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# Bis($\mu$-pentafluorobenzenethiolato-$\kappa^2S$:$S$)-*trans*-bis{(pentafluorobenzenethiolato-$\kappa S$)-[(pentafluorophenyl)diphenylphosphine-$\kappa P$]palladium(II)}

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In the title compound, $[Pd_2(C_6F_5S)_4(C_{18}H_{10}F_5P)_2]$, the molecule lies on an inversion center. The structure is characterized by a nearly planar [P,S-Pd($\mu_2$-S)$_2$Pd-S,P] moiety, with *anti* bridging thiolate ligands and terminal ligands in a mutually *trans* arrangement.

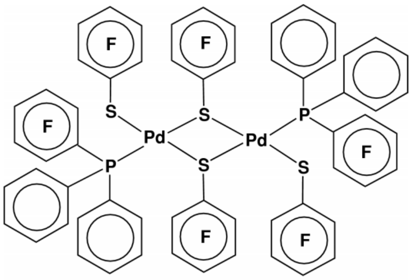
**Key indicators**

Single-crystal X-ray study
$T$ = 296 K
Mean $\sigma$(C–C) = 0.015 Å
$R$ factor = 0.047
$wR$ factor = 0.111
Data-to-parameter ratio = 12.6

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

## Comment

We have a long-standing interest in dinuclear transition metal complexes bearing fluorinated phosphines and thiolates (Claver *et al.*, 1990; García *et al.*, 1993; Arroyo *et al.*, 2000), since these compounds are relevant, for example, to the development of chemical systems involving C—F bond activation (Murai, 1999) or to the study of fluorinated biphasic catalytic processes (Barthel-Rosa & Gladysz, 1999). While working with this class of compounds, we have found that the metathetical reaction of *trans*-$[PdCl_2\{P(C_6H_5)_2(C_6F_5)\}_2]$ with $Pb(SC_6F_5)_2$ gives rise not only to the expected mononuclear complex *trans*-$[Pd(SC_6F_5)_2\{P(C_6H_5)_2(C_6F_5)\}_2]$, but also to a dinuclear compound, *trans*-$[\{P(C_6H_5)_2(C_6F_5)\}(SC_6F_5)Pd(\mu_2\text{-}SC_6F_5)_2Pd(SC_6F_5)\{P(C_6H_5)_2(C_6F_5)\}]$, (I), probably through a sterically driven rearrangement of the mononuclear species. We now report the crystal structure of this dinuclear compound.



(I)

The asymmetric unit of (I) contains one-half of the molecule ($Z' = \frac{1}{2}$) with the Pd atom lying close to an inversion center (Wyckoff position 4$c$ in space group $C2/c$), generating a centrosymmetric dinuclear complex (Fig. 1) including a planar $[Pd_2(\mu_2\text{-}S)_2]$ core. This symmetry is retained in solution, as reflected in the single signal observed in the $^{31}$P NMR spectrum (see *Experimental*). The bridging thiolate ligands display an *anti* configuration and the coordination sphere is completed by two terminal ligands, a thiolate and a phosphine, in a *trans* arrangement. The resulting coordination geometry for the Pd$^{II}$ ions is very close to square-planar (Table 1): the r.m.s. deviation from the least-squares plane defined by S1/S1$^i$/S2/P1

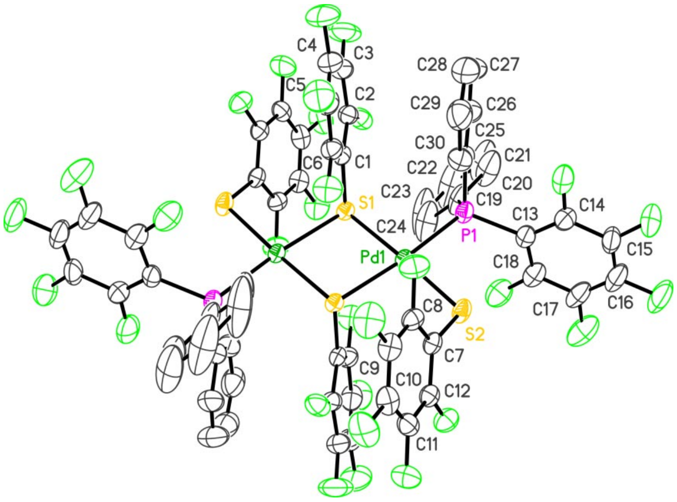


**Figure 1**
The structure of (I), with displacement ellipsoids at the 25% probability level. H atoms have been omitted for clarity. The numbering scheme is given for the asymmetric unit, omitting F atoms for which the number is the same as for the parent C atom.

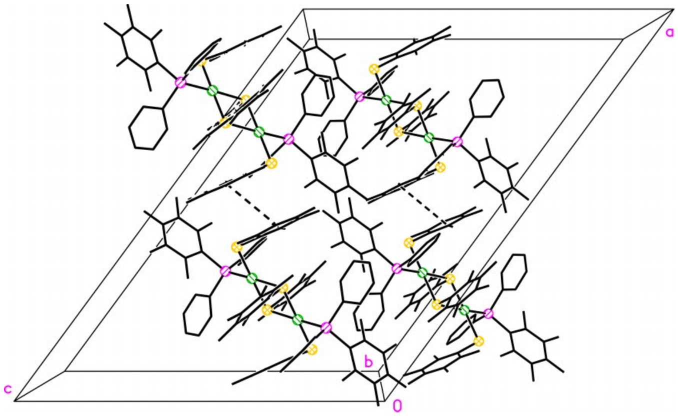


**Figure 2**
The packing of (I), viewed down the $b$ axis. Four molecules are displayed, with closest $\pi$–$\pi$ intermolecular contacts between aromatic rings represented by dashed lines. For clarity, H atoms have been omitted.

[symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$] is 0.0343 (9) Å, with atom Pd1 deviating from this plane by 0.0074 (7) Å.

The same *trans–anti* conformation was previously observed for closely related complexes, *viz*. with triphenylphosphine as terminal phosphine ligands (Fenn & Segrott, 1972), or with triphenylphosphine and benzenethiolate instead of fluorinated ligands (Nakanishi *et al.*, 1994). In other words, these complexes seem to stabilize this conformation in the solid sate, regardless of the F/H substitutions at ligands, *i.e.* regardless of the ligand basicity. Straightforward arguments based on steric considerations can explain the stabilization of this conformation. However, no far-reaching conclusions should be drawn using these observations; for example, the Pt-based complex including phenylmethanethiolate as bridging and terminal ligands and methyldiphenylphosphine as terminal phosphine ligands displays a *cis–syn* arrangement (Bird *et al.*, 1982). On the other hand, dynamic processes generated by inversion of configuration at the S-bridging atoms can take place, giving several stereoisomeric species in solution, as observed for related Pt-containing complexes (Rivera *et al.*, 2001). Therefore, in the case of (I), the possibility of crystallization of a variety of conformers should not be ruled out.

Finally, weak $\pi$–$\pi$ interactions between terminal perfluorothiolate rings are observed in the packing of (I). The closest separation between symmetry-related centroids of rings C7—C12 is 3.7541 (4) Å (symmetry code: $1-x, y, \frac{1}{2}-z$; Fig. 2).

## Experimental

Equimolar amounts of *trans*-[$PdCl_2\{P(C_6H_5)_2(C_6F_5)\}_2$] (0.226 g) and $Pb(SC_6F_5)_2$ (0.152 g) dissolved in 20 ml of acetone were mixed and kept at room temperature with magnetic stirring for 1 h. After this period, the resulting white solid ($PbCl_2$) was filtered off. The yellow solution was chromatographed through a column using silica gel as the stationary phase (Merck, 0.2–0.5 mm) and a mixture of hexane–dichloromethane (4:1) as eluant, to obtain two yellow fractions and a third colorless fraction. The first fraction contained the mononuclear complex *trans*-[$Pd(SC_6F_5)_2\{P(C_6H_5)_2(C_6F_5)\}_2$] (yield 46%). Fraction 2 contained the title compound, (I) (yield 14%). The third fraction contained the free phosphine $P(C_6H_5)_2(C_6F_5)$. Single crystals of (I) were obtained by slow evaporation of the solvent under an $N_2$ flow. Analysis found: C 42.1, H 1.1, S 7.5%; calculated for $C_{60}H_{20}F_{30}P_2Pd_2S_4$: C 42.0, H 1.2, S 7.5%. MS: $m/z$ 1714 (18%); $^{31}$P NMR (in acetone-$d_6$, referenced to external 85% $H_3PO_4$): $\delta$ 8.26 ($s$, $P_{phos}$).

### *Crystal data*

[$Pd_2(C_6F_5S)_4(C_{18}H_{10}F_5P)_2$]
$M_r = 1713.74$
Monoclinic, $C2/c$
$a = 26.807$ (3) Å
$b = 14.3442$ (18) Å
$c = 20.3758$ (15) Å
$\beta = 126.362$ (6)°
$V = 6309.4$ (13) Å$^3$
$Z = 4$
$D_x = 1.804$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 36 reflections
$\theta = 2.8$–$12.0$°
$\mu = 0.88$ mm$^{-1}$
$T = 296$ (1) K
Prism, red
0.3 × 0.3 × 0.2 mm

### *Data collection*

Bruker $P4$ diffractometer
$2\theta/\omega$ scans
Absorption correction: $\psi$ scan (Fait, 1991)
$T_{min} = 0.761$, $T_{max} = 0.841$
6476 measured reflections
5561 independent reflections
3530 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$
$\theta_{max} = 25.0$°
$h = -1 \rightarrow 31$
$k = -1 \rightarrow 17$
$l = -24 \rightarrow 19$
3 standard reflections every 97 reflections intensity decay: 4.1%

### *Refinement*

Refinement on $F^2$
$R[(F) > 2\sigma((F))] = 0.047$
$wR(F^2) = 0.111$
$S = 1.00$
5561 reflections
442 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.44$ e Å$^{-3}$
$\Delta\rho_{min} = -0.31$ e Å$^{-3}$

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**Table 1**
Selected geometric parameters (Å, °).

| | | | |
|---|---|---|---|
| Pd1—P1 | 2.2826 (16) | P1—C19 | 1.834 (7) |
| Pd1—S2 | 2.3153 (14) | P1—C13 | 1.846 (6) |
| Pd1—S1 | 2.3586 (13) | S1—C1 | 1.765 (6) |
| Pd1—S1$^{i}$ | 2.3768 (14) | S2—C7 | 1.765 (5) |
| P1—C25 | 1.810 (8) | | |
| P1—Pd1—S2 | 89.15 (5) | C19—P1—C13 | 101.3 (3) |
| P1—Pd1—S1 | 92.99 (5) | C25—P1—Pd1 | 106.9 (2) |
| S2—Pd1—S1 | 177.51 (6) | C19—P1—Pd1 | 113.9 (3) |
| P1—Pd1—S1$^{i}$ | 174.80 (5) | C13—P1—Pd1 | 117.3 (2) |
| S2—Pd1—S1$^{i}$ | 95.64 (5) | C1—S1—Pd1 | 107.78 (17) |
| S1—Pd1—S1$^{i}$ | 82.26 (5) | C1—S1—Pd1$^{i}$ | 104.12 (18) |
| C25—P1—C19 | 110.4 (4) | Pd1—S1—Pd1$^{i}$ | 97.74 (5) |
| C25—P1—C13 | 106.8 (3) | C7—S2—Pd1 | 106.48 (17) |

Symmetry code: (i) $-x+\frac{1}{2}, -y+\frac{3}{2}, -z$.

A refinement carried out using all-free parameters showed the C19—C24 phenyl ring to have a larger than usual $U_{eq}$ range [$U_{eq}(\max)/U_{eq}(\min) = 2.83$ for this group of six C atoms]. A similarity restraint (Sheldrick, 1998) was then applied to the displacement parameters of this group; atoms closer than 1.5 Å were restrained, with an s.u. value of 0.04 Å$^2$, to have the same $U_{ij}$ components [36 restraints, giving, after refinement, $U_{eq}(\max)/U_{eq}(\min) = 2.39$]. H atoms were treated as riding atoms, with $U_{iso}(H) = 1.2U_{eq}$(parent C) and C—H distances constrained to 0.93 Å.

Data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXTL-Plus* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL-Plus*; molecular graphics: *SHELXTL-Plus*; software used to prepare material for publication: *SHELXTL-Plus*.

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