# Synthesis and Crystal Structures of Antimony(III) Complexes With a Bis(amino)silane Ligand

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**Abstract.** Bis(amino)silane bearing bulky substituents on nitrogen, LH<sub>2</sub> [L = Me<sub>2</sub>Si(NDipp)<sub>2</sub>, Dipp = 2,6-diisopropylphenyl] was reacted with *n*BuLi (ratio 1:1 and 1:2) in toluene. The Me<sub>2</sub>Si(LiNDipp)<sub>2</sub> was treated with SbCl<sub>3</sub> in a 1:1 ratio to yield the four-membered SiN<sub>2</sub>Sb ring compound of composition [ $\eta^2(N,N)$ -Me<sub>2</sub>Si(NDipp)<sub>2</sub>SbCl] (1).

### Introduction

In recent years silicon containing heteroatomic compounds attract much research interest.<sup>[1]</sup> Moreover metal compounds supported by chelating bis(imido) ligands have been reported by *Brookhart* et al. and *Gibson* et al. They were used for the polymerization of olefins showing excellent activities.<sup>[2]</sup> Bis(a-mino)silane Me<sub>2</sub>Si(ArNH)<sub>2</sub> could serve as a very useful chelating ligand and may have a marked influence on the activity of the resulting complex in catalysis due to the presence of the silicon atom close to the ligating nitrogen atoms.<sup>[3]</sup>

The Si-N bonds in bis(amino)silane are rather strong, while it is desirable to attach bulky R groups to the silicon and nitrogen atoms to achieve increased kinetic stability of the lowcoordinate metal. There are a few examples reported, such as:  $[Me_2Si(NDipp)_2]ZrCl_2(THF)_2$ ,<sup>[4]</sup> { $Me_2Si(NDipp)_2$ }<sub>x</sub> $M_y$  (M =Mo, Zn, Mn, Cd),<sup>[5]</sup>  $[iPr_2Si(NDipp)_2]M$ : (M = Ge, Sn),<sup>[6]</sup>  $[\eta^2 -$ (N,N)-Me<sub>2</sub>Si(NDipp)<sub>2</sub>M·nTHF] (M = Ca, Sr, Ba),<sup>[7]</sup> [Ph<sub>2</sub>Si- $(NDipp)_{2}$ Sn,<sup>[8]</sup> { $[Me_{2}Si(NDipp)_{2}]Mg$ }<sub>2</sub>,<sup>[9]</sup> [(2,6-Et<sub>2</sub>C<sub>6</sub>H<sub>3</sub>Ni)  $(2,6-\text{Et}_2\text{C}_6\text{H}_3\text{NH})\text{SiPh}_2]$ ,<sup>[10]</sup> [ $\eta^2$ -(*N*,*N*)-*R*<sub>2</sub>Si(DippN)<sub>2</sub>*M*] (*M* = Ge, Sn, Pb),<sup>[11]</sup> { $(Me_2Si)[(2,6-R^1_2-4-R^2-C_6H_2)N]_2$ } LnN(SiMe\_3)\_2-(THF) (Ln = Yb, Y, Eu, Sm, Nd),<sup>[12]</sup> and [(Ph<sub>2</sub>Si(Nar)<sub>2</sub>)<sub>2</sub>Eu-{K(THF)<sub>2</sub>}<sub>2</sub>].<sup>[13]</sup> These compounds with a variety of backbones were prepared by the salt metathesis reaction of the appropriate dilithiated diamide with  $MCl_n$ . They show a high degree of thermal stability compared to the corresponding species with bulky substituents both at the silicon and the nitrogen

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[b] Institut für Anorganische Chemie Georg-August-Universität Göttingen Tammannstrasse 4 37077 Göttingen, Germany The mono lithiated bis(amino)silane was used to synthesize the monodentate heterotetraatomic complex [ $(\eta^1-Me_2SiNDipp)NHDippSbCl_2$ ] (2) by the reaction with SbCl<sub>3</sub>. The complexes were characterized by <sup>1</sup>H and <sup>13</sup>C NMR, elemental analysis, IR, and single-crystal X-ray structural analysis.

atoms. However most of the reported compounds contain two ligands, whereas those with one ligand are rare. Herein, we report on two Sb<sup>III</sup> compounds with a bis(amino)silane type as mono and bidentate ligand, respectively.

## **Experimental Section**

**General Procedures:** All manipulations were carried out in a purified nitrogen atmosphere using Schlenk techniques or inside a Mbraun MB 150-GI glovebox. All solvents were distilled from Na/benzophenone ketyl prior to use. LH<sub>2</sub> was prepared as described in the literature.<sup>[4]</sup> Commercially available chemicals were purchased from J&K chemical or Aldrich and used as received. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded with a Varian 400 spectrometer. Melting points were measured in sealed glass tubes and are not corrected. Elemental analyses were performed with a Elementar Vario Micro Cube.

 $[\eta^{2}(N,N)-Me_{2}Si(NDipp)_{2}SbCl]$  (1): LH<sub>2</sub> (0.410 g, 1 mmol) was dissolved in toluene (20 mL) and 2 equiv. of nBuLi (1.6 M in hexane, 1.3 mL, 2.0 mmol) were added drop by drop at 0 °C via syringe. The mixture was allowed to warm to room temperature. The suspension was stirred for 6 h at room temperature and further cooled to 0 °C, anhydrous SbCl<sub>3</sub> (0.23, 1.0 mmol) in toluene (5 mL) was added drop by drop (Scheme 1). The solution was allowed to warm to room temperature and stirred for 24 h. The solvent was removed in vacuo and the obtained solid was extracted with n-hexane (20 mL). The extraction was filtered. The filtrate was reduced in volume in vacuo and stored at -35 °C in a freezer for crystallization. Product 1 was isolated as colorless crystals. Yield: 0.50 g (88%). Mp: 171-172 °C. C26H40ClN2SbSi (565.89): calcd. C 55.18; H 7.12; N 4.95 %; found C 56.02; H 7.26; N 4.82%. <sup>1</sup>H NMR (400.18 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta = 0.34$  (s, 3 H, SiMe<sub>2</sub>), 7.14–7.37 (m, 6 H, Ar–H), 3.81–4.22 [br., 4 H, CH(CH<sub>3</sub>)<sub>2</sub>], 1.26–1.44 [m, 24 H, CH(CH<sub>3</sub>)<sub>2</sub>], 0.65 (s, 3 H, SiMe<sub>2</sub>) ppm. <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = 147.4, 137.8, 125.1, 123.8 (p-, m-, o-, i-C of Ar), 28.1 (CHMe2), 27.6 (CHMe<sub>2</sub>), 25.5 (CHMe<sub>2</sub>), 3.8 (SiMe<sub>2</sub>), 2.7 (SiMe<sub>2</sub>) ppm. IR (KBr): v = 2966 (s), 1439 (m) cm<sup>-1</sup>.

 $[(\eta^1-Me_2SiNDipp)NHDippSbCl_2]$  (2): The preparation of 2 is like that of 1 except equimolar *n*BuLi (1.6 M in hexane, 0.7 mL, 1.1 mmol)



Scheme 1. Preparation of compounds 1 and 2.

and SbCl<sub>3</sub> (0.23, 1.0 mmol) in toluene were used. Product **2** was isolated as colorless crystals. Yield: 0.49 g (82%). Mp: 143–145 °C. C<sub>26</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>2</sub>SbSi (602.35): calcd. C 51.84; H 6.86; N 4.64%; found C 51.65; H 6.52; N 4.94%. <sup>1</sup>H NMR (400.18 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = 7.18–7.37 (*m*, 6 H, Ar–*H*), 4.64 (*s*, 1 H, N–*H*), 3.87 [*septet*, 1 H, C*H*(CH<sub>3</sub>)<sub>2</sub>], 3.62 [*septet*, 1 H, C*H*(CH<sub>3</sub>)<sub>2</sub>], 3.48 [*septet*, 1 H, C*H*(CH<sub>3</sub>)<sub>2</sub>], 3.11 [*septet*, 1 H, C*H*(CH<sub>3</sub>)<sub>2</sub>], 1.15–1.52 [*m*, 24 H, CH(CH<sub>3</sub>)<sub>2</sub>], 0.31 (*s*, 6 H, SiMe<sub>2</sub>) ppm. <sup>13</sup>C NMR (100.63 MHz, CDCl<sub>3</sub>, 298 K, ppm):  $\delta$  = 147.8, 147.0, 141.2, 137.5, 125.9, 124.4, 123.5, 122.6 (*p*-, *m*-, *o*-, *i*-C of Ar), 29.0, 28.6 (CHMe<sub>2</sub>), 27.2, 26.3, 25.6, 24.2, (CHMe<sub>2</sub>), 3.5 (SiMe<sub>2</sub>) ppm. IR (KBr):  $\tilde{v}$  = 3394 (w, NH), 2966 (s), 1437 (m) cm<sup>-1</sup>.

Single Crystal X-ray Structure Determination and Refinement: The crystallographic data for 1 and 2 were collected with a Rigaku AFC10 Saturn724+ (2×2 bin mode) diffractometer equipped with graphite-monochromated Mo- $K_{\alpha}$  radiation ( $\lambda = 0.71073$  Å). Empirical absorption correction was applied using the SADABS program.<sup>[14]</sup> Structures were solved by direct methods<sup>[15]</sup> and refined by full-matrix least-squares on  $F^2$  using the SHELXL-97 program.<sup>[16]</sup> All non-hydrogen atoms were located by difference Fourier synthesis and refined anisotropically, and hydrogen atoms were included using the riding model with  $U_{iso}$  related to the  $U_{iso}$  of the parent atoms.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-897265 (1) and CCDC-897264 (2) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam. ac.uk).

#### **Results and Discussion**

LH<sub>2</sub> reacts with 2 equiv. of *n*BuLi in toluene for 6 h to LLi<sub>2</sub> without isolation (Scheme 1), then antimony(III) trichloride was added in equimolar amount, which resulted in the product  $[\eta^2(N,N)-Me_2Si(NDipp)_2SbCl]$  (1). The reaction of LH<sub>2</sub> with equimolar amount of *n*BuLi in toluene for 6 h yields L(H)Li, which was treated with antimony(III) trichloride in a molar ratio of 1:1, which resulted in the product  $[(\eta^1-Me_2SiNDipp)]$  NHDippSbCl<sub>2</sub>] (2). Compounds 1 and 2 were isolated after growing colorless crystals from the concentrated *n*-hexane solutions. All compounds are soluble in toluene, benzene, and trichloromethane.

Compounds 1 and 2 were characterized by <sup>1</sup>H and <sup>13</sup>C NMR investigation in CDCl<sub>3</sub> solution, IR, as well as by elemental analysis. In the <sup>1</sup>H NMR spectrum, compound 1 exhibits two resonances for the Si $Me_2$  protons ( $\delta = 0.34$  and 0.65 ppm) and one broad resonance for the CHMe<sub>2</sub> protons in the range 3.81– 4.22 ppm with the intensity of 3:2, showing the characteristic bis(amino)silane skeleton. Compound 2 exhibits Si $Me_2$  protons ( $\delta = 0.31$  ppm), four resonances for the CHMe<sub>2</sub> ( $\delta = 3.11, 3.48,$ 3.62, 3.87 ppm) with equal intensity, and one sharp resonance for the N–H proton ( $\delta = 4.64$  ppm), showing the characteristic aminosilane skeleton.

Compound 1 crystallizes in the orthorhombic space group  $Pna2_1$  with one molecule in the symmetric unit.<sup>[17]</sup> Compound 2 crystallizes in the triclinic space group  $P_1$  with one molecule in the asymmetric unit.<sup>[18]</sup>

The molecular structure of **1** is shown in Figure 1. Selected bond lengths and bond angles are listed in Table 1.



Figure 1. Molecular structure of 1. Thermal ellipsoids are drawn at 50% level, and the hydrogen atoms are omitted for clarity.

Table 1. Selected	bond lengths //	Å and angles /	<sup>o</sup> for com	pound 1.

Sb1-N1	2.018(4)	Sb1-N2	2.029(5)
Sb1-Cl1	2.3899(17)	Si1-N1	1.754(5)
Si1-N2	1.763(5)	N1-Sb1-N2	74.83(18)
N1-Si1-N2	88.7(2)	N1-Sb1-Cl1	98.69(17)
N2-Sb1-Cl1	101.73(13)	Si1-N1-Sb1	98.6(2)
Si1-N2-Sb1	97.9(2)		

Compound 1 adopts a  $N_2SiSb$  four-membered ring with trigonal planar coordinated nitrogen atoms. The  $SiN_2Sb$  fourmembered ring is essentially planar with the sum of inner angles of 360.03°. The bond angles around the antimony atom



of N1–Sb1–N2 (74.83°), N1–Sb1–Cl1 (101.73°), and N2–Sb1–Cl2 (98.69°) are highly distorted and could be described as a quasi-tetrahedral arrangement. The angle of N1–Sb1–N2 (74.83°) is much sharper when compared with the one in a regular tetrahedon (109°28′). This might be due to the SiN<sub>2</sub>Sb ring strain. Compound **1** presents a rare antimony heterocycle featuring a N<sub>2</sub>SiSb core structurally characterized by a X-ray single crystal structural investigation.

The molecular structure of **2** is shown in Figure 2. Selected bond lengths and bond angles are listed in Table 2. In the structure of compound **2** the antimony atom is coordinated to one nitrogen atom of the ligand, forming a complex with an acyclic N–Si–N–Sb core. The Sb–N1 bond length in **2** is 2.029 Å, whereas that of Sb–N2 is 2.66 Å, which demonstrates that there is no bonding between Sb and N2. The N1–Si–N2 angle is 97.06° in **2** and 88.7° in **1**, the Si–N–Sb angle is 110.35° in **2** and 98.25° in **1**, which shows the open structure of the N<sub>2</sub>SbSi moiety in **2**. The N–Sb–Cl angle is 95.94° in **2**, which is a little smaller when compared with that of 100.21° in **1**. To the best of our knowledge **2** is the first antimony(III) compound supported by a bis(amino)silane monodentate ligand.



Figure 2. Molecular structure of 2. Thermal ellipsoids are drawn at 50% level, and the hydrogen atoms (except N-H) are omitted for clarity.

 Table 2. Selected bond lengths /Å and angles /° for compound 2.

Sb1–N1	2.0294 (17)	Sb1-Cl1	2.3905(8)
Sb1-Cl2	2.4077(8)	Si1-N1	1.7353(18)
Si1-N2	1.775(2)	N2–H2n	0.74(2)
Cl1-Sb1-Cl2	93.79(3)	N1-Si1-N2	97.06(9)
N1-Sb1-Cl1	95.12(5)	N1-Sb1-Cl2	96.76(5)
Si1-N1-Sb1	110.35(8)		

#### Conclusions

We have synthesized and characterized two antimony(III) chloride complexes with an aminosilane ligand. One of the complexes exhibits a  $SiN_2Sb$  four-membered ring, whereas the second features an acyclic N–Si–N–Sb core. Both complexes were characterized by single-crystal X-ray structural analysis.

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- 17] Crystal data for 1:  $C_{26}H_{40}CIN_2SbSi$ , Mr = 565.89, orthorhombic, space group  $Pna2_1$ , a = 17.327(3) Å, b = 8.7112(13) Å, c = 36.648(3) Å,  $a = \beta = \gamma = 90^\circ$ , V = 5531.5(12) Å<sup>3</sup>, Z = 8,  $\rho_{calcd} = 1000$

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1.359 g·cm<sup>-3</sup>, *F*(000)= 2336, 2.35 ≤ *θ* ≤ 30.02, of 33087 reflections collected, 15047 were independent, *R*(int)= 0.0474, *R*<sub>1</sub> = 0.0641, *wR*<sub>2</sub> = 0.1548 [*I* > 2*σ*(*I*)); The residual electron density: 5.050/–1.877 e·Å<sup>-3</sup>.

[18] Crystal data for **2**: C<sub>26</sub>H<sub>41</sub>Cl<sub>2</sub>N<sub>2</sub>SbSi, *Mr* = 602.35, triclinic, space group *P*<sub>1</sub>, *a* = 8.316(2) Å, *b* = 9.705(3) Å, *c* = 18.069(6) Å, *a* = 91.953(6)°,  $\beta$  = 94.094(6)°,  $\gamma$  = 91.674(5)°, *V* = 1452.9 (7) Å<sup>3</sup>, *Z* = 2,  $\rho_{calcd.}$  = 1.377 gcm<sup>-3</sup>, *F*(000)= 620, 2.10  $\leq \theta \leq$  30.02, of

16801 reflections collected, 8294 were independent, R(int)= 0.0335,  $R_1 = 0.0336$ ,  $wR_2 = 0.0765$  [ $I > 2\sigma(I)$ ); The residual electron density: 0.673/–1.140 e·Å<sup>-3</sup>. Command "twin" was used to revise the possible racemic twin of the structure, so there's no s. u. given for the Alert Level A in the checkcif file.

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