trans-Vinylboranes from 9-Borabicyclo[3.3.1]nonane through Dehydroborylation

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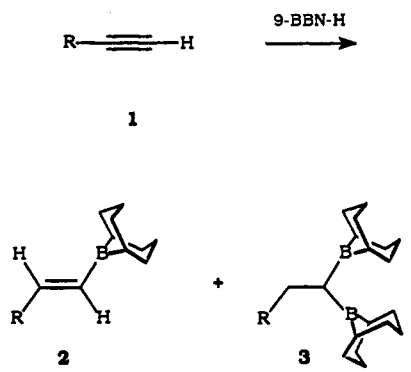
Abstract: The hydroboration of 1-alkynes (**1**) was reinvestigated by ^{11}B NMR under optimized conditions (THF, 18 h, 0 °C) and found to provide *trans*-vinyl-9-BBN adducts (**2**) together with variable amounts of 1,1-diborylalkanes (**3**) depending both upon the excess of **1** employed and the nature of alkyne substitution. By contrast, the formation of **3** with 2 equiv of 9-BBN-H is quantitative. A new completely stereoselective route to **2** from **3** was discovered with its reaction with ArCHO in an electrocyclic process (ρ = 0.42). While analogous to the Midland reduction, the term dehydroborylation is introduced to emphasize the olefination aspect of the reaction. Compound **3a** (R = Me) is smoothly dehydroborylated at 25 °C with PhCHO following second-order kinetics. Competitive rate studies reveal its reaction to be slower than that of Alpineborane (**7**) (k_7/k_{3a} = 4.5) but faster than that of *B*-siamyl-9-BBN (**6**) (k_6/k_{3a} = 0.34). The value of the dehydroborylation approach to **2** and the advantages of using 9-BBN derivatives in vinylborane reactions are demonstrated with numerous examples. Thus, 1,8-nonadiyne is converted, through a bis(vinylborane) (**11**), to pure *trans,trans*-1,9-dideuterio-1,8-nonadiene (**12**). This transformation has not been previously possible for 9-BBN-H because of competitive dihydroboration. The dihydroboration of 1-(triethylsilyl)-1-propyne, after thermal isomerization and deuterolysis, affords *trans*-(3-deuterioallyl)silane (**16**), a most remarkable overall conversion. The insertion of aromatic aldehydes into **2** was further demonstrated to provide a convenient entry to *trans*-allylic alcohols. The selective oxidation of **2** with TMANO produces *trans*-alkenyl-9-oxa-10-borabicyclo[3.3.2]decanes, **18**, which resist further reaction with ArCHO, oxidation in the atmosphere, and protonolysis. A **1** → **3** → **2** → **20** sequence was employed without the isolation of **2** in a one-pot Suzuki coupling with ArBr to provide *trans*-stilbenes (**20**, Ar = *p*-C_6H_4X, X = OMe (80%), NMe_2 (60%)).

The monohydroboration of terminal alkynes (**1**) is perhaps the simplest and most efficient route to *trans*-vinylboranes (*e.g.*, **2**).[3,4] Virtually all of the common monofunctional hydroborating agents (*i.e.*, dicyclohexylborane, disiamylborane, catecholborane, and dimesitylborane as well as complexes of dihaloboranes) can be used to carry out this conversion, the most notable exception being 9-borabicyclo[3.3.1]nonane (9-BBN-H) dimer.[3,5] With this reagent, product **2** effectively competes with **1** for 9-BBN-H which leads to the formation of significant quantities of 1,1-diboryl adducts **3** with a 1:1 (1:9-BBN-H) stoichiometry.

The dihydroboration problem notwithstanding, many of the limitations associated with other vinylborane derivatives would be overcome were an efficient route to **2** from **1** available. For instance, as a dialkylborane, 9-BBN adds to unsaturated substrates at or below room temperature, exhibiting exceptional regioselectivity, a clear advantage over oxygenated derivatives such as catecholborane.[3a] However, unlike the low thermal stabilities of other dialkyl(vinyl)boranes, **2** exhibits remarkable stability and, similar to catecholborane derivatives, can be purified by distillation without decomposition and can be fully characterized in most cases.[5,6] Available from a simple hydroboration procedure in high purity as a stable, crystalline solid,[3] 9-BBN-H dimer can be stored indefinitely, is easily handled, and is soluble in a wide variety of reaction solvents, making it a particularly convenient reagent to use.



(1)

Partial solutions to the dihydroboration problem have been found through either employing a 100% excess of **1**[5] or using silylated derivatives.[6e,h] However, these measures which sacrifice starting alkyne or add extra reaction steps are clearly unsatisfactory for many applications. In the present study, we wish to

(1) Graduate student supported by the NIH-MBRS Program.
(2) Graduate student supported by the NSF EPSCoR Program of Puerto Rico.
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Table I. Hydroboration of 1-Alkynes with 9-BBN-H[a]

series	R	ratio[b]	2,[c] %	3,[d] %
a	Me	1:1	20	40
		2:1	56	22
b	*n*-Bu	1:1	56	22
		2:1	80 (70)	10
c	Ph	1:1	92	4
		2:1	96 (79)	2
d	*i*-Pr	1:1	88	6
		2:1	94 (79)	3
e	$SiMe_3$	1:1	38	31
		2:1	74	13

[a] Reactions were carried out at 0 °C [0.5 M 9-BBN-H in THF]. [b] Molar ratio of 1:9-BBN-H employed. [c] Yields are calculated based upon 9-BBN-H and rounded up to the next highest even percentage isolated yields of **2** by distillation). [d] ^{11}B NMR (THF/C_6D_6) δ 87.0 (**3a**), 86.9 (**3b**), 87.6 (**3c**), 87.0 (**3d**), 85.1 (**3e**) (calculated from the peak areas/2).

Table II. Effect of THF on the ^{11}B NMR Chemical Shift of 2[a]

3	δ ($CDCl_3$)	δ (THF)[b]
Me	77.2	74.5
n-Bu	77.0	73.1
i-Pr	77.7	73.0
Ph	78.5	70.0
$SiMe_3$	77.6	67.4

[a] There was no significant effect upon δ for **3** with this change in solvent systems. [b] C_6D_6 (ca. 10%) was added as an internal lock.

report a convenient ^{11}B NMR-based evaluation of the hydroboration of **1** with 9-BBN-H and a new, completely stereoselective process for the preparation of **2** from **3** through a most unusual Midland-type reduction of aromatic aldehydes.[7]

Results and Discussion

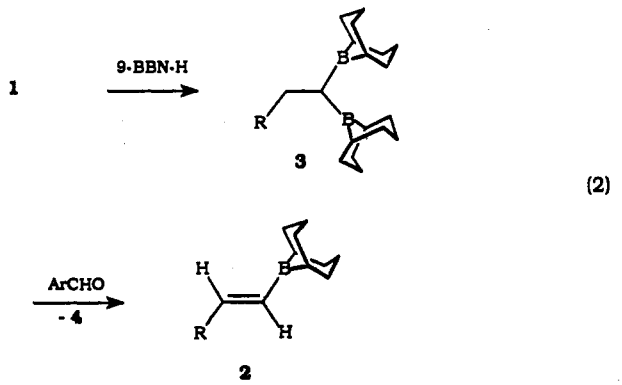
Hydroboration of 1 with 9-BBN-H. To definitively answer the question as to the extent of monohydroboration of **1** achieved with 9-BBN-H under optimal conditions (THF, 18 h, 0 °C),[5] this process was reexamined employing a 1:1 stoichiometry and using a 100% excess of **1** (Table I). With the current availability of higher NMR fields, we discovered that because **2**, but not **3**, is partially complexed by THF, its 96-MHz ^{11}B NMR signal is sufficiently shifted upfield (Table II) in this solvent to allow the product distribution to be directly assessed, thereby avoiding the extra steps associated with the GC analysis of their protonolysis and oxidation products, respectively. For **1b**, we corroborated (±2%) our results with the extensive GC available for this system[5b] and reconfirmed this by ^{13}C NMR. Like Brown,[5] we find that while the relative amounts of **2**, employing a 100% excess of **1** may be lower than was originally thought (*cf.* ref 5), this excess does significantly enhance the monohydroboration process. We isolated vinylboranes **2b-d** in pure form by their distillation from these reaction mixtures (Table I). Clearly apparent for the first time from this data is the fact that the relative amounts of **2** *vs* **3** generally increase with the size of the R group in **1**, with $SiMe_3$ exhibiting its expected, exceptional behavior.[6h,8]

Dehydroborylation of 3. The facile nature of the dihydroboration of **1** with 9-BBN-H makes the quantitative preparation of **3** from **1** with 2 equiv of 9-BBN-H a trivial process.[3,5] It occurred to us that if **3** could be quantitatively converted to **2**, only 9-BBN-H, but not **1**, would be sacrificed, and this would be a small price to pay for a general synthesis of *trans*-vinyl-9-BBN derivatives. A clue to effecting this conversion came from viewing the reduction of carbonyl compounds with trialkylboranes (Midland reductions)[7] from the opposite perspective, namely, as a new way to efficiently dehydroborylate alkylboranes in a concerted manner to produce alkenes. The limited information on the fate of the alkene byproduct in the Midland reduction was not encouraging with the reported sluggish reaction of *s*-Bu-9-BBN with aldehydes producing 2-butene as a *c*/*t* mixture (35/65).[7b] However, we had observed[9] that **3** accepts only one hydride from KH,[10] a fact which suggests that the two boron atoms may act in concert to result in unusual reactivity with aldehydes compared to that with simple trialkylboranes. Indeed, with the addition of 1 equiv of PhCHO to **3a**, in 2 h at 25 °C, *B*-$PhCH_2O$-9-BBN (**4a**) and **2a** were quantitatively formed as the only detectable products, the latter with exclusively the *trans* configuration. Moreover, the **3** → **2** conversion is quite general, occurring smoothly for all of our representative systems to produce **2** quantitatively as the *trans* isomer exclusively together with an equal quantity of **4** (Table III).

Table III. *trans*-Vinylboranes (2) via Dehydroborylation of 3

series	R	Ar	yield of 2,[a,b] %
a	Me	Ph	89[b]
		1-Naph	81[b]
b	*n*-Bu	Ph	100[c]
		1-Naph	86[b]
c	Ph	Ph	100[c]
		1-Naph	100[c]
		o-C_6H_5CHO	68[c,d]
d	*i*-Pr	1-Naph	85[b]
e	$SiMe_3$	1-Naph	82[b]

[a] Reactions were carried out in THF, 25 °C, 4 h. [b] Isolated yield of pure **2**. [c] ^{11}B NMR yield. [d] *o*-$C_6H_4(CHO)_2$/**3** = 0.5.



(2)

By changing the added aldehyde from PhCHO to 1-naphthaldehyde (1-NaphCHO), the distillative separation of **2** from **4** was greatly simplified in most cases. With the exception of **2c**, the pure vinylborane was isolated in >80% yield by distillative separation from **4**. To rule out a dehydroboration mechanism, we added styrene to **3a**, observing no detectable reaction after 1.5 h at 25 °C.[7a-e,11] However, once PhCHO is added to this mixture, the smooth production of **4a** and **2a**, but not *B*-($PhCH_2CH_2$)-9-BBN, is observed, a result which confirms the absence of free 9-BBN-H in the process.

Kinetic and Mechanistic Features. The second-order rate constants for the reaction of **3a** with five *para*-substituted benzaldehydes were determined, and this data was used for the

(7) (a) Midland, M. M.; Tramontano, A.; Zderic, S. A. *J. Organomet. Chem.* **1977**, *134*, C17. (b) Midland, M. M.; Tramontano, A.; Zderic, S. A. *J. Organomet. Chem.* **1978**, *156*, 203. (c) Midland, M. M.; Greer, S.; Tramontano, A.; Zderic, S. A. *J. Am. Chem. Soc.* **1979**, *101*, 2352. (d) Midland, M. M.; Zderic, S. A. *J. Am. Chem. Soc.* **1982**, *104*, 525. (e) Midland, M. M.; McLoughlin, J. I. *J. Org. Chem.* **1984**, *49*, 1317. (f) Midland, M. M. *Chem. Rev.* **1989**, *89*, 1553. (g) Brown, H. C.; Ramachandran, P. V.; Weissman, S. A.; Swaminathan, S. *J. Org. Chem.* **1990**, *55*, 6328. (h) Soderquist, J. A.; Anderson, C. L.; Miranda, E. I.; Rivera, I.; Kabalka, G. W. *Tetrahedron Lett.* **1990**, *31*, 4677. (i) Brown, H. C.; Ramachandran, P. V. *Accts. Chem. Res.* **1992**, *25*, 16.

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(9) We have observed that a THF solution of **3a** reacts with KH[10] to form a monoborohydride species which is observed as a broad signal by ^{11}B NMR (δ −14.7).

(10) Soderquist, J. A.; Rivera, I. *Tetrahedron Lett.* **1988**, *29*, 3195.

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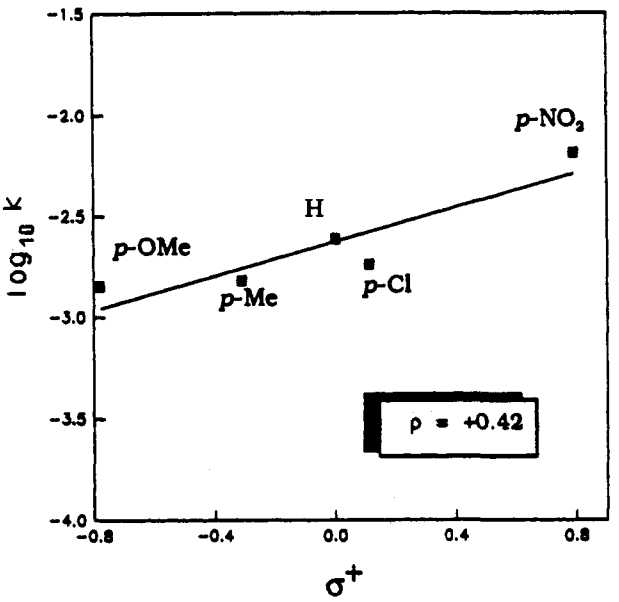
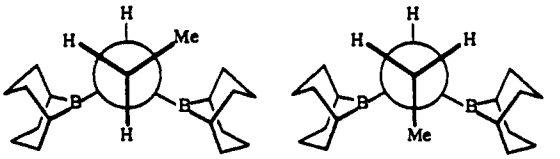


Figure 1. Hammett plot for the dehydroborylation of **3a** with p-XC_6H_4CHO at 23 °C in $CDCl_3$.

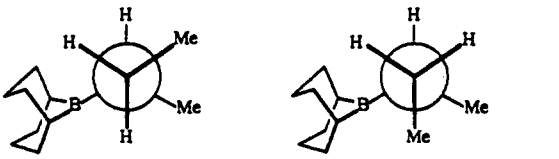
Hammett plot illustrated in Figure 1 from which a ρ value of 0.42 was calculated, very close to the 0.49 value obtained by Midland for a similar process with Alpineborane.[7d] Midland has measured the relative rates of reduction of PhCHO at 65 °C with *B*-alkyl-9-BBN derivatives, observing that both β-alkyl substitution and synperiplanar arrangement of the H–C–C–B array enhance the rate so that *B*-siamyl-9-BBN (**6**) reacts 7.3 times as fast as *B*-*s*-Bu-9-BBN (**5**); Alpineborane (**7**) is too fast to compare.[7a,c,d] We carried out competitive experiments with 1 equiv of PhCHO, **3a**, and either **5**, **6**, or **7** at 23 °C. Employing the Ingold–Shaw relationship,[12] we performed competitive rate studies that reveal an ordering of $k_7 > k_{3a} > k_6$ with relative rates of 4.5, 1.0, and 0.34, respectively. Compound **5** reduces PhCHO too slowly to compete with **3a** under these conditions. Thus, the reactivity of **3a**, with only a single β substituent and no fixed synperiplanar relationship of the H–C–C–B array as is present in **7**, is exceptionally high.

Comparing the MMX-minimized conformations[13] of **3a** with **5** and **6** (Figure 2), one observes an energetic preference for the least hindered *gauche* conformations represented on the left in Figure 2. The alternative *gauche* conformations with a β-methyl group bisecting the two α substituents is significantly higher in energy in the case of **3a** than for either **5** or **6**. Further, by comparing **3a** to **5** with a fixed synperiplanar relationship for the H–C–C–B array, there is a greater preference for the "*trans*-eclipsed" form of **3a** over its "*cis*-eclipsed" alternative than that calculated for **5** (*i.e.*, 1.5 *vs* 1.0 kcal/mol). These results suggest that the delivery of 9-BBN-H from **3a** to an aldehyde should show a greater *trans* selectivity for **3a** than for **5**, regardless of the actual arrangement of the H–C–C–B array (*i.e.*, synperiplanar or *gauche*).

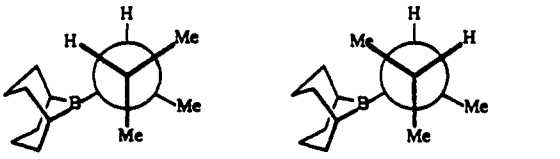
Borane reductions are thought to occur through initial *O*-complexation of the borane which produces an equilibrium concentration of the complexed species.[7c,h,14] The dynamic nature of this equilibrium can be observed in unhindered systems through an upfield shift in the time-averaged ^{11}B NMR signal for the $R_3B/(RCHO–BR_3)$ mixture. This shift is not detectable in most systems, including **3**, probably due to the very low concentration of the complexed species. However, our previous studies[7h] with 3-pinanylboranes strongly suggest that the selective formation of



3a (ΔE = +2.6 kcal/mol)



5 (ΔE = +0.7 kcal/mol)



6 (ΔE = +0.4 kcal/mol)

Figure 2. Newman projections of the *gauche* conformations of **3a**, **5**, and **6** with comparative MMX data.

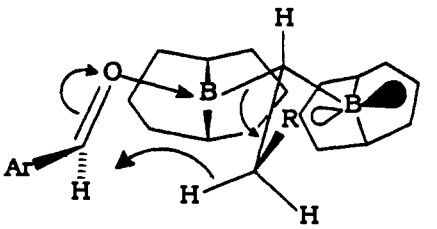


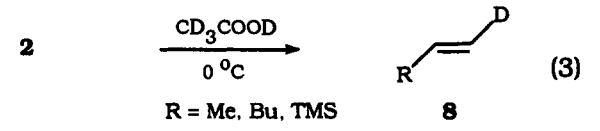
Figure 3. Proposed TS for the dehydroborylation of **3**.

this complex with *anti* geometry (*i.e.*, RC(=O)B)[15] is responsible for the preferred geometry in Midland's proposed boat-like, electrocyclic, hydride-transfer transition state.[7f] Combining these features suggests a transition-state model for the dehydroborylation process for **3** which is depicted in Figure 3.

Compared to simple *B*-alkyl-9-BBN derivatives, the unusually fast rate of reduction of ArCHO by **3** can be explained by the added stability imparted to the transition state by the empty p orbital on the boron atom in the added 9-BBN substituent.[7,16] This stabilization allows reaction to occur at much lower temperatures than that with *B*-*s*-Bu-9-BBN, a feature which favors a more selective process. Moreover, as noted above, 1,3 repulsions for the Me–C–C–(9-BBN) array are greater than that for Me–C–C–Me, an aspect of this process which disfavors the alternative transition state leading to a *cis*-vinylborane from **3** compared to the formation of *cis*-2-butene from **5**. Thus, the combination of these steric considerations with the electronically based lower reaction temperatures makes the preparation of **2** from **3** a highly efficient and selective process.

Vinylborane Conversions. To demonstrate the remarkable versatility of our new approach to **2** and to highlight the synthetic advantages of 9-BBN derivatives over other vinylboranes, selected experiments were conducted to combine these features. Undergoing protonolysis under very mild conditions with complete retention of configuration, **2** is an excellent precursor to *trans*-1-deuterioalkenes.[3,6e,h] Thus, **2a**, **2b**, and **2e**, vinylboranes which are not formed efficiently even with a large excess of **1**, were smoothly converted to **8** with CD_3COOD (or AcOD) at 0 °C.

(12) Ingold, C. K.; Shaw, R. *J. Chem. Soc.* **1927**, 2818. See also: refs 5b and 6d.
(13) PC Model: available from Serena Software, Bloomington, IN 47402-3076.
(14) Bolton, R. *Aust. J. Chem.* **1990**, *43*, 493.
(15) (a) Reetz, M. T.; Hullmann, M.; Massa, W.; Berger, S.; Rademacher, P.; Heymanns, P. *J. Am. Chem. Soc.* **1986**, *108*, 2405. (b) See also: Denmark, S. E.; Henke, B. R.; Webber, E. *J. Am. Chem. Soc.* **1987**, *109*, 2512.
(16) See, for example, (a) Gassman, P. G.; Singleton, D. A. *Tetrahedron Lett.* **1987**, *28*, 5969. (b) Gassman, P. G.; Gorman, D. B. *J. Am. Chem. Soc.* **1990**, *112*, 8623.

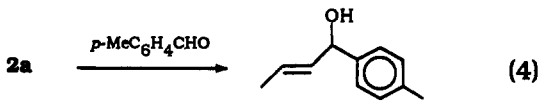


(3)

The concept of using an excess of the alkyne to enhance vinylborane formation is completely unworkable for an α,ω-diyne if both alkyne components are to be hydroborated. However, with a 4:1 9-BBN-H/**9** stoichiometry, the 1,1,9,9-tetra-9-BBN adduct, **10**, is formed cleanly from 1,8-nonadiyne (**9**). This can be contrasted to the 2:1 stoichiometry which gives a complex mixture of many products. Treatment of **10** with 2 equiv of PhCHO results in the clean formation of *trans,trans*-1,9-di-9-BBN-1,8-nonadiene (**11**) which, after deuterolysis as above, produces pure *trans,trans*-dideuterated diene **12**, which was isolated in 64% overall yield.

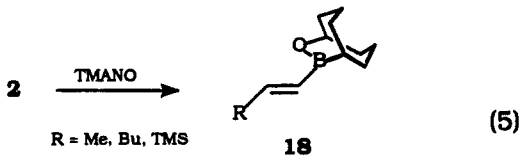
The 9-BBN ring possesses remarkable thermal stability,[3] and this feature is utilized in the one-pot conversion of **13** to *trans*-3-(deuterioallyl)silane, **16**, which was isolated in 62% overall yield. Thus, the neat dihydroboration of **13** with 2 equiv of 9-BBN-H produces a 1,2-diboryl adduct[6h] initially, and this is cleanly, thermally isomerized at 170 °C in 2 h to give 3,3-diboryl product **14**.[6h] Treatment of **14** with PhCHO gives **15**, and its deuterolysis in pentane affords **16** cleanly.

The "Grignard-like" addition to aldehydes is unique to vinyl-9-BBN derivatives because of their Lewis acidity and, unlike other alkylboranes, no competitive β-hydride reductive processes are observed.[6l,17] Thus, *p*-tolualdehyde inserts cleanly into the vinylic B–C bond of **2a** in refluxing ether (0.4 M, 12 h) to provide the corresponding *trans*-allylic alcohol **17** in 89% yield.[18]



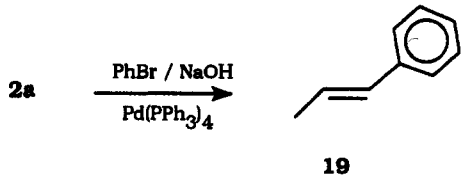
(4)

Another important feature of 9-BBN systems stems from their selective oxidation to the corresponding air-stable 9-oxa-10-borabicyclo[3.3.2]decanes **18**.[6e,m,n] This proved to be a trivial operation for **2a** (92%), **2b** (87%), and **2e** (82%) with 1 equiv of anhydrous trimethylamine *N*-oxide (TMANO)[19] in $CHCl_3$ at 0 °C. Interestingly, **18** is not only inert to atmospheric oxygen but also proved to be unreactive toward either protonolysis (HOAc, 25 °C, 8 h) or the insertion process (PhCHO, neat, 80 °C, 6 h).



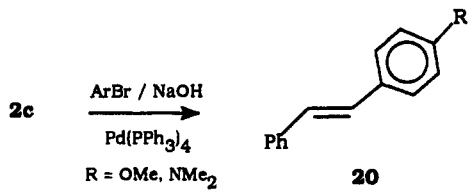
(5)

With the versatility of 9-BBN derivatives in the Suzuki coupling[20] having been demonstrated only for a limited number of vinylboranes, we were impressed with their relative efficiency and ease of product isolation in this important process.[6m-p,20e] The absence of a convenient route to **2** has severely limited the use of 9-BBN derivatives in this coupling in favor of their more accessible catechol, disiamyl, or dicyclohexyl vinylborane counterparts, reagents which have other disadvantages.[3a,20,21] However, with **2** now available, we carried out this cross-coupling with **2a** and PhBr under standard conditions (THF, 3% $Pd(PPh_3)_4$, 3 M NaOH (3 equiv), reflux, 12 h) followed by oxidation of the borane coproducts (excess 30% H_2O_2) to obtain pure *trans*-1-phenyl-1-propene (**19**) in 87% yield.



(6)

As mentioned above, **2c** is best prepared in pure form *via* Brown's hydroboration procedure,[5] but it is quantitatively produced from the dehydroborylation method (Table III). To demonstrate that the presence of **4a** would not interfere with the Suzuki coupling, the hydroboration of **1c** was carried out neat with 2 equiv of 9-BBN-H (neat, 2 h, 100 °C); PhCHO (1 equiv, 0.2 M in THF, 6 h, 25 °C) was added to effect the conversion to **2c**, and its cross-couplings with *p*-Me_2N and *p*-MeO bromobenzenes were conducted to afford the desired substituted *trans*-stilbenes (**20**) in 60 and 80% isolated yields, respectively. Therefore, it is not necessary to remove **4a** from **2** to successfully carry out the Suzuki process, and the separation of $PhCH_2OH$ (and *cis*-1,5-cyclooctanediol) is easily accomplished by filtration of **20** through alumina with pentane.



(7)

Conclusions

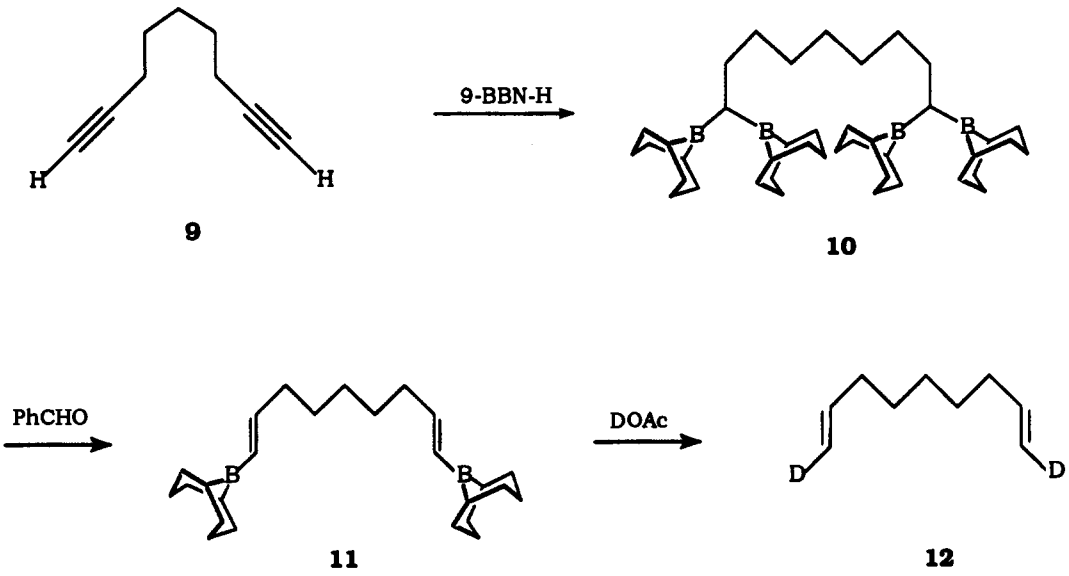
In summary, the hydroboration of excess **1** with 9-BBN-H, while an effective approach to **2** from available, inexpensive terminal alkynes with branched substituents, is not general. By contrast, the dihydroboration of **1** provides 1,1-diboryl adducts **3** cleanly, and these are converted to **2** quantitatively with ArCHO for every system examined. The term dehydroborylation is introduced to emphasize the olefination feature of the process and to differentiate it from the Midland reduction of carbonyl compounds. Compound **2** was subjected to deuterolysis, thermal isomerization, aldehyde insertion, oxidation, and Pd-catalyzed cross-coupling reactions not only to establish the value of the dehydroborylation approach but also to clearly show the advantages of using 9-BBN derivatives in vinylborane reactions. Thus, the scope and limitations of both the hydroboration and the new dehydroborylation route to *trans*-vinyl-9-BBN derivatives have been fully delineated, and several previously unknown applications to chemical synthesis were described to demonstrate their remarkable versatility.

Experimental Section

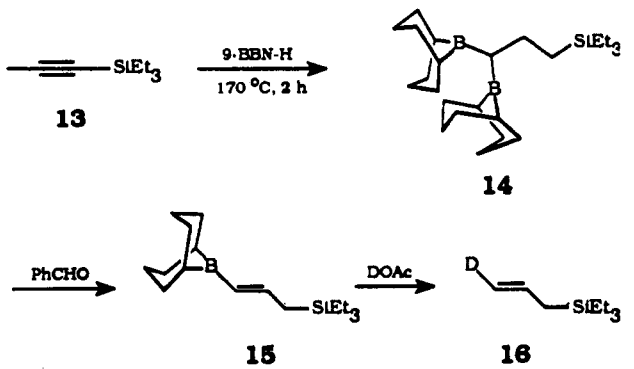
General Methods. All experiments were carried out in predried glassware (1 h, 150 °C) under a nitrogen atmosphere. Standard handling techniques for air-sensitive compounds were employed throughout this study.[3] ^1H NMR, ^{13}C NMR, and ^{11}B NMR data were recorded at 300, 75, and 96 MHz, respectively. Standard COSY, HETCOR, APT, and/or DEPT experiments were carried out for the NMR assignments for all of the compounds discussed in this work including the broadened α-boryl carbons which often were previously not observed.[6a,b,e,h,i,22] GC analyses

(17) Jacob, P., III; Brown, H. C. *J. Org. Chem.* **1977**, *42*, 579.
(18) Recognizing the sequential nature of the **3a** → **2a** → **15** process, we concluded that the high efficiency of the aldehyde insertion process observed by Jacob and Brown[17] was due, in part, to the increase in the amount of **2** over that produced from the hydroboration of **1** with 9-BBN-H by the initial dehydroborylation of **3** followed by its reaction with the excess aldehyde employed.
(19) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.* **1986**, *27*, 3961.
(20) (a) Miyaura, N.; Yamada, K.; Suginome, H.; Suzuki, A. *J. Am. Chem. Soc.* **1985**, *107*, 972. (b) Suzuki, A. *Pure Appl. Chem.* **1991**, *63*, 419. (c) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314. (d) Ishiyama, T.; Miyaura, N.; Suzuki, A. *Synlett* **1991**, 687. (e) Soderquist, J. A.; Colberg, J. C. *Synlett* **1989**, 25.
(21) Soderquist, J. A.; León-Colón, G. *Tetrahedron Lett.* **1991**, *32*, 43.
(22) Blue, C. D.; Nelson, D. J. *J. Org. Chem.* **1983**, *48*, 4538.

Scheme I



Scheme II



were performed using 6-ft × $^1/_8$-in. 20% SE-30 on DCDMS-treated Chrom W packed columns and 30-m × 0.23-mm i.d. 20% SE-30 vitreous silica open tubular columns. Columns were silylated (MSTFA) prior to analytical runs. Electron-impact (70 eV) GC/MS data were obtained employing similarly treated analytical GC columns. $CDCl_3$ and C_6D_6 were filtered through Al_2O_3 and stored in a sealed, amber bottle. Alkynes were distilled from CaH_2 and stored under nitrogen. Hexanes and pentane were purified over concentrated sulfuric acid, decanted, extracted with a solution of 5% $NaHCO_3$, dried, and distilled from $LiAlH_4$. THF, DME, and ether were distilled from Na/Ph_2CO prior to use. Other reagents were either obtained from commercial sources or prepared as described and were used without further purification.

Hydroboration of 1 with 9-BBN-H.[5] General Procedure. To 9-BBN-H (1.22 g, 10 mmol) in THF (20 mL) at 0 °C was added **1** (either 10 or 20 mmol). After the solution was stirred for 18 h at 0 °C, an aliquot was withdrawn *via* syringe and analyzed by ^{11}B NMR. For example, for the **2b**/**3b** system, integration of the 69.3 and 87.6 ppm signals for the 1:1 **1b**/9-BBN-H mixture gives a 56:44 ratio of peak areas. Dividing the 87.6 ppm area by 2 (two 9-BBN groups/**3b**) results in a 22% yield of **3b**. Corroborative ^{13}C NMR data were obtained on the concentrated mixture as previously described[4h] which resulted in a 55:23 calculated product ratio under these conditions and for which we have demonstrated the direct correlation to carefully obtained GC analysis data. It must be noted that the ^{11}B NMR technique is a very direct method which gives consistent and reliable data for the boron product distribution, minimizing additional handling or chemical operations.

***trans*-1-(9-Borabicyclo[3.3.1]non-9-yl)-1-propene (2a).** To 9-BBN-H (12.2 g, 100 mmol) in THF (200 mL) at 25 °C in a flask surmounted by a dry ice condenser was added propyne (2.0 g, 50 mmol) in THF (10 mL) slowly *via* cannula. After 1 h, the mixture was heated at reflux temperature for 2 h to ensure complete dihydroboration. To the 0 °C solution of **3a** was added 1-NaphCHO (7.81 g, 50 mmol), and the mixture was stirred at 25 °C for 12 h. Concentration followed by distillation gave 6.54 g (81%) of **2a** (bp 65–67 °C at 0.9 Torr): ^1H NMR ($CDCl_3$) δ 1.32 (m, 2H), 1.78 (m, 6H), 1.93 (m, 6H), 2.01 (dd, J = 6.3, 1.5 Hz, 3H), 6.31 (dq, J = 17.1, 1.5 Hz, 1H), 6.89 (dq, J = 17.1, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.5, 30.0, 33.8 (9-BBN[6a] ring), 21.9 (C-3), 136.5 (C-1), 150.8 (C-2); ^{11}B NMR ($CDCl_3$) δ 77.0; IR (CCl_4) 1616, 992 cm^{-1} (*t*-CH=CH); MS m/z (relative abundance) 162 ($M^{\bullet+}$, 42), 147 (10), 133 (35), 120 (65), 105 (36), 91 (100), 79 (66), 53 (85). The same procedure (200-mmol scale) using PhCHO gave **2a** (89%, bp 46–47 °C at 0.1 Torr).

***trans*-1-(9-Borabicyclo[3.3.1]non-9-yl)-1-hexene (2b).** To 9-BBN-H (24.4 g, 200 mmol) in THF (200 mL) at 25 °C was added 1-hexyne (8.22 g, 100 mmol) slowly with constant stirring. After 1 h, the mixture was heated at reflux temperature for an additional 2 h to ensure complete dihydroboration. The solution of **3b** was cooled to 0 °C, 1-NaphCHO (15.6 g, 100 mmol) was added dropwise, and the mixture was allowed to warm to 25 °C and stirred for an additional 4 h. Concentration and distillation of the residue gave 17.55 g (86%) of **2b** (bp 96–97 °C at 0.2 Torr): ^1H NMR ($CDCl_3$) δ 0.98 (t, J = 7.2 Hz, 3H), 1.43 (m, 8H), 1.86 (m, 10H), 2.33 (dq, J = 6.6, 1.2 Hz, 2H), 6.88 (dt, J = 17.1, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.6, 30.6, 33.8 (9-BBN[6a] ring), 13.9 (C-6), 22.5 (C-5), 30.7 (C-4), 35.9 (C-3), 134.4 (C-1), 156.0 (C-2); ^{11}B NMR ($CDCl_3$) δ 77.4; MS m/z (relative abundance) 204 ($M^{\bullet+}$, 18), 175 (3), 161 (9), 147 (22), 134 (40), 120 (69), 91 (100), 77 (70), 53 (75).

***trans*-1-(9-Borabicyclo[3.3.1]non-9-yl)-2-phenylethene (2c).** To 9-BBN (2.44 g, 20 mmol) in THF (37.5 mL) at 0 °C was added phenylacetylene (4.00 g, 40 mmol), and after being stirred at this temperature for 18 h, the mixture was concentrated and distilled to afford 3.54 g (79%) of **2c** (bp 130–132 °C at 0.10 Torr): ^1H NMR (C_6D_6) δ 1.10–2.05 (m, 14 H), 7.19 (d, J = 18 Hz, 1H), 7.73 (d, J = 18 Hz, 1H), 7.51–7.78 (m, 5H); ^{13}C NMR (C_6D_6) δ 23.5, 30.3, 33.8 (9-BBN[6a] ring), 127.9, 128.5, 129.2, 137.6 (*m*, *o*, *p*, *i*), 131.2 (C-1), 149.7 (C-2); ^{11}B NMR ($CDCl_3$) δ 79.

***trans*-1-(9-Borabicyclo[3.3.1]non-9-yl)-3-methyl-1-butene (2d).** To 9-BBN-H (2.454 g, 20.11 mmol) in THF (50 mL) at 25 °C in a flask surmounted by a dry ice condenser was added isopropylacetylene (0.685 g, 10.05 mmol) slowly *via* cannula. After 1 h, the mixture was heated at reflux temperature for 2 h to ensure complete dihydroboration. To the 0 °C solution of **3d** was added 1-naphthaldehyde (1.562 g, 10.05 mmol), and the mixture was stirred at 25 °C for 6 h. Concentration followed by distillation gave 1.622 g (85%) of **2d** (bp 75–76 °C at 0.2 Torr): ^1H NMR ($CDCl_3$) δ 1.08 (d, J = 6.7 Hz, 6H), 1.27 (m, 4H), 1.81 (m, 10H), 2.47 (m, 1H), 6.16 (dd, J = 17.5, 1.5 Hz, 1H), 6.79 (dd, J = 17.5, 6.2 Hz, 1H); ^{13}C NMR (C_6D_6) δ 23.6, 30.1, 33.8 (9-BBN[6a] ring), 21.7 (C-4, -5), 33.9 (C-3), 130.6 (C-1), 162.2 (C-2); ^{11}B NMR δ ($CDCl_3$) 78. In a separate experiment, the hydroboration of **1d** (100 excess, 18 h, 0 °C) with 9-BBN-H gave a 93:7 mixture of **2d**/**3d**, from which a 79% yield of pure **2d** was obtained after distillation. This product exhibited identical spectroscopic properties to that isolated from the dehydroborylation procedure.

***trans*-1-(9-Borabicyclo[3.3.1]non-9-yl)-2-(trimethylsilyl)ethene (2e).** To 9-BBN (3.66 g, 30 mmol) in THF (7.5 mL) was added (trimethylsilyl)acetylene (1.47 g, 15 mmol), and the mixture was stirred for 3 h at 25 °C. After the solution was cooled to 0 °C, *p*-anisaldehyde (2.0 g, 15 mmol) was added and the solution was stirred for 1 h, allowed to warm to 25 °C, and stirred for an additional 3 h. Concentration followed by

distillation afforded 2.7 g (82%) of **2e** (bp 85–86 °C at 1.0 Torr): ^{1}H NMR ($CDCl_3$) δ 0.10 (s, 9H), 1.15–1.95 (m, 14H), 7.24 (d, J = 21 Hz, 1H), 7.37 (d, J = 21 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.9, 30.6, 34.2 (9-BBN^{6a} ring), –1.4 (TMS), 152.2 (C-2), 157.3 (C-1); ^{11}B NMR ($CDCl_3$) δ 68.

1,1-Bis(9-borabicyclo[3.3.1]non-9-yl)propane (3a). To 9-BBN (12.2 g, 100 mmol in THF (200 mL) at 0 °C in a reaction flask surmounted by a dry ice condenser was slowly added propyne (2.0 g, 50 mmol) in THF (*ca.* 50 mL) *via* cannula. The reaction mixture was stirred for 1 h at 0 °C followed by 2 h at reflux temperature. Concentration afforded 14.2 g (100%) of **3a**: ^{1}H NMR ($CDCl_3$) δ 0.94 (t, J = 7.5 Hz, 3H), 1.67 (m, 4H), 1.32 (m, 4H), 1.86 (m, 20H), 2.01 (q, J = 7.2 Hz, 2H), 2.70 (t, J = 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.9, 32.2, 33.6, 33.9 (9-BBN^{6a} ring), 18.7 (C-3), 22.0 (C-2), 58.7 (C-1); ^{11}B NMR ($CDCl_3$) δ 84.5.

1,1-Bis(9-borabicyclo[3.3.1]non-9-yl)hexane (3b). To 9-BBN-H (12.2 g, 100 mmol) in THF (200 mL) at 0 °C in a reaction flask surmounted by a dry ice condenser was added 1-hexyne (4.107 g, 50.0 mmol) dropwise. The reaction mixture was stirred for 1 h at 0 °C followed by 2 h at reflux temperature. Concentration afforded 16.3 g (100%) of **3b**: ^{1}H NMR ($CDCl_3$) δ 0.98 (t, J = 6.6 Hz, 3H), 1.39 (m, 6H), 1.75 (m, 6H), 1.96 (m, 24H), 2.81 (t, J = 6.0 Hz, 1H); ^{13}C NMR ($CDCl_3$) 23.3, 31.6, 33.2, 33.4 (9-BBN^{6a} ring), 14.2 (C-6), 22.7 (C-5), 28.5 (C-3), 32.4 (C-4), 33.8 (C-2), 55.6 (C-1); ^{11}B NMR ($CDCl_3$) δ 87.8.

1,1-Bis(9-borabicyclo[3.3.1]non-9-yl)-2-phenylethane (3c). To 9-BBN-H (2.44 g, 20 mmol) was added phenylacetylene (1.02 g, 10 mmol). The reaction mixture was heated neat at 100 °C for 2 h to afford 6.92 g (100%) of **3c** (mp 68–70 °C, sealed tube): ^{1}H NMR ($CDCl_3$) δ 1.21 (m, 4H), 1.60 (m, 10H), 1.86 (m, 15H), 3.33 (br s, 2H), 7.29 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 23.1, 31.8, 33.0, 33.1 (9-BBN^{6a} ring), 125.2, 128.0, 128.4, 144.8 (*p*, *o*, *m*, *i*), 33.6 (C-2), 54.3 (C-1); ^{11}B NMR ($CDCl_3$) δ 88.0.

1,1-Bis(9-borabicyclo[3.3.1]non-9-yl)-3-methylbutane (3d). To 9-BBN-H (2.454 g, 20.11 mmol) in THF (50 mL) at 25 °C in a flask surmounted by a dry ice condenser was added isopropylacetylene (0.685 g, 10.05 mmol) slowly with constant stirring. After 1 h, the mixture was heated at reflux temperature for an additional 2 h to ensure complete dihydroboration. Concentration gave 3.14 g (100%) of **3d**: ^{1}H NMR ($CDCl_3$) δ 0.89 (d, J = 6.7 Hz, 6H), 1.32 (m, 6H), 1.45 (9 lines, J = 6.7 Hz, 1H), 1.69 (m, 6H), 1.87 (m, 18H), 2.88 (t, J = 5.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 23.3, 30.9, 33.2, 33.4 (9-BBN^{6a} ring), 22.8 (C-4,5), 31.8 (C-3), 37.7 (C-2), 52.9 (C-1); ^{11}B NMR ($CDCl_3$) δ 87.5.

1,1-Bis(9-borabicyclo[3.3.1]non-9-yl)-2-(trimethylsilyl)ethane (3e). From 9-BBN-H (2.44 g, 20 mmol) in THF (50 mL) and (trimethylsilyl)acetylene (0.98 g, 10 mmol) in DME (10 mL), after 2 h (precipate formed) at 25 °C, concentration followed by recrystallization from DME afforded 3.0 g (88%) of **3e** (mp 105 °C, sealed tube): ^{1}H NMR (C_6D_6) δ –0.12 (s, 9H), 1.1–1.8 (m, 30H), 2.71 (t, J = 5 Hz, 1H); ^{13}C (C_6D_6) δ 23.4, 31.8, 33.5 (9-BBN^{6a} ring), –1.4 (TMS), 13.3 (C-1), 48.6 (C-2); ^{11}B NMR (C_6D_6) δ 85.

Attempted Trapping of 9-BBN-H in the Dehydroborylation Process. To **3a** (0.284 g, 1.00 mmol) in dry $CDCl_3$ (1 mL) in a predried 5-mm NMR tube was added, *via* syringe, styrene (0.118 g, 1.0 mmol). This mixture was stirred at probe temperature (*ca.* 30 °C) for 1.5 h with no detectable reaction. To this solution was added benzaldehyde (0.108 g, 1.0 mmol) which revealed, by ^{13}C NMR, the complete conversion to **3a** and **4a** (^{13}C NMR δ 23.2, 24.5, 33.1 (9-BBN^{6a} ring), 126.5, 127.2, 128.2, 139.7 (C_6H_5, *o*, *p*, *m*, *i*), 67.5) in 2 h while the styrene remained completely unreacted. In a separate experiment, styrene (^{13}C NMR ($CDCl_3$) δ 126.2, 127.6, 128.3, 137.6 (C_6H_5, *m*, *o*, *p*, *i*), 113.4, 136.9) was hydroborated with 9-BBN-H to prepare *B*-(2-phenylethyl)-9-BBN (^{13}C NMR ($CDCl_3$) δ 23.2, 31.3, 33.2 (9-BBN^{6a} ring), 125.3, 127.8, 128.1, 144.7 (C_6H_5, *o*, *p*, *m*, *i*), 29.1, 30.5) and confirm its absence in the above dehydroborylation mixture.

General Procedure for Obtaining the Kinetic Data Used for the Hammett Plot. After thoroughly flushing an oven-dried NMR tube containing a *para*-substituted benzaldehyde (0.30 mmol) with nitrogen, $CDCl_3$ (300 μL) and silicone oil (100 μL) were added *via* syringe followed by the addition of **3a** (300 μL of a 1 M solution in $CDCl_3$, 0.30 mmol). A ^{13}C NMR (32 scan) spectrum was immediately obtained to establish the initial relative ratio of the silicone oil signal (δ 1.4) to that selected for **3a** (δ 18.4 (C-3)). Linear least-squares plots were obtained for [**3a**]$^{-1}$ *vs* time (*p*-$MeOC_6H_4CHO$: $k = 1.4 \times 10^{-3}$ M^{-1} s^{-1} ([**3a**], time (s)) (0.30, 374), (0.25, 974), (0.19, 1574), (0.15, 2174), (0.14, 2774), (0.12, 3374), (0.12, 3974), (0.10, 4574). *p*-$NO_2C_6H_4CHO$: $k = 6.5 \times 10^{-3}$ M^{-1} s^{-1} ([**3a**], time (s)) (0.41, 0), (0.27, 330), (0.21, 450), (0.19, 570), (0.16, 690), (0.13, 810), (0.14, 930), (0.10, 1050). *p*-MeC_6H_4CHO: $k = 1.51 \times 10^{-3}$ M^{-1} s^{-1} ([**3a**], time (s)) (0.38, 0), (0.30, 481), (0.25, 1081), (0.19, 1681), (0.15, 2281), (0.14, 2881), (0.14, 3481), (0.11, 4081). *p*-ClC_6H_4CHO: $k = 1.82 \times 10^{-3}$ M^{-1} s^{-1} ([**3a**], time (s)) (0.69, 0), (0.52, 248), (0.50, 348), (0.44, 448), (0.42, 548), (0.37, 648), (0.36, 748). C_6H_5CHO: $k = 2.43 \times 10^{-3}$ M^{-1} s^{-1} ([**3a**], time (s)) (1.62, 0), (0.65, 540), (0.53, 660), (0.47, 780), (0.44, 900), (0.36, 1020), (0.32, 1140), (0.29, 1260), (0.29, 1380), (0.26, 1500), (0.21, 1620)). A Hammett plot was obtained using $k_{p\text{-}X}/k_H$ *vs* σ_p^+ to result in a ρ value of 0.42.

Competitive Rate Studies. A thoroughly flushed, oven-dried NMR tube was charged with **3a** (290 μL, 0.189 g, 0.97 mmol) and **6** (210 μL, 0.187 g, 0.97 mmol), and $CDCl_3$ (100 μL), silicone oil (100 μL), and, finally, PhCHO (100 μL, 0.103 g, 0.97 mmol) were added *via* syringe. A ^{13}C NMR (32 scan) spectrum was immediately obtained to establish the initial relative ratio of the silicone oil signal (δ 1.3) to that selected for **3a** (δ 18.4 (C-3)) and **6** (δ 11.2 (C-4)). Assuming additive volumes, the concentration of each organoborane was calculated initially and, using the silicone oil as an internal standard, the change in peak heights was monitored with time to determine the concentration of both organoboranes at various intervals. Using the Ingold–Shaw relationship,[12] $k_x/k_y = (\log x_0 - \log x_t)/(\log y_0 - \log y_t)$, at various times resulted in a calculated value of 2.9 for k_{3a}/k_6 (*e.g.*, ([**3a**], [**6**], time (s)) 1.21, 1.21, 0; 0.70, 1.01, 300; 0.48, 0.88, 900). Similar experiments with **7** (δ 48) *vs* **3a** (δ 18.4) resulted in $k_7/k_{3a} = 4.5$ (*e.g.*, 1.06, 1.06, 0; 0.24, 0.76, 275; 0.20, 0.74, 395).

***trans*-1-Deuterio-1-propene (8a).** To **2a** (0.16 g, 1.0 mmol) in $CDCl_3$ (0.5 mL) at 0 °C in an NMR tube was added CH_3COOD (0.061 g, 1.0 mmol) *via* syringe, and the contents were thoroughly shaken. NMR analysis revealed the clean formation of **8a**[23] (^{1}H NMR δ 1.78 (dd, J = 6.6, 1.8 Hz, 3H), 5.07 (dq, J = 17.1, 1.8 Hz, 1H), 5.88 (dq of 3-line patterns, J = 17.1, 6.6, 1.5 Hz, 1H); ^{13}C NMR δ 19.1 (C-3), 133.4 (C-2), 115.2 (C-1, 3 lines, $^2J_{C\text{-}D}$ = 24.0 Hz)) and *B*-AcO-9-BBN (^{13}C NMR δ 23.3, 23.7, 31.9 (9-BBN^{6a} ring), 22.5, 179.5 (AcO); ^{11}B NMR δ 58).

***trans*-1-Deuterio-1-hexene (8b).** To **2b** (2.135 g, 10.46 mmol) in tetradecane (50 mL) at 0 °C CD_3COOD (0.670 g, 10.46 mmol) dropwise with rapid stirring (*B*-AcO-9-BBN precipitated). The mixture was slowly warmed to 25 °C and stirred for 3 h. Vacuum bulb-to-bulb distillation to a receiver flask at –78 °C gave 0.683 g (79%) of **8b**;[24] ^{1}H NMR ($CDCl_3$) δ 0.90 (t, J = 7.2 Hz, 3H), 1.35 (m, 4H), 2.05 (q, J = 6.9 Hz, 2H), 4.96 (dt, J = 17.1, 1.5 Hz, 1H), 5.79 (dtt, J = 17.1, 6.6, 1.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.9 (C-6), 22.2 (C-5), 31.1 (C-4), 33.4 (C-3), 139.3 (C-2), 113.8 (C-1, 3 lines, $^2J_{C\text{-}D}$ = 24.3 Hz); MS *m*/*z* (relative abundance) 85 ($M^{\bullet+}$, 33), 70 (21), 56 (100).

***trans*-1-(2-Deuterioethenyl)trimethylsilane (8e).** To **2e** (3.3 g, 15 mmol) in tetradecane (15 mL) at 0 °C was added CD_3COOD (0.93 g, 15 mmol). After 15 min, the reaction was allowed to reach 25 °C, stirred for an additional 15 min, concentrated, and distilled to afford (55–57 °C, 760 Torr) 1.05 g (70%) of **8e**: ^{1}H NMR (C_6D_6) δ 0.10 (s, 9H), 5.58 (dt, J = 20.0, 2.1 Hz, 1H), 6.10 (d, J = 20.0 Hz, 1H); ^{13}C NMR (C_6D_6) δ –2.0 (Me_3Si); 130.3 (C-2, 3 lines, $^2J_{C\text{-}D}$ = 24 Hz), 139.5 (C-1); MS (70 eV) *m*/*z* (relative abundance) 101 ($M^{\bullet+}$, 16), 100 (4), 86 (100), 73 (100), 60.0 (100), 57 (34), 56 (61), 55 (61), 54 (43), 53 (87); IR (TF) 2100 (C–D), 1595, 965 (*t*-CH=CH), 1240 (SiMe) cm^{-1}.

1,1,9,9-Tetrakis(9-borabicyclo[3.3.1]non-9-yl)nonane (10). To 9-BBN-H (2.4 g, 20 mmol) in THF (10 mL) at 25 °C was added **9** (0.6 g, 5 mmol), and the mixture was stirred for 5 h. Concentration gave 3.0 g (100%) of **10**: ^{1}H NMR (C_6D_6) δ 1.23–2.28 (m, 70 H), 2.65 (t, J = 6 Hz, 2H); ^{13}C (C_6D_6) δ 23.8, 32.1, 33.6, 33.9 (9-BBN^{6a} ring), 28.9 (C-5), 30.0 (C-4,6), 30.6 (C-2,8), 34.1 (C-3,7), 56.1 (C-1,9); ^{11}B NMR (C_6D_6) δ 86.

***trans,trans*-1,9-Bis(9-borabicyclo[3.3.1]non-9-yl)-1,8-nonadiene (11).** To **10** (3.0 g, 5.0 mmol) in THF (10 mL) at 0 °C was added PhCHO (1.06 g, 10 mmol), and after 1 h, the mixture was stirred for an additional 3 h at 25 °C and concentrated *in vacuo*. NMR revealed the clean formation of **4** (*vide ultra*) and **11** (^{1}H NMR (C_6D_6) δ 1.00–2.00 (m, 34H), 2.13 (q, J = 7 Hz, 4H), 6.25 (d, J = 17 Hz, 1H), 6.78 (dt, J = 17, 7 Hz, 1H); ^{13}C NMR (C_6D_6) δ 23.9, 30.6, 33.8 (9-BBN^{6a} ring), 28.9 (C-5), 29.7 (C-4,6), 36.5 (C-3,7), 134.9 (C-1,9), 156.3 (C-2,8); ^{11}B NMR (C_6D_6) δ 77.

***trans,trans*-1,9-Dideuterio-1,8-nonadiene (12).** To **10** (3.31 g, 5 mmol) in pentane (5 mL) was added PhCHO (2.12 g, 10 mmol), and after 5 h, the solution was cooled to 0 °C and CD_3COOD (0.64 g, 10 mmol) was added. After 15 min, the temperature was allowed to reach 25 °C, and, after an additional 15 min, ethanolamine (1.34 g, 22 mmol) was added to the vigorously stirring mixture, the solution was filtered, and the filtrate was concentrated and distilled to obtain 0.32 g (62%) of **12** (bp 140–143 °C at 760 Torr, ^{13}C NMR >95% D_2): ^{1}H NMR ($CDCl_3$) δ 1.30–1.56 (m, 6H), 2.04–2.21 (m, 4H), 4.93 (d, J = 17 Hz, 2H), 5.84 (m, 2H); ^{13}C

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($CDCl_3$) δ 29.0 (C-5), 29.2 (C-4,6), 34.0 (C-3,7), 114.3 (C-1,-9, 3 lines, $^2J_{C,D}$ = 25 Hz), 139.4 (C-2,8); IR (TF) 2110 (C–D), 1645, 990 (*t*-CH=CH) cm^{-1}. Anal. Calcd[25] for $C_9H_{14}D_2$: C, 85.63; H, 12.95. Found: C, 85.83; H, 12.79.

(3,3-Bis(9-borabicyclo[3.3.1]non-9-yl)propyl)triethylsilane (14). To 9-BBN-H (3.66 g, 30.0 mmol) was added **13** (2.31 g, 15.0 mmol), and the mixture was heated at 110 °C for 48 h with ^{13}C and ^{11}B NMR revealing the complete conversion to **14**. Distillation afforded 5.0 g (84%) of pure **14** (bp 165 °C at 0.3 Torr): ^1H NMR ($CDCl_3$) δ 0.70 (q, *J* = 8.0 Hz, 6H), 1.4–2.2 (m, 41H), 2.9 (t, *J* = 6.0 Hz, 1H); ^{13}C ($CDCl_3$) δ 3.7, 7.5 ($SiCH_2CH_3$), 16.8 (C-1), 22.5 (C-2), 60.6 (C-3), 23.4, 31.8, 33.2, 33.5 (9-BBN[6a] ring); ^{11}B ($CDCl_3$) δ 86.

***trans*-(3-(9-Borabicyclo[3.3.1]non-9-yl)-2-propen-1-yl)triethylsilane (15).** To **14** (from 9-BBN-H (2.44 g, 20 mmol) and **13** (1.54 g, 10 mmol), 170 °C, 2 h) at 0 °C was added PhCHO (1.06 g, 10 mmol), and after 1 h, the mixture was stirred an additional 3 h at 25 °C and concentrated *in vacuo*. In addition to the expected signals for **4a** (*vide ultra*), the clean formation of **15** was observed by NMR analysis: ^1H NMR (C_6D_6) δ 0.63 (q, *J* = 8 Hz, 6H), 1.03 (t, *J* = 8 Hz, 9H), 1.63 (d, *J* = 8 Hz, 2H), 1.25–2.05 (m, 14H), 6.16 (d, *J* = 17 Hz, 1H), 7.04 (dt, *J* = 17, 8 Hz, 1H); ^{13}C NMR (C_6D_6) δ 3.1, 7.5 ($SiCH_2CH_3$), 24.0 (C-1), 134.0 (C-3), 154.0 (C-2), 23.8, 30.0, 33.7 (9-BBN[6a] ring); ^{11}B NMR (C_6D_6) δ 79.

***trans*-(3-Deuterio-2-propen-1-yl)triethylsilane (16).** To a mixture of **15** and **4** (R = Ph) prepared as above in dry pentane (15 mL) at 0 °C was added CD_3COOD (0.64 g, 10 mmol), and the reaction mixture was stirred at 25 °C for 0.5 h. Ethanolamine (1.34 g, 22 mmol) was added, and the mixture was filtered through alumina, eluting with pentane, concentrated, and distilled to afford 0.98 g (62%) of **16** (bp 168-170 °C at 760 Torr): ^1H NMR ($CDCl_3$) δ 0.55 (q, *J* = 8 Hz, 6H), 0.96 (t, *J* = 8 Hz, 9H), 1.55 (dd, *J* = 8, 1.3 Hz, 2H), 4.85 (dt, *J* = 17, 1.3 Hz, 1H), 5.80 (dd, *J* = 17, 8 Hz, 1H); ^{13}C ($CDCl_3$) δ 3.4, 7.5 ($SiCH_2CH_3$), 19.7 (C-1), 112 (C-3, 3 lines, $^2J_{C,D}$ = 24 Hz), 135.3 (C-2); IR (TF) 2100 (CD), 1610 (C=C), 1249 (MeSi), 965 (*t*-CH=CH) cm^{-1}; MS *m*/*z* (relative abundance) 157 ($M^{\bullet+}$, 1), 115 (50), 100 (11), 88 (10), 87 (100). Anal. Calcd[25] for $C_9H_{19}DSi$: C, 68.76; H, 12.89. Found: C, 68.49; H, 12.78.

***trans*-1-(*p*-Tolyl)-2-propen-1-ol (17).** To **2a** (1.695 g, 10.46 mmol) was added *p*-tolualdehyde (1.257 g, 10.46 mmol), and the mixture was heated at 100–110 °C for 11 h. After the mixture was cooled to 25 °C, ether (25 mL) was added followed by the slow addition of aqueous NaOH (15 mL of 3 N) and then 30% H_2O_2 (15 mL). Ethanol (5 mL) was added, and the solution was maintained at 50 °C overnight. The ether was removed *in vacuo*, and the residue was saturated with K_2CO_3 and extracted with hexane (3 × 10 mL). Concentration gave 1.52 g (90%) of **17** as a white solid (mp 47–48 °C, lit.[26] mp 48 °C): ^1H NMR ($CDCl_3$) δ 1.70 (dd, *J* = 5.1, 0.6 Hz, 3H), 2.04 (s, 1H), 2.33 (s, 3H), 5.09 (d, *J* = 5.7 Hz, 1H), 5.6–5.8 (m, 2H), 7.15 (d, *J* = 8.1 Hz, 2H), 7.24 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 17.5 (C-4), 21.0 (*p*-Me), 74.7 (C-1), 126.6 (C-3), 133.7 (C-2), 126.0, 129.1, 136.7, 140.5 (*o*, *m*, *p*, *i*, *p*-tolyl ring); IR (KBr) 3300 (OH), 1670, 960 (*t*-CH=CH) cm^{-1}.

***trans*-10-(1-Propen-1-yl)-9-oxa-10-borabicyclo[3.3.2]decane (18a).** To **2a** (1.46 g, 9.0 mmol) in THF (5 mL) at 0 °C was added TMANO in $CHCl_3$ (4.5 mL of 2.00 M, 9.0 mmol) dropwise. The mixture was allowed to reach 25 °C over 30 min, concentrated, and distilled to give 1.477 g (92%) of **18a** (bp 85-88 °C at 1.5 Torr, 98% GC purity): ^1H NMR ($CDCl_3$) δ 1.43 (m, 4H), 1.64 (m, 4H), 1.82 (m, 5H), 1.86 (dd, *J* = 6.3, 1.5 Hz, 3H), 4.58 (m, 1H), 5.63 (dq, *J* = 17.5, 1.5 Hz, 1H), 6.59 (dq, *J* = 17.5, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.4 (br s), 22.1, 26.2, 31.7, 73.8 (OBBD ring[4e]), 21.4 (C-3), 133.3 (C-1, br s), 148.1 (C-2); ^{11}B NMR ($CDCl_3$) δ 47.2; IR (neat) 1631, 990 (*t*-CH=CH) cm^{-1}; MS *m*/*z* (relative abundance) 178 ($M^{\bullet+}$, 5), 110 (98), 95 (29), 82 (100). Anal. Calcd for $C_{11}H_{19}BO$: C, 74.24; H, 10.76. Found: C, 74.10; H. 10.73.

***trans*-10-(1-Hexen-1-yl)-9-oxa-10-borabicyclo[3.3.2]decane (18b).** To **2b** (5.156 g, 25.3 mmol) in THF (10 mL) at 0 °C was added TMANO in $CHCl_3$ (12.65 mL of 2.00 M, 25.3 mmol) dropwise. The mixture was allowed to reach 25 °C over 30 min, concentrated, and distilled to give 4.812 g (87%) of **18b** (bp 114–5 °C at 0.9 Torr). ^1H NMR ($CDCl_3$) δ 0.89 (t, *J* = 7.1 Hz, 3H), 1.38 (m, 7H), 1.60 (m, 5H), 1.84 (m, 5H), 2.17 (q, *J* = 6.3 Hz, 2H), 4.59 (m, 1H), 5.59 (d, *J* = 17.6 Hz, 1H), 6.57 (dt, *J* = 17.6, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.1, 22.4 (br s), 26.2, 31.7, 73.1 (OBBD ring[4e]), 13.8 (C-6), 22.2 (C-5), 30.6 (C-4), 35.3 (C-3), 131.2 (C-1), 153.5 (C-2); ^{11}B NMR ($CDCl_3$) δ 47.6; IR (TF) 1628, 999 (*t*-CH=CH), 1123 (CO) cm^{-1}; MS *m*/*z* (relative abundance) 220 ($M^{\bullet+}$, 0.44), 110 (25), 82 (54), 67 (100). Anal. Calcd for $C_{14}H_{25}BO$: C, 76.38; H, 11.45. Found: C, 76.15; H, 11.39.

***trans*-1-(2-(9-Oxa-10-borabicyclo[3.3.2]dec-10-yl)ethenyl)trimethylsilane (18e).** To **2e** (1.10 g, 5 mmol) in THF (5 mL) at 0 °C was added TMANO in $CHCl_3$ (3.1 mL of 1.6 M, 5.0 mmol) was added dropwise. After 1 h, the mixture was stirred for an additional hour at 25 °C, concentrated, and distilled to afford 1.12 (95%) of **18e** (bp 92–94 °C at 0.8 Torr): ^1H NMR ($CDCl_3$) δ 0.04 (s, 9H), 1.30–1.96 (m, 13H), 4.47 (m, 1H), 6.52 (d, *J* = 21.6 Hz, 1H), 7.03 (d, *J* = 21.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 22.5, 26.7 (br s), 29.7, 32.2, 73.3 (OBBD ring[4e]), −1.2 ($SiMe_3$), 150.1 (C-2, br s), 154.3 (C-1); ^{11}B NMR ($CDCl_3$) δ 47.

***trans*-1-Phenylpropene (19).** A solution of **1a** (1.782 g, 11.0 mmol), NaOH (11 mL of 3 M, 33 mmol), and THF (20 mL) was added to a mixture of bromobenzene (1.58 g, 10 mmol) and $Pd(PPh_3)_4$ (0.350 g, 0.3 mmol) in THF (30 mL). After the solution was heated at 65 °C for 12 h, 30% H_2O_2 (10 mL, 100 mmol) was added dropwise, and the mixture was heated overnight at reflux temperature to ensure the complete oxidation of the residual organoborane species. Tetradecane (1.56 g, 7.8 mmol) was added as an internal standard, and the mixture was analyzed by GC to reveal 87% yield of **19**. The mixture was extracted with pentane (3 × 10 mL), and the pentane layer was washed several times with H_2O to remove the THF. Concentration gave a mixture of **17** and *n*-$C_{14}H_{30}$, from which a pure sample of **19** was isolated by preparative GC and its structure confirmed by comparison to an authentic sample.[4n] **19**: ^1H NMR ($CDCl_3$) δ 1.87 (dd, *J* = 6.4, 1.2 Hz, 3H), 6.23 (dq, *J* = 15.9, 6.4 Hz, 1H), 6.39 (dq, *J* = 15.9, 1.2 Hz, 1H), 7.19 (m, 1H), 7.28 (m, 2H), 7.32 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 18.5 (C-3), 125.6 (C-2), 130.9 (C-1), 125.8, 126.7, 128.4, 137.9 (*o*, *p*, *m*, *i*, Ph ring); MS *m*/*z* (relative abundance) 118 ($M^{\bullet+}$, 68), 117 (100), 103 (9), 77 (7).

***trans*-1-(4-Methoxyphenyl)-2-phenylethene (20a).** To 9-BBN-H (2.507 g, 20.5 mmol) was added phenylacetylene (1.406 g, 10.24 mmol), and the mixture was heated at 100–120 °C for 2 h. Pentane (20 mL) was added followed by benzaldehyde (1.086 g, 10.2 mmol). After the solution was stirred at 25 °C for 6 h, NaOH (10 mL of 3 M, 30 mmol) was added. This mixture was transferred to a second flask containing a solution of *p*-bromoanisole (1.663, 9.0 mmol) and $Pd(PPh_3)_4$ (0.350 g, 0.3 mmol) in THF (10 mL). After the solution was heated at 65 °C for 15 h, 30% H_2O_2 (11 mL, 110 mmol) was added dropwise and the mixture was heated overnight at reflux temperature to ensure the complete oxidation of the residual organoborane species. Separation and extraction of the aqueous layer with ether (3 × 10 mL) followed by drying the combined organic extracts with Na_2SO_4 and concentration gave a residue which was recrystallized from 95% EtOH to afford 1.54 g (80%) of **20a** (mp 135-137 °C, lit.[27] mp 136.5-137.0 °C): ^1H NMR ($CDCl_3$) δ 3.84 (s, 3H), 6.92 (dt, *J* = 8.8, 1.5 Hz, 1H), 6.99 (d, *J* = 16.5 Hz, 1H), 7.09 (d, *J* = 16.5 Hz, 1H), 7.26 (m, 1H), 7.37 (m, 2H), 7.48 (dt, *J* = 8.8, 1.5 Hz, 1H), 7.53 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 55.3 (OMe), 114.1, 127.7, 130.1, 159.3 (*m*, *o*, *i*, *p*, *p*-$MeOC_6H_4$ ring), 126.2, 127.2, 128.6, 137.6 (*o*, *p*, *m*, *i*, Ph ring), 126.6 (C-2), 128.1 (C-1); MS *m*/*z* (relative abundance) 210 ($M^{\bullet+}$, 31), 165 (100).

***trans*-1-(4-(*N*,*N*-Dimethylamino)phenyl)-2-phenylethene (20b).** To **3c** (3.48 g, 10.1 mmol) (prepared as for **20a**) in THF (10 mL) was added benzaldehyde (1.07 g, 10.1 mmol). After the solution was stirred for 6 h at 25 °C, NaOH (10 mL of 3 M, 30 mmol) was added and this mixture transferred to a solution of *p*-bromo-*N*,*N*-dimethylaniline (1.80 g, 9.0 mmol) and $Pd(PPh_3)_4$ (0.350 g, 0.3 mmol) in THF (20 mL). After being heated at 65 °C for 12 h and oxidized as for **20a**, the organic material was diluted with hexanes (20 mL) and separated and the aqueous layer was extracted with hexanes (3 × 10 mL). The combined organic material was filtered through Al_2O_3 and concentrated to afforded 1.2 g (60%) of **20b** (mp 147 °C, lit.[28] mp 149 °C): ^1H NMR ($CDCl_3$) δ 3.00 (s, 6H), 6.75 (d, *J* = 9.0 Hz, 2H), 6.95 (d, *J* = 16.5 Hz, 1H), 7.09 (d, *J* = 16.5 Hz, 1H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.36 (t, *J* = 7.2 Hz, 2H), 7.45 (d, *J* = 9.0 Hz, 2H), 7.51 (d, *J* = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 40.4 (NMe_2), 112.4, 125.7, 127.5, 150.1 (*m*, *i*, *o*, *p*, *p*-$Me_2NC_6H_4$ ring), 125.9, 126.6, 128.5, 138.1 (*o*, *p*, *m*, *i*, Ph ring), 124.3 (C-2), 128.7 (C-1); MS *m*/*z* (relative abundance) 223 ($M^{\bullet+}$, 30), 78 (100).

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(25) The theoretical percentage of H was calculated as follows: for example, from the combustion of 1 mol of **12** (126.24 g), the total mass of the "water" produced would be 146.137 g (5 H_2O + 2 HOD) from which the analytical laboratory calculates 16.35 g of "H" (0.1119 g of H/g of H_2O). Dividing this by the MW of **8e** results in the theoretical value, 12.95% H. The % C is calculated in the usual manner (g C/MW × 100).

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