

**DOE Chemical Hydrogen Storage  
Center of Excellence:  
Center Overview  
&  
Los Alamos National Laboratory  
Contributions**

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5/16/06**

Project ST1

# Objective DOE Chemical Hydrogen Storage Center

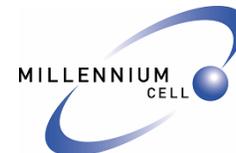
Identify, research, develop and validate advanced on-board chemical hydrogen storage systems to overcome technical barriers and meet 2010 DOE system goals with the potential to meet to 2015 goals:

- Develop materials, catalysts and new concepts to control thermochemistry and reaction pathways
- Assess concepts and systems using engineering analysis and studies
- Select most promising chemical systems for engineering development
- Develop life cycle inventory and demonstrate a 1 kg storage system

- More efficient borate-to-borohydride (B-OH to B-H) regeneration
- Alternative boron chemistry to avoid thermodynamic sinks using polyhedral boranes (B<sub>x</sub>H<sub>y</sub>) or amine-boranes
- Concepts using coupled endo/exothermic reactions, nanomaterials, heteroatom substitution for thermodynamic control



PENNSTATE



# Science of Chemical Hydrogen Storage

- **CAPACITY**

- Develop, synthesize, test compounds with high hydrogen density, proper energetics, and potential pathways
- Theory and modeling for insight

- **HYDROGEN RELEASE**

- Pathways: avoid large thermodynamic sinks, byproducts
- Rates: study mechanisms
- Develop and optimize catalysts and catalytic processes

- **REGENERATION**

- Develop pathways closer to thermodynamic limits
  - » Avoid high energy intermediates
  - » Use regenerable intermediates

*Theory* ↔ *Experiment* ↔ *Assessment*

# Center Projects

	<b>Project</b>	<b>Partners</b>
<b>1.1</b>	<b>B-O to B-H Engineering Guided Research</b>	<b>ROH, MCEL, PSU, Ala, USB, PNNL, LANL</b>
<b>1.2</b>	<b>Engineering Assessment of Hydrogen Generation Systems</b>	<b>MCEL, ROH, LANL, PNNL</b>
<b>2.1</b>	<b>Polyhedral Borane Chemistry</b>	<b>UCLA, IMX, PSU, PNNL, LANL</b>
<b>2.2</b>	<b>Amine-Borane Chemistry</b>	<b>Penn, UW, NAU, Ala, IMX, PNNL, LANL</b>
<b>2.3</b>	<b>Amine-Borane Systems Engineering, Safety</b>	<b>PNNL, NAU, LANL</b>
<b>3.1</b>	<b>Organics and Coupled Reactions</b>	<b>Ala, PNNL, LANL</b>
<b>3.2</b>	<b>Nanoparticles and Main Group Hydrides</b>	<b>UC Davis, Ala, LANL</b>

# Summary and Key Developments

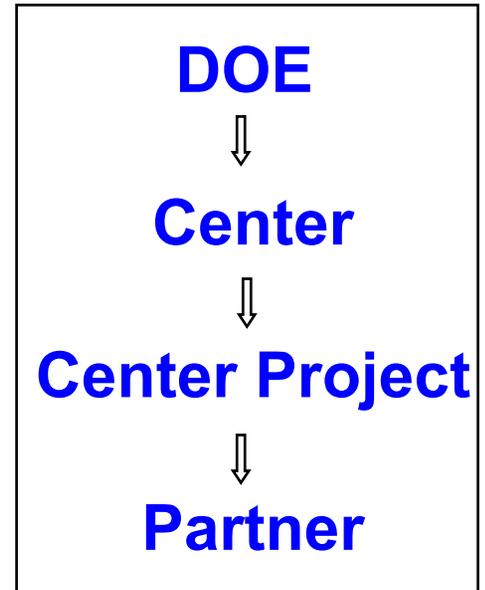
- **B-OH → B-H**
  - New concepts for electrochemical reduction of B-OH(OR) bonds
  - Options and spreadsheet (energetics)
- **On-board storage engineering**
  - Engineering assessment tools being developed and engineering analysis in progress
  - On-board generation models with SBH as a prototypical system
- **Polyhedral boranes**
  - Catalytic hydrolysis of polyhedral boranes
- **Ammonia borane (AB) dehydrogenation**
  - Inclusion in mesoporous materials alters rate and selectivity
  - Acid catalysts can lead to multiple dehydrogenation from AB
  - Rapid single dehydrogenation with Ir catalysts
  - Multiple dehydrogenation of AB is facile with homogeneous electron-rich precious metal complexes
  - The first examples of non-precious metal catalysts have been discovered

# Summary and Key Developments (cont.)

- **Ammonia borane (AB) dehydrogenation (cont)**
  - Heterogeneous catalysts have been discovered (including rapid screening)
  - Alternative reaction media can open up new reaction pathways
  - Kinetics and mechanistic studies underway
- **AB regeneration concept development/demonstration**
  - Dissolution, hydride transfer, regenerable hydrides, ligand exchange
- **Organic systems**
  - Theory on thermodynamics
  - Hydrogen release demonstrated
  - Coupled reactions
- **Nanophase materials**
  - Developing routes to H-loaded Si and  $\text{Si}_x(\text{NH}_2)_n$

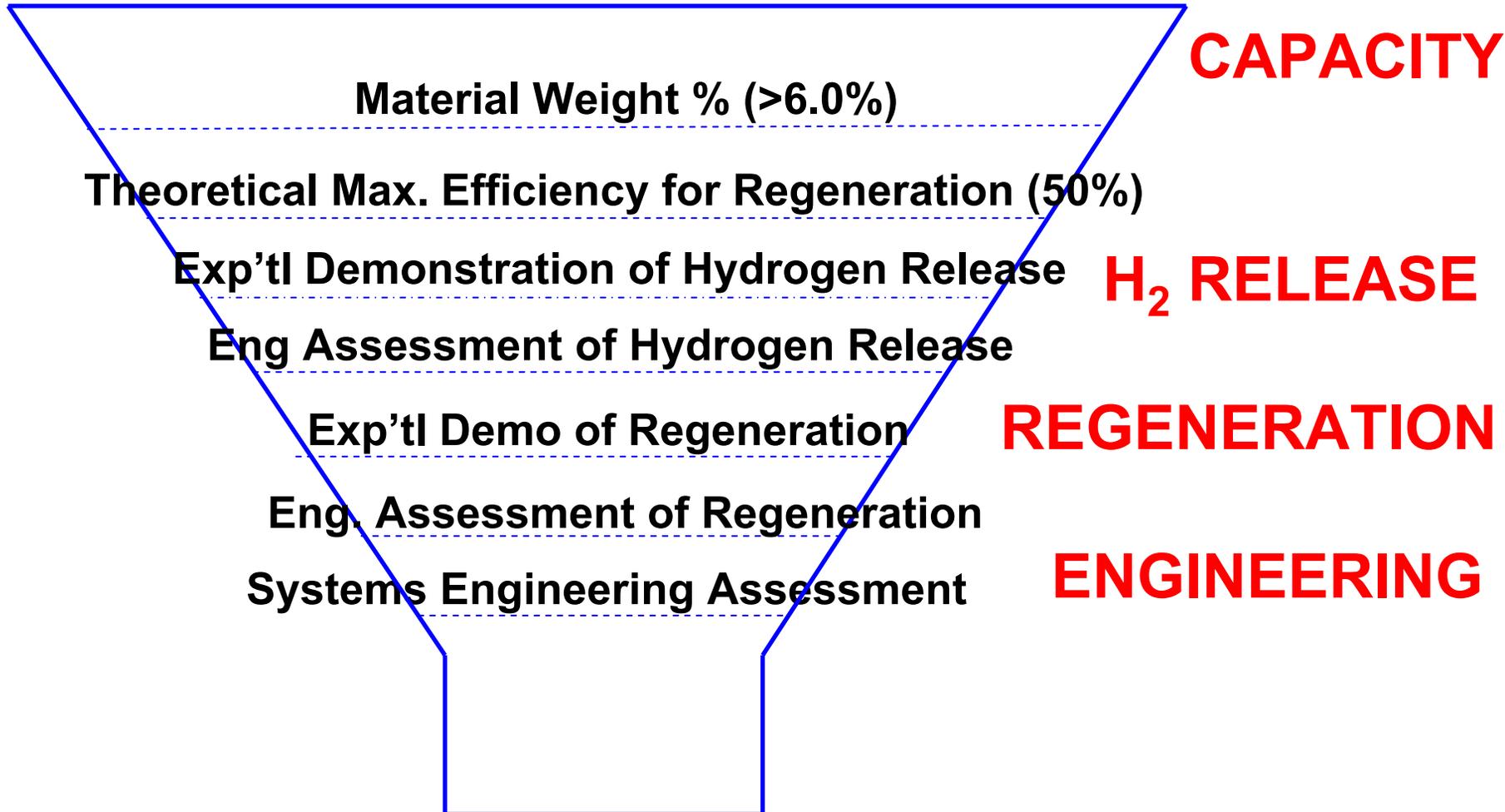
# FY06 Center Coordination

- **Planning**
  - **Develop performance-based approach**
  - Develop implementation plan
  - Develop Center and Project Milestones  
in accordance with DOE's multiyear R&D plan
- **Implementation**
  - Center and Center Project meetings
  - Site visits
  - Monthly Center Project conference calls
  - Internal website
  - Regular PI-PI communication/email
  - Personnel exchange
  - Coordinating council
    - » Establish go/no-go decision process and recommendations to DOE
    - » Communicate lessons learned and safety aspects
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    - » Promote outreach activities
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# Performance-Based Approach

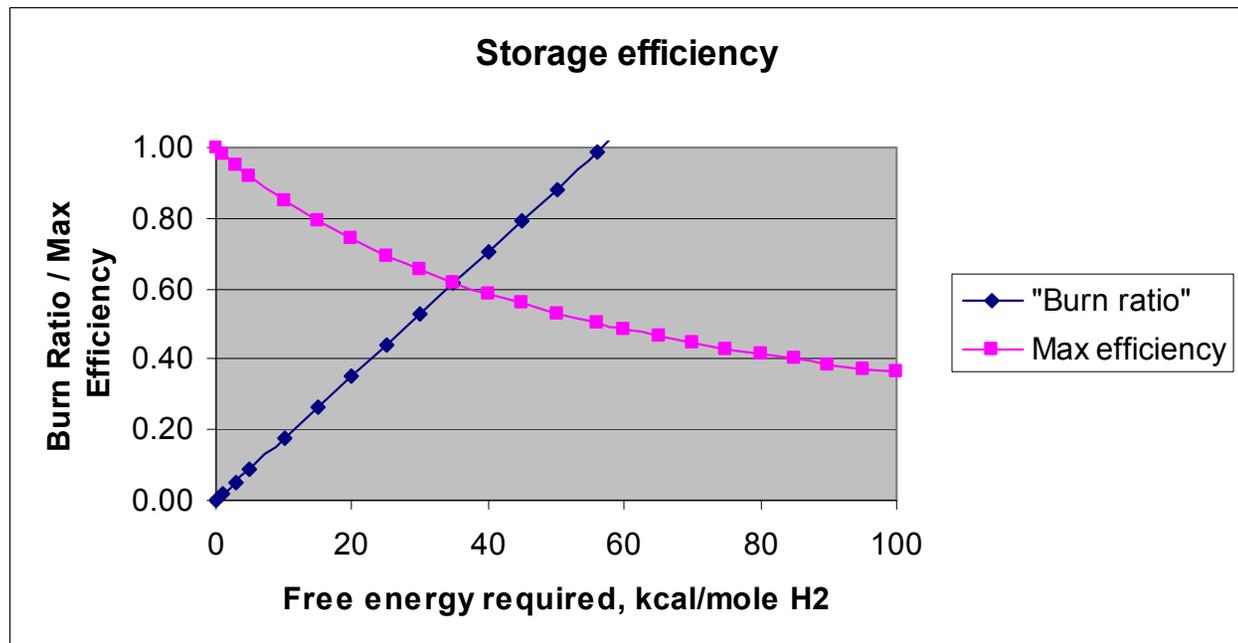
## POTENTIAL CANDIDATES



## VIABLE SYSTEMS

# Thermodynamic Maximum Storage Efficiency: “Burn ratio”

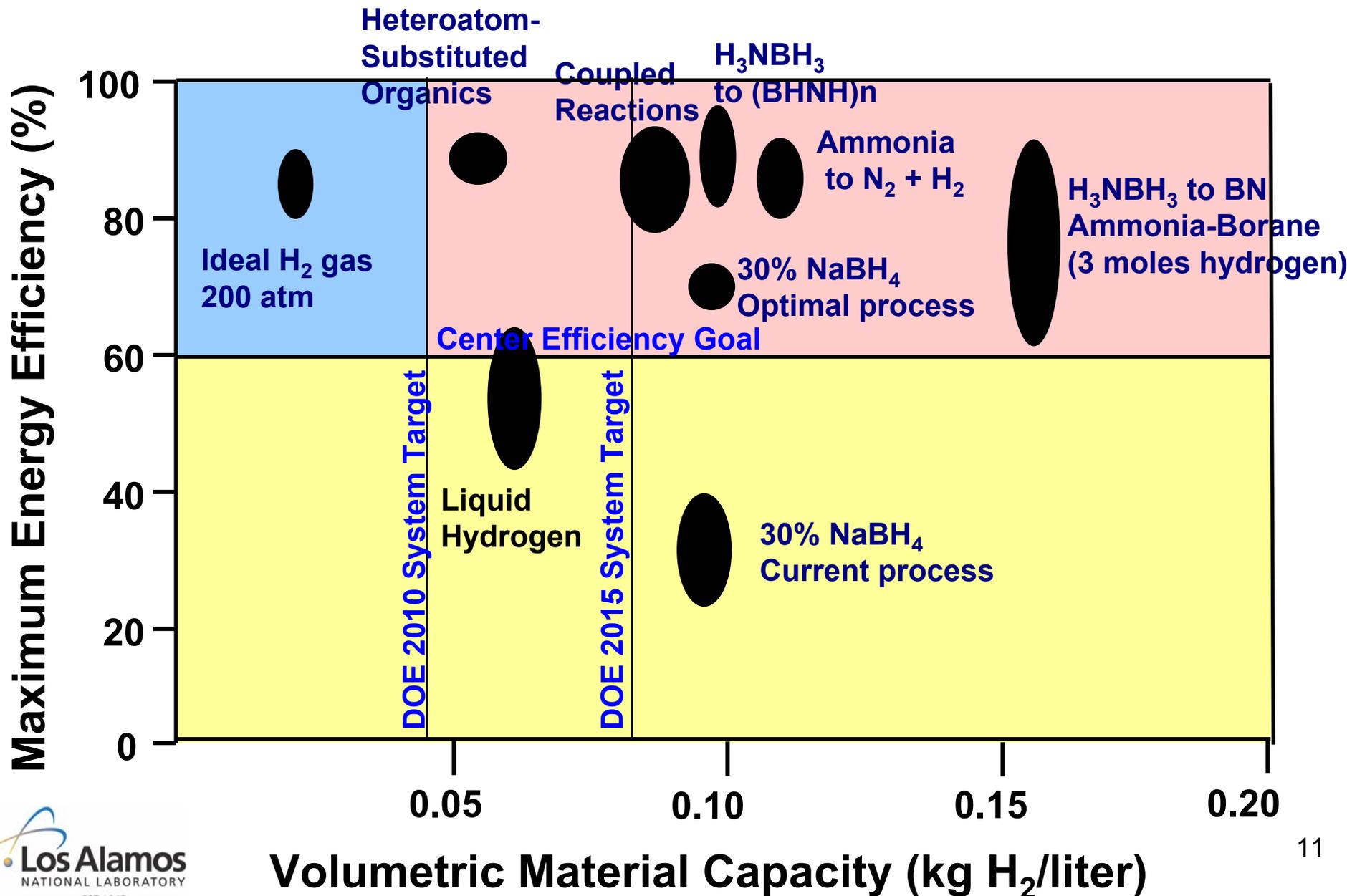
- Consider the (hypothetical) chemical regeneration process as the reverse of the hydrogen release reaction
- Calculate  $\Delta G^0$  for this process, per  $H_2$  stored
  - (use G instead of H to allow for unfavorable entropy of storing  $H_2$ )
- Define “burn ratio” as amount of  $H_2$  that must be burned to provide this  $\Delta G^0$ 
  - one  $H_2$  provides 56.7 kcal of free energy [UHV]
- Efficiency =  $1/(1+\text{burn ratio})$



# Storage Capacities and Efficiencies

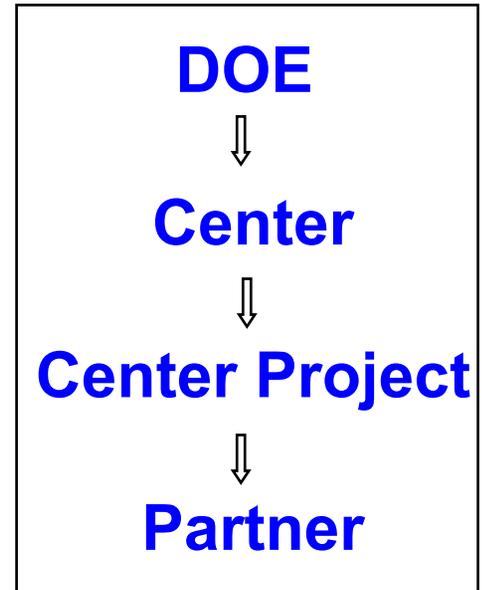
Hydrogen release reaction	Regeneration reaction	no. of H2 for release reaction as written	mwt of all reactants (including water)	density of reactants	deltaH0 of release reaction, kcal	delta G0 of release reaction, kcal	"burn ratio", higher of Delta G0 or Delta H0	max ideal efficiency	Grav density, wt% H2	Vol density, kg H per liter	volumetric target met	gravimetric target met	efficiency goal met
NaBH4 + 2 H2O	NaBO2 + 4 H2	4	73.86	1.4	-50.72	-76.00	0.34	74.9%	10.918	0.15285	2015	2015	>70%
NaBH4 + 5 H2O (approx 11 M, 30%)	NaBO2 + 4H2	4	127.9	1.4	-50.72	-76.00	0.34	74.9%	6.30493	0.08827	2015	2010	>70%
formic acid	CO2 + H2	1	46.03	1	7.55	-7.60	0.13	88.2%	4.37975	0.0438	2007	none	>70%
B10H14	10B(s) + 7 H2	7	122.22	1	6.9	-49.90	0.13	88.8%	11.5464	0.11546	2015	2015	>70%
silane condensation	Me3Si-SiMe3 + H2	1	148.4	1	-2	-8.00	0.14	87.6%	1.35849	0.01358	none	none	>70%
paraformaldehyde+H2O = CO2 +H2	CO2 + 2 H2	2	48.04	1	16.71	-8.98	0.12	89.1%	8.39301	0.08393	2015	2010	>70%
MgO.CH3OH + H2O	MgCO3 + 3 H2	3	90.36	1.4	3.45	-13.29	0.08	92.7%	6.69323	0.09371	2015	2010	>70%
hexahydrotriazine	triazine + 3 H2	3	87.12	1	17	-9.00	0.08	92.3%	6.94215	0.06942	2010	2010	>70%
BH3NH3 to BN	BN + 3 H2 = BH3NH3	3	30.87	0.76	-23.4	-45.50	0.27	78.9%	19.5918	0.1489	2015	2015	>70%
BH3NH3 to BHNH (borazine)	BHNH + 2 H2 = BH3NH3	2	30.87	0.76	-6.5	-23.10	0.20	83.1%	13.0612	0.09927	2015	2015	>70%
C6H12 -> C6H6 + 3 H2	C6H6 + 3 H2	3	84.16	1	49.08	23.35	0.24	80.7%	7.18631	0.07186	2010	2010	>70%
CH3OH + H2O -> CO2 + 3 H2	CO2+3H2	3	50.06	1	31.41	2.22	0.15	86.7%	12.0815	0.12082	2015	2015	>70%
C10H18 -> 5 H2 + C10H8	C10H8 + 5H2	5	138.25	1	85.56	39.01	0.25	80.0%	7.29114	0.07291	2010	2010	>70%
2 NH3 = N2 + 3 H2 (liquid density at bp)	3 H2 + N2 = 2 NH3	3	34.06	0.682	21.94	7.84	0.11	90.3%	17.7569	0.1211	2015	2015	>70%
MgCl2.6(NH3) = MgCl2 + 3N2 + 9H3 (assume 10 kcal binding enthalpy per NH3, 2 kcal binding free energy)	MgCl2+3N2+9H3	9	197.39	1.239	126	36	0.21	83.0%	9.19196	0.11389	2015	2015	>70%

# Chemical Hydrogen Storage



# FY06 Center Coordination

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  - Develop performance-based approach
  - **Develop implementation plan**
  - **Develop Center and Project Milestones**  
in accordance with DOE's multiyear R&D plan
- **Implementation**
  - Center and Center Project meetings
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# Center Coordination: Looking Ahead

- **Planning**

- Based on results, assessments, meetings
- Coordinate project transition and down-selection
- Negotiate project changes, technical direction

- **Key FY06 Center Decisions**

- Develop milestones and go/no-go criteria for FY07 decision on sodium borohydride
- Increase coordinated effort on catalytic dehydrogenation of ammonia-borane, including mechanisms and product characterization
- Accelerate development of BN regeneration concepts
- Integrate exploratory organic-based efforts into a Center project on non-Boron material development

# Center Path Forward

- **Go/no-go on sodium borohydride (FY07)**
  - Determine feasibility and provide a go/no-go recommendation for Sodium Borohydride (SBH) hydrolysis on-board storage system based on modeling and laboratory-scale experimental demonstration of energy efficient regeneration off-board.
  - Criteria development
  - Center milestones by quarter
- **Ammonia-borane**
  - Increase rates for AB dehydrogenation
  - Enhance spent AB regeneration scheme
- **Optimization and evaluation of other boron-containing systems**
- **Coordinated effort on non-boron organic system**
- **Exploratory research on other options**
- **Prepare for down-selection of storage material**
  - Criteria development

# FY07 Milestones

- **FY07 Milestones:**
  - Complete assessment of the most energy-efficient routes for indirect regeneration of sodium borate to sodium borohydride (complexed borates)
  - Down-select catalysts and chemical processes (2-3 candidates max) for hydrogen generation from ammonia-borane
  - Down-select to organic materials and polyhedral boranes (3-5 candidates max) along with associated processes for hydrogen generation
  - Down-select from chemical hydrogen regeneration processes for sodium borohydride.
  - Complete assessment of ammonia borane regeneration routes to assist in down selection process
  - Complete assessment of nanoparticles for hydrogen storage capacity
  - Complete assessment for regeneration of organics and polyhedral boranes to assist in down-selection process
- **Go/No Go Decision on Sodium Borohydride (4QFY07)**

# Center Partners

- **Penn: Prof. Larry Sneddon**
  - Martin Bluhm (PD), Prof. Mark Bradley, William Ewing (GS)
- **UCLA: Prof. Fred Hawthorne**
  - Satish Jalisetgi (PD), Bhaskar Ramachandran (PD), Robert Kojima (GS), Thomas Quickel (GS), Colin Carver (GS)
- **Penn State: Prof. Digby Macdonald**
  - Justin Tokash (GS), Jason McLafferty (GS), Yancheng Zhang (PD)
- **Alabama: Profs. Dave Dixon, A. Arduengo**
  - Owen Webster, Monica Vasiliu, Luigi Iconaru, Michael Phillips, Daniel Grant (GS), Jacob Batson (UGS), Myrna Hernandez Matus (PD), Prof. Minh Nguyen
- **UW: Profs. Karen Goldberg, Mike Heinekey**
  - Melanie Denney (PD), Vincent Pons (PD)
- **UC Davis: Profs. Susan Kauzlarich, Phil Power**
  - Japhe Raucher (GS), Li Yan Wang (PD)
- **NAU: Prof. Clint Lane**
- **Rohm and Haas: Sue Linehan**
  - Frank Lipiecki, Arthur Chin, John Yamamoto, Leo Klawiter,, James Vouros,, Sam November, Aaron Sarafinas, Alan Keiter, Wendy Bingaman Jay Soh, and Robert Wilczynski; Larry Guilbault and Duane Mazur (consultants)
- **Millennium Cell: Ying Wu**
  - Jeffrey Orgeta, Robert Molter, Rick Mohring, Mike Kelly, Todd Randal, Roxanne Spencer
- **Intematix: Xiao-Dong Xiang**
  - Wei Shan, Jonathan Melman
- **US Borax: Dave Schubert**
  - Jonathan Owen
- **PNNL: Chris Aardahl**
  - Tom Autrey, Maciej Gutowski, Anna Gutowska, John Linehan, Scot Rassat, Wendy Shaw, Ashley Stowe, Mike Thompson
- **LANL:**
  - R. Thomas Baker, Anthony Burrell, Fernando Garzon, P. Jeffrey Hay, Neil Henson, Kevin John, Karl Jonietz, Richard Keaton (PD) , Dan Kelly, Kevin Ott, Bobbi Roop, Dan Schwarz (PD), Frances Stephens (PD), David Thorn

**US Department of Energy EERE**

# Los Alamos National Laboratory Contributions to DOE Center

R. T. Baker

F. Stephens

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K. C. Ott

J. Stairs

J. Rau

T. Cameron

P. J. Hay

J. Webb

N. Henson

T. Semmelsberger

B. Roop

C. Macomber

W. Tumas

**May 16, 2006**

This presentation does not contain any proprietary or confidential information

# Overview

## Timeline

- Start – Jan 2005
- Finish – Jan 2010
- 28 % complete

## Budget

- FY05: \$ 1200 K
- FY06: \$ 1760 K

## Partners

DOE

Chemical Hydrogen  
Storage Center

## Barriers

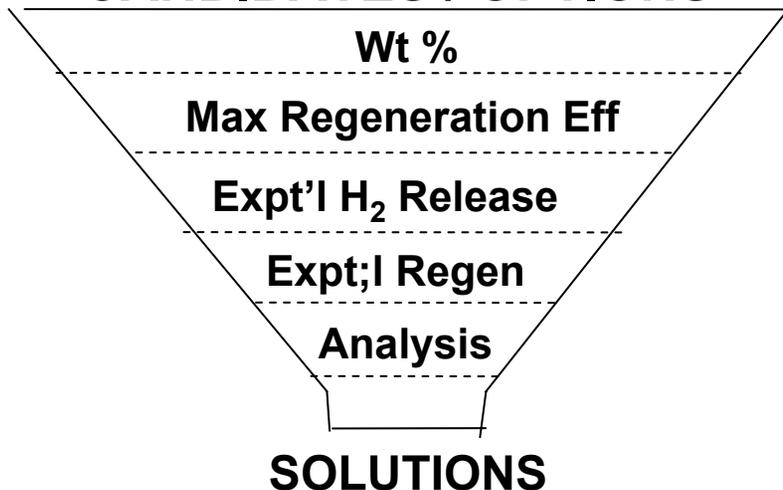
- Cost
- Weight and volume
- System Life-Cycle Assessment
- Energy Efficiency
- Regeneration Processes

	2010	2015
Gravimetric Capacity	6 wt %	9 wt %
Volumetric Capacity	.045 kg/L	0.081 kg/L
Minimum Flow Rate (g/s)/kW	0.02	0.02
Regeneration Efficiency (Center goal)	50 %	50 %

# LANL Approach and Objectives

## APPROACH

### CANDIDATES / OPTIONS



- Develop and demonstrate
- Study fundamentals
- Evaluate limits
- Assess and optimize

## OBJECTIVES

- Reduction of B-OH to B-H
  - Electrochemistry
  - Chemical reduction
- Ammonia-borane
  - Catalysis for H<sub>2</sub> release
  - Selectivity of BNH<sub>x</sub> products
  - Efficient regeneration
- Organic-based systems
  - Coupled reactions for hydrogen release
  - Hetero-atom containing organics
- Center coordination

# B-H via Electrochemical Reduction

## APPROACH

- Data mining for leads
- Electrolytically reduce  $\text{B}(\text{OH})_4^-$ 
  - Aqueous solution
  - Non protic solvents
  - Complexants
- Search for electrochemical activity
  - Electrodes, conditions
- Elucidate reaction mechanisms

## RESULTS

- Initial data mining indicates no clear path forward for the production of  $\text{BH}_4^-$  in an  $\text{H}_2\text{O}$  system.
- Number of boron compounds tested show no electrochemical activity
- ROH/PSU/MCEL/LANL identified potential routes for reduction based on proprietary ROH data

# B-H via Electrochemical/Chemical Reduction

## **Initial Compounds Tested**

(no reduction on  
C, Pt, Au electrodes)



## **FUTURE WORK**

- Work begun on advancing ROH results
- Searching for boron species that undergo boron centered reduction
- Examining electrode surfaces that could promote chemical reduction
- Indirect electrochemical reduction
- Thermal routes with regenerable hydrides and/or metals

# Ammonia-Borane for Hydrogen Storage



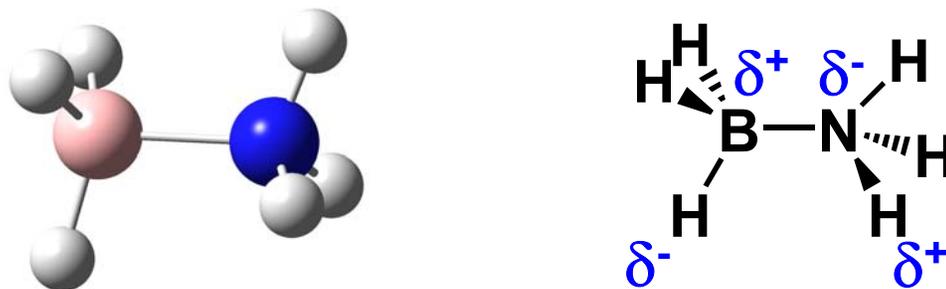
## OBJECTIVES

- Identify catalysts for rapid, controlled release of hydrogen from ammonia-borane (AB) (determine capacity, kinetics and mechanisms)
- Fully characterize dehydrogenated BNH<sub>x</sub> products obtained from different families of catalysts

## RESULTS

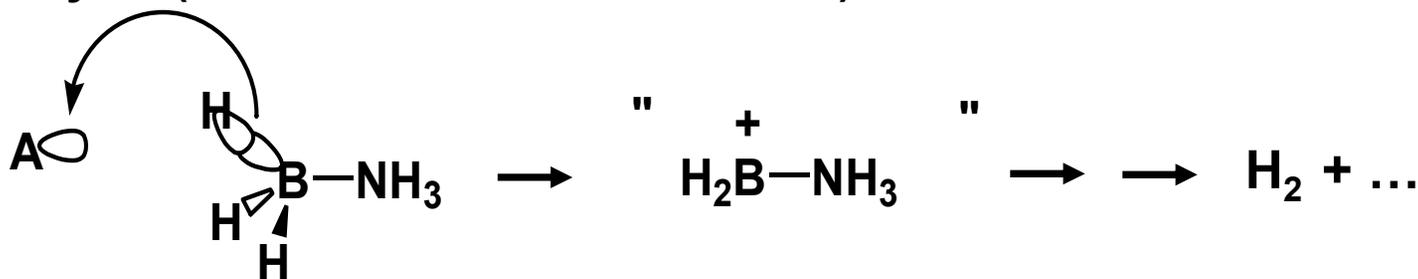
- Discovered AB dehydrogenation catalysis by strong Bronsted and Lewis acids; rates, product distribution and extent of hydrogen release depend on relative amounts of AB, acid, and solvent
- Discovered base metal carbene complexes that catalyze hydrogen release from AB to give over 2 equiv. of H<sub>2</sub>
- Obtained significant quantities of AB, cyclotriborazane [(H<sub>2</sub>BNH<sub>2</sub>)<sub>3</sub>] and borazine [(HB=NH)<sub>3</sub>] for detailed relative rate studies

# Catalytic Chemistry in Solution: Activation of AB

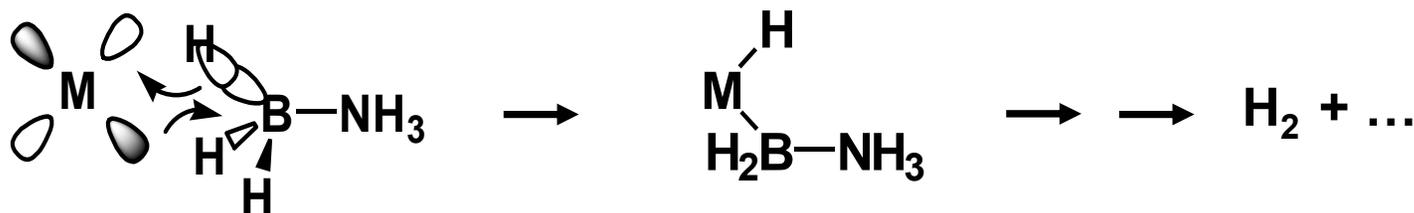


Thermal release of  $H_2$  is too slow at  $T < 100^\circ C$   
What catalyzes the process?

- Acid Catalysis (Lewis Acid or Bronsted Acid)

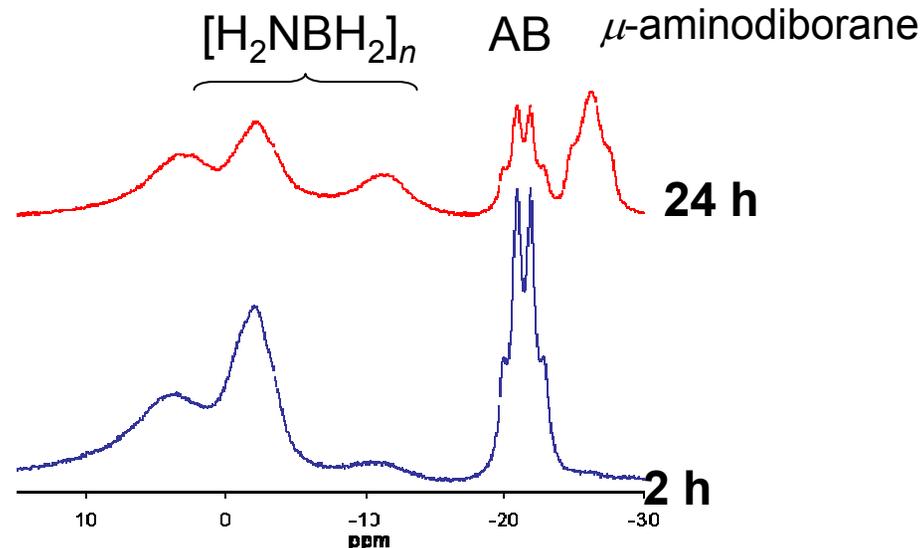


- Metal Catalysis



# Results: Acid Catalysis

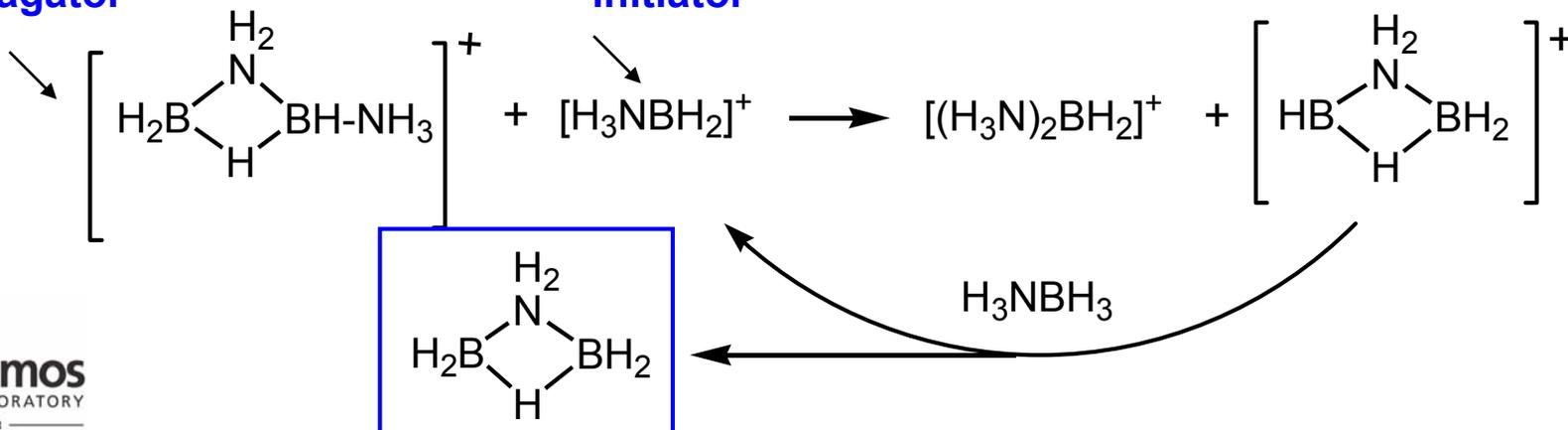
- Strong Bronsted and Lewis acids enable H<sub>2</sub> release at room temp
- Experimental and theory studies (w/ Alabama):
  - cationic initiator
  - acyclic BNH<sub>x</sub> products
  - < 1 eq. hydrogen, due to μ-aminodiborane by-product
  - By-product formation leads to free NH<sub>3</sub> which quenches cation and chain propagation



**H-coupled <sup>11</sup>B NMR of AB and 0.1 equiv. triflic acid in diglyme at 24°C**

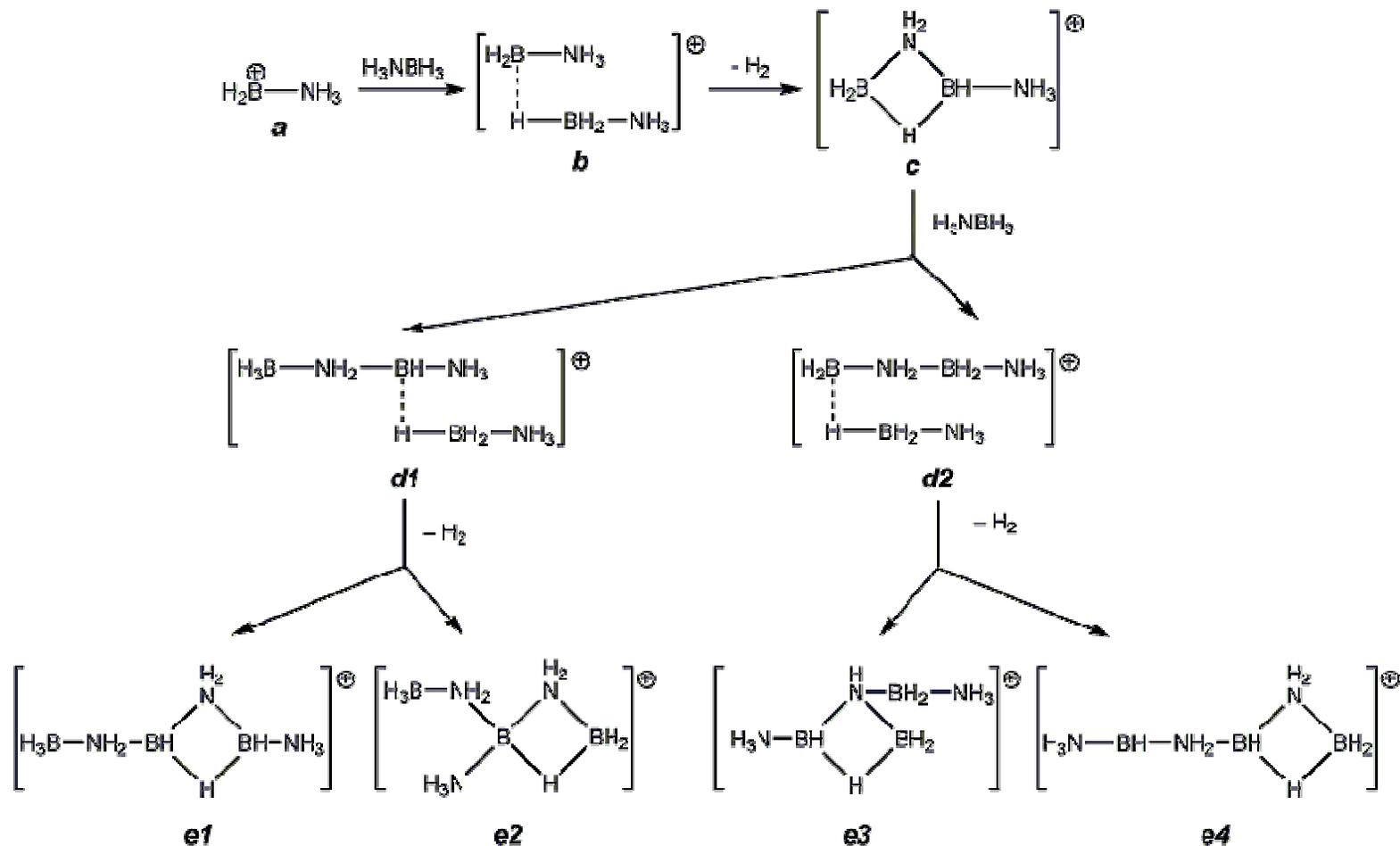
propagator

initiator



# Acid Catalysis: Reaction Pathway from Theory and Experiment

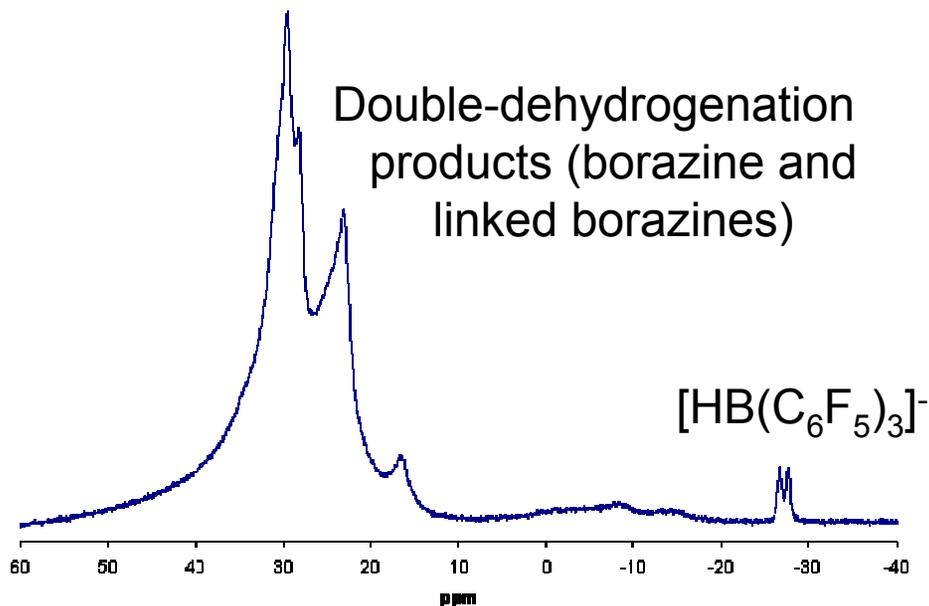
In collaboration with University of Alabama



*Lowest energy structures*

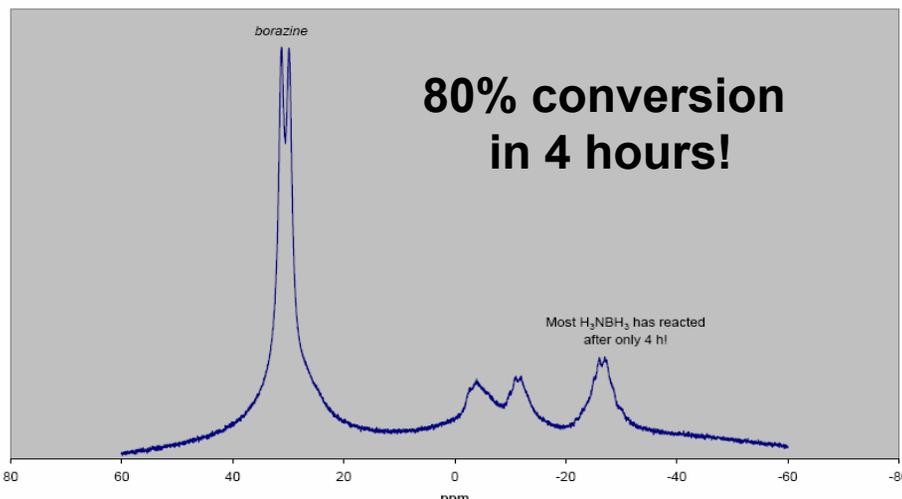
# Acid Catalysis: Concentration Effects

- Reducing acid/AB ratio eliminates  $\mu$ -aminodiborane and affords  $> 2 \text{ H}_2$
- Reducing amount of solvent gives faster rates but volatile borazine is major product



**H-coupled  $^{11}\text{B}$  NMR of AB and 0.005 eq.  $\text{B}(\text{C}_6\text{F}_5)_3$  in diglyme at  $80^\circ\text{C}$**

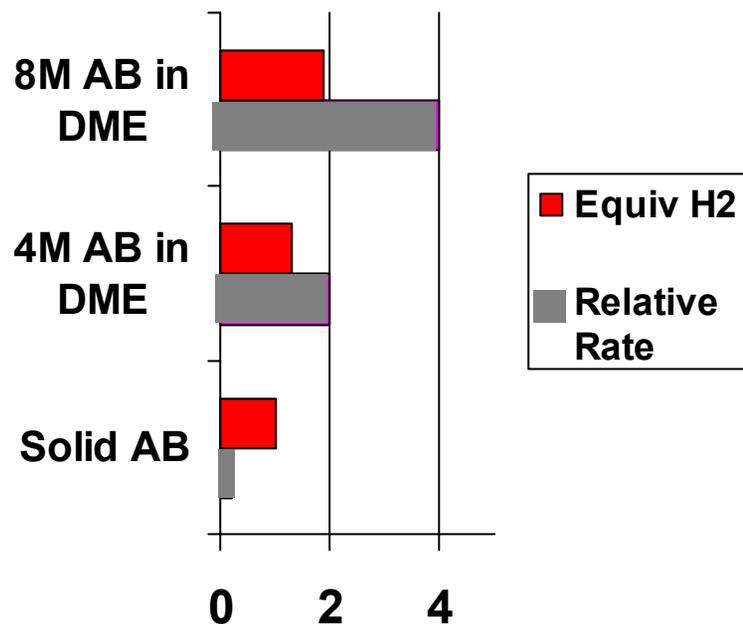
FHS-II-69:  $\text{H}_3\text{NBH}_3 + 0.005 \text{ B}(\text{C}_6\text{F}_5)_3$ , slurry in diglyme,  $80^\circ\text{C}$  for 4h



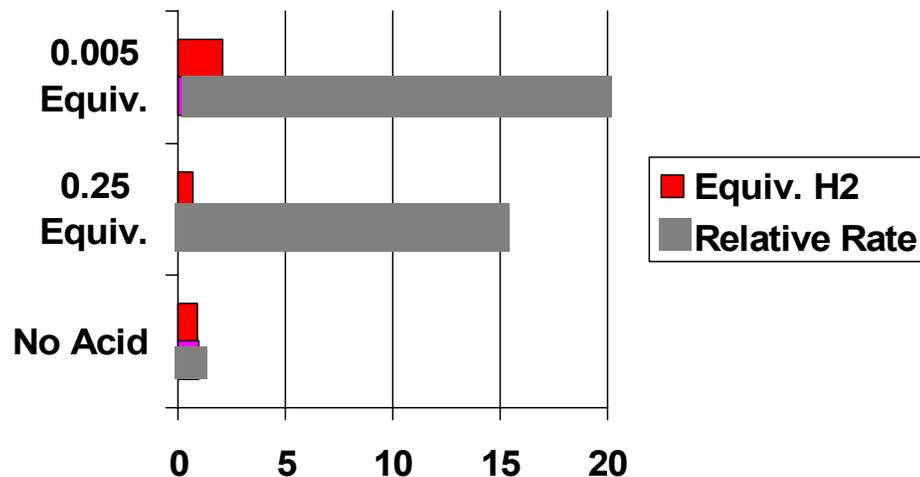
# Rate and Extent of Ammonia-Borane Dehydrogenation in Diglyme solution

- H<sub>2</sub> release rate and extent increase most with dilute acid

Concentration Effects (80 °C)



Acid Catalysis (70 °C)



- H<sub>2</sub> release rate and extent increase when AB is slurried with diglyme

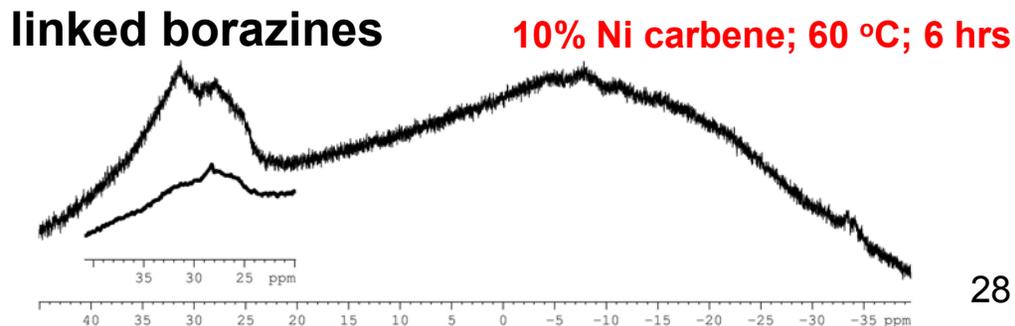
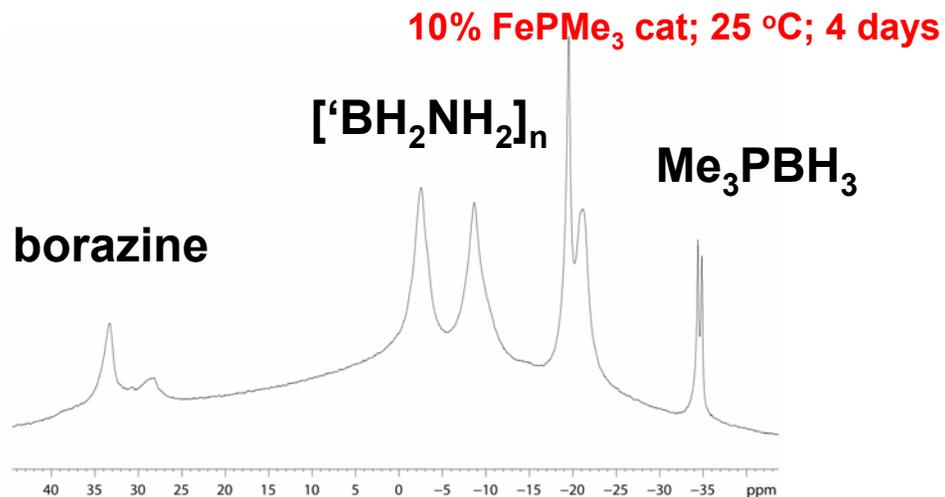
# Homogeneous Catalysts: Transition Metals

## APPROACH

- Examine electron-rich metal complexes
- “Base” metal complexes with electron-rich phosphine and carbene ligands

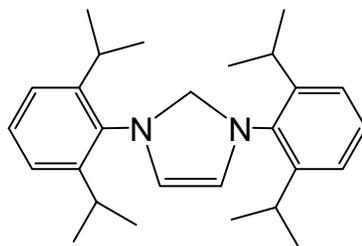
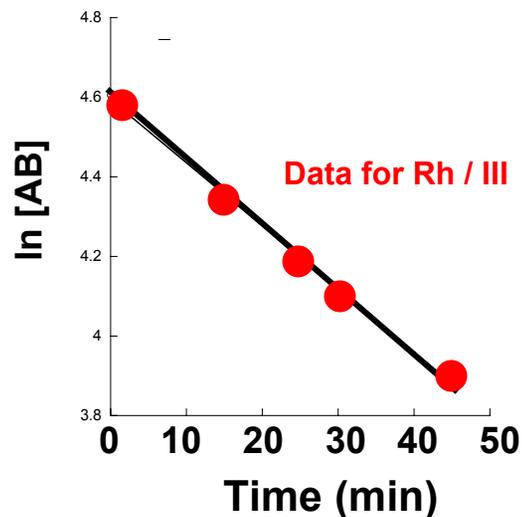
## RESULTS

- Iron and nickel phosphine complexes are slow and short-lived due to inactive metal boride formation
- Metal carbene complexes afford long-lived catalysts that afford linked borazines without build-up of  $[\text{BH}_2\text{NH}_2]_n$  intermediates



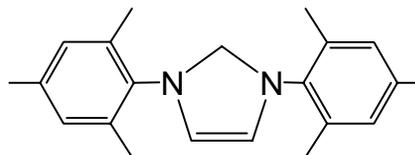
# Rates Depend on Metal and Ligands

- Kinetics of Ni, Ru, and Rh carbene complexes
- Best catalyst to date is Ni complex with Enders' triazacarbene III



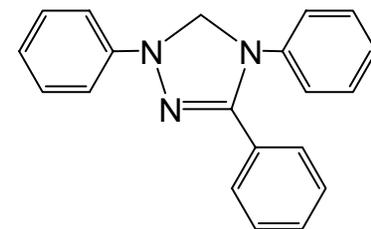
I-dipp

I



I-Mes

II



Enders'

III

Catalyst	Ni / I	Ni / II	Ni / III	Ru / III	Rh / III
Rates at 60°C (10 <sup>-3</sup> min <sup>-1</sup> )	5.6	7.3	64.6	34.7	15.8

# Summary: Catalytic Hydrogen Release from AB

- **Acid Catalysis**

- Strong Lewis and Bronsted acids promote hydrogen release even at room temperature to afford  $[\text{BH}_2\text{NH}_2]_n$  oligomers
- At low acid concentrations at 80°C linked borazines are obtained (>2 eq.  $\text{H}_2$ )
- Slurries of ammonia-borane generate twice as much hydrogen at 80°C (vs. solid)

- **Metal Catalysis**

- Base metal complexes of N-heterocyclic carbenes are unique in
  - » 1) affording long-lived dehydrogenation catalysts without metal boride formation; and
  - » 2) affording linked borazines without build-up of  $[\text{BH}_2\text{NH}_2]_n$  intermediates
- Fastest rate to date =  $0.06 \text{ min}^{-1}$  (Ni/Enders)
  - » 153 g of AB to release 0.02 g  $\text{H}_2$  per sec
  - » For AB:catalyst = 20, need 14.6 g of Ni (plus carbene)
  - » For 75 kW, need 11.5 kg of AB (1.1 kg of Ni) for target rate

# Path Forward for AB Catalysis

- **Increase rates**
- **Full product characterization**
  - Scale up catalytic reactions
- **Mechanistic studies to optimize catalysis**
  - Optimal solvent, concentration and temperature for desired rates, products and extent of hydrogen release
- **Collaborate with Center engineering assessment team to identify key parameters for solution catalysis**
  - Minimize solvent to increase capacity

# Toward Regeneration of Ammonia Borane

## OBJECTIVE

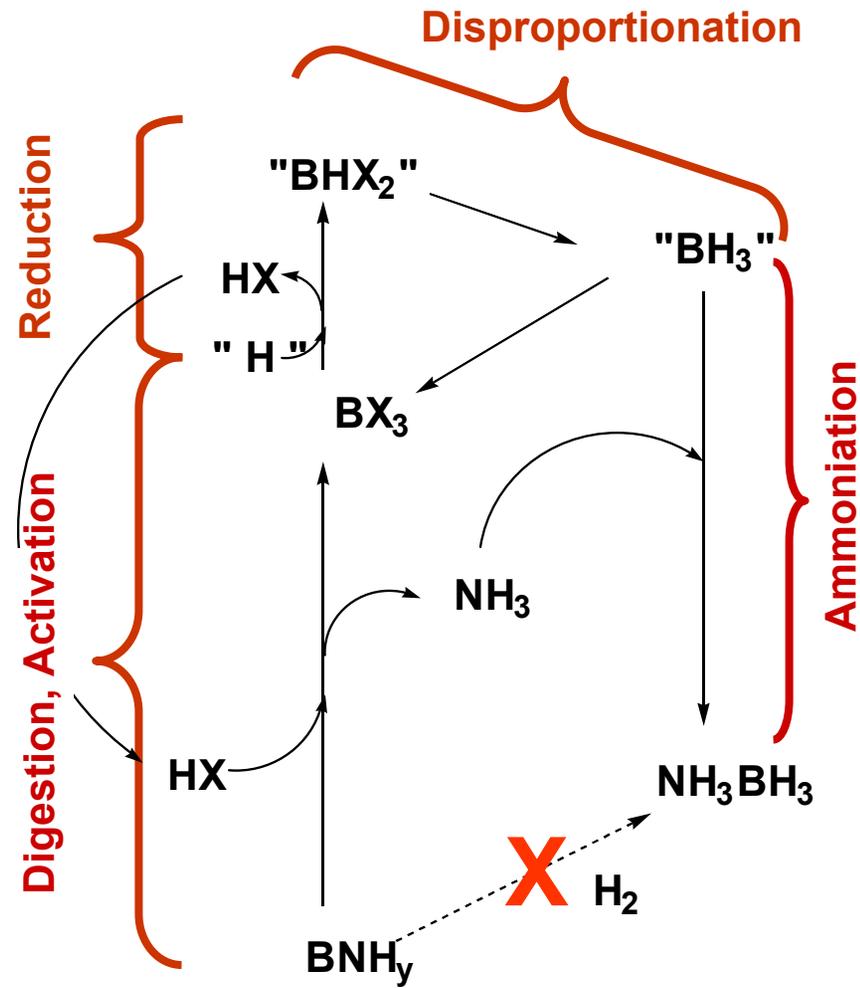
- Develop and demonstrate regeneration process for spent AB

## APPROACH (LANL/Penn)

- Digest spent material without wasting remaining B-H bonds
- Use lowest-energy, least expensive reductant possible
- Use thermoneutral or reversible steps wherever possible
- Find high yield reactions

## RESULTS

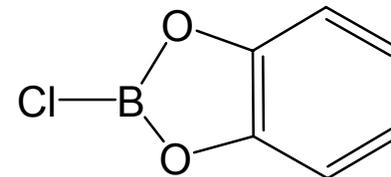
- Developed 5 step process
- Demonstrated 3 of 5 steps in lab
- Demonstrated regenerable hydride
- Identified other hydrides



# Results: Reduction of B-X to B-H

- **Digestion, activation (e.g. Penn)**

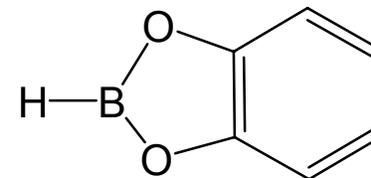
Catechol and acid (e.g. HCl)



- **Demonstrated reduction of Cl-BCat**



(hexane or neat: rapid, mildly exothermic, near-quantitative yield)



- **Metal-hydride regeneration**



(endothermic decarboxylation at 110-140 °C)

Silanes ( $\text{HSiR}_3$ )

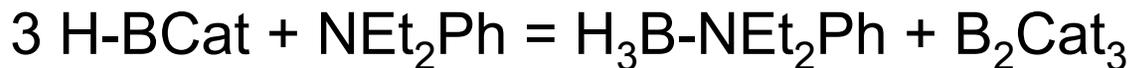
M-H on electrodes

## NET REDUCTION PROCESS



# Disproportionation Step: H-BCat to BH<sub>3</sub> species

## Diethylaniline drives disproportionation

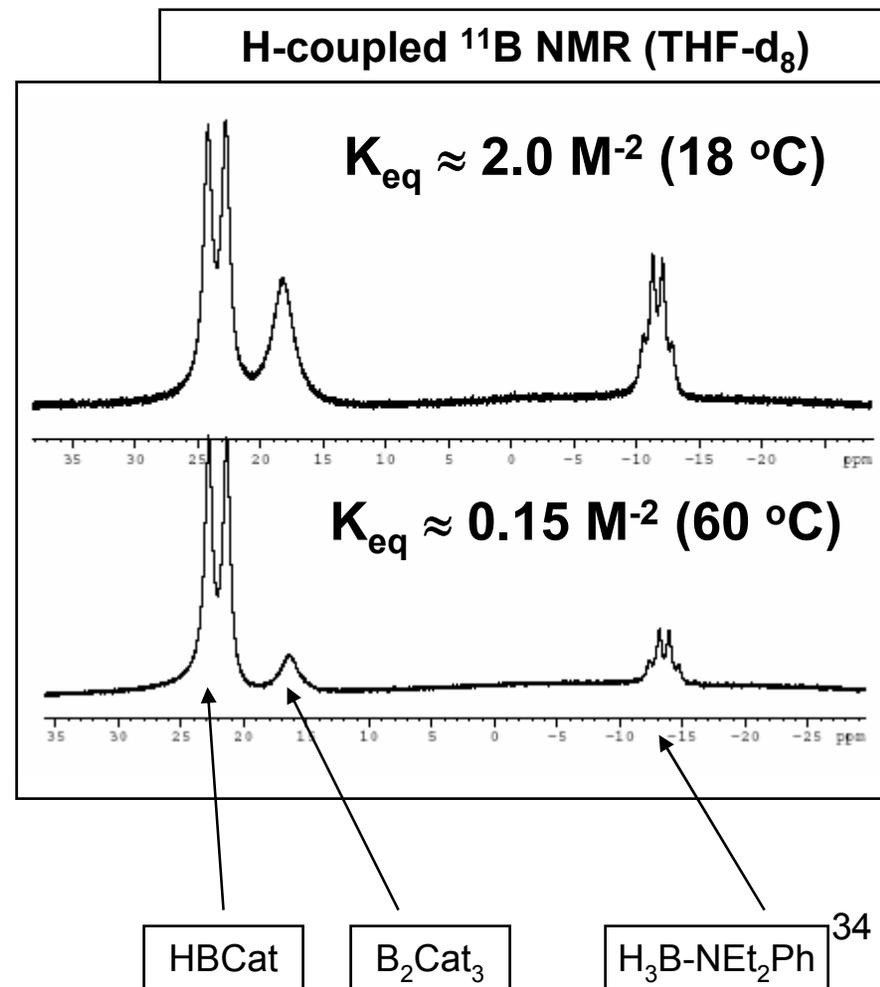


Slow, establishes clean equilibrium  
(THF solution)

$$\Delta H \approx -10 \text{ to } -13 \text{ kcal}$$

$$\Delta S \approx -35 \text{ to } -45 \text{ eu}$$

- Exothermic disproportionation is favored at lower temperature
- H<sub>3</sub>B-NEt<sub>2</sub>Ph product reacts quantitatively with ammonia to make AB
- B<sub>2</sub>Cat<sub>3</sub> co-product can be recycled (activated, then reduced)



# AB Regeneration: Path Forward

- **Process Simplification**

- Combine/integrate 5-steps
- Digestion, activation, reduction, disproportionation, ammoniation

- **Improvement in Steps**

- Will need efficient digestion yet without significant waste of residual B-H.
  - » Catechol under investigation, not optimized
  - » Anticipate that “activation” step may be troublesome/costly
- Initial leads for new concept which combines activation and reduction
- Establish other hydride systems
  - » Silanes also capable of reduction
  - » Reduction using electrochemically-generated surface hydrides
- Develop other concepts

- **Analysis and Assessment**

- How good does this overall scheme look under rigorous engineering and economic scrutiny? Relative to other routes?
  - » Project Zip:  $\text{BCl}_3/\text{H}_2$ , borates/ $\text{Al}/\text{H}_2$

# Organic-Based Materials for Hydrogen Storage

## BACKGROUND

- Organic compounds contain considerable hydrogen
- Offer potential advantages as storage materials
- Hydrogen release from most C-H bonds occurs endothermically at elevated temperature

## OBJECTIVE

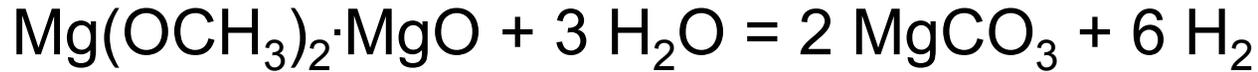
- Identify compounds and chemical reactions that release H<sub>2</sub> from organic materials with near thermoneutrality at ambient temperature

## APPROACH

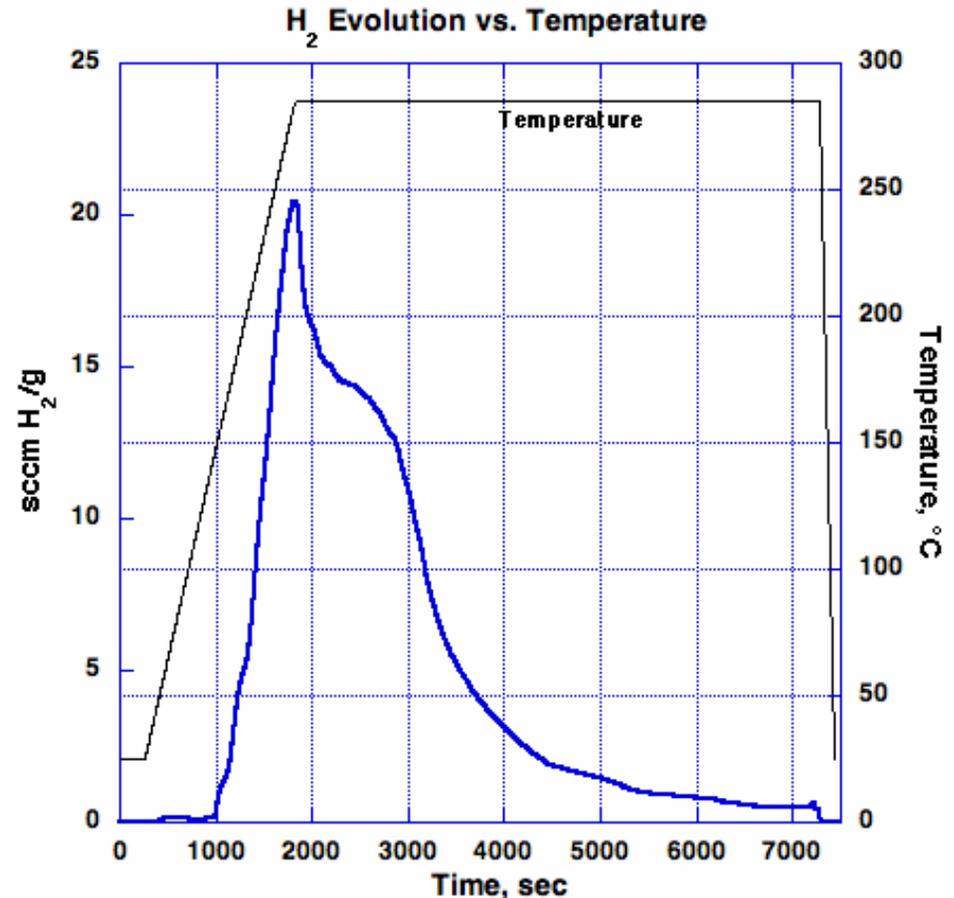
- Use simultaneous or tandem “coupled reactions” to balance an endothermic H<sub>2</sub> release with an exothermic reaction step
  - Mg(OCH<sub>3</sub>)<sub>2</sub>·MgO composites react with water to release H<sub>2</sub>,
  - More favorable enthalpy ( $\Delta H$  ca. +1 kcal/H<sub>2</sub>) than methanol reforming ( $\Delta H$  +10 kcal/H<sub>2</sub>)
- Use heteroatom substitution to lower the enthalpy of H<sub>2</sub> release
  - Dihydrobenzimidazoles act as “organic hydrides,” with acids
  - Exothermic release of H<sub>2</sub>

# Results: Coupled Reactions

- Developed  $\text{Mg}(\text{OCH}_3)_2 \cdot \text{MgO}$ -catalyst composites



- Theoretical composite material capacity = 6.7 wt%
- > 0.09 kg/  $\text{H}_2$ /L w/o water
- Demonstrated yield to date:
  - 4.4 wt%  $\text{H}_2$
  - 46% of theoretical
- Demonstrated  $\text{H}_2$  release rate: 20 sccm/g at 260 °C
- At this release rate, 600 g would provide 0.02 g  $\text{H}_2$ /sec

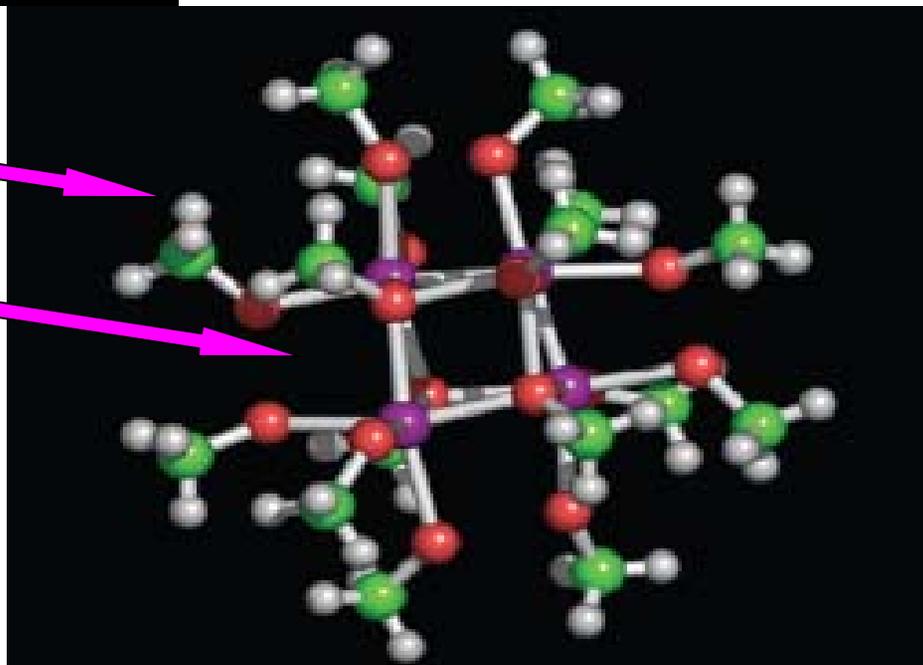


# Coupled Reactions

## THEORY

Prediction from computation:  
C-H bonds of “terminal”  
methoxide are ca. 7 kcal  
weaker than “cube corner”  
methoxide

Explore compositions having less  
“cube corner” methoxide, more  
“terminal” methoxide:  
 $[(\text{CH}_3\text{O})\text{Mg}]_4(\mu\text{-OH})_4$  ?

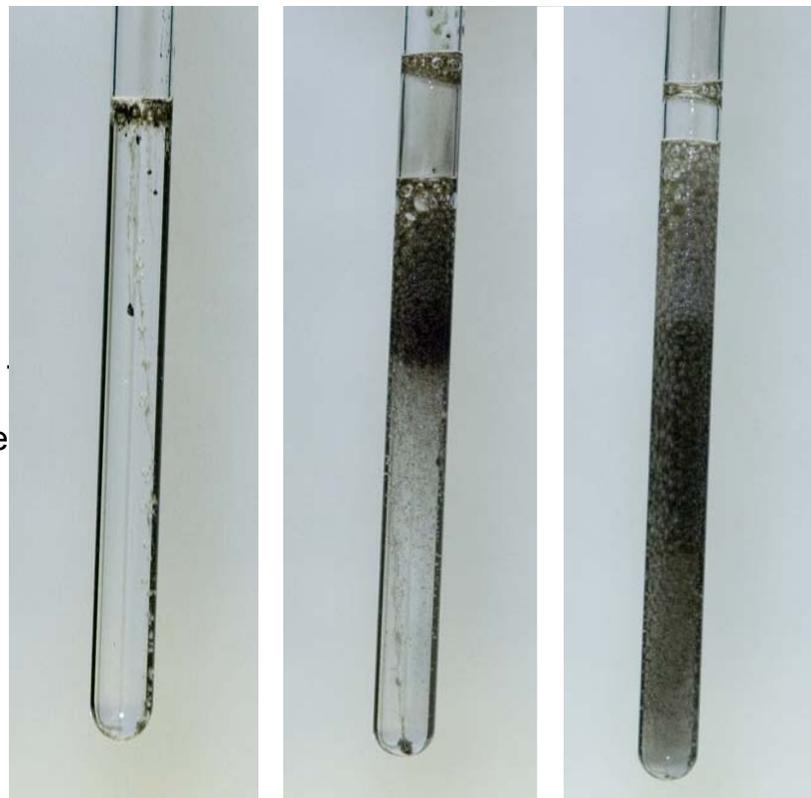
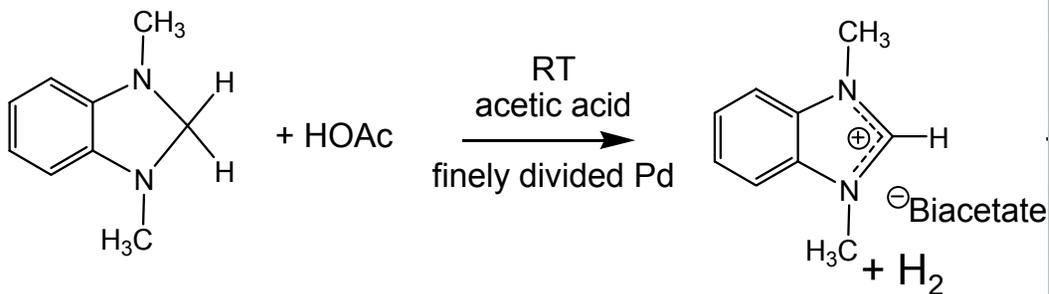


## FUTURE WORK

- Incorporate more efficient catalysts
- Reduce methanol, CO<sub>2</sub> breakthrough; optimize H<sub>2</sub> yield
- Release H<sub>2</sub> at 10-100x present rate, lower temperature
- Study other Mg(alkoxide)<sub>2</sub>·MgO-catalyst composites
- Exploit structural control of chemistry

# Results: "Organic Hydrides"

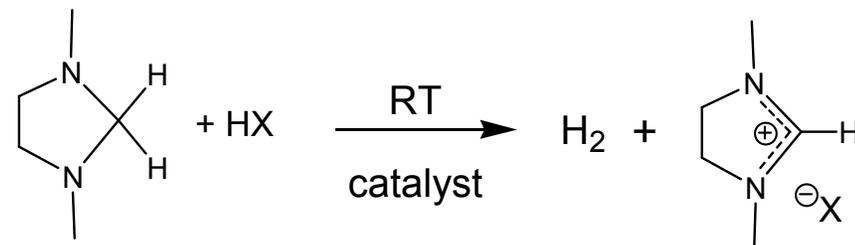
Dihydrobenzimidazoles react with acids:



- Hydrogen release is facile at room temperature (turnover rate ca. 30/min, mole/mole Pd)
- Geminal-di-heteroatom substitution makes H<sub>2</sub> release exothermic  
 $\Delta H^\circ$  ca.  $-10(3)$ ,  $\Delta G^\circ$  ca.  $-18(6)$  kcal/mole, irreversible with H<sub>2</sub> pressure alone
- H<sub>2</sub> yield is quantitative, but limited to 1 wt% H<sub>2</sub> by wt of these particular compounds

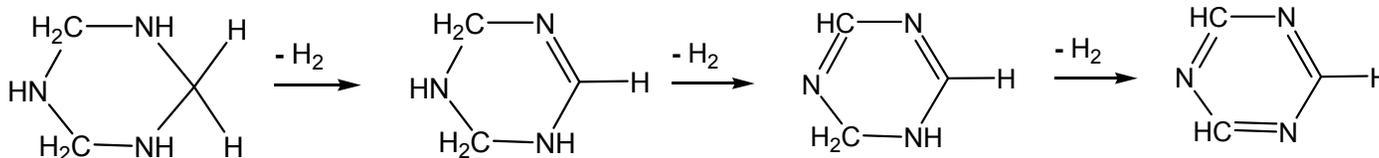
# Future Work: “Organic Hydrides”

- Increase H<sub>2</sub> capacity
- Reduce molecular weight of components
  - Have removed benzo group
  - H<sub>2</sub> release demonstrated for “staged” process, not for “one-pot” process



“staged process”: Org-H + metal-complex = Org<sup>+</sup> + H-metal-complex  
H-metal-complex + acid = H<sub>2</sub> + metal-complex

- Need to develop new catalysts that work without benzo group in “one-pot” process
- A goal: dehydrogenation of hexahydrotriazine (6.9 wt% H<sub>2</sub>)



**Combining with other Center organic material  
concepts in new developmental thrust**

# LANL Summary: Approach to Targets

<b>TARGET (2010)</b>	<b>LANL AB Current</b>	<b>AB Theor.</b>	<b>LANL Coupled Current</b>	<b>Coupled Theor.</b>	<b>LANL Org. Hydride Current</b>	<b>Organic Hydride Theor.</b>
<b>Material Gravimetric Capacity (6 wt%)</b>	<b>2.7 (with solvent, catalyst)</b>	<b>13-19%</b>	<b>4.4 (dry)</b>	<b>6.7 (with H<sub>2</sub>O)</b>	<b>0.9</b>	<b>6.9 (&gt; 8)</b>
<b>Material Volumetric Capacity 0.045 kg/L</b>	<b>0.02</b>	<b>0.12- 0.16</b>	<b>0.04</b>	<b>&gt; 0.09</b>	<b>0.015</b>	<b>0.062</b>
<b>H<sub>2</sub> Flow Rate 0.02 (g/s)/kW</b>	<b>Needs 153 g AB, 14.6 g Ni</b>	<b>-</b>	<b>Needs 600 g of material</b>	<b>-</b>	<b>Needs 2 g catalyst</b>	<b>-</b>
<b>Regeneration Efficiency (Center: 50%)</b>	<b>TBD</b>	<b>80%</b>	<b>TBD</b>	<b>92%</b>	<b>TBD</b>	<b>92%</b>

## FUTURE WORK—FY07

- **Determine if B-O to B-H is possible with better energy efficiency**
- **Increase capacity and rates of AB dehydrogenation**
- **Enhance spent AB regeneration process(es)**
- **Energy efficient metal hydrides**
- **Development of new chemistry for non-boron-based storage system with > 6-7 material wt%**
- **Mechanistically couple endothermic and exothermic reactions**

# Publications/Patents/Presentations

- **Publications**

- “Hydrogen evolution from organic hydrides.” *Chemical Communications*, 2005, (47), 5919 – 5921.
- “Acid-catalyzed dehydrogenation of ammonia-borane,” submitted.

- **Patents filed (5)**

- Composition and method for storing and releasing hydrogen
- Energy efficient synthesis of boranes
- Method and system for hydrogen evolution and storage
- Base metal dehydrogenation of amine boranes
- Acid catalyzed dehydrogenation of amine boranes

- **Presentations including**

- Posters at Inorganic/Organometallic Gordon Conferences, Aug 05
- MS&T, Pittsburgh, Sept 05
- FECHEM Conference on Organometallic Chemistry , Budapest, Sept 05
- Singapore National Chemistry Conference, Oct 05
- Pacifichem, Honolulu, HI, Dec 06
- FC Expo, Tokyo Jan 06
- AIST, NEDO, Honda, Feb 2006
- MRS Spring Meeting, San Francisco, CA Apr 06
- University seminars (5)

# Backup Slides: Center Overview

# Center Talk: Center Activities

## CENTER/PROJECT MEETINGS

- Electrochem meeting at PSU (3/05)
  - ROH, MCEL, LANL, PSU
- Center meeting at Annual Review (5/05)
  - All, DOE
- PNNL/LANL BN regen brainstorming, Berkeley (8/05)
- ACS meeting (Washington DC) (8/05)
  - PNNL, Penn, LANL, MCEL
- Engineering Meeting at PNNL (9/05)
  - MCEL, ROH, LANL, PNNL
- Semi-annual Center meeting at Salt Lake City (10/05)
  - All, DOE
- BN regen meeting at SLC (10/05)
- Analysis meeting at Argonne Natl Lab (10/05)
- US Borax B-OH = B-H
  - LANL, PNNL, PSU
- Tier 1 meeting at Rohm and Haas (12/05)
  - PNNL, LANL, MCEL, ROH
- PacifiChem meeting (Hawaii) (12/05)
  - Ala, UW, PNNL, Penn, LANL
- AB chemistry meeting at SLC (2/06)

## SITE VISITS

- PSU (3/05)
  - ROH, MCEL, LANL
- UCLA (4/05)
  - Intematix, PNNL, LANL
- US Borax (4/05)
  - LANL, PNNL, USB
- LANL, PNNL (7/05)
  - PNNL, LANL
- Intematix (8/05)
  - PNNL, LANL
- UC Davis (8/05)
  - PNNL
- UCLA (11/05)
  - PNNL, PSU, LANL
- Rohm and Haas SBH Plant Tour (1/06)
  - DOE, PNNL
- DOE Site Visits
  - LANL (7/05), PNNL (7/05), Penn (2005), Intematix (1/06), UCLA (1/06), ROH (3/06), Alabama (3/06)
- DOE HQ (several; LANL, PNNL)

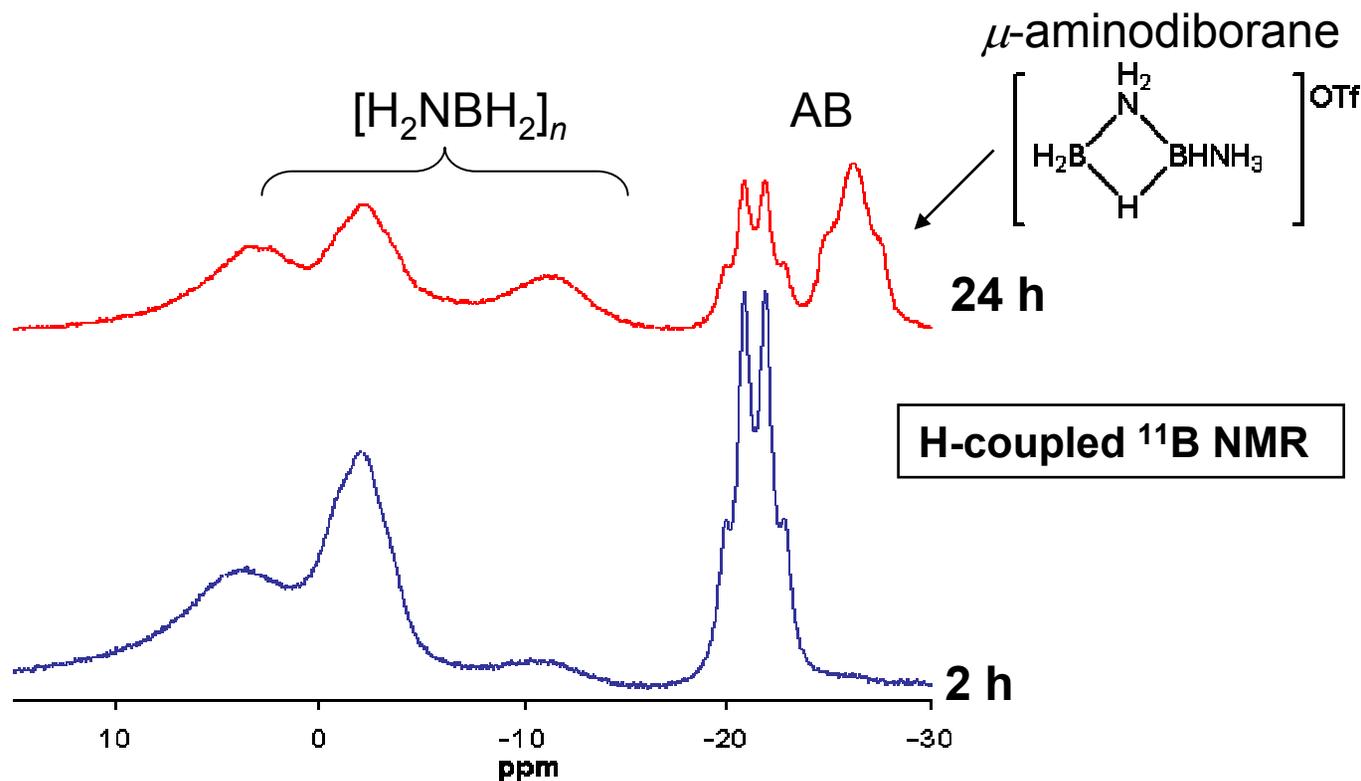
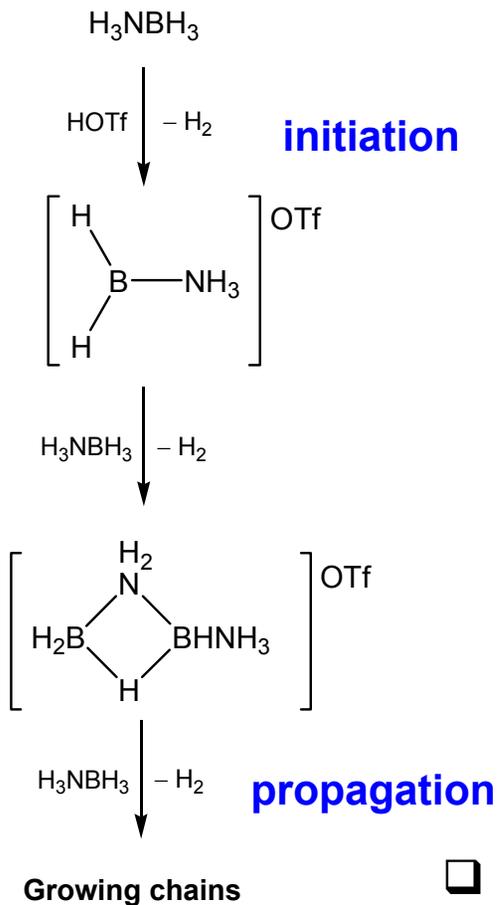
# FY07 SBH Go/No-Go Milestones

<b>Q1</b>	<b>Finish computational analysis of SBH regeneration options (chemical and electrolytic) that meet regeneration efficiency criteria and identify at least one process for laboratory demonstration.</b>
<b>Q2</b>	<b>Complete conceptual on-board system design that meets DOE 2007 targets (4.5 wt%, 1.2 kWhr/l, minimum flow rate of 0.02 g/sec/kW @ 50 kW).</b>
<b>Q3</b>	<b>Laboratory demonstration at least one of the SBH regeneration processes at an overall energy efficiency equal to or greater than 80% of the theoretical efficiency for that particular process.</b>
<b>Q4</b>	<b>Conceptual design of laboratory demonstrated SBH regeneration process and associated on-board system. Determine feasibility and provide a go/no-go recommendation for Sodium Borohydride (SBH) hydrolysis on-board storage system based on modeling and laboratory-scale experimental demonstration of energy efficient regeneration off-board.</b>

# Backup Slides: LANL Contributions

# Accomplishments: Acid Catalysts

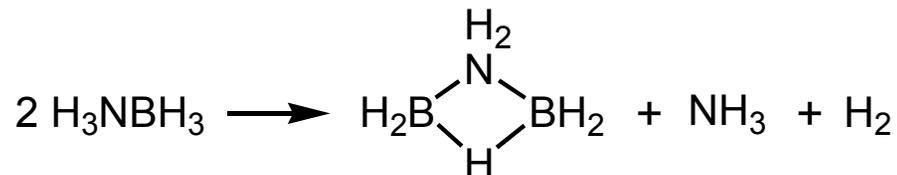
- Strong Bronsted and Lewis acids enable  $H_2$  release at room temperature



- Reaction at  $24^\circ C$  with 0.1 eq triflic acid is ca. **20 $\times$  faster** than thermolysis in 1,2-dimethoxyethane at  $85^\circ C$ . Less than one equiv.  $H_2$  formed due to unwanted by-product  $\mu$ -aminodiborane

# Results: Limitation of Acid Catalysis by Formation of $\mu$ -Aminodiborane

When  $\mu$ -Aminodiborane is formed,  
so is  $\text{NH}_3$ :

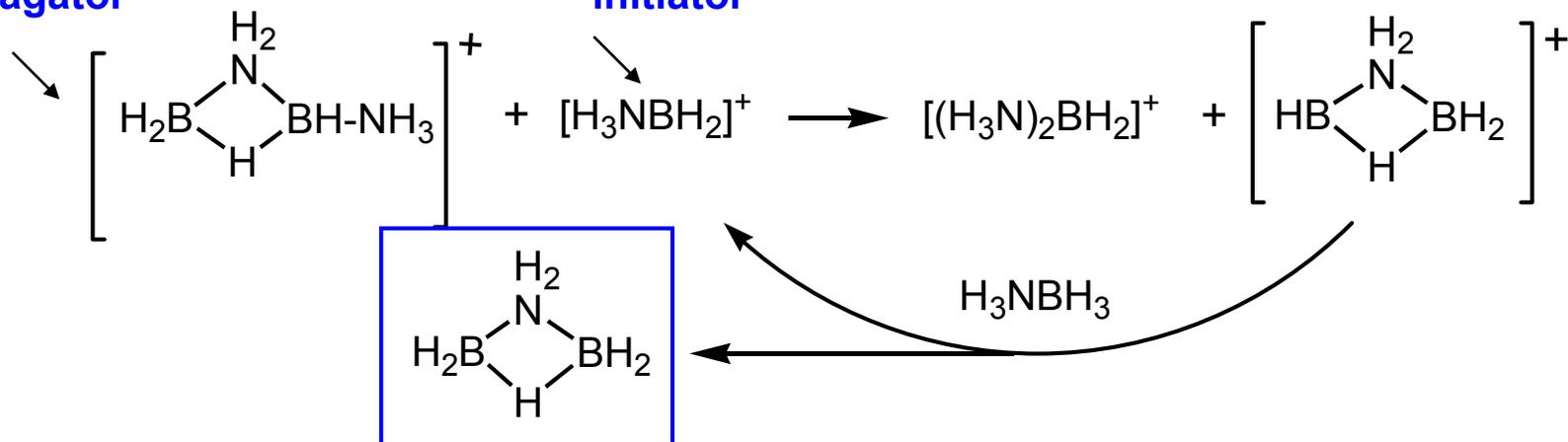


and  $\text{NH}_3$  quenches the cations that propagate the catalytic chain

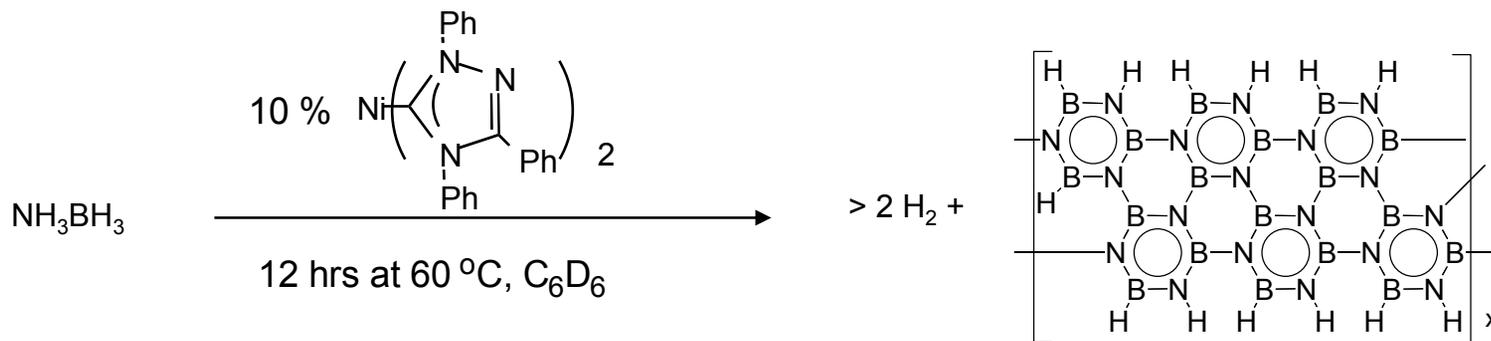
$\mu$ -aminodiborane formation results from unwanted reactions between  
initiating and propagating species:

propagator

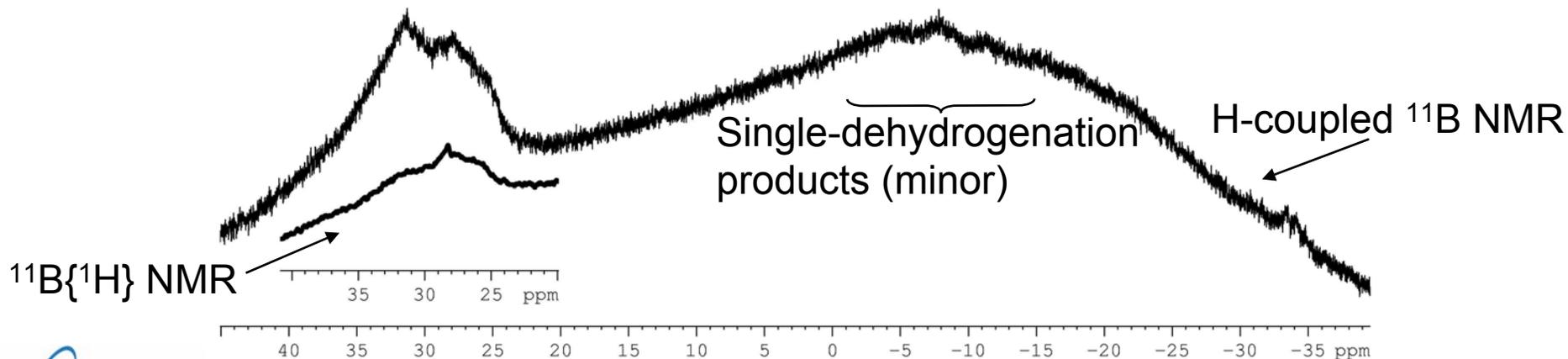
initiator



# Non-phosphine Catalyst: Ni(carbene)<sub>2</sub>

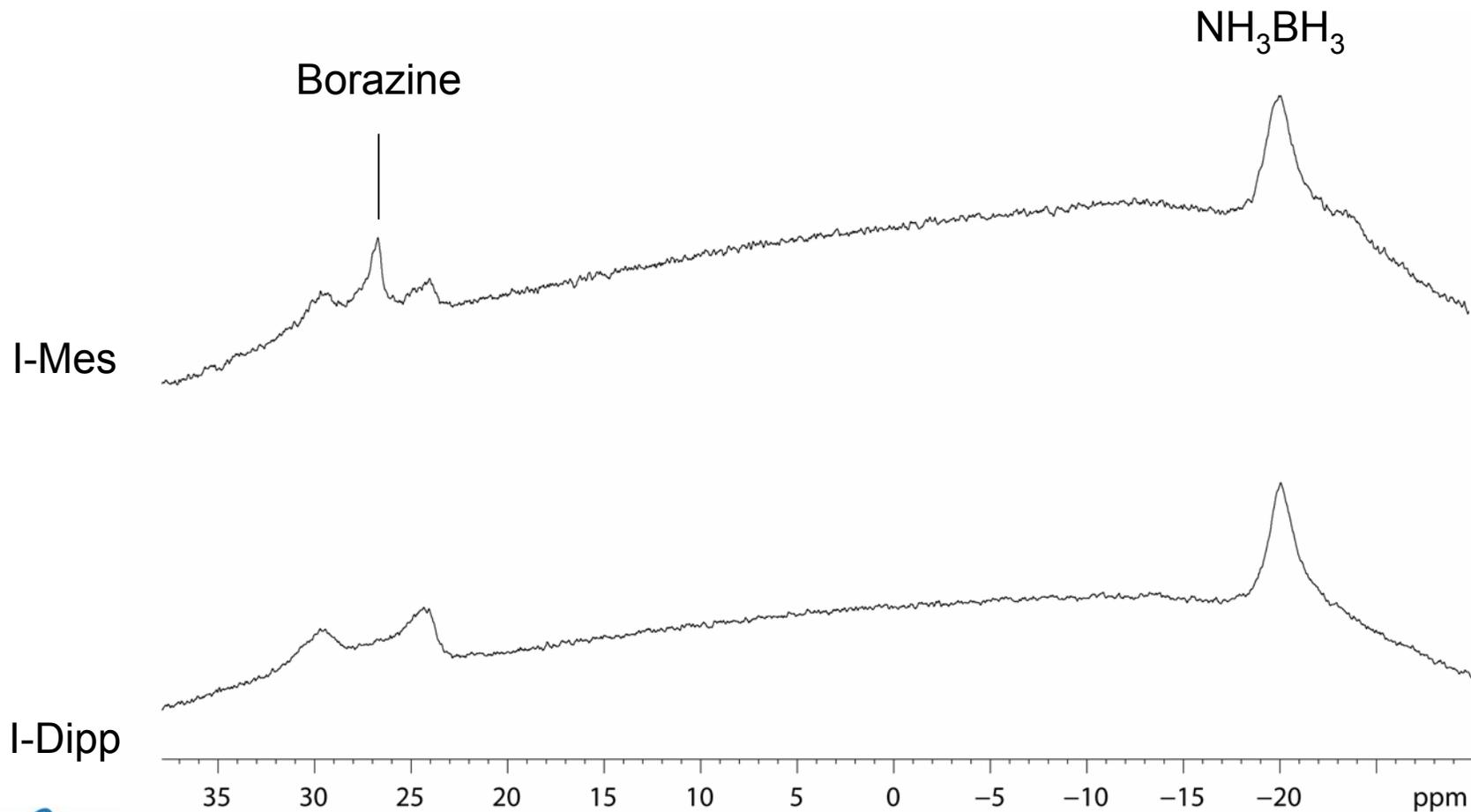


Absence of sharp spectral features  
confirms linked borazine structure,  
> double dehydrogenation of ammonia-borane



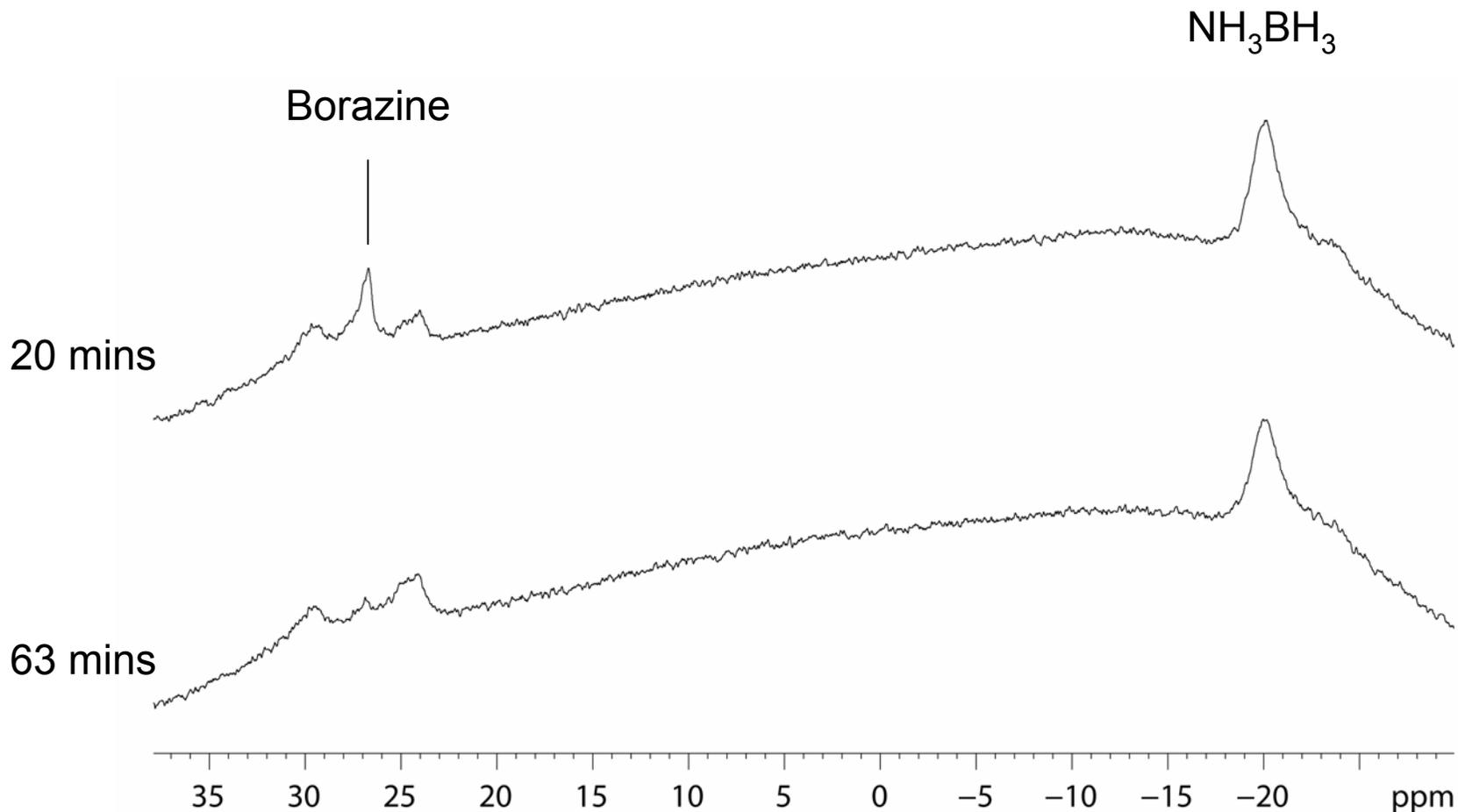
## Borazine Formation Depends on Carbene

$^{11}\text{B}\{-^1\text{H}\}$  NMR in 2:1 diglyme: $\text{C}_6\text{D}_6$  after 15 minutes at 60 °C



## Borazine Formation and Consumption

$^{11}\text{B}\{-^1\text{H}\}$  NMR of  $\text{Ni}(\text{cod})_2 + 2 \text{I-Mes}$  in 2:1 diglyme: $\text{C}_6\text{D}_6$  at 60 °C



Kinetics of borazine consumption with this catalyst system also need investigation

# Key Developments for Ammonia-Borane

- Inclusion in mesoporous materials alters rate and selectivity
- Acid catalysts can lead to multiple dehydrogenation from AB
- Rapid single dehydrogenation with Ir catalysts
- Multiple dehydrogenation of AB is facile with homogeneous electron-rich precious metal complexes
- The first examples of non-precious metal catalysts have been discovered
- Heterogeneous catalysts have been discovered (including rapid screening)
- Alternative reaction media can open up new reaction pathways
- Kinetics and mechanistic studies underway

