

Reactions of Carbaalanes with HBF_4 and HCl : A μ_3 -Bridging Fluorine Atom in $(\text{AlEt})_7(\text{C}=\text{CHPh})_2(\text{CCH}_2\text{Ph})_3(\mu_3\text{-F})$ versus a Terminal Chlorine Atom in $(\text{AlMe})_7(\text{AlCl})(\text{CCH}_2\text{Ph})_5\text{H}$

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The 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**) reacted with $\text{HBF}_4\cdot\text{OEt}_2$ to yield the fluorine derivative $(\text{AlEt})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CCH}_2\text{C}_6\text{H}_5)_3(\mu_3\text{-F})$ (**4**) by the replacement of its bridging hydrogen atom and the cleavage of a B–F bond. The fluorine atom bridges three aluminum atoms with the Al–F distances in a narrow range between 1.97 and 2.00 Å. A similar reaction was observed with the *arachno*-carbaalane $(\text{AlMe})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5\text{H}$ (**1**). However, an impure product was isolated which could not be purified by repeated recrystallization. In contrast, use of HCl instead of $\text{HBF}_4\cdot\text{OEt}_2$ as a proton donor did not result in substitution of the bridging hydrogen atom of **1**, but a methyl group at the bottom of the cluster was replaced by release of methane. The compound $(\text{AlMe})_7(\text{AlCl})(\text{CCH}_2\text{C}_6\text{H}_5)_5(\mu\text{-H})$ (**6**), which possesses a terminally bonded chlorine atom, was formed.

Introduction

The hydroalumination of dialkyl(ethynyl)aluminum derivatives with the corresponding dialkylaluminum hydrides afforded novel compounds which contain polyhedral clusters of carbon and aluminum atoms.^{1–3} Owing to obvious similarities to carbaboranes, we suggested the name *carbaalanes* for this new and now well-established class of compounds.⁴ Two different types of structures were verified by crystal structure determinations. One possessing the general formula $(\text{AlR})_8(\text{CCH}_2\text{R}')_5(\text{R}'')$ (**1**: $\text{R} = \text{Me, Et}$; $\text{R}' = \text{CH}_3, \text{Ph}$; $\text{R}'' = \text{H, C}\equiv\text{CPh, C}\equiv\text{CMe}$; Scheme 1) may be derived from a slightly distorted cube of aluminum atoms, five faces of which are bridged by $\text{C}-\text{CH}_2\text{R}'$ groups, while the sixth face is occupied by a hydrogen atom or an ethynyl ligand. These compounds have 16 cluster electron pairs, which, in accordance with the Wade rules,⁵ verify an *arachno* configuration. Incomplete hydroalumination caused the formation of $(\text{AlEt})_7(\text{C}=\text{CHPh})_2(\text{CCH}_2\text{Ph})_3\text{H}$

(**2**), which has a singular structure with two $\text{C}=\text{C}$ double bonds and one vertex of the Al_8 cube of **1** unoccupied.² The structure of the second type of carbaalanes, $(\text{AlR})_7(\text{CCH}_2\text{R}')_4(\text{R}'')$ (**3**: $\text{R}'' = \text{H, C}\equiv\text{CPh}$; Scheme 1) is closely related to that of the *closo*-borate anion $[\text{B}_{11}\text{H}_{11}]^{2-}$.⁶ However, the number of electron pairs needed for a *closo* configuration, 12, can only be calculated for the aluminum compounds if the bridging acetylenide or hydride anions were taken as *exo* ligands not involved in the cluster bonding. As was shown by quantum-chemical calculations, all these clusters require a delocalized bonding description with, however, only weak direct Al–Al interactions.³ The charge separation in the carbaalane clusters is as expected, with positively charged aluminum atoms and negative charges localized at the carbon and bridging hydrogen atoms. We have begun investigations of the chemical reactivity of these compounds and report here on reactions with protic reagents which should lead to the replacement of the bridging hydrogen atoms.

Results and Discussion

Treatment of $(\text{AlEt})_7(\text{C}=\text{CHPh})_2(\text{CCH}_2\text{Ph})_3\text{H}$ (**2**) with $\text{HBF}_4\cdot\text{OEt}_2$. Gas evolution was observed when the

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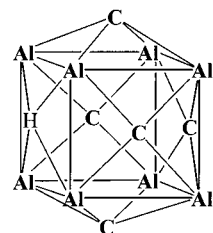
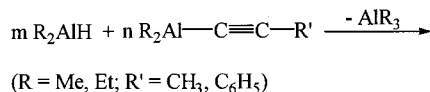
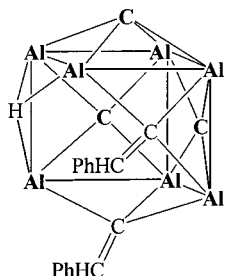
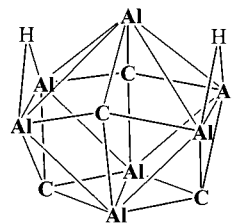
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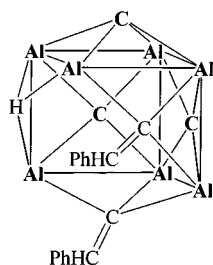
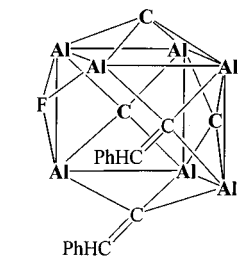
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Scheme 1

(AlMe)₈(CCH₂C₆H₅)₅H1 (Al = AlMe; C = CCH₂C₆H₅)(AlEt)₇(C=CHPh)₂(CCH₂Ph)₃H2 (Al = AlEt; C = CCH₂Ph)(AlMe)₇(CCH₂CH₃)₄H₂3 (Al = AlMe; C = CCH₂CH₃)

alkenyl carbaalane **2** was treated with a solution of tetrafluoroboric acid in diethyl ether at -50°C (eq 1).

(AlEt)₇(C=CHPh)₂(CCH₂Ph)₃H2 (Al = AlEt; C = CCH₂Ph)(AlEt)₇(C=CHPh)₂(CCH₂Ph)₃F4 (Al = AlEt; C = CCH₂Ph)

Orange crystals of the product, (AlEt)₇(C=CHPh)₂(C-CH₂Ph)₃(μ_3 -F) (**4**), were isolated after evaporation of the solvent and recrystallization of the residue from cyclopentane in 48% yield. Characterization of **4** showed that the bridging hydrogen atom was replaced by a single fluorine atom. This reaction requires the cleavage of at least one B-F bond of the tetrafluoroborate anions, which may be favored by the coordination of each fluorine atom by three aluminum atoms of the cluster. The ^1H and ^{13}C NMR spectra are very complicated, owing to the low molecular symmetry with five chemically different ethyl groups and further owing to the coupling between fluorine and carbon or hydrogen. Despite the employment of various NMR techniques we were not able to unambiguously assign all observed resonances. The alkenylidene proton is shifted to low field (δ 9.28), similar to the case for the starting compound **2**.² The carbon atoms of the terminal ethyl

groups attached to aluminum exhibit chemical shifts between 0.7 and 3.1 ppm, which is in the normal range of carbon atoms bonded to coordinatively saturated aluminum atoms.⁷ In contrast, the cluster carbon atoms not involved in C=C double bonds resonate at an unusually low field (δ 32.5 and 39.6), which is quite characteristic for carbaalanes¹⁻³ and may be caused by the particular bonding situation of the clusters. The alkenylidene carbon atoms coordinated by three aluminum atoms have a shift of 156.2 ppm.²⁷Al NMR data of organoaluminum derivatives are sensitive to the coordination numbers of aluminum atoms, and shifts of about 170 ppm were recorded for a tetrahedral coordination sphere, while an octahedral environment gave shifts of about 0 ppm.⁸ The ²⁷Al NMR shifts of carbaalanes derived from Al₈ cubes were observed in a broad range between 85 and 170 ppm.⁹ Their assignment and clear separation are difficult, owing to the line widths of the usually very broad ²⁷Al NMR resonances and the partial overlap of signals. Compound **4** showed resonances with maxima at δ 74 ($W_{1/2}$ = 12 000 Hz) and -28 ($W_{1/2}$ = 10 000 Hz). Clearly resolved shoulders were detected at about 110 and 20 ppm. Much more data must be collected in future work, in conjunction with quantum-chemical calculations, to allow the secure assignment of resonances to particular aluminum atoms of the cluster. This may be very helpful for a more sophisticated understanding of the bonding situation of carbaalanes. We were not able to detect a ¹⁹F NMR signal in the range between -100 and -160 ppm, which is characteristic of AlF groups containing μ_2 -bridging fluorine atoms (see below for quantum-chemical calculations).

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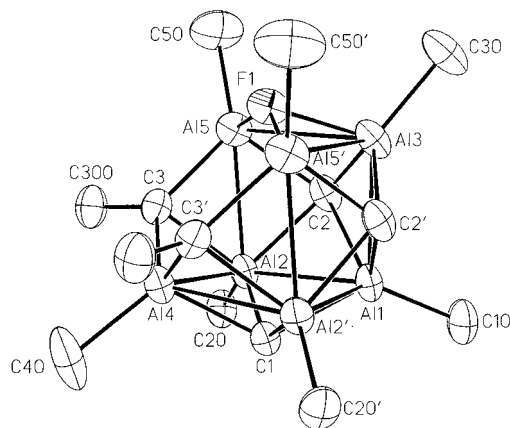


Figure 1. Molecular structure of **4**. The thermal ellipsoids are drawn at the 40% probability level. Methyl, phenyl, and benzyl groups are omitted for clarity. Important bond lengths (Å): Al(1)–Al(2) = 2.598(1), Al(1)–Al(3) = 2.552(2), Al(1)–C(1) = 2.056(5), Al(1)–C(2) = 2.152(4), Al(2)–Al(4) = 2.691(2), Al(2)–Al(5) = 2.662(2), Al(2)–C(1) = 2.042(2), Al(2)–C(2) = 2.071(4), Al(2)–C(3) = 2.128(4), Al(3)–F(1) = 1.966(4), Al(3)–Al(5) = 2.788(2), Al(3)–C(2) = 2.019(4), Al(4)–C(1) = 2.148(6), Al(4)–C(3) = 2.045(4), Al(5)–F(1) = 2.000(1), Al(5)–C(2) = 2.050(4), Al(5)–C(3) = 2.009(4), C(3)–C(300) = 1.359(5).

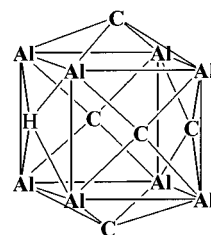
tions).¹⁰ An organogallium compound, $\text{Mes}_6\text{Ga}_6\text{F}_4\text{O}_4$, is known with a μ_3 -fluorine ligand and a pseudo- μ_3 -fluorine ligand, for which only small upfield shifts were observed compared to the μ_2 situation.¹¹ The nonobservance of a resonance due to the fluorine atom in **4** may be caused by the quadrupole moment of aluminum, the coupling to chemically different aluminum atoms, and an unusually strong line broadening.

The molecular structure of **4** is depicted in Figure 1. It contains an Al_7C_5 cluster, which may be derived from an Al_8 cube if one vertex remains unoccupied. It has three Al_4 rings which are bridged by $\text{CCH}_2\text{C}_6\text{H}_5$ groups. At the open face three Al_3 triangles result, two of which are bridged by the alkenylidene ligands and one by the fluorine atom. The structure is almost identical with that of the starting compound **2**.² The length of the C=C bonds (1.359(5) Å) corresponds to that of **2** and is only slightly longer than the standard value.¹² The Al–C distances to the terminally bonded ethyl groups are quite normal (1.95 Å on average). Longer separations (2.009(4)–2.148(6) Å) are detected in the cluster, similar to data reported before for other carbaalanes.^{1–3} Three ranges of Al–Al distances are observed (2.575, 2.677, and 2.788 Å on average). The longer ones belong to the fluorine-bridged Al_3 triangle (Al(3)–Al(5)); the shortest ones are to the aluminum atom Al(1) (Al(1)–Al(2), Al(1)–Al(3)), which is opposite to the open face and occupies the most intact part of the cluster. The fluorine atom bridges the atoms Al(3), Al(5), and Al(5') with Al–F distances of 1.966(4) Å (Al(3)) and 2.000(1) Å (Al(5)). These distances are much longer than those observed for μ_2 -Al–F–Al bridges, which usually have values between 1.78 and 1.85 Å.¹⁰ To the best of our

knowledge, a similar μ_3 bridging has not been observed before in aluminum chemistry but was found in the gallium compound $\text{Mes}_6\text{Ga}_6\text{F}_4\text{O}_4$ ¹¹ with a similar lengthening of the element–fluorine distances compared to the μ_2 situation.

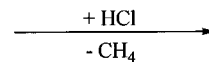
The carbaalane **2** underwent a rearrangement reaction upon heating to yield almost quantitatively an Al_7C_4 cluster (**3**).² The same reaction was not observed with the fluoro-containing cluster **4**, which is stable even at elevated temperatures. Etheral solutions of **4** are sensitive toward irradiation, and exposure to daylight gave a new product which, to date, could not be isolated and characterized. A reaction similar to that in eq 1 was observed upon treatment of the *arachno*-carbaalane **1** (R = Me, R' = Ph, R'' = H) with $\text{HBF}_4 \cdot \text{OEt}_2$. However, equimolar amounts of the acid gave a 3:1 mixture of a novel product (**5**) and the starting compound **1**, which could not be separated by repeated recrystallization. To completely consume **1**, we employed an excess of the acid. However, a solid precipitated which was insoluble in organic solvents and which could not be characterized. NMR spectra of **5** recorded of the mixture verify that the bridging hydrogen atom was replaced by a fluorine atom and that the structure of the cluster remained unchanged with a cube of eight aluminum atoms and five faces bridged by CCH_2Ph groups. A resonance at –121.4 ppm was observed in the ^{19}F NMR spectrum in the expected range for AlF compounds.¹⁰

Treatment of $(\text{AlMe})_8(\text{CCH}_2\text{Ph})_5\text{H}$ (1**) with Hydrogen Chloride.** To gain deeper insight into the reaction of the *arachno*-carbaalane **1** with protic reagents and to isolate a pure compound, we treated **1** with a small excess of an etheral solution of HCl. Gas evolution was observed at low temperature (–70 °C, eq 2). After evaporation of the solvent at –20 °C and

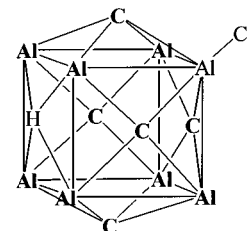


$(\text{AlMe})_8(\text{CCH}_2\text{Ph})_5\text{H}$

1 (Al = AlMe; C = CCH_2Ph)



(2)



$(\text{AlCl})(\text{AlMe})_7(\text{CCH}_2\text{Ph})_5\text{H}$

6 (Al = AlMe; C = CCH_2Ph)

recrystallization of the product **6** from toluene, a colorless, solid product was isolated which usually had an impurity of about 10% of the starting compound **1**. A pure sample of **1** was obtained in very small quantity by recrystallization from a very dilute pentane solution.

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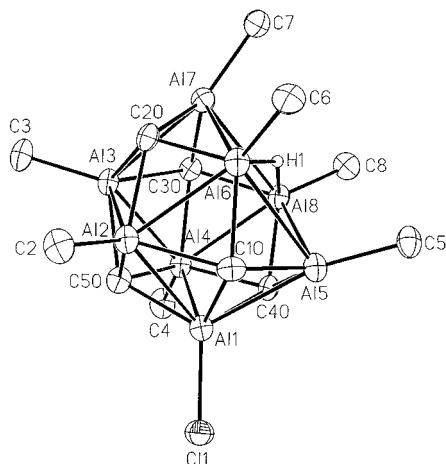


Figure 2. Molecular structure of **6**. The thermal ellipsoids are drawn at the 40% probability level. Benzyl groups are omitted for clarity. Only one of the disordered positions of the chlorine atom is shown. Important bond lengths (Å): Al(1)–Al(2) = 2.599(2), Al(1)–Al(4) = 2.588(2), Al(1)–Al(5) = 2.588(2), Al(1)–C(10) = 2.061(5), Al(1)–C(40) = 2.076(5), Al(1)–C(50) = 2.046(5), Al(1)–Cl(1) = 2.096(5), Al(2)–Al(3) = 2.603(2), Al(2)–Al(6) = 2.596(2), Al(2)–C(10) = 2.129(6), Al(2)–C(20) = 2.113(6), Al(2)–C(50) = 2.029(5), Al(3)–Al(4) = 2.599(2), Al(3)–Al(7) = 2.597(2), Al(3)–C(20) = 2.087(5), Al(3)–C(30) = 2.120(5), Al(3)–C(50) = 2.095(6), Al(4)–Al(8) = 2.580(2), Al(4)–C(30) = 2.090(5), Al(4)–C(40) = 2.114(5), Al(4)–C(50) = 2.050(5), Al(5)–Al(6) = 2.800(2), Al(5)–Al(8) = 2.795(2), Al(5)–C(10) = 2.020(5), Al(5)–C(40) = 2.015(5), Al(6)–Al(7) = 2.781(2), Al(6)–C(10) = 2.036(5), Al(6)–C(20) = 2.016(5), Al(7)–Al(8) = 2.780(2), Al(7)–C(20) = 2.005(5), Al(7)–C(30) = 2.021(5), Al(8)–C(30) = 2.037(5), Al(8)–C(40) = 2.013(5).

Increasing the excess of HCl did not result in complete consumption of **1**. Instead, the concentration of polyhalogenated byproducts increased. Five resonances in the ^1H NMR spectrum with an intensity ratio of 1:2:2:1:1 for the methyl groups attached to aluminum clearly show that the expected substitution of the bridging hydrogen atom did not occur. Its resonance is still present at δ 5.04, which is only slightly shifted compared to the corresponding signal of **1** (δ 5.23).¹ Thus, a remarkable and unexpected reaction occurred in which the proton did not attack the negatively charged hydrogen atom at the open face of the cluster; instead, a methyl group terminally attached to an aluminum atom at the opposite site of the cluster was replaced with release of methane. Thus, the chlorine atom does not occupy a bridging position between two or more aluminum atoms but prefers a terminal position. The unexpectedly different reaction behavior of HCl and $\text{HBF}_4 \cdot \text{OEt}_2$ may depend on the strength of these acids and the different Al–X bond energies, but we need to undertake more systematic studies to clearly answer that question. The replacement of one methyl group at the bottom of the cluster by a chlorine atom is in complete agreement with the NMR spectroscopic observation of five chemically different types of methyl groups. Single groups are attached to the atoms Al3, Al5, and Al7 (see Figure 2), while pairs of equivalent groups are at the opposite atoms (Al2, Al4) and (Al6, Al8), respectively. Despite the complicated molecular symmetry only a single resonance was observed in the ^{27}Al NMR spectrum (δ 132), which seems to have a

small line width ($W_{1/2} = 1500$ Hz). However, the signal has a very broad base covering a range of almost 150 ppm, which may indicate the overlap of several resonances.

The molecules of **6** showed a disorder in the solid state with the chlorine atom distributed over three positions attached to Al(1), Al(3), and Al(4). The molecule with the highest occupation factor (0.6) is shown in Figure 2. The structure of the cluster is almost unchanged in comparison with that of the starting compound **1**,¹ with the important restriction that only seven Al atoms are bonded to methyl groups, while one (Al(1)) is attached to a terminal chlorine atom. Thus, a methyl group at the closed part of the cluster is replaced, which may be caused by the higher electron density at positions completely enclosed in the electronically delocalized cluster bonding. The Al–Al distances at the hydrogen-bridged face of the cluster are very long (2.789 Å on average) compared to those of the remaining edges of the Al_8 cube (2.594 Å). The open face has a diamond-shaped distortion with two short (1.89 Å average) and two long Al–H distances (2.11(5) and 2.32(5) Å). The Al–C distances in the cluster (2.005(5)–2.129(6) Å) are longer than those observed to the terminal methyl groups. The shortest ones involved the aluminum atoms of the hydrogen-bridged face and the Al–C bonds to the carbon atom C(50) opposite to the bridging hydrogen atom. The introduction of the chlorine substituent seems to have no significant influence on the bond lengths in the cluster. Both compounds **4** and **6** are excellent starting materials for further investigations, and salt elimination reactions may provide access to a great variety of derivatives.

Quantum-Chemical Calculations. In contrast to **5**, the compound $(\text{AlEt})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CCH}_2\text{C}_6\text{H}_5)_3(\mu_3\text{-F})$ (**4**) did not give an observable resonance in the ^{19}F NMR spectrum in the expected range of -100 to -160 ppm. To verify that range for carbaalanes also, we carried out quantum-mechanical calculations on $(\text{AlH})_7(\text{C}=\text{CH}_2)_2(\text{CH})_3(\mu_3\text{-F})$ (**I**) and $(\text{AlH})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CH})_3(\mu_3\text{-F})$ (**III** and **IV**) as model clusters (see Figure 3) of the real cluster **4** and $(\text{AlH})_8(\text{CH})_5(\text{CH})_3\text{F}$ (**II**) as a model system of the impure product **5**. All calculations employed B3LYP hybrid density functional¹³ and standard double- ζ basis sets 6-31(G)d and 6-31+G(d).¹⁴ This theoretical model seems to be a reasonable compromise between accuracy and computer time in describing the fundamental properties of carbaalanes.³

In a first step, we did a full geometry optimization on structures **I** and **II** (see Figure 3) followed by calculations of the Hessian matrixes to characterize the nature of the stationary points. The B3LYP/6-31+G(d) optimized geometry of $(\text{AlH})_7(\text{C}=\text{CH}_2)_2(\text{CH})_3(\mu_3\text{-F})$ (**I**) (C_s

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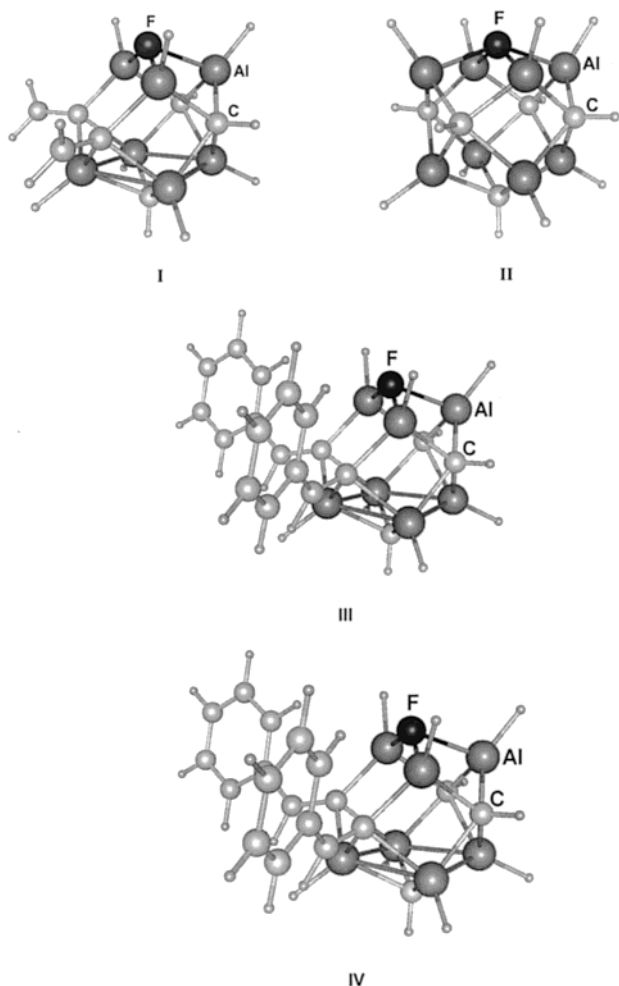


Figure 3. Optimized geometry of the model clusters $(\text{AlH})_7(\text{C}=\text{CHR})_2(\text{CH})_3(\mu_3\text{-F})$ (**I**, **III**, and **IV**; C_s symmetry) and $(\text{AlH})_8(\text{CH})_5(\text{F})$ (**II**; C_{4v} symmetry) at the B3LYP/6-31+G(d) level of theory.

symmetry) is a minimum on the potential energy surface (no imaginary frequencies). The equilibrium distances (1.968 and 2.131 Å) between the μ_3 -bridging F and the Al atoms are in agreement with experimental data. The B3LYP/6-31+G(d) optimized geometry of $(\text{AlH})_8(\text{CH})_5(\mu_4\text{-F})$ (**II**) in C_{4v} symmetry as a model system of the product $(\text{AlMe})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5\text{F}$ (**5**) shows three small ($<100\text{ cm}^{-1}$) imaginary frequencies. Releasing the symmetry constraint during the optimization moves the F atom from a symmetric μ_4 -bridging position (Al–F = 2.188 Å) to a pseudo μ_3 -bridging position (Al–F = 2.023, 2.133, 2.827 Å). This leads to a true minimum in C_s symmetry, which is 8.34 kcal/mol lower in energy than the C_{4v} symmetric third-order saddle point. Nevertheless, the calculated ^{19}F NMR resonance using the GIAO method¹⁵ is quite invariant (C_{4v} symmetry, –153 ppm; C_s symmetry, –148 ppm). Taking into account the simplicity of our model system compared to the real compound $(\text{AlMe})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5\text{F}$ (**5**) ($\delta(^{19}\text{F})$ –121 ppm), the agreement is quite good. A similar chemical shift of –160 ppm was calculated for the ^{19}F NMR resonance in $(\text{AlH})_7(\text{C}=\text{CH}_2)_2(\text{CH})_3(\mu_3\text{-F})$ (**I**) as a model compound of **4**. This verifies that we have to expect the ^{19}F

resonance of **4** in the characteristic range of Al–F compounds. The fact that we did not observe a signal may thus indeed be the consequence of an unusually strong line broadening.

In a second step, we augmented our model system and included the phenyl rings on the C=C double bonds in order to model their electronic effects on the ^{19}F shielding in $(\text{AlH})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CH})_3(\mu_3\text{-F})$ (**III**). We had to reduce the diffuse functions to a 6-31G(d) basis because of limited computing power. Starting with the X-ray geometry of $(\text{AlEt})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CCH}_2\text{C}_6\text{H}_5)_3(\mu_3\text{-F})$ (**4**), we generated our model cluster **III** (see Figure 3) in C_s symmetry. A full geometry optimization was done, ending up with the stationary point **IV**, which was characterized as a true minimum (no imaginary frequencies). According to our calculations, the ^{19}F NMR shift is more or less invariant (cluster **III**, –155 ppm; cluster **IV**, –162 ppm) to the presence or orientation of the C=CHC₆H₅ phenyl rings.

Experimental Section

All procedures were carried out under purified argon. *n*-Pentane and cyclopentane were dried over LiAlH_4 and toluene and diethyl ether over Na/benzophenone. The carbaalanes $(\text{AlMe})_8(\text{CCH}_2\text{C}_6\text{H}_5)_5\text{H}$ (**1**) and $(\text{AlEt})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CCH}_2\text{C}_6\text{H}_5)_3\text{H}$ (**2**) were synthesized according to literature procedures.^{1,2} Commercially available solutions of HBF_4 (54%) and HCl (1 M) in diethyl ether (Aldrich) were used without further purification. ^1H and ^{13}C NMR spectra were recorded on a 500 MHz NMR spectrometer at room temperature. ^{19}F NMR spectra were recorded on a 300 MHz NMR spectrometer. ^{27}Al NMR spectra were taken on a 400 MHz spectrometer. The resonances were assigned on the basis of ^1H , ^{13}C , ^{19}F , H–H-COSY, HMQC, and HMBC spectra. Shifts are reported on the δ scale in ppm relative to residual nondeuterated solvent signals (^1H) or the signals of the deuterated solvent (^{13}C) as internal standards and relative to CFCl_3 as external standard in case of the ^{19}F NMR experiments or relative to $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ as external standard for ^{27}Al NMR spectra.

Synthesis of the Fluorocarbaalane $(\text{AlEt})_7(\text{C}=\text{CHC}_6\text{H}_5)_2(\text{CCH}_2\text{C}_6\text{H}_5)_3\text{F}$ (4**).** $(\text{AlEt})_7(\text{C}=\text{CHPh})_2(\text{CCH}_2\text{Ph})_3\text{H}$ (**2**; 1.501 g, 1.66 mmol) was dissolved in 50 mL of diethyl ether and cooled to -50°C . One equivalent (227 μL) of a 54% solution of tetrafluoroboric acid in diethyl ether was added slowly. Gas evolution was observed, and a light orange solid precipitated. After the mixture was warmed to room temperature, the solvent was distilled off under vacuum. The highly viscous residue was thoroughly evacuated to completely remove all volatile impurities. It was treated with cyclopentane to give a suspension of a light orange solid, which was filtered. That solid was insoluble in organic solvents and was not characterized further. The filtrate was concentrated and cooled to -30°C . The orange product **4** precipitated, which is very hygroscopic and rapidly decomposes in solution in daylight. Yield: 0.722 g (48%). Dec pt (argon, sealed capillary): 160°C . Anal. Calcd for $\text{C}_{54}\text{H}_{68}\text{Al}_7\text{F}$ (925.0): Al, 20.4; C, 70.1; H, 7.4. Found: Al, 20.1; C, 70.5; H, 7.3. Molar mass (cryoscopically in benzene): found m/e 907. ^1H NMR (d_6 -toluene, 500 MHz; δ): benzyl group at C1, 7.51 (2 H, m, *o*-H), 7.30 (2 H, m, *m*-H), 7.15 (1 H, m, *p*-H), 3.68 (2 H, s, CH_2); benzyl groups at C2, 7.38 (4 H, m, *o*-H), 7.22 (4 H, m, *m*-H), 7.10 (2 H, m, *p*-H), 3.47 (2 H, dd, CH_2 , $^2J_{\text{HH}} = -13.7\text{ Hz}$, $^4J_{\text{HF}} = 4.3\text{ Hz}$), 3.42 (2 H, dd, CH_2 , $^2J_{\text{HH}} = -13.7\text{ Hz}$, $^4J_{\text{HF}} = 9.0\text{ Hz}$); C=CHPh groups: 7.18 and 7.06 (m, C_6H_5 , further assignment uncertain), 9.28 (2 H, s, C=CH); ethyl group at Al1*, 1.20 (3 H, t, $^3J_{\text{HH}} = 8.1\text{ Hz}$, CH_3), 0.12 (2 H, q, $^3J_{\text{HH}} = 8.1\text{ Hz}$, CH_2); ethyl groups at Al2 and Al2', 1.20 (6 H, dd, $^3J_{\text{HH}} = 8.1$ and 8.1 Hz , CH_3), 0.62 and 0.48 (each 2 H, dq, $^2J_{\text{HH}} = -14.5\text{ Hz}$, $^3J_{\text{HH}} = 8.1\text{ Hz}$,

(15) Wolinski, K.; Hilton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

CH_2); ethyl group at Al3*, 1.40 (3 H, t, $^3J_{\text{HH}} = 8.1$ Hz, CH_3), 0.75 (2 H, q, $^3J_{\text{HH}} = 8.1$ Hz, CH_2); ethyl group at Al4*, 1.32 (3 H, t, $^3J_{\text{HH}} = 8.1$ Hz, CH_3), 0.53 (2 H, q, $^3J_{\text{HH}} = 8.1$ Hz, CH_2); ethyl groups at Al5 and Al5', 0.64 (6 H, dd, $^3J_{\text{HH}} = 8.1$ and 8.1 Hz, CH_3), 0.01 and -0.18 (each 2 H, dq or m, $^2J_{\text{HH}} = -14.9$ Hz, $^3J_{\text{HH}} = 8.1$ Hz, the second resonance shows $^3J_{\text{HF}} = 11.2$ Hz, CH_2); (the asterisks denote the fact that some uncertainties exist concerning the individual assignment of the ethyl groups). ^{13}C NMR (d_8 -toluene, 125.8 MHz; δ): benzyl group at C1, 148.8 (*i*-C), 128.5 (*o*-C), 129.2 (*m*-C), 126.3 (*p*-C), 35.7 (CH_2); benzyl groups at C2 and C2', 148.7 (*i*-C), 128.5 (*o*-C), 129.8 (*m*-C), 126.7 (*p*-C), 34.3 (CH_2); phenyl groups at C300 and C300', 142.3 (*i*-C), 130.6, 129.2, 128.6, 128.3 and 125.5 (phenyl, individual assignment not possible), 184.2 ($\text{C}=\text{CHPh}$); ethyl group at Al1*, 10.0 (CH_3), 2.1 (CH_2); ethyl groups at Al2 and Al2', 10.2 (CH_3), 2.8 (CH_2); ethyl group Al3*, 10.5 (CH_3), 0.7 (CH_2); ethyl group at Al4*, 9.2 (CH_3), 2.1 (CH_2); ethyl groups at Al5 and Al5', 7.6 (CH_3), 3.1 (CH_2 , $^2J_{\text{CF}} = 17$ Hz); 32.5 (C1), 39.6 (C2, $^2J_{\text{CF}} = 11$ Hz), 156.2 ($\text{C}=\text{C}$, $^2J_{\text{CF}} = 23$ Hz) (the asterisks denote uncertain assignments). ^{27}Al NMR (d_8 -toluene, 104 MHz; δ): δ 110 (sh), 74 ($W_{1/2} = 12$ 000 Hz), 20 (sh), -28 ($W_{1/2} = 10$ 000 Hz). IR (CsBr plates, paraffin, cm^{-1}): 1945 vw, 1873 vw, 1798 vw, 1683 vw, 1598 w (phenyl); 1578 w $\nu(\text{C}=\text{C})$; 1505 m $\delta(\text{CH})$, 1457 vs, 1377 vs (paraffin); 1302 m, 1224 w, 1196 w, 1169 m, 1155 m $\delta(\text{CH})$, $\nu(\text{CC})$; 1074 w, 1029 w $\nu(\text{CC})$; 977 m, 957 br m, 930 sh, m, 907 m, 835 w (phenyl); 747 s $\delta(\text{Ph})$; 721 vs; 705 sh, s, 690 m Al-C and C-C bending modes; 653 br s, 609 m, 558 m $\delta(\text{Ph})$, $\nu(\text{AlC})$; 502 w, 474 m, 447 m, 365 br w, 288 w $\nu(\text{AlC})$, $\nu(\text{AlF})$.

Synthesis of the Impure Fluorocarbaalane (AlMe) $_8$ -(CCH $_2$ C $_6$ H $_5$) $_5$ F (5). The *arachno*-carbaalane (AlMe) $_8$ (CCH $_2$ C $_6$ H $_5$) $_5$ H $\cdot$ 0.5(cyclopentane) (**1**; 0.638 g, 0.72 mmol) was dissolved in 25 mL of diethyl ether and cooled to -50 $^\circ\text{C}$. At this temperature **1** partially precipitated. One equivalent (98 μL) of a 54% solution of tetrafluoroboric acid in diethyl ether was added slowly. Gas evolution occurred, and the precipitate dissolved upon warming to room temperature. The mixture was stirred for 4 h. A small quantity of a colorless solid precipitated, which was filtered. The solvent was removed in vacuo, and the residue was recrystallized from toluene ($+20$ to -30 $^\circ\text{C}$). An amorphous solid was obtained which contains up to 30% of the starting cluster **1**. Many attempts at recrystallization from different solvents gave no enrichment of **5**. The NMR data for **5** were recorded by employing such a mixture. ^1H NMR (C_6D_6 , 500 MHz; δ): four equivalent benzyl groups, 7.13–6.99 (20 H, m, phenyl groups, no individual assignment owing to overlap), 3.01 (8 H, d, $^4J_{\text{HF}} = 6.4$ Hz, CH_2); benzyl group opposite to the fluorine atom, 7.51 (2 H, m), 7.36 (2 H, m), 7.21 (1 H, m), 3.53 (2 H, s, CH_2); methyl groups of Al atoms attached to fluorine, -0.67 (12 H, d, $^3J_{\text{HF}} = 4.3$ Hz); remaining methyl groups, -0.27 (12 H, s). ^{13}C NMR (C_6D_6 , 125.8 MHz; δ): four equivalent benzyl groups, 148.4 (*i*-C), 130.2, 128.0, 126.6, 34.9 (CH_2); benzyl group opposite to the fluorine atom, 148.1 (*i*-C), 129.4, 129.2, 126.2, 35.1 (CH_2); methyl groups of Al atoms attached to fluorine, -11.0 ($^2J_{\text{CF}} = 12.7$ Hz); methyl groups at the remaining Al atoms, -9.1 ; cluster carbon atoms, 38.7 ($^2J_{\text{CF}} = 13.6$ Hz, four equivalent C atoms), 10.0. ^{19}F NMR (C_6D_6 , 282 MHz; δ): -121.4 . ^{27}Al NMR (C_6D_6 , 104 MHz; δ): 62 ($W_{1/2} = 6500$ Hz), -48 ($W_{1/2} \approx 13$ 000 Hz).

Synthesis of the Chlorocarbaalane (AlMe) $_7$ (AlCl)-(CCH $_2$ C $_6$ H $_5$) $_5$ H (6). 1 $\cdot$ 0.2(cyclopentane) (0.594 g, 0.69 mmol) was dissolved in 30 mL of diethyl ether and cooled to -70 $^\circ\text{C}$. That solution was treated with 1.2 equiv (0.82 mL) of a 1 M solution of HCl in diethyl ether. Gas evolution was observed. The mixture was slowly warmed to -20 $^\circ\text{C}$, and all volatile components were distilled at this temperature. Higher temperatures gave secondary reactions, yielding a mixture of products which could not be separated. After evaporation of all volatiles the product is stable in solution at room temperature. The colorless residue was thoroughly evacuated, dis-

Table 1. Crystal Data, Data Collection Parameters, and Structure Refinement Details for Compounds **4 and **6****

	4	6
formula	$\text{C}_{54}\text{H}_{68}\text{Al}_7\text{F}$	$\text{C}_{52}\text{H}_{57}\text{Al}_8\text{Cl}$
cryst syst	orthorhombic	triclinic
space group	$Pnma$; No. 62 ¹⁶	$P\bar{1}$; No. 2 ¹⁶
<i>Z</i>	4	2
temp, K	193(2)	193(2)
D_{calcd} , g/cm ³	1.187	1.195
<i>a</i> , Å	20.0859(7)	11.833(2)
<i>b</i> , Å	17.1674(7)	13.386(4)
<i>c</i> , Å	15.0162(6)	16.716(5)
α , deg	90	81.90(2)
β , deg	90	82.41(2)
γ , deg	90	85.48(2)
<i>V</i> , 10 ⁻³⁰ m ³	5177.9(3)	2593.5(12)
μ , mm ⁻¹	0.179	0.242
cryst dims, mm	0.55 $\times$ 0.45 $\times$ 0.40	0.55 $\times$ 0.40 $\times$ 0.25
radiation	Mo K α ; graphite monochromator	
2 θ range, deg	4.06–52.00	5.38–49.94
index ranges	$-24 \leq h \leq 24$ $-21 \leq k \leq 21$ $-18 \leq l \leq 18$	$-10 \leq h \leq 0$ $-11 \leq k \leq 11$ $-14 \leq l \leq 14$
no. of unique rflns	5222 ($R_{\text{int}} = 0.0825$)	6434 ($R_{\text{int}} = 0.0465$)
no. of params	306	566
$R1$ (rflns $I > 2\sigma(I)$)	0.0678	0.0741
$wR2$ (all data)	0.1962	0.1984
max/min residual	0.893/ -0.546	0.692/ -0.601
electron density, 10 ³⁰ e/m ³		

solved in toluene, and filtered. A colorless, crystalline solid, **6**, was obtained upon cooling the solution to -30 $^\circ\text{C}$. The product contained about 10% of the starting compound **1**. We did not succeed in reducing the concentration of that impurity by repeated recrystallization from different solvents. Yield: 0.335 g (56%). ^1H NMR (C_6D_6 , 500 MHz; δ): phenyl groups (a), 7.73 (2 H, m, *o*-H), 7.35 (2 H, m, *m*-H), 7.19 (1 H, m, *p*-H); phenyl groups (b), 7.31 (4 H, m, *o*-H), 7.13 (4 H, m, *m*-H), 7.01 (2 H, m, *p*-H); phenyl groups (c), 7.09 (4 H, m, *o*-H), 7.05 (4 H, m, *m*-H), 6.97 (2 H, m, *p*-H), further assignment uncertain; 3.70 (2 H, s, CH_2 and C50); remaining CH_2 groups, 3.46 and 2.94 (each 2 H, d, $^2J_{\text{HH}} = 14.0$ Hz), 3.06 and 2.95 (each 2 H, d, $^2J_{\text{HH}} = -13.5$ Hz); methyl groups at Al3, Al5, and Al7, -0.26 , -0.81 , and -1.21 (each 3 H, s); remaining methyl groups, -0.46 and -0.49 (each 6 H, s); 5.04 (1 H, s, AlH). ^{13}C NMR (C_6D_6 , 125.8 MHz; δ): δ 148.1, 148.0, 147.70, 147.67, 137.8, 130.3, 130.1, 130.0, 129.5, 129.4, 129.4, 129.3, 128.5, 127.8, 126.8, 126.7, 126.6, 126.3, 125.6 (phenyl, further assignment uncertain); 34.9 (CH_2 at C50), remaining CH_2 groups, 34.7 and 33.8; cluster carbon atoms, 34.5 and 29.4, one resonance is missing; methyl groups, -11.3 , -11.8 , and -12.3 (Al3, Al5, Al7), -12.4 and -12.9 (Al2, Al4, Al6, Al8). ^{27}Al NMR (C_6D_6 , 104 MHz; δ): δ 132 ($W_{1/2} = 1500$ Hz). IR (CsBr plates, paraffin, cm^{-1}): 1599 m, 1582 vw (phenyl); 1491 s ($\delta(\text{CH}_3)$); 1453 vs, 1377 vs (Nujol); 1301 m, 1190 s, 1154 m, 1075 w, 1029 w ($\nu(\text{CC})$); 1003 vw, 961 s, 933 m, 906 m, 823 m (phenyl); 751 vs, 712 vs, 690 vs ($\delta(\text{Ph})$, $\nu(\text{AlC})$); 586 m, 552 m, 530 m ($\nu(\text{AlC})$); 504 m, 464 m ($\nu(\text{AlCl})$); 450 vw, 429 m ($\nu(\text{AlC})$).

Crystal Structure Determinations. Single crystals of compound **4** were obtained by very slow concentration of a solution in cyclopentane at room temperature. Extraction of solid **6** with *n*-pentane and cooling of the solution to 0 $^\circ\text{C}$ gave single crystals in trace amounts. The crystallographic data of compounds **4** and **6** were collected with a STOE imaging plate diffractometer and the four-cycle CAD 4 diffractometer, respectively. Relevant crystal data, data collection parameters, and results of the structure refinement are summarized in Table 1. The structures were solved by direct methods and refined with the program SHELXL-97¹⁷ by a full-matrix least-

squares method based on F^2 . Compound **6** showed a disorder of the chlorine atom with three distinct positions: Al(1)–Cl(1) (occupation factor 61%), Al(3)–Cl(3) (16%), and Al(4)–Cl(4) (21%). The corresponding carbon and chlorine positions as well as the occupation factors were refined with restrictions of bond lengths. One *n*-pentane molecule was enclosed per formula unit of **6**.

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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-158662 (**4**) and CCDC-158663 (**6**).

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