1634 *Organometallics* **1998,** *17,* 1634−1636

Skeletal Bonding in *closo*-1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH; Y = NH_2, CH_3, H) Cages Is Dictated by Boron Substituents

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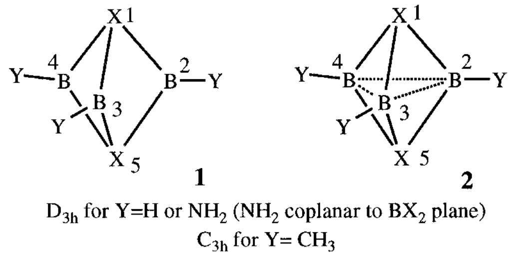
Received November 3, 1997

Summary: Bonding (NLMO bond orders and Bader's topographical analysis), energetic (homodesmotically computed stabilization energies), and magnetic (diamagnetic susceptibility exaltation and NICS) analyses for closo-1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH; Y = NH_2, CH_3, H) reveal the skeletal bonding to be decided by boron substituents.

Is the skeletal bonding in amino (NH_2)- and methyl (CH_3)-substituted five-vertex *closo*-diheteroboranes, 1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH; Y = NH_2, CH_3), classical (**1**) or nonclassical (**2**) (Figure 1)?[1] In striking contrast to most of the earlier conclusions,[2−4] our reexamination of the parent five-vertex cages (Y = H) provided a variety of evidence favoring the nonclassical, three-dimensionally delocalized structures.[4] However, donor substituents such as CH_3 and especially NH_2 (due to the π-donation from the amino group to the "formally" empty p orbital on boron)[4,5] might change the nature of the skeletal bonding, for example from *delocalized* (**2**) to *classical* (**1**). Our present ab initio structural, energetic, and magnetic analyses demonstrate that boron substituents (Y = NH_2, CH_3, H) are indeed decisive in determining the nature of the five-vertex cage bonding.

X-ray structures of several 1,5-$P_2(BNR_2)_3$ cages[6] suggested "a degree of B−N π-overlap" with the exocyclic amino substituent. Burdett and Eisenstein (BE)[3a], using the fragment molecular orbital approach and the Mulliken populations, concluded that 1,5-$P_2B_3(NH_2)_3$ and other 1,5-$X_2B_3Y_3$ molecules (X = CH, P, SiH) for the parent (Y = H, NH_2) had classical structures (**1**, Figure 1). Mulliken population analysis[7] or Wiberg bond indices and natural bond orbital analysis deduced the nonclassical bonding (**2**) for Y = H. These descriptions were supported by the energetic and magnetic criteria as well.[4] Furthermore, recent X-ray analyses of 1,5-$C_2B_3Et_5$[8,9] suggested multicenter bonding at the B−C−B face of the trigonal bipyramid.[8] On the basis of the significantly delocalized deformation electron density (DED) maps of the B−C−B faces in the 1,5-$C_2B_3Et_5$ cage, Antipin et al.[9] concluded that "the contribution of the nonclassical multicenter bonding to the electronic structure of the molecule has probably the same importance as the conventional two-center one." We now describe the results of a closer examination of the electronic structure of NH_2- and CH_3-substituted 1,5-*closo*-diheteroboranes (Figure 1). In contrast with BE's conclusion (**1** for Y = H, NH_2), we show that the bonding in Y = H and Y = NH_2 systems is quite different.



1 **2**

Figure 1. Classical (**1**) and nonclassical (**2**) bonding representations for *closo*-1,5-$X_2B_3Y_3$ cages.

The geometries of 1,5-$X_2B_3Y_3$ and the reference molecules **3**−**5** were optimized at MP2(fc)/6-31+G* (MP2).[10] Homodesmotic reactions (eqs 1−3) were used to evaluate stabilizations due to the hyperconjugation and to

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[1] A classical species can be adequately represented by a single Lewis structure involving simple 2c−2e bonds. A nonclassical species, on the other hand, cannot be represented adequately by a single Lewis structure. Nonclassical bonding is characterized by electron sharing or delocalization among three or more nuclei, rather than just two. Brown, H. C. (with comments from Schleyer, P. v. R.) *The Nonclassical Ion Problem*; Plenum Press: New York, 1977, pp 40, 49.

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S0276-7333(97)00959-X CCC: $15.00
Publication on Web 04/07/1998

Table 1. Total (Hartrees) and Zero Point Energies (ZPE, kcal/mol), Interatomic Distances (*D*, Å), Natural Localized Molecular Orbital/Natural Population Analysis Bond Orders (NLMO), and Density Values ($\rho(r)$, Au) of *closo*-1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH; Y = NH_2, CH_3, H) Molecules

				B−X			B−B		
molecule	sym	total energy[a]	ZPE[b]	*D*[a]	NLMO	$\rho(r)$[c]	*D*[a]	NLMO	$\rho(r)$[d]
$N_2B_3(NH_2)_3$	D_{3h}	−351.053 17	70.2	1.527	0.598	0.171	1.808	0.387	0.108
$C_2B_3H_2(NH_2)_3$	D_{3h}	−318.930 32	85.1	1.574	0.720	0.168	1.932	0.357	0.093
$P_2B_3(NH_2)_3$	D_{3h}	−9023.451 43	65.7	1.940	0.971	0.130	2.086	0.412	0.070
$Si_2B_3H_2(NH_2)_3$	D_{3h}	−820.835 96	75.9	2.021	0.897	0.105	2.580	0.139	0.043
$N_2B_3(CH_3)_3$	C_{3h}	−302.852 09	88.6	1.521	0.625	0.169	1.780	0.510	0.112
$C_2B_3H_2(CH_3)_3$	C_{3h}	−270.739 09	103.6	1.560	0.766	0.167	1.871	0.514	0.101
$P_2B_3(CH_3)_3$	C_{3h}	−875.255 04	83.6	1.918	1.046	0.130	1.922	0.755	0.089
$Si_2B_3H_2(CH_3)_3$	C_{3h}	−772.608 75	92.9	1.974	0.939	0.105	2.311	0.431	0.058
$N_2B_3H_3$	D_{3h}	−185.288 91	32.3	1.516	0.646	0.171	1.759	0.531	0.115
$C_2B_3H_5$	D_{3h}	−153.191 26	47.2	1.554	0.787	0.167	1.844	0.553	0.104
$P_2B_3H_3$	D_{3h}	−757.715 02	27.0	1.909	1.096	0.130	1.856	0.869	0.098
$Si_2B_3H_5$	D_{3h}	−655.074 56	35.9	1.941	0.975	0.105	2.078	0.725	0.076

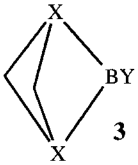
[a] MP2(fc)/6-31+G*//MP2(fc)/6-31+G*. [b] HF/6-31+G*//HF/6-31+G*. All structures correspond to minima. [c] HF/6-311+G**//MP2(fc)/6-31+G*-computed $\rho(r)$ at the (3,−1) B−X bond critical point. [d] HF/6-311+G**//MP2(fc)/6-31+G*-computed $\rho(r)$ at the (3,+1) X−B−X−B four-membered-ring critical point.

the "three-dimensional delocalization". The diamagnetic susceptibility exaltations[11] (Λ, evaluated using eq 3) and the nucleus-independent chemical shifts (NICS)[12] were computed at the CSGT-HF/6-311+G**[13] and GIAO−HF/6-311+G**[14] levels, respectively, on the MP2-optimized geometries (Tables 1 and 2). The nature of the bonding in the parent five-vertex diheteroboranes (**2**), deduced earlier[4] from the geometric, energetic, and magnetic criteria, is compared with the present results in Tables 1 and 2.

$$3\,(\mathbf{3}) \rightarrow \mathbf{1} \text{ or } \mathbf{2} + 2\,(\mathbf{5}) \qquad (1)$$

$$2\,(\mathbf{3}) \rightarrow \mathbf{4} + \mathbf{5} \qquad (2)$$

$$\mathbf{5} + 3\,(\mathbf{4}) \rightarrow \mathbf{1} \text{ or } \mathbf{2} + 3\,(\mathbf{3}) \qquad (3)$$



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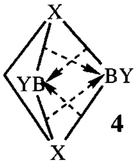

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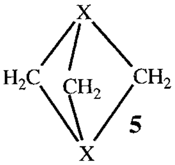

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With each substituent (Y = NH_2, CH_3, H), the trends in the B−B distances correlate well with the electronegativity difference (X = N > C > P > Si)[15] between the boron and the vertex (X) atoms. Similarly, for a given vertex (X), the B−X distances and the B−B separations consistently become shorter from Y = NH_2 to CH_3 to H (Table 1).

The exothermicities of the homodesmotic reaction (eq 1, Table 2) are due both to the "three-dimensional aromaticity"[16] and the hyperconjugative stabilization[17] from the 12 B−X···B(p) interactions (such interactions are represented schematically by dashed arrows in **4**) in 1,5-$X_2B_3Y_3$. Assuming strain effects to be balanced in the closely related reference cages, eq 2 evaluates only the hyperconjugative stabilization energy (HSE, Table 2) from the four B−X···B(p) interactions (indicated by dashed arrows in eq 2) in **4**. The magnitude of the HSE (which can be quite appreciable) depends not only on X but also on the boron substituents Y (H, CH_3, NH_2). Thus, the B−X···B(p) hyperconjugative stabilization (Table 2) of methyl-substituted diheteroboranes is comparable to that in the parent cage (Y = H). However, the amino-substituted counterparts (Y = NH_2) have diminished HSE's due to the exocyclic B═N character.[6] The electron donation from nitrogen weakens the cage hyperconjugative stabilization in **1** (or **2**) and **4** (Table 2). The hyperconjugative interactions in **1** (or **2**) are also reflected in the NLMO (natural localized molecular orbital/natural population analysis) bond orders. Thus, the significant B−B NLMO bond orders in Table 1 do not result alone from the direct interaction between the two boron centers but are consequences of the four B−X···B(p) interactions involving the two boron nuclei.[18] Bader's atoms in molecules (AIM) theory[19] shows all the B−X's to be directly bonded as (3,−1) critical points (CP's) to be located between these nuclei. The density values ($\rho(r)$) at the (3,−1) B−X CP's (Table 1) are quite insensitive to the boron substituents (Y) but vary with

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[12] (a) The nucleus-independent chemical shift (NICS) is defined as the negative of the absolute magnetic shielding. Computed, for example, at the geometrical center of a ring (cage) molecule, significant negative NICS values imply diatropic ring currents and, hence, aromaticity. Paratropic ring currents are characterized by positive NICS values at or above ring centers. (b) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

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[17] (a) Hyperconjugation is defined as the donation of electron density from the occupied symmetry-related σ-bonds to the formally empty p- or π-orbital of the conjugated fragment of a molecular entity. Thus, the C−H bond eclipsing the empty p-orbital on boron in H_3C-BH_2 (C_s) is a classic example of hyperconjugation. Similarly, the hyperconjugation in **1** or **2** and **4** involves the interaction between the formally empty p-orbital on boron, B(p), in the equatorial plane of the trigonal bipyramid and the neighboring B−X bonds (B−X···B(p)). (b) Minyaev, R. M.; Quapp, W.; Schleyer, P. v. R.; Subramanian, G.; Mo, Y. *J. Comput. Chem.* **1997**, *18*, 1792.

[18] The B−B NLMO bond orders in **4** also follow a similar pattern with no direct bonding between the borons (except for 1,5-$P_2B_3H_3$, where the NBO analysis predicts direct B−B bonding). At the HF/6-31+G*//MP2(fc)/6-31+G* level the B−B NLMO bond orders for Y = NH_2 are 0.293 (N), 0.228 (CH), 0.309 (P), and 0.082 (SiH). The corresponding values for Y = CH_3 are 0.359 (N), 0.306 (CH), 0.489 (P), and 0.113 (SiH). For the parent 1,5-$X_2B_3H_3$, they are 0.198 (N), 0.310 (CH), 0.995 (P), and 0.109 (SiH), respectively.

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Table 2. Reaction Energies from Eq 1 (RE, kcal/mol),[a] Hyperconjugative Stabilization Energy from Eq 2 (HSE, kcal/mol),[a] Stabilization Energy (SE, kcal/mol),[a] Magnetic Susceptibility Exaltation (Λ, ppm Cgs)[b] from Eq 3, and Nucleus-Independent Chemical Shifts (NICS, ppm)[c] for *closo*-1,5-$X_2B_3Y_3$ (X = N, CH, P, SiH; Y = NH_2, CH_3, H) Molecules

X	RE	HSE	SE	Λ	NICS
			Y = NH_2		
N	−29.6	−8.6	−3.8	0.6	−7.2
CH	−42.7	−11.2	−9.1	−1.4	−15.4
P	−41.9	−13.2	−2.3	−4.4	−6.5
SiH	−12.5	−2.1	−6.2	−3.9	−10.3
			Y = CH_3		
N	−46.8	−12.9	−8.1	0.1	−7.4
CH	−67.1	−16.5	−17.6	−7.2	−15.0
P	−67.1	−14.1	−24.8	−40.8	−11.6
SiH	−31.1	−4.6	−17.3	−19.0	−13.6
			Y = H		
N	−51.9	−14.5	−8.4	0.5	−10.2
CH	−75.2	−18.5	−19.7	−6.9	−17.1
P	−96.0	−24.7	−21.9	−23.3	−18.2
SiH	−46.1	−5.6	−29.3	−36.6	−22.4

[a] MP2(fc)/6-31+G*//MP2(fc)/6-31+G*. [b] CSGT-HF/6-311+G**//MP2(fc)/6-31+G*. [c] GIAO−HF/6-311+G**//MP2(fc)/6-31+G*.

the nature of X ($\rho(r)$ for N > CH > P > SiH). In contrast, (3,−1) CP's do not exist between any of the borons, supporting the absence of direct B−B connectivity. However, three (3,+1) CP's (rather than (3,−1) CP's) characterizing X−B−X−B rings are located between each pair of BB atoms. The (3,+3) CP's show 1,5-$X_2B_3Y_3$ molecules to possess cage structures. That the boron atoms in the cage are not directly bonded also concurs with the absence of significant DED peaks between the borons in 1,5-$C_2B_3Et_5$[9] and also with the DED maps obtained from spherical charge density analysis for 1,5-$C_2B_3H_5$.[2c]

The homodesmotic reaction (eq 3), obtained by reorganizing eqs 1 and 2 (eq 3 = eq 1 −3(eq 2)) balances the hyperconjugative interactions and measures the stabilization due to three-dimensional delocalization (SE). The SE's of 1,5-$X_2B_3(NH_2)_3$ cages are much smaller than 1,5-$X_2B_3(CH_3)_3$ SE's, which again are lower than 1,5-$X_2B_3H_3$ SE's (Table 2). Furthermore, 1,5-$P_2B_3(NH_2)_3$ possesses the lowest SE (2.3 kcal/mol) in the amino series (Y = NH_2) and substantiates the classical description (**1**) deduced by BE.[3] Similarly, the significant SE (17.7 kcal/mol) for 1,5-$C_2B_3H_2Me_3$ corroborates the partially nonclassical description (**2**) proposed for 1,5-$C_2B_3Et_5$.[9]

Three-dimensionally delocalized "aromatic" structures exhibit large exaltations (Λ),[11,20] as demonstrated earlier for the 1,5-$X_2B_3H_3$ species (Table 2).[3] The very low Λ values for the amino-substituted cages indicate predominantly classical bonding (**1**) with all the vertexes X. In contrast, delocalized, nonclassical behavior (**2**) is shown by the appreciable exaltations (Λ, Table 2) for the corresponding methyl analogues (Y = CH_3; X = CH, P, SiH).

Cage delocalization is indicated by the significantly negative NICS values of the 1,5-$X_2B_3Y_3$ cages (Table 2), which vary with the vertex atom X (N, CH, P, SiH), but show clear trends to more positive values along the Y = H, CH_3, NH_2 series. While a direct relationship between the SE, Λ, and NICS only exists for Y = H, all the three criteria (SE, Λ, and NICS) suggest the bonding in 1,5-$N_2B_3Y_3$ (Y = NH_2, Me) and 1,5-$P_2B_3(NH_2)_3$ to be predominantly classical (**1**). In contrast, large values for both SE and Λ for 1,5-$P_2B_3Me_3$ support a nonclassical description (**2**). The SE and NICS order is the same for the amino-substituted cages (**1**) and the NICS value is the largest for 1,5-$C_2B_3Y_3$ (Y = NH_2, CH_3).

In conclusion, the SE, Λ, and NICS data demonstrate the bonding in the amino-substituted *closo*-diheteroboranes to be predominantly classical (**1**). However, the methyl-substituted analogues (for X ≠ N) have nonclassical, three-dimensionally delocalized structures (**2**), similar to the parent (Y = H) systems. The bonding deduced for the experimentally characterized 1,5-$P_2B_3(NR_2)_3$ (classical)[4] and 1,5-$C_2B_3Et_5$ (nonclassical)[5,6] derivatives is supported by all these criteria. 1,5-$P_2B_3Me_3$ and 1,5-$C_2B_3Me_3$ (or other alkyl-substituted derivatives) are predicted to exhibit stronger cage delocalization than 1,5-$N_2B_3Me_3$ and 1,5-$Si_2B_3Me_3$. Hyperconjugation also is important in these cage molecules. For example, each B−C···B(p) interaction results in a ca. 4 kcal/mol stabilization, and there are 12 such interactions in 1,5-$C_2B_3H_5$. The computed HSE values (Table 2) reveal 1,5-$X_2B_3(CH_3)_3$ species to enjoy larger stabilization than their 1,5-$X_2B_3(NH_2)_3$ counterparts, although 1,5-$X_2B_3H_3$ (X = N, CH, P, SiH) benefits the most. With additional support from the AIM topographical analysis that demonstrates the absence of a direct B−B connectivity and the NLMO bond orders, the much debated issue of the bonding in *closo*-1,5-$X_2B_3Y_3$ cages is resolved.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie, as well as the Alexander von Humboldt Foundation (postdoctoral fellowship to G.S.). The authors also thank Dr. Jürgen Kapp, Dr. Matthias Hofmann, and Professor Eluvathingal D. Jemmis for discussions.

OM9709594

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