metal-organic papers

Bis[2-(phenylsulfanyl)benzenethiolato]palladium(II)

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In the title complex, $[Pd(C_{12}H_9S_2)_2]$, the central Pd atom has a slightly distorted *cis*-planar four-coordinate geometry defined by the two thiolate and the two sulfanyl S atoms from two 2-(phenylsulfanyl)benzenethiolate ligands. The two phenyl groups are on the same side of the PdS_4 plane and indicative of the typical arrangement of intermolecular π-stacking. Moreover, an intermolecular $C-H\cdots\pi$ stacking interaction links molecules to one another.

Key indicators

Single-crystal X-ray study
$T = 153$ K
Mean σ(C–C) = 0.004 Å
R factor = 0.023
wR factor = 0.057
Data-to-parameter ratio = 13.2

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

Comment

The cleavage of an S—S bond mediated by a transition metal agent is one of the common methods to synthesize a transition metal complex with thiolate ligands. In the course of our studies on the reactivity of acyclic polythioethers possessing a disulfide bond toward low-valent transition metals (Shimizu *et al.*, 2006), we synthesized the title compound, (I), by the reaction of $(PhSC_6H_4S)_2$ with $Pd(PPh_3)_4$, and determined its crystal structure.

(I)
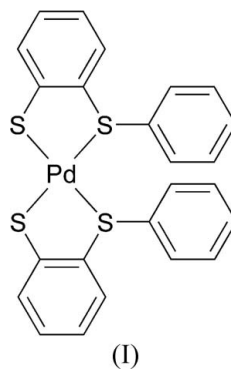
The molecular structure of (I) is shown in Fig. 1. The central Pd atom has a slightly distorted *cis*-square planar coordination to the two thiolate S atoms and the two sulfanyl S atoms of the two 2-(phenylsulfanyl)benzenethiolate ligands. The sum of the bond angles around the Pd1 atom is close to 360°. The Pd1—S1 and Pd1—S3 bond lengths are slightly shorter than those of Pd1—S2 and Pd1—S4 (Table 1). The $C_6H_4S_2PdS_2C_6H_4$ group containing the PdS_4 plane is essentially planar, with the two phenyl groups on the same side of this plane and perpendicular to it. Moreover, the two phenyl rings are nearly parallel to each other, the centroid-to-centroid separation of 3.6241 (16) Å suggesting a face-to-face π-stacking interaction.

The $C4-H3\cdots Cg(C13)^i$ angle [Cg(C13) is the centroid of the C13–C18 ring] of 152° and $H\cdots Cg$ separation of 2.77 Å indicate $C-H\cdots\pi$ stacking between neighbouring benzene rings [symmetry code: (i) $1 - x, -y, -z$].

Experimental

Tetrakis(triphenylphosphine)palladium(0) (133 mg, 0.115 mmol) was added to a benzene solution (10 ml) of bis[2-(phenylsulfanyl)phenyl] disulfide (50 mg, 0.115 mmol) (Figuly *et al.*, 1989) at 298 K. After stirring for 24 h at this temperature, the crude mixture was purified by recrystallization from a benzene/acetonitrile solution (1:1) to give single crystals of (I) (47.5 mg, 76%) [m.p. 526.0–527.0 K (decomposition)].

Crystal data

$[Pd(C_{12}H_9S_2)_2]$	$Z = 2$
$M_r = 541.02$	$D_x = 1.671$ Mg m^{-3}
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.2910$ (1) Å	Cell parameters from 3349
$b = 8.4579$ (2) Å	reflections
$c = 20.4780$ (5) Å	$\theta = 2.4$–25.5°
$\alpha = 98.7890$ (13)°	$\mu = 1.26$ mm^{-1}
$\beta = 92.7051$ (14)°	$T = 153$ (2) K
$\gamma = 91.2243$ (15)°	Prism, purple
$V = 1075.16$ (4) Å^3	$0.15 \times 0.10 \times 0.01$ mm

Data collection

Rigaku Saturn diffractometer	3587 reflections with $I > 2\sigma(I)$
ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan	$\theta_{max} = 25.5°$
(Jacobson, 1998)	$h = -7 \rightarrow 7$
$T_{min} = 0.834$, $T_{max} = 0.988$	$k = -10 \rightarrow 10$
8083 measured reflections	$l = -23 \rightarrow 24$
3985 independent reflections	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0172P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.023$	$+ 0.7132P]$
$wR(F^2) = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
3985 reflections	$\Delta\rho_{max} = 0.40$ e Å^{-3}
302 parameters	$\Delta\rho_{min} = -0.36$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Pd1—S1	2.2886 (6)	S2—C6	1.785 (2)
Pd1—S2	2.3146 (6)	S2—C13	1.790 (2)
Pd1—S3	2.2888 (6)	S3—C7	1.759 (3)
Pd1—S4	2.3186 (6)	S4—C12	1.786 (2)
S1—C1	1.758 (2)	S4—C19	1.789 (2)
S3—Pd1—S1	87.47 (2)	C1—S1—Pd1	104.66 (8)
S3—Pd1—S2	174.59 (2)	C6—S2—Pd1	104.64 (8)
S1—Pd1—S2	88.72 (2)	C13—S2—Pd1	109.61 (8)
S3—Pd1—S4	88.61 (2)	C7—S3—Pd1	104.47 (8)
S1—Pd1—S4	175.66 (2)	C12—S4—Pd1	104.55 (8)
S2—Pd1—S4	95.06 (2)	C19—S4—Pd1	108.93 (8)

All H atoms were placed in calculated positions, with C—H = 0.95 Å, and refined in riding mode, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *CRYSTALCLEAR* (Rigaku, 2004); cell refinement: *HKL2000* (Otwinowski & Minor, 1997); data reduction: *HKL2000*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996); software used to prepare material for publication: *Yadokari-XG* (Wakita, 2005).
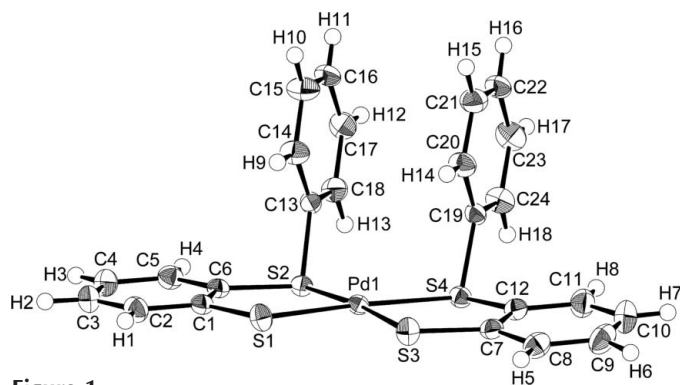

Figure 1
The molecular structure of (I), shown with 50% probability displacement ellipsoids. H atoms are represented by circles of arbitrary size.
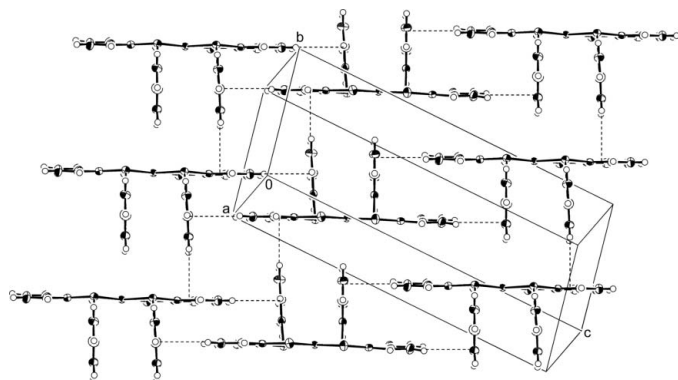

Figure 2
The molecular packing of (I), viewed edge-on to the $C_6H_4S_2PdS_2C_6H_4$ plane.

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