Synthesis and X-ray Crystal Structures of the First Lewis Base-Stabilized, Monomeric Aluminum Stibides

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*Summary: Addition of an equimolar amount of 4-(dimethylamino)pyridine (dmap) to a solution of an AlSb heterocycle $(R_2AlSb(SiMe_3)_2)_x$ (R = Me, x = 3; R = Et, i-Bu, x = 2) in hexane lead to the formation of monomeric, Lewis base-stabilized aluminum stibides $R_2AlSb(SiMe_3)_2$←dmap (R = Me, **1**; Et, **2**; i-Bu, **3**). **1** and **2** have been characterized by single-crystal X-ray diffraction.*

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Introduction

Group 13−monopnicogen compounds of the type $R_2MER'_2$ (M = Al, Ga, In; E = N, P, As, Sb, (Bi); R, R′ = organic ligand) tend to form heterocycles $(R_2MER'_2)_x$ (x = 2, 3), heterocubanes (x = 4), or more highly associated cages in solution and in the solid state. This is due to the tendency of the group 13 element to utilize its vacant p valence orbital by increasing its coordination number from 3 to 4. The heterocycles thus formed may be described as intermolecularly stabilized Lewis acid−base adducts. The degree of oligomerization of $(R_2MER'_2)_x$ depends on the steric bulk of the organic substituents R and R′. Bulky ligands favor the formation of lower associated compounds, while smaller ligands (H, Cl, Me) often lead to more highly associated cyclic or cage compounds. In the case of group 13 compounds of type $R_2MER'_2$ (M = Al, Ga, In; E = N, P, As), extremely bulky ligands (R, R′ = *t*-Bu, adamantyl, Mes* (2,4,6-*t*-Bu_3-C_6H_2), Dipp (2,6-*i*-Pr_2-C_6H_3), Cp*)) on M and E inhibit the formation of oligomers and result in the formation of kinetically stabilized monomers.[1] Monomeric monostibides, $R_2MSbR'_2$, are, to the best of our knowledge, thus far unknown. Only simple Lewis acid−base adducts R_3M←SbR'_3 and four- and six-membered heterocycles $(R_2MSbR'_2)_x$ (M = Al, Ga, In; x = 2, 3) have been prepared and structurally characterized.[2] We describe here an easy route to the first, Lewis base-stabilized, monomeric aluminum monostibides.

Experimental Section

General Considerations. All manipulations were performed in a glovebox under a N_2 atmosphere or by standard Schlenk techniques. $[Me_2AlSb(SiMe_3)_2]_3$, $[Et_2AlSb(SiMe_3)_2]_2$, and $[i\text{-}Bu_2AlSb(SiMe_3)_2]_2$ were prepared by literature methods.[2i,j] ^{1}H and $^{13}C\{^1H\}$ spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal C_6D_5H (δ^1H 7.154, δ^{13}C 128.0). Melting points were measured in sealed capillaries and are not corrected. Elemental analyses were performed at the Mikroanalytisches Labor der Universität Bonn.

General Preparation of $R_2AlSb(SiMe_3)_2$←dmap. 4-(Dimethylamino)pyridine (2 mmol) was added to a solution of the respective Al−Sb heterocycle (1 mmol of the dimer, 0.67 mmol of the trimer) in hexane, and the resulting suspension was heated at reflux for 30 min. The resulting clear yellow solution was stored at −30 °C. After 10 h, **1**−**3** were obtained as colorless or light yellow solids.

$Me_2AlSb(SiMe_3)_2$←dmap, **1** (M = 447.35 g/mol): 0.72 g, 1.60 mmol, 80%. Mp: 136 °C (dec). $C_{15}H_{34}AlN_2SbSi_2$, found (calc): C 40.11 (40.24); H 7.58 (7.66). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.10 (s, 6H, Me), 0.71 (s, 18H, $SiMe_3$), 1.88 (s, 6H, NMe_2), 5.52 (d, $^3J_{H-H}$ = 6.7 Hz, 2H, CH), 8.10 (d, $^3J_{H-H}$ = 6.7 Hz, 2H, CH). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ −3.4 (Me), 7.0 ($SiMe_3$), 38.3 (NMe_2), 106.7 (C_{Ring}), 147.0 (C_{Ring}), 155.3 (C_{Ring}).

$Et_2AlSb(SiMe_3)_2$←dmap, **2** (M = 475.40 g/mol): 0.80 g, 1.68 mmol, 84%. Mp: 93 °C (dec). $C_{17}H_{38}AlSbN_2Si_2$, found (calc): C 42.78 (42.96); H 8.00 (8.06). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.69 (q, $^3J_{H-H}$ = 8.1 Hz, 4H, CH_2), 0.70 (s, 18H, $SiMe_3$), 1.52 (t, $^3J_{H-H}$ = 8.1 Hz, 6H, Me), 1.93 (s, 6H, NMe_2), 5.60 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, CH), 8.13 (d, $^3J_{H-H}$ = 6.9 Hz, 2H, CH). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 2.3 (CH_2), 7.2 ($SiMe_3$), 10.9 (Me), 38.4 (NMe_2), 106.8 (C_{Ring}), 147.4 (C_{Ring}), 153.3 (C_{Ring}).

$i\text{-}Bu_2AlSb(SiMe_3)_2$←dmap, **3** (M = 503.16 g/mol): 0.72 g, 1.44 mmol, 72%. Mp: 81 °C (dec). $C_{21}H_{46}AlSbN_2Si_2$, found (calc): C 50.05 (50.13); H 9.12 (9.22). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.66 (s, 18H, $SiMe_3$), 0.67 (d, $^3J_{H-H}$ = 6.7 Hz, 4H, CH_2), 1.27 (d, $^3J_{H-H}$ = 6.7 Hz, 12H, CH_3), 1.92 (s, 6H, NMe_2), 2.30 (m, $^3J_{H-H}$ = 6.7 Hz, 2H, CH), 5.65 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, CH), 8.23 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, CH). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 7.2 ($SiMe_3$), 27.7 (CH_2), 27.9 (CH), 29.0 (CH_3), 29.4 (CH_3), 38.4 (NMe_2), 106.6 (C_{Ring}), 147.5 (C_{Ring}), 155.4 (C_{Ring}).

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Table 1. Crystallographic Data and Measurements for $Me_2AlSb(SiMe_3)_2$←dmap (1) and $Et_2AlSb(SiMe_3)_2$←dmap (2)

	1	2
mol formula	$C_{15}H_{34}AlN_2SbSi_2$	$C_{17}H_{38}AlN_2SbSi_2$
fw	447.35	475.40
cryst syst	monoclinic	triclinic
space group	$P2_1/n$ (No. 14)	$P\bar{1}$ (No. 2)
a, Å	14.4103(3)	9.5988(4)
b, Å	9.8166(2)	10.2709(5)
c, Å	17.3924(3)	14.1694(5)
α, deg		77.792(2)
β, deg	110.546(1)	76.440(3)
γ, deg		70.002(2)
V, Å^3	2303.90(8)	1262.87(9)
Z	4	2
radiation (wavelength, Å)	Mo Kα (0.71073)	Mo Kα (0.71073)
μ, mm^{-1}	1.337	1.224
temp, K	123(2)	123(2)
D_{calcd}, g cm^{-3}	1.290	1.250
cryst dimens, mm	0.30 × 0.25 × 0.25	0.20 × 0.20 × 0.04
$2\theta_{max}$, deg	56.6	56.6
no. of rflns rec	44 900	26 703
no. of nonequiv rflns rec	5723	6156
R_{merg}	0.034	0.081
no. of params refined	192	210
R1;[a] wR2[b]	0.018, 0.046	0.030, 0.061
goodness of fit[c]	1.054	0.989
final max, min $\Delta\rho$, e Å^{-3}	0.342, −0.562	0.524, −0.727

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

Table 2. Selected Bond Distances (Å) and Angles (deg) for $Me_2AlSb(SiMe_3)_2$←dmap (1) and $Et_2AlSb(SiMe_3)_2$←dmap (2)

distance	1	2	angle	1	2
Sb1−Al1	2.691(1)	2.679(1)	C7−Al1−C8/9	116.54(8)	115.22(2)
Sb1−Si1	2.546(1)	2.554(1)	C7−Al2−N1d	105.48(6)	105.68(9)
Sb1−Si2	2.549(1)	2.546(1)	C8/9-Al3−N1d	106.25(6)	103.96(9)
Al1−C7	1.973(2)	1.978(2)	C7−Al1−Sb1	107.28(6)	118.13(7)
Al1−C8/9	1.967(2)	1.982(2)	C8/9-Al1−Sb1	117.66(5)	107.82(8)
Al1−N1d	1.978(1)	1.980(2)	N1d-Al1−Sb1	101.91(4)	104.48(6)
			Si1−Sb1−Si2	97.55(1)	99.06(2)
			Si1−Sb1−Al1	98.09(2)	99.34(2)
			Si2−Sb1−Al1	106.80(2)	100.51(2)

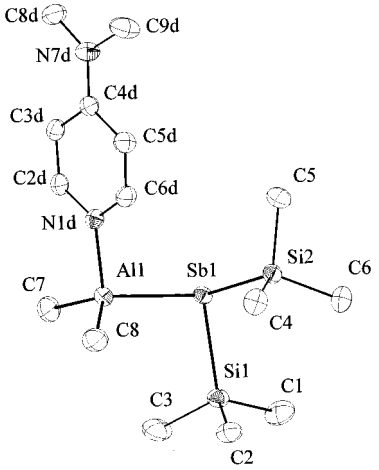

Figure 1. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **1**.

X-ray Structure Solution and Refinement. Crystallographic data of **1** and **2** are summarized in Table 1, selected bond lengths and angles in Table 2. Figures 1 and 2 show the ORTEP diagrams of the solid-state structures of **1** and **2**. Data were collected on a Nonius Kappa-CCD diffractometer. The

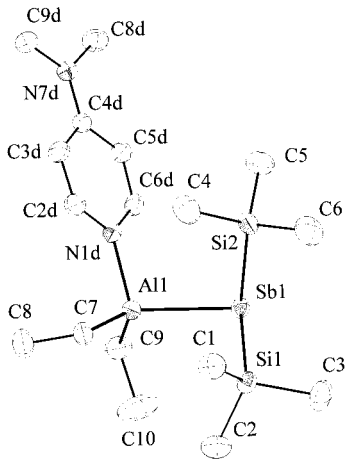

Figure 2. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **2**.

structures of **1** and **2** were solved by Patterson methods (SHELXS-97)[3] and refined by full-matrix least-squares on F^2 (SHELXL-97).[4] All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model. Empirical absorption corrections were applied. The crystallographic data of **1** and **2** (without structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-139165 (**1**) and CCDC-139164 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (Telefax: (+44) 1223/336033; e-mail: deposit@ccdc.cam-ak.uk).

Results and Discussion

Reactions of equimolar amounts of 4-(dimethylamino)-pyridine (dmap) with Al−Sb heterocycles $(R_2AlSb(SiMe_3)_2)_x$ (R = Me, x = 3; R = Et, *i*-Bu, x = 2) in refluxing hexane resulted in the formation of yellow solutions, which were extremely sensitive toward air and moisture. At −30 °C, **1**−**3** were obtained as crystalline solids.

The ^{1}H NMR spectra of **1**−**3** show resonances due to the organic ligands bound to the metal centers and the expected resonances of dmap. Integration of the signals due to the organic ligands and dmap indicated a 1:1 stoichiometry of dmap to $R_2AlSb(SiMe_3)_2$ (R = Me, Et, *i*-Bu). Compared to the starting heterocycles, the resonances due to the groups bound to Al and Sb are shifted to lower field and those of the coordinated dmap molecule to higher field, compared to free dmap.

X-ray crystallographic analyses of **1** and **2** clearly show the presence of monomeric $R_2AlSb(SiMe_3)_2$ molecules, to which one dmap is coordinated. The average Al−C (**1**, 1.970 Å; **2**, 1.980 Å) and Sb−Si (**1**, 2.548 Å; **2**, 2.550 Å) bond lengths are within the expected range. Common Al−N distances found in adducts range from 2 to 2.10 Å (e.g., Me_3Al−NMe_3, 2.10(1) Å; H_3Al−NMe_3, 2.063(8) Å (gas phase); Me_3Al−NH_3, 2.004(5) Å (powder diffraction); H_3Al(2,2,6,6-tetramethylpiperidine), 2.04-(1) Å).[5] **1** and **2** show significantly shorter Al−N distances (**1**, 1.978(1) Å; **2**, 1.980(2)). This clearly demonstrates the strong donor capacity of dmap and the

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strong Lewis acid character of the Al center. A shorter Al−N distance was found in $Cl_3Al{-}NMe_3$ (1.96(1) Å). The Al−Sb bond lengths (**1**, 2.691(1) Å; **2**, 2.680(1)) are the shortest ever observed. Due to the lack of structurally characterized, monomeric aluminum stibides, only comparisons to AlSb heterocycles $(R_2AlSbR'_2)_x$ ($R' = SiMe_3$, *t*-Bu; $x = 2$, 3), which show distances between 2.71 and 2.78 Å,[2i,j,l] can be made. The literature value for the sum of the covalent radii of Al and Sb (2.65 Å)[6] is only slightly shorter than the bond distances observed in **1** and **2**.

The formation of **1**−**3** may be explained by the HSAB principle (hard−soft-acid−base).[7] Al−pnicogen adducts show a decreasing bond strength from nitrogen to bismuth,[8] because the "hard" acid Al would rather form adducts with a "hard" N-base than with a "soft" Sb- or Bi-base. Therefore, N-bases such as dmap can displace weaker antimony bases from the Al-coordination sphere. Previous reports on Lewis base stabilized group 13/15 compounds include reactions of $H_3Al{\leftarrow}NMe_3$ with sterically bulky secundary amines, which formed Me_3N-coordinated monomeric aminoalanes.[9] To the best of our knowledge, the only examples of Lewis base stabilized monomeric group13/15 compounds containing the higher homologues of group 15 were prepared by reaction of $H_3Al{\leftarrow}NMe_3$ with $As(SiMe_3)_3$ and $H_2AlCl{\leftarrow}NMe_3$ with $LiEMes_2$ (E = P, As), leading to the formation of $H_2AlAs(SiMe_3)_2{\leftarrow}NMe_3$ and $H_2AlEMes_2{\leftarrow}NMe_3$.[10] In addition, one example of a Lewis acid and Lewis base stabilized, monomeric compound, $Cr(CO)_5[Ph_2PAl(CH_2SiMe_3)_2{\leftarrow}NMe_3]$, is known.[11] However, as far as we know, no example of a monomeric group 13/15 compound obtained by a ring cleavage reaction has been described so far.

The compounds **1**−**3** are of interest due to their potential to serve in the synthesis of bimetallic compounds by coordination of a metal fragment to the Sb atom, which is currently under investigation.

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Supporting Information Available: Tables of bond distances, bond angles, anisotropic temperature factor parameters, and fractional coordinates for **1** and **3**. This material is available free of charge via the Internet at http://pubs.acs.org.

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