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trans-Chloro(2-nitrobenzenethiolato-*S*)bis(triphenylphosphine-*P*)palladium(II) monoacetone solvate

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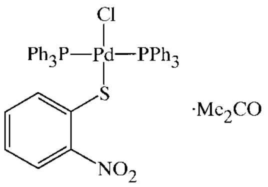
Molecules of the title compound, $[PdCl(C_6H_4NO_2S)(PPh_3)_2]\cdot C_3H_6O$, exhibit a slight distortion from exact planarity at the Pd atom towards tetrahedral, with P—Pd—P and Cl—Pd—S angles of 174.98 (3) and 174.19 (3)°, respectively. The Pd—Cl and Pd—S bonds are, respectively, long [2.3550 (11) Å] and short [2.3020 (12) Å] for their types; the S—C bond is also very short [1.744 (4) Å]. The solvating acetone molecule is linked to one of the phosphine ligands by means of a C—H···O hydrogen bond.

Comment

We have recently reported the structures of members of the $2\text{-}O_2NC_6H_4SX$ system containing the 2-nitrobenzenethiolate group, in which the α-atom of fragment X can be C or N (Low, Storey *et al.*, 2000) or S (Low, Glidewell & Wardell, 2000). In general, at the global energy minimum conformation, both the nitro group and the α-atom of group X are essentially coplanar with the aryl ring. When X is not in the plane of the aryl ring, rotation about the exocyclic C—S bond is associated with a disrotatory twist of the nitro group about the C—N bond; the occurrence of such conformations seems to depend on the presence in the structure of specific intermolecular interactions, such as C—H···O hydrogen bonds. Seeking to investigate the wider generality of this idea, we report here the structure of a further compound of type $2\text{-}O_2NC_6H_4SX$, namely *trans*-chloro(2-nitrobenzenethiolato-*S*)bis(triphenylphosphine-*P*)palladium(II), in which the α-atom of group X is Pd and which crystallizes from acetone as a 1:1 solvate, (I).

Molecules of the Pd complex (I) lie in general positions (Fig. 1). Although no bond angle at Pd involving a pair of *cis* substituents deviates from 90° by more than 1.7°, nonetheless there is a slight but significant distortion from planarity towards tetrahedral, and both bond angles at Pd involving *trans* pairs of substituents are less than 175° (Table 1). The deviations (Å) of the ligating atoms from their best plane through Pd are: Cl −0.106 (1), S −0.105 (1), P1 0.105 (1) and P2 0.106 (1). In this respect, the configuration of the *trans*-$PdClP_2S$ chromophore in (I) differs from those found in two analogous compounds retrieved from the Cambridge Structural Database (Allen & Kennard, 1993) containing *trans*-$PdCl_2P_2$ and *trans*-PdP_2S_2 chromophores. Molecules of *trans*-$[PdCl_2(PPh_3)_2]$ are centrosymmetric both in the unsolvated compound (BISKIX; Ferguson *et al.*, 1982) and in the bis-chloroform solvate (RAVYUI; Stark & Whitmire, 1997). Similarly, molecules of *trans*-$[Pd\{PH(C_6H_{11})_2\}_2(SPh)_2]$ (LETNON; Pasquali *et al.*, 1993) lie across inversion centres. Hence, in all these complexes, palladium and its four ligating atoms are strictly coplanar.



(I)

The conformation of (I) is close to that expected (Low, Storey *et al.*, 2000) for the global energy minimum. There is a slight rotation around the C—S bond away from coplanarity of the Pd atom with the nitrated aryl ring, and a disrotatory twist of the nitro group around the C—N bond. The dihedral angles between the nitrated aryl ring and the planes defined by C1—S1—Pd1—Cl1 and C6–NO_2 are 6.2 (2) and 16.3 (2)°, respectively. In centrosymmetric molecules of *trans*-$[PdCl_2(PPh_3)_2]$ (Ferguson *et al.*, 1982; Stark & Whitmire, 1997), the P—C bonds of the two phosphine ligands are necessarily exactly staggered. In contrast, in (I), these P—C bonds are almost eclipsed, with a mean deviation of 5.9 (3)° from a fully eclipsed $Ph_3P—Pd—PPh_3$ fragment. Presumably, the rotational barriers about the Pd—P bonds are low.

The two independent Pd—P distances in (I) (Table 1) are both very similar to those reported for BISKIX [2.337 (2) Å] and RAVYUI [2.343 (2) Å]. However, the Pd—Cl distance in (I) is very much longer than the corresponding distances in BISKIX [2.291 (2) Å] and RAVYUI [2.293 (2) Å]. On the other hand, the Pd—S distance in (I) is much shorter than those reported for LETNON [2.3393 (16) and 2.3366 (19) Å in two independent molecules]. These observations can all be readily rationalized in terms of the *trans* influence, $t(X)$, of a ligand X upon the properties of the metal–ligand bond *trans* to X, which arises from the competition for a common metal d orbital of the π type between ligands occupying *trans* sites. Ligands of high *trans*-influence render the metal–ligand bonds *trans* to themselves longer (Appleton *et al.*, 1973), and ligands can thus be ranked in order of $t(X)$. This is a static thermodynamic phenomenon which closely parallels the dynamic kinetic *trans* effect describing the influence on the rates of ligand substitution exerted by ligands in *trans* sites (Basolo &

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Pearson, 1962). The data for (I) and related compounds show that a Pd—S bond *trans* to Cl is much shorter than a Pd—S bond *trans* to another thiolate; hence, $t(\mathrm{S}R^-) >> t(\mathrm{Cl}^-)$. Similarly, Pd—P bonds *trans* to another P are typically much shorter than Pd—P bonds *trans* to chloride. For example, in *cis*-[$PdCl_2$(Me_2N=CH)PPh_3] (McCrindle *et al.*, 2000), the Pd—P distance is 2.2495 (7) Å, much shorter than the corresponding bonds in (I), BISKIX and RAVYUI. Likewise, in [$PdCl_2$(Me_2N=CH)PPh_3], the Pd—Cl bond *trans* to P is very much longer [2.3600 (7) Å] than those in BISKIX [2.291 (2) Å] and RAVYUI [2.293 (2) Å], so that $t(\mathrm{P}R_3) >> t(\mathrm{Cl}^-)$. The order of $\mathrm{P}R_3$ and $\mathrm{S}R^-$ can be established by comparison of analogous *cis*- and *trans*-PdP_2S_2 chromophores, as for example in LETNON and [Pd($Ph_2PCH_2CH_2PPh_2$)(SCH_2Ph)$_2$] (TERREN; Su *et al.*, 1997). On moving from *trans* to *cis* geometry, the Pd—P bonds become shorter and the Pd—S bonds become longer, hence $t(\mathrm{P}R_3) > t(\mathrm{S}R^-)$ and overall $t(\mathrm{P}R_3) > t(\mathrm{S}R^-) > t(\mathrm{Cl}^-)$.

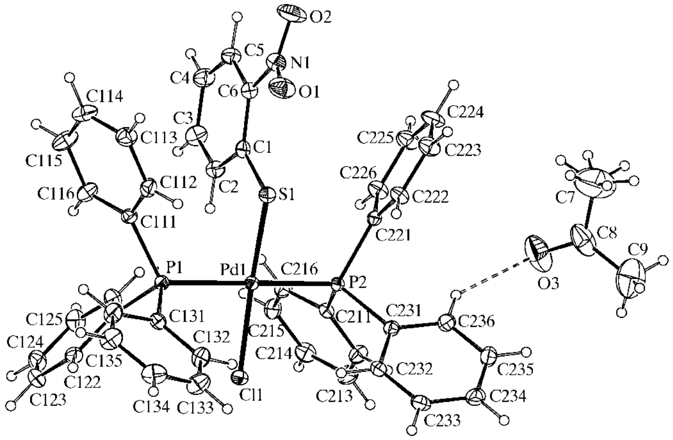

Figure 1

The asymmetric unit of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level. H atoms bonded to C7 have a site-occupation factor of 0.5.

There is evidence of C—C bond fixation in the nitrated aryl ring, where the C—C distances range from 1.358 (6) to 1.414 (5) Å. This range is greater than is usual for compounds of this type (Low, Storey *et al.*, 2000; Low, Glidewell & Wardell 2000), although the C—N distance and the O—N—O angle are both entirely typical of their types, so ruling out any *p*-quinonoid-type bond fixation, as observed in 2-O_2N-C_6H_4SCH=CHPh (Low, Storey *et al.*, 2000). On the other hand, the C—S distance is significantly shorter than those observed in previous examples of 2-$O_2NC_6H_4SX$ compounds. For comparison, the lower quartile value for a C(aryl)—S—C bond distance is 1.765 Å and, indeed, C(aryl)—S bonds as short as that in (I) are generally found only with four-coordinate S^{VI} (Allen *et al.*, 1987). The short C—S bond and the extremely small C—C—C angles *ipso* to S are together consistent with significant electron donation from S into the adjacent ring (Domenicano & Murray-Rust, 1979).

The solvating acetone molecule is linked to a phenyl group in one of the phosphine ligands of (I) by a C—H···O hydrogen bond (Table 2).

Experimental

The title compound was obtained from the reaction of *trans*-[$PdCl_2(PPh_3)_2$] and 2-$O_2NC_6H_4SSnPh_3$ in acetone solution. The compound was purified by column chromatography on silica using $CHCl_3$ as eluent. The compound obtained decomposed on heating, before melting at 478 K. Crystals suitable for single-crystal X-ray diffraction were obtained from an acetone solution.

Crystal data

[$PdCl(C_6H_4NO_2S)(C_{18}H_{15}P)_2$]·$C_3H_6O$
$M_r = 878.63$
Monoclinic, $P2_1/n$
$a = 18.292$ (7) Å
$b = 10.969$ (3) Å
$c = 21.363$ (8) Å
$\beta = 105.0928$ (17)°
$V = 4139$ (2) Å^3
$Z = 4$
$D_x = 1.410$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 11315 reflections
$\theta = 1.31$–30.48°
$\mu = 0.681$ mm^{-1}
$T = 150$ (1) K
Block, orange
0.30 × 0.10 × 0.05 mm

Data collection

Enraf–Nonius diffractometer with FAST area detector
φ and ω scans with κ offsets
Absorption correction: multi-scan (*FAST*/*MADNES*; Pflugrath & Messerschmidt, 1989)
$T_{\min} = 0.822$, $T_{\max} = 0.967$
49 325 measured reflections
11 315 independent reflections
5642 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.095$
$\theta_{\max} = 30.05°$
$h = -25 \rightarrow 25$
$k = -14 \rightarrow 15$
$l = -29 \rightarrow 30$
Intensity decay: negligible

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.053$
$wR(F^2) = 0.147$
$S = 0.943$
11 315 reflections
489 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0686P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.54$ e Å^{-3}
$\Delta\rho_{\min} = -1.10$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0026 (2)

Table 1

Selected geometric parameters (Å, °).

Pd1—S1	2.3020 (11)	S1—C1	1.744 (4)
Pd1—P1	2.3366 (13)	O1—N1	1.228 (4)
Pd1—P2	2.3303 (12)	O2—N1	1.237 (4)
Pd1—Cl1	2.3550 (11)	N1—C6	1.458 (5)
Cl1—Pd1—P1	89.56 (4)	O1—N1—O2	122.4 (4)
Cl1—Pd1—P2	88.59 (4)	C2—C1—C6	113.8 (4)
S1—Pd1—P1	90.63 (4)	C2—C1—S1	121.2 (3)
S1—Pd1—P2	91.69 (4)	C6—C1—S1	125.0 (3)
Cl1—Pd1—S1	174.19 (3)	C1—C6—C5	122.7 (4)
P1—Pd1—P2	174.98 (3)	C1—C6—N1	121.3 (4)
C1—S1—Pd1	105.52 (14)	C5—C6—N1	116.0 (4)
Cl1—Pd1—P1—C111	−165.77 (15)	Cl1—Pd1—P2—C211	51.41 (12)
Cl1—Pd1—P1—C121	−45.54 (13)	Cl1—Pd1—P2—C221	171.16 (14)
Cl1—Pd1—P1—C131	74.17 (13)	Cl1—Pd1—P2—C231	−67.66 (13)

Table 2

Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
C236—H236···O3	0.95	2.51	3.307 (6)	141

Compound (I) crystallized in the monoclinic system as a monoacetone solvate; space group $P2_1/n$ was assumed from the systematic absences. H atoms were treated as riding atoms with a C—H distance of 0.95 Å for aromatic H atoms and 0.98 Å for methyl H atoms. The acetone molecule was modelled with six half-occupancy H atoms in the methyl group defined by C7; the O and C atoms of the acetone molecule all had large displacement parameters. Examination of the refined structure with *PLATON* (Spek, 2000) showed there were no solvent-accessible voids in the structure, but that there were four symmetry-related voids, each with a volume of *ca* 11 Å^3, in the vicinity of the four solvent molecules in the unit cell. These may be associated with the large displacement parameters of the solvent molecule. The sites of maximum and minimum residual density are adjacent to the acetone and Pd atom, respectively.

Data collection: *CAD*-4-*PC Software* (Enraf–Nonius, 1992) and *FAST*/*MADNES* (Pflugrath & Messerschmidt, 1989); cell refinement: *CAD*-4-*PC Software* and *FAST*/*MADNES*; data reduction: *CAD*-4-*PC Software* and *FAST*/*MADNES*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *NRCVAX*96 (Gabe *et al.*, 1989) and *SHELXL*97 (Sheldrick, 1997); molecular graphics: *NRCVAX*96, *ORTEP*II (Johnson, 1976) and *PLATON* (Spek, 2000); software used to prepare material for publication: *NRCVAX*96, *SHELXL*97 and *WordPerfect* macro *PREP*8 (Ferguson, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1393). Services for accessing these data are described at the back of the journal.

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