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Three new enantiomerically pure ferrocenylphosphole compounds

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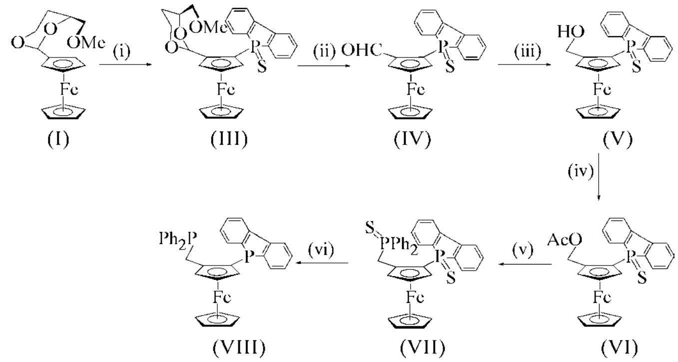
The absolute configurations of three new enantiomerically pure ferrocenylphosphole compounds, namely (2*S*,4*S*,S_{Fc})-4-methoxymethyl-2-[2-(9-thioxo-9λ^5-phosphafluoren-9-yl)ferrocenyl]-1,3-dioxane, $[Fe(C_5H_5)(C_{23}H_{22}O_3PS)]$, (III), ($S_{Fc}$)-[2-(9-thioxo-9$\lambda^5$-phosphafluoren-9-yl)ferrocenyl]methanol, $[Fe(C_5H_5)(C_{18}H_{14}OPS)]$, (V), and ($S_{Fc}$)-diphenyl[2-(9-thioxo-9$\lambda^5$-phosphafluoren-9-yl]ferrocenylmethyl]phosphine, $[Fe(C_5H_5)(C_{30}H_{23}P_2)]$, (VIII), have been unambiguously established. All three ligands contain a planar chiral ferrocene group, bearing a dibenzophosphole and either a dioxane, a methanol or a diphenylphosphinomethane group on the same cyclopentadienyl. In compound (V), the occurrence of O—H···S and C—H···S hydrogen bonds results in the formation of a two-dimensional network parallel to (001). The geometry of the ferrocene frameworks agrees with related reported structures.

Comment

Considerable efforts have been devoted to the development of new chiral ligands owing to the growing importance of transition metal-catalysed asymmetric synthesis (Ojima, 2000; Jacobsen *et al.*, 1999; Noyori, 1994). Of these chiral ligands, ferrocene-containing ligands are among the most interesting because of their stability, the easy introduction of planar chirality and the special electronic and stereoproperties of the ferrocene skeleton (Togni & Hayashi, 1995; Borman, 1996; Togni, 1996; Atkinson *et al.*, 2004). Of the chiral ferrocene-based ligands, enantiopure 1,2-disubstituted ferrocene derivatives, especially ferrocenyldiphosphine ligands, have played a dominant role (Colacot, 2003; Tang *et al.*, 2003; Barbaro *et al.*, 2004). Typical examples are TRAP ligands (Sawamura *et al.*, 1996; Kuwano *et al.*, 1999, 2000) and the diphosphine Josiphos ligands (Blaser *et al.*, 2002, and references therein), in particular the industrially important Xyliphos (Blaser, 2002, and references therein), Taniaphos (Lotz *et al.*, 2002; Spindler *et al.*, 2004) or Walphos-type ligands (Sturm *et al.*, 2003). Common characteristics of these ligands include the ferrocenylethyl backbone and the presence of both planar and central chiralities. Little attention has been paid to ligands based on the ferrocenylmethyl backbone or, more generally, to ferrocenes possessing planar chirality as their only element of chirality. Thus, we have recently investigated the family of 1,2-disubstituted planar chiral ferrocenes by the introduction of a phosphole group, leading to planar chiral ferrocenylphosphole amine ligands (Lopez Cortés *et al.*, 2006). We report here the structural characterization of three enantiomerically pure ferrocenyl derivatives containing the dibenzophosphole (9-phosphafluorene) moiety, *viz.* (III), (V) and (VIII).



(i) ^{t}BuLi, 195 K to room temperature;
1-cyanophosphole, 243 K;
S_8, CH_2Cl_2, room temperature
(ii) H^+, H_2O/CH_2Cl_2, reflux
(iii) $NaBH_4$, room temperature
(iv) $AcCl/NEt_3$, 273 K to room temperature
(v) R_2PH, toluene, reflux, S_8
(vi) $P(NMe_2)_3$, toluene, reflux

A molecular view of compound (III) is shown in Fig. 1. As expected, the phosphole ring is planar, with the largest deviation being 0.068 (2) Å for atom C112. Atom P1 deviates slightly [by 0.204 (2) Å] from the cyclopentadienyl (Cp) ring to which it is attached, whereas atom S1 is *endo* with respect to this Cp ring by 1.026 (3) Å. The dibenzophosphole system and

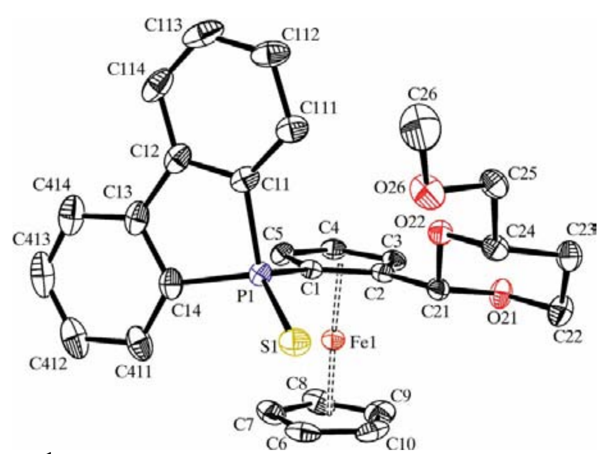


Figure 1
The molecular structure of compound (III), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

the Cp rings are nearly perpendicular, making a dihedral angle of 88.21 (5)°. The dioxane ring is distorted and the puckering parameters (Cremer & Pople, 1975) show that its conformation is close to that of a chair: the θ and φ angles calculated for the atom sequence C21–O21–C22–C23–C24–O22 are 175.4 (2) and 133 (2)°, respectively. Owing to steric hindrance, the dioxane ring is twisted with respect to the Cp ring, with C3—C2—C21—O21 and C3—C2—C21—O22 torsion angles of −5.0 (3) and 115.8 (2)°, respectively. The two Cp rings are nearly eclipsed, with a twist angle of only 3.5°.

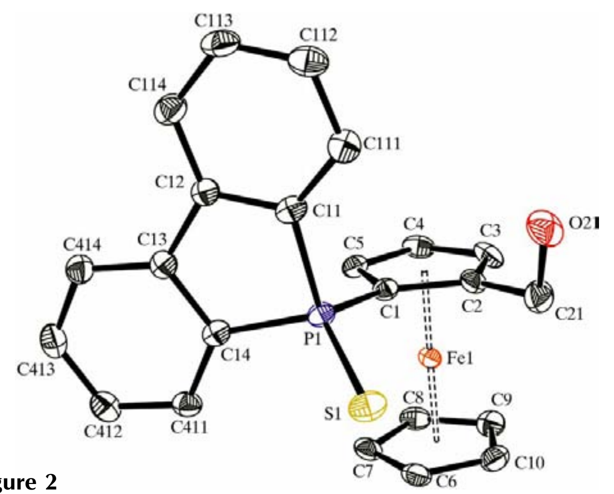


Figure 2
The molecular structure of compound (V), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

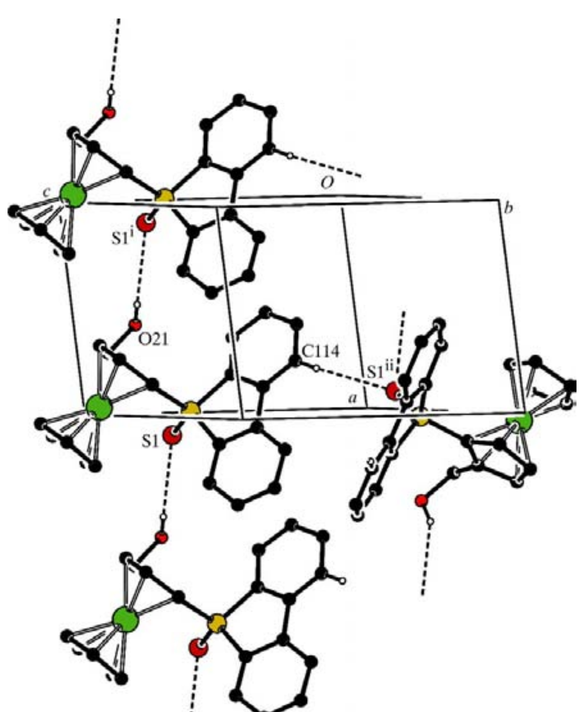


Figure 3
A packing view for compound (V), showing the O—H···S and C—H···S hydrogen-bonding interactions (dashed lines) resulting in the formation of a two-dimensional network parallel to (001). [Symmetry codes: (i) $x - 1, y, z$; (ii) $-x + 2, y + \frac{1}{2}, -z + 1$.]

A molecular view of alcohol (V) is shown in Fig. 2. As noted previously, the dibenzophosphole system is roughly planar, with the largest deviation being 0.109 (2) Å for atom C14, and it makes a dihedral angle of 87.34 (7)° with the Cp ring to which it is attached. Atom P1 is nearly coplanar with the Cp ring, deviating by only 0.088 (2) Å. Atom S1 is *endo* by 1.333 (3) Å with respect to this Cp ring. An interesting feature is the occurrence of an intermolecular O—H···S hydrogen bond linking the molecules to form a chain developing parallel to the *a* axis. It is worth pointing out that, in the related compound (S_{Fc})-[2-(3,4-dimethyl-1-thio-1*H*-1λ^5-phosphol-1-yl)ferrocenyl]methanol (Mourgues *et al.*, 2003), the O—H···S interaction is only intramolecular. Moreover, in (V) the chains are interconnected by weak C—H···S hydrogen bonds to form a two-dimensional network parallel to (001) (Table 1 and Fig. 3). The two Cp rings are twisted with respect to one another by 13.9°. This larger value compared with compound (III) might be related to the occurrence of the hydrogen bond. The alcohol group is twisted with respect to the Cp plane, with a C3—C2—C21—O21 torsion angle of 103.1 (3)°. A similar conformation of the alcohol group has been found in the related compound *rac*-2-(diphenylthiophosphoryl)ferrocenylmethanol (Stepnicka & Císarová, 2002). However, the O—H···S hydrogen bonds in that compound resulted in the formation of a pseudo-dimer through an inversion centre.

A molecular view of complex (VIII) is shown in Fig. 4. As already observed in free phosphole ligands (Tissot *et al.*, 2000; Ogasawara *et al.*, 2001; Hydrio *et al.*, 2002; Melaimi *et al.*, 2002), the P atom is located slightly above the butadiene fragment [0.129 (5) Å]. Atom P1 is roughly in the plane of the Cp ring, with a deviation from the mean plane of 0.09 (1) Å. Atom P2 is oriented *exo* with respect to the Cp ring and is located 1.62 (1) Å above it. The two Cp rings are perfectly eclipsed, with a twist angle of 0.5°. The two phenyl rings make a dihedral angle of 65.7 (2)°. It is interesting to note that the lone pairs of the two P atoms are in the correct arrangement for chelating to a metal precursor.

In all three compounds, the geometry within the ferrocene framework is roughly identical (Table 2) and agrees with that of related compounds found in the Cambridge Structural

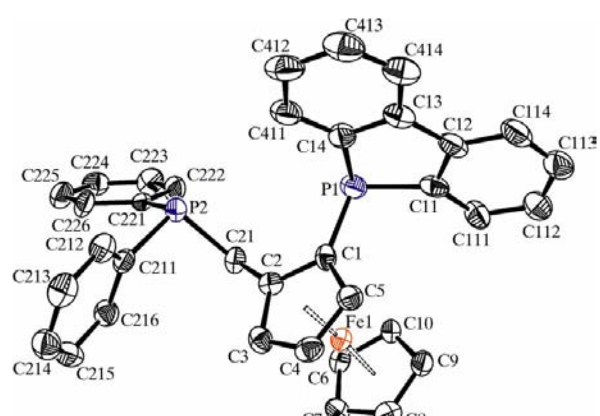


Figure 4
The molecular structure of compound (VIII), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms have been omitted for clarity.

Database (Version 5.27; Allen, 2002). For these three compounds, refinement of the Flack parameter (Flack, 1983; Bernardinelli & Flack, 1985) allowed the determination of the absolute configuration.

Experimental

Compounds (III), (V) and (VIII) were synthesized according to the procedure reported by Lopez Cortés *et al.* (2006) (see scheme). Intermediate products (IV), (VI) and (VII) were obtained as oils, whereas crystals of (III), (V) and (VIII) suitable for X-ray analyses were obtained by slow diffusion of pentane into dichloromethane solutions.

Compound (III)

Crystal data

$[Fe(C_5H_5)(C_{23}H_{22}O_3PS)]$	$Z = 2$
$M_r = 530.38$	$D_x = 1.470$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.4885$ (7) Å	$\mu = 0.81$ mm^{-1}
$b = 9.5175$ (8) Å	$T = 180$ (2) K
$c = 16.8193$ (13) Å	Prism, yellow
$\beta = 91.067$ (7)°	0.36 × 0.28 × 0.22 mm
$V = 1198.53$ (18) Å^3	

Data collection

Oxford Xcalibur diffractometer	4045 reflections with $I > 2\sigma(I)$
ω and φ scans	$R_{int} = 0.023$
10617 measured reflections	$\theta_{max} = 28.3°$
4383 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0401P)^2 + 0.0522P]$
$R[F^2 > 2\sigma(F^2)] = 0.027$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{max} = 0.002$
$S = 1.07$	$\Delta\rho_{max} = 0.33$ e Å^{-3}
4383 reflections	$\Delta\rho_{min} = -0.33$ e Å^{-3}
308 parameters	Absolute structure: Flack (1983), with 1249 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.00 (1)

Compound (V)

Crystal data

$[Fe(C_5H_5)(C_{18}H_{14}OPS)]$	$Z = 2$
$M_r = 430.26$	$D_x = 1.539$ Mg m^{-3}
Monoclinic, $P2_1$	Mo $K\alpha$ radiation
$a = 7.1110$ (13) Å	$\mu = 1.02$ mm^{-1}
$b = 12.862$ (3) Å	$T = 180$ (2) K
$c = 10.223$ (2) Å	Needle, yellow
$\beta = 96.73$ (2)°	0.48 × 0.13 × 0.12 mm
$V = 928.6$ (3) Å^3	

Data collection

Stoe IPDS diffractometer	9253 measured reflections
φ scans	3619 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	3380 reflections with $I > 2\sigma(I)$
$T_{min} = 0.598$, $T_{max} = 0.873$	$R_{int} = 0.050$
	$\theta_{max} = 26.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0359P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.026$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.061$	$(\Delta/\sigma)_{max} = 0.001$
$S = 0.98$	$\Delta\rho_{max} = 0.36$ e Å^{-3}
3619 reflections	$\Delta\rho_{min} = -0.25$ e Å^{-3}
245 parameters	Absolute structure: Flack (1983), with 1722 Friedel pairs
H-atom parameters constrained	Flack parameter: −0.015 (12)

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

D—H···A	D—H	H···A	D···A	D—H···A
O21—H21···S1^{i}	0.82	2.73	3.426 (2)	144
C114—H114···S1^{ii}	0.93	2.78	3.633 (3)	153

Symmetry codes: (i) $x-1, y, z$; (ii) $-x+2, y+\frac{1}{2}, -z+1$.

Compound (VIII)

Crystal data

$[Fe(C_5H_5)(C_{30}H_{23}P_2)]$	$Z = 4$
$M_r = 566.36$	$D_x = 1.369$ Mg m^{-3}
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 10.9693$ (10) Å	$\mu = 0.69$ mm^{-1}
$b = 11.0436$ (10) Å	$T = 180$ (2) K
$c = 22.678$ (2) Å	Prism, yellow
$V = 2747.2$ (4) Å^3	0.2 × 0.12 × 0.1 mm

Data collection

Stoe IPDS diffractometer	22007 measured reflections
φ scans	5395 independent reflections
Absorption correction: multi-scan (Blessing, 1995)	3205 reflections with $I > 2\sigma(I)$
$T_{min} = 0.852$, $T_{max} = 0.894$	$R_{int} = 0.145$
	$\theta_{max} = 26.1°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0476P)^2]$
$R[F^2 > 2\sigma(F^2)] = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{max} = 0.004$
$S = 0.93$	$\Delta\rho_{max} = 0.97$ e Å^{-3}
5395 reflections	$\Delta\rho_{min} = -0.47$ e Å^{-3}
343 parameters	Absolute structure: Flack (1983), with 2333 Friedel pairs
H-atom parameters constrained	Flack parameter: 0.01 (3)

Table 2
Selected distances (Å) within the three title compounds.

*Cg*1 and *Cg*2 are the centroids of rings C1–C5 and C6–C10, respectively.

Compound	Fe1—*Cg*1	Fe1—*Cg*2	C1—P1	P1—S1	C2—C21
(III)	1.639 (5)	1.653 (5)	1.796 (2)	1.9384 (7)	1.503 (3)
a	1.645 (9)	1.660 (10)	1.790 (3)	1.9487 (11)	1.504 (4)
(V)	1.636 (2)	1.651 (2)	1.785 (2)	1.9555 (9)	1.490 (4)
a	1.636 (8)	1.646 (8)	1.7901 (18)	1.9677 (6)	1.505 (3)
b	1.633 (2)	1.652 (2)	1.7885 (14)	1.9645 (6)	1.489 (2)
(VIII)	1.6337 (8)	1.6503 (8)	1.803 (6)		1.496 (8)
a	1.6392 (4)	1.6588 (4)	1.809 (3)		1.515 (5)
c	1.6375 (8)	1.656 (1)	1.790 (2)	1.9567 (6)	1.485 (2)
d	1.6443 (7)	1.6596 (7)	1.795 (3)	1.9561 (5)	1.505 (2)

References: (*a*) Lopez Cortés *et al.* (2006); (*b*) Mourgues *et al.* (2003); (*c*) Stepnicka & Císarová (2002); (*d*) Stepnicka & Císarová (2003).

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003) for (III); *IPDS Software* (Stoe & Cie, 2000) for (V) and (VIII). Cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003) for (III); *IPDS Software* for (V) and (VIII). Data reduction: *CrysAlis RED* for (III); *X-RED* (Stoe & Cie, 1996) for (V) and (VIII). For all compounds, 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) for (III) and (VIII); *ORTEP-3 for Windows* (Farrugia, 1997) and *PLATON* (Spek, 2003) for (V). For all compounds, software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3012). Services for accessing these data are described at the back of the journal.

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