MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1974

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CONTENTS

Manganese, Technetium and Rhenium, Annual Survey covering the year 1973 see J. Organometal. Chem., 83 (1974) 427-476.

I INTRODUCTION

In the opinion of this author, 1974 was not a particularly exciting year in the development of the organometallic chemistry of the Group VIIB elements, at least in the sense that there was few extensive new problems introduced. Published research in 1974 seemed directed primarily to elaboration on research topics that had already been established in the previous years. A number of completed studies were published which had been the subject of interesting communications last year; and several theses describing elaborate studies of work now published were made available through Dissertation Abstracts.

No trends in research efforts were obvious during the year. There seemed to be a generally good balance of synthetic work, structural studies primarily by X-ray crystallography, and studies of physical properties of these compounds. The application of several newer techniques might be noted though. Metal atom reactor syntheses, now commonplace in organometallic chemistry, were extended to this group, and PES studies received much emphasis. So also did several carbon-13 magnetic resonances studies appear in print. A review article on this latter subject, containing data on a few manganese and rhenium compounds, was published in this journal (1).

The organization of this review based on compound type will be continued again. The only variation is an additional section, at the end, which lists the compounds whose structures have been determined by X-ray crystallographic or other physical methods.

II METAL CARBONYLS AND DERIVATIVES OBTAINED BY SIMPLE LIGAND SUBSTITUTION

The radical species $Re(CO)_5$ was identified as the product arising from cocondensation of rhenium atoms and either pure carbon monoxide at 15°K or carbon monoxide in an argon matrix at 20°K (2). Earlier, this species had been detected by mass spectroscopy and it had also been postulated in photolytic work on $Re_2(CO)_{10}$, but no properties had been assigned. A matrix infrared spectrum of $Re(CO)_5$ showed $\nu(CO)$ at 1995(s) and 1977(w) cm^{-1}; a square pyramidal geometry surrounding the metal was suggested.

There was also an interesting reference to a radical species of manganese(3). Earlier a paramagnetic species, presumed to be $Mn(CO)_5$, was obtained upon sublimation of $Mn_2(CO)_{10}$ to a 77°K cold finger. Careful restudy of this process revealed, however, that the paramagnetic species was obtained only when oxygen was present. Based upon this fact, and supported by additional analogous work with dicobalt octacarbonyl, the radical was assigned by the authors of this paper to be a peroxo complex, $Mn(CO)_5O_2$.

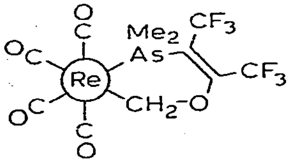
A thesis described published work on photolytic reactions of $Mn_2(CO)_{10}$ with iodine, nitric oxide, and $SnCl_2$; intermediacy of the radical species $Mn(CO)_5$ was presumed in these reactions (4). The photo-induced formation of $Mn(CO)_4NO$ from $Mn_2(CO)_{10}$ and NO in pentane was also reported from a different laboratory (5).

An electron diffraction study on $Re_2(CO)_{10}$ has been carried out (6). This molecular compound has D_{4h} symmetry and a rhenium-rhenium bond length of 3.04Å; in the previously determined solid state structure a value of 3.02Å had been reported for this bond length.

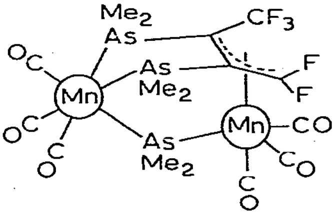
An infrared study on the dimetal decacarbonyls, $M_2(CO)_{10}$ (M = Mn, Tc, Re) was reported (7), as was carbon-13 nmr data for $Re_2(CO)_{10}$ (8). There is an interesting general MO study on metal carbonyls including those of manganese, technetium and rhenium (9).

Further study involving chelating arsines and manganese and rhenium carbonyls has been carried out. A full paper on the crystal structure determination for the compound $Mn_2(CO)_8[Me_2As\overline{C{=}C(AsMe_2)CF_2C}F_2]$ has appeared (10); this structure was the subject of a communication reported in last year's ANNUAL SURVEYS. The reactions of cis-2,3-bis(dimethylarsino)hexafluorobut-2-ene with $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ are considerably different (11). Ultraviolet irradiation of the ligand and $Re_2(CO)_{10}$, in benzene, gave a compound $\overline{Re(CO)_4AsMe_2C(CF_3){=}C(CF_3)OCH_2}$ (I) in

22% yield. The mode of formation of this substance, and particularly the origin of the -CH_2O-group interposed in the chelate ligand structure, is a mystery. Interestingly, the possibility that this group arises from a coordinated carbonyl group was not suggested. With $Mn_2(CO)_{10}$ and cis-2,3-bis(dimethylarsino)hexafluorobut-2-ene, there was yet another surprise. Fragmentation of the ligand occurred with ultimate formation of a binuclear species with a π-allylic coordination to one manganese atom. The structure is shown below (II). The structure of this compound was determined by X-ray diffraction methods.



I



II

Pittman and coworkers (12) have described work on polymer or resin supported metal carbonyls. These workers attached phosphine groups to the support, then contacted these systems with metal carbonyls including $Mn_2(CO)_{10}$ and $MeC_5H_4Mn(CO)_3$. The eventual intention in these studies is to achieve some sort of heterogeneous catalyst system, and with current emphasis on organometallics as catalysts these studies are likely to be of more than passing interest.

Vibrational spectra of several mixed metal carbonyls are reported. Bor (13) analyzed spectral data for the series of compounds $(CO)_4CoM(CO)_5$ (M = Mn, Tc, Re). Infrared and Raman spectral data on various $[(CO)_5MM'(CO)_5]^-$ complexes (M = Mn, Re; M' = Cr, Mo, W) are found in a thesis (14).

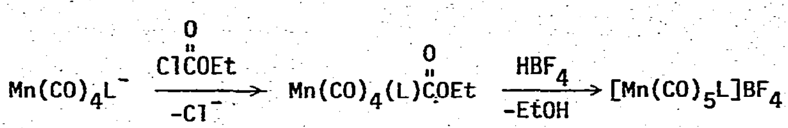
Several studies on anionic carbonyl complexes are noted. Ion cyclotron resonance studies of various metal carbonyl anions, including $Mn(CO)_5^-$, were reported by Dunbar and Hutchison (15). An infrared study on $Li[Mn(CO)_5]$ and

$Na[Mn(CO)_5]$ in various ethers has been carried out (16); data suggested that close ion pairing of cation and anion occurs in most solvents giving a species of C_{3v} site symmetry at manganese. In tetrahydrofuran, solvent separated ion pairs were believed present. Nuclear quadrupole resonance and Mossbauer spectra were investigated for the series of complexes $[M(CO)_{5-n}L_n]^x$ (L = PPh_3, $P(OMe)_3$; $M^x = Mn^{-1}$, Fe^0, Co^{+1}; n = 1, 2); field gradients at the metal nuclei were determined in this study (17).

The trinuclear anion $Mn_3(CO)_{14}^-$ was prepared in low yield by deprotonation of $H_3Mn_3(CO)_{12}$ by NaOH in ethanol (18). A crystal structure study on the tetraphenylarsonium salt of this anion was also carried out. Interestingly, the anion structure has a linear arrangement of metal atoms with overall D_{4h} symmetry; previous structural studies had shown that the analogous species $Mn_2Fe(CO)_{14}$ is linear but the protonated forms $Re_3(CO)_{14}H$ and $Re_2Mn(CO)_{14}H$ are bent. This was rationalized by steric considerations. The average manganese-manganese distance in the $Mn_3(CO)_{14}^-$ ion was found to be 2.895Å, comparable to manganese-manganese distances measured in other compounds such as $Mn_2(CO)_{10}$.

Substitution of one CO in the anionic mixed-metal compound $NEt_4[MnFe_2(CO)_{12}]$ was accomplished in refluxing acetone and the new compounds $NEt_4[MnFe(CO)_{11}L]$ (L = PPh_3, PPh_2Me, $P(OPr)_3$) were prepared (19). These complexes were assumed to have the $Fe_3(CO)_{12}$ structure with the manganese atom in the unique position. Mossbauer data showed that substitution caused the two irons to become non-equivalent in the PPh_3 complex. This suggests that substitution has occurred at iron, but this was not an unequivocal assignment; equatorial substitution at manganese could also cause the observed non-equivalence.

A number of studies have further developed the chemistry of cationic manganese carbonyls, derivatives of the parent species $[Mn(CO)_6]^+$. Two syntheses of mono-substituted complexes were described (20). The first, shown in Equation 1, originated with a carbonyl anion which was reacted with ethyl chloroformate to give a carboethoxy-manganese carbonyl; on treatment with a strong acid the cationic species was generated. The second, Equation 2, took advantage of the facile displacement of acetonitrile from $[Mn(CO)_5NCMe]^+$ by other ligands. The starting complex is readily available, of course, from the $Mn_2(CO)_{10}$-$NOPF_6$ reaction in

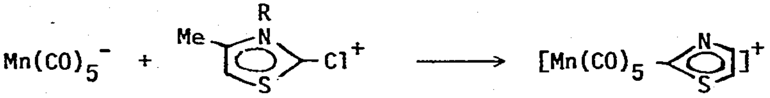


$$Mn(CO)_4L^- \xrightarrow[-Cl^-]{Cl\overset{O}{\overset{\|}{C}}OEt} Mn(CO)_4(L)\overset{O}{\overset{\|}{C}}OEt \xrightarrow[-EtOH]{HBF_4} [Mn(CO)_5L]BF_4 \qquad \text{EQ 1}$$

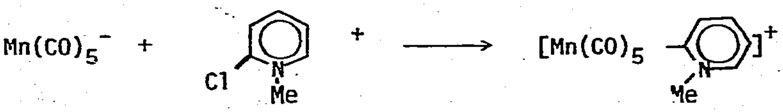
$$[Mn(CO)_5(NCMe)]^+ \ + \ L \longrightarrow [Mn(CO)_5L]^+ + MeCN \qquad \text{EQ 2}$$

acetonitrile. Complexes prepared were $[Mn(CO)_5L]^+$ (L = PPh_3, $P(OPh)_3$, $P(p\text{-}tol)_3$, $PPhMe_2$, $Ph_2PCH_2CH_2PPh_2$, pyridine).

Other papers describe $[Mn(CO)_5L]^+$ complexes where the ligands L are so-called carbenes (21, 22). The complex $Mn(CO)_5COOCH_2CH_2Cl$ reacted with $AgPF_6$ with halide loss and concurrent cyclization of the organic ligand to give $[Mn(CO)_5\overline{COCH_2CH_2O}]^+$ Similar reactions occurred with $Mn(CO)_4(L)COCH_2CH_2CH_2Cl$ (L = CO, phos) (23) and $Mn(CO)_5COO\overline{CHCHClCH_2CH_2CH_2}$ (21). A different route to carbene complexes is shown below (Equations 3,4). Here reaction of $Mn(CO)_5^-$ with 2-halothiazolium cations, or with the 2-chloromethylpyridinium cation, occurred with halide displacement (22) and complex formation.



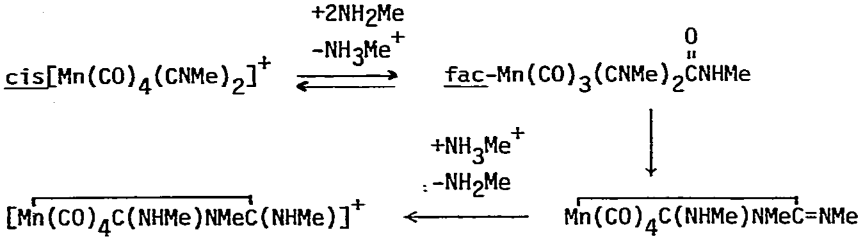
EQ 3



EQ 4

The disubstituted manganese carbonyl complex $[Mn(CO)_4(P\hat{}N)]^+$ (P^N = o-dimethylaminophenyldiphenylphosphine) was described (24). This compound was formed on direct carbonylation of $Mn(CO)_3(P^\frown N)Br$ in the presence of the halogen acceptor, $AlCl_3$. The manganese carbonyl precursor was formed by carbonyl displacement from $Mn(CO)_5Br$. The cationic carbonyl compound was shown to react with the nucleophilic reagents including the menthoxide anion; in this reaction two diastereoisomeric complexes were formed which unfortunately were not stable enough to allow their separation.

An interesting study concerning amine reactions with $[Mn(CO)_{6-n}(CNMe)_n]^+$ was recorded, which, however, raised as many questions as it answered (25). The reaction of cis-$[Mn(CO)_4(CNMe)_2]^+$ and methylamine occurred initially with addition to a carbonyl group; the product fac-$Mn(CO)_3(CNMe)_2CONHMe$ was observed in solution. This product cannot be isolated in pure form, being quite unstable. If no attempt to isolate this species is made, a further reaction ensues. The isolable product was the chelated amidinium ligand complex $[\overline{Mn(CO)_4C(NHMe)NMeC}(NHMe)]^+$, formed apparently by initial rearrangement of the carboxamido complex followed by protonation (sequence of Equations 5).



$$\begin{tikzcd}
\text{cis}[Mn(CO)_4(CNMe)_2]^+ \arrow[r, shift left, "\substack{+2NH_2Me \\ -NH_3Me^+}"] & \text{fac-}Mn(CO)_3(CNMe)_2\overset{O}{\overset{\|}{C}}NHMe \arrow[l, shift left] \arrow[d] \\
{[\overline{Mn(CO)_4C(NHMe)NMeC}(NHMe)]^+} & \overline{Mn(CO)_4C(NHMe)NMeC}{=}NMe \arrow[l, "\substack{+NH_3Me^+ \\ -NH_2Me}"']
\end{tikzcd}$$

EQ 5

The deprotonated intermediate in this rearrangement can be observed spectroscopically during this reaction but was not isolated in the direct reaction. It can be isolated by reaction of the base triethylamine with the amidinium complex however.

The reaction of fac-$[Mn(CO)_3(CNMe)_3]^+$ and methylamine was also reported to give a chelated amidinium complex, mer-$[\overline{Mn(CO)_3(CNMe)C(NHMe)NMeC}(NHMe)]^+$. Intermediacy of a carboxamido complex was not ascertained in this reaction, but is presumed; in the reaction with n-$BuNH_2$ a carboxamido complex was identified spectroscopically (25).

The compound *fac*-$[Mn(CO)_3(CNMe)_3]SO_3F$ was also reported in this study, formed on methylation of *fac*-$[Mn(CO)_3(CN)_3]^{2-}$ with methylfluorosulfonate. The *mer*-isomer had previously been made. Reaction of this species with methylamine appeared to give an unstable amidinium complex which cannot be isolated.

Substantial further study has been accorded to tri- and tetra-substituted $[Mn(CO)_{6-n}L_n]^+$ species by Reimann and Singleton (26). These workers prepared the complex *fac*-$[Mn(CO)_3(NCMe)_3]^+$ by refluxing $Mn(CO)_5Br$ in acetonitrile. Partial or complete replacement of the labile nitrile ligands (and sometimes CO as well) was then accomplished using a wide variety of trivalent phosphorus ligands, the extent of substitution being dependent on the nature of the ligand and reaction conditions. Many new complexes were characterized; stoichiometries include: *fac*-$[Mn(CO)_3(L)_n(NCMe)_{3-n}]^+$ and *cis*-$[Mn(CO)_2(L)_{4-n}(NCMe)_n]^+$ n = 1, 2 (L = phosphines, phosphonates, phosphites). Some of these complexes were oxidized to the divalent species using $NOPF_6$. Isolated dipositive species include *trans*-$[Mn(CO)_2(NCMe)_2\{PPh(OMe)_2\}_2](PF_6)_2$, formed from the *cis* isomer, *mer*-*trans*-$[Mn(CO)_2(NCMe)L_3](PF_6)_2$ (L = $P(OMe)_3$ and $PPh(OMe)_2$) from the *mer*-*cis* isomer, and *trans*-$[Mn(CO)_2\{P(OMe)_3\}_4](PF_6)_2$ from the *cis* isomer. The interconversion of *cis*-*trans* geometries in these oxidations is of particular note.

Synthesis of the complex *cis*-$[Mn(CO)_2\{P(OMe)_3\}_4]PF_6$ was accomplished by a unique process which takes advantage of this change in geometry. This reaction sequence is shown below (Equation 6).

$$[Mn(CO)_3(NCMe)_3]^+ \; + \; P(OMe)_3 = L \longrightarrow \underline{mer}\text{-}\underline{cis}\text{-}[Mn(CO)_2(NCMe)L_3]^+$$

(no *cis*-$[Mn(CO)_2L_4]^+$) EQ 6

$$\xrightarrow{NOPF_6} \underline{mer}\text{-}\underline{trans}\text{-}[Mn(CO)_2(NCMe)L_3]^{2+} \xrightarrow{N_2H_4} \underline{mer}\text{-}\underline{trans}\text{-}[Mn(CO)_2(NCMe)L_3]^+$$

$$\xrightarrow{+L} \underline{cis}\text{-}[Mn(CO)_2L_4]^+$$

the mer-cis isomer is inert to substitution by the fourth phosphite whereas the mer-trans isomer is not.

Electrochemical studies on various diphos compounds including trans-$[Mn(CO)_2(diphos)_2]^+$ (diphos = 1,2-bisdiphenylphosphinoethane) are noted (27). One electron oxidation of this complex to form trans-$[Mn(CO)_2(diphos)_2]^{2+}$ occurrec with an $E_{1/2}$ value of +1.08v (vs. Ag/AgCl reference electrode) in a cyclic voltammetry experiment.

An infrared and Raman spectral study on $[Mn(CO)_6]PF_6$ has been carried out by McLean (28).

III METAL CARBONYL HALIDE COMPLEXES AND DERIVATIVES THEREOF

Many papers have appeared describing the preparation and characterization of various complexes derived from $Mn(CO)_5X$ and $Re(CO)_5X$ (X = Cl, Br, I).

Disubstituted complexes $Mn(CO)_3(P\hat{}N)Br$ and $Mn(CO)_3(N\hat{}N)Br$ were reported, prepared by direct reactions of $Mn(CO)_5Br$ and either P^N (o-dimethylaminophenyldiphenylphosphine) or N^N (the Schiff base derived from pyridine-2-carbaldehyde and R(α)-1-phenylethylamine) (24). The former compound was converted to the cationic $[Mn(CO)_4(P\hat{}N)]^+$ by treatment with carbon monoxide and $AlCl_3$. The latter by virtue of the presence of two asymmetric carbon centers, was formed as a pair of diastereoisomers. These isomers were separated and identified.

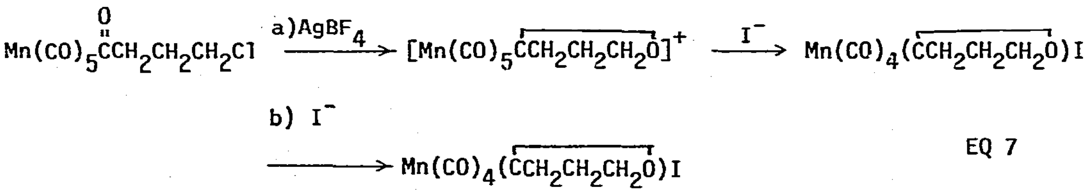
A study of the reactions of $Mn(CO)_5Br$ and $Mn(CO)_5I$ with a potentially tetradentate phosphorus ligand $[Ph_2PCH_2CH_2PPhCH_2]_2$ has been carried out (29) and a number of products were isolated. These include: two isomers of the form fac-$Mn(CO)_3(P\hat{}P\hat{}P\hat{}P)Br$, involving bidentate ligand functionality, a tridentate ligand complex, cis-$Mn(CO)_2(P\hat{}P\hat{}P\hat{}P)Br$, and a complex $[Mn(CO)_3Br]_2(P\hat{}P\hat{}P\hat{}P)$ in which the ligand coordinates in a bidentate fashion to two different metal carbonyl groups. This work is also reported in a thesis, along with similar reactions involving other polydentate phosphine ligands (30).

Another interesting study described dmpe (1,2-bisdimethylphosphinoethane) complexes wherein this ligand functions in both typical and atypical fashions (31). Reaction of $Mn(CO)_5Br$ and $Mo(CO)_5(dmpe)$ gave a complex $(CO)_5Mo(dmpe)Mn(CO)_4Br$ with the dmpe ligand bridging the two metals. Typical bidentate behavior of this ligand was achieved in the complexes $Mn(CO)_3(dmpe)X$ (Cl, Br), formed from ligand and $Et_4N[Mn(CO)_4X_2]$ in the presence of $[Et_3O]PF_4$. Also presented in this paper was the synthesis of $Mn(CO)_3(PMe_3)_2Br$ and $Mn(CO)_4(PMe_3)Br$ from the $[Mn(CO)_4Br_2]^-$ precursor and $Ag(PMe_3)NO_3$.

The reactions of Me_2PNMe_2 with various manganese carbonyl complexes including $Mn(CO)_5Br$ were run (32). A monosubstituted derivative, $Mn(CO)_4(PMe_2NMe_2)Br$ was formed; in this compound phosphorus coordinated to the metal rather than nitrogen. This compound reacted with HCl to give $Mn(CO)_4(PMe_2Cl)Br$.

A series of substituted complexes $Mn(CO)_3L_2(OCOCF_3)$ (L = pyridine, PPh_3, bipy, o-phen, $RSCH_2CH_2SR$) was formed in direct reactions of the trifluoroacetate compound, $Mn(CO)_5OCOCF_3$ (33).

Reactions of cationic $[Mn(CO)_5carbene]^+$ complexes and iodide ion gave cis-$Mn(CO)_4(carbene)I$ compounds (21, 23). These complexes may also be formed by a route wherein the cationic carbene complexes are generated as non-isolated intermediates, reacting as they are formed (23) (Equation 7).

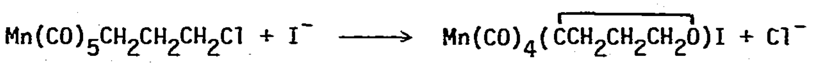


$$\mathrm{Mn(CO)_5\overset{O}{\overset{\|}{C}}CH_2CH_2CH_2Cl} \xrightarrow{a)\,AgBF_4} \mathrm{[Mn(CO)_5\overline{CCH_2CH_2CH_2O}]^+} \xrightarrow{I^-} \mathrm{Mn(CO)_4(\overline{CCH_2CH_2CH_2O})I}$$

$$\xrightarrow{b)\ I^-} \mathrm{Mn(CO)_4(\overline{CCH_2CH_2CH_2O})I}$$

EQ 7

Chloroalkylmanganesecarbonyl compounds react with iodide ion also, apparently generating iodoacylmanganesecarbonyl anion which lose chloride ion and cyclize to give similar products (Equation 8).



$$\mathrm{Mn(CO)_5CH_2CH_2CH_2Cl} + I^- \longrightarrow \mathrm{Mn(CO)_4(\overline{CCH_2CH_2CH_2O})I} + Cl^-$$

EQ 8

Mono-phosphine and phosphite complexes $Mn(CO)_3(L)(\overline{CCH_2CH_2CH_2O})I$ arose in simple variations on this reaction.

Ultraviolet and visible spectral data for $M(CO)_5X$ (Mn: X = Cl, Br, I, H, Me, SiH_3, CF_3; and Re: X = Cl, Br, I) were interpreted based upon molecular orbital theory calculations (37). Two nmr studies on manganese complexes of chelating arsines, $Mn(CO)_3(As\hat{}As)X$, ($As\hat{}As$ = $Me_2AsCRR'CRR'AsMe_2$ and $Me_2AsCH_2CHRCH_2AsMe_2$; X = Cl, Br, I) were also reported (38, 39) as was a full description of the crystal and molecular structure of fac-$Mn(CO)_3(CNPh)_2Br$ (40).

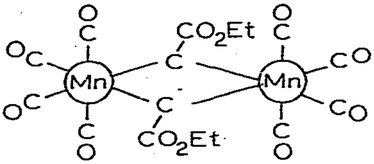
There was also quite a lot of work on derivatives of rhenium carbonyl halides. The tetrameric formulation for a compound $[Re(CO)_3Cl]_x$, described in 1973, has been determined by mass spectroscopy (41). The structure of this species thus must resemble structures of other tetrameric complexes of this stoichiometry, with metal and non-metal atoms occupying alternate corners of a cube.

An interesting reaction sequence occurred with $Re(CO)_5Br$ and diphenylthiophosphinic acid (42). Initially a monosubstituted complex $Re(CO)_4(SPPh_2OH)Br$ was formed. In this complex the thiophosphinic acid bonds to the metal through sulfur. Heating this complex at a temperature greater than 65° expelled one carbonyl, giving a fac-substituted $Re(CO)_3(SPR_2OH)Br$, with both sulfur and oxygen bonding to the metal. This complex in turn lost HBr to form the dimeric species $[Re(CO)_3(SPPh_2O)]_2$.

The syntheses of various disubstituted phosphine, amine, and nitrile complexes of rhenium, fac-$Re(CO)_3L_2X$ (L = PPh_3, $PPh_2CH_2CH_2CN$, pyridine, aniline, PhCN, MeCN), has been reported (43). These syntheses were accomplished by intermediate formation of dimeric tetrahydrofuran complexes $[Re(CO)_3(THF)X]_2$ (X = Cl, Br) by refluxing the $Re(CO)_5X$ species in this solvent; this compound was then reacted with the ligand. Complexes of o-cyanophenyldiphenylphosphine (L) having the formula $[Re(CO)_3LX]_2$ (X = Cl, Br) were reported (44). These dimeric compounds are believed to have a structure with the two cyanophenylphosphine ligands bridging the metal atoms, bridging being accomplished by coordination of phosphorus to one metal and the cyano nitrogen to the other. Raman data was presented to support nitrile coordination through nitrogen only, not through the C≡N π electron system.

The reaction of $Mn(CO)_5Br$ in refluxing acetonitrile to give $[Mn(CO)_3(NCMe)_3]^+$ was cited earlier in this review (26). Also to be noted are reactions of $Mn(CO)_5X$ (Cl, Br, I) with triphenylphosphine oxide, triphenylarsine oxide and pyridine-N-oxide, which occur with either oxidation of manganese, giving $Mn(L)_nCl_2$, or disproportionation giving $[MnL_4X][Mn(CO)_4X_2]$ (34). Finally, the reaction of <u>mer</u>-<u>trans</u>-$Mn(CO)_3[PPh(OMe)_2]_2Cl$ with nitric oxide to give $Mn(NO)_2[PPh(OMe)_2]_2Cl$ was cited (35).

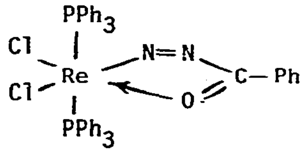
There is a reported reaction of $Mn(CO)_5Br$ and $Hg[C(=N_2)COOEt]_2$. Upon heating the latter reagent generates the carbyne species C(COOEt) which is said to be trapped by its reaction with the manganese carbonyl halide, giving the complex (III) shown below (36).



III

The disubstituted compound <u>trans</u>-$Re(CO)_3(PPh_3)_2Cl$ was obtained when the rhenium (V) complex $Re(PPh_3)_2OCl_3$ was reacted with carbon monoxide in refluxing toluene (45). Addition of excess phosphine to this reaction system improves the yield of the product, the phosphine perhaps acting as a reducing agent. When this product was heated in benzonitrile one equivalent of CO was lost and a product having the stoichiometry $Re(CO)_2(PPh_3)_2Cl$ was formed. This species is presumably dimeric but no data on the degree of aggregation was presented.

Also presented in this paper were reactions of the rhenium (III) complex $Re(PPh_3)_2Cl_2N{=}NCOPh$. Refluxing this compound in a benzene-methanol mixture gave the dinitrogen complex $Re(CO)_2(N_2)(PPh_3)_2Cl$. In benzene with carbon monoxide the reaction proceeded to a seven coordinate benzoyl diazonium rhenium complex (Equation 9) which in turn reacted with $PPhMe_2$ and $PPhEt_2$ to give $Re(CO)(PPhMe_2)_4Cl$ and $Re(CO)_2(PPhEt_2)_3Cl$ respectively.



$+ CO \xrightarrow{C_6H_6} Re(CO)_2(PPh_3)_2(NNCOPh)Cl_2$ EQ 9

Some oxidative chemistry of rhenium (1) complexes was reported here (45). The complexes $Re(CO)(phos)_4Cl$ (phos = $PPhMe_2$, diphos) were oxidized by either chlorine or $FeCl_3$ to give the 17e $[Re(CO)(phos)_4Cl]^+$; further reaction with chlorine occurred with formation of the rhenium (III) or rhenium (IV) compounds $Re(CO)(phos)_3Cl_3$ and $Re(phos)_2Cl_4$. A similar one-electron oxidation of the dinitrogen complex $Re(N_2)(phos)_4Cl$ to $[Re(N_2)(phos)_4Cl]^+$ was accomplished with $AgNO_3$. Both reactions contrast with the reaction of $Re(CO)(diars)_2Cl$ and bromine (diars = o-bisdimethylarsinobenzene) wherein electrophilic addition to the metal occurred with formation of $[Re(CO)(diars)_2Br_2]Br_3$.

The reaction of $Re(CO)_5Cl$ and diethylthiuram disulfide, $[Et_2NCS_2]_2$, may also be mentioned at this point (46). Two organometallic products were obtained, along with $Re(S_2CNEt_2)_2Cl_2$. One, a rhenium (III) species, has the 7-coordinate stoichiometry $Re(CO)(S_2CNEt_2)_3$. The second is $[Re(S_2CNEt_2)_4][Re(CO)_3(S_2CNEt_2)Cl]$, wherein the anion is the product of disubstitution of $Re(CO)_5Cl$ by the bidentate anion ligand $Et_2NCS_2^-$. This salt was found to be reactive with tetrabutylammonium iodide, giving $Bu_4N[Re(CO)_3(S_2CNEt_2)I]$.

Oxidation of $Re(CO)(PPhMe_2)_4Cl$ with excess $TiCl_4$ also gave a 7-coordinate rhenium (III) complex $Re(CO)(PPhMe_2)_3Cl_3$ (47). However, if a deficiency of $TiCl_4$ is used as a 1:2 adduct, $[Re(CO)(PPhMe_2)_4Cl]_2TiCl_4$, was obtained instead. Because of the very low ν(CO) frequencies observed for this species, it was suggested that carbonyl oxygen complexation to titanium is occurring in this species; this means there is a simple representation of the structure as a $TiCl_4 \cdot L_2$ species.

Two references to $Re(CO)_5NO_3$ reactions have appeared. This compound reacted with $Ph_4As[NO_3]$ to give the anionic cis-$Re(CO)_4(NO_3)_2^-$ (48). With various ligands (pyridine, bipy, terpy, PPh_3, $AsPh_3$) the disubstituted fac-$Re(CO)_3L_2NO_3$ can be made by direct reaction (49). Heating of these products at 180° for several hours allowed partial conversion to mer isomers.

Helium(I) photoelectron spectra for $Re(CO)_5X$ (Cl, Br, I) (50) and ultraviolet and visible spectra for the same complexes (37) were reported. Luminescence experiments on $Re(CO)_3$(o-phen)X were said to provide evidence on the lowest excited state of this molecular species (51).

IV HYDRIDO, ALKYL, AND ARYL METAL COMPLEXES

Rather diverse work has been reported on compounds of these types. In addition to some unusually varied synthetic chemistry, there are also several papers on physical properties and theory. These are abstracted here first.

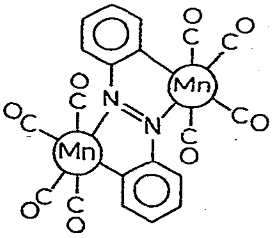
An interesting thermochemical study on $Mn(CO)_5Me$ and $Re(CO)_5Me$ was carried out by Lalage et al. (52). From measured heats of iodination of these compounds at elevated temperatures in a microcalorimeter, the values for $\Delta H_f^{298°}$ for these two compounds were determined. These values were -189.0 ± 2.0 Kcal/mole and -198.0 ± 2.0 Kcal/mole for manganese and rhenium compounds respectively. Used with data for the metal-metal bond dissociation energies for the dimetal decacarbonyls, a carbon-manganese bond energy of either 27.9 ± 2.3 Kcals or 30.9 ± 2.3 Kcals was found. (The discrepancy of these two values results from the difference in published values for the manganese-manganese bond energy). The carbon-rhenium bond energy was calculated to be 53.2 ± 2.5 Kcals.

Assignments for the photoelectron spectra of $Mn(CO)_5Me$ and $Mn(CO)_5CF_3$ have been made (53); and ultraviolet-visible spectral transitions for $Mn(CO)_5X$ (X =

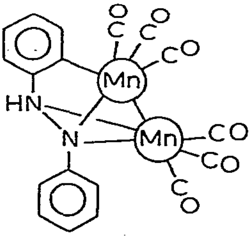
H, Me, SiH_3, CF_3) were made with assistance from MO calculations and PES data (37). Carbon(13) magnetic resonance spectra were recorded for $Mn(CO)_5CH_2Ph$, (8) and for $Mn(CO)_5CH{=}C(CN)_2$ and $Mn(CO)_5C(CN){=}C(CN)_2$ (54).

Ultraviolet irradiation of $Mn(CO)_5Me$ and $Mn(CO)_5CH_2Ph$ was carried out at -30° in the presence of nitrosodurene (55). Homolytic cleavage of the carbon-manganese bond is believed to occur with both radicals resulting from cleavage being trapped by the nitrosodurene, giving $ArNOMn(CO)_5$ and ArNOR (R = Me, CH_2Ph). These species were detected and identified by esr spectroscopy.

Four papers have appeared describing internal metallation reactions for manganese carbonyl compounds. Stone and coworkers (56) have studied the reaction of $Mn(CO)_5Me$ with a species $\overline{Mn(CO)_4N(Ph){=}N{-}C_6H_4}$ which was itself the product of internal metallation of azobenzene. The product of this reaction has the structure shown below (IV). Interestingly the analogous reaction of $Mn(CO)_5Ph$ gave a different product (V).



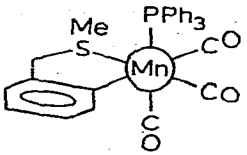
IV



V

Reaction of $Mn(CO)_5COCH_2Ph$ and triphenylphosphite occurred initially to give the benzyl-metal complex $Mn(CO)_4[P(OPh)_3]CH_2Ph$; further reaction led to elimination of toluene and formation of the internally metallated $\overline{Mn(CO)_3[P(OPh)_3]P(OPh)_2OC_6H_4}$ (57). The reaction of the phenylacetylmanganese carbonyl precursor with diphos(1,2-bisdiphenylphosphinoethane) did not take the same course however, giving instead the product $Mn(CO)_3(diphos)COCH_2Ph$.

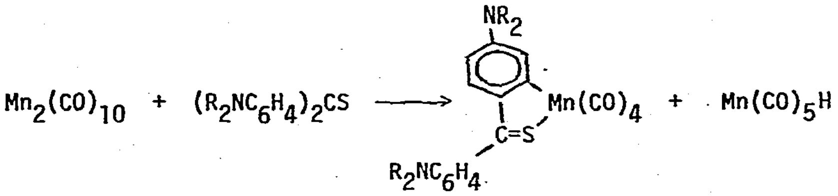
Internal metallation also occurred in the reaction of $Mn(CO)_5Me$ and benzylmethylsulfide (58). The product of this reaction was not amenable to a crystallographic study so the monotriphenylphosphine complex was obtained by direct reaction with this ligand. The structure of this complex was determined by X-ray diffraction techniques (Structure VI).



VI

An elaborate study on manganese carbonyl reactions with various thiobenzophenones was carried out by Alper (59). With 4,4'-dialkylaminothiobenzophenone, the reaction was suggested to occur according to the following sequence equations (Equations 10-12).

1)



EQ 10

2) $Mn(CO)_5H + (R_2NC_6H_4)_2CS \longrightarrow [Mn(CO)_5SCH(C_6H_4NR_2)_2]$ EQ 11

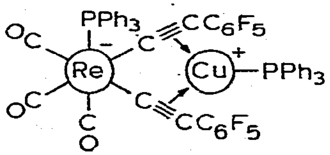
3) $Mn(CO)_5SCH(C_6H_4NR_2)_2 + Mn(CO)_5H \longrightarrow [Mn(CO)_3S]_x + (R_2NC_6H_4)_2CH_2$ EQ 12

Interestingly, a different reaction occurred with thiobenzophenones not containing p-dialkylamino groups on the aryl ring.

Several other methods leading to the formation of carbon-metal σ bonds may be reported here. A metal exchange reaction occurred between $Mn(CO)_5Cl$ and o-$PhN{=}NC_6H_4HgX$ to give $HgCl_2$ and $\overline{Mn(CO)_4N(Ph){=}NC}_6H_4$ (60), the same product as that obtained in the primary internal metallation reaction with azobenzene. Treatment of $Mn(CO)_5Cl$ with 2,3,4,5-tetrachlorodiazocyclopentadiene, $C_5Cl_4N_2$, gave two products (61). These are $C_5Cl_5Mn(CO)_3$, containing the pentahapto coordinated pentachlorocyclopentadienyl ligand, and $Mn(CO)_5C_5Cl_5$. The latter species was converted to the former upon melting at 110°. It contained a monohapto C_5Cl_5 ligand; structural verification was accomplished by a crystal structure determination.

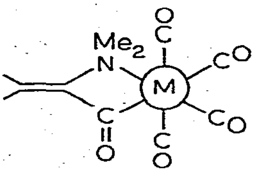
An addition reaction occurred between $M(CO)_5Br$ (Mn,Re) and the Wittig reagent triphenylphosphinemethylene giving the ionic $[M(CO)_5CH_2PPh_3]Br$ complexes (62). Further reaction with PPh_3CH_2 then occurred with proton abstraction from the methylene group in the metal complex, forming $Mn(CO)_5CH{=}PPh_3$ and $[PPh_3Me]Br$. Wittig-type reactions at a coordinated carbonyl were also found to occur between $Ph_3P{=}C{=}PPh_3$ and $M(CO)_5Br$; the resulting product had the formula cis-$M(CO)_4(C{\equiv}CPPh_3)Br$. Consideration is given to a zwitterionic representation of the structure, vis., $M^-(CO)_4(C{\equiv}C\overset{+}{P}Ph_3)Br$, and a structure with no charge separation, $M(CO)_4({=}C{=}C{=}PPh_3)Br$.

The structure of an unusual compound prepared from $Re(CO)_3(PPh_3)_2Cl$ and $Cu(C{\equiv}CC_6F_5)$ has been determined by X-ray crystallography to have the structure VII shown below (63). A zwitterion representation (negative charge on rhenium, positive charge on copper) was suggested.

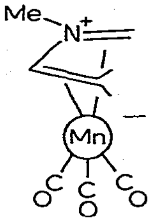


VII

King and Hodges (64) have reacted the $[M(CO)_5]^-$ anions (M = Mn, Re) with $Me_2C{=}C(NMe_2)Cl$. In the case of $Re(CO)_5^-$ simple halide displacement occurred with the vinyl-rhenium compound, $Re(CO)_5C(NMe_2){=}CMe_2$ being formed. A more complex chemistry was seen with $[Mn(CO)_5]^-$. The initial reaction gave an acyl-metal tetracarbonyl, with the amino group assuming the remaining coordination site on the metal (Structure VIII). This compound underwent substantial rearrangement on ultraviolet irradiation to give the compound with structure IX, shown below. The reaction of $Mn(CO)_5H$ and pentamethylenediaziridine to give $Mn(CO)_4CONHC(NH_2)CH_2CH_2CH_2CH_2$ was reported (65).



VIII



IX

An elaborate study on the compound $ReOMe_4$ was the subject of a communication (66) This compound was prepared in over 50% yield in the reaction of either $ReOCl_4$ or $ReOCl_3(PPh_3)_2$ with methyllithium at -35°. It is an air-sensitive, thermally stable, paramagnetic, red purple solid, m.p. 44°. A mass spectrum at 16ev ionizing voltage was reported to show the peaks associated with $ReOMe_n^+$ (n = 0, 1, 2, 3, 4), and the infrared spectrum identifies ν(ReO) at 1016 cm^{-1}. The compound was unreactive to H_2O, ROH, H_2, CO, and SO_2; with I_2, methyl iodide was formed.

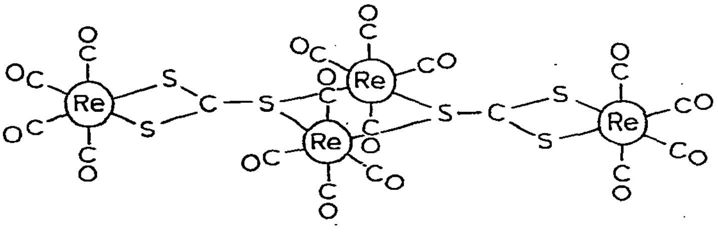
A structure for the compound $C_5H_5Re(CO)_2(Me)Br$ was determined by X-ray diffraction (67). The standard square pyramidal arrangement of ligands was found with the C_5H_5 ring in the apex, and methyl and bromide groups in trans basal positions.

Reference was made earlier in this review to the compound

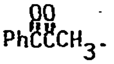
$\overline{Re(CO)_4CH_2OC(CF_3)=C(CF_3)AsMe_2}$, which was presumed to have an alkyl-rhenium structure (11).

Various studies of reactions of metal alkyl complexes have reached publication Electrophilic reactions of various 2-alkynyl and 2-alkenyl metal compounds are found in a thesis (68). Most of this work has been published and has been cited in ANNUAL SURVEYS in the previous two years. The reaction of $Mn(CO)_5Me$ and $SnCl_2$ did not give insertion into the carbon metal bond as was seen with $C_5H_5Fe(CO)_2Me$; instead cleavage occurred and the products $Mn(CO)_5SnCl_3$ and $[Mn(CO)_4Cl]_2$ were obtained (69). Rates of carbon-metal bond cleavage in liquid SO_2 (-65° to -18°C) have been studied (70) and pseudo-first order rate constants determined. Relative cleavage rates were: $C_5H_5Fe(CO)_2Me > Re(CO)_5Me > C_5H_5Ru(CO)$ $> Mn(CO)_5Me >> C_5H_5Mo(CO)_3Me >> C_5H_5W(CO)_3Me$; and $C_5H_5Cr(NO)_2CH_2Ph >>$ $C_5H_5Mo(NO)_2CH_2Ph \geq C_5H_5Fe(CO)_2CH_2Ph \gtrsim Mn(CO)_5CH_2Ph > C_5H_5Ru(CO)_2CH_2Ph >>$ $C_5H_5W(NO)_2CH_2Ph$.

The product of the reaction product of $Re(CO)_5CF_3$ and CS_2 has been characteri by X-ray diffraction techniques (71). Its structure is shown below (X)



X

Several papers have dealt partly or exclusively with metal acyl complexes. Earlier the isolation of several of these species and their use in generating carbene-metal complexes (21, 23) or cationic metal complexes (20) was noted. In addition, there were two reports on decomposition reactions of manganese acyl compounds from Casey et al. The compound erythro-2,3-dimethylpentanoylmanganese pentacarbonyl was shown to decompose thermally to give a mixture of 4-11% 3-methyl-1-pentene, 56-62% *trans*-3-methyl-2-pentene, and 31-32% *cis*-3-methyl-2-pentene (72). The same product mixture was also obtained from a mixture of the *erythro*- and *threo* compounds, and also from 4-methylhexanoyl manganese pentacarbonyl. A reaction scheme to account for these products is proposed. Nucleophilic addition of methyllithium to benzoylmanganese pentacarbonyl giving *cis*-$[Mn(CO)_4(COPh)(COMe)]^-$ was noted (73). This anion was isolated as a tetramethylammonium salt, and a crystal structure study carried out. This anion decomposed in THF (70°C) to give acetophenone, and reacted with bromine (0°C) to give  $Ph\overset{O}{\overset{\|}{C}}\overset{O}{\overset{\|}{C}}CH_3$.

A full paper on thiocarboxamido-manganese carbonyls has appeared (74); there was a communication on this work last year. Reaction of Me_2NCSCl and $Mn(CO)_4L^-$ (L = CO, PPh_3) gave $Mn(CO)_3(L)CSNMe_2$ wherein the CS group of the thiocarboxamido-group functions as a bidentate three electron donor ligand. The compound $Mn(CO)_3(PPh_3)CSNMe_2$ can be alkylated at sulfur with $[Me_3O]^+$.

Carboxamido complexes were identified as initial products in the reactions of primary amines with $[Mn(CO)_{6-n}(CNMe)_n]^+$ (n = 2, 3); isolation of these unstable products was usually not accomplished however (25). This type of addition reaction was also seen in reactions of $[RC_5H_4Mn(NO)(CO)L]^+$ (L = CO, PPh_3) with primary amines (75). For the compounds with L = CO carboxamido-metal complexes could be isolated; when L = PPh_3 stable complexes were not obtained although spectroscopic evidence suggested their presence in solution.

An unusual rearrangement occurs with the carboxamido complex $Re(NO)(PPh_3)_2(NCO)CONHCOOEt$ upon protonation; isolated were the compounds $[Re(CO)(NO)(PPh_3)_2(NCO)NH_2COOEt]BF_4$ with HBF_4, and $Re(CO)(NO)(PPh_3)_2(NCO)Cl$ with HCl (76).

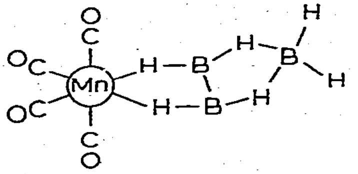
The isomerization of the optically active carbomethoxy compound, (+) or (-) $C_5H_5Mn(NO)(PPh_3)COOMe$, occurred via a 5-coordinate intermediate formed upon dissociation of the phosphine (77).

There have been few references to manganese hydride species. Reference to the ultraviolet-visible spectra of $Mn(CO)_5H$ was made earlier (37), as was the deprotonation with accompanying rearrangement of $H_3Mn_3(CO)_{12}$ (18). Two papers reported nmr studies of $C_5H_5Mn(CO)_{3-n}(PR_3)_n$ (n = 1, 2) compounds in CF_3COOH. An upfield proton resonance at 14-16τ was seen, indicative of metal protonation (78). Phosphorus(31) and carbon(13) data also support this formulation (79). The reactions of $H_3Mn_3(CO)_{12}$ and various cyclic olefins have been reported (80). In addition to $Mn_2(CO)_{10}$, a product always seen in these reactions, there were found various dienyl-manganese carbonyl compounds, and several other more complex hydrocarbon complexes. With acetylenes, oligomerization occurred. Diphenylacetylene and $H_3Mn_3(CO)_{12}$ gave 1,2,3,4-tetraphenylbutadiene; diethylacetylene, however, gave 1,2,3,4,5,6-$(C_6Et_6H)Mn(CO)_3$, a cyclohexadienylmetal tricarbonyl complex.

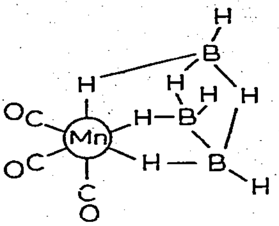
V METAL CARBONYL DERIVATIVES OF METALS AND METALLOIDS

There are only three references to complexes containing more metallic elements. Two structural studies on cadmium complexes have been reported, concerning Cd(diglyme)$[Mn(CO)_5]_2$ (81) and two Cd(N^N)$[Mn(CO)_5]_2$ complexes (N^N = bipyridine, o-phenanthroline) (82). Five coordinate geometry about cadmium was seen in the first example; distorted tetrahedral geometry around the metal was found in the complexes with nitrogen chelate ligands. The synthesis and vibrational spectra for the trans square planar compounds $M(L)_2[Mn(CO)_5]_2$ (M = Pt, L = 3-methylpyridine, 4-methylpyridine; M = Pd, L = pyridine) is noted (83). The trans-geometry was confirmed by the single infrared absorption for the manganese-metal bond.

More work has appeared concerning complexes of these metals with boron and other Group IIIA elements. An interesting communication from Gaines and Hildebrandt described the yellow volatile liquids $Mn(CO)_4B_3H_8$ (84), prepared from $[B_3H_8]^-$ and $Mn(CO)_5Br$; a similar rhenium compound was also reported. Ultraviolet irradiation of $Mn(CO)_4B_3H_8$ caused decarbonylation to give $Mn(CO)_3B_3H_8$. The structures of these two borane species involve bidentate and tridentate coordination to the metal via electron deficient B-H-Mn bridge bonds (Structures XI and XII).



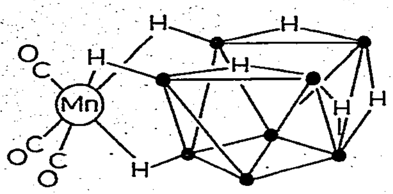
XI



XII

Interestingly, the tetracarbonyl complexes exhibit the expected ^1H and ^{11}B resonances. However $Mn(CO)_3B_3H_8$ shows only two proton resonances at 10.1τ and 21.6τ and a single ^{11}B nmr resonance. These data suggest that the hydrogen atoms bridging the metal and boron atoms are not exchanging rapidly, but requires that terminal and B-H-B bridge hydrogens on the ligand are exchanging, causing the boron atoms and these hydrogens to experience similar magnetic environments.

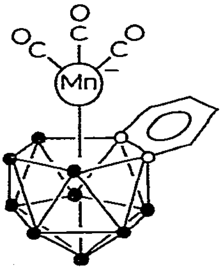
An elaborate chemistry of B_9 derivatives of manganese and rhenium emerged from the same research group (85, 86, 87, 88). Treatment of $M(CO)_5Br$ (M = Mn, Re) with $K[B_9H_{14}]^-$ in a 1:1 molar ratio gave $[6\text{-}Mn(CO)_3B_9H_{13}]^-$ which on oxidation with $HgCl_2$ or I_2 formed 2-THF-6-$Mn(CO)_3B_9H_{12}$. (The numbering system refers to the $B_{10}H_{14}$ structural prototype; here the manganese tricarbonyl group takes the B(6) position.) If the molar ratio was changed to 2:1, a third compound, 5-THF-6-$Mn(CO)_3B_9H_{12}$, was formed (85). Treatment of 2-THF-6-$Mn(CO)_3B_9H_{12}$ with triethylamine resulted in tetrahydrofuran ring cleavage; a crystal structure for the product of this reaction, 8-$Et_3N(CH_2)_4O$-6-$Mn(CO)_3B_9H_{12}$, has been determined (86). Finally, in a later paper yet another product of the $Mn(CO)_5Br + K[B_9H_{14}]$ reaction was described; this was the compound $Mn(CO)_3B_8H_{13}$ (87). An X-ray diffraction study has given its structure as well (Structure XIII, below).



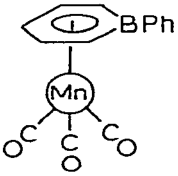
XIII

Most of this B_9 work is summarized in a thesis (88).

Manganese tricarbonyl complexes of the benzodicarbollide and the 1,4-dihydrobenzodicarbollide ions were prepared from the salts of these dianions and $Mn(CO)_5Br$ (89); they were each isolated as tetramethylammonium salts. The presumed structure of the former complex is shown below (XIV).



XIV

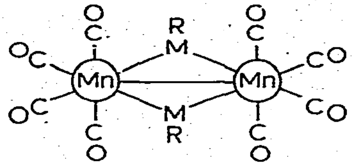


XV

A reaction product of this complex and bromine, $[C_6B_9H_{15}Mn(CO)_2Br]_2$, was also described. It is believed to be dimeric via halogen bridging atoms.

The structure of $C_5H_5BPhMn(CO)_3$ is shown above (Structure XV) (90). The borabenzene ring is essentially planar, and the manganese atom, though displaced slightly from the center of the ring away from boron, is obviously experiencing some bonding interaction with this atom.

Compounds formed from gallium or indium and either $Mn_2(CO)_{10}$, $Hg[Mn(CO)_5]_2$, or a mixture of Hg + $Mn_2(CO)_{10}$ at 180°C have the formula $M_2Mn_4(CO)_{18}$ (M = Ga, In) (91); the same compound for indium was formed on heating $In[Mn(CO)_5]_3$ at 180°C. The crystal structures of both compounds have been investigated by X-ray diffractior methods, and have been found to contain the molecular species (Structure XVI) shown below (92). An interesting feature of this structure is the long



$(M = Ga, In; R = Mn(CO)_5)$

XVI

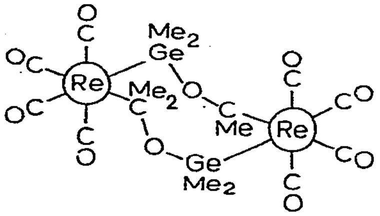
metal-metal bond 3.227 Å.

Two reports in the literature describe searches for thallium(I) complexes of manganese. Burlitch and Theyson (93) have obtained spectroscopic evidence for $Tl[Mn(CO)_5]$, formed at low temperature from $Mn(CO)_5H$ and TlOEt. This unisolable compound is not stable in solution at temperatures higher than -65°C; at room temperature decomposition to $Th[Mn(CO)_5]_3$ and thallium metal occurred. The thallium(I) species also reacted with Ph_3SnCl to give $Mn(CO)_5SnPh_3$; this suggests rather a salt-like behavior for this compound. The thallium(III) complex on photolysis gave $Mn_2(CO)_{10}$ and the $Tl[Mn(CO)_5]$ decomposition products. A prediction of the instability of thallium(I) complexes of metal carbonyls is given, based on the pKa values for the corresponding hydrides (94). Thallium(I) complexes of $-Co(CO)_4$ and $-Co(CO)_3[P(OPh)_3]$ are stable, and the corresponding hydrides are quite acidic with pKa values of ~ 1 and 4.95 respectively. On the other hand the compound $Tl[Co(CO)_3PPh_3]$ is unstable and disproportionates; and the pKa of $Co(CO)_3(PPh_3)H$ is 6.96. Since the pKa of $Mn(CO)_5H$ is about 7.5, instability of its thallium(I) complex was predicted.

A Ph.D. thesis on manganese pentacarbonyl derivatives of aluminum, gallium and indium is abstracted (95).

Still more work on Group IVA compounds of manganese and rhenium continues to appear. Much of this only involves extensions of known work, but a few things merit special notice. There was, for example, an interesting attempt to prepare germylene compounds (i.e. compounds with GeR_2 ligands) of various metals including manganese (96). Thus the reaction of $Mn(CO)_5GeMe_2Cl$ and $AgBF_4$ was attempted. Regrettably this did not give the desired product; instead $Mn(CO)_5GeMe_2F$ was isolated. Also of note is the reaction of $Na[Mn(CO)_5]$ and Me_3SnCH_2I (97). The product formed arose from reaction at the tin-carbon bond, generating $Mn(CO)_5SnMe_3$ and presumably $Na[CH_2I]$. Also obtained was a trace of $Mn(CO)_5Me$. Finally the unusual reaction of $Sn(C_5H_5)_2$ and $Mn(CO)_5H$ was reported (98); a distannane compound $[(CO)_5Mn]_2HSnSnH[Mn(CO)_5]_2$ was isolated and characterized in a crystallographic study.

Further work has been carried out on the compound $\overline{Mn(CO)_4CMeOGeMe_2}$ which exists in equilibrium with a dimeric form (99). The dimeric rhenium compound of the same formulation was the subject of a crystallographic study; its structure is shown below (XVII).

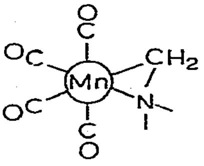

XVII

Otherwise there were few surprises in this area. Three papers concerning pentafluorophenyl substituted silicon, germanium, and tin compounds have appeared. Synthesis of the silicon compounds occurred from $Si(Ph)_{3-n}(C_6F_5)_nH$ and $Mn_2(CO)_{10}$. The analogous germanium and tin compounds, $Mn(CO)_5Ge(Ph)_{3-n}(C_6F_5)_n$ and $Mn(CO)_5Sn(Ph)_{3-n}(C_6F_5)_n$, were prepared from $Mn(CO)_5M(Ph)_{3-n}Cl_n$ and C_6F_5Li (100). Reactions of $Mn(CO)_5Sn(Ph)_{3-n}(C_6F_5)_n$ ($n = 1, 2$) with chlorine occurred giving $Mn(CO)_5Sn(C_6H_5)_nCl_{3-n}$ compounds (101). Infrared, nmr, and Mossbauer data (on the tin compounds) were recorded; mass spectra were also reported in a separate paper (102). The vinyl-tin derivatives $Mn(CO)_5Sn(CH{=}CH_2)_2OCOCF_3$ and $Sn(CH{=}CH_2)_2[Mn(CO)_5]_2$ were formed from $Na[Mn(CO)_5]$ and $Sn(CH{=}CH_2)_2(OCOCF_3)_2$ (103). The formation of compounds of the formula $Mn(CO)_4(L)Si(SiMe_3)_nMe_{3-n}$ (n = 1,2,3; L = CO, PPh_3) was accomplished either from $[Mn(CO)_5]^-$ and $Me_3SiSiMe_2Cl$, or from $[Si(SiMe_3)_nMe_{3-n}]^-$ and $Mn(CO)_4(L)Br$ (104). The syntheses of $Mn(CO)_5SnPh_3$ (93) and $Mn(CO)_5SnCl_3$ (69) were reported from $Tl[Mn(CO)_5]$ + $SnPh_3Cl$ and $Mn(CO)_5Me$ + $SnCl_2$ respectively. And the polymetallic compound $[(CO)_5ReSnBu_2]_2Os(CO)_4$ was described formed from $(ClSnBu_2)_2Os(CO)_4$ and $Na[Re(CO)_5]$ (105). In the same paper a structure determination of $(Bu_3Sn)_2Os(CO)_4$ determined that this compound had a <u>trans</u> configuration.

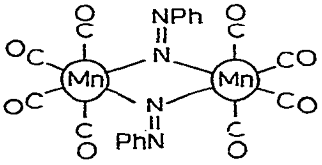
Two papers on infrared-Raman work concerning Group IV-manganese and rhenium compounds have appeared (106, 107).

VI METAL COMPLEXES OF GROUP VA and VIA LIGANDS

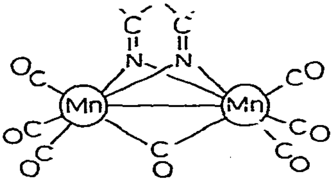
Three types of compounds of various nitrogen ligands have been prepared in Abel's laboratories and characterized by X-ray diffraction methods. Aminomethylene complexes $Mn(CO)_4CH_2NR_2$ (N = Me, Et, etc.) are formed in the reaction of $R_3SnCH_2NR_2$ and $Mn(CO)_5Br$ (108). Presumably this reaction proceeded first to a <u>cis</u>- amine substituted manganese tetracarbonyl bromide. This can then undergo facile Me_3SnBr loss to give the observed product, having both carbon and nitrogen coordinated to the metal (XVIII)



XVIII



XIX



XX

The second compound has bridging phenyl diazonium groups, as shown in structure XIX. This compound arose from $Me_3SiN{=}NPh$ and $Mn(CO)_5Br$ (109). The last compound was formed on treatment of $Mn(CO)_5Br$ and $Me_3SnN{=}C(CF_3)_2$. Again elimination of $SnMe_3Br$ occurred. The product species has the stoichiometry $Mn_2(CO)_7[N{=}C(CF_3)_2]_2$. Its structure is likened to the structure of $Fe_2(CO)_9$ (see Structure XX) with two bridging carbonyl groups replaced by $N{=}C(CF_3)_2$ groups (110).

Extensive further work has appeared describing porphyrin compounds of technetium and rhenium; some of this work had been communicated last year. Two series of compounds were described. The monometallic compounds have the general formula $HPM(CO)_3$ (where HP is the mono-hydrogen-meso-tetraphenylporphinato (HTTP) ligand, or the mono-hydrogen-mesoporphyrin(IX) dimethylesterato (HMP) ligand; and M = Tc, Re). The static structure of these substances involves coordination to the metal by three nitrogens; the fourth nitrogen retains the hydrogen. Nmr studies indicate, however, that exchange of hydrogen and hence of the metal among the four possibilities must occur rapidly (111, 112). The thermal conversion of $HMPTc(CO)_3$ to the bimetallic $MP[Tc(CO)_3]_2$ was the subject of another paper (113).

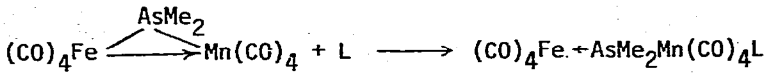
Nmr studies have also shown that fast exchange occurs at 5°C for several pyrazolylborato complexes of manganese having the formula $Mn(CO)_2L(pz)_3BR$ (R = H, pz), which caused all the coordinated pyrazolyl groups to experience identical magnetic environments (114).

Finally, mention has already been made in this review of the following nitrogen ligand complexes: $Mn_2(CO)_6(C_{12}H_{10}N_2)$ from $Mn(CO)_5Ph$ and $Mn(CO)_4C_6H_4N{=}NPh$ (56), $Re(CO)_2(PPh_3)_2(N{=}NCOPh)Cl_2$ and $Re(CO)_2(PPh_3)_2(N_2)Cl$ (45), and $Mn(CO)_5NOPh$ (trapped nitroxide radicals, not isolated) (55).

A single reference to phosphorus ligand complexes (excepting those concerned with phosphines as simple two electron donor ligands) was concerned with non-parameterized MO calculations on $[Mn_2(CO)_8(PR_2)_2]^n$ (n = 0, 1, 2) species (115).

An unusual complex with a bridging $AsMe_2$ group arose in the $Mn_2(CO)_{10}$-

<u>cis</u>-$Me_2AsC(CF_3)=C(CF_3)AsMe_2$ reaction (11). Other work on bridged arsenic ligand complexes comes out of Vahrenkamp's research group. A series of complexes $(CO)_4FeAsMe_2Mn(CO)_4L$ (L = $P(NMe_2)_3$, $P(OMe)_3$, PPh_3, $PPhMe_2$) was formed by reaction of $(CO)_4FeAsMe_2Mn(CO)_4$ (116). Their formation involved metal-metal bond breaking according to Equation 13.

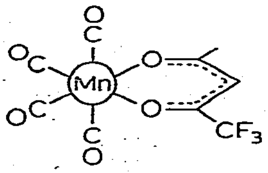


$$(CO)_4Fe\overset{AsMe_2}{\longrightarrow}Mn(CO)_4 + L \longrightarrow (CO)_4Fe \leftarrow AsMe_2Mn(CO)_4L \qquad \text{EQ 13}$$

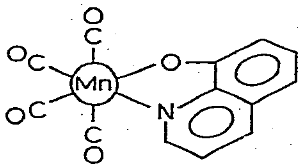
A crystal structure on the compound $C_5H_5Mn(CO)_2AsMe_2Mn(CO)_4$ was also reported (117). Noteworthy is the substantial distortion of one of the terminal carbonyl groups bonded to the C_5H_5Mn atom, a consequence of intramolecular repulsions of carbonyls on adjacent metals.

Among the various Group VIA ligand complexes, mention might first go to oxygen donor ligands. The synthesis and characterization of 1,1,1-trifluoropentadionatomanganese tetracarbonyl (Structure XXI) may be noted, from $Mn(CO)_5Br$ and the sodium salt of the diketone (118). Also of interest are manganese complexes of 8-hydroxyquinoline, formed in the same sort of reaction from $Mn(CO)_5Br$ (Structure XXII).

It is possible to effect ligand substitution in these latter complexes generating either <u>fac</u>-$Mn(CO)_3(L)(Ox)$ or $Mn(CO)_2L_2Ox$ (L = amines, pyridine, phosphines, arsines; Ox = oxine, i.e. the 8-hydroxyquinolinato ligand). The kinetics of this ligand substitution have been studied (119).



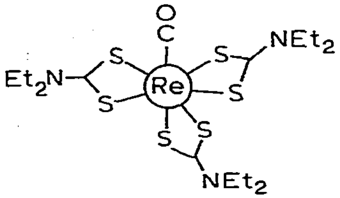
XXI



XXII

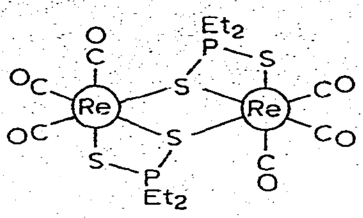
The various nitrate ion complexes cited earlier in this review (48, 49) including cis-$Re(CO)_4(NO_3)_2^-$ and $Re(CO)_3L_2NO_3$, contain the nitrate ion linked to rhenium via an oxygen.

Three general types of sulfur ligand complexes have received more than nominal attention. Dithiocarbamate complexes of rhenium, noted earlier, include $Re(CO)(S_2CNEt_2)_3$, $[Re(CO)_3(S_2CNEt_2)X]^-$ (X = Cl, I) and the dinuclear $[Re(CO)_3(S_2CNEt_2)]_2$ which has bridging dithiocarbamate ligands (46). The structure of the first of these compounds has been determined by a crystallographic study; (120) this is shown below (Structure XXIII). The geometry of substitution at the metal in this compound has a distorted pentagonal bipyramidal arrangement of ligands.



XXIII

Various references to dithio-phosphinate and -arsinate complexes have been made; this is the work of Lindner and coworkers. The monomeric complexes $M(CO)_4S_2AsMe_2$ were prepared from $M(CO)_5Br$ (M = Mn, Re)and the salt $Na[S_2AsMe_2]$ (121). Upon heating dimeric complexes $[M(CO)_3S_2AsMe_2]_2$ were formed; reaction with pyridine gave fac-$M(CO)_3(py)S_2AsMe_2$. Kinetics of reactions of $M(CO)_4S_2PR_2$ (M = Mn, Re; R = Et, Ph) have also been studied (122). With PPh_3 and pyridine; carbonyl substitution reactions are first order (in complex only); however the reaction of $AsPh_3$ is second order. The structure of $[Re(CO)_3S_2PEt_2]_2$ has been determined (123) This is shown below (Structure XXIV).



XXIV

The reaction of $Re(CO)_5Br$ and $Ph_2P(S)OH$ to give first $Re(CO)_4(SP(OH)Ph_2)Br$, and then $[Re(CO)_3SP(O)Ph_2]_2$ was cited earlier (42).

Chelating trithiocarbonate complexes, $M(CO)_4S_2CSMe$, (M = Mn, Re) were formed if the pentacarbonylmetallate anion was treated first with CS_2, and then with methyl iodide (124). A second product, $Re(CO)_4S_2CSRe(CO)_5$, was also formed in small quantity in the rhenium reaction. Its yield can be improved substantially however by adding $Re(CO)_5Br$. This result, in turn, suggested a route to a mixed manganese-rhenium species by substitution of $Mn(CO)_5Br$ for $Re(CO)_5Br$ in the final step. This proved not exactly correct however. The product of this reaction turned out to be $Mn(CO)_4S_2CSRe(CO)_5$, not $Re(CO)_4S_2CSMn(CO)_5$. It was suggested that a symmetric intermediate, $Re(CO)_5SC(=S)SMn(CO)_5$, was involved. A monodentate complex, $Re(CO)_5SCSSMe$ was also reported in this paper. This compound arose upon sequential addition of CS_2, S_8 and MeI to $[Re(CO)_5]^-$.

An unusual trithiocarbonate complex $Re_4(CO)_{16}(CS_3)_2$ was described earlier (71). It was formed in the reaction of $Re(CO)_5CF_3$ and CS_2. The bidentate thiocarboxamido complexes $Mn(CO)_3(L)CSNMe_2$ (L = CO, PPh_3) were also noted earlier (74), as were reactions of p-dialkylaminothiobenzophenones and $Mn_2(CO)_{10}$ to give internally metallated products, $[Mn(CO)_3S]_x$ and $R_2NC_6H_4CH_2C_6H_4NR_2$. In contrast, when para-amino substituent groups were not present this reaction took a different course. No internally metallated products were formed; instead the reaction products were $Ph_2C=CPh_2$ and $[Mn(CO)_3S]_x$.

VII HYDROCARBON METAL COMPLEXES

Magnetic susceptibility and esr data on manganocene and bis(methylcyclopentadienyl)manganese have been reported during the last 20 years, and it has generally been assumed that these compounds contained the metal in a high spin configuration. However, in 1972, a paper on Helium(I) photoelectron spectra for gaseous manganocene appeared which suggested a low spin state. Further work to explain or resolve this possible contradiction has now appeared from three laboratories; these are referenced chronologically here (125, 126, 127). Each study reached the same basic conclusion, that the lowest energy state is the high spin state, but the energy difference between high and low spin states was small indeed. This was illustrated nicely in the experimental work in the last article (127). Here the esr spectra of both diluted and undiluted samples were determined from 4.2° - 300°K. High spin spectra for pure $Mn(C_5H_5)_2$ and for $Mn(C_5H_5)_2$ diluted in $Mg(C_5H_5)_2$ were found, whereas low spin esr spectra were seen for the same sample diluted in $Fe(C_5H_5)_2$. Low spin spectra were also seen for diluted $Mn(C_5H_4Me)_2$ samples. The conclusion is offered that the energy difference between the high and low spin states is quite small, perhaps about 0.5 Kcal/mol; hence small changes arising in intermolecular forces may have significant influence on the nature of the system.

A Ph.D. thesis on this work was also referenced (128).

Various synthetic and physical property studies have been directed to mono- and di-substituted derivatives of $C_5H_5Mn(CO)_3$. One interesting study was concerned with reactions occurring at the coordinated phosphorus ligands in $C_5H_5Mn(CO)_2PPhCl_2$ (129). Facile exchange of chloride by other groups Y^- can be accomplished, giving $C_5H_5Mn(CO)_2PPhY_2$ (Y = CN, NCO, NCS, N_3). Further reactions can then be carried out: $C_5H_5Mn(CO)_2PPh(NCO)_2$ and ROH (R - Me, Et) or Et_2NH give $C_5H_5Mn(CO)_2PPh(NHCOOR)_2$ or $C_5H_5Mn(CO)_2PPh(NHCONEt_2)_2$, and $C_5H_5Mn(CO)_2PPh(N_3)_2$ and CO or PPh_3 gave $C_5H_5Mn(CO)_2PPh(NCO)_2$ or $C_5H_5Mn(CO)_2PPh(N_3)(NPPh_3)$. A reaction to form $C_5H_5Mn(CO)_2PMe_2NMe_2$ was also reported (32). This compound reacted with HCl to give $C_5H_5Mn(CO)_2PMe_2Cl$.

Manganese complexes of diphenylketene (130) and of phenylbenzoyl carbene were also reported (133). They both arose from $MeC_5H_4Mn(CO)_2THF$ (prepared on in situ irradiation of a solution of $MeC_5H_4Mn(CO)_3$ in THF) and either $Ph_2C=C=O$ or $PhC(N_2)COPh$ respectively.

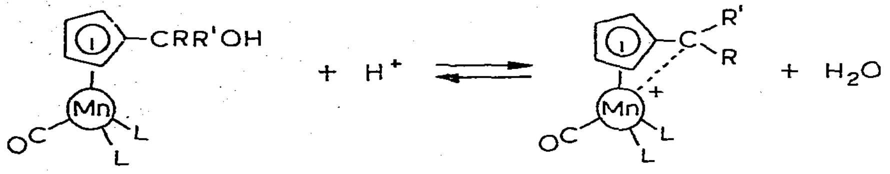
Various thiocarbonyl derivatives of $C_5H_5Mn(CO)_3$ have been prepared. Reactions of $C_5H_5Mn(CO)_2(CS)$ with phosphines, phosphites, $AsPh_3$, $SbPh_3$ gave either $C_5H_5Mn(CO)(L)(CS)$ or $C_5H_5Mn(L)_2(CS)$ complexes (132, 133, 134). A thesis on some of this work was cited (30).

The reaction of KCN and $MeC_5H_4Mn(CO)_3$ gave a mixture of two anionic complexes, $[MeC_5H_4Mn(CO)_2CN]^-$ and $[MeC_5H_4Mn(CN)_3]^{3-}$ (135). The former was not isolated as a pure salt, but reacted directly with electrophiles. Triethyloxonium salts added one or two ethyl groups on nitrogens giving $[MeC_5H_4Mn(CNEt)_{3-n}(CN)_n]^{n-}$ (n = 1,2). Protonation or methylation of $K[MeC_5H_4Mn(CO)_2CN]$ gave $MeC_5H_4Mn(CO)_2CNR$ (R = H, Me).

There is a thesis describing the synthesis, infrared spectrum and reactions of $C_5H_5Mn(CO)_2SR_2$ (136). Polymer bound phosphines displace carbon monoxide from $MeC_5H_4Mn(CO)_3$ to give a polymer-bound metal complex (12). The reaction of $Mn(CO)_5Cl$ and 2,3,4,5-tetrachlorodiazacyclopentadiene to give $C_5Cl_5Mn(CO)_3$ was noted earlier (61). Interestingly, the values of $\nu(CO)$ for this compound fall at 2050 and 1982 cm^{-1}, about 28 cm^{-1} higher than the values for $C_5H_5Mn(CO)_3$, reflecting the inductive effect of the five chlorine substituents.

Two isomeric disubstituted complexes were obtained from $C_5H_5Mn(CO)_3$ and the triphosphine $(Ph_2PCH_2CH_2)_2PPh$ (134). A crystal structure study on the complex $C_5H_5Mn(CO)(PPh_3)_2 \cdot C_6H_6$ has been carried out (137). The phosphorus-metal-phosphorus angle here is 104°, rather large, an indication of substantial repulsion of the triphenylphosphine ligands.

Trifluoroacetic acid protonation of various $(C_5H_4CRR'OH)Mn(CO)L_2$ complexes (L = CO, PPh_3, $PPr_3{}^i$, 1/2 diphos) has been reported (138). An equilibrium was apparently established between the starting materials and a cationic fulvene complex and water, vis (Equation 14).



EQ. 14

Other studies involving protonation of $CpMn(CO)_{3-n}L_n$ complexes (n = 1,2; L = phosphines) at the metal atom were mentioned earlier in this review (78, 79).

Reactions in a mass spectrograph were observed (139). When $C_5H_5Mn(CO)_3$ and various ligands were introduced simultaneously into a mass spectrograph, peaks corresponding to $[C_5H_5MnL]^+$ and $[C_5H_5Mn(CO)L]^+$ were seen (L = PF_3, H_2O, H_2S, R_2O, NH_3, hydrocarbons).

An esr study on crystals of $C_5H_5Mn(CO)_3$ which had been subjected to irradiation by 50Kv x-rays is reported (140); radical species were detected. Infrared and Raman spectra were obtained for $C_5H_5Mn(CO)_3$ (141, 142), $C_4H_4NMn(CO)_3$ (141), and $C_5D_5Mn(CO)_3$ (142). Carbon-13 nmr data were reported for the isoelectronic complexes $[C_5H_5Cr(CO)_3]^-$, $C_5H_5Mn(CO)_3$, and $[C_5H_5Fe(CO)_3]^+$. Large differences in chemical shifts were identified, and a correlation with deshielding with increased π bonding from metal to ligand was offered (143). Additional carbon-13 nmr data for substituted species $C_5H_5Mn(CO)_2L$ (L = CS, CO, PPh_3, PBu_3, $P(OPh)_3$, $P(OMe)_3$, $C_5H_{10}NH$, C_8H_{14})were reported in another paper (144). As in the earlier study there is increased deshielding of the carbonyl carbon with increased metal to carbonyl back donation. It may also be noted in passing that these data indicated that the ligand CS is a better acceptor than CO.

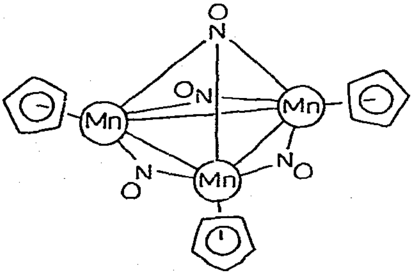
Temperature dependent proton nmr spectra for $C_5H_5Mn(CO)_2(C_2H_4)$ and $C_5H_5Mn(CO)_2(trans\text{-}C_2H_2D_2)$ have shown that there is restricted rotation around the metal-olefin bond (145). The activation parameter $\Delta G^{\ddagger}$ measured at 168°K was found to be 8.4 ± 0.2 Kcal/mole.

ESCA spectra were recorded for $C_5H_5Mn(CO)_3$, $Mn(C_5H_5)_2$ and $[C_6H_6Mn(CO)_3]BF_4$ (146).

The reaction of $Re(C_5H_5)_2H$ and $NaOCOCCl_3$ in glyme was reported in a thesis (147). Products included $Re(C_5H_5)_2Cl$ and $C_5H_5Re(CO)_3$. The structure of $C_5H_5Re(CO)_2(Me)Br$ has been determined in a crystallographic study (67).

Treatment of $[C_5H_4RMn(NO)(CO)L]^+$ (R = H, Me; L = CO, PPh_3) with primary amines appeared to give an equilibrium mixture of starting materials and the products $C_5H_4RMn(NO)(L)CONHR$ and $[RNH_3]^+$ (75). Several carboxamido complexes were isolated (L = CO only).

The structure of $(C_5H_5Mn)_3(NO)_4$ involves an equilateral triangle of metals with three NO groups bridging the edges and an NO group bridging one face (148); the structure is shown below (XXV).



XXV

An extensive spectroscopic study on $[C_6H_{6-n}Me_nMn(CO)_3]^+$ complexes was reported (149). Infrared, proton and carbon(13) nmr, and manganese(55) n.q.r. measurements were recorded; ESCA data was reported elsewhere (146).

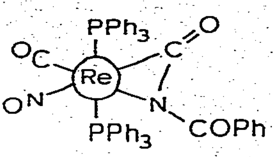
Various hydrocarbon complexes, including many dienylmanganese tricarbonyls were formed from $Mn_3(CO)_{12}H_3$ and cyclic olefins (80). The mass spectra for some of these compounds, including $C_6H_7Mn(CO)_3$, $C_7H_9Mn(CO)_3$, and two isomers of $C_8H_{11}Mn(CO)_3$, were described (150). As expected, stepwise loss of the three carbonyls was seen.

VIII VARIOUS ISOCYANIDE AND NITROSYL COMPOUNDS

Little work on isocyanide complexes has appeared; in contrast several years ago this was a major area of study. Cited already in this review are three references: to the reaction of $[Mn(CO)_{6-n}(CNMe)_n]^+$ (n = 2,3) with primary amines (25), to the structure of fac-$Mn(CO)_3(CNPh)_2Br$ (40), and to alkylation products of $K[MeC_5H_4Mn(CO)_2CN]$ and $K_3[MeC_5H_4Mn(CN)_3]$ (135). In addition, molecular orbital calculations and spectroscopic data for $[Mn(CNR)_6]^{2+}$ complexes have been reported (151).

More work has been done on nitrosyl complexes however. The photolytic reaction of $Mn_2(CO)_{10}$ and NO gave first $Mn(CO)_4NO$ (4,5) and then $Mn(NO)_3CO$ (5). Reactions of the latter species with electron donors were also reported. A thesis described an infrared study on $Mn(CO)_4NO$ as a vapor and in solution. A molecular geometry having C_{3v} symmetry was inferred (152). The compound $Mn[PPh(OMe)_2]_2(NO)_2Cl$ has been prepared from mer-trans-$Mn(CO)_3[PPh(OMe)_2]_2Cl$ and NO. Its structure is based upon a trigonal bipyramidal configuration at the metal with phosphorus ligands occupying trans-axial positions (35). The structure of $(C_5H_5Mn)_3(NO)_4$ was cited earlier in this review (148) (Structure XXV). Also mentioned were the reactions of $[MeC_5H_4Mn(NO)(CO)L]^+$ and $[C_5H_5Mn(NO)(CO)L]^+$ (L = CO, PPh_3) with primary amines to give carboxamido complexes (75).

There have appeared two papers on organometallic rhenium nitrosyl complexes. The reaction of $Re(CO)_2(PPh_3)_3H$ and Diazald, a nitrosyl donating reagent, in benzene has given $Re(CO)_2(PPh_3)_2NO$ (153). This is the first reference to a derivative of $Re(CO)_4NO$, a compound which has been sought unsuccessfully, for some time. This species was reactive, presumably owing to the tendency of rhenium to achieve a higher coordination number. With halogens, a reaction to give $[Re(CO)_2(PPh_3)_2(NO)X]X_3$ occurred. An elaborate chemistry was also developed with benzoyl azide (76). In benzene $Re(CO)(PPh_3)_2(NO)(PhCONCO)$ was formed; its structure is shown below (Structure XXVI).



XXVI

In ethanol a carboxamido complex, $Re(CO)(PPh_3)_2(NO)(NCO)CONH\overset{O}{\overset{\|}{C}}OEt$ was formed. This isomerized in $CHCl_3$ to give $Re(CO)(PPh_3)_2(NO)(NCO)NHCOOEt$ and protonated reversibly giving $[Re(CO)(PPh_3)_2(NO)(NCO)NH_2COOEt]^+$. The latter, with chloride ion (using HCl as the acid) reacted with amide displacement to give $Re(CO)(PPh_3)_2(NO)(NCO)Cl$.

X <u>STRUCTURAL STUDIES</u>

The following compounds have been the subject of structural studies by single crystal X-ray diffraction methods (or other methods as noted): $Re_2(CO)_{10}$ (electron diffraction) (6), $Mn_2(CO)_8[Me_2AsC{=}C(AsMe_2)CF_2CF_2]$ (10), $Mn_2(CO)_6(AsMe_2)_3(C_4F_5)$ (11), $Ph_4As[Mn_3(CO)_{14}]$ (18), $Mn(NO)_2(PPh_3)_2Cl$ (35), <u>fac</u>-$Mn(CO)_3(CNPh)_2Br$ (40), $\overline{Mn(CO)_3(PPh_3)C_6H_4CH_2S}Me$ (58), $Mn(CO)_5C_5Cl_5$ (61), $Re(CO)_3(PPh_3)(C{\equiv}CC_6F_5)_2Cu(PPh_3)$ (63), $C_5H_5Re(CO)_2(Me)Br$ (67), $Re_4(CO)_{16}(CS_3)_2$ (71), $Me_4N[Mn(CO)_4(COPh)(COMe)]$ (73), Cd(diglyme)$[Mn(CO)_5]_2$ (81), Cd(bipy)$[Mn(CO)_5]_2$, and Cd(o-phen)$[Mn(CO)_5]_2$ (82), 8-$Et_3N(CH_2)_4O$-6-$Mn(CO)_3B_9H_{12}$ (86), 6-$Mn(CO)_3B_8H_{13}$ (87), $C_5H_5BPhMn(CO)_3$ (90), $M_2Mn_4(CO)_{18}$ (M = Ga, In) (92), $[(CO)_5Mn]_2SnHSnH[Mn(CO)_5]_2$ (98), $Re_2(CO)_8(GeMe_2OCMe)_2$ (99), <u>trans</u>-$(Bu_3Sn)_2Os(CO)_4$ (105), $Mn(CO)_4CH_2N(CH_2)_2$ (108). $Mn_2(CO)_8(N_2Ph)_2$ (109), $Mn_2(CO)_7[NC(CF_3)_2]_2$ (110), $Re(S_2CNEt_2)_3(CO)$ (120), $[Re(CO)_3S_2PEt_2]_2$ (123), $(C_5H_5Mn)_3(NO)_4$ (148).

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