

# First structural characterization of completely alkyl-substituted Al–Sb Lewis acid–base adducts

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## Abstract

Several Lewis acid–base adducts  $R_3Al \leftarrow SbR'_3$  ( $R' = Et$ ,  $R = Me$  (**1**),  $Et$  (**2**),  $t-Bu$  (**3**);  $R' = n-Pr$ ,  $R = Me$  (**4**),  $Et$  (**5**),  $t-Bu$  (**6**);  $R' = i-Pr$ ,  $R = Me$  (**7**),  $Et$  (**8**),  $t-Bu$  (**9**);  $R' = sec-Bu$ ,  $R = Me$  (**10**),  $Et$  (**11**),  $t-Bu$  (**12**);  $R' = t-Bu$ ,  $R = Me$  (**13**),  $Et$  (**14**),  $t-Bu$  (**15**)) were obtained by reaction of aluminum trialkyls  $R_3Al$  and the corresponding antimony trialkyls  $R'_3Sb$ . For the first time, solid state structures of all-alkyl substituted Al–Sb adducts (**3**, **9**, **13**, **14**) were determined by single crystal X-ray analysis. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Main group chemistry; Aluminum; Antimony; Lewis acid–base adducts

## 1. Introduction

The tendency of Group13 trialkyls to form adducts of the type  $MR_3-D$  is a general aspect of their chemistry. Therefore, the adduct formation of Al, Ga and In trialkyls mainly with amines and phosphines was investigated intensively [1]. Very recently, the role of terminal atoms in the donor–acceptor complexes  $MX_3-D$  ( $M = Al, Ga, In$ ;  $X = F, Cl, Br, I$ ;  $D = X^-, YX_3, YH_3$ ;  $Y = N, P, As$ ) was investigated [2]. Reports on adducts with arsines are not as numerous [3] and adducts with the higher homolog, Sb, are very rare. Some compounds of the type  $X_3B \leftarrow Sb(SiMe_3)_3$  ( $X = \text{halogen}$ ),  $R_3M \leftarrow Sb(SiMe_3)_3$  ( $M = Al, Ga, In$ ;  $R = \text{alkyl}$ ) and  $R_3M \leftarrow SbR'_3$  ( $M = Ga, In$ ) have been reported [4]. In addition, reactions between  $R_3Sb$  or  $R_3SbCl_2$  and  $AlEt_nCl_{3-n}$  ( $n = 0, 1, 2, 3$ )<sup>1</sup> and reactions of  $Sb(NMe_3)_3$  with  $R_3Al$  [6] have been investigated.

Within the last years, we focused on the preparation of compounds containing Al–Sb bonds and reported

the synthesis and X-ray structures of several Al–Sb ring compounds containing two-electron two-center  $\sigma$ -bonds and Lewis acid–base adducts  $R_3Al \leftarrow Sb(SiMe_3)_3$  and  $R_2AlCl \leftarrow Sb(SiMe_3)_3$ , respectively [7]. Herein, we present the synthesis of completely alkyl-substituted Al–Sb Lewis acid–base adducts and for the first time their structural characterization by single crystal X-ray structure analysis.

## 2. Results and discussion

The simple Lewis acid–base adducts **1–15** were prepared by reaction of equimolar amounts of the Al- and Sb-trialkyl and investigated by <sup>1</sup>H- and <sup>13</sup>C-NMR spectroscopy.  $\alpha$ -H and  $\alpha$ -C shifts and differences of the chemical shifts between adduct and pure trialkyl ( $\Delta H$ ,  $\Delta C$ ) are summarized in Table 1<sup>2</sup>.

The <sup>1</sup>H-NMR spectra do not show resonances of the starting trialkyls ( $R_3Al$ ,  $R_3Sb$ ). The resonances of the organic ligands bound to the Al centers are shifted to lower field, while resonances of the organic ligands bound to Sb are shifted to higher field. Comparable

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<sup>1</sup> In Ref. [5] the preparation of  $Et_3AlSbEt_3$  is described and the electrical conductivity of the resulting mixture was measured. However, no further characterization of the product is given.

<sup>2</sup> Large linewidths observed in <sup>27</sup>Al-NMR spectra (1500–3000 Hz) made comparisons between the adducts impossible. Data are therefore not presented in this paper.

Table 1  
Selected  $^1\text{H}$ - and  $^{13}\text{C}$ -NMR shifts and  $\Delta(\text{H})$  and  $\Delta(\text{C})$  values of the Al trialkyls and the adducts **1–15** in  $\text{C}_6\text{D}_6$

| Compound   | $\delta$ $^1\text{H}^a$ | $\delta$ $^{13}\text{C}^b$ | $\Delta(\text{H})^c$ | $\Delta(\text{C})^d$ |
|--|-------------------------|----------------------------|----------------------|----------------------|
| $\text{Me}_3\text{Al}$   | −0.36                   | −6.79                      | −                    | −                    |
| $\text{Me}_3\text{Al} \leftarrow \text{SbEt}_3$ ( <b>1</b> )                 | −0.32                   | −6.38                      | 0.04                 | 0.41                 |
| $\text{Me}_3\text{Al} \leftarrow \text{Sb}(n\text{-Pr})_3$ ( <b>4</b> )      | −0.33                   | −6.67                      | 0.03                 | 0.12                 |
| $\text{Me}_3\text{Al} \leftarrow \text{Sb}(i\text{-Pr})_3$ ( <b>7</b> )      | −0.28                   | −5.39                      | 0.08                 | 1.40                 |
| $\text{Me}_3\text{Al} \leftarrow \text{Sb}(\text{sec-Bu})_3$ ( <b>10</b> )   | −0.32                   | −6.38                      | 0.04                 | 0.41                 |
| $\text{Me}_3\text{Al} \leftarrow \text{Sb}(t\text{-Bu})_3$ ( <b>13</b> )     | −0.21                   | −5.02                      | 0.15                 | 1.77                 |
| $\text{Et}_3\text{Al}$   | 0.31                    | 0.87                       | −                    | −                    |
| $\text{Et}_3\text{Al} \leftarrow \text{SbEt}_3$ ( <b>2</b> )                 | 0.35                    | 2.40                       | 0.04                 | 1.53                 |
| $\text{Et}_3\text{Al} \leftarrow \text{Sb}(n\text{-Pr})_3$ ( <b>5</b> )      | 0.33                    | 1.88                       | 0.02                 | 0.99                 |
| $\text{Et}_3\text{Al} \leftarrow \text{Sb}(i\text{-Pr})_3$ ( <b>8</b> )      | 0.37                    | 2.62                       | 0.06                 | 1.75                 |
| $\text{Et}_3\text{Al} \leftarrow \text{Sb}(\text{sec-Bu})_3$ ( <b>11</b> )   | 0.37                    | 2.54                       | 0.06                 | 1.67                 |
| $\text{Et}_3\text{Al} \leftarrow \text{Sb}(t\text{-Bu})_3$ ( <b>14</b> )     | 0.42                    | 3.70                       | 0.11                 | 2.83                 |
| $t\text{-Bu}_3\text{Al}$   | 1.08                    | 21.09                      | −                    | −                    |
| $t\text{-Bu}_3\text{Al} \leftarrow \text{SbEt}_3$ ( <b>3</b> )               | 1.27                    | 19.10                      | 0.19                 | −2.01                |
| $t\text{-Bu}_3\text{Al} \leftarrow \text{Sb}(n\text{-Pr})_3$ ( <b>6</b> )    | 1.30                    | 19.10                      | 0.22                 | −2.01                |
| $t\text{-Bu}_3\text{Al} \leftarrow \text{Sb}(i\text{-Pr})_3$ ( <b>9</b> )    | 1.26                    | 19.58                      | 0.18                 | −1.51                |
| $t\text{-Bu}_3\text{Al} \leftarrow \text{Sb}(\text{sec-Bu})_3$ ( <b>12</b> ) | 1.21                    | 20.27                      | 0.13                 | −0.82                |
| $t\text{-Bu}_3\text{Al} \leftarrow \text{Sb}(t\text{-Bu})_3$ ( <b>15</b> )   | 1.09                    | 21.24                      | 0.01                 | 0.15                 |

<sup>a</sup>  $\text{Me}_3\text{Al}$  and  $\text{Et}_3\text{Al}$ :  $\delta$   $^1\text{H}$  ( $\alpha\text{-H}$ );  $t\text{-Bu}_3\text{Al}$ :  $\delta$   $^1\text{H}$  ( $\beta\text{-H}$ ).

<sup>b</sup>  $\text{Me}_3\text{Al}$ ,  $\text{Et}_3\text{Al}$  and  $t\text{-Bu}_3\text{Al}$ :  $\delta$   $^{13}\text{C}$  ( $\alpha\text{-C}$ );  $t\text{-Bu}_3\text{Al}$ :  $\delta$   $^{13}\text{C}$  ( $\alpha\text{-C}$ ).

<sup>c</sup>  $\text{Me}_3\text{Al}$  and  $\text{Et}_3\text{Al}$ :  $\Delta(\text{H}) = \delta$  ( $\alpha\text{-H}$ )<sub>adduct</sub> −  $\delta$  ( $\alpha\text{-H}$ )<sub>trialkylalane</sub>;  $t\text{-Bu}_3\text{Al}$ :  $\Delta(\text{H}) = \delta$  ( $\beta\text{-H}$ )<sub>adduct</sub> −  $\delta$  ( $\beta\text{-H}$ )<sub>trialkylalane</sub>.

<sup>d</sup>  $\text{Me}_3\text{Al}$ ,  $\text{Et}_3\text{Al}$  and  $t\text{-Bu}_3\text{Al}$ :  $\Delta(\text{C}) = \delta$  ( $\alpha\text{-C}$ )<sub>adduct</sub> −  $\delta$  ( $\alpha\text{-C}$ )<sub>trialkylalane</sub>;  $t\text{-Bu}_3\text{Al}$ :  $\Delta(\text{C}) = \delta$  ( $\alpha\text{-C}$ )<sub>adduct</sub> −  $\delta$  ( $\alpha\text{-C}$ )<sub>trialkylalane</sub>.

results were obtained in adducts of the type  $\text{Me}_3\text{Al-NHR}_2$  [8],  $\text{Et}_3\text{Al-NHR}_2$  [1n],  $\text{Me}_3\text{Al-PR}_3$  [1d],  $\text{R}_3\text{Ga-PR}'_3$  ( $\text{R} = \text{Me}, \text{Et}$ ) [1f,9], and  $\text{Me}_3\text{In-NR}_3$  [10]. The shift extension observed for  $\alpha\text{-H-Al}$  and  $\alpha\text{-C-Al}$  resonances in  $\text{Me}_3\text{Al}$  and  $\text{Et}_3\text{Al}$  adducts correlates with the basicity of the Sb trialkyls. The biggest lowfield shift of  $\alpha\text{-H}$  and  $\alpha\text{-C}$  resonances (and therefore biggest  $\Delta(\text{H})$  and  $\Delta(\text{C})$  values) of the Al–Me and Al–Et group were observed with the *strongest* Lewis base  $t\text{-Bu}_3\text{Sb}$ , indicating **13** and **14** to be the strongest adduct within their group<sup>3</sup>.

In contrast, the resonances due to the  $t\text{-Bu}_3\text{Al}$  adducts show the biggest lowfield shift with the *weakest* Lewis base  $\text{Et}_3\text{Sb}$  (**3**). Sterically bulkier substituents at the Sb atom lead to a less intense lowfield shift and the adduct with  $t\text{-Bu}_3\text{Sb}$  (**15**) show resonances due to the organic ligands at the same shift as was found for the starting trialkyls, indicating this sterically overcrowded adduct to be completely dissociated in solution. Steric repulsion between the ligands, as indicated by the Tolman angle, reaches its maximum for the sterically most demanding  $t\text{-Bu}_3\text{Sb}$  adducts<sup>4</sup>. While this contradictory

<sup>3</sup> The proportional correlation of steric bulk of the substituents and the basicity strength of the lone pair is well known for amines  $\text{R}_3\text{N}$  and phosphines  $\text{R}_3\text{P}$ .

<sup>4</sup> In analogy to the well documented amines  $\text{R}_3\text{N}$  and phosphines  $\text{R}_3\text{P}$ , the Tolman angle increases in the following order:  $\text{Et}_3\text{Sb} \approx n\text{-Pr}_3\text{Sb} < i\text{-Pr}_3\text{Sb} \approx \text{sec-Bu}_3\text{Sb} < t\text{-Bu}_3\text{Sb}$ .

influence on the adduct strength<sup>5</sup> is less intense for the sterically less demanding  $\text{Me}_3\text{Al}$  and the  $\text{Et}_3\text{Al}$  adducts (here the basicity of  $\text{R}_3\text{Sb}$  dominates), it becomes the dominating factor for the sterically bulkier  $t\text{-Bu}_3\text{Al}$  adducts. They tend to form stronger adducts with electronically weaker, but sterically less demanding Sb trialkyls.

However, the observed chemical shifts do not necessarily have to be the chemical shift of the ‘real’ adducts because it might be an intermediate chemical shift of associated and dissociated species. If fast combination/recombination processes (on the NMR time scale) occur in solution and if the rate, at which such exchange reactions occur, is greater than the frequency separation of the resonance peaks corresponding to the two environments, the two peaks will merge into a single peak of the intermediate chemical shift. In case of  $\text{R}_3\text{Al-SbR}_3$  adducts, which contain an unfavorable combination of hard Lewis acid and weak Lewis base, it seems plausible, that the adducts are at least partially dissociated<sup>6</sup>.

Mass spectra of **1–15** do not show molecular ion peaks due to fragmentation into the corresponding aluminum- and antimony trialkyls. However, the solid adducts can be sublimed without decomposition at temperatures between 55 and 75°C at  $10^{-3}$  mbar.

## 2.1. Structural description

Crystals of four different adducts have been obtained from pentane solution at  $-30^\circ\text{C}$ .

Compounds **3**, **9**, **13** and **14** crystallize monoclinic in the space group  $P2_1/c$  (**3**, **14**) and  $P2_1/n$  (**9**, **13**), respectively. In all adducts, the ligands bound to the metal centers adopt a staggered conformation in relation to one other. The mean Al–C (**3**: 2.027 Å; **9**: 2.030 Å; **13**: 1.967 Å; **14**: 1.981 Å) and Sb–C bond lengths (**3**: 2.147 Å; **9**: 2.182 Å; **13**: 2.205 Å; **14**: 2.210 Å) are within the expected range. However, they show significant differences dependent on the steric bulk of the ligands. The mean C–Al–C (**3**: 116.2°; **9**: 115.6°; **13**: 115.7°; **14**:

<sup>5</sup> Electronically,  $t\text{-Bu}_3\text{Sb}$  is the strongest base but, due to the increased steric pressure, sometimes complexation to a Lewis acid is kinetically hindered.

<sup>6</sup> Combination of  $\text{R}_3\text{Al}$  with an excess of the antimony trialkyl (100%) yield only *one* resonance for the antimony substituents in the  $^1\text{H}$ -NMR spectra shifted to other ppm values compared to the 1:1 combination, obviously due to fast combination/recombination processes (on the NMR time scale) in solution. Low temperature NMR studies ( $-60^\circ\text{C}$ ) do not show the coalescence point of the process. Unfortunately, we weren't able to perform cryoscopic molecular weight measurements (to determine the degree of dissociation) due to the extreme sensitivity of the compounds in solution towards air and moisture.

114.6°) and C–Al–Sb bond angles (**3**: 101.4°; **9**: 102.3°; **13**: 102.1°; **14**: 103.33°) differ marginally, while the effect of bulky substituents on the C–Sb–C (**3**: 98.0°; **9**: 100.5°; **13**: 106.4°; **14**: 105.9°) and C–Sb–Al bond angles (**3**: 119.3°; **9**: 117.3°; **13**: 112.4°; **14**: 112.8°) is much stronger. In particular, the sterically overcrowded adduct **9** shows significant differences, e.g. the C–Sb–Al bond angles span the wide range of 112.2(1)–122.0(1)°.

The Al–Sb bond lengths observed in **3**, **9**, **13** and **14** clearly display the influence of steric bulk on the distances. Compound **3** (2.845(1) Å) shows the same distance as the comparable adduct Et<sub>3</sub>Al←Sb(SiMe<sub>3</sub>)<sub>3</sub> (2.841(1) Å), while the Al–Sb bond length in **14** (2.873(1) Å) is slightly elongated (3 pm). Compounds **3** and **14** show the same ligand sphere, only the ligands are swapped between Al and Sb. These adducts clearly demonstrate the different influence of bulky ligands on the Al and Sb atom. The Sb center is more sensitive towards steric bulk than the Al center, as can be seen by comparing the C–E–C bond angles (E = Al, Sb). In contrast to the C–Al–C angles, which are almost equal (average values: **3**: 116.2°; **14**: 114.6°), the C–Sb–C angles differ significantly (**3**: 98.0°; **14**: 105.9°). The somewhat bigger steric pressure in **14** leads to an elongated bond length compared to **3**.

The influence of bulky substituents on the Al–Sb bond length can be seen much clearer when **3** is compared with **9**. In these adducts the acid remains constant (*t*-Bu<sub>3</sub>Al) and only the trialkyl stibine is changed. The replacement of three Et groups (**3**) by three *i*-Pr groups (**9**) leads to an increased steric pressure, resulting in an 8 pm elongated Al–Sb distance (2.927(1)–2.845(1) Å).

Compounds **13** and **14** only differ by their Lewis acid, while the base fragment remains constant. The stronger Lewis acid Me<sub>3</sub>Al (**13**) shows a 4 pm shortened Al–Sb bond distance (**13**: 2.834(1) Å; **14**: 2.873(1) Å). **13** shows a disorder of the ligands due to the lower steric bulk of the Me groups.

### 3. Conclusions

A series of 15 adducts of Al trialkyls and Sb trialkyls have been prepared. Due to their sensitivity in solution, cryoscopic molecular weight determinations did not give reliable values. However, we believe **1–15** to be at least partially dissociated in solution. <sup>1</sup>H- and <sup>13</sup>C-NMR investigations demonstrate the influence of steric bulk on the adduct strength. For Me<sub>3</sub>Al and Et<sub>3</sub>Al adducts, the adduct strength correlates proportional to the basicity of the antimony trialkyl, while for the sterically more demanding *t*-Bu<sub>3</sub>Al adducts it correlates to the steric bulk of the ligands: the bulkier the ligands, the weaker the adducts. The dominating factor is *steric repulsion* between the ligands.

Four single crystal X-ray structures, all containing *t*-Bu<sub>3</sub>Al or *t*-Bu<sub>3</sub>Sb fragments, clearly demonstrate the existence of adducts in the solid state. The observed bond lengths, which range from 2.83 to 2.93 Å, clearly display the influence of steric bulk on the distances.

## 4. Experimental

### 4.1. General considerations

All manipulations were performed in a glovebox under N<sub>2</sub>-atmosphere or by standard Schlenk techniques. Me<sub>3</sub>Al and Et<sub>3</sub>Al were purchased from Aldrich and used as received. *t*-Bu<sub>3</sub>Al [11] and R<sub>3</sub>Sb (R = Et, *n*-Pr, *i*-Pr, *sec*-Bu) [12] were prepared by literature methods, *t*-Bu<sub>3</sub>Sb by a standard salt elimination reaction between SbCl<sub>3</sub> and *t*-BuLi at –100°C. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} spectra were recorded using a Bruker AMX 300 spectrometer and are referenced to internal C<sub>6</sub>D<sub>5</sub>H (δ <sup>1</sup>H 7.154, δ <sup>13</sup>C 128.0). Melting points were observed in sealed capillaries and were not corrected. Mass spectroscopy studies were performed but only show the starting trialkyl compounds due to dissociation in the gas phase. Therefore data are not presented.

### 4.2. General preparation of adducts R<sub>3</sub>Al–SbR'<sub>3</sub>

The aluminum trialkyl (5 mmol) and antimony trialkyl (5 mmol) were combined at room temperature in the glovebox. In the case of **3**, **6**, **9**, **13–15** a white solid was formed, which was dissolved in pentane and stored at –30°C, resulting in the formation of colorless crystals in almost quantitative yield. In the case of liquid adducts **1**, **2**, **4–8**, **10–12** they were characterized without further purification. Only the Me<sub>3</sub>Al adducts will be presented here (**1**, **4**, **7**, **10**, **13**). The Et<sub>3</sub>Al and *t*-Bu<sub>3</sub>Al adducts were deposited as supplementary material.

#### 4.2.1. Me<sub>3</sub>Al–SbEt<sub>3</sub> (**1**)

Anal. Calc. for C<sub>9</sub>H<sub>24</sub>AlSb (M = 281): C, 38.43; H, 8.54. Found: C, 38.21; H, 8.37%. <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>H, 25 °C): δ = –0.32 (s, 3H, AlCH<sub>3</sub>), 1.09–1.25 (m, 5H, Et). <sup>13</sup>C{<sup>1</sup>H}-NMR (80 MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C): δ = –6.4 (Me), 5.8 (SbCH<sub>2</sub>CH<sub>3</sub>), 11.9 (SbCH<sub>2</sub>CH<sub>3</sub>).

#### 4.2.2. Me<sub>3</sub>Al–Sb(*n*-Pr)<sub>3</sub> (**4**)

Anal. Calc. for C<sub>12</sub>H<sub>30</sub>AlSb (M = 323): C, 44.58; H, 9.29. Found: C, 44.43; H, 9.21%. <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C): δ = –0.33 (s, 3H, AlCH<sub>3</sub>), 0.93 (t, <sup>3</sup>J<sub>HH</sub> = 7.2 Hz, 3H, SbCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.30 (m, 2H, SbCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 1.45–1.57 (m, 2H, SbCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (80 MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C): δ = –6.7 (Me), 17.2 (SbCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 18.3 (SbCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 21.6 (SbCH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>).

Table 2

Crystallographic data and measurements for *t*-Bu<sub>3</sub>Al-SbEt<sub>3</sub> (**3**), *t*-Bu<sub>3</sub>Al-Sb(*i*-Pr)<sub>3</sub> (**9**), Me<sub>3</sub>Al-Sb(*t*-Bu)<sub>3</sub> (**13**), and Et<sub>3</sub>Al-Sb(*t*-Bu)<sub>3</sub> (**14**)

|  | <b>3</b>                                    | <b>9</b>                                    | <b>13</b>                                   | <b>14</b>                                   |
|--|---|---|---|---|
| Molecular formula  | C <sub>18</sub> H <sub>42</sub> AlSb        | C <sub>21</sub> H <sub>48</sub> AlSb        | C <sub>15</sub> H <sub>36</sub> AlSb        | C <sub>18</sub> H <sub>42</sub> AlSb        |
| Fw   | 407.25                                      | 449.32                                      | 365.17                                      | 407.25                                      |
| Crystal system   | Monoclinic                                  | Monoclinic                                  | Monoclinic                                  | Monoclinic                                  |
| Space group  | <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14) | <i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14) | <i>P</i> 2 <sub>1</sub> / <i>n</i> (no. 14) | <i>P</i> 2 <sub>1</sub> / <i>c</i> (no. 14) |
| <i>a</i> (Å)   | 14.1647(7)                                  | 8.7709(2)                                   | 8.5113(1)                                   | 14.1186(7)                                  |
| <i>b</i> (Å)   | 9.5559(4)                                   | 18.7738(3)                                  | 27.0387(4)                                  | 9.4706(4)                                   |
| <i>c</i> (Å)   | 16.0327(8)                                  | 15.3248(2)                                  | 9.2741(1)                                   | 16.1244(9)                                  |
| $\beta$ (°)  | 90.916(3)                                   | 99.463(1)                                   | 110.760(1)                                  | 90.909(2)                                   |
| <i>V</i> (Å <sup>3</sup> )   | 2169.85(18)                                 | 2489.09(8)                                  | 1995.72(4)                                  | 2155.75(18)                                 |
| <i>Z</i>   | 4   | 4   | 4   | 4   |
| Radiation (wavelength (Å))   | Mo-K $\alpha$ (0.71073)                     | Mo-K $\alpha$ (0.71073)                     | Mo-K $\alpha$ (0.71073)                     | Mo-K $\alpha$ (0.71073)                     |
| $\mu$ (mm <sup>-1</sup> )  | 1.31  | 1.14  | 1.41  | 1.31  |
| Temperature (K)  | 123(2)                                      | 123(2)                                      | 123(2)                                      | 123(2)                                      |
| <i>D</i> <sub>calc</sub> (g cm <sup>-3</sup> )                           | 1.25  | 1.20  | 1.22  | 1.26  |
| Crystal dimensions (mm)  | 0.40 × 0.25 × 0.20                          | 0.25 × 0.20 × 0.15                          | 0.35 × 0.30 × 0.30                          | 0.70 × 0.60 × 0.50                          |
| 2 $\theta$ <sub>max</sub> (°)  | 56.6  | 56.6  | 56.6  | 56.6  |
| Max./min. transmission   | 0.7296/0.6509                               | 0.7917/0.7200                               | 0.7092/0.5993                               | 0.6162/0.5097                               |
| No. of reflections recorded  | 13310                                       | 51001                                       | 32 812                                      | 24 112                                      |
| No. of nonequivalent reflections recorded                                | 5148  | 6164  | 4898  | 5024  |
| <i>R</i> <sub>int</sub>  | 0.038                                       | 0.043                                       | 0.047                                       | 0.036                                       |
| No. of parameters/restraints   | 182/0                                       | 208/0                                       | 131/240                                     | 181/0                                       |
| <i>R</i> <sub>1</sub> <sup>a</sup> ; <i>wR</i> <sub>2</sub> <sup>b</sup> | 0.030, 0.078                                | 0.019, 0.047                                | 0.037, 0.092                                | 0.032, 0.074                                |
| Largest difference peak and hole (e Å <sup>-3</sup> )                    | 1.427, -0.719                               | 0.473, -0.833                               | 1.161, -0.877                               | 0.579, -0.882                               |

<sup>a</sup> For  $I > 2\sigma(I)$ .<sup>b</sup> For all data.

#### 4.2.3. Me<sub>3</sub>Al-Sb(*i*-Pr)<sub>3</sub> (**7**)

Anal. Calc. for C<sub>12</sub>H<sub>30</sub>AlSb (M = 323): C, 44.58; H, 9.29. Found: C, 44.45; H, 9.22%. <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>H, 25 °C):  $\delta$  = -0.28 (s, 3H, AlCH<sub>3</sub>), 1.21 (d, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 6H, SbCH(CH<sub>3</sub>)<sub>2</sub>), 1.75 (sept, <sup>3</sup>*J*<sub>HH</sub> = 7.4 Hz, 1H, SbCH(CH<sub>3</sub>)<sub>2</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (80 MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C):  $\delta$  = -5.4 (AlCH<sub>3</sub>), 17.9 (SbCH(CH<sub>3</sub>)<sub>2</sub>), 22.7 (SbCH(CH<sub>3</sub>)<sub>2</sub>).

#### 4.2.4. Me<sub>3</sub>Al-Sb(*sec*-Bu)<sub>3</sub> (**10**)

Anal. Calc. for C<sub>15</sub>H<sub>36</sub>AlSb (M = 365): C, 49.32; H, 9.86. Found: C, 49.25; H, 9.81%. <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C):  $\delta$  = -0.32 (s, 3H, AlCH<sub>3</sub>), 0.94 (three t, <sup>3</sup>*J*<sub>HH</sub> = 7.0, 7.2, 7.4 Hz, 3H, SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.21–1.25 (three d, <sup>3</sup>*J*<sub>HH</sub> = 7.2, 7.4, 7.5 Hz, 3H, SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.43–1.56 (m, <sup>3</sup>*J*<sub>HH</sub> = 7.2, 7.4 Hz, 1H, SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 1.62–1.81 (m, <sup>3</sup>*J*<sub>HH</sub> = 7.2, 7.4, 7.5 Hz, 2H, SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H}-NMR (80 MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C):  $\delta$  = -6.4 (AlCH<sub>3</sub>), 14.0, 14.0, 14.1, 14.1 (SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 18.4, 18.5, 18.6, 18.8 (SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 25.0, 25.3, 25.7, 25.8 (SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>), 29.5, 29.8, 30.0, 30.2 (SbCH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>).

#### 4.2.5. Me<sub>3</sub>Al-Sb(*t*-Bu)<sub>3</sub> (**13**)

Yield: 90%. Anal. Calc. for C<sub>15</sub>H<sub>36</sub>AlSb (M = 365): C, 49.32; H, 9.86. Found: C, 49.27; H, 9.80%. M.p. 126°C. <sup>1</sup>H-NMR (300 MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C):  $\delta$  = -0.21 (s, 3H, AlCH<sub>3</sub>), 1.25 (s, 9H, *t*-Bu). <sup>13</sup>C{<sup>1</sup>H}-NMR (80

MHz, C<sub>6</sub>D<sub>5</sub>H, 25°C):  $\delta$  = -5.0 (AlCH<sub>3</sub>), 32.2 (SbCMe<sub>3</sub>), 34.0 (SbCMe<sub>3</sub>).

#### 4.3. X-ray structure solution and refinement

Crystallographic data are summarized in Table 2. Figs. 1–4 show the ORTEP diagrams of the solid-state structures of **3**, **9**, **13** and **14** including selected bond lengths and angles. Data were collected on a Nonius Kappa-CCD diffractometer. In all cases absorption corrections were applied. Structures were solved by direct methods (SHELXS-97) [13] and refined by full-matrix least-squares on *F*<sup>2</sup>. All non-hydrogen atoms were refined anisotropically and hydrogen atoms by a riding model (SHELXL-97) [14]. In **13**, all Me groups are disordered and refined isotropically.

#### 5. Supplementary material

The experimental data of the Et<sub>3</sub>Al and *t*-Bu<sub>3</sub>Al adducts have been deposited as supplementary information. Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 135438 (**3**), no. 135439 (**9**), no. 135440 (**13**), and no. 135441 (**14**). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: de-

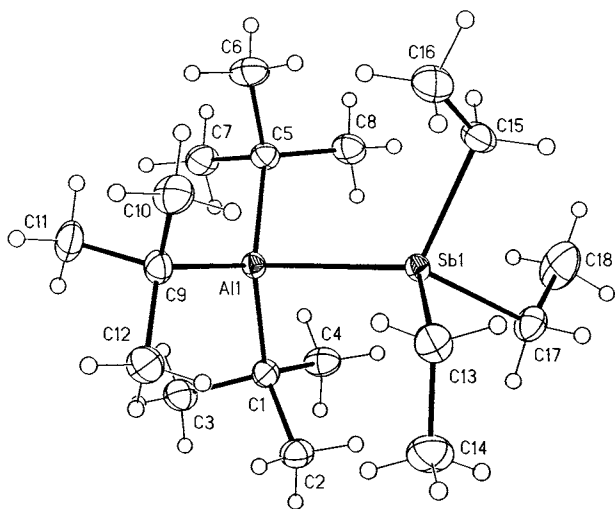


Fig. 1. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **3**; selected bond lengths (Å) and angles (°): AlI1–Sb1 2.8447(7), AlI1–C1 2.027(2), AlI1–C5 2.022(3), AlI1–C9 2.033(2), Sb1–C13 2.149(3), Sb1–C15 2.144(2), Sb1–C17 2.149(2), C1–AlI1–C5 116.32(11), C1–AlI1–C9 115.89(11), C5–AlI1–C9 116.46(11), C13–Sb1–C15 97.91(11), C13–Sb1–C17 98.30(11), C15–Sb1–C17 97.92(10), C1–AlI1–Sb1 101.00(7), C5–AlI1–Sb1 101.17(7), C9–AlI1–Sb1 101.88(8), C13–Sb1–AlI1 118.91(7), C15–Sb1–AlI1 118.57(8), C17–Sb1–AlI1 120.52(8).

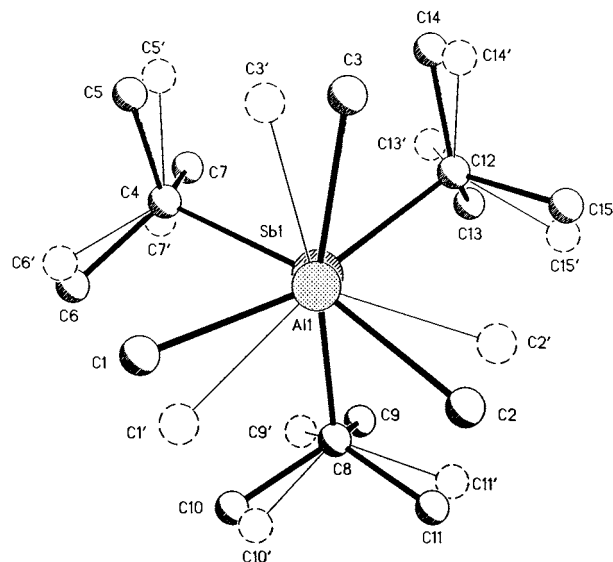


Fig. 3. Structure plot showing the staggered conformation, the distortion and the atom-numbering scheme for **13**; selected bond lengths (Å) and angles (°): AlI1–Sb1 2.8344(10), AlI1–C1\* 1.955(7), AlI1–C2\* 1.965 (7), AlI1–C3\* 1.981(7), Sb1–C4 2.205(3), Sb1–C8 2.206(3), Sb1–C12 2.205(4), C1\*–AlI1–C2\* 116.1(4), C1\*–AlI1–C3\* 116.1(4), C2\*–AlI1–C3\* 115.4(6), C4–Sb1–C8 106.20(14), C4–Sb1–C12 106.25(14), C8–Sb1–C12 106.65(15), C1\*–AlI1–Sb1 102.7(3), C2\*–AlI1–Sb1 101.8(2), C3\*–AlI1–Sb1 101.8(2), C4–Sb1–AlI1 112.39(9), C8–Sb1–AlI1 113.04(10), C12–Sb1–AlI1 111.83(10). \* Disorder part site occupancy factor = 0.514(4).

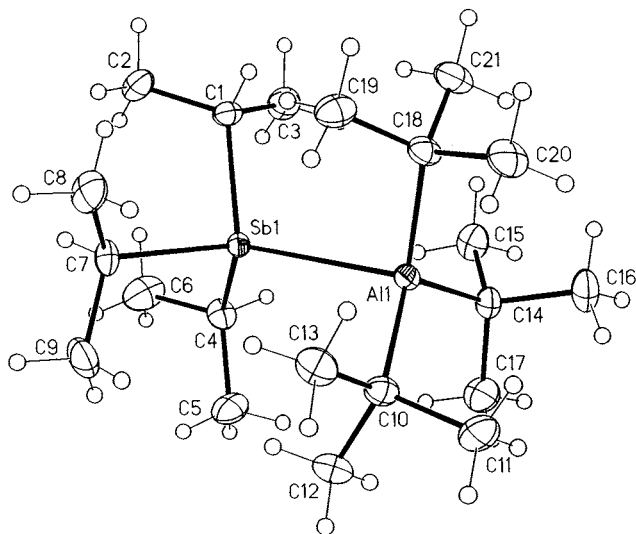


Fig. 2. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **9**; selected bond lengths (Å) and angles (°): AlI1–Sb1 2.9267(4), AlI1–C10 2.026(1), AlI1–C14 2.030(1), AlI1–C18 2.033(1), Sb1–C1 2.186(1), Sb1–C4 2.183(1), Sb1–C7 2.177(1), C10–AlI1–C14 115.22(6), C10–AlI1–C18 115.83(6), C14–AlI1–C18 115.80(6), C1–Sb1–C4 101.43(6), C1–Sb1–C7 98.85(6), C4–Sb1–C7 101.25(6), C10–AlI1–Sb1 103.25(4), C14–AlI1–Sb1 104.15(4), C18–AlI1–Sb1 99.38(4), C1–Sb1–AlI1 112.20(4), C4–Sb1–AlI1 117.76(4), C7–Sb1–AlI1 121.98(4).

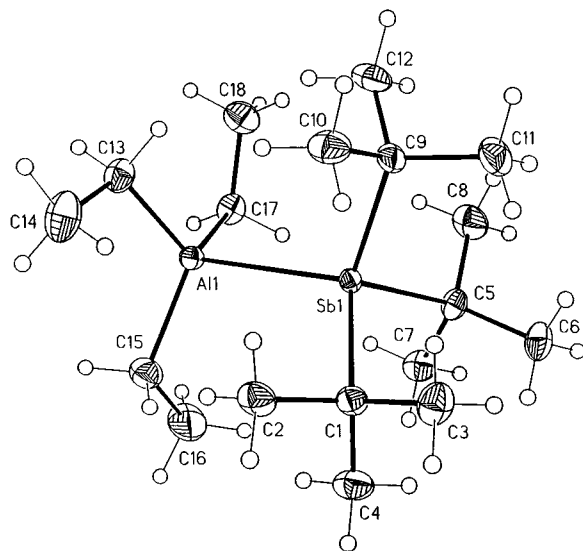


Fig. 4. ORTEP diagram (50% probability ellipsoids) showing the solid-state structure and atom-numbering scheme for **14**; selected bond lengths (Å) and angles (°): AlI1–Sb1 2.8730(9), AlI1–C13 1.981(3), AlI1–C15 1.977(3), AlI1–C17 1.984(3), Sb1–C1 2.214(3), Sb1–C5 2.210(3), Sb1–C9 2.205(3), C13–AlI1–C15 115.35(15), C13–AlI1–C17 114.36(14), C15–AlI1–C17 114.07(15), C1–Sb1–C5 106.00(12), C1–Sb1–C9 105.68(12), C5–Sb1–C9 106.15(12), C13–AlI1–Sb1 103.24(10), C15–AlI1–Sb1 105.17(11), C17–AlI1–Sb1 102.59(10), C1–Sb1–AlI1 113.00(8), C5–Sb1–AlI1 112.26(8), C9–Sb1–AlI1 113.16(8).

posit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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## References

- [1] For example, see the following and references therein: (a) M.G. Gardiner, C.L. Raston, *Coord. Chem. Rev.* 166 (1997) 1. (b) C. Jones, G.A. Koutsantonis, C.L. Raston, *Polyhedron* 12 (1993) 1829. (c) A. Haaland, *Angew. Chem.* 101 (1989) 1017; *Angew. Chem., Int. Ed. Engl.* 28 (1989) 992. (d) A.R. Barron, *J. Chem. Soc., Dalton Trans.* (1988) 3047. (e) D.A. Atwood, R.A. Jones, A.H. Cowley, S.G. Bott, J.L. Atwood, *J. Organomet. Chem.* 434 (1992) 143. (f) O.T. Beachley, Jr., J.D. Maloney, *Organometallics* 16 (1997) 4016. (g) J.E. Park, B.-J. Bae, Y. Kim, J.T. Park, I.-H. Suh, *Organometallics* 18 (1999) 1059. (h) I. Krossing, H. Nöth, H. Schwenk-Kirchner, T. Seifert, C. Tacke, *Eur. J. Inorg. Chem.* (1998) 1925. (i) J. Müller, U. Ruschewitz, O. Indris, H. Hartwig, W. Stahl, *J. Am. Chem. Soc.* 121 (1999) 4647. (j) P.T. Brain, H.E. Brown, A.J. Downs, T.M. Greene, E. Johnsen, S. Parsons, D.W.H. Rankin, B.A. Smart, C.Y. Tang, *J. Chem. Soc., Dalton Trans.* (1998) 3685. (k) R.L. Wells, A.T. McPhail, J.A. Laske, P.S. White, *Polyhedron* 13 (1994) 2737. (l) R.L. Wells, A.T. McPhail, M.F. Self, J.A. Laske, P.S. White, *Organometallics* 12 (1993) 3333. (m) D.C. Bradley, G. Coumbarides, I.S. Harding, G.E. Hawkes, I.A. Maia, M. Motevalli, *J. Chem. Soc., Dalton Trans.* (1999) 3553. (n) E.K. Styron, C.H. Lake, S.J. Schauer, C.L. Watkins, L. K. Krannich, *Polyhedron* 18 (1999) 1595.
- [2] A.Y. Timoshkin, A.V. Suvorov, H.F. Bettinger, H. F. Schaefer III, *J. Am. Chem. Soc.* 121 (1999) 5687.
- [3] For example, see the following and references therein: (a) R.L. Wells, R.A. Baldwin, P.S. White, *Organometallics* 14 (1995) 2123. (b) R.L. Wells, A.T. McPhail, L.J.J. Jones III, M.F. Self, R.J. Butcher, *Organometallics* 11 (1992) 2694. (c) R.L. Wells, A.T. McPhail, T.M. Speer, *Organometallics* 11 (1992) 960. (d) R.L. Wells, A.T. McPhail, T.M. Speer, *Eur. J. Solid State Inorg. Chem.* 29 (1992) 63. (e) L.-J. Baker, L.A. Kloo, C.E.F. Rickard, M. J. Taylor, *J. Organomet. Chem.* 545 (1997) 249. (f) B. Beagley, S.M. Godfrey, K.J. Kelly, S. Kungwankunakorn, C.A. McAuliffe, R.G. Pritchard, *J. Chem. Soc., Chem. Commun.* (1996) 2179. (g) R.L. Wells, E.E. Foos, A.L. Rheingold, G.P.A. Yap, L.M. Liable-Sands, P.S. White, *Organometallics* 17 (1998) 2869.
- [4] (a) M.S. Lube, R.L. Wells, P.S. White, *J. Chem. Soc., Dalton Trans.* (1997) 285. (b) R.A. Baldwin, E.E. Foos, R.L. Wells, P.S. White, A.L. Rheingold, G.P.A. Yap, *Organometallics* 15 (1996) 5035. (c) R.L. Wells, E.E. Foos, P.S. White, A.L. Rheingold, L.M. Liable-Sands, *Organometallics* 16 (1997) 4771. (d) S. Schulz, M. Nieger, *J. Organomet. Chem.* 570 (1998) 275. (e) L.M. Nemirowskii, B.I. Kozyrkin, A.F. Lanstov, B.G. Gribov, I.M. Skvortsov, I.A. Sredinskaya, *Dokl. Akad. Nauk SSSR* 214 (1974) 590. (f) G.E. Coates, *J. Chem. Soc.* (1951) 2003.
- [5] Y. Takashi, I. Aishima, *J. Organomet. Chem.* 8 (1967) 209.
- [6] C.J. Thomas, L.K. Krannich, C.L. Watkins, *Polyhedron* 12 (1993) 89.
- [7] (a) S. Schulz, M. Nieger, *Organometallics* 17 (1998) 3398. (b) S. Schulz, M. Nieger, *Organometallics* 18 (1999) 315.
- [8] S.J. Schauer, C.L. Watkins, L.K. Krannich, R.B. Gala, E.M. Gundy, C.B. Lagrone, *Polyhedron* 14 (1995) 3505.
- [9] A. Leib, M.T. Emerson, J.P. Oliver, *Inorg. Chem.* 4 (1965) 1825.
- [10] D.C. Bradley, H. Dawes, D.M. Frigo, M.B. Hursthouse, B. Hussian, *J. Organomet. Chem.* 325 (1987) 55.
- [11] H. Lehmkuhl, O. Olbrysch, H. Nehl, *Liebigs Ann. Chem.* (1973) 708.
- [12] M. Wieber, in: H. Bitterer (Ed.), *Gmelin Handbook of Inorganic Chemistry, Sb Organoantimony Compounds Part 1*, 8th edition, Springer, Berlin, 1981.
- [13] G.M. Sheldrick, SHELXS-97, Program for Structure Solution, *Acta Crystallogr. Sect. A* 46 (1990) 467.
- [14] G.M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, Germany, 1997.