The redox behaviour of ferrocenyl alcohols and ferrocenediyl-diols: crystal and molecular structure of ferrocenyl(2-furyl)phenylmethanol ☆

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Abstract

Cyclic voltammetry and controlled-potential coulometry show that ferrocenyl alcohols of type $(C_5H_5)Fe(C_5H_4)C(OH)RR'$ and ferrocenediols of type $Fe[(C_5H_4)CCR'(OH)]_2$ undergo quantitative and reversible one-electron oxidation at the metal centre, and that the redox potentials are controlled predominantly by the inductive effects of the substituents at the α-carbon. The crystal structure of the new alcohol ferrocenyl(2-furyl)phenylmethanol not only confirms its molecular constitution, but also demonstrates that in the solid state it forms centrosymmetric hydrogen-bonded dimers involving cyclic $(OH)_2$ bridge without any participation of the furan oxygen atom in the hydrogen bonding.

Keywords: Iron; Ferrocene; Ferrocenyl alcohols; Electrochemistry; Crystal structure

1. Introduction

One of the best known properties of ferrocene molecules is their ability to lose one electron at potential values which are a function of the electron-donating ability of the substituents attached to the cyclopentadienyl rings [2]. In many cases such electron removal gives rise to unstable ferrocenium species. In continuation of our interest in elucidating the redox properties of ferrocenes and studying the stability of their ferricenium congeners [1], we report here on the electrochemical behaviour of a series of α-ferrocenyl alcohols and the related ferrocene-1,1'-diyl diols (Scheme 1).

The crystal structures of complexes 3 [3], 4 [4], 6 [5], 11 [5], 15 [6], 17 [7], 19 [7], 20 [5], and 21 [3] have already been reported, while that of 13 is reported here. The electrochemistry of a few members of the present

series has been already briefly reported, namely 1 [8–11], 2 [11,12], 4 [13], 16 [10,14], and 17 [11,15].

2. Experimental details

2.1. Synthesis

Compounds 1–6, 10–12, and 15–21 were prepared by published procedures [3–15]. New compounds 7–9 and 14 were prepared by reaction of phenyllithium with the corresponding acylferrocenes FcCOR [16], (throughout this paper, $Fc = (C_5H_5)Fe(C_5H_4)$). In this manner were prepared:

(i) $FcCPh(OH)C_2H_5$, (7). Found: C, 71.9; H, 6.2%. $C_{19}H_{20}FeO$ requires C, 71.3; H, 6.3%. NMR (CDCl$_3$): δ_H 0.82 (t, 3H, CH$_3$); 2.11 (q, 2H, CH$_2$); 2.53 (s, br, 1H, OH); 3.96 (m, 1H), 4.12 (m, 1H), 4.24 (m, 1H), 4.36 (m, 1H) (C$_5$H$_4$); 4.21 (s, 5H, C$_5$H$_5$); 7.1–7.5 (m, 5H, C$_6$H$_5$); δ_C 29.6 (q, CH$_3$); 35.9 (t, CH$_2$); 66.5 (d), 66.6 (d), 67.6 (d), 68.0 (d) and 101.2 (s) (C$_5$H$_4$); 68.2 (d, C$_5$H$_5$); 74.5 (s, C–OH); 125.5 (d), 126.1 (d), 127.5 (d) and 145.4 (s) (C$_6$H$_5$).
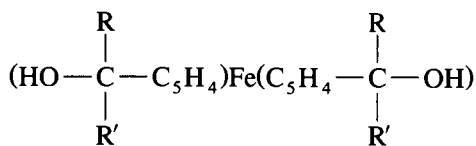

$$(C_5H_5)Fe(C_5H_4 \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}} OH)$$
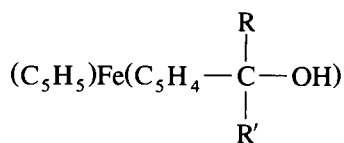
R = H,	R' = H	1	R = Ph,	R' = Me	6
	R' = Me	2		R' = Et	7
	R' = Bu^t	3		R' = Pr^n	8
	R' = Ph	4		R' = Pr^i	9
	R' = Bz	5		R' = Bu^t	10
				R' = Ph	11
				R' = Bz	12
				R' = 2-C$_4$H$_3$O	13
				R' = 2-C$_4$H$_3$S	14

R = Bu^t,　　R' = (C$_5$H$_5$)Fe(C$_5$H$_4$)　　15

$$(HO \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}} C_5H_4)Fe(C_5H_4 \overset{\overset{\displaystyle R}{|}}{\underset{\underset{\displaystyle R'}{|}}{C}} OH)$$

R = H,	R' = H	16	R = Ph, R' = Me	19
	R' = Me	17	R = Ph	20
	R' = Ph	18		
R = Me,	R' = Me	21		

Scheme 1.

(ii) FcCPh(OH)CH$_2$CH$_2$CH$_3$, (8). Found: C, 71.8; H 6.7. C$_{20}$H$_{22}$FeO requires C, 71.9; H, 6.6%. NMR (CDCl$_3$): δ_H 0.86 (t, 3H, CH$_3$); 1.54 (m, 2H, CH$_2$); 2.06 (m, 2H, CH$_2$); 2.64 (s, br, 1H, OH); 3.96 (m, 1H), 4.10 (m, 1H), 4.16 (m, 1H), 4.37 (m, 1H) (C$_5$H$_4$); 4.18 (s, 5H, C$_5$H$_5$); 7.1–7.4 (m, 5H, C$_6$H$_5$); δ_C 14.4 (q, CH$_3$); 16.9 (t, CH$_2$); 45.7 (t, CH$_2$); 66.5 (2 × d), 67.6 (d), 68.0 (d) and 101.3 (s) (C$_5$H$_4$); 68.2 (d, C$_5$H$_5$); 74.3 (s, C–OH); 120.1 (d), 123.1 (d), 126.0 (d) and 145.7 (s) (C$_6$H$_5$).

(iii) FcCPh(OH)CH(CH$_3$)$_2$, (9). Found: C, 71.8; H, 6.7%. C$_{20}$H$_{22}$FeO requires C, 71.9; H, 6.6%. NMR (CDCl$_3$): δ_H 0.71 (d 3H, CH$_3$); 1.04 (d, 3H, CH$_3$); 2.20 (septet, 1H, CH); 2.57 (s, br, 1H, OH); 3.96 (m, 1H), 4.12 (m, 1H), 4.18 (m, 1H), 4.40 (m, 1H) (C$_5$H$_4$); 4.01 (s, 5H, C$_5$H$_5$); 7.2–7.5 (m, 5H, C$_6$H$_5$); δ_C 18.3 (q, CH$_3$); 19.1 (q, CH$_3$); 39.1 (d, CH); 67.8 (d), 67.9 (d), 68.5 (d), 68.7 (d) and 99.4 (s) (C$_5$H$_4$); 69.0 (d, C$_5$H$_5$); 77.6 (s, C–OH); 126.2 (d), 126.7 (d), 127.9 (d) and 147.0 (s) (C$_6$H$_5$).

(iv) FcCPh(OH)C$_4$H$_3$S, (14). Found: C, 67.4; H, 5.1%. C$_{21}$H$_{18}$FeOS requires C, 67.4; H, 4.9%. NMR (CDCl$_3$): δ_H 3.54 (s, br, 1H, OH); 3.96 (m, 1H), 4.11 (m, 1H), 4.14 (m, 1H), 4.20 (m, 1H) (C$_5$H$_4$); 4.18 (s, 5H, C$_5$H$_5$); 6.65 (m, 1H), 6.90 (m, 1H), 7.2–7.5 (m, 6H) (C$_4$H$_3$ and C$_6$H$_5$); δ_C 67.3 (d), 67.9 (d), 68.5 (d), 69.1 (d) and 99.4 (s) (C$_5$H$_4$); 68.7 (d, C$_5$H$_5$); 75.5 (s,

C–OH); 124.4 (d), 125.5 (d), 125.9 (d) and 152.3 (s) (C$_4$H$_3$); 126.3 (d), 127.0 (d), 127.4 (d) and 146.2 (s) (C$_6$H$_5$).

In like manner, FcCPh(OH)(2-furyl) (13) was prepared from 2-furyllithium [17] and benzoylferrocene. Found: C, 70.9; H, 4.7%. C$_{21}$H$_{18}$FeO$_2$ requires C, 70.4; H, 5.0%. NMR (CDCl$_3$): δ_H 3.38 (s, br, 1H, OH); 4.1–4.4 (m, 9H, C$_5$H$_5$ and C$_5$H$_4$); 6.03 (m, 1H), 6.31

Table 1
Summary of crystal data, data collection, structure solution and refinement details for compound 13

(a) Crystal data	
Empirical formula	C$_{21}$H$_{18}$FeO$_2$
Molar mass	358.20
Colour, habit	yellow–orange, plate
Crystal size (mm)	0.35×0.30×0.10
Crystal system	triclinic
a (Å)	7.828(3)
b (Å)	11.299(2)
c (Å)	19.673(4)
α (°)	92.236(13)
β (°)	93.56(2)
γ (°)	105.35(2)
V (Å^3)	1672.0(8)
Space group	$P\bar{1}$
Z	4 (two independent molecules)
F(000)	744
d_{calc}(g cm^{-3})	1.423
μ (mm^{-1})	0.911
(b) Data acquisition [a]	
Temperature (k)	294(1)
Unit-cell reflections (θ range, °)	25 (9.3–13.3)
Max. θ(°) for reflections	26.90
hkl range of reflections	−9 9; 0 14; −25 25
Variation in 3 standard reflections	< 1.0%
Reflections measured	7237
Unique reflections	7237
Reflections with $I > 2\sigma(I)$	4382
Absorption correction type	Ψ-scans
min., max. absorption correction	0.784, 0.995
(c) Structure solution and refinement [b]	
Refinement on	F^2 with all measured data
Solution method	Patterson heavy atom
H-atom treatment	riding, C–H 0.95, O–H 0.82 Å
No. of variables in least-squares	472
k in $w = 1/(\sigma^2Fo^2 + k)$ [$P = (Fo^2 + 2Fc^2)/3$]	$(0.0899\,P)^2$
R, R_w, goodness of fit	0.054, 0.132, 0.95
Density range in final Δ-map (e Å^{-3})	−0.85, 0.62
Final shift/error ratio	0.004

[a] Data collection on an Enraf-Nonius CAD4 diffractometer with graphite monochromatised Mo-K α radiation (λ 0.7107 Å).
[b] All calculations were done on a Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs [19] and with SHELXL-93 [20] for refinement with all data on F^2.

(m, 1H) and 7.42 (m, 1H) (C$_4$H$_3$O); 7.2–7.4 (m, 5H) (C$_6$H$_5$); δ_C 66.8 (d), 68.0 (2 × d), 68.5 (d) and 97.1 (s) (C$_5$H$_4$); 68.6 (d, C$_5$H$_5$); 73.9 (s, C–OH); 107.3 (d),

109.8 (d), 141.7 (d) and 158.5 (s) (C$_4$H$_3$); 126.4 (d), 127.2 (d), 127.5 (d) and 143.9 (s) (C$_6$H$_5$). Identity confirmed and structure established by X-ray analysis.

Table 2
Atomic coordinates for compound **13** [a]

	x	y	z	U_{eq}
Fe1A	0.09108(7)	0.71346(5)	0.42321(3)	0.0415(2)
Fe1B	0.27698(6)	0.71938(5)	0.87859(3)	0.0446(2)
Cp1a	−0.04418	0.73686	0.47980	
Cp2a	0.21912	0.68864	0.36356	
Cp1b	0.08260	0.61636	0.86830	
Cp2b	0.47014	0.82534	0.88692	
O1A	0.3424(4)	0.9604(2)	0.53858(14)	0.0571(7)
O1B	0.3264(3)	0.4592(2)	0.96588(12)	0.0490(6)
O2B	0.3117(3)	0.3775(3)	0.78484(13)	0.0557(7)
C1A	0.2310(4)	0.8586(3)	0.5695(2)	0.0429(8)
C11A	0.0828(5)	0.7891(3)	0.5185(2)	0.0399(8)
C12A	−0.0072(6)	0.8442(4)	0.4684(2)	0.0542(10)
C13A	−0.1474(6)	0.7508(5)	0.4348(2)	0.0668(13)
C14A	−0.1446(5)	0.6383(4)	0.4628(2)	0.0599(11)
C15A	−0.0045(5)	0.6619(3)	0.5145(2)	0.0451(8)
C21A	0.3483(5)	0.7516(4)	0.3961(2)	0.0577(10)
C22A	0.2408(6)	0.7921(4)	0.3469(2)	0.0637(11)
C23A	0.1044(6)	0.6891(5)	0.3208(2)	0.0690(13)
C24A	0.1260(6)	0.5860(4)	0.3535(2)	0.0647(12)
C25A	0.2761(6)	0.6244(4)	0.4005(2)	0.0621(11)
C31A	0.3407(4)	0.7779(3)	0.5960(2)	0.0466(8)
O2A	0.2713(12)	0.6909(7)	0.6410(4)	0.063(3)
C32A	0.5019(11)	0.7704(12)	0.5822(9)	0.082(5)
C33A	0.5387(13)	0.6747(13)	0.6203(10)	0.097(7)
C34A	0.4043(18)	0.6371(14)	0.6593(9)	0.106(7)
O2C	0.4576(11)	0.7467(7)	0.5540(4)	0.067(3)
C32C	0.3462(17)	0.7239(10)	0.6547(3)	0.063(3)
C33C	0.4602(27)	0.6458(16)	0.6479(6)	0.095(7)
C34C	0.5343(16)	0.6690(12)	0.5892(6)	0.074(4)
C41A	0.1569(5)	0.9129(3)	0.6300(2)	0.0465(9)
C42A	0.2702(7)	1.0032(4)	0.6726(2)	0.0667(12)
C43A	0.2056(11)	1.0527(5)	0.7277(3)	0.094(2)
C44A	0.0328(11)	1.0113(6)	0.7414(3)	0.097(2)
C45A	−0.0781(9)	0.9225(6)	0.7009(3)	0.093(2)
C46A	−0.0175(6)	0.8729(4)	0.6447(2)	0.0654(12)
C1B	0.2381(4)	0.4337(3)	0.8986(2)	0.0363(7)
C11B	0.1541(4)	0.5366(3)	0.8811(2)	0.0392(8)
C12B	0.0835(5)	0.6051(4)	0.9289(2)	0.0563(10)
C13B	0.0132(5)	0.6885(4)	0.8927(3)	0.0720(14)
C14B	0.0381(5)	0.6735(4)	0.8231(3)	0.0687(13)
C15B	0.1241(5)	0.5781(3)	0.8157(2)	0.0501(9)
C21B	0.5374(5)	0.7584(4)	0.9151(2)	0.0593(11)
C22B	0.4515(7)	0.8367(5)	0.9466(3)	0.088(2)
C23B	0.3920(7)	0.9019(4)	0.8937(5)	0.106(3)
C24B	0.4413(7)	0.8576(5)	0.8323(3)	0.087(2)
C25B	0.5285(6)	0.7721(4)	0.8469(3)	0.0692(13)
C31B	0.3727(4)	0.4217(3)	0.8493(2)	0.0378(7)
C32B	0.5518(5)	0.4516(4)	0.8549(2)	0.0597(11)
C33B	0.6044(6)	0.4234(5)	0.7897(2)	0.0667(12)
C34B	0.4591(6)	0.3784(4)	0.7501(2)	0.0632(11)
C41B	0.0999(4)	0.3100(3)	0.9010(2)	0.0385(7)
C42B	0.1562(5)	0.2104(4)	0.9236(2)	0.0538(10)
C43B	0.0364(6)	0.0980(4)	0.9275(2)	0.0647(12)
C44B	−0.1400(6)	0.0817(4)	0.9083(2)	0.0687(13)
C45B	−0.1951(6)	0.1773(4)	0.8854(3)	0.0689(13)
C46B	−0.0763(5)	0.2921(4)	−0.8813(2)	0.0538(10)

[a] Site occupation factors for O(2A), C(32A), C(33A) and C(34A) refined to 0.48(2); site occupation factors for O(2C), C(32C), C(33C) and C(34C) refined to 0.52(2).

2.2. Electrochemistry

The materials and apparatus for electrochemistry have been described elsewhere [18]. All the potential values are referred to the Saturated Calomel Electrode (S.C.E.).

2.3. X-ray crystallography

Crystals of compound **13** suitable for X-ray examination were grown by slow evaporation of a solution in light petroleum (b.p. 40–60°C). Details of crystal data, data collection, structure solution and refinement are summarized in Table 1. There are two independent molecules in the asymmetric unit, here denoted by A and B. In molecule A only, the furan ring adopts two conformations, differing by a rotation of ca. 150°C about the C(1A)–C(31A) bond. In order to stabilise the refinement of these disordered rings it was necessary to constrain them to be planar with bond lengths: C–O, 1.375(1) Å, C=C, 1.330(1) Å, C–C(ring), 1.420(1) Å

Table 3
Selected molecular dimensions for **13**

(a) Bond lengths (Å)

	Molecule A	Molecule B
C(11)–C(12)	1.431(5)	1.423(5)
C(12)–C(13)	1.413(6)	1.406(6)
C(13)–C(14)	1.410(7)	1.406(7)
C(14)–C(15)	1.411(5)	1.421(6)
C(15)–C(11)	1.415(5)	1.413(5)
Fe–Cp(1)	1.644	1.648
C(21)–C(22)	1.411(6)	1.395(7)
C(22)–C(23)	1.409(7)	1.424(9)
C(23)–C(24)	1.395(7)	1.404(9)
C(24)–C(25)	1.410(6)	1.352(7)
C(25)–C(21)	1.407(6)	1.355(6)
Fe–Cp(2)	1.652	1.656
C(1)–C(11)	1.510(5)	1.521(5)
C(1)–O(1)	1.430(4)	1.436(4)
C(1)–C(31)	1.496 [a]	1.504(5)
C(1)–C(41)	1.532(5)	1.528(5)
C(31)–C(32)	1.330 [a]	1.349(5)
C(32)–C(33)	1.420 [a]	1.422(6)
C(33)–C(34)	1.330 [a]	1.309(6)
C(34)–O(2)	1.375 [a]	1.375(5)
O(2)–C(31)	1.374 [a]	1.354(4)
C(31A)–C(32C)	1.329 [a]	
C(32C)–C(33C)	1.420 [a]	
C(33C)–C(34C)	1.329 [a]	
C(34C)–O(2C)	1.374 [a]	
O(2C)–C(31A)	1.374 [a]	

(b) Torsion angles (°)

	Molecule A	Molecule B
C(1n)–Cp(1)–Cp(2)–C(2n) (mean)	−7.4(2)	−16.8(8)
O(1)–C(1)–C(11)–C(12)	−37.1(4)	−32.7(4)
C(31)–C(1)–C(11)–C(12)	−158.6(3)	−152.5(3)
C(41)–C(1)–C(11)–C(12)	80.0(4)	84.2(4)
C(11)–C(1)–C(41)–C(42)	−164.1(3)	−173.3(2)
C(11)–C(1)–C(31)–C(32)	104.6(12)	106.5(4)
C(11)–C(1)–C(31)–O(2)	−72.9(7)	−70.4(4)
C(11)–C(1)–C(31)–C(32C)	−103.0(9)	
C(11)–C(1)–C(31)–O(2C)	74.8(6)	
O(1)–C(1)–C(31)–O(2)	165.2(6)	169.2(3)
O(1)–C(1)–C(31)–O(2C)	−47.1(6)	

(c) Hydrogen–bond distances and angles

	Molecule A		Molecule B
O(1A) · · · O(1A)[I]	2.932(14)	O(1B) · · · O(1B)[II]	2.857(4)
O(1A)–H(1A) · · · O(1A)[I]	114	O(1B)–H(1B) · · · O(1B)[II]	116

Symmetry positions

I $1 - x, 2 - y, 1 - z$ II $1 - x, 1 - y, 2 - z$
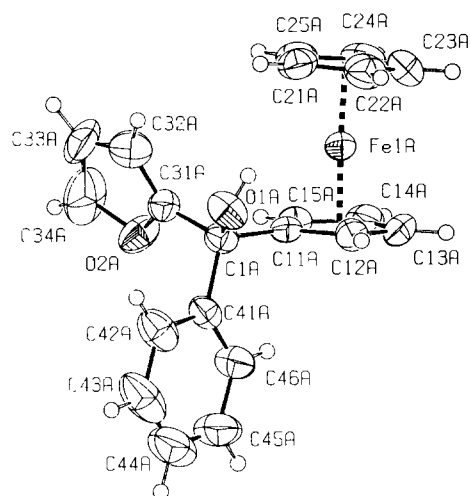
[a] Constrained refinement, see text.

Fig. 1. View of molecule A of compound 13, showing the atom-labelling scheme. Thermal ellipsoids are drawn at the 30% probability level.
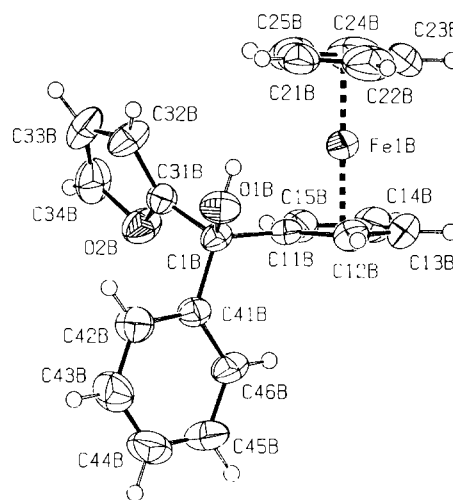

Fig. 2. View of molecule B of compound 13, showing the atom-labelling scheme. Thermal ellipsoids are drawn at the 30% probability level.

and C–C (exocyclic) 1.495(1) Å. Subject to these constraints, the site occupation factors for the two orientations refined to 0.48(2) and 0.52(2). In the Tables, the atoms comprising the second orientation are labelled O(2C), C(32C), C(33C) and C(34C). Examination of the refined structure using PLATON [21] revealed no solvent-accessible voids in the crystal structure. Final refined atom coordinates are given in Table 2: selected geometrical parameters are given in Table 3. Figs. 1 and 2 show the perspective views of the two independent molecules, with the atom-labelling schemes, and were prepared using ORTEP-II [22] as implemented in PLATON [21]. Fig. 3 shows the packing of the unit-cell contents and was prepared using PLUTON [23]. Tables of H-atom coordinates and thermal parameters, and a full list of

bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

Compounds of type FcCPh(OH)R are readily formed by reaction of phenyllithium with the corresponding acylferrocene FcCOR [4]. Further examples having R = C_2H_5 (7), $CH_2CH_2CH_3$ (8), $CH(CH_3)_2$ (9) and (2-thienyl) (14) have been prepared for the purposes of the present study. All were characterised straightforwardly by a combination of elemental analysis and ^{1}H and ^{13}C NMR spectroscopy; in each case, the stereogenic carbon atom bonded to OH causes all the carbons of the
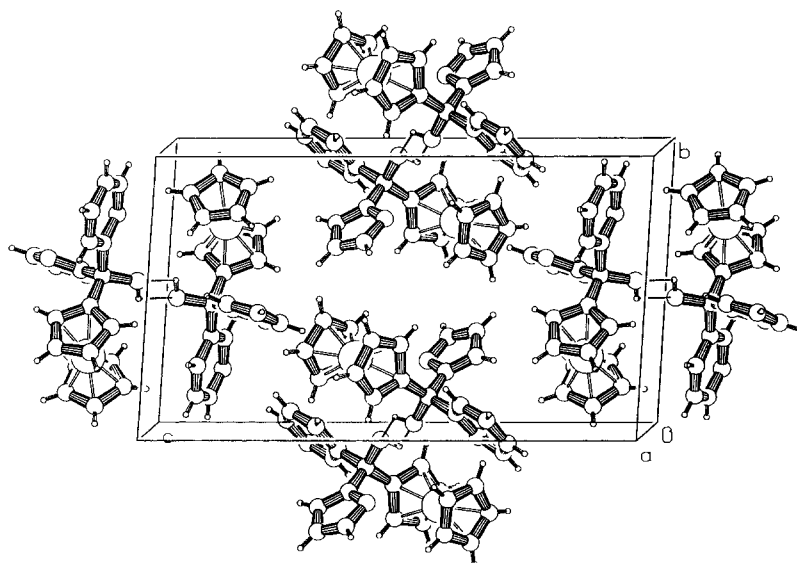

Fig. 3. A view of the crystal structure of 13.

substituted cyclopentadiene ring to be chemically and magnetically distinct, allowing easy spectral characterisation. The acylferrocene FcCO(2-furyl) is not easily accessible, and the corresponding alcohol FcCPh-(OH)(2-C_4H_3O) (13) was therefore synthesised by the complementary route using 2-furyl-lithium and benzoyl-ferrocene. The ^1H resonances of the C_5H_5 and C_5H_4 rings in compound 13 were not resolvable, nor were all the ^{13}C resonances of the C_5H_4 ring: although the analytical and spectroscopic evidence was consistent with the proposed formulation of 13 it was not definitive. Consequently, the structure of 13 was confirmed by single-crystal X-ray structure analysis.

3.1. Crystal and molecular structure of compound 13

The racemic form of ferrocenyl (2-furyl)phenyl-methanol crystallises in the triclinic space group $P\bar{1}$ with two molecules, denoted by A and B, in the asymmetric unit; the centrosymmetric space group accommodates equal numbers of the R and S enantiomers. In molecule A, the 2-furyl group adopts two conformations with site occupation factors which are equal within experimental error: these conformations differ by a rotation of 152(1)° about the C(1A)–C(31A) bond.

The molecules form centrosymmetric dimeric aggregates held together by hydrogen bonds involving only the hydroxyl groups and forming a cyclic (OH)$_2$ bridge with graph set R_2^2 (4) [24,25]. Molecules of type A form a dimer about the centre of inversion at ($\frac{1}{2}$, 0, $\frac{1}{2}$) and molecules of type B form a dimer about the centre of inversion at ($\frac{1}{2}$, $\frac{1}{2}$, 0) (Fig. 3). It is noteworthy that the oxygen atoms of the furan ring take no part in the intermolecular hydrogen bonding; this accounts for the rotational freedom about the exocyclic C–C bond of the furan in molecule A, which allows the orientational disorder. Application of Etter's postulate [24] thus suggests that the oxygen of the furan ring is less basic than the hydroxyl oxygen atom. The hydrogen-bond motif observed here is identical to that observed in the dimer of ferrocenyldiphenylmethanol, FcCPh$_2$OH [26]. However, despite the constitutional similarities between Fc-CPh$_2$OH and compound 13 and their similar molecular volumes, 445.7(1) Å^3 and 418(1) Å^3, respectively, these compounds are not isostructural, having, respectively, two and four molecules in their triclinic unit cells.

Although there are two independent molecules in the asymmetric unit of compound 13, their intramolecular bond lengths and angles are virtually identical, and apart from the rotational disorder of the furan rings in molecule A, their conformations are also very similar. For both molecular units the ferrocenyl rings are nearly eclipsed, as shown by the mean values of the C(1n)–Cp(1)–Cp(2)–C(2n) torsion angles, −7.4(2)° in molecule A and −16.8(8)° in molecule B: values of

zero and 36.0° correspond to perfect eclipsing and perfect staggering respectively. As often observed in monosubstituted ferrocenes, the mean C–C distance is significantly longer for the substituted ring, 1.415(6) Å, than for the unsubstituted ring, 1.396(7) Å. The other intramolecular distances are typical of their types [27,28].

In each molecule, the projection of the C(1)–C(41) bond (that to the phenyl ring) is almost perpendicular to the C(11)–C(15) plane, while the phenyl ring itself is almost parallel to the C(1)–C(11) bond (Table 2). Similarly, for molecule B and one conformer of molecule A, the O(1)–C(1)–C(31)–O(2) torsion angles indicate that the two oxygen atoms are *trans* to one another, effectively precluding in this conformation any intramolecular O–H ⋯ O hydrogen bonding analogous to the intramolecular O–H ⋯ N hydrogen bonding observed in diphenyl(2-pyridyl)methanol [29].

In each molecule, A and B, there is a close approach of one C–H bond of the substituted cyclopentadienyl ring to the furan oxygen atom; for the two conformations of molecule A, the C15A ⋯ O2A and C21A ⋯ O2C distances are 3.139(5) Å and 3.176(5) Å respectively, with apparent H ⋯ O distances of 2.62 Å and 2.71 Å, while in molecule B the C15B ⋯ O2B distance is 3.071(5) Å, with an apparent H ⋯ O distance of 2.55 Å. These C ⋯ O distances may be compared, on the one hand, with the close intermolecular O ⋯ C distances of 3.525(4) Å in PhCH$_2$CPh$_2$OH [30] and 3.302(3) Å in PhC≡CCPh$_2$OH [29], both of which form dimeric aggregates held together only by C–H ⋯ π(arene) interactions and on the other hand with the shortest O ⋯ C distance of 3.487(3) Å in the intramolecular O–H ⋯ π(C$_5$H$_5$) interactions involving an unsubstituted cyclopentadienyl ring observed in Fc-CPh(OH)CH$_3$ [26]. The observation of a cyclopentadienyl ring acting as a hydrogen-bond donor, rather than as a hydrogen-bond acceptor is unusual in the ferrocene series: the graph set for this interaction is S(6).
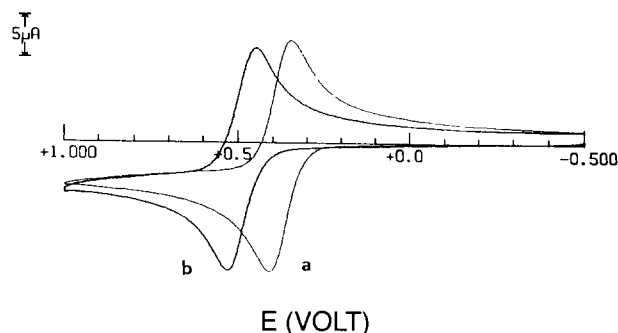

Fig. 4. Cyclic voltammograms recorded at a platinum electrode on CH$_2$Cl$_2$ solutions containing [NBu$_4$][ClO$_4$] (0.2 mol dm^{-3}) and: (a) 3 (1.1×10^{-3} mol dm^{-3}); (b) 20 (1.0×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

Table 4
Formal electrode potentials (V vs. S.C.E.) and peak-to-peak separation (in mV) for the one-electron oxidation of the series FcC(OH)RR'

R	R'	$E^{\varnothing}_{0/+}$	ΔE_p [a]	$E^{\varnothing}_{+/2+}$	ΔE_p [a]	Solvent	Reference
H	H (1)	+0.42	90			CH$_2$Cl$_2$	[b]
		+0.31				MeCN	[8]
		+0.36				MeCN	[9]
		+0.40				MeCN	[10]
		+0.39				MeCN	[11]
		+0.46				Me$_2$CO	[11]
		+0.49				DMF	[11]
		+0.40				DMSO	[11]
	Me (2)	+0.40	74			CH$_2$Cl$_2$	[b]
		+0.29				MeCN	[12]
		+0.37				MeCN	[11]
		+0.45				Me$_2$CO	[11]
	^{t}Bu (3)	+0.38	70			CH$_2$Cl$_2$	[b]
	Ph (4)	+0.41	70			CH$_2$Cl$_2$	[b]
		+0.53				CH$_2$Cl$_2$	[13]
		+0.51				THF	[13]
	Bz (5)	+0.40	78			CH$_2$Cl$_2$	[b]
Ph	Me (6)	+0.43	76			CH$_2$Cl$_2$	[b]
	Et (7)	+0.41	70			CH$_2$Cl$_2$	[b]
	^{n}Pr (8)	+0.40	82			CH$_2$Cl$_2$	[b]
	^{i}Pr (9)	+0.38	80			CH$_2$Cl$_2$	[b]
	^{t}Bu (10)	+0.40	72			CH$_2$Cl$_2$	[b]
	Ph (11)	+0.44	76			CH$_2$Cl$_2$	[b]
	Bz (12)	+0.43	68			CH$_2$Cl$_2$	[b]
	2-furyl (13)	+0.44	74			CH$_2$Cl$_2$	[b]
	2-thienyl (14)	+0.45	74			CH$_2$Cl$_2$	[b]
^{t}Bu	Fc (15)	+0.35	74	+0.52	72	CH$_2$Cl$_2$	[b]
	FcH	+0.44	88			CH$_2$Cl$_2$	[b]

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

3.2. Electrochemistry

Fig. 4 compares the response of the ferrocenyl complex 3, which bears one strong electron-donating butyl group, with that of the ferrocene-1,1'-diyl complex 20, which bears two electron-withdrawing phenyl groups. As can easily be seen, the voltammetric profiles possess features of chemical reversibility and their separation in redox potentials is of about 0.1 V.

Table 5
Formal electrode potentials (V vs S.C.E.) and peak-to-peak separation (mV) for the one-electron oxidation of the series R'RC(OH)FcdC(OH)RR' [Fcd = (C$_5$H$_4$)Fe(C$_5$H$_4$)]

R	R'	$E^{\varnothing}$	ΔE_p [a]	Solvent	Reference
H	H (16)	+0.39	60	CH$_2$Cl$_2$	[b]
		+0.40		MeCN	[10]
		+0.22		H$_2$O (pH 7)	[14]
	Me (17)	+0.37	76	CH$_2$Cl$_2$	[b]
		+0.56		CH$_2$Cl$_2$	[15]
		+0.37		MeCN	[11]
	Ph (18)	+0.42	68	CH$_2$Cl$_2$	[b]
Ph	Me (19)	+0.45	72	CH$_2$Cl$_2$	[b]
	Ph (20)	+0.49	74	CH$_2$Cl$_2$	[b]
Me	Me (21)	+0.39	78	CH$_2$Cl$_2$	[b]

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

In both cases controlled potential coulometric tests show that the anodic process involves the consumption of one electron per molecule. In confirmation of the full chemical reversibility of the ferrocene/ferrocenium step, cyclic voltammetric tests performed on the two exhaustively oxidised solutions display voltammetric profiles complementary to those shown in Fig. 4.
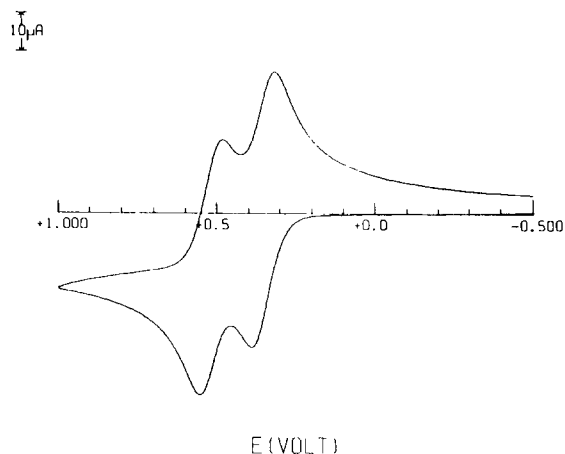

Fig. 5. Cyclic voltammogram recorded at a platinum electrode on a CH$_2$Cl$_2$ solution containing [NBu$_4$] [ClO$_4$] (0.2 mol dm^{-3}) and 15 (1.4×10^{-3} mol dm^{-3}). Scan rate 0.2 V s^{-1}.

Table 6

Visible spectrophotometric measurements on the ferrocenyl alcohols and their electrogenerated ferricenium congeners in dichloromethane solution (containing [NBu$_4$][ClO$_4$] (0.2 mol dm^{-3}))

Complex	λ_{max} (nm)	ε (M^{-1} cm^{-1})	Complex	λ_{max} (nm)	ε (M^{-1} cm^{-1})
1	435	170	[1]$^+$	628	432
2	440	161	[2]$^+$	629	614
3	438	162	[3]$^+$	627	776
4	440	219	[4]$^+$	630	545
5	452	55	[5]$^+$	631	618
6	440	200	[6]$^+$	631	664
7	440	108	[7]$^+$	632	554
8	442	182	[8]$^+$	632	630
9	442	180	[9]$^+$	638	810
10	440	162	[10]$^+$	630	850
11	445	191	[11]$^+$	633	807
12	460	300	[12]$^+$	636	634
13	441	212	[13]$^+$	638	763
14	444	139	[14]$^+$	634	984
15	457	414	[15]$^+$	620	814
			[15]$^{2+}$	629	1223
16	435	195	[16]$^+$	621	664
17	440	174	[17]$^+$	641	47 [a]
18	442	221	[18]$^+$	656	611
19	445	207	[19]$^+$	657	341
20	443	186	[20]$^+$ [b]	657	612
21	439	169			

[a] Partial decomposition of the monocation occurs.

[b] Full decomposition of the monocation occurs.

Analysis [31] of the cyclic voltammetric responses of the two complexes with scan rate varying from 0.02 to 10.24 V s^{-1} show typical parameters diagnostic of electrochemically reversible one-electron removals. As a matter of fact, in both cases, the i_{pc}/i_{pa} ratio is constantly equal to unity, the current function $i_{pa}\, v^{-1/2}$ remains constant, and the peak-to-peak separation progressively increases from 60 to 90 mV in the range from 0.02 to 0.5 V s^{-1}, then it departs to a greater extent from the value of 59 mV theoretically expected for an electrochemically reversible one-electron process. Indeed, this trend in ΔE_p was also recorded for the one-electron oxidation of unsubstituted ferrocene, and so we attribute this departure to uncompensated solution resistances. The electrochemical reversibility of the oxidation steps confirms that the electron removal does not cause significant structural reorganisation of the original molecular frameworks [3,5].

Table 7

Correlation analysis between the electronic effects of the substituents R and R' in the two series FcC(OH)RR' and R'RC(OH)FcdC(OH)RR' and the relevant redox potentials [a]

Series	ΣF vs. E^σ	ΣR vs. E^σ	$\Sigma\sigma_p$ vs. E^σ
FcC(OH)RR'	0.73	0.14	0.80
R'RC(OH)FcdC(OH)RR'	0.97	-0.33	0.35

[a] Electronic effects from Ref. [34].

All the other complexes exhibit quite similar anodic processes at potential values that, as shown in Tables 4 and 5, are not significantly affected by the nature of the substituents. With the help of Fig. 5, which shows the cyclic voltammetric profile of 15, we can comment on the redox properties of this bisferrocenyl complex, in comparison with those of the corresponding ferrocenyl derivative 3.

(i) The fact that the two ferrocenyl subunits gives rise to two separate, electrochemically reversible, one-electron oxidations suggests that the two iron(II) subunits are electronically communicating. The comproportionation constant value $K_c \approx 750$ for [15]$^+$, which can be computed from the separation between the two oxidation steps [32], suggests it should belong to the slightly delocalised, weakly interacting, Robin-Day's "Class II" mixed valent species [33].

(ii) The fact that the first anodic anodic step occurs at potential values 30 mV lower than that of 3 indicates that the ferrocenyl unit is more electron-donating than the hydrogen atom.

(iii) Finally, the fact that step-by-step controlled potential coulometry shows that both of the anodic steps are also chemically reversible provides evidence of the stability of the present framework in all the oxidation states Fe(II)Fe(II)/Fe(II)Fe(III)/Fe(III)Fe(III).

Visible spectrophotometric measurements performed before and after exhaustive anodic oxidation of all

complexes show that the corresponding (from green to blue) monocations are stable and that the electron removals are iron-centred, Table 6. Only in the case of complexes **17** and **21** was slow degradation of the corresponding monocation observed.

Attempts were made to correlate the redox potentials listed in Tables 4 and 5 with the electronic effects of the substituents R and R' in the two series FcC(OH)RR' and R'RC(OH)FcdC(OH)RR' and the relevant results are summarised in Table 7. As far as the ferrocenyl alcohols are concerned, if it is assumed that electronic effects essentially govern the localisation of the redox potential of the electron removals (neglecting for instance steric effects), we can tentatively propose that there is a predominance of inductive (F parameter) over resonance (R parameter) effects, even if the correlation coefficient of the best relationship ($\Sigma \sigma_p$ vs. E^α, where the σ_p parameter represents the sum of the two contributions) is still low. This proposal receives support from the results obtained for the corresponding ferrocendiyl alcohols.

Acknowledgements

References

[1] Preceding paper in the series: P. Zanello, G. Opromolla, G. Giorgi, G. Sasso and A. Togni, *J. Organomet. Chem.*, in press.

[2] W.E. Geiger, *J. Organomet. Chem. Libr.*, 22 (1990) 142.

[3] Y. Li, G. Ferguson, C. Glidewell and C.M. Zakaria, *Acta Cryst.*, C50 (1994) 857.

[4] G. Ferguson, J.F. Gallagher, C. Glidewell and C.M. Zakaria, *J. Organomet. Chem.*, 464 (1994) 95.

[5] G. Ferguson, J.F. Gallagher, C. Glidewell and C.M. Zakaria, *Acta Cryst.*, C49 (1993) 967.

[6] H.K. Sharma, F. Cervantes-Lee and K.H. Pannell, *J. Organomet. Chem.*, 438 (1992) 183.

[7] J.F. Gallagher, G. Ferguson, C. Glidewell and C.M. Zakaria, *Acta Cryst.*, C50 (1994) 18.

[8] H. Hennig and O. Gürtler, *J. Organomet. Chem.*, 11 (1968) 307.

[9] C. Le Vanda, K. Bechgaard, D.O. Cowan and M.D. Rausch, *J. Am. Chem. Soc.*, 99 (1977) 2964.

[10] M. Hillman and J.D. Austin, *Organometallics*, 6 (1987) 1737.

[11] H. Scholl and K. Sochai, *Electrochim. Acta*, 34 (1989) 915.

[12] T. Kuwana, D.E. Bublitz and G. Hoh, *J. Am. Chem. Soc.*, 82 (1960) 5811.

[13] N.E.N.P.R.A. Silva, A.J.L. Pombeiro J.J.R. da Silva, R. Herrmann, N. Deus, T.J. Castilho and M.F.C.G. Silva, *J. Organomet. Chem.*, 421 (1991) 75.

[14] R. Szentrimay, P. Yeh, and T. Kuwana, in: D.T. Sawyer, (ed.), *Electrochemical Studies of Biological Systems* ACS Symp. Ser., 1977 143.

[15] A. Al-Saed, E.A. Seddon, K.R. Seddon, A.A. Shimran, S. Tompkins, M.C. Grossel and J.P. Knychala, *J. Organomet. Chem.*, 347 (1988) C25.

[16] G. Ferguson, J.F. Gallagher, C. Glidewell and C.M. Zakaria, *J. Organomet. Chem.*, 464 (1994) 95.

[17] D.J. Chadwick and C. Willbe, *J. Chem. Soc., Perkin Trans.* 2 (1977) 887.

[18] A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech and H. Keller *Organometallics*, 13 (1994) 1224.

[19] E.J. Gabe, Y. Le Page, J.-P. Charland, F.L. Lee and P.S. White, *J. Appl. Cryst.*, 22 (1989) 384.

[20] G.M. Sheldrick, SHELXL-93. Program for the refinement of crystal structures, University of Göttingen, Germany.

[21] A.L. Spek, PLATON molecular geometry program, University of Utrecht, The Netherlands.

[22] C.K. Johnson, ORTEP-II, Thermal ellipsoid plot program, Tech. Rep. ORNL-538, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

[23] A.L. Spek, PLUTON molecular graphics program University of Utrecht, The Netherlands.

[24] M.C. Etter, *Acc. Chem. Res.*, 23 (1990) 120.

[25] M.C. Etter, J.C. McDonald and J. Bernstein, *Acta Crystallogr., Sect B.*, 46 (1990) 256.

[26] G. Ferguson, J.F. Gallagher, C. Glidewell and C.M. Zakaria, *Acta Crystallogr., Sect C*, 49 (1993) 967.

[27] F.H. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans 2*, (1987) S1.

[28] A.G. Orpen, L. Brammer, F.H. Allen, O. Kennard, D.G. Watson and R. Taylor, *J. Chem. Soc., Dalton Trans.*, (1989) S1.

[29] G. Ferguson, C.D. Carroll, C. Glidewell, C.M. Zakaria and A.J. Lough, *Acta Crystallogr., Sect B*, 51 (1995) 367.

[30] G. Ferguson, J.F. Gallagher, C. Glidewell and C.M. Zakaria, *Acta Crystallogr., Sect C*, 50 (1994) 70.

[31] E.R. Brown and J. Sandifer, in: B.W. Rossiter and J.F. Hamilton (eds.), *Physical Methods of Chemistry: Electrochemical Methods*, Wiley, New York, 1986, Vol. 2, Chap. 4.

[32] D.E. Richardson and H. Taube, *Inorg. Chem.*, 20 (1981) 1278.

[33] R.R. Gagné, C.A. Kowal, T.J. Smith and M.C. Cimolino, *J. Am. Chem. Soc.*, 101 (1979) 4571.

[34] C. Hansch, A. Leo and R.W. Taft, *Chem. Rev.*, 91 (1991) 165.