



# Amineborane-Based Chemical Hydrogen Storage

Department of Chemistry  
University of Pennsylvania

DOE Chemical Hydrogen  
Storage Center of Excellence

2008 DOE Hydrogen Program Review

June 10, 2008

Project ID: **ST7**

This presentation does not contain any proprietary or confidential information

# Project Overview

## Timeline

Project Start: FY 2005  
Project End: FY 2009  
Percent complete: 70%

## Budget

Total Project Funding: \$1,783,787  
DOE: \$1,417,353  
Penn: \$366,434

DOE Funding in 07: \$275,000  
DOE Funding in 08: \$300,000

## Barriers Addressed

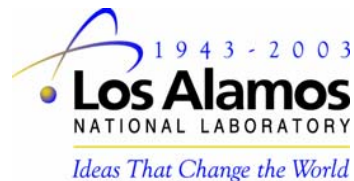
### Barriers

- A. System Weight and Volume
- B. System Cost
- E. Charging/Discharging Rates
- R. Regeneration Processes

### Targets

DOE storage targets for kg-H<sub>2</sub>/kg, kWh/L and \$/kWh

## Collaborators on Amineborane Project



# Overall Project Objectives and Approach

## Overall Center and Project Objectives

- Develop Methods for On-Demand, Low Temperature Hydrogen Release from Chemical Hydrides that Can Achieve DOE Targets
- Develop High Conversion Off-Board Methods for Chemical Hydride Regeneration

In collaboration with Center Partners, the goal of this project is to develop new methods for **Hydrogen-Release** and **Regeneration** that will enable the use of amineboranes for chemical hydrogen storage.



## Penn Project Approaches to Amineborane Hydrogen-Release and Regeneration Goals

**Hydrogen-Release:** Use the activating effects of ionic liquids, chemical promoters and/or metal-catalysts to enhance the rate and extent of hydrogen release from amineboranes.

**Regeneration:** Goals of Penn off-board  $\text{BNH}_x$  regeneration approach: (1) high yields; (2) avoid formation of B-O bonded intermediates; (3) avoid formation of hazardous diborane; (4) recover all products. Penn method converts  $\text{BNH}_x$  to boron trihalides, which are then converted to AB via sequential coordination, reduction and displacement reactions.

# 2008 Objectives and Achievements

## Penn Objectives for the Last Year

- Significantly increase the rate and wt% of AB H<sub>2</sub>-release.
- Learn how to better control AB H<sub>2</sub>-release mechanisms, intermediates and final spent fuel products.
- Further optimize the super-acid/halide-reduction regeneration process.

## Summary of Penn Achievements Since Last Review

- A greatly increased rate of H<sub>2</sub>-loss (~2.3 eqv. in 15 min) with 10.2 mat-wt% from AB/ionic-liquid mixtures was achieved at 120°C.
- A rhodium catalyzed AB H<sub>2</sub>-release in an ionic liquid was demonstrated that increases the loss rate for the first H<sub>2</sub> eqv.
- Proton sponge in ionic liquids was shown to both increase the release rate of the second AB H<sub>2</sub> eqv. and greatly reduce foaming.
- NMR, DSC and rate studies revealed that while there are different mechanistic pathways for AB H<sub>2</sub>-release, the final spent fuels all contain trigonal sp<sup>2</sup> BNH<sub>x</sub> structures thus enabling a common regeneration strategy.
- New high yield processes for the conversion of BX<sub>3</sub> to AB were developed that avoid the formation of hazardous diborane and allow complete separation and recovery of all products.



### Penn Research Team

PI: Larry Sneddon

Postdoctoral: Laif Alden

Students:

Dan Himmelberger

Bill Ewing

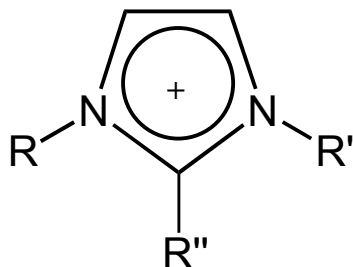
**Penn Approach to Improving Ammonia Borane H<sub>2</sub>-Release. Increase the Rate and Amount of H<sub>2</sub>-Release by Activation of AB with:**

- 1. Ionic Liquids**
- 2. Metal-Catalysts/Ionic-Liquids**
- 3. Chemical Promoters**

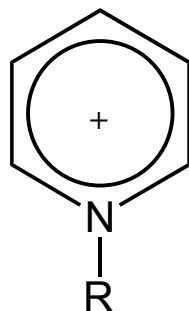
# 1. Why Ionic Liquid Solvents for Amineborane Dehydrogenations?

## Ionic Liquid Solvents

Cations:



N,N'-imidazolium



N-pyridinium

Anions:

*Reactive:*  $\text{AlCl}_4^-$ ,  $\text{Al}_2\text{Cl}_7^-$

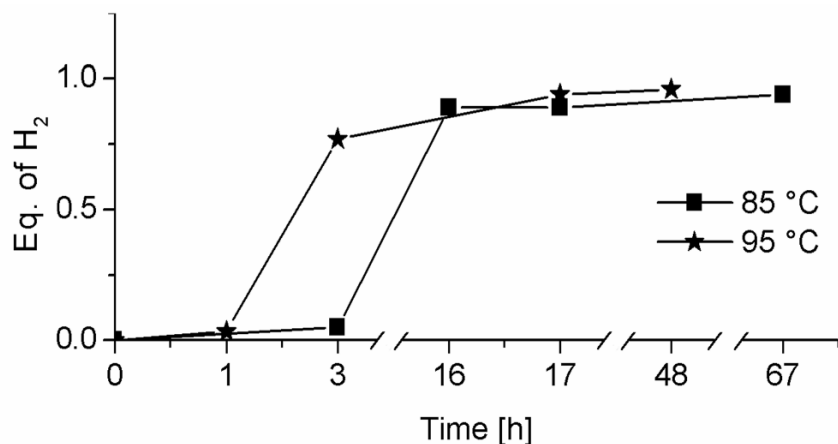
*Inert:*  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{Cl}^-$

## Advantages

- Negligible vapor pressures
- Dissolve both neutral and ionic species
- Thermally stable to elevated temperatures
- Non-coordinating anions and cations provide an inert, polar reaction medium
- **Promote the formation of ionic or polar intermediates and transition states**

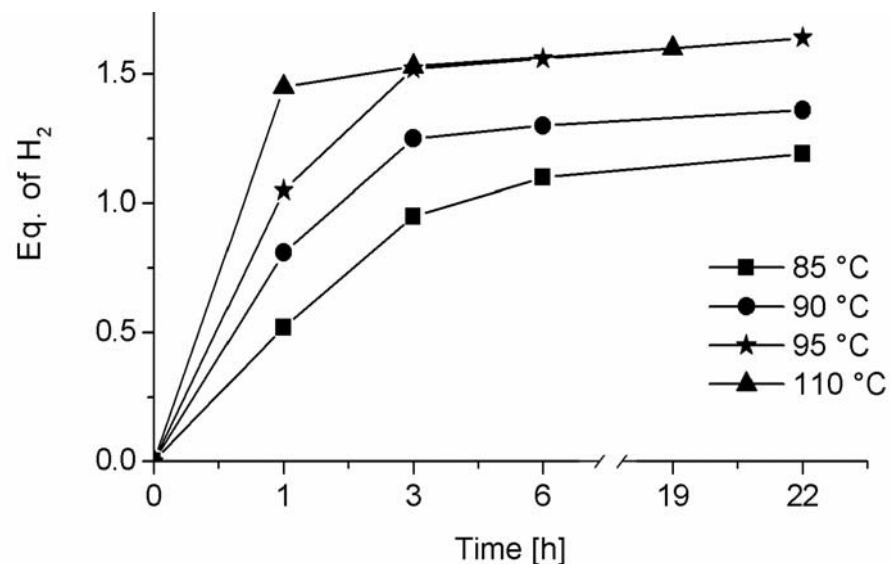
# 2006: Ionic Liquids Increase the Rate and Extent of H<sub>2</sub>-Release from AB and Eliminates Induction Period

Neat NH<sub>3</sub>BH<sub>3</sub>



NH<sub>3</sub>BH<sub>3</sub> + Ionic Liquid<sup>‡</sup>

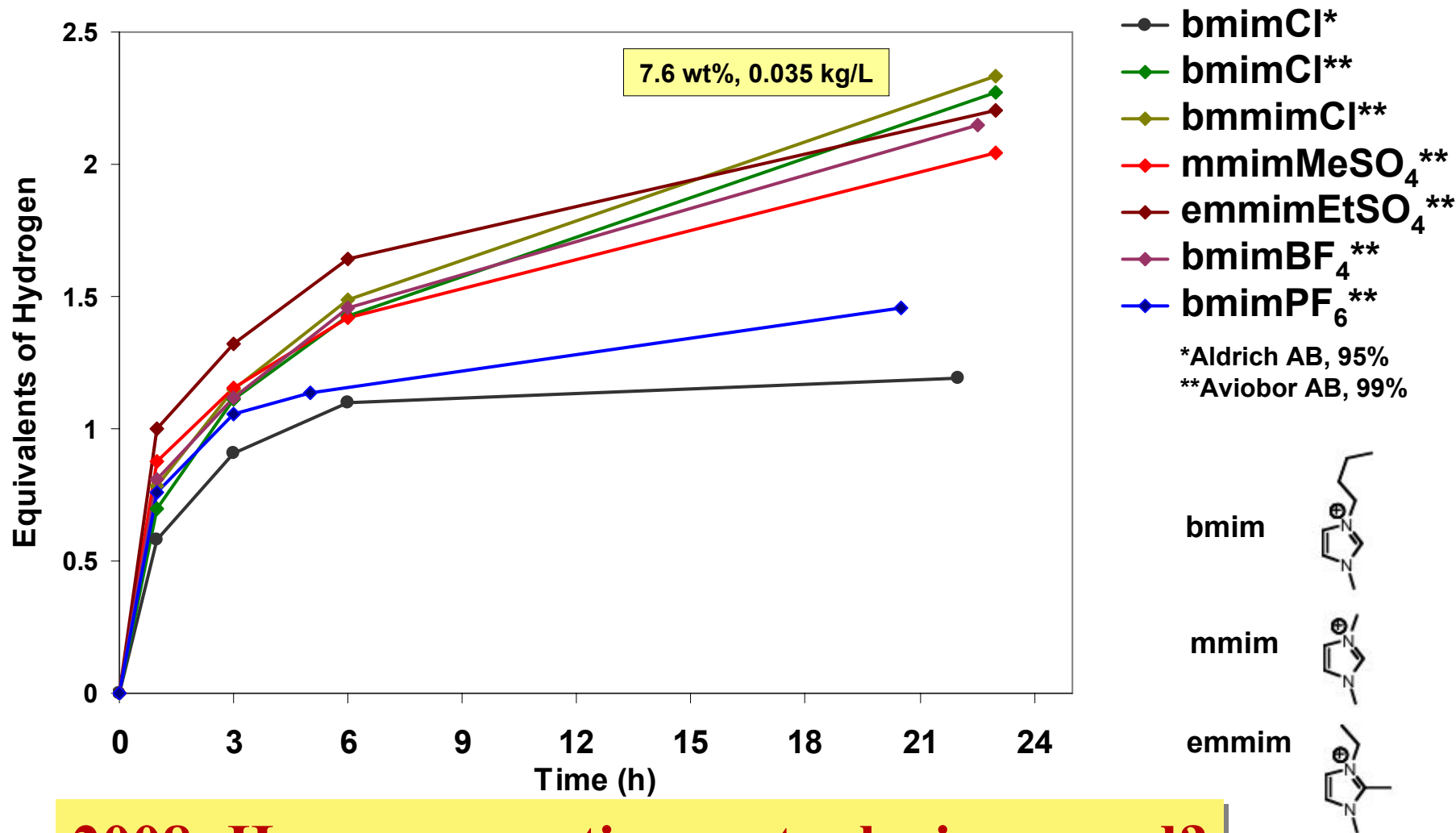
(50:50 wt% mixture)



<sup>‡</sup>1-Butyl-3-methylimidazolium chloride

Bluhm, M. E.; Bradley, M. G.; Butterick, R.; Kusari, U.; Sneddon, L. G.  
*J. Am. Chem. Soc.* **2006**, *128*, 7748-9.

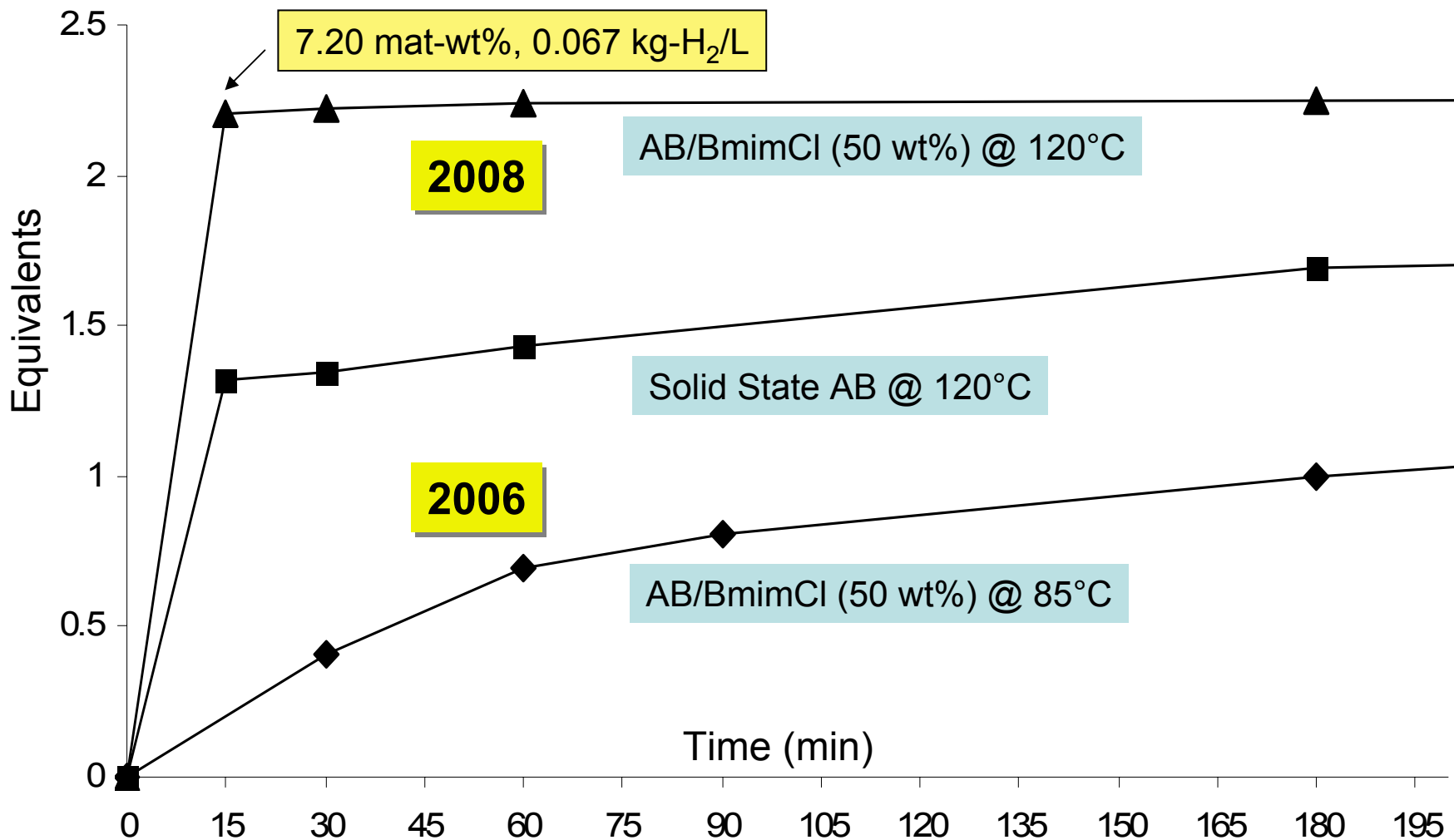
# 2007: Other Ionic Liquids Show Increased Extent and Rate of H<sub>2</sub>-Release at 85 °C



2008: How can reactions rates be increased?

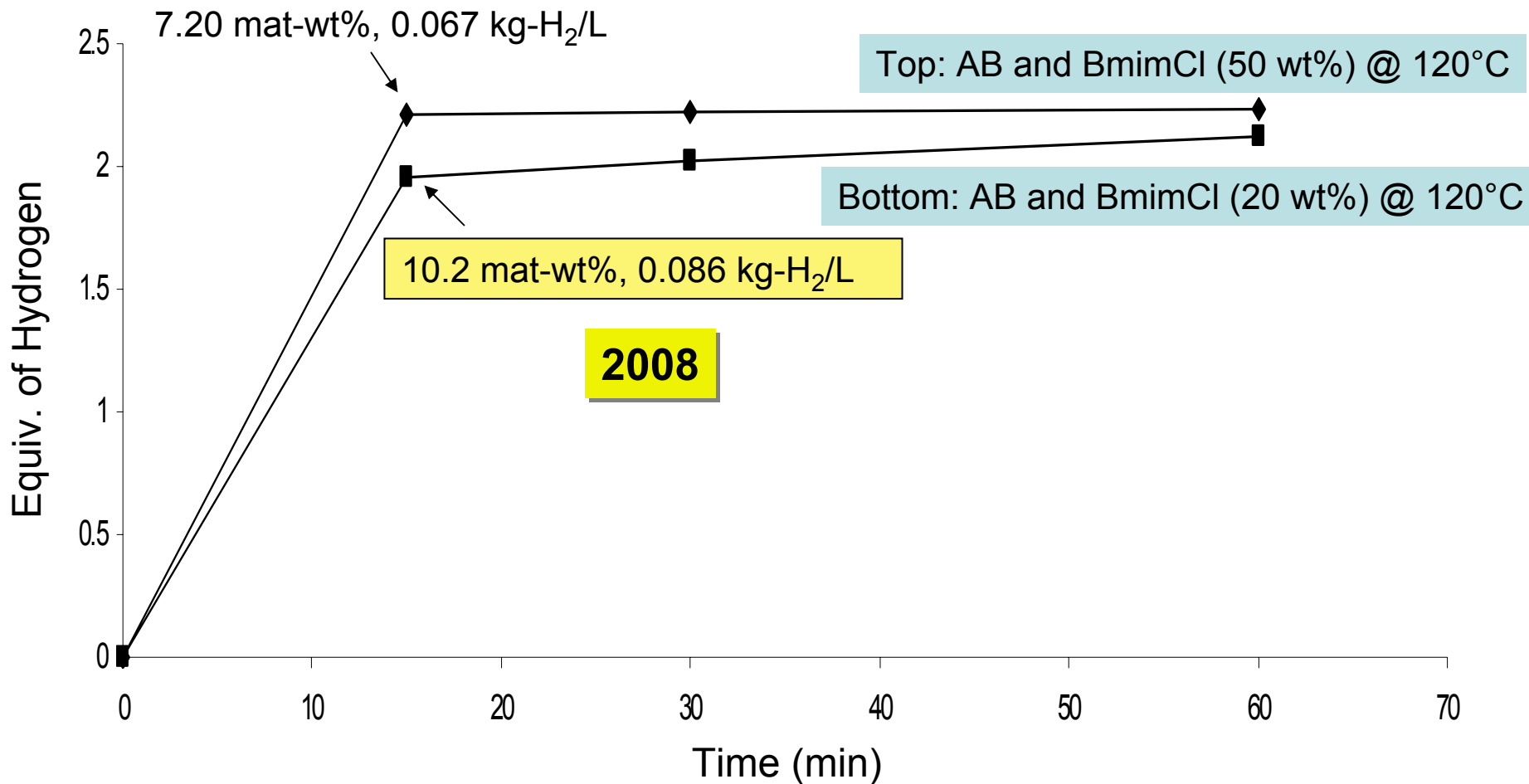


# 2008: H<sub>2</sub>-Release Rates of AB in Ionic Liquids are Greatly Increased at 120 °C



**Similar H<sub>2</sub>-Release Rates for 1st and 2nd Equivalents!**

# 2008: 10.2 Mat-wt% H<sub>2</sub> in 15 min at 120 °C is Achieved When only 20% BmimCl is Used



# 2008: Metrics for New “Best” H<sub>2</sub>-Release Systems

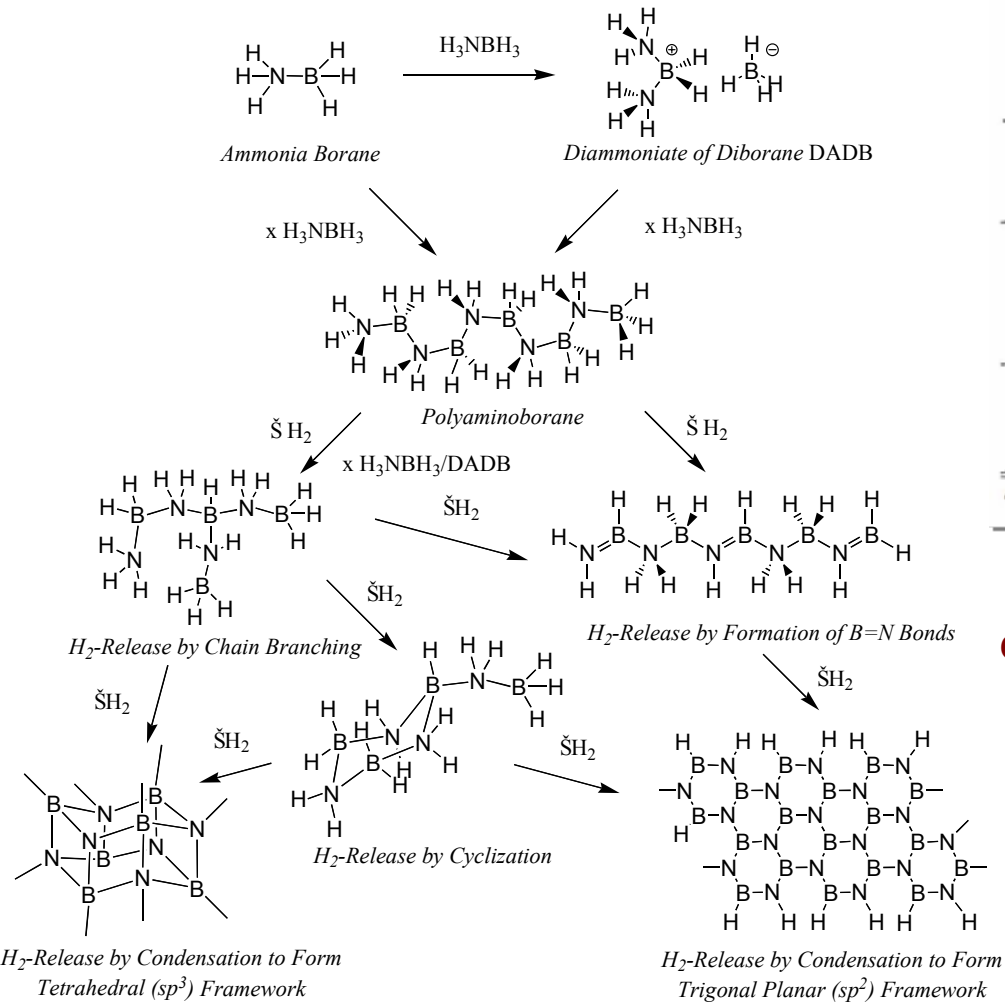
Metrics	AB Thermolysis at 120°C		
	Solution-State (15 min, ~2 Eq. H <sub>2</sub> )		
	50 wt% BmimCl	40 wt% BmimCl	20 wt% BmimCl
Grav. density (Mat. wt%)	7.2	8.7	10.2
Vol. density (Kg-H <sub>2</sub> /L Mat.)	0.067	0.078	0.086
H <sub>2</sub> Flow Rate (g/s) per kg Material	0.08	0.097	0.114
Kg of Mat. for 0.8 mol/sec	20	17	14

**DOE Total System Targets for Hydrogen Storage Systems**

<b>Gravimetric Density (wt%)</b>	<b>Volumetric Density (Kg-H<sub>2</sub>/L)</b>
4.5 (2007), 6.0 (2010), 9.0 (2015)	0.036 (2007), 0.045 (2010), 0.081 (2015)

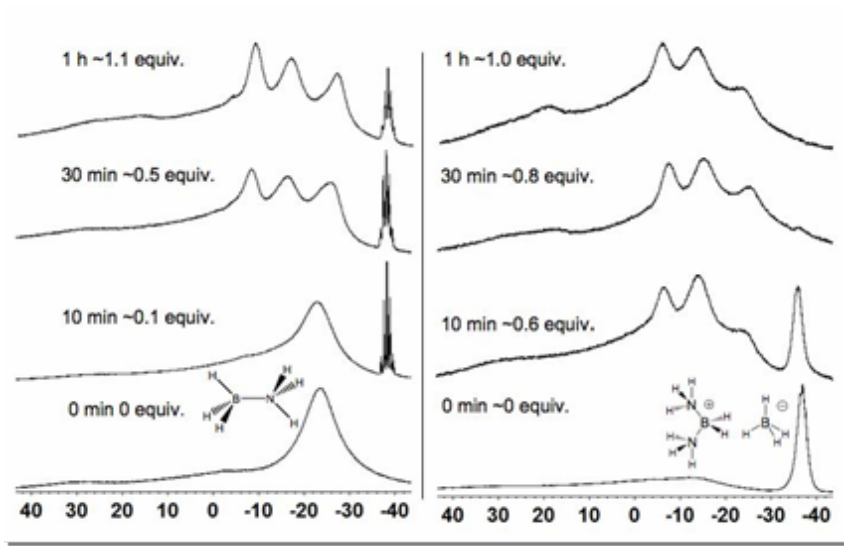
# NMR Studies Identify Initial and Final Release Products

## Possible Mechanistic Steps



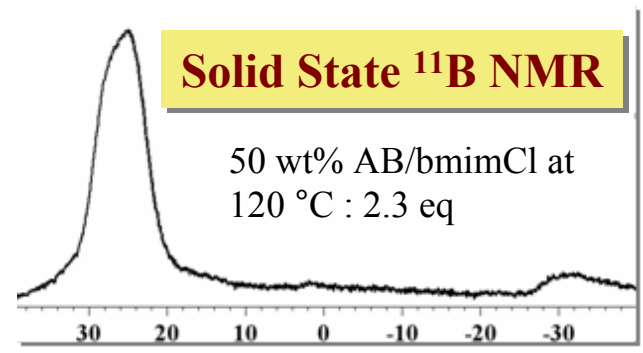
## Solution <sup>11</sup>B NMR

10 wt% AB and DADB in bmimOTf at 85°C



**Conclusion: Both DADB formation and decomposition is enhanced in ionic liquids**

## Solid State <sup>11</sup>B NMR



**Conclusion: Final Spent Fuel Product has sp<sup>2</sup>-type framework**

## 2. Why Use Metal Catalysts for Amineborane Dehydrogenations in Ionic Liquids?

Catalysts in Conjunction with Ionic Liquids Could Provide:

- (1) Faster H<sub>2</sub>-Release
- (2) Better Control of H<sub>2</sub>-Release Rates
- (3) Lower Temperature Reactions
- (4) Synergistic Release Mechanisms

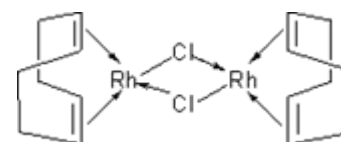
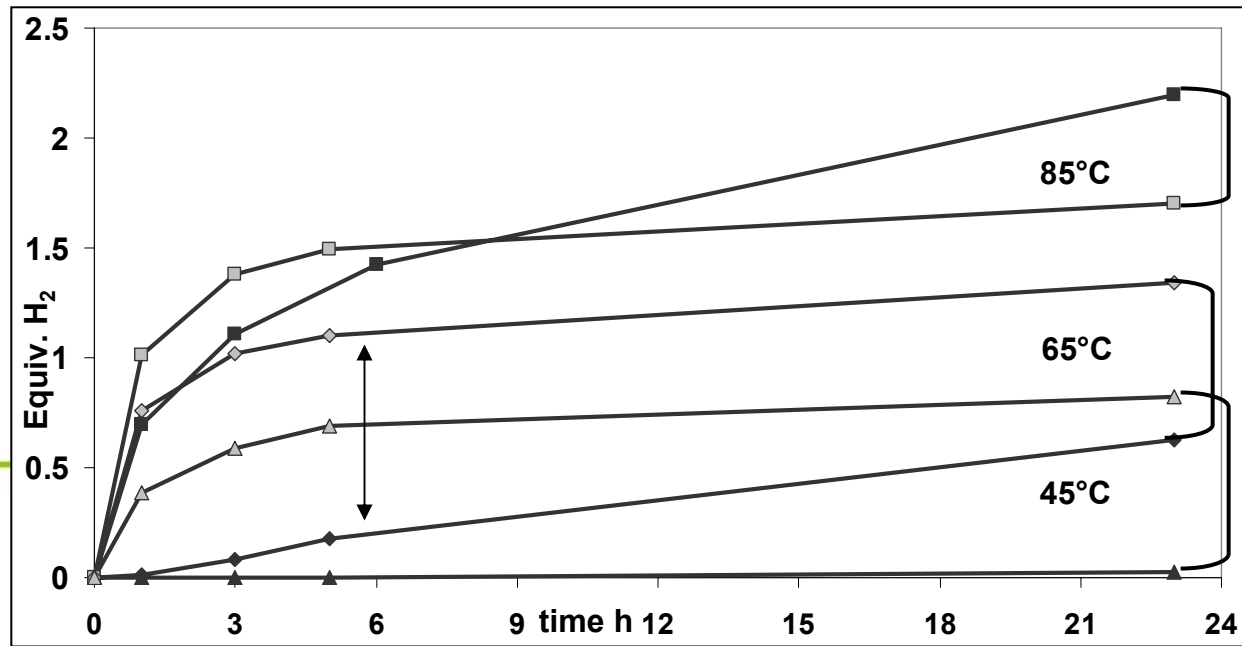
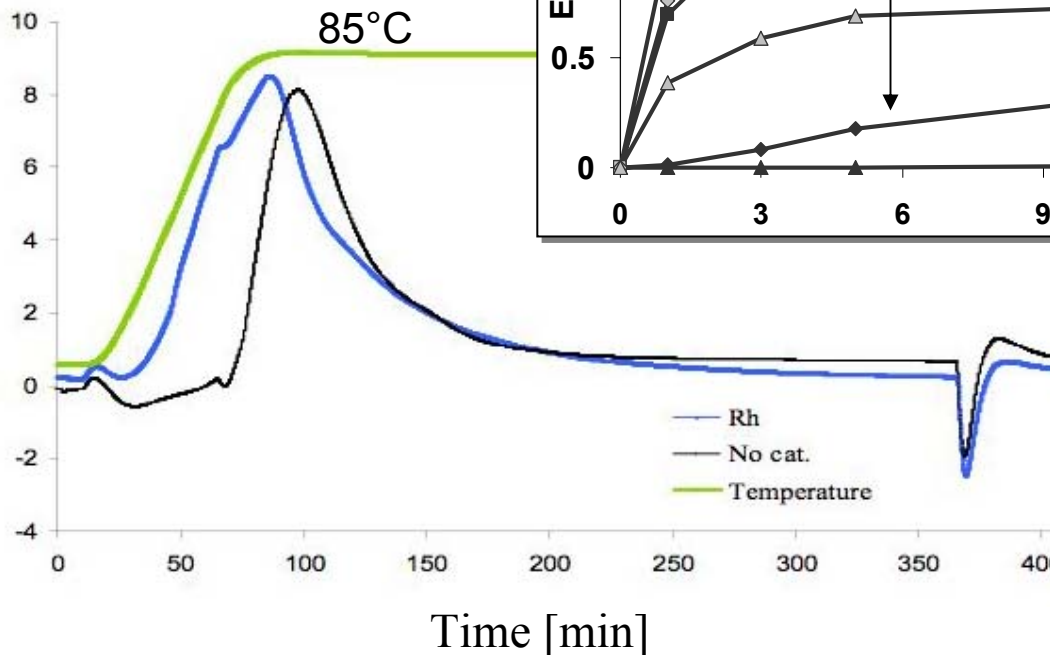
Center Partners (LANL and U Washington) have previously demonstrated metal catalyzed AB H<sub>2</sub>-release in organic solvents.

Since the last program review, AB catalyzed H<sub>2</sub>-release in ionic liquids has been achieved.

# 2008: Rh Catalyst Increases Release Rate of the First Equivalent of H<sub>2</sub> from AB in Ionic Liquids

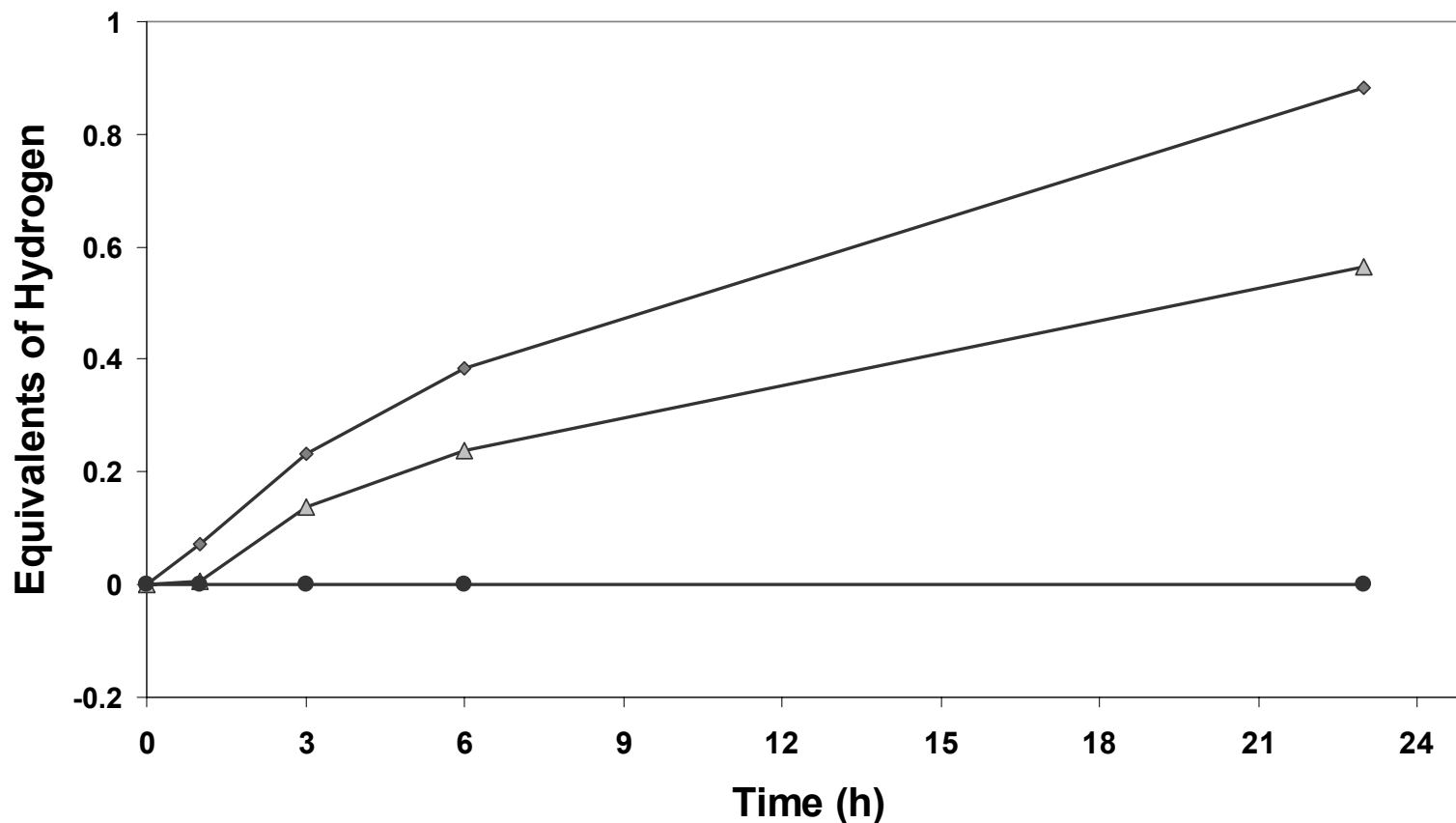
50 wt% AB  
in bmimCl  
5 mol% Rh

DSC



- 85°C
- ◆ 65°C
- ▲ 45°C
- ◻ 85°C w/ Rh
- ◊ 65°C w/ Rh
- △ 45°C w/ Rh

# 2008: Rh Catalyzes Dehydrogenation of Other Amineboranes in Ionic Liquids

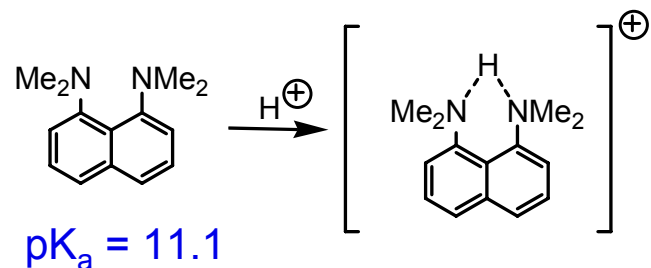
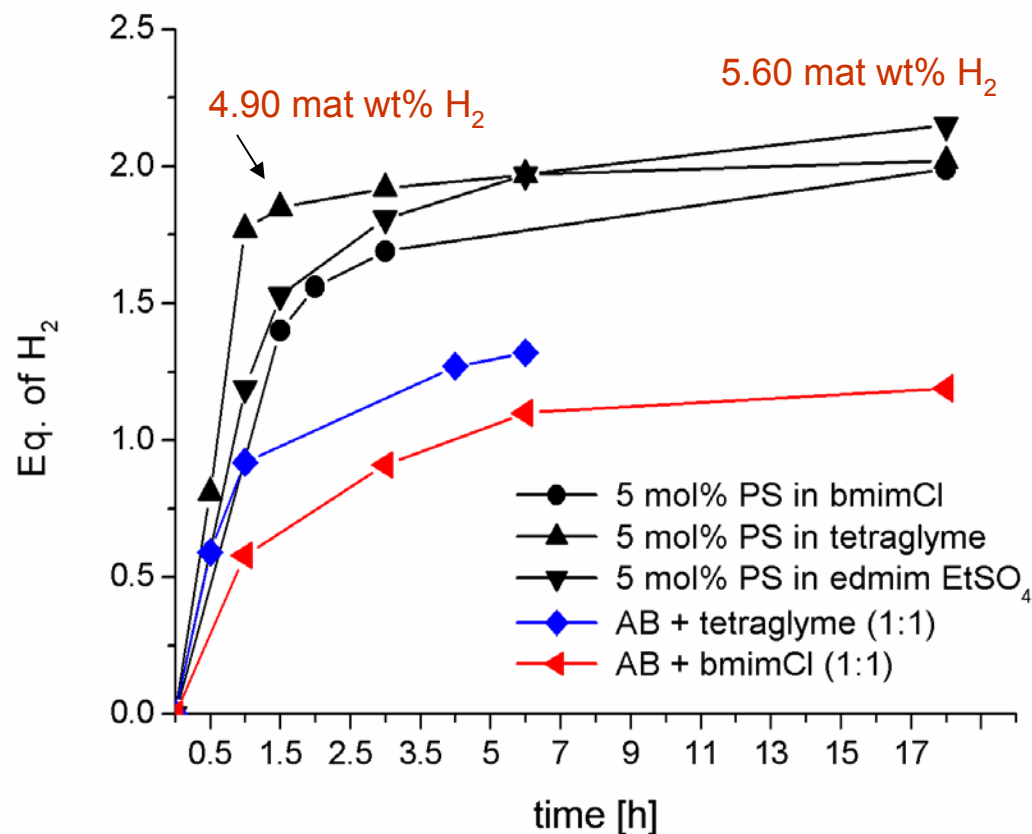


**Me<sub>2</sub>NHBH<sub>3</sub> (10wt%) in mmimMeSO<sub>4</sub> at 45°C**

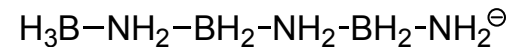
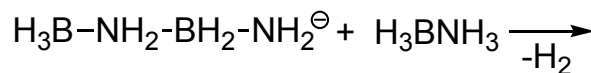
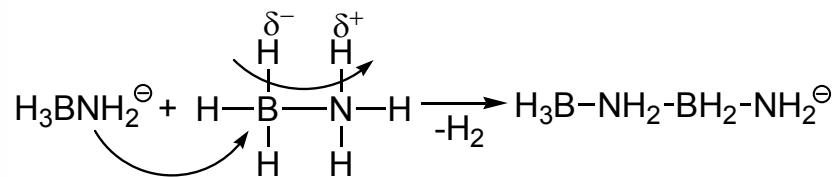
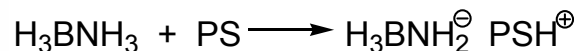
- △ 5 mol% Rh(COD)Cl
- ◇ 1 mol% Rh(COD)Cl
- 0 mol% Rh(COD)Cl

### 3. 2007: Chemical Promotors: Proton Sponge Increases H<sub>2</sub>-Release from AB in Solution and Avoids the Formation of M<sup>+</sup>BH<sub>4</sub><sup>-</sup> and NH<sub>3</sub>

NH<sub>3</sub>BH<sub>3</sub> + 5 mol % PS at 85 °C in Ionic-Liquids or Tetraglyme (250 mg) (91 mg)



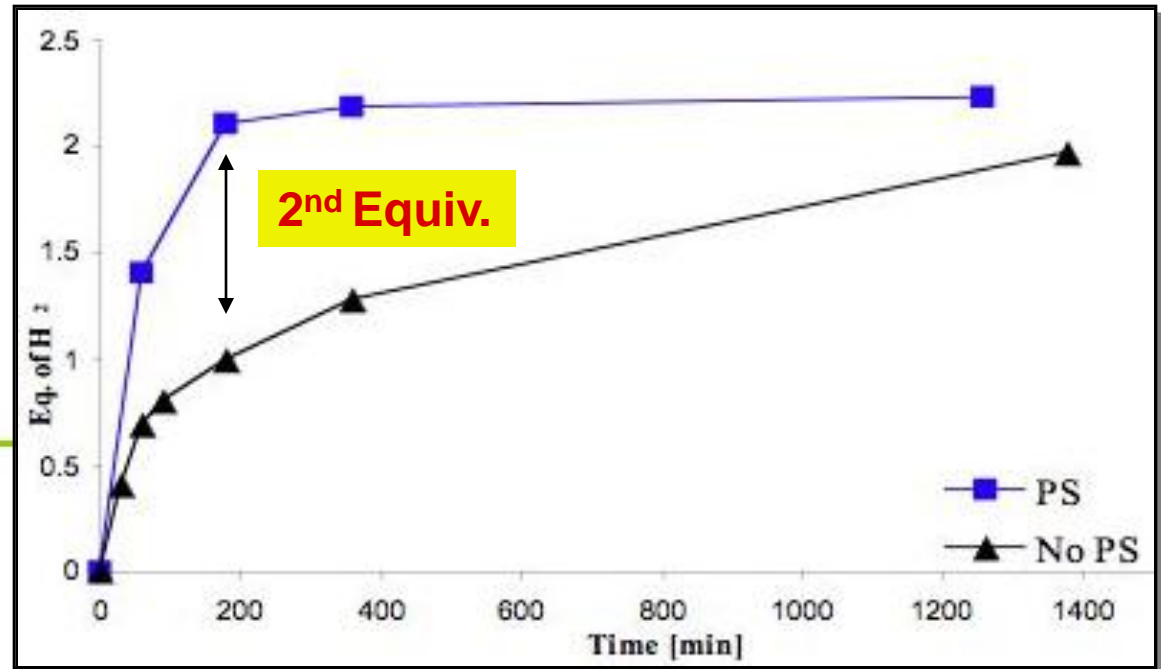
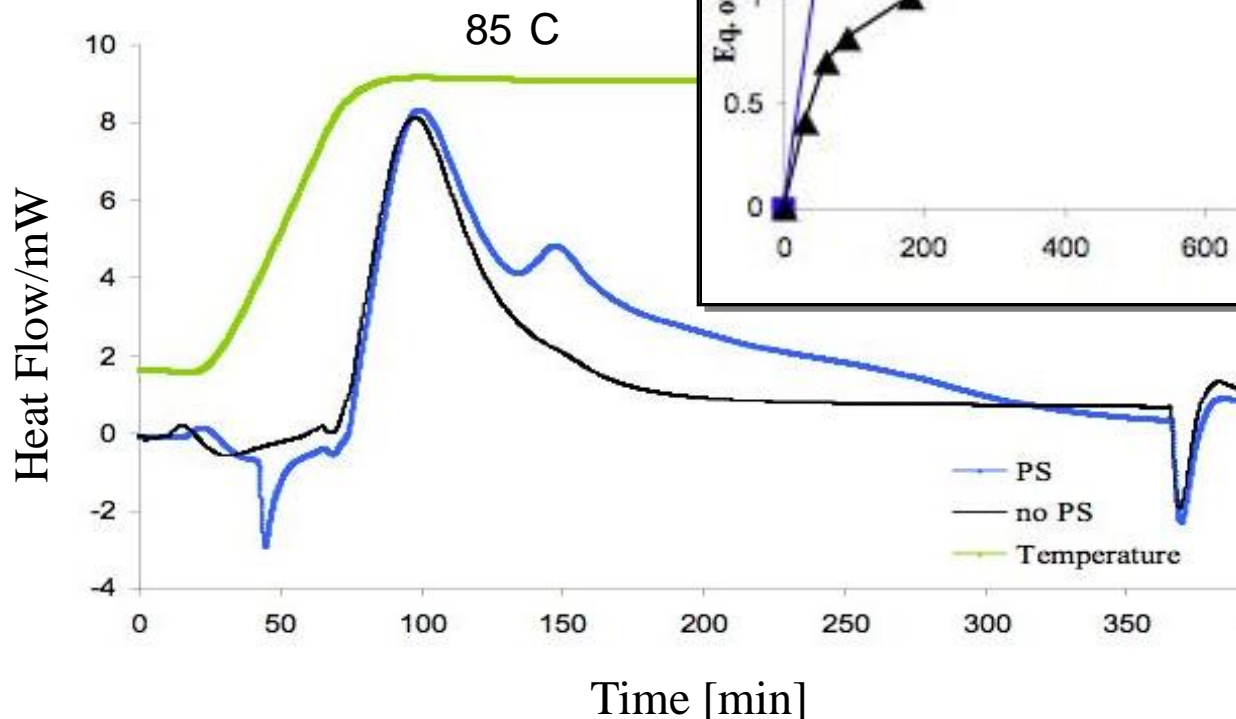
#### Proton Sponge Reaction Mechanism



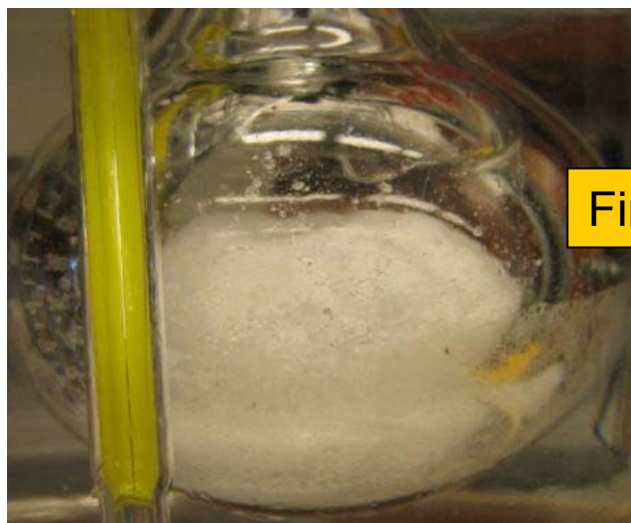


# 2008: Proton Sponge Increases the Release Rate of the Second Equivalent of H<sub>2</sub> from AB and Reduces Foaming

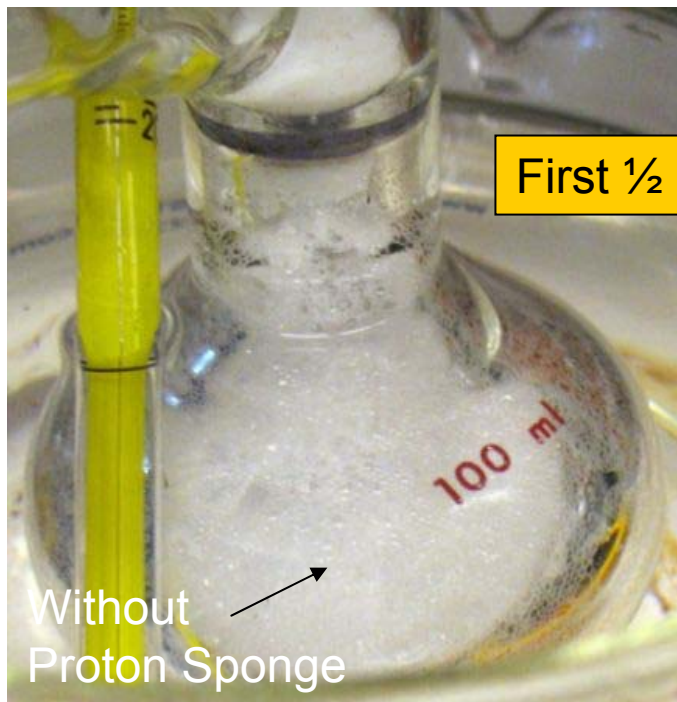
AB with 5 mol% PS  
in bmimCl at 85 °C



# 2008: Foaming Suppressed with Proton Sponge

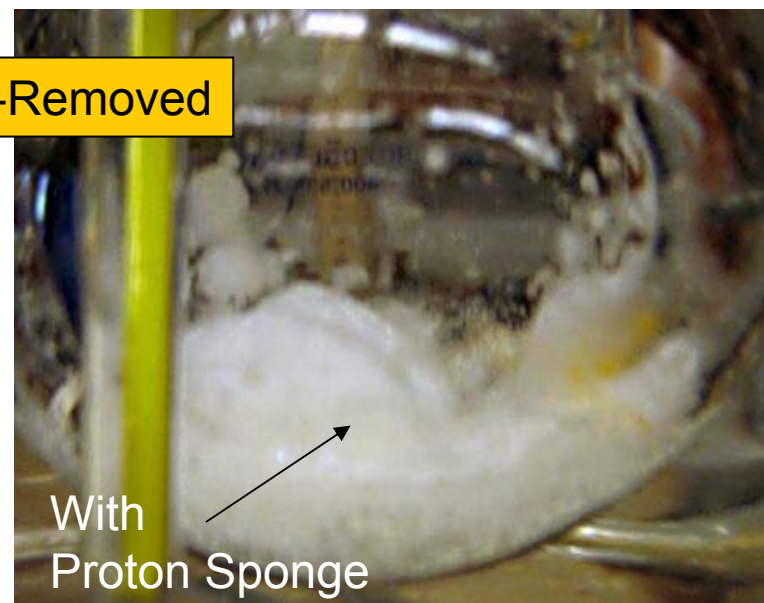


First ½ h of Reaction



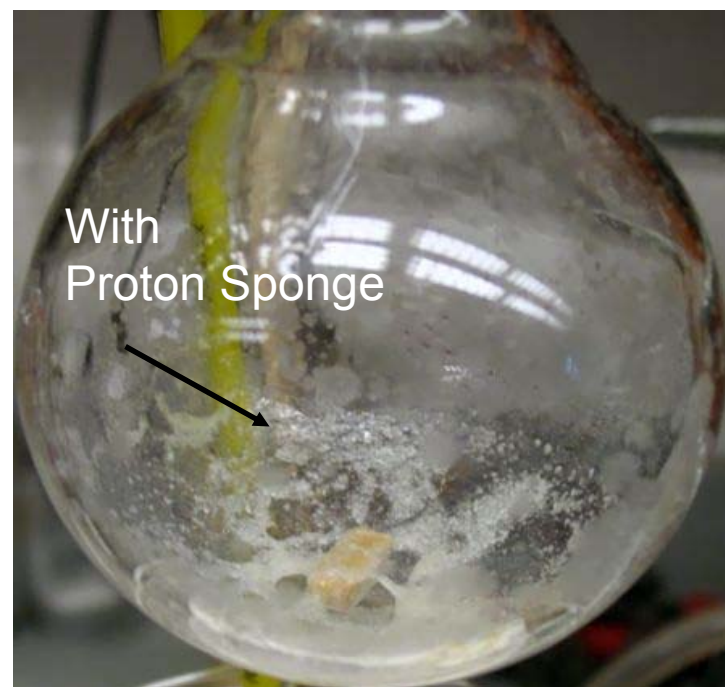
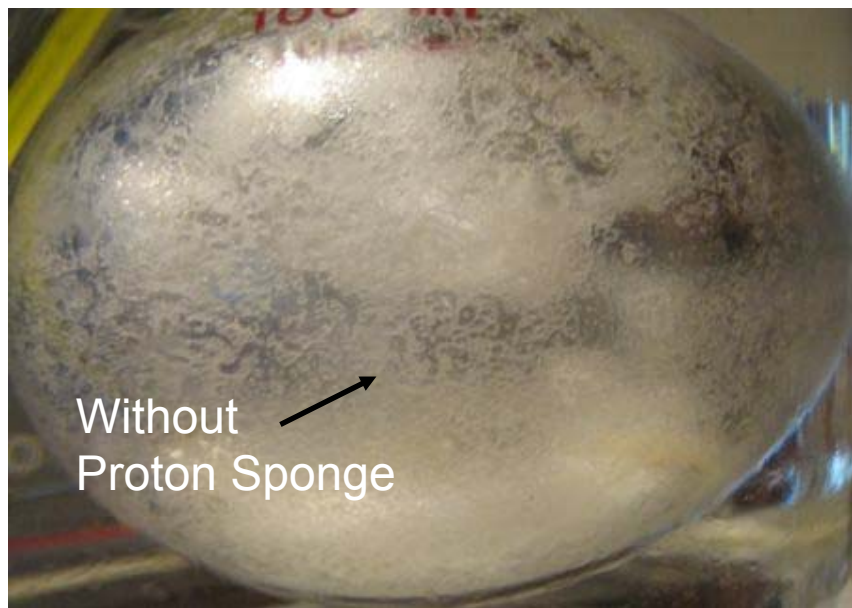
First ½ h, After H<sub>2</sub>-Removed

Without  
Proton Sponge



With  
Proton Sponge

## 2008: Foaming Suppressed with Proton Sponge



After 23 hours

# Penn Approach to Regeneration: Super-Acid/Halide-Reduction Process

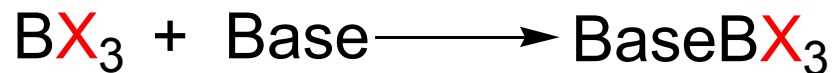
Important Goals: (1) high yields, (2) avoid the formation of B-O bonds, (3) avoid the formation of B<sub>2</sub>H<sub>6</sub>, and (4) recover all products

## First Step: Digestion of Spent Fuel by Super Acidic Halo-Acids

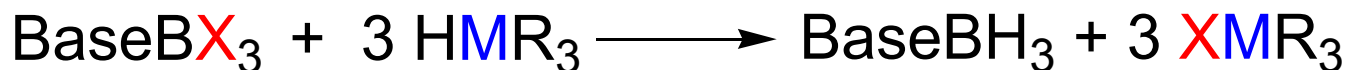


## Second Step: One-Pot Conversion of BX<sub>3</sub> to AB

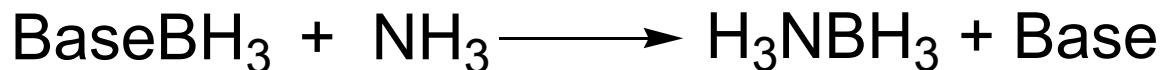
### Coordination of BX<sub>3</sub>



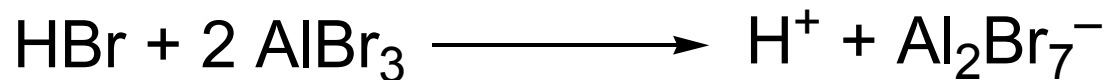
### BX Reduction



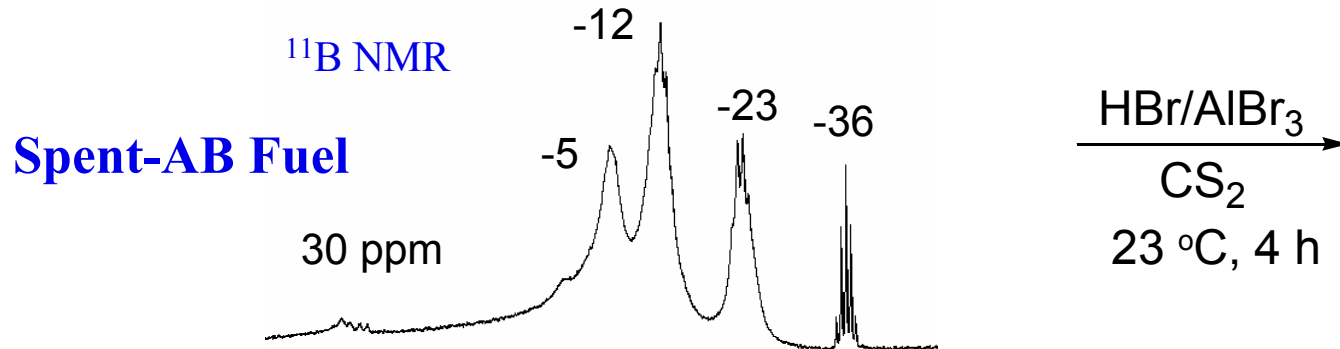
### Base Displacement by NH<sub>3</sub> Yields AB



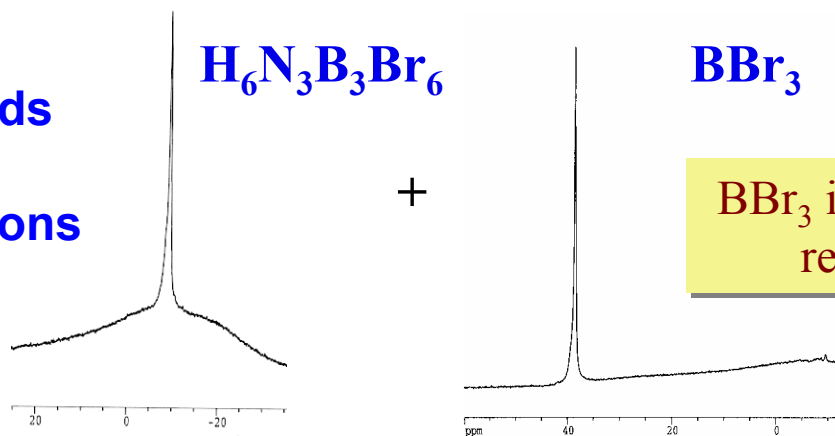
# 2007: Step 1. Digestion. Superacidic HX/AlX<sub>3</sub> Solutions Digest BNH<sub>x</sub> Spent-Fuels



Farcasiu, D.; Fisk, S. L.; Melchior, M. T.; Rose, K. D. *J. Org. Chem.* **1982**, *47*, 453-7



Product ratio depends upon spent-fuel reactants and conditions



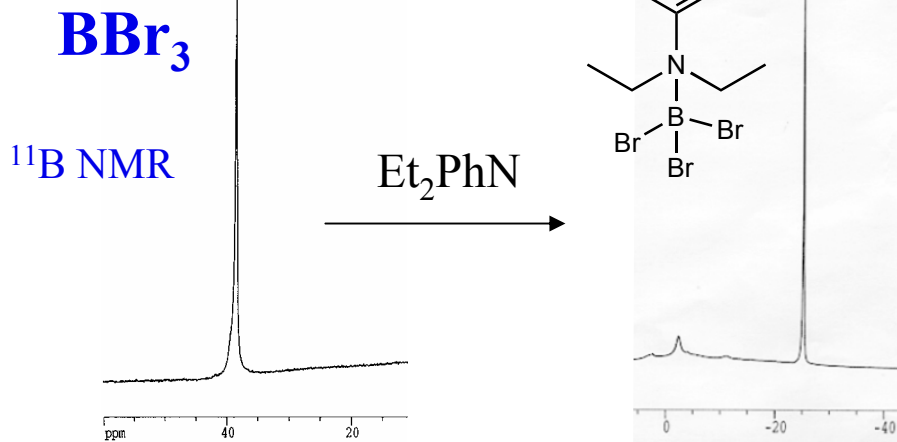
**BBr<sub>3</sub> is distilled from the reaction mixture**



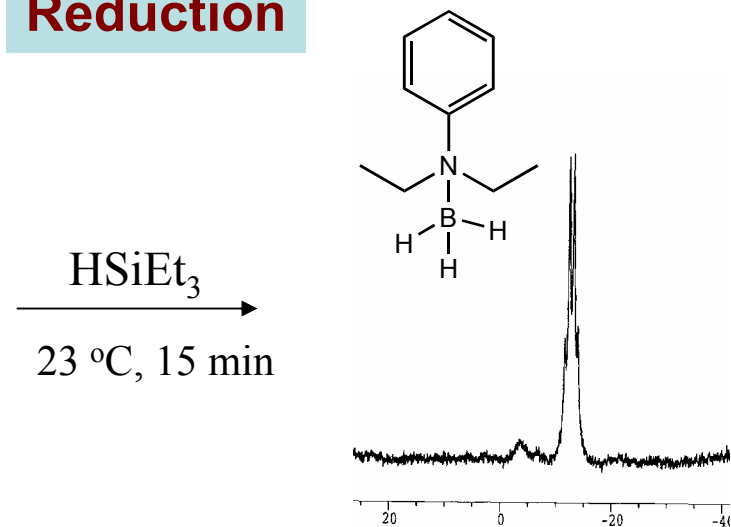
# 2007: Step 2. Coordination, Reduction and Displacement to Regenerate AB from BBr<sub>3</sub>

A One-Pot 84%-Yield of AB from BBr<sub>3</sub> Has Been Achieved via the Reduction of Diethylaniline-BBr<sub>3</sub> Followed by NH<sub>3</sub> Exchange

## Amine-Coordination



## Reduction



Alabama (Dixon) analysis indicates regeneration efficiency for total process (Steps 1 and 2) could meet 60% DOE target, depending upon reactants and heat recovery

+NH<sub>3</sub>

-Et<sub>2</sub>PhN

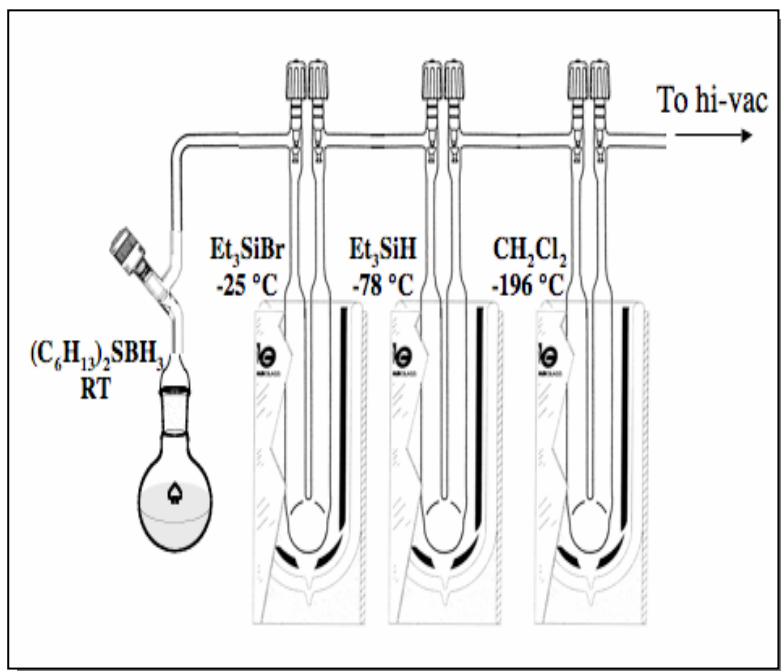
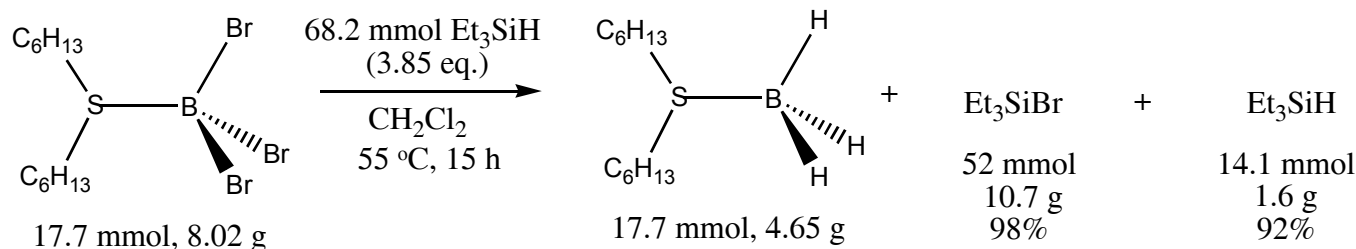
**H<sub>3</sub>NBH<sub>3</sub>**

**Exchange**

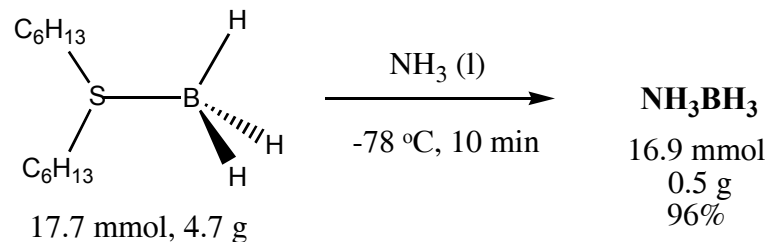
2006, Thorn, LANL

# 2008: New Reduction Processes are Quantitative and Allow Separation and Recovery of All Products

## Reduction with Silane



## Reaction with Ammonia

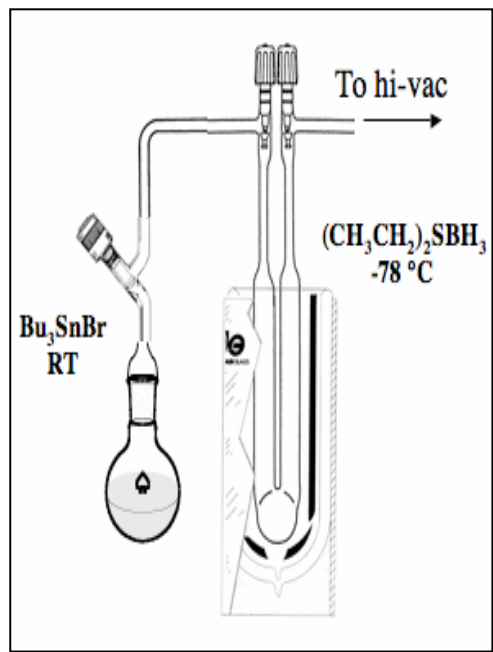
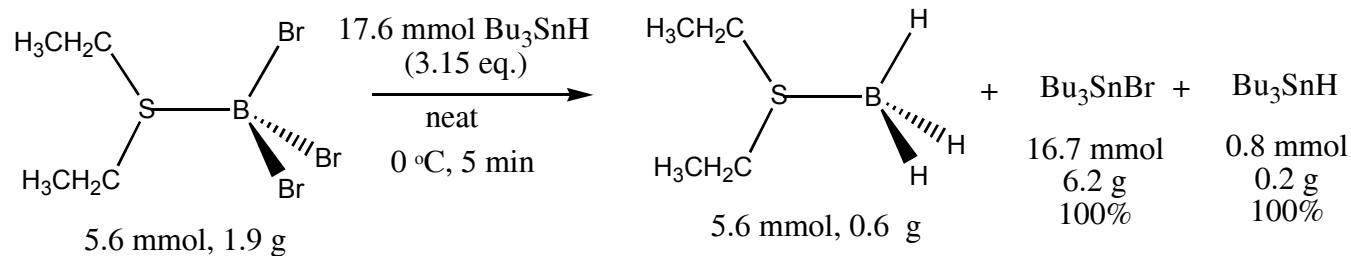


Residual ammonia is removed in-vacuo leaving a slurry of AB and hexylsulfide. Hexyl sulfide is removed by washing with hexane. AB is then collected and dried. Hexyl sulfide can be recovered by removing hexane in vacuo

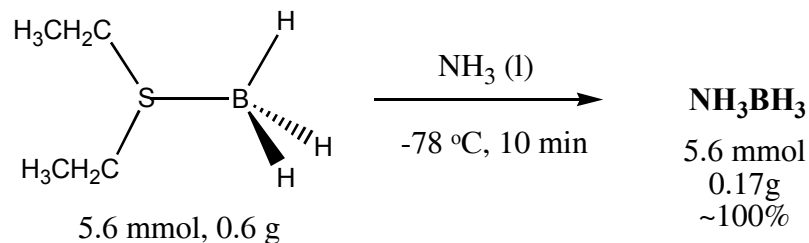
## Isolation of Reduction Products

**Overall AB Yield from BBr<sub>3</sub>; 96%**

## Reduction with Stannanes



## Reaction with Ammonia



**Overall AB Yield from BBr<sub>3</sub>: 100%**

**Isolation of Reduction Products**

**Both Procedures Avoid Handling B<sub>2</sub>H<sub>6</sub>**



# Future Studies

## AB H<sub>2</sub>-Release



## AB and MAB Regeneration

- Optimize the higher-temperature/weight-ratios for ionic liquid based H<sub>2</sub>-release systems
- Continue to develop and optimize chemical-promoter systems with improved H<sub>2</sub>-release rates
- Investigate a wider range of metal catalysts for H<sub>2</sub>-release in ionic liquids
- NMR studies focused on learning how to control H<sub>2</sub>-release mechanisms to achieve the most regenerable spent fuels
- Take advantage of synergistic mechanisms to improve H<sub>2</sub>-release rates

- **AB Digestion:** The conversion of spent fuel to BX<sub>3</sub> must be improved for this scheme to be viable. Future work will use more forcing conditions.
- **BX<sub>3</sub> Reduction:** This step is finished and optimized in the laboratory, but is it industrially feasible? Future collaborative work with Rohm and Haas will focus on process design and scalability.
- In collaboration with other center partners, new investigations of the use of the super-acid/halide-reduction process for the regeneration of other fuels such as LiNH<sub>2</sub>BH<sub>3</sub>.



DOE Hydrogen Program

# Collaborations and Technology Transfer

**Penn work on H<sub>2</sub>-Release/Regeneration is Highly Coordinated with Partners by Frequent “Brainstorming” Discussions, Laboratory Visits, and Sample and Measurement-Sharing. Partner Collaborations Provide Complimentary Expertise:**

- Penn:** new H<sub>2</sub>-release methods for AB and AT using chemical promoters and ionic liquids; solution NMR-characterization and regeneration of spent-fuel products
- LANL:** AB homogeneous and acid dehydrogenation catalysts and regeneration methods
- PNNL:** supported AB dehydrogenation catalysts and studies of key dehydrogenation steps, new hydrogen-recovery methods, solid-state NMR studies
- U. of Washington:** studies of fundamental amineborane coordination chemistry and mechanisms of homogeneously catalyzed AB dehydrogenation
- U. of Alabama:** computational studies of amineborane reaction pathways and stabilities, evaluation of the energetics of regeneration methods
- Rohm and Haas:** provides starting materials for amineborane synthesis and key expertise in process design and scalability.

**Future Studies will Now Rely Heavily on Industrial and National Laboratory Partners for Engineering and Scale-Up of Technologies**

- PNNL and LANL:** Engineering assessments and implementation of solid and liquid-based H<sub>2</sub>-release systems.
- Rohm and Haas:** Engineering assessment and scale-up of new regeneration process