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Synthesis and crystal structures of two trigonal bipyramidal Sb(V) compounds, R_2SbBr_3 and $R_3Sb(S_2PPh_2)_2$ ($R = Me_3SiCH_2$)

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Abstract

Addition of Br_2 to R_2SbBr ($R = Me_3SiCH_2$) gives R_2SbBr_3 (**1**). R_3SbBr_2 reacts with $NH_4S_2PPh_2$ to form $R_3Sb(S_2PPh_2)_2$ (**2**). The structures of **1** and **2** have been determined by single-crystal X-ray diffraction.

Keywords: Antimony; Phosphorus; X-ray structure

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1. Introduction

The trimethylsilylmethyl group is a valuable substituent for the synthesis of organometallic alkyl derivatives because it is a protecting but sterically not very demanding ligand, with the α-silyl group increasing the stability of the metal–carbon bond.

Examples of organoantimony compounds with the trimethylsilylmethyl substituent include derivatives of Sb(I): $(RSb)_4$, $(RSb)_5$ [1,2]; Sb(II): (R_4Sb_2) [3]; Sb(III): R_3Sb [4,5], $RSbH_2$, [1], $RSbCl_2$ [2], $RSbBr_2$[1], $RSbCl_3^-$ [2], and Sb(V): R_3SbX_2 ($X = Br$ [4], I [5]); $R = Me_3SiCH_2$. Three compounds, R_3Sb [4], $[Cp_2Co][RSbCl_3]$ [2], and R_3SbI_2 [4] have been characterized by X-ray crystallography.

We report here the syntheses and the crystal structures of R_2SbBr_3 (**1**) and $R_3Sb(S_2PPh_2)_2$ (**2**) ($R = Me_3SiCH_2$), two trigonal bipyramidal Sb(V) compounds with the alkyl groups in equatorial positions. Both structures correspond to known structural motifs. Closely related to **1** is the structure of Ph_2SbBr_3 [6]. However no crystal structures of trigonal bipyramidal dialkylantimony trihalides have been so far reported. The other dialkylantimony trihalide with a known structure, $(Me_2SbCl_3)_2$ [7], is a dimer with six-coordinate antimony. Structures of inorganic and organometallic antimony complexes with the Ph_2PS_2 or with related ligands have been carefully studied in recent years [8]. These investigations also included the characterization of $Me_3Sb(S_2PPh_2)_2$ [9], a compound that is closely related to **2**. However, the present study reveals interesting differences between both compounds with respect to the coordination pattern of the dithiophosphinato ligands.

2. Results and discussion

2.1. Preparation and structure of $(Me_3SiCH_2)_2SbBr_3$ (1)

Addition of 50% excess of the stoichiometric amount of Br_2 to $(Me_3SiCH_2)_2SbBr$ [1] in petroleum ether at −20°C followed by recrystallization from warm toluene gives **1** in quantitative yield as colorless crystals (m.p. 123–125°C dec.), soluble in toluene, benzene and other organic solvents.

$$Br_2 + (Me_3SiCH_2)_2SbBr \rightarrow \underset{\mathbf{1}}{(Me_3SiCH_2)_2SbBr_3} \qquad (1)$$

At room temperature the crystals of **1** are surprisingly stable in air. Even after months there is no indication of decomposition. Other dialkylantimony tribromides like Me_2SbBr_3 [10], Et_2SbBr_3 [11], and *i*-Pr_2SbBr_3 [12], but also the corresponding iodide $(Me_3SiCH_2)_2SbI_3$ [5] de-

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compose at room temperature with elimination of the corresponding alkyl halide. In the case of **1** the reductive elimination of Me_3SiCH_2Br with formation of $Me_3SiCH_2SbBr_2$ starts only when heated to melting temperature (125°C).

$$\underset{\mathbf{1}}{(Me_3SiCH_2)_2SbBr_3} \rightarrow Me_3SiCH_2SbBr_2 + Me_3SiCH_2Br \qquad (2)$$

For the preparation of $Me_3SiCH_2SbBr_2$ this route is, however, not very useful because it requires many steps. A better method of synthesis for this dibromide is the distribution reaction between R_3Sb and $SbBr_3$ [1].

The structure of **1** was determined by X-ray diffraction on a single crystal that was obtained as a side product of the reaction of R_3Sb with Br_2. The structure as shown in Fig. 1 consists of discrete molecules of **1** with two bromine atoms in axial positions and one bromine atom and two Me_3SiCH_2 groups in equatorial sites of an almost ideal trigonal bipyramid (Br(1)–Sb(1)–Br(1a) 176.31(4)°).

The Me_3Si groups point towards the equatorial bromine atom with the silicon atoms lying in the equatorial plane (mean deviation of the silicon atoms from the $BrSbC_2$ plane ± 2.75 pm). This arrangement leads to significant opening of the Si–C–Sb angles (Si(1)–C(1)–Sb(1) 119.7(3)°). As usual for a trigonal bipyramidal environment, the axial Sb–Br bonds (262.36(16) pm) are longer than the equatorial Sb–Br bond (247.5(2) pm). The bond angles in the equatorial plane are close to the ideal value of 120° (C–Sb–C 123.7(4)°, C–Sb–Br 118.17(18)°). By contrast, the distortions of the trigonal bipyramidal geometry, caused by intermolecular Sb···Br interactions, are much larger for Ph_2SbBr_3 (C–Sb–C 154°) [6]. There are no short intermolecular contacts in the structure of **1** (see Table 1).

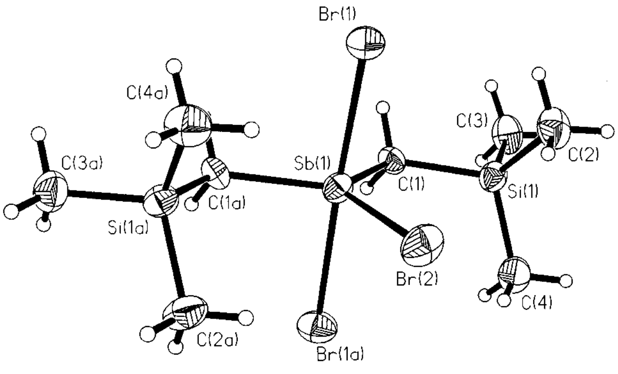

Fig. 1. Structure of **1**. Selected distances (pm) and angles (°): Sb(1)–C(1) 211.5(6), Sb(1)–Br(1) 262.36(16), Sb(1)–Br(2) 247.5(2); C(1)–Sb(1)–C(1a) 123.7(4), C(1)–Sb(1)–Br(2) 118.17(18), C(1)–Sb(1)–Br(1a) 90.42(19), Br(2)–Sb(1)–Br(1) 88.15, C(1)–Sb(1)–Br(1) 91.32(19), Br(1)–Sb(1)–Br(1a) 176.31(4), Si(1)–C(1)–Sb(1) 119.7(3).

Table 1
Crystallographic data and measurements for **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_8H_{22}Br_3SbSi_2$	$C_{36}H_{53}P_2S_4SbSi_3$
Formula weight	535.92	881.98
Color	Colorless	Yellowish
Crystal size, mm	0.6 × 0.5 × 0.3	0.9 × 0.7 × 0.6
Unit cell dimensions		
a (pm)	692.4(6)	1098.4(2)
b (pm)	692.4(6)	1197.3(3)
c (pm)	3649.5(12)	1766.8(3)
α (°)	90	72.770(10)
β (°)	90	78.340(10)
γ (°)	90	78.08(2)
Crystal system	Tetragonal	Triclinic
Space group	$P4(1)2(1)2$	$P\bar{1}$
Z	4	2
Diffractometer	Siemens P4	Siemens P4
Mo–K_α radiation (wavelength, Å)	0.71073	0.71073
Temperature (K)	173(2)	173(2)
Reflections collected	8924	10246
Independent reflections	2000 [$R_{int} = 7.23\%$]	8690 [$R_{int} = 1.96\%$]
Completeness to θ	27.62°, 98.8%	27.50°, 88%
Absorption coefficient (mm^{-1})	8.538	1.020
Absorption correction	DIFABS [15]	None
Final R [a] indices [$I > 2\sigma(I)$]	$R_1 = 0.0413$, $wR_2 = 0.095$	$R_1 = 0.0260$, $wR_2 = 0.0692$
R [a] indices (all data)	$R_1 = 0.0553$, $wR_2 = 0.1032$	$R_1 = 0.0274$, $wR_2 = 0.0701$
Goodness of fit on F^2	1.092	1.099
No. of parameters	71	428
Refinement method	Full-matrix least-squares on F^2 [16]	
Treatment of hydrogen atoms	Refined with a riding model and common isotropic temperature factor	

[a] Definition of the R values: $R_1 = (\Sigma\|F_o|-|F_c\|)/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with $w^{-1} = \sigma^2(F_o^2)+(aP)^2+bP$.

2.2. Preparation and structure of $(Me_3SiCH_2)_3Sb(S_2PPh_2)_2$ (2)

The reaction of $(Me_3SiCH_2)_3SbBr_2$ with two equivalents of ammonium diphenyldithiophosphinate yields the yellowish crystalline, air stable compound **2**:

$$(Me_3SiCH_2)_3SbBr_2 + 2(NH_4)S_2PPh_2 \rightarrow \underset{\mathbf{2}}{(Me_3SiCH_2)_3Sb(S_2PPh_2)_2} + 2NH_4Br \qquad (3)$$

This is readily soluble in organic solvents, but evidence of decomposition was observed by NMR spectroscopy when a solution was kept for long time. Compound **2** was characterized by multinuclear NMR spectroscopy, the data being consistent with the proposed formulation. In the EI mass spectrum of **2** the molecular ion was not found, but other important antimony-containing fragments could be observed (see Section 3).

Crystals of the title compound were obtained from a chloroform–*n*-hexane solution. The triclinic unit cell contains monomeric units of **2** with no intermolecular associations being observed. The molecular structure with the atom numbering scheme is depicted in Fig. 2.

Both diphenyldithiophosphinato groups act as monodentate ligands, being connected to the central antimony atom through sulfur atoms occupying the axial positions in a distorted trigonal bipyramidal environment (S(1)–Sb(1)–S(3) 175.098(16)°). The coordination polyhedron is less distorted than in $Me_3Sb(S_2PPh_2)_2$ [9] where the corresponding S–Sb–S angle is smaller, i.e. 171.1(1)°. On the other hand, the S–Sb–S angle in **2** is of the same magnitude as the O–Sb–O angle (177.7(2)°) in the monothio derivative, $Me_3Sb(OSPPh_2)_2$ [13], where the ligand units exhibit a similar monodentate coordination pattern. The Sb(1)–S(1) and Sb(1)–S(3) distances are comparable in both dithiophosphinato compounds: 263.69(8) and 261.37(8) pm in **2** and 261.1(5) pm in $Me_3Sb(S_2PPh_2)_2$ [9]. The distances between the antimony and the sulfur atoms double bonded to phosphorus are much larger in **2** (409.4 and 404.8 pm, respectively) than in $Me_3Sb(S_2PPh_2)_2$ (374.4 and 383.9 pm, respectively [9]). Moreover they are longer than the sum of van der Waals radii for S and Sb (ca. 400 pm). These data prove that in **2** the dithiophosphinato ligand acts in a monodentate fashion. This interpretation is also supported by the phosphorus–sulfur distances in the diphenyldithiophosphinato units of **2**, which are characteristic for single, P–S (205.23(8) and 206.32(8) pm) and double, P=S (195.95(8) and 195.97(8) pm) bonds (c.f. 207.7(1) and 195.4(1) pm in the free acid, Ph_2PS_2H) [14].

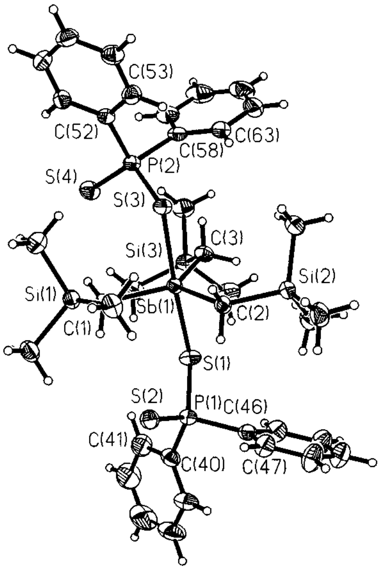

Fig. 2. Structure of **2**. Selected distances (pm) and angles (°) Sb(1)–C(1) 212.21(19), Sb(1)–C(2) 211.92(19), Sb(1)–C(3), 212.2(2), Sb(1)–S(1), 263.69(8), Sb(1)–S(3), 261.37(8), P(1)–S(1), 205.23(8), P(2)–S(3) 206.32(8), P(1)–S(2) 195.95(8), P(2)–S(4) 195.97(8); C(1)–Sb(1)–C(2) 119.92(8), C(1)–Sb(1)–C(3) 125.76(8), C(2)–Sb(1)–C(3) 114.31(8), S(1)–Sb(1)–C(1) 92.46(6), S(3)–Sb(1)–C(1) 90.82(6), S(1)–Sb(1)–C(2) 94.24(6), S(3)–Sb(1)–C(2) 87.27(6), S(1)–Sb(1)–C(3) 82.71(6), S(3)–Sb(1)–C(3) 92.42(6), S(1)–Sb(1)–S(3) 175.098(16), Sb(1)–S(1)–P(1) 111.91(3), Sb(1)–S(3)–P(2) 107.95(3), S(1)–P(1)–S(2) 117.01(4), S(3)–P(2)–S(4) 117.62(4), C(40)–P(1)–C(46) 102.80(11), C(52)–P(2)–C(58) 102.44(9).

The equatorial positions in the trigonal bipyramidal environment of antimony are occupied by the C(1), C(2) and C(3) atoms of the organic groups attached to the metal. The SbC_3 unit is planar (the sum of the C–Sb–C angles is 360°), but the C(3)–Sb(1)–C(1) angle is somewhat enlarged (125.76(8)°) at the expense of the C(2)–Sb(1)–C(3) angle (114.31(8)°). The antimony–carbon distances (212 pm, mean value) are in the same range as those found in other trimethylantimony(V) derivatives (210 pm in $Me_3Sb(S_2PMe_2)_2$, and 208 pm in $Me_3Sb(OSPPh_2)_2$).

One of the three silicon atoms of the trimethylsilylmethyl groups lies practically in the Sb(1)C(1)C(2)C(3) plane while the other two are almost symmetrically located above and under this plane (mean deviation from the SbC_3 plane for Si(1), Si(2) and Si(3) are −0.962, 0.003 and 0.917 Å respectively) (see Table 1).

3. Experimental

All the experiments were performed in an argon atmosphere, using dried solvents distilled under argon.

3.1. Synthesis of bis(trimethylsilymethyl)antimony tribromide (1)

At −20°C a solution of Br_2 (0.28 g, 1.75 mmol) in petroleum ether (20 ml) was added to $(Me_3SiCH_2)_2SbBr$ (0.44 g, 1.17 mmol) in 10 ml petroleum ether. After the addition the mixture was allowed to warm up to room temperature. The solvent was removed at reduced pressure yielding 0.62g (99%) of bis(trimethylsilymethyl)antimony tribromide. Crystallization from warm toluene afforded colorless crystals melting, with decomposition beginning at 123–125°C. ^1H-NMR (C_6D_6, 200 MHz): 0.21 s (9H, CH_3), 2.68 s (2H, CH_2). ^{13}C-NMR (C_6D_6, 50 MHz): 0.25 (CH_3), 50.24 (CH_2). MS (EI, 70eV) *m*/*z* [fragment]: 517 $[R_2SbBr_3–Me]^+$, 455 $[R_2SbBr_2]^+$, 376 $[R_2SbBr]^+$, 361 $[R_2SbBr–Me]^+$, 353 $[RSbBr_2–Me]^+$, 289 $[RSbBr]^+$ with R = Me_3SiCH_2. Anal. found: C 17.68, H 3.99. Anal. Calc. $C_8H_{22}Br_3SbSi_2$: C 17.93, H 4.14%.

3.2. Synthesis of tris(trimethylsilymethyl)antimony bis(diphenyldithiophosphinate) (2)

A stoichiometric mixture of $(Me_3SiCH_2)_3SbBr_2$ (0.45 g, 0.83 mmol) and $Ph_2PS_2NH_4$ (0.45 g, 1.66 mmol) was refluxed for 1 h in chloroform. The precipitated ammonium chloride was filtered off from the reaction mixture and the solvent was removed in vacuum from the clear yellowish solution. The solid powder was recrystallized from chloroform–*n*-hexane (1:5 by volume) and yellowish crystals of $(Me_3SiCH_2)_3Sb(S_2PPh_2)_2$ were obtained. Yield: 0.25 g (42%); m.p. 103°C. ^{1}H-NMR ($CDCl_3$, 200 MHz): 0.22 s (27H, CH_3), 2.33 s (6H, CH_2), 7.36 m (12H, C_6H_5 -meta + para), 7.95 ddd (8H, C_6H_5 -ortho, $^3J_{HH}$ 7.1 Hz, $^4J_{HH}$ 3.3 Hz, $^3J_{PH}$ 14.1 Hz). ^{13}C-NMR ($CDCl_3$, 50 MHz): 2.07s (CH_3), 26.00s (CH_2), 128.06 d (C_m, $^3J_{PC}$ 13.2 Hz), 130.61s (C_p), 130.90d (C_o, $^2J_{PC}$ 11.3 Hz), 139.50d (C_i, $^1J_{PC}$ 83.5 Hz). ^{31}P-NMR ($CDCl_3$, 81 MHz): 56.6s. MS (EI, 70eV) *m*/*z* [fragment]: 619 $[Sb(S_2PPh_2)_2^+]$, 382 $[(Me_3SiCH_2)_3Sb^+]$, 295 $[(Me_3SiCH_2)_2Sb^+]$, 208 $[Me_3SiCH_2Sb^+]$. Anal. found: C 48.84, H 6.07. Anal. Calc. $C_{36}H_{53}P_2S_4SbSi_3$: C 49.02, H 6.06%.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 119355 for compound **1** and CCDC no. 119354 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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