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Synthesis of Carbaalane Halogen Derivatives

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The carbaalane halogen derivatives $[(AlX)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (X = F (**9**), Cl (**7**), Br (**10**), I (**11**)) were prepared in toluene from $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) and $BF_3{\cdot}OEt_2$, BX_3 (X = Br, I), Me_3SnF, and Me_3SiX (X = Cl, Br, I), respectively. A partially halogenated product $[(AlH)_2(AlX)_4(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**12**) (X = Cl (∼40%), Br (∼60%)) was obtained from **5** and impure BBr_3. $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**5**) was converted to $[(AlX)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (X = F (**13**), Cl (**14**), Br (**15**), I (**16**)) using $BF_3{\cdot}OEt_2$ and Me_3SiX (X = Cl, Br, I), respectively. The X-ray single-crystal structures of **11**$\cdot C_6H_6$, **12**$\cdot 3C_7H_8$, **13**$\cdot 6C_7H_8$, and **15**$\cdot 4C_7H_8$ were determined. Compounds **7** and **9**–**11** are soluble in benzene/toluene and could be well characterized by NMR spectroscopy and MS (EI) spectrometry. The results demonstrate the facile substitution of the hydridic hydrogen atoms in **5** and **6** by the halides with different reagents.

Introduction

Since the first structural characterization of the carbaalane $[(AlMe)_8(CCH_2Ph)_5H]$ (**1**) in 1999 by Uhl and Breher,[1] numerous carbaalanes have been prepared.[2] Three halogen-substituted carbaalanes $[(AlEt)_7(C{=}CPh)_2(CCH_2Ph)_3F]$ (**2**), having a μ_3-bridged fluorine atom, $[(AlMe)_8(CCH_2Ph)_5F]$ (**3**), and $[(AlMe)_7(AlCl)(CCH_2Ph)_5H]$ (**4**) with a terminal chlorine atom and unreacted hydride were prepared by treatment of the parent carbaalane (e.g. **1** for the preparation of **3** and **4**) with HBF_4 and HCl, respectively. The crystal structures of **2** and **4** were determined.[3] We synthesized the carbaalane $[(AlH)_6(AlNMe_3)_2(CCH_2R)_6]$ (R = Ph (**5**), CH_2SiMe_3 (**6**)) in a facile reaction from the corresponding terminal alkyne and 3 equiv of the alane trimethylamine adduct in boiling toluene.[2e] Using compound **6** and BCl_3 under varying conditions, we obtained the chlorinated species $[(AlCl)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**7**) and $[(AlCl)_6(AlNMe_3)_2(CCH_2CH_2SiMe_2Cl)_6]$ (**8**), demonstrating the stepwise functionalization and the stability of the cluster.[2e] Very recently, we obtained the first carbaalanate from the reaction of ${}^{t}Bu\text{-}C{\equiv}CLi$ with a mixture of $ClAlH_2{\cdot}NMe_3$ and $AlH_3{\cdot}NMe_3$.[4]

Compounds containing aluminum hydrogen bonds can be substituted by halides using various reagents.[2e,3,5] Recently, we have converted polyhedral compounds from hydroalumination reactions to halogen derivatives.[6] In this paper we report on the synthesis and characterization of new halogen-substituted carbaalanes, which are key derivatives of carbaalane chemistry.

Results and Discussion

Preparation and Spectroscopic Characterization. For hydride metathesis, the toluene-soluble carbaalane $[(AlH)_6$-

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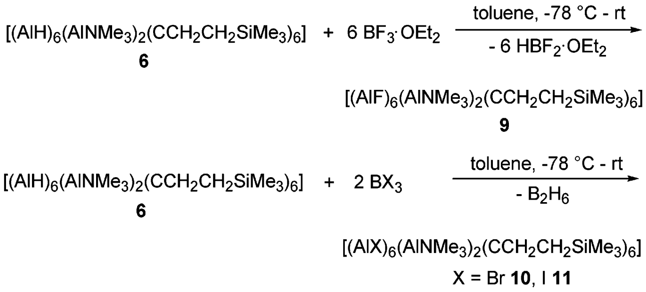
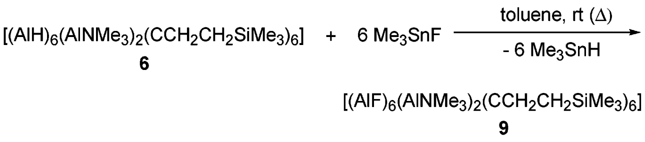
Scheme 1



$$[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\ (\mathbf{6}) + 6\ BF_3{\cdot}OEt_2 \xrightarrow[-6\ HBF_2{\cdot}OEt_2]{\text{toluene, -78 °C - rt}} [(AlF)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\ (\mathbf{9})$$

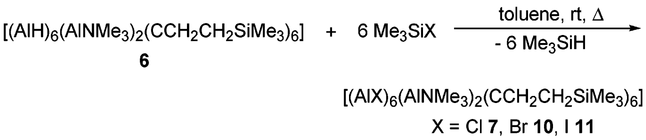
$$[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\ (\mathbf{6}) + 2\ BX_3 \xrightarrow[-B_2H_6]{\text{toluene, -78 °C - rt}} [(AlX)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\quad X = Br\ \mathbf{10},\ I\ \mathbf{11}$$

Scheme 2



$$[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\ (\mathbf{6}) + 6\ Me_3SnF \xrightarrow[-6\ Me_3SnH]{\text{toluene, rt }(\Delta)} [(AlF)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\ (\mathbf{9})$$

Scheme 3



$$[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\ (\mathbf{6}) + 6\ Me_3SiX \xrightarrow[-6\ Me_3SiH]{\text{toluene, rt, }\Delta} [(AlX)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]\quad X = Cl\ \mathbf{7},\ Br\ \mathbf{10},\ I\ \mathbf{11}$$

$(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) was treated with at least 2 equiv of $BF_3{\cdot}OEt_2$, BBr_3, and BI_3, respectively, in toluene at low temperature to yield the halogen derivative $[(AlX)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (X = F (**9**), Br (**10**), I (**11**)) in good yield (Scheme 1).The reaction of **6** with the boron halides proceeds at low temperature and is best performed at −78 °C under slow warming to room temperature. When the reaction mixture is conducted at ice bath temperature, only partially substituted halogen derivatives are formed or an excess of the boron halides is required. In the case of preparing the fluorine derivative **9**, 6 equiv of $BF_3{\cdot}OEt_2$ was used for obtaining optimal results. In another attempt we found that 2 equiv of $BF_3{\cdot}OEt_2$ was sufficient for this reaction and that all the fluorine atoms can be transfered to aluminum but this can increase the amount of partially fluorinated byproducts. A large excess of boron halides (especially BX_3, X = Cl, Br, I) and heating the reaction mixture must be avoided, otherwise compound **8** (when BCl_3 is used) and oily byproducts are formed. Compound **9** can be alternatively synthesized from **6** using Me_3SnF in toluene over a period of 3 d at room temperature or by stirring at room temperature and slowly warming the mixture to its boiling point until all the Me_3SnF has reacted (Scheme 2).

For the preparation of compounds **7**, **10**, and **11** trimethylsilyl halides can be used alternatively (Scheme 3). For these reactions, elevated reaction temperatures are necessary. In general, the reagents are combined at room temperature and the mixture is heated under reflux for up to 2 h. Compound **11** could not be prepared by slow addition of elemental iodine in toluene at 0 °C/room temperature. The reaction mixture is consuming far more than 6 equiv of I_2. We assume that intermediate HI is decomposing the cluster, which is sensitive to protic reagents.

The compounds **9**−**11** provide molecular ion peaks in the EI mass spectra like the chlorine derivatives **7** and **8** and the starting material **6** in the correct isotope pattern. Incomplete halogenation, especially for the fluorine and chlorine derivatives, can be detected by EI mass spectra of the crude products showing the intermediates as molecular ion peaks. The crude products of **9** and **10** exhibit small peaks for the pentasubstituted halogen derivatives. The NMR data for compounds **9**−**11** show results similar to those of **7**. The NMR resonances are in agreement with a symmetric structure, and the CH_2CH_2 groups show the typical multiplicity (2 × ddd) in the ^{1}H NMR spectrum. In general, the ^{1}H NMR resonances are shifted downfield within the series F, Cl, Br, and I. The ^{13}C NMR spectra exhibit the resonances for the cluster carbon atoms (δ 33.1 (**9**), δ 32.0 (**10**), and δ 29.4 (**11**)), which are close to those of the chlorine compounds **7** (δ 32.1) and **8** (δ 30.2) and are shifted downfield when compared to **6** (δ 16.8). The ^{27}Al NMR resonances of **10** (δ 143.9) and **11** (δ 144.9) are in the region of the previously characterized compounds (**6**, δ 142.3; **7**, δ 140.9; **8**, δ 141.4). However, the value for the fluorine derivative **9** is strongly shifted upfield to δ 122.3. The latter compound exhibits a broad resonance in the ^{19}F NMR spectrum at δ −181.5 with a shoulder at δ −178, which could result from a small amount of the pentafluorinated species. This resonance is in the high-field region for terminal Al−F bonds, and only the resonance of $[Me_4N][AlF_4]$ (δ −194.9) is shifted more upfield than **9** for tetracoordinated aluminum compounds.[7] Fluorinated cage compounds having AlN or $AlCH_2N$ cores from hydroalumination reactions with terminal Al−F bonds show ^{19}F NMR resonances around δ −163 and −155.7.[6c] The fluorinated carbaalane **3** exhibits a resonance at δ −121.4 in the ^{19}F NMR spectrum, while the corresponding resonance for **2** was not observed.

Recrystallization of the crude product (**7**, **9**−**11**) afforded some yellow crystals of **9**, which were not suitable for X-ray single crystal structure analysis. The previously published compound **7** could be recrystallized from toluene or diethyl ether at different temperatures forming large yellow blocks, but the crystals become opaque either when the temperature is changed or when the crystals are taken out of the solution. Some yellow-green rods of $\mathbf{11}{\cdot}C_6H_6$ were obtained from a concentrated benzene solution. However, the crude products of **7** and **9**−**11** were of good purity as shown by their ^{1}H and ^{13}C NMR spectra.

In one experiment, compound **6** was treated with an impure sample of BBr_3 at −78 °C under warming to room temperature. The expected molecular ion peak M^+ ($m/z = 1492$) of compound **10** is present in the EI mass spectrum of the crude product. However, recrystallization from toluene (50 °C/−25 °C, 4 months) afforded a small number of pale yellow single crystals of $[(AlH)_2(AlX)_4(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]{\cdot}3$toluene ($\mathbf{12}{\cdot}3C_7H_8$) with a halogen ratio of X = Cl (∼40%) and Br (∼60%) which was characterized by its X-ray single-crystal structure.

In contrast to compound **6**, compound **5** is much less soluble, and therefore, derivatization was difficult. Compound

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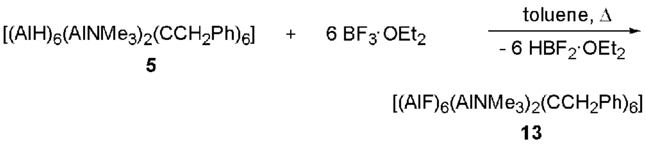
[7] Pinkas, J.; Roesky, H. W. *J. Fluorine Chem.* **2003**, *122*, 125 and references therein.

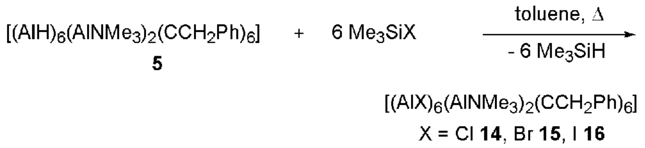
Table 1. Crystallographic Data

param	**11**·C_6H_6	**12**·3C_7H_8	**13**·6C_7H_8	**15**·4C_7H_8
diffractometer	I	II	I	I
empirical formula	$C_{54}H_{108}Al_8I_6N_2Si_6$	$C_{63}H_{122}Al_8Br_{2.38}Cl_{1.62}N_2Si_6$	$C_{96}H_{108}Al_8F_6N_2$	$C_{82}H_{92}Al_8Br_6N_2$
fw	1913.20	1539.62	1619.68	1800.88
T/K	133(2)	200(2)	133(2)	140(2)
cryst system	rhombohedral	monoclinic	monoclinic	monoclinic
space group	$R\bar{3}$	$P2_1/n$	$P2_1/n$	$P2_1/n$
unit cell dimens/Å and deg	$a = 15.4323(10)$ $b = 15.4323(10)$ $c = 29.624(2)$ $\alpha = 90$ $\beta = 90$ $\gamma = 120$	$a = 15.732(3)$ $b = 12.9036(17)$ $c = 21.286(7)$ $\alpha = 90$ $\beta = 90.59(2)$ $\gamma = 90$	$a = 11.642(2)$ $b = 31.900(6)$ $c = 11.986(2)$ $\alpha = 90$ $\beta = 102.75(3)$ $\gamma = 90$	$a = 11.822(2)$ $b = 15.823(3)$ $c = 21.216(4)$ $\alpha = 90$ $\beta = 95.55(3)$ $\gamma = 90$
V/Å^3	6109.8(7)	4320.9(16)	4341.5(15)	3949.9(14)
Z	3	2	2	2
ρ/Mg·m^{-3}	1.575	1.183	1.239	1.514
μ/mm^{-1}	2.494	1.362	0.154	3.183
F(000)	2856	1626	1712	1823
cryst size/mm^3	0.40 × 0.20 × 0.20	0.50 × 0.40 × 0.40	0.40 × 0.30 × 0.30	0.20 × 0.20 × 0.20
θ/deg	1.67−25.35	3.51−22.44	1.86−24.78	1.61−24.96
index ranges	$-18 \leq h \leq 18$, $-18 \leq k \leq 18$, $-35 \leq l \leq 35$	$-16 \leq h \leq 9$, $0 \leq k \leq 13$, $0 \leq l \leq 22$	$-13 \leq h \leq 11$, $-37 \leq k \leq 36$, $-14 \leq l \leq 14$	$-13 \leq h \leq 13$, $-18 \leq k \leq 18$, $-24 \leq l \leq 24$
reflcns collcd/unique	22 379/2479	4701/4701	27 552/7294	57 236/6830
R_{int}	0.0427	0.0000	0.1153	0.1936
completeness to θ/%	99.6	83.9	97.7	98.6
data/restraints/params	2479/0/128	4701/595/416	7294/0/575	6830/409/415
goodness-of-fit on F^2	1.089	1.039	0.956	1.029
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0153$, $wR_2 = 0.0374$	$R_1 = 0.0633$, $wR_2 = 0.1198$	$R_1 = 0.0587$, $wR_2 = 0.0841$	$R_1 = 0.0768$, $wR_2 = 0.1826$
R indices (all data)	$R_1 = 0.0168$, $wR_2 = 0.0380$	$R_1 = 0.1259$, $wR_2 = 0.1467$	$R_1 = 0.1282$, $wR_2 = 0.0946$	$R_1 = 0.1130$, $wR_2 = 0.2019$
largest diff peak and hole/e·Å^{-3}	0.402, −0.421	0.429, −0.446	0.328, −0.252	1.025, −1.797

Scheme 4



Scheme 5



5 was treated with an excess of BF_3·OEt_2 in boiling toluene (Scheme 4). Filtering the hot reaction mixture gave an impure greenish crude product, and storing the solution at room temperature resulted in shiny green-yellow rhombuses mainly containing $[(AlF)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**13**). The unit cell could not be refined due to disordering. Filtering off these crystals and storing the resulting solution at −25 °C gave another crop of crystals (plates) with the same color of composition **13**·6C_7H_8.

Compound **5** reacts with an excess of Me_3SiX (X = Cl, Br, I) in boiling toluene giving a crude product and a crystalline material of $[(AlX)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (X = Cl (**14**), Br (**15**), I (**16**)) that precipitated from the reaction mixture upon standing for a few days at room temperature or lower temperatures (Scheme 5). The crystal structure of **15**·4C_7H_8 was determined. In these reactions, the color is changing after a few minutes of refluxing. In general, the products have an intense yellow or yellow-green color. Due to the poor solubility of **13**−**16**, no satisfying NMR spectra could be recorded. Only traces of the reagents or impurities were detected. The crystalline compounds are not soluble in THF or acetonitrile, and moreover, they are not reacting with the nitrile in the way the hydrided derivative does. Corresponding to the parent compound **5**, no molecular ion was detected in the EI mass spectra of **13**−**16**. For the derivatives of **5**, neither NMR and IR spectroscopy nor mass spectrometry provides proof of their composition or structures. Obviously, only functionalization of the hydride takes place as proven by the structural analysis of **13** and **15** and the corresponding reactions using **6** as a starting material.

Crystal Structures. The X-ray single-crystal structures of **11**·C_6H_6, **12**·3C_7H_8, **13**·6C_7H_8, and **15**·4C_7H_8 were determined, and the crystallographic data are summarized in Table 1. ORTEP plots (50% thermal ellipsoids) of these compounds are shown in the Figures 1−4 in different views of the cluster core, and selected bond lengths and angles are given in the Tables 2−5. Compounds **12**·3C_7H_8, **13**·6C_7H_8, and **15**·4C_7H_8 crystallize in the monoclinic space group $P2_1/n$, and their asymmetric units show half of the molecule along with half of the solvent molecules, respectively. In contrast to that, **11**·C_6H_6 crystallizes in the rhombohedral space group $R\bar{3}$ with one sixth of the molecule in the asymmetric unit demonstrating the symmetry of the cluster. All compounds have in common that the central cluster consists of a cube of eight aluminum atoms where each face is occupied by a carbon atom attached to an organic group. Two aluminum atoms on opposite sides of the cluster are coordinating to a NMe_3 unit. The remaining aluminum atoms are bonded to halogen atoms or to a mixture of halides and hydrides in **12**·3C_7H_8. In all compounds, the Al−C bond lengths (from 2.028(4) to 2.099(4) Å in **13**·6C_7H_8) and the Al−Al distances (from 2.566(3) Å in **12**·3C_7H_8 to 2.632(3) Å in **15**·4C_7H_8)

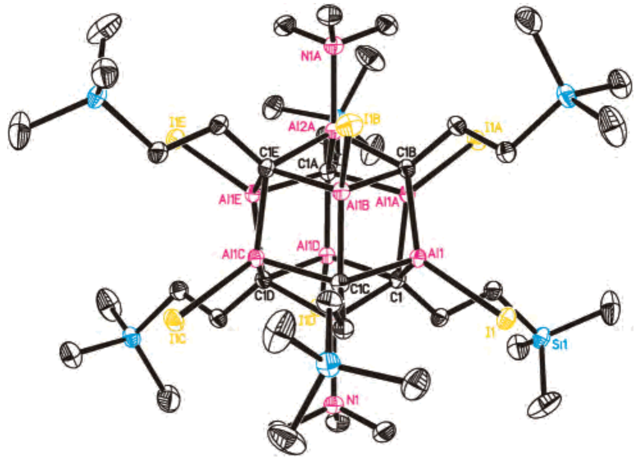


Figure 1. ORTEP drawing of the crystal structure of **11**$\cdot C_6H_6$. Hydrogen atoms and solvent molecules are not shown.

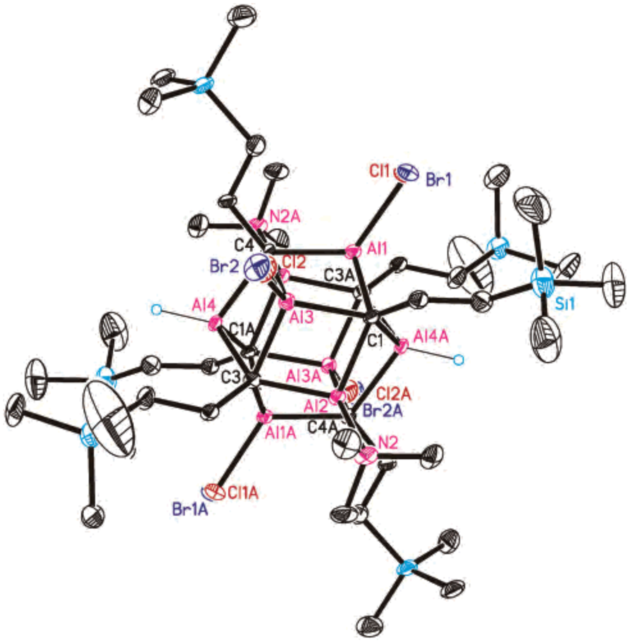


Figure 2. ORTEP drawing of the crystal structure of **12**$\cdot 3C_7H_8$. Only hydrogen atoms on aluminum are depicted. Solvent molecules are not shown.

are comparable to those reported in the literature,[2e] with the exception of one long Al−C bond length (2.131(7) Å) in **12**$\cdot 3C_7H_8$. The Al−F bond lengths in **13**$\cdot 6C_7H_8$ range from 1.667(2) to 1.669(3) Å, the Al−Br bond lengths in **15**$\cdot 4C_7H_8$ range from 2.282(2) to 2.302(2) Å, and the Al−I bond length is 2.5297(5) Å. In **12**$\cdot 3C_7H_8$, two aluminum atoms on opposite sides of the cluster are each bearing a datively bonded NMe_3 unit (Al2 and Al2A) and a hydride (Al4 and Al4A), respectively. The other four Al atoms are carrying halogen atoms and were refined with Br (∼64%) and Cl (∼36%) on Al1 and Al1A, as well as Br (∼55%) and Cl (∼45%) on Al3 and Al3A. The Al−Br bond lengths are around 2.30 Å, and the Al−Cl bond lengths are not exact enough for the discussion.

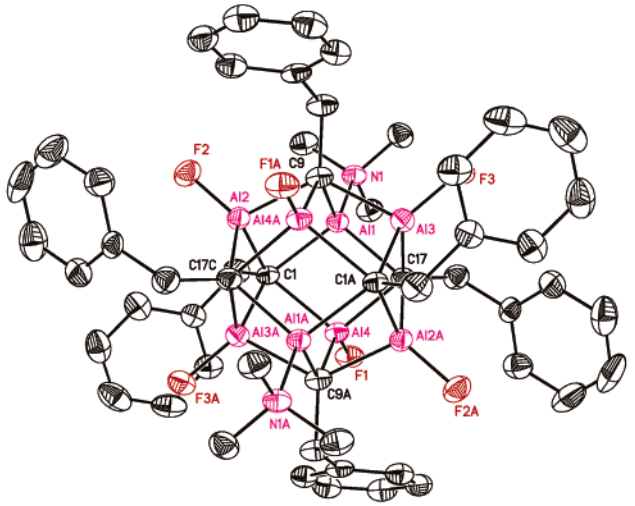


Figure 3. ORTEP drawing of the crystal structure of **13**$\cdot 6C_7H_8$. Hydrogen atoms and solvent molecules are not shown.

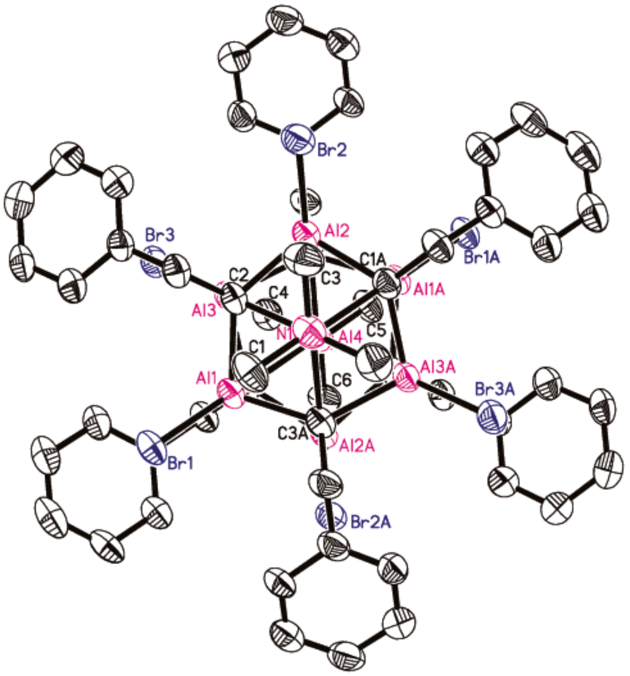


Figure 4. ORTEP drawing of the crystal structure of **15**$\cdot 4C_7H_8$. Hydrogen atoms and solvent molecules are not shown.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **11**$\cdot C_6H_6$

Al(1)−I(1)	2.5297(5)	Al(1)−C(1)	2.0860(17)
Al(1)−C(1)$^{\#1}$	2.0729(18)	Al(1)−C(1)$^{\#2}$	2.0839(17)
Al(2)−N(1)	2.005(3)	Al(2)−C(1)	2.0639(17)
Al(1)−Al(1)$^{\#1}$	2.6160(7)	Al(1)−Al(2)	2.5844(7)
C(1)−Al(1)−I(1)	110.60(5)	C(1)$^{\#1}$−Al(1)−I(1)	130.01(5)
I(1)−Al(1)−Al(2)	113.68(2)	I(1)−Al(1)−Al(1)$^{\#1}$	130.78(2)
C(1)−Al(1)−C(1)$^{\#1}$	100.36(8)	C(1)−Al(2)−C(1)$^{\#4}$	102.24(6)
Al(2)−Al(1)−Al(1)$^{\#1}$	89.149(16)	Al(1)$^{\#1}$−Al(1)−Al(4)$^{\#3}$	90.14(3)
Al(1)$^{\#2}$−Al(2)−Al(1)	91.55(3)		

There are always two small and one large X−Al−C angles (X = halogen) around each Al(X) atom, while two large and one small X−Al−Al angles are found around Al(X) in every compound. The result is that the Al(X) atoms are in a strongly distorted tetrahedral arrangement and the Al−X units are directing toward the NMe_3 groups. For example, the smallest I−Al−C angle in **11**$\cdot C_6H_6$ is 110.60(5)° and the largest is 130.01(5)° whereas the I−Al−Al angles range from 113.68(2) to 130.78(2)° and the F−Al−C angles in **13**$\cdot 6C_7H_8$ are ranging from 110.98(15) to 129.51(12)° with the F−Al−Al angles ranging from 115.42(9) to 131.98(11)°.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for **12**·3C_7H_8

Br(1)−Al(1)	2.30(2)	Cl(1)−Al(1)	2.24(9)
Br(2)−Al(3)	2.309(11)	Cl(2)−Al(3)	2.16(3)
Al(1)−C(1)	2.071(8)	Al(1)−C(4)	2.043(7)
C(1)−Al(2)	2.041(7)	Al(2)−C(3)	2.028(7)
Al(2)−C(4)$^{\#1}$	2.033(8)	Al(3)−C(3)	2.071(7)
Al(3)−C(4)	2.052(8)	C(3)−Al(4)	2.082(8)
Al(4)−C(1)$^{\#1}$	2.088(8)	Al(4)−C(4)	2.131(7)
Al(1)−Al(2)$^{\#1}$	2.581(3)	Al(1)−Al(3)	2.601(4)
Al(1)−Al(4)$^{\#1}$	2.609(3)	Al(2)−Al(3)	2.566(3)
Al(2)−Al(4)$^{\#1}$	2.570(3)	Al(3)−Al(4)	2.595(3)
Al(2)−N(2)	1.973(7)		
C(4)−Al(1)−C(1)	99.6(3)	C(1)−Al(1)−C(3)$^{\#1}$	100.6(3)
C(4)−Al(1)−Al(2)$^{\#1}$	50.5(2)	Al(1)−C(4)−Al(3)	78.9(3)
C(1)−Al(1)−Al(2)$^{\#1}$	114.9(2)	Al(1)−C(4)−Al(4)	126.1(3)
Al(2)$^{\#1}$−Al(4)−Al(1)$^{\#1}$	89.38(10)	Al(3)−Al(4)−Al(1)$^{\#1}$	90.18(10)
Al(2)$^{\#1}$−Al(4)−Al(3)	88.21(10)	Al(4)−Al(3)−Al(1)	91.44(11)
Al(2)$^{\#1}$−Al(1)−Al(3)	87.86(10)	Al(2)$^{\#1}$−Al(1)−Al(4)$^{\#1}$	88.85(10)
Al(3)−Al(1)−Al(4)$^{\#1}$	89.66(10)	Al(3)−Al(2)−Al(4)$^{\#1}$	91.31(11)
Al(3)−Al(2)−Al(1)$^{\#1}$	91.47(10)	Al(4)$^{\#1}$−Al(2)−Al(1)$^{\#1}$	92.47(11)
Al(2)−Al(3)−Al(4)	89.49(10)	Al(2)−Al(3)−Al(1)	89.65(10)
Al(4)−Al(3)−Al(1)	91.44(11)	Al(3)−Al(4)−Al(1)$^{\#1}$	90.18(10)

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **13**·6C_7H_8

Al(2)−F(2)	1.668(2)	Al(3)−F(3)	1.667(3)
Al(4)−F(1)	1.669(3)	N(1)−Al(1)	1.982(3)
Al(1)−C(1)	2.052(4)	Al(1)−C(9)	2.028(4)
Al(1)−C(17)	2.049(4)	Al(2)−C(1)	2.079(4)
Al(2)−C(9)	2.075(4)	Al(2)−C(17)$^{\#1}$	2.073(4)
Al(3)−C(1)$^{\#1}$	2.070(4)	Al(3)−C(9)	2.099(4)
Al(3)−C(17)	2.085(4)	Al(4)−C(1)	2.092(4)
Al(4)−C(9)$^{\#1}$	2.063(4)	Al(4)−C(17)	2.084(4)
Al(1)−Al(2)	2.583(2)	Al(1)−Al(3)	2.573(2)
Al(1)−Al(4)	2.579(2)	Al(2)−Al(3)$^{\#1}$	2.629(2)
Al(2)−Al(4)$^{\#1}$	2.623(2)	Al(3)−Al(4)$^{\#1}$	2.625(2)
C(9)−Al(1)−C(1)	102.14(17)	C(17)−Al(1)−C(1)	102.82(15)
C(9)−Al(1)−C(17)	103.24(16)	F(2)−Al(2)−C(1)	111.12(15)
F(2)−Al(2)−C(9)	115.10(13)	F(2)−Al(2)−C(17)$^{\#1}$	127.52(16)
F(3)−Al(3)−C(1)$^{\#1}$	128.01(15)	F(3)−Al(3)−C(17)	113.84(16)
F(3)−Al(3)−C(9)	111.97(13)	F(1)−Al(4)−C(1)	110.98(15)
F(1)−Al(4)−C(9)$^{\#1}$	129.51(12)	F(1)−Al(4)−C(17)	112.12(16)
N(1)−Al(1)−C(1)	115.84(15)	N(1)−Al(1)−C(9)	116.43(13)
N(1)−Al(1)−C(17)	114.45(16)	Al(3)−Al(1)−Al(2)	92.93(6)
Al(3)−Al(1)−Al(4)	92.31(6)	Al(4)−Al(1)−Al(2)	92.34(5)
Al(1)−Al(2)−Al(4)$^{\#1}$	88.03(6)	Al(4)$^{\#1}$−Al(2)−Al(3)$^{\#1}$	90.04(5)
Al(1)−Al(2)−Al(3)$^{\#1}$	88.61(5)	Al(1)−Al(3)−Al(2)$^{\#1}$	88.80(6)
Al(1)−Al(3)−Al(4)$^{\#1}$	88.18(6)	Al(1)−Al(4)−Al(2)$^{\#1}$	88.83(6)
Al(4)$^{\#1}$−Al(3)−Al(2)$^{\#1}$	90.24(5)	Al(2)$^{\#1}$−Al(4)−Al(3)$^{\#1}$	90.84(6)
Al(1)−Al(4)−Al(3)$^{\#1}$	88.79(5)		

Table 5. Selected Bond Lengths (Å) and Angles (deg) for **15**·4C_7H_8

Al(1)−Br(1)	2.302(2)	Al(2)−Br(2)	2.282(2)
Al(3)−Br(3)	2.286(2)	N(1)−Al(4)	1.981(7)
Al(1)−C(1)	2.067(8)	Al(1)−C(2)	2.064(8)
Al(1)−C(3)$^{\#1}$	2.060(8)	Al(2)−C(2)	2.098(7)
Al(2)−C(3)	2.054(8)	Al(4)$^{\#1}$−C(2)	2.041(8)
Al(1)−Al(2)$^{\#1}$	2.607(3)	Al(2)−Al(3)	2.632(3)
Al(1)−Al(4)$^{\#1}$	2.583(3)	Al(2)−Al(4)$^{\#1}$	2.574(3)
Br(1)−Al(1)−C(1)	132.2(2)	Br(1)−Al(1)−C(2)	110.5(2)
Br(1)−Al(1)−C(3)$^{\#1}$	109.9(2)	Br(1)−Al(1)−Al(4)$^{\#1}$	112.15(10)
Br(1)−Al(1)−Al(2)$^{\#1}$	131.28(12)	Br(1)−Al(1)−Al(3)	131.92(12)
Al(1)$^{\#1}$−Al(2)−Al(3)	90.33(10)	Al(2)$^{\#1}$−Al(4)−Al(1)$^{\#1}$	92.30(10)
Al(4)$^{\#1}$−Al(2)−Al(3)	88.46(10)		

In summary, we have prepared the halogen derivatives $[(AlX)_6(AlNMe_3)_2(CCH_2R)_6]$ (X = F, Cl, Br, I; R = Ph, CH_2SiMe_3) and one partially substituted species using various reagents and compared their spectroscopic data and properties. It is surprising that in the fluorine-containing carbaalane **9** the fluorine atoms are arranged in a terminal rather than in a bridging position. These compounds are key substances for the fast growing field of carbaalanes.

Experimental Section

All manipulations were performed under a dry and oxygen-free inert-gas atmosphere (N_2 or Ar) using Schlenk line and glovebox techniques. IR spectra were recorded in Nujol between KBr plates, and melting points are not corrected. X-ray single-crystal structural analyses were performed on the diffractometers Stoe-IPDS II (diffractometer I) or Stoe-Siemens four circle (diffractometer II) with Mo Kα radiation ($\lambda = 0.710\ 73$ Å). The structures were solved by direct methods and refined by full-matrix least squares on F^2 using the SHELX-97, G. M. Sheldrick, programs for crystal structure refinement, Universität Göttingen, 1997.

$[(AlF)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (9). Method a. $BF_3 \cdot OEt_2$ (150 μL, 165 mg, 1.17 mmol, 6.6 equiv) was added dropwise to a −78 °C cooled solution of $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) (0.18 g, 0.177 mmol, 1.0 equiv) in toluene (15 mL), and the solution turned yellow. The mixture was slowly warmed to room temperature and stirred for 30 min, and all volatiles were removed in vacuo. The product was dried in vacuo at 50 °C giving a yellow solid. Yield: 0.19 g (0.168 mmol, 95%). A sample could be recrystallized from toluene.

Method b. Toluene (15 mL) was added to a mixture of $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) (0.12 g, 0.106 mmol, 1.0 equiv) and finely powdered Me_3SnF (0.16 g, 0.87 mmol, 8.2 equiv). The suspension was roughly stirred 3 d at room temperature. The mixture turned yellow after several hours. The solution was filtered, all volatiles were removed in vacuo, and the residue was dried in vacuo at 40 °C. Yield: 0.11 g (97 μmol, 91%). Mp: 270−280 °C, color changed to orange (until 400 °C no complete dec). ^{1}H NMR (200 MHz, C_6D_6): $\delta = 0.05$ (s, 54 H, Si(C*H*$_3$)$_3$), 1.56 (ddd, *J* = 9.1, 4.3, 4.3 Hz, 12 H; Me$_3$SiC*H*$_2$), 2.18 (s, 18 H, N(C*H*$_3$)$_3$), 2.31 (ddd, *J* = 9.1, 4.3, 4.3 Hz, 12 H; CC*H*$_2$). ^{13}C NMR (126 MHz, C_6D_6): $\delta = -1.65$ (Si(*C*H$_3$)$_3$), 23.5 (Me$_3$Si*C*H$_2$), 28.0 (*C*H$_2$C), 33.1 (broad, cluster-*C*), 47.4 (N(*C*H$_3$)$_3$). ^{19}F NMR (126 MHz, C_6D_6): $\delta = -181.5$ (s, broad, shoulder at ca −178). ^{27}Al NMR (65.2 MHz, C_6D_6): $\delta = 122.3$ (s, $W_{1/2} = 750$ Hz). ^{29}Si NMR (99.4 MHz, C_6D_6): $\delta = -0.65$. MS (EI) [*m*/*z* (%)]: 1226.2 (8, M$^+$). IR: $\tilde{\nu}$ = 1412, 1319, 1259, 1247, 1183, 1103, 1020, 976, 956, 917, 864, 835, 807, 766, 690, 657, 608, 493, 370 cm^{-1}. Anal. Calcd for $C_{42}H_{96}Al_8F_6N_2Si_6$: C, 44.74; H, 8.58; N, 2.48. Found: C, 45.32; H, 8.82; N, 2.33.

$[(AlCl)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (7). A solution of Me_3SiCl (0.52 mL, 0.45 g, 4.12 mmol, 15 equiv) and $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) (0.28 g, 0.275 mmol, 1.0 equiv) in toluene (20 mL) was stirred 1 h at room temperature and refluxed for 2 h. All volatiles were removed in vacuo, and the product was dried at 40 °C in vacuo. Yield: 0.34 g (0.275 mmol, 100%), Mp: 233 °C (dec with color change); 250 °C (rapid dec with gas formation). Spectroscopic data: see ref 2e.

$[(AlBr)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (10). Method a. BBr_3 (0.43 mL of a 1.0 M hexane solution, 0.43 mmol, 2.2 equiv) was added dropwise to a −78 °C cooled solution of $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) (0.20 g, 0.196 mmol, 1.0 equiv) in toluene (15 mL) and slowly warmed to room temperature. All volatiles were removed in vacuo, and the product was dried at 40 °C in vacuo. Yield: 0.27 g (0.182 mmol, 95%).

Method b. A solution of Me_3SiBr (0.34 mL, 0.40 g, 2.59 mmol, 12 eqiuv) and $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) (0.22 g, 0.216 mmol, 1.0 equiv) in toluene (15 mL) was stirred 10 min at room temperature and slowly heated to its boiling point. The mixture was refluxed for 1 h. All volatiles were removed in vacuo, and the product was dried at 40 °C in vacuo. Yield: 0.30 g (0.203 mmol, 94%). Mp: 225 °C (dec with color change); 245 °C (further dec with gas and foam formation). ^{1}H NMR (200 MHz, C_6D_6): $\delta = 0.10$ (s, 54 H, Si(C*H*$_3$)$_3$), 1.58 (ddd, $J = 9.1, 4.3, 4.3$ Hz, 12 H; Me_3SiCH_2), 2.23 (s, 18 H, N(C*H*$_3$)$_3$), 2.39 (ddd, $J = 9.1, 4.3, 4.3$ Hz, 12 H; CCH_2). ^{13}C NMR (126 MHz, C_6D_6): $\delta = -1.52$ (Si(*C*H$_3$)$_3$), 28.0 (Me_3SiCH_2), 28.6 (CH_2C), 32.0 (broad, cluster-*C*), 48.7 (N(*C*H$_3$)$_3$). ^{27}Al NMR (65.2 MHz, C_6D_6): $\delta = 143.9$ (s, $W_{1/2} \approx 1500$ Hz). ^{29}Si NMR (99.4 MHz, C_6D_6): $\delta = 0.2$. MS (EI) [*m/z* (%)]: 1492 (89, M^+). IR: $\tilde{\nu} = 1268, 1086, 1022, 802, 728, 605$ cm^{-1}. Anal. Calcd for $C_{42}H_{96}Al_8Br_6N_2Si_6$: C, 33.79; H, 6.48; N, 1.88. Found: C, 34.64; H, 6.63; N, 1.75.

$[(AlI)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (11). Method a. BI_3 (0.22 g, 0.56 mmol, 2.5 equiv) was cooled to −196 °C, and a solution of $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (**6**) (0.23 g, 0.225 mmol, 1.0 equiv) in toluene (20 mL) was added. The mixture was brought to −78 °C, stirred at this temperature for 30 min, and slowly warmed to room temperature. All volatiles were removed, and the product was dried at 50 °C in vacuo. Yield: 0.36 g (0.203 mmol, 90%).

Method b. A mixture of Me_3SiI (0.265 mL, 0.37 g, 1.86 mmol, 10 equiv) and $[(AlH)_6(AlNMe_3)_2(CCH_2CH_2SiMe_3)_6]$ (0.19 g, 0.186 mmol, 1.0 equiv) in toluene (20 mL) was stirred 1 h at room temperature and refluxed for 30 min. All volatiles were removed in vacuo, and the product was dried at 50 °C in vacuo. Yield: 0.315 g (0.177 mmol, 95%). Mp: 262 °C (dec). ^{1}H NMR (200 MHz, C_6D_6): $\delta = 0.15$ (s, 54 H, Si(C*H*$_3$)$_3$), 1.60 (ddd, $J = 9.1, 4.3, 4.3$ Hz, 12 H; Me_3SiCH_2), 2.25 (s, 18 H, N(C*H*$_3$)$_3$), 2.39 (ddd, $J = 9.1, 4.3, 4.3$ Hz, 12 H; CCH_2). ^{13}C NMR (126 MHz, C_6D_6): $\delta = -1.30$ (Si(*C*H$_3$)$_3$), 29.1 (Me_3SiCH_2), 29.4 (broad, cluster-*C*), 32.6 (CH_2C), 49.1 (N(*C*H$_3$)$_3$). ^{27}Al NMR (65.2 MHz, C_6D_6): $\delta = 144.9$ (s, $W_{1/2} \approx 2300$ Hz). ^{29}Si NMR (99.4 MHz, C_6D_6): $\delta = 0.3$. MS (EI) [*m/z* (%)]: 1774 (3, M^+). IR: $\tilde{\nu} = 1268, 1086, 1022, 802, 728, 605$ cm^{-1}. Anal. Calcd for $C_{42}H_{96}Al_8I_6N_2Si_6$: C, 28.42; H, 5.45; N, 1.58. Found: C, 29.14; H, 5.69; N, 1.47.

$[(AlF)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (13). $BF_3{\cdot}OEt_2$ (0.18 mL, 0.20 g, 1.41 mmol, 6.7 equiv) was added to a fine suspension of $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**5**) (0.20 g, 0.209 mmol, 1.0 equiv) in toluene (20 mL) and stirred for 3 h. The mixture was refluxed for 30 min followed by hot filtration giving a greenish crude product and a yellow solution. Storing the solution at room temperature for several weeks afforded intensive green-yellow crystals of **13** with toluene and a B−F compound. Filtering these crystals off and storing the solution at −25 °C afforded another crop of crystals (plates) of **13**·6toluene with the same color. The crystals were dried in vacuo at 40 °C. Yield: ca. 100 mg (ca. 94 μmol, ca. 45%) and ca. 120 mg crude product. Mp: slow change of color above 280 °C, no melting or full dec until 400 °C. Anal. Calcd for $C_{54}H_{60}Al_8F_6N_2$: C, 62.79; H, 5.67; N, 2.63. Found: C, 63.44; H, 5.99; N, 2.43.

$[(AlX)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (X = Cl (14), Br (15), I (16)). A mixture of $[(AlH)_6(AlNMe_3)_2(CCH_2Ph)_6]$ (**5**) and an excess of Me_3SiX in toluene was stirred, refluxed for 2 h, and filtered hot giving crude products of **14**−**16** and green-yellow solutions from which the compounds precipitated as crystalline solids at room temperature and lower temperatures. Obtained crystalline products were dried in vacuo for several h at 40 °C.

14: **5** (0.29 g, 0.303 mmol, 1.0 equiv), Me_3SiCl (1.00 mL, 0.86 g, 7.92 mmol, 26 equiv), toluene (35 mL); yield ca. 90 mg (ca. 77 μmol, 26%) and ca. 220 mg of crude product; mp 280 °C (dec). Anal. Calcd for $C_{54}H_{60}Al_8Cl_6N_2$: C, 55.64; H, 5.19; N, 2.40. Found: C, 56.46; H, 5.05; N, 2.19.

15: **5** (0.22 g, 0.23 mmol, 1.0 equiv), Me_3SiBr (0.42 mL, 0.49 g, 3.22 mmol, 14 equiv), toluene (25 mL); yield ca. 100 mg (ca. 75 μmol, 33%) and ca. 210 mg of crude product; mp 262 °C (dec). Anal. Calcd for $C_{54}H_{60}Al_8Br_6N_2$: C, 45.28; H, 4.22; N, 1.96. Found: C, 43.56; H, 4.40; N, 2.08.

16: **5** (0.20 g, 0.21 mmol, 1.0 equiv), Me_3SiI (0.30 mL, 0.42 g, 2.09 mmol, 10 equiv), toluene (25 mL); yield: ca. 150 mg (ca. 88 μmol, 42%) and ca. 170 mg of crude product; mp 232 °C (dec). Anal. Calcd for $C_{54}H_{60}Al_8I_6N_2$: C, 37.83; H, 3.53; N, 1.63. Found: C, 38.13; H, 3.62; N, 1.55.

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Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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