

# Hydroboration with Haloborane/Trialkylsilane Mixtures<sup>1</sup>

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Trialkylsilanes or dialkylsilanes react rapidly with boron trichloride in the absence of ethereal solvents or other nucleophiles to form unsolvated dichloroborane. If no substrate is present, dichloroborane disproportionates to trichloroborane and two geometric isomers of chloroborane dimer, which in turn yield monochlorodiborane and, slowly but irreversibly, diborane. All of the B-H compounds in the mixture except diborane are highly active hydroborating agents. With alkenes in the presence of sufficient boron trichloride, the products are alkyldichloroboranes. These are free from detectable contamination by dialkylchloroboranes unless more than 1 mol of hydride is present. Similar hydroboration of terminal acetylenes can be controlled to yield either (*E*)-1-(dichloroboryl)alkenes or 1,1-bis(dichloroboryl)alkanes, each free from significant contamination by the other. Alkyldichloroboranes with trialkylsilanes at 25 °C produce alkylmonochloroboranes, detected by <sup>11</sup>B NMR. 1,1-Bis(dichloroboryl)alkanes similarly yield 1,1-diborylalkane dimers. An alkylmonochloroborane can hydroborate a second alkene to form a dialkylchloroborane. For this purpose, differing alkyl groups may be introduced in either order, regardless of their relative steric properties. With 2 mol of trialkylsilane, alkyldichloroboranes are converted to alkylborane dimers. Boron tribromide and its bromoborane derivatives behave similarly to the chloro compounds in the examples tested.

## Introduction

Dihaloboranes have been known to be hydroborating agents for some time. Dichloroborane was reported to be generated from hydrogen and trichloroborane over magnesium at 400–450 °C, to be trapped at –135 °C, and to react “readily and energetically with olefinic and acetylenic hydrocarbons” at 10–30 °C in 1959.<sup>2</sup> Later patents indicated best results at temperatures between 550 and 1000 °C with rapid quenching and that the dichloroborane disproportionates slowly to form diborane.<sup>3</sup> Disproportionation of dichloroborane to monochlorodiborane (ClB<sub>2</sub>H<sub>5</sub>) and boron trichloride was reported to have a half-life of 8–12 h at –4 °C,<sup>4</sup> and it was previously known that pure monochlorodiborane disproportionates slowly to boron trichloride and diborane.<sup>5</sup>

There have been a few reports that silanes reduce trihaloboranes, but diborane was the only borane product noted.<sup>6</sup> In a study of mechanisms of nucleophilic displacement at silicon, methyl-naphthylphenylsilane with boron trichloride yielded the halosilane with retention of configuration at silicon, plus diborane.<sup>7</sup>

The information published by 1966,<sup>2,6,7</sup> had it ever been considered together, would have strongly suggested that trialkylsilanes with boron halides should produce useful ether-free hydroborating agents. How-

ever, chemists may have been diverted by the knowledge that in the absence of ethers the reaction of diborane with alkenes requires temperatures above 100 °C in order to proceed at any appreciable rate and is not synthetically useful.<sup>8</sup> Dichloroborane and dibromoborane were first developed as useful hydroborating agents in the form of their etherate or dimethyl sulfide complexes.<sup>9</sup> Dissociation of the monomeric haloboranes from these complexes, the rate-limiting step in the general mechanism of hydroborations,<sup>10</sup> has turned out to be slow. Hydroborations with dichloroborane etherate require boron trichloride to capture the ether and generally require several hours to complete.<sup>9</sup>

Our work evolved from an exploratory study of boron halides with tributyltin hydride, which transferred alkyl and hydride indiscriminately, and a silane was tried instead.

(5) (a) Schlesinger, H. I.; Burg, A. B. *J. Am. Chem. Soc.* **1931**, *53*, 4321. (b) Myers, H. W.; Putnam, R. F. *Inorg. Chem.* **1963**, *2*, 655–657. (c) Cueilieron, J.; Bouix, J. *Bull. Soc. Chim. Fr.* **1967**, 2945–2949.

(6) (b) Van Dyke, C. H.; MacDiarmid, A. G. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1503–1506. (c) Drake, J. E.; Goddard, N. *Inorg. Nucl. Chem. Lett.* **1968**, *4*, 385–388. (a) Vanderwielen, A. J.; Ring, M. A. *Inorg. Nucl. Chem. Lett.* **1972**, *8*, 421–422.

(7) Attridge, C. J.; Haszeldine, R. N.; Newlands, M. J. *J. Chem. Soc., Chem. Commun.* **1966**, 911.

(8) (a) Hurd, D. T. *J. Am. Chem. Soc.* **1948**, *70*, 2053. (b) Whatley, A. T.; Pease, R. N. *J. Am. Chem. Soc.* **1954**, *76*, 835. (c) Brown, H. C. *Boranes in Organic Chemistry*; Cornell University Press: Ithaca, NY, 1972; pp 256–261.

(9) (a) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1976**, *98*, 1798–1806. (b) Brown, H. C.; Ravindran, N. *Inorg. Chem.* **1977**, *16*, 2938–2940. (c) Brown, H. C.; Ravindran, N. *J. Org. Chem.* **1977**, *42*, 2533–2534. (d) Brown, H. C.; Chandrasekharan, J. *Organometallics* **1983**, *2*, 1261–1263. (e) Brown, H. C.; Chandrasekharan, J. *J. Org. Chem.* **1988**, *53*, 4811–4814.

(10) (a) Brown, H. C.; Scouten, C. G.; Wang, K. K. *J. Org. Chem.* **1979**, *44*, 2589–2591. (b) Wang, K. K.; Brown, H. C. *J. Org. Chem.* **1980**, *45*, 5303–5306. (c) Nelson, D. J.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 4907–4912. (d) Nelson, D. J.; Blue, C. D.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 4913–4917. (e) Wang, K. K.; Brown, H. C. *J. Am. Chem. Soc.* **1982**, *104*, 7148–7155.

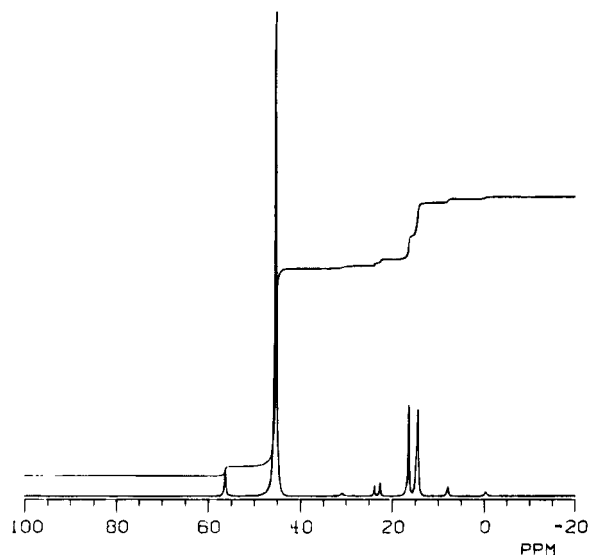
<sup>⊗</sup> Abstract published in *Advance ACS Abstracts*, August 1, 1995.

(1) A preliminary account of part this work has appeared: Soundararajan, R.; Matteson, D. S. *J. Org. Chem.* **1990**, *55*, 2274–2275.

(2) Lynds, L.; Stern, D. R. *J. Am. Chem. Soc.* **1959**, *81*, 5006. Most of the hydroborations were normal, but isobutylene yielded *tert*-butyl alcohol, which we would reinterpret as an artifact, perhaps derived via *tert*-butyl chloride from hydrogen chloride produced in the BCl<sub>3</sub>/H<sub>2</sub> reaction.

(3) (a) Pearson, R. K. U.S. Patent 3,323,867, June 6, 1967. (b) Hunt, C. D.A.; Kerrigan, J. V.; Leffler, A. J.; Martin, W. W. U.S. Patent 3,328,135, June 27, 1967.

(4) Cooper, H. B. H. U.S. Patent 3,684,462, August 15, 1972.

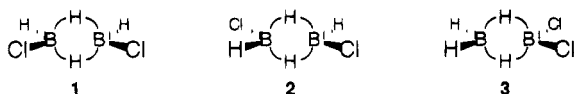


**Figure 1.** 64 MHz  $^1\text{H}$ -decoupled  $^{11}\text{B}$  NMR spectrum of an equimolar mixture of boron trichloride and diethylsilane taken after  $\sim 1$  h at  $-40^\circ\text{C}$ .

## Results

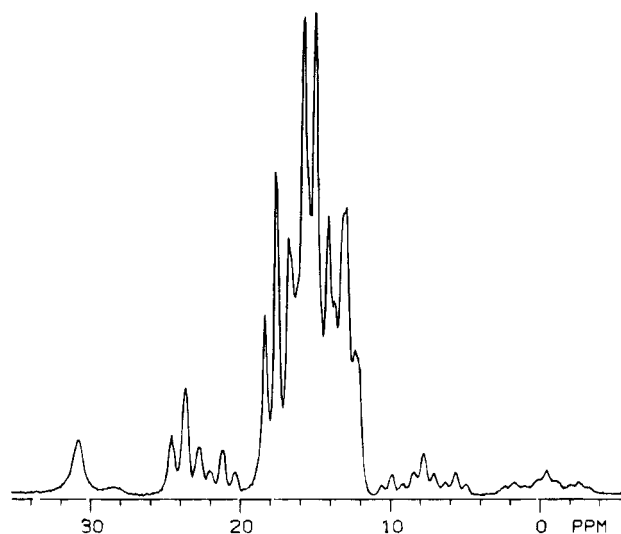
### Dichloroborane and Chloroborane Formation.

Addition of diethylsilane or a trialkylsilane to an approximately equimolar amount of boron trichloride in an NMR tube at  $-78$  to  $-40^\circ\text{C}$  produced a mixture that showed prominent absorptions in the  $^{11}\text{B}$  NMR spectrum at  $\delta$  46 (boron trichloride) and two overlapping sets of doublets of triplets at  $\delta$  14.3 and 16.2 in the  $^{11}\text{B}$  NMR spectrum, attributed to *cis*- and *trans*-1,2-dichlorodiborane **1** and **2**. Also present was monochlorodiborane,



ane,  $\text{ClHB}[\text{H}_2]\text{BH}_2$ ,  $\delta$  7.7 (t of t's) and 22.5 (d of t's), which matched the known  $^{11}\text{B}$  NMR spectrum,<sup>11</sup> a small triplet of triplets at  $\delta$   $-0.6$ , and a peak with an equal integral at  $\delta$  23.7, which in the  $^1\text{H}$ -coupled spectrum appeared to be a triplet coincident with one-half of the monochlorodiborane peak. This is the expected splitting pattern, though with unexpectedly upfield chemical shifts, for the third possible isomer **3** of dichlorodiborane. A small doublet at  $\delta$  56.1, d,  $J_{\text{BH}} = 204$  Hz, might be due to dichloroborane ( $\text{HBCl}_2$ ), though the only certainties are that dichloroborane is not present at more than a few mol % concentration as monomer and that no detectable amount of hydrogen bridged dimer,  $\text{B}_2\text{H}_2\text{Cl}_4$ , is present. The  $\sim 70:25$  ratio of  $\text{BCl}_3$  to the  $\text{BH}_2\text{Cl}$  dimers is consistent within experimental error to transfer only one hydrogen of diethylsilane to boron under these conditions. The  $^1\text{H}$ -coupled and  $^1\text{H}$ -decoupled 64-MHz  $^{11}\text{B}$  NMR spectra are illustrated in Figures 1 and 2.

When the mixture was warmed to  $-20^\circ\text{C}$ , the multiplet centered at  $\delta$  16.2 attributed to **1** or **2** decreased in intensity, the monochlorodiborane peaks increased substantially, a small amount of diborane appeared at  $\delta$  17, and the  $\delta$  56, 23.7, and  $-0.6$  peaks



**Figure 2.** Portion of a 64 MHz  $^1\text{H}$ -coupled  $^{11}\text{B}$  NMR spectrum of an equimolar mixture of boron trichloride and diethylsilane taken after  $\sim 1$  h at  $-40^\circ\text{C}$ .

increased slightly. Boron trichloride and the multiplet centered at  $\delta$  14.3 (**2** or **1**) remained constant within experimental error, and a slight splitting ( $\sim 15$  Hz) appeared in some of the peaks of the  $\delta$  14.3 multiplet, conceivably an H-B-B long-range coupling. A spectrum of a similar sample prepared from triethylsilane and boron trichloride taken at room temperature showed only the peaks attributed to boron trichloride, monochlorodiborane, and diborane.

### Hydroboration with Preformed Chloroboranes.

Mixtures containing either 1,2-dichlorodiborane or monochlorodiborane and boron trichloride readily hydroborated either cyclohexene or 1-hexene to alkyl-dichloroborane, as shown by the prompt appearance of the characteristic alkyl-dihaloborane peak<sup>12</sup> in the range  $\delta$  61–64 in the  $^{11}\text{B}$  NMR spectrum. However, in accord with the previously reported inert character of diborane,<sup>8</sup> solutions of diborane in boron trichloride, with or without added chlorotrimethylsilane, failed to hydroborate 1-hexene in a few hours at temperatures below the boiling point of the mixture.

Hydroboration of 1-hexene with premixed trimethylsilane and boron trichloride followed by oxidation yielded 1-hexanol containing 0.8% 2-hexanol, twice the proportion of 2-hexanol found when the hydroboration was carried out under the improved conditions described below.

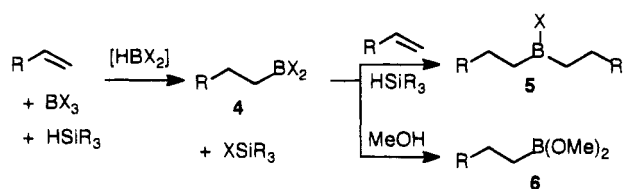
The foregoing hydroborations were carried out by first adding the trialkylsilane to boron trichloride, neat or in pentane, while being cooled with a  $-78^\circ\text{C}$  bath, then adding the alkene dropwise to the cold, stirred borane mixture. For synthetic purposes, it could be hazardous to prepare large batches of unstable haloboranes that gradually liberate gaseous, spontaneously flammable diborane above  $-40^\circ\text{C}$ . Therefore, we tested other conditions for mixing the reagents.

**Addition of Silanes to Alkene/Boron Trichloride Mixtures.** Conditions tested first involved adding an equimolar amount of an alkene to neat boron trichloride stirred at  $-78^\circ\text{C}$ , followed by introduction of an equimolar amount of trimethylsilane via cannula. After

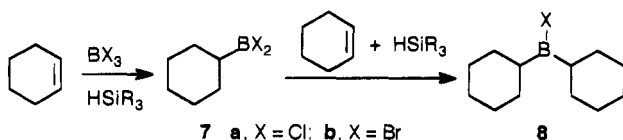
(11) Eaton, G. R.; Lipscomb, W. N. *NMR Studies of Boron Hydrides and Related Compounds*; W. A. Benjamin, Inc.: New York, 1969; pp 9–23.

(12) Brown, H. C.; Sikorski, J. A. *Organometallics* **1982**, *1*, 28–37.

5–10 min at  $-78\text{ }^{\circ}\text{C}$ , the mixture was warmed to room temperature. In this manner, 1-hexene was converted to 1-hexyldichloroborane (**4a**) and cyclohexene to cyclo-



a,  $\text{R} = \text{CH}_3(\text{CH}_2)_3$ ,  $\text{X} = \text{Cl}$ ; b,  $\text{R} = \text{CH}_3(\text{CH}_2)_3$ ,  $\text{X} = \text{Br}$ ; c,  $\text{R} = \text{H}$ ,  $\text{X} = \text{Cl}$



7 a,  $\text{X} = \text{Cl}$ ; b,  $\text{X} = \text{Br}$

hexyldichloroborane (**7a**), and the products were separated from the trimethylsilyl chloride byproduct by simple distillation. Contamination of **4a** by dihexylchloroborane (**5a**) or of **7a** by dicyclohexylchloroborane (**8a**) was not detectable ( $\leq 1\%$ ) by  $^{11}\text{B}$  NMR. Oxidation of **4a** with alkaline hydrogen peroxide yielded 1-hexanol containing only 0.4% 2-hexanol by GC analysis.

The rate of the reaction is remarkable. Diethylsilane was layered on top of 1-hexene/boron trichloride in a 5-mm NMR tube encased in a 14-mm tube at  $-98\text{ }^{\circ}\text{C}$ . After 5 min the reactants remained unmixed,  $\text{BCl}_3$   $\delta$  47, but after one inversion of the tube and a return to the  $-98\text{ }^{\circ}\text{C}$  bath in 2–3 s, the  $^{11}\text{B}$  NMR within 1 min showed only **4a**,  $\delta$  62. In another experiment, a mixture of diethylsilane and 1-hexene was added dropwise to stirred boron trichloride in pentane at approximately  $-100\text{ }^{\circ}\text{C}$ . After 1 h, methanol was added in order to destroy all haloboranes and thus stop the hydroboration before the bath was warmed above  $-100\text{ }^{\circ}\text{C}$ .<sup>13</sup> Dimethyl hexylboronate was isolated by distillation (60%).

**Ethylene Hydroboration.** Because ethylene is not condensed at  $-78\text{ }^{\circ}\text{C}$  at atmospheric pressure, a different experimental technique was tested for laboratory use. Passage of ethylene through boron trichloride at  $-78\text{ }^{\circ}\text{C}$  while slowly adding triethylsilane resulted in formation of ethyldichloroborane (**4c**), together with a significant amount of diethylchloroborane (**5c**). After being warmed to room temperature (though not at  $-78\text{ }^{\circ}\text{C}$ ) the crude reaction mixture proved pyrophoric. Addition of just enough methanol to convert the boron halides to methoxyboranes resulted in a mixture of trimethyl borate, dimethyl ethylboronate (**6c**), and methyl diethylboronate [ $\text{CH}_3\text{OB}(\text{CH}_2\text{CH}_3)_2$ ], which were incompletely separated by fractional distillation through an efficient packed column, plus recoverable trimethylchlorosilane.

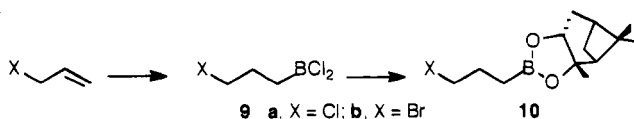
When the boron trichloride was diluted to  $\sim 3\text{ M}$  with mixed xylenes and a similar hydroboration procedure was followed, the resulting solution of ethyldichloroborane and some diethylchloroborane was not pyrophoric, but when the chloroboranes were separated from most of the xylenes and triethylchlorosilane by simple distillation, pyrophoricity returned. Placed on filter paper, the crude ethyldichloroborane ignited spontaneously but burned off with only slight darkening of the paper. The

distilled crude ethyldichloroborane was treated with methanol, and after simple distillation dimethyl ethylboronate was obtained in  $\sim 70\%$  yield (after correcting for the  $\sim 80\%$  purity), with about 9% trimethyl borate and the remainder divided between methyl diethylboronate, xylenes, and triethylchlorosilane.

Dichloromethane has been used elsewhere as the solvent for hydroboration with trialkylsilane and boron trichloride.<sup>14</sup> When the ethylene hydroboration was repeated in this solvent, the unchanged boron trichloride could be removed completely by distillation, and the mixture of dichloromethane, ethyldichloroborane (**4c**), and diethylchloroborane (**5c**) that distilled from the unchanged triethylchlorosilane was not pyrophoric. Treatment with methanol then yielded dimethyl ethylboronate containing an insignificant amount of trimethyl borate ( $< 1\%$ ), but the proportion of methyl diethylboronate in the product was  $\sim 11\%$ . Inasmuch as the boiling points of ethyldichloroborane and diethylchloroborane have been reported to differ by  $25\text{ }^{\circ}\text{C}$  at 100 Torr,<sup>15</sup> it would appear that the pure monoethylated boron species could be most easily purified as ethyldichloroborane, provided the equipment can accommodate pyrophoric substances safely.

**Addition of Silane/Alkene Mixtures to Boron Trihalides.** It is expected that acid-sensitive alkenes will be rearranged or destroyed by mixing with boron trichloride, even at low temperatures. Therefore an alternative set of reaction conditions was tested, in which the alkene and an equimolar amount of a trialkylsilane were mixed at room temperature and then added dropwise to stirred boron trichloride, either as the neat liquid or diluted with pentane, at any temperature from  $-78\text{ }^{\circ}\text{C}$  to the boiling point of boron trichloride ( $12\text{ }^{\circ}\text{C}$ ). For example, an equimolar mixture of triethylsilane and 1-hexene added dropwise to stirred, refluxing boron trichloride cleanly yielded **4a**. Boron tribromide behaved similarly, and addition of an equimolar mixture of cyclohexene and triethylsilane to boron tribromide maintained at  $20\text{ }^{\circ}\text{C}$  in a bath readily yielded cyclohexyldibromoborane (**7b**), as indicated by the  $^{11}\text{B}$  NMR peak at  $\delta$  65.

Addition of an equimolar mixture of allyl chloride or bromide with trimethylsilane (or triethylsilane) to boron trichloride at  $-78\text{ }^{\circ}\text{C}$  yielded (3-halopropyl)dichloroborane (**9**). Trimethylsilyl chloride was removed from **6**



9 a,  $\text{X} = \text{Cl}$ ; b,  $\text{X} = \text{Br}$

10

under reduced pressure, and **6** was then converted to the known<sup>16</sup> pinanediol esters **10** for characterization. There was no visible evidence of chlorine–bromine exchange in the  $^1\text{H}$  NMR spectrum of pinanediol (3-bromopropyl)boronate (**10b**).

**Dialkylhaloborane Formation.** Alkyldihaloboranes,  $\text{RBX}_2$ , react readily with trialkylsilanes to form alkylmonohaloboranes,  $\text{RBHX}$ , which also hydroborate

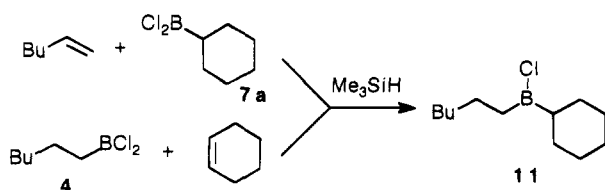
(14) Hawkins, J. M.; Loren, S.; Nambu, M. *J. Am. Chem. Soc.* **1994**, *116*, 1657–1660.

(15) Buis, V. W.; Davis, O. L.; Thomas, R. I. *J. Am. Chem. Soc.* **1957**, *79*, 337–339.

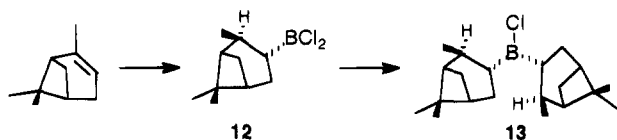
(16) Matteson, D. S.; Jesthi, P. K.; Sadhu, K. M. *Organometallics* **1984**, *3*, 1284–1288.

(13) We thank Professor H. C. Brown for suggesting this experiment.

alkenes in situ. In the absence of alkene, 1-hexylchloroborane,  $C_6H_{13}BHCl$ , disproportionated to dihexylchloroborane (**5a**) ( $^{11}B$   $\delta$  78.3) and dealkylated chlorodiboranes, including  $B_2H_5Cl$ . Symmetrical dialkylchloroboranes **5a** and **7a** were efficiently prepared from the corresponding alkene, triethylsilane, and boron trichloride in the theoretical 2:2:1 molar ratio. Disproportionation of hexylchloroborane is slow compared to its reaction with 1-hexene, as addition of an equimolar mixture of cyclohexene and triethylsilane to hexyldichloroborane (**4a**) yielded (cyclohexyl)(1-hexyl)chloroborane (**11**) which contained no **5a** or **8a** at the ~5% limit of detectability in the  $^{13}C$  NMR.



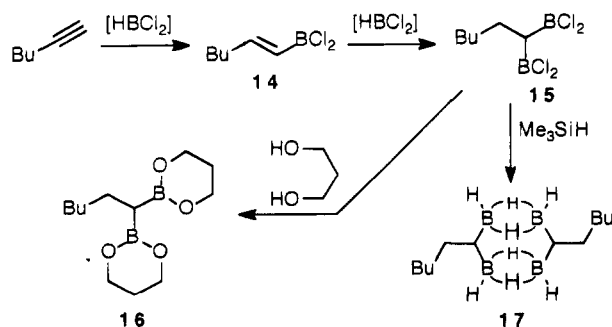
Addition of an equimolar mixture of (+)- $\alpha$ -pinene and trimethylsilane to boron trichloride at  $-78$  °C yielded isopinocampheylidichloroborane (**12**), which was char-



acterized by  $^{11}B$  NMR and oxidation to isopinocampheol (95% gc). Treatment of **12** with a second mole of boron trichloride and trimethylsilane, or addition of a mixture of 2 mol of (+)- $\alpha$ -pinene with 2 mol of trimethylsilane to 1 mol of boron trichloride yielded diisopinocampheylchloroborane (**13**), which was also converted to isopinocampheol (88% GC) for characterization.

Reduction of cyclohexyldichloroborane (**7a**) with 2 mol of trialkylsilane yielded 1,2-dicyclohexyldiborane (cyclohexylborane dimer):  $^{11}B$  NMR  $\delta$  23.7 [lit.<sup>17</sup> ( $RBH_2$ )<sub>2</sub>  $\delta$  22–24];  $^1H$ -coupled, broad d ( $J = 105$  Hz), bridge H couplings not resolved.

**Alkyne Hydroboration.** Addition of an equimolar mixture of trimethylsilane and 1-hexyne to boron trichloride yielded 1-hexenyldichloroborane (**14**), which was



found by  $^{11}B$  NMR to contain no more than 2% of the disubstitution product 1,1-bis(dichloroboryl)hexane (**15**). Addition of triethylsilane and 1-hexyne in a 2:1 molar ratio to sufficient boron trichloride efficiently yielded 1,1-bis(dichloroboryl)hexane (**15**), which was character-

ized first by NMR and finally by conversion to the known<sup>18</sup> 1,3-propanediol ester (**16**). Treatment of **15** with trimethylsilane yielded 1,1-bis(diborylhexane) dimer (**17**), which was characterized by  $^{11}B$  NMR and mass spectrometry.

**Other Silanes.** The use of diethylsilane has been noted above. Only one of the two silicon-bound hydrides reacts under the conditions used. The reaction of the inexpensive reagent dimethylchlorosilane,  $(CH_3)_2SiHCl$ , with boron trichloride and cyclohexene in pentane was shown by  $^{11}B$  NMR to yield cyclohexyldichloroborane (**7a**) slowly, requiring several hours at room temperature to complete the reaction. Attempts were made to use trichlorosilane as a hydride source, but no evidence of hydride transfer was detected by  $^{11}B$  NMR.

Tributylsilane behaved similarly to triethylsilane, though hydroboration of 1-hexene in pentane was relatively slow. Triphenylsilane and boron tribromide in pentane hydroborated 1-hexene over a period of several hours at room temperature. Triphenylsilyl bromide precipitated and could be removed by filtration.

## Discussion

**Caution.** Volatile alkylidichloroboranes ignite spontaneously in air. Butyldichloroborane has been reported as pyrophoric,<sup>15</sup> but appears to be at about the upper molecular weight limit for primary alkylidichloroborane pyrophoricity.<sup>19</sup> Secondary alkyl groups confer greater oxygen sensitivity, and cyclohexyldichloroborane (**7a**) has been reported to be pyrophoric.<sup>19</sup> We observed no flames when **7a** was handled in ordinary glassware under a blanket of argon, but the pyrophoric behavior of the more volatile ethyldichloroborane has been noted in the Results section.

The use of preformed chloroborane mixtures is not recommended for multigram synthetic purposes. Diborane is an inevitable byproduct in such mixtures. In one instance where boron trichloride and triethylsilane were mixed first at  $-78$  °C, 1-hexene was added subsequently; as the solution was warmed to 20 °C, the septum cap was expelled from the container and the vapors ignited. Similarly, a boron trihalide should never be added to a trialkylsilane or a mixture containing trialkylsilane, as excess trialkylsilane will reduce the boron trihalide all the way to diborane.

Based on standard heats of formation,<sup>20</sup> for the reaction  $SiH_4 + CH_3Cl \rightarrow CH_4 + SiH_3Cl$  (gas phase),  $\Delta H^\circ = -40.0$  kcal mol<sup>-1</sup>. Assuming similar bond energies, the stoichiometric mixture of triethylsilane with allyl chloride described in this work could conceivably liberate ~200 cal/g if accidental catalysis of halide/hydride exchange should occur. We have never seen any evidence of reaction of silanes with alkyl halides, but the safety of indefinite scaleup has not been proved. Dilution with an inert (hydrocarbon) solvent would be a straightforward precaution.

A stoichiometric mixture of diethylsilane with dichloromethane theoretically could liberate ~450 cal/g, but dichloromethane is safe with boron trichloride, and the

(18) Matteson, D. S.; Moody, R. J. *Organometallics* **1982**, *1*, 20–28.

(19) McCusker, P. A.; Ashby, E. C.; Makowski, H. S. *J. Am. Chem. Soc.* **1957**, *79*, 5182–5184.

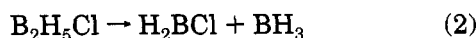
(20) (a) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables. J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. 1).

(17) Cole, T. E.; Bakshi, R. K.; Srebnik, M.; Singaram, B.; Brown, H. C. *Organometallics* **1986**, *5*, 2303–2307.

silicon and boron hydrides are consumed as quickly as an alkene/silane mixture is added to boron trichloride. Dichloromethane provides better protection than hydrocarbon solvents against the spontaneous flammability of low molecular weight alkylhaloboranes.

**Mechanism.** The first step, hydride exchange between the silane and boron halide, is rapid unless hindered by steric or electronic effects. The reaction  $\text{SiH}_4 + \frac{1}{3}\text{BCl}_3 \rightarrow \frac{1}{3}\text{BH}_3 + \text{SiH}_3\text{Cl}$  has  $\Delta H^\circ = -2.68 \text{ kcal mol}^{-1}$ , based on a high level quantum mechanical calculation of  $\Delta H_f^\circ$  for  $\text{BH}_3$ ,<sup>21</sup> or  $\Delta H^\circ = -1.49 \text{ kcal mol}^{-1}$  if the rather uncertain experimental value<sup>20</sup> is assumed. The analogous reaction  $\text{SiHCl}_3 + \frac{1}{3}\text{BCl}_3 \rightarrow \frac{1}{3}\text{BH}_3 + \text{SiCl}_4$  has  $\Delta H^\circ$  from  $-0.4$  to  $+0.9 \text{ kcal mol}^{-1}$ , insufficiently different to explain the unreactivity of trichlorosilane or the sluggish reactivity of dimethylchlorosilane, which must instead be related to activation energies. The nearly complete reduction of boron trichloride by silanes to chloroborane dimers and chlorosilanes is driven thermodynamically by the heat of dimerization.

Monomeric boranes are the active intermediates in hydroborations.<sup>10</sup> Our observations are consistent with the hypotheses that dichlorodiboranes (1–3) and monochlorodiborane dissociate readily, eqs 1 and 2 but diborane does not, and that only the monomeric boranes undergo hydride/halide exchange.



The observed disappearance of one of the isomers 1 or 2 while the other remains constant (or perhaps increases slightly) implies that the initial ratio of 1:2 is kinetically controlled and that one of the dimers, possibly the *trans*-isomer 2, is thermodynamically more stable than the other.

Because halide/hydride exchange among trigonal borane species is rapid, it makes little practical difference whether the actual hydroborating agent is dichloroborane or monochloroborane. Any alkylchloroborane,  $\text{RBHCl}$ , formed would undergo hydride–chloride exchange with boron trichloride to yield alkylchloroborane,  $\text{RBCl}_2$ . The observation that hydroboration of 1-hexene with preformed chloroboranes resulted in more attack of boron at the 2-carbon (0.8%) than did addition of the 1-hexene/trialkylsilane mixture to boron trichloride (0.4%) suggests the possibility that dichloroborane may be a bit more regioselective than monochloroborane, which in turn is known to be measurably more selective than borane–THF.<sup>22</sup> Thus, in addition to safety considerations, the addition of a mixture of the trialkylsilane and the alkene to the boron trichloride appears to yield the best chemical result.

**Alternative Hydroborating Agents.**<sup>23</sup> Etherates of dichloroborane<sup>9a</sup> and chloroborane<sup>24</sup> have been known as hydroborating agents for some time. Dichloroborane

etherate<sup>9a</sup> and dichloroborane dimethyl sulfide<sup>9c</sup> are very slow hydroborating agents unless an equivalent amount of boron trichloride is added in order to free the dichloroborane monomer. Dibromoborane dimethylsulfide complex is more reactive and gives good hydroboration rates with a catalytic amount of boron tribromide.<sup>9e</sup> Chloroborane etherate<sup>22</sup> and chloroborane dimethyl sulfide<sup>9c</sup> or haloborane dimethyl sulfide complexes<sup>25</sup> work well for making dialkylhaloboranes.

Dimethyl sulfide complexes strongly with alkylchloroboranes.<sup>9</sup> Alkylchloroborane dimethyl sulfide complexes dissociate sufficiently that the liberated dimethyl sulfide inhibits dissociation of the dichloroborane dimethyl sulfide complex and thus inhibits the hydroboration process.<sup>9e</sup> The trialkylsilane boron trichloride system was chosen in preference to the dimethylsulfide boranes for preparing free alkylchloroboranes or their crystalline complexes with chiral ketones.<sup>14</sup>

Where boronic esters are the synthetic objectives, hydroboration with catecholborane is an alternative.<sup>22,26</sup> However, these reactions are slow and require heating. The recently reported pinacolborane reacts faster, though excess reagent is required.<sup>27</sup>

The use of less expensive silanes in our process appears feasible. Our data indicate that dimethylchlorosilane would efficiently generate dichloroborane from boron trichloride at slightly elevated temperatures in a pressurized reactor.

**Limitations.** A major limitation on the synthetic use of hydroboration with haloboranes is their tendency to complex strongly with oxygen functions. Functionalized alkenes other than allyl halides have not been explored in the present investigation. Reagents such as catecholborane can be expected to work in the presence of acid-sensitive functionality that is incompatible with boron trihalides.

Unexpectedly, 3-hexyne did not yield much of the corresponding alkenylchloroborane when it was mixed with triethylsilane and added to boron trichloride.<sup>28</sup>

**Conclusions.** (1) Trialkylsilanes or dialkylsilanes with boron trichloride or boron tribromide provide a convenient source of unsolvated dichloroborane or dibromoborane, and these are very rapid in situ hydroborating agents for alkenes and 1-alkynes. (2) The best general procedure for carrying out these hydroborations is to add a mixture of equivalent amounts of the silane and alkene slowly to the stirred boron trihalide, neat or in a solvent. Any convenient temperature between  $-78^\circ\text{C}$  and the boiling point of boron trichloride ( $+12^\circ\text{C}$ ) or, for boron tribromide, room temperature, is generally satisfactory. (3) Taking into account rapidity of reaction, ease of use, cost, availability and storability of reagents, efficiency, and ease of product purification, no other means of hydroborating alkenes with dihaloboranes is competitive overall with the new technique. (4) For conversion of hydrocarbon substrates to boronic

(21) Sana, M.; Leroy, G.; Wilante, C. *Organometallics* **1991**, *10*, 264–270.

(22) Brown, H. C.; Ravindran, N. *J. Am. Chem. Soc.* **1976**, *98*, 1785–1798.

(23) For a more extensive review, see: Matteson, D. S. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F., Patai, S., Eds.; John Wiley and Sons: New York, **1987**; Vol. 4, pp 307–409.

(24) (a) Zweifel, G. *J. Organomet. Chem.* **1967**, *9*, 215–221. (b) Pasto, D. J.; Balasubramanian, P. *J. Am. Chem. Soc.* **1967**, *89*, 295–300.

(25) (a) Brown, H. C.; Ravindran, N. *Synthesis* **1977**, 695–697. (b) Brown, H. C.; Ravindran, N.; Kulkarni, S. U. *J. Org. Chem.* **1979**, *44*, 2417–2425.

(26) Brown, H. C.; Gupta, S. K. *J. Am. Chem. Soc.* **1971**, *93*, 1816–1818.

(27) Tucker, C. E.; Davidson, J.; Knochel, P. *J. Org. Chem.* **1992**, *57*, 3482–3485.

(28) We thank W. Hiscox and B. Schafman for the initial observation. Work in progress with B. Schafman indicates that this problem can be overcome by proper choice of reagents and conditions, to be published later.

esters, there is no known technique that is superior to the use of the new method followed by alcoholysis of the alkylboron dihalide. (5) Hydroboration of an alkyne by the new technique can efficiently provide either the (*E*)-alkenyldichloroborane or the 1,1-bis(dichloroboryl)alkane in a fully controlled manner. (6) Reduction of an alkyl-dihaloborane with a trialkylsilane to an alkyl-monohaloborane in the presence of an alkene provides a superior general route to dialkylhaloboranes having two different alkyl groups. The order of introduction of the two alkyl groups can be independent of their relative steric requirements. (7) Reduction of an alkyl-dihaloborane with 2 equiv of a trialkylsilane yields an alkylborane dimer.

### Experimental Section

**General Procedures.** Silanes, boron trichloride, and alkenes were purchased and used without further purification. *Caution!* Because alkylboranes, diborane, and other boron hydrides are rapidly oxidized by air and are in some cases spontaneously flammable and because haloboranes are easily hydrolyzed by atmospheric moisture, all reactions were carried out under an inert atmosphere of argon. An external boron trifluoride etherate reference was used for  $^{11}\text{B}$  NMR spectra.

**Dichloroborane and Chloroborane Formation.** Diethylsilane was added to an approximately equimolar amount of boron trichloride in an NMR tube cooled with a  $-78\text{ }^\circ\text{C}$  bath, then kept  $\sim 1$  h at  $-40\text{ }^\circ\text{C}$  and analyzed by 64 MHz  $^{11}\text{B}$  NMR. In addition to  $\text{BCl}_3$  ( $\delta$  46, 71 g-atom %, s), the major products appeared to be *cis*- and *trans*-1,2-dichlorodiborane,  $\text{ClHB}[\text{H}_2]\text{BHCl}$ , as indicated by  $^1\text{H}$ -coupled and  $^1\text{H}$ -decoupled 64 MHz  $^{11}\text{B}$  NMR data,  $\delta$  14.3 (12 g-atom %, d,  $J \approx 178$  Hz, of t's,  $J \approx 50$  Hz) and 16.2 (8 g-atom %, d,  $J \approx 170$  Hz, of t's,  $J \approx 50$  Hz). The  $^1\text{H}$ -coupled spectra overlapped so that only approximate estimates of coupling constants were possible. Other peaks included  $\delta$  56.1 (3 g-atom %, d,  $J_{\text{BH}} = 204$  Hz), attributed tentatively to dichloroborane ( $\text{HBCl}_2$ ); a set of multiplets characteristic of known<sup>11</sup> monochlorodiborane ( $\text{B}_2\text{H}_5\text{Cl}$ ),  $\delta$  7.7 (1.1%, t of t's,  $J = 45$  Hz and  $J = 137$  Hz) and 22.5 (1.1%, d,  $J = 162$  Hz, of t's,  $J = 54$  Hz); small peaks at  $\delta$   $-0.6$  (0.9%, t of t's,  $J = 141$  Hz,  $J = 41$  Hz) and 23.7 (0.9%, t,  $J \approx 58$  Hz, coincident with one t of  $\text{B}_2\text{H}_5\text{Cl}$ ), which is the expected splitting pattern, though unexpected chemical shifts, for  $\text{Cl}_2\text{B}[\text{H}_2]\text{BH}_2$ ;  $\delta$  30.8 (1.4%, s,  $(\text{RO})_3\text{B}?$ ). After  $\sim 1$  h at  $-20\text{ }^\circ\text{C}$ , the proportions of  $\text{BCl}_3$  and the  $\text{B}_2\text{H}_4\text{Cl}_2$  isomer centered at  $\delta$  14.3 were unchanged, but the  $\text{B}_2\text{H}_4\text{Cl}_2$  isomer at  $\delta$  16.2 decreased to 2.8%; each peak at  $\delta$   $-0.6$  and 23.7 ( $\text{B}_2\text{H}_5\text{Cl}$ ) increased to 2.1%; the unknown peaks at  $\delta$   $-0.6$  and 23.7 both increased to 1.4%, the  $\delta$  56 peak increased to 4.6%, and diborane appeared at  $\delta$  17 (1%). In a separate experiment, a similar mixture was prepared from boron trichloride and triethylsilane and the 64 MHz  $^{11}\text{B}$  NMR spectrum was taken at room temperature. The only BH species present were monochlorodiborane ( $\text{B}_2\text{H}_5\text{Cl}$ ),  $\delta$  9.0 (t of t's,  $J = 45$  Hz and  $J = 137$  Hz) and 24.2 (d,  $J = 162$  Hz, of t's,  $J = 54$  Hz) [lit.<sup>11</sup> similar], and diborane ( $\text{B}_2\text{H}_6$ ),  $\delta$  18.4 (t of t's,  $J = 46$  Hz,  $J = 138$  Hz).

**Dichlorohexylborane (4a).** (a) **From Triethylsilane and Boron Trichloride at  $\geq 12\text{ }^\circ\text{C}$ .** Boron trichloride (1.60 g, 13.7 mmol) was placed in a flask under a solid carbon dioxide cooled condenser and

stirred under reflux during the dropwise addition of a mixture of 1-hexene (0.78 g, 9.36 mmol) and triethylsilane (1.09 g, 9.36 mmol) from a syringe. The  $^{11}\text{B}$  NMR spectrum showed the strong peak at  $\delta$  60.3 attributed to dichlorohexylborane, with no additional peak at  $\delta$  75.6–78.3, the region characteristic of dialkylchloroboranes.<sup>29</sup> Complete consumption of the 1-hexene was indicated by the  $^1\text{H}$  NMR spectrum, which showed no evidence of olefinic hydrogen in the region near  $\delta$  5.

**Dichlorohexylborane (4a) from Tributylsilane at  $-78\text{ }^\circ\text{C}$ .** A solution of 1.91 g (16.25 mmol) of boron trichloride and 1.37 g (2.03 mL, 16.25 mmol) of 1-hexene in 5 mL of pentane at  $-78\text{ }^\circ\text{C}$  was stirred under argon during the dropwise addition of 3.26 g (4.2 mL, 16.25 mmol) of tributylsilane. The  $^{11}\text{B}$  NMR spectrum showed the only major peak at  $\delta$  63.1, characteristic of alkyl-dichloroboranes. Distillation yielded 2.4 g (88%) of dichlorohexylborane, bp  $89\text{--}90\text{ }^\circ\text{C}$  (19 Torr).

**Dimethyl 1-Hexylboronate (6a) via 4a from Diethylsilane at  $-100\text{ }^\circ\text{C}$ .** A solution of boron trichloride (9.8 g, 0.084 mol) in pentane (50 mL) was chilled in a  $-100\text{ }^\circ\text{C}$  bath (95% ethanol partially frozen with liquid nitrogen) and stirred during the addition of a mixture of 1-hexene (7.58 g, 0.090 mol) and diethylsilane (7.46 g, 0.085 mol) dropwise down the chilled side of the flask over a period of 10 min. Stirring in the  $-100\text{ }^\circ\text{C}$  bath was maintained over a period of 1 h. (In preliminary tests monitored by  $^{11}\text{B}$  NMR and not recorded in full detail, hydroboration was  $\sim 40\%$  complete in 5 min and  $\sim 85\%$  complete in 15 min at  $-100\text{ }^\circ\text{C}$ .) Methanol (9.0 g, 0.281 mol) was added dropwise down the side of the flask to the chilled, stirred solution over a period of 5 min. The magnetic stirrer froze, but was released and resumed turning well before the bath warmed past  $-78\text{ }^\circ\text{C}$ , at which point dry ice lumps in the bath resumed gas evolution. Stirring was continued, and the bath was warmed to  $25\text{ }^\circ\text{C}$  overnight, with the argon source arranged to sweep evolved hydrogen chloride into a gas trap. A dense phase (methanol) was separated ( $\sim 5$  mL), and the pentane solution was distilled. After foreruns at mainly  $49\text{--}52\text{ }^\circ\text{C}$  and  $72\text{--}83\text{ }^\circ\text{C}$  but continuous up to  $152\text{ }^\circ\text{C}$ , dimethyl hexylboronate was distilled in the range  $152\text{--}170\text{ }^\circ\text{C}$ , mostly at  $163\text{--}168\text{ }^\circ\text{C}$  ( $\sim 700$  Torr) [lit.<sup>30</sup> bp  $69\text{--}70\text{ }^\circ\text{C}$  (16 Torr)]; 8.16 g (60%); 300 MHz  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.76 (t, 2), 0.88 (t, 3), [1.0 (m,  $\sim 0.4$ , impurity)], 1.27–1.43 (m, 8), 3.53 (s, 6); 75 MHz  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 23.9, 31.8, 32.4, 51.3 (BC not observed); HRMS found 158.1482 for  $\text{C}_8\text{H}_{19}\text{BO}_2$  calcd 158.1478. It appeared that **6a** partially decomposed during GC–mass spectral analysis, yielding a large number of impurity peaks. The last significant component to elute and the second most abundant was tentatively identified as tri-*B*-hexylboroxine,  $\text{M}^+$  obsd 336 ( $\text{C}_{18}\text{H}_{39}\text{B}_3\text{O}_3$ ), easily rationalized as a hydrolysis product of **6a**. The liquid distillation residue (1.2 g) was not characterized.

**Dibromohexylborane (4b) from Triphenylsilane and Boron Tribromide at Room Temperature in Pentane.** Boron tribromide (3.3 g, 13.15 mmol), 1-hexene (1.11 g, 13.15 mmol), and a solution of triphenylsilane (3.42 g, 13.15 mmol) in a minimal amount of pentane were stirred together at room temperature.

(29) Brown, H. C.; Srebnik, M.; Ramachandran, P. V. *J. Org. Chem.* **1989**, *54*, 1577–1583.

(30) Brown, H. C.; Bhat, N. G.; Somayaji, V. *Organometallics* **1983**, *2*, 1311–1316.

After 15 min, the conversion to dibromo(1-hexyl)borane,  $^{11}\text{B}$  NMR  $\delta$  64.9, was 50%. After 4.5 h the reaction was complete as shown by the absence of any  $^{11}\text{B}$  signal for boron tribromide and any olefinic  $^1\text{H}$  signal. Bromotriphenylsilane precipitated as a crystalline solid from the reaction mixture, making isolation of the (dibromo)-(1-hexyl)borane very simple.

**Dimethyl Ethylboronate (6c).** (a) **In Dichloromethane.** A 500-mL three-neck flask was equipped with an efficient magnetic stirrer, a gas inlet tube that would reach below the surface of 200 mL of liquid, a glass stopper in the center neck, and an adapter tube for connection to an argon supply, which was vented via a T-tube to a good gas trap for acidic vapors. The detached apparatus was tared and then connected, filled with argon, and cooled with a  $-78^\circ\text{C}$  bath while boron trichloride was admitted through the gas inlet tube until approximately the right volume (80–85 mL) had condensed (wt obsd: 113.6 g, 0.97 mol). The glass stopper was replaced by a pressure-equalized addition funnel ( $\geq 125$  mL), and a dry ice cooled condenser was inserted between the flask and the argon supply. Dichloromethane (200 mL) was added. The mixture was stirred while a slow stream of ethylene was passed through, and triethylsilane (96.33 g, 0.828 mol) was added dropwise ( $\sim 80$  drops/min) over a period of 1 h. During this time a slow stream of argon was maintained so that vented ethylene was diluted, except that the argon flow was interrupted occasionally to be sure that a slight excess of ethylene was passing through the system. Ethylene was introduced for an additional 20 min, at which time it appeared that saturation had been reached. The resulting solution was not pyrophoric on paper. The flask was equipped with a distillation head having a reflux condenser and a stopcock to regulate take-off rate, the gas inlet and outlet were replaced by stoppers, and the argon supply and exit gas trap were connected to the still head. The solution was warmed slowly (boron trichloride evolved) and distilled, first fraction up to  $35^\circ\text{C}$  (10.7 g, discarded; reacted violently with water), second fraction mostly  $35$ – $60^\circ\text{C}$  [ethylchloroborane, lit.<sup>19</sup> bp  $50.8^\circ\text{C}$  (745 Torr)], some to  $136^\circ\text{C}$  [diethylchloroborane, lit.<sup>15</sup> bp  $25^\circ\text{C}$  (100 Torr)], compared with ethyldichloroborane, bp  $1^\circ\text{C}$  (100 Torr), residue mainly triethylchlorosilane (116.7 g). The second fraction was redistilled in part through a 30-cm vacuum-jacketed column packed with glass helices, bp to  $35^\circ\text{C}$  (30 g, violently reactive to water),  $35$ – $38.5^\circ\text{C}$  (46 g, moderately reactive to water), residue not pyrophoric on filter paper. The flask containing the residue was fitted with an adapter having a side arm for connection to the argon supply and trap system and a pressure-equalized addition funnel above, then cooled under argon in a  $-78^\circ\text{C}$  bath. Methanol (53.5 g, 1.67 mol) was added dropwise over a period of 15 min. Not much gas was evolved until the material was warmed to near  $0^\circ\text{C}$ , at which time the flask was reattached to the fractionating column and hydrogen chloride began to escape at a rapid rate through the argon delivery system and into the gas trap. Careful fractionation separated dichloromethane ( $35$ – $38^\circ\text{C}$ , plus intermediate cut to  $50^\circ\text{C}$ ), then yielded an apparent methanol azeotrope (mostly  $58^\circ\text{C}$ , included  $50$ – $78^\circ\text{C}$ ,  $\sim 35$  g), leaving the major product in the first residue, which was stored under argon. The methanol azeotrope was

combined with pentane (80 mL) and refractionated until azeotrope ( $28^\circ\text{C}$ ) and pentane ( $36^\circ\text{C}$ ) distillation ceased. The second residue was then purified by simple distillation (bp  $79$ – $84^\circ\text{C}$ ), and the first residue (bp  $81$ – $85^\circ\text{C}$ , a little to  $89^\circ\text{C}$ ) was distilled into the same flask, total 50.0 g, estimated by  $^1\text{H}$  NMR analysis to contain dimethyl ethylboronate<sup>31</sup> (86%–88%; yield 51%–52%), methyl diethylborinate<sup>31</sup> (11%–13%; yield 7%–8%), trimethyl borate (0.7%), and triethylsilane (0.8%).

(b) **In Xylenes.** A similar procedure to that in the foregoing paragraph was followed, using a solution of boron trichloride (129 g, 1.1 mol) in mixed xylene isomers (300 mL) and adding triethylsilane (117.2 g, 1.008 mol) over a period of 2 h. The solution was warmed to room temperature, resulting in considerable gas evolution (presumably ethylene). A sample was taken for 96 MHz  $^{11}\text{B}$  NMR and showed peaks at  $\delta$  63.69 [dichloroethylborane],  $\delta$  46.15 (boron trichloride), and  $\delta$  78.36 (diethylchloroborane) in the ratios 1.00/0.11/0.06, respectively. When the mixture was heated above room temperature, distillation began, and the first distillate was pyrophoric. Simple distillation was continued fairly rapidly, without separating any fractions, at atmospheric pressure under argon until the bp reached  $128^\circ\text{C}$  (xylenes, bp  $139^\circ\text{C}$ ; chlorotriethylsilane, bp  $144^\circ\text{C}$ ); 144 g collected. When this flask was separated from the distillation apparatus, the vapors ignited immediately though not vigorously at the mouth of the flask, which was restoppered uneventfully within 1–2 s and stored in a dry ice filled dewar. Treatment with methanol (90 mL, 2.2 mol) was followed by slow simple distillation, with a distillation head allowing partial or total reflux; methanol/methyl borate azeotrope and methyl borate, bp  $55$ – $78^\circ\text{C}$ ; impure (83%) dimethyl ethylboronate, bp  $79$ – $89^\circ\text{C}$ , 75.6 g (estimated by NMR analysis to contain 11% trimethyl borate, 3% xylenes, and 3% triethylchlorosilane); impure ( $\sim 75\%$ ) dimethyl ethylboronate, 13.7 g; total dimethyl ethylboronate in both fractions, 73 g (72%).

(c) **Without Solvent.** Boron trichloride (113 g, 0.96 mol) was condensed and stirred under argon while a slow stream of ethylene was passed through, with a dry ice condenser to retain boron trichloride, and triethylsilane (110.4 g, 0.9496 mol) was added dropwise over a period of 1.7 h. Ethylene was introduced for an additional 25 min, at which time it appeared that saturation had been reached. Methanol (62.1 g) was added dropwise, and the evolved hydrogen chloride was allowed to exit into a stream of argon leading to an aqueous trap. Simple distillation using a good distillation head yielded 1.8 g of forerun up to  $86^\circ\text{C}$ , then 105.3 g at  $86$ – $131^\circ\text{C}$ . NMR analysis indicated the presence of trimethyl borate ( $\sim 24.2$  g), dimethyl ethylboronate ( $\sim 49.4$  g), methyl diethylborinate ( $\sim 15.2$  g), and triethylsilyl chloride ( $\sim 16.4$  g). Fractionation through a 30-cm column packed with stainless steel helices yielded fractions at  $67$ – $73^\circ\text{C}$ , 20.9 g, estimated by NMR analysis to contain trimethyl borate (15.2 g) and dimethyl ethylboronate (5.7 g);  $73$ – $78^\circ\text{C}$ , 10.3 g, estimated by NMR to contain trimethyl borate (1.6 g), dimethyl ethylboronate (8.1 g), and methyl diethylbori-

(31) (a) Dimethyl ethylboronate,  $\delta$  0.69, 0.89, 3.50; methyl diethylborinate,  $\delta$  0.83, 0.85, 3.65; Nöth, H.; Vahrenkamp, H. *J. Organomet. Chem.* **1968**, *12*, 23–36. (b) Methyl diethylborinate,  $\delta$  0.87, 3.62; Köster, R.; Fenzl, W.; Seidel, G. *Justus Liebigs Ann. Chem.* **1975**, 352–372.

nate (0.6 g); 78–82 °C, 43.1 g, estimated to contain dimethyl ethylboronate (35.1 g) and methyl diethylboronate (8.0 g); 82–95 °C, 9.7 g, estimated to contain dimethyl ethylboronate (2.6 g) and methyl diethylboronate (7.1 g); total contained dimethyl ethylboronate estimated 51.5 g (53%).

**(Dichloro)(cyclohexyl)borane (7a) from Tributylsilane and Boron Trichloride at –78 °C.** Condensed boron trichloride (4.68 g, 40 mmol) was weighed in a 50-mL flask under argon, then stirred at –78 °C (acetone–solid carbon dioxide bath). Pentane (5 mL) was added as a diluent, followed by 3.28 g (40 mmol) of cyclohexene. Tributylsilane (8 g) was added dropwise from a syringe. The mixture was stirred for 5 min at –78 °C. A small portion of the mixture was transferred to an NMR tube via cannula with the aid of argon pressure. The  $^{11}\text{B}$  NMR spectrum showed a strong peak at  $\delta$  63.0 (external  $\text{BF}_3\cdot\text{Et}_2\text{O}$  reference), which is characteristic of alkyl dichloroboranes.<sup>12</sup> There was also a small peak (~3%) at  $\delta$  45.5 (boron trichloride) and a small impurity peak at  $\delta$  30.9 attributed to accidental hydrolysis of the boron halides during transfer to the NMR tube. Simple distillation of the major portion of the mixture yielded dichlorocyclohexylborane (6.2 g), bp 95 °C (30 Torr) containing ~10% tributylsilyl chloride as a contaminant as indicated by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra. Allowing for the impurity, the corrected yield of dichlorocyclohexylborane was 85%.

**Dichlorocyclohexylborane (7a) from Premixed Triethylsilane and Boron Trichloride.** To a 3.94-g (33.5-mmol) sample of boron trichloride stirred at –78 °C under argon was added 5 mL of pentane followed by 3.89 g (33.5 mmol) of triethylsilane dropwise at a rate slow enough to avoid boiling of the solution. The  $^{11}\text{B}$  NMR spectrum of this mixture indicated unchanged boron trichloride at  $\delta$  46.8, diborane at  $\delta$  18.55 (triplet of triplets,  $J = 47$  Hz and  $J = 138$  Hz), and monochlorodiborane at  $\delta$  9.07 ( $^1\text{H}$ -coupled: triplet of triplets,  $J = 45$  Hz and  $J = 138$  Hz) and 24.89 (doublet,  $J = 164$  Hz, of triplets,  $J = 55$  Hz). Addition of 33.5 mmol of cyclohexene to this solution at –78 °C resulted in rapid reaction, and the resulting solution showed the  $^{11}\text{B}$  NMR peak at  $\delta$  63.3 characteristic of (dichloro)(cyclohexyl)borane with only minor impurities at  $\delta$  31 and 34.

**Dichlorocyclohexylborane (7a) from Diethylsilane and Boron Trichloride.** A mixture of boron trichloride (25.5 mmol) and cyclohexene (25.5 mmol) in pentane at –78 °C was stirred during the dropwise addition of diethylsilane (12.75 mmol). The  $^{11}\text{B}$  NMR spectrum taken after 5 min showed complete conversion of the boron trichloride to dichlorocyclohexylborane,  $\delta$  63.3.

**Dichlorocyclohexylborane (7a) from Dimethylchlorosilane and Boron Trichloride.** A mixture of boron trichloride (2.0 g, 17.0 mmol) and cyclohexene (1.39 g, 17.0 mmol) in pentane at –78 °C was stirred during the dropwise addition of dimethylchlorosilane (1.61 g, 17 mmol). The  $^{11}\text{B}$  NMR spectrum taken after 10 min showed only 4% conversion to dichlorocyclohexylborane. After 1.1 h at room temperature in the NMR tube sealed with a rubber septum, the conversion had reached ~57%, and after 4.5 h complete conversion of the boron trichloride to (dichloro)(cyclohexyl)borane,  $\delta$  63.3, was observed.

**1,2-Dicyclohexyldiborane (Cyclohexylborane Dimer).** The solution of dichlorocyclohexylborane (33.5 mmol) prepared from premixed triethylsilane and boron trichloride was treated with 67 mmol (2 additional equiv) of triethylsilane. Analysis by  $^{11}\text{B}$  NMR indicated slow reaction, but after remaining overnight at room temperature the strong peak at  $\delta$  23.7 ( $^1\text{H}$ -coupled; broad doublet,  $J = 105$  Hz, bridge B–H couplings not resolved) indicated complete conversion to 1,2-dicyclohexyldiborane, the dimer of cyclohexylborane. In another test, dichlorocyclohexylborane was treated with triethylsilane in the absence of solvent, and  $^1\text{H}$  NMR indicated rapid conversion to 1,2-(dicyclohexyl)diborane.

**Dibromocyclohexylborane (7b) from Triethylsilane and Boron Tribromide.** Boron tribromide (3.19 g, 12.7 mmol) was stirred at 20 °C (maintained with a water bath) during the dropwise addition of a mixture of cyclohexene (1.04 g, 12.7 mmol) and triethylsilane (1.50 g, 12.7 mmol) from a syringe. The  $^{11}\text{B}$  NMR spectrum consisted of a peak at  $\delta$  65 characteristic of (alkyl)(dibromo)boranes; hence, dibromocyclohexylborane is present.<sup>30</sup>

**Dichloro(3-chloropropyl)borane (9a) and (S)-Pinanediol (3-Chloropropyl)boronate (10a).** Trimethylsilane (1.73 g, 23.3 mmol) was condensed under argon at –78 °C and mixed with allyl chloride (1.81 g, 23.3 mmol), and this mixture was added via cannula to boron trichloride (2.74 g, 23.3 mmol) stirred at –78 °C under argon. On completion of the addition the formation of  $\text{Cl}(\text{CH}_2)_3\text{BCl}_2$  was indicated by the typical alkyl dichloroborane peak<sup>29</sup> at  $\delta$  62.6 in the  $^{11}\text{B}$  NMR spectrum. (In a parallel experiment with triethylsilane in place of trimethylsilane, small amounts of  $\text{R}_2\text{BCl}$  at  $\delta$  76.7 and  $\text{BCl}_3$  at  $\delta$  46 were also observed, perhaps because the addition of the mixture of triethylsilane and allyl chloride was carried out too rapidly.) Volatile byproducts were removed at 25 °C (100 Torr) for 1 h. The residue was cooled in an ice bath, and a solution of (S)-pinanediol<sup>32</sup> (3.97 g, 23.3 mmol) in diethyl ether (15 mL) was added. After being stirred for 10 min, the mixture was distilled. The yield of (S)-pinanediol (3-chloropropyl)boronate, bp 130 °C (0.5 Torr), was 5.7 g (92% after correction for minor impurities detected by  $^1\text{H}$  NMR analysis). The  $^1\text{H}$  NMR spectrum was similar to that previously reported.<sup>16</sup>

**Dichloro(3-bromopropyl)borane (9b) and (S)-Pinanediol (3-Bromopropyl)boronate (10b).** The procedure was the same as that described in the preceding paragraph for dichloro(3-chloropropyl)borane and (S)-pinanediol (3-chloropropyl)boronate except that allyl bromide was used in place of allyl chloride. (S)-Pinanediol (3-bromopropyl)boronate distilled at 145 °C (0.25 Torr), yield 80%,  $^1\text{H}$  NMR similar to that reported previously.<sup>16</sup> It is noteworthy that the 200 MHz  $^1\text{H}$  NMR spectrum clearly indicated that only the bromopropyl group was present, and that chloride–bromide exchange to produce (3-chloropropyl)boronic ester as a byproduct had not occurred.

**Chlorodihexylborane (8a) from Tributylsilane, 1-Hexene, and Dichlorohexylborane.** A solution of 0.5 g (3 mmol) of dichlorohexylborane and 0.252 g (0.38 mL, 3 mmol) of 1-hexene in 5 mL of pentane was stirred

(32) Chemical Abstracts name: [1S-(1 $\alpha$ ,2 $\beta$ ,3 $\beta$ ,5 $\alpha$ )]-2,6,6-trimethylbicyclo[3.1.1]heptane-2,3-diol. This compound was purchased from the Aldrich Chemical Company.



under argon at room temperature during the dropwise addition of 0.60 g (0.77 mL, 3 mmol) of tributylsilane. Analysis by  $^{11}\text{B}$  NMR indicated that the reaction required some time to complete, but after 4 h the peak at  $\delta$  63 characteristic of (dichloro)(hexyl)borane had disappeared and had been replaced by a peak at  $\delta$  77.3 characteristic of chlorodihexylborane.

**Chlorodihexylborane (5a) from Diethylsilane, 1-Hexene, and Boron Trichloride.** A mixture of 1-hexene (25.5 mmol) and diethylsilane (12.75 mmol) was added dropwise to boron trichloride (8.5 mmol) at a rate slow enough to avoid any appearance of boiling in the flask, which was cooled in a  $-78^\circ\text{C}$  bath. The  $^{11}\text{B}$  NMR spectrum taken at room temperature shortly after mixing showed mostly dichlorohexylborane at  $\delta$  62.8 and chlorodihexylborane at  $\delta$  78.0 in an approximately 1:1 ratio, with a small proportion of unchanged boron trichloride at  $\delta$  46.8. After 4 h at room temperature, the peaks due to boron trichloride and dichlorohexylborane had disappeared and the only peak was that of chlorodihexylborane at  $\delta$  78. Distilled material: *m/e* calcd 216.1816, found 216.1810;  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.1, 22.7, 24.6, 29.4 (broad, BC), 31.9, 32.0

**Dichlorohexylborane (4a) and Chlorodihexylborane (5a) from 1-Hexene and Trimethylsilane.** Boron trichloride (2.0 g, 17 mmol) and 1-hexene (1.26 g, 17 mmol) were placed in a flask under a solid carbon dioxide cooled condenser and were stirred under reflux during the dropwise addition of condensed trimethylsilane (1.42 g, 17 mmol) via cannula. The  $^{11}\text{B}$  NMR spectrum immediately showed the strong peak at  $\delta$  60.3 attributed to dichlorohexylborane. A second 17 mmol of 1-hexene was added, followed by a second 17 mmol of trimethylsilane. At the end of the addition the  $^{11}\text{B}$  NMR spectrum consisted of a single peak at  $\delta$  77.3 characteristic of a dialkylchloroborane.<sup>29</sup>

**Stepwise Preparation of Dichlorohexylborane (4a) and Chlorodihexylborane (5a) from Trimethylsilane, 1-Hexene, and Boron Trichloride at Reflux Temperature.** Boron trichloride (17.0 mmol) was condensed at  $-78^\circ\text{C}$  in a flask equipped with a dry ice cooled reflux condenser, then allowed to come to reflux temperature (approximately  $12^\circ\text{C}$ ). Trimethylsilane (17.0 mmol) was condensed separately and mixed with 1-hexene (17.0 mmol), and the mixture was added dropwise to the refluxing boron trichloride. The  $^{11}\text{B}$  NMR spectrum was taken immediately and indicated the presence of dichloro(1-hexyl)borane at  $\delta$  63 with  $\leq 2\%$  chlorobis(1-hexyl)borane at  $\delta$  78.4. Treatment of this product mixture with additional trimethylsilane (17 mmol) and 1-hexene (17 mmol) resulted in complete conversion of the (dichloro)(1-hexyl)borane to chlorobis(1-hexyl)borane within 2 h at room temperature, as indicated by the  $^{11}\text{B}$  NMR signal at  $\delta$  78.4. Addition of a third equivalent of trimethylsilane (17 mmol) and 1-hexene (17 mmol) resulted in no measurable conversion of the chlorobis(1-hexyl)borane to trihexylborane in 2 h at room temperature.

**Bromodicyclohexylborane (8b) from Cyclohexene, Triethylsilane, and Dibromocyclohexylborane.** The (dibromo)(cyclohexyl)borane from the preceding experiment was treated with a mixture of 12.7 mmol of cyclohexene and 12.7 mmol of triethylsilane. The  $^{11}\text{B}$  NMR spectrum immediately showed only a

peak at  $\delta$  80.1, characteristic of bromodicyclohexylborane. Dialkylbromoboranes characteristically absorb at  $\delta$  78–83.<sup>30</sup>

**Chlorocyclohexylhexylborane (11). (a) Via Dichlorohexylborane (4a) and Cyclohexene.** A mixture of 1-hexene (30 mmol) and triethylsilane (30 mmol) was added to boron trichloride (30 mmol) at  $-78^\circ\text{C}$  in the usual manner. The  $^{11}\text{B}$  NMR spectrum indicated complete conversion of the boron trichloride to dichloro(1-hexyl)borane, and the  $^1\text{H}$  NMR indicated complete consumption of the 1-hexene. This product mixture was treated at room temperature with a mixture of triethylsilane (30 mmol) and cyclohexene (30 mmol). The  $^{11}\text{B}$  NMR signal at  $\delta$  63.0 ( $\text{RBCl}_2$ ) disappeared gradually over the course of 30 min, and was replaced by the signal at  $\delta$  78 characteristic of chlorocyclohexyl(1-hexyl)borane. The  $^1\text{H}$  NMR indicated no olefinic protons remained; 50 MHz  $^{13}\text{C}$  NMR  $\delta$  14.1, 22.7, 24.6, 26.8, 27.4, 28.1,  $\sim 28$  (broad, obscured by sharp peaks, BC), 31.8, 32.1, 37.7 (broad, BC'). Possible impurities not detected:  $\leq 5\%$  bis(*n*-hexyl)chloroborane [ $\delta$  14.1, 22.7, 24.6, 29.4 (broad, BC), 31.9, 32.0] and  $\leq 5\%$  dicyclohexylchloroborane [ $\delta$  26.7, 27.2, 27.8, 36.4 (broad, BC)].

**(b) Via Dichlorocyclohexylborane (7a) and 1-Hexene.** The procedure described in the preceding paragraph was followed, except that cyclohexene was used in place of 1-hexene in the first step. The resulting solution of dichlorocyclohexylborane was treated with triethylsilane and 1-hexene at room temperature and after 4.5 h showed disappearance of the  $^{11}\text{B}$  NMR  $\text{RBCl}_2$  signal at  $\delta$  63 and complete conversion to chlorocyclohexyl(1-hexyl)borane,  $\delta$  78, as well as disappearance of olefinic protons in the  $^1\text{H}$  NMR.

**Dichloroisopinocampheylborane (12) and Chlorodiisopinocampheylborane (13).** (+)- $\alpha$ -Pinene (98% ee) (2.92 g, 21.4 mmol) and triethylsilane (2.49 g, 21.4 mmol) were mixed and added dropwise to boron trichloride (2.51 g, 21.4 mmol), stirred, and cooled with a  $-78^\circ\text{C}$  bath. The rate of addition was kept slow enough to avoid any boiling of the boron trichloride. After 5 min, the  $^{11}\text{B}$  NMR spectrum showed only a typical  $\text{RBCl}_2$  peak at  $\delta$  62.4 and no remaining boron trichloride. The  $^1\text{H}$  NMR indicated that no olefinic protons remained;  $^{13}\text{C}$  NMR in accord with the assigned structure; *m/e* calcd 218.0800, found 218.0779. This crude dichloroisopinocampheylborane was stirred and cooled with a  $0^\circ\text{C}$  bath during dropwise addition of a mixture of (+)- $\alpha$ -pinene (2.92 g, 21.4 mmol) and triethylsilane (2.49 g, 21.4 mmol). The mixture was then stirred at room temperature overnight. After 16 h, the  $^{11}\text{B}$  NMR spectrum indicated complete conversion to chlorodiisopinocampheylborane, which showed a broad peak at  $\delta$  76.0;  $^{13}\text{C}$  NMR in accord with the assigned structure; *m/e* calcd 320.2442, found 320.2440, which with hydrogen peroxide yielded isopinocampheol, mp  $54\text{--}56^\circ\text{C}$ ,  $[\alpha]^{23}_{\text{D}} -32.5^\circ$  (*c* 10, benzene) (lit.<sup>33</sup> mp  $57^\circ\text{C}$ ,  $[\alpha]^{20}_{\text{D}} -32.0^\circ$ ; lit.<sup>34</sup>  $[\alpha]^{27}_{\text{D}} -35.79^\circ$ ).

**Dichloro(1-hexenyl)borane (14) and 1,1-Bis(dichloroboryl)hexane (15).** A 4.3-g (36.6 mmol) portion

(33) Shin-Piaw, C. C. *R. Hebd. Seances Acad. Sci.* **1936**, 202, 127.

(34) Brown, H. C.; Mandal, A. K.; Yoon, N. M.; Singaram, B.; Schwier, J. R.; Jadhav, P. K. *J. Org. Chem.* **1982**, 47, 5069–5074. We thank a referee for calling our attention to this reference. Both the melting point and rotation (92.7% of theoretical) indicate that our sample contained some impurity. The 200 MHz NMR spectra available when this work was done were inadequate to reveal the nature of the impurity.

of boron trichloride was stirred at  $-78\text{ }^{\circ}\text{C}$  under argon during the dropwise addition of a mixture of 2.13 g (18.3 mmol) of triethylsilane and 1.50 g (18.3 mmol) of 1-hexyne from a syringe. The  $^{11}\text{B}$  NMR spectrum of this mixture showed major peaks in the ratio 1:1 at  $\delta$  53.15 corresponding to dichloro(1-hexenyl)borane and  $\delta$  46.9 corresponding to the unconsumed boron trichloride. Addition of a second 2.13-g portion of triethylsilane resulted in disappearance of the peak at  $\delta$  53.15 and appearance of a new peak at  $\delta$  60.83 characteristic of 1,1-bis(dichloroboryl)hexane, with only  $\sim 2\%$ – $3\%$  remaining  $\text{BCl}_3$  at  $\delta$  45.9. Distillation yielded 3.8 g (83%) of 1,1-bis(dichloroboryl)hexane, bp  $76\text{--}77\text{ }^{\circ}\text{C}$  (3 Torr). The structure was supported by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

**1,1-Bis(dichloroboryl)hexane (15).** A 2.2-g (18.72 mmol) portion of boron trichloride was stirred at  $-78\text{ }^{\circ}\text{C}$  under argon during the dropwise addition of a mixture of 2.18 g (18.72 mmol) of triethylsilane and 0.76 g (9.36 mmol) of 1-hexyne from a syringe. The  $^{11}\text{B}$  NMR spectrum of this mixture showed a peak at  $\delta$  60.3 characteristic of 1,1-bis(dichloroboryl)hexane, with some remaining  $\text{BCl}_3$  at  $\delta$  46. No (dichloro)(1-hexenyl)borane was detected at  $\delta$  53. The  $^1\text{H}$  NMR spectrum indicated complete conversion of the hexyne to saturated product.

**1,1-Bis[2-(1,2,3-dioxaborinyl)]hexane (16).** Treatment of 1,1-bis(dichloroboryl)hexane (550 mg, 2.2 mmol) with 1,3-propanediol (338 mg, 4.4 mmol) yielded 1,1-bis[2-(1,2,3-dioxaborinyl)]hexane (360 mg, 91%) as shown

by bp  $141\text{ }^{\circ}\text{C}$  (0.5 Torr) and by  $^1\text{H}$  NMR spectral data in good agreement with the literature values.<sup>18</sup>

**1,1-Diborylhexane Dimer [1,2-bis(hexylidene)-bis(diborane)] (17).** 1-Hexyne (0.84 g, 10.2 mmol) was mixed with trimethylsilane (1.51 g, 20.4 mmol) at  $-78\text{ }^{\circ}\text{C}$  and added via cannula to 2.4 g (20.4 mmol) of boron trichloride stirred at  $-78\text{ }^{\circ}\text{C}$ . When the addition was complete, the  $^{11}\text{B}$  NMR spectrum showed a broad singlet at  $\delta$  60.8 and less than 2% unreacted boron trichloride ( $\delta$  45.5). The mixture was allowed to warm to room temperature and the trimethylsilyl chloride was evaporated for 2 h at approximately 100 Torr. The resulting 1,1-bis(dichloroboryl)hexane was stirred at  $-78\text{ }^{\circ}\text{C}$  during the addition of 3.02 g (40.8 mmol) of trimethylsilane. After 10 min, the  $^{11}\text{B}$  NMR spectrum showed less than 2% 1,1-bis(dichloroboryl)hexane ( $\delta$  60.8) and a new peak at  $\delta$  25.8. When the spectrum was proton decoupled, this peak was a broad singlet, and when it was proton coupled, the absorption became broader but was not resolved. The mass spectrum (CI,  $\text{CH}_4$ ) showed  $m/e$  220.2827 for  $\text{C}_{12}\text{H}_{32}\text{B}_4$  (calcd, 220.2876).

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