IRON AND MANGANESE COMPLEXES OF HETEROCYCLES

S U M M A R Y

The study describes the various attempts which have been made to synthesize heterocyclic derivatives of transition metals, e.g. iron and manganese, in which the heterocycle is bonded to the metal in an analogous manner to the bonding in π - cyclopentadienyl - metal compounds.

The π - pyrrolyl manganese carbonyl complexes were prepared by one or both of the following methods. In the first the pyrrole or substituted pyrrole was heated with dimanganese decacarbonyl in an inert solvent. In the second method, the potassium salt of the heterocycle was heated with bromomanganese pentacarbonyl. The latter method was found to be more widely applicable and was extended to the preparation of such complexes from pyrrole bearing functional groups, to indoles, pyrazoles and benzotriazole. In some of these cases σ - heterocycle manganese pentacarbonyl could be isolated as the first product.

Similarly the potassium salt of heterocycles containing one nitrogen, on reaction with iodo - dicarbonyl cyclopentadienyl iron gave σ - complexes, i.e. dicarbonyl - π - cyclopentadienyl - σ - heterocycle iron. These σ - bonded complexes by loss of carbon monoxide

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yielded aza ferrocenes, i.e. π - cyclopentadienyl - π - heterocyclo iron at higher temperature.

Attempts to effect electrophilic substitution of the two parent complexes, i.e. tricarbonyl - π - pyrrolyl manganese and π - cyclopentadienyl - π - pyrrolyl iron were made in order to prepare heterocyclic metal complexes with functional groups. Friedel and Crafts Acylation appeared to give a trace of acylated products, while attempted aminomethylation resulted in decomposition.

The reaction of pyrroyl chloride with sodiomanganese pentacarbonyl resulted in the formation of the σ - bonded complex, 2 - pyrrolyl manganese pentacarbonyl via pyrroyl manganese pentacarbonyl by loss of carbon monoxide. Allyl iron tricarbonyl iodide on reaction with pyrrolyl potassium gave 2 : 4 Hexadiene tricarbonyl iron. Unsuccessful attempts have been made to prepare dipyrrolyl analogous of ferrocene, cobaltocene and nickelocene. The reaction between molybdenum hexacarbonyl and pyrrolyl potassium resulted in decomposition.

T H E S I S

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SOME IRON AND MANGANESE COMPLEXES

OF

HETEROCYCLES

A C K N O W L E D G E M E N T S

CONTENTS

INTRODUCTION

ORGANOMETALLICS

Organometallic chemistry, an interesting branch of chemistry, was founded in the middle of the nineteenth century by the famous researches of Bunsen on cacodyl and organoarsenic compounds and the studies of Frankland on organoderivatives of zinc. Since then a steady development of this aspect of chemistry has produced a vast number of metal and metalloid complexes with organic residues of widely varying nature.

Besides, addition of large numbers of new compounds to the literature, the organometallic chemistry has brought changes in the fundamental modern theories of valency and chemical bonding.

Organometallics, the valuable intermediates in the synthesis of other chemicals, have found direct technological application. One can very well appreciate Grignard's revolutionary work on organomagnesium halides, Midgley's utilization of tetraethyl lead as "antiknock" in gasoline, and Ziegler's recent remarkable discovery that ethylene can be polymerised by catalysts containing organoaluminium compounds in combination with metal salts. These few examples give an idea of the significant role

played by organometallics in the present day chemistry and chemical technology.

In spite of the large amount of research in organometallic chemistry during the last century, however, it appeared that the organic derivatives of the transition metals were generally difficult to prepare, although some workers claimed the synthesis of such derivatives during this period[1].

DISCOVERY OF FERROCENE

The organic chemistry of transition metals was more or less confined to certain alkyl complexes of precious metals[2,3] and polyphenyl chromium derivatives[4], whose structures were not well understood.   In 1951 two different groups working independently discovered an entirely new type of organometallic compound, dicyclopentadienyliron[3,6] (I) which was unexpectedly very stable.   Kealy and Pauson[5] isolated dicyclopentadienyliron, from the reaction of

(I) (II)
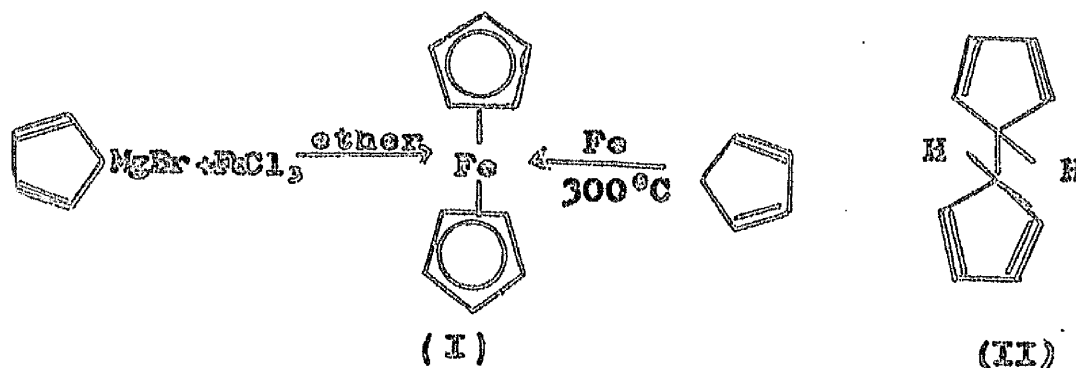
cyclopentadienylmagnesium bromide with ferric chloride
in ethereal solution in an attempt to prepare
dihydrofulvalene (II).

Miller et al; obtained dicyclopentadienyliron from
a reaction of cyclopentadiene vapour and reduced iron
at 300°C.

Since the discovery of dicyclopentadienyliron[5, 6],
the chemistry of organic complexes of transition metals
has developed at an exceedingly rapid rate.   Shortly
after the discovery of this new compound, Woodward,
Rosenblum and Whiting[7] named it "Ferrocene" (III M = Fe)
as a result of

(III)

its aromatic reactivity.   Since then numerous organo-

metallic compounds, incorporating a large majority of transition metals have been synthesised.   Dicyclopentadienyl compounds of the type (III) are now very well known for all metals of the first transition series, from titanium to nickel[8], but only ferrocene behaves as an aromatic compound, judged by its chemical reactivity.   Other members of the iron triad, ruthenocene (III M = Ru)[9], and osmocene (III M = Os)[10] also undergo the reactions typical of an aromatic compound and these together with tricarbonylcyclopentadienyl manganese[11, 12, 13, 14] (IV) tetracarbonylcyclopentadienyl vanadium[15, 16] (V) and dicarbonyl nitrosylcyclopentadienyl chromium[17] (VI) are important members of the rapidly developing family of non-benzenoid aromatic systems.
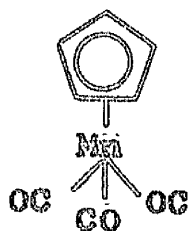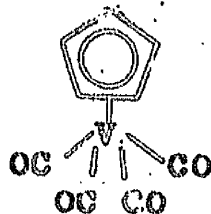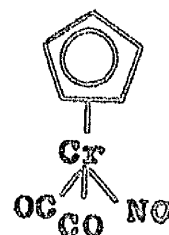
(IV)   (V)   (VI)

Several reviews[8, 18-21] have been published summarising the researches in recent years.

STRUCTURE AND SOME CHARACTERISTICS OF FERROCENE

The structure of ferrocene[22, 23] described as "a molecular sandwich" has further been confirmed by detailed X-ray crystallographic analysis, which shows that the centrosymmetrical molecule conforms to a pentagonal antiprism (VII) with the iron atom at an equal distance from all ten carbon atoms of the rings, which lie in parallel planes[24-28].
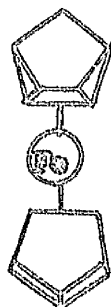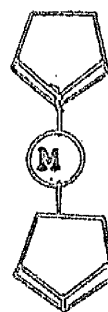
(VII)   (VIII)

Ruthenocene (VIII M = Ru) and osmocene (VIII M = Os) have the opposed conformation in their ortho-rhombic crystals, the carbon atoms of one ring "eclipsing" those of the other in the form of a prism[29, 30]. This variance is attributed to small differences in the lattice forces and to a decrease in significance of the repulsive forces between the hydrogen atoms of the different rings as they are pushed further apart by the heavy metal atom. Other neutral metallocenes form a series of isomorphous mono-clinic crystals[31-34], for which the X-ray measurements[31, 32]

demonstrate "sandwich" structures similar to ferrocene. The infra-red and nuclear magnetic resonance[33] spectra and the zero dipole moments[36, 37] of these compounds are in favour of their structural symmetry. The non-existence of rotational isomers of ferrocene derivatives bearing a substituent in each ring supports "free" rotation of the rings in the molecule[38]. The rotation has been discussed[39, 40] and this view has been favoured by the studies of proton magnetic resonance spectra[35].

Ferrocene, an orange crystalline compound melts at 173°C, sublimes readily and can be purified even by steam distillation, thus behaving as an extremely stable covalent system which has been shown[41] to be stable at 400°C.

NATURE OF BONDING IN FERROCENE

A cyclopentadienyl ring and a metal combine in three ways. Firstly, there can be transfer of an electron from the metal to the cyclopentadienyl ring, resulting in a positively charged metal atom and a negatively charged cyclopentadienyl ring, thus giving rise to an ionic bond, e.g. sodium cyclopentadienide.

Secondly, the metal and one carbon atom of the cyclopentadienyl ring can each contribute an electron for bonding, resulting in shared pair of electrons. This type of bond is a _localised_ covalent bond and is referred to as a σ - bond.

A third type of bond exists, in which, the entire cyclopentadienyl ring is bonded uniformly to the metal atom. This type of bond occurs mainly in cyclopentadienyl compounds of transition metals, e.g. dicyclo-pentadienyliron (ferrocene)[3, 6].

Bonding of this type results from the overlap of π - electrons, i.e. (the electrons, that are not involved in localised σ-bonding between the carbon atoms and between carbon and hydrogen atoms) of the cyclopentadienyl ring with the d-orbitals of the metal and can, therefore, be referred to as π-bonding.

Fischer[23, 42] and others[43, 44] have advanced the theory that the nature of the bonding in dicyclopentadienyliron (ferrocene) is similar to that found in the penetration complexes, such as the ion $[Fe(CN)_6]^{-4}$, so that the metal atom accepts three pairs of π-electrons from each cyclopentadienyl ring into its vacant 3d, 4s and 4p orbitals thus attaining the

configuration[18] of an inert gas.

Alternatively on the basis of molecular orbital theory Dunitz and Orgel[27] and later Moffit[45], proposed that the bonding depends essentially on the possession by the cyclopentadiene rings of molecular orbitals with symmetry similar to the 3d, 4s and 4p metal orbitals. Of the five 3d metal orbitals only the pair with quantum number m = ∓ 1 have the same transformation properties and approximately the same energy content, as one of the available of each cyclopentadiene ring and this is the condition for strong bonding. One each of these orbitals of the metal will therefore combine with the appropriate orbital of each ring to give a strongly bonding (and of course also an anti-bonding) molecular orbital. Thus considering the cyclopentadiene ring as a whole, a single delocalised covalent bond is produced from the metal atom to the ring as a whole[8], i.e. not to one particular carbon atom but "resonating" equally among all five carbon atoms. The molecular theory well accounts for the paramagnetic nature of nickelocene and the stability of dicyclopentadienyl titanium chloride (which cannot attain an inert gas configuration).

GENERAL PREPARATIVE METHODS FOR

FERROCENE AND OTHER METALLOCENES

The two general methods, which have been employed for the preparation of ferrocene, its derivatives and related metallocenes are:-

1. treatment of cyclopentadienyl salts with iron halides.

2. reaction between cyclopentadiene and iron carbonyl.

1. From cyclopentadienyl derivatives:-

(a) Cyclopentadienyl magnesium halides[46,47] react with ferric chloride to yield ferrocene[5,48].

(b) Cyclopentadiene reacts with mercuric chloride in presence of sodium acetate to produce dicyclopentadienyl mercury[49].

(c) The alkali metal salts of cyclopentadiene were first prepared by Thiele[50,51] in 1900. Alternately the sodium salt can be prepared using sodamide or sodium acetylide in liquid ammonia[52] and the cyclo-pentadienyllithium by treating the hydrocarbon with solutions of alkyl or aryl lithiums[48]. These react with iron halides to give ferrocene.

(d) A convenient method for preparation of ferrocene consists of direct reaction between cyclopentadiene and ferrous chloride in presence of basic solvents

such as piperidine and triethylamine or sodium

ethoxide in ethanol containing reduced iron powder[58].

2. <u>High temperature reactions</u>:-

(a) The original ferrocene synthesis[6], the high

temperature reaction between reduced iron and

cyclopentadiene, gives only poor yields of ferrocene[59]

and much better results are obtained using the metal

oxide[60].   Dicyclopentadienyl magnesium[61]   can be

prepared using metallic magnesium at high temperature.

(b) Cyclopentadiene reacts directly with iron carbonyls

at high temperatures to give ferrocene[62,63].   In a

similar fashion, thermal decomposition of the tetra-

carbonyl, (IX) or dicarbonylcyclopentadienyl halide,

(X, X = Cl) obtained by chlorination of the tetra-

carbonyl, (IX) produces ferrocene[64].

(IX)   (X)
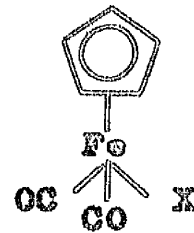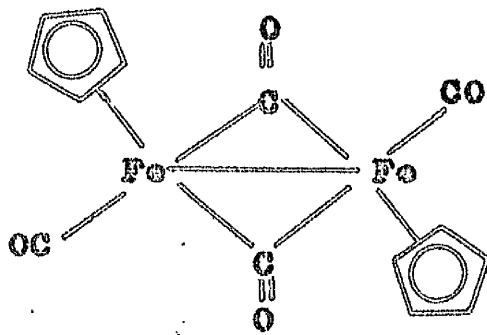
CYCLOPENTADIENYL METAL CARBONYLS

Intensive research soon after the discovery of ferrocene[3, 6], resulted in the preparation of compounds with only one cyclopentadienyl ring bonded to a transition metal.   The cyclopentadienyl carbonyl compounds of molybdenum and tungsten[65] $(C_5H_5)_2Mo(CO)_6$ and $(C_5H_5)_2W_2(CO)_6$, are the first examples of this type and these resulted from the reaction between vapours of cyclopentadiene and the metal carbonyl in a tube heated at 250-300°C.   Under similar conditions chromium carbonyl yielded dicyclopentadienyl chromium, but at lower temperature the binuclear, dicyclopentadienyl dichromium hexacarbonyl[66] (XI) was produced.
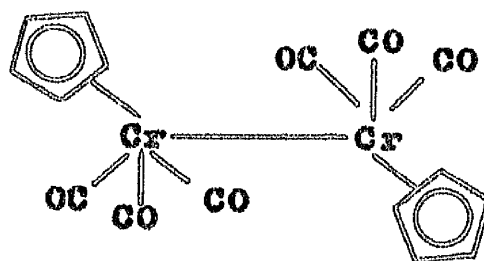
(XI)

Cyclopentadiene reacts with all iron carbonyls at 135°C to give tetracarbonyl-dicyclopentadienyl-diiron[62, 64] (IX), which on halogenation forms the halide[62] (X).   The latter on treatment with sodium cyclopentadienide[67, 68] or Grignard reagents[62, 69] yeilded dicarbonyl-π-cyclo-pentadienyl-σ-cyclopentadienyliron (XII) along with other

products.

(XII)
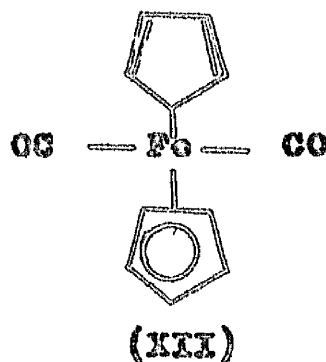
Cyclopentadiene on reaction with the carbonyls of manganese and vanadium forms the corresponding tricarbonyl cyclopentadienyl manganese[11-14] (IV), and tetracarbonyl cyclopentadienyl vanadium[15, 16] (V), while cobalt carbonyl reacts with cyclopentadiene at low temperature to form dicarbonyl-cyclopentadienyl cobalt[62, 70] (XIII) according to the following equation:-

(XIII)

$$Co_2(CO)_8 + 3C_5H_6 \rightarrow 2C_5H_5Co(CO)_2 + 4CO + C_5H_8$$
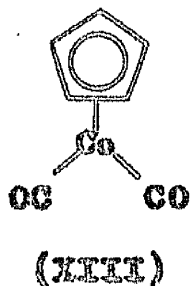
Di (carbonyl-cyclopentadienyl-nickel[71]) (XIV), is obtained from the reaction of dicyclopentadienyl-nickel[72] (III, M = Ni) and nickel carbonyl. Prolonged heating causes the reaction to yield a trinuclear species.

$$Ni(CO)_4 + (C_5H_5)_2Ni \rightarrow 2CO + [C_5H_5Ni(CO)_2]_2 \rightarrow$$

$$(C_5H_5)_3Ni_3(CO)_2$$
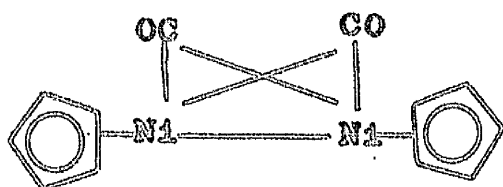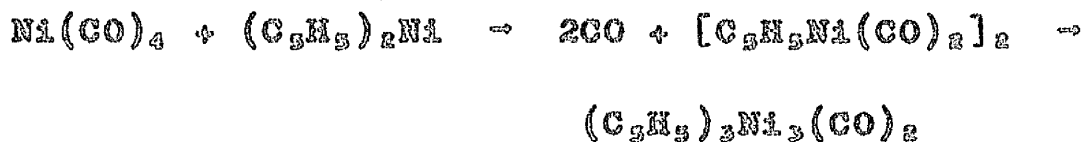
(XIV)
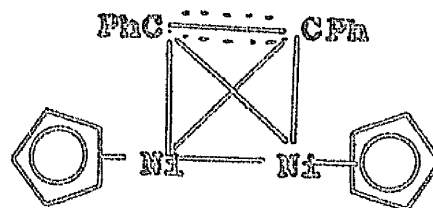
(XV)

The dimer (XIV) gives diphenyl acetylene di(cyclo-pentadienylnickel[73]) (XV) on reaction with diphenyl acetylene by loss of two molecules of carbon monoxide, suggesting that the compound (XIV) possesses a "folded structure", i.e. two bridging carbonyl groups lying in intersecting planes.

The halocyclopentadienyl metal carbonyls, (X, XVI and XVII) obtained by the halogen oxidation of the dimeric species attain their E.A.N. by having the halogen atom covalently bonded.
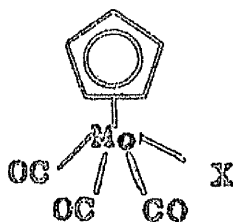
(XVI)
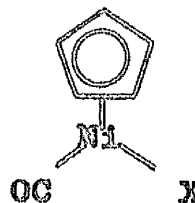
(XVII)

The displacement of one cyclopentadienyl group by carbon monoxide has been employed for the conversion of the dicyclopentadienyl derivatives of vanadium[13, 16], chromium[74], manganese[62] and cobalt[70, 75] to the corresponding cyclopentadienyl metal carbonyls. Tetracarbonyl-cyclopentadienyl vanadium (V) resists further reaction with either cyclopentadiene or carbon monoxide, while dicarbonylcyclopentadienyl cobalt (XIII) leads to cobalt carbonyl.

BIS - ARENEMETAL COMPLEXES

Hein[76] obtained a series of "polyphenyl" chromium compounds from the reaction of phenylmagnesium chloride with chromic or chromous chloride. These compounds were later recognised by Zeiss and Tsutsui[77] as "sandwich" molecules through the lithium-aluminium hydride degradation to yield the expected amounts of benzene and diphenyl. Hence e.g. the structure (XVIII) was proposed for Hein's so called tetraphenylchromium iodide.

(XVIII)   (XIX)

The dibenzene chromium cation was also identified by
Zeiss and Herwig[79] as being one of the reaction products,
and this on reduction yeilded dibenzene chromium (XIX).
Evidence for the six fold symmetry of this compound has
been reported[79]. Fischer and Hafner[80,81] found a new
and direct method for the preparation of arene metal
compounds. This method involves the reaction of the
aromatic hydrocarbon with chromic chloride in presence
of anhydrous aluminium chloride and aluminium powder at
high temperature. Fischer has extended his work to the
preparation of bis-arene compounds, for example, of
molybdenium[82], vanadium[83], rhenium[84], ruthenium[85], iron[86]
and cobalt.

ARENE METAL CARBONYLS

Chromium hexacarbonyl and dibenzene chromium (XIX)
react in benzene in a sealed system at 220°C, to give
tricarbonylbenzene chromium (XX).

(XX)   (XXI)

The most general method suitable for the preparation of
this type of complex, discovered independently by
Fischer[87], Natta[88] and Whiting[89] involves heating
together the aromatic compound with chromium carbonyl
under reflux in an autoclave under pressure in a
solvent such as diglyme.

$$\text{Arene} + \text{Cr(CO)}_6 \xrightarrow{\text{diglyme}} \text{Arene Cr(CO)}_3 + 3\text{CO}$$

A very wide range of arene metal compounds from
substituted benzene derivatives, e.g. tricarbonylbenzyl-
alcohol-chromium (XXI) and from polycyclic aromatic
systems, such as diphenyl[90], naphthalene[87,88] and
anthracene[90] are now known.   It has been shown[91] that
the metal carbonyl residue results in electron with-
drawal from the arene system.   This causes decreased
reactivity of the arene group towards electrophilic
reagents, and conversely an increase in reactivity
towards nucleophilic reagents.

MIXED "SANDWICH" COMPOUNDS

The first mixed cyclopentadienyl benzene metal complex, 2-methylcyclopentadienyl benzene manganese[92] (XXII) has been prepared by the reaction of phenyl-magnesium bromide with bis-methylcyclopentadienyl manganese.

(XXII)　　(XXIII)　　(XXIV)　　(XXV)
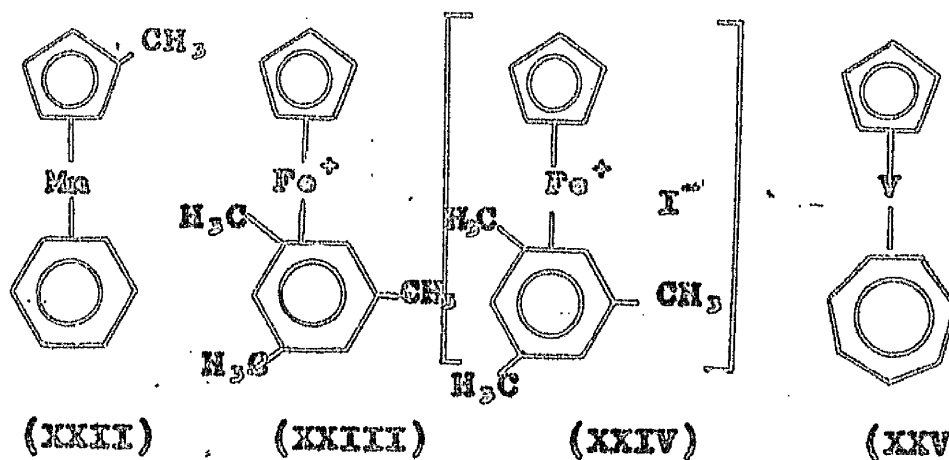
The analogous, but paramagnetic cyclopentadienyl benzene chromium[93] has also been reported.

Chlorodicarbonylcyclopentadienyliron[68] (X) and anhydrous aluminium chloride on refluxing with mesitylene produce the cyclopentadienyl mesitylenoiron cation[94] (XXIII), which on hydrolysis and subsequent treatment with potassium iodide gives the corresponding stable complex (XXIV).

Recently Stone and King[94] have obtained cyclopentadienyl-cycloheptatrienyl-vanadium (XXV), a paramagnetic compound, with one unpaired electron, by the reaction of tetracarbonylcyclopentadienyl-vanadium[15, 16] (V) with cycloheptatriene.

HETEROCYCLIC METAL COMPLEXES

The main hindrance in preparing the heterocyclic transition metal complexes, in which the heterocyclic ring is bound to the metal atoms in a similar fashion to the bonding in π-cyclopentadienyl and arene metal complexes, is the donor function associated with the presence of lone pairs of electrons on the hetero atoms. The mixed carbonyl pyridine metal complexes, which result from various reactions of pyridine with hexacarbonyls of chromium, **molybdenum** and tungsten show displacement of, up to three molecules of carbon monoxide by the same number of molecules of pyridine, and, in these complexes, **pyridine is bonded to the metal by a dative σ-bond.** The complex salts such as $[C_5H_3N^+Me][I\ Cr(CO)_5^-]$ have been prepared by blocking the donor function of the nitrogen in pyridine by forming

N-methyl pyridinium iodide and reacting the latter with chromium carbonyl[93, 96]. Pyrolysis of this salt has yielded tricarbonyl-2-methylpyridinylchromium (XXVI).
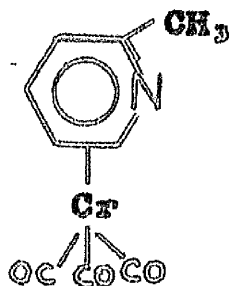
(XXVI)

Alternately blocking of the donor function of nitrogen in pyridine has also been achieved by the steric hindrance on the ring system. Whiting[97] has shown that 2 , 4 , 6 trimethylpyridine reacts with chromium carbonyl to yield tricarbonyl – 2 , 4 , 6 – trimethyl-pyridinyl chromium (XXVII)
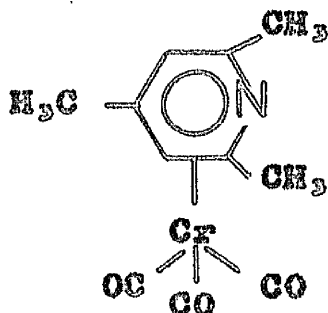
(XXVII)

Some heterocyclic complexes containing a metal, as hetero atom in the ring are now known. Reppe[98] has reported many products as a result of reaction between acetylene and iron carbonyl, particularly the product, $C_{10}H_4O_8Fe$, which results from the reaction between alkaline solution of acetylene and iron carbonyl. The structure (XXVIII)

(XXVIII)
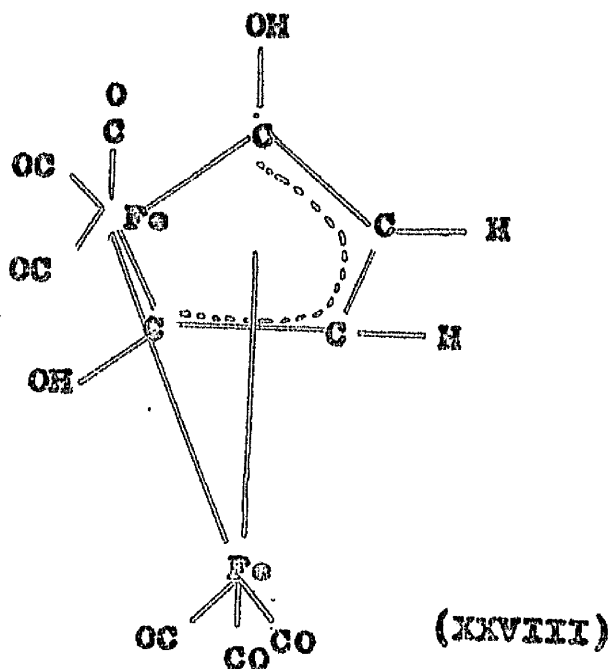
of this compound has been elucidated by X-ray measurements[99] of its dimethyl derivative as a dimethylether, obtained from but-2 yne and iron carbonyl, the presence of the fragment

$$\begin{array}{c} OH \quad R \quad R \quad OH \\ | \quad\quad | \quad\quad | \quad\quad | \\ - C - C - C - C - \end{array}$$ in the complex having been shown previously by Jones et al[100,101]. Hubel and co-workers[102-107], in their intensive research have shown that reaction of different iron carbonyls with a variety of acetylenes, especially with phenylacetylene and tolane, yield two products of the general formula $[(C_2 R_2)_2 Fe_2(CO)_6]$[103,107] and $[(C_2 R_2)_2 Fe_2(CO)_7]$[106,108]. The former has structure (XXIX) related to the butyn-2-complex.
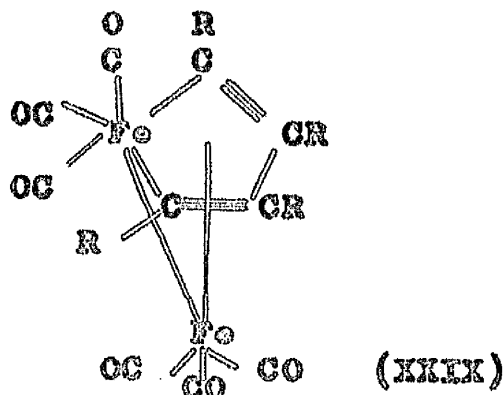
(XXIX)

Many compounds such as tropone and cyclopentadienone
iron carbonyls were also obtained in these reactions
depending on the acetylene and the conditions used.
Reaction of compound (XXIX, R = Ph) with dichloro-
phenylphosphine gives tricarbonylpentaphenylphosphole-
iron[107] (XXX, R = Ph)

(XXX)
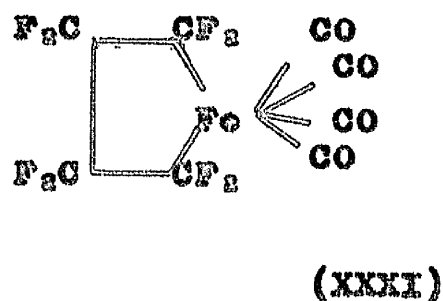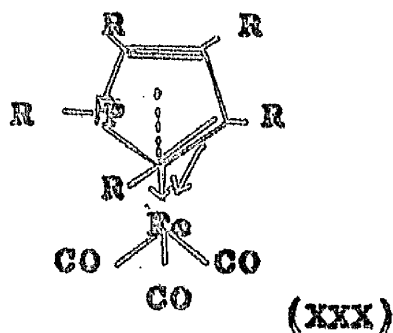
(XXXI)

The compound[109] (XXXI), in which the iron atom is bonded
to the organo group by two σ-bonds, has been obtained
from a reaction between tetrafluoroethylene and iron
pentacarbonyl. Several other systems containing a
heterocycle bonded to a transition metal have been
prepared. Compounds of the type tricarbonyl -

thiophenedioxide iron[102] (XXXII) have been

(XXXII)
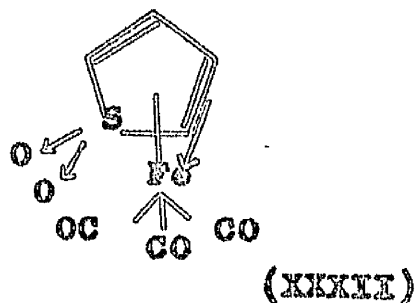
reported as a result of displacement of two molecules

of carbon monoxide in iron pentacarbonyl by thiophene-

dioxide.

Thiophene has been reported to react with iron

pentacarbonyl to produce the compound with structure[110, 111]

identical with

(XXXIII)
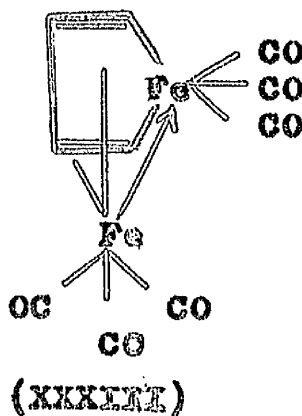
the complex[113] (XXIX, R = H) obtained from acetylene[104].

On the other hand, chromium carbonyl and thiophene react

to yield the complex, tricarbonyl thiophenyl chromium[112]

(XXXIV).

Cr
OC CO CO
(XXXIV)

Mn
OC CO CO
(IV)
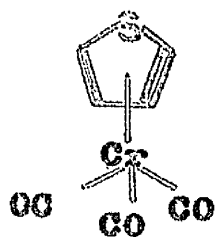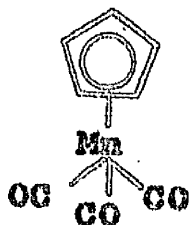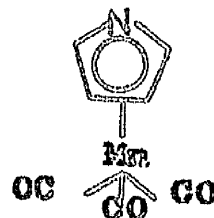
N
Mn
OC CO CO
(XXXV)

In these complexes the heterocyclic residue behaves
as a six-π-electron arene system.   An attempt by
Fischer[113] to prepare dipyrrolyl nickel $(C_4 H_4 N)_2$ Ni
via $[Ni(NH_3)_4](C_4 H_4 N)_2$ failed in contrast to the
cyclopentadienyl derivative $[Ni(NH_3)_6](C_5 H_5)_2$, which
on heating is converted to dicyclopentadienyl nickel[113].

The present work is the extension of the discovery
of a novel complex, tricarbonyl-π- pyrrolyl-
manganese[114], (XXXV); obtained by Joshi and Pauson,
by reaction between pyrrole and dimanganese decacarbonyl.
The heterocyclic ring system in the compound (XXXV) is
bonded to the transition metal, i.e. manganese in an
analogous manner to the bonding in π-cyclopentadienyl
metal compounds, e.g. tricarbonyl-π-cyclopentadienyl
manganese[11-14] (IV).

(XXXVI)

A more recent account[113] of this type of pyrrole

complex, including a pyrrole analogue of ferrocene

(azaferrocene XXXVI), has appeared.

DISCUSSION

During the past several years many workers[112][110] attempted to prepare π-pyrrolyl metal complexes by a variety of methods, but without any success and it was considered that π-pyrrolyl metal complexes may not be stable enough to exist.

In 1962 Joshi and Pauson attempted to prepare a diarene metal complex (XXXVII) by substitution in dimanganese decacarbonyl, in view of the reported complexes of the type, $(CO)_5Mn-Mn(CO)_3L$[117][110].
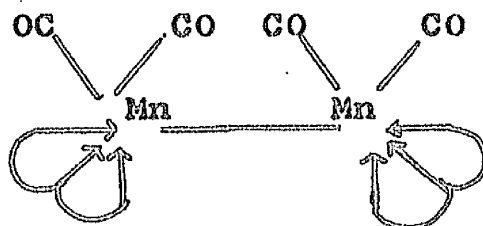
(XXXVII)

As a result of their failure to prepare such complexes, the next attempt was to make use of pyrrole and dimanganese decacarbonyl. They obtained a yellow crystalline compound from the reaction of dimanganese decacarbonyl and pyrrole, (XXXVIII; $R_1=R_2=R_3=R_4=$ H) in refluxing ethyleneglycoldiethyl ether to which was assigned the structure[114], (XXXV; $R_1=R_2=R_3=R_4=$ H) on the basis of infrared, ultraviolet and nuclear magnetic

resonance spectra and analysis.
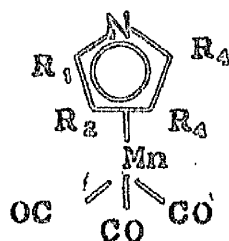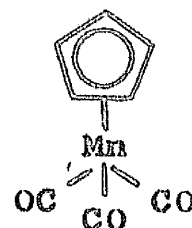
(XXXVIII)   (XXXV)   (IV)

In this compound the heterocycle is bonded to the metal in a fashion analogous to the bonding of the cyclopenta-dienyl ring in the tricarbonyl-π-cyclopentadienyl-manganese (IV).   Compound (XXXV) has been named tricarbonyl-π-pyrrolylmanganese[114].   This result indicated that π-pyrrolyl metal complexes had appreciable stability, and it was therefore decided to investigate more thoroughly the synthesis of other π-pyrrolyl derivatives.

Another aspect of the present investigations was to study more closely the various types of bonding, which might exist in pyrrole metal complexes, considering that pyrrole $C_4 H_5 N$, could react with metal carbonyls in the following fashion:-

(i)   Interaction of the lone pair on the nitrogen atom with metal carbonyls to give substitution type complexes similar to those formed by pyridine and metal carbonyls e.g. $Mo(CO)_3(C_5H_5N)$[110]. This type of reaction is unlikely in view of the low basicity of pyrrole[120].

(ii)   Interaction of the diene system with metal carbonyls similar to the reactions of 1,3-butadiene; 1,3-cyclohexadiene[121][12] etc.

(iii)   Each carbon atom contributing one electron and the nitrogen two electrons, thus giving rise to aromatic-π-bonded complexes, e.g. thiophene in tricarbonylthiophene-chromium[112].

(iv)   Replacement of the hydrogen atom attached to nitrogen atom by a metal carbonyl residue to give a sigma bonded complex.

(v)   Substitution in the α and β positions of the pyrrole ring by a metal residue.

(vi)   Via anion formation giving rise to complexes, in which the bonding of the pyrrole to the metal is analogous to that in π-cyclopentadienyl complexes of transition metals.

The reaction of pyrrole and dimanganese decacarbonyl
was repeated in ligroin (b.p. 100-120°C) to give a
slightly increased yield of the complex (XXXV; $R_1=R_2=R_3=R_4=H$)
Thus the choice of solvent appears to be of little
significance.

As a general method the reaction of pyrroles with
dimanganese decacarbonyl was found to be of only limited
use.   Thus when applied to 2,5-dimethylpyrrole (XXXVIII;
$R_1=R_4=CH_3$; $R_2=R_3= H$),   the complex (XXXV $R_1=R_4=CH_3$;
$R_2=R_3= H$) could not be obtained analytically pure,
probably due to the presence of polymerised substituted
pyrrole, which might have formed as a result of high
temperature (100-120°C) employed.

This approach also failed in an attempt to prepare
tricarbonyl-π-3,5-dicarbethoxy-2,4-dimethylpyrrolyl-
manganese (XXXV; $R_1= R_3= CH_3$; $R_2= R_4= COOCH_3$).   The
synthesis of π-cyclopentadienyl metal complexes has been
facilitated by the use of alkali salts of cyclopentadiene,
e.g. cyclopentadienylsodium (XXXIX).   Pyrrole also reacts
with potassium to give pyrrolylpotassium (XL).

Na⁺

(XXXIX)
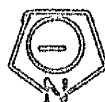
K⁺

(XL)

The only reported reaction of pyrrolylpotassium with a transition metal halide, with a view to preparing π-bonded complexes analogous to π-cyclopentadienyl metal derivatives is by Fischer and Ofele[112]. They did not observe any reaction between pyrrolylpotassium and hexammino-nickel (II)-thiocyanate. The reaction of pyrrolylpotassium with bromomanganese pentacarbonyl [Br Mn(CO)$_5$] in refluxing tetrahydrofuran, however, gave the expected complex, tricarbonyl-π-pyrrolylmanganese (XXXV; $R_1 = R_2 = R_3 = R_4 = H$).

This second method was found to be more widely applicable, and was extended not only to the preparation of many substituted pyrrolylmanganese complexes but also to other heterocyclic complexes.

By this method the substituted pyrrolylmanganese complexes,
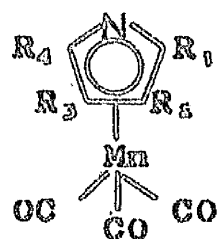
$$(XXXV)$$

(a) $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

(b) $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$

(c) $R_1 = R_2 = R_3 = R_4 = CH_3$

(d) $R_1 = R_3 = CH_3$; $R_2 = COCH_3$; $R_4 = H$

(e) $R_1 = CH_3$; $R_2 = COCH_3$; $R_3 = R_4 = H$

(XXXV, a-e) have been prepared. Their structures, analogous to that of tricarbonyl-π-pyrrolylmanganese (XXXV; $R_1 = R_2 = R_3 = R_4 = H$), have been supported by infrared spectra, showing twin MC-O stretching frequencies in the expected region, by nuclear magnetic resonance spectra and by analytical data.

When the potassium salt of 2-acetylpyrrole (XXXVIII; $R_1 = COCH_3$; $R_2 = R_3 = R_4 = H$) was treated with bromomanganese pentacarbonyl in tetrahydrofuran at <u>low temperature</u>, an unstable yellow compound was obtained. The infrared spectrum of this compound showed more than two MC-O peaks, i.e. at $2140^{cm^{-1}}$ (m); $2041^{cm^{-1}}$ (s); $2020^{cm^{-1}}$ (w) and $1941^{cm^{-1}}$ (s). A similar observation was made in the case of complex (XXXV; $R_1 = R_2 = R_3 = R_4 = C_6H_5$), where the MC-O peaks appeared at $2061^{cm^{-1}}$ (m); $2015^{cm^{-1}}$ (s); $1961^{cm^{-1}}$ (s)

and $1923^{cm^{-1}}$ (s). On the other hand the 2-acetylpyrrole (XXXVIII; R_1=COCH$_3$; R_2=R_3=R_4=H) on reaction with bromo-manganese pentacarbonyl in the same solvent at reflux temperature, yielded tricarbonyl-π-2-acetylpyrrolyl manganese (XXV; R_1=COCH$_3$; R_1=R_2=R_3=R_4=H), whose infrared spectrum showed twin MC-O peaks at $2020^{cm^{-1}}$ (s) and $1920^{cm^{-1}}$ (s), i.e. in the region of such π-complexes.

The occurrence of more than two MC-O bands in the infrared spectrum and the instability of these products formed at low temperature suggested the possibility that the σ-bonded intermediates, i.e. derivatives of penta-carbonyl pyrrolylmanganese had been isolated.

This view has been supported by the isolation and characterisation of σ-bonded iron complexes (vide infra). This suggests that the reaction always proceeds via σ-bonded intermediates, which lose two molecules of carbon monoxide to give the π-bonded tricarbonylmanganese complexes.

This second method has two main advantages over the first one.

(a) possibility of isolating σ-bonded complexes.

(b) low temperature of reaction, thus avoiding the polymerisation of pyrrole.

Presence of a functional group such as -CHO and $COCH_3$ in the α position of the pyrrole makes the corresponding complex noticeably unstable.   This effect appears to be partly offset by methyl groups.

The complexes (XXXV; f-i)

(XXXV)
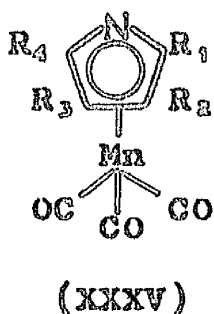
(f) $R_1 = COCH_3$; $R_2 = R_3 = R_4 = H$

(g) $R_1 = CHO$; $R_2 = R_3 = R_4 = H$

(h) $R_1 = R_3 = CH_3$; $R_2 = R_4 = COOCH_3$

(i) $R_1 = COOCH_3$; $R_2 = R_3 = R_4 = H$

were all obtained by reactions employing the second method. These products could not be purified analytically due to their instability and the difficulty of removing the pyrrole (unchanged or formed as a result of their decomposition during the attempted purification).

An attempt to prepare tricarbonyl-π-indolylmanganese (XLI; $R_1 = R_2 = R_3 = R_4 = R_5 = R_6 = H$) by heating indole with dimanganese decacarbonyl failed.

(XLI)
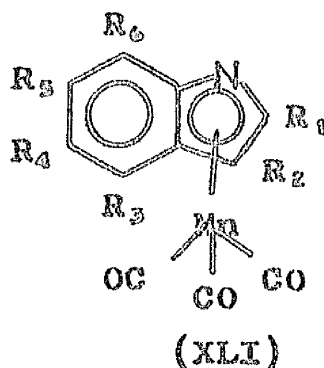
However the reaction of indolylpotassium with bromo-
manganese pentacarbonyl yielded a yellow oily product.
The infrared spectrum showed MC-O bands at $2030^{cm^{-1}}$ (vs)
and $1941^{cm^{-1}}$ (vs). The n.m.r. spectrum, [incompatible with
the structure (XLI; $R_1=R_2=R_3=R_4=R_5=R_6=H$)] and the mass
spectrum[125] showed the presence of two additional
hydrogens. A similar observation was made for a
compound[126] obtained from the reaction between bromo-
manganese pentacarbonyl and carbazolylpotassium. Both
products require further study to establish their
structures.

By contrast, alkyl-substituted indoles do give
complexes of the expected type (XLI). The dimethyl
derivative (XLI; $R_1=R_4=CH_3$; $R_2=R_3=R_5=R_6=H$) has only been
obtained in impure state. The main difficulty in the
purification of all the indole complexes was the

spreading of the free indoles on chromatographic column, making the products rather difficult to elute. Fractional sublimation and vacuum distillation were employed for purification.   Only the complex (XLI; $R_1 = CH_3$; $R_2 = R_3 = R_4 = R_5 = R_6 = H$) has been fully identified by analysis, infrared and n.m.r. spectra.   A similar complex, tricarbonyl-π-tetrahydrocarbozolylmanganese[126] has been synthesised in these laboratories.

Pyrazole and the methyl substituted pyrazoles yielded similar -π-bonded manganese complexes, of the type (XLII), which are unstable particularly in solution.   They show twin MC-O peaks in the expected region of their infrared spectra.   An attempt to obtain the complex (XLII; $R_1 = CH_3$; $R_2 = H$; $R_3 = CH_3$) failed.
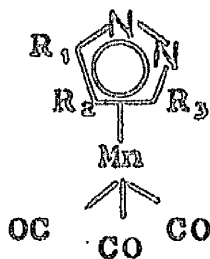
(XLII)

Analyses were rather difficult to obtain for these complexes because of their unstable nature. For example a yellow picrate prepared from the complex, tricarbonyl-

methyl-

π-3-pyrazolylmanganese (XLII; $R_1 = CH_3$; $R_2 = R_3 = H$) was shown by melting point (143°C) to be the picrate of the parent pyrazole, i.e. 3-methylpyrazole. This shows that the complexes decompose readily, regenerating the corresponding pyrazoles.

A yellow product obtained either by allowing benzotriazole to react with dimanganese decacarbonyl or by treatment of benzotriazolylpotassium with bromomanganese pentacarbonyl has not yet been characterised, although the twin MC-O bands at 2041 $^{cm^{-1}}$ (vs) and 1940 $^{cm^{-1}}$ (vs) in the infrared spectra suggest the formation of the desired tricarbonyl-π-benzotriazolylmanganese (XLIII).
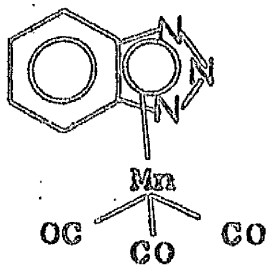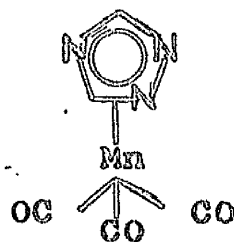
(XLIII)   (XLIV)

Similarly the unstable yellow product obtained from
1,2,4-triazole showed MC-O peaks at $2041^{cm^{-1}}$(vs) and
$1923^{cm^{-1}}$(vs) in its infrared spectrum suggesting the
formation of the corresponding tricarbonyl-π-1,2,4-
triazolylmanganese (XLIV).

All these experiments on pyrazoles and triazoles
suggest that the complexes of heterocycles containing
more than one hetero atom are highly unstable and
difficult to obtain in a pure state. (cf. the pyrrole
complexes are relatively stable).

Cyclopentadiene has been shown to react with
carbonyls of group VI metals to give bis(tricarbonyl-
cyclopentadienyl metal) complexes. Reaction of pyrrole
with molybdenum carbonyl gave a yellow solution, which
rapidly decomposed on exposure to air. Since solvent
employed was diglyme, it seems not unreasonable to assume
the formation of the diglyme metal carbonyl complex[127]
(XLV), which did not react with pyrrole and which
decomposed on exposure to air.

The hydrides of tricarbonyl-cyclopentadienyl-tungsten and molybdenum
have been prepared[128] by treatment of the sodium salt

from the reaction of the metal carbonyl and cyclopenta-
dienyl sodium, with acetic acid.   A similar reaction
was attempted with molybdenum carbonyl and pyrrolyl-
potassium.   The reaction mixture turned yellow on
addition of pyrrolyl salt to the metal carbonyl.   Treat-
ment of this reaction product with acetic acid or with
iodomethane gave only molybdenum carbonyl suggesting
that the expected hydride and the methyl derivative, if
formed, are too unstable to isolate.

Wilkinson and co-workers have treated iron (II)
and (III);, cobalt (III) and Ni (II) acetylacetonates
with cyclopentadienyl-sodium obtaining ferrocene,
cobaltocene and nickelocene respectively.   Attempts to
prepare pyrrole analogue (XLVI; M=Fe, Co, or Ni)
similarly, using 2,5-dimethylpyrrole (XXXVIII; $R_1=R_4=CH_3$;
$R_2=R_3=H$) resulted in decomposition, showing that the
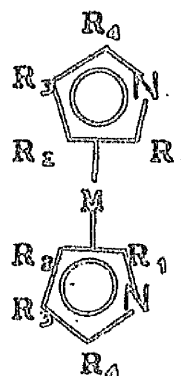
(XXXVIII)   (XLVI)

conditions employed were not favourable for the formation and isolation of the desired dipyrrolyl metal complexes.

Wilkinson[94] et al; have prepared ferrocene by treatment of cyclopentadienyl-sodium with anhydrous ferrous chloride.   An attempt to prepare bis(2,5-dimethylpyrrolyl) iron (XLVI; M=Fe; R_1=R_4=CH_3; R_2=R_3=H) by this method resulted in the formation of an unidentified yellow product in trace amount.

The desired complex might be obtainable by use of a base, e.g. trimethylamine or pyridine as in the preparation of ferrocene from cyclopentadiene[96].

In order to prepare pyrrolylnickel complexes, reactions between tetrapyridonickel-dichloride (XLVII) or allylnickel bromide[130] (XLVIII) and 2,5-dimethylpyrrole and its potassium derivatives were carried out, but failed.   The complex (XLVII) has been shown to react with cyclopentadienyl-sodium to yield π-allyl-π-cyclopentadienyl nickel[131] [132] (XLIX). .   The complex (XLIX) has also been obtained by the reaction of allylmagnesium halides with nickelocene.

Green and Nagy[133] obtained dicarbonyl-σ-allyl-π-

cyclopentadienyliron (L) from the reaction of allyl-
chloride with $Na^+[\pi-C_5H_5Fe(CO)_2]^-$. The complex (L) is
converted into monocarbonyl-π-allyl-π-cyclopentadienyl-
iron (LI) on u.v. irradiation. An attempt to prepare
similar pyrrole complexes by reaction of pyrrolylpotassium
with iodotricarbonylallyliron[134][135] (LII) resulted in the
formation of a yellow oil, which was

TABLE I

Complex	Method	Infrared $MC-O^{cm^{-1}}$
*I (a)	$C_4H_4NK + C_5H_5Fe(CO)_3I$	2038 (vs)
		1970 (vs)
(b)	$C_5H_5MgCl + C_5H_5Fe(CO)_3I$	2040 (vs)
		1970 (vs)
II[136]	CH_3 $CH=CH-CH=CH$ $CH_3+Fe(CO)_2$	2040 (vs)
		1960 (vs)
III[137] $(CO)_3Fe[CH_3CH=CH-CH$ CH $CH_2]BF_4+NaBH_4$		2042 (vs)
		1972 (vs)

*I (a) and (b) are products of the present study.

also obtained from Method I(b) in higher yield. (Table I).
The MC-O stretching frequencies of all the three products
I, II and III show similarity of their nature.   The n.m.r.

spectra of I and II, i.e. tricarbonyl-2,4-hexadiene-iron are
superimposable. The n.m.r. spectrum of product III
(obtained by Petit[136] et al) which is complex, gives
the information about the formation of a mixture of hexa-
dieneirontricarbonyls. This suggests that the complex
III is analogous to products I and II.

An unidentified unstable red compound obtained by
method I(a) showed MC-O peaks at $2095^{cm^{-1}}$ (S); $2041^{cm^{-1}}$ (VS)
and $1961^{cm^{-1}}$ (VS) in its infrared spectrum. Further study
is required to establish its structure.

An attempt to prepare tetracarbonyl-dipyrrolyldiiron
(LIII) by heating pyrrole with
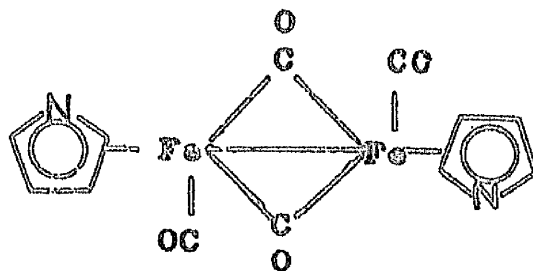
(LIII)

iron pentacarbonyl or iron dodecarbonyl in an autoclave
(cf. the preparation of tetracarbonyldicyclopentadienyl-
diiron[64]) failed as did the reaction between pyrrolyl-

potassium and iron dodecacarbonyl.   Similarly the
reaction between iron-enneacarbonyl with 2,5-dimethyl-
pyrrolylpotassium resulted in failure.

The reaction of pyrrolylpotassium with chloro-
tricarbonylcrotyliron (LIV) failed to give the desired
carbonyliron complex (LIII), although the reaction of
the complex (LIV) with diphenylcyclopentadienyl-sodium
has been shown[136] to give tetracarbonyl bis(diphenyl-
cyclopentadienyl)-diiron.   Compounds of the type
$R Fe(CO)_2C_5H_5$ have been obtained by treatment of the
halides, $C_5H_5Fe(CO)X$ with Grignard reagents or cyclo-
pentadienyl-sodium[69].   The Grignard reagents used
include methyl, ethyl and phenyl magnesium halides.
However, the syntheses involving these Grignard reagents
are inferior to the corresponding syntheses of the same
compounds from the sodium salt, $Na^+[Fe(CO)_2C_5H_5]$ and the
corresponding iodide because of a greater tendency to
side reactions such as those producing $[C_5H_5Fe(CO)_2]_2$.
The reaction between cyclopentadienyl-sodium and
iododicarbonylcyclopentadienyliron (X; X=Br or I)
produces a compound $(\sigma-C_5H_5)Fe(CO)_2(\pi-C_5H_5)$ together with

ferrocene and the dimeric complex [$C_5H_5Fe(CO)_2$]$_2$.

A similar reaction between iododicarbonylcyclo-
pentadienyliron (LV) and pyrrolylpotassium in <u>benzene</u>
at reflux temperature yielded azaferrocene, i.e.
π-cyclopentadienyl-π-pyrrolyliron (XXXVI),

    (LV)   (XL)   (XXXVI)
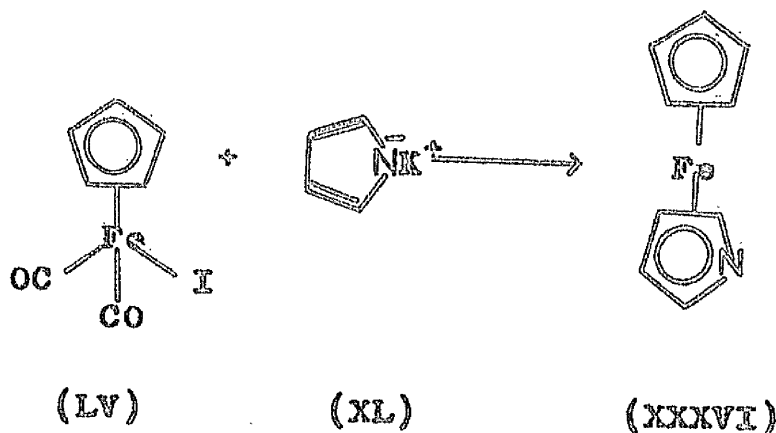
a red volatile crystalline compound along with ferrocene.

Table II shows comparison of infrared spectra of the
compound (XXXVI) and ferrocene. The infrared spectrum
contains strong 9 and 10 μ bands (1100 cm^{-1} and 1000 cm^{-1})
characteristic of an unsubstituted cyclopentadienyl group
and other bands corresponding to those of ferrocene.

TABLE II

Comparison of IR spectra

Ferrocene cm^{-1}	Azaferrocene cm^{-1}
3086 (m)	3080 (s)
2909 (w)	
1767 (w)	1745 (w)
	1715 (m)
	1700 (m)
	1660 (m)
1638 (w)	1640 (m)
1408 (m)	1409 (m)
	1386 (m)
	1342 (m)
1253 (w)	1265 (m)
1188 (w)	1185 (s)
1104 (s)	1109 (s)
1054 (w)	1062 (m)
1001 (s)	1002 (s)
854 (w)	855 (m)
844 (w)	
814 (s)	816 (s)

The compound is moderately soluble in organic solvents. Its volatility and solubility are very similar to those of ferrocene, making the separation of ferrocene and aza-ferrocene, $C_5H_5Fe\,C_4H_4N$, either by fractional crystallisation or sublimation difficult. The separation was readily effected by chromatography, ether being necessary to elute the pyrrolyl complex, while ligroin readily elutes ferrocene. This increase in polarity in substituting a π-cyclopenta-dienyl group by π-pyrrolyl group was also observed in the purification of tricarbonyl-π-pyrrolylmanganese (XXXV; $R_1=R_2=R_3=R_4=H$), which was eluted by ligroin-benzene, while tricarbonyl-π-cyclopentadienylmanganese (IV) is readily eluted with ligroin alone. The complex (XXXVI) gives an unstable yellow picrate and brown methiodide with picric acid and iodomethane respectively, in benzene.

The basicity of the complex (XXXVI) was determined potentiometrically. The value found for aza-ferrocene in aqueous ethanol (pK, 4.5) is closely similar to that of quinoline (4.65) under identical conditions. Azaferrocene dissolves in aqueous acids.

The nuclear magnetic spectrum is also in harmony
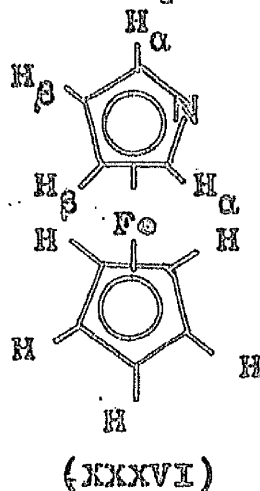
(XXXVI)

with the structure (XXXVI). The singlet resonances at

τ 4.74 and τ 5.56 each of relative intensity 2 may be

assigned to the two pairs of equivalent α and β protons

of the π-pyrrolyl ring respectively, and the singlet

resonances at τ 5.85 of relative intensity 5 to the

five equivalent protons of the π-cyclopentadienyl ring.

The resonances due to the π-pyrrolyl hydrogens appear at

higher field than the corresponding resonances[114] at

τ 3.9 and 4.8 in $C_4H_4N Mn(CO)_3$. This difference may be

attributed to the deshielding effect of the electron

withdrawing carbonyl groups, and compared, e.g. with the

chemical shift difference between the π-cyclopentadienyl

protons in $C_5H_5Mn(CO)_3$, which occur at τ 5.17[130] and those of

ferrocene, which occur at τ 5.94[139][140]. It is of interest to observe that in the n.m.r. spectra of $C_5H_5Fe\ C_4H_4N$ and $C_4H_4N\ Mn(CO)_3$, there is no observable coupling between the two different types of protons of the π-pyrrolyl ring in contrast to the n.m.r. spectrum of free pyrrole. A preliminary X-ray study[141] of aza-ferrocene (XXXVI) has shown that it is isomorphous with ferrocene. The structure is therefore disordered, with nitrogen atoms randomly placed in any of the ten positions occupied by carbon in a ferrocene molecule.

Azaferrocene (XXXVI) has also been obtained in very poor yield by the reaction of pyrrolylpotassium and cyclo-pentadienyl sodium in presence of ferrous chloride[116]. This method is inferior to the one employed in these studies as regards yield and ease of reaction.

An attempt was made to determine the aromaticity of azaferrocene. Two reactions (a) acetylation (b) amino-methylation were carried out to investigate (i) the possibility of substitution (ii) to find which of the two rings is more reactive towards the electrophilic attack. Friedel and Crafts acetylation of azaferrocene afforded

an unstable yellow gummy product.   The infrared spectrum
of this product showed two CH_3C-O peaks at $1703^{cm^{-1}}$ (vs)
and $1639^{cm^{-1}}$ (vs) but no strong 9 and 10μ bands.   This
suggests the formation of an acetylated product which
appears to be a mixture of isomers.   The reaction requires
further study.   A similar experiment using tricarbonyl-π-
pyrrolylmanganese (XXXV; $R_1 = R_2 = R_3 = R_4 = H$) afforded a trace
of reddish brown product, which decomposed quickly.

The aminomethylation of azaferrocene led to
decomposition.   This suggests the instability of the
aminomethylated product.

In view of the unfavourable behaviour of azaferrocene
towards electrophilic reagents, another route to substituted
azaferrocenes was employed.

In addition to azaferrocene the following derivatives
(XXXVI)(a-d)
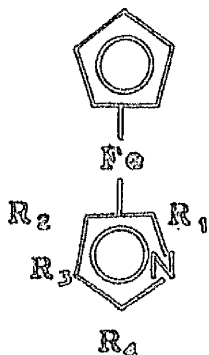
(a) $R_1 = R_3 = CH_3$; $R_2 = R_4 = H$

(b) $R_1 = R_4 = CH_3$; $R_2 = R_3 = H$

(c) $R_1 = R_2 = R_3 = R_4 = CH_3$

(d) $R_1 = R_3 = CH_3$; $R_2 = COCH_3$; $R_4 = H$

(XXXVI)

have been prepared in similar fashion, i.e. reaction
between the potassium salt of the substituted pyrrole
and iododicarbonylcyclopentadienyliron (LV).   It is
notable that the resonances of the pyrrole pattern in
the n.m.r. spectra of (XXXVI; (a)) and (XXXVI; (b))
appear at higher field than the resonances of the
corresponding pyrrolylmanganese complexes, i.e.
(XXXV; $R_1=R_3=CH_3$; $R_2=R_4=H$) and (XXXV; $R_1=R_4=CH_3$; $R_2=R_3=H$)
which in turn appear at higher field as compared with the
parent pyrroles (XXXVIII; $R_1=R_3=CH_3$; $R_2=R_4=H$) and (XXXVIII;
$R_1=R_4=CH_3$; $R_2=R_3=H$), (see Appendix).   In all these
complexes pyrrole metal bonding is analogous to that
found with the π-cyclopentadienyl complexes of transition
metals.

To explore the possibility of synthesising complexes
exhibiting a different mode of bonding of the pyrrole to
metal atom, the reaction between pyrrolylpotassium and
iododicarbonylcyclopentadienyliron (LV) was carried out
in the same solvent (benzene) but at a low temperature
(50-60°C).   On chromatography of the reaction product
dicarbonyl-π-cyclopentadienyl-σ-pyrrolyliron (LVI) was
eluted faster than π-cyclopentadienyl-π-pyrrolyliron

TABLE III

Comparison of IR Spectra

$\pi - C_5H_5Fe(CO)_2 - \sigma - CH_3$ cm^{-1}	$\pi - C_5H_5Fe(CO)_2 - \sigma - CH_4N$ cm^{-1}
2015 (vs)	2020 (vs)
1965 (vs)	1975 (vs)
1785 (w)	
1706 (w)	
1664 (v.w)	
1606 (w)	
	1505 (w)
	1413 (w)
	1353 (v.w.)
	1160 (v.w.)
	1110 (v.w.)
1086 (w)	1090 (s)
	1055 (v.w.)
	1045 (w)
	1030 (w)
1015 (m)	
1001 (m)	995 (v.w.)
	908 (m)
923 (m)	
	885 (w)
841 (w)	840 (m)
	795 (m)
705 (s)	
740 (s)	
	703 (vs)

(XXXVI). This shows that the σ-bonded complex (LVI)
is less polar than the π-bonded complex, i.e. aza-
ferrocene (XXXVI). The infrared spectrum (table III) of this
σ-bonded compound is comparable with that of dicarbonyl-
π-cyclopentadienyl-σ-cyclopentadienyliron[67][69] (XII),
showing the structural similarity of the two complexes.

This structure of the complex (LVI) is confirmed by
the n.m.r. spectrum, which shows

(LVI)
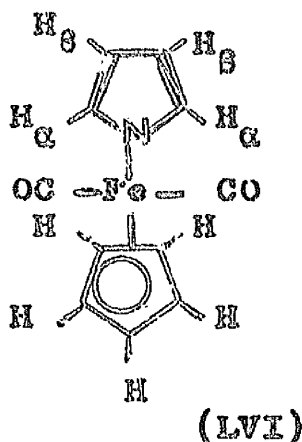
doublets centred at τ 4.0 and τ 4.15 each of relative
intensity 2, which may be assigned to two pairs of
equivalent protons (bonded to α and β carbon atoms) and
the singlet resonance at τ 5.17 of relative intensity 5
assigned to the five equivalent protons of the π-cyclo-
pentadienyl ring. It is of interest to note that

resonances due to the σ-bonded pyrrolyl ring appear
at higher field than those of the parent pyrrole
(XXXVIII; $R_1=R_2=R_3=R_4=H$) but at lower field than those
(at τ 4.74 and τ 5.56) of azaferrocene (XXXVI)(see
Appendix).

Another aspect of the n.m.r. spectrum is that the
singlet due to the π-cyclopentadienyl ring is at
appreciably lower field than that in the π-cyclopenta-
dienyl ring in azaferrocene (XXXVI = π-cyclopentadienyl-
π-pyrrolyliron at τ 5.85).

The formation of dicarbonyl-π-cyclopentadienyl-N-
pyrrolyliron has shown that complexes containing pyrrole-
σ-bonded to iron (type iv) are stable and capable of
isolation.   On heating this σ-bonded complex (LVI)
loses carbon monoxide and is converted to π-bonded
complex (XXXVI).

(XL)   (LV)   (LVI)   (XXXVI)
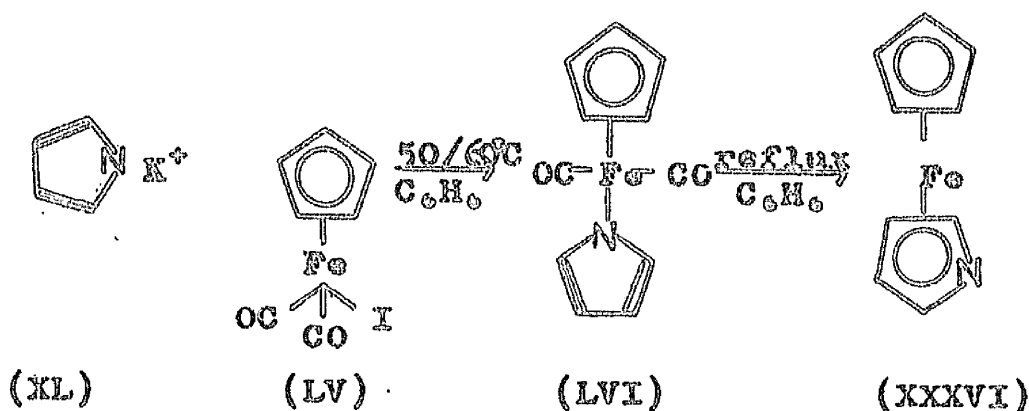
A logical extension of the preparation of the
compounds (XXXVI and LVI) appeared to be the reaction of
diiodotetracarbonyliron, $Fe(CO)_4I_2$ (LVII) with pyrrolyl-
potassium.   The complex (LVII) reacts with cyclopenta-
dienyl sodium to give ferrocene.   The reaction using
pyrrolylpotassium at $0^{\circ}C$ afforded an unidentified unstable
product in trace amounts.

The reaction of iododicarbonylcyclopentadienyliron
with other heterocyclic systems, e.g. indole and carbazole
was examined with a view to preparing the corresponding
benzo-analogues of both π- and σ-bonded pyrrolyl iron
complexes.

Thus the reaction of iododicarbonylcyclopentadienyl-
iron with indolylpotassium yielded the corresponding σ-
indolyl complex (LVIII) accompanied by a red viscous
product which appeared to be π-cyclopentadienyl-π-indolyl-
iron (LIX). The infrared spectrum of the latter showed
9 and 10 μ bands, demonstrating the presence of an
unsubstituted cyclopentadienyl ring π-bonded to iron.

<div align="center">TABLE IV</div>

Complex	π-cyclopentadienyl ring τ values
π-cyclopentadienyl-π-indolyliron	5.95
dicarbonyl-π-cyclopentadienyl-σ-indolyliron	5.16
π-cyclopentadienyl-π-pyrrolyliron	5.87
dicarbonyl-π-cyclopentadienyl-σ-pyrrolyliron	5.17

Table IV compares the resonance frequency of the cyclo-
pentadienyl protons of these two indolyl complexes with
those of the corresponding π- and σ-bonded pyrrolyliron
complexes (XXXVI and LVI).

In a similar way two different reactions at _lower temperature_ between iodocarbonylcyclopentadienyliron and the potassium salts of carbazole and tetrahydrocarbazole yielded the corresponding σ-bonded complexes, (i) dicarbonyl-π-cyclopentadienyl-N-carbazolyliron (LX) and (ii) dicarbonyl-π-cyclopentadienyl-N-tetrahydrocarbazolyl-iron (LXI) respectively.   The n.m.r. spectrum of the σ-bonded complex (LX   ) shows two resonances at τ 2.25 (complex) of relative intensity 2, which may be assigned to H_1 and H_8 of the σ-bonded carbazolyl ring and at τ 2.8 (complex) of relative intensity 6 due to the remaining six protons.   The singlet resonance

(LX)

(LXI)
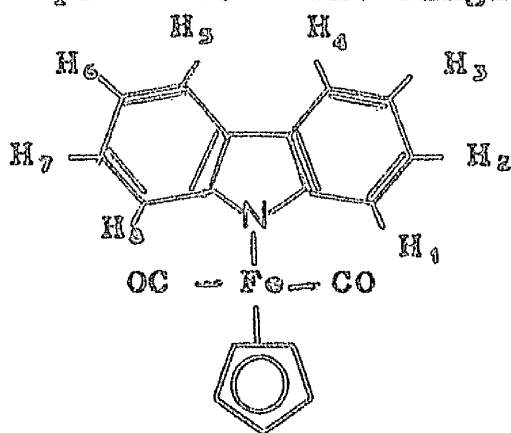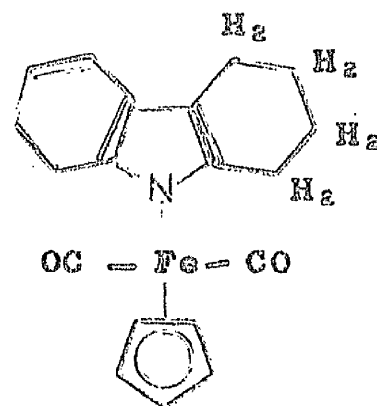
at τ 4.95 of relative intensity 5 can be assigned to the

five protons of the cyclopentadienyl ring.   Thus the
product can be reasonably assigned the stureture (LX).
The n.m.r. spectrum of the compound (LXII) is complex
and the singlet resonance at τ 4.98 can be assigned to
the five protons of the cyclopentadienyl ring.   It is
noticeable that the cyclopentadienyl resonances of these
complexes are at lower field than those of either the σ-
bonded pyrrole or σ-bonded indole complexes.

In similar reactions at higher temperature, the
potassium salts of tetrahydrocarbazole and indole afforded
products, which appeared to be π-iron complexes.   The
infrared spectra of these products showed strong 9 and 10 μ
bands, characteristic of π-cyclopentadienyl metal groups.

A similar reaction of indenyl sodium[148] with iodo-
dicarbonylcyclopentadienyliron in tetrahydrofuran afforded
the corresponding σ-bonded indenyl complex in poor yield.
The reaction of 2-formylpyrrolylpotassium with the iodide
(LV) gave no isolable product, but reaction of 2-acetyl-
pyrrolylpotassium with the iodide (LV) afforded dicarbonyl-
π-cyclopentadienyl-σ-2-acetylpyrrolyliron (LXII).
Surprisingly the $CH_3C=O$ peak in the infrared spectrum of
the latter appeared at $1575^{cm^{-1}}$ (S), shifted from its usual

position (in the parent pyrrole, i.e. 2-acetylpyrrole,
the acetyl peak appears at $1658^{cm^{-1}}$). A similar
phenomenon is apparent with the corresponding manganese
carbonyl derivative, i.e. tricarbonyl-π-2-acetylpyrrolyl-
manganese (XXXV; $R_1 = COCH_3$, $R_2 = R_3 = R_4 = H$) which showed its
CH_3C-O peak at $1587^{cm^{-1}}$.

The n.m.r. spectrum of dicarbonyl-π-cyclopentadienyl-
σ-2-acetylpyrrolyliron (LXII) shows resonances at τ 3.15;
3.45; 3.95 (all weak and broad), which may be assigned to
the 3 protons, one at α and two at β positions in the
pyrrole ring.
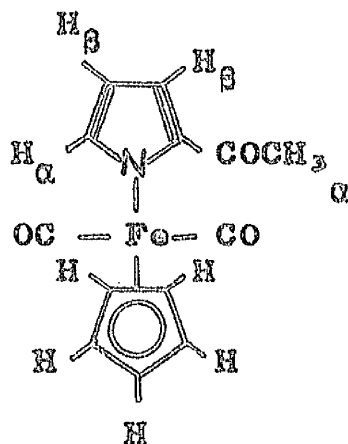
(LXII)

A singlet resonance at τ 5.25 may be assigned to five
protons on the π-bonded cyclopentadienyl ring and another
singlet resonance at τ 7.89 assigned to three protons of

the acetyl group.   The observed relative intensities are in the ratio 3 : 4.9 : 3, whereas the structure (LXIX) requires a ratio 3 : 5 : 3.   The structure (LXII) is acceptable on the basis of (i) analysis, (ii) infrared spectrum, (III) n.m.r. spectrum and (iv) mass spectrum[125] (see Appendix).

The cracking pattern has been interpreted as follows (see Appendix).
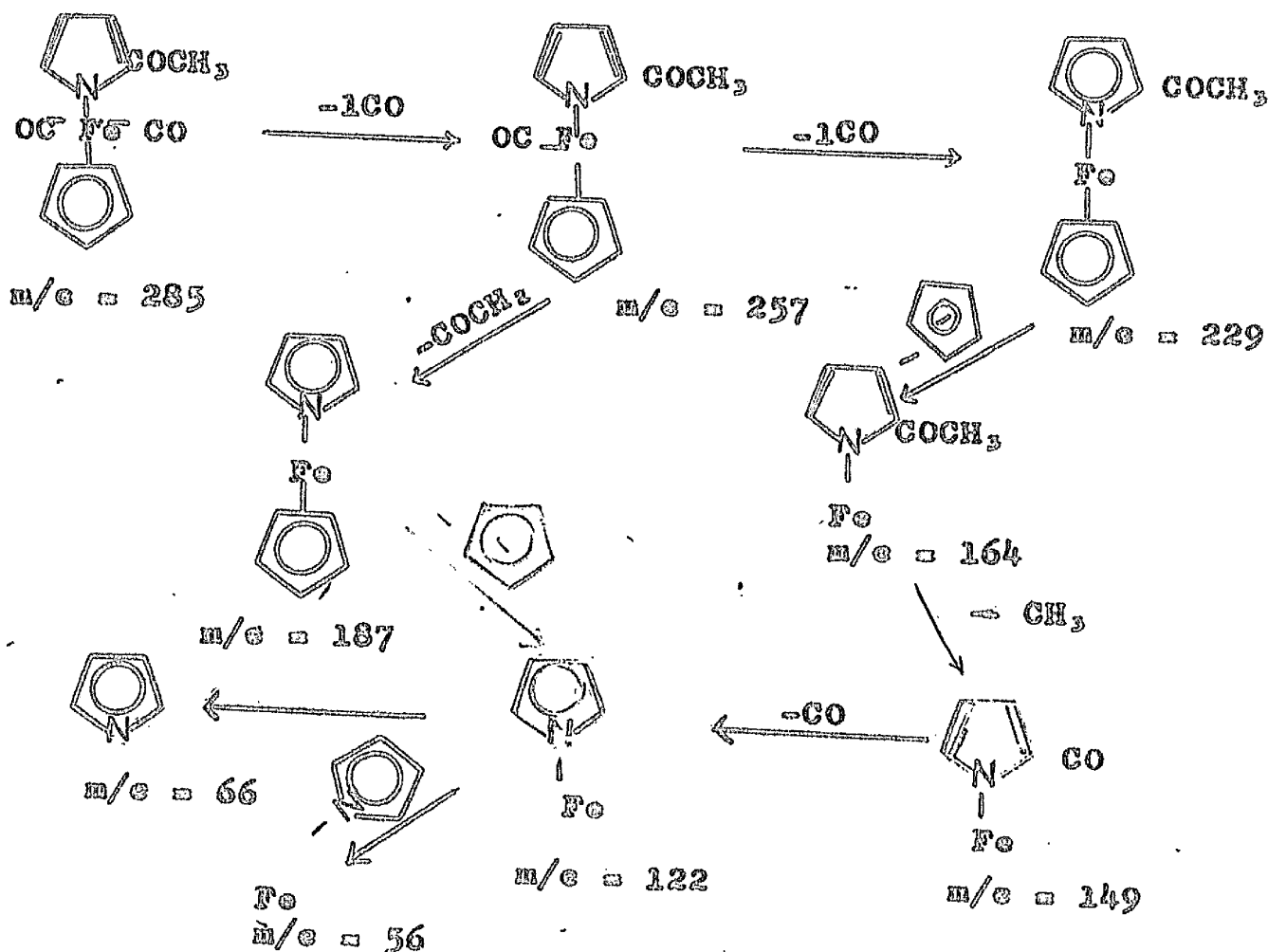
Sodiomanganesepentacarbonyl has been reported to react
with acylhalides to give complexes of the type
$RCOMn(CO)_5$[145]. Pyrroyl chloride on such treatment
afforded two yellow products. The infrared spectrum of
the less stable product exhibited MC-O peaks at 2145^{cm-1} (S);
2088^{cm-1} (S); 2050^{cm-1} (v.w); 2022^{cm-1} (V S and broad) and
1940^{cm-1} (VS) in addition to acyl peaks at 1754^{cm-1} (VS);
1683^{cm-1} (VS) and appears to be the σ-bonded acyl complex,
pyrroylmanganesepentacarbonyl ($C_9H_4Mn\ NO_6$)(LXIII)(cf.
furoylmanganesepentacarbonyl[144]). The infrared spectrum
of the second product showed MC-O peaks at 2141^{cm-1} (S);
2041^{cm-1} (VS) and 1923^{cm-1} (VS, broad) but no acyl peaks
and can be assigned the structure, 2-pyrrolylmanganese-
pentacarbonyl ($C_9H_4Mn\ NO_5$)(LXIV) formed by

(LXIII)   (LXIV)
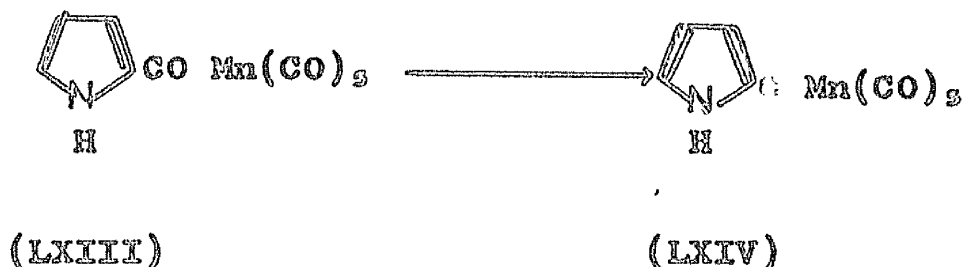
the loss of one molecule of carbon monoxide in the complex
(LXIII) in a similar fashion to 2-furylmanganesepenta-
carbonyl[141]. Analytical data support the formula (LXIV)
for the complex.

EXPERIMENTAL

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G E N E R A L

All reactions were carried out in an atmosphere of oxygen free "white spot" nitrogen.

All solvents used in reactions were carefully dried; e.g. petroleum ether (b.p. 100-120°C) was purified by washing in turn with conc. sulphuric acid, acidified potassium permanganate solution and water, drying over calcium chloride and distilling over sodium.

Ligroin refers to that fraction of petroleum ether of b.p. 60-80°C unless otherwise specified. Spence's 'Grade H' alumina was used for chromatography and was partially deactivated by exposure to air for 3-6 hours.

Neutral alumina was prepared by storing 'Grade H' alumina under ethylacetate for 1-2 days, filtering, washing with methanol and water and finally drying at 160°C for 4 hours.

All melting and boiling points are uncorrected.

All infrared spectra were recorded as potassium chloride discs unless otherwise stated.

N.M.R. spectra were recorded on Perkin-Elmer 40M/C Spectrometer (tetramethylsilane being the internal

reference) in carbondisulphide unless otherwise specified.

Percentage yields are based on unrecovered carbonyl
or halocarbonyl.

The following two methods (A) and (B) have been followed as standard ones in the preparation of heterocyclic manganese complexes.

TRICARBONYL-π-PYRROLYL-MANGANESE

(A) From pyrrole and dimanganese decacarbonyl.

Pyrrole (12 ml.) was added to a solution of dimanganese decacarbonyl (3.9 g. 10 mmoles) in ligroin (b.p. 100-120°C; 45 ml.). The mixture was stirred at reflux temperature for 14 hr, cooled, and the solvent was evaporated under reduced pressure. The residue was chromatographed on alumina. Ligroin eluted dimanganese decacarbonyl (1.7 g; 43.7%). Ligroin-benzene (4 : 1) eluted excess pyrrole. Further elution with the same solvent mixture gave tricarbonyl-π-pyrrolyl-manganese (1.5 g; 68%), which was purified by sublimation (0.01 mm at room temperature) as bright orange crystals m.p. 41.0°C [lit[114] 40.5-41.0°C].

(B) From pyrrolylpotassium and bromomanganese pentacarbonyl.

Pyrrole (0.7 g. 11 mmoles) was added dropwise to a suspension of potassium (0.39 g; 0.01 g.atom) in tetra-

hydrofuran (20 ml.). The mixture was stirred at room temperature, until all potassium had reacted (Ca 5-6 hr.) Bromomanganese pentacarbonyl (2.75 g; [145] 10 mmoles) in tetrahydrofuran (40 ml.) was added to the white suspension of potassium salt and the mixture was heated at reflux temperature with stirring for 4 hr. The mixture was cooled and filtered through kieselguhr. The solvent was evaporated in vacuo. The residue was extracted with benzene and chromatographed as under (A). Dimanganese decacarbonyl (0.77 g.) and tricarbonyl-π-pyrrolylmanganese (0.88 g; 72%) m.p. 41°C [lit [114] 40.5-41.0°C] were obtained besides some unchanged pyrrole.

TRICARBONYL-π-2,5-DIMETHYLPYRROLYL-MANGANESE

1. From dimethylpyrrole and dimanganese decacarbonyl

    2,5-dimethylpyrrole [146] (9.35 g. 100 mmoles) and dimanganese decacarbonyl (1.3 g; 4 mmoles) were refluxed for 16 hr. The reaction mixture was processed by method (A). Dimanganese decacarbonyl (0.57 g.) and unreacted dimethylpyrrole (4.32 g.) were eluted by ligroin and benzene. Elution with ether afforded a yellow liquid

(0.74 g.), which on distillation at $60°C/10^{-2}$ mm. gave tricarbonyl-π-2,5-dimethylpyrrolyl-manganese, whose spectrum showed that it was still contaminated with unchanged pyrrole. A pure sample was obtained as follows:-

2. From 2,5-dimethylpyrrolyl-potassium and bromo-manganese pentacarbonyl.

Cooled 2,5-dimethylpyrrolyl-potassium obtained (3 hr. reflux) from 2,5-dimethylpyrrole (1.37 g; 14 mmoles) and potassium (0.40 g; 0.01 g.atom) in tetrahydrofuran (30 ml.) and bromomanganese pentacarbonyl (2.92 g; 11 mmoles) in the same solvent (30 ml.) were treated under the reaction conditions (B) for 4 hr. Dimanganese deca-carbonyl (0.75 g.); unchanged 2,5-dimethylpyrrole (0.37 g.) and tricarbonyl-π-2,5-dimethylpyrrolyl-manganese (0.16 g; 12%) were obtained. The product was purified by sublimation (0.01 mm Hg at room temperature) as yellow crystals m.p.25.5-26.0°C

Found   C, 46.0;   H, 3.5   N, 5.95

$C_9 H_8 Mn NO_3$ requires   C, 46.4;   H, 3.4   N, 6.0%

Infrared peaks (liquid film) MC-O at $2022^{cm^{-1}}$ (vs) and $1923^{cm^{-1}}$ (vs)

N.M.R.peaks at τ5.1(β-H) and 7.87(α-CH$_3$), relative intensities 1 : 3.01, required intensities 1 : 3.

TRICARBONYL-π-2,4-DIMETHYLPYRROLYL-MANGANESE

Cooled 2:4-dimethylpyrrolyl-potassium, obtained (3 hr; reflux) from 2,4-dimethylpyrrole[147] (0.84 g; 9 mmoles) and potassium (0.30 g; 0.007 g.atom) in tetrahydrofuran (30 ml.) and bromomanganese pentacarbonyl (3.6 g; 13 mmoles) were treated for 3-4 hr as under (B). On chromatography, ligroin; ligroin-benzene (30 : 70) and ether eluted successively, dimanganese decacarbonyl (0.60 g.); unchanged 2,4-dimethylpyrrole, and tricarbonyl-π-2,4-dimethylpyrrolyl-manganese, as a yellow oil (0.38 g; 15%), which was purified by distillation at 45-50°C/0.01-0.05 mm.

Found : C, 46.5; H, 3.8; N, 6.0

C$_9$ H$_8$ Mn NO$_3$ requires: C, 46.4; H, 3.4; N, 6.0%

Infrared peaks (liquid film) MC-O at $2010^{cm^{-1}}$ (VS) and $1923^{cm^{-1}}$ (VS).

N.M.R. peaks (C Cl$_4$) at τ4.33(α-H); 5.13(β-H); 7.85(α-CH$_3$) and 8.03(β-CH$_3$), relative intensities 1 : 1 : 3 : 3, required intensities 1 : 1 : 3 : 3

TRICARBONYL-π-2,3,4,5-TETRAMETHYLPYRROLYL-MANGANESE

Cooled 2,3,4,5-tetramethylpyrrolyl-potassium
(14 mmoles) prepared (2-3 hr. reflux) from 2,3,4,5-
tetramethylpyrrole (1.68 g; 14 mmoles) and potassium
(0.53 g; 0.014 g.atom) in tetrahydrofuran (30 ml.) and
bromomanganese pentacarbonyl (3.8 g; 14 mmoles) in the
same solvent (40 ml.) were allowed to react for 3-4 hr.
and processed as under (B).   Elution with ligroin,
ligroin-benzene (30:70) and ether isolated dimanganese
decacarbonyl (0.42 g.), unchanged tetramethylpyrrole and
tricarbonyl-π-2,3,4,5-tetramethylpyrrolyl-manganese (1.51g.)
respectively.   The crude product on purification
(sublimation at $60°C/10^{-2}$ mm.) gave orange crystals
(0.41 g; 12%) m.p. 35.5-36°C.

Found   : C, 50.4;   H, 4.5;   N, 5.5

$C_{11}H_{12}$ Mn NO_3 requires: C, 50.6;   H, 4.6;   N, 5.4%

Infrared peaks MC-O at $2020^{cm^{-1}}$ (VS) and $2041^{cm^{-1}}$ (VS)

N.M.R. peaks at τ 7.93(α-CH_3) and 8.1(β-CH_3), relative
intensities 1 : 1,   required intensities 1 : 1.

TRICARBONYL-π-3-ACETYL-2-METHYLPYRROLYL-MANGANESE

Cooled 3-acetyl-2-methylpyrrolyl-potassium obtained (3hr. reflux) from 3-acetyl-2-methylpyrrole[149] (1.9 g; 15 mmoles) and potassium (0.53 g; 0.014 g.atom) in tetrahydrofuran (25 ml.) and bromomanganese pentacarbonyl (3.35 g; 12 mmoles) in the same solvent (50 ml.) were refluxed (5 hr.). Subsequent chromatography gave dimanganese decacarbonyl (0.76 g.) and tricarbonyl-π-3-acetyl-2-methylpyrrolyl-manganese, a yellow mass, on elution with ligroin and petrol-benzene (1 : 1) respectively. The product was purified (sublimation $40°C/10^{-2}$ mm), (0.91 g. 50%) as yellow crystals m.p. 67.5-68°C.

Found : C, 46.4; H, 3.5; N, 5.4

$C_{10}H_8$ Mn NO_4 requires : C, 46.0; H, 3.1; N, 5.4%

Infrared peaks MC-O at $2041^{cm^{-1}}$ (VS) and $1961^{cm^{-1}}$ (VS) CH_3C-O at $1681^{cm^{-1}}$ (S).

N.M.R. peaks at τ 4.08, 4.12 (α-H); 4.44, 4.48 (β-H); 7.6 (α-CH$_3$) 7.72 (β-CH$_3$), relative intensities 1 : 1 : 3 : 2.9, required intensities 1 : 1 : 3 : 3.

TRICARBONYL-Ⅱ-3-ACETYL-2,4-DIMETHYLPYRROLYL-MANGANESE

3-Acetyl-2,4-dimethylpyrrolyl-potassium (cooled),
obtained (2 hr. reflux) from 3-acetyl-2,4-dimethyl-
pyrrole (2.6 g; 9 mmoles) and potassium (0.54 g; 0.014
g.atom) in tetrahydrofuran (25 ml.) under reaction
conditions (B) with pentacarbonyl bromomanganese (3 g;
11 mmoles) for 5 hr, gave dimanganese decacarbonyl
(0.625 g.) and tricarbonyl-3-acetyl-2,4-dimethylpyrrolyl-
manganese (1.03 g.), eluted successively with ligroin
and petrol-benzene (1 : 1).   After purification by
distillation (80-82.5°C/0.02 mm) the yellow compound
(0.71 g; 45%) thus obtained was sublimed (10^{-3}mm. room
temperature) to give yellow crystals m.p. 44.5-45°C.

Found   :   N, 4.9, 5.0

$C_1 H_0$ Mn NO_4 requires   :   N, 5.1%

Infrared peaks MC-O at $2041^{cm^{-1}}$ (VS) and $1961^{cm^{-1}}$ (VS),
CH_3C-O at $1681^{cm^{-1}}$ (S).

N.M.R. peaks at $\mathcal{T}$4.28(α-H); 6.63(α-CH_3 & β-$COCH_3$) and
7.85(β-CH_3),   relative intensities 1 : 6.1 : 3.1,
required intensities 1 : 6 : 3.

ATTEMPTED REACTION OF INDOLES WITH DIMANGANESE DECACARBONYL

Indole (2.5 g; 21 mmoles) and dimanganese decacarbonyl (3.9 g; 10 mmoles) under condition (A) gave only manganese carbonyl (2.1 g; 84%) and unchanged indole spread over the column. From a similar reaction between 2-methyl-indole (2.9 g;) and manganese carbonyl (1.5 g.), unchanged manganese carbonyl (1.32 g. 88%) and some 2-methyl-indole were recovered.

REACTION OF INDOLYLPOTASSIUM WITH BROMOMANGANESE PENTA-
CARBONYL

Indolyl-potassium, obtained (3 hr. room temperature) from indole (2.73 g; 2.3 mmoles) and potassium (0.6 g; 0.016 g.atom) in tetrahydrofuran (10 ml, which was evaporated under a stream of nitrogen), was allowed to react (B) with bromomanganese pentacarbonyl (2.77 g; 10 mmoles) for 5 hr. in benzene (60 ml.). Elution with petrol and petrol-benzene (70:30) gave dimanganese deca-carbonyl (0.60 g.) and a viscous yellow oil (0.85 g.). Sublimation removed indole and subsequent high vacuum

distillation gave the product.

Found : N, 5.7

$C_1H_6Mn\,NO_3$ requires : N, 5.3; $C_1H_6Mn\,NO_3$ requires 5.45%. Infrared peaks (liquid film) MC-O at $2030^{cm^{-1}}$ (vs) and $1941^{cm^{-1}}$ (vs)

TRICARBONYL-π-2-METHYLINDOLYL-MANGANESE

2-Methylindolyl-potassium (cooled), obtained (2 hr. reflux) from 2-methylindole (2.0 g; 17.5 mmoles) and potassium (0.41 g; 0.01 g.atom) in benzene (50 ml.) on reaction (B) with bromomanganese pentacarbonyl (3.26 g; 12 mmoles) in the same solvent (50 ml.) and subsequent chromatography yielded **dimanganese decacarbonyl** (0.84 g.) unchanged 2-methylindole and a complex. Prolonged sublimation at room temperature/10^{-2} mm, removed 2-methylindole, followed at 60°C/10^{-2} mm by tricarbonyl-π-2-methylindolyl-manganese, which formed orange crystals m.p. 91.5-92°C.

Found : C, 53.1; H, 3.0; N, 5.3
$C_{12}H_8Mn\,NO_3$ requires: C, 53.3; H, 3.0; N, 5.2%

Infrared peaks MC-O at $2041^{cm^{-1}}$ (VS) and $1961^{cm^{-1}}$ (VS)
N.M.R. peaks at τ 2.6 (complex phenyl); 4.5 (3-H) and
7.78 (α-CH$_3$), relative intensities 4.1 : 1 : 3, required
intensities 4 : 1 : 3.

REACTION OF 2,5-DIMETHYLINDOLYL-POTASSIUM WITH
BROMOMANGANESE PENTACARBONYL

2,5-Dimethylindolyl-potassium (cooled) prepared
(3 hr. reflux) from 2,5-dimethylindole (1.67 g; 12 mmoles)
and potassium (0.59 g; 0.015 g.atom) in tetrahydrofuran
(10 ml. evaporated under nitrogen) was allowed to react
(B) with bromomanganese pentacarbonyl (3.2 g; 12 mmoles)
in benzene (75 ml.) Chromatography, besides dimanganese
decacarbonyl (0.72 g.), gave a small amount of yellow
product, contaminated with unchanged indole, which could
not be separated by fractional sublimation to yield the
complex in pure state, it showed infrared peaks MC-O at
$2020^{cm^{-1}}$ (VS) and $1961^{cm^{-1}}$ (VS).

ATTEMPTED REACTION OF 3,5-DICARBETHOXY-2,4-DIMETHYL-
PYRROLE WITH DIMANGANESE DECACARBONYL

3,5-Dicarbethoxy-2,4-dimethylpyrrole [150] (4.71 g;
20 mmoles) and dimanganese decacarbonyl (0.59 g; 1.5 mmoles)
on reaction (A) gave dimanganese decacarbonyl (0.24 g;
50%) and unreacted 3,5 dicarbethoxy 2,4-dimethylpyrrole
(1.62 g.)

REACTION OF 3,5-DICARBETHOXY-2,4-DIMETHYLPYRROLYL-
POTASSIUM WITH BROMOMANGANESE PENTACARBONYL

3,5-Dicarbethoxy-2,4-dimethylpyrrolyl-potassium
(cooled), obtained (3 hr. reflux) from 3,5-dicarbethoxy-
2,4-dimethylpyrrole (3.79 g; 10 mmoles) and potassium
(0.55 g; 0.014 g.atoms) in tetrahydrofuran (40 ml.)
was allowed to react (B) with bromomanganese pentacarbonyl
(4.0 g; 15 mmoles) in the same solvent (40 ml.) for 4 hr.
Chromatography, on elution with petrol, petrol-benzene
(7:3) and ether gave dimanganese decacarbonyl (0.62 g.)
the unchanged pyrrole (1.43 g.) and a yellow solid in
poor yield respectively. The yellow solid was unstable
Infrared peaks MC-O at $2041^{cm^{-1}}$ (vs) and $1941^{cm^{-1}}$ (vs)
CH_3C-OO at $1626^{cm^{-1}}$ (s), $1550^{cm^{-1}}$ (s) and $1428^{cm^{-1}}$ (s).

REACTION OF 2-METHOXYCARBONYLPYRROLYL-POTASSIUM WITH

BROMOMANGANESE PENTACARBONYL

2-Methoxycarbonylpyrrolyl potassium prepared (2 hr. room temperature) from 2-methoxycarbonylpyrrole[131] (1.03 g; 8 mmoles) and potassium (0.28 g; 0.007 g.atom) in tetrahydrofuran (30 ml.) on reaction (B) with bromomanganese pentacarbonyl (2.21 g; 8 mmoles) in the same solvent (40 ml.) for 5 hr., gave dimanganese decacarbonyl (1.04 g.) and a yellow solid, which on sublimation gave unchanged 2-methoxycarbonylpyrrole (0.400 g.).   The infrared peaks of the yellow gummy residue (unstable) are MC-O at $2020^{cm^{-1}}$ (VS) and $1941^{cm^{-1}}$ (VS); CH_3C-OO $1667^{cm^{-1}}$ (S); $1545^{cm^{-1}}$ (S) and $1420^{cm^{-1}}$ (S).

REACTION OF 2,3,4,5-TETRAPHENYLPYRROLYL-POTASSIUM WITH

BROMOMANGANESE PENTACARBONYL

2,3,4,5-Tetraphenylpyrrolyl-potassium (cooled), obtained (6 hr. reflux) from 2,3,4,5-tetraphenylpyrrole[132] (2.09 g; 5 mmoles) and potassium (0.20 g; 0.005 g.atom) in tetrahydrofuran (30 ml.), on reaction (B) with bromomanganese pentacarbonyl (1.77 g; 7 mmoles) in the same

solvent (40 ml.) for 4 hr. gave, on subsequent
chromatography, dimanganese decacarbonyl (0.35 g.);
the unreacted pyrrole (1.5 g.) and a yellow product
(unstable) in very poor yield.

Infrared peaks MC-O $2061^{cm^{-1}}$ (vs), $2015^{cm^{-1}}$ (vs), $1961^{cm^{-1}}$ (vs),
$1923^{cm^{-1}}$ (vs); C_6H_5 $1490^{cm^{-1}}$ (s), $1493^{cm^{-1}}$ (s), $1471^{cm^{-1}}$ (s)
and $1428^{cm^{-1}}$ (s) show the product as pentacarbonyl σ-
tetraphenylpyrrolyl-manganese.

REACTION OF 2-ACETYLPYRROLYL-POTASSIUM WITH BROMO-
MANGANESE PENTACARBONYL

1.   Cooled, 2-acetylpyrrolyl-potassium obtained (4 hr.
reflux) from 2-acetylpyrrole (1.65 g; 15 mmoles) and
potassium (0.50 g; 0.013 g.atom) in tetrahydrofuran
(25 ml.) and bromomanganese pentacarbonyl (3.01 g; 11 mmoles
in the same solvent (50 ml.) on reaction (B) for 4-5 hr.
gave on elution with ligroin and ether dimanganese deca-
carbonyl (0.99 g.) and tricarbonyl-π-2-acetylpyrrolyl-
manganese (0.086 g; 0.8%) as yellow crystals m.p.
60-70°C decomp.

Infrared peaks MC-O $2041^{cm^{-1}}$ (vs) and $1923^{cm^{-1}}$ (vs).
CH_3C-O $1587^{cm^{-1}}$ (s).

2.   2-Acetylpyrrolyl-potassium prepared (4 hr. room
temperature 28°C) from 2-acetylpyrrole (1.37 g; 12 mmoles)
and potassium (0.35 g; 0.008 g.atom) in tetrahydrofuran
(30 ml.) was stirred with bromomanganese decacarbonyl
(2.4 g; 8 mmoles) in the same solvent (30 ml.) at room
temperature for 3 hr.   Chromatography on neutral alumina
yielded dimanganese decacarbonyl (0.56 g.);   unreacted
pyrrole and a yellow compound (0.095 g.) which decomposed
quickly.

Infrared peaks in C Cl$_4$ MC-O at 2140$^{cm^{-1}}$(m), 2041$^{cm^{-1}}$(vs)
2020$^{cm^{-1}}$(w) and 1941$^{cm^{-1}}$(vs) and CH$_3$C-O at 1640$^{cm^{-1}}$(s)
show that this product is probably pentacarbonyl- N -
(2-acetylpyrrolyl)-manganese.

REACTION OF 2-FORMYLPYRROLYL POTASSIUM WITH BROMO-
MANGANESE PENTACARBONYL

2-Formylpyrrolyl-potassium prepared (3 hr. room
temperature) from 2-formylpyrrole (0.97 g; 10 mmoles)
and potassium (0.22 g; 0.005 g.atom) in tetrahydrofuran
(30 ml.) was stirred with bromomanganese pentacarbonyl
(2.6 g; 40 mmol) in the same solvent (40 ml.) for 4 hr.

Chromatography on silica gave dimanganese decacarbonyl
(0.70 g.) and an impure and unstable yellow product (0.21 g.)
the infrared spectrum of this product shows $MC-O$ $2020^{cm^{-1}}$ (vs)
and $1923^{cm^{-1}}$ (vs), $HC-O$ $1754^{cm^{-1}}$ (m), $1640^{cm^{-1}}$ (s) and
$1600^{cm^{-1}}$ (s, broad).

REACTION OF PYRAZOLYL-POTASSIUM WITH BROMOMANGANESE PENTACARBONYL

Pyrazolyl-potassium obtained (1 hr. room temperature)
from pyrazole (2.04 g; 25 mmoles) and potassium (0.67 g;
0.018 g.atom) in tetrahydrofuran (30 ml.) and bromo-
manganese pentacarbonyl (3.68 g; 13 mmoles) in the same
solvent (50 ml.) were treated as (B).   Chromatography
gave dimanganese decacarbonyl (0.50) and few milligrams of
a yellow product, which blackened quickly.

REACTION OF 3-METHYLPYRAZOLYL-POTASSIUM WITH BROMO-MANGANESE PENTACARBONYL

3-Methylpyrazolyl-potassium prepared (2 hr. reflux)
from 3-methylpyrazole (2.8 g; 34 mmoles) and potassium
(0.74 g; 0.019 g.atom) in tetrahydrofuran (20 ml.) was

treated (B) with bromomanganese pentacarbonyl (5.36 g; 19 mmoles) in the same solvent (50 ml.) for 8 hr. Chromatography on neutral alumina afforded dimanganese decacarbonyl (0.24 g.); an unidentified gummy unstable product (0.07 g.) and then pyrazolyl complex (0.85 g.) This forms yellow crystals m.p. 138.5-140°C. The product was further purified by sublimation (90-100°C/0.005 mm). Infrared peaks MC-O $2030^{cm^{-1}}$(VS) and $1923^{cm^{-1}}$(VS).

REACTION OF 3,5-DIMETHYLPYRAZOLYL POTASSIUM WITH BROMOMANGANESE PENTACARBONYL

3,5-Dimethylpyrazolyl-potassium obtained (3 hr. room temperature) from 3,5-dimethylpyrazole (1.54 g; 16 mmoles) and potassium (0.54 g; 0.014 g.atom) in tetrahydrofuran (30 ml.) was treated (B) with bromo-manganese pentacarbonyl (4.12 g; 40 ml.) in the same solvent for 5 hr. Chromatography on neutral alumina gave dimanganese decacarbonyl (1.53 g.) and an orange crystalline product (0.66 g.) m.p. 120-124°C decomp. Infrared peaks (CS$_2$) MC-O at $2030^{cm^{-1}}$(VS) and $1923^{cm^{-1}}$(VS).

ATTEMPTED REACTION OF 3-METHYL, 5-PHENYLPYRAZOLYL-POTASSIUM WITH BROMOMANGANESE PENTACARBONYL

Cooled, 3-methyl,5-phenylpyrazolyl-potassium obtained (4 hr. 40-50°C) from 3-methyl,5-phenyl-pyrazole (3.08 g; 16 mmoles) and potassium (0.70 g; 0.017 g.atom) in tetrahydrofuran (30 ml.) and bromo-manganese pentacarbonyl (4.8 g; 17 mmoles) in the same solvent (50 ml.) on similar reaction (B) for 4 hr. gave on chromatography only dimanganese decacarbonyl (1.82 g.), while the pyrazole spread all over the column.

REACTION OF BENZOTRIAZOLE WITH DIMANGANESE DECACARBONYL

Benzotriazole (1.49 g; 12 mmoles) and dimanganese decacarbonyl (2.55 g; 6.5 mmoles) were treated under the conditions (A). On elution with ligroin, benzene and methanol, dimanganese decacarbonyl (0.55 g.), unchanged benzotriazole and a yellow compound (0.852 g.) were successively obtained. The yellow compound when crystallised from dichloromethane and petrol afforded a product m.p. 42-43°C.

Infrared peaks MC-O at $2041^{cm^{-1}}$ (vs) and $1940^{cm^{-1}}$ (vs).

REACTION OF BENZOTRIAZOLYL-POTASSIUM WITH BROMO-
MANGANESE PENTACARBONYL

Benzotriazolyl-potassium obtained (3 hr. room
temperature) from benzotriazole (0.83 g; 7 mmoles)
and potassium (0.28 g; 7 mmoles) in tetrahydrofuran
(30 ml.) and bromomanganese pentacarbonyl (3.5 g;
13 mmoles) in the same solvent (40 ml.) on treatment
(B) for 3 hr. and subsequent chromatography gave
dimanganese decacarbonyl (0.25 g.), benzotriazole and
a yellow compound on eluting the column with petrol,
benzene and methanol.   The yellow compound was
rechromatographed and crystallised from tetrahydrofuran
and petrol to give the product m.p. 42-43°C, obtained
in the preceding experiment.
Infrared peaks MC-O at $2041^{cm^{-1}}$ (VS) and $1942^{cm^{-1}}$ (VS).

REACTION 1,2,4-TRIAZOLYL-POTASSIUM WITH BROMO-
MANGANESE CARBONYL

1,2,4-Triazolyl-potassium prepared (2 hr. room
temperature) from 1,2,4-triazole (1.50 g; 22 mmoles)
and potassium (0.30 g; 0.008 g.atom) in tetrahydrofuran

(30 ml.) on treatment (B) with bromomanganese penta-
carbonyl (3.0 g; 11 mmoles) in the same solvent (40 ml.)
gave on chromatography, dimanganese decacarbonyl (0.63 g.)
the triazole and a yellow solid (38 mg with acetone),
which decomposed quickly.

Infrared peaks MC-O 2041$^{cm^{-1}}$(VS) and 1923$^{cm^{-1}}$(VS).

ATTEMPTED REACTION OF TETRAIODOPYRROLE WITH DIMANGANESE

DECACARBONYL

Tetraiodopyrrole (1.63 g;) and dimanganese deca-
carbonyl (1.0 g.) in ethyleneglycoldiethyl ether (50 ml.)
on treatment (A) gave a black residue, from which only
dimanganese decacarbonyl (0.26 g.) was recovered on
chromatography.

REACTION OF IRON-TETRACARBONYL DIIODIDE WITH PYRROLYL-

POTASSIUM

Iron pentacarbonyl (1.5 cc) and iodine (2.66 g.)
were stirred at 0°C in ether for 2 hr. to form iron
tetracarbonyl-diiodide.   Pyrrolyl-potassium (1.35 g.)
in tetrahydrofuran (30 ml.) was added and the mixture

was stirred for another 2 hrs. at low temperature. The
residue, obtained after removal of solvent in vacuo, on
chromatography yielded a few milligrams of a yellow
compound (ether elution), which decomposed quickly.

ATTEMPTED REACTION OF PYRROLE WITH MOLYBDENUM CARBONYL

A mixture of pyrrole (5.36 g; 80 mmoles) and
molybdenum carbonyl (5.28 g; 20 mmoles) in diethylene-
glycol dimethyl ether (50 ml.) was refluxed (16 hr.).
After cooling and filtering (kieselguhr), the yellow
filtrate turned black on exposure to air. Removal of
the solvent and subsequent sublimation of the residue
gave molybdenum hexacarbonyl (1.96 g.)

REACTION OF PYRROLYL-POTASSIUM WITH MOLYBDENUM
HEXACARBONYL

Molybdenum carbonyl (5.28 g; 20 mmoles) and pyrrolyl-
potassium (obtained from pyrrole (2.97 g; 45 mmoles) and
potassium (1.17 g; 0.03 g.atom) in 4 hr. reflux) in
tetrahydrofuran (60 ml.) were stirred at reflux temperature
for 16 hr. The yellow mixture was cooled at -20°C and

acetic acid (2 g; 3 3 mmoles) was added and the mixture
allowed to warm up to room temperature with stirring
(1 hr.).   The solvent was removed in vacuo   and
iodomethane (2.9 g; 20 mmoles) in benzene (75 ml.) was
added.   The reaction mixture was refluxed again for
another 24 hr. during which the contents of the flask
blackened.   The black mass was extracted with dichloro-
methane, solvent removed and on sublimation of the
residue, molybdenum hexacarbonyl (0.27 g.) was obtained.

ATTEMPTED PREPARATION OF BIS (2,5-DIMETHYLPYRROLYL)-IRON

I.   Reaction of ferric-acetyl-acetonate[156] with 2,5 methyl-
pyrrolyl-potassium.

Ferric-acetyl-acetonate (5.24 g; 15 mmoles) and 2,5-
dimethylpyrrolyl-potassium (6.2 g; 46 mmoles) in tetra-
hydrofuran (100 ml.) were refluxed with stirring for 3 hr.
The black residue, after cooling and evaporating solvent
in vacuo on chromatography gave unchanged 2,5-dimethyl-
pyrrole leaving lot of decomposition product on the
column.

II.   Ferrous-acetyl-acetonate (2.04 g; 8 mmoles) and
2,5-dimethylpyrrolyl-potassium (2.1 g; 16 mmoles)
in tetrahydrofuran (50 ml.) under identical conditions
of experiment as described above (I) gave only 2,5-
dimethylpyrrole (0.85 g.)

III.(i) Ferric chloride (1.65 g.) and iron metal (powder;
0.8 g.) in tetrahydrofuran (30 ml.) were refluxed till
the yellow colour disappeared (Ca 4 hr.).   The cooled
solution was stirred with 2,5-dimethylpyrrolyl-potassium
(3.4 g.) at room temperature for 3 hr.   Chromatography
afforded a few milligrams of yellow crystals,
unidentified and very unstable.

(ii) In another similar reaction ferrous chloride
obtained by refluxing ferric chloride with chlorobenzene
failed to react with 2,5-dimethylpyrrolyl-potassium.

ATTEMPTED PREPARATION OF 2,5-DIMETHYLPYRROLYL COBALT

Cobalt (III)-acetyl-acetonate (2.0 g.) and 2,5-
dimethylpyrrolyl-potassium (3.16 g.) in tetrahydrofuran
(60 ml.) were refluxed for 3 hr.   After cooling and
filtering (keiselguhr), the solvent on evaporation
in vacuo gave a brown residue, which was extracted with

dichloromethane and crystallised to give a few milligrams
of a brown compound, (highly unstable) containing cobalt
and nitrogen.

ATTEMPTED PREPARATION OF 2,5-DIMETHYLPYRROLYL-NICKEL
COMPLEXES

I.   Ni(II)acetyl-acetonate (3.06 g.) and 2,5-dimethyl-
pyrrolyl-potassium (4.8 g.) in benzene (50 ml.) were
refluxed for 3 hr.   The black contents of the flask,
after cooling, filtering and evaporating the solvent
in vacuo and subsequent chromatography   gave only
unchanged 2,5-dimethylpyrrole (2.1 g.).

II.   Allyl-nickel-bromide[130] (1.0 g.) and 2,5-dimethyl-
pyrrolyl-potassium in tetrahydrofuran (30 ml.) were
stirred at room temperature.   The black contents of
the flask were filtered, solvent removed in vacuo and
the residual black gum on chromatography gave unchanged
2,5-dimethylpyrrole (0.53 g.)

III.   Tetrapyridonickel dichloride (2.36 g.) and 2,5-
dimethylpyrrolyl-potassium (2.02 g.) in benzene (60 ml.)
were refluxed for 3-4 hr.   The reaction mixture, which

turned red and then black was cooled, filtered and
the solvent evaporated _in vacuo_.   The residue on
chromatography gave unchanged 2,5-dimethylpyrrole
(0.75 g.).

IV.   Nickelocene (2.2 g.) and 2,5-dimethylpyrrolyl-
potassium obtained (3 hr. room temperature) from 2,5-
dimethylpyrrole (2.0 g.) and potassium (0.45 g.) in
tetrahydrofuran (30 ml.) were stirred for 3 hr at
room temperature.   On processing the brown reaction
mixture in the usual manner, only a few milligrams of
nickelocene and pyrrole (0.92 g.) were obtained.

ATTEMPTED REACTION OF 2,5-DIMETHYLPYRROLE WITH IRON
ENNEACARBONYL

2,5-Dimethylpyrrole (6.5 g.) and iron enneacarbonyl
(1.56 g.) were refluxed for 14 hr.   The cooled black
mass on chromatography gave unreacted 2,5-dimethylpyrrole
(3.03 g.).

ATTEMPTED REACTION OF PYRROLYL-POTASSIUM WITH IRON-DODECACARBONYL

Pyrrolyl-potassium prepared (3 hr. room temperature) from pyrrole (3 cc.) and potassium (0.52 g.) in tetrahydrofuran (30 ml.) and iron dodecacarbonyl (2.5 g.) in the same solvent (25 ml.) were stirred at room temperature for 3 hr. during which the mixture turned red. The solvent was evaporated in vacuo and the residue on chromatography gave a few milligrams of iron dodecacarbonyl along with unreacted pyrrole (1.25 g.)

ATTEMPTED REACTION OF PYRROLE WITH IRON CARBONYLS

I.   Pyrrole (40 ml.) and iron pentacarbonyl (30 ml.) were heated at 150°C in an atmosphere of carbondioxide in a rocking autoclave for 20 hr.   The reaction mixture on vacuum distillation at room temperature afforded unreacted iron pentacarbonyl (20 ml.) and then pyrrole (20 ml.) at 40°C.

II.   Pyrrole (15 ml.) and iron dodecacarbonyl (15 g.) under similar conditions as described above and subsequent chromatography gave only unchanged iron-dodecacarbonyl (10.5 g.) and pyrrole (12.2 g.).

ATTEMPTED REACTION OF PYRROLYLPOTASSIUM WITH CROTYL-IRON-TRICARBONYL-CHLORIDE

Pyrrolyl-potassium obtained (3 hr. room temperature) from pyrrole (2.5 cc.) and potassium (0.44 g.) in tetra-hydrofuran (20 ml.) was stirred with crotyl-irontricarbonyl chloride[189] (1.45 g.) in the same solvent (30 ml.) for 1 hr. The colour of the reaction mixture became blue, green and finally brown. The residue, after evaporating solvent in vacuo, on chromatography gave iron dodecacarbonyl (0.19 g.) and pyrrole (1.73 g.).

REACTION OF PYRROLYLPOTASSIUM WITH TRICARBONYL-π-ALLYL-IODO-IRON

Pyrrolylpotassium prepared (5-6 hr. reflux) from pyrrole (3.0 g; 45 mmoles) and potassium (0.62 g; 0.016 g.atom) in benzene (50 ml.) was refluxed with iodo-tricarbonyl-allyl-iron[134] (6.46 g; 21 mmoles) in benzene (50 ml.) for 5 hr. On processing the reaction mixture in the usual way petrol eluted a yellow oil as the principal product (0.65 g.), which distilled (31-31.5°C/10^{-2} mm) affording a mixture of 2:4-Hexadiene complexes (0.21 g.).

Infrared peaks (liquid film) MC-O at $2038^{cm^{-1}}$ (VS) and $1970^{cm^{-1}}$ (VS,). Further elution with the same solvent afforded a red compound (0.130 g.), which sublimes (0.005 mm. at room temperature) and is highly unstable. Infrared (liquid film) MC-O; $2041^{cm^{-1}}$ (VS) and $1961^{cm^{-1}}$ (VS). Benzene-petrol eluted unchanged pyrrole (0.36 g.)

REACTION OF ALLYL-IRON-TRICARBONYL-IODIDE WITH ALLYL-MAGNESIUM CHLORIDE

Allyl-magnesium-chloride[160] obtained (6-7 hr. at 0°C) from allylchloride (4.1g; 53 mmoles) and magnesium (1.32 g; 0.054 g.atom) in ether (30 ml.) was stirred at 0°C with allyl-iron-tricarbonyl-iodide (5.11 g; 16.5 mmoles) for 2 hr. and then refluxed for another 2 hr. The cooled, filtered (kieselguhr) solution was reduced to small bulk (in vacuo). The residue on chromatography yielded a yellow oil (0.50 g; 10%) identical to the one obtained in above experiment. Infrared peaks (liquid film) MC-O $2041^{cm^{-1}}$ (VS) and $1970^{cm^{-1}}$ (VS,b), infrared peaks lit.[137] MC-O $2042^{cm^{-1}}$ (VS) and $1972^{cm^{-1}}$ (VS,b).

(C)

GENERAL METHOD FOR THE PREPARATION OF π-CYCLOPENTA-DIENYL-π-PYRROLYLIRON AND ITS DERIVATIVES

π-CYCLOPENTADIENYL-π-PYRROLYLIRON

Pyrrolylpotassium (cooled) prepared (4 hr. reflux) from pyrrole (1.56 g; 24 mmoles) and potassium (0.76 g; 0.02 g.atom) in benzene (50 ml.) was refluxed with iodo-dicarbonylcyclopentadienyliron (6.0 g; 20 mmoles) in the same solvent (50 ml.) for 3 hr. with stirring. The mixture was cooled and solvent reduced to small bulk _in vacuo._ The residual mass was chromatographed on alumina. Ligroin eluted ferrocene (0.27 g; 7%) identified by its infrared spectrum and m.p. Benzene-petrol (1:1) eluted unreacted iodo-dicarbonylcyclopenta-dienyliron (0.25 g; 3.2%). Elution with ether afforded red crystals of π-cyclopentadienyl-π-pyrrolyliron (1.2 g; 25%) m.p. 113.5-114°C. It sublimes (10^{-2} mm room temperature). Infrared peaks $3080^{cm^{-1}}$ (S); $1109^{cm^{-1}}$ (VS) and $1002^{cm^{-1}}$ (VS). N.M.R. ($C Cl_4$) at τ 4.74(α-H); 5.56(β-H) and 5.85($-C_5H_5$) of relative intensities 2 : 2 : 5.

π-CYCLOPENTADIENYL-π-2,4-DIMETHYLPYRROLYLIRON

2,4-Dimethylpyrrolylpotassium (cooled) obtained
(4 hr. reflux) from 2,4-dimethylpyrrole (1.29g; 11 mmoles)
and potassium (0.38 g; 0.01 g.atom) in benzene (30 ml.)
and iodocarbonyl-cyclopentadienyliron (6.8 g; 22 mmoles)
in the same solvent (45 ml.) were treated for 3-4 hr. as
(c).   Chromatography gave ferrocene (0.050 g) iodo-
dicarbonylcyclopentadienyliron (2.83 g.) and π-cyclopenta-
dienyl-π-2,4-dimethylpyrrolyliron (0.84 g; 20%) a red
liquid, which was purified by vacuum distillation (b.p.80-
82°C/0.5 mm). Infra red peaks (liquid film) 1108$^{cm^{-1}}$(s)
and 1005$^{cm^{-1}}$(s).   N.M.R. (C Cl$_4$)at τ4.87(α-H); 5.63(β-H);
5.93(C_5H_5); 7.8(α-CH$_3$) and 8.03(β-CH$_3$) of relative
intensities 1 : 1 : 5 : 3 : 3.   Found N, 6.3
$C_{11}H_{13}Fe$ N requires N, 6.5%.

π-CYCLOPENTADIENYL-π-2,5-DIMETHYLPYRROLYLIRON

2,5-Dimethylpyrrolylpotassium (cooled) prepared
(4 hr. reflux) from 2,5-dimethylpyrrole (1.97 g; 22 mmoles)
and potassium (0.48 g; 0.012 g.atom) in benzene (30 ml.)
and iododicarbonylcyclopentadienyliron (4.62 g; 15 mmoles)
in the same solvent (30 ml.) were treated under conditions

(C) for 4 hr.   The resulting products were ferrocene.
(0.030 g;), iodocarbonylcyclopentadienyliron (1.4 g.)
and π-cyclopentadienyl-π-2,5-dimethylpyrrolyliron, a
thick red liquid (0.68 g; 32%) which was purified by
sublimation (50°C/10⁻² mm dry cold probe) giving red
stout crystals m.p. 12.5-13.5°C or by distillation
(40.5-41.5°C/6.2 mm); density 1.18/20°C.   Found C, 61.75;
H, 6.1; N, 6.8.   C$_1$H$_{13}$Fe N requires C, 61.4; H, 6.0;
N, 6.5%.   Infrared peaks (liquid film) 1099$^{cm^{-1}}$ (s) and
1005$^{cm^{-1}}$ (s).   N.M.R. (C Cl$_4$) at τ5.79(β-H); 5.94(C$_5$H$_5$);
7.76(α-CH$_3$) of relative intensities 2 : 5 : 6.

π-CYCLOPENTADIENYL-π-2,3,4,5-TETRAMETHYLPYRROLYLIRON

2,3,4,5-Tetramethylpyrrolylpotassium (cooled),
prepared (4 hr. reflux) from 2,3,4,5-tetramethylpyrrole
(1.41 g; 11.5 mmoles) and potassium (0.43 g; 0.011 g.atom)
in benzene (30 ml.), was treated for 3 hr. with iodo-
dicarbonylcyclopentadienyliron (3.68 g; 12 mmoles) in the
same solvent (50 ml.).   This yielded ferrocene (trace);
iododicarbonylcyclopentadienyliron (2.1 g.) and the
π-tetramethylpyrrolyl-π-cyclopentadienyliron, a brown gum

(0.085 g)with the infrared peaks at $1099^{cm^{-1}}$(s) and $1000^{cm^{-1}}$(s).

π-3-ACETYL-2,4-DIMETHYLPYRROLYL-π-CYCLOPENTADIENYL

3-Acetyl-2,4-dimethylpyrrolylpotassium (cooled) prepared (3 hr. reflux) from 3-acetyl-2,4-dimethylpyrrole (2.66 g; 19 mmoles) and potassium (0.51 g; 0.13 g.) in tetrahydrofuran (10 ml. evaporated under a stream of nitrogen) and iododicarbonylcyclopentadienyliron (4.6 g. 13 mmoles) in benzene (75 ml.) were reacted (C) for 4-5 hr. Chromatography afforded ferrocene (trace); unchanged iododicarbonylcyclopentadienyliron (2.35 g.) and a red gummy product, which on sublimation (40°C/10^{-2} mm dry cold probe) gave π-3-acetyl-2,4-dimethylpyrrolyl-π-cyclopentadienyliron (82 mgm; 4%), very unstable in air and light. Infrared spectrum (liquid film) peaks at $1105^{cm^{-1}}$(s) and $1000^{cm^{-1}}$(S). CH_3C-O at $1667^{cm^{-1}}$(S) and $1639^{cm^{-1}}$ (V). N.M.R. at τ 4.78(α-H); 5.95(ς H$_5$); 7.55 (α-CH$_3$ & -COCH$_3$); 7.85(β-CH$_3$) of measured relative intensities 1 : 4.9 : 5.7 : 3.3. required intensities 1 : 5 : 6 : 3.

ACETYLATION OF π-CYCLOPENTADIENYL-π-PYRROLYLIRON

The filtered and cooled Perrier complex [obtained
by shaking acetylchloride (0.8 g; 10 mmoles) with excess
powdered aluminium chloride in dichloromethane (25 ml.)
for 2 hr.] was added dropwise to a stirred and ice-
cooled solution of pyrrolylcyclopentadienyliron (1.2g;
6 mmoles) in the same solvent (25 ml.) over a period of
1 hr. at 0°C.   The mixture was allowed to come to room
temperature.   The organic layer separated, dried over
calcium chloride and filtered.   The solvent was
evaporated in vacuo and, the residue, extracted with
benzene.   Chromatography yielded, the acetylated product,
an unstable yellow gum (0.075 g.) with infrared peaks
(liquid film)(CH$_3$C-O) at 1703$^{cm^{-1}}$(S); 1639$^{cm^{-1}}$(S).

ATTEMPTED AMINOMETHYLATION OF π-CYCLOPENTADIENYL-π-
PYRROLYLIRON

A mixture of cyclopentadienyl-pyrrolyliron (1.87 g.)
methylene bisdimethylamine (1.0 g.); phosphoric acid (1 cc.)
and glacial acetic acid (10 ml.) was heated with stirring
on steam bath for 10 hr.   The mixture was cooled and
poured into water (20 ml.) and extracted with ether, which

removed unchanged cyclopentadienylpyrrolyliron (0.75 g.)
A black precipitate resulted, when the aqueous layer was
made alkaline with sodium hydroxide.

ATTEMPTED ACETYLATION OF TRICARBONYL-π-PYRROLYL-
MANGANESE

Aluminium chloride (2.0 g.) in carbondisulphide
(10 ml.) and acetylchloride (0.6 g.) in the same solvent
(10 ml.) were added alternately to a stirred and ice-
cooled solution of tricarbonylpyrrolylmanganese (1.5 g.)
in the same solvent (25 ml.) over 2 hr.   The mixture was
refluxed for 20 minutes, treated with ice cold HCl and
the carbondisulphide layer separated, dried over calcium
chloride and solvent evaporated _in vacuo_ after filtration.
The red residue on crystallisation from dichloromethane
and petrol gave a few milligrams of the product, which
decomposed quickly.

(D)   DICARBONYL-π-CYCLOPENTADIENYL-N-PYRROLYLIRON

Pyrrolylpotassium (cooled) prepared (5-6 hr. reflux)
from pyrrole (3.2 g; 48 mmoles) and potassium (0.70 g;
0.017 g.atom) in benzene (50 ml.) and iodocarbonylcyclo-

pentadienyliron (6.6 g; 18 mmoles) in the same solvent
(50 ml.) were heated at 50-60°C for 2-3 hrs.   After
cooling and filtering (kieselguhr), the solution was
reduced to a small bulk _in vacuo_ and the residue
chromatographed on _neutral_ alumina.   Ligroin eluted
ferrocene (0.150 g.); benzene-petrol (1:1) eluted
unreacted iododicarbonylcyclopentadienyliron (2.56 g.).
Elution with ether afforded first a brown compound
(0.6 g; 15%) which was rechromatographed to give purer
product (0.30 gm.).   The product could also be purified
by crystallisation from ether at very low temperature,
m.p. 90.5-91°C.   The sublimation (60-70°C/10^{-2} mm.)
yielded brown crystals (140 mgm) of dicarbonyl-π-cyclo-
pentadienyl-N-pyrrolyliron m.p. 91.0°C.

Found N, 5.8, 5.6;   C, H_9Fe NO_2 requires N, 5.8%
Infrared peaks C-H $3065^{cm^{-1}}$ (m), MC-O $2020^{cm^{-1}}$ (vs),
$1975^{cm^{-1}}$ (vs) others $1090^{cm^{-1}}$ (s) and $995^{cm^{-1}}$ (w).
N.M.R. at τ 4.0 (α-H); 4.15   (β-H); 5.17(C H_5) of
relative intensities 2 : 2 : 5.   Another fraction eluted
by ether, red crystals (0.97g)was obtained and identified
by its m.p. and infrared spectrum as π-cyclopentadienyl-
π-pyrrolyliron.

CONVERSION OF DICARBONYL-π-CYCLOPENTADIENYL-N-PYRROLYL-IRON INTO π-CYCLOPENTADIENYL-π-PYRROLYLIRON.

Dicarbonyl-π-cyclopentadienyl-N-pyrrolyliron (120 mgm) in benzene (50 ml.) was heated at 90°C-100°C with stirring for one hour.   After cooling, the solution was reduced in bulk *in vacuo*, and chromatographed.   Petrol eluted a trace amount of ferrocene, identified by its yellow colour, benzene-petrol (1:1) eluted red crystals (10 mg.) of tetracarbonyl-dicyclopentadienyl diiron, identified by its m.p. and infrared spectrum.   Elution with ether gave π-cyclopentadienyl-π-pyrrolyliron (56 mgm), which on subsequent sublimation yielded pure sample (38 mgm) identified by its m.p. 113.5°C and infrared spectrum.

DICARBONYL-π-CYCLOPENTADIENYL-N-INDOLYLIRON

Indolylpotassium (cooled) prepared (3 hr. reflux) from indole (5.27 g; 45 mmoles) and potassium (1.26 g; 0.04 g.atom) in tetrahydrofuran (10 ml; evaporated in a stream of nitrogen) and iododicarbonylcyclopentadienyl-iron (8.0 g; 26 mmoles) in benzene (175 ml.) were treated as under (D) for 5-6 hr.   Chromatography gave ferrocene (0.25 g.); unchanged iododicarbonylcyclopenta-

94.

dionyliron (3.87 g.) and ether eluted first, a crimson
compound, crystallising from dichloromethane and petrol
at very low temperature; dicarbonyl-π-cyclopentadienyl-
N-indolyliron formed red crystals (1.3 g; 31.5%) m.p.
114-114.5°C.   Found C, 61.1; H, 4.1; N, 4.8;
$C_{15}H_{11}FeNO_2$ requires C, 61.0; H, 3.8; N, 4.8%.
Infrared peaks C-H at $3065^{cm^{-1}}$ MC-O $2020^{cm^{-1}}$ (vs);
$1975^{cm^{-1}}$ (vs)   others $1090^{cm^{-1}}$ (s); $997^{cm^{-1}}$ (m).   N.M.R. at
$\tau 3.5$ (complex - C_8H_5) and 5.16(C_5H_5) of relative
intensities 6.05 : 5;   required intensities 6 : 5.
Another fraction was obtained as a viscous red oil (200 mgm)
with ether.   Infrared peaks (liquid film) at $1111^{cm^{-1}}$ (s)
and $1005^{cm^{-1}}$ (s).   N.M.R.at $\tau 5.95$ (C_5H_5), considered to be
π-cyclopentadienyl-π-indolyliron.

DICARBONYL-π-CYCLOPENTADIENYL-N-CARBAZOLYLIRON

Carbazolylpotassium (cooled) prepared (4 hr. reflux)
from potassium (0.67 g; 0.017 g.atom) and carbazole
(3.05 g; 18 mmoles) in tetrahydrofuran (10-15 ml.
evaporated under N_2) was treated with iododicarbonylcyclo-
pentadienyliron (4.88 g; 16 mmoles) in benzene (100 ml.)

for 5 hr. as (D).   On chromatography ferrocene (0.22 g.);
unchanged iodide (1.07 g.) and dicarbonyl-π-cyclopenta-
dienyl-N-carbazolyliron (1.08 g. 25%) red crystals m.p.
150-155°C (decomposed) were obtained.   Found C,65.9;
H, 3.9; N,4.4; $C_{19}H_{13}FeNO_2$ requires C, 66.3; H, 3.8;
N, 4.1%.   Infrared peaks MC-O at $2030^{cm^{-1}}$ (VS) and
$1978^{cm^{-1}}$ (VS).   N.M.R.at τ 2—3 (complex); 4.95(C_5H_5) of
relative intensities 2 : 6 : 5.

DICARBONYL-π-CYCLOPENTADIENYL-N-TETRAHYDROCARBAZOLYLIRON

Tetrahydrocarbazolylpotassium (cooled) obtained
(5 hr. reflux) from tetrahydrocarbazole (3.42 g; 20 mmoles)
and potassium (0.71 g; 0.018 g.atom) in tetrahydrofuran
(10-15 ml. evaporated afterwards) was treated with iodo-
dicarbonylcyclopentadienyliron (6.72 g; 25 mmoles) in
benzene (175 ml.) at 60-70°C for 5 hr. (D).   Chromatography
afforded ferrocene (0.250 g.); unchanged iodide (4.32 g.)
and dicarbonyl-π-cyclopentadienyl-N-tetrahydrocarbazolyl-
iron (0.38 g; 19%; by elution with petrol-benzene (1:1),
rechromatographed and crystallised from ether at very low
temperature) red crystals m.p. 150°C decomp.   Found C, 66.0
H, 5.3; N, 4.2; $C_{19}H_{17}FeNO_2$ requires C, 65.7;   H, 4.9;
N, 4.0%.

Infrared peaks MC-O at $2020^{cm^{-1}}$ (VS) and $1985^{cm^{-1}}$ (VS,broad) N.M.R.at τ4.98 (5 H$_5$).

π-CYCLOPENTADIENYL-π-TETRAHYDROCARBAZOLYLIRON

Tetrahydrocarbazolylpotassium obtained from tetrahydrocarbazole (4.75 g; 28 mmoles) and potassium (0.80 g; 0.02 g.atom) was treated with the iodide (7.2 g; 20 mmoles) in benzene (150 ml.) exactly under the same conditions as above but at higher temperature. This gave ferrocene (0.34 g.); iodide (4.52 g.) and the product (0.23 g; eluted with ether), a yellow brown gum, which sublimed (80-90°C/0.01 mm) to give highly unstable brown crystals. Infrared peaks 1108$^{cm^{-1}}$(s) and 1005$^{cm^{-1}}$(s).

REACTION OF 2-ACETYLPYRROLYLPOTASSIUM WITH IODO-
DICARBONYLCYCLOPENTADIENYLIRON

Cooled 2-acetylpyrrolylpotassium prepared (5 hr. reflux) from 2-acetylpyrrole (1.3 g; 12 mmoles) and potassium (0.37 g; 0.10 g.atom) in benzene (30 ml.) was treated with iododicarbonylcyclopentadienyliron (3.22 g; 10 mmoles) at 50-60°C for 3 hr. On chromatography ferrocene (0.15 g.); iodide (1.54 g.); 2-acetylpyrrole

(0.45 g.) and the <u>yellow product</u> (0.43 g; 28%)
purified by rechromatography and sublimation (80-90°C/
10^{-2} mm), yellow crystals m.p. 110-111°C.
Found C, 54.5; H, 4.0; N, 4.6; $C_3 H_1$ Fe NO requires
C, 54.8; H, 3.9; N, 4.9%. Infrared peaks MC-O at
$2020^{cm^{-1}}$ (vs) and $1990^{cm^{-1}}$ (vs). CH_3C-O $1575^{cm^{-1}}$ (s).
N.M.R. peaks at τ 3.15(α-H); 3.45(β-H); 3.95(β-H);
5.25($C_5 H_5$) and 7.89(-COCH$_3$) of relative measured intensities
3 : 4.9 : 3; required intensities 3 : 5 : 3.

ATTEMPTED REACTION 2-FORMYLPYRROLYLPOTASSIUM WITH IODO-
DICARBONYLCYCLOPENTADIENYLIRON

2-Formylpyrrolylpotassium (cooled) obtained (2 hr.
room temperature) from 2-formylpyrrole (2.1 g; 22 mmoles)
and potassium (0.52 g; 0.013 g.atom) in tetrahydrofuran
(10-15 ml. evaporated afterwards) was warmed with iodo-
dicarbonylcyclopentadienyliron (4.3 g; 14 mmoles) in
benzene (75 ml.) at 50-60°C for 5 hr. (D). Chromatography
gave ferrocene (12 mg.); unchanged iodide (1.76 g.) and
a very unstable, unidentified brown product (0.060 g.)
which could not be handled.

REACTION OF 2-METHYLINDOLYLPOTASSIUM WITH IODO-

DICARBONYLCYCLOPENTADIENYLIRON

2-Methylindolylpotassium (cooled) obtained (2 hr. reflux) from 2-methylindole (2.1 g; 18 mmoles) and potassium (0.38 g; 0.01 g.atom) in benzene (30 ml.) on treatment with iododicarbonylcyclopentadienyliron (4.2 g. 14 mmoles) in the same solvent (50 ml.) for 4 hr. (c) and subsequent chromatography gave ferrocene (0.25 g.) unchanged iodide (2.1 g.) and a brown gummy product (0.125 g.) which could not be further purified. The infrared spectrum shows peaks at 1108 cm^{-1} (s) and 1003 cm^{-1} (s) as expected in π-cyclopentadienyl-π-2-methylindolyliron.

REACTION OF SODIO-MANGANESEPENTACARBONYL WITH PYRROYL

CHLORIDE

Pyrroylchloride[129] (0.93 g; 8 mmoles) in tetrahydrofuran (15 ml.) was stirred with sodium-manganese pentacarbonyl [prepared from dimanganese decacarbonyl (1.71 g; 11 mmoles) and 20 ml. of approximately 1% sodium amalgam in the same solvent (20 ml.)] for 1 hr. After filtration (kieselguhr) and evaporation of solvent in vacuo the red gum was chromatographed on neutral alumina. Elution with petrol

afforded dimanganese decacarbonyl (0.25 g.) and ether eluted an unstable yellow compound (40 mgm). The infrared spectrum in CCl_4 containing - NH peak at $3362^{cm^{-1}}$ (S); MC-O peaks at $2145^{cm^{-1}}$ (S); $2088^{cm^{-1}}$ (S); $2050^{cm^{-1}}$ (Vw); $2022^{cm^{-1}}$ (VS,) and $1940^{cm^{-1}}$ (VS) and also acylcarbonyl bands at 1754 (VS) and 1683 (VS) shows the formation of <u>g-bonded, pentacarbonylpyrroylmanganese.</u>
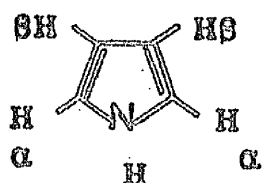
Further elution with methanol afforded another yellow compound (0.14 g.) which was crystallised from ether and ligroin, m.p. 120-130°C decomp. The infrared spectrum (K Cl) containing an NH peak at 3390 (S); MC-O peaks at $2141^{cm^{-1}}$ (S); $2041^{cm^{-1}}$ (VS); $1923^{cm^{-1}}$ (VS,) shows the formation of <u>pentacarbonyl-2-pyrrolylmanganese.</u> Found N, 5.30; 5.50; C_9H_4MnNO requires 5.4%. (Acyl complex $C_{10}H_4MnNO_6$ requires 4.9%).

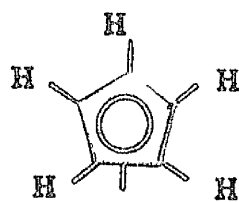# APPENDIX   I

Details of Nouclear Magnetic Resonance Spectra.
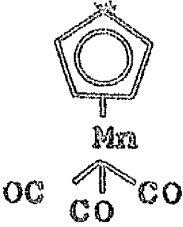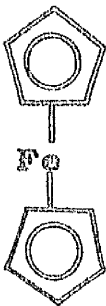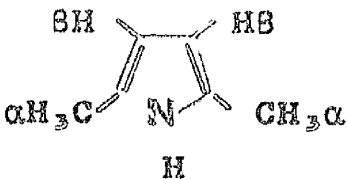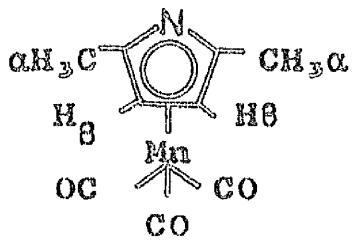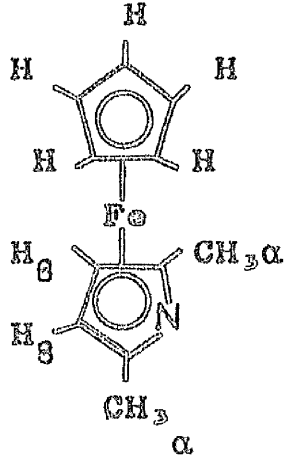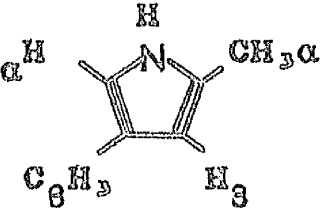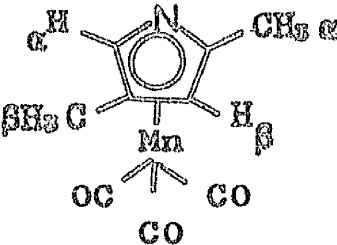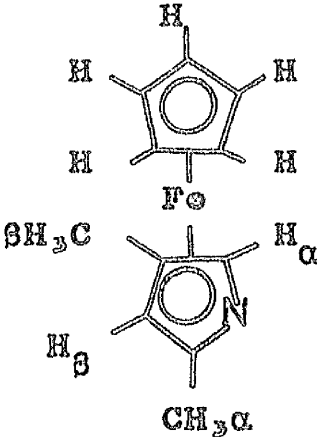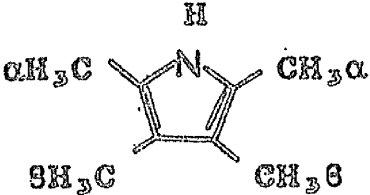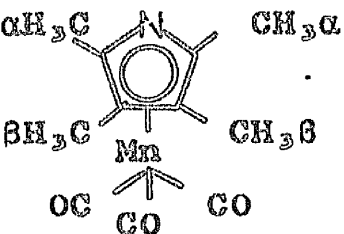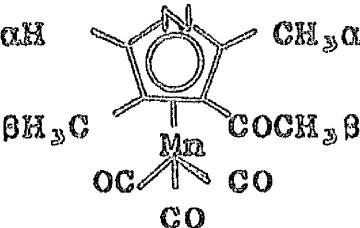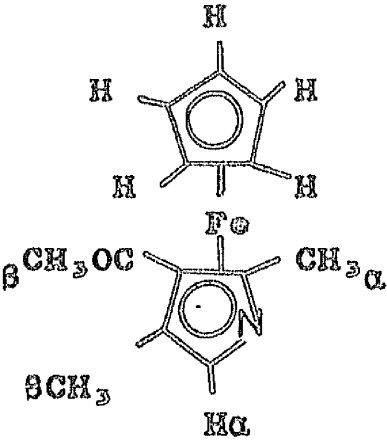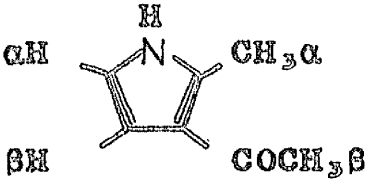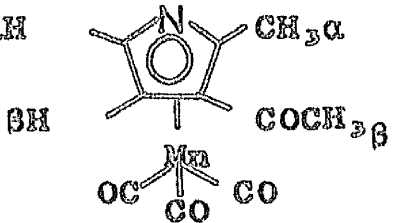
HETEROCYCLE	COMPLEX	τ VALUES	ASSIGNMENT

3.38 (D$\cdot$D) α - protons
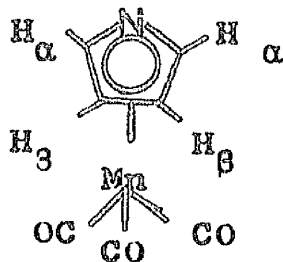
3.72 (D$\cdot$D) β - protons

3.9 (s) α - protons

4.8 (s) β - protons

4.74 (s) α - protons

5.56 (s) β - protons

5.85 (s) - C_5H_5 protons

4.0 (c) α - protons

4.15 (c) β - protons
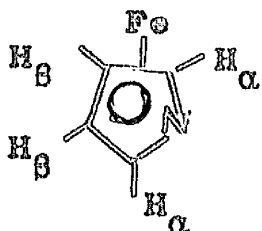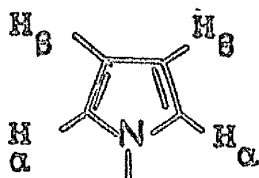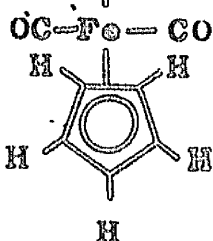
5.17 (s) - C_5H_5 protons

C = complex; d = doublet; m = multiplet; Q = quartet;

and S = singlet, D$\cdot$D = double doublet

HETEROCYCLE	COMPLEX	γ VALUES	ASSIGNMENT

NOTE:

5.17

5.95

4.33 ⎤
4.4 ⎦ (d) β - protons

7.93 (s) α-CH$_3$protons

5.1 (s) β - protons

7.87 (s) α-CH$_3$protons

5.79 (s) β - protons

5.94 (s) -C H$_3$ protons

7.76 (s) α-CH$_3$ protons

HETEROCYCLE	COMPLEX	τ VALUES	ASSIGNMENT
		3.9 (s)	α – protons
		4.42 (s)	β – proton
		7.97 (s)	α & β–CH_3 protons
		4.33 (s)	α – proton
		5.13 (s)	β – proton
		7.85 (s)	α–CH_3 protons
		8.03 (s)	β–CH_3 protons
		4.87 (s)	α – proton
		5.63 (s)	β – proton
		5.93 (s)	–C_5H_5 protons
		7.8 (s)	α–CH_3 protons
		8.03 (s)	β–CH_3 protons
		7.93 (s)	α–CH_3 protons
		8.1 (s)	β–CH_3 protons

HETEROCYCLE	COMPLEX	τ VALUES	ASSIGNMENT

Structure 1 (HETEROCYCLE): pyrrole ring with N–H; αH, CH₃α, CH₃β, COCH₃β substituents

		3.63 (s)	α – proton
		7.52 (s)	α–CH₃ protons
		7.58 (s)	β–COCH₃ protons
		7.72 (s)	β–CH₃ protons

Structure 2 (COMPLEX): Mn(CO)₃ complex; αH, CH₃α, βH₃C, COCH₃β substituents, OC, CO, CO

		4.28 (s)	α – proton
		6.63 (s)	α–CH₃ & β–COCH₃ protons
		7.85 (s)	β–CH₃ Protons

Structure 3 (COMPLEX): ferrocene-type complex, cyclopentadienyl ring (H's) over Fe over pyrrole ring with βCH₃OC, CH₃α, βCH₃, Hα

		4.78 (s)	α – protons
		5.95 (s)	–C₅H₅ protons
		7.55 (s)	α–CH₃ & β–COCH₃ protons
		7.85 (s)	β–CH₃ protons

Structure 4 (HETEROCYCLE): pyrrole ring with N–H; αH, CH₃α, βH, COCH₃β substituents

		3.45 (c)	α & β protons
		7.45 (s)	α–CH₃ protons
		7.58 (s)	β–COCH₃ protons

Structure 5 (COMPLEX): Mn(CO)₃ complex; αH, CH₃α, βH, COCH₃β substituents, OC, CO, CO

		4.1 (d)	α–proton
		4.46 (d)	β–proton
		7.58 (s)	β–COCH₃ protons
		7.72 (s)	α–COCH₃ protons

HETEROCYCLE	COMPLEX	Υ VALUES	ASSIGNMENT

		2.6 (m)	$-C_5H_5$ protons
		4.5 (s)	β - proton
		7.78 (s)	$\alpha-CH_3$ protons

complex
5.97 (s) $-C_5H_5$ protons

2.8 -
3.8 (c)

5.16 (s) $-C_5H_5$ protons

%—Abundance

100 90 80 70 60 50 40 30 20 10

m/e

50

56

79

94

100

121

149

164

187

229

257

286

150

200

230

250

923.
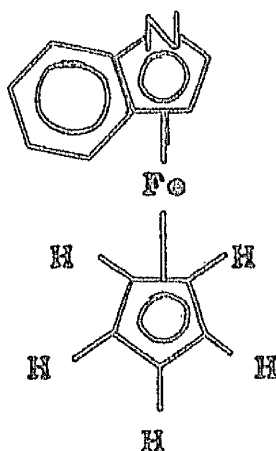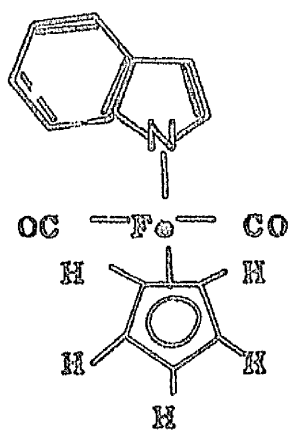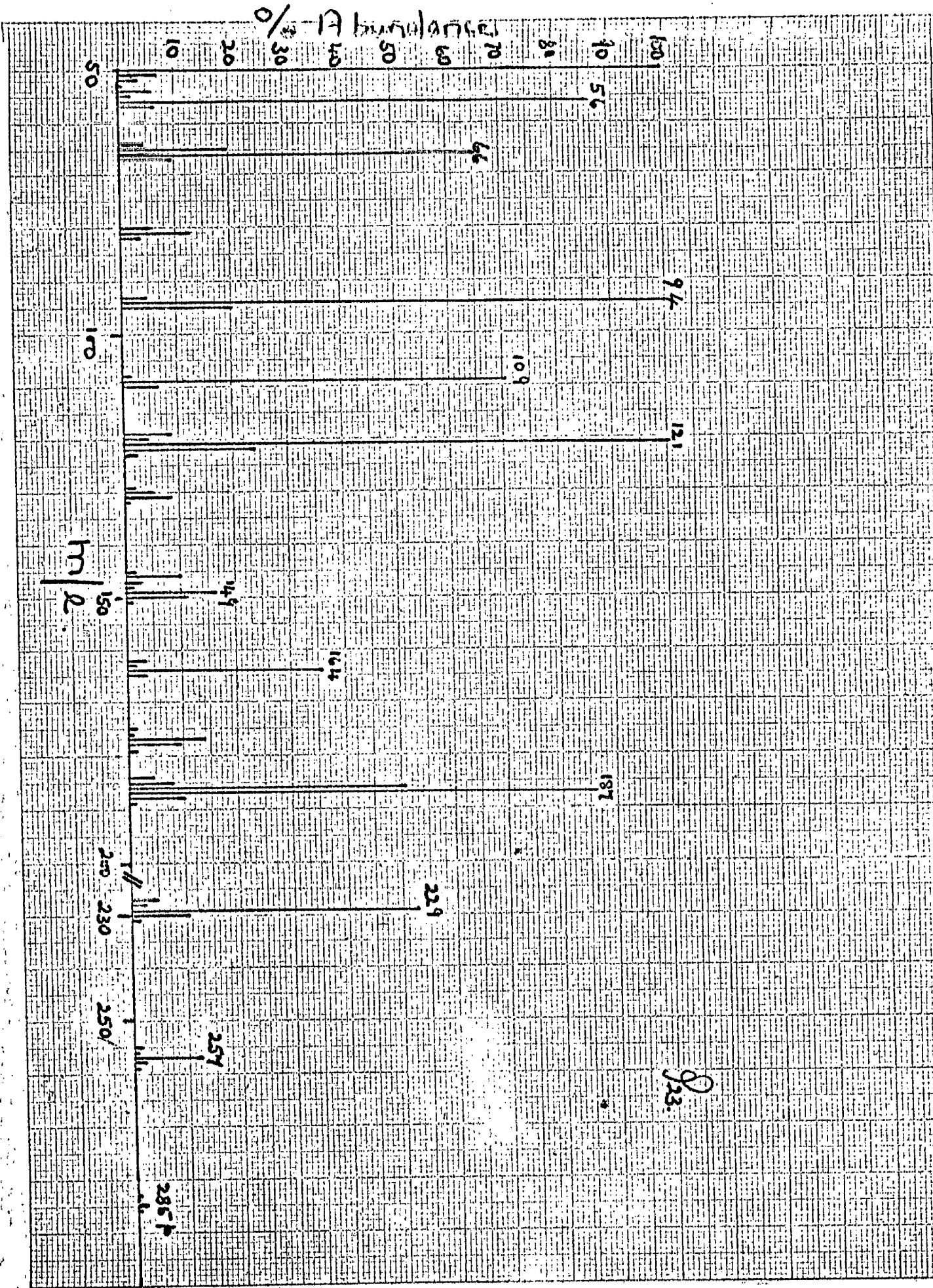
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SOME IRON AND MANGANESE COMPLEXES OF HETEROCYCLES

S U M M A R Y

The study describes the various attempts, which have been made to synthesize heterocyclic derivatives of transition metals, e.g. iron and manganese, in which the heterocycle is bonded to the metal in an analogous manner to the bonding in π - cyclopentadienyl - metal compounds.

The π - pyrrolyl manganese carbonyl complexes were prepared by one or both of the following methods. In the first the pyrrole or substituted pyrrole was heated with dimanganese decacarbonyl in an inert solvent. In the second method, the potassium salt of the heterocycle was heated with bromomanganese pentacarbonyl. The latter method was found to be more widely applicable and was extended to the preparation of such complexes from pyrroles bearing functional groups, to indoles, pyrazoles and benzotriazole. In some of these cases σ - heterocycle manganese pentacarbonyl could be isolated as the first product.

Similarly the potassium salt of heterocycles containing one nitrogen, on reaction with iodo - dicarbonyl-cyclopentadienyl-iron gave σ - complexes, i.e. dicarbonyl - π - cyclopentadienyl - σ - heterocycle iron. These σ - bonded complexes by loss of carbon monoxide

yielded aza-ferrocenes, i.e. π - cyclopentadienyl - π - heterocycle iron at higher temperature.

Attempts to effect electrophilic substitution of the two parent complexes, i.e. tricarbonyl - π - pyrrolyl manganese and π - cyclopentadienyl - π - pyrrolyl iron were made in order to prepare heterocyclic metal complexes with functional groups. Friedel and Crafts Acylation appeared to give a trace of acylated products, while attempted aminomethylation resulted in decomposition.

The reaction of pyrroyl chloride with sodiomanganese pentacarbonyl resulted in the formation of the σ - bonded complex, 2 - pyrrolyl manganese pentacarbonyl via pyrroyl manganese pentacarbonyl by loss of carbon monoxide. Allyl-iron-tricarbonyl-iodide on reaction with pyrrolyl potassium gave 2 : 4 Hexadiene tricarbonyl iron. Unsuccessful attempts have been made to prepare dipyrrolyl analogous of ferrocene, cobaltocene and nickelocene. The reaction between molybdenum hexacarbonyl and pyrrolyl potassium resulted in decomposition.