

MANGANESE, TECHNETIUM, AND RHENIUM
ANNUAL SURVEY COVERING THE YEAR 1984 *

P. M. TREICHEL

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

CONTENTS

| | |
|--|-----|
| I. Introduction | 83 |
| II. Neutral, Anionic, and Cationic Metal Carbonyl Derivatives | 84 |
| III. Metal Carbonyl Halides and Derivatives | 87 |
| IV. Metal Hydride Complexes | 89 |
| V. Complexes with Carbon Ligands | 93 |
| VI. Derivatives of Metals and Metalloids | 96 |
| VII. Complexes with Group VA and VIA Ligands | 99 |
| VIII. Derivatives of $M(CO)_3(\eta-C_5H_5)$ and $[M(NO)(CO)_2(\eta-C_5H_5)]^+$ | 103 |
| IX. Other Hydrocarbon-Metal Complexes | 106 |
| X. Isocyanide and Nitrosyl Complexes | 109 |
| XI. Structural Studies | 109 |
| XII. References | 111 |

I. INTRODUCTION

The organization of this article is the same as that in the previous year [1]. As in past years the topic of Mn, Tc, and Re organometallic chemistry remains fruitful; 223 references were assembled for this review, up slightly from last year. Extensive effort continues to be directed to complexes derived from $M(CO)_3(\eta-C_5H_5)$ and $[M(NO)(CO)_2(\eta-C_5H_5)]^+$ (Section VIII), to studies pertaining to metal-metal bond cleavage or retention in reactions of $M_2(CO)_{10-n}(L)_n$ (Section II), and to heterobimetallic and polymetallic complexes including metal cluster complexes (Section VI). There have been quite significant developments in most other areas, as will become evident in this survey.

Several review articles with pertinent material are cited. A review of electron transfer processes for mononuclear organometallic species, long needed, has appeared [2]; the organization is partially based on the metallic elements which permits rapid access to work with this group of metals. Reviews on non-homolytic cleavage of metal-metal bonds in photo-

*Previous review see J.Organomet.Chem.Library, 17(1985)365-397.

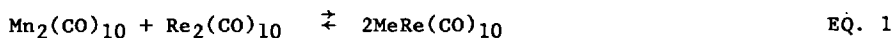
lysis [3], and on complexes with secondary phosphine chalcogenide (-R₂PS-) ligands [4] have appeared; these also contain significant numbers of references to studies involving organometallic species of manganese, technetium and rhenium.

II. NEUTRAL, ANIONIC, AND CATIONIC METAL CARBONYL DERIVATIVES

Homolytic cleavage of the metal-metal bond in M₂(CO)₁₀ (M=Mn,Tc,Re), and in species derived from these dinuclear compounds, was demonstrated over 10 years ago. It appears, however, that despite extensive study (and many published papers) the precise details of these photolyses are only now becoming clear. There is now evidence from flash photolysis experiments using Mn₂(CO)₁₀ and Re₂(CO)₁₀ in the gas phase that there are two primary photoreactions for these species; both metal-metal homolysis and CO loss appear to occur [5]. The same conclusion pertains for photolytic studies in hexane solution on a variety of Mn₂(CO)₈(L)₂ complexes (L = CO; PBu₃, PBu₃⁺, PPt₃⁺, P(OPh)₃) [6,7]. A semibridging carbonyl group is suggested to be present in the binuclear intermediates, Mn₂(CO)₇L₂. Kinetic data for recombination of these species with CO have been obtained [7]. Another paper in this area defines bimolecular kinetics of recombination for the radical species M(CO)₄(L) in hexane, and corrects an earlier report which alleged CO dissociation from M(CO)₄(L) as a secondary photoprocess [8].

Photolysis of Mn₂(CO)₁₀ in an argon matrix at 12K has been shown to give Mn₂(CO)₉. Based on spectroscopic data, a molecular structure of this species with a semibridging carbonyl group is proposed [9]. This result is in accord with proposals in the papers cited above.

Equilibrium constants were obtained for the thermal (170-190°C, decalin) reaction given as EQ. 1 below:



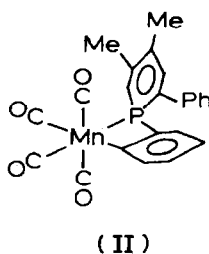
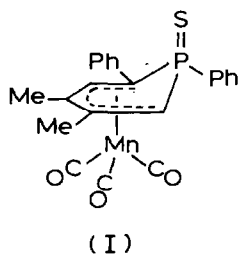
The value of ΔH^\ddagger for this process is $+34.4 \pm 1.3 \text{ kJ mol}^{-1}$, while ΔS^\ddagger is $80.3 \pm 2.5 \text{ JK}^{-1} \text{ mol}^{-1}$ [10].

The mechanism of the disproportionation reaction which occurs when mixtures of Mn₂(CO)₁₀ and nitrogen donor ligands (pyridine, NEt₃, others) are photolyzed is the subject of a paper by Steigman and Tyler [11]. Photochemical cleavage of the metal-metal bond is believed to be the first step in the reaction; rapid carbonyl replacement by the amine then ensues to give Mn(CO)_{5-n}L_n species which can react with Mn₂(CO)₁₀ by electron transfer to provide the isolated products [Mn(CO)₃(L)₃]Mn(CO)₅. Another paper from this group describes related studies [12]. Here, photolysis of [Fe(CO)₂(η-C₅H₅)₂], Mn₂(CO)₁₀ and dppe was shown to give

$[\text{Fe}(\text{CO})(\text{dppe})(\eta\text{-C}_5\text{H}_5)]\text{Mn}(\text{CO})_5$ while a photolytic reaction of $[\text{Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]_2$, $\text{Mn}_2(\text{CO})_{10}$ and diethylenetriamine (dien) yields $[\text{Mn}(\text{CO})_3(\text{dien})]\text{-Mo}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$. Proposed mechanisms of these reactions are similar to the mechanism of the $\text{Mn}_2(\text{CO})_{10}$ -amine reactions noted above. (See also the review article on this topic by these authors [2]).

A mechanism is proposed for the cleavage of $\text{M}_2(\text{CO})_{10}$ species ($\text{M} = \text{Mn, Re}$; $\text{M}_2 = \text{MnRe}$) by halogens in acetonitrile. The products of this reaction, $\text{MX}(\text{CO})_5 + [\text{M}'(\text{CO})_5(\text{MeCN})]^+$, are believed to arise in a two step sequence of attack of the electrophilic Br^+ on the metal-metal bond to give a halogen bridged dimer followed by solvolytic displacement of $\text{MBr}(\text{CO})_5$. The rate of halogen cleavage is very dependent on solvent. Relative rates of the $\text{I}_2\text{-M}_2(\text{CO})_{10}$ reaction are in the order $\text{Re}_2(\text{CO})_{10} > (\text{CO})_5\text{MnRe}(\text{CO})_5 > \text{Mn}_2(\text{CO})_{10}$, which notably is opposite to the order of metal-metal bond energies [13].

The formation of $\text{eq-Re}_2(\text{CO})_9(\text{CNBu}^t)$ from $\text{Re}_2(\text{CO})_{10}$ and $t\text{-BuNC}$ is catalyzed by PdO [14]. Further reaction yields initially $\text{eq,eq-Re}_2(\text{CO})_8(\text{CNBu}^t)_2$ which isomerizes at 50° in the presence of PdO to give $\text{fac}(\text{CO})_3(\text{CNBu}^t)_2\text{ReRe}(\text{CO})_5$ [15]. Molecular structures were determined for this product and also for $\text{eq-Re}_2(\text{CO})_9(\text{CNBu}^t)$. A monosubstituted phosphine complex, $\text{Mn}_2(\text{CO})_9(\text{L})$, is formed from $\text{Mn}_2(\text{CO})_{10}$ and 4,5-dimethyl-1,2-diphenyl-1,6-dihydrophosphorin sulfide, along with a second product, a phosphacyclohexadienyl-manganese tricarbonyl, **I**. Upon heating, the former species undergoes an orthometallation reaction to give **II** [16]. A description of syntheses of $\text{Mn}_2(\text{CO})_8(\mu\text{-dmpm})$ and $\text{Mn}_2(\text{CO})_6(\text{dmpm})_2$ in the reaction of $\text{Mn}_2(\text{CO})_{10}$ and bisdimethylphosphinomethane is contained in a thesis [17].



Note also papers on the esr spectrum of $\text{Mn}(\text{CO})_5$ in a krypton matrix at low temperature [18] and on the esr spectrum of $\text{M}(\text{CO})_4(\text{BETS})$ ($\text{M} = \text{Mn, Re}$, $\text{BETS} = \text{bisethoxythiocarbonylsulfide}$) [19]. A bonding description for

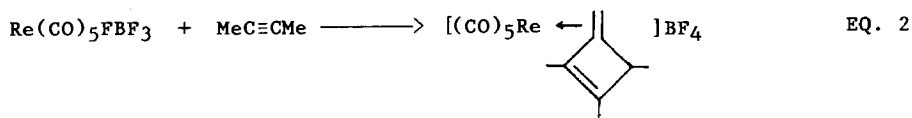
$\text{Mn}_2(\text{CO})_5(\text{dppm})_2$ is given [20].

Primary references to $[\text{Mn}(\text{CO})_5]^-$ and its derivatives are scarce, being limited to three papers. Rapid electron transfer occurs between $[\text{Mn}(\text{CO})_5]^-$ and $\text{V}(\text{CO})_6$, yielding $\text{Mn}_2(\text{CO})_{10}$ and $[\text{V}(\text{CO})_6]^-$ [21]. The kinetics of the $[\text{Mn}(\text{CO})_5]^-$ reaction with methyltrialkylammonium ions was investigated in terms of its relationship to a catalytic methanol homologation reaction [22]. A paper describing gas phase reactions of oxygen with various metal carbonyl anions including $[\text{Mn}(\text{CO})_5]^-$ has also been published [23].

Syntheses of $[\text{Re}(\text{CO})_5(\text{H}_2\text{O})]\text{Y}$ and $[\text{Re}(\text{CO})_3(\text{L})_2(\text{H}_2\text{O})]\text{Y}$ ($\text{Y} = \text{BF}_4, \text{AsF}_6$; $\text{L}_2 = \text{bipy}, \text{dppe}, \text{tmen}$; $\text{L} = \text{P}(\text{O}^i\text{Ph})_3$) were accomplished through reactions of either $\text{ReBr}(\text{CO})_5$ or $\text{ReBr}(\text{CO})_3(\text{L})_2$ with AgY in CH_2Cl_2 . Crystal structure determinations of $[\text{Re}(\text{CO})_5(\text{H}_2\text{O})]\text{AsF}_6$ and $[\text{Re}(\text{CO})_3(\text{tmen})(\text{H}_2\text{O})]\text{AsF}_6$ were part of this study which also included an assessment of the equilibrium between coordination of water and the BF_4^- counterion. The BF_4^- ion competes effectively for a coordination site on the metal with this ligand [24]. Another example of a complex with water as a ligand is $[\text{Re}(\text{CO})_3(\text{bipy})-\text{H}_2\text{O}]_3\text{SCF}_3$, prepared by solvolysis of $\text{Re}(\text{CO})_3(\text{bipy})\text{OSO}_2\text{CF}_3$. The reaction of this cationic complex with borohydride gives $\text{ReH}(\text{CO})_3(\text{bipy})$ [25].

Complexes with covalently bonded PF_6^- ligands (bonded via a fluorine lone pair) are formed by reaction of $[\text{Ph}_3\text{C}]\text{PF}_6$ with $\text{MnH}(\text{CO})_{5-n}(\text{L})_n$ ($\text{L} = \text{P}(\text{OR})_3$, $\text{R} = \text{Me}, \text{Et}, i\text{-Pr}, \text{Ph}$; $n = 2, 3, 4$). If additional ligand is added to the reaction mixture, these species are converted to cationic complexes, $[\text{Mn}(\text{CO})_{5-n}(\text{L})_{n+1}]\text{PF}_6$ [26]. Cationic complexes with nitrile ligands, $[\text{M}(\text{CO})_3(\text{RCN})_3]\text{ClO}_4$ ($\text{M} = \text{Mn}, \text{Re}$; $\text{R} = \text{Et}, \text{Pr}, \text{CH}_2\text{Ph}$), have been prepared from $\text{MBr}(\text{CO})_5$ and AgClO_4 using the nitrile as solvent. The nitrile ligands in these species are easily displaced by Group VA bases including NH_3 and dien (with manganese) and triphos (using Re). Formation of $[\text{Re}(\text{CO})_3(\text{NH}_3)_3]\text{PF}_6$ was achieved in a reaction of $[\text{Re}(\text{CO})_3(\eta\text{-C}_6\text{H}_5\text{Me})]\text{PF}_6$ with NH_3 [27]. Synthesis of *mer*- $[\text{Mn}(\text{CO})_3(\text{CNBu}^t)(\text{N}^i\text{N})]\text{ClO}_4$ and other isocyanide complexes $[\text{Mn}(\text{CO})_{3-n}(\text{CNR})_{n+1}(\text{N}^i\text{N})]\text{ClO}_4$ are reported in another paper [28]. The formation of $[\text{Re}(\text{CNR})_2(\text{MeCN})(\text{L})(\text{PPh}_3)_2]\text{BF}_4$ ($\text{R} = i\text{-Pr}, t\text{-Bu}$; $\text{L} = \text{MeCN}, \text{py}, \text{CyNH}_2, t\text{-BuNH}_2$) and $[\text{Re}(\text{CNBu}^t)_4(\text{PPh}_3)_2]\text{BF}_4$ is mentioned; oxidation of one of these species gives $[\text{Re}(\text{CNBu}^t)_2(\text{MeCN})_2(\text{PPh}_3)_2](\text{BF}_4)_2$, a compound of rhenium(II), which was also the subject of a crystallographic study [29].

Reactions of $\text{Re}(\text{CO})_5\text{FBF}_3$ with 2-butyne and 2-pentyne produce cationic complexes such as III which contain methylenecyclobutenes as ligands; See EQ. 2. The ligand is seen to arise by coupling of two acetylenes [30].

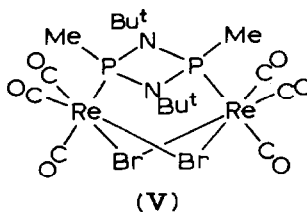
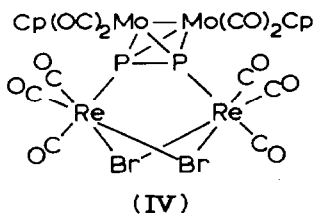


III

Reduction of $[\text{Mn}(\text{CO})_4(\text{PPh}_3)_2]^+$ by electrochemical techniques yields $[\text{Mn}(\text{CO})_4\text{PPh}_3]^-$. When the reduction is carried out in the presence of Bu_3SnH , a complex is obtained which, though uncharacterized, is believed to contain a methyl group bonded to manganese [31]. The synthesis, spectra, and redox chemistry of $[\text{Re}(\text{bipy})_2(\text{CO})_2]^+$ and $[\text{Re}(\text{CO})_2(\text{PR}_3)_2(\text{bipy})]^+$ are reported [32]. See also the review article on electron transfer reactions of mononuclear metal carbonyls [3].

III. METAL CARBONYL HALIDES AND DERIVATIVES

Carbonylation of $[\text{Re}_2\text{Cl}_4(\text{PPhMe}_2)_4](\text{PF}_6)_n$ ($n = 0, 1, 2$) in 2-methoxyethanol produces $\text{ReCl}(\text{CO})_3(\text{PPhMe}_2)_2$ in high yield. More complex reactions of these reagents occur in other solvents, with products such as $\text{ReCl}(\text{CO})_2(\text{PPhMe}_2)_3$ and $\text{ReCl}_3(\text{CO})(\text{PPhMe}_2)_3$ accompanying the aforementioned species [33]. Reactions of potentially bidentate ligand species, thioformamides, $(\text{Ph}_2\text{PCSNRMe})$ and the isomeric thioformimido esters $(\text{Ph}_2\text{PC}(\text{SMe})=\text{NR})$, with $\text{MnBr}(\text{CO})_5$ result in formation of $\text{MnBr}(\text{CO})_3(\text{L}^-\text{L})$ by carbonyl replacement [34]. Preparations of dinuclear halide bridged bimetallic species are described in several papers; products include $\text{Re}_2\text{X}_2(\text{CO})_6(\text{Ph}_4\text{E}_2)$ ($\text{X} = \text{I}, \text{Br}$; $\text{E} = \text{P}, \text{As}, \text{Sb}$) [35], $\text{Mn}_2\text{Br}_2(\text{CO})_{8-2n}(\text{POP})_n$ ($n = 1, 2$; POP is $(\text{EtO})_2\text{POP}(\text{OEt})_2$) [36], $\text{Re}_2\text{Br}_2(\text{CO})_6[\text{P}_2\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ IV, [37], and $\text{Re}_2\text{Br}_2(\text{CO})_6[(\text{MePNBu}^t)_2]$, V [38]. Reduction of $\text{Mn}_2\text{Br}_2(\text{CO})_4(\text{POP})_2$ by sodium amalgam followed by addition of H^+ yields $\text{Mn}_2(\mu\text{-Br})(\mu\text{-H})(\text{CO})_4(\text{POP})_2$ [36]; and IV reacts further with additional ligand to give $\text{ReBr}(\text{CO})_3(\mu\text{-P}^-\text{P}^+)\text{ReBr}(\text{CO})_3$ [37]. Crystal structures were obtained for $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{Ph}_4\text{Sb}_2)$ [35], $\text{Mn}_2(\mu\text{-Br})(\mu\text{-Y})(\text{CO})_4(\text{POP})_2$ ($\text{Y} = \text{Br}$ and H) [36], for IV, for $\text{ReBr}(\text{CO})_3(\mu\text{-P}^-\text{P}^+)\text{ReBr}(\text{CO})_3$ [37], and for V [38].

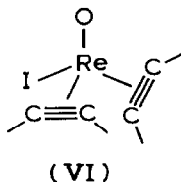


Voltammetric studies have been carried out on mer and fac- $\text{ReCl}(\text{CO})_3\text{-}(\text{PPhMe}_2)_2$, on mer- $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$ and on $\text{ReCl}(\text{CO})_2(\text{PPhMe}_2)_3$ [39]. The temperature dependence of the ^1H NMR spectra of fac- $\text{ReX}(\text{CO})_3(\text{MeSZSeMe})$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{Z} = \text{-CH}_2\text{CH}_2\text{-}$ and $\text{o-C}_6\text{H}_4$) provides information concerning barriers of inversion at sulfur and selenium [40]. The complex $\text{ReCl}(\text{CO})_3(\text{bipy})$ was found to be an efficient catalyst for the electrochemical reduction of CO_2 to CO [41].

Products in reaction of acetylenes with $\text{ReCl}(\text{dppe})_2(\text{N}_2)$ are described in two communications. Terminal acetylenes displace N_2 from this rhenium species to give trans- $\text{ReCl}(\text{dppe})_2(\text{C-CHR})$ ($\text{R} = \text{Ph}, \text{CO}_2\text{Et}, \text{Et}$); the structure of the product from phenylacetylene was characterized by crystallography [42]. The reaction of $\text{PhC}\equiv\text{CMe}$ with $\text{ReCl}(\text{dppe})_2(\text{N}_2)$ yields an η^2 complex of an allene, $\text{ReCl}(\text{dppe})_2(\eta^2\text{-H}_2\text{C=C=CHPh})$ [42], in which the hydrocarbon coordinates to the metal through the unsubstituted portion of allene.

Reactions of ethylene oxide or ethyleneimine with $\text{MX}(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$) result in complexes with carbene ligands, $\text{MX}(\text{CO})_4(\overline{\text{COCH}_2\text{CH}_2\text{Y}})$, ($\text{Y} = \text{O}, \text{NH}$) [44]. It is possible to replace a carbonyl group in $[\text{Mn}(\text{CO})_3(\eta\text{-arene})]^+$ by a halide ion photolytically to give $\text{MnX}(\text{CO})_2(\eta\text{-arene})$ (with C_6Me_6 , $\text{X} = \text{Cl}, \text{Br}, \text{I}$; and with mesitylene, $\text{X} = \text{I}$) [45].

An unusual compound, $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})_2$, VI, is formed by reaction of either $\text{ReO}_2\text{I}(\text{PPh}_3)_2$ or $\text{ReOI}_3(\text{AsPh}_3)_2$ with excess $\text{MeC}\equiv\text{CMe}$. Its structure was ascertained by crystallography [46].



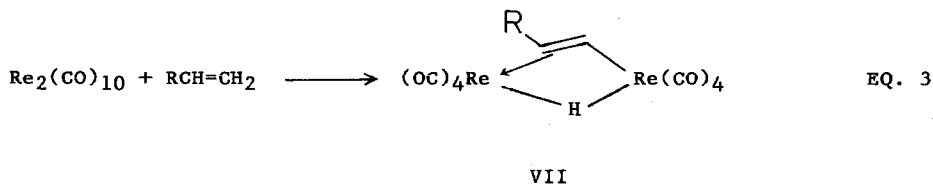
A series of quite unusual manganese(II) species, with formulas $\text{MnCl}(\text{tmed})(\eta\text{-C}_5\text{H}_5)$, ($\text{tmed} = \text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$), $[\text{MnX}(\text{THF})(\eta\text{-C}_5\text{H}_4\text{Me})]_2$ and $[\text{MnX}(\text{PET}_3)(\eta\text{-C}_5\text{H}_4\text{Me})]_2$ have been reported. The first compound is prepared from MnCl_2 , $\text{Na}[\text{C}_5\text{H}_5]$, and the amine; its crystal structure was determined [47]. Formation of $[\text{MnX}(\text{THF})(\eta\text{-C}_5\text{H}_4\text{Me})]_2$ occurs when $\text{Mn}(\eta\text{-MeCp})_2$ and MnX_2 are mixed in THF. Triethylphosphine displaces THF from these species, giving $[\text{MnX}(\text{PET}_3)(\eta\text{-C}_5\text{H}_4\text{Me})]_2$. The structure of the chloride complex was determined in a crystal structure study [48].

IV. METAL HYDRIDE COMPLEXES

Three papers by Bursten and Gatter [49-51] address the interesting dichotomy of metal hydrides concerning their acidic or hydridic character in chemical reactions. Using the Fenske-Hall method of calculation, these authors show that in anions derived by loss of H^+ from acidic metal hydride species (for example, $[\text{Cr}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)]^-$) there is a sizable HOMO-LUMO gap. With anions derived from hydridic species (e.g., $[\text{Cr}(\text{NO})_2(\eta\text{-C}_5\text{H}_5)]^-$), on the other hand, the HOMO is destabilized and the HOMO-LUMO gap is narrow. Calculations on $[\text{Mn}(\text{NO})(\text{CO})(\eta\text{-C}_5\text{H}_5)]^-$ suggested that $\text{MnH}(\text{NO})(\text{CO})(\eta\text{-C}_5\text{H}_5)$ should be intermediate in its properties [49]. This idea was extended to explain the chemistry of $\text{ReH}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$. This species is known to lose a proton to give $[\text{ReH}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$, but the resulting anion appears to be a hydride donor rather than a proton donor [50]. The third paper in this series addresses the trend in acidity of members of several series of complexes including $\text{MnH}(\text{CO})_{5-n}(\text{PPh}_3)_n$ [51].

Other theoretical papers on manganese hydride species provide SCF-X α -SW calculations for $\text{MnH}(\text{CO})_5$ [52] and address dinuclear reductive elimination reactions (such as $[\text{Mn}_2\text{H}_2(\text{CO})_8]^{2-} \rightarrow [\text{H}_2]$) [53].

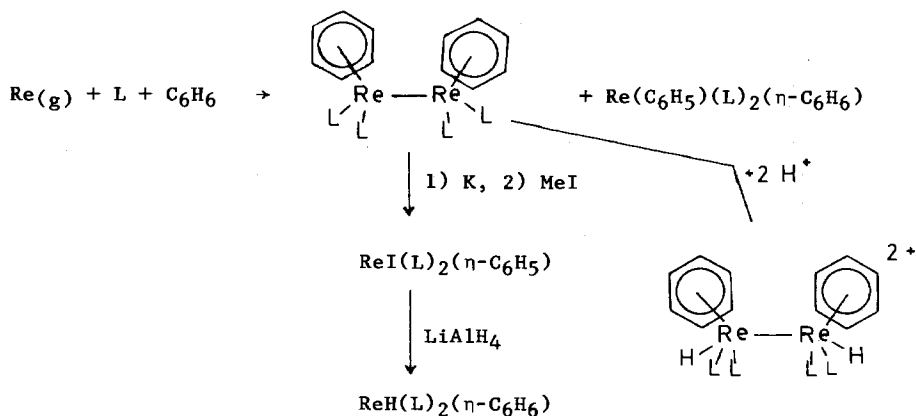
Nubel and Brown have described photolytic reactions between $\text{Re}_2(\text{CO})_{10}$ and several olefins which produce μ -hydrido- μ, η^2 -alkenyldirhenium octacarbonyl species VII. EQ. 3.



A mechanism involving intermediacy of $\text{Re}_2(\text{CO})_8(\eta\text{-RCH=CH}_2)_2$ is suggested. The products are found to be fluxional at room temperature, with the different bonds of the μ -alkenyl group interchanging between rhenium atoms. Reactions of these species with various phosphites, phosphines, and pyridine lead to elimination of the alkene; with hydrogen $\text{Re}_2(\mu\text{-H})_2(\text{CO})_8$ and the alkene are formed. Reactions with other alkenes ($\text{R}'\text{CH=CH}_2$) lead to exchange of organic groups in the molecule [54]. A later paper describes another reaction of these species with alkenes in which the end result is alkene dimerization [55].

The same authors [56] report formation of μ -alkynyl complexes $\text{Re}_2(\mu\text{-H})(\mu\text{-C}\equiv\text{CPh})(\text{CO})_8$ and subsequent reactions of these species with CO, PY, PPh_3 , and PMe_3 . The preparation of this type of complex has also been reported by another research group [57].

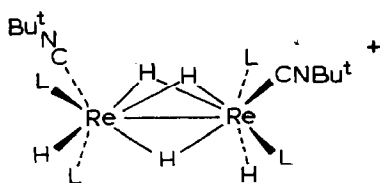
Hydride complexes are formed in reactions involving metal atoms. Co-deposition of rhenium atoms, in a metal atom reactor, with benzene and an alkane leads to complexes having the formula $(\eta\text{-C}_6\text{H}_6)\text{Re}(\mu\text{-H})_2(\mu\text{-CHR})\text{Re}(\eta\text{-C}_6\text{H}_6)$ ($\text{R} = \text{Et, Pr, Bu}^t, \text{Cy, others}$). A crystal structure study defined the geometry and molecular parameters of one of these complexes (with $\text{R} = \text{Bu}^t$) [58]. A metal hydride product, $\text{MnH}(\text{PMe}_3)_2(\eta\text{-C}_6\text{H}_6)$, is formed from $\text{Mn}(\text{g})$, PMe_3 , and the arene. The same reaction with rhenium produces $[\text{Re}(\text{PMe}_3)_2(\eta\text{-C}_6\text{H}_6)]_2$. A series of reactions carried out on the former are portrayed in the scheme below [59].



($\text{L} = \text{PMe}_3$)

An elaborate sequence of reactions starting with $\text{Re}_2(\mu\text{-H})_4\text{H}_4\text{L}_4$ ($\text{L} = \text{PPh}_3, \text{PPh}_2\text{Et, PPhEt}_2, \text{AsPh}_3$) is reported; included among characterized products from these reactions are several dinuclear species containing Bu^tNC as a ligand [60]. The crystal structure of one of these products, VIII,

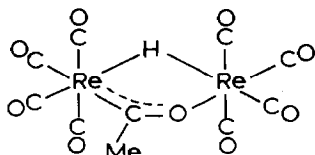
is described in another paper [61].



(VIII, L = PMe₃; PF₆⁻ salt)

Preparations of MnH(SiHPh₂)(CO)(L)(η-C₅H₄Me) (L = PR₃ with R = Me, Bu, OPh, OEt) were achieved by photolysis of Mn(CO)₂(L)(η-C₅H₄Me) with Ph₂SiH₂ [62]. Synthesis and structure of (-)-MnH(SiPhMeNp)(CO)₂(η-C₅H₄Me) were reported by another group; the paper describing this work also reports synthesis and some chemical reactions of MnH(GeR₃)(CO)₂(η-C₅H₅) [63].

Photolyses of Re₂(CO)₁₀ and RCHO (R = Me, Et) gives Re₃H₃(CO)₁₂ as a primary product, along with a small amount of Re₂(μ-H)(μ-RCO)(CO)₈; the structure of one of these species, IX, was ascertained crystallographically [64]. Photolyses of Re₃H₃(CO)₁₂ and PhC≡CPh yields Re₂(CO)₁₀, ReH(CO)₅, and three other complexes Re₂(CO)₇(PhC≡CPh)₂, Re₂(CO)₅(C₆H₄)(PhC≡CPh) and Re₂(CO)₄(C₆H₆)(PhC≡CPh). Structures of the last two were also determined [65].



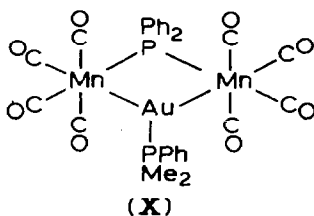
(IX)

Continuing study of reactions of [Re₃(μ-H)₄(CO)₁₀]⁻ has produced several new species including Re₃H₃(CO)₁₀(L)₂ (L = CO, MeCN, PhCN) and Re₃H₂(CO)₁₀⁻(η⁵-C₇H₉). The latter was the subject of a crystal structure study [66]. Reaction of Re₃H₃(CO)₁₀(PhCN)₂ and [Bu₄N]OH yielded Bu₄N[Re₃H₃(CO)₁₀⁻(μ, η²-OCPhNH)], whose structure was ascertained by crystallography [67].

A product $\text{Et}_4\text{N}[\text{Re}_3\text{H}_3(\text{CO})_{10}(\mu_4, \eta^2\text{-NO})\text{Re}_3\text{H}_3(\text{CO})_{10}]$ was prepared from $\text{Et}_4\text{N}[\text{Re}_3\text{H}_4(\text{CO})_{10}]$ and NOBF_4 ; its structure was also determined [68].

Mechanistic features of reactions involving C-H bond activation by $\text{ReH}_7(\text{PCy}_3)_2$ are presented with $\text{ReH}_5(\text{PCy}_3)_2$ being implicated as an intermediate [69]. Double bond isomerization and hydrogenation reactions are catalyzed by $\text{MnH}(\text{CO})_4(\text{PPh}_3)$ and also by $\text{Mn}(\text{Me})(\text{CO})_4(\text{PPh}_3)$, the latter by virtue of its reaction with D_2 under photolysis to give $\text{MnD}(\text{CO})_4(\text{PPh}_3)$ [70]. Gas phase pyrolysis of $\text{MnH}(\text{CO})_5$ with ^{13}CO is described [71].

Various bimetallic species with M-H-M' structural units are encountered including $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}(\mu\text{-H})\text{Nb}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$ and its tantalum analogue [72], $(\text{CO})_4\text{Mn}(\mu\text{-H})(\mu\text{-PPh}_2)\text{Fe}(\text{CO})(\eta\text{-C}_5\text{H}_5)$ [73], and $(\text{CO})_4\text{Mn}(\mu\text{-H})(\mu\text{-Ptol}_2)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [74,75]. Crystal structures were obtained for the Nb-Mn and Fe-Mn compounds. Deprotonation of $(\text{CO})_4\text{Mn}(\mu\text{-H})(\mu\text{-Ptol}_2)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ can be accomplished using KOH; the anion thus formed can be protonated with HBF_4 [74,75]. Deprotonation of $\text{Mn}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\text{CO})_8$ is more difficult, apparently, but is achieved using NaBH_4 . The anion produced can be isolated as a PPN^+ salt, on which a crystal study was carried out. Reactions with $\text{Cu}(\text{PET}_3)_3^+$, $\text{Ag}(\text{PET}_3)^+$, and with $\text{Au}(\text{PPhMe}_2)^+$ (giving X, the subject of a crystallographic study [76],) and with PhHgCl and HgCl_2 [77] are noted; the new metallic group ends up in a position bridging the two manganese atoms as shown in the example below.



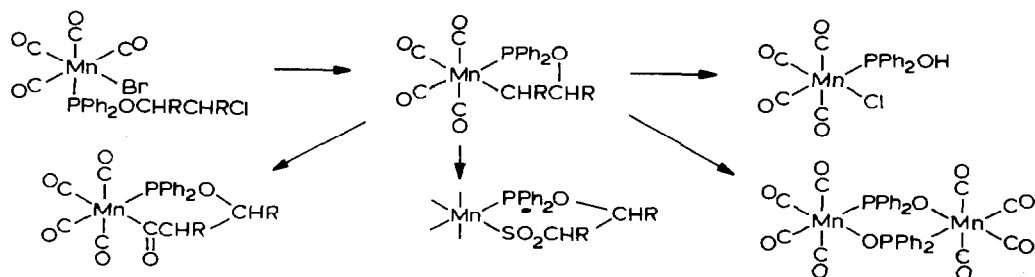
The preparation, structure, and reactions of $\text{Mn}_2(\mu\text{-H})[\mu\text{-P}(\text{NPr}_2^i)_2](\text{CO})_8$ are noted [78]. The reaction of $\text{ReH}(\text{CO})_3(\text{bipy})$ and CO_2 occurs slowly with heating but rapidly under photolysis, giving $\text{Re}(\text{CO}_2\text{H})(\text{CO})_3(\text{bipy})$ [25]. Mention was made earlier in this review of $\text{Mn}_2(\mu\text{-H})(\mu\text{-Br})(\text{CO})_4(\text{POP})_2$ [36]. A thesis (abstract) concerned with large rhenium carbonyl clusters has appeared [79].

V. COMPLEXES WITH CARBON LIGANDS

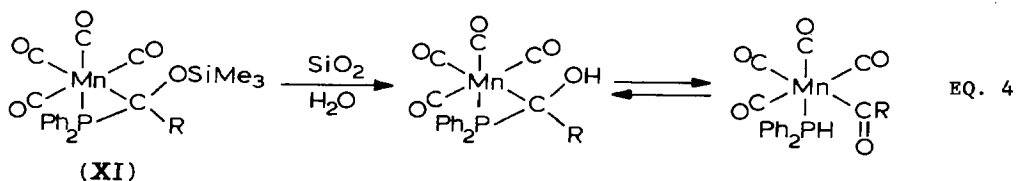
Halogen exchange between BX_3 and $Mn(CO)_5CH_xF_{3-x}$ provides access to a large variety of halomethyl complexes having formulas $Mn(CO)_5CH_xX_{3-x}$ ($X = Cl, Br, I; x = 1, 2, 3$). Similarly, $M(CO)_5CF_2CF_3$ undergoes halogen exchange to yield $M(CO)_5CX_2CF_3$ ($M = Mn, X = Cl; M = Re, X = Cl, Br$) [80]. It is possible to convert $Mn(CO)_5CBr_3$ to $Mn(CO)_5CH_xBr_{3-x}$ ($x = 1, 2, 3$) in reactions of this species with Bu_3SnH [81]. See also a thesis which includes this work along with other studies on reactions of $MnMe(CO)_5$ and Lewis acids [82].

Preparations of $Mn(CO)_5CH_2R$ ($R =$ the phthalimide and $-C_5H_4Re(CO)_3$ [84] groups) have been carried out by standard procedures starting with RCH_2X and $Na[Mn(CO)_5]$. Preparation of a series of complexes $Mn(CO)_{5-n}(L)_nC\equiv CR$ ($R = H, Ph; L = CNBu^t, PCy_3; L_2 = dppe, bipy; n = 1, 2$) was achieved by substitution of carbonyl groups in $Mn(CO)_5C\equiv CR$. One of these species, $Mn(CO)_4(PCy_3)C\equiv CPh$ was shown to form a complex via the acetylene unit with dicobalt octacarbonyl. The structure of this species was determined; it resembled dicobalt carbonyl complexes with other acetylenes [85].

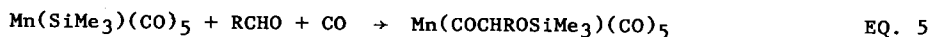
The reaction of $Mn(Me)(CO)_5$ with either bicyclo-2,2,1-heptene or cyclopentene in the presence of CO occurs with addition of $MeCO-$ and the metal group to the double bond in the hydrocarbon [86]. Carbonyl loss and dimer formation is encountered when $Mn(CO)_5(o-CH_2C_6H_4NC)$ is heated [87]. The complex $Mn(CO)_4PPh_2OCHRCHR$ can be isolated as a product when $MnBr(CO)_4-PPh_2OCHRCHRCl$ is treated with sodium amalgam. Numerous reactions were carried out on this species including CO and SO_2 insertion into the metal-carbon bond and cleavage of the organic group with HCl. When heated, olefin is eliminated and $[(CO)_4MnPPh_2O]_2$ is formed; the rates of this reaction was measured [88]. This chemistry is summarized in the scheme below.



Carbon dioxide inserts into the metal-carbon bond in $\overline{\text{Mn}(\text{CO})_4(\text{PPh}_2\text{CH}_2\text{CH}_2)}$ giving $\overline{\text{Mn}(\text{CO})_4\text{PPh}_2\text{CH}_2\text{CH}_2\text{COO}}$ [89]. Various $\text{MnR}(\text{CO})_5$ species ($\text{R} = \text{Me}, \text{CH}_2\text{SiMe}_3, \text{Ph}, \text{Np}$) react with $\text{Ph}_2\text{PSiMe}_3$ to give XI; These complexes hydrolyze on silica gel to form acyl-metal complexes in the manner shown below, EQ. 4 [90].

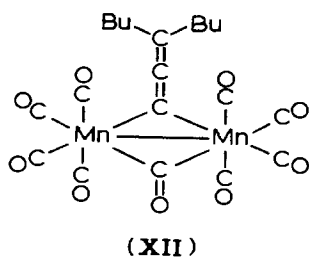


Acyl-metal complexes are also formed by insertion of aldehydes into the metal-silicon bond in $\text{Mn}(\text{SiMe}_3)(\text{CO})_5$ in the presence of CO, EQ. 5:



Similar products, i.e., siloxyacyl-manganese carbonyls, result when cyclic ethers are substituted for an aldehyde in this reaction [91].

Complexes with the formula $\text{M}(\text{C}\equiv\text{CCBu}_2^t\text{Cl})(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$) have been shown to hydrolyze to $\text{M}(\text{C}\equiv\text{CCBu}_2^t\text{OH})(\text{CO})_5$. The preparation of these species involves an initial reaction of $\text{M}_2(\text{CO})_{10}$ with $[\text{C}\equiv\text{CCBu}_2^t\text{O}]^{2-}$ followed by treatment of intermediate species with COCl_2 . Accompanying the indicated products is a second product, $\text{M}_2(\text{CO})_9(\text{C}=\text{C}=\text{CBu}_2^t)$. In the rhenium species the $\text{C}=\text{C}=\text{CBu}_2^t$ ligand coordinates as a terminal ligand, but with the manganese complex XII this group bridges two metals; this structure was verified by crystal structure study [92].

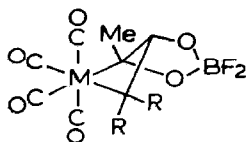


The reaction of $\text{Mn}(\text{CH}_2\text{Ph})_2(\text{THF})$ and oxygen produces $\text{Mn}_4\text{O}_4(\text{OH})_4(\text{OCH}_2\text{Ph})_4$ [93]. Infrared spectra of $\text{M}(\text{Me})(\text{CO})_5$ ($\text{M} = \text{Mn}, \text{Re}$) are the subject of a study whose concern is with the methyl group's geometry and rotation [94].

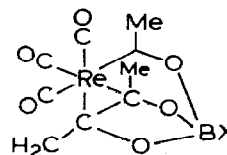
Cited previously in this review are references to $(\text{CO})_4\overline{\text{Mn-C}_6\text{H}_4\text{-PC}_5\text{H}_2\text{Me}_2\text{Ph}}$, an orthometallation product [16], $\text{Re}(\text{Ph})(\text{PMe}_3)_2(\eta\text{-C}_6\text{H}_6)$ [59], an unidentified methyl manganese complex formed by electrochemical reduction of $[\text{Mn}(\text{CO})_4(\text{PPh}_3)_2]^+$ in the presence of Bu_3SnH [31], and the use of $\text{Mn}(\text{Me})(\text{CO})_4(\text{PPh}_3)$ as a catalyst for hydrogenation and isomerization of 2-butenes [70].

Stabilization of various formyl-metal species, including $[\text{ReX}(\text{CO})_4\text{CHO}]^{--}(\text{M}^+)$ ($\text{X} = \text{MeCO}, \text{Br}$), $[\text{Mn}_2(\text{CO})_9\text{CHO}]\text{K}$ and $\text{Mn}(\text{CHO})(\text{CO})_3(\text{PPh}_3)_2$, can be accomplished by addition of Bu_3SnH ; this material hinders a radical chain decarbonylation process which forms the corresponding metal hydride [95]. Stable manganese formyl complexes mer, trans- $\text{Mn}(\text{CHO})(\text{CO})_2[\text{P}(\text{OPh})_3]_3$ and mer, trans- $\text{Mn}(\text{CHO})(\text{CO})_3[\text{P}(\text{OPh})_3]_2$ can be prepared by reduction of the appropriate cationic manganese carbonyl species with $\text{K}[\text{BH}(\text{OPr}^i)_3]$; a crystal structure study was carried out on the latter product [96].

Single crystal x-ray diffraction and (in one example) single crystal time-of-flight neutron diffraction techniques were used to affirm the anticipated structures of $\text{PhC}(\text{NH}_2)_2[\text{Re}(\text{COCH}_3)_2(\text{CO})_4]$ [97], $\text{Re}(\text{CO})_4(\text{COMe})\text{-}(\text{CMe}=\text{NH})\text{BPhCl}$ [98], and $\text{Re}(\text{CO})_4(\text{COMe})_2\text{H}$ [99]. Compounds XIII were prepared by deprotonation of $\text{M}(\text{CO})_4(\text{COMe})(\text{COR})\text{BF}_2$ ($\text{M} = \text{Mn}, \text{Re}; \text{R} = \text{Me}, \text{Pr}^i$); the structure of one of these products was determined [100]. Similar reactions starting with $\text{Re}(\text{CO})_3(\text{COR})_3\text{BX}$ ($\text{X} = \text{Cl}, \text{F}, \text{R} = \text{Me}, \text{Pr}^i$) yield complexes with structure XIV [101]. Some of this work is contained in a thesis [102].



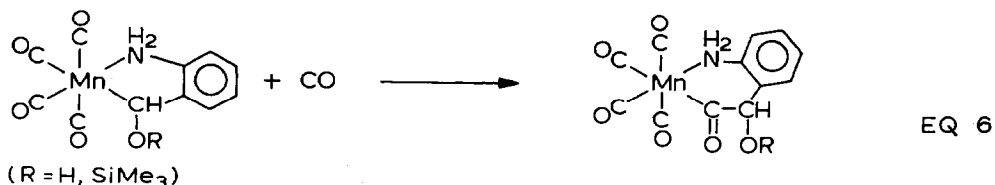
(XIII, $\text{M} = \text{Mn}, \text{Re}; \text{R} = \text{Me}, \text{Pr}^i$)



(XIV, $\text{X} = \text{Cl}, \text{F}$)

Reactions of various species of the formula $\overline{\text{HNCH}_2\text{X}}$ ($\text{X} = \text{CR}_2, \text{NH}, \text{O}$) with $\text{MnH}(\text{CO})_4(\text{L})$ ($\text{L} = \text{CO}, \text{PPh}_3$) yield $(\text{CO})_3(\text{L})\overline{\text{MnCOCH}_2\text{XNH}_2}$ [103]. Somewhat similar complexes, $(\text{CO})_4\overline{\text{ReCONR}'\text{CR}=\text{NR}'}$, ($\text{R} = \text{H}, \text{Me}, \text{Ph}; \text{R}' = \text{several aryl}$

groups), are obtained in $\text{ReX}(\text{CO})_5 + \text{Li}[\text{R}'\text{NCRNR}']$ reactions; heating these species gives two products, $(\text{CO})_4\text{ReR}'\text{NCRNR}'$ (from decarbonylation) and an orthometallated species [104]. The carbonylation reactions shown below (EQ. 6) were carried out, with the trimethylsiloxy reaction being slower by a factor of sixteen [105]. Formation of $\text{Re}(\text{CO})_3(\text{bipy})\text{CO}_2\text{H}$ was referred to earlier in this review [25].



Other complexes having carbon containing ligands to which earlier reference has been made include $\text{ReCl}(\text{dppe})_2=\text{C}=\text{CR}_2$ [42], $\text{MX}(\text{CO})_4(\overline{\text{COCH}_2\text{CH}_2\text{Y}})$ [44], $\text{Re}_2(\mu\text{-H})_2(\mu\text{-CHR})(\eta\text{-C}_6\text{H}_6)_2$ [58], $\text{Re}_2(\mu\text{-H})(\mu\text{-MeCO})(\text{CO})_8$ [64], $\text{Bu}_4\text{N}[\text{Re}_3(\mu\text{-H})_3(\mu, \eta^2\text{-OCPhNH})(\text{CO})_{10}]$ [67]; see also a paper on C-H activation using $\text{ReH}_7(\text{PCy}_3)_2$ [69]. Two papers [106,107] referencing carbyne units bridging dissimilar metals are discussed further in Section VI.

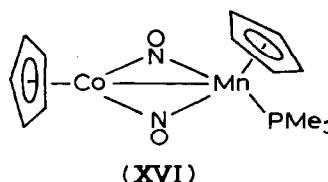
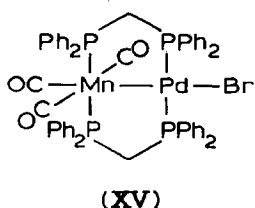
VI. DERIVATIVES OF METALS AND METALLOIDS

Initial coverage in this section is directed to dinuclear and polynuclear complexes with two different transition metals; this will be followed by a survey of Mn and Re complexes with lanthanoids. After this, references to derivatives of main group elements are presented. Overall, the activity in this area seems to have expanded substantially in the last year.

Two research groups have published reports of a complex trans- $\text{Pt}(\text{CO})_2\text{-}[\text{Mn}(\text{CO})_5]_2$. Braünstein et al. [108,109] prepared this species by displacing benzonitrile in $\text{Pt}(\text{PhCN})_2[\text{Mn}(\text{CO})_5]_2$ by CO. Shapley et al. [110] prepared this species and also the rhenium analogue from the reaction of $\text{PtMe}_2(\text{COD})$ and $\text{MH}(\text{CO})_5$; an x-ray diffraction study provided structural information on the rhenium complex. A thesis containing this work is also noted [111].

Preparation of $\text{PdPtMn}_2(\text{CO})_9(\text{dppm})_2$ was accomplished by reaction of $\text{Na}[\text{Mn}(\text{CO})_5]$ and $\text{PdPtCl}_2(\text{dppm})_2$ [112]. Dinuclear palladium-manganese species

$\text{MnPdX}(\text{CO})_3(\text{dppm})_2$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) are formed from the reactions of $\text{MnX}(\text{CO})_5$, $\text{Pd}(\text{dba})_2$ ($\text{dba} = \text{trans,trans}(\text{PhCH}=\text{CH})_2\text{CO}$) and dppm . The bromide species was the subject of a crystal structure study (XV). The exchange of the halide ion using several other anions was also reported [113]. A product of the reaction of $\text{Na}[\text{Mn}(\text{CO})_5]$ with $\text{RhCl}(\text{PPh}_3)_3$, has been characterized; it has the formula $\text{MnRh}(\text{CO})_2(\mu\text{-CO})_2(\text{PPh}_3)_3$ and is assumed to contain a manganese-rhodium double bond [114]. A cobalt-manganese complex, XVI, was prepared from $\text{Na}[\text{Co}(\text{NO})(\eta\text{-C}_5\text{H}_5)]$ and $[\text{Mn}(\text{NO})(\text{CO})(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ and its structure determined [115]. Reactions of $\text{CoMn}(\text{CO})_9$ with several acetylenes yielded $\text{MnCo}(\text{CO})_7(\text{RC}\equiv\text{CR})$ ($\text{R} = \text{Et}, \text{Me}, \text{Ph}$) [116].



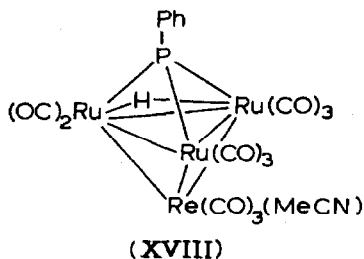
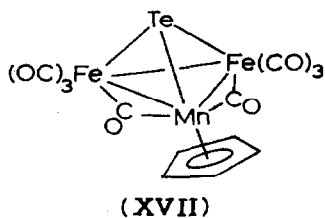
Extensive study has been accorded to products formed in a reaction sequence originating with $(\text{CO})_5\text{ReW}(\text{CO})_4\equiv\text{CtolP}$. Reduction of this species using $\text{K}[\text{BHBu}_3]^{\text{s}}$ followed by metathesis with $[\text{PPN}]\text{Cl}$ affords $\text{PPN}[(\text{CO})_4\text{Re}(\mu\text{-CHtolP})\text{W}(\text{CO})_5]$ (structure determined). Reactions with phosphines and phosphites produced a series of derived species; two, $(\text{CO})_3\text{Re}(\mu\text{-CHtol})(\mu\text{-CO})(\mu\text{-dppm})\text{W}(\text{CO})_3$ and $(\text{CO})_3\text{Re}(\mu\text{-tolCH}_2\text{CO})(\mu\text{-CO})(\mu\text{-dppm})\text{W}(\text{CO})_2[\text{P}(\text{OMe})_3]$, were characterized by crystallographic methods [107]. The complex $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}(\mu\text{-HCOCO}_2\text{Me})\text{W}(\text{CO})_4$ has also been mentioned; it is formed in the reaction between $\text{Mn}(\text{HC}\equiv\text{CCO}_2\text{Me})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $\text{W}(\text{CO})_5(\text{THF})$ [117].

Reactions of $\text{W}(\text{Ctol})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ with $\text{Re}_2(\text{CO})_{10}$ yields $\text{Re}_2\text{W}(\mu_3\text{-Ctol})(\text{CO})_{10}(\eta\text{-C}_5\text{H}_5)$. The tungsten species also reacts with $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{THF})_2$ to give $\text{Re}_2\text{W}(\mu\text{-Br})_2(\mu\text{-Ctol})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)$ and with $\text{ReBr}(\text{CO})_3(\text{MeCN})_2$ to give $\text{ReW}_2(\mu\text{-Br})(\mu_2\text{-Ctol})(\mu_3\text{-Ctol})(\mu\text{-CO})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2$ which is found to oxidize readily in air to a μ -oxo species $\text{ReW}_2(\mu\text{-Br})(\mu_2\text{-CR})(\mu_3\text{-CR})(\mu\text{-O})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$. Structures of the last two complexes were determined crystallographically [106].

Reference to formation of $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mo}(\mu\text{-H})(\mu\text{-Ptol})_2\text{Mn}(\text{CO})_4$ and to deprotonation of this species were given earlier in this review [74,75]. Also cited earlier was a paper on $(\eta\text{-C}_5\text{H}_5)_2(\text{CO})\text{M}(\mu\text{-H})\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Nb}, \text{Ta}$) [72].

The species $(\eta\text{-C}_5\text{H}_5\text{CrSBu}^t)_2\text{S}$ is a precursor to several chromium-manganese complexes. Its reaction with either $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5)$ [118] or $\text{Mn}(\eta\text{-C}_5\text{H}_5)_2$ [119] yields $[(\eta\text{-C}_5\text{H}_5\text{Cr})_2(\mu_2\text{-SBu})(\mu_3\text{-S})_2]_2\text{Mn}$, while reaction with $\text{Mn}_2(\text{CO})_{10}$ gives $(\eta\text{-C}_5\text{H}_5\text{Cr})_2(\mu\text{-SBu}^t)(\mu_3\text{-S})_2\text{Mn}(\text{CO})_3$ [120]. Structures of both species were obtained in these studies.

Bimetallic and polymetallic complexes of iron group metals with either manganese or rhenium include $(\eta\text{-C}_5\text{Me}_5\text{Mn})\text{Fe}_2(\mu\text{-CO})_2(\mu_3\text{-Te})(\text{CO})_6$, XVII [120] and a structurally analogous compound with sulfur instead of tellurium and the methylcyclopentadienyl ligand instead of the pentamethylcyclopentadienyl group [122]. Structures were determined for both species. Formation of $\text{ReRu}_3(\mu\text{-H})(\mu_3\text{-PPh})(\text{CO})_{11}(\text{MeCN})$, XVIII, from $[\text{Ru}_3(\mu\text{-H})(\mu_3\text{-PPh})(\text{CO})_9]$ and $[\text{Re}(\text{CO})_3(\text{MeCN})_3]^+$ is noted [123]. A thesis reports on various ruthenium-manganese cluster species (and other clusters as well) [124]. The complex



$(\eta\text{-C}_5\text{H}_5\text{Mn})\text{Os}_3(\mu\text{-H})(\mu\text{-CO})(\mu_2\text{-CH=CHPh})(\text{CO})_{11}$ has been prepared and structurally characterized [125,126] as has the species $\text{ReOs}_3(\mu\text{-H})(\mu, \eta^2\text{-C}\equiv\text{CPh})_2(\text{CO})_{14}$ [127].

Various gold(I)-metal complexes including $[(\text{CO})_5\text{MnAuMn}(\text{CO})_5]^-$ have been prepared; their syntheses are carried out from reaction of $\text{R}_4\text{N}[\text{AuX}_2]$ with metal carbonyl anions [128]. Complexes with copper, silver and gold [76] and mercury [77] atoms bridging two manganese tetracarbonyl units have been described earlier. The formation of $[\text{HgRe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_4$ and a description of its structure have been published [129]. A ytterbium complex, $(\text{C}_5\text{Me}_5)_2\text{YbMn}(\text{CO})_5$, was prepared; it has a polymeric structure [130].

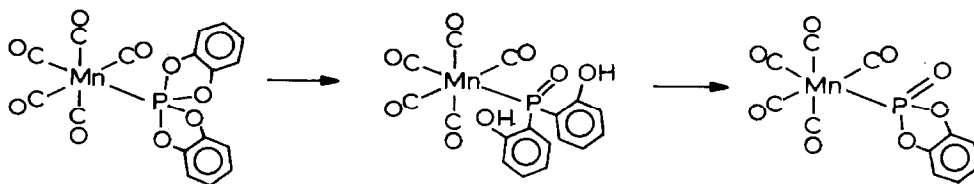
Interest in complexes between manganese and rhenium and elements in periodic groups III and IV has faded in the last year. One boron containing complex, $\text{Mn}(\eta\text{-C}_3\text{H}_3\text{BMeNBu}^t)(\text{CO})_3$, has been reported [131]. Reference to complexes with silicon-manganese bonds is limited to four citations. Three were given earlier: two were on $\text{MnH}(\text{silyl})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ species [62,63] and one on reactions of $\text{Mn}(\text{CO})_5\text{SiMe}_3$ [91]. The remaining reference [132] concerns reactions of $\text{K}[\text{Mn}(\text{MPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})]$ ($\text{Me} = \text{Si, Ge, Sn}$) with alkyl halides (MeX , EtX , PhCH_2X), giving $\text{Mn}(\text{R})(\text{MPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})$. The complex $\text{K}[\text{Mn}(\text{GeH}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ was prepared from $\text{K}[\text{GeH}_3]$ and $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5)$ [133]. This species was used as a precursor to $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}]_2\text{Ge}$ and $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}]_3\text{Ge}$ [134]; the latter species was the subject of a crystal structure determination. Two papers describe $\text{M}_2(\text{CO})_8[\mu\text{-SnXM}(\text{CO})_4(\text{PPh}_3)]_2$ species ($\text{M} = \text{Mn, Re}$, $\text{X} = \text{Cl, Br, I}$) in a study which includes reports of two crystal structures [135,136].

VII. COMPLEXES WITH GROUP VA AND VIA LIGANDS

This section collects references to species with specific Group VA and VIA ligands (but choosing to exclude substances containing ligands that function as simple two electron donors). Some of the references for this section have already been presented in conjunction with other topics, including the following: references to phosphido bridged ($\mu_2\text{-PR}_2$) species [73-78,123,124]; references to bridging sulfido, $\mu_3\text{-S}$, and to one $\mu_3\text{-Te}$ species [118-122]; a reference to a radical species $(\text{CO})_4\text{Mn}(\text{BETS})$ [19]; and a reference to a review article on complexes with $\text{-R}_2\text{PS-}$ units [4].

Bis-pyrazolylgallium complexes act as bidentate ligands to rhenium in the complex $\text{Re}(\text{CO})_4(\text{pz}_2\text{GaMe}_2)$ ($\text{pz} = \overline{\text{NCRCHCRN}}$, for $\text{R} = \text{H, Me}$). Analogous species $\overline{\text{Re}(\text{CO})_4(\text{pzGaMe}_2\text{OH})}$ [137] and $\text{M}(\text{CO})_3(\text{pzGaMe}_2\text{XCH}_2\text{CH}_2\text{Y})$ ($\text{M} = \text{Mn, Re}$; $\text{X} = \text{O, S}$; $\text{Y} = \text{NH}_2, \text{NMe}_2$) have also been reported [138]. In the latter, the tridentate coordination to the metal is from a pyrazolyl nitrogen and the X and Y donor nuclei; a crystal structure was determined for one of these latter species.

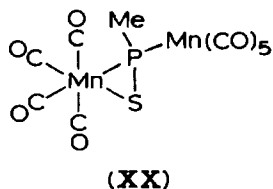
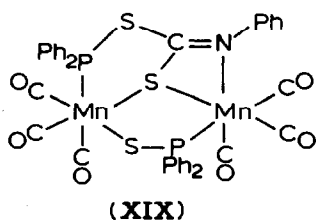
Hydrolysis of $\text{Mn}(\text{CO})_5\text{P}(\text{O}_2\text{C}_6\text{H}_4)_2$ gives $\text{Mn}(\text{CO})_5\text{PO}(\text{o-OC}_6\text{H}_4\text{OH})_2$ which can be converted to $\text{Mn}(\text{CO})_5\text{PO}(\text{O}_2\text{C}_6\text{H}_4)_2$, see the scheme below. Structures of both products were ascertained [139,140].



A reaction between $\text{MnBr}(\text{CO})_5$ and $\text{R}_2\text{NP}(=\text{NR})_2$ ($\text{R} = \text{SiMe}_3$) yields $\text{Mn}(\text{CO})_3(\text{RNPBrNR}_2\text{NR})$, a 16e species; this complex adds CO at low temperature but loses it as the temperature is raised. The structure of $\text{Mn}(\text{CO})_3[\text{RNP}(\text{OPh})(\text{NR}_2)\text{NR}]$ ($\text{R} = \text{SiMe}_3$) was determined; conversion of the former species to this complex occurs with addition of phenoxide ion [141].

Photolysis of $\text{Mn}_2(\mu\text{-PPh}_2)_2(\text{CO})_8$ leads to CO loss and formation of $\text{Mn}_2(\mu\text{-PPh}_2)_2(\mu\text{-CO})(\text{CO})_6$ (structure determined) [142]. Reactions of $\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-}\eta^2\text{-CR=CHR})(\text{CO})_8$ ($\text{R} = \text{H}, \text{Ph}$) with NaBH_4 , CNBu^t and PEt_3 have been carried out. Structures for three products were determined crystallographically and are reported in the indicated paper; these have the formulas $\text{PPN}[\text{Mn}_2(\mu\text{-H})(\mu\text{-PPh}_2)(\mu\text{-PhCH=CPhCO})(\text{CO})_6]$, $\text{Mn}_2(\mu\text{-PPh}_2)(\mu\text{-PhCH=CPhCO})(\text{CO})_6\text{-}(\text{CNBu}^t)_2$, and $\text{Mn}_2(\mu\text{-PPh}_2\text{COCPh=CHPh})(\text{CO})_6(\text{PEt}_3)$. Other complexes identified in the hydride reaction include the anionic species $[\text{Mn}_2(\mu\text{-PPh}_2)(\text{CO})_8]^-$ and $[\text{Mn}_2(\mu\text{-H})(\mu\text{-PPh}_2)_2(\text{CO})_6]^-$ [143].

Reactions between $[(\text{CO})_4\text{MnSPR}_2]_2$ ($\text{R} = \text{Me}, \text{Ph}$) and PhNCS have been described; the structure of the product, $\text{Mn}_2(\mu\text{-SPPh}_2)(\mu\text{-Ph}_2\text{PSCSNPh})(\text{CO})_6$, XIX, was ascertained through a crystallographic study [144]. The complex $\text{Mn}_2(\mu\text{-MePS})(\text{CO})_9$, XX, obtained from the reaction of MePSCl_2 , $\text{Me}_2(\text{CO})_{10}$, and Mg , was also characterized crystallographically [145].

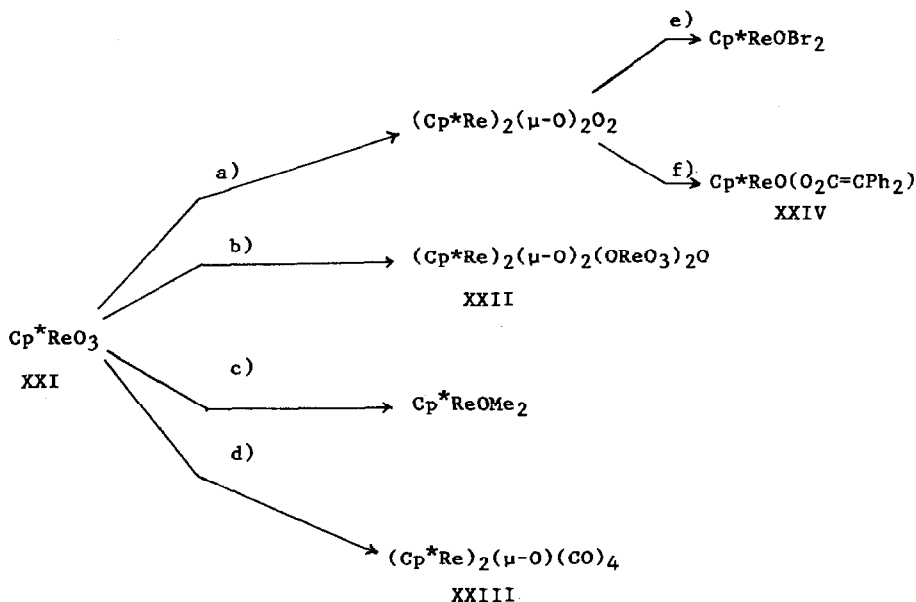


The Ph_2PO ligand group, coordinated through phosphorus, is encountered in the complex $[\text{Mn}(\text{CO})_4(\text{PPh}_2\text{O})_2]^-$. This anionic species is formed by deprotonation of $\text{Mn}(\text{CO})_4(\text{PPh}_2\text{O})_2\text{H}$ which was obtained, in turn, from the reaction between $\text{Na}_2[\text{Mn}(\text{CO})_4\text{PPh}_2]$ and SO_2Cl_2 . It was the subject of a crystal structure study [146]. The compounds $\text{M}_2[\mu-(\text{EtO})_2\text{PO}]_2(\text{CO})_8$ ($\text{M} = \text{Mn}, \text{Re}$) are formed by photolysis of $\text{M}_2(\text{CO})_{10}$ and $\text{Hg}[\text{PO}(\text{OEt})_2]_2$ [147]. A similar species, $\text{Mn}_2(\mu-\text{Ph}_2\text{PO})_2(\text{CO})_8$, forms on thermal degradation of $\text{Mn}(\text{CO})_4(\text{PPh}_2\text{OCH}_2\text{CH}_2)$ [88].

The NMR spectrum of a phosphole complex, $\text{Mn}(\text{CO})_3(\eta\text{-}3\text{MeC}_4\text{H}_3\text{P})$, is the subject of another study [148].

An arsenic complex, $[(\eta\text{-C}_5\text{Me}_5)\text{Mn}(\text{CO})_2]_2\text{AsH}$, can be obtained from the reaction of $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{Me}_5)$ and AsH_3 . Heating converts this species to $\text{Mn}_2(\mu\text{-As}_2)(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2$. Structures of both species were determined. Using $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5)$, a different complex was obtained in a reaction with AsH_3 ; it has the formula $\text{As}_2[(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_4$ [149]. The antimony complexes $[(\eta\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2]_2\text{SbBr}$ (structure determined) and $[(\eta\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2]_2\text{SbCl}$ were prepared and characterized [150].

A most interesting series of rhenium complexes with oxo ligands has been the subject of recent, intensive study. Oxygen reacts with $\text{Re}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{Me}_5)$ to give $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$ [151,152]. This species was then found to undergo numerous reactions [152,153] which are outlined in the scheme below. Structures of compounds XXI [152] and XXII-XXIV [153] were determined crystallographically.



a) PPh_3 ; b) $\text{PPh}_3 + \text{O}_2$; c) AlMe_3 ; d) CO ; e) Br_2 ; f) $\text{Ph}_2\text{C}=\text{C}=\text{O}$;
 $(\text{Cp}^* = \eta\text{-C}_5\text{Me}_5)$

In a related study, photolysis of $\text{Re}(\text{CO})_3(\eta\text{-C}_5\text{Me}_5)$ in THF was shown to yield two compounds, in addition to $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$. These are $(\eta\text{-C}_5\text{Me}_5\text{Re})_2(\mu\text{-O})(\text{CO})_4$ and $(\eta\text{-C}_5\text{Me}_5\text{Re})_2(\text{CO})_2\text{O}_2$; both are converted to $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$ if the reaction is continued [154].

In ethanol, indenylrhenium tricarbonyl and hexamethylenetetramine react to yield $[\text{HMTA-Me}]^+ [\text{Re}_2(\mu\text{-OEt})_2(\mu\text{-OMe})(\text{CO})_6]^-$; the molecular structure of this species was determined [155]. The complex $\text{Re}(\text{CO})_2(\text{PPh}_3)_2(\text{sal})^-$ (sal is the anion derived from salicylaldehyde) is formed from $\text{ReCl}(\text{CO})_3(\text{PPh}_3)_2$ and $\text{Li}[\text{sal}]$ [156]. Anionic manganese and rhenium tricarbonyl species with a $\text{P}_3\text{O}_9^{3-}$ ligand are described in a thesis [157].

One of the more interesting results in the past year is found in a paper describing $\text{Mn}(\text{CO})_2(\text{RSH})(\eta\text{-C}_5\text{H}_5)$ and a product derived from oxidation of this species. The indicated complex, obtained from $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5)$ and a mercaptan, reacts readily with oxygen to give a violet complex $\text{Mn}(\text{SR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ in which the metal has, formally, a 17 electron configuration. The molecular structure of one such complex, $\text{Mn}(\text{SBU}^t)(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)$, was determined by crystallography [158].

The complex $\text{fpCS}_2\text{Re}(\text{CO})_5$ ($\text{fp} = \text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$) can be formed from $[\text{fpCS}_2]^-$ and $\text{ReX}(\text{CO})_5$. Methylation of this species yields $\text{fp}[\text{C}(\text{SMe})\text{SRe}(\text{CO})_5]^+$; treatment with $\text{Mn}(\text{CO})_2(\text{THF})(\text{C}_5\text{H}_5)$ leads to $\text{fp}[\text{C}(\text{SMe})\text{SMn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [159].

Another paper [160] reports the reaction of $\text{fpCS}_2\text{Re}(\text{CO})_5$ with $[\text{fpCS}]\text{Br}$. This reaction gives $[\text{fpCSC}(\text{SRe}(\text{CO})_5)\text{Fe}(\text{CO})(\eta\text{-C}_5\text{H}_5)\text{S}]\text{Br}$ which was isolated and its structure determined.

The thiophene complex, $[\text{Mn}(\text{CO})_3(\eta\text{-C}_4\text{H}_4\text{S})]\text{O}_3\text{SCF}_3$, is formed from $\text{Mn}(\text{O}_3\text{SCF}_3)(\text{CO})_5$ and thiophene. It is very reactive with nucleophiles such as CN^- , giving products resulting from attack at a carbon atom of the heterocyclic ring [161]. The reaction between $\text{Re}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5)$ with S_8 (or COS) leads to a series of products: $\text{Re}(\text{CO})_2(\text{S}_2)(\eta\text{-C}_5\text{H}_5)$, $\text{Re}_2(\mu\text{-S})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2$ and $\text{Re}_2(\mu_2\text{-S}_2)(\mu\text{-S}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2$. Molecular structures were obtained for the last two species [162]. A complex $[(\eta\text{-C}_5\text{Me}_5)(\text{CO})_2\text{Mn}]_2\text{Te}$ has been prepared (structure determined.) This species reacts with $\text{R}_2\text{C}=\text{N}_2$ to give a product in which the carbene group derived from the diazo precursor bridges manganese and tellurium [163].

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

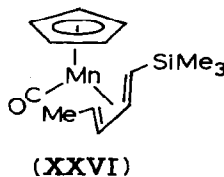
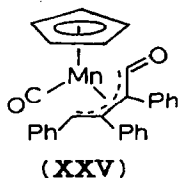
The task of assembling references in this section will be simplified by listing compounds (or topics) mentioned earlier, along with appropriate references. Even so, the list of references in this area left to be identified remains extensive. Compounds cited here previously include: $\text{MnH}(\text{CO})(\text{NO})(\eta\text{-C}_5\text{H}_5)$ [49]; $\text{ReH}_2(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $[\text{ReH}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^-$ [50]; $\text{MnH}(\text{SiHPh}_2)(\text{CO})(\text{L})(\eta\text{-C}_5\text{H}_4\text{Me})$ [62]; $\text{MnH}(\text{SiMePhNp})(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})$ [63]; $(\eta\text{-C}_5\text{H}_5)_2(\text{CO})\text{M}(\mu\text{-H})\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ ($\text{M} = \text{Nb}, \text{Ta}$) [72]; $\text{Re}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{CH}_2\text{X})$ ($\text{X} = \text{Cl}, \text{Mn}(\text{CO})_5, -(\eta\text{-C}_5\text{H}_4\text{Re}(\text{CO})_3)$) [84]; $(\text{CO})_4\text{W}(\mu\text{-HCOCOOMe})\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [117]; $(\eta\text{-C}_5\text{Me}_5)\text{MnFe}_2\text{Te}(\text{CO})_8$ [121]; $(\eta\text{-C}_5\text{H}_4\text{Me})\text{MnFe}_2\text{S}(\text{CO})_8$ [122]; $(\eta\text{-C}_5\text{H}_5\text{Mn})\text{Os}_3\text{H}(\mu\text{-CH}=\text{CHPh})(\text{CO})_{12}$ [125, 126]; $[\text{HgRe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_4$ [129]; $\text{Mn}(\text{R})(\text{MPh}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})$ [132]; $\text{K}[\text{Mn}(\text{GeH}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [133]; $\text{Ge}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_3$ [134]; products of $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{R}_5) + \text{AsH}_3$ [149]; $\text{XSb}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_2$ [150]; $\text{Mn}(\text{RSH})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ and $\text{Mn}(\text{SR})(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)$ [158]; $\text{fpC}(\text{SMe})_5\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [159]; products of $\text{Re}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_5) + \text{S}_8$ [162]; and $\text{Te}[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2$ [163].

The synthesis of $\text{Mn}(\text{CO})_3[\eta\text{-C}_5(\text{CO}_2\text{Me})_5]$ has been accomplished by reaction of $\text{MnBr}(\text{CO})_5$ with $\text{K}[\text{C}_5(\text{CO}_2\text{Me})_5]$. This is one of only a few complexes with a pentasubstituted cyclopentadienyl ligand with substituents other than hydrogen or a methyl group. Reactions of this species with several phosphines were carried out [164]. It has been determined that $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{Me}_5)$ loses CO spontaneously at room temperature, forming $(\eta\text{-C}_5\text{Me}_5)\text{Mn}(\mu\text{-CO})_3\text{Mn}(\eta\text{-C}_5\text{Me}_5)$. A crystal structure study on the product revealed a very short metal-metal distance of 2.170 Å, in accord with the formulation of a triple bond between metals in this dimer [165].

A few new derivatives of $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ in which one carbonyl has been replaced by another ligand have been reported in the literature. These include $\text{NEt}_4[\text{Mn}(\text{N}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [166], $\text{Mn}(\text{CO})_2[\text{PH}(\text{NPr}_2^i)_2](\eta\text{-C}_5\text{H}_5)$ [167], $(\eta\text{-C}_5\text{Me}_5)\text{Rh}(\text{CO})\text{Me}_2\text{PPMe}_2\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [168],

$[(\eta\text{-C}_5\text{Me}_5\text{Mo})_2\text{S}_4]\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [169], $\eta\text{-C}_5\text{H}_5\text{Mn}(\text{CO})_2\text{L}^{\wedge}\text{LMn}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ with $\text{L}^{\wedge}\text{L} = 4,4'$ -bipy and other bidentate nitrogen donor ligands [170], $p\text{-C}=\text{CHC}_6\text{H}_4\text{CH}=\text{C}$ [171] and 1,4-pyrazine [172]. The last listed compound is of interest because it can be reduced to a radical anion for which ESR data can be obtained. Complexes of the form $\text{Mn}(\text{C}\text{Ar}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})$ are obtained by reactions between $\text{Mn}(\text{CO})_2(\text{THF})(\eta\text{-C}_5\text{H}_4\text{Me})$ and Ar_2CN_2 ($\text{Ar} = \text{aryl groups}$). These species add CO which assumes a bridging position between the carbene carbon and the metal. The structures of two new complexes are reported in this study [173].

Reaction between $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ and triphenylcyclopropene yields the complex $\text{Mn}(\text{CO})(\eta^4\text{-C}_3\text{Ph}_3\text{CO})(\eta\text{-C}_5\text{H}_5)$ with structure XXV [174]. Another diene derivative, XXVI, arises out of the reaction between $\text{Me}_3\text{SiCH}=\text{CH}=\text{CHMe}$ and $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_4\text{Me})$ [175].

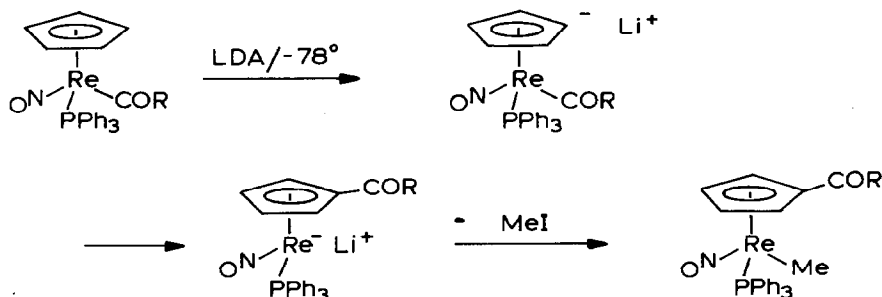


Addition of HX ($\text{X} = \text{Cl}, \text{Br}, \text{BF}_4, \text{CF}_3\text{CO}_2$) to divalent carbon ligand in $\text{Mn}(\text{CO})_2(\text{C}=\text{C}=\text{CR}_2)(\eta\text{-C}_5\text{H}_5)$ ($\text{R} = \text{Ph}, \text{Bu}^t$) converts it to a carbyne group. A crystal structure determination was carried out on one complex $[\text{Mn}(\equiv\text{CCH}=\text{CPh}_2)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$. Hydride reduction of these species produces $\text{Mn}_2(\mu\text{-C}=\text{CHR}')(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2$ [176]. A reaction of PPh_3 with the same precursor gives $\text{Mn}(\text{CO})_2(\text{C}\text{PPh}_3=\text{C}=\text{CPh}_2)(\eta\text{-C}_5\text{H}_5)$ (structure determined) [177]. A reaction of $\text{Mn}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ with the ylide $\text{Me}_3\text{PCHSiMe}_3$ results in formation of $\text{Mn}(\text{CO})_2(\text{CHSiMe}_3\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)$. Other reactions were also reported in this paper [178].

Preparations of $\text{Yb}[\eta\text{-C}_5\text{H}_4\text{Mn}(\text{CO})_3]_2$ [179] and $\text{Mn}(\text{CO})_3[\eta\text{-C}_5\text{H}_4\text{Fe}(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{CO}_2\text{H})]$ [180] have been carried out. Crystal structures of two complexes $\text{Mn}(\text{CO})_3[\eta\text{-C}_5\text{H}_4\text{Fe}(\text{CO})(\text{L})(\text{C}_5\text{H}_5)]$ ($\text{L} = \text{CO}, \text{PPh}_3$) were completed [181]. Low frequency IR and Raman spectrometry [182], mass spectrometry [183], ion-molecule reactions with a crown ether [184] and NMR in nematic crystals [185] of $\text{M}(\text{CO})_3(\eta\text{-C}_5\text{H}_5)$ are other subjects under study. The crystal structure of $\text{Mn}(\text{CO})_2(\text{CPh}_2)(\eta\text{-C}_5\text{H}_5)$ has been determined. Of interest here is the conformation of the carbene fragment and comparisons of structural parameters with those of the isoelectronic species $\text{Cr}(\text{CO})(\text{NO})(\text{CPh}_2)(\eta\text{-C}_5\text{H}_5)$ [186].

A crystal structure study on $\{\text{Re}(\text{CO})_2(\text{NHNMeC}_6\text{H}_4\text{Me})(\eta\text{-C}_5\text{H}_5)\}\text{BF}_4$ provides the molecular geometry of this species. In solution this and other hydrazido complexes exist in two stereoisomeric forms which are found to interconvert by rotation around the nitrogen-nitrogen bond [187]. This work and related studies are also contained in a Ph.D. thesis [188].

Five papers on various cyclopentadienylrhenium nitrosyl cations have appeared, three from the Gladysz group. One reference [189] identifies retention of metal stereochemistry in cleavage of the rhenium-carbon bond in $\text{Re}(\text{Me})(\text{NO})(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)$ by acids. In reactions with halogens, however, the metal stereochemistry is lost [189]. A second paper [190] examines the carbene complexes $[\text{Re}(\text{CHAR})(\text{NO})(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ ($\text{Ar} = \text{Ph}, o\text{-tol}, \text{Mes}$) with respect to the conformation of the carbene group; NMR techniques were used to study rotation around the carbon-metal bond in these species. In the third paper [191], there is a report on the interesting reaction sequence shown below. Deprotonation of the cyclopentadienyl group in the starting material is followed by migration of an acyl group from the metal; the sequence is completed by alkylation at rhenium.

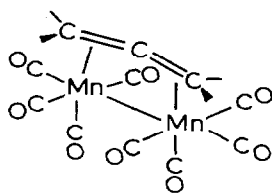


Deprotonation of $\text{ReH}(\text{NO})(\text{CO})(\eta\text{-C}_5\text{H}_5)$ has been shown to occur using $n\text{-BuLi}$ in TMEDA at -40° . The anionic species was then allowed to react with MeX , Me_3SiCl , or CO_2/H^+ to give $\text{Re}(\text{R})(\text{NO})(\text{CO})(\eta\text{-C}_5\text{H}_5)$ ($\text{R} = \text{Me}$, SiMe_3 , or CO_2H) [192]. Reactions of $[\text{Re}(\text{NO})(\text{PPh}_3)(\text{CH}_2)(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$ with PPh_3Se or KSeCN yield two products, $\text{Re}(\text{CH}_2\text{X})(\text{NO})(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)$ ($\text{X} = \text{CN}$, PPh_3^+) and $[\text{Re}(\text{NO})(\text{PPh}_3)(\eta\text{-CH}_2=\text{Se})(\eta\text{-C}_5\text{H}_5)]\text{PF}_6$; the latter was the subject of a structural investigation [193].

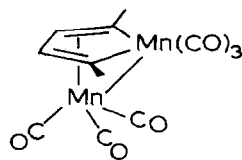
IX. OTHER HYDROCARBON-METAL COMPLEXES

Organization of this section is based on size of the hydrocarbon ligands. First considered are complexes of alkenes and acetylenes (η^2); then progress is charted through complexes with ligands of increasing size, $\eta^3 \rightarrow \eta^6$.

Most references to complexes having η^2 -alkene or acetylene ligands have already been encountered in this review in other contexts. This includes references to: η^2 -methylene-cyclobutene complexes [30]; $\text{ReCl}(\text{dppe})_2$ - $(\eta^2\text{-H}_2\text{C}=\text{C}=\text{CHPh})$ [43]; $\text{ReI}(\text{O})(\eta\text{-MeC}\equiv\text{CMe})_2$ [46]; several dirhenium carbonyl complexes with μ, η^2 -alkenyl and alkynyl groups [54-57]; complexes derived from $\text{Re}_3\text{H}_3(\text{CO})_{12}$ and $\text{PhC}\equiv\text{CPh}$ [65]; and olefin hydrogenation and isomerization catalyzed by $\text{MnH}(\text{CO})_4(\text{PPh}_3)$ [70]. In addition to these references, there is also a report of the synthesis of $\text{ReH}_3(\eta\text{-C}_2\text{H}_4)_2(\text{PR}_3)_2$ and its hydrogenation to $\text{ReH}_5(\eta\text{-C}_2\text{H}_4)(\text{PR}_3)_2$ ($\text{PR}_3 = \text{P}(\text{C-C}_5\text{H}_9)_3$ and $\text{PPhPr}_2^{\frac{1}{2}}$) [194], and the synthesis of XXVII, drawn below. This species is the product of photolysis of $\text{Mn}_2(\text{CO})_{10}$ and allene at low temperature [195].



(XXVII)



(XXVIII)

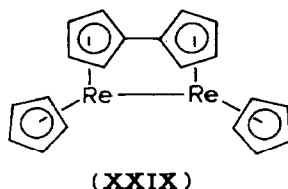
A study related to that just cited, by the same authors, involves photolysis of $\text{Mn}_2(\text{CO})_{10}$ with trans,cis-2,4-hexadiene. In addition to three compounds with η^3 -hexenyl ligands, product XXVIII is also obtained. The structure of this species has been confirmed by a crystallographic study [196]. Note also that one of the products from the $\text{Re}_3\text{H}_3(\text{CO})_{12}\text{-PhC}\equiv\text{CPh}$ reaction [65] has a structure similar to XXVIII.

A rhenium-diene complex is formed when $\text{ReH}_7(\text{PPh}_3)_2$ is heated with propene. Photolysis converts the mixture of reactants and products to $\text{ReH}(\eta^3\text{-C}_3\text{H}_5)_2(\text{PPh}_3)_2$ [197]. Extensive study is accorded to diene-rhenium species, $\text{ReH}_3(\eta^4\text{-diene})(\text{PPh}_3)_2$. An NMR study indicates fluxional behavior for the hydrocarbon unit [198]. The crystal structure of $\text{ReH}_3(\eta^4\text{-C}_6\text{H}_8)(\text{PPh}_3)_2$ was determined [199]. The ESR spectrum of $\text{Mn}(\eta^4\text{-C}_4\text{H}_6)_2(\text{PMe}_3)$ in a host matrix of the diamagnetic iron analogue has been observed. This shows that in the manganese species the unpaired electron resides primarily in the d_{z^2} orbital [200,201].

Complexes with η^5 -pentadienyl ligands include $\text{Re}_3\text{H}_2(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$, mentioned previously in this review [66]. The complex $\text{Mn}_3(\eta^5\text{-3-MeC}_5\text{H}_6)_2$ is described in a thesis [202]. Phosphines add to $\text{Mn}(\text{CO})_3(\eta^5\text{-C}_5\text{H}_7)$ at room temperature to produce $\text{Mn}(\text{CO})_3(\text{L})(\eta^3\text{-C}_5\text{H}_7)$ ($\text{L} = \text{PMe}_3, \text{PPhMe}_2, \text{PBu}_3$). The structure of the PMe_3 adduct was verified by crystallography. If the reaction mixture is heated (cyclohexane, reflux) carbonyl loss occurs to give $\text{Mn}(\text{CO})_2(\text{L})(\eta^5\text{-C}_5\text{H}_7)$ [203]. Cycloheptadienylmanganese complexes are formed upon nucleophilic addition of various enolates to $[\text{Mn}(\text{CO})_3(\eta^6\text{-1,3,5-C}_7\text{H}_8)]\text{PF}_6$ [204].

References to complexes of thiophene, $[\text{Mn}(\text{CO})_3(\eta\text{-C}_4\text{H}_4\text{S})]^+$ [161], and a complex with a phospholyl ligand, $\text{Mn}(\text{CO})_3(\eta\text{-3-MeC}_4\text{H}_3\text{P})$ [148], were given earlier in this review.

It has been shown that manganocene forms 1:1 adducts with a variety of phosphines [205] and also with nitrogen bases like pyridine (a thesis, ref [206]). Crystallographic studies have defined the molecular structures of $\text{Mn}(\text{L})(\eta\text{-C}_5\text{H}_5)_2$ ($\text{L} = \text{PMe}_3, \text{PPh}_2\text{Me}$, and dmpe). In the third species the dmpe ligand, a bidentate ligand, is found to chelate to the metal. The oxidation of $\text{Re}(\eta\text{-C}_5\text{H}_5)_2\text{Li}$ has been under study [207]; the product is a dinuclear species $\text{Re}_2(\eta\text{-C}_5\text{H}_5)_4$. Thermolysis of this species gives **XXIX**, along with $\text{ReH}(\eta\text{-C}_5\text{H}_5)_2$ while reaction with PhCH_2Br leads to metal-metal bond cleavage forming $\text{Re}(\text{CH}_2\text{Ph})(\eta\text{-C}_5\text{H}_5)_2$ and $\text{ReBr}(\eta\text{-C}_5\text{H}_5)_2$.

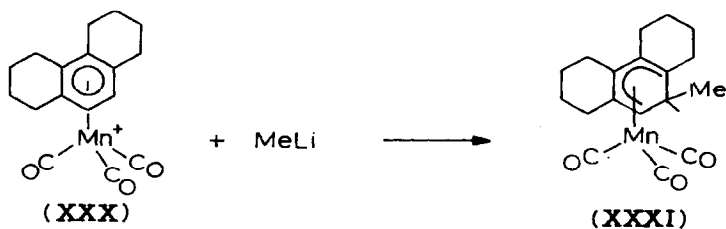


Kinetic measurements on carbonyl substitution of η^5 indenyl- and η^5 fluorenyl- manganese tricarbonyl show an associative pathway for these reactions which implicate η^3 and η^1 - intermediates [208]. The kinetics and mechanism of the $\eta^6 \rightarrow \eta^5$ haptotropic rearrangement of $\text{Mn}(\text{CO})_3(\eta^6\text{-C}_{13}\text{H}_9)$ are the subject of another paper from the same research group [209]. Reference to the reaction of $\text{Re}(\text{CO})_3(\eta^5\text{-C}_9\text{H}_7)$ with $(\text{CH}_2)_6\text{N}_4$ was given earlier [155].

Other significant complexes of these metals having cyclopentadienyl ligands include $\text{MnCl}(\text{TMEDA})(\eta\text{-C}_5\text{H}_5)$ [47] and $[\text{MnX}(\text{L})(\eta\text{-C}_5\text{H}_5)]_2$ ($\text{L} = \text{THF}$, PMe_3) [48], and $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$ and related species [151-154].

Arene complexes including $\text{MnR}(\text{PMe}_3)_2(\eta\text{-C}_6\text{H}_6)$ ($\text{R} = \text{H}$, Ph) [59] and $\text{Re}_2(\mu\text{-H})_2(\mu\text{-CHR})(\eta\text{-C}_6\text{H}_6)_2$ [58] are found as products in metal atom reactions. Another reference in this area describes the reaction of rhenium, C_6H_6 , and cyclohexene; products include $\text{ReH}(\eta^4\text{-C}_6\text{H}_8)(\eta\text{-C}_6\text{H}_6)$ and $\text{Re}_2(\mu\text{-H})_2(\eta^4\text{-C}_6\text{H}_8)_2(\eta\text{-C}_6\text{H}_6)$. Both species were subjects for structure determinations [210].

A new synthetic method for preparation of $[\text{Mn}(\text{CO})_3(\eta\text{-arene})]^+$ species involves the reaction of $\text{Mn}_2(\text{CO})_{10}$ and the arene in $\text{CF}_3\text{CO}_2\text{H}$. The acid presumably functions as an oxidizing agent [211]. Synthesis of complexes $[\text{Mn}(\text{CO})_3(\eta\text{-arene})]^+$ are explored using polycyclic arene species. The reaction of $\text{MnBr}(\text{CO})_5$ and AlCl_3 with naphthalene or anthracene yields only complexes of tetralin and 9,10-dihydroanthracene. The former can also be prepared using tetralin as the arene in this reaction. Species XXX was also formed by this type of reaction. It reacts with methyllithium to give the cyclohexadienyl-manganese complex XXXI (structure determined) [212]. The synthesis of various arene complexes $[\text{Re}(\text{CO})_3(\eta\text{-arene})]\text{AlBr}_4$



is described in another paper along with a report of the molecular structure of the mesitylene complex [213].

Sequential hydride addition and protonation starting with cationic arene manganese tricarbonyl complexes has been studied [214,215]. It is possible to deprotonate $[\text{Mn}(\text{CO})_3(\eta\text{-C}_6\text{Me}_6)]^+$, according to a thesis [216]; characterization of the products of this reaction are described.

Note also an earlier reference to carbonyl substitution in $[\text{Mn}(\text{CO})_3(\text{arene})]^+$ species [45].

X. ISOCYANIDE AND NITROSYL COMPLEXES

In the area of nitrosyl complexes there are seven references, all have been identified in earlier sections in this review. Note the reference to an unusual polynuclear complex with an μ_4, η^2 nitrosyl group [68], the reference to a species $\eta\text{-C}_5\text{H}_5\text{Co}(\mu\text{-NO})_2\text{Mn}(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)$ [115], and references to various derivatives of $[\text{M}(\text{NO})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]^+$ [189-193].

Most of the reported chemistry of complexes with isocyanide ligand groups has come from Walton and coworkers. Complexes derived from reaction of $\text{Re}_2(\mu\text{-H})_4\text{H}_4(\text{PR}_3)_4$ and isocyanides were mentioned already [60,61], as was the series of complexes formed by reactions of $[\text{ReH}(\text{MeCN})_3(\text{L})(\text{PPh}_3)_2](\text{BF}_4)_2$ with isocyanides [29]. Reactions of several aryl isocyanides with either $\text{Re}_2\text{Cl}_2(\text{OAc})_4$ or $[\text{Re}_2\text{Cl}_8]^{2-}$ (methanol, reflux) yield $[\text{Re}(\text{CNR})_6]\text{PF}_6$ complexes [R = Ph, Mes, tol, 2,6-Me₂C₆H₃]. Intermediates in these reactions can be isolated if a lower temperature is employed [217]. Raman and IR spectra of $[\text{Re}(\text{CNR})_6]\text{PF}_6$ [R = Ph, tol] are discussed in a separate paper [218]. Abstracts of three theses containing this work are available [219, 220, 221].

Two papers by Nielson and Wherland have been published. One provides information on manganese-55 to carbon-13 NMR coupling constants for $[\text{Mn}(\text{CNR})_6]\text{BF}_4$ [222] while the second contains information on the rate of electron exchange between $[\text{Mn}(\text{CNR})_6]^{n+}$ (n = 1,2), obtained from ⁵⁵Mn NMR measurements [223].

Other work on isocyanide complexes includes: formation of $\text{Re}_2(\text{CO})_{10-x}(\text{CNR})_x$ (x = 1,2) [14,15], $[\text{Mn}(\text{CO})_3(\text{CNBu})(\text{N}^+\text{N})]\text{ClO}_4$ [28] and $\text{Mn}_2(\text{CO})_8(\text{o-CH}_2\text{C}_6\text{H}_4\text{NC})_2$ [87].

XI. STRUCTURAL STUDIES

Compounds whose structures were determined by x-ray crystallography (or by other methods) are listed: $\text{eq-Re}_2(\text{CO})_9(\text{CNBu}^t)$ [14]; $\text{fac}(\text{CO})_3(\text{CNBu})_2\text{ReRe}(\text{CO})_5$ [15]; $[\text{Re}(\text{CO})_5(\text{H}_2\text{O})]\text{AsF}_6$ and $[\text{Re}(\text{CO})_3(\text{tmed})(\text{H}_2\text{O})]\text{AsF}_6$ [24]; all trans- $[\text{Re}(\text{CNBu}^t)_2(\text{MeCN})_2(\text{PPh}_3)_2](\text{BF}_4)_2$ [29]; $\text{Re}_2\text{Br}_2(\text{CO})_2(\text{Ph}_4\text{Sb}_2)$ [35]; $\text{Mn}_2(\mu\text{-Br})(\mu\text{-Y})(\text{CO})_6[(\text{EtO})_2\text{POP}(\text{OEt})_2]_2$ Y = Br, H [36]; $\text{Re}_2\text{Br}_2(\text{CO})_6(\text{P}^+\text{P})$

and $\text{ReBr}(\text{CO})_3(\mu\text{-P}^*\text{P})_2\text{ReBr}(\text{CO})_3$ with $\text{P}^*\text{P} = \text{P}_2\text{Mo}_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2$ [37]; $\text{Re}_2\text{Br}_2(\text{CO})_6[(\text{MePNBu}^t)_2]$ [38]; $\text{ReCl}(\text{dppe})_2\text{C}=\text{CHPh}$ [42]; $\text{Re}(\text{O})\text{I}(\text{MeC}\equiv\text{CMe})_2$; $\text{MnCl}(\text{tmed})(\eta\text{-C}_5\text{H}_5)$ [47]; $[\text{MnCl}(\text{PET}_3)(\eta\text{-C}_5\text{H}_4\text{Me})]_2$ [48]; $(\eta\text{-C}_6\text{H}_6)\text{Re}(\mu\text{-H})_2(\mu\text{-CHBu}^t)\text{Re}(\eta\text{-C}_6\text{H}_6)$ [58]; $[\text{Re}_2(\mu\text{-H})_3\text{H}_2(\text{CNBu})_2(\text{PMe}_3)_4]\text{PF}_6$, V, [61]; $(\text{-})\text{-MnH}(\text{SiPhMeNp})(\text{CO})_2(\eta\text{-C}_5\text{H}_4\text{Me})$ [63]; $\text{Re}_2(\mu\text{-H})(\mu\text{-MeCO})(\text{CO})_8$ [64]; $\text{Re}_2(\text{CO})_5(\text{C}_4\text{Ph}_4)(\text{PhC}\equiv\text{CPh})$ and $\text{Re}_2(\text{CO})_4(\text{C}_6\text{Ph}_6)(\text{PhC}\equiv\text{CPh})$ [65]; $\text{Re}_3\text{H}_2(\text{CO})_{10}(\eta^5\text{-C}_7\text{H}_9)$ [66]; $\text{Bu}_4\text{N}[\text{Re}_3\text{H}_3(\text{CO})_{10}(\mu, \eta^2\text{-OCPhNH})]$ [67]; $\text{Et}_4\text{N}[\text{Re}_3\text{H}_3(\text{CO})_{10}(\mu_4, \eta^2\text{-NO})\text{Re}_3\text{H}_3(\text{CO})_{10}]$ [68]; $(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}(\mu\text{-H})\text{Nb}(\text{CO})(\eta\text{-C}_5\text{H}_5)_2$ [72]; $(\text{CO})_4\text{Mn}(\mu\text{-H})(\mu\text{-PPH}_2)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)$ [73]; $\text{PPN}[\text{Mn}_2(\mu\text{-PPH}_2)(\text{CO})_8]$ and $\text{Mn}_2(\mu\text{-PPH}_2)(\mu\text{-AuPPhMe}_2)(\text{CO})_8$ [76]; $\text{Mn}_2(\mu\text{-H})(\mu\text{-P}(\text{NPr}_2)_2)(\text{CO})_8$ [78]; $\text{Co}_2(\text{CO})_6(\text{PhC}\equiv\text{CMn}(\text{CO})_4(\text{PCy}_3))$ [85]; $\text{Mn}_2(\mu\text{-CO})(\mu\text{-C}=\text{C}=\text{CBu}^t)(\text{CO})_8$, IX, [92]; mer, trans- $\text{Mn}(\text{CHO})(\text{CO})_3[\text{P}(\text{OPh})_3]_2$ [96]; $\text{PhC}(\text{NH}_2)_2[\text{Re}(\text{COMe})_2(\text{CO})_4]$, [97]; $\text{Re}(\text{CO})_4(\text{COMe})(\text{CMe}=\text{NH})\text{BPhCl}$ [98]; $\text{Re}(\text{CO})_4(\text{COMe})_2\text{H}$ [99]; $\text{Mn}(\text{CO})_4(\text{COPr}^i\text{COCMe}_2)\text{BF}_2$ [100]; $\text{ReW}_2(\mu\text{-Br})(\mu_2\text{-Cto1})(\mu_3\text{-Cto1})(\mu\text{-CO})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2$ and $\text{ReW}_2(\mu\text{Br})(\mu_2\text{-Cto1})(\mu_3\text{-Cto1})(\mu\text{-O})(\text{CO})_3(\eta\text{-C}_5\text{H}_5)_2$ [106]; $\text{PPN}[(\text{CO})_4\text{Re}(\mu\text{-CHto1P})\text{W}(\text{CO})_5]$, $(\text{CO})_3\text{Re}(\mu\text{-CHto1})(\mu\text{-CO})(\mu\text{-dppm})\text{W}(\text{CO})_3$, and $(\text{CO})_3\text{Re}(\mu\text{-to1CH}_2\text{CO})(\mu\text{-CO})(\mu\text{-dppm})\text{W}(\text{CO})_2[\text{P}(\text{OMe})_3]$ [107]; $\text{Pt}(\text{CO})_2[\text{Re}(\text{CO})_5]_2$ [110]; $\text{MnPdBr}(\text{CO})_3(\mu\text{-dppm})_2$, XXI, [112]; $(\eta\text{-C}_5\text{H}_5)\text{Co}(\mu\text{-NO})_2\text{Mn}(\text{PMe}_3)(\eta\text{-C}_5\text{H}_5)$, XIII, [114]; $[(\eta\text{-C}_5\text{H}_5\text{Cr})_2(\mu_2\text{-SBu}^t)(\mu_3\text{-S})_2]_2\text{Mn}$ [117]; $(\eta\text{-C}_5\text{H}_5\text{Cr})_2(\mu_2\text{-SBu}^t)(\mu_3\text{-S})_2\text{Mn}(\text{CO})_3$ [119]; $(\eta\text{-C}_5\text{H}_5\text{Mn})\text{-Fe}_2(\mu\text{-CO})_2(\mu_3\text{-Te})(\text{CO})_6$ [120]; $(\eta\text{-C}_5\text{H}_5\text{Mn})\text{Fe}_2(\mu\text{-CO})_2(\eta_3\text{-S})(\text{CO})_6$ [121]; $(\eta\text{-C}_5\text{H}_5\text{Mn})\text{Os}_3(\mu\text{-H})(\mu\text{-CO})(\mu\text{-CH}=\text{CHPh})(\text{CO})_{11}$ [125]; $\text{ReOs}_3(\mu\text{-H})(\mu, \eta^2\text{-C}\equiv\text{CPh})_2(\text{CO})_{14}$ [127]; $[\text{HgRe}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]_4$ [128]; $[(\text{C}_5\text{Me}_5)_2\text{YbMn}(\text{CO})_5]_x$, [129]; $[(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{Mn}]_3\text{Ge}$ [134]; $\text{Re}_2(\text{CO})_8[\text{SnXRe}(\text{CO})_4(\text{PPh}_3)]_2$ $X = \text{Cl}$ [135] and $X = \text{I}$ [136]; $\text{Re}(\text{CO})_3(\text{pzGaMe}_2\text{OCH}_2\text{CH}_2\text{NH}_2)$ [138]; $\text{Mn}(\text{CO})_5\text{PO}(\text{OC}_6\text{H}_4\text{OH})_2$ and $\text{Mn}(\text{CO})_5\text{PO}(\text{O}_2\text{C}_6\text{H}_4)$ [139, 140]; $\text{Mn}(\text{CO})_3[\text{RNP}(\text{OPh})(\text{NR}_2)\text{NR}]$ ($R = \text{SiMe}_3$) [141]; $\text{Mn}_2(\mu\text{-PR}_2)_2(\mu\text{-CO})(\text{CO})_6$ [142]; $\text{PPN}[\text{Mn}_2(\mu\text{-H})(\mu\text{-PPH}_2)(\mu\text{-PhCH}=\text{CPhCO})(\text{CO})_6]$, $\text{Mn}_2(\mu\text{-PPH}_2)(\mu\text{-PPH}_2\text{COCPh}=\text{CHPh})(\text{CO})_6(\text{PET}_3)$ and $\text{Mn}_2(\mu\text{-PPH}_2)(\mu\text{-PhCH}=\text{CPhCO})(\text{CO})_6(\text{CNBu}^t)_2$ [143]; $\text{Mn}_2(\mu\text{-SPPH}_2)(\mu\text{-Ph}_2\text{PSCSNPh})(\text{CO})_6$ [144]; $\text{Mn}_2(\mu\text{-MePS})(\text{CO})_9$ [145]; $\text{Mn}(\text{CO})_4(\text{PPh}_2\text{O})_2\text{H}$ [146]; $[(\eta\text{-C}_5\text{Me}_5)(\text{Mn}(\text{CO})_2)_2\text{AsH}]$ and $\text{Mn}_2(\mu\text{-As}_2)(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2$ [149]; $[(\eta\text{-C}_5\text{H}_4\text{Me})\text{Mn}(\text{CO})_2]_2\text{SbCl}$ [150]; $\text{ReO}_3(\eta\text{-C}_5\text{Me}_5)$ [152]; $\text{Re}_2(\mu\text{-O})(\text{CO})_4(\eta\text{-C}_5\text{Me}_5)_2$, $\text{Re}(\text{O}_2\text{C}=\text{CPh}_2)(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)$ and $(\eta\text{-C}_5\text{Me}_5\text{Re})_2(\mu\text{-O})_2(\text{OREO}_3)_2\text{O}$ [153]; $[\text{HMTAMe}][\text{Re}_2(\mu\text{-OEt})_2(\mu\text{-OMe})(\text{CO})_6]$ [155]; $\text{Mn}(\text{SBu}^t)(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)$ [158]; $[\text{fpCSC}(\text{SRe}(\text{CO})_5)\text{Fe}(\text{CO})(\eta\text{-C}_5\text{H}_5)\text{S}]\text{Br}$ [160]; $\text{Re}_2(\mu\text{-S})(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2$ and $\text{Re}_2(\mu_2\text{-S}_2)(\mu_2\text{-S}_3)(\text{CO})_2(\eta\text{-C}_5\text{H}_5)_2$ [162]; $[\text{Mn}(\text{CO})_2(\eta\text{-C}_5\text{Me}_5)]_2\text{Te}$ [163]; $(\eta\text{-C}_5\text{Me}_5)\text{Mn}(\mu\text{-CO})_3\text{Mn}(\eta\text{-C}_5\text{Me}_5)$ [165]; $\text{Mn}(\text{CO})_2(\text{L})(\eta\text{-C}_5\text{H}_5)$ in which $\text{L} = \overline{\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4}$ and $\text{Mn}(\text{CO})_2(\text{L})(\eta\text{-C}_5\text{H}_4\text{Me})$ in which $\text{L} = \text{O}-\overline{\text{C}_6\text{H}_4\text{CH}_2\text{CH}_2\text{C}_6\text{H}_4}$ [173]; $\text{Mn}(\text{CO})(\eta^3\text{-C}_3\text{Ph}_3\text{CO})(\eta\text{-C}_5\text{H}_5)$ [174]; $\text{Mn}(\text{CO})(\text{Me}_3\text{SiCH}=\text{CHCH}=\text{CHMe})(\eta\text{-C}_5\text{H}_4\text{Me})$ [175]; $[\text{Mn}(\text{CO})_2(\equiv\text{CCH}=\text{CPh}_2)(\eta\text{-C}_5\text{H}_5)]\text{BF}_4$ [176]; $\text{Mn}(\text{CO})_2(\text{GPPh}_3=\text{C}=\text{CPh}_2)(\eta\text{-C}_5\text{H}_5)$ [177]; $\text{Mn}(\text{CO})_3[\eta\text{-C}_5\text{H}_4\text{Fe}(\text{CO})(\text{L})(\text{C}_5\text{H}_5)]$ $\text{L} = \text{CO}$ and PPh_3 [181];

Mn(CO)₂(CPh₂)(η-C₅H₅) [186]; Re(CO)₂(HNNMeC₆H₄Me)(η-C₅H₅)]BF₄ [187];
 [Re(NO)(PPh₃)(η²-CH₂=Se)(η-C₅H₅)]BF₄ [193]; Mn₂(CO)₆(μ,η⁴-C₆H₁₀), XXVIII [196];
 ReH₃(η⁴-C₆H₈)(PPh₃)₂ [199]; Mn(CO)₃(PMe₃)(η³-C₅H₇) [203], Mn(PR₃)(η-C₅H₅)₂
 (PR₃ = PMe₃, PPh₂Me) and Mn(dmpe)(η-C₅H₅)₂ [205]; ReH(η⁴-C₆H₈)(η-C₆H₆) and
 Re₂(μ-H)₂(η⁴-C₆H₈)₂(η-C₆H₈)(η-C₆H₆) [210]; Mn(CO)₃(η⁵-C₁₅H₂₁) [212];
 [Re(CO)₃(η-C₆H₃Me₃)]AlBr₄ [213].

XII. REFERENCES

- 1 Annual Survey for Mn, Tc, Re for 1983: P. M. Treichel, *J. Organomet. Chem. Library*, 17 (1985) 365-397.
- 2 N. G. Connelly and W. E. Geiger, *Adv. Organomet. Chem.*, 23 (1984) 2-94.
- 3 A. E. Stiegman and D. R. Tyler, *Accts. Chem. Res.*, 17 (1984) 61.
- 4 B. Walther, *Coord. Chem. Rev.*, 60 (1984) 67.
- 5 D. G. Leopold and V. Vaida, *J. Am. Chem. Soc.*, 106 (1984) 3720.
- 6 S. P. Church, H. Hermann, F. W. Grevels, and K. Schaffner, *J. Chem. Soc., Chem. Commun.*, (1984) 785.
- 7 R. S. Herrick and T. L. Brown, *Inorg. Chem.*, 23 (1984) 4550.
- 8 H. W. Walker, R. S. Herrick, R. J. Olsen, and T. L. Brown, *Inorg. Chem.*, 23 (1984) 3748.
- 9 I. R. Dunkin, P. Harter, and C. J. Shields, *J. Am. Chem. Soc.*, 106 (1984) 7248.
- 10 A. Marcomini and A. Poe, *J. Chem. Soc. Dalton Trans.*, (1984) 95.
- 11 A. E. Stiegman and D. R. Tyler, *Inorg. Chem.*, 23 (1984) 527.
- 12 A. E. Stiegman, A. S. Goldman, D. B. Leslie, and D. R. Tyler, *J. Chem. Soc., Chem. Commun.*, (1984) 632.
- 13 S. P. Schmidt, W. C. Trogler, and F. Basolo, *J. Am. Chem. Soc.*, 106 (1984) 1308.
- 14 M. O. Albers, J. C. A. Boeyens, N. J. Coville, and G. W. Harris, *J. Organomet. Chem.*, 260 (1984) 99.
- 15 D. J. Robinson, G. W. Harris, J. C. A. Boeyens, and N. J. Coville, *J. Chem. Soc., Chem. Commun.*, (1984) 1307.
- 16 E. Deschamps, F. Mathey, C. Knobler, and Y. Jeannin, *Organometallics*, 3 (1984) 1144.
- 17 K. S. Raghuveer, Ph.D. Thesis, U. of Georgia, 1983; *Diss. Abstr.*, 44 (1984) 3400B.
- 18 S. A. Fairhurst, J. R. Morton, R. N. Perutz, and K. F. Preston, *Organometallics*, 3 (1984) 1389.
- 19 W. G. McGimpsey, M. C. Depew, and J. K. S. Wan, *Organometallics*, 3 (1984) 1684.
- 20 M. Benard, A. Dedieu, and S. Nakamura, *Nouv. J. Chim.* 8 (1984) 149.
- 21 F. Calderazzo and G. Pampaloni, *J. Chem. Soc., Chem. Commun.*, (1984) 1249.
- 22 S. A. Roth, G. D. Stucky, H. M. Feder, M. J. Chen, and J. W. Rathke, *Organometallics*, 3 (1984) 708.

- 23 K. Lane, L. Sallans, and R. R. Squires, *J. Am. Chem. Soc.*, 106 (1984) 2719.
- 24 E. Horn and M. R. Snow, *Aust. J. Chem.*, 37 (1984) 1375.
- 25 B.P. Sullivan and T. J. Meyer, *J. Chem. Soc., Chem. Commun.* (1984) 1244.
- 26 H. Berke and G. Weiler, *Z. Naturforsch.*, 39B (1984) 431.
- 27 D. A. Edwards and J. Marshalsea, *Polyhedron*, 3 (1984) 353.
- 28 F. J. Garcia Alonso, V. Riera, F. Villefane, and M. Vivanco, *J. Organomet. Chem.*, 276 (1984) 39.
- 29 J. D. Allison, P. E. Fanwick, and R. A. Walton, *Organometallics*, 3 (1984) 1515.
- 30 K. Raab and W. Beck, *Chem. Ber.*, 117 (1984) 3169.
- 31 B. A. Narayanan and J. K. Kochi, *J. Organomet. Chem.*, 272 (1984) C49.
- 32 J. V. Caspar, B. P. Sullivan, and T. J. Meyer, *Inorg. Chem.*, 23 (1984) 2104.
- 33 K. R. Dunbar and R. A. Walton, *Inorg. Chim. Acta*, 87 (1984) 185.
- 34 U. Kunze, A. Bruns, and D. Rehder, *J. Organomet. Chem.*, 268 (1984) 213.
- 35 I. Bernal, J. D. Korp, F. Calderazzo, R. Poli, and D. Vitali, *J. Chem. Soc., Dalton Trans.*, (1984) 1945.
- 36 J. Gimeno, V. Riera, M. A. Ruiz, A. M. M. Lanfredi, and A. Tiripicchio, *J. Organomet. Chem.*, 268 (1984) C13.
- 37 O. J. Scherer, H. Sitzmann, and G. Wolmershauser, *Angew. Chem. Int. Ed. Engl.*, 24 (1984) 968.
- 38 O. J. Scherer, R. Anselmann, and W. S. Sheldrick, *J. Organomet. Chem.*, 263 (1984) C26.
- 39 R. Seeber, G. A. Mazzocchin, U. Mazzi, E. Roncari, and F. Refosco, *Transit. Met. Chem.*, 9 (1984) 315.
- 40 E. W. Abel, S. K. Bhargava, K. Kite, K. G. Orrell, V. Sik, and B. L. Williams, *J. Chem. Soc., Dalton Trans.*, (1984) 365.
- 41 J. Hawacker, J.-M. Lehn, and R. Ziessel, *J. Chem. Soc., Chem. Commun.*, (1984) 328.
- 42 A. J. L. Pombiero, J. C. Jeffery, C. J. Pickett, and R. L. Richards, *J. Organomet. Chem.*, 277 (1984) C7.
- 43 D. L. Hughes, A. J. Pombiero, C. J. Pickett, and R. L. Richards, *J. Chem. Soc., Chem. Commun.*, (1984) 992.
- 44 M. M. Singh and R. J. Angelici, *Inorg. Chem.*, 23 (1984) 2699.
- 45 R. J. Bernhardt and D. P. Eyman, *Organometallics*, 3 (1984) 1445.
- 46 J.M. Mayer and T. H. Tulip, *J. Am. Chem. Soc.*, 106 (1984) 3878.
- 47 J. Heck, W. Massa, and P. Weinig, *Angew. Chem. Int. Ed. Engl.*, 24 (1984) 722.
- 48 F. H. Kohler, N. Hebenanz, U. Thewalt, B. Kanellakopoulos and R. Klenze, *Angew. Chem. Int. Ed. Engl.*, 24 (1984) 721.
- 49 B. E. Bursten and M. G. Gatter, *J. Am. Chem. Soc.*, 106 (1984) 2554.
- 50 B. E. Bursten and M.G. Gatter, *Organometallics*, 3 (1984) 941.
- 51 B. E. Bursten and M. G. Gatter, *Organometallics*, 3 (1984) 895.
- 52 C. J. Eyermann and A. Chung-Phillips, *J. Am. Chem. Soc.*, 106 (1984) 7437.

- 53 G. Trinquier and R. Hoffmann, *Organometallics*, 3 (1984) 370.
- 54 P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, 106 (1984) 644.
- 55 P. O. Nubel and T. L. Brown, *J. Am. Chem. Soc.*, 106 (1984) 3474.
- 56 P. O. Nubel and T. L. Brown, *Organometallics*, 3 (1984) 29.
- 57 K. H. Franzreb and C. G. Kreiter, *Z. Naturforsch.*, 39B (1984) 81.
- 58 J. A. Bandy, F. G. N. Cloke, M. L. H. Green, D. O'Hare, and K. Prout, *J. Chem. Soc., Chem. Commun.*, (1984) 240.
- 59 M. L. H. Green, D. O'Hare, and J. M. Wallis, *J. Chem. Soc., Chem. Commun.*, (1984) 233.
- 60 J. D. Allison and R. A. Walton, *J. Am. Chem. Soc.*, 106 (1984) 163.
- 61 J. D. Allison, F. A. Cotton, G. L. Powell, and R. A. Walton, *Inorg. Chem.*, 23 (1984) 159.
- 62 U. Schubert, G. Kraft, and C. Kalbas, *Trans. Met. Chem.*, 9 (1984) 161.
- 63 F. Carre, E. Colomer, R. J. P. Corriu, and A. Vioux, *Organometallics*, 3 (1984) 1272.
- 64 C. G. Kreiter, K. H. Franzreb, and W. S. Sheldrick, *J. Organomet. Chem.*, 270 (1984) 71.
- 65 D. B. Pourreau, R. R. Whittle, and G. L. Geoffroy, *J. Organomet. Chem.*, 273 (1984) 333.
- 66 T. Beringhelli, G. Ciani, G. D'Alfonso, P. Romiti, A. Sironi, and M. Freni, *Inorg. Chem.*, 23 (1984) 2849.
- 67 T. Beringhelli, E. Cesarotti, G. Ciani, G. D'Alfonso, and A. Sironi, *J. Organomet. Chem.*, 268 (1984) C18.
- 68 T. Beringhelli, G. Ciani, G. D'Alfonso, H. Molinari, A. Sironi, and M. Freni, *J. Chem. Soc., Chem. Commun.*, (1984) 1326.
- 69 E. H. Kelle-Zeiber, D. G. DeWit, and K. G. Caulton, *J. Am. Chem. Soc.*, 106 (1984) 7006.
- 70 P. L. Bogdan, P. J. Sullivan, T. A. Donovan, and J. D. Atwood, *J. Organomet. Chem.*, 269 (1984) C51.
- 71 N. J. Bristow, B. D. Moore, M. Poliakoff, G. J. Ryott, and J. J. Turner, *J. Organomet. Chem.*, 260 (1984) 181.
- 72 W. A. Herrmann, H. Biersack, B. Balbach, and M. L. Ziegler, *Chem. Ber.*, 117 (1984) 95.
- 73 R. P. Rosen, J. B. Hoke, R. R. Whittle, G. L. Geoffroy, J. P. Hutchinson, and J. A. Zubieta, *Organometallics*, 3 (1984) 846.
- 74 C. M. Casey and R. M. Bullock, *Organometallics*, 3 (1984) 1100.
- 75 R. M. Bullock, Ph.D. U. of Wisconsin, 1984; *Diss. Abstr.* 45 (1984) 175B.
- 76 J. A. Iggo, M. J. Mays, and P. R. Raithby, *J. Chem. Soc., Dalton Trans.*, (1984) 633.
- 77 J. A. Iggo and M. J. Mays, *J. Chem. Soc., Dalton Trans.*, (1984) 643.
- 78 R. B. King, W. K. Fu, and E. M. Holt, *J. Chem. Soc., Chem. Commun.*, (1984) 1439.
- 79 C.-M. T. Hayward, Ph.D. Thesis, U. of Illinois, 1984; *Diss. Abstr.*, 45 (1984) 178B.
- 80 T. G. Richmond and D. F. Shriver, *Organometallics*, 3 (1984) 305.

- 81 T. G. Richmond, A. M. Crespi, and D. F. Shriver, *Organometallics*, 3 (1984) 314.
- 82 T. G. Richmond, Ph.D. Thesis, Northwestern U., 1984; *Diss. Abstr.*, 45 (1984) 552B.
- 83 W. Petri and W. Beck, *Chem. Ber.*, 117 (1984) 3265.
- 84 Z. P. Valueva, M. Ya. Solodova, and N. E. Kolobova, *Izv. Akad. Nauk. SSSR, Ser. Khim.*, (Engl. Trans.) 32 (1983) 1687.
- 85 G. Carriedo, V. Riera, D. Miguel, A. M. Manotti Lanfredi, and A. Tiripicchio, *J. Organomet. Chem.*, 272 (1984) C17.
- 86 P. DeShong and G. A. Slough, *Organometallics*, 3 (1984) 636.
- 87 G. Facchin, P. Uguagliati, and R. A. Michelin, *Organometallics*, 3 (1984) 1818.
- 88 E. Lindner and A. Bronsamle, *Chem. Ber.*, 117 (1984) 2730.
- 89 A. Behr, U. Kanne, and G. Thelen, *J. Organomet. Chem.*, 269 (1984) C1.
- 90 G. D. Vaughn, K. A. Krein, and J. A. Gladysz, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 245.
- 91 K. C. Brinkman and J. A. Gladysz, *Organometallics*, 3 (1984) 147.
- 92 H. Berke, P. Harter, G. Huttner, L. Zsolnai, *Chem. Ber.*, 117 (1984) 3423.
- 93 K. Jacob, K. H. Thiele, and B. Mohai, *Z. anorg. allgem. Chem.*, 511 (1984) 89.
- 94 C. Long, A. R. Morrisson, D. C. McKean, G. P. McQuillan, *J. Am. Chem. Soc.*, 106 (1984) 7418.
- 95 B. A. Narayanan, C. A. Amatore, and J. K. Kochi, *Organometallics*, 3 (1984) 802.
- 96 H. Berke, G. Huttner, O. Scheidsteger, and G. Weiler, *Angew. Chem., Int. Ed. Engl.*, 24 (1984) 735.
- 97 P. G. Lenhart, C. M. Lukehart, P. D. Sotiropoulos, and K. Srinivasan, *Inorg. Chem.*, 23 (1984) 1807.
- 98 P. G. Lenhart, C. M. Lukehart, and K. Srinivasan, *Inorg. Chem.*, 23 (1984) 438.
- 99 A. J. Schultz, K. Srinivasan, R. G. Teller, J. M. Williams, and C. M. Lukehart, *J. Am. Chem. Soc.*, 106 (1984) 999.
- 100 P. G. Lenhart, C. M. Lukehart, and K. Srinivasan, *J. Am. Chem. Soc.*, 106 (1984) 124.
- 101 C. M. Lukehart and W. L. Magnuson, *J. Am. Chem. Soc.*, 106 (1984) 1333.
- 102 K. Srinivasan, Ph.D. Thesis, Vanderbilt U., 1984; *Diss. Abstr.*, 45 (1984) 196B.
- 103 W. Danzer, R. Hofer, H. Menzel, B. Olgemoller, and W. Beck, *Z. Naturforsch.*, 39B (1984) 167.
- 104 J. A. Clark and M. Kilner, *J. Chem. Soc., Dalton Trans.*, (1984) 389.
- 105 G. D. Vaughn and J. A. Gladysz, *Organometallics*, 3 (1984) 1596.
- 106 G. A. Carriedo, J. J. Jeffery, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, (1984) 1597.
- 107 J. C. Jeffery, A. G. Orpen, W. T. Robinson, F. G. A. Stone, and M. J. Went, *J. Chem. Soc., Chem. Commun.*, (1984) 396.

- 108 O. Bars, P. Braunstein, and J. M. Jud, *Nouv. J. Chim.*, 8 (1984) 771.
- 109 R. Bender, P. Braunstein, J.M.Jud, and Y. Dusauso, *Inorg. Chem.*, 23 (1984) 4489.
- 110 M. A. Urbancic, S. R. Wilson, and J. R. Shapley, *Inorg. Chem.*, 23 (1984) 2954.
- 111 M. A. Urbancic, Ph.D. Thesis, U. of Illinois, 1984; *Diss. Abstr.*, 45 (1985) 182B.
- 112 P. Braunstein, C. deMeric de Bellefon, and M. Ries, *J. Organomet. Chem.*, 262 (1984) C14.
- 113 B. F. Hoskins, R. J. Steen, and T. W. Turney, *J. Chem. Soc., Dalton Trans.*, (1984) 1831.
- 114 L. Carlton, W. E. Lindsell, K. J. McCullough, and P. N. Preston, *J. Chem. Soc., Dalton Trans.* (1984) 1693.
- 115 W. P. Weiner, F. J. Hollander, and R. G. Bergman, *J. Am. Chem. Soc.*, 106 (1984) 7462.
- 116 P. J. Manning and L. K. Peterson, *Inorg. Chim. Acta*, 88 (1984) L5.
- 117 N. E. Kolobova, L. L. Ivanov, and O. S. Zhvanko, *Izv. Akad. Nauk. SSSR, Ser. Khim. (Engl. Trans.)*, 32 (1983) 866.
- 118 I. L. Eremenko, A. A. Pasynskii, G. Sh. Gasanov, B. Orazsakhmatov, Yu. T. Struchkov, and V. E. Shklover, *J. Organomet. Chem.*, 275 (1984) 183.
- 119 A. A. Pasynskii, I. L. Eremenko, G. Sh. Gasanov, Yu. T. Struchkov, and V. E. Shklover, *J. Organomet. Chem.*, 276 (1984) 349.
- 120 A. A. Pasynskii, I. L. Eremenko, B. Orazsakhmatov, G. Sh. Gasanov, V. M. Novotortsev, O. G. Ellert, and Z. M. Seifulina, *J. Organomet. Chem.*, 270 (1984) 53.
- 121 W. A. Herrmann, G. Hecht, M. L. Ziegler, and T. Zahn, *J. Organomet. Chem.*, 273 (1984) 323.
- 122 A. Winter, L. Zsolnai, and G. Huttner, *J. Organomet. Chem.*, 269 (1984) C29.
- 123 M. J. Mays, P. R. Raithby, P. L. Taylor, and K. Hendrick, *J. Chem. Soc., Dalton trans.*, (1984) 959.
- 124 R. P. Rosen, Ph.D., Penn State U., 1983; *Diss. Abstr.* 45 (1984) 869B.
- 125 A. B. Antonova, S. V. Kovalenko, E. D. Korniyets, I. U. Efremova, A. A. Ioganson, S. P. Gubin, *Izv. Akad. Nauk. SSSR, Ser. Khim. (Engl. Trans.)*, 33 (1983) 1052.
- 126 A. B. Antonova, S. V. Kovalenko, E. D. Korniyets, A. A. Johansson, Yu. T. Struchkov, and A. I. Yanovsky, *J. Organomet. Chem.*, 267 (1984) 299.
- 127 A. A. Koridze, O. A. Kizas, N. E. Kolobova, V. N. Vinogradova, N. A. Ustynyuk, P. V. Petrovskii, A. I. Yanovsky, and Y. T. Struchkov, *J. Chem. Soc., Chem. Commun.*, (1984) 1158.
- 128 P. Braunstein, U. Schubert, and M. Burgard, *Inorg. Chem.*, 23 (1984) 4057.
- 129 N. E. Kolobova, Z. P. Valueva, E. I. Kazimirchuk, V. G. Andrianov, and Yu. T. Struchkov, *Izv. Akad. Nauk, SSSR Ser. Khim. (Engl. Trans.)*, 33 (1984) 847.
- 130 J. M. Boncella and R. A. Andersen, *Inorg. Chem.*, 23 (1984) 432.
- 131 G. Schmid, U. Hohner, D. Kampmann, F. Schmidt, D. Blaser, and R. Boese, *Chem. Ber.*, 117 (1984) 672.

- 132 E. Colomer, R. J. P. Corriu, and A. Vioux, *J. Organomet. Chem.*, 267 (1984) 107.
- 133 D. Melzer and E. Weiss, *Chem. Ber.*, 117 (1984) 2464.
- 134 D. Melzer and E. Weiss, *J. Organomet. Chem.*, 263 (1984) 67.
- 135 H. J. Haupt, P. Balsaa, B. Schwab, and U. Florke, *Z. Anorg. Allgem. Chem.*, 513 (1984) 22.
- 136 H. Preut, H. J. Haupt, and U. Florke, *Acta Cryst.C*, 40 (1984) 600.
- 137 B. M. Louie and A. Storr, *Can. J. Chem.*, 62 (1984) 1344.
- 138 S. J. Rettig, A. Storr, J. Trotter, and K. Ulrich, *Can. J. Chem.*, 62 (1984) 2783.
- 139 M. Lattman, B. N. Anand, S. S. C. Chu, and R. D. Rosenstein, *Organometallics*, 3 (1984) 670.
- 140 S. S. C. Chu, R. D. Rosenstein, M. Lattman, and B.N. Anand, *J. Organomet. Chem.*, 265 (1984) 45.
- 141 O. J. Scherer, J. Kerth, and W. F. Sheldrick, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 156.
- 142 T. Kawamura, T. Sowa, T. Yonezawa, T. Yamabe, H. Masuda, T. Taga, and K. Machida, *J. Organomet. Chem.*, 276 (1984) C10.
- 143 K. Henrick, J. A. Iggo, M. J. Mays, and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, (1984) 209.
- 144 E. Lindner, C. P. Krieg, W. Hiller, and D. Hubner, *Chem. Ber.*, 117 (1984) 489.
- 145 E. Lindner, K. Auch, W. Hiller, and R. Fawzi, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 320.
- 146 R. Fawzi, W. Hiller, I. P. Lorenz, J. Mohyla, and C. Zeiher, *J. Organomet. Chem.*, 262 (1984) C43.
- 147 P. Jaitner and P. Peringer, *Transit. Met. Chem.*, 9 (1984) 325.
- 148 N. Suryaprakash, A. C. Kunwar, and C. L. Khetrupal, *J. Organomet. Chem.*, 275 (1984) 53.
- 149 W. A. Herrmann, B. Kuombouris, T. Zahn, and M. L. Ziegler, *Angew. Chem., Int. Ed. Engl.*, 24 (1984) 812.
- 150 U. Weber, L. Zsolnai, and G. Huttner, *J. Organomet. Chem.*, 260 (1984) 281.
- 151 A.H. Klahn-Oliva and D. Sutton, *Organometallics*, 3 (1984) 1313.
- 152 W. A. Herrmann, R. Serrano, and H. Bock, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 383.
- 153 W. A. Herrmann, R. Serrano, U. Kusthardt, M. L. Ziegler, E. Guggolz and T. Zahn, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 515.
- 154 W. A. Herrmann, R. Serrano, A. Schafer, U. Kosthardt, M. L. Ziegler, and E. Guggolz, *J. Organomet. Chem.*, 272 (1984) 55.
- 155 N. E. Kolobova, V. I. Zdanovich, I. A. Lobanova, V. G. Andrianov, Yu. T. Struchkov, and P. V. Petrovskii, *Izv. Akad. Nauk. USSR Ser. Khim. (Engl. Trans.)*, 33 (1984) 871.
- 156 A. Duatti, R. Rossi, A. Marchi, A. Paschetto, and U. Mazzi, *Inorg. Chim. Acta*, 81 (1984) 21.
- 157 C. J. Besecker, Ph.D. Thesis, Columbia U., 1983; *Diss. Abstr.*, 44 (1984) 2418B.

- 158 A. Winter, G. Huttner, L. Zsolnai, P. Kroneck, and M. Gottlieb, *Angew. Chem. Int. Ed. Engl.*, 24 (1984) 975.
- 159 H. Stolzenberg, W. P. Fehlhammer, M. Monari, V. Zanotti, and L. Busetto, *J. Organomet. Chem.*, 272 (1984) 73.
- 160 V. G. Albano, D. Braga, L. Busetto, M. Monari, and V. Zanotti, *J. Chem. Soc., Chem. Commun.*, (1984) 1257.
- 161 D. A. Lesch, J. W. Richardson, R. A. Jacobson, and R. J. Angelici, *J. Am. Chem. Soc.*, 106 (1984) 2901.
- 162 M. Herberhold, D. Reiner, K. Ackermann, U. Thewalt, and T. Debaerdemaeker, *Z. Naturforsch.*, 39B (1984) 1199.
- 163 W. A. Herrmann, C. Hecht, M. L. Ziegler, and B. Balbach, *J. Chem. Soc., Chem. Commun.*, (1984) 686.
- 164 C. Arsenault, P. Bougeard, B. G. Sayer, S. Yeroushalmi, and M. J. McGlinchey, *J. Organomet. Chem.*, 265 (1984) 283.
- 165 I. Bernal, J. D. Korp, W. A. Herrmann, and R. Serrano, *Chem. Ber.*, 117 (1984) 434.
- 166 D. Sellmann, W. Weber, G. Liehr, and H. P. Beck, *J. Organomet. Chem.*, 269 (1984) 155.
- 167 R. B. King and W. K. Fu, *J. Organomet. Chem.*, 272 (1984) C33.
- 168 H. Werner, B. Klingert, R. Zolk, and P. Thometzek, *J. Organomet. Chem.*, 266 (1984) 97.
- 169 H. Brunner, H. Kauermann, W. Meier, and J. Wachter, *J. Organomet. Chem.*, 263 (1984) 183.
- 170 P. L. Gaus, N. Marchant, M. A. Marsinek, and M. O. Funk, *Inorg. Chem.*, 23 (1984) 3269.
- 171 N. E. Kolobova, L. L. Ivanov, and O. S. Zhvanko, *Izv. Akad. Nauk. SSSR, Ser. Khim. (Engl. Transl.)*, 33 (1984) 1528.
- 172 R. Gross and W. Kaim, *Angew. Chem. Int. Ed. Engl.*, 24 (1984) 614.
- 173 W. A. Herrmann, J. Plank, G. W. Kriechbaum, M. L. Ziegler, H. Pfisterer, J. L. Atwood, and R. D. Rogers, *J. Organomet. Chem.*, 264 (1984) 327.
- 174 K. J. Jens and E. Weiss, *Chem. Ber.*, 117 (1984) 2469.
- 175 R. Corriu, N. Escudie, and C. Guerin, *J. Organomet. Chem.*, 264 (1984) 207.
- 176 N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, O. M. Khitrova, A. S. Batsanov and Y. T. Struchkov, *J. Organomet. Chem.*, 262 (1984) 39.
- 177 N. E. Kolobova, L. L. Ivanov, O. S. Zhvanko, O. M. Khitrova, A. S. Batsanov, and Yu. T. Struchkov, *J. Organomet. Chem.*, 265 (1984) 271.
- 178 H. Blau, K. H. Griessmann, and W. Malisch, *J. Organomet. Chem.*, 263 (1984) C5.
- 179 G. Z. Suleimanov, P. V. Petrovskii, Yu. S. Bogachev, I. L. Zhuravleva, E. I. Fedin, and I. P. Beletskaya, *J. Organomet. Chem.*, 262 (1984) C35.
- 180 T. Yu. Orlova, V. N. Selkina, and D. N. Kursanov, *J. Organomet. Chem.*, 267 (1984) 309.
- 181 A. T. Batsanov and Yu. T. Struchkov, *J. Organomet. Chem.*, 266 (1984) 295.
- 182 K. Chhor and G. Lucazeau, *Inorg. Chem.*, 23 (1984) 462.
- 183 J. Muller and C. Hansch, *J. Organomet. Chem.* 262 (1984) 323.

- 184 D. V. Zagorevskii and Y. S. Nekrasov, *J. Organomet. Chem.*, 267 (1984) 121.
- 185 D. F. R. Gilson, P. J. Fitzpatrick, and I. S. Butler, *Organometallics*, 3 (1984) 387.
- 186 W. A. Herrmann, J. L. Hubbard, I. Bernal, J. D. Korp, B. L. Haymore, and G. L. Hillhouse, *Inorg. Chem.*, 23 (1984) 2978.
- 187 C. F. Barrientos-Penna, C. F. Campana, F. W. B. Einstein, J. Jones, D. Sutton, and A. S. Tracey, *Inorg. Chem.*, 23 (1984) 363.
- 188 C. F. Barrientos-Penna, Ph.D. Thesis, Simon Frazer Univ., 1983; *Diss. Abstr.*, 44 (1984) 2417 B.
- 189 J. H. Merrifield, J. M. Fernandez, W. E. Buhro, and J. A. Gladysz, *Inorg. Chem.*, 23 (1984) 4022.
- 190 W. A. Kiel, W. E. Buhro, and J. A. Gladysz, *Organometallics*, 3 (1984) 879.
- 191 P. C. Heah and J. A. Gladysz, *J. Am. Chem. Soc.*, 106 (1984) 7636.
- 192 I. A. Lobanova, V. I. Zdanovich, N. E. Kolobova, *Izv. Akad. Nauk. USSR Ser. Khim. (Engl. Trans.)*, 33 (1984) 642.
- 193 B. F. McCormick, *Organometallics*, 3 (1984) 1924.
- 194 N. H. Hazel, J. A. K. Howard, and J. L. Spencer, *J. Chem. Soc., Chem. Commun.*, (1984) 1663.
- 195 M. Leyendecker and C. G. Kreiter, *J. Organomet. Chem.*, 260 (1984) C67.
- 196 M. Leyendecker, W. S. Sheldrick, and C. G. Kreiter, *J. Organomet. Chem.*, 270 (1984) C37.
- 197 D. Baudry, J. M. Cormier, M. Ephritikhine, and H. Felkin, *J. Organomet. Chem.*, 277 (1984) 99.
- 198 D. Baudry, M. Ephritikhine, H. Felkin, and J. Zakrzewski, *J. Organomet. Chem.*, 272 (1984) 391.
- 199 D. Baudry, M. Ephritikhine, H. Felkin, Y. Dromzee, and Y. Jeannin, *J. Organomet. Chem.*, 272 (1984) 403.
- 200 J. M. McCall, J. R. Morton, and K. F. Preston, *Organometallics*, 3 (1984) 238.
- 201 J. M. McCall, J. R. Morton, Y. LePage, and K. F. Preston, *Organometallics*, 3 (1984) 1299.
- 202 D. R. Wilson, Ph.D. Thesis, U. of Utah, 1984; *Diss. Abstr.*, 45 (1984) 183B.
- 203 M. de los Angeles Paz-Sandoval, P. Powell, M. G. B. Drew, and R. N. Perutz, *Organometallics*, 3 (1984) 1026.
- 204 A. J. Pearson, P. R. Bruhn, and I. C. Richards, *Isr. J. Chem.*, 24 (1984) 93.
- 205 C. G. Howard, G. S. Girolami, G. Wilkinson, M. Thornton-Pett, and M. B. Hursthouse, *J. Am. Chem. Soc.*, 106 (1984) 2033.
- 206 J. T. Weed, Ph.D. Thesis, U. of Cal., Riverside, 1983; *Diss. Abstr.*, 44, (1984) 3779B.
- 207 P. Pasman and J. J. M. Snel, *J. Organomet. Chem.*, 276 (1984) 387.
- 208 L. N. Ji, M. E. Rerek, and F. Basolo, *Organometallics*, 3 (1984) 740.
- 209 M. E. Rerek and F. Basolo, *Organometallics*, 3 (1984) 647.
- 210 M. L. H. Green, D. O'Hare, J. A. Bandy, and K. Prout, *J. Chem. Soc., Chem. Commun.*, (1984) 884.

- 211 M. I. Rubinskaya, V. S. Kaganovich, A. R. Kudinov, *Izv. Akad. Nauk.SSSR, Ser. Khim., (Engl. Trans.)*, 33 (1984) 813.
- 212 S. R. Stobart and M. J. Zaworotko, *J. Chem. Soc., Chem. Commun.*, (1984) 1700.
- 213 F. Calderazzo, R. Pol., A. Barbati, and P. F. Zanazzi, *J. Chem. Soc., Dalton Trans.*, (1984) 1059.
- 214 M. Brookhart and A. Lukacs, *J. Am. Chem. Soc.*, 106 (1984) 4161.
- 215 A. Lukacs, Ph.D. Thesis, U. of North Carolina, 1984; *Diss. Abstr.*, 44 (1984) 3788B.
- 216 J. W. Hull, Ph.D. Thesis, U. of Minnesota, 1983; *Diss. Abstr.*; 44 (1984) 3407B.
- 217 C. J. Cameron, S. M. Tetrick, and R. A. Walton, *Organometallics*, 3 (1984) 240.
- 218 C. J. Cameron, R. A. Walton, and D. A. Edwards, *J. Organomet. Chem.*, 262 (1984) 335.
- 219 J. D. Allison, Ph.D. Thesis, Purdue, U., 1983; *Diss. Abstr.*, 45 (1984) 865B.
- 220 D. E. Wigley, Ph.D. Thesis, Purdue U., 1983; *Diss. Abstr.*, 45 (1984) 871B.
- 221 C. J. Cameron, Ph.D. Thesis, Purdue U., 1983; *Diss. Abstr.*, 45 (1984) 548B.
- 222 R. M. Nielson and S. Wherland, *Inorg. Chem.*, 23 (1984) 3265.
- 223 R. M. Nielson and S. Wherland, *Inorg. Chem.*, 23 (1984) 1338.