

# Molecular Structures of Dimeric and Trimeric Dineopentylaluminum Hydride and Trimeric Diphenylaluminum Hydride

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**Keywords:** Aluminum hydrides; Aluminum; Oligomerization; Three-center bonds

**Abstract.** The synthesis of dineopentylaluminum hydride,  $\text{H-Al}(\text{CH}_2\text{CMe}_3)_2$ , is known in the literature since 1988. We determined the crystal structure of this important starting material and found different ring sizes with dimeric versus trimeric formula units. The molecular shape depends on the polarity of the solvent used for

recrystallization (*n*-pentane or 1,2-difluorobenzene). The synthesis of diphenylaluminum hydride, which is also long known in the literature, was optimized. It has a trimeric structure in the solid state with an  $\text{Al}_3\text{H}_3$  heterocycle.

## Introduction

Dialkylaluminum hydrides are important starting compounds in preparative organic or inorganic chemistry.<sup>[1,2]</sup> Due to the coordinative unsaturation and the Lewis acidity of the aluminum atoms these hydrides usually form oligomeric species in solution and the solid state via Al–H–Al 3c–2e bonds. Molecular mass determinations verified trimeric formula units or equilibria between dimeric and trimeric forms in solution,<sup>[3]</sup> and the partial dissociation of a dimer into monomeric fragments was found with the bulky  $\text{CH}(\text{SiMe}_3)_2$  substituent.<sup>[4]</sup> Only two dialkylaluminum hydrides have been characterized by crystal structure determinations, which verified a dimeric and a trimeric compound depending on steric shielding. Monomeric derivatives have only been observed with the very bulky aryl groups 2,4,6-tri(*tert*-butyl)phenyl<sup>[5]</sup> and 2,6-dimesitylphenyl.<sup>[6]</sup> Bis(trimethylsilyl)methyl<sup>[4]</sup> or triisopropylphenyl groups<sup>[7]</sup> lead to dimeric species in the solid state. A dimer has also been observed for  $\text{Me}_2\text{Al-H}$  at a low pressure in the gas phase at 200 °C.<sup>[8]</sup> Bis(*tert*-butyl)aluminum hydride crystallizes as a trimer. In that case the preference of the trimeric form in spite of the relatively high steric shielding was explained by an approach of the packing of the approximately ball-shaped *tert*-butyl groups to a hexagonal closed array.<sup>[9]</sup> Its relatively low solubility in hydrocarbons prevented the determination of its molecular mass in benzene solution.

The facile synthesis of dineopentylaluminum hydride **1** from trineopentylaluminum and  $\text{LiAlH}_4$  has been reported in 1988 by the group of Beachley.<sup>[10]</sup> It is an important starting compound in hydroalumination reactions<sup>[1,11]</sup> and has an interme-

diated steric shielding between that of bis(*tert*-butyl)aluminum hydride and the commercially available diisobutylaluminum hydride which is a standard reagent in organic transformations. Its molecular structure in the solid state has not yet been reported. Another important starting compound for hydroalumination reactions is diphenylaluminum hydride. Compared to dialkylaluminum compounds the phenyl groups should enhance the Lewis acidity of the aluminum atoms, which may be helpful in many secondary applications. Although this hydride is known in the literature since 1964,<sup>[12]</sup> it has been applied only in a preliminary reaction with phenylethyne, which after hydrolytic work-up gave a mixture of at least four products. Its structure is still unknown.

## Results and Discussion

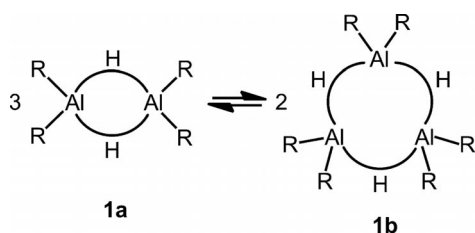
### Dineopentylaluminum Hydride

Dineopentylaluminum hydride **1** is a colorless solid, which is readily soluble in hydrocarbons such as *n*-pentane or benzene. In accordance with <sup>1</sup>H NMR spectroscopic data from Ref. [10] freshly recrystallized samples dissolved in  $\text{C}_6\text{D}_6$  show the <sup>1</sup>H and <sup>13</sup>C NMR signals of two species. Their relative intensities depend on concentration and temperature. In an NMR experiment at 220 K in  $[\text{D}_8]\text{toluene}$  the singlet signals of *tert*-butyl groups at  $\delta = 1.19$  and 1.16 ppm had an integration ratio of about 4.6:1. The intensity of the first one steadily decreased upon warming. At about 283 K both signals had the same intensity, and at 330 K the resonance at  $\delta = 1.19$  completely disappeared. The second resonance at  $\delta = 1.16$  was almost unchanged and showed only the expected continuous shift with increasing temperature ( $\delta = 1.09$  at 380 K). Same holds for the resonances of the  $\text{CH}_2$  protons at  $\delta = 0.73$  and 0.63 ppm (220 K), from which only the latter was observed at 380 K ( $\delta = 0.62$  ppm), and for the signals of the Al–H hydrogen atoms

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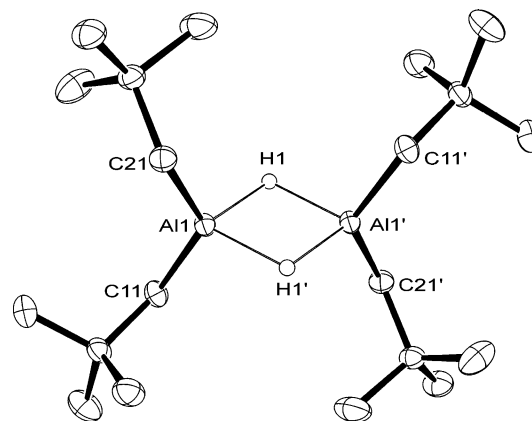
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( $\delta = 3.29$  and  $3.14$ ; the latter disappeared). Molecular mass determinations verified an equilibrium between trimeric and dimeric formula units, which was shifted towards the dimer with increasing dilution (see also Ref. [10]). In view of these results we suppose that the NMR spectra at 300 K show the resonances of the dimer [**1a**,  $\delta = 3.33$ , 1.12, 0.62.  $^{13}\text{C}$  NMR: 35.0 (CH<sub>3</sub>), 27.8 (CH<sub>2</sub>)] and the trimer [**1b**,  $\delta = 3.14$ , 1.15, 0.70.  $^{13}\text{C}$  NMR: 35.0 (CH<sub>3</sub>), 29.0 (CH<sub>2</sub>)] (Scheme 1). The trimer is the preferred species at low temperature and in concentrated solution, while the dimer is the only isomer present at higher temperature. We did not observe coalescence over the entire range of temperature. Therefore, a fast exchange between both oligomeric forms in solution can be excluded, which in addition should result in resonances with average chemical shifts at higher temperatures. We suppose that the trimer is completely transformed to the dimeric molecules upon warming.

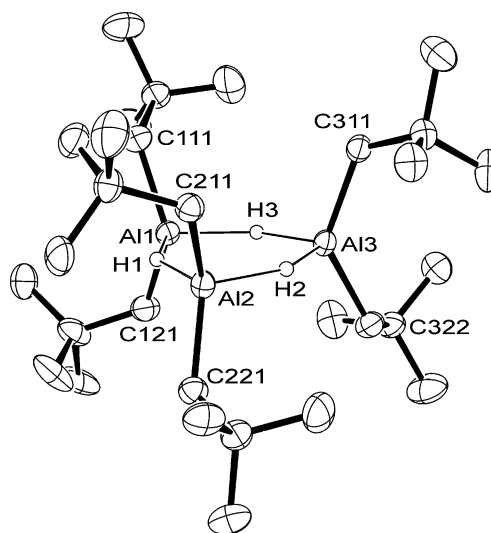


**Scheme 1.** Equilibrium between dimeric and trimeric  $\text{H-Al}(\text{CH}_2\text{CMe}_3)_2$  ( $R = \text{CH}_2\text{CMe}_3$ ).

Crystals of both forms could be isolated from different solvents. Recrystallization from *n*-pentane ( $-30\text{ }^\circ\text{C}$ ) afforded the dimer **1a** (Figure 1), while the polar non-coordinating solvent 1,2-difluorobenzene ( $-30\text{ }^\circ\text{C}$ ) yielded crystals of the trimeric molecule **1b** (Figure 2). Two or three aluminum atoms are bridged by hydrogen atoms to give  $\text{Al}_2\text{H}_2$  or  $\text{Al}_3\text{H}_3$  heterocycles. The four-membered ring is planar due to its position on a crystallographic center of symmetry, and the atoms of the six-membered heterocycle deviate only slightly from the average plane (maximum deviation of an atom 2 pm). The Al–H distances do not significantly depend on the ring size and are 170 pm on average. The endocyclic angles and transannular distances differ considerably. **1a** with the four-membered ring has relatively acute angles Al–H–Al and H–Al–H of  $101.7(7)$  and  $78.3(7)^\circ$ , while for **1b** much larger values of 144 and  $96^\circ$  (on average) were found. A very narrow transannular Al...Al contact of 262.9 pm results for the dinuclear structure of **1a** ( $\text{H}\cdots\text{H} = 214$  pm) which corresponds to the value detected for dimeric dimethylaluminum hydride in the gas phase (262.5 pm).<sup>[8]</sup> A much longer distance of 322.2 pm was observed for **1b** ( $\text{H}\cdots\text{H} = 253$  pm). These observations may reflect a different bonding situation with a closed vs. an open three-center bonding interaction. The structure of the dimer **1a** is isotopic to the previously published structure of dineopentylgallium hydride, which is exclusively dimeric in solution and does not show a dimer/trimer equilibrium.<sup>[13]</sup>



**Figure 1.** Molecular structure of **1a**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of the bridging atoms H1 and H1' are omitted. Important bond lengths /pm and angles  $^\circ$ : Al1–H1 168(1), Al1–H1' 171(1), Al1–H1–Al1' 101.7(7), H1–Al1–H1' 78.3(7), C11–Al1–C21 130.93(5); symmetry equivalent atoms generated by  $-x, -y, -z + 1$ .

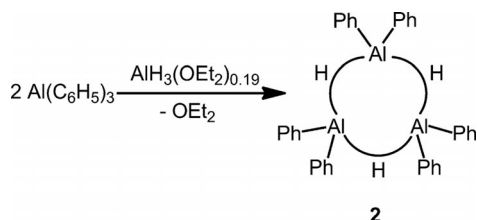


**Figure 2.** Molecular structure of **1b**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of the bridging atoms H1, H2, and H3 are omitted. Important bond lengths /pm and angles  $^\circ$ : Al–H 162(3) to 176(3), Al–H–Al 142(2) to 145(2), H–Al–H 96(1) to 97(1), C–Al–C 129.3(1) to 132.4(1).

### Diphenylaluminum Hydride 2

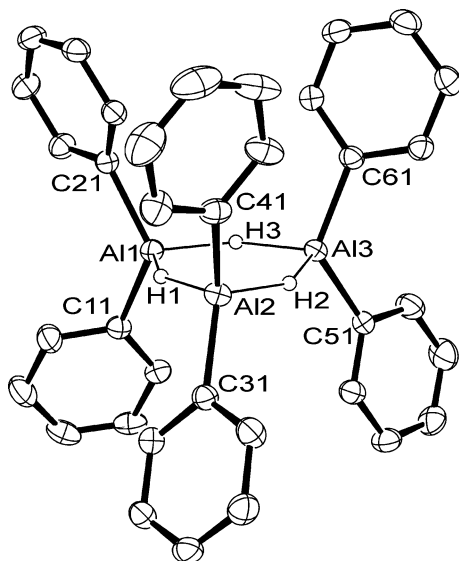
The synthesis of **2** has been reported in the literature.<sup>[12]</sup> We changed the reaction conditions to improve its reproducibility. **2** is formed by treatment of triphenylaluminum with the alane-ether adduct  $\text{AlH}_3 \cdot 0.19\text{Et}_2\text{O}$  in toluene at  $75\text{ }^\circ\text{C}$  for 3 h (Scheme 2). Higher temperatures resulted in partial decomposition by precipitation of elemental aluminum. Colorless crystals of **2** were obtained after filtration, concentration of the filtrate, and cooling to  $-20\text{ }^\circ\text{C}$  in 72% yield. The hydrogen atom bonded to aluminum gave a broad resonance in the  $^1\text{H}$  NMR spectrum at  $\delta = 4.63$ , and the IR spectrum showed a broad absorption at  $1760\text{ cm}^{-1}$  for the stretching vibration of the Al–H–Al groups. The monomeric fragment  $\text{H-Al}(\text{C}_6\text{H}_5)_2$

was detected in the mass spectrum. Pure diphenylaluminum hydride is insoluble in cyclopentane or *n*-hexane and only sparingly soluble in toluene or benzene; therefore we were not able to determine the molar mass in solution by cryoscopy. Ebulliometric measurements in benzene were reported to result in an association degree of 2.4.<sup>[12]</sup>



**Scheme 2.** Synthesis of diphenylaluminum hydride.

Crystal structure determination (Figure 3) revealed a trimeric formula unit in the solid state with an almost ideally planar  $\text{Al}_3\text{H}_3$  heterocycle. The largest deviation of an atom from the average plane is 9 pm (H2). The structural parameters are quite similar to those of the trimeric dineopentyl derivative **1b**. The endocyclic angles  $\text{Al-H-Al}$  and  $\text{H-Al-H}$  are 145 and  $94^\circ$  on average, and the transannular  $\text{Al}\cdots\text{Al}$  or  $\text{H}\cdots\text{H}$  distances are 322 and 248 pm. The  $\text{Al-C}$  bond lengths [194.3(2) to 195.2(2)] are similar to those to the terminal phenyl groups in dimeric triphenylaluminum.<sup>[14]</sup>



**Figure 3.** Molecular structure of **2**. Displacement ellipsoids are drawn at the 40% level. Hydrogen atoms with the exception of the bridging atoms H1, H2 and H3 are omitted. Important bond lengths /pm and angles  $^\circ$ :  $\text{Al-H}$  163(2) to 173(2),  $\text{Al-H-Al}$  145(1) to 146(1),  $\text{H-Al-H}$  94.1(8) to 94.5(8),  $\text{C-Al-C}$  124.1(1) to 125.9(1).

Preliminary experiments verified the exceptional reactivity of the diphenyl compound **2** and its broad applicability in hydroalumination reactions. Particularly interesting is the variation and enhancement of the Lewis-acidity of the aluminum atoms compared to that of dialkylaluminum compounds, which is caused by the relatively strong  $-\text{I}$  effect of the phenyl

groups. The stronger electron pair acceptor capability seems to favor spontaneous secondary reactions such as condensation or metallation of aromatic rings with the formation of unprecedented structural motifs.

## Experimental Section

**General:** All manipulations were carried out in a dry argon atmosphere, using standard Schlenk techniques. Toluene was dried with Na/benzophenone, *n*-pentane and *n*-hexane over  $\text{LiAlH}_4$  and 1,2-difluorobenzene over molecular sieves. NMR spectra were recorded in  $\text{C}_6\text{D}_6$  at ambient probe temperature using the following Bruker instruments: Avance I ( $^1\text{H}$ , 400.13;  $^{13}\text{C}$ , 100.62 MHz) or Avance III ( $^1\text{H}$ , 400.03;  $^{13}\text{C}$ , 100.59 MHz) and referenced internally to residual solvent resonances (chemical shift data in  $\delta$ ). The  $^{13}\text{C}$  NMR spectrum was proton-decoupled. The IR spectrum was recorded as paraffin mull between CsI plates on a Shimadzu Prestige 21 spectrometer. Dineopentylaluminum hydride,<sup>[10]</sup> triphenylaluminum,<sup>[15]</sup> and the adduct  $\text{AlH}_3\cdot 0.19\text{Et}_2\text{O}$ <sup>[16]</sup> were obtained following literature procedures.

**Synthesis of Diphenylaluminum Hydride 2:** A suspension of triphenylaluminum (1.33 g, 5.15 mmol) and  $\text{AlH}_3\cdot 0.19\text{Et}_2\text{O}$  (0.113 g, 2.56 mmol) in toluene (100 mL) was stirred at  $75^\circ\text{C}$  for 3 h. After cooling to room temperature the mixture was filtered, and the solid material was washed with toluene (20 mL). The filtrate was concentrated in vacuo. A colorless solid of **2** was obtained at  $-45^\circ\text{C}$ . It was isolated and washed with *n*-hexane. All volatiles were removed in vacuo ( $10^{-3}$  Torr). Yield: 1.01 g (72%). **Mp** (argon, sealed capillary):  $150\text{--}156^\circ\text{C}$  (dec.). **IR** (paraffin, CsI plates):  $\tilde{\nu} = 1796$  s, br., 1699 s, br.  $\nu\text{AlH}$ ; 1580 w, 1558 w phenyl; 1462 vs. (paraffin); 1420 s  $\nu\text{C}_{\text{arom}}$ ; 1378 s paraffin; 1300 vw, 1248 w, 1192 w, 1155 vw, 1099 m  $\delta\text{CH}$ ; 1084 m  $\delta\text{C}_{\text{arom}}$ ; 993 w; 885 w, br., 849 w, br.  $\delta\text{AlH}$ ; 727 paraffin; 700 vs. phenyl; 629 vw, 617 vw, 476 vs., 457 s, 446 m, 424 w  $\nu\text{AlC}$   $\text{cm}^{-1}$ .  **$^1\text{H}$  NMR** (400 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta = 7.64$  (4 H, *pseudo-d*, *ortho-H*), 7.23 (2 H, *pseudo-t*, *para-H*), 7.16 (4 H, *pseudo-t*, *meta-H*), 4.63 (1 H, br., Al-H).  **$^{13}\text{C}\{^1\text{H}\}$  NMR** (100 MHz,  $\text{C}_6\text{D}_6$ , 300 K):  $\delta = 138.2$  (br., *ipso-C* and *ortho-C*), 130.2 (*para-C*), 128.2 (*meta-C*). **MS** (EI, 20 eV, 333 K):  $m/z$  (%) = 182 (6) [ $\text{M}$  (monomer)]<sup>+</sup>, 164 (6), 154 (7) [ $\text{Ph-Ph}$ ]<sup>+</sup>, 78 (100) [ $\text{Ph-H}$ ]<sup>+</sup>.

**X-ray Crystallography:** Crystals suitable for X-ray crystallography were obtained by recrystallization from *n*-pentane ( $-30^\circ\text{C}$ ; **1a**), 1,2-difluorobenzene ( $-30^\circ\text{C}$ ; **1b**) and toluene ( $-20^\circ\text{C}$ ; **2**). Intensity data was collected with Bruker APEX II and Bruker Quasar diffractometers with monochromated  $\text{Mo-K}_\alpha$  (**1a**, **2**) and  $\text{Cu-K}_\alpha$  radiation (**1b**). Data reduction was carried out using the program SAINT+.<sup>[17]</sup> The crystal structures were solved by direct methods using SHELXTL.<sup>[18]</sup> Non-hydrogen atoms were first refined isotropically followed by anisotropic refinement by full-matrix least-squares calculation based on  $F^2$  using SHELXTL. With the exception of the bridging hydride atoms the hydrogen atoms were positioned geometrically and allowed to ride on their respective parent atoms. A *tert*-butyl group of **1b** was rotationally disordered. Its atoms were refined with site occupancy factors of 0.35, 0.30, and 0.35. Compound **2** crystallized with half a toluene molecule per formula unit. The solvent molecule was disordered across a center of symmetry. The methyl group was refined on two positions with site occupancy factors of 0.5. Further crystallographic data is summarized in Table 1.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository

**Table 1.** Crystal data and structure refinement for compounds **1a**, **1b**, and **2**.

|   | <b>1a</b>                                       | <b>1b</b>                                       | <b>2·0.5toluene</b>                               |
|---|---|---|---|
| Empirical formula                               | C <sub>20</sub> H <sub>46</sub> Al <sub>2</sub> | C <sub>30</sub> H <sub>69</sub> Al <sub>3</sub> | C <sub>39.5</sub> H <sub>37</sub> Al <sub>3</sub> |
| Crystal system                                  | triclinic                                       | monoclinic                                      | triclinic   |
| Space group                                     | <i>P</i> $\bar{1}$                              | <i>P</i> 2 <sub>1</sub> <sup>c</sup>            | <i>P</i> $\bar{1}$                                |
| Z   | 1   | 2   | 2   |
| T /K  | 153(2)  | 153(2)  | 153(2)  |
| D <sub>calc</sub> /g·cm <sup>-3</sup>           | 0.934   | 0.895   | 1.158   |
| a /pm   | 623.05(11)                                      | 1120.21(4)                                      | 1042.1(2)   |
| b /pm   | 1004.8(2)                                       | 1618.00(7)                                      | 1226.1(3)   |
| c /pm   | 1014.9(2)                                       | 1173.55(5)                                      | 1447.8(3)   |
| α /°  | 106.281(3)                                      | 90  | 68.03(3)  |
| β /°  | 90.438(3)                                       | 117.033(2)                                      | 84.40(3)  |
| γ /°  | 96.706(3)                                       | 90  | 82.84(3)  |
| V /nm <sup>3</sup>                              | 0.6051(2)                                       | 1.8947(1)                                       | 1.6995(6)   |
| μ /mm <sup>-1</sup>                             | 0.118   | 0.992   | 0.137   |
| A   | Mo-K <sub>α</sub>                               | Cu-K <sub>α</sub>                               | Mo-K <sub>α</sub>                                 |
| θ Range /°                                      | 2.09–30.02                                      | 4.23–69.00                                      | 1.52–27.93  |
| Independent reflections                         | 3480 [R <sub>int</sub> = 0.0337]                | 5589 [R <sub>int</sub> = 0.0285]                | 8043 [R <sub>int</sub> = 0.0471]                  |
| Parameters                                      | 110   | 383   | 401   |
| R <sub>1</sub> <sup>a)</sup> [I > 2σ(I)]        | 0.0445 (2953)                                   | 0.0436 (5178)                                   | 0.0397 (6096)                                     |
| wR <sub>2</sub> <sup>b)</sup> (all data)        | 0.1179  | 0.1143  | 0.1084  |
| Largest diff. peak and hole /e·nm <sup>-3</sup> | 407, -184                                       | 256, -185                                       | 505, -249   |

a)  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ . b)  $wR_2 = \{\sum w(|F_o|^2 - |F_c|^2)^2 / \sum |F_o|^2\}^{1/2}$ . c) Absolute structure parameter: 0.01(3).

numbers CCDC-962760 (**1a**), CCDC-962761 (**1b**), and CCDC-962762 (**2**) (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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