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Key indicators

Single-crystal X-ray study
T = 293 K
Mean $\sigma(\text{C}-\text{C}) = 0.006 \text{ \AA}$
R factor = 0.066
wR factor = 0.169
Data-to-parameter ratio = 14.9

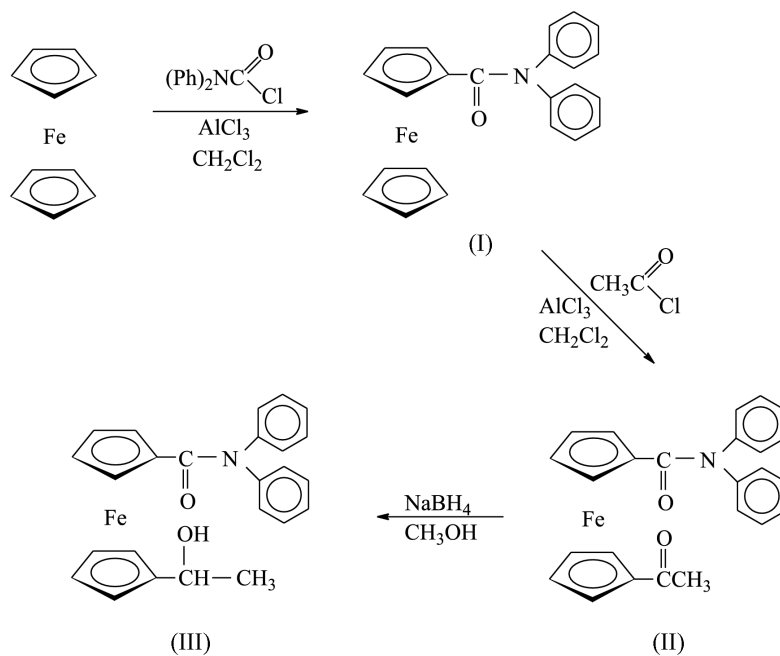
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1'-(1-Hydroxyethyl)-N,N-diphenylferrocene-1-carboxamide

In the title compound, $[\text{Fe}(\text{C}_{18}\text{H}_{14}\text{NO})(\text{C}_7\text{H}_9\text{O})]$, an *N,N*-diphenylcarboxamide moiety and a hydroxyethyl group are attached to the ferrocene skeleton. The cyclopentadienyl rings deviate only slightly from an eclipsed conformation. Two $\text{C}-\text{H} \cdots \pi$ interactions link the molecules into sheets. According to the X-ray, IR, and ^1H NMR data, the molecule also possesses an intramolecular $\text{O}-\text{H} \cdots \text{O}$ hydrogen bond.

Comment

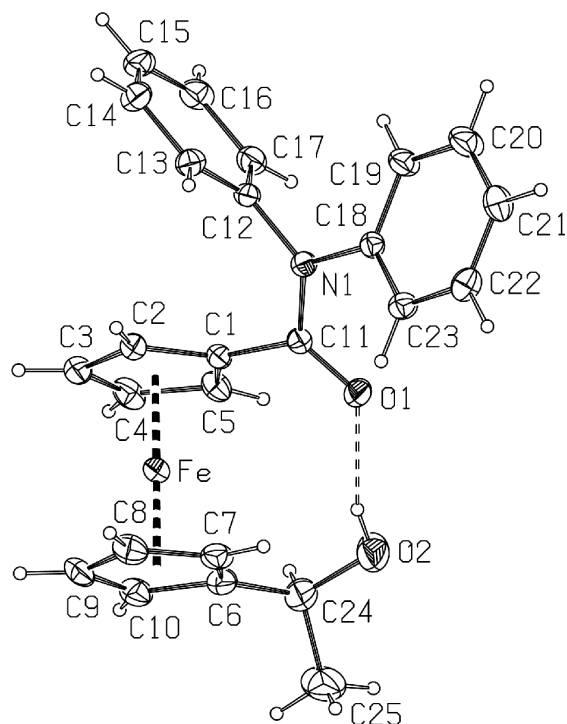
The increasing importance of transition metal-catalysed enantioselective reactions has paralleled the development of new ligands (Togni, 1996; Perea *et al.*, 1998). A variety of synthetic methods have been reported in the literature for the preparation of heteroannularly substituted derivatives of ferrocene carbinols and carboxylic acids (Little & Eisenthal, 1960, 1961). The title compound, (III), was prepared as one of the substrates for our current research on lipase-catalysed resolution of racemic ferrocene derivatives (Đaković *et al.*, 2003). Acylation of ferrocene with *N,N*-diphenylcarbonyl chloride gave *N,N*-diphenylferrocenecarboxamide, (I), which was converted into *N,N*-diphenyl-1'-acetylferrocenyl-1-carboxamide, (II), by the action of acetyl chloride/ AlCl_3 . Reduction of the ketone–amide (II) with sodium borohydride in aqueous methanol gave the alcohol–amide (III).



In (III), the cyclopentadienyl (Cp) rings bear an *N,N*-diphenylcarboxamide moiety and a hydroxyethyl group (Fig. 1).

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Ferrocene compounds, Part XLII. For part XLI, see Barišić *et al.* (2004).

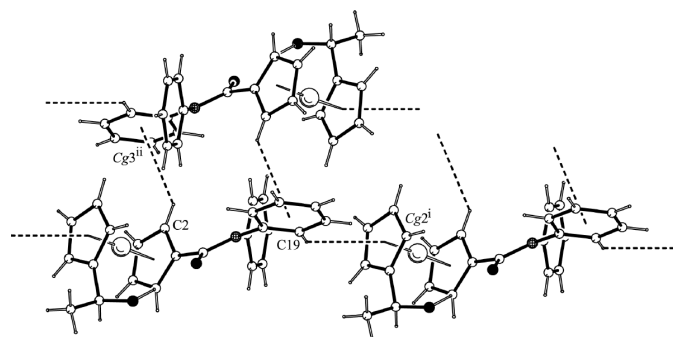

Figure 1

A view of (III), with the atom-numbering scheme. Displacement ellipsoids for non-H atoms are drawn at the 20% probability level. The hydrogen bond is shown dashed.

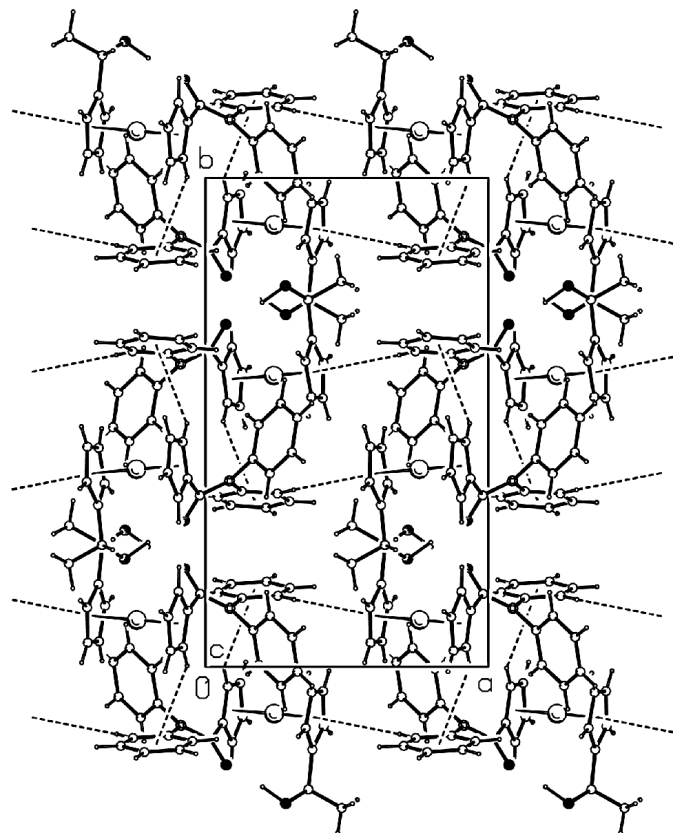
The C1–Cg1–Cg2–C6 pseudo-torsion angle is $-68.3(3)^\circ$ (Cg1 and Cg2 are the centroids of the C1–C5 and C6–C10 rings, respectively). A survey of the Cambridge Structural Database (July 2004, Version 5.25; Allen, 2002) reveals that this is the first structure that has the *N,N*-diphenylcarboxamide moiety attached to the ferrocenyl skeleton. When we compared (III) with the structures where one phenyl ring is replaced with an H atom and the phenyl ring is not part of a polycyclic structure (Oberhoff *et al.*, 1996; Shirin *et al.*, 2002; Janner *et al.*, 2003), we found that that the C11–N1 and N1–C(phenyl) bonds in (III) are slightly elongated (0.02–0.04 Å; Table 1).

The cyclopentadienyl (Cp) rings deviate only slightly from the eclipsed conformation. The values of the corresponding C–Cg1–Cg2–C pseudo-torsion angles, defined by joining two eclipsing Cp C atoms through the ring centroids range from $3.4(3)$ to $4.2(4)^\circ$. The centroids of the Cp rings are almost equidistant from the Fe atom. The Fe–Cg1 and Fe–Cg2 distances are 1.644(2) and 1.639(2) Å, respectively, and the Cg1–Fe–Cg2 angle is $178.1(1)^\circ$.

The sum of the angles around atom N1 is nearly 360° , *i.e.* the atom is sp^2 -hybridized. The carbonyl group and C1–C5 ring form an extended π -conjugated system. The coplanar arrangement of a carbonyl group attached to the ring should allow maximum interaction of the two π systems (Lin *et al.*, 1998). In (III), the C11=O1 bond is twisted out of the C1–C5 ring by $39.3(3)^\circ$, and the C1–C11 bond is longer than the equivalent bond in our previously reported structures where a carbonyl group is attached to the Cp ring (1.46–1.47 Å; Pavlović *et al.*, 2002; Barišić *et al.*, 2003; Cetina *et al.*, 2003;


Figure 2

Part of the crystal structure of (III), showing the C19–H19...Cg2ⁱ and C2–H2A...Cg3ⁱⁱ interactions (Cg2 and Cg3 are the C6–C10 and C18–C23 ring centroids) that form a chain motif and a centrosymmetric dimer. C–H... π interactions are indicated by dashed lines and the unit-cell outline has been omitted for clarity. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $-x, 1 - y, 2 - z$.]


Figure 3

A crystal packing diagram of (III), viewed along [001], showing the formation of (010) sheets built from C19–H19...Cg2ⁱ and C2–H2A...Cg3ⁱⁱ interactions. C–H... π interactions are indicated by dashed lines. [Symmetry codes: (i) $-1 + x, y, z$; (ii) $-x, 1 - y, 2 - z$.]

Pavlović *et al.*, 2003). In these, the C11=O1 bond is almost coplanar with the Cp ring. The phenyl rings are rotated out of the mean plane of the C1/C11/O1/N1 atoms by $71.6(2)$ (C12–C17 ring) and $44.0(2)^\circ$ (C18–C23 ring). Furthermore, the C18–C23 phenyl ring is almost perpendicular with respect to the C1–C5 cyclopentadienyl ring and the C12–C17 phenyl ring; the corresponding dihedral angles are $89.4(2)$ and $83.3(2)^\circ$, respectively.

Carbonyl atom O1 and the hydroxyl group at C24 are linked by an intramolecular hydrogen bond (Fig. 1 and Table 2). This finding was corroborated by spectroscopic analysis. The IR spectrum of a *ca* 10^{-2} M solution of 1-ferrocenylethanol (Goldberg *et al.*, 1963) in CH_2Cl_2 showed the narrow strong absorption at 3598 cm^{-1} corresponding to ν O—H (free); the IR spectrum of (III) showed a very weak signal at this position and an additional broad band at 3388 cm^{-1} (O—H \cdots N). In the solution ^1H NMR spectrum, the signal for the hydroxyl proton belonging to the first mentioned compound was found at δ 3.55, and the signal of the alcohol–amide (III) had been shifted to lower field (4.70 p.p.m.), which is an indication of an intramolecular hydrogen bond. It should also be noted that there are two short intramolecular contacts between the C atoms of the Cp and phenyl rings [C1 \cdots C17 = 3.114 (6) Å and C2 \cdots C12 = 3.031 (5) Å], and one between carbonyl atom O1 and phenyl-ring atom C23 [2.882 (5) Å].

The supramolecular structure of (III) contains two very weak C—H \cdots π interactions (Figs. 2 and 3). Both interactions could be classified as geometric type-III interactions, according to Malone *et al.* (1997), and exhibit almost similar geometry (Table 2). The C19—H19 \cdots Cg2ⁱ interaction (Cg2 is the C6—C10 ring centroid) generated by the translation chain motif runs along [100] [symmetry code: (i) $-1 + x, y, z$]. The H19 \cdots C10ⁱ distance is shorter than the distance between the H atom and the Cp-ring centroid. The second shortest H \cdots C contact (H19 \cdots C6) is much longer than the H19 \cdots C10ⁱ contact and the C19—H19 bond points towards ring atom C10 rather than towards the Cp-ring centroid. On the other hand, the C2—H2A \cdots Cg3ⁱⁱ interaction (Cg3 is the C18—C23 ring centroid) forms a centrosymmetric dimer [symmetry code: (ii) $-x, 1 - y, 2 - z$]. The shortest contact is H2A \cdots C23ⁱⁱ and the C2—H2A bond points more to ring atom C23 than to the phenyl-ring centroid. The molecules of (III) are linked by these two C—H \cdots π interactions to form (010) sheets (Fig. 3).

Experimental

N,N-Diphenylferrocenylcarboxamide, (I), was prepared in 54% yield starting from ferrocene and *N,N*-diphenylcarbonyl chloride (Little & Eisenthal, 1960). By Friedel–Crafts reaction of (I) and acetyl chloride/ AlCl_3 in dry CH_2Cl_2 , a 95% yield of *N,N*-diphenyl-1'-acetylferrocenyl-1-carboxamide, (II), was obtained (Little & Eisenthal, 1961). To a warm solution of (II) (1.0 g, 2.365 mmol) in methanol (28 ml) containing 50% sodium hydroxide (0.03 ml), a 10% sodium borohydride solution (3.8 ml, made up in 10% aqueous sodium hydroxide) was added. The reaction mixture was stirred at room temperature for 30 min and at gentle reflux for an additional 5 h. On cooling, the product precipitated to give 1.0 g (99.5%) of orange crystals of (III) (m.p. 386–388 K). Single crystals of the title compound were obtained by slow evaporation of a dichloromethane solution at room temperature. IR (CH_2Cl_2 , cm^{-1}): ν 3595 vw (O—H, free), 3388 *b* (O—H asoc.), 3093 *w* (C—H, Fc), 3034 *w* (C—H, Ph), 2928 *m* (C—H, aliphatic), 1630 *s* (C=O), 1592 (N—C=O) ^1H NMR (CDCl_3 , p.p.m.): δ 7.30–7.35 (*m*, 4H, H14, H16, H20, H23; Ph), 7.10–7.25 (*m*, 6H, H13, H15, H17, H19, H21, H23; Ph), 4.70 (*s*, 1H, OH) (disappeared after addition of D_2O), 4.62 (*bs*, 1H, CHFc), 4.35 (*s*, 1H, Fc), 4.09–4.25 (*m*, 5H, Fc), 4.06 (*m*, 2H, Fc), 1.39–1.41 (*d*, 3H, Me). ^{13}C NMR (CDCl_3 , p.p.m.): δ 172.27 (C11), 143.5 (C12 and C18), 126.61–

129.18 (C13–C17), 97.32 (C1), 76.58 (C6), 73.04 (C24), 71.2, 70.27, 70.18, 68.38, 68.30, 67.49, 65.28, 65.26 (C2–C5 and C7–C10), 25.41 (C25).

Crystal data

[Fe(C₁₈H₁₄NO)(C₇H₅O)]
 $M_r = 425.29$
 Monoclinic, $P2_1/c$
 $a = 11.0428$ (12) Å
 $b = 18.507$ (2) Å
 $c = 10.1462$ (11) Å
 $\beta = 104.547$ (9)°
 $V = 2007.0$ (4) Å³
 $Z = 4$

$D_x = 1.407$ Mg m⁻³
 Mo $K\alpha$ radiation
 Cell parameters from 3736 reflections
 $\theta = 11.1$ – 20.6 °
 $\mu = 0.77$ mm⁻¹
 $T = 293$ (2) K
 Prism, orange
 $0.45 \times 0.24 \times 0.13$ mm

Data collection

Oxford Diffraction Xcalibur2 diffractometer
 ω scans
 Absorption correction: numerical (*CrysAlis RED*; Oxford Diffraction, 2004)
 $T_{\min} = 0.775$, $T_{\max} = 0.906$
 16741 measured reflections

3929 independent reflections
 3473 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.055$
 $\theta_{\max} = 26.0$ °
 $h = -13 \rightarrow 13$
 $k = -22 \rightarrow 19$
 $l = -12 \rightarrow 12$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.066$
 $wR(F^2) = 0.169$
 $S = 1.17$
 3929 reflections
 263 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0814P)^2 + 1.0597P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.54\text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.37\text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Fe—C6	2.029 (4)	Fe—C3	2.049 (4)
Fe—C1	2.032 (3)	N1—C11	1.374 (4)
Fe—C5	2.029 (4)	N1—C12	1.446 (4)
Fe—C10	2.031 (4)	N1—C18	1.445 (4)
Fe—C7	2.033 (4)	O1—C11	1.219 (4)
Fe—C8	2.042 (4)	O2—C24	1.411 (6)
Fe—C9	2.044 (4)	C1—C11	1.495 (5)
Fe—C2	2.046 (4)	C6—C24	1.520 (7)
Fe—C4	2.040 (4)	C24—C25	1.443 (7)
C11—N1—C12	120.1 (3)	O1—C11—C1	121.8 (3)
C11—N1—C18	121.9 (3)	N1—C11—C1	115.8 (3)
C12—N1—C18	117.3 (3)	O2—C24—C6	111.7 (4)
O1—C11—N1	122.4 (3)	C25—C24—C6	113.1 (5)
C12—N1—C11—C1	-18.4 (5)	C7—C6—C24—O2	-20.3 (7)
C18—N1—C11—C1	171.7 (3)	C7—C6—C24—C25	101.4 (6)

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O2—H2 \cdots O1	0.82	2.08	2.876 (5)	162
C19—H19 \cdots Cg2 ⁱ	0.93	3.25	3.933 (5)	132
C19—H19 \cdots C10 ⁱ	0.93	3.09	3.931 (6)	152
C19—H19 \cdots C6 ⁱ	0.93	3.36	4.005 (6)	129
C2—H2A \cdots Cg3 ⁱⁱ	0.93	3.20	3.912 (4)	135
C2—H2A \cdots C23 ⁱⁱ	0.93	2.93	3.777 (5)	152
C2—H2A \cdots C18 ⁱⁱ	0.93	3.20	4.068 (5)	156

Symmetry codes: (i) $x - 1, y, z$; (ii) $-x, 1 - y, 2 - z$. Notes: Cg2 is the C6—C10 ring centroid and Cg3 is the C18—C23 ring centroid

All H atoms were included in calculated positions as riding atoms, with O–H = 0.82 Å and C–H = 0.93 Å for aromatic H atoms, 0.96 Å for methyl H atoms or 0.98 Å for the methine H atom. H-atom U_{iso} values were set at $1.5U_{\text{eq}}$ (carrier atom) for the hydroxyl and methyl H atoms, and at $1.2U_{\text{eq}}$ (carrier atom) for all other H atoms.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*.

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