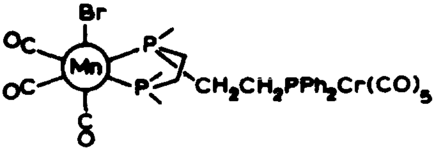
$$Mn(CO)_5Br + S{=}PR_2H \longrightarrow Mn(CO)_4(PR_2SH)Br$$

are rather interesting in that their formation requires a conversion of the secondary phosphine sulfide to the less stable isomeric diorganothiophosphinic acid. Diazomethane was used to convert $Mn(CO)_4(PR_2SH)Br$ to $Mn(CO)_4(PR_2SMe)Br$.

The reaction of triphosphine $(Ph_2PCH_2CH_2)_2PPh$ with $Mn(CO)_5Br$ to give two isomers of the formula $Mn(CO)_3$(triphos)Br was reported in a communication last year and a full paper has now appeared on this work (38). This paper describes the further reaction of this species with $P(OMe)_3$, to give $Mn(CO)_2\{P(OMe)_3\}$(triph which in turn is oxidizable to the phosphine oxide by oxygen, or converted to $Cr(CO)_5$- derivative with $Cr(CO)_5THF$. Structural characterization of the two isomeric forms of $Mn(CO)_3Br(triphos)Cr(CO)_5$ was accomplished by x-ray crystallography (39). The structures are shown below (III and IV).



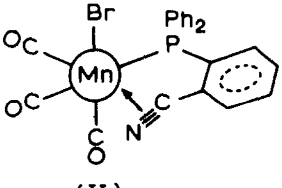
(III) (α-form)



(IV) (β-form)

The crystal structure of <u>fac</u>-$Mn(CO)_3(Me_2AsCH_2CH_2CH_2AsMe_2)Cl$ is reported (40), as has the structure of <u>fac</u>-$Mn(CO)_3(CNCH_3)_2Br$ (29). Syntheses of $Mn(CO)_{5-x}(CNCH_3)_xBr$ compounds appear in a thesis (28).

The reaction of o-cyanophenyldiphenylphosphine with manganese and rhenium pentacarbonyl bromides is reported (41,42). With the manganese compound a product $Mn(CO)_3LBr$ is formed. Its monomeric formulation is ascertained by molecular weight data, and to be in accord with the 18e rule it is suggested that the CN group is coordinated to the metal. Steric considerations dictate that this must occur using the π-electrons of this group, rather than the nitrogen lone pair (V). In contrast, however, a rhenium analogue of the same formula is found to be dimeric. Hence its structure is said to utilize the phosphine in a bridging capacity bonding through phosphorus to one rhenium and through



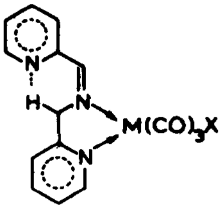
(V)

the C≡N group to the other.

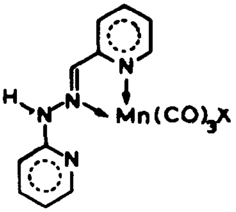
Monomeric compounds of cyanoethyldiphenylphosphine with $Mn(CO)_5X$ (X = Cl,Br), having the same formula, are also said to bond the ligand in a bidentate fashion, analogous to V. Other organonitriles ($NC(CH_2)_xCN$ x = 1,2,3; $o-C_6H_4(CN)_2$) are reported to bond to manganese in the same fashion if geometric considerations dictate it (43).

The carbene derivatives $Mn(CO)_4[C(OH)Me]X$ (X = Br, I) are isolated following protonation of $Mn(CO)_4(COMe)X^-$; the latter anions are obtained by reaction of halide ions with $Mn(CO)_5Me$ (44).

The two isomeric forms of 2-pyridine-2-carbaldehyde-2-pyridylhydrazone (z-paphy, and E-paphy) react with $Mn(CO)_5X$ (X = Cl, Br, I) to give the isomeric compounds drawn below (VI, VII); the reaction of z-paphy with $Re(CO)_5Cl$ is also noted (45).



(VI) (z-paphy complexes, M = Re
X = Cl, Br, I, M = Mn, X = Br, I)



(VII) (E-paphy complexes; X = Br, I)

Various substitution reactions of rhenium pentacarbonyl halides are mentioned. With excess phosphine or phosphite reagents and $Re(CO)_5Br$ in refluxing benzene-petroleum ether the trisubstituted derivatives <u>mer,cis</u>-$Re(CO)_2L_3Br$ (L = PMe_3, $PPhMe_2$, $PPhEt_2$, PPh_2Me, PPh_2OEt, $PPh(OMe)_2$, $PPh(OEt)_2$, and $P(OR)_3$ for R = Ph, Me, Et, i-Pr, Bu) are formed. It is also possible, using the same solvent and temperature (100-120°) and stoichiometric ratios of reactants to isolate fac-$Re(CO)_3L_2Br$ species; these are found to be converted to the mer,trans- geometries (46) upon prolonged reflux. The presence of $NaBH_4$, which has a labilizing effect on ligands, appears to facilitate this reaction. It was more difficult to effect isomerization for those compounds for which L is small such as PMe_3.

Reactions with the potentially monodentate or bidentate diarsine ligand, $Ph_2AsCH_2AsPh_2$(As^As) with $Re(CO)_5X$ (X = Cl, Br, I) are reported (47). The rates of reaction are highest for the chloride and decrease from bromide to iodide. Various products are obtained in these reactions, depending on solvent, time, and mole ratios of reactants, including $Re(CO)_4$(As^As)X and $Re(CO)_3(As\hat{}As)_2X$ where the ligand is presumed to be monodentate, coordinating via one arsenic atom only, $Re(CO)_3$(As^As)X and $Re(CO)_2$(As^As)X, requiring a chelating formulation for the ligand, $Re_2(CO)_6X_2$(As^As) wherein each arsenic atom in the ligand coordinates to a different rhenium atom which in turn are also linked by halogen bridges.

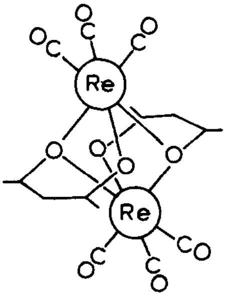
The same authors report the synthesis of a new series of metal carbonyl halides (48). When $Re(CO)_5X$ complexes (X = Cl, Br, I) are refluxed in heptane the formulation of the dinuclear $[Re(CO)_4X]_2$ species is seen to occur first; then one further carbonyl group is lost with the formation of polynuclear $[Re(CO)_3X]_n$ compounds. No molecular weights could be obtained due to the insolubility of these species in noncoordinating solvents, but the suggestion is made that they could be trimeric or tetrameric, analogous to known sulfur species $[Re(CO)_3SR]_{3,or\ 4}$. These compounds dissolve in polar solvents with reaction; for example in pyridine $Re(CO)_3(py)_2X$ compounds are formed.

Base strengths vs. Al_2Me_6 have been determined for a number of phosphine complexes of rhenium including $Re(CO)(PPhMe_2)_4Cl$; however the major thrust of these studies concerned the base strengths of rhenium dinitrogen species such as $Re(N_2)(PPhMe_2)_4Cl$ (49).

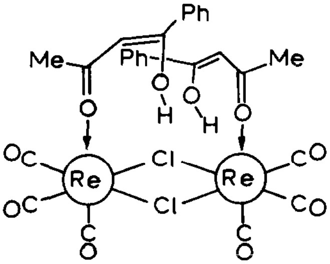
A number of studies involving oxygen donor ligands are referenced also. When $Re(CO)_5Br$ or $Re_2(CO)_8Br_2$ is refluxed in tetrahydrofuran the compounds

$Re(CO)_4(THF)Br$ and $[Re(CO)_3(THF)Br]_2$ are formed (50). These reactions can be followed spectroscopically. The halogen bridged dimer can be used as a reaction intermediate; in further reactions with $C_6H_{11}NC$ or bipyridine the species $Re(CO)_3(CNC_6H_{11})_2Br$ and $Re(CO)_3(bipy)Br$ can be obtained. A somewhat analogous observation was made using methanol as solvent (43), wherein the dimeric $[Re(CO)_3(CH_3OH)X]_2$ (X = Cl, Br) complexes could be isolated. Using dioxane, however, a complex of stoichiometry $Re(CO)_3(diox)Cl$ is formed; this loses solvent to give $[Re(CO)_3Cl]_x$.

The reactions of β-diketones and $Re(CO)_5Cl$ have provided some unusual results (51,52). The structures of two compounds from these reactions have been ascertained by x-ray crystallography. The compound $Re_2(CO)_6(dbm)_2$ (dbm = dibenzoylmethanato) group has the structure shown in VIII, below; the dbm ligands function in a bridging capacity. In the compound, $[Re(CO)_3Cl(bamH)]_2$ (bamH = benzoylacetylmethane), each diketone ligand, in its enol form, serves to coordinate in a monodentate fashion through the ketonic oxygen (IX).



(VIII) (Ph groups omitted)

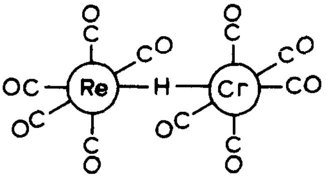


(IX)

The infrared and Raman spectra for various isotopically labeled (^{13}CO, $C^{18}O$) $Mn(CO)_5Br$ species as solids and in CH_2Cl_2 solution have been studied, vibrations were assigned and force constants calculated (53). The photoelectron spectra for the manganese carbonyl halides ($M(CO)_5X$, X = Cl, Br, I) and for $Mn(CO)_4(CNCH_3)Br$ are reported (54, 29); data correlate well with MO calculations on energies of orbitals.

IV HYDRIDO AND ALKYL (ARYL) METAL COMPLEXES

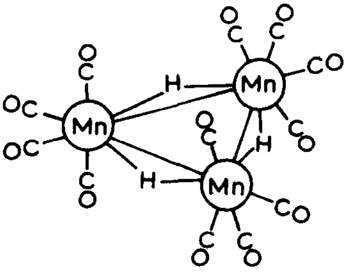
Remarkably stable hydride bridged species $(CO)_5ReHM(CO)_5$ (M = Cr, W) have been reported (55). They are prepared upon H_3PO_4 acidification of the anions $[MM'(CO)_{10}]^-$ (M = Cr, W; M' = Re), and were identified by mass spectroscopy and various spectroscopic methods. The crystal structure of one of these complexes, $(CO)_5ReHCr(CO)_5$, has been determined and is presented below (X). It is similar to the known structure of $Cr_2(CO)_{10}H^-$, and has a long metal-metal distance of 3.435(1)Å.



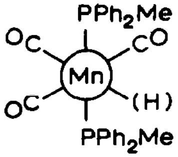
(X)

Preparation of other analogous compounds were attempted but they appear considerably less stable.

Crystal structures of two other hydrido complexes of manganese have also been reported. The structure of $Mn_3(CO)_{12}H_3$ (56) consists of a triangular arrangement of $Mn(CO)_4$ groups (XI). Bridging hydrogens were located, symmetricall situated along each edge of the triangle. The average manganese-manganese distance is 3.111(2)Å and the manganese-hydrogen distance is 1.72(3)Å. The compound $Mn(CO)_3(PPh_2Me)_2H$, (XII) formed from $Mn_2(CO)_{10}$ and the phosphine in excess in either petroleum ether (bp 100-120°) or in n-propanol, has been shown



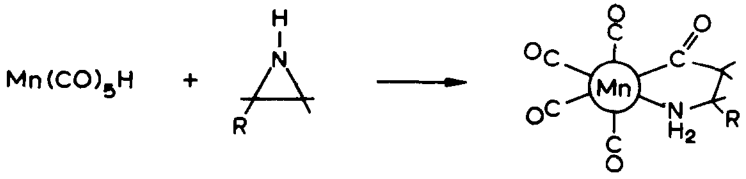
(XI)



(XII)

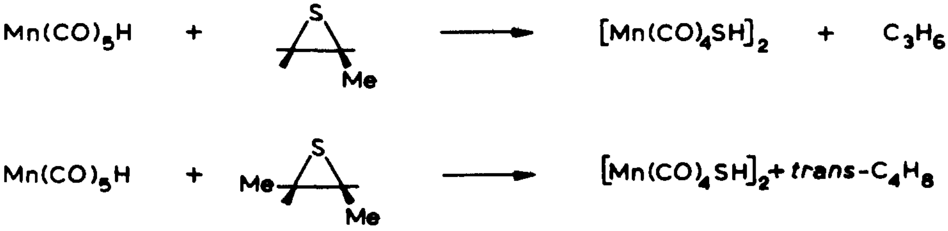
to have a distorted octahedral geometry with ligands in a mer,trans- configuration (57). The carbon-manganese angle (trans carbonyls) is only 153°. Apparently the hydride was not located precisely.

A study of manganese carbonyl hydride reactions with several three-membered heterocyclic compounds has been carried out (58). With aziridines the following reactions occur:



(R = H,Me)

The product species are identical to products characterized earlier from reactions of $Mn(CO)_5^-$ and $H_2NCH_2CH_2COCl$. With thiiranes a different reaction was noted however. An olefin is eliminated and the SH group remaining incorporated into the product.



The thiol bridged compound, believed formed via $Mn(CO)_5SH$, has three ν(SH) absorptions in its infrared spectrum suggesting that there are two isomeric forms. This could occur as a result of different S-H orientations, the groups being either in syn or anti positions with respect to each other.

An enthalpy of formation, ΔH_f, has been reported for $Mn(CO)_5H$ (and several other compounds) from mass spectral data on appearance potentials (59). A value of ΔH_f of -237 Kcal/mole is suggested. Using this value the bond energy for the Mn-H bond is determined to be 7 ± 12 Kcal/mole; this small value supports earlier claims that this bond is very weak.

Syntheses of σ-cyanocarbon and σ-fluorocarbon complexes of manganese and rhenium pentacarbonyls is mentioned. The compounds $Mn(CO)_5CX{=}C(CN)_2$ (X = H, CN, Cl) were prepared from $NaMn(CO)_5$ and the halide $ClCX{=}C(CN)_2$ (60). Preparation of perfluoro-1-methylpropenyl derivatives of manganese and rhenium from a silver salt of this group is reported in a thesis (61).

$$Ag[(-C(CF_3){=}CFCF_3)] + M(CO)_5Br \rightarrow M(CO)_5C(CF_3){=}CFCF_3$$

In contrast to the success described above in the preparation of cyanovinyl-metal carbonyls, an attempt to prepare tricyanomethyl derivatives of manganese and rhenium from $Mn(CO)_5Br$ or $Re(CO)_5Cl$ and $K[C(CN)_3]$ met with failure. Instead, a polymeric product $[Mn(CO)_3NCC(CN)_2]_x$ was formed in this reaction. The aggregation is presumably a result of the $C(CN)_3$ anion bridging two or three metal atoms. A mononuclear derivative can be formed on treatment with this polymeric compound with triphenylphosphine; its structure appears to involve the tricyanomethyl group bonding to the metal via one nitrogen, vis. $M(CO)_3(PPh_3)_2{-}N{=}C{=}C(CN)_2$ (M = Mn, Re) (62).

Similar reactions are said to occur with $K[C(COOEt)_3]$, (62) to give oxygen bonded derivatives $[M(CO)_3OC(OEt){=}C(COOEt)_2]_x$, (M = Mn, Re), and $Mn(CO)_3$-$(PPh_3)_2{-}OC(OEt){=}C(COOEt)_2$.

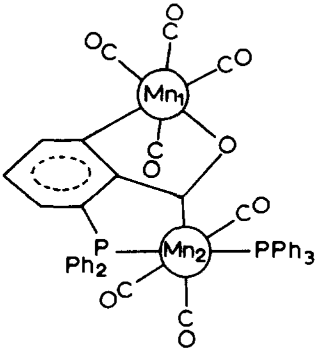
A useful method for decarbonylation of acyl-metal complexes utilizes $Rh(PPh_3)_3Cl$ as a carbonyl scavenger (63). With acetylmanganese pentacarbonyl this reaction is:

$$Mn(CO)_5COMe + Rh(PPh_3)_3Cl \rightarrow \underset{(95\%)}{Rh(PPh_3)_2(CO)Cl} + \underset{(12\%)}{Mn(CO)_5Me}$$

The yield of the manganese compound is poor so use of this reaction here is not competitive with other available methods. In other instances this is the favored reaction however.

Studies of reactions involving ortho-metallation of an aryl group were cited in the introduction of this review as one of the significant developments in the Group VIIB metal carbonyl chemistry. Further elaboration on this work follows.

When $Mn(CO)_4C_6H_4PPh_2$ and cis-$Mn(CO)_4(PPh_3)Me$ are refluxed in toluene (2 hrs) five compounds are formed (5). These compounds could be separated by chromatography. The first compound in 15-25% yield followed elution of starting material in the chromatography. It is a yellow-orange crystalline solid; a crystallographi study revealed the structure shown below (XIII).



(XIII)

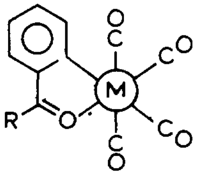
The other products of this reaction included: a product derived from XIII by loss of 3 CO which can be generated directly from XIII by heating at 170°; a product derived from XIII by substitution of one carbonyl on Mn_1 by PPh_3: $\overline{Mn(CO)_3(PPh_3)C_6H_4P}Ph_2$; and $\overline{Mn(CO)_4COC_6H_4P}Ph_2$.

The reaction of $\overline{Mn(CO)_4C_6H_4P}Ph_2$ with $Mn(CO)_5Me$ gave another product analogous to XIII, with the terminal phosphine replaced by CO, in addition to $Mn_2(CO)_{10}$. The analogous reaction with $Re(CO)_5Me$ to give a similar product (one rhenium atom replacing a manganese atom) is also noted (5).

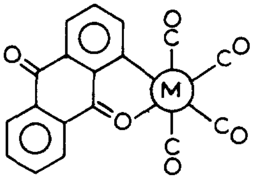
Some of the earlier work on metallations, including formation of $\overline{Mn(CO)_4C_6H_4P}Ph_2$ is detailed in a thesis (64).

Work from the same group on the metallation of aryl ketones is also noted (6). The reactions of $M(CO)_5Me$ (M = Mn, Re) with benzophenone, and of $Mn(CO)_5Me$ with acetophenone, at 80-125° for up to 12 hrs proceed with methane elimination.

The structures of the resultant products are shown below (XIV). An analogous reaction product is formed from anthroquinone and $Re(CO)_5Me$ (XV).

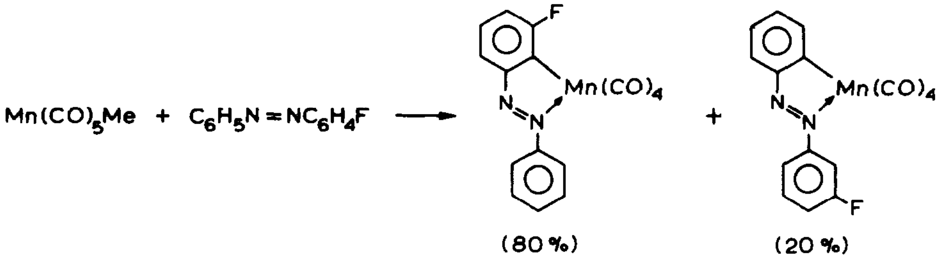


(XIV)
(Mn, R = Me, Ph
Re, R = Ph)



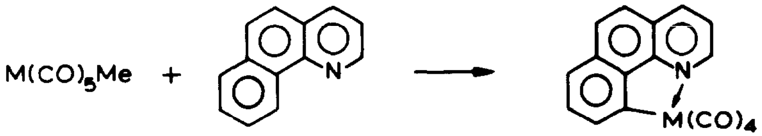
(XV)

Bruce, Goodall, and Stone have used a similar reaction to metallate azobenzenes (3) and also benzo(h)quinoline (4). With m-fluoroazobenzene, and $Mn(CO)_5Me$ two products were obtained, resulting from metallation at different rings. The product in higher yield was the one involving metallation ortho to the fluoro group substituent, which is consistent with a mechanism involving nucleophilic attack, since such a reaction should be promoted by the o-fluoro group. This result contrasts with the results of metallation

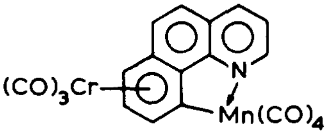


reported with $PdCl_2$, where metallation of the fluorophenyl ring in positions ortho (<1%) and para (20%) to the fluoro substituent group occurs, but metallation on the other ring occurs to the extent of 80%. This result is consistent with the palladation reaction occurring via electrophilic substitution.

The metallation of benzo(h)quinoline by both $Mn(CO)_5Me$ and $Re(CO)_5Me$ occurs according to the following reaction (4):

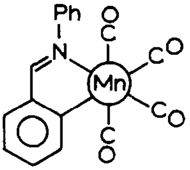


A monosubstituted phosphine complex, $Mn(CO)_3(PPh_2Me)C_{13}H_8N$ was isolated on reaction of the product with phosphine. Spectroscopic evidence for a disubstituted complex was also obtained. In addition the reaction with [benzo(h)quinoline]$Cr(CO)_3$ and $Mn(CO)_5Me$ to give a bimetallic product (XVI).

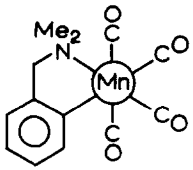


(XVI)

The crystal structures of compounds derived from benzylideneaniline (8) and benzyldimethylamine (7) and $Mn(CO)_5Me$ are reported by Little and Doedens. Structures are shown below (XVI, XVIII)

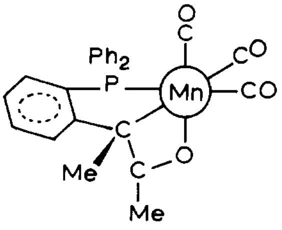


(XVII)

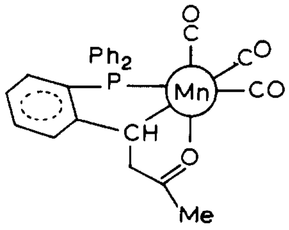


(XVIII)

A rather interesting reaction of $Mn(CO)_5Me$ with o-vinylphenyldiphenylphosphine has been reported to give two isomeric products (65), whose structures are drawn below (XIX, XX). The structure of XVIII was ascertained crystallographically. Formation of both products can be rationalized; the reaction is presumably initiated by formation of an intermediate $Mn(CO)_4(phos)COCH_3$, in a carbonyl insertion reaction typical for these systems. One product, XX, then arises from addition of the manganese-acetyl group across the vinyl double bond, the acetyl group adding to the 2-position.



(XIX)



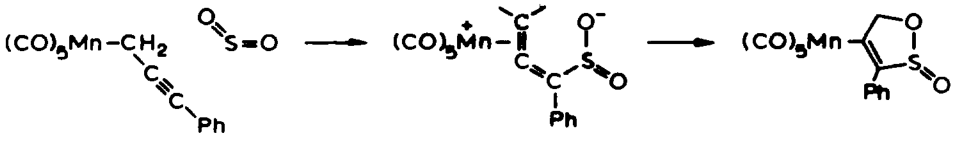
(XX)

The other product can be assumed to form via the reverse addition (i.e. the acetyl group adding to the 1-position) followed by hydrogen migration.

Several completed studies on SO_2 insertion into metal carbon σ-bonds are noted, and new information is presented with respect to mechanisms (66). When solutions of $M(CO)_5R$ (M = Mn, Re; R = Me, CH_2Ph) are prepared in liquid SO_2, or in hydrocarbon solvents containing dissolved SO_2, an initial reaction occurs to give a product identified as either $M(CO)_5O\overset{O}{S}R$ or $M(CO)_5\overset{O}{S}OR$. The authors indicate a preference to the first formulation, having a metal-oxygen bond; they suggest this structure is more in accord with the observation of facile displacement of the sulfinato group by iodide ion. This initial product is stable only in the presence of SO_2 however, and rearranges on standing or on attempted isolation to give the isolable S-sulfinato compound $M(CO)_5SO_2R$.

Further information on this subject may be found in a thesis (67).

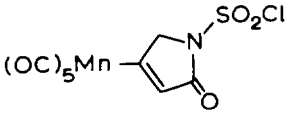
The reaction of $Mn(CO)_5CH_2C{\equiv}CPh$ with liquid SO_2 occurs to give $Mn(CO)_5\overline{C{=}CPhS({=}O)OC}H_2$, rather than simple insertion however (68). The following mechanism is proposed:



Sulfur dioxide is viewed as being electrophilic, coordinating to the acetylenic bond through sulfur. In turn this makes the oxygen nucleophilic and it is in a position to attack the $-CH_2$ group internally, giving the observed product.

The $KMnO_4$ oxidation of the product of this reaction to a metal sulfone compound, $Mn(CO)_5\text{-}\overline{C{=}CPhSO_2OC}H_2$; the same product can be obtained by the direct reaction of $Mn(CO)_5CH_2C{\equiv}CPh$ and SO_3 (68).

The reaction of $Mn(CO)_5CH_2C{\equiv}CPh$ (and other metal compounds as well), with $ClSO_2NCO$ is reported (69). The product of this reaction is shown below (XXI);



(XXI)

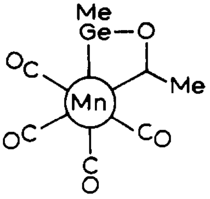
its mechanism of formation is considered to be similar to the SO_2 addition reaction described above. Diethylamine solvolyzes the $N\text{-}SO_2Cl$ bond in this species to give $Mn(CO)_5\text{-}\overline{C{=}CPh\text{-}CO\text{-}NHC}H_2$.

Interestingly, the reaction of $Mn(CO)_5CH_2CH{=}CHPh$ and $ClSO_2NCO$ gives only $Mn(CO)_5Cl$; in contrast addition reactions are found to occur with other metal systems of this σ-allyl group (69).

The carbonyl insertion into the metal carbon σ bond in $M(CO)_5R$ (R = Me, Ph) upon reaction with $M(CO)_5^-$ (M = Mn, Re) was noted earlier (16,19) in that these product species are precursors to metal carbene species.

In two other instances insertion reactions into metal-carbon σ bonds were noted. Treatment of $Mn(CO)_5Me$ with halide ion (X = Br, I) gives $Mn(CO)_4(COMe)X^-$ which can be protonated at the acyl oxygen to give the carbene complexes $Mn(CO)_4[C(OH)Me]X$. These species with cyclohexylamine give $Mn(CO)_4(C_6H_{11}NH_2)COMe$, and with water give $Mn(CO)_5Me$ (44). Treatment of $Mn(CO)_5GeR_3$ (R = Me, Ph) with methyllithium in ethyl ether generates $Li[Mn(CO)_4(GeR_3)(COMe)]$. A carbene complex $Mn(CO)_4[C(OEt)Me]GeR_3$ is obtained with triethyloxonium tetrafluoroborate; reaction with aqueous HCl generates another unusual carbene complex (XXII) (70).

Carbamoyl derivatives of manganese and rhenium have received some attention. Four different routes for the synthesis of these rhenium complexes are described (30); these include: a) the reaction of $Re(CO)_6^+$ and various



(XXII)

secondary amines; b) the reaction of $Re(CO)_6^+$ and amide ions NRR'^-; c) reactions of $Re(CO)_5^-$ and organic isocyanates, RNCO, followed by protonation; and d) solvolysis of $Re(CO)_5COOMe$ and $M(CO)_3(PPh_3)_2COOMe$ (M = Mn, Re) by secondary amines. These last reactions are reversible. Compounds described here include the following: $Re(CO)_5CONRR'$ (NR_2 = NHMe, NHEt, $NHBu^n$, NHC_6H_{11}, $NHBu^s$, $NHBu^t$, NMe_2, NEt_2, NC_4H_8, NC_5H_{10}). Reaction of the various species $M(CO)_5COOMe$ with hydrazine to give $M(CO)_5NCO$ (M = Mn, Re) species is also reported in this paper.

Further related work has probed both the equilibrium position and kinetics of the forward reaction for the following systems (31):

$$\underline{\text{trans}}\text{-}[M(CO)_4L_2]^+ + 2RNH_2 \rightleftarrows M(CO)_3L_2\overset{\overset{\displaystyle O}{\|}}{C}NHR + NH_3R^+$$

The rate law for the reaction, rate = $k_3[M(CO)_4L_2^+][RNH_2]^2$, suggests that these reactions occur via base catalyzed amine attack at a coordinated carbonyl group. Rates are found to be greater for rhenium complexes than for the analogous manganese systems. The effect of ligand variation on rate is $PPh_2Me > PPhMe_2 > PPh_3$; it is suggested that electronic effects determine the general trend in this series except that for steric reasons PPh_3 is out of order.

Equilibrium constants for the above reactions of $Mn(CO)_4L_2^+$ decrease with increasing size of L ($PPhMe_2 > PPh_2Me > PPh_3$) and with increasing size of the amine (31).

V METAL CARBONYL DERIVATIVES OF METALS AND METALLOIDS

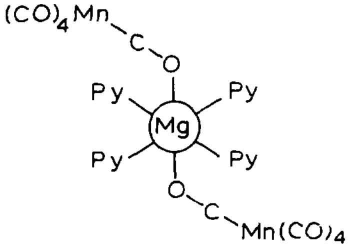
Following a period of very active interest in compounds of this type, research activity seems now to have ebbed somewhat; still there have been a few papers breaking new ground and a more substantial number filling in some additional details in this area.

An interesting communication on lanthanide derivatives of manganese pentacarbonyl has appeared (71). The electropositive metals yttrium, promethium, samarium, dysprosium, holmium, erbium and ytterbium react with $Mn(CO)_5Br$ in tetrahydrofuran in a manner analogous to magnesium. The red solutions from these reactions are air and moisture sensitive and are presumed to contain some species $M[Mn(CO)_5]_xBr_y$. These solutions are weakly conducting, show $\nu(CO)$ bands appropriate for carbonyl containing species, and undergo reactions typical of Grignard type derivatives. For example they react with $SnPh_3Cl$ to give $Mn(CO)_5SnPh_3$, and with methyl iodide to give $Mn(CO)_5Me$. On addition of a base, manganese carbonyl complexes $Mn_2(CO)_8L_2$ (L = PPh_3, 2,2'-bipy, o-phen) are formed. In one instance a lanthanide metal derivative can be isolated. Following treatment of the holmium compound with Na(acac) the compound $[Mn(CO)_5]Hoacac\cdot 2Et_2O$ can be obtained.

Crystal structures of $Hg[Mn(CO)_5]_2$ (72) and of $terpyrCd[Mn(CO)_5]_2$ (73) are reported, the former in a thesis. A discussion of zinc derivatives of manganese pentacarbonyl including $Zn[Mn(CO)_5]_2$ and $[MeOZnMn(CO)_5]_4$ is also found in a thesis (74).

Reaction of $Hg[C_5H_5Mo(CO)_3]_2$ and manganese metal in tetrahydrofuran, followed by recrystallization from pyridine gives an air-sensitive white solid $[C_5H_5Mo(CO)_3]_2Mnpy_4$ (75). The same reactions are reported for the chromium and tungsten analogues. These products are derivatives of divalent manganese and are not strictly speaking organometallic compounds of this metal since they contain no manganese-carbon bond. The manganese atom is assumed to be bonded to an oxygen atom of a carbonyl group, resulting in a very low $\nu(CO)$ value; the structures are thus analogous to that of the known magnesium compound $[C_5H_5Mo(CO)_3]_2Mgpy_4$ (76).

A compound similar to those discussed above, having the formula $[Mn(CO)_5]_2Mgpy_4$ (XXIII) has been described (76). It has ν(CO) absorptions

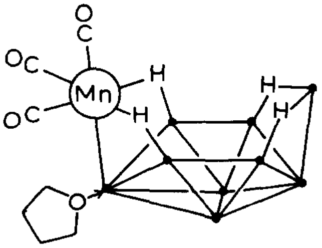


(XXIII)

at 2131(w), 1928(s), 1904(s) and 1721(s), the lower frequency absorption being due to the carbonyl coordinated through oxygen to magnesium. The $Mn(CO)_5^-$ group in this compound is a substantial nucleophile implying the bond to magnesium (II) is quite ionic; for example, the compound reacts with $SiPh_3Cl$ to give $Mn(CO)_5SiPh_3$.

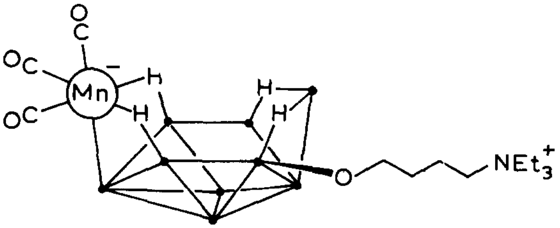
Formation of mercury derivatives of manganese pentacarbonyl, including $Mn(CO)_5HgCl$ and $Mn(CO)_5HgMe$, occurs when $Mn(CO)_5SnMe_3$ is reacted with $HgCl_2$ and MeHgCl respectively. However with PhHgCl, the known $Hg[Mn(CO)_5]_2$ forms instead (77).

Several new manganese carbonyl derivatives of borane and carborane anions have been reported. When $Mn(CO)_5Br$ and the anion, $B_9H_{14}^-$, are refluxed in tetrahydrofuran several metalloboranes are formed. The characterization of the complex $[Mn(CO)_3B_9H_{13}]^-$ as the tetramethylammonium salt, and $Mn(CO)_3(B_9H_{12}\cdot THF)$, are described in a communication (78). A crystallographic study on the latter species has defined its molecule structure. The structure (XXIV) is essentially that of decaborane, with the $Mn(CO)_3$ group replacing the boron (BH) group in position 6; the tetrahydrofuran is attached to B(2) which is also lacking a hydrogen. The former compound has an analogous structure, with a hydrogen (formally H^-) instead of tetrahydrofuran bonded to B(2).



(XXIV)

An interesting reaction has been found to occur when this compound (XXIV) is reacted with triethylamine in refluxing tetrahydrofuran (79). Instead of the expected ligand replacement ring opening of the coordinated tetrahydrofuran occurs forming the zwitterionic compound XXV, shown below;

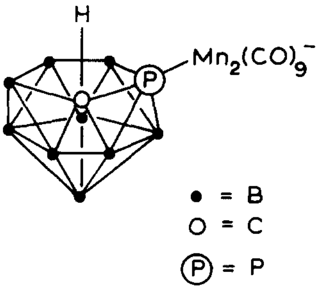


(XXV)

a skeletal rearrangement probably occurs as well to allow the butoxy group to find its way to the B(8) position.

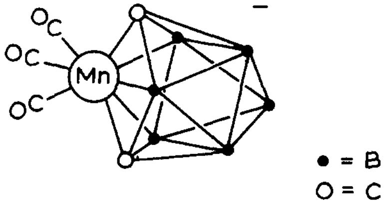
A reaction of $Me_4N[7,8\text{-}B_9H_{10}(CH)P]$ with several metal carbonyls including $Mn_2(CO)_{10}$ under ultraviolet irradiation occurs (80). The product from this reaction is $Me_4N[7,8\text{-}B_9H_{10}(CH)PMn_2(CO)_9]$; its structure is suggested to be that of an axially substituted $Mn_2(CO)_9L$ derivative, with the phosphacarborane anion bonding through phosphorus to the metal (XXVI). The reaction of $Me_4N[7,9\text{-}B_9H_{10}(CH)P]$ with $Mn_2(CO)_{10}$ under photolytic conditions gave a disubstituted product, $[Me_4N]_2[Mn_2(CO)_8\{B_9H_{10}(CH)P\}_2]$ however, its stereochemistry was not defined.

The structure of the anion $[B_6C_2H_8Mn(CO)_3]^-$, obtained as the triphenylmethylphosphonium salt was determined (81). This confirmed the earlier



(XXVI)

structural prediction made on the basis of infrared and nmr evidence. The structure, represented below (XXVII), may be viewed as a tricapped trigonal prism; the manganese tricarbonyl group is bonded to two carbon and three boron atoms.



(XXVII) $[B_6C_2H_8Mn(CO)_3]^-$

The only other reference work on Group IIIA derivatives of the manganese group metals concerns reactions of Ph_2TlCl and $PhTlCl_2$ with $NaMn(CO)_5$ to give $Mn(CO)_5TlPh_2$ and $[Mn(CO)_5]_2TlCl$ respectively (82). In addition a thesis on $M[Mn(CO)_5]_3$ compounds (M = In, Tl) is noted (83).

A number of references describing syntheses of simple Group IVA derivatives of manganese and rhenium carbonyls have appeared. The reaction of $NaRe(CO)_5$ and GeH_3Br is reported to give primarily $Re(CO)_5GeH_3$ along with a small amount of $GeH_2[Mn(CO)_5]_2$ (84). Various dimethylvinylgermyl derivatives including $Mn(CO)_5GeMe_2Vi$, $Mn(CO)_4(PPh_3)GeMe_2Vi$, and $Re(CO)_5GeMe_2Vi$, were prepared from $GeMe_2ViI$ and the appropriate carbonylmetallate anions (85). Trifluorosilyl derivatives of the same three metal carbonyl groups were prepared by reaction of the SiF_3H and either $M_2(CO)_{10}$ (M = Mn, Re) or $[Mn(CO)_4PPh_3]_2$ (86). The compound $Mn(CO)_5SiF_3$, a volatile, very thermally stable species, reacts with water to give a manganese carbonyl substituted siloxane polymer. The preparation of $[Mn(CO)_5]_2GePh_2$ from $Mn(CO)_5^-$ and Ph_2GeBr_2 and of $Mn(CO)_5GePh_2Cl$ from $Mn(CO)_5^-$ and Ph_2GeBr_2 is noted in a thesis (87); also found in a thesis is the preparation of the series of compounds $Mn(CO)_5GePh_{3-n}Cl_n$, $Mn(CO)_5Sn(C_6F_5)_{3-n}(C_6H_5)_n$ (88). From each member of the latter series of compounds on treatment with chlorine one can obtain $Mn(CO)_5Sn(C_6F_5)_{3-n}Cl_n$ derivatives. Referred to earlier in this review was the synthesis of $Mn(CO)_5SiPh_3$ from $[Mn(CO)_5]_2Mgpy_4$ and $SiPh_3Cl$ (76).

Several papers have noted reactions of Group IVA derivatives of manganese carbonyls. The compounds $Mn(CO)_5GeMe_2Vi$ on photolysis give only $Mn_2(CO)_{10}$, in contrast to results with several other metal carbonyl systems (85). Iodine cleaves the tin-manganese bond in $Mn(CO)_5SnR_3$ (R = Me, allyl) to give $Mn(CO)_5I$ and R_3SnI. Reactions of the same species occur with Me_3SiCl to give only $Mn(CO)_5Cl$ and R_3SnCl (R = Me only), with PhHgCl to give $Hg[Mn(CO)_5]_2$ and with MeHgCl to give a mixture of $SnMe_3Cl$, Me_2Hg, $SnMe_4$, and $MeHgMn(CO)_5$ (77). Chlorine or bromine with $Ph_2Pb[Mn(CO)_5]_2$ yields $K_2Pb[Mn(CO)_5]_2$, with cleavage of Pb-C and not Pb-Mn bonds. However in acetone the compound $Br_2Pb[Mn(CO)_5]_2$ undergoes the following reductive elimination reaction (89):

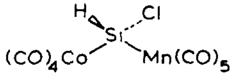
$$Br_2Pb[Mn(CO)_5]_2 \xrightarrow{\text{acetone}} Mn_2(CO)_{10} + PbBr_2$$

The compound $Mn(CO)_5PbMe_3$ undergoes disproportionation in tetrahydrofuran, giving $PbMe_4$ and $Me_2Pb[Mn(CO)_5]_2$ (89).

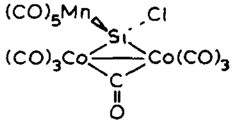
$$Mn(CO)_5PbMe_3 \xrightarrow{\text{THF}} PbMe_4 + Me_2Pb[Mn(CO)_5]_2$$

The synthesis of various silicon manganese carbonyl compounds including $H_2Si[Mn(CO)_5]_2$ and $Cl_2Si[Mn(CO)_5]_2$ is reported in a thesis (90). Reaction of several silyl-manganese carbonyls with various other metal carbonyls gives mixed metal carbonyl aggregates (90, 91). For example, the reaction of $Mn(CO)_5SiH_2Cl$ with $Co_2(CO)_8$ gives $(CO)_4Co\text{-}SiHCl\text{-}Mn(CO)_5$ and $Mn(CO)_5SiClCo_2(CO)_7$;

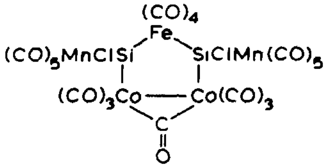
and reaction of the first product above with $Fe_3(CO)_{12}$ lead to a compound with cobalt, iron and manganese carbonyls having the formula $Fe(CO)_4[SiClMn(CO)_5]Co_2(CO)_7$. Proposed structures of these compounds are drawn below (XXVIII, XXIX, XXX).



(XXVIII)



(XXIX)



(XXX)

Irradiation of $Me_2Ge[Mn(CO)_5]_2$ gives a new compound $Me_2GeMn_2(CO)_9$. This compound shows a weak ν(CO) and a single sharp methyl proton resonance in the nmr spectrum. To explain the weak ν(CO) absorption, it is suggested that two molecular forms of the compound exist which interconvert rapidly:

The irradiation of $Mn(CO)_5GeMe_2Cl$ to give $Mn_2(CO)_8(GeMe_2)_2$ is also noted in this paper (92).

Collman _et al_. (93) have reported the synthesis of various stannane and germane-manganese (and rhenium) carbonyls from chlorostannane and chlorogermane metal complexes on reduction with iBu_2AlH. Compounds prepared include $H_2Sn[M(CO)_5]_2$, $M(CO)_5SnPh_2H$, and $M(CO)_5GePh_2H$ (M = Mn, Re). Various reactions of these species utilizing the M-H reactivity were also noted. From $Mn(CO)_5GePh_2H$ and $SnPh_3NMe_2$ the compound $Mn(CO)_5GePh_2SnPh_3$ was formed; on heating of $Mn(CO)_5GePh_2H$ the dimer $Mn_2(CO)_8(GePh_2)_2$ is obtained. Mixed metallic species were also noted, formed according to the following reactions:

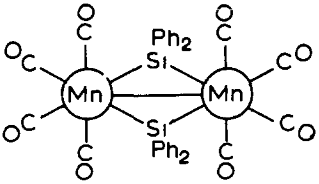
$$Mn(CO)_5GePh_2H + [C_5H_5Fe(CO)_2]_2 \longrightarrow (CO)_5MnGePh_2Fe(CO)_2C_5H_5$$

$$Mn(CO)_5GePh_2H + Fe_2(CO)_9 \longrightarrow Fe(CO)_4[GePh_2Mn(CO)_5]_2$$

$$Mn(CO)_5GePh_2H + Co_2(CO)_8 \longrightarrow Sn[Co(CO)_4]_2[Mn(CO)_5]_2$$

A preparation of $[Mn(CO)_4(GePh_3)(COMe)]^-$ and its conversion to $Mn(CO)_4$-$[C(OEt)Me]GePh_3$ and to $Ph_2GeMn(CO)_4COMe$ (see drawing XXII) was cited here earlier (70).

Two crystal structure studies have been reported; these are of the compounds $[Mn(CO)_4SiPh_2]_2$ (94) and $Mn(CO)_5Si(SiMe_3)_3$ (95). The structure of the former is shown below (XXXI). The metal-metal distance in this compound is 2.87Å.



(XXXI)

Infrared and Raman spectra of $Mn(CO)_5MMe_3$ (M = Si, Ge, Sn) are the subject of a recent study. The ν(Mn-M) vibrations were assigned at 297 cm^{-1} ν(Mn-Si), 194 cm^{-1} ν(Mn-Ge), and 178 cm^{-1} ν(Mn-Sn). Appearance potentials for the MMe_3^+ fragment were also measured, and this data used to give an approximate dissociation energy of 2.5 ev for the Mn-M bond (96). An infrared spectral study and normal coordinate analysis of $Mn(CO)_5MX_3$ (M = Si, Ge, Sn; X = Cl, Br, I) is also mentioned in another paper (97).

The manganese (55) nmr of 14 compounds $Mn(CO)_5MR_3$ (R = Cl, C_6F_5, Ph; M = Si, Ge, Sn, Pb) are reported. The chemical shift value is said to correlate with the σ donor ability of the MR_3 group (98). Other manganese (55) nmr data on $Mn(CO)_5Sn(C_6F_5)_{3-n}X_n$ (X = Ph, Cl) is found in a thesis (88).

The helium photoelectron spectra of four silyl and germyl compounds of manganese and rhenium carbonyls is noted (99).

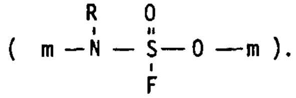
VI GROUP VA AND VIA LIGANDS (EXCEPT AS SIMPLE ELECTRON PAIR DONORS)

The bis(fluorosulfonyl)amido ion has been shown to function as a ligand to both manganese and rhenium pentacarbonyl. Synthesis of these complexes was accomplished by treatment of the silver salt of this anion with $M(CO)_5Br$ (100, 101):

$$M(CO)_5Br + Ag[N(SO_2F)_2] \longrightarrow M(CO)_5N(SO_2F)_2$$

$$M = Mn\ (100),\ Re\ (101)$$

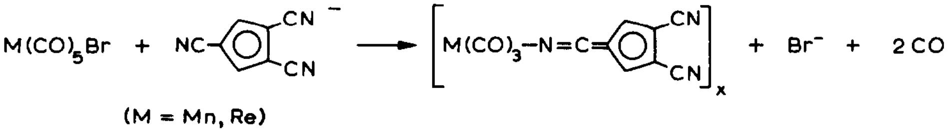
Some chemistry of these species is noted. The bis(fluorosufonyl)amidomanganese bond is solvolyzed in donor solvents such as acetonitrile, giving ionic $[Mn(CO)_5(CH_3CN)]N(SO_2F)_2$. Refluxing of $Re(CO)_5N(SO_2F)_2$ in heptane (90°C) leads to loss of CO and formation of dimer, $[Re(CO)_4N(SO_2F)_2]_2$; the synthesis of the manganese analogue directly from $Mn(CO)_5Br$ and $AgN(SO_2F)_2$ is also noted. These dinuclear species have bridging $N(SO_2F)_2$ groups, but the fashion in which this group bridges is uncertain; this could occur either through nitrogen alone (i.e. $m —NR_2— m$) or through a NSO group



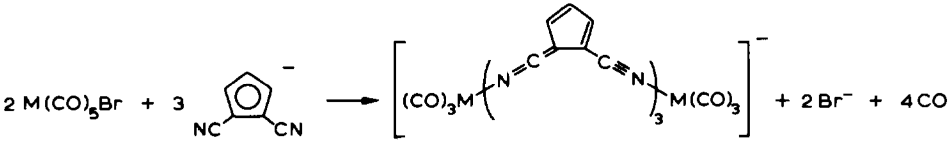
$$(m - \overset{R}{N} - \underset{F}{\overset{O}{S}} - O - m).$$

The synthesis of a heterodinuclear porphinato complex, tricarbonyltechnetium-μ-[mesoporphyrin IX dimethylesterato]tricarbonyl rhenium, $(CO)_3TcMPRe(CO)_3$, from $HMPRe(CO)_3$ and $Tc_2(CO)_{10}$ in refluxing decalin is noted (102). The structure of this compound, having $M(CO)_3$ groups above and below an essentially planar porphinato group with each group bonded to three of the nitrogen atoms, is that predicted. This structure is similar to that of μ-[mesotetraphenylporphinato]bis[tricarbonyl rhenium] reported last year.

A variety of cyanocarbons have been shown to bond to manganese and rhenium carbonyls through nitrogen. Mentioned earlier were compounds derived from the tricyanomethyl group, $[M(CO)_3—N=C=C(CN)_2]_x$ and $M(CO)_3(PPh_3)_2N=C=C(CN)_2$ (62). Presumably analogous compounds are formed with the 1,2,4-tricyanocyclopentadienide ion (103); viz*:

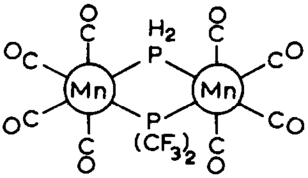


A discrete dinuclear anion is formed with the 1,2-dicyanocyclopentadienide ion, along with the species $[C_5H_3(CN)_2]M(CO)_3$ (M = Mn, Re) (104).



The photochemical syntheses of polypyrazolylborate complexes of manganese $RB(C_3H_3N_2)_3Mn(CO)_3^-$ are noted, and comparisons with $C_5H_5Mn(CO)_3$ are made in a thesis (105).

Only one reference to phosphorus ligand species is made. Manganese carbonyl and the diphosphine $H_2PP(CF_3)_2$ are reported (106) to give a mixture of $[Mn(CO)_4P(CF_3)]_2$ and $Mn_2(CO)_8P(CF_3)_2(PH_2)$ (XXXII)



(XXXII)

Extensive synthetic and structural work on some arsenic bridged complexes is reported. Treatment of $Fe_2(CO)_9$ with Me_2AsNMe_2 gives $Fe(CO)_4AsMe_2NMe_2$ which with HCl is converted to $Fe(CO)_4AsMe_2Cl$. This species

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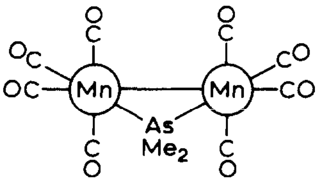
*These are probably delocalized structures, and the drawing thus represent only one of the possible canonical structures.

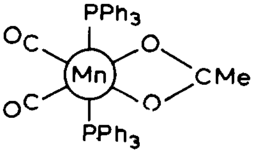
reacts with $NaMn(CO)_5$ to give $(CO)_4FeAsMe_2Mn(CO)_5$ a compound with a single $-AsMe_2-$ group bridging the metal carbonyl fragments (107). Analogous compounds $(CO)_5CrAsMe_2M(CO)_5$ (M = Mn, Re) are prepared in the same manner from $Cr(CO)_5AsMe_2Cl$ and $NaM(CO)_5$ (108). Irradiation of $(CO)_4FeAsMe_2Mn(CO)_5$ causes loss of carbon monoxide and formation of $(CO)_4FeAsMe_2Mn(CO)_4$(109). The structure of this latter species has been determined (110) it is represented below (XXXIII).



(XXXIII)

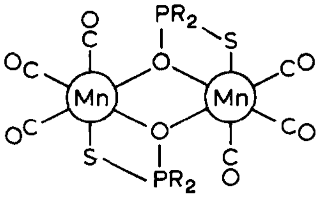
Also reported from the same research group is the compound <u>cis</u>-$(CO)_4Cr[AsMe_2Mn(CO)_5]_2$ (111). This converts on heating to the <u>trans</u> isomer. An analogous reaction with $Mo(CO)_4(AsMe_2Cl)_2$ gives only $(CO)_5MoAsMe_2Mn(CO)_5$ (tetrahydrofuran, 12 hrs, room temperature) or $[Mn(CO)_4AsMe_2]_2$ (tetrahydrofuran reflux).

Several compounds with oxygen donor ligands are described. The preparation of interesting compound $Mn(CO)_2(PPh_3)_2OCOMe$ was accomplished fortuitously (112, 113); it was formed when a manganese carbonyl anion, perhaps $Mn_3(CO)_{14}^-$, is treated with triphenylphosphine and acetic acid. It can be separated from the other products of the reaction, $Mn_2(CO)_9PPh_3$ and $Mn(CO)_3(PPh_3)_2Cl$, by chromatography. A crystallographic study verified that $Mn(CO)_2(PPh_3)_2OCOCH_3$ is monomeric, with the acetate group functioning as a bidentate ligand through both oxygen atoms (XXXIV).



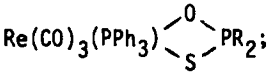
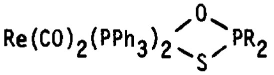
(XXXIV)

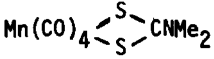
The reactions of  $R\overset{S}{\overset{\|}{P}}OH$ (R = Ph, Et) with $Mn(CO)_5Br$ and $R(CO)_5Br$ are also described (114). The initial product has the dimeric structure $M_2(CO)_6[R_2P(O)S]_2$, for which the structure proposed below is offered (XXXV).

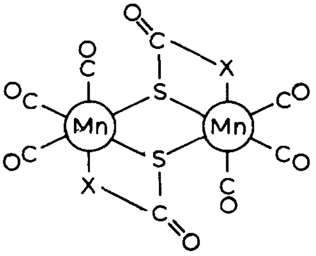


(M = Mn, Re)

(XXXV)

Treatment of this dimer (M = Re) with one mole of triphenylphosphine gives  $Re(CO)_3(PPh_3)\begin{smallmatrix}O\\S\end{smallmatrix}PR_2$; with excess phosphine $R(CO)_3(PPh_3)_2$-$SP(O)R_2$ and  $Re(CO)_2(PPh_3)_2\begin{smallmatrix}O\\S\end{smallmatrix}PR_2$ are obtained.

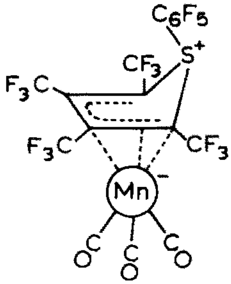
A closely related study involves the reactions of Me_3SnX derivatives ($X = -S_2CNMe_2$, $-SCONMe_2$, and $-SC(=NPh)NMe_2$) with $Mn(CO)_5X$ (115). In the first example a simple mononuclear complex  $Mn(CO)_4\begin{smallmatrix}S\\S\end{smallmatrix}CNMe_2$ was obtained. However dinuclear compounds compounds were formed in the other reactions; the structures proposed for these species are shown below (XXXVI); the similarity ot this structure and the structure for the $M_2(CO)_2[R_2P(O)S]_2$ (XXXV) compounds is apparent.



(X = O, NPh)

(XXXVI)

On treatment of $[Mn(CO)_4SC_6F_5]_2$ with $CF_3C{\equiv}CCF_3$ at 20° a complex $Mn(CO)_4[CF_3C{=}C(CF_3)SC_6F_5]$ is formed. Infrared and nmr evidence suggest that the $-CF_3C{=}C(CF_3)SC_6F_5$ group is functioning as a 3e donor coordinating to the metal via a σ bond to carbon and a μ (donor) bond to sulfur. Further reaction of this species with the acetylene at 80°, and the direct reaction of $[Mn(CO)_4SCF_3]_2$ with this acetylene give the novel manganese complexes of the sulfur heterocycle $[C_4(CF_3)_4SR]^+$ having the general formulas $Mn(CO)_3(CF_3C{\equiv}CCF_3)_2SR$ (R = CF_3, C_6F_5). A crystal structure study of the latter species (XXXVII) confirms the structure prediction offered for these species.



(XXXVII)

The sulfur atom in the heterocyclic ring is bent substantially away from the metal, the dihedral angle being 30.8°. This means the sulfur atom is well outside a predicted covalent metal-sulfur bonding distance, and in turn suggests that the simple representation as a manganese (-1) derivative (with a sulfonium cation) is reasonable (116).

The compound $Mn(CO)_5SCF_3$ is reported to be formed on irradiation of a mixture of $Mn_2(CO)_{10}$ and CF_3SSCF_3 (117). Reference to $[Mn(CO)_4SH]_2$, formed from $Mn(CO)_5H$ and propylene sulfide, was made earlier (58).

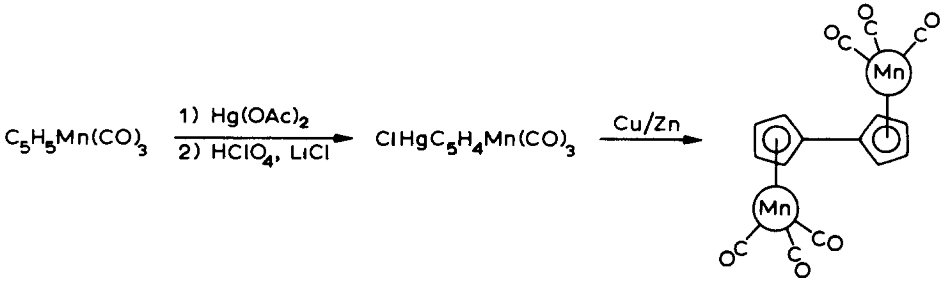
VII CYCLOPENTADIENYL-MANGANESE AND RHENIUM CARBONYLS

Let us consider the compounds having the general formula $C_5H_5M(CO)_3$ and derivatives formed from it by substitution of CO by other 2e donor ligands.

The new dicyanocyclopentadienyl compounds $[1,2\text{-}C_5H_3(CN)_2]M(CO)_3$ (M = Mn, Re) are formed with another product when the $1,2\text{-}C_5H_3(CN)_2^-$ anion is treated with $M(CO)_5Br$ (104). However, attempts to form $1,2,4\text{-}[C_5H_2(CN)_3]M(CO)_3$

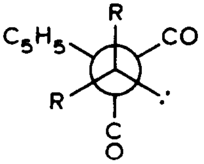
by a similar route failed (103). The reactions of $C_5Me_5Mn(CO)_3$ with triphenylphosphine to give $C_5Me_5Mn(CO)_2PPh_3$ and with $NOPF_6$ to give $[C_5Me_5Mn(CO)_2NO]PF_6$ are noted (118).

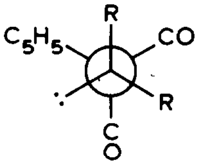
The formation of fulvalene $Mn_2(CO)_6$ by the route given below is reported (119).



The compound $[C_5H_5Mn(CO)_2]_2P_2H_4$ has been prepared from $C_5H_5Mn(CO)_2(THF)$ and P_2H_4 at -78°C (120). The preparation of $C_5H_5Mn(CO)_2PF_2NR_2$ complexes is described in a thesis (61). Structural studies on $C_5H_5Mn(CO)_2(SO_2)$ (121) and on $C_5H_5Mn(CO)_2PPh_3$ (122) are noted.

A series of sulfide complexes $C_5H_5Mn(CO)_2SR_2$ (R = Me, Et, Pr, Bu and SR_2 = $\overline{SCH_2CH_2CH_2CH_2}$) was prepared and infrared spectra of these compounds studied. Since four ν(CO) bands are seen for each species it is suggested that there exists two conformational isomers in solution which arise with respect to the S-Mn rotation (123), vis.

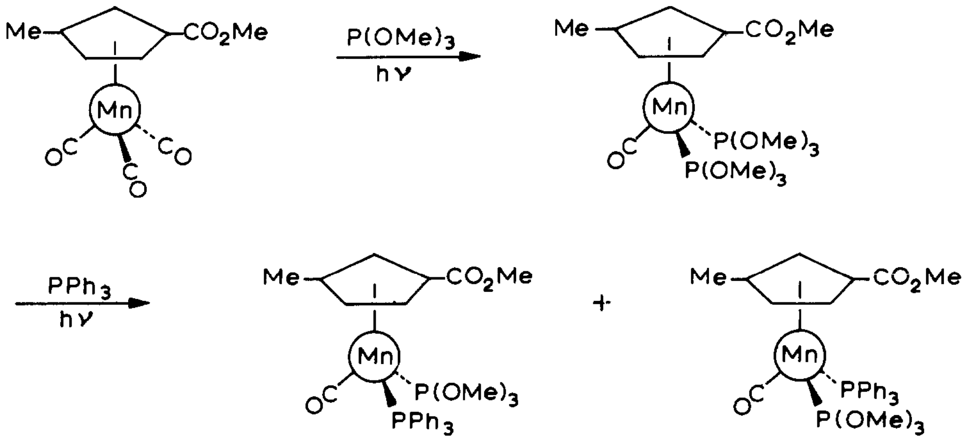




Molecular orbital calculations on $C_5H_5Mn(CO)_2N_2$ have been performed; they suggest that dinitrogen is a weaker π acceptor and a stronger σ+π donor than is CO (124). ESCA data on $C_5H_5Mn(CO)_3$, $C_5H_5Mn(CO)_2NH_3$, $C_5H_5Mn(CO)_2N_2H_4$, $[C_5H_5Mn(CO)_2]_2N_2H_2$ and $C_5H_5Mn(CO)_2N_2$ is given (125).

Kinetic data on the reaction of $C_5H_5Mn(CO)(CS)C_8H_{14}$ with triphenylphosphine to give $C_5H_5Mn(CO)(CS)(PPh_3)$ is presented. The reaction rate is first order in complex concentration, and a dissociative mechanism is suggested (126). Carbon monoxide exchange for $C_5H_5Mn(CO)_3$, $C_5H_5Mn(CO)_2(CS)$, $C_5H_5Mn(CO)_2(C_8H_{14})$ and $C_5H_5Mn(CO)(CS)(C_8H_{14})$ has been studied using labeled ^{13}CO and $C^{18}O$ (127).

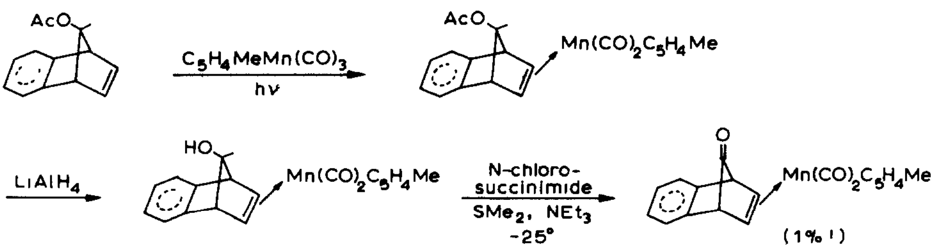
The synthesis and characterization of compounds wherein the metal is an optically active center has been the subject of two studies. LeMoigne and Dabard (128) have carried out the following sequence of reactions:



The diastereotopic compounds were separated by chromatography.

The two diastereotopic compounds $[C_5H_4Me\overset{*}{Mn}(NO)(CO)(PPh_2NMe\overset{*}{C}HMePh)]PF_6$ having asymmetric centers at manganese and at the unique methyne carbon in the amino side chain of the phosphine (the starred atoms in the formula) were also reported. They were prepared from a reaction of $[C_5H_4MeMn(NO)(CO)_2]PF_6$ and the phosphine (129).

The synthesis of a manganese complex of benzonorbornadienone was accomplished (130) by the following reaction sequence:



It is interesting to note that previous attempts to stabilize this organic ligand by coordination have been unsuccessful; for example attempts to prepare benzonorbornadiene $Cr(CO)_3$, having the $Cr(CO)_3$ group coordinated to the arene ring, gave only naphthalene $Cr(CO)_3$, which may arise from facile carbonyl expulsion from the desired species.

Studies on the interactions of acids with various cyclopentadienyl metal carbonyls have been reported. Ginsberg, et al. (131) report that $C_5H_5Re(CO)_2PPh_3$ is protonated by CF_3COOH in dichloromethane according to infrared data; ν(CO) absorptions in this solvent mixture are found at 2053 and 1922 cm^{-1}, vs. 1930 and 1859 cm^{-1} absorptions found for the starting material. Infrared data is also reported to indicate adducts of $C_5H_5Mn(CO)_2PPh_3$ and the Lewis acid $SnCl_4$ (132). The order of basicity of various hydrocarbon metal carbonyl species is said to be $C_5H_5Nb(CO)_3L$ > $C_5H_5Re(CO)_2L$ > $C_6H_6Cr(CO)_2L$ > $C_5H_5V(CO)_3L$ > $C_5H_5Mn(CO)_2L$ (131).

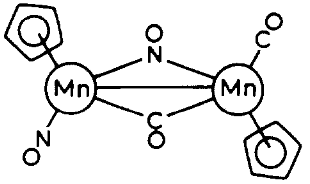
The effect of MR_3 substitution in $C_5H_5M'(CO)_2MR_3$ (M = P, As, Sb) on the hydrogen/deuterioum exchange of the ring protons has also been determined (133).

Studies on the ring proton nmr resonances in various series of cyclopentadienyl manganese carbonyls $C_5H_5Mn(CO)_2L$ (L = CO; PR_3, R = Bu, C_6H_{11}, i-C_3H_7, Ph, C_6H_4OMe, tol, OPh, CH_2Ph; $AsPh_3$; $SbPh_3$)(134) and $C_5H_4XMn(CO)_2PPh_3$ (X = Et, CH_2Ph, SMe, Cl, Br, I, COOMe, H) (135) have been carried out. Non-equivalence of protons on carbons adjacent to a chiral carbon substituent on the cyclopentadienyl ring in $C_5H_4RMn(CO)_3$ is noted (136).

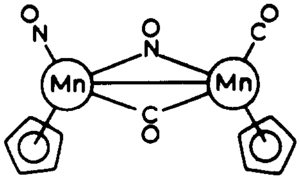
The esr spectrum of a radical anion derived from $PhCOC_5H_4Mn(CO)_3$ and sodium in tetrahydrofuran or dimethoxyethane is reported (137). Major hyperfine coupling to ^{55}Mn occurs. Polarographic reduction of $ClHgC_5H_4M(CO)_3$ and $Hg[C_5H_4M(CO)_3]_2$ (M = Mn, Re) has also been carried out (138).

Various reactions of organolithium reagents and of sodium borohydride with $[C_5H_5Mn(NO)(CO)L]PF_6$ (L = CO, PPh_3) have been carried out (139). With $[C_5H_5Mn(NO)(CO)PPh_3]PF_6$ and LiR (R = Me, Ph) attack is seen to occur at a carbonyl to give the acyl compounds $C_5H_5Mn(NO)(PPh_3)(COR)$. A different product is obtained in low yield from $[C_5H_5Mn(NO)(CO)_2]PF_6$; here exo- attack at the cyclopentadienyl ring is noted, to give exo-$RC_5H_5Mn(CO)_2NO$. The reaction of $NaBH_4$ and $[C_5H_5Mn(NO)(PPh_3)(CO)]PF_6$ leads to two products, $C_5H_6Mn(NO)(PPh_3)(CO)$ from attack at the ring, and $C_5H_5Mn(NO)(CO)COCH_3$. The latter product apparently has its origin in reduction of a carbonyl to a methyl group, but this reaction must be accompanied by a ligand redistribution reaction and carbonylation.

A substantial study on $[C_5H_5Mn(CO)(NO)]_2$ has appeared (9). The solid state structure of this compound, from X-ray crystallography, is determined to be like $[C_5H_5Fe(CO)_2]_2$, with trans cyclopentadienyl groups. Bridging and terminal carbonyls and nitrosyls are completely disordered, and not distinguished in this structure but compelling nmr and infrared evidence suggests that one CO and one NO group bridge the two metals. The metals are also linked with a metal-metal bond; the manganese-manganese distance is 2.571(1)Å. In solution, nmr data at -65° for the cyclopentadienyl protons shows the presence of two isomers in unequal concentration, with each isomer having two cyclopentadienyl proton resonances indicative of different cyclopentadienyl ring environments. One isomer is assigned to the trans compound, the second to the cis (XXXVIII, XXXIX). On warming from -65° the averaging of the C_5H_5 proton resonances for each isomer is seen. Eventually at higher temperatures there is a cis-trans interconversion as well so in the 40°C spectrum the cyclopentadienyl proton resonance appears as essentially a single peak.



(XXXVIII) *trans* isomer

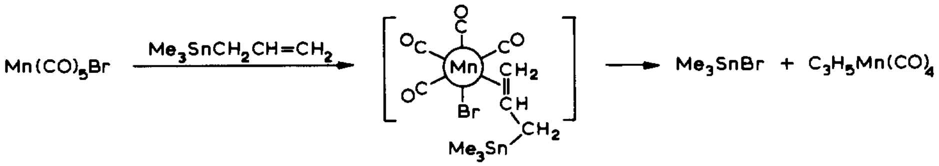


(XXIX) *cis* isomer

Comparison of *cis-trans* ratios, and of activation energies for the *cis-trans* isomerism is made for the series of compounds $[C_5H_5Cr(NO)_2]_2$, $[C_5H_5Mn(CO)(NO)]_2$ and $[C_5H_5Fe(CO)_2]_2$.

Further commentary on the $[C_5H_5Mn(CO)(NO)]_2$ rearrangements is also found (140).

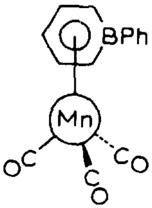
A few studies on other hydrocarbon-metal complexes are seen. The synthesis of allyl $Mn(CO)_4$ from $Mn(CO)_5Br$ and $Me_3Sn(allyl)$ in refluxing tetrahydrofuran is accomplished with 82% yield; the rhenium compound is made in 80% yield, representing an improvement on known preparations since allylrhenium tetracarbonyl is not easily made by other routes. This synthesis is believed not to proceed through a σ allyl complex. Instead the following mechanism is proposed (141):



The failure to obtain cyclopropenyl complexes of manganese from cyclopropenium salts and $NaMn(CO)_5$ was noted earlier (26).

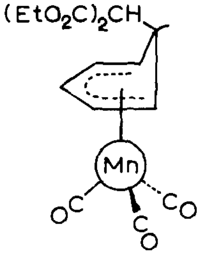
The synthesis of the interesting manganese complex of a boron heterocyclic species (XXXX) by ligand exchange from $Co(C_5H_5BPh)_2$ and $Mn_2(CO)_{10}$ is reported (142).

Reactions of $[areneMn(CO)_3]^+$ with a variety of reagents have been studied, and four different reaction pathways are found to exist (143). With phosphines (PPh_3, PBu_3, $PPhMe_2$) simple carbonyl replacment occurs



(XXXX)

to give [areneMn$(CO)_2L]^+$ (143, 144). Infrared spectra provide evidence for the additions of certain anionic nucleophiles including acac$^-$, N_3^-, OMe$^-$, PPh_2^-, and NCS$^-$ to the arene ring to give uncharged exo-substituted cyclohexadienyl–metal carbonyls. In addition the reaction of $NaCH(COOEt)_2$ and $[C_6H_6Mn(CO)_3]^+$ gave an isolable compound of the formula exo-$(EtOOC)_2CH$-$C_6H_6Mn(CO)_3$; a crystal structure study (145) has confirmed the identification of this compound (XXXXI). Finally a fourth reaction, displacement of the arene, is also noted. Thus $[C_6H_6Mn(CO)_3]^+$ in acetonitrile, in the presence of iodide ion, gives $Mn(CO)_3(NCMe)_2I$; in acetone $Mn(CO)_3(acet)_2I$ is formed though not isolated since it decomposes to $[Mn(CO)_4I]_2$.



(XXXXI)

The preparation of $[C_6H_6Mn(CO)_2PPh_2H]PF_6$ is noted. This compound can be deprotonated at phosphorus with methoxide ion, and then alkylated with methyl iodide. Alternatively it reacts with $C_5H_5Fe(CO)_2Cl$ to give $[C_6H_6Mn(CO)_2PPh_2Fe(CO)_2C_5H_5]^+$ as a PF_6 salt which cannot be separated, however, from $[C_5H_5Fe(CO)_2PPh_2Fe(CO)_2C_5H_5]PF_6$ also present (144).

The reactions of cyanide ion with (arene)$Mn(CO)_3^+$ complexes are reported in a separate paper (146). With $C_6Me_6Mn(CO)_3^+$ displacement of a carbonyl occurs, giving $C_6Me_6Mn(CO)_2CN$. Otherwise cyanide adds <u>exo</u>- to the hydrocarbon ring. Abstraction of cyanide by the trityl cation, CPh_3^+, from the cyano-cyclohexadienyl complex occurs. However ceric ion oxidation generates the free cyanoarene.

VIII VARIOUS ISOCYANIDE AND NITROSYL SPECIES

Little has appeared on isocyanide complexes of manganese and rhenium in the last year. A new synthesis of various $Mn(CNR)_6^{2+}$ and $Mn(CNR)_6^+$ species has been reported; this preparation involves treatment of $Mn(NO_3)_2 \cdot 6H_2O$ with the isocyanide in methanol, distilling off the water. The MnL_6^{2+} species is formed initially, and is reduced presumably by excess isocyanide in a slower step to MnL_6^+ (147).

The alkylation of $K_3Mn(NO)(CN)_5$ by $MeOSO_2F$ gives $[Mn(CNMe)_5NO]^{2+}$ (35). The two series of complexes $[Mn(CO)_{6-x}(CNMe)_x]PF_6$ and $Mn(CO)_{5-x}(CNMe)_xBr$ are reported in a thesis (28),as are the force constant analysis for the former series, the photoelectron spectrum of Mn(CO)4(CNMe)Br and the crystal structure of $Mn(CO)_3(CNMe)_2Br$ (29).

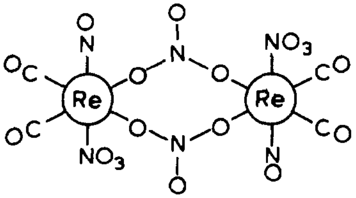
Two reports of $Mn(NO)_3PF_3$ are found.- The interesting syntnesis of this compound by cocondensing manganese atoms, NO, BF_3, and PF_3 at low temperature is noteworthy, in view of the active current use of this technique for organometallic syntheses (148). A more pendantic route to this compound by treatment of $Mn(NO)_3CO$ with excess PF_3 with irradiation is also noted (149).

Several other manganese nitrosyl species have also been prepared. The addition of $NOPF_6$ to $Mn(CO)[P(OMe)_3]_4Br$ results in the formation of $[Mn(NO)(CO)\{P(OMe)_3\ _4](PF_6)_2\}$(27). In addition, the reaction of NO with with $Mn(CO)_2[PPh(OMe)_2]_3Br$ in refluxing cyclohexane gives $Mn(NO)_2[PPh(OMe)_2]_2Br$ providing that oxygen is excluded. If oxygen is present the NO is converted to NO_2, and this serves as an oxidant instead, yielding $[Mn(CO)_2\{PPh(OMe)_2\}_3Br]^+$ (1).

Earlier in this review, mention was made of $[C_5H_5Mn(NO)(CO)]_2$ (9, 10),

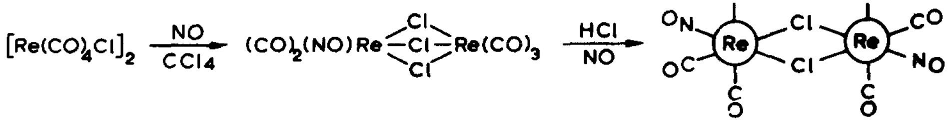
$[C_5Me_5Mn(NO)(CO)_2]PF_6$ (119), and $[C_5H_5Mn(NO)(CO)_2]PF_6$ and several derivatives thereof (129, 139).

Nitrosyls of rhenium are reported in two instances. Treatment of $Re_2(CO)_{10}$ with N_2O_4 gives a small amount of $[Re(CO)_2(NO)(NO_3)_2]_2$ in addition to the primary product $Re(CO)_5NO_3$ (150). A suggested structure for this product is given below (XXXXII).



(XXXXII)

In contrast to an earlier report of the non-reactivity of NO with $[Re(CO)_4Cl]_2$, it has now been found that a reaction will take place in CCl_4, giving $Re_2(CO)_5(NO)Cl_3$. This compound, in turn, reacts with HCl in the presence of NO to give $[Re(NO)(CO)_2Cl_2]_2$, and with LiI to give the anion $[Re(NO)(CO)_2I_3]^-$ isolable as the tetramethylammonium salt. Under forcing conditions $[Re(NO)(CO)_2Cl_2]_2$ may be reduced in an autoclave using zinc and ethanol with CO pressure; this results in formation of $Re_2(CO)_{10}$ and $Re_2(CO)_5NO(OEt)_3$ (151).



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