

Structural characterization of a completely alkyl-substituted Al–Sb Lewis acid–base adduct

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ABSTRACT

The Lewis acid–base adduct *t*-Bu₃Al–SbMe₃ (**1**), which was synthesized by reaction of equimolar amounts of *t*-Bu₃Al and trimethylstibine SbMe₃, was characterized by multinuclear NMR (¹H, ¹³C) spectroscopy, elemental analyses as well as by single crystal X-ray diffraction.

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1. Introduction

The tendency of Lewis acidic trialkylalanes AlR₃ to react with Lewis bases with subsequent formation of Lewis acid–base adducts is a general aspect of their chemistry. In particular reactions with amines and phosphines have been investigated intensely and numerous adducts of the type R₃Al–ER₃ (E = N, P) have been synthesized and structurally characterized in the last decades [1]. Moreover, their dissociation enthalpies were determined both experimentally [2] and by computational studies [3]. In sharp contrast, comparable adducts of the heavier group 15 analogues ER₃ (E = Sb, Bi) have been investigated to a far lesser extent [4] and experimental data on the thermodynamic stability of such adducts (dissociation energies) are almost unavailable. However, structural parameters as-obtained from single crystal X-ray diffraction studies were found to be useful for a rough estimation of the relative strength of the acid–base interaction [5] according to a simple structural model initially described by Haaland [6].

In the last decade we have investigated the synthesis of such adducts in detail and reported on several group 13/15 adducts including those of stibines [7], distibines [8], bismuthines [9] and dibismuthines [10]. However, these adducts were typically synthesized using group 15 complexes containing sterically bulky

substituents as is also true for transition metal stibine complexes [11]. Steric repulsion between the organic substituents generally leads to an increase of the C–Sb–C bond angles and, as a consequence, the p-character of the bonding electron pairs decreases and that of the electron lone-pair increases. The Lewis basicity of the stibine hence increases with increasing steric demand of the substituents.

Herein we describe the synthesis and single crystal X-ray analysis of the first alane–SbMe₃ adduct *t*-Bu₃Al–SbMe₃ (**1**).

2. Results and discussion

The reaction of equimolar amounts of *t*-Bu₃Al and SbMe₃ resulted in the formation of the corresponding Lewis acid–base adduct *t*-Bu₃Al–SbMe₃ (**1**), which was obtained as colorless crystalline solid. **1** was re-crystallized from a solution in *n*-pentane at –30 °C and characterized by multinuclear NMR (¹H, ¹³C) and mass spectroscopy as well as elemental analysis (Scheme 1).

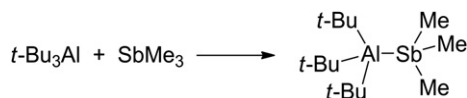
Compared to the starting alane *t*-Bu₃Al and trimethylstibine SbMe₃, the ¹H and ¹³C resonances observed for **1** are shifted to higher field (Me) or lower field (*t*-Bu), respectively. Comparable findings have been previously observed for group 13/15 adducts [12].

Crystals of **1** suitable for a single crystal X-ray diffraction study were obtained from solutions in *n*-pentane solution at –30 °C.

1 crystallizes monoclinic in the space group P2₁/n (**1**) with four molecules in the unit cell. The organic substituents bound to the metal centers adopt a staggered conformation in relation to each

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Scheme 1.

other. The mean Al–C (2.020 Å **1**) and Sb–C bond lengths (2.128 Å **1**) are comparable to those previously observed in alane–stibine adducts $t\text{-Bu}_3\text{Al-SbR}_3$ (R = Et: [7b] Al–C 2.027, Sb–C 2.147 Å; *i*-Pr: [7b] Al–C 2.030, Sb–C 2.182 Å; *i*-Bu: [8c] Al–C 2.019, Sb–C 2.156 Å) and the central Al–Sb bond length of **1** (2.8431(6) Å) belongs to the shortest Al–Sb bond lengths observed so far for these type of adducts. The steric demand of the organic substituents strongly influences the metal–carbon bond length, in particular the Sb–C distances. As a consequence, the sterically less demanding adduct $t\text{-Bu}_3\text{Al-SbMe}_3$ **1** shows the shortest Sb–C bond length, whereas the sterically most hindered adduct $t\text{-Bu}_3\text{Al-Sb}(i\text{-Pr})_3$ exhibits the longest Sb–C bond length. Comparable trends are also observed for the C–Al–C (349.9° **1**) and C–Sb–C (295.6° **1**) bond angular sums. In particular the C–Sb–C bond angles of the four adducts $t\text{-Bu}_3\text{Al-SbR}_3$ as shown in Fig. 2 differ significantly by almost 7°, which clearly reflects the more pronounced repulsive interactions between the larger *i*-Bu and *i*-Pr substituents. The increased steric interactions are also expressed by the C–Sb–Al bond angles as can be seen when comparing $t\text{-Bu}_3\text{Al-SbMe}_3$ **1** and $t\text{-Bu}_3\text{Al-Sb}(i\text{-Bu})_3$: a wide range (110.66(10)–123.38(11)°) was observed for $t\text{-Bu}_3\text{Al-Sb}(i\text{-Bu})_3$, whereas the sterically less hindered adduct $\text{Me}_3\text{Sb-Al}(t\text{-Bu})_3$ **1** shows significantly more consistent angles (117.66(7)–119.71(7)°). Fig. 2 summarizes the trends observed for central structural parameters such as the Al–Sb bond length as well as the C–Al–C and C–Sb–C bond angular sums of four structurally characterized adducts of the type $t\text{-Bu}_3\text{Al-SbR}_3$ (R = Me **1**, Et [7b], *i*-Bu [8c], *i*-Pr [7b]). The influence of the steric demand of the alkyl substituents R bound to Sb becomes quite obvious: with increasing steric demand of R (Me < Et < *i*-Bu < *i*-Pr), which should result in an increasing Lewis basicity of the stibine SbR_3 due to the increasing +*I*-effect, the Al–Sb bond lengths and the C–Sb–C bond angular sum increase whereas the C–Al–C bond angles become more acute. According to these studies, SbMe_3 is the weakest Lewis base within the trialkylstibine family. It should be noted, that the central Al–Sb bond length

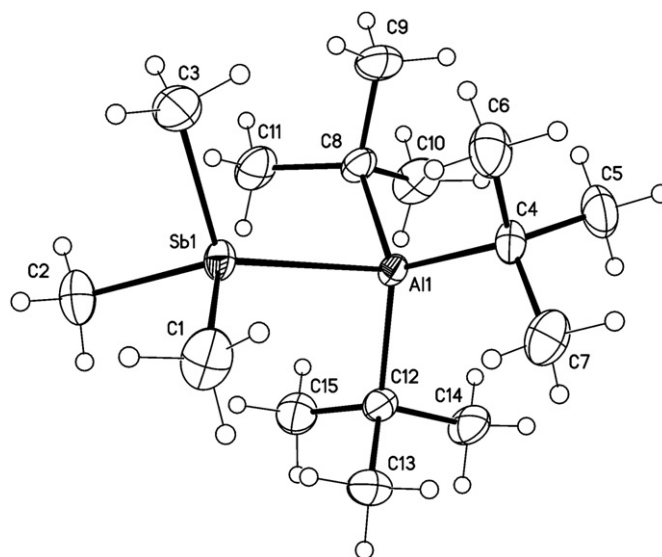


Fig. 1. Molecular structure of **1** (displacement parameters are drawn at 50% probability level) showing the solid-state structure and atom-numbering scheme; selected bond lengths (Å) and angles (°): Al1–Sb1 2.8431(6), Al1–C4 2.021(2), Al1–C8 2.019(2), Al1–C12 2.021(2), Sb1–C1 2.124(2), Sb1–C2 2.129(2), Sb1–C3 2.132(2), C4–Al1–C8 116.31(11), C4–Al1–C12 116.91(10), C8–Al1–C12 116.72(11), C1–Sb1–C2 98.22(10), C1–Sb1–C3 99.07(11), C2–Sb1–C3 98.27(11), C4–Al1–Sb1 101.44(7), C8–Al1–Sb1 99.73(6), C12–Al1–Sb1 100.86(7), C1–Sb1–Al1 119.71(7), C2–Sb1–Al1 119.53(7), C3–Sb1–Al1 117.66(7).

as obtained in the solid state by single crystal X-ray diffraction not necessarily is a valuable indicator for the strength of the Lewis acid–base interaction, in particular when repulsive steric interactions due to the presence of sterically demanding organic substituents have to be considered. Comparable trends have been reported by us [5,7] and others in previous studies. For instance, the B–N bond lengths in the two adducts HCN-BF_3 (1.638 Å) and MeCN-BF_3 (1.630 Å) as obtained in the solid state don't reflect the higher Lewis basicity of MeCN compared to HCN. In contrast, electron diffraction studies revealed significantly different B–N bond distance (247.3 vs. 201.1 Å), which strongly reflect the different Lewis basicity of both electron donor molecules [13].

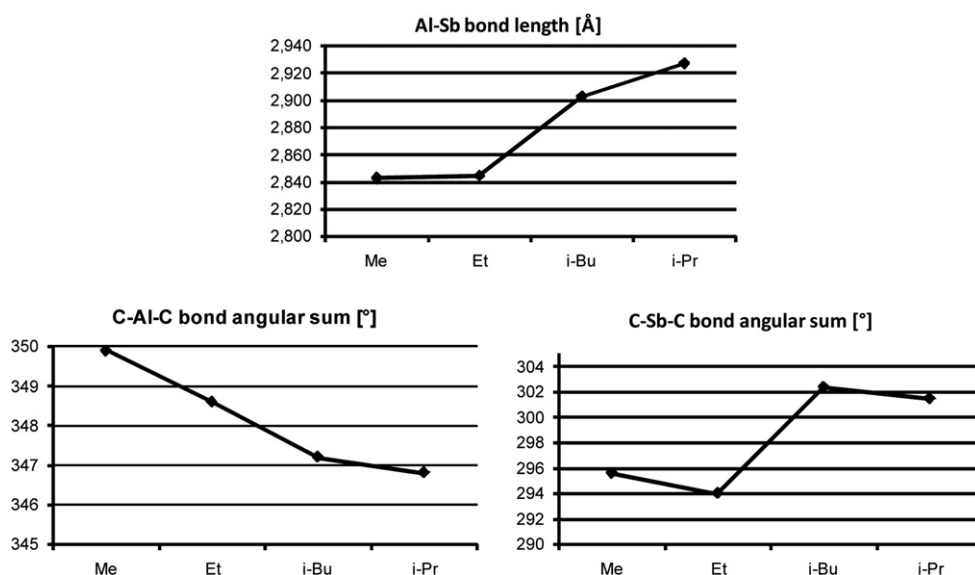


Fig. 2. Central structural parameters of four adducts of the type $\text{R}_3\text{Sb-Al}(t\text{-Bu})_3$ (R = Me, Et, *i*-Bu, *i*-Pr).

Table 1
Crystallographic data and measurements for *t*-Bu₃Al–SbMe₃ (**1**).

	1
Mol formula	C ₁₅ H ₃₆ AlSb
Fw	365.17
Crystal system	Monoclinic
Space group	P2 ₁ /n
<i>a</i> , Å	8.4970(2)
<i>b</i> , Å	12.9678(4)
<i>c</i> , Å	18.0089(6)
β, deg	97.480(2)
<i>V</i> , Å ³	1967.47(10)
<i>Z</i>	4
radiation (wavelength, Å)	Mo Kα (0.71073)
μ, mm ⁻¹	1.432
temp. K	123(2)
<i>D</i> _{calcd} , g cm ⁻³	1.233
Crystal dim. (mm)	0.40 × 0.20 × 0.10
2θ _{max} , deg	54.96
max./min. transmission	0.8700/0.5981
no. of rflns. rec.	23307
no. of nonequiv. rflns. recorded	4437
<i>R</i> _{int}	0.0665
no. of parameters/restraints	154/0
<i>R</i> ₁ ^a ; <i>wR</i> ₂ ^b	0.0250, 0.0630
Goodness of fit ^c	0.921
Largest diff. peak/hole (e Å ⁻³)	0.528, -0.707

^a $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ (for $I > 2\sigma(I)$).^b $wR_2 = \{\sum[w(F_o^2 - F_c^2)]^2 / \sum[w(F_o^2)]^2\}^{1/2}$.^c Goodness of fit = $\{\sum[w(|F_o^2 - F_c^2)|^2] / (N_{\text{observns}} - N_{\text{params}})\}^{1/2}$.

3. Experimental section

3.1. General considerations

All manipulations were performed in a glovebox under Ar-atmosphere or by standard Schlenk techniques. *t*-Bu₃Al [14] and Me₃Sb [15] were prepared according to literature methods. ¹H and ¹³C{¹H} spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal C₆D₅H (δ¹H 7.154, δ¹³C 128.0). The melting point was measured in sealed capillaries and was not corrected. The mass spectrum of **1** only showed signals due to the starting trialkyl compounds as well as typical fragmentation patterns. These results clearly indicate that **1** is fully dissociated in the gas phase.

3.2. Preparation of *t*-Bu₃Al–SbMe₃

0.66 g *t*-Bu₃Al (3 mmol) was added via syringe to a solution of 0.50 g trimethylstibine SbMe₃ (3 mmol) in 5 mL of *n*-pentane. The solution was stored at -30 °C, resulting in the formation of colorless crystals in almost quantitative yield. **1** was characterized without further purification.

t-Bu₃Al–SbMe₃ (**1**): Anal. Calc. for C₁₅H₃₆AlSb (*M* = 365.18): C, 49.34; H, 9.94. Found: C, 49.21; H, 9.87%. ¹H NMR (300 MHz, C₆D₅H, 25 °C): δ = 0.58 (s, 3H, SbCH₃), 1.22 (s, 9H, AlC(CH₃)₃). ¹³C{¹H} NMR (80 MHz, C₆D₅H, 25 °C): δ = -4.1 (SbCH₃), 24.8 (AlC(CH₃)₃), 31.3 (AlC(CH₃)₃).

3.3. X-ray structure solution and refinement

Crystallographic data are summarized in Table 1. Fig. 1 shows the ORTEP diagram of the solid state structure of **1** including selected bond lengths and angles. Data were collected on a Nonius Kappa-CCD diffractometer (**1**). A semi-empirical absorption

correction was applied. The structure was solved by direct methods (SHELXS-97) 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) [16].

Acknowledgments

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Appendix A. Supplementary material

CCDC-771020 (**1**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data-request/cif.

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