New Reactions for Old Ions: Cage Rearrangements, Hydrolysis, and Two-Electron Reduction of \textit{nido}-Decaborane in Neat 1-Ethyl-3-Methylimidazolium Acetate

Steven P. Kelley,* Giovanni P. Rachiero,§ Hatem M. Titi,‡ and Robin D. Rogers*†‖

1 Department of Chemistry, The University of Alabama, Box 870336, Tuscaloosa, Alabama 35487, United States
2 Department of Chemistry, McGill University, 801 Sherbrooke Street W., Montreal, Quebec H3A 0B8, Canada
3 Department of Chemistry, University of Missouri, 601 S. College Avenue, Columbia, Missouri 65201, United States
4 S2S Solutions, Inc., P.O. Box 2206, Tuscaloosa, Alabama 35403, United States

ABSTRACT: The access to free, unsolvated ions at high concentrations and ambient temperatures enabled by ionic liquids results in previously unobserved reactivity for even well-studied ions, demonstrated here by acetate ([OAc]−) acting as a reducing agent for B\textsubscript{10}H\textsubscript{14} but only when used as a neat liquid in \([\text{C}_2\text{mim}][\text{OAc}]\) at ambient temperature. More typical reaction products are obtained when B\textsubscript{10}H\textsubscript{14} is reacted with \([\text{C}_2\text{mim}][\text{OAc}]\) at an elevated temperature or in the presence of strong bases.

1. INTRODUCTION

Ionic liquids (ILs) are salts with low melting points (usually defined as melting below 100 °C), which distinguishes them from ionic compounds in that they can be used as solvents or in solventless reactions. As dissolution of a salt in a molecular solvent necessarily reduces the activity of the ions because of their interactions with the solvent, new avenues of reactivity in solventless reactions. As dissolution of a salt in a molecular solvent necessarily reduces the activity of the ions because of their interactions with the solvent, new avenues of reactivity can be discovered for ions by incorporating them into ILs and using them in the neat liquid state. A good example is the IL 1-ethyl-3-methylimidazolium acetate ([C\textsubscript{2}mim][OAc]), which is liquid at room temperature, where the anion naturally acts as a Brønsted or Lewis base (for instance, in the dissolution of normally insoluble biopolymers) and the cation can also act as a Lewis base and react with electrophilic molecules because of a dynamic equilibrium between the \([\text{C}_2\text{mim}]^+\) cation and the corresponding imidazole-2-ylidene. Here, we sought to expand the known main group chemistry of \([\text{C}_2\text{mim}][\text{OAc}]\) to boron by investigating its reactivity with \textit{nido}-decaborane, B\textsubscript{10}H\textsubscript{14}. Boranes have been of fundamental interest to chemists for decades because of their complex geometries and their ability to bond to a wide range of main group and transition metal elements. Functionalization of boranes is also being investigated to make advanced materials. Here, we sought to expand the known main group chemistry of \([\text{C}_2\text{mim}][\text{OAc}]\) to boron by investigating its reactivity with \textit{nido}-decaborane, B\textsubscript{10}H\textsubscript{14}. Boranes have been of fundamental interest to chemists for decades because of their complex geometries and their ability to bond to a wide range of main group and transition metal elements. Functionalization of boranes is also being investigated to make advanced materials for applications such as hydrogen storage. Decaboranes in particular have been found to show unusual reactivity toward ILs; for instance, the cage opening reaction of \textit{closo}-B\textsubscript{10}H\textsubscript{12} and substitution of the halogen atom (X) on \textit{nido}-B\textsubscript{10}H\textsubscript{12}X proceed in dialkylimidazolium ILs under unusually mild conditions. We previously found that B\textsubscript{10}H\textsubscript{14} reacted spontaneously with ions from energetic azolium ILs to form stable IL-soluble species, formed through deprotonation and rearrangement of B\textsubscript{10}H\textsubscript{14}. B\textsubscript{10}H\textsubscript{14} is therefore an interesting main group probe for reactivity with \([\text{C}_2\text{mim}][\text{OAc}]\) because it possesses Lewis acidic sites of variable nature which may prefer the [OAc]− ion or the carbene.

2. RESULTS AND DISCUSSION

We first tried solventless reactions of \([\text{C}_2\text{mim}][\text{OAc}]\) and B\textsubscript{10}H\textsubscript{14} by combining them at variable molar ratios and temperatures. The reactants were weighed out under ambient conditions and were either allowed to stand at room temperature in sealed containers or heated in unsealed containers at 60 °C. Reaction conditions are given in Table S1 (Supporting Information). Reactions at elevated temperatures proceeded rapidly with a color change from pale yellow to red-orange and visible gas evolution. The reaction of B\textsubscript{10}H\textsubscript{14} with 1 equiv of \([\text{C}_2\text{mim}]^+\)−[OAc] gave a strongly colored mixture of red-orange solids, while reactions with two or more equiv of \([\text{C}_2\text{mim}]^+\)−[OAc] gave yellow semi-solid products which were similar in appearance to each other.

Powder X-ray diffraction (PXRD) confirmed that crystalline phases were a minor component of the product. Nevertheless, two of the products formed in this set of reactions were identified by isolating crystals suitable for single crystal XRD (SCXRD) directly from crude reaction mixtures: \([\text{C}_2\text{mim}]_2[B\textsubscript{10}H\textsubscript{12}][\text{OAc}]\) isolated from the 1:1 reaction (Table S1, Supporting Information).
entry 1) and \([\text{C}_2\text{mim}]_2[\text{B}(\text{O(BOO)}_2)_2]\) isolated from the 1:5 reaction (Table S1, entry 5), both of which are known.\textsuperscript{13,14} The crystal structure of \([\text{C}_2\text{mim}]_2[\text{B}_{12}\text{H}_{12}]\) (Figure S6) was found to be a new polymorph, which is isomorphous with the perfluorinated analog \([\text{C}_2\text{mim}]_2[\text{B}_{12}\text{F}_{12}]\).\textsuperscript{15} The \([\text{B}_{12}\text{H}_{12}]^2−\) could form from disproportionation of \(\text{B}_{10}\text{H}_{14}\), as reported for other borohydrides,\textsuperscript{16} while \([\text{B}(\text{O(BOO)}_2)_2]^−\) can be made from boric acid which could have formed through hydrolysis.

Interestingly, \([\text{C}_2\text{mim}]\)[\text{OAc}] and \(\text{B}_{10}\text{H}_{14}\) reacted spontaneously at room temperature as well, although more slowly. In this case, \(\text{B}_{10}\text{H}_{14}\) fully dissolved in 1 equiv of \([\text{C}_2\text{mim}]\)[\text{OAc}] at room temperature to give a red-orange liquid. Reactions with two and 3 equiv of \([\text{C}_2\text{mim}]\)[\text{OAc}] gave yellow pastes, which were found to be composed of many single crystalline plates dispersed through a viscous matrix. \(\text{B}_{10}\text{H}_{14}\) was also observed to dissolve in 10 equiv of \([\text{C}_2\text{mim}]\)[\text{OAc}] with stirring to give a viscous yet free-flowing liquid. All reactions proceeded over the course of several hours with a visible color change of the IL from pale yellow to red-orange and the slow formation of bubbles and appeared to reach completion overnight, except for the reaction with 10 equiv of \([\text{C}_2\text{mim}]\)[\text{OAc}], which gradually faded back to yellow over a period of several weeks.

PXRD of the reaction of \(\text{B}_{10}\text{H}_{14}\) with 3 equiv of \([\text{C}_2\text{mim}]\)[-\text{OAc}] showed a larger amount of crystalline material than observed in the high temperature reaction. Furthermore, while some of the XRD peaks (including those at 16.5°–17.9° and 25° 2θ) could be assigned to \([\text{C}_2\text{mim}]_2[\text{B}(\text{O(BOO)}_2)_2]\), others (most notably the large peak at 6° 2θ) indicated the presence of at least one unidentified product which had not crystallized at high temperature (Figure 1).

A single crystal from the 1:3 reaction mixture was isolated, analyzed by SCXRD, and found to be \([\text{C}_2\text{mim}]_2[\text{B}_{10}\text{H}_{13}(\text{OAc})]\), in which the \(\text{B}_{10}\text{H}_{14}\) molecule has converted into a doubly anionic borane ester (Figure 2). The structure is notable for two reasons. First, we were unable to find any prior report of functionalization of \(\text{B}_{10}\text{H}_{14}\) with a carboxylate through a direct reaction with a carboxylate salt. The typical routes we found were cage-opening reactions with closo-decaborane\textsuperscript{17} or substitution reactions on derivatized boranes.\textsuperscript{18,19} Second, the product is not formed through a typical substitution reaction, as a cation (\(\text{H}^+\)) is being substituted by an anion ([\text{OAc}]^−) to give a doubly anionic product.

The open face of the \([\text{B}_{10}\text{H}_{13}(\text{OAc})]^2−\) anion has two endocyclic, bridging hydrogen atoms and four exocyclic ligands (three hydrogen atoms and the [\text{OAc}]^− group), which matches the structure of the \([\text{B}_{10}\text{H}_{14}]^2−\) anion, not \(\text{B}_{10}\text{H}_{14}\).\textsuperscript{20} The C–O bond distances of the acetate group are very dissymmetric [1.214(4) Å vs 1.314(4) Å] and match well with those of other borane esters.\textsuperscript{21} The two \([\text{C}_2\text{mim}]^+\) counterions form intermolecular contacts distributed all over the cluster (Figure S3, Supporting Information) and are not concentrated around the former [\text{OAc}]^− ion. All of these indicate reduction rather than substitution; the negative charge of [\text{OAc}]^− has been completely transferred to the borane cage.

The Cambridge Structural Database\textsuperscript{22} contains only two structurally characterized examples of dianions produced through similar reactions: \([\text{B}_{10}\text{H}_{14}]^2−\), prepared by reacting \(\text{B}_{10}\text{H}_{14}\) with \(\text{NaBH}_4\),\textsuperscript{20} and \([\text{B}_{10}\text{H}_{13}\text{CN}]^2−\), prepared by reacting \(\text{B}_{10}\text{H}_{14}\) with \(\text{NaCN}\).\textsuperscript{23} These reactions are postulated to proceed through deprotonation of \(\text{B}_{10}\text{H}_{14}\) to give \([\text{B}_{10}\text{H}_{13}]^−\), rearrangement of the hydrogen atoms, and addition of the anionic ligand to the cluster. The anions from these reactions, \(\text{H}^−\) (from \(\text{NaBH}_4\)) and \(\text{CN}^−\), tend to undergo very covalent bonding. Carboxylates, however, tend to bond with cations such as \(\text{H}^+\) to give carboxylic acids or metal ions to give metal complexes. The direct formation of an ester from a carboxylate is very unusual, but here, it can be rationalized by the fact that

---

**Figure 1.** Comparison of PXRD pattern of room temperature reaction mixture (red) with calculated PXRD patterns for \([\text{C}_2\text{mim}]_2[\text{B}_{10}\text{H}_{13}(\text{OAc})]\) (black) and \([\text{C}_2\text{mim}]_2[\text{B}(\text{O(BOO)}_2)_2]\) (blue) with black and blue rectangles drawn around peaks corresponding to those phases, respectively.

**Figure 2.** Left: 50% probability ellipsoid diagrams of the asymmetric/formula unit of \([\text{C}_2\text{mim}]_2[\text{B}_{10}\text{H}_{13}(\text{OAc})]\); Right: detailed view of the anion. Dashed lines indicate the shortest cation–anion contacts.
the negative charge becomes highly delocalized over the entire cluster.

We were unable to isolate [C2mim][B10H13(OAc)] for spectroscopic analysis or to determine its yield. Isolation of this compound has proven to be very challenging because it likely reacts with polar solvents, in which it would be soluble, and the IL cannot be removed by evaporation. We attempted workups on some reaction mixtures by washing with toluene, acetonitrile, or a 50:50 v/v mixture of the two. On the basis of the color changes observed, the products appeared to have no appreciable solubility in toluene and reacted with both acetonitrile-containing solvents.

The 1:10 B10H14/[C2mim][OAc] reaction mixture prepared at room temperature was analyzed by 1H, 13C, and 11B nuclear magnetic resonance (NMR) to obtain spectroscopic information on boron-containing species present. At least 13 resolvable maxima can be observed in the 11B spectrum within the range of 5 to −55 ppm (Figure 3), more than can possibly be explained by any single boron-containing species likely to be present. Unambiguous peak assignment is not possible because of the inability to accurately integrate the overlapping peaks and lack of reference data for 11B NMR in [C2mim][OAc]. The major peak at −44 ppm is in an area consistent with an open skeleton species containing bridging hydrogen atoms and may correspond to the combined signals of B1, B3, B6, and B9 of \([\text{B}_{10}\text{H}_{13}(\text{OAc})]^2\text{−}\), which are the four positions most likely to be shifted upfield by the shielding effect of bridging hydrogen atoms. Two signals at roughly half the height of the major peak are located at −8 and −25 ppm, which may be associated with two pairs of symmetry related atoms, B5/B7 and B8/B10, respectively. B2 and B4 are likely coalesced in the band of signals from 0 to −12, based on the reported chemical shifts for the analogous positions in \([\text{B}_{10}\text{H}_{14}]^2\text{−}\). The remaining peaks may be due to unreacted decaborane or other boron hydrides including \([\text{B}_{12}\text{H}_{12}]^2\text{−}\) and cannot be assigned definitively.

Although 11B NMR is ultimately ambiguous as to the identity of the boron-containing species present, 13C NMR shows definitive evidence for the presence of \([\text{B}_{10}\text{H}_{14}(\text{OAc})]^2\text{−}\). A set of new peaks emerge near the 13C NMR signals for the carbonyl and methyl carbon atoms of [OAc]−/HOAc but not for any other carbon atom, which indicates the formation of an ester (Figure S2, Supporting Information). A second set of even smaller peaks corresponding to the [OAc]− carbon atoms in the 13C spectra also appears; the symmetrical B6,B9-disubstituted \([\text{B}_{10}\text{H}_{12}(\text{OAc})_2]^2\text{−}\) seems to be the most likely assignment because both [OAc]− groups would be chemically equivalent. Because there are no other reactions with the IL besides these additions to the borane cluster, the formation of borates is most likely due to the reaction with adventitious water and suggests a possible scavenging mechanism.

We also made an attempt to force B10H14 to react with the [C2mim]+ moiety, rather than [OAc]−. Excess [C2mim][OAc] was first treated with either NaH or potassium tert-butoxide to generate the imidazole-2-ylidine quantitatively, and B10H14 was then added (Table S2, Supporting Information). The IL changed in color from red-orange to yellow over the course of several hours, after which no variation of the color was observed over a period of several weeks. To separate the
approaches for a wide range of functionalized borane products from inorganic salts, the reaction mixtures were dissolved in an acetonitrile solution, layered with benzene, and allowed to crystallize by slow evaporation at ambient temperature. Any carboranes formed were expected to be stable to this treatment, as well as B\textsubscript{10}H\textsubscript{14} itself, which reacts with acetonitrile only at an elevated temperature.\textsuperscript{25}

Colorless crystalline blocks were isolated after 1 day, analyzed by SCXRD, and determined to be \([\text{C}_2\text{mim}][\text{B}_{10}\text{H}_{10}]\) (Figure 4, left). PXRD of solids obtained from the reaction of B\textsubscript{10}H\textsubscript{14} with KO\textsubscript{Bu} indicates that \([\text{C}_2\text{mim}][\text{B}_{10}\text{H}_{10}]\) is the major crystalline product after the reaction (Figure 4, right). \([\text{B}_{10}\text{H}_{10}]^{2-}\) can be made from reactions of B\textsubscript{10}H\textsubscript{12}L\textsubscript{2} molecules (a class which B\textsubscript{10}H\textsubscript{14} can be considered a member) with bases.\textsuperscript{26} This suggests that B\textsubscript{10}H\textsubscript{14} simply protonates the ylide. It also further supports that the unusual reactivity of \([\text{OAc}]^-\) comes from accessing it at a high concentration and ambient temperature as an IL because NaH and K(t-BuO) only undergo typical chemistry when dissolved in \([\text{C}_2\text{mim}][\text{OAc}]\).

3. CONCLUSIONS

In conclusion, we have shown that B\textsubscript{10}H\textsubscript{14} can react with \([\text{C}_2\text{mim}][\text{OAc}]\) through multiple pathways to give boron clusters (\([\text{B}_{12}\text{H}_{12}]^{2-}\) and \([\text{B}_{10}\text{H}_{10}]^{2-}\)), boron oxyanions (\([\text{B}-\text{O}(\text{BOO})\text{O}])\)), and the newly reported, reduced borane ester (\([\text{B}_{10}\text{H}_{13}(\text{OAc})]^{2-}\)). The type of chemistry which led to the formation of \([\text{B}_{10}\text{H}_{13}(\text{OAc})]^{2-}\) has been previously observed in aqueous systems with covalently bonding anions such as H\textsuperscript{+} and CN\textsuperscript{-}, but we have now shown that the normally stable \([\text{OAc}]^-\) anion can also undergo this reaction when used as a neat IL. Using the IL as a solvent for other bases, however, does not give access to unusual chemistry for those bases. These observations are consistent with our previous findings that the ability to access high concentrations of free ions at ambient temperatures can be essential to their unusual reactivity, as it allows them to proceed through reactions that are normally disrupted by side reactions.\textsuperscript{26} Given the various contexts in which borane chemistry is being explored, we hope that this finding will lead to facile, IL-based approaches for a wide range of functionalized borane derivatives.

4. EXPERIMENTAL SECTION

4.1. Materials and Methods. nido-Decaborane (B\textsubscript{10}H\textsubscript{14}, Alfa Aesar, Ward Hill, MA), sodium hydride (NaH, Sigma-Aldrich, St. Louis, MO), potassium tert-butoxide (KO\textsubscript{Bu}, Sigma-Aldrich, St. Louis, MO), acetonitrile (Fisher Chemicals, Fair Lawn, NJ), and benzene (Sigma-Aldrich) were used as received. 1-Ethyl-3-methylimidazolium acetate (\([\text{C}_2\text{mim}][\text{OAc}]\), IOLITEC USA, Tuscaloosa, AL) was used as received for reactions with B\textsubscript{10}H\textsubscript{14} and was kept under oil pump vacuum at 100 °C for 24 h and degassed before reactions with B\textsubscript{10}H\textsubscript{14}/NaH or B\textsubscript{10}H\textsubscript{14}/KO\textsubscript{Bu}.

PXRD data were collected on a Bruker D2 PHASER equipped with a LynxEye linear position sensitive detector (Bruker AXS, Madison, WI). Neat samples were smeared directly onto the silicon wafer of a proprietary low-background sample holder. Data were collected using a continuous coupled \(\theta/2\theta\) scan with Ni-filtered Cu-K\textsubscript{z} radiation.

SCXRD data of \([\text{C}_2\text{mim}][\text{B}_{12}\text{H}_{12}]\), \([\text{C}_2\text{mim}][\text{B}(\text{O}-\text{BOO})\text{O}])\), and \([\text{C}_2\text{mim}][\text{B}_{10}\text{H}_{13}(\text{OAc})]\) were collected on a Bruker diffractometer equipped with a PLATFORM 3-circle goniometer and an APEX II CCD area detector (Bruker AXS) using graphite-monochromated Mo-K\textsubscript{z} radiation. Crystals were cooled to 100 K under a cold stream of nitrogen using an Oxford N-HeliX cryostat (Oxford Cryosystems, Oxford, UK). Hemispheres of data out to a resolution of at least 0.80 Å were collected by a strategy of \(\phi\) and \(\omega\) scans. Unit cell determination, data collection, data reduction, and correction for absorption were all conducted using the APEX2 software suite (Bruker AXS). The structures of \([\text{C}_2\text{mim}][\text{B}_{12}\text{H}_{12}]\) and \([\text{C}_2\text{mim}][\text{B}_{10}\text{H}_{13}(\text{OAc})]\) were solved by direct methods and refined by full-matrix least squares refinement against \(F^2\). Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms bonded to boron were located from the difference map, and their coordinates were allowed to refine while their thermal parameters were constrained to ride on the carrier atoms. Hydrogen atoms bonded to carbon were placed in calculated positions, and their coordinates and thermal parameters were constrained to ride on the carrier atoms.

SCXRD data for \([\text{C}_2\text{mim}][\text{B}_{12}\text{H}_{12}]\) were collected on a Bruker D8 ADVANCE diffractometer with a PHOTON 100 CMOS area detector and an Lu/S microfocus X-ray source (Bruker AXS) using Mo-K\textsubscript{z} radiation. All the non-hydrogen atoms were refined anisotropically. The ethyl group was modeled as being disordered over two conformations with the terminal methyl group occupying two positions. The site occupancy factors and anisotropic thermal parameters were freely refined. Structures were solved by direct methods and refined by full-matrix least squares refinement against \(F^2\). Non-hydrogen atoms were located from the difference map and refined anisotropically. Hydrogen atoms bonded to boron were located from the difference map, and hydrogen atoms bonded to carbon were placed in calculated positions. All hydrogen atom coordinates and thermal parameters were constrained to ride on the carrier atoms.

The crystal structure of \([\text{C}_2\text{mim}][\text{B}_{12}\text{H}_{12}]\) has unusually large thermal ellipsoids for carbon atoms on the cations, especially the ethyl groups, and an exceptionally short C–C single bond. These are likely artifacts of unresolved disorder. Examination of the difference map suggests that the carbon atoms of the −CH\textsubscript{2}− groups might be disordered over two positions. As the nitrogen atoms are very unlikely to form bond angles deviating from 120°, disorder at this position suggests that the entire ring may be disordered over two offset positions, which is a common form of disorder for aromatic rings. Because the overall scattering from this crystal was weak, the high angle data is mostly unobserved, and the usable fraction of the data is at too low of a resolution to allow the modeling of so many nearly overlapping partial atoms. Nevertheless, the correct identity of the structure is strongly supported by the presence of the geometrically distinct \([\text{B}_{12}\text{H}_{12}]^{2-}\) fragment, the requirements of charge balance, and isomorphism with the crystal structure of \([\text{C}_2\text{mim}][\text{B}_{12}\text{F}_{12}]\). Analysis of another crystal was not attempted; as the crystal is isomorphous with a known compound, we do not anticipate any significant findings from a higher resolution structure.

4.2. Synthetic Methods. Caution: B\textsubscript{10}H\textsubscript{14} is a volatile, highly poisonous solid, capable of causing permanent health effects at low exposure levels. Never handle unsealed containers of B\textsubscript{10}H\textsubscript{14} outside of a fume hood, and decontaminate all glassware, utensils, and materials that come into contact with B\textsubscript{10}H\textsubscript{14} before removing them.
4.3. General Procedure for the Isolation of Single Crystals of \([\text{C}_2\text{mim}][\text{B}_{10}\text{H}_{14}]\), \([\text{C}_2\text{mim}][\text{B(OH})\text{OO}]_{2}\), and \([\text{C}_2\text{mim}][\text{B}_{10}\text{H}_{13}](\text{OAc})]\). A borosilicate glass culture tube was tared, and \([\text{C}_2\text{mim}][\text{OAc}]\) was weighed into it. \(\text{B}_{10}\text{H}_{14}\) was handled exclusively in a fume hood by adding it to a tared, empty screw-cap vial, sealing the vial, weighing it, and adding or removing \(\text{B}_{10}\text{H}_{14}\) as needed until the target mass was achieved. When the needed amount of \(n\)-\(\text{B}_{10}\text{H}_{14}\) was weighed out, the contents of the vial were emptied onto a sheet of weighing paper and then transferred into the culture tube containing the IL. The culture tubes were then either sealed with Parafilm and allowed to stand at room temperature or placed in a heated sand bath while unsealed. After 1 d, portions of the vitri were isolated and analyzed. An identical procedure with butanol was charged with \([\text{C}_2\text{mim}][\text{OAc}]\) (0.502 g, 2.94 mmol). The flask was purged with \(\text{N}_2\) (Linde Gas Canada, Mississauga, ON). KO[Bu] (0.0662 g, 0.590 mmol, 0.20 equiv) was added in one portion under \(\text{N}_2\). After 4 h, \(\text{B}_{10}\text{H}_{14}\) (0.0539 g, 0.441 mmol) was added to viscous liquid in one portion under \(\text{N}_2\). The viscosity increased progressively, and the product assumed a solid consistency while the color changed from orange to yellow. After 24 h, an aliquot of the solution was layered with benzene (1:1 v/v). After 1 d, colorless crystals were isolated and analyzed. An identical procedure with NaH provided the same results.

4.4. General Procedure for the Isolation of Single Crystals of \([\text{C}_2\text{mim}][\text{B}_{10}\text{H}_{14}]\). A 100 mL round bottom Schlenk flask was charged with \([\text{C}_2\text{mim}][\text{OAc}]\) (1.241 g, 2.94 mmol). The flask was purged with \(\text{N}_2\) and stirred for 5 h until complete dissolution of \(\text{B}_{10}\text{H}_{14}\) was observed. The color of the mixture turned from colorless to a more viscous yet free-flowing yellow liquid. The resulting liquid was loaded into an NMR tube with three sealed capillaries containing DMSO-\(d_6\). \(^{1}H\), \(^{13}C\), and \(^{11}B\)-NMR spectra were recorded on a Bruker Ascend 500 spectrometer (500 MHz).

4.5. NMR Measurement. \(\text{B}_{10}\text{H}_{14}\) (0.087 g) was added to \([\text{C}_2\text{mim}][\text{OAc}]\) (1.241 g) and stirred for 5 h until complete dissolution of \(\text{B}_{10}\text{H}_{14}\) was observed. The color of the mixture turned from colorless to more viscous yet free-flowing yellow liquid. The resulting liquid was loaded into an NMR tube with three sealed capillaries containing DMSO-\(d_6\). \(^{11}B\)-NMR spectra recorded on a Bruker Ascend 500 spectrometer (500 MHz).

Acknowledgments

This material is based upon work supported by the Air Force Office of Scientific Research under AFOSR award nos. FA9550-16-1-0521 and FA9550-14-1-0306 (Iowa State University subcontract 421-21-06A). This research was undertaken, in part, thanks to funding from the Canada Excellence Research Chairs Program.

References

(1) Hallet, J. P.; Welton, T. Room-temperature ionic liquids: Solvents for synthesis and catalysis. 2. Chem. Rev. 2011, 111, 3508–3576.
(2) Wilkes, J. S.; Zaworotko, M. J. Air and water stable 1-ethyl-3-methylimidazolium based ionic liquids. J. Chem. Soc. Chem. Commun. 1992, 0, 965–967.
(3) Remsing, R. C.; Hernandez, G.; Swatloski, R. P.; Massefski, W. J.; Rogers, R. D.; Moyna, G. Solvation of carbohydrates in N,N’-dialkylimidazolium ionic liquids: A multinuclear NMR spectroscopy study. J. Phys. Chem. B 2008, 112, 11071–11078.
(4) Gura, G.; Rodriguez, H.; Kelley, S. P.; Janiczek, P.; Kalb, R. S.; Rogers, R. D. Demonstration of chemisorption of carbon dioxide in 1,3-dialkylimidazolium acetate ionic liquids. Angew. Chem., Int. Ed. 2011, 50, 12024–12026.
(5) Rodriguez, H.; Gura, G.; Holbrey, J. D.; Rogers, R. D. Reaction of elemental chalcogens with imidazolium acetates to yield imidazol-2-chalcogenones: Direct evidence for ionic liquids as proto-carbenes. Chem. Commun. 2011, 47, 3222–3224.
(6) Shore, S. G. Nido- and arachno- boron hydrides. In Boron Hydride Chemistry; Muetterties, E. L., Ed.; Academic Press, Inc.: New York, NY, 1975; pp. 79–174.
(7) Dalebrook, A. F.; Gan, W.; Grasemann, M.; Moret, S.; Laurenczy, G. Hydrogen storage: Beyond conventional methods. Chem. Commun. 2013, 49, 8735.
(8) Ewing, W. C.; Carroll, P. J.; Sneddon, L. G. Crystallographic characterization and new high-yield synthetic routes for the complete series of 6-X-\(\text{B}_{10}\text{H}_{14}\) Halodecaboranes (X = F, Cl, Br, I) via superacid-induced cage-opening reactions of closo-\(\text{B}_{10}\text{H}_{10}^+\). Inorg. Chem. 2008, 47, 8580–8582.
(9) Ewing, W. C.; Carroll, P. J.; Sneddon, L. G. Efficient syntheses of 5-X-\(\text{B}_{10}\text{H}_{14}\) Halodecaboranes via the photochemical (X = I) and/or base-catalyzed (X = Cl, Br) \(^{1}I\) isomerization reactions of 6-X-\(\text{B}_{10}\text{H}_{13}\). Inorg. Chem. 2010, 49, 1983–1994.
(10) Kusari, U.; Carroll, P. J.; Sneddon, L. G. Ionic liquid-promoted decaborane olefin-hydroboration: A new efficient route to 6-R-\(\text{B}_{10}\text{H}_{13}\) Derivatives. Inorg. Chem. 2008, 47, 9203–9215.
(11) McCrary, P. D.; Barber, P. S.; Kelley, S. P.; Rogers, R. D. Nonaborane and decaborane cluster anions can enhance the ignition delay in hypergolic ionic liquids and induce hypergolicity in molecular solvents. Inorg. Chem. 2014, 53, 4770–4776.
(12) Kelley, S. P.; McCrary, P. D.; Flores, L.; Garner, E. B.; III; Dixon, D. A.; Rogers, R. D. Structural and theoretical study of salts of the \([\text{B}_{10}\text{H}_{14}]^-\) ion: Isolation of multiple isomers and implications for energy storage. ChemPlusChem 2016, 81, 922–925.
(13) Shackelford, S. A.; Belletire, J. L.; Boatz, J. A.; Schneider, S.; Wheaton, A. K.; Wight, B. A.; Hudgens, L. M.; Ammon, H. L.; Strauss, S. H. Pairing heterocyclic cations with closo-icosahedral borane and carborane anions. I. Benchtop aqueous synthesis of binary triazolium and imidazolium salts with limited water solubility. Org. Lett. 2009, 11, 2623–2626.

Author Information

Corresponding Author
*E-mail: drd55@ua.edu (R.D.R.).

ORCID
Steven P. Kelley: 0000-0001-6755-4495
Giovanni P. Rachiero: 0000-0002-9698-3077
Hatem M. Titi: 0000-0002-0654-1292
Robin D. Rogers: 0000-0001-9843-7494

Present Address
2Active AgriScience, 209-31136 Peardonville Rd., Abbotsford, BC V2T 6K2, Canada (G.P.R.).

Notes
The authors declare no competing financial interest.
(14) Parker, T. G.; Pubbi, D.; Beehler, A.; Albrecht-Schmitt, T. E. 1-Ethyl-3-methyl-1H-imidazol-3-ium spiropentaborate. *Acta Crystallogr., Sect. E: Struct. Rep. Online* 2014, 70, o171–o172.

(15) Belleitre, J. L.; Schneider, S.; Shackelford, S. A.; Peryshkov, D. V.; Strauss, S. H. Pairing heterocyclic cations with closo-decaborodecaborate (2−). *J. Fluorine Chem.* 2011, 132, 925–936.

(16) Miller, H. C.; Miller, N. E.; Muetterties, E. L. Chemistry of boranes. XX. Syntheses of polyhedral boranes. *Inorg. Chem.* 1964, 3, 1456–1463.

(17) Miao, J.; Nie, Y.; Chen, H.; Wang, D.; Enders, M.; Siebert, W.; Sun, G.; Dou, J. Synthesis and characterization of the nido-platinaborane 7,7-(PPh3)7-7-PtB10H11-11-OC(O)Me. *Z. Naturforsch., B: J. Chem. Sci.* 2011, 66, 387–391.

(18) Fontaine, X. L. R.; Greenwood, N. N.; Kennedy, J. D.; Thornton-Pett, M.; Peiju, Z. Homobimetallic B-frame species: [(PPh3)2Ru](μ-MeCO2)3(μ-H)2{RuB10H7}], a unique diruthenaborane in which the metal atoms are linked by one-, two-, three-, and four-membered bridges. *J. Chem. Soc. Chem. Commun.* 1987, 0, 1717–1718.

(19) Peymann, T.; Lork, E.; Gabel, D. Hydroxoundecahydro-closo-decaborate(2−) as a nucleophile. Preparation and structural characterization of O-Alkyl and O-Acyl derivatives of hydroxoundecahydro-closo-decaborate(2−). *Inorg. Chem.* 1996, 35, 1355–1360.

(20) Kendall, D. S.; Lipscomb, W. N. Crystal structure of tetramethyl ammonium tetradecaborate. Structure of the B10H142− ion. *Inorg. Chem.* 1973, 12, 546–551.

(21) Li, T.; Jalisatgi, S. S.; Bayer, M. J.; Maderna, A.; Khan, S. I.; Hawthorne, M. F. Organic syntheses on an icosahedral borane surface: Closomer structures with twofold functionality. *J. Am. Chem. Soc.* 2005, 127, 17832–17841.

(22) Groom, C. R.; Bruno, I. J.; Lightfoot, M. P.; Ward, S. C. The Cambridge Structural Database. *Acta Crystallogr., Sect. B: Struct. Sci., Cryst. Eng. Mater.* 2016, 72, 171–179.

(23) Baše, K.; Alcock, W. N.; Howarth, O. W.; Powell, H. R.; Harrison, A. T.; Wallbridge, M. G. H. The structure of the arachno-[B10H13CN]2− anion; an example of endo substitution in the decaborane(14) framework. *J. Chem. Soc. Chem. Commun.* 1988, 0, 341–342.

(24) Hermanek, S. Boron-11 NMR spectra of boranes, main-group heteroboranes, and substituted derivatives. Factors influencing chemical shifts of skeletal atoms. *Chem. Rev.* 1992, 92, 325–362.

(25) Schaeffer, R. A new type of substituted borane. *J. Am. Chem. Soc.* 1957, 79, 1006–1007.

(26) Hawthorne, M. F.; Pilling, R. L.; Grimes, R. N. The Mechanism of B10H102− formation from B10H12(ligand)2 species. *J. Am. Chem. Soc.* 1967, 89, 1067–1074.

(27) Kelley, S. P.; Rogers, R. D. Isolation of uranyl dicyanamide complexes from N-donor ionic liquids. *Inorg. Chem.* 2015, 54, 10323–10334.