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(1*R*,3*R*,4*S*)-8-Phenylmenthyl (8*S*,9*S*)-8-ferrocenyl-6-methyl-1,4-dithia-6-azaspiro[4,4]nonane-9-carboxylate

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Key indicators

Single-crystal X-ray study
T = 200 K
Mean σ(C–C) = 0.011 Å
R factor = 0.054
wR factor = 0.142
Data-to-parameter ratio = 8.0

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

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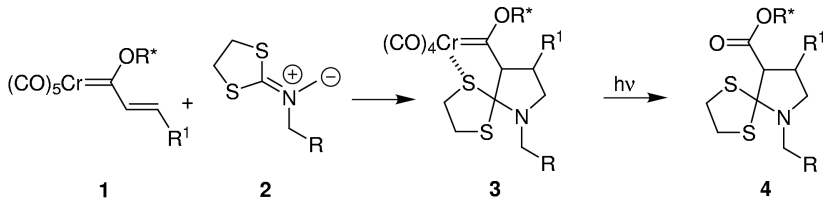
The absolute configuration of the title compound, $[Fe(C_5H_5)(C_{29}H_{38}NO_2S_2)]$, was unambigously determined, the Flack [*Acta Cryst.* (1983). A**39**, 876–881] parameter refining to a value of 0.039 (10). Several intramolecular hydrogen-bonding contacts help to stabilize the structure.

Comment

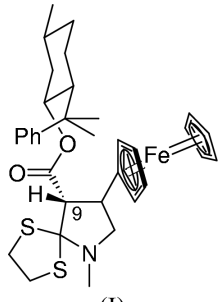
This work is part of a project directed towards the study of the regio- and diastereoselective [3+2]-dipolar cycloaddition of chiral non-racemic Fischer carbene complexes, (1), with azomethine ylides, (2) (Barluenga *et al.*, 2001), as shown in the reaction scheme below. The cycloadducts formed in these reactions were new chelated tetracarbonyl chromium carbene complexes, (3), whose oxidation by exposure to sunlight yielded, among other products, the analogous esters, (4).



1 2 3 4

R*OH = (–)-8-phenylmenthol

The absolute configuration of the title compound, (I), was unambiguously determined, the Flack (1983) parameter refining to a value of 0.039 (10). This served to determine the absolute configuration of the cycloadducts and the stereochemical course of the reaction.



(I)

Several intramolecular hydrogen-bonding contacts help to stabilize the structure. The four shortest are C9—H9*A*···O2 [*D*···*A* = 2.723 (9) Å and *D*—H···*A* = 104 (7)°], C2—H2*A*···O2 [*D*···*A* = 2.924 (9) Å and *D*—H···*A* = 107 (4)°], C18—H18*A*···O1 [*D*···*A* 2.952 (9) Å and *D*—H···*A*

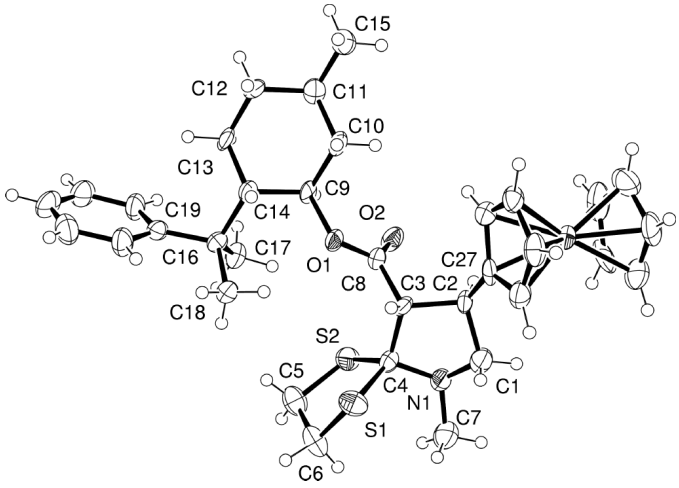


Figure 1
View of (I), with 50% probability displacement ellipsoids.

134.8 (4)°] and C7—H7*C*···S1 [*D*···*A* 3.177 (9) Å and *D*—H···*H* 105.6 (5)°].

Experimental

The title compound was prepared in 38% yield from tetracarbonyl {[(8*S*,9*R*)-8-ferrocenyl-6-methyl-1,4-dithia-6-azaspiro[4,4]nonan-9-yl]-[(1*R*,3*R*,4*S*)-8-phenylmenthyloxy]methylidene}chromium(0), by oxidation promoted by exposure to sunlight (Barluenga *et al.*, 2001). After column chromatography purification, the product was recrystallized from hexane/chloroform (20:1).

Crystal data

$[Fe(C_5H_5)(C_{29}H_{38}NO_2S_2)]$
M_r = 617.66
Orthorhombic, $P2_12_12_1$
a = 8.679 (8) Å
b = 14.784 (4) Å
c = 23.593 (15) Å
V = 3027 (3) Å^3
Z = 4
D_x = 1.355 Mg m^{-3}
Cu $K\alpha$ radiation
Cell parameters from 1251 reflections
θ = 3.5–59.0°
μ = 5.52 mm^{-1}
T = 200 (2) K
Prism, yellow
0.25 × 0.18 × 0.15 mm

Data collection

Nonius KappaCCD diffractometer
φ scans with κ offsets
Absorption correction: **empirical** (*XABS2*; Parkin *et al.*, 1995) **[empirical or refined from ΔF?]**
T_{min} = 0.238, T_{max} = 0.437
12 512 measured reflections
3218 independent reflections
2699 reflections with $I > 2\sigma(I)$
R_{int} = 0.031
θ_{max} = 59.0°
$h = -9 \rightarrow 9$
$k = -16 \rightarrow 16$
$l = -23 \rightarrow 22$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.054
$wR(F^2)$ = 0.142
S = 1.08
3218 reflections
401 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0696P)^2 + 4.833P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.36 e Å^{-3}
$\Delta\rho_{min}$ = −0.34 e Å^{-3}
Absolute structure: Flack (1983), 1005 Friedel pairs
Flack parameter = 0.039 (10)

Table 1
Selected geometric parameters (Å, °).

S1—C6	1.793 (8)	C19—C20	1.375 (10)
S1—C4	1.865 (8)	C19—C16	1.531 (10)
S2—C5	1.806 (9)	C13—C14	1.532 (10)
S2—C4	1.808 (7)	C13—C12	1.545 (10)
O1—C8	1.354 (9)	C10—C11	1.508 (10)
O1—C9	1.467 (8)	C10—C9	1.533 (11)
N1—C1	1.445 (9)	C9—C14	1.536 (10)
N1—C4	1.451 (9)	C12—C11	1.517 (10)
N1—C7	1.454 (10)	C14—C16	1.592 (10)
C2—C27	1.497 (11)	C4—C3	1.598 (10)
C2—C1	1.526 (10)	C17—C16	1.545 (11)
C2—C3	1.543 (10)	C5—C6	1.531 (11)
C15—C11	1.521 (10)	C8—C3	1.514 (10)
C18—C16	1.532 (10)		
C6—S1—C4	96.6 (3)	C13—C14—C16	113.2 (5)
C5—S2—C4	99.6 (4)	C9—C14—C16	113.7 (6)
C8—O1—C9	117.4 (6)	N1—C4—C3	102.0 (5)
C1—N1—C4	109.0 (6)	N1—C4—S2	109.0 (5)
C1—N1—C7	114.2 (6)	C3—C4—S2	118.4 (5)
C4—N1—C7	117.2 (6)	N1—C4—S1	115.7 (5)
C27—C2—C1	115.5 (6)	C3—C4—S1	105.0 (4)
C27—C2—C3	113.0 (6)	S2—C4—S1	107.1 (4)
C1—C2—C3	101.6 (6)	C2—C27—Fe1	129.1 (5)
C20—C19—C16	122.3 (7)	O2—C8—O1	124.1 (7)
C24—C19—C16	120.8 (6)	O2—C8—C3	124.7 (7)
C14—C13—C12	112.6 (6)	O1—C8—C3	111.2 (6)
C11—C10—C9	112.7 (6)	C8—C3—C2	111.4 (6)
O1—C9—C10	106.6 (5)	C8—C3—C4	113.6 (6)
O1—C9—C14	110.4 (6)	C2—C3—C4	105.5 (5)
C10—C9—C14	111.8 (6)	N1—C1—C2	102.3 (6)
C11—C12—C13	111.8 (6)	C5—C6—S1	106.0 (6)
C13—C14—C9	107.1 (6)		

Bond distances and angles within the ferrocenyl moiety are within normal ranges. H atoms were located in difference Fourier syntheses and refined isotropically with a common displacement parameter, some freely and the others riding on their parent atoms.

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

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