MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1980

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I. INTRODUCTION

The Manganese, Technetium, and Rhenium Annual Surveys articles for 1978 and 1979 have appeared (ref. 1,2). This article continues the general pattern for organization of subject matter that was established in earlier Annual Survey articles by this author. One small change has been introduced, which places general spectroscopic studies and theoretical studies in a separate section. This was done to eliminate the need to have multiple references to this type of study in several subsections of this review.

Two references of a general nature are noted here. A review article on compounds containing rhenium-rhenium bonds should be of some interest (ref. 3). Structures of 59 compounds are referenced; many of these are

Previous review see J. Organometal. Chem., 211(1981) 177–213.

organometallic species. The twentieth volume of Inorganic Synthesis provides synthetic procedures for 11 manganese and rhenium compounds (ref. 4). These compounds are listed in the Table below.

TABLE. Compounds Included in Inorganic Syntheses, Vol. 20 (ref. 4)

Compound	Authors	Pages
$Mn(CO)_3(\eta\text{-}C_5H_4X)$, X = Cl, Br, I	K. J. Reimer and A. Shaver	192-193
$Mn(CO)_5(\eta^1\text{-}C_5Cl_4X)$, X = Cl, Br	K. J. Reimer and A. Shaver	193-194
$Mn(CO)_3(\eta\text{-}C_5Cl_4X)$, X = Cl, Br	K. J. Reimer and A. Shaver	194-195
$Re(CO)_5COMe$, $Re(CO)_4(COMe)_2H$, and $Re(CO)_4(COMe)(CMeNH_2)$	K. P. Darst, C. M. Lukehart, L. Y. Warfield, and J. V. Zeile	204-206
$Mn_3(B_2H_6)(H)(CO)_{10}$	H. D. Kaesz, S. W. Kirtley	240

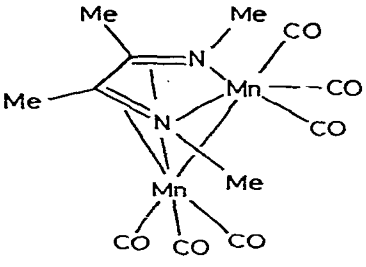
Approximately 170 articles are cited in this year's Annual Survey of Group VIIB Organometallic Compounds. This is slightly smaller than the number of articles abstracted in previous years.

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

There has been little study accorded to the anionic complexes $[Mn(CO)_{5-n}L_n]^-$. The structure of $Ph_4P[Mn(CO)_4(PPh_3)]$ was determined by x-ray diffraction methods (ref. 5). The metal atom in the anion has a distorted trigonal bipyramidal geometry with the phosphine in an axial position. The axial and equatorial metal-carbon bond lengths are equal, D(Mn-C) ave = 1.796(5)Å, unlike the structure of $[Mn(CO)_5]^-$ in which the axial Mn-C bond lengths are slightly longer than the equatorial M-C bond lengths.

The pentacarbonylmanganate(-1) ion has been used as a reducing agent in two instances. Addition of this anion to $Ru_3(CO)_{12}$ produced the anionic ruthenium carbide cluster, $[Ru_6C(CO)_{16}]^{2-}$, (ref. 6). The reaction of $[Mn(CO)_5]^-$ with a mixture of $CrCl_2$ and PEt_3 in toluene (1 hr, room temperature) gave fac-$Cr(CO)_3(PEt_3)_3$ (ref. 7). This paper made the point that direct reactions between $Cr(CO)_6$ and PEt_3 gave only cis- and trans- isomers of $Cr(CO)_4(PEt_3)_2$, and failed to produce a trisubstituted product.

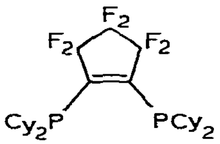
The identity of a product obtained in a reaction between $[Mn(CO)_4(CNMe)]^-$ and MeI has been discovered through a crystallographic study; the structure of this dinuclear species is shown below, (I) (ref. 8).



(I)

Booth, Haszeldine and Reynolds have reported on studies of reactions of $P(OCH_2)_3CEt(=L)$ with $Mn_2(CO)_{10}$ (ref. 9) and $Mn(CO)_5H$ (ref. 10). The products of the first reaction, which depend on reactant stoichiometry and reaction conditions, include various $Mn_2(CO)_{10-n}L_n$ compounds (n = 1,2,3,4). Each member of this series appears to exist as a mixture of geometric isomers which were not separated. It was also determined that the compound $Mn_2(CO)_6L_4$ degrades in refluxing xylene (45 min.) to give a mixture of mer,trans-$Mn(CO)_3(L)_2H$ and mer-$Mn(CO)_2(L)_3H$ in low yield. Reactions of $Re_2(CO)_{10}$ with several phosphites and phosphines have also been carried out by other workers. Diaxially substituted species, $Re_2(CO)_8L_2$, were obtained for L = $P(OPh)_3$, $P(Otol^o)_3$, $P(OC_6H_4Cl)_3$, $Ptol_3^p$ and PCy_3. With $P(OPh)_3$ the occurrence of a second product, $Re_2(CO)_7L_3$, was noted. In the phosphine reactions, the hydride complexes, mer,trans-$Re(CO)_3(L)_2H$, were also products and in the reaction with $P(Otol^o)_3$ an ortho-metallated species was obtained along with the substituted dimetallic carbonyl (ref. 11).

Several manganese carbonyl complexes of bidentate phosphine and arsine ligands were obtained from direct reactions of $Mn_2(CO)_{10}$ and the ligand (ref. 12). These compounds had the general formula $Mn_2(CO)_8(L\text{^}L)$ where L^L =



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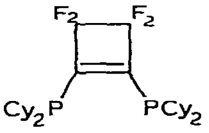

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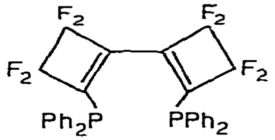

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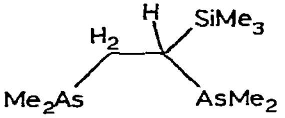


A $Mn_2(CO)_6(L\text{^}L)_2$ derivative was also obtained from the first ligand listed and several of the $Mn_2(CO)_8(L\text{^}L)$ complexes were reacted with halogens, this resulting in metal-metal bond cleavage.

The reaction between $Mn(CO)_5H$ and $AsPh_3$ in the presence of oxygen produced $Mn_2(CO)_9(AsPh_3)$. A mixture of axial and equatorial isomers was present (ref. 13). Formaldehyde was the second product. Sulfur dioxide was found to insert into the manganese-manganese bond in $Mn_2(CO)_{10}$ under photolytic conditions, giving $(OC)_5MnSO_2Mn(CO)_5$ (ref. 14).

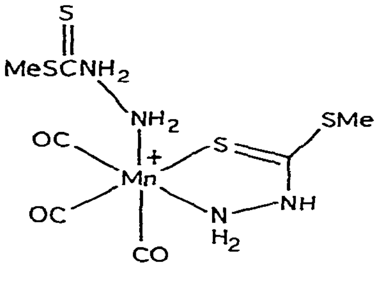
Further study on the reactive radical species derived from $Mn_2(CO)_{10}$ by metal bond cleavage has appeared. Thermal and photolytic reactions of $Mn_2(CO)_{10}$ (and $Mn(CO)_5SnMe_3$ and $Me_2Sn[Mn(CO)_5]_2$) in the presence of ortho-quinones and α-diketones produced the radical species, $Mn(CO)_4$(o-quinone) and $Mn(CO)_4$(diketone); these species were detected by esr spectroscopy. An adduct of $Mn(CO)_5\cdot$ and 2,6-di-tert-butyl-para-quinone was also identified (ref. 15). Generation of $Mn(CO)_5\cdot$ radicals in the presence of nitro compounds and PBu_3 led to the formation of the stable $Mn(CO)_{4-n}(PBu_3)_n\ O_2NR$ radical species, also studied by esr (ref. 16).

The use of $Re_2(CO)_{10}$ as a catalyst in the oxidation of cyclohexanol or various ketones to carboxylic acids was reported in a communication and a full paper (ref. 17, 18). The compound $MnCo(CO)_9$, and also mixtures of $Mn_2(CO)_{10}$ and $Co_2(CO)_8$, were reported as catalysts for the conversion of synthesis gas to various hydrocarbons (ref. 19).

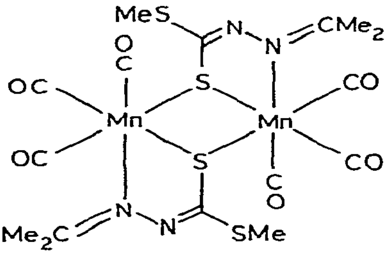
Various further study on the kinetics of reactions of the dinuclear metal carbonyls has been completed and published. Kinetic studies on reactions between iodine and $Mn_2(CO)_{10-n}L_n$ species ($n = 1$, $L = PPh_3$; $n = 2$, several phosphines and $P(OMe)_3$), $MnRe(CO)_8(PPh_3)_2$ and $Re_2(CO)_8(PPh_3)_2$ in decalin indicated a rapid initial formation of a complex between the organometallic reagent and from one to four equivalents of iodine. This is followed by electron transfer and metal-metal bond cleavage (ref. 20). Kinetic arguments were also presented for the existence of some dimeric long-lived species, in addition to the monomeric $Mn(CO)_5$ radical species, in flash photolysis experiments on $Mn_2(CO)_{10}$. Several possible structures were suggested for the dinuclear intermediate (ref. 21). Kinetic data on reactions between $MnRe(CO)_{10}$ and PPh_3, PBu_3, and $P(OPh)_3$ were presented in a third paper (ref. 22). These reactions, run in THF at room temperature, produce $(OC)_5MnRe(CO)_4L$ along with some $L(OC)_4MnRe(CO)_4L$ and a small amount of $L(OC)_4MnRe(CO)_5$ which forms at an early stage of the reaction. Interestingly, no dimanganese or dirhenium products are found. It is suggested that the reaction occurs with initial dissociation of CO from manganese. The coordinately unsaturated intermediate formed can be trapped by L, or rearrange with CO transfer from rhenium to manganese, giving a new intermediate which will add the ligand at the rhenium site. Significantly, metal-metal bond cleavage was not implicated in these experiments.

A cationic aquo complexes of manganese (I), $[Mn(CO)_5(H_2O)]ClO_4$, was formed when $Mn(CO)_5OClO_3$ and H_2O were allowed to react in CH_2Cl_2 (30 min, room temperature under N_2). This cationic species can be isolated as a tetraphenylborate salt; alternately water was displaced by ligands such as acetonitrile (ref. 23). The analogous aquo-rhenium complex has been described in another paper along with complexes of several other oxygen ligands (ref. 24). These complexes, $[Re(CO)_5L]AsF_6$ (L = H_2O, MeOH, acetone), were formed from $[Re(CO)_5(SO_2)]AsF_6$ upon addition of the designated ligands.

Syntheses of other cationic complexes have been reported in two other papers. The reaction of $[Re(CO)_3O_2PR_2]_n$ compounds (R = Me, Ph) with ethylenediamine (en) at 110° produced $[Re(CO)_3(en)_2]O_2PR_2$, compounds in which one of the diamine ligands is bidentate and the second is monodentate. A crystal structure study on the compound with R = Ph confirmed this structure (ref. 25). The compounds $[M(CO)_3(H_2NNHCS_2Me)_2]Br$ and $M(CO)_3(H_2NNHCS_2Me)Br$ (M = Mn, Re) were prepared from $M(CO)_5Br$ and H_2NNHCS_2Me, and an x-ray diffraction study carried out on the manganese compound (ref. 26). The structure is sketched below (II).



(II)



(III)

Additional different products were obtained from reactions of these reagents under basic conditions. These include $Mn(CO)_5N(NH_2)CS_2Me$, $[Re(CO)_3N(NH_2)CS_2Me]_2$ and $[Mn(CO)_3(Me_2CNNCS_2Me)]_2$. A crystal structure determination on this third compound identified its structure as (III).

Reactions between $[M(CO)_3(MeCN)_3]PF_6$ (M = Mn, Re) and $(Bu_4N)_4Nb_2W_4(CO)_{19}$ have given ionic compounds of the stoichiometry $(Bu_4N)_3[(OC)_3MNb_2W_4O_{19}]$. The oxy-anion cluster is linked via three oxygen to fac- positions on the metal (ref. 27). This work was undertaken because of the possible analogy between these compounds and complexes of the $M(CO)_3$ group with the surface of a metal oxide.

An extensive study on mechanisms of substitution reactions of $[Mn(CO)_5(MeCN)]BF_4$ has appeared in a paper (ref. 28) and in a thesis (ref. 29).

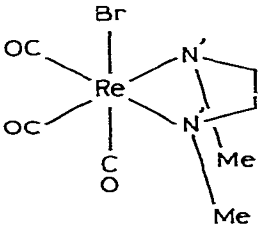
The reaction with pyridine in nitromethane produced $[Mn(CO)_3(py)_3]BF_4$ and CO_2, it was suggested that this reaction occurred with initial attack of $[CH_2NO_2]^-$ at CO. In MeCN, the reaction between pyridine and $[Mn(CO)_5(MeCN)]BF_4$ may involve nucleophilic attack at a carbonyl group by the nitrogen base which preceded MeCN loss.

A thesis (ref. 30) described study on various isocyanide containing cationic complexes; most of this work was described in publications a year ago (See 1979 Annual Surveys, ref. 2).

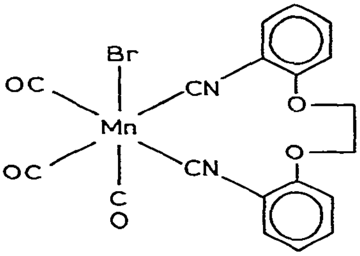
III. METAL CARBONYL HALIDES AND DERIVATIVES ($M(CO)_{5-n}L_nX$, others)

Rest and coworkers (ref. 31) have carried out photolyses of the $Mn(CO)_5X$ compounds (X = Cl, Br, I) at 12°K in a glassy matrix. The product species, $Mn(CO)_4X$, have been studied using infrared spectroscopy; a trigonal bipyramidal geometry with the halide ligand in an equatorial position was suggested.

Data on the preparation and characterization of various substituted manganese carbonyl halides appear in several papers. Abel and coworkers (ref. 32) have reported on the compounds $Re(CO)_3(N\frown N)X$ (X = Cl, Br, I; $N\frown N = MeNHCH_2CH_2NHMe$). A crystal structure study on the bromide complex identified the stereochemistry for this species, shown below (IV):



(IV)

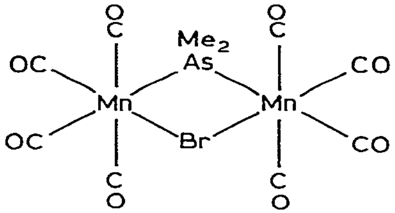


(V)

The complexes $Mn(CO)_3(DiCN)Br$ and $Mn(CO)_3(DiNC)Br$ were reported in another paper, (ref. 33). These compounds were prepared from reactions between these ligands and $Mn(CO)_5Br$. The DiNC ligand is identified in the drawing above (V); the DiCN has cyano rather than isocyano- donor groups. Additional references to the complexes $M(CO)_3(H_2NNHCS_2Me)Br$(M=Mn,Re) (ref. 26), $Mn(CO)_4(mqp)Br$ (mqp = 8-methylquinolylmethyldi-tert-butylphosphine) (ref. 34) and <u>fac</u>-$Mn(CO)_3[(NC_4H_4)Mn(CO)_3]_2I$ (ref. 35) are noted. The latter compound was obtained as an unexpected produce in a reaction between pyrrolylmanganese tricarbonyl and $Fe(C_5H_5)(CO)_2I$, and was the subject of a crystal structure determination.

The reaction between $Ni(COD)_2$ and $Mn(CO)_5Cl$ in tetrahydrofuran yielded the compound $[Mn(CO)_3(THF)Cl]_2$, and a crystallographic study was carried out on this dinuclear chloride bridged species. When $Ni(COD)_2$ and $Mn(CO)_3(P(OMe)_3)_2Cl$ were reacted, the product was $[Mn(CO)_4P(OMe)_3]_2$ (ref. 36, 37).

Preparations of a series of rhenium complexes $Re(CO)_3L_2Br$ (L = ten amino acids) from $Re(CO)_5Br$ have been described in a Russian journal (ref. 38). These complexes reacted with pyridine, giving $Re(CO)_3py_2Br$. Formation of the compounds $Mn(CO)_4(Me_2AsCl)Br$ and $Mn(CO)_3(Me_2AsCl)_2Br$ was noted (ref. 39). The former compound reacted with $[Mn(CO)_5]^-$ to give $(CO)_5MnAsMe_2Mn(CO)_4Br$ which loses CO upon heating to produce the interesting dinuclear species (VI).



(VI)

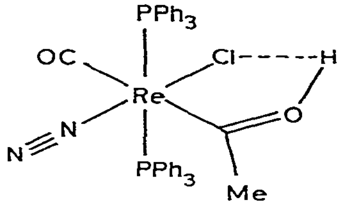
In another paper (ref. 40) the hydrolysis of $Mn(CO)_4(Me_2AsCl)Br$ was described; this reaction produced $Mn(CO)_4(Me_2AsOH)Br$.

The reaction between $Re(CO)_5R$ compounds (R = Me, Ph) and two equivalents of $AlEtCl_2$ yields a system which is an active catalyst for olefin metathesis. If this mixture was allowed to come in contact with moisture a white solid formed. This solid has been identified as a carbene complex, cis-$Re(CO)_4(CROH)Cl$. A similar product, cis-$Re(CO)_4(CEtOH)Cl$ was formed from the reaction of $Re(CO)_5Cl$ and $AlEtCl_2$ in methanol (ref. 41).

Correspondence concerning product stereochemistry in substitution reactions of octahedral metal carbonyl compounds is cited (ref. 42). The point was made that the stereochemistry of a substitution product may usually be that predicted based on the site of CO loss, even if the 16e intermediate is fluxional. Examples from $M(CO)_5Br$ (M = Mn, Re) substitution chemistry were provided.

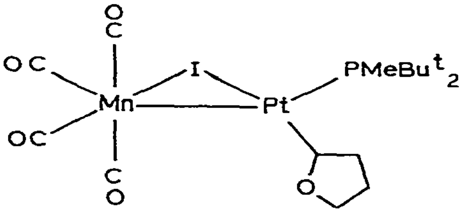
Reactions between $Mn(CO)_5X$ compounds (X = Cl, Br) and either TlF or AgF in CH_2Cl_2 gave the tetrameric species, $[Mn_4(CO)_{12}F_x(OH)_{4-x}]$. In the thallium fluoride reaction, compounds having x = 1 and 2 predominated, while with silver fluoride the primary product species have x = 2 and 3. An x-ray crystallographic study on a compound which was mainly $[Mn_4(CO)_{12}F(OH)_3]$ was carried out (OH and F disorder) (ref. 43). While on the general topic of tetrameric complexes it is appropriate to mention another reference which describes the preparation of the species $[Re(CO)_3X]_4$ (X = Br, Cl). These compounds were prepared by thermal decomposition of $\mathrm{Re(CO)_3(Ph_2S)_2X}$; interestingly, these tetramers are not available from the thermal decomposition of $\mathrm{Re(CO)_5X}$ (ref. 44).

The carbene complex, $\mathrm{Mn(CO)_4(\overline{COCH_2CH_2CH_2})I}$, reacted with $\mathrm{Pt(C_2H_4)_2(PMeBu^t_2)_2}$ to give two organometallic products. The first is the known platinum trimer, $\mathrm{Pt_3(\mu\text{-}CO)_3L_3}$; the second is a species containing platinum and manganese, characterized by x-ray crystallography as (VII), (ref. 45).



(VIII)

Other reaction chemistry concerned with metal carbonyl halides include the reaction of $\mathrm{Mn(CO)_3(bipy)Cl}$ and $\mathrm{Na[O_2SOMe]}$ in methanol (17 hr) to produce the alkylsulfito complex $\mathrm{Mn(CO)_3(bipy)OSO_2Me}$ (ref. 46) and the pyrolysis of $\mathrm{Mn(CO)_2(P(OEt)_3)_3Br}$ at 155° to give $\mathrm{Mn_6(CO)_9(OP(OEt)_2)_9}$, a compound characterized crystallographically (ref. 47). Two different types of manganese atoms are found in this structure. Three $\mathrm{Mn^{2+}}$ ions are coordinated in approximately a trigonal bipyramid by five oxygen atoms of the phosphonate ligands; the remaining are $\mathrm{Mn^{+}}$ ions coordinated by three carbonyls and three phosphorus atoms. There are no metal-metal interactions. The interaction between $\mathrm{Re(CO)_2(PPh_3)_2(N_2)Cl}$ and methyllithium followed by protonation gives (VIII) (ref. 48). In contrast the methyllithium reaction with $\mathrm{Re(CO)_3(PPh_3)_2Cl}$ produces $\mathrm{Re(CO)_3(PPh_3)_2Me}$. Reaction of methyllithium with $\mathrm{Re(CO)_5I}$ gives $\underline{\text{fac}}$-$\mathrm{[Re(CO)_3(COMe)_2I]^{2-}}$ which adds two protons to produce $\mathrm{Re(CO)_3(CMeOH)_2I}$. This compound decomposes in solution, forming $\mathrm{CH_3CHO}$ and $\mathrm{Re_2(CO)_8I_2}$ (ref. 49). A crystal structure determination was carried out on $\mathrm{Re_2(CO)_8I_2}$.



(VII)

A charge transfer exciplex is formed between $\mathrm{Re(CO)_3(4,7\text{-}Ph_2phen)Cl}$ and $\mathrm{NPhMe_2}$ (ref. 50).

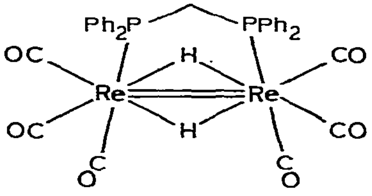
IV. METAL CARBONYL HYDRIDES ($M(CO)_{5-n}L_nH$, polynuclear hydrides)

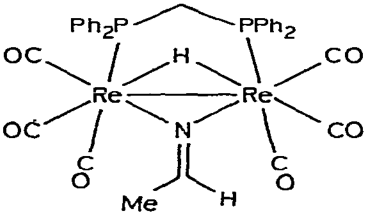
A personal account of H. D. Kaesz' research on metal hydrides appeared in the centenary edition (Vol. 200) of J. Organomet. Chem. (ref. 51). A large fraction of this work was on hydride complexes of the elements of this group, including $Tc(CO)_5H$, the various trimeric and tetrameric rhenium species and other compounds.

Reactions between $Mn(CO)_5H$ and $P(OCH_2)_3CEt$ (= L) under different conditions gave the products cis-$Mn(CO)_4(L)H$, mer,trans-$Mn(CO)_3(L)_2H$, mer,cis-$Mn(CO)_2(L)_3H$. The third compound can be converted to trans -$Mn(CO)_2(L)_3H$ by heating the solid over 100°C. The monosubstituted species was also prepared by protonation of $[Mn(CO)_4(L)]^-$, and the disubstituted compound was prepared by a $LiAlH_4$-$Mn(CO)_3(L)_2X$ reaction (ref. 10). Preparation of the di- and tri- substituted species from $Mn_2(CO)_6L_4$ (xylene, reflux) was reported separately (ref. 9). Reactions of $Re_2(CO)_{10}$ with $Ptol_3{}^P$ and PCy_3 gave, as one type of product, the mer,trans-disubstituted hydride complexes (ref. 11).

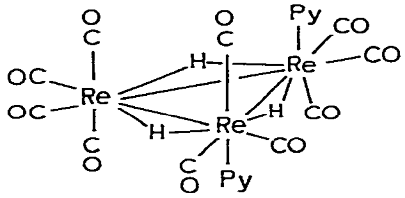
Photolysis of $Re(dppe)_2H_3$ causes hydrogen evolution and produces a reactive intermediate complex. This intermediate adds CO, C_2H_4, and N_2 (= L) to form the complexes $Re(dppe)_2(L)H$. Addition of CO_2 leads to the formate complex $Re(dppe)_2(O_2CH)$, (ref. 52). The reaction between $Mn(CO)_5H$ and $AsPh_3$ in the presence of O_2 gives cis- and trans-$Mn_2(CO)_9AsPh_3$ (ref. 13). Mixing $Fe(CNBu^t)_5$ and $Mn(CO)_5H$ produces a salt $[Fe(CNBu^t)_5H]Mn(CO)_5$, indicating the higher basicity of the iron compound relative to $[Mn(CO)_5]^-$ (ref. 53).

An UV PES study on various metal clusters with bridging hydride units has been published (ref. 54), and included among compounds studied is $Re_3(CO)_{12}H_3$. Reaction of $Re_3(CO)_{12}H_3$ with dppm in refluxing octane has yielded the new compound $Re_2(CO)_6(dppm)H_2$. This species was found to add one equivalent of various ligands to form $Re_2(CO)_6(L)(dppm)H_2$ (L = $P(OMe)_3$, MeCN, RNC). The structures of $Re_2(CO)_6(dppm)H_2$ (IX) and $Re_2(CO)_6(dppm)(NCHMe)H$ (X) were determined by x-ray diffraction studies. Pertinent information on these species include the metal-metal bond lengths, 2.893(2)Å in (IX) and 3.035(3)Å in (X) (ref. 55).


(IX)

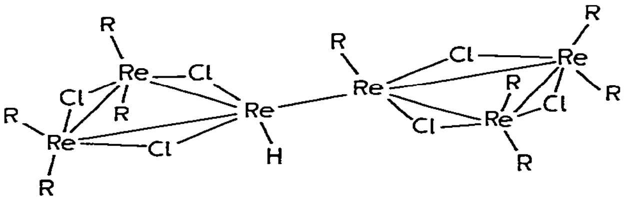

(X)

Ciani *et al.* (ref. 56) reported that the reaction between $(Et_4N)_2$-$[Re_3(CO)_{10}H_3]$ and I_2 in ethanol gave two products, $(Et_4N)[Re_3(CO)_{10}(I)H_3]$ and $(Et_4N)_2[Re_3(CO)_{10}(I)H_2]$. However, the same reaction in pyridine gave $Re_3(CO)_{10}(py)_2H_3$, a derivative of $Re_3(CO)_{12}H_3$. A crystal structure study revealed the geometry of this compound to be (XI); an average rhenium-rhenium bond length of 3.292Å was determined.



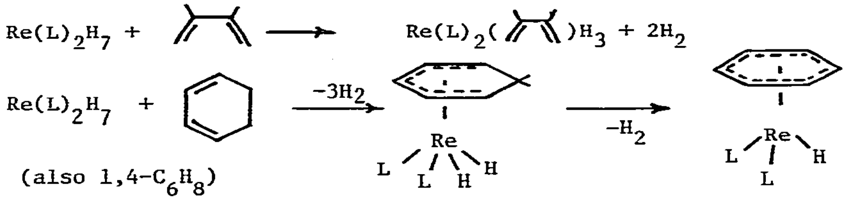
(XI)

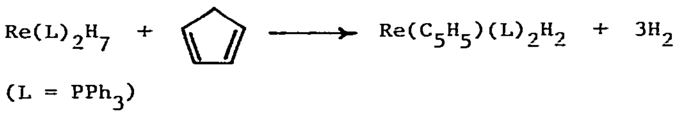
The unusual compound $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_9H$ was formed from $Re_3(\mu\text{-}Cl)_3$-$(CH_2SiMe_3)_6$ and H_2. Its structure, determined through a crystallographic study, is (XII) (ref. 57).



(XII, $R = CH_2SiMe_3$)

Two communications have been published describing hydride complexes formed from $Re(L)_2H_7$ and various hydrocarbons. The first to appear (ref. 58) described reactions of $Re(PPh_3)_2H_7$ and several dienes. Reaction chemistry is summarized by the equations below:





ıe cyclopentadienyl-rhenium compound in the third equation (and also a $PPhEt_2$ ıalogue) was also formed from cyclopentane in 3,3-dimethyl-1-butene (ref. 59). ıese cyclopentadienyl compounds were shown to add a proton, forming ${}^{\backslash}e(C_5H_5)(L)_2H_3]^+$.

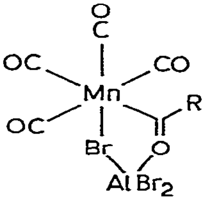
Various reactions of $Re(C_5H_5)_2H$ have been described in the literature :ef. 60). Lithiation using butyllithium gave $Re(C_5H_5)_2Li$ which was used as a :ecursor to a variety of compounds $Re(C_5H_5)_2R$ (R = D, Me, $CH_2CH{=}CH_2$, COPh). reaction with excess methyl iodide produced $[Re(C_5H_5)_2Me_2]^+$ while the ɜaction with allyl bromide yielded $[Re(C_5H_5)_2(\eta^2\text{-}CH_2{=}CHCH_3)]^+$. With CO_2 ${}^{\backslash}e(C_5H_5)_2(CO)]^+$ was formed. The reaction of the protonated complex, ${}^{\backslash}e(C_5H_5)_2H_2]^+$, with diazomethane and a nitrile (RCN) was found to form ${}^{\backslash}e(C_5H_5)_2CRNHMe]^+$.

Various references to other cyclopentadienyl-metal hydride species were ›stracted in 1980. Reduction of $Mn(C_5H_4Me)(NO)(PPh_3)I$ using $Na[AlH_2(OCH_2CH_2OMe)_2]$ ıve $Mn(C_5H_4Me)(NO)(PPh_3)H$ (ref. 61). Reduction of $[Re(C_5H_5)(CO)_2CPh]^+$ using ɩEt_2H (-30°, 3 hr) led to formation of $Re(C_5H_5)(CO)_2(H)CH_2Ph$; the structure : this product was determined in an x-ray diffraction study (ref. 62). :otonation of the metal-metal bond $Re_2(C_5H_5)_2(CO)_5$ gave $[Re_2(C_5H_5)_2(CO)_5(\mu\text{-}H)]^+$:cording to work in a thesis (ref. 63). A very extensive study (ref. 64) ı cyclopentadienylrhenium nitrosyl carbonyl systems included the decarbonyl- :ion reaction of $Re(C_5H_5)(NO)(CO)CHO$.

. METAL COMPLEXES WITH CARBON GROUPS AS LIGANDS ($M(CO)_{5-n}L_nR$, $M(CO)_{5-n}L_nCOR$, ${}^{\backslash}_n$, Complexes with Carbene and Carbyne Ligands)

The number of papers abstracted in this subsection is large, and the ɩversity of interests seen here is substantial. The general topics of ɜtal-alkyl and acyl compounds and carbene, carbyne, and alkylidene complexes ›pear to be among those few areas under most active current investigation.

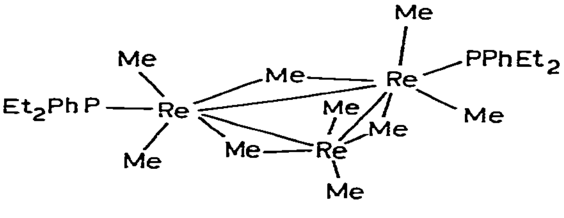
Two papers (ref. 65, 66) and a thesis (ref. 67) address Lewis acid ıtalysis of reactions involving carbonyl insertion into a metal-alkyl bond. ıriver and coworkers (ref. 65) showed that a reaction of $Mn(CO)_5R$ compounds ${}^{\backslash}$ = Me, CH_2Ph) with $AlBr_3$ occurred to give compounds (XIII), characterized , a crystallographic study (for R = Me). Further reaction with CO at low :essure (<1.0 atm) yielded $Mn(CO)_5COR$. The $AlBr_3$ appears to serve three ınctions: 1) it stabilizes the acyl group through coordination to the



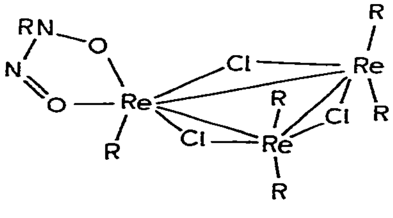
(XIII, R = Me, CH$_2$Ph)

carbonyl oxygen; 2) it acts (through a bromine atom) as a ligand; and 3) it enhances the rate of methyl migration by a substantial measure. Similarly the rate of migration of methyl to an adjacent carbonyl group (CO insertion) is enhanced by an alumina surface (ref. 66); a related mechanism is presumed.

Five papers have appeared from Wilkinson's group on various types of alkyl-rhenium and manganese compounds. Improved synthetic procedures for $ReOMe_4$, $ReMe_6$ and Li_2ReMe_8 (and other compounds) were provided in one reference (ref. 68). The synthesis of MnR_2 compounds (R = 1-adamantylmethyl) is noted (ref. 69). The compound $Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4$ was prepared from $ReCl_4{\cdot}2THF$ and Me_3SiCH_2MgCl; its structure, ascertained by a crystallographic study, contains tetrahedrally substituted metal atoms, and a planar Re_2C_2 framework with a rhenium-rhenium bond length of 2.557(1)Å, somewhat long but compatible with the predicted metal-metal double bond (ref. 70). Another paper includes structural data on $Re_3Me_9(PPhEt_2)_2$ (XIV) and $Re_3(\mu\text{-}Cl_3)(CH_2SiMe_3)_5\text{-}(ONCH_2SiMe_3NO)$ (XV). This latter compound contains the N-(trimethylsilylmethyl)-N-nitrosohydroxyaminato ligand and is formed in a reaction of $Re_3Cl_3(CH_2SiMe_3)_6$ and nitric oxide (ref. 71). The final reference in this area, to the compound $Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_9H$, was cited earlier (ref. 57).



(XIV)



(XV, R = CH$_2$SiMe$_3$)

It has been found that $M(CO)_5Ph$ compounds (M = Mn, Re) are formed by photolysis of $M_2(CO)_{10}$ and $HgPh_2$; vis:

$$HgPh_2 + 2M_2(CO)_{10} \xrightarrow{h\nu} 2M(CO)_5Ph + Hg[M(CO)_5]_2$$

Under other conditions (xylene, 144°) an ortho-metallated product, $Mn(CO)_4C_6H_4COPh$, forms instead. This and other compounds were also prepared using $Mn(CO)_5Me$ and PhCOPh. A crystallographic study was carried out on fac-$Re(CO)_3(PPh_3)C_6H_4COPh$ (ref. 72). Mention of two other ortho-metallated products (from $Re_2(CO)_{10}$ and $Ptol_3^{o}$ (ref. 11), and from $Mn(CO)_5Me$ and mqp (ref. 34)) is also made.

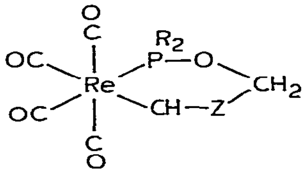
McHugh and Rest (ref. 73) have reported on the photolysis $Mn(CO)_5Me$ and $Mn(CO)_5COMe$ in a matrix at 12°K. The 16e products are believed to have equatorial substituted trigonal bipyramidal geometry.

It has been found that there is multiple deuterium incorporation in the organic product (toluene) when CF_3COOD is used to cleave the carbon-metal bond in $Mn(CO)_5CH_2Ph$ (and also in other benzyl-metal compounds). For example the percentages of d_0, d_1, d_2, and d_3 toluene obtained from $Mn(CO)_5CH_2Ph$ (25°, no solvent 180 min) are, respectively, 3%, 33%, 46%, and 18% (ref. 74).

The reaction of $Re(CO)_4(PPh_3)Br$ and methyllithium occurs to give a lithio salt initially (ref. 75). This species, $Li[Re(CO)_3(PPh_3)(COMe)Br]$, slowly eliminates LiBr, and the methyl group migrates to the metal to give the eventual product, $Re(CO)_4(PPh_3)Me$. Earlier in this review, mention was made of the reaction of $Re(CO)_5I$ and methyllithium, giving Li_2[fac-$Re(CO)_3(COMe)_2I$], (ref. 49), the reaction of methyllithium and $Re(CO)_2(N_2)(PPh_3)_2Cl$ (followed by protonation) giving $Re(CO)(N_2)(PPh_3)_2(COMe)Cl)H$, and the reaction of this organolithium compound with $Re(CO)_3(PPh_3)_2Cl$ forming $Re(CO)_3(PPh_3)_2Me$ (ref. 48).

The compound $Mn(CO)_5CH_2CO_2Bu^t$ was prepared, in anticipation of unusual behavior associated with the substituted alkyl group (ref. 76). A thesis contains work on dithionite bridged species, products derived from SO_2 addition into manganese and rhenium carbonyl compounds and other metal carbonyl compounds (ref. 77).

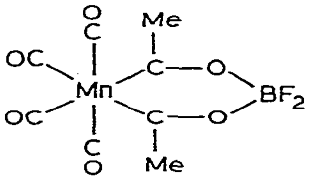
Lindner et al. (ref. 78-80) have described a series of related reactions of the anion $[Re(CO)_4OPR_2]_2^{2-}$ (R = Me, Ph) with organic species XCH_2ZCH_2X ($X = OSO_2CF_3$; Z = CH_2, C_2H_4, CMe_2). The products are the cyclic compounds shown below (XVI). Insertion reactions of these compounds with SO_2 and CO are described as is the crystal structure of $Re(CO)_4PPh_2OCH_2CMe_2CH_2$ (ref. 78,79). Analogous manganese chemistry was published by these authors separately, and the structure of $Mn(CO)_4PPh_2OCH_2CH_2CH_2$ determined (ref. 81).



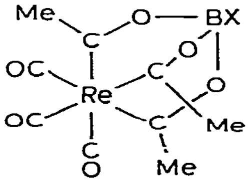
(<u>XVI</u>, R = Me, Ph, Z = CH_2, C_2H_4, CMe_2)

Gladysz <u>et</u> <u>al</u>. (ref. 82) have reported that a reaction occurs between $Mn(CO)_5SiMe_3$ and several cyclic ether compounds, ($\overline{OCH_2CH_2}$, $\overline{O\text{-}CH_2CH_2CH_2}$, THF) under CO pressure to give the products $Mn(CO)_5CO(CH_2)_nOSiMe_3$ (n = 2,3,4). Treatment of the compound with n = 3 with $[S(NEt_2)_3]SiMe_3F_2$ gives a lactone, $\overline{OCH_2CH_2CH_2CO}$.

Lukehart and coworkers continue to extend the chemistry of metallodiketonate species. The crystal structure of $Cu[Re(CO)_4(COMe)_2]_2$ was reported (ref. 83). Reactions of $Re(CO)_4(COMe)(COR)H$ (R = Me, Pr^i, CH_2Ph) with haloboranes yielded compounds having the general formulas $Re(CO)_4(COMe)(COR)BXY$ (X,Y = Ph, halogen). A manganese analogue (XVII) was prepared from $Li[Mn(CO)_4(COMe)_2]$ and BF_3 (ref. 84). The related compounds $Re(CO)_3(COMe)_3BX$ (XVIII) were obtained in reactions of $Li_2[Re(CO)_3(COMe)_3]$ and BX_3 (X = F, Cl, Br); reaction of the chloro species with $AgBF_4$ in an alcohol gave the compounds with X = OR



(<u>XVII</u>)



(<u>XVIII</u>, X = F, Cl, Br, OR)

(ref. 85). Additional information on this topic is reported in a thesis (ref. 86), which also includes report of a crystal structure study on

$Re(CO)_3(COMe)_3BCl$. A final paper in this area concerns the ^{13}C NMR spectra of a series of compounds $Re(CO)_4(COR)(CMeNHR')$ (R = Me, R' = Ph, Me, H; and R = Pr^i, R' = H) (ref. 87).

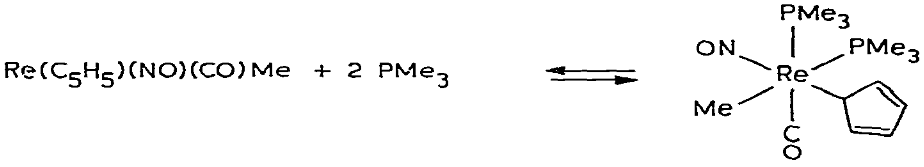
Reported in two papers by Casey and Scheck (ref. 88, 89) and in Scheck's thesis (ref. 90) are studies on reactions of $[M(CO)_4(COMe)(COPh)]^-$ (M = Mn, Re). Thermal decomposition of $NMe_4[Mn(CO)_4(COMe)(COPh)]$ with ^{13}C labels in either the (COMe) or (COPh) groups gave , with PPh_3 added, $NMe_4[Mn(CO)_4PPh_3]$ and PhCOMe. The extent of retention of the ^{13}CO label in the eliminated product, acetophenone, showed that methyl migration is preferred kinetically to phenyl migration; however the reductive elimination step must occur primarily from the intermediate $NMe_4[Mn(CO)_4(COMe)Ph]$. Further experiments on $NMe_4[Re(CO)_4(COMe)(COPh)]$ concur with this; it was determined that methyl migration is about 28 times more rapid than phenyl migration.

Liquid ammonia solvolyses of $[Mn(C_5H_4R)(NO)(CO)_2]^+$ (R = Me, Ph), $[Re(C_5H_5)(NO)(CO)_2]^+$, and several $[Mn(C_5H_5)(NO)(L)(CO)]^+$ compounds (L = PPh_3, $PPhEt_2$, $AsPh_3$, CNMe, CNEt) gave carboxamido- complexes of these metals (ref. 91). Reactions of several carboxamido-metal complexes with CS_2 and/or COS have been carried out; produced are mono- and dithiocarbamate complexes. Examples include $M(CO)_4(S_2CNHMe)$ (M = Mn, Re), formed from cis-$M(CO)_4(MeNH_2)(CONHMe)$ and CS_2, and $Re(C_5H_5)(NO)(CO)(S_2CNHMe)$, formed from $Re(C_5H_5)(NO)(CO)(CONHMe)$ (ref. 92).

The reduction of $[Re(C_5H_5)(NO)(CO)_2]PF_6$ using $K[B(OPr^i)_3H]$ has produced the metal formyl $Re(C_5H_5)(NO)(CO)CHO$, an orange unstable oil which decomposes slowly to $Re(C_5H_5)(NO)(CO)H$. A further reaction with $BH_3{\cdot}THF$ caused reduction of the formyl group to a methyl group. Reaction with $LiBHEt_3$ produced the novel complex $Re(C_5H_5)(NO)(CO)CH_2O\overset{O}{\overset{\|}{C}}Re(NO)(CO)(C_5H_5)$ as a mixture of diastereomers. Methanol solvolysis cleaved this species into $Re(C_5H_5)(NO)(CO)CH_2OMe$ and $Re(C_5H_5)(NO)(CO)CO_2Me$. The former compound reacted with aqueous acid to give $Re(C_5H_5)(NO)(CO)CH_2OH$, which can also be produced directly from $[Re(C_5H_5)(NO)(CO)_2]PF_6$ using $LiAlEt_2H_2$ (ref. 64).

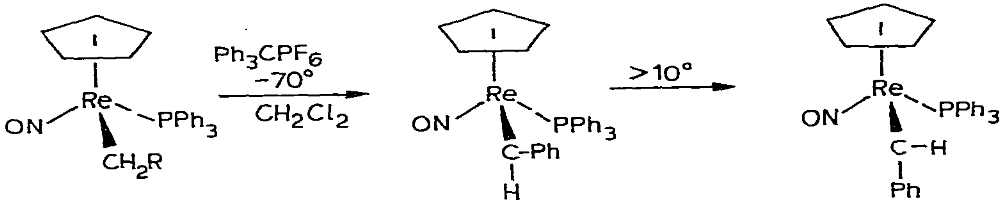
The syntheses and reactions of various other metal-formyl complexes ($[M_2(CO)_9CHO]^-$, $Re(C_5H_5)(NO)(CO)CHO$) were described in a thesis (ref. 93).

An unprecedented result was obtained by Casey and Jones (ref. 94), when $Re(C_5H_5)(NO)(COMe$ was allowed to react with PMe_3. Here, the cyclopentadienyl group was converted from η^5 to η^1 coordination. The structure of the product, $Re(NO)(CO)(PMe_3)_2(Me)(\eta^1\text{-}C_5H_5)$, (XIX) was determined by crystallography.

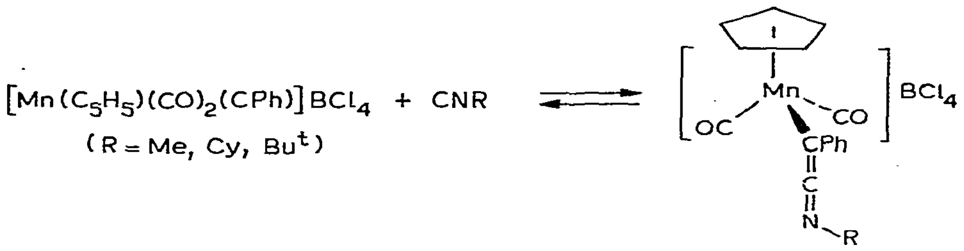


(XIX)

Gladysz et al. (ref. 95, 96) have prepared the rhenium carbene complex, $[Re(C_5H_5)(NO)(PPh_3)CHR]PF_6$ (R = Ph, Me, Et) by hydride abstraction from $Re(C_5H_5)(NO)(PPh_3)CH_2R$. At −70° ($CD_2Cl_2$, using Ph_3CPF_6) only one alkylidene isomer was formed. At $T > 10°$ this product isomerized to the thermodynamically more stable isomer. The presumed geometry of the kinetically and thermodynamically preferred isomers was suggested based on steric criteria; see the reaction sequence below.

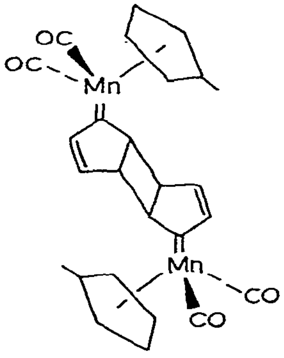


Various other carbene complexes have been prepared, primarily with cyclopentadienyl- manganese and -rhenium carbonyls. Fischer et al. (ref. 97) reacted $Re(C_5H_5)(CO)_3$ with $LiSiPh_3$; following addition to the reaction system of $MeOSO_2F$ these workers obtained $Re(C_5H_5)(CO)_2C(SiPh_3)OMe$. This compound reacts with BF_3 to produce a carbyne complex $[Re(C_5H_5)(CO)CSiPh_3]BF_4$ which subsequently was converted to $Re(C_5H_5)(CO)_2CRSiPh_3$ (R = Me, H) by reaction with methyllithium or $Bu^n_4NBH_4$. A crystallographic study defined the structure of $Re(C_5H_5)(CO)_2CHSiPh_3$. In another paper, (ref. 62), Fischer and Frank described the preparation of $Re(C_5H_5)(CO)_2CHPh$ by reduction of $[Re(C_5H_5)(CO)_2CPh]^+$ using $AlEt_2H$ at −78° (15 min). Reaction at −30° for 3 hr produced $Re(C_5H_5)(CO)_2(H)CH_2Ph$. A third paper from this research group (ref. 98) described the reactions between $[Mn(C_5H_5)(CO)_2CPh]BCl_4$ with several alkyl isocyanides, (CNR; R = Me, Cy, Bu^t) which gave dark green, thermally labile 1:1 adducts, vis.



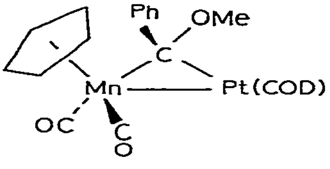
Formation of $Mn(C_5H_5)(CO)_2CPhCN$ (plus Bu^tCl and $SbCl_5$) from $[Mn(C_5H_5)(CO)_2CPh]SbCl_6$ and Bu^tNC was also noted.

Other reported carbene complexes with these metals include the series of derivatives $Mn(C_5H_4Me)(CO)(L)(CSCR{=}CRS)$ ($L = P(OMe)_3$, PMe_3, $PPhMe_2$; $R = COOMe$) (ref. 99), and $[Mn(C_5H_4Me)(CO)_2]_2C_{10}H_8$, (XX), (ref. 100). The former compounds were formed from reactions between $Mn(C_5H_4Me(CO)(L)(CS_2)$ and $RC{\equiv}CR$, the latter in the reaction of $Mn(C_5H_4Me)(CO)_2(THF)$ and $C_5H_4N_2$. Crystal structure studies have been carried out on $Mn(C_5H_5)(CO)(P(OMe)_3)(CSCR{=}CRS)$ and on (XX) to identify these compounds. Formation of several other carbene complexes, $Re(CO)_4(CROH)Cl$, ($R = Me$, Ph) was noted earlier in this review (ref. 41).

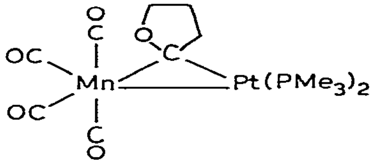


(XX)

The reaction of $Mn(CO)_4(COCH_2CH_2CH_2)I$ and $Pt(C_2H_4)_2PMeBu_2^t$ was mentioned earlier (ref. 45). The reaction of $Mn(C_5H_5)(CO)_2CPhOMe$ with $Pt(COD)_2$ was found to give (XXI), a compound having a bridging methylene group (ref. 101). A crystal structure study was carried out on this compound. Reactions of this carbene complex with $Pt(C_2H_4)_3$, $Pd(dpa)_2$ and $Ni(COD)_2$ were carried out, and products isolated following subsequent addition of two equivalents of PMe_3. These products had structures similar to (XXI) but with $M(PMe_3)_2$ ($M = Ni$, Pd, Pt) replacing the Pt(COD) unit. The related complex (XXII) was formed from $Mn_2(CO)_9(\overline{COCH_2CH_2CH_2})$ and $Pt(C_2H_4)_3$ followed by PMe_3 addition. Two isomers of this compound were subjected to crystallographic studies; the structural differences between the two isomers turned out to be small, however.



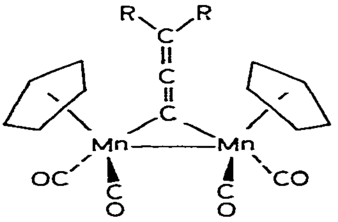
(XXI)



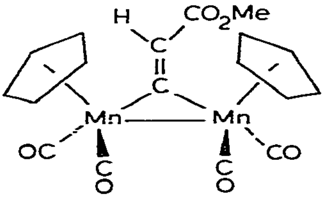
(XXII)

The carbene complex $Mn(C_5H_4Me)(CO)_2(CPhNH_2)$ was found to react with $MeC{\equiv}CNEt_2$ in benzene solvent (20-80°). The product obtained had the formula $Mn(C_5H_4Me)(CO)_2(CPhN{=}CEtNEt_2)$. A similar reaction for $Mn_2(CO)_9(CPhNH_2)$ was reported (ref. 102).

The formation of complexes $Mn(C_5H_5)(CO)_2C{=}C{=}CR_2$ ($R = Bu^t$, Cy, CH_2Ph, Ph) was accomplished by a two step reaction sequence. First, $Mn(C_5H_5)(CO)_2$-(η^2-$HC{\equiv}CCO_2Me$) was treated with three equivalents of RLi; then H^+ and $COCl_2$ was added (ref. 102). Heating these compounds, alone or with $Mn(C_5H_5)(CO)_2(OEt_2)$ (ref. 104), gave the dinuclear species (XXXIII). If $Mn(C_5H_5)(CO)_2(\eta^2$-$HC{\equiv}CCO_2Me)$ was allowed to react with one equivalent of Bu^tLi and then either HCl or $MeOSO_2F$ added, $Mn(C_5H_5)(CO)_2$ $C{=}CRCO_2Me$(R = H, Me) were obtained (ref. 105). These compounds also were converted to dinuclear species (XXIV) on heating.

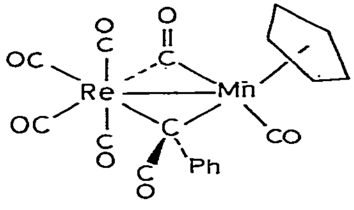


(XXIII)



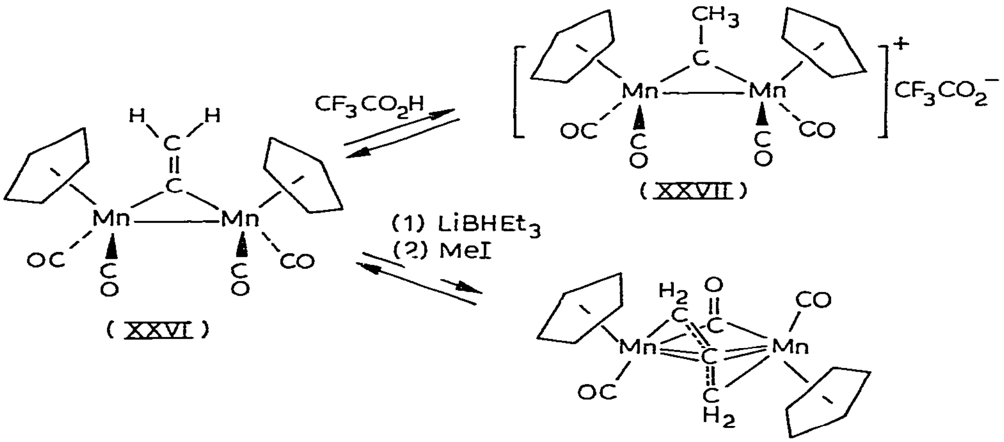
(XXIV)

The reaction of $[Mn(C_5H_5)(CO)_2CPh]BCl_4$ with $Na[Re(CO)_5]$ formed compound XXV; the structure of this unusual species was determined crystallographically (ref. 106).



(XXV)

Caulton et al. have been studying various reactions of $[Mn(C_5H_5)(CO)_2]_2$-(μ-$C=CH_2$), (XXVI), (ref. 107, 108); see also the thesis of L. N. Lewis (ref. 63). Pertinent chemical behavior is summarized below. The structure of compound (XXVIII) was determined in a crystallographic study.



(XXVI) (XXVII) (XXVIII)

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

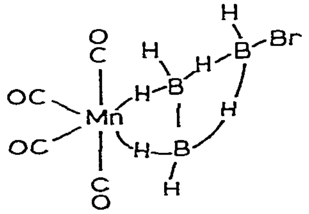
Electrochemical reductions of several manganese carbonyl derivatives of platinum were observed. Also reported was the 2-electron cathodic reduction of $Hg[Mn(CO)_5]_2$, which occurs according to the equation (ref. 109, 110):

$$Hg[Mn(CO)_5]_2 + 2e \rightarrow Hg + 2[Mn(CO)_5]^-$$

The compound $C_5H_5ZnMn(CO)_5$ was prepared in a reaction of $Zn(C_5H_5)_2$ and $Mn(CO)_5H$ (ref. 111), along with several other zinc complexes of other metals. The authors of this communication indicated that these are the first stable species with zinc-transition metal bonds.

The preparations of several different compounds having manganese-platinum σ-bonds (see (XXI) and (XXII)) were discussed earlier in this article (ref. 45, 101). A better preparative method for the compound $(C_5H_5)(CO)_2MnFe_2(CO)_6PPh$ has been given (ref. 112). The reaction of $(C_5H_5)(PMe_3)Co(\mu\text{-}CO)_2Mn(C_5H_4Me)$ with $Co(C_5H_5)(PMe_3)(CS_2)$ was reported; this gave the compound $Co_3(C_5H_5)_3(CS)(S)$ (ref. 113).

The complex $Mn_2(CO)_6(B_3H_8)(Br)$ was prepared from $Mn(CO)_3B_3H_8$ and bromine in the presence of $AlBr_3$. Its molecular structure was determined in a crystallographic study; see (XXIX), below (ref. 114, 115). The structure of $Mn(CO)_4(B_3H_7Br)$ was also determined (ref. 116). This species undergoes a fluxional process in which the hydrogen atoms bonded to boron rapidly exchange sites; for this process $\Delta G^{\ddagger} = 12.2 \pm 0.1$ Kcal. Dimanganese decacarbonyl and $Co(C_5H_5BMe)_2$ react at 160° (3 days); the product $Mn(CO)_3(\eta^6\text{-}C_5H_5BMe)_2$ was obtained. Additionally, a Friedel-Crafts reaction on this product species was reported (ref. 117). Molecular orbital calculations on π-(3)-1,2-dicarbollyl-tricarbonylmanganese were discussed in another paper (ref. 118).



(XXIX)

References to manganese- and rhenium- carbonyl derivatives containing Group IVA metalloidal elements are few in number. A reaction between $Mn(CO)_5SiMe_3$ and several cyclic ethers was mentioned earlier in this review (ref. 82). Di- and trigermane derivatives of manganese pentacarbonyl have been synthesized (ref. 119). The pentacarbonylmanganese ion was found to displace iodide ion from $2IGe_3H_7$, giving $Mn(CO)_5GeH(GeH_3)_2$, and $Mn(CO)_5GeCl(GeH_3)_2$ was formed from this compound and CCl_4. Similarly $(OC)_5MnGeH_2GeH_2Mn(CO)_5$ was prepared using $Na[Mn(CO)_5]$ and $ClGeH_2GeH_2Cl$, and $(OC)_5MnGeCl_2GeCl_2Mn(CO)_5$ was obtained from this product and CCl_4. It was also determined that sodium cleaved the germanium-manganese bond in $Mn(CO)_5GeH_2GeH_3$; after addition of methyl iodide, $Mn(CO)_5Me$, Me_2GeH_2 and $MeGeH_3$ were obtained. Preparation of the compounds $BrSn[Co(CO)_4]_2[M(CO)_5]$ (M = Mn, Re) was noted in another paper (ref. 120). Thermal and photolytic cleavage reactions of $Mn(CO)_5SnMe_3$ and $Me_2Sn[Mn(CO)_5]_2$ were carried out in the presence of α,α-diketones, which served to trap the manganese carbonyl radical fragment (ref. 15). Ground state and excited state redox chemistry of $Re(CO)_3$(o-phen)$SnPh_3$ and $Re(CO)_3$(o-phen)-$GePh_3$ was the topic of a paper published by Wrighton *et al*. (ref. 121).

VII. METAL COMPLEXES OF GROUP VA AND VIA LIGANDS

Complexes of these elements will again be considered in an order based on periodic position, starting with Group VA elements. As before, compounds in which these elements are the donor atom in simple donor-acceptor species are not included, these complexes being covered in other sections.

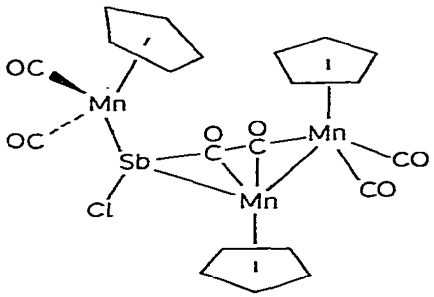
A full paper on $M_3(CO)_{12}N_2Me$ and $M_2(CO)_{10}(CH_2N_2)$ (M = Mn, Re), products obtained from $Mn(CO)_5H$ and diazomethane, has appeared (ref. 122). A communication on this work was published last year. Other papers on work communicated previously include a report on $Mn(CO)_4$(ArNCHNAr) and $Mn(CO)_4$(CONArCHNAr) (ref. 123) and a paper on $Mn_2(CO)_7(N{=}C(CF_3)_2)_2$ (ref. 124). Reactions of this latter compound with pyridine (giving $Mn_2(CO)_6(py)(N{=}C(CF_3)_2)_2$) and with several phosphines (giving the five coordinate monomeric compounds $Mn(CO)_2(L)_2$-$N{=}C(CF_3)_2$ (L = PPh_3, PPh_2Me, $PPhMe_2$)) are noted.

A communication and full paper have provided information on the structure of $[Mn(C_5H_4Me)(CO)_2(o\text{-}N_2C_6H_4CF_3)]BF_4$ (ref. 125, 126). In addition, reactions of this compound and the cyclopentadienylrhenium analogue with several anions (Cl^-, Br^-, I^-, CN^-, SCN^-) were reported; these reactions involved displacement of the aryl group, producing the dinitrogen compounds $Mn(C_5H_4Me)(CO)_2N_2$ and $Re(C_5H_5)(CO)_2(N_2)$.

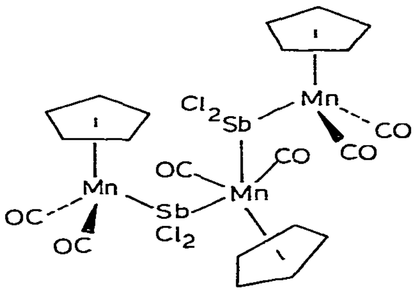
Earlier, mention was made of the characterization of $Mn_2(CO)_6(C_6H_{12}N_2)$, (I) (ref. 8) and $Re_2(CO)_6$(dppm)(NCHMe)H, (X) (ref. 55).

Vahrenkamp and coworkers have continued to expand their work on phosphido and arsenido-bridged metal complexes. Five references in this area are noted (ref. 39, 127-130). Among the more interesting compounds are $Mn_2(CO)_8(\mu\text{-}AsMe_2)(\mu\text{-}Br)$ (ref. 39), and $Mn_2(CO)_7(Cl)(\mu\text{-}AsMe_2)(\mu\text{-}As_2Me_4)$ (ref. 129). The latter species was obtained from a reaction between $K[Mn(CO)_5]$ and Me_2AsCl, and was found to have a dimeric structure with bridging Me_2As and Me_4As_2 groups, according to a crystal structure study. Another compound, the salt $[MnFe(CO)_8(\mu\text{-}AsMe_2)_2]^+[MnFe(CO)_8(Cl)(\mu\text{-}AsMe_2)]^-$ was also characterized by crystallographic techniques (ref. 130).

A modified preparation of $Mn(C_5H_5)(CO)_2Fe_2(CO)_6PPh$ was mentioned earlier (ref. 112). The preparation of $\{[Mn(C_5H_5)(CO)_2]_2BiCl\}_2$ was accomplished in a reaction between $Mn(C_5H_5)(CO)_2(THF)$ and $BiCl_3$. A crystal structure determination on this compound was carried out. Each bismuth atom is tetrahedrally coordinated, and acts as a two-electron donor to two metal groups. The bismuth atoms are linked together via chloride bridging groups (ref. 131). A similar reaction between $Mn(C_5H_5)(CO)_2(THF)$ and $SbCl_3$ produced two quite different products, also characterized by x-ray crystallography (ref. 132). These compounds have formulas $[Mn(C_5H_5)(CO)_2]_3SbCl$, (XXX), and $[Mn(C_5H_5)(CO)_2]_3$-Sb_2Cl_4, (XXXI), with structures indicated below.



(XXX)



(XXXI)

Among compounds with oxygen ligands are $Mn_4(CO)_{12}F_x(OH)_{4-x}$ (ref. 43), radical species $Mn(CO)_{4-n}(PBu_3)_nO_2NR$ (ref. 16) and $[Mn(CO)_3(O_2PR_2)]_n$ (ref. 25), all discussed earlier in this review. Additionally, the compound $[Re(CO)_3$-$(OC_6H_4N_2Ph)]_2$ should be mentioned (ref. 133). This compound was prepared by a reaction of $Re(CO)_5Br$ and o-$HOC_6H_4N_2Ph$, and was the subject of a crystallographic study.

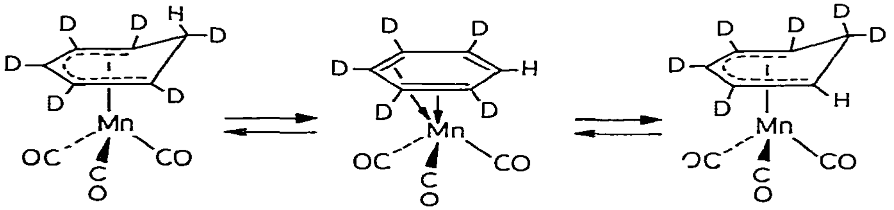
A unique complex with a bridging disulfur (S_2) ligand was prepared via the reaction of $Mn(C_5H_5)(CO)_2(THF)$ and COS, and its structure confirmed. A diselenium analogue was also reported (ref. 134). Other new sulfur-ligand complexes include $[Mn(CO)_3SCH_2CH_2PPh_2]_2$, a species believed to be dimeric via the thiolato bridging groups (ref. 135) and $Mn(CO)_4(SC{=}NRPPh_2)$ (R = Ph, Me); (ref. 136). The latter compounds were prepared from $Mn(CO)_5Cl$ and $Me_3SiNRCSPPh_2$. Mentioned earlier in this review were $[Mn(CO)_5]_2SO_2$ (ref. 14), several N-methyldithiocarbamate complexes formed in reactions of CS_2 with different carboxamido complexes (ref. 92), products derived from $M(CO)_5Br$ (M = Mn, Re) and $H_2NNHCSSMe$ (ref. 26), and the products of reactions between $Mn(C_5H_4Me)(CO)(L)(CS_2)$ ompounds and acetylenes (ref. 99).

VIII. HYDROCARBON METAL COMPLEXES ($M(C_5H_5)(CO)_3$, $M(C_6H_7)(CO)_3$, olefin, allyl complexes, others)

The molecular structure of $Mn(C_5Me_5)_2$ has been determined in an electron diffraction experiment. The average manganese-carbon distance in this low spin complex is 2.130(4)Å (ref. 137). Dissociation energies of bis(cyclopentadienyl)metal complexes were compared; these values can be related to the metal-ring distances (ref. 138). Chemistry initiated with $Re(C_5H_5)_2H$ was presented in a paper mentioned earlier in this review (ref. 60), and a thesis on properties of $Re(C_5H_5)_2R$ complexes can be identified (ref. 139).

One reference to allyl-manganese and -rhenium compounds has appeared (ref. 140). Mono- and disubstitution of carbonyl groups occurred in reactions with phosphines; products isolated included $Mn(\eta^3-C_3H_5)(CO)_3(L)$ (L = PPh_3, PCy_3, PBu_3, PPh_2Me, $AsPh_3$), $Mn(\eta^3-C_3H_5)(CO)_2(L)_2$ (L = PPh_2Me, $P(OMe)_3$, $P(OEt)_3$, and L_2 = dppm) and $Re(\eta^3-C_3H_5)(CO)_{4-n}(PPh_3)_n$ (n = 1,2). A crystal structure determination was performed on $Mn(\eta^3-C_3H_5)(CO)_2(P(OMe)_3)_2$.

The cyclohexadienyl-manganese tricarbonyl complexes $Mn(exo-1-RC_6H_6)(CO)_3$ (R = H, CN, $CH(CO_2Et)_2$) were examined using ^{55}Mn nqr (ref. 141). Brookhart and coworkers (ref. 142) have studied the process by which $Mn(exo-1-HC_6D_6)(CO)_3$ permits randomization of hydrogen using NMR. The process is believed to occur via a η^4-arene metal hydride, vis.



The barrier to this process $\Delta G^{\ddagger}$, was determined to be 34 Kcal.

Earlier in this review two references were provided to olefin, cyclopentadienyl, and cyclohexadienylrhenium compounds, (ref. 58, 59), and to the olefin complex $Re(C_2H_4)(dppe)_2H$ (ref. 52).

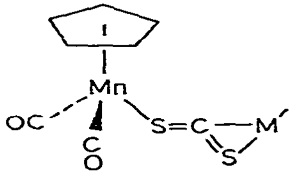
References to two papers on manganese-heterocyclic ligand complexes are included from work in 1980. The THF ligand in $Mn(C_5H_4R)(CO)_2(THF)$ can be displaced by phosphabenzenes which act as two electron donors. Photolyses of these species provided η^6- complexes of phosphabenzenes such as $Mn(C_5H_4R)(C_5H_5P)$ (ref. 143). The stibolyl complex-, $Mn(2,5-Me_2C_4H_2Sb)(CO)_3$ was prepared from $Li[2,5-Me_2C_4H_2Sb]$ and $Mn(CO)_5Br$ (ref. 144). A pyrrolyl complex was referred to at an earlier time in this review (ref. 35).

All of the remaining references (many) within this subsection are on derivatives of $M(C_5H_5)(CO)_3$ or $[M(C_5H_5)(NO)(CO)_2]^+$. Many have been cited previously in this review.

A 2:1 adduct forms between the Wittig reagent, Me_3PCH_2, and $Mn(C_5H_4Me)(CO)_3$; this has been identified as an ionic species, $PMe_4[Mn(C_5H_4Me)(CO)_2COCHPMe_3]$ (ref. 145). This compound has been carried through a reaction sequence involving two consecutive methylations (using $MeOSO_2F$) followed by deprotonation using Me_3PCH_2, to give the final product, $Mn(C_5H_4Me)(CO)_2(C(OMe)CMe{=}PMe_3)$ (ref. 146). The product of a reaction between $Mn(C_5H_5)(CO)_2(NCtol)$ and $PhMe_2PCH_2$ had the formula $Mn(C_5H_5)(CO)_2(NH{=}CtolCH{=}PPhMe_2)$, formally derived from its precursor by C-H addition across the C≡N bond of the coordinated nitrile (ref. 147). In contrast reactions of $PPh_{3-n}Me_nCHR$ with $Mn(C_5H_4Me)(CO)_2(THF)$ gave zwitterionic products $\bar{M}n(C_5H_4Me)(CO)_2CHR\overset{+}{P}Ph_{3-n}Me_n$, displacement of THF by the phosphine methylene reagent occurring (ref. 148).

Reactions of $Mn(C_5H_5)(CO)_2(\eta^2\text{-}HC{\equiv}CCO_2Me)$ with alkyllithium reagents received comment earlier in this review (ref. 103-105); mononuclear and dinuclear complexes were obtained in those studied. It was also determined, by other workers (ref. 149), that this precursor reacted with PPh_3; the product obtained was also zwitterionic, vis., $\bar{M}n(C_5H_5)(CO)_2(C\overset{+}{P}Ph_3{=}CHCO_2Me)$.

A number of new complexes, $Mn(C_5H_5)(CO)_2(L)$, can be identified. Among these are complexes in which L is the pendant sulfur atom of $\eta^2\text{-}CS_2$ ligand to another metal; see structure (XXXII) below.



(XXXII)

Metal groups represented by M' in this structure include $Rh(C_5H_5)(PMe_3)$- (ref. 150), Co(triphos)- (ref. 151), and several iron complexes $Fe(CO)_2(L)_2$-, ($L = P(OMe)_3$, $PPhMe_2$, PMe_3) (ref. 152). A crystal structure study was carried out on $Mn(C_5H_5)(CO)_2(\mu\text{-}CS_2)Fe(CO)_2(PPhMe_2)_2$. All of these compounds were prepared from $Mn(C_5H_5)(CO)_2(THF)$. In addition reference is made to compounds of $P_4(SiMe_2)_3$ which can coordinate to manganese through a phosphorus atom lone pair (ref. 153), to complexes of di- and tri-azophospholes (ref. 154), and to $(CO)_5Cr(\eta\text{-}C_6H_{11}N_2)Mn(CO)_2(C_5H_4Me)$ (ref. 155). References to $[Mn(C_5H_4Me)(CO)_2]_2C_{10}H_8$ (ref. 100) to antimony and bismuth ligand complexes (ref. 131, 132), and to disulfur and diselenium complexes (ref. 134) were given earlier.

A crystal structure determination was carried out on $[Mn(C_5H_5)(CO)_2Me_2PS]_2$. This compound contains $Mn(C_5H_5)(CO)_2$ groups bridged by the ligand $Me_2PSSPMe_2$ (ref. 156). Also the structure of $[Mn(C_5H_5)(CO)_2PMe_2]_2O$ was identified via a crystallographic study (ref. 157). This complex was obtained by hydrolysis (Et_3N, H_2O) of $Mn(C_5H_5)(CO)_2(PMe_2Cl)$.

Acetylacetone has been shown to react with $Mn(C_5H_5)(CO)_2(PhAsCl_2)$, forming a complex of the ligand $Ph\overline{AsOCMe{=}CHC({=}CH_2)O}$ (ref. 158); a similar reaction of the phosphorus analogue may be recalled. Other studies on reactions at coordinated ligands in cyclopentadienyl manganese carbonyl systems may be recalled from earlier in this review. These include the addition of acetylenes to the CS_2 ligand in $Mn(C_5H_4Me)(CO)(L)(\eta^2\text{-}CS_2)$ complexes (ref. 99) and to the carbene ligand in $Mn(C_5H_4Me)(CO)_2(CPhNH_2)$ (ref. 102). Reactions at the carbyne ligand to give carbene complexes are also noted here (ref. 62, 97, 98), as are those studies involving bridging carbene, alkylidene and carbyne ligands (ref. 63, 106-108).

Two references to the diazonium complexes $[M(C_5H_4R)(CO)_2N_2C_4H_4CF_3]BF_4$ (M = Mn, R = Me; M = Re, R = H) were included earlier (ref. 125, 126). Cyclopentadienylmetal nitrosyl complexes were extensively studied in several groups, and this work also received substantial discussion in earlier sections of this review; (See ref. 61, 64, 91-96).

Several papers are noted on chemistry at the cyclopentadienyl group in $M(C_5H_5)(CO)_3$ (M = Mn, Re) species. Formation of $Ti(C_5H_5)_2(C_5H_4Mn(CO)_3)_2$ from $Ti(C_5H_5)_2Cl_2$ and $Mn(C_5H_4Li)(CO)_3$ was reported and a structural study carried out on this species (ref. 159). Resolution of optical isomers of $Mn(C_5H_4\overset{*}{C}HMeNH_2)(CO)$ was accomplished using (+)-d-tartaric acid and the absolute configuration of a similar compound determined by crystallography (ref. 160). The formyl species, $M(C_5H_4CHO)(CO)_3$ (M = Mn, Re), were prepared in a reaction sequence involving metallation followed by reaction with $HCONMe_2$ and hydrolysis (ref. 161).

Redox potentials of the various nitrogen ligand complexes $Mn(C_5H_5)(CO)_2(L)$ ($L = N_2$, N_2H_4, NH_3) and $[Mn(C_5H_5)(CO)_2]_2(N_2H_2)$ were measured using cyclic voltammetry (ref. 162). Mass spectrometry data on $M(C_5H_4R)(CO)_3$ compounds, (M = Mn, Re), has been reported in four papers (ref. 163-166); additionally, mass spectral studies on several $Mn(C_5H_4Me)(CO)_2(L)$ and $Mn(C_5H_4Me)(CO)(CS)(L)$ compounds (ref. 167) and on $Mn(C_5H_4Me)(NO)(CS)I$ (ref. 168) have been published.

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

There are few papers on compounds containing nitrosyl ligands, and still fewer papers on isocyanide complexes. The single citation in the latter area is to a thesis (ref. 30). A number of papers on cyclopentadienyl metal nitrosyl species were identified in earlier sections, where the emphasis was primarily directed to other ligand groups (especially formyl and carbene ligand groups) (ref. 61, 64, 91-96, 168). In addition two papers on $Mn(NO)_3L$ complexes have appeared. One paper described the preparation of the compounds with L = PBu^t_3, $PBu^t_2AMe_3$, $PBu^t(AMe_3)_2$, and $P(AMe_3)_3$ (A = Si, Ge, Sn) (ref. 169). The second paper reported the structure of $Mn(NO)_3(PPh_3)$, (ref. 170).

X. GENERAL SPECTROSCOPIC STUDIES AND THEORETICAL STUDIES

This section is intended to identify those papers primarily dealing with theoretical or spectroscopic studies of a wide range of compounds. It will not generally include studies on single compounds which are more easily included in earlier sections.

Mass spectrometry on compounds of various silyl and stannyl derivatives of manganese and rhenium pentacarbonyls provided information on the metal-group IV element bond energies. For the manganese compounds there was a decrease in these bond energies in the series $SiMe_3 \geq SnMe_2Cl > SnPh_3 \simeq SnMe_3$. The bond energies for the Re-Si and Re-Sn bonds in $Re(CO)_5SiMe_3$ and $Re(CO)_5SnPh_3$ were substantially greater (ref. 171). Negative ion mass spectra at 70 ev are reported for $Mn(CO)_5X$, $Re(CO)_5X$, $Re_2(CO)_8X_2$ (X = Cl, Br, I) and for $Mn_2(CO)_8Br_2$ (ref. 172). Mass spectral data on cyclopentadienyl-manganese compounds were mentioned earlier (ref. 163-168).

Kump and Todd (ref. 173) have obtained ^{17}O NMR data on a large number of manganese carbonyl compounds, including $Mn_2(CO)_{10-n}(L)_n$ (n = 0, 1, 2; L = PPh_3), $Mn(CO)_5X$ (X = Cl, Br, I, Me) $Mn_2(CO)_8Br_2$, $Mn(CO)_4(PPh_3)Br$, and $Mn(CO)_3(PPhMe_2)_2Br$.

The manganese $2p_{3/2}$, carbon 1s and oxygen 1s binding energies in various $Mn(CO)_5X$ species (X = $Mn(CO)_5$, Me, H, MeCO, Cl, Br, I, CF_3, CF_3CO, Me_3Sn, Cl_3Si, F_3Si) were found to be linearly related to inductive parameters associated with the X group, such as σ_I values or Pauling electronegativity values (ref. 174).

An extended version of the CNDO method was used to study the mechanism of CO insertion in the carbon-R bond in $Mn(CO)_5R$ (R = H, Me, Et, CHO, CH_2CF_3). These calculations were used to rationalize differences in rates as a function of R (ref. 175).

XI. STRUCTURAL STUDIES

Compounds whose structures have been determined by x-ray crystallography (or by other methods) are listed: $\mathrm{PPN[Mn(CO)_4(PPh_3)]}$ (ref. 5); $\mathrm{Mn_2(CO)_6(C_6H_{12}N_2)}$ (I), (ref. 8); $\mathrm{[Re(CO)_3(en)_2]O_2PPh_2}$ (ref. 25); $\mathrm{[Mn(CO)_3(H_2NNHCS_2Me)_2]Br}$ (II), and $\mathrm{[Mn(CO)_3(Me_2CNNCS_2Me)]_2}$ (III), (ref. 26); $\mathrm{Re(CO)_3(MeNHCH_2CH_2NHMe)Br}$, (IV), (ref. 32); $\mathrm{Mn(CO)_3[(NC_4H_4)Mn(CO)_3]_2I}$ (ref. 35); $\mathrm{[Mn(CO)_3(THF)Cl]_2}$, (ref. 36); $\mathrm{Mn4(CO)_{12}F_x(OH)_{4-x}}$ with $x = 1$ the predominant species (ref. 43); $\mathrm{MnPtI(C_4H_6O)(CO)_4(PMeBu_2{}^t)_2}$ (VII) (ref. 45); $\mathrm{Mn_6(CO)_9(OP(OEt)_2)_9}$ (ref. 47); $\mathrm{Re_2(CO)_8I_2}$ (ref. 49); $\mathrm{Re_2(CO)_6(dppm)H_2}$ (IX) and $\mathrm{Re_2(CO)_6(dppm)(NCHMe)H}$ (X), (ref. 55); $\mathrm{Re_3(CO)_{10}(py)_2H_3}$ (XI), (ref. 56); $\mathrm{Re_6(\mu\text{-}Cl)_6(CH_2SiMe_3)_9H}$ (XII), (ref. 57); $\mathrm{Re(C_5H_5)(CO)_2(H)CH_2Ph}$, (ref. 62); $\mathrm{Mn(CO)_4(COMe)(AlBr_3)}$, (XIII) (ref. 65); $\mathrm{Re_2(\mu\text{-}CSiMe_3)_2(CH_2SiMe_3)_4}$ (ref. 70); $\mathrm{Re_3Me_9(PPhEt_2)_2}$, (XIV), and $\mathrm{Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_5(ONCH_2SiMe_3NO)}$, (XV), (ref. 71); $\overline{\mathrm{Re(CO)_3(PPh_3)C_6H_4C}}\mathrm{OPh}$ (ref. 72); $\overline{\mathrm{Re(CO)_4(Ph_2POCH_2CMe_2C}}\mathrm{H_2)}$, (ref. 78, 79); $\overline{\mathrm{Mn(CO)_4(PPh_2OCH_2CH_2C}}\mathrm{H_2)}$, (ref. 81); $\mathrm{Cu[Re(CO)_4(COMe)_2]_2}$, (ref. 83); $\mathrm{Re(CO)_3(COMe)_3BCl}$, (ref. 86); $\mathrm{Re(NO)(CO)(PMe_3)_2(Me)(\eta^1\text{-}C_5H_5)}$ (ref. 94); $\mathrm{Re(C_5H_5)(CO)_2(CHSiPh_3)}$, (ref. 97); $\mathrm{Mn(C_5H_5)(CO)(P(OMe)_3)(\overline{CSCR{=}CRS})}$, (R = COOMe), (ref. 99); $\mathrm{[Mn(C_5H_5)(CO)_2]_2C_{10}H_8}$, (XX), (ref. 100); $\mathrm{(C_5H_5)(CO)_2\text{-}Mn(\mu\text{-}CPhOMe)Pt(COD)}$ (XXI), and $\mathrm{(CO)_4Mn(\mu\text{-}\overline{COCH_2CH_2C}H_2)Pt(PMe_3)_2}$ (XXII), 2 isomers (ref. 101); $\mathrm{(CO)_4Re(\mu\text{-}CPhCO)Mn(CO)_2(C_5H_5)}$, (XXV), (ref. 106); $\mathrm{Mn_2(C_5H_5)_2(CO)_3(\mu\text{-}C_3H_4)}$ (XXVIII), (ref. 107, 108); $\mathrm{Mn_2(CO)_6(B_3H_8)(Br)}$, (XXIX) (ref. 114, 115); $\mathrm{Mn(CO)4(B_3H_7Br)}$, (ref. 116); $\mathrm{[Mn(C_5H_4Me)(CO)_2\text{-}(o\text{-}N_2C_6H_4CF_3)]BF_4}$ (ref. 125, 126); $\mathrm{Mn_2(CO)_7(Cl)(\mu\text{-}AsMe_2)(\mu\text{-}As_2Me_4)}$; (ref. 129); $\mathrm{[FeMn(CO)_8(AsMe_2)_2]^+[FeMn(CO)_8(Cl)(\mu\text{-}AsMe_2)]^-}$ (ref. 130); $\mathrm{\{[Mn(C_5H_5)(CO)_2]_2BiCl\}_2}$, (ref. 131); $\mathrm{[Mn(C_5H_5)(CO)_2]_3SbCl}$, (XXX), and $\mathrm{[Mn(C_5H_5)(CO)_2]_3Sb_2Cl_4}$ (XXXI), (ref. 132); $\mathrm{[Re(CO)_3(OC_6H_4N_2Ph)]_2}$, (ref. 133); $\mathrm{[Mn(C_5H_5)(CO)_2]_2S_2}$, (ref. 134); $\mathrm{Mn(C_5Me_5)_2}$, electron diffraction,(ref. 137); $\mathrm{Mn(\eta^3\text{-}C_3H_5)(CO)_2(P(OMe)_3)_2}$ (ref. 140); $\mathrm{Mn(C_5H_5)(CO)_2(\mu\text{-}CS_2)Fe(CO)_2(PPhMe_2)_2}$ (ref. 152); $\mathrm{[Mn(C_5H_5)(CO)_2\text{-}Me_2PS]_2}$, (ref. 156); $\mathrm{[Mn(C_5H_5)(CO)_2PMe_2]_2O}$ (ref. 157); $\mathrm{Ti(C_5H_5)_2(C_5H_4Mn(CO)_3)_2}$ (ref. 159); $\mathrm{(+)\text{-}R\text{-}Mn(C_5H_4CHMeNHCOMe)(CO)_3}$, (ref. 160); and $\mathrm{Mn(NO)3(PPh_3)}$ (ref. 170).

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