MANGANESE, TECHNETIUM, AND RHENIUM

ANNUAL SURVEY COVERING THE YEAR 1976

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CONTENTS

Manganese, technetium and rhenium; Annual Survey covering the year 1975 see J. Organometal. Chem., 126 (1977) 383-430.

I. INTRODUCTION

In last year's ANNUAL SURVEYS article (1) comments were offered on the remarkable number of papers published in 1975. There were almost 200 papers, up by ~30% from previous years. This review again abstracted a large number of papers, 190, so the last year's level of output seems to be holding constant.

It may be noted, in passing, that the large majority of primary papers abstracted here 126/182 (Diss. Abst. omitted from this tabulation) were from only four journals: the ACS journals Inorg. Chem. and J. Am. Chem. Soc., the Chemical Society (London) journal J. Chem. Soc. Dalton Trans., and this journal. Of these four this journal, J. Organometal. Chem., was very much predominant, with the number of papers abstracted exceeding the sum of papers abstracted from the other three. More than a third of the references cited in this review were from this journal. This fact is both impressive and significant, since these figures certainly must reflect a broader perspective encompassing all of transition metal organometallic chemistry. It may also be observed that the articles in this journal are of consistent high quality, a credit to referees and editors and a tribute to the reputation of this journal among organometallic chemists.

This ANNUAL SURVEY article continues to use the outline followed in previous years based on compound type.

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

Darensbourg et al. (2) have studied ion pairing in the compounds $Na[Mn(CO)_4L]$ ($L = PMe_2Ph$, PPh_3, $P(OPh)_3$, CO) in several solvents using infrared and conductivity measurements. Infrared data suggested that in typical solvents (THF, ethyl ether) there was substantial ion pairing, with the cation interacting with an oxygen atom of an equatorial carbonyl. Presence of solvents such as HMPA or a crown ether which strongly interacted with the cation diminished the extent of ion pairing. The significance of this result can be seen from kinetic measurements on reactions of these carbonylmetallates with alkyl halides. When solvents were present which strongly coordinated with the cation the anion reactivity was substantially lowered from the reactivity found in the absence of such solvents; this was defined to be a consequence of a larger negative entropy of activation.

There were three papers describing synthesis and reactions of carbonylmetallat anions. A full paper described the synthesis in situ of $Na_3[Mn(CO)_4]$, a manganese (-3) complex, and its reaction with Ph_3SnCl to give cis-$[Mn(CO)_4(SnPh_3)_2]^-$ (3); this work was also reported in a communication last year. Also described were the anion $[Mn(CO)_{5-n}(CNMe)_n]^-$ (n = 1, 2, 3), prepared by sodium amalgam reduction at -15° to -20° of the halides $Mn(CO)_{5-n}(CNMe)_nBr$ (4). A series of derivatives of these anion having the formulas $Mn(CO)_{5-n}(CNMe)_nX$ ($X = SnPh_3$, $GePh_3$, CH_2CN, HgI) and $[Mn(CO)_{5-n}(CNMe)_n]_2Hg$ were also of significance. The anions $[Mn(CO)_4(PCy_3)]^-$ and

$[Re(CO)_5]^-$ were found to interact with CS_2 to give $[Mn(CO)_4(PCy_3)CS_2]^-$ and $[Re(CO)_5CS_2]^-$ which were not isolated (5). Further reaction of the manganese complex with Ph_3SnCl gave $Mn(CO)_4(PCy_3)C(=S)SSnPh_3$; with $[Re(CO)_5CS_2]^-$ a mixture of $Re(CO)_5SnPh_3$ and $Re(CO)_5C(=S)SSnPh_3$ resulted.

Ellis (6) has isolated $AsPh_4[Mn(CO)_5]$ from a metathetical reaction between cation and anion. In contrast to this, $[Re(CO)_5]^-$ and either $[AsPh_4]Cl$ or $[PPh_4]Cl$ gave $Re_2(CO)_{10}$. It was noted that a third type of behavior was seen with $[Fe(C_5H_5)(CO)_2]^-$; this involved $Fe(C_5H_5)(CO)_2Ph$ formation.

Synthesis of $Mn_2(CO)_{10}$ in a metal atom reactor was reported in a communication (7). Also, carbonylations of two manganese carbonyl species containing nitrogen ligands, $Mn(CO)_4(NH_2Bu^n)CONHBu^n$ and $\overline{Mn(CO)_4(NPhCPhNPh)}$, were found to give $Mn_2(CO)_{10}$ (8).

Studies on the mechanisms of thermal and photolytic reactions of the dimetal decacarbonyls continued to appear, and these further reinforce earlier suggestions that metal-metal bond breaking is an initial step in these processes. One paper dealt with the thermal decomposition of $Mn_2(CO)_{10}$ in decalin, in the presence and absence of oxygen (9). A second paper from the same group reported kinetic data in decalin for the reactions: $MnRe(CO)_{10} + PPh_3$, $Tc_2(CO)_{10} + PPh_3$, $MnRe(CO)_8(PPh_3)_2 + CO$, and $Tc_2(CO)_8(PPh_3)_2 + CO$ (10). Third, photochemical reactions (313-633 nm) of $(CO)_5MM(CO)_3(o\text{-phen})$ (M = Mn, Re) and of $(CO)_5ReRe(CO)_3(\text{biquinoline})$ in a CH_2Cl_2/CCl_4 mixture yielded $M(CO)_5Cl$ and $M(CO)_3(\overset{\frown}{N\,N})Cl$ (11); again a mechanism of prior metal-metal bond cleavage was presumed.

An interesting contrast to this work, however, was contained in another paper which reported studies on the kinetics of reactions of $Re_2(CO)_9(PPh_3)$ with CO and PPh_3 (12). The PPh_3 reaction kinetics were simple, and consistent with several mechanisms, including prior ligand dissociation, metal-metal bond fission or metal migration. However the former reaction with CO had entirely different activation parameters, and for this reason the authors of this paper assumed that the fission of the metal-metal bond was not the rate determining step. It might be noted that this paper also reported characterization of monomeric species $Re(CO)_4PPh_3$ and $Re(CO)_3(PPh_3)_2$ from reactions of $Re_2(CO)_8(PPh_3)_2$ with PPh_3 in decalin.

The identity of a product from photolysis of $Mn_2(CO)_{10}$ in THF was previously a subject of some controversy, but this appears now to be settled. Studies conclusively showed that the species giving an esr signal was a manganese(II) salt (13, 14). However the route to formation of this final product must be complex (14). Apparently, photolysis initially caused metal-metal bond dissociation since the radical species $Mn(CO)_5$ can be trapped with the spin trapping agent 2,4,6-tri(t-butyl)nitrosobenzene. Evidence was also given for the formation of short-lived $Mn(CO)_5O_2$ in non-polar solvents if the trapping agent was omitted.

Photolysis in basic solvents (pyridine, DMSO, DMF) of $M_2(CO)_{10}$ (M = Mn, Re) was found to give $[M(solv)_6][M(CO)_5]$ (15); these salts were also products of thermal reactions. The authors of this paper (15) believe that these products arose from heterolytic cleavage of the metal-metal bond to give, initially, $[M(CO)_5solv][M(CO)_5]$. Photolyses of $M(CO)_5X$ complexes (Mn, X = Cl, Br, I; Re, X = Cl, Br) in the same solvents gave $[M(CO)_5]^-$.

Two papers reported other reactions of dimetal decacarbonyls involving metal-metal cleavage. Electrochemical reduction of $MnRe(CO)_{10}$ in DMF led to a mixture of $[Mn(CO)_5]^-$, $[Re(CO)_5]^-$ and $HMnRe_2(CO)_{14}$ (16). Electrochemical oxidation of $Mn_2(CO)_{10}$ in CF_3COOH gave $Mn(CO)_5OCOCF_3$ (17).

An extensive study of reactions of $Mn_2(CO)_{10}$ with phosphorus and arsenic ligands may be found in J. Chem. Soc. Dalton Trans. (18). Lower temperature thermal reactions or photolysis of these reagents gave first $Mn_2(CO)_9L$ and then $Mn_2(CO)_8L_2$ complexes. Disubstituted complexes having two different geometries, with diaxial substitution ($PPhMe_2$, PPh_2Me, $PPh(OMe)_2$, PPh_2OMe) or diequatorial substitution ($AsPhMe_2$, $AsEt_3$, $AsMe_3$) may be found. At higher temperatures, the reactions of ligand and $Mn_2(CO)_{10}$ gave mer-trans $Mn(CO)_3L_2H$ (L = PPh_2Me, PPh_2Et, $PPhMe_2$, $PPh(OMe)_2$, $P(OMe)_3$); the same products formed more easily from these reactants and $NaBH_4$ in ethanol.

Heterolytic cleavage of $Mn_2(CO)_{10}$ occurred in the reaction with the tridentate phosphine ligand $CH_3C(CH_2PPh_2)_3$(triphos). The product $[Mn(CO)_3(triphos)]$-$Mn(CO)_5$ was converted to $[Mn(CO)_3(triphos)]Y$ (Y = ClO_4^-, PF_6^-, BPh_4^-) by metathetical reactions with the appropriate anions (19).

Photolysis of $Re_2(CO)_{10}$ with thiobenzophenone gave $Re_2(CO)_9(SCPh_2)$ along with an ortho-metallated product (20). Substitution of an axial carbonyl by halide ion (F^-, Cl^-, Br^-, I^-) occurred in reactions of $Mn_2(CO)_{10}$ and the potassium halide with a crown ether present (21). A thesis (22) reported reactions of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ with fluorinated chelating diarsines. Reactions of $Mn_2(CO)_{10}$ with 1,3-dienes gave a number of products including substituted $Mn_2(CO)_{10}$ species. With butadiene, products included $Mn_2(CO)_8(C_4H_6)_2$ (presumed to be a bis-olefin complex) and $Mn_2(CO)_8(C_4H_6)$; the latter product has one olefinic group coordinated equatorially to each metal (23). From 1,3- or 1,4-cyclohexadiene reactions the analogous products were found (24). A thesis reported photochemical reactions of $Mn_2(CO)_{10}$ and other metal carbonyls (25).

Caulton and Adair (26) have studied the exchange of CO in the following reaction. Their interest in this system arose from its possible use as a catalyst for reactions of CO.

$$Mn_2(CO)_5(dpm) + CO \rightleftharpoons Mn_2(CO)_6(dpm)$$

(dpm = 1,2-bisdiphenylphosphinomethane)

He(I) and He(II) photoelectron spectra for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were reported (27). Two papers on thermochemistry may be found; the first reported a phase transition for $MnRe(CO)_{10}(s)$ at 343±1°K, with a ΔH_{343} of 3.23±0.05 Kcal (28) and the second was concerned with low temperature heat capacities of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (29). Also reported, in a thesis, was radiochemistry on ^{56}Mn and ^{186}Re for the dimetal decacarbonyls (30).

Two papers on mixed metal carbonyls have appeared. Sodium reduction of $W_2(C_5H_5)_2(CO)_5(NH_3)$ followed by addition of $Mn(CO)_5Br$ gave $(CO)_5MnW(C_5H_5)(CO)_3$ and $(CO)_5MnW(C_5H_5)(CO)_2(NH_3)$ which were separated by chromatography (31). Reactions of the carbyne complex trans-$Cr(CO)_4(CPh)Br$ and $Na[M(CO)_5]$ gave axially substituted $(CO)_5MCr(CO)_4CPh$ (M = Mn, Re). An x-ray diffraction study on the rhenium compound provided details on its molecular structure (32).

Several papers reported syntheses of new cationic carbonyl complexes of manganese and rhenium, or new routes to previously reported complexes. The stereospecific synthesis of cis- and trans-$[Mn(CO)_2(CNMe)_4]PF_6$ and of fac- and mer-$[Mn(CO)_3(CNMe)_3]PF_6$, particularly, may be noted (33). These complexes were prepared by reaction of a substituted metal carbonyl halide, $Mn(CO)_{5-n}(CNMe)_nBr$, added ligand and a halide acceptor; the added ligand stereospecifically replaced the halide ion in the metal coordination sphere. This paper further discussed the electrochemical oxidations of these complexes. The ease of oxidation of the isomeric complexes differed, a result attributed to the preference of CO over CNMe to stabilize the metal 3d orbitals. In a related paper (34) the reactions of $Mn(CO)(CNR)_4Br$ and $Mn(CNR)_5Br$ with $AgPF_6$ were discussed. In the absence of any additional ligand the cationic complexes $[Mn(CO)(CNR)_5]^+$ and $[MnL_6]^+$ were formed. When an additional ligand was present (py, CNR') the products were trans-$[Mn(CO)(CNR)_4L]^+$ and $[Mn(CNR)_5L]^+$; again the reactions appeared to be stereospecific. Electrochemical and infrared data were recorded for the products and correlations between these data were noted.

Reactions of $Mn_2(CO)_8L_2$ complexes (L = phosphorus and arsenic ligands) with $NOPF_6$ gave $[Mn(CO)_5L]PF_6$ (18). Also reported here were reactions of $Mn(CO)_3L_2H$ with HPF_6 in MeCN to give $[Mn(CO)_3L_2(NCMe)]PF_6$. The syntheses of $[Mn(CO)_3triphos]^+$ salts were mentioned earlier (19). Also noted was the complex $[Re(dpe)_2(CNMe)_2]^+$, prepared in an elaborate syntheses starting with $ReOCl_3(PPh_3)_2$ (35).

In addition to the electrochemical oxidations mentioned above (33, 34) several other chemical reactions should be noted. The complexes $[Mn(CO)_5PPhMe_2]^+$, $[Re(CO)_5NCMe]^+$ and $[Re(CO)_5py]^+$ have been shown to undergo ^{18}O exchange with $H_2{}^{18}O$ in acetonitrile solution (36). This exchange occurred exclusively for carbonyls cis- to the non-carbonyl ligand; this result was in accord with cis-labilization studies for other $M(CO)_5X$ systems. The rates of exchange were, as expected, greater for the manganese system. Noted was the synthesis of the acyl silane complex $Re(CO)_3(dpe)COSiPh_3$ from $[Re(CO)_4dpe]^+$ and Ph_3SiLi (37).

There was also a report of the failure of $[Mn(CO)_5\overline{COCH_2CH_2O}]^+$ to give ethylene carbonate in an oxidative degradation, in contrast to reactions observed for other carbene-metal complexes (38).

X-ray crystallographic studies have been completed on two cationic complexes. These are the isomeric species cis- and trans-$[Mn(CO)_2(PPh(OMe)_2)_4]PF_6$ (39). Electronic spectra for $[M(CO)_5(NH_2Me)]Cl$ (M = Mn, Re) have been recorded (40).

III. METAL CARBONYL HALIDES AND DERIVATIVES ($M(CO)_5X$; $M(C_5H_5)(CO)_2X_2$).

Two further papers on metal carbonyl fluorides have now appeared. Fluorination of $Mn(CO)_5Br$ with silver(I) fluoride gave two products, $Mn(CO)_3F_3$ and $[Mn(CO)_4F]_2$ (41). Two rhenium carbonyl fluorides were reported in the second paper (42). The first, $Re(CO)_5F$, was formed from $Re(CO)_5Cl$ and anhydrous HF. The other compound, resulting when $Re_2(CO)_{10}$ was treated with XeF_2, was assigned the stoichiometry $Re(CO)_5$-F-ReF_5; it presumably was the structure indicated in the formula, a single fluorine atom bridging the two rhenium atoms. Partial hydrolysis of this compound gave $[Re(CO)_6]ReOF_5$.

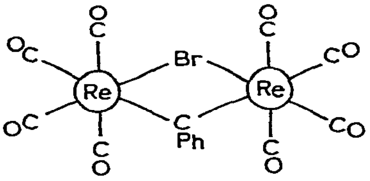
Mention is made again here of the photochemical reactions of $(CO)_5MM(CO)_3(N\frown N)$ compounds ($N\frown N$ = o-phen, biquinoline; M = Mn, Re) in CH_2Cl_2/CCl_4 in which the products $M(CO)_5Cl$ and $M(CO)_3(N\frown N)Cl$ were formed (11). Also the substitution of an axial carbonyl in $Mn_2(CO)_{10}$ by halide ion using a potassium halide and a crown ether was noted earlier (21).

Bromine cleavage of diaxially substituted $Mn_2(CO)_8L_2$ compounds (L = several phosphorus ligands) provided an unexpected reward. The initial product to be isolated was the less stable isomeric form, trans-$Mn(CO)_4(L)Br$. These compounds slowly rearranged to the more stable cis-isomers (18).

Treatment of $Re(CO)_5Cl$ with octaethylporphin ($OEPH_2$) in refluxing decalin gave two products (43), $OEP[Re(CO)_3]_2$ and the salt $[H_2OEP]^+[Re_2(CO)_6Cl_3]^-$. A crystal structure study on the latter species was carried out, revealing that the anion structure consisted of two $Re(CO)_3$ groups linked by three chloride bridges. The metal-metal distance in this compound was 3.37Å. No metal-metal bonding was necessary to accord with the 18e configuration.

Two thiocarbonyl complexes were reported (44). The first $Mn(C_5H_5)(NO)(CS)I$ formed from $[Mn(C_5H_5)(NO)(CO)(CS)]^+$ and KI. This compound may then be reduced with zinc in diglyme to give deep brown $[Mn(C_5H_5)(NO)(CS)]_2$ in about 30% yield; the nmr spectrum of this compound indicated that two geometrical isomers were present.

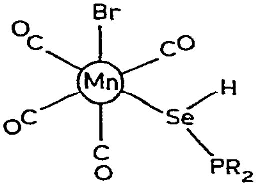
Fischer et al. (45) reported the synthesis and characterization of an unusual rhenium dinuclear complex, $Re_2(CO)_8(CPh)Br$, arising from $Re_2(CO)_9CPhOMe$ and Al_2Br_6. An x-ray crystallographic study identified the molecular structure of this compound; it has two $Re(CO)_4$ groups bridged by the carbyne group, CPh, and by a bromine atom (I).



I

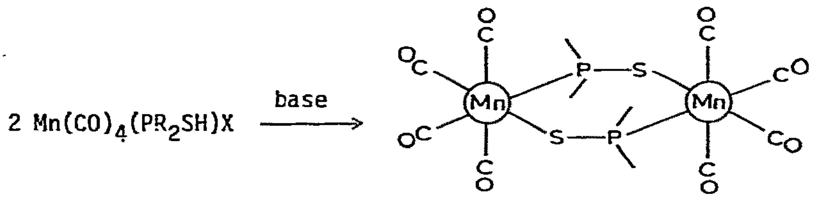
In two papers by Atwood and Brown (46, 47) and in Atwood's thesis (48) kinetic studies on reactions of manganese and rhenium carbonyl halides were discussed. The reactions of <u>cis</u>-$M(CO)_4(L)Br$ (M = Mn, Re; L = various ligands) and ^{13}CO, and the reactions of <u>cis</u>-$Mn(CO)_4(PPh_3)Br$ and $P(OPh)_3$ and $P(OBu)_3$ were followed using infrared spectroscopy (46). The reactions were first order in metal complex and zero order in ligand. The ligands <u>L</u> have different labilizing effects on <u>cis</u> carbonyls; the magnitude of this effect was in the order py > PPh_3 > $P(OPh)_3 \approx CO$. The five coordinate intermediate formed by CO dissociation was assumed to undergo rapid intramolecular rearrangement. It was suggested that the ligand <u>L</u> assumed an equatorial position in a trigonal bipyramidal structure, and that <u>L</u> stabilized this intermediate.

Four papers have appeared in this journal on derivatives of $Mn(CO)_5X$ having the isomeric ligands $R_2P(=X)H$ and R_2PXH (X = S primarily, also O, Se). The first, containing work also described last year in a communication, was on the linkage isomers $Mn(CO)_4(PR_2SH)X$ and $Mn(CO)_4(SPR_2H)X$ (R = Me, X = Cl, Br; R = Ph, X = Br). The latter, the less stable isomers, were formed in low temperature reactions (49). A latter communication (50) described the isomerization of one isomer to the other for both these compounds and also for the oxygen analogues $Mn(CO)_4(OPR_2H)Br$. In addition a selenium analogue was described; it was said to have the following structure (II):



II

Finally, two further papers (51, 52) discussed abstraction of HBr from the thiophosphinous acid complex by bases to give dinuclear complexes $[Mn(CO)_4SPR_2]_2$ (III) according to the following equation:

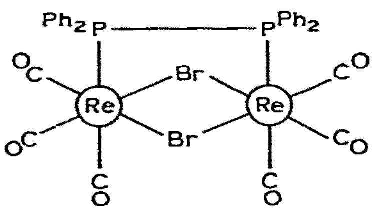


III

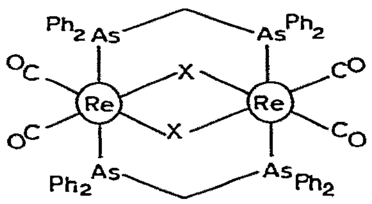
A number of new complexes derived from M(CO)$_5$X by carbonyl substitution were reported. Included are: Mn(CO)$_4$(CNBH$_2$NMe$_3$)Br (53); (CO)$_5$CrMe$_2$PPMe$_2$Mn(CO)$_4$Br (54), from Cr(CO)$_5$Me$_2$PPMe$_2$ and Mn(CO)$_5$Br; Mn(CO)$_3$($P_{neo}\frown P_{neo}$)Br ($P_{neo}\frown P_{neo}$ = (Me$_3$CCH$_2$)$_2$-PCH$_2$CH$_2$P(CH$_2$CMe$_3$)$_2$) (55); Re(CO)$_4$(L)X and Re(CO)$_3$(L)$_2$X (X = Cl, Br; L = N coordinated NCCH$_2$CH$_2$SPh) (56); M(CO)$_3$($P\frown N$)X (MX = MnCl, ReBr; $P\frown N$ = Ph$_2$P-pz, a pyrazollyl substituted phosphine) (57).

Manganese pentacarbonyl chloride and bromide reacted with 1,2-bis(diphenylarsino)methane (dam) to give first, Mn$_2$(CO)$_6$(dam)X$_2$ (X = Cl, Br). Further reaction of these products (X = Br) with dam in refluxing methanol gave mer-trans-Mn(CO)$_3$(dam)$_2$Br; here the potentially bidentate diarsines were found to coordinate as monodentate ligands (58).

A product, Re$_2$(CO)$_6$(P$_2$Ph$_4$)Br$_2$, was formed from P$_2$Ph$_4$ and [Re(CO)$_3$(THF)Br]$_2$ (59). Its structure, determined by x-ray crystallography, is shown below (IV). The somewhat related compounds, Re$_2$(CO)$_4$(dam)$_2$X$_2$, are now believed to have structure (V) (60)



IV



V

A kinetic study on the reaction of Re(CO)$_5$X (X = Cl, Br, I) with excess CN$^-$ in methanol showed that the reaction was first order in complex. A mechanism was suggested in which the reaction proceeded stepwise to the product [Re(CO)$_4$(CN)$_2$]$^-$ via the postulated intermediate [Re(CO)$_4$(CN)X]$^-$ (61). Kinetics of the reaction of cis-Mn(CO)$_4$(L)Br (L = PPh$_3$, AsPh$_3$, SbPh$_3$) with the bidentate ligands dpe, dae (1,2-bisdiphenylarsinoethane), and bipy were noted (62).

Cyclic voltammetric studies on Mn(CO)$_5$Br showed that this compound can be oxidized in CF$_3$COOH to give transient [Mn(CO)$_5$Br]$^+$. This species had a half life of between 50 and 500 milliseconds (17). Chemical reduction of Mn(CO)$_5$X (X = Cl, Br, I) and of Re(CO)$_5$X (X = Cl, Br) occurred upon photolysis in donor solvents, giving $[M(CO)_5]^-$ (15). Chemical oxidation of $Mn(CO)(CNR)_4Br$ and $Mn(CNR)_5Br$ with $AgPF_6$ could not be accomplished. Instead halide loss occurred and cationic metal complexes were generated (34).

A paper (63) and a thesis (64) described the use of $Re(CO)_5Cl$ in conjunction with an aluminum alkyl cocatalyst for olefin metathesis.

The reaction of $Re(C_5H_5)(CO)_3$ and bromine in CF_3COOH gave two isomers of $Re(C_5H_5)(CO)_2Br_2$ (65), differing in the relative orientations, cis and trans, of the bromine atoms, which were separated by chromatography. Reaction of $Re(C_5H_5)(CO)_2Br_2$ with $P(OR)_3$ (R = Me, Et, Ph), with $CNBu^t$ gave $Re(C_5H_5)(CO)(L)Br_2$. In addition, with $P(OMe)_3$, the product $Re(C_5H_5)(CO)(P(OMe)_3)(P(=O)(OMe)_2)Br$ was found, also in two isomeric forms. Another paper (66) reports the reaction of $Re(C_5H_5)(CO)_2Br_2$ with RMgBr (R = Me, Ph); a Grignard-like species, $[Re(C_5H_5)(CO)_2Br]MgBr$, was formed. This was reacted with MeCOCl and PhCOCl to give $Re(C_5H_5)(CO)_2(R)Br$ (R = COMe, Me; and Ph). With NOCl the new nitrosyl complex $Re(C_5H_5)(CO)(NO)Br$ was formed.

A complicated reaction sequence yielding unusual complexes of rhenium originated with $ReOCl_3(PPh_3)_2$ (35). Reaction of this species with CNMe gave $ReCl_3(CNMe)(PPh_3)_2$, $ReCl_3(CNMe)_3(PPh_3)$ and/or $[ReCl_2(CNMe)_4(PPh_3]^+$ (isolated as a PF_6^- salt). The first of these compounds reacted with 1,2-bisdiphenylphosphinoethane (dpe) giving $ReCl_3(CNMe)(dpe)$. This further gave $[ReCl(CONHMe)(dpe)_2]ClO_4$ with $NaClO_4$, dpe, MeOH, and H_2O. Base converted this product to $Re(dpe)_2(MeNCO)$ reversibly and from this product and CNMe, $[Re(CNMe)_2(dpe)_2]^+$ could be formed.

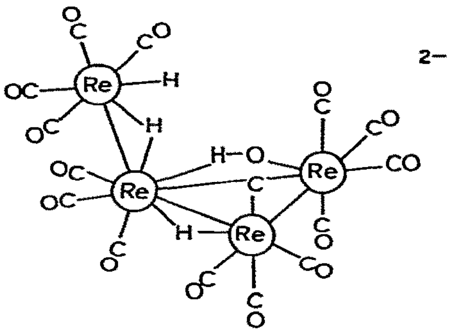
Radiochemistry evolving from ^{60}Co γ irradiation of $Mn(CO)_5X$ at 77°K has been studied (67). Also reported is the ^{119}Sn Mossbauer data for $M(CO)_4[PBu^t(SnMe_3)_2]Br$ (M = Mn, Re) (68). Noted earlier in this review were references to the electronic spectra of $Re(CO)_5X$ (X = Cl, Br, I) (40) and to the PES spectra of $M(CO)_5X$ (M = Mn, Re; X = Cl, Br, I) (27). The former reference also included discussion of the photochemistry of $Re(CO)_5X$ at 25°C.

IV. METAL COMPLEXES WITH EITHER HYDROGEN OR CARBON GROUPS AS LIGANDS ($M(CO)_5H$, $M(CO)_5R$, $M(CO)_5COR$, MR_n, polynuclear hydrides)

A structural study has been completed on the compound $Re_4(CO)_{12}H_4$ (69). The metal tricarbonyl groups formed a regular tetrahedron. The configuration of the carbonyls was staggered relative to the metal-metal bonds. This fact was taken to imply that the hydrogen atoms lie on the faces of the tetrahedron.

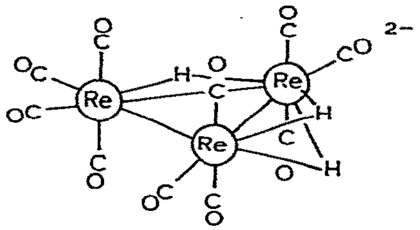
The crystal structure of $Re(NO)(PPh_3)_3H_2$ has also been determined (70). This compound was said to have a distorted octahedral geometry; the hydrogens, not seen, occupied two adjacent positions.

Four papers in this journal contained work on complex polynuclear rhenium carbonyl hydrides. The anionic complex $[Re_4(CO)_{15}H_4]^{2-}$, previously obtained from reduction of $Re_2(CO)_{10}$ was shown to have the structure below (VI) by x-ray crystallography (bis-NEt$_4^+$ salt) (71).

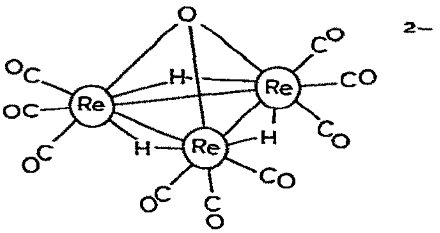


VI

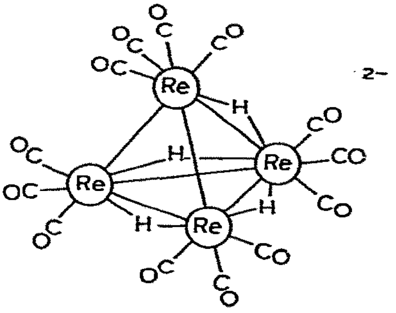
A variable temperature proton nmr study on this compound was also reported; the hydrogens were shown to undergo tautomeric exchange (72). Refluxing (NEt$_4$)$_2$[Re$_4$(CO)$_{15}$H$_4$] in ethanol led to loss of Re(CO)$_5$H and formation of (NEt$_4$)$_2$[Re$_3$(CO)$_{10}$H$_3$] (VII) in the absence of air (73); in air the same reaction gave (NEt$_4$)$_2$[Re$_3$(CO)$_9$(O)H$_3$] (VIII) and (NEt$_4$)$_2$[Re$_4$(CO)$_{13}$H$_4$] (IX) (74). Crystal structure studies have been performed on all three compounds (73, 74) locating all non-hydrogen atoms. Noteworthy was the structure of VII. The distance between the two metals presumably bridged by two hydrogens was very short, 2.797(4)Å. The remaining hydrogen was believed to be disordered between the other two metal-metal bonds; the average bond length for these two other Re-Re bonds was 3.031(5)Å.



VII



VIII



IX

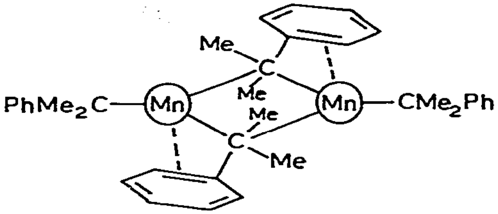
The known trinuclear compound $Re_2Mn(CO)_{14}H$ was formed with other products on electrochemical reduction of $ReMn(CO)_{10}$ (16). The reaction of $Mn_2(CO)_{10}$ with various phosphorus ligands (L) at high temperatures gave *mer-trans*-$Mn(CO)_3(L)_2H$. This reaction could be the easiest synthetic route available for many of these compounds (18). A new substituted manganese hydride, $Mn(CO)_4(L)H$ ($L = P(CF_3)_2$-$Fe(CO)_2(C_5H_5)$) was obtained by direct carbonyl substitution using L (75). The compound $Mn(CO)_3(C_6H_8)H$ (C_6H_8 = 1,3 cyclohexadiene) was one minor product in the reaction of $Mn_2(CO)_{10}$ and 1,3-cyclohexadiene (24).

Reported in theses were gas phase electron diffraction studies on $Mn(CO)_5H$ and several other metal hydrides (76), and kinetics and mechanistic interpretations for reactions of $Mn(CO)_5H$ and $Re(CO)_5H$ (77). Photoelectron spectra for $Mn(CO)_5H$ and $Mn(CO)_5CH_3$ have been recorded (78).

Protonation of $Re(C_5H_5)(PPh_3)(CO)_2$ gave *cis*- and *trans*- isomers of $[Re(C_5H_5)(PPh_3)(CO)_2H]^+$, and nmr data were recorded for these compounds (79). A similar study was accorded $Mn(C_5H_5)(PPh_3)(CO)_2$ (80). Various reactions of $Mn(C_5H_4Me)(CO)_2(H)Si^*(Me)(Ph)Np$ were run to determine the stereochemical consequences at the optically active silicon atom (81).

Wilkinson and coworkers have described further work on rhenium alkyls. The reaction of $ReOMe_4$ with Me_3Al gave green crystals of paramagnetic (d^1) $ReMe_6$. This compound regenerated $ReOMe_4$ with oxygen; both $ReMe_6$ and $ReOMe_4$ with NO gave *cis*-$ReMe_3O_2$, via a characterized intermediate $ReOMe_3(MeNO)$. Further, the reaction of $ReMe_6$ and LiMe in tetramethylethylenediamine(*tmed*) gave $Li_2Re_2Me_8$·tmed (82); the anion in this compound had a square antiprism configuration. Esr studies on $ReMe_6$ and Li_2ReMe_8 have been carried out and were reported in a separate paper (83). The reaction of LiMe and $ReCl_5$ in ether gave $Li_2Re_2Me_8 \cdot 2Et_2O$ a red crystalline diamagnetic species (84); the ether in this compound may be displaced by better donors. An x-ray crystallographic study on this compound showed the anion to be eclipsed, D_{4h} symmetry, with a very short rhenium-rhenium bond length of 2.178(1)Å; this is assumed to be of order four. Finally, the reactions of RMgCl (Me_3SiCH_2MgCl and Me_3CCH_2MgCl) with $(Re_3Cl_9)_x$ and with $ReCl_4 \cdot 2THF$ or $ReCl_5$ have been carried out. The former reaction gave $Re_3Cl_3R_6$. This compound reacted with water or pyridine to give $Re_3Cl_3R_6L_3$. The latter reactions gave transient ReR_4 which decomposed to Re_3R_{12} in an argon atmosphere, and which formed $Re_2R_8N_2$ and $ReOR_4$ in nitrogen and oxygen respectively (85).

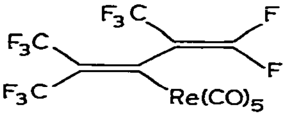
Manganese(II) chloride and RMgX or R_2Mg ($R = CH_2SiMe_3$, CH_2CMe_2Ph) gave dimeric Mn_2R_4 compounds. The former was polymeric while the latter (X) was a dimer, the lower aggragation being a consequence of the phenyl ring coordinating to the metal, according to an x-ray crystallographic study. A further reaction of MnR_2 compounds with tetramethylethylenediamine and LiR to give respectively, monomeric MnR_2·tmed and Li_2MnR_4, was noted (86).



X

Related to this work are the coupling reactions of vinyllithium reagents (87) and vinyl- and arylmagnesium halides (88) using manganese(II) salts. The former reactions were suggested to proceed via $LiMnR_3$ compounds.

Other new alkyl and alkenyl complexes of manganese and rhenium pentacarbonyls included trans-$Mn(CO)_5CH_2CH{=}CHSiMe_3$ (89) and $Fe(C_5H_5)(C_5H_4CH_2Mn(CO)_5)$ (90). Both were prepared from the organic halide by halide displacement using $[Mn(CO)_5]^-$. Several σ-bonded perfluoroorganic derivatives of rhenium carbonyl were prepared from $[Re(CO)_5]^-$ displacement of fluoride ion from fluoroorganic reagents. Two papers (91, 92) described the synthesis of a compound $Re(CO)_5C_7F_{11}$ from $[Re(CO)_5]^-$ and tetrakis (trifluoromethyl)allene; the structure of this product (XI) was determined by x-ray diffraction techniquesand was described in yet a third paper (93).



XI.

Other alkyl and aryl- metal compounds to be described included $Mn(CO)_4(C_4H_6)$-$CH_2CH{=}CHCH_3$ a product from the reaction of butadiene and $Mn_2(CO)_{10}$ (23), and several compounds of the structural type $\overline{Re(CO)_4S{=}C(Ph)C}_6H_4$ which arose on ortho-metallation of thiobenzophenone (20). While mentioning ortho-metallation it is also worthwhile to include another paper which discussed evidence for ortho-metallation arising from ^{31}P nmr data (94).

A paper dealing with kinetics of reactions of $Na[Mn(CO)_4L]$ and alkyl halides was mentioned earlier in this review (2).

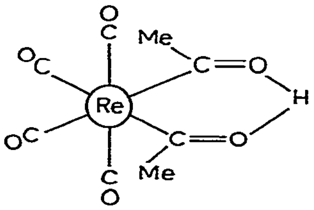
Several acyl metal carbonyl complexes were reported. Reference to a silyl-acyl compound was made earlier (37). Casey et al. (95) prepared pyruvoyl-manganese pentacarbonyl, $Mn(CO)_5COCOMe$, from $[Mn(CO)_5]^-$ and pyruvoyl chloride, and determined its structure. Studies on the decarbonylation of this compound were reported. Acyl compounds also resulted from reactions of chelating diphosphines and diarsines with $Mn(CO)_5Me$; the reaction sequence, given below

$$Mn(CO)_5Me \longrightarrow Mn(CO)_4(\overset{\frown}{L\ L})COMe \longrightarrow$$

$$Mn(CO)_3(\overset{\frown}{L\ L})COMe \longrightarrow Mn(CO)_3(\overset{\frown}{L\ L})Me$$

was followed by infrared and nmr (96). The reaction of $Mn(CO)_5R$ (R = Ph, Me) with the ligand $[GeCl_3]^-$ gave as an intermediate acyl product, the anion $[Mn(CO)_4(GeCl_3)COR]^-$; this on methylation formed the carbene complexes $Mn(CO)_4(CROMe)GeCl_3$ (97).

Two research groups have directed consideration to the reaction of RLi compounds with acyl metal carbonyls. Interestingly, these addition reactions occurred at a coordinated carbonyl and not at the acyl carbonyl. This reaction site is frontier, not charge, controlled (98); differences in energies and localization of the LUMO in the complex made nucleophilic attack at this site more likely. An x-ray diffraction study elucidated the structural features of one product $(NMe_4)[Mn(CO)_4(COMe)(COPh)]$ (99). This product was found to degrade on heating, given acetophenone; the fate of the metal was not indicated. Protonation of <u>cis</u>-$[Re(CO)_4(COMe)_2]^-$ yielded a neutral molecular species also characterized by crystallography; the structure (XII) is sketched below (100).



XII

The diacyl products of these reactions were used as bidentate ligands. A number of aluminum and gallium complexes were described (101).

The mechanism of decarbonylation of $Mn(CO)_5COCH_2CH_2COOMe$ has been studied. Two products, $Mn(CO)_5CH_2CH_2COOMe$ and $Mn(CO)_5CHMeCOOMe$, arose with the former in much larger quantity. In contrast, the decarbonylation of <u>ortho</u>-$C_6H_4(COOMe)$-$COMn(CO)_5$ occurred with concurrent loss of two carbonyls, yielding $\overline{Mn(CO)_4C_6H_4C(OR)O}$ (102).

The rearrangement of $M(CO)_5CF_2CCl{=}CF_2$ to $M(CO)_5CF{=}CClCF_3$ (M = Mn, Re) has been studied by DTA. The enthalpies of reaction for rearrangements of the manganese and rhenium compounds were determined to be -144 ± 20 kjoules and -79 ± 20 kjoules respectively (103).

Mention was made earlier of the thiocarboxylate-metal complexes $Mn(CO)_4(PCy_3)$-CS_2SnPh_3 and $Re(CO)_5CS_2SnPh_3$, formed by reaction of $[Mn(CO)_4(PCy_3)]^-$ or $[Re(CO)_5]^-$ with CS_2 followed by addition of Ph_3SnCl (5). Carbamoyl complexes were mentioned twice. The complex $Mn(CO)_4(NH_2Bu)CONHBu$ was reduced by carbon monoxide giving $Mn_2(CO)_{10}$ (8). Addition of $Mn(CO)_5H$ to pentamethylene diaziridine or an N-methyl derivative of this compound, gave $\overline{Mn(CO)_4CONHC(R_2)N}HR'$ (R_2 = pentamethylene, R' = H, Me) (104). An x-ray crystallographic study on $Mn(CO)_3(PPh_3)CSNMe_2$ and $[Mn(CO)_3(PPh_3)C(SMe)NMe_2]PF_6$ has been concluded, verifying previously postulated structures. Both carbon and sulfur of the CS group coordinated to the metal; thus this group functions as a three electron donor (105).

Reactions of $\overset{*}{Mn}(RC_5H_4)(NO)(PPh_3)COPh$ (R = Me, H) with various ligands including PPr^i_3, $P(OR)_3$, CyNC have been run giving $Mn(RC_5H_4)(NO)(L)COPh$ (106). These reactions occurred with retention of configuration at manganese.

A thesis described the cycloaddition reaction of $Mn(CO)_5CH_2C{\equiv}CPh$ with <u>trans</u>-$CF_3C(CN){=}C(CN)CF_3$, and also the reaction of this manganese complex with $RO_2CC{\equiv}CCO_2R$. The latter reaction gave a substituted cyclopentadienylmanganese tricarbonyl (107).

Also to be mentioned as a carbon ligand complex is the bridging carbyne compound $Re_2(CO)_8(CPh)Br$ (45). The carbyne complex, $[Re(C_5H_5)(CO)_2CPh]BCl_4$, obtained from $Re(C_5H_5)(CO)_2C(Ph)OMe$ and BCl_3, was found to react with methyllithium to give the carbene complex $Re(C_5H_5)(CO)_2CPhMe$ (108). Similar reactions were described for the manganese analogue, $Mn(C_5H_5)(CO)_2CMeR$ compounds (R = Me, Ph) being reported (109).

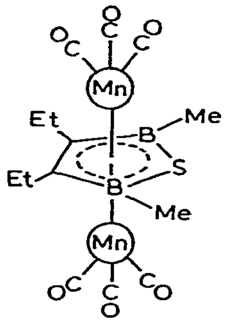
Electron diffraction results for three rhenium compounds, $Re(CO)_5Me$, $Re(CO)_5SiH_3$ and $Re(CO)_5GeH_3$, were described (110). Also the photoelectron spectra of $Mn(CO)_5Me$ was mentioned (78) as was the oxygen(1s) x-ray PES spectrum of gaseous $Mn(CO)_5COMe$. In the latter study it was possible to identify the two different oxygens (111).

V. METAL CARBONYL DERIVATIVES OF METALS AND METALLOIDS (Derivatives of electropositive metals, and of group IIIA and IVA elements).

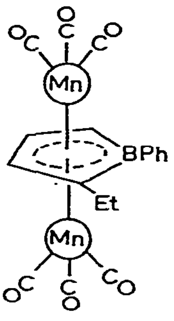
Two papers were mentioned earlier in this review on the mixed metal carbonyls $(CO)_5MnW(C_5H_5)(CO)_3$ and $(CO)_5MnW(C_5H_5)(CO)_2NH_3$ (31) and on $(CO)_5MCr(CO)_4CPh$ (M = Mn, Re) (32). Other than these references, the only covalent complexes of electropositive metals to be described were $(CO)_5MnHgCo(CO)_4$, formed in equilibrium (below) between $Hg[Mn(CO)_5]_2$ and $Hg[Co(CO)_4]_2$ (112), and $Mn(CO)_{5-n}(CNMe)_n$ HgI and $[Mn(CO)_{5-n}(CNMe)_n]_2Hg$, formed from $[Mn(CO)_{5-n}(CNMe)_n]^-$ anions (4).

$$Hg[Mn(CO)_5]_2 + Hg[Co(CO)_4]_2 \rightleftharpoons (CO)_5MnHgCo(CO)_4$$

Two new π-complexes of boron heterocyclic ligands were reported. From $Mn_2(CO)_{10}$ and $\overline{SBMeCEt{=}CEtBMe}$ the orange-red compound (XIII) was formed (113), and from $Mn_2(CO)_{10}$ and $\overline{PhBCH{=}CHCH_2CH_2CH{=}CH}$ compound (XIV) was obtained (114). A crystal structure study was carried out on the latter compound.



XIII



XIV

The reaction of $Mn_2(CO)_{10}$ and InCl in xylene gave $In_2Cl_2[Mn(CO)_5]_4$ (115). In this dinuclear compound, the indium atoms were σ-bonded to two $Mn(CO)_5$ groups and bridged by two chlorine atoms, according to crystal structure data.

Syntheses of the following manganese and rhenium complexes of Group IVA elements have been reported: $[Mn(CO)_4(COR)GeCl_3]^-$ (R = Me, Ph) from $Mn(CO)_5Me$ and Me_4NGeCl_3, and $Mn(CO)_4(C(OR)Me)GeCl_3$ from alkylation of the former compound (97);$[Mn(CO)_4(SnPh_3)_2]^-$ from $[Mn(CO)_4]^{3-}$ and Ph_3SnCl (3); $Mn(CO)_{5-n}(CNMe)_nMPh_3$ from $[Mn(CO)_{5-n}(CNMe)_n]^-$ and Ph_3MCl (n = 1-3, M = Ge, Sn, Pb) (4); $Re(CO)_4$-$(C(OEt)Me)GePh_2Me$ from $\overline{Re(CO)_4GePh_2OCMe}$ and MeLi followed by addition of $[Et_3O]^+$ (116); $[Mn(C_5H_5)(PF_3)_2MCl_3]^-$ from $Mn(C_5H_5)(PF_3)_3$ and $[MCl_3]^-$ (M = Ge, Sn) (117); and $Mn(C_5H_4Me)(CO)_2L$ (L = $:Sn(acac)_2$ and other tin(II) bis-diketonates (118), and:$GeCl_2(THF)$ or :$GeCl_2$(benzothiazole) (119). The syntheses of $Mn(CO)_5GeMe_{3-n}H_n$ (n = 3, 2, 1) by $[Mn(CO)_5]^-$ displacement of $[Co(CO)_4]^-$ from $Co(CO)_4GeMe_{3-n}H_n$ was published (120).

Three papers on reaction kinetics in this area have appeared; all are from the same research group. Two papers dealt with reactions of halogens and $Mn(CO)_5SnR_3$ (R = Me, Et, Cy) (121, 122). The third paper considered the same reaction with $Re(CO)_5SnMe_3$ (123).

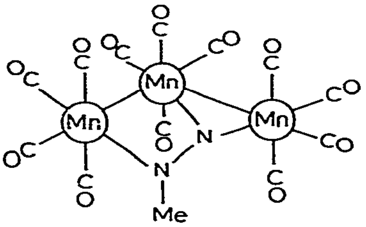
Photolysis converted $Mn(CO)_5SnMe_2Cl$ to $Mn_2(CO)_8(SnMe_3)_2$ (124). Bombardment of $Mn(CO)_5PbPh_3$ with ^{60}Co γ radiation was said to give the radical species $Mn(CO)_4PbPh_3^{\cdot}$ (125).

A relatively large number of structural studies on silicon and tin derivatives of these metals have been reported. Structures determined included: $Re(CO)_5SiMe_3$, $Re(CO)_5Si(SiMe_3)_3$ (126); trans-$Mn(CO)_4(PPh_3)SiMe_3$ (127); $Re(CO)_5SiH_3$ and $Re(CO)_5GeH_3$ by electron diffraction (110); $[(CO)_5Mn]_2BrSnSnBr$-$[Mn(CO)_5]_2$ (128); and $[Mn(CO)_4SnRBr]_2$ (R = $Mn(CO)_5$)(129).

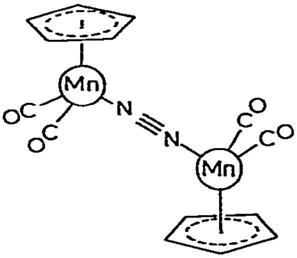
VI. METAL COMPLEXES OF GROUP VA AND VIA LIGANDS

Discussed in order in this section are complexes of nitrogen, phosphorus and arsenic followed by complexes of oxygen and sulfur.

When $Re_2(CO)_{10}$ and picolinic acid (picH) were melted together the compound $Re(CO)_3(py)pic$ was obtained (130). (The pyridine arose from decarbonylation of picolinic acid.) Added phosphorus ligands gave either fac-$Re(CO)_3(L)pic$ or $Re(CO)_2(L)_2pic$; the latter had the configuration with CO groups cis and phosphines trans. An unusual compound $CH_3N_2[Mn(CO)_4]_3$ was formed when $Mn(CO)_5H$ reacted with diazomethane (131). An x-ray diffraction study determined that this compound had the structure (XV). From 1,1,1-trifluorodiazoethane and $Mn(C_5H_4R)(CO)_2(THF)$ (R = H, Me) was obtained $[Mn(C_5H_4R)(CO)_2]_2N_2$; this structure has been determined (132). The preparation of $OEP[Re(CO)_3]_2$ ($OEPH_2$ = octaethylporphin) was mentioned earlier in this review, in conjunction with a second product of this reaction (43). Also mentioned was the carbonylation reaction of $\overline{Mn(CO)_4NPhCPhN}Ph$ to give, first, $Mn(CO)_5NPhCPh{=}NPh$ and finally $Mn_2(CO)_{10}$ (8). The He(I) photoelectron spectra of $Mn(C_5H_5)(CO)_2N_2$ and $Mn(C_5H_5)(CO)_2NH_3$ have been run and data correlated with theory (133).



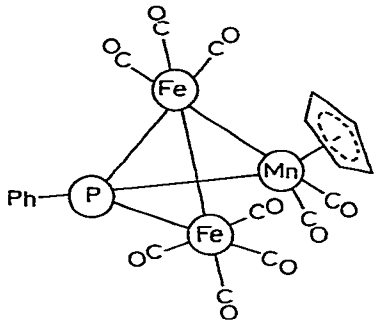
XV



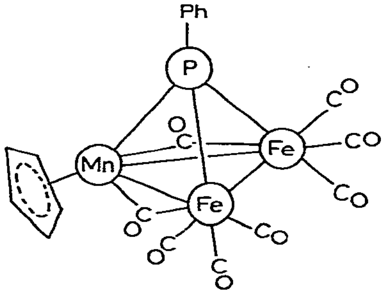
XVI

Sodium in liquid ammonia was found to reduce $Mn(C_5H_5)(CO)_2PPh_2Cl$ to $[Mn(C_5H_5)(CO)_2PPh_2]^-$ (134). This product was alkylated or protonated using MeI or H_2O, and reacted with CH_2Cl_2 (giving $Mn(C_5H_5)(CO)_2PPh_2CH_2PPh_2Mn(CO)_2(C_5H_5)$), with CCl_4 or I_2 (giving $Mn(C_5H_5)(CO)_2(PPh_2X)$) and with MeCOCl (giving a mixture of $Mn(C_5H_5)(CO)_2PPh_2COMe$ and $Mn(C_5H_4COMe)(CO)_2PPh_2COMe$). Reductions of other starting materials such as $Mn(C_5H_5)(CO)_2L$ (L = PPhEtCl, $PPhCl_2$, and NMe_2H) were also carried out and the products alkylated with MeI.

Two interesting complexes were formed from $Mn(C_5H_5)(CO)_2PPhCl_2$ and $Fe_2(CO)_9$, and their crystal structures determined by x-ray crystallography (135, 136). These structures are shown below (XVII, XVIII).



XVII (ref. 135)



XVIII (ref. 136)

Derived from $Mn(C_5H_5)(CO)_2PPhCl_2$ and $Mn(C_5H_5)(CO)_2PPhLi_2$ was another complex, meso-$C_5H_5Mn(CO)_2PPhHPHPhMn(CO)_2C_5H_5$ (137). The analogous arsenic compound was obtained by another route, starting with $Mn(C_5H_5)(CO)_2THF$ and $PhAsH_2$ (138). Structures for both were determined by x-ray diffraction.

The compounds $[Mn(CO)_4SPR_2]_2$, having bridging SPR_2 groups, were reported earlier in this Survey (51, 52). The ^{119}Sn Mossbauer spectrum of $[Re(CO)_4P(SnMe_3)_2]_2$ has been recorded (68).

Two papers described complexes having bidentate carboxylate ligands. When $Re(CO)_2(PPh_3)_3H$ reacted with RCO_2H, hydrogen was lost and one phosphine displaced giving the product $Re(CO)_2(PPh_3)_2(O_2CR)$ (139). The same products are obtained from $Re(CO)_2(PPh_3)_2NHCOR$ with $H_2O + Et_3N$. A crystal structure study was carried out for the acetate compound. Certain ligands can be added to these complexes converting the bidentate carboxylate linkage to a monodentate linkage, vis $Re(CO)_2(PPh_3)_2(L)OCOR$ (L = CO, CNtol). A formate analogue of these compounds can be obtained by the CO_2 reaction with $Re(CO)_2(PPh_3)H$ (140). Other chemistry in this paper included the synthesis of $Re(CO)_2(PPh_3)_2NHCOR$ from $Re(CO)_2(PPh_3)_3H$ and $RCON_3$. Reactions of $Re(CO)_2(PPh_3)_2NHCOR$ with CO_2 (and CS_2) in the presence of a secondary amine NR'_2H gave carbamate complexes or dithiocarbamate complexes $Re(CO)_2(PPh_3)_2X_2CNR_2$ (X = O, S); these are structurally similar to the carboxylate complexes, with chelating X_2CNR_2 groups.

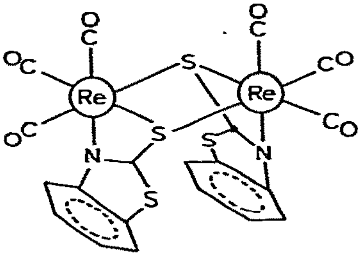
Mentioned at this point are related xanthate compounds $M(CO)_4S_2COR$ (M = Mn, Re; R = Me, Et). These compounds may be prepared by reaction of $K[S_2COR]$ and $M(CO)_5X$. They reacted with phosphines giving $Mn(CO)_3(PR_3)(S_2COR)$ (141).

One of the more interesting developments in this area during the last year was the preparation of complexes of $[SR_3]^+$ ligands. It is remarkable that complexes of such simple ligands, isoelectronic with common phosphine ligands PR_3, had not previously been mentioned. Preparation of $[Mn(C_5H_5)(CO)_2SR_2Me]^+$ was accomplished by alkylation of $Mn(C_5H_5)(CO)_2SR_2$ (SR_2 = SMe_2, SPhMe) using $MeOSO_2F$ or $[Me_3O]BF_4$ (142). The complexes proved quite reactive, common ligands readily displacing the $[R_3S]^+$ group.

The reaction of $[Mn(CO)_5]^-$ and Ph_2CS gave the dinuclear species $[Mn(CO)_4SCHPh_2]_2$; this reaction was believed to occur via charge transfer giving a radical intermediate (143). Other diarylthiones reacted similarly. Photolyses of either $N(SCF_3)_3$ or $Se_2(CF_3)_2$ gave the radicals $\cdot SCF_3$ and $\cdot SeCF_3$. If $Mn_2(CO)_{10}$ was present during these photolyses the products $[Mn(CO)_4XCF_3]_2$ (X = S, Se) could be obtained (144). The compound $[Mn(CO)_4SH]_2$ can be formed from $[Mn(CO)_4SSnMe_3]_2$ and HCl or from $[Mn(CO)_3SSnMe_3]_4$, CO, and HCl (145).

Other carbonylations like that just cited with $[Mn(CO)_3SSnMe_3]_4$ are reported. Carbon monoxide under pressure and $[Re(CO)_3SMe]_4$ gave $[Re(CO)_4SMe]_2$ (146). Carbonylation of $[Mn(CO)_4SH]_2$ and $[Mn(CO)_4SC_6F_5]_2$ gave $Mn(CO)_5SH$ (145) and $Mn(CO)_5SC_6F_5$ (146) respectively.

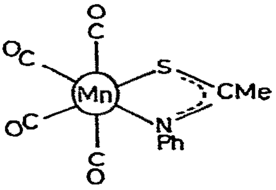
The reactions of 2-mercaptobenzothiazole with either $Mn(CO)_5Br$ or $Re_2(CO)_{10}$ gave $[M(CO)_3SC_7H_4NS]_2$ compounds (147). A crystal structure study on the rhenium compound showed the following structure (XIX):



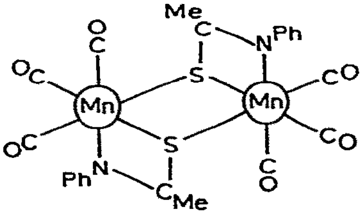
XIX

Interestingly this product had the <u>cis</u> rather than <u>trans</u> configuration

The reaction of either N-trimethylsilyl-thioacetanilide or N-phenyl-S-trimethylstannylthioacetimidate and $Mn(CO)_5Br$ gave initially a monomer $Mn(CO)_4SCMeNPh$ (XX); in turn this lost carbon monoxide forming the dimer, (XXI) (48).



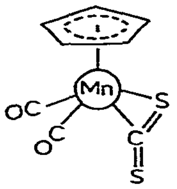
XX



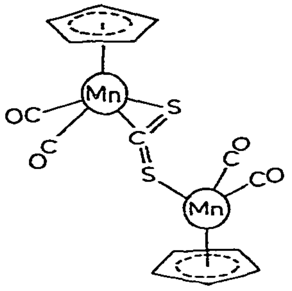
XXI

Two carbon disulfide complexes were reported in the reaction of CS_2 and $Mn(C_5H_5)(CO)_2(THF)$ (149). At low temperature in pentane (-20°) monomeric $Mn(C_5H_5)(CO)_2(CS_2)$ was formed, while at 25° using THF a dimer, $[Mn(C_5H_5)(CO)_2]_2CS_2$, was isolated. Suggested structures for these two species are sketched below

(XXII, XXIII).



XXII



XXIII

The reaction of $Mn(C_5H_5)(CO)_2THF$ and SOF_2 gave a compound $Mn(C_5H_5)(CO)_2(SOF_2)$, from which $Mn(C_5H_5)(CO)_2[SO(NEt_2)_2]$ can be prepared by addition of NEt_2H (150). Further reaction of $Mn(C_5H_5)(CO)_2[SO(NEt_2)_2]$ with HCl gave $Mn(C_5H_5)(CO)_2(SO_2)$; with elemental sulfur the sulfido bridged dimer $[Mn(C_5H_5)(CO)_2]_2S$ was obtained. In turn, this compound could be oxidized to $[Mn(C_5H_5)(CO)_2]_2SO$ (150).

Mention has already been made for the structural study on $Mn(CO)_3(PPh_3)CSNMe_2$ and $[Mn(CO)_3(PPh_3)C(SMe)NMe_2]PF_6$ (105).

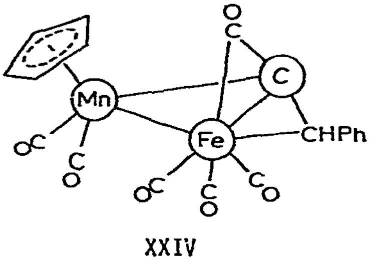
VII. HYDROCARBON METAL COMPLEXES ($M(C_5H_5(CO)_3$, $[M(C_6H_6)(CO)_3]^+$, $M(C_6H_7)(CO)_3$, olefin, allyl complexes, others)

There have been some interesting developments in this area over the past year. Of particular note are the syntheses of various substituted derivatives of $Mn(C_5H_5)(CO)_3$, having formulas $Mn(C_5H_5)(CO)_2L$, where L represents a range of unusual ligands. Mentioned already in this review were the following compounds: $[Mn(C_5H_5)(CO)_2SR_2R']^+$ (R = Me, R' = Me, Ph), synthesized by alkylation of a sulfide complex (142); $Mn(C_5H_5)(CO)_2(CS_2)$ and $[Mn(C_5H_5)(CO)_2]_2CS_2$ formed from $Mn(C_5H_5)(CO)_2(THF)$ and CS_2 at -20° and +25° respectively (149); $Mn(C_5H_5)(CO)_2(SOX_2)$ (X = F, NEt_2), $Mn(C_5H_5)(CO)_2(SO_2)$, $[Mn(C_5H_5)(CO)_2]_2S$, and $[Mn(C_5H_5)(CO)_2]_2SO$ (150); $[Mn(C_5H_5)(CO)_2]_2N_2$, the dinitrogen ligand bridging linearly the two metals (132); the complexes having divalent tin and germanium ligands $Mn(C_5H_4Me)(CO)_2L$ (L = :Sn(acac)$_2$ and related species (118) and $:GeCl_2\cdot THF$ or $:GeCl_2\cdot$benzothiazole (119)); the carbyne and carbene complexes $[M(C_5H_5)(CO)_2CR]BCl_4$ and $M(C_5H_5)(CO)_2(CRR')$ (M = Mn, Re; R = Me, R' = Me, Ph) (108, 109); meso-$Mn(C_5H_5)(CO)_2APhHAHPhMn(CO)_2C_5H_5$ (A = phosphorus (137), arsenic (138)); and $[Mn(C_5H_5)(PF_3)_2MCl_3]^-$ (M = Ge,Sn) (117).

When $Mn(C_5H_5)(CO)_2(THF)$ and PhC≡CH were reacted the compounds $Mn(C_5H_5)(CO)_2$-(C=CPhH) and $[Mn(C_5H_5)(CO)_2]_2C{=}CPhH$ were obtained (151). Structures of both were determined by x-ray crystallography. The dimer had the C=CPhH group bridging the two metals and cyclopentadienyl ligands in trans positions. Substitution of CO in the monomer by PPh_3 and $P(OPh)_3$ was reported in another paper (152).

The compound $Mn(C_5H_5)(CO)_2(HC{\equiv}CCOOMe)$ was formed by a direct ligand substitution reaction at -30°C (153). Further reaction at -20° with Bu^tLi gave the product $Mn(C_5H_5)(CO)_2(C{=}C{=}CBu_2{}^t)$.

The compound $Mn(C_5H_5)(CO)_2(C{=}CPhH)$ was found to react with $Fe_2(CO)_9$ to give a new product $Mn(C_5H_5)(CO)_2(C_2PhH)Fe(CO)_4$. A strange structure of this compound was determined by a crystallographic study; this is shown below (XXIV) (154).



XXIV

The structure of $[Mn(C_5H_5)(CO)_2]_2C_5H_6$ was determined; this is a bis(olefin) complex with the diolefin cyclopentadiene bridging the two metals (155). Also reported was a structural study on $Mn(C_5H_5)(CO)_2(Ph_2C{=}C{=}O)$. Here the ketene ligand bonds to manganese through the C=C unit (156). Structural studies on $Mn(C_5H_5)(CO)_2Fe_2(CO)_7PPh$ (135) and $Mn(C_5H_5)(CO)_2Fe_2(CO)_8PPh$ (136) were mentioned earlier.

The compound $[Mn(C_{13}H_{10})(CO)_3]PF_6$ ($C_{13}H_{10}$ = fluorene) gave up a proton from C(9) to bases such as Et_3N (157). This meant that the compound is a stronger acid than the free ligand by about ten orders of magnitude, a consequence of the stabilization of negative charge on the ligand by virtue of its delocalization to the $Mn(CO)_3$ group. The product of deprotonation was a red crystalline species with the metal still complexed to the six membered ring. It reacted slowly with alkylating agents, giving stereospecifically the exo- isomer with the $Mn(CO)_3{}^+$ group bonded to the 9-alkylfluorene. In solution or in the solid state, rearrangement of $Mn(C_{13}H_9)(CO)_3$ occurred with metal migration to the five membered ring giving the known stable fluorenylmanganese tricarbonyl.

The synthesis of $Mn(1\text{-}Ph\text{-}2,3\text{-}(MeO_2C)_2C_5H_2)(CO)_3$ in a cycloaddition reaction between $Mn(CO)_5CH_2C{\equiv}CPh$ and $MeO_2CC{\equiv}CCO_2Me$ has been reported in a thesis (107).

Protonations of $Mn(C_5H_5)(CO)_2L$ and $Re(C_5H_5)(CO)_2L$ (L = PPh_3, CO) were discussed in two papers (79, 80). Other adducts of the latter compound with the Lewis acids $SnCl_4$, $SnBr_4$ and $TiCl_4$ were also described (158).

Somewhat related to this acid-base chemistry were the CF_3COOH protonations of the hydroxymethylcyclopentadienyl metal complexes $Mn(C_5H_4CR_2OH)(CO)_2L$ (R = Me, Et, Ph, H; L = PPh_3, $PPr_3{}^i$) (158). The products of these reactions were carbonium ions, stabilized by the metal. The degree of stabilization was found to depend on L (159). A further paper (160) discussed equilibrium constant values for the system:

$$\mathrm{Mn(C_5H_4CR_2OH)(CO)_3 + H^+ \rightleftharpoons Mn(C_5H_4CR_2{}^+)(CO)_3 + H_2O}$$

Sodium reduction of $Mn(C_5H_5)(CO)_3$ in HMPA gave first $Na[Mn(CO)_5]$ and ultimately $Na_3[Mn(CO)_4]$ (3). Cyclic voltammetry in CF_3COOH showed that $Mn(C_5H_5)(CO)_3$ oxidized to the transient species $[Mn(C_5H_5)(CO)_3]^+$ which had a half life of about 10 sec. (17).

The chemistry at coordinated phosphorus or nitrogen ligands was mentioned here previously. Sodium in liquid ammonia caused reduction of $Mn(C_5H_5)(CO)_2PRR'Cl$; the anionic phosphido complexes were reacted with a variety of electrophilic reagents (134, 137).

The synthesis of the optically active compounds $Mn^*(1,3Me_2C_5H_3)(CO)(PPh_3)[P(OMe)_3]$ was accomplished in an interesting reaction sequence (161). The precursor for this was $Mn(1\text{-}Me\text{-}3\text{-}MeO_2CC_5H_3)(CO)_3$ which was first substituted by two $P(OMe)_3$ groups; then one of the $P(OMe)_3$ groups was displaced by PPh_3. The product $Mn(1\text{-}Me\text{-}3\text{-}MeO_2CC_5H_3)(CO)(PPh_3)[P(OMe)_3]$ existed in two diastereomeric forms, separable by chromatography. Treatment of each diastereomer with $LiAlH_4$ to reduce the carbomethoxy group to a methyl group gave the products. Earlier the results on the stereospecificity of borohydride and organolithium reactions at a keto-group on the cyclopentadienyl ligand (162) had been communicated.

Another paper on the cyclopentadienyl ligand group chemistry was the boronation of $Mn(C_5H_5)(CO)_3$ to give $Mn(C_5H_4BXY)(CO)_3$ (BXY = BBr_2, BI_2, BPhI, BMeI), and subsequent replacement of halogen on boron by OEt, SMe, NMe_2 or NEt_2 groups (163); the insertion of $CNtol^p$ into the nickel-carbon bond in $Ni(C_5H_5)(PPh_3)C_5H_4Mn(CO)_3$ was observed (164).

Mentioned earlier in this review was a study of reactions at optically active silicon in $Mn(C_5H_4Me)(CO)_2(H)Si^*(Me)(Ph)(\alpha Np)$ (81). Also reported was the isolation of two isomers of $Re(C_5H_5)(CO)_2Br_2$, the reaction of the <u>trans</u> isomer with phosphites and with $CNBu^t$ (65) and the formation of "Grignard-like" $[Re(C_5H_5)(CO)_2Br]MgBr$ and reactions of this compound (66).

Active study on photoelectron spectra continued, with PES data being reported for $Mn(C_5H_5)(CO)_2L$ (L = CO (165), N_2 and NH_3 (133) and CS (166)) and for $Re(C_5H_5)(CO)_3$ (165). The data on the thiocarbonyl compound was in accord with theory which suggested that CS is a better π acceptor than CO (166). Nmr data (^{13}C) on $Mn(C_5H_5)(CO)_2L$ (167) and on the metal stabilized carbonium ion species $[Mn(C_5H_4CH_2)(CO)_2L]^+$ (168) were also found, as was an infrared and laser Raman study on $Mn(C_5H_5)(CO)_{3-n}(CS)_n$ (n = 1,2) (169). The temperature dependent nmr spectra of $Mn(C_5H_5)(CO)_2$(olefin) (olefin = 1,1-, <u>cis</u>-1,2-, and <u>trans</u>-1,2- $C_2H_2(OMe)_2$ and $C_2(OMe)_4$ have been reported (170).

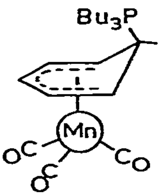
Beta decay of ^{99}Mo ($\tau_{1/2}$ = 99m) in $[Mo(C_5H_5)(CO)_3]_2$ gave primarily $^{99}Tc(C_5H_5)(CO)_3$. In addition a small amount of $^{99}Tc(CO)_5$ formed (171).

The cyclopentadienyl manganese and rhenium complexes $Mn(C_5H_5)(NO)(CS)I$ (44), $Re(C_5H_5)(NO)(CO)Br$ (66), and $[Mn(C_5H_5)(NO)(CS)]_2$ (44) were discussed previously. Reaction of $[Mn(C_5H_5)(NO)(PPh_3)(CO)]^+$ and methyllithium gave Mn(exo-MeC_5H_5)(NO)(PPh_3)(CO), whose structure has been determined by x-ray diffraction (172). The reaction of phenyllithium and $[Mn(C_5H_5)(NO)(PN^*)(CO)]^+$ (PN^* = (S)-(+)-$PPh_2NMe\overset{*}{C}HMePh$) gave two products, Mn $(C_5H_5)(NO)(PN^*)COPh$ and Mn(exo-PhC_5H_5)(NO)(PN^*)(CO), attack of the nucleophilic reagent occurring at either the C_5H_5- ring or at CO. In both products the optical activity inherent at the metal center is initially retained although the acyl compound slowly epimerized in a first order reaction (173). Reactions of $Mn(C_5H_4R)(NO)(PPh_3)COPh$ (R = H, Me) with various ligands L (PPr_3^i, $P(OR)_3$, CNCy) gave $Mn^*(C_5H_4R)(NO)(L)$-COPh; these products were formed with retention of configuration at the metal (106).

An elaborate study on optically active manganese compounds was reported in this journal by Brunner and Aclasis (174). Starting with $[Mn(C_5H_5)(NO)(CO)_2]^+$ and various phosphines, the complexes with an asymmetric metal center $[\overset{*}{Mn}(C_5H_5)(NO)(L)(CO)]^+$ were formed. Addition of the optically active menthoxy anion $[OMen^*]^-$ gave the diastereomeric products $\overset{*}{Mn}(C_5H_5)(NO)(L)(COOMen^*)$ which were separable by crystallization. In turn these were reacted with PhLi giving $\overset{*}{Mn}(C_5H_5)(NO)(L)COPh$ and $\overset{*}{Mn}$(exo-PhC_5H_5)(NO)(L)(CO) in which the optical activity at the metal was retained. Studies on the rates of racemization were then performed on these systems. While the cationic species were stable to racemization the esters and benzoyl compounds did racemize, presumably via a phosphine dissociative mechanism.

Conductance studies were performed on ClO_4^- and BPh_4^- salts of the cationic complex $[Mn(C_6H_6)(CO)_3]^+$ in both THF and acetonitrile. Results indicated only partial dissociation in these solvents (175). Two communications described the reaction of this cation, as a BF_4^- salt, with PBu_3. In the absence of light, or in the presence of light and oxygen (which quenches the photochemical reaction) an equilibrium existed between these reagents and a product of exo-addition of PBu_3 to the hydrocarbon ring:

$[Mn(C_6H_6)(CO)_3]BF_4 + PBu_3 \rightleftarrows$

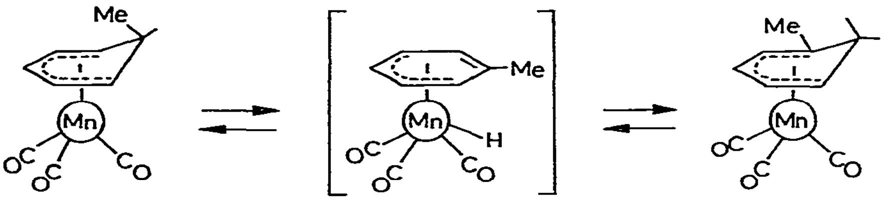


Reactions of these reagents in the presence of light led to carbonyl substitution by the phosphine (176). The second communication on this work, from the same research group, reported the rates of this addition-reaction (177) with several complexes. Reactions were bimolecular, first order in phosphine and complex. The reaction of manganese complex was the slowest among those studied.

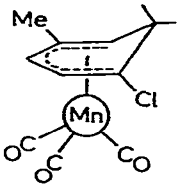
An interesting and thought provoking paper discussed the geometry of nucleophilic addition to a coordinated hydrocarbon ring such as the C_6H_6 ring in $[Mn(C_6H_6)(CO)_3]^+$ (178). It was suggested that the deformation of the ring from planarity was a consequence of electronic considerations. It was also suggested that the exo configuration was favored for substituents less electronegative than hydrogen; endo configuration should be preferred by more electronegative substituents than hydrogen.

The compound $Mn(C_6H_7)(CO)_3$, a cyclohexadienyl complex, was reported as one of the products from photolytic reaction of $Mn_2(CO)_{10}$ and 1,3- or 1,4-cyclohexadiene (24). Also reported here, for the reaction of butadiene and $Mn_2(CO)_{10}$, (23) were a number of olefin and diolefin complexes.

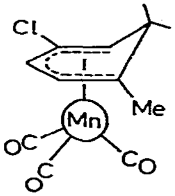
A communication (179) reported the isomerization reaction below:



At 135° an approximately equal mixture of the two products was present, but at 150° the second predominated. The exchange reaction was suggested to occur via hydrogen transfer to the metal giving $Mn[C_6H_5R](CO)_3H$ as indicated in the equation above. In the solvent 4-chlorotoluene this isomerization reaction was complicated by exchange of the coordinated arene ring with this substance, and the products shown below (XXV and XXVI) were identified as components of the reaction system.

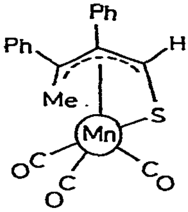


XXV



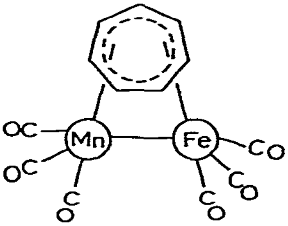
XXVI

Reactions of $[Mn(CO)_3(NCMe)_3]PF_6$ with $C_5H_4SMe_2$ and $C_5H_4PPh_3$ gave the respective products $[Mn(C_5H_4SMe_2)(CO)_3]^+$ and $[Mn(C_5H_4PPh_3)(CO)_3]^+$ (180). A compound $Mn_2(CO)_8(RC{\equiv}CNEt_2)$ (R = Me, NEt_2) was formed in the reaction of $[Mn_2(CO)_{10}$ and $RC{\equiv}CNEt_2$ (181) and a tentative structure suggested. An interesting compound, (XXVII), was reported formed in the reaction of $[Mn(CO)_5]^-$, diphenylthiopropenone, and MeI (182).



XXVII

Three papers reported cycloheptatriene and cycloheptatrienyl- manganese and rhenium compounds. Whitesides and Budnik prepared $Mn(C_7H_7)(CO)_3$ from $Mn(CO)_5COC_7H_7$ by low temperature photolysis (183). This compound exhibited fluxional behavior, and study of its nmr spectrum over several temperatures suggested that the fluxional motion consisted of a series of 1,2-shifts of the metal around the ring. The bimetallic compounds $C_7H_7Fe(CO)_3M(CO)_3$ (M = Mn, Re) were formed from $[Re(CO)_3(THF)Br]_2$ or $Mn_2(CO)_8Br_2$ and $[Fe(C_7H_7)(CO)_3]^-$ (184). The structure of the manganese compound is shown below (XXVIII). Nmr spectra on these and related compounds also demonstrated fluxional behavior.



XXVIII

The cycloheptatriene compounds of rhenium $Re_2(CO)_7(C_7H_8)$ and $Re_2(CO)_8(C_7H_8)$ were formed by photolysis of the hydrocarbon ligand and $Re_2(CO)_{10}$ (185). A third compound, cycloheptadienylrhenium tricarbonyl, $Re(C_7H_9)(CO)_3$, was also obtained in this reaction.

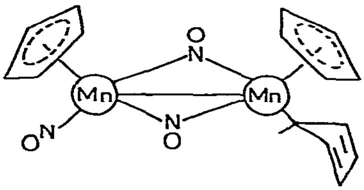
A further paper on manganocene has appeared (185). This reported CNDO-MO calculations on the ground state and excited states of this molecule and correlated this theory with PES and uv-visible absorption spectral data (186).

VIII. VARIOUS ISOCYANIDE AND NITROSYL COMPOUNDS ($[M(CNR)_6]^+$, $M(CO)_4NO$, $[M(C_5H_5)(CO)_2NO]^+$)

Most of the studies on nitrosyl containing complexes were discussed earlier in this review. These included references to the following compounds: $Re(C_5H_5)(NO)(CO)Br$ (66); $Mn(C_5H_5)(NO)(CS)I$ and $[Mn(C_5H_5)(NO)(CS)]_2$ (44);

$Mn(C_5H_4R)(NO)(L)(COPh)$ (106); $Mn($exo-$MeC_5H_5)(NO)(PPh_3)CO$ (structure) (172); $[Mn(C_5H_5)(NO)(PN^*)CO]^+$ and two products derived from it in the reaction with PhLi (173); and various $[Mn(C_5H_5)(NO)(L)CO]^+$, $Mn(C_5H_5)(NO)(L)(COPh)$, and $Mn($exo-$PhC_5H_5)(NO)(L)(CO)$ compounds used in a mechanistic study involving optical activity at the metal center (174). The manganese compound $Mn(CO)_3(L)NO$ ($L = P(CF_3)_2Fe(CO)_2(C_5H_5)$) was also described (75).

The structure of $Mn_2(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NO)_3$ is shown below (XXIX); it was determined by x-ray crystallography (187). The reduction of this compound by $LiAlH_4 + AlCl_3$ was described in another paper (188) to give $Mn_3(C_5H_5)_3(NO)_4$. Also reported was reaction of this precursor with phenyllithium. The reaction product presumably had a structure like (XXIX), with the phenyl group replacing the $\eta^1\text{-}C_5H_5$ group. This compound existed in two isomeric forms according to spectroscopic results; these isomers must have cis and trans cyclopentadienyl groups.



XXIX

Two mononuclear rhenium nitrosyls were reported. The compound $Re(CO)_2(PPh_3)_2$-NO was formed by carbonylation of $ReH_2(NO)(PPh_3)_3$ (189). A crystal structure study has been carried out on the latter compound (70). Including the hydrogens in assumed positions, this compound was represented to have a very distorted octahedral geometry.

The following isocyanide complexes were mentioned in earlier sections of this review: $Re(CO)_2(CNtol)(PPh_3)_2OCOR$ (139); $[Mn(CO)_{5-n}(CNMe)_n]^-$ (n = 1,2,3) and tin, germanium, mercury, and alkyl derivatives (4); $Re(C_5H_5)(CO)(CNBu^t)Br_2$ (65); $Mn(CO)_4(CNBH_2NMe_3)Br$ (53). Also mentioned earlier were the stereospecific syntheses of $[Mn(CO)_{6+n}(CNMe)_n]^+$ (n = 3,4) and the electrochemical oxidation potential data for these substances (33), and the reactions of MnL_5Br or $Mn(CO)(L)_4Br$ (L = CNMe, CNPh) with $AgPF_6$ and another ligand L' (34).

The reaction of MeNC and $ReOCl_3(PPh_3)_2$ gave rhenium(III) isocyanide complexes $Re(CNMe)(PPh_3)_2Cl_3$ and $Re(CNMe)_3(PPh_3)Cl_3$. Addition of dpe to the former gave $Re(CNMe)(dpe)Cl_3$. In the presence of PF_6^- the ionic complex $[Re(CNMe)_4(PPh_3)Cl_2]PF_6$ can be obtained. Addition of $NaClO_4$ and dpe, and H_2O to $Re(CNMe)(dpe)Cl_3$ gave $[Re(dpe)_2(CONHMe)Cl]ClO_4$, where OH^- has been added to the isocyanide. Treatment of this with base and more MeNC gave $[Re(dpe)_2$-$(CNMe)_2]^+$ (35).

The electronic absorption spectra for $[Mn(CNPh)_6]Cl$ and $[Mn(CNPh)_6](PF_6)_2$ were reported (190).

IX. STRUCTURAL STUDIES

The compounds whose structures have been determined by x-ray crystallography or electron diffraction are listed below: *trans*-$(CO)_5ReCr(CO)_4CPh$ (32); *cis*- and *trans*-$[Mn(CO)_2(PPh(OMe)_2)_4]PF_6$ (39); $[H_3OEP]^+[Re_2(CO)_6Cl_3]^-$ (43); $Re(CO)_8$-$(CPh)Br$ (45); $Re_2(CO)_6(P_2Ph_4)Br_2$ (59); $Re_4(CO)_{12}H_4$ (69); $(NEt_4)_2[Re_4(CO)_{15}H_4]$ (71); $(NEt_4)_2[Re_3(CO)_9H_3]$ and $(NEt_4)_2[Re_3(CO)_9(O)H_3]$ (73); $(NEt_4)_2[Re_4(CO)_{13}H_4]$ (74). $Mn(CO)_5H$ (electron diffraction) (76); $Li_2Re_2Me_8 \cdot 2Et_2O$ (84); $Mn_2(CH_2CMe_2Ph)_4$ (86), $Re(CO)_5C_7F_{11}$ (93); $Mn(CO)_5COCOMe$ (95); $NMe_4[Mn(CO)_4(COMe)(COPh)]$ (99); $Re(CO)_4(COMe)_2H$ (100); $Mn(CO)_3(PPh_3)CSNMe_2$ and $[Mn(CO)_3(PPh_3)C(SMe)NMe_2]PF_6$ (105); $Re(CO)_5Me$, $Re(CO)_5SiH_3$, $Re(CO)_5GeH_3$ (all electron diffraction) (110); EtC_4H_3BPh-$[Mn(CO)_3]_2$ (114); $In_2Cl_2[Mn(CO)_5]_4$ (115); $Re(CO)_5SiMe_3$ and $Re(CO)_5Si(SiMe_3)_3$ (126); *trans*-$Mn(CO)_4(PPh_3)SiMe_3$ (127); $[(CO)_5Mn]_2BrSnSnBr[Mn(CO)_5]_2$ (128); $[Mn(CO)_4SnRBr]_2$ (R = $Mn(CO)_5$)(129); $CH_3N_2[Mn(CO)_4]_3$ (131); $Mn(C_5H_4Me)(CO)_2]_2N_2$ (132); $Mn(C_5H_5)(CO)_2Fe_2(CO)_7PPh$ (135); $Mn(C_5H_5)Fe(CO)_8PPh$ (136); *meso*-$C_5H_5Mn(CO)_2$-$PPhHPHPhMn(CO)_2C_5H_5$ (137); *meso*-$C_5H_5Mn(CO)_2AsPhHAsHPhMn(CO)_2C_5H_5$ (138); $Re(CO)_2$-$(PPh_3)_2O_2CR$ (139); $[Re(CO)_4SC_7H_4NS]_2$ (147); $Mn(C_5H_5)(CO)_2C{=}CPhH$ and $[Mn(C_5H_5)(CO)_2]_2C{=}CPhH$ (151); $Mn(C_5H_5)(CO)_2C(CPhH)Fe(CO)_4$ (154); $[Mn(C_5H_5)(CO)_2]_2C_5H_6$ (155); $Mn(C_5H_5)(CO)_2(Ph_2C{=}C{=}O)$ (156); $Mn($*exo*-$MeC_5H_5)(NO)$-$(PPh_3)(CO)$ (172); $Mn_2(\eta^5\text{-}C_5H_5)_2(\eta^1\text{-}C_5H_5)(NO)_3$ (187); $Re(NO)(PPh_3)_3H_2$ (70).

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