Inorg. Chem. **2005**, *44*, 5854–5857

Inorganic Chemistry
Article

# Aluminum Hydride Cations Stabilized by Weakly Coordinating Carbaalanates

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Received October 8, 2004

The reactions of *t*-BuC≡CLi with a mixture of $AlH_3{\cdot}NMe_3$ and $ClAlH_2{\cdot}NMe_3$ in boiling toluene with the addition of $[t\text{-BuCH}_2(Bzl)NMe_2]Cl$, or a bulky $\beta$-diketimine instead, and $[n\text{-Bu}_4N]Cl$ led to the carbaalanates $[H_2Al(NMe_3)_2]_2[(AlH)_8(CCH_2t\text{-Bu})_6]$, **3**, and $[n\text{-Bu}_4N]_2[(AlH)_8(CCH_2t\text{-Bu})_6]$, **4**, respectively. The reaction of $Me_3N{\cdot}Al(C{\equiv}Ct\text{-Bu})_3$ **5** and $AlH_3{\cdot}NMe_3$ in boiling toluene yielded $[H(n\text{-Bu})Al(NMe_3)_2][(AlH)_7(AlNMe_3)(CCH_2t\text{-Bu})_6]$, **6**, in trace amounts. The single-crystal X-ray structures of **3** and **6** are reported. The compounds **3**, **4**, and **6** consist of well-separated ion pairs introducing carbaalanates as weakly coordinating anions and stabilizing aluminum hydride cations.

## Introduction

Weakly coordinating anions (WCAs)[1] are an attractive research field for the stabilization of reactive cationic species mainly in catalysis. Systems such as $BAr_4^-$, $Al(OR)_4^-$, and carbaboranates[2] were extensively used to study the chemistry of free cations. The *closo*-carbaboranates $CB_{11}H_6X_6$ (X = Cl, Br, etc.) show high inertness and could be isolated with $H^+$ as a super-Brönsted acid and also with extremely reactive cations.[3,4] Moreover, these anions form easily crystallizable salts and allow structural determinations. The stability arises from a $\sigma$-aromaticity in the cluster core.[2] Computed larger *closo*-carbaboranes/carbaboranates[5] are isoelectronic to the $[(AlH)_6(AlNMe_3)_2(CCH_2R)_6]$ system (**1**, R = Ph, prepared from PhC≡CH and excess $AlH_3{\cdot}NMe_3$ in boiling toluene)[6] and $[(AlH)_8(CCH_2t\text{-Bu})_6]^{2-}$ in $[\{t\text{-BuCH}_2C(AlH_2{\cdot}NMe_3)_3\text{-Li}\}_2\{(AlH)_8(CCH_2t\text{-Bu})_6\}]$, **2**.[7] In **2**, the Li atoms are coordinated to the anion through hydrides giving a contact ion pair. The carbaalane cluster compounds are not stable toward protic reagents.[6,8] Altogether, we set our interest in synthesizing carbaalanates with free anions with a potential use as WCAs.

## Results and Discussion

Compound **2** was prepared from a mixture of *t*-BuC≡CLi, $ClAlH_2{\cdot}NMe_3$, and $AlH_3{\cdot}NMe_3$ in a ratio of approximately 1:1:2 in boiling toluene. Salt metathesis and hydroalumination reactions led to the formation of the cluster during the reaction. To fully eliminate the $Li^+$ from the reaction leading to **2**, we used additives such as quaternary ammonium chlorides and a bulky $\beta$-diketimine. The ammonium chloride and *t*-BuC≡CLi were used in a ratio of 2:6. The reaction of 2 equiv of $[t\text{-BuCH}_2(Bzl)NMe_2]Cl$ with 6 equiv of *t*-BuC≡CLi in a mixture of $AlH_3{\cdot}NMe_3$ and $ClAlH_2{\cdot}NMe_3$ in boiling toluene leads to crystals of $[H_2Al(NMe_3)_2]_2[(AlH)_8(CCH_2t\text{-Bu})_6]$, **3**, in 50% yield. Applying the same synthetic procedure for **3** using $[n\text{-Bu}_4N]Cl$ instead of $[t\text{-BuCH}_2(Bzl)NMe_2]Cl$ resulted in crystals of $[n\text{-Bu}_4N]_2[(AlH)_8(CCH_2t\text{-Bu})_6]$, **4**, in 47% yield (Scheme 1). Use of $Me_3SiCl$ in the synthesis of **4** facilitates partial and selective chlorination of alane which takes place with the elimination of LiCl, which is opposite to LiH elimination. Compound **3** could be characterized by its X-ray single-crystal structure and is shown in Figure 1. An X-ray single-crystal structural analysis of **4** is of poor quality and not given, but its constitution is unambiguous.[9a] Both compounds consist of well-separated

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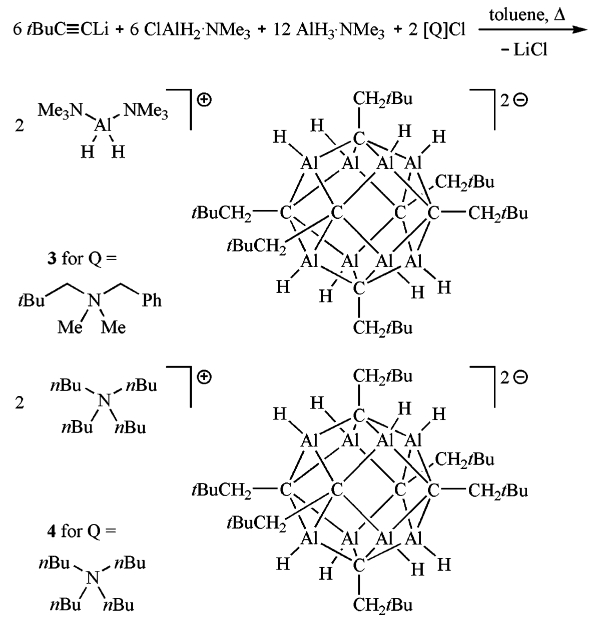
10.1021/ic048594k CCC: $30.25 © 2005 American Chemical Society
Published on Web 06/28/2005

**Scheme 1**



ion pairs with a free $[(AlH)_8(CCH_2t\text{-}Bu)_6]^{2-}$ anion. The Al−C and Al−Al distances in the carbaalane cluster of **3** (as well as those in **4**) are in the region of previously characterized compounds. Compound **3** contains two free $[H_2Al(NMe_3)_2]^+$ cations per formula unit. It has a distorted tetrahedral arrangement with a N−Al−N angle of 112.4(3)° and Al−N bond lengths of 1.977(6) and 1.981(6) Å, respectively. H atoms in **3** on Al (also at the cation) were freely refined with distance restraints of the Al−H bond length of 1.53 Å. This value is in the range of previously observed Al−H distances in neutral and anionic complexes of aluminum hydride (1.5−1.8 Å).[9b−d] The H−Al−H angle in **3** is 127(3)°, which is comparable to the H−Al−H angle[10] of 132° in amine stabilized $[H_2Al(pmdien)]^+[AlH_4]^-$, however the latter is arranged in another coordination sphere. The cation is neither stabilized by a bulky ligand nor stabilized by a high coordination number. Two complexes of the type $[LAlH_2][AlH_4]$ with chelating tri- and tetradentate amine ligands were structurally characterized with the Al atoms of the cations in a penta- and hexacoordinate coordination sphere.[10,11] Very recently, a bulky phosphinimine−amide ligand was used to stabilize aluminum hydride cations with borate anions which were not structurally characterized.[12] An aluminum hydride cation coordinated by THF molecules was structurally characterized in $[H_2Al(THF)_4][(Cp_3Yb)_2Na]$.[13] For comparison, the $[H_2Al(NMe_3)_2]^\bullet$ radical was detected by electron paramagnetic resonance (EPR) spectroscopy and was analyzed to have a quasi-trigonal bipyramidal structure.[14] Compounds **3** and **4** are nearly insoluble in organic solvents, and no significant NMR spectra could be recorded. Furthermore, electron impact (EI) mass experiments showed small C−H fragments for compounds **3** and **4** and $[Bu_4N]^+$ ion for **4**. The compounds are too sensitive for fast atom bombardment (FAB) experiments. The IR spectra of **3** and **4** show strong absorptions for the Al−H bonds of the carbaalanate anion (1751 cm$^{-1}$ for **3** and 1753 cm$^{-1}$ for **4**) as well as sharp absorptions in **3** (1874 and 1881 cm$^{-1}$) for the $[H_2Al(NMe_3)_2]^+$ cation. When treated with THF, compounds **2** and **3** lose their $NMe_3$ ligands and a small amount of gas evolution was observed. Moreover, in the elemental analysis of the resulting compound, no nitrogen was found. These results could not be supported by NMR because of the very poor solubility of the resulting compound. We used 2 equiv of the bulky β-diketimine ligand $^{\text{Dipp}}$nacnacH[15] (2-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)pent-2-ene) as an additive (instead of the quarternary ammonium chlorides), which is known to stabilize aluminum cations[16] and performed a comparable reaction (Scheme 2). Compound **3** was obtained in 58% yield, which was characterized by X-ray single-crystal structure determination as well as by IR spectroscopy. The compound $^{\text{Dipp}}$nacnacAlH$_2$[17] was detected in the remaining solution. We assume that—comparable to chemistry in water solution—several cationic species exist in the boiling reaction mixture and the ion pair with low solubility (or highest lattice energy) crystallizes.

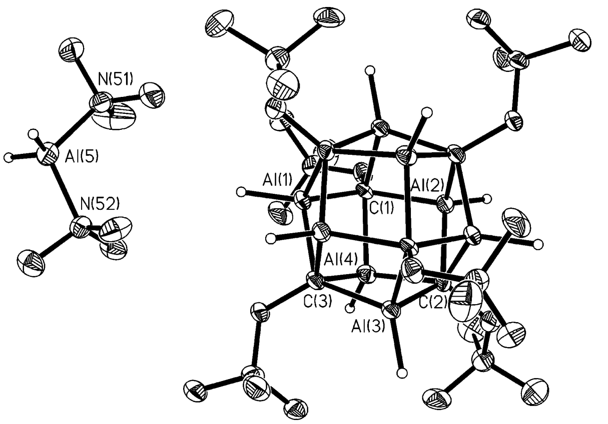


**Figure 1.** ORTEP drawing of **3** (50% thermal ellipsoids). Only one $[H_2Al(NMe_3)_2]$ cation and hydrogen atoms on Al atoms are shown. Selected bond lengths (Å) and angles (deg): Al(5)−N(51) 1.981(6), Al(5)−N(52) 1.977(6); N(52)−Al(5)−N(51) 112.4(3).

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(9) (a) Selected crystal data for **4**: $C_{68}H_{146}Al_8N_2$, $a$ = 20.325(4), $b$ = 19.064(4), $c$ = 20.841(4) Å, orthorhombic. (b) Atwood, J. L.; Bennett, F. R.; Elms, F. M.; Jones, C.; Raston, C. L.; Robinson, K. D. *J. Am. Chem. Soc.* **1991**, *113*, 8183−8185. (c) Bennett, F. R.; Elms, F. M.; Gardiner, M. G.; Koutsantonis, G. A.; Raston, C. L.; Roberts, N. K. *Organometallics* **1992**, *11*, 1457−1459. (d) Atwood, J. L.; Bennett, F. R.; Jones, C.; Koutsantonis, G. A.; Raston, C. L.; Robinson, K. D. *J. Chem. Soc., Chem. Commun.* **1992**, 541−543.

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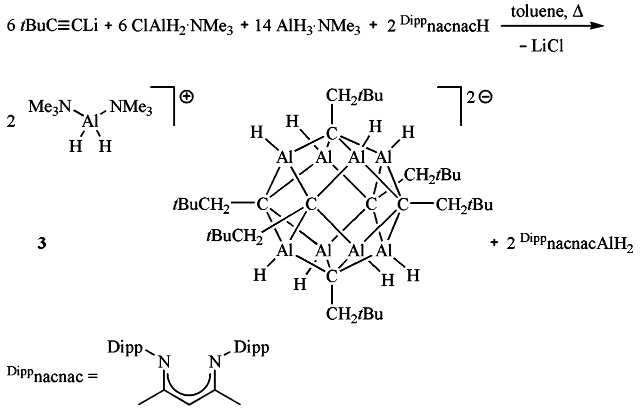
**Scheme 2**



When we treated $Me_3N{\cdot}Al(C{\equiv}Ct\text{-}Bu)_3$, **5**, prepared from $Me_3N{\cdot}AlCl_3$ and $LiC{\equiv}Ct\text{-}Bu$ in toluene, with 6 equiv of $AlH_3{\cdot}NMe_3$ in boiling toluene for 45 min, we obtained a crop of a carbaalane product at 4 °C which we could not properly characterize. However, storing the supernatant solution at −25 °C for 6 months resulted in the formation of the byproduct $[H(n\text{-}Bu)Al(NMe_3)_2][(AlH)_7(AlNMe_3)(CCH_2t\text{-}Bu)_6]$, **6**, in trace amounts. **6** was characterized by X-ray single-crystal structural analysis (Figure 2) and NMR spectroscopy. Compound **6** contains the cation $[H(n\text{-}Bu)Al(NMe_3)_2]^+$, which is the mono-*n*-butyl derivative of the cation of **3**. The *n*-butyl group obviously arises from the use of *n*-butyllithium in the preparation of $LiC{\equiv}Ct\text{-}Bu$ in hexane, although this compound was isolated from the solution by filtration. The NMR spectra of compound **5** do not show noticeable resonances for the *n*-butyl group. The monoanionic $[(AlH)_7(AlNMe_3)(CCH_2t\text{-}Bu)_6]^-$ is an intermediate between the neutral carbaalanes (e.g., **1**) and the dianionic carbaalanates. It also provides a better solubility when compared to **1**−**4**. The $^1H$ NMR spectrum of **6** shows six singlets each for the $C(CH_3)_3$ and the $CCH_2$ groups with different intensities but with a correct overall integral. The $^{13}C$ NMR spectrum always exhibits six resonances each for the different carbon atoms of comparable organic groups of the cluster anion. Only one singlet in the $^1H$ and $^{13}C$ NMR spectra is observed for the $NMe_3$ groups on the different Al atoms with the expected integration.

When we used $LiC{\equiv}CPh$ instead of $LiC{\equiv}Ct\text{-}Bu$ in a comparable reaction like the preparation for **2**, the neutral compound **1** was obtained in 64% yield (Scheme 3). Moreover, we found compound **1** to be the product of the reaction of $Me_3N{\cdot}Al(C{\equiv}CPh)_3$, **7**, with $AlH_3{\cdot}NMe_3$ in boiling toluene.[18] This indicates that not only the use of the lithium starting material and the additives are responsible for the carbaalanate formation but also the nature of the organic group of the alkynyl moiety is important. Moreover, this is in accordance with the reaction of ethynyl adamantane $AdC{\equiv}CH$ with 3 equiv of $AlH_3{\cdot}NMe_3$ in boiling toluene. No straightforward synthesis of a neutral carbaalane is observed, although this compound does not evaporate like the chemically related $t\text{-}BuC{\equiv}CH$ (bp 37−38 °C) from the reaction mixture when refluxed. Furthermore, the reaction mixture of $AdC{\equiv}CH$ and $AlH_3{\cdot}NMe_3$ and all the presented carbaalanates turn violet upon treatment with air. We have not made a comparable observation for our neutral derivatives. Possibly, an oxidation of the cluster anions occurs although we could not detect a resonance in the EPR spectrum of oxidized **2**,[7] and a diamagnetic oxidation product is probable.

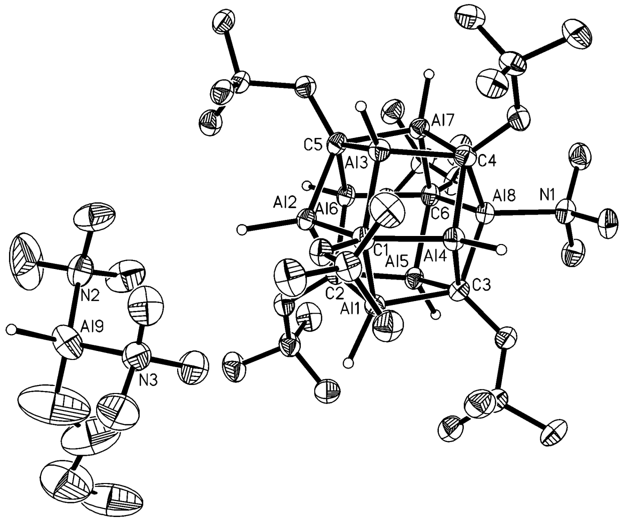
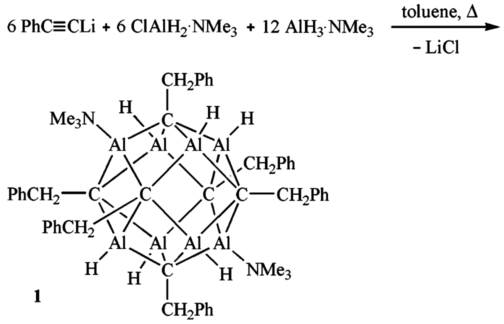


**Figure 2.** ORTEP drawing of $6{\cdot}2C_7H_8$ (50% thermal ellipsoids). Solvents molecules are omitted. Only hydrogen atoms on Al atoms are shown. Selected bond lengths (Å) and angles (deg): Al(9)−N(2) 199.7(3), Al(9)−N(3) 199.6(3), Al(9)−C(91) 192.7(6); N(3)−Al(9)−N(2) 110.03(12), C(91)−Al(9)−N(2) 110.1(3), C(91)−Al(9)−N(3) 113.0(3).

**Scheme 3**



In summary, we have introduced the class of weakly coordinating carbaalanates with the free anions $[(AlH)_8(CCH_2t\text{-}Bu)_6]^{2-}$ and $[(AlH)_7(AlNMe_3)(CCH_2t\text{-}Bu)_6]^-$ which are able to stabilize aluminum hydride cations such as $[H_2Al(NMe_3)_2]^+$ in **3**. Although they are not stable toward protic reagents, their chemical inertness in general makes them an attractive target for future applications.

## Experimental Section

**General.** All manipulations were performed with dried and degassed reagents in a dry and oxygen free atmosphere ($N_2$ or Ar) using Schlenk line and glovebox techniques. IR spectra were recorded in a Nujol mull between KBr plates. Melting points are not corrected.

**Synthesis of $[H_2Al(NMe_3)_2]_2[(AlH)_8(CCH_2t\text{-}Bu)_6]$, 3.** $Me_3SiCl$ (1.47 g, 1.72 mL, 13.6 mmol, 5.7 equiv) was added dropwise to a

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**Table 1.** Crystallographic Data

| | **3** | **6**·2 $C_7H_8$ |
|---|---|---|
| formula | $C_{48}H_{114}Al_{10}N_4$ | $C_{63}H_{126}Al_9N_3$ |
| formula weight | 1017.23 | 1168.49 |
| crystal system | monoclinic | orthorhombic |
| space group | $P2_1/n$ | $P2_12_12_1$ |
| unit cell dimensions | $a = 13.013(3)$ Å<br>$b = 15.676(4)$ Å<br>$c = 16.321(3)$ Å<br>$\beta = 94.375(17)$ deg | $a = 11.9773(11)$ Å<br>$b = 18.527(3)$ Å<br>$c = 33.662(4))$ Å |
| $V$ | 3319.9(13) Å$^3$ | 7469.8(16) Å$^3$ |
| $Z$ | 2 | 4 |
| $\rho_{\text{calculated}}$ | 1.018 mg/m$^3$ | 1.039 mg/m$^3$ |
| $m$ | 0.180 mm$^{-1}$ | 0.157 mm$^{-1}$ |
| $F(000)$ | 1120 | 2568 |
| crystal size | $0.40 \times 0.20 \times 0.20$ mm$^3$ | $0.30 \times 0.30 \times 0.30$ mm$^3$ |
| $\theta$ range for data collection | 1.80−24.76 deg | 1.63−24.80 deg |
| index ranges | $-15 \leq h \leq 15, -16 \leq k \leq 18, -19 \leq l \leq 19$ | $-14 \leq h \leq 13, -21 \leq k \leq 21, -39 \leq l \leq 39$ |
| reflctns collected | 26812 | 96085 |
| independent reflctns | 5663 [$R_{\text{int}} = 0.1384$] | 12766 [$R_{\text{int}} = 0.0694$] |
| completeness to $\theta$ | 99.5% | 99.4% |
| max and min transmission | 0.9648 and 0.9314 | 0.9545 and 0.9545 |
| data/restraints/ parameters | 5663/15/319 | 12766/15/738 |
| goodness-of-fit on $F^2$ | 1.079 | 1.026 |
| final $R$ indices [$I > 2\sigma(I)$] | $R_1 = 0.0846$, $wR_2 = 0.2008$ | $R_1 = 0.0404$, $wR_2 = 0.0996$ |
| $R$ indices (all data) | $R_1 = 0.1412$, $wR_2 = 0.2182$ | $R_1 = 0.0484$, $wR_2 = 0.1033$ |
| largest diff. peak and hole | 0.676 and −0.337 e·Å$^{-3}$ | 0.404 and −0.356 e·Å$^{-3}$ |

mixture of $AlH_3 \cdot NMe_3$ (50 mL of a 0.90 M solution in toluene, 45.0 mmol, 18.9 equiv), [*t*-$BuCH_2(Bzl)NMe_2$]Cl (1.15 g, 4.76 mmol, 2.0 equiv), and toluene (20 mL) at 0 °C and stirred at room temperature for 30 min. This mixture was added at 0 °C to solid *t*-BuC≡CLi (1.26 g, 14.3 mmol, 6.0 equiv). The suspension was stirred for 30 min at room temperature, refluxed for 45 min, and filtered hot. The solution was stored overnight at room temperature and for several weeks at 4 °C yielding two crops of colorless crystals of **3**. Yield: 1.20 g (1.18 mmol, 50%). In a similar reaction, 2.0 equiv of $^{\text{Dipp}}$nacnacH (1.99 g, 4.76 mmol) was used instead of [*t*-$BuCH_2(Bzl)NMe_2$]Cl and allowed to react with the $AlH_3 \cdot NMe_3$ prior to adding further reagents. Yield: 1.40 g (1.38 mmol, 58%). Mp: 170 °C (dec). IR: $\tilde{\nu}$ 1882 and 1874 (Al−H from $[H_2Al(NMe_3)_2]^+$), 1751 (Al−H from $[(AlH)_8(CCH_2t\text{-}Bu)_6]^{2-}$), 1262, 1033, 1002, 798, 755, 557, 516 cm$^{-1}$. Anal. Calcd for $C_{48}H_{114}Al_{10}N_4$: C, 56.67; H, 11.30; N, 5.51. Found: C, 56.32; H, 11.19; N, 5.31.

**Synthesis of $[n\text{-}Bu_4N]_2[(AlH)_8(CCH_2t\text{-}Bu)_6]$, 4.** $Me_3SiCl$ (1.67 g, 1.94 mL, 15.4 mmol, 5.7 eq) was added dropwise to a mixture of $AlH_3 \cdot NMe_3$ (60 mL of a 0.85 M solution in toluene, 51.0 mmol, 18.9 equiv) and [*n*-$Bu_4N$]Cl (1.50 g, 5.40 mmol, 2.0 equiv) at 0 °C and stirred at room temperature for 30 min. This mixture was added at 0 °C to solid *t*-BuC≡CLi (1.43 g, 16.2 mmol, 6.0 equiv). The suspension was stirred for 1 h at room temperature, refluxed for 45 min, and filtered hot. The solution was stored at room temperature affording colorless crystals of **4**. Yield: 1.51 g (1.27 mmol, 47%). Mp: 180 °C (dec). EI-MS: *m*/*z* (%): 242 ($n\text{-}Bu_4N^+$, 100). IR: $\tilde{\nu}$ 1753 (Al−H from $[(AlH)_8(CCH_2t\text{-}Bu)_6]^{2-}$), 1330, 1262, 1196, 1034, 1004, 925, 891, 754, 700, 552 cm$^{-1}$. Anal. Calcd for $C_{68}H_{146}Al_8N_2$: C, 67.62; H, 12.18; N, 2.32. Found: C, 68.27; H, 12.05; N, 2.47.

**Synthesis of $Me_3N \cdot Al(C{\equiv}Ct\text{-}Bu)_3$, 5.** Toluene (25 mL) was added at 0 °C to a mixture of $AlCl_3 \cdot NMe_3$[19] (0.63 g, 3.28 mmol, 1.0 equiv) and LiC≡C*t*-Bu (0.92 g, 10.4 mmol, 3.2 equiv) and stirred 4 h at room temperature. The mixture was filtered, all the volatiles were removed, and the residue was recrystallized from hexane/toluene (2:1) affording fine colorless needles of **5**. Yield: 0.83 g (2.53 mmol, 77%). Mp: 253 °C (sublimation starts at 200 °C). $^1$H NMR (300 MHz, $C_6D_6$): $\delta$ 1.17 (s, 27 H, $C(CH_3)_3$), 2.26 (s, 9 H, $N(CH_3)_3$). $^{13}$C NMR (126 MHz, $C_6D_6$): $\delta$ 28.3 ($C(CH_3)_3$), 31.6 ($C(CH_3)_3$), 46.7 ($N(CH_3)_3$), 89.5 (very broad, AlC≡C), 117.0 ($C{\equiv}CC(CH_3)_3$). EI-MS: *m*/*z* (%): 329 (M$^+$, 18), 314 (M$^+$ − Me, 7), 272 (M$^+$ − *t*-Bu, 78). IR: $\tilde{\nu}$ 2158 and 2130 (C≡C), 1245, 798, 653 cm$^{-1}$. Anal. Calcd for $C_{21}H_{36}AlN$: C, 76.55; H, 11.01; N, 4.25. Found: C, 76.00; H, 11.25; N, 4.33.

**Synthesis of $[H(n\text{-}Bu)Al(NMe_3)_2][(AlH)_7(AlNMe_3)(CCH_2t\text{-}Bu)_6]$, 6.** $AlH_3 \cdot NMe_3$ (8.55 mL of a 0.85 M solution in toluene, 7.27 mmol, 6.3 equiv) was added to a solution of $Me_3N \cdot Al(C{\equiv}CtBu)_3$ **5** (0.38 g, 1.15 mmol, 1.0 eq) in toluene (10 mL). The mixture was refluxed for 50 min and concentrated to ca. 10 mL. A crystalline product precipitated at room temperature and 4 °C, but the composition could not be determined. The remaining solution was concentrated to ca. 3 mL and stored at −25 °C for 6 months, yielding colorless blocks of **6**·$2C_7H_8$. Yield: ca. 10 mg (9 $\mu$mol, 1.5%). $^1$H NMR (500 MHz, $C_6D_6$): $\delta$ 0.75−1.20 (m, 7 H, *n*-Bu), 1.37, 1.39, 1.42, 1.44, 1.47, 1.53 (6 s, 54 H, $C(CH_3)_3$), 2.00 (s, 18 H, $N(CH_3)_3$), 2.24, 2.28, 2.29, 2.30, 2.32, 2.40 (6 s, $CCH_2$), ca. 5.3 (s, very broad, Al−H). $^{13}$C NMR (126 MHz, $C_6D_6$): $\delta$ 14.4, 15.5, 23.2, 29.5, 29.6 (*n*-Bu group and/or cluster C), 30.3, 30.4, 30.8, 30.9, 31.0, 31.1 ($C(CH_3)_3$), 35.4, 35.5, 35.5, 35.6, 35.8, 35.9 ($C(CH_3)_3$), 47.6 ($N(CH_3)_3$), 49.9, 50.0, 50.1, 50.8, 50.9, 51.3 ($CCH_2$).

**X-ray Crystallography.** Crystals were mounted in oil and measured on a Stoe IPDS II diffractometer at 133(2) K using Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least squares on $F^2$ using SHELX-97 programs for crystal structure refinement (Sheldrick, Universität Göttingen, 1997).

**Acknowledgment.** We are thankful for financial support of the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Göttinger Akademie der Wissenschaften.

**Supporting Information Available:** Structural data for **3** and **6**·$2C_7H_8$ is available as a CIF. This material is available free of charge via the Internet at http://pubs.acs.org.

IC048594K

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