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SYNTHESIS OF A TRIMETALLOCENE DERIVATIVE*[1,2]

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THE recently described[3] ferrocenyl ruthenocenyl ketone prompts us to report some of the results we have obtained in the course of an investigation[1] of the chemistry of cyclopentadienylmanganese tricarbonyl (I) and its derivatives.

Compound (I) reacted with (chloroformylcyclopentadienyl)-manganese tricarbonyl (II) under Friedel-Crafts conditions to yield, after the usual work-up and chromatography over alumina, yellow crystals of di-(cyclopentadienylmanganese tricarbonyl)-ketone (III) (28%) m.p. 145-145.5°. (Found: C, 46.84; H, 2.10; Mn, 24.94. $C_{17}H_{10}O_7Mn_2$ requires: C, 46.81; H, 2.31; Mn, 25.19%). The infra-red spectrum of (III) showed the terminal carbonyl absorption at 2030 and 1948 cm^{-1} as well as a ketonic carbonyl absorption at 1647 cm^{-1}. It is interesting to note that the ketonic carbonyl absorption is lower than that of either diferrocenyl ketone[3] (1612 cm^{-1}) or

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[*] Organometallic Studies - IV.

[1] Part III: M. Cais and J. Kozikowski, J.Amer.Chem.Soc. 82, 5667 (1960); Part II: A. Modiano and M. Cais, Tetrahedron Letters No. 18 31 (1960); Part I: M. Cais and A. Modiano, Chem. & Ind. 202 (1960).

[2] Presented in part at the Meeting of the Israel Chemical Society, Rehovot, 4-5 April, 1961.

[3] M. Rausch, E.O. Fischer and H. Grubert, J.Amer.Chem.Soc. 82, 76 (1960).

ferrocenyl ruthenocenyl ketone[3] (1623 cm^{-1}).

The acid chloride (II) (1.33 g) was reacted under similar conditions with ferrocene (0.93 g) and chromatography of the reaction product yielded 1.25 g of scarlet-red crystals, m.p. 148-149° and 0.13 g of purple-red crystals, m.p. 230-232°. The lower m.p. compound turned out to be the expected (cyclopentadienylmanganese tricarbonyl) (1-ferrocenyl)-ketone (IV) (Found: C, 55.15; H, 3.43. $C_{19}H_{13}O_4MnFe$ requires: C, 54.84; H, 3.15%). The infra-red spectrum showed terminal carbonyl absorptions at 2030 and 1940 cm^{-1}, ketonic carbonyl absorption at 1633 cm^{-1} and absorptions at 1003 and 1109 cm^{-1}, indicative of an unsubstituted cyclopentadienyl ring in the ferrocene moiety. The higher m.p. compound showed absorption bands (KBr pellet) at 2030, 1944 and 1929 cm^{-1} assigned to the terminal carbonyl groups, at 1628 cm^{-1} assigned to ketonic carbonyls and no absorption bands near 1000 and 1100 cm^{-1}.

On the basis of the infra-red spectrum and the elementary analysis, this compound was assigned the structure of the diketone V (Found: C, 52.14; H, 2.55; $C_{28}H_{16}O_8FeMn_2$ requires: C, 52.05; H, 2.49%).

This appears to be the first reported derivative in which three metallocene moieties are incorporated into a neutral compound.

The same compound (V) was obtained in 82% yield when the acid chloride (II) was reacted directly with the monoketone (IV), under Friedel-Crafts conditions.

Using the same series of reactions as for (I),[1,4] methylcyclopentadienylmanganese tricarbonyl (VI) was transformed into (x-methyl-y-carboxylcyclopentadienyl)manganese tricarbonyl.

Two isomeric carboxylic acids were separated, one (VIIa) m.p. 180-181°

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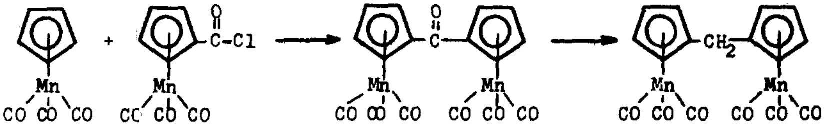
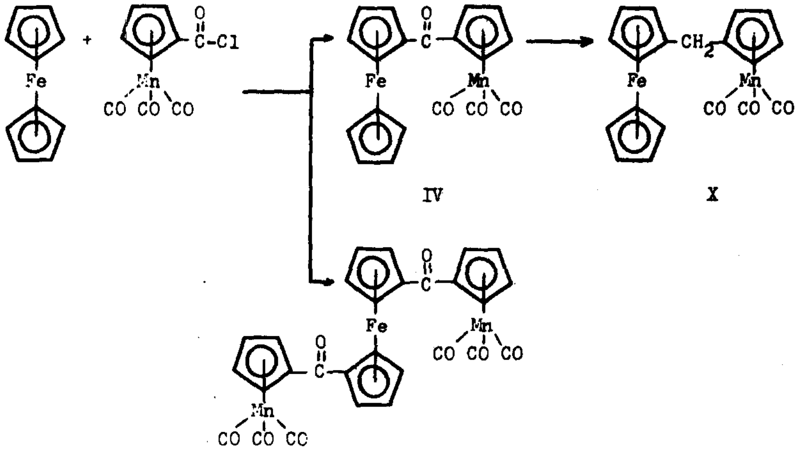
[4] J. Kozokowski and M. Cais, unpublished results.

(Found: C, 45.94; H, 2.90; Mn, 21.00. $C_{10}H_7O_5Mn$ requires: C, 45.79; H, 2.69; Mn, 20.96%) and another one (VIIb), m.p. 154-155° (Found: C, 45.93; H, 2.76; Mn, 21.44%). The higher m.p. acid (VIIa) was transformed into the acid chloride (VIII) (with thionyl chloride) and the latter reacted

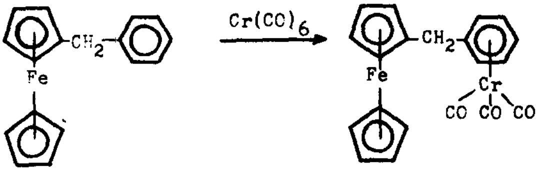


I II III



IV X

V



XI

under Friedel-Crafts conditions with ferrocene to yield over 40% of red crystals (IX). The I.R. spectrum and the elementary analysis of this compound indicated that (IX) was the disubstituted ferrocene derivative analogous to compound (V).

Clemmensen reduction of the ketone (IV) gave the corresponding substituted methane derivative (X), orange crystals, m.p. 121.5-122° (Found: C, 56.80; H, 3.85. $C_{19}H_{15}O_3FeMn$ requires: C, 56.75; H, 3.76%).

The same reduction was carried out with the ketone (III). An analogous compound to (X) was prepared by reacting benzyl ferrocene[5] with chromium hexacarbonyl to yield, among other products, 1-(benzylchromium tricarbonyl)-ferrocene (XI), m.p. 164-165°. (Found: C, 58.52; H, 3.84. $C_{20}H_{16}O_3CrFe$ requires C, 58.28; H, 3.91%).

The infra-red spectrum of (XI) shows the terminal carbonyl absorptions at 1965 and 1893 cm^{-1}, and the unsubstituted-ring absorptions of ferrocene at 1105 and 998 cm^{-1}. A study of the latter reaction as well as an investigation of the reactions of the ketones reported are in progress.

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[5] M. Rausch, M. Vogel and H. Rosenberg, J.Org.Chem. 22, 900 (1957).