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Ionic-Liquid-Promoted Decaborane Olefin-Hydroboration: A New Efficient Route to 6-R-$B_{10}H_{13}$ Derivatives

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Unlike in conventional organic solvents where transition metal catalysts are required, decaborane olefin-hydroboration reactions have been found to proceed in biphasic ionic-liquid/toluene mixtures with a wide variety of olefins, including alkyl, alkenyl, halo, phenyl, ether, ester, pinacolborane, ketone, and alcohol-substituted olefins, and these reactions now provide simple high-yield routes to 6-R-$B_{10}H_{13}$ derivatives. Best results were observed for reactions with bmimX (1-butyl-3-methylimidazolium, X = Cl^- or BF_4^-) and bmpyX (1-butyl-4-methylpyridinium, X = Cl^- or BF_4^-). Both the experimental data for these reactions and separate studies of the reactions of $B_{10}H_{13}^-$ salts with olefins indicate a reaction sequence involving (1) the ionic-liquid-promoted formation of the $B_{10}H_{13}^-$ anion as the essential initial step, (2) the addition of the $B_{10}H_{13}^-$ anion to the olefin to form a 6-R-$B_{10}H_{12}^-$ anion, and finally, (3) protonation of 6-R-$B_{10}H_{12}^-$ to form the final neutral 6-R-$B_{10}H_{13}$ product. The 6-R-$B_{10}H_{13}$ derivatives also undergo ionic-liquid-mediated dehydrogenative alkyne-insertion reactions in biphasic bmimCl/toluene mixtures, and these reactions provide high yield routes to 3-R-1,2-R'_2-1,2-$C_2B_{10}H_9$ *ortho*-carborane derivatives.

Introduction

In the preceding paper,[1] we demonstrated that decaborane dehydrogenative alkyne-insertion reactions proceed in ionic liquids with a wide variety of alkynes to give high yields of *ortho*-carborane products without the need of the added Lewis base catalyst that is required in conventional syntheses in organic solvents. In this paper, we describe complimentary studies of ionic-liquid-mediated decaborane olefin-hydroboration reactions that further illustrate the unique advantages of ionic liquids for activating polyborane reactions.

Decaborane is the most available polyborane, and its functionally substituted derivatives are potentially important in a number of applications[2,3] ranging from materials science (e.g., components in preceramic polymers) to medicine (e.g., boron neutron capture therapy). While Gaines[4,5] has reported excellent stoichiometric routes to 6-alkyl-$B_{10}H_{13}$ derivatives, these routes require multiple steps and are not suitable to produce complex functional derivatives. We have previously shown that platinum-[6] and titanium-catalyzed[7,8] decaborane olefin-hydroborations provide high yield routes to 6,9-R_2-$B_{10}H_{12}$ and 6-R-$B_{10}H_{13}$ derivatives, respectively. However, both the platinum- and titanium-catalyzed reactions are slow (typically less than one turnover per hour) and are also not useful for most functional olefins. While Wei has reported[9] an excellent route to many functional 6-R-$B_{10}H_{13}$ derivatives by utilizing the ruthenium-catalyzed metathesis reactions of 6-hexenyl-$B_{10}H_{13}$ with functional olefins, this sequence still requires the use of the slow titanium-catalyzed reaction of decaborane with 1,5-hexadiene to produce the key 6-hexenyl-$B_{10}H_{13}$ intermediate. Thus, there is still a need for the development of improved routes to more complex decaborane-derivatives.

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Recent reports that transition metal catalyzed hydrosilylation and monoborane-hydroborations of alkynes and alkenes can be carried out in ionic liquids[10] stimulated our initial interest[11] in the use of ionic liquids as noncoordinating solvents for the metal-catalyzed reactions of decaborane. We report in this paper the surprising result that when decaborane olefin-hydroboration reactions are carried out in ionic liquids, high yields of 6-R-$B_{10}H_{13}$ products are obtained *even in the absence of any metal catalysts.*

Experimental Section

General Synthetic Procedures and Materials. Unless otherwise noted, all reactions and manipulations were performed in dry glassware under nitrogen or argon atmospheres using the high-vacuum or inert-atmosphere techniques described by Shriver.[12]

$B_{10}H_{14}$ (Callery) was freshly sublimed prior to use. The $[Et_3NH^+][B_{10}H_{13}^-]$ and $[Bu_4N^+][B_{10}H_{13}^-]$ salts were prepared according to literature methods.[13] The 1-hexene, 1-octene, *cis*-4-octene, *trans*-4-octene, 1,7-octadiene, 2,5-dimethyl-2-hexene, 6-bromo-hexene, cyclohexene, *cis*-cyclooctene, allylbenzene, allyltrimethylsilane, styrene, allyl propyl ether, allyl benzyl ether, allyl alcohol, 5-hexen-2-one, norbornylene, 3-hexyne, allylboronic acid pinacol ester, and acetic acid 5-hexen-1-yl ester were purchased from Aldrich, TCI America, or Alfa Aesar, dried over CaH_2 or $MgSO_4$ as appropriate, and vacuum transferred prior to use. The ionic liquids, 1-butyl-3-methylimidazolium chloride [bmimCl], 1-butyl-3-methylimidazolium bromide [bmimBr], 1-butyl-4-methylpyridinium chloride [bmpyCl], 1-butyl-3-methylimidazolium tetrafluoroborate [$bmimBF_4$], 1-butyl-4-methylpyridinium tetrafluoroborate [$bmpyBF_4$], 1-butyl-3-methylimidazolium phosphorus hexafluoride [$bmimPF_6$], 1-ethyl-3-methylimidazolium chloride [emimCl], 1-butyl-2,3-dimethylimidazolium chloride [bdmimCl], 1-butyl-3-methylimidazolium acetate [bmimOAc], 1-butyl-3-methylimidazolium trifluoromethanesulfonate [bmimOTf], 1-ethyl-2,3-dimethylimidazolium ethyl sulfate [$emimEtSO_4$], 1,3-dimethylimidazolium methyl sulfate [$dmimMeSO_4$], and tetrabutylammonium methanesulfonate [$TBAMeSO_3$], were from Fluka. 1-Butyl-3-methylimidazolium iodide [bmimI] was from EMD Chemicals Inc. Two additional samples of $bmimBF_4$ with different chloride contents were obtained from (a) Aldrich-Fluka (catalysis grade, assay purity ≥98.5%) and (b) Alfa-Aesar (assay purity 98%+). The bis(triphenylphosphoranylidene) ammonium chloride [PPNCl], *N*,*N*,*N*′,*N*′-tetramethyl-1,8-naphthalenediamine [Proton Sponge], 2,6-dimethylpyridine, Me_4NF, Me_4NBF_4, Et_4NBF_4, Bu_4NCl, Bu_4NPF_6, Bu_4NBF_4, Bu_4NSCN, $NaBF_4$, NH_4BF_4, $NaHSO_4$, CH_3COONa, NaF, NaCl, and C_6H_5COOH (Aldrich) were used as received. All ionic liquids and Bu_4NF, tetrabutylammonium fluoride [TBAF] (Aldrich), were dried by carrying out an azeotropic distillation with toluene, followed by heating overnight under high-vacuum and storage in a dry box. Toluene, glyme (ethylene glycol dimethyl ether), and hexanes were dried by passing them through an activated alumina column prior to use. HPLC or ACS grade hexanes, toluene, Et_2O, CH_2Cl_2, NEt_3, and silica gel (Fisher) were used as received. $CDCl_3$ (D, 99.5%), C_6D_6 (D, 99.5%), and CD_2Cl_2 (D, 99.9%) (Cambridge Isotope) were used as received.

Physical Measurements. ^{1}H NMR at 400.1 MHz and ^{11}B NMR spectra at 128.4 MHz were obtained on a Bruker DMX 400 spectrometer. All ^{11}B NMR chemical shifts are referenced to external $BF_3 \cdot OEt_2$ (0.00 ppm) with a negative sign indicating an upfield shift. All ^{1}H chemical shifts were measured relative to residual protons in the lock solvents and are referenced to Me_4Si (0.00 ppm). High- and low-resolution mass spectra (HRMS and LRMS) using negative chemical ionization (NCI) techniques were recorded on a Micromass Autospec Spectrometer. Infrared spectra were recorded on a Perkin-Elmer Spectrum 100 FT-IR spectrometer using KBr pellets or NaCl plates and are listed in Table S1, Supporting Information. Elemental analyses were performed at Robertson Microlit Laboratories, Madison, NJ. Melting points were obtained on a standard melting point apparatus and are uncorrected.

Reaction of $B_{10}H_{14}$ and an Olefin in the Absence of an Ionic Liquid. A 10 mL, 2-neck round-bottom flask equipped with a septum and stir bar was charged with 0.122 g (1.0 mmol) of $B_{10}H_{14}$, 0.5 g (4.1 mmol) of 1-octene, and ~2 mL of toluene. The flask was attached to a water condenser open to argon, and the body of the flask was then submerged in a 125 °C oil bath equipped with a magnetic stir plate. After the mixture was stirred vigorously for ~8.0 h, ^{11}B NMR analysis of the toluene layer showed only unreacted $B_{10}H_{14}$.

General Experimental Procedure for Hydroboration Reactions. A 25 mL, 2-neck round-bottom flask equipped with a septum, stir bar, and vacuum adapter was charged in a dry box with an ionic liquid, inorganic salt, or nitrogen base. The flask was sealed, taken out of the box and then charged under Ar with the indicated amounts of $B_{10}H_{14}$, olefin, and ~3−4 mL of solvent (toluene or dichloroethane). Using the vacuum adapter, the flask was attached to a water condenser open to argon, and the body of the flask then submerged in a hot oil bath (typically at 85−140 °C, as indicated) equipped with a magnetic stir plate. The reactions were vigorously stirred to form an emulsion. The reaction was monitored by ^{11}B NMR analysis of the toluene layer and stopped when all starting decaborane had been consumed. The top organic-layer of the reaction mixture was separated by pipet. The ionic liquid layer was then extracted multiple times with ether. The combined organic solutions were vacuum concentrated and then flash-filtered through a silica gel column.

6-R-$B_{10}H_{13}$ Syntheses in Ionic Liquids. 6-[$CH_3(CH_2)_7$]-$B_{10}H_{13}$ (1). Reaction of 0.611 g (5.0 mmol) of $B_{10}H_{14}$ with 2.0 g (17.8 mmol) of 1-octene in biphasic toluene (~4 mL)/bmimCl (0.175 g, 1.0 mmol) at 125 °C for ~12 h gave, following elution with a 1:1 hexanes/toluene eluent from a silica gel column, 1.05 g (4.5 mmol, 90% yield) of **1** as an oily liquid. GC/MS analysis of the oil showed **1** as the only product. NCI-HRMS (*m*/*e*) calcd (M)$^-$ for $^{12}C_8{}^{11}B_{10}{}^{1}H_{30}$: 236.3278; found 236.3289. Anal. Calcd: C, 40.99; H, 12.90. Found: C, 41.67; H, 11.15. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 25.5 (s, 1, B6), 9.7 (d, 2, B1,3), 8.0 (d, 1, B9), 0.5 (d, 2, B5,7), −3.4 (d, 2, B8,10), −34.4 (d, 1, B2), −39.3 (d, 1, B4). ^{1}H NMR (400.1 MHz, $CDCl_3$, ppm): δ 1.55 (m, 2, CH_2), 1.29 (m, 12, CH_2), 0.89 (t, 3, CH_3), −1.68 (br, s, 2, B*H*B), −2.04 (br, s, 2, B*H*B).

Reaction of 0.611 g (5.0 mmol) of $B_{10}H_{14}$ with 2.0 g (17.8 mmol) of 1-octene in biphasic toluene (~4 mL)/$bmpyBF_4$ (2.5 g, 10.5 mmol) at 140 °C for ~11 h gave 1.03 g (4.4 mmol, 88% yield) of **1**. As summarized in Table S2, Supporting Information, another 4 cycles of reaction and product isolation following periodic additions over 57 h of new mixtures of 0.611 g of $B_{10}H_{14}$, 2.0 g of 1-octene,

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and 4 mL of toluene to the reaction flask containing the used bmpyBF_4 produced a total of 3.9 g (16.7 mmol, 83.5%) of **1**.

The reactions of 0.122 g (1.0 mmol) of $B_{10}H_{14}$ with 0.5 g (4.5 mmol) of 1-octene at 140 °C for ~13.3 h in a biphasic mixture of toluene (~3 mL) and 0.5 g (2.2 mmol) of either (1) Alfa-Aesar 98%+ (chloride content not reported) bmimBF_4 or (2) Fluka "catalytic grade" (~10 ppm Cl) bmimBF_4, gave comparable yields of **1**, 0.20 g (0.85 mmol, 85% yield) and 0.20 g (0.85 mmol, 85% yield), respectively.

Reactions carried out with identical amounts of decaborane and 1-octene in the presence of other ionic-liquids, salts, or conditions are compared in Table S3, Supporting Information.

6-[$(CH_3)_3Si(CH_2)_3$]-$B_{10}H_{13}$ (2). Reaction of 0.49 g (4.0 mmol) of $B_{10}H_{14}$ with 1.5 g (13.1 mmol) of allyltrimethylsilane in biphasic toluene (~3 mL)/bmimCl (0.14 g, 0.8 mmol) at 125 °C for ~11 h gave, following elution with a 1:1 hexanes/toluene eluent from a silica gel column, 0.84 g (3.6 mmol, 89% yield) of **2** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_6{}^{11}B_{10}{}^1H_{28}{}^{28}Si_1$: 238.2891; found 238.2895. Anal. Calcd: C, 30.47; H, 11.93. Found: C, 30.94; H, 12.10. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 25.6 (s, 1, B6), 9.5 (d, 2, B1,3), 8.2 (d,1, B9), 0.4 (d, 2, B5,7), −3.3 (d, 2, B8,10), −34.4 (d, 1, B2), −39.2 (d, 1, B4). $^1H\{^{11}B\}$NMR (400.1 MHz, $CDCl_3$, ppm): δ 1.56 (m, 2, CH_2), 1.18 (m, 2, CH_2), 0.61 (m, 2, CH_2), 0.07 (s, 9, CH_3), −1.68 (br, s, 2, B*H*B), −2.02 (br, s, 2, B*H*B).

Reaction of 0.49 g (4.0 mmol) of $B_{10}H_{14}$ with 1.5 g (13.1 mmol) of allyltrimethylsilane in biphasic toluene (~3 mL)/Bu_4NF (0.174 g, 0.67 mmol) at 125 °C for ~3.3 h gave 0.86 g (3.64 mmol, 91% yield) of **2**.

6-[$CH_2{=}CH(CH_2)_6$]-$B_{10}H_{13}$ (3). Reaction of 0.611 g (5.0 mmol) of $B_{10}H_{14}$ with 2.0 g (18.1 mmol) of 1,7-octadiene in biphasic toluene (~4 mL)/bmimCl (0.175 g, 1.0 mmol) at 125 °C for ~12 h gave, following elution with a 3:1 hexanes/toluene eluent from a silica gel column, 1.03 g (4.4 mmol, 89% yield) of **3** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_8{}^{11}B_{10}{}^1H_{28}$: 234.3122; found 234.3125. Anal. Calcd: C, 41.34; H, 12.14. Found: C, 41.28; H, 12.07. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 25.5 (s, 1, B6), 9.8 (d, 2, B1,3), 8.0 (d,1, B9), −0.5 (d, 2, B5,7), −3.4 (d, 2, B8,10), −34.5 (d, 1, B2), −39.3 (d, 1, B4). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 5.86 (m, 1, =CH-), 5.05 (m, 2, CH_2=), 2.12 (m, 2, CH_2), 1.61 (m, 2, CH_2), 1.42 (m, 8, CH_2), −1.63 (br, s, 2, B*H*B), −1.97 (br, s, 2, B*H*B).

Reaction of 0.611 g (5.0 mmol) of $B_{10}H_{14}$ with 2.0 g (18.1 mmol) of 1,7-octadiene in a biphasic mixture of toluene (~4 mL), Bu_4NF (0.22 g, 0.83 mmol) and bmimOTf (1.0 g, 3.5 mmol) at 125 °C for ~3.3 h gave 1.05 g (4.5 mmol, 90% yield) of **3**. As summarized in Table S4, Supporting Information, another 4 cycles of reaction and product isolation following periodic additions over 54 h of new mixtures of 0.611 g (5.0 mmol) of $B_{10}H_{14}$, 2.0 g (18.1 mmol) of 1,7-octadiene and 4 mL of toluene to the reaction flask containing the used Bu_4NF/bmimOTf mixture, produced 4.16 g (17.4 mmol, 87.0%) of **3**.

6-[$CH_3C(O)O(CH_2)_6$]-$B_{10}H_{13}$ (4). Reaction of 0.49 g (4.0 mmol) of $B_{10}H_{14}$ with 1.5 g (10.5 mmol) of acetic acid 5-hexen-1-yl ester in biphasic toluene (~3 mL)/bmimCl (0.14 g, 0.8 mmol) at 125 °C for ~12 h gave, following elution with a 2:1 hexanes/toluene eluent from a silica gel column and drying on a high-vacuum line overnight at ~125 °C, 0.95 g (3.6 mmol, 90% yield) of **4** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_8{}^{11}B_{10}{}^1H_{28}{}^{16}O_2$: 266.3020, found 266.3026. Anal. Calcd: C, 36.34; H, 10.67. Found: C, 35.43; H, 10.83. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 25.3 (s, 1, B6), 9.8 (d, 2, B1,3), 8.1 (d,1, B9), 0.4 (d, 2, B5,7), −3.4 (d, 2, B8,10), −34.5 (d, 1, B2), −39.3 (d, 1, B4). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 4.07 (t, 2, $-OCH_2-$), 2.05 (s, 3, CH_3), 1.65 (m, 2, CH_2), 1.55 (m, 2, CH_2), 1.39 (m, 6, CH_2), −1.68 (br, s, 2, B*H*B), −2.02 (br, s, 2, B*H*B).

Reaction of 0.49 g (4.0 mmol) of $B_{10}H_{14}$ with 1.5 g (10.5 mmol) of acetic acid 5-hexen-1-yl ester in biphasic toluene (~3 mL)/Bu_4NF (0.174 g, 0.67 mmol) at 125 °C for ~3.3 h gave 0.97 g (3.7 mmol, 92% yield) of **4**.

6-[$CH_3(CH_2)_2O(CH_2)_3$]-$B_{10}H_{13}$ (5). Reaction of 0.366 g (3.0 mmol) of $B_{10}H_{14}$ with 1.5 g (15.0 mmol) of allyl propyl ether in biphasic toluene (~3 mL)/bmimCl (0.105 g, 0.6 mmol) at 125 °C for ~45 h gave, following toluene elution from a silica gel column, 0.47 g (2.1 mmol, 70% yield) of **5** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_6{}^{11}B_{10}{}^1H_{26}{}^{16}O_1$: 224.2914; found 224.2910. Anal. Calcd: C, 32.41; H, 11.78. Found: C, 33.05; H, 11.71. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 26.4 (s, 1, B6), 8.7 (d, 2, B1,3), 7.0 (d,1, B9), 0.1 (d, 2, B5,7), −5.0 (d, 2, B8,10), −33.8 (d, 1, B2), −39.7 (d, 1, B4). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 3.43 (t, 2, CH_3), 3.27 (t, 2, CH_2), 1.80 (m, 2, CH_2), 1.53 (m, 2, CH_2), 1.45 (m, 2, CH_2), 0.87 (t, 3, CH_3) −1.31 (br, s, 2, B*H*B), −2.13 (br, s, 2, B*H*B).

6-[$C_6H_5(CH_2)O(CH_2)_3$]-$B_{10}H_{13}$ (6). Reaction of 0.366 g (3.0 mmol) of $B_{10}H_{14}$ with 0.90 g (6.1 mmol) of allyl benzyl ether in biphasic toluene (~4 mL)/bmimCl (0.105 g, 0.6 mmol) at 125 °C for ~40 h gave, following toluene elution from a silica gel column and drying on a high-vacuum line overnight at ~125 °C, 0.60 g (2.2 mmol, 74% yield) of **6** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M - H)^-$ for $^{12}C_{10}{}^{11}B_{10}{}^1H_{26}{}^{16}O_1$: 271.2835; found 271.2827. Anal. Calcd: C, 44.42; H, 9.69. Found: C, 45.10; H, 9.87. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 26.6 (s, 1, B6), 8.7 (d, 2, B1,3), 7.1 (d,1, B9), 0.02 (d, 2, B5,7), −3.6 (d, 2, B8,10), −33.8 (d, 1, B2), −39.5 (d, 1, B4). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 7.34 (m, 5, C_6H_5-), 4.34 (s, 2, CH_2), 3.55 (t, 2, CH_2), 1.85 (m, 2, CH_2), 1.56 (m, 2, CH_2), −1.50 (br, s, 2, B*H*B), −2.27 (br, s, 2, B*H*B).

Reaction of 0.366 g (3.0 mmol) of $B_{10}H_{14}$ with 1.0 g (6.7 mmol) of allyl benzyl ether in biphasic toluene (~4 mL)/Bu_4NF (0.13 g, 0.5 mmol) at 125 °C for ~6.3 h gave 0.63 g (2.3 mmol, 77% yield) of **6**.

6-[$HO(CH_2)_3$]-$B_{10}H_{13}$ (7). Reaction of 0.366 g (3.0 mmol) of $B_{10}H_{14}$ with 0.5 g (8.6 mmol) of allyl alcohol in biphasic toluene (~3 mL)/bmimCl (0.105 g, 0.6 mmol) at 125 °C for ~7 h gave, following CH_2Cl_2 elution from a silica gel column, 0.325 g (1.8 mmol, 55% yield) of **7** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M - H)^-$ for $^{12}C_3{}^{11}B_{10}{}^1H_{20}{}^{16}O_1$: 181.2366, found 181.2361. Anal. Calcd: C, 19.98; H, 11.18. Found: C, 20.15; H, 11.40. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 25.0 (s, 1, B6), 9.2 (d, 2, B1,3), 7.5 (d,1, B9), −0.1 (d, 2, B5,7), −3.9 (d, 2, B8,10), −35.0 (d, 1, B2), −39.8 (d, 1, B4). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 3.79 (m, 2, CH_2), 1.81 (s, 1, OH), 1.58−1.53 (m, 2, CH_2), 1.3 (m, 2, CH_2), −1.67 (br, s, 2, B*H*B), −2.02 (br, s, 2, B*H*B).

6-[$(CH_3)_4C_2O_2B(CH_2)_3$]-$B_{10}H_{13}$ (8). Reaction of 0.366 g (3.0 mmol) of $B_{10}H_{14}$ with 1.5 g (8.9 mmol) of allylboronic acid pinacol ester (2-allyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) in biphasic toluene (~3 mL)/bmimCl (0.105 g, 0.6 mmol) at 125 °C for ~9.0 h gave, following elution with a 1:1 hexanes/toluene eluent mixture from a silica gel column and drying on a high-vacuum line overnight at ~125 °C, 0.78 g (2.7 mmol, 90% yield) of **8** as an oil. NCI-HRMS (*m*/*e*) calcd $(M - H)^-$ for $^{12}C_9{}^{11}B_{11}{}^1H_{31}{}^{16}O_2$: 291.3269; found 291.3265. Anal. Calcd: C, 37.24; H, 10.76. Found: C, 36.59; H, 11.14. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 33.0 (s, 1, O−B−O), 25.3 (s, 1, B6), 9.8 (d, 2, B1,3), 8.0 (d,1, B9), 0.5 (d, 2, B5,7), −3.2 (d, 2, B8,10), −34.4 (d, 1, B2), −39.2 (d, 1, B4).

^{1}H{^{11}B} NMR (400.1 MHz, CDCl$_3$, ppm): δ 1.67 (m, 2, CH$_2$), 1.43 (m, 2, CH$_2$), 1.25 (s, 12, CH$_3$), 0.86 (m, 2, CH$_2$), −1.68 (br, s, 2, B*H*B), −2.03 (br, s, 2, B*H*B).

6-((exo)-Bicyclo-[2,2,1]-hept-2-yl)-B$_{10}$H$_{13}$ (9). Reaction of 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 1.0 g (10.6 mmol) of norbornylene in biphasic toluene (~3 mL)/bmimCl (0.105 g, 0.6 mmol) at 125 °C for ~10.3 h gave, following elution with a 1:3 hexanes/toluene eluent from a silica gel column, 0.55 g (2.55 mmol, 85% yield) of **9** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M − H)$^-$ for ^{12}C$_7$^{11}B$_{10}$^{1}H$_{24}$: 217.2730; found 217.2726. Anal. Calcd: C, 38.86; H, 11.18. Found: C, 38.30; H, 11.46. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm): δ 27.0 (s, 1, B6), 9.1 (d, 2, B1,3), 7.5 (d,1, B9), 0.1 (d, 2, B5,7), −4.6 (d, 2, B8,10), −35.0 (d, 1, B2), −39.7 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, CDCl$_3$, ppm): δ 2.33 (m, 2, CH), 1.61 (m, 4, CH), 1.44 (m, 2, CH), 1.28 (m, 2, CH), 0.92 (m, 1, CH), −1.62 (br, s, 2, B*H*B), −2.03 (br, s, 2, B*H*B).

6-[CH$_3$(CH$_2$)$_5$]-B$_{10}$H$_{13}$ (10). Reaction of 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 2.0 g (23.8 mmol) of 1-hexene in biphasic toluene (~4 mL)/Bu$_4$NF (0.13 g, 0.5 mmol) at 125 °C for ~14 h gave, following elution with a 3:1 hexanes/toluene eluent from a silica gel column, 0.50 g (2.4 mmol, 80% yield) of **10** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M)$^-$ for ^{12}C$_6$^{11}B$_{10}$^{1}H$_{26}$: 208.2965; found 208.2966. Anal. Calcd: C, 34.92; H, 12.70. Found: C, 34.86; H, 13.16. ^{11}B{^{1}H} NMR (128.4 MHz, CDCl$_3$, ppm): δ 25.5 (s, 1, B6), 9.7 (d, 2, B1,3), 7.9 (d,1, B9), 0.4 (d, 2, B5,7), −3.4 (d, 2, B8,10), −34.5 (d, 1, B2), −39.4 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, CDCl$_3$, ppm): δ 1.54 (m, 2, CH$_2$), 1.35 (m, 8, CH$_2$), 0.90 (t, 3, CH$_3$), −1.68 (br, s, 2, B*H*B), −2.03 (br, s, 2, B*H*B).

6-[2,5-(CH$_3$)$_2$-Hex-3-yl]-B$_{10}$H$_{13}$ (11). Reaction of 0.367 g (3.0 mmol) of B$_{10}$H$_{14}$ with 1.5 g (13.4 mmol) of 2,5-dimethyl-2-hexene in biphasic toluene (~3 mL)/bmpyBF$_4$ (1.5 g, 6.3 mmol) at 140 °C for ~13 h gave, following elution with a 3:1 hexanes/toluene eluent from a silica gel column, 0.60 g (2.6 mmol, 85% yield) of **11** as an light yellow oily liquid. GC/MS analysis showed **11** as the only product. NCI-HRMS (*m*/*e*) calcd (M)$^-$ for ^{12}C$_8$^{11}B$_{10}$^{1}H$_{30}$, 236.3278, found 236.3280. Anal. Calcd: C, 40.99; H, 12.90. Found: C, 41.20; H, 12.95. ^{11}B NMR (128.4 MHz, C$_6$D$_6$, ppm): δ 26.3 (s, 1, B6), 10.6 (d, 2, B1,3), 7.9 (d, 1, B9), 1.1 (d, 2, B5,7), −3.0 (d, 2, B8,10), −34.1 (d, 1, B2), −38.6 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, C$_6$D$_6$, ppm): δ 2.2 (m, 1, CH), 1.72 (m, 1, CH), 1.43 (m, 3, CHCH$_3$), 1.08 (d, 12, CH$_3$), −1.79 (br, s, 2, B*H*B), −2.25 (br, s, 2, B*H*B).

6-[Br(CH$_2$)$_6$]-B$_{10}$H$_{13}$ (12). Reaction of 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 1.5 g (9.2 mmol) of 6-bromo-1-hexene in biphasic toluene (~3 mL)/bmpyBF$_4$ (1.5 g, 6.3 mmol) at 140 °C for ~13 h gave, following elution with a 1:1 hexanes/toluene eluent from a silica gel column and drying on a high-vacuum line overnight at ~125 °C, 0.73 g (2.6 mmol, 85% yield) of **12** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M − H)$^-$ for ^{12}C$_6$^{11}B$_{10}$^{1}H$_{25}$^{81}Br$_1$: 285.1992; found 285.1998. Anal. Calcd: C, 25.26; H, 8.83. Found: C, 25.72; H, 8.94. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm): δ 25.3 (s, 1, B6), 9.8 (d, 2, B1,3), 8.1 (d,1, B9), 0.5 (d, 2, B5,7), −3.3 (d, 2, B8,10), −34.5 (d, 1, B2), −39.2 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, CDCl$_3$, ppm): δ 3.42 (t, 2, CH$_2$−Br), 1.88 (m, 2, CH$_2$), 1.59 (m, 2, CH$_2$), 1.43 (m, 6, CH$_2$), −1.68 (br, s, 2, B*H*B), −2.02 (br, s, 2, B*H*B).

6-[C$_6$H$_5$(CH$_2$)$_2$]-B$_{10}$H$_{13}$ (13). Reaction of 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 0.70 g (6.7 mmol) of inhibitor-free styrene in biphasic toluene (~4 mL)/bmpyBF$_4$ (2.0 g, 8.4 mmol) at 140 °C for ~17 h gave, following toluene elution from a silica gel column and drying on a high-vacuum line overnight at ~125 °C, 0.51 g (2.3 mmol, 75% yield) of **13** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M − H)$^-$ for ^{12}C$_8$^{11}B$_{10}$^{1}H$_{22}$: 227.2573; found 227.2570. Anal. Calcd: C, 42.45; H, 9.80. Found: C, 42.77; H, 10.14. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm): δ 24.5 (s, 1, B6), 9.6 (d, 2, B1,3), 7.7 (d, 1, B9), 0.3 (d, 2, B5,7), −3.5 (d, 2, B8,10), −34.5 (d, 1, B2), −39.3 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, CDCl$_3$, ppm): δ 7.29 (m, 5, C$_6$H$_5$), 3.02 (t, 2, CH$_2$), 1.43 (m, 2, CH$_2$), −1.80 (br, s, 2, B*H*B), −2.15 (br, s, 2, B*H*B).

6-[C$_6$H$_5$(CH$_2$)$_3$]-B$_{10}$H$_{13}$ (14). Reaction of 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 0.75 g (6.3 mmol) of allylbenzene in biphasic toluene (~3 mL)/bmpyBF$_4$ (1.5 g, 6.3 mmol) at 140 °C for ~13 h gave, following elution with a 1:1 hexanes/toluene eluent from a silica gel column and drying on a high-vacuum line overnight at ~125 °C, 0.62 g (2.6 mmol, 86% yield) of **14** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M)$^-$ for ^{12}C$_9$^{11}B$_{10}$^{1}H$_{24}$: 242.2809; found 242.2803. Anal. Calcd: C, 44.97; H, 10.06. Found: C, 45.16; H, 10.52. ^{11}B NMR (128.4 MHz, C$_6$D$_6$, ppm): δ 25.4 (s, 1, B6), 10.7 (d, 2, B1,3), 8.4 (d,1, B9), 0.1 (d, 2, B5,7), −2.7 (d, 2, B8,10), −33.4 (d, 1, B2), −38.0 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, C$_6$D$_6$, ppm): δ 7.13 (m, 5, C$_6$H$_5$), 2.42 (t, 2, CH$_2$), 1.68 (m, 2, CH$_2$), 1.06 (m, 2, CH$_2$), −2.30 (br, s, 2, B*H*B), −2.67 (br, s, 2, B*H*B).

6-[CH$_3$C(O)(CH$_2$)$_4$]-B$_{10}$H$_{13}$ (15). Reaction of 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 1.0 g (10.2 mmol) of 5-hexen-2-one in biphasic toluene (~3 mL)/bmpyBF$_4$ (1.5 g, 6.3 mmol) at ~140 °C for ~7.3 h gave, following toluene elution from a silica gel column, 0.463 g (2.1 mmol, 70% yield) of **15** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M)$^-$ for ^{12}C$_6$^{11}B$_{10}$^{1}H$_{24}$^{16}O$_1$: 222.2757; found 222.2756. Anal. Calcd: C, 32.7; H, 10.98. Found: C, 33.10; H,11.10. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm): δ 25.1 (s, 1, B6), 9.8 (d, 2, B1,3), 8.4 (d, 1, B9), 0.5 (d, 2, B5,7), −3.3 (d, 2, B8,10), −34.4 (d, 1, B2), −39.0 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, CDCl$_3$, ppm): δ 2.46 (t, 2, C*H$_2$*-CO), 2.14 (s, 3, CH$_3$), 1.59 (m, 4, CH$_2$), 1.38 (m, 2, CH$_2$), −1.65 (br, s, 2, B*H*B), −1.95 (br, s, 2, B*H*B).

6-[C$_8$H$_{15}$]-B$_{10}$H$_{13}$ (16). Reaction of 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 0.75 g (6.8 mmol) of *cis*-cyclooctene in biphasic toluene (~3 mL)/bmpyBF$_4$ (1.5 g, 6.3 mmol) at ~140 °C for ~4.0 h gave, following elution with a 3:1 hexanes/toluene eluent from a silica gel column and drying on a high-vacuum line overnight at ~125 °C, 0.62 g (2.7 mmol, 89% yield) of **16** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M)$^-$ for ^{12}C$_8$^{11}B$_{10}$^{1}H$_{28}$: 233.3043; found 233.3033. Anal. Calcd: C, 41.34; H, 12.14. Found: C, 41.31; H, 12.33. ^{11}B NMR (128.4 MHz, CDCl$_3$, ppm): δ 28.0 (s, 1, B6), 9.6 (d, 2, B1,3), 7.9 (d,1, B9), 0.5 (d, 2, B5,7), −4.0 (d, 2, B8,10), −34.8 (d, 1, B2), −39.3 (d, 1, B4). ^{1}H{^{11}B} NMR (400.1 MHz, CDCl$_3$, ppm): δ 1.90 (m, 1, CH), 1.74 (m, 4, CH$_2$), 1.55 (m, 10, CH$_2$), −1.66 (br, s, 2, B*H*B), −2.04 (br, s, 2, B*H*B).

6-R-B$_{10}$H$_{13}$ Syntheses in the Presence of Chloride or Acetate Anions. The reactions of separate samples of 0.244 g (2.0 mmol) of B$_{10}$H$_{14}$ with 1.0 g (8.9 mmol) of 1-octene in toluene (~3 mL) at 125 °C in the presence of (1) Bu$_4$NCl (0.11 g, 0.4 mmol, 10.3 h) and (2) bmpyCl (0.074 g, 0.6 mmol, 12 h) gave 0.41 (1.7 mmol, 88% yield) and 0.42 g (1.8 mmol, 89% yield), respectively, of **1**. In a similar manner, the reactions of (1) 0.366 g (3.0 mmol) of B$_{10}$H$_{14}$ with 1.5 g (13.1 mmol) of 1-octene in biphasic toluene (~3 mL)/PPNCl (3.44 g, 0.6 mmol) at 125 °C for ~17.3 h gave 0.36 g (1.53 mmol, 51% yield) of **1**; (2) 0.244 g (2.0 mmol) of B$_{10}$H$_{14}$ with 1.0 g (8.9 mmol) of 1-octene in a biphasic mixture of toluene (~4 mL), NaOAc (0.033 g, 0.4 mmol), and bmimPF$_6$ (1.0 g, 3.5 mmol) at 125 °C for ~10.0 h gave 0.38 g (1.6 mmol, 80% yield) of **1**; and (3) 0.244 g (2.0 mmol) of B$_{10}$H$_{14}$ with 1.0 g (8.9 mmol) of 1-octene in a biphasic mixture of toluene (~4 mL), bmimOAc (0.08 g, 0.4 mmol), and bmimOTf (1.0 g, 3.5 mmol) at 125 °C for ~18 h gave 0.38 g (1.6 mmol, 80% yield) of **1**.

Reaction of $B_{10}H_{14}$ with 1-Octene in bmimCl in the Presence of Acids. The reaction at 125 °C of separate samples of 0.122 g (1.0 mmol) of $B_{10}H_{14}$ with ~0.5 g (4.5 mmol) of 1-octene in biphasic toluene (~3 mL)/bmimCl (0.035 g, 0.2 mmol) containing: (1) 0.024 g (0.2 mmol) (22.3 h) of $NaHSO_4$, $pK_a = 1.92$, and (2) 0.025 g (0.2 mmol) (12.3 h) of C_6H_5COOH, $pK_a = 4.2$, gave 0.19 (0.82 mmol, 82% yield) and 0.20 g (0.86 mmol, 86% yield), respectively, of **1**. Likewise, heating 0.122 g (1.0 mmol) of $B_{10}H_{14}$ and ~0.5 g (4.5 mmol) of 1-octene in biphasic toluene (~3 mL)/bmimCl (0.035 g, 0.2 mmol) for 8 h at 125 °C while bubbling anhydrous HCl through the biphasic mixture, resulted in no reaction.

6-R-$B_{10}H_{13}$ Syntheses via $B_{10}H_{13}^-$ Salts. These reactions were carried out in the manner described in the general procedure except that once the organic (toluene or DCE) layer was separated by pipet, it was cooled at 0 °C and then acidified by the dropwise addition of ~0.5 mL of concentrated H_2SO_4. The organic layer was separated by pipet from the aqueous layer, and following multiple extractions of the aqueous layer using ether, the combined organic solutions were vacuum concentrated and then flash filtered through a silica gel column using a 1:1 hexanes/toluene eluent.

From $[Et_3NH^+][B_{10}H_{13}^-]$. ^{11}B NMR analyses showed that heating at 90 °C separate solutions of 0.447 g (2.0 mmol) of $[Et_3NH^+][B_{10}H_{13}^-]$ in 4 mL of DCE with (1) ~1.0 mL (8.9 mmol) of 1-octene (2.3 h) and (2) 1.0 g (8.9 mmol) of 2,5-dimethyl-2-hexene (3 h) produced (1) mixtures of 6-$[CH_3(CH_2)_7]$-$B_{10}H_{13}$ **1** and its conjugate anion 6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$ and (2) mixtures of 6-[2,5-$(CH_3)_2$-hex-3-yl]-$B_{10}H_{13}$ **11** and it conjugate anion 6-[2,5-$(CH_3)_2$-hex-3-yl]-$B_{10}H_{12}^-$, respectively. Following acidification and purification, 0.40 g (1.7 mmol, 85% yield) of **1** and 0.30 g (1.3 mmol, 65% yield) of **11** were obtained.

From $[Bu_4N^+][B_{10}H_{13}^-]$. Reaction of 0.73 g (2.0 mmol) of $[Bu_4N^+][B_{10}H_{13}^-]$ with ~1.0 mL (8.9 mmol) of 1-octene in ~4 mL of DCE at 90 °C for 2.3 h yielded a solution containing only the 6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$ anion. Acidification and separation gave 0.40 g (1.7 mmol, 85% yield) of **1**.

Via In Situ Generation of $[Et_3NH^+][B_{10}H_{13}^-]$ or $[PSH^+]$-$[B_{10}H_{13}^-]$. Separate reactions at 90 °C of mixtures of 0.366 g (3.0 mmol) of $B_{10}H_{14}$, toluene (~3 mL) and Et_3N (0.12 g, 1.2 mmol) with (1) 1.5 g (13.1 mmol) of 1-octene (6 h), (2) 1.5 g (13.1 mmol) of allyltrimethylsilane (5 h), (3) 1.0 g (7.0 mmol) of acetic acid 5-hexen-1-yl ester (6 h), and (4) 1.0 g (8.9 mmol) of 2,5-dimethyl-2-hexene (8 h) gave (1) 0.63 g (2.7 mmol, 89% yield) of 6-$[CH_3(CH_2)_7]$-$B_{10}H_{13}$ (**1**), (2) 0.56 g (2.4 mmol, 80% yield) of 6-$[(CH_3)_3Si(CH_2)_3]$-$B_{10}H_{13}$ (**2**), (3) 0.51 g (1.92 mmol, 64% yield) of 6-$[CH_3C(O)O(CH_2)_6]$-$B_{10}H_{13}$ (**4**), and (4) 0.47 g (2.0 mmol, 67% yield) of 6-[2,5-$(CH_3)_2$-hex-3-yl]-$B_{10}H_{13}$ (**11**), respectively.

Reaction of 0.366 g (3.0 mmol) of $B_{10}H_{14}$ with 1.5 g (13.1 mmol) of 1-octene and (0.26 g, 1.2 mmol) of Proton Sponge in toluene (~3 mL) at 90 °C for ~6 h gave 0.60 g (2.6 mmol, 85% yield) of **1**.

Reaction of 6-$[CH_3(CH_2)_7]$-$B_{10}H_{13}$ (1) with 1-Octene in bmimCl/toluene. ^{11}B NMR analysis of the reaction solution showed that no reaction took place when a mixture of 0.23 g (1.0 mmol) of **1** and 0.5 g (4.5 mmol) of 1-octene was heated in biphasic toluene (~3 mL)/bmimCl (0.035 g, 0.02 mmol) at 125 °C for 8 h.

Reactions of $[Bu_4N^+]$[6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$] and $[Et_3NH^+]$-[6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$] with 1-Octene and 3-Hexyne. ^{11}B NMR analysis showed that no reactions had occurred after heating at 90 °C for 1.3 h separate samples of 0.24 g (0.5 mmol) of $[Bu_4N^+]$[6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$] in ~3 mL of toluene with either (1) ~0.5 mL (4.5 mmol) of 1-octene or (2) ~0.4 mL (5 mmol) of 3-hexyne. Likewise, ^{11}B NMR analysis showed that there was no reaction with either the olefin or alkyne when separate samples of 0.24 g (0.5 mmol) of $[Et_3NH^+]$[6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$] in ~3 mL of toluene were heated at 90 °C for 1.3 h with either (1) ~0.5 mL (4.5 mmol) of 1-octene or (2) ~0.4 mL (5 mmol) of 3-hexyne and that there was complete conversion of the $[Et_3NH^+]$[6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$] to 6-$[CH_3(CH_2)_7]$-$B_{10}H_{13}$ with loss of Et_3N.

Reaction of $[Bu_4N^+]$[6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$] (1^-) with $B_{10}H_{14}$. Reaction of 0.24 g (0.5 mmol) of 1^- with 0.036 g (0.3 mmol) of $B_{10}H_{14}$ in ~3 mL of DCE for ~0.3 h, showed by ^{11}B NMR analysis, the complete consumption of the $B_{10}H_{14}$ to produce a mixture containing 6-$[CH_3(CH_2)_7]$-$B_{10}H_{13}$, 6-$[CH_3(CH_2)_7]$-$B_{10}H_{12}^-$, and $B_{10}H_{13}^-$.

3-R-1,2-Et_2-1,2-$C_2B_{10}H_9$ Syntheses. 3-$[CH_3(CH_2)_7]$-1,2-$(C_2H_5)_2$-1,2-$C_2B_{10}H_9$ (17). A 25 mL, 2-neck round-bottom flask equipped with a septum, stir bar, and vacuum adapter was charged under an inert atmosphere with 0.35 g (2.0 mmol) of bmimCl, 0.47 g (2.0 mmol) of **1**, 1.0 g (12.2 mmol) of 3-hexyne, and ~3 mL of toluene. The flask was attached to a water condenser open to argon, and the body of the flask was then submerged into a 100 °C oil bath equipped with a magnetic stir plate. After the mixture was stirred vigorously for ~4 h, ^{11}B NMR analysis of the toluene layer showed the absence of any unreacted 6-R-$B_{10}H_{13}$ and the formation of **17**. The reaction was then stopped, and the top organic layer of the reaction mixture was separated by pipet; then the ionic-liquid layer extracted several times with ether. The combined toluene and ether solutions were vacuum concentrated and then flash filtered on a silica gel column with toluene eluent to afford, after drying under high vacuum overnight, 0.58 g (1.8 mmol, 92% yield) of 3-$[CH_3(CH_2)_7]$-1,2-$(C_2H_5)_2$-$C_2B_{10}H_9$ (**17**) as a dark-yellow oil. GC/MS analysis of the oil showed **17** as the only product. NCI-HRMS (*m/e*) calcd $(M)^-$ for $^{12}C_{14}{}^{11}B_{10}{}^{1}H_{36}$: 314.3747; found 314.3764. Anal. Calcd: C, 53.80; H, 11.61. Found: C, 54.16; H, 12.24. ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ −0.21 (s, 1, B3), −4.2 (d, 2), −9.7 (s, 2), −11.0 (d, 3), −12.7 (d, 1), −14.4 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, C_6D_6, ppm): δ 1.56 (m, 2, CH_2), 1.50 (m, 4, CH_2), 1.36 (m, 2, CH_2), 1.27 (m, 10, CH_2), 0.88 (m, 3, CH_3), 0.63 (t, 6, CH_3).

3-$[(CH_3)_3Si(CH_2)_3]$-1,2-$(C_2H_5)_2$-1,2-$C_2B_{10}H_9$ (18). Reaction of 0.473 g (2.0 mmol) of **2** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.58 g (1.82 mmol, 91% yield) of **18** as an oily liquid. NCI-HRMS (*m/e*) calcd $(M)^-$ for $^{12}C_{12}{}^{11}B_{10}{}^{1}H_{34}{}^{28}Si_1$: 316.3360; found 316.3364. Anal. Calcd: C, 45.81; H, 10.89. Found: C, 45.77; H, 11.35. ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ −0.7 (s, 1, B3), −4.7 (d, 2), −10.1 (s, 2), −11.5 (d, 3), −12.4 (d, 1), −14.2 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, C_6D_6, ppm): δ 1.69 (m, 2, CH_2), 1.57 (m, 2, CH_2), 0.94 (m, 4, CH_2), 0.79 (t, 6, CH_3), 0.63 (t, 2, CH_2), 0.03 (s, 9, CH_3).

3-$[CH_2{=}CH(CH_2)_6]$-1,2-$(C_2H_5)_2$-1,2-$C_2B_{10}H_9$ (19). Reaction of 0.465 g (2.0 mmol) **3** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.57 g (1.82 mmol, 91% yield) of **19** as an oily liquid. NCI-HRMS (*m/e*) calcd $(M)^-$ for $^{12}C_{14}{}^{11}B_{10}{}^{1}H_{34}$: 312.3591; found 312.3587. Anal. Calcd: C, 54.15; H, 11.04. Found: C, 54.39; H, 11.25. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ −0.8 (s, 1, B3), −5.4 (d, 2), −10.6 (s, 2), −12.1 (d, 3), −12.9 (d, 1), −14.8 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, CDCl3, ppm): δ5.83 (m, 1, $=CH-$), 5.0 (m, 2, $CH_2=$), 2.05 (m, 2, CH_2), 1.43 (m, 2, CH_2), 1.32 (m, 8, CH_2), 1.32 (m, 4, CH_2), 0.89 (m, 6, CH_3).

3-$[CH_3C(O)O(CH_2)_6]$-1,2-$(C_2H_5)_2$-1,2-$C_2B_{10}H_9$ (20). Reaction of 0.53 g (2.0 mmol) of **4** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.62 g (1.8 mmol, 90% yield) of **20** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{14}{}^{11}B_{10}{}^{1}H_{34}{}^{16}O_2$: 344.3489; found 344.3478. Anal. Calcd: C, 49.09; H, 10.00. Found: C, 50.22; H, 9.57. ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ −0.7 (s, 1, B3), −4.6 (d, 2), −10.1 (s, 2), −11.4 (d, 3), −12.5 (d, 1), −14.1 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, C_6D_6, ppm): δ 3.95 (t, 2, $-OCH_2-$), 1.73 (s, 3, CH_3), 1.69 (m, 4, CH_2), 1.45 (m, 6, CH_2), 1.25 (m, 4, CH_2), 0.78 (m, 6, CH_3).

3-[$CH_3(CH_2)_2O(CH_2)_3$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (21). Reaction of 0.445 g (2.0 mmol) of **5** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.54 g (1.78 mmol, 89% yield) of **21** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{12}{}^{11}B_{10}{}^{1}H_{32}{}^{16}O_1$: 302.3384; found 302.3385. Anal. Calcd: C, 47.96; H, 10.73. Found: C, 49.02; H, 9.11. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ −0.7 (s, 1, B3), −4.5 (d, 2), −10.2 (s, 2), −11.5 (d, 3), −12.6 (d, 1), −14.4 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 3.41 (t, 2, $-O-CH_2$), 3.34 (t, 2, $-O-CH_2$), 1.85 (m, 2, CH_2), 1.58 (m, 2, CH_2), 1.43 (m, 6, CH_2), 0.90 (t, 9, CH_3).

3-[$C_6H_5(CH_2)O(CH_2)_3$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (22). Reaction of 0.54 g (2.0 mmol) of **6** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.635 g (1.8 mmol, 90% yield) of **22** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{16}{}^{11}B_{10}{}^{1}H_{32}{}^{16}O_1$: 350.3384; found 350.3379. Anal. Calcd: C, 55.14; H, 9.25. Found: C, 56.02; H, 9.62. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ −1.2 (s, 1, B3), −5.4 (d, 2), −10.6 (s, 2), −12.2 (d, 3), −12.9 (d, 1), −14.7 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 7.36 (m, 5, C_6H_5-), 4.52 (s, 2, CH_2), 3.50 (t, 2, CH_2), 2.33 (m, 2, CH_2), 1.74 (m, 2, CH_2), 1.14 (q, 4, CH_2), 0.95 (m, 6, CH_3).

3-[$HO(CH_2)_3$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (23). Reaction of 0.36 g (2.0 mmol) of **7** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.43 g (1.64 mmol, 82% yield) of **23** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M - C_4H_{10})^-$ for $^{12}C_9{}^{11}B_{10}{}^{1}H_{26}{}^{16}O_1$: 202.2131; found 202.2138. Anal. Calcd: C, 41.83; H, 10.14. Found: C, 42.42; H, 11.86. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ −0.9 (s, 1, B3), −5.5 (d, 2), −10.7 (s, 2), −12.2 (d, 3), −13.0 (d, 1), −14.8 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 3.65 (t, 2, CH), 1.8 (s, 1, OH), 1.59 (m, 2, CH), 1.29 (m, 2, CH), 1.15 (q, 4, CH), 0.89 (t, 6, CH).

3-[$(CH_3)_4C_2O_2B(CH_2)_3$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (24). Reaction of 0.58 g (2.0 mmol) of **8** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.68 g (1.82 mmol, 91% yield) of **24** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{15}{}^{11}B_{11}{}^{1}H_{37}{}^{16}O_2$: 370.3817; found 370.3825. Anal. Calcd: C, 48.91; H, 10.12. Found: C, 49.10; H, 10.40. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ 33.5 (s, O−B−O), −0.9 (s, 1, B3), −5.3 (d, 2), −10.5 (s, 2), −12.1 (d, 3), −12.8 (d, 1), −14.7 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 2.11 (m, 2, CH_2), 1.54 (m, 2, CH_2), 1.25 (s, 12, CH_3), 1.14 (q, 4, CH_2), 1.02 (m, 2, CH_2), 0.91 (m, 6, CH_2).

3-[(*exo*)-Bicyclo-[2,2,1]-hept-2-yl]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (25). Reaction of 0.43 g (2.0 mmol) of **9** and 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.54 g (1.8 mmol, 90% yield) of **25** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{13}{}^{11}B_{10}{}^{1}H_{30}$: 296.3278; found 296.3278. Anal. Calcd: C, 53.02; H, 10.27. Found: C, 53.65; H, 10.16. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ −0.9 (s, 1, B3), −5.7 (d, 2), −11.0 (s, 2), −12.3 (d, 3), −13.1 (d, 1), −14.8 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 2.29 (m, 2, CH_2), 1.52 (m, 4, CH_2), 1.20 (m, 4, CH_2), 1.13 (q, 4, CH_2), 1.00 (m, 6, CH_3), 0.84 (m, 1, CH).

3-[2,5-$(CH_3)_2$-hex-3-yl]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (26). Reaction of 0.47 g (2.0 mmol) of **11** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.58 g (1.82 mmol, 91% yield) of **26** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M - H)^-$ for $^{12}C_{14}{}^{11}B_{10}{}^{1}H_{36}$: 314.3748; found 314.3755. Anal. Calcd: C, 53.80; H, 11.61. Found: C, 54.22; H, 11.48. ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ 1.3 (s, 1, B3), −4.1 (d, 2), −10.1 (s, 2), −11.4 (d, 3), −12.4 (d, 1), −14.0 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, C_6D_6, ppm): δ 2.26 (m, 1, CH), 1.54 (m, 1, CH), 1.33 (m, 5, CH_2), 1.10 (m, 10, CH_2), 0.87 (m, 8, CH_3, CH_2), 0.60 (m, 2, CH_2).

3-[$Br(CH_2)_6$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (27). Reaction of 0.57 g (2.0 mmol) of **12** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.65 g (1.78 mmol, 89% yield) of **27** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M - Br)^-$ for $^{12}C_{12}{}^{11}B_{10}{}^{1}H_{31}{}^{81}Br_1$: 285.3356; found 285.3362. Anal. Calcd: C, 39.66; H, 8.60. Found: C, 40.37; H, 9.18. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ −1.0 (s, 1, B3), −5.3 (d, 2), −10.5 (s, 2), −12.1 (d, 3), −12.8 (d, 1), −14.7 (d, 1). ^1H $\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 3.55 (t, 2, CH_2-Br), 2.23 (m, 2, CH_2), 1.79 (m, 2, CH_2), 1.44 (m, 6, CH_2), 1.15 (q, 4, CH_2), 0.90 (m, 6, CH_3).

3-[$C_6H_5(CH_2)_2$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (28). Reaction of 0.45 g (2.0 mmol) of **13** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.55 g (1.78 mmol, 89% yield) of **28** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{14}{}^{11}B_{10}{}^{1}H_{28}$: 306.3122; found 306.3126. Anal. Calcd: C, 55.23; H, 9.27. Found: C, 55.45; H, 9.24. ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ −1.5 (s, 1, B3), −5.4 (d, 2), −10.8 (s, 2), −12.1 (d, 3), −12.9 (d, 1), −14.7 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 6.98 (m, 5, C_6H_5), 2.30 (m, 2, CH_2), 1.35 (m, 2, CH_2), 1.21 (q, 4, CH_2), 0.99 (m, 6, CH_3).

3-[$C_6H_5(CH_2)_3$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (29). Reaction of 0.481 g (2.0 mmol) of **14** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.59 g (1.82 mmol, 91% yield) of **29** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{15}{}^{11}B_{10}{}^{1}H_{30}$: 320.3278; found 320.3287. Anal. Calcd: C, 56.56; H, 9.49. Found: C, 57.03; H, 9.45. ^{11}B NMR (128.4 MHz, C_6D_6, ppm): δ −0.6 (s, 1, B3), −4.5 (d, 2), −10.0 (s, 2), −11.4 (d, 3), −12.4 (d, 1), −14.1 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, C_6D_6, ppm): δ 7.06 (m, 5, C_6H_5), 2.53 (t, 2, CH_2), 1.64 (m, 2, CH_2), 0.99 (m, 4, CH_2), 0.88 (m, 2, CH_2), 0.65 (m, 6, CH_3).

3-[$CH_3C(O)(CH_2)_4$]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (30). Reaction of 0.44 g (2.0 mmol) of **15** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.54 g (1.78 mmol, 89% yield) of **30** as an oily liquid. NCI-HRMS (*m*/*e*) calcd $(M)^-$ for $^{12}C_{12}{}^{11}B_{10}{}^{1}H_{30}{}^{16}O_1$: 300.3227; found 300.3231. Anal. Calcd: C, 48.29; H, 10.13. Found: C, 50.02; H, 9.17. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): δ −1.0 (s, 1, B3), −5.4 (d, 2), −10.7 (s, 2), −12.2 (d, 3), −13.0 (d, 1), −14.8 (d, 1). $^1H\{^{11}B\}$ NMR (400.1 MHz, $CDCl_3$, ppm): δ 2.35 (m, 2, CH_2-CO), 2.23 (s,

Table 1. Crystallographic Data Collection and Structural Refinement Information for 6-[$(CH_3)_3Si(CH_2)_3$]-$B_{10}H_{13}$ (**2**) and 6-[$CH_3C(O)(CH_2)_4$]-$B_{10}H_{13}$ (**15**)

	2	**15**
empirical formula	$C_6B_{10}H_{28}Si$	$C_6B_{10}H_{24}O$
fw	236.47	220.35
cryst class	orthorhombic	monoclinic
space group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
Z	8	16
a, Å	12.4576(9)	17.146(2)
b, Å	11.0223(8)	13.4183(11)
c, Å	24.028(2)	25.820(2)
β, deg		96.949(2)
V, Å^3	3299.3(4)	5896.7(9)
μ, cm^{-1}	1.12	0.50
cryst size, mm	0.32 × 0.10 × 0.04	0.42 × 0.25 × 0.18
D_{calcd}, g/cm^3	0.952	0.993
F(000)	1024	1888
radiation	Mo Kα ($\lambda = 0.71069$ Å)	Mo Kα ($\lambda = 0.71069$ Å)
2*θ* angle, deg	5.22−50.02	5.18−50.02
temp, K	143	143
hkl collected	$-13 \le h \le 14$ $-11 \le k \le 13$ $-23 \le 1 \le 28$	$-19 \le h \le 20$ $-13 \le k \le 15$ $-30 \le l \le 30$
reflns measured	12 587	30 288
unique reflns	2899 ($R_{int} = 0.0473$)	10 348 ($R_{int} = 0.0357$)
observed reflns, ($F > 4\sigma$)	2503	6809
reflns used in refinement	2899	10 348
params	267	826
R^a indices ($F > 4\sigma$)	$R_1 = 0.0483$ $wR_1 = 0.1180$	$R_1 = 0.0655$ $wR_1 = 0.1692$
R^a indices (all data)	$R_1 = 0.0575$ $wR_2 = 0.1254$	$R_1 = 0.1026$ $wR_2 = 0.1993$
GOF^b	1.149	1.074
final difference peaks, e/Å^3	+0.200, −0.293	+0.298, −0.191

[a] $R_1 = ||F_o| - |F_c||/|F_o|$; $wR_2 = \{w(F_o^2 - F_c^2)^2/w(F_o^2)^2\}^{1/2}$. [b] GOF = $\{w(F_o^2 - F_c^2)^2/(n - p)\}^{1/2}$ where *n* = no. of reflections; *p* = no. of parameters refined.

3, CH_3), 2.14 (m, 4, CH_2), 1.45 (m, 2, CH_2), 1.15 (q, 4, CH_2), 0.88 (m, 6, CH_3).

3-[C_8H_{15}]-1,2-(C_2H_5)$_2$-1,2-$C_2B_{10}H_9$ (31). Reaction of 0.465 g (2.0 mmol) of **16** with 1.0 g (12.2 mmol) of 3-hexyne in biphasic toluene (~3 mL)/bmimCl (0.35 g, 2.0 mmol) at 100 °C for ~4 h gave, following toluene elution from a silica gel column, 0.57 g (1.8 mmol, 90% yield) of **31** as an oily liquid. NCI-HRMS (*m*/*e*) calcd (M)$^-$ for $^{12}C_{14}{}^{11}B_{10}{}^{1}H_{34}$: 312.3591; found 312.3605. Anal. Calcd: C, 54.15; H, 11.04. Found: C, 55.02; H, 10.89. ^{11}B NMR (128.4 MHz, $CDCl_3$, ppm): *δ* 1.5 (s, 1, B3), −5.6 (d, 2), −11.0 (s, 2), −12.3 (d, 3), −12.8 (d, 1), −14.7 (d, 1). ^{1}H{^{11}B} NMR (400.1 MHz, $CDCl_3$, ppm): *δ* 2.22 (m, 1, CH), 1.80 (m, 4, CH_2), 1.55 (m, 10, CH_2), 1.19 (m, 4, CH_2), 0.97 (m, 6, CH_3).

Crystallographic Data for 2 and 15. Single crystals were grown from a 1:1 toluene/hexanes solution of **2** (Upenn no. 3280) and from a toluene solution of **15** (Upenn no. 3281) at room temperature.

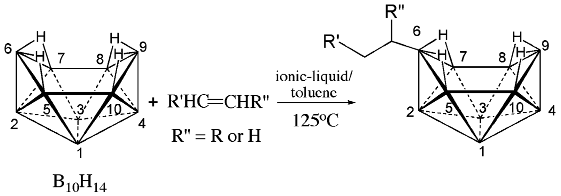
Collection and Reduction of the Data. X-ray intensity data (Table 1) were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo Kα radiation. Oscillation images were processed to produce a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the CrystalStructure program package[14] for further processing and structure solution on a Dell Pentium III computer. The intensity data were corrected for Lorentz and polarization effects and for absorption.

Solution and Refinement of the Structures. The structures were solved by direct methods (SIR97).[15] Refinements were by full-matrix least-squares based on F^2 using SHELXL-97.[16] All reflections were used during refinement (F^2 values that were experimentally negative were replaced by $F^2 = 0$). Non-hydrogen atoms were refined anisotropically; chain hydrogen atoms were refined using a "riding" model. Cage hydrogen atoms were refined isotropically, and chain hydrogen atoms were included as constant contributions to the structure factors and were not refined. Disordered structures of the substituent with different orientations were observed for **15** and were resolved accordingly. For **15**, four independent molecules of the asymmetric unit adopt different conformations with the C1−C2 single bond assuming different orientations.

Results

Syntheses of 6-R-$B_{10}H_{13}$ via the Ionic-Liquid or Salt Mediated Reactions of Olefins with $B_{10}H_{14}$. As summarized in Table 2, decaborane, $B_{10}H_{14}$, was found to hydroborate a variety of olefins in biphasic mixtures of toluene and an ionic liquid, including, 1-butyl-3-methylimidazolium chloride (bmimCl), and 1-butyl-4-methylpyridinium tetrafluoroborate ($bmpyBF_4$), or toluene and an inorganic salt, such as, anhydrous tetrabutylammonium fluoride (Bu_4NF), to give the corresponding 6-R-$B_{10}H_{13}$ products, **1**−**15**, in isolated yields ranging from 55 to 92%.

(1)



The biphasic reaction mixture, with the ionic-liquid layer at the bottom and the olefin-toluene layer at the top, was heated with vigorous stirring to form an emulsion. Reactions at 125−140 °C, using an excess of the olefin, were typically complete in ~12−40 h depending on the olefin. No reaction was observed when decaborane was heated in an olefin/toluene solution at 125 °C *without* an ionic liquid.

As shown in Figure 1 for a reaction with 1-octene in toluene/bmimBF$_4$, ^{11}B NMR spectra obtained when the $B_{10}H_{14}$ was initially added to the biphasic mixture showed the presence of $B_{10}H_{14}$ in both the $bmpyBF_4$ and toluene layers. After heating for 30 min, the toluene layer showed a characteristic color change to light yellow. As shown in Figure 2, the ^{11}B NMR spectra of the toluene layer showed 6-R-$B_{10}H_{13}$ resonances after just 2.3 h. Reactions were determined to be complete (~12 h for the reaction with 1-octene in bmimCl at 125 °C; and ~20.3 h at 125 °C, or ~12 h at 140 °C, for reactions with 1-octene in $bmpyBF_4$) when the ^{11}B NMR spectra of the toluene layer showed the complete consumption of $B_{10}H_{14}$. The toluene layer was separated by pipet, and then the ionic-liquid layer was extracted multiple times with Et_2O. The toluene and ether solutions were combined, vacuum concentrated, and then flash filtered through a silica gel column using a hexanes/toluene eluent. Removal of the solvent and excess olefin in

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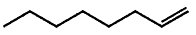
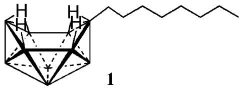
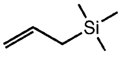
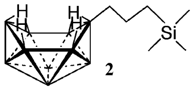
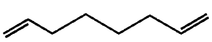
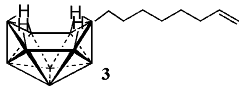
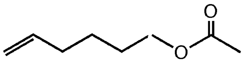
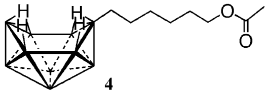
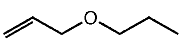
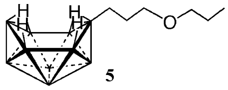
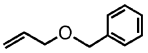
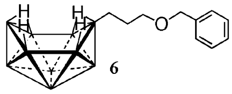
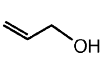
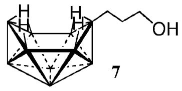
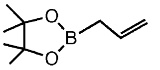
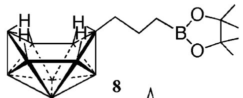
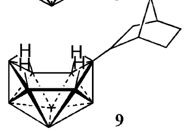
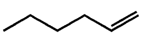
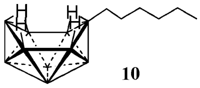
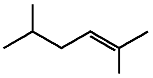
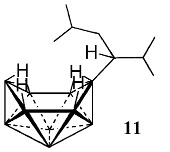
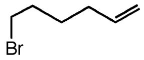
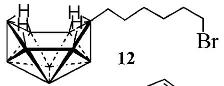
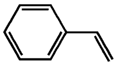
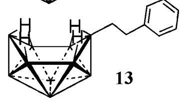
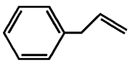
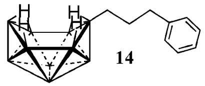
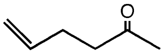
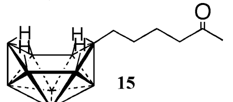
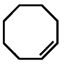
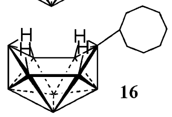
(14) *Crystal Structure, Crystal Structure Analysis Package*; Rigaku Corporation: The Woodlands, TX, 2002.

(15) For SIR97, see: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Moliterni, A.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(16) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

Table 2. Summary of 6-R-$B_{10}H_{13}$ Syntheses

Olefin	Hydroboration Product	Yield (%)
	 **1**	90
	 **2**	89
	 **3**	89
	 **4**	92
	 **5**	70
	 **6**	74
	 **7**	55
	 **8**	90
	 **9**	85
	 **10**	80
	 **11**	85
	 **12**	85
	 **13**	75
	 **14**	86
	 **15**	70
	 **16**	88

vacuo afforded final yields of ~89% of **1** for both the bmimCl and bmpyBF_4 reactions.

As typical of decaborane derivatives, compounds **1**−**15** were stable under inert atmosphere, slowly hydrolyzing upon standing in air over days. All compounds were soluble in common organic solvents like benzene, toluene, methylene chloride and ethyl acetate, with the exception of compounds **5**, **6**, **7**, **13**, and **15**, which were only partially soluble in hexanes, toluene, and benzene. The ^{11}B NMR spectra of **1**−**15** showed the peaks characteristic of 6-R-$B_{10}H_{13}$ derivatives,[4,5,7−9] and their ^{1}H NMR spectra showed the resonances expected for their attached substituents and the terminal B−H cage hydrogens, along with two broad upfield resonances arising from the two sets of intensity-two bridging hydrogens. While it is possible, as is usually observed in most uncatalyzed monoborane olefin-hydroborations,[17] that a Markovnikov addition product was produced in minor amounts, analysis of the 6-R-$B_{10}H_{13}$ products by ^{1}H NMR and GC/MS confirmed almost exclusive anti-Markovnikov addition. The crystallographically determined structures of 6-[$(CH_3)_3$-$Si(CH_2)_3$]-$B_{10}H_{13}$ (**2**), and 6-[$CH_3C(O)(CH_2)_4$]-$B_{10}H_{13}$ (**15**), shown in Figures 3 and 4, likewise confirm anti-Markovnikov addition. The distances and angles observed in these structures are all in the expected ranges.

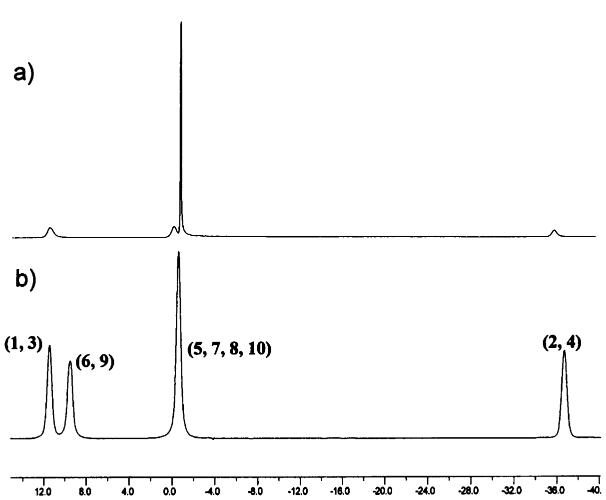


Figure 1. $^{11}B\{^{1}H\}$ NMR spectra showing decaborane dissolved in both the (a) bmpyBF_4 and (b) toluene layers. Spectrum a also shows the BF_4^- resonance of the ionic liquid at −1.7 ppm. (To record spectrum a, some CH_2Cl_2 was added to the NMR tube to reduce the viscosity of the solution).

As shown in Table S3, Supporting Information, for reactions with 1-octene, the $B_{10}H_{14}$ olefin-hydroboration reaction was found to proceed in a number of ionic liquids,

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(17) Brown, H. C.; Knights, E. F.; Scouten, C. G. *J. Am. Chem. Soc.* **1974**, *96*, 7765–70.

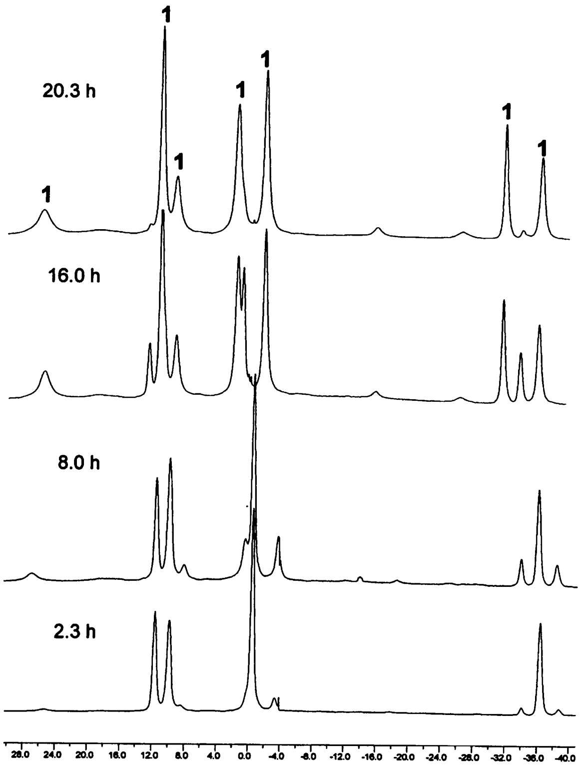


Figure 2. Reaction progression for the reaction of $B_{10}H_{14}$ with 1-octene in bmpyBF_4/toluene, as measured by the $^{11}B\{^1H\}$ NMR spectra of the toluene layer versus time. **1** = (6-octyl-$B_{10}H_{13}$) resonances.

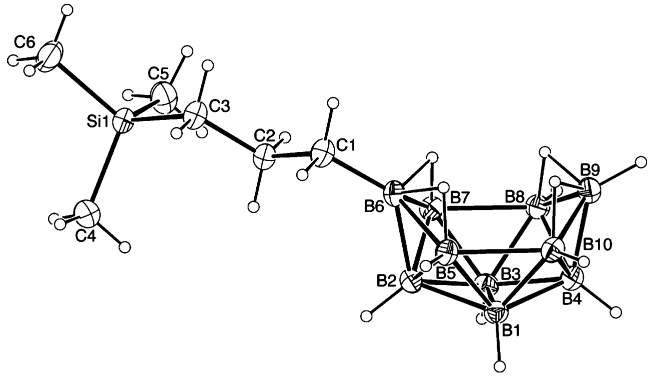


Figure 3. ORTEP representation of the structure of 6-[$(CH_3)_3Si(CH_2)_3$]-$B_{10}H_{13}$ (**2**). Selected bond lengths (Å) and bond angles (deg): C6−Si, 1.860(2); C4−Si, 1.862(2); C5−Si, 1.864(2); Si−C3, 1.870(2); C1−B6, 1.574(3); B6−B5, 1.800(3); B5−B10, 1.983(3); B6−B7,1.805(3); B7−B8, 1.977(3); B10−B9, 1.790(3); C4−Si−C5, 108.78(13); C6−Si−C3, 110.02(12); C5−Si−C3, 109.09(10); C2−C1−B6, 114.0(2); C1−B6−B2, 132.1(2); C1−B6−B7, 127.6(2); C1−B6−B5, 127.5(2); B6−B7−B8, 118.25(14); B6−B5−B10, 117.41(14).

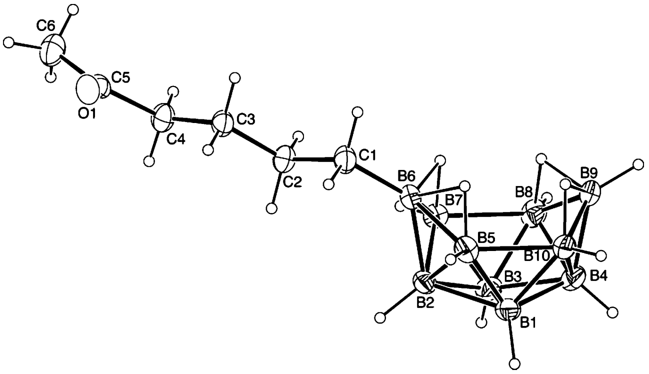


Figure 4. ORTEP drawing of the structure of 6-[$CH_3C(O)(CH_2)_4$]-$B_{10}H_{13}$ (**15**). Selected bond lengths (Å) and angles (deg): C6−C5, 1.497(3); C5−O, 1.216(2); C5−C4, 1.493(3); C1−C2, 1.519(3); C1−B6, 1.565(3); B6−B2, 1.739(3); B6−B7, 1.791(3); B6−B5, 1.791(3); B7−B8, 1.965(4); B8−B9, 1.771(4); C6−C5−C4, 117.1(2); C6−C5−O, 121.1(2); O−C5−C4, 121.9(2); C5−C4−C3, 115.1(2); C2−C1−B6, 116.4(2); C1−B6−B7, 129.2(2); C1−B6−B5, 125.7(2); C1−B6−B2, 131.4(2); B6−B2−B3, 111.5(2); B6−B2−B1, 111.3(2); B6−B5−B10, 118.3(2); B6−B7−B8, 117.1(2); B7−B8−B9, 117.5(2).

including the imidazolium and pyridinium halides (bmimCl, bmimBr, bmimI, and bmpyCl), acetates (bmimOAc), and tetrafluoroborates (bmimBF_4 and bmpyBF_4), but no reactions were observed in the phosphorus hexafluorides (bmimPF_6 or bmpyPF_6) or the trifluoromethanesulfonate (bmimOTf). For the reactions of 1-octene in ionic liquids containing the bmim cation, the relative hydroboration rates were $Cl^- > Br^- \approx OAc^- > BF_4^- > I^-$. When salts containing halide or acetate anions, for example, Bu_4NF, NaF, NaCl, NH_4Cl, or NaOAc, were added to the "inert" bmimPF_6 and bminOTf ionic liquids, these new mixed systems became active for hydroboration reactions. Likewise, it was found that upon heating, even toluene solutions of many soluble salts containing halides and tetrafluoroborates, including Bu_4NBF_4, Bu_4NF, Bu_4NCl, Bu_4NBr, Bu_4NSCN, and PPNCl, formed "ionic liquid"-like biphasic mixtures that showed good reactivities for decaborane olefin-hydroboration, whereas the Bu_4NPF_6 salt did not. For reactions with the tetrabutylammonium cation, the reaction rates decreased in the order: $F^- > Cl^- > SCN^-$. On the other hand, toluene/decaborane/olefin solutions in the presence of high melting, toluene-insoluble salts, such as $NaBF_4$, NH_4BF_4, and Me_4NBF_4, showed no reactivity.

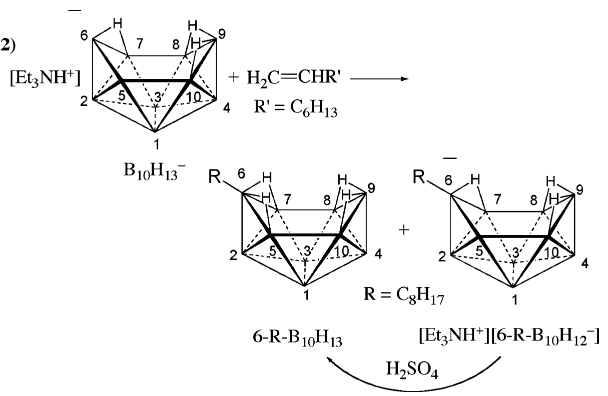
When used in catalytic amounts (~0.2−0.5 equiv relative to $B_{10}H_{14}$), bmimCl proved to be the most versatile reagent for inducing decaborane olefin-hydroboration, but its use in larger ratios resulted in lower product yields because of $B_{10}H_{14}$ degradation reactions. No $B_{10}H_{14}$ degradation was observed when using ionic liquids containing the BF_4^- anion, even at high stoichiometries. For both bmimCl and bmpyBF_4, the rate of 1-octene hydroboration was faster at higher temperatures with the upper reaction temperatures (~125−140 °C) only limited by the olefin and solvent boiling points. The possible role of Cl^- impurities in bmimBF_4, bmpyBF_4, and Bu_4NBF_4, in activating the $B_{10}H_{14}$ olefin-hydroboration reactions in these ionic liquids was also considered, but it was found that reactions in low-chloride content (10 ppm) bmimBF_4 (Fluka catalytic grade) showed no decrease in rate.

While many olefins reacted in both bmimCl and bmpyBF_4, some olefins showed significant reactivity in only one of them. For example, 6-bromo-hexene and allylbenzene reacted more effectively in bmpyBF_4, while allyl propyl and allyl benzyl ether had much higher reactivity in bmimCl. Likewise, while the hydroboration rates of terminal olefins in bmimCl were significantly higher than those of internal olefins, both terminal and internal olefins reacted at similar rates in bmpyBF_4 and bmimBF_4 with both the cis- and trans-internal olefins showing comparable rates in bmpyBF_4 (Table S5, Supporting Information). As previously observed for monoborane-olefin hydroborations,[18] decaborane hydroboration of strained cyclic olefins, like *cis*-cyclooctene, proceeded at a higher rate than those of terminal olefins. Cyclohexene hydroboration was slow, possibly because of lower ring-strain and hence a lower reactivity. Hydroborations of olefins containing acid, acid chloride, thiol, thioether, and aldehyde groups were unsuccessful in either bmimCl or bmpyBF$_4$.

Several of the ionic-liquid-mediated hydroboration systems were shown to be reusable and active over reasonable periods of time. As summarized in Tables S1 and S4, Supporting Information, reactions involving the sequential additions of ~5 mmol of decaborane (20 mmol total) every ~3−15 h to either excess 1-octene in bmpyBF$_4$/toluene or excess 1,7-octadiene in a Bu$_4$NF/bmimOTf/toluene mixture showed only small decreases in rate and ultimately gave 84 or 87% final yields of the 6-R-B$_{10}$H$_{13}$ products.

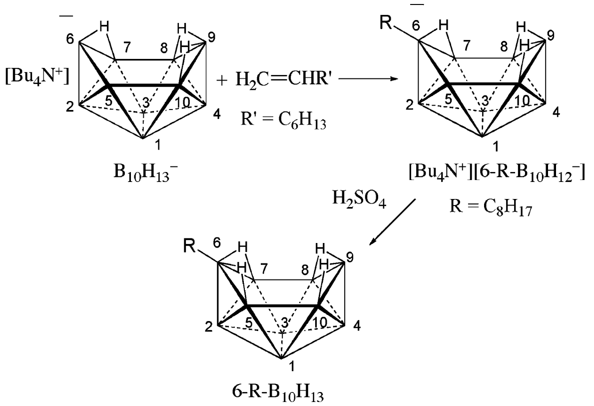
6-R-B$_{10}$H$_{13}$ Syntheses via the Reactions of Olefins with B$_{10}$H$_{13}^-$. To test the possible role of the B$_{10}$H$_{13}^-$ anion in the ionic-liquid-mediated reactions, the reactions of B$_{10}$H$_{13}^-$ with 1-octene, either starting with the isolated [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$] salt or by in situ generation of the B$_{10}$H$_{13}^-$ anion from B$_{10}$H$_{14}$ in the presence of bases such as Et$_3$N or Proton Sponge, were investigated and were found (eq 2) in each case to result in olefin-hydroboration to produce a mixture of the neutral 6-octyl-B$_{10}$H$_{13}$ product **1**, along with its 6-octyl-B$_{10}$H$_{12}^-$ conjugate anion (**1**$^-$). While acidification of these mixtures gave 6-octyl-B$_{10}$H$_{13}$ in yields comparable to the ionic-liquid reactions, the yields obtained for the reactions starting with the B$_{10}$H$_{13}^-$ anion with most internal and functional olefins were much lower than those obtained from the bmimCl reactions discussed in the previous section.

(2)



As expected, given the absence of an acidic hydrogen on the ammonium cation, reactions of [Bu$_4$N$^+$][B$_{10}$H$_{13}^-$] with 1-octene gave exclusively the [Bu$_4$N$^+$][6-octyl-B$_{10}$H$_{12}^-$] salt (eq 3). Nevertheless, subsequent acidification again converted this salt to the neutral 6-octyl-B$_{10}$H$_{13}$.

(3)



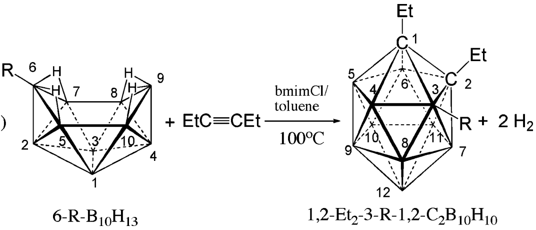
Attempted Reactions of 6-R-B$_{10}$H$_{13}$ and 6-R-B$_{10}$H$_{12}^-$ with Olefins. Consistent with the fact that the ionic-liquid-mediated decaborane olefin-hydroboration reactions were highly selective for the formation of only monosubstituted products, no reactions were observed upon heating 6-R-B$_{10}$H$_{13}$ derivatives with olefins in biphasic mixtures of an ionic liquid (either bmimCl or bmpyBF$_4$) and toluene (eq 4).

$$6\text{-R-B}_{10}\text{H}_{13} + \text{1-octene} \xrightarrow[125\ ^\circ\text{C},\ 4\ \text{h}]{\text{bmimcl or bmpBF}_4\text{/toluene}} \text{no reaction} \qquad (4)$$

Likewise, no dialkyl-products were produced when toluene solutions of 1-octene and either the [Bu$_4$N$^+$][6-R-B$_{10}$H$_{12}^-$] or [Et$_3$NH$^+$][6-R-B$_{10}$H$_{12}^-$] salts were heated at 90 °C.

Reactions 6-R-B$_{10}$H$_{13}$ with Alkynes: Ionic-Liquid-Mediated Syntheses of 3-R-1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_9$ Carboranes. Previous routes to boron-substituted *o*-carboranes have been limited in their scope and yields, having involved for example the reactions of RBX$_2$ compounds with the dicarbollide anion[19] or the metal-catalyzed reactions of Grignard reagents with iodocarboranes.[20] On the other hand, following the procedures that are described in the preceding paper,[1] the 6-R-B$_{10}$H$_{13}$ compounds were found to react with 3-hexyne in a biphasic mixture of a bottom 1-butyl-3-methylimidazolium chloride layer and a top alkyne-toluene layer to give boron-functionalized *ortho*-carboranes 3-R-1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_9$ in high yields (eq 5).

(5)



Vigorously stirred reactions at ~100 °C using an excess of 3-hexyne were typically complete in ~3−4 h. The biphasic system enabled facile product separation by simply pipetting the organic layer from the reaction mixture and then extracting any residual product in the ionic-liquid layer with ether. Flash filtration of these combined solutions through a silica gel plug, afforded high final yields for most substituted decaboranes. For example, the reaction of 3-hex-

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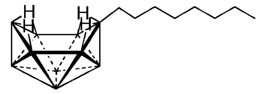
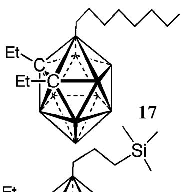
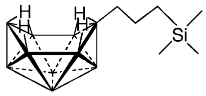
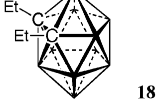
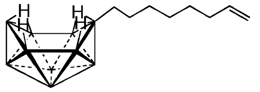
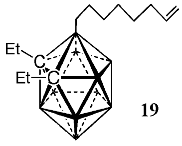
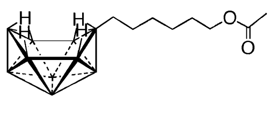
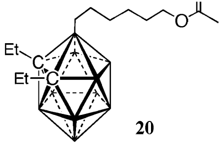
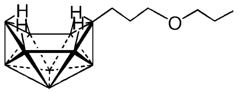
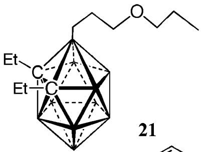
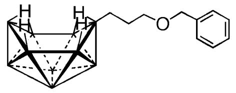
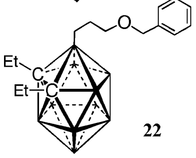
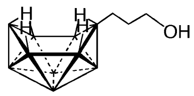
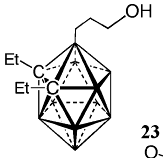
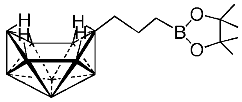
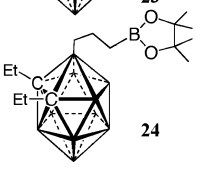
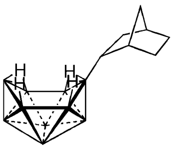
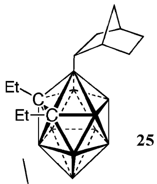
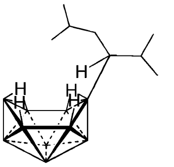
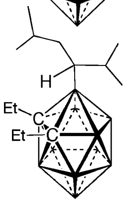
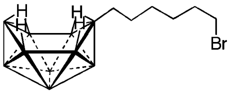
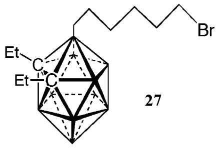
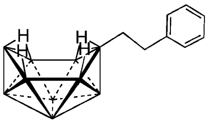
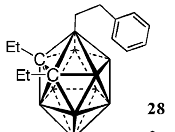
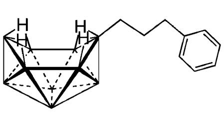
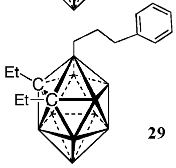
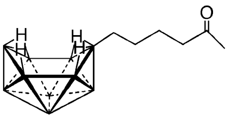
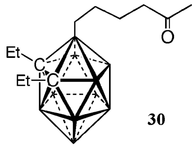
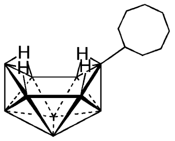
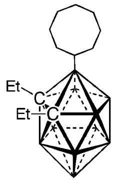
(18) Brown, H. C.; Liotta, R.; Scouten, C. G. *J. Am. Chem. Soc.* **1976**, *98*, 5297–5301.

(19) Chen, W.; Rockwell, J. J.; Knobler, C. B.; Harwell, D. E.; Hawthorne, M. F. *Polyhedron* **1999**, *18*, 1725–1734.

Table 3. Summary of 3-R-1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_9$ Syntheses

6-R-B$_{10}$H$_{13}$	3-R-1,2-(C$_2$H$_5$)$_2$-C$_2$B$_{10}$H$_9$	Yield (%)
	 **17**	92
	 **18**	91
	 **19**	91
	 **20**	90
	 **21**	89
	 **22**	90
	 **23**	82
	 **24**	91
	 **25**	90
	 **26**	91
	 **27**	89
	 **28**	89
	 **29**	91
	 **30**	89
	 **31**	90

yne with 6-[CH$_3$(CH$_2$)$_7$]-B$_{10}$H$_{13}$ in biphasic bmimCl/toluene gave 3-[CH$_3$(CH$_2$)$_7$]-1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_9$ (**17**) in ~90% yields in only ~4 h. As seen in Table 3, 6-R-B$_{10}$H$_{13}$ derivatives with a wide range of functionalities could be converted into their *ortho*-carborane analogues 3-R-1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_9$ **17**−**31**, in isolated yields ranging from 89 to 92%.

Compounds **17**−**31** were stable in air and soluble in organic solvents like benzene, toluene, methylene chloride, and ethyl acetate. Their ^{11}B NMR spectra showed peaks characteristic of 3-R-1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_9$ derivatives.[19,20] The ^{1}H NMR spectra of all compounds showed the resonances of the substituents attached at B3 and the Et-groups at the C1 and C2 atoms.

Discussion

The experimental observations for both the ionic-liquid-mediated decaborane dehydrogenative alkyne-insertion reactions reported in the preceding paper[1] and the olefin-hydroboration reactions presented in this paper, support overall reaction schemes, such as depicted in Figure 5 for an olefin hydroboration, where the ionic-liquid-mediated formation of the B$_{10}$H$_{13}^-$ anion is the essential first step in these reactions. For the-olefin-hydroboration reactions, this initial step is then followed by (2) addition of the B$_{10}$H$_{13}^-$ anion to the olefin to form a 6-R-B$_{10}$H$_{12}^-$ anion and, finally, (3) protonation of 6-R-B$_{10}$H$_{12}^-$ to form the final neutral 6-R-B$_{10}$H$_{13}$ product.

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(20) (a) Li, J.; Logan, C. F.; Jones, M., Jr. *Inorg. Chem.* **1991**, *30*, 4866–4868. (b) Zheng, Z.; Jiang, W.; Zinn, A. A.; Knobler, C. B.; Hawthorne, M. F. *Inorg. Chem.* **1995**, *34*, 2095–2100. (c) Vinas, C.; Barbera, G.; Oliva, J. M.; Teixidor, F.; Welch, A. J.; Rosair, G. M. *Inorg. Chem.* **2001**, *40*, 6555–6562.

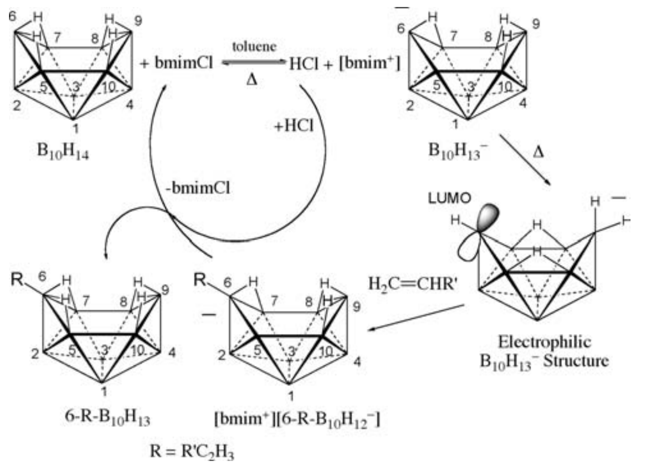

Figure 5. Possible reaction scheme for ionic-liquid-promoted $B_{10}H_{14}$ olefin-hydroboration.

Decaborane has been shown to be a monoprotic Brϕnsted acid[21] (eq 6) as a result of ionization of one bridging proton in either water (pK_a = 2.7) or polar nonaqueous solutions.

$$B_{10}H_{14} + H_2O \rightleftharpoons B_{10}H_{13}^- + H_3O^+ \tag{6}$$

As described in the Experimental Section and in the Supporting Information, the observations that (1) while decaborane remained largely undissociated in pure toluene or dichloroethane solvents, it ionized to produce acidic solutions in the presence of ionic liquids or salts containing the conjugate anion of a weak acid; (2) the hydroboration activity of both the ionic liquid and the $Bu_4N^+X^-$ salts increased as the conjugate base strength of the anionic component increased; and (3) the decaborane olefin-hydroboration reaction was retarded by the addition of acids that were stronger than decaborane, all suggest that $B_{10}H_{14}$ ionization was enhanced in the ionic liquids and that the $B_{10}H_{13}^-$ anion was the key reactive intermediate in the olefin hydroboration reaction.

Supporting the above hypothesis, it was found that the reactions of $B_{10}H_{13}^-$ salts with 1-octene, either starting with the isolated $[Et_3NH^+][B_{10}H_{13}^-]$ salt or by in situ generation of the $B_{10}H_{13}^-$ anion from $B_{10}H_{14}$ in the presence of bases such as Et_3N or Proton Sponge, resulted in 1-octene hydroboration to produce a mixture of the neutral 6-octyl-$B_{10}H_{13}$ product (**1**), along with its 6-octyl-$B_{10}H_{12}^-$ conjugate anion (**1**$^-$).

The key question that then arises is what is the nature of the attack of the $B_{10}H_{13}^-$ anion at the olefins? The following paper[22] uses computational methods to explore this question. While a fuller discussion of the possible mechanisms will be presented there, the essential finding is that in these reactions it is energetically feasible for the $B_{10}H_{13}^-$ anion to rearrange to an electrophilic-type structure (Figure 5), similar to that of the isoelectronic electrophilic SB_9H_{11} thiaborane cluster, having a LUMO orbital highly localized at the B6 boron and that olefin binding at this site, as for SB_9H_{11},[23] serves as a prelude to hydroboration.

Following hydroboration, the final step (3) in the scheme in Figure 5 involves the protonation of the 6-R-$B_{10}H_{12}^-$ anion to form the neutral product 6-R-$B_{10}H_{13}$. The dissociation of $B_{10}H_{14}$ in bmimCl would lead to the formation of $B_{10}H_{13}^-$ and HCl. While HCl, HBr, and HI are of course strong acids in water, they are only partially disassociated in many organic solvents (for example, in DCE, pK_a = 10.8, HCl; 8.7, HBr; 7.9, HI),[24] and the acidic pH observed for the DCE layer after heating $B_{10}H_{14}$ in a bmimCl/DCE mixture is consistent with the presence of dissolved HCl that could then serve as the protonating acid for the final step.

The formation of the protonated neutral 6-octyl-$B_{10}H_{13}$ (**1**) product in both the ionic-liquid and $[Et_3NH^+][B_{10}H_{13}^-]$ reactions with 1-octene suggests that the 6-octyl-$B_{10}H_{12}^-$ anion is a stronger base than the $B_{10}H_{13}^-$ anion, and indeed, it was found in a separate experiment that the reaction of 6-(octyl)-$B_{10}H_{12}^-$ with $B_{10}H_{14}$ resulted in proton transfer to produce neutral 6-(octyl)-$B_{10}H_{13}$ and the $B_{10}H_{13}^-$ anion (eq 7). Likewise, equimolar bmimCl solutions of $B_{10}H_{14}$ exhibited a significantly lower pH (pH ~2) than those of 6-(octyl)-$B_{10}H_{13}$ (pH~3.5).

$$\text{6-octyl-}B_{10}H_{12}^- + B_{10}H_{14} \rightarrow \text{6-octyl-}B_{10}H_{13} + B_{10}H_{13}^- \tag{7}$$

The stronger basicity of 6-(octyl)-$B_{10}H_{12}^-$ compared to that of $B_{10}H_{13}^-$ could explain the different reactivities of the Et_3NH^+ and Bu_4N^+ salts of $B_{10}H_{13}^-$ and 6-(octyl)-$B_{10}H_{12}^-$ salts toward olefins and alkynes. Thus, while $[Et_3NH^+][B_{10}H_{13}^-]$ reacted with 1-octene and 3-hexyne in DCE to produce 6-(octyl)-$B_{10}H_{13}$ and 1,2-Et_2-1,2-$C_2B_{10}H_{10}$, respectively, $[Et_3NH^+]$[6-(octyl)-$B_{10}H_{12}^-$] reacted with neither, becoming reprotonated instead to form neutral 6-octyl-$B_{10}H_{13}$ with loss of triethylamine. Likewise, $[Bu_4N^+]$[6-(octyl)-$B_{10}H_{12}^-$] did not react with 1-octene, whereas $[Bu_4N^+][B_{10}H_{13}^-]$ reacted to give $[Bu_4N^+]$[6-(octyl)-$B_{10}H_{12}^-$]. The stronger basicity of 6-(octyl)-$B_{10}H_{12}^-$ compared to $B_{10}H_{13}^-$ should also result in a corresponding decrease in its electrophilicity and in the degree of 6-(octyl)-$B_{10}H_{13}$ ionization. All of these differences could play a role in the fact that higher alkylated products were not observed in the ionic-liquid-mediated reactions with olefins. Thus, once formed in the sequence in Figure 5, protonation of the 6-R-$B_{10}H_{12}^-$ anions by HCl or decaborane would be expected to be more favorable than an electrophilic attack at the olefin. These factors would also seem to disfavor the reactions of 6-R-$B_{10}H_{13}$ with alkynes, but, it was found that the 6-R-$B_{10}H_{13}$ derivatives underwent ionic-liquid-mediated dehydrogenative alkyne-insertion reactions in biphasic bmimCl/toluene mixtures to produce 3-R-1,2-R'_2-1,2-$C_2B_{10}H_9$ *ortho*-carborane derivatives in high yields. Thus, the reasons for observed differences in the reactivities of the 6-R-$B_{10}H_{12}^-$ and $B_{10}H_{13}^-$ anions toward olefins and alkynes in the presence of ionic liquids is even more complex, with the ionic liquid possibly playing an additional role in alkyne activation.

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(21) (a) Guter, G. A.; Schaeffer, G. W. *J. Am. Chem. Soc.* **1956**, *78*, 3546. (b) Hawthorne, M. F.; Pitochelli, A. R.; Strahm, R. D.; Miller, J. J. *J. Am. Chem. Soc.* **1960**, *82*, 1825–1829. (c) Hermanek, S.; Plotova, H. *Collect. Czech. Chem. Commun.* **1971**, *36*, 1639–1643.

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In summary, the ionic-liquid-promoted decaborane olefin-hydroboration reactions now provide general, one-step, high yield routes to many substituted decaboranes with a wide range of functionalities including, alkenyl, halide, phenyl, ether, ester, pinacolborane, ketone, and alcohol groups. Likewise, this method can be used to hydroborate olefins with terminal, internal, or cyclic double bonds in both their cis and trans geometries, with high yields and reasonable reaction times. While $B_{10}H_{13}^-$ salts also exhibited activity for decaborane olefin-hydroboration with 1-octene, the ionic-liquid-based systems provide the most general synthetic route to 6-R-$B_{10}H_{13}$ derivatives. The subsequent ionic-liquid-promoted dehydrogenative alkyne-insertion reactions of these derivatives also provide high yield routes to B-functionalized *ortho*-carborane derivatives. The combination of the new ionic-liquid-mediated decaborane olefin-hydroboration and dehydrogenative alkyne-insertion reactions has the potential to provide a wide range of more complex *ortho*-carborane derivatives with different functionalities at the B3-boron and the cage-carbons. Finally, these results suggest that the unique properties of ionic liquids might be beneficial for other polyborane reactions.

Acknowledgment. We thank the National Science Foundation for the support of this project.

Supporting Information Available: X-ray crystallographic data for structure determinations of compounds **2** and **15** in CIF format, IR data for all compounds, tables summarizing olefin-hydroboration activities of different substrates, ionic-liquids, and salts under various conditions, and summary of qualitative solution pH measurements. This material is available free of charge via the Internet at http://pubs.acs.org.

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(23) Meneghelli, B. J.; Bower, M.; Canter, N.; Rudolph, R. W. *J. Am. Chem. Soc.* **1980**, *102*, 4355–4360.

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