Synthesis and Crystal and Molecular Structure of Tris(dimethylphenylsilyl)antimony

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Tris(dimethylphenylsilyl)antimony (**1**) was prepared in moderate yield from dimetallic "Na_3Sb" (generated in situ) and chlorodimethylphenylsilane in tetrahydrofuran at reflux temperature. The product was identified by standard analytical and spectroscopic techniques, and the crystal structure was determined by single-crystal X-ray diffraction (triclinic, space group $P\bar{1}$, $Z = 2$). The $SbSi_3$ skeleton is pyramidal (average Si–Sb–Si angle 100.2°, average Sb–Si bond length 2.558 Å), and the Me_2PhSi groups are in a staggered conformation.

Trisilylamines are structurally unique compounds[1]. All species of the type $(R_3Si)_3N$ (R = H, halogen, alkyl, aryl, alkoxy etc.) feature a planar NSi_3 skeleton, while the silyl derivatives of all heavier pnicogens have pyramidal ESi_3 cores (E = P, As, Sb, and Bi)[2]. These structural characteristics have emerged only very slowly, and some of the structures have still not been proven unambiguously. This is particularly true for the arsenic, antimony, and bismuth compounds, where structural data are limited to the gas-phase parameters of $(H_3Si)_3E$ (determined by electron diffraction)[2,3]. Although there is now agreement that the vibrational data of $(H_3Si)_3Sb$[4] also support a pyramidal skeleton $SbSi_3$, these data were initially assigned to a planar $SbSi_3$ framework[5].

Single-crystal X-ray diffraction studies of compounds containing Sb–Si bonds have been carried out, inter alia, for $LiSb(SiMe_3)_2 \cdot DME$[6] and $Sb_2(SiMe_3)_4$[7], but no structure of a tris(silyl)antimony $(R_3Si)_3Sb$ compound has been determined so far.

Tris(silyl)antimony molecules were first prepared by Amberger and collaborators[8,9] and independently by Razuvaev and coworkers[10–13] in the 1960s. The preparative chemistry was further developed in the laboratories of Bürger et al.[4,13], Becker et al.[6,7], and Breunig et al.[14–16], who also demonstrated that silylantimony compounds are useful synthons for antimonides of other elements.

The excellent leaving group properties of alkylsilyl- and arylsilyl groups open up synthetic pathways to a whole range of compounds with element-antimony bonds in metathesis reactions with halides or pseudohalides of these elements[17].

In the course of the syntheses of antimony-centered gold clusters, we therefore became interested in the use of silylantimony compounds as components for the metathesis with (phosphane)gold(I) halides. In previous studies with silylphosphanes[18–21] and -arsanes[22] the corresponding phosphorus- and arsenic-centered gold clusters could be generated with a wide variety of stoichiometries and structures and with different phosphane ligands. The present paper summarizes the results of our attempts to obtain a stable, well-defined tris(triorganosilyl)antimony compound, which subsequently could be used in gold clusters chemistry.

Preparation and Properties of Tris(dimethylphenylsilyl)antimony (1)

According to the procedures[8–13] described for other tris(silyl)antimony species, the title compound **1** was prepared from trisodium antimonide (generated in situ from antimony powder and sodium metal in tetrahydrofuran) and chlorodimethylphenylsilane in THF at reflux temperature:

$$3\,Na + Sb \rightarrow Na_3Sb \quad (1)$$

$$Na_3Sb + 3\,Me_3PhSiCl \rightarrow 3\,NaCl + (Me_2PhSi)_3Sb \quad (2)$$

The product was obtained in low yield (ca. 35%) as colorless crystals, which – if in a pure form – melt at 98 °C without decomposition. The pure compound is not sensitive to light, but decomposes rapidly in air. Solutions in THF, chlorinated hydrocarbons, and other solvents are particularly sensitive to oxygen and water, and decomposition is complete in a few seconds in the air.

For the solvent-free crystalline material satisfactory elemental analytical data have been obtained. The FAB mass spectrum (positive ions) shows the molecular ion with high intensity and the correct isotope distribution. The negative ion FAB mass spectrum shows the anion $[Sb(SiPhMe_2)_2]^-$ as the parent peak. The ^{29}Si-NMR spectrum (in chloroform at −60 °C) exhibits only one singlet resonance at $\delta = -14.2$. In the $\{^1H\}^{13}C$-NMR spectrum (recorded in benzene at 20 °C) the phenyl carbon resonances are observed at δ = 129.0 (*para*), 128.0 (*meta*), 134.0 (*ortho*), and 140.8 (ipso), and the methyl resonance appears at $\delta = 2.7$. The ^1H signals of the phenyl rings appear as multiplets at $\delta = 7.1$ (*ortho*, *para*) and 7.4 (*meta*), for the methyl group at δ = 0.48.

In agreement with an idealized C_{3v} symmetry, the methyl groups are not diastereotopic. Since a conformation with strict C_{3v} sym-

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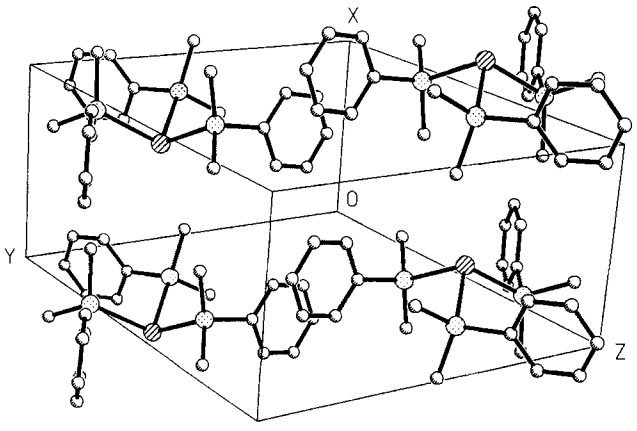
Figure 1. Crystal packing of compound **1**

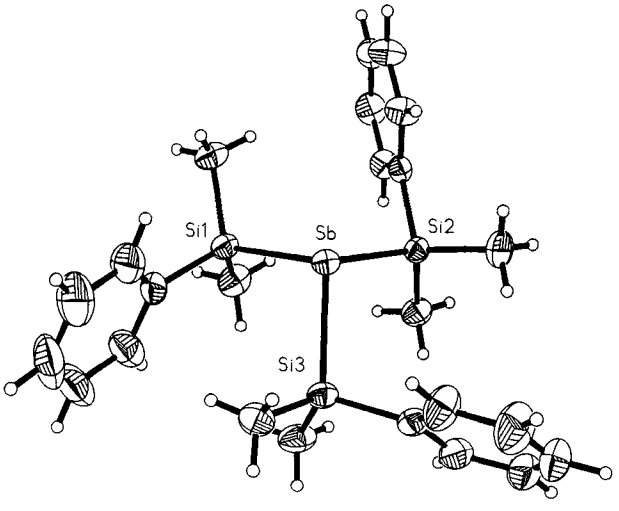


metry is unlikely on steric reasons, free rotation of the silyl groups around the Sb–Si bonds can be assumed in solution.

Crystal and Molecular Structure of Tris(dimethylphenylsilyl)antimony (1)

Compound **1** crystallizes in the triclinic space group $P\bar{1}$ (No. 2) with two formula units in the unit cell (Figure 1). The molecule has no crystallographically imposed symmetry, but the structure approaches closely the symmetry of the point group C_3 (Figure 2). The three independent Sb–Si distances are very similar (Caption to Figure 2). They are also in good agreement with previous data for a silylantimonide and a tetrakis(silyl)diantimony species[6,7]. The Si–Sb–Si angles are in the range of $100 \pm 1°$ and are thus much smaller than the tetrahedral standard.

Figure 2. Molecular structure of $(Me_2PhSi)_3Sb$ (**1**) with atomic numbering (ORTEP, 50% probability ellipsoids). Selected bond lengths [A] and angles [°]: Sb–Si1 2.5601(8), Sb–Si2 2.5543(8), Sb–Si3 2.5619(8); Si1–Sb–Si2 100.18(3), Si2–Sb–Si3 100.76(3), Si1–Sb–Si3 99.81(3)



The Si–Sb–Si angle in $(H_3Si)_3Sb$ in the gas phase was determined[2] to be as small as $88.6 \pm 0.2°$, even smaller than in stibane H_3Sb (91.3°)[23]. This difference of more than 10° relative to compound **1** is remarkable, and an explanation based on steric effects alone is not very convincing. Theoretical calculations on an advanced level are necessary to clarify this point.

The relative orientation of the three dimethylphenylsilyl groups at the antimony atom is all-staggered, with each phenyl group placed between two methyl groups of a neighboring silyl group. If the molecule were fixed in this conformation, the methyl groups would be diastereotopic. The NMR data have shown, however, that in solution the methyl groups are isochronous, indicating virtually uninhibited rotation.

In summary, the present study has shown that tris(silyl)-antimony compounds are no exception in that they adopt a pyramidal heavy-atom skeleton as found for all tris(silyl)pnicogen species except for the trisilylamines. The title compound **1** can be obtained in a pure, crystalline form and is a valuable starting material for preparative studies.

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Experimental

All experiments were performed under carefully purified and dried nitrogen, preferably in an automatized and monitored glove box. Solvents and glassware were treated accordingly. – MS: Varian MAT 311A. – NMR: Jeol GX 400, TMS as internal standard.

Tris(dimethylphenylsilyl)antimony (**1**): A mirror of sodium metal is generated on the inner surface of a round-bottom flask by gently heating and shaking 3.4 g of sodium (0.15 mol) in the reaction vessel. 6.0 g of antimony powder (0.05 mol) and a few crystals of naphthalene are placed into the flask and covered with 200 ml of dry tetrahydrofuran, which is then heated at reflux for 20 h. After cooling to ambient temp. 25.0 g of chlorodimethylphenylsilane (Fluka; 0.15 mol) is added dropwise with stirring, and the mixture is refluxed for 5 h. The dark, turbid solution thus obtained is concentrated in vacuo. 100 ml of pentane is added, the mixture is filtered through a glass frit, and the filtrate evaporated to dryness in vacuo. The remaining gray solid is washed with 50 ml of diethyl ether, taken up in dry benzene, and crystallized by slow solvent evaporation in the glove box at +20°C. Colorless crystals, m.p. 98°C (in a sealed capillary, uncorrected), yield 9.1 g (35%). – NMR: see text. – MS, pos. FAB, *m/z:* 528.4 (100%) for the most abundant isotope combination of M^+; neg. FAB, *m/z:* 391.1 (100%) for $[M-SiPhMe_2]^-$. – $C_{24}H_{33}SbSi_3$ (527.5): calcd. C 54.64, H 6.30; found C 54.94, H 6.88.

Crystal Structure Determination of **1**: The selected crystal was mounted in a glass capillary. Graphite-monochromated Mo-K_α radiation was used. The structure was solved by direct methods (SHELXTL-PC). The final cell data and specific data collection parameters are summarized in Table 1. Further details have been deposited at the Fachinformationszentrum Karlsruhe GmbH, D-76344 Eggenstein-Leopoldshafen, Germany, and may be obtained on quoting the names of the authors, the journal citation, and the depository number CSD-58874.

Table 1. Crystallographic data for tris(dimethylphenylsilyl)antimony (**1**)

$C_{24}H_{33}SbSi_3$ (527.52) crystal system: triclinic, space group (No.) $P\bar{1}$ (2), a = 6.626(1), b = 13.409(1), c = 14,836(1) Å, α = 87.37(1), β = 89.65(1), γ = 88.75(1)°, V = 1316.4 Å^3, $\rho_{calcd.}$ = 1.331 gcm^{-3}, Z = 2, $F(000)$ = 540, μ(Mo-K_α) = 11.9 cm^{-1}, crystal dimension 0.25/0.3/0.35 mm, T = −62°C, diffractometer Enraf Nonius CAD4, scan Θ-Θ, *hkl* range +8/±16/±18, measured reflections 5704, unique reflections 5651, reflections in least squares 5651, refined parameters 253, H atoms (found/calcd.) −/33, $wR2$* = 0.1204, R** = 0.0286 for 5137 reflections with $F > 4\sigma(F)$, weighting scheme *** a = 0.0504/b = 1.2695, ρ_{fin}(max/min) 1.402/−0.525 eÅ^{-3}

* $wR2 = \sqrt{\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2}$. − ** $R = \sum \| F_o | - | F_c \| / \sum | F_o |$. −

*** $w = \dfrac{q}{\sigma^2(F_o^2) + (a \cdot p)^2 + b \cdot p}$, $p = \dfrac{\mathrm{Max}(F_o^2, 0) + 2 \cdot F_c^2}{3}$.

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