Electrophilic Substitution at the NB_9 and NB_{11} *closo*-Skeletons☆

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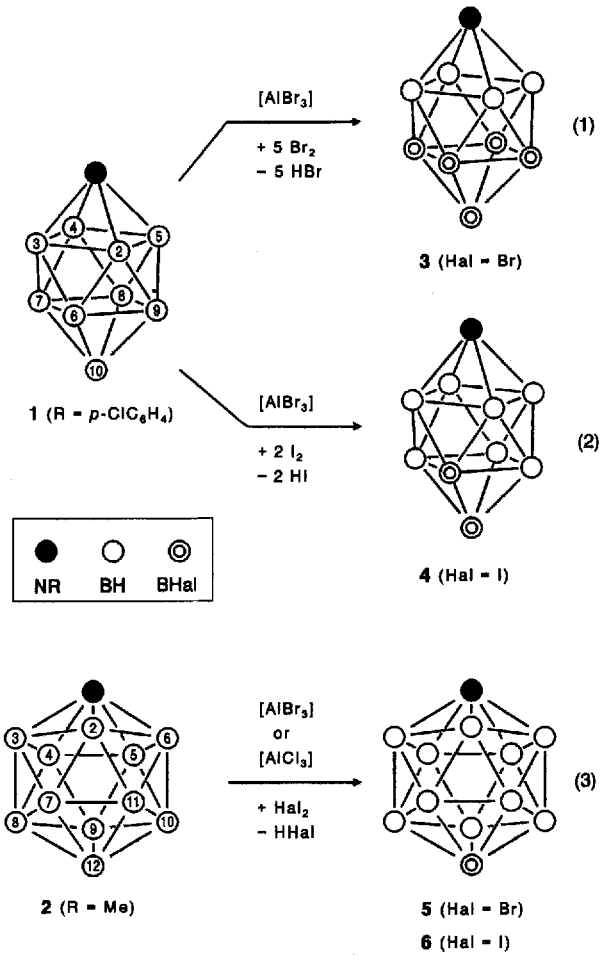
The aza-*closo*-boranes $ArNB_9H_9$ (**1**, Ar = *p*-ClC_6H_4) and $MeNB_{11}H_{11}$ (**2**) were brominated, iodinated, or methylated under Friedel-Crafts conditions to give $ArNB_9H_4Br_5$ (**3**), $ArNB_9H_7I_2$ (**4**), $ArNB_9H_4Me_5$ (**7**), $MeNB_{11}H_{10}Br$ (**5**), $MeNB_{11}H_{10}I$ (**6**), and $MeNB_{11}H_5Me_6$ (**9**), respectively. The upper boron belt adjacent to nitrogen is not involved in the substitution reactions with **1** and **2**. The antipodal position and the lower belt are attacked by electrophiles in the case of **1**; the antipodal position is the preferred one in the case of **2**. By prolongated action of triflic acid on the methylated species **7** and **9**, one methyl group is replaced by the triflate group to give $ArNB_9H_4Me_4(OTrf)$ (**8**) and $MeNB_{11}H_5Me_5(OTrf)$ (**10**) with this group in the positions 6 and 12, respectively. The NMR data indicate the cluster symmetries C_s (**4**, **8**), C_{4v} (**3**, **7**), and C_{5v} (**5**, **6**, **9**, **10**). Crystal structure investigations of **5** (space group *Cc*) and **10** (space group *C*2/*c*) showed that the molecular dimensions of the NB_{11} skeleton are comparable to those of *closo*-$(PhCH_2)NB_{11}H_{11}$.

Synthetic Results

Investigating the pattern of electrophilic substitutions at the NB_9 and NB_{11} *closo* skeletons, we did not start from the parent compounds NB_9H_{10}[1] or $NB_{11}H_{12}$[2] in order to avoid side reactions of the rather acidic NH bonds of both molecules. The *N*-organo derivatives $ArNB_9H_9$ (**1**, Ar = *p*-ClC_6H_4)[3] and $MeNB_{11}H_{11}$ (**2**)[4] appeared to be appropriate starting materials.

The bromination and iodination of **1** proceeded in CH_2Br_2 in the presence of $AlBr_3$ to give the 6,7,8,9,10-pentabromo derivative **3** [Eq. (1)] and the 6,10-diiodo derivative **4** [Eq. (2)], respectively; no products of lower or higher halogenation degree were formed in considerable amounts. – The *closo* cluster **2** allowed only one hydrogen/halogen exchange. The bromination was performed with an excess of bromine at 0°C in the presence of $AlBr_3$ and the iodination with iodine in CH_2Cl_2 in the presence of $AlCl_3$ to give the 12-halo derivatives **5** and **6**, respectively [Eq. (3)].

Aza-*closo*-decarborane **1** was methylated with an excess of methyl triflate at reflux temperature in the presence of a catalytic amount of triflic acid. The 6,7,8,9,10-pentamethyl derivative **7** [Eq. (4)] could be isolated with only 80% purity after a reaction time of four hours; byproducts were clusters of lower methylation degree as revealed by NMR data, besides unreacted starting material. The pure product **8** was obtained when the methylation of **1** was conducted for 16 hours, again with an excess of methyl triflate in the presence of triflic acid. Product **8** contains four methyl groups in the positions 7 to 10 and a triflate group in the position 6. Whereas the cluster **1** is inert toward triflic acid, **8** is also formed by the reaction of **7** with triflic acid, representing formally a nucleophilic substitution of a methyl group [Eq. (5)]. – Six methyl groups were introduced into the positions 7 to 12 of the aza-*closo*-dodecaborane **2**, when **2** was heated first at 80°C for two hours and then at 120°C for four hours in methyl triflate in the presence of triflic acid [Eq.



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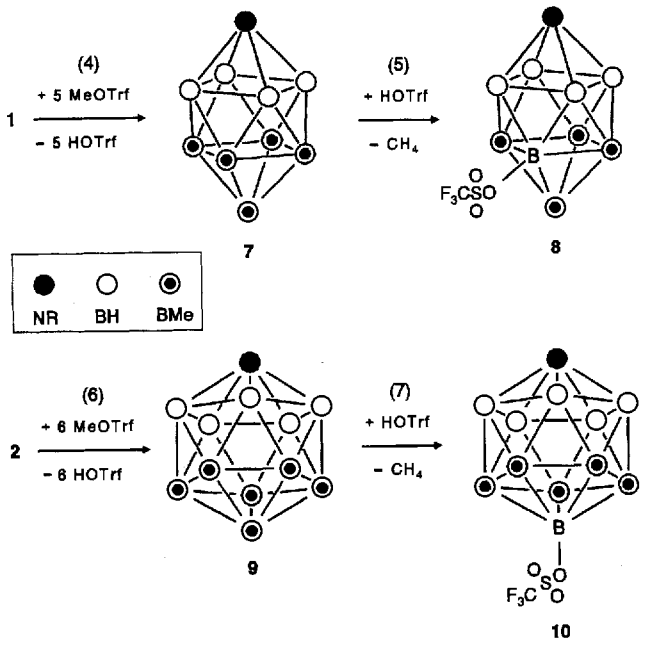
(6)]. Heating of **2** in refluxing methyl triflate for 20 hours, again in the presence of triflic acid, gave the 7,8,9,10,11-pentamethyl-12-triflato derivative **10**. Like **1** the cluster **2** is not attacked either by pure triflic acid, but treatment of **9** with this acid leads to replacement of a methyl by a triflate group in position 12 [Eq. (7)] affording **10**. Apparently, the clusters **7** and **9** are intermediates in the direct formation of **8** and **10** from **1** and **2**, respectively.



Characterization of the Products

The substitution pattern could be characterized unambiguously by NMR methods (Table 1). Six ^{11}B-NMR signals in the ratio of 2:2:2:1:1:1 were found for the molecules with C_s symmetry (**4**, **8**), three signals in the ratio of 4:4:1 or 5:5:1 for the molecules with C_{4v} symmetry (**3**, **7**) or C_{5v} symmetry (**5**, **6**, **9**, **10**). The BH vertices were identified by doublets with the characteristic coupling constants ^1J of about 160 Hz; the BX vertices with non-hydrogen ligands were recognized by the singlet structure of the ^{11}B-NMR signals. The assignment of the skeletal shifts was completed by 2D-^{11}B/^{11}B COSY-NMR spectra of the products **3**–**6**, **8**–**10**. As expected, cross-peaks were not found between the peaks of B2/3 and B4/5 of **4** and **8**, since the corresponding bonds are bridged by the N atom. – The skeletally bound H atoms give rise to clearly detectable ^{1}H{^{11}B}-NMR signals (Table 1). In the cases of C_s symmetry, the assignment of the protons was possible by 2D-^{1}H/^{11}B HMQC-NMR experiments as far as the ^{11}B-NMR signal could be assigned.

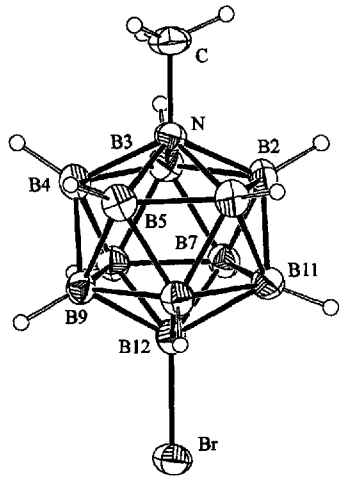
Moreover, the azaboranes **5** and **10** were characterized by X-ray structural analyses (Figures 1, 2). In the case of **10**, the distances and angles do not largely deviate from C_{5v} symmetry, as indicated by the maximal and minimal values in each zone of a bicapped pentagonal prism, which are not far away from the average value; the deviations are larger in the case of **5** (Table 2). As found for 1-benzyl-1-aza-*closo*-dodecaborane $(PhCH_2)NB_{11}H_{11}$[5], the BN distances are certainly the shortest (171.8 and 171.1 pm) and the angles at the N vertex the largest (63.4 and 63.3°) in the skeletons of **5** and **10**, respectively. The longest skeletal bonds of **10** are those in the lower pentagonal belt (181.5 pm), corresponding with large opposite angles, particularly in the antiprismatic deltahedral zone (62.3°); this may be a consequence of steric strain among the five methyl groups. In spite of certain deviations, the icosahedral overall shape of **5** and **10** can easily be recognized.

Table 1. ^{1}H- and ^{11}B-NMR shifts δ[a] of the *closo*-clusters **3**–**10**[b–d] in comparison to the parent clusters **1**[1] and **2**[2]

	H2,3	H4,5	H/Me6	H/Me7,9	H/Me8	H/Me10
1	3.02	3.02	1.33	1.33	1.33	7.69
3	3.52	3.52	-	-	-	-
4	2.96[e]	3.52[e]	-	1.99	1.80	-
7	2.87	2.87	- 0.11	- 0.11	- 0.11	1.15
8	3.00[e]	3.29[e]	-	0.18	- 0.07	1.20
	B2,3	B4,5	B6	B7,9	B8	B10
1	-0.4	-0.4	-20.3	-20.3	-20.3	63.1
3	2.3	2.3	- 8.9	- 8.9	- 8.9	47.4
4	0.8[f]	0.8[f]	-23.5	-13.9	-17.8	43.9
7	-2.0	-2.0	- 9.0	- 9.0	- 9.0	71.8
8	4.7[e]	6.0[e]	-13.1	- 5.8	6.0	63.4
	H2-6	H/Me7-11	H/Me12	B2-6	B7-11	B12
2	2.16	2.47	3.03	- 5.1	-11.2	- 0.1
5	2.56	2.42	-	- 5.0	-10.3	3.5
6	2.58	2.55	-	- 4.1	- 9.4	-12.8
9	2.17	-0.01	- 0.39	- 8.1	- 2.3	10.3
10	2.22	0.66	-	-10.1	- 4.1	14.0

[a] 499.843 and 160.364 MHz (^{1}H/TMS and ^{11}B/$Et_2O \cdot BF_3$, respectively) in CD_2Cl_2 (NB_9 clusters) and $CDCl_3$ (NB_{11} clusters). – [b] Additional ^{1}H-NMR data: δ = 3.12, 3.04, 3.10, 3.14 (NMe of **5**, **6**, **9**, **10**). – [c] ^{13}C NMR (125.639 MHz, TMS): δ = 56.7, 57.4, 56.3, 55.8 (NMe of **5**, **6**, **9**, **10**); −6.4, −5.0, −4.6 (broad signals for BMe of **8**–**10**, Me groups in unequivalent positions of **8**, **9** could not be distinguished); 118.7, 118.4 (^1J = 318 Hz, CF_3 of **8**, **10**). – [d] ^{19}F NMR (470.148 MHz, CCl_3F): δ = −77.1, −77.3 (**8**, **10**). – [e] Arbitrary assignment to positions 2/3 or 4/5. – [f] Accidental degeneracy.

Figure 1. Molecular structure of $MeNB_{11}H_{10}Br$ (**5**) with 30% probability ellipsoids



Discussion of Results

The most extensively investigated hetero-*closo*-boranes are certainly the 1,2-, 1,7-, and 1,12-isomers of $C_2B_{10}H_{12}$,

Figure 2. Molecular structure of $MeNB_{11}H_5Me_5(OTrf)$ (**10**) with 30% probability ellipsoids

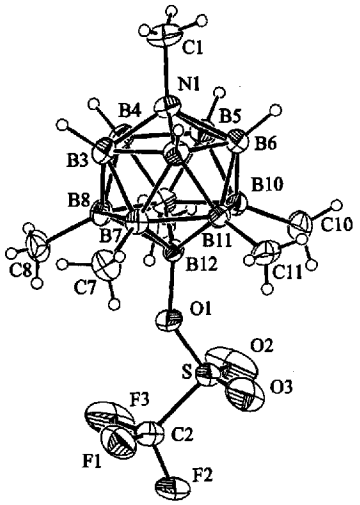


Table 2. Skeletal distances [pm] and angles [°] of **5** and **10**, averaged for zones of hypothetical equivalency[a,b]

	5			**10**		
	aver.	max.	min.	aver.	max.	min.
upper pyr. zone	171.8	174(1)	169(1)	171.1	171.6(5)	170.7(5)
upper belt	180.6	182(1)	175(1)	179.6	180.1(6)	179.3(6)
antiprism. zone	176.4	181(1)	174(1)	175.3	176.4(6)	174.6(6)
lower belt	178.6	181(1)	174(1)	181.5	181.9(6)	181.0(5)
lower pyr. zone	178.0	182(1)	174(1)	177.0	177.5(5)	176.5(5)
angles at N	63.4	64.2(5)	62.9(5)	63.3	63.6(2)	63.2(2)
angles at B2-B6	60.9	61.8(6)	59.6(5)	61.6	61.8(2)	61.4(2)
angles at B7-B11	61.6	62.7(5)	60.4(6)	62.3	62.5(2)	62.1(2)
angles at B12	60.3	61.6(5)	59.1(5)	61.7	61.9(2)	61.4(2)

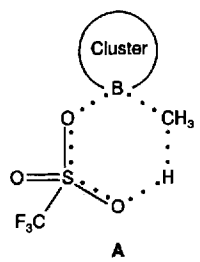
[a] According to hypothetical C_{5v} symmetry with five independent edges (two on a mirror plane, two orthogonal to it, one in general position) and four independent angles (bisected by a mirror plane). – [b] Supplementary bond distances and angles: N–C 150.4(9); B12–Br 194.9(9) (**5**). B7–C7 to B11–C11 158.8 [max. 159.9(5), min. 157.9(5)], N1–C1 151.6(5), B12–O1 147.7(4) pm; B12–O1–S 139.6(2)° (**10**).

whose electrophilic halogenation was thoroughly studied[6–11]. As a general result, the halogenation proceeds successively leading to the introduction of one or several halogen atoms, and the primary attacked B atoms are distant from both C atoms as much as possible, i.e. preferentially in the position 9 (antipodal to one of the C atoms) and preferentially in the positions 9 and 12 (antipodal to each of the C atoms) during the mono- and dihalogenation, respectively, of the 1,2-isomer. Even more similar to the structure of **1** and **2** are the thia-*closo*-boranes 1-SB_9H_9 and $SB_{11}H_{11}$. One, two, or three of the halogen atoms Cl, Br, I can be fixed to the *closo*-SB_9 skeleton by halogenation with the elements[12,13]. A general result is apparently that halogenation in position 6 occurs preferentially kinetically whereas in position 10 it occurs preferentially thermodynamically. Thus, prolonged heating of mixtures of the isomers, mono-halogenated in the 6- or 10-position, increases the amount of the 10-isomer. This is in accord with our finding that the iodination of **1** takes place in the positions 6 and 10 and the bromination in the positions 6 to 10, position 6 being equivalent to the positions 7 to 9. It is not clear, however, whether the position 6 or 10 is preferred in the first halogenation step, since we could not isolate the monohalogen derivatives of **1**. – Similarly, $SB_{11}H_{11}$ may be halogenated once, twice, or even three times[13,14]. The monochlorination occurs preferentially in position 7, the iodination gives a 4:1 mixture of the 7- and the 12-iodo species, whereas we find the 12-bromo and -iodo isomers **5** and **6** exclusively, when **2** is halogenated.

The directive effect of hetero atoms in *closo*-boranes on substitution reactions may be correlated with ground-state charge distributions, if the products are kinetically determined and the transition state is strongly influenced by the ground state. Charge distributions of XB_9H_9 and $XB_{11}H_{11}$ (X = S, NH), based on high-level calculations, are available[15], but on going from the upper belt through the lower belt to the antipodal B atoms, the Mulliken and the Löwdin charge analyses give different sequences for SB_9H_9 as well as for $SB_{11}H_{11}$. Such charge sequences do coincide, however, with NB_9H_{10} and $NB_{11}H_{12}$ and let expect a preferred cationic attack at B-6 of NB_9H_{10} and B-7 of $NB_{11}H_{12}$. This would not necessarily disagree with the experimental findings in the case of **1**, but is not in accord with the specific preference of position 12 in the case of **2**. Apparently the products **5** and **6** are thermodynamically favored.

Friedel-Crafts alkylations of $C_2B_{10}H_{12}$ have been known for many years[17,18]. Recently, the *B*-permethylation of 1,12-$C_2B_{10}H_{12}$ to give 1,12-$H_2C_2B_{10}Me_{10}$ could be achieved by applying an excess of methyl triflate in the presence of triflic acid[19]. We adapted this method to the methylation of **1** and **2**. As with the halogenation, the boron belt adjacent to nitrogen was not attacked, not even by refluxing in that most potent methylation mixture for a prolonged period.

Apparently, the permethylation of the lower boron belt and the antipodal vertex alters the electronic situation of **1** and **2** drastically. The replacement of a methyl by the triflate group according to Eqs. (5) and (7) proceeds formally as a nucleophilic substitution. Nothing is actually known about the mechanism. A concerted process via a six-membered cyclic transition state **A** would make a classification in terms of electrophilic/nucleophilic irrelevant.



A

Whereas electrophiles exclusively attack the vertices distant from nitrogen in the aza-*closo*-boranes **1** and **2**, nucleophiles exclusively approach a vertex adjacent to nitrogen, followed by either opening[3,20] or by opening and removal of one vertex (in the case of **1**)[3].

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Experimental

NMR: Varian Unity 500. – MS: Finnigan MAT 95 (EI, 70 eV). – Elemental analyses: Carlo-Erba Elemental Analyzer 1106. – All experiments were conducted under dry nitrogen; anhydrous solvents were used.

6,7,8,9,10-Pentabromo-1-(4-chlorophenyl)-1-aza-closo-decaborane (**3**): 1-(4-Chlorophenyl)-1-aza-*closo*-decaborane[3] (**1**; 0.12 g, 0.52 mmol) and bromine (0.3 ml, 5.9 mmol) are dissolved in dibromomethane (15 ml), aluminium bromide (0.14 g, 0.52 mmol) is added to the solution, and the mixture is refluxed for 16 h. The solvent is removed from the black solution in vacuo, $AlBr_3$ is sublimated off in vacuo, finally at 150°C, 15 ml of toluene is added to the black residue, and the mixture is filtered. The filtrate is passed through silica gel, and the toluene is removed from the eluate. The brownish residue is crystallized from dibromomethane/hexane to give pale yellow crystals of **3** (0.29 g, 89%). – No peaks besides those originating from **3** can be detected in the NMR spectra. In the mass spectrum of **3**, the mass pattern of $[(p\text{-}ClC_6H_4)NB_9H_3Br_6]^+$ can be observed with 5% intensity compared with the pattern of **3** (100%); the observed isotope pattern is in excellent agreement with the calculated one in both cases.

1-(4-Chlorophenyl)-6,10-diiodo-1-aza-closo-decaborane (**4**): A solution of **1** (0.16 g, 0.69 mmol), iodine (1.75 g, 6.9 mmol), and $AlBr_3$ (1.8 g, 6.8 mmol) in CH_2Br_2 (10 ml) is stirred at ambient temp. for 15 h. The work-up by sublimation gives the colorless solid **4** (0.30 g, 90%). – The mass spectrum reveals the presence of traces of the triiodo derivative $(p\text{-}ClC_6H_4)NB_9H_6I_3$.

12-Bromo-1-methylaza-closo-dodecarborane (**5**): 1-Methylaza-*closo*-dodecaborane[4] (**2**; 160 mg, 1.01 mmol), bromine (2.0 ml, 39 mmol), and $AlBr_3$ (ca. 50 mg) are mixed at 0°C. The mixture is brought to ambient temp. within 2 h and then stirred for 12 h. Volatile materials are removed in high vacuo. The dark residue is extracted with hexane, hexane is evaporated from the extract in vacuo and the colorless product sublimated (50°C/0.001 Torr). Recrystallization from CH_2Cl_2 gives pure **5** (122 mg, 51%). – The observed isotope pattern of the molecule cation 5^+ (100%) coincides with the calculated one.

12-Iodo-1-methylaza-closo-dodecaborane (**6**): A solution of **2** (160 mg, 1.01 mmol), iodine (500 mg, 1.97 mmol), and $AlCl_3$ (ca. 40 mg) in CH_2Cl_2 (5 ml) is refluxed for 2 h; the violet color of I_2 changes to the brown color of I_3^- after 30 min. After removal of the volatile materials in vacuo, the grey residue is extracted with three portions of hexane. The combined extracts contain a colorless solid from which pure **6** (180 mg, 63%) is isolated first by sublimation (80°C/0.001 Torr) and then by recrystallization from hexane at −40°C. – MS, *m/z* (%): 285 (100); $^{12}C^1H_{13}{}^{10}B_2{}^{11}B_9{}^{14}N^{127}I$: calcd. 285.118895; found 285.118880.

1-(4-Chlorophenyl)-6,7,8,9,10-pentamethyl-1-aza-closo-decaborane (**7**): A suspension of **1** (0.06 g, 0.026 mmol) in methyl triflate (2.0 ml) is refluxed for 4 h in the presence of a drop of triflic acid. After removal of all volatile materials in vacuo, the remaining colorless solid is dissolved in hexane. A solid crystallizes at −40°C that contains **7** (ca. 80%) and unreacted **1** besides traces of material less methylated than **7**, according to ^{11}B-NMR data.

1-(4-Chlorophenyl)-7,8,9,10-tetramethyl-6-(trifluoromethylsulfonyl)-1-aza-closo-decaborane (**8**): A mixture of **1** (125 mg, 0.54 mmol), methyl triflate (6 ml), and triflic acid (0.5 ml) is refluxed for 16 h. Work-up by sublimation gives a fraction (70–110°C/0.001 Torr) of colorless solid **8** (200 mg, 85%), which is pure according to the NMR spectra. – MS, *m/z* (%): 436 (100) [M^+], 287 (30) [M − O_3SCF_3], 149 (20) [$O_3SCF_3^+$], 69 (40) [CF_3^+], and other signals.

1,7,8,9,10,11,12-Heptamethylaza-closo-dodecaborane (**9**): A mixture of **7** (160 mg, 1.01 mmol), methyl triflate (1.5 ml), and triflic acid (0.4 ml) is heated at 80°C for 2 h and then at 120°C for 4 h. Excess triflate and triflic acid are removed in vacuo to give a brown oil, from which colorless solid **9** (117 mg, 48%) can be sublimated (20°C/0.001 Torr). – MS, *m/z* (%): 243 (100) [M^+], 228 (68) [M − Me], 213 (25) [M − 2 Me], 198 (8) [M − 3 Me], 183 (5) [M − 4 Me], 168 (5) [M − 5 Me], 153 (5) [M − 6 Me], and other signals.

1,7,8,9,10,11-Hexamethyl-12-(trifluoromethylsulfonyl)aza-closo-dodecaborane (**10**): A solution of the cluster **2** (190 mg, 1.19 mmol) in methyl triflate (1.5 ml) is refluxed in the presence of triflic acid (0.4 ml) for 20 h. Volatile compounds are then removed in vacuo. The black residue is extracted with three portions of hexane. The colorless extracted solid is sublimated (40°C/0.001 Torr). Pure **10** is recrystallized from hexane at −40°C (300 mg, 67%). – $C_7H_{23}B_{11}F_3NO_3S$ (377.2): calcd. C 22.29, H 6.15, N 3.71; found C 22.23, H 6.33, N 3.71.

Crystal Structure Investigations of **5** *and* **10**: Data were collected at −45°C with an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator (Cu-K_α: λ = 154.18 pm). Crystal data and convergence results are compiled in Table 3. The structures were solved with direct methods (SHELXS-86) and refined on *F* (SDP). All hydrogen atoms were located in difference Fourier maps; they were idealized (C–H 98, B–H 110 pm) and allowed to ride on their corresponding heavy atoms in the case of **5** and refined isotropically in the case of **10**. The highest residual electron density in a final difference Fourier map was 2.4 eÅ^{-3} close to the Br atom in **5** and 0.6 eÅ^{-3} close to the CF_3 group in **10**[21].

Table 3. Crystal data and refinement results

	5	**10**
Formula	$CH_{13}B_{11}BrN$	$C_7H_{23}B_{11}F_3NO_3S$
Space group (no.)	*Cc* (9)	*C2/c* (15)
a [pm]	699.6(2)	1595.9(2)
b [pm]	1257.3(3)	979.8(1)
c [pm]	1271.2(3)	2583.0(3)
β [°]	90.64(2)	100.856(8)
V [nm^3]	1.1181(5)	3.9665(8)
Z	4	8
Calcd.density [g cm^{-3}]	1.413	1.263
Crystal dimens. [mm^3]	0.15×0.15×0.12	0.35×0.30×0.30
μ [cm^{-1}]	45.30	17.16
Refls.	3356	9330
Scan range [°]	5<θ<72	5<θ<72
Indep. reflexions	2223	3899
Indep. refls. $I > 1.0\,\sigma(I)$	1774	2460
Refined parameters	126	327
R	0.062	0.075
$R_w[w^{-1} = \sigma^2(F_O)]$	0.067	0.082
GOF	1.359	1.822

☆ Dedicated to Professor *Kurt Dehnicke* on the occasion of his 65th birthday.

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[21] Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (FRG), on quoting the depository number CSD-405164 (**5**) or 405146 (**10**).

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