Inorg. Chem. **2008**, *47*, 9193−9202

Inorganic Chemistry

Article

Ionic-Liquid-Promoted Decaborane Dehydrogenative Alkyne-Insertion Reactions: A New Route to *o*-Carboranes

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Received May 31, 2008

Unlike in conventional organic solvents, where Lewis base catalysts are required, decaborane dehydrogenative alkyne-insertion reactions proceed rapidly in biphasic ionic-liquid/toluene mixtures with a wide variety of terminal and internal alkynes, thus providing efficient, one-step routes to functional *o*-carborane 1-R-1,2-$C_2B_{10}H_{11}$ and 1-R-2-R′-1,2-$C_2B_{10}H_{10}$ derivatives, including R = C_6H_5− (**1**), C_6H_{13}− (**2**), HC≡C−$(CH_2)_5$− (**3**), (1-$C_2B_{10}H_{11}$)−$(CH_2)_5$− (**4**), $CH_3CH_2C(O)OCH_2$− (**5**), $(C_2H_5)_2NCH_2$− (**6**), NC−$(CH_2)_3$− (**7**), 3-HC≡C−C_6H_4− (**8**), (1-$C_2B_{10}H_{11}$)−1,3-C_6H_4− (**9**), HC≡C−CH_2−O−CH_2− (**10**); R,R′ = C_2H_5− (**11**); R = $HOCH_2$−, R′ = CH_3− (**12**); R = $BrCH_2$−; R′ = CH_3− (**13**); R = $H_2C{=}C(CH_3)$−, R′ = C_2H_5− (**14**). The best results were obtained from reactions with only catalytic amounts of bmimCl (1-butyl-3-methylimidazolium chloride), where in many cases reaction times of less than 20 min were required. The experimental data for these reactions, the results observed for the reactions of $B_{10}H_{13}^-$ salts with alkynes, and the computational studies reported in the third paper in this series all support a reaction sequence involving (1) the initial ionic liquid promoted formation of the $B_{10}H_{13}^-$ anion, (2) addition of $B_{10}H_{13}^-$ to the alkyne to form an *arachno*-R,R′-$C_2B_{10}H_{13}^-$ anion, and (3) protonation of *arachno*-R,R′-$C_2B_{10}H_{13}^-$ to form the final neutral 1-R-2-R′-1,2-$C_2B_{10}H_{10}$ product with loss of hydrogen.

Introduction

Because of their high boron content and excellent chemical and thermal stabilities, *o*-carborane clusters are important components in applications ranging from medicine[1] (boron neutron capture therapy) to materials science.[2] The syntheses of mono- and di-C-substituted *o*-carborane derivatives have previously been most conveniently achieved (eqs 1 and 2)[3] through the reactions of alkynes with either decaborane/Lewis-base (L) mixtures or 6,9-$B_{10}H_{12}\cdot L_2$ (e.g., L = SEt_2, CH_3CN) compounds. Reaction times are normally several

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10.1021/ic800999y CCC: $40.75

hours with typical yields of <75% for terminal alkynes and with much lower yields (or not work at all) for internal alkynes.

$$B_{10}H_{14} + 2L \xrightarrow{\Delta} B_{10}H_{12}L_2\ (L = SEt_2\,\text{or}\ CH_3CN) + H_2 \quad (1)$$

$$B_{10}H_{12}L_2 + RC{\equiv}CH \rightarrow 1\text{-}R\text{-}1,2\text{-}C_2B_{10}H_{11} + 2L + H_2 \quad (2)$$

We report in this paper that, in contrast to the conventional routes, decaborane dehydrogenative alkyne-insertion reactions in biphasic ionic-liquid/toluene mixtures proceed rapidly (in many cases in less than 20 min) with both terminal and internal alkynes without the need of any added Lewis base catalyst and thus provide improved, one-step routes to an array of C-substitiuted, 1-R-1,2-$C_2B_{10}H_{11}$ and 1-R-2-R′-1,2-$C_2B_{10}H_{10}$, *o*-carborane derivatives.

Experimental Section

General 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.[4]

Phenylacetylene, 3-hexyne, 1-octyne, bis(triphenylphosphoranylidene) ammonium chloride [PPNCl], 2-methyl-1-hexen-3-yne, Bu_4NCl, 1,8-bis(dimethylamino)naphthalene [Proton Sponge, PS], Me_4NF, Bu_4NPF_6 (Aldrich), methyl propiolate, 1,8-nonadiyne (Chemical Samples), propargylpropionate, 2-butyn-1-ol (Lancaster), 3-diethylamino-1-propyne, 5-cyano-1-pentyne and *m*-diethynylbenzene (GSF Chemicals) were used as received. The literature method was used to prepare $[Et_3NH^+][B_{10}H_{13}^-]$.[5] The 1-butyl-3-methyl-imidazolium chloride [bmimCl], 1-butyl-3-methyl-imidazolium bromide [bmimBr], 1-butyl-3-methylimidazolium iodide [bmimI], 1-butyl-3-methylimidazolium hexafluorophosphate [bmimPF_6], 1-butyl-3-methylimidazolium tetrafluoroborate [bmimBF_4], trihexyl(tetradecyl)phosphonium tetrafluoroborate [thtdpBF_4], 1-butyl-4-methylpyridinium tetrafluoroborate [bmpyBF_4], 1-butylpyridimiun hexafluorophosphate [bpyPF_6], 1-butyl-3-methylimidazolium trifluoromethanesulfonate [bmimOTF] (Fluka) were dried by carrying out azetropic distillations with toluene, followed by in vacuo drying. They were then stored in the dry box until use. Decaborane, $B_{10}H_{14}$ (Callery), was sublimed prior to use. HPLC or ACS grade hexanes, toluene, ethyl acetate, CH_2Cl_2, NEt_3, and silica gel with mesh sizes of 230−400 (Fisher) were used as received. C_6D_6 (D, 99.5%) and CD_2Cl_2 (D, 99.9%) (Cambridge Isotope) were used as received.

Physical Measurements. ^1H 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 ^1H 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.

Table 1. Comparison of Decaborane Reactions with Phenylacetylene in Different Biphasic Systems[a]

ionic phase (g, mmol)	time (h) for $B_{10}H_{14}$ consumption	ionic phase (g, mmol)	time (h) for $B_{10}H_{14}$ consumption
bmimBF_4 (0.9, 3.9)	96	bmimCl (0.21, 1.2)	0.1
bmimPF_6 (1.0, 3.5)	72	bmimI (0.33, 1.2)	no reaction
thtdpBF_4 (1.1, 1.9)	48	bmimOTf (0.23, 0.8)	no reaction
bmpyBF_4 (0.9, 3.9)	24	Bu_4NCl (0.26, 0.9)	0.5
bmimBr (0.34, 0.7)	20	Bu_4NPF_6 (1.0, 2.6)	20
bpyPF_6 (0.31, 1.1)	16	PPNCl (1.1, 1.9)	1
		Me_4NF (0.18, 2.2)	20

[a] All reactions were performed at 120 °C and used ~0.4 g (3.2 mmol) of $B_{10}H_{14}$, an excess (~0.6 g, 5.9 mmol) of phenylacetylene, and ~10 mL of toluene.

Reaction of $B_{10}H_{14}$ and an Alkyne in the Absence of an Ionic Liquid. A 50 mL, 2-neck round bottom flask equipped with a septum, stir bar, and vacuum adapter was charged under an inert atmosphere with 0.102 g (0.83 mmol) of $B_{10}H_{14}$, 0.4 mL (3.6 mmol) of phenylacetylene and ~10 mL of toluene. After heating the reaction mixture at 120 °C for 1 h, analysis by ^{11}B NMR of an aliquot of the toluene layer showed only unreacted $B_{10}H_{14}$.

General Synthetic Procedures. A 50 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 $B_{10}H_{14}$, alkyne and toluene. Using the vacuum adapter, the flask was attached to a water condenser open to argon and the body of the flask then submerged in an oil bath (usually at 120 °C) equipped with a magnetic stir plate. The mixture was vigorously stirred during reaction 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 pipette. The ionic liquid layer was then extracted with 10−20 mL of ether. The combined toluene and ether extracts were vacuum concentrated and then flash-filtered through a silica gel column.

Syntheses in Ionic Liquids. 1-C_6H_5-1,2-$C_2B_{10}H_{11}$ (1).[3,6] Reaction of $B_{10}H_{14}$ (0.307 g, 2.51 mmol) with 0.674 g (6.60 mmol) of phenylacetylene in biphasic toluene (~10 mL)/bmimCl (0.209 g, 1.20 mmol) at 120 °C for 7 min gave, following hexanes elution from a silica gel column, 0.400 g (1.78 mmol, 71% yield) of **1** as a white solid. mp: 66−67 °C (lit. 66−67 °C).[6] NCI-HRMS (*m/e*) calcd for $^{12}C_8{}^{11}B_{10}{}^1H_{16}$: 222.2182; found 222.2185. Anal. Calcd: C, 43.61; H, 7.32. Found: C, 43.80; H, 7.60. The ^1H and ^{11}B NMR and IR data (Tables S1 and S2, Supporting Information) are consistent with literature values.[6]

The reactions of $B_{10}H_{14}$ (~0.4 g, 3.2 mmol) with phenylacetylene (~0.6 g, 5.9 mmol) in biphasic mixtures of toluene (~10 mL) and other ionic liquids are compared in Table 1.

1-C_6H_{13}-1,2-$C_2B_{10}H_{11}$ (2).[7] Reaction of $B_{10}H_{14}$ (0.251 g, 2.06 mmol) with 0.720 g (6.53 mmol) of 1-octyne in biphasic toluene (~10 mL)/bmimCl (0.194 g, 1.11 mmol) at 120 °C for ~7 min gave, following hexanes elution from a silica gel column, 0.430 g (1.86 mmol, 91% yield) of **2** as an oily liquid. NCI-HRMS (*m/e*) calcd for $^{12}C_8{}^{11}B_{10}{}^1H_{24}$: 230.2802; found 230.2819. Anal. Calcd:

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C, 42.07; H, 10.59. Found: C, 42.98; H, 10.43. Spectral data for **2** were not previously reported. ^{11}B NMR (128.4 MHz, C_6D_6, ppm, J = Hz): δ −3.1 (d, 1B, J 147), −6.5 (d, 1B, J 143), −10.1 (d, 2B, J 151), −12.2 (d, 2B, J 160), −13.2 (d, 2B, J undefined), −13.9 (d, 2B, J 156). ^{1}H NMR (400.1 MHz, C_6D_6, ppm, J = Hz): δ 2.53 (s, 1H, cage C−H), 1.62-1.57 (2H, CH_2), 1.24-1.15 (m, 4H, CH_2CH_2), 1.07-1.00 (m, 4H, CH_2CH_2), 0.88 (t, 3H, J 7.2, CH_3).

1-(HC≡C-(CH$_2$)$_5$)-1,2-C$_2$B$_{10}$H$_{11}$ (3). Reaction of $B_{10}H_{14}$ (0.228 g, 1.86 mmol) with 0.7 mL (~4.6 mmol) of 1,8-nonadiyne in biphasic toluene (~10 mL)/bmimCl (0.138 g, 0.79 mmol) at 120 °C for 10 min gave, following CH_2Cl_2 elution from a silica gel column, 0.282 g (1.18 mmol, 63% yield) of **3** as an oily liquid. NCI-HRMS (*m/e*) calcd for $^{12}C_9{}^{11}B_{10}{}^1H_{22}$: 240.2652; found 240.2643. ^{11}B NMR (128.4 MHz, C_6D_6, ppm, J = Hz): δ −2.8 (d, 1B, J 146), −6.1 (d, 1B, J 138), −9.8 (d, 2B, J 151), −12.1 (d, 2B, J 157), −13.0 (d, 2B, J undefined), −13.6 (d, 2B, J undefined). ^{1}H NMR (400.1 MHz, C_6D_6, ppm, J = Hz): δ 2.46 (s, 1H, cage C−H), 1.89 (m, 2H, CH_2), 1.80 (m, 2H, CH_2), 1.49 (m, 2H, CH_2), 1.22 (s, 1H, HC≡C), 1.10 (m, 2H, CH_2), 0.88 (m, 2H, CH_2).

1,1′-(CH$_2$)$_5$-(1,2-C$_2$B$_{10}$H$_{11}$)$_2$ (4).[8] Reaction of $B_{10}H_{14}$ (0.447 g, 3.66 mmol) with 0.215 g (1.79 mmol) of 1,8-nonadiyne in biphasic toluene (~10 mL)/bmimCl (0.150 g, 0.86 mmol) at 120 °C for ~10 min gave, following CH_2Cl_2 elution from a silica gel column, 0.379 g (1.06 mmol, 59% yield) of **4** as a white solid. mp: 177−179 °C (lit. 177−179 °C).[8] NCI-HRMS (*m/e*) calcd for $^{12}C_9{}^{11}B_{20}{}^1H_{32}$: 360.4364; found 360.4386. Anal. Calcd: C, 30.32; H, 9.05. Found: C, 30.60; H, 9.34. The ^{11}B and ^{1}H NMR and IR data (Tables S1 and S2, Supporting Information) are consistent with literature values.[8]

1-CH$_3$CH$_2$C(O)OCH$_2$-1,2-C$_2$B$_{10}$H$_{11}$ (5).[9] Reaction of $B_{10}H_{14}$ (0.245 g, 2.01 mmol) with 0.4 mL (~2.5 mmol) of propargylpropionate in biphasic toluene (~10 mL)/bmimCl (0.120 g, 0.69 mmol) at 120 °C for ~10 min gave, following ethyl acetate elution from a silica gel column, 0.337 g (1.46 mmol, 73% yield) of **5** as an oily liquid. NCI-HRMS (*m/e*) calcd for $^{12}C_6{}^{11}B_{10}{}^1H_{18}{}^{16}O_2$: 232.2236; found 232.2225. Anal. Calcd: C, 31.28; H, 7.92. Found: C, 31.52; H, 7.96. Spectral data for **5** were not previously reported. ^{11}B NMR (128.4 MHz, C_6D_6, ppm, J = Hz): δ 2.5 (d, 1B, J 149), −5.0 (d, 1B, J 148), −10.0 (d, 2B, J 151), −12.2 (d, 2B, J 158), −13.8 (d, 4B, J 169). ^{1}H NMR (400.1 MHz, C_6D_6, ppm, J = Hz): δ 4.00 (s, 2H, −CH_2−O−), 3.13 (s, 1H, cage C−H), 1.88 (q, 2H, J 7.5, CH_2CH_3), 0.85 (t, 3H, J 7.5, CH_3).

1-(C$_2$H$_5$)$_2$NCH$_2$-1,2-C$_2$B$_{10}$H$_{11}$ (6).[3] Reaction of $B_{10}H_{14}$ (0.170 g, 1.39 mmol) with 0.25 mL (~1.8 mmol) of 3-diethylamino-1-propyne in biphasic toluene (~10 mL)/bmimCl (0.090 g, 0.51 mmol) at 120 °C for ~30 min gave, following hexanes elution from a silica gel column, 0.146 g (0.64 mmol, 46% yield) of **6** as a white solid. mp: 33−34 °C (lit. 33−35 °C).[3] NCI-HRMS (*m/e*) calcd for $^{12}C_7{}^{11}B_{10}{}^1H_{23}{}^{14}N$: 231.2761; found 231.2764. Anal. Calcd: C, 36.66; H, 10.11; N, 6.11. Found: C, 36.51; H, 10.30; N, 5.89. Spectral data for **6** were not previously reported. ^{11}B NMR (128.4 MHz, C_6D_6, ppm, J = Hz): δ −3.1 (d, 1B, J 149), −5.6 (d, 1B, J 149), −9.5 (d, 2B, J 150), −11.9 (d, 2B, J 161), −13.6 (d, 4B, J 158). ^{1}H NMR (400.1 MHz, C_6D_6, ppm, J = Hz): 3.34 (s, 1H, cage C−H), 2.50 (s, 2H, N-CH_2), 2.03 (q, 4H, J7.1, CH_2CH_3), 0.56 (t, 6H, J 7.1, CH_3).

1-NC-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{11}$ (7).[10] Reaction of $B_{10}H_{14}$ (0.180 g, 1.47 mmol) with 0.4 mL (~3.8 mmol) of 5-cyano-1-pentyne in biphasic toluene (~10 mL)/bmimCl (0.095 g, 0.54 mmol) at 120 °C for ~30 min gave, following ethyl acetate elution from a silica gel column, 0.200 g (0.95 mmol, 65% yield) of **7** as a white solid. mp: 81−82 °C (lit. 81−82 °C).[10] NCI-HRMS (*m/e*) calcd for $^{12}C_6{}^{11}B_{10}{}^1H_{17}{}^{14}N$: 213.2291, found 213.2298. Anal. Calcd: C, 34.10; H, 8.11; N, 6.63. Found: C, 34.35; H, 8.14; N, 6.71. The ^{11}B and ^{1}H NMR and IR data (Tables S1 and S2, Supporting Information) are consistent with literature values.[10]

1-(3-HC≡C−C$_6$H$_4$)-1,2-C$_2$B$_{10}$H$_{11}$ (8). Reaction of $B_{10}H_{14}$ (0.295 g, 2.42 mmol) with 0.6 mL (~3.8 mmol) of *m*-diethynylbenzene in biphasic toluene (~10 mL)/bmimCl (0.240 g, 1.37 mmol) at 120 °C for ~20 min gave, following hexanes elution from a silica gel column, 0.250 g (1.02 mmol, 42% yield) of **8** as a light yellow solid. mp: 59−61 °C. NCI-HRMS (*m/e*) calcd for $^{12}C_{10}{}^{11}B_{10}{}^1H_{16}$: 246.2182; found 246.2187. Anal. Calcd: C, 49.16; H, 6.60. Found: C, 48.88; H, 6.62. ^{11}B NMR (128.4 MHz, C_6D_6, ppm, J = Hz): −2.4 (d, 1B, J 151), −4.6 (d, 1B, J 151), −9.4 (d, 2B, J 153), −11.7 (d, 2B, J 163), −12.3 (d, 2B, J undefined), −14.7 (d, 2B, J 158). ^{1}H NMR (400.1 MHz, CD_2Cl_2, ppm, J = Hz): δ 7.61 (m, 1H, C_6H_4), 7.50 (m, 2H, C_6H_4), 7.33 (t, 1H, J 7.8, C_6H_4), 4.07 (s, 1H, cage C−H), 3.19 (s, 1H, −C≡CH).

1,1′-(1,3-C$_6$H$_4$)-(1,2-C$_2$B$_{10}$H$_{11}$)$_2$ (9).[11] Reaction of $B_{10}H_{14}$ (0.337 g, 2.75 mmol) with 0.5 mL (0.169, 1.33 mmol) of *m*-diethynylbenzene in biphasic toluene (~10 mL)/bmimCl (0.168 g, 0.95 mmol) at 120 °C for ~20 min gave, following hexane elution from a silica gel column, 0.168 g (0.46 mmol, 35% yield) of **9** as a white solid. The ^{11}B and ^{1}H NMR data (Tables S1 and S2, Supporting Information) are consistent with the literature values.[11]

1-(HC≡C-CH$_2$-O-CH$_2$)-1,2-C$_2$B$_{10}$H$_{11}$ (10). Reaction of $B_{10}H_{14}$ (0.351 g, 2.87 mmol) with 0.7 mL (6.8 mmol) of dipropargyl ether in biphasic toluene (~10 mL)/bmimCl (0.308 g, 1.76 mmol) at 120 °C for ~20 min gave, following CH_2Cl_2/hexane (1:4 ratio) elution from a silica gel column, 0.333 g (1.56 mmol, 55% yield) of **10** as an oily liquid. NCI-HRMS (*m/e*) calcd for $^{12}C_6{}^{11}B_{10}{}^1H_{16}O$: 214.2131; found 214.2127. Anal. Calcd: C, 33.95; H, 7.60. Found: C, 34.37; H, 7.84. ^{11}B NMR (128.4 MHz, C_6D_6, ppm, J = Hz): δ −3.5 (d, 1B, J 153), −5.3 (d, 1B, J 140), −9.8 (d, 2B, J 157), −12.4 (d, 2B, J 168), −13.9 (d, 4B, J 156). ^{1}H NMR (400.1 MHz, C_6D_6, ppm, J = Hz): δ 3.47 (s, 2H, −O−CH_2−), 3.32 (s, 2H, −O−CH_2−), 3.18 (s, 1H, cage C−H), 1.98 (s, 1H, −C≡CH).

1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (11).[12] Reaction of $B_{10}H_{14}$ (0.468 g, 3.83 mmol) with 0.682 g (8.30 mmol) of 3-hexyne in biphasic toluene (~10 mL)/bmimCl (0.204 g, 1.17 mmol) at 120 °C for ~7 min gave, following hexane elution from a silica gel column, 0.537 g (2.68 mmol, 70% yield) of **11** as a white solid. mp: 74−75 °C. NCI-HRMS (*m/e*) calcd for $^{12}C_6{}^{11}B_{10}{}^1H_{20}$: 202.2802; found 202.2819. Anal. Calcd: C, 35.97; H, 10.06. Found: C, 35.91; H, 10.27. The

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^{11}B and ^{1}H NMR and IR data (Tables S1 and S2, Supporting Information) are consistent with literature values.[12]

1-HOCH$_2$-2-Me-1,2-C$_2$B$_{10}$H$_{10}$ (12).[13] Reaction of B$_{10}$H$_{14}$ (0.181 g, 1.48 mmol) with 0.402 g (5.74 mmol) of 2-butyn-1-ol in biphasic toluene (~10 mL)/bmimCl (0.113 g, 0.65 mmol) at 60 °C for ~10 h gave, following CH$_2$Cl$_2$ elution from a silica gel column, 0.179 g (0.95 mmol, 64% yield) of **12** as a white solid. mp: 270−272 °C (lit. 268−269 °C).[13] NCI-HRMS (*m/e*) calcd for ^{12}C$_4$^{11}B$_{10}$^{1}H$_{16}$^{16}O: 190.2131; found 190.2138. Anal. Calcd: C, 25.52; H, 8.57. Found: C, 25.80; H, 8.76. Spectral data for **12** were not previously reported. ^{11}B NMR (128.4 MHz, C$_6$D$_6$, ppm, *J* = Hz): δ −4.5 (d, 1B, *J* 153), −6.2 (d, 1B, *J* 144), −10.5 (d, 2B, *J* 162), −11.0 (d, 2B, *J* undefined), −11.7 (d, 4B, *J* 151). ^{1}H NMR (400.1 MHz, C$_6$D$_6$, ppm, *J* = Hz): δ 3.27 (d, 2H, *J* 7.3, CH$_2$OH), 1.29 (s, 3H, CH$_3$), 1.0 (t, 1H, *J* 7.3, OH).

1-BrCH$_2$-2-Me-1,2-C$_2$B$_{10}$H$_{10}$ (13).[3] Reaction of B$_{10}$H$_{14}$ (0.271 g, 2.22 mmol) with 0.4 mL (~4.6 mmol) of 1-bromo-2-butyne in biphasic toluene (~10 mL)/bmimCl (0.094 g, 0.54 mmol) at 120 °C for ~4 h gave, following ethyl acetate elution from a silica gel column, 0.490 g (1.95 mmol, 88% yield) of **13** as a white solid. mp: 126−127 °C (lit. 125−127 °C).[3] NCI-HRMS (*m/e*) calcd for ^{12}C$_4$^{11}B$_{10}$^{1}H$_{15}$^{80}Br: 252.1288; found 252.1269. Anal. Calcd: C, 19.14; H, 6.02. Found: C, 18.88; H, 5.92. Spectral data for **13** were not previously reported. ^{11}B NMR (128.4 MHz, C$_6$D$_6$, ppm, *J* = Hz): δ −3.8 (d, 1B, *J* 159), −5.5 (d, 1B, *J* 157), −10.4 (d, 8B, *J* undefined). ^{1}H NMR (400.1 MHz, C$_6$D$_6$, ppm, *J* = Hz): δ 3.02 (s, 2H, CH$_2$), 1.15 (s, 3H, CH$_3$).

1-H$_2$C=C(CH$_3$)-2-Et-1,2-C$_2$B$_{10}$H$_{10}$ (14). Reaction of B$_{10}$H$_{14}$ (0.129 g, 1.06 mmol) with 0.187 g (~2.0 mmol) of 2-methyl-1-hexen-3-yne in biphasic toluene (~10 mL)/bmimCl (0.120 g, 0.69 mmol) at 120 °C for ~10 min gave, following pentane elution from a silica gel column, 0.184 g (0.87 mmol, 82% yield) of **14** as an oily liquid. NCI-HRMS (*m/e*) calcd for ^{12}C$_7$^{11}B$_{10}$^{1}H$_{20}$: 214.2495; found 214.2489. Anal. Calcd: C, 39.59; H, 9.49. Found: C, 39.58; H, 9.88. ^{11}B NMR (128.4 MHz, C$_6$D$_6$, ppm, *J* = Hz): δ −4.2 (d, 1B, *J* 150), −4.9 (d, 1B, *J* 149), −10.7 (d, 4B, *J* 148), −11.8 (d, 4B, *J* 155). ^{1}H NMR (400.1 MHz, C$_6$D$_6$, ppm, *J* = Hz): δ 4.99 (d, 2H, *J* 29.7, =CH$_2$), 1.54 (q, 2H, *J* 7.6, CH$_2$CH$_3$), 1.43 (s, 3H, CH$_3$−C=CH$_2$), 0.69 (t, 3H, *J* 7.6, CH$_2$CH$_3$).

***arachno*-8-(NC)-7,8-C$_2$B$_{10}$H$_{14}^-$ (15).**[14] Analysis by ^{11}B NMR of aliquots of both the toluene and ionic liquid layers following the reaction of B$_{10}$H$_{14}$ (0.125 g, 1.02 mmol) with 0.25 mL of cyanoacetylene in biphasic toluene (~10 mL)/bmimCl (0.168 g, 0.96 mmol) at 120 °C for ~30 min showed the formation of *arachno*-8-(NC)-7,8-C$_2$B$_{10}$H$_{14}^-$.

Reaction of B$_{10}$H$_{14}$ with Phenylacetylene in Acidic bmimCl/Toluene. HCl was bubbled through a mixture of B$_{10}$H$_{14}$ (0.253 g, 2.1 mmol), bmimCl (0.157 g, 0.9 mmol), and toluene (10 mL) for 15 min; then 0.6 mL (5.4 mmol) of phenylacetylene was added, and the mixture heated at 115 °C for 20 min. Analysis by ^{11}B NMR of the toluene layer showed only unreacted B$_{10}$H$_{14}$.

Syntheses with Halide Salts. 1-C$_6$H$_5$-1,2-C$_2$B$_{10}$H$_{11}$ (1). The reaction of B$_{10}$H$_{14}$ (0.326 g, 2.67 mmol) with 0.5 mL (~4.5 mmol) of phenylacetylene and 0.689 g (2.48 mmol) of Bu$_4$NCl in toluene (~10 mL) at 120 °C for 30 min resulted in the formation of two layers. Extraction of the toluene layer gave, following hexane elution from a silica gel column, 0.196 g (0.89 mmol, 34% yield) of **1**. In a similar manner, reactions of (1) B$_{10}$H$_{14}$ (0.309 g, 2.53 mmol) with 0.5 mL (~4.5 mmol) of phenylacetylene and 1.087 g of (1.9 mmol) bis(triphenylphosphoranylidene) ammonium chloride (PPNCl) in toluene (~10 mL) at 120 °C for ~1 h gave 0.159 g (0.70 mmol, 28% yield) of **1**; (2) B$_{10}$H$_{14}$ (0.158 g, 1.29 mmol) with 0.5 mL (~4.5 mmol) of phenylacetylene and 0.176 g (1.89 mmol) of Me$_4$NF in toluene (~10 mL) at 110 °C for 10 h gave 0.065 g (0.30 mmol, 23% yield) of **1**; and (3) B$_{10}$H$_{14}$ (0.327 g, 2.68 mmol) with ~0.5 mL (~4.5 mmol) of phenylacetylene and 1.019 g (2.63 mmol) of Bu$_4$NPF$_6$ in toluene (~10 mL) at 110 °C for ~20 h gave 0.376 g (1.71 mmol, 64% yield) of **1**.

1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (11). Reaction of B$_{10}$H$_{14}$ (0.221 g, 1.81 mmol) with ~0.4 mL (~3.5 mmol) of 3-hexyne and 0.466 g (1.68 mmol) of Bu$_4$NCl in toluene (~10 mL) at 110 °C for ~0.5 h, gave 0.194 g (0.97 mmol, 53% yield) of **11**, and reaction of B$_{10}$H$_{14}$ (0.196 g, 1.60 mmol) with ~0.4 mL (~3.5 mmol) of 3-hexyne and 0.835 g (1.45 mmol) of PPNCl in toluene (~10 mL) at 110 °C for ~1 h gave 0.091 g (0.45 mmol, 28% yield) of **11**.

Syntheses via [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$] Salts. 1-C$_6$H$_5$-1,2-C$_2$B$_{10}$H$_{11}$ (1). Reaction of [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$] (0.362 g, 1.62 mmol) with ~0.5 mL (~4.5 mmol) of phenylacetylene and ~10 mL toluene at 110 °C for 10 min gave 0.233 g (1.06 mmol, 66% yield) of **1**.

1-C$_6$H$_{13}$-1,2-C$_2$B$_{10}$H$_{11}$ (2). Reaction of [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$] (0.369 g, 1.65 mmol) with 0.4 mL (~2.7 mmol) of 1-octyne in toluene (~10 mL) at 120 °C for ~10 min gave 0.215 g (0.87 mmol, 57% yield) of **2**.

1-(C$_2$H$_5$)$_2$NCH$_2$-1,2-C$_2$B$_{10}$H$_{11}$ (6). Reaction of [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$] (0.411 g, 1.84 mmol) with ~0.5 mL (~3.6 mmol) of 3-diethylamino-1-propyne in toluene (~10 mL) at 120 °C for ~10 min gave 0.134 g (0.06 mmol, 32% yield) of **6**.

1-NC-(CH$_2$)$_3$-1,2-C$_2$B$_{10}$H$_{11}$ (7). Reaction of [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$] (0.378 g, 1.69 mmol) with 0.5 mL (~4.8 mmol) of 5-cyano-1-pentyne in toluene (~10 mL) at 110°C for ~10 min, gave, following ethyl acetate elution from a silica gel column and recrystallization from hot pentane, 0.189 g (0.89 mmol, 53% yield) of **7**.

1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (11). Reaction of [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$] (0.361 g, 1.62 mmol) with 0.4 mL (~3.5 mmol) of 3-hexyne in toluene (~10 mL) at 120 °C for ~10 min gave 0.108 g (1.13 mmol, 70% yield) of **11**.

Syntheses via in Situ Generation of [PSH$^+$][B$_{10}$H$_{13}^-$] or [Et$_3$NH$^+$][B$_{10}$H$_{13}^-$]. 1-C$_6$H$_5$-1,2-C$_2$B$_{10}$H$_{11}$ (1). Reaction of B$_{10}$H$_{14}$ (0.233 g, 1.90 mmol) with 0.5 mL (~4.5 mmol) of phenylacetylene and 0.413 g (1.93 mmol) of Proton Sponge in toluene (~10 mL) at 110 °C for 1 h gave 0.086 g (0.38 mmol, 20% yield) of **1**. Likewise, reaction of B$_{10}$H$_{14}$ (0.249 g, 2.03 mmol) with ~0.4 mL (~3.4 mmol) of phenylacetylene and 0.292 g (2.8 mmol) of Et$_3$N in toluene (~10 mL) at 110 °C for ~10 min gave 0.118 g (0.54 mmol, 26% yield) of **1**.

1,2-Et$_2$-1,2-C$_2$B$_{10}$H$_{10}$ (11). Reaction of B$_{10}$H$_{14}$ (0.242 g, 1.98 mmol) with ~0.4 mL (~3.5 mmol) of 3-hexyne and 0.538 g (2.51 mmol) of Proton Sponge in toluene (~10 mL) at 110 °C for ~30 min gave 0.093 g (0.47 mmol, 23% yield) of **11**, and reaction of of B$_{10}$H$_{14}$ (0.278 g, 2.27 mmol) with ~0.5 mL (~4.4 mmol) of 3-hexyne and 0.220 g (2.2 mmol) of Et$_3$N in toluene (~10 mL) at 110 °C for ~10 min gave 0.141 g (0.70 mmol, 31% yield) of **11**.

Reaction with [Bu$_4$N$^+$][B$_{10}$H$_{13}^-$]. ^{11}B NMR analysis indicated reaction of [Bu$_4$N$^+$][B$_{10}$H$_{13}^-$] (0.249 g, 0.7 mmol) with ~0.3 mL (~2.7 mmol) of phenylacetylene in ~10 mL of toluene at 110 °C for 30 min, resulted in complete consumption of [Bu$_4$N$^+$][B$_{10}$H$_{13}^-$] to form the B$_9$H$_{14}^-$ anion.[15]

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Table 2. Crystallographic Data Collection and Structural Refinement Information for **4**, **8**, and **9**

	4	**8**	**9**
empirical formula	$C_9B_{20}H_{32}$	$C_{10}B_{10}H_{16}$	$C_{10}B_{20}H_{26}$
fw	356.55	244.33	362.51
crystal class	monoclinic	orthorhombic	monoclinic
space group	$P2_1/c$ (No. 14)	$Pca2_1$ (No. 29)	$C2/c$ (No. 15)
Z	4	4	4
a, Å	13.537(6)	11.138(2)	14.756(2)
b, Å	11.577(5)	11.504(2)	15.817(2)
c, Å	13.750(6)	10.857(2)	11.4501(13)
β, deg	106.01(3)		128.506(3)
V, Å^3	2071.3(15)	1391.1(4)	2091.3(4)
μ, cm^{-1}	0.45	0.55	0.50
cryst size, mm	0.45 × 0.27 × 0.01	0.30 × 0.18 × 0.03	0.40 × 0.28 × 0.03
D_{calcd}, g/cm^3	1.143	1.167	1.151
F(000)	744	504	744
radiation	Mo Kα	Mo Kα	Mo Kα
temp, K	143	143	143
2θ angle, deg	5.14−48.1	5.1−50.08	5.16−50.1
hkl collected	$-15 \le h \le 13$	$-12 \le h \le 13$	$-17 \le h \le 15$
	$-13 \le k \le 11$	$-13 \le k \le 12$	$-18 \le k \le 18$
	$-11 \le l \le 15$	$-12 \le l \le 11$	$-12 \le l \le 13$
reflns measured	6516	5538	7865
unique reflns	3150	2071	1852
	($R_{\mathrm{int}} = 0.0528$)	($R_{\mathrm{int}} = 0.0280$)	($R_{\mathrm{int}} = 0.0448$)
observed reflns ($F > 4\sigma$)	2046	1896	1396
reflns used in refinement	3150	2071	1852
params	263	246	189
R^a indices ($F > 4\sigma$)	R1 = 0.1180	R1 = 0.0457	R1 = 0.0553
	wR2 = 0.2601	wR2 = 0.1149	wR2 = 0.1239
R^a indices (all data)	R1 = 0.1781	R1 = 0.0507	R1 = 0.0805
	wR2 = 03136	wR2 = 0.1218	wR2 = 0.1410
GOF^b	1.136	1.041	1.110
final difference peaks, e/Å^3	+0.587, −0.407	+0.166, 0.192	+0.244, −0.190

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$; $wR2 = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$. [b] $GOF = \{\sum w(F_o^2 - F_c^2)^2/n - p)\}^{1/2}$, where n = no. of reflections and p = no. of parameters refined.

Crystallographic Data for 1,1′-$(CH_2)_5$-(1,2-$C_2B_{10}H_{11}$)$_2$ (4), 1-(3-HC≡C-C_6H_4)-1,2-$C_2B_{10}H_{11}$ (8), and 1,1′-(1,3-C_6H_4)-(1,2-$C_2B_{10}H_{11}$)$_2$ (9). Single crystals of **4** (Upenn no. 3219), **8** (Upenn no. 3267), and **9** (Upenn no. 3271) were grown from hexane solutions at room temperature.

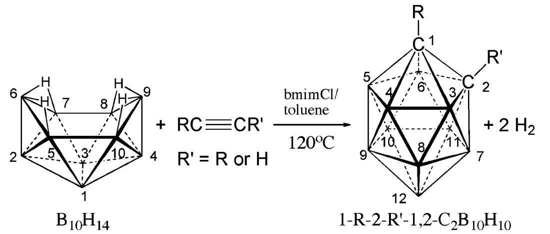
Collection and Reduction of the Data. X-ray intensity data (Table 2) were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Rotation images were processed to produce a listing of unaveraged F^2 and $\sigma(F^2)$ values, which were then passed to the CrystalStructure[16] program package 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).[17a] Refinements were by full-matrix least squares based on F^2 using SHELXL-97.[17b] 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, cage hydrogen atoms were refined isotropically, and chain hydrogen atoms were included as constant contributions to the structure factors and were not refined.

Results

As summarized in Table 3, decaborane was found to react with a variety of internal and terminal alkynes in mixtures of toluene and an ionic liquid, such as 1-butyl-3-methylimidiazolium chloride, bmimCl, to give the corresponding 1-R-1,2-$C_2B_{10}H_{11}$ and 1-R-2-R′-1,2-$C_2B_{10}H_{10}$ *o*-carborane derivatives, **1−14** (eq 3).

(3)



The biphasic reaction mixtures, with an ionic liquid layer at the bottom and the alkyne-toluene layer at the top, were heated at ~120 °C with vigorous stirring to form an emulsion. In many cases, as shown in the NMR spectra in Figure 1 for the reaction of decaborane with 1-octyne in toluene/bmimCl, reactions were complete in only a few minutes. The bottom spectrum shows the initial $B_{10}H_{14}$ starting material in the toluene layer above the ionic liquid. The 1-octyne was added, and the stirred emulsion was heated at 120 °C. The middle spectrum is of the reaction mixture after 4 min, where the peaks of the 1-C_6H_{13}-1,2-$C_2B_{10}H_{11}$ product are clearly visible. The top spectrum shows that the reaction was complete after only 7 min. The toluene layer

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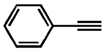
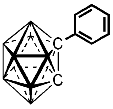
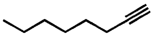
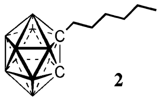
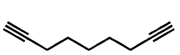
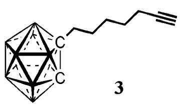
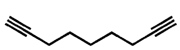
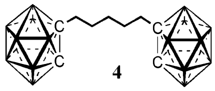
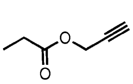
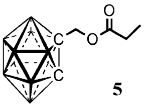
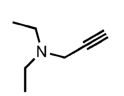
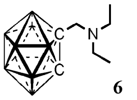
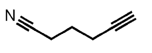
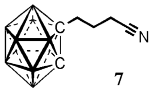
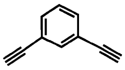
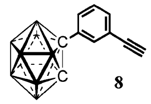
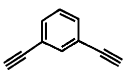
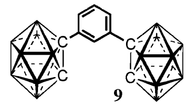
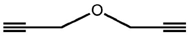
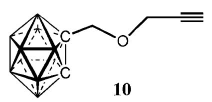
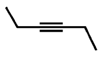
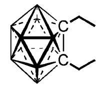
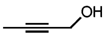
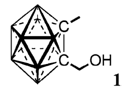
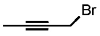
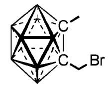
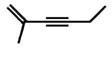
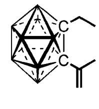
Table 3. Summary of $B_{10}H_{14}$ Dehydrogenative Alkyne Insertions in bmimCl/Toluene

Alkyne	Product	Yield (Time) *Previous Yield (Time)*
	 **1**	71% (7 min) *65-68% (10 h)*[6]
	 **2**	91% (7 min) *60% (23 h)*[7]
	 **3**	63% (7 min) *a*
	 **4**	59% (10 min) *b*
	 **5**	73% (30 min) *b*
	 **6**	46% (30 min) *4% (7.5 h)*[3]
	 **7**	65% (30 min) *74% (5d)*[10]
	 **8**	42% (10 min) *a*
	 **9**	35% (10 min) *44% (2 d)*[11]
	 **10**	55% (20 min) *a*
	 **11**	70% (10 min) *b*
	 **12**	64% (10 h at 60°C) *b*
	 **13**	88% (4 h) *36% (4h)*[3]
	 **14**	82% (10 min) *a*

[a] New compound. [b] The previous synthesis was via lithiocarborane, not by alkyne insertion.

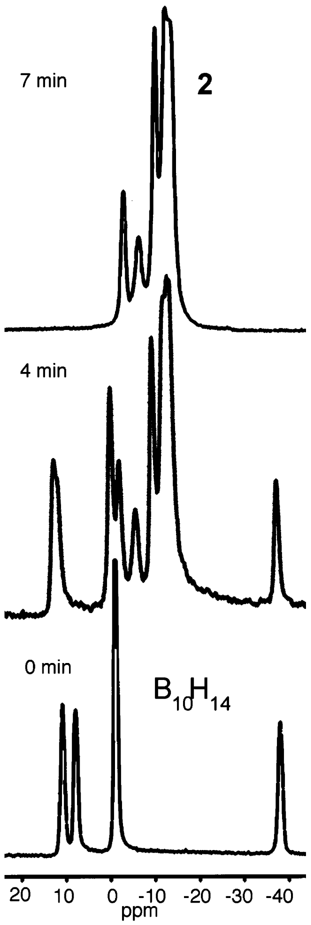


Figure 1. $^{11}B\{^1H\}$ spectra of the toluene layer showing the progress of the reaction of $B_{10}H_{14}$ with 1-octyne at 120 °C to produce 1-C_6H_{13}-1,2-$C_2B_{10}H_{11}$ (**2**) when employing bmimCl/toluene biphasic media.

was separated by pipette, and then the ionic liquid was extracted several 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 eluent. Removal of the solvent afforded a ~90% yield of **2**.

As typical of *o*-carborane derivatives, compounds **1**−**14** were air and water stable and showed good solubilities in polar solvents including THF, methylene chloride, and ethyl acetate. The less polar products **1**, **2**, **6**, **8**, **9**, **11**, and **14** were also soluble in hexanes, benzene, and toluene. Compounds **1**, **2**, **4**−**7**, **9**, and **11**−**13** were previously known, but **3**, **8**, **10**, and **14** had not been reported. All products were characterized by ^{11}B and ^1H NMR, NCI-MS, FT-IR, and elemental analysis.

The C_s symmetric monosubstituted 1-R-1,2-$C_2B_{10}H_{11}$ derivatives **1**−**10** have a mirror plane containing the C1, C2, B9, and B12 atoms and should exhibit six doublets in 1:1:2:2:2:2 ratios in their ^{11}B NMR spectra arising from the B9, B12, B8,10, B4,5, B7,11, and B3,6 boron atoms. However, overlap of the B4,5 and B7,11 resonances was usually observed producing a pattern with five doublets in 1:1:2:4:2 ratios.[18] The ~C_{2v} symmetric disubstituted 1-R-2-R′-1,2-$C_2B_{10}H_{10}$ derivatives **11**−**14** should have four doublets in

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(18) (a) Fielding, T. E. Ph.D. thesis, University of Pittsburgh, Pittsburgh, PA, 1971. (b) Todd, L. J.; Siedle, A. R. *Prog. NMR Spectrosc.* **1993**, *13*, 87–176.

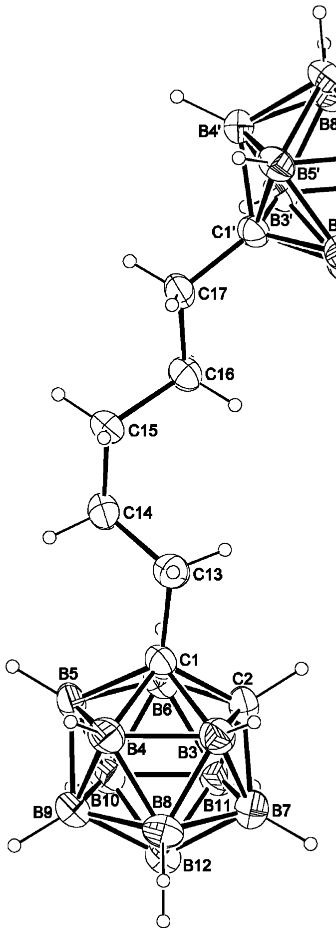


Figure 2. ORTEP drawing of the structure of 1,1′-$(CH_2)_5$-$(1,2\text{-}C_2B_{10}H_{11})_2$ (**4**).[19]

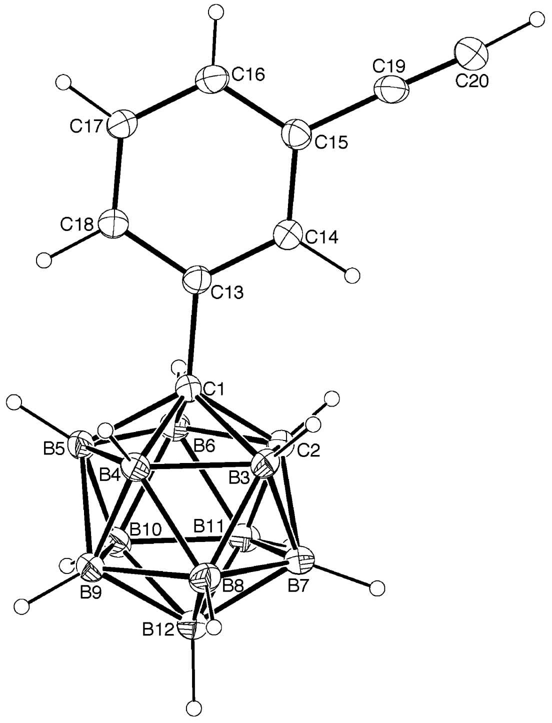
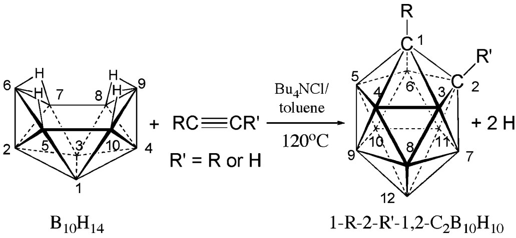


Figure 3. ORTEP drawing of 1-(3-HC≡C-C_6H_4)-1,2-$C_2B_{10}H_{11}$ (**8**). Selected bond lengths (Å) and angles (deg): C1−C13, 1.504(3); C13−C14, 1.392(4); C14−C15, 1.393(3); C15−C16, 1.404(3); C16−C17, 1.381(4); C17−C18, 1.388(4); C18−C13, 1.394(3); C15−C19, 1.437(4); C19−C20, 1.194(4); C1−C2, 1.648(3); C1−B3, 1.743(3); C1−B4, 1.720(4); C1−B5, 1.716(4); C1−B6, 1.734(4); C2−B3, 1.722(4); B3−B4, 1.790(4); B4−B5, 1.780(4); B5−B6, 1.768(4); B6−C2, 1.722(4); C13−C1−C2, 117.8(2); C13−C1−B3, 115.9(2); C13−C1−B4, 122.0(2); C13−C1−B5, 123.4(2); C13−C1−B6, 117.3(2); C1−C13−C14, 120.6(2); C13−C14−C15, 120.9(2); C14−C15−C16, 119.3(2); C16−C17−C18, 121.0(2); C18−C13−C14, 119.3(2).

2:2:4:2 ratios because of the B9,12, B8,10, B4,5,7,11, and B3,6 boron atoms, but resonances again overlap. The crystallographically determined structures of 1,1′-$(CH_2)_5$-$(1,2\text{-}C_2B_{10}H_{11})_2$ (**4**), 1-(3-HC≡C-C_6H_4)-1,2-$C_2B_{10}H_{11}$ (**8**), and 1,1′-(1,3-C_6H_4)-$(1,2\text{-}C_2B_{10}H_{11})_2$ (**9**) are shown in Figures 2−4. The distances and angles observed in these structures are all in the expected ranges.

No reaction was observed when decaborane was heated in an alkyne/toluene solution at 120°C without an ionic liquid. While many ionic liquids showed reactivity for $B_{10}H_{14}$ dehydrogenative alkyne-insertion when employed in the biphasic ionic-liquid/toluene mixtures, reactions employing bmimCl were remarkably fast. Thus as shown in Table 1 for reactions with phenylacetylene, although the bmimCl reaction was complete in 7 min, the reactions with $bmimBF_4$, $bmimPF_6$, $thtdpBF_4$, $bmpyBF_4$, bmimBr, and $bmpyPF_6$ required between 16 and 96 h for completion, with the basicity of the anionic component of the ionic liquid appearing to be the key in determining the reactivity (e.g., $Cl^- > Br^- > I^-$). In this regard, it was also found that upon heating, toluene solutions of several halide salts formed "ionic liquid"-like biphasic mixtures that promoted $B_{10}H_{14}$ dehydrogenative-alkyne insertions with both phenylacetylene and 3-hexyne. Consistent with the trend observed with the ionic liquids, the highest reactivities were for the chloride containing Bu_4NCl (eq 4) and PPNCl salts. Nevertheless, the yields with these salts were much lower (∼20−30%) than those obtained from the analogous bmimCl reactions with these alkynes (90% **1** and 70% **2**).

(**4**)



Thus, in terms of both rates and yields, the most effective agent for inducing $B_{10}H_{14}$ dehydrogenative-alkyne insertion was bmimCl. It is also important to note that the best yields were obtained when only catalytic amounts (∼0.2−0.4 equiv relative to $B_{10}H_{14}$) of bmimCl were employed. When bmimCl was used in larger amounts, the product yields dropped because of $B_{10}H_{14}$ degradation reactions.

Syntheses via the Reactions of Alkynes with $B_{10}H_{13}^-$. The reactions of several alkynes with the $B_{10}H_{13}^-$ anion were investigated to test the possible role of this anion in the ionic liquid-mediated reactions. Reactions of phenylacetylene, 1-octyne, 3-diethylamino-1-propyne, 5-cyano-1-pentyne, and 3-hexyne with the $[Et_3NH^+][B_{10}H_{13}^-]$ salt

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(19) Because of the poorer quality of the structure determination of **4**, the distances and angles information are not listed.

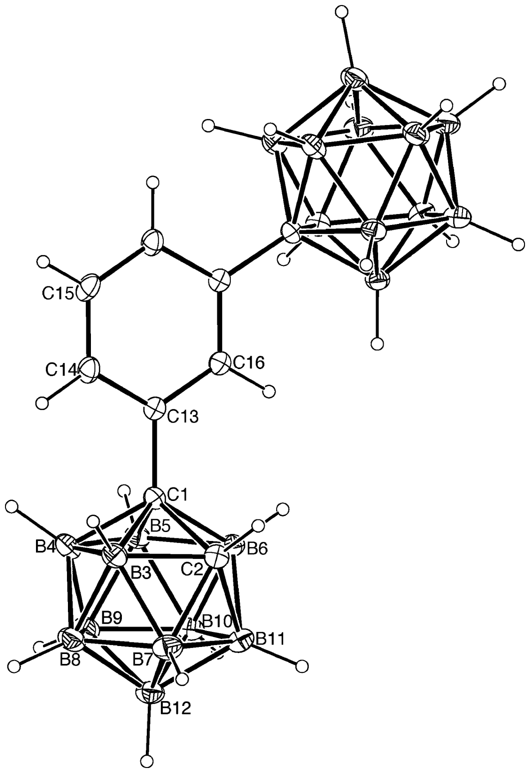
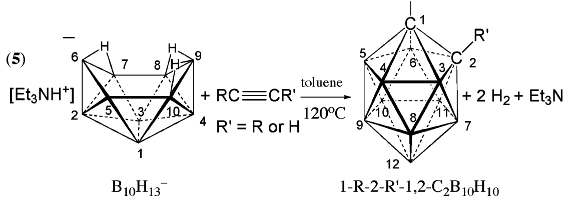
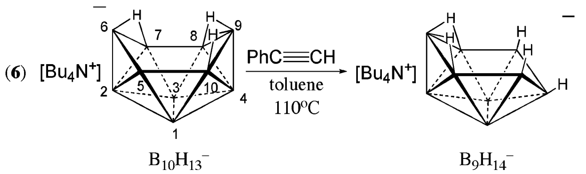


Figure 4. ORTEP drawing of 1,1′-(1,3-C_6H_4)-(1,2-$C_2B_{10}H_{11}$)$_2$ (**9**). Selected bond length (Å) and bond angles (deg): C1−C13, 1.511(3); C13−C14, 1.397(3); C14−C15, 1.382(3); C13−C16, 1.392; C1−C2, 1.692(3); C1−B3, 1.740(3); C1−B4, 1.685(3); C1−B5, 1.725(3); C1−B6, 1.723(3); C2−B3, 1.749(3); B3−B4, 1.755(3); B4−B5, 1.746(3); B5−B6, 1.744(3); B6−C2, 1.746(3); C13−C1−C2, 120.8(2); C13−C1−B3, 117.6(2); C13−C1−B4, 119.8(2); C13−C1−B5, 118.7(2); C13−C1−B6, 120.5(2); C1−C13−C14, 120.3(2); C1−C13−C16, 120.5(2); C13−C14−C15, 119.7(2); C14−C13−C16, 119.2(2).

in toluene solution gave the *o*-carborane derivatives **1**, **2**, **6**, **7**, and **11** in comparable rates, but in most cases, with somewhat lower yields than the analogous $B_{10}H_{14}$-bmimCl/toluene reactions. Reactions of phenylacetylene and 3-hexyne with the $B_{10}H_{13}^-$ anion generated in situ via the reaction of $B_{10}H_{14}$ with catalytic amounts of either Et_3N or Proton Sponge likewise produced **1** and **11** (eq 5), but the yields were much lower (∼20−30%) than either the [Et_3NH^+][$B_{10}H_{13}^-$] or $B_{10}H_{14}$-bmimCl/toluene reactions.



Unlike with [Et_3NH^+][$B_{10}H_{13}^-$] and [PSH^+][$B_{10}H_{13}^-$], when [Bu_4N^+][$B_{10}H_{13}^-$] was reacted with phenylacetylene in toluene solution, no *o*-carborane products were produced. Instead, ^{11}B NMR analysis of the solution after only 30 min at 110 °C showed cage degradation to the $B_9H_{14}^-$ anion and other minor products (eq 6).



Discussion

Ionic liquids (ILs) are generally defined as salts that are relatively low viscosity liquids at temperatures below 100°C.[20] Some of the most common ILs are composed of inorganic anions, X^-, BF_4^-, PF_6^-, and nitrogen-containing organic cations, such as RN,R′N-imidazolium or RN-pyridinium. ILs have been shown[20] to have a number of unusual properties that make them attractive substitutes for conventional solvents for organic and inorganic syntheses, including (1) negligible vapor pressures, (2) thermal stability to elevated temperatures, (3) the ability to dissolve a wide range of organic and inorganic compounds, salts, and gases, (4) immiscibility with many hydrocarbons, water, or both, thus enabling two-phase reaction systems, (5) weakly-coordinating anions and cations that provide a polar reaction medium, and (6) the ability to stabilize polar intermediates and transition states. Examples of the numerous organic reactions that have been carried out in ILs include hydrogenations, hydrodimerizations, hydroformylations, oxidations, Heck reactions, carbonylations, Suzuki-couplings, Trost−Tsuji couplings, Friedel−Crafts reactions, alkylations, halogenations, cycloaddtions, reductions, and metathesis reactions. These prior studies suggested to us that ionic liquids might have similar advantages for carrying out many polyborane transformations, including hydroborations, alkyne-insertions, dehydrogenations, dehydrocondensations, alkylations, and transition metal catalyzed reactions.[21]

The results reported herein have clearly demonstrated that decaborane dehydrogenative alkyne-insertion reactions proceed in biphasic bmimCl/toluene mixtures to give good to excellent yields of *o*-carborane products without the need of the Lewis base catalysts required in the conventional syntheses. Likewise, both terminal and internal alkynes showed comparable reactivities. Thus, as illustrated in the two examples given in Figure 5, the reactions of decaborane in bmimCl/toluene with 3-hexyne and 1-octyne gave their 1,2-Et_2-1,2-$C_2B_{10}H_{10}$ (**11**) (70%, 10 min) and 1-C_6H_{13}-1,2-$C_2B_{10}H_{11}$ (**2**) (91%, 7 min) products in good yields and comparable reaction rates. In contrast, Heying[3a] reported that 3-hexyne does not react at all using the conventional process in eqs 1 and 2.

As shown in Table 3, a variety of functionalized alkynes were found to react to produce the corresponding C-functionalized

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[20] For general reviews, see: (a) *Ionic Liquids in Synthesis*; 2nd ed.; Wasserscheid, P., Welton, T., Eds.; Wiley-VCH: Weinheim, Germany, 2007. (b) Dyson, P. J. *Appl. Organomet. Chem.* **2002**, *16*, 495–500. (c) Zhao, H.; Malhotra, S. V. *Aldrich Chim. Acta* **2002**, *35*, 75–83. (d) Sheldon, R. *Chem. Commun.* **2001**, 2399–2407. (e) Wasserscheid, P.; Keim, W. *Angew. Chem., Int. Ed.* **2002**, *39*, 3772–3789. (f) Dupont, J.; de Souza, R. F.; Suarez, P. A. Z. *Chem. Rev.* **2002**, *102*, 3667–3692.

[21] Kusari, U.; Li, Y.; Bradley, M. G.; Sneddon, L. G. *J. Am. Chem. Soc.* **2004**, *126*, 8662–8663.

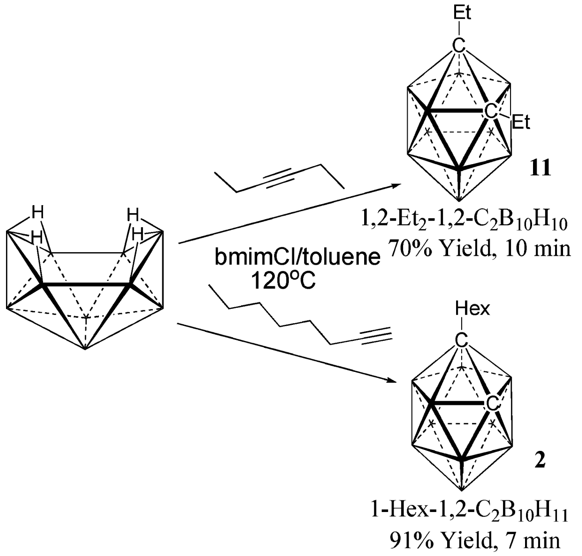

Figure 5. Reactions of $B_{10}H_{14}$ with 3-hexyne and 1-octyne in bmimCl/toluene show comparable reaction times/yields.

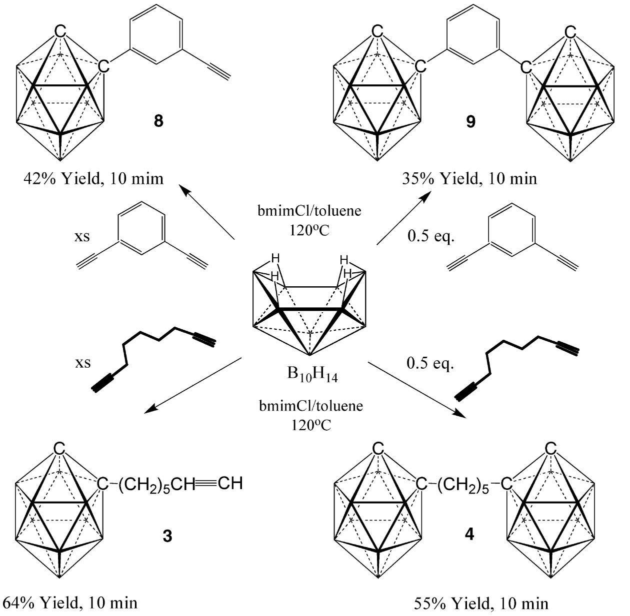

Figure 6. Depending upon the reaction stoichiometry, reactions with diynes give either mono- or di-insertion products.

o-carboranes with faster rates and with either comparable or significantly higher yields than those obtained with the conventional Lewis base methods. It should also be noted that while compounds **4**, **5**, **11**, and **12** were previously known, they have apparently not been prepared directly from alkyne/$B_{10}H_{14}$ reactions but were instead prepared via the reaction of $[Li^+][1,2\text{-}C_2B_{10}H_{11}^-]$ or $[Li^+]_2[1,2\text{-}C_2B_{10}H_{10}^{2-}]$ *o*-carborane anions with the corresponding RX reagents (**4**, $Br(CH_2)_5Br$;[8] **5**, $BrCH_2CO_2Et$;[9] **11**, EtBr[12]) and formaldehyde[13a,b] or ethylene oxide[13c] (**12**). Thus, the ionic liquid reactions are the first report of their direct preparation from decaborane.

As illustrated for the reactions with *m*-diethynylbenzene and 1,8-nonadiyne given in Figure 6, depending on the reaction stoichiometries, decaborane reactions with diynes yield either mono or dicarborane products. The crystallographically established structures of the monoinsertion product **8** and the di-insertion products **4** and **9** are shown in Figures 3, 2, and 4. Endo's previous synthesis[11] of **9** via the reaction of $B_{10}H_{14}$ with *m*-diethynylbenzene and acetonitrile in benzene solution required 2 days of reflux to achieve a 44% yield, whereas the bmimCl/toluene reaction gave a 35% yield after only 10 min.

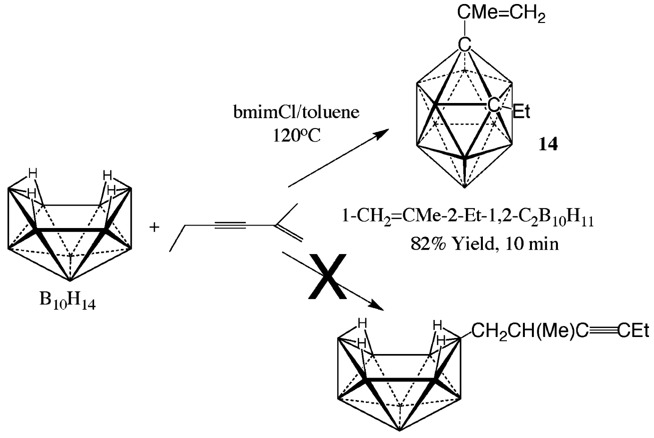

Figure 7. Reactions of enynes give only dehydrogenative alkyne-insertion rather than olefin-hydroboration products

The following paper[22] reports that ionic liquids also promote decaborane olefin-hydroboration reactions, but with rates that are much slower than those found for the ionic-liquid-promoted dehydrogenative alkyne insertion reactions. Consistent with this lower olefin reactivity, it was found (Figure 7) that the reaction of decaborane with 2-methyl-1-hexen-3-yne gave exclusively the dehydrogenative alkyne-insertion product $1\text{-}H_2C{=}C(CH_3)\text{-}2\text{-}Et\text{-}1,2\text{-}C_2B_{10}H_{10}$ **14** rather than the $6\text{-}EtC{\equiv}C(Me)CHCH_2\text{-}B_{10}H_{13}$ olefin-hydroboration product. Thus, reactions with enynes can provide convenient routes to olefin-substituted *o*-carboranes.

Decaborane has been shown to be a monoprotic Bronsted acid in polar solvents, such as water ($pK_a = 2.7$), dioxane, and acetonitrile.[23] The experimental observations for both the ionic liquid-mediated dehydrogenative alkyne-insertion reactions and decaborane-olefin hydroborations[22] indicate that the ionic liquid promoted ionization of decaborane to form the $B_{10}H_{13}^-$ anion is the essential first step in both the alkyne and olefin reactions. Supporting the above hypothesis, it was found that the reactions of $B_{10}H_{13}^-$ salts with alkynes, either starting with the isolated $[Et_3NH^+][B_{10}H_{13}^-]$ salt or with $B_{10}H_{13}^-$ generated in situ from the reactions of $B_{10}H_{14}$ with either Et_3N or Proton Sponge, resulted in dehydrogenative alkyne insertion to produce the *o*-carborane products. Both the yields and rates of the reaction with $[Et_3NH^+][B_{10}H_{13}^-]$ salts were comparable to those of the bmimCl/toluene reactions. Likewise, when the reaction of $B_{10}H_{14}$ with alkynes in bmimCl was carried out under conditions where $B_{10}H_{14}$ ionization was suppressed by the addition of added HCl acid, no reaction was observed.

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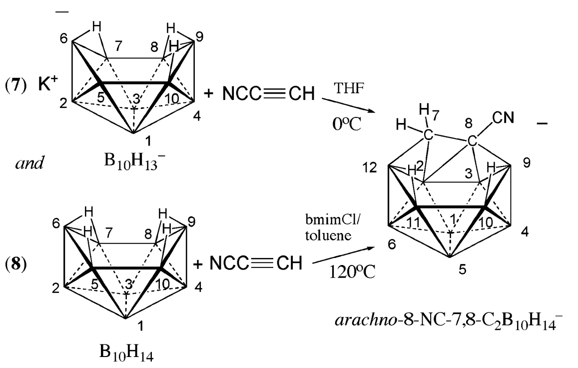
(22) Kusari, U.; Carroll, P. J.; Sneddon, L. G. *Inorg. Chem.* **2008**, *47*, 9203–9215.

(23) (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. *Coll. Czech. Chem. Comm.* **1971**, *36*, 1639–1643.

Su[14] had previously shown that $K^+B_{10}H_{13}^-$ will add to the polar-alkyne, cyanoacetylene, in THF solution to form the *arachno*-dicarbaborane anion, *arachno*-8-(NC)-7,8-$C_2B_{10}H_{14}^-$ (eq 7). We likewise confirmed (eq 8) that the reaction of $B_{10}H_{14}$ with cyanoacetylene in bmimCl/toluene gave the same *arachno*-8-(NC)-7,8-$C_2B_{10}H_{14}^-$ product, again supporting the initial bmimCl-mediated formation of $B_{10}H_{13}^-$ in the ionic liquid reactions.



However, the nature of the reaction of $B_{10}H_{13}^-$ with the strongly polarized cyanoacetylene would be expected to be quite different than its reaction with the nonpolar alkynes reported herein. Thus, in contrast to cyanoacetylene, the alkynes employed herein would be expected to be susceptible to electrophilic, not nucleophilic attacks. The third paper[24] in this series utilizes computational methods to explore both the nucleophilic and electrophilic reactions of the $B_{10}H_{13}^-$ anion, and there it is demonstrated that it is energetically feasible for $B_{10}H_{13}^-$ to rearrange to an electrophilic-type structure having a LUMO orbital highly localized at the B6 boron (Figure 8). Alkyne binding at this site serves as a prelude to the dehydrogenative alkyne-insertion reaction with the proposed structure of the key alkyne-$B_{10}H_{13}$ adduct being quite similar to that previously established[5,25] for L-$B_{10}H_{13}^-$ Lewis acid/base adducts (L = R_3N, R_3P, RCN).

The final step in the scheme in Figure 8 requires a proton source to react with the intermediate *arachno*-R,R′-$C_2B_{10}H_{13}^-$ anion to form the final neutral *o*-carborane products with loss of H_2. For reactions with $[Et_3NH^+][B_{10}H_{13}^-]$ and $[PSH^+][B_{10}H_{13}^-]$, this can be accomplished, as shown in eq 9, by proton transfer from the cations of the $[Et_3NH^+]$[*arachno*-R,R′-$C_2B_{10}H_{13}^-$] and $[PSH^+]$[*arachno*-R,R′-$C_2B_{10}H_{13}^-$] intermediates with liberation of the free amines and two equivalents of hydrogen. The requirement of a proton source in the final step explains why reactions with $[Bu_4N^+][B_{10}H_{13}^-]$ could not produce *o*-carboranes.

$$[Et_2NH^+][arachno\text{-}R,R'C_2B_{10}H_{13}^-] \rightarrow 1,2\text{-}R,R'\text{-}1,2\text{-}C_2B_{10}H_{10} + Et_3N + 2H_2 \quad (9)$$

The dissociation of $B_{10}H_{14}$ in bmimCl would lead to the formation of $B_{10}H_{13}^-$ and HCl. While HCl is of course a strong acid in water, it is only partially disassociated in many organic solvents.[26] Thus, HCl dissolved in the ionic-liquid/toluene could then serve as the proton source for the final step in the bmimCl/toluene mixture reactions. As indicated in Figure 8, this reaction would then regenerate bmimCl, which could go back into the cycle to promote the ionization of additional $B_{10}H_{14}$. The strong activating effect of Cl^- compared to the other ionic liquid anions in Table 1 is consistent with its stronger base strength relative to the other anions and, accordingly, to its ability to promote decaborane ionization.

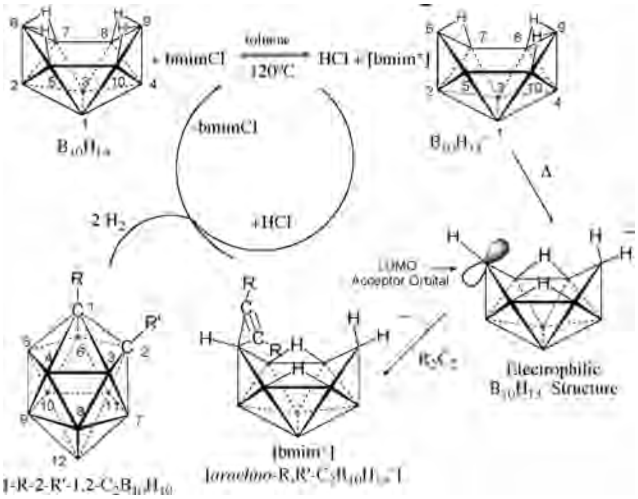


Figure 8. Proposed overall reaction scheme for ionic liquid promoted dehydrogenative alkyne-insertion

It is clear from the results reported herein that decaborane dehydrogenative alkyne-insertions are activated in ionic liquids and that these reactions now provide an important new synthetic route to a wide variety of *o*-carborane derivatives. The following two papers demonstrate that ionic liquids also activate decaborane olefin-hydroborations and, in addition, present the results of further experimental and computational studies that provide more detailed insights into the mechanistic steps involved in both the decaborane dehydrogenative alkyne-insertion and olefin-hydroboration reactions.

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

Supporting Information Available: Tables of infrared data for all compounds, NMR characterization data for the previously reported compounds **1**, **4**, **7**, **9**, and **11**, and X-ray crystallographic data structure determinations of compounds **4**, **8**, and **9** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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