ORGANOMETALLICS

Volume 18, Number 8, April 12, 1999

Communications

Synthesis, Structure, and Reducing Ability of a Stable Organotrihydroaluminate Bearing a Novel Bowl-Type Substituent

Kei Goto,*,† Junji Kobayashi, and Renji Okazaki*,‡

Department of Chemistry, Graduate School of Science, The University of Tokyo, 7-3-1 Hongo,
Bunkyo-ku, Tokyo 113-0033, Japan

Received June 18, 1998

*Summary: The reaction between BmtLi (Bmt = 4-tert-butyl-2,6-bis[(2,2″,6,6″-tetramethyl-m-terphenyl-2′-yl)-methyl]phenyl) and AlH_3NMe_3 in DME gave a stable organotrihydroaluminate, $BmtAlH_3Li(DME)_2$ (**6**), whose monomeric structure was established by X-ray analysis. Compound **6** showed high reactivity as a reducing agent toward unsaturated compounds such as benzophenone, phenyl benzoate, and benzonitrile.*

There is growing interest in the chemistry of the hydride derivatives of the heavier main group 3 elements.[1,2] In contrast to organotrihydroborates,[3] very little is known about organotrihydroaluminates because of their instability. They are known to undergo facile ligand redistribution reaction described in eq 1[4] and

$$2[AlRH_3]^- \rightarrow [AlH_4]^- + [AlR_2H_2]^- \qquad (1)$$

even *tert*-butyl[5] and 2,4,6-triisopropylphenyl[6] groups are not sufficiently bulky to suppress this reaction. Recently, it has been found that the attachment of a bulkier substituent suppresses this process,[5−7] and the structures of three compounds $[(PhMe_2Si)_3CAlH_3Li(THF)_2]_2$ (**1**),[5] $[2,4,6\text{-}Ph_3C_6H_2AlH_3Li(OEt_2)_{1.5}]_2$ (**2**),[7] and $[Mes^*AlH_3Li(THF)_2]_2$ (**3**)[7] have been characterized. It seems particularly interesting how they behave as reducing agents toward unsaturated species such as carbonyl compounds and nitriles in terms of comparison with the reactivity of other kinds of lithium aluminum hydrides. However, there has been no description on such reducing ability of organotrihydroaluminates.

We have recently developed a novel bowl-type substituent **4** (denoted as Bmt hereafter) with an all-carbon

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[†] Present address: Department of Chemistry, School of Science, Kitasato University, 1-15-1 Kitasato, Sagamihara, Kanagawa 228-8555, Japan. E-mail: goto@jet.sci.kitasato-u.ac.jp. Fax: +81-427-78-9961.

[‡] Present address: Department of Chemical and Biological Sciences, Faculty of Science, Japan Women's University, 2-8-1 Mejirodai, Bunkyo-ku, Tokyo 112-8681, Japan. E-mail: okazaki@jwu.ac.jp. Fax: +81-3-3942-6116.

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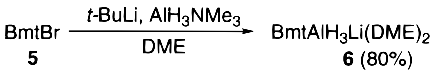
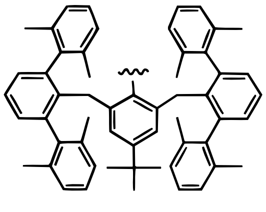
10.1021/om9805032 CCC: $18.00 © 1999 American Chemical Society
Publication on Web 03/19/1999

Scheme 1



$$\underset{\mathbf{5}}{\text{BmtBr}} \xrightarrow[\text{DME}]{t\text{-BuLi, AlH}_3\text{NMe}_3} \underset{\mathbf{6}\ (80\%)}{\text{BmtAlH}_3\text{Li(DME)}_2}$$

and acyclic framework.[8] Through its application to the synthesis of a stable sulfenic acid (RSOH), it was found that the bowl-shaped framework of **4** can prevent dimerization of a reactive species very effectively with retention of its reactivity toward other substrates.[9] Here we report the synthesis of a stable organotrihydroaluminate which has a monomeric structure in the crystalline state and its reducing ability toward the unsaturated compounds.



4 ≡ Bmt

Lithiation of bromide **5**[8] with *t*-BuLi in dimethoxyethane (DME) at −78 °C followed by treatment of AlH_3-NMe_3[10] afforded $BmtAlH_3Li(DME)_2$ (**6**), which was isolated as colorless crystals in 80% yield after recrystallization (Scheme 1).[11] Although trihydroaluminate **6** is sensitive toward moisture, it is stable over 1 month under argon atmosphere in the crystalline state, which was confirmed by the ^1H NMR measurement. No decomposition was observed in C_6D_6 and in toluene-d_8 in a sealed tube after 1 month by ^1H NMR. In the ^1H NMR (toluene-d_8) spectrum at room temperature the Al−H resonance was not confirmed, whereas a broad signal for this proton was clearly observed at 3.14 ppm at −60 °C. The ^{27}Al NMR spectrum (C_6D_6) at room temperature showed a broad peak at 102 ppm, which is indicative of a 4-coordinated organoaluminate compound.[12]

The structure of **6** was finally established by X-ray crystallographic analysis as shown in Figure 1.[13] The lithium atom is bound to one of three hydrogen atoms and two DME molecules, the remaining two hydrogen atoms being terminally bound. The Al−H distances average 1.60(6) Å, and the Li−H and Al−C distances are 1.94(5) and 2.021(6) Å, respectively. The shortest intermolecular Al···Al and Li···H distances are 7.68 and 6.29 Å, respectively, clearly indicating that **6** is monomeric in the crystalline state. Trihydroaluminates **1**, **2**, and **3** have been reported to have a dimeric structure with an eight-membered $Li_2Al_2H_4$ ring structure, where two H_3AlR units are bridged by two lithium atoms,[5,7] and there has been no example of a characterization of a monomeric organotrihydroaluminate. The unassociated structure of **6** is considered to result from the bowl-shaped framework of the molecule, where the aluminate functionality is surrounded by two *m*-terphenyl units, as well as the solvation of two DME molecules to the lithium atom. Recrystallization from THF has so far not afforded crystals suitable for an X-ray study.

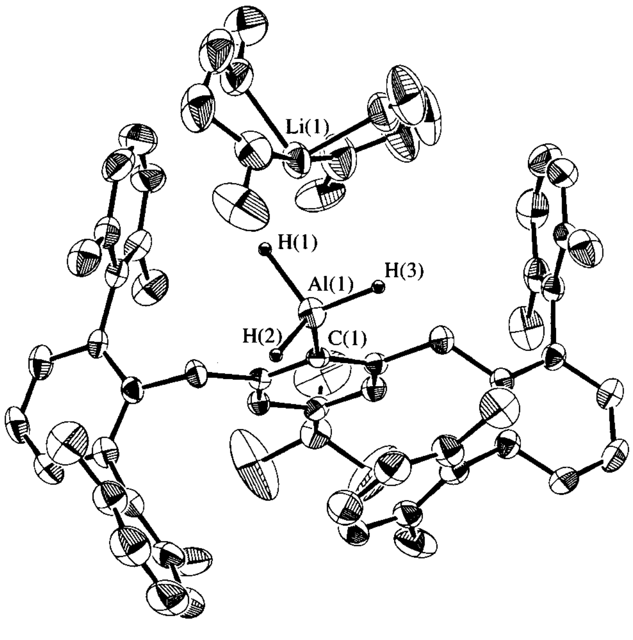


Figure 1. ORTEP drawing of **6** with thermal ellipsoid plot (30% probability). H atoms except those bound to aluminum are omitted for clarity. Selected bond lengths (Å): Al(1)−C(1) = 2.021(6), Al(1)−H(1) 1.64(5), Al(1)−H(2) = 1.60(6), Al(1)−H(3) = 1.55(7), H(1)−Li(1) = 1.94(5).

Trihydroaluminate **6** showed reducing ability toward several kinds of unsaturated species (Scheme 2). The reaction of **6** with a 3 equimolar amount of benzophenone (**7**) at room temperature afforded benzhydrol quantitatively after aqueous workup,[14] indicating that all three hydrides of **6** are effective in the reduction of **7**. The intermediary trialkoxyaluminate BmtAl-

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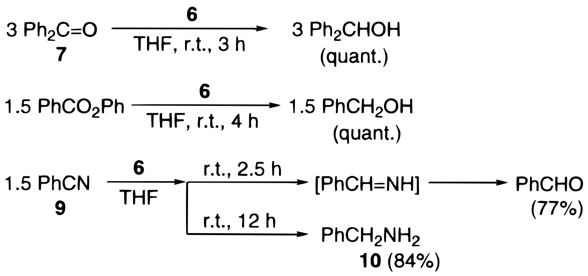
(11) **6**: A solution of *t*-BuLi in pentane (1.66 M, 1.50 mL, 2.5 mmol) was added dropwise to a solution of **5** (812 mg, 1.0 mmol) in DME (50 mL) at −72 °C. After the mixture was stirred for 8 min at the same temperature, a solution of AlH_3NMe_3 (1.05 mmol) in benzene (2.1 mL) was added. The mixture was stirred overnight at −72 °C and then allowed to warm to room temperature. After removal of the solvent, the residue was recrystallized from DME in a glovebox filled with argon to give **6** (756 mg, 80%) as colorless crystals: mp >300 °C. ^1H NMR (270 MHz, −60 °C, toluene-d_8): δ 1.28 (s, 9H), 2.28 (s, 12H), 2.38 (s, 12H), 2.70 (brs, 12H), 2.81 (brs, 8H), 3.14 (brs, Al−H, 3H), 4.18 (s, 4H), 6.57 (s, 2H), 6.83 (d, 4H, $^3J_{HH} = 7.3$ Hz), 6.98−7.08 (m, 12H), 7.18 (t, 2H, $^3J_{HH} = 7.3$ Hz). ^{13}C NMR (126 MHz, rt, C_6D_6): δ 21.5 (q), 31.7 (q), 34.5 (s), 40.2 (t), 59.0 (q), 70.6 (t), 121.0 (d), 126.3 (d), 126.8 (d), 127.7 (d), 129.3 (d), 136.5 (s), 140.7 (s), 142.2 (s), 142.8 (s), 145.1 (s), 149.0 (s). ^{27}Al NMR (130 MHz, rt, C_6D_6, reference to aqueous $Al(NO_3)_3$): δ 102 (br). Anal. Found: C, 82.18; H, 8.20. Calcd for $C_{64}H_{80}$-$AlLiO_4$: C, 81.15; H, 8.51.

(12) Akitt, J. W. In *Multinuclear NMR*; Mason, J., Ed.; Plenum: New York, 1987.

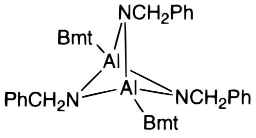
(13) Crystal data for **6**: $C_{64}H_{80}AlLiO_4$, fw = 947.26, monoclinic, space group $P2_1/n$, $a = 11.769(2)$ Å, $b = 21.482(3)$ Å, $c = 23.960(2)$ Å, $\beta = 102.856(9)°$, $V = 5905(1)$ Å^3, $Z = 4$, $D_{calcd} = 1.065$ g/cm^3, $\mu = 0.78$ cm^{-1}. The intensity data were collected on a Rigaku AFC5R diffractometer with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 69$ Å) at a temperature of 23 °C, and the structure was solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the AlH_3 moiety were refined isotropically; the rest were included but not refined. The final cycle of full-matrix least-squares refinement was based on 3236 observed reflections [$I > 3.00\sigma(I)$] and 643 variable parameters with R (R_w) = 0.061 (0.058). Full details of the crystallographic structure analysis are described in the Supporting Information.

(14) The yields were obtained by gas chromatography with naphthalene as an internal standard.

Scheme 2



$(OCHPh_2)_3Li$ (**8**)[15] was observed by ^1H and ^{27}Al NMR in the reaction of **6** with an excess amount of **7**. Phenyl benzoate was also reduced by **6** to benzyl alcohol quantitatively.[14] The reduction of benzonitrile (**9**) by **6** was found to proceed stepwise. The reaction of **6** with a 1.5 equimolar amount of **9** was stopped after 2.5 h by addition of hydrochloric acid to give benzaldehyde in 77% yield,[14] which is considered to be formed via hydrolysis of the intermediary imine. On the other hand, the prolonged reaction time of 12 h resulted in the further reduced product, benzylamine (**10**), in 84% yield.[14] All three hydrides of **6** were effective also in this reaction. It was reported that $LiAlH_4$ reduces **9** directly to **10** within 3 h under similar conditions.[16] The reason for the slow rate of the second reduction by **6** is probably because this step requires coordination of two molecules of **6** to each nitrogen atom, perhaps in a sterically hindered intermediate such as **11**, although its observation has been unsuccessful so far. The results obtained here indicate that organotrihydroaluminate **6** has high reducing ability, similar to $LiAlH_4$, except when thereaction involves two molecules of the reductant. Further investigations on its reactivity toward other substrates and isolation of the intermediates of these reactions are currently in progress.



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Acknowledgment. This work was partly supported by a Grant-in-Aid for Scientific Research (No. 08740487) from the Ministry of Education, Science, Sports and Culture, Japan. We also thank Tosoh Akzo Co., Ltd., for the generous gift of alkyllithiums.

Supporting Information Available: Crystallographic data with complete tables of bond lengths, angles, and thermal and positional parameters for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.

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[15] **8**: selected ^1H NMR data (500 MHz, rt, C_6D_6): δ 1.34 (s, 9H, *t*-Bu), 1.85 (s, 12H, $ArCH_3$), 2.29 (s, 12H, $ArCH_3$), 4.18 (s, 4H, CH_2), 5.46 (s, 3H, $OCHPh_2$). ^{27}Al NMR (130 MHz, rt, C_6D_6, $Al(NO_3)_3$): δ 61 (br).

[16] Brown, H. C.; Weissman, P. M.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1458–1463.