New Carbaalanes − $(AlMe)_8(CCH_2Me)_5(C{\equiv}C{-}Me)$ and the THF Adduct $(AlMe)_8(CCH_2Me)_5H{\cdot}2THF$

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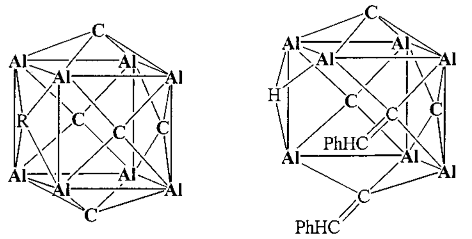
The hydroalumination of $Me_2Al{-}C{\equiv}C{-}Me$ with a large excess of Me_2AlH afforded the *arachno*-carbaalane $(AlMe)_8(CCH_2Me)_5H$ (**4**) by the release of $AlMe_3$. **4** is almost insoluble in noncoordinating solvents and could not be purified by recrystallization. On an attempt to recrystallize **4** from a THF solution, the adduct $(AlMe)_8(CCH_2Me)_5H{\cdot}2THF$ (**5**) was isolated as the first stable ether adduct of a carbaalane. Crystal structure determination revealed a cube of eight aluminium atoms, five faces of which are bridged by $C{-}CH_2Me$ groups. The sixth face is μ_2-bridged by a hydrogen atom, and two opposite aluminium atoms of this face are coordinated by one THF ligand each. When the excess of dimethylaluminium hydride was reduced and the starting compounds were employed in a 1:2.1 molar ratio, an incomplete hydroalumination reaction led to the formation of the carbaalane $(AlMe)_8(CCH_2Me)_5(\mu{-}C{\equiv}C{-}Me)$ (**6**), in which the bridging hydrogen atom of **4** is replaced by an alkynido group. ^{27}Al NMR spectroscopic data of all the characterized carbaalanes are reported and supplemented by ^{27}Al NMR chemical shift calculations.

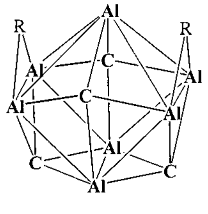
Introduction

Carbaalanes[1] constitute a new class of compounds containing clusters of aluminium and carbon atoms. They are easily obtained by hydroalumination of dialkylaluminium alkynides using an excess of the corresponding dialkylaluminium hydride.[2−4] Two completely different structure types have so far been observed. One may be described by a cube of eight aluminium atoms (**1**, Scheme 1), the six faces of which are occupied by five $C{-}CH_2{-}R$ groups and one hydrido or alkynido ligand. Compound **2** (Scheme 1) may be derived from this cubic arrangement, but it has a unique structure with one vertex unoccupied and possesses only seven aluminium atoms. The three remaining Al_4 faces are still occupied by $C{-}CH_2{-}R$ groups, while the open site of the cluster is coordinated by one hydrogen atom and two alkenido ligands containing $C{=}C$ double bonds. This structure results from an incomplete hydroalumination reaction, and the formal addition of one equivalent of ethylaluminium dihydride to complete the Al_8 cube is missing. The second principal type of carbaalane has a *closo*-configuration on the basis of its structure and electron count (**3**; Scheme 1) and is a remarkable analogue of the *closo*-borate anion $[B_{11}H_{11}]^{2-}$.[5] The bonding situation in the carbaalanes has been studied by quantum-chemical calculations.[4] They revealed a delocalized multi-centre bonding with only weak direct $Al{-}Al$ interactions. We report herein on the synthesis and structure of further carbaalane derivatives and their characterization by ^{27}Al NMR spectroscopy.



1 (**Al** = AlMe, AlEt; **C** = CCH_2Ph; R = H, CCPh)

2 (**Al** = AlMe; **C** = CCH_2Ph)



3 (**Al** = AlMe, AlEt; **C** = CCH_2Ph, CCH_2CH_3; R = H, CCPh)

Scheme 1

Results and Discussion

Synthesis of $(AlMe)_8(CCH_2Me)_5H$ (4) and its THF Adduct (5)

The reaction of dimethyl(propynyl)aluminium with a large excess of dimethylaluminium hydride has been re-

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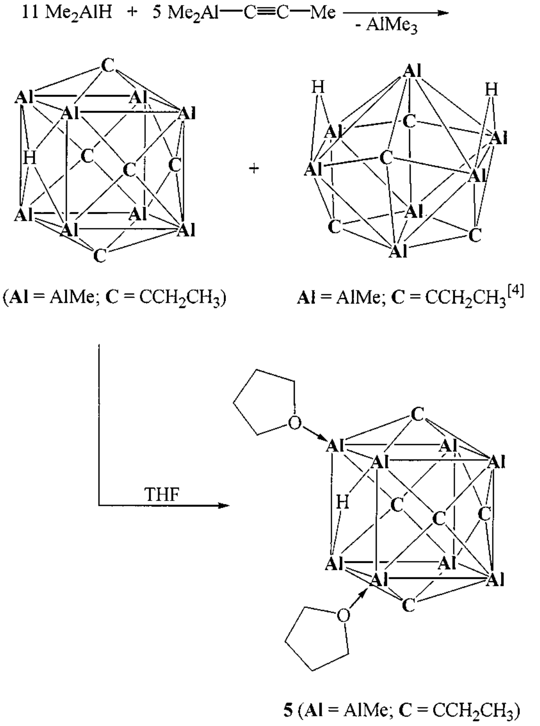
ported by our group only recently.[4] As a main product, we isolated the heptaaluminium carbaalane $(AlMe)_7(CCH_2Me)_4H_2$ in 63% yield, which possesses the *closo*-structure **3** shown in Scheme 1. In all of these reactions, we observed the formation of a hitherto uncharacterized by-product [**4**; Equation (1)], which is almost insoluble in nonpolar solvents such as pentane or toluene and could not be purified by recrystallization. It was isolated as an amorphous and highly pyrophoric powder in about 30% yield. Owing to its insolubility and unknown purity, **4** was characterized only by its ^1H NMR spectrum, which was recorded from a very dilute solution in [D_6]benzene. The data obtained were clearly indicative of an *arachno*-type structure similar to compound **1** in Scheme 1. Two resonances of equal intensity were observed for the methyl groups attached to aluminium in a quite normal range (δ = −0.20 and −0.15). The signal of the hydrogen atom bridging an Al_4 face of the cluster is shifted downfield (δ = 5.68) compared to that in dialkylaluminium hydrides containing μ_2-bridging hydrogen atoms in four- or six-membered heterocycles.[6] A similar shift has been observed in all carbaalanes isolated to date. Two triplets (δ = 1.04 and 1.33) and two quadruplets (δ = 1.93 and 2.33), each pair with an intensity ratio of 4:1, were observed for the ethyl substituents of the cluster carbon atoms. These observations are in accordance with the proposed *arachno* structure, in which four of these substituents are adjacent to the hydrogen-bonded face, while one is opposite to this face.



(1)

All attempts to recrystallize **4** from dilute solutions in noncoordinating solvents failed. In some cases, we were able to successfully recrystallize carbaalanes from THF, in which they are usually quite soluble and they do not form any kind of stable THF adduct. Clearly, the aluminium atoms of the carbaalanes are such weak Lewis acids that the coordination of THF molecules even at the open faces of these clusters has never previously been observed. Upon treatment of **4** with THF and slow evaporation of the solvent at room temperature, we obtained colourless crystals. However, an X-ray structure determination (see below) showed that a THF adduct of compound **4** had been formed in which two opposite aluminium atoms of the hydrogen-bonded face of the cluster were each coordinated by one THF molecule [**5**; Equation (1)]. The ether molecules are tightly bound to the aluminium atoms, and no dissociation was observed upon storing of the crystals in vacuo at 10^{-3} Torr and 50 °C. Compound **5** is thermally very stable and does not decompose at temperatures below 260 °C. The NMR spectroscopic characterization in [D_8]THF at room temperature showed two quite narrow singlets due to the methyl groups attached to aluminium, two triplets and two quadruplets (each pair with an intensity ratio of 4:1) due to the ethyl substituents bound to the cluster carbon atoms, and one singlet due to the bridging hydrogen atom. The chemical shift of the latter (δ = 4.19) shows the most significant deviation from the resonances of the starting compound **4** and is closer to the shifts normally observed for alkylaluminium hydrides. The cluster carbon atoms exhibit chemical shifts of δ = 20.5 and 21.5, which are strongly downfield shifted compared to the resonances normally observed with coordinatively saturated aluminium atoms (δ = −8.8 and −9.4 for the terminal methyl groups) and may be caused by the particular delocalized bonding situation in these clusters. Two resonances were observed in the ^{27}Al NMR spectrum (δ = 155 and 56), which are discussed in more detail below. Two THF molecules were detected for each formula unit of **5**, in accordance with the result of the crystal structure determination. More complicated NMR spectra were expected in view of the molecular symmetry detected in the solid state, indicating a fast exchange process in THF solution at room temperature. This process is frozen only at very low temperatures, and at −110 °C a splitting of both methyl resonances was observed [δ = −0.41 and −0.56 (coalescence at about 225 K) and δ = −0.49 and −0.51 (coalescence at about 202 K)]. The activation barrier was estimated[7] from these data to be about 45 kJ mol^{-1}.

A crystal structure determination of **5** revealed a structure similar to that of **1**[2,4] (Figure 1) with a cube of eight aluminium atoms. However, two opposite aluminium atoms of the hydrogen-bonded face are coordinated by a THF molecule. The Al−C distances to the terminal methyl groups (average 196.8 pm) do not depend on the coordination sphere of the aluminium atoms and are shorter than those within the cluster (203.8 to 213.3 pm). The Al−Al separations are 293.4 pm at the hydrogen-bonded face and 258.3 pm for the remaining eight edges of the Al_8 cube. The latter are similar to those observed for 3c−2e Al−X−Al interactions (X = H, CH_3)[8] and are shorter than those of Al−Al single bonds in tetraalkyldialuminium(4) derivatives $R_2Al-AlR_2$.[9] All these parameters were similarly determined in carbaalanes of type **1**.[2,4] The most notable devi-

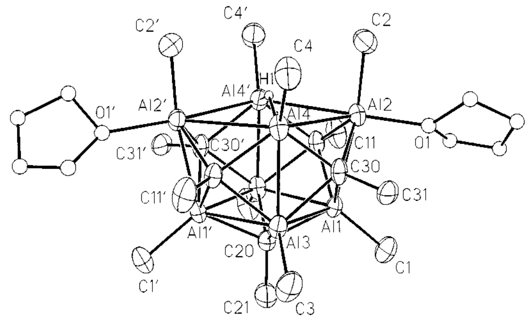
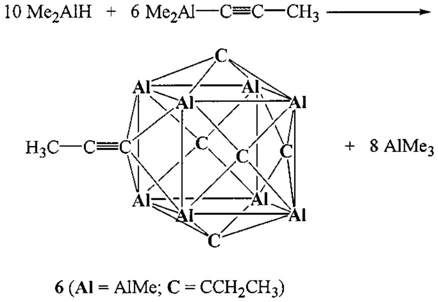


Figure 1. Molecular structure and numbering scheme for compound **5**; thermal ellipsoids are drawn at a 40% probability level; methyl groups have been omitted for clarity; hydrogen atoms are drawn with arbitrary radii; selected bond lengths (pm): Al-1−C-1 196.8(3), Al-2−C-2 197.5(4), Al-3−C-3 196.4(3), Al-4−C-4 196.3(3), Al-1−C-10 210.7(3), Al-1−C-20 205.7(2), Al-1−C-30 209.4(3), Al-2−O-1 197.9(2), Al-2−C-10 204.4(3), Al-2−C-30 205.5(3), Al-3−C-20 203.8(2), Al-3−C-30 211.5(3), Al-3−C-10′ 213.3(3), Al-4−C-30 204.8(3), Al-4−C-10′ 205.7(3), Al-4−H-1 173(1), Al-1−Al-2 259.3(1), Al-1−Al-3 258.4(1), Al-1−Al-3′ 258.4(1), Al-2−Al-4 293.0(1), Al-2−Al-4′ 293.7(1), Al-3−Al-4 257.1(1); C-10′ and Al-3′ were generated by $-x + 3/2, y, -z + 1/2$

ation from these recently published structures is a greater distortion of the hydrogen-bonded face with strongly differing transannular Al−Al distances of 483.2 pm (Al2−Al2′, unsupported) and 331.8 pm (Al4−Al4′, hydrogen bonded). The latter distance resembles that in the trimeric compound $[(Me_3C)_2AlH]_3$ containing a six-membered Al_3H_3 heterocycle with three μ_2-bridging hydrogen atoms.[10] The THF molecules are bound to the aluminium atoms Al2 and Al2′ with relatively long Al−O "dative" distances of 197.9 pm.[11] The oxygen atoms of the ether molecules lie slightly below the plane spanned by the four aluminium atoms of the hydrogen-bonded face of the cluster (37.6 pm; angle Al2′···Al2−O1 9.6°). Owing to this lateral coordination of THF, the Al(2)−C bonds are almost perpendicular to this plane (angle Al2′···Al2−C2 94.5°; for comparison Al4′···Al4−C4 54.4°).

Synthesis of $(AlMe)_8(CCH_2Me)_5(\mu\text{-}C{\equiv}C{-}Me)$ (6)

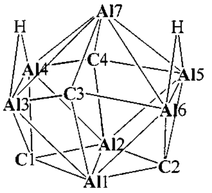
In a further reaction, we reduced the excess of dimethylaluminium hydride from about 6:1 required for the synthesis of **4** and **5** according to Equation (1) to a molar ratio of only 2.1:1. Once again, a strongly exothermic reaction was observed on stirring a mixture of the hydride and the alkynide at room temperature without a solvent and a bright-yellow solid precipitated. After 1 h at room temperature, all volatile components ($AlMe_3$) were distilled off in vacuo and the yellow residue was recrystallized from warm toluene. Bright-yellow crystals of compound **6** were isolated in 39% yield after cooling to −30 °C [Equation (2)]. According to the NMR spectra, the mother liquors still contained considerable quantities of **6**, but in all cases we were unable to isolate a second pure fraction. Compound **6** was identified as the carbaalane $(AlMe)_8(CCH_2Me)_5(\mu\text{-}C{\equiv}C\text{-}Me)$, which is similar to compound **4** but has a bridging propynido group instead of the bridging hydrogen atom. The formation of **6** according to Equation (2) requires a stoichiometric ratio of the starting compounds of 1 (alkynide) to 1.7 (hydride). Thus, we still employed a slight excess of the hydride, but further reduction of the hydride concentration did not result in an improved yield of **6**.



(2)

An absorption at 2019 cm^{-1} was detected in the IR spectrum due to the stretching vibration of the C≡C triple bond. Compared to the corresponding vibration of the starting compound $Me_2Al{-}C{\equiv}C{-}Me$ (2109 cm^{-1}),[4] a shift of about 90 cm^{-1} to lower wavenumbers was observed. An even lower value (1957 cm^{-1}) was found for a similar compound with benzyl instead of ethyl groups bound to the cluster carbon atoms.[4] In this case, the weakening of the C≡C triple bond, which may be caused by the particular μ_4-bridging arrangement in the cluster, was also verified by an increased C−C bond length and by quantum chemical calculations.[4] NMR spectroscopic characterization proved quite difficult owing to the very low solubility of **6** in organic solvents. In contrast to compound **4**, small quantities of **6** could be dissolved and handled in THF at room temperature without the formation of a stable ether adduct; thus, all spectra were recorded in dilute [D$_8$]THF solutions. The terminal methyl groups attached to aluminium exhibit two equivalent resonances in the expected ranges of the ^1H and ^{13}C NMR spectra ($\delta = -0.36, -0.44$ and $\delta = -7.7, -8.9$, respectively). The cluster carbon atoms resonate at $\delta = 21.5$ and 17.5, which, as discussed above, is further downfield than expected, and a shift of $\delta = 88.2$ was observed for the bridging carbon atom of the propynido ligand ($\delta = 117.0$ in the benzyl compound cited above).[4] Only one resonance was observed in the ^{27}Al NMR spectrum ($\delta = 153$); a shoulder may be present at $\delta \approx 130$ owing to a marked asymmetry of this signal (see below). A crystal structure determination of **6** revealed a strong disorder of the propyne group, which partially occupies all faces of the Al_8 cube (not shown). As a result of this disorder, an almost undistorted cube of eight aluminium atoms is obtained, with an average Al−Al distance of 265.8 pm; this represents a reasonable mean value between the three different distances expected for a regular structure, as discussed previously for compound **5** and the corresponding benzyl derivative.[4]

In contrast to the dimethylaluminium starting compounds, the sterically slightly more shielded ethyl derivatives diethylaluminium hydride and diethylaluminium propynide do not react exothermically at room temperature. The mixture was heated to 50 °C without a solvent for 18 h to complete the reaction. As expected, triethylaluminium was formed, which was distilled off in vacuo. An orange residue remained, which, according to its ^{1}H NMR spectrum, contained a carbaalane cluster accompanied by a considerable amount of impurities. However, we did not succeed in isolating a pure component by recrystallization or sublimation. Moreover, the sterically more shielded diisopropyl derivatives did not react exothermically at room temperature and had to be stirred at 50 °C for 18 h to complete the reaction. Owing to the low volatility of triisobutylaluminium, the mixture was subsequently heated in vacuum to 80 °C for 2 h to completely remove this by-product. The oily, light-yellow residue was redissolved in diisopropyl ether. After several weeks at −70 °C, only trace amounts of a colourless solid (**7**) were isolated. On the basis of the results of the NMR spectroscopic characterization (see Exp. Sect.), we suppose that **7** has a *closo*-type structure (Scheme 2) with two opposite Al−Al edges bridged by hydrogen atoms. As required by such a structure, we observed three clearly resolved ^{27}Al NMR resonances (see below). Single crystals suitable for a crystal structure determination were not obtained. A concentrated solution of bis(*tert*-butyl)aluminium hydride and the corresponding propynylaluminium compound in toluene was heated for 20 h at 50 °C. NMR spectroscopic monitoring of the reaction showed the complete consumption of the starting compounds, but no evidence was found for the formation of a carbaalane cluster. Despite many attempts to recrystallize the crude product from various solvents, we did not succeed in isolating any pure component of the mixture.



7 (**Al** = Al*i*Pr; **C** = CCH_2CH_3)

Scheme 2

^{27}Al NMR Spectra of Carbaalanes

For the first time, we have investigated the ^{27}Al NMR spectra of carbaalanes in a systematic manner. ^{27}Al NMR shifts are known to be very sensitive to the coordination sphere at the central aluminium atoms, and coordination numbers of three, four, five, or six give characteristic shifts of $\delta \approx 270$, 170, 120, and 0, respectively.[12] Furthermore, ^{27}Al NMR chemical shifts, in combination with quantum chemical NMR shift calculations, have previously been shown to be useful for the identification and characterization of aluminium cluster compounds.[13−15] However, the unequivocal interpretation of ^{27}Al NMR spectra is difficult owing to the quadrupole moment of aluminium and the usually broad line width of the resonances. The overlap of signals often prevents a clear assignment, especially in those cases in which chemically different aluminium atoms are present, as in the carbaalanes.

To facilitate the interpretation of the experimental spectra, we performed quantum chemical ^{27}Al NMR shift calculations for most of the carbaalanes under consideration and in this way investigated the usefulness of ^{27}Al NMR spectroscopy for the identification and characterization of carbaalanes. The results of the experimental and the computational investigations are summarized in Table 1. Experimentally, only one broad resonance is observed for most carbaalanes; this is in line with the calculations, which yield values within the rather narrow range of $\delta = 150$ to 210 for the ^{27}Al chemical shifts of all the considered carbaalanes. In some cases, shoulders could be identified, but it seems that in most cases these result from strong anisotropies of the main resonances.

As expected, the *arachno*-type compounds exhibit two Al NMR signals, which are found experimentally at around $\delta = 80$ and 140, while the calculations predict values around $\delta = 160$ and 180 to $\delta = 210$. According to the calculations, the ^{27}Al signal at lower field corresponds to the aluminium atoms close to either the bridging hydrogen atom or the bridging CCR group. The signal shows a slight, though not very pronounced, dependence on the bridging group. The resonances at higher field on the other side are due to the remaining aluminium cluster atoms. They appear to be rather insensitive to the nature of the bridging group and the substituents at the carbon atoms in the cluster.

In principle, the more open alkenido derivatives have five distinct aluminium atoms. The calculations predict ^{27}Al NMR signals for these in the range $\delta = 155$ to 172. Only for the F-containing derivative are higher values of $\delta = 184$ and 200 found for the aluminium atoms close to the bridging fluorine atom. Experimentally, very broad resonances with one (R = H) or two maxima (R = F) are observed. One of the resonances of the fluorine derivative has quite an unusual chemical shift of $\delta = -28$.

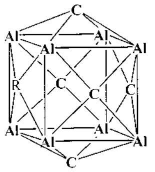
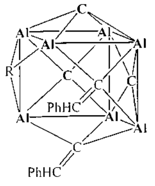
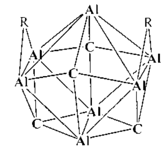
For the *closo* form, the calculations again predict values in the range of $\delta = 150$ to 170. The experimental value of $\delta = 157$ for one of the carbaalanes seems to be in satisfactory agreement with the theoretical predictions. However, three clearly resolved resonances ($\delta = 145$, 79, and -38) are observed for **7**.

Overall, it appears that the ^{27}Al NMR spectra of carbaalanes typically consist of one broad resonance, for which a clear assignment, even with the aid of quantum chemical shift calculations, is rather difficult. Our experimental and computational results also suggest that the sensitivity of the ^{27}Al NMR shifts to structural features of the carbaalanes is not very pronounced and that ^{27}Al NMR spectroscopy is not a particularly promising tool for future investigations of such compounds.

Experimental Section

General: All procedures were carried out under purified argon in dried solvents (toluene and THF over Na/benzophenone; *n*-pent-

Table 1. Experimental and computed ^{27}Al NMR spectroscopic data of carbaalanes (104.3 MHz, δ in ppm relative to $[Al(H_2O)_6]^{3+}$ as an external standard, $W_{1/2}$ in Hz, shoulders with uncertain chemical shifts in italics; the asterisk* denotes uncertain values as a consequence of impurities)

	Al	**C**	**R**	δ ($W_{1/2}$)	$δ_{computed}$	Solvent	Ref.
	AlMe	CCH_2Ph	H	142 (10200); *100*	159-164 (4x), 176-180 (2x), 209-215 (2x)	C_6D_6	[2]
	AlEt	CCH_2Ph	H	130; 85 (10900)	–	C_6D_6	[4]
	AlMe	CCH_2Ph	C≡CPh	*130*; 80 (6300)	162-166 (4x), 173-175 (2x), 206-209 (2x)	C_6D_6	[4]
	AlMe	CCH_2CH_3	$C≡CCH_3$ (**6**)	153 (3100); *130*	163-166 (4x), 187-191 (4x)	OC_4D_8	–
	AlMe	CCH_2Ph	F	62 (6500); -20 (13000)*	–	C_6D_6	[16]
	AlMe	CCH_2CH_3	H/THF (**5**)	155 (3700); 56 (6800)	160-163 (4x), 195-203 (4x)	OC_4D_8	–
	AlEt	CCH_2Ph	H	*170*; 149 (8800); *100*	159-172	C_6D_6	[3]
	AlEt	CCH_2Ph	F	*110*; 74 (12000); *20*, -28 (10000)	152, 160, 168, 184, 200	C_7D_8	[16]
	AlEt	CCH_2Ph	C≡CPh, H	*110*; 66 (4500)	156-171	C_6D_6	[3]
	AlMe	CCH_2CH_3	H	157 (4200); very broad base (up to ~ 60 ppm)	155, 164-170 (6x)	C_6D_6	[4]
	Al*i*Pr	CCH_2CH_3	H (**7**)	145 (6900); 79 (5600); -38 (> 10000)	–	C_6D_6	–

ane and *n*-hexane over $LiAlH_4$). The compounds $Me_2Al-C≡C-CH_3$,[4] Me_2Al-H,[17] Et_2Al-H,[17] iPr_2Al-H,[17] tBu_2Al-H,[10] Et_2Al-Cl,[17] iPr_2Al-Br,[17] and tBu_2Al-Cl[18] were synthesized according to literature procedures. – ^{1}H and ^{13}C NMR shifts were assigned on the basis of ^{1}H, ^{13}C, HH-COSY, HMQC, and HMBC spectra. Shifts are reported on the δ scale in ppm relative to residual nondeuterated solvent signals (^{1}H) or the signals of the deuterated solvent (^{13}C) as internal standards, or relative to $[Al(H_2O)_6]^{3+}$ (^{27}Al) as an external standard.

Synthesis of $(AlMe)_8(CCH_2Me)_5H$ (4): Dimethylpropynylaluminium (0.604 g, 6.29 mmol) was dissolved in excess dimethylaluminium hydride (2.301 g, 39.6 mmol) and the solution was stirred at room temperature. A strongly exothermic reaction occurred after some minutes and a colourless solid precipitated. After stirring for 2 h, all volatile components were distilled off in vacuo. The vessel containing the residue was thoroughly evacuated to 10^{-3} Torr and then the dried product was redissolved in toluene (40 mL). After filtration and cooling to −30 °C, an amorphous, extremely pyrophoric precipitate of the product **4** was deposited. The mother liquor contained a *closo*-carbaalane derivative similar to **3**, the isolation and characterization of which has been reported previously. Owing to its low solubility, **4** could not be purified by recrystallization from noncoordinating solvents. Yield of the crude product: 0.201 g (29% based on propynylaluminium). – ^{1}H NMR (very dilute solution in C_6D_6, 200 MHz, 298 K): δ = −0.20 and −0.15 (2 s, 12 H each, AlMe), 1.04 (t, 12 H, $^3J_{HH}$ = 7.3 Hz, CH_3 of ethyl), 1.33 (t, 3 H, $^3J_{HH}$ = 7.5 Hz, CH_3 of ethyl opposite to bridging H), 1.93 (q, 8 H, $^3J_{HH}$ = 7.3 Hz, CH_2 of ethyl), 2.33 (q, 2 H, $^3J_{HH}$ = 7.5 Hz, CH_2 of ethyl opposite to bridging H), 5.68 (s, 1 H, AlH).

Synthesis of $(AlMe)_8(CCH_2Me)_5H·2THF$ (5): Compound **4** was dissolved in THF. The solution was slowly concentrated under slightly reduced pressure at room temperature over several weeks to yield single crystals of the THF adduct **5**. M.p. (argon, sealed capillary): 260 °C (dec.). – ^{1}H NMR ([D$_8$]THF, 500 MHz, 300 K): δ = −0.44 (s, 12 H, methyl at Al-1, Al-3), −0.43 (s, 12 H, methyl at A-l2, Al-4 of the hydrogen-bonded face), 1.04 (t, 12 H, $^3J_{HH}$ = 7.3 Hz, CH_3 of ethyl), 1.05 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, CH_3 of ethyl opposite to the bridging hydrogen atom), 1.99 (q, 8 H, $^3J_{HH}$ = 7.3 Hz, CH_2 of ethyl), 2.05 (q, 2 H, $^3J_{HH}$ = 7.3 Hz, CH_2 of ethyl opposite to the bridging hydrogen atom), 4.19 (s, 1 H, AlH); coordinated THF: δ = 1.77 and 3.62 (each m), part of the THF was replaced by [D$_8$]THF and was detected as free THF in solution. – ^{1}H NMR ([D$_8$]THF, 400 MHz, 165 K): δ = −0.49 and −0.51 (2 s, 6 H each, methyl of Al-1, Al-3), −0.41 and −0.56 (2 s, 6 H each, methyl of Al-2, Al-4), 3.98 (s, 1 H, AlH), broad resonances of the ethyl groups at δ = 1.0 and 1.9. – ^{13}C NMR ([D$_8$]THF, 125.8 MHz, 300 K): δ = −9.4 and −8.8 (AlMe); 20.5 (cluster carbon atom C-20, see Figure 1), 21.5 (cluster carbon atoms C-10 and C-30), 23.1 (CH_3 of ethyl, C-12 and C-32), 24.35 (CH_2 of ethyl, C-11 and C-31), 24.40 (CH_3 of ethyl, C-22), 24.5 (CH_2 of ethyl, C-21), 68.2 (CO of coordinated THF), 26.4 ($C_β$ of THF). – ^{13}C NMR ([D$_8$]THF, 100.6 MHz, 202 K): δ = −10.6, −10.3, −8.5, and −7.8 (AlMe). – ^{27}Al NMR: See Table 1. – IR (CsBr, paraffin): $\tilde{\nu}$ = 1616 m (νAlH), 1458 vs, 1376 vs paraffin; 1314 s, 1269 m ($δCH_3$), 1196 m, 1176 s, 1078 m, 1066 m, 1025 s, 1004 s, 920 m, 874 s, 801 s (νCC, νCO, $δCH_3$) 721 vs, 679 vs [br. νAlC(Me)] 465 m, 426 m, 388 m, 344 m, 301 m, 275 m (νAlC, δCC). – $C_{31}H_{66}Al_8O_2$ (686.7): calcd. Al 31.4; found Al 31.2.

Synthesis of $(AlMe)_8(CCH_2Me)_5(μ\text{-}C≡C-Me)$ (6): Dimethylpropynylaluminium (1.665 g, 17.3 mmol) was treated with dimethylaluminium hydride (2.102 g, 36.2 mmol, 2.1 equiv.) without a solvent at room temperature. After about 1 min, a strongly exothermic reaction occurred and a bright-yellow solid precipitated. The mixture was stirred for 1 h and then all volatile components were removed in vacuo. The yellow residue was redissolved in warm toluene (50 mL). The yellow, air-sensitive product was isolated after cooling the solution to −30 °C. Yield: 0.654 g (39%), m.p. (argon, sealed capillary): 240 °C (dec.). − ^{1}H NMR ([D$_8$]THF, 500 MHz, 300 K): δ = −0.44 (s, 12 H, methyl groups of the aluminium atoms at the bottom of the cluster), −0.36 (s, 12 H, methyl groups of the aluminium atoms of the propynido-bridged face), 1.03 (t, 12 H, $^3J_{HH}$ = 7.3 Hz, CH$_3$ of ethyl), 1.08 (t, 3 H, $^3J_{HH}$ = 7.3 Hz, CH$_3$ of the ethyl group opposite to the bridging propynido group), 1.99 (q, 8 H, $^3J_{HH}$ = 7.3 Hz, CH$_2$ of ethyl), 2.07 (q, 2 H, $^3J_{HH}$ = 7.3 Hz, CH$_2$ of the ethyl group opposite to the bridging propynido group), 2.41 (s, 3 H, CH$_3$ of the propynido ligand). − ^{13}C NMR ([D$_8$]THF, 125.8 MHz, 300 K): δ = −8.9 and −7.7 (AlMe), 8.8 (CH$_3$ of the propynido ligand), 17.5 (cluster carbon atom opposite to the bridging propynido ligand), 21.5 (remaining cluster carbon atoms), 23.5 (CH$_3$ of ethyl), 24.1 (CH$_2$ of ethyl opposite to the propynido bridge), 24.3 (CH$_3$ of the ethyl group opposite to the propynido bridge), 25.0 (CH$_2$ of ethyl)*, 88.2 (bridging C of the C≡C triple bond), 162.3 (β-C of C≡C triple bond); *obscured by solvent signal. − ^{27}Al NMR: See Table 1. − IR (CsBr, paraffin): ṽ = 2019 m, 2010 m (νC≡C, splitting possibly caused by Fermi resonance) 1460 vs, 1377 vs (paraffin) 1322 s, 1186 vs, 1082 m, 1067 m, 1031 vs, 879 vs, 788 m (νCC, δCH$_3$), 663 vs [br. νAlC(Me)] 437 m, 402 w, 344 w (νAlC). − $C_{26}H_{54}Al_8$ (582.6): calcd. Al 37.1; found Al 37.2.

Synthesis of Et$_2$Al−C≡C−Me:[19] A mixture of *n*-butyllithium (15.0 mL, 1.6 M solution in *n*-hexane, 24.0 mmol) and *n*-pentane (20 mL) was cooled to −70 °C. Dried (P$_4$O$_{10}$) gaseous propyne was then passed over the solution for half an hour. A colourless solid precipitated. The resulting suspension was allowed to warm to room temperature and stirred until the gas evolution had ceased. A solution of diethylaluminium chloride (2.601 g, 21.6 mmol, 0.9 equiv.) in *n*-pentane (20 mL) was then added dropwise at room temperature. The mixture was stirred for 1 h and filtered. The solvent was removed in vacuo and the oily residue was employed directly for further reactions without purification. Yield: 1.955 g (73% based on Et$_2$AlCl). − ^{1}H NMR (C$_6$D$_6$, 300 MHz, 300 K): δ = 0.43 (q, 4 H, $^3J_{HH}$ = 8.1 Hz, CH$_2$), 1.25 (s, 3 H, C≡C−CH$_3$), 1.39 (t, 6 H, $^3J_{HH}$ = 8.1 Hz, CH$_3$ of ethyl). − ^{13}C NMR (C$_6$D$_6$, 75.5 MHz, 300 K): δ = 2.4 [AlC(Et)], 5.3 (CH$_3$ of propyne), 9.6 (CH$_3$ of ethyl), 86.3 and 134.5 (C≡C). − ^{27}Al NMR (C$_6$D$_6$, 104.3 MHz, 300 K): δ = 146 ($W_{1/2}$ = 4000 Hz). − IR (CsBr, paraffin): ṽ = 2149 s, 2101 vs (νC≡C), 1463 vs (paraffin), 1407 s, 1393 s (δCH$_3$), 1375 s (paraffin) 1303 vw, 1227 w, 1194 w, 1167 w, 1101 w, 1056 s, 988 vs, 974 sh, s, 951 s, 919 m, 899 s, 868 m, 808 m, (br. νCC, δCH$_3$) 656 vs (br. νAlC), 541 s, 469 sh, s, 406 s, br., 346 s, 312 m (νAlC, δCC).

Synthesis of *i*Pr$_2$Al−C≡C−Me: A solution of *n*-butyllithium (15.6 mL, 1.6 M in *n*-hexane, 25.0 mmol) and *n*-hexane (20 mL) was cooled to −70 °C. Dried (P$_4$O$_{10}$) gaseous propyne was passed over the solution for half an hour. A colourless solid precipitated. The mixture was then allowed to warm to room temperature and stirred until the gas evolution (butane, excess propyne) had ceased. A solution of diisopropylaluminium bromide (4.568 g, 23.7 mmol, 0.95 equiv.) was then added dropwise at room temperature. The resulting suspension was stirred for 3 h, then filtered, and all volatile components were removed from the filtrate in vacuo. The waxy residue was employed without further purification. Yield: 2.179 g (61% based on *i*Pr$_2$AlBr). − ^{1}H NMR (C$_6$D$_6$, 200 MHz, 300 K): δ = 0.76 (septet, 2 H, $^3J_{HH}$ = 7.5 Hz, AlCH), 1.32 (s, 3 H, C≡C−CH$_3$), 1.41 (d, 12 H, $^3J_{HH}$ = 7.5 Hz, CH$_3$ of isopropyl). − ^{13}C NMR (C$_6$D$_6$, 50.3 MHz, 300 K): δ = 5.9 (CH$_3$ of propyne), 12.1 [br., AlC(*i*Pr)], 21.1 (CH$_3$ of isopropyl), 136.8 (C≡C); only one resonance of the C≡C triple bond was detected. − ^{27}Al NMR (C$_6$D$_6$, 104.3 MHz, 300 K): δ = 138 ($W_{1/2}$ = 5000 Hz). − IR (CsBr, paraffin): ṽ = 2149 w, 2098 vs (νC≡C), 1461 vs, 1377 vs (paraffin), 1305 w, 1261 m, 1206 w, 1169 sh, w, 1120 m, 1055 s, 1028 sh, m, 972 s, 957 s, 910 w, 873 s, 835 w, 801 m, (br. νCC, δCH$_3$), 723 m,

Table 2. Crystal data, data collection parameters, and structure refinement of compounds **5** and **6**[a]

	5	**6**
Formula	$C_{31}H_{66}Al_8O_2$	$C_{26}H_{56}Al_8$
Crystal system	monoclinic	tetragonal
Space group	*P*2/*n*; No. 13 [20]	*I*4/*m*; No. 87 [20]
Z	2	2
Temperature [K]	193(2)	193(2)
$d_{calcd.}$ [g/cm^3]	1.175	1.172
a [pm]	1059.7(1)	1061.62(5)
b [pm]	1093.6(1)	1061.62(5)
c [pm]	1689.7(3)	1464.21(9)
β [°]	97.63(2)	90
V [10^{-30} m^3]	1940.8(5)	1650.2(2)
μ [mm^{-1}]	0.236	0.262
Crystal size [mm]	0.40 × 0.34 × 0.31	0.36 × 0.36 × 0.34
Diffractometer	STOE IPDS	
Radiation	Mo-K_α radiation; graphite monochromator	
Range [°]	2.15 to 25.93	3.84 to 25.84
Index ranges	$-12 \le h \le 12$	$-12 \le h \le 12$
	$-13 \le k \le 13$	$-13 \le k \le 12$
	$-20 \le l \le 20$	$-17 \le l \le 17$
Independent reflections	3758 [*R*(int) = 0.0406]	828 [*R*(int) = 0.0414]
Reflections $F > 4\sigma(F)$	2987	685
Parameters	257	55
$R = \Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$ [$F > 4\sigma(F)$]	0.0511	0.0553
$wR^2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$ (all data)	0.1539	0.1831
Max./min. residual [10^{30} e/m^3]	0.896/−0.567	0.318/−0.648

[a] Programs: SHELXTL-Plus, SHELXL-97;[21] solutions by direct methods; full-matrix refinement with all independent structure factors.

699 w, 622 vs (br. νAlC), 563 sh, m, 532 s, 457 s, 402 m, 350 m (νAlC, δCC).

Reaction of *i*Pr$_2$Al−H with *i*Pr$_2$Al−C≡C−Me: Diisopropylpropynylaluminium (1.090 g, 7.17 mmol) was treated with diisopropylaluminium hydride (3.466 g, 30.4 mmol) and the resulting mixture was heated to 50 °C for 18 h. In order to distil off triisopropylaluminium, the mixture was heated in vacuo to 80 °C for 2 h. The oily, light-yellow residue was treated with diisopropyl ether. After filtration, the solution was cooled to −70 °C to furnish a small quantity of a colourless solid (**7**) after several weeks. Yield: <1%. − ^{1}H NMR (C_6D_6, 500 MHz, 300 K, the numbering scheme is given in Scheme 2): ethyl groups at C-1 and C-2: $\delta = 1.19$ (t, 6 H, $^3J_{HH} = 7.4$ Hz, CH_3)*, 2.18 (q, 4 H, $^3J_{HH} = 7.4$ Hz, CH_2); ethyl groups at C-3 and C-4: $\delta = 1.19$ (t, 6 H, $^3J_{HH} = 7.4$ Hz, CH_3)*, 2.18 (q, 4 H, $^3J_{HH} = 7.4$ Hz, CH_2); isopropyl groups at Al-1 and Al-2: $\delta = 0.90$ (m, 2 H, $^3J_{HH} = 7.7$ Hz, AlCH), 1.46 (d, 12 H, $^3J_{HH} = 7.7$ Hz, CH_3); isopropyl groups at Al-3, Al-4, Al-5, and Al-6: $\delta = 0.85$ and 0.95 (2 m, each 2 H, $^3J_{HH} = 7.7$ Hz, AlCH), 1.37 and 1.38 (2 d, each 12 H, $^3J_{HH} = 7.7$ Hz, CH_3); isopropyl group at Al-7: $\delta = 0.46$ (septet, 1 H, $^3J_{HH} = 7.7$ Hz, AlCH), 1.41 (d, 6 H, $^3J_{HH} = 7.7$ Hz, CH_3); 4.53 (s, 2 H, AlH) (*assignments may be interchanged). − ^{13}C NMR (C_6D_6, 125.8 MHz, 300 K): ethyl groups at C-1, C-2, C-3, and C-4: $\delta = 21.2$ and 23.1 (CH_2), 23.9 and 25.3 (CH_3); cluster carbon atoms C-1 to C-4: $\delta = 18.0$ and 27.0; isopropyl groups at Al-1 and Al-2: $\delta = 13.0$ or 13.3 (AlC, uncertain), 21.0 (CH_3); isopropyl groups at Al-3, Al-4, Al-5, Al-6: $\delta = 6.2$ and 10.3 (AlC), 21.6 and 21.8 (CH_3); isopropyl group at Al-7: $\delta = 9.8$ (AlC), 21.7 (CH_3). − ^{27}Al NMR: See Table 1.

Synthesis of (Me$_3$C)$_2$Al−C≡C−Me: Li−C≡C−Me was synthesized as described above (5.3 mL of a 1.6 M solution of *n*-butyllithium in *n*-hexane, 8.48 mmol). A solution of bis(*tert*-butyl)aluminium chloride (1.490 g, 8.44 mmol) in *n*-hexane (20 mL) was added and the mixture was stirred at room temperature for 3 h. After filtration and concentration, a colourless solid was obtained upon cooling the solution to −30 °C. The product was further purified by recrystallization from *n*-hexane. Yield: 1.172 g (77%, based on *t*Bu$_2$AlCl); m.p. (argon, sealed capillary): 96 °C (dec.). − ^{1}H NMR (C_6D_6, 200 MHz, 300 K): $\delta = 1.31$ (s, 18 H, CMe_3), 1.49 (s, 3 H, C≡C−CH_3). − ^{13}C NMR (C_6D_6, 100.6 MHz, 300 K): $\delta = 5.6$ (CH_3 of propyne), 18.4 [br., AlC(*t*Bu)], 31.8 (CH_3 of *tert*-butyl), 135.6 (C≡C); only one resonance of the C≡C triple bond was detected. − ^{27}Al NMR (C_6D_6, 104.3 MHz, 300 K): $\delta = 130$ ($W_{1/2} = 5000$ Hz). − IR (CsBr, paraffin): $\tilde{\nu} = 2092$ vs, 2058 w, 2047 w (νC≡C), 1464 vs, 1378 vs (paraffin), 1308 m, 1262 m, 1178 m, 1127 w, 1043 m, 1002 s, 966 s, 939 s, 891 w, 846 w, 812 vs (νCC, δCH_3), 722 s, 663 vw, 631 w, 587 vs (νAlC), 541 s, 442 vs, 418 vs, 356 vs (νAlC, δCC).

Crystal Structure Determinations: Single crystals of compounds **5** and **6** were obtained by very slow concentration of solutions in THF at room temperature over several weeks. Crystal data and structure refinement parameters are given in Table 2.[22] The carbon atoms of the THF molecules and one ethyl group (C-31, C-32) of compound **5** showed a disorder; these atoms were refined in split positions. Compound **6** is severely disordered and the propynido group is distributed over all six faces of the cluster.

Quantum Chemical Calculations: The structures of the carbaalanes **1** (with Al = AlMe and R = CCPh as well as H, respectively), **2**, **3** (with Al = AlMe and AlEt, respectively), **4**, and **6** were optimized at the density-functional theory (DFT) level[23] employing the Becke−Perdew (BP86) functional[24] together with an auxiliary basis set approximation for the Coulomb energy (RI-DFT).[25] A polarized split-valence basis SV(P)[26] was used in all calculations, with the parentheses indicating that polarization functions have been considered only for non-hydrogen atoms as well as the hydrogen bonds.

^{27}Al NMR chemical shifts were computed employing the gauge-including atomic orbital (GIAO) Hartree−Fock self-consistent-field (HF-SCF) method[27] using a polarized double-zeta (dzp) basis[28] for Al, C, and F and a DZ basis for all nonbridging hydrogen atoms. Relative shifts were obtained with $[AlH_4]^-$ as an internal reference and a $\delta(^{27}Al)$ value for $[AlH_4]^-$ of $\delta = 101$ [28] (the absolute shielding computed for $[AlH_4]^-$ at the GIAO-HF-SCF/dzp level is 517.1 ppm). For the parent system of **5** (all ethyl and methyl groups replaced by hydrogens), the accuracy of the calculated shifts was checked in GIAO-HF-SCF calculations using a larger polarized triple-zeta (TZP) basis,[26] as well as in electron-correlated calculations using second-order Møller−Plesset perturbation theory, i.e. GIAO-MP2.[29] According to these calculations, the accuracy of the computed shift can be estimated to be in agreement with previous ^{27}Al NMR chemical shift calculations on aluminium cluster compounds within $\delta = 20-30$.[13,14] All calculations were carried out with the TURBOMOLE program package.[30]

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