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Dichlorido[(S,R_S)-1-diphenylphosphino-2-(ethylsulfanylmethyl)ferrocene]palladium(II)

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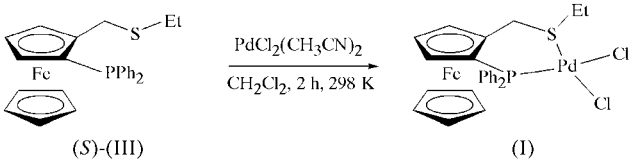
The reaction of enantiomerically pure planar chiral ferrocene phosphine thioether with bis(acetonitrile)dichloridopalladium yields the title square-planar mononuclear palladium complex as an enantiomerically pure single diastereoisomer, $[PdFe(C_5H_5)(C_{20}H_{20}PS)Cl_2]$. The planar chirality of the ligand is retained in the complex and fully controls the central chirality on the S atom. The absolute configuration, *viz*. *S* for the planar chirality and *R* for the S atom, is unequivocally determined by refinement of the Flack parameter.

Comment

Owing to the huge importance of asymmetric catalysis for academic and industrial research, considerable efforts have been devoted to the development of new chiral ligands for transition metal-catalysed asymmetric catalysis (Noyori, 1994; Jacobsen *et al.*, 1999; Ojima 2000). Chiral ferrocene-based ligands have proved to be of particular interest (Colacot, 2003; Atkinson *et al.*, 2004; Gomez Arrayas *et al.*, 2006) because of their stability, easy introduction of planar chirality (Togni, 1996; Riant & Kagan, 1997; Balavoine *et al.*, 1998; Richards & Locke, 1998) and special stereoelectronic properties of the ferrocene skeleton.



(*S*)-(III) (I)

We have recently developed new chiral ferrocene-based phosphine thioether ligands having only planar chirality, in both racemic and enantiomerically pure forms (*R* or *S* configuration) (Routaboul *et al.*, 2005; Mateus *et al.*, 2006) and briefly reported on their coordination chemistry (Malacea, Manoury *et al.*, 2006; Malacea, Daran *et al.*, 2006; Malacea *et al.*, 2007). These ligands, in enantiomerically pure forms, have been successfully applied to some asymmetric catalytic reactions, namely palladium-catalysed allylic substitution (Routaboul *et al.*, 2005, 2007) and iridium-catalysed ketone hydrogenation (Le Roux *et al.*, 2007).

The reaction of the planar chiral ligand (*S*)-(III) with one equivalent of (acetonitrile)dichloridobispalladium (see scheme) quantitatively yields the title square-planar mononuclear palladium complex, (I), as a single diastereoisomer, as shown by NMR data (^{1}H, ^{31}P and ^{13}C).

Compound (I) adopts a mononuclear square-planar geometry, with the phosphine and thioether functions in relative *cis* positions. The largest deviation from the square plane is −0.0857 (4) for atom Cl1. This plane makes a dihedral angle of 37.08 (7)° with the plane containing the substituted cyclopentadienyl (Cp) ring and atoms P1 and C21. As observed in the racemic compound and in related Pd complexes (Malacea *et al.*, 2007), the S substituent is located on the opposite side (*anti*) of the S—C—C—C—P chelate, relative to the FeCp group. Thus, the Pd atom has been selectively coordinated by one of the two lone pairs of the S atom; after coordination, the remaining lone pair is oriented *syn* to the unsubstituted Cp ring. Owing to the synthetic pathway, compound (I) is an enantiomerically pure single diastereoisomer with the configuration for planar chirality being *S*, and the configuration of the S atom being *R*. This stereochemistry has been unequivocally determined by the structural analysis, with a value of 0.01 (2) for the enantiopole parameter (Flack, 1983). The planar chirality of the ligand is then retained in the complex and fully controls the central chirality on the S atom.

As shown in Table 1, there are no significant differences in the relevant structural parameters between compound (I) and its racemic equivalent (II) (Table 1; Malacea *et al.*, 2007). Although their crystal systems are different, orthorhombic for (I) and monoclinic for (II) (Table 1), their packings are

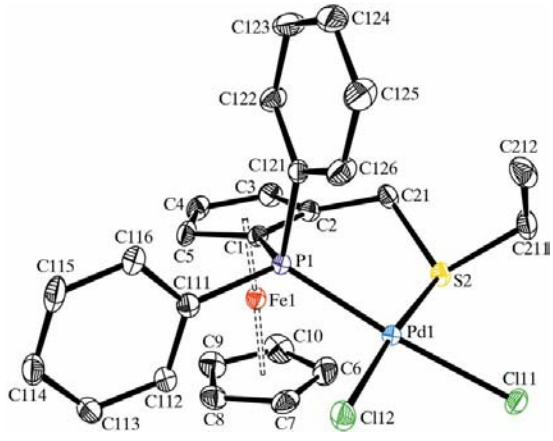


Figure 1
A molecular view of compound (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity.

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roughly similar, with four molecules within the unit cell (Figs. 2 and 3) and weak C—H···Cl interactions (Steiner, 1998) (Table 2). It may be noted that only atom Cl1 is involved in these hydrogen bonds in both compounds, which reflects the electronic *trans* effect of the P atom.

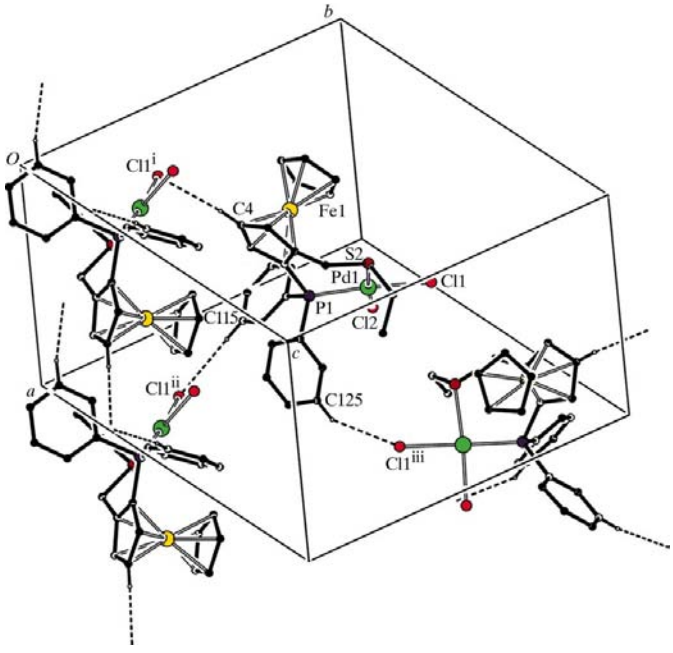

Figure 2
A partial packing view of compound (I), showing the C—H···Cl interactions as dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$.]

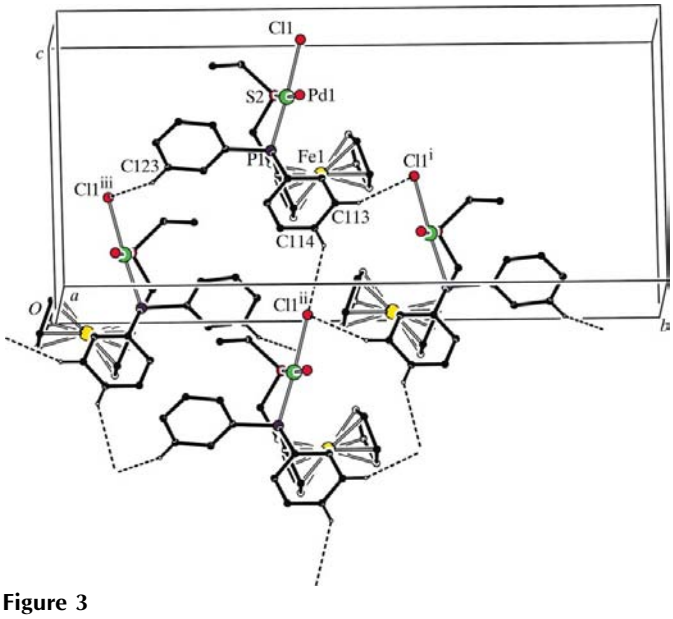

Figure 3
A partial packing view of compound (II) (Malacea *et al.*, 2007), the related racemate of (I). Hydrogen bonds are shown as dashed lines and H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (i) $x, 1-y, -\frac{1}{2}+z$; (ii) $x, y, -1+z$; (iii) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$.]

When comparing the structure of the title compound with related structures (Malacea *et al.*, 2007; García Mancheño *et al.*, 2005) (Table 1), it can indeed be noted that the Pd—S bond is longer than the Pd—P bond, and the Pd—Cl bond *trans* to P is longer than the Pd—Cl bond *trans* to S, in agreement with the stronger *trans* effect of phosphine donors compared with thioethers (Table 1). The Pd—P distances are within the previously established range (2.228–2.237 Å) for relevant compounds found in the Cambridge Structural Database (Version 5.28; Allen, 2002), whereas the Pd—S distances are slightly longer with respect to the reported range of 2.257–2.296 Å. In compounds (I), (II), (III) and (IV), the P—Pd—S, P—Pd—Cl and S—Pd—Cl angles (Table 1) seem to be influenced by the growing steric repulsion between the S substituent and the pseudo-axial phosphine phenyl group. Indeed, the largest differences are observed for compound (IV), where the S atom bears a bulky *tert*-butyl substituent. In compound (V), where the S atom is directly bonded to the Cp ring (García Mancheño *et al.*, 2005), the square-planar framework is nearly perfect, with all angles close to 90 or 180°.

Experimental

Thioether (*S*)-(III) (88 mg, 0.225 mmol) and $[PdCl_2(CH_3CN)_2]$ (58 mg, 0.225 mmol) were dissolved in dry dichloromethane (15 ml) under argon. After stirring for 2 h at room temperature, the solvent was evaporated and the resulting red solid was washed with dry pentane (yield 113 mg, 81%). Single crystals of complex (I) suitable for X-ray diffraction analysis were obtained by slow evaporation of a methanol solution. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.72–7.53 (6H, *m*, Ph), 751–7.41 (4H, *m*, Ph), 4.63 (5H, *s*, Cp), 4.56 (1H, *s* large, subst. Cp), 4.41 (1H, *s* large, subst. Cp), 3.78 [1H, *d*(AB), J_{HH} = 12 Hz, CH_2—Cp], 3.53 (1H, *s* large, subst. Cp), 3.29 [1H, *d*(AB), J_{HH} = 12 Hz, CH_2—Cp], 3.24 (2H, *q*, J_{HH} = 7 Hz, CH_2—CH_3), 1.38 (3H, *t*, J_{HH} = 7 Hz, CH_2—CH_3). ^{31}P NMR (500 MHz, $CDCl_3$): δ 21.2.

Crystal data

$[PdFe(C_5H_5)(C_{20}H_{20}PS)Cl_2]$
M_r = 621.63
Orthorhombic, $P2_12_12_1$
a = 9.7644 (7) Å
b = 14.8595 (15) Å
c = 16.9586 (12) Å
V = 2460.6 (4) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.70 mm^{-1}
T = 180 (2) K
0.58 × 0.31 × 0.1 mm

Data collection

Stoe IPDS diffractometer
Absorption correction: multi-scan (Blessing, 1995)
T_{min} = 0.565, T_{max} = 0.856
24267 measured reflections
4771 independent reflections
4539 reflections with $I > 2\sigma(I)$
R_{int} = 0.045

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.024
$wR(F^2)$ = 0.059
S = 1.03
4771 reflections
281 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.51 e Å^{-3}
$\Delta\rho_{min}$ = −0.53 e Å^{-3}
Absolute structure: Flack (1983), with 2048 Friedel pairs
Flack parameter: −0.008 (17)

All H atoms were fixed geometrically and treated as riding, with C—H = 0.93 (aromatic), 0.96 (methyl) or 0.97 Å (methylene), and with U_{iso}(H) = 1.2U_{eq}(C) or 1.5U_{eq}(methyl C).

Table 1
Comparison of selected geometric parameters (Å, °) for the title compound and related CpFe[1,2-$C_5H_3(PPh_2)\{(CH_2)_nSR\}$]$PdCl_2$ structures, where R = Et, Ph or ^{t}Bu.

*Cg*1 and *Cg*2 are the centroids of the Cp rings and δ is the twist angle between the two Cp rings.

Parameter	(I)†	(II)‡	(III)§	(IV)¶	(V)††
Space group	$P2_12_12_1$	*Cc*	$P2_1/c$	$P2_1/c$	$P2_12_12_1$
Pd1—P1	2.2302 (7)	2.2253 (16)	2.2311 (10)	2.2251 (8)	2.2427 (9)
Pd1—S2	2.2962 (8)	2.3078 (18)	2.3074 (9)	2.3215 (8)	2.3137 (9)
Pd1—Cl2	2.2971 (8)	2.3139 (18)	2.3102 (9)	2.3006 (8)	2.3022 (11)
Pd1—Cl1	2.3708 (7)	2.3621 (17)	2.3683 (10)	2.3588 (8)	2.3461 (11)
P1—Pd1—S2	94.72 (3)	93.93 (6)	95.08 (4)	96.08 (3)	90.83 (3)
P1—Pd1—Cl2	89.96 (3)	89.78 (6)	90.20 (3)	88.99 (3)	88.26 (4)
P1—Pd1—Cl1	174.74 (3)	176.50 (7)	175.56 (3)	163.68 (3)	176.95 (4)
S2—Pd1—Cl1	83.71 (3)	83.73 (6)	83.41 (3)	86.73 (3)	89.39 (4)
S2—Pd1—Cl2	174.47 (3)	176.28 (6)	173.14 (3)	169.98 (3)	176.23 (4)
Cl1—Pd1—Cl2	91.89 (3)	92.55 (7)	91.65 (4)	90.82 (3)	91.72 (5)
Fe1—*Cg*1	1.6463 (4)	1.643 (7)	1.6523 (6)	1.6581 (4)	
Fe1—*Cg*2	1.6539 (4)	1.662 (6)	1.6651 (6)	1.6657 (4)	
*Cg*1—Fe1—*Cg*2	176.03 (7)	174.8 (11)	175.67 (3)	176.96 (3)	
δ	8.4 (3)	5.6 (5)	6.8 (3)	11.8 (2)	

† For compound (I), $n = 1$, $R = C_2H_5$ (this work). ‡ For compound (II), $n = 1$, $R = C_2H_5$; data from Malacea *et al.* (2007). § For compound (III), $n = 1$, $R = C_6H_5$; data from Malacea *et al.* (2007). ¶ For compound (IV), $n = 1$, $R = C(CH_3)_3$; data from Malacea *et al.* (2007). †† For compound (V), $n = 0$, $R = C(CH_3)_3$; data from García Mancheño *et al.* (2005).

Table 2
Comparison of C—H···Cl hydrogen-bond interactions (Å, °) between compound (I) and its racemate (II).

		D—H	H···*A*	*D*···*A*	*D*—H···*A*
(I)	C4—H4···Cl1^{i}	0.93	2.68	3.603 (3)	174.0
	C115—H115···Cl1^{ii}	0.93	2.79	3.704 (4)	168.2
	C125—H125···Cl1^{iii}	0.93	2.72	3.554 (4)	149.0
(II)†	C113—H113···Cl1^{iv}	0.95	2.78	3.474 (8)	131.0
	C114—H114···Cl1^{v}	0.95	2.82	3.499 (7)	129.2
	C123—H123···Cl1^{vi}	0.95	2.69	3.560 (9)	152.2

Symmetry codes: (i) $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (ii) $2-x, -\frac{1}{2}+y, \frac{1}{2}-z$; (iii) $\frac{1}{2}+x, \frac{3}{2}-y, 1-z$; (iv) $x, 1-y, \frac{1}{2}-z$; (v) $x, y, -1+z$; (vi) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$. † Data for compound (II) taken from Malacea *et al.* (2007).

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: *ORTEPIII* (Burnett & Johnson, 1996) and *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: HJ3055). Services for accessing these data are described at the back of the journal.

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