

Electrochemical Synthesis and Structure of the First Example of a Ferrocene Dication: Propane-1,3-diyl-1,1'-bis(tetramethylcyclopentadienyl)iron(2+)

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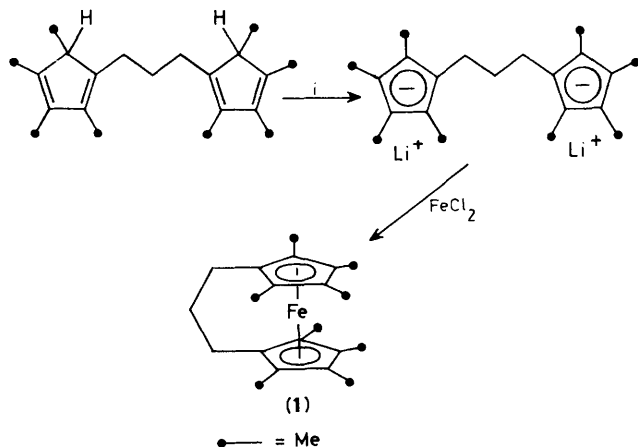
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The permethylferrocenophane [(pdmcp)Fe] [pdmcp = η^5, η^5 -C₅Me₄(CH₂)₃C₅Me₄] and its oxidised species, monocation and dication salts, were synthesised, in which the latter, [(pdmcp)Fe(NCMe)](PF₆)₂, has a substantially bent bis(cyclopentadienyl) moiety to accommodate one molecule of MeCN.

Since the first preparation of ferrocene in 1951,¹ there has been no report upon the preparation and isolation of a ferrocene dication. We have found that a permethylated ferrocenophane with the ligand, η^5, η^5 -C₅Me₄(CH₂)₃C₅Me₄ (pdmcp)² can be oxidised in acetonitrile stepwise to the corresponding dication. Moreover, the X-ray crystal structure of this dication has shown that it contains acetonitrile as an additional ligand.

The neutral ferrocenophane [(pdmcp)Fe] (1)[†] was prepared in 27% yield from the reaction of FeCl₂ and the dilithium salt Li₂(pdmcp)² (Scheme 1).

The cyclic voltammogram of (1) shows two separate oxidation waves at $E_{1/2}$ -0.049 and +1.054 V vs. standard calomel electrode (SCE) in 0.1 M Buⁿ₄NBF₄/MeCN. The first oxidation step is reversible [ΔE = 78 mV; cf. (η^5 -C₅H₅)₂Fe: ΔE = 75 mV], while the second step is quasi-reversible (ΔE = 232 mV). Two-step bulk electrolysis of (1) was successfully achieved as follows. A solution of (1) in acetonitrile with 0.1 M NH₄PF₆ as supporting electrolyte was electrolysed at a Pt plate working electrode under a nitrogen atmosphere at +0.05 V vs. SCE. After evaporation and washing the residue with water, recrystallisation from acetonitrile/ether afforded crystals of the monocation (2)[†] in 96% yield. In a similar manner, further oxidation of (2) was carried out at +1.20 V vs. SCE to give the crude dication (3)[†] in 90% yield (Scheme 2).



Scheme 1. Reagents and conditions: i, 2 BuⁿLi; ii, FeCl₂.

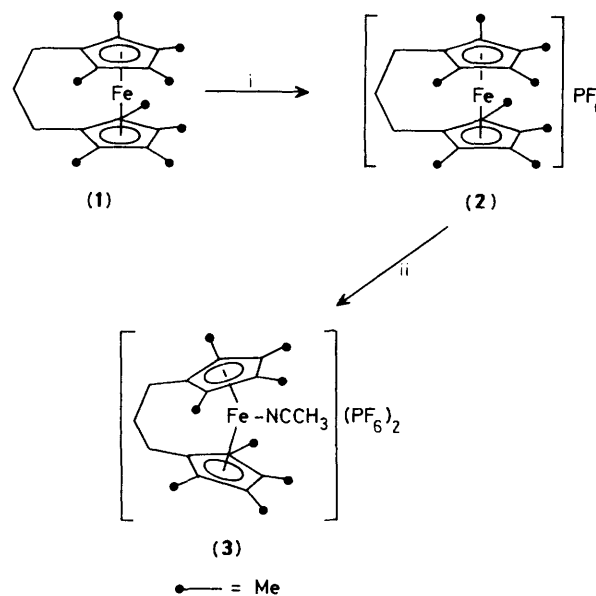
[†] Satisfactory elemental analyses were obtained for (1)–(3). (1): yellow crystals; ¹H n.m.r. (90 MHz, C₆H₆) δ 1.52 (12H, s, Me), 1.60 (12H, s, Me), 1.76 (4H, m, CH₂), 1.85 (2H, m, CH₂); ¹³C n.m.r. (22.5 MHz, C₆D₆) δ 9.5 (CH₃), 20.3 (CH₂), 34.7 (CH₂), 78.9 (C₅Me₄), 80.2 (C₅Me₄); m/z 338 (100, M⁺).

(2): greenish-blue crystals; ¹H n.m.r. (90 MHz, CD₃COCD₃) δ -52.0 (12H, br.s, Me); -42.2 (4H, br.s, CH₂), -16.5 (2H, br.s, central CH₂), 10.1 (12H, br.s, Me).

(3): dark green crystals; ¹H n.m.r. (90 MHz, CD₃CN) δ 1.38 (12H, s, Me), 1.60 (12H, s, Me), 2.34 (6H, m, CH₂).

The ¹H n.m.r. spectrum of (3) in CD₃CN shows two sharp signals of methyl groups of the pdmcp ligand at δ 1.38 and 1.60, indicating that (3) is a diamagnetic complex. It is known that 16 electron metallocenes such as (C₅H₅)₂Cr, (C₅Me₅)₂Cr, and [(C₅Me₅)₂Mn]⁺ are paramagnetic and possess the orbitally degenerate ³E_{2g}[e_{2g}³a_{1g}¹] configuration.³ Accordingly, the diamagnetic nature of (3) suggests that (3) is not a 16 electron complex but an 18 electron complex ligating an acetonitrile in solution. In contrast to (3), the ¹H n.m.r. spectral signals of the monocation (2) are broad and show large paramagnetic shifts.

The structure of (3) was determined by an X-ray crystal structure analysis.[‡] The Fe–N≡C–C unit and P atoms of (3) lie on the intersections of mirror planes. The central methylene of the trimethylene chain is disordered between two sites as shown in Figure 1.



Scheme 2. Conditions: 0.1 M NH₄PF₆ in MeCN: i, +0.05 V; ii, +1.2 V vs. SCE.

[‡] Crystal data: C₂₃H₃₃F₁₂FeNP₂, M = 669.3, orthorhombic, space group $Pmnm$ (variant of No. 59); a = 10.903(2), b = 14.804(3), c = 8.971(2) Å, U = 1448.0(5) Å³, Z = 2, D_c = 1.54 g cm⁻³, $F(000)$ = 684, $\mu(\text{Mo-K}\alpha)$ = 0.74 mm⁻¹. Diffraction data were collected in the ω - 2θ scan mode ($3^\circ < 2\theta < 60^\circ$). The structure was solved by the heavy-atom method and was refined by use of block-diagonal least-squares procedures. The 22 independent non-hydrogen atoms including two disordered fluorine atoms were refined anisotropically. All the methyl hydrogen atoms except those of MeCN were included in the refinement as isotropic scatterers. For 1483 unique reflections [$|F_o| > 3\sigma(F_o)$] the atomic parameters were refined to R = 0.063 (R_w = 0.100). Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Centre. See Notice to Authors, Issue No. 1.

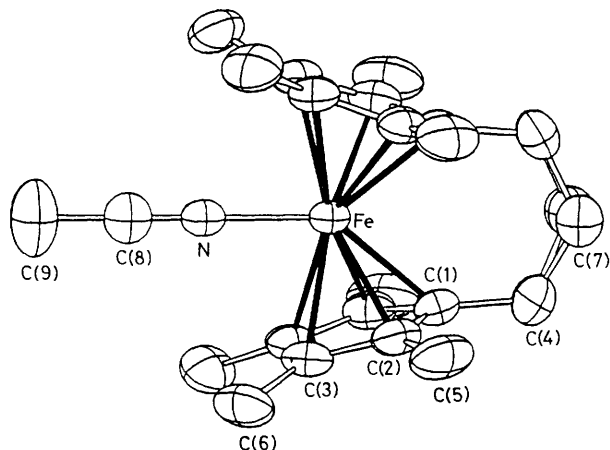


Figure 1. ORTEP view of $[(\text{pdmc})\text{Fe}(\text{MeCN})](\text{PF}_6)_2$ (**3**) with thermal ellipsoids at 30% probability level. Both the disordered methylene carbons are drawn. Selected distances (Å) and angles ($^\circ$): Fe–N 1.916(6), Fe–C(1) 2.155(5), Fe–C(2) 2.166(4), Fe–C(3) 2.179(3), C(1)–C(4) 1.483(8), C(4)–C(7) 1.457(11), N–C(8) 1.150(11), C(8)–C(9) 1.415(14); Fe–N–C(8) 180.0, N–C(8)–C(9) 180.0, C(1)–C(4)–C(7) 118.2(6), C(4)–C(7)–C(4 $'$) 121.2(12).

The most characteristic structural feature of (**3**) is the co-ordination of an acetonitrile molecule to the iron atom. Although it is known that ferrocene derivatives are protonated in strong acids⁴ or form adducts with Lewis acids such as HgCl_2 ,⁵ this is the first time that a Lewis base like acetonitrile is observed co-ordinating to the iron atom of a ferrocene unit. The acetonitrile ligand is located on the axis that maximises the overlap between the lone pair of nitrogen and the vacant $2a_1$ orbital of the ferrocene dication unit.⁶ The Fe–N [1.916(6) Å] and N≡C lengths [1.150(11) Å] are normal, whereas the exact linearity of the Fe–N–C(8) bond (180°) is rather unusual in comparison with those of other M–NCMe complexes.⁷ The dihedral angle between the least-squares planes of two cyclopentadienyl rings is 34.5° .

There are some structural characteristics due to the connection of the two permethylcyclopentadienyl rings with the trimethylene chain. In the dication (**3**), the pair of cyclopentadienyl rings are completely eclipsed in contrast with the staggered C_5Me_5 rings in $(\text{C}_5\text{Me}_5)_2\text{Fe}^8$ and $[(\text{C}_5\text{Me}_5)_2\text{Fe}]^+$.⁹ The bending of methyl and methylene groups away from the iron atom from the cyclopentadienyl ring planes (0.219 Å) is far larger than that of $(\text{C}_5\text{Me}_5)_2\text{Fe}$ (0.064 Å).

The iron–(ring carbon) distances of (**3**) [2.155(5)–2.179(3) Å] are significantly longer than those of other unsubstituted and substituted ferrocenes and ferricinium ions, which range almost from 2.01 to 2.10 Å.⁹ This bond-extension is apparently due to the large steric repulsion between the cyclopentadienyl rings and the acetonitrile ligand, but the high oxidation state of the iron of (pdmcp)Fe^{IV} (**3**) may also be responsible for this.

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