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Bis[(diphenylsulfimido)triphenylphosphonium] di-μ-bromo-bis[dibromopalladate(II)]

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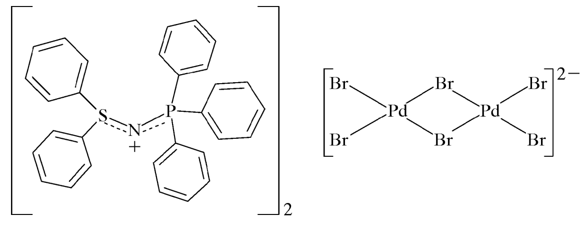
The title compound, $(C_{30}H_{25}NPS)_2[Pd_2Br_6]$ or $(Ph_3PNSPh_2)_2[Pd_2Br_6]$, was crystallized from the reaction of $(Ph_3PNSPh_2)[BPh_4]$ with $(PPh_4)_2[Pd_2Br_6]$, giving a salt rather than the intended coordination complex $[PdBr_3(Ph_3PNSPh_2)]$. The compound crystallizes in the non-centrosymmetric space group *Cc* with one complete formula unit in the asymmetric unit. One of the two independent cations is disordered. The geometry of the two cations is compared with that of the only previously crystallized example of this cation, *viz.* its $[SbCl_6]^-$ salt [Reck *et al.* (1982). *Chem. Ber.* **115**, 2981–2996]. The bond angles within the P—N—S triad in the two cations in the title compound are narrower than those observed in the literature example, while the S—N bond lengths are slightly longer in the title compound. The P—N bond length in the ordered cation shows excellent agreement with that determined by Reck and co-workers, but the P—N bond lengths are lengthened slightly in the disordered cation. Weak C—H···Br interactions create a three-dimensional network, with cations and anions alternating along the crystallographic *c* direction.

Comment

It has been known for some time that the bromosulfimide Ph_2SNBr is capable of undergoing oxidative addition to simple phosphines and sulfides to generate cations such as $Ph_3PNSPh_2^+$ and $Ph_2SNSPh_2^+$ (Furukawa *et al.*, 1978). In recent work, we have demonstrated that such reactions may be extended to polyphosphines and selenides, and we have used X-ray crystallography to characterize the novel $[1,4\text{-}(Ph_2PNSPh_2)_2(C_6H_4)]^{2+}$ and $Ph_2SNSPh_2^+$ cations (Aucott *et al.*, 2004). In the light of the relative ease of preparation and stability of such compounds, and given our ability to include a variety of main-group atoms within the basic *X*—N—*Y* core, the question of the ability of these cations to act as ligands becomes relevant. The presence of the three potential donor sites is offset by the fact that the units possess a positive charge, which may hamper their ability to coordinate to a metal centre. In order to start to address this question we have undertaken the reaction between $(Ph_3PNSPh_2)[BPh_4]$ and $(PPh_4)_2[Pd_2Br_6]$ in order to generate $(Ph_3PNSPh_2)_2[Pd_2Br_6]$ as the initial product by metathesis. Previous work has shown that the $[Pd_2Br_6]^{2-}$ anion is a very effective source of the coordinatively unsaturated $[PdBr_3]^-$ unit, which can then coordinate to a range of main-group species (*e.g.* Kelly *et al.*, 1995). If the $Ph_3PNSPh_2^+$ cation is capable of acting as a reasonably effective ligand, then previous experience would indicate that subsequent formation of $[PdBr_3(Ph_3PNSPh_2)]$ could be expected, the positive charge on the incoming unit being offset by the fact that the $[PdBr_3]^-$ unit is negatively charged, thereby providing some electrostatic encouragement to the reaction.



(I)

Crystallization of the product of the reaction results in orange crystals for which X-ray crystallography reveals the structure $(Ph_3PNSPh_2)_2[Pd_2Br_6]$, (I), *i.e.* the simple salt rather than the coordination complex $[PdBr_3(Ph_3PNSPh_2)]$. The asymmetric unit contains one complete formula unit of (I) (Fig. 1). One of the two independent $Ph_3PNSPh_2^+$ cations was found to be disordered, and the S and N atoms and the two phenyl rings bonded to atom S2 were modelled as disordered over two sets of positions (see *Experimental*). The two cations

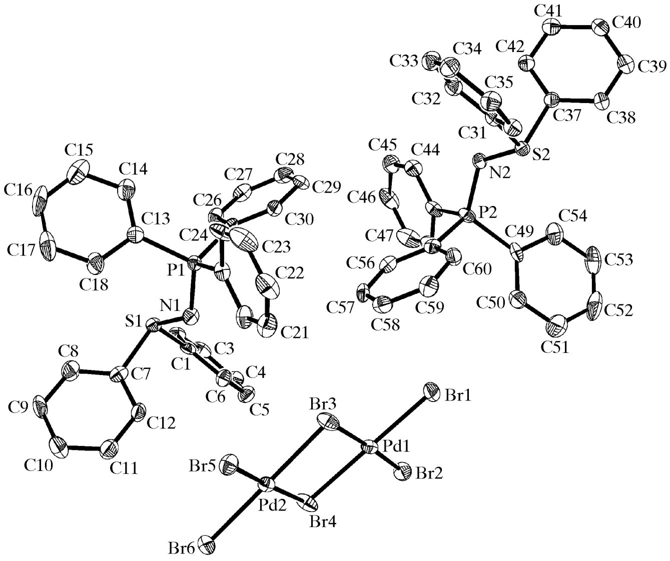


Figure 1
A view of the components of (I), showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level, and H atoms and the minor disorder component have been omitted for clarity.

have very similar geometries (Table 1), and compare well with the geometry of the same cation in the structure of $(Ph_3PNSPh_2)[SbCl_6]\cdot CH_2Cl_2$ (Table 3) (Reck *et al.*, 1982). There are small differences between the geometric parameters of the cations in (I) and those in Table 3; clearly the P—N—S bond angle is narrower in both cations present in (I) (including the disordered group) and the S—N bond lengths are slightly longer than that in the literature compound. The P—N bond lengths in the second (disordered) cation in (I) are lengthened compared with the ordered cation in (I) and the literature compound. It should be noted here that restraints were only applied to the geometries of the partially occupied phenyl components of the disordered group, but not to the P—N or S—N bond lengths or to the P—N—S geometry.

Owing to the large number of relatively acidic aryl CH groups, the presence of C—H···Br interactions (Table 2) is unsurprising. These interactions have C···Br distances in the range ~3.8–3.9 Å and C—H···Br angles greater than 140°; these ranges compare well with the mean value of 3.75 (2) Å for C···Br contact distances in Csp^2—H···Br interactions having C—H···Br angles greater than 140° (Desiraju & Steiner, 1999). These weak interactions create a three-dimensional network, with cations and anions alternating along the crystallographic *c* direction.

The fact that the cation has not broken into the structure of the bromo-bridged palladium dimer is indicative of the poor donor capabilities of the cation. Of course, this result does not entirely rule out coordination by such species and future work will investigate their reactivity towards other complexes bearing labile ligands. It may prove necessary to use low valent metal reagents such as Pt^0, which could induce concomitant reduction of the cations and the formation of anionic species more conducive to coordination, in this case to the resulting Pt^{II} centre. Indeed, the question of the nature of the reduction products of such heteronuclear cations is intriguing, and work to assess this process is underway.

Experimental

$(Ph_3PNSPh_2)Br$ was prepared by the reaction of Ph_2SNBr with PPh_3 in toluene in the same manner as the bisphosphine reactions described by Aucott *et al.* (2004). $(Ph_3PNSPh_2)[BPh_4]$ was then precipitated from a methanol solution of $(Ph_3PNSPh_2)Br$ by addition of $Na[BPh_4]$. $(Ph_3PNSPh_2)[BPh_4]$ and $(PPh_4)_2[Pd_2Br_6]$ were reacted in MeCN, producing a precipitate of $(PPh_4)[BPh_4]$. The filtrate was evaporated to dryness and redissolved in dichloromethane, and the title product was crystallized by diffusion of diethyl ether into this solution.

Crystal data

$(C_{30}H_{25}NPS)_2[Pd_2Br_6]$
$M_r = 1617.34$
Monoclinic, *Cc*
$a = 12.8250$ (13) Å
$b = 16.2000$ (16) Å
$c = 28.721$ (3) Å
$\beta = 97.318$ (2)°
$V = 5918.7$ (10) Å^3
$Z = 4$
$D_x = 1.815$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 12 077 reflections
$\theta = 2.2$–28.5°
$\mu = 4.82$ mm^{-1}
$T = 150$ (2) K
Block, dark orange
0.59 × 0.40 × 0.37 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.104$, $T_{max} = 0.168$
24 282 measured reflections
12 979 independent reflections
11 006 reflections with $I > 2\sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$
$h = -16 \rightarrow 16$
$k = -21 \rightarrow 21$
$l = -37 \rightarrow 36$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.036$
$wR(F^2) = 0.082$
$S = 1.01$
12 639 reflections
732 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.029P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.29$ e Å^{-3}
$\Delta\rho_{min} = -0.90$ e Å^{-3}
Absolute structure: Flack (1983), 5943 Friedel pairs
Flack parameter = 0.065 (6)

Table 1
Selected geometric parameters (Å, °).

Pd1—Br1	2.4102 (7)	P1—C13	1.808 (6)
Pd1—Br2	2.4086 (7)	P1—C19	1.786 (5)
Pd1—Br3	2.4550 (7)	P1—C25	1.787 (5)
Pd1—Br4	2.4437 (7)	P2—N2	1.622 (5)
Pd2—Br3	2.4505 (7)	P2—N2*X*	1.63 (3)
Pd2—Br4	2.4455 (7)	P2—C43	1.803 (5)
Pd2—Br5	2.4180 (7)	P2—C49	1.797 (6)
Pd2—Br6	2.4109 (7)	P2—C55	1.785 (5)
S1—N1	1.616 (4)	S2—N2	1.615 (5)
S1—C1	1.778 (4)	S2—C31	1.789 (5)
S1—C7	1.796 (5)	S2—C37	1.795 (5)
P1—N1	1.609 (4)		
P1—N1—S1	118.1 (3)	P2—N2—S2	119.1 (3)

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C14—H14···Br6^{i}	0.95	3.13	3.909 (6)	140
C17—H17···Br2^{ii}	0.95	2.97	3.900 (7)	167
C27—H27···Br3^{iii}	0.95	2.93	3.858 (6)	167
C39—H39···Br6^{iv}	0.95	2.92	3.827 (8)	161
C59—H59···Br4^{v}	0.95	2.93	3.830 (6)	158

Symmetry codes: (i) $x-1, y, z$; (ii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (iii) $x-\frac{1}{2}, \frac{1}{2}+y, z$; (iv) $x-1, 1-y, \frac{1}{2}+z$; (v) $x-\frac{1}{2}, y-\frac{1}{2}, z$.

Table 3
Selected bond lengths and angle (Å, °) for $(Ph_2SNPPh_3)[SbCl_6]\cdot CH_2Cl_2$ (Reck *et al.*, 1982).

S—N	1.596	S—C	1.755, 1.761
P—N	1.608	P—C	1.779, 1.788, 1.797
P—N—S	123.6		

The data set for (I) was truncated at $2\theta = 55°$, as only statistically insignificant data were present above this limit. Atoms N2 and S2 and the phenyl substituents bonded to atom S2 were found to be disordered. These groups were modelled over two sets of positions, giving a refined major occupancy of 88.5 (3)%. The C atoms in the minor component of the disorder model were refined isotropically, with restraints applied to their displacement parameters. Atoms N2*X* and S2*X* were refined anisotropically, with restraints applied to their displacement parameters. Restraints were also applied to the geometries of the phenyl substituents in the disordered group. The

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largest ΔF residual lies 1.03 Å from atom Pd1. H atoms were positioned geometrically (C—H = 0.95 Å) and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1597). Services for accessing these data are described at the back of the journal.

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