

(+)-(R,E)-2-Ethylidene-4-ferrocenylcyclopentanone

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Key indicators

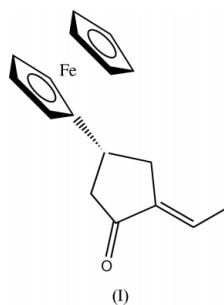
Single-crystal X-ray study
T = 120 K
 Mean $\sigma(\text{C}-\text{C})$ = 0.017 Å
R factor = 0.111
wR factor = 0.301
 Data-to-parameter ratio = 12.6

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

The absolute configuration of the title compound, $\text{C}_{17}\text{H}_{18}\text{FeO}$ or $[\text{Fe}(\text{C}_5\text{H}_5)(\text{C}_{12}\text{H}_{13}\text{O})]$, has been unambiguously determined from a data set with many Friedel pairs. Two molecules were found in the asymmetric unit, both with the same configuration.

Comment

α -Alkylidenecyclopentanones can be found in a variety of natural and biologically active compounds. Since the isolation of sarkomycin (Umezawa *et al.*, 1953), xanthocidin (Asahi *et al.*, 1966) and methylenomycin (Haneishi *et al.*, 1974), the syntheses of α -alkylidenecyclopentanones have commanded considerable attention from synthetic chemists [see Ramaiah (1984) for a review]. A range of synthetic approaches to this class of compounds exist and involve palladium-catalysed cyclizations (Nishimura *et al.*, 1999; Hegedus & Ranslow, 2000), retro-Diels–Alder reactions (Kodpinid *et al.*, 1984; Helmchen *et al.*, 1987), and intramolecular carbenoid cyclization reactions (Lee *et al.*, 1989; Kim & Lee, 1991; Kim & Uh, 1992). A new method for the synthesis of α -methylene-cyclopentanones through the cycloaddition reaction between a Fischer carbene complex and 1,3-dienes will be published elsewhere (Barluenga *et al.*, 2002). We report here the structural characterization of the title compound, (I), which has two molecules in the asymmetric unit, both with the same absolute configuration, as found from the effects of anomalous dispersion of the Fe atoms on the 1933 Friedel pairs measured. Use of *PLATON* (Spek, 1997) has shown that chiral atoms C4A and C4B adopt the *R* configuration.

**Experimental**

A mixture of [[[1*R*,2*S*,5*R*]-8-ferrocenylmenthyloxy]][(*E*)-2-phenylethenyl]methylene]pentacarbonylchromium (1 mmol, 538 mg), 1,3-butadiene (5 mmol, 270 mg) and 2,4-di-*tert*-butyl-4-methylphenol (BHT, 0.5 mmol, 83 mg) in toluene (15 ml) was introduced into a flask, which was sealed and heated to 353 K for 5.5 h. The reaction mixture was cooled to room temperature, toluene was removed under reduced pressure, and the remaining residue was dissolved in hexane

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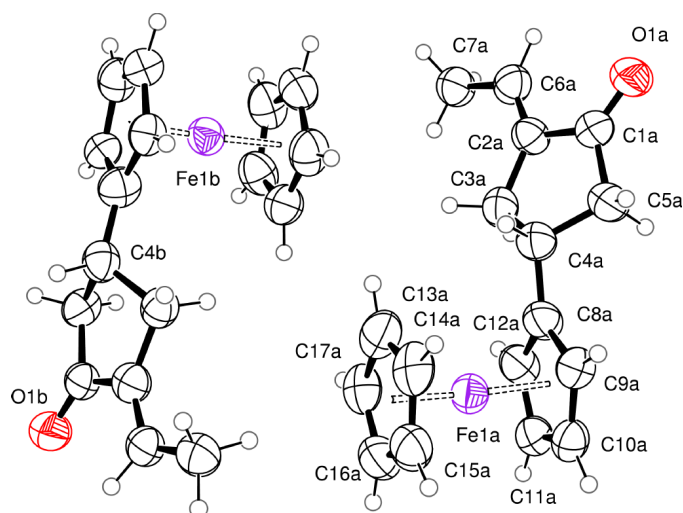


Figure 1
View of (I), shown with 50% probability displacement ellipsoids. The two molecules found in the asymmetric unit are shown.

and exposed to sunlight and air for 0.5–1.0 h to remove coordinated metal species. The resulting mixture was filtered through a short pad of Celite and the volatiles were evaporated. To a solution of the remaining oil in THF (10 ml) was added at room temperature a 2 *N* solution of HCl (1 mmol, 0.5 ml) and the mixture was stirred for 1 h. The solvent was removed under reduced pressure and the residue extracted with Et₂O. The organic phase was dried with Na₂SO₄ and concentrated. The resulting oil was purified by column chromatography (silica gel, hexane–EtOAc, 95:5) to give (I) as a pure orange solid (81%, mixture of enantiomers 9:1). The compound was recrystallized from hexane at room temperature.

Crystal data

[Fe(C₅H₅)(C₁₂H₁₃O)]
M_r = 294.16
 Triclinic, *P*1
a = 7.938 (2) Å
b = 9.5038 (14) Å
c = 9.906 (3) Å
 α = 100.765 (13)°
 β = 102.87 (2)°
 γ = 107.855 (10)°
V = 666.7 (3) Å³

Z = 2
D_x = 1.465 Mg m⁻³
 Cu K α radiation
 Cell parameters from 2303 reflections
 θ = 1.8–30.0°
 μ = 8.95 mm⁻¹
T = 120 (2) K
 Prism, orange
 0.18 × 0.13 × 0.10 mm

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
*T*_{min} = 0.223, *T*_{max} = 0.504
 20 199 measured reflections
 4363 independent reflections

3578 reflections with *I* > 2 σ (*I*)
*R*_{int} = 0.194
 θ _{max} = 69.8°
h = -9 → 9
k = -11 → 11
l = -12 → 11

Refinement

Refinement on *F*²
R [*F*² > 2 σ (*F*²)] = 0.111
wR(*F*²) = 0.301
S = 1.17
 4363 reflections
 345 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.2P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.76 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.76 \text{ e \AA}^{-3}$
 Absolute structure: Flack (1983),
 1933 Friedel pairs
 Flack parameter = -0.013 (6)

Table 1

Selected geometric parameters (Å, °).

C1A—O1A	1.196 (13)	C1B—O1B	1.216 (13)
C1A—C2A	1.501 (14)	C1B—C2B	1.486 (15)
C1A—C5A	1.520 (15)	C1B—C5B	1.502 (15)
C2A—C6A	1.331 (15)	C2B—C6B	1.363 (15)
C2A—C3A	1.500 (15)	C2B—C3B	1.492 (14)
C3A—C4A	1.552 (13)	C3B—C4B	1.552 (13)
C4A—C8A	1.504 (14)	C4B—C8B	1.478 (15)
C4A—C5A	1.524 (13)	C4B—C5B	1.517 (14)
C6A—C7A	1.494 (14)	C6B—C7B	1.485 (14)
O1A—C1A—C2A	126.4 (10)	O1B—C1B—C2B	125.8 (10)
O1A—C1A—C5A	126.4 (10)	O1B—C1B—C5B	127.3 (10)
C2A—C1A—C5A	107.1 (9)	C2B—C1B—C5B	106.9 (8)
C6A—C2A—C3A	130.7 (10)	C6B—C2B—C1B	122.2 (10)
C6A—C2A—C1A	120.1 (9)	C6B—C2B—C3B	129.1 (10)
C3A—C2A—C1A	109.2 (8)	C1B—C2B—C3B	108.6 (9)
C2A—C3A—C4A	105.2 (8)	C2B—C3B—C4B	102.4 (8)
C8A—C4A—C5A	114.5 (9)	C8B—C4B—C5B	117.6 (9)
C8A—C4A—C3A	113.8 (9)	C8B—C4B—C3B	116.6 (8)
C5A—C4A—C3A	105.2 (8)	C5B—C4B—C3B	102.9 (8)
C1A—C5A—C4A	105.4 (9)	C1B—C5B—C4B	103.4 (8)
C2A—C6A—C7A	125.1 (11)	C2B—C6B—C7B	125.9 (10)

All H atoms were found in a difference Fourier synthesis and then refined using a riding model [see Van der Maelen & Sheldrick (1996), and Van der Maelen (1999) for refinement strategies]. The quality of the crystals was not very good, and this is apparent from the final *R* and *wR* values, as well as from the *R*_{int} value, but, in spite of several attempts, it was not possible to obtain better crystals or data, so, due to the importance of the chemistry involved, we decided to solve and refine the structure with the best data available.

Data collection: COLLECT (Nonius, 1997–2000); cell refinement: HKL SCALEPACK (Otwinowski & Minor, 1997); data reduction: HKL DENZO and SCALEPACK (Otwinowski & Minor, 1997); program(s) used to solve structure: DIRDIF97 (Beurskens *et al.*, 1999); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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