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The redox behaviour of some bis-ferrocenyl compounds: crystal and molecular structures of diferrocenylmethane and diferrocenylmethanol ¹

George Ferguson ^{a,*}, Christopher Glidewell ^{b,*}, Giuliana Opromolla ^c,
Choudhury M. Zakaria ^b, Piero Zanello ^{c,*}

^a Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ont. N1G 2W1, Canada

^b School of Chemistry, University of St. Andrews, St. Andrews, Fife KY16 9ST, UK

^c Dipartimento di Chimica dell'Università di Siena, Pian dei Mantellini 44, I-53100 Siena, Italy

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Abstract

Electrochemistry of diferrocenylmethane (1), diferrocenylketone (2), diferrocenylmethanol (3), diferrocenyl(phenyl)methanol (4), bis(1-ferrocenylpropyl) ether (5), 3,3-bis(ferrocenylmethyl)pentane-2,4-dione (6), 2,2-bis(ferrocenylmethyl)cyclohexane-1,3-dione (7) and *trans*-1,2-diferrocenylethene (8) shows that one-electron oxidation of the individual ferrocenyl sub-units takes place through: (i) separated charge transfers for 2 and 4; (ii) nearly overlapping steps for 1, 3 and 8; and (iii) single steps for each of 5, 6 and 7. This reflects the extent of electronic communication between the two redox centres, which is relatively high in the first case, decreases for the second series and is negligible for the third series. The crystal structure of diferrocenylmethanol 3 demonstrates that in the solid state the molecules are aggregated into centrosymmetric pairs with an O...O distance of 3.020(3) Å. The hydroxyl hydrogen atoms are disordered, but one pattern of site occupancy gives rise to a closed (OH)₂ dimer with hydrogen-bonding graph set R₂²(4). The crystal structure of diferrocenylmethane 1 contains isolated molecules having almost the same conformation and molecular volume as 3.

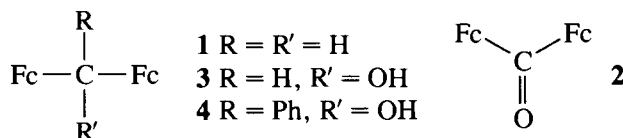
Keywords: Iron; Ferrocene; Crystal structure; Electrochemistry

1. Introduction

In a recent study of the electrochemical behaviour of a range of ferrocenyl alcohols and ferrocenediyl-diols, it was observed [2] that in the bis-ferrocenyl alcohol, 1,1-diferrocenyl-2,2-dimethylpropan-1-ol, Fc₂C(CMe₃)OH [Fc = (C₅H₅)Fe(C₅H₄)], the two ferrocenyl units gave rise to separate, electrochemically-reversible, one-electron oxidations; the two iron sub-units are electronically communicating, and the conproportionation constant $K_C \approx 750$ indicates that the monocation [Fc₂C(CMe₃)OH]⁺ is an example of the slightly delocalised, weakly-interacting class II mixed-valence

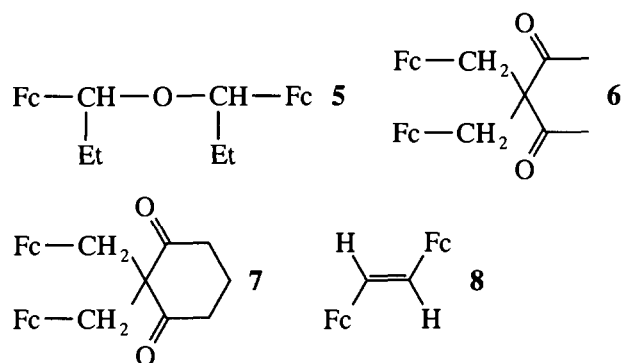
species within the Robin–Day classification [3,4]. We have now studied the electrochemical behaviour of a number of other bis-ferrocenyl compounds 1–8 in which the two ferrocenyl units are separated by a variety of different spacer units.

The crystal structures of compounds 2 [5], 4 [6] and 5 [7] have already been reported, as has that of Fc₂C(CMe₃)OH, closely-related to 4 [8], and we report here the structures of compounds 1 and 3. While the structure of compound 8, 1,2-diferrocenylethylene, has not been reported, that of the closely-related 1,2-bis(1'-ethyl-1-ferrocenyl)-1,2-dimethylethylene has been recorded [9].



* Corresponding authors.

¹ Part XII of the series "The redox behaviour of ferrocene molecules". For Part XI, see Ref. [1].



2. Experimental

2.1. Synthesis

Published procedures were used for the preparation of compounds **1** [10], **2** [11], **3** [10], **6** [12], **7** [12] and **8** [13]. NMR: **1**: $\delta(\text{C})$ 30.0 (t, CH_2); 67.2(d), 68.4(d) and 88.5(s) (C_5H_4); 68.6(d, C_5H_5). **2**: $\delta(\text{C})$ 70.0(d, C_5H_5); 70.6(d), 71.4(d) and 80.5(s) (C_5H_4); 199.3(s, CO). **3**: $\delta(\text{C})$ 66.2(d), 67.2(d), 67.7(d), 67.8(d) and 92.9(s) (C_5H_4); 68.1(d, COH); 68.5 (d, C_5H_5). **8**: $\delta(\text{C})$ 67.1(d), 69.5(d) and 85.3(s) (C_5H_4); 70.1(d, C_5H_5); 124.5(d, $-\text{CH}=\text{}$).

Compound **4** was prepared by reaction of **2** with phenyl-lithium [14]. NMR: $\delta(\text{C})$ 67.0(d), 67.3(d), 68.0(d), 68.2(d) and 99.8(s) (C_5H_4); 68.6(d, C_5H_5);

73.6(s, OH); 126.3(d), 127.0(d), 128.7(d) and 146.7(s) (C_6H_5). Identity confirmed and structure established by X-ray analysis [5].

2.1.1. Preparation of compound 5

A solution of propionylferrocene (2.42 g, 10.0 mmol) in dry tetrahydrofuran (50 cm^3) was added with stirring to a cooled solution of LiAlH_4 (0.015 g) in dry tetrahydrofuran (50 cm^3). The mixture was boiled under reflux for 2 h, and then ethyl acetate was added to destroy excess reductant. To this mixture were added in turn water (0.5 cm^3), ethanol (2.5 cm^3) and diethyl ether (5 cm^3); the resulting suspension was filtered through Hyflo-supercel, and the filtrate was dried over Na_2SO_4 . After removal of the solvent, the resulting deep-yellow oil was dissolved in a mixture of dichloromethane and light petroleum (b.p. 40–60°C). Slow evaporation gave compound **5** as orange crystals in 60% yield, m.p. 125°C. Anal. Found: C, 66.9; H, 6.5. $\text{C}_{26}\text{H}_{30}\text{Fe}_2\text{O}$ Calc.: C, 66.4; H, 6.4%. NMR: $\delta(\text{H})$ 0.80(t, 3H, CH_3); 1.62–1.98(m, 2H, CH_2); 4.15(s, 5H, C_5H_5); 4.05–4.20(m, 5H, C_5H_4 and CH); $\delta(\text{C})$ 11.0(q, CH_3); 29.3(t, CH_2); 66.2(d), 66.8(d), 67.8(d) 68.4(d) and 90.7(s) (C_5H_4); 75.3(d, CH). Identity confirmed and structure established by X-ray analysis [7].

2.2. Electrochemistry

The materials and apparatus for electrochemistry have been described elsewhere [15]. All the potential values

Table 1

Electrochemical characteristics for the oxidation processes of the bis(ferrocenes) **1**–**8** and related molecules with the Robin–Day classification of the relevant mixed-valent species

Compound	$E_{0/+}^{\circ}$ (V)	$E_{+/2+}^{\circ}$ (V)	ΔE_p (mV) ^a	K_{con}	Robin–Day class	Solvent	Ref.
1	+0.30	+0.42	106	1×10^2	II	CH_2Cl_2	^b
	+0.26 ^c	+0.37 ^c					[19]
	+0.39	+0.56					[20]
	+0.30	+0.40					90% EtOH
2	+0.55	+0.74	78	1×10^3	II	CH_2Cl_2	^b
	+0.35	+0.47					[22]
3	+0.39	+0.49	78	1×10^2	II	CH_2Cl_2	^b
	+0.34	+0.53					[22]
4	+0.36	+0.47	78	1×10^3	II	CH_2Cl_2	^b
	+0.42	+0.41 ^c					[II] ^d
6	+0.41	+0.47	78	8	[I–II] ^d	CH_2Cl_2	^b
	+0.31	+0.47					[I–II] ^d
7	+0.25 ^c	+0.41 ^c	78	5×10^2	II	CH_2Cl_2	^b
	+0.35	+0.52					[19]
$\text{Fc}_2\text{C}(\text{CMe}_3)\text{OH}$	+0.35	+0.52	120	750	II	CH_2Cl_2	[2]
$\text{FcCH}_2\text{CH}_2\text{Fc}$	+0.35	+0.46	120	22	II	CH_2Cl_2	^b
	+0.28 ^c	+0.60					[19]
	+0.37	+0.79					[20]
$\text{FcCH}_2\text{OCH}_2\text{Fc}$	+0.46	+0.60	85	2×10^2	II	CH_2Cl_2	[22]
	+0.44	+0.79					[23]
$\text{FcC}\equiv\text{CFc}$	+0.44	+0.79	85	8×10^5	III	CH_2Cl_2	[23]
$\text{Fc}-\text{Fc}$	+0.44	+0.79	85	8×10^5	III	CH_2Cl_2	[23]
FcH	+0.44	+0.79	85	8×10^5	III	CH_2Cl_2	^b

^a Peak-to-peak separation for single-stepped processes, measured at 0.2 V s^{-1} . ^b Present work. ^c Measured at -30°C . ^d See text.

are referred to the saturated calomel electrode (SCE). In situ UV–visible spectrophotometric measurements during macroelectrolysis experiments were made using a Perkin-Elmer Lambda-5 fibre-optic system. The electrochemical characteristics for the oxidation processes are reported in Table 1, and the spectrophotometric data are given in Table 2.

2.3. X-ray crystallography

Crystals of compounds **1** and **3** suitable for single-crystal X-ray diffraction were grown by slow evaporation of solutions in dichloromethane + light petroleum (b.p. 40–60°C). Repeated attempts to grow crystals of compounds **6**, **7** and **8** suitable for single-crystal diffraction have been unsuccessful.

Compounds **1** and **3** crystallised in the triclinic and monoclinic systems respectively. For **1**, the space group $P\bar{1}$ was assumed and confirmed by the analysis; for **3**, the space group $P2_1/c$ was uniquely assigned from the systematic absences. Details of crystal data and data collection and refinement are given in Table 3. For compound **3**, difference maps showed that the hydroxyl hydrogen atom was disordered over two sites with equal occupancy. The ORTEP diagrams (Figs. 2 and 3) were prepared using ORTEP-II [16], as implemented in PLATON [17]; the plot of the hydrogen-bonded dimer of compound **3** was made using PLUTON [18]. Examination of both refined structures using PLATON showed that there were no solvent-accessible voids in the crystal lattice. Refined atomic coordinates are given in Tables 4 and 5, and selected structural parameters in Table 6.

3. Results and discussion

The reduction of acyl ferrocenes FcCOR using LiAlH_4 normally proceeds smoothly to provide high yields of the corresponding racemic alcohols FcCH(OH)R [14]. However, in the case of $\text{R} = \text{C}_2\text{H}_5$, we have observed that instead of the expected FcCH(OH) C_2H_5 , the sole product formed is compound **5**, the

dehydration product from the expected alcohol. Only a single diastereoisomer of **5** was observed, and X-ray analysis showed [7] that the product was a racemic mixture of the *RR* and *SS* forms; hence, the *meso-RS* form is absent, indicating stereoselectivity in the dehydration process.

3.1. Electrochemistry

The different cyclovoltammetric responses exhibited by the present diferrocene derivatives are exemplified in Fig. 1. Under features of chemically reversible voltammetric profiles, compound **2** undergoes two distinct oxidations (with minor adsorption effects present at low scan rates on the reverse scan); compound **1** exhibits two almost overlapping oxidation processes; finally, compound **6** undergoes a single-stepped oxidation process. Controlled potential coulometry proves that in all cases the overall oxidation process consumes two electrons per molecule. These voltammetric curves suggest that the electronic communication between the two ferrocenyl units is well defined in **2**, decreases in **1** and is lacking in **6**.

The formal electrode potentials for the oxidation processes of compounds **1–8**, and for some related bis-ferrocenes [19–23], are collected in Table 1, together with the Robin–Day classification [3] of the relevant Fe(II)Fe(III) mixed-valent species. In the case of nearly overlapping processes their separation has been evaluated by the Richardson–Taube method [24]. As a matter of fact, the one-electron oxidized forms of compounds **1–4** and **8** belong to the *slightly delocalized* class II. This should also be the case for compound **5**, which undergoes a single-stepped two-electron oxidation but with a peak-to-peak separation notably higher than the 60 mV expected for a two-electron process involving non-interacting centres. Nevertheless, because of the possible effects of uncompensated solution resistances indicated by the departure from 60 mV recorded for the ΔE_p of ferrocene, the classification of compounds **5–7** has to be considered cautiously.

Table 2
Spectrophotometric results on the two-electron oxidation of the present bis(ferrocenes) which afford stable dications in dichloromethane solution

Compound	λ_{max} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)	Compound	λ_{max} (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
1	439	273	[1]²⁺	629	1114
3	450	197	[3]²⁺	631	1125
4	443	306	[4]²⁺	735	2860
5	444	400	[5]²⁺	628	1553
6	435	411	[6]²⁺	635	1578
7	439	356	[7]²⁺	636	1374

Looking at the whole series of complexes studied here it can be deduced that, relative to the rather strong conjugation between the ferrocenyl units of biferrocene, any insertion of carbon/oxygen bridges tends to attenuate their electronic communication, even if the physico-chemical properties of the bridges can impart different extents of attenuation [25]. The splitting-wave effects of π -bond conjugation in $\text{FcCH}=\text{CHFc}$ and $\text{FcC}\equiv\text{CFc}$ are easily seen when compared with the single anodic process exhibited by dferrocenylethane, while electronic effects easily account for the difference in redox potentials between **5** and $\text{FcCH}_2\text{OCH}_2\text{Fc}$; these effects, however, are not sufficient to overcome the barrier to the communication between ferrocenyl units.

In spite of the apparent chemical reversibility of the cyclic voltammetric responses of all the present dferrocenes, cyclic voltammetric tests performed on the exhaustively two-electron oxidized solutions pointed out partial decomposition of the electrogenerated dication $[\mathbf{2}]^{2+}$ and full decomposition of $[\mathbf{8}]^{2+}$. For the remaining compounds, the typical green-to-blue colour of iron-centred ferrocene oxidation processes was observed, Table 2.

3.2. Crystal and molecular structure of compound 1

Diferrocenylmethane crystallises in the centrosymmetric triclinic space group $P\bar{1}$ with one molecule in

Table 3
Summary of crystal data, data collection and refinement details

	Compound 1	Compound 3
<i>Crystal data</i>		
Empirical formula	$\text{C}_{21}\text{H}_{20}\text{Fe}_2$	$\text{C}_{21}\text{H}_{20}\text{Fe}_2\text{O}$
Molar mass	384.07	400.07
Colour, habit	orange, lath	orange, block
Crystal size (mm^3)	$0.42 \times 0.21 \times 0.14$	$0.41 \times 0.35 \times 0.22$
Crystal system	triclinic	monoclinic
a (\AA)	7.6041(6)	9.0048(9)
b (\AA)	10.352(2)	9.5947(12)
c (\AA)	11.226(3)	19.054(3)
α ($^\circ$)	112.28(2)	
β ($^\circ$)	90.16(2)	92.707(12)
γ ($^\circ$)	93.814(11)	
V (\AA^3)	815.5(2)	1644.4(4)
Space group	$P\bar{1}$	$P2_1/c$
Z	2	4
$F(000)$	396	824
d_{calc} (g cm^{-3})	1.564	1.616
μ (mm^{-1})	1.774	1.768
<i>Data acquisition</i> ^a		
Temperature (K)	294(1)	294(1)
Unit-cell reflections (2θ -range, $^\circ$)	20.80–40.50	20.00–24.80
Max 2θ ($^\circ$) for reflections	53.88	53.80
hkl range for reflections	–9, 9; 0, 13; –14, 13	–11, 11; 0.12; 0, 24
Decay in three standard reflections (%)	3.8	< 1
Reflections measured	3550	3782
Unique reflections	3550	3566
R_{int}	—	0.020
Reflections with $I > n\sigma(I)$, n	2356, 2	2440, 2
Min, max abs. corr.	0.5989, 0.7117	0.8107, 0.9887
<i>Structure solution and refinement</i> ^b		
Solution method	Patterson heavy-atom	Patterson heavy-atom
Final refinement	F^2 (all data)	F^2 (all data)
No. variables in LS	208	218
k in $w = 1/(\sigma^2 F_o + kF_o^2)$	0.0410	0.0430
R , R_w , GOF	0.0263, 0.0654, 1.136	0.0320, 0.0750, 1.148
Range in final Δ -map, $e \text{\AA}^{-3}$	0.363, –0.318	0.303, –0.301
Final shift/error ratio	0.000	0.060

^a Data collection on an Enraf–Nonius CAD-4 diffractometer with graphite monochromated Mo K α radiation ($\lambda = 0.7107 \text{\AA}$).

^b All calculations were done on an Silicon Graphics 4D-35TG computer system with the NRCVAX system of programs (E.J. Gabe, Y. LePage, J.-P. Charland, F.L. Lee and P.S. White, *J. Appl. Chem.*, 22 (1989) 384) and with SHELXL-93 (G.M. Sheldrick, SHELXL-93, *Program for the refinement of crystal structures*, University of Göttingen, Germany) for refinement with all data on F^2 .

Table 4

Atomic coordinates for Fc_2CH_2

Atom	x	y	z	U_{eq}
Fe1	0.02636(4)	-0.22590(3)	0.24633(3)	0.03738(10)
Fe2	0.45329(4)	0.26918(3)	0.26478(3)	0.03338(10)
C1	0.1451(3)	0.0253(2)	0.1571(2)	0.0430(6)
C11	0.0017(3)	-0.0572(2)	0.1965(2)	0.0348(5)
C12	-0.1005(3)	-0.1770(2)	0.1115(2)	0.0429(6)
C13	-0.2242(3)	-0.2220(3)	0.1845(3)	0.0508(6)
C14	-0.2000(3)	-0.1307(3)	0.3141(3)	0.0525(7)
C15	-0.0605(3)	-0.0289(2)	0.3215(2)	0.0401(5)
C21	0.2862(4)	-0.2622(3)	0.2411(4)	0.0679(9)
C22	0.1894(4)	-0.3777(3)	0.1512(3)	0.0668(8)
C23	0.0640(4)	-0.4273(3)	0.2187(4)	0.0737(9)
C24	0.0843(5)	-0.3431(4)	0.3491(4)	0.0826(11)
C25	0.2229(4)	-0.2384(4)	0.3633(3)	0.0741(10)
C31	0.2332(3)	0.1452(2)	0.2676(2)	0.0362(5)
C32	0.3670(3)	0.1394(3)	0.3545(2)	0.0441(6)
C33	0.4080(3)	0.2767(3)	0.4461(2)	0.0481(6)
C34	0.3015(3)	0.3678(3)	0.4177(2)	0.0458(6)
C35	0.1942(3)	0.2863(2)	0.3085(2)	0.0405(5)
C41	0.5336(3)	0.2032(3)	0.0792(2)	0.0497(6)
C42	0.6643(3)	0.1853(3)	0.1599(3)	0.0582(7)
C43	0.7143(3)	0.3190(3)	0.2562(3)	0.0627(8)
C44	0.6147(4)	0.4182(3)	0.2343(3)	0.0587(8)
C45	0.5035(4)	0.3459(3)	0.1244(2)	0.0528(7)
Cg1	-0.1167(3)	-0.1232(3)	0.2256(3)	
Cg2	0.1694(4)	-0.3297(4)	0.2647(4)	
Cg3	0.3008(3)	0.2431(3)	0.3589(2)	
Cg4	0.6061(4)	0.2943(3)	0.1708(3)	

Cg1 to Cg4 are the centroids of rings C11–C15, C21–C25, C31–C35 and C41–C45 respectively.

Table 5

Atomic coordinates for Fc_2CHOH

Atom	x	y	z	U_{eq}
Fe1	0.42577(4)	0.32064(4)	0.11096(2)	0.03561(11)
Fe2	0.08676(4)	0.17164(4)	-0.14106(2)	0.03563(11)
O1	-0.0192(2)	0.3464(2)	0.01427(10)	0.0571(6)
C1	0.1270(2)	0.2900(3)	0.01396(12)	0.0357(6)
C11	0.2258(2)	0.3755(3)	0.06283(12)	0.0318(5)
C12	0.2183(3)	0.3786(3)	0.13783(13)	0.0407(6)
C13	0.3252(3)	0.4757(3)	0.16419(14)	0.0473(7)
C14	0.3993(3)	0.5329(3)	0.10700(14)	0.0435(6)
C15	0.3369(3)	0.4715(3)	0.04469(13)	0.0359(5)
C21	0.4683(3)	0.1174(3)	0.0879(2)	0.0532(7)
C22	0.4733(4)	0.1370(3)	0.1611(2)	0.0599(9)
C23	0.5853(4)	0.2367(4)	0.1778(2)	0.0649(9)
C24	0.6478(3)	0.2769(3)	0.1145(2)	0.0638(9)
C25	0.5756(3)	0.2042(3)	0.0595(2)	0.0562(8)
C31	0.1820(2)	0.2821(2)	-0.05922(12)	0.0333(5)
C32	0.2837(3)	0.1808(3)	-0.08428(14)	0.0407(6)
C33	0.3061(3)	0.2098(3)	-0.15597(14)	0.0471(7)
C34	0.2200(3)	0.3273(3)	-0.17607(14)	0.0454(6)
C35	0.1443(3)	0.3729(3)	-0.11679(13)	0.0385(6)
C41	-0.0879(3)	0.0672(3)	-0.1022(2)	0.0544(8)
C42	0.0109(3)	-0.0272(3)	-0.1326(2)	0.0552(7)
C43	0.0215(3)	0.0090(3)	-0.2038(2)	0.0570(8)
C44	-0.0700(3)	0.1250(4)	-0.2180(2)	0.0600(8)
C45	-0.1384(3)	0.1608(3)	-0.1554(2)	0.0602(9)
Cg1	0.3011(3)	0.4468(3)	0.1033(2)	
Cg2	0.5501(3)	0.1944(3)	0.1202(2)	
Cg3	0.2272(3)	0.2746(3)	-0.1185(2)	
Cg4	-0.0528(3)	0.0670(3)	-0.1624(3)	

Cg1 to Cg4 are the centroids of rings C11–C15, C21–C25, C31–C35 and C41–C45 respectively.

the asymmetric unit. In contrast to the crystal structures of diferrocenyl ketone **2**, where the molecules lie on two-fold rotation axes [5], and of biferrocenyl Fc–Fc, where the molecules lie across centres of inversion [26], in the crystal structure of compound **1** the molecules exhibit no crystallographic symmetry. Indeed, the torsion angles C11–C1–C31–C32 and C31–C1–C11–C12 (Table 6) indicate that the molecular conformation (Fig. 2) is very far from either C_2 or C_s symmetry; in solution, however, conformational averaging leads to very simple NMR spectra. More striking is the remarkable conformational similarity between the molecules of compound **1** and those of compound **3** (Table 6 and Figs. 2 and 3), despite the fact that the two compounds crystallise in different space groups and with very different unit cells. Moreover, the molecules of **3** are aggregated by hydrogen bonding (see below); nevertheless, the effective molecular volumes of **1** and **3** are virtually identical at 408 and 411 Å³ respectively. This very close similarity between molecules of type R_3CH and R_3COH is reminiscent of the isomorphous pair $(PhCH_2)_3SiH$ [27] and $(PhCH_2)_3SiOH$ [28].

3.3. Crystal and molecular structure of compound 3

Diferrocenylmethanol crystallises in the centrosymmetric monoclinic space group $P2_1/c$ with one molecule in the asymmetric unit. The molecules are

arranged in pairs lying across a centre of inversion with an $O \cdots O$ distance of 3.020(3) Å (Figs. 3 and 4). The hydroxyl hydrogen atoms are disordered over two sites with equal populations, as judged from the peak heights in difference maps. The hydrogen-bonding patterns depend therefore upon the pattern of occupancy of the alternative hydroxyl hydrogen sites. Within any close pair of Fc_2CHOH molecules characterised by a short $O \cdots O$ distance, there can be two hydrogen bonds, forming a closed dimer with graph set $R_2^2(4)$; one hydrogen bond, forming an open dimer with graph set D ; or none. The proportions of close molecule-pairs exhibiting these patterns at any instant depends upon the extent to which the occupancies are correlated. An X-ray diffraction study of ferrocene-1,1'-diylbis(diphenylmethanol) $[Fe(C_5H_4CPh_2OH)_2]$ showed that the molecules are aggregated into dimeric units, with the hydroxyl hydrogen atoms disordered equally over two sites [29]. A subsequent study of the proton dynamics in this system, made using ²H and ¹³C VT-NMR in the solid state, showed that the hydroxyl hydrogen atoms are mobile and that their motion is highly correlated [30]. The preferred model for the proton mobility was rotation about C–O bonds, so that the hydroxyl hydrogen sites identified in the X-ray structure analysis represent the energy minima on the circular locus of each hydroxyl hydrogen atom. It is thus highly plausible that the disordered sites found here for Fc_2CHOH similarly

Table 6
Selected geometric parameters (distances (Å), angles (°))

	Fc_2CH_2	Fc_2CHOH
Fe1–Cg1	1.645(2)	1.653(3)
Fe1–Cg2	1.643(2)	1.653(3)
Fe2–Cg3	1.648(2)	1.646(3)
Fe2–Cg4	1.644(2)	1.645(3)
C1–C11	1.510(3)	1.501(3)
C1–C31	1.498(3)	1.503(3)
C1–O1		1.424(3)
Cg1–Fe1–Cg2	178.8(2)	179.0(2)
Cg3–Fe2–Cg4	179.2(2)	179.0(2)
C11–C1–C31	113.9(2)	113.1(2)
O1–C1–C11		108.1(2)
O1–C1–C31		111.6(2)
Mean C1 _n –Cg1–Cg2–C2 _n	2.6(2)	–8.2(3)
Mean C3 _n –Cg3–Cg4–C4 _n	4.1(2)	–5.1(1)
C11–C1–C31–C32	79.5(3)	88.3(3)
C11–C1–C31–C35	–98.0(3)	–91.4(3)
C31–C1–C11–C12	–178.9(2)	–166.9(2)
C31–C1–C11–C15	3.4(4)	16.4(3)
O1–C1–C11–C12		69.1(3)
O1–C1–C11–C15		–107.7(3)
O1–C1–C31–C32		–149.6(2)
O1–C1–C31–C35		30.7(3)

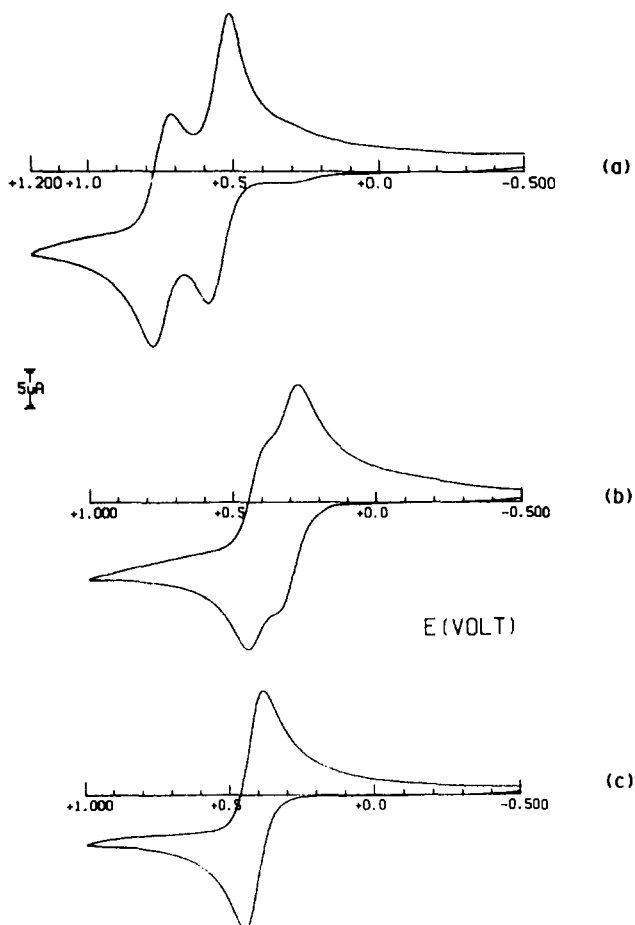


Fig. 1. Cyclic voltammograms recorded at a platinum electrode on CH_2Cl_2 solutions containing $[\text{NBu}_4][\text{PF}_6]$ (0.2 mol dm^{-3}) and: (a) **2** ($1.3 \times 10^{-3} \text{ mol dm}^{-3}$); (b) **1** ($1.1 \times 10^{-3} \text{ mol dm}^{-3}$); (c) **6** ($0.8 \times 10^{-3} \text{ mol dm}^{-3}$). Scan rate 0.1 V s^{-1} .

represent the energy minima for highly mobile hydrogen atoms. For the hydrogen sites between the oxygen atoms the $\text{O-H} \cdots \text{O}$ angle is 166° .

An extremely wide range of hydrogen-bonding patterns has been observed in the solid-state structures of monoalcohols [31,32]. In α -ferrocenyl monoalcohols, the aggregation patterns include both finite dimers and long chains, generated by screw axes (2_1 or 4_1) or by

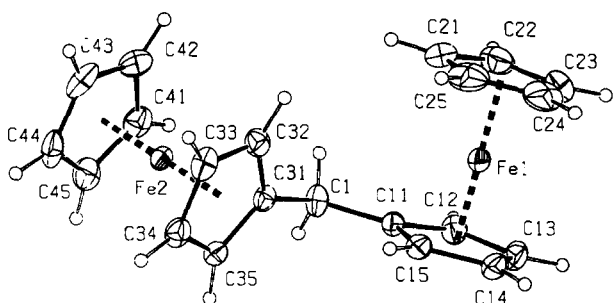


Fig. 2. A view of the molecule of **1** with our atom numbering scheme; thermal ellipsoids are drawn at the 30% probability level.

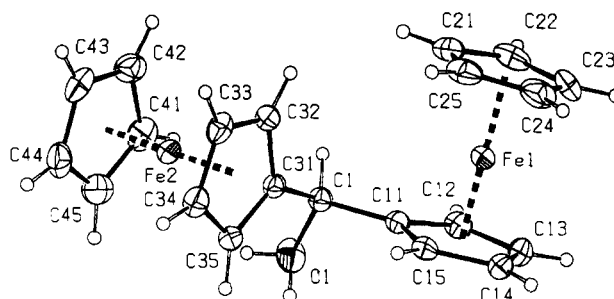


Fig. 3. A view of the molecule of **3** with our atom numbering scheme; thermal ellipsoids are drawn at the 30% probability level.

glide planes [6]. The dimers are based upon the $(\text{OH})_2$ hydrogen-bonding motif having graph set $\text{R}_2^2(4)$ [33–35]. Closed dimers containing this hydrogen-bonding motif are unknown amongst simple organic alcohols, and its occurrence has recently been described [31] as “highly improbable”. Nonetheless, in α -ferrocenyl alcohols this is actually a rather common motif, occurring in five of the 13 examples of such alcohols which have previously been structurally characterised [6].

Diferrocenylmethanol has proved to be yet a further example of the closed dimers formed in the ferrocenyl alcohol series, bringing to six the number of α -ferrocenyl alcohols which exhibit the $\text{R}_2^2(4)$ hydrogen-bonding motif; in the bis(ferrocenyl) alcohol series these comprise Fc_2CHOH , Fc_2CPhOH [6], and $\text{Fc}_2\text{C}(\text{CMe}_3)\text{OH}$ [8], and in the monoferrocenyl series they are FcCPh_2OH [29], $\text{FcCH}(\text{CH}_2\text{Ph})\text{OH}$ [6], and $\text{FcCPh}(2\text{-furyl})\text{OH}$ [2]. It is interesting to compare the aggrega-

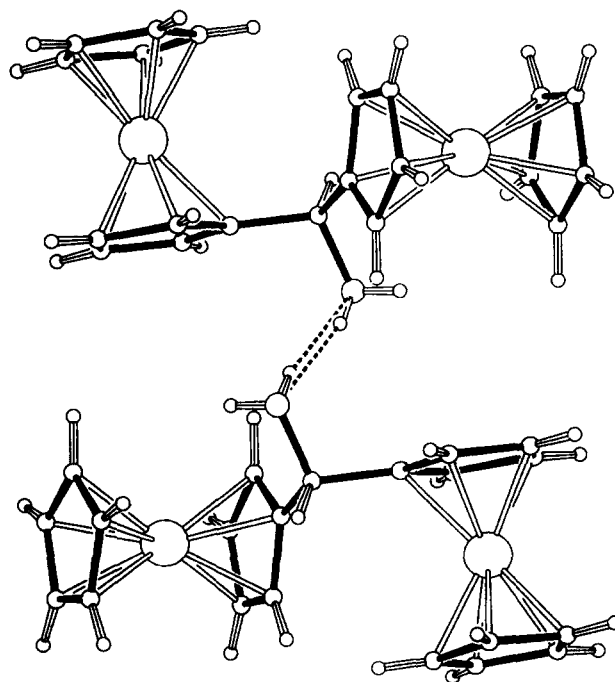


Fig. 4. A view of the hydrogen-bonded dimer of **3**.

tion patterns of the two series RCFc_2OH and RCPH_2OH , so far as these are known: whereas RCFc_2OH forms centrosymmetric dimers for both $\text{R} = \text{H}$ and $\text{R} = \text{Ph}$, the corresponding RCPH_2OH analogues form a long-chain polymer when $\text{R} = \text{H}$ [32] and a tetrahedral tetramer when $\text{R} = \text{Ph}$ [36]; while $(\text{Me}_3\text{C})\text{CFc}_2\text{OH}$ forms a centrosymmetric dimer [8], the structure of $(\text{Me}_3\text{C})\text{CPh}_2\text{OH}$ is not yet known.

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