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# Trimethylantimony(V) tetraphenyldichalcogenoimidodiphosphinates: crystal structure of $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$, a compound containing true *O*-monometallic monoconnective phosphorus ligands with XPNPY skeleton

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**Abstract**

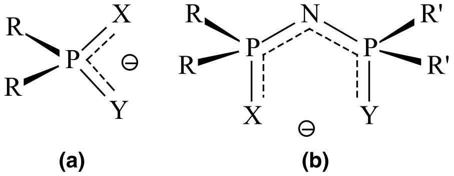
Reactions between $Me_3SbCl_2$ and $K[(SPPh_2)_2N]$, using 1:1 and 1:2 molar ratios, have been investigated. In both cases $Me\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}S$ (**1**) was isolated, as a result of the migration of a methyl group from antimony to sulfur. The *S*-Me ester was identified by NMR spectroscopy and its solid-state molecular structure was determined. Reaction of $Me_3SbCl_2$ and $K[(OPPh_2)(SPPh_2)N]$ in 1:2 molar ratio gave $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (**2**), isolated as a white solid and characterized by IR and NMR ($^1H$, $^{13}C$, $^{31}P$) spectroscopy. The molecular structure of **2** was investigated by X-ray diffraction. The crystal consists of discrete molecules, with two monothio ligands bound to the metal center only through oxygen atoms, thus resulting in a trigonal bipyramidal $C_3SbO_2$ core. The $SbC_3$ unit is planar [Σ(C—Sb—C angles) 360°] and the angle between the axial Sb—O bonds is 173.4(2)°. The coordination of the monothioimododiphosphinato ligand in the *O*-monometallic monoconnective mode is unique; such ligands usually exhibiting chelate or bridging coordination through both oxygen and sulfur atoms.

*Keywords:* Antimony(V) compounds; Imidodiphosphinato ligands; Crystal structure

## 1. Introduction

Both inorganic and organometallic complexes of antimony(III) with 1,1-dichalcogeno organophosphorus ligands of the type $[R_2PXY]^-$ (R = alkyl, aryl, alkoxy; X, Y = O, S) (**a**) are known to exhibit a wide structural diversity from monomeric molecular species to supramolecular assemblies and several practical uses have also been reported [1]. In addition, a few trialkylantimony(V) derivatives containing monodentate $[R_2PXY]^-$ ligands and planar $SbC_3$ moiety have been described, e.g., $R_3Sb[S(S)PPh_2]_2$ (R=Me [2], $Me_3SiCH_2$ [3]) and $Me_3Sb[O(S)PPh_2]_2$ [4].

By contrast, relatively few reports are available on inorganic and organoantimony(III) and -antimony(V) compounds containing tetraorganodichalcogenoimidodiphosphinato ligands $[(XPR_2)(YPR'_2)N]^-$ (R = alkyl, aryl, alkoxy; X, Y = O, S) (**b**) [5].



(a) (b)

So far, only two inorganic antimony(III) compounds, i.e., $Sb[(SePPh_2)_2N]_3$ [6] and $(\mu\text{-}S)(\mu\text{-}I)_2[Sb(SPPh_2)_2N]_2$

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[7], a few phenylantimony(III), $PhSbCl[(XPPh_2)(SPPh_2)N]$ and $PhSb[(XPPh_2)(SPPh_2)N]_2$ (X = O, S) [8], and the diphenylantimony(V) derivatives, $Ph_2SbCl_2[(OPPh_2)(YPPh_2)N]$ (Y = O, S) and $Ph_2SbCl_2[(OPMe_2)(OPPh_2)N]$ [9], have been reported. In all of these antimony compounds, the $[(XPR_2)(YPR'_2)N]^-$ anion chelates the metal center through both chalcogen atoms. Very few examples of metal compounds containing a true monodentate dichalcogenoimidodiphosphinato ligand are known [5], i.e. $[2\text{-}(Me_2NCH_2)C_6H_4]Te\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}S$ [10], (L) $Au\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}O$ (L = *P*-$(2\text{-}H_2NC_6H_4PPh_2)$ [11], *P*-$(Ph_2PNHP(O)Ph_2)$ [12]), $(L)(CH_3)Pd\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}O$ (L = *N*,*P*-$(2\text{-}H_2NC_6H_4PPh_2)$ [11]), $[(L)Pd\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}O][PF_6]$ (L = *N*,*N'*,*N''*-$(H_2HCH_2CH_2)_2$ NH [13]), $(L)Pd(S\text{-}PPh_2{=}N\text{-}PPh_2{=}O)_2$ (L = *N*,*N'*-$H_2NCH_2CH_2NH_2$ [12], *N*,*N'*-2-$(H_2NCH_2)C_5H_4N$ [13]). For all compounds containing monothio ligands, an *S*-monometallic monoconnective coordination pattern was established. Only for $Me_2TeCl[(OPPh_2)(SPPh_2)N]$ a primary coordination through the oxygen atom was establish, the sulfur atom being involved only in a weak intramolecular Te···S interaction [3.413(7) Å] [14].

Here, we report on the reactions of $Me_3SbCl_2$ with $K[(SPPh_2)_2N]$ (1:1 and 1:2 molar ratio), which afford the isolation of the ester $Me\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}S$, as result of a methyl group migration from antimony to sulfur. By contrast, it was possible to isolate $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ as a stable solid and its molecular structure, containing *O*-monometallic monoconnective phosphorus ligands, is described.

## 2. Experimental

Solvents were dried and freshly distilled prior to use. The starting materials were prepared according to reported procedures: $Me_3SbCl_2$ [15], $K[(SPPh_2)_2N]$ [16] and $K[(OPPh_2)(SPPh_2)N]$ [17]. The infrared spectra were recorded using KBr pellets on a Specord 75 IR Zeiss-Jena (DDR) instrument, in the range 4000–400 $cm^{-1}$. The $^1H$, $^{13}C$ and $^{31}P$ NMR spectra were recorded on a VARIAN GEMINI 300S instrument operating at 299.5, 75.4 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.

### 2.1. Reaction of $Me_3SbCl_2$ with $K[(SPPh_2)_2N]$ in 1:1 molar ratio

A mixture of $Me_3SbCl_2$ (0.238 g, 1.00 mmol) and $K[(SPPh_2)_2N]$ (0.478 g, 1.00 mmol) in 25 mL anhydrous toluene was stirred under reflux for 4 h, then filtered hot to remove the resulting KCl. The filtrate was concentrated to 10 mL and the precipitate separated by filtration. Recrystallization from hot toluene allowed separation of a white crystalline product. The NMR data confirmed the isolation of the ester $Me\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}S$ (**1**). Crystals suitable for X-ray studies were grown from $CH_2Cl_2$/*n*-hexane. Yield: 0.27 g (58%), m.p. 190–191 °C. IR ($cm^{-1}$): 1235vs [$\nu_{as}(P_2N)$], 603s [$\nu$ (P=S)], 548s [$\nu$ (P—S)]. $^1H$ NMR: 2.18 (d, 3H, *S*-$CH_3$, $^3J_{PH} = 13.5$ Hz), 7.30 (m, 6H, $C_6H_5 - meta + para$), 7.47 (m, 6H, $C_6H_5 - meta + para$), 7.95 (m, 8H, $C_6H_5$ – *ortho*). $^{13}C$ NMR: 12.19 (s, br, $CH_3$), 127.71 (d, $C_m$, $^3J_{PC} = 13.0$ Hz), 128.64 (d, $C_m$, $^3J_{PC} = 13.8$ Hz), 129.82 (d, $C_p$, $^4J_{PC} = 2.8$ Hz), 130.69 (d, $C_o$, $^2J_{PC} = 11.2$ Hz), 131.94 (d, $C_o$, $^2J_{PC} = 11.1$ Hz), 133.34 (d, $C_p$, $^4J_{PC} = 3.0$ Hz), 140.67 (dd, $C_i$, $^1J_{PC} = 107.3$ Hz, $^3J_{PC} = 6.2$ Hz); the resonance signal for the second type of $C_i$ carbon could not be assigned (it is probably overlapped by the other stronger carbon resonances). $^{31}P$ NMR: 27.8 (d, $Ph_2P$-S-Me, $^2J_{PP} = 6.7$ Hz), 42.0 (d, $Ph_2P$=S, $^2J_{PP} = 6.7$ Hz).

### 2.2. Preparation of $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (2)

A mixture of $Me_3SbCl_2$ (0.238 g, 1.00 mmol) and $K[(OPPh_2)(SPPh_2)N]$ (0.942 g, 2.00 mmol) in 25 mL anhydrous chloroform was stirred under reflux for 2 h, then filtered hot to remove the resulting KCl. The solvent was removed to dryness under reduced pressure, leading to a white solid, which was washed twice with 10 mL *n*-hexane. Crystals of the title compound, suitable for single-crystal X-ray studies, were grown by slow diffusion from chloroform/*n*-hexane. Yield: 0.93 g (94%). *Anal.* Found: C, 59.1; H, 4.7; N, 2.5%. Required for $C_{51}H_{49}N_2O_2P_4S_2Sb$: C, 59.4; H, 4.8; N, 2.7%. m.p. 153–154 °C. IR ($cm^{-1}$): 1226s, br [$\nu_{as}(P_2N)$], 1123s, 1100s [$\nu$(PO)], 860m, br [$\rho(SbCH_3)$], 612s [$\nu$(PS)]. $^1H$ NMR: 2.12 (s, 9H, $CH_3$), 7.28 (m, 20H, $C_6H_5$ – $meta + para$), 7.39 (t, 4H, P(O)-$C_6H_5 - para$, $^3J_{HH} = 7.2$ Hz), 7.56 (dd, 8H, P(O)-$C_6H_5$ – *ortho*, $^3J_{PH} = 13.1$, $^3J_{HH} = 8.0$ Hz), 7.90 (dd, 8H, P(S)-$C_6H_5$ –*ortho*, $^3J_{PH} = 13.5$, $^3J_{HH} = 7.7$ Hz). $^{13}C$ NMR: 17.21 (s, $CH_3$), 127.68 (d, $C_m$, $^3J_{PC} = 13.0$ Hz), 128.24 (d, $C_m$, $^3J_{PC} = 13.5$ Hz), 129.64 (s, br, $C_p$); 130.69 (d, $C_o$, $^2J_{PC} = 11.2$ Hz), 131.14 (d, $C_o$, $^2J_{PC} = 10.4$ Hz), 135.19 (dd, $C_i$, P(O)-$C_6H_5$, $^1J_{PC} = 139.9$, $^3J_{PC} = 4.7$ Hz), 141.07 (dd, $C_i$, P(S)—$C_6H_5$, $^1J_{PC} = 107.1$, $^3J_{PC} = 5.0$ Hz). $^{31}P$ NMR: 16.0 (s,$Ph_2P$ O, $^1J_{PC} = 140.3$ Hz), 40.1 (s, $Ph_2P$ S,$^1J_{PC} = 107.9$ Hz).

### 2.3. Crystal structure determinations

Colourless, block crystals of $Me\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}S$ (**1**) and $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (**2**) were mounted on a glass fibre. Data collection and processing was carried out using a Bruker SMART APEX system (Babes-Bolyai University, Cluj-Napoca) and a Siemens SMART/CCD system (University of Windsor), respectively. Cell refinement gave cell constants corresponding to a monoclinic cell for **1** and a triclinic cell for **2**, whose

Table 1
Crystal data and details of structure refinement for Me-S-$PPh_2$=N-$PPh_2$=S (**1**) and $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (**2**)

| | **1** | **2** |
|---|---|---|
| Molecular formula | $C_{25}H_{23}NP_2S_2$ | $C_{51}H_{49}N_2O_2P_4S_2Sb$ |
| *M* | 463.50 | 1031.67 |
| Temperature (K) | 300(2) | 299(2) |
| Crystal size (mm) | 0.36 × 0.24 × 0.16 | 0.32 × 0.22 × 0.15 |
| Crystal system | monoclinic | triclinic |
| Space group | *P2(1)/n* | $P\bar{1}$ |
| Radiation | Mo Kα, 0.71073 Å | Mo Kα, 0.71073 Å |
| Unit cell dimension | | |
| *a* (Å) | 14.9322(15) | 9.689(1) |
| *b* (Å) | 8.9011(9) | 12.950(1) |
| *c* (Å) | 18.5566(19) | 20.674(2) |
| α (°) | 90 | 81.27(1) |
| β (°) | 109.168(2) | 82.08(1) |
| γ (°) | 90 | 80.40(1) |
| *V* ($Å^3$) | 2329.7(4) | 2511.1(5) |
| *Z* | 4 | 2 |
| $D_{calc}$ ($g\,cm^{-3}$) | 1.322 | 1.364 |
| $F_{000}$ | 968 | 1056 |
| μ(Mo Kα) ($mm^{-1}$) | 0.379 | 0.800 |
| θ Range for data collection (°) | 1.53–26.37 | 1.61–25.03 |
| Reflections collected | 18108 | 18733 |
| Independent reflections | 4755 [$R_{int}$ = 0.0311] | 8749 [$R_{int}$ = 0.0395] |
| Max. and min. transmissions | 0.9419 and 0.8757 | 0.8894 and 0.7838 |
| Refinement method | full-matrix least-squares on $F^2$ | |
| Data/restraints/parameters | 4755/0/272 | 8749/0/562 |
| Goodness-of-fit on $F^2$ | 1.113 | 1.109 |
| Final *R* indices [$F^2 > 2\sigma(F^2)$] | $R_1 = 0.0461$, $wR_2 = 0.1128$ | $R_1 = 0.0661$, $wR_2 = 0.1656$ |
| *R* indices (all data) | $R_1 = 0.0529$, $wR_2 = 0.1171$ | $R_1 = 0.0823$, $wR_2 = 0.1733$ |
| Largest difference peak and hole (e $Å^{-3}$) | 0.448 and −0.185 | 1.729 and −0.696 |

dimensions are given in Table 1 along with other experimental parameters. An empirical absorption correction was applied which resulted in transmission factors ranging from 0.9419 to 0.8757 for **1** and 0.8894 to 0.7838 for **2**, respectively.

The structure was solved by direct methods [18] and refined using SHELX-97 [19] for **1** and the WinGX version [20] of SHELX-97 [19] for **2**. 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 positions of the higher residual peak made no chemical sense. The final cycle of full-matrix least-squares refinement converged (largest parameter shift was 0.001 times its esd).

## 3. Results and discussion

The reaction between $Me_3SbCl_2$ and $K[(SPPh_2)_2N]$ (1:1 molar ratio) was carried out in anhydrous toluene. After repeated recrystallization from toluene, a pure white, crystalline solid was isolated. The compound was identified by NMR data as the methyl ester, Me-S-$PPh_2$=N-$PPh_2$=S (**1**), formed by migration of a methyl group from antimony to sulfur, according to:

$$\begin{tikzcd} Me_2SbCl_2 + K[(SPPh_2)_2N] \arrow[r, "- KCl"'] & \{Me_3SbCl[(SPPh_2)_2N]\} \atop \text{unstable} \arrow[d] \\ & \underset{\mathbf{1}}{Me_2SbCl + Me\text{-}S\text{-}PPh_2{=}N\text{-}PPh_2{=}S} \end{tikzcd} \quad (1)$$

This compound was previously prepared by reacting the free $(SPPh_2)_2NH$ acid with diazomethane [21]. Crystals of **1** were obtained by slow diffusion from a $CH_2Cl_2$/*n*-hexane mixture and the molecular structure was determined by X-ray diffraction. An attempt to follow this reaction by $^{31}P$ NMR in situ was performed. Although the experiment was rendered difficult due to the unsoluble material (the starting $K[(SPPh_2)_2N]$ and the resulting KCl), 30 min after mixing the reagents the $^{31}P$ NMR spectrum exhibited a broad resonance (δ 53.0 ppm), which might be assigned to the $Me_3SbCl[(SPPh_2)_2N]$ intermediate product, along with weak resonances (δ 29.5, 43.8 ppm) corresponding to the methyl ester **1**. In $^{31}P$ NMR spectrum of the same reaction mixture, recorded after 4 h, this broad resonance is still present and the resonances assigned to **1** are considerably increased, thus indicating the decomposition process is in progress. Attempts to prepare the disubstituted derivative, Me3Sb$[(SPPh_2)_2N]_2$, also resulted in decomposition and the presence of the ester Me-S-$PPh_2$=N-$PPh_2$=S was established by $^{31}P$ NMR, along with other unidentified phosphorus-containing products.

In contrast to the dithioimidodiphosphinato derivatives, the trimethylantimony(V) derivative $Me_3Sb[O$-$PPh_2$=N-$PPh_2$=$S]_2$ (**3**) was obtained in good yields as an air-stable crystalline product, by reacting stoichiometric amounts of trimethylantimony(V) dichloride and the potassium salt of the organophosphorus ligand, according to:

$$Me_3SbCl_2 + 2K[(OPPh_2)(SPPh_2)N] \rightarrow \underset{\mathbf{2}}{Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2} + 2KCl \qquad (2)$$

This suggests that the presence of an oxygen atom in the phosphorus ligand moiety stabilizes the disubstituted trimethylantimony(V) derivative. The new compound was characterized by IR and multinuclear NMR ($^1H$, $^{13}C$, $^{31}P$) spectroscopy and its molecular structure was established by single-crystal X-ray diffraction.

### 3.1. Infrared spectra

For complex **2** strong infrared absorptions in the regions 1230–1220 and 1130–1100 $cm^{-1}$ and around 610 $cm^{-1}$ were assigned to $\nu_{as}(P_2N)$, $\nu(PO)$, and $\nu(PS)$ stretching vibrations, respectively, by comparison with the spectra of the free acid and its alkali metal salt [17]. The absence of strong absorptions around 2700–2600 [$\nu(NH)$] and 950–900 $cm^{-1}$ [$\nu_{as}(P_2NH)$], which are characteristic of the free $(OPPh_2)(SPPh_2)NH$ acid, is consistent with deprotonated phosphorus ligands. In addition, an absorption of medium intensity at 860 $cm^{-1}$ [$\rho(SbCH_3)$] was also observed, indicating the presence of methyl groups attached to the antimony atom. The stretching vibrations for the $SbC_3$ moiety (600–500 $cm^{-1}$) could not be assigned, being obscured by stronger $\nu(SbO)$ and aromatic group vibrations.

### 3.2. NMR spectra

The NMR data confirmed the isolation of the Me-S-$PPh_2$=N-$PPh_2$=S ester **1**. For the methyl protons a doublet resonance was observed in the $^1H$ NMR spectrum, due to the phosphorus–proton coupling [$^3J_{PH} = 13.5$ Hz]. The $^{31}P$ NMR spectrum exhibits two doublet resonances at $\delta$ 27.8 ($Ph_2P$-S-Me) and 42.0 ppm ($Ph_2P$=S), as result of the phosphorus–phosphorus coupling ($^2J_{PP} = 6.7$ Hz).

The NMR spectra of **2** provide evidences that the structure observed in the solid state (see below) is preserved in solution. The $^1H$ NMR spectrum contains only one singlet resonance for the methyl groups on antimony ($\delta$ 2.12 ppm), thus suggesting a planar $Me_3Sb$ core. The $^{31}P$ NMR spectrum exhibits the two expected resonances which appear as singlets (phosphorus–phosphorus coupling was not observed) surrounded by satellites due to phosphorus–carbon coupling. Their assignment to $P_O$ ($\delta$ 16.0 ppm) and $P_S$ ($\delta$ 40.1 ppm) atoms was based on the $^1J_{PC}$ coupling constants. The magnitude of the $P_S$ chemical shift is consistent with a P=S double bond, i.e., monodentate thioimidodiphosphinato ligands coordinated to the metal centre through the oxygen atoms, thus resulting in a trigonal bipyramidal $C_3SbO_2$ core.

### 3.3. The molecular structure of Me-S-$PPh_2$=N-$PPh_2$2=S (**1**)

The crystal of **1** consists of discrete molecules separated by normal van der Waals distances. Selected interatomic distances and angles are listed in Table 2. Fig. 1 shows the ORTEP-like view of the molecular structure of Me-S-$PPh_2$=N-$PPh_2$=S, with the atom numbering scheme.

The phosphorus–sulfur and phosphorus–nitrogen bond distances in the molecule of **1** are different, consistent with single [P(1)—S(1) 2.0712(8), P(2)—N(1) 1.610(2) Å] and double [P(2)—S(2) 1.9541(8), P(1)—N(1) 1.5622(18) Å] bond character, respectively (cf. $(SPPh_2)_2$ NH [22]: P=S 1.936(1) and 1.950(1) Å, P—N 1.684(2)

Table 2
Relevant interatomic distance (Å) and angles (°) in Me-S-$PPh_2$=N-$PPh_2$=S (**1**)

| | | | |
|---|---|---|---|
| *Interatomic distances* | | | |
| P(1)—S(1) | 2.0712(8) | P(2)—S(2) | 1.9541(8) |
| P(1)—N(1) | 1.5622(18) | P(2)—N(1) | 1.6101(18) |
| S(1)—C(1) | 1.802(3) | | |
| *Interatomic angles* | | | |
| N(1)—P(1)—S(1) | 119.81(8) | N(1)—P(2)—S(2) | 120.14(7) |
| P(1)—N(1)—P(2) | 135.76(13) | | |

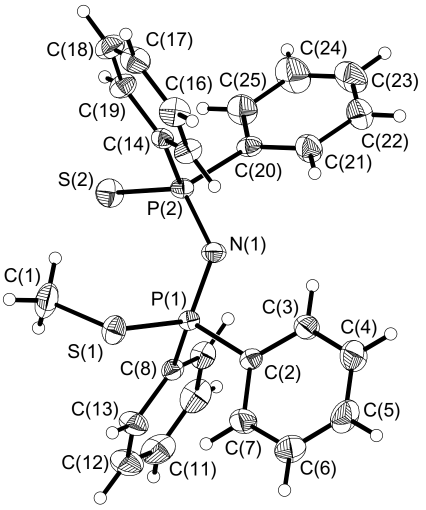
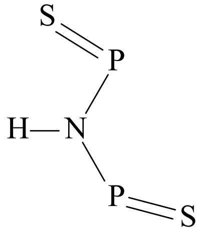


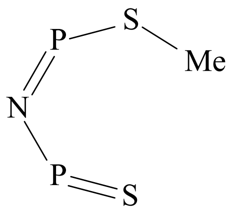
Fig. 1. ORTEP plot of the molecule of Me-S-$PPh_2$=N-$PPh_2$=S (**1**). The atoms are drawn with 30% probability ellipsoids.

and 1.671(2) Å; $Ph_2P(=S)SH$ [23]: P—S 2.077(1), P=S 1.954(1) Å; $[(Me_3Si)_2N\text{-}P(=NBu^t)S]_2$ [24]: P—N 1.662(2), P=N 1.529(2) Å). The P(1)—N(1)—P(2) [135.76(13)°] is slightly increased in **1** in comparison with the parent $(SPPh_2)_2NH$ acid [132.68(14)°], as are the the N—P—S angles [119.81(8)° and 120.14(7)° in **1** *vs* 114.73(7)° and 115.53(7)° in the free acid] [22].

The SPNPS skeleton in the free $(SPPh_2)_2NH$ acid exhibits an *anti* conformation (**c**) (S—P···P—S torsion angle of 155.7°), with the sulfur atoms placed on opposite sides of the PNP-plane [$(-,-)/(+,+)$ code, in terms of $(x,z)$ coordinates of the sulfur atoms with respect to the triatomic PNP-plane placed in the $(x,y)$-plane] [5]. In contrast, the SPNPS skeleton in **1** is twisted to bring the sulfur atoms in a *syn* conformation (**d**) (S—P···P—S torsion angle of 75.5°), the sulfur atoms being again placed on opposite sides of the PNP plane (deviations from PNP plane: S(1), −1.461; S(2), 0.907 Å).



**(c)**



**(d)**

### 3.4. The molecular structure of $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (2)

Crystals of $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (**2**) suitable for X-ray diffraction studies were grown from a mixture of chloroform/*n*-hexane. Important interatomic distances and bond angles are listed in Table 3 and Fig. 2 shows the ORTEP-like view of the molecular structure of $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$, with the atom numbering scheme. Discrete monomeric molecules, separated by normal van der Waals distances, are present in the crystal of **2**.

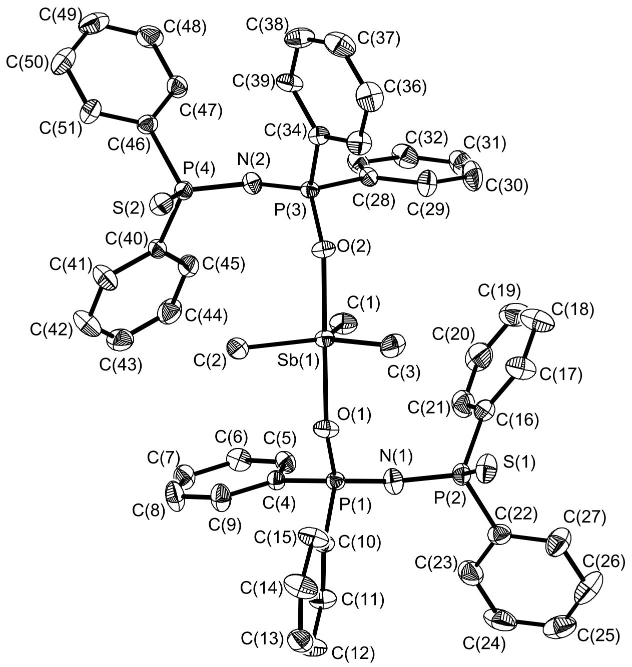


Fig. 2. ORTEP plot of the molecule of $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (**2**). The atoms are drawn with 20% probability ellipsoids. Hydrogen atoms are omitted for clarity.

In the molecule of **2** both thioimidodiphosphinato ligands are bound to the antimony atom only through the

Table 3
Relevant interatomic distance (Å) and angles (°) in $Me_3Sb[O\text{-}PPh_2{=}N\text{-}PPh_2{=}S]_2$ (**2**)

| | | | |
|---|---|---|---|
| *Interatomic distances* | | | |
| Sb(1)—C(1) | 2.100(8) | Sb(1)—C(3) | 2.082(8) |
| Sb(1)—C(2) | 2.103(8) | | |
| Sb(1)—O(1) | 2.090(5) | Sb(1)—O(2) | 2.109(5) |
| P(1)—O(1) | 1.544(6) | P(3)—O(2) | 1.556(5) |
| P(1)—N(1) | 1.571(7) | P(3)—N(2) | 1.564(6) |
| P(2)—N(1) | 1.601(7) | P(4)—N(2) | 1.618(6) |
| P(2)—S(1) | 1.962(3) | P(4)—S(2) | 1.972(3) |
| *Interatomic angles* | | | |
| C(1)—Sb(1)—C(2) | 120.5(4) | C(1)—Sb(1)—C(3) | 119.9(4) |
| C(2)—Sb(1)—C(3) | 119.6(4) | | |
| O(1)—Sb(1)—C(1) | 92.1(3) | O(2)—Sb(1)—C(1) | 94.4(3) |
| O(1)—Sb(1)—C(2) | 87.1(3) | O(2)—Sb(1)—C(2) | 90.9(3) |
| O(1)—Sb(1)—C(3) | 90.0(3) | O(2)—Sb(1)—C(3) | 85.5(3) |
| O(1)—Sb(1)—O(2) | 173.4(2) | | |
| O(1)—P(1)—N(1) | 117.4(4) | O(2)—P(3)—N(2) | 118.9(3) |
| S(1)—P(2)—N(1) | 120.0(3) | S(2)—P(4)—N(2) | 119.8(2) |
| P(1)—N(1)—P(2) | 134.1(5) | P(3)—N(2)—P(4) | 132.6(4) |
| Sb(1)—O(1)—P(1) | 147.9(4) | Sb(1)—O(2)—P(3) | 138.3(3) |

oxygen atoms. The antimony–oxygen bond lengths [Sb(1)—O(1) 2.090(5), Sb(1)—O(2) 2.109(5) Å] in **2** are of the same magnitude with those found in the related $Me_3Sb[O(S)PPh_2]_2$ derivative [2.107(5), 2.114(5) Å], which also contains monodentate monothiophosphinato ligands [4], or in the antimony(V) complex $Ph_2SbCl_2[(OPPh_2)(SPPh_2)N]$ [2.128(3) Å], in which the thioimidodiphosphinato ligand exhibits a monometallic biconnective coordination pattern [9]. The coordination geometry around the antimony atom is distorted trigonal bipyramidal, with Sb—C bonds in the equatorial positions and oxygen atoms of the monodentate thioimidodiphosphinato ligands in the axial positions [O(1)—Sb(1)—O(2) 173.4(2)°]. The $SbC_3$ unit is planar, with the C—Sb—C angles in the range 119.6(4)°–120.5(4)°. The distortion of the $C_3SbO_2$ core is reflected in the $O_{ax}$—Sb—$C_{eq}$ bond angles [85.5(3)°–94.4(3)°].

The unique *O*-monometallic monoconnective coordination pattern of the thioimidodiphosphinato ligand units in **2** is reflected by the interatomic distances within the OPNPS fragments. The phosphorus–oxygen [P(1)—O(1) 1.544(6), P(3)—O(2) 1.556(5) Å] and phosphorus–sulfur [P(2)—S(1) 1.962(3), P(4)—S(2) 1.972(3) Å] bond distances are typical for single P—O and double P=S bonds (cf. $(OPPh_2)(SPPh_2)NH$ [25]: P=O 1.491(4), P=S 1.935(2) Å, in one of the two independent molecules present in the unit cell; $Ph_2P(=S)OH$ [26]: P—O 1.582(2), P=S 1.956(1) Å; $Ph_2P(=O)OH$ [27]: P=O 1.486(6), P—O 1.526(6) Å). Consequently, the phosphorus–nitrogen bonds within a ligand moiety are not equivalent; the shorter corresponding to double $P_O$=N [1.571(7)/1.564(6) Å] and the longer to single $P_S$—N [1.601(7)/1.618(6) Å] bonds. The bond distances within the OPNPS skeletons in **2** are of the same magnitude as observed in $Me_2TeCl[(OPPh_2)(SPPh_2)N]$ [P—O 1.56(1), $P_O$=N 1.56(1), $P_S$—N 1.64(2), P=S 1.973(8) Å]; in this case, however, although the monothio ligand is bound to the tellurium atom through its oxygen, a weak intramolecular Te···S interaction [3.413(7) Å] is also established [14]. The O···S interatomic distances for a ligand moiety in **2** (3.795, 3.922 Å) are much larger than in $Ph_2SbCl_2[(OPPh_2)(SPPh_2)N]$ (3.374 Å) [9] and are consistent with the high flexibility of the OPNPS skeleton, reflecting versatility of this type of ligand in responding to various coordination requirements of the antimony atom.

The O—P—N, N—P—N and N—P—S bond angles within the OPNPS skeletons (Table 3) generally follow a similar trend, i.e., they are slightly larger than in the parent $(OPPh_2)(SPPh_2)NH$ acid [113.5(2)°/131.4(3)°/115.7(2)°] [25] or in the bidentate ligand moiety of $Ph_2SbCl_2[(OPPh_2)(SPPh_2)N]$ [116.7(2)°/132.3(3)°/117.9(2)°] [9]. A consequence of the monodentate behaviour of the thioimidodiphosphinato ligands in **2** is the significantly larger Sb—O—P angles [Sb(1)—O(1)—P(1) 147.9(4)°, Sb(1)—O(2)—P(3) 138.3(3)°] in comparison with that found in the *six-membered* $SbOSP_2N$ ring [Sb—O—P 132.6(2)°] formed as result of the *O,S*-chelating nature of the same ligand moiety in $Ph_2SbCl_2[(OPPh_2)(SPPh_2)N]$ [9].

## 4. Supplementary material

Crystallographic data for the structural analysis of compounds **1** and **2** have been deposited with the Cambridge Crystallographic Data centre [CCDC No. 186321 (**1**), 182711 (**2**)]. 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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