# Aluminium Atoms at High Connectivity Sites in Polyhedral Polyborane Analogous Clusters: From Aluminaboranes to Carbaalanes

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**Keywords:** Carbaalanes / Cluster compounds / Electron deficiency / Aluminium / Boron

Cluster chemistry in the third main group has long been restricted to compounds of the lightest element boron. However, about 30 years ago the first compounds were synthesized and characterized in which single aluminium atoms adopted positions of high connectivity in polyhedral borane or carbaborane clusters. The next successful step in these efforts to establish a chemistry analogous to that of the polyboranes with the heavier elements of the third main-group was the synthesis of *closo*-dodecaaluminate $[Al_{12}iBu_{12}]^{2-}$ at the beginning of the nineties, which was the first homonuclear aluminium analogue of a polyborate anion and had a core exclusively formed by aluminium atoms. Another class of interesting new aluminium compounds was formed by the carbaalanes, which were synthesized and characterized for the first time only recently. They have clusters of aluminium and carbon atoms, and are similar to the carbaborane analogues in that their structures seem to be determined by the number of electron pairs in their molecular centers in accordance with the Wade rules.

## Introduction

Polyhedral compounds containing clusters of boron atoms have been well-known since the pioneering work of Alfred Stock at the beginning of this century.[1] Usually, the boron atoms in these clusters have a high connectivity[2] and are attached to up to six other boron atoms, as observed for a boron atom located above a boat-shaped six-membered ring in $[B_{11}H_{11}]^{2-}$.[3] Essentially, the configuration of these clusters is determined by the number of electron pairs delocalized in their molecular cores;[2][4] the addition of more electrons gives more open clusters. They can all be derived from the corresponding *closo* polyborate anions, in which the number of electron pairs exceeds the number of vertices by one. Two and three extra electron pairs are required for the electron count in *nido* or *arachno* compounds, respectively. The syntheses[5] of those polyborate anions or polyborane molecules often starts with diborane(6) ($B_2H_6$) or the borate anion $[BH_4]^-$, but in many cases the very sophisticated procedures yield the products in only poor yields. Nevertheless, these polyboron compounds form a class of well-characterized and highly interesting species with fascinating structures and bonding situations

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**MICROREVIEWS:** This feature introduces the readers to the authors' research through a concise overview of the selected topic. Reference to important work from others in the field is included.

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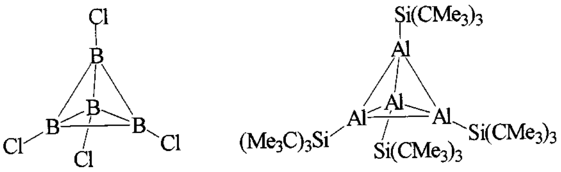
in their clusters, and were thoroughly investigated by conventional physical methods of structure determinations and quantum chemical calculations.[2]

Many years after the first synthesis of polyhedral polyboranes the carbaboranes were obtained as a new class of compounds; they have one or more boron atoms of the clusters replaced by carbon atoms. Often, they were synthesized by the reaction of polyboranes or some activated derivatives with alkynes,[2,5,6] but once again the yields are very low in most cases. The hydroboration of borylalkynes as a facile method for the synthesis of carbaboranes will be discussed in more detail later on. The structures and the bonding situation of these carbaboranes are quite similar to those of the pure boranes and this became clearer after the isolobality between the fragments $BH^-$ and CH was recognized in the Sixties.[2] Carbaboranes are now known in huge numbers with a large variety of different structures and of carbon to boron ratios. They have been used to synthesize many fascinating derivatives with elements of the main group or transition metals enclosed in their clusters,[5] of which, as an example, only the dicarbollide ligand[7] will be mentioned, which gives coordination compounds similar to cyclopentadienyl complexes.

In contrast to these well-established classes of polyhedral cluster compounds, no comparable chemistry has been developed with aluminium which is the next heavier homologue of boron in the third main group. Only a few compounds have been described in the literature, in which one aluminium atom occupies a vertex in a borane or carbaborane cluster or which has a skeleton of aluminium atoms similar to the *closo* borate anions. Both these classes of compounds will be described in the next sections in more detail. Carbaalanes, which have clusters exclusively formed by aluminium and carbon atoms, analogous to the carbaboranes, have been obtained and completely characterized for the first time only recently by our group, they will be discussed in the last section of this Microreview.

Tetrahedral and neutral cluster compounds such as the rare examples containing boron, $B_4Cl_4$[8] (Scheme 1) or $B_4(CMe_3)_4$,[9] will not be considered here as they do not fit in the classic scheme of ordering in borane or carbaborane chemistry. This type of clusters has found considerable interest in current organoaluminium chemistry and several remarkable compounds with tetrahedra of aluminium atoms such as $Al_4Cp^*_4$[10] (Cp* = pentamethylcyclopentadienyl), $Al_4[Si(CMe_3)_3]_4$[11] (Scheme 1), $Al_4[C(SiMe_3)_3]_4$,[12] or $Al_4[Si(SiMe_3)_3]_4$[13] have been reported in the literature. The cluster compound $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$ was synthesized starting with aluminium(I) chloride and has three polyhedral shells of Al atoms and will also not be considered here.[14] The rapidly growing and fascinating chemistry of monovalent aluminium as well as the similar chemistry of the heavier homologues gallium, indium and thallium has been reviewed several times before.[15–17] Furthermore, we will not discuss compounds derived from these $Al^I$ derivatives, which formally obey the Wade rules[4] for *closo* clusters like $Al_3Cp^*_3As_2$ with a trigonal bipyramidal $Al_3As_2$ cluster[18] and which, from quantum chemical calculations, have a delocalized electronic system in their molecular cores.

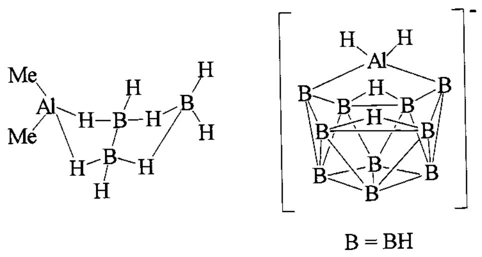


Scheme 1

## Aluminaboranes and Aluminacarbaboranes

Few compounds are known in which single aluminium atoms occupy the positions of boron atoms in polyboranes. The simplest one (**1**) is derived from tetraborane(10), in which one bridging $BH_2$ group is replaced by an $AlMe_2$ group (Scheme 2). This compound was synthesized in high yield by the reaction of $[B_3H_8]^-$ with dimethylaluminium chloride,[19][20] and its structure was confirmed by an electron diffraction experiment in the gas phase.[20][21] Its conformation is quite similar to that of tetraborane(10),[22] although the inner B−B bond is lengthened. The Al−B distance of the Al−H−B three center bonds was found to be 231.6 pm which, as expected, is much longer than the Al−B distances observed in the other cage compounds discussed here. Decaborane(14) gave the aluminapolyborate anion $[AlH_2B_{10}H_{12}]^-$ (**2**) upon treatment with trimethylamine alane or monochloroalane adducts $AlXH_2{\cdot}NMe_3$ (X = H, Cl).[23][24] The structure is derived from that of $B_{10}H_{14}$ with the aluminium atom bridging the boron atoms in the 2,6 position of the boron polyhedron (Scheme 2). Compound **2** was claimed in 1965 to be the first compound containing a direct Al−B bond. Aluminium boranate $Al(BH_4)_3$ was reported to react with diborane(6), pentaborane(9) or tetraborane(10) with the formation of three different polyhedral aluminaboranes, for which the compositions $AlB_4H_{11}$, $AlB_5H_{12}$, and, after a decomposition reaction, $AlB_6H_{13}$ were given.[25] The structures of these compounds are uncertain, although a polymeric structure with Al−H bridges was suggested from some physical and chemical properties. A *closo* aluminaboranate anion (**3**) analogous to $[B_{12}H_{12}]^{2-}$ was obtained according to Equation 1.[26] It possesses an icosahedron of eleven boron atoms and one aluminium atom (Figure 1). The B−B distances (176.0 to 185.6 pm) are within the normal range reported for polyboranes, the longer ones were observed for the pentagon bridged by the Al atom. As expected, the five B−Al distances are almost equidistant (213.1 to 214.0 pm) and the Al−C vector is only slightly tilted (by 2°) from the normal of that plane, which is formed by the five nearest boron atoms.

Much more information is available concerning carbaborane derivatives containing one aluminium atom, and much of the work has been done by the group of Hawthorne. A 3-alumina-1,2-dicarba-*closo*-dodecaborane **(4)**, obtained by the treatment of 1,2-dicarbaundecaborane with triethylaluminium (Equation 2),[27] has an icosahedral



**1** **2**

Scheme 2

$$\mathrm{Na_2[B_{11}H_{13}]} + \mathrm{Al(CH_3)_3} \xrightarrow{\substack{110^\circ\mathrm{C}\\ \text{4 days}}} \mathrm{Na_2[B_{11}H_{11}AlCH_3]} + 2\ \mathrm{CH_4} \qquad (1)$$

**3**

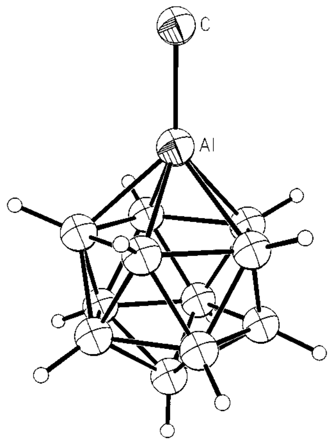


Figure 1. Molecular structure of $[\mathrm{MeAlB_{11}H_{11}}]^{2-}$ **3**;[26] hydrogen atoms of the methyl group are omitted; boron atoms (not shaded) are not labelled

structure with the Al atom coordinated to both carbon atoms and three boron atoms as well as the terminal ethyl group (Figure 2). The Al−B and Al−C bond lengths in the cluster are 217.3 and 213.7 pm, respectively. As expected, the terminal Al−C bond is much shorter and has a length of 193.0 pm. The terminal Al−C bond is tilted from the normal of the $B_3C_2$ plane by 19.5°, so that the methylene group of the disordered ethyl substituent approaches both carbon atoms of the cluster. Compound **4** may be described as a dicarbollyl complex with a carbaboranate ligand coordinated to an Al atom; indeed, such compounds were later used as dicarbollyl transfer reagents.[28] The Al atom of **4** is electrophilic and, upon treatment with THF[29] or phosphanes,[30] adducts are formed in which the connectivity of the Al atoms is reduced to a normal value of four as shown by a crystal structure determination of a phosphane derivative (Figure 3). The cluster is attached to the Al atom by only one boron atom, and the Al−B distance is 212.8 pm, which is shorter than the three Al−B separations observed in the *closo* cluster **4**. The contacts of the Al atom to both remaining boron atoms are much longer (248.0 pm on average) and indicate no further significant bonding interaction. A similar reduction of the connectivity of the Al atoms was observed in some other cluster compounds, which had $AlR_2$ or AlRL (L = $Et_2O$) groups in bridging positions[29,30−33] and which are not discussed here in detail.

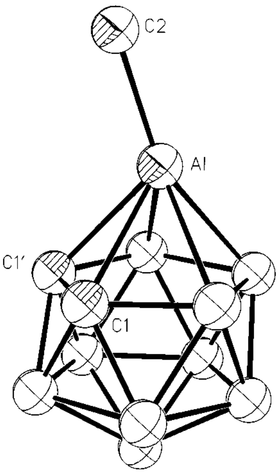


Figure 2. Molecular structure of $[\mathrm{EtAlB_9C_2H_{11}}]$ **4**;[27] hydrogen atoms and the methyl group of the ethyl substituent are omitted; boron atoms (not shaded) are not labelled

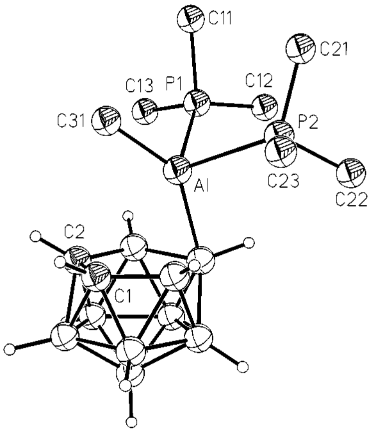


Figure 3. Molecular structure of $[\mathrm{EtAl(PEt_3)_2B_9C_2H_{11}}]$;[30] hydrogen atoms of the alkyl groups are omitted; only the α carbon atoms of the ethyl groups are drawn; boron atoms (not shaded) are not labelled

$$\text{(3)-1,2-}\mathrm{B_9C_2H_{13}} + \mathrm{Et_3Al} \xrightarrow{50^\circ\mathrm{C}\,/\,1\ \mathrm{h}} \text{1,2-}\mathrm{B_9C_2H_{12}AlEt_2} + \mathrm{C_2H_6}$$

$$\text{1,2-}\mathrm{B_9C_2H_{12}AlEt_2} \xrightarrow{77^\circ\mathrm{C}\,/\,25\ \mathrm{h}} \text{1,2-}\mathrm{B_9C_2H_{11}AlEt} + \mathrm{C_2H_6} \qquad (2)$$

**4**

Two remarkable bis(dicarbollide)aluminium sandwich compounds were described by the group of Hawthorne,[30,34–36] and may be named as *commo*-3,3′-bis(3-alumina-1,2-dicarba-*closo*-dodecaboranate) (Figure 4). One compound was obtained by the treatment of the aluminacarbaborane **4** with carbon monoxide.[30][34] It has an *exo* diethylaluminium group coordinated by two hydrogen atoms to one of the carbaborane clusters. The second compound (**5**) was synthesized by the reaction of diethylaluminium chloride with a thallium salt of the corresponding carbaborane (Equation 3).[30][35] An anionic symmetric sandwich compound (**5**, Figure 4) was isolated, in which two *closo* aluminacarbaboranes have a common Al atom. As expected, the Al−C and Al−B distances (224 to 230 pm and 214 to 229 pm, respectively) are longer than the distances observed in the monodicarbollyl compound **4**, which is probably caused by the greater connectivity of the Al atom (ten in **5**, six in **4**). Further *commo* derivatives with smaller carbaborane moieties are also known from the literature.[30,37,38] The aluminium atoms in these compounds have, however, normal coordination numbers of four. In one compound, the Al atom bridges two *nido*-6,9-dicarbadecaboranate ligands via their carbon atoms.[37] The metal atom resides above the six-membered $B_4C_2$ heterocycles with a boat conformation and is tetrahedrally coordinated by all four carbon atoms. The Al−C distances are 206 pm, which is longer than expected for tetracoordinated Al atoms. The Al−B distances are much longer (253 pm) indicating a very weak bonding interaction. In the second compound two *nido*-2,7-dicarba-octaboranate units are bridged by a common Al atom.[38] Once again the metal atom is tetrahedrally coordinated by the four carbon atoms of the ligands. The distance between both carbon atoms of one ligand is smaller than that in the carbaborate cage discussed before and, probably due to the lower steric strain, the Al−C distances are shorter (201.8 pm). Two of the Al−B distances are quite short (228 pm on average) and may indicate a further bonding interaction.

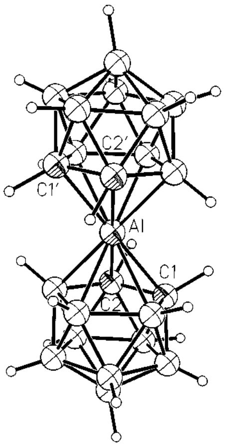
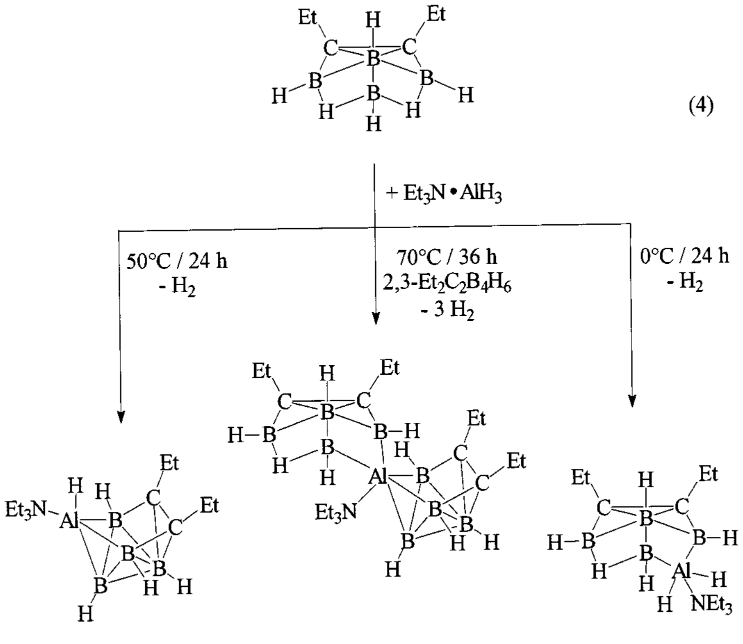


Figure 4. Molecular structure of $[Al(B_9C_2H_{11})_2]^-$ **5**;[34] boron atoms (not shaded) are not labelled

$$2\ \mathrm{Tl_2[7,8\text{-}C_2B_9H_{11}]} \quad + \quad 4\ \mathrm{Et_2AlCl} \longrightarrow \underset{\mathbf{5}}{\mathrm{Tl[Al(C_2B_9H_{11})_2]}} \quad + \quad 2\ \mathrm{Tl[AlEt_3Cl]} \quad + \quad \mathrm{Tl[AlEt_2Cl_2]} \qquad (3)$$

Small aluminacarbaborane clusters not stabilized by donor atoms, beside the *commo* compounds just cited, are rare. One article reported the reaction of the anionic cababorane $[2,3\text{-}C_2B_4H_7]^-$ with dimethylaluminium chloride,[39] which should yield μ-dimethylaluminium-2,3-*nido*-dicarbahexaborane(8). It was described as a very unstable compound in the liquid form or in solution and was thermolyzed in the gas phase to yield the unstable *closo* compound $MeAlC_2B_4H_6$. Remarkably, the gallium analogues of both compounds are much more stable and were isolated and



(4)

characterized.[39][40] Another reaction has been published, in which *nido*-$Et_2C_2B_4H_6$ was treated with the triethylamine alane adduct and from which, depending on the reaction conditions, three different products were obtained (Equation 4).[41] In accordance with the NMR and IR spectroscopic data, as well as elemental analyses, the authors suggested the structures given in Equation 4, which all have Al atoms with a higher connectivity than four.

## The Icosahedral Compound $[Al_{12}iBu_{12}]^{2-}$ (6)

Compound **6** is the only known polyhedral organoelement compound containing only aluminium atoms which obeys the Wade rules for a *closo* cluster. It was obtained and characterized by a crystal structure determination in our group in 1991.[42] In 1976 the reduction of di(isobutyl)aluminium chloride with elemental potassium was reported to yield tetra(isobutyl)dialane(4) with an Al−Al bond.[43] The compound was isolated as a brown oil and characterized by a hydrolysis experiment. However, in our experience, very large substituents are required to stabilize such dialuminium compounds, which contain bivalent aluminium atoms, against disproportionation reactions; we succeeded in isolating the first stable and completely characterized dialane(4), when we employed bulky bis(trimethylsilyl)methyl groups.[44] Therefore, we reinvestigated the synthesis of the isobutyl derivative and found a completely different result (Equation 5).[15] The main product is not the dialumium derivative originally proposed, but a potassium chloride adduct of tri(isobutyl)aluminium, which may be formed by a disproportionation reaction. A solid precipitated out of the reaction mixture, from which two products were extracted by treatment with toluene. One of these was identified as $K[Cl_2AliBu_2]$. The other one (**6**) was isolated as dark red crystals in a very low, but reproducible, yield of about 2%, and was identified as $K_2[Al_{12}iBu_{12}]$ by a crystal structure determination (Figure 5).[42] Compound **6** possesses an almost undistorted icosahedron of twelve aluminium atoms and is isoelectronic with the *closo*-borate anion $[B_{12}H_{12}]^{2-}$. The Al−Al distances are in a narrow range of 267.9 to 269.6 pm and are only slightly lengthened relative to the Al−Al single bonds in tetraalkyldialane(4) compounds (264 to 266 pm).[44][45] As shown in Figure 5, four triangles of each $Al_{12}$ cluster are bridged by potassium ions to give a three-dimensional network in the solid state with tetrahedrally coordinated cluster anions and linearly coordinated potassium cations. Thus, the arrangement of anions and cations is quite different to that in solid $K_2[B_{12}H_{12}]$.[46]

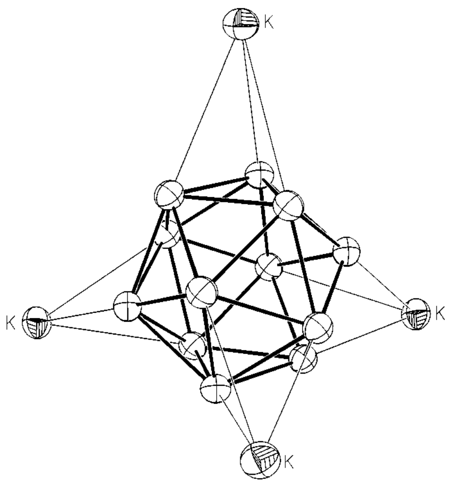
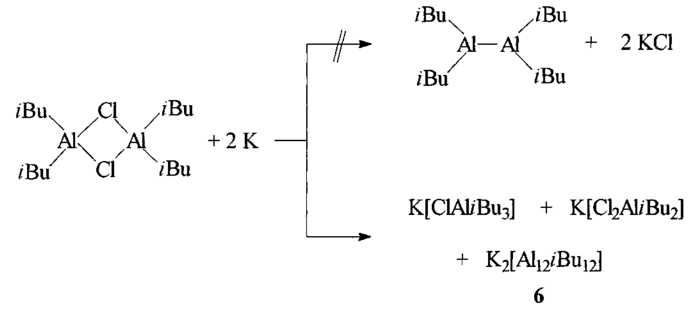


Figure 5. Crystal structure of $K_2[Al_{12}iBu_{12}]$ **6**;[42] isobutyl groups are omitted; each icosahedron is surrounded by four potassium ions to give a three-dimensional network

Compound **6** is only moderately stable in solution and decomposes slowly with the precipitation of elemental aluminium. In the crystalline form, it is much more stable with a decomposition point of 150 °C. The crystals can be stored in air for about two hours with no obvious signs of decomposition, but then slowly a colorless substance, probably aluminium hydroxide, is formed on their surfaces. Cyclovoltammetry revealed a reversible one-electron oxidation process, followed by a second irreversible oxidation.[47] In this respect the dodecaaluminate is similar to the corresponding boron compounds.[48]

A further anionic polyhedral cluster compound formed exclusively from aluminium atoms has been postulated by the group of Schnöckel, but until now it has not been isolated in a pure form or structurally characterized.[49] The reaction of aluminium(I) chloride with *tert*-butyllithium yielded a dark red, quite stable product of, presumably, a neutral oligomeric *tert*-butylaluminium(I) compound. Treatment of this intermediate with sodium/potassium alloy gave a radical anion (Equation 6) which, from an ESR spectroscopic characterization and quantum chemical calculations, was identified as the octahedral hexaaluminium compound $[Al_6(CMe_3)_6]^-$.[49] Furthermore, theory showed that the hypothetical neutral hexamer is much more stable



(5)

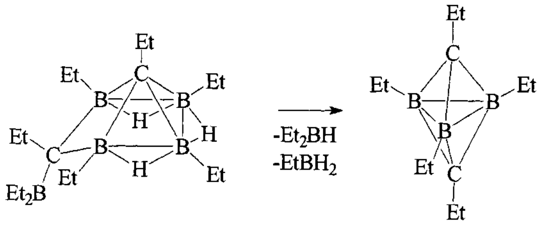
than the monomeric fragments (540 kJ/mol), and that the molecule is further stabilized by the addition of an electron and the formation of the radical anion by 140 kJ/mol.[16][49]

$$n\,\mathrm{AlCl} + n\,\mathrm{LiCMe_3} \longrightarrow \mathrm{Al}_n(\mathrm{CMe_3})_n \xrightarrow{\mathrm{Na/K}} [\mathrm{Al_6(CMe_3)_6}]^{\bullet -} \qquad (6)$$

## Hydroboration for the Synthesis of Carbaboranes; Some Remarks on Hydroalumination

The reaction of polyboranes with alkynes is the standard method for the synthesis of polyhedral carbaboranes.[5] However, mixtures are often formed and the isolation of pure products, even in a poor yield, is extremely difficult. The hydroboration of dialkylborylalkynes or bis(dialkylboryl)ethynes, followed by condensation reactions, offers an alternative route for the synthesis of carbaboranes, and several recent reports described such reactions, which yielded the products in some cases in a moderate to high yield.[50−57] For instance, treatment of diethylborylethyne with a large excess of diethylboron hydride afforded 1-carba-*arachno*-pentaborane(10) **(7)** (Equation 7), which by loss of diethylboron hydride and ethylboron dihydride gave *closo* dicarba-pentaborane(5) **(8)**.[51] Other products were identified, when the selectivity of the reaction was reduced.[55]

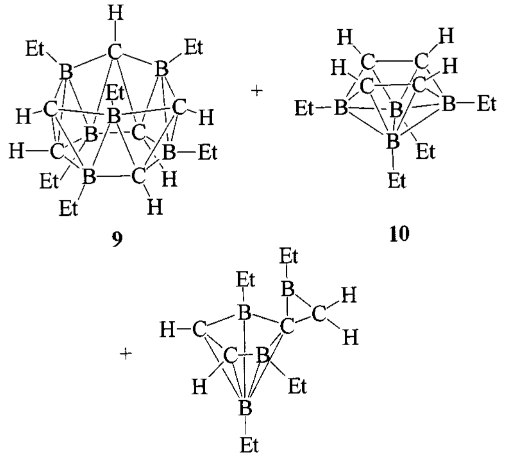
$$\mathrm{Et_2B{-}C{\equiv}C{-}Me} + \mathrm{Et_2BH}\ (\mathrm{excess}) \xrightarrow[\mathrm{-Et_3B}]{} \qquad (7)$$



**7** **8**

A mixture of carbaboranes was formed by the reaction of a diborylethyne with an excess of dialkylboron hydride (Equation 8), from which three products were isolated and characterized by NMR spectroscopy, one crystal structure determination and comparison of the observed data with those obtained by quantum chemical calculations.[54,56,57] Compound **9** was identified as a hexacarba-*arachno*-dodecaborane(12), which has a hexagonal antiprism of carbon and boron atoms.[56] The tetracarba-*nido*-octaborane(8) derivative **(10)** was isolated in a yield of 9% and contains a hexagonal face in a boat form, which has two pairs of carbon atoms bridged by two boron atoms.[54] The third compound **11** was isolated and characterized as a mixture with **10**. It was identified as a spiro compound, in which a 2,3,5-tricarba-*nido*-hexaborane cluster was connected to a three-membered $C_2B$ heterocycle by a common carbon atom.[57] Some further examples, which are not discussed here in detail, show that the hydroboration reaction is a powerful method for the synthesis of such carbaborane clusters.

$$\mathrm{Et_2B{-}C{\equiv}C{-}BEt_2} + \mathrm{Et_2BH}\ (\mathrm{excess}) \xrightarrow[\mathrm{-Et_3B}]{} \qquad (8)$$



**9** **10** **11**

Similar to hydroboration is hydroalumination, which has been used in the synthesis of alkylaluminium derivatives and in preparative organic chemistry.[58][59] In many cases, the products obtained by the addition of Al−H bonds to alkynes were, however, not isolated and characterized, but hydrolyzed to liberate the corresponding hydrocarbons.[59] Thus, only poor information concerning the structure of most of the organoaluminium intermediates is available in the literature. To the best of our knowledge, the hydroalumination of aluminium alkynides, which is similar to the reactions of the boron compounds cited above, and may open the route to the formation of cluster compounds, has been described in only two papers. In a conference report, Wilke and Schneider described the reaction of diethylaluminium hydride with diethylaluminium butynide,[60] which in a first step yielded the product of a twofold hydroalumination $(Et_2Al)_3C{-}CH_2{-}C_2H_5$. This compound was characterized by deuterolysis and oxidation and decomposes upon heating to 50 or 60 °C with the formation of triethylalane and an unknown residue. A similar reaction with dimethylaluminium hydride and dimethylaluminium propynide afforded a solid which, in addition to hydrolysis, was characterized by elemental analysis and molar mass determination. These results were interpreted in terms of the formation of an adamantane-like cage compound ("pseudo-aluminoadamantane"), which has seven Al atoms and four C atoms. Two of the Al atoms should be bridged by hydride ions. Remarkably, this compound showed no tendency to form adducts with diethyl ether.[60] The hydroalumination of dimethylaluminium ethynide, generated in situ, with dimethylaluminium hydride was reported to afford $(AlMe)_6(CCH_3)_4$ with a true adamantane structure in which the tricoordinated Al atoms occupy the bridging positions.[60] In view of the results discussed below, it seems probable that the Wilke group had synthesized the first carbaalanes in 1963 without recognizing, however, their true structure and the importance of their particular and fascinating bonding situation.

Similar reactions were carried out by a Russian group in 1988.[61] They treated some diethylaluminium alkynides with isobutylaluminium hydride and obtained oily residues, which by hydrolysis experiments were identified as the products of the twofold hydroalumination, similar to the intermediate discussed in the preceding paragraph. In our opinion, however, it is not clear from these experiments whether they indeed had these trialuminium compounds or whether their reactions already gave cluster derivatives. In our experience, the reactions of differently substituted aluminium starting compounds, as described in ref.,[61] afford complicated mixtures of products by dismutation reactions. Thus, we suppose that they never had a pure component in their oily residues.

## Carbaalanes

We began to investigate hydroalumination reactions because we were interested in an effective method for the synthesis of polyaluminium compounds, which are useful as chelating Lewis-acids in phase transfer processes or in anion recognition.[62] We succeeded in synthesizing these compounds by the reaction of polyalkynes with dialkylaluminium hydrides. The trialuminium derivatives, which were obtained by a twofold hydroalumination of aluminium alkynides as cited above, are of particular interest for such investigations, although we never observed a reaction at room temperature or in solution when we employed aluminium phenylethynides as starting compounds.

A hydroalumination reaction was observed when we dissolved dimethylaluminium phenylethynide in a slight excess of dimethylaluminium hydride (Equation 9) and heated the mixture to 80 °C for two days.[63] As shown by NMR spectroscopy, a large quantity of trimethylaluminium was formed, which was distilled off at room temperature in vacuo. Recrystallization of the residue afforded the colorless product $(AlMe)_8(CCH_2Ph)_5H$ (**12**). Compound **12** possesses a unique molecular structure (Figure 6), which comprises a cluster of eight aluminium and five carbon atoms. The aluminium atoms occupy the vertices of a slightly distorted cube, of which five faces are bridged by carbon atoms. The sixth face is bridged by a hydrogen atom. Each aluminium atom is further coordinated to one methyl group, and each carbon atom of the cluster is further attached to a benzyl group. Long Al−Al distances are observed for the hydrogen bonded face (279.7 pm), while the remaining eight edges of the cube are shorter (260.5 pm). The short distances are similar to those found in dimeric trimethylaluminium $(AlMe_3)_2$ (261 pm)[64] containing a 3c-2e Al−C−Al bond, and they are shorter than the Al−Al single bond in tetraalkyl compounds $R_2Al-AlR_2$.[44][45] Thus, they are consistent with a multicenter bonding interaction in the cluster. The Al−C separations within the cluster range between 201.8 pm and 214.1 pm and depend on the coordination sphere of the aluminium atoms. The shortest ones are observed to the Al atoms of the hydrogen bonded face and the longest to the carbon atom C14 at the opposite site of the cube. All are longer than the terminal Al−Me distances (195.0 pm). The formation of **12** may be described by the repeated hydroalumination of the starting aluminium ethynide and by condensation reactions with the release of trimethylalane. Furthermore, methylaluminium dihydride may be formed by the dismutation equilibrium of dimethylaluminium hydride and may be important at least for the introduction of the bridging hydride ion.

$$11\ Me_2AlH \quad + \quad 5\ Me_2Al{-}C{\equiv}C{-}Ph \longrightarrow \underset{\mathbf{12}}{(AlMe)_8(CCH_2Ph)_5H} \quad + \quad 8\ AlMe_3 \tag{9}$$

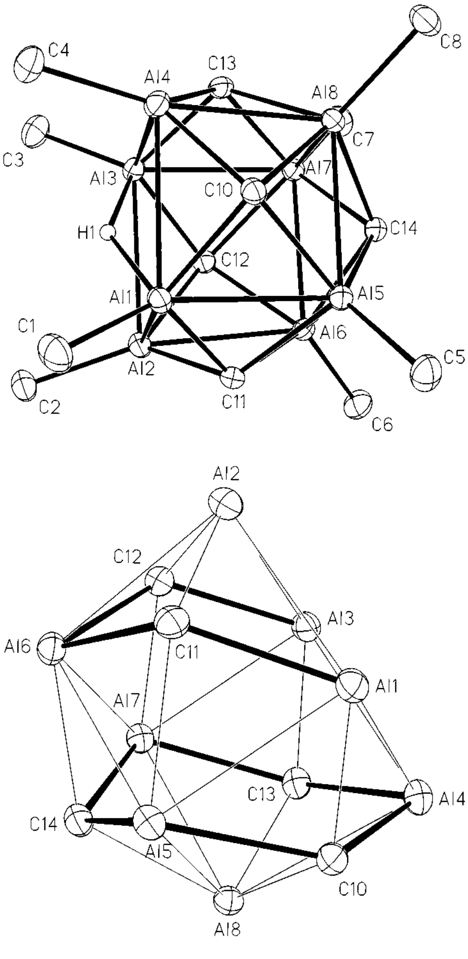


Figure 6. (a) Molecular structure of $(AlMe)_8(CCH_2C_6H_5)_5H$ **12**;[63] hydrogen atoms with the exception of H1 and benzyl groups are omitted. (b) The carbon and aluminium atoms of the rotated cluster with Al8 at the bottom, the bold lines characterize the planes discussed in the text

Each aluminium atom contributes two electrons and each carbon atom three electrons to the bonding in the cluster. Including the electron of the bridging hydrogen atom, a total electron count of 16 electron pairs results, which, in accordance with Wade's rules, gives an *arachno* configuration for the 13 vertex cluster of **12**. The corresponding *closo* polyborate $[B_{15}H_{15}]^{2-}$ is known only from quantum chemical calculations.[65] It has a hexagonal antiprism in its molecular center, of which the hexagonal faces are bridged by one and two boron atoms, respectively. The cluster of **12** can be derived from this structure, which is best recognized when it is placed on the aluminium atom Al8 (Figure 6). This atom bridges a six-membered heterocycle (Al4, Al5, Al7, C10, C13 and C14) in a chair form. The next plane comprises only five atoms (Al1, Al3, Al6, C11 and C12), and one vertex remains unoccupied, which is the approximate position of the bridging hydrogen atom H1. The atom Al2 resides above this plane. Thus, two vertices are unoccupied in comparison with *closo* $[B_{15}H_{15}]^{2-}$, which is in accordance with an *arachno* structure. However, **12** does not adopt an antiprismatic molecular center − owing to the large differences between the Al−Al and Al−C distances the planes are in an almost eclipsed conformation. Compound **12** was the first well-characterized cluster compound containing exclusively aluminium and carbon atoms to be reported in the literature. Owing to the obvious similarity between this compound and polyboranes or carbaboranes with respect to its structure and electronic configuration, we suggested the name carbaalanes[66] for this new class of organoaluminium derivatives.

When we reduced the excess of dimethylaluminium hydride, **12** was formed only as a minor by-product,[67] and a dark red compound $(AlMe)_8(CCH_2Ph)_5(C{\equiv}CPh)$ **(13)** was isolated in a yield of 40%; this compound has no hydrogen atoms attached to aluminium (Equation 10). The molecular structure of **13** (Figure 7) is quite similar to that of the colorless hydrido-bridged cluster **12**, except that the sixth face of the $Al_8$ cube is bridged by a phenylethynido ligand. Despite the different bridging atoms, the bond lengths in the cluster are almost indistinguishable from those of **12**, and the Al−Al separations of the ethynido-bridged face are longer (282.9 pm) than the remaining Al−Al distances (258.2 to 262.2 pm). The hydrido- or ethynido-bridged face of each cube is distorted to a rhombus with different distances between aluminium and the bridging atoms (Al−H: 191 and 221 pm in **12**; Al−C: 217.4 and 241.1 pm in **13**). Thus, these bridges may be interpreted as 3c-2e bonds with weak secondary interactions. The C−C bond length of the ethynide group (124.1 pm) is slightly longer than the standard bond length of a C≡C triple bond (120 pm[68]), and accordingly the absorption of the C≡C triple bond in the IR spectrum is shifted to 1956 $cm^{-1}$, which is more than 100 $cm^{-1}$ lower than usually observed (e.g. in compound **15** discussed below with an exo ethynide group). These observations verify a particular bonding and electronic situation at the open face of the cluster, which may be compared with that of carbaboranes. Thus, we expect that, similar to the carbaboranes, the carbaalanes may show an interesting and unprecedented chemical reactivity.

Other products were formed when diethylaluminium derivatives were employed for the hydroalumination reaction.

$$10\ Me_2AlH + 6\ Me_2Al{-}C{\equiv}C{-}Ph \longrightarrow \underset{\mathbf{13}}{(AlMe)_8(CCH_2Ph)_5(C{\equiv}CPh)} + 8\ AlMe_3 \qquad (10)$$

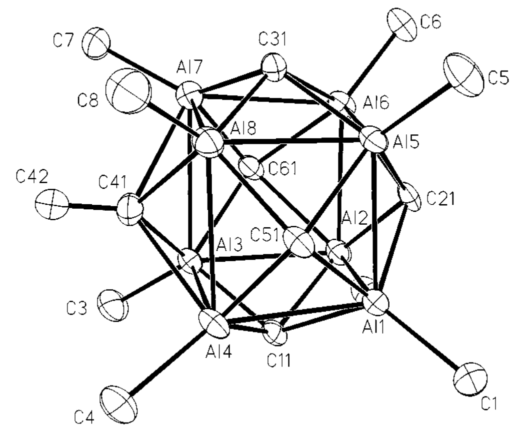


Figure 7. Molecular structure of $(AlMe)_8(CCH_2C_6H_5)_5(C{\equiv}C{-}C_6H_5)$ **13**;[67] hydrogen atoms, the phenyl group attached to C42 and benzyl groups are omitted

An orange-red product (**14**) was isolated after heating a mixture of the corresponding ethynide and hydride to 50 °C for 18 hours (Equation 11).[69] Once again, trialkylaluminium ($AlEt_3$) was detected as a main product, which was distilled off in vacuo. Although the crude product contained **14** in a high concentration, the crystalline compound was obtained in only a 36% yield. A crystal structure determination confirmed the compound to be $(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H$ (Figure 8), which has seven Al and five carbon atoms in its cluster and may be derived from compound **12** with one vertex of the $Al_8$ cube unoccupied. The five carbon atoms are in two different positions: three of them bridge four Al atoms, while two reside above a triangle of Al atoms. The first ones belong to $C{-}CH_2{-}C_6H_5$ groups, similar to the bridging groups in compound **12**, while the second ones (C3,C3′) are alkenylidene carbon atoms of C=C double bonds. One further $Al_3$ triangle is bridged by a hydrogen atom. Thus, only one hydroalumination step with $EtAlH_2$ is missing to obtain a compound analogous to **12**. The Al−Al distances of the carbon- or hydrogen-bonded faces (268.2 and 270.7 pm, respectively) are shorter than those observed for the hydrogen-bonded face in **12**, while the remaining Al−Al separations are quite similar (256.9 and 260.0 pm). The C=C double bonds (136.0 pm on average) are only slightly lengthened relative to the standard bond length.[68] The alkenylidene groups adopt an orientation, in which a part of the π-orbitals overlaps the open face of the cluster. If the π-electrons are added to the number of cluster electrons, 16 electron pairs are obtained, which are in accordance with a *hypho* structure. Indeed, the cluster of **14** can be derived from that of the *closo*-borate $[B_{15}H_{15}]^{2-}$[65] with three vertices unoccupied. The molecular structure has five different ethyl groups, two different benzyl groups and the ethenylidene groups, and some of the $CH_2$ groups are diastereotopic. Thus, very complicated NMR spectra resulted, some of their more important aspects are discussed later on.

$$9\ Et_2AlH + 5\ Et_2Al{-}C{\equiv}C{-}Ph \longrightarrow \underset{\mathbf{14}}{(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H} + 7\ AlEt_3 + (\mathbf{15}) \qquad (11)$$

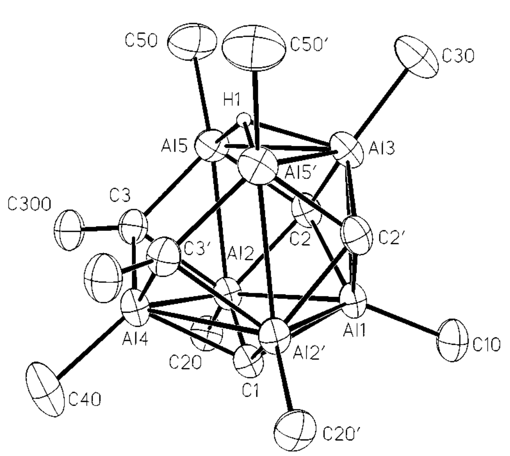


Figure 8. Molecular structure of $(AlEt)_7(CCH_2C_6H_5)_3(C{=}CHC_6H_5)_2H$ **14**;[69] hydrogen atoms with the exception of H1, phenyl and benzyl groups and the methyl groups of the ethyl substituents are omitted; the molecule is located on a crystallographic mirror plane

A second product (**15**) was isolated from the mother liquor after the separation of **14**.[69] Compound **14** was completely converted into **15** by heating a benzene solution to 60 °C for several days. Monitoring of the rearrangement by NMR spectroscopy gave a first order reaction, which has an estimated rate constant of $k \approx 4 \times 10^{-5}\ sec^{-1}$ and a free enthalpy of activation of $\Delta G^{\neq} \approx 110$ kJ/mol. A much faster reaction was observed when the crude product from the reaction was heated to 110 °C for one hour (Equation 12). Compound **15** is isomeric with **14**, but has a different structure with a cluster of seven Al and four C atoms [$(AlEt)_7(CCH_2Ph)_4(C{\equiv}CPh)H$, Figure 9]. One edge of the cluster (Al3−Al6) is bridged by a hydrogen atom and a second one (Al2−Al5) by an ethynide group. The $Al_7C_4$ molecular core has twelve electron pairs, which is in accordance with a *closo* configuration. Indeed, the structure of the cluster is analogous to that of *closo*-$[B_{11}H_{11}]^{2-}$[3] and has a six-membered heterocycle in a boat conformation bridged by an Al atom as a very characteristic structural motif. With the exception of the distances to the unique Al atom Al7, short Al−Al separations were observed, which are between 258.1 and 259.4 pm for the unsupported Al−Al edges, while they are little lengthened for the bridged ones (261.2 and 267.5 pm). Much longer distances of 281.8 to 292.1 pm were observed to the atom Al7 above the boat shaped $Al_4C_2$ heterocycle. A similar lengthening of the B−B distances to that unique position was observed in the undecaborate dianion (B−B = 200.9 pm).

$$\underset{\mathbf{14}}{(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H} \xrightarrow{\Delta} \underset{\mathbf{15}}{(AlEt)_7(CCH_2Ph)_4(C{\equiv}CPh)H} \qquad (12)$$

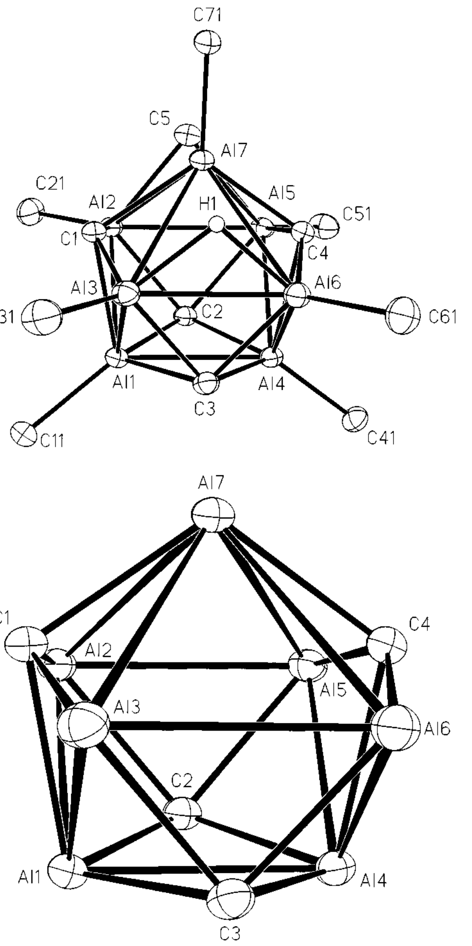


Figure 9. Molecular structure of $(AlEt)_7(CCH_2C_6H_5)_4(C{\equiv}C{-}C_6H_5)H$ **15**;[69] (a) shows the cluster with the exo hydrogen and ethyne (C5) ligands and the α carbon atoms of the ethyl substituents; (b) gives the naked cluster and shows the remarkable analogy to $[B_{11}H_{11}]^{2-}$

As described above, compound **14** containing seven Al atoms and two C=C double bonds may be converted into an *arachno* derivative analogous to **12** by a single hydroalumination step with $EtAlH_2$. However, only alkyl or aryl aluminium dihydrides with very bulky substituents are available.[70] Dihydrides bearing smaller substituents may be formed in trace amounts by the dismutation equilibrium of dialkylaluminium hydrides, and we suppose that they are intermediates in the hydroalumination reactions described here. Therefore, we treated compound **14** with an excess of diethylaluminium hydride in order to hydroaluminate **14** and to synthesize the corresponding *arachno* compound. The mixture of the starting materials was heated to 60 °C for 18 hours without additional solvent, and triethylaluminium was formed as detected by NMR spectroscopy. All volatile components were removed in vacuo, and recrystallization of the residue from *n*-pentane afforded colorless crystals of product **16** in a yield of 69% (Equation 13). The molecular structure is analogous to that of **12** containing a cube of eight Al atoms, of which five faces are bridged by carbon atoms and one face is occupied by a hydrogen atom. The reaction according to Equation (13) gives an important insight into the mechanism of the formation of these carbaalane clusters.

$$\underset{\mathbf{14}}{(AlEt)_7(C{=}CHPh)_2(CCH_2Ph)_3H} + Et_2AlH\ \text{(excess)} \xrightarrow[-\ Et_3Al]{} \underset{\mathbf{16}}{(AlEt)_8(CCH_2Ph)_5H} \qquad (13)$$

The complete characterization by NMR spectroscopy and assignment of resonances to all atoms of these compounds was extremely difficult, and despite the application of advanced NMR spectroscopic techniques (H,H COSY, HMQC and HMBC NMR spectra) not all resonances could clearly be assigned to particular atoms. However, those resonances which are important for the discussion of these clusters, were clearly resolved and assigned. $^{27}$Al NMR spectroscopic data have not yet been recorded. The $^{13}$C NMR resonances of the cluster carbon atoms show a strong shift to low field ($\delta$ = 21 to 35). Similar shifts were calculated for a carbaborane cluster which has an alternating arrangement of boron and carbon atoms (see above).[56] A chemical shift of 0 ppm is usually observed for compounds which have carbon atoms attached to aluminium with a higher coordination number than three. Those shifts were detected here for the $\alpha$-carbon atoms of the terminally coordinated methyl or ethyl substituents. Similarly, the bridging hydrogen atoms show a low-field shift in the $^{1}$H NMR spectra and resonate at about 4.7 to 5.3 ppm, while in the starting dimethyl or diethyl aluminium hydrides the hydrido bridges have resonances of $\delta$ = 2.92 and 2.79, respectively. The resonances of the $CH_2$ protons of the benzyl groups are also shifted to a lower field ($\delta$ = 3.0 to 3.7). We have not yet succeeded in the unambiguous assignment of absorptions in the IR spectra to cluster vibrations. All IR spectra show some weak absorptions in the typical range for Al−C bonds ($\approx$ 450 to 550 cm$^{-1}$) and intense, broad absorptions at 660 to 710 cm$^{-1}$, which, however, is the range of deformation vibrations of the phenyl groups. Thus, their more intuitive assignment to cluster vibrations can only be discussed with reservation. Polyhedral carbaalanes without phenyl groups may help to clarify this point.

## Concluding Remarks

A deficiency of electrons causes the singular property of boron to form clusters which require a delocalized bonding description. As described here, similar compounds are now available with its heavier homologue aluminium, in which Al atoms occupy positions of high connectivity in delocalized electronic systems; these compounds obey the same rules concerning structure and electron count. Nevertheless differences between both kinds of compounds should not be ignored. The aluminium derivatives are often more reactive and less stable than the boron clusters. This may be due to the low electronegativity of aluminium, which leads to a significant charge separation in all heteronuclear bonds. Steric shielding, which has been used for the preparation of so many compounds with unusual structures in main group chemistry, seems to have only a minor influence here, instead the stabilization of these clusters may be caused mainly by the delocalization of electron density. The investigation of the chemical reactivity of the carbaalanes as a new class of compounds is just beginning, but a broad application in research such as in catalytic processes seems to be possible, in particular due to their facile synthesis. Future work will show whether this type of aluminium chemistry will reach a similar importance and diversity as that of boron

## Acknowledgments

We are grateful to the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for generous financial support.

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Received August 3, 1999
[I99285]