

Heterocyclic π -Complexes of the Transition Metals

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Introduction.

The ability of the common heteroatoms such as N, O, S, etc., to form σ -complexes with transition metals is well established and plays a significant role in various aspects of analytical, biological, theoretical, and general chemistry. When such atoms are part of the basic structure of more complex molecules that contain π -systems, e.g., pyridine, thiophene, adenine, etc., the nonbonding electron pairs of the heteroatom are still available for Lewis-base chemical reactivity. In most cases, these nonbonding electron pairs have lower ionization potentials and are more readily available for bonding than the electrons in π -molecular orbitals. Thus, when compared to organic aromatic and π -compounds that exhibit a very extensive π -bonding capacity toward the transition metals, heteroaromatic and hetero π -compounds form predominantly σ -bonded complexes.

However, there are a growing number of examples of π -bonded heteroaromatic complexes of considerable interest. There are several reasons for this recent interest: a) Stabilization of reactive heterocyclic intermediates. b) Isomerization reactions. c) Complexes of biologically significant compounds. d) Modification of heterocyclic chemistry upon complexation. e) Theoretical models of electronic structure and bonding. Finally of somewhat more interest to the inorganic chemist is the modification

of the chemical and physical properties of the metal center upon coordination to the heterocyclic molecule.

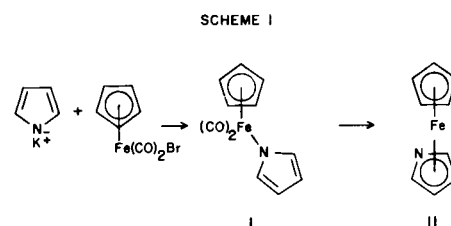
It is the aim of this article to review the area of π -bonded heterocyclic compounds bringing together the diverse studies and outlining the generalities of the subject matter. In this fashion, we hope to introduce the area to organic heterocyclic chemists and stimulate their activity in the field which should lead to the synthesis of more such complexes. Also, the information obtained from such studies can contribute to continued growth and understanding of heterocyclic chemistry (2).

1. Pyrrole Complexes.

Pyrrole may be thought of as π -isoelectronic with cyclopentadiene. Thus, given the large array of cyclopentadienyl transition metal complexes, e.g., ferrocene, many π -pyrrole metal complexes might be expected. Although there are such examples in the literature, the number is very small and there are even surprisingly few σ -complexes reported.

Three main routes are reported for the formation of π -pyrrole complexes: 1) Salt elimination reactions involving the pyrrolide anion and a transition metal halide. 2) Direct use of pyrrole and a suitable transition metal complex. 3) Reaction of pyrrole and a transition metal halide in the presence of a Lewis acid, resulting in the formation of cationic complexes.

The pyrrolide anion, isoelectronic with $C_5H_5^-$, has been shown to react with metal carbonyl halides to form a σ -complex, which then may be converted *via* loss of two carbon monoxide ligands into the corresponding η^5 -complex as outlined in Scheme 1, using cyclopentadienyl

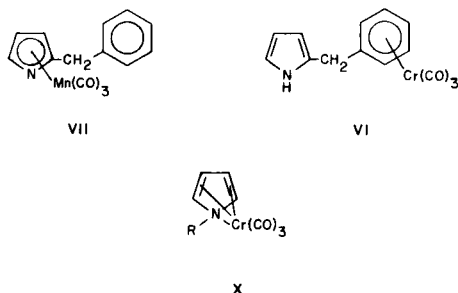


iron dicarbonyl bromide as an example (3). The intermediate σ -bonded complexes vary in stability, and ability to transform into η^5 -complexes, as a function of substituent on the pyrrole ring. While complex I rearranges to the (η^5 -pyrrolyl) (η^5 -cyclopentadienyl) iron complex, azaferrocene II, under very mild conditions (40°), 2-acetylpyrrole, indole, and carbazole all exhibit greater thermodynamic stability in the form of the corresponding

σ -complexes, and indeed both the indole and carbazole complexes resist transformation into isolable π -complexes. Such substituent effects are probably a result of the variation of π -energy levels upon substitution since these substituents will lower the levels making them less accessible for π -bonding (4). Conversely, electron-donating substituents, *e.g.*, alkyl groups, enhance π -bonding ability (4). A further example of this substituent effect with a different metal is obtained from a study on the reactions of the various pyrrolide anions with manganese pentacarbonyl bromide (5). In these cases no intermediate σ -complexes are observed, and contrary to the case with iron, an η^5 -indole complex is reported with an alkyl substituent in the pyrrole ring; *i.e.*, $[(\eta^5\text{-2-methylindole})\text{Mn}(\text{CO})_3]$ (IV). 1,2,3,4-Tetrahydrocarbazole also forms such a η^5 -Mn(CO)₃ complex (V).

The reaction between potassium indolide and Mn(CO)₅Br does not lead to a π -complex but rather an interesting nitrogen abstraction takes place to give an uncharacterized product C₉H₈Mn(CO)₃ which needs further investigation (5).

The reaction of the 2-benzylpyrrolide anion with Mn(CO)₅Br affords $[\eta^5\text{-(C}_6\text{H}_5\text{CH}_2\text{C}_4\text{H}_3\text{N)}\text{Mn}(\text{CO})_3]$ (VII) with the Mn(CO)₃ group bonded to the pyrrolyl ring, whereas reaction of benzylpyrrole with Cr(CO)₆ leads to $[\eta^6\text{-(C}_6\text{H}_5\text{CH}_2\text{C}_4\text{H}_3\text{N)}\text{Cr}(\text{CO})_3]$ (VI) with the Cr(CO)₃ bonded to the carbocyclic ring. Subsequent reaction of either VI or VII with Mn₂(CO)₁₀ or Cr(CO)₆, respectively, leads to the formation of a bimetallic complex, $[(\text{C}_6\text{H}_5\text{CH}_2\text{C}_4\text{H}_3\text{N})(\text{Mn}(\text{CO})_3)(\text{Cr}(\text{CO})_3)]$ (VIII). The same complex may be obtained by direct reaction of 2-benzylpyrrole with a mixture of Cr(CO)₆ and Mn₂(CO)₁₀ illustrating the important selectivity of metals for various π -systems (6), the Cr(CO)₃ group coordinating only to the 6 electron carbocyclic aromatic system, the Mn(CO)₃ to the 6 electron pyrrolyl system. In the case where the aromatic ring is fused directly to the heterocyclic ring, *e.g.*, carbazole and indole, it has been shown that Cr(CO)₆ will form stable Cr(CO)₃ η^6 -complexes with the carbocyclic ring, (XVII, XVIII) no interactions with the hetero ring being observed (7). Several η^5 -pyrrolyl Mn(CO)₃ complexes including $(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ itself, (IX), are reported by direct reaction of Mn₂(CO)₁₀ and the appropriate pyrrole (8,9).



Pyrrole, *N*-methylpyrrole and *N*-phenylpyrrole react with L₃Cr(CO)₃, L = CH₃CN or CO, to form the corresponding yellow diamagnetic (η^5 -pyrrole) Cr(CO)₃, (X, Xa,b) (10). For the *N*-phenyl derivatives the reaction is only successful when L = CH₃CN, when L = CO the Cr(CO)₃ group bonds preferentially to the benzene ring (XI). These η^5 -pyrrole derivatives are extremely unstable with respect to molecular oxygen, and also the pyrrole ligand is very easily displaced by donor solvents, *e.g.*, tetrahydrofuran or benzene. An interesting side observation from this study was that attempts to form the η^5 -pyrrole complexes from Cr(CO)₆ at elevated temperatures and pressures led to fragmentation and rearrangement of the pyrrole ring to form benzene and pyridine and ultimately (η^6 -benzene) Cr(CO)₃ and (pyridine) Cr(CO)₅ complexes.

A third synthetic route involving Mn(CO)₅I, *N*-methylpyrrole, and AlCl₃ has been reported to yield the cationic complex, $[\eta^5\text{-C}_4\text{H}_4\text{NCH}_3)\text{Mn}(\text{CO})_3]^+\text{I}^-$, (XII) (9). This is an isolated example of this route, although the resulting *N*-methyl salts may be available by direct methylation of the pyrrole complexes as reported for azaferrocene (9).

Mills (11) has mentioned that azaferrocene is isomorphous with ferrocene but no details have appeared on this compound although the structure of tricarbonyl (*N*-methylpyrrole) chromium(0) has been solved (12). The pyrrole ring remains planar and no significant changes in bonding parameters are observed with the exception that the *N*-methyl group is bent out of plane 9° away from the Cr(CO)₃ group. Overall, the structure illustrates the weak nature of the pyrrole Cr interaction. Contrary to the above x-ray study, an interesting ⁵⁵Mn NQR study of $(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ (13), has suggested that the pyrrole ring is considerably distorted upon coordination to manganese, with the metal asymmetrically placed with long Mn-C β bonds and short Mn-C α and Mn-N bonds. This suggests that the π -interaction may be thought of as a combination of an η^2 -olefinic metal interaction and an η^3 -aza-allylic four-electron bond (XIII). Such a structure



VIII

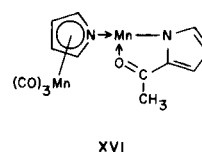
might imply somewhat specific potential activation of the β -carbon atoms upon coordination; however, without a good x-ray structure of the manganese complex this remains simply an interesting suggestion. There are no reactivity data reported in the literature to back up possible metal activation of coordinated pyrrole, and indeed a detailed vibrational spectral analysis of $(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ indicates a structure very closely resembling that of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_3$ (14). Optical isomers of $(\text{CH}_3\text{C}_4\text{H}_3\text{N})\text{FeC}_5\text{H}_5$ (IIb) were resolved and the absolute configuration of the forms determined using

ORD, CD and ultraviolet techniques (15,16).

Although distinctly less stable and possessing lower melting points, the physical properties of π -pyrrolyl complexes are generally very similar to those of their π -cyclopentadienyl counterparts. Infrared (17) and pmr (18) studies on various complexes indicate quite unambiguously that substituting a pyrrolyl ligand for a cyclopentadienyl ligand results in less electron density residing upon the metal center. Thus, the infrared stretching frequencies for the carbonyl groups in $(\eta^5\text{-C}_4\text{H}_4\text{N})(\text{PPh}_3)\text{Mn}(\text{CO})_2$ (XIV) are at 1940 and 1870 cm^{-1} compared to 1930 and 1861 cm^{-1} for the corresponding $(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)\text{Mn}(\text{CO})_2$ (17). This increase in stretching frequency results from a decrease in retrodonative π -bonding from the metal to the carbonyl π^* -orbitals, in turn indicating that the pyrrolyl group is either a less efficient σ -donor or a superior π -acceptor when compared to the cyclopentadienyl ligand, a combination of both probably being responsible for the overall result.

Mass spectral studies on azaferrocene (19,20) have provided some information concerning the strength of the pyrrolyl metal π -bond and also clues as to the reasons for the general lack of heterocyclic aza π -complexes. The most abundant ion in the mass spectrum of azaferrocene is the parent ion $[(\text{C}_4\text{H}_4\text{N})\text{Fe}(\text{C}_5\text{H}_5)]^+$, m/e 187. Fragmentation of this ion is mostly with loss of pyrrole to form $[(\text{C}_5\text{H}_5)\text{Fe}]^+$, m/e 121. There are very few ions which involve retention of a nitrogen containing species illustrating the basic lack of thermodynamic stability of the Fe-N bond in this system (19). From ionization and appearance potential studies it was estimated that the strength of the pyrrolyl iron π bond cannot exceed 65 kcal/mole, which is considerably less than the Fe- $(\eta^5\text{-C}_5\text{H}_5)$ bond. Further, the bond strength of the Fe- $(\eta^5\text{-C}_4\text{H}_4\text{N})$ is greater in the cation $[(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Fe}(\eta^5\text{-C}_5\text{H}_5)]^+$, illustrating that as in ferrocene, in azaferrocene the highest occupied MO is of antibonding character (20).

This last observation would imply a certain stability for the azaferrocenium cation similar to that known for the ferrocenium cation. Various attempts to illustrate this chemically have not met with success. An example is the attempted formation of $[(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_2\text{NO}]^+$ *via* the reaction of the tricarbonyl with NO^+ . No products or starting materials were recovered from such a reaction possibly because of prior NO^+ electrophilic attack at the heteroatom (17); however, it was established in early studies that the pyrrole nitrogen atom in $(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ is very non-basic (9). Recent chemical studies on H-D exchange reactions of $(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ in acid media showed that all four positions on the ring are highly reactive toward exchange, and that the exchange process involves intermediate Mn-H cationic species (21, 22) (XV). Attempted acylation on $(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ produced a surprising product (23) (XVI).



XVI

Acylation clearly occurs on the α -carbon atom, however, this causes the π -pyrrole complex to change to an N -bonded σ complex (as expected from the earlier comments on electronic effects), while the acyl keto group acts as a ligand. The empty coordination site of the Mn is occupied by another $(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_3$ molecule bonding *via* the N atom (24). As implied above in discussing spectral data on the tricarbonyl manganese system, it has been possible to replace CO groups in complex IX by trivalent ligands of group V, but this displacement does not carry over to other neutral Lewis base systems. For example, acetylenes react readily with the system, but no isolable products or starting materials were obtained contrasting the ready formation of $(\eta^5\text{-C}_5\text{H}_5)\text{Mn}(\text{CO})_2$ (acetylene) complexes (17).

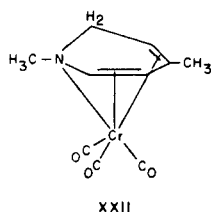
2. Pyridine Complexes.

A single unsubstituted π -pyridine metal complex is reported in the literature, $(\eta^6\text{-C}_5\text{H}_5\text{N})\text{Cr}(\text{PF}_3)_3$, (XIX) (26,27) synthesized using the cocondensation reaction of "hot" chromium atoms with pyridine and trifluorophosphine. The yield is very low (1%) and the reaction produces mainly σ -bonded complexes. The sandwich complex, *bis*-(2,6-dimethylpyridine) chromium, (XX), results from the reaction of chromium atoms and 2,6-dimethylpyridine, but pyridine itself did not yield any characterized products from such a reaction (28).

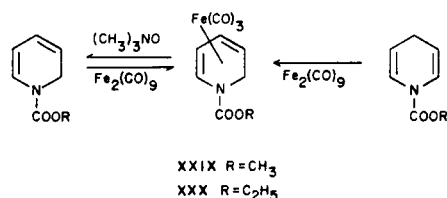
2,6-Dimethyl-, 2,4,6-trimethyl-, 2,3,5,6-tetramethyl-, and pentamethylpyridine (29,30) also react with $\text{Cr}(\text{CO})_6$ in dioxane at 120°, to produce yellow crystalline air stable complexes, $[(\eta^6\text{-(CH}_3)_n\text{C}_5\text{H}_5\text{-}_n\text{N})\text{Cr}(\text{CO})_3]$ (XXI, XXIa,b,c). No σ -complexes were reported, thus not only does the methyl substituent effect mentioned previously seem operative, but also the 2,6-substitution seems to sterically inhibit N -bonded σ -complex formation.

The blocking of the N atom lone pair sterically has a counterpart in the blocking *via* chemical substitution on the nitrogen, preventing σ -complex formation and helping π -complex formation. *N*-Methylpyridinium iodide reacts with $\text{Cr}(\text{CO})_6$ to form initially the pentacarbonyl salt $[\text{CH}_3\text{NC}_5\text{H}_5]^+[\text{M}(\text{CO})_5\text{I}]^-$. Thermal treatment of this complex under vacuum leads to the formation of 1-methyl-1,2-dihydropyridine tricarbonyl chromium, (XXIII), where the metal is coordinated to the ligand *via* chelation involving a η^2 -alkenyl and a η^3 -4 electron vinylamine system (33). [This complex was originally incorrectly formulated as *C*-methylpyridine chromium tricarbonyl complex (31).] The same complex may be obtained more unambiguously *via* the reaction of $\text{Cr}(\text{CO})_6$

with the parent 1-methyl-1,2-dihydropyridine. Also prepared by this route, or by using $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ instead of $\text{Cr}(\text{CO})_6$, were 1,3,4-trimethyl- and 1,4,5-trimethyl-1,2-dihydropyridine tricarbonyl chromium (XXIIIa,b), both of which were prepared from 1,3,4-trimethyl-1,2-dihydropyridine. When heated to 100° , both the 1,3,4- and 1,4,5-chromium complexes transformed into a mixture of the two, thus illustrating the ability of the metal to catalyze the 1,3(1.5)-intramolecular hydrogen shift (31-34). The structure of 1,4-dimethyl-1,2-dihydropyridine chromium tricarbonyl, (XXII) involves a 5 atom planar interaction with the Cr atom, the methylene group being bent out of the plane away from the Cr by 45° (35).

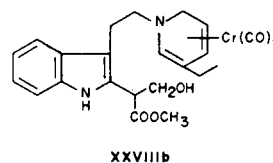


The reaction between *N*-methyl-3-ethyl-1,2-dihydropyridine and $\text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3$ yields a mixture of *N*-methyl-3-ethyl-1,2- and 1,6-dihydropyridine $\text{Cr}(\text{CO})_3$ complexes (XXIV, XXIVa) (36). The 1,6-dihydro complex is formed in a larger amount and illustrates an interesting isomer preference. In a similar reaction, *N*-methyl-dihydroquinoline or -isoquinoline give $\text{Cr}(\text{CO})_3$ complexes, however, the metal is complexed to the carbocyclic ring (XXV, XXVI) (34). The attempted use of $\text{Fe}(\text{CO})_5$ and $\text{Ni}(\text{CO})_4$ for the possible formation of dihydropyridine complexes resulted in no complex formation and the generation of reactive carbonyl metallate anions, $[\text{Fe}_4(\text{CO})_{13}]^{2-}$ and $[\text{Ni}_4(\text{CO})_9]^{2-}$ (34). Recently it has been reported that the use of $\text{Fe}_2(\text{CO})_9$ with *N*-carbalkoxy-1,2- or 1,4-dihydropyridines produced as the only product in each case, *N*-carbalkoxy-1,2-dihydropyridine $\text{Fe}(\text{CO})_3$ (XXIX, XXX) (37). The $\text{Fe}(\text{CO})_3$ group is bonded to the diene portion of the molecule, and in common with most $\text{Fe}(\text{CO})_3$ diene type complexes may be readily displaced using trimethylamine oxide (37), as may the $\text{Cr}(\text{CO})_3$ group be displaced from the various $\text{Cr}(\text{CO})_3$ dihydropyridine complexes by, for example, pyridine (38).

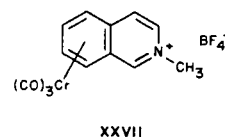


The facile liberation of the metal moiety suggests that such complexes may be useful reagents for the *in situ* generation of the dihydropyridines in a fashion similar to the use of cyclobutadiene $\text{Fe}(\text{CO})_3$ as the preferred reagent for the generation of cyclobutadiene. Thus

N-methyl-3-ethyl-1,2-dihydropyridine may be readily alkylated and reduced in the 5 position upon liberation from a $\text{Cr}(\text{CO})_3$ complex. It is interesting to note that release of the ligand is not accompanied by isomerization and further, when the dihydropyridine is in a large molecule (e.g., XXVIII), the $\text{Cr}(\text{CO})_3$ preferentially binds to the dihydropyridine portion of the structure rather than the indole portion (39). This stabilization of the dihydropyridine moiety in such biological molecules argues well for the use of metal derivatives in complex natural product synthesis, and for studies in the redox system of NADH (39).



The *N*-methylisoquinoline $\text{Cr}(\text{CO})_3$ (XXVI) complexes have been shown to be more reactive than their uncomplexed counterparts since the enamine portion of the molecule is isolated by the complexation of the aromatic phenyl group. Thus, these complexes are readily transformed into the corresponding *N*-methylisoquinolinium tetrafluoroborate salts, (XXVII) (34). Many carbocyclic

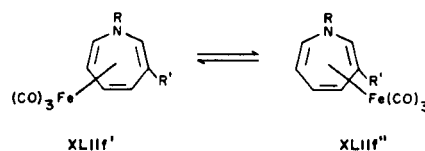


bonded metal carbonyl complexes of polynuclear mono- and diazaheterocycles have been reported, (XXXI-XLI).

3. Azepine Complexes.

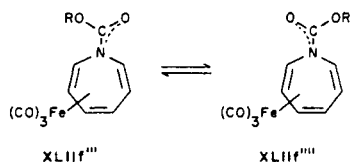
(a) Monoazepine.

Thermal and/or photochemical reactions of $\text{Fe}(\text{CO})_5$ and/or $\text{Fe}_2(\text{CO})_9$ with *N*-carbethoxyazepines yield the appropriate $\text{Fe}(\text{CO})_3$ (*N*-carbethoxyazepine) complex in good yields (XLII) (42,43). The $\text{Fe}(\text{CO})_3$ group is π -bonded to the ligand *via* a diene interaction and thus these complexes exhibit the potential for fluxional behavior as illustrated below, $\text{R}' = \text{H}$, $\text{R} = \text{COOC}_2\text{H}_5$, (XLII f).



Evidence for such behavior comes from the pmr data for the complexes ($\text{R}' = \text{H}$) and shows that at room temperature both (XLII f') and (XLII f'') are present, but cooling to around 0° freezes out a single structure. Further cooling refines the structure relative to restricted rotations about the amide C-N bond (XLII f''' \rightleftharpoons XLII f'''),

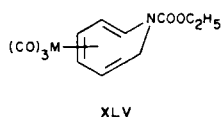
and at temperatures between -30 and -60° , the limiting structure is obtained (42,44). An x-ray crystal structure of $C_8H_9NO_2Fe(CO)_3$ (XLIIa) (45) has been determined and confirmed that the $Fe(CO)_3$ group is complexed in a *cis*-fashion with respect to the keto group and has no direct interaction with the *N* atom. Such fluxional behavior is greatly reduced when $R' \neq H$, e.g., = $COCH_3$, (XLIVd) (46). Alkaline hydrolysis of the *N*-carbomethoxy



complexes yields the corresponding N-H $Fe(CO)_3$ complexes (XLIIg, XLIIIf) (43).

The reaction of the group VI carbonyls with azepine proceeds in a different manner. In the case of *N*-carbomethoxyazepine itself, an interesting *N* extrusion occurs to yield (η^6 -benzene) tricarbonyl chromium and urethane (43). If, however, the 2,4,6-trimethyl-*N*-carbomethoxyazepine derivative is used, again ring closure occurs to yield a benzene derivative, but the C-N bond is kept intact to yield (η^6 -mesitylurethane) tricarbonyl chromium. If *N*-carbomethoxyazepine reagent is reacted with $M(CO)_3(CH_3CN)_3$ $M = Cr, Mo, W$ then related but non-ring closed, η^6 - $M(CO)_3$ complexes are formed (XLVa,b,c) (47).

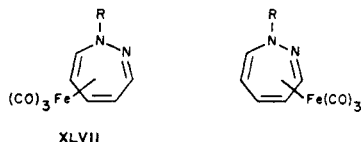
The iron tricarbonyl complexes being essentially diene



complexes give rise to a single localized double bond. This has been utilized in the synthesis of 3-substituted acyl azepine derivatives $R' = COCH_3, COC_2H_5,$ and CHO , from $R' = H$. It is the only such direct synthesis and illustrates the activating influence of the $Fe(CO)_3$ group (46).

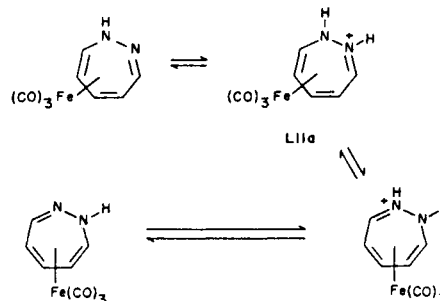
(b) Diazepines.

Iron tricarbonyl derivatives of diazepine have been reported. Unlike the azepine system, $Fe(CO)_3$ derivatives of *N*-substituted diazepines are not expected to exhibit fluxional behavior involving simple $Fe(CO)_3$ movement since the two diene π -systems are not equivalent (49), i.e.,



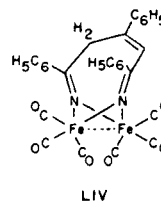
Since the π diene system involving the C=N bond will be lower in energy than that involving two C=C bonds

the complex (XLVII) (50) would be expected, and indeed such complexes are obtained. The complexes $R = H$ do, however, exhibit fluxional behavior that involves protropy and valence isomerization, with intermediate iminium complexes (LIIa) (51) that are capable of simple $Fe(CO)_3$ migration fluxional behavior.



These iminium complexes are formed *via* intermolecular hydrogen exchange and the process occurs rapidly in non-polar solvents, e.g., carbon tetrachloride, while in a polar solvent like methanol, the hydrogen bonding and solvation properties of the solvent disturb such association and slow down the process. It is an acid-catalyzed process and nmr data for the intermediate iminium cation have been obtained. When *N*-methyl-diazepine complexes are studied, no such fluxional behavior is observed.

The reaction of $Fe_2(CO)_9$ with 4*H*-1,2-diazepines, e.g., 3,5,7-triphenyl-4*H*-1,2-diazepine, does not produce simple $Fe(CO)_3$ diene complexes, but rather a *N-N* bond cleavage occurs to yield a novel bicyclic 8 membered metallocyclic complex (LIV) (52). The same ligand can react without



cleavage of the *N-N* bond to produce a simple σ -*N* bonded complex with $[Rh(CO)_2Cl]$ (53).

Sodium borohydride reductions of 1-acetyl or 1-carbomethoxy-1,2-diazepine iron tricarbonyl complexes yielded the corresponding 2,3-dihydro derivatives. While the acyl complex (LVa) is stable, the carbomethoxy complex (LVb) was too unstable for characterization, and was readily converted to the stable acetyl complex (LVI) (54).

This is the only synthetic study on azepine complexes; however, mass spectral fragmentation evidence suggests some extra utility may be forthcoming. The mass spectra of various *N*-substituted alkoxy- or carbalkoxydiazepine $Fe(CO)_3$ or $Ru(CO)_3$ complexes exhibit large abundances of the ion m/e 94, which by accurate mass measurement illustrates the presence of the elusive $C_5H_6N_2$, 1-*H*-1,2-diazepine. Since this compound has, as yet, defied synthesis, it was suggested that metal-catalyzed reactions

involving intermediate tricarbonyls may be possible, especially with Ru where the ion m/e 94 carried a very large percentage of the ion current (50).

The mass spectrum of the variously substituted diazepine complexes also exhibited abundant peaks signifying transformation to pyridines. It has been established that 3,5,7-triphenyl-4*H*-1,2-diazepine and 1-methyl-3,5,7-triphenyl-1*H*-1,2-diazepine are thermally converted to 2,4,6-triphenylpyridine, thus such ions are not unexpected; however, a by-product from the *low temperature* reactions of these diazepines with $\text{Fe}_2(\text{CO})_9$ is the same 2,4,6-triphenylpyridine suggesting some extra metal enhancement of this rearrangement. Other fragmentations involving the totally expected losses of HCN, RCN, etc., are also observed, but surprisingly, unlike the fragmentation of 1-ethoxycarbonyl-1*H*-1,2-diazepine itself, no cyclopentadiene derivatives resulting from N_2 loss are observed. Since cyclopentadienyl ions might be stabilized by the metal atoms this implies that a certain amount of metal nitrogen bonding may weaken the *N-N* bond as has been observed to be the case in the fragmentation of σ -metal complexes of pyridazine. In this latter example successive loss of 2 molecules of HCN is observed for the metal coordinated ligand, *c.f.* loss of N_2 for the free pyridazine ligand (55).

4. Oxepin Complexes.

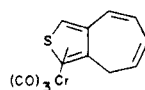
Iron tricarbonyl complexes of oxepin, 2,7-dimethyloxepin and 1-benzoxepin have been prepared *via* photochemical irradiation of the starting ligands with $\text{Fe}(\text{CO})_5$, (LVIIa,b, LVIII) (56). As with the azepine complexes, these oxepin complexes (LVIIa,b) exhibit fluxional behavior (57). A chromium tricarbonyl complex of benzoxepin involving η^6 - $\text{Cr}(\text{CO})_3$ carbocyclic bonding has been reported (58), (LIXa). Trace amounts of a novel diiron ring opened complex have also been obtained, which possesses an unusual ketocarbene metal bond, (LIX) (57).

5. Thiophene Complexes.

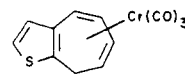
Many complexes of the type $\text{LCr}(\text{CO})_3$ ($L =$ thiophene and substituted thiophenes LXII) have been prepared by two synthetic routes: a) direct reaction of the ligand with $\text{Cr}(\text{CO})_6$, often at elevated temperatures and pressures, b) reaction of the ligand with $\text{L}_3\text{Cr}(\text{CO})_3$, $L = \text{CH}_3\text{CN}$, pyridine. The latter produces significantly better yields and is the preferred synthetic route. The corresponding selenophene and tellurophene complexes have also been prepared using the same techniques (LXXX, LXXXI). All the complexes are yellow, diamagnetic solids of moderate stability in air. However, they are not as stable as the related arene complexes, *e.g.*, $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$, *vide infra* (59-63, 76).

Variouly fused aromatic thiophenes have also been used as ligands, but generally the metal complexes to the

carbocyclic aromatic ring. The benzo[*b*]thiophene, dibenzothiophene, and benzo[*b*]naphtho[2,1-*d*]thiophene all form stable complexes with $\text{Cr}(\text{CO})_3$ group bound to the phenyl or naphthyl group, (LXXVII-LXXIX). Similar π -arene complexes are found with 2- and 3-phenylthiophenes, (LXIII) and (LXIV). An interesting exception to this generality is the report of $\text{Cr}(\text{CO})_3$ complexes of cycloheptatriene[*c* or *b*]thiophenes (63). The *c* derivatives complex *via* the thiophene ring, (LXV), while the *b* derivatives complex *via* the cycloheptatriene ring system, (LXVI), illustrating that the S atom is only complexed when the geometry of the unsaturated system precludes tridentate olefin bonding.

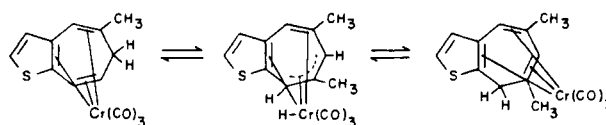


LXV



LXVI

It was noted in this system, that regardless of the particular isomeric structure of the starting *c* ligand, *e.g.*, 4*H* or 6*H*-dimethyl-5,7-cyclohepta[*c*]thiophene, or *b* ligand, *e.g.*, 4*H*, 6*H*, or 8*H*-dimethyl-5,7-cyclohepta[*b*]thiophene, only a single *c* or *b* thiophene complex is obtained. It was suggested that these ligand isomerizations, which do not occur in the absence of metal complexation, proceed *via* intermediate hydrido chromium tricarbonyl complexes.



LXVII

Removal of the complexed metal by other ligands, *e.g.*, aniline, from a single complex generates a mixture of the appropriate ligand, illustrating a potential catalytic process in this system. Treatment of 5,7-dimethylcyclohepta[*b*]thiophene chromium tricarbonyl with trityl perchlorate results in proton abstraction to yield a novel thieno-2,3-tropylium cation complexed to the $\text{Cr}(\text{CO})_3$ group (LXVII) (63).

Cationic thiophene manganese tricarbonyl (64,65) complexes have been prepared by the reaction of $\text{Mn}(\text{CO})_5\text{Cl}$, thiophenes and AlCl_3 , the complexes being isolated as perchlorate salts after washing the reaction mixture with NH_4ClO_4 . The yields of such salts vary from a meager 3% of thiophene itself, (LXVIIIh) up to a respectable 33% for the tetramethylthiophene complex, (LXVIIIa).

In a similar procedure to that above, tetramethylthiophene, FeCl_2 and AlCl_3 followed by hydrolysis with NH_4PF_6 yields *bis*-tetramethylthiophene iron (II) hexafluorophosphate, an analog of ferrocene, (LXIXa) (66). A mixed (η^5 -tetramethylthiophene) (η^5 -cyclopentadiene)

Fe (LXIX) complex has been reported *via* the reaction of ferrocene, AlBr_3 , Al and the ligand (66b).

Attempts to make thiophene metal complexes *via* the "hot atom" technique have not yet proved successful. Using either Fe or Cr atoms together with thiophene and permitting warm up in a CO atmosphere results in an immediate desulfurization reaction that leads for Fe to the formation of ferracyclopentadienyl iron tricarbonyl, $\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_6$, (LXX) (67). An exactly similar reaction has been reported to occur when thiophene reacts at elevated temperatures with the various iron carbonyls (68,69). Such heteroatom extractions are a major reason why more heterocyclic complexes are not known; however, better results may be forthcoming if more substituted thiophenes are used in these reactions.

The structure of thiophene $\text{Cr}(\text{CO})_3$ has been determined, and it has been shown to be isomorphous with benzene $\text{Cr}(\text{CO})_3$ (70). The disorder of the crystal made accurate molecular parameters unavailable; however, the sulfur atom was clearly always *trans* with respect to one of the terminal carbonyl groups, which themselves were orthogonal in an O_h symmetry situation. These observations were confirmed by a more recent structural study on the cyclohepta[*c*]thiophene $\text{Cr}(\text{CO})_3$ complex (LXVa) (70a). This structure was further refined than the simple $(\text{C}_4\text{H}_4\text{S})\text{Cr}(\text{CO})_3$ structure and it was noted that the thiophene ring was no longer planar upon complexation, the S atom being displaced 0.13 Å toward the Cr atom. It was also noted that the various C-C bond lengths had changed so as to make all C-C bonds more equivalent, *i.e.*, a greater delocalization of the π -system had occurred upon complexation.

Similar conclusions concerning the effect of complexation upon the thiophene ring have been arrived at using nmr spectroscopy (71,72). It was observed that the α protons are more affected by complexation than the β protons, and by noting the variations in the various coupling constants between the protons in thiophene and its methylated derivatives, and comparing these values to those obtained in the complexes, it has been suggested that the complexed thiophene resembles an isolated butadiene moiety and a distinct sulfur atom rather than a delocalized 6 electron unit. It should be noted, however, that the molecular parameters for the cyclohepta[*c*]thiophene complex do not necessarily extrapolate to the simple thiophene complex, due to the electronic π -interactions between the diene unit in the carbocycle and the thiophene ring. Indeed, dipole moment measurements (73) upon simple thiophene $\text{Cr}(\text{CO})_3$ complexes have been successfully interpreted on the basis of a planar thiophene complexed to Cr, while infrared studies on the various vibrational modes of the complexed thiophene have illustrated a remarkable equivalence to those of $(\eta^6\text{-C}_6\text{H}_6)\text{Cr}(\text{CO})_3$ (74,75) with the ring vibrations

lowered by some 80 cm^{-1} upon complexation. The dipole moment study on the thiophene $\text{Cr}(\text{CO})_3$ system, coupled with an infrared study on the related [thiophene $\text{Mn}(\text{CO})_3$] $^+$ complexes illustrates the effective increasing basicity and reduced retrodative acidity of the variously methyl substituted ligands, as tabulated below (Table I).

Table I

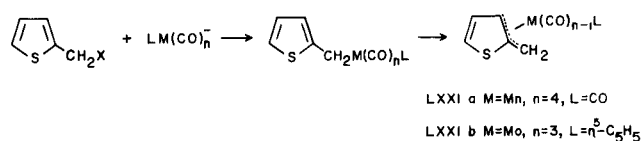
L	μ [$(\text{L})\text{Cr}(\text{CO})_3$], D	$\nu(\text{C}\equiv\text{O})$ [$(\text{L})\text{Mn}(\text{CO})_3$] $^+$, cm^{-1}	
$\text{C}_4\text{H}_4\text{S}$	5.95	2068	2008
2- $\text{CH}_3\text{C}_4\text{H}_3\text{S}$	6.19	2067	2008
2,5-(CH_3) $_2\text{C}_4\text{H}_2\text{S}$	6.38	2063	2009, 1991
2,3,5-(CH_3) $_3\text{C}_4\text{HS}$	6.49	2059	1994
(CH_3) $_4\text{C}_4\text{S}$	6.75	2054	1995, 1983

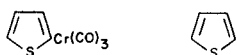
Similar infrared studies on the $\text{Cr}(\text{CO})_3$ of variously substituted thiophene complexes have also been reported (64).

A single brief report of the electronic spectra of thiophene $\text{Cr}(\text{CO})_3$ complexes has appeared (76); however, no significant analysis was offered. Some mass spectral fragmentation data on the complexes have also been published illustrating a general phenomenon for metal heterocycle complexes involving direct metal heteroatom bonding subsequent to elimination of the carbon skeleton (77a). It has been also noted that the nature of the metal often can cause dramatic variations in the fragmentation pattern of such complexes (77b).

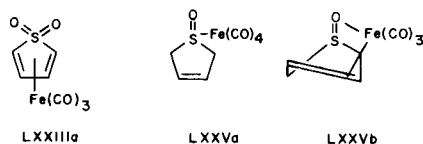
Few reactivity studies on these various π -thiophene complexes are reported. It has been shown that the π -ligand is easily displaced by carbon aromatics in the gas phase, *e.g.*, benzene, to form π -arene $\text{Cr}(\text{CO})_3$ complexes. The rate of displacement, and the rate of decomposition of the π -thiophene complexes decreases markedly upon methyl substitution of the thiophene (78). It has also been shown that the benzothiophene $\text{Cr}(\text{CO})_3$ complexes are photochemically susceptible to decomposition involving release of the ligand (77c).

Reactions of transition metallates, $[(\text{L})\text{M}(\text{CO})_n]^-$, with 2- or 3-halomethylthiophenes lead to the formation of complexes that may be transformed into π -complexes (LXXIa,b; LXXIIa,b) utilizing one of the double bonds of the thiophene ring in a three electron π -allyl bond to the metal. Such bonding breaks the aromaticity of the thiophene, but as yet no reactivity studies have been reported on the system (79).





There has been some very recent activity in stabilizing normally unstable thiophene derivatives *via* metal complexation. Thiophene 1,1-dioxide may be generated *in situ* with $\text{Fe}(\text{CO})_5$ in benzene and irradiation of the resulting mixture yields complex (LXXIII) where the $\text{Fe}(\text{CO})_3$ coordinates with the butadiene portion of the ligand (80,81).



Similarly, 2,5-dihydrothiophene-1-oxide may be stabilized by reaction with $\text{Fe}_2(\text{CO})_9$. Initially an $\text{Fe}(\text{CO})_4$ complex is obtained which involves a (S=O) Fe π -bond, but this complex may be readily converted to a $\text{Fe}(\text{CO})_3$ derivative involving a C=C metal π -bond and an oxygen-Fe σ -bond (82), (*i.e.*, LXXVa \rightarrow LXXVb).

The isomerized ligand may be readily removed upon either uv irradiation or treatment with a superior ligand, *e.g.*, $(\text{CH}_3)_3\text{NO}$ (83).

6. Complexes with Boron-Containing Heterocycles.

Boron π complexes can be divided into three main groups: a) Borazine derivatives. b) Borole derivatives. c) Borabenzene derivatives.

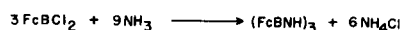
a) Borazine Derivatives.

There are examples of heterocycles containing no ring carbon atoms forming transition metal complexes having the general formula, $\text{LCr}(\text{CO})_3$, (LXXXII) L = hexaalkylborazine (alkyl groups may be the same or different) (84). There are three main routes for the preparation of π -borazine complexes: a) by photochemical reaction of $\text{Cr}(\text{CO})_6$ with appropriate ligand at low pressure (84), b) reaction of the ligand with $(\text{CH}_3\text{CN})_3\text{Cr}(\text{CO})_3$ in dioxane or without solvent (85-87), c) ring ligand exchange method (87,88). The structure of the (hexaethylborazine) tricarbonyl chromium(0) has been determined (90-92), showing the presence of a puckered borazine ring, (Cr-B and Cr-N bond lengths are 2.31 and 2.22 Å respectively), with the $\text{Cr}(\text{CO})_3$ moiety centrally bound, and the nitrogen atoms staggered with respect to the CO groups.

The borazine ring is a significantly poorer π -acceptor ligand than is an arene group (93), although both ligands have similar donor characteristics. This weak π -borazine bond is in accord with a theoretical study of π -complexes of heteroaromatic systems that predicted π -complexes of borazines to be less stable than the corresponding complexes of benzene (94). Borazine displacement reactions

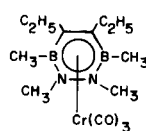
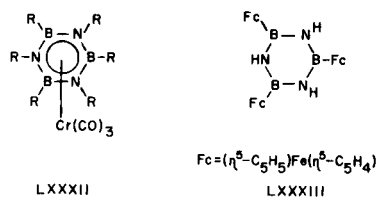
using phosphines, phosphites (89), methyl cyanides and dioxane (86) have been reported to occur under very mild conditions. When L = trialkyl phosphines and trialkyl or triaryl phosphites, complexes of the general composition *cis*- $\text{Cr}(\text{CO})_3\text{L}_3$ are formed, whereas for L = triphenyl- and tricyclohexylphosphine, disproportionation complexes, *trans*- $\text{Cr}(\text{CO})_4\text{L}_2$, are obtained.

B-Triferrocenylborazine, $[(\eta^5\text{-C}_5\text{H}_5)\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{BNH})]_3$ (LXXXIII) has been prepared by the reaction of ferrocenyl dichloroborane with ammonia in toluene. LXXXIII



undergoes a reversible three electron oxidation at +0.37V vs. S.C.E., while under the same conditions ferrocene undergoes a reversible, one electron oxidation at +0.48V vs. S.C.E., suggesting that a π -interaction between the borazine ring and the ferrocenyl group may be extremely important. This conclusion is consistent with the mass spectrum of the compound which gave no fragmentation, only the molecular ion and the doubly charged molecular ion being observed (95).

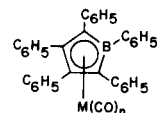
Recently a diboron compound, 1,2-diaza-3,6-dibora-4-cyclohexene $\text{Cr}(\text{CO})_3$ (LXXXIV) (96), has been reported.



LXXXIV

b) Borole Derivatives.

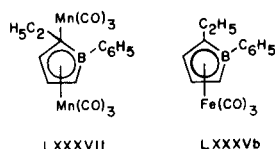
Unsubstituted borole is unknown whereas pentaphenylborole is known (97). Pentaphenylborole reacts with $\text{Fe}_2(\text{CO})_9$ to give tricarbonyl (η^5 -pentaphenylborole) iron (LXXXVa) and with $\text{Ni}(\text{CO})_4$ to give dicarbonyl (η^5 -pentaphenylborole) nickel (98) (LXXXVI).



LXXXVa M=Fe, n=3
LXXXVI M=Ni, n=2

1-Phenyl-4,5-dihydroborepine undergoes ring contraction in complexation reactions carried out under drastic conditions. Thus reaction of 1-phenyl-4,5-dihydroborepine with $\text{Mn}_2(\text{CO})_{10}$ in boiling mesitylene forms μ -(1-phenyl-

2-ethylborole)-*bis*-(tricarbonyl) manganese (99) (LXXXVII) and with $\text{Fe}(\text{CO})_5$ yields tricarbonyl (2-ethyl-1-phenylborole) iron (LXXXVb) (98) and a mixture of stereoisomeric *bis*-(2-methyl-1-phenylborinato) iron complexes which need further investigation. The borole ligands in the complexes are bound to the metal as pentahapto four electron ligands. Pentaphenylborole is extremely water-sensitive whereas its complexes are stable towards air.

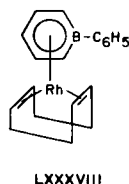


The structure of (LXXXVII) has been determined and corresponds to a pentagonal bipyramidal structure, the apical positions occupied by $\text{Mn}(\text{CO})_3$ groups and the four carbon atoms and boron atom of the borole ring occupying the equatorial positions (99). The compound is closely related to metal carborane complexes, and unusual in the apparent displacement of four CO groups by a formal 4 electron ligand.

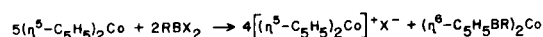
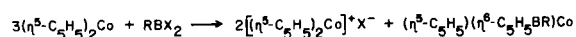
c) Borabenzene Derivatives.

Borabenzene is unknown whereas the derivative, 1-phenylborabenzene anion is known (100). There are four main routes reported for the synthesis of π -borabenzene derivatives: a) salt elimination reactions involving the phenyl borabenzene anion and a transition metal halide, b) direct use of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$ with organoboron halides leading to the formation of *mono*- or *bis*-borabenzene cobalt complexes, c) reaction of *bis*-(borabenzene) cobalt with metal carbonyls forming the corresponding metal carbonyl borabenzene derivatives, d) reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$ with organoboron halides in the presence of halide acceptors resulting in the formation of cationic complexes.

The borinates analogously to the alkali metal cyclopentadienides may be used for a large variety of complexation reactions. For example, from the potassium salt, $\text{K}[\text{C}_5\text{H}_5\text{B-C}_6\text{H}_5]$ and di- μ -chlorodi(1,5-cyclooctadiene) dirhodium, (1-phenylborinato)(1,5-cyclooctadiene) rhodium (LXXXVIII) was obtained (101).

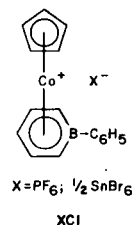


Mono- or *bis*-borabenzene cobalt complexes LXXXIX, XC have been prepared by the direct reaction of $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$ with organoboron halides as shown below (102):



The paramagnetic *bis*-(borinato) cobalt complexes which contain an excess electron and thus labilized ring metal bonds is an excellent starting material for ligand transfer reactions. For example, *bis*-(1-phenylborinato) cobalt reacts with $\text{Mn}_2(\text{CO})_{10}$ in boiling toluene with formation of metallic Co and (1-phenylborinato) $\text{Mn}(\text{CO})_3$ (XCII) (103).

Cationic complexes (104) (XCI) have been prepared when $(\eta^5\text{-C}_5\text{H}_5)_2\text{Co}$ reacts with $\text{C}_6\text{H}_5\text{BBr}_2$ at -50° in toluene to give $(\eta^5\text{-C}_5\text{H}_5)_2\text{CoBr}$ and a red unstable solution. Salts separate upon treatment with halide acceptors at room temperature. Thus addition of SnBr_4 produces the hexabromostannate which can be converted into the hexafluorophosphate by hydrolysis and subsequent precipitation with NH_4PF_6 .

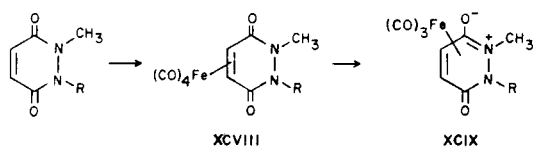


The structures of *bis*-(1-methoxyborinato) cobalt (XCIIIc) and *bis*-(1-methylborinato) cobalt (XCb) show that both molecules are centrosymmetric, with nearly planar parallel rings forming sandwich type complexes (105-106). The atomic distances in both the systems are identical, indicating a certain degree of cyclic conjugation for the ligands. The structure of di- μ -carbonyl (dicarbonyl) *bis*-(1-methylborinato) diiron (107), (XCIV) shows that it has *cis* configuration and C_{2v} symmetry whereas in (1-phenylborinato) manganese tricarbonyl, (XCIII) the plane of the ligand is twisted by 14° with respect to the plane of the phenyl substituent. In these complexes the distances within the ligands indicate cyclic conjugation. The ESR spectrum (108) of *bis*-(1-phenylborabenzene) cobalt-(II) suggests that the bonding is very similar to that in ferrocene with 0.7 electron back donated to each borabenzene ring.

7. Miscellaneous.

a) Pyridazine.

The reaction of 1,2-dimethyl- and 1-methyl-2-phenyl-1,2-dihydropyridazine-3,6-diones with iron carbonyls forms iron tetracarbonyl complexes (XCVIII) which are converted to iron tricarbonyls (XCIX). The x-ray structure of 1,2-dimethyl-1,2-dihydropyridazine-3,6-dione iron tricarbonyl shows the iron atom bonded to the heterodiene fragment of probable zwitterionic structure (109).



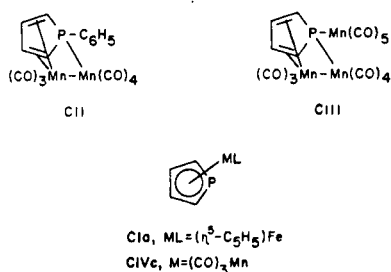
b) Diazoles and Triazoles.

The reaction of $\text{Fe}_2(\text{CO})_9$ with 4-butyroyl-1,2,3-triazole; 4-benzoyl-1,2,3-triazole and 3,5-dimethylpyrazole give red solutions from which the complexes $(\text{C}_3\text{H}_7\text{COC}_2\text{H}_2\text{N}_3)_2\text{Fe}$, (C) and $(\text{C}_6\text{H}_5\text{COC}_2\text{H}_2\text{N}_3)_2\text{Fe}$, (Ca) are precipitated by adding C_6H_4 , and $[(\text{CH}_3)_2\text{C}_3\text{H}_2\text{N}_2]_2\text{Fe}(\text{CO})$ (Cb) by evaporation of the solvent under vacuum. Infrared analysis has been interpreted to indicate the presence of π -bonded species (109).

c) Phosphorus Derivatives.

Reaction of $[\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ with phospholes in boiling xylene at 150° gives phosphaferecenes (CIa,b) (111). Attempts were made to synthesize tetraphenyl-substituted phosphaferecene by the reaction of potassium 2,3,4,5-tetraphenylphospholyl with cyclopentadienyl dicarbonyl iron iodide, the σ -complex $\eta^5\text{-C}_5\text{H}_5\text{Fe}(\text{CO})_2\text{L}$ thus formed was stable and did not lose CO upon heating to give the expected phosphaferecene (112). This stands in sharp contrast to observations when $\text{L} = \text{pyrrolyl}$ (synthesis of azaferrocene) (3).

However, when the corresponding phospholes are irradiated with uv light with $\text{Mn}_2(\text{CO})_{10}$, σ -complexes of the type $\text{L}_m\text{Mn}_2(\text{CO})_{10-m}$ ($\text{L} = 1\text{-phenylphosphole}$ or $1\text{-phenyl-3,4-dimethylphosphole}$; $m = 1$ or 2) are obtained. The novel complexes $\text{LMn}_2(\text{CO})_7$ (CII) in which phospholes act as tridentate ligands *via* their P atoms and their dienic systems are also obtained. Further irradiation of $\text{Mn}_2(\text{CO})_{10}$ and $\text{LMn}_2(\text{CO})_7$ ($\text{L} = 1\text{-phenyl-3,4-dimethylphosphole}$) yields $\text{L}'\text{Mn}_3(\text{CO})_{12}$ (CIII) ($\text{L}' = 3,4\text{-dimethylphospholyl}$) in which $\text{P-C}_6\text{H}_5$ is replaced by a $\text{P-Mn}(\text{CO})_5$ bond. The mass spectrum of CIII shows that it decomposes mainly into $\text{L}'\text{Mn}(\text{CO})_3$ and, not surprisingly, when pyrolyzed at 150° yields $\text{L}'\text{Mn}(\text{CO})_3$ (CIVa) (115). Indeed the complexes (CIV) are more conveniently prepared by direct thermal reactions between $\text{Mn}_2(\text{CO})_{10}$ and the corresponding phospholes (114).

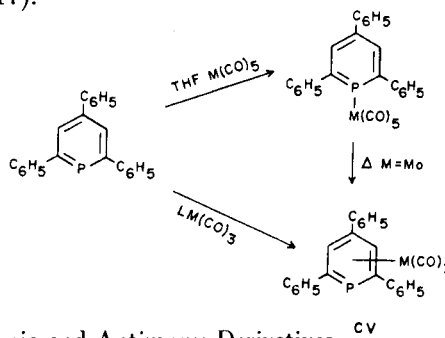


Phospholyl $\text{Mn}(\text{CO})_3$ and phosphaferecene undergo acetylation to give the acetyl derivatives, (CIVd, CIc) (111,114) behaving as ferrocene in this respect.

The x-ray structure of (CIb) indicates that the iron atom is sandwiched between a π bonded cyclopentadienyl ring and a π -bonded phospholyl group so as to attain an eclipsed conformation (111). 2,4,6-Triphenylphosphabenzene yields $\eta^6\text{-M}(\text{CO})_3$ complexes, $\text{M} = \text{Cr}$ (CV); Mo (CVa) when the ligand reacts with $\text{L}_3\text{M}(\text{CO})_3$ or $\text{L}'\text{M}(\text{CO})_3$, $\text{L} = \text{pyridine}$, $\text{L}' = \text{mesitylene}$ for Mo , or with $\text{Cr}(\text{CO})_6$ (115). The crystal structure determination of CV shows that the $\text{Cr}(\text{CO})_3$ group is centrally bonded to the phosphabenzene ring, but unlike the related structure of thiophene- and cyclohepta[c]thiophene $\text{Cr}(\text{CO})_3$ (LXIIa, LXVa, respectively) there is no special trans orientation of a terminal CO group with respect to the hetero atom (116).

The η^6 -complex CVa may also be obtained *via* the thermal $\sigma \rightarrow \pi$ transformation of the related $\sigma\text{-Mo}(\text{CO})_5$ complex (115).

Unsubstituted phosphabenzene, $\text{C}_5\text{H}_5\text{P}$, has also been utilized to form the $\text{Mo}(\text{CO})_5$ derivative but this complex resists thermal transformation into an $\eta^6\text{-Mo}(\text{CO})_3$ complex (117).



d) Arsenic and Antimony Derivatives.

Tricarbonyl manganese and rhenium tetraphenylarsole (CVIa, CVIb) are known. The x-ray structure of $(\text{Ph}_4\text{C}_4\text{As})\text{Mn}(\text{CO})_3$ (CVIa) shows the presence of the arsole ring π -bonded to the tricarbonyl Mn group with the plane containing the carbon atoms of the carbonyl groups effectively parallel to the arsole ring (118). The arsole ring is planar with the phenyl substituents twisted out of the plane by $40\text{-}60^\circ$. Arsabenzene, along with the Sb analog both form $\eta^6\text{-Mo}(\text{CO})_3$ complexes (CVIIa,b) related to the phosphabenzene complexes mentioned above, formed by a $\sigma \rightarrow \pi$ conversion from the appropriate $\sigma\text{-Mo}(\text{CO})_5$ complex (117).

e) Heterocyclic Complexes with a Cyclopentadienyl Ring.

There are several ferrocenyl derivatives of heterocycles reported of the type Fc-L , (CVIIIa-g), $\text{Fc} = (\eta^5\text{-C}_5\text{H}_5)\text{Fe}$ ($\eta^5\text{-C}_5\text{H}_4$); $\text{L} = 1\text{-, 2-},$ and 3-pyrrolyl , 2-thiazolyl , 1- and 3-indolyl , and $4\text{-}(2\text{-methylthiazolyl})$ (119).

The thiazole derivative is obtained from the reaction outlined below:

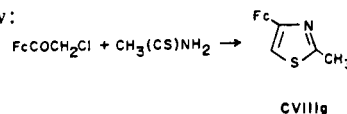


Table II

Heterocyclic π -Complexes of Transition Metals

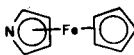
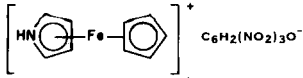
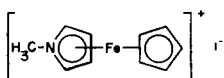
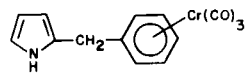
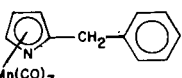
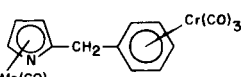
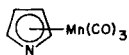

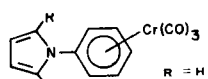
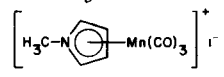
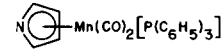
No.	Complex	Reference	Synthesis (a)
1. Pyrrole			
II		(9,18,19,20)	(C,b)
IIa	$(\eta^5\text{-2-acetyldiole})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$	(3)	(C)
IIb	$(\eta^5\text{-2-CH}_3\text{C}_4\text{H}_3\text{N})(\eta^5\text{-C}_5\text{H}_5)\text{Fe}$	(15,16)	(C)
IIc	$[\eta^5\text{-3-CH}_3\text{CO-2,4-(CH}_3)_2\text{C}_4\text{HN}](\eta^5\text{-C}_5\text{H}_5)\text{Fe}$	(5)	(C)
III		(9)	(c)
IIIa		(9)	(d)
IV	$(\eta^5\text{-2-methylindole})\text{Mn}(\text{CO})_3$	(5)	(C)
V	$(\text{tetrahydrocarbazoly})\text{Mn}(\text{CO})_3$	(5)	(C)
VI		(6)	(A)
VII		(6)	(C)
VIII		(6)	(A)
IX		(8,9,13)	(A,C)
IXa	$(1\text{-CH}_3\text{C}_4\text{H}_3\text{N})\text{Mn}(\text{CO})_3$	(9)	(A)
IXb	$[1,3\text{-(CH}_3)_2\text{C}_4\text{H}_2\text{N}]\text{Mn}(\text{CO})_3$	(9)	(A)
IXc	$[1,4\text{-(CH}_3)_2\text{C}_4\text{H}_2\text{N}]\text{Mn}(\text{CO})_3$	(9)	(A)
IXd	$[(\text{CH}_3)_4\text{C}_4\text{N}]\text{Mn}(\text{CO})_3$	(9)	(A)
IXe	$(2\text{-CH}_3\text{-3-CH}_3\text{CO-C}_4\text{H}_2\text{N})\text{Mn}(\text{CO})_3$	(5)	(C)
IXf	$[2,4\text{-(CH}_3)_2\text{-3-CH}_3\text{CO-C}_4\text{HN}]\text{Mn}(\text{CO})_3$	(5)	(C)
X		(10)	(B')
Xa	R = CH ₃ ; R ₁ = H	(10)	(A)
Xb	R = C ₆ H ₅ ; R ₁ = CH ₃	(10)	(B')
XI		(10)	(A)
XIa	R = CH ₃	(10)	(A)
XII		(9)	(D)
XIV		(17)	(E)
XIVa	$(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_2[\text{As}(\text{C}_6\text{H}_5)_3]$	(17)	(E)
XIVb	$(\eta^5\text{-C}_4\text{H}_4\text{N})\text{Mn}(\text{CO})_2[\text{Sb}(\text{C}_6\text{H}_5)_3]$	(17)	(E)

Table II (Continued)

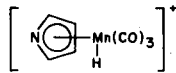
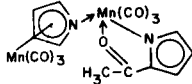
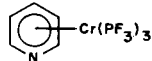
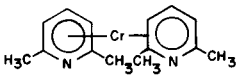
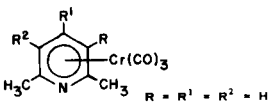
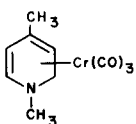
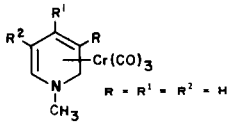
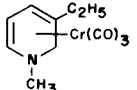
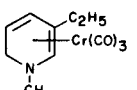
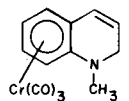
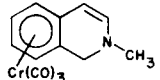
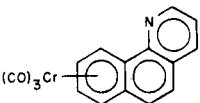
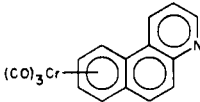
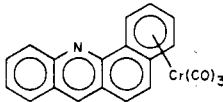
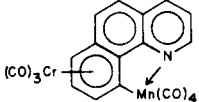
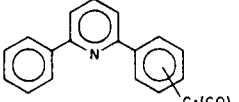
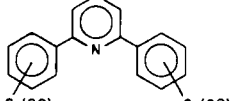
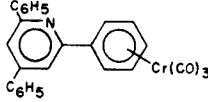
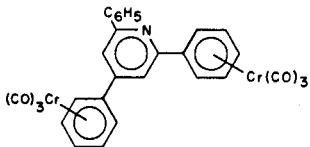
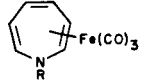
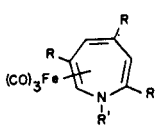
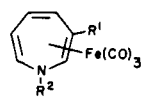
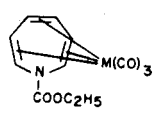
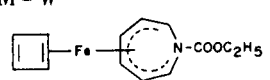
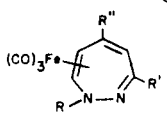
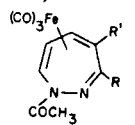
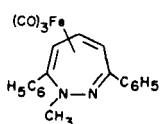
No.	Complex	Reference	Synthesis (a)
XV		(21,22)	(e)
XVI		(23)	(f)
XVII	(η^6 -indole)Cr(CO) ₃	(17)	(A,B')
XVIII	(η^6 -carbazole)Cr(CO) ₃	(17)	(A,B')
	2. Pyridine		
XIX		(26,27)	(F)
XX		(28)	(F)
XXI		(29)	(A)
XXIa	R ¹ = CH ₃ ; R = R ² = H	(30)	(A)
XXIb	R = R ² = CH ₃ ; R ¹ = H	(29)	(A)
XXIc	R = R ¹ = R ² = CH ₃	(30)	(A)
XXII		(35)	(B')
XXIII		(33)	(A,B')
XXIIIa	(R ¹ = R ² = CH ₃ ; R = H)	(34)	(B')
XXIIIb	(R = R ¹ = CH ₃ ; R ² = H)	(34)	(B')
XXIV		(36)	(B')
XXIVa		(36)	(B')
XXV		(34)	(B')
XXVI		(34)	(B')

Table II (Continued)

No.	Complex	Reference	Synthesis (a)
XXVII		(34)	(g)
XXVIII		(39)	(z)
XXVIIIa		(39)	(z)
XXVIIIb		(39)	(z)
XXIX		(37)	(h)
XXX		(37)	(h)
XXXI		(41)	(A)
XXXII		(41)	(A)
XXXIII		(41)	(A)
XXXIV		(41)	(A)
XXXV		(41)	(A)

No.	Complex	Reference	Synthesis (a)
XXXVI		(7)	(A)
XXXVII		(7)	(A)
XXXVIII		(7)	(A)
XXXIX		(41a)	(i)
XL		(41b)	(A)
XLa		(41b)	(A)
XLI		(41b)	(A)
XLla		(41b)	(A)
XLlb	2,4,6- $[\eta^5(\text{CO})_3\text{Cr-C}_6\text{H}_5]_3\text{C}_5\text{H}_2\text{N}$	(41b)	(A)
XLII	3. Azepines 		
XLIIa	R = COOCH ₃	(42)	(A)
XLIIb	R = COOC ₆ H ₅	(42)	(A)
XLIIc	R = SO ₂ CH ₃	(42)	(A)
XLIIId	R = COOC(CH ₃) ₃	(42)	(A)
XLIIe	R = COOCH ₂ C ₆ H ₅	(42)	(A)

No.	Complex	Reference	Synthesis (a)
XLII f	R = COOC ₂ H ₅	(43)	(A)
XLII g	R = H	(43)	(j)
XLIII			
XLIII a	R = CH ₃ , R' = COOC ₂ H ₅	(43)	(A)
XLIII b	R = CH ₃ , R' = H	(43)	(j)
XLIV			
XLIV a	R ¹ = COCH ₃ ; R ² = COOC ₂ H ₅	(46)	(k)
XLIV b	R ¹ = CHO; R ² = COOC ₂ H ₅	(46)	(l)
XLIV c	R ¹ = COCH ₃ ; R ² = CH ₃	(46)	(m)
XLIV d	R ¹ = COCH ₃ ; R ² = H	(46)	(j)
XLIV e	R ¹ = COC ₃ H ₇ ; R ² = COOC ₂ H ₅	(46)	(k)
XLV			
XLV a	M = Cr	(47)	(B')
XLV b	M = Mo	(47)	(B''')
XLV c	M = W	(47)	(B')
XLVI		(48)	(o)
XLVII			
XLVII a	R = H; R' = CH ₃ ; R'' = H	(49,51)	(j)
XLVII b	R = R' = H; R'' = CH ₃	(49)	
XLVII c	R = CH ₂ C ₆ H ₅ ; R' = R'' = H	(49,58a)	(G)
XLVII d	R = COCH ₃ ; R' = R'' = H	(49,50,58a)	(A,G)
XLVII e	R = COOC ₂ H ₅ ; R' = R'' = H	(49,49a)	(A)
XLVII f	R = COCH ₃ ; R' = CH ₃ ; R'' = H	(49)	
XLVII g	R = COCH ₃ ; R' = H; R'' = CH ₃	(49)	
XLVII h	R = R' = R'' = H	(49,51,58a)	(j)
XLVII i	R = COO <i>i</i> -C ₃ H ₇ ; R' = R'' = H	(50)	
XLVII j	R = COOCH ₃ ; R' = R'' = H	(50)	
XLVII k	R = COC ₆ H ₅ ; R' = R'' = H	(58a)	(G)
XLVII l	R = COCH = CHC ₆ H ₅ ; R' = R'' = H	(58a)	(G)
XLVII m	R = COCH ₂ Cl; R' = R'' = H	(58a)	(G)
XLVII n	R = COOCH ₂ CCl ₃ ; R' = R'' = H	(58a)	(G)
XLVII o	R = CH ₂ CH = CH ₂ ; R' = R'' = H	(58a)	(G)
XLVII p	R = COCF ₃ ; R' = R'' = H	(58a)	(p)
XLVII q	R = CN; R' = R'' = H	(58a)	(q)
XLVIII			
XLVIII a	R = R' = H	(50)	(A)
XLVIII b	R = CH ₃ ; R' = H	(50)	(A)
XLVIII c	R = H; R' = CH ₃	(50)	(A)
XLIX		(50)	(A)

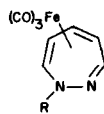
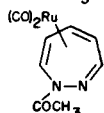
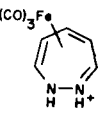
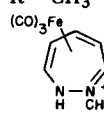
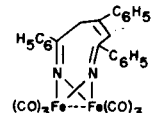
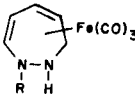
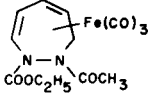
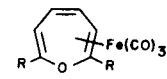

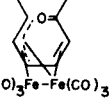
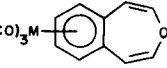
No.	Complex	Reference	Synthesis (a)
L			
La	R = SO ₂ C ₇ H ₇	(50)	(A)
Lb	R = COC ₆ H ₅	(50)	(A)
Lc	R = CH ₃	(51,58a)	(G)
LI		(50)	(A)
LII			
LIIa	R = H	(51)	(r)
LIIb	R = CH ₃	(51)	(r)
LIII		(51)	(s)
LIV		(52)	(A)
LV			
LVa	R = COCH ₃	(54)	(t)
LVb	R = COOC ₂ H ₅	(54)	(t)
LVI		(54)	(u)
	4. Oxepin		
LVII			
LVIIa	R = H	(56)	(A)
LVIIb	R = CH ₃	(56,57)	(A)
LVIII		(56)	(A)
LIX		(57)	(A)
LX			
LXa	M = Cr	(58)	(B')
LXb	M = Mo	(58)	(B''')
LXc	M = W	(58)	(B')

Table II (Continued)


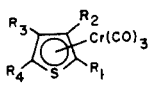
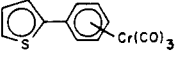
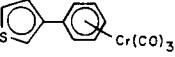
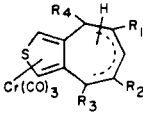
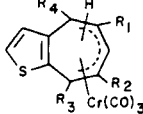
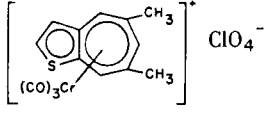
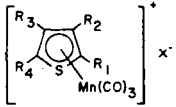
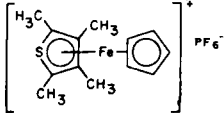
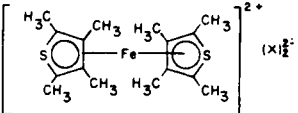
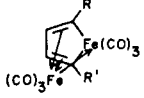
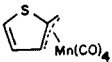
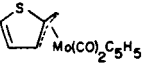


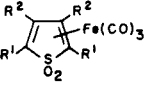
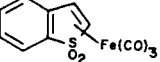
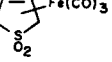
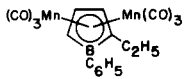
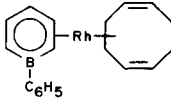
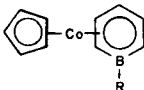
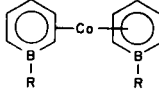
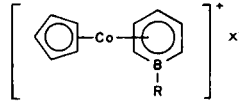
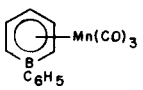
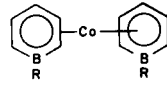
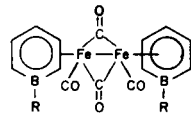
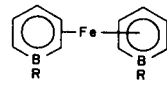
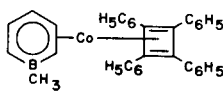
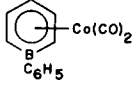
No.	Complex	Reference	Synthesis (a)
LXI		(48)	(o)
5. Thiophene			
LXII			
LXIIa	$R_1 = R_2 = R_3 = R_4 = H$	(59,60a,63,76)	(A,B')
LXIIb	$R_1 = CH_3; R_2 = R_3 = R_4 = H$	(60,60a,63,76)	(A,B')
LXIIc	$R_1 = C_2H_5; R_2 = R_3 = R_4 = H$	(60a)	(A,B')
LXII d	$R_1 = \eta-C_3H_7; R_2 = R_3 = R_4 = H$	(60a)	(B')
LXIIe	$R_1 = i-C_3H_7; R_2 = R_3 = R_4 = H$	(60a)	(A,B')
LXII f	$R_1 = t-C_4H_9; R_2 = R_3 = R_4 = H$	(60a)	(A,B')
LXII g	$R_1 = R_3 = R_4 = H; R_2 = CH_3$	(60a,63,76)	(A,B')
LXII h	$R_2 = t-C_4H_9; R_1 = R_3 = R_4 = H$	(60a)	(A,B')
LXII i	$R_1 = R_2 = CH_3; R_3 = R_4 = H$	(60a,63)	(A,B')
LXII j	$R_1 = R_3 = CH_3; R_2 = R_4 = H$	(60a,63)	(A,B')
LXII k	$R_1 = R_4 = CH_3; R_2 = R_3 = H$	(60a,63)	(A,B')
LXII l	$R_1 = R_4 = H; R_2 = R_3 = CH_3$	(60a,63)	(A,B')
LXII m	$R_1 = R_4 = t-C_4H_9; R_2 = R_3 = H$	(60a)	(B')
LXII n	$R_1 = CH_3; R_2 = R_3 = H; R_4 = OCH_3$	(60a)	(B')
LXII o	$R_1 = R_2 = R_4 = CH_3; R_3 = H$	(63)	(A)
LXII p	$R_1 = R_2 = R_3 = R_4 = CH_3$	(63)	(A)
LXII q	$R_1 = COOCH_3; R_2 = CH_3; R_3 = R_4 = H$	(63)	(A)
LXII r	$R_1 = OCH_3; R_2 = R_3 = R_4 = H$	(76)	(B'')
LXII s	$R_1 = R_3 = R_4 = H; R_2 = OCH_3$	(76)	(B'')
LXII t	$R_1 = Br; R_2 = R_3 = R_4 = H$	(76)	(B'')
LXII u	$R_2 = Br; R_1 = R_3 = R_4 = H$	(76)	(B'')
LXII v	$R_1 = COOCH_3; R_2 = R_3 = R_4 = H$	(76)	(B'')
LXII w	$R_1 = R_3 = R_4 = H; R_2 = COOCH_3$	(76)	(B')
LXIII		(63)	(A)
LXIV		(63)	(A)
LXV			
LXVa	$R_1 = R_2 = CH_3; R_3 = R_4 = H$	(63)	(A)
LXVI			
LXVIa	$R_1 = R_2 = CH_3; R_3 = R_4 = H$	(63)	(A)
LXVIb	$R_1 = R_2 = R_4 = CH_3; R_3 = H$	(63)	(A)
LXVIc	$R_1 = R_2 = R_3 = CH_3; R_4 = H$	(63)	(A)
LXVII		(63)	(g)

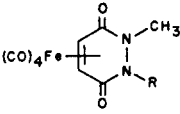
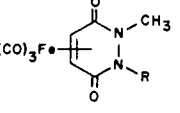
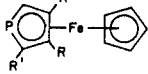
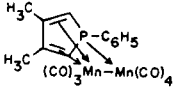
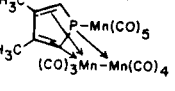
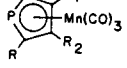
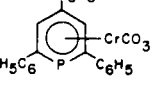
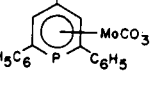
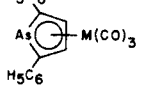
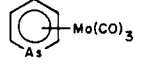
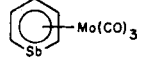
Table II (Continued)

No.	Complex	Reference	Synthesis (a)
LXVIII			
LXVIIIa	$R_1 = R_2 = R_3 = R_4 = \text{CH}_3$; $X^- = \text{ClO}_4$	(64,65)	(D)
LXVIIIb	$R_1 = R_2 = R_3 = R_4 = \text{CH}_3$; $X^- = \text{IO}_4$	(64,65)	(D)
LXVIIIc	$R_1 = R_2 = R_3 = R_4 = \text{CH}_3$; $X^- = [\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$	(64,65)	(D)
LXVIIId	$R_1 = R_2 = R_4 = \text{CH}_3$; $R_3 = \text{H}$; $X^- = [\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$	(64)	(D)
LXVIIIe	$R_1 = R_4 = \text{CH}_3$; $R_2 = R_3 = \text{H}$; $X^- = [\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$	(64)	(D)
LXVIIIf	$R_2 = \text{CH}_3$; $R_1 = R_3 = R_4 = \text{H}$; $X^- = [\text{Cr}(\text{NH}_3)_2(\text{SCN})_4]$	(64)	(D)
LXVIIIg	$R_1 = \text{CH}_3$; $R_2 = R_3 = R_4 = \text{H}$	(64)	(D)
LXVIIIh	$R_1 = R_2 = R_3 = R_4 = \text{H}$	(64)	(D)
LXIX		(66b)	(v''')
LXIXa		(66a)	(v)
LXIXb	$X^- = \text{PF}_6$	(66a)	(v')
LXIXc	$X^- = \text{H}$	(66a)	(v'')
LXX			
LXXa	$R = R' = \text{H}$	(67,68,69)	(A,F)
LXXb	$R = \text{H}$; $R' = \text{CH}_3$	(67)	(F)
LXXIa		(79)	(w)
LXXIb		(79)	(w')
LXXIIa		(79)	(w)
LXXIIb		(79)	(w')
LXXIII			
LXXIIIa	$R^1 = R^2 = \text{H}$	(80)	(A)
LXXIIIb	$R^1 = \text{CH}_3$; $R^2 = \text{H}$	(80)	(A)
LXXIIIc	$R^1 = R^2 = \text{C}_6\text{H}_5$	(80)	(A)
LXXIV		(81)	(A)
LXXVb		(82)	(A)

No.	Complex	Reference	Synthesis (a)
LXXVI		(83)	(x)
LXXVII		(7)	(A)
LXXVIII		(7)	(A)
LXXIX		(7)	(B')
LXXX			
LXXXa	R = H	(61)	(B)
LXXXb	R = CH ₃	(61)	(B)
LXXXI		(62)	(B')
6. Boron			
LXXXII			
LXXXIIa	R ¹ = C ₂ H ₅ ; R = CH ₃	(84,86)	(A)
LXXXIIb	R ¹ = CH ₃ ; R = C ₂ H ₅	(84,93)	(A)
LXXXIIc	R ¹ = R = CH ₃	(85,86,93)	(B')
LXXXIId	R ¹ = η-C ₃ H ₇ ; R = CH ₃	(87)	(B')
LXXXIIe	R ¹ = CH ₃ ; R = η-C ₃ H ₇	(87)	(B')
LXXXIIIf	R ¹ = i-C ₃ H ₇ ; R = CH ₃	(87)	(B')
LXXXIIg	R ¹ = CH ₃ ; R = i-C ₃ H ₇	(87)	(B')
LXXXIIh	R ¹ = R = C ₂ H ₅	(87)	(B',x')
LXXXIIi	R ¹ = CH ₃ ; R = H	(88)	(x')
LXXXIIj	(C ₆ H ₅)(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃ Cr(CO) ₃	(93)	(A,B')
LXXXIIk	(C ₂ H ₅)(CH ₃) ₂ B ₃ N ₃ (CH ₃) ₃ Cr(CO) ₃	(93)	(A,B')
LXXXIII		(95)	(x'')
	Fc = ferrocenyl		
LXXXIV		(96)	(B')
LXXXV			
LXXXVa	R ¹ = R ² = R ³ = R ⁴ = C ₆ H ₅	(98)	(A)
LXXXVb	R ¹ = R ² = R ³ = R ⁴ = H	(98)	(A)
LXXXVI		(98)	(A)

Table II (Continued)

No.	Complex	Reference	Synthesis (a)
LXXXVII		(99)	(A)
LXXXVIII		(101)	
LXXXIX			
LXXXIXa	R = C ₆ H ₅	(102)	
LXXXIXb	R = CH ₃	(102)	
XC			
XCa	R = C ₆ H ₅	(102)	
XCb	R = CH ₃	(102)	
XCI			
XCIa	R = C ₆ H ₅ ; X ⁻ = PF ₆ ⁻ or 1/2 SnBr ₆ ²⁻	(102,104)	
XCIb	R = CH ₃ ; X ⁻ = PF ₆ ⁻	(102)	
XCI		(103)	(A)
XCI			
XCIa	R = Br	(102a)	
XCIb	R = OH	(102a)	
XCIc	R = OCH ₃	(102a)	
XCI			
XCIa	R = CH ₃	(107a)	(A)
XCIb	R = C ₆ H ₅	(107a)	(A)
XCV			
XCVa	R = CH ₃	(107a)	(z')
XCVb	R = C ₆ H ₅	(107a)	(z')
XCVI		(107b)	
XCVII		(107c)	(A)

No.	Complex	Reference	Synthesis (a)
	7. Miscellaneous		
XCVIII			
XCVIIIa	R = CH ₃	(109)	(A)
XCVIIIb	R = C ₆ H ₅	(109)	(A)
XCIX			
XCIXa	R = CH ₃	(109)	(A)
XCIXb	R = C ₆ H ₅	(109)	(A)
C	[(CH ₃) ₂ C ₃ H ₂ N ₂] ₂ Fe(CO)]	(110)	(A)
CI			
CIa	R = H; R ¹ = H	(111)	(A)
CIb	R = CH ₃ ; R ¹ = H	(111)	(A)
CIc	R = CH ₃ ; R ¹ = COCH ₃	(111)	(u')
CII		(113)	(A)
CIII		(113)	(A)
CIV			
CIVa	R ₁ = R ₂ = CH ₃ ; R = H	(114)	(A)
CIVb	R ₁ = CH ₃ ; R = R ₂ = H	(114)	(A)
CIVc	R ₁ = R ₂ = R = H	(113,114)	(A)
CIVd	R ₁ = R ₂ = CH ₃ ; R = COCH ₃	(114)	(u')
CVa		(115)	(B)
CVb		(115)	(B)
CVI			
CVIa	M = Mn	(115)	(y)
CVIb	M = Re	(115)	(y)
CVIIa		(120)	(α)
CVIIb		(120)	(α)

No.	Complex	Reference	Synthesis (a)
CVIIIa		(120)	(z'')
CVIIIb		(119)	(z''')
CVIIIc		(119)	(z''')
CVIIId		(119,120)	(z'', z''')
CVIIIe		(119,120)	(z'', z''')
CVIII f		(119)	(z''')
CVIIIg		(121)	(y')
	Fc = ferrocenyl		
CIXa		(119)	(z''')
CIXb		(119)	(z''')
CIXc		(119)	(z''')

(a) General synthetic methods of preparation are as follows: A. Ligand + metal carbonyl; B. Ligand + L₃ metal (CO)₃, B'L' = CH₃CN; B''L' = pyridine; B''', L' = C₄H₁₄O₃; C. Ligand anion + metal carbonyl halide; D. Ligand + metal carbonyl halide + AlX₃; E. Complex + EPh₃ [E = P, As, Sb]; F. Metal atom + ligand (S); G. Complex + alkyl or aryl halide. (b) FeCl₂ + C₅H₅Na + (C₄H₄N)⁻. (c) II + picric acid. (d) II + CH₃I. (e) IX + H⁺. (f) IX + (CH₃CO)₂O + H₃PO₄. (g) Complex + trityl salt. (h) + Fe₂(CO)₉ or +

Fe₂(CO)₉. (i) Cr(CO)₃(π-benzo[h]quinoline) + Mn(CO)₅Me. (j) Complex + sodium alkoxide. (k) XLIIf + (RCO)₂O + HBF₄ + base or XLIIf + (RCO)₂ + SnCl₄. (l) XLIIf + NN-DMF + POCl₃. (m) XLIIId + CH₃I + NaH. (o) Cyclobutadiene Fe(CO)₃ + L. (p) XLVIIIh + (CF₃CO)₂O. (q) XLVIIIh + BrCN. (r) Complex + trifluoroacetic acid. (s) Complex + methyl fluorosulfonate. (t) Complex + NaBH₄. (u) Complex + AC₂O. (u') Complex + CH₃COCl + AlCl₃. (v) FeCl₂ + L + AlCl₃. (v') FeCl₂ + L + AlCl₃ + NH₄PF₆. (v'') FeCl₂ + L + AlCl₃ + NaBH₄. (v''') FcH + L + AlBr₃ + Al. (w) σ-C₄H₃SCH₂Mn(CO)₅ $\xrightarrow{\text{vac. distillation}}$ (w') σ-C₄H₃SCH₂Mo(CO)₃C₅H₅ $\xrightarrow{h\nu}$

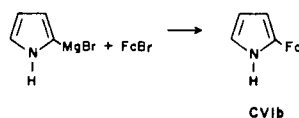
(x) LXXIIIb + (CH₃)₃NO. (x') LXXXIIa + R₃B₃N₃R₃' (R = C₂H₅ or CH₃ and R' = C₂H₅ or H). (x'') 3FcBCl₂ + 9NH₃.

(y) (C₆H₅)₄C₄AsM(CO)₅ $\xrightarrow{h\nu}$ [(C₆H₅)₄C₄AsM(CO)₄]₂ $\xrightarrow{h\nu}$ (C₆H₅)₄C₄AsM(CO)₃. (y') FcCOCH₂Cl + CH₃(CS)NH₂.

(z) Ligand + $\begin{matrix} 1. \text{NaBH}_4 \\ 2. \text{Cr}(\text{CO})_3(\text{CH}_3\text{CN})_3 \end{matrix}$. (z') Decomposition of XCIV at 230°. (z'') FeBr + ligand anion. (z''') FeBr + RMgBr (R = thienyl, pyrrol, or indolyl). (z''') Bromoacetylcyclopentadienyl-Mn(CO)₃ + RNH₂ (R = CH₃CO, CH₃CS, C₆H₅). (α) LM(CO)₅ $\xrightarrow{\Delta}$ η⁶-LM(CO)₃.

If the method of preparation is not mentioned in a footnote, it is discussed in the text and/or the details can be found in the original literature.

The other derivatives are prepared by salt elimination reactions as exemplified by the formation of the 2-pyrrolyl derivatives (119).



Related cyclopentadienyl manganese tricarbonyl complexes with 2-methylthiazole, 2-methylloxazole, and indole (CVIVa-c) have also been obtained using $(\eta^5\text{-C}_5\text{H}_4\text{COCH}_2\text{Br})\text{Mn}(\text{CO})_3$ as starting material (122). Little work has been performed on those complexes. It has been noted that the heterocycles were overall electron acceptors relative to the $(\eta^5\text{-C}_5\text{H}_4)\text{Mn}(\text{CO})_3$ group (122); however, electrochemical oxidations on the ferrocene derivatives show that ease of oxidation of ferrocene is increased thus suggesting some interesting electronic heteroatom-metal interactions (121).

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- (2) To save space, many formulae of the complexes appear in the review only once. If the formula of a complex cannot be found in the text, it is given in Table II at the end of the review.
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