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***cis*- $\mu$ -Chloro- $\mu$ -*p*-toluenethiolato-bis  
[chloro(triethylphosphine)palladium]**

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The title compound, *cis*-[Pd<sub>2</sub>Cl<sub>3</sub>(C<sub>7</sub>H<sub>7</sub>S)(C<sub>6</sub>H<sub>15</sub>P)<sub>2</sub>], has bridging chloro and arylthiolato groups, with the phosphines being *trans* to the bridging chloro group. The four-membered metallocyclic Pd<sub>2</sub>ClS ring is unexpectedly non-planar, with a dihedral angle of 133.8 (1)° between the PdCl<sub>2</sub>SP coordination planes. Principal dimensions include Pd—Cl<sub>t</sub> 2.316 (3) and 2.329 (3), Pd—Cl<sub>b</sub> 2.442 (3) and 2.432 (3), Pd—S 2.280 (3) and 2.282 (3), and Pd—P 2.233 (3) and 2.236 (3) Å (where Cl<sub>t</sub> and Cl<sub>b</sub> are terminal and bridging chloro ligands, respectively).

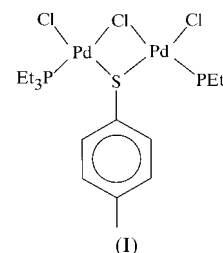
**Comment**

The *cis*-[M(SR')<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] compounds (where M = Pd or Pt, R = alkyl or aryl groups) are well known as synthons for preparing binuclear compounds (Jain *et al.*, 1993). The [Pd(SR')<sub>2</sub>(PR<sub>3</sub>)<sub>2</sub>] complexes also exist in the *trans* form, but the utility of the *trans* isomer for corresponding transformations to dimeric species is not known.

The four-membered metallocyclic Pd<sub>2</sub>XS ring in the dinuclear palladium(II) complexes [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -X)( $\mu$ -SR')(PR<sub>3</sub>)<sub>2</sub>] (X = Cl or SR'; R and R' are alkyl or aryl) is reported to adopt either planar or non-planar conformations depending upon the nature of the R' group on the S atom. The arylthiolato-bridged compounds [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)( $\mu$ -SR)(PMe<sub>3</sub>)<sub>2</sub>] (where R = Me or 'Bu) (Padilla *et al.*, 1991), [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)( $\mu$ -SEt)(PMe<sub>2</sub>Ph)<sub>2</sub>] (Jain *et al.*, 1989) and [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)( $\mu$ -SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl)(PMe<sub>3</sub>)<sub>2</sub>] (Yamamoto *et al.*, 1991) have non-planar four-membered metallocyclic rings. A search of the April 2000 release of the Cambridge Structural Database (CSD; Allen & Kennard, 1993) with ConQuest showed no other related compounds and the coordinates available there allowed us to calculate values of the fold angle [dihedral angle between the coordination planes (PdCl<sub>2</sub>SP) of the Pd atoms] as 146 (R' = Me; CSD refcode JUNXEV; Padilla *et al.*, 1991), 134 (R' = Et; KIFDAE; Jain *et al.*, 1989), 155 (R' = CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl; JITYIU; Yamamoto *et al.*, 1991) and 138° (R' = 'Bu; JUNXIZ; Padilla *et al.*, 1991). In the arylthiolato

compound [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)( $\mu$ -SPh)(PMe<sub>3</sub>)<sub>2</sub>] (Padilla *et al.*, 1991), the fold angle from the data in the CSD is 172° (rather than the reported value of 180°; JUNXOF; Padilla *et al.*, 1991).

In the course of our synthetic studies of organochalcogenide compounds of Pd<sup>II</sup> (Alyea *et al.*, 1998), we prepared the title compound, (I); principal dimensions are in Table 1. The ranges of the principal dimensions in the previously reported related structures with aliphatic bridging SR groups are: Pd—Cl<sub>b</sub> 2.41–2.45, Pd—S<sub>b</sub> 2.26–2.29, Pd—Cl<sub>t</sub> 2.32–2.34, Pd—P 2.21–2.23 Å, with mean values Pd—Cl<sub>b</sub> 2.433 (14), Pd—S<sub>b</sub> 2.277 (7), Pd—Cl<sub>t</sub> 2.331 (7) and Pd—P 2.220 (7) Å (where Cl<sub>t</sub> and Cl<sub>b</sub> are terminal and bridging chloro ligands, respectively). The dimensions in Table 1 are clearly in accord with these values.



The reported dimensions for the one previously reported arylthiolato compound, [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)( $\mu$ -SPh)(PMe<sub>3</sub>)<sub>2</sub>] [Pd—Cl<sub>b</sub> 2.391 (2) and 2.401 (2), Pd—S<sub>b</sub> 2.288 (2) and 2.301 (2), Pd—Cl<sub>t</sub> 2.296 (2) and 2.310 (2), and Pd—P 2.214 (2) and 2.222 (2) Å] are slightly shorter (Pd—Cl<sub>t</sub> and Pd—Cl<sub>b</sub>), slightly longer (Pd—S<sub>b</sub>) and within the same range (Pd—P) as those reported for the arylthiolato species.

The four-membered Pd<sub>2</sub>ClS ring in (I) is markedly folded [fold angle 133.8 (1)°]; this is at the low end of the 'aliphatic thiolato' range, defined by dinuclear species with the mono-thiolato bridge being —SEt (135.5°) and —SCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>Cl (156.4°), and quite different from the almost planar conformation of the S-phenyl structure (172°).

This is contrary to a previous prediction (Padilla *et al.*, 1991) which related the occurrence of metallocycle non-planarity with the presence of shorter Pd—S bonds for the aliphatic bridging —SR cases. The enhanced Pd—S bonding involving sulfur *p*(z) and metal *d*(*x*<sup>2</sup> — *y*<sup>2</sup>) orbitals was considered the reason for distortion from planarity in the Pd—Cl—Pd—S core. This electronic rationale must be considered tenuous given the present result for a second arylthiolato complex. At best, there is a trend of increasing fold angle with increasing Pd—S distance (with concomitant shorter Pd—Cl<sub>t</sub> and Pd—Cl<sub>b</sub> bonds and larger Pd—Cl—Pd and Pd—S—Pd angles). This of course does not preclude other factors (*e.g.* steric and intermolecular packing effects) playing a role in determining the exact conformation of the Pd<sub>2</sub>ClS ring.

**Experimental**

Stoichiometric amounts of *trans*-[Pd(S—C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>-*p*)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] and [Pd<sub>2</sub>Cl<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>(PEt<sub>3</sub>)<sub>2</sub>] were stirred in dichloromethane (25 ml) for 5 h. The solution was evaporated in vacuum and the residue dissolved in dichloromethane (5 ml) and filtered. To the filtrate, methanol was added (1 ml) and the solution left for crystallization. The solution on

evaporation yielded a yellow crystalline product which was filtered, washed with methanol, and dried. This product was recrystallized from dichloromethane/methanol and identified by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy as the title compound. The supernatant solution on evaporation yielded an orange coloured product which was identified as  $[\text{Pd}_2(\mu\text{-S-C}_6\text{H}_4\text{CH}_3\text{-P})_2(\text{PEt}_3)_2]$ . The distinguishing  $^{31}\text{P}$  NMR signal in  $\text{CDCl}_3$  occurred at 31.0 p.p.m. for the latter dithiolato-bridged compound *versus* 38.7 p.p.m. for the monobridged species and 18.8 p.p.m. for  $[\text{PdCl}_2(\text{PEt}_3)_2]$  (present as an impurity in the supernatant solution).

Crystal data



$M_r = 678.69$

Monoclinic,  $P2_1$

$a = 7.8564$  (7) Å

$b = 17.4629$  (16) Å

$c = 9.7865$  (16) Å

$\beta = 92.132$  (9)°

$V = 1341.7$  (3) Å<sup>3</sup>

$Z = 2$

$D_x = 1.680$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

Cell parameters from 25 reflections

$\theta = 10.00\text{--}18.25^\circ$

$\mu = 1.841$  mm<sup>-1</sup>

$T = 294$  (1) K

Plate, colourless

$0.43 \times 0.16 \times 0.07$  mm

Data collection

Enraf-Nonius CAD-4 diffractometer

$\theta/2\theta$  scans

Absorption correction: Gaussian (*ABSO* in *NRCVAX*; Gabe *et al.*, 1989)

$T_{\min} = 0.746$ ,  $T_{\max} = 0.883$

2652 measured reflections

2457 independent reflections

1842 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.016$

$\theta_{\text{max}} = 25.04^\circ$

$h = -9 \rightarrow 9$

$k = 0 \rightarrow 20$

$l = 0 \rightarrow 11$

3 standard reflections

frequency: 120 min

intensity variation: 1.0%

Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.038$

$wR(F^2) = 0.068$

$S = 0.975$

2457 reflections

245 parameters

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0270P)^2]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.48$  e Å<sup>-3</sup>

$\Delta\rho_{\text{min}} = -0.55$  e Å<sup>-3</sup>

Absolute structure: Flack (1983), no

Friedel pairs

Flack parameter = 0.01 (5)

Table 1

Selected geometric parameters (Å, °).

Pd1—P1	2.236 (3)	Pd2—P2	2.233 (3)
Pd1—S1	2.282 (3)	Pd2—S1	2.280 (3)
Pd1—Cl1	2.316 (3)	Pd2—Cl2	2.329 (3)
Pd1—Cl12	2.442 (3)	Pd2—Cl12	2.432 (3)

P1—Pd1—S1	87.69 (10)	P2—Pd2—Cl2	88.36 (12)
P1—Pd1—Cl1	93.84 (10)	S1—Pd2—Cl2	176.97 (12)
S1—Pd1—Cl1	172.99 (14)	P2—Pd2—Cl12	175.93 (11)
P1—Pd1—Cl12	172.96 (10)	S1—Pd2—Cl12	85.59 (9)
S1—Pd1—Cl12	85.31 (9)	Cl2—Pd2—Cl12	93.16 (11)
Cl1—Pd1—Cl12	93.02 (10)	Pd2—S1—Pd1	89.78 (9)
P2—Pd2—S1	93.07 (10)	Pd2—Cl12—Pd1	82.67 (8)

Molecule (I) crystallized in the monoclinic system; space group  $P2_1$  or  $P2_1/m$  was suggested by the systematic absences and  $P2_1$  was assumed and confirmed by the analysis. H atoms were treated as riding atoms (C—H 0.93–0.97 Å). Examination of the structure with *PLATON* (Spek, 2000) showed that there were no solvent-accessible voids in the crystal lattice.

Data collection: *CAD-4-PC* (Enraf-Nonius, 1992); cell refinement: *SET4* and *CELDIM* (Enraf-Nonius, 1992); data reduction: *DATRD2* in *NRCVAX96* (Gabe *et al.*, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *NRCVAX96* and *SHELXL97* (Sheldrick, 1997); software used to prepare material for publication: *NRCVAX96*, *SHELXL97* and *WordPerfect* macro *PREP8* (Ferguson, 1998).

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