MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1981*

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I. INTRODUCTION

This year's Annual Survey article contains over two hundred references to work on the organometallic chemistry of Manganese, Technetium, and Rhenium; this is up substantially from previous years. The high level of productivity seen recently in this area has not only been sustained but has been enhanced. Interesting and significant work on a broad range of topics has appeared in this past year, as will be evident in this review.

The organization of this article follows the outline used in the past year. A few changes have been made in writing formulas to be in accord with current practice.

It is appropriate to mention two specific review articles in this introduction. Caulton (ref. 1) has constructed an excellent review on the coordination chemistry of $M(CO)_2(\eta\text{-}C_5H_5)$ groups (M = Mn, Re). This article should prove valuable to workers in this field; an article in this area has long been needed. The second reference is to an article by Lukehart (ref. 2) in Accts. Chem. Res. This article summarizes this author's work in the area of metallo-β-diketonates.

The 1979 Annual Surveys article in this area appeared during 1981 (ref. 3). At the time of this writing, the 1980 article is still in press.

* Manganese, technetium and rhenium; Annual Survey covering the year 1980 see J. Organometal. Chem., 237 (1982) 61-93.

II. NEUTRAL, ANIONIC, AND CATIONIC METAL CARBONYL DERIVATIVES

The solid state structures of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were redetermined, providing much more accurate values for the metal-metal bond lengths (ref. 4). Values obtained are: d(Mn-Mn) = 2.9038(6) Å and d(Re-Re) = 3.0413(11) Å. Infrared spectra for these compounds were recorded at high temperature. It was suggested that these molecules have D_{4h} symmetry under high pressure, in contrast to the D_{4d} molecular symmetry at one atmosphere (ref. 5).

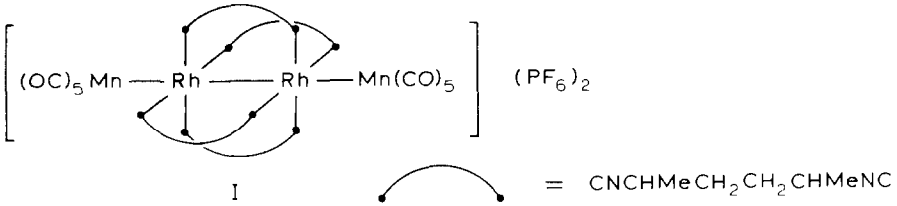
The mixed metal carbonyls, $MnTc(CO)_{10}$ and $ReTc(CO)_{10}$ were prepared by the following reactions:

$$[M(CO)_5]^- + TcBr(CO)_5 \rightarrow MTc(CO)_{10} + Br^-$$

(M = Mn, Re)

Conditions were established to provide optimum yields and the products were characterized by infrared spectroscopy and mass spectrometry (ref. 6). The formation of $Mn_2(CO)_{10}$ in reactions between $MnBr(CO)_5$ and sodium or lithium acetylide was mentioned (ref. 7). Reference was made to $Re_2\{P(OMe)_3\}_{10}$ and $ReH\{P(OMe)_3\}_5$ in a thesis (ref. 8).

Photolysis of $Mn_2(CO)_{10}$ with pyridine and several substituted pyridines gives $Mn_2(CO)_9(py)$ and $[Mn(CO)_3(py)_3]Mn(CO)_5$ initially. Continued photolysis eventually leads to $[Mn(py)_6][Mn(CO)_5]_2$. The mechanism of this reaction is believed to involve the initial cleavage of the metal-metal bond (ref. 9). There have been a number of other studies in which metal-metal bond cleavage is believed to play a role. Photolysis of a solution of $Mn_2(CO)_{10}$ and $[Rh_2(TM4\text{-bridge})_4](PF_6)_2$ in acetone produces $[Rh_2(TM4\text{-bridge})_4Mn_2(CO)_{10}](PF_6)_2$, (I); this product is believed to arise by facile addition of $Mn(CO)_5$ radicals to the rhodium-rhodium bonded precursor. A crystal structure determination was carried out on (I), (ref. 10).



I

Flash photolysis of $Mn_2(CO)_{10}$ (M = Mn, Re) under pressure of one atmosphere of CO or more has been shown to generate $M(CO)_5$ radicals. These radicals recombine in a rapid bimolecular process for which rate constants have been determined.

In degassed solutions, under low pressure of CO, the behavior is more complicated. Both $M_2(CO)_8$ and $M_2(CO)_9$ intermediates are implicated; their formation is believed to arise by CO dissociation from $M(CO)_5$ followed by recombination of $M(CO)_4$ and $M(CO)_5$ radicals (ref. 11). Additional information on flash photolysis experiments involving mixtures of $M_2(CO)_{10}$ (M = Mn, Re) and $Co_2(CO)_6(L)_2$ (L = CO, PBu_3) is found in a thesis (ref. 12).

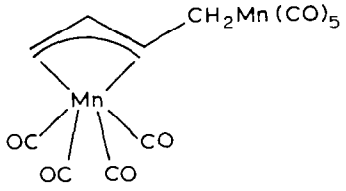
Wrighton and Hepp (ref. 13) have investigated the one electron oxidation of photochemically generated $M(CO)_5$ radicals (M = Mn, Re). They proposed that these reactions produce 16 electron species, $[M(CO)_5]^+$ which then add an additional ligand, ClO_4^- or CH_3CN, to give the final 18 electron products, $Re(OClO_3)(CO)_5$ and $[Mn(CO)_5(CH_3CN)]^+$. Poë, et al. (ref. 14) have studied substitution reactions of photochemically generated $Re(CO)_5$ determining that these reactions are second order and not dissociative.

An initial correspondence from Poë (ref. 15) concerning the mechanism of substitution reactions of $MnRe(CO)_{10}$ was followed by an answer and his further response (ref. 16, 17). The point of contention is whether the mechanism of the reaction involves initial homolytic cleavage of the metal-metal bond.

The radical species $Mn(CO)_5$ has been generated in a solid CO matrix at 10-20K by photolysis of $MnH(CO)_5$. Infrared spectral data indicated that this radical has a square pyramidal geometry (ref. 18).

The formation of $Mn_2(CO)_9[S\{Cr(SBu^t)(\eta\text{-}C_5H_5)\}_2]$ by irradiation of a THF solution of $Mn_2(CO)_{10}$ and $[Cr(SBu^t)(\eta\text{-}C_5H_5)]_2S$ has been described. A crystal structure study was carried out on this species (ref. 19).

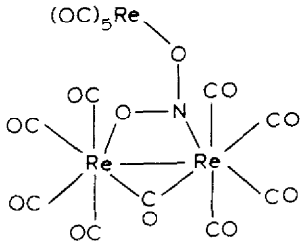
Three products were obtained on irradiation of solutions of $Mn_2(CO)_{10}$ and 1,3-butadiene (ref. 20). These are $Mn_2(CO)_9(\eta^2\text{-}C_4H_6)$, $Mn_2(CO)_8(C_4H_6)$, and $Mn(CO)_4\{\eta^3\text{-}C_3H_4CH_2Mn(CO)_5\}$, (II). The second product contains a bridging



II

trans-butadiene bonded in a η^2-fashion to each manganese atom. Reactions between $Re_2(CO)_{10}$ and several dienes (cyclooctatetraene, 1,4-pentadiene, along with 1,3-butadiene) produce a number of similar products, with the compound $Re_2(CO)_8(C_4H_6)$ being the subject of a crystal structure study (ref. 21). A

plethora of products were obtained in low yields by irradiating $Re_2(CO)_{10}$ and NO, in both the presence and absence of 1,3,5-cyclooctatriene (ref. 22). These include $Re_2(CO)_8(C_4H_6)$, $Re_2(CO)_9(C_3H_6)$, $Re_3(CO)_{14}(NO_2)$ (III), $Re_3(CO)_{14}(CO_2H)$, $Re_3H(CO)_{14}$, and $Re_4H_4(CO)_{12}$. The structure of III was determined, as was the structure of the metallocarboxylic acid derivative. The latter structure resembles (III), with a CO_2H group replacing the NO_2 group.



III

The use of $Mn_2(CO)_{10}$ as an initiator for radical addition reactions was reported in two papers (ref. 23, 24). These papers were followed by an ESR study on the interaction of $M_2(CO)_{10}$ (M = Mn, Re) with silicon-hydride compounds (ref. 25). Dirhenium decacarbonyl was included as one of many organometallic catalysts studied in cyclopropanation reactions (ref. 26).

The preparation of $[PhCH_2NEt_3]Mn(CO)_5$ was accomplished in a phase transfer reaction between $[PhCH_2NEt_3]Br$, $MnBr(CO)_5$, and $NaBH_4$, using a H_2O/CH_2Cl_2 two phase system. The anionic complex, in CH_2Cl_2, was then allowed to react with Ph_3SnCl, providing a 95% isolated yield of $Mn(SnPh_3)(CO)_5$. An analogous phase transfer reaction using $MnCl(CO)_4(PPh_3)$ produced cis-$MnH(CO)_4(PPh_3)$ (ref. 27, 28).

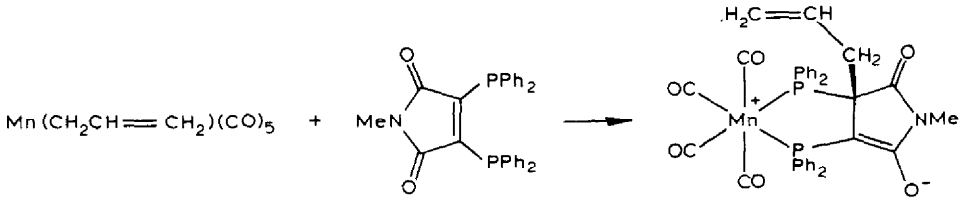
A photochemical reaction between $NbH_3(\eta\text{-}C_5H_5)_2$ and $Mn_2(CO)_{10}$ gives an ionic product, $[Nb_2H(CO)_2(\eta\text{-}C_5H_5)_4]Mn(CO)_5$ whose crystal structure was determined. The focus of attention in this paper is the cation; structural parameters for the anion are not exceptional (ref. 29).

Infrared data on several $Mn_2(CO)_8(L)_2$ compounds (L = PPh_2H, $PPh(OPh)_2$, $PPh(NEt_2)_2$, PPr^i_3, $P(C_6H_4F)_3$) and on $Re_2(CO)_8(PPh_2H)_2$, suggests that all except $Mn_2(CO)_8(PPh_2H)_2$ possess D_{4h} or D_{4d} symmetry. The diphenylphosphine-manganese complex appears to be asymmetrically substituted, i.e., $(CO)_5MnMn(CO)_3(PPh_2H)_2$; the reasons for this are not apparent (ref. 30). Additional discussion on infrared and NMR data for other carbonyl compounds is included in this paper.

Many new cationic complexes, derivatives of the manganese (I) species $[Mn(CO)_6]^+$, have been described in a series of four papers by Riera and co-workers (ref. 31-34). The synthetic scheme reported is the one ordinarily used, involving a metal carbonyl halide, halide acceptor, and ligand. Much of this work involved bidentate ligands, and there was apparent interest in syntheses and conversions of isomers. The complexes fac-$[Mn(CO)_3\{Ph_2P(CH_2)_n PPh_2\}(L)]ClO_4$ (n = 1-4; L = various phosphines, phosphites) were prepared from fac-$MnBr(CO)_3(Ph_2P(CH_2)_n PPh_2)$, $AgClO_4$, and L. On heating these isomers, and with a large excess of ligand they are converted to trans-$[Mn(CO)_2(Ph_2P(CH_2)_n PPh_2)(L)_2]ClO_4$ species (ref. 31). Syntheses of either cis,trans-$[Mn(CO)_2(L)_2(N\hat{}N)]ClO_4$ or $[Mn(CO)(L)_3(N\hat{}N)]ClO_4$ (N^N = bipy, phen; L = $P(OMe)_3$, $P(OEt)_3$, $PPh(OMe)_2$, $PPh(OEt)_2$) were accomplished by reacting $Mn(OClO_3)(CO)_3(N\hat{}N)$ with the appropriate ligand in ethanol, the specific product obtained being dependent on the identity of L (ref. 32). The same reactions with a potentially chelating ligand produce the complexes $[Mn(CO)_3(N\hat{}N)(L\hat{}L)]ClO_4$ and $[Mn(CO)_3(N\hat{}N)(\mu\text{-}L\hat{}L)Mn(CO)_3(N\hat{}N)](ClO_4)_2$ with the chelating ligand functioning in either a monodentate or bridging capacity (ref. 33). Using $TlPF_6$ or $AgClO_4$ as a halide acceptor, cis,cis-$MnBr(CO)_2(dppe)(L)$ and L' produced either cis,cis- or trans-$[Mn(CO)_2(L)(L')(dppe)]X$ (X = PF_6, ClO_4; L,L' = phosphines and/or phosphites; isomer designations are the authors) (ref. 34).

The syntheses of several cationic rhenium carbonyls has been reported (ref. 35) These procedures start with either $ReH(CO)_5$ or $ReMe(CO)_5$ which with Ph_3CBF_4 produces $Re(FBF_3)(CO)_5$. Added ligands (L = Me_2CO, MeCN, CO, C_2H_4, C_3H_6, C_5H_{10}) may then be used to displace the BF_4^- ion, giving $[Re(CO)_5(L)]BF_4$. The synthesis of $[Re(CNBu^t)_6]Cl$ by the reaction of $Re_2(OAc)_4Cl_2$ and Bu^tNC has been described (ref. 36, 37).

A zwitterionic compound, IV, is formed in the reaction between $Mn(CH_2CH{=}CH_2)(CO)_5$ and the designated chelating phosphine. Its structure is known through a crystallographic study (ref. 38).



IV

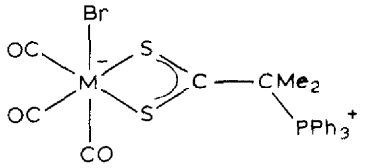
The complex $[Re(CO)_3(MeCN)(phen)]^+$ is inert to thermal substitution, but substitution can be accomplished photochemically. It is suggested that a substitution-labile excited state is generated during photolysis (ref. 39).

The cationic complexes $[M(CO)_3(MeCN)_3]PF_6$ (M = Mn, Re) are precursors to some interesting complexes with oxyanions. These cations react with $P_3O_9^{3-}$ to produce $[Mn(CO)_3(P_3O_9)]^{2-}$, isolable as a Bu_4N^+ salt, (ref. 40). A similar reaction between $[(\eta\text{-}C_5H_5)TiMo_5O_{18}]^{3-}$ and $[Mn(CO)_3(MeCN)_3]PF_6$ produces $(Bu_4N)_4[(\eta\text{-}C_5H_5)TiMo_5O_{18}Re(CO)_3]$ (ref. 41). The structures of these species have tridentate coordination of three terminal oxygen atoms of the anion to fac-positions on the metal.

The rate of ^{17}O exchange between $H_2{}^{17}O$ and $[Re(CO)_6]PF_6$ in MeCN was measured using ^{17}O NMR. A rate law was determined, the rate being first order in complex and second order in H_2O (ref. 42).

III. METAL CARBONYL HALIDES AND DERIVATIVES

The preparations of the following compounds by carbonyl substitution reactions are reported: $ReBr(CO)_4(PPh_2\overset{\frown}{N}CMe{=}CH{-}\overset{\frown}{C}Me)$ (ref. 43); $MBr(CO)_4(L)$, (M = Mn, Re; L = $PBu^t_{3-n}(AMe_3)_n$, n = 2,3, A = Si, Ge, Sn) (ref. 44); fac-$MnBr(CO)_3(P\hat{}P)$ ($P\hat{}P$ = $Fe(\eta\text{-}C_5H_4SiMe_2CH_2PPh_2)_2$) (ref. 45); $MnBr(CO)_{5-n}(L\hat{}L)_n$ (n = 1,2) and $MnBr(CO)_4(\mu\text{-}L\hat{}L)MnBr(CO)_4$ (L = 1,3- and 1,4- $C_6H_4(NC)_2$, p-$CNC_6H_4C_6H_4NC$, p-$CNC_6H_4CH_2C_6H_4NC$) (ref. 46); $[RhA_4]Cl$ (A = μ-$CNC_6H_4C_6H_4NC$-$MnBr(CO)_4$) (ref. 47); $ReX(CO)_3(Me_2Se)_2$ (X = Cl, Br, I) and $ReCl(CO)_3(Me_2S)_2$ (ref. 48); cis-$(CO)_4M(\mu\text{-}A_2Me_4)_2MnBr(CO)_3$ (M = Cr, Mo, W, A = P, As) (ref. 49); trans-$(CO)_4Cr(\mu\text{-}P_2Me_4MnBr(CO)_4)_2$ and $MnBr(CO)_3(\mu\text{-}P_2Me_4Cr(CO)_5)_2$ (ref. 50); and $MX(CO)_3(S_2CCMe_2PPh_3)$ (M = Mn, Re; X = Cl, Br) (ref. 51). Crystal structure studies were carried out on two of the last compounds (Va and b)



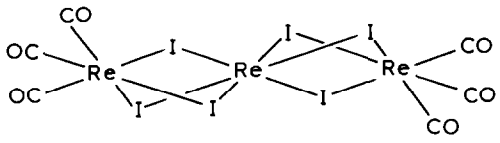
a) M = Mn ; b) M = Re

V

Reactions of fac-$MnBr(CO)_3(dppe)$ and fac-$MnBr(CO)_3(dppm)$ with various phosphorus ligands provided the compounds cis,cis-$MnBr(CO)_2(L)(P\hat{}P)$ (L = $P(OR)_3$, R = Ph,Me,Et; $PPh(OMe)_2$, PEt_3). Oxidation of several complexes using either $NOPF_6$ or NO_2 produced unstable 17 electron species, trans-

$[MnBr(CO)_2(L)(dppe)]^+$; these could be reduced back to 18 electron complexes trans-$MnBr(CO)_2(L)(dppe)$ which are isomers of the original complexes (ref. 34).

The reaction of $Re_2(CO)_{10}$ and Et_4NBH_4 in a phase transfer system (H_2O, CH_2Cl_2) produces $[Re_2Cl(CO)_9]^-$ (ref. 28). Similar reactions with $MnBr(CO)_5$ and $Mn_2(CO)_{10}$ lead to in situ formation of the anionic reactant, $[Mn(CO)_5]^-$, while a similar reduction of $MnBr(CO)_4(PPh_3)$ produces $MnH(CO)_4(PPh_3)$ (ref. 27, 28). A reaction of $Re_2I_2(CO)_8$ and iodine (heptane reflux, 2d.) gives a product $Re_3I_6(CO)_6$ (VI) while the reaction between $Re_2I_2(CO)_6(THF)_2$ and iodine at room temperature yields $Re_4I_8(CO)_6$. Molecular structures were obtained for both compounds by x-ray crystallography (ref. 52). The structures of compound VI is shown below; the second compound is described as having two hexacoordinate $Re(CO)_3$ groups bridged by the $Re_2I_8^{2-}$ anion.



VI

Reactions between $MnBr(CO)_5$ and $R_2PCSNHPh$ (R = Me, Et, Ph, Cy) produce various complexes, including cis-$MnBr(CO)_4(PCy_2H)$, $\overline{Mn(CO)_4\{SC(NPh)PPh_2\}}$, and $\overline{MnBr(CO)_3\{SC(NHPh)PR_2\}}$. As indicated, bidentate coordination from the phosphinothioformamide and phosphinothioformamidium ions is believed to occur through phosphorus and sulfur atoms (ref. 53).

Structural determinations by x-ray diffraction methods have been reported for $Re_2Br_2(CO)_6(Te_2Ph_2)$ (ref. 54), and for fac-$ReBr(CO)_3(NHR_2)_2$ (R = Me, Et) (ref. 55). The rates of fac- $\rightleftarrows$ mer- isomerization of $[ReCl(CO)_3(PPhMe_2)]^+$ have been studied using electrochemical techniques (ref. 56). Resonance Raman spectra were reported for several diimine complexes, $ReX(CO)_3(N\hat{}N)$, (ref. 57). Photolysis of $ReCl(CO)_5$ in a low temperature MeTHF matrix produces $ReBr(CO)_4(MeTHF)$, according to infrared data, and not $Re(CO)_5$ or $[Re(CO)_5]^+$ as had been suggested earlier (ref. 58). The use of $ReCl(CO)_3(phen)$ as a catalyst for hydrogen peroxide and organic peroxide decomposition has been studied (ref. 59).

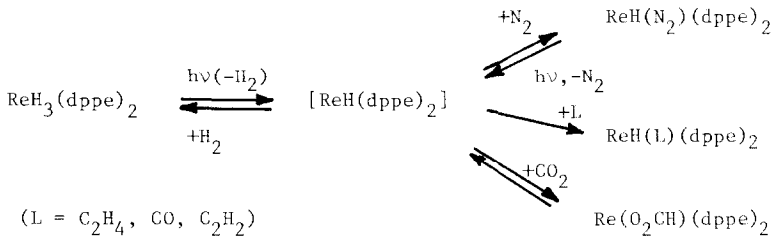
An extensive study on the chemistry of $MnI(NO)(CO)(\eta\text{-}C_5H_5)$ has been published. Reactions with several phosphines give substituted derivatives of this species whereas with harder bases such as amines and ethers dinuclear products having the formula $Mn_2I(NO)_3(\eta\text{-}C_5H_5)_2$ are formed. The synthesis of

$ReI(NO)(CO)(\eta\text{-}C_5H_5)$ was accomplished by iodine cleavage of the methyl-rhenium bond in $ReMe(NO)(CO)(\eta\text{-}C_5H_5)$ (ref. 60). This compound has also been reported to be formed by reaction of $[Re(NO)(CO)_2(\eta\text{-}C_5H_5)]^+$ with iodine ion. Cyanide, bromide, and iodide ions were reported to react with $[Mn(NO)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ to produce $MnX(NO)_2(PPh_3)_2$ (X = CN, Br, I) (ref. 61).

Chlorine adds to $Re(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$ at -15° in CCl_4 to give the $[ReCl(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ ion, isolable after metathesis as a BF_4^- salt. Heat converts the chloride salt to $ReCl_2(CO)_2(\eta\text{-}C_5H_5)$ (ref. 62). The reduction of $ReBr_2(CO)_2(\eta\text{-}C_5H_5)$ using zinc and acetic acid produces $ReH_2(CO)_2(\eta\text{-}C_5H_5)$ (ref. 63).

IV. METAL HYDRIDE DERIVATIVES

Some of the more interesting chemistry in this area, from four research groups, concerns polyhydrido-rhenium phosphine complexes. Geoffroy and coworkers (ref. 64) photolyzed $ReH_3(dppe)_2$ giving a reactive intermediate believed to be $ReH(dppe)_2$. Reactions of this species are summarized in the scheme below. When photolyzed in C_6D_6, this complex rapidly undergoes H/D exchange between C_6D_6 and the ortho hydrogens on the phenyl rings. Photolysis



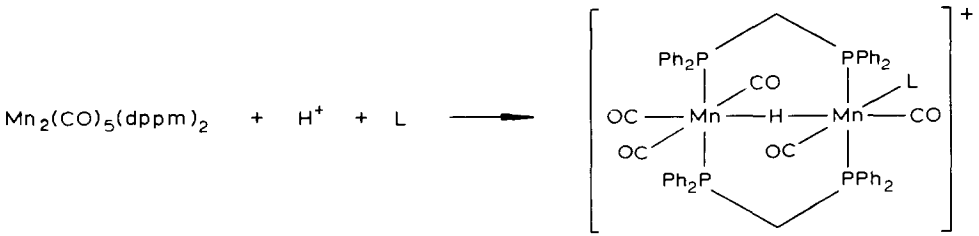
studies were also carried out on ReH_5L_3 and ReH_3L_4 complexes (L = PPh_3, PPh_2Me, $PPhMe_2$) with phosphine dissociation being the primary initial photoprocess. If hydrogen is present ReH_3L_4 complexes are converted first to ReH_5L_2 and then to ReH_7L_2 upon photolysis (ref. 65).

Other work in this area has originated in Felkin's (ref. 66) and Caulton's (ref. 67) laboratories. The former group described the reaction of $ReH_7(PPh_3)_2$ with CH_2=$CHBu^t$ and benzene to give $ReH_2(PPh_3)_2(\eta^5\text{-}C_6H_7)$ while the latter described reactions of photogenerated $ReH_5(PPhMe_2)_2$. This species reacts with cyclopentene forming $ReH_3(PPhMe_2)_3(\eta^2\text{-}C_5H_8)$; upon further photolysis C_5H_{10}, $ReH_2(PPhMe_2)_2(\eta\text{-}C_5H_5)$ and $ReH_4(PPhMe_2)(\eta\text{-}C_5H_5)$ are formed. The intermediate $ReH_5(PPhMe_2)_2$ also reacts with C_6H_6, CH_2=$CHBu^t$ and N_2 giving $Re(CH_2CH_2CMe_3)(PPhMe_2)_2(\eta\text{-}C_6H_6)$ and fac-$Re(o\text{-}C_6H_4PMe_2)(PPhMe_2)_3(N_2)$. Crystal

structure studies were carried out on $ReH_2(PPh_3)_2(\eta^5\text{-}C_6H_7)$ (ref. 66), $ReH_3(PPhMe_2)_3(\eta^2\text{-}C_5H_8)$ and fac-$\overleftarrow{Re(o\text{-}C_6H_4PMe_2}(PPhMe_2)_3(N_2)$, (ref. 67).

Walton et al. (ref. 68) described the one electron oxidation of dark red $Re_2H_8(PPh_3)_4$ to give blue $[Re_2H_8(PPh_3)_4]^+$. Reactions of ReH_7L_2 (L = PPh_3, PPh_2Et) with cyclohexyl and tert-butyl isocyanides with added KPF_6 give the products $[Re(CNR)_4(L)_2]PF_6$.

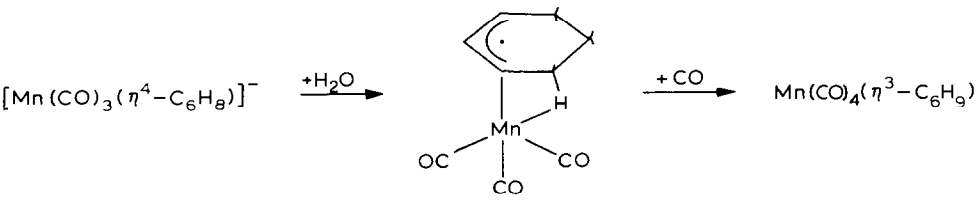
It is possible to protonate the metal-metal bond in $Mn_2(CO)_5(dppm)_2$, with concurrent addition of another ligand. The isolable products $Mn_2H(X)(CO)_5(dppm)$ (X = CN, Br) and $[Mn_2H(L)(CO)_5(dppm)_2]^+$, VII (L = CO, CNtol, MeCN) may be converted back to the starting material by a reaction with $LiBHEt_3$ (ref. 69).



VII

The rhenium-rhenium bond in $Re_2(CO)_5(\eta\text{-}C_5H_5)_2$ can also be protonated at low temperature, using a strong acid, CF_3SO_3H (ref. 70).

Lemanna and Brookhart (ref. 71) have shown that an anionic complex $K[Mn(CO)_3(\eta^4\text{-}C_6H_8)]$ is formed by reaction of $KBHEt_3$ with either $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ or $Mn(CO)_3(\eta^5\text{-}C_6H_7)$. This complex exhibits ν(CO) absorptions at 1930, 1840, and 1789 cm^{-1}. Addition of water to this species produces $Mn(CO)_3(\eta^3\text{-}C_6H_9)$ for which structure VIII was proposed. This compound is fluxional on the NMR time scale. It will add CO, breaking the unique electron deficient Mn-H-C bond. Similar chemistry starting with $Mn(CO)_3(\eta^5\text{-exo-1-}RC_6H_6)$ (R = Me,Ph) has also been described (ref. 72).



(VIII)

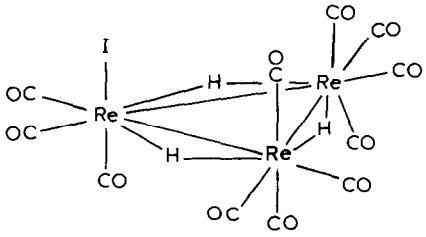
Elaborate and extensive chemistry resulting from H_2 addition to $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ has been reported (ref. 73). Crystal structure studies were carried out on two compounds prepared in this work, $R_5(\mu\text{-}Cl)_3Re_3Re_3(\mu\text{-}Cl)_3(H)R_4$ and $Re_3(\mu\text{-}Cl)_3(Cl)(H)(PPh_3)R_4$ (R = CH_2SiMe_3). The same group reported on reactions of $ReCl_3(NPh)(PMe_3)_2$, with Na/Hg (giving $ReH(CH_2PMe_2)(PMe_3)_2(NHPh)$), with CO (giving $Re(NHPh)(CO)_2(PMe_3)_3$) and with butadiene (giving $Re(NHPh)(\eta^4\text{-}C_4H_6)(PMe_3)_3$) (ref. 74).

The reactions of $PPN[VH(CO)_3(\eta\text{-}C_5H_5)]$ and $MoH(CO)_3(\eta\text{-}C_5H_5)$ with various metal carbonyl species has been studied. Reactions of the former hydride complex with $ReMe(CO)_5$ and $Re(COMe)(CO)_5$ at 50°C are particularly interesting, forming two rhenium complexes, $[ReH(Me)(CO)_4]^-$ and $[ReH(COMe)(CO)_4]^-$ along with $V(CO)_4(\eta\text{-}C_5H_5)$. These species could not be isolated and were characterized by IR and NMR spectroscopy, and by their reaction with CO to give $[Re(CO)_5]^-$ (ref. 75).

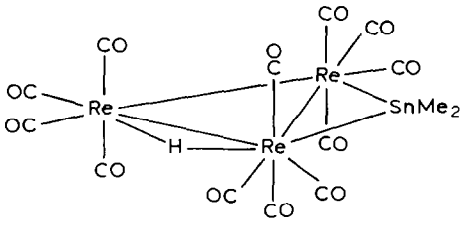
Results of an extensive study on the low temperature photolyses of several bis-cyclopentadienyl rhenium compounds in Ar or Ar/CO matrices were described in a communication (ref. 76). The photolysis reaction of $Re(CO)_2(\eta^2\text{-}C_5H_6)(\eta\text{-}C_5H_5)$ without CO present proceeds through three intermediates to $ReH(\eta\text{-}C_5H_5)_2$. The photolysis of $ReH(\eta\text{-}C_5H_5)_2$ in Ar/CO is dependent on conditions giving either a new monocarbonyl species (uncharacterized) or $Re(\eta\text{-}C_5H_5)_2$.

A useful synthesis of $MnH(CO)_4(PPh_3)$ by a phase transfer reaction was described earlier in this review (ref. 27, 28). The compounds $Re_3H(CO)_{14}$, $Re_3H_3(CO)_{12}$, and $Re_4H_4(CO)_{12}$ were identified among products of photolysis of $Re_2(CO)_{10}$, NO, and 1,3,5-C_8H_{10} (ref. 22). A preparation of $ReH_2(CO)_2(\eta\text{-}C_5H_5)$ was also mentioned (ref. 63).

Studies on polynuclear hydride species have continued. The preparation of $Et_4N[Re_3H_3(OEt)(CO)_9]$ from $Et_4N[Re_3H_4(CO)_{10}]$ and EtOH and its structural characterization by x-ray diffraction have been reported (ref. 77). Reactions of either $NEt_4[Re_4H_4(I)(CO)_{15}]$ or $NEt_4[Re_4H_4(CO)_{15}]$ with iodine in ethanol at room temperature produce $Et_4N[Re_3H_3(I)(CO)_{11}]$ (IX) along with two other species. A crystal structure determination was carried out on compound IX (ref. 78). The reaction of $[Ph_4As]_2[Re_3H(CO)_{12}]$ with Me_2SnCl_2 gives (X) whose molecular structure was also determined (ref. 79). The structural characterization of $Re_3H_3(CO)_{11}(PPh_3)$ was also reported, the PPh_3 group is in an equatorial position, unlike the iodide ion in complex X (ref. 80). Gas phase PES spectra have been reported for $Re_3H_3(CO)_{12}$, $Re_4H_4(CO)_{12}$ (ref. 81) and $Mn_3H_3(CO)_{12}$ (ref. 82) and excited state decay properties of $(Bu_4N)_2[Re_4H_6(CO)_{12}]$ have been described (ref. 83). Further description and classification



IX



X

of metal carbonyl cluster systems (including $Re_4H_4(CO)_{12}$) was presented (ref. 84).

The use of $MnH(CO)_5$ as a stoichiometric hydroformylation reagent was described (ref. 85). The reagent was also seen to hydrogenate anthracene derivatives. A study on this reaction supported a free radical mechanism (ref. 86).

Gas phase proton affinities have been determined for several compounds including $MnMe(CO)_5$ (188 Kcal mol^{-1}), $ReMe(CO)_5$ (191 Kcal mol^{-1}), $MnH(CO)_5$ (204 Kcal mol^{-1}), and $Mn(CO)_3(\eta\text{-}C_5H_4Me)$ (203 Kcal mol^{-1}), (ref. 87).

Various silanes add oxidatively to $Re(CO)_3(\eta\text{-}C_5H_5)$, producing cis-$ReH(SiR_3)(CO)_2(\eta\text{-}C_5H_5)$ (SiR_3 = $SiPh_3$, $Si(CH_2Ph)_3$, $SiPh_2H$). The products can be easily deprotonated; reprotonation produces the trans- isomer (ref. 88). A similar oxidative addition reaction between Ph_2SiH_2 and $Mn(CO)_3(\eta\text{-}C_5H_4Me)$ yields $MnH(SiPh_2H)(CO)_2(\eta\text{-}C_5H_4Me)$. Treatment of this compound with PCl_5 in CCl_4 gives $MnH(SiPh_2Cl)(CO)_2(\eta\text{-}C_5H_4Me)$ and pyrolysis of this species causes reductive elimination of Ph_2SiHCl. The manganese compound was regarded by the authors of this paper as a protecting group in this silane synthesis (ref. 89).

V. COMPLEXES WITH CARBON LIGANDS

Two papers have appeared describing reactions of homoleptic rhenium alkyl compounds. Hexamethylrhenium reacts with Bu^tNC and NO. The product of the former reaction is $Re(CNBu)_2(CMe{=}NBu)_3$ (ref. 90). A stable, orange-red crystalline product having the formula $Re(NO)Me_6$ is formed if the latter reaction is run in petroleum ether at -78°; however in ether at room temperature the product is ReO_2Me_3. Nitric oxide also reacts with Li_2ReMe_8 and $[Re(CH_2SiMe_3)_4]_2N_2$ (ref. 91). The reaction between $Mn(CH_2Ph)_2$ and NO was reported, giving a product of stoichiometry $Mn(NO)CH_2Ph$ (ref. 92). Extensive chemistry of $Re_3(\mu\text{-}Cl)_3(CH_2SiMe_3)_6$ was mentioned earlier in this review (ref. 73).

Various alkyl compounds of these metals were synthesized during the last year. Chloromethyl-manganese and -rhenium compounds were prepared from the pentacarbonylmetallate anions and either ICH_2Cl (for $Mn(CH_2Cl)(CO)_5$) or $MeOCH_2Cl$ (for $Re(CH_2Cl)(CO)_5$). $Re(CH_2OMe)(CO)_5$ is also obtained in the latter reaction, in approximately the same amount as the chloromethyl-rhenium complex. The manganese compound reacts with PPh_3 over several days giving $MnCl(CO)_3(PPh_3)_2$; the rhenium analogue is unreactive toward PPh_3 under similar conditions (ref. 93). Photolysis of $Mn_2(CO)_{10}$, $MnBr(CO)_5$, and $ReBr(CO)_5$ with $TiMe_2(\eta\text{-}C_5H_5)_2$ gives $MMe(CO)_5$ and $Mn(CO)_3(\eta\text{-}C_5H_5)$ (ref. 94). The preparation of $Fe[\eta^6\text{-}C_6Me_5CH_2Mn(CO)_5](\eta\text{-}C_5H_5)$ from $Fe(\eta^6\text{-}C_6Me_5CH_2)(\eta\text{-}C_5H_5)$ and $MnBr(CO)_5$ was reported (ref. 95). The species $(CO)_5ReCH_2CH_2Re(CO)_5$ is obtained in a reaction between $[Re(CO)_5(\eta\text{-}C_2H_4)]^+$ and $[Re(CO)_5]^-$; its structure was determined in a crystallographic study (ref. 35, 96). Also reported in the latter paper are the compounds $(CO)_5ReCH_2CH_2M(CO)_3(\eta\text{-}C_5H_5)$ (M = Mo, W) (ref. 96).

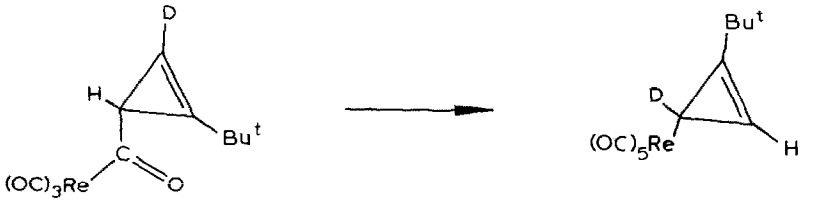
The preparations of various manganese and rhenium compounds of the formula $M(PPh_2(CH_2)_nCH_2(CO)_4$ (M = Mn, n = 0-3; M = Re, n = 1-3) were reported (ref. 97). These syntheses were accomplished from $MBr(PPh_2(CH_2)_nCH_2Cl)(CO)_4$ and sodium amalgam. Two of the products were subjects of crystallographic studies. A thermal rearrangement of $Mn(PPh_2CH_2CH_2CH_2CH_2)(CO)_4$ to $Mn(PPh_2CH_2CH_2CHCH_3)(CO)_4$ occurred at 100° (hexane, sealed tube). Both CO and SO_2 were shown to insert into the metal-carbon bond in the product. Crystal structure studies on both isomers were also reported (ref. 98,99).

Reduction of $MBr(CO)_4(PR_2SH)$ (M = Mn, R = Me; M = Re, R = Me, Ph) by sodium amalgam first gives $Na_2[M_2(PR_2S)_2(CO)_8]$. With an excess of sodium, these dinuclear compounds are further reduced to produce $Na_2[M(CO)_4(PR_2S)]$. The dianionic complexes react with dimethyl sulfate or 1,3-dibromopropane to produce $MMe(PR_2SMe)(CO)_4$ and $M(PR_2SCH_2CH_2CH_2)(CO)_4$, respectively (ref. 100). Analogous reactions between $Na_2[Mn(CO)_4PR_2O]$ (R = Me, Ph) and several α-ω-dihalide produce similar products, two of which were subjects of crystallographic studies (ref. 101).

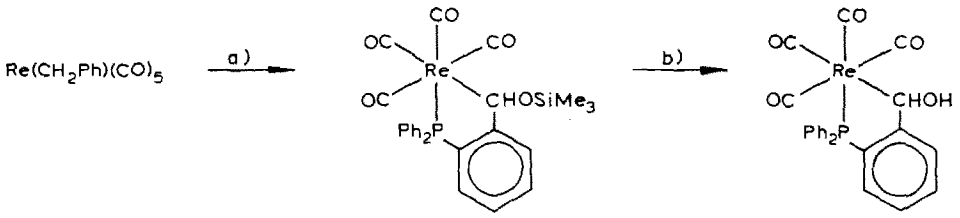
The synthesis of several compounds having the formulas $Mn(CH_2COR)(CO)_5$ (R = Me, Ph, OMe) is accomplished from reactions of $[Mn(CO)_5]^-$ and the appropriate organic halide. A similar reaction with $[Mn(CO)_4(PPh_3)]^-$ provides cis-$Mn(CH_2COMe)(CO)_4(PPh_3)$, whose structure was determined by x-ray diffraction. A short carbon-carbon bond in the $-CH_2\overset{O}{\overset{\|}{C}}-$ group of 1.453(8) Å was taken as an indication of an interaction between the metal and the β-carbon in the organic group (ref. 102).

Two rhenium-acyl compounds, $Re(COCHCPh{=}CPh)(CO)_5$ and $Re(COCHCD{=}CBu)(CO)_5$, were prepared from the appropriate acyl chloride and $Na[Re(CO)_5]$. These

complexes decarbonylate smoothly at 20° to give cyclopropenyl-rhenium complexes. This decarbonylation is accompanied by an allylic rearrangment; this is illustrated by the equation below (ref. 102).



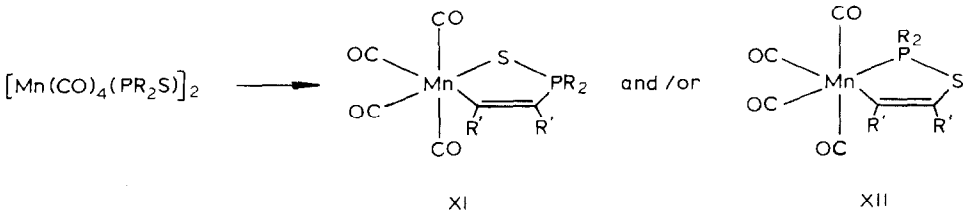
Vaughan and Gladysz (ref. 104) have presented three synthetic routes to hydroxymethyl-rhenium and -manganese carbonyl complexes. These are: the borane reduction ($BH_3 \cdot THF$) of an acyl-metal complex followed by hydrolysis; the reaction of $Re(CH_2Ph)(CO)_5$ and $Ph_2P(o\text{-}C_6H_4CHO)$; and the reaction of $Re(CH_2Ph)(CO)_5$ and $Ph_2P(o\text{-}C_6H_4CH_2OSiMe_2Bu^t)$ followed by hydrolytic cleavage of the siloxy group. This last route is described in the reaction scheme below.



a) $Ph_2P(o\text{-}C_6H_4CH_2OSiMe_2Bu^t)$; $-PhCH_3$; b) $Et_4NF \cdot H_2O$; $-Me_2Bu^tSiF$

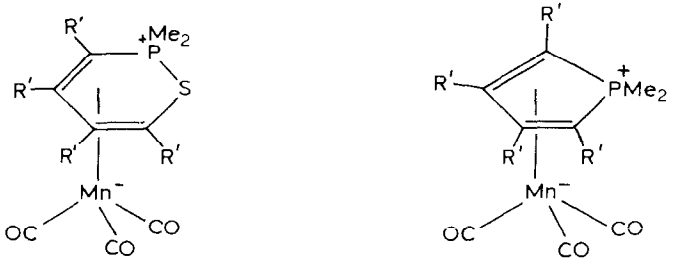
The addition of $Mn(SiMe_3)(CO)_5$ to benzaldehyde (2 wks, 5°C) produces a 65-90% yield of $Mn(CHPhOSiMe_3)(CO)_5$. This compound decomposes at 80° to give $Mn_2(CO)_{10}$. The reaction of $Mn(SiMe_3)(CO)_5$ and C_3H_7CHO did not give an analogous product, but produced $MnH(CO)_5$; however under 10 atm CO the acyl compound $Mn(COCHROSiMe_3)(CO)_5$ is formed; it is suggested that the alkyl-manganese compound is an unstable intermediate in this reaction.

The compounds $[M(CO)_4(PR_2S)]_2$ (M = Mn, Re; R = Me, Ph) add one equivalent of activated acetylene to give the two isomeric products shown below (XI, XII), (ref. 106, 107).



XI XII

Further reaction of XI (M = Mn, R = Me, R' = CO_2Me) with the acetylene then gives XIII. The structures of $[Mn(CO)_4(PMe_2S)]_2$ (ref. 108) and XI (M = Mn,



XIII (R' = CO_2Me) XIV (R' = CO_2Me)

R = Me, R' = CO_2Me) were determined by crystallography. Reactions of XIII with $(NH_4)_2Ce(NO_3)_6$ causes degradation to a substituted thiophene, while Raney nickel causes desulfurization of the compound, producing XVI. The molecular structure of XIV was also determined (ref. 109).

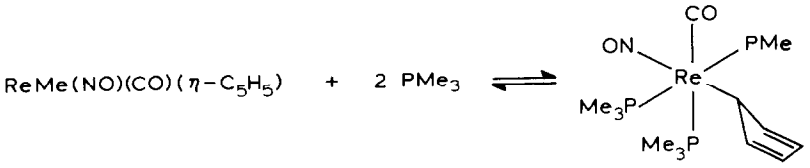
The metal atom stereochemistry for CO insertion into the methyl-manganese bond in $MnMe(CO)_5$ was determined using ^{13}C NMR spectroscopy. Data were consistent with methyl migration to an adjacent carbonyl group (ref. 110, 111). Protonic acids cause an acceleration of methyl migration in $MnMe(CO)_5$ (ref. 112). Rates of 3 + 2 cycloaddition reactions in $Mn(CH_2C{\equiv}CR)(CO)_4(L)$ (L = CO, PPh_3) and other metal complexes, have been measured. The phosphine complex reacts more rapidly (ref. 113). Study of cyclization and other reactions was presented in a thesis (ref. 114).

The preparations of a variety of formyl derivatives and a study of their rates and mechanisms of decomposition are contained in a paper by Gladysz et al. (ref. 115). This study included the anionic complexes $[MnR(CHO)(CO)_4]^-$ (R = PhCO, $MeOCH_2CO$, MeOCO, CF_3CO, CF_3, $SnPh_3$) and $[ReR(CHO)(CO)_4]^-$ (R = Br, Ch_2Ph). An earlier reference was made in this article to $[ReH(COMe)(CO)_4]^-$,

formed by a hydride transfer reaction (ref. 75). The review on metalla-β-diketonates was cited in the introduction (ref. 2). Cyclic voltammetry experiments on $Cr[Re(CO)_4(COMe)_2]_3$, $Fe[Re(CO)_4(COMe)_2]_3$, and $Cu[Re(CO)_4(COMe)_2]_2$ have been reported (ref. 116).

Gas-phase metal-carbon bond energies were determined for metals in the first transition series. This was done by measurement of the energetics of reactions between the univalent gaseous ions and various molecular species. Comparisons among the various metals were provided (ref. 117).

Several derivatives of cyclopentadienyl-rhenium nitrosyl complexes deserve mention at this point. Casey et al. (ref. 118) demonstrated that $ReMe(NO)(CO)(\eta\text{-}C_5H_5)$ and trimethylphosphine exist in equilibrium with a σ-cyclopentadienyl-rhenium complex, XV, in solution:



XV

An intermediate 1:1 adduct of these reactants was detected in solution. A σ-cycloheptatrienyl-rhenium complex has been prepared by Sweet and Graham (ref. 119) in a two step reaction. Addition of $ReH(NO)(CO)(\eta\text{-}C_5H_5)$ to $C_7H_7BF_4$ initially produces an olefin complex $[Re(NO)(CO)(\eta^2\text{-}C_7H_8)(\eta\text{-}C_5H_5)]BF_4$; this complex reacts with Et_3N to give $Re(NO)(CO)(\eta^1\text{-}C_7H_7)(\eta\text{-}C_5H_5)$. The carbene complex $[Re(CH_2)(CO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ adds dialkyl sulfides to give $[Re(CH_2SR_2)(NO)(PR_3)(\eta\text{-}C_5H_5)]PF_6$ (R = Me, $PhCH_2$). The sulfide can be displaced with PPh_3, giving $Re(CH_2PPh_3)(NO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$, and with SMe^-, giving $Re(CH_2SMe)(NO)(PPh_3)(\eta\text{-}C_5H_5)$. A further reaction of the latter compound with the carbene complex was recorded (ref. 120).

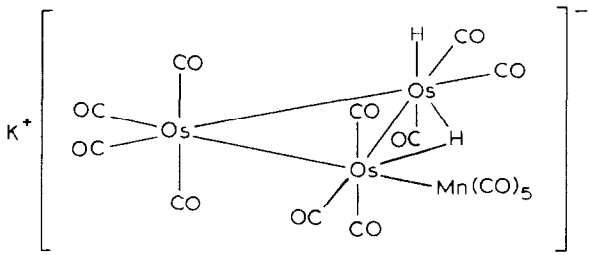
Methyllithium reacts with $ReCl(CO)_2(N_2)(PPh_3)_2$; after protonation a carbene complex $ReCl(CO)(CMeOH)(N_2)(PPh_3)_2$ can be isolated (ref. 121). The preparation of the diphenylcarbene complex, $Mn(CO)_2(CPh_2)(\eta\text{-}C_5H_5)$ from $W(CO)_5(CPh_2)$ and $Mn(CO)_2(THF)(\eta\text{-}C_5H_5)$ was mentioned (ref. 122). The compound reacts with trans-RCH=CHR (R = CO_2Et) to produce the expected substituted cyclopropane. X-ray diffraction studies were reported for $Mn(CO)_2(C{=}C{=}CCy_2)(\eta\text{-}C_5H_5)$ (ref. 123) and for $Mn(CO)_2(C{=}CMe_2)(\eta\text{-}C_5H_5)$ (ref. 124). A discussion of the reactions of the former complex with various nucleophiles including

Bu^tLi (ref. 124), PPh_3, PEt_3, Bu^tS^- and NMe_2^- (ref. 123) is included in these papers. The formation of the carbyne complex $[ReCl(CNHMe)(dppe)_2]BF_4$ occurs on protonation of $ReCl(CNMe)(dppe)_2$; the structure of this product was elucidated by x-ray crystallography (ref. 125).

The molecular structure of the complex $Mn_2(CO)_4(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2$ was identified in a crystallographic study (ref. 126). PES on this compound (ref. 127) and on the methylcyclopentadienyl analogue (ref. 128) were reported. Molecular orbital calculations were presented for a series of carbyne complexes, $[Mn(CR)(CO)_2(\eta\text{-}C_5H_5)]^+$ (R = Me, Si, Me_3, Ph, NEt_2) in another paper (ref. 129). Four papers on compounds having carbyne groups bridging manganese and another metal have appeared from Stone and coworkers (ref. 130-133); this work is discussed further in the next section.

VI. DERIVATIVES OF METALS AND METALLOIDS

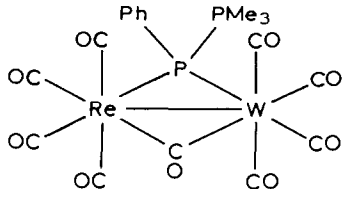
Various compounds having simple σ bonds between manganese or rhenium and another transition metal have been encountered. Compound (I), $[Rh_2(TM4\text{-bridge})_4Mn_2(CO)_{10}](PF_6)_2$, was mentioned earlier in this review (ref. 10). A compound having the formula $K[Os_3MnH_2(CO)_{15}]$ was formed by the reaction of $Os_3H_2(CO)_{10}$ and $K[Mn(CO)_5]$; the anion was believed to have structure XVI (ref. 134).



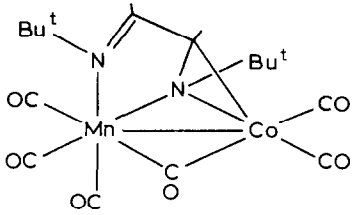
XVI

A compound of similar structure, $Os_3ReH(CO)_{15}(MeCN)$ was formed when $Os_3Re_2H_2(CO)_{20}$ was heated in MeCN (ref. 135, 136). Its structure was confirmed in a crystallographic study (ref. 137). Reactions of $Os_3ReH(CO)_5(MeCN)$ were reported with various reagents including CO (which gives $Os_3ReH(CO)_{12}$, a molecular species containing a tetrahedron of metal atoms).

Data on the infrared and Raman spectra of $(CO)_5ReM(CO)_4CPh$ (M = Cr, Mo, W) have been published (ref. 138). The compounds $(CO)_5ReM(CO)_4CPh$ (M = Cr, W) react with PMe_3 to give dinuclear products $(CO)_4Re(\mu\text{-}CO)(\mu\text{-}CPhPMe)_3M(CO)_4$; a crystal structure determination was carried out on one of these compounds, XVII (ref. 139).



XVII

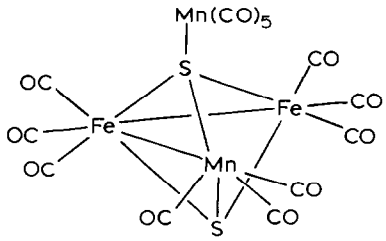


XVIII

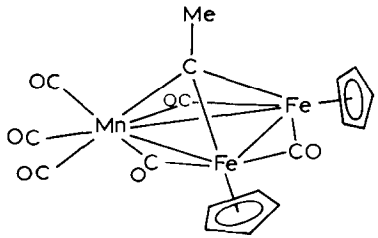
The unusual structure of $MnCo(CO)_6(tBuN{=}CHCH{=}NBu^t)$ XVIII, is shown above; this was determined by x-ray diffraction (ref. 140). This and related complexes had been prepared earlier by reaction of $[Co(CO)_4]^-$ with $MnBr(CO)_3(DAB)$ (DAB = various 1,4 diazabutadienes). The fluxionality of these species was studied by ^{13}C NMR techniques (ref. 141). Field desorption mass spectra of these compounds were described in a separate paper (ref. 142).

Complete assignments of the IR absorptions for the three compounds $MCo(CO)_9$ (M = Mn, Tc, Re) have been made (ref. 143).

Photolysis of $Mn_2(CO)_{10}$ and $Fe_2(CO)_6S_2$ in THF leads to the formation of a new tetrametallic compound, $Mn_2Fe_2S_2(CO)_{14}$. The structure of this species was established to be XIX, below (ref. 144). A manganese-iron cluster compound, $(\eta\text{-}C_5H_5Fe)_2Mn(CO)_6(\mu\text{-}CMe)$, XX, was prepared from $Fe_2(CO)_3(\mu\text{-}C{=}CH_2)(\eta\text{-}C_5H_5)_2$ and $Mn_3H_3(CO)_{12}$ (ref. 130). The reaction of $Mn(CO)_3(\eta\text{-}C_5H_4Me)$ and $Co(CO)(PMe_3)(\eta\text{-}C_5H_5)$ yielded $C_5H_5Co(PMe_3)(\mu\text{-}CO)_2Mn(CO)(\eta\text{-}C_5H_4Me)$ (ref. 145).



XIX



XX

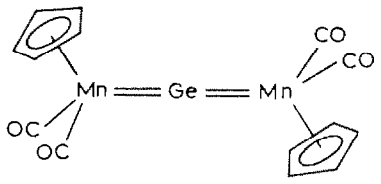
The structural determination of three compounds having phosphido-groups bridging manganese and platinum was the subject of a paper by Braunstein et al. (ref. 146). These compounds were obtained in the reaction between $cis\text{-}PtCl_2(PPh_2Cl)$ and $Na[Mn(CO)_5]$. Complexes having carbene and carbyne

ligands bridging manganese and platinum were described (ref. 131-133).

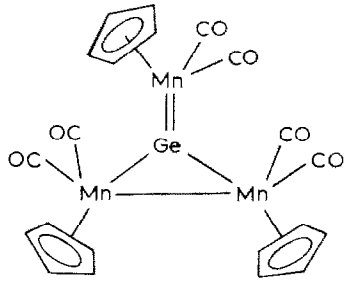
The synthesis and structural characterization of two manganese-mercury derivatives was reported. The complex $(CO)_5MnHg(N_3R_2)$ ($R = o\text{-}C_6H_4Cl$) was prepared in a disproportionation reaction between $Hg[Mn(CO)_5]_2$ and $Hg(N_3R_2)$ (ref. 147). A cyclic tetramer, $[HgMn(CO)_2(\eta\text{-}C_5H_4Me)]_4$, was obtained from $K[Mn(GeH_3)(CO)_2(\eta\text{-}C_5H_5)]$ and Hg^{2+} (ref. 148). The precursor was prepared by the reaction of $K[GeH_3]$ and $Mn(CO)_3(\eta\text{-}C_5H_4Me)$, (ref. 149). Short Hg-Hg distances of 2.888 Å were identified in $[HgMn(CO)_2(\eta\text{-}C_5H_4Me)]_4$, suggesting delocalized bonding between these atoms.

Several group IVA derivatives of manganese and rhenium have been mentioned in earlier discussions; these include $Mn(H)(SiPh_2X)(CO)_2(\eta\text{-}C_5H_4Me)$ (X = H, Cl) (ref. 89), $ReH(SiR_3)(CO)_2(\eta\text{-}C_5H_5)$ (R = Ph, $PhCH_2$) and $ReH(SiPh_2H)$-$(CO)_2(\eta\text{-}C_5H_5)$, (ref. 88). These rhenium complexes are formed by photolysis of $Re(CO)_3(\eta\text{-}C_5H_5)$ and the specific silane. They are acids, giving up a proton to various bases. The anionic complexes $[Re(SiR_3)(CO)_2(\eta\text{-}C_5H_5)]^-$ which form were shown to react with a variety of species R'X to give $Re(R')(SiR_3)(CO)_2(\eta\text{-}C_5H_5)$ compounds (R' = Me, Cl, Br, I, SnR_3). The complex $Re_3H(SnMe_2)(CO)_{12}$ was referred to earlier, with synthesis and structure determination being described (ref. 79). Also mentioned was a reaction of $Mn(SiMe_3)(CO)_5$ and benzaldehyde to form $Mn(CHPhOSiMe_3)(CO)_5$ (ref. 105).

The attempted protonation of $K[Mn(CO)_2(GeH_3)(\eta\text{-}C_5H_4Me)]$ with acetic acid at room temperature produces $Ge[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_2$ (XXI). This compound reacts with Hg^{2+} ion to give a second new species, $Ge[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_3$ (XXII). Crystal structure studies were carried out on both compounds (ref.150).



XXI



XXII

The preparation of $\overline{Mn(SiF_2CH{=}CBu^tSiF_2)}(CO)_2(\eta\text{-}C_5H_4Me)$ was accomplished by photolyzing $Mn(CO)_3(\eta\text{-}C_5H_4Me)$ and the disilacyclobutene (ref. 151). Redistribution reactions between organo-lead derivatives of manganese and rhenium have been studied;

$$Me_4Pb + Me_2Pb[M(CO)_5]_2 \rightleftharpoons 2Me_3PbM(CO)_5$$

(M = Mn, Re)

the rate for the reaction of the manganese complex is faster, and the rates for both manganese and rhenium complexes depend on solvent (ref. 152). A crystallographic study was carried out on the compound $ClSn[Mn(CO)_4(PPh_3)]_3$ (ref. 153).

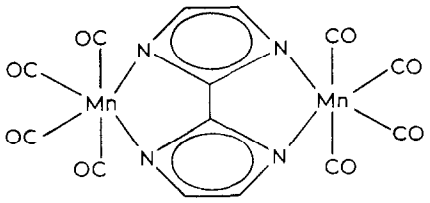
The reaction between $MnH(CO)_5$ and $Ph_2(Me)SnH$ gives a 40% yield of $Mn(SnPh_2Me)(CO)_5$, $Mn_2(CO)_{10}$ was also obtained. When the same reaction was carried out with an optically active tin compound, $\overset{*}{Sn}(Ph)(Me)(CH_2CPhMe_2)H$, optical activity was not retained in the product (ref. 154). The compound trans-$Mn[\overset{*}{Sn}(Ph)(Me)(\alpha\text{-Np})](CO)_4(PPh_2N\overset{*}{M}eC\overset{*}{H}MePh)$ was prepared. The two diastereomeric forms could be separated by fractional crystallization (ref. 155).

VII. COMPLEXES WITH GROUP VA AND VIA LIGANDS

In accord with previous Annual Survey articles by this author, the coverage in this section will not consider complexes with simple Group VA and Group VIA donor ligands. Emphasis is placed on those complexes in which organo derivatives of these elements function in some other capacity, such as bridging two or more metals or as part of a delocalized ligand. This classification includes compounds of many and various structural types. Coverage in this section is presented in the order: N, P and As, O, S and Se.

A group of compounds having the formula $Re(CO)_2(PPh_3)_2(N_3R_2)$ (R = Ph, tol, p-C_6H_4F, p-C_6H_4Cl) was prepared from $Li[N_3R_2]$ and $ReCl(CO)_3(PPh_3)_2$, (ref. 156). A structural study was carried out on the tolyl derivative; rhenium assumes octahedral coordination, and the diaryl triazenide anion functions as a bidentate ligand. The phosphines are cis to this ligand, and trans to each other (ref. 157).

The bibenzoimidizolate and bisimidizolate dianions are capable of bridging two metal atoms. The structure of one such complex, $Mn_2(CO)_8(C_6H_4N_4)$ is shown below, XXIII (ref. 158). A crystal study was carried out for the compound $Mn(N{=}N{=}CR_2)(CO)_2(\eta\text{-}C_5H_5)$ (R = CO_2Me). This compound was prepared from $Mn(CO)_2(THF)(\eta\text{-}C_5H_5)$ and the disubstituted diazoalkane (ref. 159). The nitrogen atom in pyrrolylmanganese tricarbonyl can function as a ligand, and the complexes $Mn(CO)_3\{\eta^5\text{-}C_4H_4NM(CO)_5\}$ (M = Cr, Mo, W) were prepared (ref. 160). Molecular orbital calculations have been carried out on slipped and skewed out of plane metalloporphyrin complexes $[Re(CO)_3]_2N_4$ (N_4 = porphyrin) and derived species (ref. 161).

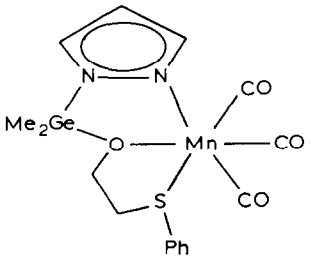


XXIII

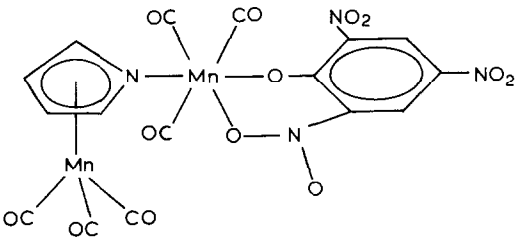
Other references to complexes having nitrogen ligands were cited in earlier sections of this review (see ref. 114, 140-142).

Manning et al. (ref. 162) observed that when $Mn_2(CO)_8(AsPh_3)_2$ is heated in butanol, a degradation occurs with the organometallic product, $Mn_2(\mu\text{-}AsPh_2)_2(CO)_8$, being obtained. They suggest a mechanism for this reaction involving intermediate formation of $Mn(CO)_4(AsPh_3)$ radicals followed by As-C bond cleavage. This reaction is not found with phosphine complexes. Dinuclear $M_2(\mu\text{-}PR_2)_2(CO)_8$ species (M = Mn, Re; R = $GeMe_3$, Bu^t) were sometimes obtained in reactions between $MBr(CO)_5$ and $PBu^t_2GeMe_3$ and $P(GeMe_3)_3$ (ref. 44). An electrochemical study on complexes with bridging phosphido and arsenido complexes, $Mn_2(\mu\text{-}AMe_2)_2(CO)_8$ (A = P, As), has been completed (ref. 163). Two papers on the preparations and structures of several complexes with phosphido-groups bridging between manganese and other elements were cited previously in this article (ref. 50, 146), as were six papers on complexes with $-PR_2S-$ bridging groups (ref. 100, 101, 106-109).

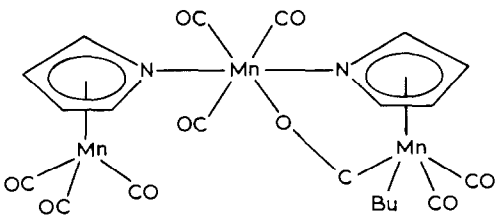
The crystal structure of a phosphabenzene complex, $Mn(\eta\text{-}C_5H_5)(\eta\text{-}2,4,6\text{-}PC_5Ph_3H_2)$, was identified (ref. 164). Raman and infrared spectra on several phospholyl-manganese tricarbonyl complexes indicate that the C_4H_4P ring is a weaker π-donor than the C_5H_5 ring (ref. 165). A paper describing reactions, spectra, and structures of $XAs[Mn(CO)_2(\eta\text{-}C_5H_5)]_2$ compounds (X = Ph, Cl, I) has appeared (ref. 166). Molecular structures of $Me_2Ge(OCH_2CH_2SPh)(C_3HMe_2N_2)\text{-}Mn(CO)_3$, XXIV, (ref. 167), $Mn(CO)_3\{C_4H_4NMn(CO)_3(C_6H_2(NO_2)_3O)\}$, XXV, (ref. 168), and $Mn(CO)_3\{C_4H_4NMn(CO)_3NC_4H_4Mn(CO)_3Bu\}$ XXVI, (ref. 169) were obtained through crystallographic studies. Synthetic procedures for XXV and XXVI were also reported.



XXIV



XXV



XXVI

X-ray diffraction techniques were also used to identify the structures of $Et_4N[Re_3H_3(\mu\text{-}OEt)(CO)_9]$ (ref. 77), $[Re(CO)_3OH]_4 \cdot 2C_6H_6$ (ref. 170), and $Mn(O_2CCF_3)(CO)_5$ and $Mn(O_2CCF_3)(CO)_3(py)_2$ (ref. 171). Other complexes with ligands having oxygen donor functions were cited earlier in this review; this includes the anionic complexes $(Bu_4N)_2[Mn(CO)_3(P_3O_9)]$ (ref. 40) and $(Bu_4N)_2[C_5H_5TiMo_5O_{18}Re(CO)_3]$ (ref. 41). Various sigma bonded perchlorate complexes $Mn(OClO_3)(CO)_3(L\hat{}L)$ were used as precursors in syntheses of many cationic carbonyl complexes (ref. 31, 32, 33).

The diethylcarbamate complex, $Re(O_2CNEt_2)(CO)_3(NHEt_2)$, was prepared from $ReBr(CO)_3(NHEt_2)_2$ and CO_2 (ref. 55). A 17 electron complex $Re(CO)_4(3,5\text{-}Bu^t_2\text{-}C_6H_2O_2)$, has been isolated and its esr spectrum recorded (ref. 172). Derivatives of 17 electron complexes having optically active phosphine ligands have also received recent study (ref. 173).

The reaction between $ReBr(CO)_5$ and cesium-dithiooxalate gives $Cs_4[Re_2(CO)_6(C_2S_2O_2)_3]$. The anionic complex is believed to contain both chelating and bridging dithiooxalate ligands (ref. 174). Photolysis of

$Mn_2(CO)_{10}$ with Ph_2S and Ph_2Se produces the pseudo-cubane complexes, $[Mn(CO)_3SPh]_4$ and $[Mn(CO)_3SePh]_4$ (ref. 175). Manganese and rhenium carbonyls react with $(R_2NCSe)_2Se$ compounds (n = 1,3, R_2N=Et_2N, $O(CH_2CH_2)_2NH$) giving the dimers, $[M(CO)_3(Se_2CNR_2)]_2$ (ref. 176, 177). The seven-coordinate rhenium(III) species, $Re(CO)(Se_2CNR_2)_3$, were also characterized. Various manganese and rhenium carbonyl complexes having formulas $M(CO)_4(SPPh_2CSNR)$ and $[M(CO)_3(SPPh_2CSNR)]_2$ were prepared from $MCl(CO)_5$ and $NHRCSPSPh_2$ (ref. 178, 179). The complexes $MBr(CO)_3(S_2CCMe_2PPh_3)$, (M = Mn, Re), were mentioned at an earlier point in this review (ref. 51). Also identified earlier was the compound $Fe_2Mn_2S_2(CO)_{14}$, a compound with bridging sulfido groups (ref. 144), and various compounds derived from the ligands $[R_2PCS_2]^-$ and $[R_2PCSNR]^-$ (ref. 53).

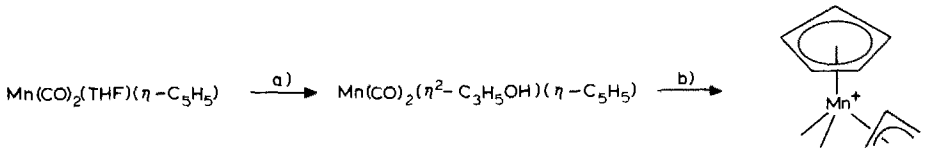
VIII. HYDROCARBON COMPLEXES

Again, as in past years, studies on cyclopentadienylmanganese tricarbonyl derivatives dominate this area. Many articles have already been cited including a valuable review in this area (ref. 1). The following references have been discussed already: the preparation and reactions of several cumulene derivatives, $Mn(CO)_2(C{=}C{=}CR_2)(\eta\text{-}C_5H_5)$ (ref. 123, 124); the preparation of $Mn(CPh_2)(CO)_2(\eta\text{-}C_5H_5)$ from $W(CO)_5(CPh_2)$ (ref. 122); the preparation and structure of $Mn(CO)_2(N{=}N{=}CR_2)(\eta\text{-}C_5H_5)$, (R = CO_2Me) (ref. 159); reactions of $ClAs[Mn(CO)_2(\eta\text{-}C_5H_5)]_2$ (ref. 166); the preparation of $K[Mn(GeH_3)(CO)_2(\eta\text{-}C_5H_5)]$ and reactions of this species (ref. 148-150); the preparation and reactions of several complexes of the form $ReH(SiR_3)(CO)_2(\eta\text{-}C_5H_5)$, (ref. 88, 89), a preparation of $Mn(SiF_2CBu^t{=}CHSiF_2)(CO)_2(\eta\text{-}C_5H_4Me)$ (ref. 151); the preparation, reactions, and structural characterization of various cyclopentadienylmanganese-platinum complexes (ref. 132, 133) and the preparation of bimetallic manganese-chromium (ref. 50) and manganese-cobalt related species (ref. 145); the reaction of $Re(CO)_2(PPh_3)(\eta\text{-}C_5H_5)$ with chlorine (ref. 62); and an MO study on a number of carbyne complexes, $[Mn(CR)(CO)_2(\eta\text{-}C_5H_5)]^+$ (ref. 129). Also mentioned earlier was the preparation of $ReH_2(CO)_2(\eta\text{-}C_5H_5)$ (ref. 63) and the protonation of $Re_2(CO)_5(\eta\text{-}C_5H_5)_2$ (ref. 70). The dinuclear compound, $Mn_2(CO)_4(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2$, was the subject of a crystal structure determination and two PES studies (ref. 126-128).

The compound $Mn(CO)_3(\eta\text{-}C_5H_5)$ was obtained as one of two organometallic products from the photolysis of $Mn_2(CO)_{10}$ and $TiMe_2(\eta\text{-}C_5H_5)_2$ (ref. 94). A number of new derivatives of $Mn(CO)_3(\eta\text{-}C_5H_5)$ have been prepared and characterized. This includes $[Cr_2(SBu^t)_2(\eta\text{-}C_5H_5)_2S]Mn(CO)_2(\eta\text{-}C_5H_5)$, a compound in which the lone sulfur atom bridging the two chromium atoms acts as a ligand to manganese. The structure of this compound was determined by crystallography

(ref. 180). The compound $(\eta\text{-}C_5H_5)(CO)_2Mn(Me_2PPMe_2)Mn(CO)_2(\eta\text{-}C_5H_5)$ was reported (ref. 49), as were several isocyanide complexes including $Mn(CNCOPh)\text{-}(CO)_2(\eta\text{-}C_5H_5)$ (ref. 181). The indenyl complexes $Mn(CO)_3(\eta\text{-}C_9H_6X)$ (X = Cl, Br, I) were prepared by reactions of $C_9H_6N_2$ with $MnX(CO)_5$ (ref. 182).

It is possible to prepare an olefin compound of manganese by the reaction of allyl alcohol and $Mn(CO)_2(THF)(\eta\text{-}C_5H_5)$. Protonation at oxygen followed by loss of water gives the cationic allyl complex, XXVII. This species exists in two isomeric forms, the exo isomer being shown, (ref. 183).



a) $CH_2{=}{=}CHCH_2OH$; b) $H^+, -H_2O$

XXVII

A paper on the redetermination of the structure of $Mn(CO)_3(\eta\text{-}C_5H_5)$ has been published (ref. 184), as has a paper on the structure of $Re(CO)_3(\eta\text{-}C_5H_5)$ (ref. 185). Crystal structure determinations were reported on two η^2-olefin compounds, $Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)$ (ref. 186) and $Mn(CO)_2(\eta^2\text{-}C_7H_8)(\eta\text{-}C_5H_5)$ (ref. 187). Helium I and II PES spectra have been recorded for $Mn(CO)_3(\eta\text{-}C_5H_{5-n}Me_n)$ (M = Mn, Re; n = 1-5) (ref. 188) and for the olefin derivatives $Mn(CO)_2(\eta^2\text{-olefin})(\eta\text{-}C_5H_{5-n}Me_n)$ (olefin = C_2H_4, C_3H_6) (ref. 189). A mass spectral study on various $Re(CO)_3(\eta\text{-}C_5H_4R)$ derivatives has been published (ref. 190). Photolysis of $Mn(CO)_3(\eta\text{-}C_5H_5)$ in glassy solids at 77K leads to $Mn(CO)_2(\eta\text{-}C_5H_5)$ and $Mn(CO)(\eta\text{-}C_5H_5)$ (ref. 191).

Various types of studies concerned with the cyclopentadienyl ring in $Mn(CO)_3(\eta\text{-}C_5H_5)$ and its derivatives have been carried out. The compound $Mn(CO)_3\{\eta\text{-}C_5H_4CPh{=}SMn(CO)_2(\eta\text{-}C_5H_5)\}$ was prepared and its structure determined by crystallography; the carbon (13) NMR spectrum on this compound was also discussed (ref. 192). The identity of L in $[Mn(CO)(L)_2(\eta\text{-}C_5H_4CR_2^+)]$ (L = PPh_3, dppe, CO), markedly influences the stabilities of these carbonium ion species (ref. 193). The new compound $Mn(CO)_3(\eta\text{-}C_5H_4CH_2CH_2C{\equiv}CH)$ has been made; photolysis of this compound displaces CO and the acetylenic group of side chains on the cyclopentadienyl ligand coordinates to the metal (ref. 194). Metallation (using butyllithium) of the ring in $Mn(CO)_3(\eta\text{-}C_5H_4CH_2NMe_2)$ occurs in the 2-and/or 3- positions. Several derivatives were prepared from the

lithiated intermediates (ref. 195). An esr study was carried out on the radical species $Mn(CO)_3(\eta^5\text{-}C_5H_4C_6H_2Bu^t_2O\cdot)$ (ref. 196).

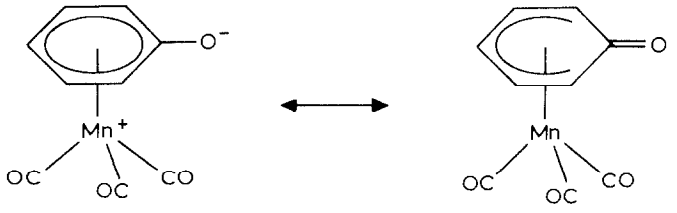
Various studies on cyclopentadienyl-metal nitrosyl complexes and their derivatives have already received comment in this review. This includes: preparation and reactionsof $[Mn(NO)(CO)(L)(\eta\text{-}C_5H_5)]^+$ and $[M(NO)(CO)(L)\text{-}(\eta^5\text{-}C_9H_7)]^+$ (L = CO, PPh_3, C_9H_7 is the indenyl ligand), (ref. 61); various reactions of $MnI(NO)(CO)(\eta\text{-}C_5H_5)$ (ref. 60); the reaction of $ReMe(NO)(CO)\text{-}(\eta\text{-}C_5H_5)$ and PMe_3 (ref. 118); the preparation of $[Re(NO)(CO)(\eta^2\text{-}C_7H_8)(\eta\text{-}C_5H_5)]\text{-}BF_4$ and $Re(\eta^1\text{-}C_7H_7)(NO)(CO)(\eta\text{-}C_5H_5)$ (ref. 119); and various reactions of $[Re(CH_2)(NO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ with sulfides (ref. 120). Diasteromers of the compound $[Mn(NO)(norphos)(\eta\text{-}C_5H_5)]PF_6$ were prepared and separated by fractional crystallization from benzene (ref. 197).

Complexes with arenes coordinated to a metal are considered next. Two useful preparative methods for $[Mn(CO)_3(\eta^6\text{-arene})]^+$ complexes have been described. The first method uses the $AlBr_3$ catalyzed exchange of the methylcyclopentadienyl group in $Mn(CO)_3(\eta\text{-}C_5H_4Me)$ with an arene. The low cost of the precursor is advantageous; the reaction is limited to arenes which are compatible with aluminum halides (ref. 198). It was also shown subsequently that some methyl benzenes ($C_6H_{6-n}Me_6$) isomerize and undergo intermolecular methyl exchange using these reaction conditions (ref. 199). The second method involves the reaction of $Mn(OClO_3)(CO)_5$ and an arene in CH_2Cl_2 (ref. 200). The σ- perchlorate ligand is easily displaced. This method is useful for preparations of complexes of arenes having electronegative substituent groups; viz.

$$Mn(OClO_3)(CO)_5 + C_6H_5R \rightarrow [Mn(CO)_3(\eta\text{-}C_6H_5R)]ClO_4 + 2CO$$

(C_6H_5R: R = H, F, $N(CH_2)_5$, OEt, OH)

The phenol complex undergoes deprotonation with base giving $Mn(CO)_3(\eta\text{-}C_6H_5O)$. Bonding in this species is described in terms of the two resonance structures shown below.



Various complexes with the general formula $Mn(CO)_2(CN)\{\eta^6\text{-arene}(CH_2)_nX\}$ were prepared by standard methods (ref. 201). Interest in these compounds centers on their ability to undergo internal reactions to form isocyanide derivatives.

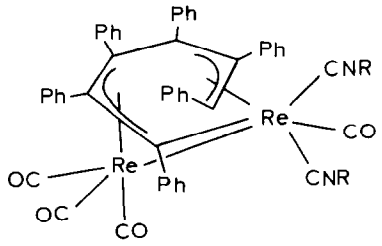
Kinetics of reactions between $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ and several nucleophiles (N_3^-, OH^-, CN^-) were investigated. The relative rates of these reactions are in the order given, with the reaction of azide being the fastest. Rate laws were determined for the reactions of OH^- and CN^- (ref. 202).

Field desorption mass spectra were recorded for several manganese-hydrocarbon complexes (ref. 203).

Papers have appeared from two groups describing the synthesis of pentadienyl-manganese (ref. 204) and -rhenium (ref. 205) tricarbonyls. The same method was used in each case; this utilizes a reaction of $Me_3SnCH_2CH{=}CHCH{=}CH_2$ and $MBr(CO)_5$ (M = Mn, Re).

Three compounds are described from a reaction between $Re_2(CO)_{10}$ and PhC≡CPh (ref. 206). These have the formulas $Re_2(CO)_7(C_2Ph_2)_2$, $Re_2(CO)_6(C_2Ph_2)_3$, and $Re_2(CO)_4(C_2Ph_2)_4$ whose structure was identified in a crystallographic study and shown below (XXVIII).

Various allyl-manganese compounds have been made in phase transfer catalysis reactions. For example, $Mn(CO)_3(PPh_3)(\eta^3\text{-}C_3H_5)$ can be made from $MnBr(CO)_3(PPh_3)_2$, allyl bromide, and hydroxide ion with a tetraalkylammonium bromide salt as the phase transfer reagent (ref. 207). PES data for several η^3-allyl-manganese compounds were presented in another paper (ref. 208)



XXVIII

Other references to hydrocarbon-metal complexes have already been mentioned. Various olefin, diolefin, and allyl compounds were prepared by photolysis of manganese and rhenium carbonyls with several dienes (ref. 20-22). Other olefin, diene, and dienyl complexes have been reported as products in reactions of phosphine-rhenium hydrides (ref. 64, 66, 67). Also mentioned was the interesting reaction sequence starting with hydride addition to either $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ or $Mn(CO)_3(\eta^5\text{-}C_6H_7)$, from which diene- and allyl-manganese carbonyl species evolved (ref. 71,72). Reactions of the ethylene complex $[Re(CO)_5(\eta^2\text{-}C_2H_4)]^+$ with $[Re(CO)_5]^-$ gives $(CO)_5ReCH_2CH_2Re(CO)_5$ (ref. 35,96). Brief mention was made of two diene complexes, $Re(CO)_2(\eta^4\text{-}C_5H_6)(\eta\text{-}C_5H_5)$, (ref. 76), and $Re(NHPh)(\eta^4\text{-}C_4H_6)(PMe_3)_3$ (ref. 74).

Complexes of π-heterocyclic molecules as ligands have been considered in this review. This includes complexes of the pyrrolyl (ref. 160, 168, 169) and phospholyl (ref. 165) ligands, of a phosphabenzene (ref. 164), and of a phosphorus-sulfur containing six-membered heterocycle (ref. 107, 109).

INDO-SCF molecular orbital calculations on $Mn(\eta\text{-}C_5H_5)_2$, $[Fe(\eta\text{-}C_5H_5)_2]^+$ and $[Cr(\eta\text{-}C_5H_5)_2]^-$ have been mentioned (ref. 209).

IX. ISOCYANIDE AND NITROSYL COMPLEXES

Gladfelter, et al. (ref. 210) have identified $[PPN]NO_2$ as a mild versatile nitrosating reagent in dipolar solvents. Its reaction with $[Mn(CO)_6]^+$, at -40° in MeCN, occurs rapidly to give $Mn(NO)(CO)_4$; subsequently $PPN[Mn(NO)_2(CO)_2]$ forms upon addition of a second equivalent of this reagent. The PES spectrum and molecular orbital calculations (Xα-SW) on $Mn(NO)(CO)_4$ are reported in another paper (ref. 211). Other references to nitrosyl complexes include two papers on the reaction of NO with homoleptic metal alkyl species (ref. 91, 92), and several papers on the various complexes derived from $[Mn(NO)(CO)_2(\eta\text{-}C_5H_5)]^+$ (ref. 60, 61, 118-120, 197).

All papers on complexes with isocyanide ligands have been cited earlier in this review. The preparations of $[Re(CNBu^t)_6]^+$ (ref. 36, 37) and $[Re(CNR)_4(PPh_3)_2]^+$ (R = Bu^t, Cy) (ref. 68) were described. Complexes from several diisocyanides and $MnBr(CO)_5$ were mentioned (ref. 46, 47). Other complexes cited include $Re(CNBu^t)_2(CMe{=}NBu^t)_3$ (ref. 90), $[Mn_2(CO)_5(CNtol)(dppm)_2H]^+$ (ref. 69), $ReCl(CNR)(dppe)_2$ (R = Me, Bu^t) (ref. 125), $Mn(CO)_2(CNCOPh)(\eta\text{-}C_5H_5)$ (ref. 181) and $Re_2(CO)_4(CNCH_2SO_2C_6H_4Me)_2(C_2Ph_2)_3$ (ref. 206).

X. STRUCTURAL STUDIES

Compounds whose structures were determined by x-ray crystallography, or by other diffraction methods are listed: $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (ref. 4); $[Rh_2(TM4\text{-bridge})_4Mn_2(CO)_{10}](PF_6)_2$, (I), (ref. 10); $Mn_2(CO)_9[S\{Cr(SBu^t)(\eta\text{-}C_5H_5)\}_2]$ (ref. 19); $Re_2(CO)_8(C_4H_6)$ (ref. 21); $Re_3(CO)_{14}(NO_2)$ and $Re_3(CO)_{14}(CO_2H)$

(ref. 22); $[Nb_2H(CO)_2(\eta\text{-}C_5H_5)_4]Mn(CO)_5$ (ref. 28); $MBr(CO)_3S_2CCMe_2PPh_3)$, M = Mn, Re (ref. 51); $Re_3I_6(CO)_6$, VI, and $Re_4I_4(CO)_6$ (ref. 52); $Re_2Br_2(CO)_6(Te_2Ph_2)$, (ref. 54); $ReBr(CO)_3(NHR)_2$, R = Me, Et, (ref. 55); $ReH_2(PPh_3)_2(\eta^5\text{-}C_6H_7)$ (ref. 66); fac-$\overbrace{Re(o\text{-}C_6H_4PMe_2)}(PPhMe_2)_3(N_2)$ and $ReH_3(PPhMe_2)_3(\eta^2\text{-}C_5H_8)$ (ref. 67); $R_5(\mu\text{-}Cl)_3Re_3Re_3(\mu\text{-}Cl)_3(H)R_4$ and $Re_3(\mu\text{-}Cl)_3(Cl)(H)(PPh_3)R_4$, R = CH_2SiMe_3 (ref. 73); $Et_4N[Re_3H_3(OEt)(CO)_9]$(ref. 77); $Et_4N[Re_3H_3(I)(CO)_{11}]$ (ref. 78); $Re_3H(SnMe_2)(CO)_{12}$ (ref. 79); $Re_3H_3(CO)_{11}(PPh_3)$ (ref. 80); $(CO)_5ReCH_2CH_2Re(CO)_5$ (ref. 96); $\overbrace{Mn(PPh_2CH_2CH_2CH_2)}(CO)_4$ and $\overbrace{Re(PPh_2CH_2CH_2)}(CO)_4$ (ref. 97); $\overbrace{Mn(PPh_2CH_2CH_2CH_2CH_2)}(CO)_4$ and $\overbrace{Mn(PPh_2CH_2CH_2CHCH_3)}(CO)_4$ (ref. 99); $\overbrace{Mn(PMe_2OCH_2)}$-$(CO)_4$ and $\overbrace{Mn(PMe_2OCH_2CH_2CH_2)}(CO)_4$ (ref. 101); cis-$Mn(CH_2COMe)(CO)_4(PPh_3)$ (ref. 102); $\overbrace{Mn(SPMe_2CR{=}CR)}(CO)_4$, R = CO_2Me (ref. 105, 106); $Mn(CO)_3(\eta^4\text{-}C_4R_4PMe_2)$, R = CO_2Me (ref. 109); $Mn(CO)_2(C{=}C{=}CCy_2)(\eta\text{-}C_5H_5)$ (ref. 123); $Mn(CO)_2(C{=}CMe_2)$-$(\eta\text{-}C_5H_5)$ (ref. 124); $Mn_2(CO)_4(\mu\text{-}CH_2)(\eta\text{-}C_5H_5)_2$ (ref. 125); $Mn(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}CS)$-$Pt(PPh_2Me)_2$ (ref. 130); $[Mn(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}Ctol^P)Pt(PMe_3)_2]BF_4$ (ref. 131); $[MnPt\{\mu\text{-}C(PMe_3)tol^P\}(CO)_2(PMe_3)_2(\eta\text{-}C_5H_5)]BF_4$ and $MnPt(Stol^P)\{\mu\text{-}C(PMe_3)tol^P\}$-$(\mu\text{-}CO)(PMe_3)(\eta\text{-}C_5H_5)$ (ref. 132); $Os_3ReH(CO)_{15}(MeCN)$ (ref. 136); $(CO)_4Re(\mu\text{-}CO)$-$(\mu\text{-}CPhPMe_3)W(CO)_4$ (ref. 138); $MnCo(CO)_6(Bu^tN{=}CHCH{=}NBu^t)$ (ref. 139); $Mn_2Fe_2S_2(CO)_{14}$ (ref. 144); $Mn_2Pt(PPh_2)_2(CO)_9$, $Mn_2PtH(PPh_2)_3(CO)_8$ and $Mn_2Pt_2(PPh_2)_4(CO)_8$ (ref. 146); $(CO)_5MnHg(N_3R_2)$, R = $o\text{-}ClC_6H_4$, (ref. 147); $[HgMn(CO)_2(\eta\text{-}C_5H_4Me)]_4$ (ref. 148); $Ge[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_2$ and $Ge[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_3$ (ref. 150); $ClSn[Mn(CO)_4(PPh_3)]_3$ (ref. 153); $Re(CO)_2(PPh_3)_2(N_3tol_2)$ (ref. 157); $Mn(N_2CR_2)(CO)_2(\eta\text{-}C_5H_5)$ (ref. 159); $Mn(\eta\text{-}C_5H_5)(\eta\text{-}2,4,6\text{-}C_5PPh_3H_2)$ (ref. 164); $Me_2Ge(OCH_2CH_2SPh)(C_3HMe_2N_2)Mn(CO)_3$ (ref. 167); $Mn(CO)_3\{C_4N_4NMn(CO)_3(C_6H_2(NO_2)_3O)\}$ (ref. 168); $Mn(CO)_3$-$\{C_4H_4NMn(CO)_3NC_4H_4Mn(CO)_3Bu\}$ (ref. 169); $[Re(CO)_3OH]_4{\cdot}2C_6H_6$ (ref. 170); $Mn(O_2CCF_3)(CO)_5$ and $Mn(O_2CCF_3)(CO)_3(py)_2$ (ref. 171); $[Cr_2(SBu^t)_2(\eta\text{-}C_5H_5)_2S]$-$Mn(CO)_2(\eta\text{-}C_5H_5)$ (ref. 180); $Mn(CO)_3(\eta\text{-}C_5H_5)$ (ref. 184); $Re(CO)_3(\eta\text{-}C_5H_5)$ (ref. 185); $Mn(CO)_2(\eta^2\text{-}C_8H_8)(\eta\text{-}C_5H_5)$ (ref. 186); $Mn(CO)_2(\eta^2\text{-}C_7H_8)(\eta\text{-}C_5H_5)$ (ref. 187); $Mn(CO)_2\{\eta\text{-}C_5H_4CPh{=}SMn(CO)_2(\eta\text{-}C_5H_5)\}$ (ref. 192); $Re_2(CO)_4(CNCH_2SO_2C_6H_4Me)_2(C_2Ph_2)_3$ (ref. 206).

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