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[2-(Isopropylthio)benzoato-*O*,*S*]phenyl(triphenylphosphine)palladium(II) tetrahydrofuran solvate

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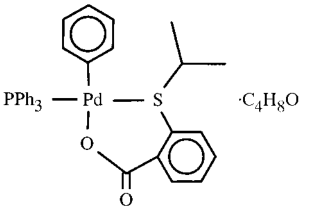
In the title compound, $[Pd(C_6H_5)(C_{10}H_{11}O_2S)(C_{18}H_{15}P)]\cdot C_4H_8O$, an isopropylthiobenzoate ligand is coordinated in a bidentate fashion to the central Pd atom through the O and S atoms. The square-planar geometry of the Pd atom is completed by a phenyl ligand and a triphenylphosphine group but is distorted by the bidentate ligand, which forms a six-membered chelate ring. This ring deviates strongly from planarity, which is illustrated by the plane through the phenyl portion of the chelate ring forming a dihedral angle of 62.3 (1)° with the coordination plane.

Comment

The title compound, (I), was synthesized for its potential catalytic properties in C—C linkage reactions, such as the oligomerization of ethene. P—O hemilabile ligands coordinated to nickel are well known in such reactions, and the catalytic mechanism proposed by Rauchfuss *et al.* (1975) can also be applied to S—O hemilabile ligands. The hemilabile ligand may be either monodentate (coordinated only through an O atom) or bidentate (coordinated through both S and O atoms). In the presence of a substrate molecule the S atom of the complex containing the bidentate ligand will decoordinate leaving a vacant coordination site. Since the hemilabile ligand is still bound to Pd through the O atom, the S atom is close enough to recoordinate to Pd once the catalytic reaction has taken place.



(I)

The synthesis and characterization of a series of Pd complexes containing potentially hemilabile S—O ligands, of the type *trans*-$[Pd(OOC\text{-}C_6H_4\text{-}2\text{-}SR\text{-}\kappa O)(C_6H_5)\{P(C_6H_5)_3\}_2]$, have been reported previously [R = Et was described by Meyer *et al.* (1998), while the two conformational isomers of R = Me were discussed by Kruger *et al.* (2000)]. Although the hemilability of the complexes has been proven in solution, all the previously reported crystal structures were of the monodentate form. This paper presents the first example of a crystal structure of a Pd complex with bidentate coordination of the S—O ligand, through both the S and O atoms.

The molecular structure and atom-numbering scheme for (I) are shown in Fig. 1. The majority of the bond lengths and angles agree with those found in the previously determined ethylthiobenzoate and methylthiobenzoate structures, although the Pd—P bond length of 2.279 (1) Å is shorter. This suggests that the *trans* influence of the S atom is smaller than that of the P atom (the *trans* ligand in the previously determined structures).

The conformation of the chelate ring agrees with the findings of Corey & Bailar (1959). They determined that enhanced puckering of a six-membered ring occurred when a metal–N bond distance was greater than 2 Å and the bite angle of the chelate was close to 90°. This increased the interactions of *cis* substituents, thus destabilizing the ring, particularly when bulky substituents were present. This is clearly the case in the present structure, where the bond angle is close to 90° and the chelate ring is extremely buckled, whereas the previous monodentate methylthiobenzoate and ethylthiobenzoate

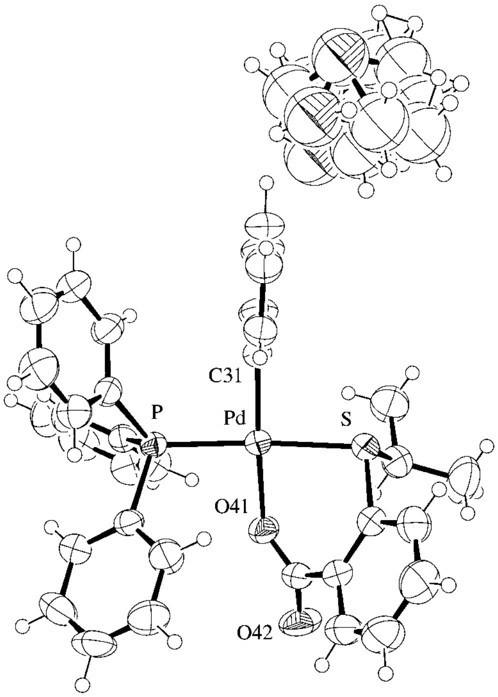


Figure 1
The molecular conformation of (I) showing the atom-numbering scheme and the disordered solvent molecule. Displacement ellipsoids are shown at the 50% probability level and H atoms are drawn as spheres of arbitrary radii.

ligands were planar. The extent of the puckering is illustrated by the phenyl portion of the ligand (C42–C47), which is tilted at an angle of 62.3 (1)° to the molecular plane containing the Pd atom, and by the deviations from 0 or 180° in the torsion angles shown in Table 1.

Although the bond angles around the Pd atom do not deviate substantially from the expected 90 and 180°, the planarity of the square-planar conformation around it is affected by the puckered ligand, giving a tetrahedral distortion. A calculation of the best plane through the Pd and the four atoms bonded to it showed that the Pd atom lies only 0.009 (1) Å above the plane, whereas the *trans* C31 and O41 atoms lie 0.173 (2) and 0.180 (2) Å, respectively, above the plane, and the P and S atoms lie 0.182 (1) and 0.181 (1) Å, respectively, below the plane.

Experimental

Thallium 2-isopropylthiobenzoate was obtained by stirring thallium carbonate with the stoichiometric amount of 2-isopropylthiobenzoic acid in methanol at *ca* 313 K for 30 min and removing the solvent *in vacuo*. The salt was then added in 20% excess to a solution of [Pd(tmeda)(C_6H_5)I] (tmeda = tetramethylethylenediamine) in tetrahydrofuran (THF) and the mixture stirred for 1 h at room temperature. A solution of the stoichiometric amount of triphenylphosphine in THF was added dropwise to the suspension over a period of 1 h. After stirring overnight, the precipitated thallium iodide was removed by filtration through Celite. The volume of the solution was reduced to one-third and layered with *n*-pentane. Single crystals of (I) were obtained at room temperature in a yield of 30% with no further crystallization.

Crystal data

$[Pd(C_6H_5)(C_{10}H_{11}O_2S)(C_{18}H_{15}P)]\cdot C_4H_8O$
$M_r = 713.12$
Triclinic, $P\bar{1}$
$a = 9.8574$ (6) Å
$b = 10.9503$ (6) Å
$c = 16.5057$ (10) Å
$\alpha = 100.142$ (1)°
$\beta = 95.803$ (1)°
$\gamma = 96.244$ (1)°
$V = 1730.2$ (2) Å^3

$Z = 2$
$D_x = 1.369$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 7829 reflections
$\theta = 1.26$–25.00°
$\mu = 0.677$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.30 × 0.25 × 0.20 mm

Data collection

Siemens SMART CCD area detector diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.82$, $T_{max} = 0.87$
7829 measured reflections

5613 independent reflections
5028 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25°$
$h = -11 \rightarrow 11$
$k = -10 \rightarrow 13$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.097$
$S = 1.103$
5613 reflections
386 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0318P)^2 + 2.4317P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.019$
$\Delta\rho_{max} = 0.66$ e Å^{-3}
$\Delta\rho_{min} = -0.50$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pd—C31	1.988 (4)	Pd—P	2.2788 (10)
Pd—O41	2.098 (3)	Pd—S	2.3611 (10)
C31—Pd—O41	170.24 (14)	C31—Pd—S	90.71 (11)
C31—Pd—P	90.77 (11)	O41—Pd—S	87.47 (8)
O41—Pd—P	92.60 (8)	P—Pd—S	170.55 (4)
O41—C41—C42—C43	141.3 (4)	C42—C47—S—C51	−67.5 (4)
O41—C41—C42—C47	−41.5 (6)		

The THF molecule was found to be disordered. This was resolved by a rigid-body refinement of an ideal molecule, which showed that the disorder could be described by three different conformations in the ratio 40:27:33. Each conformation was refined with common isotropic displacement parameters.

Data collection: *SMART* (Siemens, 1996); data reduction: *SAINT* (Siemens, 1996); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1232). Services for accessing these data are described at the back of the journal.

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