# Syntheses of the Antimonides $R_2Sb^-$ (R = Ph, Mes, *t*Bu, *t*Bu<sub>2</sub>Sb) and $Sb_7^{3-}$ by Reactions of Organoantimony Hydrides or *cyclo*-(*t*BuSb)<sub>4</sub> with Li, Na, K, or BuLi

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Dedicated to Professor Gerd-Volker Röschenthaler on the Occasion of his 60th Birthday

**Abstract.** Reactions of R<sub>2</sub>SbH with BuLi at -70 °C in tetrahydrofuran (thf) lead to [R<sub>2</sub>SbLi(thf)<sub>3</sub>] [R = Ph (1) or R = Mes (2)]. The antimonides [*t*Bu<sub>2</sub>SbK(pmdeta)] (3) (pmdeta = pentamethyldiethylenetriamine), [Li(tmeda)<sub>2</sub>][*t*Bu<sub>4</sub>Sb<sub>3</sub>]·benzene (4) (tmeda = tetramethylethylenediamine), and [*t*Bu<sub>4</sub>Sb<sub>3</sub>Na(tmeda,thf)] (5) result from the reduction of *cyclo*-(*t*BuSb)<sub>4</sub> by Li, Na, or K with pmdeta or tmeda in thf. The primary stibanes RSbH<sub>2</sub> [R = Mes (6), 2-

### Introduction

Alkalimetal diorgano antimonides,  $R_2SbM$  (R = alkyl, aryl) are well known reagents which are prepared by metalation of secondary stibanes, R<sub>2</sub>SbH with organo lithium compounds or by reactions of tertiary stibanes or distibanes with alkali metals [1-3]. Antimony mono anions result also from reactions of cyclo-(tBuSb)<sub>4</sub> with alkali metals. Antimonides are often used in situ for further reactions, however with auxiliary ligands also crystals are obtained. Crystal structures were determined for salt like compounds with separated antimonide anions, eg [Li(12-crown- $(4)_{2}$ [Ph<sub>2</sub>Sb]·<sup>1</sup>/<sub>3</sub>thf [4], [Li(12-crown-4)<sub>2</sub>][Ph<sub>4</sub>Sb<sub>3</sub>]·thf [4], [K(pmdedta)<sub>2</sub>][tBu<sub>4</sub>Sb<sub>3</sub>] [5], and for complexes with coordination of antimonido ligands on the alkali metal centers,  $[(Me_3Si)_2SbLi(dme)]$  (dme = 1,2-dimethoxyethane) [6],  $[RR'SbLi(thf)_2], RR'SbNa(tmeda) [R = (Me_3Si)_2CH,$  $R' = 2-(Me_2NCH_2)C_6H_4$  [7], [(*t*Bu<sub>2</sub>Sb)<sub>2</sub>SbM(pmdeta)] (M = Na, K) [8],  $[(tBu_2Sb)(tBu)SbK(pmdeta)]$  [8],  $[(CyP)_4SbNa(tmeda)(Me_2NH)]$  (Cy = C<sub>6</sub>H<sub>11</sub>) [9]. The latter complex and  $[{Sb(PCy)_3}_2Li_6(Me_2NH)_6]$  decompose to the Zintl compounds  $[Sb_7Na_3(tmeda)_3(thf)_3],$ [Sb<sub>7</sub>Li<sub>3</sub>(HNMe<sub>2</sub>)<sub>6</sub>] and [Sb<sub>7</sub>Li<sub>3</sub>(tmeda)<sub>3</sub>]·toluene [9-11].  $[Sb_7Na_3(2,2,2-crypt))_3]$  and  $[Sb_7K_3(2,2,2-crypt))_3 \cdot 2en]$  are formed from alkalimetal/antimony alloys [12, 13].

Very little is known of alkali metal monoorgano antimonides or related species [1-3]. Metalation of the stable stibane RSbH<sub>2</sub> (R =  $[2,4,6-iPr_3C_6H_2]_2C_6H_3$ ) with BuLigives RSb(Li)H [14]. Complex mixtures of lithium phenylantimonides were obtained from PhSbH<sub>2</sub> and organoli-

Institut für Anorganische und Physikalische Chemie, Universität Bremen, 28334 Bremen, Germany Fax: + 49/(0)421/2184042 E-mail: breunig@chemie.uni-bremen.de  $(Me_2NCH_2)C_6H_2$  (7)] are synthesized by reactions of RSbCl<sub>2</sub> with LiAlH<sub>4</sub>. PhSbH<sub>2</sub> reacts with BuLi, and tmeda in toluene to give  $[Sb_7Li_3(tmeda)_3]$ ·toluene (8).  $[Sb_7Na_3(pmdeta)_3]$ ·toluene (9) is obtained from PhSbH<sub>2</sub>, Na in liqu. NH<sub>3</sub>, pmdeta and toluene. Crystal structures are reported for 1–5 and 9.

Keywords: Antimony; Alkali metals; Hydrides

thium reagents [15]. PhSbNa<sub>2</sub> and (PhSb)<sub>2</sub>Na<sub>2</sub> are produced by reactions of PhSbH<sub>2</sub> or (PhSb)<sub>6</sub>·C<sub>6</sub>H<sub>6</sub> and sodium in liquid ammonia [15, 16].

In the course of investigations of organometallic compounds with Sb-alkali metal bonds [7-8] we studied reactions of organoantimony hydrides and cyclostibines with Li, Na, K or BuLi leading to derivatives of Sb<sub>7</sub><sup>3-</sup> and organoantimony mono anions.

#### **Results and Discussion**

Solutions of Ph<sub>2</sub>SbLi or Mes<sub>2</sub>SbLi were prepared by metalation of Ph<sub>2</sub>SbH or Mes<sub>2</sub>SbH with *n*BuLi in thf [4, 17, 18]. Cooling concentrated solutions gave red, air sensitive crystals of [Ph<sub>2</sub>SbLi(thf)<sub>3</sub>] (1), or [Mes<sub>2</sub>SbLi(thf)<sub>3</sub>] (2). The novel complexes are stable only in an inert atmosphere at low temperatures. They decompose above 29 °C (1) or 36 °C (2) with formation of black solids. The crystal structures of 1 and 2 consist of discrete R<sub>2</sub>SbLi(thf)<sub>3</sub> molecules with coordination of the antimony atoms on the lithium centers (Figures 1 and 2). In crystals of 2 there are two independent molecules with almost similar bond lengths and angles.

The antimony atoms have a trigonal pyramidal geometry ( $\Sigma$ (bond angles at Sb)  $\approx 289^{\circ}$  in 1 and 307° in 2), while the lithium atoms are in tetrahedral environments. The Sb-Li bond lengths [2.881(4) Å in 1 and 2.945(13), 2.893(15) Å in 2] correspond well to values for the Sb-Li bond lengths found in [(Me<sub>3</sub>Si)<sub>2</sub>SbLi(dme)], 2.933(4) [6], [Sb<sub>7</sub>Li<sub>3</sub>(HNMe<sub>2</sub>)<sub>6</sub>], 2.90(2) – 2.90(2) [10], and [Sb<sub>7</sub>Li<sub>3</sub>-(tmeda)<sub>3</sub>]  $\cdot$  toluene, 2.86(2) – 2.90(2) Å [10]. The geometries of the diarylantimony groups in 1 and 2 and in [Li(12-crown-4)<sub>2</sub>][Ph<sub>2</sub>Sb]·<sup>1</sup>/<sub>3</sub>thf [4] and [Mes<sub>2</sub>SbCuPMe<sub>3</sub>]<sub>2</sub> [17] are also similar.

 $[(tBu_2Sb)K(pmdeta)]$  (3) was obtained by reacting *cyclo*-(tBuSb)<sub>4</sub> with pieces of potassium in refluxing thf for 2 h 45', addition of pmdeta, and removal of the solvent.

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Figure 1 Structure of 1 in the crystal; the ellipsoids represent 40 % probability; selected bond lengths/Å and angles/°:



Figure 2 Structure of one of the independent molecules in the asymmetric unit of 2 in the crystal; the ellipsoids represent 40 % probability; selected bond lengths/Å and angles/°:

Shorter reaction times lead to derivatives of  $tBu_4Sb_3^-$  and  $tBu_3Sb_2^-$  in the sequence of reactions described in Scheme 1. The progress of the reaction can be monitored by <sup>1</sup>H-NMR spectra of samples taken from the reaction mixture

[8]. The <sup>1</sup>H-NMR signal of  $(tBu_2Sb)K$  in C<sub>6</sub>D<sub>6</sub> appears at  $\delta = 1.58$ .

3 is a red-brown solid, which is air and moisture sensitive, but stable in an inert atmosphere. Crystals were grown by cooling thf solutions at -28 °C. The structure of 3 (Figure 3) was determined by single crystal X-ray structure analysis.

The structure consists of polymers where  $tBu_2Sb$  groups and pmdeta-K units are in bridging positions between each other and (Sb-K)<sub>x</sub> zig-zag-chains result. The coordination around the Sb atom is distorted tetrahedral. The Sb-K bond lengths are 3.686(2) and 3.705(2) Å. These values lie in the range of the Sb-K bond lenghts found in  $[(tBu_2Sb)_2SbK(pmdeta)],$ 3.997(6) 3.833(6), and  $[tBu_3Sb_2K(pmdeta)]$  3.5655(9) Å [8]. The reduction of  $cyclo-(tBuSb)_4$  with formation of  $[(tBu_2Sb)_2Sb]^-$  is also achieved by lithium or sodium in tetrahydrofuran. The reaction time is however much longer for Li (3 d) than for K (2 h) or Na (4 h). Crystals of  $[\text{Li}(\text{tmeda})_2][(t\text{Bu}_4\text{Sb}_3)] \cdot \text{ben-}$ zene (4) and  $[(tBu_4Sb_3)Na(tmeda)(thf)]$  (5) are obtained after addition of tmeda and cooling. The structures of 4 and 5 are shown in the Figures 4 and 5.

Crystals of 4 consist of two pairs of well separated  $[Li(tmeda)_2]^+$  and  $tBu_4Sb_3^-$  ions and non coordinating benzene molecules. The coordination sphere of the Li<sup>+</sup> ions is fully occupied by the tmeda ligands. The structure of 5 contains discrete molecular complexes where the triantimonide ligands are coordinated to the sodium atoms through both terminal antimony atoms. The Sb<sub>3</sub>Na heterocycle in 5 is almost planar; the Na-Sb-Sb/Sb-Sb-Sb dihedral angle is 175.5°. The bond lengths and angles [4, Sb-Sb 2.768(1)-2.771(1) Å; Sb<sub>3</sub> 89.37(1)°; **5**, Sb-Na 3.241(3), 3.429(3) Å; Sb-Sb 2.763(1), 2.754(1) Å, Sb<sub>3</sub> 88.33(3)] are similar with the corresponding values found in  $[K(pmdeta)_2][(tBu_2Sb)_2Sb]$  [Sb-Sb 2.7643(9), 2.7669(7) Å, Sb<sub>3</sub> 86.23(3)°] [5] and  $[(tBu_2Sb)_2SbNa(pmdeta)]$  [Sb-Na 3.304(2), 3.225 (2); Sb-Sb 2.720(8) - 2.776(2) Å; Sb<sub>3</sub> 89.80(7), 91.4(2)°] [8].

The primary stibanes  $RSbH_2$  [R = Ph, Mes (6), 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>2</sub> (7)] were prepared by reaction of the corresponding dichlorides with LiAlH<sub>4</sub> in Et<sub>2</sub>O. 6 and 7 are light and air sensitive colourless liquids, which are unstable at room temperature but stable at -30 °C in an inert atmosphere in absence of light. They were characterized by <sup>1</sup>H-NMR [ $\delta$  SbH 3.11 (6), 4.43 (7)], IR [ $\nu$  SbH 1863 (6), 1806 (7) cm<sup>-1</sup>] and mass spectrometry. Preliminary data of a crystal structure analysis of 6 were reported recently [19].

The reaction of a solution of PhSbH<sub>2</sub> in thf with *n*BuLi in hexane (molar ratio 1:2) and tmeda in toluene in the temperature range -70 to 0 °C leads to the formation of red solutions. Crystallisation at -28 °C gives red crystals of [Sb<sub>7</sub>Li<sub>3</sub>(tmeda)<sub>3</sub>] toluene (**8**) in approximately 60 % yield. This reaction provides a novel low temperature access to this Zintl compound. We have redetermined the structure of **8** and found conformity with the published data [10]. The mechanism of the formation of **8** is not known. Attempts to stabilize intermediates of the metalation by the use of primary stibines [**6**, **7**, (Me<sub>3</sub>Si)<sub>2</sub>CHSbH<sub>2</sub>] which provide better



Scheme 1



Figure 3 Part of the zig-zag-chain structure of 3 in the crystal; the ellipsoids represent 40 % probability; selected bond lengths/Å and angles/°:

sterical protection were not successful, compound **8** being the only isolated product [19]. Red crystals of  $[Sb_7Na_3(pmdeta)_3]$ ·toluene (**9**) were obtained by reacting PhSbH<sub>2</sub> with sodium inliquid ammonia and pmdeta in toluene. The structure of **9** was determined by single crystal X-ray diffraction. The structure is shown in Figure 6.

Crystals of **9** contain discrete cage molecules in which  $\text{Sb}_7{}^{3-}$  ions are coordinated through the equatorial Sb atoms to three pmdeta solvated Na<sup>+</sup> cations. The Sb-Na bond lengths range from 3.217(5) to 3.273(4) Å and the values for the Sb-Sb bond lengths lie between 2.737(1) and 2.880(2) Å. The other known complex of  $\text{Sb}_7{}^{3-}$  with ion-contacts between Na and Sb is  $[\text{Sb}_7\text{Na}_3(\text{tmeda})_3(\text{thf})_3]$ . In the latter complex there is an asymmetrical coordination of the Na<sup>+</sup> cations and two of them form weak interactions with the apical Sb atom [9]. In **9** the arrangement of the coordinating Sb atoms and the Na<sup>+</sup> ions is almost planar.



**Figure 4** Structure of the [Li(tmeda)<sub>2</sub>] [ $tBu_4Sb_3$ ] unit in crystals of **4**; the ellipsoids represent 40 % probability; selected bond lengths/ Å and angles/°:

#### Conclusion

The metalation of Ph<sub>2</sub>SbH or Mes<sub>2</sub>SbH with BuLi is a straight forward process leading to crystalline samples of diarylantimonides. By contrast metalations of  $RSbH_2$  (R = Ph, Mes, 2-(Me<sub>2</sub>NCH<sub>2</sub>)C<sub>6</sub>H<sub>2</sub>, (Me<sub>3</sub>Si)<sub>2</sub>CH) result in the migration of the organic groups, formation of Sb-Sb bonds, and open a convenient low temperature route to Zintl compounds containing the  $Sb_7^{3-}$  ion. Further investigations are necessary to gain insight into this multi step process. Much more is known of the reactions of the cyclostibane cyclo-(tBuSb)<sub>4</sub> with alkali metals, where the fission of Sb-Sb bonds is accompanied by alkyl group migration reactions and the successive formation of tri-, bi- and mononuclear antimonides is well documented. The crystallographic characterization of dianionic organo antimonides remains a challenge for future research. The organo mono antimonides and the trianionic  $\text{Sb}_7^{3-}$  ions are good ligands for the



**Figure 5** Structure of the  $[(tBu_4Sb_3)Na(tmeda)(thf)]$  unit in crystals of **5**; the ellipsoids represent 40 % probability; selected bond lengths/Å and angles/°:

 $\begin{array}{l} & \text{Sb}(1)\text{-C}(1)\ 2.232(7);\ \text{Sb}(1)\text{-C}(5)\ 2.238(7);\ \text{Sb}(1)\text{-Sb}(2)\ 2.7631(10);\ \text{Sb}(1)\text{-Na}(1)\\ & 3.429(3);\ \ \text{Sb}(3)\text{-C}(13)2.233(9);\ \ \text{Sb}(3)\text{-C}(9)2.235(8);\ \ \text{Sb}(2)\text{-Sb}(3)2.7542(8);\\ & \text{Sb}(3)\text{-Na}(1)3.241(3);\ \text{Na}(1)\text{-O}(1)\ 2.275(6);\ \text{Na}(1)\text{-N}(1)\ 2.440(7);\ \text{Na}(1)\text{-N}(2)\\ & 2.502(7),\ \ \text{C}(1)\text{-Sb}(1)\text{-C}(5)\ 104.0(3);\ \ \text{C}(1)\text{-Sb}(1)\text{-Sb}(2)\ 102.5(2);\ \ \text{C}(5)\text{-Sb}(1)\\ & \text{Sb}(2)\ 100.7(2);\ \ \text{C}(1)\text{-Sb}(1)\text{-Na}(1)\ 127.6(2);\ \ \text{C}(5)\text{-Sb}(1)\text{-Na}(1)\ 118.6(2);\ \text{Sb}(2)\\ & \text{Sb}(1)\text{-Na}(1)\ 98.19(6);\ \ \text{C}(13)\text{-Sb}(3)\text{-C}(9)\ 104.6(4);\ \ \text{C}(13)\text{-Sb}(3)\text{-Sb}(2)\ 103.3(3);\\ & \text{C}(9)\text{-Sb}(3)\text{-Sb}(2)\ 102.8(2);\ \ \text{C}(13)\text{-Sb}(3)\text{-Na}(1)\ 108.8(3);\ \ \text{C}(9)\text{-Sb}(3)\text{-Na}(1)\\ & 131.2(2);\ \ \text{Sb}(2)\text{-Sb}(3)\text{-Na}(1)\ 102.97(6);\ \ \text{Sb}(3)\text{-Sb}(2)\ \text{-Sb}(1)\ 88.33(3);\ \ \text{O}(1)\text{-Na}(1)\text{$ 



Figure 6 Structure of the  $[Sb_7Na_3(pmdeta)_3]$  unit in the structure of **9** in the crystal; one of the pmdeta ligands is omitted for clarity; the ellipsoids represent 40 % probability; selected bond lengths/Å: Sb(1)-Sb(4) 2.7922(13); Sb(1)-Sb(2) 2.7926(12); Sb(1)-Sb(3) 2.7959(15); Sb(2)-Sb(5) 2.7371(13); Sb(3)-Sb(7) 2.7512(15); Sb(4)-Sb(6) 2.7457(15); Sb(5)-Sb(7) 2.8630(14); Sb(5)-Sb(6) 2.8682(14); Sb(6)-Sb(7) 2.8802(19); Sb(2)-Na(2) 3.225(5); Sb(2)-Na(3) 3.240(5); Sb(3)-Na(2) 3.221(5); Sb(3)-Na(1) 3.231(4); Sb(4)-Na(3) 3.217(5); Sb(4)-Na(1) 3.273(4).

coordination on alkali metal ions. Alkalimetal antimonides with separated ions result only when the coordination sphere of the cations is saturated by efficient multidentate auxiliary ligands.

#### **Experimental Section**

General. Syntheses were carried out under argonusing dried solvents freshly distilled under argon. NMR spectra were recorded

with a Bruker DPX 200 spectrometer. The products 1-8 were characterised by single crystal X-ray diffraction (1-5, 8), NMR, IR, and mass spectrometry. The compounds were not chararacterized by elemental analyses because they are too unstable. The crystal structure measurement and refinement data for 1-5 and 9 are given in Tables 1 and 2. The data were collected on a Siemens P4 four-circle or a Stoe IPDS diffractometer using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). For this purpose the crystals were attached with Kel-F oil to a glass fibre and cooled in a nitrogen stream to 173 K. The structures were solved by direct methods. All non-hydrogen atoms were refined with anisotropic thermal parameters. Structure solutions and refinements were carried out using the software packages SHELX-93 or SHELX-97. 2 was refined as a racemic twin. Diagrams were created using the Diamond program by Crystal Impact GbR. CCDC-246281 (1), -246282 (2), -246285 (3), -246283 (4), -246284 (5) and -246280 (9) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Synthesis of [Ph<sub>2</sub>SbLi(thf)<sub>3</sub>] (1). A solution of Ph<sub>2</sub>SbH (3.00 g, 10.83 mmol) in thf (50 mL) was treated dropwise with *n*-BuLi (6.76 mL, 1.6 M in hexane) at -70 °C. The red solution was warmed to -10 °C with stirring. Reducing the volume of the solution in *vacuo* to 20 mL and cooling overnight at -28 °C gave 4.20 g (78 %) red crystals of 1 (dec. 29 °C).

<sup>1</sup>**H-NMR** (200 MHz, C<sub>6</sub>D<sub>6</sub>): 1.39 (12H, thf), 3.56 (12H, thf), 7.03 – 7.09 (m, 6H, C<sub>6</sub>H<sub>5</sub> – m + p), 7.41 – 7.46 (m, 4H, C<sub>6</sub>H<sub>5</sub>–o).

Synthesis of [Mes<sub>2</sub>SbLi(thf)<sub>3</sub>] (2). A solution of Mes<sub>2</sub>SbH (3.00 g, 8.31 mmol) in 50 mL thf was treated dropwise with *n*-BuLi (5.19 mL, 1.6 M in hexane) at -70 °C. The red solution was warmed to -10 °C with stirring. Reducing the volume of the solution in *vacuo* to 20 mL and cooling overnight at -28 °C gave 2.97 g (61 %) orange crystals of 2 (dec. 36 °C).

<sup>1</sup>**H-NMR** (200 MHz,  $C_6D_6$ ): 1.32 (12H, thf), 2.30 (s, 6H,  $CH_3 - p$ ), 2.73 (s, 12H,  $CH_3 - o$ ), 3.45 (12H, thf), 6.97 (s, 4H,  $C_6H_2 - m$ ).

Synthesis of [( $tBu_2Sb$ )K(pmdeta)] (3). To a solution of *cyclo*-(tBuSb)<sub>4</sub> (1.00 g, 1.4 mmol) in 40 mL thf, 0.30 g (7.7 mmol) small pieces of K were added and stirred with reflux for  $2^{1}/_{2}$  h. To the refluxing solution 0.88 mL (4.2 mmol) pmdeta were added, the redbrown solution was cooled with stirring to r. t. and filtered through a frit covered with kieselgur. Removal of the solvent under reduced pressure gave 0.17 g (15 %) of **3** as a red-brown solid (dec. 113–117 °C). Suitable crystals for X-ray analysis were grown by cooling thf solutions at -28 °C.

<sup>1</sup>**H-NMR** (200 MHz,  $C_6D_6$ ): 1.58 (s, 18H,  $C(CH_3)_3$ ), 2.08 (s, 12H,  $N(CH_3)_2$ ), 2.12 (s, 3H,  $NCH_3$ ), 2.23–2.41 (m, 8H,  $CH_2$ ). <sup>13</sup>C-NMR (50 MHz,  $C_6D_6$ ): 29.59 (s,  $C(CH_3)_3$ ), 31.93 (s,  $C(CH_3)_3$ ), 42.96 (s,  $NCH_3$ ), 45.98 (s,  $N(CH_3)_2$ ), 56.85 (s,  $CH_2$ ), 58.22 (s,  $CH_2$ ).

Synthesis of  $[(tBu_4Sb_3)][Li(tmeda)_2]$ -benzene (4). To a solution of *cyclo*-(tBuSb)<sub>4</sub> (1.00 g, 1.40 mmol) in 40 mL thf 0.97 g (138.6 mmol) Li wire ( $\Phi = 0.6$  mm) were added and stirred with reflux for 3 days. After addition of 0.61 mL (4.13 mmol) tmeda with 0.1 mL benzene and further stirring for 1 h at room temperature, the reaction mixture was filtered through a frit covered with kieselgur. Cooling at -28 °C gives 0.20 g (17 %) of 4 as red crystals (67 - 71 °C dec.).

<sup>1</sup>**H-NMR** (200 MHz,  $C_6D_6$ ): 1.83 (s, 36H,  $C(CH_3)_3$ ), 2.08 (s, 24H,  $N(CH_3)_2$ ), 2.20 (s, 8H,  $CH_2$ ). <sup>13</sup>**C-NMR** (50 MHz,  $C_6D_6$ ): 32.56 (s,  $C(CH_3)_3$ ), 35.42 (s,  $C(CH_3)_3$ ), 48.31 (s,  $N(CH_3)_2$ ), 59.27 (s,  $CH_2$ ).

## Table 1 Data for the X-ray structure determinations of 1 - 3

	1	<b>2</b> <sup>a)</sup>	3
formula	C24H24LiO3Sb	CaoH46Li 03Sb	C17H41KN3Sb
formula weight	499.20	583.36	448.38
colour	red	red	red
temperature/K	173(2)	173(2)	173(2)
crystal size /mm	0.60 x 0.50 x 0.40	0.50 x 0.40 x 0.20	0.60 x 0.30 x 0.10
crystal system	triclinic	monoclinic	monoclinic
space group	ΡĪ	P21	$P2_1/c$
a /Å	9.149(1)	10.079(2)	6.748(1)
b/Å	9.395(1)	18.368(3)	17,901(4)
c /Å	15.957(2)	16.729(2)	20.510(4)
$\alpha /^{\circ}$	95.38(1)		
β /°	100.63(1)	103.27(1)	94.24(3)
γ /°	113.73(1)		
Ż	2	4	4
d calc /g cm <sup>-3</sup>	1.367	1.285	1.205
$\mu/\text{mm}^{-1}$	1.158	0.941	1.287
F(000)	512	1216	936
$\theta$ range /°	2.51-27.50	2.50 - 27.50	3.02 - 27.50
Index ranges	$-11 \le h \le 11$ ,	$-1 \le h \le 13$ ,	$-1 \le h \le 8$ ,
	$-11 \le k \le 11$ .	$-1 \leq k \leq 23$ .	$-1 \le k \le 23$ .
	$-20 \le 1 \le 20^{-1}$	$-21 \le 1 \le 21$	$-26 \le 1 \le 26$
No. of measured data	6635	8887	7626
No. of unique data [R(int)]	5500 [R(int) = 0.0185]	7491 [R(int) = $0.0305$ ]	5652 [R(int) = 0.0386]
Data / restraints / parameters	5500 / 0 / 264	7491 / 2 / 646	5652 / 0 / 213
Absorption correction	DIFABS	DIFABS	DIFABS
R1 $[I > 2\sigma(I)]$	0.0271	0.0377	0.0601
$wR2$ [I>2 $\sigma$ (I)]	0.0694	0.0917	0.1311
R1 (all data)	0.0298	0.0447	0.1239
wR2 (all data)	0.0710	0.0965	0.1576
goodness-of-fit on F <sup>2</sup>	1.054	1.028	1.010
residual density /e.Å <sup>-3</sup>	0.517, -0.744	1.183, -0.920	0.787, -1.295

<sup>a)</sup> **2** was refined as a racemic twin.

## Table 2 Data for the X-ray structure determinations of 4, 5, and 9

	4	5	9
formula	$C_{34}H_{74}LiN_4Sb_3$	C <sub>33</sub> H <sub>68</sub> N <sub>2</sub> NaOSb <sub>3</sub>	C34H77N9Na3Sb7
formula mass	911.16	897.13	1533.27
colour	red	red	red
temperature / K	173(2)	173(2)	173(2)
crystal size /mm	0.70 x 0.40 x 0.10	0.60 x 0.30 x 0.25	0.8 x 0.6 x 0.6
crystal system	monoclinic	monoclinic	orthorhombic
space group	P2/c	$P2_1/n$	P212121
a /Å	17.802(2)	13.345(3)	14.762(7)
b /Å	17.084 (2)	19.079(4)	17.616(2)
c /Å	14.622(2)	16.754(3)	21.908(3)
β /°	93.60(2)	96.28(3)	90
Z	4	4	4
$d_{calc}/g \text{ cm}^{-3}$	1.364	1.405	1.788
$\mu / \text{mm}^{-1}$	1.837	1.931	3.321
F(000)	1848	1808	2936
θ range /°	2.58 - 27.50	2.13-25.00	2.59 - 27.49
index ranges	$-23 \le h \le 23$ ,	$-15 \le h \le 1$ ,	$-18 \le h \le 1$ ,
C	$-22 \le k \le 1$ ,	$-22 \le k \le 1$ ,	$-22 \le k \le 1$ ,
	$-18 \le 1 \le 18$	$-19 \le l \le 19$	$-28 \le 1 \le 1$
no. of measured data	12187	9149	8668
no. of unique data [R(int)]	10095 [R(int) = 0.0234]	7437 [R(int) = 0.0375]	8249 [R(int) = 0.0316]
data / restraints / parameters	10095 / 0 / 404	7437 / 1 / 370	8249 / 0 / 499
absorption correction	DIFABS	DIFABS	DIFABS
R1 $[I>2\sigma(I)]$	0.0386	0.0506	0.0457
$wR2 [I > 2\sigma(I)]$	0.0758	0.0811	0.0876
R1 (all data)	0.0659	0.1135	0.0828
wR2 (all data)	0.0855	0.0981	0.1061
goodness-of-fit on F <sup>2</sup>	1.004	0.998	1.036
residual density /e.Å <sup>-3</sup>	0.785, -0.968	0.463, -0.493	0.622, -0.714

Synthesis of  $[(tBu_4Sb_3)Na(tmeda)(thf)]$ -toluene (5). 1.00 g (1.4 mmol) *cyclo*-(*t*BuSb)<sub>4</sub> was reacted for 4 h with small pieces of Na (0.4 g, 17.4 mmol) in 40 mL thf. Afterwards 0.30 mL (2.06 mmol) tmeda were added and stirred for 1 h until r.t.. After filtration and removal of the solvent under reduced pressure 0.82 g of red solid (78-84 °C dec.) was obtained. After recrystallization from toluene at -28 °C 0.60 g (54 %) of 5 formed as red crystals.

<sup>1</sup>**H-NMR** (200 MHz,  $C_6D_6$ ): 1.77 (s, 36H,  $C(CH_3)_3$ ), 1.95 (s, 4H,  $CH_2$ ), 2.02 (s, 12H, NCH<sub>3</sub>). <sup>13</sup>**C-NMR** (50 MHz,  $C_6D_6$ ): 25.75 (s, thf), 30.42 (s,  $C(CH_3)_3$ ), 34.89 (s,  $C(CH_3)_3$ ), 46.05 (s,  $N(CH_3)_2$ ), 57.77 (s,  $CH_2$ ), 67.80 (s, thf).

Synthesis of MesSbH<sub>2</sub> (6). A solution of  $[2,4,6-(CH_3)_3C_6H_2]SbCl_2$ (2.00 g, 6.43 mmol) in Et<sub>2</sub>O (30 mL) was added dropwise to a cold (-80 °C) suspension of LiAlH<sub>4</sub> (0.52 g, 13.89 mmol) in Et<sub>2</sub>O (20 mL). The mixture was warmed to -10 °C and filtered through a cooled (-10 °C) frit covered with kieselgur. Removal of the solvent under reduced pressure at -10 °C gave 1.42 g (92 %) of  $[2,4,6-(CH_3)_3C_6H_2]SbH_2$  as a white solid unstable at room temperature (m.p. -18 °C; dec. 15-18 °C). Suitable crystals for X-ray diffraction studies were grown by cooling a Et<sub>2</sub>O solution of MesSbH<sub>2</sub> at -28 °C.

<sup>1</sup>**H-NMR** (200 MHz,  $C_6D_6$ ): 2.10 (s, 3H,  $CH_3-p$ ), 2.23 (s, 6H,  $CH_3-o$ ), 3.11 (s, 2H, Sb $H_2$ ), 6.75 (s, 2H,  $C_6H_2-m$ ). <sup>13</sup>C-NMR (50 MHz,  $C_6D_6$ ): 20.88 (s,  $CH_3-p$ ), 27.90 (s,  $CH_3-o$ ), 128.07 (s,  $C_6H_2$ ), 128.29 (s,  $C_6H_2$ ), 137.84 (s,  $C_6H_2$ ), 144.11 (s,  $C_6H_2$ ). **IR** (Et<sub>2</sub>O):  $v_{(Sb-H_1)}$  1863 cm<sup>-1</sup> br. MS (EI, 70 eV) m/z (%): 242 (43) [M<sup>+</sup>], 119 (100) [Mes<sup>+</sup>], 105 (86) [Mes<sup>+</sup>-CH<sub>3</sub>], 91 (40) [Mes<sup>+</sup>-CH<sub>3</sub>], 91 (40) [Mes<sup>+</sup>-CH<sub>3</sub>], 91 (40) [Mes<sup>+</sup>-2CH<sub>3</sub>] Mes = 2,4,6-(CH<sub>3</sub>)<sub>3</sub>C<sub>6</sub>H<sub>2</sub>. **HRMS** (EI, 70 eV): 242.00528 (calcd 242.00555 amu,  $C_9H_{13}Sb^{121}$ ).

Synthesis of  $[2-(Me_2NCH_2)C_6H_4]SbH_2$  (7). A solution of 1.00 g (3.05 mmol) of  $[2-(Me_2NCH_2)C_6H_4]SbCl_2$  in Et<sub>2</sub>O (30 mL) was added dropwise to a cold (-80 °C) suspension of LiAlH<sub>4</sub> (0.25 g, 6.57 mmol) in Et<sub>2</sub>O (20 mL). The mixture was warmed to -30 °C and filtered through a cooled (-30 °C) D4 frit covered with kieselgur. Removal of the solvent under reduced pressure gave 0.68 g (87 %) of  $[2-(Me_2NCH_2)C_6H_4]SbH_2$  as a white powder, unstable at room temperature (m.p. -23 °C; dec. 11-14 °C).

<sup>1</sup>**H-NMR** (200 MHz,  $C_6D_6$ ): 1.98 (s, 6H, N(CH<sub>3</sub>)<sub>2</sub>), 3.18 (s, 2H, CH<sub>2</sub>N), 4.43 (s, 2H, SbH<sub>2</sub>), 6.86 (d, 1H,  $C_6H_4$ ,  ${}^{3}J_{HH} = 7.2$  Hz), 7.19 – 7.32 (m, 2H,  $C_6H_4$ ), 8.03 (d, 1H,  $C_6H_4$ ,  ${}^{3}J_{HH} = 6.7$  Hz).  ${}^{13}$ **C-NMR** (50 MHz,  $C_6D_6$ ): 45.14 (s, N(CH<sub>3</sub>)<sub>2</sub>), 65.46 (s, CH<sub>2</sub>N), 124.27 (s,  $C_6H_4$ ), 126.79 (s,  $C_6H_4$ ), 128.30 (s,  $C_6H_4$ ), 138.56 (s,  $C_6H_4$ ), 145.25 (s,  $C_6H_4$ ). 1R (Et<sub>2</sub>O): v<sub>(Sb-H</sub>) 1806 cm<sup>-1</sup> br. **MS** (EI, 70 eV) *m*/z (%): 255 (65) [RSb<sup>+</sup>], 179 (28) [Me<sub>2</sub>NCH<sub>2</sub>Sb]<sup>+</sup>, 134 (40) [R<sup>+</sup>], 58 (100) [Me<sub>2</sub>NCH<sub>2</sub><sup>+</sup>] R = Me<sub>2</sub>NCH<sub>2</sub>C<sub>6</sub>H<sub>4</sub>.

Synthesis of  $[Sb_7Li_3(tmeda)_3]$ -toluene (8). A solution of 2.00 g (9.95 mmol) PhSbH<sub>2</sub> in 30 mL thfwas cooled to -70 °C and *n*-BuLi (12.44 mL, 1.6 M in hexane) was added *via* syringe. The solution was allowed to warm to 0 °C with stirring. At this temperature tmeda (2.96 mL) in 10 mL toluene was added drop wise and the mixture was stirred for 1 h. Cooling to -28 °C afforded 1.21 g (65 %) red crystals of 8.

Synthesis of  $[Sb_7Na_3(pmdeta)_3]$ -toluene (9). A solution of 2.00 g PhSbH<sub>2</sub> in 30 mL thf was added to 0.22 g (9.56 mmol) Na in 20 mL liquid NH<sub>3</sub> and the colour of the solution became red. After ad-

dition of 2.07 mL (9.94 mmol) pmdeta in 10 mL toluene mixture was allowed to warm to room temperature and ammonia was evaporated. Cooling to -28 °C gave 1.14 g (56 %) of **9** as red crystals.

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