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Hydrogen Bonding in α-Ferrocenyl Alcohols: Structures of 1-Ferrocenylethanol, 1-Ferrocenyl-2-phenylethanol, 1-Ferrocenyl-1-phenylpropan-1-ol, 1-Ferrocenyl-1-phenyl-2-methylpropan-1-ol, 1-Ferrocenyl-1-phenyl-2,2-dimethylpropan-1-ol, 1-Ferrocenyl-1,2-diphenylethanol and Diferrocenyl(phenyl)methanol

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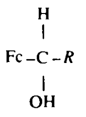
Abstract

The structure of 1-ferrocenylethanol (1*a*), $C_{12}H_{14}FeO$, tetragonal, $I4_1cd$, $a = 23.3334(18)$, $c = 7.7186(11)$ Å, $Z = 16$, $R = 0.025$ for 850 observations [$I > 3\sigma(I)$], contains spiral chains generated by a 4_1 axis, in which the molecules are connected by O—H···O hydrogen bonds in a motif with graph set $C(2)$ with an O···O distance of 2.724 (3) Å. 1-Ferrocenyl-2-phenylethanol (1*f*), $C_{18}H_{18}FeO$, orthorhombic, *Pnaa*, $a = 9.8589(7)$, $b = 15.2800(17)$, $c = 19.1399(17)$ Å, $Z = 8$, $R = 0.036$ for 1508 observations [$I > 3\sigma(I)$], crystallizes as dimeric aggregates lying across a crystallographic twofold axis and held together by O—H···O hydrogen bonds in a motif with graph set $R_2^2(4)$ with an O···O distance of 2.868 (8) Å; there are also intramolecular O—H···$\pi(C_5H_5)$ interactions. 1-Ferrocenyl-1-phenylpropan-1-ol (2*b*), $C_{19}H_{20}FeO$, monoclinic, $P2_1/c$, $a = 10.2443(13)$, $b = 10.5811(17)$, $c = 14.2487(12)$ Å, $\beta = 100.190(9)°$, $Z = 4$, $R = 0.029$ for 2289 observations [$I > 3\sigma(I)$], crystallizes as isolated molecules containing O—H···$\pi(C_5H_5)$ interactions. In 1-ferrocenyl-1-phenyl-2-methylpropan-1-ol (2*c*), $C_{20}H_{22}FeO$, monoclinic, *Cc*, $a = 25.387(4)$, $b = 7.6825(6)$, $c = 17.803(3)$ Å, $\beta = 108.217(17)°$, $Z = 8$, $R = 0.022$ for 3286 observations [$I > 3\sigma(I)$], there are two molecules in the asymmetric unit, but the structure consists of isolated molecules containing O—H···$\pi(C_5H_5)$ interactions. 1-Ferrocenyl-1-phenyl-2,2-dimethylpropan-1-ol (2*d*), $C_{21}H_{24}FeO$, monoclinic, $P2_1/n$, $a = 8.007(4)$, $b = 13.002(2)$, $c = 66.24(1)$ Å, $\beta = 91.96(3)°$, $Z = 16$, $R = 0.072$ for 4130 observations [$I > 3\sigma(I)$], has four molecules in the asymmetric unit, but there is no intermolecular hydrogen bonding. The structure of 1-ferrocenyl-1,2-diphenylethanol (2*f*), $C_{24}H_{22}FeO$, monoclinic, $C2/c$, $a = 26.229(2)$, $b = 5.889(2)$, $c = 24.553(2)$ Å, $\beta = 104.114(11)°$, $Z = 8$, $R = 0.036$ for 1733 observations [$I > 2.5\sigma(I)$], consists of isolated molecules in which the hydroxyl H atom is disordered unequally over three sites, each of which is *trans* to one of the C—C bonds involving C1; H atoms in two of these sites are involved in intramolecular O—H···$\pi(C_5H_5)$ interactions and the H atom in the third is involved in an O—H···π(arene) interaction. The structure of diferrocenyl(phenyl)methanol (2*g*), $C_{27}H_{24}Fe_2O$, triclinic, $P\bar{1}$, $a = 9.3999(11)$, $b = 11.1988(16)$, $c = 11.9720(16)$ Å, $\alpha = 117.844(11)$, $\beta = 98.890(10)$, $\gamma = 102.362(11)°$, $Z = 2$, $R = 0.031$ for 3435 observations [$I > 2.5\sigma(I)$], consists of centrosymmetric dimers held together by O—H···O hydrogen bonds in a motif with graph set $R_2^2(4)$ with an O···O distance of 2.926 (4) Å; there are also intramolecular O—H···$\pi(C_5H_5)$ interactions. Closed dimers containing the $R_2^2(4)$ $(OH)_2$ hydrogen-bonding motif, while unknown for purely organic alcohols, are a common occurrence in α-ferrocenyl alcohols (five examples from 13 known structures).

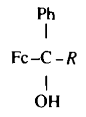
1. Introduction

Simple, unfunctionalized monoalcohols *R*OH can exhibit an extremely wide range of intermolecular aggregation patterns in the solid state. Hydrogen bonding of the type O—H···O can lead to finite aggregates which are dimeric (Sgarabotto, Ugozzoli, Sorriso & Malarski, 1988*a*), trimeric (Karlsson, 1976; Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995), tetrameric (Sultanov, Shnulin & Mamedov, 1985; Sgarabotto, Ugozzoli, Sorriso & Malarski, 1988*b*; Ferguson, Gallagher, Glidewell, Low & Scrimgeour, 1992; Ferguson, Glidewell & Zakaria, 1994) or hexameric (Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995). Such O—H···O hydrogen bonding can also lead to the formation of extended chains generated by crystallographic screw axes (Gupta & Gupta, 1975; McMillan, Paul, Caccamese & Rinehart, 1976; Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995). Other modes of aggregation involve hydrogen bonding of the types O—H···F (DesMarteau, Xu & Witz, 1992) or O—H···π(arene) (Ferguson, Gallagher, Glidewell & Zakaria, 1994*a*; Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995). On the other hand, examples are known where no intermolecular aggregation occurs (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*). Amongst α-ferrocenyl alcohols, such as (1) and (2), examples have been observed of dimers [2*e* (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*) and $[(C_5H_5)Fe(C_5H_4)]_2C(OH)CMe_3$ (Sharma, Cervantes-Lee & Pannell, 1992)] of chains generated both by 2_1 screw axes [1*d* (Li, Ferguson, Glidewell & Zakaria, 1994)] and by glide planes [1*e* (Ferguson, Gallagher, Glidewell & Zakaria, 1994*b*)], all characterized by intermolecular O—H···O interactions; and of monomers containing intramolecular O—H···$\pi(C_5H_5)$ interactions [2*a* (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*)]. These examples, and others (Ferguson, Gallagher, Glidewell & Zakaria, 1993*c*; Glidewell, Ferguson, Lough & Zakaria, 1994), indicate that the hydrogen-bonding patterns in ferrocenyl alcohols are still very difficult to predict. Continuing this study, we report here the structures of 1-ferrocenylethanol (1*a*), 1-ferrocenyl-2-phenylethanol (1*f*), 1-ferrocenyl-1-phenylpropan-1-ol (2*b*), 1-ferrocenyl-1-phenyl-2-methylpropan-1-ol (2*c*), 1-ferrocenyl-1-phenyl-2,2-dimethylpropan-1-ol (2*d*), 1-ferrocenyl-1,2-diphenylethanol (2*f*) and diferrocenyl-(phenyl)methanol (2*g*).



$\underset{\mathrm{OH}}{\overset{\mathrm{H}}{\mathrm{Fc{-}C{-}}R}}$

(1)



$\underset{\mathrm{OH}}{\overset{\mathrm{Ph}}{\mathrm{Fc{-}C{-}}R}}$

(2)

(*a*) $R = CH_3$
(*b*) $R = C_2H_5$
(*c*) $R = CHMe_2$
(*d*) $R = CMe_3$
(*e*) $R = Ph$
(*f*) $R = CH_2Ph$
(*g*) $R = Fc$

$[Fc = (C_5H_5)Fe(C_5H_4)]$

2. Experimental

2.1. *Synthesis*

Samples of (1*a*) and (1*f*) were prepared by $LiAlH_4$ reduction of acetylferrocene and (phenylacetyl)ferrocene, respectively, and samples of (2*b*), (2*c*), (2*d*) and (2*f*) were prepared by reaction of phenyllithium with the appropriate acylferrocene (Ferguson, Gallagher, Glidewell & Zakaria, 1994*b*). Compound (2*g*) was prepared by reaction of phenyllithium with diferrocenyl ketone (Pauson & Watts, 1962); ^{13}C NMR ($CDCl_3$): 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*, C—OH); 126.3 (*d*), 127.0 (*d*), 128.7 (*d*) and 146.7 (*s*, C_6H_5). Crystals of (2*c*) suitable for X-ray examination were grown by slow evaporation of a solution in dry acetone; all other crystals were grown from solutions in dichloromethane/light petroleum (b.p. 313–333 K).

2.2. *Data collection and refinement*

Details of cell data, data collection and refinement are summarized in Table 1. For (1*a*), the systematic absences (hkl absent when $h + k + l = 2n + 1$; $0kl$ absent when $l = 2n + 1$; hhl absent when $2h + l \neq 4$) allow the space group to be uniquely identified as $I4_1cd$ (No. 110). For (1*f*), the space group was uniquely identified as *Pnaa* (No. 56) from the systematic absences ($hk0$ absent when $h = 2n + 1$; $h0l$ absent when $h = 2n + 1$; $0kl$ absent when $k + l = 2n + 1$). The space group of (2*b*) was uniquely identified as $P2_1/c$ (No. 14) from the systematic absences ($h0l$ absent when $l = 2n + 1$; $0k0$ absent when $k = 2n + 1$). Compound (2*c*) crystallized in the monoclinic system and the systematic absences (hkl absent if $h + k = 2n + 1$; $h0l$ absent if $1 = 2n + 1$) permitted the space group to be either $C2/c$ (No. 15) or Cc (No. 9). Initial attempts to solve the structure in the centrosymmetric space group $C2/c$ afforded no sensible solution, but the structure was readily solved in the non-centrosymmetric space group Cc, with two molecules in the asymmetric unit. The space group Cc is polar and calculations with the opposite hand to that described here converged with R and wR values (0.024 and 0.036, respectively) slightly higher than those given in Table 1, but with no significant differences in the dimensions. Crystals of (2*d*) are monoclinic; initial attempts to determine cell dimensions using Mo *Kα* radiation indicated that one of the repeat vectors was around 60 Å, but this could not be established precisely, because of insufficient resolution of the reflections: subsequent investigation of this compound was therefore undertaken using Cu *Kα* radiation. The systematic absences ($h0l$ absent if $h + 1 = 2n + 1$; $0k0$ absent if $k = 2n + 1$) identified the space group uniquely as $P2_1/n$ (No. 14). In addition, it was observed that the $00l$ reflections were all absent unless $1 = 4n$; however, detailed comparison of the intensities of the $h0l$ and $h0l$ reflections confirmed that the Laue group was indeed $2/m$ rather than mmm, so that the behaviour of the $00l$ reflections is not an indicator of space-group symmetry. Compound (2*f*) crystallized in the monoclinic system and the systematic absences (hkl absent if $h + k = 2n + 1$; $h0l$ absent if $1 = 2n + 1$) permitted the space group to be either $C2/c$ or Cc; $C2/c$ was chosen and confirmed by successful analysis. Compound (2*g*) crystallized in the triclinic system, with possible space groups $P1$ (No. 1) and $P\bar{1}$ (No. 2); $P\bar{1}$ was chosen and confirmed by successful analysis. The diagrams were prepared using *ORTEP*II (Johnson, 1976); final fractional coordinates are given in Table 2, selected dimensions in Table 3 and significant inter- and intramolecular distances involving hydroxyl H atoms in Table 4.*

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* Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry, and stereoviews and packing diagrams have been deposited with the IUCr (Reference: AB0340). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Experimental details*

	(1*a*)	(1*f*)	(2*b*)	(2*c*)	(2*d*)	(2*f*)	(2*g*)
Crystal data							
Chemical formula	$C_{12}H_{14}FeO$	$C_{18}H_{18}FeO$	$C_{19}H_{20}FeO$	$C_{20}H_{22}FeO$	$C_{21}H_{24}FeO$	$C_{24}H_{22}FeO$	$C_{27}H_{24}Fe_2O$
Chemical formula weight	230.09	306.19	320.22	334.24	348.27	382.29	476.20
Cell setting	Tetragonal	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$I4_1cd$	*Pnaa*	$P2_1/c$	*Cc*	$P2_1/n$	$C2/c$	$P\bar{1}$
a (Å)	23.3334 (18)	9.8589 (7)	10.2443 (13)	25.387 (4)	8.007 (4)	26.229 (2)	9.3999 (11)
b (Å)	23.3334 (18)	15.2800 (17)	10.5811 (17)	7.6825 (6)	13.002 (2)	5.889 (2)	11.1988 (16)
c (Å)	7.7186 (11)	19.1399 (17)	14.2487 (12)	17.803 (3)	66.24 (1)	24.553 (2)	11.9720 (16)
α (°)	90.0	90.0	90.0	90.0	90	90.0	117.844 (11)
β (°)	90.0	90.0	100.190 (9)	108.217 (17)	91.96 (3)	104.114 (11)	98.890 (10)
γ (°)	90.0	90.0	90.0	90.0	90	90.0	102.362 (11)
V ($Å^3$)	4202.4 (7)	2883.3 (5)	1520.1 (3)	3298.2 (7)	6891 (3)	3678.0 (13)	1040.2 (2)
Z	16	8	4	8	16	8	2
D_x (Mg m^{-3})	1.455	1.411	1.399	1.346	1.343	1.381	1.520
Radiation type	Mo *K*α	Mo *K*α	Mo *K*α	Mo *K*α	Cu *K*α	Mo *K*α	Mo *K*α
Wavelength (Å)	0.7107	0.7107	0.7107	0.7107	1.5418	0.7107	0.7107
No. of reflections for cell parameters	25	25	25	25	25	25	25
2θ range (°)	25–40	18–34	20–32	19–35	27–39	16–28	23–45
μ (mm^{-1})	1.40	1.04	0.99	0.91	7.015	0.83	1.41
Temperature (K)	294 (1)	294 (1)	294 (1)	294 (1)	293 (1)	294 (1)	294 (1)
Crystal form	Needle	Plate	Plate	Block cut from needle	Plate	Plate	Plate
Crystal size (mm)	0.41 × 0.22 × 0.17	0.36 × 0.35 × 0.10	0.39 × 0.39 × 0.10	0.39 × 0.38 × 0.37	0.600 × 0.200 × 0.050	0.36 × 0.30 × 0.12	0.39 × 0.33 × 0.13
Crystal colour	Orange	Yellow	Orange	Orange	Orange	Orange	Orange
Data collection							
Diffractometer	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4	Nonius CAD-4	AFC-7*S*	Nonius CAD-4	Nonius CAD-4
Data collection method	θ/2θ	θ/2θ	θ/2θ	θ/2θ	ω/2θ	θ/2θ	θ/2θ
Absorption correction	Empirical, ψ-scans	Empirical, ψ-scans	Empirical, ψ-scans	Empirical, 4 ψ-scans, 4° steps	Empirical, ψ-scan	Empirical, ψ-scans	Empirical, ψ-scans
T_{min}	0.9532	0.8622	0.7291	0.7008	0.519	0.7857	0.6057
T_{max}	0.9894	0.9866	0.9931	0.7609	1.000	0.8267	0.7415
No. of measured reflections	2410	3137	3485	6549	11 640	4082	4507
No. of independent reflections	1228	3137	3309	3655	10 759	4010	4507
No. of observed reflections	850	1508	2289	3286	4130	1733	3435
Criterion for observed reflections	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 3.0\sigma(I)$	$I > 2.5\sigma(I)$	$I > 2.5\sigma(I)$
R_{int}	0.015	—	0.012	0.006	0.0493	0.026	—
θ_{max} (°)	26.88	26.88	26.92	26.92	60.08	26.91	26.87
Range of *h*, *k*, *l*	$-29 \rightarrow h \rightarrow 29$ $-3 \rightarrow k \rightarrow 21$ $-9 \rightarrow l \rightarrow 0$	$0 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 19$ $0 \rightarrow l \rightarrow 24$	$-13 \rightarrow h \rightarrow 12$ $0 \rightarrow k \rightarrow 13$ $0 \rightarrow l \rightarrow 18$	$0 \rightarrow h \rightarrow 32$ $-9 \rightarrow k \rightarrow 9$ $-22 \rightarrow l \rightarrow 22$	$0 \rightarrow h \rightarrow 9$ $0 \rightarrow k \rightarrow 14$ $-74 \rightarrow l \rightarrow 74$	$-33 \rightarrow h \rightarrow 32$ $0 \rightarrow k \rightarrow 7$ $0 \rightarrow l \rightarrow 31$	$-11 \rightarrow h \rightarrow 11$ $0 \rightarrow k \rightarrow 14$ $-15 \rightarrow l \rightarrow 13$
No. of standard reflections	3	3	3	3	3	3	3
Frequency of standard reflections	120	60	120	120	120	120	120
Intensity decay (%)	<1.0	<1.0	<1.0	1.0	<1.0	<1.0	1.1
Refinement							
Refinement on	*F*	*F*	*F*	*F*	*F*	*F*	*F*
R	0.025	0.036	0.029	0.022	0.0720	0.036	0.031
wR	0.029	0.047	0.042	0.035	0.0680	0.044	0.043
S	0.99	1.15	1.14	1.11	3.710	1.08	1.14
No. of reflections used in refinement	850	1508	2289	3286	4130	1733	3435
No. of parameters used	130	185	194	404	830	235	275
H-atom treatment	C—H riding, 0.95 Å, O—H. All H-atom parameters refined	C—H riding, 0.95 Å, O—H. All H-atom parameters refined	C—H riding, 0.95 Å, O—H. All H-atom parameters refined	C—H riding, 0.95 Å, O—H. All H-atom parameters refined	H-atom parameters not refined	H atoms riding, C—H 0.95 Å, O—H 0.90 Å	H atoms: C—H riding 0.95 Å, O—H. All H-atom parameters refined
Weighting scheme	$w = 1/[\sigma^2(F) + 0.0004F^2]$	$w = 1/[\sigma^2(F) + 0.0008F^2]$	$w = 1/[\sigma^2(F) + 0.0008F^2]$	$w = 1/[\sigma^2(F) + 0.0008F^2]$	$w = 1/[\sigma^2(F) + 0.0008F^2]$	$w = 1/[\sigma^2(F) + 0.0008F^2]$	$w = 1/[\sigma^2(F) + 0.0008F^2]$

Table 1 (*cont.*)

	(1*a*)	(1*f*)	(2*b*)	(2*c*)	(2*d*)	(2*f*)	(2*g*)
$(\Delta/\sigma)_{max}$	0.000	0.001	0.000	0.004	0.390	0.000	0.001
$\Delta\rho_{max}$ (e Å^{-3})	0.15	0.29	0.23	0.22	0.55	0.25	0.45
$\Delta\rho_{min}$ (e Å^{-3})	−0.16	−0.21	−0.22	−0.17	−0.68	−0.23	−0.35
Extinction method	None	None	None	Larson (1970)	Zachariasen type 2 Gaussian isotropic	None	None
Extinction coefficient	–	–	–	7523 (699)	2.98375	–	–
Source of atomic scattering factors	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)	*International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)
Computer programs							
Data collection	*CAD*-4 software (Enraf–Nonius, 1989)	*CAD*-4 software (Enraf–Nonius, 1989)	*CAD*-4 software (Enraf–Nonius, 1989)	*CAD*-4 software (Enraf–Nonius, 1989)	MSC/AFC Diffractometer Control	*CAD*-4 software (Enraf–Nonius, 1989)	*CAD*-4 software (Enraf–Nonius, 1989)
Cell refinement	Enraf–Nonius *SET*4 and *CELDIM*	Enraf–Nonius *SET*4 and *CELDIM*	Enraf–Nonius *SET*4 and *CELDIM*	Enraf–Nonius *SET*4 and *CELDIM*	MSC/AFC Diffractometer Control	Enraf–Nonius *SET*4 and *CELDIM*	Enraf–Nonius *SET*4 and *CELDIM*
Data reduction	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)	*TEXSAN* (MSC, 1992)	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)	*DATRD*2 in *NRCVAX*94 (Gabe, Le Page, Charland, Lee & White, 1989)
Structure solution	*NRCVAX*94 and Patterson heavy-atom method	*NRCVAX*94 and Patterson heavy-atom method	*NRCVAX*94 and Patterson heavy-atom method	*NRCVAX*94 and Patterson heavy-atom method	*TEXSAN* and direct methods	*NRCVAX*94 and Patterson heavy-atom method	*NRCVAX*94 and Patterson heavy-atom method
Structure refinement	*NRCVAX*94	*NRCVAX*94	*NRCVAX*94	*NRCVAX*94	*TEXSAN*	*NRCVAX*94	*NRCVAX*94
Preparation of material for publication	*NRCVAX*94 and WordPerfect	*NRCVAX*94 and WordPerfect	*NRCVAX*94 and WordPerfect	*NRCVAX*94 and WordPerfect	*TEXSAN*	*NRCVAX*94 and WordPerfect	*NRCVAX*94 and WordPerfect

3. Results and discussion

3.1. *Description of structures*

3.1.1. *Structures dominated by O—H···O hydrogen bonding*. Crystals of racemic 1-ferrocenylethanol (1*a*, Fig. 1) are tetragonal, space group $I4_1cd$, with one molecule in the asymmetric unit. The molecules are linked together by hydrogen bonds of the O—H···O type into infinite spiral chains, generated by the 4_1 screw axis (Fig. 2); the shortest O···O distance within the helix is 2.724 (3) Å. Four such helices run through each unit cell, two of each hand accommodating the equal numbers of *R* and *S* molecules present in the racemic mixture. Within a given helix, however, all the molecules are of the same chirality. The anomalously high incidence of high-symmetry space groups (taken to be those other than triclinic, monoclinic and orthorhombic) for hydrogen-bonded organic alcohols has recently been established (Brock & Duncan, 1994): of these, the majority are trigonal, and particularly tetragonal. Other recent trigonal examples include Me_2CHCPh_2OH ($P31c$) and $(C_6F_5)_2CHOH$ ($R\bar{3}$) (Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995). Although the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) does not yet contain any examples of simple organic alcohols in hexagonal and cubic space groups, the series $Ph_x(4\text{-}CH_3C_6H_4)_{3-x}COH$, for $x = 0, 1, 2$, all crystallize in the cubic space group $Pa3$ with a Z' value (Brock & Dunitz, 1994) of 4/3 (Ferguson, Glidewell & Patterson, 1995).

The racemic form of (1*f*), 1-ferrocenyl-2-phenylethanol, crystallizes in the centrosymmetric orthorhombic space group *Pnaa*, with one molecule in the asymmetric unit. The molecules at (*x*, *y*, *z*) and (x, $\frac{1}{2} - y$, $\frac{1}{2} - z$), which are related by a crystallographic rotation axis and thus have the same chirality, are linked by O—H···O hydrogen bonds into cyclic dimeric aggregates having twofold rotational symmetry (Fig. 3); the action of the **a** glide planes generates a further dimer in which the two molecules are both of opposite chirality to those in the initial dimer. In addition to the intermolecular O—H···O hydrogen bond, there is also a weak intramolecular O—H···π(C_5H_5) interaction involving, as in (2*a*) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*), the unsubstituted cyclopentadienyl ring of the ferrocenyl group, with the intramolecular distance O···C21 of 3.548 (7) Å, so that the hydroxyl H atom is, in effect, participating in three-centre (Taylor, Kennard & Versichel, 1984) hydrogen bonding. There are well documented examples of intramolecular O—H···π(C═C) interactions (Schweizer, Dunitz, Pfund, Ramos Tombo & Ganter, 1981; Zimmerman & Zuraw, 1989) and intermolecular O—H···π(arene) interactions as the sole force towards intermolecular aggregation (Baran, Kanters, Lutz, Van der Maas, Schouten & Wierzejewska-Hnat, 1990; Ferguson, Gallagher, Glidewell & Zakaria, 1994*a*; Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995). The participation of cyclopentadienyl rings, themselves more electron rich than either C═C bonds or arene rings, in

Table 2. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
(1*a*)				
Fe1	0.12164 (2)	0.10180 (2)	0.0	0.0473 (3)
O1	0.19177 (16)	0.24807 (13)	−0.2837 (5)	0.063 (2)
C1	0.14499 (18)	0.21890 (18)	−0.2010 (6)	0.054 (2)
C2	0.0942 (2)	0.2234 (2)	−0.3221 (9)	0.092 (4)
C11	0.16253 (17)	0.15834 (17)	−0.1596 (6)	0.048 (2)
C12	0.19854 (16)	0.14233 (17)	−0.0186 (7)	0.056 (3)
C13	0.20616 (18)	0.08193 (18)	−0.0235 (10)	0.069 (3)
C14	0.1756 (2)	0.06092 (18)	−0.1669 (8)	0.070 (3)
C15	0.1486 (2)	0.10725 (18)	−0.2494 (8)	0.061 (3)
C21	0.0466 (3)	0.1380 (3)	0.0701 (12)	0.104 (5)
C22	0.0817 (3)	0.1340 (2)	0.2131 (11)	0.095 (5)
C23	0.0945 (2)	0.0772 (2)	0.2396 (9)	0.073 (3)
C24	0.0674 (2)	0.0450 (2)	0.1160 (10)	0.077 (3)
C25	0.0371 (2)	0.0830 (3)	0.0083 (11)	0.099 (5)
H0	0.2096 (18)	0.2621 (19)	−0.209 (6)	0.049 (15)
(1*f*)				
Fe1	0.57745 (6)	0.45090 (4)	0.13587 (3)	0.0419 (3)
O1	0.5474 (6)	0.2287 (3)	0.1770 (2)	0.079 (3)
C1	0.5513 (5)	0.2476 (3)	0.1037 (2)	0.049 (2)
C2	0.6216 (5)	0.1698 (3)	0.0688 (3)	0.056 (3)
C11	0.6222 (4)	0.3325 (3)	0.0912 (2)	0.039 (2)
C12	0.7352 (5)	0.3651 (3)	0.1287 (2)	0.048 (2)
C13	0.7703 (5)	0.4474 (3)	0.0998 (3)	0.059 (3)
C14	0.6808 (6)	0.4655 (3)	0.0450 (2)	0.059 (3)
C15	0.5902 (5)	0.3953 (3)	0.0389 (2)	0.048 (2)
C21	0.4107 (5)	0.4415 (4)	0.2000 (3)	0.066 (3)
C22	0.5283 (6)	0.4627 (3)	0.2386 (2)	0.065 (3)
C23	0.5796 (6)	0.5419 (3)	0.2134 (2)	0.064 (3)
C24	0.4952 (7)	0.5697 (3)	0.1577 (3)	0.073 (4)
C25	0.3921 (6)	0.5085 (4)	0.1505 (3)	0.075 (4)
C31	0.6105 (4)	0.1711 (3)	−0.0095 (2)	0.043 (2)
C32	0.5003 (5)	0.1323 (3)	−0.0418 (2)	0.052 (3)
C33	0.4861 (6)	0.1340 (3)	−0.1135 (3)	0.063 (3)
C34	0.5809 (6)	0.1743 (3)	−0.1542 (2)	0.066 (3)
C35	0.6901 (6)	0.2129 (3)	−0.1226 (3)	0.068 (3)
C36	0.7059 (5)	0.2118 (3)	−0.0513 (3)	0.057 (3)
H0	0.553 (8)	0.263 (5)	0.196 (3)	0.13 (4)
(2*b*)				
Fe1	0.34401 (3)	0.12719 (3)	0.15774 (2)	0.03980 (18)
O1	0.0091 (2)	0.05882 (18)	0.17093 (15)	0.0584 (12)
C1	0.0398 (2)	0.1911 (2)	0.17478 (16)	0.0389 (11)
C2	0.0594 (2)	0.2378 (3)	0.27850 (17)	0.0519 (13)
C3	−0.0603 (3)	0.2192 (3)	0.3255 (2)	0.0690 (18)
C11	0.1620 (2)	0.2134 (2)	0.13032 (16)	0.0376 (10)
C12	0.2645 (2)	0.3042 (2)	0.15779 (19)	0.0499 (14)
C13	0.3537 (3)	0.2977 (3)	0.0929 (2)	0.0606 (17)
C14	0.3074 (3)	0.2049 (3)	0.02481 (19)	0.0595 (16)
C15	0.1892 (2)	0.1527 (3)	0.04694 (17)	0.0490 (13)
C21	0.3476 (3)	−0.0076 (3)	0.26097 (19)	0.0600 (15)
C22	0.4380 (3)	0.0898 (3)	0.2927 (2)	0.0710 (17)
C23	0.5306 (3)	0.0962 (3)	0.2302 (3)	0.0710 (19)
C24	0.4968 (3)	0.0035 (3)	0.1604 (2)	0.0648 (17)
C25	0.3838 (3)	−0.0611 (3)	0.1797 (2)	0.0596 (15)
C31	−0.0783 (2)	0.2582 (2)	0.11453 (15)	0.0364 (11)
C32	−0.1985 (2)	0.1978 (2)	0.08412 (19)	0.0498 (13)
C33	−0.3035 (2)	0.2637 (3)	0.03083 (19)	0.0604 (16)
C34	−0.2912 (3)	0.3886 (3)	0.00825 (18)	0.0563 (15)
C35	−0.1738 (3)	0.4489 (3)	0.03848 (17)	0.0506 (13)
C36	−0.0672 (2)	0.3848 (2)	0.09140 (16)	0.0423 (11)
H0	0.076 (3)	0.020 (3)	0.179 (2)	0.079 (11)
(2*c*)				
Fe1	0.239164 (17)	0.33091 (5)	0.10601 (2)	0.0363 (2)
Fe2	1/2	0.66830 (5)	1/2	0.0368 (2)
O1	0.20908 (9)	0.7258 (3)	0.19222 (14)	0.0460 (10)
O2	0.52639 (10)	0.2676 (3)	0.61194 (15)	0.0507 (12)
C1	0.25177 (10)	0.6192 (3)	0.24291 (15)	0.0363 (12)
C2	0.29516 (12)	0.7481 (3)	0.29506 (16)	0.0437 (13)
C3	0.26990 (18)	0.8697 (5)	0.3421 (2)	0.066 (2)
C4	0.32543 (16)	0.8541 (4)	0.2498 (2)	0.0600 (19)
C5	0.48435 (11)	0.3793 (3)	0.62423 (17)	0.0398 (13)
C6	0.43870 (13)	0.2555 (4)	0.6352 (2)	0.0500 (16)
C7	0.46335 (18)	0.1291 (5)	0.7034 (3)	0.069 (2)
C8	0.40843 (17)	0.1538 (5)	0.5613 (3)	0.071 (2)
C11	0.27706 (10)	0.5094 (3)	0.19227 (14)	0.0365 (12)
C12	0.28085 (14)	0.5623 (4)	0.11697 (18)	0.0460 (15)
C13	0.30933 (13)	0.4313 (4)	0.08866 (19)	0.0522 (17)
C14	0.32349 (14)	0.2976 (5)	0.1457 (2)	0.0464 (17)
C15	0.30395 (11)	0.3444 (3)	0.20939 (16)	0.0391 (12)
C21	0.15881 (15)	0.2931 (6)	0.1009 (2)	0.0581 (19)
C22	0.16071 (16)	0.3619 (5)	0.0307 (2)	0.0596 (19)
C23	0.19013 (17)	0.2565 (8)	−0.0021 (2)	0.085 (3)
C24	0.20788 (18)	0.1126 (7)	0.0472 (5)	0.108 (4)
C25	0.1884 (2)	0.1350 (6)	0.1135 (3)	0.093 (3)
C31	0.22825 (12)	0.5063 (3)	0.29549 (15)	0.0400 (12)
C32	0.17173 (13)	0.4973 (4)	0.28434 (19)	0.0518 (16)
C33	0.15059 (16)	0.3918 (6)	0.3312 (2)	0.069 (2)
C34	0.1847 (2)	0.2935 (5)	0.3903 (3)	0.070 (2)
C35	0.24150 (19)	0.3024 (5)	0.4044 (2)	0.062 (2)
C36	0.26327 (13)	0.4094 (4)	0.35807 (17)	0.0473 (15)
C41	0.46133 (10)	0.4916 (3)	0.55090 (15)	0.0373 (12)
C42	0.45848 (14)	0.4398 (4)	0.47304 (18)	0.0485 (16)
C43	0.43089 (14)	0.5712 (4)	0.41933 (17)	0.0527 (16)
C44	0.41721 (14)	0.7066 (5)	0.4637 (2)	0.0470 (17)
C45	0.43567 (11)	0.6584 (3)	0.54452 (16)	0.0388 (13)
C51	0.58148 (15)	0.7032 (6)	0.5677 (2)	0.0578 (19)
C52	0.57916 (15)	0.6364 (6)	0.4939 (3)	0.063 (2)
C53	0.54996 (17)	0.7501 (9)	0.4370 (3)	0.089 (3)
C54	0.53290 (18)	0.8907 (7)	0.4735 (5)	0.103 (4)
C55	0.55287 (17)	0.8608 (6)	0.5563 (4)	0.084 (3)
C61	0.50846 (12)	0.4902 (4)	0.69771 (15)	0.0408 (13)
C62	0.56498 (14)	0.4974 (4)	0.73698 (19)	0.0542 (16)
C63	0.58659 (17)	0.6029 (6)	0.8029 (2)	0.072 (2)
C64	0.5530 (2)	0.7049 (5)	0.8310 (2)	0.073 (3)
C65	0.49651 (19)	0.6985 (4)	0.7943 (2)	0.062 (2)
C66	0.47425 (14)	0.5907 (4)	0.72907 (17)	0.0497 (15)
H01	0.1969 (18)	0.674 (5)	0.151 (3)	0.060 (12)
H02	0.5416 (18)	0.313 (5)	0.590 (2)	0.056 (12)
(2*d*)				
Fe1	0.2380 (3)	0.9694 (2)	0.46992 (3)	0.0504
Fe2	0.7417 (3)	0.5332 (2)	0.47028 (3)	0.0519
Fe3	0.7580 (3)	0.1789 (2)	0.28097 (3)	0.0550
Fe4	0.2449 (3)	0.1158 (2)	0.22118 (4)	0.0536
O11	−0.145 (1)	0.9184 (7)	0.4450 (1)	0.0600
O21	0.343 (1)	0.5831 (7)	0.4481 (1)	0.0613
O31	0.383 (1)	0.2317 (7)	0.3052 (1)	0.0646
O41	0.627 (1)	0.0640 (7)	0.1982 (1)	0.0595
C11	−0.056 (2)	0.999 (1)	0.4355 (2)	0.0540
C12	−0.189 (2)	1.080 (1)	0.4279 (2)	0.0619
C13	−0.303 (2)	1.026 (1)	0.4115 (3)	0.0854
C14	−0.111 (2)	1.175 (1)	0.4187 (2)	0.0785
C15	−0.297 (2)	1.114 (1)	0.4452 (2)	0.0782
C21	0.444 (2)	0.510 (1)	0.4374 (2)	0.0497
C22	0.311 (2)	0.431 (1)	0.4286 (2)	0.0582
C23	0.179 (2)	0.484 (1)	0.4148 (2)	0.0693
C24	0.391 (2)	0.342 (1)	0.4166 (2)	0.0715
C25	0.218 (2)	0.380 (1)	0.4460 (2)	0.0732
C31	0.479 (2)	0.153 (1)	0.3146 (2)	0.0595
C32	0.356 (2)	0.073 (1)	0.3232 (2)	0.0646
C33	0.242 (2)	0.129 (1)	0.3389 (2)	0.0893
C34	0.438 (2)	−0.022 (1)	0.3333 (2)	0.0949
C35	0.238 (2)	0.034 (1)	0.3059 (3)	0.0902
C41	0.527 (2)	0.141 (1)	0.1879 (2)	0.0526
C42	0.657 (2)	0.222 (1)	0.1800 (2)	0.0597
C43	0.773 (2)	0.167 (1)	0.1653 (2)	0.0790
C44	0.573 (2)	0.311 (1)	0.1684 (2)	0.0896
C45	0.764 (2)	0.268 (1)	0.1973 (2)	0.0708
C111	0.064 (2)	1.0431 (10)	0.4518 (2)	0.0480

Table 2 (*cont.*)

	x	y	z	U_{eq}
C112	0.026 (2)	1.052 (1)	0.4726 (3)	0.0538
C113	0.156 (2)	1.100 (1)	0.4832 (2)	0.0660
C114	0.284 (2)	1.125 (1)	0.4695 (3)	0.0572
C115	0.223 (2)	1.089 (1)	0.4504 (2)	0.0551
C121	0.257 (3)	0.820 (1)	0.4603 (2)	0.0633
C122	0.204 (2)	0.823 (1)	0.4803 (3)	0.0643
C123	0.336 (3)	0.874 (1)	0.4917 (2)	0.0665
C124	0.461 (2)	0.903 (1)	0.4788 (3)	0.0690
C125	0.407 (2)	0.869 (1)	0.4595 (3)	0.0645
C131	0.042 (2)	0.954 (1)	0.4180 (2)	0.0619
C132	0.016 (2)	0.853 (1)	0.4121 (3)	0.0778
C133	0.099 (3)	0.808 (1)	0.3962 (3)	0.0910
C134	0.208 (3)	0.867 (2)	0.3852 (3)	0.0984
C135	0.235 (2)	0.967 (2)	0.3906 (3)	0.0959
C136	0.154 (2)	1.011 (1)	0.4065 (3)	0.0744
C211	0.562 (2)	0.462 (1)	0.4524 (3)	0.0506
C212	0.529 (2)	0.450 (1)	0.4732 (3)	0.0590
C213	0.667 (2)	0.398 (1)	0.4830 (2)	0.0568
C214	0.785 (2)	0.379 (1)	0.4686 (3)	0.0598
C215	0.725 (2)	0.414 (1)	0.4498 (2)	0.0609
C221	0.752 (2)	0.686 (1)	0.4619 (3)	0.0670
C222	0.715 (2)	0.675 (1)	0.4823 (3)	0.0662
C223	0.847 (3)	0.624 (1)	0.4920 (3)	0.0763
C224	0.960 (2)	0.599 (1)	0.4776 (4)	0.0736
C225	0.904 (3)	0.636 (1)	0.4593 (3)	0.0732
C231	0.531 (2)	0.567 (1)	0.4200 (2)	0.0563
C232	0.490 (2)	0.669 (1)	0.4164 (2)	0.0612
C233	0.574 (3)	0.725 (1)	0.4017 (3)	0.0865
C234	0.693 (3)	0.680 (2)	0.3907 (3)	0.0883
C235	0.735 (2)	0.580 (2)	0.3935 (3)	0.0819
C236	0.651 (2)	0.522 (1)	0.4083 (3)	0.0711
C311	0.598 (2)	0.103 (1)	0.2989 (2)	0.0519
C312	0.545 (2)	0.093 (1)	0.2783 (3)	0.0642
C313	0.679 (3)	0.044 (1)	0.2679 (3)	0.0746
C314	0.810 (2)	0.022 (1)	0.2822 (3)	0.0726
C315	0.759 (2)	0.056 (1)	0.3010 (2)	0.0556
C321	0.779 (3)	0.330 (1)	0.2901 (3)	0.0736
C322	0.718 (2)	0.324 (1)	0.2694 (3)	0.0671
C323	0.845 (3)	0.273 (1)	0.2587 (3)	0.0784
C324	0.974 (2)	0.248 (1)	0.2724 (4)	0.0807
C325	0.936 (2)	0.280 (1)	0.2920 (3)	0.0724
C331	0.586 (2)	0.199 (1)	0.3323 (3)	0.0690
C332	0.562 (2)	0.302 (1)	0.3381 (2)	0.0787
C333	0.660 (3)	0.349 (1)	0.3541 (3)	0.1008
C334	0.775 (3)	0.291 (2)	0.3653 (3)	0.1358
C335	0.803 (3)	0.190 (2)	0.3602 (3)	0.1313
C336	0.710 (2)	0.144 (1)	0.3442 (3)	0.0784
C411	0.412 (2)	0.191 (1)	0.2035 (2)	0.0506
C412	0.461 (2)	0.2005 (10)	0.2244 (2)	0.0543
C413	0.328 (2)	0.251 (1)	0.2349 (2)	0.0650
C414	0.198 (2)	0.273 (1)	0.2205 (3)	0.0640
C415	0.247 (2)	0.237 (1)	0.2015 (2)	0.0586
C421	0.229 (3)	−0.036 (1)	0.2122 (3)	0.0652
C422	0.289 (2)	−0.033 (1)	0.2321 (3)	0.0714
C423	0.163 (3)	0.018 (1)	0.2433 (3)	0.0848
C424	0.034 (2)	0.049 (1)	0.2303 (4)	0.0705
C425	0.073 (3)	0.014 (1)	0.2103 (3)	0.0820
C431	0.423 (2)	0.086 (1)	0.1703 (2)	0.0647
C432	0.461 (2)	−0.016 (1)	0.1662 (3)	0.0795
C433	0.368 (3)	−0.071 (2)	0.1513 (3)	0.1163
C434	0.247 (3)	−0.019 (2)	0.1406 (4)	0.1191
C435	0.206 (2)	0.084 (2)	0.1433 (3)	0.1105
C436	0.300 (2)	0.138 (1)	0.1588 (3)	0.0812
(2*f*)				
Fe1	0.39159 (2)	0.18751 (13)	0.05639 (2)	0.0399 (4)
O1	0.35818 (11)	0.4434 (6)	−0.07806 (12)	0.0463 (18)
C1	0.34737 (15)	0.2047 (9)	−0.07813 (16)	0.036 (2)
C2	0.39345 (16)	0.0712 (9)	−0.09142 (16)	0.044 (2)
C11	0.34035 (15)	0.1439 (8)	−0.02025 (16)	0.036 (2)
C12	0.35167 (17)	−0.0681 (9)	0.00763 (18)	0.046 (3)
C13	0.33666 (18)	−0.0558 (10)	0.05888 (19)	0.054 (3)
C14	0.31559 (16)	0.1615 (11)	0.06254 (19)	0.056 (3)
C15	0.31763 (15)	0.2842 (9)	0.01412 (18)	0.047 (3)
C21	0.4570 (2)	0.3522 (14)	0.0474 (2)	0.078 (4)
C22	0.46960 (19)	0.1358 (13)	0.0689 (3)	0.082 (5)
C23	0.4564 (2)	0.1199 (11)	0.1192 (3)	0.076 (4)
C24	0.4345 (2)	0.3207 (13)	0.1291 (2)	0.069 (4)
C25	0.4341 (2)	0.4681 (10)	0.0856 (3)	0.070 (4)
C31	0.29633 (15)	0.1558 (8)	−0.12271 (16)	0.035 (2)
C32	0.27602 (15)	0.3121 (9)	−0.16441 (17)	0.046 (3)
C33	0.22994 (18)	0.2644 (9)	−0.20477 (18)	0.054 (3)
C34	0.20452 (17)	0.0620 (11)	−0.20454 (19)	0.053 (3)
C35	0.22467 (18)	−0.0963 (9)	−0.1639 (2)	0.050 (3)
C36	0.27044 (17)	−0.0504 (9)	−0.12348 (18)	0.046 (3)
C41	0.40524 (15)	0.1306 (7)	−0.14702 (17)	0.037 (2)
C42	0.43294 (17)	0.3253 (10)	−0.1538 (2)	0.055 (3)
C43	0.4432 (2)	0.3737 (9)	−0.2051 (3)	0.065 (4)
C44	0.4270 (2)	0.2324 (11)	−0.2495 (2)	0.067 (4)
C45	0.3993 (2)	0.0405 (11)	−0.2439 (2)	0.069 (4)
C46	0.38847 (18)	−0.0098 (9)	−0.1930 (2)	0.055 (3)
H0*a**	0.331	0.521	−0.070	0.0556
H0*b**	0.388	0.474	−0.052	0.0556
H0*c**	0.362	0.485	−0.112	0.0556
(2*g*)				
Fe1	0.10277 (4)	−0.12015 (4)	0.26601 (4)	0.0351 (2)
Fe2	−0.45278 (4)	−0.37853 (4)	−0.15558 (3)	0.0361 (2)
O1	−0.1204 (2)	−0.0856 (2)	0.0224 (2)	0.0437 (14)
C1	−0.1988 (2)	−0.1026 (2)	0.1108 (2)	0.0305 (14)
C11	−0.1231 (3)	−0.1711 (3)	0.1756 (2)	0.0341 (15)
C12	−0.0706 (3)	−0.2887 (3)	0.1099 (3)	0.0492 (18)
C13	−0.0168 (3)	−0.3257 (3)	0.2027 (4)	0.063 (3)
C14	−0.0348 (3)	−0.2332 (4)	0.3244 (4)	0.060 (3)
C15	−0.1005 (3)	−0.1370 (3)	0.3090 (3)	0.0441 (19)
C21	0.2365 (3)	0.0350 (3)	0.2456 (3)	0.051 (2)
C22	0.2886 (3)	−0.0832 (4)	0.2045 (3)	0.066 (2)
C23	0.3274 (3)	−0.1015 (4)	0.3131 (4)	0.062 (3)
C24	0.2983 (3)	0.0047 (4)	0.4199 (3)	0.056 (2)
C25	0.2429 (3)	0.0880 (3)	0.3783 (3)	0.0508 (19)
C31	−0.3619 (3)	−0.1975 (2)	0.0286 (2)	0.0295 (13)
C32	−0.4599 (3)	−0.1740 (3)	−0.0573 (2)	0.0377 (16)
C33	−0.6073 (3)	−0.2755 (3)	−0.1038 (3)	0.0455 (18)
C34	−0.6020 (3)	−0.3607 (3)	−0.0469 (3)	0.0424 (16)
C35	−0.4510 (3)	−0.3125 (3)	0.0355 (2)	0.0341 (14)
C41	−0.2843 (4)	−0.4236 (4)	−0.2405 (3)	0.067 (2)
C42	−0.3962 (6)	−0.4103 (3)	−0.3222 (3)	0.075 (3)
C43	−0.5369 (4)	−0.5136 (4)	−0.3549 (3)	0.066 (3)
C44	−0.5095 (4)	−0.5904 (3)	−0.2931 (3)	0.058 (2)
C45	−0.3541 (4)	−0.5337 (3)	−0.2214 (3)	0.059 (2)
C51	−0.2004 (3)	0.0432 (2)	0.2180 (2)	0.0326 (15)
C52	−0.0854 (3)	0.1688 (3)	0.2596 (3)	0.0505 (19)
C53	−0.0830 (4)	0.2982 (3)	0.3639 (4)	0.064 (2)
C54	−0.1964 (4)	0.3034 (3)	0.4235 (3)	0.061 (2)
C55	−0.3121 (4)	0.1829 (3)	0.3818 (3)	0.054 (2)
C56	−0.3136 (3)	0.0521 (3)	0.2794 (3)	0.0422 (17)
H0	−0.047 (4)	−0.069 (4)	0.049 (3)	0.053 (11)

* Atoms H0*a*, H0*b* and H0*c* are the three components of the disordered hydroxyl H atom with occupancies 0.19, 0.35 and 0.46, respectively (from peak heights in difference maps).

O—H· · ·$\pi(C_5H_5)$ interactions should therefore occasion no surprise. Although the IR spectra of a number of α-metallocenylcarbinols have been interpreted in terms of O—H· · ·*M* (*M* = Fe, Ru, Os) interactions (Shubina, Epstein, Timofeeva, Struchkov, Kreindlin, Fadeeva & Rybinskaya, 1991; Shubina, Epstein, Kreindlin, Fadeeva & Rybinskaya, 1991), similar spectral features were also observed in $[(C_5H_5)Fe(C_5H_4)]_2C(OH)CMe_3$ (Sharma, Cervantes-Lee & Pannell, 1992), which was subsequently shown by X-ray analysis to form cyclic $R_2^2(4)$

Table 3. *Selected molecular dimensions (Å, °)*

(*a*) (1*a*), (1*f*), (2*b*) and (2*f*)

	(1*a*)	(1*f*)	(2*b*)	(2*f*)
C11—C12	1.424 (7)	1.414 (6)	1.425 (3)	1.420 (7)
C12—C13	1.421 (6)	1.416 (7)	1.411 (4)	1.409 (6)
C13—C14	1.404 (9)	1.399 (8)	1.403 (5)	1.406 (9)
C14—C15	1.404 (7)	1.402 (7)	1.417 (4)	1.403 (7)
C15—C11	1.417 (6)	1.422 (6)	1.421 (3)	1.413 (6)
C21—C22	1.378 (14)	1.413(8)	1.406 (5)	1.389 (11)
C22—C23	1.374 (8)	1.397 (7)	1.412 (5)	1.366 (11)
C23—C24	1.368 (10)	1.417 (8)	1.397 (5)	1.362 (10)
C24—C25	1.407 (10)	1.388 (10)	1.413 (4)	1.374 (9)
C25—C21	1.387 (12)	1.406 (8)	1.397 (4)	1.408 (10)
C1—C11	1.505 (6)	1.493 (6)	1.518 (3)	1.520 (6)
C1—O1	1.436 (5)	1.434 (6)	1.433 (3)	1.434 (6)
C2—C2	1.514 (7)	1.529 (7)	1.537 (3)	1.542 (6)
C2—C3	—	—	1.510 (4)	—
C1—C31	—	—	1.529 (3)	1.536 (6)
C2—C31	—	1.504 (7)	—	—
C2—C41	—	—	—	1.513 (6)
O···O$^{\mathrm{i}}$	2.724 (3)	—	—	—
O···O$^{\mathrm{ii}}$	—	2.868 (8)	—	—
O1—C1—C11—C12	77.1 (7)	36.5 (5)	−145.2 (4)	−150.4 (8)
C2—C1—C11—C12	−163.4 (10)	−82.5 (7)	−23.3 (2)	−30.7 (4)
C31—C1—C11—C12	—	—	98.9 (4)	91.5 (7)
H0—O1—C1—C11	−90 (6)	24 (11)	36 (4)	—

(*b*) (2*c*)

C11—C12	1.432 (4)	C41—C42	1.422 (4)
C12—C13	1.420 (5)	C42—C43	1.416 (5)
C13—C14	1.410 (5)	C43—C44	1.414 (5)
C14—C15	1.418 (5)	C44—C45	1.416 (4)
C15—C11	1.427 (4)	C45—C41	1.426 (4)
C1—C11	1.516 (4)	C5—C41	1.521 (4)
C1—O1	1.431 (3)	C5—O2	1.439 (3)
C1—C31	1.528 (4)	C5—C61	1.520 (4)
C21—C22	1.372 (6)	C51—C52	1.394 (6)
C22—C23	1.352 (6)	C52—C53	1.367 (7)
C23—C24	1.395 (10)	C53—C54	1.396 (10)
C24—C25	1.426 (11)	C54—C55	1.421 (10)
C25—C21	1.409 (7)	C55—C51	1.393 (6)
C1—C2	1.554 (4)	C5—C6	1.558 (4)
C2—C3	1.523 (4)	C6—C7	1.528 (5)
C2—C4	1.513 (5)	C6—C8	1.517 (5)
O1—C1—C11—C12	30.5 (3)	O2—C5—C41—C42	30.0 (3)
C2—C1—C11—C12	−85.2 (4)	C6—C5—C41—C42	−85.4 (4)
C31—C1—C11—C12	152.3 (5)	C61—C5—C41—C42	151.4 (5)
H01—O1—C1—C11	29 (5)	H02—O2—C5—C41	36 (5)

(*c*) (2*d*)

	$m = 1$	$m = 2$	$m = 3$	$m = 4$
Cm11—Cm12	1.42 (3)	1.42 (3)	1.42 (3)	1.43 (3)
Cm12—Cm13	1.38 (3)	1.43 (3)	1.45 (3)	1.45 (3)
Cm13—Cm14	1.43 (3)	1.39 (3)	1.42 (3)	1.42 (3)
Cm14—Cm15	1.42 (3)	1.40 (3)	1.40 (3)	1.41 (3)
Cm15—Cm11	1.41 (3)	1.46 (3)	1.43 (3)	1.45 (3)
Cm21—Cm22	1.41 (3)	1.40 (3)	1.44 (3)	1.39 (3)
Cm22—Cm23	1.44 (2)	1.39 (3)	1.42 (3)	1.44 (3)
Cm23—Cm24	1.39 (3)	1.38 (3)	1.39 (3)	1.38 (3)
Cm24—Cm25	1.40 (3)	1.37 (3)	1.41 (3)	1.45 (3)
Cm25—Cm21	1.36 (3)	1.39 (3)	1.41 (3)	1.41 (3)
Cm1—Cm11	1.54 (2)	1.49 (2)	1.57 (2)	1.55 (2)
Cm1—Cm31	1.54 (2)	1.55 (2)	1.55 (2)	1.58 (2)
Cm1—Om1	1.42 (2)	1.45 (2)	1.41 (2)	1.44 (2)
Cm1—Cm2	1.57 (2)	1.58 (2)	1.54 (2)	1.58 (2)
Cm2—Cm3	1.55 (2)	1.53 (2)	1.58 (2)	1.52 (2)
Cm2—Cm4	1.53 (2)	1.56 (2)	1.55 (2)	1.53 (2)
Cm2—Cm5	1.52 (2)	1.54 (2)	1.55 (2)	1.54 (2)
Om1—Cm1—Cm11—Cm12	−35 (1)	26 (2)	−35 (1)	32 (1)
Cm2—Cm1—Cm11—Cm12	80 (1)	−84 (1)	84 (1)	−83 (1)
Cm31—Cm1—Cm11—Cm12	−153 (1)	148 (1)	−154 (1)	149 (1)
Cm11—Cm1—Cm2—Cm3	−179 (1)	174 (1)	−179 (1)	177 (1)
Cm11—Cm1—Cm2—Cm4	59 (1)	−63 (1)	55 (2)	−64 (1)
Cm11—Cm1—Cm2—Cm5	−61 (1)	55 (1)	−62 (1)	58 (1)

Table 3 (*cont.*)

(*d*) (2*g*)

C11—C12	1.424 (4)	C31—C32	1.428 (3)
C12—C13	1.418 (5)	C32—C33	1.420 (4)
C13—C14	1.402 (6)	C33—C34	1.412 (4)
C14—C15	1.418 (4)	C34—C35	1.422 (4)
C15—C11	1.425 (4)	C35—C31	1.424 (3)
C1—O1	1.439 (3)	C1—C31	1.519 (3)
C21—C22	1.407 (5)	C41—C42	1.404 (6)
C22—C23	1.414 (6)	C42—C43	1.415 (6)
C23—C24	1.396 (5)	C43—C44	1.410 (5)
C24—C25	1.398 (5)	C44—C45	1.408 (5)
C25—C21	1.398 (4)	C45—C41	1.403 (5)
C1—C11	1.522 (3)	C1—C51	1.540 (3)
O1—C1—C11—C12	−43.1 (2)	O1—C1—C31—C32	−52.1 (2)
C31—C1—C11—C12	75.0 (3)	C11—C1—C31—C32	−172.5 (4)
C51—C1—C11—C12	−165.1 (4)	C51—C1—C31—C32	67.1 (2)
H0—O1—C21—C11	−36 (4)	H0—O1—C1—C31	−156 (4)

Symmetry codes: (i) $y, \frac{1}{2}-x, \frac{1}{4}+z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}-z$. Torsional angles are described as, for example, C*xn*—Cp*x*—Cp*y*—C*yn*, where *n* is an atom descriptor (typically $n = 1$–5) and *x*, *y* are ring descriptors: usually $n = 1$ or 2, but in 2*c* $n = 1$, 2, 4 or 5; in 2*g*, $n = 1$, 2, 3 or 4; in 2*d*, $x = m1$ or $m2$, where *m* is a molecule descriptor with $m = 1$, 2, 3 or 4.

Table 4. *Significant intra- and intermolecular dimensions*

	D	H	*A*	*D*—H	H···*A*	*D*—*A*	*D*—H···*A*
(1*a*)	O1	H0	O1$^{\mathrm{i}}$	0.78 (5)	1.95 (5)	2.724 (3)	170 (4)
	O1		C21			5.053 (4)	
	O1		Fe1			4.373 (3)	
(1*f*)	O1	H0	O1$^{\mathrm{ii}}$	0.64 (6)	2.44 (6)	2.868 (8)	126 (7)
	O1	H0	C21	0.64 (6)	3.06 (7)	3.548 (7)	135 (8)
	O1	H0	Fe1	0.64 (6)	3.09 (7)	3.498 (4)	124 (7)
(2*b*)	O1	H0	C21	0.79 (3)	2.84 (3)	3.549 (3)	151 (3)
	O1	H0	Fe1	0.79 (3)	3.03 (3)	3.544 (2)	124 (3)
	O1		O1$^{\mathrm{iii}}$			4.999 (4)	
(2*c*)	O1	H01	C21	0.81 (4)	3.12 (4)	3.745 (5)	136 (2)
	O1	H01	Fe1	0.81 (4)	3.04 (3)	3.588 (2)	127 (3)
	O1		O2$^{\mathrm{iv}}$			5.811 (3)	
	O2	H02	C51	0.72 (4)	3.23 (4)	3.804 (5)	139 (4)
	O2	H02	Fe2	0.72 (4)	3.17 (4)	3.615 (2)	122 (4)
	O2		O1$^{\mathrm{v}}$			5.811 (3)	
(2*d*)	O11		C121			3.58 (2)	
	O11		Fe1			3.49 (1)	
	O21		C221			3.64 (2)	
	O21		Fe2			3.53 (1)	
	O31		C321			3.60 (2)	
	O31		Fe3			3.51 (1)	
	O41		C241			3.61 (2)	
	O41		Fe4			3.52 (1)	
(2*f*)	O1	H0*a*	C15	0.90	2.59	2.882 (6)	100
	O1	H0*b*	C21	0.90	2.75	3.549 (6)	148
	O1	H0*b*	Fe1	0.90	3.13	3.539 (3)	110
	O1	H0*c*	C42	0.90	2.51	3.093 (5)	123
	O1		O1$^{\mathrm{vi}}$			5.889 (2)	
2(*g*)	O1	H0	O1$^{\mathrm{iii}}$	0.66 (3)	2.61 (3)	2.926 (4)	111 (3)
	O1	H0	C21	0.66 (3)	2.86 (3)	3.484 (4)	159 (4)
	O1	H0	Fe1	0.66 (3)	3.11 (3)	3.545 (2)	127 (3)

Symmetry codes (i) $y, \frac{1}{2}-x, \frac{1}{4}+z$; (ii) $x, \frac{1}{2}-y, \frac{1}{2}-z$; (iii) $-x, -y, -z$; (iv) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; (vi) $x, 1+y, z$.

dimers containing O—H···O hydrogen bonds: clearly, IR data are of limited value for the elucidation of solid-state aggregation patterns in compounds of this type.

The formation by (1*f*) of dimers having C_2 symmetry may be contrasted with the formation of extended chains by both (1*d*) (Li, Ferguson, Glidewell & Zakaria, 1994) and (1*e*) (Ferguson, Gallagher, Glidewell & Zakaria, 1994*b*) and with the formation of centrosymmetric dimers by (2*e*) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*). Although the closed $(OH)_2$ motif is unknown in simple unfunctionalized organic alcohols, C_nH_mOH, and has been described as 'highly improbable' (Brock & Duncan 1994), this motif is found not only in (1*f*) but also in (2*e*), (2*g*) (see below), $[(C_5H_5)Fe(C_5H_4)]_2C(OH)CMe_3$ (Sharma, Cervantes-Lee & Pannell, 1992) and ferrocenyl(2-furyl)phenylmethanol (Ferguson, Glidewell, Opromolla, Zakaria & Zanello, 1995): thus, although unknown in purely organic alcohols, this motif is actually rather common in α-ferrocenyl alcohols. The molecular volume of (1*f*), 360.4 (5) Å^3, is significantly larger than that, 352.5 (1) Å^3, of the isomeric compound (2*a*) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*).

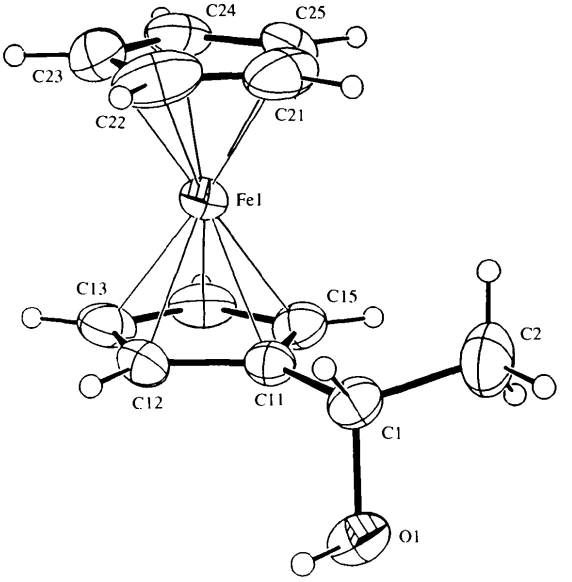

Fig. 1. View of the molecule of 1-ferrocenylethanol (1*a*) showing the atom-labelling scheme. Thermal ellipsoids are drawn at the 30% level for non-H atoms; H atoms are shown as small spheres of arbitrary size.

Crystals of (2*g*) are monoclinic, space group $P\bar{1}$, with one molecule in the asymmetric unit (Fig. 4). Pairs of molecules are thus related by a centre of inversion (Fig. 5), with an intermolecular O· · ·O distance of 2.926 (4) Å, within the range observed for weak hydrogen bonds. However, the hydroxyl H atoms, as well as participating in $(OH)_2$ hydrogen bonding as observed both in the related compound $[(C_5H_5)Fe(C_5H_4)]_2C(OH)CMe_3$ (Sharma, Cervantes-Lee & Pannell, 1992) and in (1*f*) and (2*e*), form intramolecular O—H· · ·$\pi(C_5H_5)$ interactions involving, as in (1*f*), an unsubstituted cyclopentadienyl ring from one of the ferrocenyl groups where the shortest intramolecular disance, O· · ·C21, is 3.484 (4) Å.

3.2. *Structures showing no O—H· · ·O hydrogen bonding*

Along with (2*a*) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*), the structures of (2*b*)–(2*d*) complete the series $FdCPh(OH)CH_{3-x}(CH_3)_x$ ($x = 0$–3), all of which are monomeric in the solid state. The racemic forms of (2*b*) and (2*c*) both crystallize in the monoclinic system, (2*b*) in the centrosymmetric space group $P2_1/c$ with one molecule in the asymmetric unit (Fig. 6) and (2*c*) in the non-centrosymmetric space group *Cc*, with two molecules per asymmetric unit (Fig. 7). In these crystals, the equal numbers of molecules of *R* and *S* configurations are accommodated by the centre of inversion and the glide plane, respectively. In (2*c*), the two independent molecules have the same chirality and virtually identical

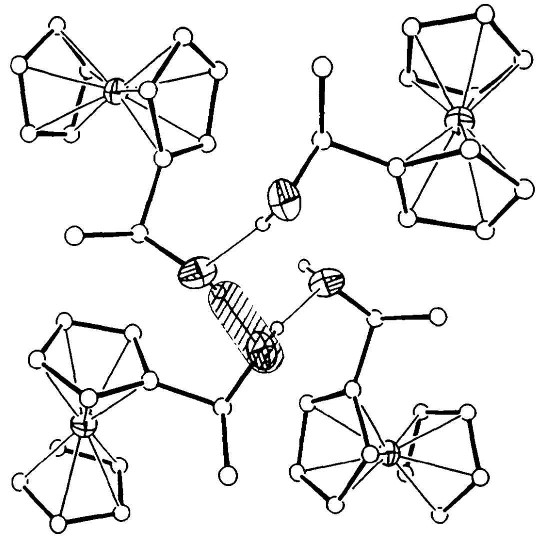

Fig. 2. View of the hydrogen bonding in (1*a*), viewed along the 4_1 screw axis, showing the *C*(2) motif.

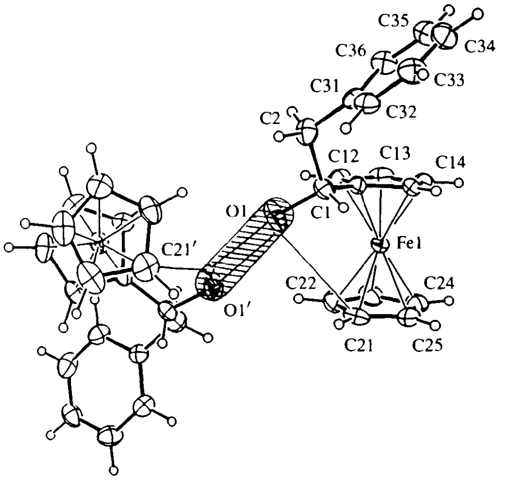

Fig. 3. View of the dimeric aggregate of 1-ferrocenyl-2-phenylethanol (1*f*), showing the $R_2^2(4)$ motif; atoms are depicted as in Fig. 1.

dimensions and conformations: nonetheless, there is no inversion centre present and indeed the structure could not be solved in the centrosymmetric space group $C2/c$. The structures of (2*b*) and (2*c*) show a number of features in common, both with each other and with (2*a*) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*). There is no O—H···O hydrogen bonding in 2(*a*)–(*c*), despite the fact that the steric demands about the unique central C1 atom are probably less in this series than in (2*e*), which forms centrosymmetric dimers held together by O—H···O hydrogen bonds (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*); the closest intermolecular O···O distances are: in (2*a*), 3.768 (3) Å; in (2*b*), 4.999 (4) Å; in (2*c*), 5.811 (3) Å, in every case precluding the formation of O—H···O hydrogen bonds. In each of (2*a*)–(*c*), the hydroxyl H atom instead points towards the π-system of the unsubstituted cyclopentadienyl ring. The closest O···C distances are: in (2*a*), 3.487 (3); in (2*b*), 3.549 (3); in (2*c*), 3.745 (5) and 3.804 (5) Å in the two independent molecules, associated with apparent (O)H···Fe distances of 2.98 (3) Å in (2*a*); 3.03 (3) in (2*b*); 3.04 (4) and 3.17 (4) Å in (2*c*). The corresponding O···Fe distances are: in (2*a*), 3.464 (3); in (2*b*), 3.544 (2); and in (2*c*), 3.588 (2) and 3.615 (2) Å.

The racemic form of (2*d*) crystallizes in the centrosymmetric monoclinic space group $P2_1/n$, which can accommodate equal numbers of molecules having *R* and *S* configurations. There are four molecules in the asymmetric unit (Fig. 8), labelled in Tables 2–4 as $n = 1$–4; of these, the molecules labelled $n - 1$ and 3 are of opposite chirality from those labelled $n = 2$ and 4, so that the asymmetric unit itself accommodates the racemic nature of (2*d*). In view of the unusual cell dimensions

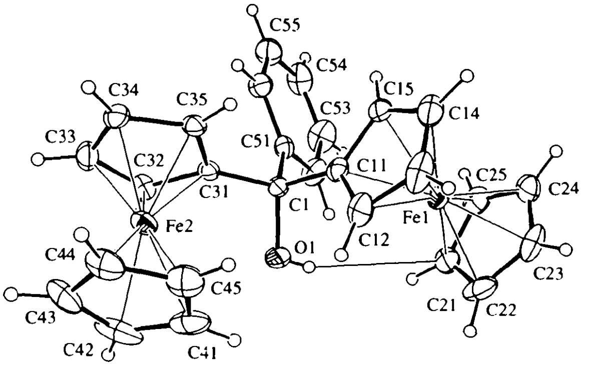

Fig. 4. View of the molecule of diferrocenyl(phenyl)methanol (2*g*); atoms are depicted as in Fig. 1. The $R_2^2(4)$ motif contains the O atoms of the molecules at (x, y, z) and $(-x, -y, -z)$ and their associated H atoms: the $S(7)$ motif contains the atoms C21, Fe1, C12, C11, C1, O1 and the hydroxyl H atom.

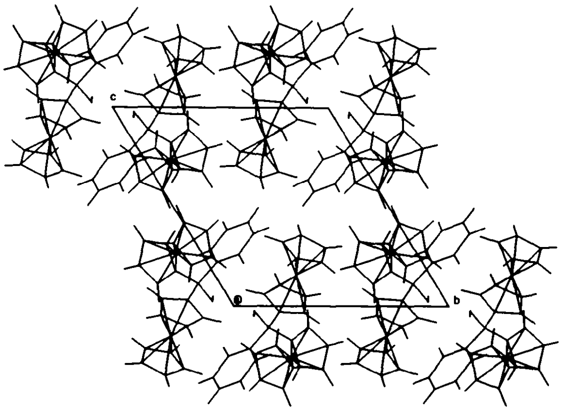

Fig. 5. View of the unit-cell contents of (2*g*), viewed along the *a* direction.

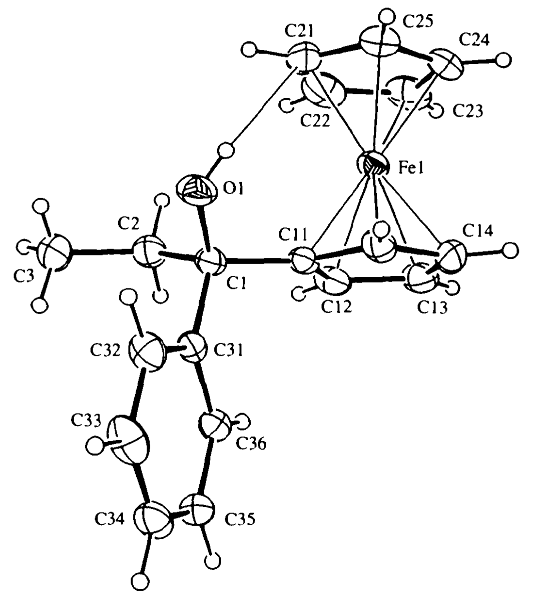

Fig. 6. View of the molecule of 1-ferrocenyl-1-phenylpropan-1-ol (2*b*); atoms are depicted as in Fig. 1.

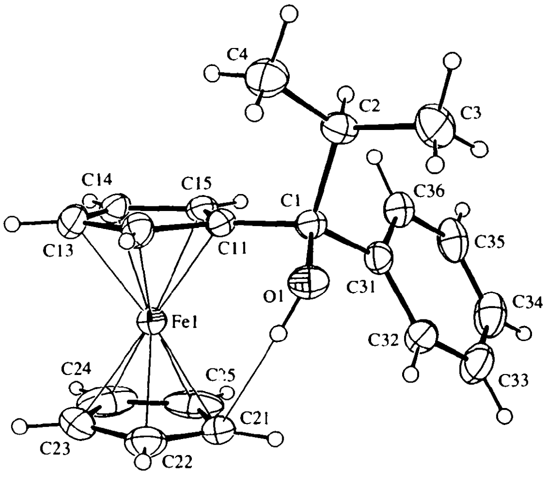

Fig. 7. View of one of the two independent molecules of 1-ferrocenyl-1-phenyl-2-methylpropan-1-ol (2*c*); atoms are depicted as in Fig. 1.

and the large asymmetric unit containing both enantiomers, a careful search for possible missing symmetry elements was made, once the refinement was complete, using both *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989) and *PLATON* (Spek, 1994) routines, but none was found: no alternative unit cell could be found, and the Laue group was confirmed as $2/m$. The arrangement of the molecules in the unit cell (Fig. 9) gives rise to four groups, each of four molecules whose Fe atoms have their z-coordinates within ±0.031 of 0.000, 0.250, 0.500 and 0.750, respectively: this arrangement and the large scattering power of the iron atoms are together responsible for the effective absence of the 001 reflections, except when $l = 4n$. There is no intermolecular aggregation; although the hydroxyl H atoms could not be located, the shortest intermolecular O···O distance of 5.85 (2) Å precludes any O—H···O hydrogen bonding; however, the On1···Cn21 distances, in the range 3.58 (2)–3.64 (2) Å, do not rule out the possibility of intramolecular O—H···$\pi(C_5H_5)$ interactions. The related molecule (1*d*) forms spiral chains, around a 2_1 screw axis (Li, Ferguson, Glidewell & Zakaria, 1994), but with the *R* and *S* enantiomers disordered within the chain so that any O—H···O hydrogen bonding probably arises adventitiously within a structure dominated by the packing of the large organic substituents. In (2*d*), there are three organic substituents around the central stereogenic C atom, having different steric demands: the ferrocenyl, phenyl and *t*-butyl groups are, respectively, approximately cylindrical, discoid and spherical and these substituents effectively shield the hydroxyl groups from contact with other molecules and, presumably, dominate the molecular packing. Within the series $FcCPh(OH)CH_{3-x}(CH_3)_x$ (x = 0–3), the effective molecular volumes are 352.5 (1), 393.0 (5), 412.3 (7) and 431 (3) Å^3 for x = 0–3, respectively.

Racemic (2*f*) crystallizes in the centrosymmetric space group $C2/c$, containing equal numbers of *R* and *S* molecules in the unit cell. The structure consists of isolated monomers (Fig. 10), in which the hydroxyl H atom is disordered over three sites, with site occupation factors estimated from difference maps as 0.19, 0.35 and 0.46, respectively. Each of these hydrogen sites is *trans* to one of the C—C bonds involving C1, so that there is perfect staggering about the C1—O1 bond: since the three organic substituents bonded to C1 are all different (phenyl, benzyl, ferrocenyl), equal population of the three hydroxyl hydrogen sites is not to be expected. Similar perfect staggering of disordered hydroxyl hydrogen sites occurs in tribenzylmethanol, $(PhCH_2)_3COH$ (Ferguson, Gallagher, Glidewell & Zakaria, 1993*a*), where the molecules, although lying in general positions, exhibit approximate threefold rotational symmetry and the disordered sites are again unequally populated. In each of its three sites the hydroxyl H atom in (2*f*) forms a close contact with a carbon of one of the aromatic systems (Fig. 10 and Table 4); H0*a* and H0*b* are engaged in O—H···$\pi(C_5R_5)$ interactions, with the substituted and unsubstituted cyclopentadienyl groups, respectively, while H0*c* is involved in an O—H···π(arene) interaction with the

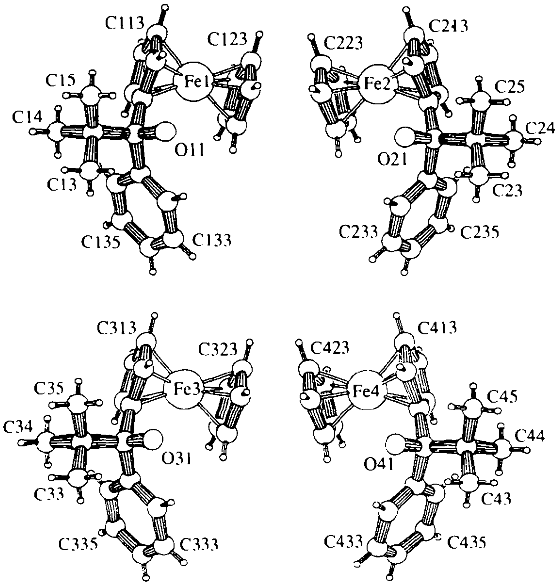

Fig. 8. Views of the four independent molecules of 1-ferrocenyl-1-phenyl-2,2-dimethylpropan-1-ol (2*d*).

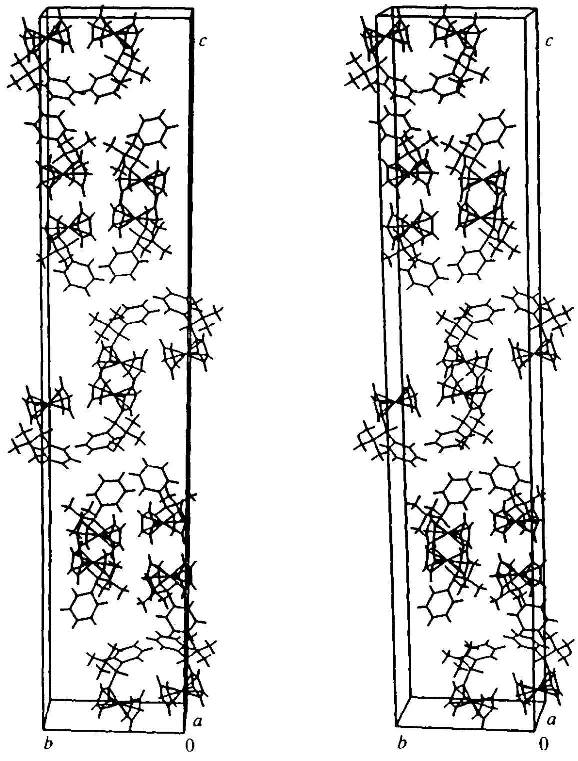

Fig. 9. Stereoview of the unit-cell contents of (2*d*).

benzyl group. The monomeric nature of (2*f*), when compared with the dimeric (2*e*), is consistent with the increased steric hindrance arising from a benzyl group, compared with a phenyl group, which we have noted previously (Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995; Glidewell & Lightfoot, 1995).

3.3. *Molecular dimensions and conformations*

Because of the comparatively low precision of the refined values of the bond lengths and angles in (2*d*), these values are excluded from the following discussion of the metrical data. Within the molecular units, the C—C bond lengths in the cyclopentadienyl rings range from 1.352 (6) to 1.426 (11) Å (both in 2*c*) in the unsubstituted rings and from 1.402 (7) in (1*f*) and 1.402 (6) in (2*g*) to 1.432 (4) Å in (2*c*) in the substituted rings: nevertheless, there is a clear pattern, consistently observed, that the mean C—C distance is always greater in the substituted than in the unsubstituted ring (Table 3). The C—O bond lengths are all very similar, ranging only from 1.431 (3) Å in one of the independent molecules in (2*c*) to 1.439 (3) Å in the other molecule of (2*c*) and in (2*g*): there is no trend of increasing C—O bond length with increasing steric congestion around C1, as found for example in compounds of the type RCPh$_2$OH (Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995).

The remaining intramolecular bonded distances are typical of their types, with no significant deviations outside the ranges defined by the upper and lower quartile values (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987; Orpen, Brammer, Allen, Kennard, Watson & Taylor, 1989). The orientation of the two cyclopentadienyl rings of each ferrocene fragment always deviates slightly from precisely parallel: the angle between the C_5 planes varies from 1.2 (3) in (2*f*) to 4.5 (2)° in (1*f*). The ring conformation of the ferrocenyl units, as defined by the mean value of the torsion angles C*xn*—Cp*x*—Cp*y*—C*yn* (where Cp represents the centroid of a cyclopentadienyl ring and *x*,*y* are ring descriptors), is always close to eclipsed (Table 3); a value of zero for such a torsion angle corresponds to complete eclipsing of the rings, while complete staggering of the rings is characterized by a torsion angle of 36°.

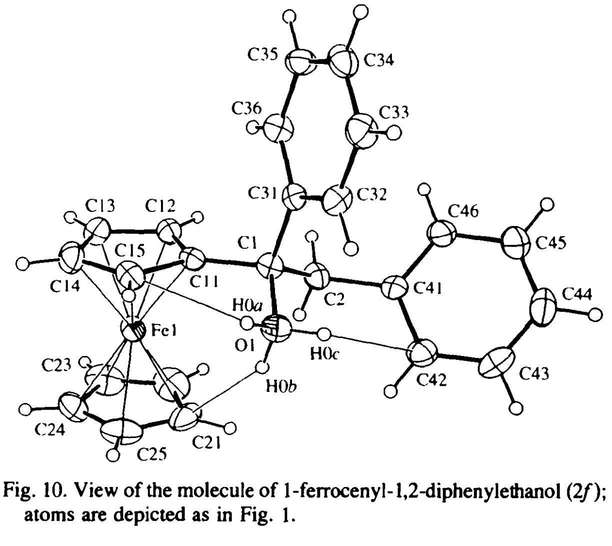

Fig. 10. View of the molecule of 1-ferrocenyl-1,2-diphenylethanol (2*f*); atoms are depicted as in Fig. 1.

3.4. *Hydrogen-bonding motifs*

The hydrogen-bond motif in (1*a*) has graph set $C(2)$ (Etter, 1990, 1991; Etter, MacDonald & Bernstein, 1990; Bernstein, Davis, Shimoni & Chang, 1995), as generally found in alcohols forming chains or helices (Brock & Duncan, 1994), and the O···O distance is 2.724 (3) Å. The O···O distance in (1*a*) is significantly shorter than the values found in other chain-forming ferrocenyl alcohols, *e.g.* 2.802 (11) Å observed in (1*d*) (Li, Ferguson, Glidewell & Zakaria, 1994), and the two independent values of 3.059 (2) and 3.150 (2) Å found in (1*e*) (Ferguson, Gallagher, Glidewell & Zakaria, 1994*b*): the hydrogen bonds in (1*d*) and (1*e*) are both to be regarded as weak (Novak, 1974; Emsley, 1980), while the O···O distance in (1*a*) represents hydrogen bonds of intermediate strength in the Emsley and Novak classifications. The cyclic dimer of (1*f*) lies across a crystallographic twofold axis and the graph set for the hydrogen-bonding motif is $R_2^2(4)$, with an O···O distance of 2.868 (8) Å. This distance is identical within experimental uncertainty to the distance of 2.876 (2) Å found (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*) in the centrosymmetric cyclic dimer of (2*e*), but much longer than the mean of 2.75 Å found in the cyclic dimer of $[(C_5H_5)Fe(C_5H_4)]_2C(OH)CMe_3$ (Sharma, Cervantes-Lee & Pannell, 1992), which is also centrosymmetric. In (2*g*) there are two hydrogen-bonding motifs. There is an intramolecular motif arising from the O—H···$\pi(C_5H_5)$ interaction, and having graph set $S(7)$: in addition, the molecules are linked into centrosymmetric pairs *via* O—H···O hydrogen bonds in an $R_2^2(4)$ motif, so that the overall motif is $R_2^2(4)[S(7)]$. The O···O distance within the dimer of (2*g*), 2.926 (4) Å, is as in (1*f*), much longer than that in the dimer of $[(C_5H_5)Fe(C_5H_4)]_2C(OH)CMe_3$: hence the hydrogen bonds in both (1*f*) and (2*g*) must be regarded as weak, while those in $[(C_5H_5)Fe(C_5H_4)]_2C(OH)CMe_3$ are of intermediate strength (Novak, 1974; Emsley, 1980).

The predominant hydrogen-bonding patterns in simple organic alcohols C_nH_mOH, aside from those showing no molecular aggregation, are (Brock & Duncan, 1994): cyclic tetramers and hexamers containing $R_4^4(8)$ and $R_6^6(12)$ rings, although we have recently reported both an $R_3^3(6)$ trimer (Ferguson, Carroll, Glidewell, Zakaria & Lough, 1995) and a tetrahedral tetramer (Ferguson, Gallager, Glidewell, Low & Scrimgeour, 1992); chains, particularly those generated by 2_1 axes, and helices, including those generated by 4_1 axes; open dimers in which only one hydroxyl H atom per dimer unit is involved in an O—H···O interaction, while the other hydroxyl H atom plays no part in the hydrogen bonding. By contrast, in α-ferrocenyl alcohols, there are as yet no known examples containing $R_3^3(6)$, $R_4^4(8)$ or $R_6^6(12)$ rings; on the other hand, $R_2^2(4)$ dimers are commonly found. Five of the 13 structurally characterized α-ferrocenyl alcohols [1*a*, 1*d*, 1*e*, 1*f*, 2*a*–*g*, $[(C_5H_5)Fe(C_5H_4)]C(OH)CMe_3$ (Sharma, Cervantes-Lee & Pannell, 1992), and ferrocenyl(2-furyl)phenylmethanol (Ferguson, Glidewell, Opromolla, Zakaria & Zanello, 1995)] exhibit the $R_2^2(4)$ motif unknown for simple alcohols.

Compounds (2*a*)–(*d*) and (*f*), although notably not (2*e*) (Ferguson, Gallagher, Glidewell & Zakaria, 1993*b*), all crystallize as monomeric units without intermolecular aggregation. In each of (2*a*)–(*c*), there are intramolecular O—H···$\pi(C_5H_5)$ interactions, with graph set *S*(6) in each case. In (2*f*) there are three different hydrogen-bonding motifs, formed by the three different hydroxyl hydrogen sites (Fig. 10); the graph set for the motif containing H0*a* is *S*(5), while the graph sets for the two different motifs involving H0*b* and H0*c* are both *S*(6).

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