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(2*S*,4*S*,S_{Fc})-2-[2-(Diphenylthiophosphinoyl)ferrocenyl]-4-methoxymethyl-1,3-dioxane

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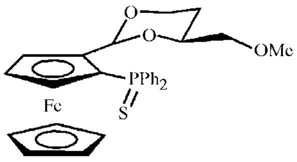
The title compound, $[Fe(C_5H_5)(C_{23}H_{24}O_3PS)]$, is a very useful intermediate for the synthesis of enantiomerically pure (*S*)-2-[(diphenylthiophosphinoyl)ferrocenyl]methanol or (*S*)-2-(diphenylthiophosphinoyl)ferrocenecarboxaldehyde. The dioxane ring has a chair conformation and is twisted with respect to the cyclopentadienyl ring to which it is attached. There is an intermolecular C—H···O hydrogen-bonding interaction which links the molecules into *C*(8) chains developing parallel to the *a* axis. Owing to this weak interaction, the two cyclopentadienyl rings are twisted with respect to each other by 16.0 (3)°, and so have a conformation which might be regarded as intermediate between eclipsed and staggered. The absolute configuration deduced from the X-ray analysis fully confirms the sterochemistry expected from the chemical pathway.

Comment

In recent decades, ferrocene derivatives have attracted tremendous interest (Togni & Hayashi, 1995) because of their numerous fields of application. Among these compounds, those which exhibit planar chirality are especially important because of their involvement in asymmetric catalysis and materials chemistry (Richards & Locke, 1998; Balavoine *et al.*, 1998; Riant & Kagan, 1997). One of the most efficient methods to synthesize enantiomerically pure ferrocene derivatives has been developed by Kagan *et al.* (Riant *et al.*, 1997). We used this method to synthesize the title compound, (I). This compound proved to be a very useful intermediate for the synthesis of enantiomerically pure (*S*)-2-(diphenylthiophosphinoylferrocenyl)methanol or (*S*)-2-(diphenylthiophosphinoyl)ferrocenecarboxaldehyde, which we have used to develop new ligands for asymmetric catalysis (Routaboul *et al.*, 2005; Mateus *et al.*, 2006; Malacea *et al.*, 2006).



(I)

A molecular view of compound (I) is shown in Fig. 1. Atom P1 is slightly *exo* [by 0.237 (5) Å] with respect to the cyclopentadienyl (Cp) ring to which it is attached. This slight deviation from planarity with the Cp ring may be related to steric hindrance occurring between the dioxane ring and the phenyl rings. Indeed, there is a short contact of 2.51 Å between atom C111 and the H atom attached to atom C2. However, it could also result from an intramolecular C—H···O interaction between atom C122 of one of the phenyl rings and atom O1 of the dioxane (Table 1). As observed in related (diphenylthiophosphinoyl)ferrocenyl derivatives (López Cortés *et al.*, 2006, and references therein), atom S1 is *endo* [by 0.878 (7) Å] with respect to this Cp ring.

The dioxane ring is distorted and the puckering parameters (Cremer & Pople, 1975) show that its conformation is close to that of a chair: the total puckering amplitude Q and the θ angle calculated for the atom sequence C2–O2–C3–C5–C4–O1 are 0.569 (3) Å and 177.1 (3)°, respectively. Such a chair conformation seems to be general for a dioxane ring attached to ferrocenyl derivatives, whatever the number of substituents on the ferrocene framework (Table 2). Owing to steric hindrance, the dioxane ring is twisted with respect to the Cp ring, with C13—C12—C2—O1 and C13—C12—C2—O2 torsion angles of 84.8 (4) and −34.5 (4)°, respectively. This twist is also reflected by the dihedral angle of 63.3 (1)° between the Cp

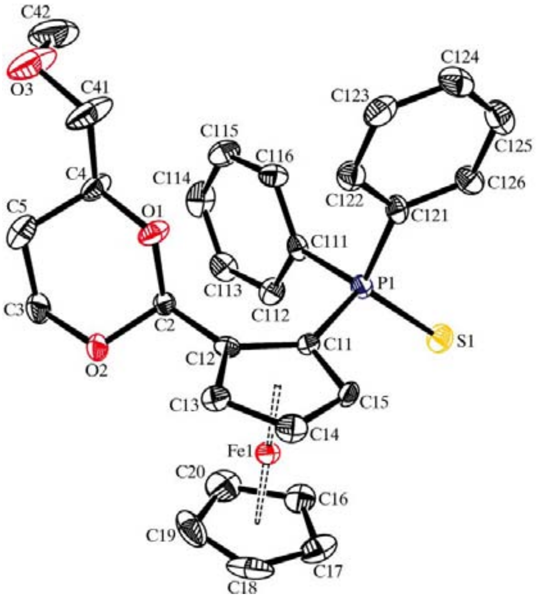


Figure 1
The molecular structure of compound (I), showing the atom-labelling scheme. Displacement parameters are drawn at the 50% probability level. H atoms have been omitted for clarity.

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ring and the O1/C3/C4/O2 mean plane. These different geometric parameters are greatly dependent on the nature of the substituted ferrocenyl derivatives (Table 2). The larger twist is observed for the 1,2-disubstituted ferrocenes with bulky substituents in the 2 position on the same Cp ring, as outlined in Table 2 [Cambridge Structural Database (CSD), Version 5.27; Allen, 2002]. The terminal methoxy group is twisted with respect to the C4—C41 bond, with a torsion angle of −71.0 (5)°.

The two Cp rings are twisted with respect to each other by 16.0 (3)°, and so have a conformation which might be regarded as intermediate between eclipsed and staggered. Such a conformation may be induced by the occurrence of an intermolecular C—H···O hydrogen-bonding interaction, which links the molecules into a *C*(8) chain (Etter *et al.*, 1990) running parallel to the *a* axis (Table 1, Fig. 2).

The geometry within the (diphenylthiophosphinoyl)ferrocenyl framework agrees with related compounds found in the CSD. Some selected bond distances, angles and puckering parameters are reported in Table 3. In all of these compounds, the S atoms appear to be *endo* with respect to the Cp ring bearing the thiophosphinoyl group.

The refinement of the Flack parameter (Flack, 1983; Bernardinelli & Flack, 1985) allowed the determination of the absolute configuration and fully confirmed the stereochemistry expected from the chemical pathway. The two stereogenic centres, C2 and C4, have an *S* configuration, and the chiral planarity is *S*.

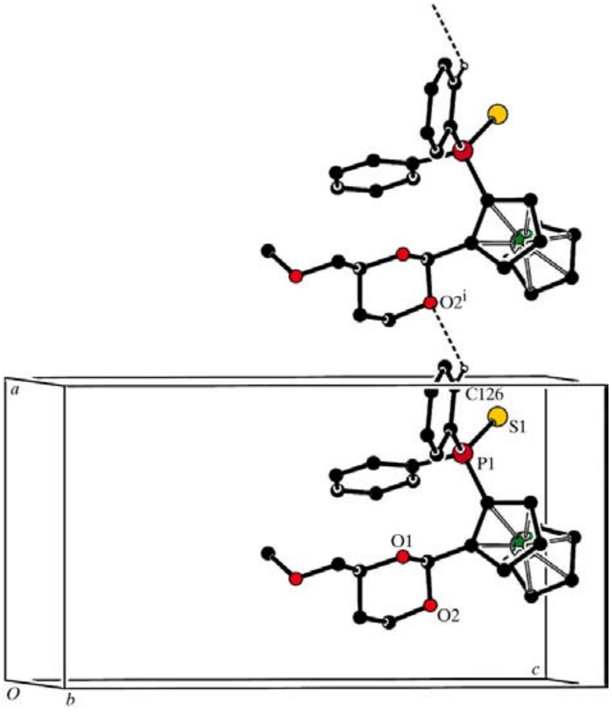

Figure 2
A packing view of compound (I), showing the weak C—H···O hydrogen-bonding interactions resulting in the formation of a *C*(8) chain. [Symmetry code: (i) 1 + *x*, *y*, *z*.]

Experimental

In a Schlenk tube under argon, (2*S*,4*S*,*S*$_{Fc}$)-2-(diphenylphosphinoylferrocenyl)-4-methoxymethyl-1,3-dioxane [16.5 g, 33.1 mmol; prepared according to Riant *et al.* (1997)] was dissolved in dry dichloromethane (1.3 l). Sulfur (5.7 g, 178 mmol, 5.4 equivalents) was then added and the solution was kept at reflux for 2 h. After cooling to room temperature, dichloromethane (1 l) was added to the suspension and the mixture was filtered on Celite and washed with dichloromethane. After evaporation of the solvent, the crude material was purified by flash chromatography on silica gel and eluted with a pentane–diethyl ether mixture (80:20 *v*/*v*), yielding 14.8 g (84%) of an orange solid. Single crystals of (I) suitable for X-ray diffraction studies were obtained by slow diffusion of hexane into a dichloromethane solution of the title compound.

Crystal data

$[Fe(C_5H_5)(C_{23}H_{24}O_3PS)]$
$M_r = 532.39$
Orthorhombic, $P2_12_12_1$
$a = 9.4886 (12)$ Å
$b = 15.2217 (17)$ Å
$c = 17.071 (2)$ Å
$V = 2465.7 (5)$ Å^3
$Z = 4$
$D_x = 1.434$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.79$ mm^{-1}
$T = 180 (2)$ K
Needle, yellow
0.49 × 0.09 × 0.06 mm

Data collection

Stoe IPDS diffractometer
φ scans
Absorption correction: multi-scan (*SORTAV*; Blessing, 1995)
$T_{min} = 0.561$, $T_{max} = 0.865$ (expected range = 0.620–0.956)
19961 measured reflections
3962 independent reflections
3266 reflections with $I > 2\sigma(I)$
$R_{int} = 0.047$
$\theta_{max} = 24.3°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.056$
$S = 0.96$
3962 reflections
308 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0172P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}
Absolute structure: Flack (1983), with 1691 Friedel pairs
Flack parameter: −0.016 (17)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C126—H126···O2^i	0.95	2.48	3.157 (4)	128
C122—H122···O1	0.95	2.69	3.570 (5)	155

Symmetry code: (i) $x + 1, y, z$.

All H atoms were positioned geometrically and treated as riding on their parent atoms, with C—H = 0.93 (C$_{ar}$) or 0.96 Å (C$_{Me}$) and O—H = 0.82 Å, and with U_{iso}(H) = $1.2U_{eq}$(C$_{ar}$,O) or $1.5U_{eq}$(C$_{Me}$).

Data collection: *IPDS Software* (Stoe & Cie, 2000); cell refinement: *IPDS Software*; data reduction: *X-RED* (Stoe & Cie, 1996); program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Table 2

Comparison of dihedral and torsion angles (°), and puckering parameters θ (°) and Q, within the dioxane ring in compound (I) and in related ferrocenyl derivatives.

Ψ_1 is the C2—C1—C11—O1 torsion angle, Ψ_2 is the C2—C1—C11—O2 torsion angle and Δ is the dihedral angle between the C_2O_2 plane and the Cp ring.

Reference	Δ	Ψ_1	Ψ_2	θ	Q
(I)†	63.3 (1)	−90.8 (4)	149.9 (3)	177.1 (3)	0.569 (3)
a†	75.9	−101.0	138.1	175.86	0.562
b‡	75.4	103.7	−135.4	178.15	0.562
c§	39.8	68.6	−169.8	176.26	0.557
c§	56.6	−93.3	28.0	177.23	0.551
d¶	48.2	103.1	−18.6	2.73	0.551
d¶	10.2	−38.5	−162.2	2.58	0.551
e¶	8.3	36.3	159.2	2.90	0.562
f¶	35.9	−113.3	6.4	179.35	0.567
f¶	7.9	148.4	26.4	4.32	0.560
f¶	36.3	174.0	−65.0	178.70	0.571
f¶	39.9	−110.2	10.5	175.59	0.564
f¶	44.7	−164.8	74.4	173.75	0.562
g††	41.4	70.8	−166.7	174.4	0.567

† 1,2-Disubstituted ferrocenyl derivatives. ‡ 1,2,1′-Trisubstituted ferrocenyl derivatives. § 1,2,5-Trisubstituted ferrocenyl derivatives. ¶ 1,1′-Disubstituted ferrocenyl derivatives. †† 1-Monosubstituted ferrocenyl derivatives. References: (*a*) Riant *et al.* (1997); (*b*) Iftime *et al.* (1996); (*c*) Chiffre *et al.* (2002); (*d*) Iftime *et al.* (1998); (*e*) Chiffre *et al.* (2001); (*f*) Hartinger *et al.* (2003); (*g*) Chiffre *et al.* (1999).

Table 3

Selected distances (Å) and angles (°) in the $FcPS(Ph)_2$ framework for compound (I) and related ferrocenyl derivatives.

δ is the distance of the S atom from the Cp ring, $Cg1$ is the centroid of the C11–C15 ring and $Cg2$ is the centroid of the C16–C20 ring.

Compound	Fe—*Cg*1	Fe—*Cg*2	*Cg*1—Fe—*Cg*2	C2—P	P—S	δ
(I)	1.639 (5)	1.653 (5)	176.16 (3)	1.800 (3)	1.9529 (13)	0.879 (7)
a	1.627	1.647	178.2	1.792	1.944	1.063
a	1.636	1.652	175.7	1.811	1.951	1.395
b	1.638	1.656	177.1	1.790	1.957	0.543
c	1.644	1.660	175.4	1.795	1.956	1.270
d	1.650	1.650	180.0	1.795	1.938	0.886
e	1.653	1.653	180.0	1.795	1.944	0.891

References: (*a*) Butler *et al.* (1986); (*b*) Stepnicka & Císarová (2002); (*c*) Stepnicka & Císarová (2003); (*d*) Fang *et al.* (1995); (*e*) Pilloni *et al.* (1997).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3026). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.

Balavoine, G. G. A., Daran, J.-C., Iftime, G., Manoury, E. & Moreau-Bossuet, C. (1998). *J. Organomet. Chem.* **567**, 191–198.

Bernardinelli, G. & Flack, H. D. (1985). *Acta Cryst.* A**41**, 500–511.

Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.

Butler, I. R., Cullen, W. R., Herring, F. G., Jagannathan, N. R., Einstein, F. W. B. & Jones, R. (1986). *Inorg. Chem.* **25**, 4534–4541.

Chiffre, J., Averseng, F., Balavoine, G. G. A., Daran, J.-C., Iftime, G., Lacroix, P. G., Manoury, E. & Nakatani, K. (2001). *Eur. J. Inorg. Chem.* pp. 2221–2226.

Chiffre, J., Coppel, Y., Balavoine, G. G. A., Daran, J.-C. & Manoury, E. (2002). *Organometallics*, **21**, 4552–4555.

Chiffre, J., Manoury, E., Daran, J.-C. & Balavoine, G. G. A. (1999). *Acta Cryst.* C**55**, 2045–2047.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.

Fang, Z.-G., Hor, T. S. A., Wen, Y.-S., Liu, L.-K. & Mak, T. C. W. (1995). *Polyhedron*, **14**, 2403–2409.

Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.

Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Hartinger, C. G., Nazarov, A. A., Chevchenko, V., Arion, V. B., Galanski, M. & Keppler, B. K. (2003). *Dalton Trans.* pp. 3098–3102.

Iftime, G., Daran, J.-C., Manoury, E. & Balavoine, G. G. A. (1996). *Organometallics*, **15**, 4808–4815.

Iftime, G., Manoury, E., Daran, J.-C. & Balavoine, G. G. A. (1998). *J. Organomet. Chem.* **565**, 115–124.

López Cortés, J. G., Vincendeau, S., Daran, J.-C., Manoury, E. & Gouygou, M. (2006). *Acta Cryst.* C**62**, m188–m191.

Malacea, R., Manoury, E., Routaboul, L., Daran, J.-C., Poli, R., Dunne, J. P., Withwood, A. C., Godard, C. & Duckett, S. B. (2006). *Eur. J. Inorg. Chem.* pp. 1803–1816.

Mateus, N., Routaboul, L., Daran, J.-C. & Manoury, E. (2006). *J. Organomet. Chem.* **691**, 2297–2310.

Pilloni, G., Longato, B., Bandoli, G. & Corain, B. (1997). *J. Chem. Soc. Dalton Trans.* pp. 819–823.

Riant, O. & Kagan, H. B. (1997). *Advances in Asymmetric Synthesis*, edited by A. Hassner, Vol. 2, pp. 189–235. Greenwich: JAI Press.

Riant, O., Samuel, O., Flessner, T., Taudien, S. & Kagan, H. B. (1997). *J. Org. Chem.* **62**, 6733–6745.

Richards, C. J. & Locke, A. J. (1998). *Tetrahedron Asymmetry*, **9**, 2377–2407.

Routaboul, L., Vincendeau, S., Daran, J.-C. & Manoury, E. (2005). *Tetrahedron Asymmetry*, **16**, 2685–2690.

Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Stepnicka, P. & Císarová, I. (2002). *New J. Chem.* **26**, 1389–1396.

Stepnicka, P. & Císarová, I. (2003). *Organometallics*, **22**, 1728–1740.

Stoe & Cie (1996). *X-RED*. Version 1.08. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (2000). *IPDS Software*. Version 2.93. Stoe & Cie, Darmstadt, Germany.

Togni, A. & Hayashi, T. (1995). In *Ferrocenes*. Weinheim: VCH.