# ORGANOMETALLIC STUDIES

## IX*. THE HALOGEN DERIVATIVES OF CYCLOPENTADIENYLMANGANESE TRICARBONYL**

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Attempts to halogenate ferrocene directly have so far led to oxidative rupture of the ring–metal bond[1] or to the formation of halogen-containing complexes[3]. Similar results have been observed[4] in the attempted direct halogenation of cyclopentadienylmanganese tricarbonyl.

However, whereas halogenated ferrocenes have been accessible for several years now by indirect routes via mercurated ferrocenes[3] or ferroceneboronic acids[5] it was only a short time ago that a halogen derivative of cyclopentadienylmanganese tricarbonyl, namely the iodo compound, was synthesized via a mercurated intermediate[6]. The availability of aminocyclopentadienylmanganese tricarbonyl[7] prompted us to attempt using this compound as starting material for the synthesis of the halogen derivatives of cyclopentadienylmanganese tricarbonyl.

In contrast to aminoferrocene which has been reported to be destroyed by nitrous acid, no diazonium salt being detectable[8], we have found that aminocyclopentadienylmanganese tricarbonyl, (I), forms diazonium salts, (II), which are stable enough to allow for their isolation. This is achieved by using isoamyl nitrite as nitrosating agent and working in anhydrous conditions. The diazonium salts, (II), appear to be practically insoluble in anhydrous ether and in this manner they can be precipitated out of the alcohol solution of the reaction mixture. The diazonium salt of aminocyclopentadienylmanganese tricarbonyl reacts smoothly with an aqueous solution of potassium iodide to form iodocyclopentadienylmanganese tricarbonyl; however, upon reacting the diazonium salt (II) with cuprous chloride or cuprous bromide under the usual Sandmayer conditions, the major reaction product was the unsubstituted cyclopentadienylmanganese tricarbonyl (IV), only traces of the expected chloro or bromo derivatives having been formed. This result was not wholly unexpected since aminocyclopentadienylmanganese tricarbonyl had been shown to be a rather weak base[7] due to the electron-withdrawing properties of the $Mn(CO)_3$ group. Electron-withdrawing groups are known to promote the replacement of the diazonium group by hydrogen[9]; moreover it has been reported[10] that the Sandmayer reaction has proved to be unsatisfactory for the preparation of chloro- and bromo-

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* Part VIII, see ref. 7.

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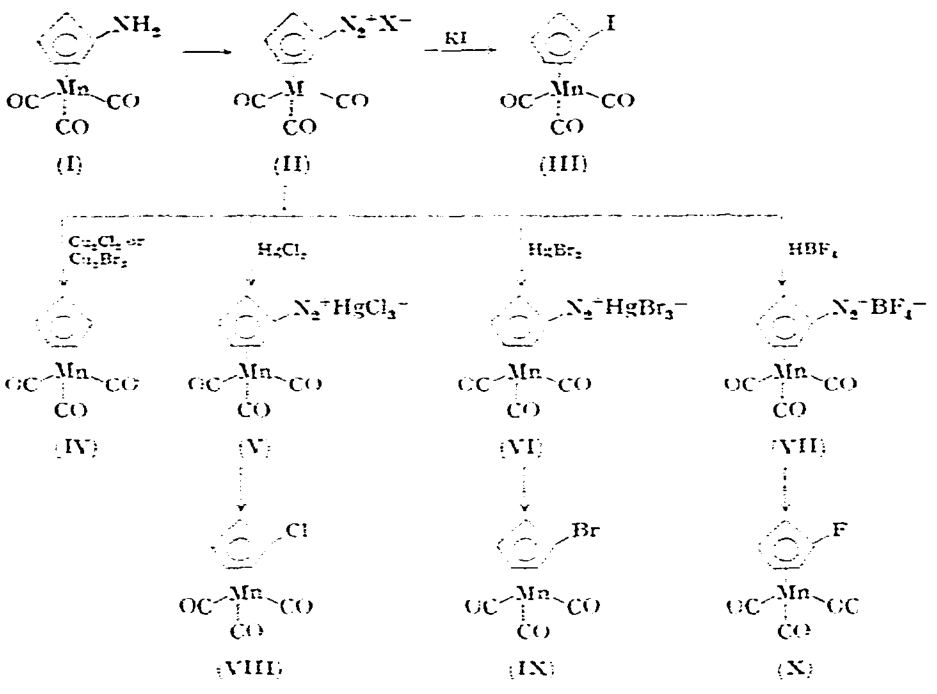
phenanthrenes from the diazonium salts of the weakly basic aminophenanthrenes. These latter halides were obtained by using the procedure of Schwechten[11] which involves the intermediate formation and subsequent decomposition of a complex formed by interaction of the diazonium salt and mercuric halide and potassium halide. By a slight modification of the above procedure as described by Bachmann[10] we were able to prepare chloro- and bromocyclopentadienylmanganese tricarbonyl, (VIII) and (IX) respectively.

The remaining halogen derivative, fluorocyclopentadienylmanganese tricarbonyl, (X), was prepared by the Schiemann reaction[12], which involves decomposition of the diazonium fluoborate salt, (VII).

REACTION SCHEME I



Further reactions of the potentially versatile diazonium salt, (II), are currently being investigated.

All four halogen derivatives of cyclopentadienylmanganese tricarbonyl are yellow-coloured, very volatile and low melting compounds (Table 1). They appear to be quite stable in air at room temperature.

The carbonyl stretching frequencies of cyclopentadienylmanganese tricarbonyl and several of its derivatives, $X{-}C_5H_4Mn(CO)_3$ are compared in Table 1. As can be seen the introduction of an electron-withdrawing group X (X = F, Cl, Br, I, COOH) causes, as expected[13,14], a shift to higher frequencies, as opposed to a lowering of the frequency caused by an electron-donating group ($X = NH_2$)[7]. However there appears to be no effect on the carbonyl frequencies on going down the group from F to I.

The ultraviolet spectra of the halogen derivatives show a bathochromic shift of the MC (metal–carbon) band[15] as compared to the parent compound.

TABLE 1

SOME PHYSICAL CONSTANTS OF $X-C_5H_4Mn(CO)_3$

| *X* | *M.p.* (°*C*) | $\nu_{CO}$[a] (*cm*$^{-1}$) | $\lambda_{max}$ ($\varepsilon$)[b] (*mμ*) |
|---|---|---|---|
| H | 78–79 | 2028 1931 | 327 (1145) |
| F | 49–51 | 2032 1953 | 330 (1240) |
| Cl | 24–25 | 2032 1953 | 332 (1030) |
| Br | 42 | 2034 1953 | 332 (1130) |
| I | 34–35 | 2032 1949 | 333 (1082) |
| $NH_2$ | 77 | 2018 1928 | 324 (1390) |
| COOH | 194–195 | 2037 1956 | 338 (1260) |

[a] Measured on Perkin-Elmer Model 21 spectrophotometer in chloroform solutions with calcium fluoride prism. [b] Measured on Carry Model 14 recording spectrophotometer in ethanol solutions.

## EXPERIMENTAL

### 1) *Iodocyclopentadienylmanganese tricarbonyl*

Freshly distilled isoamyl nitrite (0.3 ml) was added dropwise, with stirring, to a cooled (ice-bath) solution of aminocyclopentadienylmanganese tricarbonyl (0.44 g, 0.002 mole) in 3 ml isopropanol saturated with gaseous hydrochloric acid. After stirring for 10 min, dry ether (15 ml) was added to precipitate the diazonium salt. The liquid phase was removed by decantation and the yellow solid washed twice with 5 ml portions of dry ether. The remaining yellow solid was dissolved in water (1 ml) and the resulting solution was treated with a solution of potassium iodide (0.6 g) dissolved in a minimum amount of water. Evolution of nitrogen gas took place almost immediately and stirring was continued for 10 min at room temperature. This was followed by heating on water bath (~ 60°) for 2 min, cooling and extraction with ether (3 × 30 ml). The ether solution was washed first with an aqueous solution of sodium thiosulphate, then with water, dried ($Na_2SO_4$) and evaporated (vacuum) to dryness to produce 0.47 g of a brown oil which appeared to crystallize on standing. This was chromatographed over silica gel (20 g) and elution with hexane/benzene (1:1) produced 0.16 g of yellow oil. Upon distillation in vacuum (oven temperature 40°/0.02 mm Hg) there were obtained yellow crystals of iodocyclopentadienylmanganese tricarbonyl, m.p. 34–35° (lit.[6] 33–34°). (Found: C, 29.30; H, 1.03; I, 38.42. $C_8H_4IMnO_3$ calcd.: C, 29.13; H, 1.22; I, 38.47%.)

The infrared spectrum (KBr): 2940, 2036, 1941, 1718, 1652, 1626, 1538, 1450, 1418, 1379, 1350, 1145, 1054, 1020, 865, 830 cm$^{-1}$. The ultraviolet spectrum: $\lambda_{max}$ 333 mμ (log $\varepsilon$ 3.03). The NMR spectrum: a multiplet in the region $\tau$ 4.90–5.33

Further elution with benzene yielded 0.19 g of the starting material, aminocyclopentadienylmanganese tricarbonyl.

### 2) *Fluorocyclopentadienylmanganese tricarbonyl*

Aminocyclopentadienylmanganese tricarbonyl (0.33 g) was diazotized following the procedure described in experiment (*1*), up to, and including, dissolving of the solid diazonium salt in 1 ml water. To this solution there were added 4 ml of a solution of fluoboric acid (prepared by dissolving 1 ml of 50 % fluoboric acid, $HBF_4$, in 5 ml water and then making up to a total volume of 10 ml with water) and the solution stirred, with cooling (ice-bath), for 1 h. The precipitated diazonium fluoborate salt was filtered and dried in a vacuum desiccator (over Drierite) to obtain 260 mg of yellow brown powder. This was suspended in 50 ml petroleum ether (100–120°) and warmed slowly in an oil bath. When the temperature reached about 80°, there was observed the evolution of a gas. Heating was continued till reflux and the reaction mixture was maintained at this temperature for 15 min. After cooling and filtration, the filtrate was evaporated in vacuum (water pump) and the residue chromatographed over silica gel (20 g). Elution with hexane/benzene (1:1) produced 88 mg of yellow oily material which was sublimed in vacuum (40°/0.05 mm Hg) to yield the analytical sample of fluorocyclopentadienylmanganese tricarbonyl, m.p. 49.5–51°. (Found: C, 43.37; H, 1.78; Mn, 23.64. $C_8H_4FMnO_3$ calcd.: C, 43.20; H, 1.81; Mn, 24.75 %.)

The infrared spectrum (KBr): 2940, 2020, 1960, 1481, 1379, 1351, 1234, 1058, 1025, 1015, 940, 830 cm$^{-1}$. The ultraviolet spectrum: $\lambda_{max}$ 330 m$\mu$ (log $\varepsilon$ 3.09).

### 3) *Bromocyclopentadienylmanganese tricarbonyl*

To a solution of aminocyclopentadienylmanganese tricarbonyl (0.2 g) in absolute ethanol (2 ml) there were added 0.75 ml of a 30 % solution of hydrobromic acid in acetic acid. After stirring at room temperature for 10 min, the reaction mixture was cooled (ice-bath) and isoamyl nitrite (0.15 ml) was added dropwise. Stirring was continued for another 10 min and after the addition of dry ether (25 ml), followed by decantation of the liquid phase there was obtained as a yellow solid, the diazonium bromide salt. A solution, prepared by dissolving 2 g of potassium bromide in 3 ml water and the addition of solid mercuric bromide until the solution was saturated, was added to the diazonium bromide salt and the mixture was stirred, under cooling (ice-bath) for 1 h. The yellow-brown precipitate was filtered and dried in a vacuum desiccator (over $P_2O_5$) overnight to obtain 1 g of material. This was suspended in 50 ml petroleum ether (100–120°) and heated slowly in an oil-bath. Decomposition was observed to take place at about 70°. Heating was continued till reflux and the reflux maintained for 15 min. After filtration, the organic solvent was evaporated and the residue chromatographed over silica gel (20 g). Elution with hexane produced 55 mg of a yellow oil which upon sublimation (40°/0.1 mm Hg) yielded the analytical sample of bromocyclopentadienylmanganese tricarbonyl, m.p. 42.0–42.2°. (Found: C, 34.11; H, 1.34; Br, 28.14. $C_8H_4BrMnO_3$ calcd.: C, 33.97; H, 1.42; Br, 28.25 %.)

The infrared spectrum (KBr): 2940, 2020, 1930, 1709, 1639, 1422, 1351, 1197, 1152, 1020, 877, 840 cm$^{-1}$. The ultraviolet spectrum: $\lambda_{max}$ 332 m$\mu$ (log $\varepsilon$ 3.01). The NMR spectrum: multiplet between $\tau$ 5.11–5.46.

### 4) *Chlorocyclopentadienylmanganese tricarbonyl*

The diazonium chloride salt of aminocyclopentadienylmanganese tricarbonyl (0.22 g) was prepared as in expt. (*1*), up to, and including, the decantation of the ether washings. The solid salt was then treated with 5 ml of a saturated aqueous solution of mercuric chloride and stirred for 1 h. After decanting the liquid phase, the crystals were dried in a vacuum desiccator (over $P_2O_5$) and then decomposed in petroleum ether (100–120°) and the reaction mixture was worked up as in experiment

(3). Chromatography over silica gel (20 g) and elution with hexane produced 160 mg of a yellow oil which upon sublimation (40°/0.05 mm Hg) yielded the analytical sample of chlorocyclopentadienylmanganese tricarbonyl, m.p. 24–25°. (Found: C, 40.46; H, 1.94; $C_8H_4ClMnO_3$ calcd.: C, 40.29; H, 1.69 %.)

The infrared spectrum (KBr): 2940, 2040, 1960, 1680, 1438, 1388, 1360, 1169, 1020, 892, 840, 800 $cm^{-1}$. The ultraviolet spectrum: $\lambda_{max}$ 332 m$\mu$ (log $\varepsilon$ 3.01). The NMR spectrum multiplet between $\tau$ 5.04–5.41.

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## SUMMARY

The fluoro, chloro, bromo and iodo derivatives of cyclopentadienylmanganese tricarbonyl have been prepared through decomposition of the diazonium salts of aminocyclopentadienylmanganese tricarbonyl.

All four halo derivatives are low-melting, volatile, yellow-coloured compounds.

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