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Nonaborane and Decaborane Cluster Anions Can Enhance the Ignition Delay in Hypergolic Ionic Liquids and Induce Hypergolicity in Molecular Solvents

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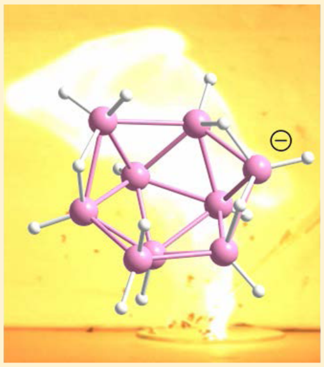
Supporting Information



ABSTRACT: The dissolution of *nido*-decaborane, $B_{10}H_{14}$, in ionic liquids that are hypergolic (fuels that spontaneously ignite upon contact with an appropriate oxidizer), 1-butyl-3-methylimidazolium dicyanamide, 1-methyl-4-amino-1,2,4-triazolium dicyanamide, and 1-allyl-3-methylimidazolium dicyanamide, led to the *in situ* generation of a nonaborane cluster anion, $[B_9H_{14}]^-$, and reductions in ignition delays for the ionic liquids suggesting salts of borane anions could enhance hypergolic properties of ionic liquids. To explore these results, four salts based on $[B_{10}H_{13}]^-$ and $[B_9H_{14}]^-$, triethylammonium *nido*-decaborane, tetraethylammonium *nido*-decaborane, 1-ethyl-3-methylimidazolium *arachno*-nonaborane, and *N*-butyl-*N*-methylpyrrolidinium *arachano*-nonaborane were synthesized from *nido*-decaborane by reaction of triethylamine or tetraethylammonium hydroxide with nido-decaborane in the case of salts containing the decaborane anion or via metathesis reactions between sodium nonaborane ($Na[B_9H_{14}]$) and the corresponding organic chloride in the case of the salts containing the nonaborane anion. These borane cluster anion salts form stable solutions in some combustible polar aprotic solvents such as tetrahydrofuran and ethyl acetate and trigger hypergolic reactivity of these solutions. Solutions of these salts in polar protic solvents are not hypergolic.

INTRODUCTION

Hypergolic ionic liquids (ILs), a class of salts with melting points below 100 °C that spontaneously ignite upon contact with an oxidizer,[1−3] have been previously proposed as replacements for hydrazine as a rocket bipropellant; however, key properties, such as heat of combustion,[4] ignition delay (ID),[2] and low temperature viscosity,[5] need improvement to match the performance of hydrazine.[6] In our own research to understand the chemistry of hypergolic ILs and their analogues, instead of focusing entirely on the ions within the IL, we have sought to improve the performance of hypergolic ILs by incorporation of catalytic nanoparticle additives, such as B(0)[7,8] or Ti(0)[9] to improve overall energetic content or graphene[10] to improve low-temperature viscosity. One key challenge with these nanoparticulate systems has been colloidal stability (<2−3 days in many cases).[7−10] We hypothesized that the stability of energetic additives could be improved by reducing their size from suspended nanoparticles to solutions of molecular clusters on the order of angstroms rather than nanometers.

Given the increased flame height that we obtained by incorporating B(0) nanoparticles in hypergolic ILs,[7] we wondered whether neutral or charged borane clusters could be dissolved in ILs in a catalytic ratio to enhance the energetic properties. Recently, several molecules containing the B−H functional group have been demonstrated as hypergolic salts,[3,11] and BH_3 hydrazine adducts have been utilized in high concentrations as ignition delay enhancers by dissolving them in hypergolic ILs.[12] During the preparation of this manuscript, it was also demonstrated that a triethylammonia borane adduct ($N(Et)_3{\cdot}BH_3$) can act as an ignition delay enhancer if added to known hypergolic ILs.[13]

Boranes are known for their potential to form air stable clusters[14] (including anionic species[15]) and to be oxidized readily[16] in hypergolic ignition reactions. Indeed, boranes have been explored in the past as potential fuels,[17,18] but interest waned due to issues with high volatility, toxicity, reactivity with many organic solvents, and solid product formation (B_2O_3) upon oxidation.[16] However, many of the properties inherent to many ILs, such as improved stability and low volatility, might be exploited by transforming neutral boranes into salts of borane anions.

While our initial interest in utilizing molecular borane clusters as energetic additives stemmed from their high reported reactivity with oxidizers,[16] we were also interested in exploring how the dissolved borane clusters would interact with complex hypergolic IL solvents, much like our previous explorations of the surface reactivity of nanomaterials with hypergolic ILs.[7−10] We selected *nido*-decaborane ($B_{10}H_{14}$) as our molecular borane source because it is air stable as a crystalline solid[19] and reacts to form anionic species by acting as a Brønsted acid (pK_a 2.7[20]) in the presence of various bases.[21] This has previously been utilized to synthesize $[B_{10}H_{13}]^{-}$[22,23] and $[B_9H_{14}]^{-}$[24,25] (Figure 1). Decaborane has

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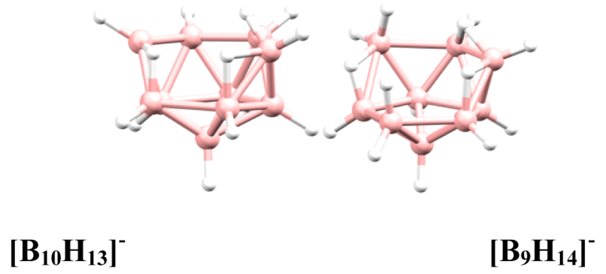


Figure 1. Diagrams of stable borane cluster anions generated from crystallographic coordinates in the Cambridge Structural Database for entries SATDOG ($[PhCH_2(CH_3)_3N][B_{10}H_{13}]$)[23] and MOTGIL ($K[B_9H_{14}]$).[24]

also been reported to react with the slightly basic chloride anion in 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) via an acid−base reaction to form $[B_{10}H_{13}]^-$ as an intermediate in the synthesis of *o*-carboboranes.[26,27]

Here we report our efforts to explore and understand the reactivity between the borane cluster $B_{10}H_{14}$ and dicyanamide-based hypergolic ILs and the composition and energetic role of the generated species. We also discuss our findings that salts of borane cluster anions not only can reduce the ignition delay of hypergolic ionic liquids in which they are dissolved but also can act as hypergolic triggers leading to combustion of non-hypergolic aprotic solvents in which they can be solubilized.

■ EXPERIMENTAL SECTION

Caution! Although no accidents were experienced in the studies reported here, special care is needed prior to and during the handling of all borane hydride compounds. Toxicity, volatility, shock sensitivity, and impact sensitivity are common in molecular boranes and borohydrides; thus extreme caution should be exercised when handling these materials.

Materials. 1-Chlorobutane, triethylamine, allyl chloride, iodomethane, tetraethylammonium hydroxide, and chloroethane were purchased from Sigma-Aldrich (St. Louis, MO) and used as received. 1-Methylimidazole was purchased from Sigma-Aldrich (St. Louis, MO) and distilled prior to use. *nido*-Decaborane, 4-NH_2-1,2,4-triazole, sodium dicyanamide, silver nitrate, and sodium hydroxide were purchased from Alfa-Aesar (Ward Hill, MA) and used as received. 1-Butyl-1-methylpyrrolidinium chloride ($[Pyrr_{14}]Cl$) was purchased from EMD Chemicals (Darmstadt, Germany) and utilized as received. 1-Ethyl-3-methylimidazolium chloride ($[C_2mim]Cl$) was purchased from BASF (Ludwigshafen, Germany) and was recrystallized from dichloromethane prior to use. Absolute ethanol, acetonitrile, anhydrous methanol, and anhydrous diethyl ether were purchased from Fischer Scientific (Hampton, NH) and used without any further purification.

Synthesis of Ionic Liquid Precursors.[7,28] *1-Butyl-3-methylimidazolium Chloride ($[C_4mim]Cl$).* $[C_4mim]Cl$ was prepared following the synthesis in ref 7. 1-Methylimidazole (150.00 g, 1.83 mol) was distilled into a flask containing a 1.1 molar excess of 1-chlorobutane (204.64 g, 2.00 mol), and the resulting mixture was refluxed under argon gas through Schlenk-line techniques. The reaction was monitored by NMR until all traces of 1-methylimidazole were no longer visible (96 h). The excess 1-chlorobutane was removed under reduced pressure, and the product was slowly cooled forming a white, crystalline solid. Melting point: 68 °C. ^1H NMR (360 MHz, DMSO-d_6) δ ppm: 9.12 (1H, s), 7.93 (1H, s), 7.85 (1H, s), 4.22 (2H, t), 3.90 (3H, s), 1.77 (2H, quintet), 1.25 (2H, sextet), 0.890 (3H, t). ^{13}C NMR (125 MHz, DMSO-d_6) δ ppm: 137.6, 124.5, 123.1, 49.3, 36.6, 32.3, 19.6, 14.2.

1-Methyl-4-amino-1,2,4-triazolium Iodide ([MAT]I). [MAT]I was prepared following the synthesis in ref 7. 4-Amino-1,2,4-triazole (100 g, 1.19 mol) was weighed out and added piecewise into a 1 L reaction flask containing 0.5 L of reagent grade acetonitrile under agitation with a Teflon stirbar. The flask was slowly heated to 35 °C during the addition. Once the 4-amino-1,2,4-triazole was completely dissolved (∼3 h), the flask was covered to minimize light exposure. While at 35 °C, iodomethane (422 g, 2.98 mol) was added slowly dropwise over ∼2 h, keeping the temperature of the solution under 40 °C during the addition. At the end of the iodomethane addition, the heat was turned off, and the reaction mixture was allowed to cool while stirring overnight. When the reaction was complete as determined by ^1H NMR, the flask was cooled to 0 °C, and a solid precipitated. The crude solids were recrystallized from absolute ethanol to yield a white crystalline solid. Melting point: 98 °C.[7,29] ^1H NMR (360 MHz, DMSO-d_6) δ ppm: 10.12 (1H, s), 9.16 (1H, s), 6.93 (2H, s), 4.02 (3H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ ppm: 145.1, 143.0, 39.1.

1-Allyl-3-methylimidazolium Chloride ([Amim]Cl). [Amim]Cl was prepared following the synthesis in ref 28 and was only modified in scale. Allyl chloride (150 mmol, 11.478 g) was dropwise added to freshly distilled 1-methylimidazole (120 mmol, 9.852 g) at room temperature, and the solution was stirred at 55 °C for 18 h. The excess allyl chloride was removed under reduced pressure to obtain an amber, viscous liquid. ^1H NMR (360 MHz, DMSO-d_6) δ ppm: 9.65 (1H, s), 7.90 (1H, s), 7.88 (1H, s), 6.04 (1H, tdd), 5.31 (1H, dd), 5.28 (1H, dd), 4.94 (2H, d), 3.91 (3H, s). ^{13}C NMR (125 MHz, DMSO-d_6) δ ppm: 137.3, 132.4, 124.2, 122.8, 120.5, 51.1, 36.2.

Silver Dicyanamide (Ag[DCA]). Sodium dicyanamide (13.35 g, 150 mmol) was dissolved in 20 mL of DI water and added dropwise to a saturated aqueous solution of silver nitrate (25.48 g, 150 mmol) in a 100 mL round-bottom flask with a Teflon-coated magnetic stirbar. The mixture was stirred overnight in darkness at room temperature, and the resulting white solid was vacuum filtered and washed with DI water followed by methanol. The solid was dried in a vacuum oven at 70 °C for 24 h.

Metathesis Reactions and Drying for $[DCA]^-$ ILs.[2,7] *1-Butyl-3-methylimidazolium Dicyanamide ($[C_4mim][DCA]$).* The method for the synthesis of all $[DCA]^-$ ILs was obtained from ref 2 and was only modified for the scale of the synthesis as presented in ref 7. In a metathesis procedure common to all of the $[DCA]^-$ ILs prepared, $[C_4mim]Cl$ (8.734 g, 50.0 mmol) was dissolved in 25 mL of dry methanol and transferred to a 250 mL round-bottom flask containing a 1.1 molar excess of Ag[DCA] (11.193 g, 55.0 mmol) containing 175 mL of anhydrous methanol.[2] An excess of Ag[DCA] was used to ensure complete conversion due to the limited solubility in methanol. The flask was covered with aluminum foil and stirred for 3 days. AgCl and remaining Ag[DCA] were filtered, and the filtrate was evaporated under reduced pressure. The resulting clear oil was dissolved in a minimal amount of methanol and filtered again to remove trace amounts of AgCl dissolved in the IL. The methanol was removed under reduced pressure.

The IL was dried using high vacuum (1×10^{-4} Torr) at 70 °C and then degassed using three separate freeze−thaw cycles with liquid nitrogen under high vacuum. A clear, nonviscous liquid was obtained. The water content was less than 500 ppm as determined by Coulometric Karl Fischer titration utilizing a Mettler-Toledo (Columbus, OH) C20 Coulometric KF Titrator. All other ILs were dried in the same manner.

^1H NMR (500 MHz, neat liquid) δ ppm: 9.08 (1H, s), 7.74 (1H, s), 7.67 (1H, s), 4.16 (2H, s), 3.85 (3H, s), 1.78 (2H, quintet (triplet of triplets)), 1.27 (2H, sextet), 0.90 (3H, t). ^{13}C NMR (125 MHz, neat liquid) δ ppm: 137.0, 124.0, 122.7, 119.6, 49.1, 36.2, 31.8, 19.3, 13.6.

1-Methyl-4-amino-1,2,4-triazolium Dicyanamide ([MAT][DCA]). The iodide anion in [MAT]I (22.602 g, 100.0 mmol) was exchanged for the $[DCA]^-$ anion with Ag[DCA] (22.385 g, 110 mmol) and dried as described above. ^1H NMR (500 MHz, neat liquid) δ ppm: 10.67 (1H, s), 9.74 (1H, s), 7.39 (2H, s, NH_2), 5.00 (3H, s). ^{13}C NMR (125 MHz, neat liquid) δ ppm: 146.2, 144.0, 120.1, 40.4.

1-Allyl-3-methylimdazolium Dicyanamide ([Amim][DCA]). The chloride anion in [Amim]Cl (7.932 g, 50.0 mmol) was exchanged for the $[DCA]^-$ anion with Ag[DCA] (11.193 g, 55.0 mmol) and dried as described above. ^1H NMR (500 MHz, neat liquid) δ ppm: 9.09 (1H, s), 7.22 (1H, s), 7.20 (1H, s), 6.03 (1H, tdd), 5.36 (1H, dd), 5.31 (1H, dd), 4.31 (2H, d). ^{13}C NMR (125 MHz, neat liquid) δ ppm: 137.1, 132.2, 124.3, 122.8, 120.6, 119.6, 51.3, 36.3.

Loading of $B_{10}H_{14}$ into Hypergolic ILs. Decaborane (0.01 mmol, 0.0012 g to 0.1 mmol, 0.0122 g) was added to a 2 dram vial containing the IL (0.1 to 10 mmol) corresponding to the desired molar ratio of decaborane/IL from 1:1 to 1:1000. The vials were immediately capped and mixed with a vortex mixer for 5 s. Upon mixing, the vial warmed and a gas was produced. The vial was opened in a hood to prevent the gas from pressurizing the vial. The clear to yellow IL started to turn bright orange, and the cap was placed back on the vial. On standing, a black precipitate was produced and separated after sedimentation.

Synthesis of Borane Salts.[30] *1-Ethyl-3-methylimidazolium arachno-Nonaborane ([C_2mim][B_9H_{14}]).* Decaborane (3 mmol, 0.3666 g) dissolved in dry ethanol was added dropwise to an aqueous solution of NaOH (3 mmol, 0.1200 g). Upon addition, the solution turned bright yellow and emitted a small amount of gas. [C_2mim]Cl (3 mmol, 0.440 g) dissolved in a minimum amount of water was added dropwise to the solution containing the newly generated Na[B_9H_{14}]. [C_2mim][B_9H_{14}] immediately precipitated out of solution as a yellow powder. ^{1}H NMR (CD_3CN): 8.41 (s, 1H, C2−H), 7.40 (s, 1H, C4−H), 7.35 (s, 1H, C−H), 4.18 (q, 2H, N-$\underline{CH_2}CH_3$), 3.84 (s, 3H, N−CH_3), 1.48 (t, 3 H, −$CH_2\underline{CH_3}$), 0.50−2.50 (q, 9H, B−H terminal as overlapping 1:1:1:1 quartets), −1.50 (m, 5H, exchanging B−H). ^{11}B NMR (CD_3CN): −8.7 (d, 3B), −21.0 (d, 3B), −24.2 (d, 3B).

N-Butyl-N-methyl-pyrrolidinium arachno-Nonaborane ([$Pyrr_{14}$][B_9H_{14}]). Decaborane (3 mmol, 0.3666 g) dissolved in dry ethanol was added dropwise to an aqueous solution of NaOH (3 mmol, 0.1200 g). Upon addition, the solution turned bright yellow and bubbled. [$Pyrr_{14}$]Cl (3 mmol, 0.533 g) dissolved in a minimal amount of water was added dropwise to the solution containing the newly generated Na[B_9H_{14}]. [$Pyrr_{14}$][B_9H_{14}] immediately precipitated out of solution as a yellow powder. ^{1}H NMR (CD_3CN): 3.42 (m, 4H), 3.24 (t, 2H), 2.96 (s, 3H), 2.18 (m, 4H), 1.73 (quintet, 2H), 1.40 (sextet, 2H), 0.99 (t, 3H), 0.50−2.50 (q, 9H, B−H terminal as overlapping 1:1:1:1 quartets), −1.49 (m, 5H, exchanging B−H. ^{11}B NMR (CD_3CN): −8.9 (d, 3B), −21.3 (d, 3B), −24.6 (d, 3B).

Triethylammonium nido-Decaborane ([H−N_{222}][$B_{10}H_{13}$]). Decaborane (3 mmol, 0.3666 g) dissolved in diethyl ether was added dropwise to a solution of triethylamine (3 mmol, 0.3036 g) in diethyl ether. Immediately upon addition, a yellow solid precipitated. The solid was separated by vacuum filtration and washed with 3 equiv of anhydrous diethyl ether to yield a bright yellow crystalline powder. The resulting powder was recrystallized by dissolving the yellow solid into EtOAc followed by the slow addition of diethyl ether until precipitation was observed, which resulted in a pale yellow crystalline powder. ^{1}H NMR (CD_3CN): 6.62 (t, 1H, $\underline{H}$-N(Et)$_3$), 3.18 (dq, 6H, H−N(-C$\underline{H_2}$-CH$_3$)$_3$), 1.5−3 (q, 8H, B−H Terminal), 1.28 (t, 9H, H−N(−CH$_2$−C$\underline{H_3}$)$_3$), 0.05 (q, 2H, B−H Terminal), −2.86 (broad, 1H, B−H Bridging), −3.76 (broad, 2H, B−H Bridging). ^{11}B NMR (CD_3CN): 7.2 (d), 2.8 (d), −4.8 (d), −35.9 (d) (neutral $B_{10}H_{14}$ and a small amount of [B_9H_{14}]$^-$ were observed in the ^{11}B NMR).

Tetraethylammonium nido-Decaborane ([N_{2222}][$B_{10}H_{13}$]). Decaborane (3 mmol, 0.3666 g) dissolved in diethyl ether was dropwise added to a solution of [N_{2222}]OH (3 mmol, 0.7784 g) in methanol. Immediately upon addition, a yellow solid precipitated. The solid was separated by vacuum filtration and washed with 3 equiv of anhydrous diethyl ether to yield a bright yellow crystalline powder. The resulting powder was recrystallized by dissolving the yellow solid into EtOAc followed by the slow addition of diethyl ether until precipitation was observed, which resulted in a pale yellow crystalline powder. ^{1}H NMR (CD_3CN): 6.62 (t, 1H, $\underline{H}$-N(Et)$_3$), 3.18 (dq, 6H, H−N(-C$\underline{H_2}$-CH$_3$)$_3$), 1.5−3 (q, 8H, B−H Terminal), 1.28 (t, 9H, H−N(−CH$_2$−C$\underline{H_3}$)$_3$), 0.05 (q, 2H, B−H Terminal), −2.86 (broad, 1H, B−H Bridging), −3.76 (broad, 2H, B−H Bridging). ^{11}B NMR (CD_3CN): 6.2 (d), 2.0 (d), −5.6 (d), −35.9 (d) (neutral $B_{10}H_{14}$ and a small amount of [B_9H_{14}]$^-$ were observed in the ^{11}B NMR).

Characterization and Testing. *Spectroscopy.* All NMR spectra were recorded utilizing a Bruker Avance spectrometer, Bruker/Magnex UltraShield 500 MHz (Madison, WI), or a Bruker Spectrospin DRX 360 MHz Ultrashield spectrometer (Madison, WI). ^{1}H, ^{13}C, and ^{11}B NMR spectra were collected using DMSO-d_6 or CD_3CN as the lock solvents with TMS and $BF_3 \cdot Et_2O$ as the internal standards. All shifts are reported in δ (ppm) relative to the internal standards. Infrared (IR) spectra were collected using a Bruker AlphaFTIR (Madison, WI) by direct measurement via attenuated total reflectance of the neat samples (or ILs loaded with borane clusters) on a diamond crystal.

Differential Scanning Calorimetry. Solid and melting transitions were evaluated with a Mettler Toledo (Columbus, OH) DSC 1. The calorimeter was calibrated for temperature and cell constants using In, Zn, H_2O, and *n*-octane. Samples were weighed and sealed in aluminum pans (5−15 mg) and heated at a rate of 5 °C/min to 75 °C. Following the initial heating cycle, the samples were cooled to −50 °C via a recirculating chiller followed by a heating cycle to 75 °C at a rate of 5 °C/min. After each dynamic temperature ramp, a 15 min isotherm was employed to ensure equilibration of the temperature in the cell. The entire cycle was repeated three times, and the values for phase changes were analyzed. Each sample was referenced to an empty aluminum pan.

Hypergolic Ignition Tests. Liquid hypergol ignition tests were conducted as in ref 2 by the addition of a single drop (10 μL) of fuel (either neat IL or IL with added borane clusters) via Hamiltonian syringe to a vial containing 500 μL of 99.5% white fuming nitric acid (WFNA). In the case of the 1:10 sample of [B_9H_{14}]$^-$ in [MAT][DCA], the viscosity of the sample was so high that, instead, the sample of [MAT][DCA] was placed on a 10 cm watch glass and a single drop of WFNA was added to the watch glass.

In the hypergolic ignition tests of the solid borane clusters and the borane clusters dissolved in molecular solvents, 2−3 drops of WFNA was dropped on a 10 cm watch glass containing the solid borane clusters (~10 mg) or the borane clusters dissolved in molecular solvents (~10 mg/mL). A Redlake MotionPro Y4 (Tallahassee, FL) high speed CCD camera at 1000 frames/s was utilized to follow the ignition drop test in each case. The ignition delay was measured as the time in milliseconds for ignition to occur after the initial contact of fuel and oxidizer. Samples were replicated 3 times, the values for ignition delay were averaged, and the standard deviation was calculated. In the case of the 1:10 sample of [B_9H_{14}]$^-$ in [C_4mim][DCA], only a single run was conducted because the walls of the Hamiltonian syringe were inadvertently shattered while setting up the second run.

■ RESULTS AND DISCUSSION

Reactivity of $B_{10}H_{14}$ with Hypergolic ILs. Our investigations began with attempts to dissolve $B_{10}H_{14}$ in the known hypergolic ILs,[2] 1-butyl-3-methylimidazolium dicyanamide ([C_4mim][DCA]), 1-allyl-3-methylimidazolium dicyanamide ([Amim][DCA]), and 1-methyl-4-amino-1,2,4-triazolium dicyanamide ([MAT][DCA]). The ILs were synthesized through metathesis reactions between the respective halide precursors and silver dicyanamide in methanol,[2,7] and each IL was dried to <500 ppm H_2O. The ILs were added dropwise to a corresponding amount of solid $B_{10}H_{14}$ in a preweighed 2 dram vial followed by vortex mixing for 15 s to give 1:1000, 1:100, and 1:10 $B_{10}H_{14}$−IL molar compositions. Upon addition, a black precipitate and gaseous product were formed, and [C_4mim][DCA] and [Amim][DCA] turned bright orange, while [MAT][DCA] obtained a cloudy orange hue. In all three ILs, the more concentrated solutions had darker orange hues, higher viscosities, and larger amounts of gaseous product and black precipitate. Apart from the observation of the black precipitates, which were easily separated after sedimentation to the bottom of the vial, the orange solutions (Figure 2) did not show any signs of further degradation or precipitation on the time scale of publication (>12 months).

The black precipitates suggested an acid−base reaction between $B_{10}H_{14}$ and the [DCA]$^-$ anion, which would result in the *in situ* formation of a reduced borane species[19] and the protonation of [DCA]$^-$, which would lead to formation of

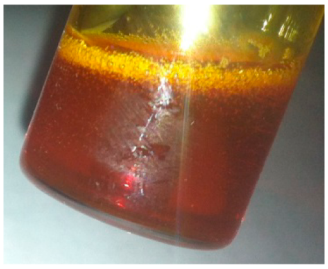


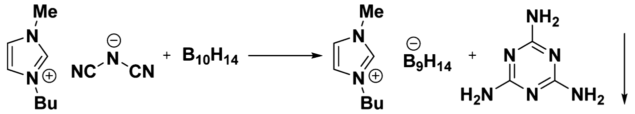
Figure 2. Stable orange solution formed when $B_{10}H_{14}$ was added to $[C_4mim][DCA]$ at a 1:100 ratio.

melamine.[20] In order to determine the structural identity of the borane cluster, infrared (IR) spectra of the IL solutions were compared to a solid sample of neat $B_{10}H_{14}$. A single, very weak B−H stretch was observed in each spectra at a lower wavenumber (2500−2520 cm^{-1}) relative to the several B−H stretches observed in neat $B_{10}H_{14}$ (2530−2600 cm^{-1}). A highly concentrated sample was then prepared by combining [MAT][DCA] with an equimolar portion of $B_{10}H_{14}$, which resulted in a dark orange gel after a large amount of bubbling and precipitation. The isolated gel yielded a single B−H stretch at 2488 cm^{-1} in the IR spectrum indicative of the generation of a more reduced[31] or negatively charged species (Figure S12, Supporting Information). Additionally, the stretches corresponding to the symmetric and asymmetric −CN stretches from the $[DCA]^-$ were shifted to a higher wavenumber, which indicated the generation of a more neutral species.

Each of the 1:100 loaded ILs were further characterized neat by ^{11}B, ^{1}H, and ^{13}C NMR spectroscopy using a sealed capillary tube of the sample surrounded by an external locking solvent ($CDCl_3$) and compared with each pure IL. ^{11}Boron NMR revealed three doublets at −8.4, −21.1, and −24.2 ppm, which were identified to be the $[B_9H_{14}]^-$ anion (Supporting Information, Figure S9) based on a spectral match to the peaks present in the known compound $K[B_9H_{14}]$.[24] No shifts were observed in any of the signals associated with the neat ILs in either the ^{1}H or ^{13}C NMR spectra upon the addition of $B_{10}H_{14}$. However, a new peak at 0.09 ppm in the ^{1}H NMR in all three solutions integrated to be approximately 14 hydrogen atoms at a concentration of 1:100, which corresponds to the presence of the $[B_9H_{14}]^-$ anion. Importantly, no differences in the borane cluster were observed based on which IL cation was studied, and key IR stretches, such as the shift in the B−H stretch to lower wavenumbers and the shift of the −CN stretches to higher wavenumbers, suggested that the reactivity was likely between $B_{10}H_{14}$ and the $[DCA]^-$ anion. Additionally, the $[B_{10}H_{13}]^-$ anion has also been previously reported to be susceptible to nucleophilic attack[32] and to form the $[B_9H_{14}]^-$ anion.[33] Taken together, these observations suggest the overall reaction shown in Scheme 1.

$[B_9H_{14}]^-$ in IL Solution. Hypergolic ignition tests (Table 1) for the nine $[B_9H_{14}]^-$ IL solutions were conducted utilizing a standard IL hypergolic drop test.[2] A single aliquot (10 μL) of fuel (IL) was added via Hamiltonian syringe to a vial containing 500 μL of 99.5% white fuming nitric acid (WFNA), and the resulting ignition was monitored with a Redlake MotionPro Y4 high speed camera at 1000 frames/s. Ignition delays (IDs) were measured as the time from when the oxidizer first came into contact with the fuel until ignition was observed. Due to the high viscosity of the most concentrated (1:10) [MAT][DCA] solution, testing of this system was conducted by placing ∼10−20 mg onto a 10 cm watch glass and directly dropping a 2−3 drop aliquot of WFNA onto the sample (Supporting Information, Figure S14). Flames with a light green hue, indicative of the oxidation of B−H bonds to boron oxide,[16] were observed upon ignition in all cases.

Scheme 1. Proposed Reaction Pathway for the *in Situ* Generation of $[B_9H_{14}]^-$



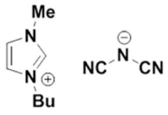
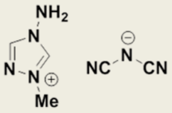
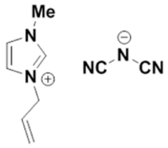
While the viscosity of these IL solutions was not directly measured due to previous reports of shock sensitivity of similar compounds,[16] the viscosity of the ILs dramatically increased visually upon the addition of $[B_9H_{14}]^-$. Thus, the slightly longer IDs observed in the 1:1000 samples might be expected due to mixing effects;[10] however, at the 1:100 loadings the IDs were shortened 15−20% despite the even higher viscosities. At the 1:10 loadings of $[C_4mim][DCA]$ and [Amim][DCA], even greater reductions (89−90%) in the ignition delay were observed with respect to the neat ILs. The viscosity was high enough to limit the ability to use a syringe to conduct the IL drop test for the 1:10 loadings of [MAT][DCA], but the mixture still led to a reduction of the ignition delay by 72% compared with the neat IL (Figure S13−S21, Supporting Information).

Synthesis of Borane Salts. To understand the composition, mechanism of formation, and reactivity of the reduced borane species, we prepared salts containing $[B_{10}H_{13}]^-$ and $[B_9H_{14}]^-$ anions. Our initial strategy was to maximize the oxidation potential of $B_{10}H_{14}$ by abstracting a single proton in a direct acid−base reaction with either a soft nitrogen base or a hard oxygen-containing base (Scheme 2a). Triethylammonium ($[H{-}N_{222}]^+$) and tetraethylammonium ($[N_{2222}]^+$) were selected based on previous reports utilizing these cations to isolate borane anions from $B_{10}H_{14}$.[20,21]

First, a solution of $B_{10}H_{14}$ in diethyl ether was added dropwise to a stirred solution of triethylamine in an equimolar ratio, whereupon a pale yellow powder precipitated. The precipitate was recrystallized by dissolution in EtOAc followed by the slow addition of diethyl ether, which resulted in pale yellow crystalline needles. ^{1}H and ^{11}B NMR of the isolated needles dissolved in CD_3CN confirmed formation of $[H{-}N_{222}][B_{10}H_{13}]$ (^{1}H, N−H triplet 6.7 ppm; ^{11}B, four unique doublets 7.2, 2.8, −4.8, −14.8 ppm; 2:1:5:2 matching previous ^{11}B results for this anion;[34,35] Supporting Information). The ^{11}B NMR also suggested the presence of small amounts of $B_{10}H_{14}$ and $[B_9H_{14}]^-$, which could not be removed by further purification.

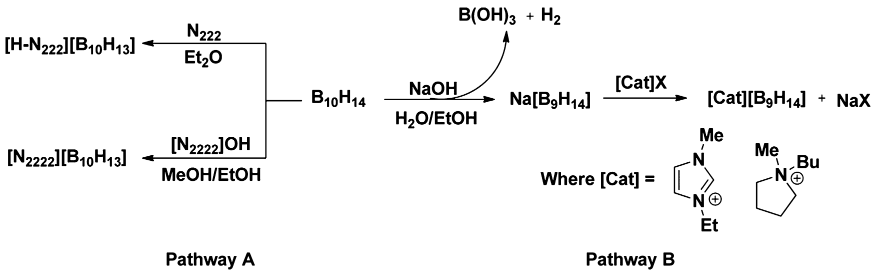
In a second reaction, an aprotic salt was prepared by reaction of $[N_{2222}]OH$ in methanol with $B_{10}H_{14}$ dissolved in absolute ethanol. Upon the dropwise addition of the $B_{10}H_{14}$ solution, a light yellow crystalline solid immediately precipitated. After recrystallization of the solid through the slow addition of diethyl ether to a dissolved sample in EtOAc, a yellow powder, composed of very small needles, was isolated. ^{11}B NMR of the isolated salt dissolved in CD_3CN displayed four unique doublets at 6.2, 2.0, −5.6, and −15.9 ppm (2:1:5:2 intensity) confirming formation of $[N_{2222}][B_{10}H_{13}]$ (See Supporting Information). Again, small amounts of $B_{10}H_{14}$ and $[B_9H_{14}]^-$

Table 1. Ignition Delays Observed for Three Hypergolic ILs and their $[B_9H_{14}]^-$ Solutions

Ionic Liquid	Neat	1:1000	1:100	1:10
		Molar ratio of $[B_9H_{14}]^-$-IL		
		Ignition delay (ms)		
 $[C_4mim][DCA]$	48(4)	58(3)	42(2)	5[a]
 [MAT][DCA]	39(2)	53(6)	31(1)	11(4)[b]
 [Amim][DCA]	35(5)	33(4)	30(6)	4(1)

[a] Only one ignition delay obtained as a result of high viscosity. [b] The drop test was performed in a watch glass instead of a vial as a result of high viscosity. Values in parentheses denote the standard deviation of three averaged tests.

Scheme 2. Synthesis of Hypergolic Borane Salts



were identified in the ^{11}B NMR spectrum but could not be removed by further purification.

To prepare $[B_9H_{14}]^-$ salts with organic cations that are typically paired with hypergolic ILs,[2,7] a sodium salt was first made by adding a solution of $B_{10}H_{14}$ in anhydrous ethanol dropwise to a stirred, equimolar solution of NaOH[33] in aqueous ethanol (Scheme 2b). Upon addition, the solution turned a bright yellow indicative of the formation of $Na[B_{10}H_{13}]$, but after stirring for 12 h, the solution became clear. Solutions of 1-ethyl-3-methylimdazolium chloride ($[C_2mim]Cl$) or *N*-butyl-*N*-methylpyrrolidinium chloride ($[Pyrr_{14}]Cl$) in ethanol were then added dropwise yielding immediate light yellow precipitates. Each water insoluble powder was collected by vacuum filtration. ^1H and ^{11}B NMR on solutions of the isolated powders in CD_3CN confirmed them to be $[C_2mim][B_9H_{14}]$ and $[Pyrr_{14}][B_9H_{14}]$. Three doublets observed at 8.7, −21.0, and −24.2 ppm ($[C_2mim][B_9H_{14}]$) and 8.9, −21.3, and −24.6 ppm ($[Pyrr_{14}][B_9H_{14}]$) in the ^{11}B NMR matched previous experimental[24] and theoretical[36] literature values (see Supporting Information) for the $[B_9H_{14}]^-$ anion.

In the ^1H NMR spectra of $[C_2mim][B_9H_{14}]$ and $[Pyrr_{14}][B_9H_{14}]$, a broad peak at −1.50 ppm was observed that corresponded to five hydrogen atoms, which are rapidly exchanging in solution. These five fluxional hydrogen atoms correspond to the hydrogen atoms along the open face of the borane cluster whose exact orientation and location in the solid state are still in debate today.[24,25,36] The remaining nine terminal B−H hydrogen atoms along the base of the borane "bowl" were observed between 2.5 and 0.5 ppm as overlapping 1:1:1:1 quartets based on the isotopic abundance and nuclear spin of ^{11}B.

Reactivity of Borane Salts. All four of the new salts, $[H\text{−}N_{222}][B_{10}H_{13}]$, $[N_{2222}][B_{10}H_{13}]$, $[C_2mim][B_9H_{14}]$, and $[Pyrr_{14}][B_9H_{14}]$, were tested for hypergolic reactivity with a variety of oxidizers. In each case, a small portion (∼10−20 mg)

Table 2. Reactivity with WFNA and Solubility in Molecular Solvents

compound	THF	EtOAc	MeOH	EtOH
$B_{10}H_{14}$	soluble, not hypergolic	soluble, not hypergolic	N/A	N/A
$[H-N_{222}][B_{10}H_{13}]$	soluble, hypergolic	soluble, hypergolic	soluble, not hypergolic	soluble, not hypergolic
$[N_{2222}][B_{10}H_{13}]$	soluble, hypergolic	soluble, hypergolic	soluble, not hypergolic	soluble, not hypergolic
$[C_2mim][B_9H_{14}]$	soluble, hypergolic	soluble, hypergolic	not soluble	not soluble
$[Pyrr_{14}][B_9H_{14}]$	soluble, hypergolic	soluble, hypergolic	not soluble	not soluble

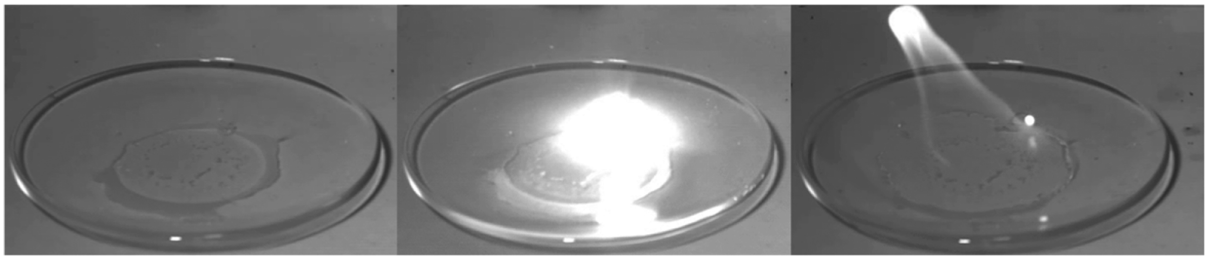


Figure 3. $[H-N_{222}][B_{10}H_{13}]$ as a trigger additive induces hypergolicity in solutions of EtOAc: (left) 0 ms, initial contact with oxidizer; (center) 2 ms, hypergolic ignition; (right) dilute green flame visible.

of the solid salt was placed on a 10 cm watch glass. An aliquot (2−3 drops) of each oxidizer (WFNA, inhibited red fuming nitric acid (IRFNA); 70% nitric acid (NA)) was dropped directly onto the samples, and the resulting ignition was monitored. Upon contact with the oxidizers, all four salts exhibited essentially instantaneous ignition (ID < 3 ms) with a green flame. The small impurities present in $[H-N_{222}][B_{10}H_{13}]$ and $[N_{2222}][B_{10}H_{13}]$ did not seem to result in decreased reactivity, suggesting that extensive purification may not be required. Other more dilute oxidizers such as 1 M nitric acid, 30% H_2O_2, and 50% H_2O_2, were tried but did not result in ignition, perhaps due in part to the low water solubility of the borane salts.

Given the rather dramatic reduction in ID of hypergolic ILs when $[B_9H_{14}]^-$ was formed *in situ* simply by adding $B_{10}H_{14}$, the four borane salts prepared here were tested to determine whether they could *induce* hypergolicity in nonhypergolic molecular solvents. Small portions (~10−20 mg) of each salt and of $B_{10}H_{14}$ were placed on a 10 cm watch glass and dissolved in approximately 10 mL of molecular solvents that could serve as potential fuels. The solvents screened were chosen based on known energetic properties and potential for reactivity with the anion. Chlorinated solvents were avoided due to the potential hazard of generation of shock sensitive primary explosives[16] and low combustibility due to high chlorine contents. DMSO and acetonitrile were also not utilized due to known reactivity with neutral $B_{10}H_{14}$ and similar anions.[37] Water, diethyl ether, and hydrocarbon based nonpolar solvents did not dissolve any of the four isolated salts. Polar protic solvents (e.g., MeOH and EtOH) were able to dissolve $[H-N_{222}][B_{10}H_{13}]$ and $[N_{2222}][B_{10}H_{13}]$ but neither of the $[B_9H_{14}]^-$ salts. Only polar aprotic solvents (e.g., THF and EtOAc) dissolved all four borane salts, which led to a total of 14 testable fuel−borane solutions (Table 2).

Several drops of oxidizer (WFNA, IR, and NA) were dropped directly onto each of the six prepared solutions on the watch glasses, and the resulting ignition was monitored with the high speed camera as previously discussed. Neutral $B_{10}H_{14}$ was not hypergolic either as a neat solid or in THF or EtOAc. Similarly, none of the salts were hypergolic when dissolved in the protic polar solvents. However, freshly prepared solutions of $[H-N_{222}][B_{10}H_{13}]$, $[N_{2222}][B_{10}H_{13}]$, $[C_2mim][B_9H_{14}]$, and $[Pyrr_{14}][B_9H_{14}]$ in THF or EtOAc were all hypergolic with WFNA, igniting instantaneously on contact. For example, $[H-N_{222}][B_{10}H_{13}]$ in EtOAc ignited instantaneously (Figure 3 and Table S2, Supporting Information) and burned for several hundred milliseconds until all of the solvent was consumed. Lower concentrations of nitric acid (e.g., IFNA, NA) did not result in hypergolic ignition.

Interestingly, even though the $[B_9H_{14}]^-$ or $[B_{10}H_{13}]^-$ salts prepared were insoluble in water, the presence of water did not prevent ignition. Floating any of the four salts on water followed by addition of the oxidizer (WFNA) resulted in ignition. This might allow some design flexibility if these salts were used in current propellant formulations, such as RP-1.[38]

■ CONCLUSIONS

The results provided here demonstrate that dissolution of *nido*-decaborane, $B_{10}H_{14}$, in ionic liquids containing the dicyanamide anion leads to *in situ* generation of a nonaborane cluster anion, $[B_9H_{14}]^-$, through a direct acid−base reaction. Additionally, borane cluster anions, $[B_{10}H_{13}]^-$ and $[B_9H_{14}]^-$, either generated *in situ* from $B_{10}H_{14}$ or synthesized as pure salts, can form stable solutions in ILs and polar molecular solvents leading to enhanced ignition in known hypergols, such as dicyanamide ionic liquids, or induced hypergolicity in certain nonhypergolic polar aprotic molecular solvents. This new class of hypergolic trigger additives, on the order of angstroms rather than nanometers, can easily be customized for specific requirements of solubility, reactivity, and physical properties by the choice of cation. This could provide control over the energetic content of virtually any fuel.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional characterization and hypergolic data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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