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[1,1′-Bis(diphenylphosphino)ferrocene-κ^2P,P']bis(2,3,4,5,6-pentafluorobenzenethiolato)platinum(II)

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The title compound, $[PtFe(C_6F_6S)_2(C_{17}H_{14}P)_2]$, was obtained from the metathesis reaction of $[Pt(dppf)Cl_2]$ and $[Pb(SC_6F_5)_2]$ in CH_2Cl_2 [dppf is 1,1′-bis(diphenylphosphino)ferrocene]. Two independent molecules are found in the asymmetric unit. The Pt^{II} centers have a distorted square-planar environment with the P atoms of the dppf ligand coordinating to the metal centers in a bidentate fashion. The coordination of each Pt atom is completed by two $-SC_6F_5$ ligands in an *anti* conformation. The crystal packing exhibits interesting C—H$\cdots\pi$ stacking.

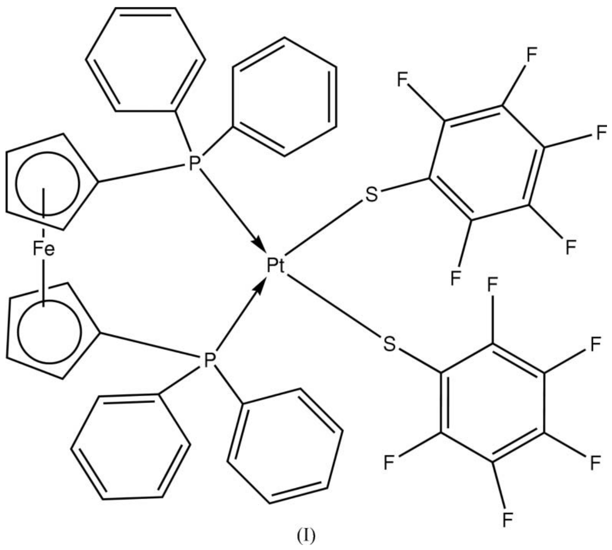
Key indicators

Single-crystal X-ray study
T = 291 K
Mean σ(C–C) = 0.009 Å
R factor = 0.037
wR factor = 0.082
Data-to-parameter ratio = 13.0

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

Comment

Since 1,1-bis(diphenylphosphino)ferrocene (dppf) was first synthesized (Bishop *et al.*, 1971), this compound has been employed extensively for the synthesis of complexes otherwise difficult or in some cases almost impossible to isolate with other diphosphines, *e.g.* with dppe [1,1-bis(diphenylphosphino)ethane; Bandoli & Dolmella, 2000]. In recent years, this capability of stabilization has been applied to the synthesis of species with potential applications in homogeneous catalysis (Canseco-Gónzalez *et al.*, 2003; Colacot, 2001, and references therein; Gan & Hor, 1995; Herrera-Alvarez *et al.*, 2004). In addition, platinum group metal complexes containing ferrocene and thiolate ligands are rare (Maisela *et al.*, 2001; Crespo *et al.*, 1999) due to the well known tendency of these compounds to polymerize, in most cases leading to insoluble solids (Dilworth & Hu, 1994).



(I)

Thus, given our continuing interest in the synthesis of transition metal complexes bearing thiolates (Morales-

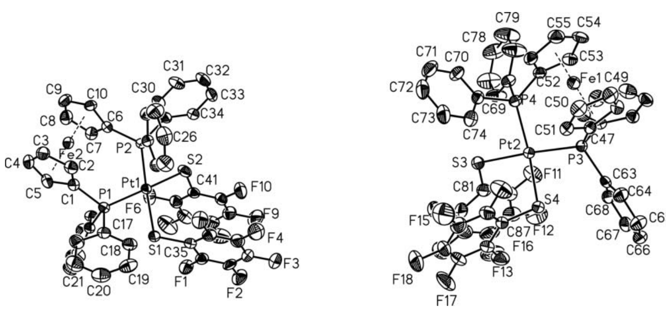


Figure 1
The structures of the two independent molecules in (I) with the atom-labeling scheme. Displacement ellipsoids are shown at the 40% probability level. H atoms have been omitted for clarity.

Morales *et al.*, 2001; Morales-Morales, Redón *et al.*, 2002; Morales-Morales Rodríguez-Morales *et al.*, 2002; Dilworth *et al.*, 2002; García *et al.*, 1993; Gómez-Benítez *et al.*, 2003; Canseco-Gónzalez *et al.*, 2004; Redon *et al.* 2001, 2002, 2003), we have obtained crystals of the platinum(II) complex [Pt(dppf)($SC_6F_5)_2$], (I), the crystal structure of which is described here.

Two independent molecules are found in the asymmetric unit of (I). The labeling scheme is shown in Fig. 1, and selected bond distances and angles are given in Table 1.

There are geometrical and conformational differences between the two molecules. The Pt atoms in both molecules exhibit a distorted square-planar geometry, with an r.m.s. deviation of 0.142 (1) Å for the P1/P2/S1/S2/Pt1 plane (molecule 1), and of 0.192 (2) Å for the P3/P4/S3/S4/Pt2 plane (molecule 2). The phenyl rings in both dppf ligands, denoted as *A* (C11–C16), *B* (C17–C22), *C* (C23–C28), *D* (C29–C34), *E* (C57–C62), *F* (C63–C68), *G* (C69–C74) and *H* (C75–C80), are practically planar. In molecule 1 the dihedral angle between the *A* and *B* rings is 71.4 (2)°, and that between the *C* and *D* rings is 66.5 (2)°, while in molecule 2 the dihedral angles are larger, *viz*. 81.1 (2)° between the *E* and *F* rings, and 80.9 (2)° between the *G* and *H* rings. Moreover, the pentafluorophenylthiolate ligands are almost coplanar in molecule 1, leading to a dihedral angle of 2.7 (2)° between ring 1-I (C35–C40) and ring 1-II (C41–C46). These ligands are rotated around the C—S bond by 63.3 (1) and 64.9 (1)°, respectively. In molecule 2, the pentafluorophenyl groups 2-III (C87–C92) and 2-IV (C81–C86) form a dihedral angle of 9.8 (3)°, and in this case the rings are also rotated by 63.7 (2) and 73.5 (1)° around the corresponding C—S bond. For both molecules, the pentafluorophenyl thiolate ligands are found in an *anti* conformation with respect to the coordination planes of the metal centers.

The molecules are linked by weak inter- and intramolecular C—H$\cdots$F and C—H$\cdots\pi$ interactions between 2.38 (3) and 2.68 (3) Å (Table 2 and Fig. 2).

Experimental

To a solution of [Pt(dppf)(Cl)$_2$] (50.0 mg, 0.068 mmol) in CH_2Cl_2 (10 ml), a solution of [Pb($SC_6F_5)_2$] (41.3 mg, 0.068 mmol) in acetone (20 ml) was added dropwise with stirring. The resulting red-brick solution was stirred overnight. It was then filtered through a short plug of Celite and the solvent was removed under vacuum. The residue was recrystallized from a CH_2Cl_2/hexane (1:1) mixture to yield (I) as yellow crystals. Yield 90%. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.95–7.25 (*m*, Ph, 20H), 4.43 (*s*, Cp, 4H), 4.27 (*s*, Cp, 4H); ^{31}P{^{1}H} NMR (121 MHz, CDCl$_3$): δ 28.16 (*s*, P); ^{19}F{^{1}H} NMR (282 MHz, CDCl$_3$): δ −135.08 (*d*, ^3JF*o*-F*m* = 22.01 Hz, *o*-F), −164.56 (*t*, ^3JF*m*-F*p*= 22.01 Hz, *p*-F), −166.87 (*m*, ^4JF*o*-F*p*= 4.79, *m*-F). Elemental analysis calculated for $C_{46}H_{28}F_{10}Fe_1P_2Pt_1S_2$: C 52.17, H 2.66%; found: C 52.14, H 2.68%. MS–FAB+ [*M*+] = 1059 *m*/*z*.

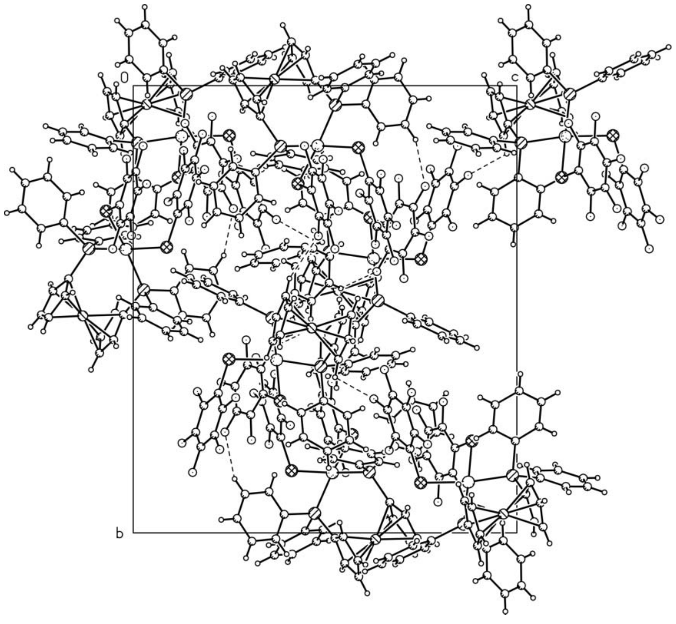


Figure 2
Crystal packing of (I) in a projection along the *a* axis. Broken lines indicate weak C—H$\cdots$F interactions. Atom code: Fe atoms medium sized hatched spheres, C atoms small hatched spheres, P atoms large hatched spheres, S atoms chequered spheres, Pt atoms double dotted large spheres, F atoms one dotted spheres, H atoms small black rimmed spheres.

Crystal data

[PtFe($C_6F_6S)_2(C_{17}H_{14}P)_2$]
M_r = 1147.68
Monoclinic, $P2_1/n$
a = 19.7466 (9) Å
b = 22.0846 (10) Å
c = 19.7669 (9) Å
β = 106.8070 (10)°
V = 8252.0 (7) Å^3
Z = 8
D_x = 1.848 Mg m^{-3}
Mo $K\alpha$ radiation
μ = 4.00 mm^{-1}
T = 291 (2) K
Prism, yellow
0.20 × 0.16 × 0.08 mm

Data collection

Bruker SMART APEX CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1998)
$T_{\min}$ = 0.502, $T_{\max}$ = 0.740
67222 measured reflections
14535 independent reflections
11545 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.066
$\theta_{\max}$ = 25.0°

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.037
$wR(F^2)$ = 0.082
S = 1.01
14535 reflections
1117 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0356P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max}$ = 0.003
$\Delta\rho_{\max}$ = 1.07 e Å^{-3}
$\Delta\rho_{\min}$ = −0.45 e Å^{-3}

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Table 1
Selected geometric parameters (Å, °).

Pt1—P2	2.2833 (13)	Pt2—P3	2.2696 (13)
Pt1—P1	2.2951 (13)	Pt2—P4	2.3006 (14)
Pt1—S2	2.3495 (14)	Pt2—S4	2.3724 (14)
Pt1—S1	2.3783 (14)	Pt2—S3	2.3744 (14)
S1—C35	1.744 (5)	S3—C81	1.762 (6)
S2—C41	1.752 (5)	S4—C87	1.766 (5)
P1—C1	1.812 (5)	P3—C47	1.798 (5)
P1—C11	1.826 (5)	P3—C57	1.814 (5)
P1—C17	1.830 (5)	P3—C63	1.822 (5)
P2—C6	1.800 (5)	P4—C52	1.819 (5)
P2—C29	1.816 (5)	P4—C75	1.823 (6)
P2—C23	1.823 (5)	P4—C69	1.826 (5)
P2—Pt1—P1	97.82 (5)	P3—Pt2—P4	96.79 (5)
P2—Pt1—S2	85.18 (5)	P3—Pt2—S4	86.36 (5)
P1—Pt1—S2	171.16 (6)	P4—Pt2—S4	168.65 (5)
P2—Pt1—S1	174.45 (5)	P3—Pt2—S3	171.50 (5)
P1—Pt1—S1	82.87 (5)	P4—Pt2—S3	87.36 (5)
S2—Pt1—S1	94.95 (5)	S4—Pt2—S3	90.99 (5)
C35—S1—Pt1	109.06 (19)	C81—S3—Pt2	104.0 (2)
C41—S2—Pt1	112.09 (18)	C87—S4—Pt2	105.65 (18)
C1—P1—Pt1	121.89 (17)	C47—P3—Pt2	112.64 (16)
C11—P1—Pt1	104.99 (17)	C57—P3—Pt2	112.61 (17)
C17—P1—Pt1	120.44 (18)	C63—P3—Pt2	115.30 (16)
C6—P2—Pt1	115.39 (17)	C52—P4—Pt2	119.09 (17)
C29—P2—Pt1	116.98 (17)	C75—P4—Pt2	120.89 (18)
C23—P2—Pt1	110.64 (17)	C69—P4—Pt2	107.48 (19)

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C18—H18···F5	0.93	2.69 (1)	3.61	176
C19—H19···F14	0.93	2.38 (1)	3.22	151
C25—H25···F15	0.93	2.78 (1)	3.70	169
C51—H51···F20	0.93	2.75 (1)	3.65	163
C74—H74···F20	0.93	2.43 (1)	3.31	158
C56—H56···F17^{i}	0.93	2.54 (1)	3.03	113
C71—H71···F13^{i}	0.93	2.68 (1)	3.50	148
C28—H28···F2^{i}	0.93	2.66 (1)	3.50	151
C21—H21···F3^{ii}	0.93	2.56 (1)	3.32	140
C13—H13···F16^{ii}	0.93	2.74 (1)	3.23	114
C31—H31···F20^{iii}	0.93	2.71 (1)	3.02	100
C54—H54···F3^{iv}	0.93	2.65 (1)	3.42	141
C61—H61···F11^{iv}	0.93	2.45 (1)	3.23	142
C48—H48···F10^{iv}	0.93	2.54 (1)	3.39	153
C56—H56···F8^{v}	0.93	2.68 (1)	3.46	142
C66—H66···F7^{vi}	0.93	2.72 (1)	3.58	155

Symmetry codes: (i) $x-\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (ii) $-x+\frac{3}{2}, y-\frac{1}{2}, -z+\frac{3}{2}$; (iii) $x+\frac{1}{2}, -y+\frac{1}{2}, z-\frac{1}{2}$; (iv) $-x+1, -y+1, -z+1$; (v) $x-1, y, z$; (vi) $-x+\frac{3}{2}, y+\frac{1}{2}, -z+\frac{3}{2}$.

H atoms were included in calculated positions (C—H = 0.93 Å), and refined using a riding model, with $U_{\rm iso}$(H) = 1.2$U_{\rm eq}$(C). The highest residual electron density peak is 0.99 Å away from atom Pt2.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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