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Note

Synthesis and crystal structure of 1,1′-bis[4-(2,2′:6′,2″-terpyridin-4′-yl)phenyl]octamethylferrocene

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Abstract

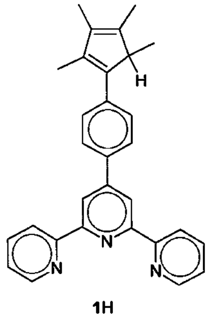
1,1′-Bis[4-(2,2′:6′,2″-terpyridin-4′-yl)phenyl]octamethylferrocene was prepared from iron(II) chloride and lithiated 4′-[4-(2,3,4,5-tetramethylcyclopenta-1,3-dien-1-yl)phenyl]-2,2′:6′,2″-terpyridin and was structurally characterised by X-ray diffraction, which revealed pronounced π-stacking of the six-membered aromatic rings. Its electrochemistry was investigated by cyclic voltammetry and controlled potential coulometry and compared with that of related compounds. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopentadienes; Iron; Oligopyridine ligands; π-Stacking; Cyclic voltammetry

1. Introduction

Donor-functionalised ferrocenes are of great current interest. They have been utilised, inter alia, as catalysts, sensors, thermotropic liquid crystals and non-linear optical materials [1]. A wide variety of ferrocenes containing *N*-heterocyclic substituents such as pyridyl, bipyridyl and terpyridyl units have been reported in this context [2]. The most straightforward way of preparing ferrocenes starts from a cyclopentadiene, which is deprotonated and subsequently allowed to react with iron(II) chloride. In fact, this method has been widely used for the preparation of a large variety of ferrocenes containing N-, P-, O- and S-donor functionalities [3]. However, since oligodentate *N*-heterocyclic groups are excellent ligands for iron(II), ferrocenes containing such substituents have exclusively been prepared by a less direct method, namely by functionalisation of ferrocene.

We have been interested in the limitations of the direct approach and have investigated this by utilising the terpyridyl-functionalised cyclopentadiene **1**H as the starting material.



1H

In view of the extremely large complex formation constant of $[Fe(tpy)_2]^{2+}$ (tpy = 2,2′:6′,2″-terpyridine) this represents a rather extreme case [4].

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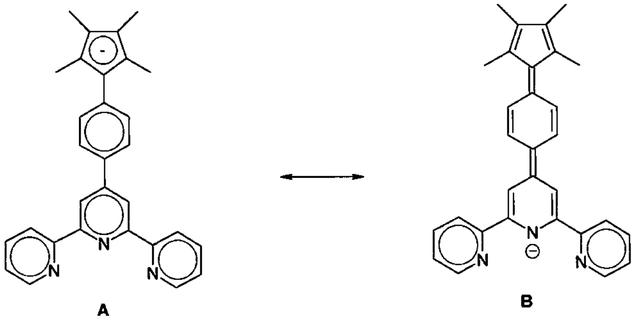
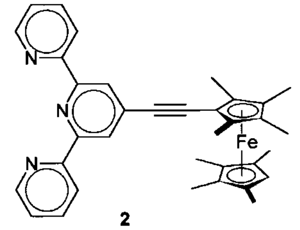
2. Results and discussion

Deprotonation of a colourless solution of **1**H in THF–hexane with LDA at −95 °C afforded a dark green solution. Upon warming of the solution to room temperature, **1**Li precipitated as a brownish black solid, which was collected by filtration, washed with toluene and dried in vacuo. Reaction of the solid with D_2O gave **1**D in quantitative yield. **1**Li is essentially insoluble in all common organic solvents, except DMSO, where it gives a dark blue solution. The intensely dark colour of **1**Li is indicative of an extended chromophore such as that present in the quinoid resonance structure **B**, which appears to be more important than the cyclopentadienide structure **A**.



Series of reactions of **1**Li with iron(II) chloride in THF, diethyl ether and THF–hexane were performed at temperatures between −80 and 25 °C, but failed to yield even trace amounts of the ferrocene $(\mathbf{1})_2$Fe. In each case a black, insoluble solid was obtained, which proved to be paramagnetic. However, when the reaction was performed in toluene in the absence of polar solvents, the desired ferrocene was indeed formed, albeit in very low yield (2–3%). The main part of the product again consisted of a black, paramagnetic solid. Owing to the insolubility of the starting materials in toluene, rather forcing reaction conditions were required (100 °C, 4 days).

The structure of $(\mathbf{1})_2$Fe was determined by a single-crystal X-ray diffraction study and is reminiscent of that of 1,1′-bis(2,2′:6′:2″-terpyridyl)ferrocene, which had previously been prepared by functionalisation of ferrocene [5]. A view of the molecule is shown in Fig. 1.



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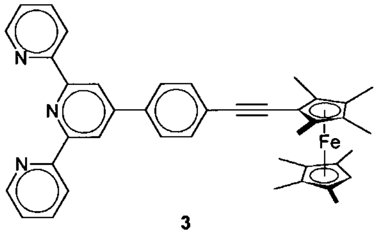

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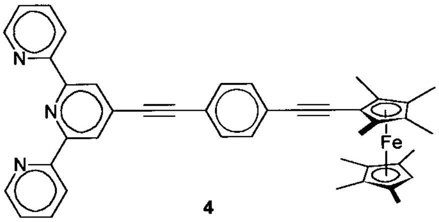

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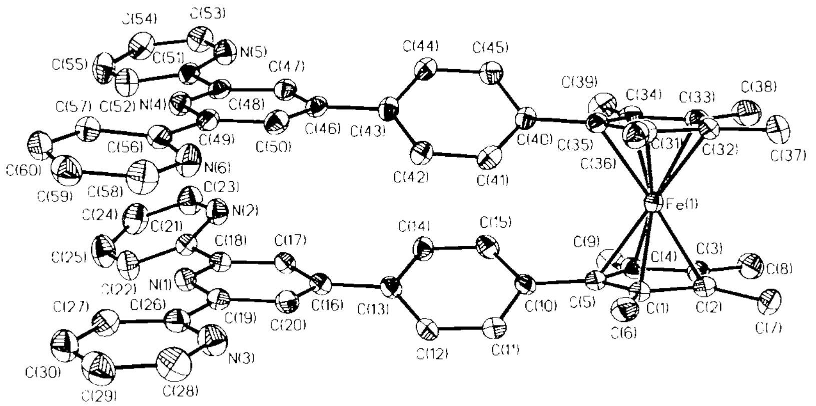

Fig. 1. Molecular structure of $(\mathbf{1})_2$Fe in the crystal. Selected bond lengths (pm): N(1)–C(18) 134.3(4), N(1)–C(19) 134.8(4), N(2)–C(21) 134.1(4), N(2)–C(23) 134.0(4), N(3)–C(26) 135.2(4), N(3)–C(28) 133.6(4), N(4)–C(48) 134.0(4), N(4)–C(49) 135.0(4), N(5)–C(51) 133.6(4), N(5)–C(53) 133.9(4), N(6)–C(56) 134.6(4), N(6)–C(58) 133.8(4), C(5)–C(10) 147.7(4), C(10)–C(11) 139.4(4), C(10)–C(15) 140.0(4), C(11)–C(12) 138.3(4), C(12)–C(13) 139.1(4), C(13)–C(14) 139.4(4), C(13)–C(16) 148.6(4), C(14)–C(15) 138.6(4), C(16)–C(17) 138.9(4), C(16)–C(20) 139.0(4), C(17)–C(18) 139.3(4), C(18)–C(21) 149.3(4), C(19)–C(26) 149.0(4), C(21)–C(22) 138.5(4), C(22)–C(25) 138.0(5), C(23)–C(24) 137.6(5), C(24)–C(25) 137.2(5), C(26)–C(27) 138.7(5), C(27)–C(30) 137.3(5), C(28)–C(29) 137.2(5), C(29)–C(30) 138.6(5), C(35)–C(40) 147.9(4), C(40)–C(41) 139.3(4), C(40)–C(45) 140.6(4), C(41)–C(42) 138.0(4), C(42)–C(43) 139.9(4), C(43)–C(44) 139.4(4), C(43)–C(46) 148.9(4), C(44)–C(45) 138.8(4), C(46)–C(47) 139.7(4), C(46)–C(50) 139.3(4), C(47)–C(48) 139.3(4), C(48)–C(51) 149.9(4), C(49)–C(50) 138.3(4), C(49)–C(56) 149.0(4), C(51)–C(52) 138.7(4), C(52)–C(55) 138.7(5), C(53)–C(54) 138.6(5), C(54)–C(55) 137.0(5), C(56)–C(57) 139.0(4), C(57)–C(60) 137.6(4), C(58)–C(59) 137.8(5), C(59)–C(60) 138.6(5).

Table 1
Formal electrode potentials (V, vs. SCE) and peak-to-peak separation (mV) for the one-electron oxidation of the ferrocene derivatives under study (dichloromethane solution, n-Bu_4NPF_6 (0.2 M) supporting electrolyte)

Compound	$E^{\circ\prime}$	ΔE_p [a]
$(\mathbf{1})_2$Fe	+0.03	63
2	+0.18	170
3	+0.06	62
4	+0.14	73
Cp^*_2Fe	−0.10	70

[a] Measured at 0.1 V s^{-1}.

Despite the presence of two large substituents, the ferrocene nucleus is almost undistorted. The cyclopentadienyl ring tilt angle is only 2.3°. The iron–carbon bond lengths range from 206.0(3) to 208.0(3) pm, the iron–ring centroid distances being 167 pm, which is essentially identical to the values observed for ferrocene and decamethylferrocene [6]. The cyclopentadienyl ring C–methyl C distances are indistiguishable within experimental error (average value 150.3 pm). In contrast to decamethylferrocene [7], the cyclopentadienyl rings of $(\mathbf{1})_2$Fe are arranged in an eclipsed conformation, which is most likely due to the extensive π-stacking observed for the six-membered rings in this compound. It is well documented that such intramolecular stacking in ferrocenes may be pronounced in case of electron-poor aryl substituents [8]. The nature of π–π interactions in metal complexes with aromatic nitrogen-containing ligands was recently reviewed [9]. Bond lengths and angles are unexceptional for the six-membered rings (C–C distances range from 137.0(5) to 140.6(4) pm and C–N distances from 133.6(4) to 135.2(4) pm). The closest approach between the two aromatic decks occurs between C(15) and C(41), whose distance is only 314.5(4) pm. This is considerably shorter than the van der Waals distance between the two π-systems (335 pm for graphite) [10]. Each six-membered ring of one terpyridylphenyl substituent is approximately parallel to its counterpart of the other terpyridylphenyl substituent. The three C_5N rings of each terpyridyl unit are arranged in the *trans–trans* conformation expected for 2,2′:6′,2″-terpyridines [11]. The values of the angle between each central C_5N ring and the best plane of the cyclopentadienyl ring connected to it by a phenylene ring are 9.0 and 9.2°, respectively. For steric reasons, each phenylene ring is tilted considerably out of the planes of the two rings attached to it (angles to C_5 rings are 33.7 and 40.1° respectively; angles to C_5N rings are 26.6 and 30.9°, respectively), indicating that in agreement with electrochemical results (vide infra) π-delocalisation is attenuated by the C_6 rings.

As expected, cyclic voltammetry on the orange dichloromethane solution of $(\mathbf{1})_2$Fe ($\lambda_{max} = 480$ nm) shows an oxidation process displaying features of chemical (i_{pc}/i_{pa} constantly equal to 1 with scan rate) and electrochemical (peak-to-peak separation close to 60 mV) reversibility. Controlled potential coulometry ($E_w = +0.2$ V) consumes one electron/molecule. The resulting yellow–green solution shows a broad and very flattened band centred at about 840 nm with the concomitant disappearance of the original absorption band. In addition, it exhibits a cyclic voltammetric profile quite complementary to the original one, thus confirming the complete stability of the monocation $[(\mathbf{1})_2\mathrm{Fe}]^+$. Table 1 compiles the relevant formal electrode potential also in comparison with those of the closely related ferrocenyl derivatives **2**, [12] **3** [2d] and **4**, [12] which bear a single terpyridyl substituent, as well as with decamethylferrocene [6].

Not surprisingly, all three terpyridyl-functionalised ferrocenes are much more difficult to oxidise than decamethylferrocene. It is the nature of the spacer unit between the ferrocene nucleus and the terpyridyl unit, which governs the redox potential. An acetylene unit is very effective for π-delocalisation (cf. **2**), whereas a phenylene ring is not, if it is prevented from forming small angles with neighbouring π-systems (cf. $(\mathbf{1})_2$Fe and **3** [2d]). The redox potential of $(\mathbf{1})_2$Fe, which contains two terpyridyl units, is almost identical to that of **3**, which contains only one terpyridyl group. However, **3** contains a spacer unit consisting of rather electronegative sp-hybridised C atoms (χ 2.99) [13] instead of the less electronegative sp^2-hybridised C atoms (χ 2.66) [13] present in $(\mathbf{1})_2$Fe. In **2** and also in **4** π-delocalisation and spacer electronegativity go hand in hand, leading to remarkably large $E^{0\prime}$ values of +0.18 and +0.14 V, respectively.

3. Experimental

3.1. General considerations

All manipulations were performed in an inert atmosphere (purified argon or dinitrogen) by using standard Schlenk and cannula techniques or a conventional glovebox. Solvents and reagents were appropriately dried and purified by using standard procedures. NMR spectra were recorded at 300 K with a Bruker DRX 500 spectrometer operating at 500.13 MHz for ^{1}H-NMR; TMS was used as external reference for ^{1}H- and ^{13}C-NMR, and 1.0 M LiCl in D_2O was used for ^{7}Li. Materials and apparatus used for the electrochemical investigations have been described elsewhere [14]. Elemental analyses were performed by the Microanalytical Laboratory of the Universität Bielefeld.

3.2. Synthesis of **1**Li

A solution of **1**H [15] (710 mg, 1.65 mmol) in a mixture of THF (20 ml) and *n*-hexane (10 ml) was cooled to −95 °C. A solution of LDA (115 mg, 1.80 mol) in THF (10 ml) was added dropwise with stirring. The dark-green reaction mixture was allowed to warm to room temperature (r.t.) overnight. Volatile components were removed in vacuo. The remaining solid was stirred with toluene (50 ml), filtered off, washed with toluene (3 × 2 ml) and finally dried in vacuo. Yield: 500 mg (70%). ^{1}H-NMR (DMSO-d_6): $\delta = 1.90$ (s, 6H, Me), 2.12 (s, 6H, Me), 7.13 (d, 2H, apparent $J = 8.4$ Hz, C_6H_4), 7.48 (m, 2H, terpyridyl 5,5″-H), 7.59 (d, 2H, apparent $J = 8.5$ Hz, C_6H_4), 8.00 (m, 2H, terpyridyl 4,4″-H), 8.63 (d, 2H, $J = 8.0$ Hz, terpyridyl 3,3″-H), 8.65 (s, 2H, terpyridyl 3′,5′-H), 8.75 (d, 2H, $J = 4.4$ Hz, terpyridyl 6,6″-H). ^{13}C{^{1}H}-NMR (DMSO-d_6): $\delta = 12.1$, 14.4, 108.7, 112.5, 115.4, 115.6, 120.7, 122.8, 124.1, 125.1, 126.0, 137.2, 145.7, 149.2, 149.7, 155.1. ^{7}Li-NMR (DMSO-d_6): $\delta = -1.14$.

3.3. Synthesis of **1**D

D_2O (2.00 g, 100 mmol) was added to a stirred suspension of **1**Li (100 mg, 0.23 mmol) in THF (10 ml). After 1 h volatile components were removed in vacuo. The remaining solid was stirred with toluene (5 ml). Insoluble material was removed by filtration and washed with toluene (3 × 1 ml). The combined toluene solutions were reduced to dryness in vacuo, affording a light yellow solid. Yield: 99 mg (quantitative). ^{1}H-NMR ($CDCl_3$): $\delta = 0.98$ (s, 3H, Me), 1.87 (s, 3H, Me), 1.94 (s, 3H, Me), 2.08 (s, 3H, Me), 7.32 (m, 2H, terpyridyl 5,5″-H), 7.36 (‘d’, 2H, apparent $J = 8.2$ Hz, C_6H_4), 7.85 (m, 2H, terpyridyl 4,4″-H), 7.90 (‘d’, 2H, apparent $J = 8.2$ Hz, C_6H_4), 8.66 (d, 2H, $J = 7.8$ Hz, terpyridyl 3,3″-H), 8.71 (d, 2H, $J = 4.5$ Hz, terpyridyl 6,6″-H), 8.76 (s, 2H, terpyridyl 3′,5′-H). EIMS; *m*/*z* (%): 430 (100) [M^+], 415 (33) [$M^+ - Me$]. Anal. Found: C, 83.59; H, 6.31; N, 9.58. Calc. for $C_{30}H_{26}DN_3$ (430.57): C, 83.69; H + D, 6.55; N, 9.76%.

Table 2
Crystal data and structure refinement parameters for (**1**)$_2$Fe

Empirical formula	$C_{62}H_{54}Cl_6FeN_6$
Formula weight	1151.66
Crystal system	Monoclinic
Space group	$P2(1)/n$
Unit cell dimensions	
a (Å)	14.2649(7)
b (Å)	14.2793(7)
c (Å)	27.3792(13)
β (°)	102.749(1)
V (Å^3)	5439.5(5)
Z	4
ρ_{calc} (g cm^{-3})	1.406
Absorption coefficient (μ, mm^{-1})	0.619
F(000)	2384
Index ranges	$-18 \le h \le 18$, $-18 \le k \le 18$, $-33 \le l \le 35$
θ range for data collection (°)	3.0–27.1
Reflections collected	51 009
Independent reflections	11 811 [$R_{int} = 0.0767$]
Data/restraints/parameters	11811/0/684
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0587$, [a] $wR_2 = 0.1272$ [b]
Goodness-of-fit on F^2	1.063
Largest difference peak and hole (e Å^{-3})	0.638 and −0.552

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

3.4. Synthesis of (**1**)$_2$Fe

Toluene (100 ml) was added to $FeCl_2$ (356 mg, 2.81 mmol) and **1**Li (2.45 g, 5.63 mol) and the mixture stirred at 100 °C for 4 days. The dark solid was removed by filtration. The volume of the filtrate was reduced to ca. 20 ml. The crude product was precipitated by slow addition of Et_2O (20 ml) and isolated by filtration. It was dissolved in CH_2Cl_2 (10 ml). Slow addition of Et_2O (10 ml) at 0 °C afforded pure (**1**)$_2$Fe as an orange, microcrystalline solid. Yield: 60 mg (2.3 %). ^{1}H-NMR ($CDCl_3$): $\delta = 1.75$ (s, 12H, Me), 1.88 (s, 12H, Me), 7.19 (m, 4H, terpyridyl 5,5″-H), 7.30 (‘d’, 4H, apparent $J = 7.9$ Hz, C_6H_4), 7.67 (‘d’, 4H, apparent $J = 8.0$ Hz, C_6H_4), 7.75 (m, 4H, terpyridyl 4,4″-H), 8.46 (d, 4H, $J = 7.9$ Hz, terpyridyl 3,3″-H), 8.54 (d, $J = 4.0$ Hz, terpyridyl 6,6″-H), 8.60 (s, 4H, terpyridyl 3′,5′-H). ^{13}C{^{1}H}-NMR ($CDCl_3$): $\delta = 9.8$, 10.9, 78.6, 80.8, 85.3, 118.3, 121.1, 123.4, 126.1, 131.1, 135.0, 136.6, 138.0, 147.7, 148.9, 155.5, 156.2. MS (LSIMS, NBA matrix); *m*/*z* (%): 913 (5) [$(M + H)^+$]. Anal. Found: C, 78.50; H, 5.81; N, 9.22. Calc. for $C_{60}H_{52}FeN_6$ (912.96): C, 78.94; H, 5.74; N, 9.21%.

3.5. Crystal structure determination

An orange single crystal of (**1**)$_2$Fe·2CHCl$_3$ (dimensions 0.3 × 0.1 × 0.1 mm^3), which was obtained by slow evaporation of a chloroform solution, was used for data collection at 183 K on a Siemens SMART CCD area detector diffractometer with graphite-monochromated Mo–K$_\alpha$ radiation ($\lambda = 0.71073$ Å). The structure was solved by direct methods. Programs used were Siemens SHELXTL PLUS [16] and SHELXL 97 [17]. Full-matrix least-squares refinement on F^2 was carried out anisotropically for the non-hydrogen atoms. Hydrogen atoms were included at calculated positions using a riding model. Further crystallographic data are given in Table 2.

4. Supplementary material

Crystallographic data for the structural analysis (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 153715 for compound $(\mathbf{1})_2$Fe. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

Acknowledgements

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