Reactivity of Aluminum Trialkyls R₃Al, Diorganoaluminum Chlorides R₂AlCl (R = Me, Et, *t*-Bu), and Me₂AlH toward Sb(SiMe₃)₃: Synthesis and Structural Characterization of Al−Sb Compounds Containing σ or Dative Bonds

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Reactions of Sb(SiMe₃)₃ with different aluminum trialkyls, R₃Al (R = Me, Et, *t*-Bu), and diorganoaluminum chlorides, R₂AlCl (R = Me, Et, *t*-Bu), in a 1:1 molar ratio are described. Aluminum trialkyls form simple Lewis acid−base adducts, R₃Al←Sb(SiMe₃)₃ (R = Me (**1**), Et (**2**), *t*-Bu (**3**)). Reactions of Me₂AlCl and Me₂AlH lead to the six-membered-ring systems cyclo-[Me(Cl)AlSb(SiMe₃)₂]₃ (**4**) and cyclo-[Me₂AlSb(SiMe₃)₂]₃ (**7**), while the sterically more crowded Et₂AlCl and *t*-Bu₂AlCl form Lewis acid−base adducts of the type R₂AlCl←Sb(SiMe₃)₃ (R = Et (**5**), *t*-Bu (**6**)). The solid-state structures of **2**, **6,** and **7** were determined by single-crystal X-ray diffraction.

Introduction

The potential applications of Sb-containing III−V semiconductors for optoelectronic devices, operating in the infrared region, and high-speed devices has prompted extensive studies of potential precursor systems for these materials.[1] We are particularly interested in the synthesis and structural characterization of AlSb single-source precursors of the type R₃Al←SbR′₃ and [R₂AlSbR′₂]ₓ (x = 2, 3), due to their potential advantages in CVD processes compared to Al and Sb alkyls or hydrides. They are less pyrophoric and toxic, and film growth often is possible at lower temperatures.[1b]

Within the past decade, several synthetic pathways for group 13−15 single-source precursors have been developed and numerous compounds, mainly amides, phosphides, and arsenides, have been synthesized.[2] In contrast, only a handful of group 13 antimonides have been reported. Ga and In antimonides can be prepared by salt elimination, dehalosilylation, and dehydrosilylation reactions.[3] In contrast, organometallic Al−Sb

compounds have been studied to a far lesser extent.[4] Very recently, we reported the synthesis and structural characterization of the novel compounds [R₂AlSb(SiMe₃)₂]₂ (R = Et, *i*-Bu), prepared by dehydrosilylation reactions of Sb(SiMe₃)₃ with the corresponding organoaluminum hydrides R₂AlH in a 1:1 molar ratio.[5] Herein, we report our investigations concerning reactions of Sb(SiMe₃)₃ with R₃Al, R₂AlCl, and Me₂AlH.

Experimental Section

General Considerations. All manipulations were performed in a glovebox under an N₂ atmosphere or by standard Schlenk techniques. Neat Me₃Al, Me₂AlCl, and Et₃Al were purchased from Aldrich and used as received. Sb(SiMe₃)₃,[6] Et₂AlCl,[7] *t*-Bu₃Al,[8] *t*-Bu₂AlCl,[8] and Me₂AlH[9] were prepared by literature methods. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ¹H and ¹³C{¹H} spectra were referenced to internal C₆D₅H (δ(¹H) 7.154, δ(¹³C) 128.0). Mass spectra were recorded on a VG Masslab 12-250 spectrometer in the electron impact mode at 20 eV. Melting points were observed in sealed capillaries and were not corrected. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.[10]

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Table 1. Crystallographic Data and Measurements for Et₃Al←Sb(SiMe₃)₃ (2), *t*-Bu₂AlCl←Sb(SiMe₃)₃ (6), and [Me₂AlSb(SiMe₃)₂]₃ (7)

	2	**6**	**7**
mol formula	$C_{15}H_{42}AlSbSi_3$	$C_{17}H_{45}AlClSbSi_3$	$C_{24}H_{72}Al_3Sb_3Si_6$
fw	455.49	517.98	975.55
cryst syst	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	$Pca2_1$ (No. 29)	$P2_1/n$ (No. 14)
a, Å	14.9677(2)	22.6792(4)	9.5066(2)
b, Å	9.9885(1)	12.1298(1)	20.8121(7)
c, Å	16.9987(3)	20.1905(4)	24.2137(8)
β, deg	91.719(1)	$\alpha = \beta = \gamma = 90$	96.210(2)
V, Å³	2540.24(6)	5554.29(15)	4762.6(2)
Z	4	8	4
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm⁻¹	1.256	1.250	1.909
temp, K	123(2)	123(2)	123(2)
D_{calcd}, g cm⁻³	1.191	1.239	1.361
crystal dimens (mm)	0.35 × 0.35 × 0.20	0.35 × 0.25 × 0.15	0.20 × 0.15 × 0.10
$2\theta_{max}$, deg	56.6	56.6	56.6
total no. of rflns	38 127	59 326	28 108
no. of nonequiv rflns recorded	5401	13003	7613
R_{merge}	0.024	0.040	0.041
no. of params refined	181	415	332
R1,ᵃ wR2ᵇ	0.021, 0.051	0.020, 0.035	0.022, 0.041
goodness of fitᶜ	1.107	0.962	0.802
final max, min Δρ, e Å⁻³	0.424, −0.761	0.473, −0.558	0.777, −0.487

ᵃ R1 = $\Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ (for $I > 2\sigma(I)$). ᵇ wR2 = $\{\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]\}^{1/2}$. ᶜ Goodness of fit = $\{\Sigma[w(|F_o{}^2| - |F_c{}^2|)^2]/(N_{observns} - N_{params})\}^{1/2}$.

General Synthesis of Adducts R₃Al←Sb(SiMe₃)₃. R₃Al (2 mmol) and Sb(SiMe₃)₃ (0.68 g, 2 mmol) were combined in the glovebox. Immediately a colorless solid was formed in quantitative yield. Recrystallization of **1**–**3** from pentane at −30 °C yields colorless crystals. **1**–**3** can be sublimed without decomposition between 50 and 60 °C at 10⁻³ mbar.

Me₃Al←Sb(SiMe₃)₃ (1). Mp: 135−138 °C. Anal. Calcd (found) for C₁₂H₃₆AlSbSi₃: C, 34.86 (33.72); H, 8.78 (8.28). ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ −0.23 (s, 9H, Me), 0.36 (s, 27H, SiMe₃). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ 4.54 (s, SiMe₃). MS (EI, 20 eV): *m/z* (%) 340 (60) [Sb(SiMe₃)₃⁺], 73 (100) [SiMe₃⁺], 72 (35) [AlMe₃⁺].

Et₃Al←Sb(SiMe₃)₃ (2). Mp: 156 °C. Anal. Calcd (found) for C₁₅H₄₂AlSbSi₃: C, 39.55 (39.92); H, 9.29 (9.03). ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ 0.35 (s, 27H, SiMe₃), 0.42 (q, ³J₍H–H₎ = 8.1 Hz, 6H, CH₂), 1.45 (t, ³J₍H–H₎ = 8.1 Hz, 9H, Me). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ 1.73 (s, CH₂), 4.44 (s, SiMe₃), 11.29 (s, Me). MS (EI, 20 eV): *m/z* (%) 340 (80) [Sb(SiMe₃)₃⁺], 114 (30) [AlEt₃⁺], 73 (100) [SiMe₃⁺].

_t_-Bu₃Al←Sb(SiMe₃)₃ (3). Mp: 163 °C. Anal. Calcd (found) for C₂₁H₅₄AlSbSi₃: C, 46.74 (46.24); H, 10.09 (10.13). ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ 0.39 (s, 27H, SiMe₃), 1.31 (s, 27H, *t*-Bu). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ 5.04 (s, SiMe₃), 33.36 (s, CH₃). MS (EI, 20 eV): *m/z* (%) 340 (75) [Sb(SiMe₃)₃⁺], 198 (35) [*t*-Bu₃Al⁺], 73 (100) [SiMe₃⁺].

cyclo-[Me(Cl)AlSb(SiMe₃)₂]₃ (4). A solution of Me₂AlCl (0.19 g, 2 mmol) and Sb(SiMe₃)₃ (0.68 g, 2 mmol) in hexane (50 mL) was heated at reflux for 3 h with stirring, reduced in vacuo to 20 mL, and stored at −30 °C. **4** was obtained as a colorless solid (0.59 g, 85%). Mp: 164 °C. Anal. Calcd (found) for C₂₁H₆₃Al₃Cl₃Sb₃Si₆: C, 24.32 (26.96); H, 6.12 (6.00). ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ −0.09 (s, 3H, Me), 0.36 (s, 18H, SiMe₃). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ 4.48 (s, SiMe₃). MS (EI, 20 eV): *m/z* (%) 839 (1) [M⁺ − 2Me₃Si − Cl − Me (=Al₃Sb₃(SiMe₃)₄Me₂Cl₂⁺)], 592 (25) [Al₃Sb₃(SiMe₃)₂⁺], 534 (30) [Al₃Sb₃(SiMe₃)Me⁺], 446 (5) [Al₃Sb₃⁺], 340 (75) [Sb(SiMe₃)₃⁺], 73 (100) [SiMe₃⁺].

General Synthesis of R₂AlCl←Sb(SiMe₃)₃. R₂AlCl (2 mmol) and Sb(SiMe₃)₃ (0.68 g, 2 mmol) were combined in the glovebox and heated to 120 °C for 20 min. Cooling to 25 °C gave a dark brown solid, which was dissolved in 20 mL of pentane and the solution was filtered. The resulting light yellow solutions of **5** and **6** were reduced to 10 mL and stored at −30 °C, resulting in the formation of colorless crystals of **5** and **6**.

Et₂AlCl←Sb(SiMe₃)₃ (5). The solid was dissolved in pentane (30 mL), and the solution was filtered, reduced in vacuo to 10 mL, and stored at −30 °C, yielding colorless crystals of **5** (0.78 g, 85%). Mp: 101 °C. Anal. Calcd (found) for C₁₃H₃₇AlClSbSi₃: C, 32.28 (32.65); H, 8.01 (7.94). ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ 0.37 (s, 27H, SiMe₃), 0.46 (q, 4H, CH₂), 1.37 (t, 6H, CH₃). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ 4.48 (s, SiMe₃), 9.84 (s, CH₃). MS (EI, 20 eV): *m/z* (%) 340 (45) [Sb-(SiMe₃)₃⁺], 120 (25) [Et₂AlCl⁺], 73 (100) [SiMe₃⁺].

_t_-Bu₂AlCl←Sb(SiMe₃)₃ (6). The solid was dissolved in pentane (30 mL), and the solution was filtered, reduced in vacuo to 10 mL, and stored at −30 °C, yielding colorless crystals of **6** (0.77 g, 75%). Mp: 89 °C. Anal. Calcd (found) for C₁₇H₄₅AlSbSi₃Cl: C, 38.44 (38.88); H, 7.79 (7.91). ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ 0.39 (s, 27H, SiMe₃), 1.25 (s, 18H, *t*-Bu). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ 4.90 (s, SiMe₃), 31.07 (s, CH₃). MS (EI, 20 eV): *m/z* (%) 340 (50) [Sb(SiMe₃)₃⁺], 176 (30) [*t*-Bu₂AlCl⁺], 73 (100) [SiMe₃⁺].

cyclo-[Me₂AlSb(SiMe₃)₂]₃ (7). Me₂AlH (0.12 g, 2 mmol) was added at 25 °C to Sb(SiMe₃)₃ (0.68 g, 2 mmol), resulting in gas evolution. After 30 s, a white solid was formed, which was heated to 45 °C (10 min) to complete the reaction. The solid was dissolved in 40 mL of hot pentane and the solution stored at −10 °C, yielding colorless crystals of **7** in quantitative yield (0.63 g, 97%). Mp: 229 °C dec. Anal. Calcd (found) for C₂₄H₇₂Al₃Sb₃Si₆: C, 29.55 (29.07); H, 7.44 (7.35). ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ 0.06 (s, 6H, Me), 0.53 (s, 18H, SiMe₃). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ 5.67 (s, SiMe₃). MS (EI, 20 eV): *m/z* (%) 887 (1) [M⁺ − Me₄Si], 536 (100) [Al₃Sb₃-Me₆⁺], 324 (70) [Me₂AlSb(SiMe₃)₂⁺], 73 (40) [SiMe₃⁺].

X-ray Structure Solution and Refinement. Crystallographic data of **2**, **6**, and **7** are summarized in Table 1; selected bond lengths and angles are given in Table 2. Figures 1−3 show the ORTEP diagrams of the solid-state conformations of **2**, **6**, and **7**; Figure 4 gives the conformation of the central six-membered ring system in **4**. Data were collected on a Nonius Kappa-CCD diffractometer. Structures were solved by direct methods (SHELXS-90)¹¹ and refined by full-

(10) Due to the extreme sensitivity of the compounds toward air and moisture, elemental analyses were performed three times for every compound and the average value is given. In addition, analyses of recrystallized or sublimed samples (**1**–**3**) were performed but did not give better results.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 2, 6, and 7

	Et₃Al←Sb(SiMe₃)₃ (2)		
Al1–Sb1	2.841(1)	Sb1–Si1	2.557(1)
Al1–C10	1.988(2)	Sb1–Si2	2.561(1)
Al1–C12	1.987(2)	Sb1–Si3	2.561(1)
Al1–C14	1.978(2)		
Si1–Sb1–Al1	115.46(2)	C10–Al1–Sb1	101.73(6)
Si2–Sb1–Al1	115.09(2)	C12–Al1–Sb1	100.47(6)
Si3–Sb1–Al1	113.95(2)	C14–Al1–Sb1	103.95(6)
C10–Al1–C12	115.48(8)	Si1–Sb1–Si2	103.71(2)
C10–Al1–C14	115.99(8)	Si1–Sb1–Si3	104.74(2)
C12–Al1–C14	115.80(9)	Si2–Sb1–Si3	102.38(2)

	t-Bu₂AlCl←Sb(SiMe₃)₃ (6)		
Al1–Sb1	2.821(1)	Al1′–Sb1′	2.798(1)
Al1–C10	1.989(2)	Al1′–C10′	1.991(2)
Al1–C14	1.992 (2)	Al1′–C14′	1.997(2)
Al1–Cl1	2.182(1)	Al1′-Cl1′	2.183(1)
Sb1–Si1	2.557 (1)	Sb1′-Si1′	2.582(1)
Sb1–Si2	2.561(1)	Sb1′-Si2′	2.581(1)
Sb1–Si3	2.561(1)	Sb1′-Si3′	2.579(1)
Si1–Sb1–Si2	102.87(2)	Cl1–Al1–Sb1	97.74(2)
Si1–Sb1–Si3	106.27(2)	C10′-Al1′-Sb1′	108.94(6)
Si2–Sb1–Si3	103.50(2)	C14′-Al1′-Sb1′	106.56(6)
Si1–Sb1–Al1	111.87(2)	Cl1′-Al1′-Sb1′	97.49(2)
Si2–Sb1–Al1	111.99(2)	Si1′-Sb1′-Si2′	102.55(2)
Si3–Sb1–Al1	118.85(2)	Si1′-Sb1′-Si3′	106.34(2)
C10–Al1–Cl1	109.44(6)	Si2′-Sb1′-Si3′	100.25(2)
C14–Al1–Cl1	111.23(7)	Si1′-Sb1′-Al1′	119.63(2)
C10–Al1–C14	119.96(9)	Si2′-Sb1′-Al1′	115.74(2)
C10–Al1–Sb1	108.89(5)	Si3′-Sb1′-Al1′	110.23(2)
C14–Al1–Sb1	107.21(6)		

	[Me₂AlSb(SiMe₃)₃]₃ (7)		
Sb1–Al1	2.7384(9)	Al1–C1	1.959(2)
Sb1–Al3	2.7362(8)	Al1–C2	1.968(2)
Sb2–Al1	2.7025(8)	Al2–C3	1.968(2)
Sb2–Al2	2.7068(8)	Al2–C4	1.954(3)
Sb3–Al2	2.7133(9)	Al3–C5	1.974(3)
Sb3–Al3	2.7161(8)	Al3–C6	1.967(3)
Sb1–Si1	2.566(1)	Sb2–Si4	2.5589(8)
Sb1–Si2	2.5675(7)	Sb3–Si5	2.5682(7)
Sb2–Si3	2.5448(7)	Sb3–Si6	2.5604(8)
Al1–Sb1–Al3	128.24(2)	Si2–Sb1–Al3	108.22(2)
Al1–Sb2–Al2	118.53(3)	Sb1–Al1–Sb2	103.48(3)
Al2–Sb3–Al3	125.26(2)	Sb2–Al2–Sb3	104.66(3)
Si1–Sb1–Si2	102.00(2)	Sb1–Al3–Sb3	106.52(3)
Si3–Sb2–Si4	102.29(3)	C1–Al1–C2	120.60(11)
Si5–Sb3–Si6	100.67(3)	C3–Al2–C4	119.46(12)
C1–Al1–Sb2	104.87(8)	C5–Al3–C6	113.69(13)
Si1–Sb1–Al1	109.58(3)	C2–Al1–Sb1	107.64(9)
Si2–Sb1–Al1	105.36(3)	C1–Al1–Sb1	109.89(9)
Si1–Sb1–Al3	100.62(2)	C2–Al1–Sb2	109.04(8)

Figure 1. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **2**.
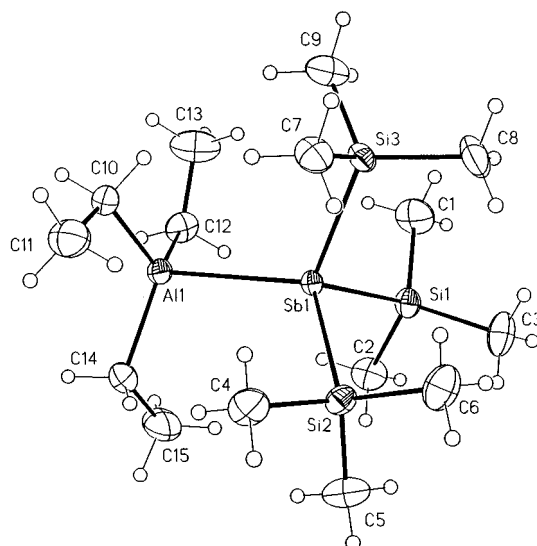
matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[12] In **6** the absolute structure was determined by refinement of the Flack parameter $x = 0.06(1)$.

Results and Discussion

Lewis acid–base adducts R₃Al←Sb(SiMe₃)₃ (R = Me (**1**), Et (**2**), *t*-Bu (**3**)) were prepared in quantitative yield by adding R₃Al to an equimolar amount of Sb(SiMe₃)₃ in the glovebox. Wells et al. prepared analogous group 13–Sb adducts by reactions of Ga– and In–trialkyls with Sb(SiMe₃)₃ in pentane.[3a,b] In contrast, our synthesis requires no solvent. To obtain single crystals, the compounds were recrystallized from pentane. The reac-

tion of Sb(SiMe₃)₃ with either Et₂AlCl or *t*-Bu₂AlCl also gave the adducts R₂AlCl←Sb(SiMe₃)₃ (R = Et (**5**), *t*-Bu (**6**)). Even in the absence of solvent at higher temperature (up to 120 °C), no dehalosilylation reaction occurred.[13] Wells et al. showed that R₂AlCl species react analogously with As(SiMe₃)₃ (R = Me, *i*-Bu;[14a] R = Et[14b]) and with P(SiMe₃)₃ (R = Et, *i*-Bu)[2a] to form simple 1:1 adducts. In contrast, similar Ga compounds, (Me₃-CCH₂)₂GaCl,[3a] *t*-Bu₂GaCl,[3b] and Me₂GaCl,[15] undergo reactions with Sb(SiMe₃)₃, which result in dehalosilylation to form four- and six-membered-ring systems, [R₂GaSb(SiMe₃)₂]ₓ (R = *t*-Bu, Me₃CCH₂, x = 2; R = Me, x = 3).

Me₂AlCl reacted with Sb(SiMe₃)₃ in refluxing hexane under elimination of Me₄Si[16] to give the six-membered-ring system cyclo-[Me(Cl)AlSb(SiMe₃)₂]₃ (**4**). The same product was obtained in a reaction of Me₂AlCl with Sb-(SiMe₃)₃ at room temperature for 3 h as well as in the absence of solvent at 80 °C for 30 min. It is not obvious why Me₂AlCl reacts in this manner but Me₃Al and Et₂-AlCl do not. Ziegler suggested that in solution R₂AlCl is in equilibrium with RAlCl₂ and R₃Al,[17] but we could not detect Me₃Al in solution (¹H NMR). In addition, the yield we obtained is too high (50% would be expected). The reaction of MeAlCl₂ with Sb(SiMe₃)₃ did not lead to **4**.

Me₂AlH reacted with Sb(SiMe₃)₃ with elimination of Me₃SiH to form cyclo-[Me₂AlSb(SiMe₃)₂]₃ (**7**) in quantitative yield. In contrast to reactions of Sb(SiMe₃)₃ with Et₂AlH or *i*-Bu₂AlH, giving four-membered-ring systems,[5] the sterically less crowding Me groups lead to the formation of a six-membered ring. Single crystals of **7** were formed in pentane at −10 °C.

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(16) After the reaction, the volatiles were trapped and analyzed by mass spectroscopy. Me₄Si was identified.
(17) Ziegler, K. In *Organometallic Chemistry*; Zeiss, H., Ed.; ACS Monograph 147; Reinhold: New York, 1960. Et₂AlCl reacts with P(SiMe₃)₃ in a 2:1 mole ratio, forming the adduct EtAlCl₂←P(SiMe₃)₃.[2a]
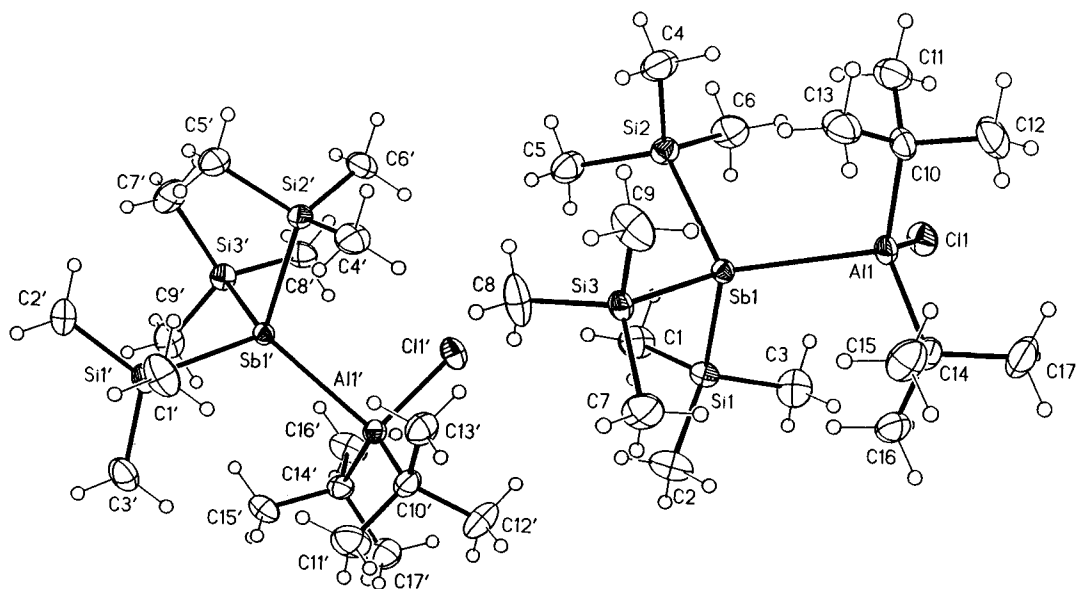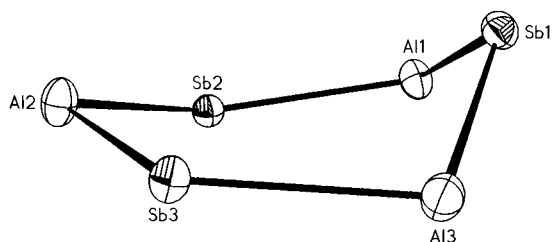
Figure 2. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **6**.
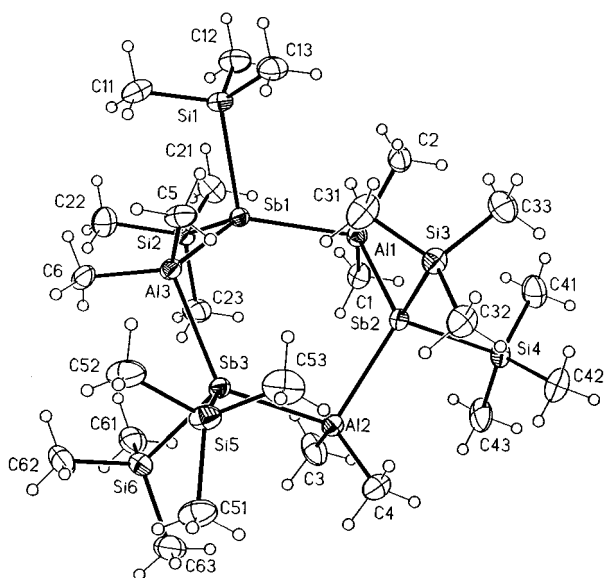
Figure 3. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **7**.

Figure 4. Solid-state structure of **4** showing the central six-membered-ring system.

The ^{1}H NMR spectra of **1**−**7** show signals due to the organic substituents on Al shifted to lower field compared to the starting compounds and the resonance for the SiMe$_3$ groups shifted to slightly higher field. Although the adducts can be sublimed without decomposition at temperatures below 60 °C (10^{-3} mbar), the mass spectra show no molecular ion peaks due to fragmenta-

tion into Sb(SiMe$_3$)$_3$ and the remaining Al fragment. The peak with the highest mass observed for **4** is a fragment at m/z 839 (M$^+$ − 2Me$_3$Si − Me − Cl). A peak at m/z 446, indicating the central Al$_3$Sb$_3$ unit, and other fragments show the ring to be stable under these conditions. **7** shows a peak at m/z 887 (M$^+$ − Me$_4$Si) and other fragments with lower mass, also indicating this ring to be stable.

Single crystals of **2**, **4**, **6,** and **7** were obtained from solutions in pentane at −30 °C (**2**, **4**, **6**), or −10 °C (**7**). To the best of our knowledge, **2** and **6** are the first examples of structurally characterized Al−Sb Lewis acid−base adducts, while **4** and **7** represent the first crystal structures of Al$_3$Sb$_3$ six-membered-ring systems.

The Ga and Sb atoms in **2** reside in a distorted-tetrahedral environment, resulting in average bond angles of 103.6(1)° for Si−Sb−Si, 114.8(1)° for Si−Sb−Al, 102.1(1)° for C−Al−Sb, and 115.8(1)° for C−Al−C. The ligands bound to the metal centers adopt a staggered conformation in relation to one other. As expected for a Lewis acid−base adduct, the observed Al−Sb bond length of 2.841(1) Å is longer than that in [R$_2$AlSb-(SiMe$_3$)$_2$]$_2$ (R = Et, 2.726(1) Å; R = *i*-Bu, 2.745(1) Å).^{5} The average bond length for Al−C of 1.983(2) Å and that for Sb−Si of 2.560(1) Å are within the expected range.

6 crystallizes in the orthorhombic space group *Pca2*$_1$ (No. 29) with two independent molecules in the elemental cell. Its structure is very similar to that of **2**, except for the Al−Sb bond distance (2.821(1) and 2.798(1) Å). This is significantly shorter than in **2** (2.841(1) Å). Obviously, the sterically less demanding Cl atom does not lead to an overcrowded Al center, allowing the base Sb(SiMe$_3$)$_3$ to come closer and to interact more strongly, resulting in a shorter Al−Sb bond length. Analogous to **2,** the ligands adopt a staggered orientation in relation to another. The average bond lengths of Al−C (1.991-(2) and 1.994(2) Å), Sb−Si (2.560(1) and 2.581(1) Å), and Al−Cl (2.182(1) and 2.183(1) Å) are within the expected ranges.

Because **2** and **6** are the first structurally character-ized compounds containing Al−Sb dative bonds, no

comparisons to related Al–Sb compounds can be made. The analogous Ga compound Et$_3$Ga←Sb(SiMe$_3$)$_3$[3a] shows nearly the same values for bond distances and angles due to the comparable atomic radii of Ga and Al, while the sterically more crowded t-Bu$_3$Ga←Sb(SiMe$_3$)$_3$ derivative show a significantly longer Ga–Sb bond length (3.027(2) Å),[3b] due to the bulky t-Bu ligands.

Single crystals of **4** were formed in pentane at −30 °C. **4** crystallizes in the monoclinic space group $P2_1/n$, but its solid-state conformation could not be determined in detail due to the disorder of the Cl and Me groups.[18] The collected data set undoubtedly confirms the presence of a six-membered-ring system as well as the presence of two SiMe$_3$ groups bound to each Sb atom, but the chlorine atom and methyl group bound to the Al atom could not be refined. A crystallographic distinction between Cl and Me was not possible, but the composition of **4** was proven by the elemental analysis and ^{1}H NMR spectrum.

Single crystals of **7** were formed in pentane at −10 °C. **7** is isostructural with **4**. The Al–Sb bond lengths in **4** (2.685−2.723 Å) and **7** (2.703(1)−2.738(1) Å) are comparable to the average bond lengths found in the four-membered-ring systems [R$_2$AlSb(SiMe$_3$)$_2$]$_2$ (R = Et, 2.726(5) Å; R = i-Bu, 2.744(5) Å).[5] [Me$_2$GaSb(SiMe$_3$)$_2$]$_3$ shows almost the same range in bond distances (2.677(5)−2.714(5) Å).[14] The Al–Sb–Al (**4**, 117.0−126.3°; **7**, 118.5(1)−128.2(1)°) and Sb–Al–Sb (**4**, 105.1−109.3°; **7**,

103.5(1)−106.5(1)°) bond angles are within the expected range. Due to the VSEPR model they are significantly greater at the Al center and smaller at the Sb center than the ideal tetrahedral values. Comparable Al–pnicogen trimers such as [Me$_2$AlAs(CH$_2$SiMe$_3$)Ph]$_3$ (118.2(2)−122.2(2)° for Al–As–Al and 102.6(2)−104.8-(2)° for As–Al–As),[19] [Me$_2$AlAsPh$_2$]$_3$·2C$_7$H$_8$ (118.1(1)−122.7(1)° for Al–As–Al and 99.1(1)−101.1(1)° for As–Al–As),[18] and [Me$_2$AlN(CH$_2$)$_2$]$_3$ (119.9(5)° for Al–N–Al and 102.0(5)° for N–Al–N)[20] and the Ga–Sb trimer [Me$_2$GaSb(SiMe$_3$)$_2$]$_3$ (118.3(2)−127.6(2)° for Ga–Sb–Ga and 103.7(2)−107.3(2)° for Sb–Ga–Sb)[14] show nearly the same bond angle values. The average Si–Sb–Si bond angles and bond distances are 102.7° and 2.565 Å (**4**) and 101.7(1)° and 2.561(1) Å (**7**), respectively. The average Al–C bond length and angle in **7** are within the expected range (1.965(3) Å, 117.9(1)°).

Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **2**, **6,** and **7** (25 pages). Ordering information is given on any current masthead page.

OM980824D

(18) Crystal data of **4**: $P2_1/n$ (No. 14), a = 9.4873(2) Å, b = 20.8663-(5) Å, c = 24.0804(6) Å, $β$ = 95.828(2)°, V = 4742.4(1) Å^3, Z = 4. Refinement of the data set dealing with a model of Cl/Me disorder (1:1) at each Al atom leads to R1 = 0.037.

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