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SYNTHESIS AND STRUCTURAL CHARACTERIZATION OF 3,5-[1,1′-FERROCENEDIYL]-1,7-DIOXO-1,7-DI(2-PYRIDYL)-4-(2-PYRIDYLCARBONYL)HEPTANE; AN UNEXPECTED COMPOUND OBTAINED FROM THE REACTION OF FERROCENE-1,1′-DICARBALDEHYDE WITH 2-ACETYLPYRIDINE

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Abstract—The reaction of ferrocene-1,1′-dicarbaldehyde with 2-acetylpyridine at room temperature for 24 h results in the synthesis of 3,5-[1,1′-ferrocenediyl]-1,7-dioxo-1,7-di(2-pyridyl)-4-(2-pyridylcarbonyl)heptane instead of the expected enone or 1,5-dicarbonyl. The crystal structure of this compound has been determined by single-crystal X-ray methods. The complex is electroactive and exhibits a reversible iron(II)/(III) process at +0.014 V vs ferrocene.

We are currently interested in the introduction of a variety of functionalized domains into metallosupramolecular systems.[1,2] Recently we have been particularly interested in the attachment of redox-active domains.[1-4] As a part of these studies we have developed compounds in which the reversible redox-active ferrocenyl substituents have been directly attached to oligopyridine metal-binding domains.[5-7] Such systems have proved to be suitable building blocks for the synthesis of redox-active supramolecular systems by self-assembly upon interaction with suitable metal centres. Using this approach we have reported the synthesis of 2,2′ : 6′,2″-terpyridine (tpy),[5] 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗-quinquepyridine (qpy)[6] and 2,2′ : 6′,2″ : 6″,2‴ : 6‴,2⁗ : 6⁗,2⁗′-sexipyridine (spy)[7] derivatives bearing ferrocenyl groups. In each case ferrocenecarbaldehyde was used as the organometallic starting material. Recently we have also explored the possibility of attaching suitable coordination centres to both of the cyclopentadienyl rings of a ferrocene unit, to give polydentate ligands in which the ferrocene can act as a redox-active ball-bearing group. By using this approach we have prepared 1,1′-[2,2′ : 6′,2″-terpyridin-4′-yl]ferrocene from the intermediate enone obtained from the reaction of ferrocene-1,1′-dicarbaldehyde with 2-acetylpyridine.[8] In the course of our studies on related ligand systems, we became

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aware that the reactions of 2-acetylpyridine with aromatic aldehydes could give rise to a range of products,[9,10] We wish to report here the compound 3, 5-[1,1′-ferrocenediyl]-1,7-dioxo-1,7-di(2-pyridyl)-4-(2-pyridylcarbonyl)heptane which may be obtained from the reaction of ferrocene-1,1′-dicarbaldehyde with 2-acetylpyridine.

EXPERIMENTAL

IR spectra were recorded on a Philips PU9624 Fourier-transform spectrophotometer, with the samples as compressed KBr disks, electronic spectra on a PU8730 spectrophotometer and proton NMR spectra on a Bruker WM-250 spectrometer. Fast atom bombardment (FAB) spectra were recorded on a Kratos MS-50 spectrometer. Electrochemical experiments were performed using a Autolab PGSTAT20 instrument. A conventional three-electrode configuration was used with platinum-bead working and auxiliary electrodes and a Ag–Ag$^+$ electrode as a reference. The solvent was purified dichloromethane and the supporting electrolyte was $[NBu_4][BF_4]$ (0.1 mol dm^{-3}) recrystallized twice from ethanol–water. Ferrocene was added at the end of each experiment as internal standard. Ferrocene-1,1′-dicarbaldehyde was prepared by the literature method.[11]

Preparations

3,5-[1,1′-Ferrocenediyl]-1,7-dioxo-1,7-di(2-pyridyl)-4-(2-pyridylcarbonyl)heptane (**4**). 2-Acetylpyridine (0.6 cm^3, 5 mmol) was added to a solution of ferrocene-1,1′-dicarbaldehyde (242 mg, 1 mmol) in ethanol (15 cm^3). After 2 min, an aqueous solution of sodium hydroxide (4 cm^3, 2 M) was added and the mixture stirred at room temperature for 24 h. After this period a yellow precipitate was obtained which was collected by filtration, washed well with water and dried *in vacuo* to yield **4** (435 mg, 76%). Found: C, 70.0; H, 4.7; N, 7.3. Calc. for $C_{33}H_{27}N_3O_3Fe$: C, 69.6; H, 4.8; N, 7.4%. IR: 1702 s, 1685 s, 1583 m, 1438 s, 1406 m, 1385 s, 1304 m, 1281 m, 1234 m, 1222 m, 1034 m, 996 m, 805 m, 773 s, 743 m, 507 m cm^{-1}. ^{1}H NMR ($CDCl_3$, δ): 3.06–5.35 (C_5H_4, CH, CH_2, 15 H, m), 7.35–8.77 (C_6H_4N, 12 H, m).

Crystal structural determination of **4**

Crystal data. $C_{34}H_{29}Cl_2FeN_3O_3$, $M = 654.35$, triclinic, space group $P\bar{1}$, $a = 7.478(4)$, $b = 10.725(5)$, $c = 18.627(9)$ Å, $\alpha = 90.89(3)$, $\beta = 92.66(3)$, $\gamma = 93.29(3)^\circ$, $U = 1489.6(13)$ Å^3, $Z = 2$, $F(000) = 676$, $D_c = 1.459$ g cm^{-3}, λ(Mo-K_α) = 0.71073 Å, $T = 120(2)$ K, μ(Mo-K_α) = 0.727 mm^{-1}. Full details are given in Table 1.

Data collection and refinement. Data were collected on a Siemens–Stoe AED four-circle diffractometer using a crystal of dimensions $0.27 \times 0.26 \times 0.19$ mm by the $2\theta/\omega$ method ($7.0 \leqslant 2\theta \leqslant 45.0^\circ$). Of a total of 4020 reflections, 3860 were unique ($R_{int} = 0.0973$). The structure was solved by direct methods (SHELXTL PLUS)[12] and refined by full-matrix least-squares analysis on F^2 (SHELX93)[13] to R_1 0.0381 [$I > 2\sigma(I)$, for 3517 reflections] and wR_2 0.1633 (all data) $\{R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma wF_o^4]^{1/2}$, $w = 1/[\sigma^2(F_o^2)+(xP)^2+yP]$, $P = (F_o^2+2F_c^2)/3\}$. The largest peak and hole in the final difference map were +0.80, −1.15 e Å^{-3}, respectively. Bond angles and bond distance are given in Table 2.

RESULTS AND DISCUSSION

Scheme 1 shows two potential routes that we considered for the synthesis of 1,1′-[2,2′:6′,2″-terpyridin-4′-yl]ferrocene (**1**). Route 1 uses the Krohnke methodology[14] in which the enone 1,1′-di[3-oxo-3-(2-pyridyl)propyl]ferrocene (**2**), obtained from the reaction of ferrocene-1,1′-dicarbaldehyde with 2 equiv. of 2-acetylpyridine is isolated as an intermediate.[8] Short reaction times and stoichiometric amounts of 2-acetylpyridine favour the formation of **2**, which is smoothly converted to **1** upon reaction with N-[2-oxo-2-(2-pyridyl)-ethyl]pyridinium iodide and an excess of ammonium acetate.[8] In the second route, we envisaged the formation of the 1,5-dione (**3**) from the reaction of ferrocene-1,1′-dicarbaldehyde with 4 equiv. of 2-acetylpyridine.[15] The formation of **3** was expected to be favoured when an excess of 2-acetylpyridine and long reaction times were used. We have previously shown that the reaction of ferrocenecarbaldehyde and 2-acetylpyridine under these conditions yields 3-ferrocenyl-1,5-bis-(2-pyridyl)-1,5-pentanedione.[5]

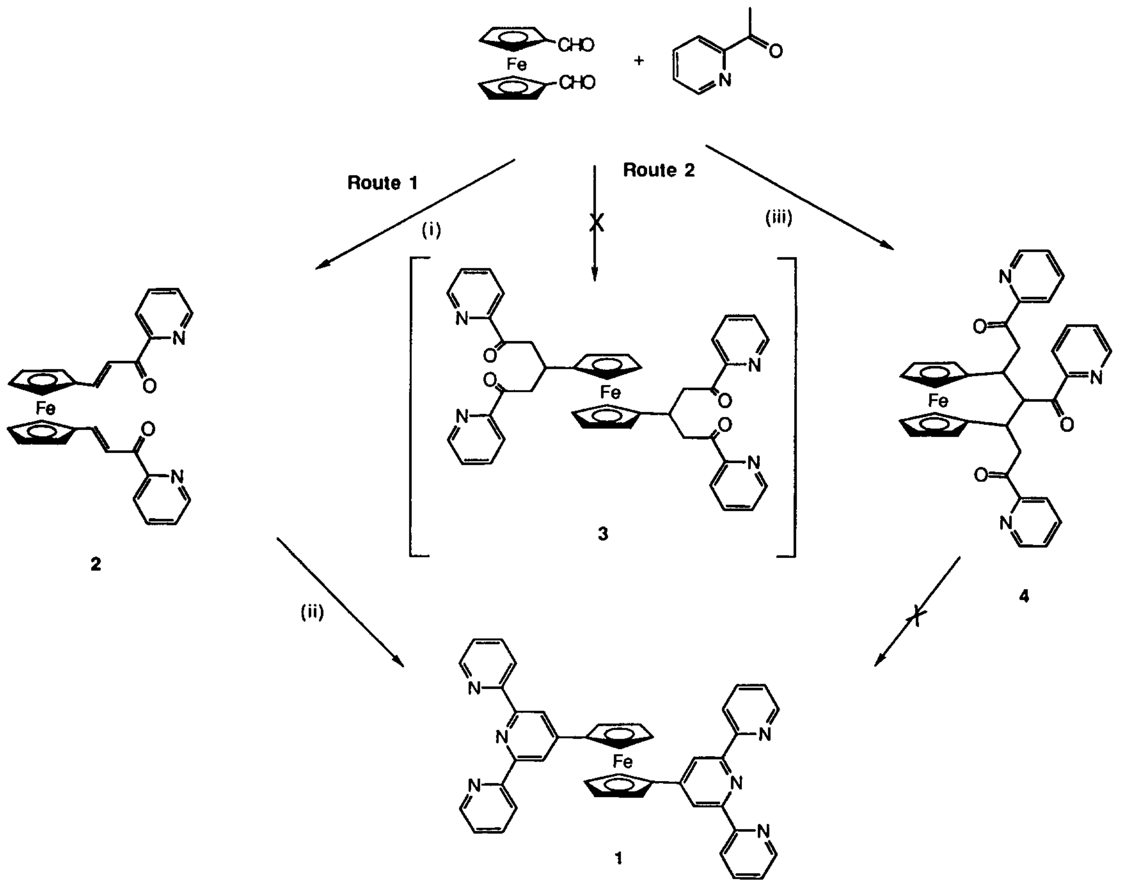
After reacting for 24 h in basic aqueous ethanol, a mixture of ferrocene-1,1′-dicarbaldehyde and 5 equiv. of 2-acetylpyridine precipitated a yellow crystalline solid (**4**). The IR spectrum of this compound shows two strong bands in the carbonyl region at 1702 and 1685 cm^{-1}, along with several absorptions characteristic of 2-pyridyl and ferrocenyl groups. The ketone **3** is expected to exhibit only a single absorption in the carbonyl region at about 1695 cm^{-1},[5,6,9,10,15,16] and the existence of several bands strongly suggests the presence of two or more different types of ketone group. The ^{1}H NMR spectrum of a $CDCl_3$ solution of the yellow com-

Table 1. Crystal data and structure refinement for **4**

Identification code	ram12
Empirical formula	$C_{34}H_{29}Cl_2FeN_3O_3$
Formula weight	654.35
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit-cell dimensions	$a = 7.478(4)$ Å, $\alpha = 90.89(3)°$
	$b = 10.725(5)$ Å, $\beta = 92.66(3)°$
	$c = 18.627(9)$ Å, $\gamma = 93.29(3)°$
V (Å^3)	1489.6(13)
Z	2
Density (calculated) (Mg m^{-3})	1.459
Absorption coefficient (mm^{-1})	0.727
$F(000)$	676
Crystal size (mm)	0.27 × 0.26 × 0.19
θ range for data collection (°)	3.54–22.50
Index ranges	$-8 \leqslant h \leqslant 8$, $-11 \leqslant k \leqslant 11$, $0 \leqslant l \leqslant 20$
Reflections collected	4020
Independent reflections	3860 ($R_{int} = 0.0973$)
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3858/0/388
Goodness-of-fit on F^2	1.317
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0381$, $wR_2 = 0.1184$
R indices (all data)	$R_1 = 0.0562$, $wR_2 = 0.1633$
Largest diff. peak and hole (e Å^{-3})	0.803 and −1.148

Table 2. Selected bond lengths (Å) and angles (°) for **4**

Fe(1)—C(1)	2.006(3)	Fe(1)—C(1′)	2.021(3)
Fe(1)—C(5)	2.023(4)	Fe(1)—C(2′)	2.032(3)
Fe(1)—C(5′)	2.035(3)	Fe(1)—C(4′)	2.047(3)
Fe(1)—C(3′)	2.046(3)	Fe(1)—C(3)	2.052(4)
Fe(1)—C(4)	2.054(4)	Fe(1)—C(2)	2.037(4)
C(1)—C(43)	1.512(5)	C(1′)—C(46)	1.511(5)
C(15)—C(44)	1.511(5)	C(21)—C(41)	1.506(5)
C(31)—C(48)	1.511(5)	C(41)—O(1)	1.219(4)
C(41)—C(42)	1.513(5)	C(42)—C(43)	1.529(5)
C(43)—C(45)	1.580(5)	C(44)—O(3)	1.218(4)
C(44)—C(45)	1.513(5)	C(45)—C(46)	1.554(5)
C(46)—C(47)	1.540(5)	C(47)—C(48)	1.511(5)
C(48)—O(2)	1.215(4)		
O(1)—C(41)—C(21)	119.6(3)	O(1)—C(41)—C(42)	122.3(3)
C(21)—C(41)—C(42)	118.1(3)	C(41)—C(42)—C(43)	112.5(3)
C(1)—C(43)—C(42)	111.4(3)	C(1)—C(43)—C(45)	112.7(3)
C(42)—C(43)—C(45)	111.6(3)	O(3)—C(44)—C(15)	120.0(3)
O(3)—C(44)—C(45)	123.1(3)	C(15)—C(44)—C(45)	116.8(3)
C(44)—C(45)—C(46)	114.6(3)	C(44)—C(45)—C(43)	105.1(3)
C(46)—C(45)—C(43)	114.2(3)	C(1′)—C(46)—C(47)	108.8(3)
C(1′)—C(46)—C(45)	110.5(3)	C(47)—C(46)—C(45)	110.7(3)
C(48)—C(47)—C(46)	112.7(3)	O(2)—C(48)—C(31)	119.4(3)
O(2)—C(48)—C(47)	122.2(3)	C(31)—C(48)—C(47)	118.4(3)



Scheme 1. (i) ETOH, NaOH (2 M in water), 0°C, 30 min; (ii) ETOH, N-[1-oxo-2-(2-pyridyl)ethyl]pyridinium iodide, $[NH_4][O_2CCH_3]$, 2 h, 80°C; (iii) EtOH, NaOH (2 M in water), room temperature, 24 h, excess of 2-acetylpyridine.

pound shows two group of resonances in the ranges δ 3.06–5.35 and 7.35–8.77. The signals in the range δ 3.06–5.35 integrate to a total of 15 H, but we have not been able to achieve a complete assignment of them. However, the group of signals integrating to 12H in the region where pyridine ring protons are expected clearly shows the presence of three non-equivalent 2-pyridyl groups. Signals at δ 8.77, 8.60 and 8.53 appear as doublets ($J_{5,6} \approx 6$ Hz) and are assigned to the H_6 protons of three 2-pyridyl groups. The overlapping sets of signals at 7.50 (3H) 7.42 (3H) and 7.35 (3H) are assigned to the H_5, H_4 and H_3 protons of three 2-pyridyl rings.

The above data strongly suggest that instead of **3**, a compound with only three pyridyl groups has been obtained. This is supported by the FAB mass spectrum which showed no peaks asigned to **3**, but a parent ion at m/z 569. The mass spectrum is compatible with a product formed from the condensation of 1 equiv. of ferrocene-1,1′-dicarbaldehyde with 3 equiv. of 2-acetylpyridine and the loss of two molecules of water. We also noted that the reaction of the yellow compound with an excess of ammonium acetate did not result in the formation of **1**.

In order to fully characterize this product we have undertaken a single-crystal determination of **4**. Suitable crystals were grown by the slow diffusion of hexane into a dichloromethane solution of the compound. The structural determination reveals **4** to be 3,5-[1,1′-ferrocenediyl]-1,7-dioxo-1,7-di(2-pyridyl)-4-(2-pyridylcarbonyl)heptane. The compound crystallizes with a molecule of dichloromethane in the lattice. A view of the molecule is presented in Fig. 1 and bond distances and angles are listed in Table 2. The structure confirms the formation of a product from 1 equiv. of ferrocene-1,1′-dicarbaldehyde and 3 equiv. of 2-acetylpyridine. The two cyclopentadiene rings are linked by a three-carbon bridge, to give a central 1,3-(1,1′-ferrocenediyl)propane moiety. To each of the terminal carbon atoms of the bridge, a 2-oxo-2-pyridyl group is attached, Finally, the central carbon of the bridge bears a 2-pyridylcarbonyl substituent. The

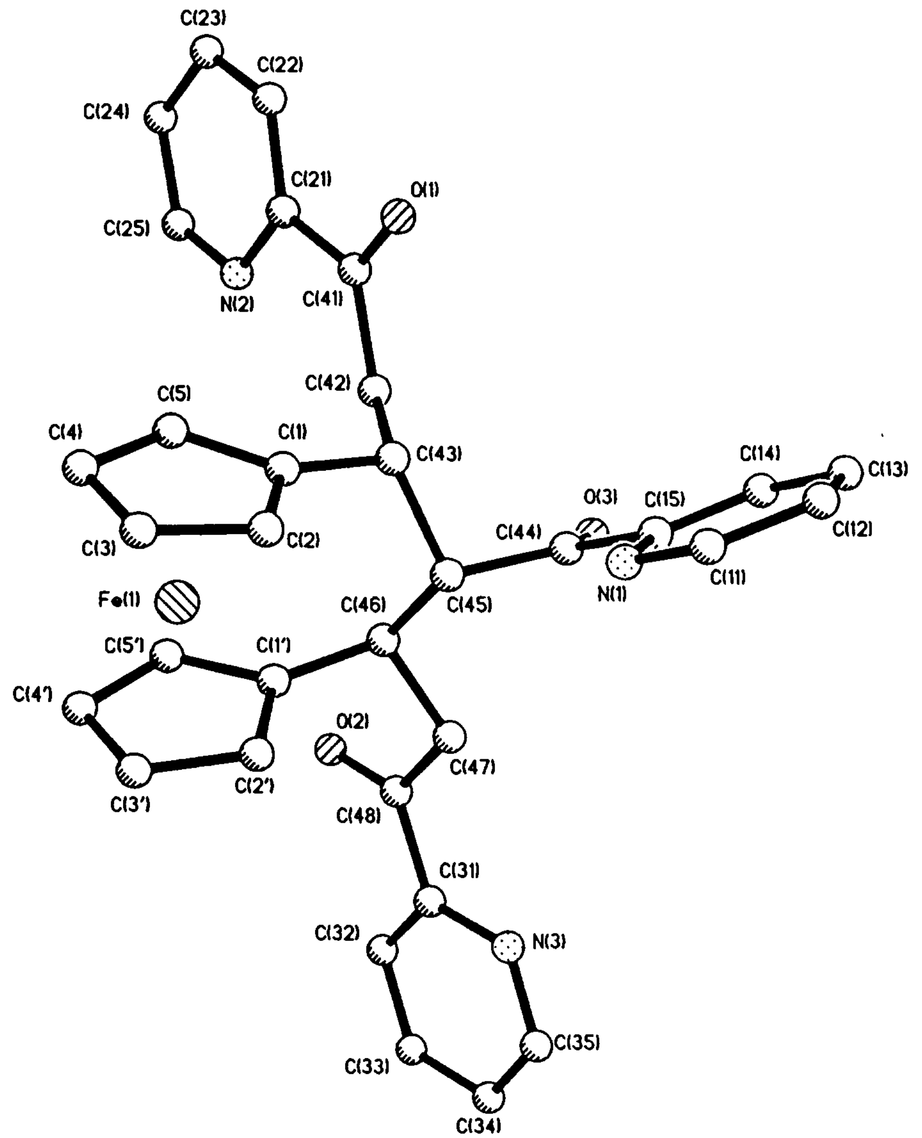
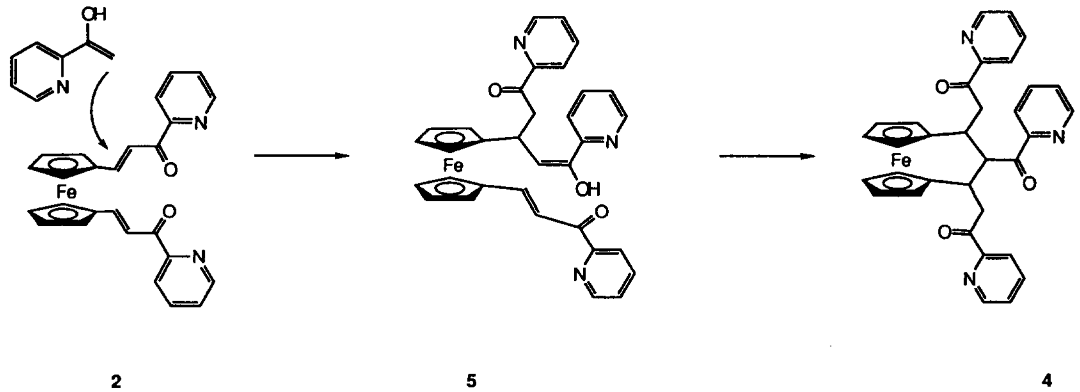


Fig. 1. Crystal and molecular structure of **4** showing the numbering scheme adopted.



Scheme 2. A possible scheme for the formation of **4**.

two cyclopentadienyl rings are not co-planar, and there is an angle between the C(1)—C(5) and C(1′)—C(5′) planes of 9.1° as a consequence of the three carbon bridge. The cyclopentadienyl intraring C—C distances are typical and range from 1.437(5) to 1.427(5) Å. The dimensions within the pyridyl rings are typical. Solvent loss at room temperature resulted in degradation of the crystals and the data were collected using low-temperature procedures. The three carbons in the propyl group are chiral, and it is interesting to note that of all the different diastereoisomers that could have been isolated the unique enantiomeric pair in **4** was obtained. There was no evidence for the formation of any other diastereomers in the reaction.

Although we have no mechanistic data, we suggest that **4** arises from **2** through an intermediate of type **5** (Scheme 2).

The electrochemical behaviour of compound **4** in CH_2Cl_2 solution has been studied. Cyclic voltammetry experiments show a single reversible iron(II)/(III) process at +0.014 mV vs the ferrocene–ferrocenium couple. The ΔE_p value was close to that obtained for ferrocene and i_a/i_c ratio equal to unity. No well defined processes were obtained at negative potentials within the solvent window.

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Note added in proof: After this work was submitted, an independent report of the same compound appeared.[17]

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