Synthesis, Properties, and Hydroboration Activity of the Highly Electrophilic Borane Bis(pentafluorophenyl)borane, $HB(C_6F_5)_2$[1]

Daniel J. Parks,[†] Warren E. Piers,*[,†] and Glenn P. A. Yap[‡]

Department of Chemistry, University of Calgary, 2500 University Drive N.W., Calgary, Alberta, Canada T2N 1N4, and X-ray Laboratory, University of Ottawa, Pavillon d'Iorio Hall, 10 Marie Curie Avenue, Ottawa, Ontario, Canada K1N 6N5

Received August 5, 1998

Two reliable and efficient routes to bis(pentafluorophenyl)borane, **1**, are described. A three-step procedure uses the $-C_6F_5$ transfer agent $Me_2Sn(C_6F_5)_2$ to produce the chloroborane $ClB(C_6F_5)_2$, which is subsequently converted to **1** by treatment with a silane, and proceeds with an overall yield of 62%. Alternatively, **1** can be made in 69% yield from $B(C_6F_5)_3$ and Et_3SiH by heating the two reagents at 60 °C for 3 days in benzene. Borane **1** is dimeric in the solid state, as determined by X-ray crystallographic analysis. However, in aromatic solvents, detectable amounts of monomeric borane are present (ratio of dimer:monomer ≈4.5:1). The ease of dimer dissociation to monomer coupled with the high electrophilicity of the borane makes **1** a very reactive hydroboration reagent in aromatic solvents. Hydroborations do not proceed in donor solvents such as tetrahydrofuran. A survey of a variety of olefin and alkyne substrates shows that **1** hydroborates with comparable regio- and chemoselectivities to commonly used reagents such as 9-BBN, but at a much faster rate. A second unique feature of the reagent is the facility with which boryl migration takes place in the products of olefin hydroboration. This property can be used to access thermodynamic products of hydroboration where other reagents give diastereomeric kinetic products. Alkynes can be selectively monohydroborated; terminal alkyne substrates will react with a second equivalent of **1**, while internal alkynes are immune to further hydroboration. Two procedures for the oxidation of the products of hydroboration were developed. Since the organobis(pentafluorophenyl)boranes are susceptible to protonolyis, oxidation must be carried out in a two-phase system using highly alkaline hydrogen peroxide or with a nonaqueous procedure using Me_3NO as the oxidant. Hydroboration/oxidation can be carried out rapidly in a one-pot procedure which gives alcohol or carbonyl products in good to excellent yields.

Introduction

Although the hydroboration reaction was discovered many years ago, it remains one of the most effective means of functionalizing carbon−carbon double and triple bonds today.[2−4] Part of the success this chemistry has enjoyed is due to the many methods available for transforming organoboranes into a wide variety of functional groups. However, the features of the hydroboration reaction itself and the development of a library of hydroboration reagents have also contributed to the utility of this process in organic chemistry.

Much of the early work in hydroboration was carried out using diborane.[2] On a practical level, hydroboration with "BH_3" or its tetrahydrofuran (THF) adduct is sufficient for simple substrates, but the reagent exhibits poor regio- and diastereoselectivity for substrates where these factors are at issue. Where BH_3 has proven most useful is as a precursor to other, more selective reagents such as 9-BBN,[5] Sia_2BH,[6] or thexylborane,[7] via in situ hydroboration of 1,5-cyclooctadiene, 2-methyl-2-butene, or tetramethylethylene, respectively. These diorganobo-

* To whom correspondence should be addressed. Telephone: 403-220-5746. FAX: 403-289-9488. E-mail: wpiers@chem.ucalgary.ca.
† University of Calgary.
‡ University of Ottawa.

(1) Dedicated to Prof. Edward Piers on the occasion of his 60th birthday. Happy Birthday, Dad!

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10.1021/om980673e CCC: $15.00
Publication on Web 11/07/1998

ranes, and others,[8] generally hydroborate unsymmetrical and prochiral substrates much more selectively than BH_3 due primarily to their greater steric bulk. The corollary to this is that they are also significantly less reactive than BH_3·THF and hydroborations with these reagents can be very slow in some circumstances.

We recently reported the novel borane reagent bis(pentafluorophenyl)borane, $HB(C_6F_5)_2$, **1**.[9] Pentafluorophenyl substituted boranes, although known for some time,[10] have recently come to prominance as strong Lewis acids capable of initiating olefin polymerization reactions in conjunction with group 4 organometallic compounds.[11] It was in this connection that we first prepared **1**,[12] but we also became interested in its utility as a new hydroboration reagent. We found that it shares the selectivity of the several diorganoboranes mentioned above but that it is significantly more reactive in terms of rate in comparison to these more commonly used reagents. As such, it is able to hydroborate difficult substrates rapidly and selectively, where other reagents fail. Furthermore, the organoborane products formed with this reagent are prone to rapid equilibration to thermodynamically stable diastereomers through retrohydroboration/rehydroboration sequences.

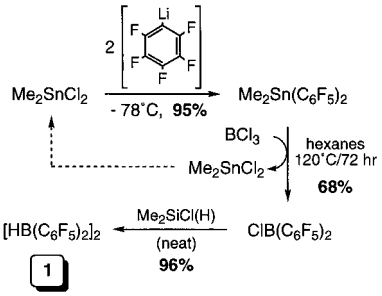
A primary concern as far as the utility of **1** is concerned resides in its accessibility to synthetic chemists. Herein we report the details of its synthesis on a multigram scale from the chloroborane $ClB(C_6F_5)_2$.[13] In addition, a new route starting from the commercially available tris(pentafluorophenyl)borane, $B(C_6F_5)_3$, has been developed, improving its availability. We also report details on its physical properties, its behavior in common solvents, and its hydroboration activity toward olefinic and acetylenic substrates.

Results and Discussion

Synthesis of $HB(C_6F_5)_2$, 1. We include details of two reliable routes to borane **1**. The first relies on the known compound $ClB(C_6F_5)_2$, while the second stems from the commercially available borane $B(C_6F_5)_3$. Both routes allow for access to multigram quantities of highly pure **1**.

Scheme 1 outlines the chemistry involved in the method we originally published. While generation of **1** from the chloroborane $ClB(C_6F_5)_2$ is straightforward and high yielding, the preparation of $ClB(C_6F_5)_2$ itself is somewhat tedious. The stannyl C_6F_5 transfer agent $Me_2Sn(C_6F_5)_2$, was originally prepared using the Grignard reagent $BrMgC_6F_5$ and Me_2SnBr_2. We have found that use of the organolithium reagent LiC_6F_5 and the less expensive tin precursor Me_2SnCl_2 gives $Me_2Sn(C_6F_5)_2$

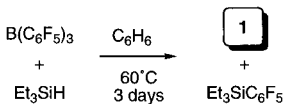
Scheme 1



in higher purity and better yield than the Grignard route. In addition, this method allows for recycling of the tin source Me_2SnCl_2 since it is an isolable byproduct of the next step in the sequence.

We have also modified the original method used for converting $Me_2Sn(C_6F_5)_2$ and BCl_3 to $ClB(C_6F_5)_2$. Rather than reacting BCl_3 and the tin reagent neat, we employ hexanes as a solvent such that the concentration of reactants is close to 0.2 M. Longer heating at a higher temperature drives the reaction to completion, and, upon cooling, up to 80% of the Me_2SnCl_2 byproduct crystallizes out of the reaction medium. The product $ClB(C_6F_5)_2$ is highly soluble in hexanes and remains in the mother liquor, which is decanted away from the precipitated Me_2SnCl_2. By removal of most of the tin in this fashion, rather than through fractional sublimation, losses of the desired $ClB(C_6F_5)_2$ product are minimized. The residual 20% of the Me_2SnCl_2 is separated via fractional sublimation, and analytically pure, tin-free chloroborane is obtained in 68% yield. Conversion of this material to **1** is trivially accomplished by dissolving the chloroborane in $Me_2SiCl(H)$ and stirring for 30 min; **1** precipitates quantitatively and can be isolated by filtration. If the reaction is allowed to stir for longer, the product borane is contaminated with up to 5% of a second borane which we believe to be the mixed dimer $[(C_6F_5)_2B(\mu\text{-}H)_2B(H)(C_6F_5)]$ on the basis of its ^{19}F NMR spectrum.[14] Short reaction times obviate this side product whose presence is in any case not detrimental on a practical level. The overall yield is 62% starting from LiC_6F_5 and Me_2SnCl_2.

A one-step procedure to **1** using commercially available borane $B(C_6F_5)_3$ and Et_3SiH occurs with roughly the same efficiency but is less labor intensive and convenient if the cost of $B(C_6F_5)_3$ is not an issue. As shown in eq 1, heating a 1:1 mixture of borane and



(1)

silane in benzene at 60 °C for several days leads to production of **1** and $Et_3SiC_6F_5$.[15] Upon cooling, **1** precipitates out of solution in 69% yield. After washing away the silane byproduct, the borane's purity is comparable to that obtained via the route in Scheme 1, although dimer $[(C_6F_5)_2B(\mu\text{-}H)_2B(H)(C_6F_5)]$ always comprises about 5% of the product mixture.

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(14) The spectrum indicates the presence of three inequivalent C_6F_5 groups, as would be expected for the mixed dimer $[(C_6F_5)_2B(\mu\text{-}H)_2B(H)(C_6F_5)]$: −130.25, −132.80, −133.2 (obscured) (F_o); −148.1, −148.7, −149.55 (F_p); −160.5, −160.7 (other signal obscured).

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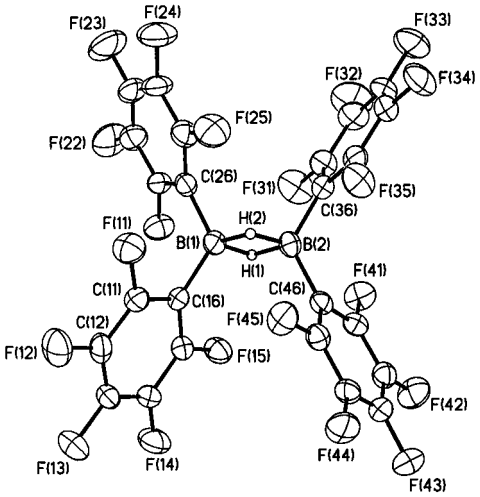

Figure 1. ORTEP diagram of $[HB(C_6F_5)_2]_2$ **1** (thermal ellipsoids are at the 50% probability level).

Table 1. Selected Metrical Parameters for 1 and Comparative Data for Other $[R_2BH]_2$ Dimers

param	**1**	$B_2H_2Mes_4$	$(9\text{-BBN})_2$	B_2H_6
B−H[a] (Å)	1.26(1)	1.285(20)	1.25(2)	1.245(20)
B−C[a] (Å)	1.576(6)	1.602(3)	1.567(2)	
B···B (Å)	1.799(7)	1.851(3)	1.818(3)	1.76(1)
C−B−C[a] (deg)	121.6(4)	123.2(1)	111.8(3)	
H−B−H[a] (deg)	90(2)	88(1)	86(2)	90(1)
B−H−B[a] (deg)	92(3)	93(2)	94(2)	

[a] Average value.

Solution and Solid-State Properties of 1. Borane **1** is a white, microcrystalline solid that is stable indefinitely under an inert atmosphere. In the presence of protic agents, it reacts rapidly to eliminate hydrogen and form $XB(C_6F_5)_2$ derivatives. For example, it serves as a precursor to the useful bis(pentafluorophenyl)boryl compounds $HOB(C_6F_5)_2$ [16] and $CF_3SO_3B(C_6F_5)_2$ [17] upon treatment with 1 equiv of water or triflic acid, respectively. The borane is sparingly soluble in aromatic solvents at room temperature, but since it reacts with donor solvents in which it is more soluble (vide infra), benzene or toluene is the solvent of choice for its use.

As is typical for diorganoboranes of modest steric bulk,[18] in the solid **1** exists as a dimer. This is indicated by the IR spectrum which displays a strong absorption at 1550 cm^{-1}, characteristic of a bridging $B-(\mu\text{-}H)_2-B$ moiety.[19] No absorption due to a terminal B−H (2500−2600 cm^{-1}) is present. Crystals of **1** grown from benzene were subjected to X-ray crystallographic analysis, which confirmed the dimeric nature of the compound. An ORTEP depiction of the molecular structure is shown in Figure 1, and selected metrical data are given in Table 1 along with comparative data from the borane dimers dimesitylborane,[20] 9-BBN dimer,[21] and diborane,[22] updating a table originally compiled by Power, et al.[20] The parameters associated with the structure of **1** are similar to its sister compounds and will not be further discussed.

Although a dimer in the solid, boron and fluorine NMR studies suggest that a significant amount of monomeric borane is accessible in solution. For example, the ^{11}B NMR spectrum of dilute solutions of **1** in C_6D_6 (all material dissolved) displays two resonances, one due to a minor species (20%) at 60 ppm and the other to a major species (80%) at 18 ppm. These resonances appear in the spectral regions[18,23] associated with neutral, three-coordinate boron[24] and neutral, four-coordinate boron, respectively. For comparison, the definitively monomeric borane $HB(Trip)_2$ (Trip = 2,4,6-^{i}Pr$_3$C$_6$H$_2$) is characterized by a ^{11}B chemical shift of δ 73.5 ppm in C_6D_6.[20]

The presence of monomer is also evidenced in the ^{19}F NMR spectrum of **1**, which exhibits resonances for both the major and minor components. The chemical shift difference between the *para*- and *meta*-fluorine resonances is sensitive to the coordination environment about boron in C_6F_5 substituted boranes and borates.[25] In the spectrum of **1**, $\Delta\delta_{m,p} = 12.7$ for the major component and $\Delta\delta_{m,p} = 18.3$ ppm for the minor species. The latter value is in the range expected for three-coordinate boranes, while the former is consistent with the four-coordinate boron associated with a dimeric structure. As the temperature is raised, the intensity of the resonances for the minor species increase, indicating that dissociation into monomer becomes more favored upon heating. A regime in which monomer/dimer exchange was rapid on the ^{19}F NMR time scale was not reached.

Extensive kinetic[26] and computational[27] studies suggest that, for diorganoboranes, hydroboration of olefins occurs through a monomeric species formed upon dissociation of $R_2B(\mu\text{-}H)_2BR_2$ dimers. Since the barrier to addition of the B−H bond across C=C is low for most boranes,[26−28] the overall rate of hydroboration for a given reagent is largely dictated by the barrier to dimer dissociation. In the case of diborane, the barrier to dimer dissociation has been estimated[29] to be ≈36 kcal mol^{-1} on the basis of the observed and calculated stabilization energy obtained for the reverse process (i.e., dimerization of two molecules of BH_3), which has virtually no barrier. Thus, hydroboration with B_2H_6 itself is relatively slow because of the substantial energetic impedance to dimer dissociation. For diorganoboranes, this process is somewhat more favorable (but still quite endothermic) due to greater nonbonding interactions

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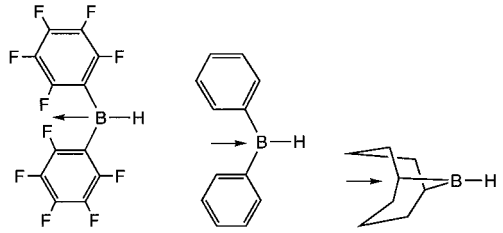


Dipole	0.77 debye		0.83 debye		0.43 debye		
Mulliken Charge	**B**	0.38	**B**	0.28	**B**	0.41
	H	0.03	**H**	-0.05	**H**	-0.03
	C	-0.30	**C**	-0.11	**C**	-0.33

Figure 2. Ab intio calculated dipole moments and selected Mulliken charges of borane monomers (RHF 6-31G*) using MacSpartan Plus software. The arrow indicates the direction of the dipole moment.

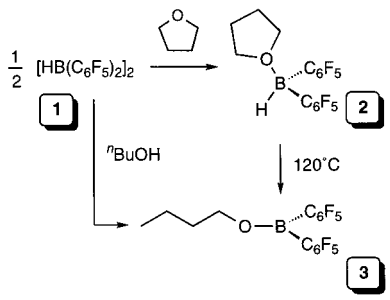
between alkyl groups on the two boron centers. For example, kinetic studies on hydroboration with 9-BBN suggest that the monomer/dimer equilibrium strongly favors the dimer and dissociation proceeds with a rate constant on the order of 1.5×10^{-4} s^{-1} and an estimated barrier of 22 kcal mol^{-1} at room temperature.[26]

In this light, the presence of observable amounts of monomeric borane in solutions of **1** accounts for its extremely high hydroboration reactivity relative to other boranes (vide infra). Overall, the rate of hydroboration with **1** likely still depends on the rate of dimer dissociation, but given the high activity of **1**, this process must be much more favorable for $[HB(C_6F_5)_2]_2$ than $[9\text{-BBN}]_2$. Indeed, a rough calculation of K_{eq} for dimer dissociation in **1**, using the NMR data discussed above, yields a value of $\approx 4 \times 10^{-4}$, corresponding to a $\Delta G°_{298}$ of $\approx$5 kcal mol^{-1}. Even with a modest barrier to dimerization of $HB(C_6F_5)_2$, the barrier to dimer dissociation in $[HB(C_6F_5)_2]_2$ would be markedly lower than that of 9-BBN dimer.

The lower barrier to dimer dissociation in **1** relative to other boranes is due to a destabilized dimer, a stabilized monomer, or a combination of both factors. Ab initio calculations carried out at the 6-31G* level on the monomeric boranes 9-BBN, Ph_2BH, and $(C_6F_5)_2BH$ show that the polarity of the BH bond drops for the pentafluorophenyl substituted species; indeed the direction of the dipole moment inverts in this compound (Figure 2). The C_6F_5 groups increase the effective electronegativity of the boron nucleus, reducing the nucleophilicity of the B−H bond which could diminish the strength of the three-center, 2-electron bonds necessary to hold the dimer together, allowing for more facile dissociation. On the monomer side of the equilibrium, it is conceivable that monomeric **1** is more effectively solvated by aromatic solvents than other boranes through C_6H_6/C_6F_5 π-stacking interactions[30] or perhaps even a weak interaction with benzene itself in a manner similar to that observed for Et_3Si^+.[31] While $HB(C_6F_5)_2$ is not as Lewis acidic as the triethylsilylium ion, we note that (pentafluorophenyl)boranes are capable of partially activating trialkylsilanes through abstraction of H^-.[32]

For 9-BBN dimer, hydroboration rates are increased approximately 10-fold when weak Lewis bases are added,[26] the rationale being that donors break up the dimer and make active monomer more accessible in solution. While boosting compound **1**'s performance is not necessary for practical purposes, we wanted to explore its utility in donor solvent media. Hydroborations with **1** are possible in chlorinated solvents such as dichloromethane, but it forms strong adducts with Lewis bases such as THF and Et_2O which are not active as hydroboration reagents. For example, **1** rapidly forms the adduct $HB(C_6F_5)_2$·THF, **2**, upon dissolution in THF; **2** can be isolated as a white solid (Scheme 2). Adduct **2** is unreactive toward olefins at 25 °C, and the elevated temperatures necessary to induce THF dissociation (k_{ex} = 434(4) s^{-1} at 85 °C by ^1H NMR line shape analysis[33]) coincide with the conditions where retrohydroboration is facile (vide infra). Furthermore, in this temperature regime adduct **2** undergoes gradual decomposition via the reductive ring-opening of THF to bis(pentafluorophenyl) butylborinate ^{n}BuOB$(C_6F_5)_2$, **3** (Scheme 2). This process is accelerated with the addition of extra portions of **1**, suggesting that the mechanism involves liberation of catalytic amounts of **1** via dissociation of THF.[11,34] The relatively high endothermicity apparently associated with dissociation of THF from **1** again attests to its strongly Lewis acidic character.

Scheme 2



Hydroboration of Alkenes and Alkynes Using 1. As mentioned above, borane **1** is an extremely active hydroboration reagent toward a variety of alkene (Table 2) and alkyne (Table 3) substrates. The reactions summarized in these tables were performed in benzene-d_6 and monitored by NMR spectroscopy; with few exceptions, the reactions were clean and regioselective and complete within minutes of substrate addition to suspensions of borane reagent. Reactions were judged to be complete upon clearing of the suspension. Most of the alkylborane products were not isolated (although it is possible to do so if desired) but completely characterized by ^1H, ^{11}B, ^{13}C, and ^{19}F NMR spectroscopy. Some of the entries (entries 2−4, Table 2; entries 1 and 7, Table 3) appeared in our original report without NMR data and are included here (Experimental section) for completeness.

For ethylene (Table 2, entry 1), reaction is complete in ≈1 h at room temperature after exposure of **1** in benzene to 1 atm of ethylene. Treatment of styrene with

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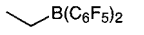
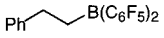
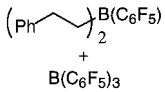
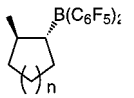
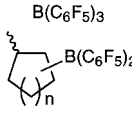
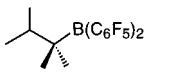
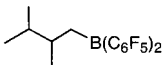
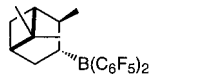
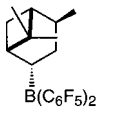
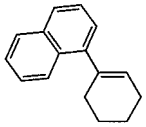
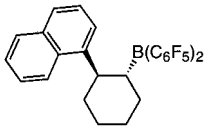
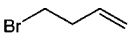
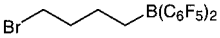
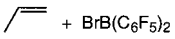
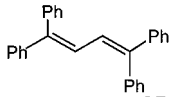
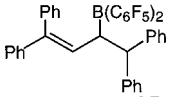
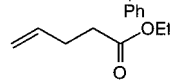
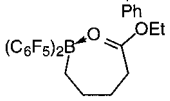
(33) Sandstrom, J. *Dynamic NMR Spectroscopy*; Academic Press: New York, 1982.

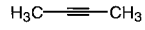
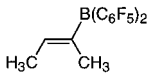
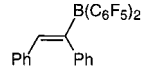
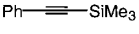
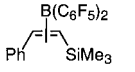
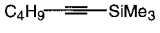
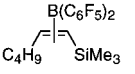
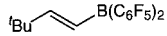
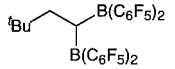
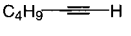
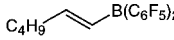
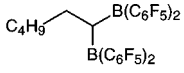
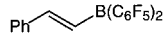
(34) The utility of this ring opening process was surveyed with several other oxygen containing heterocycles; unfortunately, most of these reactions were not selective and gave complex product mixtures. We thus abandoned this chemistry and focused on hydroboration applications.

Table 2. Hydroboration of Alkene Substrates Using $HB(C_6F_5)_2$, 1

entry	substrate	product: kinetic	product: thermodynamic
1			
2[a]			
3[b]			
4			
5[c]			
6			
7			
8			
9			
10			

[a] ≈5% of 2-boryl product present. [b] $n = 1$ and 2. [c] The final ratio of kinetic:thermodynamic ≈ 1:1.

Table 3. Hydroboration of Alkyne Substrates Using $HB(C_6F_5)_2$, 1

entry	substrate	product: monohydroboration	product: dihydroboration
1			no reaction
2			no reaction
3[a]			[b]
4[a]			[b]
5			
6			
7			
8			[b]

[a] Product is a 1:1 mixture of regioisomers. [b] Reactions not attempted.

1 gives predominantly the terminal isomer $PhCH_2CH_2B(C_6F_5)_2$ (96:4). Styrene is a benchmark substrate for evaluating regiochemical behavior of borane reagents;[2] **1** gives comparable results to common dialkylboranes such as 9-BBN, but with a much higher rate of hydroboration.

Scheme 3

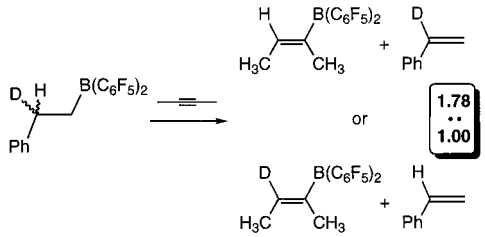
Studies on retrohydroboration from $PhCH_2CH_2B(C_6F_5)_2$ (vide infra) brought to light the tendency of these organobis(pentafluorophenyl)boranes to undergo slow disproportionation in solution over the course of several days. In the ^1H NMR spectrum a new product arises in which the resonances of the two methylene groups are shifted upfield ($\delta_{CH_2} = 2.67$, 1.86 ppm) relative to those of the kinetic product of styrene hydroboration ($\delta_{CH_2} = 2.77$, 2.29 ppm). This is consistent with the presence of $(PhCH_2CH_2)_2BC_6F_5$ since the phenethyl groups in this compound are associated with a less electrophilic boron center. The presence of equimolar amounts of $B(C_6F_5)_3$ was confirmed by ^{19}F NMR spectroscopy. Fortunately, this disproportionation reaction is not kinetically significant enough to disrupt other applications of **1**.

The substrates of entries 3−6 are illustrative of a unique feature of olefin hydroboration with $HB(C_6F_5)_2$. In each example, a kinetic product arising from direct H−B addition to C=C is observed but isomerization to a more thermodynamically stable product mixture via a retrohydroboration/rehydroboration sequence occurs at room temperature. In other boranes, boryl migration is observed only at temperatures in excess of 150 °C.[35] For the methylcycloalkenes of entry 3, rapid, regioselective hydroboration was followed by a slower migration of the $-B(C_6F_5)_2$ around the ring *at room temperature*, forming an essentially statistical mixture of isomers.[36] The kinetic product of hydroboration of tetramethylethylene (entry 4) isomerizes much more rapidly (migration occurs even at −30 °C) and exclusively to the final product shown. Indeed, reactions of borane $(CH_3)_3CHC(CH_3)_2B(C_6F_5)_2$ with trapping agents such as 2-butyne or THF occur upon mixing (Scheme 3), suggesting that although the equilibrium lies toward the hydroborated species, retrohydroboration in this system is extremely facile. Brown et al. have observed that boryl migrations in boranes of general formula R_2B-(3-hexyl) are strongly influenced by the steric properties of R; i.e., migration becomes more facile as R increases in steric bulk.[35b−d] While the $-C_6F_5$ is of moderate steric bulk, the facility of boryl migrations in the hydroboration products of **1** is undoubtedly related to the highly electrophilic nature of the boron center.

(35) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1966**, *88*, 1433. (b) Brown, H. C.; Racherla, U. S.; Taniguchi, H. *J. Org. Chem.* **1981**, *46*, 4314. (c) Brown, H. C.; Racherla, U. S. *Organometallics* **1982**, *1*, 765. (d) Brown, H. C.; Racherla, U. S. *J. Organomet. Chem.* **1983**, *241*, C37.

(36) We were unable to ascertain whether this mixture consisted of exclusively trans isomers. Boryl migration in cyclic systems has been observed previously and proposed to occur without dissociation of the olefin from the boron on the basis of the absence of cis isomers from the mixture.

Scheme 4

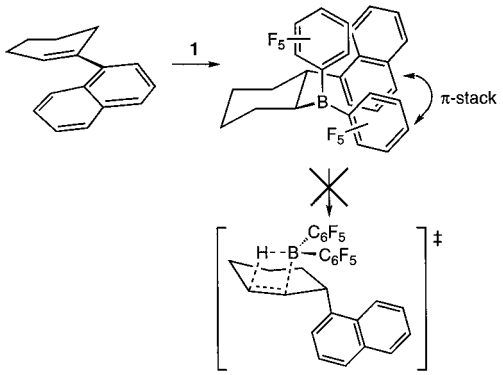


These observations suggest that **1** might find application in the hydroboration of substrates where functional group migration is desired. Selectivity in such reactions will depend on the number of possible isomers available and their relative stabilities. For example, hydroboration of (+)-α-pinene gave the kinetic product shown in entry 5 as a result of hydroboration of the less hindered *endo* face of the C=C bond. Although only one migration product can be formed in this system, the two isomers must be similar in energy since equilibration results in an essentially 1:1 mixture. A more positive illustration of how this feature can be used constructively is the hydroboration/oxidation of *β*-pinene discussed below.

Parallels can be drawn between retrohydroboration in these systems and the *β*-elimination reaction studied by Bercaw et al. for organoscandium compounds of general formula $Cp^*_2ScCH_2CH_2R$.[37] As in the transition metal systems, eliminated **1** could be rapidly and irreversibly trapped with an excess of 2-butyne and the rate of organoborane disappearance monitored over time. Under these conditions, k_{obs} can be taken as the rate of retrohydroboration.[37] Accordingly, disappearance of $PhCH_2CH_2B(C_6F_5)_2$ exhibited first-order behavior with an observed rate constant on the order of $1.9(1) \times 10^{-2}$ h^{-1}.[38] Furthermore, an isotope effect of 1.78(5) on retrohydroboration was obtainable using the experiment shown in Scheme 4. This compares favorably to the k_H/k_D value of 2.0(3) observed for *β*-elimination from $Cp_2^*ScCH_2CHDPh$. Together these results suggest a similar, but perhaps more constrained (*i.e.*, B···H−C deviating more severely from linearity than Sc···H−B), transition state for retrohydroboration than that proposed by Bercaw for *β*-elimination. This also agrees with the accepted picture for the transition state of the microscopic reverse, hydroboration.[27,39]

Turning back to Table 2, arylcycloalkenes are a generally difficult class of substrates to hydroborate with conventional reagents; even monoorganoboranes react sluggishly with phenylcyclohexene.[40] Our reagent, on the other hand, rapidly hydroborates these substrates, as illustrated by the naphthyl derivative shown in entry 6. One regioisomer is produced and, unlike the products of entry 3, bis(pentafluorophenyl)-*trans*-2-α-naphthylcyclohexylborane does not undergo boryl migration; it is indefinitely stable in solution. The resistance to boryl migration in this product may be attributable to favorable *π*-stacking interactions[30] between the α-naphthyl substituent and a C_6F_5- group, which must be disrupted in order to attain the transition state for the retrohydroboration leading to boryl migration (Scheme 5). The inability of methyl versus naphthyl to *π*-stack accounts for the predilection for migration in the products of entry 3.

Scheme 5



The remaining entries of Table 2 explore the functional group tolerance of the hydroboration reaction. Bromides do not interfere with the reaction unless bonded directly to the olefin, in which case debromination[41] occurs rapidly. The conjugated diene of entry 9 is selectively hydroborated as shown, despite the general reluctance of dienes to undergo hydroboration due to the resulting loss of resonance stabilization.[42] This again demonstrates the potential of **1** as the reagent of choice for otherwise unreactive substrates. The final entry of Table 2 shows that ester functions may be tolerated in certain instances; ethyl 4-pentenoate cleanly forms the product shown upon treatment with **1**. Spectral data for this product, most notably the ^{11}B (δ 6.8 ppm) and ^{19}F NMR spectra ($\Delta\delta_{m,p} = 5.7$ ppm), indicate that the ester carbonyl group is coordinated to the boron center.[30b] Similar substrates with aldehyde and ketone carbonyl functions do not react cleanly with **1** as these groups react competitively with **1**, forming alkyl borinates.

Alkynes may be hydroborated to vinyl boranes, which can subsequently be transformed into *cis*-alkenes, aldehydes, or ketones,[43] or employed as dienophiles for Diels−Alder reactions.[44] As the retrohydroboration chemistry discussed above implies, borane **1** irreversibly reacts with symmetrical internal alkynes (Table 3, entries 1, 2). In contrast to 9-BBN but similarly to dimesitylborane,[45] dihydroboration products were not

(37) Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

(38) Unfortunately, the disproportionation reaction mentioned above prevented us from completing a full kinetic study on this retrohydroboration process. For example, hydroborated *p*-nitrostyrene underwent slow elimination of **1**, such that disproportionation was competitive. Thus, judgments as to the relative polarity of the transition state were not possible using this method.

(39) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1960**, *82*, 4708. (b) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 2544. (c) Pasto, D. J.; Kang, S.-Z. *J. Am. Chem. Soc.* **1968**, *90*, 3797.

(40) (a) Mandal, A. K.; Jadhav, P. K.; Brown, H. C.; *J. Org. Chem.* **1980**, *45*, 3543. (b) Brown, H. C.; Jadhav, P. K.; Mandal, A. K. *J. Org. Chem.* **1982**, *47*, 5074. (c) Brown, H. C.; Vara Prasad, J. V. N.; Gupta, A. K.; Bakshi, R. K. *J. Org. Chem.* **1987**, *52*, 310. (d) Evans, D. A.; Muci, A. R.; Stürmer, R. *J. Org. Chem.* **1993**, *58*, 5307.

(41) (a) Binger, P.; Köster, R. *Tetrahedron Lett.* **1961**, *4*, 156. (b) Brown, H. C.; Knights, E. F. *J. Am. Chem. Soc.* **1968**, *90*, 4439. (c) Brown, H. C.; Knights, E. F. *Isr. J. Chem.* **1968**, *6*, 691.

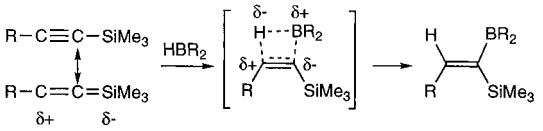
(42) Brown, H. C.; Liotta, R.; Kramer, G. W. *J. Org. Chem.* **1978**, *43*, 1058.

(43) (a) Brown, H. C.; Zweifel, G. *J. Am. Chem. Soc.* **1961**, *83*, 3834. (b) Brown, H. C.; Basavaiah, D.; Kulkarni, S. V. *J. Organomet. Chem.* **1982**, *225*, 63. (c) Zweifel, G.; Polston, N. L.; Whitney, C. C. *J. Am. Chem. Soc.* **1968**, *90*, 6243. (d) Brown, H. C.; Coleman, R. A. *J. Am. Chem. Soc.* **1969**, *91*, 4606. (e) Matteson, D. S.; Moody, R. J. *J. Org. Chem.* **1980**, *45*, 1091.

(44) Singleton, D. A.; Martinez, J. P.; Watson, J. V. *Tetrahedron Lett.* **1992**, *33*, 1017.

(45) Pelter, A.; Singaram, S.; Brown, H. C. *Tetrahedron Lett.* **1983**, *24*, 1433.

Scheme 6



detected; indeed, the vinylborane products were inert to further reaction with **1**. This is likely due to a combination of steric effects and deactivation of the π-bond caused by resonance with the electrophilic boron center.[46]

Reaction of **1** with unsymmetrical alkynes (entries 3, 4) was essentially nonspecific, giving mixtures of the two possible products despite the presence of an $SiMe_3$ group which tends to direct boron to the silicon substituted carbon by polarizing the C≡C bond as shown in Scheme 6.[47] Obviously, there is little kinetic selectivity in these reactions using **1**, perhaps due to the lower susceptibility of the B−H bond in **1** to be directed by weak electronic effects.[46] Since equilibrating retrohydroboration/rehydroboration pathways are not available to the vinylboranes, the kinetic ratio of products is the best that can be done with this reagent. Thus, the use of very sterically demanding reagents such as dimesitylborane remains the method of choice for effecting regioselective monohydroboration of unsymmetrical alkynes.[45]

Terminal alkynes are hydroborated cleanly with 1 equiv of **1** to produce the corresponding (*E*)-1,2-disubstituted vinylboranes (entries 5−8) almost exclusively.[48] Dihydroboration products are not detected until a second equivalent of **1** is added, resulting in the regiospecific formation of the terminal *gem*-diboryl species.[49] Qualitatively, the second hydroboration proceeds at a slower rate, the first addition being complete after ≈2 min, the second requiring approximately 30 min to complete, attesting to the deactivating effect of the electron withdrawing $B(C_6F_5)_2$ group. Dihydroboration of terminal alkynes with **1** provides an attractive route to a variety of *gem*-diboryl species,[50] which can be used to synthesize weakly coordinating counterions for Ziegler−Natta polymerization catalyst activators.[51]

Hydroboration/Oxidation Procedures Using 1. The utility of organoboranes in organic synthesis hinges on the variety of methods available for their conversion to other functional groups, the most common being oxidation to alcohols or carbonyl compounds. This can be accomplished with numerous oxidizing reagents, such as basic hydrogen peroxide,[2] amine-*N*-oxides,[52] and peracids,[2] each method offering certain advantages for particular substrates.

The organoboranes produced from **1** are somewhat sensitive to protic agents,[53] and standard oxidizing conditions using dilute alkaline peroxide lead to significant amounts of RH in addition to the desired alcohol or carbonyl products. Amine-*N*-oxides can be used under anhydrous conditions, but complete oxidation usually requires elevated temperatures, conditions where boryl migration is facile for some of the hydroborated olefins reported herein. In these instances, this method leads to mixtures of alcohols and is therefore applicable only to systems where retrohydroboration is not an issue. To suppress protonolysis, a procedure was developed where a concentrated, highly alkaline (pH ≈12) aqueous solution of potassium hydroxide (0.2 M) and H_2O_2 (4.4 M) was used to effect oxidation in a two-phase system. Using this procedure, a variety of alkene and alkyne substrates were hydroborated and oxidized, with minimal or no RH side products, giving alcohols or carbonyl compounds in good to excellent yields (Table 4).

Some of the examples included illustrate the extent to which boryl migration can be used to control selectivity. For example, hydroboration/oxidation of (−)-β-pinene (entry 2) gave only one diastereomer, which was determined to be (−)-*trans*-myrtanol.[54] This contrasts with the results of hydroboration/oxidation of β-pinene with BH_3, in which *cis*-myrtanol is exclusively formed *unless* the organoborane is thermolyzed prior to oxidation.[55] The opposite selectivities observed for **1** and BH_3 may be attributed to the ability of **1** to undergo rapid retrohydroboration and equilibrate to the thermodynamically more favored trans isomer obtained upon H−B addition to the face of the olefin directed to the methyl groups (Scheme 7). This conversion requires higher temperature for BH_3 reduction, since retrohydroboration does not occur as readily with this borane reagent.

Entries 3−5 in Table 4 involve olefins where boryl migration is reasonably facile. To a limited extent, the reaction may be controlled if oxidation is performed immediately after hydroboration, although yields tend to suffer in these cases. Most likely, leakage occurs through retrohydroboration and loss of $HB(C_6F_5)_2$ reagent through reaction with water; this is particularly significant for tetramethylethylene (entry 5), where yields of the desired alcohol are very low. If isomerization to the thermodynamic borane is allowed to occur prior to oxidation, however, the yield improves dramatically (entry 6), illustrating that borane **1** may be an effective reagent for functional group migration of tetrasubstituted double bonds in instances where one isomer is clearly favored.

For the naphthylcyclohexene substrate where retrohydroboration was negligible (vide supra) the oxidation

(46) Structural evidence that $B(C_6F_5)_2$ groups in conjugation with C=C can lower its bond order can be found in: Köhler, K.; Piers, W. E.; Xin, S.; Feng, Y.; Bravakis, A. M.; Jarvis, A. P.; Collins, S.; Clegg, W.; Yap, G. P. A.; Marder, T. B. *Organometallics* **1998**, *17*, 3557.

(47) (a) Uchida, K.; Utimoto, K.; Nozaki, H. *J. Org. Chem.* **1976**, *41*, 2941. (b) Uchida, K.; Utimoto, K.; Nozaki, H. *Tetrahedron* **1977**, *33*, 2987. (c) Hoshi, M.; Masuda, Y.; Arase, A. *J. Chem. Soc., Perkin Trans. 1* **1990**, 3237.

(48) Detectable (2−4%) amounts of the 1,1 regioisomers were produced. It appears that these isomers react much more sluggishly with further portions of **1** than the major 1,2 substituted vinyl boranes. Collins, S.; Jarvis, A. P. Personal communication.

(49) (a) Brown, H. C.; Scouten, C. G.; Liotta, R. *J. Am. Chem. Soc.* **1979**, *101*, 96. (b) Zweifel, G.; Arzoumanian, H. *J. Am. Chem. Soc.* **1967**, *89*, 291.

(50) The product of dihydroboration of phenylacetylene undergoes decomposition in solution to a number of unidentified products. Alkynes with aliphatic groups yield stable products.

(51) Jia, L.; Yang, X.; Stern, C.; Marks, T. J. *Organometallics* **1994**, *13*, 3755.

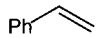
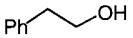
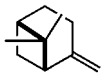
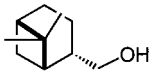
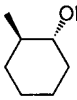
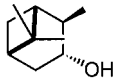
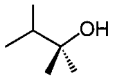
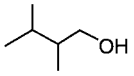
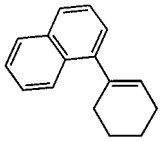
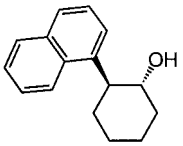
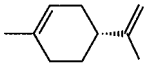
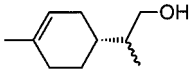
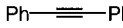
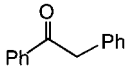
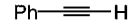
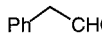
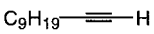
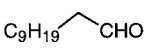
(52) (a) Soderquist, J. A.; Najafi, M. R. *J. Org. Chem.* **1986**, *51*, 1330. (b) Kabalka, G. W.; Hedgecock, H. C., Jr. *J. Chem. Educ.* **1975**, *52*, 745. (c) Kabalka, G. W.; Hedgecock, H. C. Jr. *J. Org. Chem.* **1975**, *40*, 1776. (d) Köster, R.; Morita, Y. *Liebigs Ann. Chem.* **1967**, *704*, 70. (e) Köster, R.; Morita, Y. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 580.

(53) For example, the compound $PhCH_2CH_2B(C_6F_5)_2$ was hydrolyzed over the course of 2−3 h when treated with water. Acidification of the sample resulted in much faster hydrolysis.

(54) Coxon, J. M.; Hydes, G. J.; Steel, P. J. *J. Chem. Soc., Perkin Trans. 2* **1984**, 1351.

(55) Braun, J. C.; Fisher, G. S. *Tetrahedron Lett.* **1960**, *21*, 9.

Table 4. One-Pot Hydroboration/Oxidation of Olefinic and Acetylenic Substrates Using $HB(C_6F_5)2$, 1

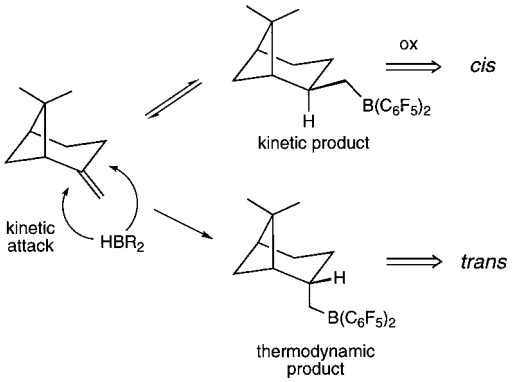
entry	substrate[a]	product[b]	yield[c]
1			93[d]
2			82
3			53
4			62
5			14
6			88
7			98
8			93[e]
9			97
10			49
11[f]			67

[a] General procedure 3 (see Experimental Section) was employed for these reactions except for E11. [b] Compounds were identified through comparison to literature NMR data. E1: Pouchert, C. J. *The Aldrich Library of NMR Spectra*, 2nd ed.; Aldrich Chemical Co., Inc.: Milwaukee, WI, 1983; Vol. 1, p 956. E3: *ibid.*; p 150. E4: *ibid.;* p 158. E8: *ibid.;* p 148. E9: *ibid.;* p 12. E2: Reference 52. E5: House, H. O.; Frank, G. A. *J. Org. Chem.* **1965**, *30*, 2948. E6: Khripach, V. A.; Zhabinskii, V. N.; Ol'khovik, V. K.; Lakhvich, F. A. *J. Org. Chem. USSR* **1990**, *26*, 1699. E7: Basavaiah, D.; Rao, P. D. *Tetrahedron: Asymm.* **1994**, *5*, 223. E10: Chikashita, H.; Morita, Y.; Itoh, K. *Synth. Commun.* **1987**, *17*, 677. E11: Inokuchi, T.; Matsumoto, S. Torii, S. *J. Org. Chem.* **1991**, *56*, 2416. [c] Percent isolated yield. [d] 96:4 mixture of 1- and 2-isomers. [e] 1:1 mixture of diastereomers. [f] Nonaqueous oxidation with $ONMe_3$ was employed for this substrate.

product was isolated in very high yield (entry 7). The hydroboration/oxidation of (+)-limonene (entry 8) illustrates that reaction at the less substituted double bond is preferred despite the high reactivity of $HB(C_6F_5)_2$.

Hydroboration/oxidation of alkynes (entries 9−10) is also possible with **1**, but even with highly alkaline peroxide, protonolysis becomes an important side reaction for terminal alkyne substrates. The low yield of aldehyde in entry 10 can be attributed to this effect. Nonaqueous oxidation using anhydrous trimethylamine oxide offers an improvement as illustrated in entry 11. No 1-undecene was detected in this experiment, suggesting that protonolysis is effectively suppressed using this oxidation procedure.

Scheme 7



Conclusions

To be of use to a wide variety of synthetic chemists, a new hydroboration reagent should have one or more of the following characteristics: (1) it should be cheap, readily available, and easily handled; (2) it must be demonstratably superior to other boranes for routine applications, and (3) it must be effective in hydroborations where standard reagents fail or perform poorly. In this paper, we have attempted to show that bis(pentafluorophenyl)borane scores highly in all three categories.

Boranes which are not available directly from BH_3 have second tier status as hydroboration reagents and are generally relegated to specialty applications; a case in point is dimesitylborane. Our originally published route to **1**, while reliable, is tedious enough to represent a significant roadblock to the average synthetic chemist. The new synthesis of **1** in one step from two commercially available reagents improves the compound's availability, and although $B(C_6F_5)_3$ is a relatively expensive reagent, its price has come down significantly over the past couple of years. The properties of **1** are such that, once prepared, any laboratory capable of storing and handling moderately air- and moisture-sensitive reagents should be able to handle **1** with little difficulty.

There is little doubt that **1** is as good or better a hydroboration reagent than those currently available. Selectivities are competitive with, for example, 9-BBN, and the reagent shows reasonable functional group tolerance. Its primary advantage is its activity; hydroborations with **1** are extremely rapid in comparison with other boranes. There are two primary reasons for this: a more rapid and thermodynamically favorable dissociation of borane dimer to reactive monomer and the high electrophilicity of the boron center. Even sterically hindered olefins, which are not touched by more common reagents, are rapidly hydroborated by **1**.

Finally, we have shown that the facility of boryl migration in the products of hydroboration with **1** makes this reagent attractive for transformations of certain specialty substrates. For example, the rapid interconversion of kinetic and thermodynamic hydroboration products of cyclic hydrocarbons with *exo*-methylene functions allows for excellent selectivity for the thermodynamic isomers. Further, hydroboration and controlled boryl migration for tri- and tetrasubstituted olefinic substrates is a potentially exploitable means for functionalizing these normally difficult double bonds.

Experimental Section

General. General procedures have been described in detail elsewhere.[30b] Olefin and alkyne substrates were purchased from the Aldrich-Sigma Chemical Co. and purified by passage through a column of activated, basic alumina (Brockmann I, 150 mesh) or via standard methods.[56] Compounds **1** and **1**$-d_1$ were prepared according to our original report[9] or via the new method described below. $B(C_6F_5)_3$ was purchased from Boulder Scientific Co. and dried by treatment with Me_3SiCl prior to resublimation.

Synthesis of $Me_2Sn(C_6F_5)_2$. The known compound $Me_2Sn(C_6F_5)_2$ [57] was prepared by a different route to that reported in the literature. This procedure involves the generation and use of C_6F_5Li at low temperature. *CAUTION!! Under no circumstances should this reagent be isolated or warmed above −30* °C in solution! Bromopentafluorobenzene (5.0 mL, 40.1 mmol) was added via syringe to a 100 mL two-necked round-bottom flask equipped with a large egg shaped stir bar. The flask was evacuated, and Et_2O (15−20 mL) was condensed into the vessel at −78 °C. The apparatus was back-filled with argon, and the solution was stirred to dissolve the solidified C_6F_5Br. Butyllithium (25 mL of a 1.6 M hexanes solution, 40.1 mmol) was added dropwise via syringe under an argon purge over 10 min. The reaction was stirred at −78 °C for 45 min, and Me_2SnCl_2 (4.4 g, 20.05 mmol) was added to the solution either as a concentrated ether solution or as a solid. The reaction was stirred for 15 min at −78 °C, then allowed to warm to ambient temperature, and stirred for an additional 12 h.

A small volume of untreated, reagent grade (i.e., wet) hexanes (5 mL) was added to the white suspension to quench any unreacted C_6F_5Li. The solvent was removed under reduced pressure, and the solid was extracted with hexanes (3 × 30 mL). The solvent was removed from the collected extracts; distillation of the residue under reduced pressure gave a clear, colorless liquid that crystallized on standing (9.19 g, 19.0 mmol) in 95% yield. ^{1}H NMR: δ 0.88 (s, 6H, ^{117}Sn (7.7%) and ^{119}Sn (8.4%) satellites, J = 31.9 Hz and J = 32.4 Hz). ^{19}F NMR: δ −122.2 (dd, J = 8.7 Hz and J = 25.0 Hz, F_o), −150.4 (tt, J = 2.3 Hz and J = 20.0 Hz, F_p), −159.5 (m, F_m).

Synthesis of $ClB(C_6F_5)_2$. $ClB(C_6F_5)_2$ was prepared by a modified procedure from the literature preparation.[13] The procedure may be doubled in scale-keeping reaction concentrations constant. $Me_2Sn(C_6F_5)_2$ (9.19 g, 19.0 mmol) was placed in a 100 mL thick-walled glass bomb and evacuated. Hexanes (∼50 mL) was condensed into the vessel, and the bomb was tared on a balance. Weighing by difference, BCl_3 (2.23 g, 19.0 mmol) was condensed into the vessel. Once the appropriate amount of BCl_3 was condensed into the bomb, the vessel was back-filled with argon and closed. After the contents were stirred at room temperature for 1 h, the bomb was placed in a thermostated oil bath set to 120.0 °C and heated for 48 h.

The bomb was removed from the oil bath and allowed to cool to ambient temperature during which time crystals of Me_2SnCl_2 formed. After allowing crystallization to occur for several hours, the supernatant liquid was removed from the crystals via cannula into a vessel flushed with argon. The crystals in the glass bomb were washed once with hexanes (10 mL), and then the wash was transferred to the vessel via cannula. The solvent was removed under reduced pressure, leaving a residue that was transferred to a sublimation apparatus.

Residual Me_2SnCl_2 was removed by sublimation under an atmosphere of argon at an oil bath temperature of 35 °C. The crystals of Me_2SnCl_2 were removed from the coldfinger, and the procedure was repeated until no more Me_2SnCl_2 was obtained. Sublimation of the remaining white powder under full vacuum at an oil bath temperature of 60 °C produced $ClB(C_6F_5)_2$ as a colorless, crystalline solid (4.90 g, 12.9 mmol) in 68% yield. ^{19}F NMR: δ −129.6 (dtt, J = 4.9 Hz, J = 6.6 Hz, and J = 20.9 Hz, F_o), −143.9 (tt, J = 6.6 Hz and J = 21.2 Hz, F_p), −160.4 (m, F_m). ^{11}B NMR: δ 59.1 (360). The ^{19}F NMR spectrum was in good agreement with the literature.

Synthesis of $HB(C_6F_5)_2$, 1. Tris-(pentafluorophenyl)borane (1.0 g, 1.95 mmol) and triethylsilane (0.23 g, 1.98 mmol) were dissolved in benzene (20 mL) and placed in a reactor bomb. The reaction was heated at 60 °C for 3 days. The solution was transferred hot via cannula to a swivel frit apparatus, including a 1 × 10 mL rinse of the reactor bomb. The solution was concentrated to ≈15 mL and allowed to cool, causing precipitation of **1**. The solid was isolated by filtration and washed once with benzene to remove residual $Et_3SiC_6F_5$;[15] yield, 0.47 g, 69%. The material was spectroscopically identical to samples prepared from $ClB(C_6F_5)_2$.[9]

General Procedure 1 for the Hydroboration of Alkenes and Alkynes. A suspension of $HB(C_6F_5)_2$ (ca. 0.15 mmol) in C_6D_6 (0.5 mL) was prepared in a NMR tube. The substrate (1 equiv) was then added to the suspension. The tube was capped with a rubber septum, and the suspension was vigorously shaken until all of the solid had dissolved (approximately 2 min). The sample was assayed by ^{1}H NMR spectroscopy.

General Procedure 2 for the Dihydroboration of Terminal Alkynes. A suspension of $HB(C_6F_5)_2$ (ca. 0.2 mmol) in C_6D_6 (0.5 mL) was prepared in a NMR tube. The substrate (0.5 equiv) was then added to the suspension. The NMR tube was capped with a rubber septum, and the suspension was vigorously shaken until all of the solid had dissolved (approximately 15−20 min). The sample was assayed by ^{1}H NMR spectroscopy.

General Procedure 3 for the Hydroboration/Oxidation of Alkenes and Internal Alkynes. A solution of 30% H_2O_2 (10 mL), deionized H_2O (10 mL), and KOH (0.25 g) was freshly prepared giving a 4.4 N H_2O_2 solution containing 5% KOH.

A suspension of **1** (0.3 mmol) in benzene (1.0 mL) was prepared in a 1 dram vial. The substrate (0.3 mmol) was added to the rapidly stirred suspension, and then the vial was capped with a rubber septum. After the solids had completely dissolved, THF (1 mL) and 0.3 mL of the freshly prepared H_2O_2 solution (1.5 mmol of H_2O_2 and 0.07 mmol KOH) were added to the solution via syringe in sequence. The resulting emulsion was stirred for 1 h.

The mixture was poured into 15 mL of 0.25 M KOH solution diluted with 15 mL of saturated NaCl solution. The aqueous layer was extracted with Et_2O (4 × 15 mL). The combined organic extracts were dried over anhydrous $MgSO_4$. After filtration, the solvent was removed in vacuo, leaving behind the crude product. Purification was effected by column chromatography and/or distillation.

General Procedure 4 for the Hydroboration/Oxidation of Terminal Alkynes. $HB(C_6F_5)_2$ (0.3 mmol) was suspended in benzene (5 mL) in a 10 mL round-bottom flask. Under a flow of argon, the substrate (0.3 mmol) was added to the stirred suspension via syringe. After all of the borane had dissolved, solid trimethylamine oxide (0.9 mmol) was added to the stirred solution under an argon purge. The reaction was stirred for 1 h, and then the solution was heated to reflux for 5 min. The reaction was stirred at room temperature for an additional hour, and then THF/H_2O (5 mL of a 7:3 mixture by volume) was added. After 15 min, the mixture was poured into saturated NaCl solution (10 mL) and the organic layer was separated. The aqueous phase was extracted with Et_2O (2 × 10 mL), and then the combined organic extracts were washed with 0.1 M NaOH (3 × 10 mL) and saturated NaCl solution (10 mL). The organic layer was dried over anhydrous $MgSO_4$ and filtered, and the solvent was removed under reduced pressure. The crude product was purified by Kugelrohr distillation.

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Synthesis of $HB(C_6F_5)_2$·THF, 2. $HB(C_6F_5)_2$ (0.200 g, 0.578 mmol) was placed in a 10 mL round-bottom flask and dissolved in THF (5 mL). The solution was stirred for 5 min, and the solvent was removed under reduced pressure, leaving a white, foamy residue which became powdery upon suspension in hexanes (5 mL). The reaction flask was sonicated to free the solid from the walls of the flask, and the precipitate was isolated by filtration and washed with clean hexanes (2 × 1 mL). Isolation of the solid from the frit afforded **2** (0.225 g, 0.538 mmol) as a white powder in 93% yield. IR (KBr pellet; cm^{-1}): 2996 (m, CH), 2446 (s, BH), 1646 (s, C=C), 1517, 1471, 1291, 1137, 976. ^{1}H NMR: δ 4.2 (br s, B*H*), 3.26 (m, 4H, OCH_2), 1.01 (m, 4H, CH_2). ^{13}C NMR: δ 148.3, 141.6, 136.6, and 116.1 (C_6F_5); 76.1 (OCH_2), 24.5 (CH_2). ^{19}F NMR: δ −134.0 (d, J = 20.2 Hz, F_o), −157.1 (t, J = 20.4 Hz, F_p), −163.8 (m, F_m). ^{11}B NMR: δ −1.6 (200). Anal. Calcd for $C_{22}H_9BF_{15}O$: C, 45.97; H, 2.17. Found: C, 46.09; H, 2.02.

Separate Synthesis of ^{n}BuOB$(C_6F_5)_2$, 3. A suspension of $HB(C_6F_5)_2$ (50 mg, 0.145 mmol) in C_6D_6 (0.5 mL) was prepared in an NMR tube. 1-Butanol (13 μL, 0.145 mmol) was added to the suspension, resulting in vigorous evolution of hydrogen gas, giving borinate **3**. ^{1}H NMR: δ 3.77 (t, J = 5.9 Hz, 2H, OCH_2), 1.41 (m, 2H, OCH_2CH_2), 1.32 (m, 2H, CH_2CH_3), 0.79 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR: δ 150.1, 145.8, 140.2, and 135.0 (C_6F_5), 70.4 (OCH_2), 33.2 (OCH_2CH_2), 18.9 (CH_2CH_3), 13.6 (CH_3). ^{19}F NMR: δ −132.7 (dd, J = 9.1 Hz and J = 23.4 Hz, F_o), −149.2 (t, J = 20.2 Hz, F_p), −161.1 (m, F_m). ^{11}B NMR: δ 39.5 (360).

Retrohydroboration Kinetics. A suspension of $HB(C_6F_5)_2$ (53 mg, 0.153 mmol) in C_6D_6 (0.5 mL) was prepared in an NMR tube, and then styrene (16.6 μL, 0.145 mmol) was added. The solution was vigorously shaken until the solid dissolved ([borane] = 0.29(1) M); 3-hexyne (165 μL, 1.45 mmol) was added, and the tube was flame sealed. The tube was placed in a thermostated water bath with a set temperature of 25.0(1) ,°C. The rate of disappearance of $C_6H_5CH_2CH_2B(C_6F_5)_2$ was monitored over several half-lives by ^{1}H NMR spectroscopy. A first-order plot of $\ln[C_6H_5CH_2CH_2B(C_6F_5)_2]$ vs time was linear with a slope of $-1.89(7) \times 10^2$ (R^2 = 0.985).

Determination of the Deuterium Kinetic Isotope Effect of Retrohydroboration. The deuterated borane C_6H_5-CH(D)$CH_2B(C_6F_5)_2$ was prepared from $DB(C_6F_5)_2$ and styrene in toluene and isolated as a white powder by recrystallizing from hexanes. A sample of pure $C_6H_5CH(D)CH_2B(C_6F_5)_2$ was loaded into a sealable NMR tube, dissolved in C_6D_6, and attached to a vacuum line. The sample was degassed, and an excess of 2-butyne (ca. 8 equiv) was condensed into the tube at −78 °C. The tube was flame sealed, and the solution was warmed to room temperature. The isotope effect, k_H/k_D, was calculated from the ratio of styrene to styrene-d_1 obtained by integration of the proton resonance due to the vinyl proton cis to the phenyl group, which gave a k_H/k_D = 1.7(1). The "cut-and-weigh" method gave a k_H/k_D of 1.78(5).

$CH_3CH_2B(C_6F_5)_2$. Borane **1** (0.687 g, 1.99 mmol) was suspended in benzene in a 25 mL round-bottom flask and attached to a vacuum line. The vessel was evacuated, and purified ethylene was admitted to 1 atm. The reaction was stirred for 1 h at room temperature during which time the precipitate dissolved. The solvent was removed, leaving a yellow oil that crystallized on standing. Sublimation under a full, static vacuum at 35−40 °C gave $CH_3CH_2B(C_6F_5)_2$ as a colorless, crystalline solid or oil. ^{1}H NMR: δ 1.77 (q, J = 7.5 Hz, 2H, CH_2), 0.93 (t, 3H, CH_3). ^{13}C NMR: δ 147.6, 143.9, 138.0, and 114.3 (C_6F_5), 24.6 (CH_2), 8.5 (CH_3). ^{19}F NMR: δ −130.7 (dd, J = 6.1 Hz and J = 19.1 Hz, F_o), −147.7 (dt, J = 3.6 Hz and J = 20.5 Hz, F_p), −161.2 (m, F_m). ^{11}B NMR: δ 74.9 (350).

$PhCH_2CH_2B(C_6F_5)_2$. General procedure 1 was used to prepare this compound from styrene (16.7 μL, 0.146 mmol) and **1** (50.5 mg, 0.146 mmol). ^{1}H NMR: δ 7.20 (t, J = 7.3 Hz, 2H, CH_m), 7.11 (m, J = 7.3 Hz, 1H, CH_p), 7.08 (d, J = 7.3 Hz, 2H, CH_o), 2.77 (t, J = 8.0 Hz, 2H, CH_2B), 2.29 (t, 2H, CH_2). ^{13}C NMR: δ 147.1, 143.6, 137.5, and 114.2 (C_6F_5), 142.7 (C_{ipso}), 128.9, 128.0, and 126.5 (C_6H_5), 33.3 (BCH_2), 31.0 (CH_2). ^{19}F NMR: δ −132.1 (d, J = 21.1 Hz, F_o), −148.9 (t, J = 22.8 Hz, F_p), −162.8 (m, F_m). ^{11}B NMR: δ 73.3 (770).

Bis(pentafluorophenyl)(*trans*-2-methyl-1-cyclopentyl)-borane. General procedure 1 was used to prepare this compound from 1-methylcyclopentene (16.4 μL, 0.156 mmol) and **1** (53.9 mg, 0.156 mmol). ^{1}H NMR: δ 2.26 (ddd, J = 9.4 Hz, J = 9.5 Hz, and J = 9.8 Hz, 1H, BC*H*), 1.92, 1.80−1.40 (m, 5H, ring protons), 1.10 (dq, J = 11.9 and 8.5 Hz, 1H, C*H*), 0.91 (d, J = 8.5 Hz, 3H, CH_3). ^{13}C NMR: δ 146.4, 142.0, 137.6, and 114.0 (C_6F_5), 49.0 (B*C*H), 39.0 (*C*H), 37.2, 27.9, and 26.9 (CH_2), 21.1 (CH_3). ^{19}F NMR: δ −132.2 (d, J = 15.4 Hz, F_o), −150.4 (t, J = 21.4 Hz, F_p), −162.9 (m, F_m). ^{11}B NMR: δ 73.6 (630).

Bis(pentafluorophenyl)(*trans*-2-methyl-1-cyclohexyl)-borane. General procedure 1 was used to prepare this compound from 1-methylcyclohexene (17.4 μL, 0.147 mmol) and borane **1** (51.1 mg, 0.147 mmol). ^{1}H NMR: δ 2.01 (m, J = 11.5 Hz, 1H, BC*H*), 1.47−1.72, 1.05−1.35, 0.80−0.92 (m, 9H, ring protons), 0.78 (d, J = 6.4 Hz, 3H, CH_3). ^{13}C NMR: δ 146.0, 142.9, 137.7, and 114.8 (C_6F_5), 47.9 (B*C*H), 36.2 (*C*H), 34.1, 27.0, 26.3, and 25.1 (CH_2), 24.2 (CH_3). ^{19}F NMR: δ −132.2 (d, J = 18.4 Hz, F_o), −150.4 (t, J = 23.0 Hz, F_p), −162.7 (m, F_m). ^{11}B NMR: δ 76.3 (770).

Bis(pentafluorophenyl)(1,1,2-trimethylpropyl)borane. General procedure 1 was used to prepare this compound from 2,3-dimethyl-2-butene (16.7 μL, 0.140 mmol) and **1** (48.5 mg, 0.140 mmol). ^{1}H NMR: δ 1.86 (sp, J = 6.7 Hz, 1H, C*H*), 0.89 (s, 6H, CH_3), 0.77 (d, 6H, CH_3). ^{13}C NMR: δ 144.3, 141.4, 137.6, and 114.1 (C_6F_5), 40.4 (BC_{quat}), 34.4 (*C*H), 19.1 and 17.5 (CH_3). ^{19}F NMR: δ −131.8 (d, J = 21.4 Hz, F_o), −152.8 (t, J = 21.3 Hz, F_p), −162.7 (m, F_m). ^{11}B NMR: δ 73.6 (670).

Bis(pentafluorophenyl)(2,3-dimethylbutyl)borane. A solution of bis-(pentafluorophenyl)-1-(1,1,2-trimethylpropyl)-borane was allowed to sit at room temperature for 24 h, producing this isomeric borane. ^{1}H NMR: δ 1.83 (br m, 2H, BCH_2), 1.74, 1.38 (m, 1H, 1H, C*H*), 0.88 (d, J = 6.8 Hz, 3H, CH_3), 0.81, 0.80 (d, J = 6.4, 6.8 Hz, 6H, CH_3). ^{13}C NMR: δ 147.6, 142.7, 137.7, and 114.5 (C_6F_5), 39.7 and 34.9 (*C*H), 38.4 (BCH_2), 21.0, 19.7, and 19.5 (CH_3). ^{19}F NMR: δ −130.8 (d, J = 25.9 Hz, F_o), −147.5 (t, J = 20.9 Hz, F_p), −161.0 (m, F_m). ^{11}B NMR: δ 73.2 (800).

Bis(pentafluorophenyl)-3-pinanylborane. General procedure 1 was used to prepare this compound from α-pinene (13.3 μL, 0.084 mmol) and **1** (29.0 mg, 0.084 mmol). ^{1}H NMR: δ 2.72 (m, J = 9.0 and 10.6 Hz, 1H, BC*H*), 2.23, 2.15 (m, 1H, C*H*), 1.60−2.00 (m, 4H, CH_2), 1.14, 1.08 (s, 3H, CH_3), 0.94 (d, J = 7.0 Hz, 3H, CH_3), 0.66 (d, J = 9.9 Hz, 1H). ^{13}C NMR: δ 145.9, 142.7, 137.7, and 113.8 (C_6F_5), 47.8 ($C(CH_3)_2$), 41.1 and 39.2 (*C*H), 38.4 (B*C*H), 38.2 (*C*HCH_3), 33.6 and 28.4 (CH_2), 25.9, 23.4, and 22.6 (CH_3). ^{19}F NMR: δ −132.7 (d, J = 18.3 Hz, F_o), −150.7 (t, J = 20.1 Hz, F_p), −162.5 (m, F_m). ^{11}B NMR: δ 71.9 (1000).

Bis(pentafluorophenyl)(*trans*-2-naphthyl-1-cyclohexyl)-borane. General procedure 1 was used to prepare this compound from 1-naphthyl-1-cyclohexene (17.0 mg, 0.082 mmol) and **1** (28.0 mg, 0.082 mmol) and **1** (28.0 mg, 0.082 mmol). ^{1}H NMR: δ 7.80 (br d, J = 9.0 Hz, 1H, aromatic C*H*), 7.47, 7.35, 7.10−7.30 (m, 6H, aromatic C*H*), 3.53 (br m, J = 10.5 Hz, 1H, BC*H*), 2.93 (dt, J = 2.2 Hz and J = 11.6 Hz, 1H, C*H*), 1.20−2.00 (m, 8H, CH_2). ^{13}C NMR: δ 146.6, 141.5, 137.3, and 114.7 (C_6F_5), 145.1, 133.9, and 131.3 (C_{quat}), 128.9, 126.8, 126.0, 125.9, 125.8, 122.0, and 123.4 (aromatic *C*H), 46.6 (B*C*H), 40.3 (*C*H), 36.6, 28.4, 28.1, and 27.3 (CH_2). ^{19}F NMR: δ −130.7 (dd, J = 7.6 Hz and J = 23.6 Hz, F_o), −149.6 (tt, J = 3.6 Hz and J = 20.4 Hz, F_p), −161.4 (m, F_m). ^{11}B NMR: δ 77.0 (1200).

Bis(pentafluorophenyl)(4-bromo-1-butyl)borane. General procedure 1 was used to prepare this compound from

4-bromo-1-butene (7.3 μL, 0.072 mmol) and borane **1** (25.0 mg, 0.072 mmol). ^{1}H NMR: δ 2.90 (t, J = 6.3 Hz, 2H, CH_2Br), 1.68 (br t, J = 7.6 Hz, 2H, BCH_2), 1.45−1.60 (m, 4H, CH_2CH_2). ^{13}C NMR: δ 147.1, 143.7, 137.7, and 114.0 (C_6F_5), 35.3 (CH_2Br), 32.6 (CH_2), 30.9 (BCH_2), 23.4 (CH_2). ^{19}F NMR: δ −130.5 (d, J = 20.0 Hz, F_o), −146.9 (t, J = 20.7 Hz, F_p), −160.8 (m, F_m). ^{11}B NMR: δ 72.7 (360).

Bis(pentafluorophenyl)-3-(1,1,4,4-tetraphenylbut-1-enyl)borane. General procedure 1 was used to prepare this compound from 1,1,4,4-tetraphenyl-1,3-butadiene (62.2 mg, 0.173 mmol) and **1** (60.0 mg, 0.173 mmol). ^{1}H NMR: δ 7.37 (d, J = 6.5 Hz, 2H, aromatic CH), 6.87−7.28 (m, 16H, aromatic CH), 6.41 (d, J = 7.2 Hz, 2H, aromatic CH), 6.28 (d, J = 10.5 Hz, 1H, vinyl CH), 4.99 (dd, J = 10.5, 11.2 Hz, 1H, BCH), 4.36 (d, 1H, CH). ^{13}C NMR: δ 145.5, 141.7, 137.0, and 113.4 (C_6F_5), 154.4 (alkenyl C_{quat}), 143.6, 143.5, 142.2, and 138.7 (C_{ipso}), 130.1 (alkenyl CH), 127.9, 127.9, 127.8, 127.6, 127.4, 127.2, 127.1, 127.0, 126.8, and 125.8, 125.8 (aromatic CH, others obscured by solvent), 54.3 (CH), 48.3 (BCH). ^{19}F NMR: δ −129.5 (d, J = 17.9 Hz, F_o), −150.0 (t, J = 20.6 Hz, F_p), −161.7 (m, F_m). ^{11}B NMR: δ 13.5 (400).

Ethyl 5-(Bis(pentafluorophenyl)boryl)pentanoate. General procedure 1 was used to prepare this compound from ethyl 4-pentenoate (17.0 mg, 0.082 mmol) and **1** (28.0 mg, 0.082 mmol). ^{1}H NMR: δ 3.83 (q, J = 7.2 Hz, 2H, OCH_2), 1.86 (m, 2H, CH_2CO), 1.57 (m, 2H, CH_2), 1.40 (br m, 2H, BCH_2), 1.07 (m, 2H, CH_2), 0.70 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR: δ 187.0 (CO), 149.2, 146.9, 137.8, and 119.7 (C_6F_5), 67.9 (CH_2, OCH_2), 34.1 (CH_2CO), 26.4 and 24.0 (CH_2), 21.2 (BCH_2), 13.0 (CH_3). ^{19}F NMR: δ −134.5 (d, J = 23.1 Hz, F_o), −158.1 (t, J = 20.6 Hz, F_p), −163.8 (m, F_m). ^{11}B NMR: δ 6.8 (360).

Bis(pentafluorophenyl)((*Z*)-1-methyl-1-propenyl)borane. Borane **1** (54.6 mg, 0.158 mmol) was loaded into a sealable NMR tube, suspended in C_6D_6 (0.6 mL), and attached to a vacuum line. The sample was degassed, and 2-butyne (86 Torr/34.2 mL, 0.087 mmol) was condensed into the tube, which was then flame-sealed and warmed to room temperature. The solution was shaken vigorously during which time the solid dissolved, giving *Z*-$CH_3CH{=}C(CH_3)B(C_6F_5)_2$ as the only product. ^{1}H NMR: δ 6.59 (q, J = 6.8 Hz, 1H, CH), 1.64 (s, 3H, C(B)CH_3), 1.48 (d, 3H, C(H)CH_3). ^{13}C NMR: δ 161.8 (CH), 145.9, (CB), 146.2, 142.7, 137.5, and 114.3 (C_6F_5), 16.6 and 15.1 (CH_3). ^{19}F NMR: δ −133.0 (dd, J = 12.2 and 24.4 Hz, F_o), −151.6 (t, J = 18.3 Hz, F_p), −163.1 (m, F_m). ^{11}B NMR: δ 62.0 (640).

Bis(pentafluorophenyl)((*Z*)-1,2-diphenylethenyl)borane. General procedure 1 was used to prepare this compound from diphenylacetylene (20.1 mg, 0.113 mmol) and **1** (39.0 mg, 0.113 mmol). ^{1}H NMR: δ 7.62 (s, 1H, vinyl CH), 7.09 (d, J = 7.3 Hz, 2H, H_o), 7.02 (d, J = 7.0 Hz, 2H, H_o), 6.98 (t, J = 7.3 Hz, 2H, H), 6.91 (t, J = 7.0 Hz, 1H, H_p), 6.86 (t, J = 7.3 Hz, 1H, H_p), 6.80 (t, J = 7.0 Hz, 2H, H_m). ^{13}C NMR: δ 146.3, 142.9, 137.7, and 114.7 (C_6F_5), 157.8 (CH), 150.6 (BC), 141.2 and 135.5 (C_{ipso}), 132.1, 131.2, 129.2, 128.7, 128.6, and 127.6 (aromatic CH). ^{19}F NMR: δ −132.3 (dd, J = 6.1 Hz and J = 24.4 Hz, F_o), −150.7 (t, J = 19.8 Hz, F_p), −162.9 (m, F_m). ^{11}B NMR: δ 65.1 (770).

Bis(pentafluorophenyl)(*trans*-3,3-dimethyl-1-butenyl)-borane. General procedure 1 was used to prepare this compound from 3,3-dimethyl-1-butyne (5.3 μL, 0.043 mmol) and **1** (15.0 mg, 0.043 mmol). ^{1}H NMR: 6.95, 6.81 (AB_q, J = 17.6 Hz, 2H, vinyl CH), 0.93 (s, 9H, CH_3). ^{13}C NMR: δ 180.4 (=CH), 147.7, 143.3, 137.6, and 114.0 (C_6F_5), 130.1 (BCH), 36.5 (CCH$_3$), 28.1 (CCH$_3$). ^{19}F NMR: δ −130.0 (dd, J = 7.6 Hz and J = 25.7 Hz, F_o), −148.4 (tt, J = 4.1 Hz and J = 20.6 Hz, F_p), −161.4 (m, F_m). ^{11}B NMR: δ 58.6 (960).

Bis(pentafluorophenyl)(*trans*-1-hexenyl)borane. General procedure 1 was used to prepare this compound from 1-hexyne (9.0 μL, 0.078 mmol) and **1** (27.1 mg, 0.078 mmol). ^{1}H NMR: δ 6.83 (br m, 2H, vinyl CH), 2.07 (m, 2H, =CHCH_2), 1.24 (m, 2H, CH_2), 1.17 (m, 2H, CH_2), 0.79 (t, J = 7.2 Hz, 3H, CH_3). ^{13}C NMR: δ 147.7, 143.2, 137.7, and 114.1 (C_6F_5), 172.4 (=CH), 136.0 (BCH), 36.8 (=CHCH$_2$), 29.9 and 22.5 (CH_2), 13.8 (CH_3). ^{19}F NMR: δ −130.1 (dd, J = 7.8 Hz and J = 25.5 Hz, F_o), −148.7 (tt, J = 3.6 Hz and J = 20.6 Hz, F_p), −161.5 (m, F_m). ^{11}B NMR: δ 58.1 (900).

Bis(pentafluorophenyl)(*trans*-2-phenylethenyl)borane. General procedure 1 was used to prepare this compound from phenylacetylene (15.7 μL, 0.143 mmol) and **1** (49.4 mg, 0.143 mmol). ^{1}H NMR: d 7.51 (br m, 2H, vinyl CH); 7.34, 7.03 (m, 5H, C_6H_5). ^{13}C NMR: δ 163.4 (=CH), 147.7, 143.2, 137.7, and 114.0 (C_6F_5), 136.2 (C_{ipso}), 132.2, 129.6, and 129.3 (C_6H_5), 131.9 (BCH). ^{19}F NMR: δ −131.5 (dd, J = 18.1 Hz and J = 6.4, F_o), −150.2 (t, J = 21.3 Hz, F_p), −163.1 (m, F_m). ^{11}B NMR: δ 58.3 (770).

1,1-Bis(bis(pentafluorophenyl)boryl)-3,3-dimethylbutane.[51] General procedure 2 was used to prepare this known compound from 3,3-dimethyl-1-butyne (5.3 μL, 0.043 mmol) and **1** (30.0 mg, 0.086 mmol). ^{1}H and ^{19}F NMR data were essentially identical to that reported in the literature. ^{13}C NMR: δ 145.96, 143.3, 137.7, and 113.8 (C_6F_5), 57.8 (CB_2), 47.0 (CH_2), 31.3 (CCH$_3$), 29.1 (CCH$_3$). ^{11}B NMR: δ 70.0 (1500).

1,1-Bis(bis(pentafluorophenyl)boryl)hexane. General procedure 2 was used to prepare this compound from 1-hexyne (9.0 μL, 0.078 mmol) and **1** (54.2 mg, 0.156 mmol). ^{1}H NMR: δ 3.55 (t, J = 5.5 Hz, 1H, CHB$_2$), 2.06 (dt, J = 5.5 Hz and J = 7.4 Hz, 2H, CHCH_2), 1.32, 1.13, 1.09 (m, 6H, CH_2), 0.77 (t, J = 7.1 Hz, 3H, CH_3). ^{13}C NMR: δ 148.5, 146.0, 138.8, and 111.9 (C_6F_5), 60.1 (CB$_2$), 33.2 (CHCH$_2$), 32.5, 31.1, and 22.6 (CH_2), 13.8 (CH_3). ^{19}F NMR: δ −130.7 (d, J = 17.1 Hz, F_o), −146.6 (t, J = 20.5 Hz, F_p), −160.1 (m, F_m). ^{11}B NMR: δ 82.8 (400).

1,1-Bis(bis(pentafluorophenyl)boryl)-2-phenylethane. General procedure 2 was used to prepare this compound from phenylacetylene (6.9 μL, 0.063 mmol) and **1** (43.6 mg, 0.126 mmol) in CD_2Cl_2 (0.6 mL). ^{1}H NMR (CD_2Cl_2):δ 7.08−7.18 (m, 3H, aromatic CH), 6.86−6.91 (m, 2H, aromatic CH), 4.18 (t, J = 6.7 Hz, 1H, CHB$_2$), 3.38 (d, 2H, CH_2). ^{13}C NMR (C_6D_6): δ 146.2, 143.4, 137.6, and 113.6 (C_6F_5), 141.2 (C_{ipso}), 131.9, 129.3, and 127.5 (C_6H_5), 59.1 (CB), 35.0 (CH_2). ^{19}F NMR (CD_2Cl_2): δ −130.3 (d, J = 16.1 Hz, F_o), −147.7 (t, J = 19.9 Hz, F_p), −160.9 (m, F_m). ^{11}B NMR (CD_2Cl_2): δ 75.0 (1030).

Ethyl *trans*-5-(*Bis*(pentafluorophenyl)boryl)-4-pentenoate. General procedure 1 was used to prepare this compound from ethyl 4-pentynoate (11.0 mg, 0.087 mmol) and **1** (30.0 mg, 0.087 mmol). ^{1}H NMR: δ 6.74 (m, J = 17.4 Hz and J = 1.2 Hz, 1H, BCH), 6.49 (dt, J = 5.7 Hz, 1H, =CH), 3.94 (q, J = 7.1 Hz, 2H, OCH_2), 2.28 (dt, J = 6.7 Hz, 2H, =CHCH_2), 2.16 (t, 2H, CH_2CO), 0.92 (t, 3H, CH_3). ^{13}C NMR: δ 174.1 (CO), 162.9 (=CH), 147.7, 142.8, 137.7, and 114.2 (C_6F_5), 136.5 (BC), 62.1 (OCH_2), 32.2 and 31.3 (CH_2), 13.9 (CH_3). ^{19}F NMR: δ −130.3 (dd, J = 9.4 Hz and J = 23.5 Hz, F_o), −149.2 (t, J = 19.8 Hz, F_p), −161.5 (m, F_m). ^{11}B NMR: δ 51.7 (1155).

X-ray Crystallography. Measurements were made on a Bruker AXS SMART CCD area-detector diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). The structures was solved by direct methods and refined on F^2 values by full-matrix least-squares for all unique data. Table

Table 5. Summary of Data Collection and Structure Refinement Details for 1

formula	$C_{24}H_2B_2F_{20}$	Z	8
fw	691.88	F(000)	2688
space group	$C2/c$	d_{calc}, mg m^{-3}	1.832
cryst syst	monoclinic	μ, mm^{-1}	0.211
a, Å	43.925(7)	no. of reflcns	8724
b, Å	6.527(1)	ind. reflcns	3212
c, Å	18.770(3)	R_1	0.0584
β, deg	111.215(2)	R_{w2}	0.1219
V, Å^3	5016.4(5)	GOF	1.081

(58) Sheldrick, G. M. *SHELXTL*, version 5; Bruker AXS Inc.: Madison, WI, 1994.

5 gives further details. Programs used were standard Bruker SMART (control) and SAINT (integration), SHELXTL[58] for structure solution, refinement and molecular graphics, and local programs.

Acknowledgment. Funding for this work from the Natural Sciences and Engineering Research Council of Canada in the form of a Research Grant to W.E.P. and Scholarship support to D.J.P. (1994−8). W.E.P. also thanks the Alfred P. Sloan Foundation for a Research Fellowship (1996−2000).

Supporting Information Available: Tables giving full listings of crystallographic data, atomic parameters, hydrogen parameters, atomic coordinates, and complete bond distances and angles for **1** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

OM980673E