MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1986 *

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CONTENTS

I. INTRODUCTION

A conscious attempt has been made to be concise in writing this Annual Surveys article. Primarily, this has been done by avoiding repetition when reporting on various papers in two or more sections, by being more brief in reporting on each paper, and by decreasing the number of figures. In addition, Diss. Abstr. has been omitted from coverage (about 20 citations per year.) Readers will note that there are 206 articles referenced; the 1985 Annual Surveys for this group of elements contained 247 references.

The 1984 [1] and 1985 [2] Annual Surveys on this group have appeared in print since the last survey. Several individuals have written review articles pertinent to this area, including the following: Herrmann [3] (rhenium oxo species), Kochi [4] (electron transfer and radicals in organometallic chemistry), Kelly and Woollins [5] (-NS and -NSX compounds, many with rhenium), and Chivers and Edelmann [6] (-NS ligand chemistry), Kreiter ($M_2(CO)_{10}$-diene photochemistry [7].

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* Previous review see J. Organomet. Chem., 318(1987)121-156.

II. NEUTRAL, ANIONIC, AND CATIONIC METAL CARBONYL DERIVATIVES

Using pulsed time resolved photoacoustic calorimetry, Vaida et al [8] have determined a value for the metal-metal bond energy in $Mn_2(CO)_{10}$, 38.0 ± 5 kcal. Frequency and time resolved infrared fluorescence studies on $Mn_2(CO)_{10}$ have been reported in a communication [9]. Papers on pulsed laser photolysis of this species [10], and on its gas phase infrared spectrum have been published. Parameters for recombination kinetics for the radical species $Mn(CO)_5$, generated from $Mn_2(CO)_{10}$ by laser photolysis [11, 12], have been determined. A similar study was carried out with species containing bidentate ligands bridging two metals, $Re_2(CO)_8(L^\wedge L)$, ($L^\wedge L = R_2P(CH_2)_nPR_2$, R = Me, Ph, Cy, n = 2 —> 6) [13]. In another paper, a study on the flash photolysis of $Re_2(CO)_8(L)_2$ (L = CO, PR_3, $P(OR)_3$) was detailed with the monometallic radical which is formed being allowed to react with halocarbons and tri-n-butyltin hydride [14].

A single crystal x-ray diffraction study on $MnRe(CO)_{10}$ revealed a metal-metal bond distance of 2.909 Å [15]. This is shorter, by about 0.05 Å, than a value reported earlier for this compound and rather close to the distance between metals in $Mn_2(CO)_{10}$. The synthesis of $MnRe(CO)_{10}$ containing ^{13}CO enrichment in carbonyls bonded to rhenium was accomplished by reaction of labeled $Re(^*CO)_5O_3SCF_3$ and $K[Mn(CO)_5]$. Rates of migration of ^{13}CO between the metals were then measured [16]. The PdO catalyzed synthesis of $(CO)_5MnRe(CO)_4(CNR)$ (R = Cy, i-Pr, t-Bu, xylyl) has been published [17]. Photolysis of $MnRe(CO)_{10}$ in a matrix produces $MnRe(CO)_9$ which was determined by IR to contain bridging carbonyl groups [18].

Photolysis of $Mn_2(CO)_{10}$ and 1,2-bis-diethylphosphinoethane (depe) produces an equilibrium mixture of $Mn(CO)_3$(depe) and its dimer, the latter in larger amounts. A facile reaction with alkyl halides traps the monomer [19]. The reaction of $Mn_2(CO)_{10}$ with $(EtO)_2POP(OEt)_2$ (tedip) gives $Mn_2(CO)_8$(tedip) and $Mn_2(CO)_6(tedip)_2$, which were isolated, along with other uncharacterized products [20]. A reaction of the parent carbonyl compound with $Me_2PCH_2PMe_2$ (dmpm) gives mer, fac- and mer, mer- isomers of the compound $Mn_2(CO)_6(dmpm)_2$; both species can be oxidized to form ESR active monocations [21]. A mechanistic study of the photolytic disproportionation of $Mn_2(CO)_{10}$ with oxygen and nitrogen ligands has been published; 19 electron intermediates are postulated for this reaction which yields either $[MnL_6]^{2+}$ or $[Mn(CO)_3(L)_3]^+$ along with $[Mn(CO)_5]^-$ [22]. Electrochemical techniques were chosen to probe mechanisms of reduction and oxidation of $Mn_2(CO)_{10}$, $Mn(CO)_5$ being implicated as an intermediate [23]. Free radical reactions are reported to occur when $Re_2(CO)_{10}$ and CCl_4 or cyclohexane are photolyzed [24].

A crystallographic study on trans-$Re_2(CO)_9(L)$ (L = a carbene ligand, $=\overline{CCH_2CH_2TiCp_2O}$) and synthesis of manganese and rhenium compounds from the parent carbonyl and $Ti(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)$ is noted [25]. A report on Raman and infrared spectra for $Re_2(CO)_{10-n}(CNR)_n$ (n = 1—>4; R = Me, t-Bu, benzyl) has appeared [26]. It is found that $M_2(CO)_{10}$ (M = Mn, Re) and $Re_2(CO)_8(PPh_3)_2$ catalyzes ring chlorination of toluene [27].

An ionic complex, $[Re(CO)_3(L{\wedge}L{\wedge}L)]Br$, forms from $ReBr(CO)_5$ and 1,4,7-triazanonane; further chemistry of this species will be described later in this review [28]. A simple preparation of $[M(CO)_5(SO_2)]AsF_6$ (M = Mn, Re) has been reported from the metal carbonyl and AsF_5 in liquid SO_2 [29]. An unstable complex with a MeSSMe ligand, $[Mn(CO)_5(MeSSMe)]^+$, is detected in solution [30]. Cis, trans-$[Mn(CO)_2(dipy)\{P(OPh)_3\}_2]^+$ reacts with halide ions with phosphite displacement. A synthesis of $[\{Mn(CO)_3(bipy)\}_2(\mu\text{-}CN)]PF_6$ is found in this paper [31]. Reduction of various $[Mn(CO)_5(L)]^+$ cations (L = CO, MeCN, py, PR_3) gives either $Mn_2(CO)_{10}$ (in the case L = CO) or hydride species, $Mn(CO)_4(L)H$ [32].

III. METAL CARBONYL HALIDES AND DERIVATIVES

Syntheses of various manganese and rhenium carbonyl halides upon photolysis of the parent metal carbonyl in the presence of a halocarbon have been noted already [14, 19, 24]. Syntheses of several complexes of the formula $Cl(CO)_3Re(\mu\text{-}bipym)Re(CO)_3Cl$ (bipym = several bipyrimidines) were carried out and the absorption and emission spectra of these species recorded [33]. The compounds $ReX(CO)_4(PPh_2SiMe_3)$ (X = Cl, Br) were prepared from $Re(CO)_5X$ and the silylphosphine; their reactions with water produce $Re(CO)_4(PPh_2H)X$. The silylphosphine complex reacts further with $MBr(CO)_5$ to give $MRe(\mu\text{-}Br)(\mu\text{-}PPh_2)(CO)_8$ (M = Re, Mn) [34]. The compounds $MnBr(CO)_4(PPhMeCO_2R)$ (R = CCl_3, $CHCl_2$, CH_2Cl) were prepared; magnesium reduction of the $-CH_2Cl$ derivative causes cyclization of metal and ligand, giving $(OC)_4\overline{Mn(CH_2OCOP}PhMe)$ [35].

The reaction of $ReCl(CO)_5$ with $AgReO_4$ gives $Re(CO)_5OReO_3$; from infrared data on this species one concludes the ReO_4^- ligand is a good electron acceptor [36]. The reaction of $ReCl(CO)_5$ with $KB(OPr^i)_3H$ gives a metal-formyl species whose reactions were further studied. Halide loss from $[Re(Br)(CHO)(CO)_4]^-$ is facile giving $ReH(CO)_5$; with phosphines, halide displacement occurs giving $Re(CHO)(CO)_4(PR_3)$ [37]. Light induced reduction of CO_2 is catalyzed by $ReCl(CO)_3(bipy)$ [38]. Isomerization of $MnBr(CO)_2\{P(OPh)_3\}(dppm)$ (trans carbonyls) to the all cis isomer is oxidatively catalyzed, occurring via the one electron oxidation product [39]. The reaction of $ReCl(CO)_5$ and 1,4,7-triazanonane was mentioned previously [28].

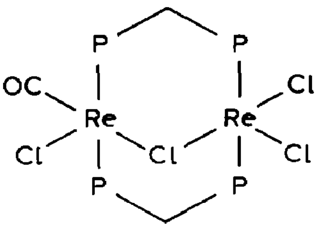
The reaction between $Ir(\eta\text{-}C_5Me_5)(CO)_2$ and $Re_2(\mu\text{-}Br)_2(CO)_8$ in dichloromethane (60°C, 5 d) yields $[Ir(\eta\text{-}C_5Me_5)(CO)_2(CH_2Cl)]^+$ and $[Re_2(\mu\text{-}Cl)_n(\mu\text{-}Br)_{3-n}(CO)_6]^-$; a crystal structure study was carried out on the chloride salt [40]. The formation of $[Mn_2(\mu\text{-}I)(CO)_{10-2n}(dppm)_n]^+$ from the reaction of $I(py)_2^+$ and the appropriate dimanganese precursor is noted [41].

Several papers have presented work on complexes of manganese with pseudohalide ligands (CN^-, SCN^-). Cited earlier in this article was a paper on reactions of cis, trans- $[Mn(CO)_2(bipy)\{P(OPh)_3\}_2]^+$ with X^-, formation of $Mn(CO)_2(bipy)\{P(OPh)_3\}X$ (X = CN, SCN, I, Br) being the result [31]. From the same research group, another paper describes cyanide and thiocyanate complexes formed from $MnBr(CO)_3(dppm)$ and KCN or KSCN [42].

A ^{55}Mn NMR study on various manganese carbonyl halides is identified [43].

A collection of papers concerning phosphine-rhenium halides is noted next. Carbonylation of $Re_2Cl_4(PEt_3)_4$ gives a complicated mixture of products. Separated and then characterized by x-ray crystallography were the compounds $ReCl_2(CO)_2(L)_2$, mer-$ReCl(CO)_3(L)_2$, cis-$ReCl(CO)_4(L)$, and trans-$ReCl_4(L)_2$ (L = PEt_3) [44]. Addition of isocyanides to $Re_2X_4(dppm)_2$ gives $Re_2Cl_4(dppm)_2(CNR)$ (X = Cl, Br; R = Me, t-Bu, xylyl) [45]. In the presence of PF_6^-, these reagents react to produce $[Re_2Cl_3(dppm)_2(CNR)_2]PF_6$ or $[Re_2Cl_3(dppm)_2(CNR)_3]PF_6$; further reactions, electrochemistry, spectra, and a crystal structure are reported in this paper [46]. Carbonylation of the precursor was shown to produce $Re_2Cl_4(dppm)_2(CO)$, I, (crystal structure determination); further reactions of the product with xylyl isocyanide (crystal structure of $Re_2Cl_4(dppm)_2(CO)(CNxy)$) and with nitriles in the presence of $TlPF_6$ were also carried out [47]. Isocyanides were shown to reduce $[Re_2Cl_4(dppe)_2]PF_6$ and then react to give $[Re_2Cl_3(dppe)_2(CNR)]PF_6$, II, which are oxidized by $NOPF_6$ forming $[Re_2Cl_3(dppe)_2(CNR)](PF_6)_2$. Related compounds are formed from the starting material and nitriles in the presence of $TlPF_6$ [48].

Sections VIII and IX identify further articles on arene- and cyclopentadienyl-metal complexes with halide ligands.



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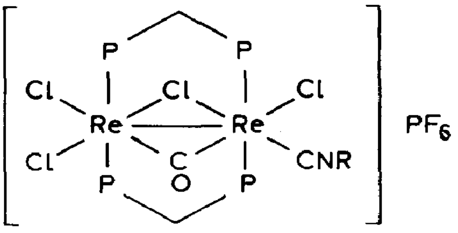


II

IV. METAL HYDRIDE COMPLEXES

Norton et al [49] have obtained pKa values for $ReH(CO)_5$ (21.1) and $MnH(CO)_5$ (15.1) in acetonitrile.

The reaction between $MnH(CO)_5$ and $AuMe(PPh_3)$ yields $(PPh_3)AuMn(CO)_5$ [50]. A radical mechanism has been proposed for reactions of $MnH(CO)_5$ and dienes [51] and allenes [52]. A kinetic study on the insertion of CO_2 into the Re-H bond in fac-$ReH(CO)_3(bipy)$ has reached publication [53].

Synthesis of rhenium carbonyl hydrides by flash photolysis of $Re_2(CO)_8(L)_2$ in the presence of tri-n-butyltin hydride [14] and the formation of $ReH(CO)_5$

from $KB(OPr^i)_3H$ reduction of $ReBr(CO)_5$ [37] were reported earlier in this review. Electrochemical reduction of $[Mn(CO)_5(L)]^+$ (L = CO, NCMe, py, phosphines) results in formation of $MnH(CO)_4(L)$ [32]. The complex $[Re_2(CO)_9(CHO)]^-$ decomposes to $[Re_2(H)(CO)_9]^-$ by a radical chain process [54]. Photolysis of $Re_2(CO)_{10}$ and olefins gives $Re_2(\mu\text{-}H)(\mu\text{-}CH{=}CHR)(CO)_8$ (R = H, Ph) as primary products with smaller amounts of other species [55]. The compound $MnH(CO)_4(PPh_2CH_2CH_2CHO)$ was synthesized from $MnH(CO)_5$ by carbonyl substitution; it was found not to cyclize. The product that would have been obtained from cyclization is known, formed in a different sequence of reactions [56]:

$$\overline{Mn(CO)_4(COCH_2CH_2NH_2)} + BH_3{:}thf \longrightarrow \overline{Mn(CO)_4(CHOHCH_2CH_2NH_2)}$$

Three papers report mechanistic studies on reactions between manganese or rhenium carbonyl hydrides and alkylmanganese or rhenium carbonyls which produce aldehydes and the dinuclear metal carbonyl [57, 58, 59].

Reactions between $Mn_2(CO)_{10}$ and two secondary phosphines, PCy_2H [60], and $P(NPr^i{}_2)_2H$ [61], are reported, products being the dinuclear species $Mn_2(\mu\text{-}H)(\mu\text{-}PR_2)(CO)_8$. Dinuclear complexes containing hydride ligands bridging between manganese and either platinum [62] or molybdenum [63] are described in the cited papers. Photolysis of the latter species with an olefin (ethylene, cyclohexene) led to M-H addition to this organic substrate resulting in formation of a coordinately unsaturated species which reversibly adds CO, vis:

$$(CO)_3Mn(\mu\text{-}COR)(\mu\text{-}PPh_2)Mo(CO)_2(\eta\text{-}Cp) + CO \longrightarrow$$
$$(OC)_4Mn(\mu\text{-}H)(\mu\text{-}COR)Mo(CO)_2(\eta\text{-}Cp)$$

Further chemistry of polynuclear rhenium carbonyl hydride anions has been presented. Reaction of $Et_4N[Re_3(\mu\text{-}H)_4(CO)_{10}]$ with phosphines has been shown to produce $Et_4N[Re_3(\mu\text{-}H)_2(CO)_{10}(PR_3)_2]$; a single crystal x-ray diffraction study on the PPh_3 derivative defined a structure for this anion based on the known $[Re_3(\mu\text{-}H)_2(CO)_{12}]^-$ structure with phosphines in non-equivalent equatorial positions [64]. Further reactions of the $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ anion are described in another paper; prepared and characterized were $Et_4N[Re_3(\mu\text{-}H)_4(CO)_8(L)_2]$ (L = NCMe, py, PPh_3). Structures of the last two complexes were defined by x-ray diffraction also; these species have the $[Re_3(\mu\text{-}H)_4(CO)_{10}]^-$ structure with the non-carbonyl ligands residing on axial positions of the unique rhenium [65]. The third paper by this research group characterized $Et_4N[Re_3(\mu\text{-}H)_4(CO)_9(L)]$ (L = MeCN, Me_3NO) and $Et_4N[Re_3(\mu\text{-}H)_3(CO)_9(\mu^3\text{-}OH)]$ (structure determined for the last species) as products of reactions of the same precursor with Me_3NO and poor donor ligands [66].

Related work, also from this group, includes papers on the reaction of $(Et_4N)_2[Re_3(\mu\text{-}H)_4(CO)_{10}]$ with $AuCl(PPh_3)$ [67], and on the reaction between

$Et_4N[ReH_2(CO)_4]$ with $Re_3(\mu\text{-}H)_3(CO)_{10}(NCMe)_2$ [68]. The product of the former is $Et_4N[Re_3(\mu\text{-}H)_3(\mu\text{-}AuPPh_3)(CO)_{10}]$; from the latter reaction the product $Et_4N[Re_4(\mu\text{-}H)_5(CO)_{14}]$ is obtained. Both were characterized by crystallography.

The infrared spectrum [69] and Raman spectrum [70] of $Mn_3(\mu\text{-}H)_3(CO)_{12}$, and the vibrational spectra of $Re_3(\mu\text{-}H)_3(CO)_{12}$ [71] are found in a series of papers in Inorg. Chem. Desorption CI mass spectra of ten rhenium compounds have been reported [72]. A molecular beam study on the reaction of $[Mn(CO)_3]^-$ and PH_3 is noted [73].

Refer to Sections VIII and IX for additional hydrides of these metals (cyclopentadienyl, cyclohexadienyl, and arene-metal compounds).

V. COMPLEXES WITH CARBON LIGANDS

Many references to complexes in this group which are derived from cyclopentadienyl- or arene-metal carbonyls are found in Sections VIII and IX and are not cross-referenced here.

A reaction of $MnCl_2(thf)_2$ with $PhSCH_2Li$, followed by addition of tetramethylethylenediamine (tmeda) gives the compound $Mn_2(\mu\text{-}Cl)_2((tmeda)_2(CH_2SPh)_2$ [74]. Synthesis of the compound $Re_2(\mu\text{-}O)_2(O)_2(Me)_2$ was accomplished by reaction of $ReOCl_3(PPh_3)_2$ and $ZnMe_2$ [75]. Structures of both products were determined by single crystal x-ray diffraction methods.

The reaction of $[Re(CO)_5]^-$ with several diimides followed by protonation yields $Re(CO)_4(C(=NHR)NRCO)$. Addition of a further proton yields a diaminocarbene complex which eliminates amine to give an isocyanide complex as shown below [76]:

$$[Re(CO)_5]^- + PhN{=}C{=}NR + H^+ \longrightarrow Re(CO)_4\{C(=NPh)NRCO\}\ (+H^+) \longrightarrow$$

$$[Re(CO)_5(C\{NHR\}\{NHPh\})]^+ \longrightarrow [Re(CO)_5(CNPh)]^+ + RNH_2$$

(R = i-Pr, t-Bu)

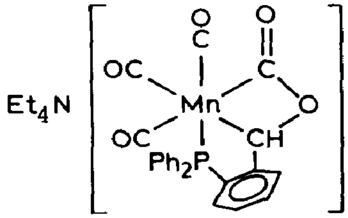
A kinetic study on the reactions between $[M(CO)_5]^-$ and C_6F_6 and C_6F_5CN has appeared [77]. Syntheses of allyl [51], -vinyl [55]], and $-CO_2H$ [53] derivatives of manganese and rhenium were cited earlier.

Gladysz, et al [78] have used the reaction between $MR(CO)_5$ (M = Mn, Re) and PPh_2SiMe_3 to prepare $M(CO)_4(CR\{OSiMe_3\}PPh_2)$. and this complex hydrolyzes to give $M(CO)_4(CR(OH)PPh_2)$. Another hydroxyalkyl-rhenium complex was described in a separate paper [79]. Synthesis of $Re(CO)_4(CH_2Ph)(PPh_2C_6H_4CH_2OSiMe_3)$ was first carried out; hydrolysis using Et_4NF gave an anionic species (whose crystal structure was established, III) which hydrated on a silica gel column, as shown below:

$$Re(CO)_4(CH\{OSiMe_3\}C_6H_4PPh_2) \longrightarrow III \longrightarrow Re(CO)_4(CH(OH)C_6H_4PPh_2)$$

An alternative synthesis of this species involving borane reduction of an acylrhenium complex was also mentioned. A third reference from this research group concerning a hydroxyalkyl complex is also noted [56].

Oxidative cleavage (Ce^{4+}, CD_3CO_2D) and halogen cleavage of the carbon manganese bond in $Mn(CO)_4(C_6H_4COMe)$ has been reported [80]. Addition of $PhPMe_2$ to $Os_3(\mu\text{-}H)(CO)_{10}(C_3Ph_2)Re(CO)_4$ produced the rearranged product, IV, shown below [81]. A paper describing 3 + 2 cycloadditions of $Mn(CO)_5CH_2C{\equiv}CH$ has appeared [82].



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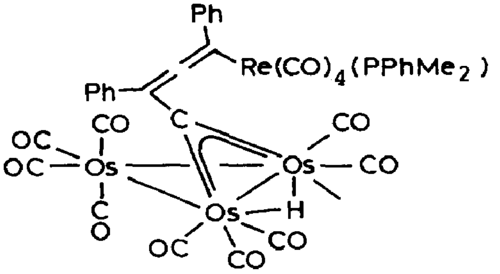


IV

Two isomers of $Mn(CO)_4Me$ were identified by infrared data, this species forming upon photolysis of $Mn(CO)_5Me$ in a low temperature matrix [83]. A monohapto to trihapto rearrangement of gaseous allylmanganese carbonyl ions was postulated from mass spectrometry data [84]. Two other papers contain information on mass spectra of mixtures of $Mn(CO)_5CH_2CH{=}CH_2$ and $C_2(CN)_4$ [85, 86]. Kinetic data on the reaction of $Mn(CO)_3(diars)Me$ and trimethylphosphite are reported [87]. Mono- and di- orthometallation of $PhCH{=}N\text{-}N{=}CHPh$ is the subject of a study [88]. Infrared spectra of $Mn(CO)_5(^{12}CH_3)$ and $Mn(CO)_5(^{13}CH_3)$ were reported [89]. The phosphorus-31 chemical shift in $Mn(CO)_4(CH_2(CH_2)_nPPh_2)$ correlates with steric restraints, ie., with the value of n [90]. A theoretical study on $Mn(CO)_4(CX)R$ species ($X = O, S, CH_2$; $R = H, Me$) is noted [91].

Two papers dealing with metal-formyl species were cited earlier [37, 54] as were three papers on formation of aldehydes from reactions of metal hydrides with metal acyl species [57, 58, 59]. It is possible to convert $Mn(CO)_5COtol$ to $Mn(CO)_5CO^*CH_2tol$ using H_2 and $^*CO$ under pressure, the asterisk identifying carbon-13 from labelled carbon monoxide [92].

Gladysz et al [93] have carried out $LiBEt_3H$ reduction of $Mn(CO)_5COCOPh$, characterizing by x-ray crystallography the initial anionic product, V, as a PPN^+ salt. This species reacts with acid or Me_3SiCl with ring opening. Decarbonylation of the hydroxyacyl species yields $PhCHO$ and $MnH(CO)_5$; decarbonylation of the silylacyl- complex gives $Mn(CO)_5CHPhOSiMe_3$ from which aldehyde and metal carbonyl hydride are formed on hydrolysis.

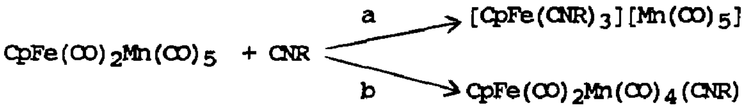
Decarbonylation of $(OC)_5MnCOCF_2CF_2COMn(CO)_5$ occurs with rearrangement to

$Mn_2(\mu\text{-}CF_2)_2(CO)_8$; this product was subject to a crystal structure determination [94]. Davis and Lukehart [95] have shown the $Re(CO)_4(CMeO)_2H$ can be derivatized in a manner making it suitable for use as a heavy metal labeling reagent; a related paper from this group reports adapting another complex of this type for derivatization of sulfhydryl and amino groups [96].

VI. DERIVATIVES OF METALS AND METALLOIDS

Special interest in complexes with different metals has continued through 1986. There are a number of interesting papers in this section.

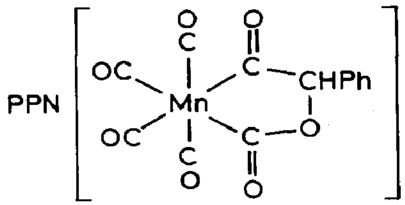
Rhodium octaethylporphyrin dimer and $Mn_2(CO)_{10}$ undergo a con-proportionation to form the bimetallic species, $(OEP)RhMn(CO)_5$. With CO and hydrogen, this compound is converted to $MnH(CO)_5$, $Rh(OEP)H$, and $Rh(OEP)CHO$ [97]. The reaction of $CpFe(CO)_2Mn(CO)_5$ with several isocyanides has been studied. In the dark, in benzene, ionic products of the formula $[CpFe(CNR)_3]^+[Mn(CO)_5]^-$ (R = t-Bu, xylyl) are formed; in contrast, in acetonitrile with added trimethylamine oxide, one can obtain $CpFe(CO)_2Mn(CO)_4(L)$. The latter type of reaction was also shown to occur with diphenylmethylphosphine and trimethylphosphite, and the products of these reactions could also be obtained from reactions between $[CpFe(CO)_2]_2$ and $[Mn(CO)_4(L)]_2$. Rhenium-iron analogues were also mentioned [98].



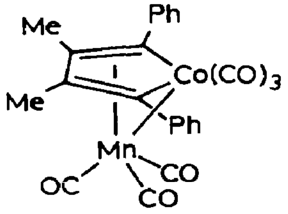
a) dark, in benzene; b) MeCN, $ONMe_3$, also PPh_2Me, $P(OMe)_3$

The reaction of $Mn(CO)_5CBr_3$ and $PPN[Co(CO)_4]$ gives $MnCo_2(CO)_9(\mu^3\text{-}CO)$ [99]. Compound VI, shown below, was obtained from $CoMn(CO)_9$ and $PhC{\equiv}CMe$ [100]. Both cobalt-manganese compounds were subjects of crystal structure determinations.

Three papers from Jeffery et al [101, 102, 103] report on reactions of $ReM(CO)_9(Ctol)$ (M = Cr, Mo, W). Reduction by $KBH(Bu^i)_3$, followed by metathesis gives $PPN[ReM(\mu\text{-}CHtol)(CO)_9]$ (structure of W compound determined) and these complexes were subject to further reactions [101]. The reaction of $ReCr(CO)_9(Ctol)$ with $Fe_2(CO)_9$ gives trimetallic $ReCrFe(\mu\text{-}Ctol)(\mu\text{-}CO)(CO)_{11}$ (structure determined) [102], while species with 5 metal atoms (three different metals), $Re_2M_2M'(\mu\text{-}Ctol)(CO)_{18}$, arise in reactions of the precursor with either $Pt(\eta\text{-}C_2H_4)_3$ or $Ni(COD)_2$. The third listed paper also describes trimetallic complexes, products of reaction of these precursors with $Pt(PMe_3)_2(\eta\text{-}C_2H_4)$ or $Pt(PCy_3)(\eta\text{-}C_2H_4)_2$ [103].



V



VI

A series of compounds with platinum and manganese atoms were prepared starting with $(OC)_3Mn(\mu\text{-dppm})_2PtCl$. Reactions of this species with $PhC{\equiv}CLi$, $NaBH_4$, $CNBu^t$, and with CO + $TlPF_6$ are noted [104]. Molybdenum-rhenium complexes were the products of reactions between $[CpMo(CO)(PR_3)(RC{\equiv}CR')]^+$ and $[Re(CO)_5]^-$ (crystal structures on two compounds, including VII) [105].

Several papers referenced earlier contribute additional examples in this area [40, 62, 63, 81].

Fac-$Mn(CO)_3(dppe)C{\equiv}CBu^t$, CuCl, and $TlPF_6$ react to give the product, $[\{Mn(CO)_3(dppe)C{\equiv}CBu^t\}_2Cu]PF_6$, a bis-alkyne-copper (I) complex whose structure was determined [106]. Along with a gold-manganese [50] and a gold-rhenium [67] complex already referenced are two other references to rhenium cluster compounds containing gold, papers on $(Ph_4As)_2$ $[Re_7C(CO)_{21}Au(PPh_3)]$ [107] and $[Au_4ReH_4(PPh_3)_7]PF_6$ [108]. The synthesis of $(PPh_3)_2(C_6Cl_5)PtMn(CO)_5$ was described [109] as was the synthesis of a uranium-rhenium species, $(PPh_3)_2ReH_6UCp_3$ [110].

A report on boron-manganese complexes, $\mu,\eta^5C_4H_4BR[Mn(CO)_3]_2$, (R = Me, Ph) has been published [111]. Various manganese-tin compounds of the form $(OC)_4(L)MnSnCl_2\text{-}M$ (M = $Co(CO)_4$, $Fe(CO)_3(NO)$, L = CO, $PPhEt_2$) were described by Behrens et al [112]. Sodium bis-trimethylsilylamide reacts with $Ph_2M[Mn(CO)_5]_2$ (M = Sn, Pb); following addition of $[Me_3O]BF_4$ one can isolate $Ph_2M[Mn(CO)_4(CNMe)]_2$ [113]. Cleavage of the acyl group in $Mn(CO)_4(PPh_3)COMe$ with either Bu_3SiH or Ph_3SnH gives MeCHO and $Mn(CO)_4(PPh_3)MR_3$ as products [114]. A previously cited reference [37] mentions $Re_2(\mu\text{-}Bu_2SnOSnBu_2)(CO)_8$. Reactivity of $Mn(CO)_5MPh_3$ (M = Si, Ge, Sn) in the gas phase was studied by CI mass spectrometry techniques [115].

See Section VIII for additional references pertinent to this topic.

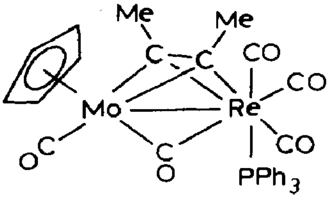
VII. COMPLEXES WITH GROUP VA AND VIA LIGANDS

Nitrogen The synthesis of nitrogen bonded succinimido compounds including $Mn(CO)_5(\overline{NCOCH_2CH_2CO})$ from $MnBr(CO)_5$ and thallium succinimide was reported [116]. Anionic manganese complexes with bibenzimidazolate ligands were prepared from $K_2bibzim$ and $[MnBr_2(CO)_4]^-$; subsequent reactions of this species with phosphorus ligands (carbonyl substitution) and methyl iodide (alkylation at uncoordinated nitrogen) are noted [117]. Complexes of the form $M(CO)_4(O^{\wedge}N)$ were described, where $O^{\wedge}N$ is the anion of an alpha amino acid (histadinate, ornithinate, lysinate) [118].

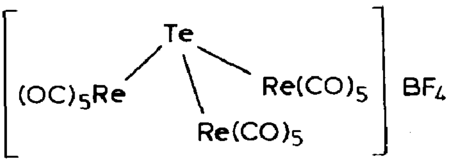
Phosphorus Four references to complexes with phosphido ligands bridging two metals were cited earlier [34, 60, 61, 63]. An additional reference to a biphosphole complex of manganese is noted [119].

Oxygen The bimetallic complex $Re(CO)_5OReO_3$ was identified earlier in this review [36]. The anionic complex, $[CpCo\{PO(OEt)_2\}_3]^-$, serves as a tridentate ligand, bonding via three phosphonate oxygens to a rhenium tricarbonyl group [120].

Sulfur, Selenium, Tellurium Reactions of $PPN[Mn(CO)_5]$ with disulfides have been studied. The nucleophilic anion initially displaces RS^- from the organosulfur compound to give $Mn(CO)_5SR$ (R = Me, Ph) which is not isolated due to subsequent reactions with thiolate ions forming $[Mn_2(\mu\text{-}SR)_3(CO)_6]^-$ [121]. A second paper describes reactions of $[Me_2SSMe]BF_4$ as an RS^+ donor toward $[Mn(CO)_5]^-$ and $Mn(CO)_5(SR)$ [30]. The reaction of $Re(CO)_5BF_4$ with an X^{2-} ion results in formation of the interesting species $[X\{Re(CO)_5\}_3]BF_4$ (X = S, Se, Te); a crystal structure study was carried out on the tellurium complex, VIII. Reported also was a hydrolysis product of this species, $Re(CO)_5OBF_3$ [122]. The preparation and characterization of $(OC)_5MnS_2CC_6H_4CS_2Mn(CO)_5$ has been described [123]. The reaction of $RPSCl_2$ with $Mn_2(CO)_{10}$ in the presence of Mg gives $RPS_2Mn_2(CO)_9$ [124]. Thionyl chloride was shown to react with $MnH(CO)_4(PPh_3)$ giving $[Mn(CO)_4(PPh_3)]_2SO$ which is oxidizable to $[Mn(CO)_4(PPh_3)]_2SO_2$ [125].



VII



VIII

This section was significantly shortened due to deferral of additional references on cyclopentadienyl-metal species with group VA and VIA ligands to Section VIII.

VIII. DERIVATIVES OF $M(CO)_3(\eta\text{-}C_5H_5)$ AND $[M(NO)(CO)_2(\eta\text{-}C_5H_5)]^+$

As seen in recent years, this section contains the largest fraction of references in this review.

$Mn(CO)_3(\eta\text{-}C_5H_5)$ derivatives The reaction between pentamethylcyclopentadiene and $Mn_2(CO)_{10}$ was found to give 77% $Mn(CO)_3(\eta\text{-}C_5Me_5)$ and 23% $Mn(CO)_3(\eta\text{-}C_5Me_4H)$

[126]. The use of $TlC_5H_4CF_3$ in the preparation of $Mn(CO)_3(\eta\text{-}C_5H_4CF_3)$ has been reported [127], as has use of $Tl_2[C_5H_4\text{-}C_5H_4]$ to prepare $(OC)_3Mn(\mu,\eta\text{-}C_5H_4C_5H_4)\text{-}Mn(CO)_3$ [127, 128]. The synthesis of $(OC)_3Mn(\mu,\eta\text{-}C_5H_4CH_2C_5H_4)Mn(CO)_3$ from a dithallium salt of the appropriate hydrocarbon is also noted [129]. A bimetallic species, $Me(OC)_3W(\mu,\eta\text{-}C_5H_4\text{-}C_5H_4))Mn(CO)_3$ was prepared from $WMe(CO)_3\text{-}(\eta\text{-}C_5H_4\text{-}C_5H_4)$, NaH, and $Mn_2(\mu\text{-}Br)_2(CO)_8$ [130]. Optically active species $Mn(CO)_3(\eta\text{-}C_5H_4R^*)$ have been characterized [131]. SCCC calculations for $Mn(CO)_3\text{-}(\eta\text{-}C_5H_4XPh)$ ($X = CO$, CH_2, CH_2CH_2) are noted [132].

Monosubstituted derivatives $Mn(CO)_2(L)(\eta\text{-}C_5H_5)$ ($L = PPh_2\text{-}C_6H_5Cr(CO)_3$ [133] and sulfur bonded $Co(PMe_3)(S{=}C{=}CR_2)(\eta\text{-}C_5H_5)$ [134]) were isolated from appropriate reactions of the metallic species and $Mn(CO)_3(\eta\text{-}C_5H_5)$ in THF. Two compounds, $Mn(CO)_2(Ph_2PC{\equiv}CPPh_2)(\eta\text{-}C_5H_5)$ and $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2(\mu\text{-}Ph_2PC{\equiv}CPPh_2)$, were prepared using similar methodology and the crystal structure of the latter was determined [135]. Likewise, mono- and di-coordinated pyrazine derivatives, $Mn(CO)_2(N\hat{}N)(\eta\text{-}C_5H_5)$ and $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2(\mu\text{-}N\hat{}N)$ ($N\hat{}N = C_4H_4N_2$) have been made; methylcyclopentadienyl and pentamethylcyclopentadienyl analogues are also reported in this paper. These species are reducible to ESR active anions [136]. The reaction of $Bu^t{}_2C{=}C{=}S$ and $Mn(CO)_2(thf)(\eta\text{-}C_5H_5)$ in situ gives $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2(\mu\text{-}S{=}C{=}CBu^t{}_2)$; a crystal structure determination showed that the sulfur atom in the ligand bridged the two metals [137]. Similarly, the group VIA element in R_2X (X = S, Se, Te) bridges two metals in the species $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2XR_2$ (R = Me, $(CH_2)_n$ for $n = 3, 4$). These species were synthesized from a 2:1 reaction of metal complex and R_2X. A bimetallic complex of the formula $Mn(CO)_2(\eta\text{-}C_5H_5)(\mu\text{-}SMe_2)Cr(CO)_5$ was also described [138].

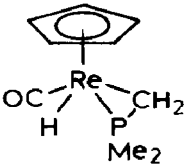
The synthesis of a mixture of $[Mn(CO)_2(\eta\text{-}C_5H_4R)]_2CH_2$ and $Mn(CO)_2(\eta\text{-}C_2H_4)\text{-}(\eta\text{-}C_5H_4R)$ (R = H, Me) from the reaction of $Mn(CO)_2(thf)(\eta\text{-}C_5H_4R)$ and $Me_2NSR({=}CH_2)({=}O)$ has been described [139].

The mono- and bis- complexes of 1,4-diethynylbenzene (DEB), $Mn(CO)_2(DEB)\text{-}(\eta\text{-}C_5H_5)$ and $[Mn(CO)_2(\eta\text{-}C_5H_5)]_2DEB$, were prepared and reactions of these species studied [140]. Reactions of $Mn(CO)_2(PH(NPr^i{}_2\}_2)(\eta\text{-}C_5H_5)$ with HBr, giving $Mn(CO)_2(PHBr_2)(\eta\text{-}C_5H_5)$, and with methanol, giving $Mn(CO)_2\{P(OMe)_2H\}(\eta\text{-}C_5H_5)$ and $Mn(CO)_2\{PH(OMe)(NPr^i{}_2)\}(\eta\text{-}C_5H_5)$, were described. The last complex was found to react with HCl to give $Mn(CO)_2(PHCl(NPr^i{}_2\})(\eta\text{-}C_5H_5)$ [141]. In a second paper, this latter complex was reported to react with $Na[Fe(CO)_2(\eta\text{-}C_5H_5)]$to form a bimetallic product, $(\eta\text{-}C_5H_5)Fe(CO)_2PH(NPr^i{}_2)Mn(CO)_2(\eta\text{-}C_5H_5)$; this species lost CO upon photolysis giving $(\eta\text{-}C_5H_5)(CO)Fe(\mu\text{-}CO)(\mu\text{-}PH(NPr^i{}_2)Mn(CO)(\eta\text{-}C_5H_5)$ [142]. A similar compound was reported to be the product in the reaction of $Na[Mn(CO)_2(SiPh_2Me)(\eta\text{-}C_5H_4Me)]$ with $FeI(CO)_2(\eta\text{-}C_5H_5)$ [143]. Also reported in this paper are gold and mercury derivatives, $Mn(CO)_2(SiPh_2Me)(M)(\eta\text{-}C_5H_4Me)$ ($M = AuPPh_3$, HgPh). Oxidation of $M(CO)_2(S_2)(\eta\text{-}C_5Me_5)$ (M = Mn, Re) using m-chloroperbenzoic acid yields $M(CO)_2(S_2O)(\eta\text{-}C_5Me_5)$; then, $M(CO)_2(S_2O_2)(\eta\text{-}C_5Me_5)$ forms on prolonged treatment with the oxidant [144]. Another compound with a bridging sulfur oxide ligand, $[Mn(CO)_2(\eta-C_5H_5)]_2SO$, was cited earlier in this review [125]. A dinuclear complex, $(\eta-C_5H_4Me)_2Mn_2(CO)_3[\mu-CO(NHCH_2Ph)N_2]$, forms in the reaction of $Mn(CO)_2(thf)(\eta-C_5H_4Me)$ and $PhCH_2N_3$; its structure was ascertained by x-ray crystallography [145]. Reactions of $Mn(CO)_2(PX_3)(\eta-C_5H_5)$ (X = Cl, Br) with $Co_2(CO)_8$ [146] and with $Fe_2(CO)_9$ [147] give the compounds $Co_3(CO)_9PMn(CO)_2(\eta-C_5H_5)$ and $Fe_3(CO)_9P_2[Mn(CO)_2(\eta-C_5H_5)]_2$, respectively; various further chemistry of these and related species was also reported in these papers. Reduction of $Mn(CO)_2(MeOC_6H_4PCl_2)(\eta-C_5H_5)$ using t-butyllithium and tmeda, followed by addition of methyl iodide, forms the phosphinylidene complex $MeOC_6H_4P[Mn(CO)_2(\eta-C_5H_5)]_2$ (structural determination); using a similar synthetic method, the complex $(\eta-C_5H_5)Mn(CO)_2(\mu-PHMePHMe)Mn(CO)_2(\eta-C_5H_5)$ was prepared from the $MePCl_2$ precursor. Its structure was also ascertained [148]. Reduction of $Mn_2(\mu-TePh)_2(CO)_4(\eta-C_5H_5)_2$ to a mono-anion and oxidation to a mono-cation was carried out, both radical species being isolated. A crystal structure determination was carried out on the cation which was found to have a lengthened metal-metal bond relative to the neutral precursor [149].

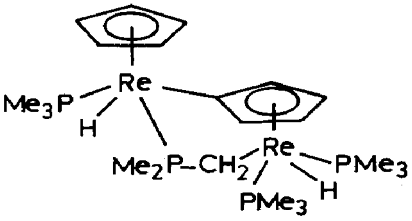
A reference to Mossbauer (^{125}Te) spectra on three tellurium manganese species [150], and a paper on ^{29}Si NMR spectra of $MnH(CO)_2(SiR_3)(\eta-C_5R_5)$ compounds [151] are noted. The latter paper also reports a neutron diffraction study on $MnH(CO)_2(SiPh_2F)(\eta-C_5H_4Me)$ and an x-ray diffraction study on $MnH(CO)(PMe_3)(SiPh_2H)(\eta-C_5Me_5)$.

Iodine reacts with $Re(CO)_3(\eta-C_5Me_5)$ to form $[ReI(CO)_3(\eta-C_5Me_5)]I_3$ which on photolysis is converted to $ReI_2(CO)_2(\eta-C_5Me_5)$. Cis- $ReX_2(CO)_2(\eta-C_5Me_5)$ is obtained when $Re(CO)_2(N_2)(\eta-C_5Me_5)$ reacts with HX (X = Cl, Br, I); upon photolysis, conversion to the trans isomer is noted. Crystal structure studies on the cis diiodide and trans dibromide were also reported here [152]. The product of the reaction of $Re(CO)_2(N_2)(\eta-C_5Me_5)$ and $[Me_3O]BF_4$ in acetone is $Re(CO)_2(\eta-Me_2C{=}CHCOMe)(\eta-C_5Me_5)$; the identity of this unexpected product was confirmed by independent synthesis from the olefin and $Re(CO)_2(thf)(\eta-C_5Me_5)$ and by a crystal structure [153]. Sulfur and selenium compounds of the formula $[Re(CO)_2(\eta-C_5Me_5)]_2(\mu-X)$ are obtained from the reaction of $Re(CO)_2(thf)(\eta-C_5Me_5)$ and the element. The selenium compound's structure was reported [154].

A two step procedure was used for synthesis of $Re(CO)(PMe_3)(N_2)(\eta-C_5Me_5)$. The known compound $[Re(CO)(NCMe)(N{=}NC_6H_4OMe)(\eta-C_5Me_5)]BF_4$ was first treated with PMe_3 and then t-butyllithium was added. This compound is very reactive, oxidatively adding benzene and reacting with N-bromosuccinimide to give $ReBr_2(CO)(PMe_3)(\eta-C_5Me_5)$. Photolysis of this compound in hexane gave IX, a product of internal addition of a C-H bond in one of the ligands to the metal [155]. The compound $Re(PMe_3)_3(\eta-C_5H_5)$, prepared from $ReCl_3(PMe_3)_3$, C_5H_6, and Na/Hg, is similarly reactive. It oxidatively adds to C-H bonds in benzene, ethylene, and saturated hydrocarbons including cyclohexane, cyclopentane, and cyclopropane. Phosphine loss accompanies this reaction. Upon photolysis, the compound also undergoes an internal oxidative addition to a phosphine ligand C-H group; the resulting product is found to dimerize slowly to the product shown below, X [156]. Photolysis of $ReH_2(PPh_3)_2(\eta-C_5H_5)$ results in a product in situ which catalyzes H/D exchange in benzene, thf, and alkanes [157].



IX



X

Neopentyllithium abstracts a cyclopentadienyl ring proton in $ReH(SiPh_3)(CO)_2(\eta-C_5H_5)$, at -78°C. This is followed by rapid migration of the silyl group to the ring to give $[ReH(CO)_2(\eta-C_5H_4SiPh_3)]^-$ which protonates (also at -78°) to give cis-$ReH_2(CO)_2(\eta-C_5H_4SiPh_3)$. The cis isomer rearranges to the trans isomer on warming to room temperature, with half life of about 12 hr. [158].

$[Re(CO)_2(NO)(\eta-C_5H_5)]^+$ Derivatives Fenske et al [[159, 160] have used MO theory to study the series of reactions in which a coordinated carbonyl group in $[Re(CO)(PPh_3)(NO)(\eta-C_5H_5)]^+$ is reduced to a methyl group.

The reaction of $[Re(CO)_2(NO)(\eta-C_5R_5)]^+$ (R = H, Me) with $Li[PR(Bu^t)(SiMe_3)]$ gives $Re(CO)(NO)(C\{=PBu^t\}OSiMe_3)(\eta-C_5R_5)$; crystal structure determinations were carried out on both the cyclopentadienyl and the pentamethylcyclopentadienyl compounds [161]. Tso and Cutler [162] have prepared and characterized two bimetallic rhenium-zirconium species, $(\eta-C_5H_5)(CO)(NO)Re(\mu-CO_2)ZrCl(\eta-C_5H_5)_2$ and $(\eta-C_5H_5)(CO)(NO)ReCH_2OZrCl(\eta-C_5H_5)_2$.

Gladysz et al continue to be actively involved in this area and six papers originate from work by this group. Addition of Me_2S, py, or PPh_3 to $[Re(NO)(PPh_3)(=CH_2)(\eta-C_5H_5)]^+$ occurs giving $[Re(NO)(PPh_3)(CH_2-L)(\eta-C_5H_5)]^+$. Thiolate ions react in the same fashion to form $Re(NO)(PPh_3)(CH_2SR)(\eta-C_5H_5)$ and these compounds were deprotonated at the methylene group [163]. Deprotonation of $[Re(NO)(PPh_3)(CH_2PPh_3)(\eta-C_5H_5)]PF_6$ with butyllithium and tmeda gives a Wittig-like species, $Re(NO)(PPh_3)(CHPPh_3)(\eta-C_5H_5)$ which was alkylated [164]. Oxidation of the same precursor using PhIO gave a formaldehyde complex, $[Re(NO)(PPh_3)(\eta-H_2C{=}O)(\eta-C_5H_5)]PF_6$, and various reactions of this species were described including aldehyde ligand displacement by acetonitrile and halide, addition of phosphines to the CH_2 group of the coordinated aldehyde, and reduction of the coordinated ligand group to a methoxy group [165]. Another paper reports selective binding of aldehydes at one enantioface and activation of the aldehyde ligand in these systems; the crystal structure of [Re(NO)-

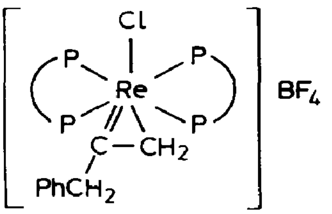
$(PPh_3)(\eta^2\text{-}PhCH_2CHO)(\eta\text{-}C_5H_5)]PF_6$ is reported in this paper [166]. Formation of various chiral products starting with $[Re(NO)(PPh_3)_2(\eta\text{-}C_5H_5)]^+$ is noted [167]. Deprotonation of $Re(NO)(COR)(PPh_3)(\eta\text{-}C_5H_5)$ (R = Me, H, CH_2Ph) using LDA occurs at the cyclopentadienyl ring and is followed by acyl transfer giving $[Re(NO)\text{-}(PPh_3)(\eta\text{-}C_5H_4COR)]^-$ which can then be alkylated with methyl iodide. In contrast, deprotonation of $Re(NO)(PPh_3)(COCH_2R)(\eta\text{-}C_5Me_5)$ occurs at the methylene group to give $[Re(NO)(PPh_3)(COCHR)(\eta\text{-}C_5Me_5)]^-$ and this anionic species alkylates at the carbanionic site [168].

IX. OTHER HYDROCARBON METAL COMPLEXES

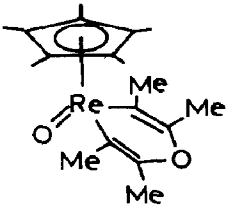
$\underline{\eta^2\text{-}C_2 \text{ and } \eta^3\text{-}C_3 \text{ Complexes}}$ Protonation of $ReCl(dppe)_2(\eta^2\text{-}H_2C{=}C{=}CHPh)$ using HBF_4 gives a product described by the figure below, XI [169]. Reference has already been made to the complexes $Re_2(\mu\text{-}H)(\mu,\eta\text{-}CH{=}CH_2)(CO)_8$ [55]. Two papers by Kreiter et al [170, 171] report on a group of (primarily) η^3-allyl-manganese carbonyls formed from reactions of $Mn_2(CO)_{10}$ and allenes. A PES study on $Mn(CO)_3(\eta^3\text{-}C_6H_9)$ was carried out, with specific interest in the activation of the C-H group bridging the ring and the metal and in the fluxionality of this species [172].

$\underline{\eta^5C_5 \text{ Complexes}}$ Cyclopentadienyl-rhenium oxo species enjoy continued interest. There is a review article for this area [3]. Lithium aluminum hydride reduction of $ReOCl_2(\eta\text{-}C_5Me_5)$ followed by addition of methanol gives a product, $ReH_6(\eta\text{-}C_5Me_5)$; this molecule is fluxional on the NMR time scale at room temperature but the fluxionality is arrested at -90°C [173]. Diphenylketene reacts with $ReO_3(\eta\text{-}C_5Me_5)$, the product $\overline{ReO(OCOCPh_2O)}(\eta\text{-}C_5Me_5)$ being obtained, and with $[ReO_2(\eta\text{-}C_5Me_5)]_2$ to give $ReO(O_2C{=}CPh_2)(\eta\text{-}C_5Me_5)$; further, the reaction of $[ReO_2(\eta\text{-}C_5Me_5)]_2$ with PhNCO gives $\overline{ReO(OCONPh)}(\eta\text{-}C_5Me_5)$. Crystal structure determinations were done on all of these products [174]. Reductive carbonylation of $ReOCl_2(\eta\text{-}C_5Me_5)$ gives $ReCl_2(CO)_2(\eta\text{-}C_5Me_5)$, while a similar reaction with $ReO(O_2C{=}CPh_2)(\eta\text{-}C_5Me_5)$ gives $Re(CO)_2(O_2CCPh_2)(\eta\text{-}C_5Me_5)$; a structural study was carried out on the latter species [175]. Formation of $ReOX_2(\eta\text{-}C_5Me_5)$ from $[ReO_2(\eta\text{-}C_5Me_5)]_2$ by reaction of HX (X = F, Cl, Br) occurs via a hydroxy bridged intermediate which can be isolated. The same paper also presents information on the reaction of $ReOCl_2(\eta\text{-}C_5Me_5)$ with trimethylaluminum, giving $ReOMe_2(\eta\text{-}C_5Me_5)$ [176]. The reaction of $ReO_3(\eta\text{-}C_5Me_5)$ with various cyclopentadienylzirconium species is reported to give either $ReOCl_2(\eta\text{-}C_5Me_5)$ or $[ReO_2(\eta\text{-}C_5Me_5)]_2$ [177]. The reaction of $ReO_3(\eta\text{-}C_5Me_5)$ with acetylenes gives first $ReO(\eta^2\text{-}RC{\equiv}CR')(\eta\text{-}C_5Me_5)$ and then $\overline{ReO(RC{=}CROCR{=}CR)}(\eta\text{-}C_5Me_5)$ (Structure, compound XII with R = R' = Me) [178]. A theoretical description of $[Re_3(\mu\text{-}O)_6\text{-}(\eta\text{-}C_5Me_5)_3]^{2+}$ has been presented [179, 180].

A study on a series of bis-cyclopentadienylmanganese compounds focused on high spin-low spin dependence on the substituent group [181]. Vibrational spectra of solution and matrix isolated $ReH(\eta\text{-}C_5H_5)_2$ and $[ReH_2(\eta\text{-}C_5H_5)_2]^+$ have been reported [182].



XI



XII

The preparation of a cyclohexadienyl compound, $ReH_2(PPh_3)_2(\eta^5-C_6H_7)$, [183] and the protonation-deprotonation reaction sequence for this species [184] are mentioned. Pentadienyl complexes of manganese [185] and rhenium [186], with formulas $M(L)_3(\eta^5-C_5H_7)$ (M = Mn, Re) and $Re(L)_3(\eta^5-2,4-Me_2C_5H_5)$ (L = phosphines) are seen to be fluxional on the NMR time scale.

Kinetic data on the addition of phosphorus and nitrogen donors at the cyclohexadienyl ring in $[Mn(NO)(CO)(L)(\eta^5-C_5H_6)]^+$ [187] and at the cycloheptadienyl ring in $[Mn(NO)(CO)(L)(\eta^5-C_7H_9)]^+$ (L = CO, phosphines) [188, 189] are presented.

<u>η^6-C_6 Complexes</u> The addition of $Na[OP(OR)_2]$ to the coordinated benzene ring in $[Mn(CO)_3(\eta-C_6H_6)]^+$ occurs with exo stereochemistry initially, but the compound rearranges to the endo isomer on standing [190]. The regiochemistry of the reaction of organomagnesium halides with $[Mn(CO)_3(\eta-1-MeO-2,4-Me_2C_6H_3)]^+$ has been studied; the reaction occurs at C(5) with vinylmagnesium halides and at C(3) with methylmagnesium halides [191]. There is a correlation between the regiochemistry of nucleophilic reactions and the force constants of associated carbonyls [192].

Two papers have appeared describing rhenium metal atom reactions with arenes [193, 194]. Dinuclear products, $(\eta\text{-Arene})Re(\mu-H)_2(\mu-CHR)Re(\eta\text{-Arene})$, are obtained when only arene is present in the reaction system; if the arene is mixed with either 1,3 or 1,5-cyclooctadiene then an arene-metal species containing a ligand derived from the second hydrocarbon is obtained. When rhenium atoms are cocondensed with indene, and KH is added in a second step, the product isolated is $K[Re(\eta^6-C_9H_7)(\eta^5-C_9H_7)]$ [195]. Condensation of rhenium atoms with benzene and PMe_3 produces $[Re(PMe_3)_2(\eta-C_6H_6)]_2$; extensive further chemistry was conducted on this species [196].

The reaction of $[Mn(CO)_3(\eta-C_6Me_6)]^+$ with NaX(aq) gives $MnX(CO)_2(\eta-C_6Me_6)$. Borohydride reduction converts this to a hydride which can be reduced to $[Mn(CO)_2(\eta-C_6Me_6)]^-$; the anion was then alkylated [197]. The compound $MnH(CO)_2(\eta-C_6Me_6)$, on treatment with CO, gives endo-$Mn(CO)_3(\eta^5-C_6Me_6H)$ (structure determined) [198]. Reduction of $MnI(CO)_2(\eta-C_6H_6)$ (using Na/NH_3) gives $[Mn(CO)_2(\eta-C_6H_6)]^-$; alkylation using RX (R = Me, Et, i-Pr, CH_2Ph, $SiMe_3$) gives $MnR(CO)_2(\eta-C_6H_6)$ which converts to the endo isomer, $Mn(CO)_2(PPh_3)(\eta-C_6H_6R)$ when treated with triphenylphosphine [199].

Jones and Fan have found that photolysis of $ReH(PPh_3)_2(\eta-C_6H_6)$ causes loss of one phosphine and formation of an in situ species which catalyzes H/D exchange of C_6D_6 [200].

X. ISOCYANIDE AND NITROSYL COMPLEXES

References to the following compounds have previously been given here: $MnRe(CO)_9(CNR)$ [17], $Re_2(CO)_{10-n}(CNR)_n$ [26], $[Re(CO)_5(CNR)]PF_6$ [76], $(\eta-C_5H_5)(OC)_2FeMn(CO)_4(CNR)$ [98], and $Ph_2E[Mn(CO)_4(CNMe)]_2$ (E = Sn, Pb) [113].

Parameters (concentration, electrolyte, temperature) which govern electron self-exchange in $[Mn(CNR)_6]^{+,2+}$ (R = tol, $p-MeOC_6H_4-$) have been reported [201] as has the volume of activation for this process [202]. Light induces ligand substitution in $[Re(CNR)_6]^+$ (R = xylyl), the halide complexes $ReX(CNR)_5$ being characterized in this paper [203]. The technetium complex, $[Tc(CNBu^t)_6]^+$ reacts with $NOPF_6$ to form $[Tc(CNBu^t)_5(NO)](PF_6)_2$ [204]. In contrast, $[Mn(CNR)_6]^+$ species are oxidized by this reagent. In the same paper, the synthesis and structure of $Tc(NO)Br_2(CNBu^t)_3$ was described. Preparation of this species was accomplished by reaction of the isocyanide with $[Tc(NO)Br_4]^-$.

References to the rhenium nitrosyl species, $[Re(NO)(CO)_2(N\hat{}N\hat{}N)](BF_4)_2$ [28] and $[Re(NO)(CO)_2(L\text{-histidinate})]PF_6$ [118], were cited earlier in this review.

A series of references on dirhenium complexes with chelating diphosphines and one or more isocyanide ligands is noted [45, 46, 47, 48].

Synthesis of $ReCl(dppe)_2(CNSiMe_3)$ from the isocyanide and $ReCl(dppe)_2(N_2)$ is reported. Acids, and even methanol, convert this species to $ReCl(dppe)_2(CNH)$ which protonates further to give $[ReCl(dppe)_2(C{=}NH_2)]^+$; the structure of the tetrafluoborate salt of this cation was identified [205]. The reaction of $ReCl(dppe)_2(CNMe)$ with $TlBF_4$ and $NaBH_4$ gives $Re(BH_4)(dppe)_2(CNMe)$ [206].

XI. STRUCTURAL STUDIES

Compounds whose structures were determined by x-ray crystallography (or other methods) are listed: $MnRe(CO)_{10}$ [15], $Mn_2Br_2(CO)_6(tedip)_2$ [20], $Re_2(CO)_9{=}CCH_2CH_2TiOCp_2$ [25], $Re_2(CO)_8(\mu-Bu_2SnOSnBu_2)$ [37], $[Ir(CH_2Cl)(CO)_2(\mu-C_5Me_5)][Re_2(\mu-Cl)_3(CO)_6]$ [40], $[Mn_2(\mu-I)(CO)_8(dppe)]BF_4$ [41], $fac-Mn(NCS)(CO)_3(dppm)$ [42], $[Re_2(\mu-Cl)(\mu-C{=}NHBu^t)(dppm)_2(CNBu^t)_2]PF_6$ [46], $Re_2Cl_4(dppm)_2(CO)$ [47], $Mn_2(\mu-H)(\mu-PCy_2)(CO)_{8-n}(PMe_3)_n$ (n = 1, 2) [60], $Mn_2(\mu-H)(\mu-P\{NPr^i{}_2\}_2)(CO)_8$ [61], $(OC)_4Mn(\mu-H)(\mu-CO)Pt(PEt_3)_2$ [62], $Mo(\mu-C_5H_5)(CO)_2(\mu-PPh_2)(\mu-CyCO)Mn(CO)_3$ and $Mo(\eta-C_5H_5)(CO)_2(\mu-PPh_2)(\mu-PrCO)Mn(CO)_4$ [63], $Et_4N[Re_3(\mu-H)_2(CO)_{10}(PPh_3)_2]$ [64], $Et_4N[Re_3(\mu-H)_4(CO)_9(L)]$ (L = PPh_3, py) [65], $Et_4N[Re_3(\mu-H)_3(\mu-OH)(CO)_9]$ [66], $Et_4N[Re_3(\mu-H)_3(CO)_9(AuPPh_3)]$ [67], $Et_4N[Re_4(\mu-H)_5(CO)_{14}]$ [68], $Mn_2(\mu-Cl)_2(CH_2SPh)_2(tmeda)_2$ [74], $Re_2O_2(\mu-O)_2(Me)_4$ [75], $Et_4N[Re(CO)_3(CO_2CHC_6H_4PPh_2)]$ [79], $Os_3H(CO)_9(PhC{=}C{=}CPh)Re(CO)_4(PPhMe_2)$ [81], $Mn(CO)_4(C_6H_4CH{=}N-N{=}CHPh)$ [88], $PPN[Mn(CO)_4(COCHPhOCO)]$ [93], $Mn_2(\mu-CF_2)_2(CO)_8$ [94], $MnCo_2(\mu-CCO)(CO)_9$ [99],

$\mathrm{MnCo(CO)_6(MeC{\equiv}CPh)_2}$ [100], $\mathrm{PPN[ReW(\mu{-}CHtol)(CO)_9]}$, $\mathrm{ReW(\mu{-}CH_2tol)(dppm)(CO)_7}$, and $\mathrm{ReW(\mu{-}OCCH_2tol)(\mu{-}dppm)(CO)_6(P\{OMe\}_3)}$ [101], $\mathrm{CrReFe(\mu{-}Ctol)(\mu{-}CO)(CO)_{11}}$ [102], $\mathrm{ReWPt(\mu{-}Ctol)(CO)_9(PMe_3)_2}$ [103], $\mathrm{CpMo(CO)(\mu{-}CO)(\mu{-}PhC{\equiv}CPh)Re(CO)_3(P\{OMe\}_3)}$ and $\mathrm{CpMo(CO)(\mu{-}CO)(\mu{-}MeC{\equiv}CMe)Re(CO)_3(PPh_3)}$ [105], $\mathrm{[Cu\{PhC{\equiv}CMn(CO)_3(dppe)\}_2]PF_6}$ [106], $\mathrm{(Ph_4As)_2[Re_7C(CO)_{21}AuPPh_3]}$ [107], $\mathrm{[Au_5ReH_4(PPh_3)_7]PF_6}$ [108], $\mathrm{Ph_2Sn{-}[Mn(CO)_4(CNMe)]_2}$ [113], $\mathrm{[S\{Re(CO)_5\}_3]BF_4}$ [122], $\mathrm{[Mn(CO)_2(\eta{-}C_5H_5)]_2(\mu{-}X)}$ (X = SO [125], $\mathrm{PPh_2C{\equiv}CPPh_2}$) [135], $\mathrm{S{=}C{=}CBu^t_2}$ [137], $\mathrm{\overline{SCH_2CH_2CH_2}}$ [138]), $\mathrm{Mn(CO)_2(\eta^2{-}HC{\equiv}C{-}C_6H_4CBr{=}CH_2)(\eta{-}C_5H_5)}$ [140], $\mathrm{Mn_2(CO)_3(\mu{-}CO\{NHCH_2Ph\}N_2)(\eta{-}C_5H_4Me)_2}$ [145], $\mathrm{(OC)_3Co{-}(\mu{-}PHPh)Mn(CO)_2(\eta{-}C_5H_5)}$ and $\mathrm{(OC)_9Co_3PMn(CO)_2(\eta{-}C_5H_5)}$ [146], $\mathrm{(OC)_9Fe_3(P)_2{-}[Mn(CO)_2(\eta{-}C_5H_5)]_n}$ (n = 1, 2) and $\mathrm{(OC)_9Fe_3P_2[Mn(CO)_2(\eta{-}C_5H_5)][Fe_2(CO)_6]}$ [147], $\mathrm{MeOC_6H_4P[Mn(CO)_2(\eta{-}C_5H_5)]_2}$ and $\mathrm{(\mu{-}MePHPHMe)[Mn(CO)_2(\eta{-}C_5H_5)]_2}$ [148], $\mathrm{[PhTe\{Mn(CO)_2(\eta{-}C_5H_5)\}_2]PF_6}$ [149], $\mathrm{MnH(SiPh_2H)(CO)(PMe_3)(\eta{-}C_5H_4Me)}$ [151], $\mathrm{Re(CO)_2(\eta^2{-}Me_2C{=}CHCOMe)(\eta{-}C_5Me_5)}$ [153], $\mathrm{Re_2(\mu{-}Se)(CO)_4(\eta{-}C_5Me_5)_2}$ [154], $\mathrm{[ReH(PMe_3)(CH_2PMe_2)(\eta{-}C_5H_5)]_2}$ [156], $\mathrm{Re(CO)(NO)(C\{{=}PBu^t\}OSiMe_3)(\eta{-}C_5R_5)}$ (R = H, Me) [161], $\mathrm{[\{Re(NO)(PPh_3)(\eta{-}C_5H_5)\}_2(\mu{-}CH_2SMeCH_2)]I}$ [163], $\mathrm{[Re(NO)(PPh_3)(\eta^2{-}O{=}CHR)(\eta{-}C_5H_5)]PF_6}$ (R = H [165], $\mathrm{CH_2Ph}$ [166]), $\mathrm{[ReCl(dppe)_2({=}C\{CH_2\}CH_2Ph)]BF_4}$ [169], $\mathrm{Mn(CO)_3(\eta^3{-}C_{15}H_{23})}$ and $\mathrm{Mn_2(CO)_6(\mu^2,\eta^3{-}C_{10}H_{16})}$ [170], $\mathrm{Mn_2(CO)_8(\mu^2,\eta^2C_3H_4)}$ and $\mathrm{Mn_2(CO)_8(\mu^2,\eta^3{-}C_6H_8)}$ [171], $\mathrm{\overline{ReO(OCOCPh_2O})(\eta{-}C_5Me_5)}$, $\mathrm{ReO(O_2C{=}CPh_2)(\eta{-}C_5Me_5)}$ and $\mathrm{\overline{ReO(OCON}Ph)(\eta{-}C_5Me_5)}$ [174], $\mathrm{\overline{Re(CO)_2(OCOC}Ph_2)(\eta{-}C_5Me_5)}$ [175], $\mathrm{ReOCl_2(\eta{-}C_5Me_5)}$ [176], $\mathrm{\overline{ReO(MeC{=}CMeOCMeC}Me)(\eta{-}C_5Me_5)}$ [178], $\mathrm{Mn(\eta{-}C_5H_4SiMe_3)_2}$ [181], $\mathrm{Re(PPhMe_2)_3{-}(\eta^5{-}2,4{-}Me_2C_5H_5)}$ [186], $\mathrm{MnCl(CO)_2(\eta{-}C_6Me_6)}$ [197], endo-$\mathrm{Mn(CO)_3(\eta{-}C_6HMe_6)}$ [198], $\mathrm{TcBr_2(NO)(CNR)_3}$ [204], $\mathrm{[ReCl(dppe)_2(C{=}NH_2)]BF_4}$ [205].

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