Bis-(π-arene-π-cyclopentadienyliron) Dications

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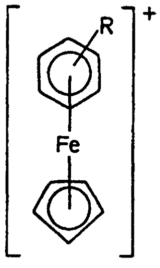
Summary Treatment of the π-arene-π-cyclopentadienyl cations (**1a,b**) and (**2**) with ferrocene in the presence of a Lewis acid affords the novel bis-(π-arene-π-cyclopentadienyliron) dications (**3a,b**) and (**4**).

ARENECYCLOPENTADIENYLIRON CATIONS (**1**) are readily synthesised by Lewis acid-induced cleavage of ferrocene in the presence of an arene,[1] but when polyaromatics such as biphenyl and fluorene were employed as substrates,[1b] only one of the aromatic rings took part in the ligand exchange process. We report here syntheses of bis-(π-arene-π-cyclopentadienyliron) dications in which both the aromatic ings of the substrate are co-ordinated to iron.

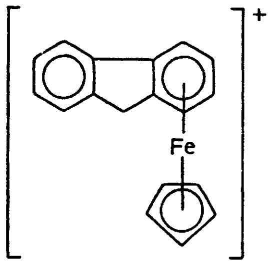
Using the method of Nesmeyanov *et al.*,[1] the corresponding arenecyclopentadienyliron cations, (**1a,b**) and (**2**) derived from biphenyl, diphenylmethane, and fluorene respectively, were synthesised and isolated as their hexafluorophosphate (PF_6^-) salts. These salts were then reacted further with excess ferrocene to co-ordinate the remaining "free" aromatic ring. Typically, a mixture of the PF_6^- salt (0·01 mol), ferrocene (0·03 mol), aluminium chloride (0·06 mol), and aluminium (0·17 mol) in decalin (50 ml) was vigorously stirred whilst heating (150—190°) under nitrogen overnight (17—24 h). Addition of NH_4PF_6 to the processed aqueous phase obtained from ice-quenching the cooled reaction residue yielded a mixture of starting material and the analogous bis hexafluorophosphate, (**1a** → **3a**, **1b** → **3b**, **2** → **4**). The latter were isolated in reasonable purity by ether-induced fractional precipitation from an acetonitrile solution of the mono and bis salt mixture. Identification was readily made on the basis of ^1H n.m.r. spectroscopy.†

In general appearance, the ^1H n.m.r. spectrum of each bis salt was identical to that of the analogous mono complex except that the resonances due to the uncomplexed arene protons of the latter were absent. In the mono salts (**1a,b**) and (**2**) the complexed arene ring protons were shifted upfield compared to the parent arene, due either to the proximity of the shielding iron atom[2] or perturbation of the arene π-electrons.[2,3] There was a concomitant downfield shift of the remaining "free" arene ring protons compared with the parent arene. Similarly the methylene protons of (**1b**) and (**2**) were shifted downfield. This can be explained in terms of the inductive influence of the co-ordinated arene ring.[3] Bis co-ordination increased the downfield shift of the methylene protons, the arene protons, and the cyclopentadienyl ring protons as was expected.

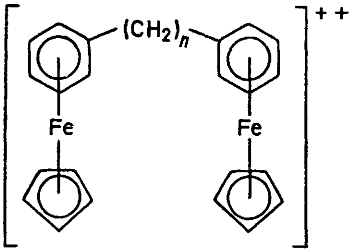
The fluorenyl series of complexes is of interest in that two possible structures *cis*-(**4a**) and *trans*-(**4b**) exist for the bis salt. The *trans* structure (**4b**) is assigned on the following basis. The methylene protons of the mono salt (**2**) comprise a doublet resonance (δ 4·10, dd, *J* 23 Hz, ΔV 4 Hz) because of their *exo-endo* relationship to the iron atom. However in the bis complex (**4**), they resonate as a singlet (δ 4·39,s) as in the parent arene (δ 3·86,s) and this equivalence can readily be explained in terms of the *trans* structure (**4b**).



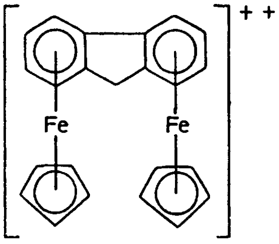
(**1**)
a; R = Ph
b; R = CH$_2$Ph



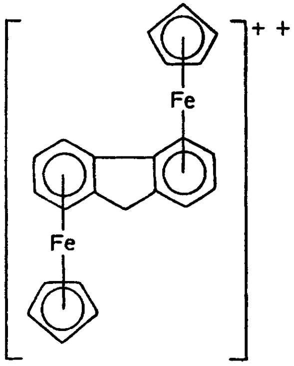
(**2**)



(**3**)
a; *n* = 0
b; *n* = 1



cis – (**4a**)



trans – (**4b**)

Further proof of the dicationic nature of the bis salts was obtained by mass spectral investigation of the unstable neutral species obtained from each on treatment with $NaBH_4$. The hydride-reduced products from (**3a,b**) and (**4**) exhibited a molecular ion at *m/e* 398, 412, and 410 respectively, corresponding to a respective molecular formula of $C_{22}H_{22}Fe_2$, $C_{23}H_{24}Fe_2$, and $C_{23}H_{22}Fe_2$ in keeping with the addition to each of two hydride ions. For further confirmation, one of the bis salts (**3a**) was treated with

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† ^1H n.m.r. spectra were recorded in acetonitrile on a Varian T-60 (60 MHz) spectrometer with tetramethylsilane as an internal standard.

$LiAlD_4$. The neutral product obtained exhibited a molecular ion at *m/e* 400, an increase in mass number of 2 over the analogous hydride-reduced product ($C_{22}H_{22}Fe_2$) corresponding to a molecular formula of $C_{22}H_{20}D_2Fe_2$.

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[1] (a) A. N. Nesmeyanov, N. A. Vol'kenau, and I. N. Bolesnova, *Tetrahedron Letters*, 1963, 1725; *Doklady Akad. Nauk S.S.S.R.*, 1963, **149**, 615; (b) *ibid.*, 1966, **166**, 607; (c) A. N. Nesmeyanov, N. A. Vol'kenau, and L. S. Shilovtseva, *ibid.*, 1965, **160**, 1327; (d) E. I. Sirotkina, A. N. Nesmeyanov, and N. A. Vol'kenau, *Izvest. Akad. Nauk S.S.S.R., Ser. khim.*, 1969, 1524.

[2] (a) I. U. Khand, P. L. Pauson, and W. E. Watts, *J. Chem. Soc. (C)*, 1968, 2257; (b) *ibid.*, p. 2261; (c) *ibid.*, 1969, 116, (d) *ibid.*, p. 2024.

[3] A. N. Nesmeyanov, I. F. Leschova, Yu. A. Ustynyuk, Ye I. Sirotkina, I. N. Bolesnova, L. S. Isayeva, and N. A. Vol'kenau, *J. Organometallic Chem.*, 1970, **22**, 689.