containing five-coordinate tin and a central Sn_2O_2 ring as is observed for **1**. It has a crystallographic center of inversion in the center of the Sn_2O_2 ring. An ORTEP plot of the compound is shown in Figure 1; selected bond distances and angles are given in Tables II and III, respectively.

Surprisingly, the five individual heterocycles of the (dimeric) molecule are essentially coplanar. Of course, planarity would be expected for the pyrazolyl rings. On the other hand, several members of the pentacyclic system should be considered as either sp^3 hybridized (boron and oxygen atoms) or sp^3d hybridized (tin atoms), and still the polycyclic system is almost coplanar. The boron atoms deviate most from the mean plane (9.3 pm); the bond angles are close to tetrahedral (109.5 ± 3.0°). The B-C distances are similar to those found in pyrazaboles,[10] but the B-O bond of 1.54 Å is rather long and even on the long side when compared to those of borates containing tetrahedral boron atoms.[11]

The oxygen atoms may be viewed as sp^3 hybridized, as is indicated by the sum of their three bond angles (328.8 versus 328.5° for the ideal case). However, the individual bond angles exhibit quite significant deviations from a tetrahedral bond angle, especially the rather acute angle of only 74.7 (1)° for Sn-O-Sn(a), while the other two, with values of 124.9 and 129.8°, respectively, would seem to be in better agreement with sp^2 hybridization.

The sharp Sn-O-Sn(a) angle forces the tin atoms fairly close together. Thus, the Sn-Sn distance within the four-membered Sn_2O_2 ring is only 3.32 Å, corresponding to a mere 18% increase over the Sn-Sn distance in metallic tin (2.80 Å). Hence, there may be bonding interaction between the two tin atoms. However, the tin is clearly five-coordinate. Inspection of the bond angles indicates a distorted trigonal-bypyramidal coordination sphere, since the sum of the bond angles between the equatorial atoms C(6), C(7), and O(1) is 359.5°, while the bond angle to the axial atoms deviates by 28.6° from the ideal value of 180°. The tin atoms contribute one axial and one equatorial bond to the formation of the central dioxadistannetane ring. As is to be expected for this kind of geometry, a short (equatorial) and a long (axial) Sn-O bond were found, although both values are on the short side of known Sn-O bond distances.[12]

The Sn-bonded nitrogen of the pyrazolyl group is in axial position; hence, the Sn-N distance is long as compared to other known Sn-N bonds.[13] Also, the B-N bond is quite long as compared to that of pyrazaboles containing the skeletal $B(\mu\text{-pz})_2B$ arrangement.[10]

In principle, the molecule belongs to a class of tin compounds of the general formula $(CH_3)_2Sn(OR)X$, where X is an electron-withdrawing group. This results in an increase of the Lewis acidity at the tin center and leads to acid-base interaction with the lone pairs of electrons at the oxygen atom, thus leading to an increase in the coordination of tin.[14]

Acknowledgment. This work was supported by the Office of Naval Research (K.N.). The assistance of Dr. A. Linti in the crystal structure determination is gratefully acknowledged.

Supplementary Material Available: Tables of atomic coordinates and isotropic displacement coefficients for hydrogen atoms and anisotropic displacement coefficients (2 pages); a table of observed and calculated structure factors for $[(C_2H_5)_2B(\mu\text{-O})(\mu\text{-pz})Sn(CH_3)_2]_2$ (8 pages). Ordering information is given on any current masthead page.

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[13] Sn-N bond distances to five-coordinate tin are on the order of 2.2-2.4 Å; see, for example: Allmann, R.; Olejnik, S.; Wakowska, A. *Z. Kristallogr.* **1981**, *154*, 244-245. Matsubayashi, G.; Tanaka, T.; Nishigaki, S.; Nakatsu, K. *J. Chem. Soc., Dalton Trans.* **1979**, 501-505.

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Ene Reactions of 1,2-Dehydro-*o*-carborane[1]

Qiurong Huang, Henry L. Gingrich, and Maitland Jones, Jr.*

Received March 7, 1991

1,2-Dehydro-*o*-carborane undergoes the ene reaction with a variety of hydrocarbon substrates. This reaction appears to be a concerted 2 + 4 process.

Introduction

o-Carborane, $C_2B_{10}H_{12}$ (**1**), is a three-dimensional analogue of benzene. Carborane **1** accommodates 26 electrons in a system of 13 filled bonding molecular orbitals and thus resembles its simpler two-dimensional aromatic cousin benzene.[2] This similarity in molecular orbital description results in vast thermodynamic stability for **1**,[2] as well as reactivity reminiscent of benzene (aromatic substitution).[3] The aromaticity of the icosahedral carboranes has been remarked many times.[2,4]

1

In this and all subsequent figures the dots represent carbon. All other vertices are boron, and there is an unshown hydrogen at each vertex.

We have recently generated 1,2-dehydro-*o*-carborane (**2**), the carborane version of benzyne,[5] and described its reactions with a variety of dienes.[4] Some of these revealed **2** to be especially

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[1] Support for this work by the National Science Foundation through Grant CHE-8800448 and by the donors of the Petroleum Research Fund, administered by the American Chemical Society, is gratefully acknowledged.

[2] (a) Olah, G. A.; Surya Prakash, G. K.; Williams, R. E.; Field, L. D.; Wade, K. *Hypercarbon Chemistry*; Wiley: New York, 1987. (b) Muetterties, E. L. *Boron Hydride Chemistry*; Academic: New York, 1975. (c) Grimes, R. N. *Carboranes*; Academic: New York, 1970. (d) Onak, T. *Organoborane Chemistry*; Academic: New York, 1975.

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[4] Gingrich, H. L.; Ghosh, T.; Huang, Q.; Jones, M., Jr. *J. Am. Chem. Soc.* **1990**, *112*, 4082. Ghosh, T.; Gingrich, H. L.; Kam, C. K.; Mobraaten, E. C.; Jones, M., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 1313.

[5] Comment seems in order on the nature of the "extra" bond in **2**. Many seem caught up in the question of whether this is a "double" or "triple" bond. The answer is a resounding "neither!". As in dehydrobenzene, a pair of singly occupied orbitals extends radially from the framework. Questions of "doubleness" or "tripleness" are not productive and in this case are essentially meaningless, as the carborane framework is constructed from three-center, two-electron bonding. The question addressed in ref 4, as well as in this work, is the extent of overlap in the "extra" bond. Future questions (computational work in progress) concern the C-C bond length in **2**.

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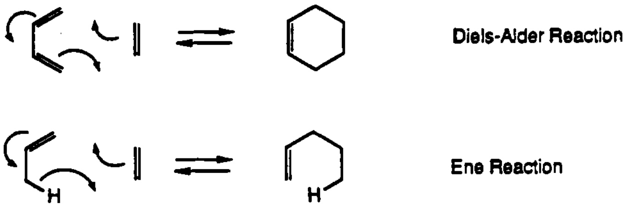
2

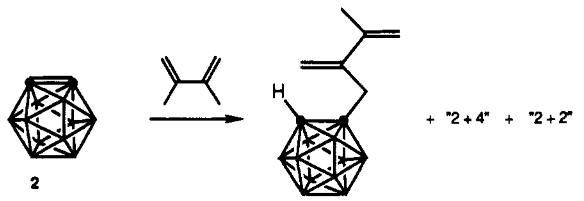
active in ene reactions. In this paper we present experiments designed to probe the mechanism of the ene process and to compare the ene reactions of **2** with those of benzyne.

Although generally something of a poor relation in the house of thermal reactions, the ene reaction is nonetheless closely related to the more extensively documented "diene" or Diels–Alder reaction. The main difference is that in the ene reaction the role of one double bond of the diene is played by a carbon–hydrogen bond of the ene.[6] Both the ene and Diels–Alder reactions are 2 + 4 cycloadditions, and therefore both are likely to be concerted.[7] Investigations of the mechanism of the ene process have shown that this is generally the case.[8,9] The critical experiments were carried out by the groups of Hill,[8] Arnold,[9] and Dolbier,[10] who used a variety of labeling experiments to determine that the best representation for the mechanism of several disparate ene reactions was a concerted one.

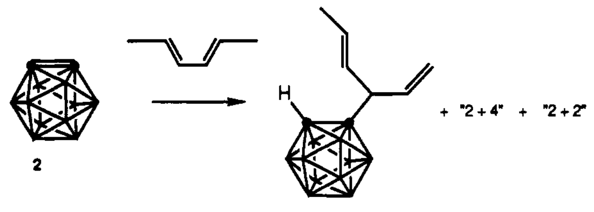


Ene Reactions of 1,2-Dehydro-*o*-carborane (2)

We have already shown that the reaction of **2** with dienes gives substantial amounts of the products of ene reaction, along with compounds formed by 2 + 2 and 2 + 4 cycloadditions.[4] There is a general correspondence with the reactions of benzyne, although detailed differences in the product mixtures certainly appear.[11,12]

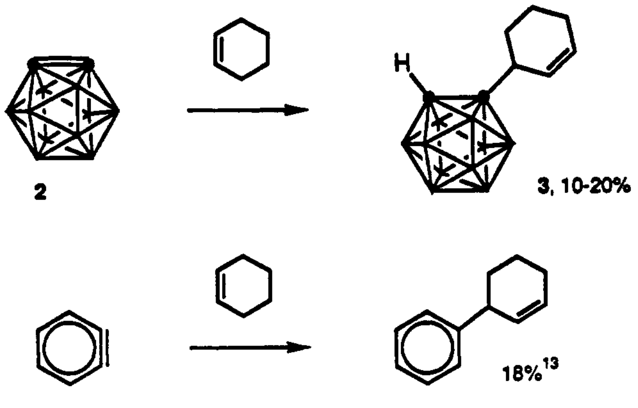


ene product,	74%	8%	18%
[benzyne:[11]	73%	13%	13%]



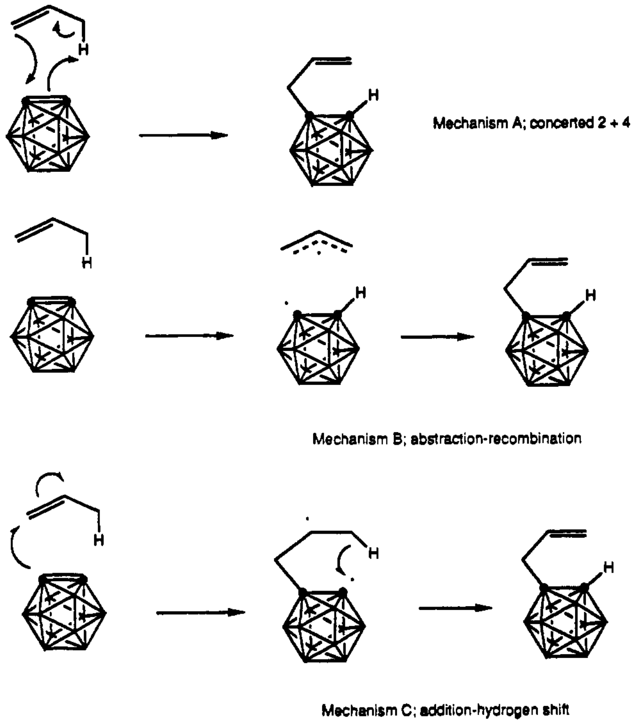
ene product,	23%	21%	56%
[benzyne:[12]	10%	85%	5%]

The provenance of the ene reaction of benzyne with unconjugated alkenes is somewhat complicated, but it is now clear that this intermediate reacts with the prototypal cyclohexene exclusively by ene reaction.[13] This is the case for **2** as well. Compound **3** is the sole adduct formed when **2** is generated in cyclohexene. No mechanistic information is available from these experiments, which do no more than demonstrate that the ene reaction is especially prominent in the chemistry of **2**.



Mechanism of the Ene Reaction of 2

Three general mechanisms can be written: a concerted 2 + 4 cycloaddition (A), an abstraction–recombination process (B), and an addition–hydrogen shift mechanism (C). Reaction of **2** with 2,3-dimethyl-2-butene was used as a test of mechanism B, abstraction–recombination. Mechanism A, the concerted 2 + 4 reaction, predicts a single product, **4**, whereas mechanism B predicts both **4** and **5**. The only adduct isolated was **4**. Authentic **5** was made in two ways. It is one of the products from ene reaction of **2** with 2,3-dimethyl-1-butene, and it can be made through a displacement of the allylic bromine of **6** by 1-lithio-*o*-carborane (**7**). With **5** in hand, it was easy to determine that



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(8) Hill, R. K.; Morgan, J. W.; Shetty, R. V.; Synerholm, M. E. *J. Am. Chem. Soc.* **1974**, *96*, 4201.

(9) Garsky, V.; Koster, D. F.; Arnold, R. T. *J. Am. Chem. Soc.* **1974**, *96*, 4207.

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(11) Wittig, G.; Dürr, H. *Liebigs Ann. Chem.* **1964**, *672*, 55.

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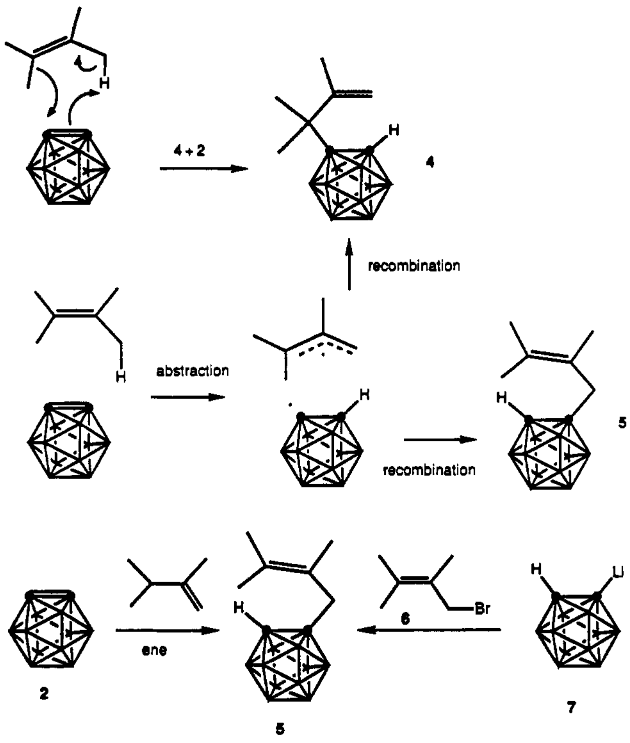
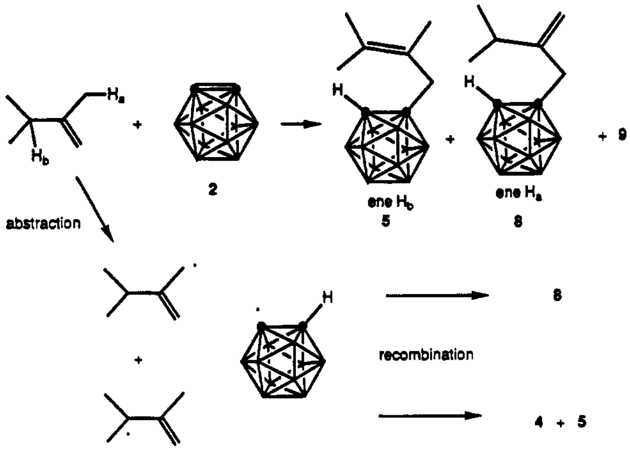
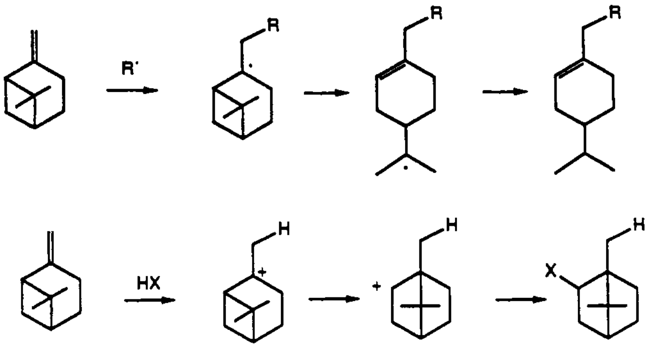


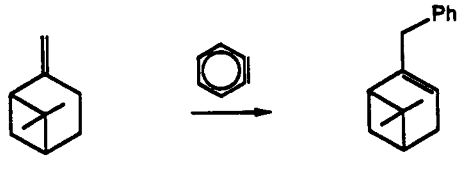
less than about 1% could have been detected in the reaction of **2** with 2,3-dimethyl-2-butene. It seems that mechanism B cannot be important. A similar conclusion can be reached from the ene reaction of 2,3-dimethyl-1-butene with **2**. Three products can be isolated, the aforementioned **5** (17%), **8** (74%), and an unidentified compound, **9**, which, though of unknown structure, is definitely not **4**. As we have compound **4** in hand, it is easy to show that it is not formed in the reaction in amounts greater than about 1%. The concerted ene reaction can form both **5** and **8**, whereas the abstraction–recombination mechanism predicts the unobserved **4** as well. The 9% of the product of uncertain structure **9** can be best characterized at this point only by showing what it is not. It is neither **4** nor a product of 2 + 2 cycloaddition. It may well be the result of reaction with an especially active minor impurity (starting alkene greater than 99% pure, as determined by ^{1}H NMR spectroscopy and gas chromatography). The overall conclusion remains that abstraction–recombination mechanisms cannot be important in reactions of **2**.



Mechanism C is more difficult to eliminate. In other contexts, addition to β-pinene has been used to choose between concerted and addition–abstraction processes. It has been long known that both radical and cationic reactions of β-pinene lead to extensive rearrangement. For example, the radical-induced addition of carbon tetrachloride to β-pinene leads to ring-opened material in "substantially quantitative" yield.[14] Cationic processes induce a different kind of skeletal rearrangement, a Wagner–Meerwein shift to give molecules containing the camphane skeleton.[15]



The absence of these rearrangements has been used to eliminate radical and cationic processes in favor of concerted mechanisms. For example, Arnold and co-workers found the reaction of benzyne with β-pinene to give 10-phenyl-α-pinene (**10**) and held this result to be inconsistent with an addition–abstraction mechanism.[9] Hill and co-workers reached similar conclusions in the study of the reaction of maleic anhydride with β-pinene.[8] We have borrowed this technique and examined the reaction of **2** with β-pinene. A radical-like addition should lead to ring-opened products such as **11**. Ionic addition should lead first to **12** and then either to ring formation as in **13** or to alkene **14**.



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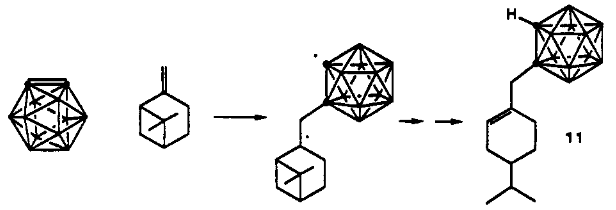

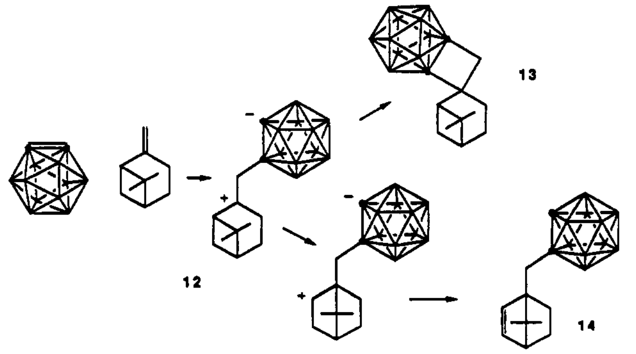

Instead, by far the major product is **15**, the carborane version of **10**. Identification rests upon analysis of NMR spectra and in particular on comparison with the reported ^{1}H NMR spectrum of **10**.[9] The presence of a pair of singlet, "bridge" methyl groups is a particularly compelling piece of evidence that the product cannot be **11**. The presence of a signal for a *single* olefinic hydrogen in the ^{1}H NMR spectrum eliminates either **13** or **14**

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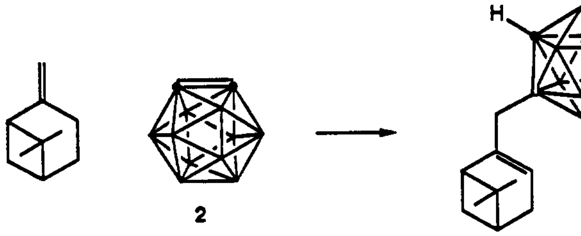

2

15

as a possible structure. There are many minor products in this reaction, but none seems to have the required molecular weight of **11**, the putative product of a radical-induced, stepwise, "mechanism C" reaction. It is not possible for us to remove the possibility that one of the minor products has the structure of **13** or **14**. However, if **13** or **14** is formed at all in this reaction, it is in much smaller amount than **15**, in sharp contrast to known[14,15] stepwise reactions in which rearranged compounds are by far the major products. Neither mechanism B nor C seems able to explain the experimental observations. By contrast, mechanism A, the concerted 2 + 4 ene process, does very well and seems to us the best candidate.

Experimental Section

General Procedures. ^{1}H NMR and ^{13}C NMR spectra were recorded on a General Electric QE 300 spectrometer at 300 and 75 MHz, respectively, with signals referenced to Me_4Si, using C_6D_6 or $CDCl_3$ as solvent. Precise masses were measured on a KRATOS MS 50 RFA high-resolution mass spectrometer. Analytical gas chromatography (AGC) was performed on a Hewlett-Packard 5890A gas chromatograph (6 m × 0.75 mm × 1.0 mn SPB-1 glass capillary column; carrier gas helium). GC/MS was performed on a Hewlett-Packard 5992 B instrument (6 ft × $^1/_4$ in. glass column packed with 3% OV-17 on Chromosorb W 100/200; carrier gas helium). Preparative gas chromatography (PGC) was performed on a GOW-MAC GC 580 instrument (8 ft × $^1/_4$ in. stainless steel column packed with 20% DC-710 on Chromosorb W 8/100; carrier gas helium). Thin-layer chromatography (TLC) and column chromatography were carried out with silica gel plates and columns. Elemental analyses were performed by Robertson Laboratories, Madison, NJ 07940.

In general, reactions were run under an argon atmosphere. The reaction systems were kept as dry as possible, and all solvents were purified and dried by standard procedures.

Generation of 2. To a solution of butyllithium (10 mL, 2 M solution in pentane; 20 mmol) in ether (10 mL) at 0 °C under an argon flow was added dropwise with stirring a solution of *o*-carborane (1.44 g, 10 mmol) in ether (10 mL). After the reaction mixture containing a curdy white crystalline precipitate was stirred at room temperature for 1 h then cooled to 0 °C, bromine (1.60 g, 10 mmol) was added very slowly. The resulting clear solution was stirred at 0 °C for an additional 0.5 h. The reaction mixture was expected to generate **2** (~10 mmol) and was used immediately to run the following reactions.

Reaction of 2 with Cyclohexene. To the reaction mixture used for generating **2** (10 mmol) was added a solution of cyclohexene (8.22 g, 100 mmol) in ether (10 mL). The solution was warmed to room temperature, stirred for 1 h, and then heated at reflux for 12 h. Upon cooling, the reaction mixture was treated with water (15 mL). The ethereal layer was separated from the mixture washed with water until pH = 7, and dried over anhydrous $MgSO_4$. The solvent and excess cyclohexene were removed under reduced pressure by using a rotary evaporator to give a dark brown liquid (1.76 g). The crude product contained a single ene reaction product **3**, in 10–20% yield. A further purification by PGC (20% DC-710 column, 100–240 °C) provided an analytical sample of **3**, a colorless liquid. ^{1}H NMR (C_6D_6): δ (ppm) 5.38 (m, 1 H), 5.08 (m, 1 H), 2.71 (s, 1 H), 2.32 (s, 1 H), 1.49 (br s, 2 H), 1.28 (m, 2 H), 0.97 (m, 2 H), 1.3–3.7 (br m, 10 H, BH). ^{13}C NMR (C_6D_6): 130.5, 125.9, 79.9, 60.0, 40.6, 29.3, 24.1, 20.9. Anal. Calcd for $B_{10}C_8H_{20}$: C, 42.83; H, 8.98. Found: C, 43.19; H, 9.03.

Reaction of 2 with 2,3-Dimethyl-2-butene. To the reaction mixture used for generating **2** (~5 mmol) was added a solution of 2,3-dimethyl-2-butene (8.42 g, 100 mmol) in ether (5 mL). The solution was warmed to room temperature, stirred for 1 h, and then heated at reflux for 24 h. Upon cooling, the reaction mixture was treated with water (8 mL). The ethereal layer was separated from the mixture, washed with water until pH = 7, and dried over anhydrous $MgSO_4$. The solvent and excess 2,3-dimethyl-2-butene were removed under reduced pressure by using a rotary evaporator to give a dark brown liquid (1.95 g) that contained a single ene reaction product **4**, in 20–35% yield. A further purification by PGC (20% DC-710 column, 100–240 °C) provided an analytical sample of **4**, mp 97–100 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.07 (s, 1 H), 4.99 (s, 1 H), 3.67 (br s, 1 H), 1.83 (s, 3 H), 1.42 (s, 6 H), 0.8–3.5 (br m, 10 H, BH). Anal. Calcd for $B_{10}C_8H_{22}$: C, 42.43; H, 9.81. Found: C, 42.46; H, 9.58.

Reaction of 2 with 2,3-Dimethyl-1-butene. To the reaction mixture used for generating **2** (~5 mmol) was added a solution of 2,3-dimethyl-1-butene (4.21 g, 50 mmol) in ether (5 mL). The solution was warmed to room temperature, stirred for 1 h, and then heated at reflux for 12 h. Upon cooling, the reaction mixture was treated with water (8 mL). The ethereal layer was separated from the mixture, washed with water until pH = 7, and dried over anhydrous $MgSO_4$. The solvent and excess 2,3-dimethyl-1-butene were removed under reduced pressure by using a rotary evaporator to give a dark brown liquid (1.25 g) that contained two ene reaction products, **8** (10–20% yield) and **5** (3–5% yield). Further purification by PGC (20% DC-710 column, 100–240 °C) provided pure samples of **8** and **5**. Compound **8** was a colorless liquid. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.04 (s, 1 H), 4.82 (s, 1 H), 3.56 (br s, 1 H), 2.97 (s, 2 H), 2.25 (m, 1 H), 1.03 (d, J = 6.6 Hz, 3 H), 0.8–3.5 (br m, 10 H, BH). Precise mass: calcd for $C_8H_{22}{}^{11}B_8{}^{10}B_2$, 226.2725; found, 226.2702. Compound **5** contained 69% of **5** and 30% of an unknown compound (m/e = 290). ^{1}H NMR ($CDCl_3$): δ (ppm) 3.50 (br s, 1 H), 3.01 (s, 2 H), 1.70 (s, 3 H), 1.68 (s, 6 H), 0.8–3.5 (br m, 10 H, BH). The unknown compound (m/e = 290) was shown to be neither **8** nor **5** by AGC, GC/MS, and ^{1}H NMR spectroscopy.

Preparation of 6. A mixture of 2,3-dimethyl-2-butene (3.37 g, 40 mmol), *N*-bromosuccinimide (1.78 g, 10 mmol) and carbon tetrachloride (50 mL) was stirred under an argon flow at room temperature for 1.5 h and then refluxed under UV irradiation for 5 h. The succinimide produced in the reaction was separated by suction filtration. The carbon tetrachloride and excess 2,3-dimethyl-2-butene were removed from the filtrate by distillation under reduced pressure. The dark brown residue was chromatographed over a 2.0 cm × 25 cm column of silica gel (~24 g) with an 80:20 pentane:ether mixture as eluent. Fractions 1–6 were combined and evaporated under a reduced pressure to give **6**, a light yellow liquid (0.88 g, 49% yield, ca. 90% pure). ^{1}H NMR ($CDCl_3$): δ (ppm) 4.08 (s, 2 H), 1.77 (s, 6 H), 1.71 (s, 3 H).

Preparation of 5 from 6 and 7. To a stirred solution of *o*-carborane (0.72 g, 5 mmol) in ether (10 mL) at 0 °C under an argon flow was added dropwise a solution of butyllithium (3 mL, 2 M solution in pentane; 6 mmol) in ether (3 mL). The mixture was warmed to room temperature, stirred for 1 h, and then cooled again to 0 °C. A solution of **6** (0.88 g (90%), ~5 mmol) in ether (5 mL) was added dropwise to the reaction mixture described above, which contained ca. 5 mmol of **7**. The resulting mixture was warmed to room temperature, stirred for 2 h, and then heated at reflux for 3 h. Upon cooling, the reaction mixture was treated with water (10 mL). The ethereal layer was separated from the mixture, washed with water until pH = 7, dried over $MgSO_4$, and then evaporated under reduced pressure by using a rotary evaporator to give 1.13 g of a dark orange liquid containing **5**. A further purification by PGC (20% DC-710 column, 100–240 °C) provided an analytical sample of **5**, a white solid, mp 66–68 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 3.50 (br s, 1 H), 3.01 (s, 2 H), 1.70 (s, 3 H), 1.68 (s, 6 H), 0.8–3.5 (br m, 10 H, BH). Precise mass: calcd for $C_8H_{22}{}^{11}B_8{}^{10}B_2$, 226.2725; found, 226.2724.

Reaction of 2 with β-Pinene. To the reaction mixture used for generation of **2** (~5 mmol) was added a solution of β-pinene (10.9 g, 80 mmol) in ether (10 mL). The solution was warmed to room temperature, stirred for 1 h, and then heated at reflux for 12 h. Upon cooling, the reaction mixture was treated with water (10 mL). The ethereal layer was separated from the mixture, washed with water until pH = 7, and dried over anhydrous $MgSO_4$. The solvent and part of the β-pinene were removed under reduced pressure by using a rotary evaporator to give a blood red liquid (10.2 g) that contained a single ene reaction product **15**. A further purification by PGC (20% DC-710 column, 100–240 °C) provided an analytical sample of **15**, a white solid, mp 106–109 °C. ^{1}H NMR ($CDCl_3$): δ (ppm) 5.42 (br s, 1 H), 3.54 (br s, 1 H), 2.91 (AB q, J = 14.3 Hz, $\Delta\nu_{AB}$ = 62 Hz, 2 H), 2.1–2.5 (m, 5 H), 1.28 (s, 3 H), 1.15 (d, 1 H, J = 8.8 Hz), 0.78 (s, 3 H), 0.7–3.2 (br m, 10 H, BH). Precise mass: calcd for $C_{12}H_{26}{}^{11}B_8{}^{10}B_2$, 278.3038; found, 278.3048.