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3-Ferrocenylprop-2-enal

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Key indicators

Single-crystal X-ray study
T = 183 K
Mean σ(C–C) = 0.003 Å
R factor = 0.017
wR factor = 0.051
Data-to-parameter ratio = 10.5

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

The title compound, [Fe(C_5H_5)(C_8H_7O)], is produced by the reaction of ferrocene with 1,1,3,3-tetramethoxypropane. It crystallizes in the noncentrosymmetric space group $P2_12_12_1$. The α,β-unsaturated aldehyde moiety adopts an *s-trans* configuration. The crystal structure is stabilized by intermolecular C—H···O interactions.

Comment

One of the applications of ferrocene groups is their ability to act as electron donor sites in conjugated systems. This property is a prerequisite for the construction of non-linear optic (NLO) materials, and several ferrocene derivatives have been investigated because of their potential in that field (Nock *et al.*, 1993; Wright & Toplikar, 1993; Polin *et al.*, 1997; Ratera *et al.*, 2001; Powell *et al.*, 2003; Hurst *et al.*, 2003; Shin *et al.*, 2003). Another important condition for the realisation of NLO effects is that the compounds must crystallize in a noncentrosymmetric space group. Some years ago I published the synthesis of an imine derived from ferrocenylpropenal and cyclohexylamine (Imhof, 1998) crystallizing in space group $P2_1$, so my research group was interested in the crystal structure of the corresponding α,β-unsaturated aldehyde, which has not hitherto been described. Several α,β-unsaturated ferrocene derivatives, in which neither the C═C double bond nor the C═*X* (*X* = O and N) double bond is part of a cyclic system, may be found in the Cambridge Structural Database (Version 5.24; Allen, 2002). Most of them are derivatives of ferrocenylacrylic acid (Skrzypczak-Jankun *et al.*, 1980; Tao *et al.*, 2001; Molina *et al.*, 1996, 1997, 1998; Rongjun *et al.*, 1991; Zhu, 1993) or of 3-ferrocenylpropenones (Woisetschlager *et al.*, 1999; Erasmus *et al.*, 1996; Constable *et al.*, 1994, 1995). Only one α,β-unsaturated ferrocenylcarbaldehyde has been structurally characterized up to now, namely 3-chloro-3-ferrocenylpropenal (Schottenberger *et al.*, 2001). Unfortunately, all of the compounds mentioned above crystallize in centrosymmetric space groups.

This communication reports the structure of 3-ferrocenylprop-2-enal, (I), crystallizing in the noncentrosymmetric space group $P2_12_12_1$. The compound was prepared by a previously reported method (Dudnik *et al.*, 1969) from ferrocene and 1,1,3,3-tetramethoxypropane in the presence of a strong Lewis acid. The molecular structure of the title compound is presented in Fig. 1; the most important bond lengths and angles are summarized in Table 1. As expected, the α,β-unsaturated side chain adopts an *s-trans* configuration with respect to the central C1—C2 single bond. The bond lengths in this side chain are alternating, although the formal C1—C2 single bond is slightly shortened, as is C3—C4, whereas the C2═C3 double bond is elongated compared with typical C═C double-bond lengths.

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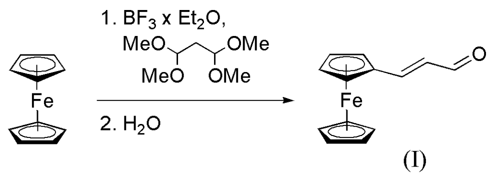

(I)

The crystal structure of 3-ferrocenylpropenal is depicted in Fig. 2. The crystal structure is stabilized mainly by four different C—H···O interactions involving the O atom of the aldehyde function. The corresponding distances and angles are shown in Table 2, where the C—H distances have been normalized to 1.08 Å. There is a bifurcated interaction of O1 with the H atoms at C2 and C8 of the same neighbouring molecule, building up infinite chains of molecules. These chains are interconnected into an infinite three-dimensional network by two additional C—H···O contacts towards CH functions of Cp ligands of different molecules. There are no interactions of the CH groups with the π system of the Cp ligands shorter than 3.28 Å.

Experimental

3-Ferrocenylpropenal was prepared according to the procedure of Dudnik *et al.* (1969), by the treatment of a solution of ferrocene and 1,1,3,3-tetramethoxypropane in $CHCl_3$ at 273 K with a slight excess of BF_3–Et_2O. After stirring the reaction mixture at 273 K for 1 h, it was refluxed for an additional hour. The solution was cooled to room temperature, poured into water and extracted three times with diethyl ether. The organic phase was washed with water until the aqueous phase reached pH 7 and was then evaporated to dryness, yielding 69.7% 3-ferrocenylpropenal as a deep-red powder.

Crystal data

$[Fe(C_5H_5)(C_8H_7O)]$
$M_r = 240.08$
Orthorhombic, $P2_12_12_1$
$a = 7.9192$ (2) Å
$b = 11.1648$ (3) Å
$c = 12.4204$ (4) Å
$V = 1098.17$ (5) Å^3
$Z = 4$
$D_x = 1.452$ Mg m^{-3}

Mo $K\alpha$ radiation
Cell parameters from 1570 reflections
$\theta = 3.8$–23.3°
$\mu = 1.34$ mm^{-1}
$T = 183$ (2) K
Block, red
0.5 × 0.2 × 0.2 mm

Data collection

Nonius KappaCCD diffractometer
ω scans
Absorption correction: none
2961 measured reflections
1570 independent reflections
1541 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.016$
$\theta_{\rm max} = 23.3°$
$h = 0 \rightarrow 8$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.017$
$wR(F^2) = 0.051$
$S = 1.11$
1570 reflections
149 parameters
Only displacement parameters of H atoms refined

$w = 1/[\sigma^2(F_o^2) + (0.0319P)^2 + 0.0364P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.13$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Absolute structure: Flack (1983), 624 Friedel pairs
Flack parameter = 0.444 (19),

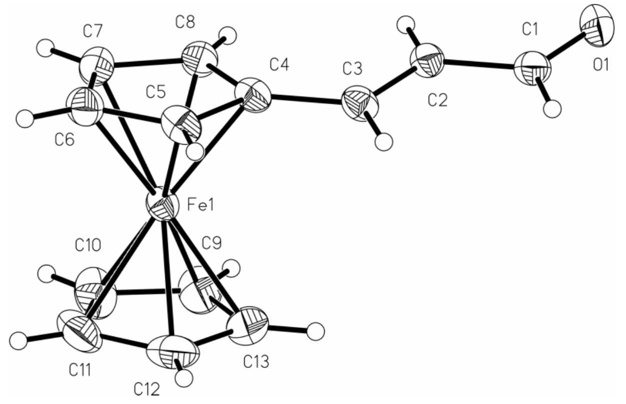

Figure 1
Molecular structure of 3-ferrocenylpropenal. Displacement ellipsoids are drawn at the 40% probability level.

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.220 (2)	C7—C8	1.421 (3)
C1—C2	1.446 (2)	C9—C13	1.408 (3)
C2—C3	1.344 (2)	C9—C10	1.427 (3)
C3—C4	1.452 (2)	C10—C11	1.418 (3)
C4—C8	1.437 (3)	C11—C12	1.408 (3)
C4—C5	1.438 (2)	C12—C13	1.425 (3)
C5—C6	1.426 (3)	Fe1—$C_{\rm Cp}$ (mean)	2.051 (2)
C6—C7	1.421 (3)		
O1—C1—C2	124.63 (17)	C8—C7—C6	108.61 (17)
C3—C2—C1	121.34 (16)	C7—C8—C4	107.78 (16)
C8—C4—C5	107.60 (15)	C13—C9—C10	107.75 (18)
C8—C4—C3	126.76 (14)	C11—C10—C9	107.96 (19)
C5—C4—C3	125.61 (16)	C12—C11—C10	108.04 (18)
C6—C5—C4	107.80 (16)	C11—C12—C13	108.12 (19)
C5—C6—C7	108.20 (16)	C9—C13—C12	108.12 (18)

Table 2
Shortest intermolecular contacts and angles (Å, °) in the crystal structure of 3-ferrocenylpropenal.

The C—H distances have been normalized to 1.08 Å.

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
C2—H2···O1$^{\rm i}$	2.545	3.609	168
C8—H8···O1$^{\rm i}$	2.308	3.369	167
C5—H5···O1$^{\rm ii}$	2.395	3.283	137
C6—H6···O1$^{\rm iii}$	2.496	3.560	168

Symmetry codes: (i) $x - \frac{1}{2}, \frac{5}{2} - y, -z$; (ii) $\frac{3}{2} - x, 2 - y, \frac{1}{2} + z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$.

The crystal is an inversion twin; the relative batch scale factor was refined to 0.444 (19). All H atoms were constrained in idealized positions during the refinement (C—H = 0.93 Å); the isotropic displacement parameters of all H atoms were refined without constraint.

Data collection: *COLLECT* (Nonius, 1998); cell refinement: *DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL*97.

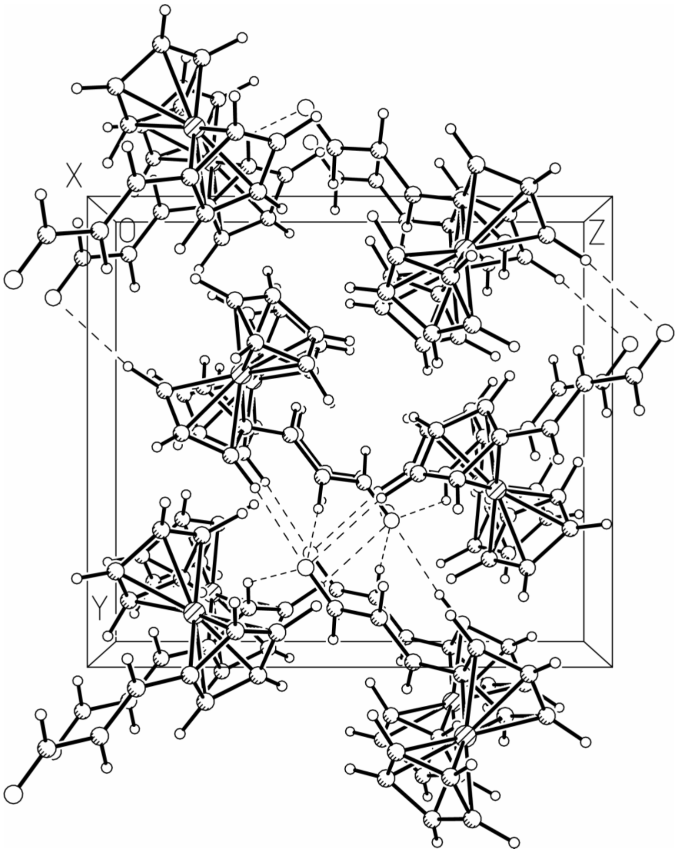

Figure 2
Packing diagram of 3-ferrocenylpropenal. Dashed lines indicate C—H···O intermolecular interactions.

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