Articles

Dicarbaheteroborane Chemistry. Representatives of Two Eleven-Vertex Dicarbaazaundecaborane Families: *nido*-10,7,8-$NC_2B_8H_{11}$, Its N-Substituted Derivatives, and *arachno*-1,8,11-$NC_2B_8H_{13}$

Jaromír Plešek,[†] Bohumil Štíbr,*,[†] Drahomír Hnyk,[†] Tomáš Jelínek,[†] Stanislav Heřmánek,[†] John D. Kennedy,[‡] Matthias Hofmann,[§] and Paul v. R. Schleyer[§]

Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic, 250 68 Řež,
The Czech Republic, School of Chemistry, University of Leeds, Leeds LS2 9JT, England, and Computer
Chemistry Center, Institute of Organic Chemistry, University Erlangen−Nürnberg, Nägelbachstrasse 25,
D-91052 Erlangen, Germany

Received December 4, 1997

Treatment of an acidified solution of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion ($\mathbf{1}^-$) with $NaNO_2$ at 0 °C in the presence of benzene resulted in the formation of two eleven-vertex azadicarbaboranes, *nido*-10,7,8-$NC_2B_8H_{11}$ (**2**) and *arachno*-1,8,11-$NC_2B_8H_{13}$ (**3**), isolated in yields of 15 and 35%, respectively, together with a small amount (0.9%) of 5-Ph-*nido*-7,8,10-$C_2NB_8H_{10}$ (5-Ph-**2**). Compound **3** was converted in 68% yield into **2** by reaction with PS (PS = “proton sponge”; 1,8-(dimethylamino)naphthalene and acetone. Deprotonation of **2** at the N(10)H vertex gave the [*nido*-10,7,8-$NC_2B_8H_{10}$]$^-$ anion ($\mathbf{2}^-$), which was easily alkylated with Me_2SO_4 or $PhCH_2Br$ to produce the N-alkylated derivatives of **2**, 10-R-*nido*-10,7,8-$NC_2B_8H_{10}$, where R = Me (10-Me-**2**, 86%) and $PhCH_2$ (10-$PhCH_2$-**2**, 69%). The geometries of the parent dicarbazaboranes **2** and **3** were optimized at the MP2(fc)/6-31G* level, and the structures of all compounds were thence confirmed by the excellent agreement between experimental data and IGLO/NMR calculations of the ^{11}B chemical shifts for the parent compounds at the DZ//6-31G*, DZ//MP2/6-31G*, and II′//MP2/6-31G* levels.

Introduction

There is burgeoning current interest and activity in the chemistry of eleven-vertex borane-cluster compounds that contain three main-group heteroatoms within the cluster structure. All the nido compounds of this family that have been reported so far adopt the classical eleven-vertex nido cluster geometry **I**, which is formally derived by the removal of one vertex from the twelve-vertex closo icosahedron (see Scheme 1, upper part).[1] All these nido compounds have the three heteroatoms in the open face of the cage. Of the two possible isomeric arrangements for this, the 7,8,9-configuration has been very recently established for the “tricarbollide” anion [7,8,9-$C_3B_8H_{11}$]$^-$ for the neutral tricarbaborane 7,8,9-$C_3B_8H_{12}$, and for several of their derivatives,[2] and it has also been proposed for the neutral diarsaheteroboranes 7,8,9-$As_2EB_8H_8$ (where E = S, Se).[3] The alternative 7,8,10-configuration is adopted by the tricarbollide anion [7,8,10-$C_3B_8H_{11}$]$^-$ and its derivatives,[2c−f] and by dicarbaheteroboranes of general formulation 10,7,8-$EC_2B_8H_{10}$ (where E = NH,[4] S,[5,6] Se[7]).

A more complex structural situation can arise in the eleven-vertex *arachno* family, for which three different cluster configurations have been established (general structures **II**, **III**, and **IV** in Scheme 1). Each of these is derived from the thirteen-

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* Corresponding author.

[†] Academy of Sciences of the Czech Republic.

[‡] University of Leeds.

[§] University of Erlangen.

(1) For electron count and structural pattern recognition see, for example: (a) Wade, K. *J. Chem. Soc., Chem. Commun.* **1971**, 792−793. (b) Wade, K. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 1. (c) Wade, K.; O’Neill, M. E. *Compr. Organomet. Chem.* **1987**, *1*, 25. (d) Williams, R. E. *Inorg. Chem.* **1971**, *10*, 210. (e) Rudolph, R. W.; Pretzer, W. R. *Inorg. Chem.* **1972**, *11*, 1974. (f) Wade, K. *Chem. Br.* **1975**, *11*, 177. (g) Williams, R. E. *Adv. Inorg. Chem. Radiochem.* **1976**, *18*, 67. (h) Rudolph, R. W. *Acc. Chem. Res.* **1976**, *9*, 446. (i) Williams, R. E. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; pp 11−93. (j) Wade, K.; O’Neill, M. E. In *Metal Interactions with Boron Hydrides*; Grimes, R. N., Ed; Plenum: New York, 1982; Chapter 1, pp 1−41. (k) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177.

(2) Štíbr, B.; Holub, J.; Teixidor, F.; Viñas, C. *J. Chem. Soc., Chem. Commun.* **1995**, 795. (b) Štíbr, B.; Holub, J.; Císařová, I.; Teixidor, F.; Viñas, C.; Fusek, J., Plzák, Z. *Inorg. Chem.* **1996**, *35*, 3635. (c) Štíbr, B.; Holub, J.; Císařová I.; Teixidor, F.; Viñas C. *Inorg. Chim. Acta* **1996**, *245*, 129. (d) Rousseau R.; Canadell, E.; Lee, S.; Teixidor, F.; Viñas, C.; Štíbr, B. *New J. Chem.* **1996**, *20*, 277−281. (e) Holub, J.; Štíbr, B.; Hnyk, D.; Fusek, J.; Císařová, I.; Teixidor, F.; Viñas, C.; Plzák, Z.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1997**, *119*, 7750. (f) Shedlow, A. M.; Carroll, P. J.; Sneddon, L. G. *Organometallics* **1995**, *14*, 4046−4047.

(3) Siedle, A. R.; Todd, L. J. *J. Chem. Soc. Chem. Commun.* **1973**, 914. (b) Barriola, A. M.; Hanusa, T. P.; Todd, L. J. *Inorg. Chem.* **1980**, *19*, 2801.

(4) Plešek, J.; Štíbr, B.; Heřmánek S. *Chem. Ind. (London)* **1974**, 662.

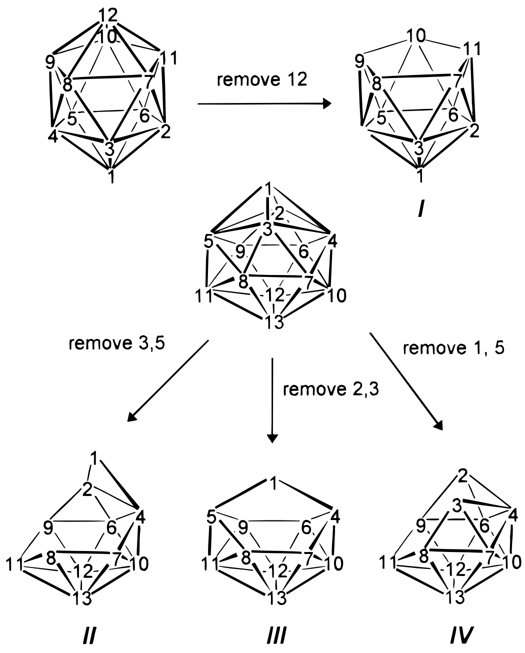
(5) Brattsev, V. A.; Knyazev, S. P.; Danilova, G. N.; Stanko, V. I. *Zh. Obshch. Khim.* **1975**, *45*, 1393.

(6) Hnyk, D.; Hofmann, M.; Schleyer, P. v. R.; Bühl, M.; Rankin, D. W. H. *J. Phys. Chem.* **1996**, *100*, 3435.

(7) Baše, K.; Štíbr, B. *Chem. Ind. (London)* **1977**, 919.

S0020-1669(97)01526-7 CCC: $15.00

Scheme 1



vertex closed deltahedron by the removal of two vertexes. For convenience of comparison in this present paper, these are numbered[8] based on the debor system and the numbering of the thirteen-vertex closed deltahedron as depicted in Scheme 1. Of these, the a,b edge-bridged structure **II** has been proposed for the dicarbaazaborane1,8,11-$NC_2B_8H_{13}$[4] whereas the a,d face-bridged structure **III** has been suggested for the syn and anti isomers of 1-Bu^t-1,6,9-$NC_2B_8H_{12}$ (numbering as in Scheme 1).[9] As far as we are aware, no triheteroborane of structure **IV** has been reported to date although this cluster geometry has definitively been established for the [2,3-$S_2B_9H_{10}$]$^-$ dithiaborane anion.[10] No triheteroborane, or indeed any other compound, of an eleven-vertex hypho type has been reported.

Here we now report full experimental details of the synthesis of the two eleven-vertex azadicarbaboranes, *nido*-10,7,8-$NC_2B_8H_{11}$ and *arachno*-1,8,11-$NC_2B_8H_{13}$, together with an investigation of some of their further chemistry. Preliminary aspects of some of the work were reported some time ago.[4] The work is now complemented by unambiguous NMR assignments, and wave-mechanical ab initio MP2(fc)/6-31G* geometry optimizations of the parent (i.e. unsubstituted) compounds, these two approaches being correlated by an excellent agreement between the experimental data and IGLO/NMR calculations of the ^{11}B chemical shifts for these parent compounds at the DZ//6-31G*, DZ//MP2/6-31G*, and II′//MP2/6-31G* levels.

Experimental Section

General Procedures. All reactions were carried out with use of standard vacuum or inert-atmosphere techniques, for example as summarized by Shriver,[11] although some operations, such as preparative TLC and column chromatography, were carried out in air. A solution of the starting anion $\mathbf{1}^-$ was prepared as reported previously.[12] 1,2-dimethoxyethane (glyme) was dried over Na/benzophenone, benzene, hexane, and CH_2Cl_2 over CaH_2, and all were freshly distilled before use. Other substances were of reagent or analytical grade and were used as purchased. Preparative TLC was carried out using silica gel G (Aldrich, type 254 nm) as the stationary phase on layers of dimensions 200 × 200 × 1 mm, made on glass plates from aqueous slurries followed by drying in air at 80 °C, and column (2.5 × 30 cm) chromatography was carried out on silica gel (Aldrich 200−400 mesh). The purity of individual chromatographic fractions was checked by analytical TLC on Silufol (Kavalier, silica gel on aluminum foil; detection by diiodine vapor, followed by 2% aqueous $AgNO_3$ spray). Melting points were measured in sealed capillaries under nitrogen and are uncorrected. Low-resolution mass spectra (70 eV, EI ionization) were obtained using a Finnigan MAT MAGNUM ion-trap quadrupole mass spectrometer equipped with a heated-inlet option, as developed by Spectronex AG (Basle, Switzerland). Proton (^1H) and boron (^{11}B) NMR spectroscopy was performed at 9.40 and 11.75 T on Bruker AM400 and Varian XL-500 instruments, respectively. The [$^{11}B-^{11}B$]-COSY,[13] [$^1H-^1H$]COSY,[14] and $^1H\{^{11}B(\text{selective})\}$[15] NMR experiments were essentially as described in other papers from our laboratories.[16] Chemical shifts δ are given in ppm to high-frequency (low-field) of Ξ = 32.083 971 MHz (nominally $F_3B \cdot OEt_2$ in $CDCl_3$) for ^{11}B (quoted ±0.5 ppm) and Ξ = 100 MHz ($SiMe_4$) for ^1H (quoted ±0.05 ppm), Ξ being defined as in ref 17. Solvent resonances were used as internal secondary standards. Coupling constants $^1J(^{11}B-^1H)$ are taken from resolution-enhanced ^{11}B spectra with digital resolution 8 Hz and are given in Hz. IR spectra were obtained on an EU 9512 Pye-Unicam Fourier transform spectrometer. Elemental analyses were performed at the Analytical Laboratory of the Institute of Inorganic Chemistry of the Academy of Sciences of the Czech Republic.

***nido*-10,7,8-$NC_2B_8H_{11}$ (2), 5-Ph-*nido*-7,8,10-$C_2NB_8H_{10}$ (5-Ph-2), and *arachno*-1,8,11-$NC_2B_8H_{13}$ (3).** A 1 M aqueous solution of K^+[*nido*-7,8-$C_2B_9H_{12}$]$^-$ ($\mathbf{1}^-$) (25 mL, 25 mmol) was diluted with 25 mL of water and acidified with 15 mL of concentrated hydrochloric acid. After 50 mL of benzene had been added, the mixture was treated dropwise with 1.0 M aqueous $NaNO_2$ (30 mL, 30 mmol) under intensive stirring and cooling to ~0 °C. The stirring was continued for 2 h, and the organic layer was separated, dried with $MgSO_4$, filtered, and evaporated to dryness. The residue was separated by column chromatography in 50% CH_2Cl_2−hexane (1:1) to collect four fractions of R_f (anal.; benzene−hexane 1:2) ~0.6 (A), 0.25 (B), 0.20 (C), and 0.03 (D).

Fraction A was further purified by preparative TLC in hexane (R_f = 0.15) to isolate 31 mg (1%) of *nido*-5,6-$C_2B_8H_{12}$, which was identified by NMR spectroscopy.[18c]

Fraction B was evaporated to dryness, and the solid residue was sublimed in vacuo at ~50 °C (bath) to obtain a white, crystalline sublimate (509 mg, 15%), which was identified as *nido*-10,7,8-$NC_2B_8H_{11}$ (**2**). For **2**: mp 178 °C. IR (KBr) 3348 (s), 3064 (w), 2912 (w), 2592 (s), 1274 (m), 1198 (m), 1124 (m), 1106 (m), 1048 (m), 1032 (sh), 994 (m), 950 (m), 936 (m), 888 (w), 858 (w), 810 (w), 776 (w), 762 (sh), 740 (w), 716 (w), 702 (w), 686 (w), 558 (w), 516 (w), 474 (w), 396 (w) cm^{-1}. Anal. Found: C, 17.22; H, 8.05. Calcd: C, 17.70; H, 8.17. MS in *m*/*z* (relative intensity (%) and assignment in parentheses): found 137 (25, [M]$^+$), 135 (100, [M]$^+$ − 2H).

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(8) For numbering see: Casey, J. B.; Evans, W. J.; Powell, W. H. *Inorg. Chem.* **1981**, *20*, 1333.

(9) Janoušek, Z.; Fusek, J.; Štíbr, B. *J. Chem. Soc., Dalton Trans.* **1992**, 2649.

(10) Holub, J.; Wille, A. E.; Štíbr, B.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **1994**, *33*, 4920.

(11) Shriver, D. F.; Drezdon, M. A. *Manipulation of Air-Sensitive Compounds*, 2nd ed.; Wiley: New York, 1986.

(12) Plešek, J.; Heřmánek, S.; Štíbr, B. *Inorg. Synth.* **1983**, *22*, 231.

(13) Hutton, W. C.; Venable, T. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1984**, *106*, 29.

(14) Fontaine, X. L. R.; Kennedy, J. D. *J. Chem. Soc., Chem. Commun.* **1986**, 779.

(15) Fontaine, X. L. R.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1987**, 1573.

(16) See, for example: Plešek J.; Štíbr, B.; Fontaine, X. L. R.; Kennedy, J. D.; Heřmánek, S.; Jelínek, T. *Collect. Czech. Chem. Commun.* **1991**, *56*, 1618.

(17) McFarlane, W. *Proc. R. Soc. London, Ser. A* **1968**, *306*, 185.

(18) Plešek, J.; Heřmánek, S. *Chem. Ind. (London)* **1971**, 267. (b) Plešek, J.; Heřmánek, S. *Collect. Czech. Chem. Commun*. **1974**, *39*, 821. (c) Štíbr, B.; Heřmánek, S.; Janoušek, Z.; Dolanský, J.; Plzák, Z.; Plešek, J. *Polyhedron* **1982**, *1*, 822. (d) Štíbr, B.; Holub, J.; Jelínek, T.; Grüner, B.; Fusek, J.; Plzák, Z.; Teixidor, F.; Viñas, C.; Kennedy, J. D. *Collect. Czech. Chem. Commun*. **1997**, *62*, 1229.

Fraction C was repurified by preparative TLC in CH_2Cl_2−hexane (1:3) to collect the main fraction of R_f 0.25, from which 5-Ph-*nido*-10,7,8-$NC_2B_8H_{10}$ (5-Ph-**2**; 50 mg, 0.9%), was isolated by evaporation and vacuum sublimation at ∼90 °C (bath) as a white solid. Anal. Found for 5-Ph-**2**: C, 45.82; H, 6.95. Calcd: C, 45.37; H, 7.13. MS in *m*/*z* (relative intensity (%) and assignment in parentheses): found 213 (22, $[M]^+$), 211 (100, $[M]^+ - 2H$).

Fraction D was evaporated to dryness, and the residual solid was crystallized from benzene to give a white crystalline solid, which was identified as *arachno*-1,8,11-$NC_2B_8H_{13}$ **(**compound **3**, 1204 mg, 35%). For **3**: mp 147−148 °C (decomp). IR (KBr) 3512 (br), 3352 (s), 3288 (s), 2612 (m), 2568 (sh), 2532 (s), 1550 (m), 1522 (sh), 1442 (br), 1300 (w), 1212 (w), 1128 (s), 1092 (m), 1032 (s), 1014 (s), 994 (sh), 918 (m), 894 (m), 874 (w), 852 (m), 794 (w), 756 (m), 736 (m), 708 (w), 662 (w), 462 (w) cm^{-1}. Anal. Found: C, 17.12; H, 8.92. Calcd: C, 17.44; H, 9.52. MS in *m*/*z* (relative intensity (%) and assignment in parentheses): found 139 (12, $[M]^+$), 137 (100, $[M]^+ -$ 2H).

***nido*-10,7,8-$NC_2B_8H_{11}$ (2) from *arachno*-1,8,11-$NC_2B_8H_{13}$ (3).** A solution of compound **3** (400 mg, 2.88 mmol) in 30 mL of CH_2Cl_2 was treated with PS (675 mg, 3 mmol), and the mixture was heated at reflux under stirring for 2 h. After it had cooled to ambient temperature, 1.5 mL of acetone was added and the mixture was left to stand for 12 h. The volatiles were evaporated, the oily residue dissolved in 20 mL of CH_2Cl_2, and the resulting solution treated dropwise with 20 mL of 5% aqueous hydrochloric acid under shaking and cooling. The CH_2Cl_2 layer was separated, reduced in volume, dried with $MgSO_4$, and placed onto a silica gel column. Development with CH_2Cl_2−hexane (1:3) led to the isolation of the main fraction of R_f (anal.; benzene−hexane 1:2) ∼0.25, from which *nido*-10,7,8-$NC_2B_8H_{11}$ (**2**; 270 mg, 68%) was isolated as in the preceding experiment.

$[NMe_4]^+$[*nido*-10,7,8-$NC_2B_8H_{10}$]$^-$ (2^-). Compound **2** (100 mg, 0.73 mmol) was dissolved in 10 mL of hexane, and the solution was treated with 20 mL of water and 10 mL of 1 M NMe_4OH under stirring for 1 h to precipitate a white, crystalline solid. This was isolated by filtration and dried in vacuo at ambient temperature for 12 h to give 139 mg (91%) of $[NMe_4]^+$[*nido*-10,7,8-$NC_2B_8H_{10}$]$^-$ ($\mathbf{2}^-$). For $\mathbf{2}^-$: IR (KBr) 3416 (br), 3260 (br), 2596 (s), 1618 (sh), 1484 (sh), 1402 (s), 1308 (s), 1152 (m), 1114 (m), 1068 (m), 1022 (m), 948 (sh), 916 (s), 772 (m), 708 (m), 472 (m) cm^{-1}. Anal. Found: C, 34.10; H, 9.81. Calcd: C, 34.52; H, 10.62.

Solution of Na^+[*nido*-10,7,8-$NC_2B_8H_{10}$]$^-$ (2^-). Compound **2** (100 mg, 0.73 mmol) was dissolved in 20 mL of glyme, and the solution was treated with NaH (∼60 mg of a 60% mineral oil dispersion, corresponding to ∼1.5 mmol) under stirring and cooling. The mixture was filtered using a Schlenk apparatus to obtain a solution of anion $\mathbf{2}^-$ which was used for the further syntheses below.

10-Me-*nido*-10,7,8-$NC_2B_8H_{10}$ (10-Me-2). A solution of anion $\mathbf{2}^-$ from the preceding experiment was treated with Me_2SO_4 (300 mg, 2.4 mmol), and the mixture was stirred at ambient temperature for 12 h and then filtered. The filtrate was evaporated, and the residual oil separated on a silica gel column using hexane as mobile phase. The fraction of R_f (anal.) 0.39 was collected and subjected to further purification by preparative TLC in hexane. The main fraction of R_f (prep.) ∼0.5 was removed by extraction with CH_2Cl_2, the CH_2Cl_2 evaporated, and the residue sublimed in vacuo at ∼90 °C (bath) to isolate 10-Me-*nido*-10,7,8-$NC_2B_8H_{10}$ (10-Me-**2**) as a white solid (95 mg, 86%). For 10-Me-**2**: mp 121−123 °C. IR (KBr) 3408 (br), 3064 (w), 3008 (w), 2956 (m), 2920 (sh), 2592 (s), 1456 (m), 1424 (sh), 1374 (w), 1264 (w), 1168 (s), 1132 (sh), 1096 (w), 1044 (m), 992 (w), 960 (m), 944 (m), 926 (sh), 914 (m), 894 (w), 864 (m), 782 (w), 756 (w), 742 (w), 514 (sh), 492 (w) cm^{-1}. Anal. Found: C, 24.92; H, 8.33. Calcd: C, 24.07; H, 8.75. MS in *m*/*z* (relative intensity (%) and assignment in parentheses): found 151 (25, $[M]^+$), 149 (100, $[M]^+ - 2H$).

10-$PhCH_2$-*nido*-10,7,8-$NC_2B_8H_{10}$ (10-$PhCH_2$-2). A glyme solution of anion $\mathbf{2}^-$ (see above) was treated with $PhCH_2Br$ (300 mg, 1.75 mmol), and the mixture was stirred at ambient temperature for 12 h and then filtered. The filtrate was evaporated and the residual oil separated on a silica gel column using hexane as mobile phase. The fraction of R_f (anal.) 0.22 was collected and subjected to further purification by preparative TLC in hexane. The main fraction of R_f (prep.) ∼0.35 was removed by extraction with CH_2Cl_2 and evaporated, and the residue was distilled in vacuo at ∼130 °C (bath) to isolate 10-$PhCH_2$-*nido*-10,7,8-$NC_2B_8H_{10}$ (10-$PhCH_2$-**2**) as a viscous liquid which solidified to give a white solid (115 mg, 69%). For 10-$PhCH_2$-**2**: mp 58−59 °C, bp ∼110 °C/10^{-2} Torr. IR (KBr) 3416 (br), 3056 (w), 3028 (w), 2584 (s), 2548 (sh), 1602 (w), 1490 (w), 1438 (m), 1366 (m), 1284 (w), 1272 (sh), 1204 (m), 1138 (s), 1126 (sh), 1042 (w), 1026 (m), 990 (w), 960 (m), 940 (m), 916 (m), 894 (m), 862 (m), 816 (w), 786 (w), 754 (w), 730 (s), 694 (s), 630 (w), 534 (w), 516 (w), 484 (w) cm^{-1}. Anal. Found: C, 48.12; H, 7.32. Calcd: C, 47.87; H, 7.59. MS in *m*/*z* (relative intensity (%) and assignment in parentheses): found 227 (50, $[M]^+$), 226 (100, $[M]^+ - H$).

Computational Methods. The geometries of compounds **2** and **3** were fully optimized to C_s symmetry using standard ab initio methods[19] beginning at the SCF level with the 3-21G and 6-31G* basis sets. The 6-31G* frequency calculations confirmed the structures to be energy minima on their respective potential hypersurfaces. The final optimization employed second-order Møller−Plesset (MP2) perturbation theory in the frozen-core approximation [denoted as MP2(fc)/6-31G*] with fc omitted in the following for simplicity. All calculations were carried out on a Cray YMP-8 computer using Gaussian 94.[20] Chemical shieldings were computed with an IGLO (individual gauge for localized orbitals) program[21] using Huzinaga basis sets:[22] first DZ, i.e. (7s3p) contracted to [4111, 21] for boron and carbon and (3s) contracted to [21] for hydrogen, and second II′, i.e. (9s5p1d) contracted to [51111, 2111, 1] for boron and carbon and (3s) contracted to [21] for hydrogen. The calculated relative nuclear shieldings are presented in Table 2 below (only the results with the II′ basis set are presented). DZ results were obtained with an IGLO lobe version whereas for II′ calculations the direct IGLO program (DIGLO)[21d] was used.

Results and Discussion

Treatment of an acidified aqueous solution of the [*nido*-7,8-$C_2B_9H_{12}$]$^-$ anion ($\mathbf{1}^-$) with $NaNO_2$ at 0 °C in the presence of benzene, followed by chromatographic separation of the benzene-soluble products on a silica gel column, resulted in the isolation of two main products which were identified as the eleven-vertex azadicarbaboranes *nido*-10,7,8-$NC_2B_8H_{11}$ (**2**) and *arachno*-1,8,11-$NC_2B_8H_{13}$ (**3**), isolated in yields of 15 and 35%, respectively (see Scheme 2). Two side products from this reaction were identified as 5-Ph-*nido*-10,7,8-$NC_2B_8H_{10}$ (5-Ph-**2**) (yield 0.9%) and the previously reported[18] and well-recognized ten-vertex nido species 5,6-$C_2B_8H_{12}$ (yield 1%):

$$\underset{\mathbf{1}^-}{[C_2B_9H_{12}]^-} + NO^+ + 2H_2O \rightarrow \underset{\mathbf{2}}{C_2NB_8H_{11}} + B(OH)_3 + H_2 \qquad (1)$$

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(19) See, for example: Hehre, W.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986 and references therein.

(20) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomprets, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, L.; Stewart, J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*, Revision B.2; Gaussian Inc.: Pittsburgh, PA, 1995.

(21) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Kutzelnigg, W.; Schindler, M.; Fleischer, U. *NMR: Basic Principles and Progress*; Springer-Verlag: Berlin, New York, 1990; Vol. 23, p 165. (d) Meier, U.; van Wüllen, Ch.; Schindler, M. *J. Comput. Chem.* **1992**, *13*, 551.

(22) Huzinaga, S. *Approximate Atomic Wave Functions*; University of Alberta: Edmonton, Canada, 1971.

Table 1. Salient MP2(fc)/6-31G* ab Initio Optimized Interatomic Distances (Å) and Angles (deg) for the Parent Dicarbaazaboranes **2** and **3**

Compound **2**			
distance[a]			
B(1)−B(2)	1.779	B(1)−B(3)	1.779
B(1)−B(5)	1.765	B(2)−B(6)	1.732
B(2)−C(7)	1.720	B(3)−B(4)	1.770
B(3)−C(7)	1.710	B(4)−B(9)	1.786
B(5)−B(6)	1.821	B(5)−B(9)	1.812
B(5)−N(10)	1.709	C(7)−C(8)	1.546
C(7)−B(11)	1.584	B(9)−N(10)	1.586
mean C−H	1.087	N(10)−H	1.022
mean B−H	1.188		
bond angles			
C(7)−C(8)−B(9)	109.8	B(9)−N(10)−B(11)	111.3
fold angles[e]			
φ	8.6[c]	θ	4.1[d]
Compound **3** (Distances)			
N(1)−B(2)	1.557	N(1)−B(4)	1.583
B(2)−B(4)	1.973	B(2)−B(6)	1.776
B(2)−B(9)	1.807	B(4)−B(6)	1.832
B(4)−B(7)	1.996	B(4)−B(10)	1.774
B(6)−B(9)	1.787	B(6)−B(10)	1.800
B(6)−B(12)	1.759	B(7)−C(8)	1.525
B(7)−B(10)	1.752	B(7)−B(13)	1.777
C(8)−C(11)	1.484	C(8)−B(13)	1.671
B(9)−C(11)	1.710	B(9)−B(12)	1.795
B(10)−B(12)	1.775	B(10)−B(13)	1.785
C(11)−B(12)	1.678	C(11)−B(13)	1.717
B(12)−B(13)	1.751	N(1)−H (mean)	1.018
B−H (mean)	1.191	B(2)−μH	1.350
B(9)−μH	1.300	C−H	1.089

[a] The number of distances is reduced due to the C_s symmetry. [b] Defined with respect to the B(2)−B(3)−B(4)−B5)−B(6) plane (also see ref 27). [c] For the C(10)−B(9)−B(11) plane. [d] For the C(7)−C(8)−B(9)−B(11) plane.

Although the reaction mechanisms have not yet been studied in detail, reasonable stoichiometries can be written down as in eqs 1 and 2. Scheme 3 illustrates steps that may be significant in these processes. Thus, in this scheme, the NO^+ cation is hydroborated by the H(10) "extra" hydrogen atom in $\mathbf{1}^-$ to produce a neutral, twelve-vertex nido intermediate $C_2N(OH)B_9H_{11}$ (**4**) which, upon exchanging the OH group for the H(10) hydrogen atom and after hydrolytic removal of the resulting {BOH} vertex, generates the nido dicarbaazaboranes **2** (eq 1). An otherwise analogous process, involving the exchange of H(9) rather than H(10) with the OH group, generates the arachno dicarbaazaborane **3** (eq 2). In the overall process of Scheme 3 the cage hydrogen atoms, assisted by H_2O hydrogen atoms, ultimately effect a complete reductive cleavage of the N≡O triple bond, which, in the final stages, is followed by or is concomitant with the insertion of the nitrogen atom into the cluster.

As also shown in Scheme 2, the arachno compound **3** can be converted into the nido species **2** in 68% yield by heating at reflux in CH_2Cl_2 solution with the nonnucleophilic base PS (eq 3), followed by oxidation with acetone and acidification:

$$\underset{\mathbf{3}^-}{[C_2NB_8H_{12}]^-} + Me_2CO \rightarrow \underset{\mathbf{2}^-}{[C_2NB_8H_{10}]^-} + Me_2CHOH \quad (3)$$

The reaction is consistent with the more intimate assimilation of the nitrogen atom by the cluster according to the representation in Scheme 4. The formation of **2** may be supposed to entail a rearrangement of the B(2) vertex of the $[C_2NB_8H_{12}]^-$ anion $\mathbf{3}^-$ into the area identified by the C(8), C(11), and B(9) atoms, followed by nitrogen-atom insertion into the cluster. There is precedent for this in the vertex-flip mechanism previously reported for ten-vertex cages.[23]

We have so far been unable to grow crystals of the parent dicarbaazaboranes **2** and **3** suitable for X-ray diffraction studies. However, an increasingly valuable tool to help in the determination of the structures of boron cluster compounds is the accurate theoretical calculation of molecular geometries followed by the calculation of molecular magnetic nuclear shielding properties associated with these geometries, and the correlation of these results with the experimentally determined ^{11}B chemical shifts. Using this approach, known as the combined ab initio/IGLO[21]/NMR method,[24,25] the molecular geometries, even of relatively large boron cluster compounds, can be established. In this approach, since ^{11}B chemical shifts are often very sensitive to small changes in molecular geometry, the suitability of structures calculated ab initio can be assessed by comparing the computed with the observed chemical shifts. Many structural assignments using this method have achieved a confidence level that is often held to rival more direct structural determinations by gas-phase or single-crystal diffraction techniques.[26] As MP2(fc)/6-31G*-derived geometries have so far given the best results,[24,25] this electron-correlated level was employed here for the optimization of the geometries of the two parent dicarbazaboranes, *nido*-**2** and *arachno*-**3**. The resulting molecular structures are in Figures 1 and 2, and selected intracluster distances are in Table 1.

The computed intercarbon, interboron, and boron−carbon interatomic distances in **2** (see Table 1) compare well to the corresponding distances as previously computed for the isostructural tricarbollide anion, [*nido*-7,8,10-$C_3B_8H_{11}]^-$, and its derivatives.[2c−f] The carbon−boron and nitrogen−boron distances are generally shorter than the interboron distances, as expected, and so the open pentagonal face in **2** is not planar but is folded into an envelope conformation (see fold angles[27] in Table 1). The B(9) and B(10) atoms are situated 0.123 Å above the plane defined by the three open-face heteroatoms.

As seen in Figure 2 and as previously predicted in our preliminary communication,[4] the basic cluster geometry of the arachno compound **3** is based on that of the ten-vertex dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ in which the 8,9-bridging hydrogen atom has been replaced by a bridging {NH_2} group. The dicarbaborane *nido*-5,6-$C_2B_8H_{12}$ itself is not structurally characterized by X-ray work, but interatomic distances may be compared to the equivalent distances in the {*nido*-5,6-$C_2B_8H_{11}$} subcluster of the structurally characterized $C_4B_{18}H_{22}$ isomer 8-(3′-*closo*-1,2-$C_2B_{10}H_{11}$)-*nido*-5,6-$C_2B_8H_{11}$.[28] Here it is im-

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(23) Štíbr, B.; Plešek, J.; Zobáčová, A. *Polyhedron* **1982**, *1*, 824. (b) Nestor, K.; Štíbr, B.; Kennedy, J. D.; Thornton-Pett, M.; Jelínek, T. *Collect. Czech. Chem. Commun.* **1992**, *57*, 1262. (c) Jones, J. H.; Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M.; Štíbr, B.; Langhoff, H. *J. Organomet. Chem.* **1993**, *445*, C15.

(24) See, for example: (a) Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477 and references therein. (b) Mebel, A. M.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 463. (c) McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712. (d) Onak, T.; Tran, D.; Tseng, J.; Diaz, M.; Arias, J.; Herrera, S. *J. Am. Chem. Soc.* **1993**, *115*, 9210. (e) For a comprehensive bibliography of applications of the ab initio/IGLO/NMR method, see: Diaz, M.; Jaballas, T.; Arias, J.; Lee, H.; Onak, T. *J. Am. Chem. Soc.* **1996**, *118*, 4405.

(25) For electron correlation effects on computed ^{11}B chemical shifts, see: (a) Bühl, M.; Gauss, J.; Hofmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 12385. (b) Schleyer, P. v. R.; Gauss, J.; Bühl, M.; Greatrex, R.; Fox, M. A. *J. Chem. Soc., Chem. Commun.* **1993**, 1766.

(26) Onak, T.; Tseng, J.; Diaz, M.; Tran, D.; Arias, J.; Herrera, S.*Inorg. Chem.* **1993**, *32*, 487.

(27) Smith, D. E.; Welch, A. J. *Acta Crystallogr.* **1986**, *C42*, 1717.

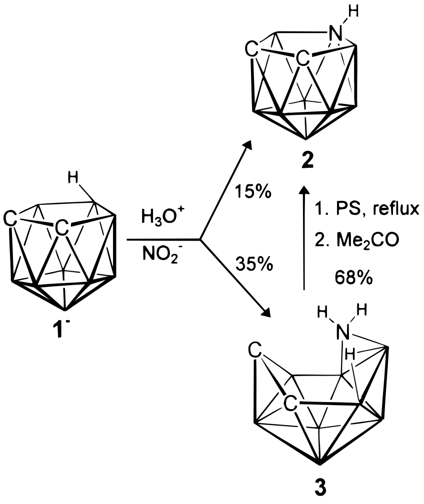
(28) Šubrtová, A.; Línek, A.; Hašek, J. *Acta Crystallogr.* **1982**, *B38*, 3147.

Table 2. NMR Data

compound	nucleus	δ (assignment, $^1J_{BH}$ (Hz))
nido-10,7,8-$NC_2B_8H_{11}$ (**2**)	^{11}B[a]	−9.4 (B3,5,6, ∼169[b]), −13.8 (B9,11, 162), −21.1 (B2,4, 159), −48.1 (B1, 152)
	^{11}B−^{11}B[c]	crosspeaks: B5,6−B9,11; B5,6−B2,4; B5,6−B1; B3−B2,4; B3−B1; B9,11−B2,4; B2,4−B1
	^{1}H[d]	3.20[e] (H10, J_{NH} = 55 Hz), 2.51 (H9,11), 2.41 (H5,6), 2.37 (H3), 2.19 (H7,8), 1.63 (H2,4), 0.60 (H1)
	^{11}H−^{11}H [f]	selected crosspeaks: H10−H9,11; H7,8−H3; H7,8−H9,11; H7,8−H2,4
5-Ph-*nido*-10,7,8-$NC_2B_8H_{10}$ (5-Ph-**2**)	^{11}B[a]	−5.2[g] (B5), −7.7 (B3, 171), −9.8 (B6,9, ∼169[b]), −14.1 (B11, 162), −19.8 (B4, 159), −22.6 (B2, 160), −47.0 (B1, 152)
	^{11}B−^{11}B[c]	crosspeaks: B5−B4; B5−B1; B3−B4; B3−B1; B6,9−B4; B6,9−B2; B6,9−B1; B11−B2; B4−B1; B2−B1
	^{1}H[d]	7.47[h] (Ph, 2 H), 7.34[h] (Ph, 3 H), 3.40[e] (H10, J_{NH} = 50 Hz), 2.64 (H3), 2.59 (H11), 2.48 (H9), 2.40 (H6), 2.39 (H8), 2.27 (H7), 1.91 (H4), 1.67 (H2), 0.72 (H1)
	^{11}H−^{11}H [f]	selected crosspeaks: H7−H3; H7−H11; H7−H2; H7−H8; H8−H3; H8−H9; H8−H4
$[NMe_4]^+$[*nido*-10,7,8-$NC_2B_8H_{10}]^-$ (**2**$^-$)[i]	^{11}B[a]	−10.7 (B3, ∼135[b]), −11.4 (B5,6, ∼145[b]), −13.7 (B9,11, 159), −21.9 (B2,4, 155), −48.3 (B1, 147)
	^{11}B−^{11}B[c]	crosspeaks: B3−B2,4; B3−B1; B5,6−B9,11; B5,6−B2,4; B5,6−B1; B9,11−B2,4; B2,4−B1
	^{1}H[d]	3.08 (NMe_4^+, 12 H), 2.24 (H9,11), 2.15 (H3), 2.06 (H5,6), 2.03 (H7,8), 1.37 (H2,4), 0.27 (H1)
10-Me-*nido*-10,7,8-$NC_2B_8H_{10}$ (10-Me-**2**)	^{11}B[a]	−5.2 (B5,6, 171), −12.1 (B9,11, 162), −12.8 (B3, ∼175[b]), −22.1 (B2,4, 159), −48.0 (B1, 150)
	^{11}B−^{11}B[c]	crosspeaks: B5,6−B9,11; B5,6−B2,4; B5,6−B1; B9,11−B2,4; B3−B2,4; B3−B1; B2,4−B1
	^{1}H[d]	2.80 (10-*Me*, 3 H), 2.49 (H5,6), 2.48 (H9,11), 2.27 (H3), 2.16 (H7,8), 1.59 (H2,4), 0.57 (H1)
10-$PhCH_2$-*nido*-10,7,8-$NC_2B_8H_{10}$ (10-$PhCH_2$-**2**)	^{11}B[a]	−4.9 (B5,6, 165), −12.3 (B3, ∼170[b]), −13.5 (B9,11, 164), −21.4 (B2,4, 159), −47.8 (B1, 150)
	^{11}B−^{11}B[c]	crosspeaks: B5,6−B9,11; B5,6−B2,4; B5,6−B1; B3−B2,4; B3−B1; B9,11−B2,4; B2,4−B1
	^{1}H[d]	7.4 (*Ph*CH_2, m, 5 H), 3.91 (PhCH_2, 2H), 2.62 (H5,6), 2.55 (H9,11), 2.29 (H3), 2.12 (H7,8), 1.63 (H2,4), 0.62 (H1)
arachno-1,8,11-$NC_2B_8H_{13}$ (**3**)	^{11}B[a]	22.1 (B7, 150), 18.6 (B12, 156), −1.1 (B4, 144), −13.6 (B2, 153), −16.5 (B10, 147), −25.5 (B9, 145/51 [j]), −28.2 (B13, 175), −33.7 (B6, 143)
	^{11}B−^{11}B[c]	crosspeaks: B7−B4; B7−B10; B7−B13; B12−B10; B12−B9; B12−B13; B12−B6; B4−B10; B4−B6; B2−B9; B2−B6; B10−B13; B10−B6; B9−B6
	^{1}H[d]	5.51 (H8), 4.47 (H7), 4.27 (H12), 3.82 (H11), 2.96 (H4), 2.79 (*exo*-H1), 2.62 (H2), 2.52 (*endo*-H1), 1.70 (H10), 1.62 (H9), 1.29 (H13), 0.72 (H6), −1.05 μH(2,9)

[a] $\delta(^{11}B)$ values in $CDCl_3$ determined from $^{11}B\{^1H(\text{broadband})\}$ measurements with assignments by [$^{11}B-^{11}B$] COSY NMR spectroscopy; all signals are doublets in normal ^{11}B spectra. [b] Values uncertain due to peak overlap. [c] Measured under the conditions of $\{^1H(\text{broadband})\}$ decoupling. [d] Assignments by $^1H\{^{11}B(\text{broadband})\}$ and $^1H\{^{11}B(\text{selective})\}$ NMR spectroscopy; all signals are singlets in the $^1H\{^{11}B(\text{broadband})\}$ NMR spectrum. [e] Broad triplet. [f] Measured under the conditions of $\{^{11}B(\text{broadband})\}$ decoupling. [g] Singlet. [h] Multiplet splitting. [i] Measured in CD_3CN. [j] Additional μH splitting.

Scheme 2



$$[C_2B_9H_{12}]^- + NO^+ + 2H_2O \rightarrow C_2NB_8H_{13} + B(OH)_3 \quad (2)$$
$$\underset{\mathbf{1}^-}{} \qquad\qquad\qquad\qquad \underset{\mathbf{3}}{}$$

mediately apparent that there are significant variations in otherwise equivalent interatomic distances when the two clusters are compared in detail.

The most marked differences are for the nitrogen-bridged interboron distance B(2)−B(4) of 1.973 Å, some 20 Å longer than the hydrogen-bridged distance of 1.782 Å, and indicating a much weaker interboron bonding interaction. Comparison of literature values for the corresponding bridged B(5)−B(6) open-face connectivities in other *nido*-type ten-vertex clusters reveals considerable variation: 2.69 Å in $[B_{10}H_{13}(\mu\text{-}PPh_2)]$,[29] 2.08 Å in $[B_{10}H_{12}(N_3)(\mu\text{-}NH_2)]$,[30] 2.211 in $[5\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{12}(\mu\text{-}NEt_2)]$,[31] 2.096 Å in $[6\text{-}(\eta^5\text{-}C_5Me_5)RhB_9H_{12}(\mu\text{-}NEt_2)]$,[31] 1.872 Å in $[B_{10}H_{12}\text{-}\mu\text{-}PHC(Bu^t)B_{10}H_{12}(SMe_2)]$,[32] 1.776 Å for the BHB bridge in $B_{10}H_{14}$ itself,[33] and 1.74 Å in the gold-bridged compound $[\{\mu\text{-}Au(PPh_3)\}B_{10}H_{13}]$.[34]

There is obviously considerable variation in bonding character here. In the (μ-PPh_2) species the interboron distance of 2.69 Å is clearly nonbonding, but in the N-bridged compounds, although the bridged interboron distances are much shorter than this, they are still somewhat longer than typical cluster interboron distances. They may therefore have bonding schemes inter-

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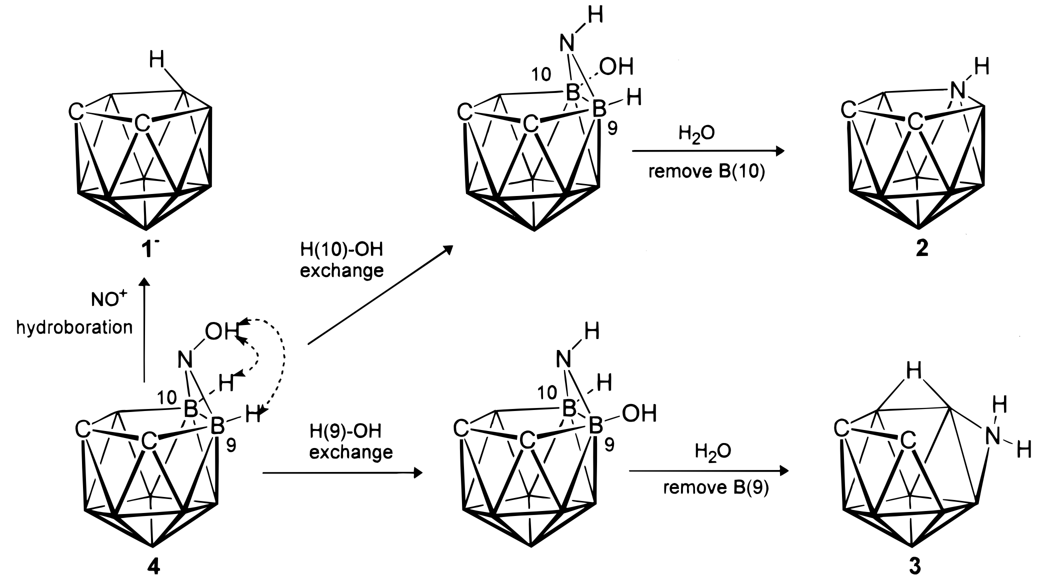
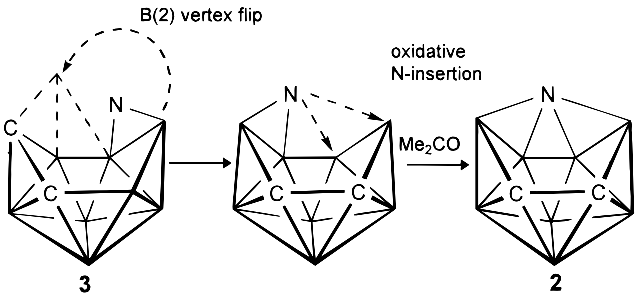
(29) Friedman, L. B.; Perry, S. L. *Inorg. Chem.* **1973**, *12*, 288.
(30) Müller, J.; Paetzold, P.; Boese, R. *Heteroatom Chem.* **1990**, *1*, 461.
(31) Dörfler, U.; Clegg, W.; Kennedy, J. D.; Thornton-Pett, N. *J. Chem. Soc., Dalton Trans.* **1998**, 2353.
(32) Meyer, F.; Paetzold, P.; Englert, U. *Chem. Ber.* **1994**, *127*, 93.
(33) Tippe, A.; Hamilton, W. C. *Inorg. Chem.* **1969**, *8*, 464.
(34) Wynd, A. J.; Caren, A. J.; Reed, D.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1987**, 2761. (b) Wynd, A. J.; Welch, A. J.; Parish, R. V. *J. Chem. Soc., Dalton Trans.* **1990**, 2185.

Scheme 3



Scheme 4



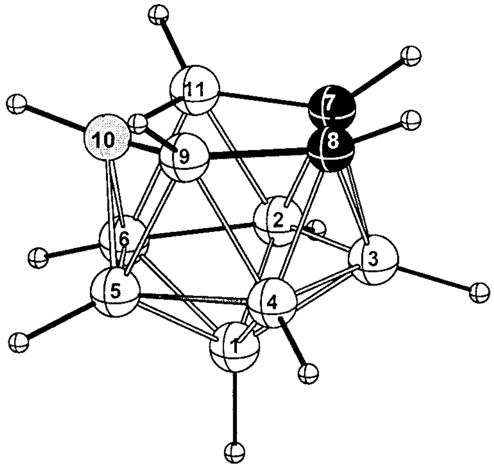


Figure 1. Geometry-optimized MP2(fc)/6-31G* structure of *nido*-10,7,8-$NC_2B_8H_{11}$ (**2**).

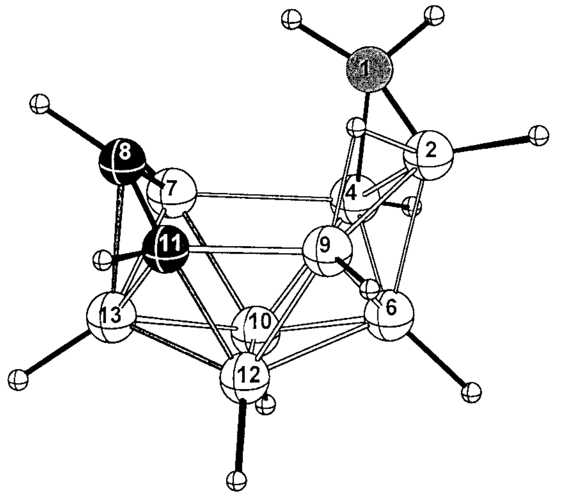


Figure 2. Geometry-optimized MP2(fc)/6-31G* structure of *arachno*-1,8,11-$NC_2B_8H_{13}$ (**3**).

mediate between two-electron three-center BBN character and one involving both available electron pairs on the nitrogen atom. This extra electron-pair would thereby engender elements of ten-vertex arachno character for the $\{C_2B_8\}$ unit. Perhaps in accord with this there are other significant differences between the cluster geometry of **3** and that of the unbridged $\{C_2B_8H_{11}\}$ subcluster of $C_4B_{18}H_{22}$.[30] Thus, links to the nitrogen-bridged boron atoms are generally on average some 0.035 Å longer than on the unbridged cluster, and there are variations of either sign up to $+ 0.027$ and -0.041 Å throughout the rest of the molecule. This indicates a difference in cluster electronic structure, perhaps again suggesting a tendency to eleven-vertex arachno character from ten-vertex nido and in any event confirming that the effect of the bridging amine group is not completely localized at the bridging site.[35]

In contrast to the behavior of the arachno compound **3**, of which the deprotonation by PS leads to a complex anionic mixture, treatment of the nido compound **2** with either of the bases PS or NaH leads to a straightforward removal of the nitrogen-bonded H(10) proton to form the [*nido*-10,7,8-$NC_2B_8H_{10}]^-$ anion $\mathbf{2}^-$. This anion is reasonably supposed to contain an exopolyhedral free electron pair on the nitrogen center, being thus a nucleophile. In accord with this presumption, anion $\mathbf{2}^-$ can be easily alkylated to produce the N-alkylated analogues of **2**. Thus, for example, Me_2SO_4 and $PhCH_2Br$ give 10-R-*nido*-10,7,8-$NC_2B_8H_{10}$ (where R = Me (10-Me-**2**) and $PhCH_2$ (10-$PhCH_2$-**2**), respectively) in good yields (86 and 69%, respectively). The structure of 10-$PhCH_2$-**2** was determined crystallographically a long time ago,[36] but no complete structural details have yet been generally available.

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(35) Beckett, M. A.; Kennedy, J. D. *J. Chem. Soc., Chem Commun.* **1983**, 575. (b) Thornton-Pett, M.; Beckett, M. A.; Kennedy, J. D. *J. Chem. Soc., Dalton Trans.* **1986**, 303.

(36) Plešek, J.; Heřmánek, S.; Huffman, J.; Ragatz, P.; Schaeffer, R. *J. Chem. Soc., Chem. Commun.*, **1975**, 935.

Table 3. Experimentally Determined and Calculated IGLO ^{11}B NMR Chemical Shifts[a] for the Parent Dicarbaazaboranes **2** and **3**

Assignments for **2**

level of theory//geometry	B(1)	B(2,4)	B(3)	B(5,6)	B(9,11)
DZ//6-31G*	−49.9	−24.8	−9.5	−11.0	−15.7
DZ//MP2/6-31G*	−49.7	−24.3	−10.0	−10.6	−16.2
II′//MP2/6-31G*	−50.6	−22.2	−6.7	−8.7	−14.6
experiment (CDCl$_3$)	−48.5	−22.5	−9.5	−10.5	−14.5
experiment (CD$_3$CN)	−48.8	−21.9	−10.4	−10.4	−14.4

Assignments for **3**

level of theory//geometry	B(2)	B(4)	B(6)	B(7)	B(9)	B(10)	B(12)	B(13)
II′//MP2/6-31G*	−16.0	−2.5	−38.8	22.8	−27.1	−17.2	19.5	−30.8
experiment	−13.6	−1.1	−33.7	22.1	−25.4	−16.5	16.6	−28.9

[a] In ppm relative to BF$_3$·OEt$_2$.

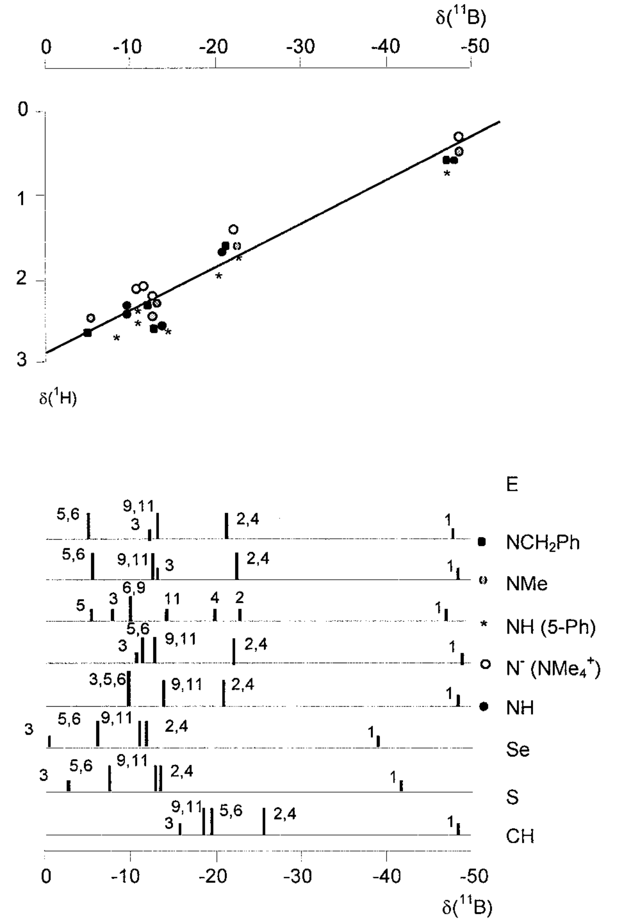

Figure 3. The bottom diagram is a stick representation and comparison of the ^{11}B NMR chemical shifts and relative intensities for the eleven-vertex *nido*-dicarbaheteroboranes of general formulation *nido*-10,7,8-EC$_2$B$_8$H$_{10}$ [where E = CH$^-$ (data from refs 2c and 2d); S (data from ref 6); Se (data from ref 7); NH, **2**; N$^-$ (NMe$_4^+$ salt), **2**$^-$; NH (5-Ph derivative), 5-Ph-**2**; NMe, 10-Me-**2**; and NCH$_2$Ph, 10-PhCH$_2$-**2**]. The upper diagram is a plot of $\delta(^1H)$ versus $\delta(^{11}B)$ for **2** and its N-substituted derivatives.

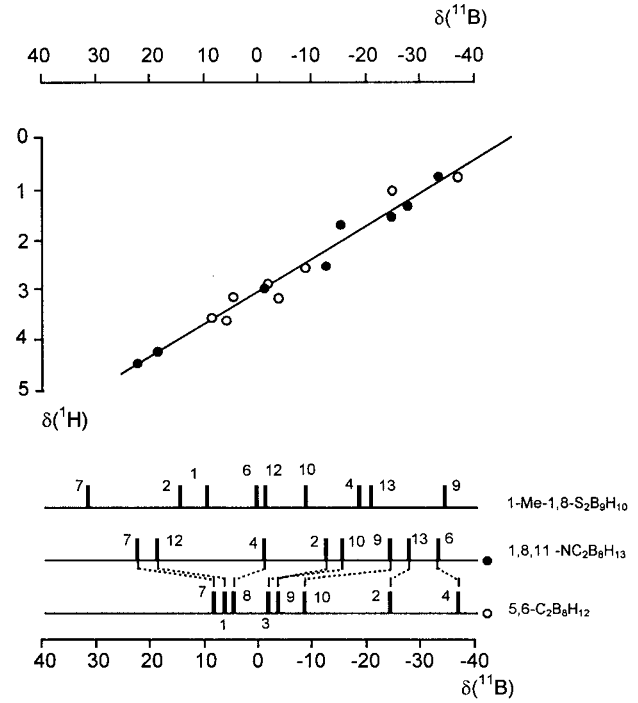

Figure 4. The bottom diagrams are stick representations of the ^{11}B NMR chemical shifts and relative intensities for *nido*-5,6-C$_2$B$_8$H$_{12}$ (data from ref 18c) and for the quasi-isostructural eleven-vertex arachno compounds 1,8,11-NC$_2$B$_8$H$_{13}$ (**3**) and 1-Me-*arachno*-1,8-S$_2$B$_9$H$_{10}$ (data from ref 10). The upper diagram is a plot of $\delta(^1H)$ versus $\delta(^{11}B)$ for individual {BH} units for the last two compounds.

For all compounds encountered in this study, [^{11}B−^{11}B]-COSY[13] and ^{1}H{^{11}B(selective)}[15] NMR experiments, combined in some cases with [^{1}H−^{1}H] COSY[14] measurements, have led to the complete assignments of all the ^{11}B and ^{1}H resonances to their individual {BH} and {CH} cluster units. The experimental NMR data are in Table 2, and Table 3 shows the good agreement between experimental and IGLO-calculated ^{11}B NMR chemical shift values, the latter being given for various levels of computation. As shown in Figure 3 (lower diagram), **2** and its substituted derivatives exhibit largely very similar ^{11}B shielding behavior. The differences arise principally from α, *β*, and antipodal substituent effects. In accord with their C_s symmetry, the parent compound **2** and its N(10)-substituted derivatives exhibit 2:1:2:2:1 patterns of doublets, whereas the asymmetrically substituted 5-Ph derivative 5-Ph-**2** shows eight different resonances. An interesting feature is the antipodal shielding[37] of the ^{11}B(3) and ^{1}H(3) nuclei by the substituent at the N(10) site; inspection of Figure 3 and Table 2 reveals antipodal shielding[38] effects decreasing along the series of substituents: $\Delta\sigma(^{11}B)_A$ Me (3.4) > PhCH$_2$ (2.5) > LP (lone electron pair) (1.3) > H (0) and $\Delta\sigma(^1H)_A$ LP (0.22) > Me (0.1) > PhCH$_2$ (0.08) > H (0). Figure 3 also correlates ^{11}B shielding behavior in the more extensive isostructural (and isoelectronic) series of dicarbaheteroboranes of general formulation *nido*-10,7,8-EC$_2$B$_8$H$_{10}$, where E is a formal isolobal unit, {CH}$^-$, NH, S, or Se. These also show mutually closely related ^{11}B NMR shielding properties, with a clear tendency for a decrease in shielding of the ^{11}B(3) nucleus antipodal to the changing heteroatom site E($\Delta\sigma(^{11}B)_A$ values in parentheses): {CH}$^-$ (0) > NH (−6.2) > S (−12.8) > Se (−15.4) (data from refs 2c, 6, and 7). As also seen from Figure 3 (upper part), there is an approximately linear correlation between $\delta(^{11}B)$ and $\delta(^1H)$(exo) for all the nido compounds of type **2**.

Figure 4 (bottom part) intercorrelates the ^{11}B shielding behavior of compound **3** with that of the structurally similar compounds *nido*-5,6-C$_2$B$_8$H$_{12}$ and 1-Me-*arachno*-1,8-S$_2$B$_9$H$_{10}$10 (numbering as in structure **II**). Inspection of the figure shows

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(37) See, for example: Heřmánek, S. *Chem. Rev.* **1992**, *92*, 325 and references therein.

(38) Defined as $\sigma_A = \sigma_H - \sigma_R$ (where symbols H and R relate to the parent and R-substituted compound, respectively).

that there is a similar ordering of individual resonances for the first two compounds, demonstrating some electronic parallels, and again justifying the originally proposed[4] structural formulation of **3** as a bridged 8,9-μ-NH_2 derivative of *nido*-5,6-$C_2B_8H_{12}$. However, the absolute differences in chemical shifts are, in most instances, somewhat too high to be simply attributed to substituent effects (α and β) of a "bridging" $\{NH_2\}$ unit. Thus, although the directly bridged ^{11}B α sites are shielded somewhat, by 5 and 10 ppm, the adjacent $^{11}B(9)$ and $^{11}B(10)$ β sites are even more shielded, by 16 and 15 ppm, respectively, and the other β site $^{11}B(7)$, and the more remote $^{11}B(12)$ γ site, are substantially deshielded, by 15 and 10 ppm, respectively. These shielding changes are not trivial and therefore indicate a deviation from straightforward ten-vertex nido character. Therefore they can also perhaps be invoked to support the proposed ten- and eleven-vertex arachno character for **3** as discussed above with regard to interatomic dimensions. In terms of such comparisons, it is interesting that there is almost no reasonable correlation of corresponding resonances between **3** and the ostensibly isostructural dithia analogue $MeS_2B_9H_{10}$.[10] Here the *differential* effects of the {CH} and {S} vertexes on the cluster bonding and resultant ^{11}B shielding must be very significant, even though the S-bridged B−B distance is, at 1.920 Å,[10] comparable to that in **3** (1.973 Å). It is thereby interesting that the perturbation of the cluster by the bridging group is significantly dependent upon cluster constituents relatively remote from the bridged site.

Acknowledgment. Contribution No. 66 from the Řež−Leeds Anglo−Czech Polyhedral Collaboration (ACPC). The Grant Agency of the Czech Republic (Grant No. 203/97/0060), the Grant Agency of the Czech Academy of Sciences of the Czech Republic (Grant No. A4032502), the EPSRC (United Kingdom) (Grant Nos. GR/F/43215 and GR/J/56929) and the Royal Society (London), the Deutsche Forschungsgemeinschaft, the Fonds der Chemischen Industrie, and the Deutscher Akademischer Austauschdienst (scholarship to D.H.) provided support. We also thank the Leibnitz Rechenzentrum in München for granting computer time on a Cray YMP-8 computer, Professor W. Kutzelnigg, Dr. M. Schindler, Dr. U. Fleischer, and Dr. Ch. van Wüllen for the IGLO and DIGLO programs, Dr. M. Bühl (Universität Zürich) for performing the II′//MP2/6-31G* calculations, Dr. E. Večerníková for IR measurements, Dr. Z. Plzák for mass spectra, and Drs. J. Holub and Z. Janoušek for revisions of some experiments.

Supporting Information Available: Listings of MP2/6-31G* calculated coordinates for **2** and **3** (1 page). Ordering information is given on any masthead page.

IC971526W