Synthesis and Reactivity of the Carbaalanes $(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$ and $(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6$: X-ray Crystal Structure of $(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$[†]

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The synthesis of the aluminum carbide clusters $(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$ (**1**), containing an assembly of ferrocenylmethylene substituents, and $(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6$ (**2**) was carried out by the hydroalumination of FcC≡CH (Fc = ferrocenyl) and $(PhC{\equiv}C)_3Al{\cdot}NMe_3$, respectively, with $AlH_3{\cdot}NMe_3$. Compound **1** is made up of an Al−C framework with eight aluminum atoms occupying the corners of a rhombic cube while the six carbon atoms cap the faces of the cube. The reaction of $(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6$ (**2**) with FcC≡CH and PhC≡CH leads to the formation of $(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6$ (**3**) and $(PhC{\equiv}C)_3Al{\cdot}NMe_3$ (**4**), respectively. Reaction of **4** with $AlH_3{\cdot}NMe_3$ results in the formation of **2**.

Introduction

Carboranes[1] burst into the chemical scene in the mid 1960s. These are cluster compounds containing boron and carbon and have been very well studied, in view of their interesting structures and bonding properties. Their congeners, carbaalanes, have been much less investigated. Wilke and co-workers have originally investigated the hydroalumination reaction involving trialkylaluminums or dialkylaluminum hydrides with dialkylaluminum acetylides.[2] However, they did not succeed in isolating and characterizing polyhedral carbaalanes. In 1999 Uhl and co-workers reported the synthesis of the polyhedral carbaalane $(AlMe)_8(CCH_2Ph)_5H$ by the hydroalumination reaction between dimethylaluminum hydride and dimethylaluminum phenylacetylide.[3] This was followed by the extension of this approach to studying the reactions between other substituted aluminum acetylides and dialkylaluminum hydrides.[4] We have been interested in hydroalumination reactions and have been pursuing this topic for some time. Recently, we reported the reactions of monosubstituted acetylenes with dimeric (pyrazolato)aluminum dihydrides in which terminal acetylides are formed.[5] To synthesize hydride-rich aluminum derivatives, we have been focusing our attention on the hydroalumination of nitriles[6] and isonitriles[7] as well as terminal acetylenes[8] with $AlH_3{\cdot}NMe_3$. Accordingly, we report here the hydroalumination of FcC≡CH with $AlH_3{\cdot}NMe_3$, which leads to the formation of the new carbaalane $(AlH)_6$-

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[†] Dedicated to Professor Marius Andruh on the occasion of his 50th birthday.

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$(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6$ (**1**). In addition, we also report reactivity studies of the analogous derivative $(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6$ (**2**) toward $FcC{\equiv}CH$ and $PhC{\equiv}CH$. Compound **2** reacts with $FcC{\equiv}CH$ to afford $(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6$ (**3**). On the other hand, reaction of **2** with $PhC{\equiv}CH$ leads to the formation of $(PhC{\equiv}C)_3Al{\cdot}NMe_3$ (**4**).[9] Interestingly, reacting **4** with $AlH_3{\cdot}NMe_3$ results in the formation of the carbaalane **2**.

Experimental Section

All experimental manipulations were carried out under an atmosphere of dry nitrogen using standard Schlenk techniques. The samples for spectral measurements were prepared in a drybox. Solvents were purified according to conventional procedures and were freshly distilled prior to use. Ferrocenylacetylene[14] and $AlH_3{\cdot}NMe_3$[15] were prepared as described in the literature. IR spectra were recorded on a Bio-Rad Digilab FTS7 spectrometer. Melting points were obtained on a HWS-SG 3000 apparatus and are uncorrected. CHN analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry, Göttingen, Germany. Solid-state NMR spectra for the nuclei ^1H, ^{13}C, and ^{27}Al were recorded at Max-Planck-Institut für Biophysikalische Chemie, Göttingen, Germany. ^{27}Al NMR chemical shifts are reported with reference to $AlCl_3$.

X-ray Crystallography. Suitable crystals of compounds **1**−**4** were mounted on a glass fiber and coated with paraffin oil. Diffraction data for all the crystals were collected on a STOE IPDS II diffractometer at 133(2) K. The measurement was made with graphite-monochromated Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structure was solved by direct methods using SHELXS-97[16] and refined against F^2 on all data by full-matrix least squares with SHELXL-97.[17] All non-hydrogen atoms were refined anisotropically. Neutral-atom scattering factors (including anomalous scattering) were taken from ref 18. Hydrogen atoms were included at geometrically calculated positions and refined using a riding model. The hydrogen atoms at the aluminum atoms were refined without any restraints.

Synthesis of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6]$ (1). $AlH_3{\cdot}NMe_3$ (19 mL, 0.50 M solution in toluene) was added with stirring to a solution of ferrocenylacetylene (0.60 g, 2.86 mmol) in toluene (30 mL) at room temperature. The reaction mixture was stirred for 1 h at room temperature and then heated at reflux until the evolution of NMe_3 and H_2 ceased. The resulting solution was kept for crystallization at room temperature for 24 h. Reddish brown crystals of **1** (0.51 g, 67% yield with respect to ferrocenylacetylene) formed. Mp: 257 °C dec. ^1H NMR (600 MHz, 23 kHz, MAS (magic angle spinning)): δ 1.9 (br, 12H; CH_2), 2.7 (br, 18H; $N(CH_3)_3$), 3.8 (br, 6H; Al−H), 5.0 ppm (br, 54H; $C_5H_4FeC_5H_5$).^{13}C NMR (600 MHz, 23 KHz, MAS): δ 27.6 (cluster C), 28.9 (CH_2C), 44.0 ($N(CH_3)_3$), 65.0 ppm ($C_5H_4FeC_5H_5$). ^{27}Al NMR (600 MHz, 23 KHz, MAS, $AlCl_3$): δ 140.0 ppm. IR (KBr, Nujol): $\tilde{\nu}$ 1802 (br, Al−H), 1279, 1261, 1230, 1103, 1038, 1002, 977, 920, 809, 759, 728 cm^{-1}. Anal. Calcd for $C_{78}H_{96}Al_8Fe_6N_2$ (1612.53): C, 58.10; H, 6.00; N, 1.74. Found: C, 58.62; H, 5.88; N, 1.27.

Synthesis of $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (2). This compound was prepared earlier by us by the hydroalumination of $PhC{\equiv}CH$ with $AlH_3{\cdot}NMe_3$.[8] Herein, we report an alternative procedure for the synthesis of **2**. $AlH_3{\cdot}NMe_3$ (10 mL, 0.50 M solution in toluene) was added to a solution of $(PhC{\equiv}C)_3Al{\cdot}NMe_3$ (0.60 g, 1.54 mmol) at room temperature. The reaction mixture was stirred for 1 h at room temperature before refluxing it until the evolution of H_2 and NMe_3 had ceased. The resultant solution was filtered and kept for crystallization at 0 °C to obtain colorless crystals of **2** (0.50 g, 72% yield with respect to $(PhC{\equiv}C)_3Al{\cdot}NMe_3$). The spectroscopic and analytical data of **2** match perfectly with those of the reported carbaalane.[8]

Reaction of 2 with $FcC{\equiv}CH$ To Give $(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6$ (3). To a suspension of **2** (0.60 g, 0.62 mmol) in toluene (30 mL) was added ferrocenylacetylene (0.80 g, 3.80 mmol) at room temperature. The reaction mixture was stirred for 1 h at room temperature. Subsequently it was refluxed until the evolution of H_2 ceased. The resulting solution was filtered and kept for crystallization at room temperature to obtain reddish brown crystals of **3** (0.75 g, yield 67% with respect to **2**). Mp: 254 °C dec. ^1H NMR (600 MHz, 26 KHz, MAS): δ 1.9 (br, 12H; CH_2), 2.7−3.0 (br, 18H; $N(CH_3)_3$), 4.0 (br, 2H; Al−H), 5.0 (br, $C_5H_4FeC_5H_5$), 7.2 ppm (br, 30H, C_6H_5). ^{13}C NMR (600 MHz, 26 KHz, MAS): δ 30.0 (cluster C and CH_2C), 40.0 ($N(CH_3)_3$), 65.0 ($C_5H_4FeC_5H_5$), 120.0−130.0 ppm (C_6H_5). ^{27}Al NMR (600 MHz, 26 KHz, MAS, $AlCl_3$): δ 40.0−130.0 ppm. IR (KBr, Nujol): $\tilde{\nu}$ 2119, 1808, 1600, 1261, 1233, 1106, 1023, 976, 915, 801, 753, 699, 674, 582, 534 cm^{-1}. Anal. Calcd for $C_{102}H_{98}Al_8Fe_4N_2$: C, 68.40; H, 5.51; N, 1.56. Found: C, 67.90; H, 5.57; N, 1.52.

Reaction of 2 with $PhC{\equiv}CH$ To Give $(PhC{\equiv}C)_3Al{\cdot}NMe_3$ (4). Compound **2** (1.00 g, 1.00 mmol) was dissolved in toluene (20 mL), and phenylacetylene (3.20 g, 30.0 mmol) was added at room temperature. The reaction mixture was heated at reflux for 1 h, during which period the evolution of NMe_3 and H_2 was observed and the solution became dark red. The volume of the solvent was reduced in vacuo to about 10 mL, and the residual solution was stored overnight at −20 °C to obtain colorless crystals of **4** (2.21 g, yield 68% with respect to **2**). The spectroscopic and analytical data of **4** prepared by the above procedure matched exactly with those of an authentic sample obtained in the reaction of $AlH_3{\cdot}NMe_3$ with excess $PhC{\equiv}CH$.[9]

Results and Discussion

The reaction of ferrocenylacetylene with an excess of $AlH_3{\cdot}NMe_3$ in refluxing toluene resulted in the formation of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6]$ (**1**) (Scheme 1). During the reaction, evolution of NMe_3 and H_2 was observed. Reddish brown crystals of compound **1** were obtained as the only isolable product when the reaction mixture was kept at room temperature after the heating period. The mechanism of hydroalumination of ferrocenylacetylene is believed to be similar to that described earlier.[8] Thus, as shown in Scheme 1, the first step is envisaged as the formation of $FcC{\equiv}CAlH_2{\cdot}NMe_3$ accompanied by the elimination of H_2. Subsequent hydroalumination of this intermediate would lead to the formation of $FcCH_2C(AlH_2{\cdot}NMe_3)_3$, which can undergo

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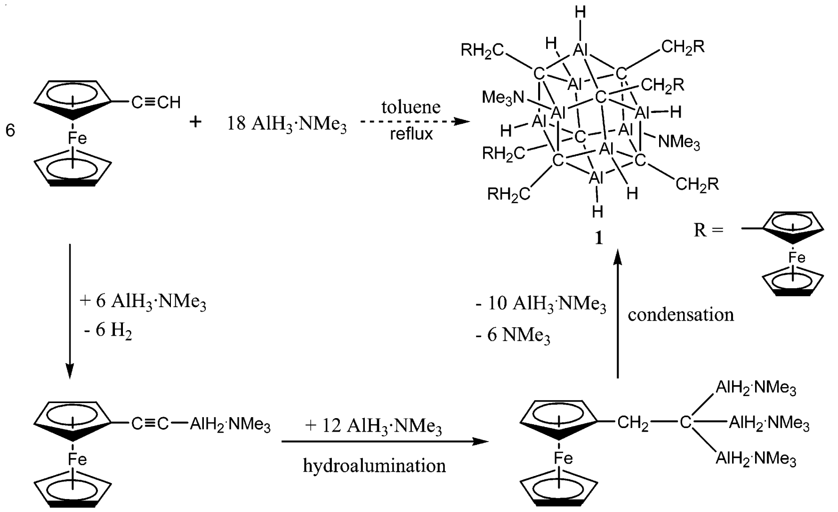
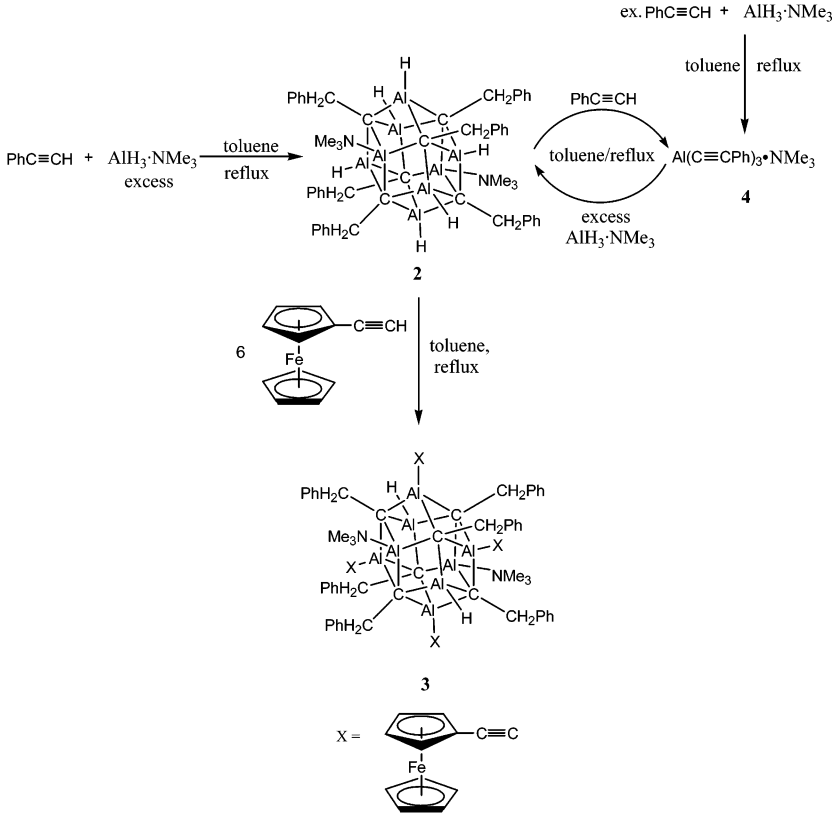
Scheme 1. Synthesis and Mechansim of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6]$ (1)



Scheme 2. Synthesis and Reactivity of 2



a condensation reaction to afford the carbaalane **1**. Compound **1** is an air-/moisture-sensitive solid which was characterized by single-crystal X-ray structural analysis, IR spectroscopy, and elemental analysis. ^{1}H and ^{13}C NMR spectra of **1** in solution could not be recorded, due to its very poor solubility in benzene, toluene, acetonitrile, and THF. Also, **1** decomposes in trichloromethane. Although there are two chemically different aluminum atoms, the solid-state ^{27}Al NMR spectrum of compound **1** shows only one prominent broad resonance at δ 140.0 ppm. It was difficult to further quantify the quadrupolar sites due to the significant degree of structural disorder. The solid-state ^{13}C NMR resonances of the cluster carbon and $N(CH_3)_3$ appear at δ 28.0 and δ 44.0 ppm, respectively. In the solid-state ^{1}H NMR spectrum of **1** the methylene groups attached to the cluster carbon atoms resonate at δ 1.9 ppm and the methyl groups of $N(CH_3)_3$ are observed at δ 2.7 ppm. Further resolution of the spectra in ^{1}H−^{13}C 2D HETCOR (heteroatom correlation spectra) showed this more clearly. A correlation typical for the CH_3 group could be found at δ(^{1}H) 2.7 ppm and δ(^{13}C) 44 ppm. Similarly, the correlation (δ(^{1}H) 5.0 ppm and δ(^{13}C) 65 ppm) could be attributed to the ferrocenyl moiety. The absence of a strong absorption band at 2119 cm^{-1} in the IR spectrum indicates the absence of a ν(C≡C)[10] stretching frequency. The presence of a broad absorption band at 1802 cm^{-1} can be attributed to the Al−H bond. We could not explore the electrochemistry[11] and reactivity of the Al−H bonds of **1** due to its very poor solubility.

Recently,[8] we reported that the aluminum−carbon cluster compound $(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6$ (**2**) can be prepared by treatment of PhC≡CH with an excess of AlH_3·NMe_3 in refluxing toluene (Scheme 2). Compound **2** can also be prepared by carrying out a reaction between $(PhC{\equiv}C)_3Al$·NMe_3 (**4**) and an excess of AlH_3·NMe_3 in refluxing toluene until the evolution of H_2 and NMe_3 ceased (Scheme 2). The resulting solution was filtered, and the product was allowed to crystallize at room temperature, giving colorless crystals of **2**. We have found earlier that compound **2** reacts with BCl_3,[8] BF_3·OEt_2,[12] BX_3 (X = Br, I),[12] Me_3SnF,[12] and Me_3SiX (X = Cl, Br, I)[12] with complete replacement of all the six hydride substituents on aluminum atoms to afford $(AlX)_6(AlNMe_3)_2(CCH_2Ph)_6$ (X = F, Cl, Br, I). It was of interest to explore the reactivity of Al−H bonds in **2** toward substituted acetylene, RC≡CH. Consequently, we studied the reaction of **2** with FcC≡CH and PhC≡CH, respectively (Scheme 2).

The reaction of **2** with 6 equiv of ferrocenylacetylene in refluxing toluene proceeds with the evolution of hydrogen and affords $(AlH)_2(FcC{\equiv}CAl)_4(AlNMe_3)_2(CCH_2Ph)_6$ (**3**). Compound **3** is formed from **2** as a result of the substitution of four Al−H bonds (out of a total of six). It was not possible to obtain any other product, even when the reaction was carried out (a) with an excess of ferrocenylacetylene and (b) in higher boiling solvents such as *p*-xylene and mesitylene. The characterization of **3** is based on its analytical data as well as solid-state NMR and IR spectra. Absorption bands at 2115 and 1808 cm^{-1} in the IR spectrum of **3** can be attributed to ν(C≡C) and ν(Al−H) stretching frequencies. The solid-state ^{27}Al NMR spectrum of **3** showed a weak resonance at δ 40 ppm and a strong one at δ 130 ppm. The ^{13}C NMR spectrum exhibits a broad resonance at δ 40 ppm, which can be attributed to $N(CH_3)_3$. The ferrocene moieties and the phenyl groups resonate at δ 65 and 120−130 ppm, respectively. In the ^1H NMR spectrum the presence of a broad signal at δ 4 ppm is due to the presence of unreacted Al−H bonds and the resonances corresponding to CCH_2, $N(CH_3)_3$, $C_5H_4FeC_5H_5$, and C_6H_5 groups are observed at δ 1.9, 2.7−3.0, 4.5, and 7.2 ppm, respectively.

In contrast to the above, in the reaction of **2** with phenylacetylene we were able to isolate only the tris(acetylide) $(PhC{\equiv}C)_3Al$·NMe_3 (**4**). To assess if the cluster **2** was undergoing decomposition in solution, as a control experiment, we heated it without any other reagent. The cluster retains its integrity even after refluxing it for 5 h. Compound **4** was the only isolable product when the reaction was carried out either in a 1:6 stoichiometric ratio (compound **2**: PhC≡CH) or even when an excess of phenylacetylene was used. The yield of **4** has been optimized in this reaction to 68% (see Experimental Section). It is of interest to note that **4** was originally prepared by the reaction of an excess of phenylacetylene with AlH_3·NMe_3.[9] Although the precise reasons for the difference in reactivity between FcC≡CH and PhC≡CH elude us at the moment, it is possible that the steric requirements of ferrocenylacetylene do not allow the reaction to proceed beyond **3**.

X-ray Crystal Structure Data of $[(AlH)_6(AlNMe_3)_2(CCH_2C_5H_4FeC_5H_5)_6]$ (1). The molecular structure of **1** in the solid state was determined by single-crystal X-ray structural analysis (Table 1). **1** crystallizes in the triclinic space group $P\bar{1}$ with two halves of the molecule and 2.5 molecules of toluene in the asymmetric unit. In one cluster molecule all Fe units are disordered (nearly 60:40). An ORTEP plot of **1** is shown in Figure 1. The carbaalane polyhedron contains an Al−C framework with eight aluminum atoms occupying the corners of the

Table 1. Crystallographic Data for the Structurally Analyzed Compound 1

compd	**1**·2.5PhMe
formula	$C_{95.50}H_{110}Al_8Fe_6N_2$
fw	1836.80
T/K	133(2)
λ/Å	0.710 73
cryst syst	triclinic
space group	$P\bar{1}$
a/Å	12.708(5)
b/Å	14.885(6)
c/Å	25.994(10)
α/deg	91.41(3)
β/deg	96.97(3)
γ/deg	113.82(3)
V/Å^3	4450.4(3)
Z	2
D(calcd)/g cm^{-3}	1.371
μ(Mo Kα)/cm^{-1}	1.078
F(000)	1914
θ range/deg	3.00−50.00
index range	$-15 \le h \le 14$ $-17 \le k \le 17$ $-30 \le l \le 30$
no. of rflns collected	85 305
no. of indep rflns	15 545
refinement method	full-matrix least squares on F^2
no. of data/restraints/params	15 545/0/807
R1, wR2 ($I > 2\sigma(I)$)[a]	0.0672, 0.1640
R1, wR2 (all data)[a]	0.0880, 0.1774
S	1.018
$\Delta\rho$(min), $\Delta\rho$(max)/e Å^3	1.397, −0.929

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = [\sum w(|F_o{}^2| - |F_c{}^2|)^2/\sum w|F_o{}^2|^2]^{1/2}$.

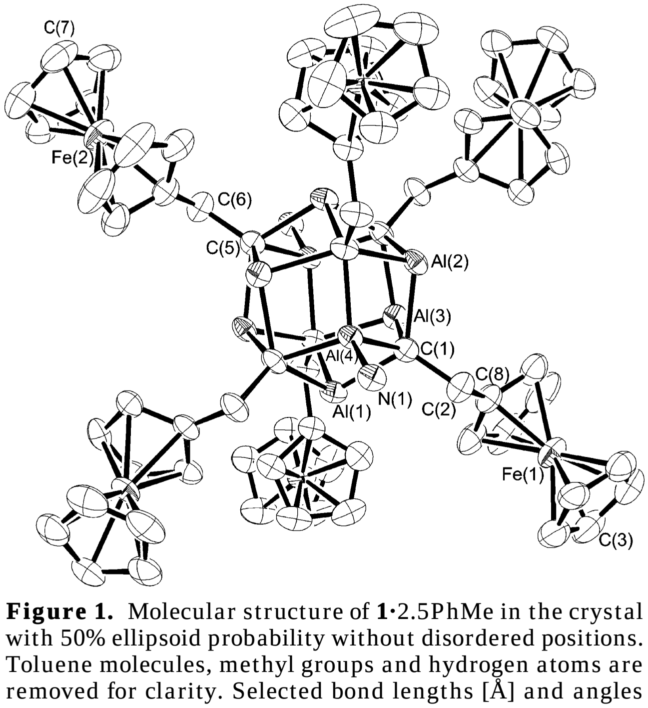


Figure 1. Molecular structure of **1**·2.5PhMe in the crystal with 50% ellipsoid probability without disordered positions. Toluene molecules, methyl groups and hydrogen atoms are removed for clarity. Selected bond lengths [Å] and angles [°]: Al(1)−Al(3) = 2.645 (2), Al(1)−Al(4) = 2.584 (2), Al(4)−N(1) = 2.001 (4), Al(4)−C(1)−Al(2) = 77.97 (17), Al(4)−C(1)−Al(3) = 123.83 (1), Al(1)−C(1)−Al(2) = 127.34 (2), Al(2)−C(1)−Al(3) = 78.37 (17).

rhombic cube, while the six carbon atoms bearing the ferrocenylmethylene groups cap the faces of the cube. Six of the eight aluminum atoms carry a hydrogen atom, and the remaining two, which are positioned opposite to each other in the cluster, are bonded to the NMe_3 groups. The opposite pairs of ferrocenylmethylene groups are trans to each other. The average bond distances between the Al atoms bonded to the NMe_3 groups and the closest cluster carbon atoms (2.017(5), 2.025(5), 2.032(5) Å) are significantly shorter than the corresponding bond distances from the Al atoms bonded to the hydrogen atoms (2.076(5), 2.094(5), 2.099(5) Å). Similarly, the average bond distances between the Al atoms coordinated to the NMe_3 groups and the Al atoms bonded to the hydrogen atoms (2.578(2), 2.584(2) Å) are shorter than the corresponding bond distances between the aluminum atoms bearing the hydrogen atoms (2.645(2), 2.641(2) Å). These Al−Al bond lengths are comparable with those of the dimeric aluminum trimethyl.[13] The average bond angles are found to be similar to those of the reported carbalanes[4,8] (Al(4)−C(1)−Al(3) = 123.83(2)°, Al(1)−C(1)−Al(2) = 127.34(2)°, Al(2)−C(1)−Al(3) = 78.37(17)°). The diameter of the cluster measured between two ferrocenylmethylene groups of the cluster, which are trans to each other, is 1.648 nm (C(7)−C(3)). All the bond parameters are comparable to those of compound **2**.[8] Crystallographic data for the compounds **2**[8] and **4**[9] have been reported earlier. Compound **3** crystallizes in the triclinic space group $P\bar{1}$. The crystal structure of this compound could not be determined completely, due to severe disorder between the ferrocenylacetylide and toluene molecules.

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Supporting Information Available: Tables and figures giving single-crystal X-ray structural data of compound **1** and solid-state NMR spectra for compounds **1** and **3**; X-ray data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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