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MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1987

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CONTENTS

I. Introduction	291
II. Neutral, Anionic and Cationic Metal Carbonyl Derivatives	292
III. Metal Carbonyl Halides and Derivatives	297
IV. Metal Hydride Complexes	298
V. Complexes with Carbon Ligands	300
VI. Derivatives of Metals and Metalloids	303
VII. Complexes with Group VA and VIA Ligands	305
VIII. Derivatives of $M(CO)_3(\eta-C_5H_5)$ and $[M(NO)(CO)_2(\eta-C_5H_5)]^+$	307
IX. Other Hydrocarbon Complexes	311
X. Isocyanide and Nitrosyl Complexes	314
XI. Structural Studies	314
XII. References	316

I. INTRODUCTION

The format of previous Annual Surveys has been maintained since it seems to provide a fairly concise representation of the material. A short discussion on the format was presented in the 1986 Annual Surveys article [1]. Two hundred twenty-five articles were abstracted for this review, contrasting with 206 articles abstracted for the 1986 article.

Before entering into the content of this article let me report that this will be the last Annual Survey on Manganese and Rhenium that I will author. I have been an author for 16 years since taking over this role in 1972, and I have found it a useful exercise. I also hope that readers have found these surveys valuable.

Several review articles pertinent to this area have appeared in 1987 on the following topics: "Organometallic Oxides: Trioxo(pentamethylcyclopentadienyl)rhenium(VII)", Herrmann, et al. [2], "Ion Pairing Effects in Transition Metal Anions", M. Darensbourg [3], and

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"Metalla-Derivatives of Beta-Diketones", Lukehart [4]. Two other articles of general interest are noted: "A Statistical Analysis of Magic Numbers of Valence Electrons in Small Clusters of Transition Metals ... using the Cambridge Crystal Structure Database" [5], and "Estimation of Standard Enthalpies of Formation of Crystalline Inorganic and Organometallic Complexes" [6].

Volumes 3 and 4 of Organometallic Syntheses [7] contain a number of significant procedures for the synthesis of manganese and rhenium organometallic compounds, listed in a table on the next page.

II. NEUTRAL, ANIONIC, AND CATIONIC METAL CARBONYL DERIVATIVES

Experimentation continues to extend our understanding of mechanisms of reactions that occur upon photolysis of the dimetal decacarbonyls. Three papers in this area are mentioned. Prinslow and Vaida [8] report that the results obtained from photolysis of $Mn_2(CO)_{10}$ (CO dissociation or Mn-Mn bond cleavage) depend on the frequency of the incident light. Poe [9], in a letter, discusses the mechanistic dilemma in determining whether CO dissociation or isomerization occurs in these systems. Poliakoff, Turner et al. [10] report on the photolysis of $MnRe(CO)_{10}$ in a low temperature argon matrix and in solution.

Gas phase ion and molecule chemistry has also progressed in the last year. Laser induced photodissociation of ion cluster fragments $[Mn_2(CO)_y]^+$ was reported [11]. The nucleophilicity of $[Mn(CO)_5]^-$ in the gas phase toward alkyl halides was measured [12]. Elsewhere, it was shown that $[Mn(CO)_3]^-$ (also gas phase) reacts with both O-H and C-H bonds in methanol; this experiment involves mass spectrometric detection of product species from this reaction.

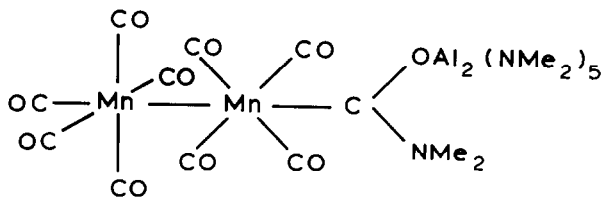
A detailed mechanistic study was presented on reactions of $[Mn(CO)_4(L)]^-$ species ($L = CO, PPh_3, P(OPh)_3$) with a series of cations $[Mn(CO)_5(L')]^+$ ($L = CO, py, MeCN, PPh_3$) [14]. From several of the $[Mn(CO)_5]^- + [Mn(CO)_5(L')]^+$ reactions ($L = CO, MeCN, py$) only one product, $Mn_2(CO)_{10}$, is obtained. Products of other reactions of this type include the various possible dinuclear species $Mn_2(CO)_8(L)(L')$. In the case of the phosphine and phosphite substituted reactants, reactions appear to occur by initial electron transfer, as judged by the scrambling of carbonyl and phosphorous ligands. A related study, from another lab, showed that $[Co(CO)_3(PPh_3)_2]^+$ and $PPN[Mn(CO)_5]$ react to give $Mn_2(CO)_8(PPh_3)$, primarily, with a smaller amount of $Mn_2(CO)_{10}$; the cobalt containing product was $Co_2(CO)_6(PPh_3)_2$ [15].

Table: Synthetic Procedures in Organometallic Syntheses [7]

Compound	Volume	Page
$(\eta\text{-C}_5\text{Me}_5)_2\text{Mn}_2(\text{CO})_3$	3	43
$(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2(\text{C-C-CBu}^t)_2$	3	239
$\text{Mn}(\text{CO})_3(\eta^5\text{-3,4-Me}_2\text{-1-PC}_4\text{H}_2)$	3	256
$(\eta\text{-C}_5\text{H}_5)_2\text{Mn}_2(\text{CO})_4(\mu\text{-H}_2\text{C-S})$	3	270
$(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\text{S}_2)$	3	276
$(\eta\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2(\text{S}_2)$	3	279
$(\eta\text{-C}_5\text{Me}_5)\text{MnFe}_2(\text{CO})_8(\text{Te})$	3	304
$\text{Mn}(\eta\text{-C}_5\text{H}_4\text{Bu}^t)_2$	4	96
$\text{Na}_3[\text{M}(\text{CO})_4]$ (M = Mn, Re)	4	100
$\text{Mn}(\text{CO})_4(\text{PPh}_3)\text{CHO}$	4	104
$\text{Mn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2\text{CHO}$	4	106
$\text{Mn}(\text{CO})_3(\eta^5\text{-exo-1-Ph-C}_6\text{H}_6)$	4	108
$[\text{Mn}(\text{CO})_2(\text{NO})(\eta^5\text{-exo-1-Ph-C}_6\text{H}_6)]\text{PF}_6$	4	109
$[\text{Mn}(\text{dppe})(\text{NO})(\eta^5\text{-exo-1-Ph-C}_6\text{H}_6)]\text{PF}_6$	4	111
$\text{Mn}(\text{CO})_2(\text{NO})(\text{exo-1-Ph-}\eta^4\text{-C}_6\text{H}_6)$	4	110
$\text{Mn}(\text{CO})(\text{PBu}_3)(\text{NO})(\text{exo-1-Ph-exo-2R-}\eta^4\text{-C}_6\text{H}_6)$ (R = $\text{CH}(\text{CO}_2\text{Me})_2$)	4	111
$[\text{Mn}(\text{CO})_3(\eta^5\text{-C}_7\text{H}_8)]\text{PF}_6$	4	113
$[\text{Mn}(\text{CO})_2(\text{NO})(\eta^5\text{-C}_7\text{H}_8)]\text{PF}_6$	4	114
$[\text{Re}(\text{CO})_2(\text{NO})(\eta^5\text{-C}_6\text{Me}_7)]\text{PF}_6$	4	116
$[\text{Mn}(\text{CO})_2(\text{solv})(\eta\text{-C}_6\text{Me}_6)]\text{PF}_6$ (solv = THF, MeCN, C_3H_8)	4	117
$\text{Mn}(\text{CO})_3(\text{B}_3\text{H}_8)$	4	121
nido-2- $[(\text{OC})_3\text{Mn}]\text{B}_5\text{H}_{10}$	4	125
$\text{Me}_4\text{N}[\text{nido-6}[(\text{OC})_3\text{Mn}]\text{B}_9\text{H}_{13}]$	4	130

The reaction of $\text{Re}_2(\text{CO})_{10}$ with the Grignard reagent, $\text{H}_2\text{C-CCH}_2\text{CH}_2\text{MgBr}$, followed by alkylation leads to a rhenium carbonyl complex with a carbene ligand. The axially substituted species thus formed, with the formula $\text{Re}_2(\text{CO})_9[\text{C}(\text{OEt})(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)]$, upon heating or photolysis, is found to lose CO to produce $\text{Re}_2(\text{CO})_8[\text{C}(\text{OEt})(\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2)]$, a molecular species in which the pendant alkene group has replaced a carbonyl on rhenium [16]. Synthesis of a tetramethylthiourea (tmtu) complex, $\text{Mn}_2(\text{CO})_9(\text{tmtu})$, was accomplished by carbonyl substitution of the appropriate precursor [17].

The structure of axial- $\text{Mn}_2(\text{CO})_9[\text{C}(\text{NMe}_2)(\text{OAl}_2(\text{NMe}_2)_5)]$ (I) was defined in a crystallographic study. This compound is produced in a reaction between $\text{Mn}_2(\text{CO})_{10}$ and $\text{Al}_2(\text{NMe}_2)_6$ [18].



(I)

The crystal and molecular structure of $\text{Mn}_2(\text{CO})_8[\text{P}(\text{NMe}_2)_3]_2$ (the ax,ax isomer) was reported; a long metal-metal bond, 294.6(1) pm, is seen [19].

A further report on the oxidation and substitution kinetics of $\text{Re}_2(\text{CO})_8(\text{PPh}_3)_2$ (with $\text{C}_{15}\text{H}_{33}\text{I}$, $\text{P}(\text{OPh})_3$, and $\text{P}(\text{OEt})_3$) has been published [20]. Two papers from Lee and Brown [21, 22] on reactions of the rhenium radical species $\text{Re}(\text{CO})_4(\text{L})$ are noted. The first reports the nature of halogen atom transfer (for the species with $\text{L} = \text{PMe}_3$, $\text{P}(\text{OPr}^t)_3$). The second provides kinetic information on electron transfer reactions of these species ($\text{L} = \text{CO}$, PR_3 , $\text{P}(\text{OR})_3$) with $[\text{p-NCC}_5\text{H}_4\text{NMe}]\text{BF}_4$ and includes information on the effect of the ligand on rates. Also defined are influences of ion pairing and solvent.

A rhenium(I) semiquinone complex, $\text{Re}_2(\text{CO})_7(\text{phenSQ})_2$, was prepared by photolysis of $\text{Re}_2(\text{CO})_{10}$ and 9,10-phenanthroquinone and its esr spectrum and a crystal structure were obtained [23]. The mechanism of a photochemical reaction involving $\text{Mn}_2(\text{CO})_{10}$ with o- and p-quinones has been discussed [24].

It has been reported that $\text{Mn}_2(\text{CO})_{10}$, $\text{MnRe}(\text{CO})_{10}$, and $\text{Re}_2(\text{CO})_{10}$ fail to react with anionic strong oxidants such as $\text{Fe}(\text{CN})_6^{3-}$ and IrCl_6^{2-} in acetonitrile. This contrasts with known reactions of these metal carbonyls with cationic oxidizing agents of comparable strength [25].

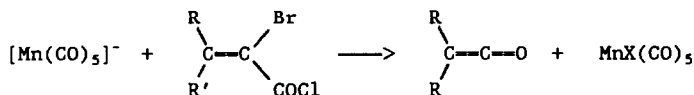
Supported transition metals and transition metal oxides are catalysts for carbonyl substitution in the dimetal decacarbonyls in this group by isonitriles and phosphines. The catalytic effects are ranked: $\text{Pd} > \text{Pt} > \text{Ru} > \text{Rh}$ and $\text{PdO} > \text{PtO}_2$. These reactions are said to be radical, non-chain processes [26].

Several papers refer to catalytic effects of the carbonyls of this group of elements. The catalytic activity of ruthenium halides toward conversion of CO and H_2 to glycol is enhanced by $\text{Re}_2(\text{CO})_{10}$ [27]. Dimanganese decacarbonyl is a catalyst for homologation of methanol in alkali metal formate/methanol solutions using mixtures of CO and H_2 [28]. Dirhenium decacarbonyl (and also $\text{Re}_3\text{H}_3(\text{CO})_{12}$ and $\text{Re}_4\text{H}_4(\text{CO})_{12}$) in conjunction with alkylaluminum compounds are

catalysts for alkane and cycloalkane hydrogenolysis [29].

Technetium(99) NMR spectra (^{99}Tc , $I = 9/2$, 100% abundance) have been reported for the compounds $\text{Tc}_2(\text{CO})_{10}$, $\text{TcCl}(\text{CO})_5$, and $\text{TcCl}(\text{CO})_3(\text{PPh}_3)_2$ [30].

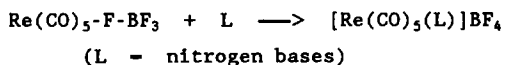
The pentacarbonylmanganate(-1) - alpha-bromoacrylyl chloride reaction results in the generation, in situ, of methylene-ketenes; $\text{MnX}(\text{CO})_5$ ($X = \text{Cl}$, Br) compounds are formed in this process [31].



Oxidation of $[\text{Mn}(\text{CO})_3(\text{L})_2]^-$ ($\text{L} =$ phosphines, phosphites) to radical species is seen to be reversible in THF. The radical species can be trapped using Bu_3SnH [32].

Dirhenium decacarbonyl reacts with XeF_2 giving $[\text{Re}(\text{CO})_6]\text{ReF}_6$ which can also be prepared from $\text{Re}(\text{CO})_5\text{-F-ReF}_5$ and CO . The latter species can be converted to other cationic complexes $[\text{Re}(\text{CO})_5(\text{L})]^+$, by addition of a ligand (PF_3 or CH_3CN) in liquid HF [33].

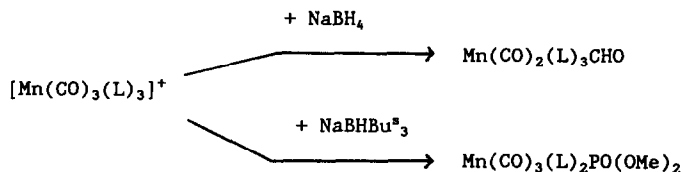
Tetrafluoroborate ion is easily displaced from the coordination sphere in $\text{Re}(\text{CO})_5\text{-F-BF}_3$. A series of complexes, $[\text{Re}(\text{CO})_5(\text{L})]\text{BF}_4$, in which the ligands L are nitrogen containing heterocyclic species (imidizoles, pyridines, pyrazoles, pyrimidine, pyrazine, 4,4-bipyridine) have been synthesized by this route, [34]. Various N-bonded nitrile and thiocyanate complexes were prepared in this way also; some of the compounds described include $[\text{Re}(\text{CO})_5(\text{L})]\text{BF}_4$ ($\text{L} = \text{EtSCN}$, NCCH_2CN , NCNH_2 which is bonded through the nitrile, TCNQ which bonds to two $\text{Re}(\text{CO})_3$ groups through two trans nitrile nitrogen atoms in this ligand.) The same paper also reports syntheses and crystal structure data on $\text{Re}(\text{CO})_5\text{N=C=C}(\text{CN})_2$ and $\text{Re}(\text{CO})_5(\text{NCN})$ [35].



Riera and coworkers have actively pursued study of cationic manganese carbonyl species with particular interest in oxidative and isomerization chemistry. A paper cited earlier described the synthesis of a tetramethylthiourea complex $[\text{Mn}(\text{CO})_4(\text{tmtu})_2]\text{ClO}_4$, [17]. Diphenylphosphine complexes with the formulas $[\text{Mn}(\text{CO})_{6-n}(\text{PPh}_2\text{H})_n]\text{ClO}_4$ ($n = 1 \rightarrow 4$) and $[\text{Mn}(\text{P}^{\wedge}\text{P})(\text{CO})_{4-n}(\text{PPh}_2\text{H})_n]\text{ClO}_4$ ($\text{P}^{\wedge}\text{P} = \text{dppm}$ and dppe , $n = 1, 2$) were prepared. On heating, fac species are seen to isomerize to the mer configuration and cis dicarbonyl species can be converted to the trans isomers [36]. The reaction of fac- $\text{Mn}(\text{CO})_3(\text{tmed})\text{Br}$ with AgClO_4 and a phosphite ($\text{tmed} =$

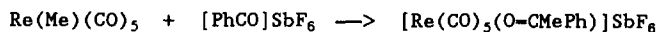
tetramethylethylenediamine; $L = P(OR)_3$, $R = Me, Et, Pr^i$) gave mer- $[Mn(CO)_3(tmcd)(L)]ClO_4$ when the reaction is carried out at ambient temperature; at $0^\circ C$ the fac isomer is formed and can be isolated [37]. X-ray crystallographic studies were carried out on cis- $[Mn(CO)_2(dppm)_2]Br \cdot 1/3H_2O$ and on trans- $[Mn(CO)_2(dppm)_2]ClO_4 \cdot 1/2CH_2Cl_2$. Reactions of these species with CN^- and SCN^- are also reported in this paper [38]. A cyclic voltammetric study on the cyanide bridged species $[Mn(CO)_2-(dppm)(L)]_2-\mu-CN^+$ and $[Mn(CO)_4(L)]_2-\mu-CN^+$ is noted [39]. One-electron oxidation of a series of compounds $[Mn(CO)(L)(dppm)_2]^+$ was reported, with potentials for oxidation dependent on the nature of the ligand [40]. Reduction ($Na/Hg + CH_3CN$) followed by oxidation by dioxygen converts cis, cis- $[Mn(CO)_2(CNBU^t)_2(bipy)]ClO_4$ to the cis, trans isomer. A similar procedure converted the fac isomer of $[Mn(CNBU^t)_3(CO)(bipy)]ClO_4$ to a mer complex [41]. A report on the crystal structure of fac- $[Mn(CO)_3(o-phen)(CNBU^t)]ClO_4$ has been published [42].

Conversion of cationic carbonyl complexes to formyl species has been reported in two different studies. Reduction of the complex $[Mn(CO)_3(P(OMe)_3)_3]^+$ by $NaBH_4$ gives $Mn(CO)_2(P(OMe)_3)_3CHO$ on which further chemistry has been carried out. Reduction of the precursor using $KBHBU^t_3$ had a different outcome; reaction occurred at the phosphite ligand and resulted in the formation of $Mn(CO)_3(P(OMe)_3)_2PO(OMe)_2$ [43].



Reductions (with $NaBH_4$) of cationic rhenium carbonyl phosphite complexes gives metal formyl complexes and the structure of one species, mer, cis- $Re(CO)_2(P(OEt)_3)_3(CHO)$, was defined by a crystallographic study. The reaction of one of these species with $Li[CuMe_2]$ giving $Re(CO)_2(P(OR)_3)_3(COMe)$ was also reported. Synthesis of the various precursors used in this study is also presented in this paper [44].

The reaction of $ReMe(CO)_5$ with $[PhCO]SbF_6$ (typically a hydride abstracting reagent) yields an oxygen bonded ketone complex, $[Re(CO)_5(O-CMePh)]SbF_6$.



The synthesis of the acetaldehyde complex, $[Re(CO)_5(O-CHMe)]BF_4$ by displacement of BF_4^- from $Re(CO)_5-F-BF_3$ was also described in this work [45].

Electrochemical reduction of $[\text{Mn}(\text{CO})_3(\text{L})_{3-n}(\text{CH}_3\text{CN})_n]^+$ (L = phosphines) in the presence of the phosphorus ligand yields $\text{MnH}(\text{CO})_3(\text{L})_2$. The mechanism of this reaction is believed to involve an initial electrochemically catalyzed substitution followed by reduction to the manganese(0) species. This radical intermediate then abstracts a hydrogen atom to give a formyl compound after which the loss of acetonitrile accompanied by migration of the hydrogen from the formyl group gives the final product [46].

NMR was used to study the barrier to inversion at sulfur in $[\text{Re}(\text{CO})_3(\text{L})\text{O}_2\text{SCF}_3]$ (L = 1,2-dihydrothiophene) [47].

The complex, $[\text{Re}(\text{CO})_3(\text{bipy})(\text{py})]\text{BF}_4$ supported on a clay mineral (aqueous environment) is a catalyst for the visible light photoproduction of H_2 from water [48].

III. METAL CARBONYL HALIDES AND DERIVATIVES

Several papers report preparation and study of various substituted derivatives of $\text{MnX}(\text{CO})_5$ and $\text{ReX}(\text{CO})_5$. Compounds mentioned include: $\text{MnBr}(\text{CO})_3(\text{S}_2\text{CPCy}_3)$, which was made by two routes and its structure determined [49]; $\text{ReX}(\text{CO})_3(\text{Me}_2\text{AsSAsMe}_2)$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [50]; from the same authors, $\text{ReX}(\text{CO})_3(\text{AsMe}_2\text{SMe})_2$, ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [51]; a series of complexes $\text{MnRe}(\text{CO})_4(\text{M}^+ \text{salen}^-)$ in which the *salen* ligand is a metal coordination complex of the *N,N'*-ethylenebisimino-bis-salicylidimino ligand ($\text{M} = \text{Zn}, \text{Cu}, \text{Ni}, \text{Co}, \text{Pd}, \text{Sn}$) [52]; $\text{MnX}(\text{CO})_3(\text{PPh}_3)_n(\text{SiMe}_3)_2$ ($n = 0 \rightarrow 3$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$), along with a structure determination on $\text{Mn}(\text{CO})_3(\text{PPh}_2\text{SiMe}_3)_2$ [53]; complexes with multidentate nitrogen ligands, having formulas $\text{N}[\text{CH}_2\text{bipyReCl}(\text{CO})_3]_3$ [54]; and $\text{ReBr}(\text{CO})_3(\text{L})_2$ where L is an axial ligand via 3,4-bis(2,6-*tert*-butylphenyl)-2,3,4,5-tetraphenyl-2 λ -1,2,3-bisazaphosphole [55]. In the latter study, the *meso* form was separated from the enantiomeric Δ, Λ form of the complex and single crystal x-ray diffraction studies were carried out on both species.

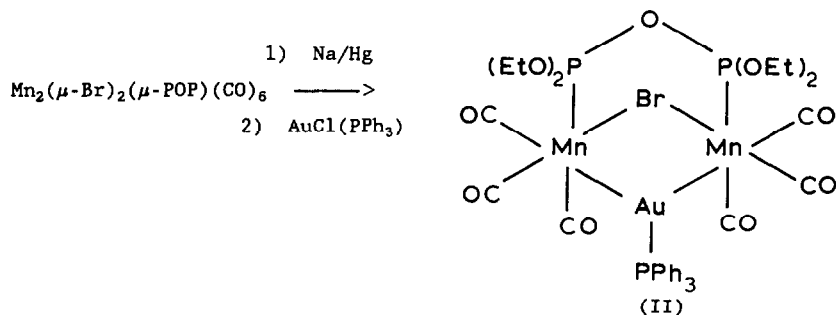
Structural studies have now been reported on $\text{ReCl}(\text{CO})_3(\text{Ph}_2\text{PCH}_2)_2\text{-CMe}(\text{CH}_2\text{PPh}_2)$ [56], $\text{MnCl}(\text{CO})_3(\text{bipy})$ [57], and $\text{Re}_2(\mu\text{-Cl})_2(\text{CO})_6(\mu\text{-SeCH}_2\text{CMe}_2\text{CH}_2\text{Se})$ [58]. The ligand field luminescence of $\text{ReCl}(\text{CO})_4(\text{L})$ ($\text{L} = \text{NH}_3$, piperidine, PPh_3) [59] and the photobleaching of $\text{ReCl}(\text{CO})_3(\text{bipy})$ by Et_3N are described in separate papers [60].

Reduction of $\text{MnBr}(\text{CO})_4(\text{PR}_2\text{H})$ by $\text{K}[\text{BHBu}^a_3]$ gives $\text{K}[\text{Mn}(\text{CO})_4(\text{PR}_2\text{H})]$ ($\text{R} = \text{Bu}^t, \text{Ph}, \text{Cy}$, and $\text{PR}_2\text{H} = \text{PMePhH}$); these anionic complexes were then used as reagents in further syntheses [61]. A rhenium carbene complex, $\text{ReBr}(\text{CO})_4(\text{COCH}_2\text{CH}_2\text{O})$, was found to react with PPh_3 to give $\text{ReBr}(\text{CO})_3(\text{COCH}_2\text{CH}_2\text{O})(\text{PPh}_3)$ (structure determined by crystallography); a further reaction with this phosphine gave $\text{ReBr}(\text{CO})_2(\text{COCH}_2\text{CH}_2\text{O})(\text{PPh}_3)_2$. The reaction of *dpe* (1,2-bis(diphenylphosphino)ethane) with the starting carbene complex was also reported [62]. The complex $\text{ReCl}(\text{CO})_2(\text{dppm})_2$, with one monodentate and

one bidentate phosphine reacts with $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$ giving a bimetallic (Re-Rh) species which was then subjected to various reactions [63]. A mechanistic study on the photoinduced reduction of CO_2 to CO mediated by $\text{ReCl}(\text{CO})_3(\text{bipy})$ has been published [64].

Reductions of $\text{Mn}_2(\mu\text{-Cl})_2(\text{CO})_6(\text{POP})$ and $\text{Mn}_2(\mu\text{-Cl})_2(\text{CO})_4(\text{POP})_2$ ($\text{POP} = (\text{EtO})_2\text{POP}(\text{OEt})_2$) give anions which form bridging hydrido complexes when protonated. Reactions of these anions with $\text{Au}(\text{PPh}_3)\text{Cl}$ were shown to yield complexes with bridging $\text{Au}(\text{PPh}_3)$ units [65]; the structure of (II), shown below, was obtained crystallographically.

Walton and coworkers have published several papers [66, 67, 68] and a brief review [69] on the chemistry of $\text{Re}_2\text{Cl}_4(\text{dppm})_2$ and related species derived from this starting material having carbonyl and isonitrile ligands.

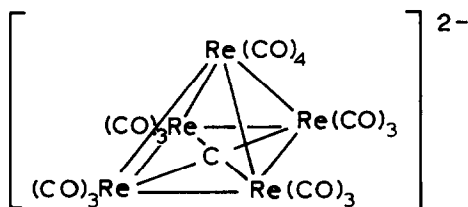


IV. METAL HYDRIDE COMPLEXES

Several references to formation of hydrido complexes were mentioned earlier in this review: addition of $[\text{Mn}(\text{CO})_3]^-$ (g) to C-H and O-H bonds [13]; reactivity of the 17 electron radical species, $\text{Mn}(\text{CO})_3(\text{L})_2$, toward $(n\text{-Bu})_3\text{SnH}$ [32]; the electrochemical reduction of $[\text{Mn}(\text{CO})_3(\text{L})_{3-n}(\text{MeCN})_n]^+$ giving $\text{MnH}(\text{CO})_3(\text{L})_2$ [46]; and the use of several rhenium carbonyl hydride species ($\text{Re}_3(\mu\text{-H})_3(\text{CO})_{12}$ and $\text{Re}_4(\mu\text{-H})_4(\text{CO})_{12}$) as catalysts for alkane and cycloalkane hydrogenolysis [29]. Also, note the references to dinuclear complexes with bridging hydride ligands, $\text{Mn}_2(\mu\text{-H})(\mu\text{-X})(\mu\text{-POP})_n(\text{CO})_{8-2n}$ [63] and $\text{Re}(\text{CO})_2(\mu\text{-H})(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{H})(\text{Cl})$ [65], mentioned above.

Several other papers refer to dinuclear compounds that contain metal atoms bridged by a hydrido ligand. A study on $\text{Mn}(\text{CO})_4(\mu\text{-H})(\mu\text{-PPh}_2)\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2$ has appeared; this compound was formed in a reaction of $(\text{OC})_5\text{MnMo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ and PPh_2H [70]. Another paper describes the compounds $\text{Re}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_{8-n}(\text{PPh}_3)_n$ ($n = 0, 2$); the octacarbonyl species is a product of the reaction of $\text{Re}_2(\text{CO})_{10}$ and PPh_2H in xylene at 190°C , while the triphenylphosphine compounds are formed from this product on substitution of carbonyl groups by this phosphine [71]. A reaction is reported [72] between $\text{Re}_2(\mu\text{-H})(\mu\text{-CH=CHEt})(\text{CO})_8$ and 1,1-dimethylcyclopropene (and with other reagents

$[\text{Re}_4\text{H}_5(\text{CO})_{12}]^{2-}$ gives the 58 electron species, $[\text{Re}_4\text{H}_5(\text{CO})_{12}]^-$, which was isolated as the tetraethylammonium salt and characterized by single crystal x-ray diffraction [79]. Complexes containing carbide ion are formed from $\text{Re}_2(\text{CO})_{10}$ upon reduction with sodium in triglyme; isolated species were $[\text{Et}_4\text{N}]_3[\text{Re}_6\text{H}(\text{C})(\text{CO})_{18}]$ and $[\text{Et}_4\text{N}]_2[\text{Re}_5\text{H}(\text{C})(\text{CO})_{16}]$. The latter species, (IV), contains a square pyramidal arrangement of metal atoms with the carbon atom centered in the basal plane [80].



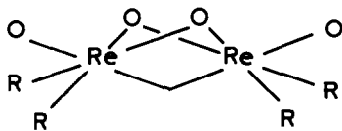
(IV)

V. COMPLEXES WITH CARBON LIGANDS

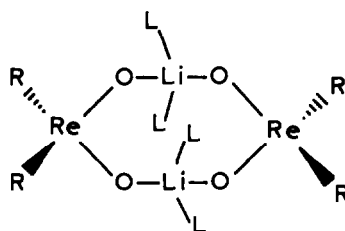
Some interesting work from two research groups has led to new sigma bonded mesityl complexes of these metals. Morris and Girolami [81] have prepared the species $\text{Mn}(\text{mes})\text{Br}_2(\text{PMe}_3)_2$ by a reaction between MnBr_2 and $\text{Mg}(\text{mes})_2(\text{THF})_2$ in the presence of the phosphine and dioxygen. A crystallographic study indicated square planar geometry with the two phosphine ligands in trans positions. Several rhenium-mesityl complexes were described by Wilkinson et al [82]. Reaction of the mesityl Grignard reagent, mesMgBr , with ReOCl_4 gives $\text{ReO}(\text{mes})_4$ as the primary product along with a trace of $\text{ReO}_2(\text{mes})_2$. Reaction of this Grignard reagent with $[\text{Me}_3\text{NH}]\text{ReO}_4$ yields a rhenium (V) species, $[\text{ReO}_2(\text{mes})_2]_2\text{Mg}(\text{THF})_2$, which is converted upon oxidation to paramagnetic $\text{ReO}_2(\text{mes})_2$; structure determinations of this species and square pyramidal $\text{ReO}(\text{mes})_4$ were also included in this study.

Three other papers describe oxo-rhenium alkyl species. The product of a reaction between $\text{ReO}_3(\text{OSiMe}_3)$ and 1.5 equiv. of tris-neopentylaluminum is the d^1-d^1 oxo-bridged dimer $\text{Re}_2\text{O}_2(\mu\text{-O})_2(\text{R})_4$, ($\text{R} = \text{CH}_2\text{CMe}_3$) (V) obtained in 43% yield. Reduction of this species by lithium or sodium amalgam gives an alkali metal salt of the anion, $[\text{ReO}_2\text{R}_2]^-$; a structural determination of the $\text{Li}(\text{MeCN})_2^+$ salt (VI) was carried out. Structures of these two species are drawn below [83]. The compound $\text{ReO}(\text{PMe}_3)(\text{CH}_2\text{SiMe}_3)_3$ was prepared from the phosphine, $\text{ReO}(\text{OEt})\text{Cl}_2(\text{py})_2$ and the appropriate Grignard reagent. If CO is used in place of the phosphine, the product is a carbonyl insertion product, $\text{ReO}(\text{py})(\eta^2\text{-COR})(\text{R})_2$ [84]. The final reference in this group is to the

compound $\text{Re}(\text{NAR})_2(\text{CH}_2\text{CMe}_3)\text{Cl}_2$; it is prepared from the analogous trichloride using the diorgano-zinc reagent, $\text{Zn}(\text{CH}_2\text{CMe}_3)_2$ [85].



(V)

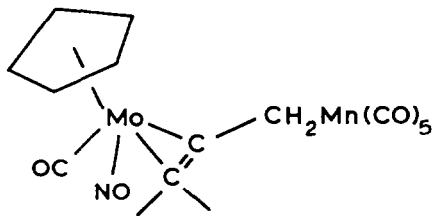


(VI)

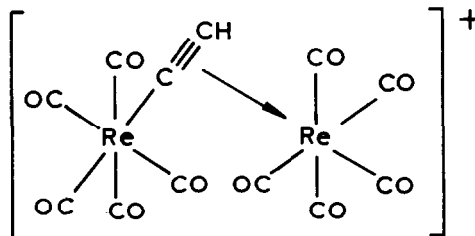
Several new metal pentacarbonyl complexes were reported including dioxocyclobutenyl species $\text{C}_4\text{O}_2[\text{M}(\text{CO})_5]_2$ ($\text{M} = \text{Mn}, \text{Re}$) and $\text{ClC}_4\text{O}_2[\text{Mn}(\text{CO})_5]$ [86], and the bimetallic species, $\text{CpFe}[\eta\text{-C}_5\text{H}_4\text{Mn}(\text{CO})_5]$ [87]. Carbonyl substitution reactions of the latter species with PPh_3 and CNBu^+ were carried out and the oxidation of the iron center to a ferrocenium ion was reported in the latter paper. There is also mention of the compound, $\text{CH}_2=\text{CH}=\text{CH}-\text{CH}_2\text{Mn}(\text{CO})_5$, an isolated precursor to η^3 -allyl and η^5 -pentadienyl species [88]. Related chemistry was reported earlier in this review [75]. Rates were measured for the reactions of the $[\text{M}(\text{CO})_5]^-$ anions ($\text{M} = \text{Mn}, \text{Re}$) with $\text{C}_3\text{N}_3\text{F}_2\text{Mn}(\text{CO})_5$, in order to determine the affect of counterions and solvent [89].

Reactions of $[\text{M}(\text{CO})_5]^-$ ($\text{M} = \text{Mn}, \text{Re}$) with $[\text{CpMo}(\text{CO})_2(\eta^4\text{-C}_4\text{H}_6)]^+$ gave $\text{CpMo}(\text{CO})_2[\eta^3\text{-C}_3\text{H}_4\text{CH}_2\text{M}(\text{CO})_5]$; similar results with related molybdenum precursors were also reported [90]. A second paper from the same research group presented results on the reactions of $[\text{M}(\text{CO})_5]^-$ ($\text{M} = \text{Mn}, \text{Re}$) with $[\text{CpMo}(\text{CO})(\text{NO})(\eta^3\text{-C}_3\text{H}_5)]^+$; in this case the products are the alkene molybdenum species (VII) [91].

A novel complex, $(\text{OC})_3\text{Re}-\text{C}\equiv\text{C}-\text{Re}(\text{CO})_5$, was formed in a two step synthesis. The reaction of $\text{Re}(\text{CO})_5\text{-F-BF}_3$ with $\text{H-C}\equiv\text{C-SiMe}_3$ yields an intermediate, $[(\text{OC})_3\text{Re}(\mu, \eta^1, \eta^2\text{-C}\equiv\text{C-H})\text{Re}(\text{CO})_5]\text{BF}_4$, (VIII); this forms the indicated product species when it is deprotonated by ethoxide ion [92].



(VII)



(VIII)

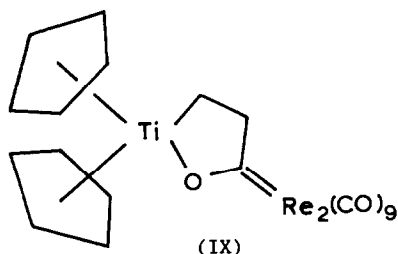
Protonation of $[\text{Re}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{CO})(\text{NO})(\text{Me})]^+$ ($\text{N}^{\wedge}\text{N}^{\wedge}\text{N} = 1,4,7$ -triazacyclononane) occurs at an amine nitrogen, forming a 16 electron species which is not isolable. Subsequent addition of chloride ion to the solution generates $[\text{Re}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{CO})(\text{NO})\text{Cl}]^+$ [93]. An iodide salt of the cation, after 10 days in aqueous solution in the presence of dioxygen, undergoes conversion to the unusual complex, $[(\text{OC})(\text{NO})(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})\text{ReCH}_2\text{OCH}_2\text{Re}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{CO})(\text{NO})]\text{I}_2$; the structure of this species was confirmed by an x-ray diffraction study. The process by which this species is formed requires both I_2 and dioxygen, and does not occur with only one of these reagents. In studies to elucidate a mechanism, it was shown that I_2 in non-aqueous conditions converts the starting complex to $\text{Re}(\text{N}^{\wedge}\text{N}^{\wedge}\text{N})(\text{CO})(\text{NO})\text{CH}_2\text{I}$ which hydrolyzes when water is added to give the product.

Additional examples of ortho-metallation have appeared. Reactions between $\text{MnMe}(\text{CO})_5$ and various N-methyl-1-phenylimidazoles [94] and between $\text{Mn}(\text{CH}_2\text{Ph})(\text{CO})_5$ and $[\text{CpRu}(\text{PPh}_3)_2=\text{C}=\text{CPh}-\text{N}=\text{NPh}]\text{PF}_6$ [95] were shown to occur with ortho-metallation. Cleavage of the carbon-manganese bond in two ortho-metallated products is effected by HgCl_2 [96].

A MO calculation was used to probe the mechanism of the carbonyl insertion reaction, tracing the process involving methyl group migration in $\text{MnMe}(\text{CO})_5$ to an adjacent carbonyl. The calculated activation barrier to this process is 17 kcal. The specific interest in this work was to determine whether the calculations would implicate an η^2 -COMe group. This appears to be a likely possibility since this species was calculated to be 11 kcal more stable than the monodentate 16 electron acyl intermediate [97].

Reactions of several manganese-formyl complexes including $\text{Mn}(\text{CO})_3[\text{P}(\text{OPh})_3]_2\text{CHO}$, with electrophiles were studied. With H^+ , the product is $\text{Mn}(\text{CO})_3(\text{L})[\text{P}(\text{OPh})_2\text{OC}_6\text{H}_4\text{CH}_2]$; in this reaction the carbonyl group in the formyl ligand is converted to the methylene group [98], in a mechanism believed to involve a metal-hydroxyalkylidene intermediate. In certain situations it is possible to intercept related intermediates, metal complexes which are esters of these species. Formation of the formyl compounds by hydride addition to a carbonyl in $[\text{Mn}(\text{CO})_{6-n}(\text{L})_n]^+$ ($\text{L} =$ phosphites, $n = 2, 3$) was noted earlier in this review [43, 44]. Conversion of $[\text{Mn}(\text{CO})_{6-n}(\text{L})_n]^+$ to $\text{Mn}(\text{CO})_{5-n}(\text{L})_n\text{COMe}$ ($n = 2, 3$) can be carried out with either LiCuMe_2 [44] or MeLi [74].

A 1:2 adduct between tert-butyl isocyanide and the carbene complex $\text{Cp}_2\text{TiCH}_2\text{CH}_2\text{C}(\text{=M}_2(\text{CO})_9)\text{O}$ was characterized by x-ray crystallographic techniques; it has a novel zwitterion structure (IX) [99]. The carbene complexes $\text{Re}(\text{CO})_4(\text{SnPh}_3)(\text{CROEt})$ ($\text{R} = \text{Ph}, \text{NET}_2, \text{NPr}^1_2$) were made in the standard two step procedure (addition of RLi to a carbonyl followed by addition of $(\text{EtO})_3\text{O}^+$) [100]. Boron triiodide and HI were then shown to cleave the tin-phenyl groups in these compounds [101].



Two papers report on carbide cluster species. A spectroscopic study, concentrated on vibrational modes which derive from the interstitial carbide group is described in one paper [102]. A synthesis paper describes the oxidative conversion of $[\text{Re}_7\text{C}(\text{CO})_{21}]^{3-}$ to $[\text{Re}_7\text{C}(\text{CO})_{22}]^-$ using tropylium ion [103], the structure of this product also being ascertained in this study. Finally, a reference to another rhenium carbide cluster was noted earlier in this review in connection with other clusters [80].

VI. DERIVATIVES OF METALS AND METALLOIDS

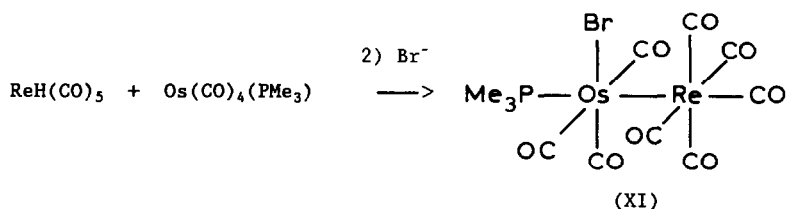
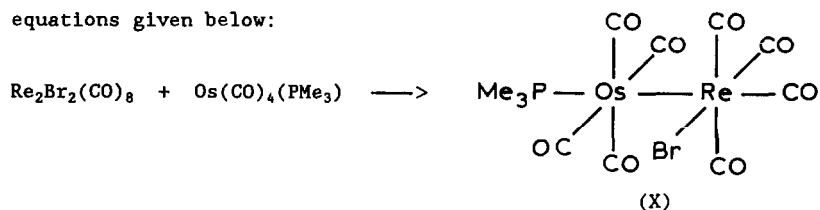
Gallium: Two crystal structures are presented in papers from Haupt and coworkers, on $\text{Re}_2(\text{CO})_4(\text{PPh}_3)_2(\mu\text{-I})_2[\mu\text{-GaRe}(\text{CO})_5]$ [104], and on $\text{Re}_2(\text{CO})_8[\mu\text{-GaRe}(\text{CO})_5]_2$ [105].

Silicon, tin: Reactions between $[\text{Re}(\text{CO})_5]^-$ and halosilanes were used to prepare $\text{ReR}(\text{CO})_5$ ($\text{R} = \text{Si}_2\text{Me}_5$, $n\text{-Si}_3\text{Me}_7$, and $i\text{-Si}_3\text{Me}_7$) [106]. A reaction of $\text{Li}[\text{Si}(\text{SiMe}_3)_3]$ (LiTTSS) and MnCl_2 was used to prepare $\text{Li}(\text{THF})_2[\text{Mn}(\text{TTSS})_2\text{Cl}]$; on further treatment with $\text{Me}_3\text{SiOSO}_2\text{CF}_3$ in dimethoxyethane, $\text{Mn}(\text{dme})[\text{Si}(\text{SiMe}_3)_3]_2$ ($\text{dme} = \text{dimethoxyethane}$) is formed [107]. In the previous section, mention was made of syntheses [100] and reactions [101] of several complexes of the formula $\text{Re}(\text{CO})_4(\text{CROEt})\text{SnPh}_3$.

Transition elements: Pope and Wrighton [108] observed substitution of a phosphine for one carbonyl group on manganese in the compound $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_5$, in a photochemical reaction run at low temperature. The same authors looked at the photolysis of $\text{CpMo}(\text{CO})_3\text{Mn}(\text{CO})_5$ in a low temperature matrix, a reaction in which two isomers are formed. The carbonyl groups exchange sites in this molecule in solution [110]. Coville et al. [110] studied substitution of carbonyl groups in $\text{CpFe}(\text{CO})_2\text{M}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$) with CNBu^t . They report that with the rhenium species $\text{CpFe}(\text{CO})_2\text{Re}(\text{CO})_4(\text{L})$ is formed directly in this reaction; in contrast the reaction of the manganese analogue led to the salts $[\text{CpFe}(\text{CO})_{3-n}(\text{L})_n][\text{Mn}(\text{CO})_5]$. However, the compound $\text{CpFe}(\text{CO})_2\text{Mn}(\text{CO})_4(\text{L})$ could be made if Me_3NO was used to promote CO loss. There is a report on the reaction of $\text{CpMo}(\text{CO})_3\text{Mn}(\text{CO})_5$ with PPh_2H ; one of two products of this reaction is $\text{CpMo}(\text{CO})_2(\mu\text{-H})(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_4$; the other is a dimolybdenum species. Reactions several phosphorus ligands give mono- and di-substitution of carbonyls in the bimetallic product [70].

The species $\text{Fe}(\text{CO})_4(\text{dppm})$ (with a monodentate diphosphine) reacts with $\text{MnBr}(\text{CO})_5$ giving $(\text{OC})_4\text{Fe}(\mu\text{-dppm})\text{MnBr}(\text{CO})_3$ [111]. From the same research group comes a report of the reaction of $\text{MnCl}(\text{CO})_2(\text{dppm})_2$ (one monodentate and one bidentate dppm ligand) with $\text{Rh}_2\text{Cl}_2(\text{CO})_4$. This gives, after hexafluorophosphate ion addition, $[\text{Mn}(\text{CO})_2(\mu\text{-Cl})(\mu\text{-dppm})_2\text{Rh}(\text{CO})_2]\text{PF}_6$, a manganese rhodium species with bridging dppm ligands [112]. Similar compounds were mentioned in an earlier reference [63].

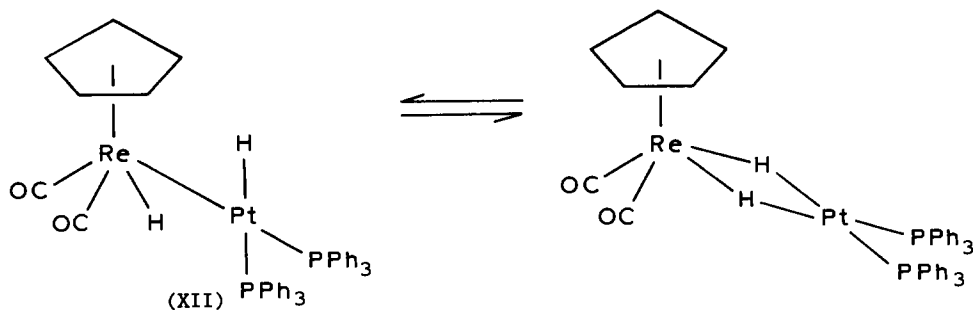
The structural determination of two rhenium-osmium carbonyl isomers, (X) and (XI), was reported [113]. Syntheses were carried out according to the equations given below:



Syntheses of various copper and gold complexes have been reported; these species have the coinage metals coordinated to a sigma bonded manganese-acetylenic group. One compound, $[\text{Ag}(\text{Mn}(\text{CO})_3(\text{dppe})\text{-C}\equiv\text{C}\text{Bu}^t)]_2\text{PF}_6$, was characterized by crystallographic methods [114]. Several gold manganese compounds, $\text{M}_2(\mu\text{-AuPPh}_3)(\mu\text{-X})(\mu\text{-POP})_n(\text{CO})_{8-2n}$ ($\text{M} = \text{Mn, Re; } n = 1, 2$) were reported in a paper cited earlier in this review [65].

To conclude this section, five references to mixed metal complexes in which the manganese or rhenium part is derived from cyclopentadienyl-rhenium or manganese carbonyl are mentioned. The trinuclear complex, $(\eta\text{-C}_5\text{H}_4\text{MeMn})(\text{CpFe})\{\text{Fe}(\text{CO})_3(\mu\text{-CO})_3(\mu^3\text{-COMe})\}$, was prepared from $\text{Fe}(\text{CO})_3(\text{COT})$ and the dinuclear iron-manganese complex $(\eta\text{-C}_5\text{H}_4\text{MeMnCO})(\text{CpFeCO})(\mu\text{-CO})(\mu\text{-COMe})$. It reacts with diazomethane giving a product with a bridging methylene group [115]. Further examples of Fe_2Mn clusters, $[(\eta\text{-C}_5\text{H}_4\text{MeMn})(\text{CpFe})_2(\mu\text{-CO})_2(\mu\text{-NO})_2]^n$ ($n = 0, +1$) were prepared and characterized by Dahl and coworkers [116]. The reduction of a triply bridged NO group to a species with a triply bridged N-H group was described in this paper. Reactions to prepare $(\eta\text{-C}_5\text{H}_4\text{Me})(\text{CO})_2\text{Mn}(\mu\text{-PBu}^t)_2\text{M}(\text{COD})$ ($\text{M} = \text{Rh, Ir}$) are reported [117]. The addition of one Re-H bond in $\text{ReH}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ to zerovalent platinum in $\text{Pt}(\text{PPh}_3)_2(\eta\text{-C}_2\text{H}_4)$

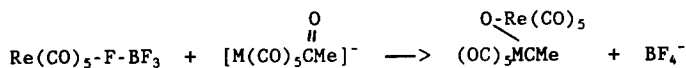
gives a novel species, $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(\text{H})\text{RePtH}(\text{PPh}_3)_2$ (XII); exchange of hydrogens between the two metals is rapid, as shown below [118].



Formation of a linear trinuclear (Mn-Pt-Mn) species with hydrides bridging the metals occurs by the reaction of $[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})(\text{SiR}_3)]\text{Li}$ and $\text{PtCl}_2(3\text{-pic})_2$ [119].

VII. COMPLEXES WITH GROUP VA AND VIA LIGANDS

Oxygen donors: Reactions of $\text{Re}(\text{CO})_5\text{-F-BF}_3$ and $[\text{M}(\text{CO})_5(\text{COMe})]^-$ ($\text{M} = \text{Cr}, \text{W}$) occur as shown in the equation below; a crystal structure of the chromium-rhenium complex was carried out [120]. Various sulfonic acids effect the cleavage of the alkyl group from $\text{M}(\text{CO})_5\text{R}$ ($\text{M} = \text{Mn}, \text{Re}$), leading to oxygen bonded sulfonate complexes, $\text{M}(\text{CO})_5\text{OSO}_2\text{R}$ ($\text{R} = \text{F}, \text{CF}_3, \text{C}_3\text{F}_7, \text{C}_6\text{F}_{13}$) [122]. A single crystal x-ray diffraction study was carried out to determine the structure of $\text{Mn}(\text{CO})_5\text{OTeF}_5$. Reactions of this species, and several others with labile anionic ligands with THF give $\text{Mn}(\text{CO})_3(\text{THF})_2\text{X}$ ($\text{X} = \text{OTeF}_5, \text{CF}_3\text{SO}_3, \text{ClO}_4$) [122].



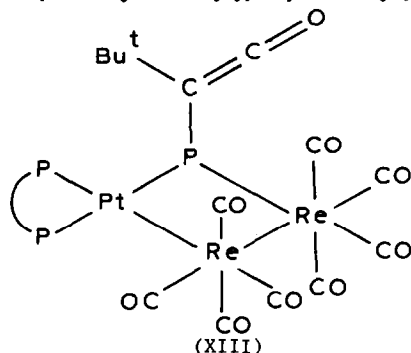
Nitrogen donors: The reaction of $\text{PPN}[\text{Mn}(\text{CO})_5]$ with phthSPh (phth is the N-bonded phthalimide group) gives a good yield of $\text{PPN}[\text{Mn}(\text{CO})_4(\text{phth})_2]$ along with a second complex, $\text{PPN}[\text{Mn}_2(\mu\text{-SPh})_3(\text{CO})_6]$. In the former, the phthalimido ligands are in cis positions, bonded to the metal via the imide nitrogen [123]. The compound $\text{Re}(\text{CO})_2(\text{psal})(\text{PPhMe}_2)_2$ (psal = N-phenylsalicylaminate ion) was characterized in a crystallographic study [124]. The compound $\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{MAT})$ (MAT = 2-methylaminothiazolate ion) reacts with RNCS ($\text{R} = \text{Ph}, \text{tol}$) to give $\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{S}_2\text{CNHR})$; reactions of related species are described in this paper along with a crystal structure study on a cocrystallized mixture of mono- and di-thiocarbamate complexes [125].

The compound $Mn(RNBmes_2)_2$ ($R = Me, Ph$), formed from $Li[RNBmes_2]$ and $MnCl_2$, was shown in a crystallographic study to contain the metal atom with approximately square planar coordination, bonded to two nitrogens from the ligand (in trans positions around manganese) with a further bonding interaction between the metal and two carbons of a mesityl ligand from each anion [126].

Four references from Storr and coworkers [127-130] provide a further elaboration on the chemistry of manganese and rhenium tricarbonyl complexes of a variety of tridentate pyrazolylgallate ligands. Two papers on rhenium carbonyl complexes with phosphorus imide/amide ligands have been published; each paper contains details on three crystal structures [131, 132]. A paper on the ^{55}Mn NMR spectrum of $Mn(CO)_3(\eta^2-tmpo)$ ($tmpo = tetramethylpiperidyl-1-oxide$) has been published [133].

Phosphorus donors: Three papers (on the phosphido bridged complexes $Re_2(\mu-H)(\mu-PPh_2)(CO)_{8-n}(PPh_2)_n$ ($n = 1, 2$) [70], $CpMo(CO)_2(\mu-H)(\mu-PPh_2)Mn(CO)_4-n(L)_n$ ($n = 0, 1, 2$) [69], and $Mn_2(\mu-PPh_2)(\mu-CR-CHR)(CO)_8$ [72]) were previously cited in this review. Extensive further chemistry was reported in the third paper cited above [72]. The species $Mn_2(\mu-SPh)(\mu-PPh(SPh))(CO)_8$ is formed in a prolonged reaction between $[Mn(CO)_5]^-$ and $PhPCl(SPh)$. Two unstable species, $Mn(CO)_5(P(SPh)Ph)$ and $Mn(CO)_5SPh$, were detected as intermediates in this reaction. A crystal structure determination was carried out on the final product [134]. A structure determination on $Mn_2(\mu-PPh_2)_2(CO)_8$ is also noted [135].

The reaction between $Pt(dppe)(P\equiv CBut^t)$ and $Re_2(\mu-H)_2(CO)_8$ gives a compound $(dppe)PtRe_2(CO)_8(PCBu^tCO)$ (XIII), in which the phosphido group bridges one rhenium and the platinum atom [136]. There is mention of a phosphorus (V) complex of manganese, $Mn(CO)_5PO(OMe)_2$; this species is formed on reduction of $[Mn(CO)_3\{P(OMe)_3\}_3]^+$ by $KBHBU_3$ [43].



Arsenic, Bismuth Ligands: The synthesis and structure of $Re_2(\mu-AsPh_2)_2(CO)_8$ have been reported [137]. From the group reporting that work

comes a further paper on a molecule with a tris-homocubane structure, $(AsMe)_7(As)[Re(CO)_4]Re_2(CO)_6$ [138]. The compound $Bi[Mn(CO)_5]_3$ has been prepared and characterized [139].

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

This section has now grown to considerable length as researchers have used these very stable metal species in studies of ligand reactions.

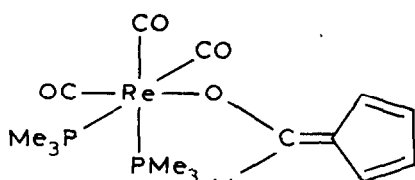
$M(CO)_3(\eta-C_5H_5)$ Derivatives: Various new complexes with the formula $M(CO)_2(L)(\eta-C_5H_5)$ have been reported, synthesized most often by carbonyl or other ligand substitution; this list includes: the η^2 -azoarene complexes $Re(CO)_2(\eta-C_5Me_5)(\eta-ArN=NAr)$ for $Ar = Ph, p\text{-tol}, p\text{-C}_6\text{H}_4\text{F}$ [140]; $Mn(CO)_2(\eta-C_5H_4R)(P(SiMe_3)_2Fe(CO)_2Cp)$ [141], and the analogous PH_2 bridged species, derived by acidic cleavage of the trimethylsilyl group from phosphorus [142]; $Mn(CO)_2(L)(\eta-C_5Me_5)$ ($L = CNMe, CNCF_3, CS_2$) [143]; $Mn(CO)_2(\eta-C_5H_4Me)(\overline{CCH_2CH_2(CH_2)_2-nO})$ formed on photolysis of $Mn(CO)_3(\eta-C_5H_4Me)$ and the acetylene, $HC\equiv C(CH_2)_nOH$ [144]; two isomers $Mn(CO)_2(L)(\eta-C_5H_4Me)$ for $L = p\text{-cyanopyridine}$, plus the bimetallic complex with this ligand bridging the metals [145]; and $NEt_4[Mn(phth)(CO)_2(\eta-C_5H_4Me)]$ ($phth = phthalimide\ anion$) [146]. The manganese complex, $Mn(CO)_2(L)(\eta-C_5H_5)$ (L is the cobalt complex, $(CpCo)_2(\mu-PMe_2)_2(\mu-S)$) has been prepared; the cobalt species coordinates to manganese via sulfur [147]. The compounds ${}^tBu_2E-N-S-N-EBu^t_2$ ($E = P, As$) coordinate two cyclopentadienylmanganese dicarbonyl units through phosphorus or arsenic atoms [148]. Tetracyanoethylene and tetracyano-p-quinone were reacted with $Mn(CO)_2(THF)(\eta-C_5Me_5)$ to give various mixed valence compounds [149]. The reaction of this manganese precursor with $P\equiv C-Bu^t$ forms a species with four $Mn(CO)_2(\eta-C_5Me_5)$ units complexed to a bis-phosphavinyl ether [150]. Preparations of manganese complexes with optically active phospholanes were described in another study [151]. The disubstituted complexes $Mn(CO)(P^{\wedge}P)(\eta-C_5H_4Me)$ ($P^{\wedge}P = o\text{-C}_6\text{H}_4(P(OR)_2)_2$), formed by photolysis of $Mn(CO)_3(\eta-C_5H_4Me)$ with these ligands, are also noted [152].

Structures of several of the products mentioned above were determined in the course of the cited work; see section XI in this review for a list of these species.

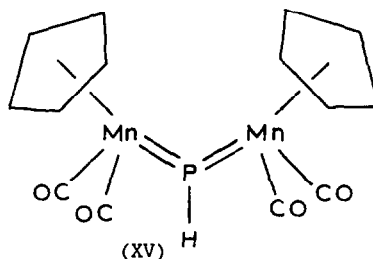
Pertinent to this section is the syntheses of a number of bi- and polymetallic complexes, mentioned earlier, which are derived from $M(CO)_3(\eta-C_5H_5)$ ($M = Mn, Re$) precursors [115-119].

Ligand substitution of the fulvalene species, $(OC)_3Mn(\mu-\eta^5, \eta^5-C_5H_4-C_5H_4)Mn(CO)_3$, was carried out using photolysis; mono- and di-substitution of olefins, phosphines, pyridine, and diphenylacetylene are reported to occur at each metal site [153].

The photolysis of $\text{Re}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{Me}_5)$ and MeSSMe results in oxidative addition of the disulfide to the metal and the formation of a novel rhenium (III) species, $\text{Re}(\text{CO})(\text{SMe})_2(\eta\text{-C}_5\text{Me}_5)$ [154]. Addition of trimethylphosphine to $\text{Re}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{COMe})$ leads to the interesting rhenium-enolate complex, $\text{Re}(\text{CO})_3(\text{PMe}_3)_2(\text{OC}(\text{Me})=\text{C}_5\text{H}_4)$, (XIV) [155]. Photolysis of $\text{Mn}(\text{CO})_2(\text{PH}_3)(\eta\text{-C}_5\text{Me}_5)$ gives $\text{HP}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2$, (XV). Deprotonation of the phosphine complex with KH followed by addition of $\text{CpFe}(\text{CO})_2\text{I}$ produces $(\eta\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2(\mu\text{-PH}_2)\text{Fe}(\text{CO})_2\text{Cp}$. A crystal structure of this species was described [156]. Theoretical calculations on $\text{Fe}_2(\text{CO})_6[\text{P}=\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$ are also noted [157].



(XIV)



(XV)

Hydrogen telluride adds oxidatively to $\text{Re}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{Me}_5)$ giving $\text{Re}(\text{CO})_2(\text{TeH})(\text{H})(\eta\text{-C}_5\text{Me}_5)$; two other compounds, $\text{Re}_2(\mu\text{-Te})(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2$ and $\text{Re}_2(\mu\text{-Te})_2(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2$, were also obtained in this reaction. Photolysis of $\text{Re}(\text{H}((\text{TeH})(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)))$ results in formation of an isomer of the third species, $(\eta\text{-C}_5\text{Me}_5)\text{Re}(\text{CO})_2(\mu, \eta^1\eta^2\text{-Te}_2)\text{Re}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)$. Crystal structure studies on all four compounds were presented in this paper [158]. The reaction between $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_4\text{Me})$ and $\text{Pb}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]_2$ yields $\text{Pb}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]_3$, also characterized using crystallography [159].

Other papers reported results on reactions occurring at coordinated ligands. Synthesis of $[\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{-})]_3\text{SiMe}$ was carried out using $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{Li})$ and MeSiCl_3 [160]. Methyl lithium adds to the tellurium in planar $\text{Te}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_3$ to give an anionic species, $[\text{MeTe}(\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5))_3]^-$. This was isolated as a PPN^+ salt and the tellurium atom in the complex was determined to have tetrahedral coordination, according to an x-ray diffraction study [161].

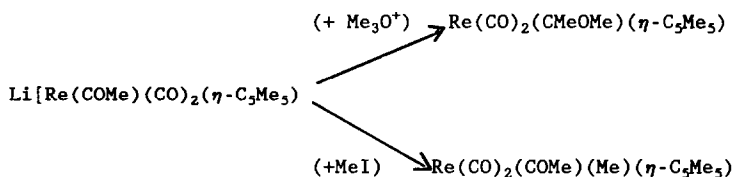
Photolysis of $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{Me})$ with $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{SiHR}_2$ ($\text{R} = \text{Me}, \text{Ph}$) first gives the expected mono-substituted metal complex, the phosphine group replacing one carbonyl. Prolonged photolysis resulted in loss of an additional carbonyl and oxidative addition of the Si-H bond to the metal [162]. A paper presenting a theoretical analysis of Si-H additions vs possible 3-center interactions of an Si-H group with a metal should be accorded significant attention [163]. There is a report by Hill and Wrighton on the photolysis of $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{Me}_5)$ at low temperature and of reactions of

the product of this photolysis, a matrix stabilized dicarbonyl, with a silane [164].

Evidence has been presented that laser flash photolysis of $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ in an alkane matrix at low temperature gives an alkane complex, $\text{Mn}(\text{CO})_2(\text{S})(\eta\text{-C}_5\text{H}_5)$ along with the dinuclear species, $\text{Mn}_2(\text{CO})_5(\eta\text{-C}_5\text{H}_5)_2$ [165].

Oxidation of $\text{PPN}[\text{Mn}(\text{CO})_2(\text{COTol})(\eta\text{-C}_5\text{H}_4\text{Me})]$ by ferrocinium ion gives a 17 electron uncharged paramagnetic species, stable at low temperature; the reaction of this species with NO at -78°C gave the 18 electron and diamagnetic $\text{Mn}(\text{CO})(\text{NO})(\text{COCOTol})(\eta\text{-C}_5\text{H}_4\text{Me})$, the addition of NO being accompanied by CO insertion into the metal-acyl bond [166]. Another paper reports isolation of a stable paramagnetic, 17 electron species, $\text{Mn}(\text{CO})_2(\text{NHC}_6\text{H}_4\text{NH}_2)(\eta\text{-C}_5\text{H}_4\text{Me})$ by oxidative deprotonation of the complex of p-phenylenediamine [167].

Carbene complexes, $\text{Mn}(\text{CO})_2(\text{CPhOSiMe}_2\text{R})(\eta\text{-C}_5\text{H}_4\text{Me})$, have been prepared from the anionic acyl-manganese precursor [168]. The reaction of $\text{Li}[\text{Re}(\text{CO})_2(\text{COMe})(\eta\text{-C}_5\text{H}_5)]$ with trimethyloxonium ion gives the expected carbene complex while with methyl iodide the product obtained is $\text{Re}(\text{CO})_2(\text{Me})(\text{COMe})(\eta\text{-C}_5\text{H}_5)$. Photolysis of the latter product gives MeCOCOMe while thermal degradation leads to the formation of acetone [169].



Molecular orbital calculations have been carried out on the electronic structures of several compounds including $\text{Mn}_2(\mu\text{-CH}_2)(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2$ [170]. An electrochemical study on this compound indicated a one electron oxidation to produce a cation radical which undergoes slow decomposition on standing [171].

Absorptions in the electron transition spectrum of $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ have been assigned based on MS $X\alpha$ calculations [172]. A series of three papers in J. Organomet. Chem. from the same group report the mass spectra of rhenium [173] and manganese [174] and IR and ^{17}O , ^{13}C , and ^1H NMR [175] on rhenium complexes of the general formula, $\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5\text{-nMe}_n)$.

$[\text{M}(\text{CO})_2(\text{NO})(\eta\text{-C}_5\text{H}_5)]^+$ Derivatives: Over 75% (10 of 13) of the references in this section are to papers from Gladysz's research group. Let us review these first.

The rhenium compound $\text{Re}(\text{Me})(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ was shown to protonate ($\text{HBF}_4\text{:OEt}_2$, -78°C) to give a species stable below -20°C . Addition of an alkyl

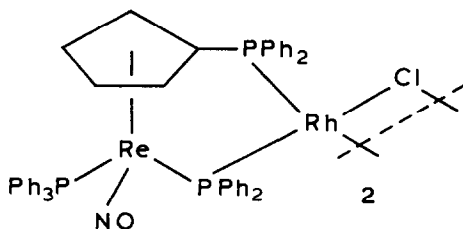
iodide to the protonated intermediate gives a complex of the formula $[\text{Re}(\text{NO})(\text{PPh}_3)(\text{RI})(\eta\text{-C}_5\text{H}_5)]^+$ ($\text{R} = \text{Me}, \text{Et}, \dots, \text{CH}_2\text{SiMe}_3$), with the alkyl iodide ligand coordinated through a lone pair on iodine. A crystal structure study on the complex with a trimethylsilylmethyl iodide ligand was carried to unequivocally establish its structure. Not surprisingly, the alkyl iodide is easily displaced (this being seen in a reaction with MeCN); however, the reaction with another potential ligand, PPh_3 , occurred with the phosphine simply being alkylated [176].

One electron oxidation of $\text{Re}(\text{Me})(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ using ferricinium ion occurs at -78°C . Upon warming to -46°C gas evolution is seen; at -15°C it is possible to identify $[\text{Re}(\text{CH}_2)(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ and $[\text{Re}(\text{NCMe})(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ among the products. On warming to room temperature the intermediate species convert to $[\text{Re}(\eta\text{-C}_2\text{H}_4)(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ [177]. An electrochemical study on related species $[\text{Re}(\text{R})(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$, $\text{R} = \text{benzyl}, \text{-CHMePh}, \text{-CH}_2\text{CHMe}_2$ indicates a one electron oxidation to a cation radical which decomposed by an EC mechanism [178]. Evidence has been presented for an initial electron transfer from these species in hydride abstraction reactions [179].

Another paper from the Gladysz group [180] gives syntheses, structures, and reactivity of a series of compounds with the formula $\text{Re}(\text{NO})(\text{PPh}_3)(\text{CO}_2\text{ML}_n)(\eta\text{-C}_5\text{H}_5)$ ($\text{ML}_n = \text{Li}, \text{K}, \text{and } \text{M}'\text{Me}_3, \text{with } \text{M}' = \text{Ge}, \text{Sn}, \text{Pb}$). Group IVA metal complexes are believed to have structures with the $\text{M}'\text{R}_3$ group symmetrically coordinated to both oxygen atoms of the carboxylate group. A Grignard reagent, ArMgI ($\text{Ar} = 3,5\text{-(MeO)}_2\text{C}_6\text{H}_3\text{-}$), was found to react with $\text{Re}(\text{NO})(\text{PPh}_3)(\text{CO}_2\text{Me})(\eta\text{-C}_5\text{H}_5)$ giving $\text{Re}(\text{NO})(\text{PPh}_3)(\text{COAr})(\eta\text{-C}_5\text{H}_5)$. The acyl group in this product is reduced by $\text{BH}_3\text{:THF}$ giving a $\text{M-CH}_2\text{Ar}$ species, from which a cationic carbene complex is formed by hydride abstraction [181]. The reaction of $[\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2)(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ with S-PPh_3 yielded two complexes, $[\text{Re}(\text{NO})(\text{PPh}_3)(\eta^2\text{-CH}_2\text{-S})(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ and $[\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$. A crystal structure study and further reaction chemistry was performed using the former compound [182]. Crystal structure studies were carried out on $\text{Re}(\text{NO})(\text{PPh}_3)(\text{COR})(\eta\text{-C}_5\text{H}_5)$ ($\text{R} = \text{H}, \text{CHMeCH}_2\text{Ph}$) [183].

The reaction between NO_2^- and $[\text{Re}(\text{CO})_2(\text{Ctol})(\eta\text{-C}_5\text{H}_5)]\text{BCl}_4$, at 0°C in dichloromethane, yields $\text{Re}(\text{NO})(\text{CO})(\text{COTol})(\eta\text{-C}_5\text{H}_5)$. When the reaction is run at lower temperature, an intermediate in the reaction is detected. The species could be isolated; it was determined by an x-ray diffraction study that the compound possessed a -COCOPh ligand; i.e., the intermediate is $\text{Re}(\text{NO})(\text{CO})(\text{COCOTol})(\eta\text{-C}_5\text{H}_5)$ [184]. Reaction of the paramagnetic complex, $\text{Mn}(\text{CO})_2(\text{COTol})(\eta\text{-C}_3\text{H}_4\text{Me})$, with NO was found to give $\text{Mn}(\text{NO})(\text{CO})(\text{COCOTol})(\eta\text{-C}_3\text{H}_4\text{Me})$ [166].

Lithiation (using butyllithium) at the cyclopentadienyl ring in $\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPh}_2)(\eta\text{-C}_5\text{H}_5)$, followed by addition of PPh_2Cl gives $\text{Re}(\text{NO})(\text{PPh}_3)(\text{PPh}_2)(\eta\text{-C}_5\text{H}_4\text{PPh}_2)$. This species can act as a bidentate ligand via the two phosphino-groups; a rhodium complex of this ligand was synthesized and characterized (XVII) [185]. A further paper reports syntheses, structures, and reactions of *cis/trans* $\text{Re}(\text{NO})(\text{PPh}_3)(\text{CX}=\text{CHR})(\eta\text{-C}_5\text{H}_5)$ [186].

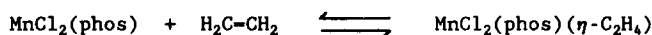


(XVII)

Weber and Meine have carried out a reaction of $\text{LiP}(\text{SiMe}_3)_2$ with $[\text{Mn}(\text{NO})(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]\text{BF}_4$, $\text{Mn}(\text{NO})(\text{CO})(\text{COP}(\text{SiMe}_3)_2)(\eta\text{-C}_5\text{Me}_5)$ being formed. This species can then be converted to a diphosphenyl complex of manganese by reaction with 2,4,6-(Bu^t) $_3\text{C}_6\text{H}_2\text{PCl}_2$ [187]. Derivatives of $\text{Re}(\text{NO})(\text{PPh}_3)(\text{COCH}_2\text{Li})(\eta\text{-C}_5\text{Me}_5)$ were prepared by O'Connor, et al., [188] via reactions with $\text{M}(\text{CO})_5\text{OSO}_2\text{CF}_3$ ($\text{M} = \text{Mn}, \text{Re}$).

IX. OTHER HYDROCARBON COMPLEXES

η^2 Complexes: An equilibrium is established between $\text{MnCl}_2(\text{phos})$ (phos = PPr_3 , PBu_3 , PPhMe_2 , PPhEt_2) and ethylene, and a 1:1 adduct of these species in THF [189].



Reactions of various nitrogen ligands L ($\text{L} = \text{py}$, bipy) and $\text{ReO}(\text{I})(\text{RC}\equiv\text{CR})_2$ with AgSbF_6 yield $[\text{ReO}(\text{RC}\equiv\text{CR}')_2(\text{L})]\text{SbF}_6$ [190]. Reactions of the same precursors, $\text{ReO}(\text{I})(\text{RC}\equiv\text{CR})_2$ ($\text{R} = \text{Me}, \text{Et}$), with $\text{Zn}(\text{Bu}^t)_2$ gave $\text{Re}_2\text{O}_2(\text{RC}\equiv\text{CR})_4$, while the reactions with Bu^tZnCl gave this species along with a second product $\text{Re}_2(\mu\text{-O})(\mu\text{-RC}\equiv\text{CR})(\text{RC}\equiv\text{CR})_4$ [191]. References were provided earlier in the review to several complexes with bridging alkene [72, 73] and alkyne ligands [92].

η^3 Complexes: Reduction of $\text{Mn}(\text{CO})_4(\eta\text{-C}_3\text{H}_4\text{Me})$ produces $[\text{Mn}(\text{CO})_4(\eta^3\text{-H}_2\text{C}=\text{CHC}_2\text{H}_5)]^-$; further reactions of the product were then studied [192]. Allylic species were mentioned in two earlier references [72, 88].

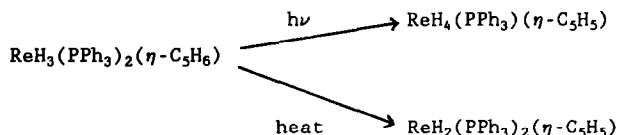
η^5 -Complexes: Mono- and di-metallic complexes of indacene derivatives have been described and structurally characterized [193]. The addition of the

Re-H bond of $\text{ReH}(\eta\text{-C}_5\text{H}_5)_2$ to various activated acetylenes is noted. The initial stereochemistry of this addition was determined to be *cis*; heat or acid caused conversion to the *trans* isomer. In some cases insertion of a second alkyne into the metal carbon bond of the initial product is also seen [194, 195].

Compounds $\text{MnI}(\text{PMe}_3)_2(\eta\text{-C}_5\text{H}_5\text{-nR}_n)$ and $[\text{MnI}(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5\text{-nR}_n)]_2$ have been characterized [196] as has the species $\text{Na}[\text{Mn}(\eta^1\text{-C}_5\text{H}_5)_{4\text{-n}}(\eta\text{-C}_5\text{H}_5)_n]$ [197]. Studies on low-spin/high-spin equilibria in $\text{Mn}(\eta\text{-C}_5\text{H}_4\text{R})_2$ (R = H, Me, Et) by NMR techniques are presented in two papers [198, 199].

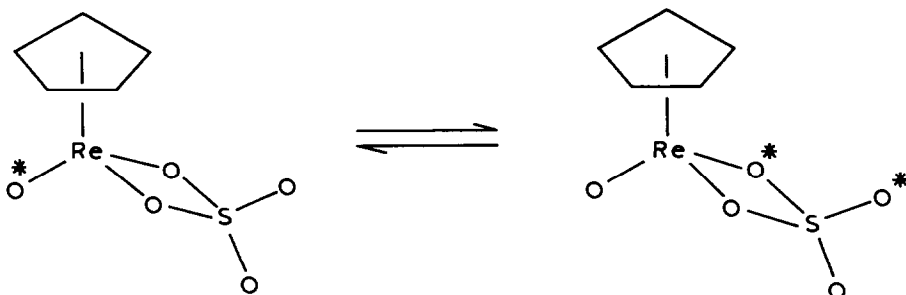
The reaction of the η^5 -pentadienyl complex, $\text{Re}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_7)$, with triethylphosphine produces an alkyl (η^1) rhenium species, $\text{Re}(\text{CO})_3(\text{L})_2(\text{CH}_2\text{CH}=\text{CH}-\text{CH}=\text{CH}_2)$. In the product the double bond is in a *cis* configuration; this slowly converts to the *trans* isomer on standing. In the presence of excess ligand the complex undergoes further substitution, giving a dicarbonyl complex [200]. The protonation of $\text{Mn}(\text{triphos})(\eta^5\text{-C}_5\text{H}_7)$ (triphos = $\text{MeC}(\text{CH}_2\text{PMe}_2)_3$) gives a species with an agostic hydrogen [201]. Addition of $[\text{Re}(\text{CO})_5]^-$ to the ring in $[\text{Mn}(\text{CO})_3(\eta^6\text{-C}_7\text{H}_8)]^+$ produces a cycloheptadienyl complex, $(\eta^5\text{-C}_7\text{H}_8\text{Mn}(\text{CO})_3)\text{Re}(\text{CO})_5$ [202].

Cyclopentadiene and $\text{ReH}_7(\text{L})_2$ (L = PPh_3) react to form $\text{ReH}_3(\text{L})_2(\eta^4\text{-C}_5\text{H}_6)$. Photolysis converts this species to $\text{ReH}_4(\text{L})(\eta\text{-C}_5\text{H}_5)$ whereas heating at 60°C gives $\text{ReH}_2(\text{L})_2(\eta\text{-C}_5\text{H}_5)$. The latter reaction appears to occur by initial transfer of the endo hydrogen to the metal [203].



A second paper by the same authors (Jones and Maguire) charts further reactions of the cyclopentadiene-rhenium complex with various phosphines, CO, and isocyanides [204]. Finally, from the same research group comes the report of one electron oxidation of $\text{ReH}_2(\text{L})_2(\eta\text{-C}_5\text{H}_5)$; in this study, compounds with several different triarylphosphine ligands were used [205].

The remainder of this subsection considers oxo-, halo-, and related complexes of rhenium, work primarily from Herrmann's group. Carbonate and sulfate complexes, $\text{ReO}(\text{SO}_4)(\eta\text{-C}_5\text{Me}_5)$ (XVIII) and $\text{ReO}(\text{CO}_3)(\eta\text{-C}_5\text{Me}_5)$, are formed in reactions of $\text{ReOCl}_2(\eta\text{-C}_5\text{Me}_5)$ with Ag_2SO_4 and Ag_2CO_3 , respectively. Using an oxygen label (O^{17}) it was shown that there is exchange between the oxo group and sulfate [206].



(XVIII)

The same rhenium precursor can be converted to a 1,2-diolate complex, $\text{ReO}(\text{OCH}_2\text{CH}_2\text{O})(\eta\text{-C}_5\text{Me}_5)$ on treatment with $\text{Na}[\text{OCH}_2\text{CH}_2\text{OH}]$. This product was converted on heating to $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$ and a dinuclear species, $(\eta\text{-C}_5\text{Me}_5)(\text{OReO}_3)_2\text{Re}(\mu\text{-O})_2\text{Re}(\text{OCH}_2\text{CH}_2\text{O})(\eta\text{-C}_5\text{Me}_5)$; the crystal structure of the latter complex was determined [207]. Reduction of $\text{ReCl}_4(\eta\text{-C}_5\text{Me}_5)$ in the presence of diethylacetylene gave $\text{ReCl}_2(\text{EtC}\equiv\text{CEt})(\eta\text{-C}_5\text{Me}_5)$. In the absence of the acetylene, reduction with aluminum and activated mercuric chloride gave a mixture of $[\text{ReCl}_3(\eta\text{-C}_5\text{Me}_5)]_2$ and $[\text{ReCl}_2(\eta\text{-C}_5\text{Me}_5)]_2$. The latter, containing two bridging chlorides and a rhenium-rhenium double bond, is cleaved by trimethylphosphine giving $\text{ReCl}_2(\text{PMe}_3)_2(\eta\text{-C}_5\text{Me}_5)$ [208].

A methyl derivative of $\text{ReCl}_4(\eta\text{-C}_5\text{Me}_5)$ is formed by the reaction of this species with MeMgCl ; $\text{ReMe}_4(\eta\text{-C}_5\text{Me}_5)$ is stable at -78°C but above that it decomposes giving ethane [209]. The methylation reaction using tetramethyltin gives $\text{ReMeCl}_3(\eta\text{-C}_5\text{Me}_5)$; this species was shown to hydrolyze in water. The precursor species, $\text{ReCl}_4(\eta\text{-C}_5\text{Me}_5)$, will also add one molecule of trimethylphosphine [210]. The reaction of $\text{ReOCl}_2(\eta\text{-C}_5\text{Me}_5)$ with the di-Grignard reagent $\text{BrMgCH}_2\text{CMe}_2\text{CH}_2\text{MgBr}$ gave a metallocyclobutane complex, $\text{ReO}(\text{CH}_2\text{CMe}_2\text{CH}_2)(\eta\text{-C}_5\text{Me}_5)$; discussion in this paper relates this complex to intermediates in the olefin metathesis reaction [211]. There is a theoretical paper on high-valent d^2 complexes, including $\text{ReOMe}_2(\eta\text{-C}_5\text{Me}_5)$ [212]. The reaction of $[\text{ReCl}_3(\eta\text{-C}_5\text{Me}_5)]_2$ and dimethylacetylene gave two products. One, $\text{ReCl}_2(\text{MeC}\equiv\text{CMe})(\eta\text{-C}_5\text{Me}_5)$, was a precursor in a further reaction with AgSbF_6 and additional acetylene to give $[\text{ReCl}(\text{MeC}\equiv\text{CMe})_2(\eta\text{-C}_5\text{Me}_5)]\text{SbF}_6$ [213].

η^6 -Complexes: Metal atom reactor procedures were used to prepare $\text{MnH}(\text{PMe}_3)_2(\eta\text{-C}_6\text{H}_6)$ [214], $\text{Re}_2(\mu\text{-H})_2(\mu\text{-CH}_2)(\eta\text{-C}_6\text{H}_6)_2$ along with other products [215] from the metal, benzene, an alkane and the phosphine. A collection of benzene and cyclohexadiene rhenium species made by similar procedures were described in another paper [216].

η -Heterocyclic Ligands: Four references to pyrrolyl and substituted pyrrolyl complexes have appeared. In two papers, Zakrzewski has reported the synthesis of $\text{ReH}_2(\text{PPh}_3)_2(\eta\text{-C}_4\text{H}_4\text{N})$ along with further reactions of this species

[217, 218]. Data from a kinetic study on carbonyl substitution in two dimethylpyrrolyl-manganese tricarbonyl compounds suggests an η^5 to η^3 ring slippage facilitated this reaction [219]. A further study from the same group suggested that concurrent first order (ring slippage) and second order process can occur [220]. Hydride addition to $[\text{Mn}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_4\text{S})]^+$ gives a neutral complex, $\text{Mn}(\text{CO})_3(\eta^4\text{-C}_4\text{H}_5\text{S})$. Exo-hydride abstraction from this species regenerates the starting complex [221]. A triple decker complex, with a $\text{Mn}(\text{CO})_3^+$ group attached to one ring in $[\text{Co}(\eta^5\text{-C}_4\text{H}_4\text{BPh})_2]^-$ has been characterized [222].

X. ISOCYANIDE AND NITROSYL COMPLEXES

Syntheses, magnetic susceptibility, IR and ESR were reported on the species $\text{MnX}_2(\text{CNBu}^t)$ ($X = \text{Cl, Br, I, NCS}$) [223]. Rhenium compounds, $[\text{ReH}_4(\text{CNBu}^t)(\text{PPh}_3)_3]\text{PF}_6$ were prepared and their reactions studied [224]. In another paper, the species $\text{ReX}(\text{N}_2)(\text{CNMe})(\text{PPhMe}_2)_3$ ($X = \text{Cl, S}_2\text{PPh}_2$) were described [225]. Several other references to species with isocyanide ligands have been mentioned already [87, 110, 143].

References to nitrosyl complexes have been presented earlier in other contexts [93, 141, 142, 166, 176-188].

XI. STRUCTURAL STUDIES

Molecular structures for the following compounds have been determined: *cis*- $[\text{Mn}(\text{CO})_4(\text{tmtu})_2]\text{ClO}_4$ (tmtu = tetramethylthiourea) [17]; *ax*- $\text{Mn}_2(\text{CO})_9\text{C}(\text{NMe}_2)\text{OAl}_2(\text{NMe}_2)_5$ [18]; *ax,ax*- $\text{Mn}_2(\text{CO})_8[\text{P}(\text{NMe}_2)_3]_2$ [19]; $\text{Re}_2(\text{CO})_7(\text{PhenSQ})_2$ [23]; $[\text{Re}(\text{CO})_5(\text{L})]\text{BF}_4$ ($\text{L} = \text{NCN-C}(\text{NH}_2)_2, \text{NCC}(\text{CN})_2, \text{NCNCN}$) [35]; *cis*- $[\text{Mn}(\text{CO})_2(\text{dppm-PP}')_2]\text{Br} \cdot 1/3\text{H}_2\text{O}$ [38]; *fac*- $[\text{Mn}(\text{CO})(\text{CNBu}^t)_3(\text{bipy})]\text{ClO}_4$ [41]; *fac*- $[\text{Mn}(\text{CO})_3(\text{o-phen})(\text{CNBu}^t)]\text{ClO}_4$ [42]; $\text{Mn}(\text{CO})_3[\text{P}(\text{OMe})_3]_2\text{H}$ [43]; $\text{Mn}(\text{CO})_2[\text{P}(\text{OEt})_3]_3\text{CHO}$ [44]; $[\text{Mn}(\text{CO})_3(\text{S}_2\text{CPCy}_3)_2]\text{ClO}_4$ [49]; $\text{Mn}(\text{CO})_4(\text{PPh}_2\text{SiMe}_3)\text{I}$ [53]; *meso*- and *d,l*- $\text{Mn}(\text{CO})_3(\text{L})_2\text{Br}$ (for chiral $\text{L} = \text{cis-3,4-dihydro-2,3,4,5-tetraphenyl-2H-1,2-diazaphosphole}$) [55]; $\text{Re}(\text{CO})_3(\text{triphos})\text{Cl}$ (triphos is $\text{MeC}(\text{CH}_2\text{PPh}_2)_3$, here acting as a bidentate ligand) [56]; $\text{Mn}(\text{CO})_3(\text{bipy})\text{Cl}$ [57]; $\text{Re}_2(\mu\text{-Cl})_2(\mu\text{-Se}_2\text{CH}_2\text{CMe}_2\text{CH}_2)(\text{CO})_6$ [58]; $\text{ReBr}(\text{CO})_3(\text{PPh}_3)(\text{COCH}_2\text{CH}_2\text{O})$ and $[\text{ReBr}(\text{CO})_3(\text{COCH}_2\text{CH}_2\text{O})_2(\mu\text{-dppe})]$ [62]; $\text{ReRh}(\mu\text{-Cl})_2(\mu\text{-dppm})_2(\text{CO})_2(\eta\text{-C}_2\text{H}_4)$ [63]; $\text{Mn}_2(\mu\text{-Br})_2(\mu\text{-POP})(\mu\text{-AuPPh}_3)(\text{CO})_6$ [65]; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CNBu}^t)]\text{PF}_6$, $\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_2(\text{CNPr}^+)$ [66]; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})(\text{CNBu}^t)_2]\text{PF}_6$ [67]; $[\text{Re}_2\text{Cl}_3(\text{dppm})_2(\text{CO})_3]\text{PF}_6$ [68]; $\text{CpMo}(\text{CO})(\mu\text{-dppm})(\mu\text{-H})(\mu\text{-PPh}_2)\text{Mn}(\text{CO})_3$ [70]; $\text{Re}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_6(\text{PPh}_3)_2$ [71]; $\text{Re}_2(\mu\text{-}\sigma\text{-}\eta\text{-CHCHCMe}_2)(\text{CO})_n$ ($n = 8, 9$) [72]; $\text{PPN}[\text{Mn}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-COCH=CHPh})(\text{CO})_6]$, $\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-CH=CHR})(\text{CO})_6$, ($R = \text{H, Ph}$) and two other related species [73]; $\text{Et}_4\text{N}[\text{Re}_2(\mu\text{-H})(\text{H})_2(\text{CO})_8]$ [76]; $(\text{Et}_4\text{N})_2[\text{Re}_3(\mu\text{-H})_3(\mu, \eta^2\text{-CH}_2\text{O})(\text{CO})_9]$ [78]; $\text{Et}_4\text{N}[\text{Re}_4\text{H}_5(\text{CO})_{12}]$ [79];

$(Et_4N)_2[Re_3H(CO)_{16}]$ [80]; $Mn(mes)Br_2(PMe_3)_2$ [81]; $ReO_2(mes)_2$ [82]; $Re_2O_2(\mu-O)_2(R)_4$ and $Li(MeCN)_2[ReO_2R_2]$ ($R = CH_2CMe_3$) [83]; $C_4O_2[Re(CO)_5]_2$ [86]; $CpMo(NO)(CO)[\mu-CH_2CHCH_2Re(CO)_5]$ [91]; $[(Re(N^{\wedge}N^{\wedge}N)(CO)(NO))_2(\mu-CH_2OCH_2)]I_2$ [93]; $Cp_2Ti(CNBu^t)[\mu-Bu^tNCCH_2CH_2COR_2(CO)_9]$ [99]; $Re(CO)_4(C(OEt)(C_6H_4NMe_2))(SnPh_3)$ [100]; $Et_4N[Re_7C(CO)_{22}]$ [103]; $Re_2(\mu-I)_2(\mu-GaRe(CO)_4(PPh_3))(CO)_4(PPh_3)_2$ [104]; $Re_2(\mu-GaRe(CO)_5)_2(CO)_8$ [105]; $CpFe(CO)_2M(CO)_4(CNBu^t)$ ($M = Mn, Re$) [110]; the isomers $(Me_3P)Os(CO)_4Re(CO)_4Br$ and $(Me_3P)OsBr(CO)_3Re(CO)_5$ [113]; $[Cu\{\text{Bu}^tC\equiv C\}Mn(dppe)(CO)_3]_2PF_6$ [114]; $(CpFe)(MeCpMn)(Fe(CO)_3)(\mu-CO)_2(\mu-X)(\mu-COMe)$ ($X = CO, CH_2$) [115]; $[(MeCpMn)(CpFe)_2(\mu-CO)_2(\mu-NO)_2]^n$ ($n = 0, +1$) [116]; $(MeCp)(CO)_2Mn(\mu-PPh_2)M(COD)$ ($M = Rh, Ir$) [117]; $CpRe(CO)_2(H)[PtH(PPh_3)_2]$ [118]; $(OC)_5CrC(Me)OR_2(CO)_5$ [120]; $Mn(CO)_5OTeF_5$ [122]; $PPN[Mn(CO)_4(phth)_2]$ [123]; $Re(CO)_2(psal)(PPhMe_2)_2$ ($psal = N\text{-phenylsalicylideneaminato}$) [124]; $Re(CO)_2(PPh_3)_2(SCXNHPh)$ (mixture of two cocrystallized species, $X = S, O$) [125]; $Mn[PhNBmes_2]_2$ [126]; $[Me_2Ga(pz)(OC_6H_4NH_2)]Re(CO)_3$ [128]; $[Me_2Ga(pz)(SC_3H_3N_2)]Re(CO)_3$ [129]; $[Me_2Ga(pz)(OC_5H_3NCH_2NMe_2)]Re(CO)_3$ [130]; $Re(CO)_4(CH_2SiMe_2NRP(NR)_2P(-NR)(NR_2))$ ($R = SiMe_3$) and three other related species [131, 132]; $Mn_2(SPh)(PPhSPh)(CO)_8$ [134]; $Mn_2(\mu-PPh_2)_2(CO)_8$ [135]; $Re_2(CO)_8(Ptdppe)(PCBu^tCO)$ [136]; $Re_2(\mu-AsPh_2)_2(CO)_8$ [137]; $Re_3(CO)_{10}(As)(AsMe)_7$ [138]; $Bi[Mn(CO)_5]_3$ [139]; $Re(CO)_2(PhN-NPh)(\eta-C_5Me_5)$ [140]; $[Mn(CO)_2(\eta-C_5H_5)]_2(\mu-Bu^t_2XN-S-NXBu^t_2)$ ($X = P, As$) [148]; $[Mn(CO)_2(\eta-C_5H_5)]_4(\mu-Bu^tCH-POP-CHBu^t)$ [150]; $Mn(CO)(P^{\wedge}P)(\eta-C_5H_5Me)$ ($P^{\wedge}P = ortho-C_6H_4\{P(OMe)_2\}_2$) [152]; $(OC)_2Mn(\mu-C_5H_4-C_5H_4)Mn(CO)_2(\mu-dppm)$ [153]; $Re(CO)(SMe)_2(\eta-C_5Me_5)$ [154]; $Re(CO)_5(OCMe-C_5H_4)$ [155]; $Mn(CO)_2(PH_3)(\eta-C_5Me_5)$ and $(C_5Me_5)(CO)_2MnPH_2Fe(CO)_2Cp$ [156]; $Re(CO)_2(H)(TeH)(\eta-C_5H_5)$, $Re_2(\mu-Te)(CO)_4(\eta-C_5H_5)_2$ and two other rhenium-tellurium species [158]; $Pb[Mn(CO)_2(\eta-C_5H_5)]_3$ [159]; $PPN[MeTe\{Mn(CO)_2(\eta-C_5H_5)\}_3]$ [161]; $[Re(NO)(PPh_3)(ICH_2SiMe_3)(\eta-C_5H_5)]BF_4$ [176]; $[Re(NO)(PPh_3)(H_2C-S)(\eta-C_5H_5)]PF_6$ [182]; $Re(NO)(PPh_3)(CHO)(\eta-C_5H_5)$ [183]; $Mn(CO)(NO)(COCOtol)(\eta-C_5H_5Me)$ [184]; $[Re(NO)(PPh_3)(PPh_2)(\eta-C_5H_4PPh_2)RhCl]_2$ [185]; Z and E $Re(NO)(PPh_3)(COMe-CHCH_2Ph)(\eta-C_5H_5)$ [186]; $(\eta-C_5H_5)(NO)(PPh_3)ReCOCH_2COMn(CO)_4$ [188]; $ReO(MeC\equiv CMe)_2(py)]SbF_6$ [190]; two isomers of $Re_2O_2(MeC\equiv CMe)_4$ [191]; two complexes derived from indacene, $C_{12}H_9Mn(CO)_3$ and $C_{12}H_9[Mn(CO)_3]_2$ [193]; *cis* and *trans* $Cp_2ReCR-CHR$ ($R = CO_2Me$) [194]; $Re(CO)_3(PMe_3)_2(CH_2CH=CHCH=CH_2)$ [200]; $[ReH(CO)_2(PPhMe_2)(\eta^5-C_5H_7)]PF_6$ [201]; $Re(PPh_3)_4(\eta-C_5H_5)$ and $Re(PPh_3)_2H_2(\eta-C_5H_5)$ [203]; $ReH(PMe_3)_5$ and $ReH_2(PEt_3)_3(PPh_2C_6H_4)$ [204]; $[ReH(PPh_3)_2(NCMe)(\eta-C_5H_5)]PF_6$ [205]; $Re(-O)(OCH_2CH_2O)(\eta-C_5H_5)$ and $(\eta-C_5H_5)Re(OR_2)_2(\mu-O)_2Re(OCH_2CH_2O)(\eta-C_5H_5)$ [207]; $[(\eta-C_5Me_5)ReCl_2]_2$ and $(\eta-C_5Me_5)ReCl_2(EtC\equiv CET)$ [208]; $ReMe_4(\eta-C_5Me_5)$ [209]; $ReMeCl_3(\eta-C_5Me_5)$ [210]; $Re_2(\mu-H)_2(\mu-CHBu^t)(\eta-C_6H_6)_2$ [215]; $ReH(\eta^4-C_6H_6)(\eta-C_6H_6)$ [216]; $Mn(CO)_3(\eta-3,4-Me_2C_4H_2N)$ [219]; $Re(S_2PPh_2)(N_2)(CNMe)(PPhMe_2)_3$ [225].

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