Structural Characterization of a Completely Alkyl-substituted Al-Sb Lewis Acid-Base Adduct

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Summary

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.

Keywords: Aluminum, Antimony, Lewis acid-base adduct

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1. Introduction

The tendency of Lewis acidic trialkylalanes AlR_3 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 has been investigated intensely and numerous adducts of the type $\text{R}_3\text{Al-ER}_3$ ($\text{E} = \text{N}, \text{P}$) 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 ER_3 ($\text{E} = \text{Sb}, \text{Bi}$) 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 parameter 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 et al.[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 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 $-30\text{ }^\circ\text{C}$ and characterized by multinuclear NMR (¹H, ¹³C) and mass spectroscopy as well as elemental analysis

((Scheme 1 here))

Compared to the starting alane $t\text{-Bu}_3\text{Al}$ and trimethylstibine SbMe_3 , the ^1H and ^{13}C resonances observed for **1** are shifted to higher field (Me) or lower field ($t\text{-Bu}$), 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 $-30\text{ }^\circ\text{C}$.

((Figure 1 here))

((Table 1 here))

1 crystallizes monoclinic in the space group $P2_1/n$ (**1**) with four molecules in the unit cell. The organic substituents bound to the metal centers adopt a staggered conformation in relation to each other. The mean Al-C ($2.020\text{ \AA}$ **1**) and Sb-C bond lengths ($2.128\text{ \AA}$ **1**) are comparable to those previously observed in alane-stibine adducts $t\text{-Bu}_3\text{Al-SbR}_3$ ($\text{R} = \text{Et}$:[7b] Al-C 2.027 , Sb-C $2.147\text{ \AA}$; $i\text{-Pr}$:[7b] Al-C 2.030 , Sb-C $2.182\text{ \AA}$; $i\text{-Bu}$:[8c] Al-C 2.019 , Sb-C $2.156\text{ \AA}$) and the central Al-Sb bond length of **1** ($2.8431(6)\text{ \AA}$) belongs to the shortest Al-Sb bond distances 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 $i\text{-Bu}$ and $i\text{-Pr}$ 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 ($110.66(10) - 123.38(11)^\circ$) 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 ($117.66(7) - 119.71(7)^\circ$). Fig. 2 summarizes the trends observed for central structural parameter 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 $t\text{-Bu}_3\text{Al-SbR}_3$ ($\text{R} = \text{Me}$ **1**, Et,^[7b] $i\text{-Bu}$,^[8c] $i\text{-Pr}$ ^[7b]). The influence of the steric demand of the alkyl substituents R bound to Sb becomes quite obvious: with increasing steric demand of R ($\text{Me} < \text{Et} < i\text{-Bu} < i\text{-Pr}$), 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* 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 ($1.638 \text{ \AA}$) and MeCN-BF_3 ($1.630 \text{ \AA}$) 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. $201.1 \text{ \AA}$), which strongly reflect the different Lewis basicity of both electron donor molecules.[13]

((Figure 2 here))

3. Experimental Section

3.1. General Considerations.

All manipulations were performed in a glovebox under N₂-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 yields. **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. Figure 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] Crystallographic data of **1** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-771020 (**1**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internal) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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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 K α (0.71073)
μ , mm ⁻¹	1.432
temp. K	123(2)
D _{calcd} , g cm ⁻³	1.233
Crystal dim. (mm)	0.40 x 0.20 x 0.10
2 θ _{max} , deg	54.96
max./ min. transmission	0.8700 / 0.5981
no. of rflns. rec.	23307
no. of nonequiv. rflns. recorded	4437
R _{int}	0.0665
no. of parameters/ restraints	154 / 0
R1 ^a ; wR2 ^b	0.0250, 0.0630
goodness of fit ^c	0.921
Largest diff. peak / hole (eÅ ⁻³)	0.528, -0.707

^a $RI = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$ (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 = $\{\Sigma[w(|F_o^2| - |F_c^2|)^2]/(N_{\text{observns}} - N_{\text{params}})\}^{1/2}$

Figure Captions

Figure 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).

Figure 2. Central structural parameters of four adducts of the type $R_3Sb-Al(t-Bu)_3$ (R = Me, Et, *i*-Bu, *i*-Pr)

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