

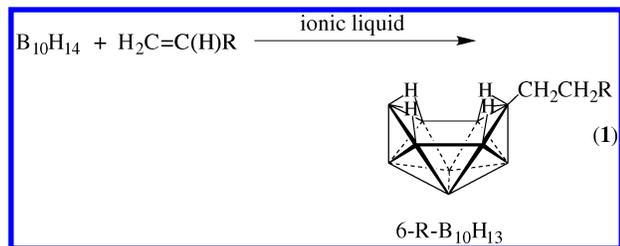
Polyborane Reactions in Ionic Liquids: New Efficient Routes to Functionalized Decaborane and *o*-Carborane Clusters

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Ionic liquids (IL) are salts that are liquid at low temperatures (<100 °C) and have relatively low viscosities. The unique properties of ILs have made them attractive substitutes for conventional solvents for organic and inorganic syntheses, as well as for metal-catalyzed reactions.² The recent report by Vaultier³ that transition metal-catalyzed hydrosilylation and hydroboration of alkynes and alkenes can be carried out in various ionic liquids stimulated our interest in the use of ILs as noncoordinating solvents for the metal-catalyzed reactions of decaborane. Much to our surprise, we found that, unlike in conventional organic solvents where either platinum or titanium catalysts are required,⁴ when decaborane olefin-hydroboration reactions (eq 1) are carried out in ILs, they give high yields of hydroboration products *even in the absence of a metal catalyst!*



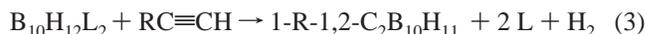
Best results were found for reactions in either 1-butyl-3-methylimidazolium (bmim) or 1-butyl-4-methylpyridium (bmpy) salts containing the BF₄⁻ anion. Because hydrocarbons are insoluble in both of these ILs, the reactions can be carried out under biphasic conditions. Thus, when decaborane, olefin, and toluene are added to (bmim)BF₄, a two-layer system is formed. NMR analysis of the IL layer showed that decaborane partially dissolves in (bmim)BF₄. The reaction mixture is then heated at 125 °C while being stirred vigorously enough to form an emulsion. As the 6-R-B₁₀H₁₃ product is formed, it is extracted into the toluene. When the reaction is complete, the product is removed in the toluene layer. Any residual IL can be separated by running the toluene solution down a short silica gel column. The resulting 6-R-B₁₀H₁₃ products are obtained in excellent yields (~90%) and purities.⁵ It is also important to note that, unlike the metal-catalyzed decaborane olefin-hydroboration reactions,⁴ the IL reaction method works well for both internal and functionalized olefins. Initial studies have shown reactions with a range of olefins, including 1-octene, allylsilane, styrene, allylbenzene, 6-bromo-1-hexene, acetic acid-5-hexen-1-yl ester, ethyl 2-methylpent-4-enoate, 1,5-cyclooctadiene, 1,7-octadiene, *cis*-cyclooctene, 2,3-dimethyl-2-butene, and vinylmethylcyclotetrasiloxane.

In the (bmim)BF₄ reactions, only the monoalkylated 6-R-B₁₀H₁₃ product forms. The absence of higher alkylated species undoubtedly arises because of the low solubility of the 6-R-B₁₀H₁₃ products in (bmim)BF₄. On the other hand, reactions in (bmpy)BF₄ showed that with extended reaction times 6,9-R₂-B₁₀H₁₂ species are formed.

These differences suggest that efficient polyalkylations may be achievable in other ILs in which alkylboranes are more soluble.

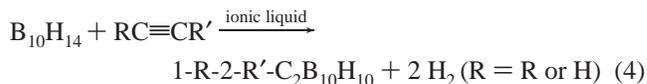
Equally important as the above results, we have found that decaborane reactions with alkynes in ILs do not yield hydroboration products but instead result in alkyne-insertion, thereby providing an important new route to *o*-carboranes.

Previously, *o*-carboranes have been best synthesized by the base-promoted, two-step process given in eqs 2 and 3.⁶



The reactions involve in situ formation of the B₁₀H₁₂L₂ adduct followed by alkyne insertion to yield the carborane product. Reaction times are normally 4–5 h, and typical yields for terminal alkynes range from 6 to 75%. This reaction method gives much lower yields (or does not work at all) for many internal alkynes.

In contrast to reactions in conventional solvents, decaborane reacts readily with both terminal and internal alkynes in ILs *without a base catalyst* to produce *o*-carborane compounds in high yields (eq 4).



As shown in the NMR spectra in Figure 1 for the reaction of 5 mmol of decaborane with 1-octyne in (bmim)Cl,⁷ reaction times can be on the order of only a few minutes. The bottom spectrum shows the initial decaborane starting material in the toluene layer above the IL. The 1-octyne was then added and the stirred emulsion heated at 120 °C. The middle spectrum shows the reaction mixture after 4 min where the peaks of the 1-(C₆H₁₃)-1,2-C₂B₁₀H₁₁ product are clearly visible. The top spectrum shows that after only 7 min the reaction has gone to completion. Workup as described above then gave a ~90% isolated yield of product. Initial screening reactions have shown similar reactions for a variety of both internal (including, for example, 3-hexyne, diphenylethyne, and 2-butyne-1-ol) and terminal alkynes. The IL route provides a new one-step, high-yield route to functionalized *o*-carboranes, and we are expanding our studies to include reactions of decaborane with a wide range of substituted acetylenes.

The reactions of alkynes with the 6-substituted decaborane derivatives that are now readily available through the new IL route given in eq 1 also provide a new general route to B-substituted *o*-carboranes. Previously, B-substituted *o*-carborane derivatives have been shown to have potential anticancer (BNCT) applications⁸ but could only be produced by reactions of RBCl₂ with the dicarbollide anion or by a multistep process involving initial carborane iodination, followed by reaction with Grignards in the presence of

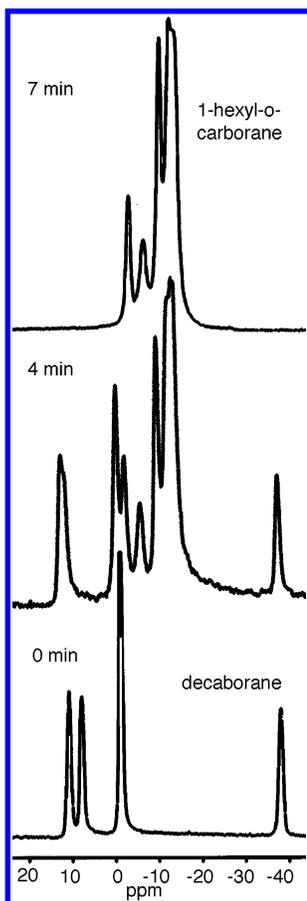
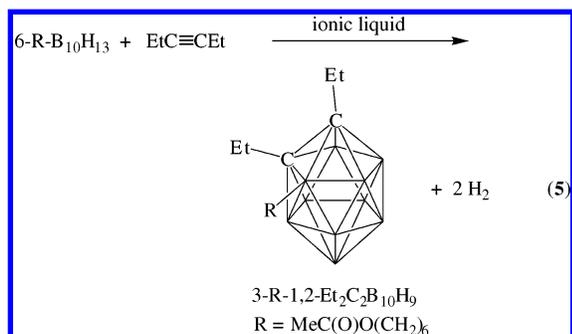


Figure 1. $^{11}\text{B}\{^1\text{H}\}$ NMR spectra showing the progress of the reaction of decaborane with 1-octyne at $120\text{ }^\circ\text{C}$ when employing (bmim)Cl/toluene biphasic media.

palladium reagents.^{8,9} In contrast to the previous routes, the new ester derivative shown in eq 5 is efficiently synthesized in high yield by the reaction of the previously unknown ester-functionalized decaborane with 3-octyne under (bmim)Cl/toluene biphasic reaction conditions.¹⁰



The exact role that the ILs play in inducing the reactions in eqs 1, 4, and 5 is still to be determined. The ILs may be simply providing an inert reaction medium that allows thermal activation of decaborane, but the fact that the olefin-hydroboration and

alkyne-insertion reactions occur in different ionic liquids suggests the ILs may have a more complex function. Regardless of the detailed mechanism of activation, it is clear that, in ILs, decaborane exhibits reactivities not found in conventional organic solvents and that these reactions now provide important new synthetic pathways to both substituted decaborane and *o*-carborane derivatives. These results strongly suggest that advantageous IL-based reactions can be developed for the syntheses of an even wider range of polyboranes, as well as for other classes of inorganic compounds. We are presently exploring these possibilities.

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- (5) In a typical reaction, 0.30 g (2.5 mmol) of decaborane and 0.70 g (4.9 mmol) of acetic acid-5-hexen-1-yl ester were reacted under Ar in a biphasic mixture of toluene (3 g) and (bmim)BF₄ (1.0 g) at $125\text{ }^\circ\text{C}$ for 14 h to give, following toluene elution from a silica gel column, 0.57 g (2.2 mmol, 87.3% yield) of 6-(acetic acid-hexyl ester)-B₁₀H₁₃ (oily liquid). Exact mass $^{12}\text{C}_8\text{H}_{28}\text{B}_{10}\text{O}_2$: *m/z* calcd, 266.3019; measd, 266.3026. ^{11}B NMR (160.5 MHz, C₆D₆) δ 25.6 (s, B6), 10.2 (d, B1, 3), 8.9 (d, B9), 0.33 (d, B5, 7), -3.2 (d, B8, 10), -33.9 (d, B2), -38.5 (d, B4). ^1H NMR (500.1 MHz, C₆D₆) δ 4.10 (m, OCH₂), 1.91 (s, CH₃), 1.83 (m, CH₂), 1.60 (m, CH₂), 1.38 (m, CH₂), 0.37 (m, CH₂CH₂), -1.7 (br, 2 BHB), -2.1 (br, 2 BHB). IR (NaCl plates, cm⁻¹) 2900(vs), 2860(s), 2560(vs), 1920(b,w), 1720(vs), 1560(m), 1520(s), 1510(s), 1460(s), 1430(s), 1390(m), 1360(s), 1260(vs), 1100(m), 1040(s), 1000(s), 960(m), 930(w), 860(w), 840(w), 810(m), 730(m).
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- (7) Reaction of 0.25 g (2.1 mmol) of decaborane and 0.72 (6.5 mmol) of 1-octyne under Ar in a biphasic mixture of toluene (~5 mL) and (bmim)Cl (0.204 g) with vigorous stirring at $120\text{ }^\circ\text{C}$ for 7 min gave, following hexanes elution from a silica gel column, 0.43 g (1.86 mmol, 90.8% yield) of the known compound 1-hexyl-1,2-C₂B₁₀H₁₁.^{6c}
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- (10) Reaction of 0.50 g (1.9 mmol) of 6-(acetic acid hexyl ester)-B₁₀H₁₃ and 0.61 g (7.6 mmol) of 3-hexyne under Ar in a biphasic mixture of toluene (2.0 g) and (bmim)Cl (0.5 g) with vigorous stirring at $95\text{ }^\circ\text{C}$ for 4 h gave, following CH₂Cl₂ elution from a silica gel column, 0.60 g (1.75 mmol, 92.6% yield) of 3-(acetic acid-hexyl ester)-1,2-diethyl-C₂B₁₀H₉ (oily liquid). Exact mass $^{12}\text{C}_{14}\text{H}_{34}\text{B}_{10}\text{O}_2$: *m/z* calcd, 344.3489; measd, 344.3478. ^{11}B NMR (160.5 MHz, C₆D₆) 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 NMR (500.1 MHz, C₆D₆) δ 3.99 (m, OCH₂), 1.75 (m, CH₂), 1.69 (s, CH₃), 1.67 (m, CH₂), 1.52 (m, CH₂), 1.4 (m, CH₂), 1.25 (m, CH₂), 1.0–0.65 (m, CH₃, CH₂). IR (NaCl plates, cm⁻¹) 2940(vs), 2860(sh,vs), 2590(vs), 1740(vs), 1460(s), 1390(s), 1370(s), 1250(vs), 1180(m), 1120(m), 1040(s), 940(vw), 910(w), 890(w), 850(vw), 740(m).

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