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Phenylantimony(III) derivatives of tetraphenyldichalcogenoimidodiphosphinic acids. Crystal and molecular structure of $PhSb[(XPPh_2)(SPPh_2)N]_2$ (X = O, S)

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Abstract

The reactions between $PhSbCl_2$ and $M[(XPPh_2)(YPPh_2)N]$ (M = Na, K; X, Y = O, S), using 1:1 and 1:2 molar ratios, have been investigated. $PhSbCl[(XPPh_2)(YPPh_2)N]$ and $PhSb[(XPPh_2)(YPPh_2)N]_2$ were isolated as microcrystalline powders and were characterized using IR and NMR (^1H, ^{31}P) spectroscopy. On standing in chloroform solution the chloro derivative $PhSbCl[(SPPh_2)_2N]$ was found to rearrange to $PhSb[(SPPh_2)_2N]_2$. The molecular structures of $PhSb[(XPPh_2)(SPPh_2)N]_2$ (X = O, S) were investigated by X-ray diffraction. The crystals of both compounds contain monomeric units with asymmetric chelating ligand fragments, resulting in a square pyramidal $CSbX_2S_2$ core with an apical phenyl group. The antimony lone pair of electrons appears to be stereochemically active and is located *trans* to the phenyl group, as suggested by the displacement of the metal atom from the best basal plane formed by the chalcogens in the opposite direction with respect to the apical carbon. For the monothio derivative, the molecule displays different ligand behaviour, i.e. *O*- and *S*-primary coordinations, respectively.

Keywords: Phenylantimony(III) compounds; Imidodiphosphinato ligands

1. Introduction

The use of organophosphorus ligands of the type $[R_2PXY]^-$ (R = alkyl, aryl, alkoxy; X, Y = O, S) often affords the isolation of inorganic and organometallic derivatives of antimony(III) exhibiting a large variety of structures [1]. Two factors often considered to be of importance in contributing to distortion of the metal coordination core are the small bite of the ligand and/or the stereochemical activity of the antimony lone pair of electrons. For most organoantimony(III) derivatives of phosphorus ligands, the primary bonds to the metal center form the usual trigonal pyramidal geometry. However, if the secondary Sb···chalcogen interactions and the possible stereochemical activity of the lone pair are considered, the distorted coordination polyhedron can be described as either *pseudo*-trigonal bipyramid or *pseudo*-octahedron. Thus, in the case of the monomeric $PhSb[S(S)P(OPr^i)_2]_2$ the dithiophosphorus ligands are asymmetric monometallic biconnective, with *cis* short and long metal–sulfur distances, respectively, forming the basal plane of a square pyramid. The antimony lone pair of electrons was suggested to be stereochemically active, occupying the axial position *trans* to the phenyl group [2]. In the molecule of the related $PhSb[S(O)CCH_3]_2$ the monothio ligands are primary bonded to the metal center through the sulfur atoms and the oxygen atoms are involved in secondary intramolecular Sb···O interactions, thus resulting in a similar distorted square pyramidal $CSbS_2O_2$ core [3]. However, intermolecular Sb···S interactions *trans* to the phenyl group give weak dimer associations in solid state and therefore it was suggested that the lone pair is probably inactive in this case.

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Tetraorganodichalcogenoimidodiphosphinato anions, $[(XPR_2)(YPR'_2)N]^-$ are versatile chelating ligands able to adjust to various coordination geometries required by metal centers because of the flexibility of the XPNPY skeleton [4–7]. Therefore, they are good candidates for investigation of the ligand bite influence on the distortion degree of the coordination polyhedron around a metal center. The use of such ligands in organometallic chemistry of main group metals has been mainly limited to Sn [8–12] and Te compounds [13–19]. Only two inorganic antimony(III) compounds, i.e. $Sb[(SePPh_2)_2N]_3$ [20] and $(\mu\text{-}S)(\mu\text{-}I)_2[Sb(SPPh_2)_2N]_2$ [21], and few diphenylantimony(V) derivatives, $Ph_2SbCl_2[(OPPh_2)(XPPh_2)N]$ (X = O, S) and Ph_2SbCl_2-$[(OPMe_2)(OPPh_2)N]$ [22], have been reported so far.

Here we report on the synthesis and spectroscopic characterization of some phenylantimony(III) compounds, $PhSbCl[(XPPh_2)(YPPh_2)N]$ and $PhSb[(XPPh_2)$-$(YPPh_2)N]_2$ (X = O, S), as well as the crystal and molecular structures of $PhSb[(SPPh_2)_2N]_2$ and PhSb-$[(OPPh_2)(SPPh_2)N]_2$.

2. Results and discussion

2.1. Preparation

The title compounds were prepared according to Eqs. (1) and (2), by reacting stoichiometric amounts of phenylantimony chlorides and the alkali salt of the appropriate organophosphorus ligand:

$$PhSbCl_2 + M[(XPPh_2)(YPPh_2)N] \rightarrow PhSbCl[(XPPh_2)(YPPh_2)N] + MCl \quad (1)$$

1 X = Y = S

2 X = O, Y = S

3 X = Y = O

$$PhSbCl_2 + 2M[(XPPh_2)(YPPh_2)N] \rightarrow PhSb[(XPPh_2)(YPPh_2)N]_2 + 2MCl \quad (2)$$

4 X = Y = S

5 X = O, Y = S

6 X = Y = O

All compounds were isolated as air-stable crystalline products. The dithio derivative **1** and **4** are yellow, while the other compounds are white solids. They were characterized by IR and NMR (^1H, ^{31}P) spectroscopy. During attempts to grow crystals of the chloro derivative $PhSbCl[(SPPh_2)_2N]$ from a chloroform–hexane solvent mixture, a rearrangement process occurred leading to the isolation of yellow crystals of the disubstituted derivative $PhSb[(SPPh_2)_2N]_2$ as was shown by NMR spectroscopy and X-ray diffraction. The crystal and molecular structures of $PhSb[(SPPh_2)_2N]_2$ and $PhSb$-$[(OPPh_2)(SPPh_2)N]_2$ were determined by single crystal X-ray diffraction.

2.2. IR spectra

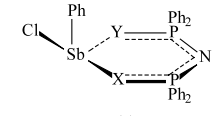
The absence of strong absorptions around 2700–2600 [ν(NH)] and 950–900 cm^{-1} [assigned to $\nu_{as}(P_2NH)$], which are characteristic of the free $(XPPh_2)(SPPh_2)NH$ acids, along with the presence of strong absorptions in the regions 1240–1200 cm^{-1}, assigned to the $\nu_{as}(P_2N)$ stretching vibrations, indicate that the phosphorus ligands are coordinated to the metal center in the deprotonated form.

2.3. NMR spectra

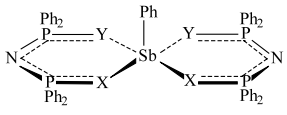
The ^1H-NMR spectra of the $PhSbCl[(XPPh_2)$-$(YPPh_2)N]$ (**1**–**3**) and $PhSb[(XPPh_2)(YPPh_2)N]_2$ (**4**–**6**) derivatives show the expected resonances for the phenyl groups bonded to antimony and phosphorus atoms.

For the complexes containing symmetric ligand units, only one broad ^{31}P resonance was observed at room temperature. This could be indicative of fluxional behavior of molecules of type (**a**) and (**b**) (X = Y), respectively, with imidodiphosphinato ligands asymmetrically coordinated through both chalcogen atoms to antimony. However, an attempt to record the low-temperature ^{31}P-NMR spectrum for a freshly prepared $PhSbCl$-$[(SPPh_2)_2N]_2$ (**1**) sample resulted only in a broader resonance at −40 °C (the quality of the spectrum prevented us from recording it at lower temperature).

The ^{31}P-NMR spectrum of $PhSbCl[(OPPh_2)$-$(SPPh_2)N]$ (**2**) exhibits two singlet resonances (phosphorus–phosphorus coupling was not resolved). The magnitude of the chemical shifts [δ (ppm) 27.6 (Ph_2PO), 33.4 (Ph_2PS)] indicates *O*, *S*-chelate coordination of the asymmetric imidodiphosphinato ligand moiety, with the oxygen *trans* to the chlorine atom (structure **a**) [cf. $Ph_2SbCl_2[(OPPh_2)(SPPh_2)N]$ [22]: δ 26.5 (Ph_2PO), 32.1 (Ph_2PS)]. For the disubstituted complex $PhSb[(OPPh_2)$-$(SPPh_2)N]_2$ (**5**) the ^{31}P spectrum exhibits four broad resonances of 1:1:2 intensity ratio (signals at δ 21.8 and 23.5 ppm are partially overlapped), a pattern consistent with a structure of type (**c**) in solution, with non-equivalent P_S and P_O atoms, as established in the solid state by X-ray diffraction.



(a)



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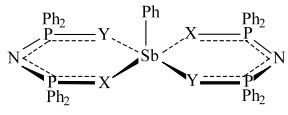


(c)

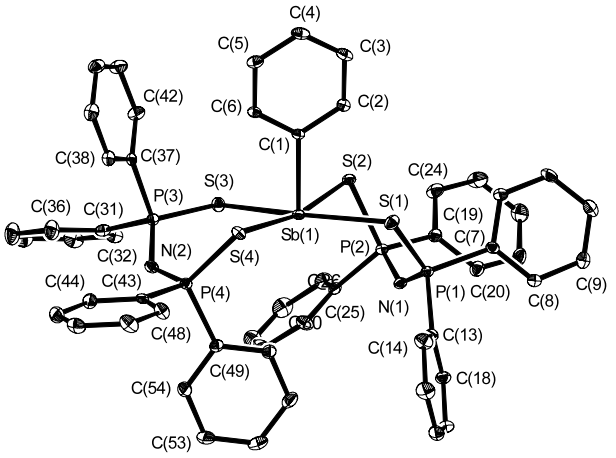


Fig. 1. ORTEP plot of the molecule $PhSb[(SPPh_2)_2N]_2$ (**4**). The atoms are drawn with 20% probability ellipsoids except for the hydrogen atoms.

2.4. Crystal and molecular structure of $PhSb[(SPPh_2)_2N]_2$ (4) and $PhSb[(OPPh_2)(SPPh_2)N]_2$ (5)

The molecular structures of compounds **4** and **5** with the atom numbering scheme are shown in Figs. 1 and 2, respectively, and selected interatomic distances and angles are listed in Table 1. The crystal structures of both compounds consist of discrete monomeric molecular units separated by normal van der Waals distances.

The structures of compounds **4** (Fig. 1) and **5** (Fig. 2) reveal some common trends. Thus, the coordination geometry around the antimony atom is distorted square pyramidal with an apical phenyl group and asymmetric monometallic biconnective dichalcogenoimidodiphosphinato ligands [*trans* S(1)–Sb(1)–S(3) 170.2(1)°, S(2)–Sb(1)–S(4) 169.5(1)° for **4**, and O(1)–Sb(1)–O(2) 169.1(7)°, S(1)–Sb(1)–S(2) 172.5(1)° for **5**]. In compound **4** the antimony atom is displaced −0.107 Å from the best basal plane formed by the sulfur atoms (sulfur atom deviations ranging from −0.136 to 0.144 Å) in the opposite direction with respect to the apical carbon of the $CSbS_4$ core [C–Sb(1)–S range 83.8(1)–96.2(1)°]. A quite similar geometry was observed for the $CSbO_2S_2$ core in **5**, where the chalcogen atoms are basically coplanar and the metal atom lies about −0.161 Å under the basal plane [C–Sb(1)–chalcogen range 83.8(3)–88.2(3)°].

The ligand moieties are coordinated through both sulfur atoms in compound **4** with a *cis* arrangement of the short Sb(1)–S [2.666(1), 2.690(1) Å, S(2)–Sb(1)–S(3) 80.73(3)°] and long Sb(1)–S bonds [2.778(1), 2.810(1) Å, S(1)–Sb(1)–S(4) 93.76(4)°], respectively. The anisobidentate coordination of the ligand moieties in the molecule of **4** is not dramatically reflected in the magnitude of the P–S [range 2.011(1)–2.030(1) Å] and P–N [range 1.587(3)–1.596(3) Å] bonds which are equal, within the experimental errors, and intermediate between single and double phosphorus–sulfur and phosphorus–nitrogen bonds [cf. the free acid $(S{=}PPh_2)_2NH$ [23]: P=S 1.937(1), 1.950(1), P–N 1.683(2), 1.672(2) Å; $[2\text{-}(Me_2NCH_2)C_6H_4]Te{-}S{-}PPh_2{=}N{-}PPh_2{=}S$ [19]: P–S 2.057(1), P=S 1.945(1), P–N 1.612(3), P=N 1.557(3) Å]. The conformation of both inorganic SbS_2P_2N rings is distorted boat, but with different atom types in the apices; the metal and N(1) atoms in one and P(3) and S(4) atoms in the other, in both cases bringing the nitrogen atoms below the basal plane. A significant difference in the magnitude of the Sb–S–P angles within the two rings, i.e. 97.52(5), 93.80(5) versus 107.87(5), 101.62(5)°, should be also noted.

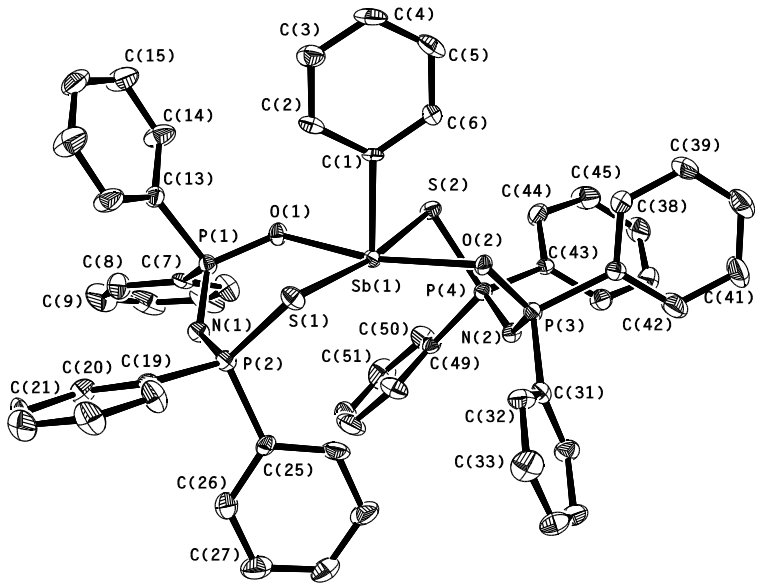
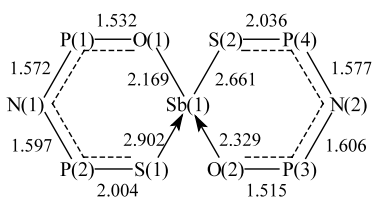


Fig. 2. ORTEP plot of the molecule $PhSb[(OPPh_2)(SPPh_2)N]_2$ (**5**). The atoms are drawn with 20% probability ellipsoids except for the hydrogen atoms.

Table 1
Selected interatomic distances (Å) and angles (°) in $PhSb[(SPPh_2)_2N]_2$ (**4**) and $PhSb[(OPPh_2)(SPPh_2)N]_2$ (**5**)

$PhSb[(SPPh_2)_2N]_2$ (**4**)				$PhSb[(OPPh_2)(SPPh_2)N]_2$ (**5**)			
Sb(1)–C(1)	2.192(3)			Sb(1)–C(1)	2.162(7)		
Sb(1)–S(1)	2.7778(11)	Sb(1)–S(3)	2.6901(11)	Sb(1)–O(1)	2.169(5)	Sb(1)–O(2)	2.329(5)
Sb(1)–S(2)	2.6659(12)	Sb(1)–S(4)	2.8097(12)	Sb(1)–S(1)	2.902(2)	Sb(1)–S(2)	2.661(2)
S(1)–P(1)	2.0111(15)	S(3)–P(3)	2.0169(15)	P(1)–O(1)	1.532(5)	P(3)–O(2)	1.515(5)
P(1)–N(1)	1.596(3)	P(3)–N(2)	1.590(3)	P(1)–N(1)	1.572(6)	P(3)–N(2)	1.606(6)
P(2)–N(1)	1.587(3)	P(4)–N(2)	1.596(3)	P(2)–N(1)	1.597(6)	P(4)–N(2)	1.577(6)
S(2)–P(2)	2.0304(14)	S(4)–P(4)	2.0114(13)	P(2)–S(1)	2.004(3)	P(4)–S(2)	2.036(3)
C(1)–Sb(1)–S(1)	85.04(10)	C(1)–Sb(1)–S(3)	96.22(10)	C(1)–Sb(1)–O(1)	88.2(3)	C(1)–Sb(1)–O(2)	83.8(3)
C(1)–Sb(1)–S(2)	86.61(10)	C(1)–Sb(1)–S(4)	83.84(10)	C(1)–Sb(1)–S(1)	85.5(2)	C(1)–Sb(1)–S(2)	88.0(2)
S(1)–Sb(1)–S(2)	89.63(4)	S(3)–Sb(1)–S(4)	96.06(3)	O(1)–Sb(1)–S(1)	88.66(14)	O(2)–Sb(1)–S(2)	85.11(13)
S(1)–Sb(1)–S(4)	93.76(4)	S(2)–Sb(1)–S(3)	80.73(3)	O(1)–Sb(1)–S(2)	87.35(14)	O(2)–Sb(1)–S(1)	97.92(13)
S(1)–Sb(1)–S(3)	170.17(3)	S(2)–Sb(1)–S(4)	169.55(3)	O(1)–Sb(1)–O(2)	169.15(17)	S(1)–Sb(1)–S(2)	172.46(7)
Sb(1)–S(1)–P(1)	97.52(5)	Sb(1)–S(3)–P(3)	107.87(5)	Sb(1)–O(1)–P(1)	130.3(3)	Sb(1)–O(2)–P(3)	118.0(3)
Sb(1)–S(2)–P(2)	93.80(5)	Sb(1)–S(4)–P(4)	101.62(5)	Sb(1)–S(1)–P(2)	96.12(11)	Sb(1)–S(2)–P(4)	94.79(10)
S(1)–P(1)–N(1)	118.37(13)	S(3)–P(3)–N(2)	119.41(13)	O(1)–P(1)–N(1)	118.1(3)	O(2)–P(3)–N(2)	116.9(3)
P(1)–N(1)–P(2)	135.6(2)	P(3)–N(2)–P(4)	134.3(2)	P(1)–N(1)–P(2)	134.6(4)	P(4)–N(2)–P(3)	131.5(4)
S(2)–P(2)–N(1)	117.14(12)	S(4)–P(4)–N(2)	118.07(12)	S(1)–P(2)–N(1)	117.4(2)	S(2)–P(4)–N(2)	117.3(3)

In the case of **5** the ligand units are again coordinated asymmetrically through both chalcogens to the metal. Surprisingly the primary coordination is established by different atoms for the two ligand moieties of a molecule as suggested by the Sb(1)–O versus Sb(1)–S bond lengths for a $SbOSP_2N$ ring [Sb(1)–O(1) 2.169(5), Sb(1)–S(1) 2.902(2) Å, and Sb(1)–O(2) 2.329(5), Sb(1)–S(2) 2.661(2) Å, respectively], with the shorter Sb–O and Sb–S bonds in *cis* positions [O(1)–Sb(1)–S(2) 87.3(1)°]. This unexpected asymmetric coordination behavior seems to be preserved in solution too and might explain the non-equivalence of the phosphorus atoms bearing the same chalcogen atom in $PhSb[(OPPh_2)(SPPh_2)N]_2$ (see Section 2.3.). The *O*- versus *S*-primary coordinations of the asymmetric bidentate ligand units in the molecule of **5** resulted in different bond lengths within the OPNPS skeletons (scheme d) which is consistent with a slightly higher degree of double bonding in the P(2)–S(1), P(3)–O(2), P(1)–N(1) and P(4)–N(2) bonds than in the others [cf. the free acid $(O{=}PPh_2)(S{=}PPh_2)NH$ [24]: P=S 1.935(2), (S)P–N 1.694(4), (O)P–N 1.668(5), P=O 1.491(4) Å]:



(**d**)

The conformation of the inorganic $SbOSP_2N$ rings is similar to that observed for the molecule of the dithio derivative **4**, i.e. distorted boat with different atom types occupying the apex positions [P(1)/S(1) and Sb(1)/N(2) atoms, respectively] and both nitrogen atoms below the basal plane. It should also be noted that there is significant opening up of the Sb–O–P bond angle [130.3(3)°] in comparison with the Sb←O=P angle [118.0(3)°], whereas the corresponding Sb←S=P [96.1(1)°] and Sb–S–P [94.8(1)°] bond angles are of same magnitude.

3. Conclusions

New $PhSbCl[(XPPh_2)(YPPh_2)N]$ and $PhSb[(XPPh_2)(YPPh_2)N]_2$ derivatives were prepared and characterized using IR and NMR (^1H, ^{31}P) spectroscopy. The molecular structures of $PhSb[(XPPh_2)(SPPh_2)N]_2$ [X = S(**4**), O(**5**)] were investigated by X-ray diffraction. Both compounds are monomeric, with asymmetric chelating ligand fragments, thus resulting in square pyramidal $CSbX_2S_2$ cores. For the monothio derivative, the molecule displays different ligand behaviour, i.e. *O*- and *S*-primary coordinations, respectively. The displacement of the antimony atom from the best basal plane of the four chalcogens in the opposite direction with respect to the apical carbon atom suggests that the antimony lone pair of electrons is stereochemically active and located *trans* to the phenyl group.

4. Experimental

4.1. Materials and procedures

All manipulations were carried out under Ar by Schlenk techniques. Solvents were dried and freshly

distilled prior to use. Phenylantimony(III) dichloride was prepared from Ph_3Sb and $SbCl_3$ (molar ratio 1:2, in the absence of a solvent) [25]. The starting materials were prepared according to literature methods: $Na[(OPPh_2)_2N]$ [26], $K[(SPPh_2)_2N]$ [8] and $K[(OPPh_2)(SPPh_2)N]$ [11]. Infrared spectra were recorded in the range 4000–250 cm^{-1} as KBr pellets on a Jasco FT/IR-615 instrument. The ^1H- and ^{31}P-NMR spectra were recorded on a Varian Gemini 300S instrument operating at 299.5 and 121.4 MHz, respectively, using solutions in dried $CDCl_3$. The chemical shifts are reported in ppm relative to TMS and H_3PO_4 85%, respectively.

4.2. Preparation of the title compounds, $PhSbCl[(XPPh_2)(YPPh_2)N]$ and $PhSb[(XPPh_2)(YPPh_2)N]_2$ (Table 2)

Mixtures of $PhSbCl_2$ and alkali salt, $M[(XPPh_2)(YPPh_2)N]$ (1:1 and 1:2 molar ratios) in 30 ml anhydrous $CHCl_3$ were stirred for 6 h, then filtered under Ar atmosphere to remove the resulting MCl. The filtrate was evaporated under reduced pressure and a solid was obtained. Details of the preparations and the melting points are given in Table 2. Microanalyzes (C, H, N) and NMR spectra are consistent with the given composition of the isolated products.

4.2.1. $PhSbCl[(SPPh_2)_2N]$ (**1**)

Anal. Found: C, 52.70; H, 3.89; N, 1.97. Calc. for $C_{30}H_{25}ClNP_2S_2Sb$: C, 52.77; H, 3.69; N, 2.05%. IR (cm^{-1}): 1200s [$\nu_{as}(P_2N)$]. ^1H-NMR: δ 7.40m (15H, P–C_6H_5 + Sb–C_6H_5, *meta* + *para*), 7.83s,br (8H, P–C_6H_5-*ortho*), 8.09dd (2H, Sb–C_6H_5-*ortho*, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.2 Hz); ^{31}P-NMR: δ 37.3s,br.

4.2.2. $PhSbCl[(OPPh_2)(SPPh_2)N]$ (**2**)

Anal. Found: C, 53.90; H, 3.94; N, 2.07. Calc. for $C_{30}H_{25}ClNOP_2SSb$: C, 54.04; H, 3.78; N, 2.10%. IR (cm^{-1}): 1215s [$\nu_{as}(P_2N)$]. ^1H-NMR: δ 7.41m (15H, P–C_6H_5 + Sb–C_6H_5, *meta* + *para*), 7.72ddd [4H, P(S)-C_6H_5-*ortho*, $^3J_{PH}$ 12.9, $^3J_{HH}$ 6.9, $^4J_{HH}$ 1.5 Hz], 7.85dd [4H, P(O)–C_6H_5-*ortho*, $^3J_{PH}$ 14.4, $^3J_{HH}$ 7.5 Hz], 8.10dd (2H, Sb–C_6H_5-*ortho*, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.5 Hz); ^{31}P-NMR: δ 27.6s (Ph_2PO), 33.4s (Ph_2PS).

4.2.3. $PhSbCl[(OPPh_2)_2N]$ (**3**)

Anal. Found: C, 55.51; H, 3.73; N, 2.03. Calc. for $C_{30}H_{25}ClNO_2P_2Sb$: C, 55.38; H, 3.87; N, 2.15%. IR (cm^{-1}): 1230s [$\nu_{as}(P_2N)$]. ^1H-NMR: δ 7.27m (11H, P–C_6H_5-*meta*, Sb–C_6H_5-*meta* + *para*), 7.40t (4H, P–C_6H_5-*para*, $^3J_{HH}$ 7.2 Hz), 7.67dd (8H, P–C_6H_5-*ortho*, $^3J_{PH}$ 12.6, $^3J_{HH}$ 7.8 Hz), 7.94m (2H, Sb–C_6H_5-*ortho*); ^{31}P-NMR: δ 24.9s,br.

4.2.4. $PhSb[(SPPh_2)_2N]_2$ (**4**)

Anal. Found: C, 59.37; H, 3.98; N, 2.45. Calc. for $C_{54}H_{45}N_2P_4S_4Sb$: C, 59.19; H, 4.14; N, 2.56%. IR (cm^{-1}): 1210vs [$\nu_{as}(P_2N)$]. ^1H-NMR: δ 7.22m (27H, P–C_6H_5 + Sb–C_6H_5, *meta* + *para*), 7.70s,br (16H, P–C_6H_5-*ortho*), 8.24m (2H, Sb–C_6H_5-*ortho*); ^{31}P-NMR: δ 38.2s,br.

4.2.5. $PhSb[(OPPh_2)(SPPh_2)N]_2$ (**5**)

Anal. Found: C, 60.75; H, 4.03; N, 2.57. Calc. for $C_{54}H_{45}N_2O_2P_4S_2Sb$: C, 60.97; H, 4.26; N, 2.63%. IR (cm^{-1}): 1240vs [$\nu_{as}(P_2N)$]. ^1H-NMR: δ 7.30m (27H, P–C_6H_5 + Sb–C_6H_5, *meta* + *para*), 7.63m [10H, P(S)–C_6H_5 + Sb–C_6H_5, *ortho*], 7.87m [8H, P(O)–C_6H_5-*ortho*]; ^{31}P-NMR: δ 21.8s, 23.5s,br (Ph_2PO), 35.1s, 57.5s,br (Ph_2PS).

4.2.6. $PhSb[(OPPh_2)_2N]_2$ (**6**)

Anal. Found: C, 62.98; H, 4.26; N, 2.93. Calc. for $C_{54}H_{45}N_2O_4P_4Sb$: C, 62.87; H, 4.40; N, 2.71%. IR (cm^{-1}): 1240vs [$\nu_{as}(P_2N)$]. ^1H-NMR: δ 7.15m (19H, P–C_6H_5-*meta*, Sb–C_6H_5-*meta* + *para*), 7.35t (8H,

Table 2
Preparation and IR data for $PhSbCl_n[(XPPh_2)(YPPh_2)N]_{2-n}$ derivatives

Starting materials		Product [yield: g (%)]	m.p. (°C)
$PhSbCl_2$ (g $mmol^{-1}$)	$M[(XPPh_2)(YPPh_2)]$ (g $mmol^{-1}$)		
	$K[(SPPh_2)_2N]$	$PhSbCl[(SPPh_2)_2N]$ (**1**)	92
0.270/1.00	0.487/1.00	0.62 (91)	
	$K[(OPPh_2)(SPPh_2)N]$	$PhSbCl[(OPPh_2)(SPPh_2)N]$ (**2**)	160–162
0.256/0.9	0.447/0.9	0.54 (86)	
	$Na[(OPPh_2)_2N]$	$PhSbCl[(OPPh_2)_2N]$ (**3**)	68–84
0.270/1.00	0.439/1.00	0.65 (100)	
	$K[(SPPh_2)_2N]$	$PhSb[(SPPh_2)_2N]_2$ (**4**)	199–200
0.270/1.00	0.974/2.00	0.92 (86)	
	$K[(OPPh_2)(SPPh_2)N]$	$PhSb[(OPPh_2)(SPPh_2)N]_2$ (**5**)	185–188
0.270/1.00	0.942/2.00	0.83 (78)	
	$Na[(OPPh_2)_2N]$	$PhSb[(OPPh_2)_2N]_2$ (**6**)	219–221
0.224/0.83	0.729/1.66	0.44 (51)	

Table 3
X-ray crystal data and structure refinement for **4** and **5**

	4	**5**
Empirical formula	$C_{54}H_{45}N_2P_4S_4Sb$	$C_{54}H_{45}N_2O_2P_4S_2Sb$
Formula weight	1095.88	1063.67
Temperature (K)	173(2)	299(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
Unit cell dimension		
a (Å)	11.330(2)	11.157(2)
b (Å)	11.678(1)	11.634(2)
c (Å)	21.070(6)	20.864(4)
α (°)	74.98(1)	77.82(3)
β (°)	77.97(2)	79.57(3)
γ (°)	68.40(1)	68.60(3)
V (Å^3)	2483.6(9)	2448.5(8)
Z	2	2
D_{calc} (g cm^{-3})	1.465	1.443
Absorption coefficient (mm^{-1})	0.892	0.823
F (000)	1116	1084
Crystal size (mm)	$0.7 \times 0.5 \times 0.4$	$0.22 \times 0.20 \times 0.20$
θ range for data collection (°)	2.23–27.50	1.01–23.25
Reflections collected	12257	17509
Independent reflections	10616 [$R_{int} = 0.0308$]	6924 [$R_{int} = 0.1070$]
Data/restraints/parameters	10616/0/588	6924/0/586
Goodness-of-fit on F^2	0.990	1.081
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.0437$; $wR_2 = 0.0937$	$R_1 = 0.0853$; $wR_2 = 0.0899$
R indices (all data)	$R_1 = 0.0699$; $wR_2 = 0.1050$	$R_1 = 0.1518$; $wR_2 = 0.1050$
Largest difference peak and hole (e Å^{-3})	0.605 and −0.769	0.452 and −0.494

P–C$_6H_5$-*para*, $^3J_{HH}$ 7.2 Hz), 7.70dd (16H, P–C$_6H_5$-*ortho*, $^3J_{PH}$ 12.1, $^3J_{HH}$ 7.6 Hz), 7.94m (2H, Sb–C$_6H_5$-*ortho*); ^{31}P-NMR: δ 22.1s,br.

4.3. X-ray structure determination

Block crystals of PhSb[(SPPh$_2$)$_2$N]$_2$ (**4**, yellow) and PhSb[(OPPh$_2$)(SPPh$_2$)N]$_2$ (**5**, colorless) were mounted on a glass fibers. Data collection and processing were carried out using a Siemens P4 four-cycle diffractometer (Bremen Universität) and a Siemens SMART/CCD system (University of Windsor), respectively. Cell refinements gave cell constants corresponding to triclinic cells whose dimensions are given in Table 3 along with other experimental parameters. An empirical absorption correction was applied for **5** which resulted in transmission factors ranging from 0.8527 to 0.8397. For **4** no absorption correction was applied.

The structures were solved by direct methods [27]. All of the non-hydrogen atoms were treated anisotropically. Hydrogen atoms were included in idealized positions with isotropic thermal parameters set at 1.2 times that of the carbon atom to which they were attached. The final cycle of full-matrix least-squares refinement [28] converged (largest parameter shift was 0.001 times its estimated S.D.).

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre CCDC no. 161031 for compound (**4**), and 160918 for compound (**5**). Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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References

[1] C. Silvestru, I. Haiduc, Coord. Chem. Rev. 147 (1996) 117.
[2] R.K. Gupta, A.K. Rai, R.C. Mehrotra, V.K. Jain, B.F. Hoskins, E.R.T. Tiekink, Inorg. Chem. 24 (1985) 3280.
[3] M. Hall, D.B. Sowerby, C.P. Falshaw, J. Organomet. Chem. 315 (1986) 321.
[4] J.D. Woollins, J. Chem. Soc. Dalton Trans. (1996) 2893.
[5] C. Silvestru, J.E. Drake, R. Rösler, J. Yang, A. Silvestru, I. Haiduc, Phosphorus Sulfur Silicon Relat. Elem. 124/125 (1997) 63.
[6] I. Haiduc, Coord. Chem. Rev. 158 (1997) 325.
[7] C. Silvestru, J.E. Drake, Coord. Chem. Rev. 223 (2001) 117.
[8] R. Rösler, C. Silvestru, I. Haiduc, M. Gielen, F. Kayser, B. Mahieu, Main Group Metal Chem. 16 (1993) 435.
[9] I. Haiduc, C. Silvestru, H.W. Roesky, H.-G. Schmidt, M. Noltemeyer, Polyhedron 12 (1993) 69.
[10] K.C. Molloy, M.F. Mahon, I. Haiduc, C. Silvestru, Polyhedron 14 (1995) 1169.
[11] R. Rösler, J.E. Drake, C. Silvestru, J. Yang, I. Haiduc, J. Chem. Soc. Dalton Trans. (1996) 391.
[12] L. Flores-Santos, R. Cea-Olivares, S. Hernandez-Ortega, R.A. Toscano, V. Garcia-Montalvo, J. Novosad, J.D. Woollins, J. Organomet. Chem. 544 (1997) 37.
[13] S. Husebye, K. Maartmann-Moe, O. Mikalsen, Acta Chem. Scand. 44 (1990) 802.
[14] A. Silvestru, I. Haiduc, R.A. Toscano, H.J. Breunig, Polyhedron 14 (1995) 2047.
[15] J.E. Drake, A. Silvestru, J. Yang, I. Haiduc, Inorg. Chim. Acta 271 (1998) 75.
[16] J. Novosad, S.V. Lindeman, J. Marek, J.D. Woollins, S. Husebye, Heteroatom Chem. 9 (1998) 615.
[17] J.E. Drake, R.J. Drake, A. Silvestru, J. Yang, Can. J. Chem. 77 (1999) 356.

[18] D.J. Birdsall, J. Novosad, A.M.Z. Slawin, J.D. Woollins, J. Chem. Soc. Dalton Trans. (2000) 438.
[19] J.E. Drake, M.B. Hursthouse, M. Kulcsar, M.E. Light, A. Silvestru, J. Organomet. Chem. 623 (2001) 153.
[20] R. Cea-Olivares, V. Garcia-Montalvo, J. Novosad, J.D. Woollins, R.A. Toscano, G. Espinosa-Perez, Chem. Ber. 129 (1996) 919.
[21] M. Arca, A. Garau, F.A. Devillanova, F. Isaia, V. Lippolis, G. Verani, Z. Anorg. Allg. Chem. 625 (1999) 517.
[22] C. Silvestru, R. Rösler, I. Haiduc, R.A. Toscano, D.B. Sowerby, J. Organomet. Chem. 515 (1996) 131.
[23] S. Husebye, K. Maartmann-Moe, Acta Chem. Scand. A37 (1983) 439.
[24] J. Yang, J.E. Drake, S. Hernandez-Ortega, R. Rösler, C. Silvestru, Polyhedron 16 (1997) 4061.
[25] M. Nunn, D.B. Sowerby, D.M. Wesolek, J. Organomet. Chem. 251 (1983) C45.
[26] R.O. Day, R.R. Holmes, A. Schmidpeter, K. Stoll, L. Howe, Chem. Ber. 124 (1991) 2443.
[27] G.M. Sheldrick, Acta Crystallogr. Sect. A 46 (1990) 467.
[28] G.M. Sheldrick, SHELXL97, University of Göttingen, Germany, 1997.