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[Ferrocene-1,1′-diylbis(diisopropylphosphine-*P*)]bis(phenylthio)palladium(II)

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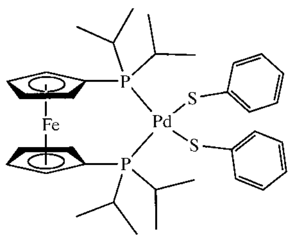
The Pd atom in the title compound, $[\mathrm{Pd(C_6H_5S)_2(C_{22}H_{36}FeP_2)}]$, possesses a distorted square-planar geometry. The phenyl rings attached to the S atoms are located on opposite sides of the plane defined by the Pd and two S atoms. The Pd—S bonds are statistically significantly different, with values of 2.3703 (7) and 2.3887 (7) Å.

Comment

Since the first synthesis of 1,1′-bis(diphenylphosphino)ferrocene (dppf) in 1971 (Bishop *et al.*, 1971), bimetallic complexes of dppf and its alkyl derivatives have been used as catalysts in organic cross-coupling reactions (Hayashi *et al.*, 1984) and in olefin hydrogenation reactions (Cullen *et al.*, 1985). We recently started using Group 10 metals dppf and dippf [dippf is bis(diisopropylphosphino)ferrocene] dihalides as starting materials in the synthesis of dithiolato metal complexes. During the course of this study, we attempted to prepare $[\mathrm{Pd(dippf)(SC_6H_4Te)}]$, by first generating $\mathrm{LiSC_6H_4TeLi}$ and reacting the dilithio salt with $\mathrm{Pd(dippf)Cl_2}$. The lithium salt was prepared by following the procedure reported by Giolando *et al.* (1987). Unexpectedly, the product isolated from our reaction was $[\mathrm{Pd(dippf)(SC_6H_5)_2}]$, (I), whose structure is reported here.



(I)

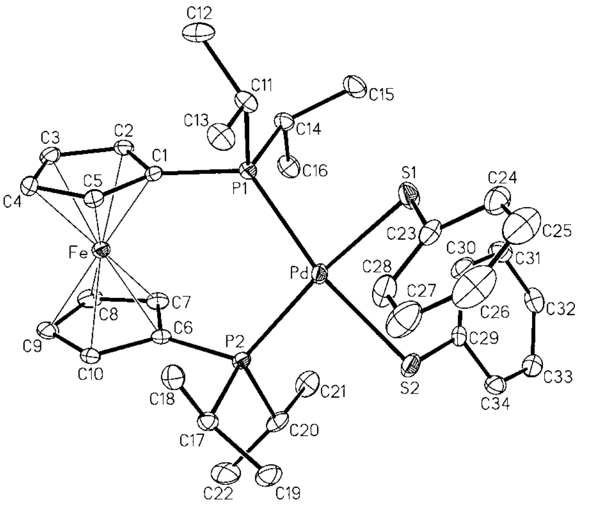


Figure 1
The molecular structure of (I) with displacement ellipsoids shown at the 30% probability level.

The molecular structure of (I) is shown in Fig. 1. Selected bond distances and angles are presented in Table 1. The Pd atom in (I) exhibits a square-planar geometry with the *cis* angles in the range 85.78 (2)–101.09 (2)° and the *trans* angles in the range 168.45 (2)–170.55 (2)°. The presence of two alkyl substituents on the P atoms results in expansion of the P—Pd—P angle to 101.09 (2)° with concomitant reduction of the S—Pd—S angle to 87.69 (2)°. The corresponding angles in $\mathrm{PdCl_2(dppf)}$ [dppf is 1,1′-bis(diphenylphosphino)ferrocene; Hayashi *et al.*, 1984], (II), measured 99.07 (5) and 87.8 (1)°, while in $[\mathrm{Pd(SC_6H_4S)(dppf)}]$, (III) (Maisela & Darkwa, 1999), they were 97.24 (3) and 88.34 (3)°, respectively. In (I), atoms Pd, S1, S2 and P2 are planar within 0.07 Å, while phosphorous P1 is displaced 0.570 (1) Å out of that plane. The Pd—P distances are slightly different [2.3303 (6) and 2.3463 (7) Å], with the Pd—P1 distance being 0.0160 (3) Å shorter. This difference is statistically significant. Similar deviation from planarity in the coordination sphere of the Pd center was observed in (II), with one P atom lying 0.21 Å out of the Pd—S—S—P plane. However, the Pd—P bond length to the P atom located out of the plane [2.301 (1) Å] was 0.018 (1) Å longer than the other Pd—P bond. In contrast, the Pd, two S and two P atoms in (III) are planar within 0.02 Å. The Pd—P bond lengths in (I) are somewhat longer than the 'normal' Pd—P bond of 2.29 (5) Å. The latter value was obtained by averaging 2422 Pd—P distances in complexes reported in the Cambridge Structural Database (CSD; Allen & Kennard, 1993). The Pd—S distances in (I) [2.3887 (7) and 2.3703 (7) Å] are also statistically different with the Pd—S bond *trans* to atom P2, being 0.0184 (7) Å longer. Both Pd—S distances in (I) appreciably exceed the length of the 'typical' Pd—S distance [2.30 (3) Å] obtained by averaging 340 Pd—S distances found in relevant complexes reported in the CSD. The S···S separation in (I) is rather short [3.297 (1) Å] compared with the sum of van der Waals radii of S atoms (3.6 Å; Porterfield, 1988). The phenyl groups on the S atoms point to the opposite sides of the plane defined by the Pd and two S atoms. The Pd—S—C angles are close to the ideal tetrahedral value of 109.4°. The ferrocene moiety is quite typical. The cyclopentadienyl rings are almost perfectly parallel, with the dihedral angle between the Cp planes being 1.39 (19)° and the Cp–Cp interplanar distance measuring 3.28 (2) Å. The Cp rings are staggered and the Fe atom is closer to the C1–C5 plane [1.637 (1) Å] than to the C6–C10 plane [1.639 (1) Å]. In contrast, the Fe–centroid distances are very similar and average 1.639 (3) Å, with the centroid—Fe—centroid angle spanning 178.3 (1)°.

Experimental

A Schlenk tube was charged with Pd(dippf)Cl_2 (0.73 g, 1.23 mmol) and flushed with nitrogen for about 15 min. Degassed toluene (30 ml) was added to give an orange solution to which thiophenol (0.25 ml, 2.46 mmol) and Et_3N (0.5 ml) were added. The orange solution immediately turned maroon with some precipitation. The mixture was filtered to remove $Et_3NH^+Cl^-$ as by-product. The filtrate was evaporated to dryness and the residue recrystallized from a CH_2Cl_2/hexane (1:2) mixture. Single crystals of (I) were grown by layering its CH_2Cl_2 solution with hexane, followed by slow diffusion of the hexane at 258 K (yield = 0.62 g, 68%). Analysis calculated for $C_{34}H_{46}FeP_2PdS_2\cdot CH_2Cl_2$: C 50.77, H 5.84%; found: C 50.80, H 5.99%. ^{1}H NMR ($CDCl_3$, p.p.m.): δ 7.30 (*m*, 4H, C_6H_5), 6.92 (*m*, 6H, C_6H_5), 4.47 (*s*, 8H, C_5H_4), 3.01 [*sept*, 4H, $HC(CH_3)_2$], 1.49 [*q*, 12H, J_{HH} = 7.0 Hz, $HC(CH_3)_2$], 1.19 [*q*, 12H, J_{HH} = 7.0 Hz, $HC(CH_3)_2$]. ^{31}P{H} NMR ($CDCl_3$, p.p.m.): δ 25.94.

Crystal data

$[Pd(C_6H_5S)_2(C_{22}H_{36}FeP_2)]$
$M_r = 743.02$
Monoclinic, $P2_1/n$
$a = 10.5873 (4)$ Å
$b = 17.5830 (7)$ Å
$c = 18.0564 (7)$ Å
$\beta = 93.303 (1)°$
$V = 3355.7 (2)$ Å^3
$Z = 4$
$D_x = 1.471$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7356 reflections
θ = 2–25°
$\mu = 1.210$ mm^{-1}
$T = 173 (2)$ K
Block, yellow
0.40 × 0.30 × 0.20 mm

Table 1
Selected geometric parameters (Å, °).

Pd—P1	2.3303 (6)	Pd—S2	2.3703 (7)
Pd—P2	2.3463 (7)	Pd—S1	2.3887 (7)
P1—Pd—P2	101.09 (2)	P1—Pd—S1	85.78 (2)
P1—Pd—S2	168.45 (2)	P2—Pd—S1	170.55 (2)
P2—Pd—S2	86.56 (2)	S2—Pd—S1	87.69 (3)

Data collection

CCD area-detector diffractometer
φ and ω scans
Absorption correction: empirical (*SADABS*; Blessing, 1995)
$T_{min} = 0.643$, $T_{max} = 0.794$
27 957 measured reflections
6858 independent reflections
5180 reflections with $I > 2\sigma(I)$
$R_{int} = 0.040$
$\theta_{max} = 26.37°$
$h = -13 \rightarrow 13$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 22$
Intensity decay: <1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.052$
$S = 1.040$
6858 reflections
369 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0100P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.41$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Data collection: *SMART* (Siemens, 1996); cell refinement: *SMART*; data reduction: *SHELXTL* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1253). Services for accessing these data are described at the back of the journal.

References

Allen, F. H. & Kennard, O. (1993). *Chem. Des. Autom. News*, **8**, 31–37.
Bishop, J. J., Davidson, A., Katscher, M. L., Lichtenberg, D. W., Merril, R. E. & Smart, J. C. (1971). *J. Organomet. Chem.* **27**, 241–249.
Blessing, R. H. (1995). *Acta Cryst.* A**51**, 33–38.
Cullen, W. R., Kim, T.-J., Einstein, F. W. B. & Jones, T. (1985). *Organometallics*, **4**, 346–351.
Giolando, D. M., Rauchfuss, T. B. & Rheingold, A. L. (1987). *Inorg. Chem.* **26**, 1636–1638.
Hayashi, T., Konishi, M., Kobori, Y., Kumada, M., Higuchi, T. & Hirotsu, K. (1984). *J. Am. Chem. Soc.* **106**, 158–163.
Maisela, L. L. & Darkwa, J. (1999). In preparation.
Porterfield, W. W. (1988). *Inorganic Chemistry*, 2nd ed. San Diego, CA: Academic Press.
Sheldrick, G. M. (1997). *SHELXTL Reference Manual.* Version 5.03. Bruker AXS Inc., Madison, Wisconsin, USA.
Siemens (1996). *SMART Software Reference Manual.* Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.