MANGANESE, TECHNETIUM, AND RHENIUM

ANNUAL SURVEY COVERING THE YEAR 1975

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CONTENTS

Manganese, Technetium, and Rhenium; Annual Survey covering the year 1974 see J. Organometal. Chem., 115 (1976) 177-220.

I INTRODUCTION

This author was impressed, first of all, by the increase in the number of papers in the area of Group VIIB organometallic chemistry. Almost 200 papers were abstracted for the 1975 ANNUAL SURVEYS article; in contrast, approximately 150 articles were abstracted in each of the last three years. Research interest in this area has continued to expand in scope. Perhaps the most interesting new developments are several attractive photochemical studies on metal carbonyl species. Some kinetic and mechanistic work has also appeared which merits special consideration. These topics will be discussed in their appropriate sections of this review.

Articles surveying various individual's work have appeared; these papers, usually papers presented at scientific conferences, are cited here. Papers from the Ettal Symposium honoring Professor W. Hieber, held in Ettal, West Germany, in July, 1974, appeared in this Journal, Vol. 94. The papers by Behrens (1), Bigorgne (2), Brunner (3), Connor (4), and Schriver (5) dealt with some aspects of the organometallic chemistry of these metals carried out in these authors' laboratories. There is another series of conference papers, from a New York Acade of Sciences meeting, which included papers from Brunner (6), Legzdins and coworker (7), Dobson (8), Tsutsui and Hrung (9) and Wojcicki (10). One paper appeared from the Bressanone, Italy, Conference in August, 1974 on rhenium chemistry (11). Two reviews of particular note on metal atom syntheses (12,13), part of a larger series on this topic, appeared in Angewandte Chemie.

Two general review articles were also published; the first discussed metal complexes containing sulfur ligands (14), the second metal complexes containing Group III elements (15). In both areas a substantial amount of work has been done involving manganese and rhenium carbonyls.

II METAL CARBONYLS, AND DERIVATIVES OBTAINED BY CARBONYL SUBSTITUTION

A study on the reaction of manganese atoms with CO using matrix isolation techniques has produced interesting results described in detail in a full paper (16), and mentioned in a review (13). When a CO/Mn ratio of $< 10^4$ is used, dimanganese decacarbonyl is found as the product. Manganese vapor as produced in this experiment is essentially monoatomic, and the dilution of metal atoms is such that mononuclear metal complexes would be unlikely to diffuse in the solid state to give dimers. It is proposed that dimer formation occurs by a surface diffusion process, diffusion occurring in a "quasi-liquid" state occurring in the transition between vapor and solid. When substantial dilution of CO in argon is made, retaining however the manganese to CO ratio such that dimanganese species are expected, the new species $Mn_2(CO)$ and $Mn_2(CO)_2$ are formed; they are identified spectroscopically. The infrared spectrum of the former species shows absorptions both in the bridging CO and terminal CO regions, and two isomeric species are suggested to be present. According to the infrared data, the structure of $Mn_2(CO)_2$ has bridging CO groups, coplanar to the metal-metal bond.

If a CO/Mn ratio $> 10^4$ is used then the monometallic species $Mn(CO)_5$ is observed to be formed. Analysis of its infrared spectrum indicates a square pyramidal structure. Varying dilution ratios of CO, other monometallic $Mn(CO)_x$ ($x = 1$-4) species can also be identified.

The photolytic reactions of $Re_2(CO)_{10}$ using 311nm and 350nm radiation is reported by Byers and Brown (17). Such reactions are believed to occur via initial metal-metal bond cleavage to give the radical species $Re(CO)_5$. Reactions with PBu_3 and $P(OMe)_3$ are found to give dimeric $Re_2(CO)_9L$ and $Re_2(CO)_8L_2$, and monomeric $Re(CO)_3L_2$. In the presence of H_2, $Re_3(CO)_{14}H$ is the primary product of the 311nm radiation reaction. With 358nm radiation the products include $Re_3(CO)_{12}H_3$. A mechanism proposed for this reaction, which involves formation of $Re(CO)_5$ followed by CO loss giving $Re(CO)_4$ which undergoes oxidative addition with H_2 to give $Re(CO)_4H_2$. The important feature of this mechanism is the activation of molecular hydrogen.

Other work on the photolysis of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $ReMn(CO)_{10}$, $Mn_2(CO)_9PPh_3$, and $Mn_2(CO)_8(PPh_3)_2$ in carbon tetrachloride to give the corresponding metal carbonyl chlorides, $M(CO)_4(L)Cl$ ($L=CO,PPh_3$), consistent with initial metal-metal bond cleavage (18). Also reported are photolyses of the $M_2(CO)_{10}$ species with I_2 giving $M(CO)_5I$ (M = Mn, Re), and photolyses with benzylchloride or tritylchloride, which give the more stable benzyl and trityl radicals. Kinetics of photolysis of $Mn_2(CO)_8(PPh_3)_2$ at 39.9° with $P(OPh)_3$ have been studied; the product is $Mn_2(CO)_8(PPh_3)[P(OPh)_3]$. Evidence suggests that dissociation of $Mn_2(CO)_8(PPh_3)_2$ to $Mn(CO)_4PPh_3$ precedes ligand exchange and recombination.

In contrast to these photolyses studies the thermal reactions of $M_2(CO)_8(f_4$far (M = Mn, Re, $f_4$fars = $Me_2As\overline{C=C(AsMe_2)CF_2C}F_2$) or $MnRe(CO)_8(f_4fars)$ with iodine are noted. Bimolecular kinetics are observed in each reaction, suggesting that a metal-metal dissociation is not the rate determining step (20). Comparison of the ratio of the cleavage reaction of the manganese compound with its rate of thermal isomerization is made (21).

Photolysis of $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ with $[C_5H_5M(CO)_3]_2$ (M = Mo, W) is found to give the bimetallic species $(CO)_5MnM(CO)_3C_5H_5$ and $(CO)_5ReM(CO)_5C_5H_5$ (22). The photolytic reactions of the pure bimetallic product species also generates the carbonyls $Mn_2(CO)_{10}$ or $Re_2(CO)_{10}$ and $[C_5H_5M(CO)_3]_2$ when an inert solvent is used; in CCl_4 the metal pentacarbonyl chloride and cyclopentadienylmetal tricarbony chloride are formed (23). All of these results are in accord with a general mechanism involving metal-metal bond cleavage as the initial step.

An interesting controversy has developed concerning the analysis of esr data obtained for solutions of $Mn_2(CO)_{10}$ which have been subjected to photolysis. An earlier reference had suggested that photolysis at 350nm gave a relatively long lived species $Mn(CO)_5$, formed on metal-metal bond cleavage. However this is contested in a paper by Lappert and coworkers (24). They find that irradiation of $Mn_2(CO)_{10}$ dissolved in a dry, degassed tetrahydrofuran in an esr spectrometer cavity gives an esr signal which doesn't fade with time. The signal is identified as due to a Mn^{2+} compound, presumably formed in a disproportionation reaction:

$$2\ Mn_2(CO)_{10} + 12\ Solv. \rightarrow 2\ Mn(Solv)_6^{2+} + 4\ Mn(CO)_5^- + 10\ CO$$

However this suggestion is contested in a later paper by Kwan and Kochi (25); they support the earlier supposition that $Mn(CO)_5$ is the paramagnetic species present.

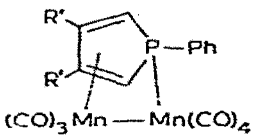
Semiempirical molecular orbital calculations have been carried out for $M_2(CO)_{10}$ (M = Mn, Re) and for $MnRe(CO)_{10}$, and the results correlated with electronic spectral data. For $Mn_2(CO)_{10}$ the 29,400 cm^{-1} absorption is assigned to a $\sigma \rightarrow \sigma^*$ transition for the Mn-Mn bond. Also assigned are the 33,000 cm^{-1} and 38,000 cm^{-1} absorptions to $\sigma \rightarrow \pi^*(CO)$ and $d\pi \rightarrow \pi^*(CO)$ transitions, respectively. The very intense 50,000cm^{-1} absorption is assigned as $d\pi \rightarrow \pi^*(CO)$ (26).

Another paper discusses MO calculations on $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ (27). Semi-bridged carbonyls are implied for the manganese compound but not for $Re_2(CO)_{10}$.

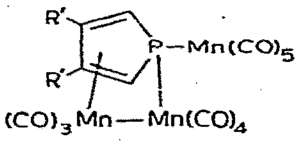
Bridging isocyanide ligands are the topic of another paper. Adams and Chodish (28) have looked at the variable temperature pmr spectrum for the compound $Mn_2(CO)_7(CNMe)_3$, in the range 36°-118°C. In the low temperature spectra two methyl resonances are seen, having relative intensity of 2:1. At the higher temperature these resonances coalesce to a single resonance, indicating that the three methyl groups have assumed the same average environment. The process by which this is achieved is assigned to exchange of the isocyanides between metals, an intermediate having bridging isocyanides being a reasonable supposition.

Substantial reaction chemistry of manganese and rhenium decacarbonyls is discussed. In the review of Professor Hieber's work cited earlier (1) the syntheses of $Re_2(CO)_{10}$, $Mn(CO)_5H$, and $Mn(CO)_5X$ are mentioned; the disproportion of $Mn_2(CO)_{10}$ with pyridine is also discussed. Further work on carbonyl ligand substitution is seen. Reactions of $Mn_2(CO)_{10}$ with MeNC and t-BuNC give $Mn_2(CO)_{10-x}L_x$ species (x = 1, 2, 3, 4); from a reaction of $Mn_2(CO)_8[P(OPh)_3]_2$ and t-BuNC the compound $Mn_2(CO)_7[P(OPh)_3]_2(CNBu^t)$ can be prepared (29). Reaction of $Mn_2(CO)_{10}$ and $[Et_4N]Cl$ in $CHCl_3$, with irradiation, gives two compounds $Et_4N[Mn_2(CO)_9Cl]$ and $Et_4N[Mn_2(CO)_6Cl_3]$ (30, 31); the structure of the second anionic complex presumably has two $Mn(CO)_3$ groups linked through three bridging chlorine atoms. The route by which this compound is formed, involving a formal oxidation of the metal, is not clear.

Reactions of $Mn_2(CO)_{10}$ and various phospholes ($L = R\overline{PCH=CR'CR'=CH}$) are complicated (32). Irradiation of these reactants leads to $Mn_2(CO)_9L$ and $Mn_2(CO)_8L_2$, unstable orange oils, whose structures are like those of other phosphine complexes having these stoichiometry. A third compound, $Mn_2(CO)_7L$, assigned structure I below, is also obtained. This latter species can be converted to another species $Mn_3(CO)_{12}L'$, structure II, which on heating in vacuum converts to compound III. This last compound is the phosphorus analoque of the known nitrogen compound, pyrrolylmanganese tricarbonyl.



I



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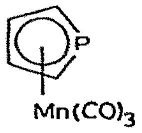


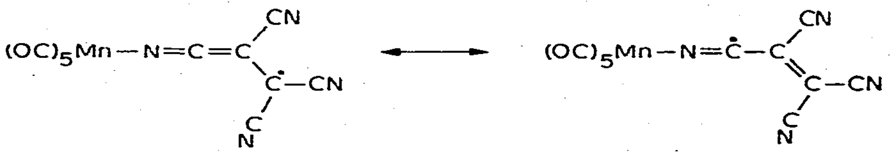
III

A reaction between $Mn_2(CO)_{10}$ and poly-1-vinyl-2 pyrrolidinone results in complete loss of CO, giving a polymeric complex of stoichiometry $[Mn(C_6H_9NO)_5]_n$ (33). Reactions of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$ and $MnRe(CO)_{10}$ with several chelating arsine and phosphine ligands ($f_4$fars, f_4'fos, $f_6$fars) are reported in a thesis (34).

When $Mn(CO)_5Me$ is treated with $Re(CO)_5^-$ and methyl fluorosulfonate added subsequently, the carbene complex $MnRe(CO)_9[CMe(OMe)]$ is formed (35). A crystal structure study on this compound shows a carbene ligand bonded to rhenium, cis to the metal-metal bond. Mechanisms of transfer of the carbene from one metal to the other are considered. Syntheses of other carbene complexes are also mentioned.

Oxidative cleavage of $Mn_2(CO)_{10}$ is reported to occur with tetracyanoethylene

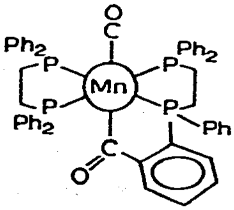
(36). An oxygen-free tetrahydrofuran solution of these reagents has an esr spectrum which is due to the presence of the tetracyanoethylene anion radical and another product. The addition of a large excess of $Mn_2(CO)_{10}$ causes diminution of the $TCNE^{\overline{\cdot}}$ concentrations and enhances the concentration of the second species. Esr evidence is presented in support of the second species being the radical $Mn(CO)_5NC\text{-}C(CN)\text{=}C(CN)_2$; (IV) represents the bonding in such a species using valence bond terminology.



IV

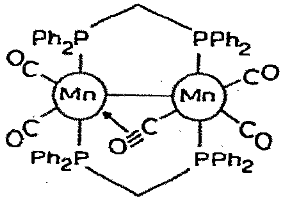
Oxidative cleavage of metal-metal bonds is a fairly common reaction. Electrochemical oxidation of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ in acetonitrile at a platinum electrode occurs in this fashion giving $[M(CO)_5(NCMe)]^+$ (37). It may be noted that the first step in the reaction of $Mn_2(CO)_{10}$ and TCNE mentioned above (36) is also believed to proceed in the same way, with one electron loss by $Mn_2(CO)_{10}$ generating $[Mn(CO)_5solv]^+$ and $Mn(CO)_5$; the later species then combines with TCNE to give $Mn(CO)_5(TCNE)$, the species identified based on esr evidence.

Reactions of $Mn_2(CO)_{10}$ and chelating diphosphines have been investigated. A red crystalline product previously believed to be a paramagnetic monomer, $Mn(CO)(DPE)_2$ (DPE = 1,2-bisdiphenylphosphinoethane), has been shown to be mischaracterized. It is diamagnetic; x-ray crystallography has identified it as having structure V



V

below (38). Reactions of $Mn_2(CO)_{10}$ and DPM (DPM = 1,2-bisdiphenylphosphinomethane) or the arsenic analogue give $Mn_2(CO)_8DPM$, $Mn_2(CO)_6(DPM)_2$, or $Mn_2(CO)_5(DPM)_2$, along with traces of $Mn(CO)_3(DPM)H$ (39). The third compound, $Mn_2(CO)_5(DPM)_2$ is the most interesting of this group. It has an unusually low ν(CO) absorption, at 1645 cm^{-1}, which arises from an unsymmetrically bridging CO group. X-ray crystallography has defined the structure of this species as VI (40, 41).



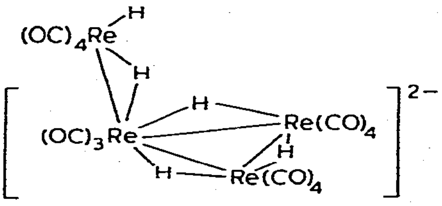
VI

Various vibrational spectroscopic investigations on the Group VIIB metal carbonyls are reported; these include studies on infrared and Raman spectra of $MnRe(CO)_{10}$ (42, 43), and the Raman spectrum of $Re_2(CO)_{10}$ (44). Solvent dependence of the infrared spectra of $Mn_2(CO)_{10}$ and $Mn_2(CO)_8L_2$ (L = PEt_3, $P(OPh)_3$) is also mentioned (45).

In work on anionic metal carbonyl complexes, the most surprising results have been the characterization of the trinegative anions $Mn(CO)_4{}^{3-}$ and $Re(CO)_4{}^{3-}$ (46). These species, isolated as $Na(HMPA)^+$ salts, are obtained by sodium reduction of the metal carbonyls in hexamethylphosphorus triamide. As expected, these anions possess very low ν(CO) absorptions; for the manganese anion ν(CO) falls at 1805w and 1670vs,b, and for the rhenium analogue the values are 1825w and 1690vs. Some reaction chemistry of the manganese compound is described with Ph_3MCl (M = Ge, Sn, the complexes trans-$Mn(CO)_4(GePh_3)_2{}^-$, cis-$Mn(CO)_4(SnPh_3)_3{}^-$, cis-$Mn(CO)_4(PbPh_3)_2{}^-$ are formed. With $Au(PPh_3)Cl$ the unusual compound $(Ph_3PAu)_3Mn(CO)_4$ is found as a product.

Work from the same research group describes reductive reactions of the metal carbonyls in tetrahydrofuran; the primary products are the pentacarbonylmetallates (47). Electrochemical reduction to these species is also reported (37).

When $Re_2(CO)_{10}$ is refluxed in methanol with added KOH, an anionic complex is formed which may be precipitated on addition of $[Et_4N]I$ (48). The formula $[NEt_4]_3[Re_4H_4(OMe)(CO)_{16}]$ is assigned to this substance, but no structure is suggested. If this compound is allowed to stand in ethanol another complex $[NEt_4]_2[Re_4(CO)_{15}H_4]$ is obtained, whose structure has been determined by an x-ray crystallographic study to be VII, below.



VII

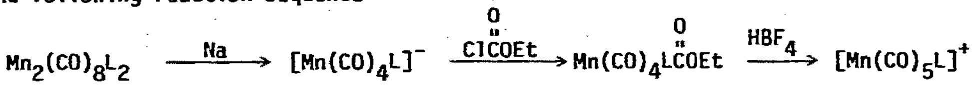
Another study on the photolysis of $Re_2(CO)_{10}$ in diethyl ether in the presence of water is reported (49). The reaction products are $Re_3(CO)_{12}H_3$ and $[Re(CO)_3OH]_4$; the former appears to be converted to the latter species as the reaction continues.

Cationic complexes, derivatives of $[M(CO)_6]^+$, were studied extensively in the last year. In one paper the syntheses of the compounds $[M(CO)_5(SO_2)]AsF_6$ (M = Mn, Re) are reported (50); these compounds are formed from $M(CO)_5Br$ and $AgAsF_6$ in liquid SO_2. They are particularly useful precursors to other cationic species, since SO_2 is easily displaced by other ligands. Complexes prepared include $[M(CO)_5L]AsF_6$ (L = NSF_3, N_4S_4, PF_2NMe_2, H_2O, MeOH, acetone). Heating of $[M(CO)_5SO_2]AsF_6$ to 50° also results in SO_2 loss; covalent fluoride-bridged species $M(CO)_5FAsF_5$ are products of this reaction.

The synthesis of $[Re(CO)_5(NSF_3)]AsF_6$ is described in a separate note (51).

The oxidative cleavage of manganese carbonyl in acetonitrile using electrochemical techniques giving $[Mn(CO)_5(NCMe)]^+$ was mentioned earlier (37). The same reaction can be accomplished chemically, using $[NO]PF_6$ as an oxidizing agent (52). The chemistry of $[Mn(CO)_5(NCMe)]^+$ has been explored further. Reaction with pyridine occurs with CO loss to form $[Mn(CO)_3(py)_2(NCMe)]^+$; above 50° the product of this reaction is $[Mn(CO)_3(py)_3]^+$. The reaction with DPE gives $[Mn(CO)_3(DPE)(NCMe)]^+$.

Other cationic derivatives of manganese are also described (52), obtained in the following reaction sequence



$$Mn_2(CO)_8L_2 \xrightarrow{Na} [Mn(CO)_4L]^- \xrightarrow{Cl\overset{O}{\overset{\|}{C}}OEt} Mn(CO)_4L\overset{O}{\overset{\|}{C}}OEt \xrightarrow{HBF_4} [Mn(CO)_5L]^+$$

(L = phosphines, py)

A full paper and a thesis describe cationic carbene complexes which are obtained on alkylation of various acyl-manganese complexes with methylfluorosulfona (53, 54). These include $[Mn(CO)_3(DPE)CR(OMe)]^+$ (R = Me, m-FC_6H_4, p-FC_6H_4), $[Mn(CO)_3\{P(OMe)_3\}_2CMe(OMe)]^+$, and $[Mn(CO)_4(PPh_3)CMe(OMe)]^+$. These compounds behave as typical "onium" complexes, donating $[Me]^+$ to many basic reagents such as phosphi However two different types of reactions are observed with added isocyanides. The DPE compounds react with carbene displacement whereas the trimethylphosphite compounds react by insertion of the isocyanide into the metal carbene bond.

$$[Mn(CO)_3(DPE)L]^+ + CNR \longrightarrow [Mn(CO)_3(DPE)CNR]^+ + L$$

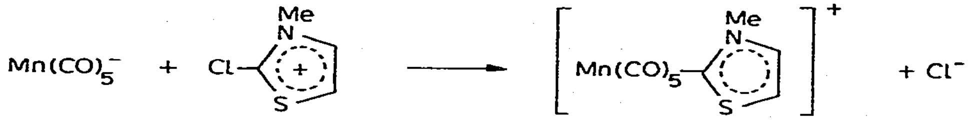
$$[Mn(CO)_3\{P(OMe)_3\}_2L]^+ + CNR \xrightarrow{+MeOH} [Mn(CO)_3\{P(OMe)_3\}_2C(NHR)C(OMe)_2Me]^+$$

Other reaction chemistry of cationic metal carbonyl complexes includes the addition of primary amines to give carbamoyl—metal complexes (52) and addition reactions with a Grignard reagent (55). The latter reactions are found to be complex. For example $[Mn(CO)_6]^+$ and $PhCH_2MgCl$ give $Mn(CO)_5COCH_2Ph$, but in the presence of additional Grignard a second and then a third addition can occur,

$$[Mn(CO)_6]^+ \xrightarrow{RMgX} Mn(CO)_5COR \xrightarrow{RMgX} Mn(CO)_4(COR)_2^- \xrightarrow{RMgX} Mn(CO)_3(COR)_3^{2-}$$

Oxygen destroys the tris-acyl complex, generating the diacyl species. Infrared evidence is used to ascribe cis and fac configurations to the second and third complexes respectively. The same reactions with $[Mn(CO)_5L]^+$ (L = $PPhMe_2$, $P(OMe)_3$) are also reported. The former complex gives first cis-$Mn(CO)_4(L)COCH_2Ph$, and then [fac-$Mn(CO)_3(L)(COCH_2Ph)_2]^-$; from the latter only the neutral cis-complex, $Mn(CO)_4(L)COCH_2Ph$ is obtained.

Reaction of $Mn(CO)_5^-$ with N-methyl-2-chlorothiazolium salts has been used to prepare a carbene-manganese carbonyl compound (56):



Reactions of this species with H_2O in the presence of Et_3N gives the hydride $Mn(CO)_4(L)H$. A carbene complex of manganese is also the product of the following reaction (57):

$$Mn(CO)_5^- + [Me_2NCCl_2]Cl \longrightarrow [Mn(CO)_5C(Cl)NMe_2]^+ + 2Cl^-$$

Displacement of arenes from $[Mn(arene)(CO)_3]^+$ complexes occurs readily if the arene is substituted with certain electronegative functional groups including NEt_2, Cl, Br, I, or OMe (58). The known complex $[Mn(CO)_3(NCMe)_3]^+$ is characterized as a product from these reactions.

The oxidative reaction of another cationic carbene complex $[Mn(CO)_5\overline{COCH_2CH_2O}]^+$ with iodosobenzene or pyridine-N-oxide has been carried out. The carbene is displaced and oxidized giving ethylene carbonate (59).

The syntheses of $[Mn(CO)_5L]^+$ (L = C_2H_4, CO) from $Mn(CO)_5Cl$,$AlCl_3$ and added ligand are mentioned in a review paper (5).

A lone technetium compound is reported. Carbonylation of [trans-$TcX_2\{P(OEt)_2Ph\}_4]ClO_4$ gives a mixture of cis and trans-$[Tc(CO)_2\{P(OEt)_2$-

$Ph]_4]ClO_4$; a crystal structure study on the cis compound has been done (60).

The infrared spectra of $[V(CO)_6]^-$, $W(CO)_6$, and $[Re(CO)_6]^+$ are discussed in a paper from the Ettal Symposium (2). Phosphorus-31 nmr spectra are reported (61) for a number of manganese complexes including the cationic species $[Mn(CO)_3L_2(NCMe)]^+$ (L_2 = DPE, DPM, and the arsenic analogue of DPE). Carbon-13 nmr data for $[Re(CO)_5(NCMe)]^+$ shows that the trans carbonyl carbon is less shielded than are the cis carbonyl carbons (62).

An empirical correlation is made between electrochemical $E_{1/2}$ values for various metal complexes and parameters determined by the nature of the ligands and the extent of substitution and the solvent (63). Among the complexes of various metals considered were the cationic manganese complexes $[Mn(CO)_{6-n}(CNR)_n]^+$ which are known to undergo one electron oxidations. Approximate MO calculations for this same series of complexes have also been reported by Sarapu and Fenske (64) who find, interestingly, that the measured $E_{1/2}$ values for these oxidations correlate well with the calculated HOMO energy level values.

There are a few references to complexes wherein manganese or rhenium carbonyl groups are linked to other transition metal carbonyls. Photochemical studies on reactions forming and degrading $(CO)_5MM'(CO)_3C_5H_5$ (M = Mn, Re; M' = Mo, W) were mentioned earlier (22, 23). Also of interest is the synthesis of a compound with a vanadium-manganese bond, $(CO)_5MnV(CO)_4(Diars)$, from $V(CO)_4(Diars)^-$ and $Mn(CO)_5Br$ (65). Absorption and laser Raman spectra of $(CO)_5ReM(CO)_5^-$ (M = Cr, Mo, W) are reported. The metal-metal linkage was of primary interest in this work (66).

III METAL CARBONYL HALIDES AND DERIVATIVES

Some of the most significant organometallic chemistry reported last year is to be found in a thorough study of ^{13}CO exchange with $Mn(CO)_5Br$ and $Re(CO)_5Br$ (67). It is found that this process is first order in complex concentration, the rate depending on CO dissociation to give a 16 electron intermediate. Loss of a carbony cis to bromine is substantially preferred, by a factor of at least 10. This labilization by a group which is a poor π-bonding ligand is apparently a general phenomenon, related to the enhanced π-bonding to the carbonyl *trans* to the group. The 16 electron 5-coordinate intermediates are assigned a trigonal bipyramidal geometry, with bromine in an axial position; kinetic evidence indicates that these species are fluxional.

The phenomenon of *cis*-labilization had been noted in another reference (8).

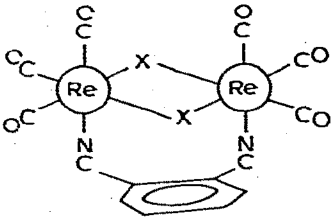
Also studied was the $C^{18}O$ exchange in the complexes *cis*-$Mn(CO)_4(L)Br$ (L = PPh_3, $AsPh_3$, $SbPh_3$) (68). For the PPh_3 complex, preferential exchange occurs for the two carbonyls in mutually *trans* positions, *cis* to bromine and phosphine. The arsine and stibine complexes react in a more complex fashion, both CO and L exchanging.

Several syntheses of metal carbonyl halides can be cited. The photochemical formation of $M(CO)_5Cl$ and $M(CO)_4LCl$ (M = Mn, Re) from the appropriate dinuclear carbonyls in $CHCl_3$ appears to have synthetic advantages (18). The photochemical preparation of the $M(CO)_5I$ compounds is also mentioned (18). Adams (28) has reported the reaction of $Mn_2(CO)_7(CNMe)_3$ and bromine to give equal quantities of $Mn(CO)_4(CNMe)Br$ and $Mn(CO)_3(CNMe)_2Br$. The halogenation of $Mn(CO)_4(\overline{CSCHCHN}Me)H$ by several haloalkanes is reported (56), as are reactions of these species with the phosphorus ligands PPh_3 and $P(OCH_2CH_2)_3CR$ (=L') to give $Mn(CO)_3(\overline{CSCHCHN}Me)(L')H$. Bridged fluoro- complexes of manganese and rhenium, $M(CO)_5FAsF_5$ arise on heating of $[M(CO)_5SO_2]AsF_6$ (50). Reference was made earlier to the dinuclear chloro-complexes $[Mn_2(CO)_9Cl]^-$ and $[Mn_2(CO)_6Cl_3]^-$ (30, 31). The latter reference, a thesis abstract, also describes the reaction of $[Mn(CO)_5(NCMe)]^+$ with KI in the presence of a crown ether:

$$[Mn(CO)_5(NCMe)]^+ + KI + \text{crown ether} \rightarrow Mn(CO)_5I + K(\text{crown ether})^+ + MeCN$$

and the photolytic syntheses of $M(CO)_4X_2^-$ (M = Mn, Re; X = Cl, Br, I) anions.

Several papers on carbonyl substitution reactions of the metal carbonyl halides are noted here. The formation of *fac*-$M(CO)_3(L\frown L)X$ compounds occurs (M = Mn, Re; X = Cl, Br, NO_3) from 1,8-naphthydridine and 1,10-phenanthroline and substituted derivatives of the chelating ligands (69). The tridentate triphosphine $(Me_2PCH_2CH_2)_2PPh$ (= $P_MP_FP_M$) and $Mn(CO)_5Br$ yield $Mn(CO)_2(P_MP_FP_M)Br$ (70). Ortho-dicyanobenzene (= L) is said to react with $Mn(CO)_5X$ (X = Br, I) and $Re(CO)_5Br$ to give complexes $M(CO)_3L_2X$, wherein the ligand is monodentate, coordinating through the nitrogen lone pair (71). This result, if correct, contradicts earlier work in this area. The reactions of $Re(CO)_5X$ (X = Cl, I) occur in a different fashion, giving dimeric $Re_2(CO)_6LX_2$, for which structure VIII is one possible formulation.



VIII

Analogous compounds $Re_2(CO)_6(DAM)X_2$ are formed in prolonged reactions of the reagents $Re(CO)_5X$ and DAM (DAM = $Ph_2AsCH_2AsPh_2$) in refluxing heptane (72). The reactions of $Re(CO)_5Br$ in tetrahydrofuran is described in a review, giving first $Re(CO)_4(THF)Br$, and then an equilibrium mixture of $Re(CO)_3(THF)_2Br$ and $[Re(CO)_3(THF)Br]_2$; the latter is dimeric via halogen bridges (11). Other ligands then can displace THF and the halide bridges to give $Re(CO)_3(L^\frown L)Br$. Thiophosphite esters, $P(SR)_3$ (R = Me, Et, Ph) have been used as ligands for the first time with metals of this group (73). Reactions with $Mn(CO)_5Br$ or $Mn(CO)_5Cl$ give sequentially cis-$Mn(CO)_4LX$ and then mer-trans $Mn(CO)_3L_2X$; with $Re(CO)_5X$ (X = Br, Cl the fac isomers $Re(CO)_3L_2X$ are obtained.

The reactions of the thiophosphinous acid PMe_2SH with $Mn(CO)_5X$ (X = Cl, Br) are temperature dependent (74). At lower temperatures (T < 45° for X = Cl, T < 50 for X = Br) complexes of the secondary phosphine sulfide, $Mn(CO)_4(SPMe_2H)X$, are formed. At higher temperatures rearrangements occur to give the complex bonded to phosphorus, vis, $Mn(CO)_4(PMe_2SH)X$.

There is a communication describing electrochemistry of several manganese complexes $Mn(CO)_{5-n}L_nX$ (n = 5, X = Cl, Br, $SnCl_3$; n = 3, 4, X = I). These complexes exhibit one electron electrochemical oxidations; the values of $E_{1/2}$, reflecting the ease of oxidation, vary widely. Trends of $E_{1/2}$ values reflect the relative electron donor power of the ligands (75).

Photolysis of $Re(CO)_3L_2X$ (X = Cl, Br; L = a substituted pyridine, trans 3- or 4- $PhCH{=}CH{-}C_5H_4N$) leads to trans - cis interconversion of the vinyl group on the ligand (76).

King and coworkers (77) have shown that the compound $C_5H_5Re(CO)_2Br_2$ can be separated into its two isomeric forms by chromatography. The first isomer is obtained as maroon plates, mp 221-3°, and is said to have bromine groups in diagonal positions in the base of the square pyramidal geometry with C_5H_5 in the apex. The second isomer, dark brown microcrystals, mp 117-120°, is the lateral isomer, bromine atoms being in adjacent positions. The isomers do not interconvert when heated in an inert solvent at 110°, but in refluxing chloroform isomerization occurs in minutes. Another paper by different authors describes 1:1 and 2:1 $AlCl_3$ adducts of $C_5H_5Re(CO)_2Br_2$ (78).

There is an interesting study describing the oxidations of $[Re(CO)_3X]_4$ compounds (X = Cl, Br) by halogens (79); Rhenium (III) complexes, $[Re(CO)_2X_4]^-$, are produced. These species have cis octahedral geometries and are paramagnetic to the extent expected for compounds of the metal in this oxidation state.

A rhenium(I) carbonyl chloride species, $Re(CO)(PMe_2Ph)_2(N_2Ph)Cl_2$, is reported (80). It is obtained by carbonylation of $Re(PMe_2Ph)_2(NH_3)(N_2Ph)Cl_2$; this precursor arises on treatment of mer- $Re(PMe_2Ph)_3Cl_3$ with phenylhydrazine; vis:

$$Re(PMe_2Ph)_3Cl_3 \xrightarrow[NH_3\,(liq.)]{PhN_2^+} Re(PMe_3Ph)_2(NH_3)(N_2Ph)Cl_2 \xrightarrow{CO} Re(CO)(PMePh_2)(N_2Ph)Cl_2$$

Structural studies by single crystal x-ray diffraction are recorded for the isomeric species mer-trans and fac- $Mn(CO)_3[PPh(OMe)_2]_2Br$ (81).

Approximate MO calculations on the compounds $Mn(CO)_{5-x}(CNMe)_xBr$ ($x = 1$-4) have been reported (65). Work has been underway recording PES spectra of various compounds of metals in this group and interpreting these data in conjunction with theoretical and chemical studies. It is appropriate to cite papers here concerning PES spectra for $Re(CO)_5X$ compounds (X = Cl, Br, I) (82, 31) and of various rhenium complexes of dinitrogen (83,84). The latter study provides a correlation of electrochemical oxidation potentials of these compounds with electronic charge density distribution as determined through the PES study.

Several papers on other spectroscopic studies are noted. A tabulation of carbon-13 nmr spectral data for various $Re(CO)_5X$ species including $Re(CO)_5Br$ is recorded (62). Also reported is the carbon-13 study of isocyanide complexes of manganese, such as $Mn(CO)(CNPh)_4Cl$ (85). Phosphorus-31 spectra of many phosphine complexes including $Mn(CO)_2(P_MP_FP_M)Br$ ($P_MP_FP_M = (Me_2PCH_2CH_2)_2PPh$) are noted (86), as are the temperature dependent nmr spectra of fac-$Mn(CO)_3(L\frown L')X$ ($X = Br, Cl$, $L\frown L' = Me_2AsCF_2CFHAsMe_2$, and $x = Cl$, $L\frown L' = Me_2AsCFHCFHAsMe_2$) (87). Anomalous infrared and Raman data for $Mn(CO)_5Br$ is mentioned (88).

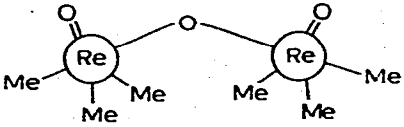
IV METAL COMPLEXES WITH EITHER HYDROGEN OR CARBON GROUPS AS LIGANDS

Much of the work which has appeared on metal carbonyl hydrides has been cited already in this review. Earlier citations on synthetic work include: $Mn(CO)_5H$ syntheses describing historical work, from the Ettal Symposium (1,5); polynuclear hydrides of rhenium obtained either from reactions of $Re_2(CO)_{10}$ with base (48), photolysis of this carbonyl in water-ether mixtures (49), or photolysis of $Re_2(CO)_{10}$ in the presence of hydrogen (17); syntheses of traces of $Mn(CO)_3(dam)H$ ($dam = Ph_2AsCH_2AsPh_2$) (39); and synthesis and halogenation reactions of $Mn(CO)_4(L)H$ where L is the 2-thiazolium group (56).

Byers and Brown (89) have studied the reaction of $Re(CO)_5H$ and PBu_3. Using very pure reagents and with light exclusion no reaction occurs, as expected for the very inert hydride species. Using less care however, one observes reactions at varying rates to give $Re(CO)_4(PBu_3)H$ and $Re(CO)_3(PBu_3)_2H$. A radical reaction sequence is suggested, whereby $Re(CO)_5$ is first generated as an intermediate; this species then reacts with the phosphine and abstracts hydrogen to give the products. Oxygen is found to inhibit the reaction, probably by scavenging $Re(CO)_5$, with formation of $Re(CO)_5O_2$.

Two references have appeared on PES work on $Re(CO)_5H$ (82) and $Mn(CO)_5H$ (4). The PES spectra of various compounds including $Mn(PF_3)_5H$ may also be mentioned here (90). Manganese-55 nqr for $Mn(CO)_5D$ (91) and spin echo double resonance detection of the deuterium quadrupole resonance in this compound (92) are reported.

Five papers have appeared from Wilkinson's group, dealing with alkyl manganese and rhenium complexes. The thermally stable manganese compounds $Mn(CH_2R)_2$ (R = t-Bu, CMe_2Ph, $SiMe_3$) are formed from the appropriate organolithium species and manganese halide (93). They are reported to react with O_2 to give unstable green manganese(IV) complexes, possibly having the formula MnR_4. The manganese(II) complex, $Li(S)_2[MnMe_4]$ (S = solvent, either tetrahydrofuran or tetramethylethylenediamine) can be isolated using excess MeLi and MnX_2. Synthesis of $ReOMe_4$ from MeLi and $ReOCl_4$ or $ReOCl_3(PPh_3)_2$ is reported (94). This air sensitive paramagnetic species is assigned a square pyramidal (C_{4v}) geometry. With Me_3SiCH_2MgX and $ReOCl_3(PPh_3)_2$ the compounds $ReO(CH_2SiMe_3)_4$ and $Re_2O_3(CH_2SiMe_3)_6$ are formed. The latter, though a rhenium(VI) compound, is diamagnetic and is assigned structure IX. Esr and electronic absorption spectra of $ReOMe_4$ and $ReO(CH_2SiMe_3)_4$ are reported in a separate paper (95).

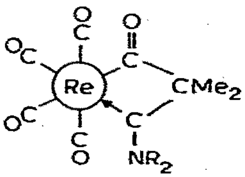


IX

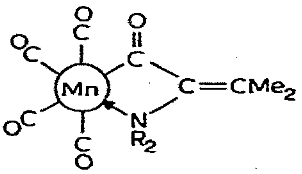
Hexamethylrhenium is noted as the product from reaction of $ReOMe_4$ and Me_3Al (96). This paramagnetic, d^1 compound exists as green volatile crystals. Also reported is the oxidation $ReOMe_4$ with NO giving the diamagnetic, d^0 species ReO_2Me_3. This compound is a yellow liquid at room temperature, solidifying at +10°C.

A WARNING ABOUT POSSIBLE EXPLOSIONS OF $ReMe_6$ IS NOTED (97).

There are a few other papers concerned with syntheses of alkyl- and acyl-metal carbonyl species. The reaction of $Mn(CO)_5Cl$ and diazotetrachlorocyclopentadi to give $Mn(CO)_5C_5Cl_5$ and $Mn(CO)_3(h^5\text{-}C_5Cl_5)$ is noted (98); a communication on this work appeared last year. Reactions of $Na[Mn(CO)_5]$ and $Na[Re(CO)_5]$ with 1-chloro-1-dimethylamino-2-methylpropene lead to several unusual compounds (99). Initial products in these reactions are shown below (<u>X</u>, <u>XI</u>) :

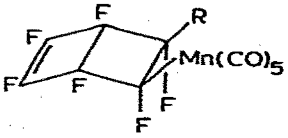


X



XI

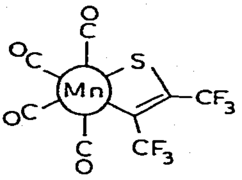
The rhenium compound is found to undergo an interesting thermal rearrangement on heating to give the vinyl metal compound $Re(CO)_5C(NMe_2)=CMe_2$. This work also is reported in a thesis abstract (100). Nucleophilic replacement of fluoride in 2,2,0-hexafluorobicyclohexadiene(C_6F_6) by $Mn(CO)_5^-$ gives $Mn(CO)_5C_6F_5$ (101). Reported in the same paper are the addition reactions of $Mn(CO)_5R$ (R = Ph, Me) and the fluorinated Dewar benzene giving <u>XII</u>, below:



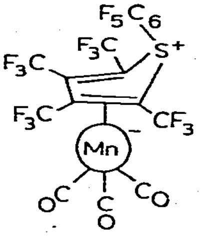
XII (R = Me, Ph)

Reactions of $[Mn(CO)_4SC_6F_5]_2$ with $CF_3C\equiv CCF_3$ give two different products depending on temperature, XIII arising at 25°, XIV at higher temperatures.

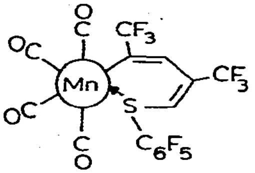
The reaction of $[Mn(CO)_4SC_6F_5]_2$ with $CF_3\equiv CH$ gives a third type of product (XV). Each product arises by incorporation of the acetylene and the -SR group



XIII



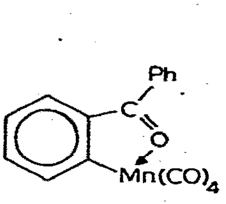
XIV



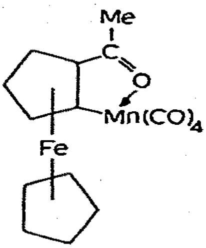
XV

The synthesis of $Mn(CO)_2(P_MP_FP_M)COMe$ by direct reaction of the tridentate phosphine $(Me_2PCH_2CH_2)_2PPh$ and $Mn(CO)_5COMe$ is also reported (70).

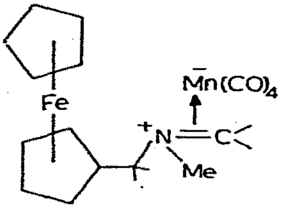
By far the most extensive work on reactions of alkyl-metal carbonyls is concerned with internal metallation (ortho-metallation) reactions. Some of this work was reported last year in communications; other studies are obvious extensions of this type of reaction. Primarily three research groups have been active in this area. The Kaesz group describes the reactions of $M(CO)_5Me$ (M = Mn, Re) with aryl ketones such as acetophenone and benzophenone (103). An x-ray crystallographic study on the acetophenone compound shows it to have the structure XVI (104). A similar reaction with acetylferrocene give the product XVII (105). From dimethylaminomethylferrocene and $Re(CO)_5Me$ an ortho-metallated product is formed. However the expected analogous reaction of $Mn(CO)_5Me$ does not occur, and another reaction product, XVIII,is isolated instead.



XVI



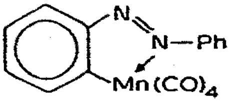
XVII



XVIII

Two other papers from this group present the synthesis and characterization of various primary and secondary products derived from thermal reactions of $Mn(CO)_4(PR_3)CH_3$ (106, 107). Much of this work is contained in two theses abstracted in Dissertation Abstracts (108, 109). Similar work is presented by Bruce and coworkers who have described the metallations of benzylmethylsulfide (110) and of various nitrogen aromatics (111, 112). The structure of a triphenylphosphine derivative of the product from benzylmethylsulfide has been determined by x-ray crystallography and is reported separately (113). Other ortho-metallation work by Bruce, Stone and coworkers, concerning various azobenzenes is reported in two papers. Reactions of $PhN{=}NC_6F_5$ occur with metallation of the Ph-ring (114); reactions of azobenzene with a large number of $Mn(CO)_5R$ compounds (R = alkyl, acyl, aryl, perfluoroaryl) are also described (115), giving XIX.

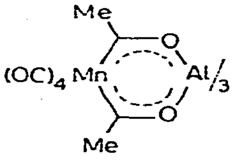
It has been determined that the red complex previously identified as $Mn(CO)(DPE)_2$ (DPE = 1,2-bis(diphenylphosphino)ethane) is in fact an acyl complex, V (38). Possibly the formation of this complex occurs by a mechanism related to the <u>ortho</u>-metallation reaction. The precursor to this product may be the salt $[Mn(CO)_2(DPE)_2]Mn(CO)_5$ which on heating loses the elements of $HMn(CO)_5$ giving the product.



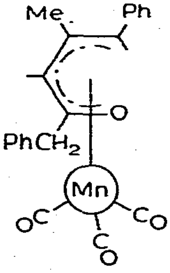
XIX

Other work concerning reactions of the alkyl and acyl metal carbonyls spans a wide range of interests. Some of this work was mentioned earlier. Of interest are the reactions of $Mn(CO)_5Me$ anions with various metal carbonyl anions (35). With $Mn(CO)_5^-$ or $Re(CO)_5^-$, the anionic acyl complexes $[MM'(CO)_9(COMe)]^-$ arise. However with the more nucleophilic $C_5H_5Fe(CO)_2^-$, only methyl transfer occurs giving $Mn(CO)_5^-$ and $C_5H_5Fe(CO)_2Me$. Also mentioned earlier were reactions of the acyl compounds $Mn(CO)_3L_2COR$ ($L = P(OMe_3)$, L_2 = DPE) and $MeOSO_2F$ to give cationic carbene complexes (53). The reactions of $[Mn(CO)_4L]^-$ anions with ClCOOEt to give $Mn(CO)_4(L)COOEt$ are noted. These compounds on protonation give $[Mn(CO)_5L]^+$ species which in turn react with primary amines to form carboxamide complexes $Mn(CO)_4(L)CONHR$ (52).

Two different studies describe acyl manganese carbonyl reactions with nucleophilic organometallic reagents. The syntheses of $[Mn(CO)_4(COCH_2Ph)_2]^-$ and $[Mn(CO)_3(COCH_2Ph)_3]^{2-}$ from $Mn(CO)_5COCH_2Ph$ and $PhCH_2MgCl$ was mentioned earlier (55). It has been noted that [cis-$Mn(CO)_4(COR)_2]^-$ complexes resemble 1,3-diketones and might themselves function as ligands. Reaction of the above complex (R = Me) with $AlCl_3$ yields the interesting substance $[Mn(CO)_4(COMe)_2]_3Al$, XX (116).



XX



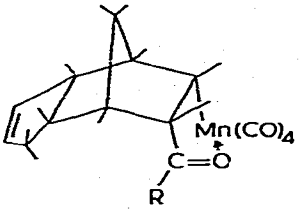
XXI

Another paper reports the aldol condensation of $MeCOCH_2Ph$ induced by $Mn(CO)_5Me$ (117). The product is assigned structure XXI.

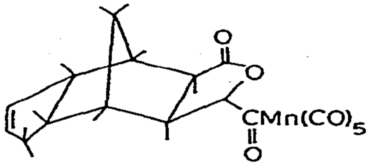
Stereochemistry of carbonyl substitution in $Mn(CO)_5CH_2Ph$ and $Mn(CO)_5COCH_2Ph$

by PPh_3 and $P(OPh)_3$, and the stereochemistry of the reaction products from $[Mn(CO)_4L$ and $PhCH_2COCl$ are reported (55).

The compounds $Mn(CO)_5R$ (R = Me, Ph) have been shown to add in a 1:1 and 1:2 fashion to dicyclopentadiene and bicyclo-2,2,1-heptadiene (118). The structure of the 1:1 adduct of dicyclopentadiene is shown below (XXII). In the 1:2 adduct

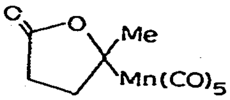


XXII

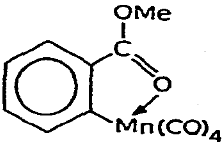


XXIII

the coordination of the ketonic oxygen to manganese is believed not to occur; instead the second molecule of dicyclopentadiene coordinates directly to the metal through an olefinic group. A related paper by the same authors is concerned with reactions of $Mn(CO)_5COR$ (R = Me, Ph) and dicyclopentadiene (119). Again 1:1 and 2:1 adducts are formed. The structure of the product formed is shown in XXIII. Its formation is rationalized in mechanistic terms. A similar product XXIV is formed in the reaction of $Mn(CO)_5^-$ and $MeCOCH_2CH_2COCl$.

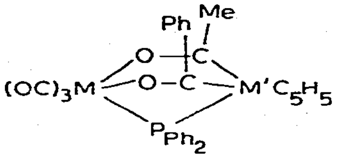


XXIV

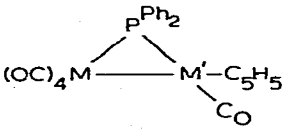


XXV

On heating, the compound o-carbomethoxybenzoylmanganese pentacarbonyl $Mn(CO)_5COC_6H_4COOMe$, undergoes an unexpected loss of two carbonyls instead of one the product being XXV (120). No mono-decarbonylation is observed. The reaction of this acyl complex with $P(OCH_2)_3CEt$ gives only $Mn(CO)_3LC_6H_4COOMe$, a phosphite substituted derivative of the decarbonylated product XXV. A remarkable reaction occurs between $M(CO)_5Me$ (M = Mn, Re) and $C_5H_5M'(CO)PPh_3$ (M' = Ir, Rh) (121). Two substances, XXVI and XXVII, are identified as reaction products.

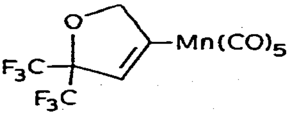

(M = Mn,Re;
M' = Rh,Ir)

XXVI


(M = Mn,Re;
M' = Rh,Ir)

XXVII

Insertion and cycloaddition reactions of various metal-alkyl compounds are described in a general review paper (10). Particular note is directed in this work to complexes of manganese and iron. Another paper has appeared presenting some of this work (122). The reaction of $Mn(CO)_5CH_2C{\equiv}CR$ and CF_3COCF_3 is found to give a 1:1 cycloaddition product, as is the reaction of this fluorinated ketone with $Mn(CO)_5CH_2CH{=}CHPh$. The former species are represented as metal dehydrofuranato complexes XXIX; the latter are the related hydrogenated complexes having a σ-tetrahydrofuranato ligand group.


XXIX

The unusual bridging carbyne complex $Mn_2(CO)_8(CCOOR)_2$, is described in a full paper (123). Communication of this work occurred last year.

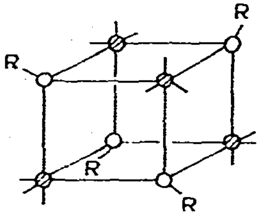
Among physical studies on complexes having alkyl or acyl metal bonds are PES studies of several $Mn(CO)_5R$ (34) and $Re(CO)_5R$ (82) compounds. The former reference (34) also provides thermochemical data on $M(CO)_5Me$ (M = Mn, Re) and $Mn(CO)_5COPh$. Extensive carbon-13 nmr data for $Re(CO)_5R$ species are recorded in another paper (62).

V METAL CARBONYL DERIVATIVES OF METALS AND METALLOIDS

This section will first consider complexes of electropositive metals bonded to manganese and rhenium; then coverage will proceed from Group IIIA to Group VIA element derivatives of these metals.

There are few references to covalent derivatives of other metals bonded to the elements of this group. A review of reactions of lanthanide elements with $Mn(CO)_5Br$ was mentioned earlier in this survey (7). Vibration spectral data for palladium, platinum and gold complexes of the $-Mn(CO)_5$ group have been reported and frequency assignments to Mn-M' bonds made (124). The reaction of $Mn(CO)_5Br$ and $RHgC(N_2)COOR$ is described to give $Mn_2(CO)_8(CCOOR)_2$ compounds; also obtained as products in this reaction are $Mn(CO)_5HgBr$ and $Mn(CO)_4(ROOCC{\equiv}CCOOR)$ (123).

A review of Group IIIA complexes of transition metals was mentioned at the beginning of this survey (15). This review contains much work on manganese and rhenium complexes of these elements. Two full papers describe work on indium-rheni complexes which was the subject of a communication last year. In the first paper the reaction of indium and rhenium carbonyl is described (125) to give two compounds The first is $Re_2(CO)_8[\mu\text{-}InRe(CO)_5]_2$, and is characterized by a crystal structure study (126). The second is also characterized crystallographically. It has the formula $Re_4(CO)_{12}[\mu\text{-}InRe(CO)_5]_4$ (125), having the Re_4In_4 unit in the shape of a cube (XXX).



⊘ = $Re(CO)_3$

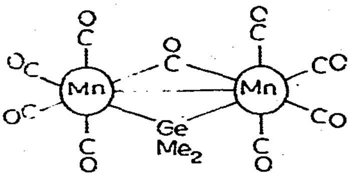
O–R = $InRe(CO)_5$

XXX

More work is reported on Group IVA derivatives. The first lead-manganese compounds to be reported, $Mn(CO)_4(PPh_3)PbR_3$ and $[Mn(CO)_4(PPh_3)]_2PbR_2$ (R = Me, Ph), were prepared from the reaction of $[Mn(CO)_4PPh_3]^-$ and $PbR_{4-n}X_n$ (127). Other syntheses are reported for the fac isomer, $Mn(CO)_3(Me_2AsCH_2CH_2CH_2AsMe_2)GeCl_3$, from $Mn(CO)_3(Me_2AsCH_2CH_2CH_2AsMe_2)Cl$ and $GeCl_4$ and for mer-$Mn(CO)_3(DPE)GeCl_3$ from $Mn(CO)_3(DPE)Br$ and $GeCl_4$ (128). Reaction chemistry of some Group IVA compounds is also described. Treatment of $Mn(CO)_5MPh_3$ (M = Si, Sn) with halogens leads either to M—Mn or M—Ph cleavage. With $Mn(CO)_5SiPh_3$ and either Br_2 or Cl_2 the Si-Mn bond is cleaved; with $Mn(CO)_5SnPh_3$, the cleavage of the Sn-Ph bond is preferred, and the compounds $Mn(CO)_5SnPh_{3-n}X_n$ (X = Cl, Br, I) are isolated (129). A kinetic study of the reaction of I_2 and $Mn(CO)_5SnPh_3$ is reported (130). Halogenations of Ge-H bonds in $Mn(CO)_5GeMeH_2$ and $Mn(CO)_5GeH_3$ by $CHCl_3$, CCl_4, or Br_2 are reported (131). From reactions of the former organometallic complex and $CHCl_3$ three products are found; these are starting material 22%, $Mn(CO)_5Ge(Me)HCl$ 39%, and $Mn(CO)_5Ge(Me)Cl_2$ 39%. Bromine gives only $Mn(CO)_5Ge(Me)Br_2$. With CCl_4, $Mn(CO)_5GeH_3$ yields $Mn(CO)_5GeCl_3$. Substitution reactions of $Mn(CO)_5SnR_3$ (R = Me, Ph) with PPh_3, $AsPh_3$, and $SbPh_3$ are reported in another paper (132) to give monosubstituted $Mn(CO)_4(L)SnR_3$.

Four papers on structural studies for representative compounds have appeared. Electron diffraction results for $Mn(CO)_5SiH_3$ and $Mn(CO)_5GeH_3$ show that the Mn-Si and Mn-Ge bonds are about 0.1Å shorter than expected (133). This result is attributed to a Si-Mn or Ge-Mn bond multiplicity greater than one, resulting from π bonding. The structure of $Mn(CO)_5SiF_3$, also determined by electron diffraction (134), shows an even shorter Mn-Si bond length. The small difference between $Mn(CO)_5SiF_3$ and $Mn(CO)_5SiH_3$, is suggested to be due either to π or σ bonding differences.

A structure determination by x-ray crystallography has been carried out on the compound $Mn(CO)_5SnCl_3$ (135). The Sn-Mn distance of 2.590(5)Å is 0.08Å shorter than the reported Sn-Mn distances in $Mn(CO)_5SnR_3$ (R = Me, Ph) complexes. Crystallography has been used to characterize the distannane compound $[Sn\{Mn(CO)_5\}_2H]_2$ (136); this product arises in the reaction of $Mn(CO)_5H$ and $Sn(C_5H_5)_2$. The structure of $Mn_2(CO)_9GeMe_2$ has also been determined (137); its molecular geometry is sketched below, XXXI.

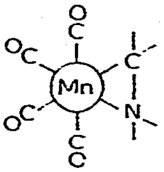


XXXI

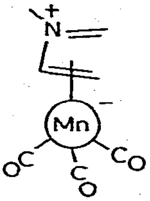
Bond energy values for the Re-M bond in $Re(CO)_5MMe_3$ (M = Si, Ge, Sn) have been obtained using mass spectrometric appearance potentials (138). Values obtained are 3.1, 3.2, and 3.7 ev for the Re-Si, Re-Ge, and Re-Sn bonds. In contrast the Mn-M bond energies for $Mn(CO)_5MMe_3$ are about 2.5 ev.

Carbon-13 nmr on $Re(CO)_5MMe_3$ (M = Si, Ge, Sn, Pb) and on $Re(CO)_5SiCl_3$ are noted (62). Magnetic shielding, determined by heteronuclear double resonance experiments are reported for 35 organotin-transition metal compounds including $Me_{4-x}Sn[Mn(CO)_5]_x$ (x = 1,2,3) and $Me_2Sn[Re(CO)_5]_2$ (139).

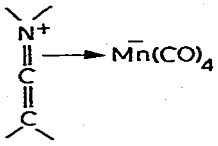
Moving on to Group VA derivatives of these elements, the next consideration may be directed to nitrogen ligands. Here again there are some interesting and diverse studies. Particular note is made here first of several papers dealing with unsaturated carbon-nitrogen ligands. Abel and Rowley (140) describe reaction products derived from $M(CO)_5X$ (M = Mn, Re) and $Me_3SnCH_2NR_2$ (R = Me, Et, C_6H_{11}, H). A general molecular formula $Mn(CO)_4(CH_2NR_2)$ is assigned, with structure XXXII being suggested. A somewhat similar product, $Mn(CO)_4(CH_2N(Me)CH_2Ph)$ was mentioned earlier (105). This compound was obtained from $PhCH_2NMe_2$ and $Mn(CO)_5Me$ in an attempted ortho-metallation reaction. Also of note is the compound, XXXIII (99). This compound is obtained from $\overline{Mn(CO)_4COC(=CMe_2)NR_2}$ on thermal decarbonylation. Compound XXXIV was also reported in this paper.



XXXII



XXXIII

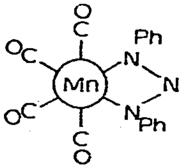


XXXIV

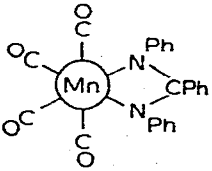
It was obtained from the same precursor on treatment with $Fe_2(CO)_9$.

Two papers which are concerned with metal porphyrin complexes have appeared. The first is a general review (9). The second (141) deals with rhenium and technetium complexes derived from the dinuclear carbonyl and either meso-porphyrin (IX) dimethyl ester (H_2MP) or meso-tetraphenylporphin (H_2TPP). Complexes of the formulas $TPP[M(CO)_3]_2$ (M = Mn, Re) are reported; structural studies by x-ray crystallography have been done for both compounds. The complexes $M(HMP)(CO)_3$ are also reported. These are found to be fluxional by nmr studies, the metal and hydrogen exchanging between the ligand sites.

Diphenyltriazenido complexes of several metals including manganese and rhenium were prepared. These complexes, $M(CO)_4(PhN_3Ph)$, structure XXXV, are formed from the metal carbonyl halide and $Na[PhN_3Ph]$ (142). Another complex, somewhat related, is prepared by photolysis of $\overline{Mn(CO)_4CONPhCPhNPh}$, which is itself prepared from $Mn(CO)_5X$ and $Li[PhNCPhNPh]$. This compound probably has structure XXXVI (143).

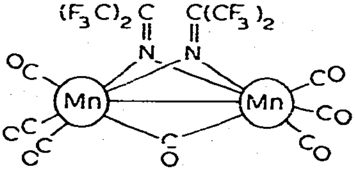


XXXV

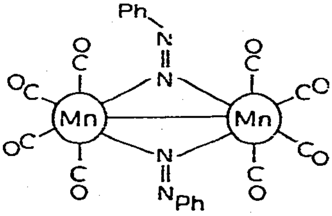


XXXVI

The reaction products of $Mn(CO)_5Br$ with $Me_3SnN{=}C(CF_3)_2$ and with $Me_3SiNNPh$ having the stoichiometries $Mn_2(CO)_7[NC(CF_3)_2]_2$ and $Mn_2(CO)_8(NNPh)_2$, respectively. They are found to have the structures XXXVII (144) and XXXVIII (145) by x-ray crystallography.



XXXVII



XXXVIII

The chemistry of $-P(CF_3)_2$ or $-As(CF_3)_2$ complexes of manganese is the subject of a recent study. Reactions of $Mn(CO)_5H$ and $A_2(CF_3)_4$ (A = P, As) give the complexes $Mn(CO)_5A(CF_3)_2$, which may be decarbonylated by heating or ultraviolet irradiation, giving $Mn_2(CO)_8[A(CF_3)_2]_2$. The mixed complex $Mn_2(CO)_8[P(CF_3)_2]$-$[As(CF_3)_2]$ is also described (146). Gas and liquid phase infrared and Raman spectra of the monomers $Mn(CO)_5A(CF_3)_2$ are reported in another paper (147).

The synthesis (121) and a structure study (148) of an unusual compound $Mn(CO)_3(PPh_2)(OCMe)(OCPh)IrC_5H_5$ are reported. The complex reaction sequence when $Mn_2(CO)_{10}$ is reacted with phospholes is the subject of another study, cited earlier (32). Noteworthy is the phospholyl compound $C_4H_4PMn(CO)_3$.

An x-ray crystallographic study has determined the structure of $MnFe(CO)_8PPh_2$ (149). The manganese-iron bond in this compound is rather long, because of steric hindrance between carbonyls on adjacent metals.

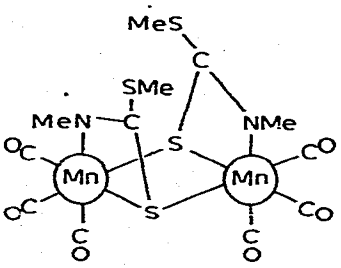
The structure of the complex $Mn_2(CO)_6(AsMe_2)_3C_4F_5$ has been ascertained by crystallographic methods (150). The synthesis of this compound was described last year. Kinetics of the thermal rearrangement of $Mn_2(CO)_8(Me_2AsC(CF_3)C(CF_3)AsMe_2)$ to form this compound are noted (21).

Several reports occur concerning derivatives of rhenium carbonyl with β-diketones as ligands. The reaction of $Re(CO)_5Cl$ and Tl(acac) in monoglyme gives the red to yellow crystalline complexes $[Re(CO)_3acac]_2\cdot solv$ (151). The solvent could not be removed. Further reaction with added PPh_2Me gives mononuclear $Re(CO)_3(PPh_2Me)acac$. Other authors report the similar formation of the dinuclear complex as a dihydrate from methanol-water with added methoxide (152). Ligand reactions to give $Re(CO)_3Lacac$ or $Re(CO)_2L_2acac$ occur with APh_3 (A = P, As, Sb) and with $P(OPh)_3$. A third paper on the reaction of $Re(CO)_5Cl$ and β-diketones reports formation of $[Re(CO)_3acac]_2$ along with $[Re(CO)_3Cl\cdot acacH]_2$ (153). The second product is suggested to be a halide bridge dimer, with one coordination position on each metal occupied by an oxygen donor atom of the diketone in the enol form.

An anionic complex with a bridging OMe group was tentatively characterized (48). This compound is formed from $Re_2(CO)_{10}$ and basic methanol. The tetranuclear $[Re(CO)_3OH]_4$ was also mentioned earlier (49).

The topic of organosulfur ligand complexes of metal carbonyls has been reviewed (14). Several sulfur containing complexes, products of addition of either $CF_3C{\equiv}CCF_3$ or $CF_3C{\equiv}CH$ to $[Mn(CO)_4SC_6F_5]_2$, are reported and the crystal structure of one of these products, $Mn[C_4(CF_3)_4SC_6F_5](CO)_3$ has been determined (154). The attempted ortho-metallation of $PhCH_2SMe$ by $Re(CO)_5Me$ gives $[Re(CO)_3SCH_2Ph]_4$ instead (110).

The pentacarbonylmanganate ion is found to add to methylisothiocyanate (155); methylation of the product with MeI gives the dinuclear species $[Mn(CO)_3\{SC(SMe)NMe\}]_2$ in 31% yield. Its structure is shown below, XXXIX.



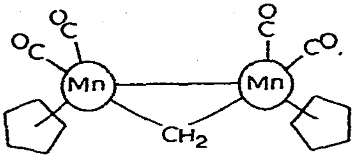
XXXIX

Also reported is the synthesis of $Mn_2(CO)_8S_2$ from $Mn_2(CO)_{10}$ and $(FCO)_2S_2$ (156), and the synthesis of dithio- and diseleno-carbamate derivatives $Mn(CO)_4(X_2CNMe_2)$ (X = S, Se). These decarbonylate on heating to give dimeric compounds $[Mn(CO)_3X_2CNMe_2]_2$ (157).

VII HYDROCARBON-METAL COMPLEXES

As in previous years much has been reported on cyclopentadienyl-metal tricarbonyl complexes and their derivatives. However, there have been other interesting developments as well which concern the complexes of other hydrocarbon groups. The former subject will be considered first.

Papers have appeared which describe compounds obtained from $C_5H_5Mn(CO)_2THF$, added ligand displacing the weakly coordinated ether group. For example the syntheses of various acetylene derivatives $C_5H_5Mn(CO)_2L$ (L = $PhC{\equiv}CMPh_3$ for M = Si, Ge, Sn, $PhC{\equiv}CH$) and $C_5H_5Mn(CO)_2(PhC{\equiv}C\text{-}C{\equiv}CPh)Mn(CO)_2C_5H_5$ is accomplished by this route (158, 159). A pentamethylene-diazirine complex is also formed from $MeC_5H_4Mn(CO)_2THF$ (160). The curious reaction of $C_5H_5Mn(CO)_2THF$ (and $MeC_5H_4Mn(CO)_2$ and CH_2N_2 at low temperature is noted (161) wherein two products are formed. The first is $C_5H_5Mn(CO)_2(C_2H_4)$, the olefinic group being formed by coupling of two methylene groups. The second is the dinuclear compound $[C_5H_5Mn(CO)_2]_2CH_2$, a compo having the CH_2 group bridging the two metals and accompanied by a metal-metal bond The geometry of the complex dictates that isomers of this compound should exist depending on relative orientations of the C_5H_5 rings in cis or trans configurations (XXXX).



XXXX (*cis* isomer)

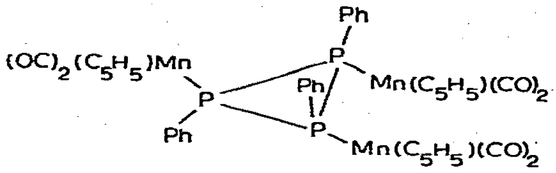
A seleno carbonyl derivative of $C_5H_5Mn(CO)_2CSe$ is described by Butler et al. (162). This is obtained by reaction of $C_5H_5Mn(CO)_2THF$, CSe_2 and PPh_3.

Various complex reactions of diazonium compounds with $C_5H_5Mn(CO)_2THF$ or $MeC_5H_4Mn(CO)_2THF$ are the subject of another study (163). Using $MeCOC(N_2)Me$, a single product is obtained having the formula $MeC_5H_4Mn(CO)_2(CH_2{=}CHCOMe)$. The vinyl methyl ketone is complexed through the olefinic bond. Reaction with $PhCOC(N_2)Ph$ give first the carbene complex $C_5H_5Mn(CO)_2C(COPh)Ph$. A crystal structure study of this compound is reported in a separate paper (164). On irradiation this compound rearranges to a complex of diphenyl ketene, $C_5H_5Mn(CO)_2$-$(Ph_2C{=}C{=}O)$. A diphenylcarbene complex is also obtained from Ph_2CN_2; this has the formula $C_5H_5Mn(CO)_2(CPh_2)$. Some chemical behavior of this complex is described. Thermal degradation gives $Ph_2C{=}CPh_2$, and ceric ion oxidation gives Ph_2CO.

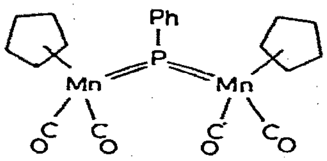
Several vinyl ketone complexes $C_5H_5Mn(CO)_2L$ ($L = CH_2{=}CHCOMe$, trans-$PhCH{=}CHCOMe$, cyclohexenone) are reported, obtained from reactions of the ligand and $C_5H_5Mn(CO)_2THF$ (165). A crystal structure study on the first compound has been carried out (166).

A kinetic study on substitution reactions of $C_5H_5Mn(CO)_2SR_2$ (R - Me, Et) is reported (167). Reactions involving displacement of the sulfide by phosphines and phosphites were studied, and found to be first order in complex.

A series of four papers from Huttner and coworkers reports reactions of $C_5H_5Mn(CO)_2PPhH_2$ and $MeC_5H_4Mn(CO)_2PPhH_2$. Lithiation with butyllithium occurs to give either the mono- or dilithio species. These may be deuterated with D_2O (168). However, a more interesting reaction is seen with $C_6H_{11}NCl_2$ which gives the compound $P_3Ph_3[Mn(CO)_2C_5H_5]_3$ (169). The structure of this substance has a P_3Ph_3 ring with each phosphorus bonded to a manganese atom. Structure XXXXI (note stereochemistry) has been verified by a crystal structure study. Heating this compound at 110° in vacuo gives another compound $PhP[Mn(CO)_2C_5H_5]_2$. A structural study shows it to be a phosphinidene complex XXXXII (170). The P-Mn bond in this species is unusually short, indicating multiple bonding. When $C_5H_5Mn(CO)_2PPhH$ is treated directly with $C_6H_{11}NCl_2$ two compounds, $C_5H_5Mn(CO)_2PPh(H)Cl$ and $C_5H_5Mn(CO)_2PPhCl_2$ are obtained (171). The former is not obtained pure, it is shown to react with $C_6H_{11}NH_2$ to give $C_5H_5Mn(CO)_2PPh(NHC_6H_{11})H$. Also reported in this paper is the reaction of $C_5H_5Mn(CO)_2PPhH_2$ with I_2 in THF; an unusual compound $C_5H_5Mn(CO)_2PPh(H)OCH_2CH_2CH_2CH_2I$ is the product.



XXXXI



XXXXII

Reactions of diazocyclopentadiene and $Mn(CO)_5X$ produce $C_5H_4XMn(CO)_3$ (X = Cl, Br, I) (172). The analogous reaction with tetraphenyl diazocyclopentadiene and $Mn(CO)_5Cl$ to give $C_5Ph_4ClMn(CO)_3$ also is reported. The synthesis of $C_5Cl_5Mn(CO)_3$ by a similar route (98) has been mentioned earlier in this review.

Studies on $AlCl_3$ adduct formation with $C_5H_5Mn(CO)_{3-x}(PPh_3)_x$ (x = 0, 1, 2) are reported (78). This work complements earlier studies on the basicities of these species toward protonic acids.

Oxidative chemistry of substituted cyclopentadienyl manganese carbonyls has drawn some attention. The one-electron oxidation of $C_5H_5Mn(CO)(DPE)$ to the paramagnetic, d^5, complex $[C_5H_5Mn(CO)(DPE)]^+$ by Ag^+ is noted in a communication (75) and in a thesis (54). The methylcyclopentadienyl compound reacts in like manner. These oxidations had to be anticipated based on electrochemical data. Oxidations of mono- and bis- substituted $C_5H_5Mn(CO)_3$ and $C_5H_5Re(CO)_3$ compounds have also been studied using electrochemistry (173). Again one electron oxidations appear to be facile processes. The complex $C_5H_5Mn(CO)_2Ph_2PCH_2CH_2PPh_2$, in which the potentially bidentate phosphine bonds to the metal through one phosphorus, is subjected to chemical oxidation. The phosphine oxide complex $C_5H_5Mn(CO)_2Ph_2PCH_2CH_2POPh_2$ is formed (174).

Acyl substituted compounds $RCOC_5H_4M(CO)_3$ have received special attention. Crystal structure studies on the acetyl compounds of manganese and rhenium, $MeCOC_5H_4M(CO)_3$ (R = Mn, Re) are reported (175). These two compounds differ slightly based on the orientation of the CO groups relative to the ring substituent. The acyl carbonyl group is coplanar with the ring. Ultraviolet and visible spectroscopy and nmr spectroscopy have been used to examine $XC_6H_4COC_5H_4Mn(CO)_3$ (176). The radical anion, $[PhCOC_5H_4Mn(CO)_3]^{\cdot}$ has been prepared, its esr spectrum recorded, and these results compared with Huckel MO calculations (177).

Molecular orbital calculations for the series of compounds $C_6H_6Cr(CO)_3$, $C_5H_5Mn(CO)_3$, and $C_4H_4Fe(CO)_3$ are reported (178). An attempt is made to correlate these calculations with relative reactivities.

Parker (179) reports on a study of the vibrational spectrum of $MeC_5H_4Mn(CO)_3$. Deuteration of the ring allows assignment of the MeC_5H_4-vibrational modes. A study of the intensities of $\nu(CO)$ and $\nu(CS)$ in $C_5H_5Mn(CO)_2CS$ is noted (180). Mass spectra are reported for $RC_5H_4Mn(CO)_2CX$ (R = Me, H; X = O, S, Se) (181). These data confirm that the dissociation energy of the M-CS bond is much greater than for the M—CO bond; this had also been suggested by chemical behavior.

Two variable temperature pmr spectral studies are to be noted. The first is on the compound $C_5H_5Mn(CO)_2[C_2(OMe)_4]$ (182), the second on $C_5H_5Mn(CO)_2L$ (L = dimethylmaleate and fumarate) compounds (183). Both studies note that there is hindered rotation for the metal olefin bond. For the latter compounds a barrier to rotation ($\Delta G^{\ddagger}$) of 11-12 Kcals is determined. Phosphorus-31 chemical shift and coupling constant data is present for several compounds including $MeC_5H_4Mn(CO)(\widehat{L\,L})$ ($\widehat{L\,L}$ = DPE, DPM, and DPA) (61) and also a series of $C_5H_5Mn(CO)_2L$ (L = $PPh_{3-x}Me_x$, $AsPh_3$, $SbPh_3$, $P(OPh)_3$) compounds (184).

Reference was made at an earlier point in this review to two studies on $C_5H_5Re(CO)_2Br_2$ (77,78). A mass spectral study on these and analogous compounds, $RC_5H_4Re(CO)_2XY$ (R = H, Me, COOMe; X,Y = several combinations of H, Me, COMe, Br, I, HgCl) has been concluded (185). Fragmentation occurs in two pathways, with either carbonyl or X,Y loss.

Various studies on $[C_5H_5Mn(NO)(CO)_2]^+$ and on compound derived from this species are reported. Two general survey papers by Brunner, conference abstracts, were noted earlier (3,6). A full paper from Brunner and Langer (186) reports reactions of $[C_5H_5Mn(NO)(CO)PPh_3]^+$ with organolithium compounds. Two products are obtained. The first is an acyl-manganese compound, arising by addition of R^- to the carbonyl; the second is a cyclopentadiene compound, formation occurring by R^- addition to the C_5H_5 ring. The acyl compounds are generated from optically active starting material without loss of configuration. They are found to racemize slowly by phosphine dissociation. Synthesis of $[R_5CH_4Mn(NO)(CO)CS]^+$ (R = H, Me) compounds from $RC_5H_4Mn(CO)_2CS$ and $[NO]SbF_6$ or $[NO_2]PF_6$ has been reported (187). These complexes react with APh_3 (A = P, As, Sb) with carbonyl displacement. The phosphorus-31 nmr of $[C_5H_5Mn(NO)\{P(CH_2CH_2PPh_2)_3\}]P$ is described (86).

Complexes of various other hydrocarbons are next considered here. The synthesis of $Mn(C_5H_5)(C_6H_6)$ and derivatives thereof using metal atom reactor techniques is reviewed (12). The mass spectrum of this compound was recorded, wherein the secondary ion formation ($Mn_2(C_5H_5)_2C_6H_6^+$, $Mn_2(C_5H_5)_2^+$, $Mn(C_5H_5)_2^+$

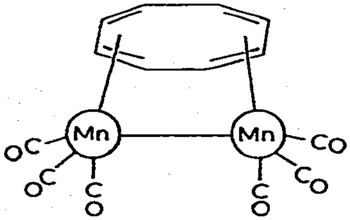
and $Mn_2(C_5H_5)^+$) is of specific interest (188).

The compound $Mn(C_5H_5)C_7H_8$ has been prepared photolytically from $C_5H_5Mn(CO)_3$ (189). Formation appears to occur stepwise with sequential loss of CO. Using 7-substituted C_7H_7R compound the compounds $Mn(C_5H_5)(C_7H_7R)$ are formed primarily as exo isomers. The compound $Mn(C_5H_5)(C_7H_8)$ loses hydride ion to $[CPh_3]^+$, giving $[Mn(C_5H_5)(C_7H_7)]^+$; however exo-substituted $Mn(C_5H_5)(C_7H_7R)$ compounds resist hydride loss. Lithium aluminum hydride regenerates $Mn(C_5H_5)(C_7H_8)$. Cyclooctatriene and a cycloctatetraene derivatives are also mentioned in this study.

A study on the PES spectra of various fluxional manganese compounds ($C_7H_7Mn(CO)_3$, Mn(pentadienyl)$(CO)_3$) are reported, and data correlated with molecular orbital calculations (190). For $C_7H_7Mn(CO)_3$ it is suggested that there is a low lying virtual level resulting from interaction of a ring π* and a a" metal orbital (e_2) which may play an important role in the fluxional process.

At low temperature several isomers are observed by nmr for the compounds $Mn[C_5H_5(CH_2)_x](CO)_{3-x}L_x$ (L = $P(OCH_2)_3CEt$; $C_5H_5(CH_2)_x$ = cyclohexadienyl, cycloheptadienyl, etc. (197). These isomers arise because of the orientation of the ligands relative to the hydrocarbon group. At room temperature the isomers are not discernable, owing to a scrambling process.

A crystal structure is reported for $C_8H_8Mn_2(CO)_6$, compound XXXXIII below (192). A long Mn-Mn bond 3.045(2)Å is found; this is compared to 2.923Å in $Mn_2(CO)_{10}$.



XXXXIII

Directive effects toward ring substitution are noted in reactions of the compounds $[Mn(transMeC_6H_4X)(CO)_3]^+$ with organolithium compounds and $LiAlH_4$ (193). Isomers arise by ring substitution at carbon adjacent either to Me or to X (X = halide, OR, NR_2). The syntheses of $[Mn(C_6H_5X)(CO)_3]^+$ by nucleophilic substitution of chloride in $[Mn(C_6H_5Cl)(CO)_3]^+$ by OMe^-, OPh^-, N_3^-, and NRH^- are reported (58). The complexes $[Mn(C_6H_5NHR)(CO)_3]^+$ deprotonate readily and reversibly.

The photolytic reaction of $Mn(CO)_4NO$ and butadiene is reported to give three products (194). These are known $Mn(CO)(NO)_3$, $Mn(C_4H_6)(NO)(CO)_2$ a yellow volatile oil, and $Mn(CO)(C_4H_6)_2$. The last substance is paramagnetic and has been the subject of a crystal structure study (195).

The complex $Mn(PhCHCMeCHC(CH_2Ph)O)(CO)_3$, XXI, was mentioned earlier, arising from an aldol condensation of $MeCOCH_2Ph$ using $Mn(CO)_5Me$ (117).

The pmr study of $Re(allyl)(CO)_4$ in a nematic phase has been carried out (196).

VIII VARIOUS ISOCYANIDE AND NITROSYL COMPOUNDS

The only paper in the area of isocyanide-complexes which has not previously been cited is concerned with descriptive isocyanide-rhenium chemistry (197). Freni and Romiti find that reaction of $KReI_6$ with p-tolylNC gives either $Re(CNR)_5I$ if excess isocyanide is used or $Re(CNR)_4I_3$ and $Re(CNR)_3I_3$ if there is a deficiency of this reagent. Reaction of $KReBr_6$ and this ligand gives only $Re(CNR)_3Br_3$. Carbonylation of $Re(CNR)_3I_3$ in ethanol is said to give the unusual rhenium(II) complex $Re(CNR)_4(CO)I_2$. A diamagnetic non-electrolyte, $Re(CO)_4(CNR)_2I$, is describ as the product of the reaction of $[Re(CO)_4I_2]^-$ and isocyanide, whereas the isocyani reaction with $[Re(CO)_2I_4]^-$ gives ionic $[ReL_4(CO)_2]I$.

Other work on isocyanide metal complexes cited earlier includes: formation of $Mn_2(CO)_{10-x}L_x$ (29); MO calculations on $[Mn(CO)_{6-x}(CNMe)_x]^+$ and $Mn(CO)_{5-x}(CNMe)_x$ (64); the carbon-13 nmr of $Mn(CNPh)_4(CO)Cl$ (85); and reactions of CNR with several manganese carbene complexes (53).

A new synthesis of the nitrosyl compound $\mathrm{Mn(NO)(CO)_4}$ from $\mathrm{Mn(CO)_5^-}$ and NOCl is reported (193). Reactions of this compound with butadiene were carried out and a new derivative of this compound, $\mathrm{Mn(NO)(C_4H_6)(CO)_2}$, was prepared (194). Various studies on $\mathrm{[C_5H_5Mn(NO)(CO)_2]^+}$ were cited already (3, 6, 86, 186, 187).

IX STRUCTURAL STUDIES

The compounds that have been subjects of structural studies by x-ray crystallography and electron diffraction are listed below: *cis*$\mathrm{(CO)_5MnRe(CO)_4CMe(OMe)}$ (35); $\mathrm{Mn(CO)(DPE)(Ph_2PCH_2CH_2PPhC_6H_4CO)}$ (38); $\mathrm{Mn_2(CO)_5(DPM)_2}$ (40, 41); $\mathrm{(Et_4N)_2}$-$\mathrm{[Re_4(CO)_{15}H_4]}$ (48);*cis*-$\mathrm{[Tc(CO)_2\{PPh(OEt)_2\}_4]ClO_4}$ (60); *fac* and *mer*-*trans*-$\mathrm{Mn(CO)_3[PPh(OMe)_2]_2Br}$ (81); $\mathrm{Mn(CO)_4C_6H_4CO}$ (104), $\mathrm{Mn(CO)_3(PPh_3)(C_6H_4CH_2SMe)}$ (113); $\mathrm{Al[Mn(CO)_4(COMe)_2]_3}$ (116); $\mathrm{Re_4(CO)_{12}[InRe(CO)_5]_4}$ (125); $\mathrm{Re_2(CO)_8[InRe(CO)_5]_2}$ (126); *fac*-$\mathrm{Mn(CO)_3(Me_2AsCH_2CH_2CH_2AsMe_2)GeCl_3}$ (128); $\mathrm{Mn(CO)_5SiH_3}$ and $\mathrm{Mn(CO)_5GeH_3}$, electron diffraction (133); $\mathrm{Mn(CO)_5SiF_3}$, electron diffraction (134); $\mathrm{Mn(CO)_5SiCl_3}$ (135); $\mathrm{Sn_2H_2[Mn(CO)_5]_4}$ (136); $\mathrm{Mn_2(CO)_7GeMe_2}$ (137); $\mathrm{TPP[Tc(CO)_3]_2}$ and $\mathrm{TPP[Re(CO)_3]_2}$ TPP = tetraphenylporphin (141); $\mathrm{Mn_2(CO)_7[NC(CF_3)_2]_2}$ (144); $\mathrm{Mn_2(CO)_8(N_2Ph)_2}$ (145); $\mathrm{Mn(CO)_3PPh_2(COMe)(COPh)IrC_5H_5}$ (148); $\mathrm{MnFe(CO)_8PPh_2}$ (149); $\mathrm{Mn_2CO)_6(AsMe_2)_3C_4F_5}$ (150); $\mathrm{Mn(CO)_3C_4(CF_3)_4SC_6F_5}$ (151);$\mathrm{[Mn(CO)_3\{SC(SMe)NMe\}]_2}$ (155); $\mathrm{C_5H_5Mn(CO)_2CPh(OPh)}$ (164), $\mathrm{C_5H_5Mn(CO)_2(CH_2{=}CHCOMe)}$ (166); $\mathrm{[C_5H_5Mn(CO)_2]_3P_3Ph_3}$ (159); $\mathrm{PhP[Mn(C_5H_5)(CO)_2]_2}$ (170); $\mathrm{MeCOC_5H_4Mn(CO)_3}$ and $\mathrm{MeCOC_5H_4Re(CO)_3}$ (175); $\mathrm{C_8H_8Mn_2(CO)_6}$ (194); and $\mathrm{Mn(CO)(C_4H_6)_2}$ (197).

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