Inorg. Chem. **1985**, *24*, 765-767 **765**

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Ab Initio Study of Additivity. 3. Application to Transition States for Rearrangements of B_5H_9

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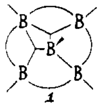
The MNDO semiempirical molecular orbital method yields five optimized structures for B_5H_9, each of which is predicted to be more stable than the observed structure of C_{4v} symmetry. When polarization functions (d orbitals on B) and correlation corrections (Møller–Plesset perturbation of the SCF wave function to orders 2 and 3) are included, the observed nonclassical structure is predicted to be the most stable of all of these structures. Models for rearrangement of 1-substituted (apex) to 2-substituted pentaboranes are suggested from two of these less stable structures. The one of C_2 symmetry has a vacant orbital and may be favored as an intermediate when a Lewis base is available, while the other of C_s symmetry is based on the DSD rearrangement mechanism and may be favored for isomerization in the absence of a Lewis base.

Introduction

Of the many reactions of B_5H_9, exemplified in some references,[1-16] the rearrangements of the 1-alkyl,[1] 1-halo,[3,4] and 1-deuterio,[2,5] derivatives to the 2-position are intramolecular. These isomerizations occur at elevated temperatures in the absence of a Lewis base and at or near room temperature in its presence.[1,10-15] Catalysis by a Lewis base L suggests an intermediate of the type B_5H_9L, for which $B_5H_{10}^-$ is an isoelectronic analogue, or of the type $B_5H_9L_2$ for which the hypho $B_5H_{11}^{2-}$ is an analogue.[17] Structures of $B_5H_9L_2$ where L is $P(CH_3)_3$ have been established by X-ray diffraction methods[18] (Figure 1).

In the absence of Lewis base, an early proposal[19] for the rearrangement of B_5H_8X, where the B–X bond remains unbroken, is here extended to include metastable intermediates. The first candidate for a metastable intermediate is the structure **6**, which was reported by the MNDO method[20] to be more stable than the observed structure of C_{4v} symmetry[1] by 9 kcal/mol. In the MNDO study,[20] diagonalization of the Hessian (force constant) matrix for the C_{4v} structure revealed several imaginary modes. Distortion along one of these modes led to structure **6**. Our study, reported below, has led to several structures **2–6**, which at the MNDO level are incorrectly predicted to be more stable than the observed structure. There may be a general tendency for MNDO to overestimate the stability of classical structures as compared with nonclassical structures.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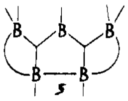
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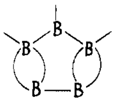
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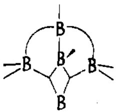
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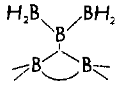
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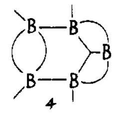
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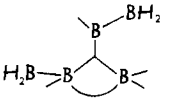
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Theoretical Methods

The MNDO method was used to locate and optimize (within the indicated symmetry) the six structures, which were further examined at the PRDDO (partial retention of diatomic differential overlap) method. Also, from the 6-31G or STO-3G levels, increments in energy were calculated at the 6-31G* and STO-3G* levels (d orbitals on B) and at the MP2/6-31G and MP3/STO-3G levels in order to obtain polarization and correlation corrections. The additivity principle (addition of polar-

Table I. Comparison of Calculated and Observed C_{4v} Geometries of B_5H_9 (Distances in Å; B_1, Apical Boron; B_2 and B_3, Basal Borons)

parameter	3-21G[a]	PRDDO[b]	MNDO[c]	expt[d]
B_2B_3	1.828	1.791	1.863	1.803
B_2B_1	1.709	1.648	1.712	1.690
B_2H_2	1.174	(1.208)[e]	1.160	1.186
B_1H_1	1.175	(1.201)[e]	1.156	1.181
B_2H_μ	1.349	1.356	1.384	1.352

[a] This work. [b] Halgren, T. A.; Kleier, D. A.; Hall, J. H., Jr.; Brown, L. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* 1978, *100*, 6595. [c] Reference 18. [d] Schwock, D.; Burg, A. B.; Beaudet, R. A. *Inorg. Chem.* 1977, 16, 3219. [e] Assumed.

Table II. Relative Energies (kcal/mol) at Different Levels

struct	MNDO	PRDDO	STO-3G	6-31G	[MP2/ 6-31G*]	[MP3/ STO-3G*][a]
1	0.0	0.0	0.0	0.0	0.0	0.0 (0.0)
2	−4.4	9.5	20.6	27.1	59.4	60.5 (53.9)
3	−26.3	−26.4	−11.1	−0.4	46.6	51.9 (41.2)
4	−8.6	11.8	22.4	24.4	39.8	41.2 (39.2)
5	−8.2	7.7	17.8	21.6	40.1	47.5 (43.7)
6	−9.7	2.6	12.4	15.2	31.5	35.6 (32.8)

[a] The first value includes polarization and correlation corrections estimated from the STO-3G basis and used with 6-31G relative energies; the second number (in parentheses) is the relative energy based on corrections from the STO-3G basis (i.e., [MP3/STO-3G*]). All energies are relative to zero for the C_{4v} structure.

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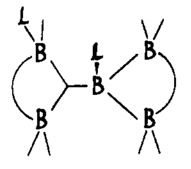

Figure 1. Structure of $B_5H_9·2P(CH_3)_3$.[18] A resonance hybrid is implied in which the three-center bond and the two single bonds are interchanged.

Table III. Contributions from Correlation and Polarization to Relative Energies (kcal/mol) at Different Levels[a]

	STO-3G			6-31G		
struct	correln cor (MP3/ STO-3G)	polarizn cor (STO-3G*)	total cor	correln cor (MP2/ 6-31G)	polarizn cor (6-31G*)	total cor
1	27.9	24.4	52.3	30.3	16.7	47.0
2	6.3	12.7	19.0	3.7	11.1	14.8
3	0.0	0.0	0.0	0.0	0.0	0.0
4	16.4	19.1	35.5	16.8	14.7	31.6
5	12.9	13.5	26.4	17.0	11.5	28.5
6	19.2	12.7	31.9	22.4	8.2	30.6

[a] Here, Structure **3** has been taken as the reference for relative energies because it is the most classical. Positive numbers indicate greater stabilization.

ization and correlation corrections) was then used to approximate the [MP2/6-31G*] or [MP3/STO-3G*] results.[21] We have found that this approximate additivity yields errors of only a few kcal/mol in isomerizations.[22-24] The basis sets refer to the GAUSSIAN 80 program.[25]

Results and Discussion

Geometries of B_5H_9 (C_{4v}) were optimized at the MNDO, 3-21G, and PRDDO levels as indicated in Table I, where the results are compared with experiment. Even though the MNDO method[26-31] indicates that the C_{4v} structure is the least stable, the geometry of this structure is given reasonably well. When the C_{4v} structure was optimized at the 3-21G level, its energy was only 2.5 kcal/mol more stable than that of a 6-31G level result calculated for the geometry that was optimized at the MNDO level. It is, of course, not known whether all six of these structures (**1**–**6**) are at stationary points (maxima or minima) on the potential energy surface. This question can be addressed at a higher level of calculation when budgets for computing permit.

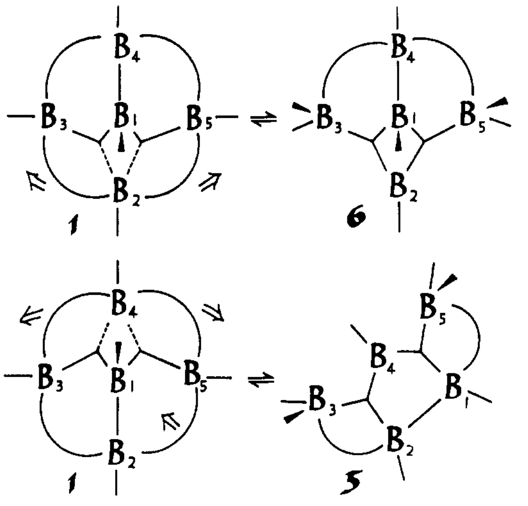

Figure 2. Possible rearrangements of the C_{4v} structure of B_5H_9 to **6** and **5**. As a distorted 3-4-1-2 square forms, the 1-3 bond breaks and the 2-4 bond forms. The 2-5 interaction is broken as the 2-5 bridge shifts to 1-5.

In Table II we summarize the relative energies of the six isomers at the MNDO, PRDDO, STO-3G, and 6-31G levels. Even at the SCF double-ζ level, 6-31G, the classical structure **3**, which has three trigonal boron atoms, is marginally more stable than the C_{4v} structure. We did not study the various isomers of **7** because we expect them to be considerably less stable when polarization and correlation corrections are added. Indeed, when these two corrections are made independently and then added to the 6-31G level (Table II, next to last column), the observed C_{4v} structure is considerably more stable than any of the other structures. The same stabilization is obtained when the two corrections are estimated from the STO-3G basis and then added to the 6-31G basis or when the two corrections are made to the STO-3G basis directly and then added (Table II, last column). The accuracy of this last procedure is fairly reasonable for these boron hydrides and allows extension of the additivity principle to much more complex molecules and reactions. Of course, this last procedure should be used with extreme caution in systems where in–out flexibility is better described by a double-ζ basis set.[22]

In Table III we exhibit separately the contributions from polarization and correlation, starting from either STO-3G (single-ζ) or 6-31G (double-ζ) levels. The two contributions are comparable in magnitude.

The discovery of classical or semiclassical structures for nonclassical molecules by these devious methods may be of value in finding transition states or reaction intermediates, a principle previously realized in this laboratory.[32] The present study is the first computational effort to study the rearrangement mechanisms of B_5H_9. The gas-phase isomerization occurs at about 200 °C, and the Lewis base catalyzed isomerization occurs at or near room temperature. In both mechanisms the apex and equatorial borons are scrambled, but there is no evidence that the substituents on boron are rearranged independently of the boron atoms to which they are attached. Of the several structures, **3** is eliminated because one boron has lost its terminal hydrogen. Structure **2**, the early prediction of Pitzer[33] for the structure of B_5H_9, lies too high in energy (59.4 kcal/mol) for an isomerization at 200 °C

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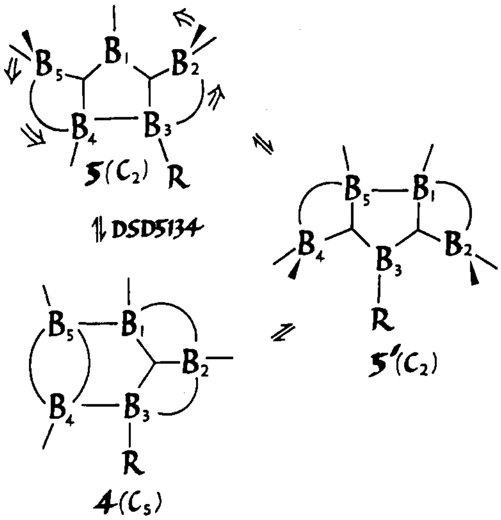

Figure 3. Illustration of scrambling of apical bond positions for the **5** (C_2) and **4** (C_s) structures. The **5** to **5′** conversion involves the indicated hydrogen motions. Two bridging hydrogens (5-4 and 3-2) adopt terminal positions (4 and 2) while two terminal hydrogens (5 and 2) migrate to bridging positions (5-4 and 2-1, respectively). The diamond–square–diamond (DSD)[34] transformation involves the formation of a 5-1-3-4 square and the formation of two bridge hydrogens (2-1 and 5-4) from terminal hydrogens (2 and 5, respectively).

(35–40 kcal/mol), provided that the entropy change is small. Structure **6** does not interchange apical and equatorial boron atoms and is therefore not suitable. The remaining structures are **4** (C_s) and **5** (C_2).

Structure **5** is a reasonable candidate for the low-temperature rearrangement in the presence of a Lewis base, because of the vacant orbital on the middle boron. The transient nature of this complex is consistent with absence of evidence for B_5H_9L adducts under conditions that a stable complex might be expected.[13] Structure **4** does not have a vacant orbital as written, although it could easily develop one if the three-center BBB bond becomes a two-center bond, leaving a vacant orbital on the boron atom at the right. If so, a ligand could bind in a transient intermediate. Finally, two ligands could act simultaneously, yielding intermediates that could be modeled by the X-ray diffraction studies of $B_5H_9L_2$ compounds.[19]

For the high-temperature rearrangement uncatalyzed by a Lewis base, structure **4** is one reasonable candidate. This structure combines a dsd mechanism[34] with a filled orbital structure, retains B–H$_t$ bonds, and does rearrange the apex and equatorial BH units.

In Figures 2 and 3 we summarize motions of atoms that might plausibly occur in these proposed rearrangements, in the expectation that further experimental and theoretical studies will be stimulated.[35]

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Registry No. B_5H_9, 19624-22-7.

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(35) Added Feb 1, 1985: At the 1984 International Chemical Congress of Pacific Basin Societies, Honolulu, HI, Dec 16–21, 1984, D. F. Gaines reported experimental evidence for retention of BH units in the rearrangement of B_5H_9 (paper 07L19), and he suggested a geometrical rearrangement mechanism similar to ours. Also at this meeting, R. Hoffmann suggested that the outer pathway of Scheme I for the rearrangement of $C_5H_5^+$ may give further clues about the rearrangement of B_5H_9 (Stohrer, W.-D.; Hoffmann, R. *J. Am. Chem. Soc.* **1972**, *94*, 1661, especially p 1664). Our preliminary examination of this pathway modified for B_5H_9 in place of $C_5H_5^+$ indicates an intermediate consisting of a BH apex having two hydrogen bridges to a B_4H_8 unit. This C_{2v} structure is 97 kcal/mol less stable than the C_{4v} structure at the [MP2/6-31G*] level after optimization at the 3-21G level. Our mechanism for rearrangement of B_5H_9 may be worth extending to the $C_5H_5^+$ system.

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Kinetics and Mechanisms of the Outer-Sphere Oxidation of *cis*-Aquaoxovanadium(IV) Complexes Containing Quadridentate Amino Polycarboxylates. Interpretation of the Difference in Activation Parameters with the Charge Type of Reactants

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Kinetics of the outer-sphere oxidation of *cis*-aquaoxovanadium(IV) complexes, $[V^{IV}O(pmida)(H_2O)]$ (H_2pmida = [(2-pyridylmethyl)imino]diacetic acid) and $[V^{IV}O(nta)(H_2O)]^-$ (H_3nta = nitrilotriacetic acid), with one-electron oxidants, $[Ir^{IV}Cl_6]^{2-}$ and $[(en)_2Co^{III}(\mu\text{-}NH_2,O_2^-)Co^{III}(en)_2]^{4+}$ (en = ethylenediamine), have been studied by the stopped-flow method in aqueous solution at I = 0.1–1.0 M ($NaClO_4$) (1 M = 1 mol dm^{-3}), pH 3.5–5.0 (acetate buffer, total acetate concentration 0.01 M), and 15–45 °C, under pseudo-first-order conditions with the vanadium complex in large excess. The observed rate law is rate = $(k_{H_2O} + k_{OH}K_a[H^+]^{-1})[V^{IV}][\text{oxidant}]$, where K_a is the acid-dissociation constant for the aqua ligand and k_{H_2O} and k_{OH} are the second-order rate constants for the oxidation of the aqua and the hydroxo complexes, respectively. ΔS^* rather than ΔH^* seems to be responsible for the fact that k_{OH} is ca. 10^3 times bigger than k_{H_2O} for each of the four redox couples. This is explained by the difference in electronic interaction between the redox couples at the transition state (nonadiabaticity) rather than the difference in the Franck–Condon barrier between the aqua and hydroxo complexes. Importance of the solvation for these reactions is discussed on the basis of the dependence of ΔH^* and ΔS^* on the charge product of redox couple.

Transition-metal ions of quadrivalent or higher oxidation states in aqueous media usually possess coordinated oxide ion(s), of which the number tends to increase as the oxidation number increases.[1-3] Oxidation of the metal ions to such higher oxidation states in aqueous solution is mostly accompanied by the formation of an "oxo–metal" bond. "Oxo–metal" bond formation on oxidation of aquated metal ions is coupled with release of the hydrogen ion as exemplified by vanadium(III):[4,5]

$$[V^{III}(H_2O)_6]^{3+} \xrightarrow[-2H^+]{-e^-} [V^{IV}O(H_2O)_5]^{2+} \xrightarrow[-2H^+]{-e^-} [V^V(O)_2(H_2O)_n]^+ \quad (1)$$

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