Synthesis and X-ray Structures of Novel Organoaluminum−Antimony Compounds

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*Summary: Dehydrosilylation reactions between Sb($SiMe_3$)$_3$ with diorganoaluminum hydrides Et_2AlH and i-Bu_2AlH in 1:1 molar ratio leads under elimination of Me_3SiH to the novel Al−Sb compounds [$Et_2AlSb(SiMe_3)_2$]$_2$ (**1**) and [i-$Bu_2AlSb(SiMe_3)_2$]$_2$, respectively (**2**). Compounds **1** and **2** have been fully characterized by NMR, IR, and mass spectroscopy as well as by single-crystal X-ray diffraction.*

Introduction

During the past decade, research on group 13−15 compounds (III−V compounds) has concentrated on Al−N, Al−P, Ga−P, Ga−As, In−P, and InAs compounds with 1:1 molar ratios of the group 13−15 elements. These compounds are of interest owing to their potential application as single-source precursors for the MOCVD process, which is a rapidly growing industrial technology for the formation of thin films of the corresponding semiconducting materials.[1] Numerous compounds, particularly the arsenides and phosphides of Al, Ga, and In, have been synthesized and structurally characterized, most of them in the form of simple Lewis acid−base adducts $R_3M \leftarrow ER'_3$ (M = group 13 element; E = group 15 element) or dimers $(R_2MER'_2)_2$ and trimers $(R_2MER'_2)_3$ with M−E σ bonds.[2] Interestingly, only a handful of group 13 antimonides have been investigated. Ga− and In−antimonides can be prepared either by salt elimination[3] or by dehalosilylation reactions between diorganogallium or indium halogenides with $Sb(SiMe_3)_3$ or *t*-$Bu_2SbSiMe_3$.[4] In contrast, Al−Sb compounds have been studied for a far lesser extent. Only one example containing an Al−Sb bond has been prepared, but its structure could not be investigated in detail.[5]

We were interested in developing a general pathway for organometallic Al−antimonides as well as studying their solid-state structures to get basic information about the as yet unknown bonding situation in Al−Sb compounds. Herein we report the synthesis and structural characterization of [$Et_2AlSb(SiMe_3)_2$]$_2$ (**1**) and [*i*-$Bu_2AlSb(SiMe_3)_2$]$_2$ (**2**), two novel Al−Sb compounds containing four-membered Al_2Sb_2 ring systems by a dehydrosilylation reaction.

Experimental Section

General Considerations. All manipulations were performed in a glovebox under N_2-atmosphere or by standard Schlenk techniques. *i*-Bu_2AlH was purchased from Aldrich and used as received. $Sb(SiMe_3)_3$ [6] and Et_2AlH [7] were prepared by literature methods. A Bruker AMX 300 spectrometer was used for NMR spectroscopy. ^1H and $^{13}C\{^1H\}$ spectra were referenced to internal C_6D_5H (δ^1H 7.154, $\delta^{13}C$ 128.0). Infrared spectra were recorded in Nujol between KBr plates with a Nicolet Magna 550 and are reported in reciprocal centimeters. Mass spectra were recorded on a VG Masslab 12-250 spectrometer in the electron ionization 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.

Preparation of [$Et_2AlSb(SiMe_3)_2$]$_2$ (1). Et_2AlH (0.17 g, 2 mmol) was added to $Sb(SiMe_3)_3$ (0.68 g, 2 mmol) in the glovebox and heated for 30 min at 50 °C, while a gas evolution was observable. **1** was obtained as a colorless solid (0.69, 1 mmol, 100%). Single crystals were formed in pentane at −30 °C. Mp: 156 °C. Anal. Calcd (Found) for $C_{20}H_{56}Al_2Sb_2Si_4$: C 33.12 (34.00); H 7.73 (7.99). ^1H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.50 (s, 9H, $SiMe_3$), 0.59 (q, $^3J_{H-H}$ = 7.9 Hz, 2H, CH_2), 1.40 (t, $^3J_{H-H}$ = 7.9 Hz, 3H, Me). $^{13}C\{^1H\}$ NMR (80 MHz, C_6D_5H, 25 °C): δ 5.76 (s, $SiMe_3$), 10.97 (s, CH_2), 11.90 (s, Me). MS (EI, 20 eV): *m/z* (%) 633 (3) [$M^+ - SiMe_3$], 353 (30) [$M^+/2$], 280 (45) [$M^+/2 - SiMe_3$], 73 (100) [$SiMe_3$]. IR (Nujol): ν 1251, 980, 954, 841 cm^{-1}.

Preparation of [*i*-$Bu_2AlSb(SiMe_3)_2$]$_2$ (2). *i*-Bu_2AlH (0.24 g, 2 mmol) was added to $Sb(SiMe_3)_3$ (0.68 g, 2 mmol) and heated for 1 h at 140 °C. Starting at 95 °C, a gas evolution was observable. **2** was obtained as a

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Table 1. Crystallographic Data and Measurements for $[Et_2AlSb(SiMe_3)_2]_2$ (1) and $[i\text{-}Bu_2AlSb(SiMe_3)_2]_2$ (2)

	1	**2**
mol formula	$C_{20}H_{56}Al_2Sb_2Si_4$	$C_{28}H_{72}Al_2Sb_2Si_4$
fw	706.47	818.68
cryst syst	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*P*2$_1$/*n* (No. 14)
a, Å	18.1472(2)	12.1479(2)
b, Å	9.5734(1)	11.2493(2)
c, Å	20.8920(3)	16.1183(4)
β, deg	98.690(1)	95.648(1)
V, Å^3	3587.91(7)	2191.96(8)
Z	4	2
radiation (wavelength, Å)	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	1.695	1.396
temp, K	123(2)	123(2)
D_{calcd}, g cm^{-3}	1.308	1.240
cryst dimens, mm	0.50 × 0.50 × 0.40	0.30 × 0.25 × 0.10
T_{max}, T_{min}	0.53094, 0.48460	none
$2\theta_{max}$, deg	56.5	56.5
no. of rflns recorded	20 938	33 491
no. of nonequiv rflns recorded	3675	4673
R_{merg}	0.016	0.027
no. of parameters refined	128	164
$R1^a$; wR^b	0.019, 0.046	0.022, 0.056
goodness of fit^c	1.15	1.07
max shift/esd in final least-squares cycle	0.002	0.004
final max, min $\Delta\rho$, e Å^{-3}	0.615, −0.423	0.712, −0.889

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

colorless solid (0.80 g, 1 mmol, 100%). Single crystals were formed in pentane at −30 °C. Mp: 210 °C (dec). Anal. Calcd (Found) for $C_{28}H_{72}Al_2Sb_2Si_4$: C 40.42 (41.08); H 8.62 (8.86). ^{1}H NMR (300 MHz, C_6D_5H, 25 °C): δ 0.54 (s, 9H, SiMe$_3$), 0.71 (d, $^3J_{H-H} = 7.4$ Hz, 2H, CH$_2$), 1.24 (d, $^3J_{H-H} = 6.5$ Hz, 6H, 2Me), 2.18 (m, $^3J_{H-H} = 6.7$ Hz, 1H, CH). ^{13}C{^{1}H }NMR (80 MHz, C_6D_5H, 25 °C): δ 5.76 (s, SiMe$_3$), 28.68 (s, Me). MS (EI, 20 eV): *m*/*z* (%) 408 (30) [M$^+$/2], 352 (20) [M$^+$/2 − Me$_2$C═CH$_2$], 296 (100) [M$^+$/2 − 2Me$_2$C═CH$_2$], 222 (40) [M$^+$/2 − 2Me$_2$C═CH$_2$ − SiMe$_3$]. IR (Nujol): ν 1246, 1150, 1058, 1006, 842 cm^{-1}.

X-ray Structure Solution and Refinement. Crystallographic data are summerized in Table 1 and selected bond lengths and angles in Table 2. Figure 1 shows the ORTEP diagram of the solid-state confirmation of **2**. Data were collected on a Nonius Kappa-CCD diffractometer. In **1** and **2**, extinction corrections were applied. Structures of **1** and **2** were solved by direct methods (SHELXS-90)[8] and refined by full-matrix least squares on F^2. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97).[9]

Results and Discussion

1 and **2** were prepared by reactions of equimolar amounts of Sb(SiMe$_3$)$_3$ with the corresponding diorganoaluminum hydride in the absence of solvent. For the first time, Al−Sb compounds were synthesized by this so-called dehydrosilylation reaction under elimination of Me$_3$SiH. This pathway, which is known to be successful in the syntheses of B−P,[10] Al−N,[11] and Al−P,[2c,12] as well as Ga−P and Ga−As[2b,13] compounds, has some major advantages in relation to dehalosilylation reactions and to salt elimination reactions: solvents and Me$_3$SiCl do not have to be removed in vacuo; filtration of formed salts is not necessary; the product is obtained in quantitative yield and analytically pure and can be used without purification for further reactions.

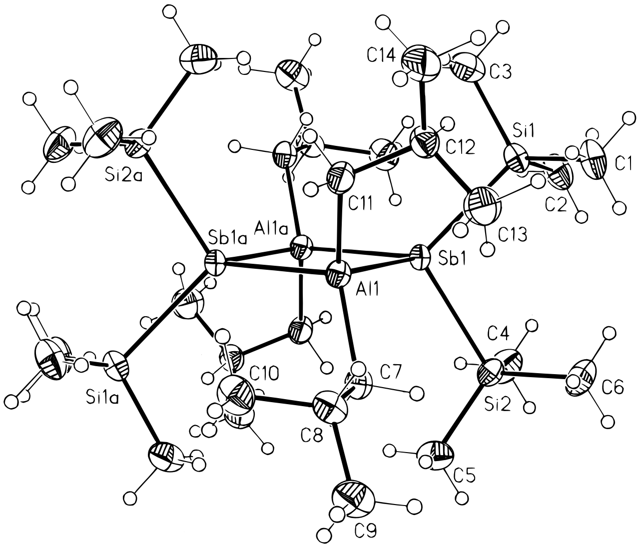

Figure 1. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom numbering scheme for **2**.

$$2R_2AlH + 2Sb(SiMe_3)_3 \xrightarrow[2Me_3SiH]{} [R_2AlSb(SiMe_3)_2]_2 \quad (R = Et, i\text{-Bu}) \quad (1)$$

1 and **2** were both fully characterized by ^{1}H and ^{13}C{^{1}H} NMR and IR and mass spectroscopy. In addition, single-crystal X-ray analyses were performed.

^{1}H NMR spectra of **1** and **2** show signals for the organic substituents shifted to lower field compared to the hydrides and the resonance for the SiMe$_3$ groups. In the mass spectra, no molecule ion peaks were detected due to fragmentation of the compounds. The signals with the highest mass are fragments for M$^+$ − SiMe$_3$ (*m*/*z* 633, **1**) and for M$^+$/2 (*m*/*z* 408, **2**).

To the best of our knowledge, **1** and **2** are the first examples of structurally characterized compounds containing Al−Sb bonds. Single-crystal X-ray structure determinations confirmed **1** and **2** to be dimers in the solid state.

Single crystals of **1** were obtained from a solution in pentane at −30 °C. **1** crystallizes in the monoclinic space group *C*2/*c*. The central unit is the planar four-membered Al$_2$Sb$_2$ ring with the Ga and Sb in a distorted tetrahedral environment. The endocyclic bond angles

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Table 2. Selected Bond Lengths and Angles for 1 and 2

$[Et_2AlSb(SiMe_3)_2]_2$ (**1**)		$[i\text{-}Bu_2AlSb(SiMe_3)_2]_2$ (**2**)	
	Bond Lengths (Å)		
Al(1)−Sb(1)	2.7228(5)	Al(1)−Sb(1)	2.7429(5)
Al(1*)−Sb(1)	2.7292(5)	Al(1*)−Sb(1)	2.7460(5)
Sb(1)−Si(1)	2.5442(5)	Sb(1)−Si(1)	2.5499(5)
Sb(1)−Si(2)	2.5437(5)	Sb(1)−Si(2)	2.5562(5)
Al(1)−C(7)	1.9711(19)	Al(1)−C(7)	1.9846(17)
Al(1)−C(9)	1.9719(18)	Al(1)−C(11)	1.9823(18)
	Bond Angles (deg)		
Al(1)−Sb(1)−Al(1*)	91.680(15)	Al(1)−Sb(1)−Al(1*)	93.660(15)
Si(1)−Sb(1)−Si(2)	107.299(18)	Si(1)−Sb(1)−Si(2)	102.746(17)
Si(1)−Sb(1)−Al(1)	109.512(16)	Si(1)−Sb(1)−Al(1)	120.008(16)
Si(2)−Sb(1)−Al(1)	115.931(16)	Si(2)−Sb(1)−Al(1)	112.538(16)
Si(1)−Sb(1)−Al(1*)	115.002(16)	Si(1)−Sb(1)−Al(1*)	118.340(16)
Si(2)−Sb(1)−Al(1*)	116.874(16)	Si(2)−Sb(1)−Al(1*)	109.683(16)
Sb(1)−Al(1)−Sb(1*)	88.320(15)	Sb(1)−Al(1)−Sb(1*)	86.340(15)
C(7)−Al(1)−C(9)	117.28(8)	C(7)−Al(1)−C(11)	121.22(8)
C(7)−Al(1)−Sb(1)	113.25(6)	C(7)−Al(1)−Sb(1)	108.00(6)
C(9)−Al(1)−Sb(1)	111.35(6)	C(11)−Al(1)−Sb(1)	113.38(6)

are 91.680(15)° for Al−Sb−Al and 88.320(15)° for Sb−Al−Sb. Compared to four-membered Ga_2Sb_2 ring systems, the distortion is slightly smaller.[4] The average Al−Sb bond length of 272.6 pm compares well with the sum of the covalent radii of 273 pm for Al and Sb. The average bond lengths for Al−C of 197.1 pm and Sb−Si of 254.3 pm are within the expected range.

Single crystals of **2** were obtained from a solution in pentane at −30 °C. **2** crystallizes monoclinic in the space group $P2_1/n$. Due to the higher steric demand of the *i*-Bu groups compared to the Et groups, the average bond lengths for Al−C (198.3 pm) and Al−Sb (274.4 pm) are slightly longer in **2**. In addition, the C−Al−C bond angle is bigger (121.22(8)° in **2** compared to 117.28(8)° in **1**), the bond angles for Sb−Al−Sb smaller (86.340(15)° (**2**) to 88.320(15)° (**1**)), for Al−Sb−Al bigger (93.660(15)° (**2**) to 91.680(15)° (**1**)), and for Si−Sb−Si smaller (102.746(17)° (**2**) compared to 107.299(18)° in (**1**)) due to the higher steric demand. This agrees very well with the corresponding values found in the related compounds $[R_2AlP(SiMe_3)_2]_2$ (R = Me,[14] Et,[2g] *i*-Bu[12d]), which show the same tendency.

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Supporting Information Available: Tables of crystal data, bond distances, bond angles, anisotropic temperature factor parameters, fractional coordinates, torsion angles, and ORTEPs for **1** and **2** (14 pages). Ordering information is given on any current masthead page.

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