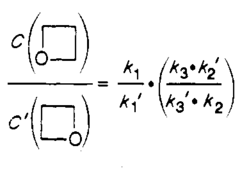
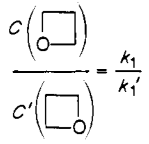

(9)


(10)

For the reaction of dioxol **5** in the high-temperature region an entropy-determined selection ($\Delta\Delta S^{\ddagger} \gg 0$, $\Delta\Delta H^{\ddagger} > 0$) is observed (Figure 1, Table II). According to Price and Hammett,[20] transition states ($\Delta G^{\ddagger}$) resulting from reactants with highly populated degrees of freedom as strongly influenced by entropy. The same considerations have to be made for comparisons of transition states from competitive reaction pathways ($\Delta\Delta G^{\ddagger}$). Nevertheless the selection mechanism corresponds to those described above, because these reactions belong to systems with isoselective points (Figures 1 and 7), which is characteristic for an identical basic mechanism.[15] Thus the matter of isoinversion is based on the same mechanistic pattern.

## Conclusion

It is obvious that this observed competition between enthalpy- and entropy-determined partial selection steps in complex chemical systems may very likely be a general principle, which allows optimization of selectivity either by changing reaction temperature, by structural adaption of a system for a given temperature or by a combination of both.

## Experimental Section

$^1$H NMR and $^{13}$C NMR spectra were recorded on a Varian VXR-300 in $CDCl_3$ as solvent and TMS as internal standard. The solvents and chemicals were purified by general methods.

Racemic *trans*-2-phenylcyclohexanol and *trans*-2-benzylcyclohexanol were synthesized from cyclohexene oxide and the corresponding Grignard reagents according to ref 21. The optically pure alcohols were obtained by enzymatic racemic resolution.[22] (−)-Menthol was kindly provided by Haarmann & Reimer (Holzminden). The phenylglyoxalates **a–c** were synthesized by a modified Stadler method.[23] The dioxols **3** and **4** were obtained by Field's route; dioxol **5** was prepared by our method.[25] Furan (**6**) (Fa. Merck) was distilled under nitrogen and used without further purification.

All temperature-dependent irradiations were carried out under nitrogen in a photoreactor which was fitted with an immersion well (vacuum jacket, Pyrex glass) and a high pressure mercury lamp HPK 125 W (Philips). The photoreactor was plunged in a thermostated bath.

**Irradiation of the Phenylglyoxalates a–c with the 2,2-Disubstituted 1,3-Dioxols 3–5.** Solutions of the esters **a–c** (7 mmol) in toluene (200 mL, 0.035 M) were flushed with nitrogen in the photoreactor. The dioxols **3–5** (8 mmol, 0.04 M) were added after 30 min of thermostatisation. After 8 h of irradiation, the conversion was complete. The solvent was evaporated and the residue was dissolved in dichloromethane, percolated over 25 g of silica gel, and eluated with 250 mL of dichloromethane. The filtate was evaporated and the residue was dried in high vacuum. The diastereomeric oxetane mixtures were obtained as colorless syrups.

**Irradiation of the Phenylglyoxalates a–c with Furan (6).** The photoreactor was charged with the reaction solution (7 mmol of the respective ester **a–c** in 200 mL of furan (**6**), 0.035 M). After 30 min of thermostatisation under nitrogen, the solution was irradiated for 24 h. The furan adducts were obtained as white crystalline solids. The workup was the same as above.

Under the described reaction conditions no further byproducts were formed. The yield of oxetane was nearly quantitative. The diastereomeric ratio of the products was determined by $^{13}$C NMR spectra.[13] Depending on the system, 14–16 signals could be used for the determination of the de values. The values given in the Eyring plots (Figure 1, parts i–v) are the average values, which minimize the influence of different NOE and of spin-relaxation effects. Each point in the Eyring plots (Figure 1, parts i–v) was confirmed by three independent measurements.

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(25) Meier, L.; Scharf, H.-D. *Synthesis* **1987**, 517.

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# The Mechanism of Rearrangement of the Icosahedral Carboranes[1]

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*Received September 19, 1988. Revised Manuscript Received February 7, 1989*

**Abstract:** The bridged *o*-carborane **5** rearranges on heating to all four possible isomers in which the three-carbon bridge spans adjacent positions. These are the new ortho isomer **6** and the three possible *m*-carboranes **7–9**. After 30 min at 450 ± 5 °C, the ratios of **5**/**6**/**7**/**8**/**9** = 39/16/5/16/25. The meta compounds do not interconvert under these conditions. Although the further rearrangement of **6** does take place, the ratio of the three meta compounds changes only slightly with time and can be summarized as **7**/**8**/**9** = 9/34/57. The formation of **9** as the major product is inconsistent with the popular "diamond–square–diamond" mechanism. The extended triangle rotation mechanism, which focuses on the preservation of triangular faces throughout the rearrangement, is suggested to rationalize both data from the literature and the results from the pyrolysis of **5**.

Framework rearrangements are characteristic of polyhedral boranes and heteroboranes, and there have been many attempts to determine the mechanisms of these reactions.[2] The effort to provide a general mechanism capable of rationalizing all data and

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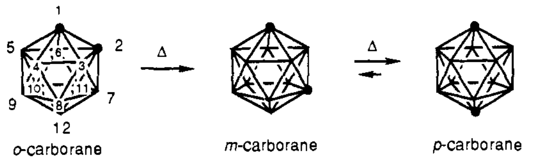
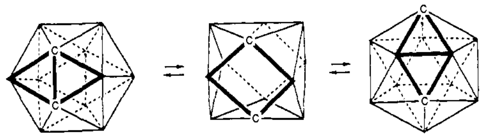


**Figure 1.** The thermal rearrangements of the icosahedral carboranes. The dots refer to CH; all other vertices are BH. The numbering system is given for *o*-carborane.

**Scheme I.** The Interconversion of *o*- and *m*-Carborane through a Cuboctahedral Intermediate



of making trenchant predictions has been frustrated by the complexity of the process, as well as earlier analytical difficulties. At present, the most general mechanism is the "diamond–square–diamond" process, championed mainly by Lipscomb and his co-workers, augmented by weighted rotations of some triangular faces in the postulated cuboctahedral intermediate.[2a,3] Despite the flexilbility afforded by the weighting factors, this complex mechanistic picture still has difficulty explaining some experimental results. We provide here some fresh data bearing upon the existing proposals as well as a new, unifying mechanistic hypothesis.

We will first give brief reviews of the early experimental work and proposed mechanisms. Second, we will present the results from our experiments and discuss the mechanistic significance of these results. Finally, we will elaborate on the role of the triangle-rotation process to establish a general mechanism which provides a unified picture of both the "diamond–square–diamond" and "triangle-rotation" mechanisms.

**The Discovery of Framework Rearrangements.**[4,5] In 1963, Grafstein and Dvorak first reported the thermal isomerization of *o*-carborane to *m*-carborane.[6] A year later, the higher temperature rearrangement of *m*-carborane to the para isomer was described by Papetti and Heying.[7] Numerous studies were subsequently devoted to the rearrangements of icosahedral carboranes and their derivatives under different conditions.[2e] It has been now well-established that the thermodynamic stability of icosahedral carborane isomers increases in the sequence $o\text{-} < m\text{-} < p\text{-}C_2B_{10}H_{12}$ and that at approximately 450 °C *o*-carborane isomerizes wholly to the meta isomer. The para isomer is formed at higher temperature (approximately 600 °C and above) and an equilibrium is established between the 1,7- (*m*-) and 1,12- (*p*-) carboranes (Figure 1).[2e] The enthalpy of activation for the rearrangement of *o*-carborane to *m*-carborane has been reported to be about 62 kcal/mol, with an entropy of activation of about +7.2 eu at 455 °C.[8]

It is necessary to use boron-substituted *o*-carboranes in order to detect interconversions between different ortho isomers. Indeed, studies of boron-halogenated carboranes soon revealed that rearrangements between ortho isomers occur under the conditions of ortho to meta isomerizations.[3]

**Mechanistic Proposals.** Prior to the publication of the experimental discovery of the isomerization of icosahedral carboranes, Lipscomb and his co-workers had proposed a mechanism by which *o*-carboranes could be isomerized to *m*-carboranes.[9] This mechanism (shown in Scheme I) involves a cuboctahedral intermediate (or, conceivably, transition state), and now is generally termed the DSD (diamond–square–diamond) mechanism.

As we know, this proposal was beautifully verified by later experiments when $m\text{-}C_2B_{10}H_{12}$ was reported as the product of heating of $o\text{-}C_2B_{10}H_{12}$ to 425–450 °C.[6] Almost no $p\text{-}C_2B_{10}H_{12}$ was formed under these conditions. The absence of the para isomer was in accord with the DSD mechanism, which cannot give *p*-carborane from either *m*- or *o*-carborane. Following these intellectual and experimental successes, Lipscomb and co-workers elaborated the DSD mechanism to encompass rearrangements in all the known polyhedra.[2a] As shown in Scheme I, the major emphasis of these initial mechanisms is the concept of stretching two common triangulated faces to a square face. The intermediate polyhedron with square faces may then revert to the original polyhedron with no net rearrangement of atoms or achieve a rearrangement by an orthogonal return to triangulated faces.

However, later experiments clearly showed that the thermal rearrangements of icosahedral carboranes were much more complicated than what the DSD mechanism predicted. (We will discuss some of these experiments later.) The discovery of the rearrangement of *m*-carborane to its para isomer at higher temperature was particularly compelling, as the simple DSD process provides no route to *p*-carborane, either from the ortho or from the meta isomer.[7] Therefore, several other mechanisms have been proposed to account for these new experimental results. Among them, four, shown in Scheme II, are the most frequently discussed.

A mechanism based on a cuboctahedral intermediate, but modified by the assumption that the trigonal faces in this intermediate can rotate, is shown in Scheme IIa. This "modified DSD" mechanism can explain the formation of *p*-carborane from *m*-carborane and was originally proposed by Lipscomb and co-workers to account for the composition of the isomer mixture formed in the rearrangement of boron-halogenated *o*-carboranes.[3] These experiments will be discussed later in more detail.

A third mechanism (Scheme IIb), which was proposed by Grafstein and Dvorak[6] and later by Zakharkin and Kalinin,[10] involves the mutual rotation of pentagonal pyramidal halves of the icosahedral cage ("pentagonal rotation"). This mechanism is applicable to the isomerization of *o*-carborane to the meta isomer as well as to the conversion of *m*- to *p*-carborane. The lower barrier for the isomerization of the ortho isomer is explicable on the basis of the relatively high positive charge density on the vicinal carbon atoms. There is, of course, a decreased opposition of charge in the meta isomer, and so the barrier is accordingly higher for its conversion to the final, thermodynamically most favored species, the para compound.

The fourth mechanism (Scheme IIc) involves the rotation of triangular faces in the icosahedral ground state ("120° triangle rotation"). This mechanism, which was proposed by Zakharkin and Kalinin[10] as well as Muetterties and Knoth,[11] also explains the formation of both *m*- and *o*-carborane.

The fifth and last mechanism for the rearrangements of icosahedral molecules differs fundamentally from the others. It was proposed by Wong and Lipscomb and involves the opening of the icosahedral closo cage to give a nido structure which is a fragment

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(1) We are grateful for the support for this work by the National Science Foundation through Grants CHE 86 17590 and 8800448. Professor J. E. Jackson provided most helpful comments on the manuscript. S.-h. Wu thanks the W. R. Grace Company for a Fellowship.

(2) (a) Lipscomb, W. N. *Science* **1966**, *153*, 373. (b) Muetterties, E. L. *Rec. Chem. Prog.* **1970**, *31*, 51. (c) Muetterties, E. L. *MTP Int. Rev. Sci. Inorg. Ser.* **1972**, *9*, 37. (d) Stanko, V. I.; Brattsev, V. A.; Knyazev, S. P. *Russ. Chem. Rev.* **1979**, *48*, 130. (e) Muetterties, E. L. *Boron Hydride Chemistry*; Academic Press: New York, 1975.

(3) Kaesz, H. D.; Bau, R.; Beall, H. A.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1967**, *86*, 4218.

(4) The two-dimensional cousins of the carboranes, the classically aromatic benzenes, undergo their own related automerization, although under much more severe conditions. The mechanism is not fully worked out, but benzvalenes seem likely to be intermediates. A mechanism in which the ring is opened seems not to be involved.[5]

(5) Scott, L. T. *Acc. Chem. Res.* **1982**, *15*, 52. See also: Scott, L. T.; Roelofs, N. H.; Tsang, T.-H. *J. Am. Chem. Soc.* **1987**, *109*, 5456.

(6) Grafstein, D.; Dvorak, J. *Inorg. Chem.* **1963**, *2*, 1123.

(7) Papetti, S.; Heying, T. L. *J. Am. Chem. Soc.* **1964**, *86*, 2295.

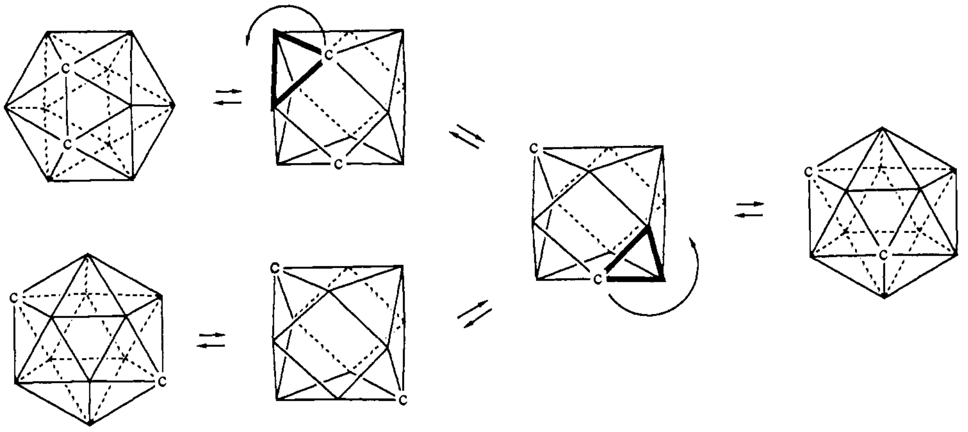
(8) Salinger, R. M.; Frye, C. L. *Inorg. Chem.* **1965**, *4*, 1815.

(9) Kaczmarczyk, A.; Dobrott, R. D.; Lipscomb, W. N. *Proc. Natl. Acad. Sci. U.S.A.* **1962**, *48*, 729.

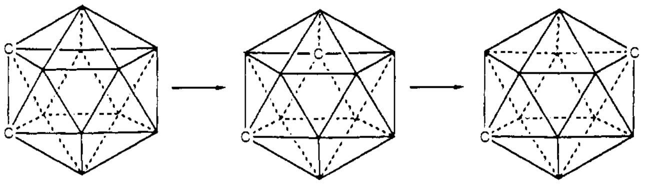
(10) Zakharkin, L. I.; Kalinin, V. N. *Dokl. Akad. Nauk SSSR* **1966**, *169*, 590.

(11) Muetterties, E. L.; Knoth, W. H. *Polyhedral Boranes*; Marcel Dekker: New York, 1968; p 55.

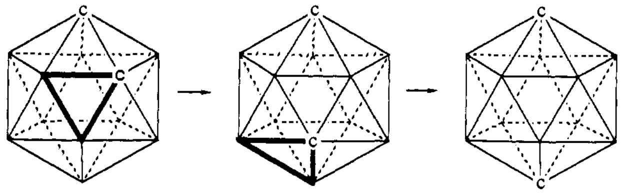
**Scheme II**



(a) Two 120° counterclockwise rotations of the emphasized triangles in the cuboctahedral intermediates leads *o*-carborane to *p*-carborane, probably through *m*-carborane as an intermediate.



(b) The most simple way to generate *m*-carborane from *o*-carborane is to rotate the upper pentagon counterclockwise. A second counterclockwise rotation gives *p*-carborane.



(c) Clockwise rotation of the bold-face triangle 120° gives *m*-carborane, which can undergo a second 120° clockwise rotation, again of the emphasized triangle, to give the para isomer.

**Table I.** Relative Yields (Percent) for the Rearrangement of 9-Bromo-*o*-carborane at 420–425 °C

| *T*, min | 9-Br-*o*- | 8-Br-*o*- | 4-Br-*o*- | 3-Br-*o*- | 9-Br-*m*- | 5-Br-*m*- | 4-Br-*m*- | 2-Br-*m*- |
|---|---|---|---|---|---|---|---|---|
| 30 | 68 | 21 | 3 | 0 | 3 | 4 | 1 | 0 |
| 60 | 52 | 23 | 8 | 1 | 6 | 7 | 3 | 0 |
| 210 | 20 | 14 | 8 | 4 | 15 | 18 | 17 | 4 |
| 330 | 0 | 0 | 0 | 0 | 24 | 28 | 35 | 13 |

of a 13-vertex polyhedron.[12] The reclosure of the polyhedron in other directions leads to the formation of different isomeric products. More recently, Johnson has argued that the rearrangement of a polyhedron might be expected to follow a pathway in which the change in cohesive energy is kept to a minimum.[13] However, it seems that without the imposition of boundary conditions, the "opening-closure" mechanism, being one of the most general, will predict the formation of all possible isomers, and permit the rationalization of any product mixture.

To summarize, there are now five mechanisms on the table: the original, pure DSD reaction, the "modified DSD", "pentagonal-rotation", and "120° triangle rotation" mechanisms and a fundamentally different process, the "opening-closure" mechanism.

We shall now look at early experiments and how they bear upon these mechanistic hypotheses.

**Early Mechanistic Experiments.** In 1966, Zakharkin and Kalinin discovered that more than one meta product was formed in the isomerization of B-9-halogenated *o*-carboranes at 400–420 °C.[10] It was demonstrated by Lipscomb and co-workers in 1967 that a pure DSD mechanism can give only one product, a B-5-labeled *m*-carborane, from a B-9 labeled *o*-carborane.[3]

This 1967 paper also described a more complete experimental investigation of the isomerization of halogenated carboranes. The Lipscomb group found all possible isomers of *B*-monobromo-*o*-carborane during the isomerization of 9-bromo-*o*-carborane (**1**) in the temperature range 395–425 °C and all possible *B*-monobromo-*m*-carboranes in the final reaction products. It was confirmed that the meta products neither reform ortho compounds nor isomerize to other meta products. The ortho carboranes, however, continue to rearrange in this temperature range. These results are summarized in Table I, which gives the percentage yields of reaction products at different times. As the simple DSD mechanism failed to explain these observations, a modified DSD mechanism, which involved selective triangle rotation in the cuboctahedral intermediate (shown in Scheme IIb), was postulated by Lipscomb and co-workers.[3] In order to fit the observed product distribution, two assumptions were made in this modified mechanism: (1) preferential rotation of those triangles furthest removed from carbon and (2) conversion of only 10% of the cuboctahedral intermediates existing at any one time to *m*-carborane products.

In 1969, the study of the rearrangements of icosahedral carboranes was extended to the higher temperature isomerizations

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(12) Wong, H. S.; Lipscomb, W. N. *Inorg. Chem.* **1975**, *14*, 1350.
(13) Johnson, B. F. G. *J. Chem. Soc., Chem. Commun.* **1986**, 27.

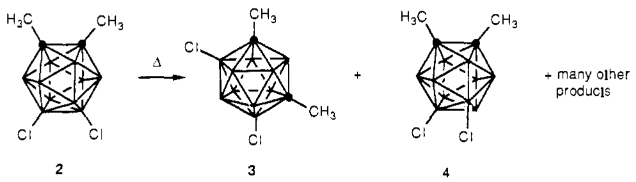

**Figure 2.** The thermal rearrangement of 1,2-dimethyl-9,12-dichloro-*o*-carborane.

that yield *p*-carboranes. Hart and Lipscomb reported that in the rearrangement of any isomer of *B*-monochloro-*m*-carborane at 560–570 °C an equilibrium between all possible meta and para isomers was established.[14] The *initial* product mixture (within the first hour) is clearly different for different starting carboranes. Some of the transformations can be explained by the simple DSD mechanism, but triangle rotations in the cuboctahedral intermediates are required in order to convert 5-chloro-*m*- and -*p*-carboranes to their products. To fit the experimental data, the rotation of those BBC triangles bearing a chlorine was assumed to be favored.[14]

In 1973, the examination of the thermal rearrangements of icosahedral carboranes was extended by Hart and Lipscomb to a dilabeled molecule, 9,12-dichloro-1,2-dimethyl-*o*-carborane, **2**.[15] Because the number of possible rearrangement isomers has now grown to 37 (16 ortho, 16 meta, and 5 para isomers), the study of initial transformations between these isomers, as well as the final product distributions of these reactions, can reveal much more information about the reaction mechanism than any experiment with monolabeled carboranes. Despite difficulties in isolation and identification of the many products, it was shown by X-ray structure analysis that the *principal* compound formed in the isomerization of **2** was 5,12-dichloro-1,7-dimethyl-*m*-carborane, **3** (Figure 2), the *only* one expected from the simple DSD mechanism. At least 15 other meta and ortho products were observed, however. These minor products must result from routes other than the pure DSD. For instance, one of the initial ortho products from **2** is 8,9-dichloro-1,2-dimethyl-*o*-carborane, **4**, which cannot arise from the simple DSD mechanism but could be obtained from triangle rotation in the cuboctahedral intermediate ("modified DSD" mechanism) or triangle rotation in the ground-state icosahedron ("120° triangle rotation" mechanism).

On the basis of the studies of thermal rearrangements of both the mono- and dihalocarboranes discussed above, Wong and Lipscomb suggested that the major mechanism governing the polyhedral isomerization is the DSD process and that products in addition to those produced by the DSD mechanism arose principally from the rotations of triangular faces in the cuboctahedron.[12] Two alternative mechanisms that involve either the rotation of pentagonal pyramids ("pentagonal-rotation" mechanism) or the rotation of a triangular face of the icosahedron ("120° triangle rotation" mechanism) might also contribute to the formation of minor products, but these were not considered important processes.

However, it is clear that introduction of electronic or geometric distortion into the icosahedron might cause a drastic shift in the rearrangement mechanism. For example, the pentagonal-rotation mechanism has been suggested for the icosahedral phosphacarborane $CHPB_{10}H_{10}$. (We will deal with this seemingly odd rearrangement at the end of this paper).

**Comments on the Early Experiments. Our Experimental Approach.** Although it is clear that the use of labels, such as halogen substituents, on various positions of carboranes provides a powerful tool for the study of the rearrangements of these molecules, some criticism of these halogen-labeling experiments has appeared. For example, Zakharkin and Kalinin presented evidence for intermolecular hydrogen–halogen exchange in *B*-iodo- and *B*-bromo-*o*-carboranes under the conditions of polyhedral rearrangements.[16]

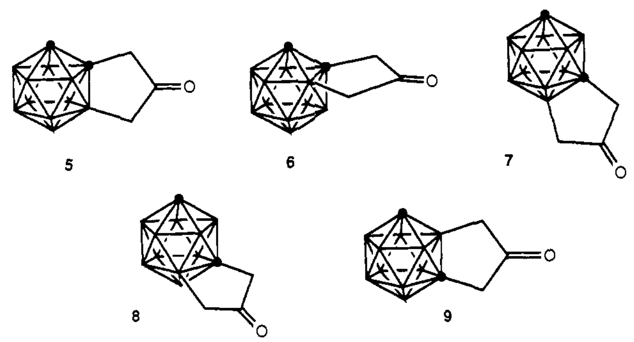

**Figure 3.** There are only four possible ortho and meta isomers of **5**.

**Table II.** Relative Yields (Percent) for the Rearrangement of **5** at 450 ± 5 °C

| *T*, min | **5** | **6** | **7** | **8** | **9** | **7/8/9** |
|---|---|---|---|---|---|---|
| 15 | 86.2 | 0.1 | 1.3 | 4.8 | 7.6 | 1/3.7/5.8 |
| 30 | 38.8 | 16.3 | 4.9 | 15.9 | 24.5 | 1/3.2/5.0 |
| 60 | 20.0 | 14.3 | 6.1 | 22.5 | 37.1 | 1/3.7/6.1 |
| 120 | 1.5 | 5.4 | 7.6 | 30.9 | 54.6 | 1/4.1/7.2 |
| 360 | 0 | 0 | 8.6 | 31.7 | 58.9 | 1/3.7/6.8 |

**Table III.** Relative Yields (Percent) for the Rearrangement of a 1/1 Sample of **5**/**6** at 450 ± 5 °C.

| *T*, min | **5** | **6** | **7** | **8** | **9** | **7/8/9** |
|---|---|---|---|---|---|---|
| 60 | 0 | 13.4 | 4.5 | 20.6 | 61.6 | 1/5/14 |

In view of these observations, the possibility that the rearrangements of halogenated carboranes proceed through either intermolecular or intramolecular hydrogen–halogen exchange reactions must be considered. Intermolecular exchange can be easily checked, and usually this was done. However, we see no easy experiments which can assess the extent of intramolecular hydrogen–halogen exchange reactions. At least one can comment that no examples are known in which a substituent moves from carbon to boron or boron to carbon, a reaction that might have been expected were intramolecular rearrangements facile.[17] It is also usually the case that isolation and identification of the products is very difficult. Thus, many of these early experimental results, some of which must have involved heroic efforts in analytical chemistry, were based upon identification of the various carborane isomers by chromatographic elution times, which, it was assumed, are a direct function of the dipole moments of the compounds. This correlation, however, may not be completely reliable, as shown by chromatographic data on tri- and tetrachloro-*p*-carboranes in which a few differences have been noted between the observed elution times and those expected from dipole moments.[18] We benefit greatly by the passage of time which has seen a vast increase in routine analytical capacity. Further, in our experiments, we have used the bridged *o*-carborane **5** in which a three atom chain connects a cage carbon ($C_1$) to one of its adjacent borons ($B_4$) (Figure 3).[19,20]

There are several advantages in the use of the bridged compound **5** as a model compound in the study of this complex mechanistic problem. Because the bridge in **5** is too short to span meta positions of the icosahedron, the two bridged atoms ($C_1$ and $B_4$) in **5** must remain adjacent throughout all rearrangements. Therefore, the number of possible ortho and meta structures is dramatically reduced from 12, in a hypothetical C,B-dilabeled *o*-carborane, to five, the two ortho and three meta isomers **5–9** (Figure 3). Moreover, the presence of the carbonyl group makes

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(14) Hart, H. V.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1969**, *91*, 771.

(15) Hart, H. V.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 2644.

(16) Zakharkin, L. I.; Kalinin, V. N. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1969**, *3*, 607.

(17) However, Z.-h. Li (Princeton University) has unpublished evidence for such a reaction.

(18) Sieckhaus, J. F.; Semenuk, N. S.; Knowles, T. A.; Schroeder, H. *Inorg. Chem.* **1969**, *8*, 2452.

(19) Wu, S.-h.; Jones, M., Jr. *Inorg. Chem.* **1986**, *25*, 4802.

(20) Wu, S.-h.; Van Engen, D.; Jones, M., Jr. Submitted to *Acta Crystallogr.*

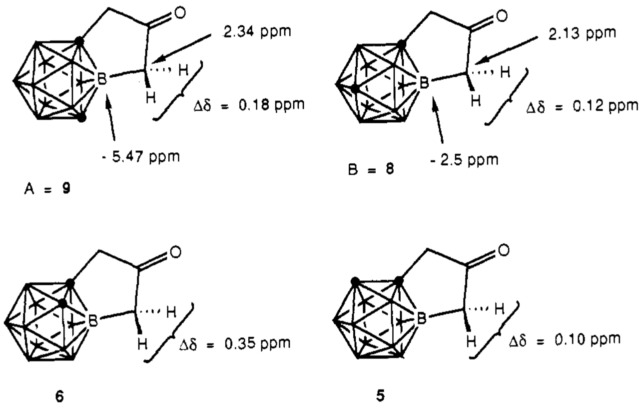


**Figure 4.** In **9**, the framework boron atom bearing the bridge should appear at higher field and the attached methylene at lower field than the corresponding signals in **8**. Also shown are the chemical shift differences ($\Delta\delta$) in the methylene hydrogens adjacent to the bridgehead boron for **8** and **9** and the reference compounds **5** and **6**.

interpretation of the $^1$H NMR spectra relatively easy, as the two methylene groups are isolated and distinct. The isolation and identification of the products are therefore much easier than in earlier work.

## Results

Percentage yields of rearrangement products arising from **5** at 450 °C for various times are shown in Table II. Four new products (**6**–**9**) start to appear early; one of them, **6**, disappears when the reaction goes to completion. The relative amounts of **7**–**9** remain approximately the same after different time periods, with a slight increase in **9** as the reaction proceeds.

The possibility of interconversion among the meta isomers (**7**–**9**) was tested by heating a pure sample of **9**. No rearrangement was observed at 450 °C over 20 h, although there was some decomposition. A sample of an approximately 1/1 mixture of **5** and **6** was also subjected to rearrangement. Table III shows the product distribution after heating for 1 h. The relative percentage of **9** increases significantly in comparison with that from the pyrolysis of **5** alone (Table II).

In order to compare the rate of isomerization of **5** to its meta isomers with that of the conversion of *o*-carborane to *m*-carborane, a mixture of **5** and *o*-carborane was heated. Analysis of the product mixture revealed a 3-fold rate enhancement for **5**. For example, when 81% of **5** has rearranged to its three meta isomers **7**–**9**, only 26% of *o*-carborane has been converted to *m*-carborane.

Identification of **6** and **7** is relatively simple. Compound **6** must be the only possible new ortho isomer because **6** disappears upon allowing the reaction to go to completion. Coinjection of the reaction mixture under various gas chromatographic (GC) conditions with an authentic sample of **6** (produced as a side product in the original synthesis of **5**) further confirms this assignment.

Examination of the structures of the three possible meta isomers reveals that only one of the three has $C_s$ symmetry. Compound **7** is assigned as this isomer, because only **7** displays magnetic equivalences of the two protons in each methylene group, as required by the $C_s$ symmetry. Two singlet resonances (2.68 and 1.98 ppm) appear in the $^1$H NMR spectrum of **7**.

Assignments for **8** and **9** are derived from their $^{11}$B NMR spectra. The only structural difference between the two possibilities is that in one, A, the bridged boron atom is directly bonded to both cage carbon atoms, while in the other isomer, B, the bridged boron atom is directly attached to only one cage carbon atom. Thus in the $^{11}$B NMR spectrum the chemical shift of the substituted boron in A must show an upfield shift relative to that of B.[21] Therefore, **9** (substituted boron resonance at ca. −5.47 ppm) is assigned as A, and **8** (substituted boron resonance at ca. −2.5 ppm) is assigned as B (Figure 4).

**Table IV.** Predicted Initial Distribution from the Pyrolysis of **5** by the Three Different Mechanisms, in Comparison with the Experimentally Observed Initial (15 min) Distribution

| | 6 | 7 | 8 | 9 |
|---|---|---|---|---|
| DSD | 1 | 0 | 1 | 0 |
| pentagonal rotation | 1 | 1 | 1 | 0 |
| 120° triangle rotation | 2 | 1 | 2 | 1 |
| exptl (15 min) | 0.1 | 1.3 | 4.8 | 7.6 |

The assignments of **8** and **9** are supported by the chemical shifts of their methylene protons adjacent to boron. The chemical shift (2.34 ppm) of the methylene protons which are next to the cage $B_2$ in **9** shows a downfield shift relative to that (2.13 ppm) of the methylene protons which are attached to the cage $B_4$ in **8**. This observation can be explained by the nature of the electron-density distribution over the *m*-carborane cage.[22] As there is a significant presence of partial positive charge on the $B_{2,3}$ atoms and a relative absence of the charge on $B_{4,6,8,11}$ in the *m*-carborane nucleus, the 2-*m*-carboranyl group usually displays an electron-withdrawing character, while the 4-*m*-carboranyl group possesses neither electron-withdrawing nor electron-donating properties.[23] Accordingly, we would expect the methylene group attached to $B_2$ to appear at lower field than the methylene attached to $B_4$, as is the case (Figure 4).

There is another subtle distinction between the $^1$H NMR spectra of **8** and **9**, which depends upon the asymmetric character of the molecules and which further confirms the assignments of structure. The two methylene protons adjacent to the bridgehead boron in **9** show a bigger difference in their chemical shifts ($\Delta\delta$ = 0.18 ppm) than the methylene protons in **8** ($\Delta\delta$ = 0.12 ppm). This is consistent with the structural assignments, as the free cage carbon, which is responsible for the asymmetry of the molecules, is closer to the methylene attached to the bridgehead boron in **9** than is the free carbon in **8**. This relationship has been previously observed, for example, in **5** and **6**. The chemical shift differences of the two protons in each methylene in **5** and **6** have been rationalized by examining the relative positions of the free cage carbon to each methylene group (Figure 4).[19,24]

## Discussion

Some striking features of the thermal rearrangement of **5** can be summarized as following:

1. All four possible isomers (**6**–**9**) were formed from **5** in the initial stages of the reaction (see Table II). The meta isomer **9** is the major product not only in the final composition, but also in the early phases of the reaction.

2. A nonstatistical distribution of three meta isomers **7**–**9** was obtained in the final products (see Table II). Recall that **9** does not rearrange to any other isomers under the reaction conditions.

3. Although the trend of the three meta isomers (**9** > **8** > **7**) remains unchanged at different reaction times, the relative distribution changes slightly as the reaction proceeds (see Table II). This can be rationalized by the increased contribution of the new ortho isomer **6** to the formation of the three final meta products. In accord with the observation that the ratios of **9**/**8** and **9**/**7** slightly increase as the reaction proceeds, **6** must give higher ratios of **9**/**8** and **9**/**7** than **5** does. This is consistent with the data in Table III, which shows higher ratios of **9**/**8** and **9**/**7** (**9**/**8**/**7** = 14/5/1) in comparison with the data in Table II (**9**/**8**/**7** = (5–7)/(3–4)/1).

Obviously, any proposed mechanism for the rearrangement of **5** must be able to account for these observed features. However, it is quite surprising that both the simple DSD mechanism and the pentagonal-rotation mechanism fail to explain these experimental results. As Table IV shows, the simple DSD mechanism predicts the formation of only **8** and **6** from the initial transfor-

---

(21) Recently, Teixidor et al. established some empirical rules for predicting the $^{11}$B NMR spectra of *closo*-boranes and *closo*-heteroboranes. See: Teixidor, F.; Vinas, C.; Rudolph, R. W. *Inorg. Chem.* **1986**, *25*, 3339.

(22) Hoffmann, R.; Lipscomb, W. N. *J. Chem. Phys.* **1962**, *36*, 3489.

(23) Kalinin, V. N.; Kobel'kova, N. I.; Zakharkin, L. I. *J. Organomet. Chem.* **1979**, *172*, 391.

(24) Wu, S.-h. Unpublished observation.

**Table V.** Predicted Initial Distribution from the Pyrolysis of **6** by the Three Different Mechanisms

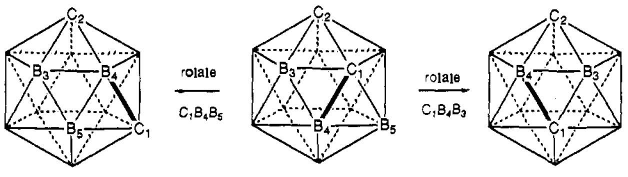
| | **5** | **7** | **8** | **9** |
|---|---|---|---|---|
| DSD | 1 | 0 | 0 | 1 |
| pentagonal rotation | 1 | 0 | 0 | 1 |
| 120° triangle rotation | 2 | 0 | 1 | 2 |

mation of **5**, while the rotating-pentagon mechanism allows the formation of **6**–**8**. Both mechanisms predict zero yield for isomer **9** in the initial transformation of **5**! However, it is exactly the isomer **9**, in sharp contrast to these predictions, that is observed as the major product from **5** in the initial stages of the rearrangement.

To predict the final product distribution, one must consider the possible isomerization of the new ortho isomer **6** to its meta products. Both the DSD mechanism and the pentagonal-rotation mechanism, as shown in Table V, give **9** as the only meta product from **6**. Thus, the DSD mechanism should predict a zero yield for **7** in the final products, and this, of course, is not observed, as all three meta isomers were found. On the other hand, although the rotating-pentagon mechanism predicts all three possible meta isomers from **5** and **6** in the final products, the inclusion of the isomerization from **6** should not change the relative ratio of **7** and **8**, as **6** produces only **9** by this mechanism. This is not consistent with the observation that the ratio between **7** and **8** does change significantly when a sample of a 1/1 mixture of **5** and **6** was subjected to the rearrangement (see Tables II and III).

The formation of **9** from **5**, however, can occur in a single step through the mechanism based upon the rotation of a triangular face in the icosahedron ("120° triangle rotation"). The predicted initial yield distributions from the transformation of **5** and **6** by this triangle-rotation mechanism, in which all triangles were allowed to rotate 120° on the icosahedron with equal probabilities, are also shown in Tables IV and V, respectively. All three meta isomers **7**–**9**, as well as the new ortho isomer, **6**, are predicted to be formed from the initial transformation of **5**, as is consistent with the experimental results (Table II), and the two meta isomers, **8** and **9**, are predicted to be formed from the isomerization of **6**, as the experimental data in Table IV show. Although the triangle-rotation mechanism is in good agreement with the gross product distribution, it fails to predict the detailed ratios of the three meta isomers. For example, the 120° triangle rotation mechanism predicts **8**, not **9**, as the major product from the initial transformation of **5**. This disagreement, however, very likely could arise from the unrealistic assumption that all triangles were allowed to rotate on the icosahedron with equal probabilities. As the triangles on the icosahedron are somewhat different electronically, (for example, CBB is different from BBB), some preference for rotation of certain triangles on the icosahedron must exist, as Lipscomb and co-workers recognized in their work.[3,14] Those triangle rotations which lead to the major product **9** must be kinetically favored compared to those which lead to the other two meta isomers, **7** and **8**. Examination of **5** reveals that only the rotations of those triangles ($C_1B_3B_4$ and $C_1B_4B_5$) which contain both bridged atoms ($C_1$ and $B_4$) can produce the major meta isomer **9** (Figure 5). Thus it seems that the rotations of triangles bearing substituents are kinetically favored over the rotations of those triangles which contain only unsubstituted carbon and/or boron atoms. This idea was suggested before by Hart and Lipscomb[14] and is now supported by the observed rate enhancement of the isomerization of **5** over that of the parent *o*-carborane.

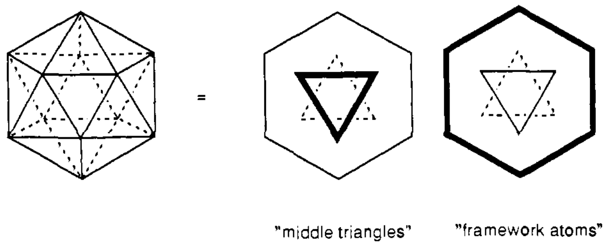
The origin of this substituent effect remains unclear, although a plausible explanation was suggested by Hart and Lipscomb.[14] We note here that subtle but significant X-ray structural evidence might now also be considered. X-ray structure determinations have shown that bonds which involve the bridgehead atoms are slightly longer than the rest of the bonds within the same class.[20] Thus it could be the case that the weakened bonding character with other skeletal atoms makes the bridgehead atoms relatively easy to rearrange.



**9** **5** **9**

**Figure 5.** The formation of **9** from 120° triangle rotations in **5**. Remember that in this compound the bridge is the only label and all borons except for $B_4$ are therefore unlabeled. Only rotations of triangles $C_1B_3B_4$ or $C_1B_4B_5$ can produce **9**. The dark line shows the position of the bridge between $C_1$ and $B_4$.

**Scheme III.** An Icosahedron Can Be Factored into "Middle Triangles"[a] and Framework Atoms"



[a] Only one of the pairs is emphasized in the drawing.

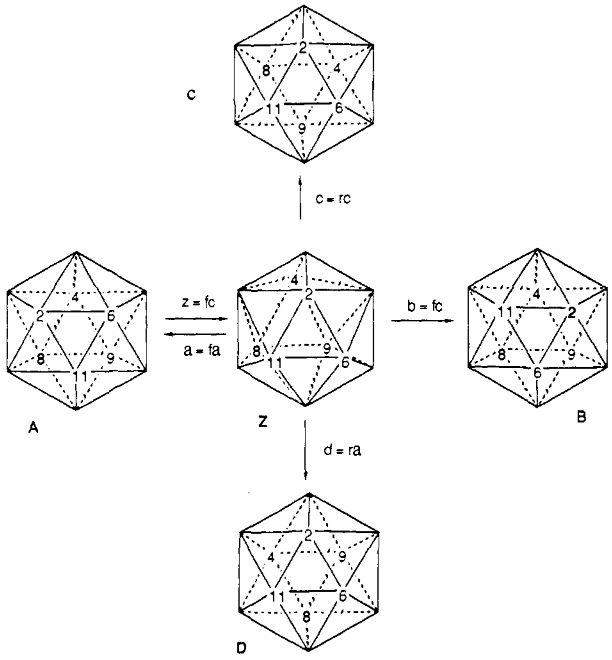
**The Extended Triangle Rotation (ETR) Mechanism.** As discussed earlier, there have been several proposals for the mechanism of the thermal isomerization of icosahedral carboranes.[2] None of them alone can explain the complicated features of the experimental results. Nevertheless, a combined mechanism, the DSD process accompanied by triangle rotation in the intermediate ("modified DSD"), appears promising in its ability to model the experimental data. Lipscomb and co-workers used this hybrid process to rationalize the observed data from the experiments with halogen-labeled carboranes. They suggested that the major transformation proceeds through the pure DSD pathway, and that products in addition to those produced by the pure DSD arise principally from triangle rotations occurring only during the lifetime of the cuboctahedral intermediates.

However, some comment on the hybrid version of the DSD pathway accompanied by triangle rotation ("modified DSD") is permitted by our new results. The observation of **9**, a non-DSD product, as the *major* product in both the initial transformation of **5** and the final product mixture clearly indicates that the triangle-rotation pathway plays a *principal* role in the reaction process and is not merely a necessary adjunct to account for the minor products. Furthermore, it is not the first time that a contradiction was found between the products predicted by the hybrid process and the observed results. Good examples can be taken from the literature. For instance, in the thermal rearrangement of 9-bromo-*o*-carborane the major initial product, 8-bromo-*o*-carborane, is not the one which the pure DSD pathway requires (Table VI).[3] In addition, although the pure DSD pathway must give 5-bromo-*m*-carborane as its only product, there is not even a significant excess of 5-bromo-*m*-carborane over another meta product, 9-bromo-*m*-carborane. Similar examples exist in the literature.[12,14,15] As our experimental results strongly suggest that triangle rotation plays an important role in the ico-

**Table VI.** Experimentally Observed Initial (30 min) Distribution from the Pyrolysis of 9-Bromo-*o*-carborane, Compared with the Predicted Distribution from the DSD Mechanism

| | 8-Br-*o*- | 4-Br-*o*- | 3-Br-*o*- | 9-Br-*m*- | 5-Br-*m*- | 4-Br-*m*- | 2-Br-*m*- |
|---|---|---|---|---|---|---|---|
| DSD | 0 | 0 | 0 | 0 | 1 | 0 | 0 |
| exptl | 21 | 3 | 0 | 3 | 4 | 1 | 0 |

**Scheme IV.** Four Possible Pathways Converting the Intermediate Z into Icosahedra



**Scheme V.** The Sixteen Possible Icosahedron–Intermediate–Icosahedron Transformations

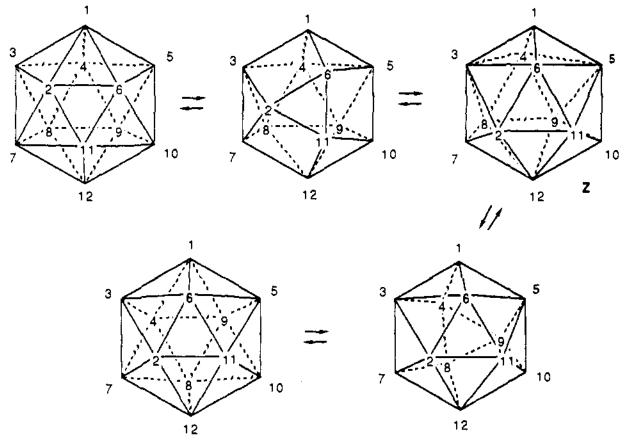
| | | | | | | | |
|---|---|---|---|---|---|---|---|
| fcfc | fcfa | fcrc | fcra | fafc | fafa | farc | fara |
| rcfc | rcfa | rcrc | rcra | rafc | rafa | rarc | rara |

sahedral framework rearrangement, it is useful to consider the triangle-rotation mechanism more carefully, by inspecting the possible transition states and intermediates involved in this process. As we do this we will build up a new mechanism, the "extended triangle rotation" or "ETR" process. We shall call the outlined triangles in Scheme III "middle triangles". The six other atoms can be shown as a hexagon (the "framework" atoms) surrounding the pair of "middle triangles" (Scheme III).

A half-way rotation (clockwise 60°, path z called "fc") of the front-side middle triangle (atoms 2, 6, and 11) in the icosahedron A gives intermediate Z (Scheme IV). Further clockwise rotation (60°) of the same triangle (path b, also called "fc") converts the intermediate Z to a stable icosahedron B, in which one triangle (2,6,11) has been rotated 120° from its position in the original molecule A. However, since the most symmetrical form of intermediate Z has pseudo $C_s$ symmetry with a plane passing through six framework atoms,[25] the rotation of the backside triangle (triangle 4,8,9) should be also possible. Thus, path c (60° rotation of rear-side triangle 4,8,9 clockwise, or "rc") leads to molecule C, and path d (60° rotation of rear-side triangle 4,8,9 anticlockwise, or "ra") leads to molecule D. Therefore, including path a, by which the intermediate Z is returned to its starting point A, there are four possible pathways (path a, b, c, and d, or fa, fc, rc, and ra) which can convert the intermediate Z to the stable icosahedral structures (A, B, C, and D).

Let's first consider a simple picture by assuming that all triangles in the polyhedron A rotate with equal probabilities. For a given molecule A, there are 10 triangle pairs which have a para relationship on the polyhedral surface. For each of these triangle pairs, there are four possible routes to reach four similar intermediates in a single step: front-side–clockwise (fc); front-side–anticlockwise (fa); rear-side–clockwise (rc) and rear-side–anticlockwise (ra). As each of these intermediates has four possible routes to stable icosahedra, the number of possible icosahedron–intermediate–icosahedron transformations for each triangle pair is 16 (Scheme V). Therefore, for a fully labeled polyhedron A, the 10 possible triangle pairs give a total of 40 possible different intermediates and 160 possible paths for icosahedron–intermediate–icosahedron interconversions. Actually the 16 possible transformations in Scheme V can be divided into four groups.

**Scheme VI.** The Intermediate Z Is Reached through a Transition State Formed by 30° Rotation of Any Triangle



Group 1: those involving only one triangle with 120° rotation, fcfc, fafa, rcrc, and rara. There is a direct correlation between this process and the mechanism called "120° triangle rotation", and the products from this group *are* the "120° triangle rotation" products. There are 40 (4 × 10) of these pure triangle rotation products.

Group 2: those involving rotation of one triangle, but which lead to no net change, fcfa, fafc, rcra, and rarc. The total number of these "no-change routes" is also 40.

Group 3: those involving triangle pairs, with 60° conrotatory rotation of two triangles in the pair, fcrc, (rcfc), fara, (rafa). Because the products from this kind of transformation are not affected by the order of the two different triangle rotations (for example, fcrc = rcfc), the possible number of products of this kind of transformation is at most only 20, although there are still 40 possible routes to them.

Group 4: those also involving both triangles in a pair, but with 60° disrotation, fcra (rafc), farc, (rcfa). These processes also give at most only 20 transformations out of 40 possible routes.

The most intriguing conclusion derived from this discussion is that all simple DSD transformations based on the original proposal of Lipscomb[2a] can be achieved by rotations of a triangle pair if each triangle rotates 60° in a conrotatory fashion. In other words, the 20 transformations in group 3 create five different transformations which are exactly equivalent to the five possible DSD transformations. Group 3 represents "pure Lipscomb DSD" transformations.

Furthermore, it turns out that the equivalence between the DSD mechanism and the transformations made by 60° conrotatory rotations of triangle pairs is no accident. In our formulation, the intermediate Z can be reached through a transition state formed by a 30° rotation of any triangle (Scheme VI). A second 30° rotation can either return us to starting material or lead further to Z. Conrotation of the triangle "para" to the one first rotated leads over another transition state to a new icosahedron (Scheme VI). A pure DSD process accomplishes the same change. The numbering of Scheme VI recapitulates that of Lipscomb's original formulation of the DSD mechanism.[2a,3] In the supplemental material is a scheme illustrating the five different "pure DSD" transformations.

Scheme VI can be extended to a complete representation of the physical processes for all transformations included in the four groups. For a given triangle pair in an icosahedron A, there are four different transition states, $A^{I}$, $A^{II}$, $A^{III}$, and $A^{IV}$. In Scheme VII movement to the right respresents front-side clockwise rotation

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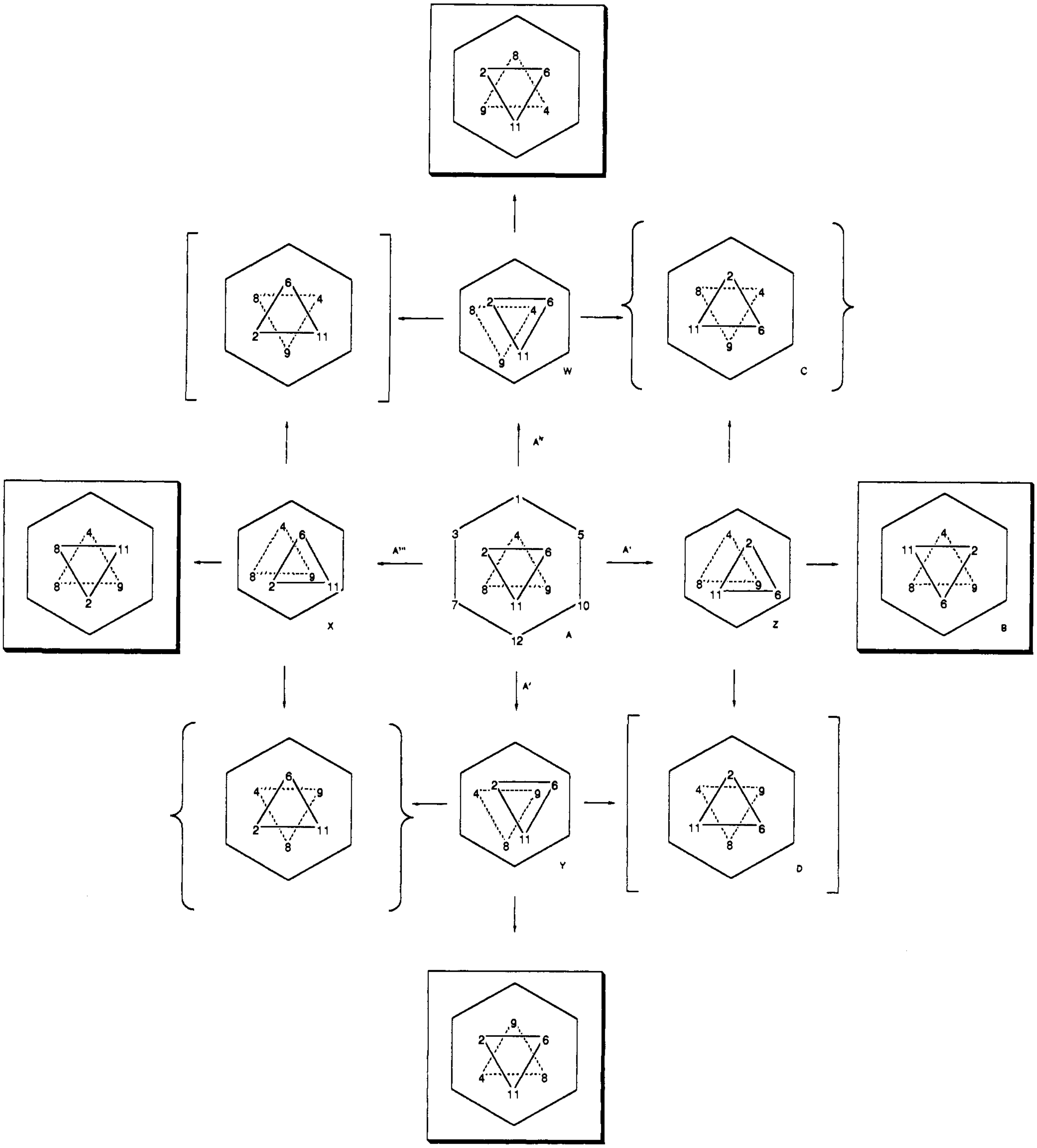
[25] In this process the framework atoms undergo a chair–plane–chair motion. We are embarking on a theoretical project designed to see if this most symmetrical picture is the best representation and whether our postulated transition state and intermediate (Z) are an appropriate energy maximum and minimum, respectively.

**Scheme VII**[a]



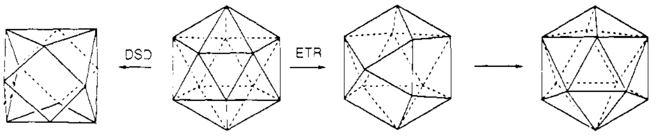
[a] Group 1 products are boxed, group 3 products are enclosed in "{}", and group 4 products are in "[ ]".

and movement to the left represents front-side anticlockwise rotation. Movement up represents rear-side clockwise rotation and movement down represents rear-side anticlockwise rotation. There are four motions of group 1 type in Scheme VII. Similarly, Scheme VII shows the two possible group 3 and two possible group 4 products. Of course, group 2 motions result in no change and are represented in the scheme by the return paths from intermediates Z, Y, X, and W to A. Scheme VII shows the eight possible transformations for only one triangle pair. A complete map of the 80 transformations for all 10 pairs of triangles can be found in the supplemental material.

The following features of the ETR mechanism can be summarized:

1. Although the ETR mechanism can reproduce the rearrangement pattern of the DSD process, it differs fundamentally from the DSD in the physical motions used to move the atoms occupying vertices on the icosahedron to their new positions. Rather than stretching two common triangular faces to a square face as in the DSD, the ETR mechanism emphasizes motions in which the integrity of the triangular faces is maintained as much as possible. Although in the transition state A′ the rotation of a triangular face converts six triangles to three squares, the remaining part of the bonding system preserves substantial triangular interaction, as 14 of the original 20 triangles are retained in A′.[26]

**Scheme VIII.** Geometrical Consequences of the DSD and ETR Processes



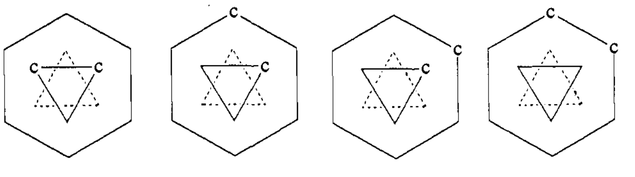
The cuboctahedral intermediate in the DSD process has six square faces and only eight triangular faces.

The starting icosahedron, A, contains 20 triangular faces.

The transition state in the ETR process, A', has three square faces and 14 triangular faces.

The intermediate in the ETR process, Z, contains 20 triangular faces as does A.

**Scheme IX.** The Three Structural Patterns for Triangle Rotation in the ETR Process



Pattern A. Both carbons occupy middle triangle positions.

Pattern B. One carbon is on the framework and the other on a middle triangle.

Pattern C. Both carbons are on the framework.

The intermediate Z is a deltahedron, and therefore contains 20 triangles, as does the starting icosahedron. As three-center, two-electron bonding is central to the stability of boron cluster compounds,[28] the ETR path should be less energy demanding than the pure DSD (Scheme VIII).

2. The ETR mechanism provides 65 potential rearrangement patterns for a fully labelled icosahedron in which all triangles can rotate. These 65 come from the 40 pathways of group 1, the 5 of group 3, and the 20 of group 4. The ETR process is much more complex than the DSD, which gives only five possible rearrangement patterns.[3] The DSD is simple—the icosahedron need only "breathe" to form the cuboctahedral intermediate and "exhale" to give rearrangement product (Scheme I). Yet we have already seen that this simplicity leads to problems. The five possible rearrangement patterns are inadequate to duplicate the experimental data. Random interconversion of neighbors on the icosahedral surface leads to 7 983 360 possible isomers. Therefore, although the ETR mechanism is more complex than the DSD, it is surely vastly more simple than random motion.

3. The analysis of the ETR mechanism can be further simplified by looking at the general features of the rotational patterns. There are only three possible structural patterns for the triangle-rotating process of the parent *o*-carborane (Scheme IX). The two carbons may occupy positions on the rotating middle triangle pair (Scheme IX, pattern A), one carbon can be on a middle triangle and one on the framework (Scheme IX, pattern B), or both carbons may hold adjacent positions on the framework (Scheme IX, pattern C). The full set of 10 triangle pairs can be divided into two of pattern A, six of pattern B, and two of pattern C. Only pattern B is capable of converting an *o*-carborane to *both* a meta and an ortho isomer. In patterns A and C the two carbons are fated to occupy forever adjacent positions in both the intermediate and the product.

If the perturbations introduced by the "exopolyhedral" substituents are small relative to the energy changes introduced by the "endopolyhedral" differences shown in Scheme IX, then the automerization process will mainly be controlled by the different energies involved in the three different triangle-rotation patterns of patterns A, B, and C. It is not the substituents attached to the framework atoms that exert control over the reaction, but the differences within the cage.

**Table VII.** Experimentally Observed Initial (15 min) Distribution from the Pyrolysis of **5**, in Comparison with the Predicted Distribution by the Three Groups of the ETR Process[a]

| | **6** | **7** | **8** | **9** |
|---|---|---|---|---|
| group 1 (120°) | 4 | 2 | 4 | 2 |
| group 3 (DSD) | 8 | 0 | 8 | 0 |
| group 4 | 8 | 2 | 6 | 0 |
| exptl | 0.1 | 1.3 | 4.8 | 7.6 |

[a] Figures given are the numbers of paths of the total of 160 ETR transformations.

Having established this new scenario to describe the thermal rearrangements of icosahedral carboranes, we can now easily understand why a hybrid mechanism such as the modified DSD (DSD accompanied by triangle rotation) theme can generally fit the observed data quite well. If the combination of the DSD and the triangle-rotation processes seems somewhat arbitrary, the articulation between these two processes now appears very natural in the "extended triangle rotation" mechanism. The products from the pure Lipscomb DSD mechanism (group 3 in ETR) and the pure triangle rotation transformations of group 1 arise from a common reaction intermediate. For example, in Scheme IV, the pure DSD product C and the 120° triangle rotation product B are both formed from the common intermediate Z. The whole ETR process, which includes the Lipscomb DSD mechanism, is unified by the motion involved in triangle rotation.

Moreover, a general prediction of the relative importance of group 1 (120° triangle rotation) and group 3 (DSD) processes can now be derived from the ETR mechanism. This prediction, that 120° rotation will be more important than the DSD process, is exactly opposite to that derived from the hybrid (modified DSD) mechanism.

Only for a fully symmetrical icosahedron will all triangles rotate with equal facility. Once asymmetry is introduced, by substitution either in or on the framework (exo- or endopolyhedral), some triangle or set of equivalent triangles will become the most favored in the rotation to form intermediate Z. Although there are four different routes from this intermediate Z to the final products, it is generally likely that rotation of this same triangle will remain most favored. This argument, therefore, leads to the clear notion that 120° triangle rotation (group 1) should contribute more to the observed final products than the other types of transformation such as pure Lipscomb DSD (group 3) or group 4. Clearly, this prediction is different from that derived from the modified DSD, which predicts that the pure DSD process (group 3) will contribute more than other kinds of transformations to the final products.

**Correlation with Experiments.** In this section we will first establish whether the general prediction of the ETR mechanism, that 120° triangle rotation should usually be the most important process, is correct. Second, we will look at some detailed experimental data to see what information we can gain about relative stabilities of intermediates and/or the transition states leading to them. Then we will use this information to see if we can rationalize further detailed experimental data.

Our general prediction is indeed supported by our experimental data on **5**, as well as by data reported by Lipscomb and co-workers. Table VII shows the observed data from our experiments on the thermal rearrangements of **5**, compared with the predicted initial yield distributions from three different groups (1, 3, and 4) of transformations.

Clearly, neither group 3 nor group 4 can be major contributors. It seems that group 1, the 120° triangle rotation transformation, contributes most to the observed product yield. Equally clearly, a random group 1 process is not the only thing happening. The fit between the data and prediction is only approximate, and there must be contributions from group 3 and/or group 4 as well as rotations of particularly favored triangle pairs of the group 1 type.

Similar conclusions can be reached by consideration of data in the literature. Table VIII shows the experimentally observed initial product distribution from the thermal isomerization of

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(26) The DSD intermediate (the cuboctahedron) and the ETR intermediate (Z) also differ in the coordination states of the different atoms at the vertices. In Z, the middle triangles are all five endocoordinate and the framework atoms are four and six endocoordinate. In the cuboctahedron all positions are four endocoordinate.[27]

(27) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781. Jemmis, E. D. *J. Am. Chem. Soc.* **1982**, *104*, 7017.

(28) Stone, A. J. *Inorg. Chem.* **1981**, *20*, 563; *Polyhedron* **1984**, *3*, 1299.

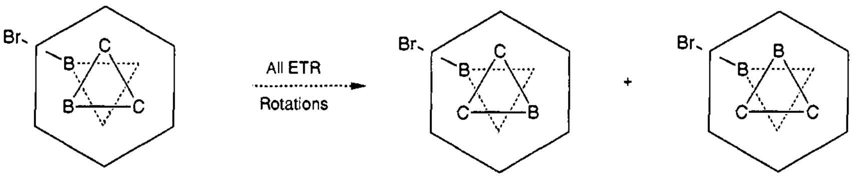
**Table VIII.** Experimentally Observed Initial Distribution from the Rearrangement of 9-Bromo-*o*-carborane, Compared with the Distribution Predicted by the Three Groups of the ETR Process

| | 8-Br-*o*- | 4-Br-*o*- | 3-Br-*o*- | 9-Br-*m*- | 5-Br-*m*- | 4-Br-*m*- | 2-Br-*m*- |
|---|---|---|---|---|---|---|---|
| group 1 (120°) | 8 | 4 | 0 | 4 | 4 | 0 | 0 |
| group 3 (DSD) | 0 | 0 | 0 | 0 | 8 | 0 | 0 |
| group 4 | 8 | 4 | 0 | 4 | 4 | 0 | 0 |
| exptl | 21 | 3 | 0 | 3 | 4 | 1 | 0 |

**Table IX.** The Possible Products from the Rearrangement of 9-Bromo-*o*-carborane, Derived from the ETR Rotations for Patterns A and B

| | 9-Br-*o*- | 8-Br-*o*- | 4-Br-*o*- | 3-Br-*o*- | 9-Br-*m*- | 5-Br-*m*- | 4-Br-*m*- | 2-Br-*m*- |
|---|---|---|---|---|---|---|---|---|
| pattern A | 16 | 8 | 0 | 0 | 0 | 0 | 0 | 0 |
| pattern B | 32 | 8 | 8 | 0 | 8 | 16 | 0 | 0 |

**Scheme X.** In the Rearrangement of 9-Bromo-*o*-carborane, All the ETR Rotations of Pattern A Produce Only One New Product

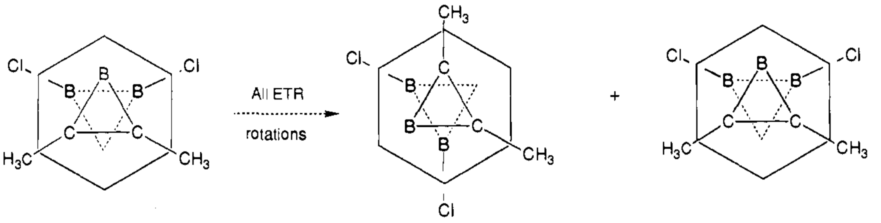


Pattern A of 9-Bromo-o-carborane. The B-Br is meta to one carbon and para to the other.

8-Bromo-o-carborane. The B-Br is meta to both carbons.

This is still 9-bromo-o-carborane.

**Scheme XI.** In the Rearrangement of 1,2-Dimethyl-9,12-dichloro-*o*-carborane, All the ETR Rotations of Pattern A Produce Only One New Product

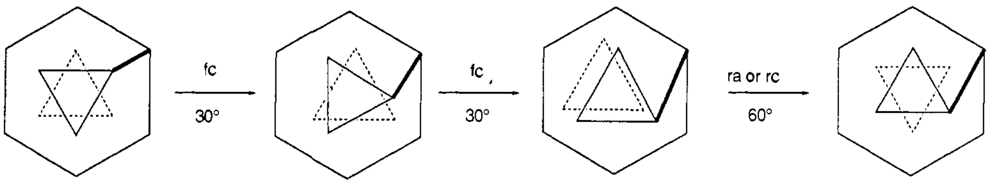


Pattern A of
1,2-Dimethyl-9,12-dichloro-o-carborane

1,2-Dimethyl-8,9-dichloro-o-carborane

Still
1,2-Dimethyl-9,12-dichloro-o-carborane

**Scheme XII.** Pattern A for the Rearrangement of **5**[a]



Transition state

Intermediate

[a] The dark line indicates the position of the bridge.

9-bromo-*o*-carborane, as well as the predicted initial yield distributions from the three different groups of transformations.[3]

Once again, the pure DSD mechanism does not make the major contribution to the mechanism, as the 120° triangle rotation transformation (group 1) seems to reproduce the observed data better than the pure DSD (group 3) does.

Now that we have discussed the general predictions made by our ETR mechanism, we will examine the detailed experimental data, to see what we can learn about the structures and energies of the intermediates.

We would like to establish the relative importance of rotations in the three patterns shown in Scheme IX. We will start with the rearrangement of 9-bromo-*o*-carborane.[3] In the thermal rearrangement of this compound, the most intriguing feature is the large amount of 8-bromo-*o*-carborane formed in the initial product mixture (see Table VIII). The DSD mechanism (group 3) has no way to produce one ortho product from another for 9-labeled *o*-carboranes and so has no way to explain the major product of the reaction. In addition, the 120° triangle rotation mechanism (group 1) predicts a 2/1 ratio of 8-bromo-*o*-carborane to 4-bromo-*o*-carborane and so an increased contribution from this process also fails to predict accurately the detailed product mixture (Table VIII). Let us analyze here the possibly ways to convert one ortho isomer to another based on our ETR formulation using the three patterns of Scheme IX.

For a $B_9$-labeled *o*-carborane, pattern A can only give starting material and the $B_8$-labeled *o*-carborane (Scheme X). Pattern B can also give the $B_8$-labeled ortho isomer, but many other products are possible as well. Pattern C cannot give a new product, and we will not be able to comment upon its importance. Table IX shows the possible products from ETR rotations (groups 1, 3, and 4) for patterns A and B. The major new product can be 8-bromo-*o*-carborane in only two ways. Pattern A must give 8-bromo-*o*-carborane as the major product. Pattern B *can* give 8-bromo-*o*-carborane, but some new factor must be supplied which kinetically favors this product over the others which should

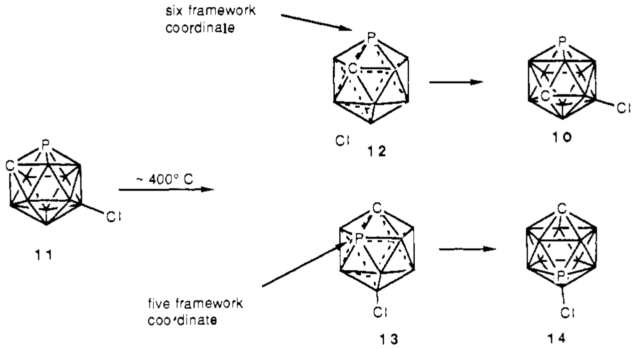


**Figure 6.** The ETR mechanism can explain the preferential formation of **10** from **11**.

dominate on a statistical basis. We prefer to wield Ockham's razor and to accept the more simple first explanation. Without further experiments we cannot say why pattern A dominates, but we will go on to show how the choice of pattern A is supported by the chemistry of our bridged intermediate **5**.

If pattern A *is* favored, we should be able to rationalize other data in the literature. For example, Lipscomb noted especially that thermal rearrangement of 1,2-dimethyl-9,12-dichloro-*o*-carborane gave as major product 1,2-dimethyl-8,9-dichloro-*o*-carborane.[15] Pattern A predicts exactly this (Scheme XI). Once more, pattern B predicts other ortho and meta isomers, and we are unable to comment upon the importance of pattern C.

If this formal picture is an accurate representation, it should also be possible to introduce perturbations which would change the product distribution in a predictable fashion. This is what the bridge in **5** does. An ortho–ortho rearrangement of pattern A, which was the major source of product in the acyclic molecules just discussed, involves a transition state in which the bridge spans middle triangle and framework positions (Scheme XII). This transition state is destabilized by the required distortion of the small bridging ring as the middle triangle rotates and the icosahedron flexes to form the transition state with three square faces.

Formation of new ortho products no longer competes effectively with that of meta isomers in the pyrolysis of **5** (Table VII) because the routes to ortho which are productive in acyclic compounds (patterns A and possibly C) are reduced in importance by the presence of the bridge. Now, ortho and meta products are formed in comparable amounts through pattern B, which becomes the major contributor. This experiment is consistent with our earlier decision that pattern A is the main source of ortho products.

The ETR mechanism also removes the necessity to invoke special mechanisms to explain individual odd results. An example is the rearrangement of the icosahedral phosphacarborane **11** mentioned earlier. It had been argued that the nearly exclusive formation of 9-Cl-1,7-$CHPB_{10}H_9$ (**10**) from 12-Cl-1,2-$CHPB_{10}H_9$ (**11**) could be best explained through a pentagonal-rotation mechanism.[12] It was thought that the distortion induced by the phosphorus atom in the cage induced the mechanistic change. However, no special mechanism is required. The ETR mechanism leads from **11** to either **12** or **13**. The important difference between **12** and **13** is the position occupied by the phosphorus atom. In **12** it is 6-framework coordinate, whereas in **13** it is 5-framework coordinate, a less favorable situation. It is the favored intermediate **12** that leads to the observed major product, **10**, whereas **13** gives **14**, an observed minor product of the reaction (Figure 6).

## Summary

When we began this work, the conceptually simple diamond–square–diamond mechanism for the automerization of carboranes had been modified to include weighted triangle rotations in order to rationalize much experimental data. Yet, as recognized explicitly by Lipscomb, there were still observations that could not be explained by the "modified DSD" mechanism. A number of different, if related, mechanisms existed, each with virtues, but each inadequate in at least some cases. Other mechanisms, such as the pentagonal-rotation process, were used to explain individual odd reactions, such as the rearrangement of the phosphorus-containing carborane **11**.

We have done two things. First, we simplified the experimental situation by introducing a bridge between a framework carbon and a boron at the 4-position on the cage. The small bridge cannot span meta or para positions and therefore sharply limits the possible products of rearrangement. It is clear from our experiments that triangle rotation is no secondary process but the major contributor in the mechanism for rearrangement.

Second, we have tried to simplify the mechanistic picture with a unifying proposal which emphasizes motion in which the integrity of the triangular faces is maintained as much as possible. This extended triangle rotation process is used to rationalize the results of our experiments as well as data in the literature.

We shall surely not have the last word. For instance, although we have made some attempts, the existing data base is too narrow to permit a detailed analysis of which kinds of triangle rotation are of lowest energy. Much new experimentation is warranted and we hope to rekindle interest in this subject with our mechanistic proposal. Both recent and older theoretical analyses have occasionally cautioned that the DSD process may not be correct for certain carboranes.[29,30] It seems clear that the time is appropriate for a new theoretical treatment of the suggested mechanisms for the isomerization.

Muetterties summarized the situation well as early as 1975 when he wrote in the introduction to the fine book *Boron Hydride Chemistry*,[2e] "Perspective in this important and complicated 12-atom case must be maintained. Keep in mind that the number of distinguishable (permutationally distinguishable) mechanisms is very large (the permutational group is isomorphous with the symmetric group $S_{12}$ of order 12! or 479 001 600.) Hence, our assessment of this rearrangement in terms of physical models has not even begun to scratch the surface of possibilities, *although it is possible that in fact the most plausible models have already been considered or proposed* (italics Muetterties).".

## Experimental Section

**Thermal Isomerization of 5.** The bridged *o*-carborane **5** was prepared by the procedure described in the literature. Samples for isomerization were weighed (each was about 5 mg) into Pyrex tubes which were subsequently sealed under vacuum. The sealed tubes ($^1/_4$ in. by about 2.5 in.) were placed in a furnace at 450 ± 5 °C for the desired time, removed, quickly cooled to room temperature, and later cracked open for chromatographic analysis. Isomerization products so obtained were dissolved in chloroform and chromatographed on a Hewlett-Packard 5890A gas chromatograph with helium as carrier gas, using 6 ft, 0.085 in. i.d. stainless steel columns. The ratios of two ortho isomers (**5** and **6** together) and three meta isomers (**7–9**) were resolved on a column packed with 10% Carbowax 20M absorbed on 80/100 Chromosorb W-HW, operating between 160 and 210 °C. The ratios of the two ortho isomers (**5** and **6**) were resolved on a column packed with 3% OV-101 and 80/100 Chromosorb W-HP, operating between 100 and 250 °C. The three final products (**7–9**) were isolated in their pure states by the use of a $^1/_4$ in. by 4 ft aluminum column packed with 15% Carbowax on 80/100 Chromosorb W-HP.

Precise mass spectra were obtained on a KRATOS MS 50 RFA high-resolution mass spectrometer. Calculated for $C_5{}^{10}B_2{}^{11}B_8H_{14}O$ 198.2047, found **7**, 198.2065; **8**, 198.2059; **9**, 198.2055.

The $^1H$ NMR spectra were recorded on a Bruker WM 250 spectrometer at 250 mHz, and signals were referenced to $Me_4Si$. **6**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.20 (br s, 1 H), 3.11 (d, 1 H; $J$ = 19.1 Hz), 2.81 (d, 1 H; $J$ = 19.2 Hz), 2.46 (d, 1 H; $J$ = 19.8 Hz), 2.11 (d, 1 H; $J$ = 19.5 Hz). **7**: $^1H$ NMR ($CDCl_3$) $\delta$ 2.97 (br s, 1 H), 2.68 (s, 2 H), 1.98 (s, 2 H). **8**: $^1H$ NMR ($CDCl_3$) $\delta$ 3.04 (br s, 1 H), 2.79 (d, 1 H; $J$ = 18.7 Hz), 2.59 (d, 1 H; $J$ = 18.8 Hz), 2.19 (d, 1 H; $J$ = 20.1 Hz), 2.07 (d,

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(29) For examples, see: Cheung, C.-C. S.; Beaudet, R. A.; Segal, G. A. *J. Am. Chem. Soc.* **1970**, *92*, 4158. King, R. B. *Inorg. Chim. Acta* **1981**, *49*, 237. Gimarc, B. M.; Ott, J. J. *Inorg. Chem.* **1986**, *25*, 83.

(30) For recent and older treatments of rearrangement mechanisms for small carboranes which focus on the conversion of "nonclassical" three-center bonds into "classical" two-electron bonds in an intermediate or transition state, see: Camp, R. N.; Marynick, D. S.; Graham, G. D.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1978**, *100*, 6781, and McKee, M. L. *J. Am. Chem. Soc.* **1988**, *110*, 5317.

1 H; $J$ = 19.9 Hz). **9**: $^1$H NMR (CDCl$_3$) $\delta$ 3.26 (br s, 1 H), 2.81 (d, 1 H; $J$ = 18.8 Hz), 2.67 (d, 1 H; $J$ = 18.9 Hz), 2.44 (d, 1 H; $J$ = 19.7 Hz), 2.25 (d, 1 H; $J$ = 19.5 Hz).

The $^{11}$B NMR spectra were recorded on a Bruker WM 250 spectrometer (80 mHz for $^{11}$B), and signals were referenced to external boron trifluoride etherate. Chemical shifts were measured on decoupled spectra and multiplicities on coupled spectra. **7**: $^{11}$B NMR (CDCl$_3$) $\delta$ 3.6 (s, 1 B), -8.7 (d, 3 B), -9.6 (d, 2 B), -10.5 (d, 2 B), -13.4 (d, 2 B). **8**: $^{11}$B NMR (CDCl$_3$) $\delta$ -2.1 (d, 2 B), -2.5 (s, 1 B), -10.8 (d, 2 B), -13.4 (d, 2 B), -15.2 (d, 2 B). **9**: $^{11}$B NMR (CDCl$_3$) $\delta$ -3.3 (d, 1 B), -5.5 (s, 1 B), -8.3 (d, 2 B), -10.4 (d, 2 B), -12.2 (d, 3 B), -13.5 (d, 1 B).

**Supplementary Material Available**: A complete map of the 80 possible transformations for all 10 pairs of triangles and a scheme illustrating the five different "pure DSD" transformations (11 pages). Ordering information is given on any current masthead page.

# Is Triquinacene Homoaromatic? A Computational Study

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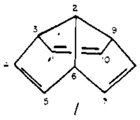
*Received October 5, 1988. Revised Manuscript Received March 6, 1989*

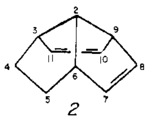
**Abstract**: AM1, ab initio, and MM2 calculations indicate triquinacene shows no significant homoaromatic stabilization, in contrast to conclusions drawn by Liebman et al. from thermochemical measurements. The discrepancy is attributed to the fact that the five-membered rings in di-, tetra-, and hexahydrotriquinacene are twisted and it can be accounted for quantitatively in this way. A discrepancy between a recent ab initio study by Miller et al. and experiment is attributed to computational errors.

Ever since the concept of homoaromaticity was first introduced by Adams and Winstein[1] some 40 years ago, it has been the subject of much interest to both experimentalists and theoreticians.[2] A variety of criteria have been suggested and applied as evidence for its presence or absence in given systems, the most direct being the observation of a ring current by $^1$H NMR spectroscopy.[3] The others involve molecular properties whose values differ from those expected for "normal" molecules, the properties in question including molecular geometries,[4] values of overlap integrals between the "nonbonded" atoms,[5] ionization energies measured by photoelectron spectroscopy,[6] and heats of hydrogenation.[7] This work has indicated that homoaromatic stabilization is mainly a property of ionic systems, the stabilization energies of neutral ones usually being very small, and convincing theoretical explanations have been given[2] for this difference.

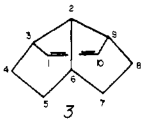
However, Liebman, Paquette, Peterson, and Rogers[7] (cited here as LPPR) have recently claimed that triquinacene (**1**, tricyclo-[5.2.1.0$^{4,10}$]deca-2,5,8-triene) is a homoaromatic species with a small (4.5 kcal/mol) stabilization energy on the basis of measurements of the heats of hydrogenation of **1** and its dihydro (**2**) and tetrahydro (**3**) derivatives to hexahydrotriquinacene (**4**). This result seems very surprizing, given that **1** is a neutral hydrocarbon and that aromaticity in it would involve cyclic conjugation in a ring containing *three* weak homoconjugative interactions. We therefore decided to investigate the matter further, by carrying out AM1, ab initio, and MM2 calculations for **1–4**.



*1*



*2*



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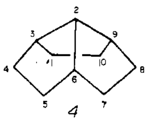

*4*

After the paper reporting our results had been submitted, two papers reporting geometry-optimized ab initio calculations for **1–4** appeared in print.[8] According to these, the heats of hydrogenation for the individual steps in the series **1** → **2** → **3** → **4** should all be equal, implying that **1** is not significantly stabilized and hence that one or more of the experimental heats of hydrogenation must have been in error by amounts well outside the expected limits. We have therefore revised our paper to take this additional information into account, arriving at a possible explanation for the experimental results.

## Theoretical Procedure

Our studies involved use both the AM1[9] semiempirical model, as implemented in the AMPAC program[10] and the ab initio SCF MO procedures embodied in the GAUSSIAN82[11] program. All geometries were fully optimized, using the methods included in AMPAC and GAUSSIAN82. The AM1 geometries were used as starting geometries in the ab initio

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(1) Adams, R.; Winstein, S. *J. Am. Chem. Soc.* **1948**, *70*, 838.

(2) For recent reviews, see: (a) Paquette, L. A. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 106. (b) Childs, R. F. *Acc. Chem. Res.* **1984**, *17*, 347.

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