Gas-Phase Hydroboration of Allene, Other Olefins, and Acetylenes

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Abstract: Terminal addition of diborane to allene results in the formation of the cyclic 1,2-trimethylenediborane. Polymerization of this compound occurs rapidly in liquid phase and is attributed, in part, to release of ring strain. Poly(μ-trimethylene)diborane depolymerizes quantitatively at 60° *in vacuo*, thus establishing the reversibility of the reaction $n\text{-}B_2C_3H_{10} \rightleftarrows [(CH_2)_3\text{-}B_2H_4]_n$ which probably proceeds *via* mobile bridge hydrogens. The gas-phase hydroboration of simple monoolefins is shown to be a general method for the synthesis of mono- and 1,1-dialkyldiboranes in yields of 55–65 and 30–40%, respectively, when carried out at 60–65° using a 5:1 diborane–olefin molar ratio. Nonvolatile organoboron polymers, the structure of which is discussed in the case of 2-butyne, are formed nearly quantitatively by gas-phase hydroboration of acetylenes with excess diborane; in addition, small fractions of alkyldiboranes are isolated.

Olefin hydroboration has been studied extensively in the liquid phase and in solvent systems,[1–4] but little in the gas phase.[5] In previous studies, hyboration was allowed to proceed to the trialkylborane stage without deliberate attempts to isolate the intermediate alkyldiboranes in preparative yields. Because alkyldiboranes are customarily prepared by equilibration of trialkylboranes with diborane,[6,7] it was anticipated that these compounds could be prepared directly from monoolefins and diborane if a sufficiently high molar ratio of B_2H_6 to olefin is used.

Weiss, *et al.*, have shown the gas-phase reaction of 1,3-butadiene with diborane in the presence of H_2 to result in the formation of cyclic organoboranes.[8] By analogy, it is not unreasonable to expect 1,2-trimethylenediborane to form by 1′,3′ addition of diborane to allene. However, the work of Devaprabhakara and Gardner indicate that the dihydroboration of allenes in solvents results in the preferential addition of the boron atoms to the central carbon atom.[9] Since solvent and gas-phase reactions frequently lead to different products, as is clearly demonstrated in the 1,3-butadiene dihydroboration reaction,[2,8,10–14] the gas-phase allene dihydroboration reaction was carried out with some expectation that 1′,3′ diaddition would occur.

Though there are apparently no reports about the isolation of organoboranes obtained from dihydroboration of acetylenes, these products are generally considered to have a complex polymeric structure derived from the bifunctional organic molecule and the trifunctional borane.[1,15–17] However, this situation also exists for the dihydroboration of 1,3-butadiene and allene, and yet, volatile compounds are formed in reasonable yields. In the case of acetylenes, cyclic organoboranes such as 1,2-dimethylenediborane and its C-alkyl derivatives were not expected for steric reasons; but formation of other volatile compounds in the gas phase could not be ruled out completely; and also, investigations seemed desirable for general comparisons with the gas-phase hydroboration of olefins reported in this work.

Experimental Section

Materials. All starting materials were checked for purity by infrared analyses. Diborane was fractionated before use through a −135° trap to remove higher boranes. Ethylene, propene, 1-butene, 1,3-butadiene, propyne, and 2-butyne (all CP, Matheson) were used without further purification. Allene (CP, Matheson) was separated from minor amounts of 2-chloropropene by glc; acetylene was fractionated through a −120° trap to remove acetone; diacetylene (C_4H_2) was prepared according to the procedure given by Armitage, *et al.*,[18] and was purified by glc.

Analyses. Infrared spectra of all materials were recorded using a Beckman IR-5 spectrometer and a 100-mm gas cell with attachments which allowed for controlled variation of pressure. All spectra were calibrated with polyethylene film. Combustion analyses were made by Elek Microanalytical Laboratories, Torrance, Calif. Gas chromatographic separations (glc) were carried out using a 30% Kel-F on firebrick column[19] normally operated at 50°.

Apparatus. Standard high-vacuum techniques were used in all experiments. Gas reactions were carried out either in reaction bulbs equipped with a cold finger and break-off seal or, if more than a 2-l. volume was required, in a closed circulation system. Over-all pressures of the gas mixtures were calculated not to exceed 1 atm at reaction temperature.

Gas-Phase Hydroboration of Monoolefins. A. Ethylene. Diborane (60 mmoles) and ethylene (12 mmoles) were condensed into a 2-l. reaction flask. After sealing from the high-vacuum line, the flask was heated to 60–65° for 24 hr and reattached to the line. All condensable gases were frozen into the cold finger with liquid

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nitrogen. The flask was then opened by cracking the breakseal after which a small amount of noncondensables were removed by pumping. By raising the cold finger to −135° unreacted diborane and ethylene were vacuum transferred to a trap at −190°. The content (46.5 mmoles) of the −190° trap was found to be nearly all diborane by infrared analysis. The residual material in the cold finger of the flask was found to be a mixture of ethyldiborane (I) and 1,1-diethyldiborane (II), which was cleanly separated by glc. The yields of I and II were 7.8 (65% yield based on ethylene consumed) and 1.8 mmoles (30%), respectively. An infrared analysis[20–23] showed only trace amounts of the 1,2-diethyldiborane as a contaminant in the isolated 1,1 isomer.

B. **Propene.** In a manner analogous to part A, diborane (25 mmoles) was allowed to react with propene (5 mmoles). The contents of the reaction bulb was heated to 65° for 18 hr, and, after cooling to ambient temperature, colorless droplets appeared at the walls. Using the same fractionation method as described in part A, 20.5 mmoles of B_2H_6 was recovered from the reaction mixture. No propene was detectable in the infrared spectrum of this fraction. Using both fractional condensation and glc separation techniques, 2.85 mmoles (57% yield based on propene) of n-$C_3H_7B_2H_5$ (IV) and 1.05 mmoles (42% yield) of 1,1-(n-$C_3H_7)_2B_2H_4$ (V) were isolated from the remaining contents of the flask. From an infrared analysis,[23] only a trace amount of 1,2 isomer was present in V. The most characteristic infrared absorptions of IV were found at 3650 w, 2967 s, 2882 s, 2597 s, 2519 s, 2320 w, 2119 w, 2049 w, 1916 w, 1773 w, 1689 m, 1592 vs, 1471 w, 1348 w, 1255 w, 1166 m sh, 1131s, ~925 w, ~850 w cm^{-1}. In a second run, 20 mmoles of B_2H_6 and 10 mmoles of C_3H_6 yielded 12.8 mmoles of unreacted B_2H_6, 4.3 mmoles (43%) of IV, and 2.4 mmoles (48%) of V. In the gas phase IV decomposes rapidly yielding B_2H_6 and higher alkylated diboranes.

C. **1-Butene.** A mixture of 15 mmoles of B_2H_6 and 3 mmoles of 1-butene in a 500-ml flask was brought to react at 60–65° for 19 hr, and, after cooling to ambient temperature, yellowish droplets appeared at the walls. Using the same procedure as described above, 9.0 mmoles of unreacted diborane and 2.1 mmoles (63% yield based on C_4H_8) of n-$C_4H_9B_2H_5$ (VII) were obtained. Oily residues in the reaction flask were not further investigated.

1,2-Diethyldiborane (III) was prepared by the disproportionation of ethyldiborane (I) using the method of Solomon, *et al.*[24] Final purification was accomplished with glc. At 50° the relative retention volumes of the ethyldiboranes (including II from part A above) are: I, 13; II, 34; and III, 38, respectively.[25]

Gas-Phase Hydroboration of Allene. Using an all-glass flow system, a mixture of 82.5 mmoles of B_2H_6 and 32 mmoles of allene was diluted with 250 mm of helium (total pressure, 475 mm) and circulated through a reactor at 90–95°. (It should be noted that severe decomposition to nonvolatile yellow solids occurs at about 100°.) By employing two −78° traps in the system, the less-volatile products were continuously removed from further circulation. After 16 hr the pressure had decreased by 106 mm, indicating that approximately 54 mmoles of gas had reacted. Only a 2-mm further decrease in pressure was noted after an additional 24 hr. Helium was removed from the condensable gases by slow passage through four traps cooled with liquid N_2. The condensed material was then vacuum fractionated through traps at −97 and −190°. The −190° trap contained 55 mmoles of diborane and no detectable amount of allene by infrared analysis. Application of glc to the contents of the −97° trap gave 13.4 mmoles (42% yield based on allene) of 1,2-trimethylenediborane (VIII) and 4.3 mmoles (13% yield) of n-$C_3H_7B_2H_5$ (IV). A considerable amount of polymeric material which did not depolymerize at 60° under high vacuum remained in the reactor. *Anal.* Calcd for $B_2C_3H_{10}$ (VIII) (mol wt, 67.75): C, 53.18; H, 14.88. Found: C, 53.88; H, 14.77 (best pair of results obtained from six analyses: the medium C value of all six analyses was 53.06). Vapor pressures were 132 ± 1 mm (26°) and 43.5 ± 1 mm (0°). All samples of VIII polymerized while warming up from −190 to *ca.* 25°, forming highly viscous liquids. During continued storage at ambient temperature, some samples transformed further to white solids. These solids were readily and quantitatively depolymerized by heating to 60° under high vacuum, and from such degradations only VIII and traces of B_2H_6 could be detected by glc. Relative glc retention volumes at 50° were found to be: IV, 17–19; VIII, 27–28.[25] Gas-phase infrared absorptions for VIII were: 3546, w, 3484 w sh, 2959 vs, 2890 s sh, 2841 w sh, 2551 vs, 2193 w, 2070 w, 1703 w, 1767 w, 1664 m, 1565 m sh, 1550 s sh, 1506 vs, 1429 m, 1416 m, 1316 w, 1256 m, 1145 s, 1045 vs, 1018 m, 961 w, 942 w, 845 m, 781 w, 771 m, 760 w, and 640 m cm^{-1}.

Gas-Phase Hydroboration of 1,3-Butadiene. A mixture of diborane (69 mmoles) and 1,3-butadiene (23 mmoles) was circulated through a reactor at 85° for 4 hr during which the pressure dropped from 190 to 78 mm. The less-volatile products were continuously removed from the gas phase by employing two −60° traps. Vacuum fractionation yielded 48.5 mmoles of unreacted B_2H_6 and a mixture, trapped at −135°, of 1,2-tetramethylenediborane (IX) and 1,2-(1′-methyltrimethylene)diborane (X). After repeated glc, 4.1 mmoles of IX and 2.4 mmoles of X were obtained. X slowly polymerized on warming from −190° to ambient temperature.

Infrared spectra of the gaseous compounds were checked and found identical with those reported.[8] Relative glc retention volumes at 50° were found to be: X, 34–39; IX, 48–52.[25] In contrast to previous findings,[8] X appears to be quite stable at 50° under these conditions.

Gas-Phase Hydroboration of Alkynes. A. Acetylene. Diborane (5 mmoles) and acetylene (5 mmoles) were condensed into a 1-l. reaction bulb which was then pressurized with 300 mm of He, sealed off, and heated to 85° for 5 hr. Near 70° the gas mixture became cloudy and yellowish solid materials precipitated at the walls. Continued formation of solids was observed through 85°. Subsequent fractionation yielded 0.3 mmole of unreacted B_2H_6 and 0.12 mmole of volatile organoboranes, which contained mostly $C_2H_5B_2H_5$ and 1,1-$(C_2H_5)_2B_2H_4$, in addition to B_5H_9 and n-butane (infrared[20–23] and mass spectroscopic analyses). Approximately 9 mmoles of H_2 was formed.

B. **Propyne.** Diborane (2 mmoles) and propyne (2 mmoles) were allowed to react in a 500-ml bulb under additional pressure of 300 mm of He. At 70°, the gas mixture began to form droplets and was then heated to 100° for 2 hr. Subsequent fractionation yielded 0.65 mmole of unreacted B_2H_6 and, trapped at −135°, a small amount of n-$C_3H_7B_2H_5$ which was identified by comparing its infrared spectrum with that of IV obtained from propene hydroboration (*vide supra*). Nonvolatile oils remained in the flask. Additional runs using B_2H_6/C_3H_4 molar ratios of 2:1 and 3:1, respectively, and a 1:1 run without diluent He, resulted in sudden decomposition of the gas mixtures after exceeding 85°.

C. **2-Butyne.** Diborane (15 mmoles) and 2-butyne (3 mmoles) were condensed into a 1-l. reaction bulb, equipped with a break-off seal, a cold finger, and a 5-mm thick-wall nmr tube. The gases were mixed by rapid vaporization at 25°; reaction began immediately, forming droplets of viscous oils which moved slowly down into the nmr tube over a period of 24 hr. After cooling the nmr tube to −78°, the break-seal was opened and volatile materials were fractionated through −140 and −190° traps. From the latter trap 12.7 mmoles of B_2H_6 was recovered. According to infrared analysis, no 2-butyne was present in the −140° trap which contained 0.35 mmole of unidentified organoboranes. The nmr tube contained the major part of the polymeric material and was sealed off under vacuum. In a second run, 5 mmoles of 2-butyne was allowed to react with 7.5 mmoles of B_2H_6 under the same conditions. By subsequent fractionation 4.5 mmoles of B_2H_6 was recovered. The nonvolatile polymer product obtained (2-butyne:diborane ratio 1.67) showed a higher viscosity than the product of run 1 (2-butyne:diborane 1.36). Both nmr samples solidified slowly when stored at 25°.

D. **Diacetylene.** In a 500-ml reaction bulb, a mixture of 2 mmoles of B_2H_6, 2 mmoles of C_4H_2, and He (350-mm pressure at 25°) was heated to 100° for 3 hr. Formation of colorless solids began soon and was most evident at 85–90°. Subsequent fractionation yielded 0.3 mmole of unreacted B_2H_6, but neither C_4H_2 nor volatile organoboranes were found. In a second run using a 2:1 B_2H_6/C_4H_2 molar ratio, severe decomposition occurred shortly after exceeding 80°; in addition to yellowish materials, black solids (carbon?) were formed.

Results and Discussion

1. Gas-Phase Hydroboration of Allene.

Allene is found to react with excess diborane in the gas phase at

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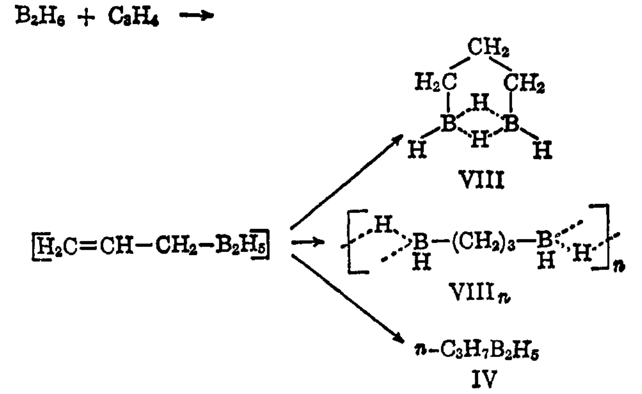
90–95°. And although the presence of allyldiborane is not detected, it is the most likely initial addition product, which is then further hydroborated to yield the cyclic compound 1,2-trimethylenediborane (VIII) or its polymer VIII$_n$. Interestingly, there is no evidence for the formation of a volatile compound with boron atoms attached to the central carbon of C_3H_4 such as the theoretically possible (and presumably volatile) cyclic dimer of 2,2′-diboranylpropane.



A remarkable amount of *n*-propyldiborane (IV) is isolated from the product mixture. Since glc-pure allene was used, it appears likely that IV is formed *via* a gas-phase hydrogenation by diborane (or its decomposition products). Such hydrogenations are apparently common as side reactions of gas-phase hydroborations, for alkanes are formed from alkenes and alkyldiboranes from alkynes, respectively. Relevantly, hydrogenolysis of B–C bonds has been reported by Koester.[26]

Major interest was devoted to VIII. It was easily identified by H^1 and B^{11} nmr[27] as well as by gas-phase infrared spectra. Table I provides a survey of the characteristic infrared stretching frequencies of terminal (H_t) and bridge (H_b) hydrogens attached to boron for VIII and three related compounds. The trends to increase $B–H_t$ and to decrease $B–H_b$ stretching frequencies with increasing ring strain are apparent.[8] Indeed VIII and X display the lowest $B–H_b$ stretching asymmetrical in-phase frequencies known in diborane derivatives. The divarication of $B–H_t$ and $B–H_b$ frequencies is reasonably explained by assuming that less overlap of the boron atomic orbitals participating in three-center bridge bonds of the strained systems increases the electron density about the $B–H_t$ bond.

Table I. Selected Infrared Absorption Frequencies of Cyclic Organodiboranes[a]

Compound	$B–H_t$ stretch, cm^{-1}	$B–H_b$ stretch,[b] cm^{-1}	Ref
III 1,2-Diethyldiborane	2506	1595	21, 23
IX 1,2-Tetramethylenediborane	2510 (2538)	1580	8
X 1,2-(1′-Methyltrimethylene)-diborane	2530 (2544)	1510	8
VIII 1,2-Trimethylenediborane	(2551)	(1506)	

[a] Compound III is included for comparison. The frequencies in parentheses are from the present work. [b] Asymmetrical in-phase.

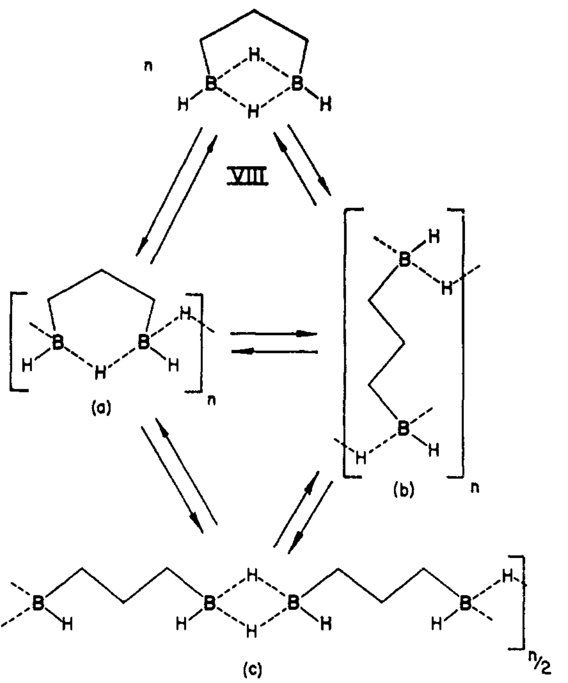


Figure 1. Possible structures and pathways for the polymerization of 1,2-trimethylendiborane (VIII).

In the gas phase, VIII behaves in a manner expected of the 1,2-trimethylenediborane monomer (Experimental Section). In the liquid phase, however, VIII exhibits somewhat surprising behavior. Samples which are allowed to warm quickly from −190 to 25° appear as mobile liquids for a short time, then gradually become quite viscous and on occasion solidify. However, the latter modifications are readily converted to monomeric VIII by heating to about 60° under vacuum.

An infrared spectrum of the polymeric product indicates that only minor changes of the molecular structure of VIII occur with polymerization. The appearance of a strong band at 2220 cm^{-1} which is completely absent in the gas spectrum of VIII is probably due to the normally very weak $B–H_b$ symmetrical in-phase vibration. The H^1 and B^{11} nmr spectra of VIII and VIII$_n$[27] confirm the cyclic structure for the monomer and are not inconsistent with a chain structure with diborane-like double hydrogen bridges for the polymer.

The ring strain of VIII, forcing the bridge hydrogens out of plane to prevent major distortions of boron sp^3 hybridization, is considered to be the driving force for the polymerization. Indeed, a mechanism involving only mobile bridge hydrogens best accounts for the observed reversibility of the polymerization process (Figure 1). It is not required to break B–C bonds.

Two additional observations support the assumption that polymerization of VIII results from a tendency to release ring strain. Firstly, IX does not polymerize; its alkyl bridge with one more methylene group than VIII is sufficiently long to allow two possible nonplanar arrangements with little or no ring strain. Secondly, X, which should have similar or equal ring strain to that of VIII, is found to polymerize in the liquid phase. However, this polymerization takes place less readily and

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extensively than with VIII, probably owing to a steric effect of the exposed methyl group.

2. Gas-Phase Hydroboration of Monoolefins. The gas-phase hydroboration of simple olefins with diborane is of considerable preparative value for the synthesis of mono- and 1,1-dialkyldiboranes. However, temperature control is quite important in the reactions of monoolefins. When a temperature range of 60–65° is exceeded, the mixture tends to decompose to give yellowish solid products of unknown composition and a considerable quantity of hydrogen. Additionally, alkanes and higher boron hydrides are found from the reactions at higher temperatures.

Gas-phase hydroborations of ethylene, propene, and 1-butene lead to formation of mono- and dialkyldiboranes in yields of 55–65 and 30–40%, respectively, using a 5:1 ratio of diborane:olefin. If less diborane is used, the yield of $R_2B_2H_4$ is increased; in the case of a 2:1 mixture of diborane and propene the product distribution is 43% propyldiborane and 48% dipropyldiborane. From infrared[21–23] and nmr data,[27,28] the dialkyldiborane isolated from the product mixtures is the 1,1 isomer with only small amounts of the 1,2 isomer present. In comparison to the findings of Hurd,[5] trialkylboranes are not produced in noticeable amounts from the 5:1 or from the 2:1 diborane:olefin reactions. However, trialkylboranes equilibrate rather rapidly with diborane;[6,7] therefore, it is difficult to show that they are not involved as intermediates on the way to the observed products. Of course, in the presence of a large excess of B_2H_6 the trialkylborane stage may not, and need not, be reached at all.

From an evaluation of the observed $R_2B_2H_4$ isomer ratio, no conclusions can be reached about whether the second alkylation takes place at the substituted or the unsubstituted boron atom of B_2H_6, respectively. The latter process would lead to the 1,2 isomer; however, this isomer participates in the secondary equilibrium

$$2RB_2H_5 \rightleftarrows B_2H_6 + 1,2\text{-}R_2B_2H_4$$

$$(K_p = 0.039 \text{ for } R = C_2H_5{}^{24})$$

which allows only very small amounts of 1,2-$R_2B_2H^4$ to coexist with high diborane concentrations.

In all, the similarity of the product distribution from the hydroboration reaction with that from the R_3B–B_2H_6 equilibration is quite striking. Unfortunately, equilibrium constants have been determined only for the trimethylborane–diborane exchange;[29] however, if it is assumed that variations in the alkyl group make only minor modifications on the values of the constants, a favorable comparison can be made. Both monoalkylated and 1,1-dialkylated diboranes are predicted as the major products from such a consideration. For the 5:1 diborane:olefin hydroboration, a product mixture containing 56% monoalkyldiborane and 44% 1,1-dialkyldiborane (percentages based on olefin[30]) is calculated from the equilibrium

$$2RB_2H_5 \rightleftarrows B_2H_6 + 1,1\text{-}R_2B_2H_4$$

$$(K \approx 3 \text{ for } R = CH_3{}^{29})$$

This compares favorably with the observed amounts (*vide supra*).

3. Gas-Phase Hydroboration of Acetylenes. In the presence of equal or excess mole amounts of B_2H_6, acetylenes react nearly quantitatively to give primarily nonvolatile organoboron polymers and small amounts of volatile products. Acetylene reacts at 75–90°, forming yellowish solid products and a volatile fraction containing B_5H_9, $C_2H_5B_2H_5$, 1,1-$(C_2H_5)_2B_2H_4$, and butane. Analogous results are found with propyne and with diacetylene.

When 2-butyne is allowed to react with B_2H_6, highly viscous colorless oils are readily formed at 25°. When an excess of B_2H_6 is used, the reaction does not occur in a 1:1 molar ratio; instead, the polymeric material obtained is made up of a 2-butyne:diborane ratio of 1.3–1.6:1, depending on reaction conditions. Similar results were previously reported for the dihydroboration of 3-hexyne.[15] It is reasonable to assume that nearly all unsaturated carbon–carbon bonds are hydroborated when excess B_2H_6 is used. Each diborane molecule, therefore, loses 2.6–3.2 B–H bonds. This should lead to formation of a rather irregular network of C_4 units linking the boron atoms of different diborane units, the hydrogen bridges of which are probably still present. Indeed, such a structure is indicated by the H^1 nmr spectrum of the polymer. Resonances of both terminal (H_t) and bridge (H_b) hydrogens appear as broad singlets;[27] although the H_b peak partially overlaps into the strong C–H resonance, it is clear that the H_b:H_t ratio is approximately in accord with the 2:1.4–0.8 ratio derived from the above assumptions. Since the resonance of the alkyl protons is only poorly resolved, no conclusions can be reached as to whether the two boron atoms are bonded to one or both carbon atoms of the former triple bond.

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(30) The relative quantities at equilibrium are calculated to be: B_2H_6, 4.22; RB_2H_5, 0.56; $R_2B_2H_4$, 0.22. In agreement with experimental observations it is safely assumed that all the olefin is consumed and that no other products are present in significant amounts.