Polyborane reactions in ionic liquids*

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Abstract: In contrast to reactions that have been observed in traditional organic solvents, decaborane olefin-hydroboration and alkyne-insertion reactions proceed in ionic liquid (IL) solvents without the need of a catalyst. These reactions now provide important new, high-yield synthetic pathways to functionalized decaborane and *ortho*-carborane clusters. As illustrated by the synthesis of n-$B_{18}H_{22}$, ILs can also provide an inert reaction medium for carrying out dehydrocondensation reactions leading to higher fused cage compounds.

Keywords: ionic liquids; decaborane; *o*-carborane; octadecaborane; hydroboration; alkyne insertion.

INTRODUCTION

Ionic liquids (ILs) are salts that are liquids at low temperatures (<100 °C) [1–5]. They are usually composed of inorganic anions and nitrogen-containing organic cations, such as N,N'-imidazolium or N-pyridinium. Reactive ILs contain anionic Lewis acidic metal halides, such as chloroaluminates, whereas inert ILs contain, for example, BF_4^-, PF_6^-, or SbF_6^- anions.

Cations: **Anions:**

N,N'-imidazolium   N-pyridinium

Reactive: $AlCl_4^-$, $Al_2Cl_7^-$

Inert: PF_6^-, BF_4^-, $CF_3SO_3^-$
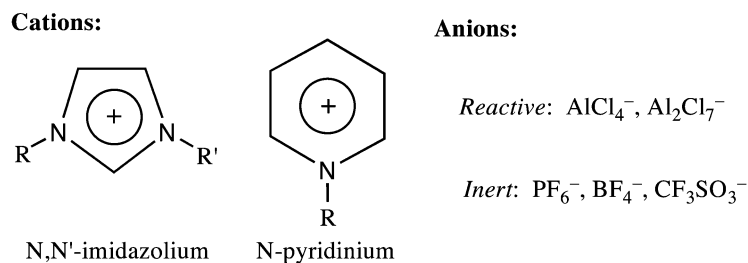
Scheme 1

ILs 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 and/or water, thus enabling two-phase reaction systems; and (5) weakly coordinating anions and cations that provide a polar, inert reaction medium.

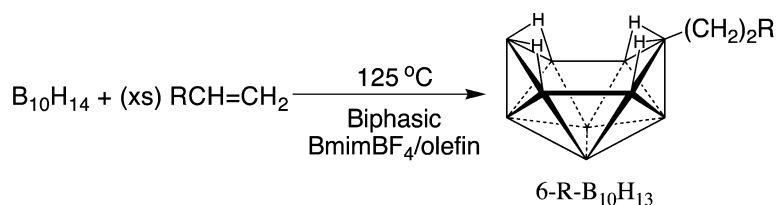
Examples of the numerous organic reactions that have been carried out in ILs include hydrogenations, hydrodimerizations, hydroformylations, oxidations, Heck reactions, carbonylations, Suzuki couplings, Trost–Tsuji couplings, Friedel–Crafts reactions, alkylations, halogenations, cycloadditions, reductions, and metathesis reactions [1–5].

These prior studies suggested to us that ILs might provide similar advantages for carrying out many polyborane transformations, including hydroboration, alkyne-insertion, dehydrogenation, dehydrocondensation, alkylation, and transition-metal-catalyzed reactions.

DECABORANE OLEFIN HYDROBORATION REACTIONS IN IONIC LIQUIDS

We have previously shown that platinum-catalyzed decaborane-olefin hydroborations yield 6,9-$R_2B_{10}H_{12}$ derivatives in high yield [6], while titanium-catalyzed decaborane-olefin hydroboration reactions provide excellent routes to both monoalkyl- and monoalkenyl-decaboranes, including new types of decaborane linked-cage compounds [7,8]. However, both the platinum- and titanium-catalyzed reactions are slow (typically less than one turnover per h) and there is a need for improved routes to these important compounds. A recent report [9] that transition-metal-catalyzed hydrosilylation and monoborane-hydroborations of alkynes and alkenes can be carried out in ILs stimulated our interest in the use of ILs as noncoordinating solvents for the metal-catalyzed reactions of polyboranes. Much to our surprise, we found [10] that when decaborane-olefin hydroboration reactions (Scheme 2) are carried out in ILs, high yields of products are obtained *even in the absence of a catalyst*!!

$$B_{10}H_{14} + (xs)\ RCH=CH_2 \xrightarrow[\substack{\text{Biphasic} \\ \text{BmimBF}_4/\text{olefin}}]{125\ ^\circ C}$$
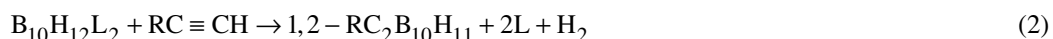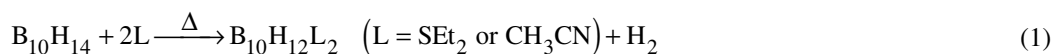
6-R-$B_{10}H_{13}$

Scheme 2

The best results were found for reactions with either the 1-butyl-3-methyl-imidiazolium (Bmim) or 1-butyl-4-methyl-pyridium (Bmpy)BF_4 salts. Because hydrocarbons are insoluble in both of these ILs, the reactions can be carried out under biphasic conditions. Thus, in a typical reaction, decaborane is added to the (Bmim)BF_4 along with the olefin and toluene to form a two-layer system. NMR analysis of the IL layer showed that decaborane partially dissolves into the (Bmim)BF_4. The reaction mixture is then heated at 125 °C while being stirred vigorously enough to form an emulsion. As the 6-R-$B_{10}H_{13}$ product is formed, it is extracted into the toluene. When the reaction is complete, the product is separated in the toluene layer. Any residual IL can be removed by running the toluene down a short silica gel column.

The resulting 6-R-$B_{10}H_{13}$ products are then obtained in excellent yields (~90 %) and purities. Similiar reactions have been found with a range of olefins, including 1-octene, allylsilane, styrene, allylbenzene, bromohexene, acetic acid 5-hexen-1-yl ester, ethylmethylpentenoate, cyclooctadiene, 2,3-dimethyl-2-butene, and vinylmethylcyclotetrasiloxane. In the (Bmim)BF_4 reactions, only the monoalkylated 6-R-$B_{10}H_{13}$ product is produced. The absence of higher alkylated species undoubtedly arises because of the low solubility of the 6-R-$B_{10}H_{13}$ products in (Bmim)BF_4 (they cannot be detected in the IL layer by NMR analysis).

## ALKYNE-INSERTION REACTIONS IN IONIC LIQUIDS: A NEW ROUTE TO CARBORANES

In contrast to the reactions with olefins described in the previous section, 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 *ortho*-carboranes [10].

Previously, *ortho*-carboranes have been best synthesized by the base-promoted, two-step process [11–13] outlined in eqs. 1 and 2.

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

$$B_{10}H_{12}L_2 + RC \equiv CH \rightarrow 1,2 - RC_2B_{10}H_{11} + 2L + H_2 \tag{2}$$

The reactions involve the in situ formation of the $B_{10}H_{12}L_2$ adduct followed by alkyne insertion to yield the carborane product. Reaction times are normally 4–5 h, and typical yields for terminal alkynes are 6–75 %. This reaction method either does not work or gives much lower yields for many internal alkynes.

Unlike reactions in conventional solvents, decaborane reacts readily with both internal and terminal alkynes *without the need of a base catalyst* in a biphasic toluene/1-butyl-3-methylimidiazolium chloride (Bmim)Cl system to produce *ortho*-carborane compounds in good yields (Scheme 3).
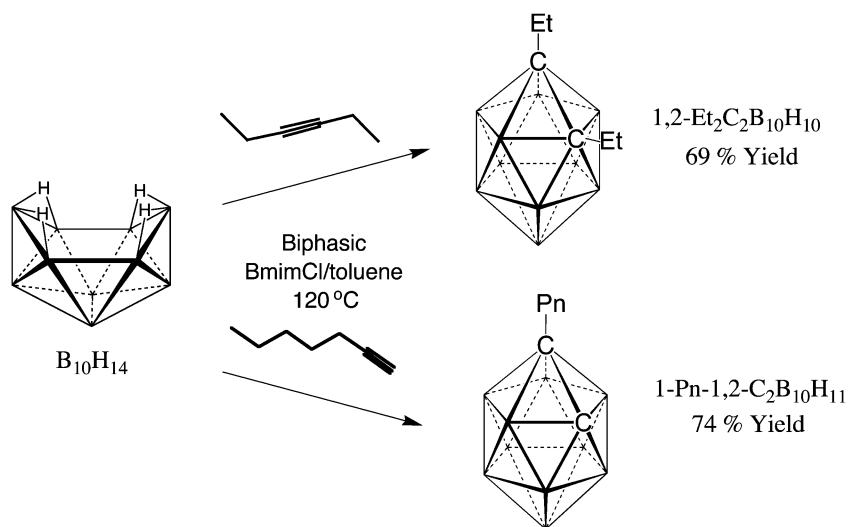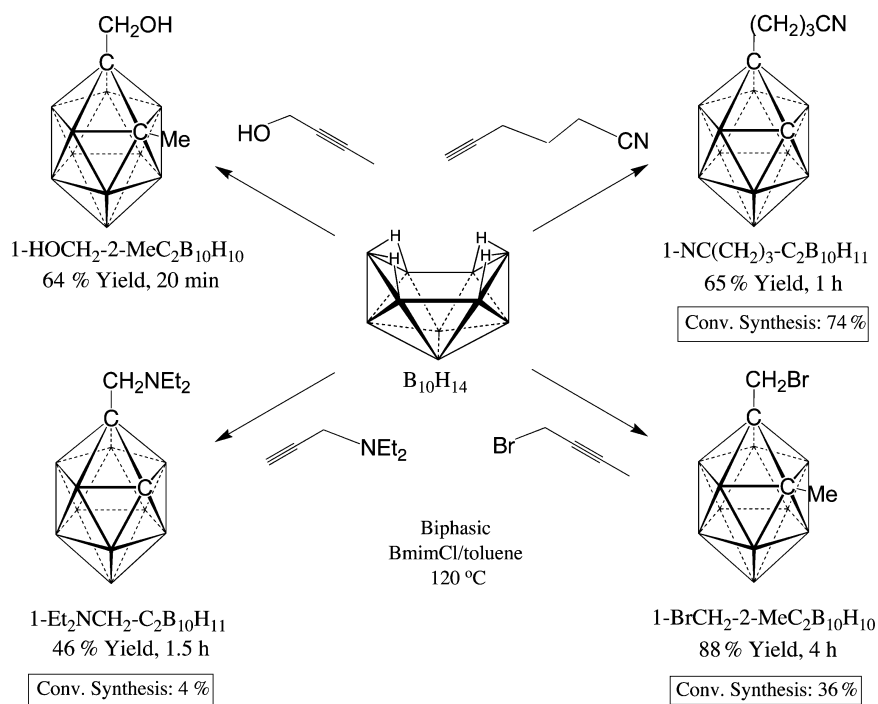

Scheme 3

As shown in the NMR spectra in Scheme 4 for the reaction of decaborane with 1-octyne in (Bmim)Cl, 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 was heated at 120 °C. The middle spectrum shows the reaction mixture after 4 min where the peaks of the $1\text{-}(C_6H_{13})\text{-}1,2\text{-}C_2B_{10}H_{11}$ product are clearly visible. The top spectrum shows that after only 7 min the reaction has gone to completion. Work-up as described above for the decaborane/olefin reactions then gave ~90 % yield of product.
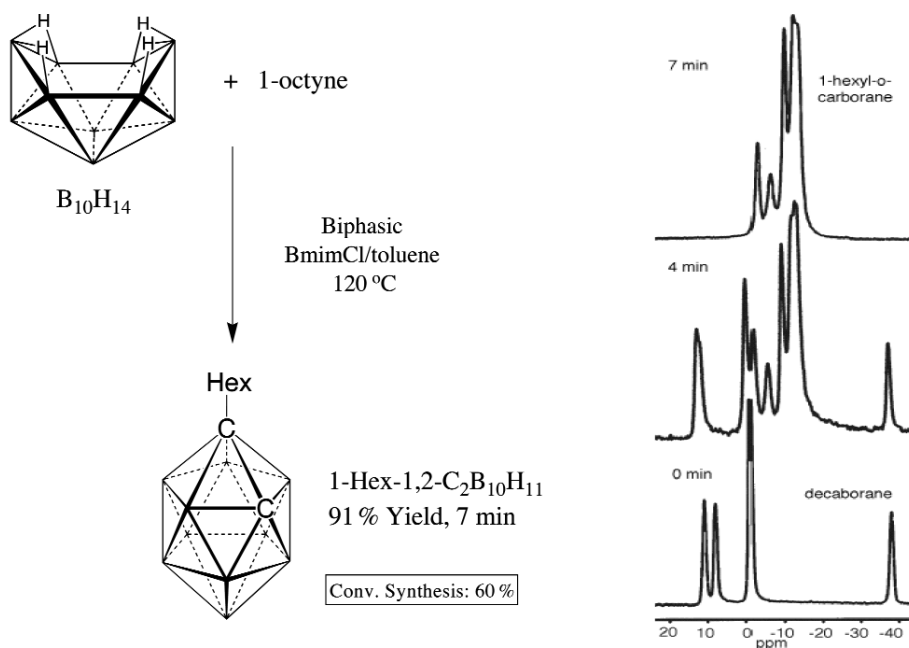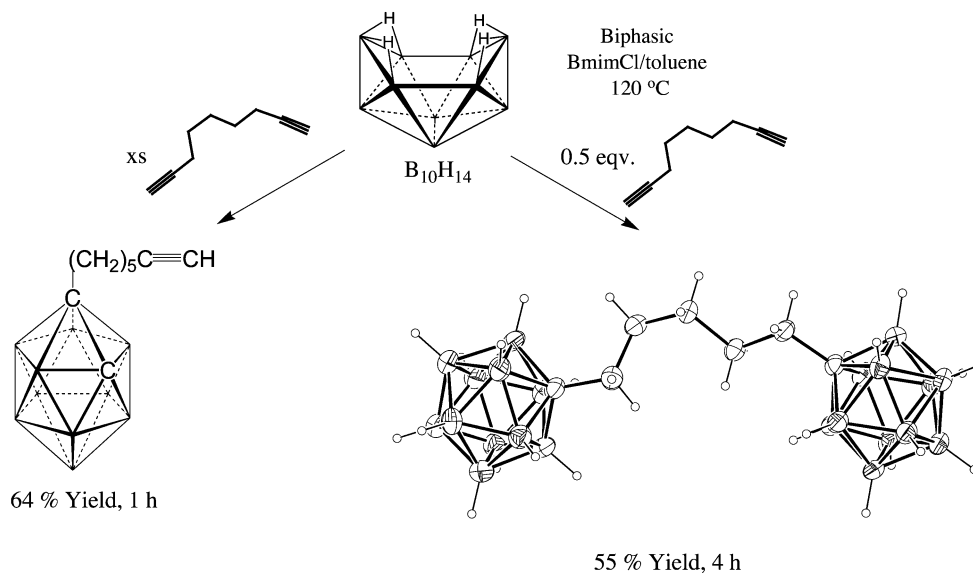
Scheme 4

As shown in the examples in Scheme 5, similar reactions have now been observed for a wide variety of functionalized alkynes.
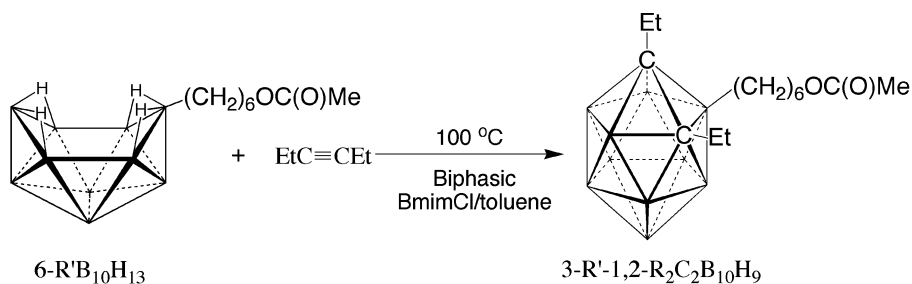

Scheme 5

As indicated in Scheme 6, depending on the reaction stoichiometries, decaborane reactions with diynes yield either mono or dicarborane products.

xs

$(CH_2)_5C\equiv CH$

Biphasic
BmimCl/toluene
120 °C

$B_{10}H_{14}$

0.5 eqv.

$(CH_2)_5C\equiv CH$

64 % Yield, 1 h

55 % Yield, 4 h

Scheme 6

The reactions of alkynes with the 6-substituted decaborane derivatives that are now readily available through the new route given in Scheme 2 also provide efficient routes to B-substituted *ortho*-carboranes, such as the new ester derivative shown in Scheme 7 which is efficiently synthesized in high yield by the reaction of the previously unknown ester-functionalized decaborane with 3-hexyne under (Bmim)Cl/toluene biphasic reaction conditions.
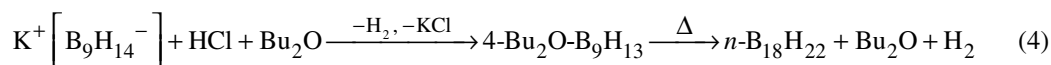

$(CH_2)_6OC(O)Me$

+ $EtC\equiv CEt$

100 °C
Biphasic
BmimCl/toluene

Et

$(CH_2)_6OC(O)Me$

Et

6-R'$B_{10}H_{13}$

3-R'-1,2-$R_2C_2B_{10}H_9$

Scheme 7

B-substituted *o*-carborane derivatives have been shown to have potential anticancer boron neutron capture therapy (BNCT) applications [14], but could only be produced by reactions of RBCl$_2$ with the dicarbollide anion or by a multi-step process involving initial carborane iodination, followed by reaction with Grignards in the presence of palladium reagents [14–16]. The IL route thus provides a new general route to these types of functionalized *ortho*-carboranes.

POLYBORANE DEHYDROCONDENSATION REACTIONS IN IONIC LIQUIDS

Dehydrocondensation reactions are key steps in many polyborane transformations leading to the formation of higher cage systems. For example, as shown in eq. 3 the thermally induced dissociation of dimethylsulfide from $4\text{-}Me_2S\text{-}B_9H_{13}$ has been shown to produce a Lewis acidic B_9H_{13} fragment, which can then undergo fusion, accompanied by dehydrogenation, with another such fragment to produce $n\text{-}B_{18}H_{22}$. Regardless of whether the reaction was carried out in vacuo or in xylene solution, only ~20–28 % yields of $n\text{-}B_{18}H_{22}$ were obtained along with a complex mixture of other polyboranes [17,18]. A similar pyrolysis of in situ generated $4\text{-}Bu_2O\text{-}B_9H_{13}$ was reported to give a 34 % yield [19].

$$4\text{-}Me_2S\text{-}B_9H_{13} \xrightarrow{\Delta} n\text{-}B_{18}H_{22} + B_{10}H_{14} + B_{16}H_{20} + B_5H_9 + Me_2SBH_3 + H_2 \qquad (3)$$

$$K^+\left[B_9H_{14}{}^-\right] + HCl + Bu_2O \xrightarrow{-H_2, -KCl} 4\text{-}Bu_2O\text{-}B_9H_{13} \xrightarrow{\Delta} n\text{-}B_{18}H_{22} + Bu_2O + H_2 \qquad (4)$$
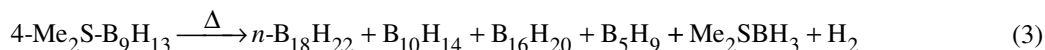
The inert, polar reaction medium provided by IL solvents could provide significant advantages over the conventional reaction conditions employed for carrying out polyborane dehydrogenation and dehydrocondensation reactions. Indeed, we have now found (eq. 5) that when the $4\text{-}Me_2S\text{-}B_9H_{13}$ pyrolysis is conducted in 1-butyl-3-methylimidazolium chloride (BmimCl) under biphasic conditions, the yield of $n\text{-}B_{18}H_{22}$ increases significantly and only $B_{10}H_{14}$ is produced as a side product.

$$4\text{-}Me_2S\text{-}B_9H_{13} \xrightarrow{\Delta} n\text{-}B_{18}H_{22} + B_{10}H_{14} \qquad (5)$$

Reactions were carried out by vigorously stirring a mixture of $4\text{-}Me_2S\text{-}B_9H_{13}$, BmimCl and xylene at 130 °C for 2 h. The xylene layer was then separated and the IL layer extracted with ether. The solvents and $B_{10}H_{14}$ impurity were removed from the combined extracts in vacuo at room temperature. Sublimation at 110 °C then gave the crystalline $n\text{-}B_{18}H_{22}$ product in ~50 % yields.

CONCLUSIONS AND FUTURE STUDIES

The exact role that the ILs play in inducing the polyborane reactions reported herein is still to be determined. In some cases, the ILs may be simply providing an inert reaction medium that allows thermal activation of the polyboranes, but the fact that the decaborane olefin-hydroboration and alkyne-insertion reactions occur in different ILs suggests the ILs may have a more complex function. Regardless of the detailed mechanism of activation, it is clear that in ILs, polyboranes exhibit reactivities not found in conventional organic solvents and that these reactions now provide important new synthetic pathways to both substituted decaborane and *ortho*-carborane derivatives, as well as higher cage systems such as $n\text{-}B_{18}H_{22}$. 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.

ACKNOWLEDGMENTS

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