Partial Insertion of the 9-BBN Unit into the *nido*-B$_{10}$ Framework: Preparation and Structural Characterization of (9-BBN)B$_{10}$H$_{13}$ and [(9-BBN)B$_{10}$H$_{12}$]$^{-}$ [†]

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Na[B$_{10}$H$_{13}$] reacts with 9-Br-BBN (9-BBN = 9-bora[3.3.1]bicyclononane) in CH$_2$Cl$_2$ to produce (9-BBN)B$_{10}$H$_{13}$, **1**, in high yield. Single-crystal X-ray diffraction analysis shows that the boron atom of the 9-BBN unit in **1** is partially inserted into the *nido*-B$_{10}$ structure through a highly asymmetric bridge between B(5) and B(6) on the B$_{10}$ cluster with distances of B(BBN)−B(5) = 1.740(6) Å and B(BBN)−B(6) = 2.079(6) Å. There is also an *agostic* interaction of the terminal H(5b) on B(5) with B(BBN). NMR studies confirm that this interaction is maintained in solution. Compound **1** is unstable in coordinating solvents, resulting in some cases in the cleavage of the 9-BBN unit from the decaborane skeleton. When **1** is placed in Et$_2$O, NMR spectra suggest that (Et$_2$O)-(9-BBN)B$_{10}$H$_{13}$, **2**, is formed in which an Et$_2$O molecule associates with the boron B(BBN) of the 9-BBN unit while the interactions of that boron with B(6) and with H(5b) are eliminated, leaving only a direct bond between B(BBN) and B(5). Reaction of **1** with "Proton Sponge", 1,8-bis(dimethylamino)naphthalene, in CH$_2$Cl$_2$ gives [PSH][(9-BBN)B$_{10}$H$_{12}$], **3**, (PSH = protonated "Proton Sponge"). Single-crystal X-ray diffraction analysis of **3** indicates a structure similar to that of *nido*-[B$_{11}$H$_{14}$]$^{-}$, with the boron of the 9-BBN unit approximately occupying a vertex site of the pentagonal face of a *nido*-B$_{11}$ cluster. The B(BBN) boron is inserted into a bridging site between B(5) and its crystallographically imposed mirror equivalent B(10′) of the decaborane cluster with B(BBN)−B(5)/B(BBN)−B(10′) distances of 1.884(4) Å and a B(5)−B(10′) distance of 1.823(5) Å. On the other hand the distance of the B(BBN) boron to B(6) and to the mirror equivalent B(9′) is an abnormally long 2.142(4) Å, which indicates that the B(BBN) boron is not fully accommodated in the formation of a *nido*-[B$_{11}$H$_{14}$]$^{-}$ analogue. The novel interaction of the 9-BBN fragment with the decaborane cluster in **1** and the partial insertion of the 9-BBN moiety into the *nido*-B$_{10}$ unit observed in **3** are the first examples of such interactions observed between a monoboron unit and a decaborane cluster. Crystal data: **1**, *Pbca* (No. 61), *a* = 11.924(3) Å, *b* = 13.205(6) Å, *c* = 19.655(5) Å, *Z* = 8; **3**, *Pnma* (No. 62), *a* = 15.359(3) Å, *b* = 13.932(3) Å, *c* = 12.565(4) Å, *Z* = 4.

Introduction

The addition of a main group atom to a boron hydride cluster has been studied extensively. Three distinct, nonterminal interactions with the *nido*-decaborane system have been recognized thus far: one in which the atom spans the region between two edge boron atoms, replacing a bridging hydrogen (Chart 1a);[1−4] another in which the added atom is associated with more than two cluster atoms but is not considered to be an integral component of the cluster (Chart 1b);[5−14] and one in

Chart 1
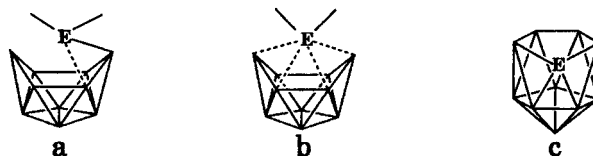
which the heteroatom is fully incorporated into the cluster, as a vertex site, often accompanied by migration or cleavage of the groups attached to the added atom (Chart 1c).[15−27]

[†] Dedicated to Professor Dr. Walter Siebert on the occasion of his sixtieth birthday.
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(1) Aftandilian, V. D.; Muetterties, E. L. *Inorg. Chem.* **1962,** *1*, 731.
(2) Amberger, E.; Leidl, P. *Chem. Ber.* **1969,** *102*, 2764.
(3) Schroeder, H. *Inorg. Chem.* **1963,** *2*, 390.
(4) Friedman, L. B.; Perry, S. L. *Inorg. Chem.* **1973,** *12*, 288.
(5) (a) Loffredo, R. E.; Norman, A. D. *J. Am. Chem. Soc.* **1971,** *93*, 5587. (b) Loffredo, R. E.; Norman, A. D. *Inorg. Nucl. Chem. Lett.* **1977,** *13*, 599.
(6) Beckett, M. A.; Kennedy, J. D. *Chem. Commun.* **1983,** 575.
(7) Petricek, V.; Cisarova, I.; Subitova, V. *Acta Crystallogr. C* **1983,** *39*, 1070.
(8) Travers, N. F.; Greenwood, N. N. *J. Chem. Soc. A* **1971,** 3257.
(9) Sharrocks, D. N.; Greenwood, N. N. *J. Chem. Soc. A* **1969,** 2334.
(10) McGinnety, J. A.; Greenwood, N. N. *J. Chem. Soc. A* **1966,** 1090.
(11) Youll, B.; Greenwood, N. N. *J. Chem. Soc., Dalton Trans.* **1975,** 158.

(12) Greenwood, N. N.; Thomas, B. S.; Waite, D. W. *J. Chem. Soc., Dalton Trans.* **1975,** 299.
(13) Greenwood, N. N.; Howard, J. A. *J. Chem. Soc., Dalton Trans.* **1976,** 177.
(14) Little, J. L.; Wong. A. C. *J. Am. Chem. Soc.* **1971,** *93*, 522.
(15) Little, J. L.; Pao, S. S.; Suganthan, K. K. *Inorg. Chem.* **1974,** *13*, 75.
(16) Little, J. L.; Whitesell, M. A.; Kester, J. G.; Folting, K.; Todd, L. J. *Inorg. Chem.* **1990,** *29*, 804.
(17) Little, J. L. *Inorg. Chem.* **1976,** *16*, 114.
(18) Yamamoto, T.; Todd, L. J. *J. Organomet. Chem.* **1974,** *67*, 75.
(19) Meyer, F.; Paetzold, P.; Englert, U. *Chem. Ber.* **1994,** *127*, 93.
(20) Bridges, A. N.; Hayashi, R. K.; Gaines, D. F. *Inorg. Chem.* **1994,** *33*, 1243.
(21) Bridges, A. N.; Gaines, D. F. *Inorg. Chem.* **1995,** *34*, 4523.
(22) Dopke, J. A.; Bridges, A. N.; Schmidt, M. R.; Gaines, D. F. *Inorg. Chem.* **1996,** *35*, 7186.
(23) Getman, T. D.; Shore, S. G. *Inorg. Chem.* **1988,** *27*, 3439.

Scheme 1
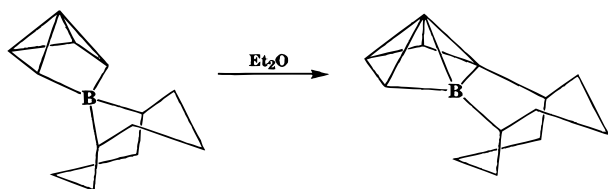
The bonding between the heteroatom (E) and the borane cluster depends on a number of factors including cluster size, the available heteroatom valence electrons, and the ability of the cluster to accommodate changes in the skeletal electron count.
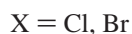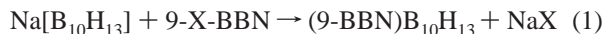
The insertion of a boron moiety into a boron bond in *arachno*-[B$_4$H$_9$]$^-$ and *nido*-[B$_5$H$_8$]$^-$ to form an edge-bridged adduct is well-established.[28] However, earlier attempts to insert a borane unit into the boron−boron bond that bridges the B(5)−B(6) positions of *nido*-[B$_{10}$H$_{13}$]$^-$ did not produce a B(5)−B(6)-bridged adduct.[20]

A recent investigation[27] showed that [B$_5$H$_8$]$^-$ reacts with 9-X-BBN (9-BBN = 9-bora[3.3.1]bicyclononane = BC$_8$H$_{14}$; X = Cl, Br) to produce 2,3-μ-9-BBNB$_5$H$_8$, a stable intermediate. In the presence of Et$_2$O, the species rearranges to a B$_6$ cluster in which the bridging boron has inserted into the cage, accompanied by migration of one of the bridgehead carbons of the bicyclononane to a neighboring basal boron atom (Scheme 1).

Results with the B$_5$ system encouraged us to explore similar reactions of 9-X-BBN with the [B$_{10}$H$_{13}$]$^-$ system. Herein we report the results of our investigations.

Results and Discussion

Preparation of (9-BBN)B$_{10}$H$_{13}$. Earlier attempts to prepare (9-BBN)B$_{10}$H$_{13}$ through reactions of [Bu$_4$N]$^+$, [Ph$_3$PMe]$^+$, and [PSH]$^+$ (PS = "Proton Sponge" = 1,8-bis(dimethylamino)-naphthalene; [PSH]$^+$ = protonated "proton sponge") salts of *nido*-[B$_{10}$H$_{13}$]$^-$ with 9-X-BBN (X = Cl, Br) were unsuccessful.[29] However, we found that the heterogeneous reaction of 9-X-BBN with ether-free Na[B$_{10}$H$_{13}$] in CH$_2$Cl$_2$ over several hours produced (9-BBN)B$_{10}$H$_{13}$, **1** (eq 1).

$$\text{Na[B}_{10}\text{H}_{13}] + \text{9-X-BBN} \rightarrow \text{(9-BBN)B}_{10}\text{H}_{13} + \text{NaX} \quad (1)$$

$$\text{X} = \text{Cl, Br}$$

Compound **1** is readily soluble in hexanes, benzene, and CH$_2$Cl$_2$, but these solutions are unstable, and noticeable decomposition to B$_{10}$H$_{14}$ occurs over a period of several days. The solid is air- and moisture-sensitive, but it appears to be stable under an atmosphere of nitrogen, as it shows no sign of decomposition at room temperature.

Molecular Structure of (9-BBN)B$_{10}$H$_{13}$, 1. Crystals of **1** were grown via slow diffusion of a CH$_2$Cl$_2$ solution into hexanes at −40 °C. Crystallographic data are listed in Table 1, and

Table 1. Crystallographic Data for (9-BBN)B$_{10}$H$_{13}$, **1**, and [PSH][(9-BBN)B$_{10}$H$_{12}$], **3**

	C$_8$B$_{11}$H$_{27}$, **1**	C$_{22}$H$_{45}$B$_{11}$N$_2$, **3**
empirical formula	C$_8$B$_{11}$H$_{27}$, **1**	C$_{22}$H$_{45}$B$_{11}$N$_2$, **3**
fw	242.23	456.51
space group	*Pbca* (No. 61)	*Pnma* (No. 62)
a, Å	11.924(3)	15.359(3)
b, Å	13.205(6)	13.932(3)
c, Å	19.655(5)	12.565(4)
V, Å^3	3094.9	2688.7
Z	8	4^e
d (calcd), g cm^{-3}	1.040	1.128
temp, °C	25	−60
λ, Å	Mo Kα (0.710 73)	Mo Kα (0.710 73)
μ, mm^{-1}	0.04	0.058
R	0.036^a	0.0454^c
R$_w$	0.046^b	0.1310^d

^{a} $R_F = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_{wF} = \{\sum w[|F_o| - |F_c|]^2/\sum w|F_o|^2\}^{1/2}$. ^{c} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{d} w$R_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$. ^{e} There are 4 molecules per unit cell, but the asymmetric unit consists of $^1/_2$ a molecule. Thus there are 8 asymmetric units per unit cell.

atom positional parameters and selected bond lengths and angles are given in Tables 2 and 3. Two views of the molecular structure of **1** are shown in Figure 1.

The molecular structure of **1** contains a 9-BBN unit that is partially inserted into the *nido*-B$_{10}$ structure through a highly asymmetric bridge between the B(5) and B(6) atoms with distances of B(BBN)−B5 = 1.740(6) Å and B(BBN)−B6 = 2.079(6) Å, a value at the high end of the range, 1.6−2.0 Å, observed for boron−boron distances.[30] Noteworthy is an apparent *agostic* interaction between the terminal hydrogen on B(5) and the boron of the 9-BBN unit. The B(5)−H(5b) distance, 1.10(4) Å, is normal for a terminal B−H interaction, and the B(BBN)−H(5b) distance, 1.43(3) Å, suggests a bridging interaction between B(BBN) and B(5). NMR spectra indicate that the *agostic* interaction of the hydrogen on B(5) is preserved in solution. The B(5)−B(6) distance is 1.687(6) Å, and there are no short nonbonded inter- or intramolecular contacts that would account for the significant asymmetry of the B(5)−B(BBN)−B(6) bond. With the existence of only a 3-center B(5)−B(BBN)−B(6) interaction, the boron of the 9-BBN unit would be associated with only six valence electrons. The distortion of the B(5)−B(BBN)−B(6) bridge favors the formation of the *agostic* interaction, thereby providing two more valence electrons to complete the octet of the 9-BBN boron atom. An analogous situation has been observed[31] in the case of ((PPh$_3$)$_2$Cu)(B$_5$H$_8$Fe(CO)$_3$). In this case the (PPh$_3$)$_2$Cu unit is inserted into the basal boron−boron bond of the pentagonal pyramidal B$_5$H$_8$Fe(CO)$_3$ cluster. The resulting B−Cu−B bond is distorted so that an *agostic* interaction occurs between a terminal hydrogen on a boron atom and the copper atom. With the *agostic* interaction, the copper atom achieves an 18 electron configuration.

The remainder of the structure of **1** is consistent with prior structural data on the B$_{10}$ cluster.[32−34] There are two symmetrical bridging hydrogen atoms spanning both the B(6)−B(7) vertexes (B(6)−H(6b), 1.26(3) Å; B(7)−H(6b), 1.27(3) Å) and the B(9)−B(10) vertexes (B(9)−H(9b), 1.28(3) Å; B(10)−

(24) Getman, T. D.; Deng. H.; Hsu, L. Y.; Shore, S. G. *Inorg. Chem.* **1989**, *28*, 3612.

(25) Whitaker, C.; Romerosa, A.; Teixidor, F.; Rius, J. *Acta Crystallogr. C* **1995**, *51*, 188.

(26) Wesemann, L.; Englert, U.; Seyferth, D. *Angew. Chem., Int. Ed. Engl.* **1995**, 2236.

(27) Edvenson, G. M.; Harris, H. A.; Campana, C. F.; Gaines, D. F. *Organometallics* **1990**, *9*, 401.

(28) Remmel, R. J.; Johnson, H. D., II; Jaworiwsky, I. S.; Shore, S. G. *J. Am. Chem. Soc.* **1975**, *97*, 5395.

(29) Bridges, A. N. Ph.D. Thesis, University of Wisconsin−Madison, 1995.

(30) Beaudet, R. A. The Molecular Structures of Boranes and Carboranes. Chapter 20 in *Advances in Boron and Boranes*; Liebmann, J. F., Greenberg, A., Williams, R. E., Eds.; VCH: New York, 1988.

(31) Mangion, M.; Ragaini, J. D.; Schmitkons; T. A.; Shore, S. G. *J. Am. Chem. Soc.* **1979**, *101*, 754.

(32) Kasper, J. S.; Lucht, C. M.; Harker, D. *J. Am. Chem. Soc.* **1948**, *70*, 881.

(33) Sneddon, L. G.; Huffman, J. C.; Schaeffer, R. O.; Streib, W. E. *Chem. Commun.* **1972**, 474.

(34) Wynd, A. J.; Welch, A. J. *Acta Crystallogr. C.* **1989**, *45*, 615.

Table 2. Positional Parameters and Their Estimated Standard Deviations for (9-BBN)$B_{10}H_{13}$

atom	x	y	z	B (Å^2)^{a,b}
C(1)	0.2307(3)	0.7727(2)	0.0135(2)	3.13(7)
C(2)	0.1911(3)	0.8041(3)	−0.0577(2)	3.89(8)
C(3)	0.2343(3)	0.9069(3)	−0.0810(2)	3.80(8)
C(4)	0.2184(3)	0.9897(3)	−0.0284(2)	3.90(9)
C(5)	0.2501(3)	0.9608(2)	0.0449(2)	3.04(7)
C(6)	0.3756(3)	0.9435(3)	0.0580(2)	4.27(9)
C(7)	0.4266(3)	0.8565(3)	0.0186(2)	4.58(9)
C(8)	0.3587(3)	0.7596(3)	0.0186(2)	3.99(9)
B	0.1921(3)	0.8586(3)	0.0639(2)	2.50(8)
B(1)	−0.0335(3)	0.8738(3)	0.1730(2)	3.6(1)
B(2)	0.0443(4)	0.7598(3)	0.1775(2)	3.53(9)
B(3)	0.0049(4)	0.8238(3)	0.2527(2)	4.1(1)
B(4)	−0.0121(4)	0.9567(3)	0.2439(2)	4.1(1)
B(5)	0.0822(3)	0.8577(3)	0.1221(2)	2.77(8)
B(6)	0.1828(3)	0.7846(3)	0.1571(2)	3.27(9)
B(7)	0.1420(4)	0.7801(3)	0.2444(2)	4.0(1)
B(8)	0.0971(4)	0.9052(4)	0.2919(2)	4.3(1)
B(9)	0.1140(4)	1.0149(3)	0.2419(2)	4.1(1)
B(10)	0.0485(3)	0.9846(3)	0.1636(2)	3.51(9)
H(11)	0.200(2)	0.708(2)	0.025(1)	3.4(7)
H(21)	0.104(2)	0.807(2)	−0.058(1)	4.3(7)
H(22)	0.218(2)	0.753(2)	−0.091(1)	5.4(8)
H(31)	0.321(2)	0.902(2)	−0.092(1)	3.9(7)
H(32)	0.199(2)	0.918(2)	−0.122(1)	4.5(7)
H(41)	0.267(3)	1.051(2)	−0.044(1)	6.0(9)
H(42)	0.136(2)	1.008(2)	−0.026(1)	4.1(7)
H(51)	0.230(2)	1.014(2)	0.074(1)	1.4(5)
H(61)	0.384(2)	0.932(3)	0.112(2)	8(1)
H(62)	0.421(2)	1.006(2)	0.045(1)	4.9(8)
H(71)	0.436(2)	0.873(2)	−0.033(2)	5.4(8)
H(72)	0.503(2)	0.841(2)	0.038(1)	4.0(7)
H(81)	0.384(3)	0.714(2)	−0.024(2)	7(1)
H(82)	0.377(2)	0.723(2)	0.060(1)	4.5(7)
H(1)	−0.113(2)	0.877(2)	0.149(1)	3.9(7)
H(2)	0.009(2)	0.691(2)	0.166(1)	4.4(7)
H(3)	−0.042(2)	0.785(2)	0.288(1)	2.9(6)
H(4)	−0.084(2)	0.991(2)	0.263(1)	4.5(7)
H(5b)	0.072(2)	0.859(2)	0.067(1)	3.9(7)
H(6)	0.247(3)	0.732(2)	0.142(1)	5.4(8)
H(6b)	0.220(2)	0.823(2)	0.211(1)	3.4(6)
H(7)	0.173(3)	0.720(2)	0.274(2)	6.6(9)
H(8)	0.107(2)	0.906(2)	0.347(1)	4.6(7)
H(9)	0.137(2)	1.092(2)	0.256(2)	4.9(8)
H(8b)	0.182(2)	0.940(2)	0.271(2)	5.4(8)
H(9b)	0.150(2)	0.996(2)	0.182(1)	3.4(6)
H(10)	0.020(2)	1.044(2)	0.131(1)	2.7(6)

^{a} Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \gamma)B(1,2) + ac(\cos \beta)B(1,3) + bc(\cos \alpha)B(2,3)]$. ^{b} Hydrogen atoms were located and refined isotropically.

H(9b), 1.27(3) Å). One unsymmetrical bridging hydrogen exists between the B(8) and B(9) vertexes (B(8)−H(8b), 1.18(4) Å; B(9)−H(8b), 1.40(4) Å). The distances between boron and terminal hydrogen atoms range from 1.03(4) to 1.10(4) Å. The two longest B−B distances are the B(5)−B(10), 1.906(6) Å, and B(7)−B(8), 1.971(8) Å, while the remaining B−B distances range from 1.687(6) to 1.791(8) Å.

NMR Spectroscopic Studies of (9-BBN)$B_{10}H_{13}$, 1. NMR spectra of **1** indicate that its structure in solution is like that in the solid state. The ^{11}B NMR spectrum of **1** at 96.3 MHz in hexanes (Figure 2) displays all 11 expected resonances, with the upfield region of the spectrum reminiscent of other asymmetrically substituted *nido*-decaboranes.[29]

The extreme downfield singlet at +53.1 ppm, assigned to the boron of the 9-BBN unit, is in the range common for trigonally coordinated boron environments, albeit at the high-field extreme.[35] This is believed to reflect the contribution of electron density of the *agostic* interaction with the terminal

hydrogen on B(5) and is appreciably farther upfield than the resonance of the bridging 9-BBN unit reported[27] for 2,3-μ-BBNB$_5$H$_8$ (+103 ppm). The remaining upfield resonances are all doublets, indicative of a terminal hydrogen on each boron atom and suggesting no terminal substitution on the decaborane skeleton.

At higher field (160.2 MHz), the ^{11}B NMR spectrum shows that the signal at +10.4 ppm has a considerably smaller B−H coupling constant ($J_{B−H}$ = 85 Hz) than the other boron signals. Terminal B−H coupling constants normally fall within the range of 130−160 Hz, while $J_{B−H\mu}$ coupling constants fall well below 85 Hz.[35] A coupling constant that falls between these two ranges could result from a terminal hydrogen acting as a "semibridging" hydrogen to a second boron atom. In view of the fact that the X-ray structure indicates an *agostic* hydrogen between B(5) and B(BBN), the signal at +10.4 ppm is assigned to the B(5) position.

Resonances in **1** were further assigned from the ^{11}B−^{11}B COSY NMR spectrum (Figure 3).

Noteworthy is the absence of cross-coupling between the 9-BBN boron at +53.1 ppm and the adjacent B(5) signal. Bridging hydrogens are known to disturb the magnetization along B−B connectivities in borane clusters, masking cross-coupling in 2-D spectra.[36,37] In addition, no cross-coupling is observed between B(BBN) and B(6), which might be due to the extended distance between these two vertexes observed in the solid-state structure.

The ^{13}C NMR spectrum of **1** at −50 °C gives no indication of rotation of the bicyclooctyl unit about the B(BBN)−B(5) bond on the ^{13}C NMR time scale. With increasing temperature, the broad signal at 33.2 ppm, assigned to the bridgehead carbons C(1) and C(5), broadens into the baseline due to increased scalar coupling with the 9-BBN boron atom. The remaining carbon signals begin to coalesce with increasing temperature, and at 50 °C, only two carbon signals at +33.8 and +23.4 ppm are observed in a ratio of 4:2. The spectrum is nearly identical with that of 9-Br-BBN,[29] which suggests free rotation about the B(BBN)−B(5) bond has been achieved. The ^{11}B NMR spectrum appears unaffected at this temperature, though slow decomposition is observed.

The 300.1 MHz ^{1}H{^{11}B} NMR spectrum of **1** is complicated but displays three distinct regions of interest. Seven signals in the downfield region, between +3.0 and +4.5 ppm, are assigned to eight of the B−H terminal hydrogens of the decaborane framework, with two overlapping signals at +3.26 ppm. Since the pattern of the terminal hydrogen signals should be similar to that of the ^{11}B NMR signal pattern, it is reasonable to assign these hydrogens to the eight downfield vertexes on the decaborane framework. The region between +1.0 and +2.5 ppm is ascribed to the complicated pattern of the bicyclooctyl ring unit. The two remaining B−H terminal hydrogen resonances, the B(2) and B(4) vertexes, are believed to correspond to the broadened signals at δ = +0.77 and +0.63 ppm, a result of inefficient decoupling due to limitations of the decoupler channel. The upfield portion of the spectrum consists of three signals of intensity one at δ = −1.80, −2.85, and −3.83 ppm, attributed to the three bridging hydrogens on the decaborane cage.

(35) Kennedy, J. D., Mason, J., Eds. *Multinuclear NMR*; Plenum Press: New York, 1987.
(36) Venable, T. L.; Hutton, W. C.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.
(37) Edvenson, G. M.; Hill, T. G.; Adams, B. R.; Gaines, D. F. *Inorg. Chem.* **1987**, *26*, 1813.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for (9-BBN)B$_{10}$H$_{13}$

Bond Lengths

C(1)−C(2)	1.532(6)	B(3)−B(8)	1.721(8)	B(1)−B(2)	1.771(7)	B(7)−H(6b)	1.27(3)
C(1)−C(8)	1.539(6)	B(3)−H(3)	1.03(3)	B(1)−B(3)	1.761(7)	B(7)−H(7)	1.05(4)
C(1)−B	1.575(6)	B(4)−B(8)	1.746(8)	B(1)−B(4)	1.791(8)	B(8)−B(9)	1.761(8)
C(2)−C(3)	1.522(6)	B(4)−B(9)	1.689(8)	B(1)−B(10)	1.768(7)	B(8)−H(8)	1.10(4)
C(3)−C(4)	1.516(6)	B(4)−B(10)	1.775(7)	B(1)−H(1)	1.06(3)	B(8)−H(8b)	1.18(4)
C(4)−C(5)	1.537(5)	B(4)−H(4)	1.04(4)	B(2)−B(3)	1.765(7)	B(9)−B(10)	1.772(7)
C(5)−C(6)	1.535(6)	B(5)−B(6)	1.687(6)	B(2)−B(5)	1.751(7)	B(9)−H(9)	1.09(4)
C(5)−B	1.561(6)	B(5)−B(10)	1.906(6)	B(2)−B(6)	1.732(7)	B(9)−H(8b)	1.40(4)
C(6)−C(7)	1.513(6)	B(5)−H(5b)	1.10(4)	B(2)−B(7)	1.777(7)	B(9)−H(9b)	1.28(3)
C(7)−C(8)	1.514(6)	B(6)−B(7)	1.786(7)	B(2)−H(2)	1.03(4)	B(10)−H(9b)	1.27(3)
B−B(5)	1.740(6)	B(6)−H(6)	1.07(4)	B(3)−B(4)	1.775(8)	B(10)−H(10)	1.07(3)
B−H(5b)	1.43(3)	B(6)−H(6b)	1.26(3)	B(3)−B(7)	1.740(8)		
B−B(6)	2.079(6)	B(7)−B(8)	1.971(8)				

Angles

C(2)−C(1)−C(8)	113.3(4)	C(4)−C(5)−C(6)	115.6(4)	B(1)−B(5)−B(10)	58.2(3)	B(3)−B(8)−H(8)	121.(2)
C(2)−C(1)−B	106.8(4)	C(4)−C(5)−B	109.2(3)	B(1)−B(5)−H(5b)	119.(2)	B(3)−B(8)−H(8b)	130.(2)
C(8)−C(1)−B	109.2(4)	C(6)−C(5)−B	105.3(3)	B(2)−B(5)−B(6)	60.5(3)	B(4)−B(8)−B(7)	105.8(4)
C(1)−C(2)−C(3)	114.4(4)	C(5)−C(6)−C(7)	114.8(4)	B(2)−B(5)−B(10)	109.2(3)	B(4)−B(8)−B(9)	57.6(3)
C(2)−C(3)−C(4)	113.2(4)	C(6)−C(7)−C(8)	115.2(4)	B(2)−B(5)−H(5b)	127.(2)	B(4)−B(8)−H(8)	128.(2)
C(3)−C(4)−C(5)	115.5(4)	C(1)−C(8)−C(7)	115.8(4)	B(6)−B(5)−B(10)	118.6(3)	B(4)−B(8)−H(8b)	108.(2)
C(1)−B−C(5)	110.1(3)	B(1)−B(3)−B(2)	60.3(3)	B(6)−B(5)−H(5b)	119.(2)	B(7)−B(8)−B(9)	113.2(4)
C(1)−B−B(5)	129.0(3)	B(1)−B(3)−B(4)	60.9(3)	B(10)−B(5)−H(5b)	113.(2)	B(7)−B(8)−H(8)	117.(2)
C(1)−B−H(5b)	108.(1)	B(1)−B(3)−B(7)	106.6(4)	B(2)−B(6)−B(5)	61.6(3)	B(7)−B(8)−H(8b)	86.(2)
C(5)−B−B(5)	119.8(3)	B(1)−B(3)−B(8)	109.3(4)	B(2)−B(6)−B(7)	60.6(3)	B(9)−B(8)−H(8)	123.(2)
C(5)−B−H(5b)	117.(1)	B(1)−B(3)−H(3)	130.(2)	B(2)−B(6)−H(6)	129.(2)	B(9)−B(8)−H(8b)	52.(2)
B(5)−B−H(5b)	39.(1)	B(2)−B(3)−B(4)	115.0(4)	B(2)−B(6)−H(6b)	103.(2)	H(8)−B(8)−H(8b)	104.(3)
B(2)−B(1)−B(3)	60.0(3)	B(2)−B(3)−B(7)	60.9(3)	B(5)−B(6)−B(7)	102.5(4)	B(4)−B(9)−B(8)	60.8(3)
B(2)−B(1)−B(4)	113.9(4)	B(2)−B(3)−B(8)	120.3(4)	B(5)−B(6)−H(6)	140.(2)	B(4)−B(9)−B(10)	61.6(3)
B(2)−B(1)−B(5)	60.3(3)	B(2)−B(3)−H(3)	118.(2)	B(5)−B(6)−H(6b)	112.(2)	B(4)−B(9)−H(9)	130.(2)
B(2)−B(1)−B(10)	114.8(3)	B(4)−B(3)−B(7)	115.2(4)	B(7)−B(6)−H(6)	116.(2)	B(4)−B(9)−H(8b)	101.(2)
B(2)−B(1)−H(1)	122.(2)	B(4)−B(3)−H(3)	59.9(3)	B(7)−B(6)−H(6b)	45.(2)	B(4)−B(9)−H(9b)	103.(2)
B(3)−B(1)−B(4)	60.0(3)	B(7)−B(3)−H(3)	120.(2)	H(6)−B(6)−H(6b)	103.(2)	B(8)−B(9)−B(10)	104.4(4)
B(3)−B(1)−B(5)	105.2(4)	B(7)−B(3)−B(8)	69.4(3)	B(2)−B(7)−B(3)	60.2(3)	B(8)−B(9)−H(9)	131.(2)
B(3)−B(1)−B(10)	105.0(4)	B(7)−B(3)−H(3)	114.(2)	B(2)−B(7)−B(6)	58.2(3)	B(8)−B(9)−H(8b)	42.(2)
B(3)−B(1)−H(1)	130.(2)	B(8)−B(3)−H(3)	111.(2)	B(2)−B(7)−B(8)	107.4(4)	B(10)−B(9)−H(9)	123.(2)
B(4)−B(1)−B(5)	114.5(4)	B(1)−B(4)−B(3)	59.2(3)	B(2)−B(7)−H(6b)	100.(2)	B(10)−B(9)−H(8b)	117.(2)
B(4)−B(1)−B(10)	59.8(3)	B(1)−B(4)−B(8)	106.8(4)	B(2)−B(7)−H(7)	121.(2)	B(10)−B(9)−H(9b)	46.(1)
B(4)−B(1)−H(1)	117.(2)	B(1)−B(4)−B(9)	112.7(4)	B(3)−B(7)−B(6)	109.6(4)	H(9)−B(9)−H(8b)	114.(3)
B(5)−B(1)−B(10)	66.3(3)	B(1)−B(4)−B(10)	59.5(3)	B(3)−B(7)−B(8)	54.8(3)	H(9)−B(9)−H(9b)	110.(3)
B(5)−B(1)−H(1)	118.(2)	B(1)−B(4)−H(4)	116.(2)	B(3)−B(7)−H(6b)	126.(2)	H(8b)−B(9)−H(9b)	93.(2)
B(10)−B(1)−H(1)	115.(2)	B(3)−B(4)−B(8)	58.5(3)	B(3)−B(7)−H(7)	122.(2)	B(1)−B(10)−B(4)	60.7(3)
B(1)−B(2)−B(3)	59.7(3)	B(3)−B(4)−B(9)	110.5(4)	B(6)−B(7)−B(8)	120.1(4)	B(1)−B(10)−B(5)	55.6(3)
B(1)−B(2)−B(5)	58.3(3)	B(3)−B(4)−B(10)	104.1(4)	B(6)−B(7)−H(6b)	45.(2)	B(1)−B(10)−B(9)	109.9(4)
B(1)−B(2)−B(6)	109.0(3)	B(3)−B(4)−H(4)	120.(2)	B(6)−B(7)−H(7)	117.(2)	B(1)−B(10)−H(9b)	126.(2)
B(1)−B(2)−B(7)	104.6(3)	B(8)−B(4)−B(9)	61.7(3)	B(8)−B(7)−H(6b)	94.(2)	B(1)−B(10)−H(10)	119.(2)
B(1)−B(2)−H(2)	122.(2)	B(8)−B(4)−B(10)	104.9(4)	B(8)−B(7)−H(7)	118.(2)	B(4)−B(10)−B(5)	106.5(3)
B(3)−B(2)−B(5)	103.6(4)	B(8)−B(4)−H(4)	126.(2)	H(6b)−B(7)−H(7)	111.(3)	B(4)−B(10)−B(9)	56.9(3)
B(3)−B(2)−B(6)	110.9(4)	B(9)−B(4)−B(10)	61.5(3)	B(3)−B(8)−B(4)	61.6(3)	B(4)−B(10)−H(9b)	99.(2)
B(3)−B(2)−B(7)	58.9(3)	B(9)−B(4)−H(4)	123.(2)	B(3)−B(8)−B(7)	55.7(3)	B(4)−B(10)−H(10)	124.(2)
B(3)−B(2)−H(2)	120.(2)	B(10)−B(4)−H(4)	124.(2)	B(5)−B(10)−B(9)	118.5(4)	B(6)−H(6b)−B(7)	90.(2)
B(5)−B(2)−B(6)	57.9(3)	B−B(5)−B(1)	170.9(4)	B(5)−B(10)−H(9b)	91.(2)	B(8)−H(8b)−B(9)	86.(2)
B(5)−B(2)−B(7)	100.3(3)	B−B(5)−B(2)	127.5(3)	B(5)−B(10)−H(10)	117.(2)	B(9)−H(9b)−B(10)	88.(2)
B(5)−B(2)−H(2)	129.(2)	B−B(5)−B(6)	74.7(3)	B(9)−B(10)−H(9b)	46.(2)	B(5)−B−B(6)	51.5(2)
B(6)−B(2)−B(7)	61.2(3)	B−B(5)−B(10)	115.8(3)	B(9)−B(10)−H(10)	120.(2)	B−B(5)−B(6)	74.7(3)
B(6)−B(2)−H(2)	121.(2)	B−B(5)−H(5b)	55.(2)	B(8)−B(9)−H(9b)	113.(2)	B−B(6)−B(5)	53.8(2)
B(7)−B(2)−H(2)	124.(2)	B(1)−B(5)−B(2)	61.4(3)	H(9b)−B(10)−H(10)	113.(2)	B−H(5b)−B(5)	86(2)
B(1)−B(5)−B(6)	113.9(4)	B(3)−B(8)−B(9)	109.7(4)	B−H(5b)−B(5)	86.(2)		

    None of the seven downfield B−H terminal hydrogen signals can be assigned with any certainty, but the signal at +3.73 ppm displays an unexpected coupling pattern, which may identify it as the B(9) terminal hydrogen. The quartet pattern was originally attributed to an extremely small coupling ($J = 9$ Hz) to one boron atom ($I = ^3/_2$). However, this small "quartet" pattern has also been observed in the {^{11}B}^{1}H NMR spectra of other boron hydride systems, namely B$_{10}$H$_{14}$ and B$_{18}$H$_{22}$,[38] in which the signals have been unambiguously assigned to the terminal hydrogens on the B(6,9) and B(9,9′) vertexes, respec-

tively. In each case the terminal hydrogen occupies a vertex directly adjacent to two bridging hydrogens. The quartet pattern is most likely a doublet of doublets, the result of coupling to nonequivalent bridging hydrogens. Apparently in the absence of coupling to a ^{11}B nucleus, the small $J = 1.5-2$ coupling can be observed under certain circumstances. Structurally, the H(8−9) and H(9−10) bridging hydrogens in **1** are inequivalent.

    The proximity of the 9-BBN fragment to the terminal hydrogen on the B(5) vertex, perhaps the most unusual aspect of the solid-state structure, is most likely responsible for the absence of cross-coupling in the ^{11}B−^{11}B COSY NMR and the diminished B(5)−H(5b) coupling observed in the 1-D ^{11}B NMR.

(38) Fontaine, X. L. R.; Greenwood, N. N. Kennedy, J. D.; MacKinnon, P. J. *J. Chem. Soc., Dalton Trans.* **1988**, 1785.

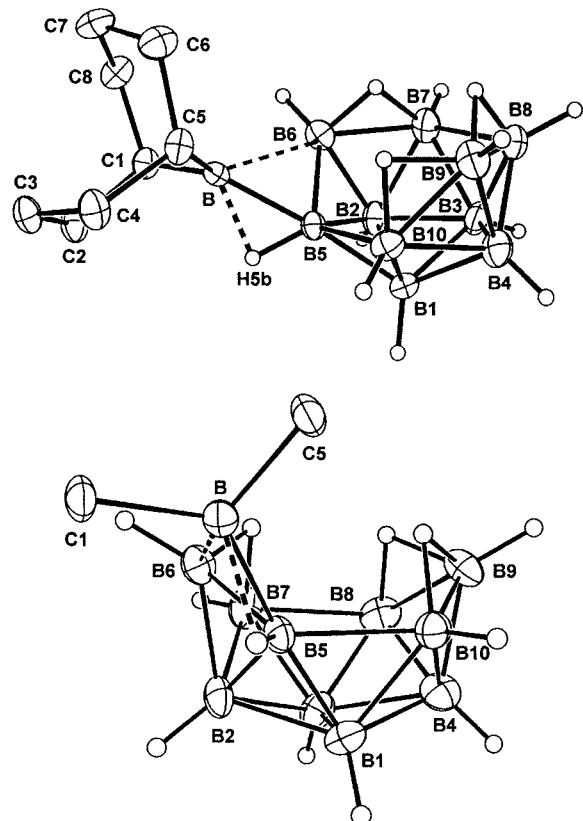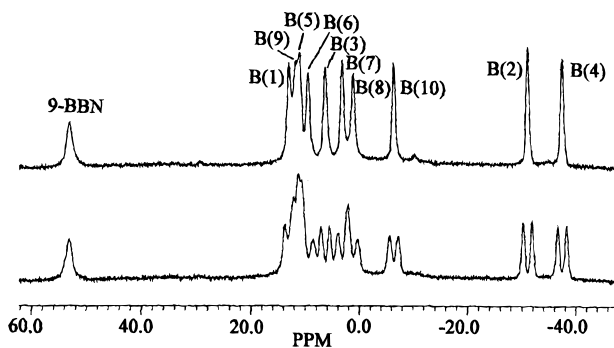**Figure 1.** Molecular structure of (9-BBN)$B_{10}H_{13}$, **1**.

Figure 2. ^{11}B and $^{11}B\{^1H\}$ NMR spectra of (9-BBN)$B_{10}H_{13}$, **1**, in hexanes at 93.6 MHz.

Conversion (9-BBN)$B_{10}H_{13}$, 1, to (Et$_2$O)(9-BBN)$B_{10}H_{13}$, 2. Compound **1** is sensitive to coordinating solvents. The solvents CH_3CN and THF are sufficiently basic to strip the 9-BBN unit from the B_{10} skeleton, leaving $[B_{10}H_{13}]^-$ and $B_{10}H_{14}$ in various ratios. However, when **1** is dissolved in the more weakly coordinating solvent Et$_2$O, a new species forms over a period of several hours as indicated in the ^{11}B NMR spectrum in benzene (Figure 4).

The symmetry pattern and chemical shifts of the spectrum indicate that the new species, **2**, has asymmetrical substitution. The pattern of the upfield resonances suggests a 5-substituted derivative, as it is quite similar to that of various 5-R-$B_{10}H_{13}$ derivatives.[29] It is believed that an incoming Et$_2$O molecule adds to the boron of the 9-BBN unit, thereby displacing the bridging hydrogen between the 9-BBN boron and B(5) atom, causing the hydrogen atom to move to a bridging site between B(5) and B(6). The 9-BBN unit is now bound to the B_{10} cage solely through a terminal bond to the B(5) atom (Chart 2) that is assigned to the singlet at +16.9 ppm in the ^{11}B NMR spectrum. The chemical shift of the downfield signal (+56.3
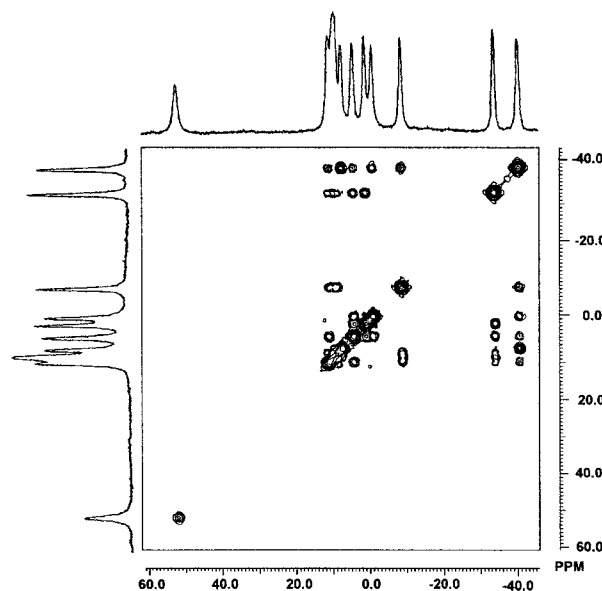

Figure 3. $^{11}B-^{11}B$ COSY NMR spectrum ($t_1 \times t_2 = 128 \times 256$ words) of (9-BBN)$B_{10}H_{13}$ in hexanes at 80.2 MHz. The ^1H-decoupled 1-D spectrum is plotted on F_1 and F_2 to aid in identifying resonances along the diagonal and interpreting cross-peaks in the 2-D array.
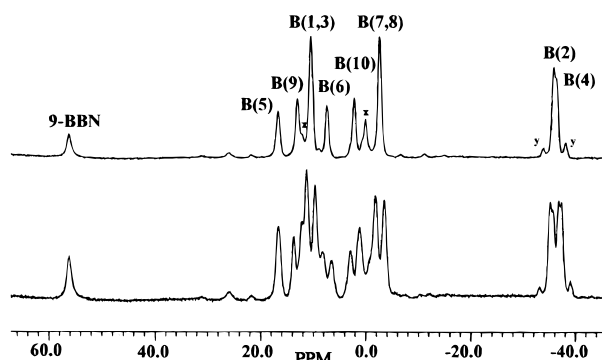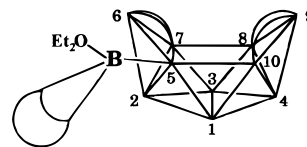

Figure 4. ^{11}B NMR spectrum of (Et$_2$O)(9-BBN)$B_{10}H_{13}$, **2**.

Chart 2

ppm) is similar to that of B(BBN) in the starting material, which suggests that the 9-BBN group in this species is in a similar chemical environment.

The $^1H\{^{11}B\}$ NMR spectrum of **2** at 300.1 MHz in benzene supports the presence of a bound Et$_2$O molecule, with a quartet at +3.78 ppm and a triplet at +1.07 ppm in a ratio of 2:3. These chemical shifts are significantly different from those of free Et$_2$O in benzene (3.25 ppm, quartet; 1.07 ppm, triplet). The three multiplets at $\delta = +1.83$, +1.39, and +1.04 ppm in a ratio of 8:2:4 are similar to those observed for 9-Br-BBN. The bridging region consists of three broadened resonances at $\delta = -2.10$, −2.65, and −2.71 ppm in a ratio of 1:1:2, which is consistent with the proposed structure (Chart 2).

The ^{13}C NMR spectrum of **2** in benzene at 62.5 MHz displays two intense resonances at 33.5 and 23.6 ppm, in a ratio of 2:1. On the basis of comparisons to the ^{13}C NMR spectra of both 9-Br-BBN and 2,3-μ-BBNB$_5$H$_8$,[27] the signals are attributed to the C(2,4,6,8) and C(3,7) atoms, respectively, and free rotation

Table 4. Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for the [(9-BBN)B$_{10}$H$_{12}$]$^-$ Anion

atom	x	y	z	U(eq)^a
C(21)	−7(2)	2500	154(3)	39(1)
C(22)	−206(2)	1588(2)	−504(2)	49(1)
C(23)	−1155(2)	1376(2)	−699(3)	69(1)
C(24)	−1754(2)	1575(2)	219(2)	49(1)
C(25)	−1584(2)	2500	843(3)	34(1)
B(1)	−350(3)	2500	3722(3)	34(1)
B(2)	209(2)	1450(2)	3341(2)	37(1)
B(3)	801(3)	2500	3652(4)	40(1)
B(5)	−716(2)	1846(2)	2604(2)	32(1)
B(6)	130(2)	1323(2)	1965(2)	37(1)
B(7)	1112(2)	1789(2)	2574(2)	42(1)
B	−585(3)	2500	1301(3)	32(1)
H(1)	−733(20)	2500	4451(26)	39(9)
H(2)	202(14)	822(16)	3877(18)	42(6)
H(3)	1275(23)	2500	4288(28)	52(10)
H(5)	−1317(14)	1479(15)	2667(16)	31(6)
H(6)	86(15)	647(18)	1544(18)	47(7)
H(7)	1716(16)	1425(18)	2532(19)	52(7)
H(67)	803(15)	1810(16)	1696(18)	41(6)

^{a} U(eq) is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 5. Selected Bond Lengths (Å) and Angles (deg) for the [(9-BBN)B$_{10}$H$_{12}$]$^-$ Anion^a

Bond Lengths			
C(21)−C(22)	1.547(3)	B(2)−H(2)	1.10(2)
C(21)−B	1.693(5)	B(3)−B(7)	1.745(5)
C(22)−C(23)	1.507(4)	B(3)−H(3)	1.08(4)
C(23)−C(24)	1.501(4)	B(5)−B(6)	1.692(4)
C(24)−C(25)	1.532(3)	B(5)−B(10′)	1.823(5)
C(25)−B	1.639(5)	B(5)−B	1.884(4)
B(1)−B(3)	1.770(6)	B(5)−H(5)	1.06(2)
B(1)−B(7)	1.763(4)	B(6)−B(7)	1.811(4)
B(1)−B(5)	1.767(4)	B(6)−H(6)	1.08(2)
B(1)−H(1)	1.09(3)	B(6)−H(67)	1.28(2)
B(2)−B(3)	1.766(4)	B−B(6)	2.142(4)
B(2)−B(6)	1.742(4)	B(7)−B(8′)	1.982(6)
B(2)−B(7)	1.754(4)	B(7)−H(7)	1.06(2)
B(2)−B(5)	1.784(4)	B(7)−H(67)	1.20(2)

Angles			
C(22)−C(21)−C(22)#1	110.5(3)	B(3)−B(1)−H(1)	126(2)
C(22)−C(21)−B	110.6(2)	B(6)−B(2)−B(7)	62.4(2)
C(23)−C(22)−C(21)	116.0(2)	B(6)−B(2)−B(1)	108.6(2)
C(24)−C(23)−C(22)	115.7(2)	B(7)−B(2)−B(1)	108.1(2)
C(23)−C(24)−C(25)	116.3(2)	B(6)−B(2)−B(3)	109.8(2)
C(24)−C(25)−C(24)#1	114.6(3)	B(7)−B(2)−B(3)	59.4(2)
C(24)−C(25)−B	109.9(2)	B(1)−B(2)−B(3)	60.2(2)
C(24)#1-C(25)−B	109.9(2)	B(6)−B(2)−B(5)	57.3(2)
C(24)−C(25)−H(25)	107.4(2)	B(7)−B(2)−B(5)	105.1(2)
B(2)#1-B(1)−B(2)	112.2(3)	B(1)−B(2)−B(5)	59.8(2)
B(2)#1-B(1)−B(5)	111.6(3)	B(3)−B(2)−B(5)	105.6(2)
B(2)−B(1)−B(5)	60.7(2)	B(6)−B(2)−H(2)	121.6(12)
B(5)−B(1)−B(10′)	62.1(2)	B(7)−B(2)−H(2)	123.8(12)
B(2)−B(1)−B(3)	60.0(2)	B(1)−B(2)−H(2)	119.2(12)
B(5)−B(1)−B(3)	106.2(3)	B(3)−B(2)−H(2)	121.8(12)
B(2)−B(1)−H(1)	119.5(5)	B(5)−B(2)−H(2)	123.6(12)
B(5)−B(1)−H(1)	119.8(13)	B(7)−B(3)−B(8′)	69.2(3)
B(7)−B(3)−B(2)	59.9(2)	B(2)−B(6)−H(67)	98.8(11)
B(7)−B(3)−B(2)#1	116.1(3)	B(7)−B(6)−H(67)	41.5(10)
B(2)−B(3)−B(2)#1	111.8(3)	H(6)−B(6)−H(67)	112(2)
B(7)−B(3)−B(1)	108.2(3)	B(3)−B(7)−B(2)	60.7(2)
B(2)−B(3)−B(1)	59.8(2)	B(3)−B(7)−B(6)	107.7(2)
B(7)−B(3)−H(3)	113(2)	B(2)−B(7)−B(6)	58.5(2)
B(2)−B(3)−H(3)	120.7(5)	B(3)−B(7)−B(8′)	55.39(13)
B(1)−B(3)−H(3)	130(2)	B(2)−B(7)−B(8′)	105.61(14)
B(6)−B(5)−B(1)	110.7(2)	B(6)−B(7)−B(8′)	110.98(14)
B(6)−B(5)−B(2)	60.1(2)	B(3)−B(7)−H(7)	123.4(14)
B(1)−B(5)−B(2)	59.5(2)	B(2)−B(7)−H(7)	126.3(14)
B(6)−B(5)−B(10′)	115.48(14)	B(6)−B(7)−H(7)	122.5(14)
B(1)−B(5)−B(10′)	58.94(11)	B(8′)−B(7)−H(7)	118.6(13)
B(2)−B(5)−B(10′)	108.00(13)	B(3)−B(7)−H(67)	126.2(11)
B(6)−B(5)−B	73.4(2)	B(2)−B(7)−H(67)	101.5(11)
B(1)−B(5)−B	114.0(2)	B(6)−B(7)−H(67)	44.9(11)
B(2)−B(5)−B	121.0(2)	B(8′)−B(7)−H(67)	88.6(11)
B(10′)−B(5)−B	61.06(10)	H(7)−B(7)−H(67)	108(2)
B(6)−B(5)−H(5)	119.9(11)	C(25)−B−C(21)	101.0(3)
B(1)−B(5)−H(5)	117.8(11)	C(25)−B−B(5)	101.8(2)
B(2)−B(5)−H(5)	120.4(11)	C(21)−B−B(5)	142.7(2)
B(10′)−B(5)−H(5)	118.9(11)	B(10′)−B−B(5)	57.9(2)
B−B(5)−H(5)	113.1(12)	B(10′)−B−B(5)	57.9(2)
B(5)−B(6)−B(2)	62.6(2)	B(9′)−B−B(6)	99.9(2)
B(5)−B(6)−B(7)	106.6(2)	B(5)−B−B(6)	49.2(1)
B(2)−B(6)−B(7)	59.1(2)	B−B(5)−B(10′)	61.1(1)
B(5)−B(6)−H(6)	123.9(13)	B−B(5)−B(6)	73.4(2)
B(2)−B(6)−H(6)	125.3(12)	B−B(6)−B(5)	57.4(2)
B(7)−B(6)−H(6)	124.8(13)	B−B(6)−B(7)	108.5(2)
B(5)−B(6)−H(67)	121.2(10)	B(6)−B(7)−B(8′)	111.0(1)

^{a} B(8′) is generated from B(7) through the symmetry operation x, $−y + ^1/_2$, z; B(9′) is generated from B(6) through the symmetry operation x, $−y + ^1/_2$, z; B(10′) is generated from B(5) through the symmetry operation x, $−y + ^1/_2$, z.

is apparent about the B(BBN)−B(5) connection. Additional signals at $\delta = 13.6$ and 61.3 ppm are assigned to the methyl and methylene carbons of an Et$_2$O molecule. The intensities of the signals corresponding to the Et$_2$O molecule in both the ^{1}H and ^{13}C NMR spectra are not consistent with a ratio of 1:1 with the 9-BBN resonances. They are, in fact significantly less, which suggests that the ether molecule is not strongly coordinated to the boron hydride and is labile.

Conversion of 1 to [PSH][(9-BBN)B$_{10}$H$_{12}$], 3. When **1** is placed in CH$_2$Cl$_2$ with a molar excess of "Proton Sponge", the solution becomes deep orange and a light-yellow precipitate forms. The ^{11}B NMR spectrum reveals the presence of a small amount [B$_{10}$H$_{13}$]$^-$ and a new species **3,** which is sparingly soluble in CH$_2$Cl$_2$ and is the principal component of the precipitate. The new species was filtered out and extracted with CH$_2$Cl$_2$ to remove the small amount of PSH[B$_{10}$H$_{13}$]. Compound **3** is moderately soluble in THF and CH$_3$CN and is very soluble in DMF. Although indefinitely stable in the solid state under nitrogen, solutions of **3** that are exposed to air decompose after a short period of time.

Molecular Structure of [PSH][(9-BBN)B$_{10}$H$_{12}$], 3. Crystals of **3** were grown by slow evaporation of a DMF solution under vacuum at 0 °C. Crystallographic data is given in Table 1, and atomic coordinates and selected bond lengths and angles are listed in Tables 4 and 5. Two views of the structure of [(9-BBN)B$_{10}$H$_{12}$]$^-$ are displayed in Figure 5.

A crystallographically imposed mirror plane passes through the structure at atoms C(21), C(25), B(BBN), B(1), and B(3). The anion has a "nest"-type structure similar to that of the *nido*-[B$_{11}$H$_{14}$]$^-$ anion with the B(BBN) boron of the 9-BBN approximately occupying a vertex site of the pentagonal face of the *nido*-B$_{11}$ cluster. It is not fully accommodated in the formation of the *nido*-[B$_{11}$H$_{14}$]$^-$ analogue. It resides 0.247 Å above the least-squares plane of the face. In the formation of **3**, upon removal of a bridge proton from the B$_{10}$H$_{13}$ component, the 9-BBN unit of **1** moves from a postition that bridges B(5)−B(6) to a position between B(5) and B(10′), boron atoms related by the crystallographic mirror plane. The distances B(5)−B(10′) (1.823(5) Å), B(BBN)−B(5)/B(BBN)−B(10′) (1.884(4) Å), and B(5)−B(6)/B(10′)−B(9′) (1.6942(4) Å) are normal boron−boron distances. However, the distances for B(BBN)−B(6)/

B(BBN)−B(9′), 2.142(4) Å, are abnormally long, which suggests weak interactions with B(BBN) and B(6)/B(9′). NMR spectra in solution indicate weak coupling between B(BBN) and B(6)/B(9′). Examination of the short intramolecular nonbonded
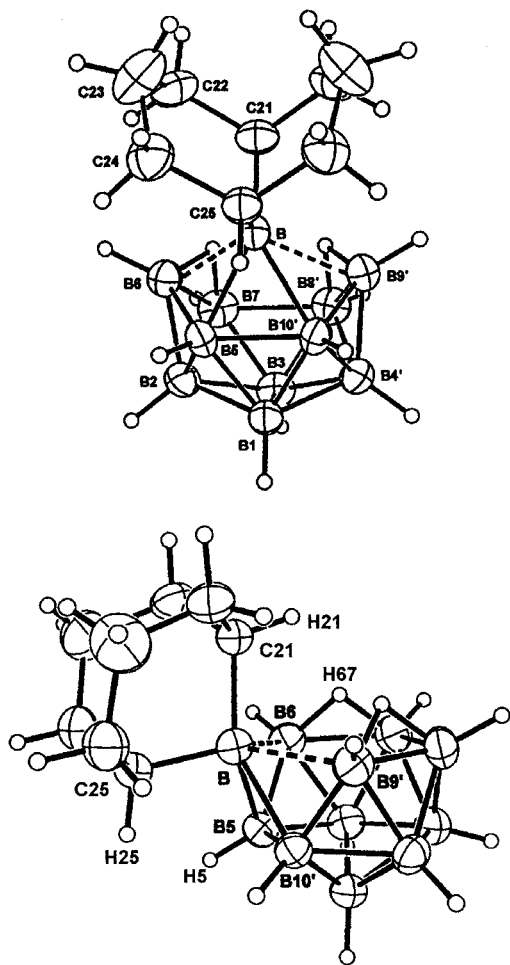
Figure 5. Molecular structure of [(9-BBN)B₁₀H₁₂]⁻, **3**.

Figure 6. ^{11}B and ^{11}B{^{1}H} NMR spectra of [PSH][(9-BBN)B$_{10}$H$_{12}$], **3**, in DMF-d_7 at 96.3 MHz.

Figure 7. ^{11}B–^{11}B COSY NMR spectrum ($t_1 \times t_2 = 128 \times 256$ words) of [PSH][(9-BBN)B$_{10}$H$_{12}$], **3**, in DMF-d_7 at 80.2 MHz. The ^{1}H-decoupled 1-D spectrum is plotted on F$_1$ and F$_2$ to aid in identifying resonances along the diagonal and interpreting cross-peaks in the 2-D array.

contacts suggests that there is a steric effect that effectively "locks" the 9-BBN unit into its observed position and prevents the boron atom of that unit from moving closer to the B(6)/ B(9′) boron atoms. The nonbonded contacts and their mirror equivalents, H(25)- - -H(5) (2.32(4) Å), C(25)- - -B(5) (2.739(4) Å), and C(25)- - -H(5) (2.73(2) Å), inhibit the 9-BBN unit from pivoting away from the open face of the B$_{10}$ cluster, while the nonbonded contacts and their mirror equivalents, H(21)- - -H(67) (1.98(4) Å), C(21)- - -B(6) (2.813(4) Å), and C(21)- - -H(67) (2.50(2) Å), inhibit the 9-BBN unit from moving closer to the B6, B9′ boron atoms. In essence, the 9-BBN unit resides on the mirror plane of the structure and is "nestled" between the atoms cited above and their mirror equivalents.

NMR Spectroscopic Studies of PSH[BBNB$_{10}$H$_{12}$], 3. The ^{11}B NMR spectrum of **3** in DMF consists of six doublets and a singlet (Figure 6).

This spectrum is consistent with the mirror symmetry of [9-BBNB$_{10}$H$_{12}$]⁻ observed in the solid state (Figure 5). This spectrum is similar to those of the related isoelectronic complexes Me$_2$EB$_{10}$H$_{12}$ (E = Si, Ge, Sn) and [Me$_2$EB$_{10}$H$_{12}$]⁻ (E = In, Tl) reported by Norman[5,6] and Greenwood.[13,14]

The ^{11}B–^{11}B COSY NMR spectrum supports the structure (Figure 7).

No cross-coupling is observed between the B(6,9) and B(7,8) signals, which is to be expected since bridging hydrogens span those boron atoms in the solid-state structure. This arrangement has been proposed for the Me$_2$EB$_{10}$H$_{12}$ derivatives[5,6] and is confirmed in [HCB$_{10}$H$_{12}$]⁻ and [Me-SiB$_{10}$H$_{12}$]⁻.[26,27] While the 9-BBN boron of **3** shows strong coupling to the B(5,10) atoms,

coupling to the B(6,9) atoms is very weak, being detectable only with careful adjustment of the COSY parameters. This is consistent with the fact that the distance between these sites (2.142(4) Å) is considerably greater than in a typical *nido*-undecaborane cluster. However, the ^{11}B NMR chemical shift of the 9-BBN boron (+11.7 ppm) is consistent with its being in a cluster environment, while a trigonally coordinated boron atom in a bridging environment would be expected to resonate much farther downfield (e.g. +103 ppm for the 9-BBN boron in 2,3-μ-B$_5$H$_8$).[27]

Summary and Conclusions

The 9-BBN⁺ synthon binds to the *nido*-B$_{10}$ cluster in three types of interactions not previously observed between a monoborane and a *nido*-B$_{10}$ cluster. (1) The boron of the 9-BBN⁺ unit is partially inserted between the B(5) abd B(6) atoms to form an highly asymmetric bridge. It also is involved in an *agostic* interaction with the terminal H(5b) in its reaction with [B$_{10}$H$_{13}$]⁺ to form (9-BBN)B$_{10}$H$_{13}$, **1**. (2) When **1** is placed in Et$_2$O, an Et$_2$O molecule apparently coordinates to the boron of 9-BBN causing it to move to a terminal position on B(5) and end its *agostic* interaction with H(5b). Treatment of **1** with

"Proton Sponge" results in deprotonation of the complex to give [PSH][(9-BBN)B$_{10}$H$_{13}$], **3**. In this complex, an analogue of *nido*-[B$_{11}$H$_{14}$]$^-$, the boron of the 9-BBN is not fully incorporated as a component of a *nido*-B$_{11}$ cluster. It occupies an approximate vertex site on the pentagonal face of the *nido*-B$_{11}$ cluster. Compounds **1** and **3** are considered to represent analogues of *meta*-stable intermediates in the stepwise insertion of a monoborane moiety into a *nido*-decaborane cluster. Their structures provide the most detailed picture to date of the adjustments (movements) that can occur during the insertion process.

Experimental Section

Apparatus. All manipulations were conducted under high vacuum or in a glovebox in an atmosphere of dry, oxygen-free nitrogen. ^{11}B NMR spectra were obtained on either a Brucker AM-500 or a Brucker AM-250 spectrometer operating at 160.4 or 80.2 MHz, respectively. ^{1}H NMR spectra were obtained on a Brucker MSL-300 spectrometer operating at 300.1 MHz and equipped with an external ^{11}B synthesizer operating at 96.3 MHz. ^{13}C NMR spectra were obtained on a Brucker AM-250 spectrometer operating at 62.5 MHz. ^{11}B NMR chemical shifts are referenced to BF$_3$·OEt$_2$ with positive values downfield. NMR spectra were observed at ambient temperature unless otherwise noted.

Materials. All solvents were dried using standard procedures and distilled into vacuum bulbs prior to use. Na[B$_{10}$H$_{13}$] was prepared in the usual manner from NaH and B$_{10}$H$_{14}$ in Et$_2$O. 9-Br-BBN (1 M solution in CH$_2$Cl$_2$) and the Proton Sponge [1,8-bis(dimethylamino)-naphthalene] were purchased from Aldrich Chemical Co. and used as received.

Preparation of (9-BBN)B$_{10}$H$_{13}$, 1. Na[B$_{10}$H$_{13}$], 0.930 g (6.46 mmol), was placed in a vacuum reactor equipped with a side port and affixed to a vacuum extractor with receiver flask. The system was evacuated and kept under vacuum for 1 day to remove traces of Et$_2$O. Then, 75 mL of CH$_2$Cl$_2$ was condensed into the flask and allowed to warm to room temperature to form a suspension. The system was cooled to −196 °C, and under N$_2$ flow, 7.0 mL of a 1 M solution of Br-9-BBN in CH$_2$Cl$_2$ was injected onto the frozen slug. The system was resealed, evacuated, warmed to room temperature, and stirred vigorously overnight. The next day the CH$_2$Cl$_2$ was removed and replaced with 150 mL of hexanes. The residue was stirred briskly for 2 h and then filtered to leave a yellow-white solid. Extraction of this solid several times with hexanes followed by removal of the solvent from the filtrate gave 1.463 g of bright-yellow product (93.8%). ^{11}B NMR (hexanes): +53.1 s (-) [1B]; +13.2 d (167) [1B]; +11.8 d (195) [1B]; +10.4 d (85) [1B]; +9.5 d (166) [1B]; +6.2 d (147) [1B]; +3.0 d (160) [1B]; +1.2 d (156) [1B]; −6.4 d (151) [1B]; −31.0 d (154) [1B]; −37.6 d (154) [1B]. ^{13}C{^{1}H}NMR (CD$_2$Cl$_2$, −50 °C): 36.2 [1C]; 34.9 [1C]; 33.2 [1C]; 33.2 [1C]; 32.0 [1C]; 30.0 [1C]; 23.3 [1C]; 23.0 [1C]. ^{1}H{^{11}B}NMR (CD$_2$Cl$_2$)data are as follows. BBN: +2.15 mult. [2H]; +2.07 br. [4H]; +1.92 br.[2H]; +1.81 br. [2H]; +1.56 br. [1H]; +1.53 br. [2H]; +1.39 br. [1H]; +1.19 br. [1H]. BH: +4.38 [1H]; +3.88 [1H]; +3.73 q (9) [1H]; +3.26 [2H]; +3.10 [1H]; +3.02 [1H]; +2.47 [1H]; +0.77 br. [1H]; +0.63 br. [1H]; −1.80 [1H]; −2.85 [1H]; −3.83 [1H].

Conversion of (9-BBN)B$_{10}$H$_{13}$, 1, to (Et$_2$O)(9-BBN)B$_{10}$H$_{13}$, 2. When **1**, 0.239 g (0.988 mmol), was left in contact with 15 mL of

Et$_2$O overnight in a vacuum, conversion to **2** occurred. The next day the Et$_2$O was removed under vacuum and the residue was dissolved in benzene. The solution was transferred to a microdistillation apparatus, the benzene removed, and the residue sublimed under vacuum to give 0.207 g of product in a 62.9% yield. ^{11}B NMR (C$_6$D$_6$): +56.3 s (-) [1B]; +16.9 s (−) [1B]; +12.7 d (148) [1B] +10.8 d (155) [1B]; +7.9 d (163) [1B]; +2.6 d (174) [1B]; −2.3 d (155) [2B]; −35.9 d (153) [1B]; −36.1 d (155) [1B]. ^{13}C NMR (C$_6$D$_6$): 33.5 [4C]; 23.6 [2C] (Et$_2$O (resid.): +61.3 [2C]; +13.6 [2C]). ^{1}H{^{11}B} NMR (C$_6$D$_6$; BBN): +1.83 mult. [8H]; +1.39 mult. [2H] +1.04 mult. [4H].

Preparation of [PSH][(9-BBN)B$_{10}$H$_{12}$], 3. A portion of **1**, 0.318 g (1.31 mmol), was charged to a vacuum reactor equipped with a sidearm tipper tube and a vacuum extractor system. The tipper-tube was loaded with 0.574 g (2.68 mmol) of Proton Sponge. The system was evacuated, and about 20 mL of CH$_2$Cl$_2$ was condensed into the flask. The reactor was warmed to room temperature, and the Proton Sponge was tipped into the solution. A deep-orange color developed, and a light-yellow precipitate formed after 5 min. The reaction was stirred briskly overnight. The next day the system was filtered and the precipitate was extracted several times with CH$_2$Cl$_2$ to give 0.426 g of PSH[η^4-6,5,10,9-(BBN)-B$_{10}$H$_{12}$] in a 75.3% yield. ^{11}B NMR (DCON-(CD$_3$)$_2$): +17.1 d (143) [2B]; +11.7 s (-) [1B]; +5.4 d (137) [2B]; +2.8 d (129) [1B]; −2.4 d (137) [2B]; −8.6 d (141) [2B]; −28.9 d (137) [2B]. ^{13}C{^{1}H}NMR (DCON(CD$_3$)$_2$) data are as follows. PSH$^+$: 145.3 [2C]; 135.6 [1C]; 129.3 [2C]; 127.3 [2C]; 122.1 [2C]; 119.7 [1C]; 46.0 [4C]. BBN: 40.1 [2C]; 39.3 [2C]; 31.0 [2C]; 24.5 [2C].

X-ray Crystal Structure Determination of 1 and 3. Crystals of suitable size were mounted in glass capillaries and sealed under nitrogen. The crystallographic data were collected on an Enraf-Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation. Unit cell parameters were obtained by a least-squares refinement of the angular settings from 25 reflections, well distributed in reciprocal space and lying in a 2θ range of 24−30°. All reflection data were corrected for Lorentz and polarization effects.

The structure of **1** was solved by the direct methods MULTAN 11/82 and difference Fourier synthesis with analytical atomic scattering factors used throughout the structure refinement with both the real and imaginary components of the anomalous dispersion included for all non-hydrogen atoms using MolEN[39] on a DEC Vax Station 3100 computer. The molecular structure of **3** was solved by SHELXTL[40] on a Compaq computer. Full-matrix least-squares refinements were employed. After all of the non-hydrogen atoms were located and refined; hydrogen atoms were located from the difference map. All hydrogen atoms were refined isotropically, and all non-hydrogen atoms were refined anisotropically.

Supporting Information Available: Tables of crystallographic data, positional and *B* parameters, completed bond lengths and bond angles, and anisotropic thermal parameters (14 pages). Ordering information is given on any current masthead page.

IC980171T

(39) MOLEN Crystal Structure Analysis Program, Enraf-Nonius, 1990.
(40) SHELXTL (version 5), Siemens Energy & Automation, Inc., 1994.