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2-Propenyl 4-ferrocenyl-4-oxobutanoate

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The title compound, $C_{17}H_{18}FeO_3$ or $[Fe(C_5H_5)(C_{12}H_{13}O_3)]$, has the cyclopentadienyl rings essentially eclipsed and nearly parallel, forming a 2.5 (2)° dihedral angle. The Fe atom lies 1.6388 (8) Å out of the plane of the substituted ring and 1.6472 (9) Å out of the unsubstituted ring plane. The torsion angle about the central C—C bond of the 4-oxobutanoate group is −79.7 (2)°, and the $O—C—C═CH_2$ torsion angle is 131.0 (2)°.

Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.091
Data-to-parameter ratio = 23.2

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

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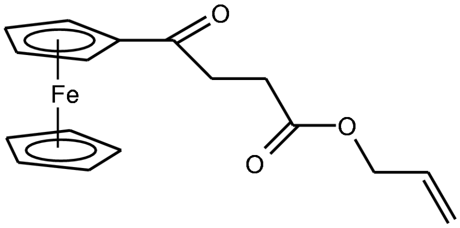
Comment

With the rapid development of solid-phase synthesis, there is a great deal of interest in developing new solid-phase linkers. We report here the synthesis of 2-propenyl 4-ferrocenyl-4-oxobutanoate, (I) (Fig. 1), a ferrocenylamide-based linker precursor. This allyl ester ferrocene derivative was prepared for use as a linker in solid-phase peptide synthesis (SPPS). The mild conditions used to remove allyl groups are compatible with classical Fmoc/^{t}Bu methods (Kates *et al.*, 1993; Trzeciak & Bannwarth, 1992; Merrifield, 1995). The allyl ester serves as a protecting group and is easily cleaved without disrupting the other protecting groups by using palladium catalysts under neutral conditions. Upon reductive amination of the ketone and peptide synthesis, the ferrocenyl–amine bond will be easily cleaved (Blanchet *et al.*, 2000) making the ferrocenyl cation, which is more stable than the traditional benzylic cations used in SPPS (Watts, 1979). The crystal structure of the title compound was determined to prove its successful synthesis.



(I)

The cyclopentadienyl (Cp) rings are essentially eclipsed, forming C—Centroid—Centroid—C torsion angles which average 3.3 (2)°. The rings are nearly parallel, forming a 2.5 (2)° dihedral angle. The Fe atom lies 1.6388 (8) Å out of the plane of Cp ring C1–C5 and 1.6472 (9) Å out of the plane of Cp ring C13–C17. These are typical geometric features [see, for example, Gallagher *et al.* (1997)]. The carbonyl C6═O1 is twisted by 11.2 (3)° out of the plane of the Cp ring to which it is attached. The conformation of the remainder of the substituent on Cp ring C1–C5 (Table 1) is such that the ester

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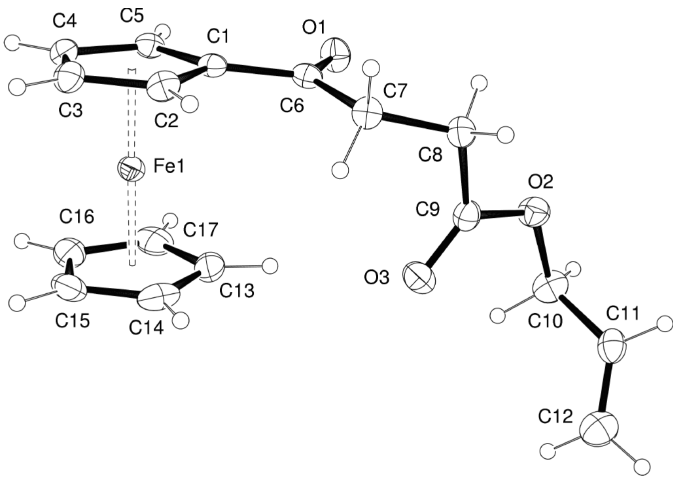

Figure 1
The atom-numbering scheme and ellipsoids at the 50% probability level for (I).

carbonyl O3 atom forms an intramolecular C—H···O hydrogen bond with the unsubstituted Cp ring. The C13···O3 distance is 3.289 (2) Å, the H···O distance is 2.39 Å, and the angle about H is 159°.

Experimental

To a solution of 4-ferrocenyl-4-oxobutanoic acid (0.95 g, 3.3 mmol) in 20 ml acetone, K_2CO_3 (1.58 g,12 mmol) and allyl bromide (2.66 g, 22 mmol) were added under argon. The mixture was refluxed at 373 K overnight. After cooling, HCl (10 ml, 4 *N*) was added to the mixture and extracted with (3 × 20 ml) dichloromethane. The organic layers were combined and dried over sodium sulfate and evaporated *in vacuo*. The product was purified by column chromatography (2:1, hexane–ethyl acetate). Diffraction-quality crystals were grown by dissolving the solid material in a hot ethanol solution, followed by slow evaporation of the solvent. Yield 0.91 g (85%). MS, *m*/*e* (M^+): 326.

Crystal data

$[Fe(C_5H_5)(C_{12}H_{13}O_3)]$
$M_r = 326.16$
Orthorhombic, *Pbca*
$a = 7.7561$ (1) Å
$b = 10.8931$ (2) Å
$c = 34.0120$ (6) Å
$V = 2873.60$ (8) Å^3
$Z = 8$
$D_x = 1.508$ Mg m^{-3}

Mo *Kα* radiation
Cell parameters from 4495 reflections
$\theta = 2.5$–31.9°
$\mu = 1.06$ mm^{-1}
$T = 120$ K
Plate, orange
0.32 × 0.20 × 0.05 mm

Data collection

KappaCCD diffractometer (with Oxford Cryosystems Cryostream cooler)
ω scans with κ offsets
Absorption correction: multi-scan (*HKL SCALEPACK*; Otwinowski & Minor, 1997)
$T_{\min} = 0.844$, $T_{\max} = 0.949$

19 653 measured reflections
4409 independent reflections
3031 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.038$
$\theta_{\max} = 31.9°$
$h = -9 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -48 \rightarrow 49$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.091$
$S = 1.01$
4409 reflections
190 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0325P)^2 + 1.0286P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.003$
$\Delta\rho_{\max} = 0.33$ e Å^{-3}
$\Delta\rho_{\min} = -0.58$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Fe1—C1	2.0260 (18)	Fe1—C4	2.0517 (16)
Fe1—C2	2.033 (2)	Fe1—C3	2.0534 (19)
Fe1—C5	2.0339 (17)	O1—C6	1.222 (2)
Fe1—C17	2.038 (2)	O2—C9	1.345 (2)
Fe1—C13	2.0386 (18)	O2—C10	1.459 (2)
Fe1—C14	2.0399 (18)	O3—C9	1.205 (2)
Fe1—C16	2.040 (2)	C11—C12	1.308 (3)
Fe1—C15	2.0415 (19)		
C5—C1—C6—O1	11.2 (3)	C10—O2—C9—C8	174.14 (15)
O1—C6—C7—C8	−8.9 (3)	C7—C8—C9—O2	158.09 (15)
C6—C7—C8—C9	−79.7 (2)	O2—C10—C11—C12	131.0 (2)

H atoms were placed in calculated positions with C—H bond distances in the range 0.95–0.99 Å and $U_{\rm iso} = 1.2U_{\rm eq}$ of the attached atom, and thereafter treated as riding.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *HKL SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *HKL DENZO* (Otwinowski & Minor, 1997) and *SCALEPACK*; program(s) used to solve structure: *SIR*97 (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEP*-3 *for Windows* (Farrugia, 1997); software used to prepare material for publication: *SHELXL*97.

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References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Blanchet, J., Bonin, M., Mocouuin, L. & Husson, H.-P. (2000). *J. Org. Chem.* **65**, 6423–6426.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Gallagher, J. F., Ferguson, G., Ahmed, S. Z., Glidewell, C. & Lewis. A. (1997). *Acta Cryst.* C**53**, 1772–1775.
Kates, S. A., Sole, N. A., Johnson, C. R., Hudson, D., Barany, G. & Albericio, F. (1993). *Tetrahedron Lett.* **34**, 1549–1552.
Merrifield, B. (1995). In *Peptides: Synthesis, Structures, and Applications*, edited by B. Gutte, ch. 3, pp. 93–169. New York: Academic Press.
Nonius (2000). *COLLECT*. Nonius BV, Delft, The Netherlands.
Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter & R. M. Sweet, pp. 307–326. London: Academic Press.
Sheldrick, G. (1997). *SHELXL*97. University of Göttingen, Germany.
Trzeciak, A. & Bannwarth, W. (1992). *Tetrahedron Lett.* **33**, 4557–4560.
Watts, W. E. (1979). *J. Organomet. Chem. Libr.* **7**, 399–459.