Hydroboration. 50. Hydroboration of Representative Alkynes with 9-Borabicyclo[3.3.1]nonane—a Simple Synthesis of Versatile Vinyl Bora and *gem*-Dibora Intermediates

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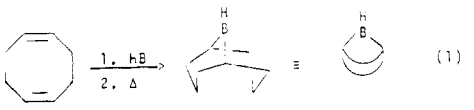
Abstract: Internal alkynes, such as 5-decyne, are readily converted into the *B*-vinyl derivatives in yields of 90–96% by treatment at 0 °C in tetrahydrofuran with an equimolar quantity of 9-borabicyclo[3.3.1]nonane (9-BBN). However, under these conditions simple terminal alkynes, such as 1-decyne, undergo significant dihydroboration. Fortunately, this difficulty can be overcome by use of excess of the terminal alkyne, making possible the preparation of the corresponding *B*-alkenyl-9-BBN derivatives in yields of 90–100%. Protonolysis of the *B*-vinyl-9-BBN derivatives provides the corresponding alkenes. The protonolysis of the product from 5-decyne and 9-BBN yields only *cis*-5-decene. The absence of any trans isomer indicates that the addition of the B–H bond to the alkyne must occur exclusively cis, yielding *B*-(*cis*-5-decenyl)-9-BBN. The *B*-alkenyl-9-BBN derivatives undergo rapid protonolysis, but they can be oxidized successfully to the corresponding ketone or aldehyde under aprotic conditions with trimethylamine *N*-oxide or under protic conditions by inverse addition to buffered hydrogen peroxide. Deuterolysis of the monohydroboration product from 1-heptyne and 9-BBN yields pure *trans*-1-*d*-1-heptene, also corresponding to a simple cis hydroboration. The hydroboration of internal acetylenes by 9-BBN is greatly influenced by steric factors, so that in many cases the least hindered product constitutes the major product. Treatment of a terminal alkyne with 2 equiv of 9-BBN in THF at 25 °C for 6 h affords the corresponding 1,1-diborylalkane in essentially quantitative yield. The reaction of internal alkynes is slower, but here also the *gem*-dibora derivatives are essentially realized in quantitative yield in 24 h at 25 °C. Consequently, the hydroboration of acetylenes by 9-BBN can be readily controlled to yield either the *B*-vinyl-9-BBN derivatives or the corresponding *gem*-dibora derivatives.

The reaction of 1,5-cyclooctadiene with diborane produces a bicyclic borane derivative of remarkable thermal stability, 9-borabicyclo[3.3.1]nonane,[2] and unusual regioselectivity (eq 1).[3-6] We have explored its behavior in the hydro-



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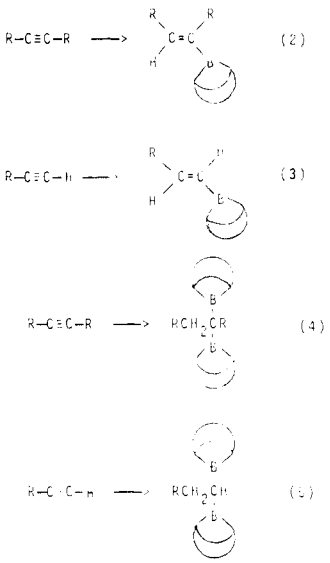
boration of acyclic olefins,[2,3] cyclic olefins,[4] conjugated dienes,[5] and nonconjugated dienes.[6] (9-BBN exists in solution as the dimer. However, it is more convenient in discussion to represent it as the monomer and that practice will be followed here.)

The hydroboration of acetylenes with 9-BBN offered the possibility of providing a route to the *B*-vinyl-9-BBN derivatives (eq 2, 3), as well as to the *gem*-dibora derivatives (eq 4, 5). (We also considered the possibility of realizing the synthesis



of vicinal dibora derivatives.[7] However, since we did not observe the formation of such derivatives, we do not show this possible reaction course in the above reactions.)

Accordingly, we undertook a systematic exploration of the reactions of 9-BBN with representative acetylenes, both terminal and internal.

Results and Discussion

Stoichiometry of Alkyne Hydroboration with 9-BBN. 5-Decyne and 1-decyne were selected as representative internal and terminal alkynes. In order to examine the stoichiometry of the hydroboration, equimolar quantities of the alkyne and 9-BBN (monomer) were maintained at 25 °C in THF until tests of aliquots with methanol for residual hydride were negative.

In the case of 5-decyne, complete reaction required 8 h (~0.5 M 9-BBN, ~0.5 M 5-decene). The product was then protonolyzed with acetic acid. GC analysis revealed the presence of 90% *cis*-5-decene, no *trans*-, and 5% residual 5-decyne. This result clearly established that the reaction had proceeded 90% toward the formation of the simple vinyl derivative (eq 2, R = *n*-C_4H_9), isomerically pure *B*-(*cis*-5-decene-5-yl)-9-BBN, with 5% of the 5-decyne and 10% of the 9-BBN undergoing reaction to form a dihydroborated product (eq 4, R = *n*-C_4H_9).

Under the same conditions, the reaction of 9-BBN with 1-decyne was considerably faster, essentially complete in 3 h. However, protonolysis yielded only 44% of 1-decene. Lowering the temperature produced only a modest improvement: 0 °C, 48% 1-decene; −15 °C, 59% 1-decene. In the latter case the reaction required 3 days to proceed to completion. It is evident that the *B*-(1-decenyl)-9-BBN, formed in the first hydroboration step, must compete effectively with 1-decyne for the remaining 9-BBN.

Fortunately, the presence of an excess of the 1-decyne in the reaction mixture achieves satisfactory production of the monohydroboration product. Thus, addition of 100% excess of 1-decyne to a stirred slurry of 9-BBN in THF at 0 °C achieved

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Table I. Hydroboration of Alkynes by 9-BBN in THF[a]

alkyne	9-BBN, mmol	alkyne, mmol	temp, °C	reaction time, h	monohydroboration,[b] %	dihydroboration,[b] %
1-pentyne	5	10	0	18	92	4
1-hexyne	5	10	0	18	94	3
1-decyne	5	10	0	18	94	3
3,3-dimethyl-1-butyne	5	10	0	18	96	2
cyclohexylethyne	5	10	0	18	96	2
phenylethyne	5	10	0	18	90	5
2-hexyne	5	5	25	6	90	5
3-hexyne	5	5	25	6	90	5
5-decyne	5	5	25	8	90	5
4-methyl-2-pentyne	5	5	25	8	92	4
4,4-dimethyl-2-pentyne	5	5	25	12	99	
1-cyclohexylpropyne	5	5	25	8	96	2
1-phenylpropyne	5	5	25	12	90	5

[a] Each reagent is 0.5 M in THF. [b] Analysis by GC following protonolysis or oxidation, and percent based on 9-BBN.

complete uptake of the 9-BBN in 18 h. Protonolysis gave 94% yield of 1-decene. Consequently, dihydroboration could have been no more than 3%.

Similar results were realized with a representative selection of acetylenes (Table I). Consequently, these two procedures provide general methods to achieve the clean monohydroboration of acetylenes, both internal (25 °C, 1:1) and terminal (0 °C, 2:1).

The monohydroboration products are quite stable thermally and are readily isolated and purified (in an inert atmosphere). Typical procedures are described in the Experimental Section. However, in most cases it is more convenient to prepare and utilize them in situ, without isolation.

Facile Protonolysis of *B*-Alkenyl-9-BBN Derivatives. Oxidation Procedure. The oxidation of *B*-alkenylboranes to aldehydes or ketones is usually accomplished without difficulty using hydrogen peroxide at 0 °C under slightly basic conditions (pH 8).[8,9] However, our initial attempts to oxidize under these conditions *B*-(*trans*-1-hexen-1-yl)-9-BBN produced in the monohydroboration of 1-hexyne gave none of the aldehyde anticipated. Instead, a quantitative yield of the protonolysis product, 1-hexene, was obtained. In contrast, the oxidation of *B*-(1-hexen-1-yl)-disiamylborane under identical conditions gives an essentially quantitative yield of 1-hexanal.[8]

The oxidation of *B*-(*cis*-5-decen-5-yl)-9-BBN under these conditions produced a mixture of products, 65% 5-decanone and 30% *cis*-5-decene. Evidently, in the case of this more hindered derivative protonolysis is slower so that oxidation can compete.

It was discovered that the competing protonolysis could be circumvented by reversing the procedure. The slow addition of the *B*-alkenyl-9-BBN in THF to the buffered hydrogen peroxide oxidizing solution effectively suppresses the undesired protonolysis reaction and favors the oxidation pathway, achieving the formation of the desired aldehyde or ketone in yields of 90–96%. Consequently, we used both protonolysis and oxidation to establish the regiospecificity of the monohydroboration products from terminal acetylenes with oxidation preferred to establish the position taken by the boron atom in the monohydroboration of unsymmetrical internal acetylenes (Table II).

The oxidation of *B*-alkenyl-9-BBN may also be accomplished under anhydrous conditions with trimethylamine *N*-oxide,[10,11] using the procedures developed for the corresponding alkyl derivatives.

Regioselectivity of Alkyne Hydroboration with 9-BBN. Oxidation of the products from the monohydroboration of 1-alkynes with 9-BBN gave the corresponding aldehydes, with no evidence of the presence of the isomeric 2-alkanones.

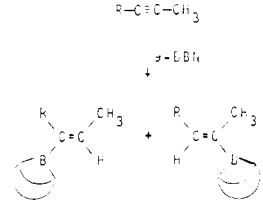
The structure of the adduct from the 1-alkyne was also established by examining the deuterolysis product. Thus deuterolysis (CH_3CO_2D) of the vinyl borane from 1-heptyne and 9-BBN under these conditions afforded a 96% yield of 1-heptene-d_1, which was isolated by GC and examined by NMR. The vinyl protons appear as a doublet (ca. δ 4.93) and a doublet of triplets (ca. δ 5.8) of equal intensities. These signals are attributed to single vinyl protons on C_1 and C_2, respectively. The equal intensities establish the presence of deuterium at C_1. The magnitude of the coupling constant ($J_{1,2}$ = 18 Hz) between the vinyl protons clearly indicates their trans geometry. These results identify the deuterolysis product as *trans*-1-*d*-1-heptene, and establish the trans geometry of the vinyl borane, *B*-(*trans*-1-hepten-1-yl)-9-BBN, produced in the monohydroboration of 1-heptyne via eq 3. Therefore, the hydroboration proceeds regiospecifically to place the boron at the terminal position of the 1-alkyne (eq 3). In this respect, the behavior of 9-BBN resembles that of disiamylborane.[8]

Table II. Directive Effects in the Hydroboration of Methyl-Substituted Alkynes by 9-BBN[a]

$RC{\equiv}CCH_3$ R	$RCOCH_2CH_3$ in ketone product, %	RCH_2COCH_3 in ketone product, %	total yield of ketone, %
n-propyl	22	78	90
isopropyl	4	96	92
tert-butyl	0	>99	>99
cyclohexyl	4	96	96
phenyl	65	35	90

[a] Analysis was performed by GC after the *B*-alkylborane was oxidized to the corresponding ketone. A small amount of dihydroboration product was observed in all cases.

On the other hand, hydroboration of unsymmetrical internal alkynes with 9-BBN produces a mixture of regioisomers (eq 6). Oxidation of the two isomeric products produces the isomeric ketones, readily analyzed by GC.



It is interesting to note how the attachment of boron to the more hindered position (α to R) decreases as the steric bulk of R increases: 22% for R = *n*-Pr, 4% for R = *i*-Pr, and 0% for R = *t*-Bu.

Table III. Directive Effects in the Hydroboration of 4-Methyl-2-pentyne and 2-Hexyne with Several Hydroborating Agents

hydroborating agent	alkyne[a] $CH_3C(CH_3)C{\equiv}CCH_3$ ↑ ↑	alkyne[a] $CH_3CH_2C{\equiv}CCH_3$ ↑ ↑
diborane[8]	25 75	40 60
thexylborane[8]	19 81	39 61
disiamylborane[8]	7 93	39 61
dicyclohexylborane[8]	8 92	33 67
9-BBN	4 96	22 78

[a] The distribution is deduced from the ketones produced following oxidation of the *B*-alkenylborane product.

Table IV. Directive Effects in the Hydroboration of 1-Phenylpropyne by Several Hydroborating Agents

	$PhC{\equiv}CCH_3$[a] ↑ ↑
diborane[b]	74 26
9-BBN[c]	65 35
thexylborane[b]	43 57
dicyclohexylborane[b]	29 71
disiamylborane[b]	19 81

[a] The distribution is deduced from the ketones produced following oxidation of the *B*-alkenylborane product. [b] Reference 9. [c] This study.

These results on the regioselectivities realized in the hydroboration of representative acetylenes, $RC{\equiv}CCH_3$, are summarized in Table II. It should be noted that the regioselectivities achieved in the monohydroboration of such acetylenes by thexylborane,[12] dicyclohexylborane,[12] disiamylborane,[12] and catecholborane[13] are similar to, but less pronounced than, that realized by 9-BBN.

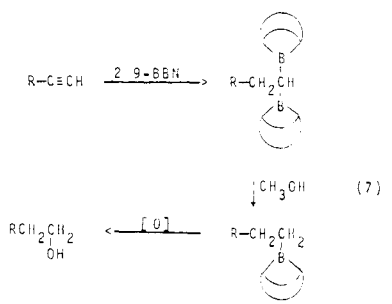
The greater regioselectivity exhibited by 9-BBN is revealed by the comparison of the distribution of isomers realized in the hydroboration of 4-methyl-2-pentyne and 2-hexyne with various hydroborating agents (Table III).

On the other hand, the directive effect of the phenyl group in 1-phenylpropyne is quite different from that predicted on the basis of the large steric requirement of this group. There occurs a major shift in the regioselectivity, with 65% of the boron adding to the triple bond α to the phenyl group (Table II).

Clearly, the effect of the phenyl group must be electronic, similar to the influence it exerts on the direction of hydroboration of styrene and substituted styrenes.[3,14] A comparison of the behavior of various hydroborating agents reveals that 9-BBN is not only most sensitive to the steric environment (Table III), but it is also most sensitive to the electronic environment[3] among the alkylborane reagents examined (Table IV).

Dihydroboration of Alkynes with 9-BBN. It appeared appropriate to establish the conditions to achieve the dihydroboration of representative acetylenes and to examine the structure of the products, whether geminal (eq 4 and 5) or vicinal.[7] As representative terminal alkynes we selected 1-hexyne, 3,3-dimethyl-1-butyne, and cyclohexylethyne. We utilized 3-hexyne and 5-decyne as the internal alkynes.

In the case of the above terminal alkynes, we observed that essentially complete uptake of 9-BBN was realized in 6 h at 25 °C in reaction mixtures in THF containing the two reactants in their stoichiometric ratio (2 9-BBN/RC≡CH). The products rapidly undergo protonolysis to the *B*-alkyl-9-BBN derivative (eq 7). Consequently, oxidation of the reaction



mixtures with alkaline hydrogen peroxide affords the corresponding primary alcohol as the sole identifiable product in yields of 95–100%.

Had dihydroboration yielded a significant amount of the 1,2 adduct, oxidation should have given the corresponding glycol.[8] However, conversion of the products to the trimethylsilyl ethers, followed by GC examination, failed to reveal the presence of any glycol derivative. Consequently, we conclude that the hydroboration of terminal acetylenes proceeds cleanly to the formation of the 1,1-dibora derivatives.

As anticipated, the dihydroboration of internal acetylenes with 9-BBN is somewhat slower. Nevertheless, quantitative hydroboration was achieved by treating the alkyne with 2 mol of 9-BBN (monomer) in THF at 25 °C for 24 h. Here also oxidation produces the corresponding alcohol attributed to the rapid protonolysis of one 9-BBN group. Here also the absence of any glycol derivative from the acetylene in the oxidation product establishes the absence of any vicinal dibora derivative.

Potential of the Intermediate. The present study has established simple means of achieving both mono- and dihydroboration of acetylenes, both terminal and internal, by 9-BBN. It has established that in such hydroboration 9-BBN exhibits an enhanced sensitivity to both steric and electronic factors, allowing considerable control in the regioselective hydroboration of internal acetylenes.

The *B*-vinyl-9-BBN derivatives exhibit enhanced reactivities. Thus, they readily undergo protonolysis in methanol, in contrast to the marked stability of the *B*-alkyl-9-BBN derivatives. The *B*-vinyl-9-BBN derivatives readily undergo 1:2 addition to aldehydes[15] and undergo 1:4 addition to methyl vinyl ketone and related derivatives.[16] Finally, they are readily transformed into the vinyl copper reagents.[17]

The *gem*-diboraalkanes are also promising reagents. Thus, under the influence of an appropriate base they undergo synthetically useful reactions leading to olefins via a novel Wittig-type reaction,[18] to secondary alkyl organoboranes via alkylation with alkyl halides,[19] to malonic acids via carbonylation,[20] and to *B*-cycloalkyl-9-BBN derivatives when the *gem*-dibora derivative bears an ω-halo or ω-tosyl substituent.[21,22]

Consequently, the present study makes available the *B*-vinyl-9-BBN and the *gem*-dibora derivatives, both promising structural types for further study and for intermediates in organic synthesis.

Experimental Section

All manipulations were carried out under an atmosphere of prepurified nitrogen (Airco). Glassware, syringes, and needles were dried for several hours at 150 °C before use. Syringes were assembled and fitted with needles while hot, then cooled as the assembled units. Glassware was assembled hot and flushed with nitrogen while cooling. GLC analyses were carried out using a Varian-Aerograph Model 1200 FID chromatograph, which was equipped with the indicated column. Prepurified nitrogen was employed as the carrier gas. Peak integration was carried out using a Disc mechanical integrator.

Materials. The purification of solvents, the preparation of 9-BBN, and the preparation of a standard solution of 9-BBN (0.5 M in 9-BBN) were carried out as previously described.[2] The *n*-alkanes (Phillips Pure Grade) employed as internal standards were used as

received, after checking the refractive indexes. The alkynes were obtained commercially (Farchan or Chemical Samples) and were used as received after checking the refractive indexes and verifying the purity by GLC ($\frac{1}{8}$ in. × 12 ft 10% SE-30 on 100–120 mesh Varaport 30 and $\frac{1}{8}$ in. × 6 ft 10% adiponitrile on 100–120 mesh Varaport 30). The methanol (Mallinckrodt, spectroquality) employed as the quenching agent was used as received. The other materials were obtained commercially, and were of analytical reagent quality.

Stoichiometry Studies. The procedure given below for the monohydroboration of 5-decyne with 9-BBN in THF at 0 °C is typical.

A dry, nitrogen-flushed 50-mL volumetric flask was capped with a serum stopple and charged via syringe with 13.82 g (100 mmol) of 5-decyne and 5.0 mL of *n*-nonane (internal standard). The mixture was then diluted to the mark with anhydrous THF, added via syringe.

A dry 50-mL flask with an injection port was equipped with a magnetic stirring bar and a gas inlet tube attached to a low-pressure (atmospheric + 55 mmHg) nitrogen supply. As the flask cooled, it was flushed with nitrogen. The injection port was capped with a rubber serum stopple and the flask was immersed in an ice–water bath (taking care not to wet the stopple). The flask was charged via syringe with 10 mL of the standard 9-BBN solution (0.5 M 9-BBN in THF). As the solution cooled, the 9-BBN precipitated. The resulting slurry of 9-BBN was stirred for 15 min to ensure thorough cooling.

The reaction was initiated by injecting 2.50 mL of the alkyne (2 M) solution into the stirred slurry of 9-BBN. The reaction mixture was maintained at 0 °C for 24 h in a cold room to allow complete reaction. The reaction mixture was now clear and colorless. The flask, still in its ice bath, was attached to a gas buret and 1 mL of methanol was added. No gas was evolved indicating that the uptake of 9-BBN was complete. Glacial acetic acid (0.0 mL, 16 mmol) was then added to protonolyze the *B*-(*cis*-5-decenyl)-9-BBN, and the stirred reaction mixture was warmed to room temperature. After 3 h, aqueous 6 M NaOH was added to remove the residual acid, the layers were separated, and the clear upper layer was analyzed by GC ($\frac{1}{8}$ in. × 12 ft 10% SE-30 on 100–120 mesh Varaport 30). The analysis indicated the presence of 4.76 mmol of 5-decene and 0.14 mmol of unreacted 5-decyne. No *trans*-5-decene could be detected. Other results are summarized in Table I.

Oxidation of *B*-(*cis*-5-Decen-5-yl)-9-BBN. The oxidation of this *B*-alkenyl-9-BBN derivative serves as a general procedure for the preparation of either ketones or aldehydes from *B*-alkenylboranes.

The hydroboration of 5-decyne (5 mmol) with an equivalent amount of 9-BBN was carried out at 0 °C to give the monohydroboration product in 95% yield. A buffer solution of pH 8 was prepared by adding 6 M NaOH to an aqueous 5 M solution of NaH_2PO_4. An aliquot of this buffer solution (5 mL) and 1.5 mL of 30% H_2O_2 were mixed at 0 °C. To this stirred solution the *B*-(*cis*-5-decenyl)-9-BBN in THF was slowly added. The mixture was stirred for 2 h at 0 °C before separating the organic and aqueous layers. Analysis of the organic layer by GC ($\frac{1}{8}$ in. × 12 ft 10% SE-30 on 100–120 mesh Varaport 30) revealed the presence of 90% 5-decanone. The ketone was identified by coinjection with an authentic sample, by isolation (preparative GC), and by comparison of its IR and ^{1}H NMR spectra with those of authentic samples.

Dihydroboration Procedure. The dihydroboration of 1-hexyne serves to illustrate the general procedure. A dry, nitrogen-flushed 100-mL flask with an injection port and a magnetic stirring bar was charged via syringe with 20 mL of a 0.5 M solution of 9-BBN (10 mmol) in THF. To this stirred solution was added 2.5 mL of a THF solution containing 1-hexyne (5 mmol) and *n*-octane (0.25 mL, internal standard). After the solution was stirred for 6 h at 25 °C, the lack of gas evolution upon the addition of water (0.5 mL) indicated complete reaction of the 9-BBN. The organoboranes were oxidized by adding successively 2 mL of 6 M NaOH and 4 mL of 30% hydrogen peroxide. The aqueous layer was saturated with potassium carbonate, a technique known to effect complete transfer of diols to the THF layer.[23] The clear upper layer was separated and dried over anhydrous potassium carbonate. The presence of 1-hexanol (98% yield), and the absence of 1-hexyne or 1-hexene (from protonolysis of monohydroboration product), were indicated by GC analysis ($\frac{1}{8}$ in. × 12 ft 10% SE-30 on 100–120 mesh Varaport 30). A 0.1-mL sample was added to 0.5 mL of Tri-Sil Z (Pierce Chemical Co.) to convert the alcohols into the corresponding trimethylsilyl ethers, and analyzed by GC using the column described above. No detectable amount of the 1,2-hexanediol trimethylsilyl ether was found. Comparable results were obtained with other alkynes discussed in the text.

Preparation of *B*-(*trans*-1-Hexen-1-yl)-9-BBN.[24] Predried 200-mL and 300-mL round-bottom flasks, each equipped with a connecting tube and Teflon-coated magnetic stirring bar, were assembled hot and cooled under a stream of dry nitrogen. To the 200-mL flask was added 7.53 g (62 mmol) of solid 9-BBN with the transfer conducted in a glovebag maintained under an N_2 atmosphere. The solid 9-BBN was then dissolved in a minimum amount of dry THF (~100 mL). The 300-mL flask was charged with 15.6 mL (136 mmol, 120% excess) of 1-hexyne and 20 mL of dry THF, then was cooled in an ice/water bath. The 9-BBN solution was then added to the 1-hexyne solution over a period of 25–30 min during which time some solid 9-BBN precipitated from the cold reaction mixture. The reaction mixture was then stirred at 0 °C until the precipitated 9-BBN had completely disappeared (~3–4 h). The clear solution was then allowed to sit at 0 °C overnight (15 h). After first warming to room temperature and stirring for 1 h, the unreacted 1-hexyne and THF were removed under a protected water aspirator vacuum.

The crude material was then decanted via a double-ended needle to a short-path distillation apparatus and distilled under reduced pressure. There was obtained 9.76 g (47.8 mmol, 77%) of a clear, colorless liquid, bp 72–74 °C (0.03 mm).

^{1}H NMR: δ 0.68 (dt, 1 H, J = 5.9, 17.2 Hz), 6.32 (d, 1 H, J = 17.2 Hz), 1.82 (s, cyclooctyl ring), 1.2–1.78 (m), 0.91 (t, 3 H, J = 6 Hz).

^{11}B NMR ($CDCl_3$): +78.4 ppm (from BF_3·OEt_2).

Preparation of *B*-(*cis*-3-Hexen-3-yl)-9-BBN.[24] *B*-(*cis*-3-Hexen-3-yl)-9-BBN was prepared in a manner analogous to that described above. Solid 9-BBN (4.84 g, 40 mmol) was dissolved in 70 mL of dry THF. The resulting solution was added slowly to a cold (0 °C), stirred solution containing 3.61 g of 3-hexyne (44 mmol, 10% excess) in 15 mL of dry THF. The reaction mixture, which contained precipitated 9-BBN, was stirred at 0 °C until the solid had completely dissolved (7–8 h), then was maintained at 0 °C for an additional 16 h to ensure complete reaction. The reaction mixture was then warmed to 25 °C and stirred for an additional 1 h. After evaporation of the solvent and unreacted alkyne, short-path distillation of the residue afforded the vinyl borane, 5.92 g (29 mmol, 74%), as a clear, colorless oil, bp 60–62 °C (0.03 mm).

^{1}H NMR ($CDCl_3$): δ 6.50 (t, 1 H, J = 7.2 Hz), 2.38 (m), 1.84 (s, cyclooctyl ring H's), 1.07 (t, J = 7.2 Hz), 0.93 (t, J = 7.5 Hz)

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