MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1982

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CONTENTS

I. Introduction 69
II. Neutral, Anionic, and Cationic Metal Carbonyl Derivatives 70
III. Metal Carbonyl Halides and Derivatives 73
IV. Metal Hydride Complexes 75
V. Complexes with Carbon Ligands 79
VI. Derivatives of Metals and Metalloids 86
VII. Complexes with Group VA and VIA Ligands 88
VIII. Hydrocarbon-Metal Complexes 90
IX. Isocyanide and Nitrosyl Complexes 92
X. Structural Studies 92
XI. References 93

I. INTRODUCTION

Over two hundred references are included in this year's Annual Survey article on Manganese, Technetium, and Rhenium Organometallic Chemistry. This is the second consecutive year that the number of references has exceeded two hundred. A wide range of topics are represented in this collection, as always. However there appears to be a particular concentration of effort on studies of reactions occurring via radical pathways, on polymetallic and mixed metal systems, and on complexes having $M(CO)_2(\eta\text{-}C_5H_5)$ groups. A review article from a year ago may have had some influence in sustaining the active effort in this last area.

Several review articles have appeared which will be of at least peripheral interest to persons involved in the organometallic chemistry of these metals. Summaries of papers on coordination chemistry of the elements published in 1979-80 (manganese [1], technetium and rhenium [2]) appeared in Coordination Chemistry Reviews; these articles include some references to organometallic chemistry. This is a continuing series which runs somewhat parallel with these Annual Surveys and which overlaps in coverage to a minor extent.

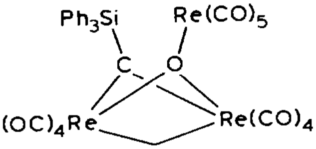
There is also a good review article on transition metal formyl complexes by Gladysz [3] and an extensive review of methylene bridged binuclear complexes by Herrmann [4]. Much of the work in both areas involves manganese and rhenium, and both authors are leaders in the respective areas.

The 1980 [5] Annual Surveys of Manganese, Technetium, and Rhenium chemistry appeared during 1982; the article for 1981 [6] has also appeared at the time the 1982 article was written.

II. NEUTRAL, ANIONIC, AND CATIONIC METAL CARBONYL DERIVATIVES

Fischer and coworkers have investigated several carbene and carbyne derivatives of $Re_2(CO)_{10}$. The reaction of $Re_2(CO)_{10}$ and $Li[SiPh_3]$ produces an anionic species, $Li[Re_2(CO)_9COSiPh_3]$ which can be alkylated by $MeOSO_2F$ or $[Et_3O]BF_4$ giving eq-$Re_2(CO)_9[C(OR)SiPh_3]$ (R = Me, Et). A trace of a second compound, $Re_3(CO)_{14}SiPh_3$, I, is also produced in this reaction sequence; it was characterized by crystallography [7]. Reactions of $Re_2(CO)_9[C(OR)SiPh_3]$ with $AlCl_3$ produce the complex ax-$[Re_2(CO)_9CSiPh_3]AlCl_4$, which contains a carbyne ligand group; this complex reacts with alcohols and amines giving the axially substituted complexes $Re_2(CO)_9[C(X)SiPh_3]$ (X = OMe, OEt, NMe_2, NEt_2) [8]. The molecular structures of eq-$Re_2(CO)_9[C(OR)SiPh_3]$ and eq,ax-$Re_2(CO)_8[C(OEt)SiPh_3]_2$ were determined in a crystallographic study [9].

The complex $Re_2(CO)_9(H_2O)$ has been prepared photolytically from $Re_2(CO)_{10}$ and H_2O in THF. Upon irradiation with 366 nm light, this aquo complex is converted to $ReH(CO)_5$ and $Re_4(OH)_4(CO)_{12}$. The disubstituted complex $Re_2(CO)_8(H_2O)_2$ is suggested as an intermediate in the latter conversion [10]. Studies on reactions of $Re_2(CO)_{10}$ and various ligands using photolytic conditions have appeared from the same research group. Both monosubstituted species eq-$Re_2(CO)_9(L)$ (L = MeCN, py, $EtNH_2$, and $MeNH_2$) and disubstituted species eq,eq-$Re_2(CO)_8(L)_2$ (L = MeCN, py) were characterized; in addition, the complexes $[Re(CO)_3(py)_3][Re_4H(CO)_{16}]$, and $Re_2(\mu\text{-}H)(\mu\text{-}C_5H_4N)(CO)_8$ were obtained in the reaction with pyridine. In each case the primary initial photoprocess is said to be metal-metal bond cleavage [11].



(I)

Various supported catalyst systems (Pt, Pd, Ru, Rh, PdO, PtO_2) have been shown to catalyze carbonyl substitution reactions. Using this procedure, $Re_2(CO)_8(PPh_2Me)_2$ and $Mn_2(CO)_9(CNCy)$ were prepared in high yield [12,13]. The complex $Re_2[P(OMe)_3]_{10}$ was prepared from $ReCl_4(py)_4$ or $ReOCl_3(py)_2$, potassium metal, and the ligand. The hydride $ReH[P(OMe)_3]_5$ was an accompanying product in these reactions [14].

Reactions of $Mn_2(CO)_{10}$ with $Et_2PCH_2PEt_2$ (depm) and with $Cy_2PCH_2PCy_2$ (dcpm) yield $Mn_2(CO)_6(depm)_2$ and $Mn_2(CO)_5(dcpm)_2$. The steric profile of the bidentate phosphine appears to determine the preferred product [15]. The reactions between $Mn_2(CO)_5(dppm)_2$ and several potential ligands (SO_2, $PhN_2{}^+$, CS_2, H^-) were reported; the ligand groups add into a bridging position between the metals. Boron trifluoride also reacts with the dimanganese complex; the 1:1 adduct may have the boron atom complexed to oxygen of the bridging carbonyl group [16].

Carbon-13 NMR spectra were recorded for $Mn_2(CO)_6(dppm)_2$ and $Mn_2(CO)_5(dppm)_2$ (dppm = $Ph_2PCH_2PPh_2$). Both complexes are fluxional in these NMR experiments and activation parameters were obtained [17].

A complicated reaction occurs upon photolysis of a solution containing $Mn_2(CO)_{10}$ and $FeH(CO)(PPh_3)(\eta-C_5H_5)$. Six products were characterized including $Mn_2(CO)_9(PPh_3)$, $Mn_2(CO)_8(PPh_3)_2$, $MnH(CO)_4(PPh_3)$ and $(CO)_5MnFe(CO)_2(\eta-C_5H_5)$ [18]. Photolysis of a mixture of $Re_2(CO)_{10}$ and butadiene produces six products including $Re_2(CO)_8(\mu-C_4H_6)$, a derivative of the parent carbonyl complex [19]. A paper on the analogous reaction of $Mn_2(CO)_{10}$ has appeared also [20].

A variety of sophisticated studies have had as their primary focus the possible cleavage of the metal-metal bond in the dimetal decacarbonyls. A picosecond absorption spectrometric experiment on photolyzed solutions of $Mn_2(CO)_{10}$ detected two products, one of which is the radical $Mn(CO)_5$. The second product is perhaps $Mn_2(CO)_9$ [21]. The sensitization of $Mn_2(CO)_{10}$ to photolytic cleavage giving $Mn(CO)_5$ by biacetyl is reported, as is the quenching of photophosphorescence of UO_2^{2+} by $Mn_2(CO)_{10}$; both experiments argue for the presence of radical species in these photolyses [22]. Pulsed laser irradiation of $Mn_2(CO)_{10(g)}$ at specific wavelengths was found to induce initial fragmentation; this is followed by ionization and ion-molecule reactions [23]. Likewise, flash photolysis of $Re_2(CO)_{10}$ in isooctane produces $Re(CO)_5$. This radical has an absorption maximum in the visible region (535 nm, ε 1000±100 $M^{-1}cm^{-1}$). Rates of recombination and rates of halogen abstraction from CCl_4 by this radical and by $Mn(CO)_5$ were measured [24].

Crossover experiments on substitution reactions of $Re_2(CO)_{10}$ in decalin at 130°C indicate that metal-metal bond is not broken. For $MnRe(CO)_{10}$, the metal-metal cleavage route is at best a secondary pathway [25]. A thesis has appeared elsewhere on rates of substitution of $MnRe(CO)_{10}$ [26].

It is possible to generate $M(CO)_5$, $M(CO)_4(PPh_3)$, $M(CO)_3(PPh_3)_2$ (M = Mn,Re), $Mn(CO)_3[P(OPh)_3]_2$ and $Mn(CO)_2[P(OMe)_3]_3$ by one electron oxidation of the corresponding anions. These radical species either dimerize or abstract hydrogen from the solvent [27]. Photolysis of $MnH(CO)_5$ in a matrix produces $Mn(CO)_5$ along with H and HCO radicals. An ESR spectrum of the manganese radical suggests that the unpaired spin is primarily centered at the metal [28].

The radical species $Mn(CO)_3(PR_3)_2$ ($R = Bu^n$, Bu^i, Pr^i, OPr^i) were shown to react with CCl_4 producing *mer,trans*-$MnCl(CO)_3(PR_3)_2$. With Bu_3SnH, $MnH(CO)_3(PR_3)_2$ complexes are the principal products, along with small amounts of $Mn(SnBu_3)(CO)_3(PR_3)_2$. A kinetic study on the latter reaction indicated that there is a first order dependence on both reagents [29]. A thesis containing some of this work was identified [30].

A kinetic study on the reaction of $Mn(CO)_3(PBu_3{}^i)_2$ *and CO has been carried* out. The displacement of phosphine by CO is first order in both reactants suggesting an associative mechanism for this reaction [31]. Other quantitative and semiquantitative kinetic data on $M_2(CO)_8(L)_2$ (M = Mn, Re) reactions have been analyzed to provide further information on the carbonyl substitution rates for various $M(CO)_4(L)$ species [32].

Electron addition to $Mn_2(CO)_{10}$ and $Mn_2(CO)_8(PR_3)_2$ ($R = Bu^n$, OEt) was accomplished by subjecting solid samples to ionizing radiation. An ESR experiment identified the products [33]. Electron spin resonance studies on various paramagnetic complexes of 1,2-diketones, $M(CO)_4$(diketone) (M = Mn, Re), have been described in three papers [34,35,36].

A further crystallographic study of $Mn_2(CO)_{10}$ has appeared [37]. This study has as its goal the determination by experiment of the charge density in the metal-metal bond region. A microcalorimetric study on many organomanganese carbonyls including $Mn_2(CO)_{10}$ was carried out to determine ΔH_f^{o} [38]. An x-ray PES study on $Mn_2(CO)_{10}$ and other species has been concluded [39].

Catalytic reduction of $PhNO_2$ to $PhNH_2$ occurs in the presence of $Mn_2(CO)_{10}$ and Bu_4NF [40]. The chlorination of cycloalkanes is catalyzed by $Re_2(CO)_{10}$ [41].

Several new derivatives of $[Mn(CO)_5]^-$ have been characterized. Of particular interest is the complex $[Mn(CO)_3(\eta^4\text{-}C_6H_8)]^-$, prepared by addition of hydride ion to $Mn(CO)_3(\eta^5\text{-}C_6H_7)$, or by the addition of two hydride ions to $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ [42]. This work will receive additional comment in Part VIII. The complexes $[Mn(L)(\eta^4\text{-}C_4H_6)_2]^-$ ($L = PMe_3$, PEt_3, $P(OMe)_3$, CO) were prepared by sodium reduction of $Mn(L)(\eta^4\text{-}C_4H_6)_2$. The phosphite complex was isolated as the $Na(18\text{-crown-}6)^+$ salt [43].

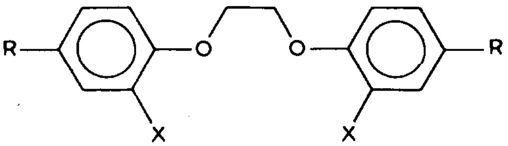
A reference to the nucleophilicity of $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$ and other anionic carbonyl metallates was overlooked in the Annual Surveys of two years ago. Rates of displacement of $OTos^-$ and I^- from MeOTos and MeI were measured. This study provides much improved data on this significant reaction [44].

A few new cationic complexes, derivatives of $[Mn(CO)_6]^+$, have been prepared. Addition of $TlPF_6$ and CO to cis,cis-$MnBr(CO)_2(dppm)_2$ gives mer-$[Mn(CO)_3(dppm)_2]PF_6$, a complex in which one of the dppm ligands is monodentate. If CO is omitted in this reaction, cis-$[Mn(CO)_2(dppm)_2]PF_6$ forms in preference. Photolysis converts this complex to the trans-isomer, while heating of the trans isomer effects conversion back to the cis form [45]. Several isocyanide complexes have been prepared, including $[Re(CNR)_6]^+$ and $[Re(CNR)_4(L)_2]^+$ species (R = Bu^t, Cy; L = PPh_3, PPh_2Et) [46]. A paper has appeared analyzing PES and electrochemistry data based upon additivity of ligand parameters. A part of the data in this paper is from work on isocyanide derivatives of manganese(I) [47]. The x-ray PES of $[Re(CNBu^t)_6]PF_6$ [48] and oxygen-17 NMR of the $[Re(CO)_6]^+$ cation [49,50] have also been described in the literature.

III. METAL CARBONYL HALIDES AND DERIVATIVES

Rhenium atoms, generated in a metal atom reactor, are oxidized by oxalyl chloride to produce a 40% yield of $Re_2Cl_2(CO)_8$, making this a viable synthetic route to this species [51]. Photolysis of $Mn_2(CO)_{10}$ and a tetraalkylammonium chloride in CH_2Cl_2 produces $[Mn(CO)_5]^-$ and $[MnCl_2(CO)_4]^-$. The complex $[Mn_2Cl(CO)_9]^-$ is postulated to be an intermediate in this reaction [52]. When $ReBr(CO)_5$ is heated in nonane, a cluster complex $Re_6Br(CO)_{14}$ is said to result. This complex has ν(CO) values of 2051 and 1940 cm^{-1}. A reaction of $ReBr(CO)_5$ and mesitylene to give $[Re(CO)_3(\eta\text{-mes})][Re_2Br_3(CO)_6]$ was also reported in this paper.

Various substituted metal carbonyl halides received attention. Preparation of cis,cis-$MnBr(CO)_2(dppm)_2$ from $MnBr(CO)_5$ and dppm (toluene, reflux) was mentioned; one of the dppm ligands is monodentate in this species [45]. Complexes with chelating diisocyanide and dicyanide ligands were reported by Angelici and coworkers [54]; these have the formula $MnBr(CO)_3(diNC)$ and $MnBr(CO)_3(diCN)$, with the substituting ligand being of the form:



(X = NC, CN; R = H, Bu^t)

Halogen atom extraction from CCl_4 by $Mn(CO)_3(L)_2$ radicals (L = PBu_3^n, PBu_3^i, PPr_3^i, $P(OPr^t)_3$) produces primarily mer,trans-$MnCl(CO)_3(L)_2$ [29,30].

Manganese complexes ($MnCl(CO)_4(L)$ and $MnCl(CO)_3(L)_2$) were also reported, in which the ligand L is an isocyanide functionality attached to a polystyrene polymer [55]. A derivative of $ReBr(CO)_5$ was obtained by substitution of CO by the terminal nitrogen in glycylglycine, viz. *cis*-$ReBr(CO)_4(H_2NCH_2CONHCH_2CO_2H)$. Upon heating in dioxane, the complexes *fac*-$ReBr(CO)_3(diox)(H_2NCH_2CONHCH_2CO_2H)$ and $Re(CO)_3(diox)(OCOCH_2NHCOCH_2NH_2)$ were obtained, the latter arising upon elimination of HCl [56,57].

Resonance Raman spectra were reported for *fac*-$ReCl(CO)_3(L)_2$ compounds (L = RN=CHCH=NR, R = p-tol, mes) [58]. NMR was used to study inversion processes at sulfur in $ReBr(CO)_3(MeS(CH_2)_nSMe)$ (n = 2,3); the selenium analogues were also investigated [59]. The molecular structure of *fac*-$MnBr(CO)_3[SC(PPh_2)NHPh]$ was obtained by x-ray crystallography [60].

Wilkinson and coworkers have published a series of papers on organorhenium complexes in the recently renamed journal, Polyhedron [61,62,63,64]. The first two papers describe chemistry originating with the complex $ReCl_3(NPh)(PMe_3)_2$. Reaction of this species with $HgMe_2$ gives $ReMe_3(NPh)(PMe_3)_2$. This in turn reacts with HBF_4 giving $ReMe_2F(NPh)(PMe_3)_2$ and with the starting material giving $ReMe_{3-n}Cl_n(NPh)(PMe_3)_2$ [61]. Reduction of $ReCl_3(NPh)(PMe_3)_2$ using Na[Hg] and additional ligands (CO, PMe_3, C_4H_6) yields a large number of new complexes; several of which were subjects for crystallographic study [62]. Reduction of $ReCl_4(THF)_2$ using Na[Hg] in the presence of added ligand molecules was broadly studied. These reactions produce a number of new species, some of which were also subjects for crystallographic studies. Halo-rhenium products characterized include $ReCl(PMe_3)_5$, $[ReH(Cl)(PMe_3)_5]BF_4$, $ReCl(CO)_2(PMe_3)_3$, $ReCl(N_2)(PPhEt_2)_4$, $[ReI(NHPh)(PMe_3)_4]I$, and $[ReI(Me)(PMe_3)_4]I \cdot PMe_4I$ [63]. Chemistry described in the fourth paper originated with $ReCl(PMe_3)_5$ which can be converted to $ReCl(CNBu^t)_2(PMe_3)_3$ and $ReCl(CNBu^t)_3(PMe_3)_2$ by reaction with Bu^tNC. Both products were subjected to structural characterization by x-ray diffraction methods. Their chemical behavior was briefly investigated; for example, both are protonated by HBF_4 giving $[ReH(Cl)(CNBu^t)_3(PMe_3)_2]BF_4$ and $[ReH(Cl)(CNBu^t)_2(PMe_3)_3]BF_4$.

A complex originally identified as $ReCl_2NO(PPh_3)_2$ has now been reformulated as $ReCl_2(OMe)(NO)(PPh_3)_2$. This species is reduced by $NaBH_4$ in ethanol in the presence of PPh_3 to give $ReH_2(NO)(PPh_3)_3$ which reacts with HBF_4 or $HClO_4$ to yield $ReF(CO)(NO)(PPh_3)_3]^+$; a crystal structure study was carried out on the perchlorate salt. A reaction of HCl with $ReH_2(NO)(PPh_3)_3$ produces $ReCl_2(NO)(PPh_3)_3$ which with CO and CNR give $ReCl_2(CO)(NO)(PPh_3)_2$ and $ReCl_2(NO)(CNR)_2(PPh_3)$ respectively [65].

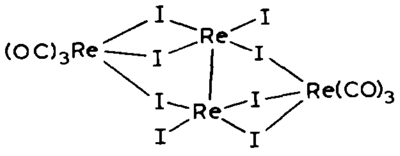
The complexes *mer*-$ReCl(N_2)(CNMe)[P(OMe)_3]_3$ and $ReCl(N_2)(CNMe)(PPh_3)[P(OEt)_3]_2$ were prepared from organodiazenide-rhenium precursors, $ReCl_2(N_2COPh)[P(OMe)_3]_3$ and $ReCl_2(N_2COPh)[P(OEt)_3]_2$, and *mer*-$ReCl(N_2)(PPh_3)[P(OMe)_3]_3$

was formed from $ReCl_2(N_2COPh)(PPh_3)_2$ [66]. The molecular structure of $ReCl(N_2)$-$(CNMe)[P(OMe)_3]_3$ was reported in this paper. Reactions between $ReCl(N_2)(dppe)_2$ and several isocyanides (RNC; R = Me ,Bu^t,tol) gave $ReCl(CNR)(dppe)_2$ [67].

Rhenium isocyanide complexes with the formula $[Re(CNR)_5X_2]^+$(R = Bu^t, Cy; X = Cl, Br) form from $(Bu_4N)_4Re_2X_8$ - RNC reactions, and these cationic species were isolated as PF_6^- salts. Several derivatives in which phosphines ($PEtPh_2$, dppe) replace isocyanides were also made [46].

Photolysis of $ReCl(CO)(dppe)_2$ generates a species presumed to be the 16e complex $ReCl(dppe)_2$. This compound reacts with methanol, producing a mixture of $ReCl(CO)(dppe)_2$ and $ReHCl_2(dppe)_2$. The reaction may involve oxidative addition of either C-H or O-H bonds of the alcohol to the coordinately unsaturated intermediate as the initial step [68].

Iodine oxidizes $Re_2I_2(CO)_6(THF)_2$ to form $ReI_3(CO)_3$ and $Re_4I_8(CO)_6$ (II); this halogen also reacts with $Re_2I_2(CO)_8$ to give $Re_3I_6(CO)_6$. X-ray crystallography was used to identify the structures of the two polynuclear products. In compound (II), the $Re_2I_8^{2-}$ anion is linked via iodide bridges to two rhenium tricarbonyl fragments; the Re-Re distance is 2.279(1) Å, not much perturbed from the free ion value [69].



(II)

Products of electron addition to $ReBr(CO)_5$ and $ReI(CO)_5$ are detected by ESR when samples of these substances are subjected to γ-radiation [70]. Values of ΔH_f° for $MnX(CO)_5$ (X = Br, I) have been measured [38], and an ^{17}O NMR spectrum recorded for $MnBr(CO)_5$ [49].

IV. METAL HYDRIDE COMPLEXES

The interaction between metal carbonyl hydrides and Lewis acids was the subject of an interesting study by Shriver et al. [71]. Manganese pentacarbonyl hydride and BCl_3 exist in equilibrium with a 1:1 adduct, detectable by NMR. It is suggested that the hydride ligand group acts as a base, a bridging hydride structure, $(CO)_5Mn$-H-BCl_3, being proposed for the adduct. In contrast, the reaction of $MnH(CO)_5$ and $AlBr_3$ produced $Mn(CO)_5AlBr_4$, while the reactions of $MnH(CO)_4(PPh_3)$ and BCl_3 or $AlBr_3$ give $MnX(CO)_4(PPh_3)$, (X = Cl, Br).

Formation of $MnH(CO)_5$ is noted in the reaction of $[Mn(CO)_5]^-$ and HCOF. Presumably product formation occurs via the metal formyl intermediate [72]. Rhenium pentacarbonyl hydride was identified as one product of photolysis of $Re_2(CO)_9(H_2O)$ along with $Re_4(OH)_4(CO)_{12}$ [10]. Formation of various phosphine substituted metal carbonyl hydrides through hydrogen abstraction by various 17e radical species, $Mn(CO)_{5-n}(L)_n$, was mentioned earlier [27]. Reduction of $ReCl_4(py)_4$ or $ReOCl_3(py)_2$ in the presence of $P(OMe)_3$ gave $ReH[P(OMe)_3]_5$ as one of four products; a second product was identified as $ReH[P(OMe)_3]_3[(MeO)_2POP(OMe)_2]$. Reactions of $ReH[P(OMe)_3]_5$ with CO, giving $ReH(CO)[P(OMe)_3]_4$, and with H^+, giving $[ReH_2\{P(OMe)_3\}_5]^+$, are mentioned [14].

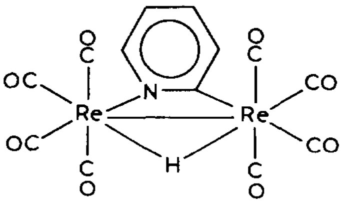
Photolysis of $MnH(CO)_5$ and $[Mo(CO)_3(\eta\text{-}C_5H_5)]_2$ produces $Mn_2(CO)_{10}$ and $MoH(CO)_3(\eta\text{-}C_5H_5)$. It was suggested that this reaction occurs through abstraction of hydrogen in $MnH(CO)_5$ by the $Mo(CO)_3(\eta\text{-}C_5H_5)$ radical [73]. Photolysis of $MnH(CO)_5$ in a solid matrix produces $Mn(CO)_5$, HCO, and H [28]. A kinetics study on the reaction between $MnH(CO)_5$ and $Mn(CH_2C_6H_4OMe)(CO)_5$ was carried out. A mechanism was proposed in which the initial step is decarbonylation of the alkyl-manganese compound followed by addition of $MnH(CO)_5$ and uptake of CO to give $Mn_2(CO)_{10}$ and $MeOC_6H_4CH_3$ [74]. A mechanism has also been developed for the reaction of $MnH(CO)_5$ with substituted cyclopropenes, which involves an intermediate caged ion pair [75].

Calculations (SCF-Xα-SW) on $MnH(CO)_5$ and on other organometallic species were developed in a thesis [76].

Various rhenium hydride species were mentioned in papers cited earlier in this review; these include: $ReH_2(NHPh)(PMe_3)_4$ and $ReH(NHPh)(\eta\text{-}CH_2PMe_2)(PMe_3)_4$ [62]; $ReH(PMe_3)_5$, $[ReH(Cl)(PMe_3)_5]BF_4$. $ReH_3(PMe_3)_4$, and $[ReH_4(PMe_3)_4]BF_4$ [63]; and $ReHCl_2(dppe)_2$ [68]. The compound $Re_2H(CO)_8(NC_5H_4)$, III, which has a hydride bridging the two metals, is one product from the photolysis of $Re_2(CO)_{10}$ and pyridine [11].

Further study has appeared on the reactivity of various phosphine-rhenium hydrides, with aliphatic C-H bonds being activated in some instances. For example $ReH_7(PPh_3)_2$ reacts with C_5H_{12} in the presence of $CH_2{=}CHCMe_3$ to produce $ReH_3(PPh_3)_2(\eta^4\text{-}C_5H_8)$ [77]. The same complex (and related complexes with other phosphine ligands) cause the dehydrogenation of cycloalkanes [78]. Dienes also react with $ReH_7(PPh_3)_2$ to produce $ReH_3(PPh_3)_2(\eta^4\text{-diene})$ species. Addition of H^+ degrades these species giving saturated hydrocarbon products [79].

Photolyses of mixtures of $Re_2(CO)_{10}$ and several terminal alkenes yield the products, IV, shown below:



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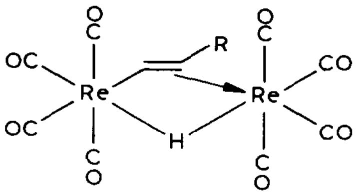
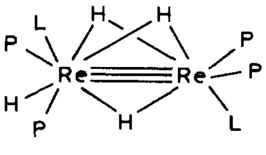


(IV) (R = H,Me,Et)

A mechanism of formation is proposed involving an intermediate species, $Re_2(CO)_8(olefin)_2$; after dissociation of one olefin, the oxidative addition of a C-H bond to the coordinately unsaturated rhenium atom gives the product. Treatment of any of these complexes with ethylene, leads to exchange of the μ-CH=CHR group by a μ-(-CH=CH_2) group. Similarly, phenylacetylene also replaces the alkenyl group to give a μ-alkynyl complex [80].

A reaction between $Re_2H_8(PPhMe_2)_4$ and $P(OCH_2)_3CEt$ (=L) gave $Re_2H_4(PPhMe_2)_4(L)_2$, V ; this complex was protonated, yielding $[Re_2H_5(PPhMe_2)_4(L)_2]BF_4$, VI. Structures of both complexes were determined crystallographically; bond lengths of about 2.6Å are in accord with a metal-metal triple bond in each compound [81]. Reactions of $Re_2H_2(CO)_6(L^\wedge L)$ ($L^\wedge L$ = dppm, $(EtO)_2POP(OEt)_2$) with



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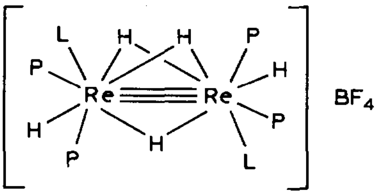
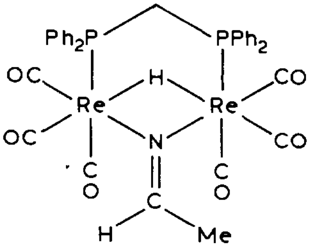


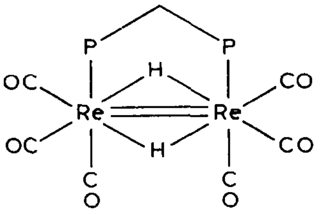
(VI)

$P(OMe)_3$, Bu^tNC and several other isocyanides, and with MeCN produced 1:1 adducts. A crystal structure study on one of these compounds identified the molecular structure shown below [82] (VII).



(VII)

Reactions were reported between $Re_3H_3(CO)_{12}$ and several bidentate ligands including dppe, dppm and $(EtO)_2POP(OEt)_2$[83]. A variety of different products were formed including mononuclear, dinuclear, and trinuclear species. X-ray diffraction data on $Re_2H_2(CO)_6(dppm)$, VIII, and on $Re_3H_3(CO)_8[(EtO)_2POP(OEt)_2]$, IX, were presented. A later paper presented results of a neutron diffraction study on IX [84].



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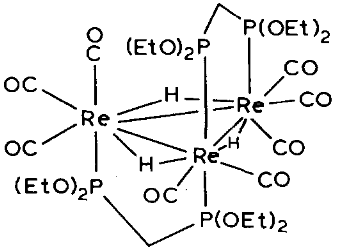
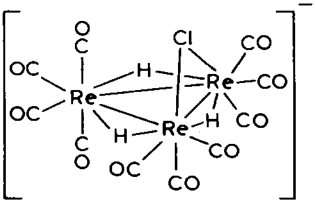


(IX)

Two papers have appeared, each describing products obtained by pyrolysis of $NEt_4[ReH_2(CO)_4]$ in η-$C_{14}H_{30}$. The earlier paper reports the complex $[Re_7C(CO)_{21}]^{3-}$, which was isolated as a tris(tetraphenylphosphonium) salt. Its structure, (x-ray diffraction) consists of a monocapped octahedron of metal atoms with a carbide carbon in the center [85]. A second product, also the subject of a x-ray crystallographic study, had the formula $(NEt_4)_2[Re_8C(CO)_{24}]$. The carbide containing anion in this species has a bicapped octahedral framework of metal tricarbonyl groups [86].

In related studies, the same research group has investigated reactions of $NEt_4[Re_3H_4(CO)_{10}]$. This species was found to react with acids, HX (X^-= Cl^-, Br^-, I^- [87]; X^- = HCO_2^-, $CF_3CO_2^-$, $CH_3CO_2^-$ [88]) yielding products having the general formula $NEt_4[Re_3H_3(X)(CO)_{10}]$. X-ray diffraction studies identified the structures with chloride, X, formate, XI, and trifluoroacetate anions. The reaction product between $NEt_4[Re_3H_4(CO)_{10}]$ and t-BuSH gave a slightly different product, XII, which was also characterized structurally [89].



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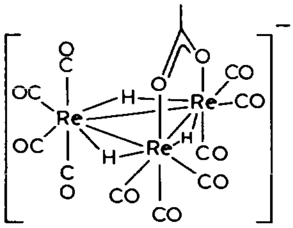

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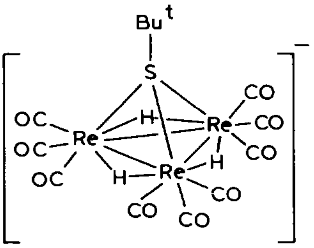


(XII)

Photolysis of $Re(CO)_3(\eta-C_5H_5)$ and Et_2SiH_2 gave $ReH(SiHEt_2)(CO)_2(\eta-C_5H_5)$. When this is dissolved in $CHCl_3$, conversion to $ReH_2(CO)_2(\eta-C_5H_5)$ occurs. This latter species was deprotonated by KOH in ethanol, giving $K_2[Re(CO)_2(\eta-C_5H_5)]$, a useful reagent for further study [90]. The reactivity of $ReH_2(CO)_2(\eta-C_5H_5)$ toward diazonium salts was tested in another study. No reaction occurred at -35°C; in contrast, a slow (2 day) reaction occurred at room temperature [91].

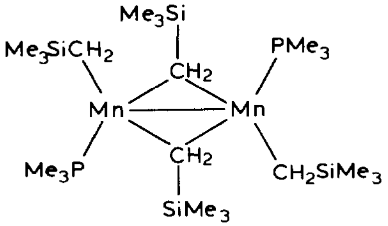
The structure of $MnH(SiPh_2F)(CO)_2(\eta-C_5H_4Me)$ was obtained in a neutron diffraction experiment [92]. The significant feature in this molecule is the position of the hydride ligand which appears to be bridging manganese and silicon.

The complex $ReH(CO)(NO)(\eta-C_5H_5)$ was formed in a reaction between $[Re(CO)_2(NO)(\eta-C_5H_5)]BF_4$ and Et_3N/H_2O, $Re(CO_2H)(CO)(NO)(\eta-C_5H_5)$ being presumed as an intermediate in this reaction. Some reactions of the hydride were reported including bromine-hydrogen exchange using CBr_4 and hydride abstraction using Ph_3C^+ [93].

V. COMPLEXES WITH CARBON LIGANDS

A diverse array of compounds are considered in this section of the review. Initial coverage will be provided to simple alkyl and acyl (including formyl) metal species; this will be followed by coverage of complexes with carbene and carbyne ligands, bridging methylene and ethylidene ligands, and other species.

The homoleptic metal alkyl complex, $[Mn(CH_2SiMe_3)_2]_x$, was found to react with PMe_3 giving a dinuclear product $Mn_2(CH_2SiMe_3)_4(PMe_3)_2$, XIII. The structure of this species (x-ray diffraction) is shown below [94]. Formation of a new homoleptic complex was accomplished by reaction of $MnBr_2$ with the diphosphorus diylide; its structure, XIV, was also determined crystallographically [95].



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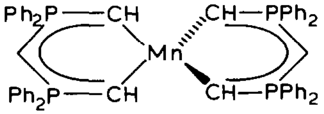
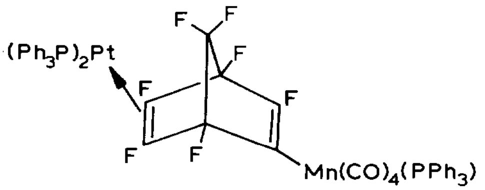


(XIV)

An unusual complex, $Mn_3(C_6H_9)_4$, was determined to be the product of a reaction between $MnCl_2$ and the 3-methylpentadienyl anion [96]. It was characterized by x-ray methods. Schrock and Edwards have prepared $ReMe_3(NBu^t)_2$ from $ReCl_3(NBu^t)_2$, and indicated it had trigonal bipyramidal (D_{3h}) symmetry. They also prepared $Re(CH_2Bu^t)(CHBu^t)(NBu^t)_2$, $Re(CBu^t)(CHBu^t)(OBu^t)_2$ and a halide bridged dinuclear species $[ReCl_2(CHBu^t)(CBu^t)(NH_2Bu^t)]_2$ [97]. The preparation of a number of rhenium alkyl species by Wilkinson and coworkers was mentioned earlier in this review. Among the compounds described by this group were $ReMe_3(NPh)(PMe_3)_2$, $ReMe_2F(NPh)(PMe_3)_2$, $ReMe(OAc)_2(NPh)(PMe_3)_2$ and $ReOR_3Re(PMe_3)_4ReO_2R$ (R = CH_2SiMe_3) [61] and $Re(CNBu^t)_5R$ (R = Me, Et) [64].

Several papers primarily concerned with the syntheses of alkyl-, alkenyl-, and alkynyl-metal carbonyls have appeared. Sodium salts of $[Mn(CO)_5]^-$ and $[Mn(CO)_4(PPh_3)]^-$ react with CH_2ClI to give chloromethylmanganese carbonyl compounds. The pentacarbonylrhenate anion reacts with $ClCH_2OMe$ giving a mixture of $Re(CH_2Cl)(CO)_5$ and $Re(CH_2OMe)(CO)_5$ [98]. Reactions of $Na[Mn(CO)_5]$ and $Na[Re(CO)_5]$ with $[PhC{\equiv}CPPh_3]Br$ give $M(C{\equiv}CPh)(CO)_5$ species; in the case of $Na[Re(CO)_5]$, $ReH(CO)_4(PPh_3)$ is also a product [99]. The reaction between $Na_2[Mn(CO)_4(PMe_2O)]$ and $(CF_3SO_3CH_2)_2CMe_2$ gives $\overline{Mn(CH_2CMe_2CH_2OPMe_2)}(CO)_4$. Similar reactions were carried out with $Na_2[M(CO)_4PPh_2O]$ (M = Mn, Re). Sulfur dioxide insertion reactions into the metal-carbon bond of the new compounds were successful. Crystal structures of two products were reported [100]. Preparations of $\overline{M[(CH_2)_nAsR_2]}(CO)_4$ (M = Mn, Re; n = 3,4; R = Me, Ph) were accomplished by dehalogenation of $MBr(CO)_4[R_2As(CH_2)_nCl]$ and the SO_2 insertion reaction was studied for these species also. A crystal structure study on $\overline{Mn(CH_2CH_2CH_2AsPh_2)}(CO)_4$ was included in this work [101]. Fluoride ion is displaced from octafluorobicyclo-2,2,1-heptadiene by $[Mn(CO)_5]^-$ and $[Re(CO)_5]^-$

giving $M(C_7F_7)(CO)_5$. The manganese species reacts further with $Pt(PPh_3)_4$, giving a bimetallic product, XV [102]. A related reaction using a partially fluorinated precursor was reported in a second paper; this also described the reaction of $MnMe(CO)_5$ with this bicycloheptadiene to give XVI [103].



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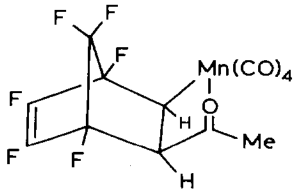


(XVI)

The preparation of η^1-cycloheptatrienylrhenium pentacarbonyl was accomplished in two ways. Photolysis of $Re(COC_7H_7)(CO)_5$ at -78° gave this product as did the reaction between $Na[Re(CO)_5]$ and $[C_7H_7]BF_4$. The metal-carbon bond energy was estimated at 30.4±0.3 Kcal/mole, and a crystal structure study was carried out on this substance [104].

A complex $MnMe(CO)_2(\eta\text{-}C_6H_6)$ was prepared by methylation of $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ using $LiCuMe_2$ [105]. The complex $ReMe_2(CO)_2(\eta\text{-}C_5H_5)$ was prepared from $K_2[Re(CO)_2(\eta\text{-}C_5H_5)]$ and CH_3I [90].

A reaction between $K[Mn(CO)_5]$ and Me_3SiOCH_2I yields $Mn(CH_2OSiMe_3)(CO)_5$. This compound could not be formed by insertion of H_2CO into the silicon-manganese bond in $Mn(SiMe_3)(CO)_5$, and an attempt to form this compound from $Mn(CH_2OMe)(CO)_5$ and Me_3SiI also failed, this reaction producing $Mn(CH_2I)(CO)_5$ and Me_3SiOMe instead [106].

A single carbonyl group in $MnMe(CO)_5$ is displaced by $CF_3SO_2N{=}S{=}NSO_2CF_3$ (=L), one nitrogen in the latter species serving as the donor group in the product, $MnMe(CO)_4(L)$ [107]. Cyclo-metallation reactions using $MnR(CO)_5$ as a precursor were the subject of a thesis [108]. Methylmanganese pentacarbonyl was found to catalyze the reduction of CO by B_2H_6; alkanes and olefins up to C_4 were found as products. The addition of BF_3 to this reaction mixture increased the amounts of longer chain saturated hydrocarbons [109,110]. This latter effect is presumably related to the fact that Lewis acids induce insertion of CO into a metal-carbon bond (alkyl migration). There is a paper from the group working this latter project which reports a kinetic study on the Lewis acid induced alkyl migration reaction [111].

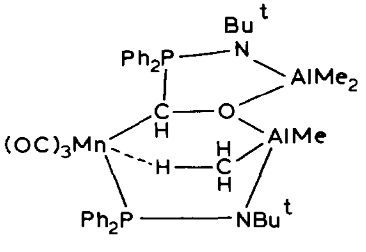
A kinetic study on the reaction between $MnMe(CO)_5$ and $MeO_2CC{\equiv}CCO_2Me$ suggests that concurrent unimolecular and bimolecular processes are operating [112]. Microcalorimetry provided values of $\Delta H_f{}^\circ$ for various manganese complexes including the alkyl and acyl species $MnR(CO)_5$, (R = Me, Ph, CH_2Ph, CF_3, COMe, $COCF_3$, COPh) [38].. A x-ray PES study of $MnR(CO)_5$ (R = Me,Pr, $CH_2CH{=}CH_2$) was reported [39], as was the ^{13}C NMR for $ReMe(CO)_5$ [113].

Metal complexes with formyl groups continue to be a topic of active involvement. A review article on this topic has appeared [3]. Graham and Sweet have described their work on $NaBH_4$ reduction of $[Re(NO)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ in THF, with H_2O present; the reaction proceeds through the metal formyl and hydroxymethyl complexes to the eventual product, $ReMe(NO)(CO)(\eta\text{-}C_5H_5)$. Similar results are found starting with the analogous pentamethylcyclopentadienyl complex [114]. Gladysz et al. have described the formation of $Re(CHO)(NO)(CO)(\eta\text{-}C_5H_5)$ from $[Re(NO)(CO)_2(\eta\text{-}C_5H_5)]^+$ using $NaBHEt_3$ as a reducing agent. A "transformylation" reaction has also been used to make this complex. Other formyl complexes ($Mn(CHO)(CO)_3(PPh_3)_2$, $Re(CHO)(CO)_4(PPh_3)$) were made by similar routes [115]. Further reduction of $Re(CHO)(NO)(PPh_3)(\eta\text{-}C_5H_5)$ can be accomplished using $BH_3{\cdot}THF$, to produce $ReMe(NO)(CO)(\eta\text{-}C_5H_5)$ [116]. A sequence of reactions of this alkyl rhenium species was carried out, starting with hydride abstraction by $[CPh_3]BF_4$ to give $[Re(CH_2)(NO)(PPh_3)(\eta\text{-}C_5H_5)]BF_4$ in situ. This complex was stabilized by addition of base (yielding $[Re(CH_2B)(NO)(PPh_3)(\eta\text{-}C_5H_5)]BF_4$, (B = py, PPh_3), or $Re(CH_2OMe)(NO)(PPh_3)(\eta\text{-}C_5H_5)$). Methyl triflate reacts with the last species to give $[Re(CHOMe)(NO)(PPh_3)(\eta\text{-}C_5H_5)]O_3SCF_3$. Other related chemistry was described in this lengthy paper, with a discussion of the implications of this work to the catalytic reduction of CO also being included.

A formyl-manganese complex, $Mn(CHO)(CO)_3[P(OMe)_3]_2$, was produced in a reaction between $[Mn(CO)_3\{P(OMe)_3\}_2]^-$ and HCOOCOMe. Hydrolysis of this species yielded $MnMe(CO)_3[P(OMe_3)]_2$ and $Mn_2(CO)_6[P(OMe)_3]_4$; a mechanism for this reaction was proposed [117]. The formyl complex, $Mn(CHO)(CO)_5$, was proposed as an intermediate in the formation of $MnH(CO)_5$ from $[Mn(CO)_5]^-$ and HCOF [72].

An acyl-rhenium compound, $Re[COC(CF_3){=}C(CF_3)AsMe_2](CO)_4$, was formed in a reaction between $Re_2(CO)_{10}$ and cis-$Me_2AsC(CF_3){=}C(CF_3)AsMe_2$; its structure was determined by diffraction methods [118]. The unusual product obtained in the reaction of $MnH(CO)_5$ and $Ph_2PNBu^tAlMe_2$ was shown to have the structure drawn below, XVII [119].

Diastereomers were formed upon reaction of $[Re(NO)(CO)(PPh_3)(\eta\text{-}C_5H_5)]BF_4$ and R-α-$H_2NCH(Me)(Np)$. Separation followed by acid degradation of the carboxamido group produced both optical isomers of $[Re(NO)(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$. The integrity of optical center at the metal was retained in a sequence of reactions which produced various alkyl and carbene derivatives by either replacement or



(XVII)

reaction with the CO group. A crystal structure study was performed on the compound (-)-R-Re(CH_2Ph)(NO)(PPh_3)(η-C_5H_5) [120].

Another paper from the same research group described the synthesis of chiral rhenium vinylidene and acetylide complexes in which chirality is transferred through the C≡C group [121].

Decarbonylation of Re(COC_3Ph_2H)$(CO)_5$ and Re($COC_3H_2Bu^t$)$(CO)_5$ produces cyclopropenyl-rhenium pentacarbonyls. The mechanism of decarbonylation involves an allylic migration of the metal group [122].

Dirhenium decacarbonyl reacts with NO in the presence of various hydrocarbons under photolytic conditions. A number of products can be isolated from these reactions including $Re_3(CO)_{14}CO_2H$ and $Re_3(CO)_{14}NO_2$. Structural data on these species were obtained by crystallography [123]. Base hydrolysis of $Re(CO)_5BF_4$ at 20°C, was originally reported to give $Re(OH)(CO)_5$; this work has now been reinterpreted and the complex formulated as $[(CO)_5ReCO_2Re(CO)_4]_2$; a solid state structure was determined for this species by x-ray diffraction [124].

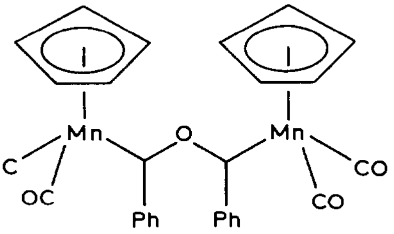
Graham and Sweet [93] converted [Re(NO)$(CO)_2$(η-C_5H_5)]BF_4 to Re(CO_2H)(NO)-(CO)(η-C_5H_5) by aqueous base hydrolysis; the product precipitates from this solvent. This compound is stable in THF, but catalytic amounts of base cause loss of CO_2 and conversion to ReH(CO)(NO)(η-C_5H_5). In water, Re(CO_2H)(NO)(CO)-(η-C_5H_5) can be deprotonated and the anion, $[Re(CO)_2(NO)(CO)(η\text{-}C_5H_5)]^-$ is considerably more stable than expected toward CO_2 loss.

Two further papers have appeared from Lukehart's group on metallo-β-diketonates. The complexes $Re(CO)_4$(MeCO)(MeC=NH)BX_2 were prepared from the reaction between $[Re(CO)_4(MeC{=}O)(MeC{=}NH)]^-$ and BX_3 (X = Cl, Br, I) [125].

Second, complexes with the formula $Re(CO)_4(MeC{=}O)(MeC{=}NCHCH_2CH_2Z)$ were prepared; Z in the formula signifies a group of biological significance [126]. A full paper on the stereochemistry of the decarbonylation reactions of $NMe_4[Re(CO)_4(COMe)(COPh)]$ has been published [127]; a communication of this work was identified last year.

Many papers have described the syntheses, structures, and properties of complexes having carbene and carbyne ligands. Early in this review the complexes ax- and eq-$Re_2(CO)_9[C(OR)SiPh_3]$, ax-$[Re_2(CO)_9CSiPh_3]AlCl_4$ [7,8], $Re_3(CO)_{14}SiPh_3$ [7], and ax-,eq-$Re_2(CO)_8[C(OEt)SiPh_3]_2$ [9] were mentioned. Carbene complexes of the formulas $[Re(CXY)(NO)(L)(\eta\text{-}C_5H_5)]$ (X,Y = H, Me, Ph; L = CO, PPh_3) were discussed in earlier referenced papers from the Gladysz group [116, 120, 121]. Further studies on these species by the same workers have been reported in two other papers. The complex $[Re(CHPh)(NO)(PPh_3)(\eta\text{-}C_5H_5)]PF_6$ is formed as two isomers, one kinetically favored isomer and a second thermodynamically more stable (>99:1) isomer. The isomers interconvert to 45:55 mixture upon photolysis [128]. The kinetic product is stable at -78°, the temperature of formation, but converts to the other isomer when warmed above this temperature. Crystal structures have been determined for both isomers [129].

Fischer's group has reported further work in this area. Reactions of a carbyne complex, $[Re(CSiPh_3)(CO)_2(\eta\text{-}C_5H_5)]BF_4$, with several alcohols (or amines) produce the carbene complexs $Re[C(X)SiPh_3](CO)_2(\eta\text{-}C_5H_5)$ (X = MeO, EtO, Me_2N). Some $Re(CHOR)(CO)_2(\eta\text{-}C_5H_5)$, a product of silyl group cleavage, was also obtained in these reactions. This paper also reported the crystal structure of ax-$Re_2(CO)_9(CHOMe)$ [130]. The Fischer group also reported the complexes $Mn[C(OEt)fc](CO)_2(\eta\text{-}C_5H_5)$ (fc = $Fe(\eta\text{-}C_5H_5)(\eta\text{-}C_5H_4\text{-})$), $[Mn(Cfc)(CO)_2(\eta\text{-}C_5H_5)]BCl_4$ [131], $[Re(CPh)(CO)(\eta\text{-}C_5H_5)]_2O$ and $[Mn(CPh)(CO)_2(\eta\text{-}C_5H_5)]_2O$, XVIII [132]; the structure of the last species was obtained by crystallography. An x-ray diffraction study has also identified the molecular structure of $Mn(CPhOEt)(CO)_2(\eta\text{-}C_5H_5)$ [133]. Molecular orbital calculations were performed on $Mn(CRR')(CO)_2(\eta\text{-}C_5H_5)$ (CRR' = CMe_2, CPhOMe), and on $[Mn(CPh)(CO)_2(\eta\text{-}C_5H_5)]^+$ [134].



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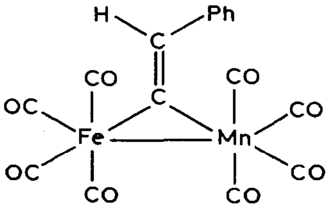
The reaction of $[Mn(CPh)(CO)_2(\eta\text{-}C_5H_5)]BF_4$ with PMe_3 produces $[Mn\{CPh(PMe_3)_n\}(CO)_2(\eta\text{-}C_5H_5)]BF_4$ (n = 1,2), both of which were isolated and characterized. Excess phosphine causes cleavage of the metal-carbon bond, however, to give $Mn(CO)_2(PMe_3)(\eta\text{-}C_5H_5)$ and $[PhC(PMe_3)_2]BF_4$ [135]. The complexes $[Mn(NO)(carbene)(L)(\eta\text{-}C_5H_5)]PF_6$ (L = CO, $P(OPh)_3$, CNCy; carbene = $\overline{COCH_2CH_2NH}$ and $\overline{COCH_2CH_2O}$) were prepared from $[Mn(NO)(CO)(L)(\eta\text{-}C_5H_5)]PF_6$ and either $[H_3NCH_2CH_2Br]^+$ or $HOCH_2CH_2Br$ [136]. Methyl manganese and rhenium pentacarbonyls react with Ph_3GeLi to give $[M(CO)_4(GePh_3)(COMe)]^-$, isolable as the Et_4N^+ salts. Treatment of the anion with $[Et_3O]BF_4$ gives the carbene complexes, $M(GePh_3)(CO)_4(CMeOEt)$. A crystal structure study was carried out on $Mn(GeMePhNp)(CO)_4(CMeOEt)$, a complex prepared in a similar manner starting with $[Ge(Ph)(Me)(Np)]Li$ [137].

A review article on complexes with bridging methylene groups was identified earlier in this review [4]. Crystal structure studies on $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2CH_2$ [138] and $[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_2CH_2$ [139] have been concluded. A PES study on the former complex is included as part of a thesis [140]. Core binding energies for this compound have also been measured [141]. The molecular structure of $(CO)_4Mn(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(CO)(\eta\text{-}C_5H_5)$ was determined by crystallography [142].

The bridging ethylidene complex, $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2C{=}CH_2$ was the subject of a recent paper [143] and a thesis [144]. This complex was prepared by a reaction of $Li[Mn(COPh)(CO)_2(\eta\text{-}C_5H_5)]$, $[CF_3SO_2]_2O$ and a proton acceptor, and its reactions were studied. Reaction of the phenylethylidene complex, $Mn(C{=}CHPh)(CO)_2(\eta\text{-}C_5H_5)$ with $Pt[P(OEt)_3]_4$ produced a bimetallic complex with a bridging phenylethylidene ligand [145]. A related reaction with $Fe_2(CO)_9$ gave two isomers of a bimetallic manganese-iron species. The molecular structure of one isomer was determined in a crystallographic study to be XIX [146]; the second isomer differs in the orientation of the phenyl groups. Reactions of this starting material with phosphites give olefinic complexes of manganese [147].

The anionic carbide complexes $[Re_7C(CO)_{21}]^{3-}$ [85] and $[Re_8C(CO)_{24}]^{2-}$ [86] were mentioned earlier in this review.



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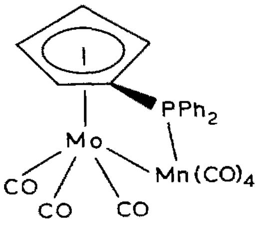
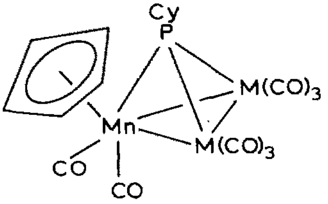
VI. DERIVATIVES OF METALS AND METALLOIDS

Numerous references have appeared to complexes having manganese or rhenium bonds to other transition metals, some having been mentioned earlier in other contexts. For example, there is the reference to $(CO)_5MnFe(CO)_2(\eta-C_5H_5)$, one of six products obtained when $Mn_2(CO)_{10}$ and $FeH(CO)_2(\eta-C_5H_5)$ are photolyzed [18]. Also there are the references to $(CO)_4Mn(\mu-CO)(\mu-CH_2)(Fe(CO)(\eta-C_5H_5)$ [142], to the complexes with bridging alkylidene groups, $[(EtO)_3P]_2Pt(-\mu-C{=}CHPh)Mn(CO)_2(\eta-C_5H_5)$ [145] and $(CO)_4Fe(\mu-C{=}CHCO_2Me)Mn(CO)_2(\eta-C_5H_5)$ [146], and to an ^{17}O NMR study which included the three complexes $[(CO)_5MMn(CO)_5]^-$ (M = Cr, Mo, W) [49].

Bimetallic compounds with metal-metal bonds were obtained from reactions of $Li[Mo(CO)_3(\eta-C_5H_4PPh_2)]$ and either $Mn_2Br_2(CO)_8$ or $ReBr(CO)_5$ [148]. A structural study on the manganese compound proved its structure to be XX. Manganese-iron and manganese-ruthenium clusters were obtained from reactions of $Mn(CO)_2(PCyCl_2)(\eta-C_5H_5)$ and $M_3(CO)_{12}$; structures of both were determined by x-ray crystallography to be XXI [149]. Manganese iron compounds with a bridging $SiCl_2$ group have been described in a thesis [150].



(XX)

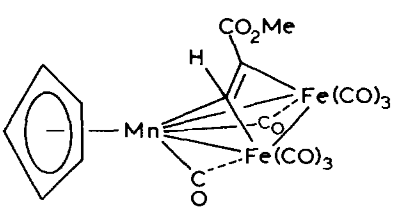


(XXI) (M = Fe,Ru)

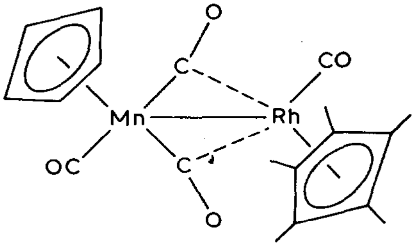
A manganese-diiron complex, XXII, was formed by reaction of $Mn(CO)_2(\eta^2-HC{\equiv}CCO_2Me)(\eta-C_5H_5)$ and $Fe_2(CO)_9$. Its structure, determined crystallographically, is shown below [150]. There is mention earlier in this review of another compound formed by reaction of these reagents.

The reaction between $Mn(THF)(CO)_2(\eta-C_5H_4Me)$ and $Co(CS)(PMe_3)(\eta-C_5H_5)$ yields two products, $(\eta-C_5H_5)(PMe_3)Co(\mu-CO)[\mu-CSMn(CO)_2(\eta-C_5H_4Me)]Mn(CO)(\eta-C_5H_4Me)$ and $(\eta-C_5H_5)(PMe_3)Co(\mu-CO)(\mu-CS)Mn(CO)(\eta-C_5H_4Me)$. The former compound can be converted to the latter by addition of PMe_3, to displace the metal coordinated to the bridging CS group. The sulfur on the bridging CS group can also be alkylated using CH_3OSO_2F [152]. Other compounds with bridging CS groups between manganese (rhenium) and platinum have been formed by reactions of $Mn(CS)(CO)_2(\eta-C_5H_5)$ and $Pt(\eta-C_2H_4)L_2$ (L = $PPhMe_2$, PPh_2Me).

The structure of one of these complexes was determined crystallographically. An NMR experiment indicates that this compound is fluxional in solution [153]. A crystal structure study from the same group was carried out on the complex $(\eta\text{-}C_5H_5)(CO)_2MnRh(CO)(\eta\text{-}C_5Me_5)$, XXIII. A significant aspect of this structure is the semi-bridging carbonyl groups [154]. The synthesis of another rhodium-manganese complex, trans-$(PPh_3)(CO)_2Mn(\mu\text{-}CO)_2Rh(PPh_3)_2$, was carried out by reacting $Na[Mn(CO)_5]$ and $RhCl(PPh_3)_3$. The authors of the communication on this work suggest a structure with bridging carbonyls and a metal-metal bond based on spectroscopic data and by analogy to a molybdenum-rhodium complex whose crystal structure had been elucidated [155].



(XXII)



(XXIII)

Bimetallic complexes with manganese and Group VB elements were described in two papers. Photolysis of $Mn_2(CO)_{10}$ and $TaH_3(\eta\text{-}C_5H_5)_2$ produces $(\eta\text{-}C_5H_5)_2Ta(\mu\text{-}H)Mn_2(CO)_9$ [156], and the reaction of $Nb(BH_4)(\eta\text{-}C_5H_5)_2$ and $Mn_2(CO)_{10}$ in the presence of Et_3N gives $(\eta\text{-}C_5H_5)_2Nb(CO)(\mu\text{-}CO)Mn(CO)_4$ [157]. Molecular structures of both products were deduced by x-ray crystallography.

Derivatives of metals of Group IIB, main group metals, and metalloids are next considered in this subsection. There have been fewer articles in this area. Methanolysis of $Zn[Mn(CO)_5]_2$ was described by Burlitch et al. [158], and a tetramer, $[MeOZnMn(CO)_5]_4$, was formulated as the product of this reaction. A structure of this species was suggested based on the structure of a related iron carbonyl derivative. The mercury complex $Hg[Mn(CO)_3(PMe_3)_2]_2$ was obtained from a reaction of $Mn(SSnMe_3)(CO)_3(PMe_3)_2$ and HgO by Vahrenkamp and Kury [159]. A paper documents He(I) and He(II) PES spectra for the various $M[Mn(CO)_5]_2$ species (M = Zn, Cd, Hg) [160].

Indium-manganese carbonyl derivatives are described in the literature [161]. Various gallium and indium complexes having the general formula $Na[Cl_{4-n}M\text{-}\{Mn(CO)_5\}_n]$ [M = Ga, In; n = 1, 2, 3] were characterized as products from the reactions of $Na[Mn(CO)_5]$ with $GaCl_3$ or $InCl_3$. Thallium(I) chloride and

$Na[Re(CO)_5]$ react, forming unstable $Tl[Re(CO)_5]$ which undergoes disproportionation to thallium metal and $Tl[Re(CO)_5]_3$ [162].

Several silyl-manganese and -rhenium complexes received mention earlier in this review including $ReH(SiHEt_2)(CO)_2(\eta\text{-}C_5H_5)$ [90], $MnH(SiPh_2F)(CO)_2(\eta\text{-}C_5H_4Me)$ [92], $(CO)_4FeH(\mu\text{-}SiCl_2)Mn(CO)_5$ and $(CO)_4Fe(\mu\text{-}H)(\mu\text{-}SiCl_2)Mn(CO)_4$ [150]. The failure of $Mn(SiMe_3)(CO)_5$ to add formaldehyde onto the silicon-manganese bond was also noted [106].

Reactions of $Mn(SiMe_3)(CO)_5$ with ten methyl ketals were carried out, producing Me_3SiOMe, $MnH(CO)_5$, and methyl enol ethers. A mechanism is proposed in which the silyl group is transferred to a ketal oxygen; elimination of Me_3SiOMe gives a cation-anion pair which eliminates $MnH(CO)_5$ to form the organic product. The reaction of $Mn(SiMe_3)(CO)_5$ with acetals is more complex. If this reaction is carried out under CO pressure an intermediate manganese species can be trapped as an acyl-metal complex, however [163].

Organogermanium derivatives of manganese and rhenium, $M(GeR_3)(CO)_4(CMeOEt)$ were obtained in a two step reaction sequence [137]. Complexes with asymmetric germanium atoms were described in this study. Cleavage of the germanium-manganese or -rhenium bond in these species was then studied, with interest focusing on retention or racemization of configuration at the metalloidal element [164, 165]. The new complexes $(CO)_5MnGeCo_3(CO)_9$ and $(CO)_5MnGeMeCo_2(CO)_7$ have been prepared and characterized [166].

Acid cleaves phenyl-tin or -lead bonds in $Ph_{4-n}M[Mn(CO)_5]_n$ (M = Sn, Pb; n = 1, 2) [167]. The synthesis of $Cl[Os(CO)_4]_3SnCl_2Re(CO)_5$ has been reported [168]. An x-ray crystallographic study on $BrSn[Mn(CO)_4(PPh_3)]_3$ was carried out, defining its molecular structure [169]. Molecular orbital calculations on $Ge[Mn(CO)_2(\eta\text{-}C_5H_5)]_2$ were performed which suggest that there is no multiple bonding between germanium and manganese. Thus rotation around this bond should not be restricted [170].

VII. COMPLEXES WITH GROUP VA AND VIA LIGANDS

This section contains references to complexes having Group VA and VIA ligands except that complexes with simple two electron donor ligands (phosphines, amines, sulfides, etc.) are not covered. Coverage will be directed first to Group VA, then to VIA, with elements in each group taken in order of atomic weight.

Nitrogen. Organo-rhenium complexes with imido (=NR) and amido (-NHPh) ligands were cited earlier; typical examples include $ReMe_3(NBu^t)_2$ and $Re(NHPh)(CO)_3(PMe_3)_2$ [62, 63, 97]. Complexes with a dinitrogen ligand were also mentioned [66],and one was the subject of an MO study [170]. Two papers on dinuclear complexes are noted; in the first $Mn_2(CO)_5(dppm)_2(\mu\text{-}CH_2N_2)$ is reported [16] while in the second there is a description of $Re_2H(CO)_6(dppm)$-(μ-N=CHMe) [82].

Oxidation of $Mn(CO)_2(H_2Ntol^m)(\eta\text{-}C_5H_5)$ by H_2O_2 or O_2 gives the stable paramagnetic species $Mn(CO)_2(NHtol^m)(\eta\text{-}C_5H_5)$ [171]. The structure of $Re(PhNCHNPh)(CO)_2(PPh_3)_2$ was determined by crystallography [172]. The reaction of $Li_2[(RN)_2CO]$ and $MnBr(CO)_5$ gives an anionic complex $Li[Mn(RNCONR)(CO)_4]$; a rhenium complex was prepared similarly [173].

Phosphorus, Arsenic. The cluster complexes $(\eta\text{-}C_5H_5)(CO)_2Mn(\mu\text{-}PCy)M_2(CO)_6$ (M = Fe, Ru) were described earlier [149]. Complexes with bridging arsenido ligands have been described in two papers; these were on the preparation of $MeCCo_3(CO)_8AsMe_2Mn(CO)_4(L)$ (L = CO, PMe_3) [174] and on the characterization of the cation-radical species $[Mn_2(AsPh_2)_2(CO)_8]^+$ [175]. The preparation and structure (x-ray diffraction) of $(\eta\text{-}C_5H_5)(CO)_2MoAs[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_2$ have been reported [176].

Oxygen. Most of the work was previously cited; this includes: ESR studies on paramagnetic metal carbonyl complexes with 1,2-diketone ligands [34,35,36]; the synthesis of $Re_4(OH)_4(CO)_{12}$ [10]; and the synthesis of complexes of N-methyl and N-phenyl-salicylideniminato- and 8 hydroxyquinolinato complexes, $Re(CO)_2(L)_2(O\hat{}N)$ [177].

Sulfur. The single reference to technetium organometallic chemistry in this review is to a paper describing the synthesis and structure of $Tc(CO)(S_2CNEt_2)_3$ [178]. An x-ray crystallographic study indicates that the metal atom has a distorted pentagonal bipyramidal structure.

The complex $Mn_2(SH)_2(CO)_8$ was synthesized in a reaction between $MnH(CO)_5$ and propylene sulfide [179]. Photolysis of a mixture of $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, and PhSSPh yields $Mn_3Re(SPh)_4(CO)_{12}$ [180]. The synthesis of $NEt_4[Re_3H_3$-$(\mu\text{-}SBu^t)(CO)_9]$ from $NEt_4[Re_3H_4(CO)_{10}]$ and Bu^tSH has already been mentioned [89]. Hydrogen chloride cleaves the tin-sulfur bonds in $[(CO)_4MSSnMe_3]_2$, $M(SSnMe_3)$-$(CO)_3(PMe_3)_2$, and $M(SSnMe_3)(CO)_2(PMe_3)$ (M = Mn, Re) to form analogous complexes with SH groups. Cleavage of this group also occurs using Me_2AsCl and MeOCSCl, giving products with SR (R = $AsMe_2$, CSOMe) groups [159, 181].

Manganese and rhenium complexes of the general formula $M(CO)_4S_2CSnPh_3$ (M = Mn, Re) can be made by reactions of $Li[Ph_3SnCS_2]$ with $MnBr(CO)_5$ and $ReBr(CO)_5$. In the case of rhenium an intermediate species, $Re(CO)_5S_2CSnPh_3$, was detected [182]. In related work, complexes with the formula $MBr(CO)_4S_2C$-CMe_2PPh_3 were prepared from $Ph_3PCMe_2CS_2$ and $MBr(CO)_5$ [183]. Structures for both the manganese and rhenium compounds were obtained. Reactions between $[Fe(CS_2)(CO)_2(\eta\text{-}C_5H_5)]^-$ and $MBr(CO)_5$ (M = Mn, Re) give $(\eta\text{-}C_5H_5)(CO)_2FeCS_2M(CO)_4$ complexes; depending on conditions the rhenium complex $(\eta\text{-}C_5H_5)(CO)_2FeCS_2Re(CO)_5$ was also isolated from the latter reaction. Alkylation using methyl triflate converts this species to $[(\eta\text{-}C_5H_5)(CO)_2FeC(SMe)SRe(CO)_5]^+$ [184, 185].

Two dithiocarbamate complexes are formed in approximately equal amounts in the reactions $M(CONHMe)(NH_2Me)(CO)_4$ and R'NCS (M = Mn, Re; R' = Me, Ph). These have the formulas $M(CO)_4(S_2CNHR')$ and $M(CO)_3(CNMe)(S_2CNHR')$ [186].

X-ray crystallographic techniques were used to determine the structures of $Mn(CO)_4[SC(=NPh)PPh_2]$ and $M(CO)_4[SPPh_2C(=NPh)S]$ [187]. The ^1H and ^{13}C NMR spectra of these and related complexes were published in a separate paper [188].

VIII. HYDROCARBON METAL COMPLEXES

More than half the papers assigned to this section have already been identified in this review in other contexts. These papers will be briefly identified first; then the other papers will be reviewed in greater depth as appropriate.

The following references are to papers on the indicated aspects of the chemistry originating with $[M(NO)(CO)_2(\eta\text{-}C_5H_5)]^+$: rhenium formyl derivatives [114, 115, 116]; manganese and rhenium carbene complexes [128, 129, 136]; and rhenium acyl, carboxamido and carboxylato species [93, 120, 121]. Carbene and carbyne derivatives of $M(CO)_3(\eta\text{-}C_5H_5)$ are the subject of seven papers [130-135, 138], and complexes with methylene and alkylidene groups bridging two manganese atoms are considered in five papers [139-141, 143, 144]. Various heterobimetallic complexes with a $Mn(CO)_n(\eta\text{-}C_5H_5)$ group as one principal metal were considered in seven papers [145, 146, 149, 151-154]. Other references of importance are to papers on MO calculations for $X[Mn(CO)_2(\eta\text{-}C_5H_5)]_2$, (X = Ge, PPh) and $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2N_2$ [170], the paramagnetic species $Mn(NHtol^m)(CO)_2\text{-}(\eta\text{-}C_5H_5)$ [171], the complex $(\eta\text{-}C_5H_5)(CO)_2MoAs[Mn(CO)_2(\eta\text{-}C_5H_5)]_2$ [176], and the various $Mn(X)(Y)(CO)_2(\eta\text{-}C_5H_5)$ species (X, Y = H, [90, 91]; X = H, Y = $SiPh_2H$ [90]; X = H, Y = $SiPh_2F$ [92]). Reactions of $Mn_2(CO)_{10}$ [20] and $Re_2(CO)_{10}$ [19] with butadiene provided a number of products having η^4-diene or η^3-allylic ligands. Diene-rhenium hydride complexes were the major interest of two papers [77,79], and mentioned in a third paper [62]. The formation of $[Re(CO)_3(\eta\text{-mes})]Re_2Br_3(CO)_6$ [53] and the reaction of $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ with $LiCuMe_2$ [105] are noted. Dirhenium carbonyl complexes with a μ-vinyl group were obtained in reactions of $Re_2(CO)_{10}$ and terminal olefins [80]. The formation of $Mn(L)(\eta^4\text{-}C_4H_6)_2$ and its chemistry has been reported [43]. Hydride ion reacts with $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ to produce first a cyclohexadienyl metal complex and then $[Mn(CO)_3(\eta^4\text{-}C_6H_8)]^-$. Protonation of this anion gives a neutral species in which there is a metal-hydrogen-carbon bridging group; this species exhibits fluxional behavior in its NMR spectrum [42]. The unusual complex $Mn_3(C_6H_9)_4$ was characterized by crystallographic study [96].

In addition to references listed in the preceding paragraph, there are numerous other references to derivatives of $M(CO)_3(\eta\text{-}C_5H_5)$. The abundance of success in this area relates to the high degree of stability inherent in these species. Syntheses of the following complexes were reported for the first time: two isomers of $Mn(CO)_2(L)(\eta\text{-}C_5H_4Me)$ in which L is either $\underline{N}$ or $\underline{\pi}$ bonded 2-vinylpyridine [189]; radical species $M(CO)_2(PhNO)(\eta\text{-}C_5H_5)$, (M = Mn, Re) [190]; $Mn(CO)_2(S{=}C{=}CR_2)(\eta\text{-}C_5H_5)$ [191]; $Mn(CO)_2(Ph_2C_2CS)_2(\eta\text{-}C_5H_5)$, in which the ligand is a sulfur bonded dimer of 1,2-diphenylcyclopropenethione [192]; and $Mn(CO)_2(\eta\text{-}C_5H_4CH_2OCH{=}CH_2)$ [193]. Friedel Crafts alkylation of $Mn(CO)_3(\eta\text{-}C_5H_5)$ using $Bu^tCl/AlCl_3$ gave mono- and disubstitution (alkylation and acylation) in the cyclopentadienyl ring [194]. The reaction of $Mn(CO)_2(THF)(\eta\text{-}C_5H_5)$ and $CH_2{=}\overline{CCH_2CO}O$ gave an η^2-allene complex which reacted further with $Mn(CO)_2(THF)(\eta\text{-}C_5H_5)$ to form $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2C_3H_4$. A crystal structure study was carried out on this species [195]. Triphenylphosphine reacts with $Mn(CO)_2(\eta^2\text{-}HC{\equiv}CCO_2Me)(\eta\text{-}C_5H_5)$, forming $Mn(CO)_2[C(CO_2Me){=}CHPPh_3](\eta\text{-}C_5H_5)$, whose molecular structure was determined [196]. Photolysis of $Re(CO)_3(\eta\text{-}C_5Me_5)$ yields $Re_2(CO)_5(\eta\text{-}C_5H_5)_2$ and $Re_2(CO)_3(\eta\text{-}C_5Me_5)_2$; the latter compound has a rhenium-rhenium triple bond [197].

An extensive study of the chemistry of $[Re(CO)_2(N_2Ar)(\eta\text{-}C_5H_5)]BF_4$ was carried out by Sutton et al. [198]. The diazonium ligand in these complexes is reduced by $NaBH_4$ to a coordinated aryldiazine. In contrast, the reaction with MeLi produces $Re(CO)_2(N{=}NMeAr)(\eta\text{-}C_5H_5)$, a compound which adds a proton in acidic medium to form a hydrazide complex, $[Re(CO)_2(NHNMeAr)(\eta\text{-}C_5H_5)]^+$. The structure of $Re(CO)_2(N{=}NMeC_6H_4OMe)(\eta\text{-}C_5H_5)$ identified crystallographically has a bent metal hydrazide(2-) skeleton.

Crystal structures were obtained for $Mn(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)$ [199] and $Mn(CO)_3[\eta\text{-}C_5H_4COCH_2W(CO)_3(\eta\text{-}C_5H_5)]$ [200]. Mass spectra of various $Mn(CO)_3(C_5H_4R)$ compounds were described [201]. The rate of substitution of PPh_3 for MeCN in $Mn(CO)_2(MeCN)(\eta\text{-}C_5H_4Me)$ is enhanced by a small anodic current [202]. Photolysis of $Mn(CO)_3(\eta\text{-}C_5H_5)$ in a low temperature matrix produces $Mn(CO)_2(\eta\text{-}C_5H_5)$ and $Mn(CO)(\eta\text{-}C_5H_5)$ which were characterized by infrared spectroscopy [203].

The molecular structure of a fluorenylmanganese compound, $Mn(CO)_3(\eta^6\text{-}C_{13}H_9)$ was determined from x-ray diffraction data. The metal atom is coordinated to one six membered ring which is significantly distorted out of planarity. It is possible to protonate C(9) of the complex $Mn(CO)_3(\eta^5\text{-}C_{13}H_9)$; this reaction is accompanied by a concurrent shift of the metal to a six membered ring, according to infrared and NMR data.

Grignard reagents (MeMgCl, PhMgBr) and several ketone enolates add to the coordinated arene ring in $[Mn(CO)_3(\eta^6\text{-}C_6H_6)]^+$, giving exo-substituted cyclohexadienyl-manganese tricarbonyls. Jones reagent (CrO_3/H_2SO_4) oxidizes these compounds to $[Mn(CO)_3(\eta\text{-}C_6H_5R)]^+$. This reaction sequence was also carried out on several complexes with substituted benzenes as ligands, with the regioselectivity of the addition reactions being easily predicted. It was suggested that this reaction sequence may have synthetic utility [207].

A similar addition of $[PhSOCH_2]^-$ to $[Mn(CO)_3(\eta\text{-}C_6H_6)]^+$ forms the expected cyclohexadienyl-metal carbonyl [208]. Complexes of the formula $[Mn(CO)_2(NO)(\eta\text{-}C_6H_7)]PF_6$ can by synthesized from $Mn(CO)_3(\eta^5\text{-}C_6H_7)$ and $NOPF_6$. They react with phosphites to substitute a carbonyl group. However hydride ($NaBH_4$) and phosphine nucleophiles add to the cyclohexadienyl ligand producing the cyclohexadiene-metal compounds, $Mn(CO)_2(NO)(\eta^4\text{-}C_6H_8)$ and $[Mn(CO)_2(NO)(\eta^4\text{-}C_6H_7PR_3)]^+$; *exo*-stereochemistry is seen for this reaction [209].

Field desorption mass spectra [210] and inelastic neutron scattering [211] studies on $[Mn(CO)_3(\text{arene})]^+$ species are noted.

The reaction of $Mn(NO)(CO)_4$ and $PhC{\equiv}CPh$ produces a small amount of $Mn(NO)(CO)_2(\eta^4\text{-}C_4Ph_4)$. A crystal structure study was carried out on this species [212]. Sodium pentacarbonylmanganate and triphenylcyclopropenyl tetrafluoroborate react to give primarily $Mn_2(CO)_{10}$ and $(C_3Ph_3)_2$; in addition a small amount of $Mn(CO)_4(\eta^3\text{-}C_3Ph_3CO)$ is formed [213]. The synthesis and electronic structure of the first row decamethylmetallocenes was reported [214], as was the reactivity of $[Re(\eta\text{-}C_5H_5)_2]Li$ [215].

IX. ISOCYANIDE AND NITROSYL COMPLEXES

A fair amount of work on $[Mn(NO)(CO)_2(\eta\text{-}C_5H_5)]^+$ (M = Mn, Re) and compounds derived from these species was discussed earlier in this review [93, 114-116, 120, 121, 128, 129, 186]. In addition the complex $Mn(NO)(CO)_2(\eta^4\text{-}C_4Ph_4)$ was identified [212], and chemistry originating with $ReCl_2(OMe)(NO)(PPh_3)_2$ [65] was considered.

Rhenium complexes with isocyanide ligands ($[ReL_6]^+$, $[ReL_5X_2]^+$, $[ReL_4(PR_3)_2]^+$, $ReClL_3(PMe_3)_2$, $ReCl(L)(dppe)_2$) were discussed [46, 48, 64, 67]. Electrochemistry of isocyanide complexes was analyzed in terms of ligand parameters [47]. Syntheses of $Mn_2(CO)_9(CNCy)$ [12], complexes of chelating diisocyanides [54] and complexes of polymer bound isocyanides [55] were considered earlier. Synthesis of $Mn(CO)_3(CNR)(S_2CNHR')$ from $M(CONHMe)(NH_2Me)(CO)_4$ and RNCS was reported [186].

X. STRUCTURAL STUDIES

Compounds whose structures were identified by x-ray crystallography (or by other methods) are listed: $Re_3(CO)_{14}SiPh_3$, I [7]; *eq*-$Re_2(CO)_9(CORSiPh_3)$ (R = Me, Et) and *ax,eq*-$Re_2(CO)_8(COEtSiPh_3)_2$ [9]; $Mn(CO)_3(\eta^3\text{-}C_6H_9)$ [42]; *fac*-$MnBr(CO)_3[SC(PPh_2)NHPh]$ and $Mn(CO)_4[SC(PPh_2)NPh]$ [60]; $ReOR_3ORe(PMe_3)_4ReO_2R$, R = CH_2SiMe_3 [61]; *trans*-$Re(NHPh)(N_2)(PMe_3)_4$ and $Re(NHPh)(PMe_3)_3(\eta\text{-}C_4H_6)$ [62];

$\mathrm{[ReH(Cl)(PMe_3)_5]BF_4}$, $\mathrm{[Re(\eta^5\text{-}C_5H_2Ph_2)(PMe_3)_3]_2C_2H_2Ph_2}$, $\mathrm{[ReI(NHPh)(PMe_3)_4]I}$, $\mathrm{Re(CH_2PMe_2)(PMe_3)_4}$, and $\mathrm{[ReI(Me)(PMe_3)_4]I{\cdot}Me_4PI}$ [63]; *mer*,*trans*-$\mathrm{ReCl(CNBu^t)_2(PMe_3)_3}$ and *mer*,*trans*-$\mathrm{ReCl(CNBu^t)_3(PMe_3)_2}$ [64]; $\mathrm{[ReF(CO)(NO)(PPh_3)_3]ClO_4}$ [65]; $\mathrm{ReCl(N_2)(CNMe)[P(OMe)_3]_3}$ [66]; $\mathrm{Re_3I_6(CO)_6}$ and $\mathrm{Re_4I_8(CO)_6}$, II, [69]; $\mathrm{Re_2H_4(PPhMe_2)_4(L)_2}$, V,and $\mathrm{[Re_2H_5(PPhMe_2)_4(L)_2]BF_4}$, VI, ($\mathrm{L = P(OCH_2)_3CEt}$) [81]; $\mathrm{Re_2H(CO)_6(dppm)(\mu\text{-}N{=}CHMe)}$, VII, [82]; $\mathrm{Re_2H_2(CO)_6(dppm)}$, VIII, and $\mathrm{Re_3H_3(CO)_8[(EtO)_2POP(OEt)_2]_2}$, IX, [83]; neutron diffraction on IX [84];$\mathrm{(PPh_4)_3[Re_7C(CO)_{21}]}$, [85];$\mathrm{(NEt_4)_2[Re_8C(CO)_{24}]}$, [86]; $\mathrm{NEt_4[Re_3H_3(Cl)(CO)_{10}]}$, X, [87]; $\mathrm{NEt_4[Re_3H_3(O_2CR)(CO)_{10}]}$ ($\mathrm{R = H, CF_3}$), XI, [88]; $\mathrm{NEt_4[Re_3H_3(SBu^t)(CO)_9]}$, XII, [89]; $\mathrm{MnH(SiPh_2F)(CO)_2(\eta\text{-}C_5H_4Me)}$, neutron diffraction [92];$\mathrm{Mn_2(CH_2SiMe_3)_4(PMe_3)_2}$,XIII, [94]; $\mathrm{Mn(C_9H_7P_2Ph_4)_2}$, XIV, [95]; $\mathrm{Mn_3(C_6H_9)_4}$ [96]; $\mathrm{\overline{Re(SO_2CH_2CMe_2CH_2P}Ph_2)(CO)_4}$ and $\mathrm{\overline{Mn(CH_2CMe_2CH_2OP}Me_2)(CO)_4}$ [100]; $\mathrm{\overline{Mn(CH_2CH_2CH_2As}Ph_2)(CO)_4}$ [101]; $\mathrm{Re(\eta^1\text{-}C_7H_7)(CO)_5}$, [104]; $\mathrm{\overline{Re[COC(CF_3){=}C(CF_3)As}Me_2](CO)_4}$, [118]; $\mathrm{Mn(CO)_3(CHO)(PPh_2NBuAlMe_2)_2}$, XVII, [119]; (–)-R-$\mathrm{Re(CH_2Ph)(NO)(PPh_3)(\eta\text{-}C_5H_5)}$ [120]; $\mathrm{Re_3(CO)_{14}CO_2H}$ and $\mathrm{Re_3(CO)_{14}NO_2}$ [123]; $\mathrm{[(CO)_5ReCO_2Re(CO)_4]_2}$ [124]; two isomers of $\mathrm{[Re(CHPh)(NO)(PPh_3)(\eta\text{-}C_5H_5)]BF_4}$ [129]; $\mathrm{Re_2(CO)_9(CHOMe)}$ [130]; $\mathrm{[Mn(CPh)(CO)_2(\eta\text{-}C_5H_5)]_2O}$ XVIII [131]; $\mathrm{Mn(CPhOEt)(CO)_2(\eta\text{-}C_5H_5)}$ [133]; $\mathrm{Mn(GeMePhNp)(CO)_4(CMeOEt)}$ [137]; $\mathrm{[Mn(CO)_2(\eta\text{-}C_5H_5)]_2CH_2}$ [138]; $\mathrm{[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_2CH_2}$ [139]; $\mathrm{(CO)_4Mn(\mu\text{-}CO)(\mu\text{-}CH_2)Fe(CO)(\eta\text{-}C_5H_5)}$ [142]; $\mathrm{(CO)_4Fe(\mu\text{-}C{=}CHCO_2Me)Mn(CO)_2(\eta\text{-}C_5H_5)}$, XIX, [146]; $\mathrm{(OC)_4\overline{MnMo(CO)_3(\eta\text{-}C_5H_4P}Ph_2)}$, XX, [148]; $\mathrm{(\eta\text{-}C_5H_5)(CO)_2Mn(\eta^3\text{-}PCy)M_2(CO)_6}$, ($\mathrm{M = Fe, Ru}$), XXI, [149]; $\mathrm{Fe_2(CO)_6(HC{\equiv}CCO_2Me)Mn(CO)_2(\eta\text{-}C_5H_5)}$, XXII, [151], $\mathrm{(\eta\text{-}C_5H_5)(CO)_2Mn(\mu\text{-}CS)Pt(PPh_2Me)_2}$ [153]; $\mathrm{(\eta\text{-}C_5H_5)(CO)_2MnRh(CO)(\eta\text{-}C_5Me_5)}$, XXIII, [154]; $\mathrm{(\eta\text{-}C_5H_5)_2Ta(\mu\text{-}H)Mn_2(CO)_9}$, [156]; $\mathrm{(\eta\text{-}C_5H_5)_2Nb(CO)(\mu\text{-}CO)Mn(CO)_4}$ [157]; $\mathrm{BrSn[Mn(CO)_4(PPh_3)]_3}$ [169]; $\mathrm{Re(PhNCHNPh)(CO)_2(PPh_3)_2}$ [172]; $\mathrm{\eta\text{-}C_5H_5Mo(CO)_2As[Mn(CO)_2(\eta\text{-}C_5H_4Me)]_2}$ [176]; $\mathrm{Tc(CO)(S_2CNEt_2)_3}$ [178]; $\mathrm{MBr(CO)_3(S_2CCMe_2PPh_3)}$ ($\mathrm{M = Mn, Re}$) [183]; $\mathrm{\overline{Mn(CO)_4[SC({=}NPh)P}Ph_2]}$ and $\mathrm{\overline{Mn(CO)_4[SPPh_2C({=}NPh)S}]}$ [187]; $\mathrm{[Mn(CO)_2(\eta\text{-}C_5H_5)]_2C_3H_4}$ [195]; $\mathrm{Mn(CO)_2[C(CO_2Me){=}CHPPh_3](\eta\text{-}C_5H_5)}$ [196]; $\mathrm{Re_2(CO)_3(\eta\text{-}C_5Me_5)_2}$ [197]; $\mathrm{Re(CO)_2[N{=}NMe(}p\mathrm{\text{-}C_6H_4OMe)(\eta\text{-}C_5H_5)}$ [198]; $\mathrm{Mn(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)}$ [199]; $\mathrm{Mn(CO)_3[\eta\text{-}C_5H_4COCH_2W(CO)_3(\eta\text{-}C_5H_5)]}$ [200]; $\mathrm{Mn(NO)(CO)_2(\eta^4\text{-}C_4Ph_4)}$ [212].

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