N-Alkylation of Ammine–Undecahydro-*closo*-dodecaborate(1–)☆

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The reactions of the ammine–undecahydro-*closo*-dodecaborate(1–) anion with alkyl halides have been studied in detail. The degree of alkylation of the nitrogen was found to be dependent upon the steric demands of the alkyl groups. The derivatives were characterized by NMR and infrared spectroscopy. Four compounds were crystallized for single crystal X-ray diffraction studies. The tetrahedral coordination of the nitrogen atom of the bis-alkylated derivatives was found to deviate towards planarity with increasing steric hindrance of the substituents. – The syntheses, crystal structures, and spectral properties of four *N*-alkyl derivatives of $[H_3N-B_{12}H_{11}]^-$, ammine–undecahydro-*closo*-dodecaborate(1–) (**3**), are reported. Alkylation of **3** with ethyl iodide was achieved in dimethyl sulfoxide using potassium hydroxide as a base. This led to orthorhombic crystals of $[N(n\text{-}C_4H_9)_4][(CH_3CH_2)_3N-B_{12}H_{11}]$ (**4**). The reaction of **3** with benzyl chloride resulted in the bisbenzylated product, isolated as triclinic crystals of $[PPN][(C_6H_5CH_2)_2NH-B_{12}H_{11}]$ (**5**). The alkylation of **3** with 2-bromopropane gave a mixture of the mono- and bisalkylated products. The monoalkylated derivative $[PPN][(CH_3)_2CH)NH_2-_{12}H_{11}]$ (**6**, crystallized in the triclinic space group $P\bar{1}$) and the bisalkylated product $[PPN]\{[(CH_3)_2CH]_2NH-B_{12}H_{11}\}$ (**7**, monoclinic, $P2_1/c$) were separated on the basis of their different water solubilities. The solid-state structures of the compounds **4**–**7** revealed a slight distortion of the B_{12} icosahedron. The length of the B(1)–N(1) bond was found to be dependent on the steric requirements of the attached amine, e.g. primary amine < secondary amine < tertiary amine. This is demonstrated by the variation in the B–N bond lengths; from 157.8(2) pm for **6**, 158.5(5) pm for **5**, 160.0(3) pm for **7**, to 163.7(6) pm for **4**.

Introduction

Recently we described the reactions of the monochalkogen derivatives of dodecahydro-*closo*-dodecaborate(2–), $[HO-B_{12}H_{11}]^{2-}$ (**1**)[1] and $[HS-B_{12}H_{11}]^{2-}$ (**2**)[2], with electrophiles. In the case of the derivatives of **1**, the length of the B–O bond was influenced by the organic group R {the bond length varies from 144.2(5) pm for $[CH_3CH_2O-B_{12}H_{11}]^{2-}$ to 152.8(4) pm for the tetrahydropyran adduct $[(CH_2)_5O-B_{12}H_{11}]^-$}[1]. This difference in the bond lengths was explained in terms of increasing steric requirements. Alkylation and acylation of **2** afforded surprisingly stable sulfonium salts and thioesters, respectively[2].

To continue the investigations on reactions of monosubstituted B_{12} clusters with electrophiles, we studied the chemistry of $[H_3N-B_{12}H_{11}]^-$, amine–undecahydro-*closo*-dodecaborate(1–) (**3**). Hertler and Raasch prepared **3** by reaction of $[B_{12}H_{12}]^{2-}$ with hydroxylamine-*O*-sulfonic acid, and isolated its protonated form $[H_3N-B_{12}H_{11}]^-$ (instead of $[H_2N-B_{12}H_{11}]^{2-}$). This was the case even from alkaline solution[3].

Various *N*-substituted $[B_{12}H_{12}]^{2-}$ derivatives have already been described. *N*-alkylated B_{12} clusters were obtained by the reactions of amines with diborane[4] at higher temperatures. The reaction of trimethylamine–borane with diborane at 175°C gave $[(CH_3)_3N-B_{12}H_{11}]^-$, and the reaction of ethyldimethylamine and diborane gave $[CH_3CH_2(CH_3)_2N-B_{12}H_{11}]^-$. $[(CH_3CH_2)_3N-B_{12}H_{11}]^-$, isolated as its potassium salt, was obtained by the reaction of decaborane(14) with triethylamine in triethylamine–borane[5].

Here we report reactions of **3** with alkyl halides, under basic conditions, that lead to amine-substituted B_{12} clusters. The new compounds were characterized by X-ray structure analysis, IR and NMR spectroscopy, and elemental analysis.

Results

Syntheses

N-Alkylation of **3** with alkyl halides was accomplished using dimethyl sulfoxide as solvent in the presence of potassium hydroxide. In all cases the alkylation products contained a positively charged nitrogen, as expected because **3** is itself isolated in its protonated form[3]. The degree of *N*-alkylation of **3** depended on the type of alkyl halide used. As revealed by ^{1}H-NMR data, the reaction of **3** with ethyl iodide gave triethylamine–undecahydro-*closo*-dodecabo-

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rate(1−) (**4**). Compound **4** has been synthesized before in the reaction of triethylamine−borane with decaborane(14) at elevated temperatures[4,5,8], and was characterized by IR data and by its crystal structure as the potassium[5] and tetramethylammonium[8] salt. We obtained crystals of the tetrabutylammonium salt that were suitable for X-ray crystallography. The anion **4** consists of a slightly distorted icosahedron with the triethylamine molecule coordinated, through nitrogen, to the boron cluster (Table 1). The B−B distances vary from 174.2(7) to 180.6(7) pm, and the B(1)−N(1) bond length is 163.7(6) pm (see Table 2). The potassium and tetramethylammonium salts of **4** exhibit similar structures to the anion, with B(1)−N(1) distances of 165(1) and 163(1) pm, respectively. No vibrational frequency ν(N−H) was found in the IR spectra of **4**, which is dominated by a band for ν(B−H) at 2492 cm^{-1}.

Table 1. Crystallographic data and data collection for compounds **4**−**7**

	4	**5**	**6**	**7**
formula	$C_{22}H_{62}B_{12}N_2$	$C_{50}H_{56}B_{12}N_2P_2$	$C_{39}H_{50}B_{12}N_2P_2$	$C_{42}H_{56}B_{12}N_2P_2$
fw	484.5	876.6	738.5	780.6
space group	$P2_12_12_1$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$
a, pm	1144.3(7)	955.8(1)	1028.3(2)	1628.1(4)
b, pm	1416.3(9)	1321.3(1)	1285.6(1)	1571.5(3)
c, pm	2059.2(18)	1997.6(2)	1631.2(3)	1906.7(5)
α, deg	90	105.41(1)	93.70(1)	90
β, deg	90	94.016(1)	107.33(2)	113.81(1)
γ, deg	90	92.276(1)	90.05(1)	90
V, nm^3	3.3373(41)	2.42165(4)	2.0538(6)	4.4631(18)
ρ(calcd), gcm^{-3}	0.952	1.202	1.194	1.162
Z	4	2	2	4
μ, mm^{-1}	0.048	0.128	0.138	0.131
T, K	293	293	173	203
R	0.076	0.066	0.047	0.043
wR_2	0.188	0.173	0.123	0.110
GOF	0.89	1.08	0.97	1.07
2θ range [°]	3.50–48.02	2.12–46.52	5.18–54.98	2.74–46.54
h, *k*, *l*	$-13 \le h \le 13$	$-10 \le h \le 10$	$-1 \le h \le 13$	$-16 \le h \le 18$
	$-16 \le k \le 13$	$-13 < k \le 14$	$-16 \le k \le 16$	$-17 \le k \le 17$
	$-22 \le l \le 17$	$-22 \le l \le 22$	$-21 \le l \le 20$	$-19 \le l \le 21$
Measured refl.	7146	10905	11188	17582
Unique refl.	5001	6755	9439	6312
$F > 4\sigma(F)$	2454	5414	7495	5252
Struct. soln.	Direct method	Direct method	Direct method	Direct method
Variables	367	643	514	563
Largest residual electron density [$eÅ^{-3}$]	0.35	0.27	0.77	0.32

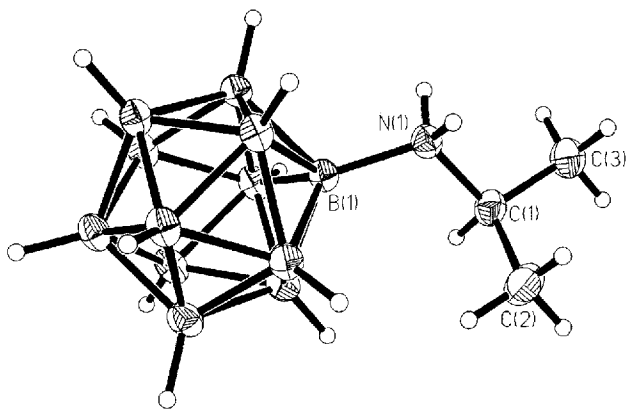
Table 2. Selected bond lengths [pm] of anions **4**−**7**

	4	**5**	**6**	**7**
B–B	174.2(7)–180.6(7)	174.9(6)–178.8(7)	176.3(2)–179.6(2)	175.5(4)–178.4(4)
B(1)–N(1)	163.7(6)	158.5(5)	157.8(2)	160.0(3)

Dibenzylamine−undecahydro-*closo*-dodecaborate(1−) (**5**) was synthesized by reaction of **3** with benzyl chloride. Crystals suitable for X-ray analysis were obtained from its PPN salt. The ^{1}H-NMR data of **5** are consistent with dibenzylation. The two signals at δ = 3.9 and δ = 4.6 constitute two AB systems, which are assigned to the two diastereotopic methylene protons. The infrared spectrum is dominated by a strong B−H stretching band at 2500 cm^1, and an absorption at 3209 cm^1 is assigned to the N−H vibration. The boron bonding situation [174.9(6)−178.8(7) pm] of the icosahedron is consistent with other B_{12} derivatives. The B(1)−N(1) bond [158.5(5) pm] is significantly shorter than for the anion **4**. The two C−N(1)−B(1) angles are almost equal [112.0(3)° and 112.7(3)°]. The three angles about N(1) sum to 340.7°.

The reaction of 2-bromopropane with **3** yielded two products which, when separated by HPLC, proved to be the mono- and diisopropylamine derivatives **6** and **7**. The ^{1}H-NMR spectrum of **6** exhibited a broad singlet at δ = 5.9, a septet at δ = 3.0, and a doublet at δ = 1.2, with an intensity ratio of 2:1:6. The ^{13}C-NMR spectrum gave two singlets for the anion, at δ = 49.4 and 21.3. Considering the ^{1}H-NMR integration and the fact that the carbons of the methyl groups gave a singlet in the ^{13}C-NMR spectrum, the structure was assigned to the monoisopropyl derivative. This was confirmed by the NMR data of the diisopropylamine derivative **7**. Its ^{13}C-NMR spectrum displayed two signals, at δ = 19.9 and δ = 19.2 ppm, for the diastereotopic methyl groups. The ^{1}H-NMR spectrum (broad singlet at δ = 5.7, septet at δ = 3.7, two doublets at δ = 1.4, intensity ratio 1:2:12) showed the intensity ratio of a diisopropyl derivative. To prove the assignment of the degree of substitution, the solid-state structures of **6** and **7** were elucidated by X-ray analysis. A view of the molecular structure of **6** is given in Figure 1. Selected bond lenghts and angles are given in Table 3.

Figure 1. Molecular structure of **6**: the thermal ellipsoids represent a 30% probability level



As expected the B(1)−N(1) distance [157.8(2) pm] of **6** is the shortest found for the compounds **4**−**7**. The boron cluster is only slightly distorted. B−B distances vary from 176.3(2) to 179.6(2) pm. Widening of the B(1)−N(1)−C(1) angle [117.8(1)°] compared to the value for sp^3 geometry is probably due to steric reasons. The structure of **7** is shown in Figure 2. Table 4 gives selected bond lengths and angles.

The B−B bond lengths [175.5(4)−178.4(4) pm] and the B(1)−N(1) distance [160.0(3) pm] are comparable to those of compound **5**. However, the sum of the bonding angles about N(1) has increased to 347.8°, showing the steric effect of both the $B_{12}H_{11}$ and two isopropyl groups. The second difference is found in the B(1)−N(1)−C angles, which differ

Table 3. Selected bond lengths [pm] and angles [°] for anion **6**

N(1)–C(1)	151.2(2)	N(1)–B(1)	157.8(2)
N(1)–B(1)	157.8(2)	C(1)–C(3)	152.1(2)
C(1)–C(2)	152.2(2)	B(1)–B(4)	176.3(2)
B(1)–B(2)	177.0(2)	B(1)–B(6)	176.7(2)
B(1)–B(5)	177.2(2)	B(2)–B(7)	178.2(2)
B(2)–B(11)	178.3(3)	B(1)–B(3)	177.3(2)
B(2)–B(6)	179.3(2)	B(2)–B(3)	179.6(2)
B(3)–B(8)	177.9(2)	B(3)–B(7)	178.0(2)
B(3)–B(4)	178.4(2)	B(4)–B(8)	178.1(2)
B(4)–B(5)	178.0(2)	B(4)–B(9)	178.1(2)
B(5)–B(10)	177.3(2)	B(5)–B(9)	177.4(2)
B(5)–B(6)	178.9(2)	B(6)–B(11)	177.6(2)
B(6)–B(10)	179.0(2)	B(7)–B(12)	177.8(3)
B(7)–B(11)	178.1(2)	B(7)–B(8)	178.3(3)
B(8)–B(12)	178.3(2)	B(8)–B(9)	178.6(2)
B(9)–B(12)	178.3(2)	B(9)–B(10)	178.5(2)
B(11)–B(12)	177.5(2)		
C(1)–N(1)–B(1)	117.8(1)	N(1)–C(1)–C(3)	110.6(1)
N(1)–C(1)–C(2)	109.9(1)	C(3)–C(1)–C(2)	111.9(1)

Figure 2. Molecular structure of **7**; the thermal ellipsoids represent a 30% probability level

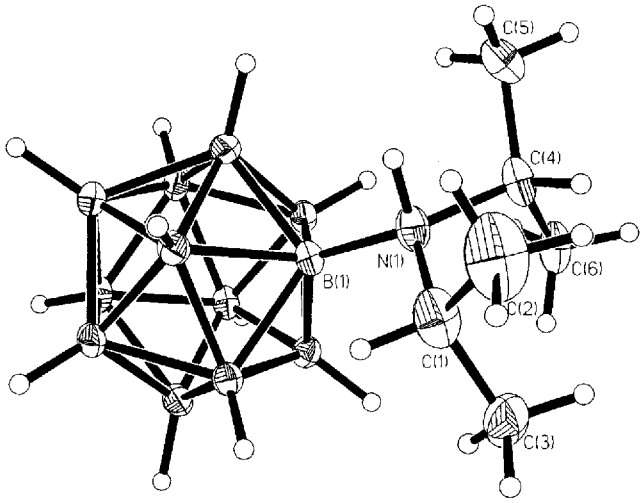


Table 4. Selected bond lengths [pm] and angles [°] for anion **7**

N(1)–C(1)	151.4(4)	N(1)–C(4)	153.4(3)
N(1)–B(1)	160.0(3)	B(1)–B(4)	175.5(4)
B(1)–B(5)	176.1(4)	B(1)–B(6)	177.5(4)
B(1)–B(2)	177.4(4)	B(1)–B(3)	177.6(4)
B(2)–B(8)	177.0(4)	B(2)–B(7)	177.7(4)
B(2)–B(3)	177.7(4)	B(2)–B(6)	178.2(4)
B(3)–B(9)	177.2(4)	B(3)–B(8)	177.9(4)
B(3)–B(4)	177.9(4)	B(4)–B(10)	177.1(4)
B(4)–B(9)	177.8(4)	B(4)–B(5)	178.2(4)
B(5)–B(10)	176.4(4)	B(5)–B(11)	177.0(4)
B(5)–B(6)	177.9(4)	B(6)–B(11)	176.5(4)
B(6)–B(7)	177.7(4)	B(7)–B(12)	177.1(4)
B(7)–B(8)	177.8(4)	B(7)–B(11)	178.4(4)
B(8)–B(12)	176.9(4)	B(8)–B(9)	177.8(4)
B(9)–B(12)	177.1(4)	B(9)–B(10)	177.5(4)
B(10)–B(12)	177.7(4)	B(10)–B(11)	177.4(4)
B(11)–B(12)	176.6(4)		
C(1)–N(1)–C(4)	113.2(2)	C(1)–N(1)–B(1)	114.2(2)
C(4)–N(1)–B(1)	120.4(2)		

in **7** by 6.2° [114.2(2) and 120.4(2)°], whereas **5** shows two almost identical B(1)–N(1)–C angles.

Discussion

Alkylation of **3** was realized under strong basic conditions because the amino group is itself very basic. Alkylated anions **5**–**7** were found to be protonated as expected. In contrast to reactions of $[HO-B_{12}H_{11}]^{2-}$, which usually afforded the monoalkylated product (with the exception of the reaction with dibromopentane, which gave the bisalkylated anion $[(CH_2)_5O-B_{12}H_{11}]^{-}$[1]), and reactions of $[HS-B_{12}H_{11}]^{2-}$, which generally gave the disubstituted derivative[2], the degree of alkylation of **3** depends on the type of alkyl halide used. The reactions are controlled by steric factors, which increase in the order ethyl < benzyl < isopropyl.

In the solid state, the degree of alkylation influences the B(1)–N(1) bond length only slightly. The difference between the bond length in **6** and **4** is 4.9 pm. We assume that the distance between the *ipso*-boron atom and the ligating heteroatom in influenced by steric factors that result in lengthening of the B(1)–N(1) bond. The B–B bond distances of compounds **4**–**7** are comparable to those found for derivatives of **1**[1] and to those of the unsubstituted $B_{12}H_{12}^{2-}$ cluster. This indicates that the monosubstitution affects the icosahedral geometry to only a small extent.

In order to estimate the influence that the icosahedral cluster has on the configuration of the attached amines, we compared the crystal structures of compounds **4**–**7** to the structures of the analogues ammonium salts. As observed before, for ligands attached through oxygen to the B_{12} cluster[1], negligible differences were found on comparing the C–N(1) bond lengths of protonated amines with the distances described in this paper for compounds **4**–**7** (see Table 5).

Table 5. C–N bond lengths of compounds **4**–**7** and analogous ammonium salts

Ammonium salt	C–N bond length (pm)	Boron cluster	C–N bond length (pm)
$NEt_3 \cdot HCl$[a]	148.4(7)	**4**	147.5(8)–153.0(6)
$[NH_2Bn_2][CuCl_4]$[b]	155.2(10), 150.7(11)	**5**	151.6(5), 151.7(4)
$[NH_3i\text{-}Pr]_3[P_3O_9]$[c]	150.0(5)	**6**	151.2(2)
$NH(i\text{-}Pr)_2 \cdot HCl$[d]	150.4(4)	**7**	151.1(4), 153.4(3)

[a] M. A. James, T. S. Cameron, O. Knop, M. Neumann, M. Falk, *Can. J. Chem.* **1985**, *63*, 1750–1758. – [b] G. Zeng, M. Qin, Y. Lin, S. Xi, *Acta Crystallogr.* **1994**, *C50*, 200–202. – [c] M. T. Averbuch-Pouchot, A. Durif, J. C. Guitel, *Acta Crystallogr.* **1988**, *C44*, 1907–1909. – [d] P. Prince, J. A. Miller, F. R. Fronczek, R. D. Gandour, *Acta Crystallogr.* **1990**, *C46*, 336–338.

Table 6 lists the ^{13}C-NMR resonances of compounds **4**–**7** and some amine hydrochlorides. In general the α-carbon of the amine moiety is shifted downfield, whereas the β-carbon does not appear to be influenced, when compared to the analogous protonated amines. The downfield shift ranges from 9.2 ppm for the dibenzylamine derivative **5** to 4.1 ppm for the monoisopropyl derivative **6**. We attribute the deshielding effect to the electron deficiency of the B_{12} cluster.

The ^{11}B-NMR data (see Table 7) of compounds **3**–**7** exhibit deshielding for B(1), but the chemical shifts of vertices B(2–12) are the same in the cases of **4** and **5** and similar

Table 6. ^{13}C-NMR data of compounds **4**–**7** and their analogous amine hydrochlorides

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$NH(i\text{-}Pr)_2 \cdot HCl$[d]	150.4(4)	**7**	151.1(4), 153.4(3)

[a] Sadtler Research Laboratories, Inc., *Sadtler Standard Carbon-13 NMR Spectra*, Researchers, Philadelphia, USA, **1976**, No. 1020C. – [b] Sadtler Research Laboratories, Inc., *Sadtler Standard Carbon-13 NMR Spectra*, Researchers, Philadelphia, USA, **1985**, No. 18862C. – [c] Sadtler Research Laboratories, Inc., *Sadtler Standard Carbon-13 NMR Spectra*, Researchers, Philadelphia, USA, **1976**, No. 375C. – [d] Sadtler Research Laboratories, Inc., *Sadtler Standard Carbon-13 NMR Spectra*, Researchers, Philadelphia, USA, **1979**, No. 7391C.

for **6** and **7**. In contrast to $[HO{-}B_{12}H_{11}]^{2-}$ derivatives[1], the B(12) vertex of compounds **4**–**7** is not shifted to higher field. Only for compound **3** was the typical 1:5:5:1 pattern, as is usually observed for $[HO{-}B_{12}H_{11}]^{2-}$ derivatives[1], found.

Table 7. ^{11}B-NMR chemical shifts (δ scale) of compounds **3**–**7**

Substituent		B(1)	B(2–6)	B(7–11)	B(12)
NH_3	**3**	–2.5	–11.7	–12.1	–13.8
$N(C_2H_5)_3$	**4**	1.6	–12.5	–12.5	–12.5
$NH(CH_2C_6H_5)_2$	**5**	0.8	–12.5	–12.5	–12.5
$NH_2CH(CH_3)_2$	**6**	–1.7	–12.2	–12.2	–13.3
$NH[CH(CH_3)_2]_2$	**7**	–0.9	–11.9	–12.2	–12.2

Interesting features of the two bisalkylated compounds **5** and **7** were observed. With the increasing steric demands of the two alkyl groups, the nitrogen geometry seems to deviate from tetrahedral towards planar coordination. The sum of the three bonding angles around the nitrogen is found to increase from 340.7° (for the dibenzylamine derivative **5**) to 347.8° (for the diisopropylamine derivative **7**). A similar effect was observed in the case of $[(CH_2)_5O{-}B_{12}H_{11}]^{2-}$, with a total of 356.1° about oxygen[1].

Conclusions

The present study has shown that it is possible to alkylate $[H_3N{-}B_{12}H_{11}]^-$ under strongly basic conditions. Different degrees of alkylation were observed, depending on the type of halide used. The crystal structures of derivatives of **3** revealed that the B–N bond length was slightly influenced by the different steric requirements of the organic group R. As observed for bisalkylated oxygen in $R_2OB_{12}H_{11}$, greater steric demands force the bis-substituted nitrogen atom closer to planar coordination.

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Experimental Section

Dimethyl sulfoxide was dried (molecular sieve) prior to use. Moisture was removed from $[N(CH_3)_4][H_3N{-}B_{12}H_{11}]$[3] by heating for 2 h at 200°C under vacuum. The reactions were carried out under conditions where moisture was excluded ($CaCl_2$ drying tube). – The NMR spectra were recorded in $[D_6]$DMSO at room temperature: ^{11}B-NMR spectra [$\delta(Et_2OBF_3) = 0.0$] were recorded at 115.5 MHz on a Bruker WH 360 spectrometer; ^{1}H NMR [δ(TMS) = 0.0] and ^{13}C-NMR spectra [δ(TMS) = 0.0] were obtained at 360.1 and 90.1 MHz, respectively. The NMR data of the cations and a broad multiplet in the ^{1}H-NMR spectra (δ = 2.2–0.6) for the 11 B–H protons are not given in the experimental section. – Infrared spectra were determined on KBr pellets on a Biorad FTS-7 spectrometer. – Microanalyses were performed by Analytische Laboratorien, Prof. Dr. H. Malissa and G. Reuter GmbH, Gummersbach, Germany. – Data collection for the single-crystal X-ray diffraction of compounds **4**–**7** was performed by using a Siemens P4 diffractometer operating with a graphite monochromator and Mo-K_α radiation, λ = 71.073 pm. Computations were performed by using the SHELXTL PC[6] or SHELXL 93[7] program packages. – Melting points determined on a Gallenkamp melting point apparatus are uncorrected. – PPN is used as an abbreviation for the (μ-nitrido)bis(triphenylphosphonium)(1+) cation.

Synthesis of $[N(n\text{-}C_4H_9)_4][(CH_3CH_2)_3N{-}B_{12}H_{11}]$ (**4**): A 200-mg sample of **3** (0.86 mmol) and 242 mg of potassium hydroxide (5.38 mmol) were stirred in 8 ml of dimethyl sulfoxide. To this solution was added 0.7 ml of ethyl iodide (8.60 mmol). After stirring for 24 h at room temperature the solvent was removed in vacuo and the orange residue dissolved in acetonitrile. After the insoluble material was filtered off, the filtrate was added to 250 ml of diethyl ether and the resulting precipitate was removed by filtration. The material obtained as a gummy solid was dissolved in acetonitrile, filtered, and the filtrate was combined with a solution of 720 mg tetrabutylammonium chloride (2.60 mmol) in 50 ml of water. A yellow precipitate formed, which was collected and recrystallized from ethanol to yield 224 mg (0.63 mmol, 73% yield) of **4** [m.p. 194°C; the literature value[5] is (due to a typographical error?) 295°C]. Crystals suitable for X-ray structure analysis were obtained from acetonitrile/diethyl ether. – ^{1}H NMR: δ = 3.3 (q, CH_2), 1.4 (t, CH_3). – $^{13}C\{^1H\}$ NMR: δ = 54.0 (CH_2), 10.3 (CH_3). – IR: $\tilde{\nu}$ = 3749, 2963, 2934, 2872, 2492 (BH), 1470, 1383, 1319, 1175, 1147, 1046, 970, 881, 825, 733 cm^{-1}. – $C_{22}H_{62}B_{12}N_2$ (484.5): calcd. C 54.54, H 12.90, N 5.78, B 26.78; found C 54.60, H 12.81, N 5.60, B 26.57.

Synthesis of $[N(CH_3)_4][(C_6H_5CH_2)_2NH{-}B_{12}H_{11}]$ (**5**): A 315-mg sample of **3** (1.36 mmol) and 360 mg of potassium hydroxide (6.40 mmol) were stirred in 10 ml of dimethyl sulfoxide. To this solution 1.63 ml (14.20 mmol) of benzyl chloride was added. The solution turned slightly pink. After stirring for 5 h at room temperature the solvent was removed in vacuo and the residue was stirred in 250 ml of diethyl ether. The diethyl ether was decanted and the resulting solid was then heated in 50 ml of water. Acetonitrile was added until the solid dissolved. Acetonitrile was evaporated in vacuo to precipitate 430 mg (1.04 mmol, yield 77%) of **5** (m.p. 236°C). To obtain crystals suitable for X-ray analysis, **5** was converted to the PPN salt, which was dissolved in dichloromethane. Ethanol was added. Crystals were formed by slowly evaporating the volatile constituents at room temperature. – ^{1}H NMR: δ = 7.3–7.2 (m, C_6H_5), 6.7 (s, br., NH); 4.6, 3.9 (2 dd, CH_2). – $^{13}C\{^1H\}$ NMR: δ = 134.3 (2 C-1); 129.8, 128.0 (2 C-2, 2 C-3); 127.9 (2 C-4); 59.0 (2 CH_2). – IR: $\tilde{\nu}$ = 3209 (NH), 3030, 2500 (BH), 1483, 1455, 1398, 1374, 1199, 1049, 1015, 990, 947, 884, 756, 699, 500 cm^{-1}. – $C_{18}H_{38}B_{12}N_2$ (412.2): calcd. C 52.45, H 9.29, N 6.80, B 31.47; found C 52.70, H 9.04, N 3.91, B 31.18. The low

value determined for nitrogen is probably due to boron nitride formation.

Syntheses of $[N(n\text{-}C_5H_9)_4][(CH_3)_2CHNH_2\text{–}B_{12}H_{11}]$ **(6)** *and* $[N(n\text{-}C_4H_9)_4]\{[(CH_3)_2CH)]_2NH\text{–}B_{12}H_{11}\}$ **(7)**: A 584-mg sample of **3** (2.52 mmol) and 707 mg of potassium hydroxide (12.56 mmol) were stirred in 20 ml of dimethyl sulfoxide. To this solution 1.18 ml of 2-bromopropane (12.56 mmol) was added. After stirring for two days at room temperature the solvent was removed in vacuo and the residue was dissolved in 10 ml of acetonitrile. This solution was filtered and the filtrate was added dropwise to 250 ml of diethyl ether, precipitating a slightly yellow solid that was isolated by filtration. Water (20 ml) was added to the solid, dissolving the monoalkylated derivative **6**. The aqueous solution was filtered and 700 mg of tetrabutylammonium chloride (2.52 mmol) was added, resulting in a precipitate that was filtered off. Recrystallization from ethanol gave 193 mg (0.44 mmol, 17% yield) of needle-like crystals of **6** (m.p. 184°C). The water-insoluble residue contained the bisalkylated derivative **7**. This was recrystallized from water and dissolved in water/acetonitrile. A solid was precipitated by addition of 700 mg of tetrabutylammonium chloride (2.52 mmol) and recrystallization from ethanol to give 172 mg (0.35 mmol, 14% yield) of **7** (m.p. 226°C). Crystals of the PPN salts of **6** and **7** suitable for X-ray diffraction were obtained from dichloromethane/ethanol. – **6**: ^{1}H NMR: δ = 5.9 (s, br., NH_2); 3.0 (sept, CH); 1.2 (d, CH–CH_3). – ^{13}C{^{1}H} NMR: δ = 49.4 (CH), 21.3 (CH–CH_3). – IR: $\tilde{\nu}$ = 3219 (NH), 3109, 2961, 2869, 2486 (BH), 1567, 1467, 1381, 1354, 1292, 1167, 1043, 1006, 894, 737, 715, 579, 526 cm^{-1}. – $C_{39}H_{50}B_{12}N_2P_2$ (738.5): calcd. C 63.43, H 6.82, N 3.79, B 17.57; found C 63.60, H 6.69, N 3.57, B 17.33.

7: ^{1}H NMR: δ = 5.7 (s, br., NH), 3.7 (sept, CH), 1.4 (2 d, CH–CH_3). – ^{13}C{^{1}H} NMR: δ = 53.2 (CH), 20.2, 19.9 (CH–CH_3). – IR: $\tilde{\nu}$ = 3749, 3239 (NH), 2963, 2935, 2873, 2492 (BH), 1471, 1384, 1255, 1168, 1122, 1043, 979, 949, 884, 729 cm^{-1}. – $C_{22}H_{62}B_{12}N_2$ (484.5): calcd. C 54.54, H 12.90, N 5.78, B 26.78; found C 54.32, H 12.86, N 5.62, B 26.51.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: internat. +44(0)1223/336-033, e-mail: teched@chemcrys.cam.ac.uk) on quoting the depository numbers CSD-100068 and -100121.

☆ Dedicated to Prof. Dr. *Walter Siebert* on the occasion of his 60th birthday.

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