

New Carbaalanes Containing Clusters of Aluminum and Carbon Atoms: $(\text{AlEt})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5\text{H}$, $(\text{AlMe})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5(\text{C}\equiv\text{C}-\text{C}_6\text{H}_5)$, and $(\text{AlMe})_7(\text{CCH}_2\text{CH}_3)_4\text{H}_2$. Quantum Chemical Characterization

Werner Uhl* and Frank Breher

Fachbereich Chemie der Philipps-Universität, Hans-Meerwein-Strasse,
D-35032 Marburg, Germany

Jörg Grunenberg

Institut für Organische Chemie, Technische Universität Braunschweig, Hagenring 30,
D-38106 Braunschweig, Germany

Arne Lützen and Wolfgang Saak

Fachbereich Chemie, Carl-von-Ossietzky Universität, Postfach 2503,
D-26111 Oldenburg, Germany

Received March 20, 2000

The open carbaalane cluster $(\text{AlEt})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CCH}_2\text{C}_6\text{H}_5)_3\text{H}$ (**2**), which was obtained in our group only recently, reacted with an excess of diethylaluminum hydride with hydroalumination of its C=C double bonds and formation of the compound $(\text{AlEt})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5\text{H}$ (**4**). The central cluster of the product comprises a cube of eight Al atoms, five faces of which are occupied by C-benzyl groups; the sixth face is bridged by a hydrogen atom. The carbaalane $(\text{AlMe})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5(\text{C}\equiv\text{CC}_6\text{H}_5)$ (**5**) was obtained by hydroalumination of $\text{Me}_2\text{AlC}\equiv\text{CC}_6\text{H}_5$ by Me_2AlH at 60 °C. Its structure is similar to that of **3**, but the bridging hydrido ligand has been replaced by an ethynyl group, which is coordinated to four Al atoms and shows a quite unusual C≡C stretching vibration of 1956 cm^{-1} . The first carbaalane possessing only aliphatic substituents, $(\text{AlMe})_7(\text{CCH}_2\text{CH}_3)_4\text{H}_2$ (**6**), was obtained by the reaction of $\text{Me}_2\text{AlC}\equiv\text{CCH}_3$ with Me_2AlH . Its structure contains an Al_7C_4 cluster, which is quite similar to that of the *closo*-borate $[\text{B}_{11}\text{H}_{11}]^{2-}$. An intense emission of a cluster vibration characteristic for carbaalanes was assigned at about 325 cm^{-1} in the Raman spectra. The structure and bonding of *arachno*-type cluster compounds related to **4** were investigated by quantum chemical calculations. A delocalized multicenter bonding situation was verified with only weak direct Al–Al interactions.

Introduction

The addition of Al–H bonds to C=C double bonds of alkenes or C≡C triple bonds of alkynes has been used in preparative organic chemistry as a simple method for the synthesis of cyclic or chainlike hydrocarbon compounds.¹ Usually, the organoaluminum intermediates of these reactions were not isolated or characterized but were hydrolyzed in situ to liberate the organic compounds. Therefore, there is very little information concerning the constitution of those aluminum derivatives. Alkynylaluminum compounds, in which dialkylaluminum groups are attached to a C≡C triple bond, were employed in hydroalumination reactions in only very few cases.^{2,3} Oily residues were obtained upon

the reactions of alkynyl-diethylaluminum compounds with diisobutylaluminum hydrides. These probably contained mixtures of products and were characterized only by hydrolysis and subsequent analysis of the hydrocarbons formed.² In the early 1960s, Wilke and Schneider reacted dimethyl- or diethylaluminum hydrides with the corresponding alkynyl-dialkylaluminum compounds and isolated solid products, which were characterized by hydrolysis and by elemental analysis and molar mass determination.³ They concluded that cage compounds must have been formed without, however, recognizing the true structure and bonding of these compounds.

(1) (a) Winterfeldt, E. *Synthesis* **1975**, 617. (b) Marek, I.; Normant, J.-F. *Chem. Rev.* **1996**, *96*, 3241.

(2) Kuchin, A. V.; Markova, S. A.; Lomakina, S. I.; Tolstikov, G. A. *J. Gen. Chem. USSR (Engl. Transl.)* **1988**, *58*, 1395; *Zh. Obshch. Khim.* **1988**, *58*, 1567.

(3) Wilke, G.; Schneider, W. *Bull. Soc. Chim. Fr.* **1963**, 1462.

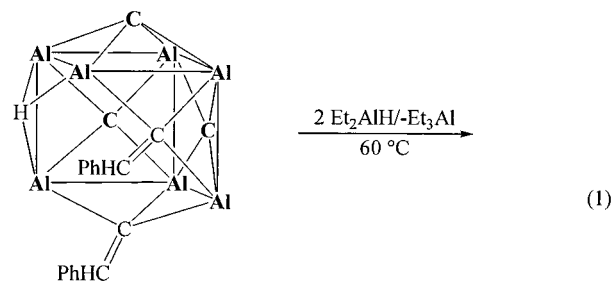
We started with investigations of hydroalumination, because we sought an easy route for the synthesis of polyaluminum compounds. In the course of these studies we also employed alkynylaluminum compounds and isolated crystalline products which had structures unprecedented in organoaluminum chemistry and which, owing to some similarities to carboranes, were named carbaalanes.⁴ The compound $(\text{AlMe})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5\text{H}$ (**1**), obtained by the reaction of dimethyl(phenylethynyl)aluminum with dimethylaluminum hydride,⁵ contains a cube of eight aluminum atoms, five faces of which are bridged by C-benzyl groups and one face of which is bridged by a hydrogen atom. A total of 16 cluster electron pairs results, which is in accordance with an *arachno* configuration of the Al_8C_5 cluster in **1**. If the methyl groups of the starting compounds were replaced by ethyl groups, two new compounds were formed under similar conditions which contained Al_7C_5 and Al_7C_4 clusters, respectively: $(\text{AlEt})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CCH}_2\text{C}_6\text{H}_5)_3\text{H}$ (**2**) and $(\text{AlEt})_7(\text{CCH}_2\text{C}_6\text{H}_5)_4(\text{C}\equiv\text{CC}_6\text{H}_5)\text{H}$ (**3**).⁶ The structure of compound **2**, which contains two C=C bonds, may be derived from that of **1** with one vertex of the Al_8 cube unoccupied. Compound **3** possesses a *closo* cluster in accordance with the number of electrons and adopts a structure very similar to that of the *closo*-borate $[\text{B}_{11}\text{H}_{11}]^{2-}$.⁷ We report here the hydroalumination of the open cluster **2** with an excess of diethylaluminum hydride, a reaction carried out in order to obtain an *arachno* cluster similar to **1**. Furthermore, we were interested in isolating one of the byproducts of the synthesis of **1** by systematically changing the reaction conditions. All carbaalanes obtained so far bear benzyl substituents on their cluster carbon atoms. Therefore, we tried to synthesize compounds with exclusively simple alkyl group substituents. This was of particular interest, owing to the obvious influence of the substituents on the size and structure of those carbaalanes.

Results and Discussion

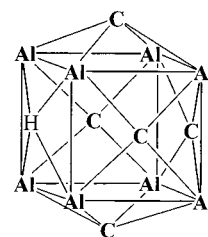
Hydroalumination of 2. As described above, the structure of the carbaalane **2** containing seven Al atoms and two C=C double bonds may be derived from that of the *arachno* Al_8C_5 cluster **1** if one vertex of the Al_8 cube remains unoccupied. Thus, just one hydroalumination step with ethylaluminum dihydride seemed to be needed to obtain an *arachno* cluster with the aluminum atoms substituted by ethyl groups. Such a reaction would give an important insight into the mechanism of formation of these cluster compounds. However, alkyl- or arylaluminum dihydrides are known only with very bulky substituents.⁸ Dihydrides bearing smaller substituents may be formed

in trace amounts by the dismutation equilibrium of dialkylaluminum hydrides, and we suppose that they are intermediates in the hydroalumination reactions of ethynylaluminum compounds, in which the corresponding trialkylaluminum derivatives were formed as byproducts in all cases.

We treated the orange-red compound **2** with an excess of diethylaluminum hydride in the absence of solvent at 60 °C for 18 h (eq 1). The color of the mixture changed



2 (Al = AlEt; C = CCH₂Ph)



4 (Al = AlEt; C = CCH₂Ph)

to yellow, and a colorless product precipitated. Triethylaluminum was formed, as detected by ¹H NMR spectroscopy. All volatile components were removed in vacuo, and the residue was recrystallized from *n*-pentane, giving the colorless compound **4** in 69% yield.

The constitution of compound **4** was established by a crystal structure determination (Figure 1). It has a structure similar to that of compound **1** (described above) with a slightly distorted cube of eight Al atoms, five faces of which are bridged by C-benzyl groups, while the sixth face is occupied by a hydrogen atom. The Al–H distances are long (1.87(4)–2.29(4) Å); the shortest ones are observed for the opposite Al atoms Al(1) (1.87 Å) and Al(3) (2.09 Å). Owing to the large standard deviations of 0.04 Å, we abstain from a more detailed discussion of the Al–H distances. The Al–Al distances of the hydrogen-bridged face (2.808 Å on average) are much longer than those of the carbon-bridged faces (2.609 Å). The latter distances are similar to the Al···Al separation in dimeric trimethylaluminum, which contains a 3c–2e Al–C–Al bridge bond (2.61 Å),⁹ and they are shorter than the Al–Al single bonds in tetraalkyl- or tetraaryldialuminum derivatives (>2.64 Å).¹⁰ Thus, the Al···Al distances in **4** are consistent with

(4) Uhl, W.; Breher, F. *Eur. J. Inorg. Chem.* **2000**, 1.

(5) Uhl, W.; Breher, F. *Angew. Chem.* **1999**, *111*, 1578; *Angew. Chem., Int. Ed.* **1999**, *38*, 1477.

(6) Uhl, W.; Breher, F.; Lützen, A.; Saak, W. *Angew. Chem.* **2000**, *112*, 414; *Angew. Chem., Int. Ed.* **2000**, *39*, 406.

(7) (a) Volkov, O.; Dirk, W.; Englert, U.; Paetzold, P. *Z. Anorg. Allg. Chem.* **1999**, *625*, 1193. (b) Wong, E. H.; Prasad, L.; Gabe, E. J.; Gatter, M. G. *Inorg. Chem.* **1983**, *22*, 1143.

(8) (a) Wehmschulte, R. J.; Grigsby, W. J.; Schiemenz, B.; Bartlett, R. A.; Power, P. P. *Inorg. Chem.* **1996**, *35*, 6694. (b) Wehmschulte, R. J.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 5611. (c) Wehmschulte, R. J.; Ellison, J. F.; Ruhlandt-Senge, K.; Power, P. P. *Inorg. Chem.* **1994**, *33*, 6300.

(9) (a) Vranka, R. G.; Amma, E. L. *J. Am. Chem. Soc.* **1967**, *89*, 3121.

(b) Huffman, J. C.; Streib, W. E. *J. Chem. Soc. Chem. Commun.* **1971**, 911.

(10) (a) Uhl, W. *Z. Naturforsch., B. Chem. Sci.* **1988**, *43*, 1113. (b) Wehmschulte, R. J.; Ruhlandt-Senge, K.; Olmstead, M. M.; Hope, H.; Sturgeon, B. E.; Power, P. P. *Inorg. Chem.* **1993**, *32*, 2983. (c) A long Al–Al bond (2.751 Å) was observed in the silyl derivative tetrakis(tri-*tert*-butylsilyl)dialane(4): Wiberg, N.; Amelunxen, K.; Blank, T.; Nöth, H.; Knizek, J. *Organometallics* **1998**, *17*, 5431.

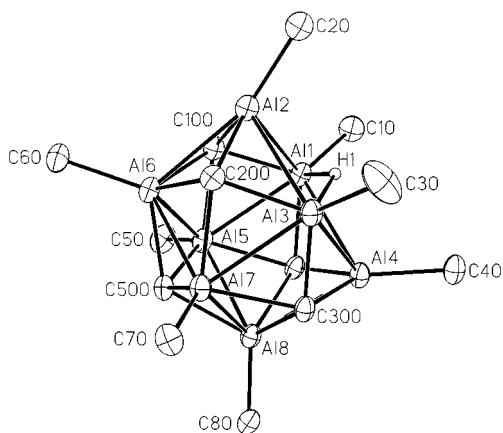


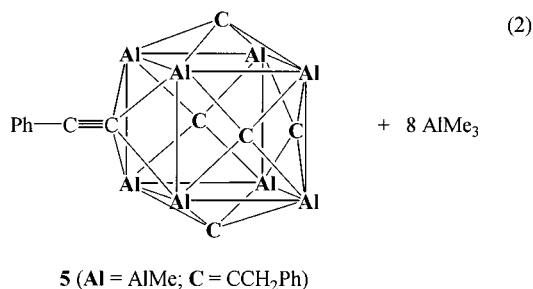
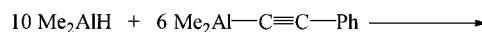
Figure 1. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å): Al(1)–Al(2) = 2.858(2), Al(2)–Al(3) = 2.787(2), Al(3)–Al(4) = 2.787(2), Al(1)–Al(4) = 2.800(2), Al(1)–Al(5) = 2.585(2), Al(2)–Al(6) = 2.604(2), Al(3)–Al(7) = 2.604(2), Al(4)–Al(8) = 2.606(2), Al(5)–Al(6) = 2.601(2), Al(6)–Al(7) = 2.622(2), Al(7)–Al(8) = 2.620(2), Al(5)–Al(8) = 2.631(2), C(100)–Al(1) = 2.025(5), C(100)–Al(2) = 2.021(4), C(100)–Al(5) = 2.126(4), C(100)–Al(6) = 2.121(4), C(200)–Al(2) = 2.022(4), C(200)–Al(3) = 2.020(5), C(200)–Al(6) = 2.072(4), C(200)–Al(7) = 2.156(4), C(300)–Al(3) = 2.027(4), C(300)–Al(4) = 2.018(4), C(300)–Al(7) = 2.134(4), C(300)–Al(8) = 2.112(4), C(400)–Al(1) = 2.040(4), C(400)–Al(4) = 2.009(4), C(400)–Al(5) = 2.099(4), C(400)–Al(8) = 2.151(4), C(500)–Al(5) = 2.063(4), C(500)–Al(6) = 2.095(4), C(500)–Al(7) = 2.049(4), C(500)–Al(8) = 2.088(5).

multicenter bonding interactions in the cluster. The terminal Al–C₂H₅ distances (1.959 Å on average) are shorter than those in the cluster (2.009(4)–2.156(4) Å), the shortest ones of which are observed for the Al atoms of the hydrogen-bridged face. The number of electron pairs in the Al₈C₅ cluster is 16, which, owing to the Wade rules,¹¹ is in accordance with an *arachno* configuration. As described before,^{4,6} the structure may be derived from that of the *closo*-borate [B₁₅H₁₅]²⁻, which is known only from the results of quantum chemical calculations and whose structure is that of a tricapped hexagonal antiprism.¹²

The NMR spectroscopic characterization of compound **4** gave some unusual results, similar to the cluster compounds published before. The bridging hydrogen atom H(1) shows a resonance at very low field (δ 5.28) compared to that of the starting compound diethylaluminum hydride (δ 2.79). Similarly, the resonances of the CH₂ hydrogen atoms of the benzyl groups are shifted to low field (δ 3.84 for the benzyl group at C(500) and δ 3.39 for the remaining four benzyl groups at C(100)–C(400)). The carbon atoms of the Al₈C₅ cluster appear in a quite unusual range in the ¹³C NMR spectrum at δ 23.9 (C(500)) and δ 31.3 (C(100)–C(400)). In contrast, the CH₂ hydrogen and carbon atoms of the terminally attached ethyl groups show quite normal shifts of δ 0.3 and 2.3 on average in the ¹H and ¹³C NMR spectra,

respectively. A Raman spectrum was recorded of the methyl cluster **1**, which is isostructural with **4**, to reduce the number of emissions and to allow a sure assignment of cluster vibrations. The most intense emission of the cluster (symmetric breathing mode) was detected in the expected range at 325 cm⁻¹. Further modes, which may be assigned to cluster vibrations, were observed at 305, 292, 212, 195, and 129 cm⁻¹. The Al–C stretching vibration of the terminal Al–C bonds to the methyl groups occurred at 628 cm⁻¹.

Synthesis of Compound 5. The carbaalane **1** cited above⁵ was obtained by the reaction between dimethyl(phenylethynyl)aluminum and an excess of dimethylaluminum hydride (molar ratio 1:5.3, vs 1:2.2 required by stoichiometry) in the absence of solvent at 80 °C for 48 h. It was isolated as a colorless solid in about 60% yield. Further products were detected in the mother liquor by ¹H NMR spectroscopy, but none of these could be isolated in pure form by recrystallization. By systematically changing the reaction conditions and the molar ratio of the starting compounds, we tried to enrich and isolate further components of the reaction mixture. The red crystalline compound **5** finally was isolated as the only further product of this reaction, when we treated dimethyl(phenylethynyl)aluminum with Me₂AlH in a 1:2 molar ratio under less drastic reaction conditions (60 °C, 24 h, eq 2).



As was shown by a crystal structure determination, **5** has a structure quite similar to that of the carbaalanes **1** and **4** with a bridged cube of eight Al atoms, but the hydrido bridge of **1** and **4** is replaced by a phenylethynyl ligand (Figure 2). The structural parameters of the cluster are almost indistinguishable from those of compound **4** discussed above and need only a short discussion. Two different ranges of Al–Al distances are observed (2.829 and 2.609 Å on average). The longer ones belong to that face which is bridged by the phenylethynyl ligand. The Al–C distances in the Al₈C₅ skeleton of the cluster are longer than the terminal Al–C bonds (1.948 Å), and values between 2.009(7) and 2.150(6) Å were determined. The Al–C distances to the carbon atom of the phenylethynyl group (C(41)) are different, as observed before with the bridging hydrogen atom; two short distances (2.174 Å) are found between the opposite Al atoms Al(3) and Al(8), while longer ones (2.411 Å) are observed to Al(4) and Al(7). Thus, the bridged face of the cube is distorted in all cases to give a diamond-shaped parallelogram. The C≡C triple bond is lengthened (1.241(8) Å) compared to the standard C≡C bond length of 1.20 Å.¹³ In

(11) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1.

(12) (a) Bicerano, J.; Marynick, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1978**, *17*, 3443. (b) Gielen, M. *Polyhedron* **1988**, *7*, 363. (c) Schleyer, P. v. R.; Najafian, K.; Mebel, A. M. *Inorg. Chem.* **1998**, *37*, 6765.

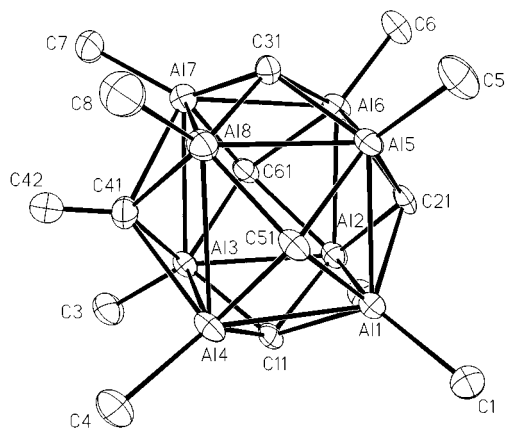


Figure 2. Molecular structure of **5**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å): Al(3)–Al(4) = 2.779(3), Al(4)–Al(8) = 2.839(3), Al(3)–Al(7) = 2.849(3), Al(7)–Al(8) = 2.849(3), Al(3)–Al(2) = 2.602(2), Al(4)–Al(1) = 2.606(2), Al(7)–Al(6) = 2.594(3), Al(8)–Al(5) = 2.582(3), Al(1)–Al(2) = 2.642(3), Al(2)–Al(6) = 2.622(3), Al(6)–Al(5) = 2.607(3), Al(1)–Al(5) = 2.618(3), C(11)–Al(1) = 2.087(5), C(11)–Al(2) = 2.136(6), C(11)–Al(3) = 2.026(6), C(11)–Al(4) = 2.016(6), C(21)–Al(1) = 2.075(6), C(21)–Al(2) = 2.045(6), C(21)–Al(5) = 2.033(6), C(21)–Al(6) = 2.070(6), C(31)–Al(5) = 2.080(6), C(31)–Al(6) = 2.137(6), C(31)–Al(7) = 2.011(6), C(31)–Al(8) = 2.036(6), C(51)–Al(1) = 2.147(7), C(51)–Al(4) = 2.021(5), C(51)–Al(5) = 2.106(5), C(51)–Al(8) = 2.048(7), C(61)–Al(2) = 2.150(6), C(61)–Al(3) = 2.053(5), C(61)–Al(6) = 2.100(5), C(61)–Al(7) = 2.009(7), C(41)–Al(3) = 2.166(7), C(41)–Al(4) = 2.378(7), C(41)–Al(7) = 2.444(6), C(41)–Al(8) = 2.182(6), C(41)–C(42) = 1.241(8).

accordance with this observation, the C≡C stretching vibration is shifted to an unusually low value¹⁴ of 1957 cm⁻¹. Similar absorptions were observed in ionic acetylides such as KC≡CH¹⁵ or in some compounds in which the ethynyl groups bridge two or more transition-metal atoms.¹⁶ The CH₂ protons of the benzyl groups gave singlets in the ¹H NMR spectrum at δ 3.24 (at C(11), C(31), C(51), and C(61)) and 3.52 (at C(21)), similar to those discussed in the case of **4** above. The carbon atoms of the Al₈C₅ skeleton were observed in the ¹³C NMR spectrum of **5** with chemical shifts of δ 20.9 (C(21)) and δ 35.1 (C(11), C(31), C(51), C(61)). The ethynyl carbon atoms have resonances of δ 89.5 (C(41)) and δ 117.0 (C(42)).

Synthesis of the First Carbaalane with Exclusively Aliphatic Substituents. Up to now, only (phenylethynyl)aluminum compounds were used as starting materials for the synthesis of carbaalanes. To investigate the chemical and spectroscopic properties of such compounds more systematically, we were interested in synthesizing aliphatic derivatives bearing small substituents on the carbon atoms as well as on the Al atoms. With propyne, *n*-butyllithium, and dimethylaluminum bromide as starting materials, Me₂AlC≡CCH₃

(13) March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985.

(14) Weidlein, J.; Müller, U.; Dehnicke, K. *Vibration Frequencies I*; Thieme Verlag: Stuttgart, Germany, 1981.

(15) Nast, R.; Gremm, J. *Z. Anorg. Allg. Chem.* **1963**, *325*, 62.

(16) Osakada, K.; Takizawa, T.; Yamamoto, T. *Organometallics* **1995**, *14*, 3531.

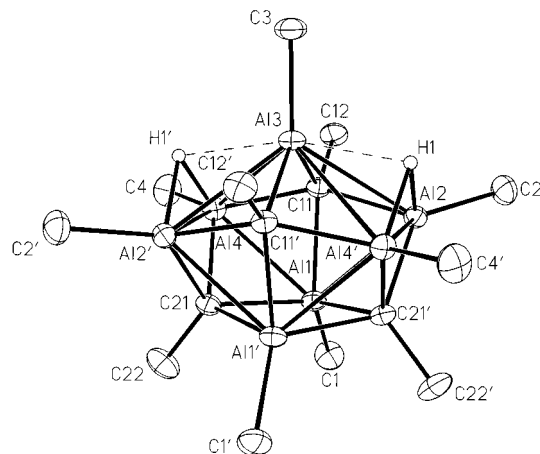
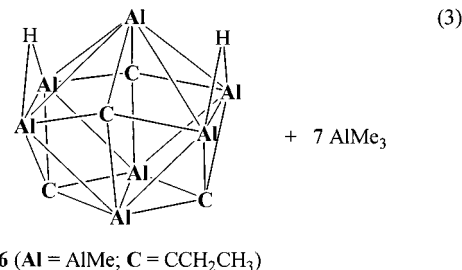
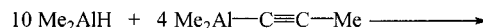


Figure 3. Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Methyl groups are omitted for clarity. Important bond lengths (Å): Al(1)–Al(1') = 2.576(1), Al(1)–Al(2) = 2.5739(8), Al(1)–Al(4) = 2.5693(8), Al(2)–Al(4') = 2.6228(9), Al(3)–Al(2) = 2.8160(7), Al(3)–Al(4) = 2.8026(7), C(11)–Al(1) = 2.143(2), C(11)–Al(2) = 2.025(2), C(11)–Al(3) = 2.055(2), C(11)–Al(4) = 2.025(2), C(21)–Al(1) = 2.099(2), C(21')–Al(1) = 2.064(2), C(21')–Al(2) = 2.042(2), C(21)–Al(4) = 2.039(2) (equivalent atoms generated by $-x, y, -z + 1/2$).

was obtained in high yield. The latter was treated with dimethylaluminum hydride (eq 3). An exothermic reac-



tion was observed at room temperature, and in contrast to the phenylethynyl derivatives described before, no heating was required for the completion of the reaction. Two products were obtained, one of which crystallized from a very dilute solution in toluene in 29% yield. Its ¹H NMR spectrum showed two resonances of equal intensity for the methyl groups attached to aluminum and two triplets and quartets for the ethyl groups in 4:1 ratios. A bridging hydrogen atom was observed at δ 5.69. Thus, we suppose that an *arachno* type compound, (AlMe)₈(CCH₂CH₃)₅H, similar to **1** and **4** has been formed. Further characterization has failed up to now, because attempted purification of this product by recrystallization has to date been unsuccessful.

The main product of the reaction, (AlMe)₇(CCH₂CH₃)₄H₂ (**6**), was isolated after recrystallization from cyclopentane in 63% yield. Its molecular structure in the solid state with an Al₇C₄ cluster similar to compound **3** is depicted in Figure 3. A four-membered Al₂C₂ heterocycle on the base is bridged by a boat-shaped six-membered Al₄C₂ heterocycle, which is capped by the

seventh Al atom (Al(3)). Two hydrogen atoms are in an *exo* position and bridge two opposite Al–Al edges (Al(2)–Al(4')) but are directed toward the Al atom Al(3) at the top of the cluster. The Al(3)–H(1) distances (2.14(2) Å) are longer than the Al(2)–H(1) or Al(4')–H(1) distances (1.76(2) and 1.83(2) Å, respectively) and indicate a weaker bonding interaction to Al(3). Thus, the situation may be described as a semibridging of a triangular Al₃ face. The 11-atom cluster in the molecular center has 12 electron pairs, and a *closo* configuration may be derived according to the Wade rules.¹¹ Indeed, there is a remarkable analogy between the structure of **6** and that of the *closo* borate [B₁₁H₁₁]²⁻,⁷ in particular owing to the boat-shaped six-membered ring bridged by a high-connectivity atom. The bond lengths are similar to those observed before for other carbaalanes, and the Al–C distances in the cluster (2.025(2)–2.143(2) Å) are longer than those to the terminally coordinated methyl groups (1.949 Å on average). The Al–Al separations differ markedly. Similar to [B₁₁H₁₁]²⁻, very long ones are observed to the Al atom at the top of the cluster (2.809 Å), while the remaining Al···Al distances (2.593 Å) are in the normal range of Al–C–Al or Al–H–Al three-center bonding interactions (see above). The longest Al–Al distances in that range (2.6228(9) Å) are found in the hydrogen-bridged edges of the cluster. They are quite similar to those in Me₂Al(μ-H)₂AlMe₂ in the gas phase.¹⁷

The results of the NMR spectroscopic characterization are in complete agreement with the crystal structure. The carbon atoms of the terminally attached methyl groups were observed in the ¹³C NMR spectrum at δ –8.5 (Al(1)), –15.0 (Al(2), Al(4)) and –20.2 (Al(3)), while those of the cluster are shifted to low field (δ 15.4 of C(11) and δ 26.1 of C(21)). A Raman spectrum of **6** verified the assignment given above for the *arachno* cluster of **1**. The symmetric breathing mode of the cluster was observed at 327 cm⁻¹ as a very intense emission. Further vibrations of the cluster are observed at 300, 271, 235, 214, and 129 cm⁻¹. Thus, the size, the structure and the substituents of the clusters seem to have only a minor influence on the vibrations observed in the Raman spectra.

Quantum Chemical Calculations. We performed quantum chemical calculations in order to study the compounds Al₈H₈(CH)₅H and Al₈H₈(CH)₅C≡CH as model systems of the real carbaalane clusters **4** and **5**. In all our calculations we used Becke's three-parameter hybrid exchange function (B3)¹⁸ together with the correlation function of Lee, Yang, and Parr (LYP)¹⁹ with a standard 6-31+G(d) basis as imple-

Table 1. Theoretical and Experimental Values of Selected Structural Parameters of the Carbaalanes **4 and **5****

	distance (Å)	
	Al ₈ Et ₈ (CCH ₂ -C ₆ H ₅) ₅ H (4) ^a	Al ₈ H ₈ (CH) ₅ H ^b
Al–H(hydrido)	1.87–2.29	2.10
Al–Al	2.585–2.858	2.618–2.817
Al–C(cluster)	2.009–2.156	2.008–2.126

	distance (Å)	
	Al ₈ Me ₈ (CH ₂ C ₆ H ₅) ₅ -C≡CC ₆ H ₅ (5) ^a	Al ₈ H ₈ (CH) ₅ (–C≡CH) ^b
Al–C(ethynyl)	2.166–2.444	2.38
Al–Al	2.582–2.849	2.610–2.889
Al–C (cluster)	2.009–2.150	2.011–2.126

^a From experimental crystal data. ^b From B3LYP/6-31+G(d) calculations.

mented in the GAUSSIAN 98 package of programs.²⁰ To our knowledge, there are no quantum chemical studies on carbaalane clusters of this size in the literature. Thus, in a first step, we checked the ability of the B3LYP/6-31+G(d) theoretical model to reproduce the main geometrical features of the real carbaalane clusters. We started all our geometry optimizations with a distorted (C_{2v} symmetry) Al₈H₈(CH)₅R (R = H, C≡CH) structure. The stationary points were characterized as minima on the energy hypersurface by analytical frequency calculations.²¹

(a) Geometry and Spectroscopic Data. The B3LYP/6-31+G(d) optimized geometries of our model systems show four identical Al–R (R = hydrido or ethynyl) distances (see Table 1). The computed values of the Al–R distances are 2.10 Å (R = –H) and 2.38 Å (R = –C≡CH), respectively. They are just between the measured Al–R distances in the real carbaalane clusters. The slight distortion of the Al₈ cube of the real structure may be due to crystal packing effects, because we could not localize a stationary point with symmetry lower than C_{4v} on the B3LYP/6-31+G(d) hypersurface. Our computations reproduce the difference between the experimental average Al–Al distances of the hydrido (or ethynyl)-bridged face and the Al–Al distances of the carbon-bridged faces, as well as the different Al–C distances of the carbon-bridged faces (Table 1).

As a further check of our theoretical model, we calculated the harmonic cluster vibrations and compared these theoretical results with the experimental Raman and IR data. We computed the stretching vibration of the C≡C triple bond in the ethynyl group of **5** at 1957 cm⁻¹ (experimental value 1956 cm⁻¹) without any scaling. Of course, such a perfect conformity of experiment and theory is mainly due to error cancellation (harmonic approximation, incomplete basis set, etc.). Nevertheless, the experimental as well as the theoretical data indicate an unusually weak C≡C triple bond in the ethynyl group of cluster **5**. In a further step, we computed the Raman intensities of the cluster vibrations in **1** or **4**. Analyzing the calculated normal mode of the most intense Raman emission (414 cm⁻¹,

(17) Almendingen, A.; Anderson, G. A.; Forgaard, F. R.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 2315.

(18) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.7; Gaussian, Inc.: Pittsburgh, PA, 1998.

(19) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(20) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(21) The Al₈H₈(CH)₅C≡CH cluster has a small negative eigenvalue corresponding to a high flexibility of the ethynyl group at this level of theory. Nevertheless, this negative eigenvalue should disappear in a more "real" model system such as Al₈H₈(CH)₅(–C≡CH).

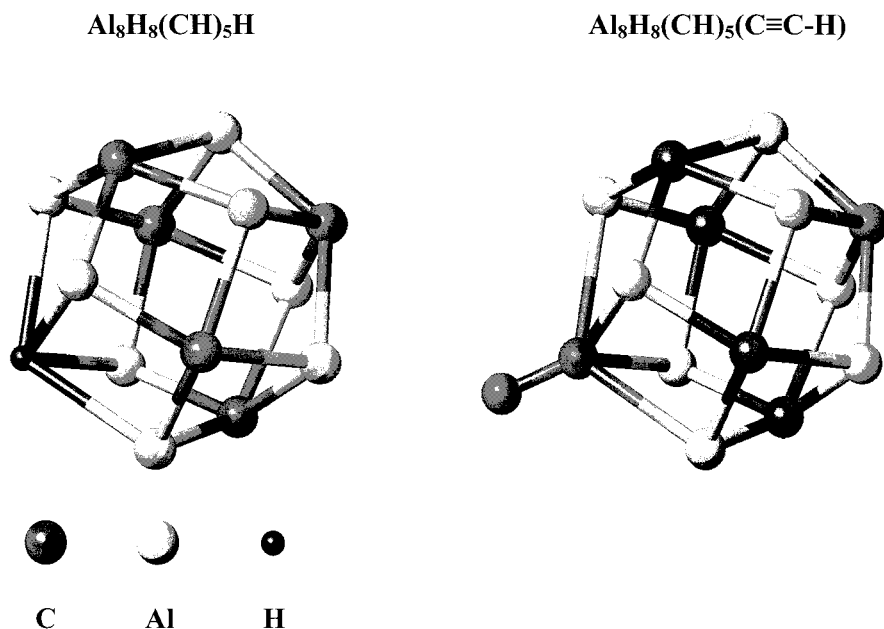


Figure 4. Bond paths of the multicenter bond in the carbaalane model systems calculated by using the B3LYP/6-31+G* densities. Each tube represents the existence of a bond critical point (BCP). The terminal hydrogen atoms are omitted.

no scaling), we assigned this vibration to the totally symmetric “breathing” mode (experimental 325 cm^{-1}). We also computed the chemical shift of the hydrido bridge in $\text{Al}_8\text{H}_8(\text{CH})_5\text{H}$ at the GIAO/B3LYP 6-31+G* level of theory. The computed value of δ 6.4, using TMS as reference, indicates a strongly deshielded bridging hydrogen atom, which is in line with the measured unusually low field shift (δ 5.2). Keeping the simplifications and approximations of our model calculations in mind, the quality of the B3LYP/6-31+G(d) wave function should be good enough to allow an analysis of the electronic structure of the carbaalanes.

(b) Electronic Structure. The topological analysis of the charge distribution proved to produce a precise picture of the bonding situation in a wide range of carbaboranes.²² We used Bader’s atoms in molecules approach,²³ to study the electronic structure in our carbaalane model compounds $\text{Al}_8\text{H}_8(\text{CH})_5\text{R}$ ($\text{R} = \text{H}, \text{C}\equiv\text{CH}$). Figure 4 shows the main features of our topological analysis of the computed (B3LYP/6-31+G(d)) charge density $\rho(\mathbf{r})$ (terminal hydrogen atoms are omitted). The tubes, connecting two atoms, represent the existence of a bond critical point (BCP) between this pair of atoms. Each carbon atom is connected to one hydrogen atom and four aluminum atoms via bond paths. Each aluminum atom is connected to one hydrogen atom and three carbon atoms. The bridging hydrogen atom is connected to four aluminum atoms by bond critical points. Note that there is no bond critical point between any two aluminum atoms of the Al_8 cube, which is in line with a averaged Wiberg bond index (WBI) of 0.08 between the aluminum atoms.²⁴

For comparison, we also studied the electronic structure of the boron cluster $\text{B}_8\text{H}_8(\text{CH})_5\text{H}$.²⁵ The C_{4v} symmetric $\text{B}_8\text{H}_8(\text{CH})_5\text{H}$ geometry represents a third-order

Table 2. Comparison of the Electronic Structures (B3LYP/6-31+G* Geometry) between $\text{Al}_8\text{H}_8(\text{CH})_5\text{H}$ and $\text{B}_8\text{H}_8(\text{CH})_5\text{H}$ (C_{4v} Symmetry)

	X = B	X = Al
distance $r_{\text{X}-\text{X}}$, Å ^a	2.000–2.177	2.618–2.817
BCP $_{\text{X}-\text{X}}$ ^b	no	no
WBI $_{\text{X}-\text{X}}$ ^c	0.125–0.178	0.077–0.082
WBI $_{\text{X}-\text{H}}$ ^c	0.231	0.192
WBI $_{\text{X}-\text{C}}$ ^c	0.568–0.651	0.412–4.706

^a X = B/Al. ^b Existence of bond critical points. ^c Wiberg bond index.

saddle point on the B3LYP/6-31+G energy hypersurface (three imaginary frequencies). In contrast to the C_{4v} symmetric $\text{Al}_8\text{H}_8(\text{CH})_5\text{H}$ cluster, the global minimum structure for $\text{B}_8\text{H}_8(\text{CH})_5\text{H}$, has C_s symmetry. The hydrogen “cap” is bridging only two boron atoms. Although the global minimum structure for $\text{B}_8\text{H}_8(\text{CH})_5\text{H}$ is around 20 kcal/mol lower in energy, we did our analysis of the wave function according to the C_{4v} symmetric saddle point for a fair comparison with the $\text{Al}_8\text{H}_8(\text{CH})_5\text{H}$ minimum structure. Following Bader’s atoms in molecules approach, the topology of the charge density shows the same features as the $\text{Al}_8(\text{CH})_5\text{H}$ cluster: there is no bond critical point between any two boron atoms even if the calculated Wiberg index points to a stronger interaction due to the smaller interatomic distance (see Table 2).

Experimental Section

All procedures were carried out under purified argon. *n*-Pentane and cyclopentane were dried over LiAlH_4 ; toluene was dried over Na/benzophenone. Dimethylaluminum hydride,²⁶ dimethyl(phenylethynyl)aluminum,⁵ diethylaluminum

(22) Bader, R. F. W.; Legare, D. A. *Can. J. Chem.* **1992**, *70*, 657.

(23) Bader, R. F. W. *Atoms in Molecules: A Quantum Theory*; Clarendon Press: Oxford, U.K., 1990.

(24) Wiberg, K. B. *Tetrahedron* **1968**, *24*, 1083.

(25) For a recent discussion of the bonding in carbaboranes, see: Casanova, J., Ed. *The Borane, Carborane, Carbocation Continuum*; Wiley: New York, 1998.

(26) Lehmkuhl, H.; Ziegler, K. In *Methods of Organic Chemistry (Houben-Weyl)*, 4th ed.; Thieme Verlag: Stuttgart, 1970; Vol. XIII/4; pp 58–59.

hydride,²⁶ dimethylaluminum bromide,²⁶ and the carbaalane **2**⁶ were synthesized according to literature procedures. Commercially available *n*-butyllithium (Chemetall) was used without further purification; propyne (Lancaster) was dried over P₄O₁₀ prior to use. NMR spectra were recorded on a 500 MHz NMR spectrometer at 300 K. The resonances were assigned on the basis of ¹H, ¹³C, H–H-COSY, HMQC, and HMBC spectra; shifts are reported on the δ scale relative to residual nondeuterated solvent signals as internal standard.

Synthesis of the Carbaalane (AlEt)₂(CCH₂C₆H₅)₃H (4). The orange-red cluster compound **2** (0.279 g, 0.308 mmol) was treated with a large excess of diethylaluminum hydride (2 mL, 1.62 g, 18.8 mmol) in the absence of solvent. The mixture was heated at 60 °C for 18 h. The color changed to yellow, and a colorless solid precipitated. All volatile components (excess hydride, triethylaluminum) were distilled off, and the residue was recrystallized from *n*-pentane (20/–30 °C). Yield: 0.206 g (69%), air-sensitive solid. Dec pt (argon, sealed capillary): 124 °C. Anal. Calcd for C₅₆H₇₆Al₈ (965.07): Al, 22.4. Found: Al, 22.0. Molar mass (cryoscopically in benzene): 930. ¹H NMR (C₆D₆, 500 MHz; δ): benzyl group at C(500), 7.63 (2 H, m, *o*-H), 7.36 (2 H, m, *m*-H), 7.22 (1 H, m, *p*-H), 3.84 (2 H, s, CH₂); benzyl groups at C(100)–C(400), 7.28 (8 H, m, *o*-H), 7.21 (8 H, m, *m*-H), 7.09 (4 H, m, *p*-H), 3.39 (8 H, s, CH₂); ethyl groups at Al(1)–Al(4), 1.10 (12 H, t, ³J_{HH} = 8.1 Hz, CH₃), 0.10 (8 H, q, ³J_{HH} = 8.1 Hz, CH₂); ethyl groups at Al(5)–Al(8), 1.36 (12 H, t, ³J_{HH} = 8.1 Hz, CH₃), 0.51 (8 H, q, ³J_{HH} = 8.1 Hz, CH₂); 5.28 (1 H, s, AlH), ¹³C NMR (C₆D₆, 125.8 MHz; δ): benzyl group at C(500), 148.0 (*i*-C), 129.3 (*o*-C), 129.0 (*m*-C), 126.4 (*p*-C), 35.5 (CH₂); benzyl groups at C(100)–C(400), 147.9 (*i*-C), 129.8 (*o*-C), 128.4 (*m*-C, covered by solvent), 126.7 (*p*-C), 34.7 (CH₂); ethyl groups at Al(1)–Al(4), 10.5 (CH₃), 1.9 (CH₂); ethyl groups at Al(5)–Al(8), 10.4 (CH₃), 2.7 (CH₂); 31.3 (C(100)–C(400)), 23.9 (C(500)). IR (CsBr plates, paraffin; cm⁻¹): 1940 vw, 1867 vw, 1824 vw, 1769 vw, 1597 m phenyl; 1463 vs, 1403 m, 1377 vs paraffin; 1295 m (ν (AlH)(?)); 1226 w, 1189 vw, 1171 w, 1153 w, 1074 w, 1048 vw, 1030 w, 991 m, 959 s, 900 m, 822 m (ν (CC), δ (CH₃), δ (CH₂)); 747 vs, 701 vs, 673 vs, 641 s, 617 s, 594 s, 560 m, 502 m (δ (CC), δ (phenyl), ν (AlC)); 451 vw, 428 w, 414 w, 355 w (ν (AlC)). UV/vis (*n*-hexane; λ_{\max} , nm (log ϵ): 250 (3.9).

Raman Spectrum of the Carbaalane (AlMe)₂(CCH₂C₆H₅)₃H (1). Single crystals, excitation 647.1 nm, cm⁻¹: 1599 s, 1580 w (ν (CC) phenyl); 1491 vw, 1452 w, 1444 w, 1424 vw (δ (CH₂), δ (CH₃)); 1331 vw, 1300 w, 1206 w (δ (CH) benzyl); 1203 w (δ (s)(CH₃(Al))); 1186 w, 1181 w (δ (CH) benzyl); 1158 vw, 1152 vw (δ (CH₂) benzyl); 1029 (ν (CH₂) phenyl); 1002 s, 988 vw, 963 vw, 952 vw (ν (CC) phenyl); 931 vw, 908 vw, 883 w (δ , γ (CH) benzyl); 822 m; 749 vw (ρ (CH₂), γ (CH) benzyl); 710 vw (ρ (CH₃–(Al))); 686 w, 673 vw, 660 vw (δ , γ (CC) phenyl); 628 w (ν (AlC)); 620 m, 582 vw, 551 m, 525 w, 515 w (δ (CC) phenyl); 442 vw, 428 w, 369 vw, 345 w (γ (CC) phenyl); 325 s, 305 m, 292 m (ν (breathing) cluster); 246 vw, 234 vw; 212 w, 195 w, 129 m (δ (cluster)).

Synthesis of the Carbaalane (AlMe)₂(CCH₂C₆H₅)₃(C≡CC₆H₅) (5). Dimethyl(phenylethynyl)aluminum (0.472 g, 2.99 mmol) was treated with 0.346 g (5.97 mmol) of dimethylaluminum hydride. The mixture was heated at 60 °C for 24 h. All volatile components were removed under vacuum. The residue was recrystallized from toluene (20/–50 °C). Yield: 0.189 g (40%), moderately air-stable red solid. Dec pt (argon, sealed capillary): 204 °C. Anal. Calcd for C₅₆H₆₄Al₈ (952.98): Al, 22.7. Found: Al, 22.4. ¹H NMR (C₆D₆, 500 MHz; δ): benzyl group at C(21), 7.50 (2 H, m, *o*-H), 7.36 (2 H, m, *m*-H), 7.22 (1 H, m, *p*-H), 3.52 (2 H, s, CH₂); benzyl groups at C(11), C(31), C(51), and C(61), 7.26 (8 H, m, *o*-H), 7.21 (8 H, m, *m*-H), 7.09 (4 H, m, *p*-H), 3.24 (8 H, s, CH₂); phenylethynyl group, 7.34 (2 H, m, *o*-H), 6.65 (2 H, m, *m*-H), 6.77 (1 H, m, *p*-H); methyl groups at Al(1), Al(2), Al(5), and Al(6), –0.33 (12 H, s); methyl groups at Al(3), Al(4), Al(7), and Al(8), –0.48 (12 H, s). ¹³C NMR (C₆D₆, 125.8 MHz; δ): benzyl group at C(21), 148.5 (*i*-

C), 129.34 (*o*-C), 129.30 (*m*-C), 126.0 (*p*-C), 36.0 (CH₂); benzyl groups at C(11), C(31), C(51), and C(61): 147.5 (*i*-C), 129.5 (*o*-C), 128.8 (*m*-C), 126.3 (*p*-C), 36.2 (CH₂); phenylethynyl group, 165.9 (*i*-C), 132.9 (*o*-C), 129.3 (*m*-C), 134.0 (*p*-C), 117.0 (C(42)), 89.5 (C(41)); methyl groups at Al(1), Al(2), Al(5), and Al(6), –10.9; methyl groups at Al(3), Al(4), Al(7), and Al(8): –8.1; cluster carbon atoms, 35.1 (C(11), C(31), C(51), C(61)), 20.9 (C(21)). IR (CsBr plates, paraffin; cm⁻¹): 1977 w, 1957 m (ν (C≡C)); 1865 vw, 1799 vw, 1597 m, 1590 m, 1580 w phenyl; 1489 m; 1456 vs, 1377 vs paraffin; 1301 m, 1184 s, 1092 vw, 1072 w, 1028 w, 978 m, 953 vs, 923 m, 905 s, 820 s (ν (CC), δ (CH₃), δ (CH₂)); 750 vs, 706 vs, 688 vs, 659 vs, 580 s, 568 s, 552 s, 533 m, 513 m (δ (CC), δ (phenyl), ν (AlC)); 447 w, 422 m, 337 w, 291 w (ν (AlC)). UV/vis (*n*-hexane; λ_{\max} , nm (log ϵ): 250 (3.8), 380 (sh, 3.3).

Synthesis of Me₂AlC≡CMe. A mixture of 15 mL of a solution of *n*-butyllithium in *n*-hexane (1.6 M, 24.0 mmol) and 20 mL of *n*-pentane was cooled to –70 °C. Dried (P₄O₁₀) gaseous propyne was passed over the stirred solution for 30 min, and the precipitation of a solid showed the beginning of the reaction. The suspension was warmed to room temperature and stirred until the evolution of gas (excess of propyne, butane) stopped. A solution of dimethylaluminum bromide (3.00 g, 21.9 mmol) in 20 mL of *n*-pentane was added at room temperature. The mixture was stirred for 3 h and filtered. Colorless and very air-sensitive crystals of the product were isolated after concentration of the solution to about 10 mL and cooling to –50 °C. Yield: 1.957 g (93%). Mp (argon, sealed capillary): 48 °C. Anal. Calcd for C₅H₉Al (96.1): Al, 0.28. Found: Al, 0.27. ¹H NMR (C₆D₆, 300 MHz; δ): 1.12 (3 H, s, C–CH₃), –0.15 (6 H, s, Al–CH₃). ¹³C NMR (C₆D₆, 75.5 MHz; δ): 133.4 (ethynyl), the second resonance was not observed, 5.2 (C–CH₃), –7.8 (br, Al–CH₃). IR (CsBr plates, paraffin; cm⁻¹): 2152 vw, 2109 vs (ν (C≡C)); 1948 w, 1867 w, 1762 w; 1456 vs, 1377 vs (paraffin); 1305 m, 1249 w, 1190 vs, 1012 m, 974 vs, 903 m (ν (CC), δ (CH₃)); 696 vs, br, 571 s (δ (CC), δ (CH₃), ν (AlC)); 472 m, 393 s, 343 vs (ν (AlC)).

Synthesis of the Carbaalane (AlMe)₂(CCH₂CH₃)₄H₂ (6). Dimethylpropynylaluminum (0.604 g, 6.29 mmol) was dissolved in 2.3 g (39.7 mmol) of dimethylaluminum hydride, and the mixture was stirred at room temperature for 2 h. A colorless product precipitated. All volatile components were removed under vacuum. The residue was dissolved in 40 mL of toluene and cooled to –30 °C. An amorphous and highly pyrophoric solid was isolated in a yield of 0.201 g (29%), which probably contains the *arachno* cluster (AlMe)₈(CCH₂CH₃)₅H. The mother liquor was evaporated, the residue was dissolved in 10 mL of cyclopentane, and this solution was cooled to –30 °C to obtain colorless, pyrophoric crystals of **6**. Yield: 0.455 g (63%). Dec pt (argon, sealed capillary): 274 °C. Anal. Calcd for C₁₉H₄₃Al₇ (460.42): Al, 41.0. Found: Al, 40.8. Molar mass (cryoscopically in benzene): 490. ¹H NMR (C₆D₆, 500 MHz; δ): ethyl groups at C(11) and C(11'), 2.01 (4 H, q, ³J_{HH} = 7.3 Hz, CH₂), 1.03 (6 H, t, ³J_{HH} = 7.3 Hz, CH₃); ethyl groups at C(21) and C(21'), 1.99 (4 H, q, ³J_{HH} = 7.3 Hz, CH₂), 1.12 (6 H, t, ³J_{HH} = 7.3 Hz, CH₃); methyl groups, –0.10 (6 H, s, Al(1) and Al(1')), –0.24 (12 H, s, Al(2), Al(2'), Al(4), and Al(4')), –0.40 (3 H, s, Al(3)); 4.91 (2 H, s, AlH), ¹³C NMR (C₆D₆, 125.8 MHz; δ): ethyl groups at C(11) and C(11'), 23.6 (CH₂), 23.5 (CH₃); ethyl groups at C(21) and C(21'), 21.6 (CH₂), 23.7 (CH₃); cluster carbon atoms, 15.4 (C(11) and C(11')), 26.1 (C(21) and C(21')); methyl groups, –8.5 (C(1), C(1')), –15.0 (C(2), C(2'), C(4), and C(4')), –20.2 (Al(3)). IR (CsBr plates, paraffin; cm⁻¹): 1321 s, 1310 s, 1277 m, 1260 m, 1207 sh br (ν (AlH)(?)), 1189 vs, 1134 s br (ν (AlH)(?)), 1092 s, 1067 s, 1046 s, 1018 s, 897 s, 878 vs, 848 s br (δ (AlH)(?)), 794 vs (ν (CC), δ (CH₃), δ (CH₂)); 719 vs, 683 vs, 659 vs br (δ (CC), ν (AlC)); 462 m, 427 m, 409 m, 391 m, 363 m, 337 m (ν (AlC)). Raman spectrum (single crystals, excitation 647.1 nm; cm⁻¹): 1472 w (ν (AlHAl)(?)); 1444 m (δ_{as} –(CH₃(Al))); 1372 (δ (CH₂)); 1191 s, 1181 m (δ_{s} (CH₃)); 1067 w, 1054 m, 1019 m (δ (CH₃), ν (CC)); 897 vw, 881 vw (δ , ρ (CH₂));

Table 3. Crystal Data, Data Collection Parameters, and Structure Refinement for the Compounds 4·(*n*-pentane), 5·(cyclopentane), and 6

	4·(<i>n</i> -pentane)	5·(cyclopentane)	6
formula	C ₆₁ H ₈₈ Al ₈	C ₆₁ H ₇₄ Al ₈	C ₁₉ H ₄₃ Al ₇
cryst syst	monoclinic	triclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i> (No. 14) ²⁷	<i>P</i> 1̄ (No. 2) ²⁷	<i>C</i> 2/ <i>c</i> (No. 15) ²⁷
<i>Z</i>	4	2	4
temp, K	193	193	193
<i>D</i> _{calcd.} , g/cm ³	1.143	1.188	1.117
<i>a</i> , Å	21.2859(14)	10.6473(7)	11.5003(7)
<i>b</i> , Å	11.0000(4)	14.4128(11)	14.4577(8)
<i>c</i> , Å	26.4323(16)	20.1533(15)	16.4668(12)
α, deg	90	77.204(8)	90
β, deg	103.056(7)	86.352(8)	90.312(8)
γ, deg	90	71.565(8)	90
<i>V</i> , 10 ⁻³⁰ m ³	6029.0(6)	2861.0(4)	2737.9(3)
μ, mm ⁻¹	0.172	0.180	0.270
cryst dimens, mm	0.75 × 0.31 × 0.08	0.48 × 0.3 × 0.07	1.1 × 0.65 × 0.13
radiation		Mo Kα; graphite monochromator	
2θ range, deg	4 ≤ 2θ ≤ 52	4 ≤ 2θ ≤ 52	4.5 ≤ 2θ ≤ 52
index ranges	-26 ≤ <i>h</i> ≤ 26 -12 ≤ <i>k</i> ≤ 12 -32 ≤ <i>l</i> ≤ 30	-13 ≤ <i>h</i> ≤ 13 -17 ≤ <i>k</i> ≤ 17 -24 ≤ <i>l</i> ≤ 24	-12 ≤ <i>h</i> ≤ 12 -17 ≤ <i>k</i> ≤ 17 -20 ≤ <i>l</i> ≤ 20
exposures; Δφ, deg	206; 0.9	258; 1.2	136; 1.4
no. of unique rflns	11 187	10 452	2514
no. of params	593	605	129
R1 (rflns <i>I</i> > 2σ(<i>I</i>))	0.0545 (4687)	0.0715 (3769)	0.0368 (2012)
wR2 (all data)	0.1648	0.2258	0.1202
max/min resid electron density, 10 ³⁰ e/m ³	0.593/-0.613	0.507/-0.551	0.753/-0.338

697 w, 672 vw, 645 w (δ(CC), ρ(CH₂), ρ(CH₃); 632 w (ν(AlCH₃)); 588 vw, 564 vw (δ(CC)); 336 sh, 327 vs, 300 w (ν(pulsation) cluster); 271 m, 235 m, 214 s, 159 vw, 129 m, 116 m (δ(cluster)). UV/vis (*n*-hexane; λ_{max}, nm (log ε)): 240 (3.5).

Crystal Structure Determination. Single crystals of the compound 4·(*n*-pentane) were obtained from a saturated solution in *n*-pentane at 0 °C. Crystals of compound 5·(cyclopentane) came from a dilute solution in cyclopentane upon slow cooling to -22 °C. Crystals of 6 were obtained by very slow (4 weeks) concentration of a solution in *n*-pentane under vacuum at room temperature. The crystallographic data of all compounds were collected with a STOE imaging plate diffractometer. The structures were solved by direct methods and refined with the program SHELXL-93²⁸ by a full-matrix least-squares method based on *F*². The crystals of 4 include one molecule of *n*-pentane (disordered over two positions) and those of 5 one molecule of cyclopentane each formula unit. The

molecule of 6 is located on a crystallographic 2-fold rotation axis. Crystal data, data collection parameters, and structure refinement details are given in Table 3.

Acknowledgment. We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support. Further, we are very indebted to Prof. Dr. J. Weidlein (University of Stuttgart) for recording the Raman spectra of compounds 1 and 5.

Supporting Information Available: Tables of atomic coordinates, isotropic and anisotropic displacement parameters, and all bond lengths and angles. This material is available free of charge via the Internet at <http://pubs.acs.org>. Further details of the crystal structure determinations are available from the Cambridge Crystallographic Data Center on quoting the depository numbers CCDC-141817 (4), -141818 (5) and -141819 (6).

OM000244S

(27) Hahn, T. Ed. *International Tables for Crystallography, Space Group Symmetry*; Kluwer Academic: Dordrecht, Boston, London, 1989; Vol. A.

(28) Sheldrick, G. M. SHELXL-97: Program for the Refinement of Structures; Universität Göttingen, Göttingen, Germany, 1997.