

Caldwell et al.⁵⁹ noted a surprisingly large deuterium isotope effect of approximately 2 for the cis-trans isomerization of 1-phenylcyclohexene. The authors found little evidence of tunneling and attributed the bulk of this large effect to zero-point vibrations. Other workers⁶⁰ found much smaller isotope effects, barely larger than unity, in bond rotation of formamide and moreover ascribed most of this effect to excitation terms. We have examined this question for the C-N bond rotation that converts our complex IIIa to IIIb and find a situation intermediate between these two extremes. Restricting our discussion first to 300 K, we find that replacement of a single H atom of the NH₃ group by D leads to a value for k_H/k_D of 1.11 whereas full deuteration of all hydrogens yields a larger value of 1.36. In either case, both ZPE and EXC make comparable contributions to the total. Tunneling, as estimated by the Wigner correction, is negligible at 300 K. As the temperature is reduced, k_H/k_D increases; ZPE becomes progressively more dominant and EXC less so. Taking 75 K as an example, the KIE is equal to 1.19 for the singly deuterated case

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and 1.45 for the fully deuterated case. In either case, this value is comprised almost exclusively of ZPE. Wigner tunneling raises both quantities significantly at this lower temperature, to 1.26 and 1.71, respectively. Raising the temperature above 300 K has an opposite effect in that the full k_H/k_D continues to diminish and EXC becomes the sole contributor.

In summary, distorted H-bonds lead to nonlinear transition states. A certain amount of angular strain is allowed before the barrier rises much. The higher barriers are responsible for greatly slowed proton transfer and for larger kinetic isotope effects. There is no justification found for the notion that isotope effects of nonlinear transition states are less pronounced or suffer from reduced sensitivity to temperature.

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Registry No. NH₂CH₂NH₃⁺, 62901-70-6; NH₂(CH₂)₂NH₃⁺, 26265-69-0; NH₂(CH₂)₃NH₃⁺, 26265-70-3; CH₃NH₃⁺, 17000-00-9; D₂, 7782-39-0.

Ab Initio Study of Rearrangement in 1-CH-1,2-C₂B₁₀H₁₁. Evaluation of the Cage Expansion Mechanism

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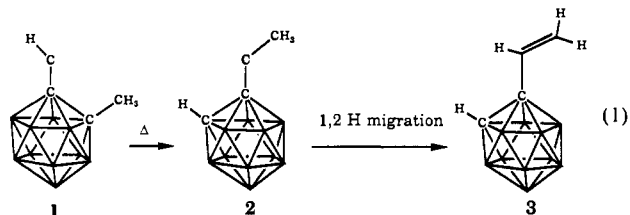
Abstract: Two 13-vertex closo carboranes of molecular formula C₃B₁₀H₁₂ are calculated and compared to the carboranylcarbene, 1-CH-1,2-C₂B₁₀H₁₁, to determine the feasibility of an expanded cage mechanism in the degenerate rearrangement of the carbene. At the MP2/6-31G**/3-21G+ZPC level, an expanded cage is only 3.4 kcal/mol higher than the carbene, which suggests that the mechanism suggested by Jones is indeed possible. Calculations are also reported for the dianion *nido*-C₂B₁₀H₁₂²⁻, which is related to the 13-vertex closo cage by removal of a C²⁺ vertex.

Introduction

As advances are made in carborane chemistry, it can be expected that rational synthetic routes will be developed for the formation of specific cages. One possible means is through cage expansion either by the condensation of coupled cages^{1,2} or by the insertion of an exo substituent into a cage. Jones and co-workers³⁻⁵ have explored the chemistry that results from the attachment of a carbene center to a carbon vertex of *o*-carborane. If the carbene is attached by a flexible tether, a bridge can form by insertion of the carbene into a C-H or B-H bond.⁵ With a short tether, insertion into a C-H or B-H bond becomes more difficult, resulting in a strained three-membered ring when the carbene is

directly attached to the carbon. An alternative pathway might be the insertion of the carbene directly into a boron-boron bond, thereby expanding the cage by one vertex.

The rearrangement of 2-methyl-*o*-carboranylcarbene (1) to 1-vinyl-*o*-carborane (3) as shown in eq 1 was observed by Jones and co-workers.³ A possible mechanism would involve the in-



intermediate 2 which would be expected to undergo 1,2 hydrogen migration to form the observed product 3. While the intermediate 2 was not trapped, conversion of 1 → 3 by a pathway involving direct reaction of the carbene center with the methyl group was shown not to occur by ¹³C labeling.³ Noting that "it would be presumptuous to speculate too much in the absence of further experiments," Jones cautiously suggests³ that the mechanism could involve a cage expansion induced by the divalent carbon to a 13-vertex cage. Interestingly, the analogous 2-methyl-*m*-

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Table I. Absolute (hartrees), Zero-Point (kcal/mol), and Relative Energies (kcal/mol) of Species on the C₂B₁₀H₁₂²⁻ and C₃B₁₀H₁₂ Potential Energy Surfaces

	sym	HF/3-21G	HF/6-31G*	MP2/6-31G*	ZPE(NIF) ^a
2,4-C ₂ B ₁₀ H ₁₂ ²⁻ (4)	C _s	-327.626 87 0.0	-329.476 08 0.0	-330.699 40 0.0	110.44 (1) 0.0
2,5-C ₂ B ₁₀ H ₁₂ ²⁻ (5)	C _s	-327.625 71 0.7	-329.475 56 0.3	-330.694 25 3.2	110.81 (0) 3.5
<i>o</i> -carboranylcarbene (6)	C _s	-365.267 22 0.0	-367.352 98 0.0	-368.662 19 0.0	117.42 (0) 0.0
1,2,4-C ₃ B ₁₀ H ₁₂ (7)	C _s	-365.229 94 23.4	-367.305 92 29.5	-368.654 34 4.9	115.74 (1) 3.4
1,2,5-C ₃ B ₁₀ H ₁₂ (8)	C _s	-365.192 55 46.8	-367.273 14 50.1	-368.628 93 20.9	116.23 (2) 19.8

^aThe number of imaginary frequencies is given in parentheses.

carboranylcarbene does not rearrange to 1-vinyl-*m*-carborane, which might suggest that the C_{carbene}-C_{cage}-C_{cage} linkage in 1 is necessary for rearrangement to occur. The present study explores the feasibility of the cage expansion mechanism.

Methods

All calculations have been made by using the GAUSSIAN 88/90 program systems.⁶ Geometries have been fully optimized in the C_s point group at the HF/3-21G level.⁷ Analytical force constants have been calculated to determine the nature of the stationary point as well as to make zero-point corrections (0.9 weighing factor). Single-point calculations have been made at the MP2/6-31G* level. The latter calculations involved 219 basis functions for C₃B₁₀H₁₂ species and would not have been possible without the development of direct methods which eliminate the need to store 2-electron integrals.⁸

Absolute energies and zero-point energies are given in Table I. Unless otherwise indicated, the energy differences used in the discussion below will be at the MP2/6-31G*/3-21G+ZPC level of theory.

Results and Discussion

The current study builds upon a previous theoretical study of the first two members of the carboranylcarbene series, 1-CH-1,2-C₂B₃H₄ and 1-CH-1,2-C₂B₄H₅.⁹ A carbene center was attached to the smaller carboranes, 1,2-C₂B₃H₅ and 1,2-C₂B₄H₆, rather than *o*-carborane (1,2-C₂B₁₀H₁₂), where experimental observations³ are available, due to computational considerations. Both smaller carboranes have directly bonded carbons in common with *o*-carborane, a fact that may be important since the rearrangement in eq 1 does not occur when cage carbons are non-adjacent.

The global minimum on the potential energy surface for C₃B₃H₅ and C₃B₄H₆ was a cage expanded by one vertex, isoelectronic and isostructural with the next larger carborane.⁹ For 1-CH-1,2-C₂B₃H₄ the expanded cage is isoelectronic with 1,6-C₂B₄H₆ (Figure 1a). The bare carbon atom has an exocyclicly directed lone pair and contributes two electrons toward cage bonding, which makes it isolobal with B-H. In a similar fashion, the global minimum for 1-CH-1,2-C₂B₄H₅ is a carborane isostructural with the seven-vertex carborane, 2,4-C₂B₅H₇ (Figure 1b). It was suggested⁹ that the extra stabilization of the C₂B₁₀H₁₂ cage might stabilize the carboranylcarbene to the point that it was more stable than the 13-vertex expanded cage. At that point, the expanded cage would be a good candidate as an intermediate or transition state in the rearrangement shown in eq 1. One requirement for

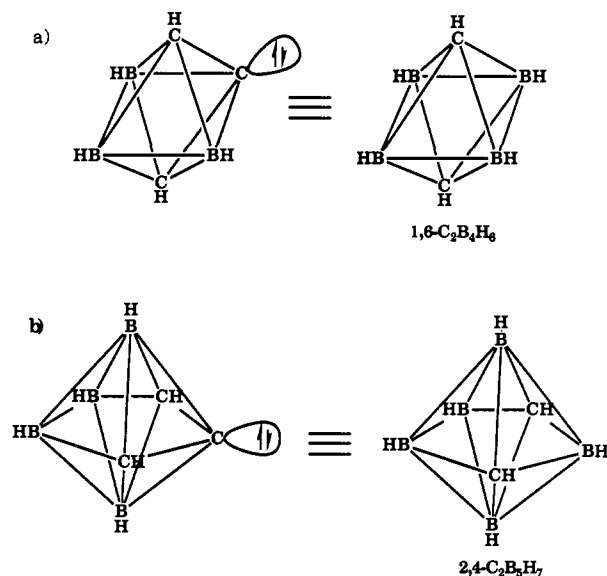


Figure 1. A bare carbon atom with an exocyclicly directed lone pair is isolobal with B-H (i.e. both contribute 2 electrons to cage bonding). (a) The expanded cage of C₃B₃H₅ is isoelectronic with 1,6-C₂B₄H₆. (b) The expanded cage of C₃B₄H₆ is isoelectronic with 2,4-C₂B₅H₇.

a candidate expanded-cage intermediate/transition state is that the two CH groups must be equivalent which would allow their exchange.

As a starting point, two structures of the nido carborane, C₂B₁₀H₁₂²⁻, were calculated. While the structure of the dianion, C₂B₁₀H₁₂²⁻, is unknown, the protonated species, C₂B₁₀H₁₃⁻, is known to exist in two forms: an "unreactive" form where the extra hydrogen is attached to a carbon and a "reactive" form where the extra hydrogen bridges two boron atoms on an open six-membered face.¹¹ An X-ray structure of the dimethyl derivative of the "reactive" form indicates an unsymmetrical hydrogen bridge with one four-coordinate cage carbon and one five-coordinate cage carbon.¹² Experimental NMR chemical shifts, on the other hand, are consistent with either rapidly interconverting unsymmetrical anions or a single stable symmetrical anion.¹¹ On the basis of known structures of metallocarboranes containing the C₂B₁₀H₁₂²⁻ ligand and the structure of the "reactive" form of C₂B₁₀H₁₃⁻, Hawthorne and co-workers¹² anticipate that *nido*-C₂B₁₀H₁₂²⁻ will have a similar structure, i.e. an open six-membered face.

Two structures were considered for C₂B₁₀H₁₂²⁻, both having an open six-membered face with two carbons substituted into the open face in the 2,4 or 2,5 positions (see Figure 2 for numbering and Table II for interatomic distances; the 1-position corresponds to the missing vertex). While the 2,4-isomer is slightly (Table I, 3.5 kcal/mol) more stable than the 2,5-isomer, the calculated vibrational frequencies reveal one imaginary frequency, indicating

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Table II. Calculated Bond Distances at the HF/3-21G Level for the *nido*-C₂B₁₀H₁₂²⁻ Cage (4, 5) and *closo*-C₃B₁₀H₁₂ Cage (7, 8)^a

	2,4-C ₂ B ₁₀ H ₁₂ ²⁻	1,2,4-C ₃ B ₁₀ H ₁₂ (7)	2,5-C ₂ B ₁₀ H ₁₂ ²⁻ (5)	1,2,5-C ₃ B ₁₀ H ₁₂ (8)
C ₁ B ₃		1.684	C ₁ C ₂	2.217
C ₁ C ₄		2.298	C ₁ B ₃	1.830
C ₁ B ₅		1.879	C ₁ B ₇	1.825
C ₁ B ₆		1.526	C ₂ B ₃	1.722
B ₃ B ₈	2.049	2.175	B ₃ B ₄	1.694
C ₄ B ₈	1.959	1.798	C ₂ B ₇	1.574
C ₄ B ₉	1.735	1.635	B ₅ B ₇	1.645
B ₅ B ₉	1.842	1.842	C ₂ B ₈	1.728
B ₅ H ₁₀	1.837	1.796	B ₃ B ₈	1.854
B ₆ B ₁₀	1.767	1.867	B ₃ B ₉	1.881
B ₈ B ₉	1.902	1.894	B ₈ B ₉	1.747
B ₉ B ₁₀	1.759	1.801	B ₈ B ₁₂	1.853
B ₁₀ B ₁₁	1.767	1.846	B ₁₁ B ₁₂	1.828
B ₉ B ₁₃	1.770	1.926	B ₈ B ₁₃	1.793
B ₉ B ₁₃	1.781	1.774	B ₉ B ₁₃	1.813
B ₁₀ B ₁₃	1.838	1.796	B ₁₁ B ₁₃	1.788
				1.836
				1.783

^a All distances are in Å. The numbering convention is found in Figure 2. For the *nido* cages, the vertex at the 1-position is missing.

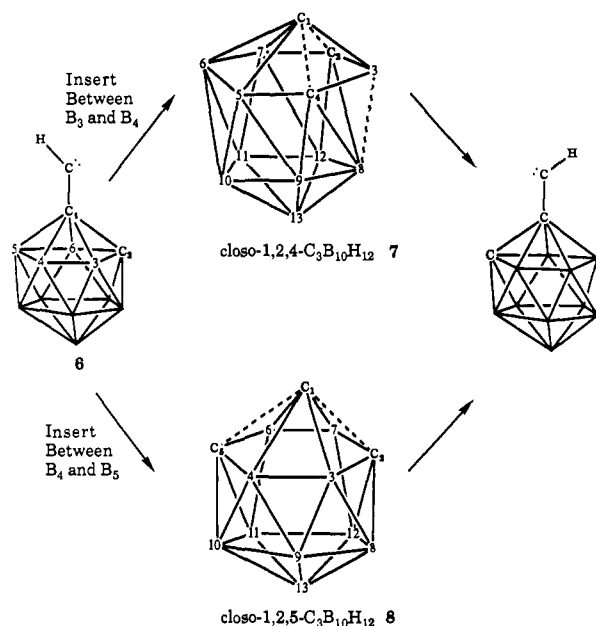


Figure 2. Illustration of possible involvement of an expanded cage in the degenerate rearrangement of the carboranylcarborane, 1-CH-1,2-C₂B₁₀H₁₁. In the top pathway, the expanded cage could form by insertion of the carbene into the B₃B₄ bond while the bottom pathway corresponds to the carbene insertion into the B₄B₅ bond. Structures 7 and 8 represent possible intermediate/transition state candidates in the rearrangement pathway. All atoms have one terminal hydrogen except C₁. The numbering system is used in Table II to designate interatomic distances. Atoms C₁B₃B₈B₁₃B₄ specify the molecular plane in 7 and atoms C₁B₃B₁₃ specify the molecular plane in 8.

an even more stable structure (at the HF/3-21G level) if the symmetry is reduced from C_s to C₁.

Geometry optimization for the expanded cage was started from the C₂B₁₀H₁₂²⁻ structure with a C²⁺ carbon capping the six-membered face. The 2,4-C₂B₁₀H₁₂²⁻ *nido* cage capped with C²⁺ will form the *closo* cage 1,2,4-C₃B₁₀H₁₂ (7), while the 2,5-C₂B₁₀H₁₂²⁻ *nido* cage capped with C²⁺ will form 1,2,5-C₃B₁₀H₁₂ (8). At the HF/3-21G level, 7 is 23.4 kcal/mol less stable than the carboranylcarbene 6 while 8 is 46.8 kcal/mol less stable than

6 (Table I). At the HF/6-31G* level, the differences increase slightly to 29.5 and 50.1 kcal/mol, respectively. Inclusion of electron correlation (MP2/6-31G*) increases the stability of the expanded cages considerably, resulting in 7 and 8 being only 4.9 and 20.9 kcal/mol above 6, respectively. The "best" values with zero-point corrections are 3.4 and 19.8 kcal/mol, respectively.

In both capped cages (7 and 8), the C–C bonds lengthen during geometry optimization to the extent that they appear broken (Table II: C₁C₂ and C₁C₄ distances in 7, C₁C₂ and C₁C₃ distances in 8). However, cage rearrangements often involve substantial geometry changes, and the C–C bond could easily be reformed with little activation. The expanded cage 1,2,4-C₃B₁₀H₁₂ (7) is lower in energy than 8 and is therefore a better candidate for the intermediate/transition state in the rearrangement shown in eq 1. Unless 7 represents an intermediate with a high activation barrier to reform the carboranylcarbene, the degenerate rearrangement 6 → 7 → 6 is expected to occur quite readily. One imaginary frequency is calculated for 7 at the HF/3-21G level, and the corresponding eigenvector has a large displacement of the apical carbon toward one of the CH units.

Conclusion

The size of the system under consideration and the level of theory used (MP2/6-31G**//3-21G+ZPC) preclude an extensive search of the potential energy surface. However, it is clear that an expanded cage is a viable candidate for the intermediate/transition state in the observed rearrangement which interchanges a cage carbon and carbene carbon. Furthermore, the small energy difference between the carboranylcarbene and the expanded cage suggests that with an appropriate substituent on the carbene center, the expanded cage might become an observable product. Calculations indicate that the carbene carbon in carboranylcarbene is positively charged while the equivalent carbons in the 13-vertex cages are negatively charged. Perhaps replacing the hydrogen on the carbene with an electron-withdrawing group such as chlorine would stabilize the 13-vertex cage relative to the carboranylcarbene.

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