



# Amineborane-Based Chemical Hydrogen Storage

Department of Chemistry  
University of Pennsylvania

DOE Chemical Hydrogen  
Storage Center of Excellence

2007 DOE Hydrogen Program Review

May 17, 2007

Project ID: **ST27**

This presentation does not contain any proprietary or confidential information

# Project Overview

## Timeline

Project Start: FY 2005  
Project End: FY 2009  
Percent complete: 50%

## Budget

Total Project Funding: \$1,727,356  
DOE: \$1,381,886  
Penn: \$345,470

DOE Funding in 06: \$250,000  
DOE Funding in 07: \$275,000

## 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 **Amineborane Hydrogen-Release and Regeneration Reactions** that will enable their use 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 ammonia borane, ammonia triborane and their mixtures.

**Regeneration:** Develop new methods for the off-board regeneration of  $\text{BNH}_x$  spent fuels which avoid formation of B-O bonded intermediates. Method currently under development converts  $\text{BNH}_x$  to boron trihalides which then are converted to ammonia borane via sequential coordination, reduction and displacement reactions.

# 2007 Objectives and Achievements



## Penn Objectives for the Last Year

- Characterize the dehydrogenation products and improve the extent and rate of hydrogen release from ammonia borane (AB)
- Determine if ammonia triborane (AT) is a candidate for hydrogen storage by either hydrolytic or thermolytic reactions
- Develop new methods for amineborane regeneration

## Summary of Penn Achievements Since Last Review

- Acids and metal-catalysts induce fast hydrolytic hydrogen release from AT under mild conditions with 6.1 materials-wt% H<sub>2</sub> achieved from concentrated aqueous solutions.
- Ionic liquids, lithium amide, lithium hydride and nitrogen bases each increase the extent and rate of thermolytic hydrogen release from both AB and AT and several systems have been identified that have potential to meet DOE targets.
- A new process for ammonia borane regeneration that avoids the formation of B-O intermediates has been developed.



## Penn Research Team

PI: Larry Sneddon

Postdoctoral: Laif Alden

Students:

Chang Yoon

Dan Himmelberger

Bill Ewing

# Why Amineboranes for Hydrogen Storage?

Because of their protonic N-H and hydridic B-H hydrogens, amineboranes are unique in their ability to store and release hydrogen

## Materials wt%

	$\text{NH}_4\text{BH}_4$	(24.5 wt%, 0.20 kg/L $\text{H}_2$ )
→	$\text{NH}_3\text{BH}_3$	(19.6 wt%, 0.16 kg/L $\text{H}_2$ )
	$\text{B}_3\text{N}_3\text{H}_{12}$	(14 wt%, 0.11 kg/L $\text{H}_2$ )
	$\text{B}_3\text{N}_3\text{H}_6$	(7.5 wt%, 0.06 kg/L $\text{H}_2$ )
→	$\text{NH}_3\text{B}_3\text{H}_7$	(17.8 wt%, 0.14 kg/L $\text{H}_2$ )

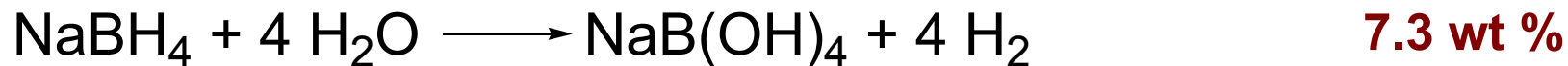
## DOE Total System Targets

**2007:** 4.5 wt%, 0.036 kg- $\text{H}_2$ /L; **2010:** 6.0 wt%, 0.045 kg- $\text{H}_2$ /L;

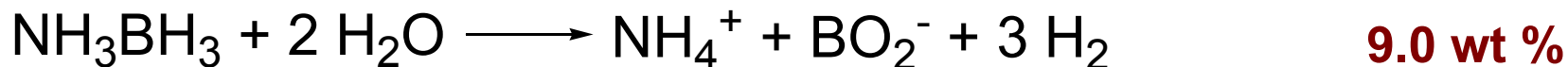
**2015:** 9.0 wt%, 0.081 kg- $\text{H}_2$ /L

# Amineborane H<sub>2</sub>-Release Can Be Achieved by Either Hydrolytic or Thermolytic Processes

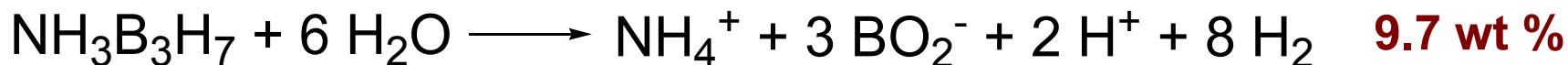
**Hydrolysis: Fast hydrogen release, but lower potential capacities**



*Int J Hydrogen Energy* **2003**, 28, 1095



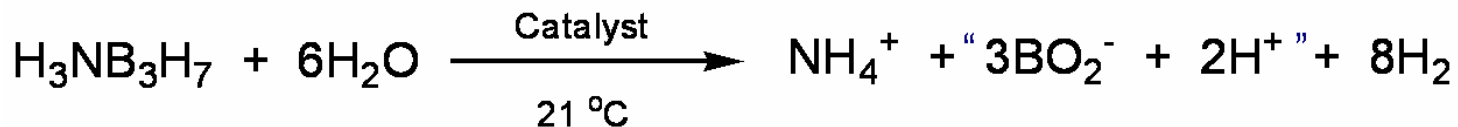
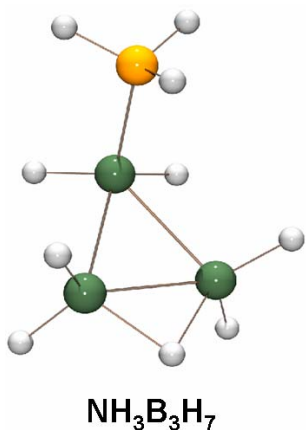
*J. Power Sources* **2006**, 159, 855



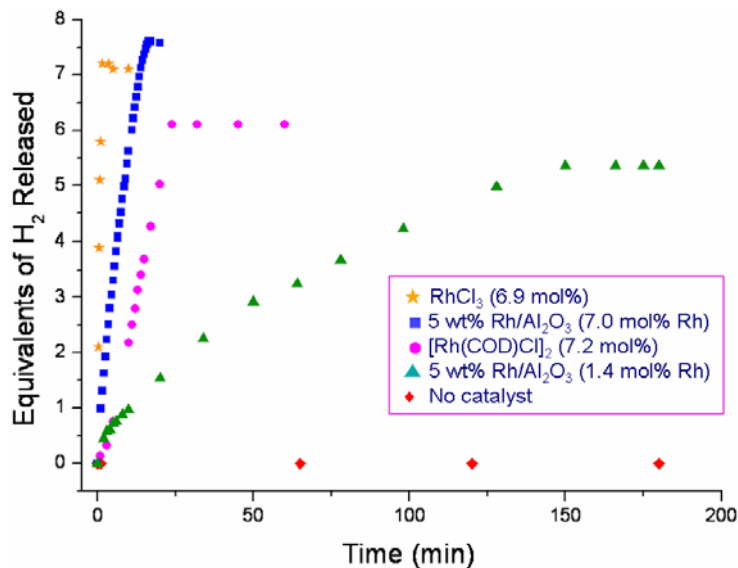
**Thermolysis: High potential capacities, but (to date) slower hydrogen release**



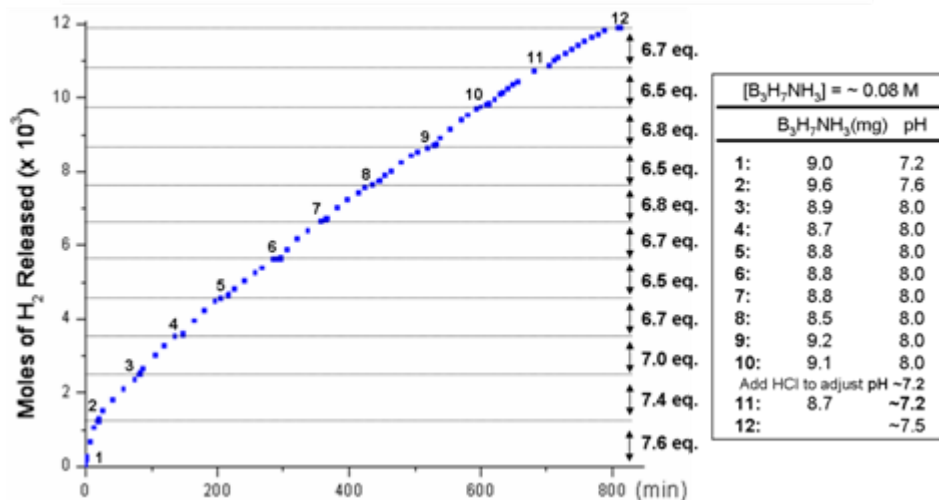
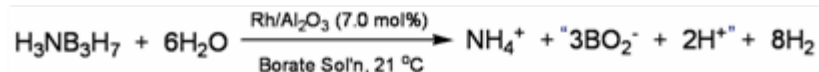
# 2006: Metals Catalyze $\text{NH}_3\text{B}_3\text{H}_7$ Hydrolytic Hydrogen Release



**Rh-Based Catalysts Exhibit Excellent Activities**

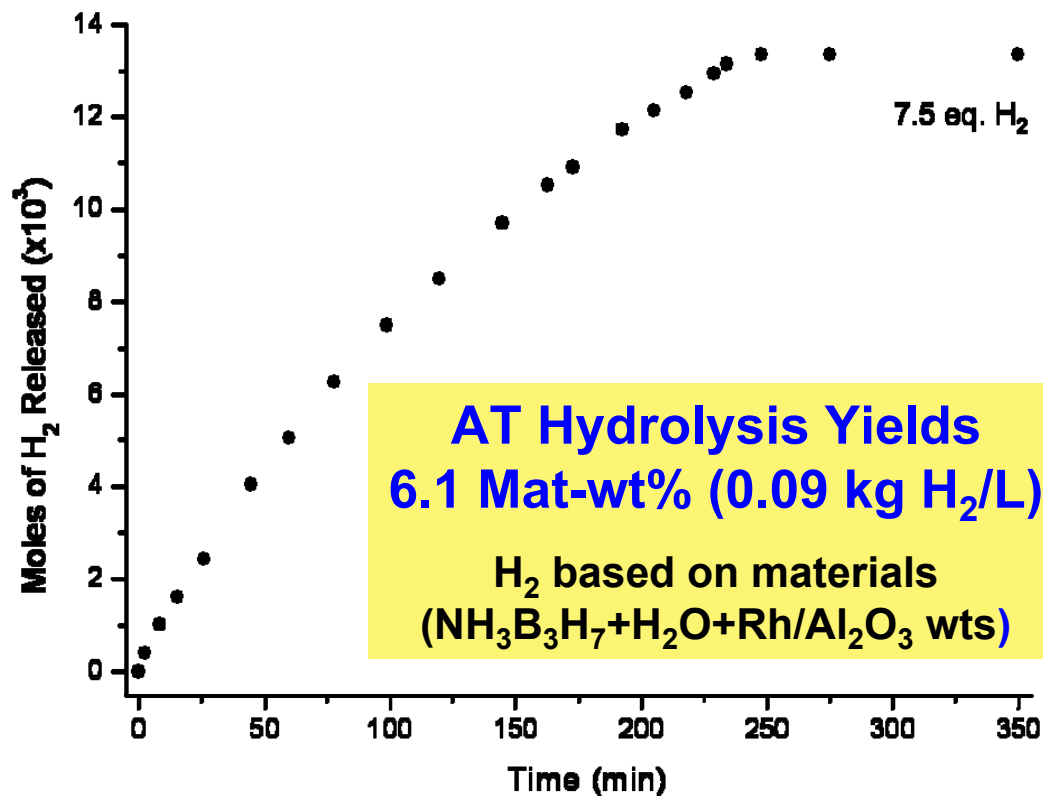
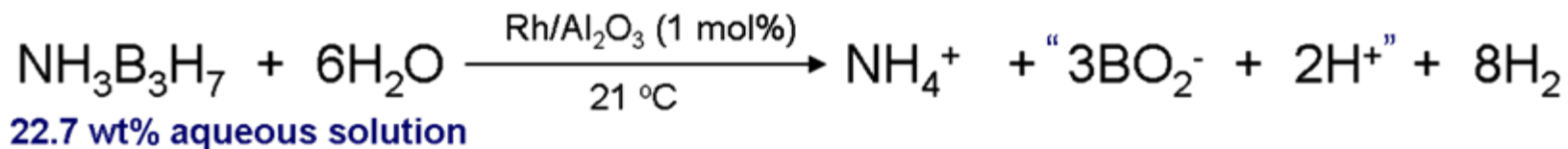


**Rh-Catalysts Have Extended Lifetimes**



H<sub>2</sub> release following 11-additions of AT to an aqueous solution containing 5wt%-Rh/Al<sub>2</sub>O<sub>3</sub>.

# 2007: Can Ammonia Triborane Hydrolysis Be Used To Achieve DOE Targets?



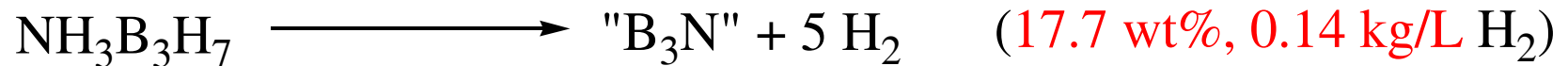
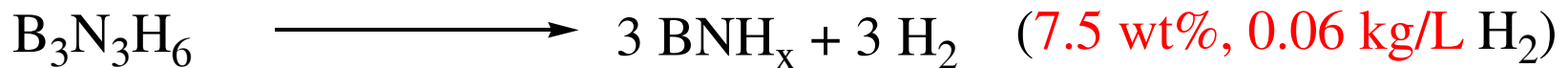
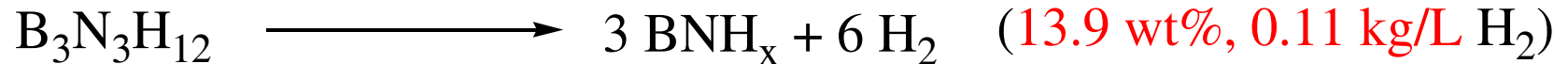
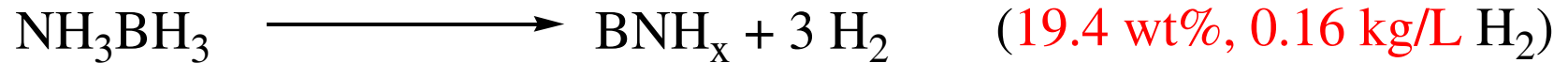
DOE total-system targets:

**2007, 4.5 wt%;** 2010, 6.0 wt%;  
2015, 9.0 wt%

**DOE 2007 wt%-target may be possible, but 2010 and 2015 targets will not be attainable with a hydrolysis-based system!**



# Thermolytic Hydrogen Release from Amineboranes Could Meet DOE Targets



## Key questions that we have been addressing since the last review:

- How can both the extent and rate of hydrogen release from ammonia borane and ammonia triborane be increased?
- How can the dehydrogenation products be regenerated?

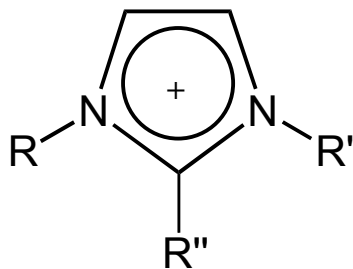
# **2007: The Extent and Rate of H<sub>2</sub>-Release from AB and AT Can Be Increased By:**

- 1. Ionic Liquids**
- 2. Chemical Promoters**

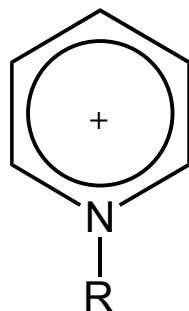
# 1. Why Ionic Liquid Solvents for Amineborane Dehydrogenations?

## Ionic Liquid Solvents

**Cations:**



N,N'-imidazolium



N-pyridinium

**Anions:**

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

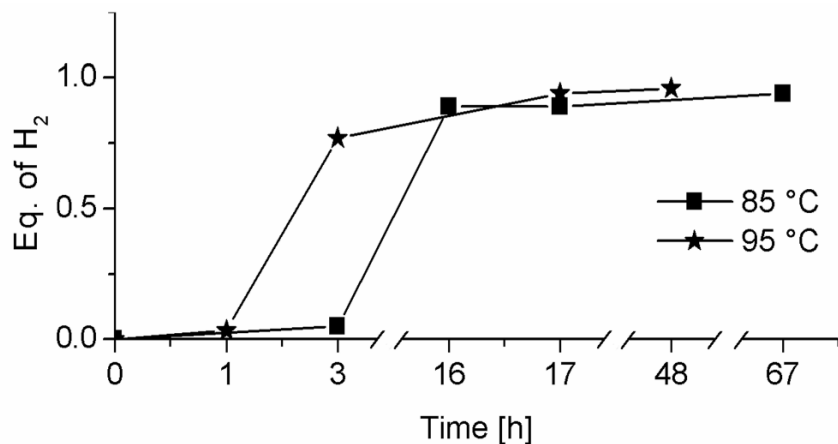
*Inert:*  $\text{PF}_6^-$ ,  $\text{BF}_4^-$ ,  $\text{Cl}^-$

## 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<sub>11</sub>

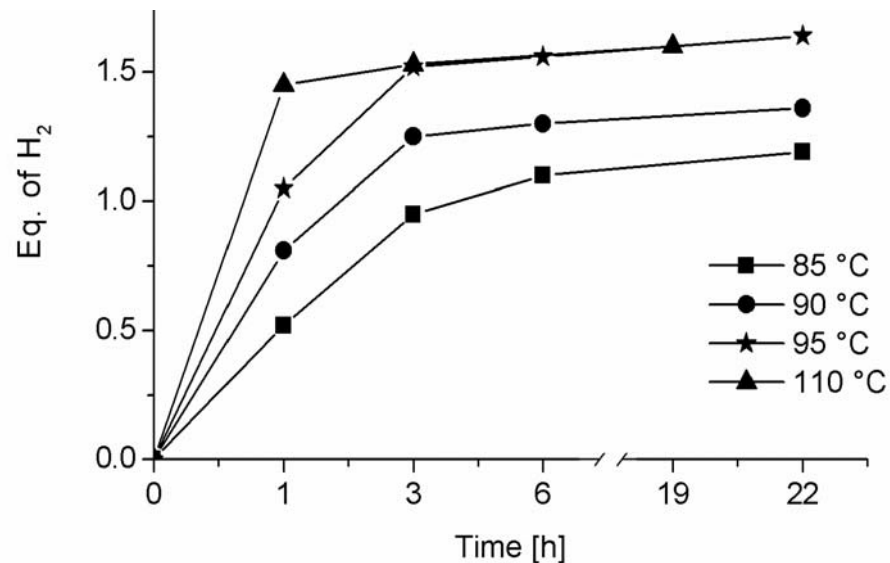
# 2006: Ionic Liquids Increase the Rate and Extent of H<sub>2</sub>-Release from AB and Eliminates Induction Period

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



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

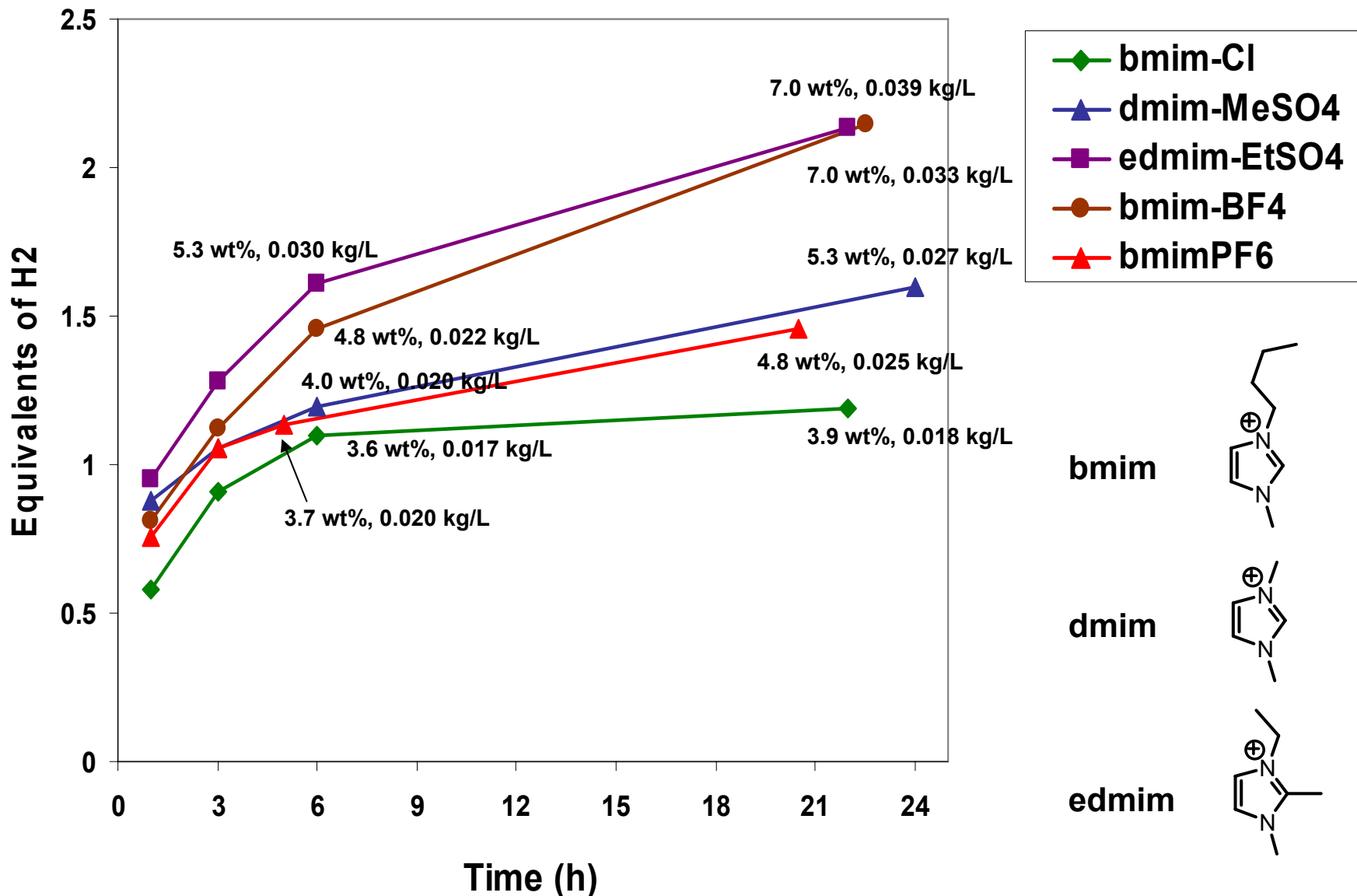
(50:50 wt% mixture)



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

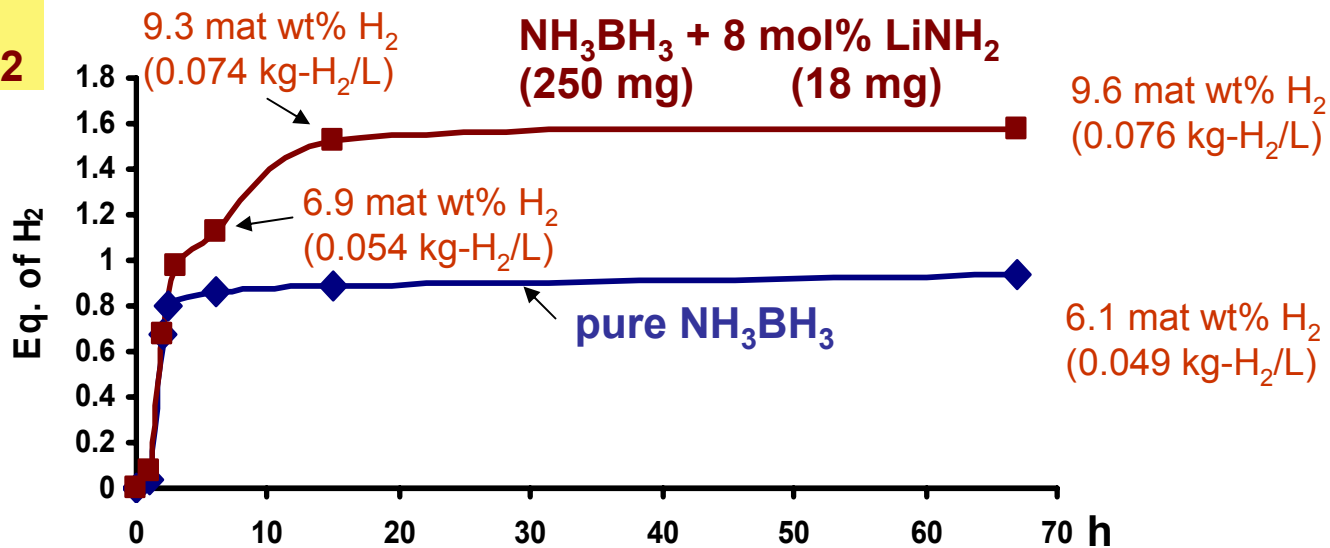
Bluhm, M. E.; Bradley, M. G.; Butterick, R.; Kusari, U.; Sneddon, L. G.  
*J. Am. Chem. Soc.* **2006**, *128*, 7748-9.

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

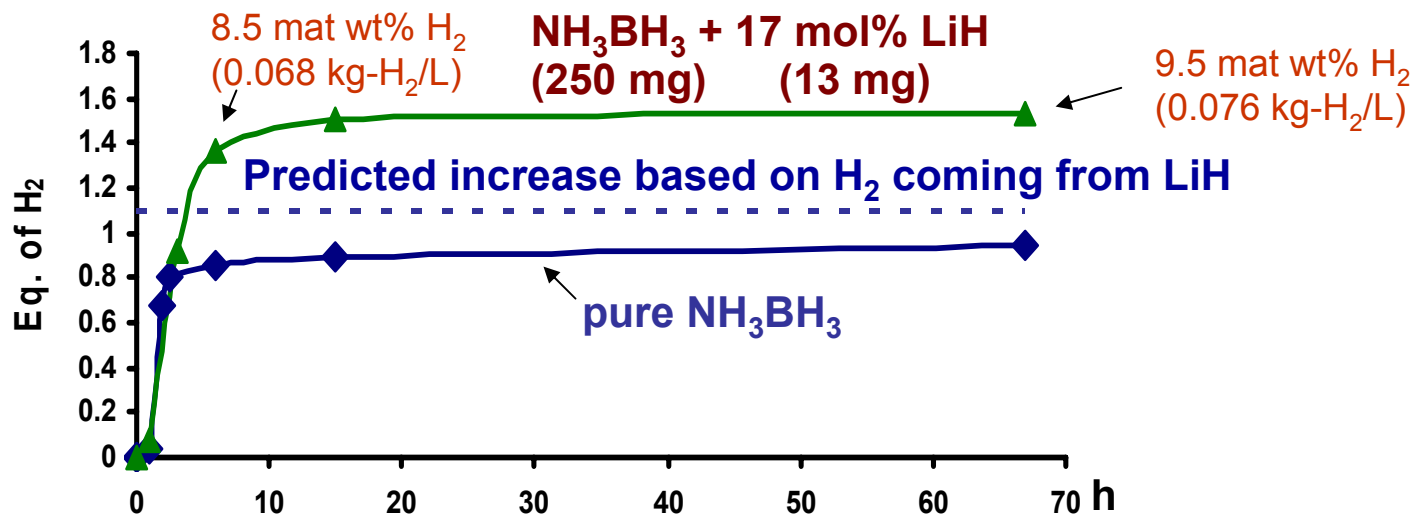


## 2. 2007: Solid-State AB Releases 9.5 Mat-Wt% H<sub>2</sub> at 85 °C with LiNH<sub>2</sub> and LiH Chemical Promoters

**AB/LiNH<sub>2</sub>**

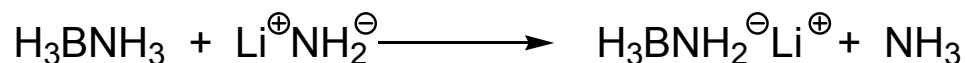


**AB/LiH**

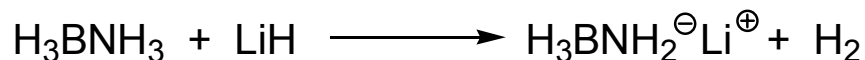


# 2007: Studies Reveal Possible Mechanisms for AB/LiNH<sub>2</sub> and AB/LiH H<sub>2</sub>-Release Reactions

## First Step: Proton Abstraction to Produce an Amine Borane Anion

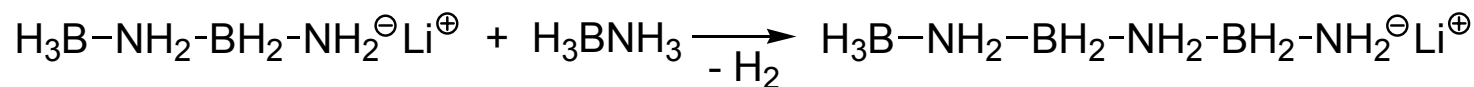
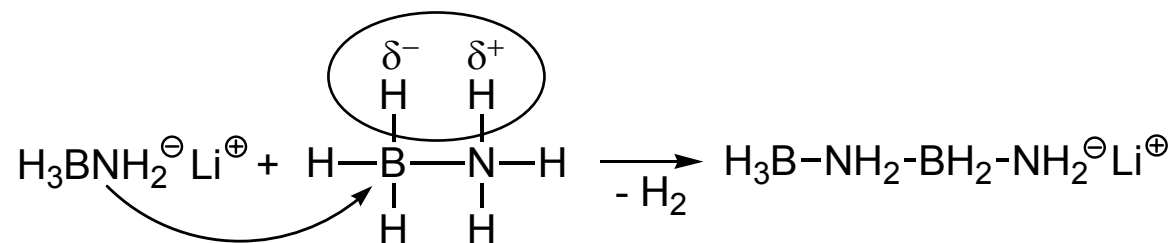


or

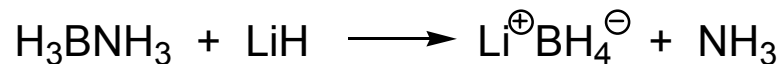
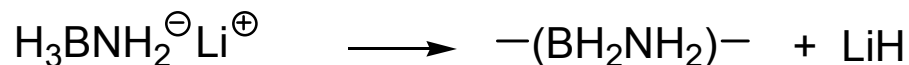


Computational studies of this mechanism are underway at Alabama (Dixon)

## Second Step: Anionic Dehydropolymerization



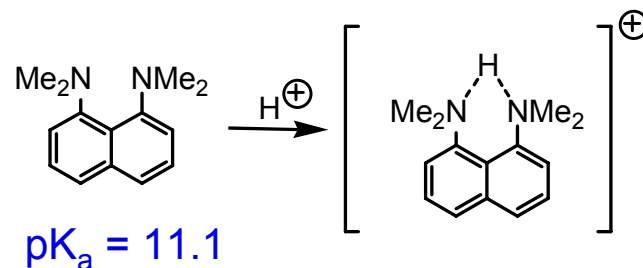
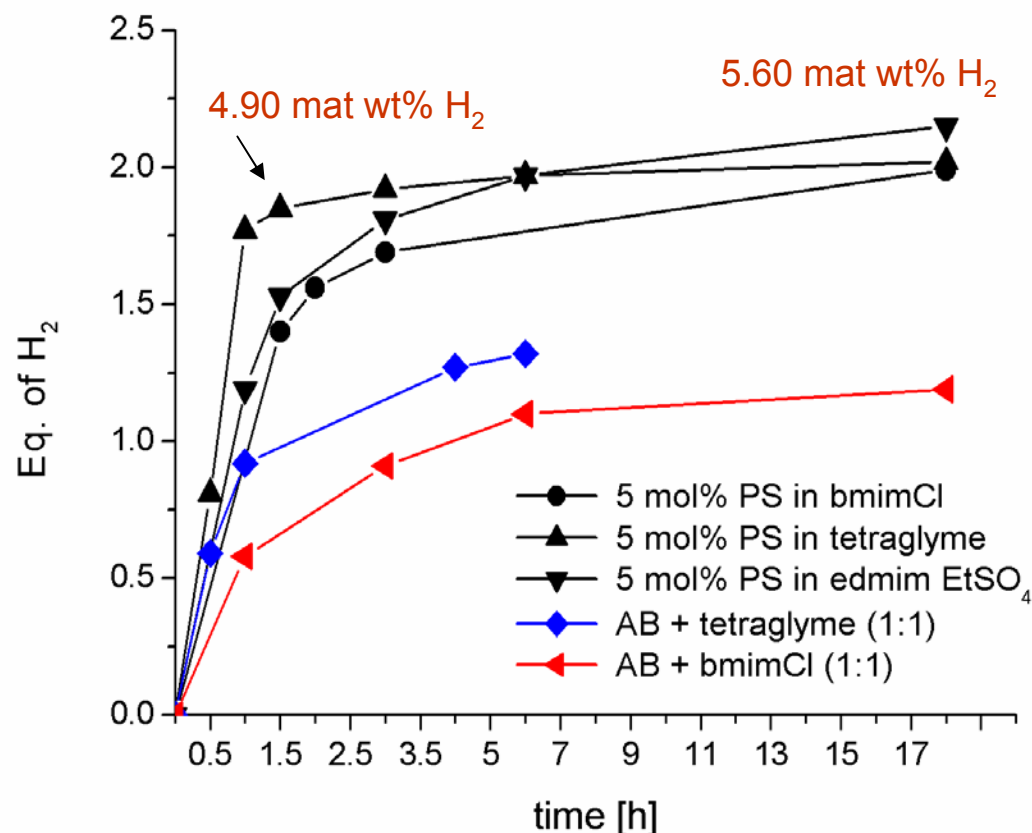
## Side Reactions Leading to the Formation of BH<sub>4</sub><sup>-</sup>:



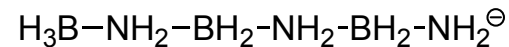
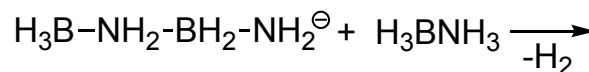
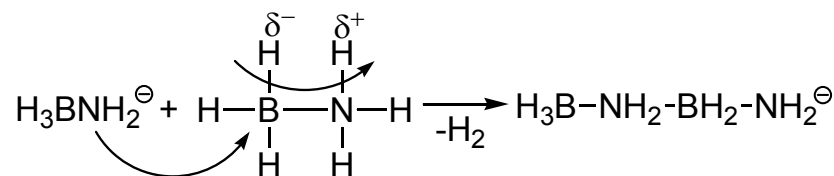
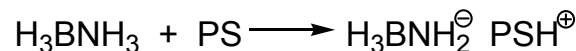
**Important Conclusion:**  
Formation of M<sup>+</sup>BH<sub>4</sub><sup>-</sup> and NH<sub>3</sub> must be eliminated to improve H<sub>2</sub>-release!

# 2007: Proton Sponge Increases H<sub>2</sub>-Release from AB Solutions 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)

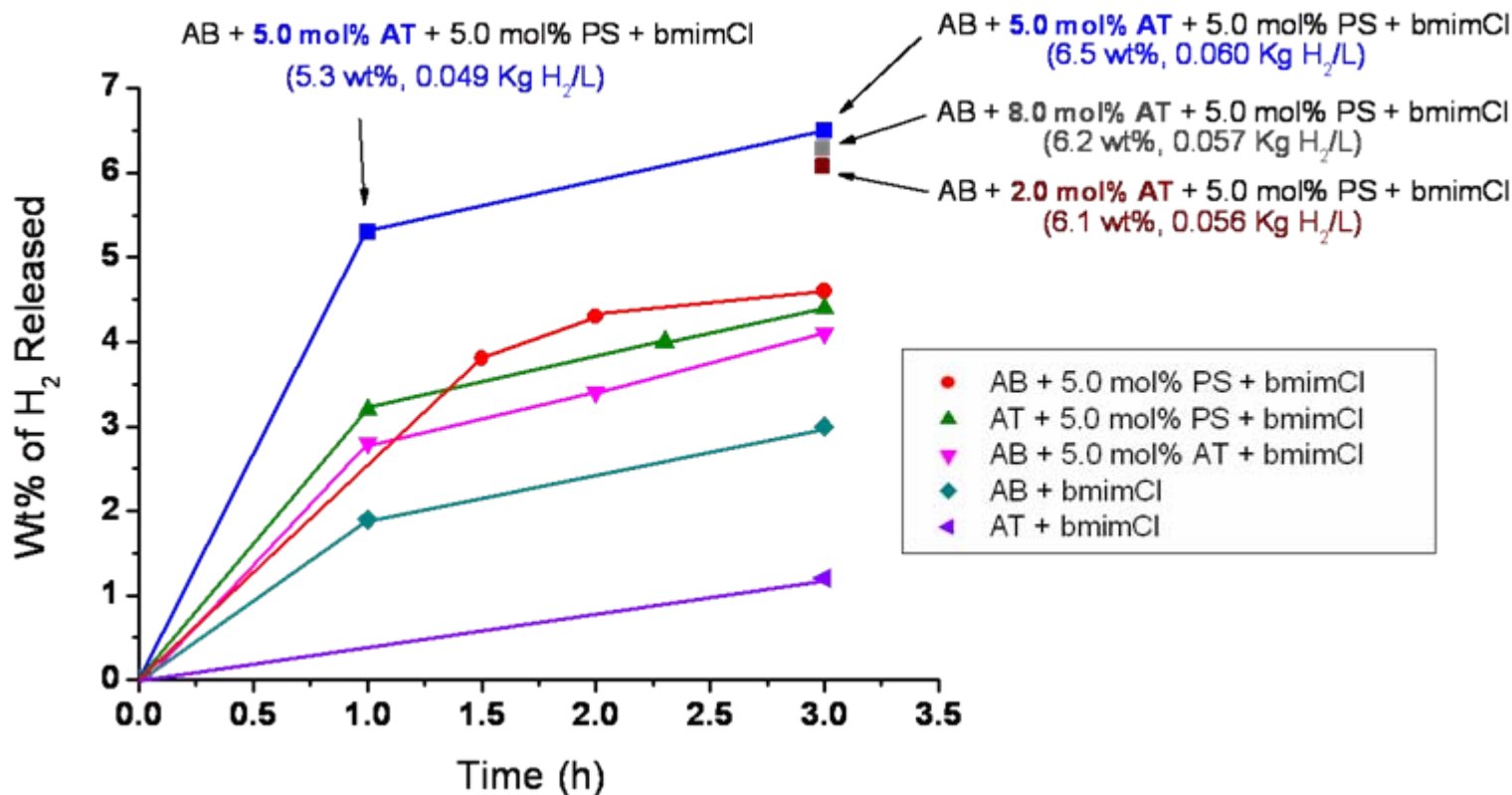


## Proton Sponge Reaction Mechanism





# 2007: PS Also Enhances H<sub>2</sub>-Release from NH<sub>3</sub>B<sub>3</sub>H<sub>7</sub> and NH<sub>3</sub>B<sub>3</sub>H<sub>7</sub>/NH<sub>3</sub>BH<sub>3</sub> Mixtures



**Conclusion: AB/AT mixtures may prove to be better for fast hydrogen release**

# System Comparisons and Progress Towards DOE Storage Targets

Metrics	Hydrolysis 22 °C	Thermolysis at 85 °C					
		Solid-State			Solution-State		
	22.7 wt% aq. AT (1.1 mol%Rh)	AB/LiNH <sub>2</sub> (9 mol%)	AB/LiH (17 mol%)	AB/AT(5mol%) /PS(5mol%)	AB/PS(5mol%) /bmimCl	AB/edmimCl	AB/AT(5mol%) /PS(5mol%)/bmimCl
Grav. density (Mat. wt%)	6.1, 4h	5.9, 3h 9.3, 15h	5.7, 3h 9.4, 15h	5.1, 1h 6.9, 3h	5.1, 3h 5.8, 6h	3.1, 1h 4.2, 3h 5.3, 6h	5.3, 1h 6.5, 3h
Vol. density (Kg-H <sub>2</sub> /L Mat.)	0.090, 4h	0.047, 3h 0.074, 15h	0.045, 3h 0.073, 15h	0.044, 1h 0.059, 3h	0.047, 3h 0.054, 6h	0.018, 1h 0.023, 3h 0.030, 6h	0.049, 1h 0.060, 3h
H <sub>2</sub> Flow Rate (g/s) per kg Material	0.0042, 4h	0.0055, 3h 0.0017, 15h	0.0053, 3h 0.0017, 15h	0.014, 1h 0.0064, 3h	0.0047, 3h 0.0027, 6h	0.0086, 1h 0.0038, 3h 0.0024, 6h	0.015, 1h 0.0060, 3h
Kg of Mat. for 0.8 mol/sec	377, 4h	295, 3h 938, 15h	304, 3h 931, 15h	114, 1h 250, 3h	342, 3h 599, 6h	186, 1h 420, 3h 670, 6h	108, 1h 267, 3h

**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)

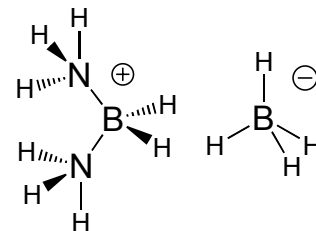
# **Amineborane-Based Chemical Hydrogen Storage**

## **Regeneration**

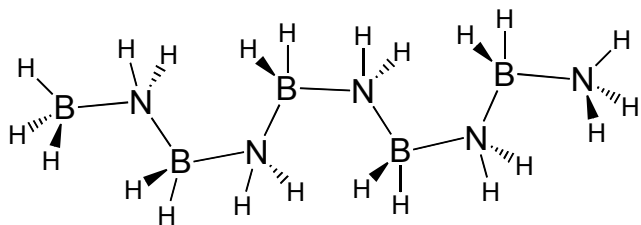
# Why is Regeneration A Difficult Problem?

**2006 DFT/GIAO/NMR Studies Showed That AB H<sub>2</sub>-Release Yields A Wide Range of Products with Greatly Differing Reactivities**

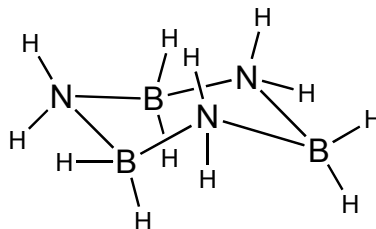
Bluhm, M. E.; Bradley, M. G.; Butterick, R.; Kusari, U.; Sneddon, L. G.  
*J. Am. Chem. Soc.* **2006**, *128*, 7748-9



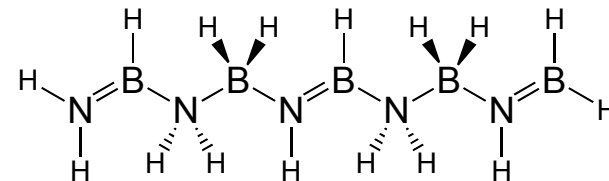
**Diammoniate of Diborane**



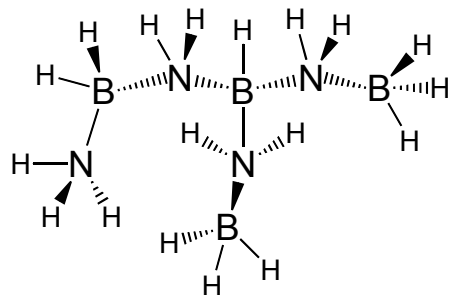
**Polyaminoborane**



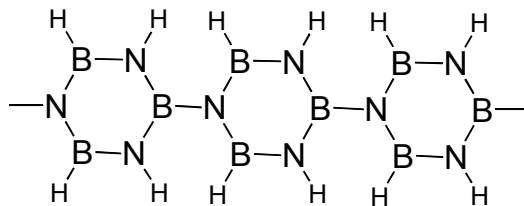
**Cyclotriborazane**



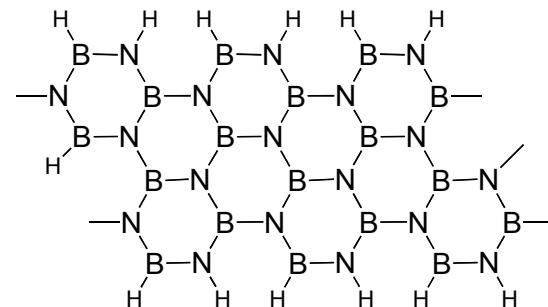
**Polyiminoborane**



**Branched Polyaminoborane**



**Polyborazylene**



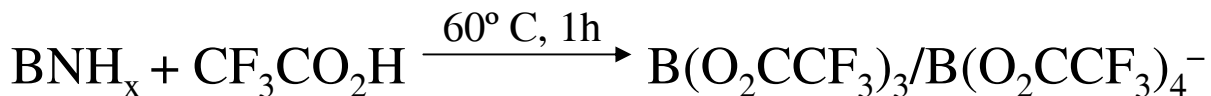
**Crosslinked Polyborazylene**

**A Viable Regeneration Method Must Be Efficient, Have Easy to Handle Reagents and Work for All Possible Spent-Fuel Species**

# 2006: Initial Penn Regeneration Method

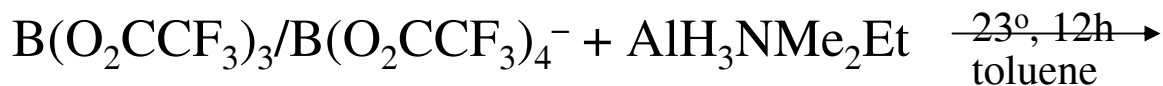
## Employed Strong Organic Acids

### Digestion



- The spent-fuel is completely digested by trifluoroacetic acid

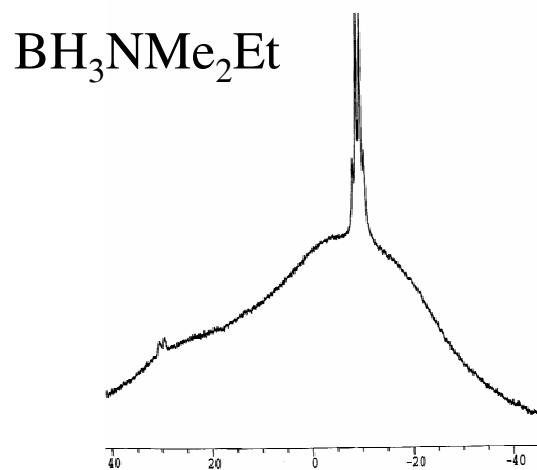
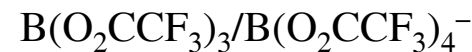
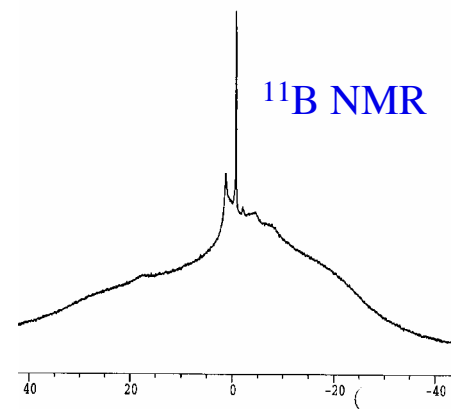
### Reduction to Borane



- Reduction regenerates a borane amine adduct

### Major Problems

- Trifluoroacetic acid is expensive and difficult to handle
- Ammonia is not recovered
- The reduction of B-O bonds requires a strong (and expensive!) reducing agent



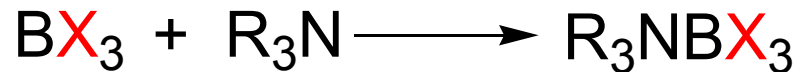
# 2007: New Penn Regeneration Process Avoids The Formation of B-O Bonds

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

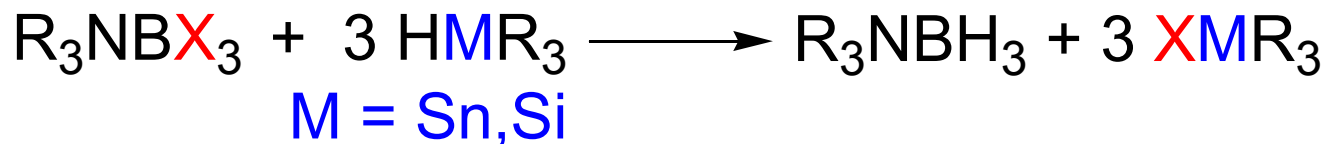


## Second Step: One-Pot Conversion of $\text{BX}_3$ to AB

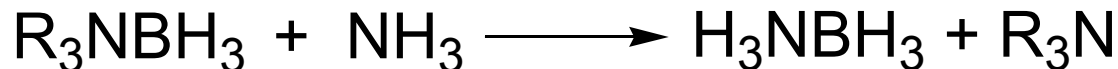
### Amine-Coordination of $\text{BX}_3$



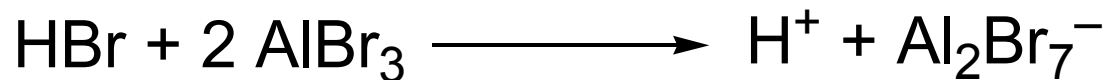
### BX Reduction



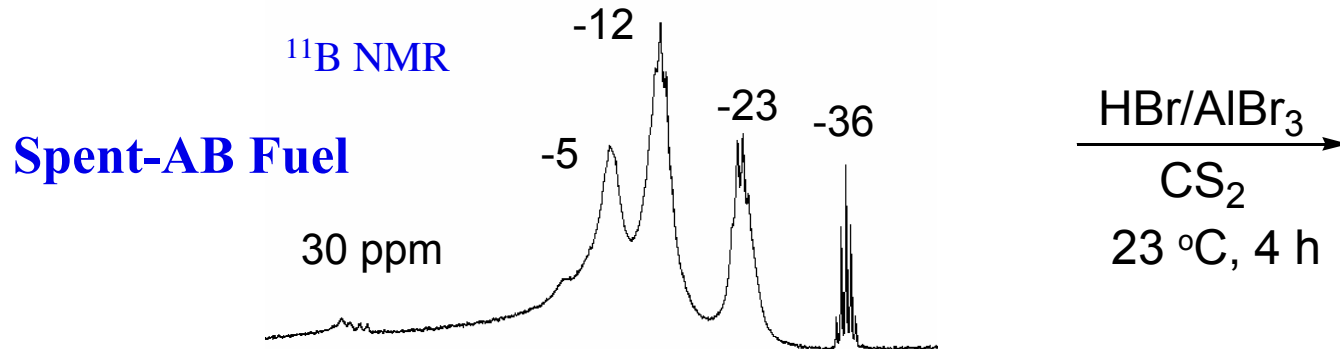
### Amine Displacement by $\text{NH}_3$ Yields AB



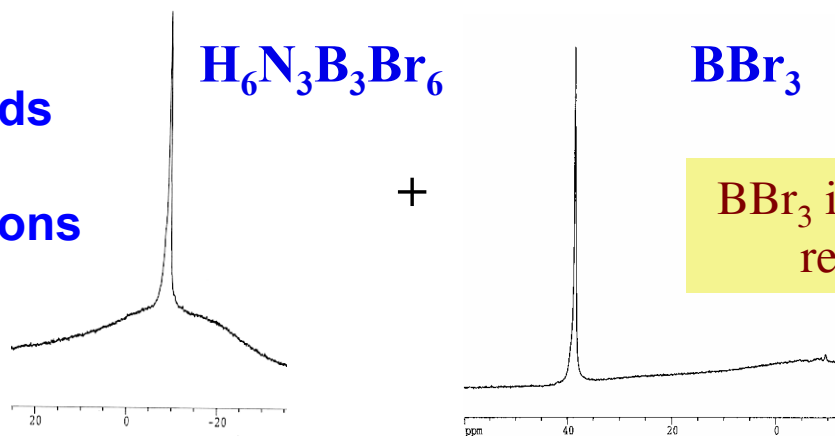
# 2007: Step 1. Digestion. Superacidic HX/AlX<sub>3</sub> Solutions Digest BNH<sub>x</sub> Spent-Fuels



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



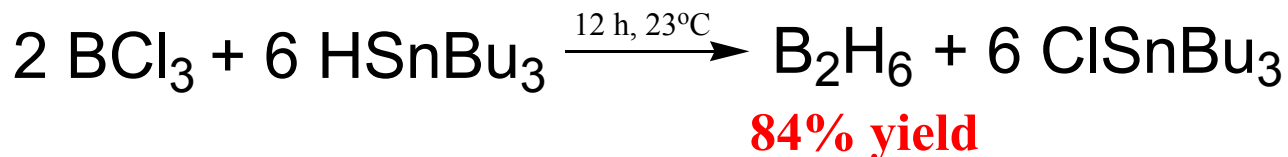
Product ratio depends upon spent-fuel reactants and conditions



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

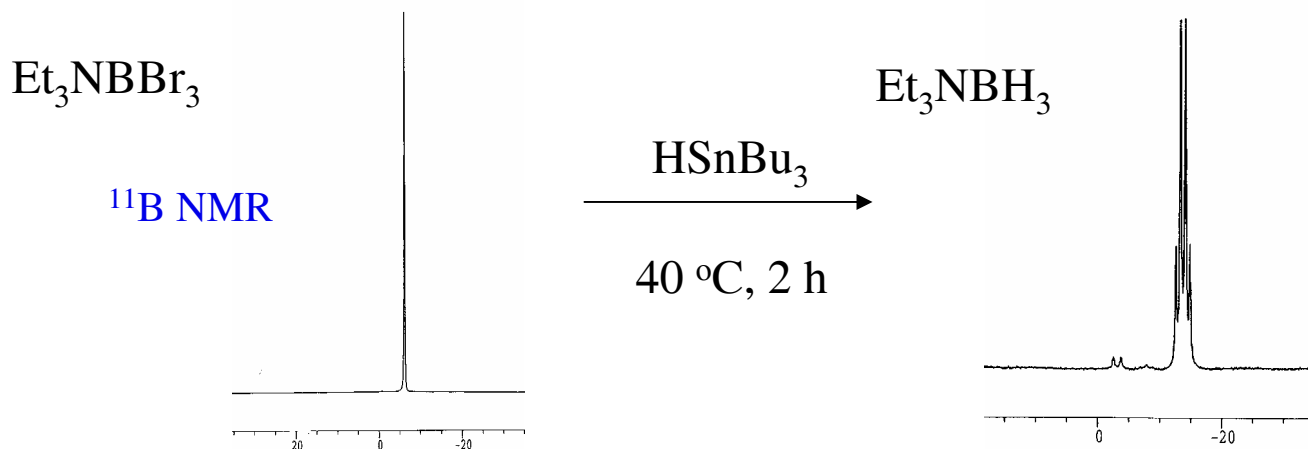
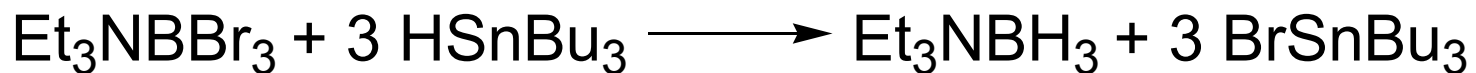
## 2007: Step 2. Coordination and Reduction. B-X Bonds Can Be Reduced by $\text{HMR}_3$ ( $\text{M} = \text{Sn}, \text{Si}$ )

High Yield  $\text{BCl}_3$  Reduction to Diborane by  $\text{HSnBu}_3$  Already Reported



Gaines, D. F.; Kunz, J. C.; Kulzick, M. J. *Inorg. Chem.* **1985**, *24*, 3336-8.

2007: Reduction of Amine-Coordinated  $\text{BBr}_3$  Has Now Been Achieved. This Step Avoids the Production and Handling of Hazardous Diborane

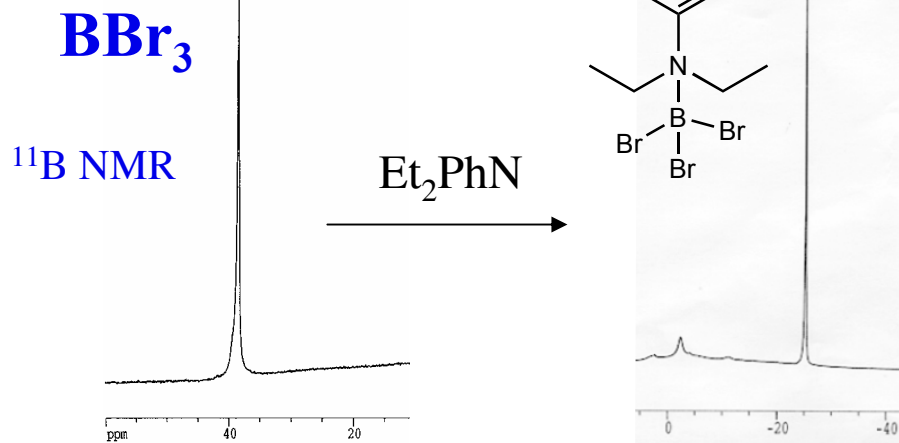




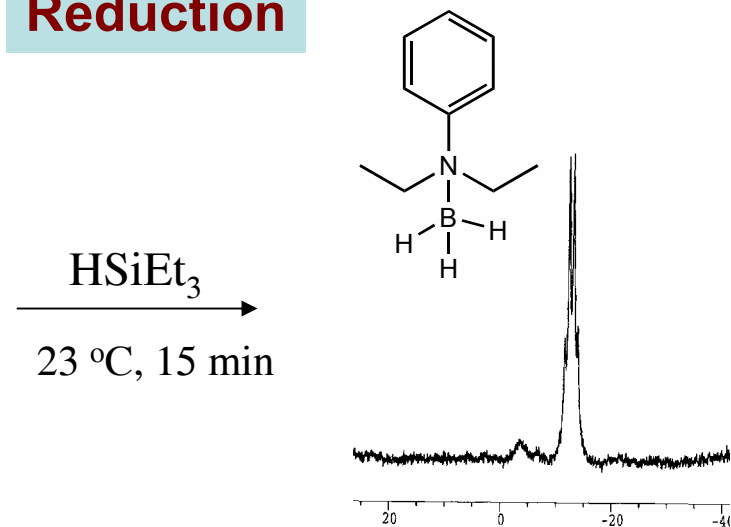
# 2007: Completed Step 2. Coordination, Reduction and Displacement to Regenerate AB from BBr<sub>3</sub>

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

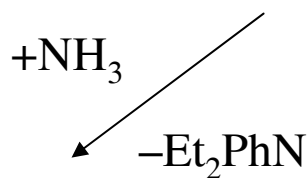
## Amine-Coordination



## 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



## Exchange



2006, Thorn, LANL

# 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
- Northern Arizona U.:** amineborane syntheses and properties, new liquid fuels
- Rohm and Haas:** provides starting materials for amineborane synthesis and general expertise in boron chemistry

**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 both solid and liquid-based H<sub>2</sub>-release systems and regeneration processes
- Rohm and Haas:** Engineering assessment and scale-up of new regeneration process

# Summary and Future Studies

## Achievements



## Ongoing and Future Studies

- Chemical additives, ionic liquids and metal catalysts have each been shown to increase the extent and rate of hydrogen release from amineboranes and several systems have been identified that have potential to meet DOE targets.
- Mechanistic studies indicate that  $\text{LiNH}_2$ ,  $\text{LiH}$  and Proton Sponge induce the anionic polymerization of AB, but that PS avoids the formation of  $\text{LiBH}_4$  and  $\text{NH}_3$ .
- A new process for ammonia borane regeneration has been demonstrated.

- Continue to develop and optimize chemical-additive systems with improved hydrogen release rates for thermolytic processes.
- Optimize mixed AB/AT and new AB/methylamine-borane processes.
- Determine which of the AB or AT dehydrogenation products have the highest regeneration activities.
- Work with Center partners to refine and optimize the new AB regeneration process.