Synthesis and Fluxional Behaviour of Cycloheptatrienylmanganesetricarbonyl and Cycloheptatrienylirontricarbonyl Cation

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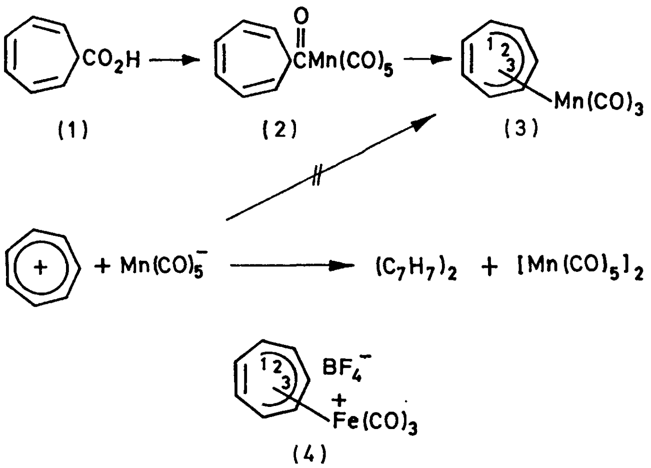
Summary The synthesis of h^5-cycloheptatrienylmanganesetricarbonyl by low temperature photochemical decarbonylation of the acyl manganese species (**2**) is described, and the properties of this molecule are compared to those of the isoelectronic iron cation.

WE report the synthesis of h^5-cycloheptatrienylmanganesetricarbonyl (**3**), whose fluxional behaviour[1] allows interesting comparisons with the isoelectronic iron tricarbonyl cation (**4**).[2] The synthesis of (**3**) is shown in the Scheme. The known acid (**1**)[3] was converted *via* the acid chloride[3] and reaction with manganese pentacarbonyl anion in tetrahydrofuran into the manganese acyl species (**2**) (67%) m.p. 83° (decomp.); ν_{CO} 2115, 2050, 2005, and 1652 cm^{-1}; n.m.r. δ (C_6D_6) 2·79 (1H), 4·97 (2H), 6·3 (2H), and 6·18 (2H). Photolysis of this species in hexane at room temperature gave only bitropyl and decacarbonyldimanganese. A similar result was obtained by direct reaction of manganese pentacarbonyl anion with tropylium ion or tropyl bromide.[4] However, when the photolysis of (**2**) was carried out at −68° (**3**) was isolated in 10·5% yield as orange, air-stable crystals, m.p. 63° (after preparative thick-layer chromatography and sublimation); ν_{CO} 2025, 1951, and 1930 cm^{-1}, M^+ 230. The n.m.r. spectrum $[(CD_3)_2CO]$ of this compound at 88° showed a single sharp line at δ 4·85. At lower temperatures, this peak broadened, then split into several lines. The low-temperature limiting spectrum, obtained at −47°, is consistent with the *pentahapto*-species (**3**) (*vide infra*). The coalescence temperature (at which the spectrum was broadest) was 27 ± 10°.



SCHEME

We have prepared (**4**) by a minor modification of the published[2] procedure and have established its nonrigidity. In $(CD_3)_2CO$ the limiting spectrum (−80°) shows signals at the positions indicated in the Table. These signals coalesce at about −50 ± 10°, and at 10° or above only a single sharp resonance (δ 6·10) is observed.

The temperature dependence of the spectra of these two fluxional molecules indicate a difference in activation energies for the fluxional process of 3—8 kcal mol^{-1}, reflecting the effect of an increase in the nuclear charge of the metal on the energetics of the tautomerism. That an increase in charge speeds up the reaction suggests that the degree of backbonding is an important determinant of the rate of rotation; the stronger the backbond, the slower the rate.

Comparison of the cyclohexadienyl- and cycloheptadienyl-manganese[5,6] and iron[7,8] complexes shows that the shift associated with the formation of the cationic species is −0·7 to −1·5 p.p.m., as might be expected. This difference is maintained in the cycloheptatrienyl complexes; here the shift is between −1·3 and −1·6 p.p.m. However, there is an additional shift in both of the trienyl species relative to their saturated analogues of between −0·3 and −1·6 p.p.m. This shift is that expected of a compound with an appreciable ring current, and suggests that considerable aromaticity is maintained by the C_7H_7 ring in the complex.

TABLE. *N.m.r. chemical shifts* (δ) *of the pentadienyl complexes*

	(**3**)[a,b]	(**4**)[a,b]	Δ[c]
H^1	3·53	5·13	−1·6
H^2	5·42	6·70	−1·3
H^3	7·10	8·48	−1·4

[a] In acetone. [b] Additional resonances for the uncomplexed olefinic protons were at 4·70(**3**) and 5·48δ(**4**). [c] $\Delta = \delta_{Mn} - \delta_{Fe}$.

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