

Base-stabilized monomeric stibinoalane dmap-Al(Et₂)Sb(^tBu)₂

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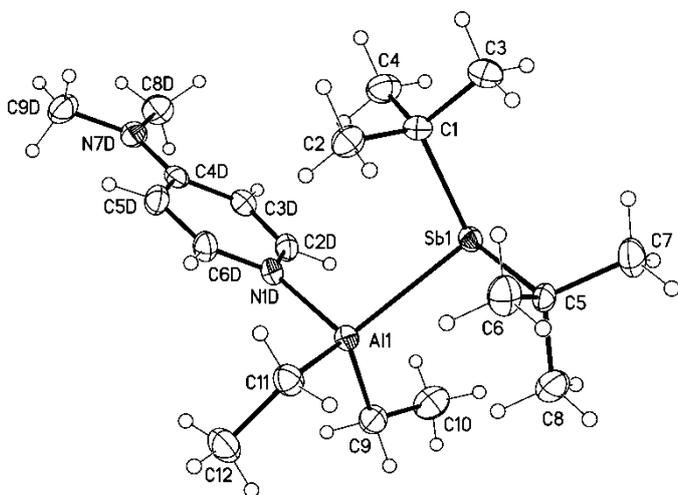
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Base-stabilized monomeric stibinoalane $\text{dmap-Al(Et}_2\text{)Sb}(t\text{-Bu)}_2$

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The synthesis and single crystal X-ray analysis of the first completely alkyl-substituted monomeric complex $\text{dmap-Al(Me}_2\text{)Sb}(t\text{-Bu)}_2$, which was obtained from the ring cleavage reactions of $[\text{Me}_2\text{AlSb}(t\text{-Bu)}_2]_3$ with dmap , is described.



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Abstract The six-membered heterocycle [Me₂AlSb(*t*-Bu)₂]₃ was reacted with the strong Lewis-base 4-dimethylaminopyridine (dmap), yielding the first completely alkyl-substituted monomeric complex dmap—Al(Me₂)Sb(*t*-Bu)₂ **1**. **1** was characterized by NMR spectroscopy and single crystal X-ray diffraction. **1** is monoclinic, space group *P*2₁/*n* with *a* = 9.9004(2) Å, *b* = 16.8166(3) Å, *c* = 13.8400(3) Å, *β* = 100.746(1)° and *Z* = 4.

Keywords Lewis-base · X-ray crystal structure · Monomeric stibinoalane

Short title: Base-stabilized stibinoalane

Introduction

Monomeric group 13/15 compounds received growing interest over the last decades due to their fascinating bonding properties [1] and their potential application as *single-source-precursors* for the preparation of the corresponding binary materials by MOCVD process [2]. Compounds of the type $R_2MER'_2$ ($M = Al, Ga, In$; $E = N, P, As, Sb, Bi$) typically form heterocycles ($x = 2, 3$), heterocubanes ($x = 4$) or more highly associated cages ($x > 4$) as a result of the tendency of the triele atom, to utilize its vacant p-valence orbital by increasing its coordination number from 3 to 4. Monomeric group 13/15 compounds $R_2MER'_2$ are only formed with sterically extremely bulky ligands on both M and E, which inhibit the formation of oligomers and lead to the formation of kinetically stabilized monomers [3]. Moreover, monomeric compounds can be electronically stabilized by use of strong Lewis bases such as 4-dimethylaminopyridine (dmap). Ring cleavage reactions of the heterocyclic $[R_2ME(SiMe_3)_2]_x$ with dmap yielded monomeric organoaluminum and organogallium phosphides, arsenides, stibides and bismuthides of the type $dmap-M(R_2)E(SiMe_3)_2$ [4]. The triele atom is coordinatively and electronically saturated by interaction with the strong base, while the *lone pair* of the pentedele atom is still active for coordination chemistry. Consequently, these monomers may serve as building blocks for the synthesis of bimetallic complexes of the type $dmap-M(R_2)E(SiMe_3)_2-M'L_n$ ($M = \text{triele}$; $E = \text{pentedele}$; $M' = Ni, Fe, Cr$), in which the pentedele atom bridges a "soft" transition metal and a "hard" main-group metal fragment [5]. Complexes of this type can be considered as transition-metal derivatives of an amphoteric main-group element ligand [6].

We herein present for the first time the single crystal X-ray analysis of the completely alkyl-substituted monomeric complex $dmap-Al(Me_2)Sb(t-Bu)_2$ **1**. **1** was obtained from the ring cleavage reactions of $[Me_2AlSb(t-Bu)_2]_3$, which can be described as *head-to-tail adduct* of three monomeric units, with the strong σ -donor dmap.

Experiments

Manipulations were performed in a glove box under an Ar-atmosphere or with standard Schlenk techniques. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. A Bruker Advance 300 spectrometer was used for NMR spectroscopy. 1H and $^{13}C\{^1H\}$ NMR spectra were referenced to internal C_6D_5H (1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$). Melting points were measured in sealed capillaries and were not corrected. Elemental analyses were performed at the Elementaranalyse Labor of the University of Bonn.

Synthesis of $\text{dmap-Al(Me}_2\text{)Sb}(t\text{-Bu)}_2$ **1**

A solution of 4-Dimethylaminopyridine (3 mmol, 0.37 g) and $([\text{Me}_2\text{AlSb}(t\text{-Bu)}_2]_3)$ (1 mmol, 0.88 g) in *n*-hexane was heated under reflux for 30 min. The resulting clear yellow solution was stored at -30 °C. After 10 h, **1** was obtained as light yellow crystals (1.14 g, 86%. m.p. 124 °C). Elemental analysis $\text{C}_{19}\text{H}_{38}\text{AlN}_2\text{Sb}$ ($M = 415.19$ g/mol), Found (calc.): C 49.03 (49.21); H 8.17 (8.29). Spectroscopic analysis: $^1\text{H-NMR}$ (500 MHz, C_6D_6 , 25 °C): $\delta = 0.09$ (s, 6 H, AlMe_2), 1.82 (s, 18 H, *t*-Bu), 1.94 (s, 6 H, NMe_2), 5.54 (d, $^3J_{\text{H-H}} = 6.2$ Hz, 2 H, C(3)-H), 8.09 (d, $^3J_{\text{H-H}} = 6.2$ Hz, 2 H, C(2)-H). $^{13}\text{C}\{^1\text{H}\}$ -NMR (75 MHz, C_6D_6 , 25 °C): $\delta = -3.2$ (Me), 32.4 (CMe_3), 35.1 (CMe_3), 38.4 (NMe_2), 106.7 (C(3)-H), 148.2 (C(2)-H), 155.1 (C(4)).

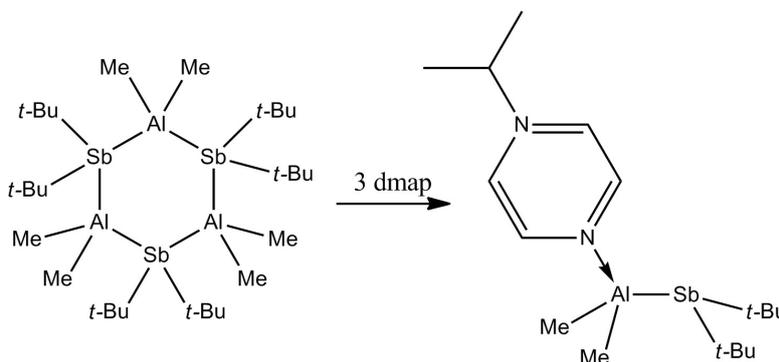


Figure 1. Synthesis of $\text{dmap-Al(Me}_2\text{)Sb}(t\text{-Bu)}_2$ **1** by ring cleavage reaction of $([\text{Me}_2\text{AlSb}(t\text{-Bu)}_2]_3)$.

The $^1\text{H-NMR}$ spectrum of **1** shows resonances due to the organic ligands bound to the metal centers and the expected resonances of dmap. Integration of these resonances indicated a 1:1 stoichiometry of $\text{dmap:Me}_2\text{AlSb}(\text{SiMe}_3)_2$. Compared to the starting heterocycle $([\text{Me}_2\text{AlSb}(t\text{-Bu)}_2]_3)$, the resonances of the metal-bonded substituents are shifted to lower field, whereas those of the coordinated dmap molecule are shifted to higher field compared to free dmap.

Crystallization of **1**

A solution of 0.50 g **1** in 20 mL of *n*-hexane was stored at -30 °C. Single crystals suitable for a single crystal X-ray analysis were obtained after 24 h. Table 1 illustrates the crystal data and structure refinement of **1**.

Crystal structure of **1**

Data were collected on a Nonius Kappa-CCD diffractometer using graphite-monochromated $\text{Mo-K}\alpha$ radiation ($\lambda = 0.71073$ Å) at $T = -150$ °C and the structures were solved by Patterson methods and refined by full-matrix least-squares on F^2 . A semi-empirical absorption correction was applied. All non-hydrogen atoms in **1** were refined anisotropically and hydrogen atoms were located from ΔF maps and refined at idealized positions using a riding model with C-H distances in the

range 0.95 and 0.99 Å and $U_{\text{iso}}(\text{H}) = x U_{\text{eq}}(\text{C})$ with $x = 1.5$ for methyl H and 1.2 for all other H atoms [7]. CCDC-770507 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by contacting The Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; email: deposit@ccdc.cam.ac.uk.

((Table 1 here))

Results and Discussion

1 crystallizes in the monoclinic space group $P2_1/n$ (No. 14). Single crystals were obtained from solutions in pentane at -30 °C. The Al atom shows a distorted tetrahedral environment whereas the Sb atom adopts a pyramidal environment. The substituents bound to Al and Sb adopt staggered conformations relative to one another as was previously observed for such complexes.

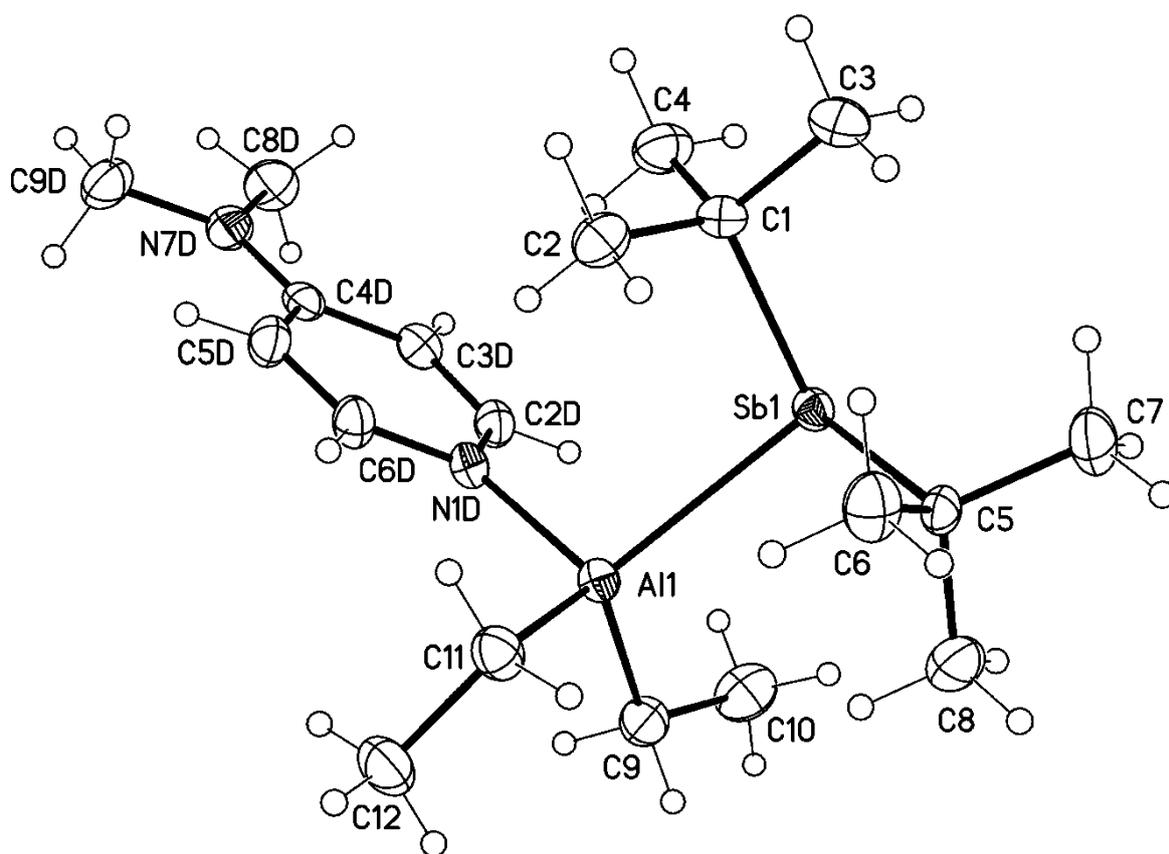


Figure 2

The solid-state structure and atom-numbering scheme for $\text{dmap-Al}(\text{Me}_2)\text{Sb}(\text{t-Bu})_2$ **1**. Displacement ellipsoids are drawn at the 50% probability level.

The mean Al-C (1.988 Å) and Sb-C (2.230 Å) bond lengths in **1** are within the expected range and the Al-Sb bond length of 2.708(1) Å is only slightly elongated compared to those observed for $\text{dmap-Al(R)Sb(SiMe}_3)_2$ (R = Me 2.691(1); Et 2.680(1) Å), which exhibit the shortest Al-Sb bond lengths ever observed [4a]. AlSb heterocycles such as $[\text{R}_2\text{AlSb(R')}_2]_x$ (R = Me, Et, *i*-Bu; R' = SiMe₃, *t*-Bu; x = 2, 3) show distances between 2.73 and 2.78 Å [8]. The Al-N bond length (2.989(2) Å), which is also typical for this type of compound, is shorter than those observed for Me₃Al-NMe₃ (2.045 Å (single crystal) [9], 2.10(1) Å (electron diffraction) [10]), H₃Al-NMe₃ (2.09(2), 2.02 (2), 2.03 (2) Å (single crystal) [11], 2.063(8) Å (electron diffraction) [12]), and Me₃Al-NH₃ 2.004(5) Å (powder diffraction) [13], respectively. This clearly demonstrates the strong σ -donor capacity of *dmap* and the strong Lewis acid character of the Al center. The bond angular sum at the threefold-coordinated Sb center of 306.8° is slightly larger compared to that in $\text{dmap-Al(R)Sb(SiMe}_3)_2$ (R = Me: 302.4°; Et: 298.9°), most likely due to shorter Sb-C (Ø2.230 Å) compared to Sb-Si (R = Me: Ø2.547; Et: 2.540 Å) bond lengths. As a consequence, *t*-Bu groups exhibit a higher steric demand compared to a SiMe₃ substituents.

((Table 2 here))

Conclusion

We have demonstrated that monomeric group 13-15 complexes can be stabilized by addition of a strong Lewis-base such as *dmap*, which electronically stabilizes these compounds. The formation of **1** may be explained by the HSAB principle (hard-soft-acid-base), according to which the "hard" acid Al rather prefers to form an adduct with a "hard" nitrogen σ -donors than with a "soft" Sb-base.

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Table 1 Crystal data and structure refinement of **1**

CCDC deposit no.	770507
Empirical formula	C ₁₉ H ₃₈ AlN ₂ Sb
Formular weight	443.24
Temperature	123(2) K
Wavelength	0.71073 Å
Crystal system	monoclinic
Space group	P2 ₁ /n
Unit cell dimensions	a = 9.9004(2) Å b = 16.8166(3) Å c = 13.8400(3) Å β = 100.746(1)°
Volume	2263.83(8) Å ³
Z	4
Density (calculated)	1.300 Mg m ⁻³
Absorption coefficient	1.260 mm ⁻¹
F(000)	920
Crystal size	0.35 x 0.25 x 0.20 mm
Theta range for data collection	28.30°
Index range	-13 ≤ h ≤ 13, -22 ≤ k ≤ 22, -18 ≤ l ≤ 18
Reflections collected	39779
Independent reflections	5582; 4774 reflections with I > 2 _σ (I) (R _{int} = 0.044)
Completeness to theta = 56.60°	99.1%
Max. and min. transmission	0.8646 and 0.6655
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	5582/0/210
goodness-of-fit on F ²	1.03
Final R indices [I > 2σ(I)]	R1 = 0.021, wR2 = 0.050
R indices (all data)	R1 = 0.027, wR2 = 0.052
Largest diff. peak and hole	0.595 and -0.881 e Å ⁻³

Table 2 Selected geometric parameters (Å, °).

Sb1-C1	2.2279(14)	Al1-C11	1.9880(16)
Sb1-C5	2.2329(14)	Al1-N1D	1.9892(13)
Al1-C9	1.9894(15)	Sb1-Al1	2.7077(4)
<hr/>			
C1-Sb1-C5	104.94(5)	C9-Al1-N1D	107.03(6)
C1-Sb1-Al1	102.85(4)	C11-Al1-N1D	105.25(6)
C5-Sb1-Al1	98.88(4)	C9-Al1-Sb1	109.71(5)
C9-Al1-C11	112.26(7)	C11-Al1-Sb1	120.12(5)
N1D-Al1-Sb1	100.98(4)		

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