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Structural Studies of *nido*-(μ-Me$_2$B)B$_5$H$_8$, the Unusual Bridging Hydrogens in *nido*-2-MeB$_6$H$_9$, and *nido*-2,3-Me$_2$B$_6$H$_8$ and the Predicted Structure of *nido*-2,4-Me$_2$B$_6$H$_8$ via the *Ab Initio*/IGLO/NMR Method

Thomas P. Onak[*,†] **and Robert E. Williams**[*,‡]

Loker Hydrocarbon Research Institute, University of Southern California, Los Angeles, California 90089, and Department of Chemistry and Biochemistry, California State University at Los Angeles, Los Angeles, California 90032

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Gaines' structure of *nido*-$\mu_{2,3}$-(Me$_2$B)-B$_5$H$_8$, **A**, with a doubly electron deficient boron, as well as Shore's structure for *nido*-2-MeB$_6$H$_9$-$\langle\mu$-3,4-H$\rangle$, **Bb**, with unsymmetrical bridge hydrogens have been reconfirmed via the *ab initio*/IGLO/NMR method. The ^{11}B NMR data of *nido*-2,3-Me$_2$B$_6$H$_8$, **C**, indicate that the $\langle\mu$-3,4-H$\rangle$-, **Cb**, and $\langle\mu$-4,5-H$\rangle$-isomers, **Ca**[1] are of nearly equivalent stability. *nido*-2,4-Me$_2$B$_6$H$_8$-$\langle\mu$-5,6-H$\rangle$, **Da**, with symmetrical bridge hydrogens, is predicted to be more stable than the **Ca** and **Cb** isomers. These results allow an assessment of some of the factors determining bridge hydrogen placement and substitution patterns in the polyboranes.

1. Introduction

Myriad polyboranes and carboranes have been discovered over the past four decades,[2] and most of their structures have been satisfactorily determined to a ball and stick level[3] of accuracy by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy. Many of these structures have also been determined to the higher accuracy afforded by X-ray, electron diffraction and/or microwave spectroscopy. As more and more of these cluster compounds have become known, the majority have become identified as individual members of larger groups or series of compounds. The structural similarities within the various groups or series mutually reinforce each other. On the other hand a considerably smaller number of unusual compounds have accumulated which do not belong to groups or series and seemingly have one-of-a-kind structures or which exhibit one-of-a-kind features within their structures.

A disquieting thought surfaces from time to time: Are these unusual compounds truly unique or could some of them possibly be members of groups or series of compounds and simply be mischaracterized? A number of these unique compounds are not amenable to X-ray structural studies, and a few are suspected of having different structures in solution as opposed to the crystalline phase.

A three-step procedure, the *ab initio*/IGLO/NMR technique,[4] has recently been reduced to practice. This method involves (a) the *ab initio* geometry optimization[5] of candidate structures after which (b) the chemical shift values are calculated (^{11}B and/or ^{13}C in the case of carboranes; ^{11}B in the case of polyboranes[6]), via the IGLO program, for each of the various *ab initio* optimized structures. The final step (c) is to compare the IGLO-calculated chemical shift values for the various candidate structures with the experimentally observed NMR chemical shift values. The degree of correspondence between the experimental NMR spectra and the calculated spectra for the known-to-be-correct isomers is truly impressive.[7]

Recently we have been able, via the *ab initio*/IGLO/NMR technique, to confirm in some cases and to deny in other cases the correctness of several of the one-of-a-kind structures proposed for a number of unique polyboranes and carboranes where structures in solution could not previously be unambiguously determined.[8]

In the present study we expand our consideration of one-of-a-kind compounds to include the structure of Gaines' unique

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[†] California State University at Los Angeles.

[‡] University of Southern California.

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(1) As four of the five candidate locations for bridge hydrogens are always filled with bridge hydrogens we choose to identify the one vacant location which does not have a bridge hydrogen rather than the four that are filled and thus would label our preferred isomer, **Ba**, in Figure 2 as 2-MeB$_6$H$_9$-$\langle\mu$-4,5-H$\rangle$. We indicate this both by placing the absent group within the symbols, $\langle\,\rangle$, which implies a negative quantity or a loss in formal business accounting practices, rather than between parentheses, ( ), and by placing the notation at the end of the formula rather than at the front. The species, presumed to be progressively less stable than **Ba**, are **Bb**, 2-MeB$_6$H$_9$-$\langle\mu$-3,4-H$\rangle$, and **Bc**, 2-MeB$_6$H$_9$-$\langle\mu$-2,3-H$\rangle$. The larger the numbers identifying the site missing the bridging hydrogen indicates that the vacant location is farther from the methyl group, i.e. **Ba**-$\langle\mu$-4,5-H$\rangle$ > **Bb**-$\langle\mu$-3,4-H$\rangle$ > **Bc**-$\langle\mu$-2,3-H$\rangle$.

(2) (a) Williams, R. E. Adv. *Inorg. Chem. Radiochem.*, **1976**, *18*, 67. (b) Williams, R. E. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991, Chapter 2, pp 11−93. (c) Williams, R. E. *Chem. Rev.* **1992**, *92*, 177−207. (d) Williams, R. E. *Adv. Organometallic Chem.* **1994**, *36*, 1 and references therein for all of the above.

(3) (a) It is generally considered by many synthetic chemists that if one knows the atom connectivity within a molecule, i.e. what atoms are "bonded to what other atoms", then the correct structure is known, whereas (b) many physical chemists and most theoretical chemists consider the structure is not known until the bonding distances and angles are determined.

(4) The IGLO method employed here was designed by (a) Kutzelnigg, W. *Isr. J. Chem.* **1980**, *19*, 193. (b) Schindler, M.; Kutzelnigg, W. *J. Chem. Phys.* **1982**, *76*, 1919. (c) Schindler, M.; Kutzelnigg, W. *J. Am. Chem. Soc.* **1983**, *105*, 1360−1370. (d) Schindler, M.; W. *J. Am. Chem. Soc.* **1987**, *109*, 1020−1033. (e) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Springer Verlag: Berlin, 1990; Vol. 23, pp 165−262.

(5) GAUSSIAN-90. Frisch, M. J.; Head-Gordon, M.; Trucks, G. W.; Foresman, J. B.; Schlegel, H. B.; Raghavachari, K.; Robb, M.; Binkley, J. S.; Gonzalez, C.; Defrees, D. J.; Fox, D. J.; Whiteside, R. A.; Seeger, R.; Melius, C. F.; Baker, J.; Martin, R. L.; Kahn, L. R.; Stewart, J. J. P.; Topiol, S.; Pople, J. A.; Gaussian, Inc., Pittsburgh PA. Hehre, W. J.; Radon, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley-Interscience: New York, **1986**.

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compound *nido*-μ-(2,3-Me_2B)B_5H_8, **A**,[14] and the novel bridge hydrogen distributions in Shore's *nido*-2-MeB_6H_9, **B**,[15] as well as Gaines' *nido*-2,3-$Me_2B_6H_8$, **C**,[14] and the predicted to be more stable *nido*-2,4-$Me_2B_6H_8$, **D**.

Compound **A** was first synthesized and isolated from the reaction of Me_2BCl and $B_5H_8^-$.[14] It was proposed to have the structure illustrated in Figure 1, (dimethylboryl)pentaborane, *nido*-$\mu_{2,3}$-(Me_2B)-B_5H_8.

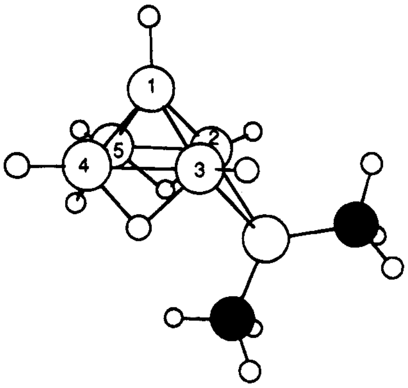

Figure 1. Proposed structure for (dimethylboryl)pentaborane, *nido*-$\mu_{2,3}$-(Me_2B)B_5H_8, **A**. The large white circles are boron atoms; the small white circles are hydrogens; the black circles represent carbon.

In recent decades two kinds of electron deficiency have been described as applying to boron and carbon compounds. The first type is the classical unsaturated electron deficiency and involves tricoordinate boron and carbon atoms that have access to six electrons, via 3 two center two electron (2c2e) bonds, e.g. Me_3C^+, and BMe_3. The second type may be called multicenter bond electron deficiency and involves penta- and hexacoordinate borons and carbons that have access to an octet of electrons via four bonds but one or more of the bonds is a multicenter 3c2e bond (or greater, e.g. 4c2e etc.) which accounts for the greater than four-coordinate borons and carbons. Examples are *nido*-diborane, B_2H_6, and *arachno*$-C_7H_{11}^+$ (2-norbornyl carbonium ion).[16]

To our knowledge only Gaines' unique compound[14] has been proposed to have a boron atom involved in both unsaturated and multicenter bond electron deficiency simultaneously. The boron in the μ-(Me_2B) group of Gaines' *nido*-$\mu_{2,3}$-(Me_2B)-B_5H_8, **A**, (Figure 1) was proposed to be affiliated with the B_5H_8 moiety via one 3c2e bond and to be connected to the two Me groups by two 2c2e bonds (six electrons in all).

There was no reason to question Gaines' proposed structure of *nido*-$\mu_{2,3}$-(Me_2B)-B_5H_8, **A**—e.g. the $\delta(^{11}B) = >90$ shift for the boron in the Me_2B group would not be unexpected for such a grouping—but since it was a one-of-a-kind compound and since, despite decades of acceptance, the structures of other one-of-a-kind compounds had been found to be incorrect,[6m,13] we felt compelled to see if the structure could be confirmed by the *ab initio*/IGLO/NMR method.

1.1. Assumptions. Our early work[17,18] as well as studies by Ryschkewitsch et al.[19] on the electrophilic Friedel–Crafts methylation of B_5H_9 revealed that methylation of the apex boron was preferred; i.e., 1-MeB_5H_8 was the kinetically favored product. We have always assumed that the apex boron (five-coordinate and involved in one 3c2e bond) was more negatively charged (since confirmed by calculations) than the four basal borons (six-coordinate and involved in 2.5 3c2e bonds). Both elevated temperatures and Lewis base catalysis quantitatively convert 1-MeB_5H_8 into the more thermodynamically stable 2-MeB_5H_8. It has long been assumed that methyl groups tend to act inductively as electron donors on electron deficient polyborane clusters and that charge smoothing is maximized

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(6) For examples of the application of IGLO to boron compounds see (a) Schleyer, P. v. R.; Bühl, M.; Fleischer, U.; Koch, W. *Inorg. Chem.* **1990**, *29*, 153. (b) Bühl, M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 886. (c) Bühl, M.; Schleyer, P. v. R. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, **1991**, Chapter 4, p.113. (d) Williams, R. E. In *Electron Deficient Boron and Carbon Clusters*; Olah, G. A., Wade, K., Williams, R. E., Eds.; Wiley: New York, 1991; Chapter 4, p 91 (see footnote 83). (e) Bühl, M.; Schleyer, P. v. R.; McKee, M. L. *Heteroat. Chem.* **1991**, *2*, 499–506. (f) Bühl, M.; Schleyer, P. v. R.; Havlas, Z.; Hnyk, D.; Hermanek, S. *Inorg. Chem.* **1991**, *30*, 3107–3111. (g) Bühl, M.; Steinke, T.; Schleyer, P. v. R.; Boese, R. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1160–1161. (h) Bühl, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1992**, *114*, 477–491. (i) Kutzelnigg, W.; Fleischer, U.; Schindler, M. In *NMR, Principles and Progress*; Springer Verlag: Berlin, 1990; Vol. 23, pp 210–212. (j) Köster, R. Seidel, G.; Wrackmeyer, B.; Blaeser, D.; Boese, R.; Bühl, M.; Schleyer, P. v. R. *Chem. Ber.* **1992**, *125*, 663; *Chem. Ber.* **1991**, *24*, 2715–2724. (k) Kang, S. O.; Bausch, J. W.; Carroll, P. J.; Sneddon, L. G. *J. Am. Chem. Soc.* **1992**, *114*, 6248–6249. (l) Bausch, J. W.; Prakash, G. K. S.; Bühl, M.; Schleyer, P. v. R.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3060–3062. (m) Bausch, J. W.; Prakash, G. K. S.; Williams, R. E. *Inorg. Chem.* **1992**, *31*, 3763–3768. (n) Bühl, M.; Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1992**, *31*, 3769–3775. (o) Onak, T.; Tseng, J.; Tran, D.; Herrera, S.; Chan, B.; Arias, J.; Diaz, M. *Inorg. Chem.* **1992**, *31*, 3910–3913. (p) Onak, T.; Tseng, J.; Diaz, M.; Tran, D.; Arias, J.; Herrera, S.; Brown, D. *Inorg. Chem.* **1993**, *32*, 487–489. (q) Mebel, A. M.; Charkin, O. P.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 463–468. (r) Mebel, A. M.; Charkin, O. P.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 469–473. McKee, M. L.; Bühl, M.; Schleyer, P. v. R. *Inorg. Chem.* **1993**, *32*, 1712–1715.

(7) In fact the numerical concurrence between theoretical values and experimental values (for the correct isomers) is so precise, and has been repeated in so many cases, that even experimentalists (heretofore theoretical-agnostics) are driven to conclude reluctantly that the underlying *ab initio* structural assignments must not only be correct but that the structural dimensions are almost as good as, equivalent to, or in some cases, suspected of being superior to those determined by X-ray crystallography, as the latter may be distorted by crystal packing forces. For example the structures of *arachno*-B_5H_{11} and *arachno*-B_6H_{12} were reconfirmed[6c] and highly refined during these studies. The dramatic differences between the observed experimental values and the theoretical values projected for the known-to-be-incorrect isomers are equally persuasive.

(8) (a) These include the solution phase structures for *nido*-$C_2B_6H_{10}$,[6l] *closo*-$C_2B_6H_8$, *closo*-$CB_7H_8^-$, and *closo*-$B_8H_8^{2-}$,[6m] and *nido*-μ-(Me_2-NBH)-$C_2B_4H_6$[9] which have been confirmed or reconfirmed as having the proposed or anticipated structures while, to our surprise, gross mismatches between theory and experiment dictate that the proposed structures for *closo*-$C_3B_5H_7$,[6m] and *arachno*-$C_2B_6H_{12}$[10] cannot be correct.[11] (b) One of us[2] has always felt the NMR evidence[12] for a dimethyl derivative of *closo*-1,2-$C_2B_3H_5$, i.e. *closo*-C,3-Me_2-1,2-$C_2B_3H_3$, is unacceptable and indeed the *ab initio*/IGLO/NMR procedure confirms the proposed structure is incorrect.[13]

(9) Onak, T.; Tseng, J.; Diaz, M.; Tran, D.; Arias, J.; Herrera, S.; Brown, D. *Inorg. Chem.*, **1993**, *32*, 487–489.

(10) Corcoran, E. W.; Sneddon, L. G., *J. Am. Chem. Soc.* **1985**, *107*, 7446.

(11) *Ab initio*/IGLO/NMR calculations by (a) Onak and Williams, (b) Bausch and Sneddon and (c) by Schleyer and Hoffman confirm that the proposed structure for *arachno*-$C_2B_6H_{12}$[10] cannot be correct in spite of its intuitive appeal and years of acceptance.

(12) (a) Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 1070. (b) Bramlett, C. L.; Grimes, R. N. *J. Am. Chem. Soc.* **1966**, *88*, 4269. (c) Grimes, R. N. *Carboranes*; Academic Press: New York; 1970; pages 33–42.

(13) *Ab initio*/IGLO/NMR calculations by Bausch and Williams and by Schleyer and McKee confirm that the proposed structure *closo*-*C*,3-Me_2-1,2-$C_2B_3H_3$ is incorrect.

(14) (a) Gaines, D. F.; Iorns, T. V. *J. Am. Chem. Soc.* **1970**, *92*, 4571. (b) Edvenson, G. M.; Gaines, D. F.; Harris, H. A.; Campana, C. F. *Organometallics* **1990**, *9*, 401.

(15) Brice, V. T.; Johnson II, H. D.; Shore, S. G. *J. Am. Chem. Soc.* **1973**, *95*, 6629.

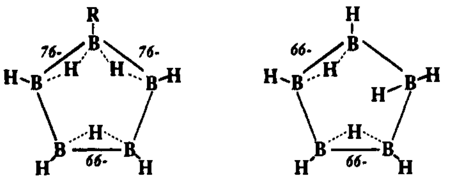
(16) Olah, G. A.; Prakash, G. K. S.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley-Interscience: New York, 1987.

(17) ^{11}B NMR in the late 1950s showed that 1-MeB_5H_8 was produced spontaneously from warming a mixture of $(MeO)_3B$ and B_5H_9 in the presence of a large excess of $AlCl_3$; apparently we were using a superelectrophile [18] but did not know it!

(18) Olah, G. A. *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 767.

(19) Ryschkewitsch, G. E.; Harris, J. J.; Sisler, H. H. *J. Am. Chem. Soc.* **1963**, *2*, 190.

Scheme 1. Comparison of the Pentagonal Open Faces of $RB_{11}H_{13}-$ and $B_{11}H_{14}^-$



$RB_{11}H_{13}]^-$ $B_{11}H_{14}]^-$

by methyl group electron donation to the more electron deficient 2-position (six-coordinate and involved in 2.5 3c2e bonds) than the 1-position (five-coordinate and only involved in one 3c2e bond). This crude rationale, while it may be roughly correct, when differences in kind are involved, is much less dependable when differences in degree are considered. For example, both Onak and Lipscomb have found 2,3-$Me_2B_5H_7$ to be more stable than 2,4-$Me_2B_5H_7$ both experimentally[20] and calculationally.[21] We cannot explain this result.

1.2. Presumptions. In order to artificially impose some semblance of order in evaluating the bridge hydrogen locations in Shore's *nido*-2-MeB_6H_9, **B**, Gaines' *nido*-2,3-$Me_2B_6H_8$, **C**, and the predicted *nido*-2,4-$Me_2B_6H_8$, **D**, we have generated the following four presumptions which we would have anticipated in the past would predict the locations of the methyl groups and bridge hydrogens, prior to the collection of any experimental data and making the *ab initio*/IGLO/NMR calculations. This allows us to point out where there is agreement with these crude presumptions and where there is disagreement. In this fashion at least the structural options can be presented in an organized fashion.

1.2.1. Crude Methyl Group/Bridge Hydrogen Presumptions in Fluxional Polyborane Clusters. (1) When structural alternatives exist for polyborane clusters which are fluxional , or can be made fluxional, the resulting clusters will tend to have the methyl (alkyl) groups located on those borons involved in the greatest number of 3c2e bonds and are coordinated with the most neighboring atoms. (Exceptions are not known.)

(2) Other things being equal, multiple bridging hydrogens will tend to occupy nonadjacent sites. (An exception is known, i.e. *nido*-B_8H_{12}.)

(3) Other things being equal, multiple methyl groups will locate on nonadjacent boron atoms in the most stable isomers. (An exception is known.[20,21])

(4) Other things being equal, multiple bridging hydrogens will tend to occupy locations as near to the boron attached methyl groups as possible. (Exceptions are illustrated in this study.)

Having long assumed that alkyl groups tend to inductively donate electron density into polyborane skeletons the recently published structure of Gaines' *nido*-7-$RB_{11}H_{13}^-$ is revealing. Both the parent compound, Shore's $B_{11}H_{14}^-$, and $RB_{11}H_{13}^-$ [22] incorporate three skeletal hydrogens. In the $B_{11}H_{14}^-$ two 66-bridge hydrogens (3c2e bonds) and one endo hydrogen (2c2e bond) are distributed as far apart as possible about a five-membered open face. The 66-indicates that both bridge hydrogens are associated with two six-coordinate boron atoms. See Scheme 1.

Table 1. Energies of $(CH_3)B_6H_9$ and $(CH_3)_2B_6H_8$ Isomers at the 3-21G Level

compound	tot. energy, au	rel energy, kcal/mol	ZPE(NF), kcal/mol	Δ3-21G// 3-21G+ZPE, kcal/mol
2-MeB_6H_9 = B				
⟨μ-4,5-H⟩ Ba	−191.77365	1.10	98.50	1.40
⟨μ-3,4-H⟩ Bb	−191.77541	0.00	98.21	0.00
⟨μ-2,3-H⟩ Bc	−191.77408	0.83	98.37	0.99
2,3-$Me_2B_6H_8$ = C				
⟨μ-4,5-H⟩ Ca	−230.60950	2.64	117.42	2.88
⟨μ-3,4-H⟩	−230.60951	2.63	117.34	2.79
⟨μ-2,3-H⟩ Cc	−230.60838	3.34	117.41	3.58
2,4-$Me_2B_6H_8$ = D				
⟨μ-5,6-H⟩ Da	−230.61142	1.43	117.10	1.35
⟨μ-4,5-H⟩ Db	−230.60844	3.31	117.53	3.65
⟨μ-2,3-H⟩ Dc	−230.61371	0.00	117.18	0.00
$\mu_{2,3}$-$BMe_2B_5H_8$ = A	−230.59642	10.84	115.49	9.16

Heretofore stable 76-bridge hydrogens have not been reported in such compounds. In $RB_{11}H_{13}^-$ all three skeletal hydrogens are bridge hydrogens, one 66-bridge hydrogen and two (necessarily adjacent) 76-bridge hydrogens. In accordance with presumptions 1, 2, and 4 the alkyl group is on the highest 7-coordinated boron, between the two necessarily adjacent 76-bridge hydrogens. Presumption 3 is inapplicable. The alkyl group apparently donates electrons into the neighboring boron atom which in turn attracts the electron-seeking bridge hydrogens and in this case allows a different structure to be produced.

2. Experimental Section

CalculationalMethods for the Geometry Optimizations and for IGLO/NMR Chemical Shift Determinations. *Ab initio* geometry optimizations, *involving alternative bridge hydrogen placements*, were carried out for the three isomers of *nido*-2-MeB_6H_9, **B**, three isomers of *nido*-2,3-$Me_2B_6H_8$, **C**, and three isomers of *nido*-2,4-$Me_2B_6H_8$, **D**, as well as for *nido*-μ-(Me_2B)-B_5H_8, **A**, using the Gaussian-90 code[5] at both the 3-21G and 6-31G* levels of theory. Each geometry optimization resulted in a vibrationally stable optimized structure; the energies for each compound are given in Tables 1 and 2. The Gaussian calculations were carried out, variously, on Alliant FX-2800 and Multiflow-Trace minisupercomputers. The structures for the molecules were verified by constructing ball and stick models of each species directly from the optimized coordinates using the Molecular Editor application on a Mac-IIci computer.

The (Gaussian) geometry optimized coordinate output for each molecule was subsequently used as the input coordinate set for IGLO calculations which were then carried out at the DZ level. The projected ^{11}B chemical shielding values, determined from IGLO calculations, were referenced to B_2H_6 as the primary reference point, and these δ values were then converted to the standard F_3B:OEt_2 scale using the experimental value of $\delta = +16.6$ ppm for (B_2H_6),[23] Tables 3 and 4.

3. Results and Discussion

3.1. *nido*-$\mu_{2,3}$-(Me_2B)-B_5H_8, A. Application of the *ab initio*/IGLO/NMR technique to *nido*-$\mu_{2,3}$-(Me_2B)B_5H_8, **A**, see Tables 3 and 4, results in very good agreement between calculational and experimental results and reconfirms the structure proposed by Gaines (Figure 1) for this unusual compound.[14] In particular, the low-field ^{11}B chemical shift of the bridging boron is forecast quite well at both the DZ//3-21G and DZ//6-31G* levels of theory.

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(20) (a) Onak, T.; Friedman, L. B.; Hartsuck, J. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1966**, *88*, 3439−3440. (b) Onak, T.; Dunks, G. B.; Searcy, I. W.; Spielman, J. *Inorg. Chem.* **1967**, *6*, 1465−1471.

(21) Onak, T.; Diaz, M.; Tseng, M.; Herrera, S.; Correa, *M. Main Group Metal Chem.* **1993**, *16*, 271−290.

(22) (a) Gaines, D, F.; Bridges, A. N.; Hayashi, R. K. *Inorg. Chem.* **1994**, *33*, 1243. (b) Getman, T. D.; Krause, J. A.; Shore, S. G. *Inorg. Chem.* **1988**, *27*, 2398.

(23) Onak, T.; Landesman, H. L.; Williams, R. E.; Shapiro, I. *J. Phys. Chem.* **1959**, *63*, 1533.

(24) Brice, V. T.; Shore, S. *Inorg. Chem.* **1973**, *12*, 309.

(25) Remmel, R. J.; Denton, D. L.; Leach, J. B.; Toft, M. A.; Shore, S. G. *Inorg. Chem.* **1981**, *20*, 1270.

Table 2. Energies of $(CH_3)B_6H_9$ and $(CH_3)_2B_6H_8$ Isomers at the 631G* Level

compound	tot. energy, au	rel. energy, kcal/mol	ZPE(NF), kcal/mol	Δ6-31G*//6-31G*+ZPE, kcal/mol
$2\text{-}MeB_6H_9$ = B				
⟨μ-4,5-H⟩ Ba	−193.57605	0.81	99.03	1.00
⟨μ-3,4-H⟩ Bb	−193.57734	0.00	98.83	0.00
⟨μ-2,3-H⟩ Bc	−193.57539	1.23	98.84	1.23
$2,3\text{-}Me_2B_6H_8$ = C				
⟨μ-4,5-H⟩ Ca	−231.92796	1.22	117.99	1.44
⟨μ-3,4-H⟩ Cb	−231.92715	1.73	117.83	1.79
⟨μ-2,3-H⟩ Cc	−231.92558	2.71	117.91	2.86
$2,4\text{-}Me_2B_6H_8$ = D				
⟨μ-5,6-H⟩ Da	−231.92990	0.00	117.77	0.00
⟨μ-4,5-H⟩ Db	−231.92649	2.14	117.97	2.34
⟨μ-2,3-H⟩ Dc	−231.92813	1.11	117.75	1.09
$\mu_{2,3}\text{-}BMe_2\text{-}B_5H_8$ = A	−231.91106	11.82	115.84	9.90

Table 3. IGLO ^{11}B Chemical Shifts (ppm): DZ//3-21G

	B1	B2	B3	B4	B5	B6
$2\text{-}MeB_6H_9$ = B						
⟨μ-4,5-H⟩ Ba	−52.3	21.2	21.2	16.5	4.5	16.5
⟨μ-3,4-H⟩ Bb	−51.1	23.2	18.7	30.2	−8.7	16.4
⟨μ-2,3-H⟩ Bc	−51.8	34.0	18.7	18.3	−9.1	13.9
exptl[a]	−49.4	18.0	18.0	29.8	−5.8	18.0
⟨μ-4,5-H⟩ Ca	−50.8	2.5	28.0	17.6	21.5	15.1
⟨μ-3,4-H⟩ Cb	−50.3	25.7	28.5	19.3	16.4	−10.3
⟨μ-2,3-H⟩ Cc	−51.0	29.5	29.5	14.6	−10.6	14.6
Ca + Cb av[b]	−50.5	21.1	21.1	10.4	18.9	10.4
exptl	−48.4	20.2	20.2	13.1	17.8	13.1
$2,4\text{-}Me_2B_6H_9$ = D						
⟨μ-5,6-H⟩ Da	−49.6	28.5	−9.7	28.5	19.0	19.0
⟨μ-4,5-H⟩ Db	−51.3	2.8	12.9	32.3	17.0	16.8
⟨μ-2,3-H⟩ Dc	−50.2	12.3	−10.4	30.7	14.8	34.3

	B1	B2	B3	B4	B5	Bμ
$\mu_{2,3}\text{-}BMe_2B_5H_8$ = A	−38.3	0.5	0.5	−5.7	−5.7	97.8
A = exptl	−33.3	−4.4	−4.4	−10.4	−10.4	96.5

[a] See ref 15. [b] See Figure 5 and text.

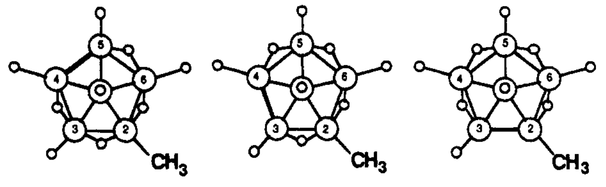
Table 4. IGLO ^{11}B Chemical Shifts (ppm): DZ//6-31G*

	B1	B2	B3	B4	B5	B6
$2\text{-}MeB_6H_9$ = B						
⟨μ-4,5-H⟩ Ba	−52.7	20.0	20.0	17.5	3.5	17.5
⟨μ-3,4-H⟩ Bb	−51.7	21.4	18.4	29.6	−8.3	17.3
⟨μ-2,3-H⟩ Bc	−52.3	31.3	18.2	18.8	−9.0	15.1
exptl[a]	−49.4	18.0	18.0	29.8	−5.8	18.0
$2,3\text{-}Me_2B_6H_9$ = C						
⟨μ-4,5-H⟩ Ca	−51.2	1.9	27.9	17.2	19.9	16.3
⟨μ-3,4-H⟩ Cb	−50.8	25.7	26.8	18.4	17.2	−10.0
⟨μ-2,3-H⟩ Cc	−51.3	29.8	29.8	16.0	−14.5	16.0
Ca + Cb av[b]	−50.0	20.5	20.5	10.4	18.5	10.4
exptl	−48.4	20.2	20.2	13.1	17.8	13.1
$2,4\text{-}Me_2B_6H_9$ = D						
⟨μ-5,6-H⟩ Da	−50.2	28.3	−9.1	28.3	18.2	18.2
⟨μ-4,5-H⟩ Db	−51.8	1.8	14.3	29.9	16.6	17.9
⟨μ-2,3-H⟩ Dc	−50.8	13.8	−10.0	29.8	15.2	31.1

	B1	B2	B3	B4	B5	Bμ
$\mu_{2,3}\text{-}BMe_2\text{-}B_5H_8$ = A	−40.6	−0.4	−0.4	−7.5	−7.5	95.3
A experimental	−33.3	−4.4	−4.4	−10.4	−10.4	96.5

[a] See ref 15. [b] See Figure 5 and text.

Compound **A** was found to rearrange[14] into a more stable dimethyl hexaborane derivative, **C** (or possibly **D**). We have optimized the geometry of the three plausible isomeric structures for *nido*-$2,3\text{-}Me_2B_6H_8$, **C**, and the three plausible isomeric structures for *nido*-$2,4\text{-}Me_2B_6H_8$, **D**, at both the 3-21G and 6-31G* levels of theory. Similarly we have carried out calculations both at the 3-21G and at the 6-31G* level on three candidate structures for *nido*-$2\text{-}MeB_6H_9$, **B**.



Ba (<μ-4,5-H>) Bb (<μ-3,4-H>) Bc (<μ-2,3-H>)

Figure 2. Three isomeric 2-methylhexaboranes, *nido*-MeB_6H_9, **B**. The large white circles are boron atoms; the small white circles are hydrogens.

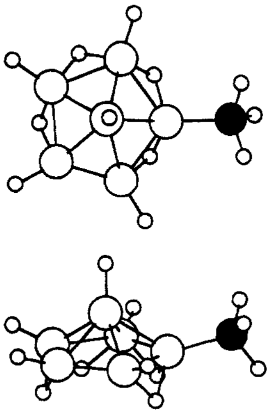
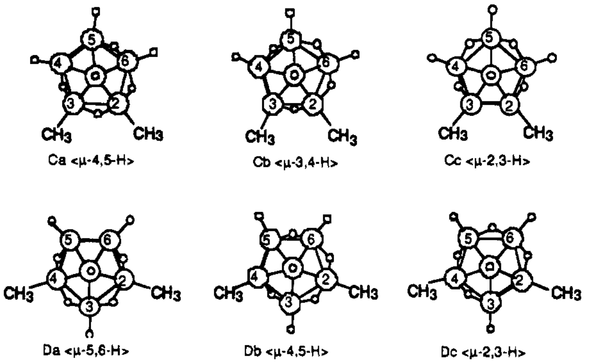


Figure 3. Two perspectives of *nido*-$2\text{-}MeB_6H_9$-⟨μ-3,4-H⟩, **Bb**. The large white circles are boron atoms; the small white circles are hydrogens; the black circle represents a carbon atom. The B−B bond without a bridging hydrogen is located between positions 3 and 4 for the most stable arrangement of bridging hydrogens relative to the *B*-methyl position.

3.2. *nido*-$2\text{-}MeB_6H_9$, B. It was expected, *assuming presumption 4 was correct*, that all four bridging hydrogens in *nido*-$2\text{-}MeB_6H_9$, **B**, would prefer locations closest to the boron to which the methyl group was attached, in spite of the potential steric hindrance of the methyl group, and that the most symmetrical structure would be favored. If this pattern had been correct then it would follow that the various isomers of *nido*-$2\text{-}MeB_6H_9$, **B**, would be progressively less stable in the order **Ba** > **Bb** > **Bc** as displayed in Figure 2.

The bridge hydrogen position isomers, **Ba**, **Bb**, and **Bc**, are identified by the *one basal location lacking a bridge hydrogen* rather than the four locations where bridge hydrogens are present.[1] The low temperature NMR results of Shore et al.[15] are compatible only with the unsymmetrical structure **Bb** (Figure 3) as the correct structure in solution. We were concerned about this structural assignment only because it seemed to be a one-of-a-kind exception with respect to the placement of bridging



Ca <μ-4,5-H> Cb <μ-3,4-H> Cc <μ-2,3-H>

Da <μ-5,6-H> Db <μ-4,5-H> Dc <μ-2,3-H>

Figure 4. Six isomeric dimethylhexaboranes, *nido*-$Me_2B_6H_8$; three isomers of **C** (methyls on adjacent basal boron atoms); and three isomers of **D** (methyls on nonadjacent basal boron atoms). The large white circles are boron atoms; the small white circles are hydrogens.

hydrogens (see above). However, our *ab initio*/IGLO/NMR results, Tables 3 and 4, fully support Shore's structural assignment.

It is important that qualitative rules rationalizing bridge hydrogen location and preferences be developed, and thus Shore's unsymmetrical structure may have far ranging implications with respect to the underlying rules governing bridge (or "agostic" hydrogen dispositions in many reactions and structures involving not only polyboranes and carboranes but also including carbocations and organometallic compounds in general. Several types of bridging hydrogens (associated with two other atoms via 3c2e bonds) are recognized, including the hydrogens in H_3^+, the unique HCH group in CH_5^+, and the BHB groups in the polyboranes. The agostic hydrogens of organometallic chemistry are a simple extension of this pattern and include MHC groups where all three atoms furnish one orbital to a 3c2e bond.

Bridging hydrogens do occupy sites directly neighboring the boron to which the Me group is attached in **Bb** (as anticipated by presumption 4) but it appears that the effect does not extend to the more remote sites, otherwise **Ba** would be most stable. Presumption 4 is thus limited and must be viewed with suspicion. The very small energy differences calculated between **Ba**, **Bb**, and **Bc** in Tables 1 and 2, e.g. $\Delta = 1.0$ and $\Delta = 1.23$ kcal/mol, may be considered almost negligible, however, it is satisfying that the total energy of Shore's isomer, **Bb**, is lower than that for the other two isomers.

3.3. *nido*-2,3-$Me_2B_6H_8$, C. The *ab initio*/IGLO/NMR calculated chemical shift values for any one of the "static" or individually fluxional species (**Ca**, **Cb**, **Cc**, **Da**, **Db**, **Dc** in Figure 4) are not compatible with the experimental data. However, if a rapid equilibrium is occurring (Figure 5) between an approximate equimolar mixture of the two isomers, *nido*-2,3-$Me_2B_6H_8$-⟨μ-4,5-H⟩, **Ca**, and *nido*-2,3-$Me_2B_6H_8$-⟨μ-3,4-H⟩, **Cb**, (and their mirror images, **Ca′** and **Cb′**), all four of which contain one bridging hydrogen between their neighboring BMe groups, then reasonable agreement is found between the calculated values and the experimental chemical shift values. The tiny energy difference between isomers **Ca** and **Cb**, ≤ 0.25 kcal/mol (Tables 1 and 2), supports the assumption of (nearly) equimolar quantities. Interconversion between **Ca** and **Cb** (and their mirror images) may be easily achieved by simple bridge hydrogen tautomerism around the B−B edges of the pentagonal open face of the hexaborane pyramid. The isomer **Cb**, 2,3-$Me_2B_6H_8$-⟨μ-3,4-H⟩, has the vacant site next to one of the BMe groups which casts further doubt on presumption 4. Low temperature studies of *nido*-2,3-$Me_2B_6H_8$, **C**, would be of great interest.

3.4. *nido*-2,4-$Me_2B_6H_8$, D. That *nido*-2,3-$Me_2B_6H_8$, **C**, was produced is probably the result of kinetic control as it is felt (presumption 2) that *nido*-2,4-$Me_2B_6H_8$, **D**, will ultimately be found to be more stable than **C**. We anticipate, *but in light of the present study are not totally confident*, that the *nido*-2,4-$Me_2B_6H_8$-⟨μ-5,6-H⟩ isomer, **Da**, will be most stable.

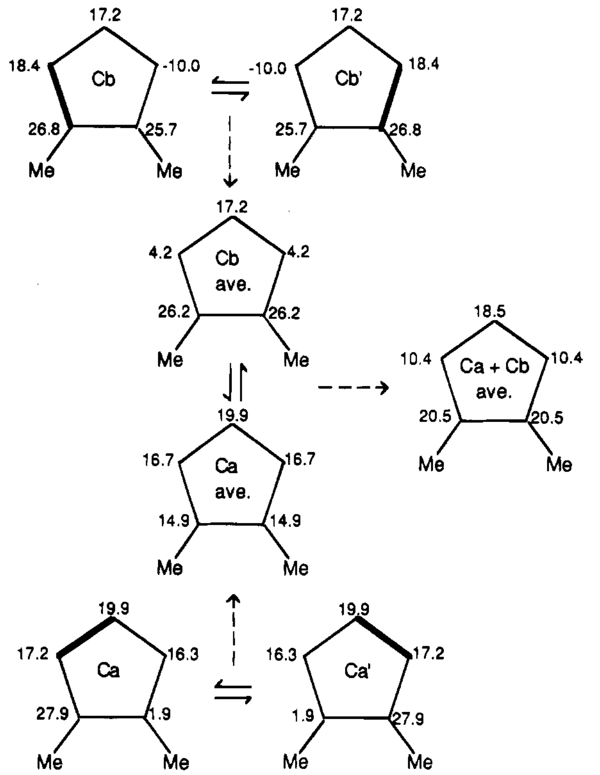


Figure 5. IGLO (DZ//6-31G*) ^{11}B chemical shift values for the *nido*-2,3-$Me_2B_6H_8$ isomers, **Ca** and **Cb**, and averages, upon considering the indicated positions of the B−B ⟨μ-H⟩ bond (darkened line).

4. Distance Measurements

Distance measurements (in Å) derived from geometry optimizations at the 6-31G* level of theory are displayed in Figure 6.

5. Conclusions

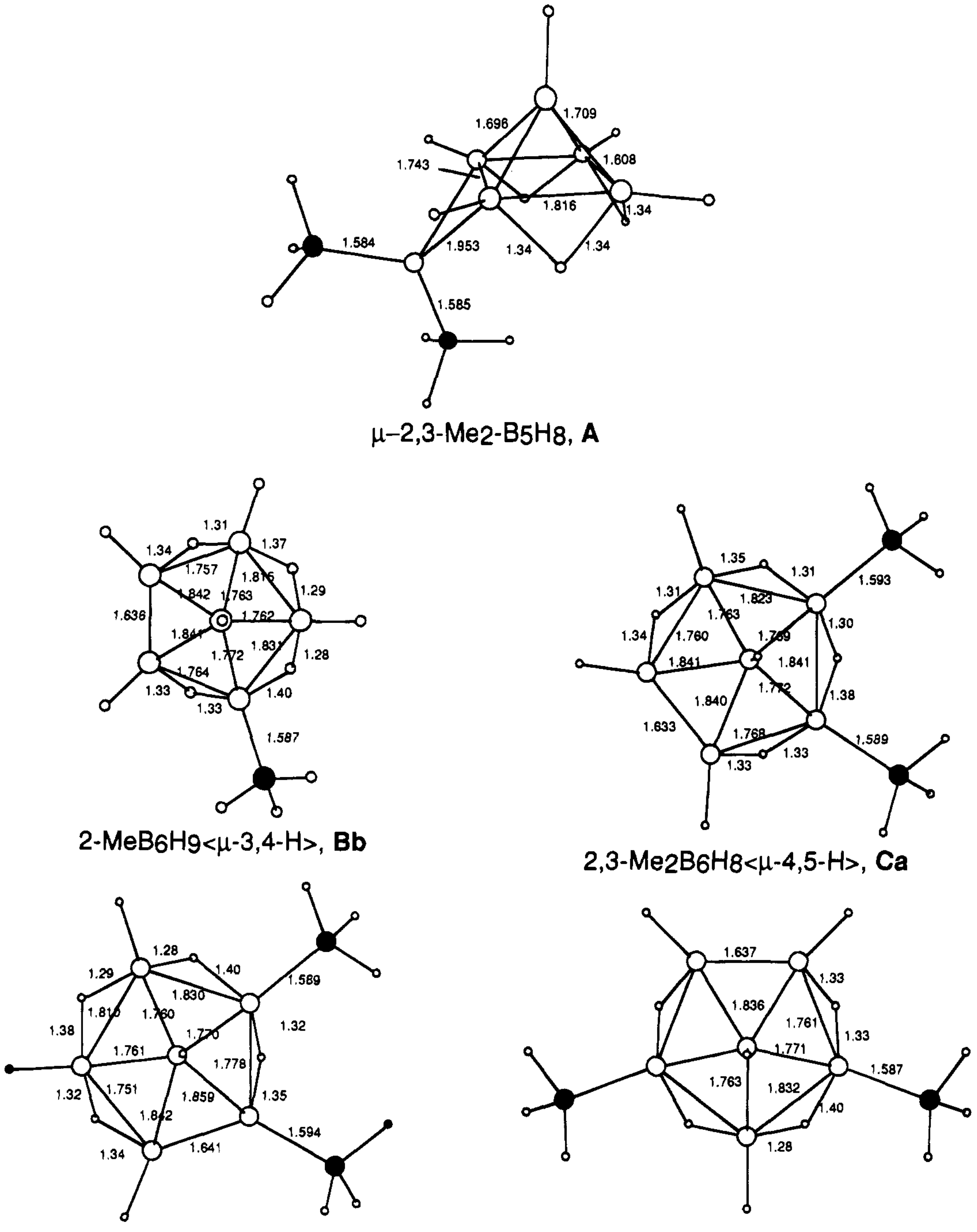
(**a**) Crude presumption number 4 would indicate that *nido*-2-MeB_6H_9-⟨μ-4,5-H⟩, **Ba**, *should have been* more stable than **Bb**. As *nido*-2-MeB_6H_9-⟨μ-3,4-H⟩, **Bb**, is actually most stable, as proposed by Shore[15] and reconfirmed here, it must be concluded that the presumed bridge hydrogen attraction for methyl groups, or the methyl attraction for bridging hydrogens, presumption 4, does not dependably extend beyond nearest neighbors.

(**b**) It appears that *nido*-2,3-$Me_2B_6H_8$-⟨μ-3,4-H⟩, **Cb** is as stable or almost as stable as *nido*-2,3-$Me_2B_6H_8$-⟨μ-4,5-H⟩, **Ca** (Figure 4). As isomer **Cb** has the vacancy next to one BMe group, it must be concluded that presumption 4 does not always apply *even* to nearest neighbors (see point a above).

(**c**) Alternatively, when two adjacent BMe groups are present, **Ca** and **Cb**, one bridge hydrogen is always (thus far) found between the adjacent MeB groups which supports a limited version of presumption 4.

(**d**) Presumption number 3 suggests that *nido*-2,4-$Me_2B_6H_8$, **D**, should be more stable than *nido*-2,3-$Me_2B_6H_8$, **C**. *nido*-2,4-$Me_2B_6H_8$, **D**, will one day be synthesized; we anticipate, with some reservations, that **D** will have the structure, *nido*-2,4-$Me_2B_6H_8$-⟨μ-5,6-H⟩, **Da**.

(**e**) We conclude that low temperature studies in solution of the structures of compounds such as *nido*-2-$MeB_5H_7^-$,[24] *nido*-2,3-$Me_2B_5H_6^-$, *nido*-2-$MeB_6H_8^-$,[25] *nido*-2,3-$Me_2B_6H_7^-$, and



μ-2,3-Me$_2$-B$_5$H$_8$, **A**

2-MeB$_6$H$_9$<μ-3,4-H>, **Bb**

2,3-Me$_2$B$_6$H$_8$<μ-4,5-H>, **Ca**

2,3-Me$_2$B$_6$H$_8$<μ-3,4-H>, **Cb**

2,4-Me$_2$B$_6$H$_8$<μ-5,6-H>, **Da**

Figure 6. Distance measurements (in Å) derived from geometry optimizations at the 6-31G* level of theory.

nido-2,4-Me$_2$B$_6$H$_7^-$ may shed light on the complexities of bridge hydrogen distribution patterns; all have alternative bridge hydrogen or agostic hydrogen vacancies.

(f) Application of the *ab initio*/IGLO/NMR technique to *nido*-$\mu_{2,3}$-(Me$_2$B)-B$_5$H$_8$, **A**, reconfirms the structure proposed by Gaines[14] (Figure 1) for this unusual compound.

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