MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1972

P. M. Treichel
Department of Chemistry, University of Wisconsin, Madison,
Wisconsin 53706 (U.S.A.)

CONTENTS

I INTRODUCTION

This section of ANNUAL SURVEYS is organized in a fashion somewhat different to that of previous years. The sequential treatment of material here is based entirely on compound type; within the discussion of each class of compounds is contained syntheses and chemical behavior, structural studies and bonding, and spectroscopic observations. A topical outline is provided in the Table of Contents, above.

It is noted that a transition between authors for this section may lead to minor overlap between this volume and the last, or alternatively there may arise some discontinuity in the coverage of certain journals. It is hoped that these effects will be minimal. This author hopes to continue the tradition of excellence established in earlier volumes of this series by Professor Wojcicki.

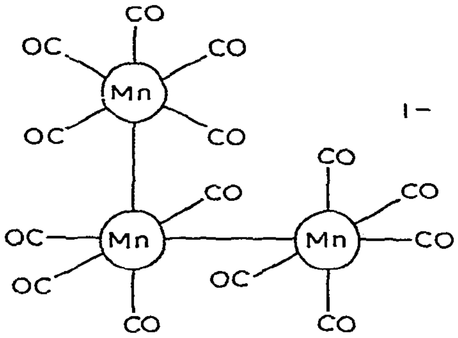
One review article pertinent to this area has appeared (1) during the last year; this is a review of the organometallic chemistry of rhenium. There is also a general review of hydride-metal complexes (2) which contains a good section on manganese and rhenium carbonyl hydrides, and a review on nitrogen fixation by Sellmann (3) which deals extensively with his work on nitrogen derivatives of manganese and rhenium. There is also a review of transition metal catalyzed olefin disproportionation reactions, including reactions involving rhenium oxide catalysts (4).

II THE METAL CARBONYLS, AND DERIVATIVES OBTAINED BY SIMPLE LIGAND SUBSTITUTION

Within this section there will be considered the manganese, technetium and rhenium species having only carbon monoxide as a ligand; in addition complexes derived from these species by simple substitution of a ligand for CO are included. This treatment limits consideration primarily to three types of complexes: $M(CO)_5^-$, $M_2(CO)_{10}$, and $M(CO)_6^+$, and their derivatives.

Ibers has continued his interest in the structural aspects of five coordination, and has published with B. A. Frenz a paper (5) describing the crystal and molecular structure of the salt $[Ni(o\text{-}phen)_3][Mn(CO)_5]_2$. The x-ray diffraction data were collected at low temperature (-123°). There are two crystallographically non-equivalent $Mn(CO)_5^-$ anions within this structure; both anions have an approximate trigonal bipyramidal arrangement of ligands around the central metal atom with only very minor distortions being noted. Fairly accurate metal-carbon bond length information was obtained; these data show the axial metal carbonyl distances to be slightly greater (∿0.02 Å) than the equatorial metal carbonyl bond lengths. This is in contrast to a number of known structures of other five-coordinate d^8 and d^9 metal complexes. The bond length data can be rationalized, however, based upon a consideration of two counterbalancing effects, the valence shell electron pair repulsion, which would lead to longer axial bond lengths, and the asymmetry of the metal d electron shell, which particularly for d^8 systems can lead to decreased electronic repulsions along the z axis and shorter axial bond lengths.

The new trinuclear manganese carbonyl anion, $Mn_3(CO)_{14}^-$, has been characterized (6) as the product in the reaction of $Mn(CO)_5^-$ and $Mn_2(CO)_{10}$; its structure is suggested to be (I), which is analogous to the $M_3(CO)_{14}H$ structures but lacking a bridging hydride.



I

Further commentary on the structure of $Re_2(CO)_{10}$ has appeared. In an earlier study (7) this molecule was stated to have a staggered (D_{4d}) configuration in the solid state; this conclusion was based only on two dimensional x-ray diffraction data however, noting the isomorphism of this compound and $Mn_2(CO)_{10}$. Now an electron diffraction study on gaseous $Re_2(CO)_{10}$ has appeared (8). From this work an eclipsed molecular configuration (D_{4h}) is proposed, with a Re-Re bond length of 3.04 Å, vs. 3.02 Å determined in the solid state studies.

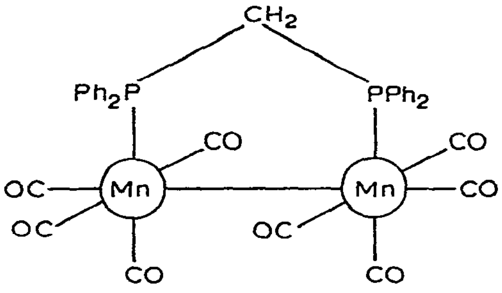
Lemoine, et al (9) have noted from powder pattern studies on $Re_2(CO)_{10}$ a reversible phase transition at 92°C. They speculate that in the solid state, below that temperature, the molecule has the staggered configuration, whereas the eclipsed configuration is found above 92°C. This conjecture is not documented however.

Extended Hückel MO calculations on the three carbonyls, $M_2(CO)_{10}$ (M = Mn, Tc, Re) are reported (10). Single crystal broadline nmr studies on $Mn_2(CO)_{10}$, $MnRe(CO)_{10}$ and $Re_2(CO)_{10}$ (11) have been carried out.

The solubility of $Re_2(CO)_{10}$ in liquid $Ni(CO)_4$ from 0.5-42.6° has been ascertained (12). The solubility increases with temperature.

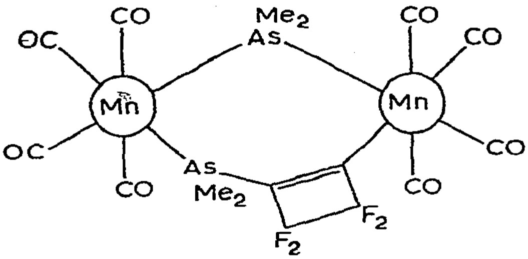
A number of derivatives of $Mn_2(CO)_{10}$ have been reported. Reaction of this carbonyl with phosphine, PH_3, under ultraviolet irradiation yields $Mn_2(CO)_9(PH_3)$ which with tetrahydrofuran gives $Mn_2(CO)_9(THF)$ (13). The reaction of $Mn_2(CO)_{10}$ and triferrocenylphosphine (Pfc_3), gives $Mn_2(CO)_9(Pfc_3)$. (14) A mixture (not separated) of several trifluorophosphine complexes, $Mn_2(CO)_{10-x}(PF_3)_x$ (15) is obtained from $Mn(CO)_5Br$ and $Ni(PF_3)_4$.

Reactions of $Mn_2(CO)_{10}$ and the chelating diphosphine ligands $Ph_2PCH_2CH_2PPh_2$ (diphos) and $Ph_2PCH_2PPh_2$ (DPM) have been studied (16). Refluxing a solution of either ligand (P^P) and $Mn_2(CO)_{10}$ (2:1 ratio) in benzene for an extended period of time gives the complexes $[Mn(CO)_3(P^\wedge P)]_2$; metal-metal bond cleavage in this species by bromine provides $Mn(CO)_3(P^\wedge P)Br$. Reactions of these diphosphines and $Mn_2(CO)_{10}$ for shorter times, or under ultraviolet irradiation give different results however. Utilizing diphos the monomeric and presumably paramagnetic species $Mn(CO)_3(diphos)$ is reportedly obtained. With excess diphos the complex $Mn(CO)(diphos)_2$ is obtained in two forms; a yellow form, m.p. 173-174° is obtained in the photochemical reaction, whereas a red form, m.p. 217-220°, is formed in the thermal reaction. With DPM and $Mn_2(CO)_{10}$ the only product obtained using the thermal or photochemical reaction conditions has the formula $Mn_2(CO)_8(DPM)$; bromine cleavage of the metal-metal bond yields $[Mn(CO)_4Br]_2$-μ-DPM, which suggests the structure of $Mn_2(CO)_8DPM$ is (II) below. This has the same general structural features of the complex $Mn_2(CO)_8f_4fars$ (see below) whose structure is known from a crystallographic study (17).



II

Compounds similar to (II) are obtained in reactions of a chelating diarsine ligand, $\overline{CF_2CF_2C(AsMe_2)C}(AsMe_2)$ (f_4fars), with manganese and rhenium carbonyls (18). The conditions used were somewhat different, with the product $Mn_2(CO)_8(f_4fars)$ being formed using ultraviolet irradiation, and the rhenium analogue $Re_2(CO)_8(f_4fars)$ being formed in a thermal reaction, in refluxing xylene (5 hr). Iodine is reported to react with the manganese species with metal-metal bond cleavage giving $[Mn(CO)_4I]_2$-μ-f_4fars. Both manganese and rhenium compounds can be converted by heating (xylene reflux, 5 hrs (Mn) 87 hrs (Re)) to a second isomeric species for which structure (III) was proposed.



III

A reaction of $Mn(CO)_5^-$ and $ClCH_2CH_2CH_2COCl$ is reported to give the acyl-metal species, $Mn(CO)_5COCH_2CH_2CH_2Cl$, which could be isolated; this reacts with additional $Mn(CO)_5^-$ to give the carbene complex $Mn_2(CO)_9(\overline{COCH_2CH_2CH_2})$ (19). Another study (20) reports that this carbene complex, and other carbene complexes as well, are deprotonated with s-butyllithium at -78° at the $-CH_2-$ group adjacent to the carbon bonded to the metal. Deuteration, using DCl in deuteromethanol generates primarily the mono-deuterated species $Mn_2(CO)_9\overline{COCH_2CH_2CH}$ (84% D_1; 4% D_2; 12% D_0). The overall conversion is only 50% however. A reaction of the same intermediate with $MeOSO_2F$ has also been observed, giving $Mn_2(CO)_9\overline{COCH_2CH_2CH}Me$.

Reactions of $Re_2(CO)_{10}$ with methyl- and phenyllithium give the complexes $[Re_2(CO)_9COR]Li$ which on treatment with trimethyloxonium ion give the carbene complexes $Re_2(CO)_9[C(OMe)R]$ (21). Analogous reactions with $Tc_2(CO)_{10}$ are also described. Interestingly, this reaction sequence with the mixed metal complex $(CO)_5MnRe(CO)_5$ leads to the complex $(CO)_5MnRe(CO)_4[C(OMe)R]$ in addition to dimanganese and dirhenium species $M_2(CO)_9[C(OMe)R]$ (M = Mn, Re). In all instances these compounds have a configuration with carbene and $M(CO)_5-$ groups coordinated to the $M'(CO)_4-$ unit in cis- positions.

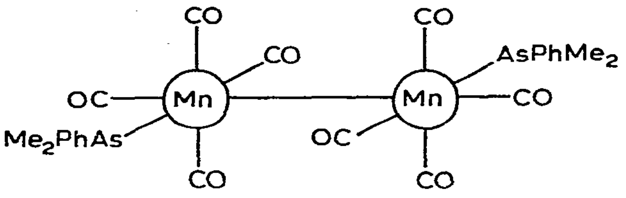
An interesting survey of the kinetics of reactions of various carbonyls having metal-metal bonds has been published (22); this was presented as a summary of a paper presented at the International Conference on Stability and

Reactivity of Coordination Compounds in Bressanone, Italy, Sept., 1971. Herein it is noted that activation energies for reactions of various bimetallic complexes with phosphines and oxygen (decalin, 110°-155°) is in the order $Mn_2(CO)_{10}$ < $(CO)_5MnRe(CO)_5$ < and $Re_2(CO)_{10}$. A correlation between activation energy, $\Delta H^{\ddagger}$, for these reactions and the ultraviolet transition energy assigned as $\sigma \rightarrow \sigma^*$ for the species $M_2(CO)_{10}$ is also proposed. The same correlation is extended to the series of compounds $M_2(CO)_{10}$, $M_2(CO)_9(PPh_3)$, $[M(CO)_4PPh_3]_2$. The $\Delta H^{\ddagger}$ and $\sigma \rightarrow \sigma^*$ transition energies are tabulated below (Table 1). The authors suggest that their data can fit satisfactorily with a mechanism involving metal migration, i.e., migration of an $M(CO)_5$ group to the carbonyl of the adjacent metal atom, as the first step of the reaction.

TABLE 1: Activation Energies for $M_2(CO)_{10-x}L_x + Br_2$ Reactions and $\sigma \rightarrow \sigma^*$ Transitions for $M_2(CO)_{10-x}L_x$ (ref. 22)

Compound	$\Delta H^{\ddagger}$	$\sigma \rightarrow \sigma^*$
$Mn_2(CO)_{10}$	36.2 kcal/mole	29,100 cm^{-1}
$MnRe(CO)_{10}$	38.2	30,800
$Re_2(CO)_{10}$	38.6	32,300
$Mn_2(CO)_9(PPh_3)$	34	28,500
$[Mn(CO)_4PPh_3]_2$	28	25,600
$Re_2(CO)_9(PPh_3)$	34.8	31,200
$[Re(CO)_4PPh_3]_2$	38.8	33,300

The structure of $Mn_2(CO)_9[C(OMe)Ph]$ has been determined (23) by x-ray crystallography, as have the structures of $Mn_2(CO)_8L_2$ (L = PPh_2Me, $AsPhMe_2$) (24), and $Mn_2(CO)_8(C_4H_6)$ (25). The structure of $Mn_2(CO)_8(PPh_2Me)_2$ is like the structure for the analogous triethylphosphine complex, derived from the $Mn_2(CO)_{10}$ structure with the two phosphines trans to the metal-metal bond. The complex $Mn_2(CO)_8(AsPhMe_2)_2$ has a different structure, however; the molecular geometry is depicted below (IV).



IV

One notes the approximate eclipsed configuration, with arsine ligands cis to the manganese-manganese bond. The bond length in this complex is 2.94 Å, compared with a 2.90 Å distance for $Mn_2(CO)_8(PPh_2Me)_2$, and a 2.92 Å value in $Mn_2(CO)_{10}$.

The butadiene complex, $Mn_2(CO)_8(C_4H_6)$ is found to have two $Mn(CO)_4$ groups linked by a trans butadiene group (25).

The only derivatives of $M(CO)_6^+$ (M = Mn, Re) to be reported are $[Mn(CO)_5(NCCH_3)]PF_6$ (26), the carbene complexes $[M(CO)_5\overline{COCH_2CH_2O}]PF_6$ (M = Mn, Re) (19), several amine complexes, $[M(CO)_{6-x}(am)_x]Y$ (x = 1,3; M = Mn, Re; am = various amines) (27,28), and a number of methyl isocyanide complexes $[Mn(CO)_{6-x}(CNCH_3)_x]PF_6$ (x = 1-6) (29).

The complex $[Mn(CO)_5(NCCH_3)]PF_6$ is obtained from $Mn(CO)_5Br$ and $NOPF_6$ in acetonitrile. The latter reagent has turned out to be a particularly versatile species, and is now known to react in various systems in the fashion indicated here (formally as a halide acceptor), as an oxidizing agent with evolution of NO, or as a source of NO in the formation of nitrosyl-metal complexes.

The complex $[Mn(CO)_5\overline{COCH_2CH_2O}]PF_6$, and the analogous rhenium complex, are obtained from $Mn(CO)_5CO_2CH_2CH_2Cl$ on treatment with $AgPF_6$. When treated with chloride ion in methanol, carbon monoxide from this cationic species is evolved giving $M(CO)_4(\overline{COCH_2CH_2O})Cl$ (M = Mn, Re).

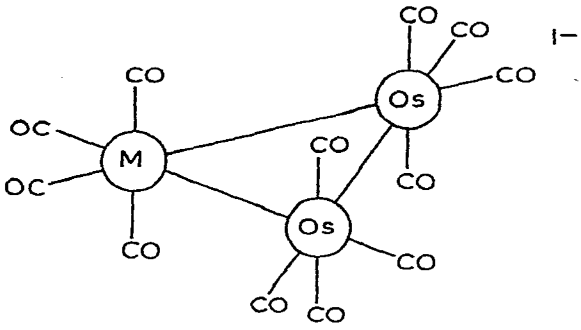
The complexes $[Mn(CO)_{6-x}(NH_3)_x]Y$ are obtained in protonation reactions of various carboxamido-manganese carbonyls. Thus the 60° reaction of $Mn(CO)_4(NH_3)CONH_2$

in liquid ammonia with NH_4Cl gives $[Mn(CO)_3(NH_3)_3]Cl$. Hydrogen chloride reacts with $Mn(CO)_4(NH_3)CONH_2$ in an inert solvent to give $[Mn(CO)_5NH_3]Cl$ (27). The cationic $[Mn(CO)_3(C_6H_{11}NH_2)_3]^+$ and $[Re(CO)_3(iPrNH_2)_3]^+$ are formed by the amine reactions with $[C_6H_6Mn(CO)_3]^+$ and $[C_6Me_6Re(CO)_3]^+$ respectively (28).

The cationic isocyanide substituted species $[Mn(CO)_{6-x}(CNCH_3)_x]PF_6$ (29) are obtained in two ways. The compound for x = 5 as the bromide salt, can be obtained from the prolonged reaction of $Mn(CO)_5Br$ and methyl isocyanide in refluxing tetrahydrofuran; it can be converted to the hexafluorophosphate salt by a metathetical reaction. The other species, x = 1, 2, 3, 4; are obtained using a standard route starting with a halide $Mn(CO)_{5-x}(CNCH_3)_xBr$, a halide acceptor $AlCl_3$, and CO, followed by PF_6^- addition. Each member of the series $[Mn(CO)_{6-x}(CNCH_3)_x]PF_6$ ($x = 1 \rightarrow 6$) and also $[Mn(CO)_{6-x}(CNC_6H_5)_x]PF_6$ (x = 5,6) are observed to undergo a one electron oxidation electrochemically to give $[Mn(CO)_{6-x}(CNR)_x]^{2+}$, and in addition for the compounds with x = 5,6 a second one electron oxidation, presumably to the $[Mn(CO)_{6-x}(CNR)_x]^{3+}$ species is also observed. Chemical oxidation of $[Mn(CO)(CNR)_5]PF_6$ ($R = CH_3$, C_6H_5) may also be accomplished using nitric acid.

The preparation of the mixed metal species $(CO)_4CoMn(CO)_5$ from $TlCo(CO)_4$ and $Mn(CO)_5Br$ is reported (30), and a triphenylphosphine derivative of this substance, $(CO)_3(PPh_3)CoMn(CO)_5$, can be obtained by ligand substitution (31). The identity of this latter species was supported by its reaction with bromine, giving $Mn(CO)_5Br$ and $Co(CO)_3(PPh_3)Br$.

The reactions of $M(CO)_5^-$ (M = Mn, Re) with $M'_3(CO)_{12}$ (M' = Fe, Ru, Os) turns out to be extraordinarily complex (32). In refluxing diglyme both $M(CO)_5^-$ anions react with $Os_3(CO)_{12}$ to give $MOs_2(CO)_{12}^-$ isolated as tetramethylammonium salts. These have the structures (V) below. Acidification of this solution gave a mixture of hydride species $HMOs_2(CO)_{12}$, $HMOs_3(CO)_{16}$, and $HMOs_3(CO)_{15}$. The last complex, along with $H_3MOs_3(CO)_{13}$, may be obtained from the same reagents using tetrahydrofuran as a solvent. Structures for each substance are proposed.



V M = Mn, Re

The reactions of both $M(CO)_5^-$ anions with $Fe_3(CO)_{12}$ lead only to polynuclear iron carbonyl anions, as did the reaction of $Mn(CO)_5^-$ and $Ru_3(CO)_{12}$. From the $Re(CO)_5^-$-$Ru_3(CO)_{12}$ reaction, however, is characterized an anionic species $ReRu_3(CO)_{16}^-$ which on acidification gives $H_2Re_2Ru(CO)_{12}$ and $H_2Re_2Ru_2(CO)_{16}$

The synthesis of ^{13}CO labeled $Mn_2(CO)_{10}$, from $Mn(CO)_4(^{13}CO)Br$ and $Mn(CO)_5^-$ is reported (33) and the infrared and Raman spectra of this species recorded. Detailed assignments of the various absorptions are made, and force constant calculations carried out which essentially confirmed the validity of earlier calculations using the Cotton-Kraihanzel method. Additional studies on a variety of other ^{13}CO enriched metal carbonyls, including $MnRe(CO)_{10}$, $(CO)_4CoM(CO)_5$ (M = Mn, Re) and $Mn_2Fe(CO)_{14}$, are described in a thesis (34).

Rhenium carbonyl, under 365 nm radiation, will polymerize acrylonitrile and methylmethacrylate (35). The esr spectra of γ-irradiated $Mn_2(CO)_{10}$ and $Mn(CO)_5Br$ indicate the presence of anion radicals (36).

III METAL CARBONYL HALIDE COMPLEXES AND DERIVATIVES

The major thrust of the research on the Group VIIB metal carbonyl halides in the last year seems to be the continued elaboration on ligand substitution for carbonyl or halide ions in these species. Only a few studies stand out as being particularly unusual.

One of the more interesting studies, by Berry and Brown (37), further delineates the carbonyl exchange processes for $Mn(CO)_5Br$. Utilizing ^{13}CO and following reaction rates by means of infrared spectral monitoring, these workers showed that axial CO exchange is 0.74 times as fast as radial CO exchange when the reaction was run in hexane, 24°. Utilizing 400 nm radiation statistical exchange in axial and radial positions is observed. The non-statistical thermal exchange is interpreted in terms of a dissociative mechanism, with the dissociation of an axial CO being slightly preferred. The data specifically rules out any rapid axial-radial exchange, or a mechanism involving bromine migration to CO giving a coordinately unsaturated $Mn(CO)_4(COBr)$ species.

The microcalorimetric determination of various enthalpies for manganese carbonyl reactions was reported (38). This study covered the reactions of $Mn_2(CO)_{10}$ and iodine, and also the reactions of $Mn(CO)_5X$ (X = Cl, Br) with I_2; in addition heats of thermal decomposition of the $Mn(CO)_5X$ species were determined. From these data, bond dissociation energies for the Mn-Cl and Mn-Br bonds in the metal pentacarbonyl halide species were determined to be 73 and 61 kcals respectively, which were about 20 kcal less than the metal halogen bond energies in $MnX_2(g)$ species.

Bamford et al (39) have investigated the two equilibria below (EQ 1 and 2).

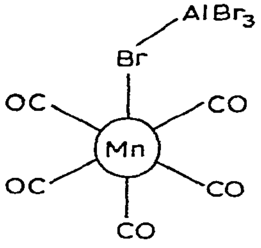
$$2\ Mn(CO)_5X \rightleftarrows Mn_2(CO)_8X_2 + 2\ CO \qquad \text{(EQ 1)}$$

$$Mn(CO)_3L_2X \rightleftarrows Mn_2(CO)_6L_2X_2 + 2\ L \qquad \text{(EQ 2)}$$

Ultraviolet spectra were used to ascertain equilibrium positions (benzene) which obviously depend on CO and L concentration.

The interactions of $Mn(CO)_5Cl$ with $FeCl_3$, and of $Mn(CO)_5X$ and AlX_3 (X = Br and I) were studied (40). No products are isolated but infrared evidence favors the existence of adducts in solution. Thus a mixture of $Mn(CO)_5Br$, which has

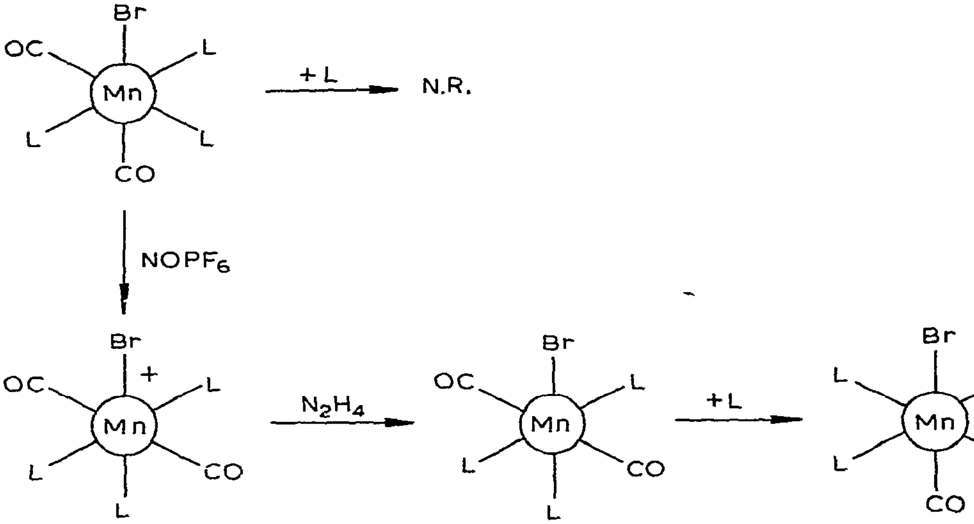
ν_{CO} values of 2136w, 2050vs, 2005s, and $AlBr_3$ shows a new set of ν_{CO} values at 2153w, 2104vw, 2071vs, 2032s. The increase in ν_{CO} frequencies is noteworthy, suggesting an increased transfer of negative charge from the metal to the non-carbonyl ligand; this is in reasonable accord with the structure shown below (VI).



VI

Liquid ammonia solvolyses of $Mn(CO)_5Cl$, $Mn(CO)_4(PPh_3)Cl$, and $Mn(CO)_3(PPh_3)_2Cl$ are reported (27) to give the carboxamido-manganese species <u>cis</u>-$Mn(CO)_4(NH_3)CONH_2$, <u>fac</u>-$Mn(CO)_3(PPh_3)(NH_3)CONH_2$, and <u>fac</u>-$Mn(CO)_3(PPh_3)_2CONH_2$. The actual mechanism of these reactions is unclear but could involve H_2N-H addition to a carbonyl group followed by loss of HCl. Of course some ligand reorganization to form the last species is required. Two different decomposition reactions of the species $Mn(CO)_4(NH_3)CONH_2$ are reported. At -33°, in liquid ammonia, a slow dehydration to $Mn(CO)_4(NH_3)CN$ is seen; at 60°, however, the reaction product is $Mn(CO)_3(NH_3)_2NCO$. This difference is sufficiently novel to merit further investigation.

Reimann and Singleton (41) have reported reactions of $Mn(CO)_5Br$ with various phosphines, phosphites, and arsines ($P(OEt)_3$, PMe_3, $PPhMe_2$, $AsPhMe_2$ = L). They challenge an earlier suggestion that the electronic influence of the substituting ligand L is important in accomplishing substitution of more than two ligands for CO, suggesting instead that the prerequisite for such a reaction is that L be small and that the CO being replaced be *trans* to CO and not *trans* to L. They describe an interesting experiment wherein $Mn(CO)_2L_3Br$ (L groups all *cis* to Br), which is unreactive toward further ligand substitution, may be converted to a second isomer $Mn(CO)_2L_3Br$ (both CO's *cis* to Br and *trans* to each other) which can then be further substituted (EQ 3).



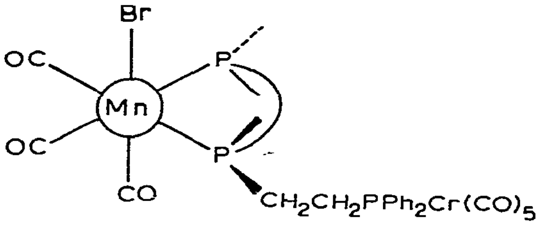
(EQ 3)

The conversion of one isomer to another via the non-EAN rule compound, $[MnL_3(CO)_2Br]^+$, is particularly nice. The oxidation to this species from uncharged $MnL_3(CO)_2Br$ is accomplished by $NOPF_6$.

Both $Mn(CO)_5Br$ and $Re(CO)_5Br$ were reacted with $P(OPh)_3$ (41). In the former instance an equilibrium between di- and tri-substituted species is established, whereas for the rhenium complex the product is $Re(CO)_2[P(OPh)_3]_3Br$. A more extensive study of $Mn(CO)_5X$ (X = Cl, Br) - phosphite reactions is also reported (42). In each instance $Mn(CO)_2L_3X$ species are isolated. Analogous complexes $Mn(CO)_2(triphos)Br$ (triphos = $(Ph_2PCH_2CH_2)_2PPh$) and $Mn(CO)_2(PPhMe_2)_3Br$ are also reported. The mixed ligand complexes $Mn(CO)_2[P(OPh)_3](A\hat{}A)X$ (A^A =

diphos, X = Cl, Br; A^A = diars, X = Br) are reported, arising from reactions of $Mn(CO)_3[P(OPh)_3]_2Br$ and A^A.

In another study Butler, et al, (43) reported two unseparable isomers of the complex fac-$Mn(CO)_3$(triphos)Br. The center phosphorus and one end phosphorus atom coordinate to manganese in these complexes, and the isomers are presumably differentiated by the orientation of the non-coordinated $-CH_2CH_2PPh_2$ group. Further reaction with $Cr(CO)_5THF$ yielded the complex shown below (VII) for which a crystal structure was determined.



VII

King and Kapoor (44) report the synthesis of $Mn(CO)_2[(Ph_2AsCH_2CH_2)_2PPh]Br$, analogous to one of the triphos complexes mentioned above. The reaction of $Mn(CO)_5Br$ and PMe_2CH_2Ph to give $Mn(CO)_3(PMe_2CH_2Ph)_2Br$ is noted (45).

The reaction of $Mn(CO)_5CO(CH_2)_3Cl$ and LiI gives a carbene complex cis-$Mn(CO)_4(\overline{COCH_2CH_2CH_2})I$. A mechanism for this reaction can be written, involving I^- displacement of a carbonyl followed by displacement of Cl^- by the acyl carbonyl oxygen to give the product (19).

Reactions of $Mn(CO)_5X$ (X = Cl, Br, I) with methyl isocyanide are reported (29) to occur with sequential substitution of carbonyls and eventually the displacement of the halide (EQ 4). The reactions for different halides show some variation in rate, with Cl > Br > I. In general the reaction conditions may be chosen to maximize the product of choice. The use of the $Mn(CO)_{5-x}L_xX$

$$Mn(CO)_5X \xrightarrow{+2L} Mn(CO)_3L_2X \xrightarrow{+L} Mn(CO)_2L_3X \xrightarrow{+L} Mn(CO)L_4X$$

$$\xrightarrow{L} [Mn(CO)L_5]X \xrightarrow{+L} [MnL_6]X \qquad \text{(EQ 4)}$$

species in syntheses of the cationic $[Mn(CO)_{6-x}L_x]PF_6$ complexes was noted earlier.

A considerably earlier study of the reactions of $Mn(CO)_5X$ (X = Cl, Br, I) and phenyl isocyanide was extended (29) and some errors in the earlier work corrected. In particular the previously reported compound $Mn(CNPh)_5Br$, was identified as a mixture of $[Mn(CNPh)_6]Br$ and $[Mn(CO)(CNPh)_5]Br$ through a combination of infrared and analytical data, and a new species $Mn(CNPh)_5Cl$, was found to arise from $Mn(CO)_5Cl$ and phenyl isocyanide; this had not been detected earlier.

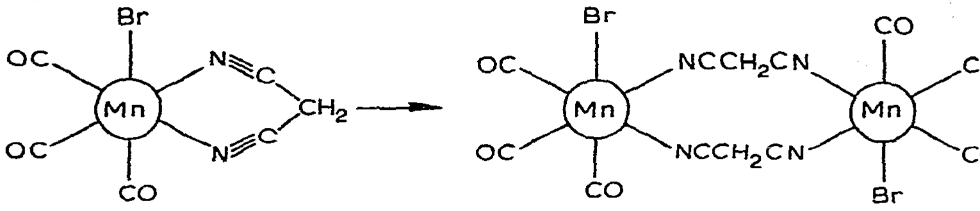
Interesting experiments on coordinated phosphine ligand reactivities have received some attention (46). The diphenylphosphine compound $Mn(CO)_4(PPh_2H)Br$ can be deprotonated using n-butyllithium to give the anionic $[Mn(CO)_4(PPh_2)Br]^-$. This can then be alkylated (→ $Mn(CO)_4(PPh_2Me)Br$); alternatively tetrahydrofuran reflux converts the species over a 6 day period to the known $[Mn(CO)_4PPh_2]_2$ in good yield (EQ 5).

$$Mn(CO)_4(PPh_2H)Br \xrightarrow{BuLi} [Mn(CO)_4(PPh_2)Br]^- \xrightarrow{6\ days} 1/2[Mn(CO)_4PPh_2]_2 + Br^-$$

(EQ 5)

Several other complexes, $Mn(CO)_4(L)Br$ (L = $PPhH_2$) and $Mn(CO)_3L_2Br$ (L = PPh_2H and $PPhH_2$) are also reported in this work.

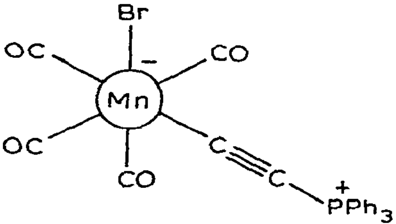
Farona and Kraus (47) report that kinetically favored $Mn(CO)_3(NCCH_2CN)Br$ slowly converts to the thermodynamically more stable dimer $[Mn(CO)_3(NCCH_2CN)Br]_2$ (EQ 6).



(EQ 6)

The substituted manganese carbonyl halides $[Mn(CO)_4I]_2$-μ-$f_4$fars (18) and $[Mn(CO)_4Br]_2$-μ-DPM (16) were mentioned earlier. The reaction of $Mn(CO)_5Br$ and excess diphos is reported (18) to give $Mn(CO)(diphos)_2Br$.

The structures of *fac*-$Mn(CO)_3(CNCH_3)_2Br$ (48) and *cis*-$Mn(CO)_4(\overline{COCH_2CH_2O})Cl$ (19) were determined by x-ray diffraction techniques. The structure of *cis*-$Mn(CO)_4(C{\equiv}CPPh_3)Br$ has also been reported (49), and is shown below (VIII). The carbon-carbon distance in the molecule is 1.216 Å, representing essentially a triple bond, so the resonance structure shown seems to be the primary contributor in bonding.



VIII

The structure of the reaction product of $Mn(CO)_5I$ and triphenylphosphine oxide has been determined by an x-ray crystallographic study (50) to be a salt $[Mn(OPPh_3)_4I][Mn(CO)_4I_2]$. The structure of the non-organometallic cation is probably the more interesting result of this study; this cation has a square pyramidal geometry, with the iodide occupying the apical position. The anion has iodides in *cis* positions.

Theoretical calculations on the anionic species $Mn(CO)_4X_2^-$ (X = Cl, Br) appear as part of a Ph.D. thesis (51).

The reactions of neutron irradiated $Mn(CO)_5Br$ and $Mn(CO)_5I$ are also reported (52).

One of the more interesting observations in rhenium carbonyl halide chemistry is the preparation and description of a new rhenium carbonyl fluoride (53). Carbonyl fluorides are generally scarce of course. This species, of empirical formula $Re(CO)_3F_3$, was prepared from ReF_6 and $Re_2(CO)_{10}$ in HF in Kel-F apparatus. Tungsten hexafluoride was used as a solvent in subsequent operations. The product, a dark brown solid, is insoluble in non-polar solvents, slightly soluble in alcohol and acetone, and soluble in H_2O. The infrared spectrum shows ν_{CO} absorptions at 2120, 2070, and 2040 cm^{-1} and ν_{ReF} at 650 and 580 cm^{-1}. The compound is paramagnetic at room temperature to the extent of 1.0 B.M.

Reports of several substituted rhenium carbonyl halides have appeared. Complexes of the formulas $Re(CO)_4LI$ and $Re(CO)_3L_2I$ (L = PH_3, $PPhH_2$, PPh_2H, PPh_3, $AsPh_3$, $SbPh_3$) are formed in reactions of $[Re(CO)_4I]_2$ and L (54). The reaction of $Re(CO)_5Br$ and $Ni(PF_3)_4$ gives $Re(CO)_3(PF_3)_2Br$ (15). From $Re(CO)_5X$ (X = Br, Cl) and $PPh_2CH_2CH_2CN$ is obtained dimeric species, $[Re(CO)_3(PPh_2CH_2CH_2CN)X]_2$, whose structures contain bridging $PPh_2CH_2CH_2CN$ groups (55). Further reaction with pyridine, PPh_3, or additional $PPh_2CH_2CH_2CN$ (= L) leads to mononuclear $Re(CO)_3(PPh_2CH_2CH_2CN)(L)X$, in which coordination of the cyano group of the β-cyanoethyldiphenylphosphine is not retained. Two trisubstituted complexes $Re(CO)_2[P(OPh)_3]_3Br$ (41) and $Re(CO)_2(PPhMe_2)_3Cl$ (56) are also described, the former being obtained by direct reaction of ligand and metal pentacarbonyl halide, the latter by carbonylation of $Re(N_2)(PPhMe_2)_4Cl$. X-ray photoelectron spectroscopy data on various $Re(CO)_3L_2Cl$ species have been reported (57).

The area of rhenium carbonyl halide anions has received extensive treatment in three papers. Colton and Knapp (58) describe the reactions of

ReX_6^{2-} (X = Cl, Br, I) with HX in refluxing formic acid. Initially the products $Re(CO)_5X$ are formed, but on continued reflux the anions $Re(CO)_4X_2^-$ and $Re(CO)_3X_3^{2-}$ are generated; these anions can be isolated as cesium salts. Alternatively, evaporation of the acid solution containing the $Re(CO)_4X_2^-$ anions gives $[Re(CO)_4X]_2$, whereas from $Re(CO)_3X_3^{2-}$ on evaporation the interesting complexes $Re(CO)_3(H_2O)_2X$ (X = Cl, Br) are formed.

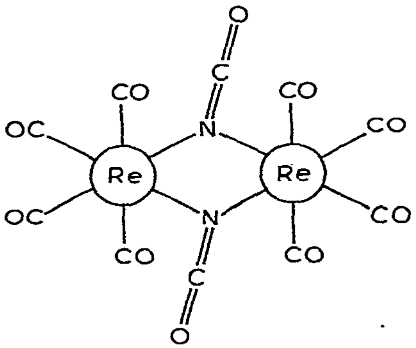
The reactions of $[Re(CO)_4I]_2$ with $[PPh_3Me]I$ are also reported to give anionic species (59), with the nature of the reaction product being determined by the stoichiometry. The products $Re_2(CO)_7I_3^-$ (I^- substituted for one CO in the halide bridged dimer), $Re(CO)_4I_2^-$, and $Re(CO)_3I_3^{2-}$ are obtained for the $[Re(CO)_4I]_2$:$[PPh_3Me]I$ ratios 1:1, 1:2, and 1:4 respectively.

Carbonylation of K_2ReI_6 in acetone yields initially a green, diamagnetic rhenium (III) anion, $Re(CO)_2I_4^-$, isolated as a tetrabutylammonium salt (60). Further carbonylation gives the known $Re(CO)_4I_2^-$. In ethanol, in the presence of KOH the species $Re(CO)_2I_4^-$ appears to undergo a disproportionation, giving orange $[Re(CO)_2I_4]^{2-}$, a rhenium(II) species also isolable as the tetrabutylammonium salt, and the perrhenate ion, ReO_4^-.

The reaction of $Re(CO)_5Cl$ and NO has been studied by Norton and is reported in a Ph.D. dissertation (61). Initially a dinuclear species, $Re_2(CO)_5(NO)Cl_3$, is formed; this is believed to have three bridging chlorine atoms. From this compound, with HCl in ethanol, one can obtain $[Re(NO)(CO)_3Cl_2]_2$, which under attempted reductive carbonylation (Zn + CO in ethanol, 125°/6 hrs) gives $Re_2(CO)_5(NO)(OEt)_3$ structurally analogous to the chlorine bridged species. (Further data on this work has since appeared in early 1973; see J. R. Norton and G. Dolcetti, Inorg. Chem., 12 (1973) 485.)

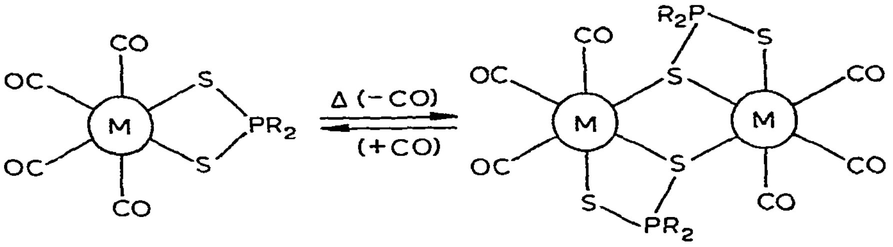
The reaction of $[Re(CO)_4(PPh_3)]_2$ and N_2O_4 at 0°C gives a mixture of cis- and trans $Re(CO)_4(PPh_3)NO_3$, whereas at room temperature only the trans isomer is found (62). Further reaction of $Re(CO)_4(PPh_3)NO_3$ with triphenylphosphine, or alternatively the reaction of (known) $Re(CO)_5NO_3$ with triphenylphosphine, leads to fac-$Re(CO)_3(PPh_3)_2NO_3$.

Prolonged reflux of $Re(CO)_5NCO$ in cyclohexane for 8 hrs generates a dimeric $[Re(CO)_4NCO]_2$ species for which the structure below is suggested (IX) (63).



IX

The dithiophosphonate salts of manganese and rhenium tetracarbonyl lose one CO on heating in vacuo giving $[M(CO)_3S_2PR_2]_2$ (64). The reaction may be reversed by CO addition (EQ 7).

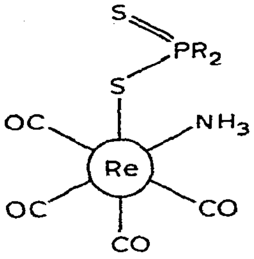


(EQ 7)

(M = Mn, Re ; R = Et, Ph)

Alternatively addition of other ligands than carbon monoxide will generate the new species $M(CO)_3LS_2PR_2$. The rhenium complex, $Re(CO)_4S_2PEt_2$ reacts with

NH_3 at -60° (in liquid ammonia), to give $Re(CO)_4(NH_3)SP(S)R_2$ (X); at 25° the



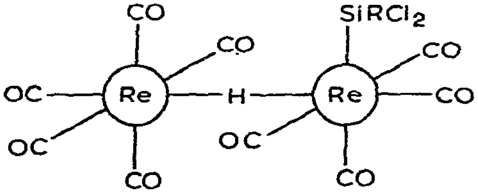
X

dithiophosphonate ligand is displaced by additional ammonia to give $[Re(CO)_4(NH_3)_2]S_2PEt_2$ (65). Other ligands (Py, PPh_3, $AsPh_3$, $SbPh_3$, 1/2 diphos) give carbonyl replacement however, with formation of $Re(CO)_3(L)S_2PEt_2$.

IV HYDRIDE AND ALKYL METAL COMPLEXES

A general review article on metal hydride species was noted earlier (2).

The most spectacular work on the Group VIIB metal hydrides in the last year has come from the group of W. A. G. Graham. Here (66) the reactions of $Re_2(CO)_{10}$ with various $RSiCl_2H$ species (R = Me, Ph, Cl) utilizing ultraviolet radiation were described. The products of these reactions have the general formula $Re_2(CO)_9(RSiCl_2)(H)$; they are white crystalline solids with moderate to high thermal stability. Spectroscopic data is used to suggest a structure, (XI), below; the similarity between this structure and that of $Re_2Mn(CO)_{14}H$

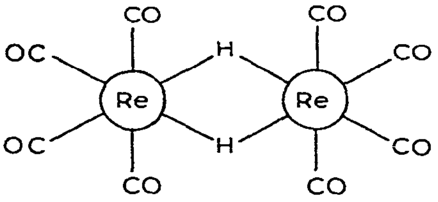


XI

is noted. Speculation on the mechanism of formation of these compounds is provided. It is suggested that ultraviolet irradiation generates a coordinately unsaturated species, perhaps $Re_2(CO)_9$, which undergoes oxidative addition to the Si-H bond; this intermediate then rearranges to give the final product.

Other reactions of $Re_2(CO)_{10}$ and either SiR_2ClH or SiR_3H were attempted, but products analogous to those described above were not obtained. From $SiPh_3H$ and $Re_2(CO)_{10}$ two different products could be obtained depending on temperature. The reaction below 20° gives good yields of $Re_3(CO)_{14}H$, whereas the only product above 60° is $Re(CO)_5SiPh_3$. The former reaction is presented as a convenient synthesis of the trinuclear hydride. In this reaction the fate of the $SiPh_3$-group is not determined.

The same research group has further defined the degradation of the unique compound $Re_2(CO)_8(SiPh_2H_2)$ in chloroform and silicic acid giving $Re_2(CO)_8H_2$, a moderately air-stable crystalline product (67). The structural characterization of this compound is reported as well. The molecular species contains two $Re(CO)_4$ groups linked via two Re-H-Re bridging units (XII). The particularly

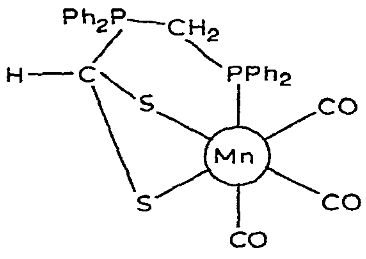


XII

interesting aspect of this molecule is the bonding within the Re_2H_2 unit. Possible bonding schemes include the presence of no formal metal-metal bonds (as in the drawing XII) with the two halves of the molecule linked only by three-center two electron bonds; alternatively one might choose to include a single or double metal-metal bond in addition to the hydrogen bridges. The short bond length (2.90 Å *vs.* 3.02 Å for the rhenium-rhenium bond length in $Re_2(CO)_{10}$) is suggested as evidence for this latter formulation. Though favoring this representation the authors note that the structural evidence is not unequivocal. With $Re(CO)_5^-$ and triphenylchlorosilane (6), the species $Re_2(CO)_8(H)(Cl)$ is found; it is an interesting compound in its own right and may be considered as a member of the series $Re_2(CO)_8Cl_2$, $Re_2(CO)_8(H)(Cl)$ and $Re_2(CO)_8H_2$.

Protonation of various $C_5H_5Mn(CO)_2L$ and $C_5H_5Mn(CO)L_2$ species (L = phos) by CF_3COOH was observed spectroscopically. Protonation is favored by substitution of electron donating alkyl groups on the cyclopentadienyl ring and by increased electron donor strength of the phosphine (68).

Another interesting report in metal carbonyl hydride chemistry concerns the reactions of $M(CO)_3(diphos)H$ and $M(CO)_3(DPM)H$ (M = Mn, Re) and carbon disulfide (69) and the structural characterization of the products. The structures of these products are somewhat surprising. The structure of $Mn(CO)_3(DPM)(HCS_2)$, determined by single crystal x-ray diffraction techniques, is illustrated below (XIII).



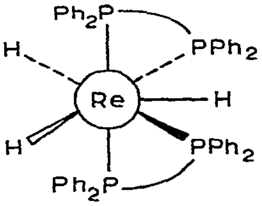
(XIII)

The polymetallic carbonyl hydrides $HMOs_2(CO)_{12}$, $HMOs_3(CO)_{16}$, $H_3MOs_3(CO)_{12}$, (M = Mn, Re), $H_2Re_2Ru(CO)_{12}$ and $H_2Re_2Ru_2(CO)_{16}$ were mentioned earlier (32).

A MO study on $Mn(CO)_5H$ and $Mn(CO)_5Me$ is reported, and these theoretical results correlated with photoelectron spectra of these species (70).

The complex $Mn(CO)_4(PPh_3)H$ is offered as a useful reducing agent for room temperature conversions of carbon-halogen to carbon-hydrogen bonds (71). Examples cited include the conversion of $CH_2{=}CHCH_2Cl$ to propene, and of CCl_4 to $CHCl_3$. An alternative dehalogenation reaction of $CF_3CFBrCF_2Br$ to C_3F_6 is also noted. Reactivities of halogen compounds were found by competition studies to be CI > CBr > CCl and $CX_4 > CHX_3 > CH_2X_2 > CH_3X$.

Though they deal with compounds which are not organometallic, two additional studies on metal hydride complexes might be noted. A crystal structure has been completed on the complex $Re(diphos)_2H_3$ (72) for which a distorted pentagonal bipyramidal structure is noted (XIV). The reaction of an analogous complex $Re(PPh_3)_4H_3$ with nitric oxide has been mentioned also (73). This reaction first yields a very unstable species $Re(NO)_2(PPh_3)_2H$; analogous halide species $Re(NO)_2(PPh_3)_2X$ (X = halogen) may also be obtained from $ReO(OEt)(PPh_3)_2X_2$ and nitric oxide. In the presence of halide ions this latter reaction gives $ReNO(PPh_3)_2X_3$.



XIV

Stewart, Okamoto, and Graham (74) have communicated the results of several reactions with the cationic species $[C_5H_5Re(CO)_2NO]^+$. They note that with sodium borohydride a single product $C_5H_5Re(CO)(NO)CH_3$ is obtained. This product could only have arisen from reduction of a carbonyl group.

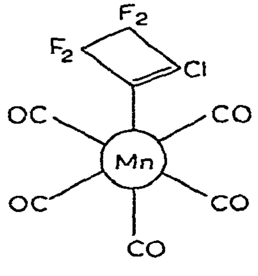
This is the second report of such a reaction, the first being the $[C_5H_5M(CO)_3(PPh_3)]^+$-borohydride reaction to give $C_5H_5M(CO)_2(PPh_3)CH_3$ (M = Mo, W). Also of note is the formation of an analogous hydride species $C_5H_5Re(CO)(NO)$ from $[C_5H_5Re(CO)_2NO]^+$ and triethylamine in aqueous acetone.

The reactions of PMe_2CH_2Ph and its arsenic analogue with $Mn(CO)_5CH_3$ gives primarily $Mn(CO)_3(AMe_2CH_2Ph)_2CH_3$ (A = P, As), along with a small amount of $[Mn(CO)_3(AMe_2CH_2Ph)_2]_2$ (45). The stereochemistry of the alkyl-manganese product has both ligands *cis* to methyl and *trans* to each other. The syntheses of $Mn(CO)_5CO(CH_2)_3Cl$ and $Mn(CO)_5CO_2CH_2CH_2Cl$ were mentioned earlier (19) in conjunction with their use as carbene metal complex precursors.

The kinetics of carbonylation of mono and disubstituted methyl- and acetyl-manganese carbonyls is discussed in a thesis (75).

A structural study on the complex $Mn(CO)_4(PPh_3)CH_3$ has been carried out (76). There are two independent molecules of this species within the unit cell; one of these molecules possesses a *cis* geometry, the other is a disordered mixture of the *cis* and *trans* molecules.

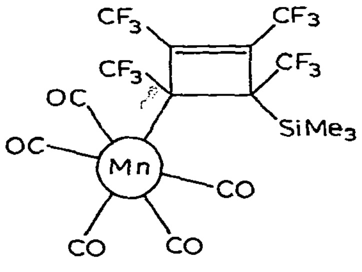
A number of new fluorocarbon-manganese carbonyls are reported. King and Efraty (77) reacted 1,2-dichlorotetrafluorocyclobut-1-ene with $Mn(CO)_5^-$, replacing one chlorine atom by the metal group (XV). King and Zipperer report the reaction of $Mn(CO)_5Br$ and *trans*-$CF_3CF{=}C(Ag)CF_3$ to give *trans*-$Mn(CO)_5C(CF_3){=}CFCF_3$ (78). The latter reaction is suggested to be a potentially useful route to fluorocarbon



XV

metal complexes in that the fluorocarbon group in $CF_3CF{=}C(Ag)CF_3$ is sufficiently anionic (nucleophilic) to be used in these reactions, and yet the compound is also somewhat more stable than the usual lithium or magnesium reagents which might have been considered for the same purpose.

Clark and Hauw (79) have subjected $Mn(CO)_5SiMe_3$ and the analogous germanium derivative and various fluoroolefins to ultraviolet irradiation. With tetrafluoroethylene the complex $Mn(CO)_5CF_2CF_2SiMe_3$ is formed by insertion of the olefin into the metal-silicon bond. Other reactions, more often than not, are complex however. Thus from $Mn(CO)_5SiMe_3$ and $CF_2{=}CFH$ the products obtained are cis $Mn(CO)_5CF{=}CFH$, $Mn(CO)_5CF{=}CFSiMe_3$, and $Mn_2(CO)_{10}$. The first two products are presumably formed by initial addition of the silicon-manganese bond to the olefin followed by elimination of $SiMe_3F$ or HF. From C_3F_6, the product obtained is cis $Mn(CO)_5CF{=}CFCF_3$. With $CF_3C{\equiv}CCF_3$ a product involving a cyclic dimer of the acetylene (XVI) is obtained.



XVI

A σ-cyanocarbon manganese carbonyl species is reported (80). This compound, $Mn(CO)_5CCl{=}C(CN)_2$, is formed from $Cl_2C{=}C(CN)_2$ by nucleophilic attack of $Mn(CO)_5^-$.

Molecular orbital calculations on $Mn(CO)_5Me$ and $Mn(CO)_5CF_3$ are noted in a paper and later in a thesis (51,81). This work clears up a misunderstanding with respect to bonding in the fluorocarbon-transition metal complexes.

Previously spectroscopic studies, and to some extent bond length data, had been used to support the contention that there is in such species some multiple metal-carbon bonding. This theoretical treatment shows this idea not to be correct, however. The information on these compounds can best be viewed as the result of two features. First, the high inductive effect of fluorine leaves a substantial positive charge on the CF_3 carbon, which in turn leads to more effective electron withdrawal from the metal within the σ-bond framework. This causes the shift of ν_{CO} to higher frequency. Second, the metal to carbon bonding orbital must be strictly represented as being somewhat antibonding with respect to the carbon-fluorine bonds. This results in carbon-fluorine bond weakening, and the lower values for ν_{CF} observed.

A correlation of MO calculations for $Mn(CO)_5Me$ and the photoelectron spectrum of this substance has appeared (70).

The vibrational (infrared and Raman) spectra of both $Mn(CO)_5CH_2CH{=}CH_2$ (82) and π $C_3H_5Mn(CO)_4$ (83) have been studied and assignments made.

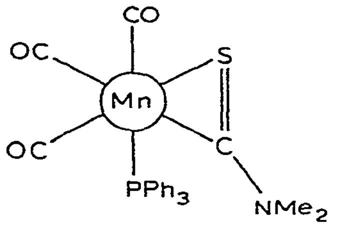
Angelici and Blacik have described reactions of arene-manganese (and rhenium) tricarbonyl cations with various amines; they postulated the existence of an equilibrium (EQ 8) in solution (28) between cation and amine and a carboxamido species. Qualitatively this equilibrium favors product formation

$$[\text{AreneMn(CO)}_3]^+ + 2RNH_2 \rightleftarrows [\text{AreneMn(CO)}_2\text{CONHR}] + RNH_3^+ \qquad \text{(EQ 8)}$$

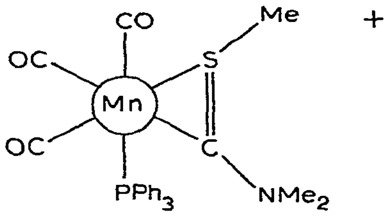
for those species chosen for arenes with fewer methyl groups ($C_6H_6 > C_6H_5Me > C_6H_4Me_2 \cdots$). This result is interpreted in terms of the electron donation by the methyl groups. Only three carboxamido complexes were isolated in this study, and those were isolated presumably due to their insolubility. These included $C_6Me_6Mn(CO)_2CONHR$ (R = H, C_6H_{11}) and (Mesitylene)$Mn(CO)_2CONH_2$. In two reactions the arene was displaced from the metal by an amine giving $[M(CO)_3(am)_3]^+$ species; these reactions were mentioned earlier. The reaction of $C_6Me_6Mn(CO)_3{}^+$ and N_2H_4 gave $C_6Me_6Mn(CO)_2NCO$, presumably by an initial solvolysis reaction to give $C_6Me_6Mn(CO)_2CONHNH_2$, followed by NH_3 elimination and rearrangement.

The reactions in liquid NH_3 of $Mn(CO)_3(NH_3)(L)CONH_2$ (L = CO, PPh_3) with acids to give cationic $[Mn(CO)_{6-x}(am)_x]^+$ were noted earlier (27).

The results of a study on reactions of metal carbonyl anions and $ClCSNMe_2$ proved to be quite unexpected (84). For example, from $Mn(CO)_5{}^-$ and $ClCSNMe_2$ is obtained the product $Mn(CO)_4CSNMe_2$. The analogous complex $Mn(CO)_3(PPh_3)CSNMe_2$ is obtained from $Mn(CO)_4PPh_3{}^-$. These species have unusual stoichiometries, apparently lacking one carbonyl; to rationalize this, it is proposed that the sulfur of the thiocarbonyl group is coordinated to the metal (XVII). These species react with trimethyloxonium tetrafluoroborate to give cationic complexes, e.g., $[Mn(CO)_3(PPh_3)C(SMe)NMe_2]^+$ (XVIII).

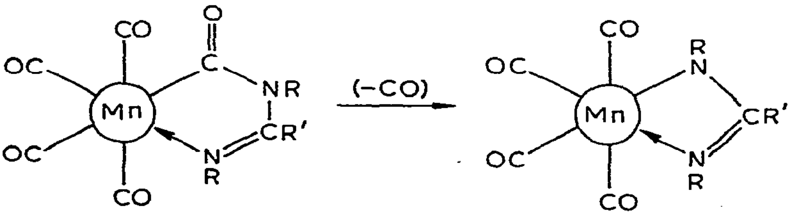


XVII



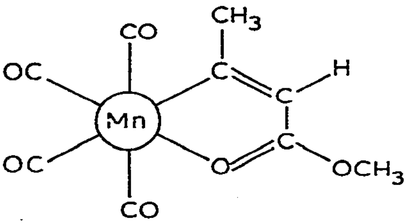
XVIII

The reaction (85) of $Mn(CO)_5Br$ and Li[RN–CR'=NR], (R = Ph, R' = Ph, Tol) gives a type of carboxamido-complex (XIX). On heating or under ultraviolet irradiation this compound loses CO to form (XX).

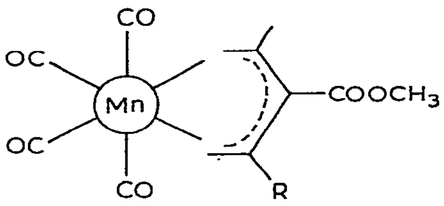


XIX XX

Reaction of $Mn(CO)_5CH_2C{\equiv}CH$ with methanol gives the compound (XXI), whereas the analogous reaction with $Mn(CO)_5CH_2C{\equiv}CR$ (R = Me, Ph) lead to π-allyl species (86) (XXII).



XXI



XXII

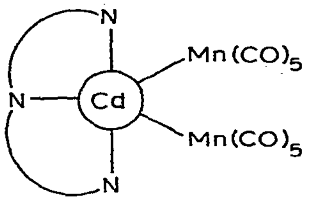
V METAL CARBONYL DERIVATIVES OF METALS AND METALLOIDS

Manganese carbonyl and $Mn_2(CO)_8(PPh_3)_2$ have been shown to react with a magnesium amalgam, using a basic solvent, solid magnesium salts $B_xMg[Mn(CO)_5]_2$ and $B_xMg[Mn(CO)_4PPh_3]_2$ (B = tetrahydrofuran, tetramethylethylenediamine) being isolated (87). The conductivity of these species in solution is quite low indicating little dissociation to ions, in contrast to observations on analogous complexes of other metals.

A number of metal carbonyl complexes of zinc, including $Zn[Mn(CO)_5]_2$, have been shown to degrade in methanol or ethanol (88) according to the equation below (EQ 9)

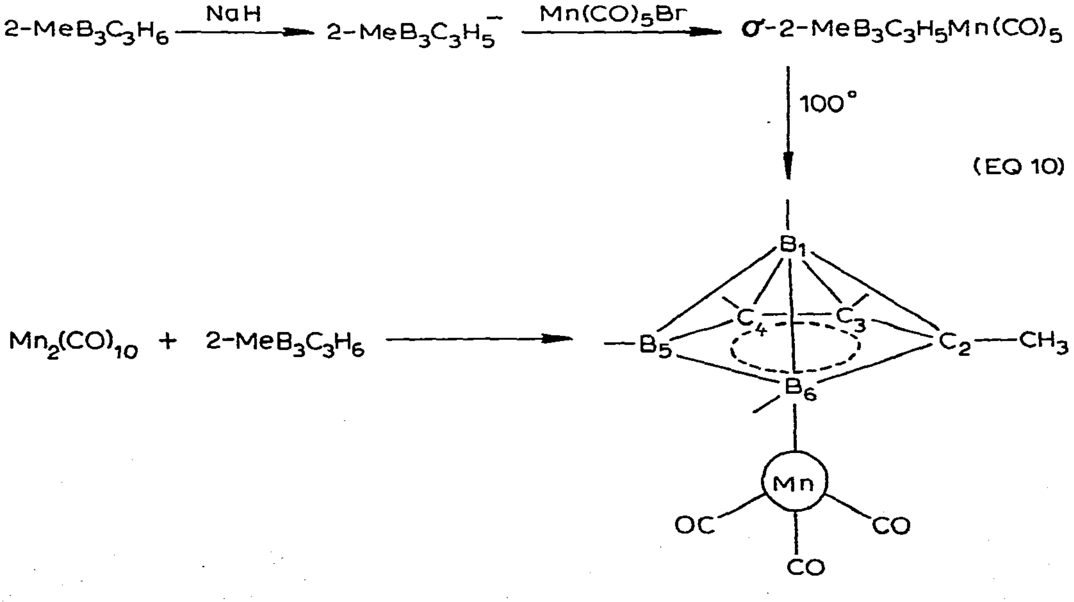
$$Zn[Mn(CO)_5]_2 + ROH \rightarrow 1/4[ROZnMn(CO)_5]_4 + HMn(CO)_5 \qquad \text{(EQ 9)}$$

Crystal structure studies on $Hg[Mn(CO)_5]_2$ (89) and $terpyrCd[Mn(CO)_5]_2$ (90) have been reported. The structure of the latter species is shown below (XXIII). Infrared spectral assignments on $Hg[Mn(CO)_5]_2$, or on $M(py)_2[Mn(CO)_5]_2$ (M = Pt, Pd) are reported (91).



(XXIII) (N⁀N⁀N= terpyridyl)

Howard and Grimes report the synthesis of tricarbahexaboranylmanganese carbonyl complexes by two different routes (92). The first involves generation of an anion from methyl substituted 2,3,4-tricarbahexaborane(7) by treatment with sodium hydride. One of these anionic species (the 2-methyl derivative) is shown to react with $Mn(CO)_5Br$ to form initially an unstable σ bonded species (EQ 10), $MeB_3C_3H_5Mn(CO)_5$; at 100° carbon monoxide is lost from this compound to give π-$MeB_3C_3H_5Mn(CO)_3$ (XXIV). The same compound is also obtained from 2-methyltricarbahexaborane(7) and $Mn_2(CO)_{10}$ as is the related 2,3-dimethyltricarbahexaborane(7) complex; the same reaction with $Re_2(CO)_{10}$ fails to give a product however.

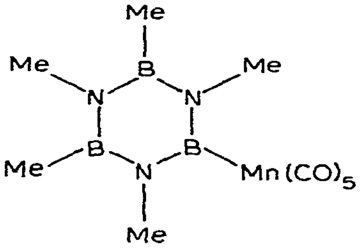


(EQ 10)

XXIV

Carbonyl substitution reactions of trispyrazolylborate complexes of manganese with various phosphines and phosphites are reported (93). Monosubstituted species $RBpz_3Mn(CO)_2L$ (R = H, pz; L = various phosphines and phosphites) are generally obtained; a disubstituted complex is formed only for triphenylphosphite.

A manganese pentacarbonyl-substituted borazole, (XXV), is reported in a thesis (94); the $Mn(CO)_4PPh_3$-derivative is also described.



XXV

The reaction of metallic gallium with $Mn_2(CO)_{10}$ in a sealed tube (120°, 2-4 days) is reported to give a red crystalline compound $Ga_2[Mn(CO)_5]_4$ (95). From infrared and Raman data the presence of both Ga-Mn and Ga-Ga bonds is inferred, and on this basis a structural characterization as $[(CO)_5Mn]Ga{-}Ga[Mn(CO)_5]_3$ is suggested. Soxhlet extraction of this compound with acetone leads to an interesting disproportionation, yielding $GaMn(CO)_5$ and $Mn_2(CO)_{10}$.

The same paper (95) reports that $In[Mn(CO)_5]_3$ may be prepared in the same fashion, from indium metal and $Mn_2(CO)_{10}$. The same compound is also reported (96) to be formed in an exchange reaction from indium and $Tl[Mn(CO)_5]_3$ in tetrahydrofuran at room temperature, and also from $Mn(CO)_5^-$ and an anhydrous indium trihalide in either tetrahydrofuran or water. The product, as orange crystals, is purified by sublimation. It is stable as a solid but degrades in solution quite rapidly.

The complexes $X_{3-n}In[Mn(CO)_5]_n$ (n = 1, 2) are also described (96). Each species may be obtained from InX_3 and the required stoichiometric amount of $Mn(CO)_5^-$; alternative preparations of each are possible by the insertion of InX into the Mn-X bond in $Mn(CO)_5X$ or the Mn-Mn bond in $Mn_2(CO)_{10}$. The cleavage of Mn-In bonds in $In[Mn(CO)_5]_3$ by stoichiometric amounts of halogen will also give these species. The compounds do not sublime up to 160°/0.001 Torr. The authors suggest that the low volatility indicates some degree of association in the solid state and they propose the presence of discrete halogen bridged dimers. However mass spectral data show only the mononuclear species, and surprisingly no molecular weight data are recorded.

The complexes $X_{3-n}In[Mn(CO)_5]_n$ are extensively ionized in DMF to give the $Mn(CO)_5^-$ anion. In acetonitrile, each of the three complexes, $X_{3-n}In[Mn(CO)_5]_n$ (n = 1, 2, 3) give the same infrared spectrum, (ν_{CO}) which is assigned to the cationic complex $(CH_3CN)_2In[Mn(CO)_5]_2^+$. This species is isolable from the reaction of $XIn[Mn(CO)_5]_2$ and $AgClO_4$ in acetonitrile. From the acetonitrile complex other $L_2In[Mn(CO)_5]_2^+$ species (L = py, o-phen) can be prepared. Halide ion also reacts with $X_{3-n}In[Mn(CO)_5]_n$ complexes giving a number of anionic species $X_{4-n}In[Mn(CO)_5]_n^-$ (n = 1, 2, 3) which can be isolated as tetraalkylammonium salts.

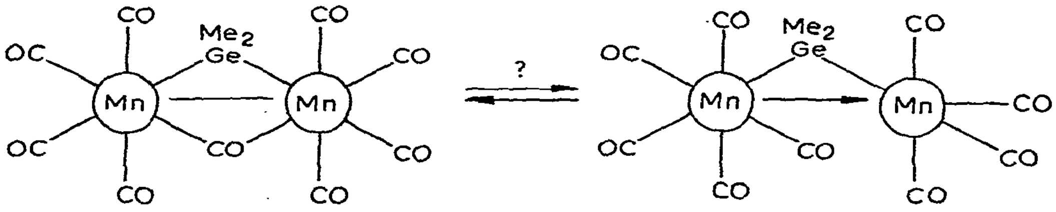
Several indium derivatives of rhenium pentacarbonyl are also reported (97). The complexes $Cl_{3-n}In[Re(CO)_5]_2$ are reported from $InCl_3$ and appropriate amounts of $Re(CO)_5^-$ (n = 1, 2, 3) or from insertion of InCl into either the Cl-Re or Re-Re bonds in $Re(CO)_5Cl$ or $Re_2(CO)_{10}$. The interesting preparation of $In[Re(CO)_5]_3$ from $InMe_3$ and $Re(CO)_5H$ is also given (EQ 11).

$$InMe_3 + 3Re(CO)_5H \rightarrow In[Re(CO)_5]_3 + 3MeH \qquad \text{(EQ 11)}$$

The complex $Tl[Mn(CO)_5]_3$ is obtained in quantitative yield from $Mn(CO)_5^-$

and TlCl (98). The reaction is believed to proceed via the thallium(I) complex $TlMn(CO)_5$ which undergoes disproportionation giving thallium metal and the observed product.

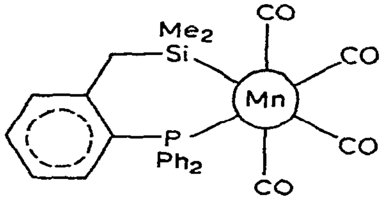
Curtis and Job (99, 100) have studied photolytic reactions of several germanium metal carbonyl species. They observe that irradiation of $Mn(CO)_5GeMe_2Cl$ generates $[Mn(CO)_4GeMe_2]_2$, a yellow crystalline complex. The complexity of the infrared spectrum of this species is said to eliminate from consideration the most likely structure having metal tetracarbonyl units bridged by two $GeMe_2$ groups and a metal-metal bond. The only other possibility however seems to be a structure having one or two terminal $GeMe_2$ groups, wherein the divalent germanium group is behaving as a two electron donor, akin to carbene ligands known previously. From $[Mn(CO)_5]_2GeMe_2$ another complex $Mn_2(CO)_9GeMe_2$ is formed on irradiation. The structure of this complex is also an enigma. The complex has an infrared absorption, ν_{CO}, at 1835 cm^{-1} suggestive of a bridging carbonyl. However the absorption is quite weak and the authors believe that some tautomerism between the structure having a bridging carbonyl (XXVI) and a structure without this functionality (probably XXVII) may be involved.



XXVI XXVII

Job's Ph.D. thesis (100) describes the synthesis of a number of $Me_2(Y)X\text{-}Mn(CO)_4L$ species (Y = halogen, vinyl; X = Sn, Ge; L = CO, PPh_3) in addition to the above work.

The reaction of o-$C_6H_4(PPh_2)(CH_2SiMe_2H)$ with $Mn_2(CO)_{10}$ in benzene (50°) gives (XXVIII), whereas the same reagent with $Re_2(CO)_{10}$ at 150° gives a silyl rhenium pentacarbonyl, o-$PPh_2C_6H_4CH_2SiMe_2Re(CO)_5$ (101). The reaction of $SnMe_3H$ and $Mn_2(CO)_{10}$ gives a poor yield of $Mn(CO)_5SnMe_3$ (102). This compound is stable to water and base; one or more methyl groups can be replaced by chlorines in reactions with CF_3COCl or $SiHCl_3$ (→ $Mn(CO)_5SnMe_2Cl$) or with $SnCl_4$ (→ $Mn(CO)_5SnCl_3$). Mercuric chloride cleaves the tin-manganese bond as does $C_2H_4Br_2$, giving $SnMe_3X$ and $Hg[Mn(CO)_5]_2$, and $Mn(CO)_5Br$ respectively. The synthesis of $Mn(CO)_5GeH_3$ from $Mn(CO)_5^-$ and GeH_3Br is recorded (103).



XXVIII

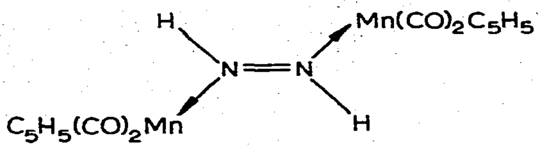
Rather an interesting enigma from previous years was the failure to obtain a compound, $Mn(CO)_5SiR_3$, from solution reactions of $Mn(CO)_5^-$ with trisorganochlorosilanes (although in the absence of solvent this product is known to form). Curtis (6) has now been able to clarify the situation considerably. He has shown that the reaction of $Mn(CO)_5^-$ and $SiPh_3Cl$ in tetrahydrofuran leads to hexaphenyl disiloxane, and a new polynuclear manganese carbonyl anion $Mn_3(CO)_{14}^-$. Its structure was described earlier in this review (I). Other metal carbonyl anion reactions with $SiPh_3Cl$ were also attempted; there seemed to be no consistent pattern of behavior however. Using $Mn(CO)_4PPh_3^-$ two products, $Mn(CO)_3(PPh_3)_2Cl$ and $[Mn(CO)_4(PPh_3)]_2$ are obtained. Only in one instance, using $Co(CO)_3PPh_3^-$, was a silyl metal complex, $Co(CO)_3(PPh_3)SiPh_3$ isolated along with other products.

Addition of $Mn(CO)_5SiMe_3$ to tetrafluoroethylene, giving $Mn(CO)_5CF_2CF_2SiMe_3$, was discussed earlier (79) as were reactions of $RSiCl_2H$ species and $Re_2(CO)_{10}$ (66) and the thermal degradation of $Re_2(CO)_8(SiR_2H_2)$ (67).

Mössbauer studies (involving the ^{119}Sn nucleus) are reported (104, 105, 106, 107) for a variety of tin-manganese and tin-rhenium carbonyls (and for carbonyls of other metals as well). Compounds considered included the particular series $Mn(CO)_5SnR_{3-x}Y_x$ (Y = halogens) (104, 107) and $[Mn(CO)_5]_nSnR_{4-n}$ (R = Cl, Br, I, Et, Ph; n = 1, 2) (107). Solvent effects on the infrared spectra of various $[Mn(CO)_5]_nSnR_{4-n}$ species are noted (108). Infrared and Raman studies of the complexes $Mn(CO)_5SnI_3$, prepared from $Mn(CO)_5SnCl_3$ and NaI in tetrahydrofuran (109) and $Mn(CO)_5LSnPh_3$ (L = CO, PPh_3) (109a), are noted. For the $Mn(CO)_5SnX_3$ species the frequency of ν_{Sn-Mn} is a linear function of the electronegativity of X (109).

VI GROUP VA AND VIA DERIVATIVES (EXCEPT AS SIMPLE ELECTRON PAIR DONORS)

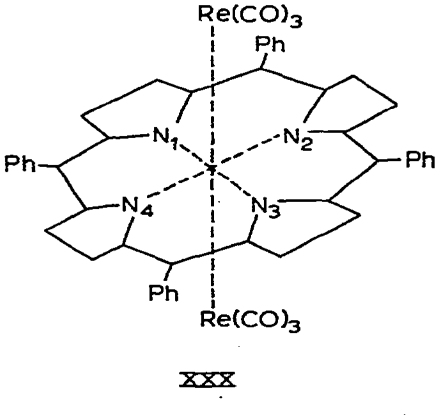
Sellmann (3) has reviewed his work on nitrogen fixation involving cyclopentadienylmanganese and rhenium complexes. He has also published communications on two interesting observations. First he notes the formation of $C_5H_5Re(CO)_2N_2$ from the oxidation of coordinated hydrazine in the complex $C_5H_5Re(CO)_2N_2H_4$ (110). The oxidation is accomplished with hydrogen peroxide in the presence of copper(II) salts in tetrahydrofuran at -20°. The product shows appropriate infrared absorptions, ν_{N_2} falling at 2141 cm^{-1}, and ν_{CO} at 1970 and 1915 cm^{-1}. Sellmann had earlier reported that the analogous oxidation of $C_5H_5Mn(CO)_2N_2H_4$ evolved nitrogen. Presumably the complex $C_5H_5Mn(CO)_2N_2$ is formed and is unstable. In this reaction he notes a blue solution being formed. Further investigation (111) of the solution has now led to the isolation and identification of an intermediate, blue $[C_5H_5Mn(CO)_2]_2N_2H_2$, in this solution. The presumed structure of this complex is shown below (XXIX).



XXIX

An infrared study of various metal-dinitrogen complexes has shown a linear correlation of ν_{N_2} and intensity (112). An explanation is made that increased delocalization of electronic charge to the ligand by π-bonding will change the ν_{N_2} frequency, and at the same time will lead to a greater charge transfer when the bond is stretched hence leading to a greater intensity for the absorption. The suggestion is made that those dinitrogen complexes which have high ν_{N_2} intensities should be more susceptible to Lewis acid attack. This in turn renders the substance more amenable to reduction of the dinitrogen ligand.

The structural characterization of meso-tetraphenylporphinato-bis-tricarbonylrhenium has been accomplished by single-crystal x-ray diffraction methods (113). This structure is certainly unexpected; it is shown below (XXX).



XXX

The porphinato group is substantially distorted; the N_1-N_3 distance, 3.60 Å, is much less than the N_2-N_4 distance of 4.62 Å. The Re-Re distance is somewhat long, at 3.15 Å, but is indicative of some degree of metal-metal bonding.

A crystal structure determination on the complex $(CO)_5CrAsMe_2Mn(CO)_5$ has shown the expected bent Cr-As-Mn geometry (114).

Ehrl and Vahrenkamp have prepared several organosulfur manganese and rhenium complexes, as well as complexes of other metals (115). Starting from the complex $C_5H_5Mn(CO)_2MeSSnMe_3$ (prepared from $C_5H_5Mn(CO)_3$ and $SnMe_3SMe$) and $C_5H_5Fe(CO)_2Cl$, the product $C_5H_5Fe(CO)_2SMeMn(CO)_2C_5H_5$ can be obtained. From $Li[W(CO)_5SMe]$ and $Re(CO)_5Cl$ the two products $[Re(CO)_4SMe]_2$ and $(CO)_5WSMeRe(CO)_5$ are formed. The reaction of $Re(CO)_5Cl$ and $W(CO)_5MeSSnMe_3$ leads to $[Re(CO)_4SMe]_2$.

Reported in a thesis (116) is the preparation of the compounds $[Re_2MoC_5H_5(CO)_8]S[SMoC_5H_5(CO)_3]$, and $Re_6S_3(CO)_{12}$, and their structures as determined by crystallographic studies. The structures of $Re_4(CO)_{12}(SMe)_4$ (117) and $[Mn(CO)_4SeCF_3]_2$ (118) are also reported.

Fenster and Butler (119) have prepared the three compounds $C_5H_5Mn(CO)_{3-x}(CS)_x$ (x = 1, 2, 3). This method of preparation involves successive reactions of a cyclooctene complex of the metal with CS_2 and PPh_3. Equation 12 illustrates the first reaction in this sequence.

$$C_5H_5Mn(CO)_2C_8H_{14} + PPh_3 + CS_2 \rightarrow C_5H_5Mn(CO)_2CS + SPPh_3 + C_8H_{14} \qquad \text{(EQ 12)}$$

VII CYCLOPENTADIENYL-MANGANESE AND RHENIUM CARBONYLS AND THEIR DERIVATIVES: OTHER π HYDROCARBON COMPLEXES

King and Efraty have prepared pentamethylcyclopentadienyl complexes of a number of metals (120). They describe the complex $C_5Me_5Mn(CO)_3$, arising from $Mn_2(CO)_{10}$ and C_5Me_5COMe. The complex $Me_3SiC_5H_4Re(CO)_3$ has been prepared from

$Re(CO)_5Br$ and 1,1-$(Me_3Si)_2C_5H_4$; a crystal structure study on this compound is reported (121).

Exchange reactions involving LiC_5D_5 with $Mn(C_5H_5)_2$, and $Ni(C_5H_5)_2$ with $Mn(C_5H_5)_2$, have been carried out (122).

A large number of new derivatives of $C_5H_5Mn(CO)_3$, having various ligands substituted for one or more carbonyls, have been reported. These include the three thiocarbonyl species $C_5H_5Mn(CO)_{3-x}(CS)_x$ mentioned earlier (119). The reaction of $C_5H_5Mn(CO)_3$ and phosphorus trifluoride in tetrahydrofuran using ultraviolet irradiation gives $C_5H_5Mn(PF_3)_3$ with the complexes $C_5H_5Mn(CO)_2THF$ and $C_5H_5Mn(CO)(THF)_2$ suggested to be intermediates (123). The ferrocenyl carbene complex, $MeC_5H_4Mn(CO)_2C(OMe)fc$ (fc = the ferrocenyl group, $C_5H_5FeC_5H_4$-) is reported (124). King et al. (125) have prepared disubstituted species $C_5H_5Mn(CO)(PF_2NR_2)_2$ (NR_2 = NMe_2 or NC_5H_{10}), from the ligand and $C_5H_5Mn(CO)_3$ under irradiation. Various complexes of the ligands $As(MMe_3)_3$ (M = Si, Ge, Sn) including $C_5H_5Mn(CO)_2As(MMe_3)_3$ have been prepared (126).

A number of new $C_5H_5Mn(CO)_2L$ species (L = $As(OR)_3$, $Sb(OR')_3$; R = Me, Et, Bu, Ph; R' = Et, Bu, Ph) are described by Brill (127). From the positions of the ν_{CO} absorption in the infrared spectra, it is suggested that the donor ability of the ligands are in the orders $E(OR)_3 > E(OAr)_3$ and $Sb(OR)_3 \geq P(OR)_3 > As(OR)_3$. Further comment on ν_{CO} intensities and on ^{55}Mn nqr spectra for these species has also appeared (128).

Two papers describe reactions at coordinating phosphines. Treichel, et al, (129) report the deprotonation of $MeC_5H_4Mn(CO)_2PPh_2H$ with butyllithium to give $[MeC_5H_4Mn(CO)_2PPh_2]^-$, which may be alkylated with methyl iodide to give $MeC_5H_4Mn(CO)_2PPh_2Me$. Hofler and Schnitzler (130) studied reactions of $C_5H_5Mn(CO)_2PPh(NEt_2)_2$ with hydrohalic acids, to give $C_5H_5Mn(CO)_2PPhX_2$ (X = Cl, Br, I), and with benzoyl fluoride to give $C_5H_5Mn(CO)_2PPh(F)NEt_2$. This latter species could then react further with HCl to give $C_5H_5Mn(CO)_2PPh(F)Cl$.

The photolysis of $MeC_5H_4Mn(CO)_3$ in a glass at low temperature has been carried out (131); infrared data suggests that the species $MeC_5H_4Mn(CO)_2$ is present. The latter has absorptions for ν_{CO} at 1955 and 1886 cm^{-1} compared to the values of ν_{CO} for $MeC_5H_4Mn(CO)_3$ at 2026 and 1938 cm^{-1}. In another study the kinetics of photolysis of $C_5H_5Mn(CO)_3$ were reported (132).

A copper(I) derivative of $C_5H_5Mn(CO)_3$ has been prepared (133); it is formed from the boronic acid derivative $(HO)_2BC_5H_4Mn(CO)_3$ and copper(II) acetate. This compound is reactive toward protonic acids, regenerating $C_5H_5Mn(CO)_3$ and toward mercury(II) chloride giving $ClHgC_5H_4Mn(CO)_3$. This copper reagent has also been found to react with haloferrocenes to give $C_5H_5FeC_5H_4$-$C_5H_4Mn(CO)_3$ (134).

The reported (68) protonations of $C_5H_5Mn(CO)_{3-x}L_x$ (x = 1, 2) was discussed earlier in this review.

Carbon(13) nmr data for $Mn(CO)_5Me$ and $MeC_5H_4Mn(CO)_3$ were obtained by adding a trace of $Cr(acac)_3$ to solutions of these compounds (135). Other nmr studies on related systems involving the measurement of the relative rates of exchange of $\underline{\alpha}$ and $\underline{\beta}$ protons by deuterium for various $XC_5H_4Mn(CO)_2(PPh_3)$ species (X = Cl, SMe, COOEt) have been carried out. This exchange is promoted by deuterio-trifluoroacetic acid and boron trifluoride etherate (136). The observation of dissimilarity of the diastereotopic $\underline{\alpha}$ and $\underline{\alpha}'$, and $\underline{\beta}$ and $\underline{\beta}'$ protons in $(MeC^*OHPh)C_5H_4Mn(CO)_3$ is noted (137).

The ^{19}F nmr chemical shifts for m- and p- $FC_6H_4C_5H_4Mn(CO)_3$ and its rhenium analogue were measured (138). From these data Hammett constants for the metal substituted groups were calculated; for the manganese group-$C_5H_4Mn(CO)_3$ σ_i is +0.21, and $\sigma_R{}^{\circ}$ is -0.06. The rhenium group -$C_5H_4Re(CO)_3$ σ_i and $\sigma_R{}^{\circ}$ are +0.27 and -0.06 respectively. Qualitatively this means that these groups are π donors and σ acceptors (relative to hydrogen).

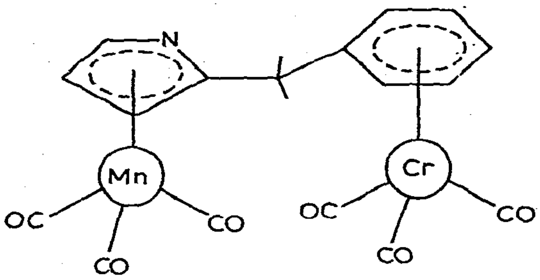
Nuclear quadrupole coupling constant data for ^{55}Mn in $C_5H_5Mn(CO)_3$ are reported (139). Infrared and Raman data on $C_5H_5Re(CO)_3$ have also been determined and assignments made (140).

Marks and Kristoff (141) have studied the compounds *cis*- and *trans*-$[C_5H_5Mn(CO)NO]_2$. The *cis*- *trans*- differentiation arises due to the relative orientations of the C_5H_5 rings. There is also one NO and one CO ligand in a bridging position, so that the manganese atoms in a molecule are dissimilar, being bonded either to terminal NO or CO groups. In the solid state the compound is found to exist as the *trans* isomer only; in solution, however, both *cis* and *trans* isomers are present. Polar solvents are seen to favor the *cis* isomer. At low temperature, -62°, the pmr spectrum of this compound shows fo C_5H_5 proton resonances, as expected for the two molecular species in their static conformation. As the temperature is raised one observes equilibration of these protons by virtue of a rapid intermolecular interconversion until at +40° only a single cyclopentadienyl proton resonance is seen. A mechanism of this interconversion of isomeric forms is postulated from these data to involve a structure with no bridging ligands.

The attempt to make an analogous rhenium compound from $[C_5H_5Re(CO)_2NO]^+$ and triethylamine in aqueous acetone gave only the new hydride species $C_5H_5Re(CO)(NO)H$; the methyl compound $C_5H_5Re(CO)(NO)CH_3$ is prepared from the same starting material with $NaBH_4$ (74).

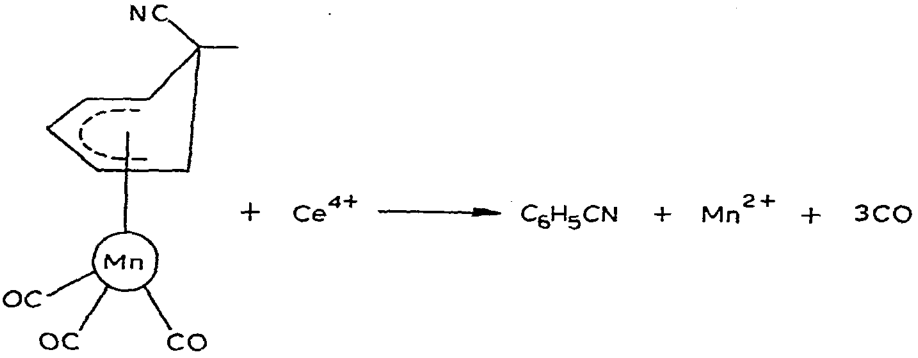
Reaction of $C_5H_5Mn(NO)(L)(L')^+$ with $NaBH_4$ ($L = L' = CNCH_3$), published at an earlier time, are now reported in a thesis (142). Unreported as yet in the literature is a study of the reactivities of these species ($L = CO$, L' = phosphines or phosphites) with C_6F_5Li, in which either ring attack yielding $C_6F_5C_5H_5Mn(NO)(CO)L$, or carbonyl attack yielding $C_5H_5Mn(NO)(L)COC_6F_5$ occurs. Ring attack is favored by good electron donors such as PEt_3; carbonyl attack occurs when L is a ligand such as $P(OMe)_3$ having some capacity for electron withdrawal from the metal.

The compound (XXXI) below may be prepared in two ways (143), either by heating the ligand α-benzyl pyrrole with a mixture of $Mn_2(CO)_{10}$ and $Cr(CO)_6$, or alternatively by first preparing α-benzylpyrrolylmanganese tricarbonyl and then reacting this with $Cr(CO)_6$.



XXXI

Walker and Mawby (144) report that a number of exo-substituted $YC_6H_6Mn(CO)_3$ compounds (Y = $CH(COOMe)_2$, $CH(COOEt)_2$, N_3, OMe, PPh_2, NCS) can be formed from Y^- and $C_6H_6Mn(CO)_3^+$; methyl substituted arene-manganese carbonyl complexes react in the same fashion. When the compounds with Y = CN are oxidized with ceric(IV) ion the aryl nitrile can be obtained (EQ 13).



(EQ 13)

Both benzonitrile and mesityl nitrile are prepared in this way. It is interesting that hydride abstracting reagents such as the triphenylmethyl carbonium ion will not give these products, but will rather abstract the group Y^- instead.

The amine solvolysis of arenemanganese tricarbonyl cations to carboxamido species was noted earlier (28).

VIII ISOCYANIDE METAL COMPLEXES

A study of the reactions of $Mn(CO)_5X$ with methyl and phenyl isocyanides received comment earlier in this review (29). Both uncharged $Mn(CO)_{5-n}L_nX$ and cationic $[Mn(CO)_{6-n}L_n]^+$ species were described.

Extensive electrochemical studies on the related series of complexes $[Mn(CO)_{6-n}(CNMe)_n]PF_6$ (29) and on $[Mn(CNR)_6]^+$ (R = Me, Ph, $p\text{-}ClC_6H_4$, $p\text{-}MeOC_6H_4\text{-}$ $p\text{-}CH_3C_6H_4\text{-}$)(145) have been reported. The ease of oxidation for the carbonyl species increases with increasing substitution of isocyanide for carbon monoxide, a factor primarily related to the different electron withdrawing capabilities of the ligands. For the $[Mn(CNR)_6]^+$ species cyclic voltammetry detected two one-electron oxidations. The first oxidation corresponded to the known chemical process $[MnL_6]^+ \rightarrow [MnL_6]^{2+} + e$. The ease of oxidation for the methyl isocyanide complex, as measured by the $E_{1/2}$ value, is considerably greater than the ease of oxidation of the aryl isocyanide complexes; the differences in $E_{1/2}$ are on the order of 500 mv. Within the series of aryl isocyanide complexes the ease of oxidation reflected the donor power of the p-substituent group in the order $p\text{-}CH_3 > H > p\text{-}OMe > p\text{-}Cl$.

King and Saran (146) report a poor yield of the complex $[Mn(CNBu^t)_5PPh_3]PF_6$ from $[Mn(CNBu^t)_6]PF_6$ and PPh_3 in refluxing diglyme. The pmr spectrum of this species shows methyl protons in a 1:4 ratio as expected. Bailey (147) describes an advanced undergraduate chemistry experiment involving the synthesis of $[Mn(CNBu^t)_6]X$, its oxidation to a paramagnetic dication, and the measurement of its magnetic susceptibility by Gouy and nmr methods.

The synthesis of $[Re(CNMe)_6]^{2+}$ complexes by methylation with methyl iodide of $Ag_4Re(CN)_6$ is reported (148). An initial product is $[Re(CNMe)_6]I_2 \cdot 8AgI$, which is converted to the nitrate salt $[Re(CNMe)_6](NO_3)_2$ by treatment with $AgNO_3$ and HNO_3. Aqueous base treatment degrades the complex with methyl isocyanide formation.

IX VARIOUS NITROSYL METAL SPECIES

Various nitrosyl complexes have already been mentioned here in other contexts. This includes the species $Re(NO)_2(PPh_3)_2X$ and $ReNO(PPh_3)_2X_3$ (73), $C_5H_5Re(NO)(CO)CH_3$ and $C_5H_5Re(NO)(CO)H$ (74), $[C_5H_5Mn(NO)(CO)]_2$ (141). Reactions of several $[C_5H_5Mn(NO)(L)(L')]^+$ species were also noted (142).

The synthesis of $Mn(CO)_3(L)NO$ ($L = PPh_3, AsPh_3$) by photolysis of $Mn(CO)_4NO$ and the ligand is mentioned (149). Further infrared studies on $Mn(CO)_4NO$ have been reported to provide evidence for the C_{2v} symmetry structure (150) and the C_{3v} structure (151).

The photochemical reaction of $Mn_2(CO)_{10}$ and NO is reported (152) to give first $Mn(CO)_4NO$ and then $Mn(NO)_3CO$, and finally a new very volatile green manganese nitrosyl having $\nu_{NO} = 1666\ cm^{-1}$ (THF). The identity of this last product is unknown.

X REFERENCES

1. H. C. Lewis and B. N. Storhoff, J. Organometal. Chem., 43 (1972) 1.
2. H. D. Kaesz and R. B. Saillant, Chem. Rev., 72 (1972) 231.
3. D. Sellmann, Angew.Chem. Internat. Ed. Engl., 11 (1972) 534.
4. W. B. Hughes, Organometal. in Chem. Syn., 1 (1972) 341.
5. B. A. Frenz and J. A. Ibers, Inorg. Chem., 11 (1972) 1109.
6. M. D. Curtis, Inorg. Chem., 11 (1972) 802.
7. L. F. Dahl, E. Ishishi, and R. E. Rundle, J. Chem. Phys., 26 (1957) 1750.
8. N. I. Gatpotchenko, N. V. Alekseev, N. E. Kolobova, K. N. Anisimov, I. A. Ronova, and A. A. Johansson, J. Organometal. Chem., 35 (1972) 319.
9. P. Lemoine, M. Gross, and J. Boissier, J. Chem. Soc. Dalton, (1972) 1626.
10. D. V. Korol'kov, Zh. Strukt Khim., 13 (1972) 689.
11. E. S. Mooberry, H. W. Spiess, and R. K. Sheline, J. Chem. Phys., 57 (1972) 813.

12. A. K. Baev, L. F. Fedulova and N. E. Kolobova, Obshch. Prikl. Khim., 4 (1972) 5; CA., 77 (1972) 106169s.
13. E. O. Fischer and W. A. Herrman, Chem. Ber., 105 (1972) 286.
14. C. U. Pittman and G. O. Evans, J. Organometal. Chem., 43 (1972) 361.
15. R. B. King and A. Efraty, J. Amer. Chem. Soc., 94 (1972) 3768.
16. R. H. Reimann and E. Singleton, J. Organometal. Chem., 38 (1972) 113.
17. L. Chan, Diss. Abstr. Int. B., 33 (1972) 98.
18. J. P. Crow, W. R. Cullen, and F. L. Hou, Inorg. Chem., 11 (1972) 2125.
19. M. Green, J. R. Moss, I. W. Nowell and F. G. A. Stone, J. Chem. Soc. Chem. Commun., (1972) 1339.
20. C. P. Casey, R. A. Boggs, and R. L. Anderson, J. Amer. Chem. Soc., 94 (1972) 8947.
21. E. O. Fischer, E. Offhaus, J. Muller, and D. Nothe, Chem. Ber., 105 (1972) 3027.
22. D. DeWit, J. P. Fawcett, A. J. Poë, and M. V. Twigg, Coord. Chem. Rev., 8 (1972) 81.
23. G. Huttner and D. Regler, Chem. Ber., 105 (1972) 1230.
24. M. Laing, T. Ashworth, P. Sommerville, E. Singleton, and R. Reimann, J. Chem. Soc. Chem. Commun., (1972) 1251.
25. H. E. Sasse and M. L. Ziegler, Z. anorg. allgem. Chem., 392 (1972) 167.
26. N. G. Connelly and J. D. Davies, J. Organometal. Chem., 38 (1972) 385.
27. H. Behrens, E. Lindner, D. Maertens, P. Wild, and R.-J. Lampe, J. Organometal. Chem., 34 (1972) 367.
28. R. J. Angelici and L. J. Blacik, Inorg. Chem., 11 (1972) 1754.
29. P. M. Treichel, G. E. Dirreen, and H. J. Mueh, J. Organometal. Chem., 44 (1972) 339.
30. S. E. Pedersen, W. R. Robinson, and D. P. Schussler, J. Organometal. Chem., 43 (1972) C44.
31. G. Sbrignadello, G. Bor, and L. Maresca, J. Organometal.Chem., 46 (1972) 345.

32. J. Knight and M. J. Mays, *J. Chem. Soc. Dalton*, (1972) 1023.

33. W. T. Wozniak and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **34** (1972) 3765.

34. W. T. Wozniak, *Diss. Abst. Int. B.*, **32** (1972) 6284B.

35. C. H. Bamford and M. U. Mahmud, *J. Chem. Soc. Chem. Commun.*, (1972) 762.

36. O. P. Anderson and M. C. R. Symons, *J. Chem. Soc. Chem. Commun.*, (1972) 1020.

37. A. Berry and T. L. Brown, *Inorg. Chem.*, **11** (1972) 1165.

38. J. A. Connor, H. A. Skinner, and Y. Virmani, *J. Chem. Soc. Faraday Trans.*, **1** (1972) 1754.

39. C. H. Bamford, J. W. Burley, and M. Coldbeck, *J. Chem. Soc. Dalton*, (1972) 1846.

40. M. Pankowski, B. Demerseman, G. Bouquet, and M. Bigorgne, *J. Organometal. Chem.*, **35** (1972) 155.

41. R. H. Reimann and E. Singleton, *J. Organometal. Chem.*, **44** (1972) C18.

42. I. S. Butler, N. J. Coville, and H. K. Spendjian, *J. Organometal. Chem.*, **43** (1972) 185.

43. M. L. Schneider, N. J. Coville, and I. S. Butler, *J. Chem. Soc. Chem. Commun.*, (1972) 799.

44. R. B. King and P. N. Kapoor, *Inorg. Chim. Acta*, **6** (1972) 391.

45. R. L. Bennett, M. I. Bruce, and F. G. A. Stone, *J. Organometal. Chem.*, **38** (1972) 325.

46. P. M. Treichel, W. K. Dean, and W. M. Douglas, *J. Organometal. Chem.*, **42** (1972) 145.

47. M. Farona and K. F. Kraus, *J. Chem. Soc. Chem. Commun.*, (1972) 513.

48. A. C. Sarapu and R. F. Fenske, *Inorg. Chem.*, **11** (1972) 3021.

49. S. Z. Goldberg, E. N. Duesler, and K. N. Raymond, *Inorg. Chem.*, **11** (1972) 1397.

50. G. Ciani, M. Manassero, and M. Sansoni, *J. Inorg. Nucl. Chem.*, **34** (1972) 1760.

51. M. B. Hall, Diss. Abstr. Int. B, 32 (1972) 4468B.

52. I. G. DeJong and D. R. Wiles, Can. J. Chem., 50 (1972) 961.

53. T. A. O'Connell and K. A. Phillips, Inorg. Chem., 11 (1972) 2563.

54. K. Moedritzer, Syn. Inorg. Metal-org. Chem., 2 (1972) 121.

55. B. N. Storhoff, J. Organometal. Chem., 43 (1972) 197.

56. D. J. Darensbourg, Inorg. Nucl. Chem. Letters, 8 (1972) 529.

57. V. I. Nefedov, M. A. Porai-Koshits, I. A. Zakharova, and M. E. Dyatkina, Proc. Acad. Sci. USSR, 202 (1972) 78.

58. R. Colton and J. E. Knapp, Austr. J. Chem., 25 (1972) 9.

59. K. Moedritzer, Syn. Inorg. Metal-Org. Chem., 2 (1972) 209.

60. M. Fremi, P. Romiti, V. Valenti, and P. Fantucci, J. Inorg. Nucl. Chem., 34 (1972) 1195.

61. J. R. Norton, Diss. Abst. Int. B, 32 (1972) 6895B.

62. R. Davis, J. Organometal. Chem., 40 (1972) 183.

63. R. B. Saillant, J. Organometal. Chem., 39 (1972) C71.

64. E. Lindner and K.-M. Matajcek, J. Organometal. Chem., 34 (1972) 195.

65. E. Lindner and H. Berke, J. Organometal. Chem., 39 (1972) 145.

66. J. K. Hoyano and W. A. G. Graham, Inorg. Chem., 11 (1972) 1265.

67. M. J. Bennett, W. A. G. Graham, J. K. Hoyano, and W. L. Hutcheon, J. Amer. Chem. Soc., 94 (1972) 6232.

68. B. V. Lokshin, A. G. Ginsberg, V. N. Setkina, D. N. Kursanov, and I. B. Nemirovskaya, J. Organometal. Chem., 37 (1972) 347.

69. F. W. Einstein, E. Enwall, N. Flitcroft, and J. M. Leach, J. Inorg. Nucl. Chem., 34 (1972) 885.

70. M. B. Hall, M. F. Guest, and I. H. Hillier, Chem. Phys. Lett., 15 (1972) 592.

71. B. L. Booth and B. L. Shaw, J. Organometal. Chem., 43 (1972) 369.

72. V. G. Albano and P. L. Bellon, J. Organometal. Chem., 37 (1972) 151.

73. D. Giusto and G. Cova, Gazz. Chim. Ital., 102 (1972) 265.

74. R. P. Stewart, N. Okamoto, and W. A. G. Graham, J. Organometal. Chem., 42 (1972) C32.

75. J. W. Davis, Diss. Abst. Int. B, 33 (1972) 1477.

76. A. Mawby and G. E. Pringle, J. Inorg. Nucl. Chem., 34 (1972) 877.

77. R. B. King and A. Efraty, J. Fluor. Chem., 1 (1972) 283.

78. R. B. King and W. C. Zipperer, Inorg. Chem., 11 (1972) 2119.

79. H. C. Clark and T. L.Hauw, J. Organometal. Chem., 42 (1972) 429.

80. R. B. King and M. S. Saran, J. Amer. Chem. Soc., 94 (1972) 1784.

81. M. B. Hall and R. F. Fenske, Inorg. Chem., 11 (1972) 768.

82. H. L. Clarke and N. J. Fitzpatrick, J. Organometal. Chem., 40 (1972) 379.

83. G. Davidson and D. C. Andrews, J. Chem. Soc. Dalton, (1972) 126.

84. P. M. Treichel and W. K. Dean, J. Chem. Soc. Chem. Commun. (1972) 804.

85. T. Inglis, M. Kilner and T. Reynoldson, J. Chem. Soc. Chem. Commun., (1972) 774.

86. J. L. Roustan, C. Charrier, J. Y. Merour, J. Benaim, and C. Giannotti, J. Organometal. Chem., 38 (1972) C37.

87. G. B. McVicker and R. S. Matyas, J. Chem. Soc. Chem. Commun., (1972) 972.

88. J. M. Burlitch and S. E. Hayes, J. Organometal. Chem., 42 (1972) C13.

89. M. L. Katcher and G. L. Simon, Inorg. Chem., 11 (1972) 1651.

90. W. Clegg and P. J. Wheatley, J. Chem. Soc. Chem. Commun., (1972) 760.

91. P. Braunstein and J. Dehand, J. Chem. Soc. Chem. Commun., (1972) 164.

92. J. W. Howard and R. N. Grimes, Inorg. Chem., 11 (1972) 263.

93. A. R. Schoenberg and W. P. Anderson, Inorg. Chem., 11 (1972) 85.

94. L. A. Melcher, Diss. Abst. Int. B, 32 (1972) 5674B.

95. H. J. Haupt and F. Neumann, Z. anorg. allgem. Chem., 394 (1972) 67.

96. A. T. T. Hsieh and M. J. Mays, J. Chem. Soc. Dalton, (1972) 516.

97. A. T. T. Hsieh and M. J. Mays, J. Organometal. Chem., 37 (1972) 9.

98. A. T. T. Hsieh and M. J. Mays, J. Organometal. Chem., 38 (1972) 243.

99. M. D. Curtis and R. C. Job, J. Amer. Chem. Soc., 94 (1972) 2153.

100. R. J. Job, Diss. Abst. Int. B., 32 (1972) 6274B.

101. H. G. Ang and P. T. Lau, J. Organometal. Chem., 37 (1972) C4.

102. R. A. Burnham, F. Glockling, and S. R. Stobart, J. Chem. Soc. Dalton, (1972) 1991.

103. R. D. George, K. M. Mackay and S. R. Stobart, J. Chem. Soc. Dalton, (1972) 1505.

104. G. M. Bancroft, K. D. Butler, and A. T. Rake, J. Organometal. Chem., 34 (1972) 137.

105. G. M. Bancroft, K. D. Butler, A. T. Rake and B. Dale, J. Chem. Soc. Dalton, (1973) 2025.

106. S. Onaka and H. Sano, Bull. Chem. Soc. Japan, 45 (1972) 1271.

107. S. R. A. Bird, J. D. Donaldson, A. F. Le C. Holding, B. Ratcliff, and S. Cenini, Inorg. Chim. Acta, 6 (1972) 379.

108. S. Cenini, B. Ratcliff, A. Fusi, and A. Pasini, Gazz. Chim. Ital., 102 (1972) 141.

109. S. Onaka, Nippon Kagaku Kaishi, (1972) 1978.

109a. H. J. Buttery, S. F. A. Kettle, G. Keeling, I. Paul, P. J. Stamper, J. Chem. Soc. Dalton, (1972) 2487.

110. D. Sellmann, J. Organometal. Chem., 36 (1972) C27.

111. D. Sellmann, J. Organometal. Chem., 44 (1972) C46.

112. D. J. Darensbourg, Inorg. Chem., 11 (1972) 1436.

113. D. Cullen, E. Meyer, T. S. Srivastava, and M. Tsutsui, J. Amer. Chem. Soc., 94 (1972) 7603.

114. H. Vahrenkamp, Chem. Ber., 105 (1972) 1486.

115. W. Ehrl and H. Vahrenkamp, Chem. Ber., 105 (1972) 1471.

116. P. J. Vergamini, Diss. Abst. Int. B., 32 (1972) 6283.

117. W. Harrison, W. C. Marsh, and J. Trotter, J. Chem. Soc. Dalton, (1972) 1009.

118. C. J. Marsdens and G. M. Sheldrick, J. Organometal. Chem., 40 (1972) 175.

119. A. E. Fenster and I. S. Butler, Can. J. Chem., 50 (1972) 598.

120. R. B. King and E. Efraty, J. Amer. Chem. Soc., 94 (1972) 3773.

121. W. Harrison and J. Trotter, J. Chem. Soc. Dalton, (1972) 678.

122. M. E. Switzer and M. F. Rettig, J. Chem. Soc. Chem. Commun., (1972) 687.

123. T. Kruck and V. Krause, Z. Naturforsch., 27b (1972) 302.

124. J. A. Connor and J. P. Lloyd, J. Chem. Soc. Dalton, (1972) 1470.

125. R. B. King, W. C. Zipperer, and M. Ishaq, Inorg. Chem., 11 (1972) 1361.

126. H. Schumann, G. Pfeifer, and H. Roser, J. Organometal. Chem., 44 (1972) C10.

127. T. B. Brill, J. Organometal. Chem., 40 (1972) 373.

128. W. P. Anderson, T. B. Brill, A. R. Schoenberg, and C. W. Stanger, J. Organometal. Chem., 44 (1972) 161.

129. P. M. Treichel, W. M. Douglas, and W. K. Dean, Inorg. Chem., 11 (1972) 1615.

130. M. Hofler and M. Schnitzler, Chem. Ber., 105 (1972) 1133.

131. P. S. Braterman and J. D. Black, J. Organometal. Chem., 39 (1972) C3.

132. R. Grelius and U. Volker, Z. Chem., 12 (1972) 264.

133. A. N. Nesmeyanov, V. A. Sazonova, and N. N. Sedova, Proc. Acad. Sci. USSR (transl), 202 (1972) 49.

134. A. N. Nesmeyanov, V. A. Sazanova, N. N. Sedova, and L. S. Klimenko, Izv. Akad. Nauk. SSSR Ser. Khim., 3 (1972) 735.

135. O. A. Gansow and A. R. Burke, J. Chem. Soc. Chem. Commun., (1972) 456.

136. A. I. Khatami, M. N. Nefedova, V. N. Setkina, and D. N. Kursanov, Proc. Acad. Sci. USSR, 203 (1972) 353.

137. D. N. Kursanov, Z. N. Parnes, N. M. Loim, N. E. Kolobova, I. B. Zlotina, P. V. Ptrovskii, and E. I. Fedin, J. Organometal. Chem., 44 (1972) C15.

138. S. P. Gubin, A. A. Koridze, N. A. Ogorodnikova, and B. A. Kvasov, Proc. Acad. Sci. USSR, 205 (1972) 571.

139. M. G. Clark, Chem. Phys. Lett., 13 (1972) 316.

140. B. V. Lokshin, Z. S. Klemenkova, and Yu. V. Makarov, Spectrochim. Acta, 28 (1972) 2209.

141. T. J. Marks and J. S. Kristoff, J. Organometal. Chem., 42 (1972) C91.

142. J. J. Benedict, Diss. Abst. Int. B, 32 (1972) 3828B.

143. N. J. Gogan and C. S. Davies, J. Organometal. Chem., 39 (1972) 129.

144. P. J. C. Walker and R. J. Mawby, J. Chem. Soc. Chem. Commun., (1972) 330.

145. P. M. Treichel and G. E. Dirreen, J. Organometal. Chem., 39 (1972) C20.

146. R. B. King and M. S. Saran, Inorg. Chem., 11 (1972) 2112.

147. R. A. Bailey, J. Chem. Ed., 49 (1972) 297.

148. S. Sarkar, J. Indian Chem. Soc., 49 (1972) 189.

149. D. P. Keeton and F. Basolo, Inorg. Chim. Acta, 6 (1972) 33.

150. A. Poletti, G. Paliani, R. Cataliotti, A. Toffani, and A. Santucci, J. Organometal. Chem., 43 (1972) 377.

151. G. Barna and I. S. Butler, Can. J. Spectrosc., 17 (1972) 2.

152. M.Herberhold and A. Razavi, Angew. Chem. Internat. Ed. Engl., 11 (1972) 1092.