

METAL COMPLEXES OF HETEROCYCLES

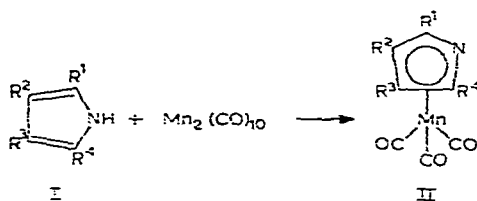
I. THE PREPARATION OF PYRROLYL MANGANESE AND IRON DERIVATIVES

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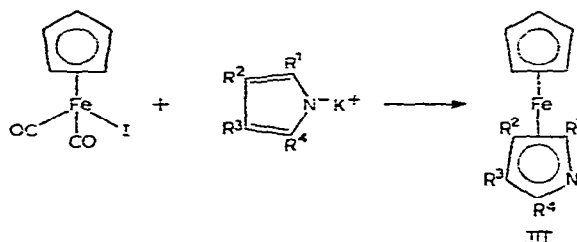
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Although thiophene¹ and methylpyridine² analogues of benzenechromium tricarbonyl were described not long after this benzene complex, heterocyclic analogues of the cyclopentadienyl-metal complexes have proved more elusive. The first example, the preparation of pyrrolylmanganese tricarbonyl (IIa) from dimanganese decacarbonyl and pyrrole (Ia) was described in our preliminary communication³. We now describe the extension of this reaction to a series of alkyl derivatives (*Method I*).

(a) $R^1 = R^2 = R^3 = R^4 = H$ (b) $R^1 = CH_3; R^2 = R^3 = R^4 = H$ (c) $R^1 = R^3 = CH_3; R^2 = R^4 = H$ (d) $R^1 = R^4 = CH_2; R^2 = R^3 = H$ (e) $R^1 = R^2 = R^3 = R^4 = CH_3$

The same compounds (II) have also been obtained by the reaction of bromomanganese pentacarbonyl, $BrMn(CO)_5$ with the potassium salt of the appropriate pyrrole (*Method II*). Moreover it has proved possible to extend this reaction to dicarbonylcyclopentadienyliron iodide which reacts with pyrrolylpotassium to yield azaferrocene (IIIa).

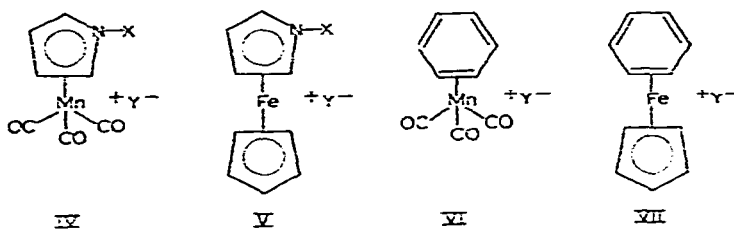


The compounds (IIa) and (IIIa) are distinctly less stable than their cyclopentadienyl analogues. Their melting points are considerably lower, but in most other respects (*e.g.* colour, solubility, IR spectra) the resemblance in physical properties is remarkably close (*cf.* Table 3). Preliminary X-ray study⁴ of a crystal of azaferrocene

(IIIa) 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.

Attempts have been made to measure the basicities of the unsubstituted compounds potentiometrically. The value found for azaferrocene in aqueous ethanol ($pK = 4.5$) is closely similar to that for quinoline (4.65) under identical conditions. The manganese compound was too weakly basic to obtain more than a crude estimate (1.6) under the same conditions. The sharp difference must be attributed to the strong electron-withdrawing effect of the carbonyl groups in (IIa).

In accord with these basicities all the compounds (II and III) dissolve readily in dilute aqueous acids. Azaferrocene (IIIa) affords a crystalline picrate [V ; $X = H$; $Y = C_6H_2(NO_2)_3O^-$] and reacts with methyl iodide to give a rather unstable salt,



presumably (V ; $X = Me$; $Y = I$). The less basic manganese complex (IIa) appears unaffected by methyl iodide under mild conditions. The corresponding metho-salt (IV ; $X = Me$; $Y = I$) is, however, obtained from halomanganese pentacarbonyl on reaction with *N*-methylpyrrole in the presence of aluminium chloride. This reaction is modelled on the preparation⁵ of benzenemanganese tricarbonyl salts (VI). Indeed the salts (IV and V ; $R = H$ or Me) are related to the latter (VI) and to the similarly prepared benzenecyclopentadienyliron salts (VII) by replacement of benzene by pyrrole *viz.* *N*-methylpyrrole respectively.

Solutions of azaferrocene in dilute nitric acid or in other acids to which oxidising agents have been added only slowly undergo a colour change reminiscent of that undergone by ferrocene on oxidation to ferricinium salts. Less ready oxidation is, of course, in harmony with the presence of the molecule as a positive ion in these solutions. We have so far failed to effect electrophilic substitutions of azaferrocene. Here again deactivation is expected to result from salt (V) formation in the systems studied. Even the neutral molecule (IIIa) is probably much less reactive than ferrocene, to which it bears the same formal relation as pyridine does to benzene.

EXPERIMENTAL

All preparations were carried out under nitrogen. Alumina used for chromatography was Spence's Gade H, deactivated by 3–4 h exposure to the atmosphere. Melting points are uncorrected.

Preparations

These are summarized in Table I and follow the methods:

TABLE I

| | | <i>R</i> | mmoles | <i>R</i> | mmoles | Solvent* | (ml) | Reaction time (h) | Product | Yield** |
|-------------------|------|----------|--------|-------------------|--------|----------|------|-------------------|---------|---------|
| | | <i>R</i> | mmoles | <i>R</i> | mmoles | | | | | g % |
| (a) Method I | | | | | | | | | | |
| Pyrrole | | | | $Mn_2(CO)_{10}$ | | | | | | |
| (Ia) | 11 | 130 | 3.9 | 10 | L | 45 | 14 | (IIa) | 1.4 | 66 |
| (Ib) | 4.9 | 60 | 0.97 | 2.5 | E | 20 | 12 | (IIb) | 0.064 | 12 |
| (Id) | 9.35 | 100 | 1.34 | 4 | L | 100 | 16 | (IIc) | 0.74 | (crude) |
| (b) Method II | | | | | | | | | | |
| K salt of Pyrrole | | | | $BrMn(CO)_5$ | | | | | | |
| (Ia) | 2.1 | 20 | 2.75 | 10 | T | 20 + 40 | 4 | (IIa) | 0.18 | 9 |
| (Ic) | 1.14 | 9 | 3.6 | 13 | T | 30 + 30 | 3-4 | (IIc) | | 15 |
| (Id) | 1.77 | 13 | 2.02 | 11 | T | 30 + 30 | 4 | (IIc) | 0.16 | 12 |
| (Ic) | 2.2 | 13 | 3.6 | 14 | T | 30 + 40 | 3-4 | (IIc) | 0.41 | 12 |
| (c) Azafereocenes | | | | | | | | | | |
| K salt of Pyrrole | | | | $C_6H_6Fe(CO)_2I$ | | | | | | |
| (Ia) | 1.05 | 10 | 3 | 10 | B | 30 + 30 | 3 | (IIa) | 0.41 | 22 |
| (Ic) | 1.04 | 8 | 6.8 | 2.2 | B | 30 + 45 | 3-4 | (IIc) | 0.84 | 20 |
| (Id) | 1.97 | 15 | 4.62 | 15 | B | 30 + 30 | 3-4 | (IIc) | 0.68 | 32 |

* B = benzene; E = ethylene glycol diethyl ether; L = ligroin, b.p. 100-120°; T = tetrahydrofuran.
 ** Percentage yields are based on unrecovered carbonyl or halocarbonyl.

TABLE 2
ANALYSES

| Compound | m.p. or b.p. | Found % | | | Required % | | |
|----------|-------------------|---------|-----|------|------------|-----|-----|
| | | C | H | N | C | H | N |
| (IIa) | 41° | 41.0 | 1.8 | 6.7 | 41.0 | 2.0 | 6.8 |
| (IIc) | 45-50°/0.05 mm | 46.5 | 3.8 | 6.1 | 46.4 | 3.4 | 6.0 |
| (IIc) | 25.5-26° | 46.0 | 3.5 | 5.95 | 46.4 | 3.4 | 6.0 |
| (IIe) | 35-36° | 50.4 | 4.5 | 5.5 | 50.6 | 5.6 | 5.4 |
| (IIIa) | 112° | 57.7 | 5.0 | 7.4 | 57.8 | 4.9 | 7.4 |
| (IIIc) | 80-82°/0.5 mm | | | 6.3 | 61.4 | 6.0 | 6.5 |
| (IIIc) | 12-13° | | | | | | |
| (IIIc) | 59.5-61.5°/3.5 mm | 61.75 | 6.1 | 6.8 | 61.4 | 6.0 | 6.5 |

I. The pyrrole and manganese carbonyl were refluxed in the solvent and for the time specified in the table. The solvent was then removed *in vacuo*, the residue dissolved in ligroin and chromatographed on alumina to separate unchanged carbonyl from the product. The latter was purified by crystallisation from pentane (compound IIa), vacuum sublimation (IIa, IIb, IIc, IIe, IIIa, IIIc) or vacuum distillation (IIe, IIIc).

II. To potassium suspended under the solvent specified, a 10-20% excess of the pyrrole was added and the mixture was refluxed until all potassium had reacted (4-6 h). After cooling, the halocarbonyl was added in the second quantity of solvent and the mixture was refluxed for the specified time. The products were worked up as specified under I above.

TABLE 3
COMPARISON OF IR SPECTRA

| $(C_5H_5)_2Mn(CO)_3$ | $(C_4H_4N)_2Mn(CO)_3$ |
|----------------------|-----------------------|
| 4115 w | 4050 w |
| 4032 m | 3960 m |
| 3908 m | 3890 m |
| 3145 s | 3090 s |
| 2451 s | 2450 s |
| 2353 m | |
| 2023 vs | 2002 vs |
| 1979 vs | 1980 vs |
| 1431 s | 1412 s |
| 1362 s | 1360 s |
| | 1272 m |
| | 1195 m |
| 1114 m | 1117 m |
| 1059 m | 1074 s |
| 1013 s | |
| 1005 s | 1010 s |
| 955 m | 910 m |
| 844 s | 805 s |
| 835 s | 845 s |
| 664 s | 666 s |
| | 650 m |
| 630 s | 630 s |
| 542 s | 533 s |

IR spectra: The principal peaks of azaferrocene (IIIa) occur at 3940 (w), 3080 (s), 1745 (w), 1715 (m), 1700 (m), 1660 (m), 1640 (m), 1409 (m), 1386 (m), 1342 (m), 1265 (m), 1185 (s), 1109 (s), 1062 (m), 1002 (s), 855 (m), 816 (s).

The principal peaks of tricarbonylpyrrolylmanganese (Ia) are compared with those of tricarbonylcyclopentadienylmanganese in table 3.

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SUMMARY

Pyrrrole and its alkyl derivatives react with manganese carbonyl giving (alkyl) pyrrolylmanganese tricarbonyls. These products are also accessible from bromomanganese pentacarbonyl and potassium salts of the pyrroles. The latter react similarly with dicarbonylcyclopentadienyliron iodide to give azaferrocenes.

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