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trans-(2-Methylthiobenzoato-*O*)-phenylbis(triphenylphosphine)-palladium(II), two conformational isomers

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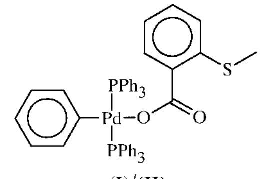
The title compound, *trans*-[Pd(C_6H_5)($C_8H_7O_2S$)($C_{18}H_{15}P$)$_2$], crystallizes in two modifications differing only in the orientation of the 2-methylthiobenzoato ligand. In both cases, this ligand binds to the metal centre *via* one O atom in a monodentate fashion. The only significant difference is a rotation about the C(Ph)—COO bond, with O—C—C—C torsion angles having values of 6.3 (7) and 157.3 (3)° in the two isomeric forms.

Comment

Organometallic catalysts often incorporate hemilabile ligands, *i.e.* ligands that could bind either in a monodentate or a bidentate fashion, so as to facilitate the liberation of one coordination site of the metal centre under the conditions of the catalytic reaction. The title compound is an example of a phenylpalladium compound containing such a hemilabile ligand, namely a methylthioethercarboxylate S—O ligand. Due to their importance in industrial catalytic processes, Pd compounds containing hemilabile P—O ligands have been investigated extensively (Bader & Lindner, 1991). Examples of compounds with hemilabile S—O ligands are, however, quite rare (Britovsek *et al.*, 1996).

We have recently described (Meyer *et al.*, 1998) the synthesis of a series of compounds containing this type of ligand, namely *trans*-[Pd(OOC–C_6H_4–2-S*R*-κ*O*)(C_6H_5){P(C_6H_5)$_3$}$_2$] with *R* = Me, Et, ^{i}Pr and ^{t}Bu. The crystal structure of one of the compounds in this series, *i.e.* where *R* = Et, was reported and it was shown that the last two complexes, *i.e.* with *R* = ^{i}Pr and ^{t}Bu, are hemilabile in solution.

The title compound (with *R* = Me) forms two distinct polymorphs, co-crystallizing from the same solution and easily distinguishable by their dissimilar crystal shapes. Their habits are monoclinic prismatic for the form we called isomer (I) and spindle-shaped monoclinic prismatic for our isomer (II). We observed the crystals of form (II) to be in the majority in a ratio of about 3:1 between the two forms. The crystal structures of both modifications were determined and are reported and compared in this paper.



(I)/(II)

It was expected that, since the S—O ligands are potentially bidentate, the structures would differ in the way in which the ligands bind to the metal centres. However, they were found to be mono-coordinated in both cases. The molecular configurations are the same in the two forms, *i.e.* a square-planar substitution of the Pd atom by the four ligands, with deviations from the best plane of less than 0.13 Å. The phenyl group and the S—O ligand are *trans* to each other and the S—O ligand bonds through the carboxylate-O rather than the S atom.

The difference between the two modifications lies in the orientation of the S—O ligands. In form (I), the S of the carboxylate ligand is adjacent to the O atom bonded to the Pd atom (O41 in Fig. 1). In form (II), the ligand is rotated around the C(carboxylate)—C(phenyl) bond to bring the S atom in close proximity to the carbonyl O atom (O42 in Fig. 2). The phenyl ligands are oriented perpendicular to the square plane, whereas the S—O ligands tilt at angles of 63.86 (7) and 42.40 (5)° to the molecular plane in forms (I) and (II), respectively. The orientations of the triphenylphosphines are very similar for both forms, as can be seen in the figures and from the torsion angles listed in Tables 1 and 2.

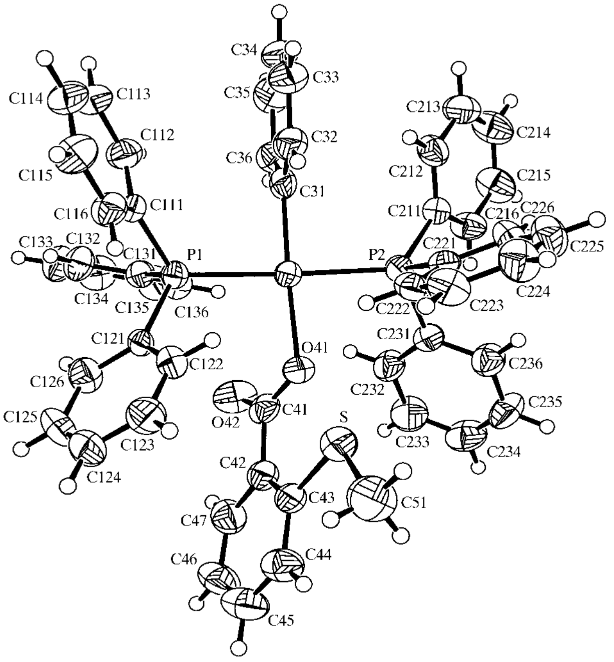


Figure 1
The molecular conformation of form (I) of the title compound, with anisotropic displacement ellipsoids shown at 50% probability level.

No significant intermolecular interactions can be observed in either of the two crystal structures. The packing of the molecules is such that in the case of isomer (I), the phenyl and the sulfur ligands point towards each other, while in the case of isomer (II), the sulfur ligands point towards pockets formed between the triphenylphosphine ligands of neighbouring molecules.

The conformation of modification (I) of the title compound (S oriented towards carboxyl O) is similar to that of its ethyl analogue *trans*-[Pd(OOC–C_6H_4-2-SC_2H_5-κO)(C_6H_5){P(C_6H_5)$_3$}$_2$] (Meyer *et al.*, 1998). The bond lengths and angles (not involving hydrogen) found for the three comparable molecular structures, the latter and forms (I) and (II) of the title compound, agree exceptionally well (all observations are within three standard deviations from the average).

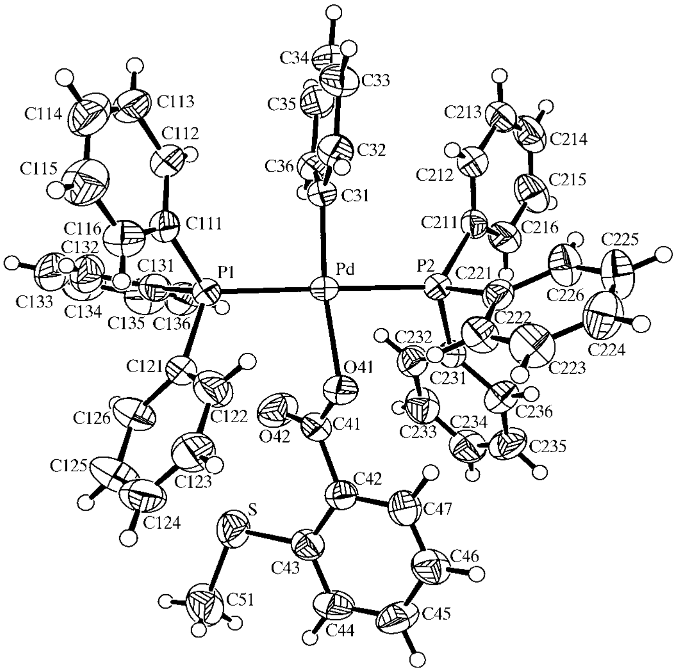


Figure 2

The molecular conformation of form (II) of the title compound, with anisotropic displacement ellipsoids shown at 50% probability level.

Experimental

The title compound was prepared by stirring *trans*-[PdCl(C_6H_5){P(C_6H_5)$_3$}$_2$] with TlOOC–C_6H_4-2-SCH_3 in tetrahydrofuran (THF) with subsequent filtration of TlCl and crystallization from THF/pentane as reported previously (Meyer *et al.*, 1998).

Isomer (I)

Crystal data

[Pd(C_6H_5)($C_8H_7O_2S$)($C_{18}H_{15}P$)$_2$]
$M_r = 875.24$
Monoclinic, $P2_1/c$
$a = 18.055$ (6) Å
$b = 14.661$ (5) Å
$c = 17.598$ (6) Å
$\beta = 116.12$ (5)°
$V = 4182$ (2) Å^3
$Z = 4$

$D_x = 1.390$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 43 reflections
$\theta = 4.3$–12.9°
$\mu = 0.61$ mm^{-1}
$T = 293$ (2) K
Prism, colourless
0.25 × 0.13 × 0.10 mm

Data collection

Philips PW1100 diffractometer
ω–2θ scans
Absorption correction: by integration (*Xtal*3.6; Hall *et al.*, 1999)
$T_{\min} = 0.93$, $T_{\max} = 0.95$
11 945 measured reflections
7379 independent reflections
4566 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.074$
$\theta_{\max} = 25°$
$h = -17 \rightarrow 21$
$k = -7 \rightarrow 17$
$l = -20 \rightarrow 19$
3 standard reflections every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.093$
$S = 0.999$
5827 reflections
505 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0294P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.51$ e Å^{-3}
$\Delta\rho_{\min} = -0.46$ e Å^{-3}

Table 1

Selected geometric parameters (Å, °) for (I).

Pd—C31	1.993 (5)	Pd—P1	2.3348 (15)
Pd—O41	2.126 (3)	Pd—P2	2.3494 (15)
C31—Pd—O41	169.92 (19)	C31—Pd—P2	89.87 (14)
C31—Pd—P1	87.55 (14)	O41—Pd—P2	88.29 (10)
O41—Pd—P1	94.52 (10)	P1—Pd—P2	176.99 (5)
O41—C41—C42—C43	6.3 (7)	C31—Pd—P2—C111	29.7 (2)
C31—Pd—P1—C111	−34.7 (2)	Pd—P2—C211—C212	59.6 (5)
Pd—P1—C111—C112	81.9 (4)	Pd—P2—C221—C222	23.7 (4)
Pd—P1—C121—C122	41.0 (4)	Pd—P2—C231—C232	34.6 (4)
Pd—P1—C131—C132	−167.6 (4)		

Isomer (II)

Crystal data

[Pd(C_6H_5)($C_8H_7O_2S$)($C_{18}H_{15}P$)$_2$]
$M_r = 875.24$
Monoclinic, $P2_1/c$
$a = 12.5741$ (6) Å
$b = 20.5817$ (9) Å
$c = 16.0672$ (8) Å
$\beta = 99.186$ (1)°
$V = 4104.8$ (3) Å^3
$Z = 4$

$D_x = 1.416$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8107 reflections
$\theta = 1.62$–28.30°
$\mu = 0.62$ mm^{-1}
$T = 293$ (2) K
Spindle, light yellow
0.35 × 0.20 × 0.18 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.86$, $T_{\max} = 0.89$
27 445 measured reflections

10 119 independent reflections
8107 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.024$
$\theta_{\max} = 28.30°$
$h = -16 \rightarrow 16$
$k = -23 \rightarrow 27$
$l = -17 \rightarrow 21$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.108$
$S = 1.042$
10 119 reflections
505 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0331P)^2 + 6.2933P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.002$
$\Delta\rho_{\max} = 2.13$ e Å^{-3}
$\Delta\rho_{\min} = -1.31$ e Å^{-3}

In isomer (II), the largest peak and the deepest hole in the residual electron-density function are unusually large, but are in close proximity to the Pd atom (at distances of 0.78 and 0.67 Å, respectively, from the Pd atom directly above and below the molecular plane). As the internal consistency of the data set is excellent, no obvious explanation for the phenomenon could be found.

Table 2
Selected geometric parameters (Å, °) for (II).

Pd—C31	1.982 (3)	Pd—P2	2.3499 (8)
Pd—O41	2.129 (2)	Pd—P1	2.3505 (8)
C31—Pd—O41	170.35 (10)	C31—Pd—P1	90.94 (8)
C31—Pd—P2	89.81 (8)	O41—Pd—P1	94.97 (6)
O41—Pd—P2	84.45 (6)	P2—Pd—P1	178.56 (3)
O41—C41—C42—C43	157.3 (3)	C31—Pd—P2—C111	37.10 (16)
C31—Pd—P1—C111	−38.17 (15)	Pd—P2—C211—C212	55.4 (3)
Pd—P1—C111—C112	64.1 (3)	Pd—P2—C221—C222	32.6 (3)
Pd—P1—C121—C122	56.3 (3)	Pd—P2—C231—C232	54.4 (3)
Pd—P1—C131—C132	−164.0 (3)		

Data collection: *PWPC* (Gomm, 1998) for isomer (I), *SMART* (Siemens, 1996) for isomer (II); cell refinement: *PWPC* for (I), *SAINT* (Siemens, 1996) for (II); data reduction: *Xtal*3.6 (Hall *et al.*, 1999) for (I), *SAINT* for (II); for both isomers, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.2

We wish to thank the Department of Chemistry of the University of the Witwatersrand for the data collection of isomer (II) on their Siemens diffractometer.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1231). Services for accessing these data are described at the back of the journal.

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