

Preliminary communication

An intramolecularly base-stabilized monomeric
organoaluminum dihydride

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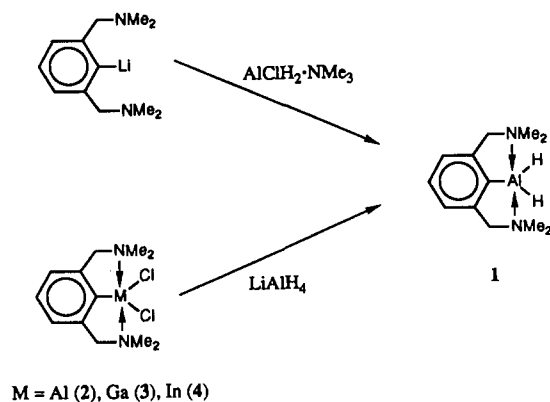
Abstract

The intramolecularly base-stabilized arylaluminum dihydride [2,6-(Me₂NCH₂)₂C₆H₃]AlH₂ (**1**) has been prepared by the metathesis reaction of the corresponding lithium aryl with AlH₂Cl·NMe₃. Alternative methods for the synthesis of **1** are transmetalation or reduction reactions of [2,6-(Me₂NCH₂)₂C₆H₃]MCl₂ (M = Al (**2**), Ga (**3**), In (**4**)) with LiAlH₄. The X-ray crystal structures of **1** and **2** have been determined: **1**, orthorhombic, *Pbca*, with *a* = 17.179(3), *b* = 9.014(20), *c* = 12.707(3) Å, *V* = 2794(1) Å³ and *Z* = 8; **2**, monoclinic, *C2/c*, with *a* = 8.2880(10), *b* = 17.022(2), *c* = 14.381(3) Å, β = 99.46(1)°, *V* = 2001.2(5) Å³, and *Z* = 4. Compounds **1** and **2** are monomeric in the solid state.

Keywords: Aluminium; Hydrides; X-ray structure

Aluminum hydride moieties have been detected on surfaces during thin film growth from organoaluminum sources [1]. Monomeric organoaluminum hydrides could, in principle, serve as useful models for further understanding of the reaction chemistry of surface-bound AlH_{*n*} groups. However, it is known that base-free organoaluminum hydrides show a strong tendency to oligomerize even when the organo substituents are relatively bulky [2]. We report the synthesis and X-ray crystal structure of an intramolecularly base-stabilized arylaluminum dihydride featuring a terminal AlH₂ group. Previous structural assays are confined to cationic species of the type [H₂AIL]⁺ where L represents a multidentate ligand [3].

A solution of H₂AlCl·NMe₃ (400 mg, 3.3 mmol) in 50 ml of Et₂O was treated with a solution of Li[2,6-(Me₂NCH₂)₂C₆H₃] (3.3 mmol) [4] in 30 ml of Et₂O at –78°C. The reaction mixture was allowed to warm to 25°C, following which it was stirred for an additional 3 h at this temperature. After filtration, removal of the solvent under reduced pressure left a white residue,



Form. 1.

which was recrystallized from toluene at –40°C to afford colorless crystals of [2,6-(Me₂NCH₂)₂C₆H₃]AlH₂ (**1**), m.p. 87–88°C, in 55% yield. Elemental analysis for C₁₂H₂₁AlN₂: calculated C 65.43%, H 9.61%, N 12.72%; found C 63.90%, H 9.49%, N 12.60%. The presence of a hydride resonance of relative area 2 in the ¹H NMR spectrum [5] and the equivalence of the NMe₂ methyl resonances in the ¹H and ¹³C{¹H} NMR spectra were suggestive of a monomeric formulation

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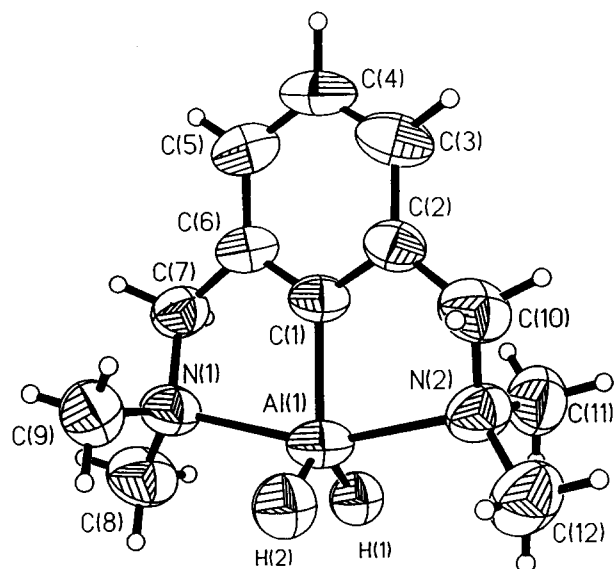


Fig. 1. View of the structure of **1**. Important bond lengths (Å) and angles (deg): Al(1)–C(1) 1.949(5), Al(1)–N(1) 2.277(5), Al(1)–N(2) 2.233(5), Al(1)–H(1) 1.512(38), Al(1)–H(2) 1.488(42), N(1)–Al(1)–N(2) 157.8(2), H(1)–Al(1)–H(2) 118.8(21), H(1)–Al(1)–C(1) 1.228(15), H(2)–Al(1)–C(1) 118.4(15).

for **1**. Further support for such a structure assignment stemmed from the following observations: (i) the highest m/z peak in the EI mass spectrum occurred at 220 amu, and (ii) the presence of overlapping bands at 1767 and 1774 cm^{-1} in the IR spectrum which can be assigned to asymmetric and symmetric terminal Al–H stretching vibrations respectively. An X-ray analysis was considered desirable to establish the connectivity of the “arms” of the ligand, for example.

Crystal data: $\text{C}_{12}\text{H}_{21}\text{AlN}_2$, $M = 220.3$, orthorhombic, space group $Pbca$, $a = 17.179(3)$, $b = 9.014(2)$, $c = 18.042(4)$ Å, $V = 2794(1)$ Å³, $D_c = 1.047$ g cm^{-3} , $Z = 8$, $\lambda(\text{Mo-K}\alpha) = 1.71073$ Å, $\mu(\text{Mo-K}\alpha) = 1.20$ cm^{-1} . 1838 independent reflections were collected on a Siemens R3m/V diffractometer at 298 K with 2θ between 3.5 and 45.0° using the θ – 2θ scan mode. The data were corrected for absorption (semiempirical) and Lorentz-polarization effects. The structure was solved by direct methods and refined (full-matrix least-squares) using 1238 reflections with $I > 4.0\sigma(I)$. The final R and R_w values were 7.27 and 8.68% respectively. The X-ray analysis reveals that **1** is monomeric (Fig. 1) and that there are no unusually short intermolecular contacts. Both CH_2NMe_2 “arms” of the aryl ligand are coordinated; however, the $\text{N} \rightarrow \text{Al}$ dative bond lengths (av. 2.255(5) Å) are somewhat longer than those in other amine–alane adducts, e.g. 2.063(8) Å in Me_3NAlH_3 (gas phase) [6]. Both hydrides were located in the final difference map and the average Al–H bond length (1.50(4) Å) is similar to those reported for terminal Al–H bonds [7]. The overall geometry at the pentacoordinate aluminum center is trigonal bipyramidal.

However, while the H_2AlCl moiety is planar within experimental error (sum of angles at Al = 360.0(21)°), the axial ligands are distinctly non-linear ($\text{N}(1)\text{–Al}(1)\text{–N}(2) = 157.8(2)^\circ$) owing to the constraints of the ligand system.

The new dichloride $[2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]\text{AlCl}_2$ (**2**) was synthesized via the reaction of $\text{Li}[2,6\text{-(Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3]$ with an equimolar quantity of aluminum chloride using a very similar procedure to that described above for **1**. Characterization of colorless, crystalline **2** [m.p. 70°C (dec)] is based on ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy, mass spectroscopy [5], and X-ray analysis. Compound **2** crystallizes with one molecule of benzene per formula unit.

Crystal data: $\text{C}_{12}\text{H}_{19}\text{AlCl}_2\text{N}_2 \cdot \text{C}_6\text{H}_6$, $M = 367.3$, monoclinic, space group $C2/c$, $a = 8.2880(10)$, $b = 17.022(2)$, $c = 14.381(3)$ Å, $\beta = 99.46(1)^\circ$, $V = 2001.2(5)$ Å³, $D_c = 1.219$ g cm^{-3} , $Z = 4$, $\lambda(\text{Mo-K}\alpha) = 0.71073$ Å, $\mu(\text{Mo-K}\alpha) = 3.69$ cm^{-1} . 1608 independent reflections were collected on a Siemens R3m/V diffractometer at 298 K with 2θ between 3.5 and 45.0° using the θ – 2θ scan mode. The data were corrected for absorption (semi-empirical) and Lorentz-polarization effects. The structure was solved by Patterson methods and refined (full-matrix least-squares) using 701 reflections with $I > 4.0\sigma(I)$. The final R and R_w values were 5.23 and 5.58% respectively. The monomeric structure of **2** is very similar to that described above for **1** with the following metrical parameters for the pentacoordinate $\text{CAI}(\text{Cl})_2\text{N}_2$ moiety: Al–C = 1.911(7), Al–Cl = 2.150(2), Al–N = 2.261(5) Å, and N–Al–N = 158.8(3)°.

Treatment of **2** with an excess of LiAlH_4 in Et_2O solution at 25°C affords, after workup and recrystallization from toluene, a virtually quantitative yield of **1**. Interestingly, $\text{Ar}'\text{GaCl}_2$ [8] and $\text{Ar}'\text{InCl}_2$ [9] undergo facile transmetalation reactions since treatment of these dichlorides with LiAlH_4 in Et_2O solution at 25°C also results in high yields of **1**.

Supplementary material is available from the Cambridge Crystallographic Data Center.

Acknowledgments

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- [5] ^1H NMR (300.15 MHz, 298 K, C_6D_6): **1**, δ = 2.22 (s, 12H, NMe_2), 3.29 (s, 4H, CH_2), 4.28 (s, br, 2H, AlH_2), 6.91 (d, 2H, 3,5 H-ring, J = 7.2 Hz), 7.27 (t, 1H, 4 H-ring, J = 7.2 Hz); **2**, δ = 2.21 (s, 12 H, NMe_2), 3.15 (s, 4H, CH_2), 6.79 (d, 2H, 3,5 H-ring, J = 7.2 Hz), 7.20 (t, 1H, 4 H-ring, J = 7.2 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.67 MHz, 298 K, C_6D_6): **1**, δ 46.9 (NMe_2), 66.5 (CH_2), 122.4 (3,5 C-ring), 129.3 (4 C-ring), 145.8 (2,6-C-ring). The *ipso* carbon was not detected; **2**, δ 47.1 (NMe_2), 65.6 (CH_2), 123.2 (3,5 C-ring), 129.9 (4 C-ring), 145.3 (2,6 C-ring). The *ipso* carbon was not detected. MS(Cl , CH_4): **1**: m/z 219 ($\text{M}^+ - \text{H}$, 100%), 193 ($\text{M}^+ - \text{AlH}_2 + 2\text{H}$, 13%), 175 ($\text{M}^+ - \text{NMe}_2$, 3%); **2**: m/z 289 ($\text{M}^+ + \text{H}$, 18%), 253 ($\text{M}^+ - \text{Cl}$, 100%).
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