Hydrogen Storage Engineering CENTER OF EXCELLENCE

uOttawa

# Fluid Phase $H_2$ Storage Material Development

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2013 Annual Merit Review, May 15th

Los Alamos National Laboratory

LA-UR-13-22354

**Project ID # ST040**

This presentation does not contain any proprietary or confidential information

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Los Alamos Materials

# Overview

## Timeline

- Project Start Date: Oct 1st 2010
- Project End Date: 2014
- Percent Complete: 73%

## Barriers

- Barriers Addressed
  - A. Weight/Volume
  - C. Efficiency
  - D. Durability/Operability
  - E. Discharging Rates

## Budget

- Total project funding
  - DOE share: $ 225k
- Funding received in FY12: $ 330k
- Funding for FY13: $ 225k

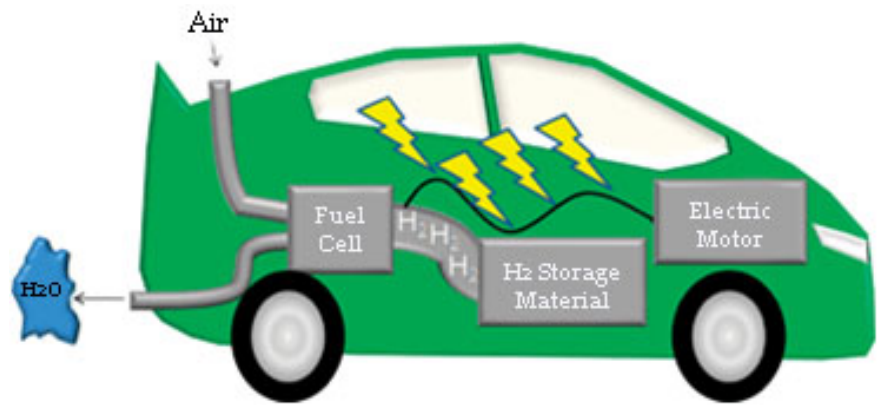
## Partners

- LANL (lead)
- University of Ottawa

## Relevance

Materials with good $H_2$ storage capacity and efficient regeneration are required for transportation, stationary, and portable power applications.

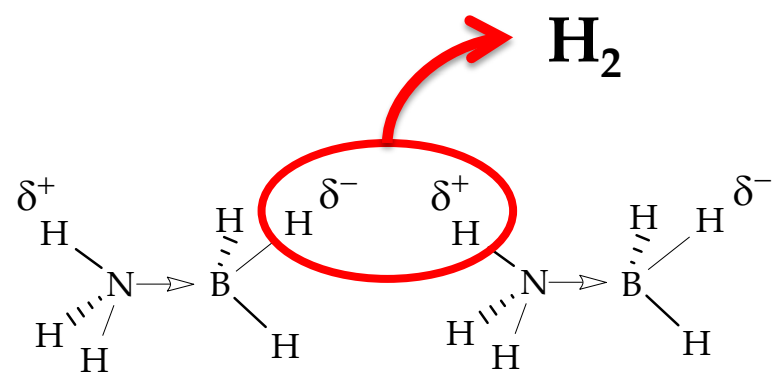
2017 system target = 5.5 wt. %; ultimate 7.5 wt. %




## Objectives

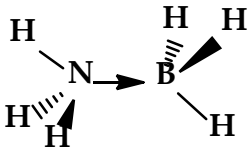
Develop liquid ammonia-borane (~15 wt. % usable $H_2$)/ionic mixtures that have sufficient $H_2$ capacity, release kinetics, stability, and fluid phase properties upon $H_2$ release.

Integrate design specifications from Hydrogen Storage Engineering Center of Excellence (HSECoE) and ensure compatibility with system designs.




Ammonia Borane

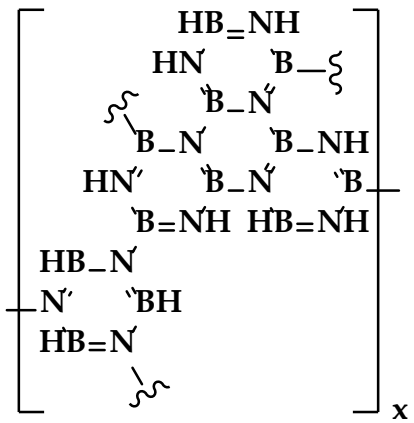
# AB/IL: Good Capacity, Kinetics



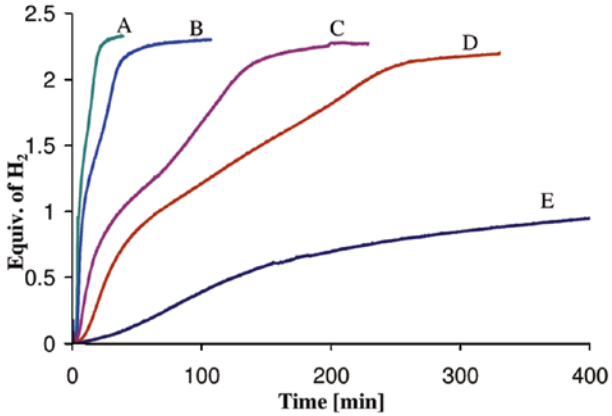
Colorless solid
@ RT

60-120 C

BmimCl
(m.p. 70 C)



7-11 wt. % $H_2$




A - 110 C
B - 105 C
C - 95 C
D - 85 C
E - 75 C

Larry Sneddon, UPENN

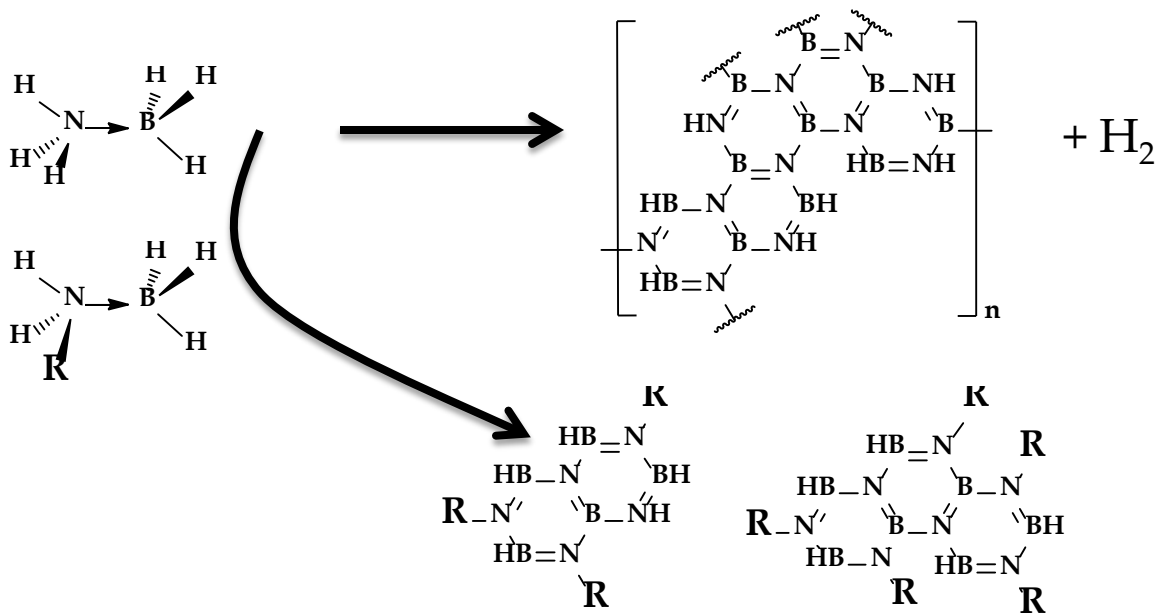
# *Approach*

Technical Limitation: Ammonia borane mixtures can form insoluble products after extensive $H_2$ release

**Our Method**: Use additives which react with ammonia borane, yielding smaller molecular weight products that are less prone to precipitation. By adjusting the functionality of the additive, we can control solubility of the products in various media

**2013 Goals**:

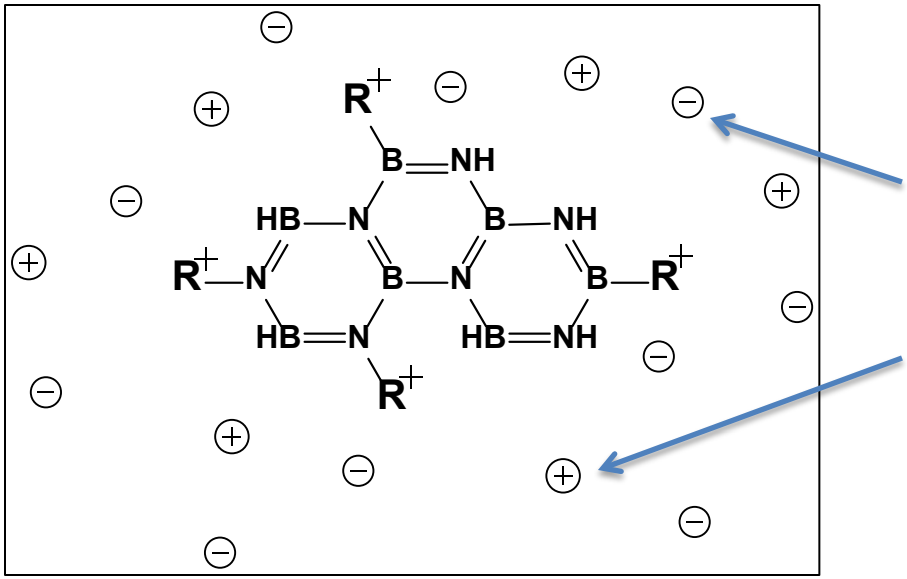
1) Design and synthesize amine-boranes tethered to ionic liquids
2) Characterize neutral functionalized amine-boranes and AB blends




**Two different classes of additives will be used to address phase change**

# *Approach – Ionic Additives*

Advantage: excellent solubility in ionic liquids; less impurities




Ionic liquid represented by positive, negative symbols

Disadvantage: unknown compounds, must be synthesized

**Ionic additives give better solubility in ionic liquids**

# *Approach – Neutral Additives*

Advantage: easy to synthesize; liquid products; good $H_2$ capacity

AB/hexylAB

$$\xrightarrow[\text{6 wt. \% } H_2]{140°C}$$

Copolymer product (@ 20°C)

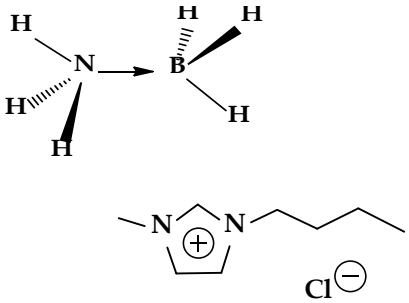
Disadvantage: may generate volatile intermediates

**Neutral Additives Yield Promising Results in FY12**

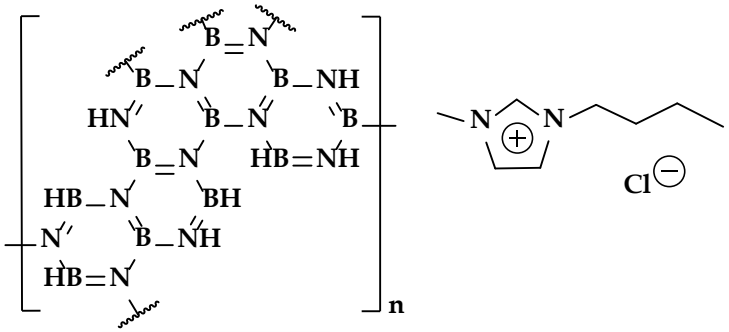
# Ionic Additive Development

# *Approach*

## Initial Sneddon Mixture:

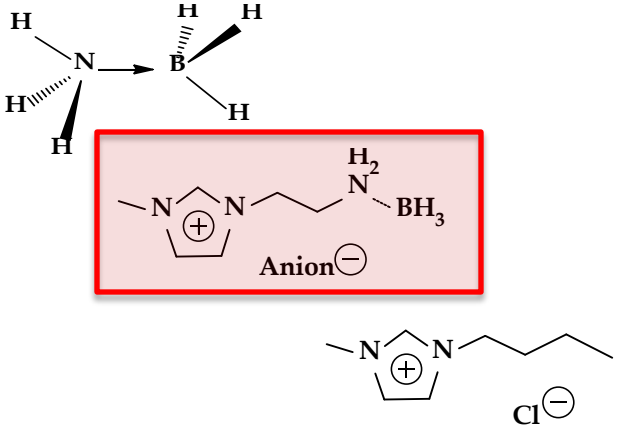


## Final Sneddon Products:

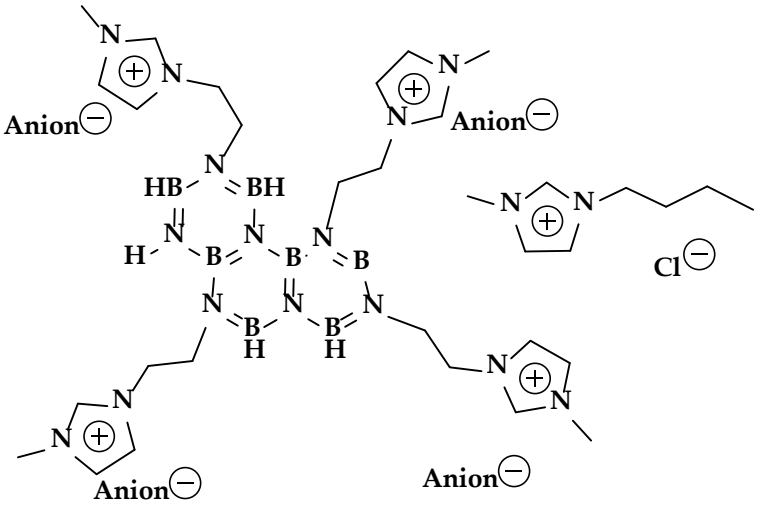


**Insoluble**

## Proposed Target:



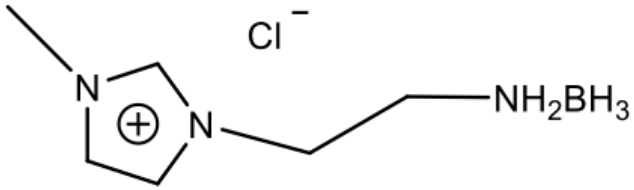
## Proposed Products:



# Attempted three independent syntheses

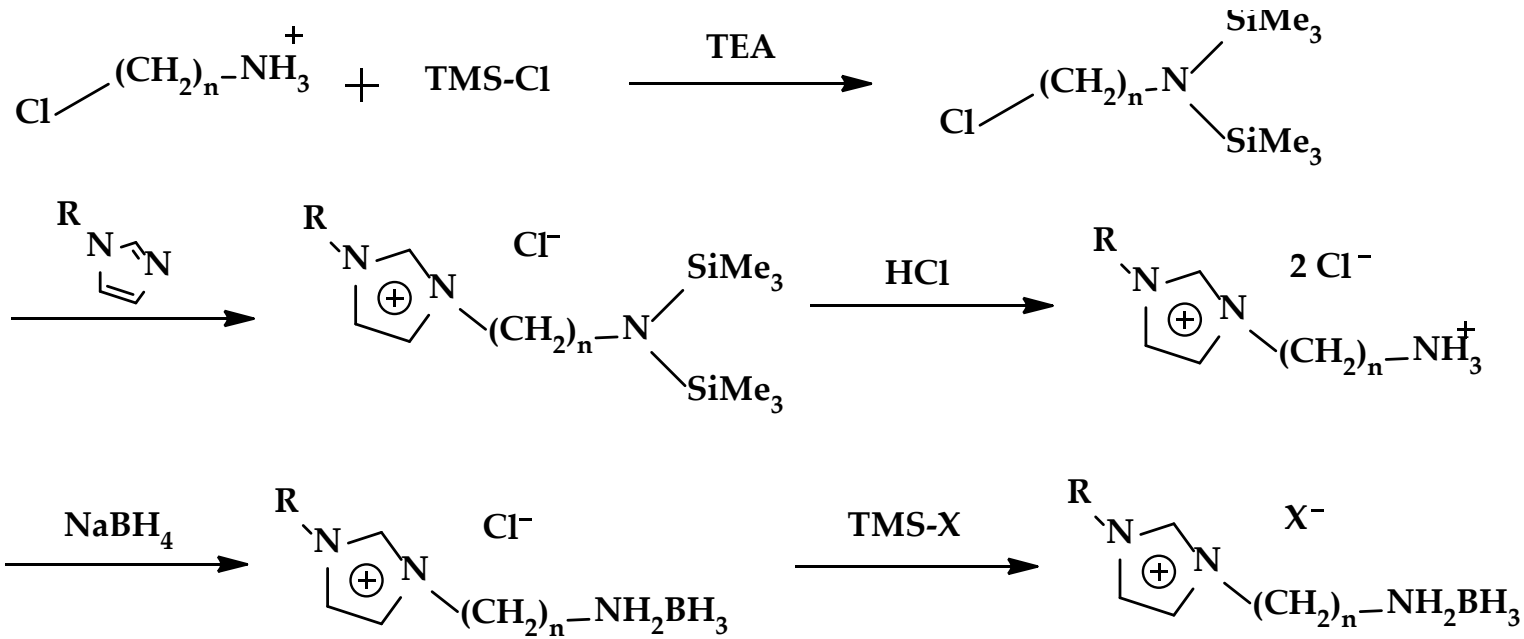
Gabriel Synthesis

Silyl Protecting Groups



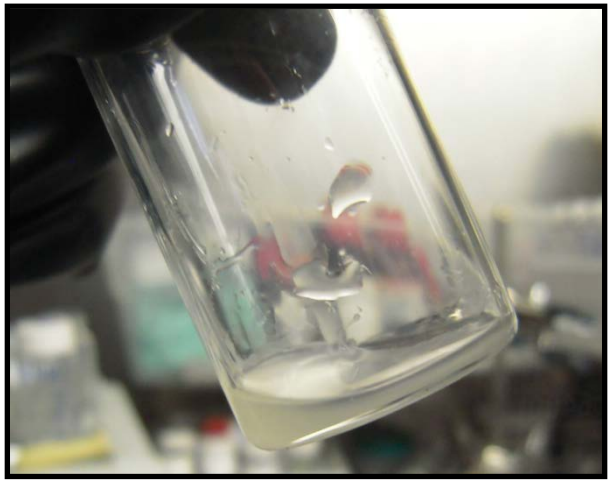

Nitrile Precursors

# Successful Synthesis of Amine-Borane tethered to an Ionic Liquid

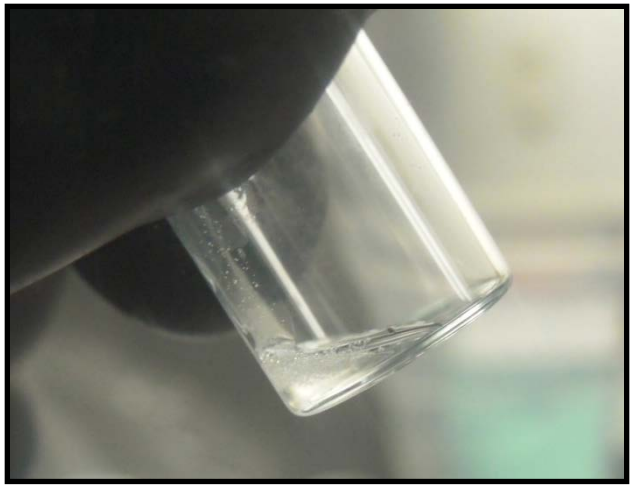



US Nonprovisional Application (#13850959)

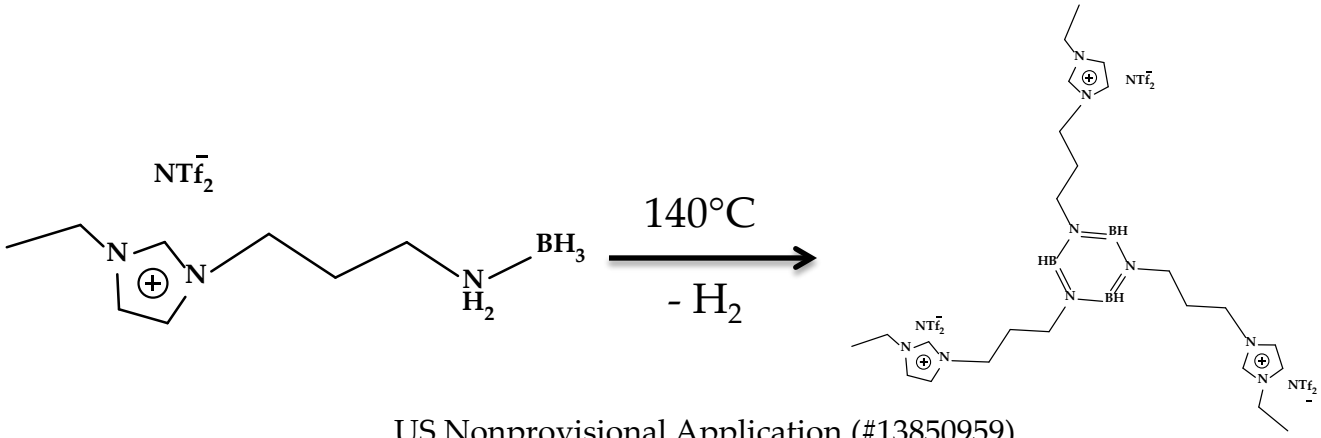
# Tethered Ionic liquid/Amineboranes Remain Liquid!



$H_2$ Charged State (@ 20°C)

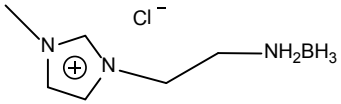
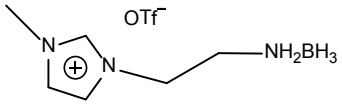
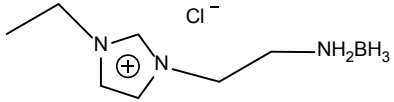
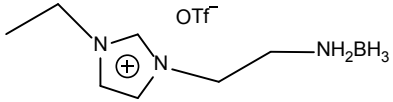
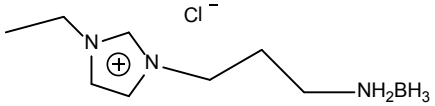
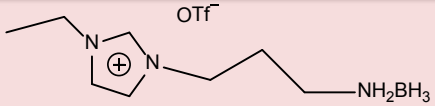
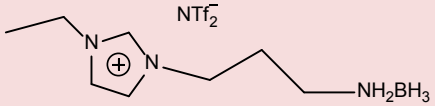


$H_2$ Released State (@ 20°C)



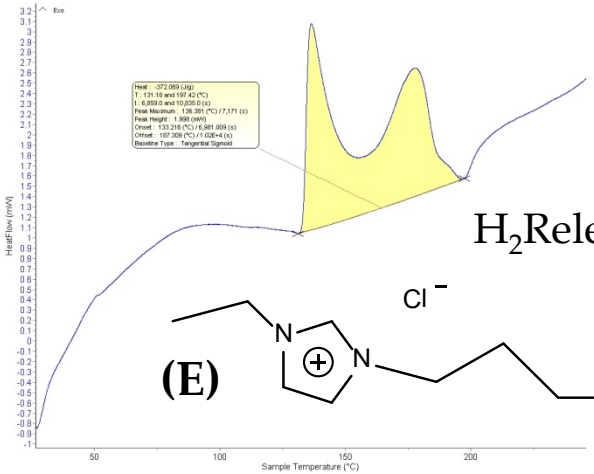

US Nonprovisional Application (#13850959)

# First Round of Derivatives

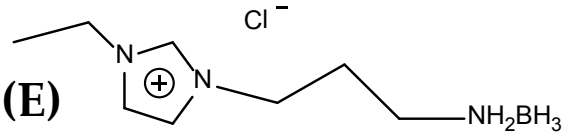
| Additive | Identifier | Initial State(20°C) | Spent State (20°C) | Wt. % $H_2$ |
|---|---|---|---|---|
|  | **A** | Solid | Solid | 2.5 |
|  | **B** | Solid | Solid | 1.5 |
|  | **C** | Solid | Solid | 2.3 |
|  | **D** | Oily Wax | Solid | 1.4 |
|  | **E** | Solid | Solid | 2.1 |
|  | **F** | Liquid | Viscous liquid | 1.4 |
|  | **G** | Liquid | Liquid | 1.0 |

US Nonprovisional Application (#13850959)

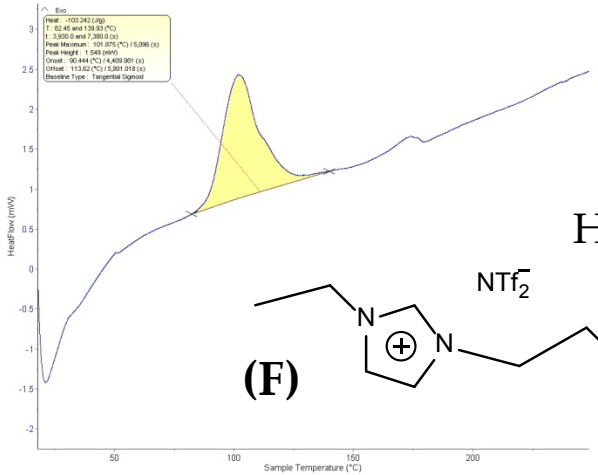
# Anion Choice Has Pronounced Effect on Properties



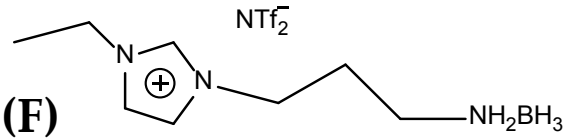

$H_2$Release: 133°C



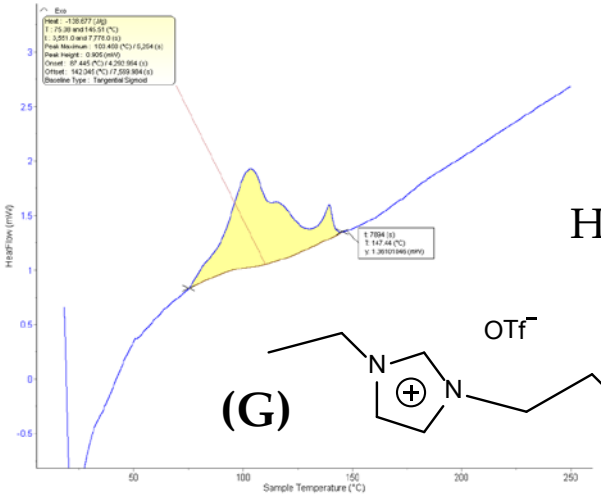

**(E)**



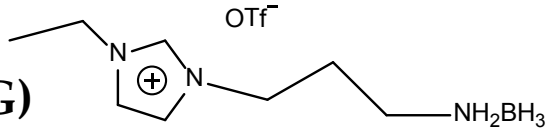

$H_2$ Release: 82°C




**(F)**




$H_2$ Release: 75°C

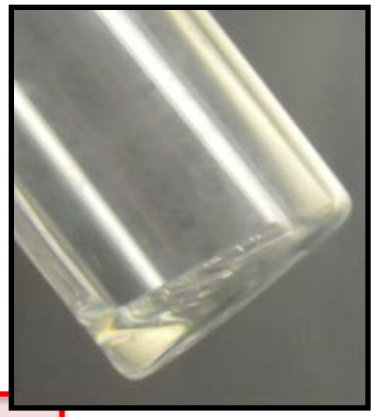



**(G)**

**Control $H_2$ release with anion choice; better match with AB = less impurities**

# Amineborane-IL/AB mixtures

| Material | AB/Additive | Initial State (20°C) | Spent State (20°C) | Wt. % $H_2$ |
|---|---|---|---|---|
| **B** | 0.5 | Solid | Solid | 2.0 |
| **F** | 0.5 | Milky Suspension | Solid | 1.8 |
| **F** | 1 | Milky Suspension | Flaky Solid | 2.3 |
| **G** | 0.5 | Milky Suspension | Viscous Liquid | 1.3 |



**Ionic Additives blended with AB yields fluid phase products**

US Nonprovisional Application (#13850959)

# Neutral Additive Development

# Surveyed Alternative AmineBoranes

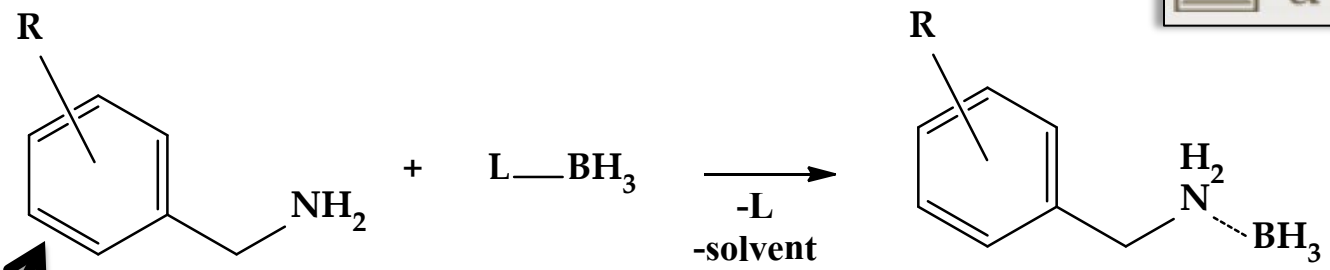
| | n-C4 | iso-C4 | sec-C4 | tert-C4 | n-C5 | iso-C5 | sec-C5 | 1,2-DMP | neo-C5 | n-C6 |
|---|---|---|---|---|---|---|---|---|---|---|
| $NRH_2$ b.p. ( C) | 78 | 68 | 63 | 45 | 104 | 95 | 93 | 85 | 83 | 130 |
| $RH_2N \bullet BH_3$ m.p. | 10 | 65 | 0 | 96 | 5 | 85 | -5 | - | - | ~-20 |

Synthesized by Ottawa

| Amine | n-C5 | iso-C5 | sec-C5 | 1,2-DMP | neo-C5 | n-C6 |
|---|---|---|---|---|---|---|
| 50g ($) | 97 | 70 | 1390 | 128 | 264 | 17 |

**Initial survey of related substituents did not reveal obvious solutions**

# Benzylamine-borane Pursued

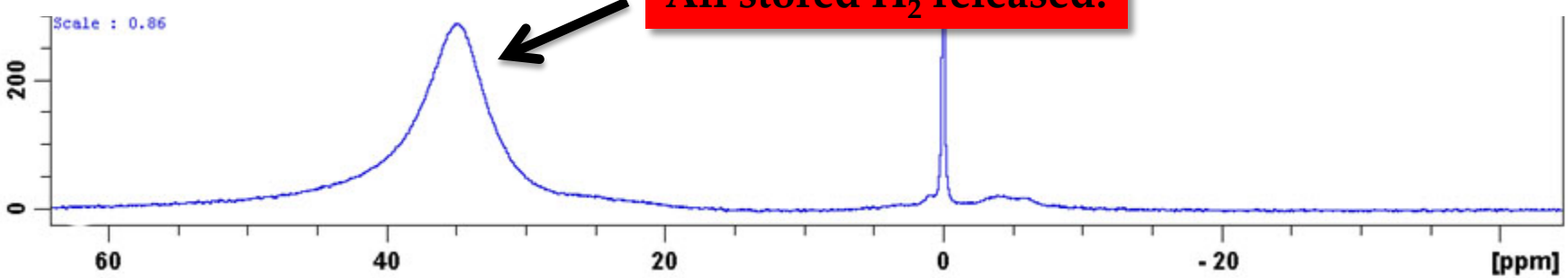



R = H, m.p. 10$ "
R = o-CH3, m.p. = < 20°C
b.p. ~200°C

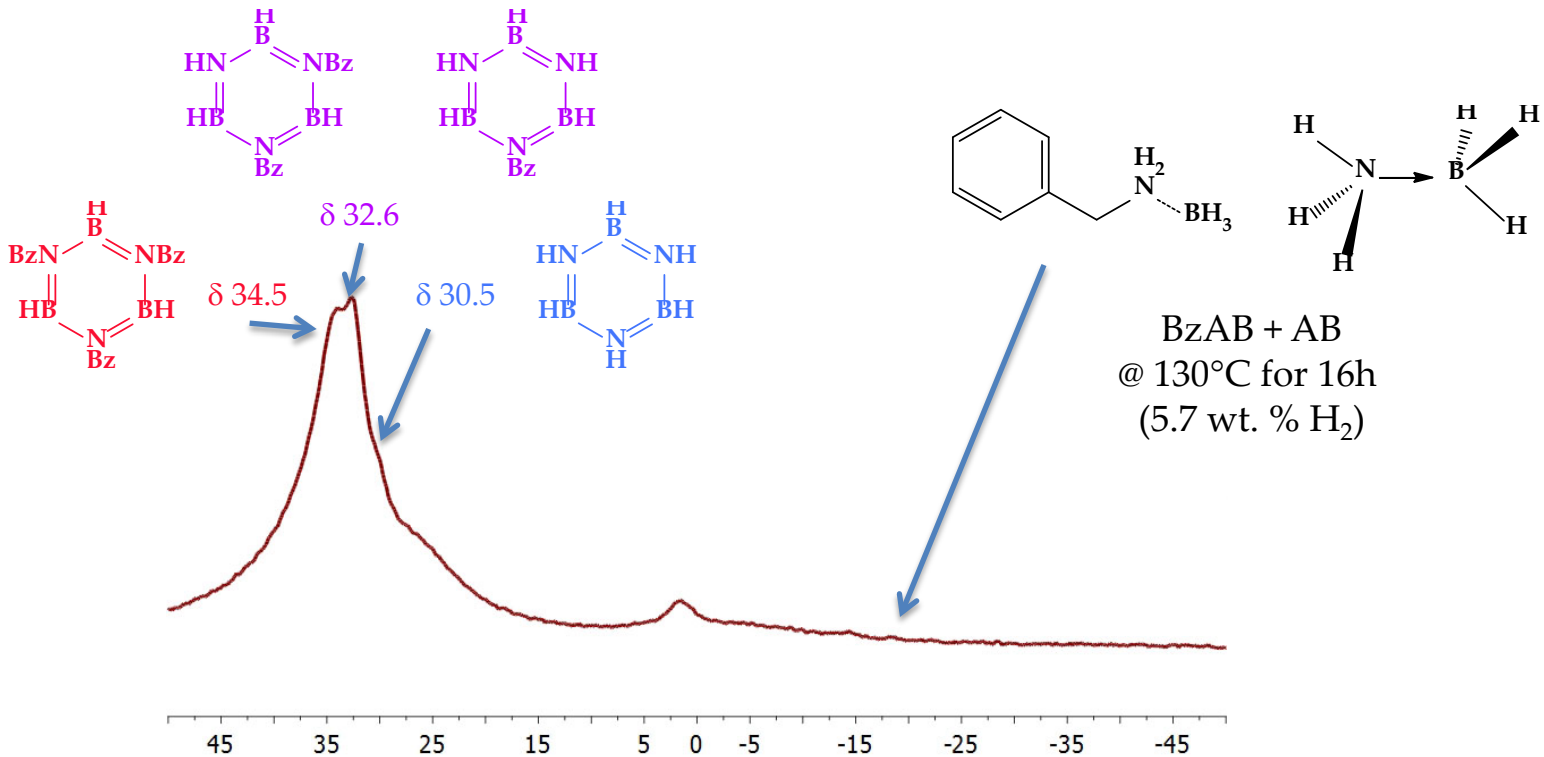
R = H, m.p. 57°C
R = o-CH3, m.p. = 110°C

**Interact with ionic liquids = greater solubility**

**All stored $H_2$ released!**



# Benzylamine-borane/AB Mixtures




Spent fuel of BzAB + AB in [EMIm]$EtSO_4$ (1.8 wt. % $H_2$) still flows while above 100°C!

**Evidence of copolymerization; 2 wt. % IL mixture flows above 100°C**

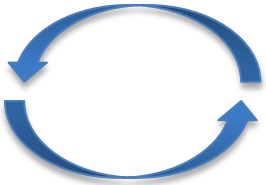
# Benzylamine-Boranes Outselected

| Fuel Blend | time (h) | temp ( C) | solvent | Spent Phase? | Wt. % $H_2$ |
|---|---|---|---|---|---|
| BzAB/AB | 24 | 80 | neat | RT: solid<br>80 C: liquid | 5.7 |
| BzAB/AB | 18 | 130 | neat | RT: solid<br>130 C: solid | 5.7 |
| BzAB/AB | 22 | 130 | [EMIm]EtSO$_4$ | RT: liquid<br>130 C: liquid | 0.5 |
| BzAB/AB | 18 | 130 | [EMIm]EtSO$_4$ | RT: solid<br>130 C: liquid | 1.8 |
| 2-MeBzAB/AB | 7 | 130 | neat | RT: liquid<br>130 C: liquid | 0.5 |
| 2-MeBzAB/AB | 18 | 130 | [EMIm]EtSO$_4$ | RT: solid<br>130 C: liquid | 1.7 |

**Benzylamineboranes outselected for future work**

# Volatility Limits Conversion

Materials Development



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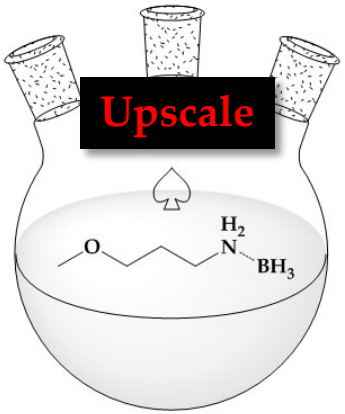
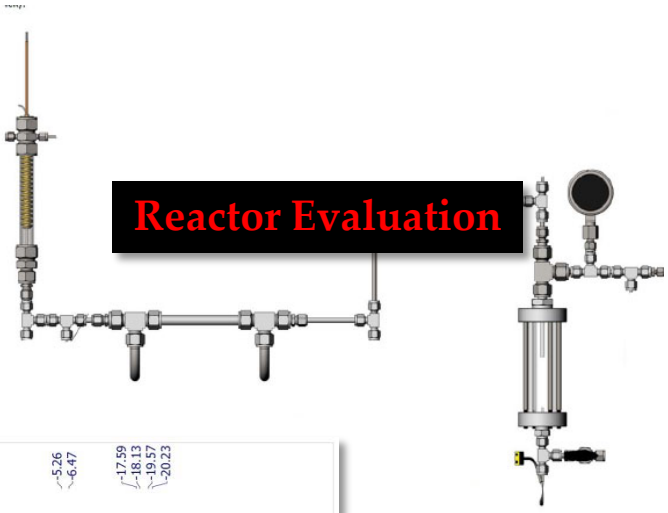
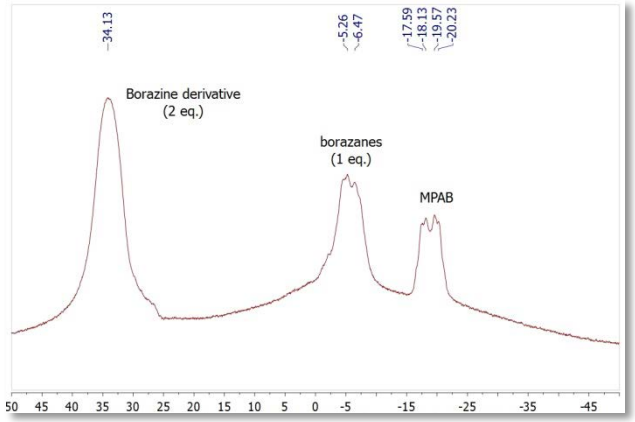
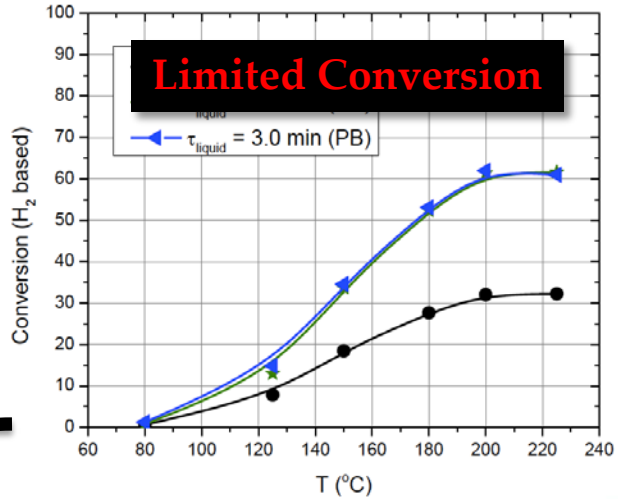


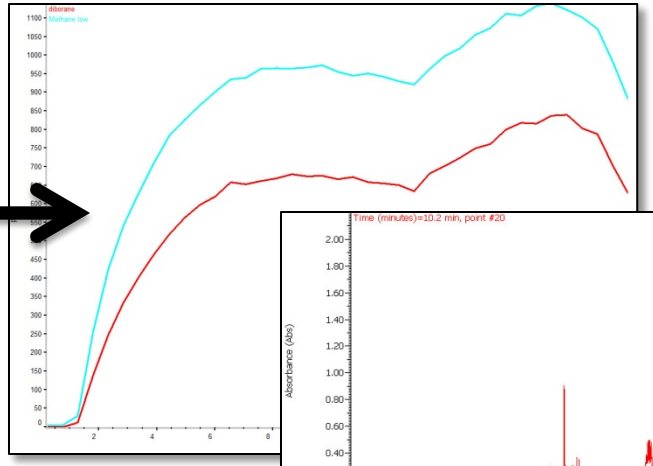



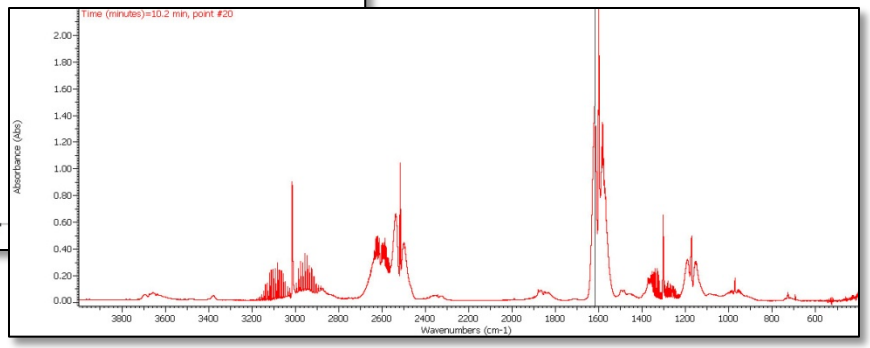



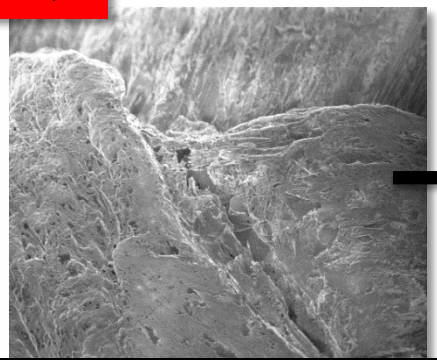

**Non-volatile additives may facilitate greater conversion and prevent phase change**

# Neutral AmineBorane/AB Blends: Batch Evaluation

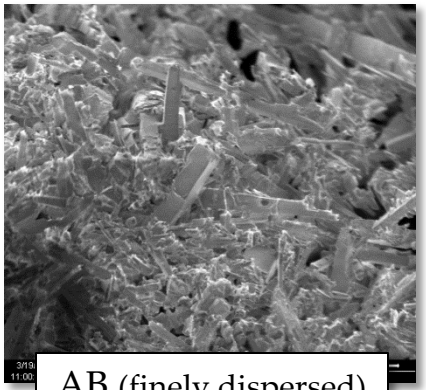



**Heating to 130°C releases 98% of stored $H_2$ (assume 2.5 eq. for AB)**



AB (JSC Aviobor, as received)

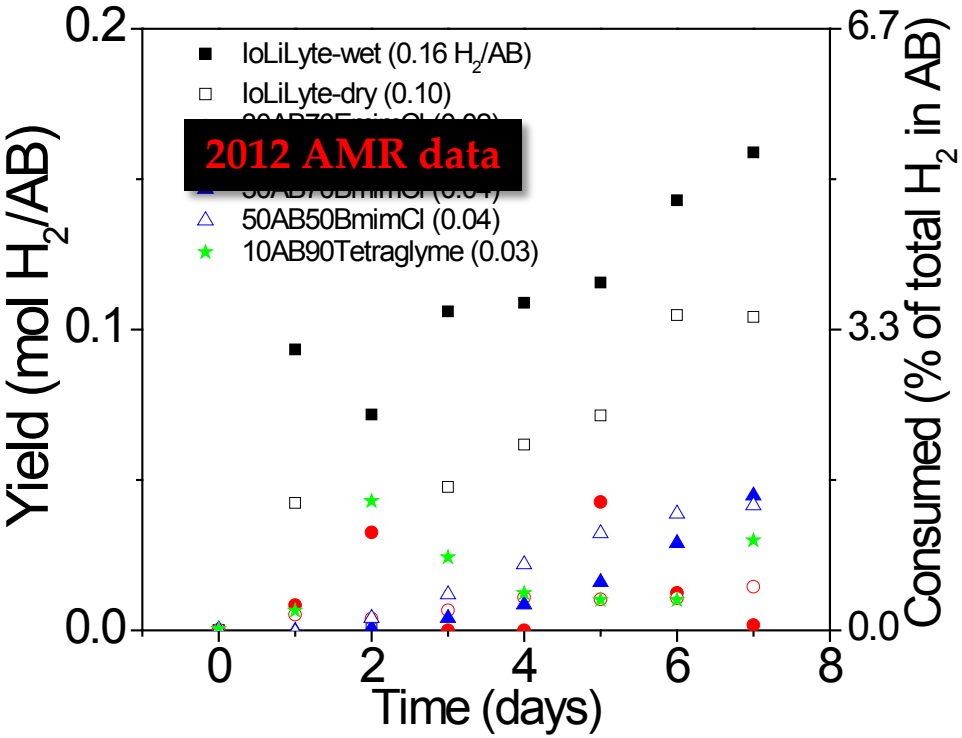


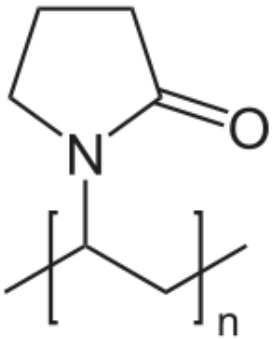
AB (finely dispersed)

**Excellent $H_2$ release; Some impurities detected; Better AB mixing for future runs**

# Stability Additive Development

# Stability Additives




PVP – inert, nonvolatile

↓

prevents isomerization and resulting $H_2$ release from glyme solutions at room temperature

**PVP improves AB stability; related additives may work in ionic liquids**

# *Collaborations*

| External Collaborators | Effort | Contact |
|---|---|---|
| $H_2$ Codes and Standards | General Guidance | C. Padro (LANL) |
| Centre for Catalysis Research and Innovation | Neutral Additive Design, Characterization | T. Baker (Ottawa) |
| Chemical Hydrogen System Architect (HSECoE) | System Designs | Troy Semelsberger (LANL) |
| Los Alamos Applied Energy Office | Fuel Cell Expertise, General Guidance | Rod Borup (LANL) |

# *Proposed Future Work*

Continue amine-borane/ionic liquid additive development

**FY13 Upscale synthesis; determine maximum AB loading**
**FY13-FY14 Assess $H_2$ release, phase of AB blends**
**FY13-FY14 Incorporate ECoE feedback for better additive design**

Assess efficacy of diaminoborane additives

**FY13 Synthesize known materials**
**FY13 Evaluate product phase with borazine, polyborazylene**
**FY14 Generate AB blends and perform batch experiments**

Interface with HSECoE

**FY13-FY14 Upscale candidate materials for HSECoE reactor/component testing**

# *Project Summary*

**Relevance**: Developing materials that store $H_2$, supporting the HSECoE effort to meet the 2017 system target of 5.5 wt. %; 7.5 wt. % ultimate

**Approach**: Create amineborane additives which, when blended with ammonia borane, yield a good storage capacity material that remains fluid after $H_2$ release. Ionic and neutral additives were targeted.

**Accomplishments and Progress**: synthesized first amineborane/ionic liquid additive; demonstrated blends with AB remain liquid post $H_2$ release; searched for new neutral additives; evaluation of neutral additives in HSECoE reactor suggests volatility may limit conversion

**Collaborations**: Hydrogen Storage Engineering Center of Excellence

**Proposed Future Research**: Continue amineborane/ionic liquid additive development; investigate diaminoborane additives

**Benjamin Davis**
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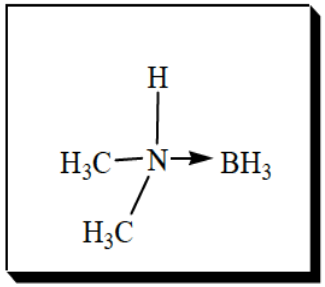
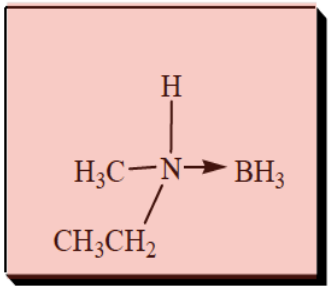
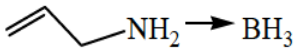
# Technical Back Up Slides

# Previous Additive Development

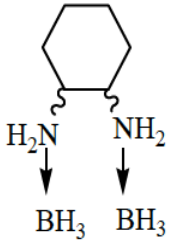
- Explored alkylamine boranes to solubilize AB

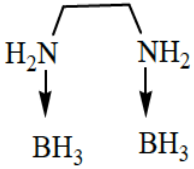



liquid at RT




solid at RT

- UPENN evaluated amine additives and substituted borazines to maintain fluid phase (2011)

AB/IL + 5% dipentylamine $\xrightarrow{85\ C}$ solid (2.2 eq. $H_2$ released)

AB/IL + 5% trimethylborazine $\xrightarrow{85\ C}$ solid (2.3 eq. $H_2$ released)