

MANGANESE, TECHNETIUM, AND RHENIUM  
ANNUAL SURVEY COVERING THE YEAR 1985 \*

P. M. TREICHEL

Department of Chemistry, University of Wisconsin-Madison  
Madison, WI 53706 (U.S.A.)

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I. INTRODUCTION

This article was written on a somewhat earlier schedule than in previous years, to make it available at the earliest possible date. Although all numbers of the 1985 volumes of major journals in organometallic chemistry were available, several lesser journals were still incomplete at the time of this writing. Thus, a few articles from late 1985 will be missing in this review; they will be included in next year's Annual Survey. At this time the 1984 Annual Survey article on Mn, Tc, and Re is in press; the 1983 article did appear in 1985 [1].

Even with a foreshortened schedule 247 articles were abstracted for this review, up 10% from previous years.

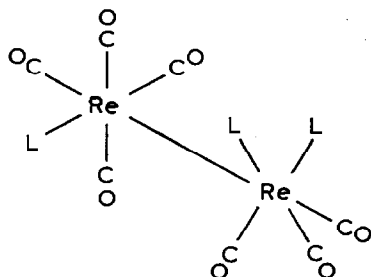
Pertinent review articles have appeared on cyclometallation reactions [2] and on light induced disproportionation of dimeric metal carbonyls [3]. The most recent volume of Inorganic Syntheses contains procedures for synthesis of  $Mn_2(\mu-X)_2(CO)_8$  [4] and  $ReX(CO)_5$  [5] compounds (X = Cl, Br, and I).

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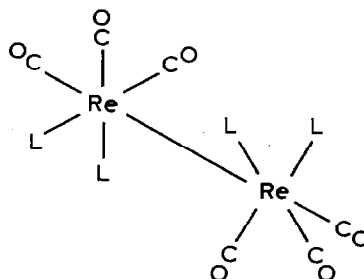
\*Previous review see p. 83.

## II. NEUTRAL, ANIONIC, AND CATIONIC METAL CARBONYL DERIVATIVES

There are a group of papers concerned with carbonyl substitution reactions of  $\text{Mn}_2(\text{CO})_{10}$  species. Catalysis by PdO of the reactions between  $\text{Re}_2(\text{CO})_{10}$  and several isocyanides (CNR; R = Me,  $\text{Bu}^t$ ,  $\text{PhCH}_2$ , Cy, 2,6-dimethylphenyl) has been described and various products of the formulas  $\text{Re}_2(\text{CO})_{10-n}(\text{CNR})_n$  ( $n = 1-4$ ) have been characterized [6]. X-ray diffraction techniques were used to identify the stereochemistry of four of these products: cis- $\text{Re}_2(\text{CO})_9(\text{CNBu}^t)$ , cis,cis- $\text{Re}_2(\text{CO})_8(\text{CNR})_2$ ,  $\text{Re}_2(\text{CO})_7(\text{CNR})_3$  and  $\text{Re}_2(\text{CO})_6(\text{CNR})_4$  (R = 2,6- $\text{Me}_2\text{C}_6\text{H}_3$ ), the third and fourth compounds having substitution patterns shown below (I, II) [7]. In further work the authors of the previous

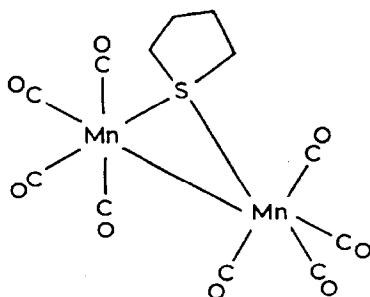


(I)



(II)

reference have shown that PdO and other palladium catalysts assist in the substitution of carbonyl groups in  $\text{Re}_2(\text{CO})_{10}$  by phosphines, mono- and di-substituted products being isolated. Substitution in  $\text{Re}_2(\text{CO})_{10}$  can also be accelerated chemically using  $\text{Me}_3\text{NO}$  in  $\text{CH}_2\text{Cl}_2$ , but  $\text{ReCl}(\text{CO})_3(\text{PR}_3)_2$  species accompany the dinuclear  $\text{Re}_2(\text{CO})_{10-n}(\text{PR}_3)_n$  ( $n = 1,2$ ) products in these reactions. A structural study on trans,trans- $\text{Re}_2(\text{CO})_8(\text{PPhMe}_2)_2$  is included in this paper [8]. Photolysis of  $\text{Re}_2(\text{CO})_{10}$  and  $\text{P}(\text{OPh})_3$  is reported to produce  $\text{Re}_2(\text{CO})_{10-n}(\text{L})_n$  ( $n = 3,4,6$ ) in addition to  $\text{ReH}(\text{CO})_3(\text{L})_2$  [9]. The molecular structure of trans,trans- $\text{Re}_2(\text{CO})_8[\text{P}(\text{OMe})_3]_2$  was determined [10]. Reactions of  $\text{Mn}_2(\text{CO})_{10}$  or  $\text{Re}_2(\text{CO})_{10}$  with tetrahydrothiophene lead to the products cis- $\text{Mn}_2(\text{CO})_9(\text{SC}_4\text{H}_8)$  and  $\text{M}_2(\text{CO})_8(\text{SC}_4\text{H}_8)$  (III). Structures of both manganese complexes were obtained in crystallographic studies; the unusual structure of III is shown below [11]. Dimanganese decacarbonyl reacts with pyrazole and imidazole to give monosubstituted products; in addition to two products of disproportionation,  $\text{Mn}(\text{pzH})_4[\text{Mn}(\text{CO})_5]_2$  and  $\text{Mn}(\text{pzH})_4[\text{Mn}_2(\mu\text{-pz})_3(\text{CO})_6]_2$  were characterized (pzH = pyrazole,  $\text{pz}^-$  = pyrazolyl anion) [12].



( III )

Syntheses of  $\text{Re}_2(\text{CO})_6(\text{dppm})_2$ ,  $\text{Re}_2(\text{CO})_6(\text{dmpm})_2$  and  $\text{Re}_2(\text{CO})_6(\text{dmpm})(\text{dppm})$  ( $\text{dppm}$  = 1,2-bisdiphenylphosphinomethane;  $\text{dmpm}$  = 1,2-bisdimethylphosphinomethane) having been described; these species were used as starting materials for further reaction with  $\text{PhC}\equiv\text{CH}$ . These latter reactions produced bimetallic products containing bridging hydrido- and phenylethynyl ligands [13]. A communication [14] describes the separation of mer,mer- and mer,fac- isomers of  $\text{Mn}_2(\text{CO})_6(\text{dmpm})_2$ . The latter species can be oxidized to give a paramagnetic monocation (not isolated) whose esr spectrum was recorded.

Reactions between  $\text{M}_2(\text{CO})_{10}$  ( $\text{M} = \text{Mn}, \text{Re}$ ) and ethylene oxide were shown to yield the products  $\text{M}_2(\text{CO})_9(\text{L})$  and  $\text{Re}_2(\text{CO})_8(\text{L})_2$  ( $\text{L} = \text{COCH}_2\text{CH}_2\text{O}$ ) [15].

Below 200K, photolysis of  $(\text{CO})_5\text{MM}'(\text{CO})_3(\text{diimine})$  complexes ( $\text{M}, \text{M}' = \text{Mn}, \text{Re}$ ) causes disproportionation while above this temperature there is homolysis of the metal-metal bond [16]. A related study from the same group on the reaction of the bimetallic precursor with  $\text{Bu}_3\text{P}$  is reported in a separate paper, evidence being presented for the product  $[\text{Mn}(\text{CO})_3(\text{diimine})(\text{PBu}_3)]\text{Mn}(\text{CO})_5$  which results from disproportionation [17]. The review article on photolytic disproportionation [3], and an article on the same type of process in reactions of  $\text{M}_2(\text{CO})_{10}$  species and diazoles [12], have been mentioned here already.

Kinetic measurements confirmed that the transient species  $\text{Mn}(\text{CO})_5$  undergoes substitution via an associative mechanism [18]. Rates of reactions of photolytically generated  $\text{Mn}(\text{CO})_4(\text{L})$  and  $\text{Mn}(\text{CO})_3\text{L}_2$  with  $\text{RX}$  ( $\text{L}$  = several phosphines and phosphites,  $\text{RX}$  = chloroalkanes,  $\text{PhCH}_2\text{Br}$ ) were measured, these reactions yielding  $\text{MnX}(\text{CO})_{5-n}\text{L}_n$  compounds as products [19]. A paper from another group provides contrasting results, in that both  $\text{MnR}(\text{CO})_4(\text{L})$  and  $\text{MnX}(\text{CO})_4(\text{L})$  ( $\text{L} = \text{PEt}_3, \text{PBu}_3, \text{P}(\text{OEt})_3$ ) are identified as products of photolysis of  $\text{Mn}_2(\text{CO})_8(\text{L})_2$  and  $\text{RX}$  [20]. The rates of reaction of  $\text{Mn}_2(\text{CO})_8(\text{PPh}_3)_2$  with a number of species ( $\text{O}_2, \text{NO}, \text{P}(\text{OEt})_3, \text{C}_2\text{H}_2\text{Cl}_4, \text{C}_{16}\text{H}_{33}\text{I}, \text{PBu}_3$ ) are described in a paper by Pöe and Sekhar [21].

Other papers on a variety of physio-chemical studies on the dimetal decacarbonyls  $M_2(CO)_{10}$  ( $M = Mn, Re$ ) include: laser photolysis of  $M_2(CO)_{10}$  [22,23], assignment of the UV PES spectrum of  $MnRe(CO)_{10}$  [24] and the Raman spectrum of  $Re_2(CO)_{10}$  at 67K [25], measurement of relative rates for ion-molecule reactions of  $Mn_2(CO)_{10}$  and  $MnRe(CO)_{10}$  [26], reactions of  $M_2(CO)_{10}$  ( $M = Mn, Re$ ) and  $MnRe(CO)_{10}$  with thermal electrons [27], and pulse radiolysis of  $M_2(CO)_{10}$  [28]. In addition, the  $^1He$  and  $^2He$  PES spectra of  $(CO)_5MM'(CO)_3$ - (diimine) complexes are reported [29]. Hartree-Fock-Slater calculations were performed on various  $d^8$  metal carbonyls including those complexes of metals in this triad (i.e.,  $[M(CO)_5]^-$  for  $M = Mn, Tc,$  and  $Re$ ) [30].

The preparation of various cationic manganese and rhenium species can be accomplished by displacement of the triflate anion from  $M(CO)_5O_3SCF_3$  [31,32]. Synthetic procedures for a series of complexes  $[Mn(CO)(dppe)_2(L)]A$  ( $L = CNR, NCR$ ;  $A = ClO_4, PF_6$ ) are described [33], as are the preparation and redox properties of  $[Re(L)_2(dppe)_2]BF_4$  ( $L = CO, CNR$ ) [34].

### III. METAL CARBONYL HALIDES AND DERIVATIVES.

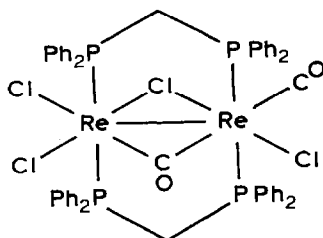
Descriptions of synthetic procedures to obtain  $Mn_2(\mu-X)_2(CO)_8$  [4] and  $ReX(CO)_5$  [5] are provided in Inorganic Syntheses. Cocondensation of rhenium atoms with oxalyl chloride results in formation of  $Re_2(\mu-Cl)_2(CO)_8$  [35]. Photolysis of mixtures of  $Mn_2(CO)_8(PR_3)_2$  and  $Co_2(\mu-X)_2(NO)_4$  yields, among other products,  $MnX(CO)_4(PR_3)$  ( $PR_3 = PPh_2Et, PBu_3, P(OPr^i)_3$ ;  $X = Cl, Br, I$ ) [36]. Substitution of one or two carbonyl groups by  $Ph_2PCH_2SiMe_2CH=CH_2 (=L)$  gives  $MnBr(CO)_4(L)$  and  $MnBr(CO)_3(L)$  [37].

Characterization of  $[Re_2(\mu-F)(CO)_{10}]PF_6$  is reported, this compound being produced in the reaction between  $ReMe(CO)_5$  and  $[Ph_3C]PF_6$ . This fluoride ion-bridged species undergoes solvolysis in acetonitrile to form  $ReF(CO)_5$  and  $[Re(CO)_5[MeCN]]PF_6$ ; attack on this species by aqueous alkali produces  $[Re_2(\mu-CO_2)(CO)_{10}]PF_6$  [38].

Oxidative addition of bromine to  $ReBr(CO)_3(PR_3)_2$  gives  $ReBr_3(CO)_2(PR_3)_2$ , if the phosphine ligands in the complex are not bulky. A crystal structure study was carried out on  $ReBr_3(CO)_2(PPhMe_2)_2$  [39]. A synthesis of  $ReCl(dppe)_2(\eta^2-CS_2)$  is noted [40], as is the formation of a series of  $ReCl(N_2)(CNR)[P(OMe)_3]_3$  complexes ( $R = Me, Et, Bu, tol, p-C_6H_4Cl$ ). The structure of the methyl isocyanide complex is found in this paper [41]. A structural determination was carried out on  $ReCl(dppe)_2(CNBut^t)$  [42].

Carbonylation of  $Re_2Cl_4(dppm)_2$  leads to  $Re_2Cl_4(dppm)_2(CO)_2$  whose structure is drawn below (IV) [43]. Reactions of this species with  $TlPF_6$  and either  $RNC$  or  $RCN$  result in formation of  $[Re_2Cl_3(dppm)_2(CO)_2(L)]PF_6$ , a species which can be reduced to neutral  $Re_2Cl_3(dppm)_2(CO)_2(L)$  by cobaltocene. The structure

of the cationic propionitrile species was determined [44]. A thesis contains some of this work [45].



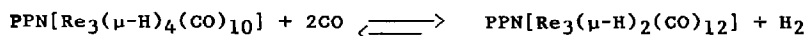
(IV)

The compound  $\text{ReCl}(\text{CO})_3(\text{v-bipy})$  ( $\text{v-bipy} = 4\text{-methyl-4'-vinyl-2,2'bipy}$ ) can be electropolymerized on a platinum electrode. The resulting electrochemical system functions as an effective apparatus for photo-electrolytic reduction of  $\text{CO}_2$  to  $\text{CO}$  [46]. The photoreduction of  $\text{CO}_2$  to  $\text{CO}$  catalyzed by  $\text{ReCl}(\text{CO})_3(\text{bipy})$  had been described in a communication preceding this reference [47].

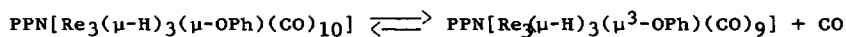
The PES spectra for a series of  $\text{ReCl}(\text{CO})_3(\text{diimine})$  species (diimines are 1,4-diaza-1,3-butadienes) were discussed [48]. Papers on the formation of various  $\text{MX}(\text{CO})_{5-n}(\text{L})_n$  species by photolysis of metal dimers with haloalkanes has been identified earlier in this review [19,20,21].

#### IV. METAL HYDRIDE COMPLEXES

A trinuclear rhenium carbonyl hydride anion with the formula  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$  continues to be a focal point of research in this area. The structure of the bis(triphenylphosphine)iminium salt,  $\text{PPN}[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]$ , was determined. This species was shown to undergo the reversible conversion involving  $\text{CO}/\text{H}_2$  exchange shown below [49]:



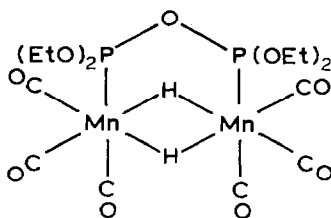
Another paper [50] documents reactions of this species with phenol, giving  $\text{PPN}[\text{Re}_3(\mu\text{-H})_3(\mu\text{-OPh})(\text{CO})_{10}]$  (under mild conditions) or  $\text{PPN}[\text{Re}_2(\mu\text{-OPh})_3(\text{CO})_6]$  when the reaction mixture is heated. The former species loses carbon monoxide reversibly, viz:



Structures of two compounds,  $\text{Et}_4\text{N}[\text{Re}_3(\mu\text{-H})_3(\text{OC}_6\text{F}_5)(\text{CO})_{10}]$  and  $\text{Et}_4\text{N}[\text{Re}_2(\mu\text{-OPh})_3(\text{CO})_6]$ , were reported in this paper. Two further papers from this research group, detailing  $^{13}\text{C}$  NMR studies on  $[\text{Re}_3(\mu\text{-H})_4(\text{CO})_{10}]^-$  [51] and on  $[\text{Re}_3(\mu\text{-H})_3(\text{CO})_{10}]^{2-}$ , [52], have been published.

Protonation of  $\text{Mn}_2(\mu\text{-CO})(\text{CO})_4(\text{dppm})_2$  by  $\text{HBF}_4$  in  $\text{Et}_2\text{O}$  at  $-80^\circ$  yields  $[\text{Mn}_2(\mu\text{-H})(\mu\text{-CO})(\text{CO})_4(\text{dppm})_2]^+$  [53]. At higher temperature the product of this protonation is  $[\text{Mn}_2(\mu\text{-H})(\text{CO})_6(\text{dppm})_2]^+$ , the additional carbon monoxide scavenged from products of concurrent decomposition. When  $\text{HCl}$  is used as an acid, addition of this reagent occurs, giving  $\text{Mn}_2(\mu\text{-H})(\text{Cl})(\text{CO})_5(\text{dppm})_2$  [54].

An elaborate array of reactions involving  $\text{Mn}_2(\mu\text{-H})_2(\text{CO})_6(\text{POP})$ , V, is reported ( $\text{POP} = (\text{EtO})_2\text{POP}(\text{OEt})_2$ ) [55]. This compound was prepared from  $\text{Mn}_2(\mu\text{-Br})_2(\text{CO})_6(\text{POP})$  and  $\text{LiBHET}_3$ .



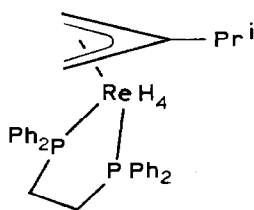
(V)

A reaction with tetrahydrothiophene results in hydrogen loss and formation of  $\text{Mn}_2(\mu\text{-SC}_4\text{H}_8)(\text{CO})_6(\text{POP})$  (c.f.,  $\text{Mn}_2(\mu\text{-SC}_4\text{H}_8)(\text{CO})_8$  [11]). Sodium amalgam reduction followed by addition of  $\text{M}(\text{PPh}_3)\text{Cl}$  ( $\text{M} = \text{Cu}, \text{Ag}, \text{Au}$ ) gives  $\text{Mn}_2(\mu\text{-MPPH}_3)_2(\text{CO})_6(\text{POP})$ ; the compound  $\text{Mn}_2(\mu\text{-H})(\mu\text{-AuPPh}_3)(\text{CO})_6(\text{POP})$  was also characterized. Structures of these species retain the original framework geometry of V but incorporate the metal group in place of the bridging hydride ligands. Reactions of V with either solid  $\text{CuCl}$  or  $\text{CuI}$  give  $\text{Mn}_2(\mu\text{-H})(\mu\text{-X})(\text{CO})_6(\text{POP})$  and  $\text{Mn}_4\text{Cu}_2\text{H}_6(\text{CO})_{12}(\text{POP})_2$ ; the latter was characterized in a crystallographic study.

ESR spectra are reported for  $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_6(\text{dppm})]^\mp$  and  $[\text{Re}_2(\mu\text{-H})_2(\text{CO})_7]^\mp$  [56] and for  $[\text{Mn}_3(\mu\text{-H})_3(\text{CO})_{12}]^\mp$  [57] in low temperature matrices.

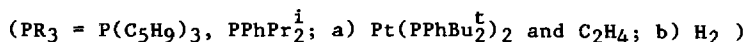
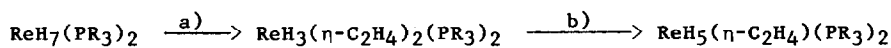
Extensive chemistry involving rhenium polyhydride species is assembled in several papers. Jones and Maguire [58] report the preparation of  $\text{ReH}_3(\text{PPh}_3)_2(\eta^4\text{-C}_5\text{H}_6)$  from  $\text{ReH}_7(\text{PPh}_3)_2$  and cyclopentadiene. The structure

of this species was determined. A variable temperature NMR study showed that this molecule was fluxional. The same authors report separately a further reaction of this species with  $\text{IrBr}(\text{CO})(\text{dppe})$  [59]; products of this reaction are  $\text{ReH}_2(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)$  and  $\text{IrH}_2\text{Br}(\text{CO})(\text{dppe})$ . A compound similar to  $\text{ReH}_3(\text{PPh}_3)_2(\eta^4\text{-C}_5\text{H}_6)$  is obtained from acenaphthylene ( $\text{C}_{12}\text{H}_8$ ) and  $\text{ReH}_7(\text{PCy}_3)_2$ ; the structure of this species,  $\text{ReH}_3(\text{PCy}_3)_2(\eta^4\text{-C}_{12}\text{H}_{10})$ , was determined. There has been, apparently, an intramolecular transfer of hydrogen from the metal to the hydrocarbon in the process of its formation [60]. Reactions between  $\text{ReH}_7(\text{dppe})$  and 2,3-dimethylbutadiene in the presence of a base,  $\text{KOBu}^t$ , take still a different course; the structure of one product,  $\text{ReH}_4(\text{dppe})(\eta^3\text{-C}_6\text{H}_{11})$ , is drawn below (VI) [61].



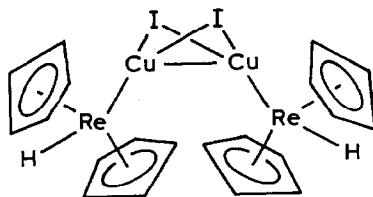
(VI)

A  $\pi$ -pyrrolyl complex,  $\text{ReH}_2(\text{PPh}_3)_2(\eta\text{-C}_4\text{H}_4\text{N})$ , obtained from the reaction of  $\text{ReH}_7(\text{PPh}_3)_2$  and pyrrole in the presence of *t*-butylethylene, can be converted to  $\text{ReHI}(\text{PPh}_3)_2(\eta\text{-C}_4\text{H}_4\text{N})$  using  $\text{I}_2$  and  $\text{K}_2\text{CO}_3$ . In turn, this species was shown to undergo regioselective nucleophilic C-alkylation on the coordinated pyrrolyl ring [62]. Ethylene complexes of rhenium are obtained in the following reaction sequence [63].



Reactions of alkynes with  $\text{Re}_2(\text{CO})_6(\text{P}^*\text{P})_2$  [13], with  $\text{Re}_2(\text{CO})_8(\text{P}^*\text{P})$  and with  $\text{Re}_2(\text{CO})_7(\text{P}^*\text{P})(\text{NCMe})$  ( $\text{P}^*\text{P} = \text{dppm}, \text{dmpm}$ ) [64] have been studied. Two products reported in the second paper were characterized by crystallography. Photolysis of  $\text{Re}_2(\text{CO})_9(\text{L})$  ( $\text{L} = \text{PMe}_3, \text{PPh}_3$ ) with ethylene leads to formation of  $\text{Re}_2(\mu\text{-H})(\mu\text{-}\eta^1, \eta^2\text{-C}_2\text{H}_3)(\text{CO})_7(\text{L})$  [65].

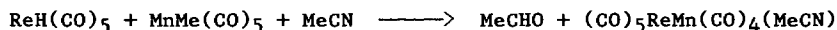
The preparation of  $(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{Ta}(\mu\text{-H})\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  has been reported [66]. Synthesis of  $[(\eta\text{-C}_5\text{Me}_5)_2\text{ReHCuI}]_2$  from  $\text{ReH}(\eta\text{-C}_5\text{Me}_5)_2$  and  $\text{CuI}$  was described [67]; the structure of this species, VII, is drawn below.



(VII)

In contrast,  $\text{ReH}(\eta\text{-C}_5\text{H}_5)_2$  and  $\text{CuCl}_2$  are found to react giving  $[\text{Re}(\eta\text{-C}_5\text{H}_5)_2]^{+}\text{CuCl}_2^{-}$  [68]. Crystal structures were determined for both rhenium species. Carbonylation of  $\text{ReH}_2(\text{NO})(\text{PPh}_3)_3$  in methanol in the presence of perchloric acid yields  $\text{ReH}(\text{OMe})(\text{CO})(\text{NO})(\text{PPh}_3)_2$  and  $[\text{ReH}(\text{CO})(\text{NO})(\text{PPh}_3)_3]\text{ClO}_4$  [69]. It is possible to prepare  $\text{ReH}(\text{PMe}_3)_2(\eta\text{-C}_6\text{H}_6)$  by cocondensation of rhenium atoms with  $\text{PMe}_3$  and cyclohexane [70]. Syntheses and reactions  $\text{MH}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)$  ( $\text{M} = \text{Mn, Re}$ ) are presented in a thesis [71].

Extensive study has been accorded to reactions of  $\text{MH}(\text{CO})_5$  with  $\text{MR}(\text{CO})_5$  in  $\text{MeCN}$  ( $\text{M} = \text{Mn, Re}$ ;  $\text{R} = \text{Me, Et}$ ; see equation below). The goal of this work was to formulate a reaction mechanism [72].



Unlike most acids,  $\text{MnH}(\text{CO})_5$  was found to be unreactive toward  $\text{Al}_2(\text{Bu}^i)_4$  [73].

## V. COMPLEXES WITH CARBON LIGANDS

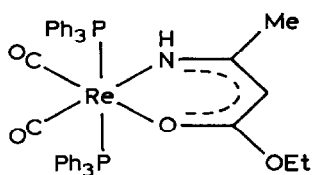
The synthesis of  $\text{MnMe}_2(\text{dmpe})_2$  from  $\text{MnX}_2(\text{dmpe})_2$  ( $\text{X} = \text{Br, I}$ ) and  $\text{LiMe}$  or  $\text{MgMe}_2$  has been described by Wilkinson et al. [74]. Reactions of  $\text{MnBr}_2(\text{dmpe})_2$  with other lithium and magnesium alkyls were reported separately [75], a variety of products being obtained including  $\text{MnH}(\eta\text{-C}_2\text{H}_4)(\text{dmpe})_2$ , from  $\text{MgEt}_2$ , and  $\text{Mn}_2(\mu\text{-C}_6\text{H}_{11})_2(\text{C}_6\text{H}_{11})_2(\text{dmpe})_2$  using  $\text{Mg}(\text{C}_6\text{H}_{11})_2$ . Tert-butyllithium deprotonates the methyl group in coordinated  $\text{dmpe}$  in  $\text{MnMe}_2(\text{dmpe})_2$ . The reaction of  $\text{MnBr}_2(\text{dmpe})_2$  with  $\text{LiAlH}_4$  leads to  $[\text{Mn}(\text{AlH}_4)(\text{dmpe})_2]_2$  as a product; this species hydrolyzes to yield  $\text{MnH}_3(\text{dmpe})_2$ . Several of the products listed here were characterized crystallographically.

Manganese(II) chloride reacts with  $\text{Li}[\text{C}(\text{SiMe}_3)_3]$  to give either  $\text{MnR}_2$  [76] or  $\text{Li}(\text{THF})_4[\text{Mn}_3\text{Cl}_4\text{R}_3(\text{THF})]$  [77]; both products were subjects of crystal structure studies. The isolation of  $\text{Li}_2\text{Mn}(\text{CH}=\text{CH}_2)_4$  and  $\text{Li}_2\text{Mn}(\text{CH}_2\text{CH}=\text{CH}_2)_4$ ,

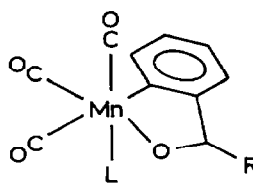


both obtained with dioxane of solvation, is noted [78]. Vinyl-manganese intermediates are implicated in  $\text{MnCl}_2$  catalyzed reactions of acetylenes and  $\text{LiSiMe}_3$  [79]. Extensive study has been accorded to reactions of  $\text{RMgX}$  ( $\text{R} = \text{Me}$ ,  $\text{CH}_2\text{SiMe}_3$ ) with various high oxidation state rhenium oxide species including  $\text{Re}_2\text{O}_7$ ,  $[\text{ReO}_4]^-$ ,  $\text{ReOCl}_4$  and  $\text{ReOCl}_3(\text{PPh}_3)_2$ . Products characterized in this paper include  $\text{Mg}(\text{THF})_4[\text{OReMe}_4]_2$ ,  $\text{Mg}(\text{THF})_4[\text{ORe}(\text{CH}_2\text{SiMe}_3)_4]_2$ ,  $\text{Re}_2\text{O}_3\text{Me}_6$  and  $\text{Re}_2\text{O}_3(\text{CH}_2\text{SiMe}_3)_6$  [80].

Many significant references to metal carbonyl alkyl, aryl, and acyl complexes have been published. A review on ortho-metallation has already been mentioned here [2]. The compound trans- $(\text{CO})_5\text{ReCH}_2\text{CH}=\text{CHCH}_2\text{Re}(\text{CO})_5$  was made by reaction of  $[\text{Re}(\text{CO})_5(\eta^2\text{-CH}_2=\text{CHCH}=\text{CH}_2)]\text{BF}_4$  and  $\text{Na}[\text{Re}(\text{CO})_5]$  and its structure determined [81]. Compounds of the formula  $\text{Mn}(\text{C}\equiv\text{CR})(\text{CO})_3(\text{L})_2$  ( $\text{R} = \text{H, Ph}$ ;  $\text{L}_2 = \text{dppe, dppm}$ , or  $\text{L} = \text{PCy}_3$ ) were prepared from  $\text{MnX}(\text{CO})_3(\text{L})_2$  and a silver or copper acetylide; they could also be obtained by substitution of carbonyl groups in  $\text{Mn}(\text{C}\equiv\text{CR})(\text{CO})_5$  by these phosphines [82]. The pentacarbonyl-metallate ions,  $\text{Na}[\text{M}(\text{CO})_5]$  ( $\text{M} = \text{Mn, Re}$ ), were shown to react with  $\text{MeC}(\text{CH}_2\text{X})_3$  ( $\text{X} = \text{Br, I}$ ) yielding products of the form  $(\text{CO})_5\text{MCH}_2\overline{\text{CMeCH}_2}\text{CH}_2$ . The reaction using  $[\text{Re}(\text{CO})_5]^-$  also gave  $[\text{Re}_2\text{I}(\text{CO})_9]^-$ , an x-ray diffraction study on the  $\text{NEt}_4^+$  salt confirming the identity of this species [83]. Complexes of the formula  $(\text{CO})_5\text{ReCH}_2\text{CO}_2\text{Et}$  were shown to react at  $110^\circ$  with  $\text{PPh}_3$  and acetonitrile in an interesting fashion, giving VIII; a structural analysis was carried out on this species [84].



(VIII)

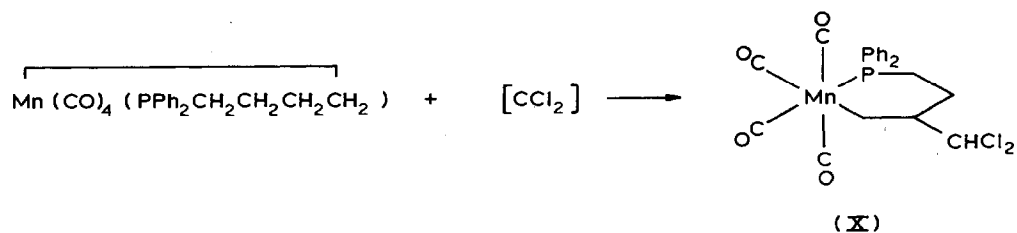


(IX)

The interesting species  $(\text{CO})_5\text{MCOCOM}(\text{CO})_5$  ( $\text{M} = \text{Mn, Re}$ ) are prepared by reaction of  $\text{Na}[\text{M}(\text{CO})_5]$  with oxalyl chloride. A crystal structure study on the rhenium species confirmed a trans-planar geometry of the bridging group [85]. Products of reactions between  $\text{HgPh}_2$  and several  $\text{MnR}(\text{CO})_4(\text{L})$  complexes ( $\text{R} = \text{Me, Et, Ph}$ ;  $\text{L} = \text{CO, PPh}_3, \text{AsPh}_3, \text{SbPh}_3, \text{P}(\text{OPh})_3$ ) have structure IX,

confirmed by structural determinations on two compounds reported in this paper [86]. The pentacarbonylrhenate anion reacts with  $\text{Ph}_2\text{C}=\text{C}=\text{CNR}$  ( $\text{R} = \text{Ph}, \text{Me}$ ) to give a product of regiospecific 2 + 2 cycloaddition; alkylation at oxygen then yields an isolable neutral molecular complex  $\overline{\text{Re}(\text{CO})_4\text{C}(\text{OR})\text{NRC}=\text{CPh}_2}$  [87]. The formation of a rhenacyclopentane complex,  $\text{Re}(\text{C}_4\text{H}_8)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ , occurs when  $\text{ReH}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  and  $\text{I}(\text{CH}_2)_4\text{I}$  are reacted in the presence of an amine; the molecular structure of this species was ascertained [88].

A procedure for the synthesis of cis,cis- $\overline{\text{Mn}(\text{CO})_2(\text{dppm})\text{PPh}_2\text{CH}_2\text{CH}_2}$  was described; this utilizes sodium amalgam reduction of  $\text{MnBr}(\text{CO})_2(\text{dppm})(\text{PPh}_2\text{CH}_2\text{CH}_2\text{Cl})$ . Acid cleavage of the manganese-carbon bond and a CO insertion reaction were carried out, the structure of the product from CO insertion was determined [89]. Similar reduction processes forming metal alkyl species were reported using  $\text{MBr}(\text{CO})_4\text{PPh}_2(\text{CH}_2)_n\text{Cl}$  ( $\text{M} = \text{Mn}, \text{Re}$ ,  $n = 5, 6$ ) [90] and  $\text{MnBr}(\text{CO})_3\text{-}(\text{PPh}_3)(\text{PPh}_2\text{OCH}_2\text{CH}_2\text{Cl})$  [91]. A curious reaction between a dihalocarbene and the products using phase transfer conditions is summarized in the equation below; the product is X.



Structural descriptions of two compounds were included in this paper [92].

Two papers report kinetic and mechanistic information on reactions between metal alkyl and metal hydride species to form aldehydes [72,93]. Reactions between  $\text{MnH}(\text{CO})_5$  and  $\text{MnR}(\text{CO})_5$  ( $\text{R} = \text{CH}_2\text{CO}_2\text{Et}$ ,  $\text{CO}_2\text{Et}$ ), producing acetate or formate esters along with  $\text{Mn}_2(\text{CO})_{10}$ , are described in another paper [94].

Flash vacuum pyrolysis of  $\text{Mn}(\text{CH}_2\text{Ph})(\text{CO})_5$  is described and a mechanism proposed for the reaction [95]. Kinetic measurements were made on the reactions of  $\text{Mn}(\text{CH}_2\text{C}_6\text{H}_4\text{X})(\text{CO})_5$  with phosphines, interest focusing on the effect of the arene substituent on reactivity [96]. Reactions of phosphines with  $(\text{CO})_5\text{Mn}(\text{CH}_2)_4\text{Mn}(\text{CO})_5$  are noted [97]. Photolysis of  $\text{MnMe}(\text{CO})_5$  in  $\text{C}_6\text{D}_6$  yields both  $\text{CH}_4$  and  $\text{CH}_3\text{D}$ ; photolyses of other  $\text{MnR}(\text{CO})_5$  species ( $\text{R} = \text{Ph}, \text{CH}_2\text{Ph}$ ) are also described in this reference [98]. Two theses contain descriptions of studies concerned with reactions of  $\text{Re}(\text{CH}_2\text{Ph})(\text{CO})_5$  with siloxyarylphosphines [99] and cleavage of  $\text{MPh}(\text{CO})_{5-n}(\text{L})_n$  species by acid [100].

Structural studies have been carried out on  $\text{Mn}(\text{CH}_2\text{CMe}_3)_2$  (by electron diffraction) [101], on  $\text{PPN}[\text{Re}_4\text{C}(\text{CO})_{15}\text{I}]$  [102], and on  $\text{Re}_2(\text{CO})_6(\text{PPh}_3)-(\text{PPh}_2\text{C}_6\text{H}_4\text{CO})$  [103]. ICR and PES data were used to calculate a value of  $32 \pm 5$  Kcals for the metal-carbon bond energy in  $\text{Mn}(\text{CH}_2\text{Ph})(\text{CO})_5$  [104].

## VI. DERIVATIVES OF METALS AND METALLOIDS

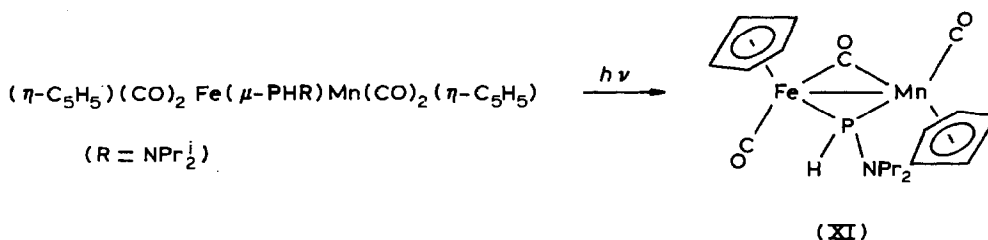
There has been a general surge of interest in hetero-bimetallic organometallic complexes during the past several years, and the references in this section clearly document this fact. Emphasis on complexes of quite dissimilar transition metals is especially evident. The papers on this topic are considered first in this section, with the organization based on the periodic group of the second metal.

Bimetallic complexes involving tantalum,  $(\eta\text{-C}_5\text{H}_4\text{R})_2\text{Ta}(\text{CO})(\mu\text{-H})\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  ( $\text{R} = \text{H}, \text{Bu}^t$ ) were identified earlier in this review [66].

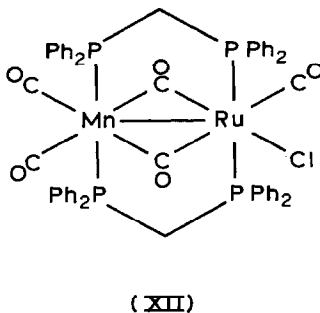
Geoffroy et al. have described the formation of  $(\text{CO})_5\text{WPPh}_2\text{Re}(\text{CO})_5$  in the reaction of  $\text{Li}[\text{W}(\text{CO})_5\text{PPh}_2]$  and  $\text{ReBr}(\text{CO})_5$  [105]. Loss of CO from this compound gives  $(\text{CO})_5\text{W}(\mu\text{-PPh}_2)\text{Re}(\text{CO})_4$ , a species shown by crystallography to have a metal-metal bond. Reactions of this compound with several potential ligands ( $\text{MeCN}$ ,  $\text{PPh}_2\text{Me}$ ) and with metal hydride or alkyllithium reagents are reported. Another paper contains a report on the reaction of this species with  $\text{PPh}_2\text{H}$ , giving  $(\text{CO})_5\text{WPPh}_2\text{Re}(\text{CO})_4(\text{PPh}_2\text{H})$ . Heating converts this compound to  $(\text{CO})_4\text{W}(\mu\text{-PPh}_2)_2\text{ReH}(\text{CO})_3$ . It is possible to deprotonate this latter species with bases giving an anion which can be alkylated. The structure of one complex formed by this type of reaction was identified [106]. For further information consult a thesis on this work [107].

Reactions of  $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_4$  with several dienes and with acetylene were carried out, and structures of the starting material and two isolated products were identified [108]. Other papers report syntheses and structures of  $\text{Co}_2\text{W}(\mu^3\text{-Cto1})(\text{CO})_{10}\text{Re}(\text{CO})_5$  [109]  $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}(\mu\text{-C}=\text{C}-\text{CHCO}_2\text{R})\text{-W}(\text{CO})_4$ , and  $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}]_2(\mu\text{-C}=\text{C}-\text{CHCO}_2\text{Me})_2\text{Mo}(\text{CO})_2$  [110].

Characterization of  $\text{PPh}_4[\text{Fe}_2\text{Mn}(\text{CO})_{12}]$  is noted [111]. Two papers describe products of reactions between  $[\text{FeH}(\text{CO})_4]^-$  and  $\text{MBr}(\text{CO})_3(\text{N}^*\text{N})$  ( $\text{N}^*\text{N} =$  several 1,2-diimines), two being characterized by crystallography [112,113]. King et al. [114] have prepared  $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Fe}(\mu\text{-PHNPr}_2^1)\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ; photolyses of this species causes CO loss and formation of  $(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{-Fe}(\mu\text{-PHNPr}_2^1)(\mu\text{-CO})\text{Mn}(\text{CO})(\eta\text{-C}_5\text{H}_5)$ , XI. Other iron-manganese bimetallic species under study include  $(\eta\text{-C}_5\text{H}_5)\text{MnFe}_2(\mu^3\text{-X})(\text{CO})_8$ , with the bridging ligand group being either phenylphosphide [115] or sulfide [116].

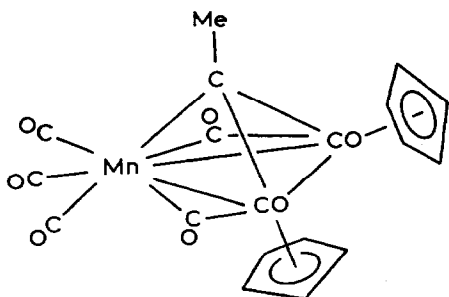


The reaction of a pentacarbonylmanganate ion with  $\text{RuCl}_2(\text{dppm})_2$  was used to synthesize  $(\text{CO})_2\text{Mn}(\mu\text{-CO})_2(\mu\text{-dppm})_2\text{Ru}(\text{CO})\text{Cl}$ , XII. Reactions of  $[\text{Mn}(\text{CO})_5]^-$  with other ruthenium halide complexes gave contrasting results. Using  $\text{RuCl}_2(\text{PMe}_3)_4$  as a precursor, one obtains  $[\text{Ru}_2(\mu\text{-Cl})_3(\text{PMe}_3)_6]\text{Mn}(\text{CO})_5$  while with  $\text{RuCl}_2(\text{PPh}_3)_3$  the isolated product is  $(\text{CO})_3(\text{PPh}_3)\text{Ru}(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_3(\text{PPh}_3)$  [117].

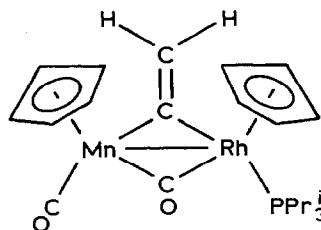


The complex  $\text{MnCo}_2(\mu\text{-CMe})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2$ , XIII, was found as the product of a reaction between  $\text{MnH}(\text{CO})_5$  and  $(\eta\text{-C}_5\text{H}_5\text{CoCO})_2(\mu\text{-C=CH}_2)$ , a crystallographic study being performed to identify the molecular geometry [118]. The formation and structure of  $(\eta\text{-C}_5\text{H}_5)(\text{PPr}_3^i)\text{Rh}(\mu\text{-CO})(\mu\text{-C=CH}_2)\text{Mn}(\text{CO})(\eta\text{-C}_5\text{H}_5)$  XIV are found in another paper [119].

There are reports of the synthesis [120] and reactions [121] of  $(\text{PPh}_3)_2\text{Pt}(\mu\text{-C=CHPh})\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ . Shaw et al. [122] report a series of platinum-manganese complexes in which the two metals are linked by two dppm ligands.



(XIII)



(XIV)

Entrance into this area is with  $\text{MnCl}(\text{CO})_2(\text{dppm})_2$ , a complex with one monodentate and one bidentate ligand. Reactions of this species (or the bromide analogue) with  $\text{Pt}(\text{PPh}_3)_4$  or  $\text{PtHCl}(\text{PPh}_3)_2$  yield  $(\text{CO})_3\text{Mn}(\mu\text{-dppm})_2\text{PtCl}$  and  $\text{Cl}(\text{CO})_2\text{Mn}(\mu\text{-dppm})_2\text{PtHX}$  respectively. Protonation of the former species, or carbonylation of the latter in the presence of  $\text{TlBF}_4$ , result in formation of  $[(\text{CO})_3\text{Mn}(\mu\text{-dppm})_2\text{PtHCl}]\text{BF}_4$ . A crystallographic study provided structural information on the bromide species.

A reaction between  $[\text{Re}(\text{NO})(\text{CO})(\text{PCy}_2\text{H})(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$  and  $\text{Pt}(\text{PPh}_3)_2(\eta\text{-C}_2\text{H}_4)$  occurs with initial oxidative addition of the P-H bond to platinum followed by ethylene loss. On heating this complex rearranges to  $[(\text{PPh}_3)_2\text{Pt}(\mu\text{-PCy}_2)\text{-ReH}(\text{NO})(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$ . This species was shown to rearrange in the presence of  $\text{Cl}^-$  ion to give  $[(\text{PPh}_3)_2\text{Pt}(\mu\text{-H})(\mu\text{-PCy}_2)\text{Re}(\text{NO})(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$  whose structure was determined by crystallography [123].

The copper, silver and gold containing complexes,  $\text{Mn}_2(\mu\text{-MPPh}_3)_2(\text{CO})_8$  and  $\text{Mn}_2(\mu\text{-H})(\mu\text{-AuPPh}_3)(\text{CO})_8$  have been characterized [55]. Another paper, cited earlier in this article, described  $[(\text{C}_5\text{Me}_5)_2\text{Re}(\text{H})(\text{CuI})]_2$  [67]. The complex,  $\text{NBu}_4[\{\text{Re}_7\text{C}(\text{CO})_{21}\text{Ag}\}_2\text{Br}]$ , was characterized by x-ray crystallography. Its synthesis and syntheses of related copper and gold complexes is also described [124]. A reaction between  $\text{Hg}[\text{Mn}(\text{CO})_5]_2$  and  $\text{SnCl}_2(\text{tpp})$  ( $\text{tpp}$  = tetraphenylporphyrin) produces a species  $(\text{tpp})\text{SnMn}(\text{CO})_4\text{HgMn}(\text{CO})_5$ ; its structure was elucidated [125].

There is a single reference about several lanthanide-manganese and -rhenium carbonyl species  $\text{M}(\text{THF})_x[\text{M}'(\text{CO})_5]_3$  [ $\text{M} = \text{Yb}, \text{Sm}, \text{Tm}$ ;  $\text{M}' = \text{Mn}, \text{Re}$ ] [126].

Five references to boron containing organometallic manganese or rhenium species have been found. Described are an improved synthesis of  $\text{B}_5\text{H}_{10}\text{Mn}(\text{CO})_3$  and the synthesis of previously unreported  $\text{B}_5\text{H}_{10}\text{Re}(\text{CO})_3$  [127,128].

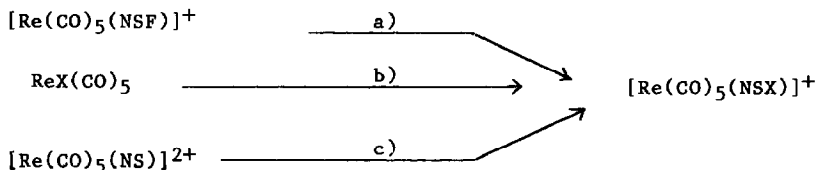
A paramagnetic compound having the formula  $\text{Mn}(\text{CO})(\eta\text{-C}_4\text{H}_4\text{BNPr}_2^{\frac{1}{2}})_2$  was prepared from  $\text{Li}_2[\text{C}_4\text{H}_4\text{BNPr}_2^{\frac{1}{2}}]$  and  $\text{MnCl}(\text{CO})_5$  [129]. Two papers describe a zwitterionic 1,2-dicarbollylrhenium complex,  $\text{B}_9\text{C}_2\text{H}_{10}\text{CH}_2\text{Re}(\text{CO})_3$ . This complex is formed by acid promoted solvolysis of  $\text{Me}_4\text{N}[(\text{B}_9\text{C}_2\text{H}_{10}\text{CH}_2\text{OH})\text{Re}(\text{CO})_3]$ ; a structural study suggests metal stabilization of the carbocation [130,131].

Two rhenium carbonyl complexes containing gallium are formed by photolysis of  $\text{Re}_2(\text{CO})_{10}$  and  $\text{GaCl}_3$ . They have the formulas  $\text{Re}_4(\text{CO})_{12}[\mu_3\text{-GaRe}(\text{CO})_5]_4$  and  $\text{Re}_2(\text{CO})_8[\mu_2\text{-GaRe}(\text{CO})_5]_2$  [132]. Photolysis of  $\text{M}_2(\text{CO})_{10}$  ( $\text{M} = \text{Mn, Re}$ ) with a silylphosphine  $\text{o-HSiMe}_2\text{C}_6\text{H}_4\text{PPh}_2$  results in the formation of  $\text{Mn}(\text{CO})_4\text{PPh}_2\text{C}_6\text{H}_4\text{SiMe}_2$  [133], while silane and  $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{Me}_5)$  have been shown to react giving  $[(\eta\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2\text{H}]_2\text{-}\mu\text{-SiH}_2$ . The structure of this species was ascertained [134]. A reaction of the manganese precursor with  $\text{GeH}_4$  in the presence of  $\text{H}_2\text{SO}_4$  yields  $\mu\text{-Ge}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2$ . A crystallographic study indicates that there are two different conformers in this solid crystalline material [135]. Syntheses of  $\text{Re}(\text{SnMe}_n\text{Cl}_{3-n})(\eta\text{-C}_5\text{H}_5)_2$  ( $n = 1, 2, 3$ ) were described, using reactions of  $\text{ReH}(\eta\text{-C}_5\text{H}_5)_2$  with  $\text{SnMe}_n\text{Cl}_{4-n}$  in the presence of triethylamine. Crystallographic data are given on all three species [136]. Photolysis of  $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$  and  $\text{PbCl}_2$  in THF produced  $\mu\text{-Pb}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$ ; a structural study on this substance showed a linear  $\text{Mn}=\text{Pb}=\text{Mn}$  formulation [137].

#### VII. COMPLEXES WITH GROUP VA AND VIA LIGANDS

A crystal structure study on fac- $\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{pz}_2\text{BMe}_2)$  ( $\text{pz}_2\text{BMe}_2 =$  dimethyl(bis)pyrazolyborate) was reported [138]. Tris-pyrazolylgallate derivatives of manganese and rhenium, and complexes of the form  $\text{M}(\text{CO})_3\text{-}(\text{pzGaMe}_2\text{XCH}_2\text{CH}_2\text{Y})$  ( $\text{X} = \text{S, O}$ ;  $\text{Y} = \text{NH}_2, \text{NMe}_2, \text{SEt}, \text{SPh}$ ) have been prepared; and two members of this group of complexes were subjects of crystallographic study [139]. See also a Ph.D. thesis on this work [140].

Halide exchange occurs between  $[\text{Re}(\text{CO})_5(\text{NSF})]^+$  and  $\text{SiX}_4$  ( $\text{X} = \text{Cl, Br}$ ), giving  $[\text{Re}(\text{CO})_5(\text{NSX})]^+$ ; both products were isolated as  $\text{AsF}_6^-$  salts. Two other routes are available for the synthesis of these species; these are the insertion of  $\text{NS}^+$  into the  $\text{Re-X}$  bond in  $\text{ReX}(\text{CO})_5$  and the addition of halide ion to  $[\text{Re}(\text{CO})_5(\text{NS})]^{2+}$  [141].



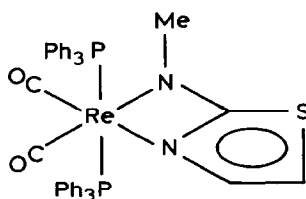
a)  $\text{SiX}_4$ ; b)  $\text{NS}^+$ ; c)  $\text{X}^-$  ( $\text{X} = \text{Cl, Br}$ ) [141].

Several examples of complexes with bridging phosphido ( $\mu_2$ -PR<sub>2</sub>, or  $\mu_3$ -PR) groups have already been mentioned in this review in conjunction with the coverage of bimetallic complexes in Section VI [105-108, 114, 115, 117]. Other references on phosphido bridged species are noted here. Complexes of the formula  $Mn_2(\mu-PH_2)_2(CO)_8$  and  $Mn_3(\mu-PH_2)_3(CO)_{12}$  are obtained from reactions between  $MnCl(CO)_5$  and  $Me_3SiPH_2$ . These species are converted to  $Mn_2(\mu-PX_2)_2(CO)_8$  (X = Cl, Br, I) or to  $Mn_3(\mu-PCl_2)_3(CO)_{12}$  when contacted with  $CX_4$ . Formation of  $Mn_2(\mu-PF_2)_2(CO)_8$  has also been accomplished, by Cl-F exchange using  $AgBF_4$  [142]. A report on <sup>55</sup>Mn NMR for a series of complexes,  $Mn_2(\mu-X)(\mu-A)(CO)_8$  (X = halogens, A = P(CF<sub>3</sub>)<sub>2</sub>, As(CF<sub>3</sub>)<sub>2</sub>, SCF<sub>3</sub>, SeCF<sub>3</sub>, TeCF<sub>3</sub>), is noted [143]. Dirhenium decacarbonyl reacts with  $Ni(PMeCl_2)_4$  to give  $Re_4(\mu-Cl)_2(MePPMePMe)(CO)_{15}$ , characterized by x-ray diffraction [144]. This species has been shown to react further with  $Re_2(CO)_{10}$  to yield  $Re_5(CO)_{14}(\mu_4-PMe)(\mu_2-PMe_2)(\mu_3PRe(CO)_5)$  and  $Re_6(CO)_{18}(\mu_4-PMe)_3$ ; both were characterized by crystallographic techniques [145].

Substitution of one carbonyl group in a phosphoranyl-manganese carbonyl gives *cis*- $Mn(CO)_4(L)P(O_2C_6H_4)_2$ ; the crystal structure of the product of P(OPh)<sub>3</sub> substitution was obtained [146]. Reactions of t-butyllithium with  $Mn(CO)_2(RPCl_2)(\eta-C_5H_5)$  or the arsenic analogue, in the presence of  $Me_2NCH_2CH_2NMe_2$  give  $RP[Mn(CO)_2(\eta-C_5H_5)]_2$  or  $RAS[Mn(CO)_2(\eta-C_5H_5)]_2$  [147]. The formation of  $HAS[Mn(CO)_2(\eta-C_5Me_5)]_2$  from  $AsH_3$  and  $Mn(CO)_2(THF)(\eta-C_5Me_5)$ , and its structure, are reported by Herrmann et al. [148]. Further chemistry of this species includes reactions with diazoalkanes, and thermolysis to give  $\mu-As_2[Mn(CO)_2(\eta-C_5Me_5)]_2$  (structure determined) and  $As_2[Mn(CO)_2(\eta-C_5Me_5)]_4$ . A congener of the later species, with  $C_5H_5$  groups, was prepared by reduction of  $ClAs[Mn(CO)_2(\eta-C_5H_5)]_2$  and its structure also obtained [149].

A series of 12 complexes containing a phosphorus, arsenic, or antimony atom bridging three metals has been prepared. Included in this list are  $[(CO)_5Cr]_2AsMn(CO)_5$  and  $(CO)_9Cr_2AsMn(CO)_5$ . Also described in this paper is the unusual species  $Mn_2[\mu-AsMn(CO)_2(\eta-C_5H_4Me)]_2(CO)_2(\eta-C_5H_4Me)_2$  [150].

The facile replacement of the triflate ion from  $M(O_3SCF_3)(CO)_5$  (M = Mn, Re) was mentioned earlier [31, 32]. Similar species,  $M(O_3SF)(CO)_5$  (M = Mn, Re), have been prepared from  $MX(CO)_5$  and  $AgO_3SF$ . Heating of the manganese compound to 70°C causes CO loss to give  $Mn(CO)_4(O_3SF)$  [151]. The reaction of  $ReCl(CO)_3(PPh_3)_2$  with  $Li[Ph_2CHCO_2]$  yields  $Re(O_2CCHPh_2)(CO)_2(PPh_3)_2$ , a species containing a bidentate carboxylate ligand. Similar reactions are seen with other lithium salts in which the anion is capable of functioning as a bidentate ligand. The structure of one species derived from lithium amino-thiazolate is shown below, XV [152].



(XV)

The complex  $\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{HNMeCHCOOEt})$  was described earlier in this review [84].

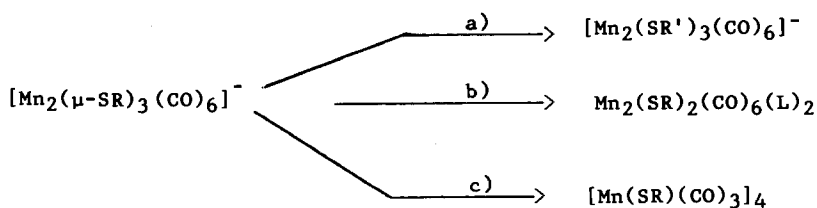
Preparations of  $(\text{Bu}_4\text{N})_2[\text{M}(\text{CO})_3(\text{P}_3\text{O}_9)]$  ( $\text{M} = \text{Mn, Re}$ ) [153] and  $(\text{Bu}_4\text{N})_3[\text{M}(\text{CO})_3\text{Nb}_2\text{W}_4\text{O}_{19}]$  [154] are reported; both procedures rely on displacement of the nitrile ligands of  $[\text{M}(\text{CO})_3(\text{MeCN})_3]^+$  by the oxyanion. A crystal structure of  $(\text{Bu}_4\text{N})_3[\text{Mn}(\text{CO})_3\text{Nb}_2\text{W}_4\text{O}_{19}]$  was also completed for the latter study. The anionic species  $[\eta\text{-C}_5\text{H}_5\text{Co}\{\text{PO}(\text{OR})_2\}_3]^-$  ( $\text{R} = \text{Me, Et}$ ) can also function as a chelating ligand to manganese or rhenium, bonding through the three phosphoryl oxygens. Syntheses of these species are accomplished by reactions of the anionic cobalt species and  $\text{MBr}(\text{CO})_5$  ( $\text{M} = \text{Mn, Re}$ ) [155].

Alkoxy bridged complexes  $\text{Et}_4\text{N}[\text{Re}_3(\mu\text{-OR})(\text{CO})_9]$  and  $\text{Et}_4\text{N}[\text{Re}_2(\text{OPh})_3(\text{CO})_6]$  were described earlier in this review [50]. A communication and a full paper report on  $[\text{Re}(\text{OH})(\text{CO})_3]_4$  supported on silica. When this system is heated, the resulting material is a metathesis catalyst [156,157].

A typical reaction of  $\text{Re}(\text{CO})_5\text{FBF}_3$  involves facile displacement of  $\text{BF}_4^-$ . This fact makes this species useful as a precursor to mononuclear  $\text{Re}(\text{X})(\text{CO})_5$  species ( $\text{X} = \text{SCN, SeCN, ONO}_2, \text{NO}_2, \text{O}_2\text{CH, CN, and p-SC}_6\text{H}_4\text{NO}_2$ ) or to binuclear species like  $(\text{CO})_5\text{ReC}_2\text{O}_4\text{Re}(\text{CO})_5$  [38].

Papers from two groups describe the complex  $\text{Et}_4\text{N}[\text{Mn}_2(\mu\text{-SPh})_3(\text{CO})_6]$  [158,159]. Several routes are available for the syntheses of this very stable species. Cyclic voltammetry reveals two one-electron oxidation processes but the products of oxidation lack stability and have not been isolated. These species are useful reagents for preparations of other manganese thiolate complexes; examples of use are given in the scheme below.



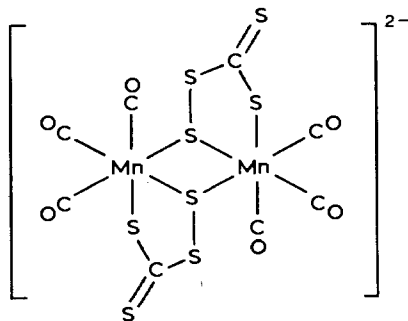


a) R'SH, H<sup>+</sup>; b) L, H<sup>+</sup>; c) H<sup>+</sup>, heat (R, R' = Me, Ph; L = CO, Phos).

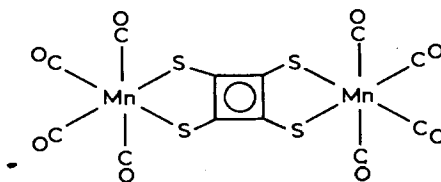
Preparation and study of a paramagnetic species Mn(SR)(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>) and Mn(SeR)(CO)<sub>2</sub>(η-C<sub>5</sub>Me<sub>5</sub>) has proven quite interesting. The paper reporting this work also describes the structure of the dinuclear species (η-C<sub>5</sub>H<sub>5</sub>)(CO)Mn-(μ-SBu<sup>t</sup>)(μ-CO)Mn(CO)<sub>4</sub> and the preparation of (η-C<sub>5</sub>Me<sub>5</sub>)MnFe<sub>2</sub>(μ-S)(CO)<sub>8</sub> [116].

Rhenium(III) thiolates, Re(SR)<sub>3</sub>(MeCN)<sub>2</sub>, are obtained in a reaction of K<sub>2</sub>ReCl<sub>6</sub>, RSH, NEt<sub>3</sub> and MeCN (R = 2,6-C<sub>6</sub>H<sub>3</sub>Pr<sub>2</sub><sup>1</sup>). Carbonylation converts these species to Re(SR)<sub>3</sub>(CO)<sub>2</sub> [160].

Adducts between CS<sub>2</sub> and MnX<sub>2</sub>(PR<sub>3</sub>) are assigned the stoichiometry [MnX<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>CS<sub>2</sub>]; a similar reaction between MnX<sub>2</sub>(THF)<sub>2</sub>(PR<sub>3</sub>) and CS<sub>2</sub> is also noted. These products are believed to have structures with the CS<sub>2</sub> bridging group linked to the two metals through sulfur and carbon [161]. The reaction of [Mn<sub>2</sub>Br(CO)<sub>9</sub>]<sup>-</sup>, prepared in situ from MnBr(CO)<sub>5</sub> in a phase transfer process utilizing [PhCH<sub>2</sub>NEt<sub>3</sub>]Cl and NaOH, reacts with elemental sulfur to give (PhCH<sub>2</sub>NEt<sub>3</sub>)<sub>2</sub>[Mn<sub>2</sub>(CS<sub>4</sub>)<sub>2</sub>(CO)<sub>6</sub>]. A crystal structure study reveals structure XVI, a complex with perthiocarbonate anions, CS<sub>4</sub><sup>2-</sup>, as ligands [162]. Complexes with a tetrathiosquarate ion as a ligand have been described [163]. Compounds described in this reference include Mn<sub>2</sub>(CO)<sub>8</sub>(μ-C<sub>4</sub>S<sub>4</sub>) XVII, [Re<sub>2</sub>Cl<sub>2</sub>(CO)<sub>6</sub>(μ-C<sub>4</sub>S<sub>4</sub>)<sup>2-</sup>, C<sub>4</sub>S<sub>4</sub>[Re(CO)<sub>5</sub>]<sub>4</sub>(BF<sub>4</sub>)<sub>2</sub> and C<sub>4</sub>S<sub>4</sub>[Re(CO)<sub>5</sub>]<sub>2</sub>. The synthesis of [Mn(CO)<sub>2</sub>(η-C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>](μ-SO) from Mn(CO)<sub>3</sub>(η-C<sub>5</sub>H<sub>5</sub>) and C<sub>2</sub>H<sub>4</sub>SO, and the structure of this product, are reported [164].



(XVI)



(XVII)

Three papers describe complexes with phosphinothioformamide and/or phosphinothioformimidate ligands. The first paper deals with syntheses of these species [165], while the second reports carbonyl substitution reactions [166] and the third, the  $^{55}\text{Mn}$  NMR [167].

A study reports  $^{13}\text{C}$  hyperfine coupling in the esr spectrum of  $\text{Mn}(\text{CO})_4^-$  (BETS) (BETS =  $[(\text{EtO})_2\text{CO}]_2\text{S}$ ) [168].

The reaction of  $\text{Te}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_3$  with methyllithium gives  $[\text{MeTe}\{\text{Mn}(\text{CO})_2(\eta\text{-Cp})\}_3]^-$ ; this species was isolated as a  $\text{PPN}^+$  salt [169].

#### VIII. DERIVATIVES OF $\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ AND $[\text{M}(\text{NO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^+$

This continues to be a very active area of involvement. There are many facets to research under this general heading.

For example, consider the subject of complexes containing two or more metals. A number of such species containing  $\text{CpM}(\text{CO})_x$  units having main group element bridging ligands have been described in the literature, and were mentioned already in this article in Sections V, VI, and VII (a hydrido-bridged complex [66]; phosphido bridged species [114,115], sulfido complexes [116], a silyl bridged complex [134]; alkylidene bridged complexes [110,119, 120,121]; germanium [135]; lead [137], phosphorane (RP) [147], arsenorane (RAs) diarsenic ( $\text{As}_2$ ) [148,149,150], sulfuryl (SO) [164], and telluride bridged complexes [169].)

In conjunction with the last article note the formation and structure determination of a complex  $\text{Mn}(\text{CO})_2(\text{Sefp}_2)(\eta\text{-C}_5\text{H}_5)$  [170]. This complex is made from  $\text{fp}_2\text{Se}$ , ( $\text{fp} = \text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ) [169], and  $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5)$ . One reference from the list above [147] describes reactions of  $\text{Mn}(\text{CO})_2(\text{PR}_2\text{X})(\eta\text{-C}_5\text{H}_5)$  with various organolithium reagents; the result is either alkylation at phosphorus or lithium-halogen exchange in cases where large alkyl groups are involved. The lithiated organometallic species react with alkyl halides and  $\text{Me}_3\text{SnCl}$  to yield  $\text{Mn}(\text{CO})_2(\text{PR}_2\text{R}')(\eta\text{-C}_5\text{H}_5)$ . Another reference to the thermolysis of bimetallic complexes with bridging alkylidene ligands is noted [171].

Chemical reactions of  $[\text{Mn}(\text{CO})_2(\text{CR})(\eta\text{-C}_5\text{H}_4\text{Me})]\text{BCl}_4$  are described in four papers. Fischer et al. reacted one of these complexes ( $\text{R} = \text{fc}$ , the ferrocenyl group) with  $\text{PhS}^-$ ,  $\text{PhSe}^-$ , and  $\text{PhTe}^-$  forming carbene complexes of manganese  $\text{Mn}(\text{CO})_2(\text{CRXPh})(\eta\text{-C}_5\text{H}_4\text{Me})$  [172]; with  $\text{Na}[\text{Co}(\text{CO})_4]$  it reacts to give the bimetallic compound  $\text{Mn}(\text{CO})_2[\text{CRCo}(\text{CO})_4](\eta\text{-C}_5\text{H}_4\text{Me})$  [173]. The product from reactions of  $\text{K}[\text{Mn}(\text{CO})_5]$  is different; it is  $(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})\text{Mn}(\mu\text{-CO})(\mu\text{RCCO})\text{-Mn}(\text{CO})_4$  ( $\text{R} = \text{Ph}, \text{fc}$ ). The structure of the ferrocenyl derivative was determined [173]. Other workers reacted  $[\text{Mn}(\text{CO})_2(\text{CPh})(\eta\text{-C}_5\text{H}_4\text{Me})]\text{BCl}_4$  with allylamine, giving the expected aminocarbene species. This complex loses CO

upon photolysis, with the double bond of the allyl group coordinating to the metal (x-ray structure) [174]. The reaction of the precursor with  $\text{Li}[\text{CSNMe}_2]$  yielded the isolable complex  $\text{Mn}(\text{CO})_2(\text{S}=\text{CPhSCH}_2\text{CSNMe}_2)(\eta\text{-C}_5\text{H}_4\text{Me})$ , also a subject for a structure determination [175].

Attention is further directed to pentamethylcyclopentadienylrhenium oxo species. The formation of  $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$  by  $\text{H}_2\text{O}_2$  oxidation of  $\text{Re}(\text{CO})_3(\eta\text{-C}_5\text{Me}_5)$  is described, [176], as are reactions with  $\text{PPh}_3$  [177, 178, 179], with tetrachloro ortho-quinone [180] and with ketenes [181]. Products characterized include  $\text{Re}_3(\mu\text{-O})_6(\eta\text{-C}_5\text{Me}_5)_3(\text{ReO}_4)_2$  (x-ray) [177, 178],  $\text{Re}_2\text{O}_4(\eta\text{-C}_5\text{Me}_5)_2$ ,  $\text{Re}_2\text{O}_3(\text{OReO}_3)_2(\eta\text{-C}_5\text{Me}_5)_2$  (x-ray) [178];  $\text{Re}(\text{O}_2\text{C}_6\text{Cl}_4)_2(\eta\text{-C}_5\text{Me}_5)$  (x-ray) and  $\text{ReO}(\text{O}_2\text{C}_6\text{Cl}_4)(\eta\text{-C}_5\text{Me}_5)$  [180], and  $\text{ReO}(\text{OCOCPh}_2\text{O})(\eta\text{-C}_5\text{Me}_5)$  (x-ray) [181]. Chlorine reacts with  $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$ . However the reaction of  $\text{Me}_3\text{SiCl}$  and  $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$  forms  $\text{ReCl}_4(\eta\text{-C}_5\text{Me}_5)$ . A 1:1 adduct of this species with trimethylphosphine was structurally characterized [179].

Acetylene complexes,  $\text{Re}(\text{CO})_2(\eta^2\text{-PhC}\equiv\text{CR})(\eta\text{-C}_5\text{H}_5)$ , ( $\text{R} = \text{Ph, Me}$ ) were prepared from  $\text{Re}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5)$ . A crystal structure study on the  $\text{PhC}\equiv\text{CPh}$  complex showed that the acetylene is bent, the  $\text{C-C}\equiv\text{C}$  angle being about  $150^\circ$  [182]. A species with a bridging benzene ligand  $[\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2\text{-}\mu\text{-}\eta^2, \eta^2\text{-C}_6\text{H}_6$ , forms initially upon photolysis of  $\text{Re}(\text{CO})_3(\eta\text{-C}_5\text{Me}_5)$  in benzene. Further irradiation gives  $\text{Re}_2(\text{CO})_5(\eta\text{-C}_5\text{Me}_5)_2$  and  $\text{Re}(\eta\text{-C}_6\text{H}_6)(\eta\text{-C}_5\text{Me}_5)$ . The structure of the binuclear species was obtained through a crystallographic study [183].

The tetrahedral cluster species,  $(\eta\text{-C}_5\text{H}_5\text{Ni})\text{Co}(\text{CO})_3(\text{BuC}\equiv\text{P})$ , functions as the ligand in  $\text{Mn}(\text{CO})_2(\text{L})(\eta\text{-C}_5\text{H}_5)$ , [184]. A series of diphosphines ( $\text{P}^*\text{P} = \text{dppe, diop, norphos}$ ) have been used as ligands to make  $\text{Mn}(\text{CO})_2(\text{P}^*\text{P})(\eta\text{-C}_5\text{H}_5)$  and  $[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2\text{-}\mu\text{-}\text{P}^*\text{P}$ ; these species are cocatalysts in conjunction with  $[\text{RhCl}(\text{COD})]_2$  in asymmetry hydrogenations [185]. A crystallographic study on  $\text{Mn}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  has been published [186]. Three different products could be obtained from reactions of p-cyanopyridine and  $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_4\text{Me})$ . These were characterized as the pyridine bonded and nitrile bonded monomers and a dimer with the ligand bridging two metal groups [187]. The complex  $\text{Mn}(\text{CO})_2(\text{H}_2\text{Ntol})(\eta\text{-C}_5\text{H}_5)$  can be deprotonated using  $\text{Na}[\text{N}(\text{SiMe}_3)_2]$ ; oxidation of the anion then gives a blue paramagnetic species  $\text{Mn}(\text{CO})_2(\text{HNtol})(\eta\text{-C}_5\text{H}_5)$ , [188].

A series of oxidative addition reactions of carbon-hydrogen bonds to rhenium is reported in a communication [189]. Three rhenium precursors,  $\text{Re}(\text{PMe}_3)_3(\eta\text{-C}_5\text{H}_5)$ ,  $\text{Re}(\text{CO})_2(\text{PMe}_3)(\eta\text{-C}_5\text{Me}_5)$  and  $\text{Re}(\text{CO})(\text{PMe}_3)_2(\eta\text{-C}_5\text{Me}_5)$ , were used, with the initial step of the process being loss of  $\text{PMe}_3$  (in the first species) or  $\text{CO}$  (in the others).

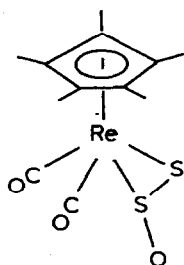
Oxidative addition of silanes ( $\text{Ph}_2\text{SiH}_2$ ,  $(\text{p-ClC}_6\text{H}_4)_2\text{SiH}_2$ ) to several  $\text{Mn}(\text{CO})_2(\text{L})(\eta\text{-C}_5\text{H}_4\text{Me})$  compounds ( $\text{L} = \text{PR}_3$ ;  $\text{R} = \text{Me, Bu, Ph, tol, p-ClC}_6\text{H}_4\text{-}$ , and  $\text{PPhMe}_2$ ) occurs upon photolysis [190]. See also another reference on the

$\text{SiH}_4\text{-Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$  reaction [134]. The preparation of the metallocycle  $\text{Re}(\text{C}_4\text{H}_8)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$  and reductive elimination of the hydrocarbon fragment on heating with phosphines is noted [88].

Protonation of  $\text{Mn}(\text{CO})_2(\eta^2\text{-C}_6\text{H}_8)(\eta\text{-C}_5\text{H}_5)$  has been shown to give  $[\text{Mn}(\text{CO})_2(\eta^3\text{-C}_6\text{H}_9)(\eta\text{-C}_5\text{H}_5)]^+$ . Allyl-manganese species of similar structure are obtained by protonation (and loss of  $\text{H}_2\text{O}$ ) in  $\text{Mn}(\text{CO})_2(\eta^2\text{-CH}_2=\text{CHCH}_2\text{OH})(\eta\text{-C}_5\text{H}_5)$  [191].

The basicity of  $\text{Mn}(\text{CO})_{3-n}(\text{L})_n(\eta\text{-C}_5\text{H}_5)$  ( $\text{L} = \text{CO}$ , phosphines) toward  $\text{H}^+$  [192] and  $\text{AlBr}_3$  or  $\text{GaBr}_3$  [193] has been investigated further. Some  $^{31}\text{P}$  NMR spectra of various  $\text{Mn}(\text{CO})_{3-n}(\text{Phos})_n(\eta\text{-C}_5\text{H}_5)$  compounds are reported [194]. An explanation of  $\sigma$  and  $\pi$  components of the metal phosphorus bond in these species has been presented [195]. A theoretical study which includes the compound  $\text{Mn}(\text{CO})_2(\text{CMe}_2)(\eta\text{-C}_5\text{H}_5)$  is of interest [196]. Criteria defining the stability of paramagnetic manganese (II) complexes derived from  $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$  are assessed [197].

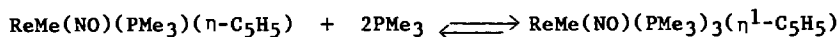
Air oxidation of  $\text{Re}(\text{CO})_2(\text{S}_2)(\eta\text{-C}_5\text{Me}_5)$  yields  $\text{Re}(\text{CO})_2(\text{S}_2\text{O})(\eta\text{-C}_5\text{Me}_5)$ . The structure, XVIII, determined by diffraction techniques, is drawn below [198].



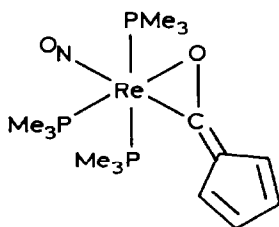
( XVIII )

Reactions of  $[\text{Re}(\text{CO})_2(\text{N}_2\text{Ar})(\eta\text{-C}_5\text{R}_5)]\text{BF}_4$  ( $\text{Ar} = p\text{-C}_6\text{H}_4\text{OMe}$ ,  $p\text{-C}_6\text{H}_4\text{NMe}_2$ ,  $p\text{-tol}$ ;  $\text{R} = \text{H}$ ,  $\text{Me}$ ) with nucleophiles are described in two papers. One carbonyl is displaced from this species by certain anions ( $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{NCO}$ ) while alkoxide and amide ions add to a coordinated carbonyl group [199]. Addition of a stoichiometric amount of hydroxide results in formation of a  $\text{Re}(\text{CO})(\text{CO}_2\text{H})(\text{N}_2\text{Ar})(\eta\text{-C}_5\text{H}_5)$  species which can be isolated. Under certain circumstances these species decompose with loss of  $\text{CO}_2$ . If excess  $\text{OH}^-$  is used then deprotonation occurs and isolable dinuclear species with a bridging carboxylato group are formed [200].

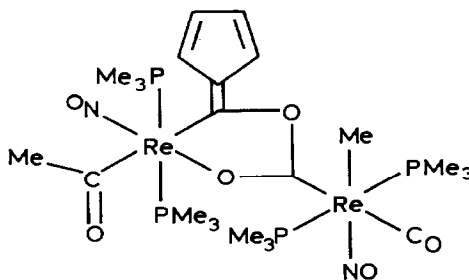
The equilibrium given in the equation below is established when  $\text{PMe}_3$  and  $\text{ReMe}(\text{NO})(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)$  are mixed. Prolonged heating of this mixture for 48



hours with excess  $\text{PMe}_3$  present leads to formation of  $[\text{ReMe}(\text{NO})(\text{PMe}_3)_4]\text{C}_5\text{H}_5$ , an ionic complex with uncoordinated ( $\eta^0$ ) cyclopentadienide anion (crystal structure reported) [201]. Further chemistry of this system is reported in another paper [202]. Compound XIX, shown below, was isolated and its reactions with  $\text{HCl}$  and with acetone described. Carbonylation of the  $\eta^1$ -cyclopentadienyl complex gives a different product, XX; its crystal structure was determined. Finally, a reaction of  $\text{PMe}_3$  and  $\text{ReH}(\text{NO})(\text{CO})(\text{PMe}_3)_2(\eta^1\text{-C}_5\text{H}_5)$  gives  $\text{Re}(\text{NO})(\text{CO})(\text{PMe}_3)_3$ .



(XIX)



(XX)

Gladysz and coworkers have continued a major research effort involving  $[\text{Re}(\text{NO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^+$  derivatives that generated six papers during the last year. The formation of the phosphido complex,  $\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)$  was described, along with its molecular structure and reactions [203]. In another paper these authors describe the facile inversion at phosphorus in this and related species [204]. The electrochemistry of 12  $\text{Re}(\text{R})(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  complexes was investigated; a one electron oxidation is the primary redox process for these systems [205]. Butyllithium deprotonates  $\text{Re}(\text{CH}_2\text{CN})(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ , and stereospecific alkylation of the anion is accomplished using methyl triflate [206]. The same set of authors also describe deprotonation of  $\text{ReH}(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  at the cyclopentadienyl ring and the subsequent rearrangement of this species to give  $\text{Li}[\text{Re}(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ . Reactions of both anions with electrophiles were then carried out [207]. Reactions of chiral  $\text{Re}(\text{NO})(\text{PPh}_3)(\text{COMeCHR})(\eta\text{-C}_5\text{H}_5)$  with alkyl halides and a crystal structure of one of the products were subjects of the final paper in this group [208].

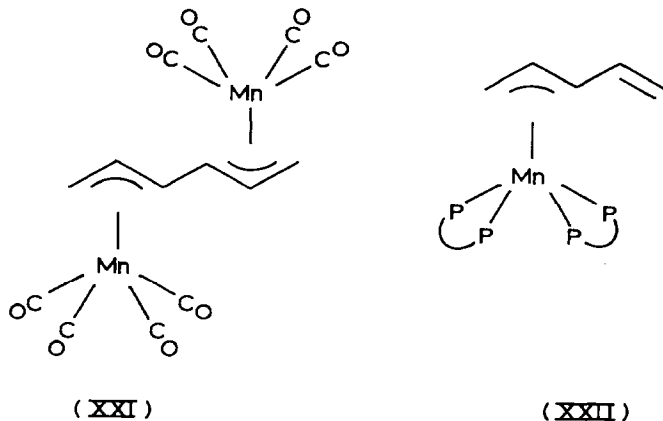
Reactions of  $[\text{Re}(\text{NO})(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]^+$  with  $\text{LiPRSiMe}_3$  result, initially, in addition of the phosphide group to a coordinated carbonyl group. This species then rearranges with migration of the silyl group to oxygen, giving  $\text{Re}(\text{NO})(\text{CO})\text{-}[\text{C}(\text{OSiMe}_3)=\text{PR}](\eta\text{-C}_5\text{Me}_5)$  in two isomeric forms [209].

A reference to a rhenium-platinum bimetallic species was described earlier in this review [123]. Conformation-reactivity relationships of a number of related species including  $\text{ReR}(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  are the topic of a theoretical paper [210].

#### IX. OTHER HYDROCARBON METAL COMPLEXES

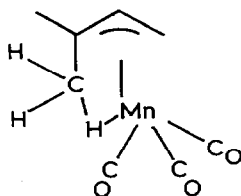
Complexes derived from reactions between  $\text{Re}_2(\text{CO})_{10}$  or its derivatives and olefins or acetylenes have been mentioned earlier; these complexes contain an alkenyl or alkynyl group bridging  $(\mu, \eta^2\text{-})$  two metal atoms [13, 64, 65]. Two related compounds (isomers) were reported as products of the reaction of  $\text{Re}_2(\text{CO})_{10}$  and 1,3,5-cycloheptatriene. The more stable isomer was the subject of a crystal structure study [211]. Other  $\eta^2$ -hydrocarbon complexes include the species  $\text{ReH}_3(\eta^2\text{-C}_2\text{H}_4)_2(\text{PR}_3)_2$  and  $\text{ReH}_5(\text{C}_2\text{H}_4)(\text{PR}_3)_2$  [63],  $\text{MnH}(\eta\text{-C}_2\text{H}_4)(\text{dmpe})_2$  [75], and  $[\text{Re}(\text{CO})_5(\eta^2\text{-butadiene})]\text{BF}_4$  [81]. A completed study on the synthesis and structure of  $\text{ReOI}(\text{MeC}\equiv\text{CMe})_2$  is noted [212].

Photolysis of  $\text{Mn}(\eta^1\text{-C}_3\text{H}_5)(\text{CO})_5$  in a low temperature matrix results in CO loss to give  $\text{Mn}(\text{CO})_4(\eta^3\text{-C}_3\text{H}_4)$ . Continued irradiation leads to loss of another CO group, and if the matrix consists of molecular  $\text{N}_2$ , this species adds to the vacant coordination site [213]. Photolysis of  $\text{Mn}_2(\text{CO})_{10}$  with several dienes produces a mixture of  $\eta^3$ -dienyl and  $\eta^3$ -alkenyl-metal complexes [214]. A similar procedure using 1,3,5-hexatriene results in formation of two isomeric forms of a dimanganese species, XXI [215]. The reaction between  $\text{MnBr}_2$ , dmpe, and pentadienylpotassium gives XXII, whose structure was obtained by crystallography [216]. An  $\eta^3$ -allyl species, noted earlier, is the product of the reaction of  $\text{ReH}_7(\text{dppe})$ , 2,3-dimethylbutadiene and  $\text{KOBu}^t$  [61].



Rates of carbonyl substitution for several  $\text{Mn}(\text{CO})_4(\eta^3\text{-allyl})$  species were measured. The reactions are first order in complex and zero order in ligand, arguing against an  $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$  mechanism [217].

Hydride reduction of  $[\text{Mn}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)]^+$  occurs stepwise, giving first an  $\eta^5$ -hexadienyl complex and then an  $\eta^4$ -cyclohexadiene-manganese tricarbonyl anion. This species can be protonated or alkylated, resulting in  $\eta^3$ -cyclohexenyl complexes [218]. Similar chemistry occurs using the toluene and xylene complexes [219]. Heating  $\text{Mn}(\text{CO})_4(\eta^3\text{-CH}_2\text{CHCMe}_2)$  causes loss of CO and formation of  $\eta^3$ -allylic species similar to those in the previous references in that they are found to contain (agostic) hydrogens bridging a carbon atom and the metal XXIII. An NMR study on these species indicates fluxional behavior [220, 221].



( XXIII )

The reaction of  $\text{Mn}(\text{CO})_5\text{FBF}_3$  and 2-butyne is reported to give  $[\text{Mn}(\text{CO})_4(\eta^4\text{-C}_4\text{Me}_4)]\text{BF}_4$  [222].

A series of diene-rhenium complexes containing phosphine and hydride ligands of formula  $\text{ReH}_3(\text{L})_2(\eta^4\text{-diene})$  have been mentioned already [58, 59, 69].

Most cyclopentadienyl-manganese and rhenium species were mentioned in the last section and will not be cited again here. Three references concerning bimetallic complexes originating from  $\text{ReH}(\eta\text{-C}_5\text{H}_5)_2$  have also been identified earlier in this review [67, 68, 136].

Cocondensation of rhenium metal and  $\text{C}_5\text{Me}_5\text{H}$  resulted in the formation of  $\text{ReH}(\eta\text{-C}_5\text{Me}_5)_2$  which could be reduced to  $[\text{Re}(\eta\text{-C}_5\text{Me}_5)_2]^-$ . Alkylation of this anion using methyl iodide then gave  $\text{ReMe}(\eta\text{-C}_5\text{Me}_5)_2$  [223].

Cyclohexadienyl-manganese complexes undergo carbonyl substitution reaction by phosphines. Subsequently it was shown that  $\text{Mn}(\text{CO})(\text{dppe})(\eta^5\text{-1-PhC}_6\text{H}_6)$  can be oxidized to a stable monocation [224]. Structures of the neutral precursor and the paramagnetic cation were obtained. In another paper, it was shown that substitution of  $\text{NO}^+$  for CO is possible in certain of these species. Nucleophiles add to  $[\text{Mn}(\text{NO})(\text{CO})_2(\eta\text{-C}_6\text{H}_7)]^+$  to give  $\text{Mn}(\text{NO})(\text{CO})_2(\eta^4\text{-C}_6\text{H}_7\text{Nu})$  [225, 226, 227]. The third listed reference contains two crystal structures.

A one step method of preparation of  $\text{Re}(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)$  is reported using  $\text{Re}_2(\text{CO})_{10}$  and indene [228]. The same research group described lithiation [229] and protonation [230] studies on  $\text{Mn}(\text{CO})_3(\eta\text{-C}_9\text{H}_7)$ . Addition of  $\text{PMe}_3$  to  $\text{Re}(\text{CO})_3(\eta\text{-C}_9\text{H}_7)$  causes fast conversion to an  $\eta^1$ -indenyl product [231].

Cocondensation of rhenium atoms with cyclohexane and  $\text{PMe}_3$  leads to  $\text{ReH}(\text{PMe}_3)_2(\eta\text{-C}_6\text{H}_6)$  [70]. Using a mixture of  $\text{C}_6\text{H}_6$  and  $\text{C}_7\text{H}_8$  with rhenium in a metal atom reactor, it is possible to prepare a mixture containing  $\text{Re}(\eta\text{-C}_6\text{H}_6)(\eta^5\text{-C}_7\text{H}_7)$  and  $\text{Re}(\eta\text{-C}_6\text{H}_6)(\eta^5\text{-C}_7\text{H}_9)$  [232]. A thesis describing  $\text{MnH}(\text{CO})_2(\eta\text{-C}_6\text{Me}_6)$  was cited earlier [71]. The structure of  $[\text{Mn}(\text{CO})_3(\eta^6\text{-C}_{18}\text{H}_{24})]\text{BF}_4$  was ascertained by crystallography [233]. Reactions of nucleophiles with  $[\text{Mn}(\text{CO})_2(\text{L})(\eta^6\text{-C}_7\text{H}_8)]^+$  ( $\text{L} = \text{CO}, \text{PPh}_3$ ) proceed with exo addition to the hydrocarbon ring; a crystal structure confirms this fact in one instance [234].

Manganese and rhenium complexes with boron containing hydrocarbon ligands were noted earlier [129-131]. Kinetics of CO substitution in pyrrolyl- and indolyl-manganese tricarbonyl were monitored; the process is first order in complex and first order in ligand [235]. Formation of  $\text{Mn}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_4\text{H}_4\text{N})$  is noted. This compound was shown to function as a ligand with the nitrogen donating its lone pair to palladium in  $\text{PdL}_2\text{Cl}_2$  ( $\text{L} = \text{Mn}(\text{CO})_3(\eta\text{-C}_4\text{H}_4\text{N})$ ) [236]. Additional types of chemical processes for  $\text{ReH}_2(\text{PR}_3)_2(\eta\text{-C}_4\text{H}_4\text{N})$ , most involving the pyrrolyl ligand, are also cited here [62].

#### X. ISOCYANIDE AND NITROSYL COMPLEXES

The lone reference to technetium in this year's Annual Surveys is to  $[\text{Te}(\text{CNR})_6\text{X}]^+$  complexes ( $\text{R} = \text{Me}, \text{Bu}^t$ ;  $\text{X} = \text{Cl}, \text{Br}$ ). These species are formed by reaction of the elemental halogen with  $[\text{Te}(\text{CNR})_6]^+$ . They were shown to undergo dealkylation upon heating to form  $[\text{Te}(\text{CNR})_5(\text{CN})\text{X}]^+$ ; a similar reaction with rhenium was also seen [237].

Papers describing  $^{55}\text{Mn}$  NMR experiments on  $[\text{Mn}(\text{CNR})_6]^+$  species are reported [238, 239]. The same authors report IR and Raman spectra and electrochemical data on these species in a separate paper [240]. See also a thesis on this work [241].

Reactions between t-butyl isocyanide and  $\text{Re}_2\text{X}_4(\text{dppm})_2$  are described in a communication and a paper [242, 243]. A rhenium(II)-rhenium(III) bimetallic product was characterized structurally. Compounds of the formula  $[\text{Re}_2\text{Cl}_3(\text{CNBu})_3(\text{dppm})_2]\text{PF}_6$  are also identified. Another paper which describes a dirhenium isocyanide complexes was mentioned earlier in another context [44]. Substitution of carbonyl groups in  $\text{Re}_2(\text{CO})_{10}$  by isocyanides yield various  $\text{Re}_2(\text{CO})_{10-x}(\text{L})_x$  species [6,7]. The characterization of



[Mn(CO)(CNR)(dppe)<sub>2</sub>]PF<sub>6</sub> [33] and [Re(CNR)<sub>2</sub>(dppe)<sub>2</sub>]PR<sub>6</sub> [34] were also mentioned at an earlier point in this review.

Nitrosyl compounds under study include Mn(NO)<sub>3</sub>L (L = THF [36], CO, PR<sub>3</sub> [244]). Both references contain <sup>55</sup>Mn NMR data. An electron diffraction study on Mn(NO)<sub>3</sub>(CO) is of interest [245]. The complex PPN [Mn(CO)<sub>2</sub>(NO)<sub>2</sub>] is described in a thesis [246]. The thionitrosyl complex [Re(CO)<sub>5</sub>(NS)] was described earlier in this review [141] as were the complexes ReH(OR)(CO)(NO)-(PPh<sub>3</sub>)<sub>2</sub> and [ReH(CO)(NO)(PPh<sub>3</sub>)<sub>3</sub>]ClO<sub>4</sub> [69]. Protonation of Mn<sub>3</sub>(NO)<sub>4</sub>-( $\eta$ -C<sub>5</sub>H<sub>4</sub>Me)<sub>3</sub> is reported in a thesis [247].

## XI. STRUCTURAL STUDIES

Compounds whose structures were determined by x-ray crystallography (or by other methods) are listed: cis-Re<sub>2</sub>(CO)<sub>9</sub>(CNBu<sup>t</sup>), cis,cis-Re<sub>2</sub>(CO)<sub>8</sub>(CNR)<sub>2</sub>, cis, fac-Re<sub>2</sub>(CO)<sub>7</sub>(CNR)<sub>3</sub> and fac, fac-Re<sub>2</sub>(CO)<sub>6</sub>(CNR)<sub>4</sub> (R = 2,6-Me<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) [7]; trans,trans-Re<sub>2</sub>(CO)<sub>8</sub>(L)<sub>2</sub> (L = PPhMe<sub>2</sub> [8] and P(OMe)<sub>3</sub> [10]); Mn<sub>2</sub>(CO)<sub>9</sub>(SC<sub>4</sub>H<sub>8</sub>) and Mn<sub>2</sub>( $\mu$ -SC<sub>4</sub>H<sub>8</sub>)(CO)<sub>8</sub> [11]; ReBr<sub>3</sub>(CO)<sub>2</sub>(PPhMe<sub>2</sub>)<sub>2</sub> [39]; ReCl(N<sub>2</sub>)(CNMe)[P(OMe)<sub>3</sub>]<sub>3</sub> [41]; ReCl(dppe)<sub>2</sub>(CNBu<sup>t</sup>) [42]; Re<sub>2</sub>Cl<sub>4</sub>(dppm)<sub>2</sub>(CO)<sub>2</sub> [43]; [Re<sub>2</sub>Cl<sub>3</sub>(dppm)<sub>2</sub>-(CO)<sub>2</sub>(EtCN)]PF<sub>6</sub> [44]; PPN[Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>10</sub>] [49]; Et<sub>4</sub>N[Re<sub>3</sub>( $\mu$ -H)<sub>3</sub>(OC<sub>6</sub>F<sub>5</sub>)(CO)<sub>10</sub>] and Et<sub>4</sub>N[Re<sub>3</sub>( $\mu$ -H)<sub>4</sub>(CO)<sub>10</sub>] [49]; Et<sub>4</sub>N[Re<sub>3</sub>( $\mu$ -H)<sub>3</sub>(OC<sub>6</sub>F<sub>5</sub>)(CO)<sub>10</sub>] and Et<sub>4</sub>N-[Re<sub>2</sub>( $\mu$ -OPh)<sub>3</sub>(CO)<sub>6</sub>] [50]; Mn<sub>4</sub>Cu<sub>2</sub>H<sub>6</sub>(CO)<sub>12</sub>(POP)<sub>2</sub> [55]; ReH<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>( $\eta^4$ -C<sub>5</sub>H<sub>6</sub>) [58]; ReH<sub>3</sub>(PCy<sub>3</sub>)<sub>2</sub>( $\eta^4$ -C<sub>12</sub>H<sub>10</sub>) [60]; ReH<sub>4</sub>(dppe)( $\eta^3$ -C<sub>6</sub>H<sub>11</sub>) [61]; Re<sub>2</sub>( $\mu$ -H)( $\eta^1$ -C $\equiv$ CPh)-(CO)<sub>7</sub>(dmpm) and Re<sub>2</sub>( $\mu$ - $\eta^1$ , $\eta^2$ -CH=CH<sub>2</sub>)( $\mu$ - $\eta^1$ , $\eta^2$ -C $\equiv$ CPh)(CO)<sub>5</sub>(dppm) [64]; [( $\eta$ -C<sub>5</sub>Me<sub>5</sub>)<sub>2</sub>ReHCuI]<sub>2</sub> [67]; [Re( $\eta$ -C<sub>5</sub>H<sub>5</sub>)<sub>2</sub>]<sup>+</sup>CuCl<sub>2</sub><sup>-</sup> [68]; Mn<sub>2</sub>( $\mu$ -C<sub>6</sub>H<sub>11</sub>)<sub>2</sub>(C<sub>6</sub>H<sub>11</sub>)<sub>2</sub><sup>-</sup>(dmpe)<sub>2</sub>, Li<sub>4</sub>[MnH( $\eta$ -C<sub>2</sub>H<sub>4</sub>)(Me<sub>2</sub>PCH<sub>2</sub>CHPMe<sub>2</sub>)<sub>2</sub>]<sub>2</sub>·2Et<sub>2</sub>O and [Mn(AlH<sub>4</sub>)(dmpe)<sub>2</sub>]<sub>2</sub> [75]; MnR<sub>2</sub> [76] and Li(THF)<sub>4</sub>[Mn<sub>3</sub>Cl<sub>4</sub>R<sub>3</sub>(THF)] (R = C(SiMe<sub>3</sub>)<sub>3</sub>) [77]; Mg(THF)<sub>4</sub>-[ORMe<sub>4</sub>]<sub>2</sub>, Mg(THF)<sub>2</sub>[OR(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>4</sub>]<sub>2</sub>, Re<sub>2</sub>O<sub>3</sub>Me<sub>6</sub>, and Re<sub>2</sub>O<sub>3</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>6</sub> [80]; trans-(CO)<sub>5</sub>ReCH<sub>2</sub>CH=CHCH<sub>2</sub>Re(CO)<sub>5</sub> [81]; NEt<sub>4</sub>[Re<sub>2</sub>I(CO)<sub>9</sub>] [83]; Re(CO)<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>HN=CMeCHCOEt VIII, [84]; (CO)<sub>5</sub>ReCOCORe(CO)<sub>5</sub> [85]; Mn(CO)<sub>4</sub>C<sub>6</sub>H<sub>4</sub>COEt and Mn(CO)<sub>3</sub>(AsPh<sub>3</sub>)C<sub>6</sub>H<sub>4</sub>COPh [86]; Re(C<sub>4</sub>H<sub>8</sub>)(CO)<sub>2</sub>( $\eta$ -C<sub>5</sub>H<sub>5</sub>) [88]; Mn(CO)<sub>2</sub>(dppm)PPh<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CO [89]; Mn(CO)<sub>4</sub>PPh<sub>2</sub>(CH<sub>2</sub>)<sub>n</sub>CH(CHCl<sub>2</sub>)CH<sub>2</sub> (n = 1,2) [92]; Mn(CH<sub>2</sub>CMe<sub>3</sub>)<sub>2</sub> by electron diffraction [101]; PPN[Re<sub>4</sub>C(CO)<sub>15</sub>I] [102]; Re<sub>2</sub>(CO)<sub>6</sub>(PPh<sub>3</sub>)(PPh<sub>2</sub>C<sub>6</sub>H<sub>4</sub>CO) [103]; (CO)<sub>5</sub>W( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>Re(CO)<sub>4</sub> [105]; (CO)<sub>4</sub>W-( $\mu$ -PPh<sub>2</sub>)<sub>2</sub>ReMe(CO)<sub>3</sub> [106]; ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mo( $\mu$ -PPh<sub>2</sub>)Mn(CO)<sub>4</sub>, ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mo-( $\mu$ -PPh<sub>2</sub>)( $\mu$ - $\sigma$ : $\eta^3$ -CH<sub>2</sub>CMeCHMe)Mn(CO)<sub>3</sub>, and ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)( $\mu$ - $\sigma$ : $\eta^4$ -CHCH<sub>2</sub>CH<sub>2</sub>CHPPh<sub>2</sub>)-Mn(CO)<sub>3</sub> [108]; Co<sub>2</sub>W( $\mu$ -Cto1)(CO)<sub>10</sub>Re(CO)<sub>5</sub> [109]; ( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mn( $\mu$ -C=C-CHCO<sub>2</sub>Me)-W(CO)<sub>4</sub> and [( $\eta$ -C<sub>5</sub>H<sub>5</sub>)(CO)<sub>2</sub>Mn]<sub>2</sub>( $\mu$ -C=C-CHCO<sub>2</sub>Me)<sub>2</sub>Mo(CO)<sub>2</sub> [110]; MnFe( $\mu$ -H)-( $\mu$ , $\mu'$ -to1NCHCHNHto1)(CO)<sub>6</sub> [112]; MnFe( $\mu$ -H)( $\mu$ -N=CHCH-C<sub>5</sub>H<sub>4</sub>N)(CO)<sub>6</sub> [113];

$(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{Mn}(\mu\text{-SBU}^t)(\mu\text{-CO})\text{Mn}(\text{CO})_4$  [116];  $\text{MnCo}_2(\mu\text{-CMe})(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$  [118];  
 $(\eta\text{-C}_5\text{H}_5)(\text{PPr}_3^i)\text{Rh}(\mu\text{-CO})(\mu\text{-C=CH}_2)\text{Mn}(\text{CO})(\eta\text{-C}_5\text{H}_5)$  [119];  $[(\text{CO})_3\text{Mn}(\mu\text{-dppm})_2\text{PtHCl}]\text{-}$   
 $\text{BF}_4$ ;  $[(\text{PPh}_3)_2\text{Pt}(\mu\text{-H})(\mu\text{-PCy}_2)\text{Re}(\text{NO})(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$ ;  $\text{NBu}_4[\{\text{Re}_7\text{C}(\text{CO})_{21}\text{Ag}\}\text{Br}]$  [124];  
 $(\text{ttp})\text{SnMn}(\text{CO})_4\text{HgMn}(\text{CO})_5$  [125];  $[\text{B}_9\text{C}_2\text{H}_{10}(\text{CH}_2)]\text{Re}(\text{CO})_3$  [131];  $[(\eta\text{-C}_5\text{Me}_5)\text{-}$   
 $\text{Mn}(\text{CO})_2\text{H}]\text{-}\mu\text{-SiH}_2$  [134];  $\mu\text{-Ge}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2$  [135];  $\text{Re}(\text{SnMe}_n\text{Cl}_{3-n})(\eta\text{-C}_5\text{H}_5)_2$   
 $(n = 1, 2, 3)$  [136];  $\mu\text{-Pb}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$  [137];  $\text{Re}(\text{CO})_3(\text{PPh}_3)(\text{pz}_2\text{BMe}_2)$  [138];  
 $\text{Re}(\text{CO})_3(\text{pzGaMe}_2\text{OCH}_2\text{CH}_2\text{NMe}_2)$  and  $\text{Re}(\text{CO})(\text{pzGaMe}_2\text{OCH}_2\text{CH}_2\text{SPh})$  [139];  
 $\text{Re}_4(\mu\text{-Cl})_2(\text{MePPMePMe})(\text{CO})_{15}$  [144];  $\text{Re}_5(\text{CO})_{14}(\mu_4\text{-PMe})(\mu_2\text{-PMe}_2)(\mu_3\text{PRE}(\text{CO})_5)$   
and  $\text{Re}_6(\text{CO})_{18}(\mu_4\text{-PMe})_3$  [145];  $\text{Mn}(\text{CO})_4[\text{P}(\text{OPh})_3]\text{P}(\text{O}_2\text{C}_6\text{H}_4)_2$  [146];  
 $\text{HAs}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2$  and  $\mu\text{-As}_2[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2$  [148];  $\text{As}_2[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_4$   
[149];  $\text{Mn}_2[\mu\text{-AsMn}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]_2(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})_2$  [150];  $\text{Re}(\text{CO})_2(\text{PPh}_3)_2\text{-}$   
 $(\text{MeNC}_2\text{SNH}_2)$  [154];  $(\text{PhCH}_2\text{NEt}_3)_2[\text{Mn}_2(\text{CS}_4)_2(\text{CO})_6]$  [162];  $[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2\text{-}$   
 $(\mu\text{-SO})$  [164];  $\text{Mn}(\text{CO})_2(\text{Sefp}_2)(\eta\text{-C}_5\text{H}_5)$  ( $\text{fp} = \text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ) [170];  
 $\text{Mn}(\text{CO})(\text{CPhNHCH}_2\text{CH=CH}_2)(\eta\text{-C}_5\text{H}_4\text{Me})$  [174];  $\text{Mn}(\text{CO})_2(\text{S=CPhSCH}_2\text{CSNMe}_2)(\eta\text{-C}_5\text{H}_4\text{Me})$   
[175];  $[\text{Re}_3(\mu\text{-O})_6(\eta\text{-C}_5\text{Me}_5)_3](\text{ReO}_4)_2$  [177];  $\text{Re}_2\text{O}_3(\text{OREO}_3)_2(\eta\text{-C}_5\text{Me}_5)_2$  [178];  
 $\text{ReCl}_4(\text{PMe}_3)(\eta\text{-C}_5\text{Me}_5)$  [179];  $\text{Re}(\text{O}_2\text{C}_6\text{Cl}_4)_2(\eta\text{-C}_5\text{Me}_5)$  [180];  $\text{ReO}(\text{OCOCPh}_2\text{O})(\eta\text{-C}_5\text{Me}_5)$   
[181];  $\text{Re}(\text{CO})_2(\eta^2\text{-PhC}\equiv\text{CPh})(\eta\text{-C}_5\text{H}_5)$  [182];  $[\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2\text{-}\mu\text{-}\eta^2, \eta^2\text{-C}_6\text{H}_6$   
[183];  $\text{Mn}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  [186];  $\text{Re}(\text{CO})_2(\text{S}_2\text{O})(\eta\text{-C}_5\text{Me}_5)$  [198];  
 $[\text{ReMe}(\text{NO})(\text{PMe}_3)_4]\text{C}_5\text{H}_5$  [201];  $\text{Re}(\text{COMe})(\text{NO})(\text{PMe}_3)_2\text{C}_6\text{H}_4\text{OCORE}(\text{Me})(\text{NO})(\text{CO})(\text{PMe}_3)_2$   
[202];  $\text{Re}(\text{NO})(\text{PPh}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$  [203];  $(\text{SR}, \text{RS})\text{-Re}(\text{NO})(\text{PPh}_3)(\text{COCHMeCH}_2\text{Ph})\text{-}$   
 $(\eta\text{-C}_5\text{H}_5)$  [208];  $\text{Re}_2(\mu\text{-H})(\mu, \eta^2\text{-C}_7\text{H}_7)(\text{CO})_8$  [211];  $\text{ReOI}(\text{MeC}\equiv\text{CMe})_2$  [212];  
 $\text{Mn}(\text{dmpe})_2(\eta^3\text{-C}_5\text{H}_7)$  [216];  $\text{Mn}(\text{CO})(\text{dppe})(\eta\text{-1-PhC}_6\text{H}_6)$  and  $[\text{Mn}(\text{CO})(\text{dppe})\text{-}$   
 $(\eta\text{-1-PhC}_6\text{H}_6)]\text{PF}_6$  [224];  $\text{Mn}(\text{NO})(\text{CO})_2(\eta^4\text{-C}_6\text{H}_8)$  and  $\text{Mn}(\text{NO})(\text{CO})_2(\eta^4\text{-1-Me-2-Ph-4-}$   
 $\text{COPh-C}_6\text{H}_5)$  [226];  $[\text{Mn}(\text{CO})_3(\eta^6\text{-C}_{18}\text{H}_{24})]\text{BF}_4$  [232];  $\text{Mn}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_8\text{PPh}_3)$  [233];  
 $\text{PdCl}_2(\text{L})_2$ , for  $\text{L} = \text{Mn}(\text{CO})_2(\text{PPh}_3)(\eta\text{-C}_4\text{H}_4\text{N})$  [236];  $[\text{Re}_2\text{Cl}_2(\mu\text{-Cl})(\mu\text{-CNHBU}^t)\text{-}$   
 $(\text{CNBU}^t)_2(\text{dppm})_2]\text{PF}_6$  [242];  $\text{Mn}(\text{NO})_3(\text{CO})$ , electron diffraction [245].

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