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The Reaction of Decaborane with Hydrazoic Acid: A Novel Access to Azaboranes

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ABSTRACT

The reaction of $B_{10}H_{12}(SMe_2)_2$ (**1**) *with* HN_3 *yields* arachno-$B_{10}H_{12}(N_3)(NH_2)$ (**2**), *a product with a* μ-NH_2 *group. Compound* **2** *can be hydrolysed to give the known* arachno-$B_9H_{13}(NH_3)$ (**3**). nido-$NB_9H_{11}(N_3)$ (**4**) *is formed from* **2** *by a deprotonation/protonation sequence. The azaborane* nido-$NB_{10}H_{13}$ (**5**) *is a product of the thermolysis of* **2**. *The structures of* **2–5** *are elucidated by 2-D COSY* ^{11}B–^{11}B *NMR spectra; the structure of* **2** *is also elucidated by an X-ray structure analysis.*

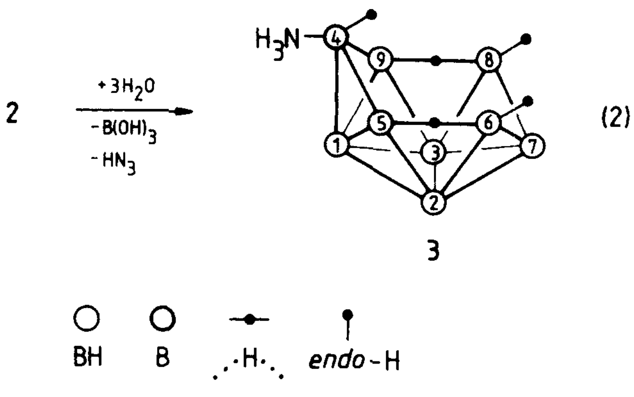
An access to larger azaboranes NB_xH_y ($x \geq 8$) is gained by the reaction of $B_{10}H_{14}$ with $NaNO_2$ or with Me_2N—NS [1], whereas organic derivatives of smaller azaboranes ($x \leq 6$) are available starting from iminoboranes RB≡NR′ [2]. In this paper we report a novel synthesis of larger azaboranes.

arachno-$B_{10}H_{12}(N_3)(NH_2)$: THE KEY SUBSTANCE

The reaction of $B_{10}H_{12}(SMe_2)_2$ (**1**) [3] with excess HN_3 gives $B_{10}H_{12}(N_3)(NH_2)$ (**2**) in 60% yield (Equation 1).

$$B_{10}H_{12}(SMe_2)_2 + 2\ HN_3 \rightarrow B_{10}H_{12}(N_3)(NH_2) + N_2 + 2\ SMe_2 \quad (1)$$

The structure of **2** in solution (C_6D_6) is in accord with the crystal structure (Figure 1). ^{11}B–^{11}B couplings between all neighboring boron atoms are found as cross peaks in the 2-D COSY NMR spectrum with the exception of those pairs of boron atoms that are bridged by NH_2 (B5/B6) or H (B8/B9, B9/B10); small couplings between bridged B atoms are known to make the corresponding cross peaks either weak or undetectable [4]. There are normal couplings between B and terminal H atoms (139–159 Hz), and there is an additional small coupling (50 Hz) between the *endo*-H atom and B7. The lack of BH coupling reveals the position of the N_3 group at B6. Typical IR absorptions are found for the N_3 and NH_2 groups. The borane **2** is closely related to *arachno*-$C_2B_8H_{11}(NH_2)$, which contains an NH_2 bridge in a similar position [5].



SCHEME 1

The hydrolysis of **2** proceeds according to Equation 2 (Scheme 1) to give the known product $B_9H_{13}(NH_3)$

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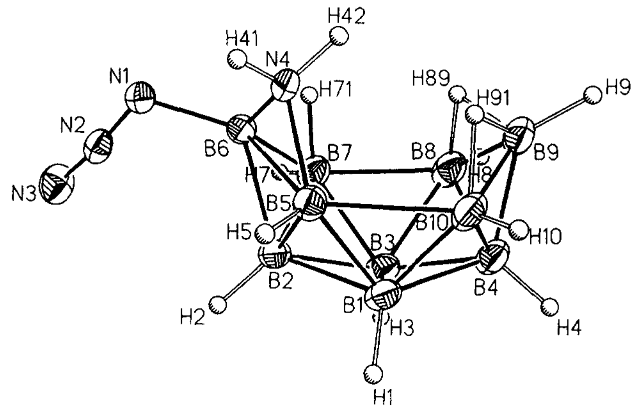


FIGURE 1 Structure of **2**

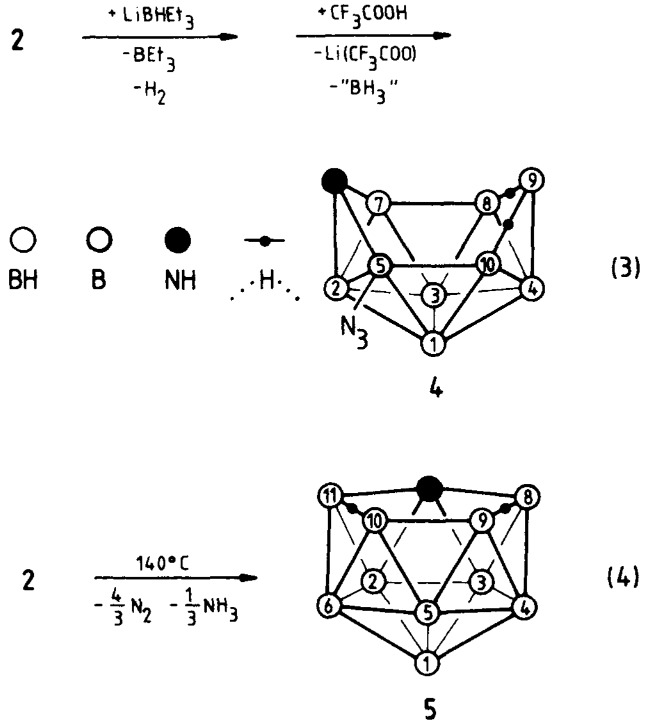
(**3**), originally prepared by the acidic hydrolysis of $Na[B_{10}H_{13}(NH_3)]$ [6]. We identified **3** by its known ^{11}B NMR spectrum [7]. The 2-D COSY version of this spectrum can be compared to that of $B_9H_{13}(SMe_2)$ [8]. In both cases, there is a lack of cross peaks for B5–B6 and B8–B9 (BHB bridges), and for B6–B7 and B7–B8. *endo*-H atoms are to be expected in an *arachno*-borane and are bonded to B6 and B8 in crystalline $B_9H_{13}(NCMe)$, which is closely related to **3** [9]. The doublets for B6 and B8 of **3**, caused by coupling with terminal H atoms, indicate some coupling with such *endo*-H atoms by broadenings. The situation is different from **2**, where a distinct coupling between B7 and *endo*-H71 as well as cross peaks for coupling between B6 and B7 (corresponding to B6–B7 and B7–B8 of **3**) are found.

STRUCTURE OF 2

The crystal and molecular structure of **2** has been analyzed at 125 K (Figure 1, Tables 1 and 2). Going from $B_{10}H_{14}$ [10] to **2**, the molecular symmetry is reduced from C_{2v} to C_1 and, instead of seven, there are twenty-one different B–B bond lengths in **2**. The cluster is widely opened by extra long bonds B5–B10 (2.03 Å) and B7–B8 (1.97 Å), as in $B_{10}H_{14}$ (1.97 Å for both). The NH_2 bridging group lengthens the B5–B6 bond from 1.77 ($B_{10}H_{14}$) to 2.08 Å (**2**). All other B–B bond lengths are found at 1.71–1.82 Å (1.71–1.78 Å in $B_{10}H_{14}$). The distances of 1.19 Å for B7–H71 and of 1.43 Å for B6–H71 indicate an *endo* position and not a bridging position for the atom H71. B–H distances of 1.26–1.30 Å between the H89 and H91 atoms and the neighboring B atoms, on the other hand, are typical for BHB bridge bonding. The B–H bond lengths for the nine terminal H atoms are found at 1.06–1.12 Å. The nearly linear azido group (< N1–N2–N3 174°) is bonded to the cluster in a terminal way (< B2–B6–N1 121°) by a typical BN single bond (1.48 Å).

nido-$NB_9H_{11}(N_3)$ FROM 2

The B_{10} cluster unit of **2** can be transformed into the NB_9 skeleton of **4** by a deprotonation/protonation sequence (Equation 3). Product **4** is the azido derivative of the well-known *nido*-NB_9H_{12} [11], which has recently been characterized by a 2-D COSY ^{11}B–^{11}B NMR spectrum [12]. In accord with a C_1 symmetry, we find eight ^{11}B NMR peaks, with one having a doubling of intensity apparently because of accidental degeneracy. A complete set of BB connectivities can be worked out of the 2-D COSY ^{11}B–^{11}B NMR spectrum. Again, no cross peaks were detected for the bonds B8–B9 and B9–B10, which are both bridged by hydrogen, or for the bonds B2–B5 and B2–B7 that belong to BBN triangles. Small BB cross peaks in triangles of this type could be invoked by concentrating the sample and by increasing the signal-to-noise ratio [12]. The eight chemical shifts of **4** and the six chemical shifts of NB_9H_{12} (symmetry group C_s) are found at comparable values. The N_3 group is easily identified by its IR stretching vibrations. Its position at B5 corresponds to the singlet among the eight ^{11}B signals (Scheme 2).



SCHEME 2

nido-$NB_{10}H_{13}$ FROM 2

The thermolysis of **2** in boiling xylene gives a mixture from which a colorless solid of $NB_{10}H_{13}$ can be sublimed in a yield of 5% (Equation 4). The structure of **5** is elucidated by spectroscopic data. Six

TABLE 1 Selected Bond Lengths [Å] and Bond Angles [°] and Their Estimated Standard Deviations (in Parentheses) for **2**

N1–N2	1.240(2)	B3–B1–B4	59.8(1)	B2–B6–B5	58.3(1)
N1–B6	1.481(2)	B2–B1–B5	65.2(1)	N1–B6–B7	119.7(1)
N2–N3	1.125(2)	B3–B1–B5	113.0(1)	N4–B6–B7	123.0(1)
N4–H41	0.879(20)	B4–B1–B5	120.0(1)	B2–B6–B7	59.9(1)
N4–H42	0.941(18)	B2–B1–B10	123.1(1)	B5–B6–B7	100.7(1)
N4–B5	1.582(2)	B3–B1–B10	110.1(1)	N1–B6–H71	113.9(6)
N4–B6	1.510(2)	B4–B1–B10	60.6(1)	N4–B6–H71	100.1(7)
B1–H1	1.104(16)	B5–B1–B10	71.1(1)	B2–B6–H71	97.8(7)
B1–B2	1.757(2)	B1–B2–B3	60.3(1)	B5–B6–H71	112.7(6)
B1–B3	1.773(2)	B1–B2–B5	57.4(1)	B7–B6–H71	40.8(7)
B1–B4	1.792(2)	B3–B2–B5	106.7(1)	B2–B7–B3	60.1(1)
B1–B5	1.759(2)	B1–B2–B6	116.8(1)	B2–B7–B6	58.8(1)
B1–B10	1.726(2)	B3–B2–B6	113.2(1)	B3–B7–B6	112.4(1)
B2–H2	1.081(15)	B5–B2–B6	68.8(1)	B2–B7–B8	105.0(1)
B2–B3	1.774(2)	B1–B2–B7	106.7(1)	B3–B7–B8	56.1(1)
B2–B5	1.895(2)	B3–B2–B7	58.5(1)	B6–B7–B8	118.6(1)
B2–B6	1.777(2)	B5–B2–B7	109.1(1)	B2–B7–H71	106.8(8)
B2–B7	1.797(2)	B6–B2–B7	61.3(1)	B3–B7–H71	132.5(8)
B3–H3	1.094(16)	B1–B3–B2	59.4(1)	B6–B7–H71	51.6(8)
B3–B4	1.778(3)	B1–B3–B4	60.6(1)	H7–B7–H71	107.1(12)
B3–B7	1.744(2)	B2–B3–B4	114.5(1)	B8–B7–H71	90.3(7)
B3–B8	1.756(2)	B1–B3–B7	108.3(1)	B3–B8–B4	60.2(1)
B4–H4	1.070(17)	B2–B3–B7	61.4(1)	B3–B8–B7	55.5(1)
B4–B8	1.790(3)	B4–B3–B7	119.3(1)	B4–B8–B7	107.9(1)
B4–B9	1.713(3)	B1–B3–B8	106.1(1)	B4–B8–B9	57.0(1)
B4–B10	1.776(3)	B2–B3–B8	115.6(1)	B3–B8–B89	127.7(7)
B5–H5	1.092(15)	B4–B3–B8	60.9(1)	B4–B8–H89	99.2(8)
B5–B6	2.077(2)	B7–B3–B8	68.3(1)	B7–B8–H89	95.7(7)
B5–B10	2.027(2)	B1–B4–B3	59.6(1)	B9–B8–H89	45.0(8)
B6–B7	1.823(2)	B1–B4–B8	103.9(1)	B4–B9–B8	61.2(1)
B6–H71	1.429(16)	B3–B4–B8	59.0(1)	B4–B9–B10	60.7(1)
B7–H7	1.060(18)	B1–B4–B9	108.9(1)	B8–B9–B10	105.4(1)
B7–B8	1.966(2)	B3–B4–B9	112.1(1)	B4–B9–H91	103.3(7)
B7–H71	1.193(17)	B8–B4–B9	61.8(1)	B8–B9–H91	120.0(7)
B8–H8	1.047(19)	B1–B4–B10	57.9(1)	B10–B9–H91	44.6(7)
B8–B9	1.801(3)	B3–B4–B10	107.7(1)	B8–B9–H89	45.0(8)
B8–H89	1.273(17)	B8–B4–B10	106.8(1)	B4–B9–H89	103.2(8)
B9–H9	1.118(17)	B9–B4–B10	62.0(1)	B10–B9–H89	117.3(7)
B9–B10	1.797(2)	N4–B5–B1	133.7(1)	H91–B9–H89	96.8(10)
B9–H91	1.299(17)	N4–B5–B2	98.6(1)	B1–B10–B4	61.5(1)
B9–H89	1.274(17)	B1–B5–B2	57.3(1)	B1–B10–B5	55.2(1)
B10–H10	1.090(17)	N4–B5–B6	46.4(1)	B4–B10–B5	107.7(1)
B10–H91	1.262(16)	B1–B5–B6	103.1(1)	B1–B10–B9	108.1(1)
N2–N1–B6	117.0(1)	B2–B5–B6	52.9(1)	B4–B10–B9	57.3(1)
N1–N2–N3	174.4(1)	N4–B5–B10	104.4(1)	B5–B10–B9	115.2(1)
H41–N4–H42	109.9(16)	B1–B5–B10	53.7(1)	B1–B10–H91	127.1(7)
H41–N4–B5	109.1(11)	B2–B5–B10	102.6(1)	B4–B10–H91	101.6(8)
H42–N4–B5	121.3(11)	B6–B5–B10	117.5(1)	B5–B10–H91	91.0(7)
H41–N4–B6	113.2(11)	N1–B6–N4	113.7(1)	B9–B10–H91	46.3(8)
H42–N4–B6	116.9(12)	N1–B6–B2	121.4(1)	B9–H91–B10	89.1(10)
B5–N4–B6	84.4(1)	N4–B6–B2	106.8(1)	B6–H71–B7	87.6(10)
B2–B1–B3	60.3(1)	N1–B6–B5	132.7(1)	B8–H89–B9	90.0(11)
B2–B1–B4	114.7(1)	N4–B6–B5	49.3(1)		

^{11}B NMR signals between −31 and 7 ppm in a 2:1:2:2:2:1 ratio prove the presence of ten B atoms in a molecule of **5**, two of which lie on a two-fold symmetry element. (Twenty B atoms and a four-fold symmetry axis are improbable and are excluded by the largest MS peak of **2** at *m/z* = 135.) All six ^{11}B NMR signals are doublets and therefore correspond to B–H groups. The presence of one NH fragment, necessarily situated on the symmetry element, is concluded from elemental analysis and from an absorption at 3324 cm^{-1} in the IR spectrum. All of six atoms (1N, 2B, 3H) cannot lie on a C_2 axis;

TABLE 2 Positional Parameters and Their Estimated Standard Deviations (in Parentheses) for **2**

	x	y	z	U^a
N1	−1621(2)	40(1)	1012(1)	20(1)
N2	−3175(2)	274(1)	1115(1)	21(1)
N3	−4620(2)	434(1)	1136(1)	31(1)
N4	1528(2)	665(1)	1332(1)	20(1)
B1	1254(2)	2982(1)	2586(1)	23(1)
B2	−621(2)	2126(1)	2195(1)	20(1)
B3	86(2)	2313(2)	3568(1)	25(1)
B4	2369(2)	2600(2)	3859(1)	27(1)
B5	1430(2)	2056(1)	1481(1)	21(1)
B6	−265(2)	668(1)	1725(1)	18(1)
B7	−603(2)	909(2)	3115(1)	24(1)
B8	1457(3)	1189(2)	4152(1)	29(1)
B9	3611(3)	1355(2)	3724(2)	30(1)
B10	3360(2)	2422(2)	2662(1)	26(1)

[a] Isotropic equivalent thermal parameter calculated as one third of the trace of the orthogonal tensor U_{ij}.

the symmetry element must therefore be a mirror plane. A broad ^{1}H NMR signal at −2.80 needs to be assigned to one BHB bridge in a symmetrical position or to two such bridges in a general position. Final clarity of the structure comes from the 2-D ^{11}B–^{11}B and ^{11}B–^{1}H NMR spectra, which allow an unambiguous assignment of the six signals to structural positions, again on the assumption that ^{11}B–^{11}B cross peaks are not observed between the B atoms connected by hydrogen bridges or between the B atoms in each of the two BBN triangles.

Compound **5** is isoelectronic with the known *nido*-$NC_2B_8H_{11}$ [5]. (The *nido*-skeleton of **5** invites closure of the cage, for example, according to **5** + $BH_3 \rightarrow$ *closo*-$NB_{11}H_{12}$ + 2 H_2.) We had expected *closo*-$NB_{11}H_{10}R_2$ to be the product of closing the *arachno*-skeleton of **1** by the addition of iminoboranes RB≡NR [13] because the dicarba analogue, *closo*-$C_2B_{10}H_{12}$, is known to be formed from **1** and the dicarba analogue of the parent iminoborane, HC≡CH. We found, however, that the oligomerization of RB≡NR is a much faster reaction than its cage-closure with **1**.

EXPERIMENTAL

Physical Measurements

NMR spectra were obtained with a Varian VXR 300 spectrometer, using standard references; 2-D ^{11}B–^{11}B NMR spectra: mixing pulse width 45°, data processing with sine bell squared; solvent: C_6D_6. (We are grateful to Dr. J. Runsink, Institut für Organische Chemie of Technische Hochschule Aachen, for making the NMR spectra available.) IR spectra were recorded with a Perkin Elmer FT-IR 1720 (solvent: CH_2Cl_2) and mass spectra with a MAT CH5 spectrometer.

5,6-μ-Amino-6-azido-arachno-decaborane(14) (**2**)

NaN_3 (20.00 g, 307.6 mmol) was dissolved in 70 mL of aqueous H_2SO_4 (50%). This solution was extracted in portions by 500 mL of toluene at 0°C. The extract was dried by the addition of Na_2SO_4, then 8.00 g (32.8 mmol) of **1** were added. The solution was stirred at room temperature for 60 h then filtered, and the filtrate was concentrated to 30 mL in vacuo. At −40°C, 3.50 g (60%) of pure crystalline **2** were obtained. Caution is recommended: the extremely explosive $NH_4[B(N_3)_4]$ may be a side product. ^{1}H NMR: δ = −3.60 (broad, 1 μH), −3.20 (broad, 1 μH), −0.90 (s, 1H, NH), 1.55 (s, 1H, NH), 0.4–4.4 (10H, BH). ^{11}B NMR (^{11}B peaks that give cross peaks with a certain ^{11}B peak are indicated in parentheses after this peak in the order of decreasing field strength): δ = −40.7 (d, J = 154.1 Hz, B4 (B1, B8, B9, B3/10)), −30.6 (d, J = 145.0 Hz, B2 (B7, B5, B1, B3, B6)), −22.8 (dd, J = 145.0, 50.4 Hz, B7 (B2, B8, B3, B6)), −8.1 (d, J = 149.6 Hz, B5 (B2, B1, B10)), 2.1 (d, J = 140.4 Hz, B1 (B4, B2, B5, B3/10)), 3.3 (d, J = 138.8 Hz, B8 (B4, B7, B3)), 6.7 (d, J = 158.6 Hz, B9 (B4)), 9.3 (d, J = 151.1 Hz, B3, and B10 in accidental degeneracy (B4, B2, B7, B5, B1, B8)), 11.1 (s, B6 (B2, B7)). IR: $\bar{\nu}$ = 3351 (m, NH_2), 3288 (m, NH_2), 2558 (s, BH_t), 2137 (s, N_3), 1559 (m, NH_2), 1330 cm^{-1} (s, N_3) etc. Anal. Calcd. for $B_{10}H_{14}N_4$: 7.92 (H), 31.43 (N). Found: 7.95 (H), 30.85 (N).

4-Ammine-arachno-nonaborane(13) (**3**)

A mixture of 0.57 g (3.2 mmol) of **2** in 10 mL of toluene and 2 mL of H_2O was stirred for 90 min at room temperature. Volatile materials were removed in vacuo. The solid products were digested in 20 mL of CH_2Cl_2, boric acid was collected by filtration, and the filtrate was cooled to −40°C. Long needles of $B_9H_{13}(NH_3)$ crystallize (0.30 g, 74%). ^{11}B NMR (for indication of cross peaks see above (**2**)): δ = −39.6 (d, J = 149.6 Hz, B2 (B6, B5, B1, B7)), −23.9 (d, J = 128.2 Hz, B4 (B5, B1)), −20.3 (d (broad), J = 140.4 Hz, B6 (B2)), −17.8 (d, J = 158.7 Hz, B5 (B2, B4, B1)), 4.4 (d, J = 134.2 Hz, B1 (B2, B4, B5)), 15.9 (d, J = 152.6 Hz, B7 (B2)); B3, B8, B9 are equivalent with B2, B6, B5, respectively, doubling the peak intensity and giving the same cross peaks with corresponding meaning. IR: $\bar{\nu}$ = 3318 (m, NH_3), 3252 (m, NH_3), 2528 (s, BH_t), 1597 cm^{-1} (w, NH_3) etc.

5-Azido-nido-6-azadecaborane(12) (**4**)

A 1 molar solution of $NaBHEt_3$ (20.8 mL) in THF was added dropwise to a solution of 3.70 g (20.76 mmol) of **2** in 20 mL of THF at −78°C. After stirring for 20 min at room temperature, all volatile components were removed in vacuo. The remaining solid was dissolved in 15 mL of THF, and 5.0 mL of

CF_3COOH was added at -78°C. After stirring the solution for 3.5 h at room temperature, the solvent was removed in vacuo, and the residue was extracted in portions with 150 mL of hexane. Crude product, gained from the hexane phase, was sublimed at 40°C (0.001 Torr) yielding 1.13 g (33%) of **4**. ^{1}H NMR: $\delta = -3.66$ (broad, 2 μH) 0.2 – 4.5 (8BH, NH). ^{11}B-NMR (for indications of cross peaks see above (**2**)): $\delta = -30.7$ (d, J = 152.5 Hz, B2 and B4 (accidental degeneracy; two-centered cross peaks with B1, B3; simple cross peaks with B8, B10, B9)), -17.5 (d, J = 152.6 Hz, B8 (B4, B3, B7)), -13.5 (d, J = 155.6 Hz, B10 (B4, B1, B5)), -8.0 (d, J = 143.5 Hz, B1 (one two-centered cross peak with B2, B4; simple cross peaks with B10, B3, B5)), -0.3 (d, J = 146.5 Hz, B3 (one two-centered cross peak with B2, B4; simple cross peaks with B8, B1, B7)), 3.7 (d, J = 164.8 Hz, B7 (B8, B3)), 15.2 (s, B5 (B10, B1)), 15.8 (d, J = 146.5 Hz, B9 (B4)). IR: $\bar{\nu}$ = 3329 (m, NH), 2578 (m, BH_t), 2147 (s, N_3), 1375 cm^{-1} (s, N_3). Anal. Calcd. for $B_9H_{11}N_4$: 6.74 (H), 34.08 (N). Found: 6.64 (H), 34.21 (N).

nido-7-Azaundecaborane(13) (**5**)

A solution of 4.00 g (22.4 mmol) of **2** was refluxed in 60 mL of xylene for 1 h. Gaseous products (33.9 mmol) were evolved (91% of the idealized gaseous products in Equation 4). After removal of the volatile products in vacuo, the product mixture was extracted in portions with 100 mL of hexane. The volume of the extract was reduced to 20 mL and cooled to -40°C. A pale, yellow solid precipitated. The sublimation at 40°/0.001 Torr yielded 0.14 g of **5** (5%). ^{1}H NMR: $\delta = -2.80$ (broad, μH), 1.23 (H at B4, B6), 2.11 (H at B9, B10), 2.15 (H at B8, B11), 2.27 (H at B1), 2.43 (H at B2, B3), 3.55 (H at B5); the assignments were achieved on the basis of a 2D ^{11}B–^{1}H NMR spectrum. ^{11}B NMR (for indications of cross peaks see above (**2**)): $\delta = -31.4$ (d, J = 149.6 Hz, B4 (B1, B9, B8, B3, B5)), -24.8 (d, J = 152.6 Hz, B1 (B4, B3, B5)), -18.1 (d, J = 158.7 Hz, B9 (B4, B5)), -8.7 (d, J = 158.7 Hz, B8 (B4)), -4.9 (d, J = 177.0 Hz, B3 (B4, B1)), 7.1 (d, J = 149.6 Hz, B5 (B4, B1, B9)); B2, B6, B10, B11 are equivalent with B3, B4, B9, B8, respectively, doubling the peak intensity and giving the same cross peaks with corresponding meaning. A change of the given assignments of B2/B3 with B9/B10 and of B1 with B5 would also be in accord with all ^{11}B NMR data but is excluded by the 2D ^{11}B–^{1}H NMR spectrum, which shows that the ^{11}B NMR peaks at -18.1 and -8.7 ppm are correlated to the ^{1}H NMR peaks of the bridging protons at -2.80 ppm. IR: $\bar{\nu}$ = 3324 (m, NH), 2585 cm^{-1} (s, BH_t) etc. MS: m/z = 135 (58%, M^+), 133 (100%, $M^+ - 2$ H) etc. Anal. Calcd. for $B_{10}H_{13}N$: 9.69 (H), 10.36 (N). Found 9.73 (H), 9.63 (N).

X-Ray Structure Analysis of **2**

Crystal size: $0.63\cdot0.18\cdot0.21$ mm^3. Diffractometer: Nicolet R3m/V, λ = 0.71069 Å (MoK_α), μ = 0.05 mm^{-1}, T = 125 K. Cell data from 50 reflections (15° $\leq 2\Theta \leq$ 25°): a = 7.6631(7), b = 11.2628(13), c = 12.6357(15) Å, β = 96.130(8)°, V = 1084.4(2) Å^3, Z = 4, D_c = 1.092 g cm^{-3}, space group $P2_1/n$. 1921 independent reflections, 1576 of which observed ($F_0 \geq 4\ \sigma(F)$) in the range 3° $\leq 2\Theta \leq$ 50°. Refinement with 183 parameters. R = 0.038, R_w = 0.041. A request for additional data may be directed to Fachinformationszentrum Karlsruhe, D-7514 Eggenstein-Leopoldshafen with a citation of the registration number CSD 320 128, the names of the authors, and the journal.

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