1-Alkyl-1-aza-*closo*-dodecaborane: A Novel Access to the Icosahedral NB_{11} Skeleton†

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arachno-$B_9H_{13}(SMe_2)$ was transformed into *arachno*-$B_9H_{13}(NRH_2)$ (**1a–d**; R = nBu, tBu, $tBuCH_2$, $PhCH_2$) by reaction with primary amines. The thermal dehydrogenation of **1a–d** gave *nido*-RNB_9H_{11} (**2a–d**). The addition of C≡NtBu to the azaboranes **2b,d** gave *arachno*-$RNB_9H_{11}(CNtBu)$ (**3b,d**). The azaboranes **2c,d** were heated with an excess of $Me_2S{\cdot}BH_3$ at 170 °C in decalin, yielding *closo*-$RNB_{11}H_{11}$ (**4c,d**). Aza-*closo*-dodecaboranes of the same type (**4e–g**; R = Et, iPr, iBu) were also obtained by alkylating the azadodecaborate $[Et_3HN][NB_{11}H_{11}]$ with $[Et_3O]BF_4$ or with the triflates RO_3SCF_3 (R = iPr, iBu), respectively. All of the products were characterized by ^1H and ^{11}B NMR, using 2-D $^{11}B/^{11}B$ techniques in the case of **1c**, **2b**, and **4e**. The structure of the *closo* cluster **4d** was shown to represent a distorted icosahedron. The N atom is distinctly closer to the polyhedral center M (M–N = 1.535 Å) than the atom B12 (M–B12 = 1.651 Å). The neighboring B–H bonds are shifted from the radial direction toward the N atom. Crystal data for **4d**: space group $P2_1/n$, $Z = 4$, $a = 9.041(4)$ Å, $b = 14.651(7)$ Å, $c = 11.224(4)$ Å, $\beta = 96.14(3)°$, $R = 0.053$.

Introduction

Recently, we reported[1] the synthesis of aza-*closo*-dodecaborane(12) ($NB_{11}H_{12}$), the isoelectronic analogue of dicarba-*closo*-dodecaborane(12) ($C_2B_{10}H_{12}$), thus proving that even the remarkably electronegative nitrogen can be incorporated into an electron-deficient cluster skeleton of 5-fold connectivity. The first step in our four-step synthesis requires handling of explosive hydrazoic acid in order to transform $B_{10}H_{12}(SMe_2)_2$ into $B_{10}H_{12}(N_3)(NH_2)$, whose subsequent thermal transformation into *nido*-$NB_{10}H_{13}$[2] suffers from the low yield of only 5%. The closure of the *nido*-NB_{10} skeleton by the action of $Et_3N{\cdot}BH_3$ proceeds more conveniently, yielding the *closo* anion $NB_{11}H_{11}^-$ first,[1] which finally gives *closo*-$NB_{11}H_{12}$ upon protonation. Our efforts[3] to close the *nido*-NB_9 instead of the *nido*-NB_{10} skeleton by reacting *nido*-NB_9H_{12} with $Et_3N{\cdot}BH_3$ in a 1:2 molar ratio gave a mere substitution of the N-bonded hydrogen with the formation of $Et_3N{-}BH_2{-}NB_9H_{11}$.

Here we report the synthesis of 6-alkyl-6-aza-*nido*-decaboranes (RNB_9H_{11}) by a novel route. The absence of an N-bonded proton allows a one-step closure of the NB_9 skeleton to give *closo*-$RNB_{11}H_{11}$ upon reaction with two BH_3 units. We also report the molecular and crystal structure of 1-benzyl-1-aza-*closo*-dodecaborane(12) in order to supplement structural evidence for the NB_{11} skeleton, which up to now has been restricted to an electron diffraction study of the parent azadodecaborane(12) in the gas phase.[4]

Results and Discussion

Synthesis. We started from dimethyl sulfide–*arachno*-nonaborane(13) ($Me_2S{\cdot}B_9H_{13}$)[5] and substituted the sulfane ligand by primary amines, a procedure well-known for other bases.[6] The products, alkylamine–nonaboranes **1a–d**, undergo an elimination of H_2 at 140 °C which is accompanied by the incorporation of the NR moiety into the cluster skeleton, giving the 6-alkyl-6-aza-*nido*-decaboranes **2a–d** in 18–24% yields. We had explored[3] this reaction for the parent compound $H_3N{\cdot}B_9H_{13}$ and had suggested an *exo*/*endo* interchange of the ligands NH_3 and H at the atom B4 as the first step. The reaction then proceeds through a stereochemically clear path: the formation of bonds between N and two adjacent B atoms at the expense of two N–H bonds, one B–H_{endo}, and one B–H–B bridge bond. In Scheme I, the products of type **2** are shown in two different perspectives in order to elucidate their formation as well as their structural relation to the familiar decaborane(14). (Note that the numbering procedure changes by going from **1** to **2**!) The *tert*-butyl and the benzyl derivatives **2b,d**, abitrarily selected among the products **2a–d**, readily add *tert*-butyl isocyanide to give *arachno*-$RNB_9H_{11}{\cdot}CNtBu$ (**3b,d**). The addition of Lewis bases in general and of isocyanides in particular to the parent compound *nido*-NB_9H_{12} is well-known.[7]

The skeletal closure of the aza-*nido*-decaboranes RNB_9H_{11} to give aza-*closo*-dodecaboranes $RNB_{11}H_{11}$ can be achieved by the use of an excess of $Me_2S{\cdot}BH_3$ under rather drastic conditions: 2-h reflux in decalin at ca. 170 °C. The yield of *closo* species is fairly good (R = $tBuCH_2$, 42%; R = $PhCH_2$, 53%). The *nido* cluster **2b** (R = tBu) gives a mixture of unknown products out of which no *closo* cluster **4b** can be sublimed. We did not test the *N*-butyl species **2a** because the yield of only 6%, starting from $Me_2S{\cdot}B_9H_{13}$, makes the access of **2a** inconvenient. The overall yields of the three-step syntheses of **4c,d**, $Me_2S{\cdot}B_9H_{13} \rightarrow RH_2N{\cdot}B_9H_{13} \rightarrow RNB_9H_{11} \rightarrow RNB_{11}H_{11}$, are 7 and 6%, respectively. The known *closo*-azaborane $MeNB_{11}H_{11}$[8] had been produced in an overall yield of only 1.1% by the four-step route $B_{10}H_{12}(SMe_2)_2 \rightarrow B_{10}H_{12}(N_3)(NH_2) \rightarrow NB_{10}H_{13} \rightarrow NB_{11}H_{11}^- \rightarrow MeNB_{11}H_{11}$, including the unpleasant use of HN_3.

In spite of the low-yield availability of the aza-*closo*-dodecaborate $[Et_3NH][NB_{11}H_{11}]$, we tested several procedures in order to alkylate the N atom of the anion. Alkyl triflates, RO_3SCF_3, are successful alkylation agents, not only for R = Me[8] but also for R = iPr, iBu. Triethyloxonium tetrafluoroborate may be used for R = Et. Alkyl halides, on the contrary, cannot be used since halide anions X^- open the aza-*closo*-dodecaborane skeleton[8] by nucleophilic attack with the formation of *nido* anions

† Dedicated to Professor Otto J. Scherer on the occasion of his 60th birthday.
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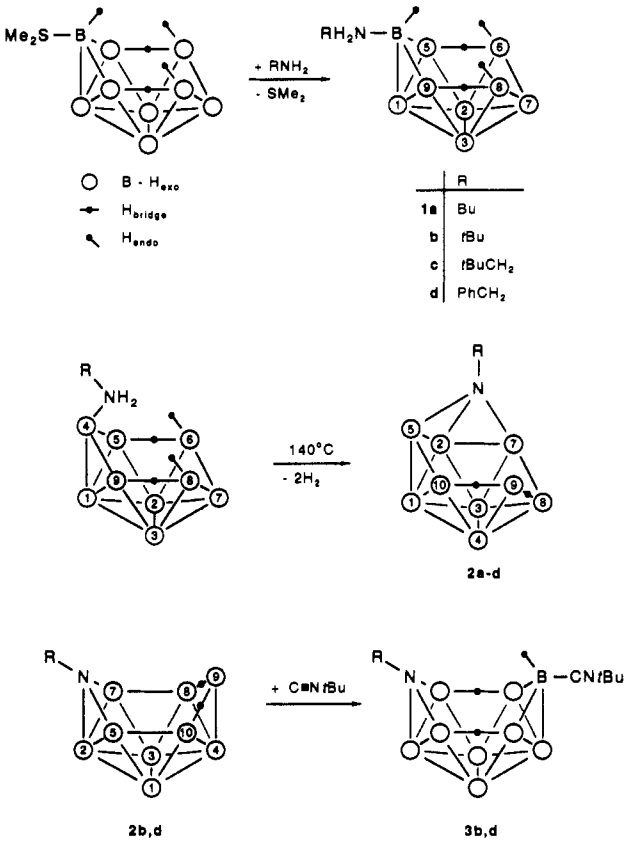
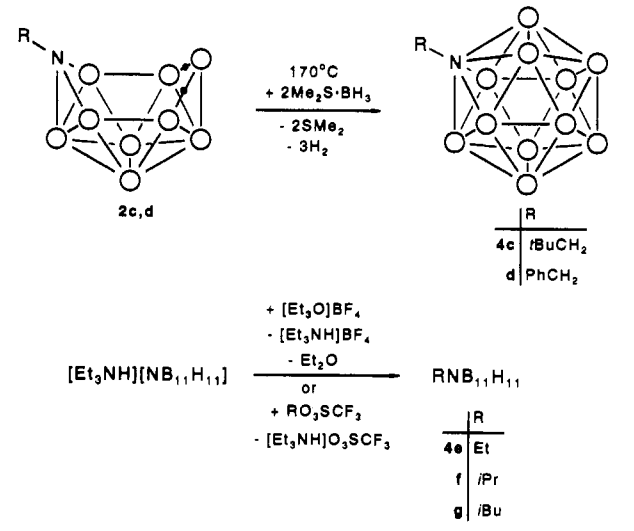
Scheme I



Scheme II



$RNB_{11}H_{11}X^-$. Trimethylsilyl and di-*n*-butylboryl triflates do not react with the anion $NB_{11}H_{11}^-$, presumably because of steric reasons. The N-bonded H atom of the parent borane $NB_{11}H_{12}$ has been shown by electron diffraction[4] to be shielded by the five neighboring H atoms, first because the small N atom is situated closer to the icosahedral center than the larger B atoms and second because the five neighboring B–H bonds are tilted from the radial direction toward the N–H bond. Therefore, rather bulky groups like Me_3Si or nBu_2B cannot approach the N atom of $NB_{11}H_{11}^-$. The failure to transform *nido*-$tBuNB_9H_{11}$ into *closo*-$tBuNB_{11}H_{11}$ may be attributed to the steric demand of the *tert*-butyl group.

NMR Characterization of the Products. The ^{11}B and ^1H NMR shifts of the boranes $RH_2N{\cdot}B_9H_{13}$ (**1a–d**), RNB_9H_{11} (**2a–d**), $RNB_9H_{11}{\cdot}CNtBu$ (**3b,d**), and $RNB_{11}H_{11}$ (**4c–g**) are summarized in Tables I and II. For the *arachno* clusters **1a–d**, the assignment of the ^{11}B NMR signals is based on a 2-D COSY $^{11}B/^{11}B$ NMR experiment on the neopentyl species **1c** and on a comparison with the assignments given[2,9] for the parent species $H_3N{\cdot}B_9H_{13}$. No cross peaks are observed between the resonances of B atoms which are connected by hydrogen bridges,[10] and there are also no cross peaks between B7 and B6/8, neither in **1c** nor in $H_3N{\cdot}B_9H_{13}$. The assignment of the $^1H\{^{11}B\}$ NMR signals is in accord with the known assigment[11] for $Me_2S{\cdot}B_9H_{13}$.—The ^{11}B and $^1H\{^{11}B\}$ NMR signals of the *nido* clusters **2a–d** can be assigned by comparison with the parent cluster NB_9H_{12}[12] and with the *N*-boryl derivative $Et_3N{-}BH_2{-}NB_9H_{11}$.[3] In the 2-D COSY $^{11}B/^{11}B$ NMR spectrum of **2b**, one can detect weak cross peaks for the hydrogen-bridged bonds B8/10–B9 and for the bonds B2–B5/7 which are opposite to the N atom. Unexpectedly, no cross peak appears for the bonds B1–B5 and B3–B7.—The assignment of the ^{11}B and $^1H\{^{11}B\}$ NMR signals of the *arachno* clusters **3b,d** corresponds well with the data for $Et_3N{-}BH_2{-}NB_9H_{11}{\cdot}CNtBu$[3].—The NMR data for the *closo* clusters **4c–g** are in excellent agreement with the known data for $NB_{11}H_{12}$[1] and $MeNB_{11}H_{11}$.[8] Triplets in the ^1H NMR spectra resulting from coupling with the cluster ^{14}N atom are observed in the case of β-methyl groups (R = Et, iPr), the coupling constants $^3J(HN)$ amounting to 4% of $^1J(HN)$, observed with $NB_{11}H_{12}$.[1] None of the groups R in $RNB_{11}H_{11}$ displays 5-fold symmetry, but these groups do not perturb such high symmetry in the NB_{11} skeleton of **4c–g** with respect to the NMR time scale, thus allowing the observation of only three ^{11}B and ^1H NMR signals in the characteristic 5:5:1 intensity ratio.

X-ray Crystallographic Study. Data were collected on the aza-*closo*-dodecaborane **4d**. Information on data collection and data processing is presented in Table III, and atomic coordinates are given in Table IV; further details are provided as supplementary material. Figure 1 depicts the molecular structure. The 30 skeletal bond distances in the NB_{12} icosahedron can be divided into five groups of similar values (see Table V). These groups correspond to the five zones of edges that are equivalent by C_{5v} symmetry in the parent $NB_{11}H_{12}$. The small atomic radius of the N atom causes deviations of the NB_{11} skeleton from ideal icosahedral geometry. The five B–N distances represent the series of shortest bonds (average value of 1.72 Å in **4b** versus 1.71 Å from an HF–SCF calculation for $NB_{11}H_{12}$ with a 6-31G* basis set[14]), followed by the ten edges in the antiprismatic zone (1.75 versus 1.77 Å). The sequence continues with the five edges from B12 to B7–B11 (1.77 versus 1.80 Å), the five edges in the corresponding pentagon (1.77 versus 1.81 Å), and finally the five edges in the pentagon of the NB_5 pyramid (1.80 versus 1.82 Å). The pentagonal plane close to the N atom is larger than the opposite one, caused by the position of the N atom which is distinctly closer to the center M of the polyhedron (M–N = 1.535 Å) than the opposite atom B12 (M–B12 = 1.651 Å). Consequently, the five atoms B2–B6 are farther away from M (1.701 Å) than the five atoms B7–B11 (1.673 Å). Such distortions of the pentagonal antiprism as well as the electronic attraction by the N atom may be the reason that the five B–H bonds around the N atom are shifted out of the radial direction toward the N apex by 12–18°, as documented by the angles M–B2–H2 to M–B6–H6 (Table V). The triangles around the B12 vertex are close to regularity; the five angles at B12, e.g., have an average value of 60.1°. The triangles in the pentagonal antiprismatic

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Table I. ^{11}B NMR Data[a]

$RH_2N{\cdot}B_9H_{13}$[b]	B1	B4	B7	B2/3	B5/9	B6/8
1a (R = nBu)	4.3/134	−20.1/110	15.6/104	−39.9/147	−18.0/159	−20.1/110
1b (R = tBu)	3.8/134	−22.7/122	15.7/159	−39.6/146	−16.9/147	−20.2/159
1c (R = $tBuCH_2$)	4.9/134	−19.7/110	16.0/122	−39.9/147	−18.0/147	−20.2/116
1d (R = $PhCH_2$)	4.6/134	−19.8/?	15.7/147	−39.9/147	−17.9/153	−20.3/?

RNB_9H_{11}[c]	B1/3	B2	B4	B5/7	B8/10	B9
2a (R = nBu)	−0.7/147	−28.4/171	−28.4/171	13.8/159	−13.0/159	14.7/147
2b (R = tBu)	−1.9/146	−28.3/171	−26.8/159	12.2/159	−13.0/159	14.3/159
2c (R = $tBuCH_2$)	0.4/146	−29.6/183	−28.4/171	15.4/159	−13.0/146	15.4/159
2d (R = $PhCH_2$)	−0.7/147	−27.8/159	−27.8/159	13.8/159	−12.9/147	14.8/159

$RNB_9H_{11}{\cdot}CNtBu$[b]	B1/3	B2	B4	B5/7	B8/10	B9
3b (R = tBu)	−40.6/147	−9.3/159	5.8/147	−13.4/134	−36.0/147[d]	−40.2/147
3d (R = $PhCH_2$)	−39.9/147	−8.6/183	4.8/134	−9.8/147	−35.7/147	−38.6/183

$RNB_{11}H_{11}$[c]	B2–B6	B7–B11	B12	$RNB_{11}H_{11}$[c]	B2–B6	B7–B11	B12
4c (R = $tBuCH_2$)	−3.9/171	−10.9/159	3.1/146	**4f** (R = iPr)	−5.1/171	−10.8/147	4.0/147
4c (R = $PhCH_2$)	−5.4/171	−10.9/147	2.2/147	**4q** (R = iBu)	−4.3/171	−10.4/153	2.9/147
4e (R = Et)	−6.1/171	−11.5/159	1.4/159				

[a] Chemical shifts δ (160.364 MHz; in ppm relative to $BF_3{\cdot}OEt_2$, positive values downfield) and coupling constants $^1J(BH)$ (in Hz), written as couples δ/J. [b] $CDCl_3$ solution. [c] C_6D_6 solution. [d] $^1J(BH_{endo}) = 37$ Hz.

Table II. ^1H NMR Data[a]

$RH_2N{\cdot}B_9H_{13}$[b]	H1	H2/3	H4	H5/9	H6/8	H7	μ-H[c]	*endo*-H	NH_2[c]
1a (R = nBu)	2.86	0.33	0.64	1.65	1.99	3.96	−3.59	−0.22	4.15
1b (R = tBu)	2.85	0.42	0.62	1.63	2.01	4.05	−3.50	−0.19	4.05
1c (R = $tBuCH_2$)	2.88	0.42	0.61	1.68	2.01	3.95	−3.64	−0.20	3.95
1d (R = $PhCH_2$)	2.93	0.36	0.73	1.67	1.98	3.95	−3.52	−0.17	4.51

RNB_9H_{11}[d]	H1/3	H2 or H4[e]	H5/7	H8/10	H9	μ-H[c]
2a (R = nBu)	3.49	1.40/1.69	3.90	2.53	3.90	−3.24
2b (R = tBu)	3.41	1.39/1.81	4.13	2.55	3.85	−3.41
2c (R = $tBuCH_2$)	3.58	1.32/1.69	3.96	2.54	3.96	−3.01
2d (R = $PhCH_2$)	3.45	1.53/1.60	4.03	2.43	3.65	−3.41

$RNB_9H_{11}{\cdot}CNtBu$[f]	H1/3	H2	H4	H5/7	H8/10	H9	μ-H[c]
3b (R = tBu)	0.46	2.52	3.09	2.40	0.61	0.61	−2.33
3d (R = $PhCH_2$)	0.52	2.39	2.99	2.39	0.61	0.27	−2.06

$RNB_{11}H_{11}$[g]	H2–6	H7-11	H12	$RNB_{11}H_{11}$[g]	H2–6	H7–11	H12
4c (R = $tBuCH_2$)	2.55	2.60	3.31	**4f** (R = iPr)	2.42	2.60	3.38
4d (R = $PhCH_2$)	2.35	2.58	3.26	**4g** (R = iBu)	2.42	2.61	3.28
4e (R = Et)	2.28	2.59	3.24				

[a] Chemical shifts δ (499.843 MHz; in ppm), ^{11}B decoupled. [b] $CDCl_3$ solution. Signals of R: $\delta = 0.96, 1.40, 1.73, 3.11$ (3:2:2:2; t, sext, quint, quint, $J = 7.0$ Hz, throughout; R = nBu); $\delta = 1.47$ (s, R = tBu); $\delta = 1.03, 2.42$ (9:2; s, m; R = $tBuCH_2$); $\delta = 4.27, 7.38–7.49$ (2:5; R = $PhCH_2$). [c] Broad signals. [d] C_6D_6 solution. Signals of R: $\delta = 0.55, 0.66, 0.93, 2.91$ (3:2:2:2; t, sext, quint, t, $J = 7.3$ Hz, throughout; R = nBu); $\delta = 0.83$ (s; R = tBu); $\delta = 0.38, 2.84$ (9:2; 2s; R = $tBuCH_2$); $\delta = 4.03, 6.73–7.10$ (2:5; R = $PhCH_2$). [e] No assignment possible for the two signals of H2 and H4, respectively. [f] $CDCl_3$ solution. Signals of R and tBu: $\delta = 1.15, 1.55$ (1:1; s, t, $^3J(HN) = 2.0$ Hz; R = tBu); $\delta = 1.53, 3.94, 7.11–7.31$ (9:2:5; t, s, m, $^3J(HN) = 2.0$ Hz; R = $PhCH_2$). [g] C_6D_6 solution. Signals of R: $\delta = 0.35, 2.60$ (9:2; 2s; R = $tBuCH_2$); $\delta = 3.44, 6.50–6.93$ (2:5; R = $PhCH_2$); $\delta = 0.17, 2.21$ (3:2; t/t, q, $^3J(HH) = 7.4$ Hz, $^3J(HN) = 2.6$ Hz; R = Et); $\delta = 0.38, 2.61$ (6:1; d/t, sept, $^3J(HH) = 6.7$ Hz, $^3J(HN) = 2.4$ Hz; R = iPr); $\delta = 0.24, 1.21, 2.39$ (6:1:2; d, m, d, $J = 6.7$ and 5.8 Hz, respectively; R = iBu).

zone deviate slightly from regularity with mean values of 61.9° at the vertices B7–B11 and 61.1° at B2–B6. The angles at the N vertex are distinctly larger, 63.0° on an average, because of the penetration of the N apex into the inner cluster sphere. An extralong N–C bond distance of 1.537(1) Å is observed, as compared to the corresponding N–C bond distance of 1.464(5) Å in the anion $[MeNB_{11}H_{11}(OMe)]^-$,[8] which is close to the normal N–C bond length of 1.47 Å found in alkylamines. We assume that such a long N–C bond length is rather due to that penetration than to the uncommon electronic situation of a 6-fold-coordinated N atom. In *C*-alkyldicarba-*closo*-dodecaboranes, $R_2C_2B_{10}H_{10}$, the C–C bond distances between the cluster and the adjacent alkyl C atoms are found close to 1.52 Å, that is a rather small value in the normal C–C single-bond range, thus showing that the participation of a 6-fold coordinated cluster C atom in a C–C single bond does not distinctly alter the normal bond distance.

Concluding Remarks

Considering the anion $B_{12}H_{12}^{2-}$ as parent species, numerous derivatives with heteroatoms in the skeleton had been synthesized that all obey the electron-counting rules for an icosahedral *closo* cluster. Besides a variety of metallic heteroatoms, the most prominent nonmetallic ones had been carbon, phosphorus, and sulfur. The chemistry of dicarba-*closo*-dodecaborane, $C_2B_{10}H_{12}$, has emerged in a way that makes the three isomers top molecules in textbooks. The synthesis, 30 years ago, taught the chemists definitely that even carbon, the model element for classical octet bond descriptions, can behave like boron in electron-deficient cluster structures with 5-fold connectivity. The synthesis and structural characterization of aza-*closo*-dodecaborane and its derivatives expand the series of nonmetallic candidates for building electron-deficient clusters by the strongly electronegative nitrogen. This paper contributes a novel and transparent incorporation of

Table III. Experimental X-ray Diffraction Parameters and Crystal Data[a]

empirical formula	$B_{11}C_7H_{18}N$
fw	235.1
cryst dimens, mm	0.5 × 0.5 × 0.2
λ(Cu Kα), Å	1.5418
T, K	298
space group	$P2_1/n$
a, Å	9.041(4)
b, Å	14.651(7)
c, Å	11.224(4)
β, deg	96.14(3)
V, Å^3	1478(2)
Z	4
μ, cm^{-1} (Cu Kα)	3.22
D(calcd), g cm^{-3}	1.057
no. of reflcns measd	3104
no. of indpd reflcns, $I > 2\sigma(I)$	2468
no. of refined params	245
R	0.053
R_w	0.064
goodness of fit	3.404
final diff ρ_{max}, e/Å^3	0.18

[a] Structure solution by direct methods using MULTAN 80 in the SDP package;[10] all hydrogen atoms were found in the difference Fourier map and were refined isotropically.

Table IV. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Hydrogen Atoms in $(PhCH_2)NB_{11}H_{11}$ (**4d**)

	x	*y*	*z*	U_{eq}
N	0.3662(1)	0.12450(7)	0.2343(1)	46.9(3)
B2	0.4026(3)	0.0736(1)	0.3730(2)	67.4(6)
B3	0.4922(2)	0.1772(1)	0.3387(2)	63.5(5)
B4	0.3654(2)	0.2413(1)	0.2358(2)	57.0(5)
B5	0.1948(2)	0.1772(1)	0.2072(2)	57.5(5)
B6	0.2208(2)	0.0729(1)	0.2916(2)	62.0(5)
B7	0.4125(3)	0.1653(1)	0.4727(2)	72.5(6)
B8	0.3900(2)	0.2679(1)	0.3889(2)	61.8(5)
B9	0.2098(2)	0.2677(1)	0.3094(2)	58.6(5)
B10	0.1206(2)	0.1638(1)	0.3433(2)	67.1(6)
B11	0.2474(3)	0.1012(2)	0.4437(2)	78.1(7)
B12	0.2384(3)	0.2216(1)	0.4557(2)	66.7(6)
C1	0.4379(2)	0.0771(1)	0.1327(1)	58.5(4)
C2	0.3427(2)	0.06993(9)	0.0160(1)	48.7(4)
C3	0.3539(2)	0.1340(1)	−0.0728(1)	62.9(5)
C4	0.2736(2)	0.1233(1)	−0.1843(2)	80.5(6)
C5	0.1808(2)	0.0490(2)	−0.2059(2)	83.9(6)
C6	0.1700(2)	−0.0144(1)	−0.1180(2)	74.5(5)
C7	0.2503(2)	−0.0045(1)	−0.0083(1)	59.2(4)

nitrogen into an icosahedral skeleton and the first X-ray crystallographic determination of its structure. A striking feature of carbaborane chemistry is the greater tendency of carbon than of boron to decrease a given high connectivity. This tendency is expected to be still greater for nitrogen. It will be a challenge to verify such expectation experimentally.

Experimental Section

Instrumentation. ^{11}B (160.364 MHz) and ^1H (499.843 MHz) NMR spectra were acquired on a Varian Unity 500 spectrometer. The measurements for the X-ray structure determination were carried out on an Enraf-Nonius CAD 4 diffractometer. Elemental analyses (C, H, N) were obtained with a Carlo-Erba elemental analyzer, Model 1106. Column chromatography was conducted on silica gel 60 (Fluka).

Materials and Procedures. The solvents benzene, xylene, and decalin were distilled from sodium, pentane and hexane were distilled from potassium, and dichloromethane was distilled from calcium hydride prior to use; trichlorodeuteriomethane and hexadeuteriobenzene were anhydrous grade and were stored over 4-Å molecular sieves. *n*-Butyl-, *tert*-butyl-, neopentyl-, and benzylamine, dimethyl sulfide, *tert*-butyl isocyanide, and dimethyl sulfide–borane were commercially available and were distilled before use. Isopropyl[15] and isobutyl trifluoromethanesulfonates[16] and

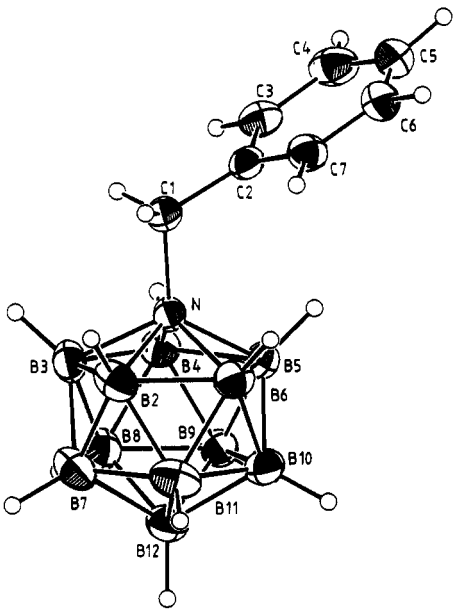

Figure 1. Molecular structure of $(PhCH_2)NB_{11}H_{11}$ (**4d**) with 30% probability ellipsoids.

Table V. Skeletal Distances and Angles for $(PhCH_2)NB_{11}H_{11}$ (**4d**)[a]

	av[b]	max	min
	Distances (Å)[c]		
N–B2 to N–B6	1.719/5	1.729(1)	1.701(7)
B2–B3 to B6–B2	1.796/5	1.805(2)	1.782(2)
B2–B7 to B2–B11	1.745/10	1.753(2)	1.732(2)
B7–B8 to B11–B7	1.773/5	1.783(2)	1.763(2)
B7–B12 to B11–B12	1.770/5	1.776(2)	1.767(2)
M–N	1.535		
M–B2 to M–B6	1.701/5	1.715	1.695
M–B7 to M–B11	1.673/5	1.680	1.666
M–B12	1.651		
	Angles (deg)[c]		
B2–N–B3 to B6–N–B2	63.00/5	63.29(6)	62.13(6)
B2–B7–B3 to B6–B11–B2	61.95/5	62.15(6)	61.44(7)
B7–B3–B8 to B11–B2–B7	61.07/5	61.40(7)	60.83(6)
B7–B12–B8 to B11–B12–B7	60.11/5	60.39(7)	59.76(7)
M–N–C1	176.0		
M–B2–H2 to M–B6–H6	165.3/5	167.8	161.9
M–B7–H7 to M–B11–H11	178.6/5	179.7	176.8
M–B12–H12	178.9		

[a] Average of distances and angles in zones of equivalency, according to hypothetical C_{5v} symmetry. The point M marks the icosahedral center, its coordinates are calculated as the arithmetic mean of the atomic coordinates of N and B2–B12. [b] The number of averaging values is mentioned behind the bar. [c] Supplementary bond distances and angles: N–C1 = 1.537(1), C1–C2 = 1.492(1), C–C(phenyl) = 1.366(2)–1.387(2) Å; N–C1–C2 = 115.68(7)°.

arachno-dimethyl sulfide–nonaborane(13)[5] were prepared as described in the literature. All synthetic procedures were conducted in an atmosphere of dry nitrogen.

Synthesis of 4-($nBuNH_2$)B_9H_{13} (1a). $Me_2S{\cdot}B_9H_{13}$ (6.1 g, 35.4 mmol) was dissolved in 60 mL of benzene, and after the addition of $nBuNH_2$ (3.9 mL, 39.3 mmol), the mixture was heated to reflux for 5 h. All volatile components were removed under vacuum at room temperature. The resulting yellow oil was taken up in 2:1 dichloromethane–hexane and column-chromatographed in the same solvent. Addition of hexane resulted in the separation from the mixture of a colorless oil, which was washed twice with hexane and dried under vacuum to give **1a** (1.12 g, 6.4 mmol, 18% based on $Me_2S{\cdot}B_9H_{13}$). Anal. Calcd for $C_4H_{24}B_9N$: C, 26.18; H, 13.18; N, 7.63. Found: C, 26.14; H, 13.61; N, 7.41.

Synthesis of 4-($tBuNH_2$)B_9H_{13} (1b). $Me_2S{\cdot}B_9H_{13}$ (6.5 g, 37.7 mmol) was dissolved in 50 mL of benzene, and after the addition of $tBuNH_2$ (4.4 mL, 41.7 mmol), the mixture was heated to reflux for 5 h. All volatile

(15) Beard, C. D.; Baum, K.; Grakauskas, V. *J. Org. Chem.* **1973**, *38*, 3673.

(16) Salomon, M. F.; Salomon, R. G.; Gleine, R. D. *J. Org. Chem.* **1976**, *41*, 3983.

components were removed under vacuum at room temperature. The residue was taken up in dichloromethane, and hexane was added to the solution, whereupon a white precipitate formed. This was isolated by filtration, washed twice with hexane, and dried to give **1b** (4.91 g, 26.8 mmol, 71% based on $Me_2S{\cdot}B_9H_{13}$) as a colorless crystalline product. Anal. Calcd for $C_4H_{24}B_9N$: C, 26.18; H, 13.18; N, 7.63. Found: C, 26.22; H, 13.17; N, 7.54.

Synthesis of 4-($tBuCH_2NH_2$)B_9H_{13} (1c). The same procecure was followed by employing 4.9 g (28.4 mmol) of $Me_2S{\cdot}B_9H_{13}$ and 3.6 mL (30.8 mmol) of $tBuCH_2NH_2$, yielding **1c** (4.1 g, 20.7 mmol, 73% based on $Me_2S{\cdot}B_9H_{13}$) as a colorless crystalline product. Anal. Calcd for $C_5H_{26}B_9N$: C, 30.40; H, 13.26; N, 7.09. Found: C, 30.47; H, 13.52; N 7.11.

Synthesis of 4-($PhCH_2NH_2$)B_9H_{13} (1d). The same procedure was followed by employing 10.8 g (62.3 mmol) of $Me_2S{\cdot}B_9H_{13}$ and 7.5 mL (68.6 mmol) of $PhCH_2NH_2$, yielding **1d** (7.7 g, 35.4 mmol, 57% based on $Me_2S{\cdot}B_9H_{13}$) as a colorless crystalline product. Anal. Calcd for $C_7H_{22}B_9N$: C, 38.65; H, 10.19; N, 6.44. Found: C, 38.68; H, 10.92; N, 5.93.

Synthesis of 6-$nBuNB_9H_{11}$ (2a). A solution of **1a** (4.31 g, 23.5 mmol) in 70 mL of xylene was heated to 140 °C for 4 h. After cooling of the reaction mixture to 0 °C, the solvent was evaporated under vacuum. The resulting orange residue was extracted in portions with 80 mL of hexane, and the solvent was removed from the combined extracts. Distillation at 25-40 °C (0.001 Torr) gave 0.76 (4.23 mmol, 18%) of crude **2a**. For further purification, the product was dissolved in hexane, and the solution was treated with an excess of SMe_2. At −40 °C a white adduct precipitated, which was isolated by filtration at that temperature. The adduct melted away under dissociation when held under vacuum at 0 °C for 1 h. Repeated distillation at 25–40 °C (0.001 Torr) afforded 0.52 g (2.90 mmol, 12 %) of pure **2a** as a colorless oil.

Synthesis of 6-$tBuNB_9H_{11}$ (2b). A solution of **1b** (3.80 g, 20.71 mmol) in 50 mL of xylene was heated to 140 °C for 4 h. After cooling of the reaction mixture to 0 °C, the solvent was evaporated under reduced pressure. The resulting orange residue was extracted in portions with 80 mL of hexane, and the solvent was removed from the combined extracts. Sublimation at 20–30 °C (0.001 Torr) gave 0.71 g (3.93 mmol, 19%) of colorless **2b**. Anal. Calcd for $C_4H_{20}B_9N$: C, 26.77; H, 11.23; N, 7.80. Found: C, 26.48; H, 11.62; N, 7.09.

Synthesis of 6-$tBuCH_2NB_9H_{11}$ (2c). The same procedure was followed by employing 3.84 g (19.43 mmol) of **1c**. Sublimation at 30–50 °C (0.001 Torr) gave 0.90 g (4.66 mmol, 24%) of colorless **2c**. Anal. Calcd for $C_5H_{22}B_9N$: C, 31.03; H, 11.46; N, 7.24. Found: C, 30.00; H, 11.84; N, 6.83.

Synthesis of 6-$PhCH_2NB_9H_{11}$ (2d). Following the same procedure, we started with 7.20 g (33.10 mmol) of **1d**. Distillation at 35-50 °C (0.001 Torr) gave 1.41 g (6.62 mmol, 20 %) of **2d** as a colorless oil.

Synthesis of 6-$tBuNB_9H_{11}$·CNtBu (3b). **2b** (0.072 g, 0.40 mmol) was dissolved in 6 mL of hexane, and *tert*-butyl isocyanide (0.045 mL, 0.40 mmol) was added dropwise at −30 °C, a white precipitate being immediately formed. The solution was warmed to room temperature, and stirring was continued for 10 min. After evaporation to dryness, the residue was taken up in dichloromethane and column-chromatographed in the same solvent. The product was crystallized from dichloromethane–hexane at −40 °C to give 0.077 g (0.29 mmol, 73%) of colorless **3b**. Anal. Calcd for $C_9H_{29}B_9N_2$: C, 41.16; H, 11.13; N, 10.67. Found: C, 42.06; H, 11.42; N, 10.54.

Synthesis of 6-$PhCH_2NB_9H_{11}$·CNtBu (3d). The same procedure used to prepare **3b** was followed by employing 0.120 g (0.56 mmol) of **2d** and 0.063 mL (0.56 mmol) of *tert*-butyl isocyanide. Crystallization from dichloromethane–hexane at −40 °C gave 0.125 g (0.42 mmol, 75%) of colorless **3d**.

Synthesis of $tBuCH_2NB_{11}H_{11}$ (4c). A solution of **3c** (0.26 g, 1.34 mmol) and $Me_2S{\cdot}BH_3$ (0.3 mL, 3.2 mmol) in 8 mL of decalin was heated to 170 °C for 2 h. After the mixture was cooled to room temperature, all volatile components were removed under vacuum. The remaining residue was extracted in portions with 80 mL of hexane, and the combined extracts were evaporated to dryness. Sublimation at 60 °C (0.001 Torr) yielded 0.12 g (0.56 mmol, 42% based on **3c**) of colorless **4c**. Further purification was achieved by crystallization from hexane at −40 °C. Anal. Calcd for $C_5H_{22}B_{11}N$: C, 27.91; H, 10.31; N, 6.51. Found: C, 27.89; H, 10.49; N, 6.38.

Synthesis of $PhCH_2NB_{11}H_{11}$ (4d). The same procedure was followed by employing 0.35 g (1.64 mmol) of **3d** and 0.4 mL (4.3 mmol) of $Me_2S{\cdot}BH_3$. Sublimation at 70 °C (0.001 Torr) afforded colorless crystals of **4d** (0.205 g, 0.87 mmol, 53% based on **3d**). Anal. Calcd for $C_7H_{18}B_{11}N$: C, 35.76; H, 7.72; N, 5.96. Found: C, 35.82; H. 7.57; N, 5.85.

Synthesis of $EtNB_{11}H_{11}$ (4e). A solution of 0.410 g (1.67 mmol) of $[Et_3HN][NB_{11}H_{11}]$ in 5 mL of dichloromethane was added to a solution of 1.28 g (6.4 mmol) of $[Et_3O]BF_4$ in 5 mL of dichloromethane. After 3 h of stirring at room temperature, all volatile components were removed under vacuum. The remaining solid was extracted in portions with 80 mL of pentane, and the combined extracts were evaporated to dryness. Sublimation at 40 °C (0.001 Torr) gave 0.131 g (0.76 mmol, 45% based on $[Et_3HN][NB_{11}H_{11}]$) of colorless **4e**. Anal. Calcd for $C_2H_{16}B_{11}N$: C, 13.88; H, 9.32; N, 8.09. Found: C, 13.72; H, 9.65; N, 7.95.

Synthesis of $iPrNB_{11}H_{11}$ (4f). A solution of 0.128 g (0.52 mmol) of $[Et_3HN][NB_{11}H_{11}]$ in 6 mL of dichloromethane was treated dropwise with 0.110 g (0.57 mmol) of $iPrO_3SCF_3$ at 0 °C. After 4 h of stirring at room temperature, all volatile components were removed under vacuum. The residue was extracted in portions with 80 mL of pentane, and the combined extracts were evaporated to dryness. Sublimation at 40 °C (0.001 Torr) yielded 0.027 g (0.14 mmol, 28% based on $[Et_3HN][NB_{11}H_{11}]$) of colorless **4f**.

Synthesis of $iBuNB_{11}H_{11}$ (4g). The same procedure used to prepare **4f** was followed by employing 0.244 g (0.99 mmol) of $[Et_3HN][NB_{11}H_{11}]$ and 0.225 g (1.09 mmol) of $iBuO_3SCF_3$. Sublimation at 40 °C (0.001 Torr) gave 0.049 g (0.24 mmol, 25% based on $[Et_3HN][NB_{11}H_{11}]$) of colorless **4g**.

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Supplementary Material Available: Tables of data collection and refinement parameters, hydrogen positional parameters, general displacement parameters, bond distances, bond angles, and least-squares planes and packing diagrams (11 pages). Ordering information is given on any current masthead page.