metal-organic papers

5-Ferrocenyl-5-methyltetrahydrofuran-2-one, the product of the Friedel–Crafts reaction of ferrocene with γ-methylenebutyrolactone

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In the molecular structure of 5-ferrocenyl-5-methyltetrahydrofuran-2-one, [Fe(C$_5$H$_5$)(C$_{10}$H$_{11}$O$_2$)], the five-membered heterocyclic ring adopts a distorted envelope conformation. The ferrocenyl substituent is in an equatorial position with respect to this ring. In the crystal structure, there are close C—H···O and C—H···π intermolecular contacts.

Comment

We have reported on the Friedel–Crafts reaction of ferrocene with diketene (Plażuk *et al.*, 2001). This reaction proceeds with an opening of the four-membered ring of diketene and leads to acetoacetylferrocene or the BF$_2$-chelated compound. We perceived that this outcome might be due to the strain present in diketene and that, therefore, it would be of interest to study the reactivity of ferrocene toward the essentially unstrained ω-methylene lactones, such as γ-methylene-γ-butyrolactone. We found that ferrocene reacts with this lactone in dichloromethane at room temperature in the presence of BF$_3$ and Et$_2$O (molar ratio ferrocene:lactone:acid 1:2:4) to afford the addition product of the metallocene to the exocyclic olefinic bond, namely 5-ferrocenyl-5-methyldihydrofuran-2-one, (I), in 23% isolated yield. A better yield of (I) (73%) was obtained when BF$_3$ and Et$_2$O were replaced by CF$_3$SO$_3$H.
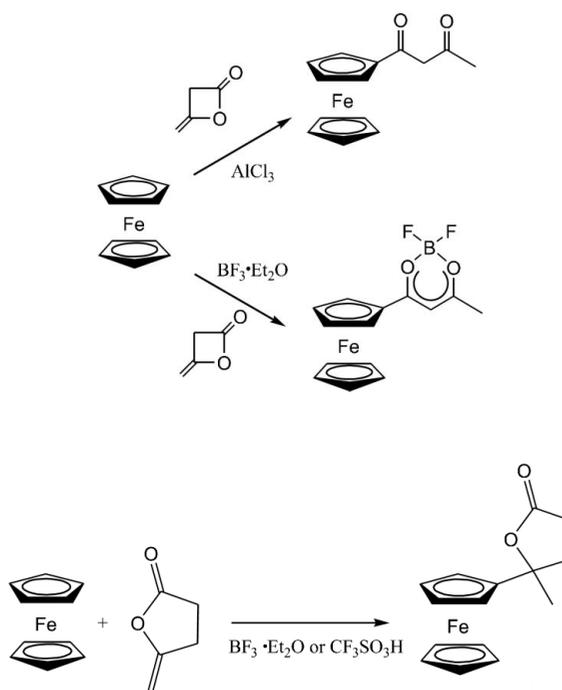
The title compound has been reported previously, prepared in 50% yield by the reaction of ferrocene with the isomeric
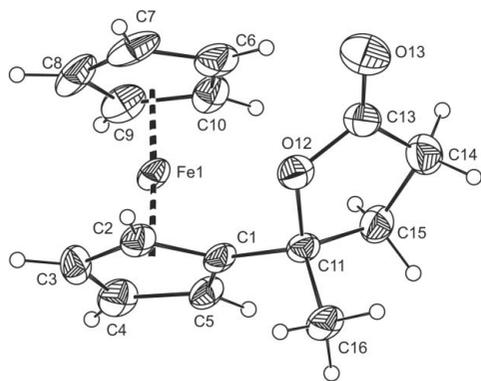
doi:10.1107/S1600536805006239

Figure 1
A view of the molecule of (I), showing the atomic numbering scheme. Displacement ellipsoids are drawn at the 40% probability level and H atoms are shown as small spheres of arbitrary radii.

γ-methylene-γ-butyrolactone, angelica lactone, in the presence of AlCl$_3$ (Sališova *et al.*, 1987). However, its crystal structure has not been reported until now.

Fig. 1 shows a displacement ellipsoid plot of (I), with the atom-labelling scheme. The molecule of (I) consists of the ferrocenyl moiety substituted with a five-membered heterocyclic lactone ring. The ferrocene adopts an eclipsed conformation, with an average C—$Cg1$—$Cg2$—C torsion angle of 4.2 (4)° ($Cg1$ and $Cg2$ are the centroids of the C1–C5 and C6–10 rings, respectively). The overall geometry of this molecular fragment shows no unexpected features. The cyclopentadienyl rings are essentially planar within experimental error and the C—Fe distances range from 2.029 (6) to 2.054 (6) Å.

The heterocyclic ring of (I) is not planar, as three C atoms (C11, C14 and C15) are sp^3 hybridized. The total puckering amplitude calculated for the five atoms of this ring is $q_2 = 0.210$ (5) Å and the maximum deviation from the least-squares plane is 0.179 (1) Å for atom C14. Analysis of the puckering parameters [$\varphi_2 = -0.39$ (2)°] (Cremer & Pople, 1975), as well as the asymmetry parameters [$\Delta_s = 0.09$ (3)] (Nardelli, 1996), indicates that the lactone ring adopts a distorted envelope conformation, with a psuedo-mirror passing through atom C15 and the midpoint of the O12—C13 bond.

The unexpected molecular feature of (I) is the equatorial position of the ferrocenyl group with respect to the heterocyclic ring. Atom C16 deviates from the lactone mean plane by 1.533 (3) Å, while atom C1 is situated much closer but on the opposite side, at a distance of 0.905 (4) Å from the plane. The molecular conformation can be confirmed by the C1—C11—O12—C13 and C16—C11—O12—C13 torsion angles (Table 1). In addition, the dihedral angle between the least-squares planes of the lactone and the substituted cyclopentidienyl rings is 41.07 (3)°. To determine the reason for this molecular arrangement we examined closely the intermolecular interactions which may stabilize the conformation observed in the crystalline state.

Weak C—H⋯O hydrogen bonds link molecules related by 2_1 screw axes into extended chains parallel to the [010] direction (Table 2). This topological motif corresponds to the
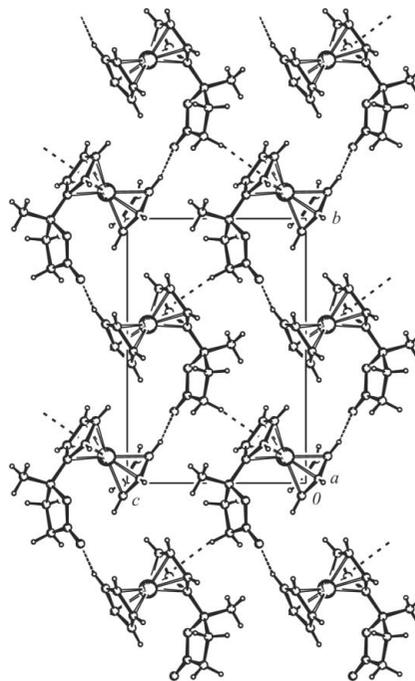

Figure 2
The crystal packing of (I), viewed along the *a* axis, with the intermolecular contacts indicated by dashed lines.

first level graph-set descriptor $C(9)$ (Etter *et al.*, 1990). In addition, the axially substituted H14 atom acts as a donor in a C—H⋯π interaction (Table 2) to link chains into sheets parallel to the *bc* plane. The resulting pattern of intermolecular interactions is shown in Fig. 2.

Interestingly, compound (I) crystallizes in the non-centrosymmetric $P2_1$ group, despite the non-stereospecific synthesis, in which both configurations should be obtained. It is probable that the sample underwent spontaneous resolution upon crystallization. In the crystal structure of (I), the chiral centre at C11 has the *R* configuration. It can be argued that the space-group symmetry is required to give intermolecular interactions and efficient crystal packing of molecules.

Experimental

To a solution of ferrocene (187 mg, 1 mmol) in dichloromethane (10 ml) was added trifluoromethanesulfonic acid (600 mg, 4 mmol) and then, dropwise, a solution of γ-methylene-γ-butyrolactone (196 mg, 2 mmol) in dichloromethane (5 ml). The reaction mixture was stirred for 5 h at room temperature and poured into water. The organic layer was separated and the aqueous layer extracted three times with dichloromethane. After flash chromatography (silica gel/chloroform), the organic extracts afforded the product, (I) (yield 206 mg, 73%). Spectroscopic analysis: ^{1}H NMR (200 MHz, CDCl$_3$, δ, p.p.m.): 1.74 (*s*, 3H), 2.22–2.49 (*m*, 2H), 2.66–2.74 (*m*, 2H), 4.13 (*bs*, 3H), 4.20 (*bs*, 6H); ^{13}C NMR (50 MHz, CDCl$_3$, δ, p.p.m.): 2 8.06, 29.65, 35.95, 65.33, 66.08, 68.37, 68.50, 69.06, 85.41, 93.22, 176.71; IR (KBr, ν, cm^{-1}): 1761. Analysis calculated for C$_{15}$H$_{16}$FeO$_2$: C 63.41, H 5.68%; found: C 62.98, H 5.74%. Orange crystals of compound (I) suitable for X-ray diffraction were obtained after recrystallization from layered dichloromethane–hexane by slow evaporation of the solvents at room temperature.

Crystal data

$[Fe(C_5H_5)(C_{10}H_{11}O_2)]$
$M_r = 284.13$
Monoclinic, $P2_1$
$a = 5.8067 (10)$ Å
$b = 12.7007 (14)$ Å
$c = 8.7274 (7)$ Å
$\beta = 99.643 (14)°$
$V = 634.54 (14)$ Å^3
$Z = 2$

$D_x = 1.487$ Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 34.9–38.2°$
$\mu = 9.45$ mm^{-1}
$T = 293 (2)$ K
Block, orange
$0.35 \times 0.25 \times 0.25$ mm

Data collection

Rigaku AFC-5S diffractometer
ω scans
Absorption correction: analytical
  (de Meulenaer & Tompa, 1965)
  $T_{min} = 0.137$, $T_{max} = 0.201$
4444 measured reflections
2253 independent reflections
1856 reflections with $I > 2\sigma(I)$

$R_{int} = 0.065$
$\theta_{max} = 68.0°$
$h = -6 \rightarrow 6$
$k = -14 \rightarrow 15$
$l = -10 \rightarrow 10$
3 standard reflections
  every 150 reflections
  intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.049$
$wR(F^2) = 0.127$
$S = 1.09$
2253 reflections
165 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0506P)^2 + 0.5135P]$
  where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.0053 (8)
Absolute structure: Flack (1983), with 1045 Friedel pairs
Flack parameter: −0.011 (9)

Table 1
Selected geometric parameters (Å, °).

C1—C11	1.481 (9)	O12—C13	1.339 (7)
C11—O12	1.483 (6)	C13—O13	1.206 (8)
C11—C16	1.517 (7)	C13—C14	1.486 (10)
C11—C15	1.547 (8)	C14—C15	1.508 (9)
C1—C11—O12	106.7 (4)	C13—O12—C11	111.3 (5)
C1—C11—C16	112.3 (5)	O13—C13—O12	119.8 (7)
O12—C11—C16	106.7 (4)	O13—C13—C14	129.1 (7)
C1—C11—C15	114.2 (5)	O12—C13—C14	111.1 (6)
O12—C11—C15	103.9 (4)	C13—C14—C15	104.8 (5)
C16—C11—C15	112.3 (5)	C14—C15—C11	104.4 (5)
C5—C1—C11—O12	149.8 (5)	C11—O12—C13—O13	178.5 (6)
C2—C1—C11—O12	−34.5 (7)	C11—O12—C13—C14	−1.4 (7)
C5—C1—C11—C16	−93.7 (6)	O13—C13—C14—C15	−165.4 (7)
C2—C1—C11—C16	82.0 (7)	O12—C13—C14—C15	14.5 (7)
C5—C1—C11—C15	35.6 (7)	C13—C14—C15—C11	−20.7 (6)
C2—C1—C11—C15	−148.7 (5)	C1—C11—C15—C14	135.8 (5)
C1—C11—O12—C13	−133.0 (5)	O12—C11—C15—C14	19.9 (5)
C16—C11—O12—C13	106.9 (5)	C16—C11—C15—C14	−94.9 (6)
C15—C11—O12—C13	−11.9 (6)		

Table 2
Hydrogen-bond geometry (Å, °).

$Cg1$ is the centroid of the C1–C5 ring.

$D—H\cdots A$	$D—H$	$H\cdots A$	$D\cdots A$	$D—H\cdots A$
C8—H8$\cdots$O13^i	0.93	2.47	3.290 (9)	147
C14—H14A$\cdots$Cg1^{ii}	0.97	2.89	3.777 (9)	153

Symmetry codes: (i) $-x + 1, y + \frac{1}{2}, -z + 2$; (ii) $-x + 1, y - \frac{1}{2}, -z + 1$.

All H atoms were introduced in calculated positions with idealized geometry and refined using a riding model, with C—H distances of 0.97 Å (CH$_3$), 0.96 Å (CH$_2$) or 0.93 Å (aromatic CH), and with U_{iso}(H) = 1.2U_{eq}(C) (in the case of secondary or aromatic C) or 1.5U_{eq}(C) (for tertiary C).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1989); cell refinement: *MSC/AFC Diffractometer Control Software;* data reduction: *TEXSAN* (Molecular Structure Corporation, 1989); program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97*, *WinGX* (Farrugia, 1999) and *PARST97* (Nardelli, 1996).

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