# Center of Excellence for Chemical Hydrogen Storage: LANL Tasks and Collaborations

Los Alamos National Laboratory

May 23, 2005

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Project ID #
STP61

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# Overview

## Timeline

Project Start Date: FY05
Project End Date: FY09
New Start

## Barriers Addressed

Cost
Weight and volume
Energy efficiency
System life-cycle assessment
Spent material removal
Regeneration processes
Heat removal

## Budget

Total project funding (requested)
- $ 8.7 M DOE share

Funding for FY05: $ 1.2 M

## Partners

Chemical Hydrogen Storage
Center of Excellence Partners

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# Objectives

- Identify, research, develop and validate the best chemical hydrogen storage systems to overcome barriers and meet 2010 DOE goals
- Develop materials, catalysts, catalytic processes and new concepts for hydrogen release and regeneration
- Design, synthesize, and test structures and compositions to control thermochemistry of $H_2$ release and spent fuel regeneration
- Provide experimental tools to Center partners
- Collaborate with Center partners where appropriate and synergistic
- Contribute to demonstration of 1 kg storage system
- Coordinate research, development and engineering efforts within each Tier and overall Center

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# Three Tier Structure of Center

- Tier I:
  - Develop borate-to-borohydride (BO to BH) regeneration alternatives and assess economics and life cycle analysis of borohydride/water to hydrogen
    - **Millennium Cell, Rohm and Haas, Penn State, Alabama, PNNL, LANL**
- Tier II:
  - Avoid water and thermodynamic sinks. Alternative boron chemistry approaches include polyhedral boranes ($B_xH_y$), amine-boranes and BCNP chemistry
    - **Penn, Penn State, UCLA, Washington, Northern Arizona, Alabama, Intematix, PNNL, LANL**
- Tier III:
  - Beyond boron:
    - Develop concepts for coupled endo/exothermic reactions, Investigate nanomaterials
    - Use heteroatom substitution for thermodynamic control
    - **UC Davis, Alabama, Intematix, PNNL, LANL**
- Core Capabilities:
  - **Computation, engineering assessment, complex instrumentation (PNNL, LANL, Rohm and Haas, Alabama)**
  - **IP management (IP Management Committee)**
  - **Safety (PNNL, LANL, Northern Arizona)**
  - **Center coordination, meetings, technical planning (LANL)**

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# Approach: Tier 1 B-O → B-H

- Engineering Guided Research
  - Data mining on efficient routes for regeneration of B-H from borates
  - Down-selection of new experimental approaches for regeneration of B-H
    - **with US Borax, Millennium Cell, PNNL, Penn State, Rohm and Haas**
- Investigation of complexation of borates for reduction chemistry/electrochemistry
    - **with PNNL, Rohm and Haas**
- Electrochemical studies of borates and complexed borates
    - **with Rohm and Haas, Penn State**

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# Approach: Tier 2 Novel Boron Chemistry

– Polyhedral Borane Chemistry
  - Validation of leads and assistance for rapid throughput catalyst development for hydrolysis of polyhedral boranes
    - **with Intematix, UCLA, PNNL**
  - Electrochemical studies of polyhedral boranes
    - **with PSU, UCLA**
  - Aminolysis of polyhedralboranes
    - **with UCLA, PNNL**

– Amine-Borane Chemistry
  - Catalyst development for dehydrogenation of amine-boranes; selectivity, activity, non-precious metals
    - **with Penn, Ala, NAU, PNNL**
  - Mechanisms of amine-borane dehydrogenation/regeneration
    - **with Penn, UW, PNNL**

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# Approach: Tier 3
# Innovation Beyond Boron

- Coupled chemical reactions
  - Develop new concepts coupling endothermic and exothermic reactions with high hydrogen storage capacity
- Heteroatom substituted organics
  - Develop molecular systems with appropriate thermochemistry for hydrogen release and regeneration
  - Develop new mechanisms for hydrogen release from organic molecules
    - **with Alabama, PNNL**
- Nanoscale materials
  - B, BN and doped-B, Si nanoparticles for hydrogen storage
    - **with UC Davis**
  - Metal-based nanoparticles by gas-solid synthesis
    - **with Intematix**

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# Technical Accomplishments/ Progress/Results

- New start in FY05 (1/20/05)
- Collaborative R&D project plans developed for all projects
- Preliminary data mining started for Tier 1
- Promising preliminary results already obtained for Tier 2 and 3

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# Tier 1: First Year Milestones

- Data mining ( B-O to B-H )
  - with ROH, MCEL, USB, PNNL, PSU
- Survey of complex borates
  - with PNNL, USB, ROH
- Selection of analytical and electrochemical methods for $BH_4$ determination.
  - with ROH, MCEL, USB, PNNL, PSU

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# Future Work: Tier 1

- Implement experimental approaches for regenerating B-H, as identified from data mining and downselection
  - **with US Borax, Millennium Cell, PNNL, Penn State, Rohm and Haas**

- Prepare most-promising borate complexes, as identified from computation and data mining, and determine reduction chemistry
  - **with PNNL, Rohm and Haas, Alabama**

- Determine electrochemical behavior of borate complexes
- Fabricate electrode materials for electrochemical borate reduction
  - **with Rohm and Haas, Penn State**

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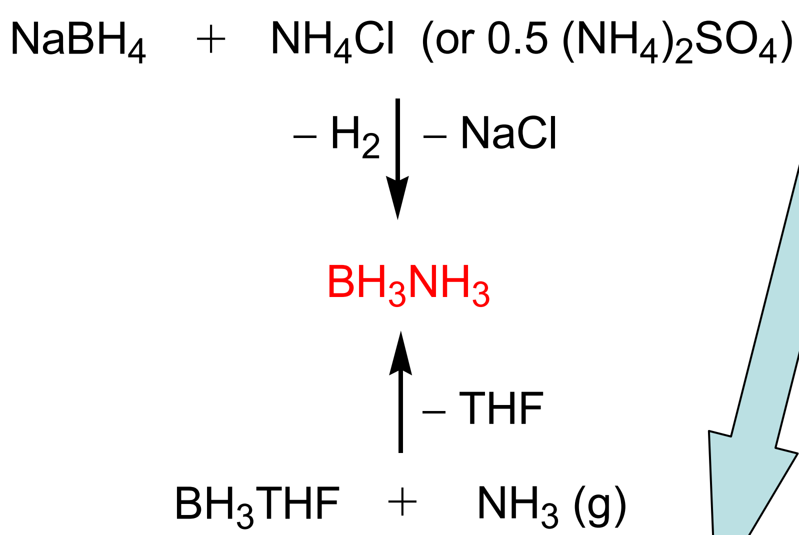
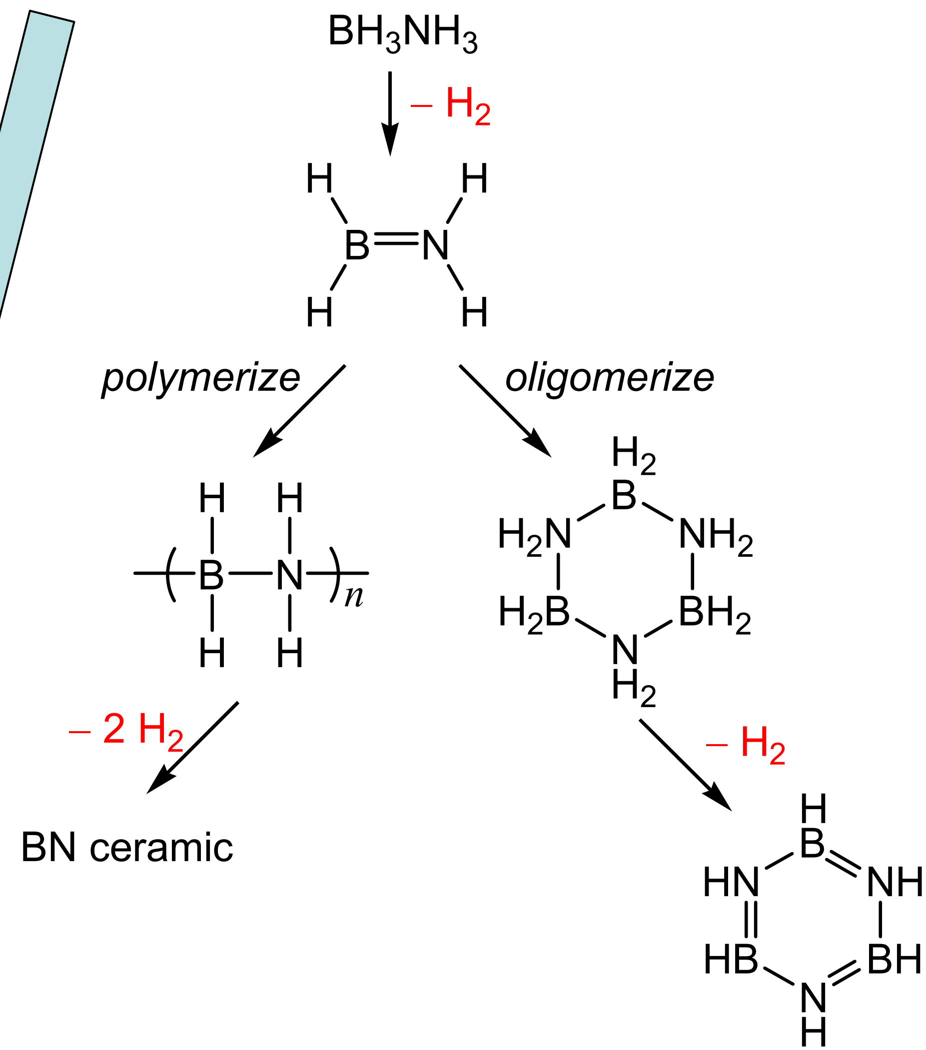
# Preliminary Results: Tier 2
# Hydrogen Production Using Ammonia-Borane

- Ammonia-borane is easily synthesized from commercially available starting materials.
- Low molecular weight paired with the loss of several equivalents of hydrogen gives $BH_3NH_3$ an ideal hydrogen storage capacity of 19.6 wt%.




*Polymerization or oligomerization of $BH_3NH_3$ requires addition of energy (> 80 °C).*

*Can we find a catalyst to lower the temperature?*

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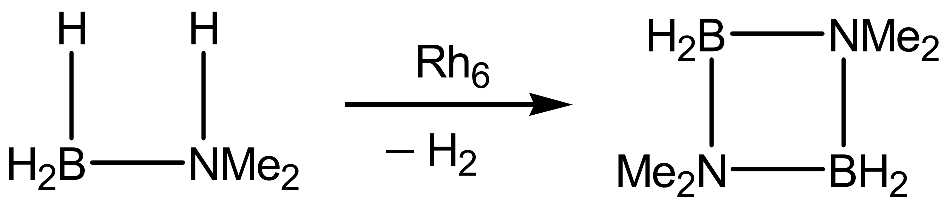
# Catalyst Development for $H_2$ Production




Manners et al. *JACS* **2003**, *125*, 9424
Fulton, Autrey, et al. *JACS* **2005**, *127*, 3254

*Rhodium and other late metal catalysts are expensive*

General characteristics of LANL Proprietary catalysts:

- Commodity chemicals
- Generally air-stable
- Lower molecular weight than transition metal catalysts

Reactions of $BH_3NH_3$ with 10 mol% catalyst (or less!) can be observed at *room temperature*, whereas $BH_3NH_3$ is stable indefinitely at 25 °C (when rigorously anhydrous, air-free conditions are utilized).

*Yes: Our new catalyst system lowers the temperature at which $H_2$ is evolved from $BH_3NH_3$*

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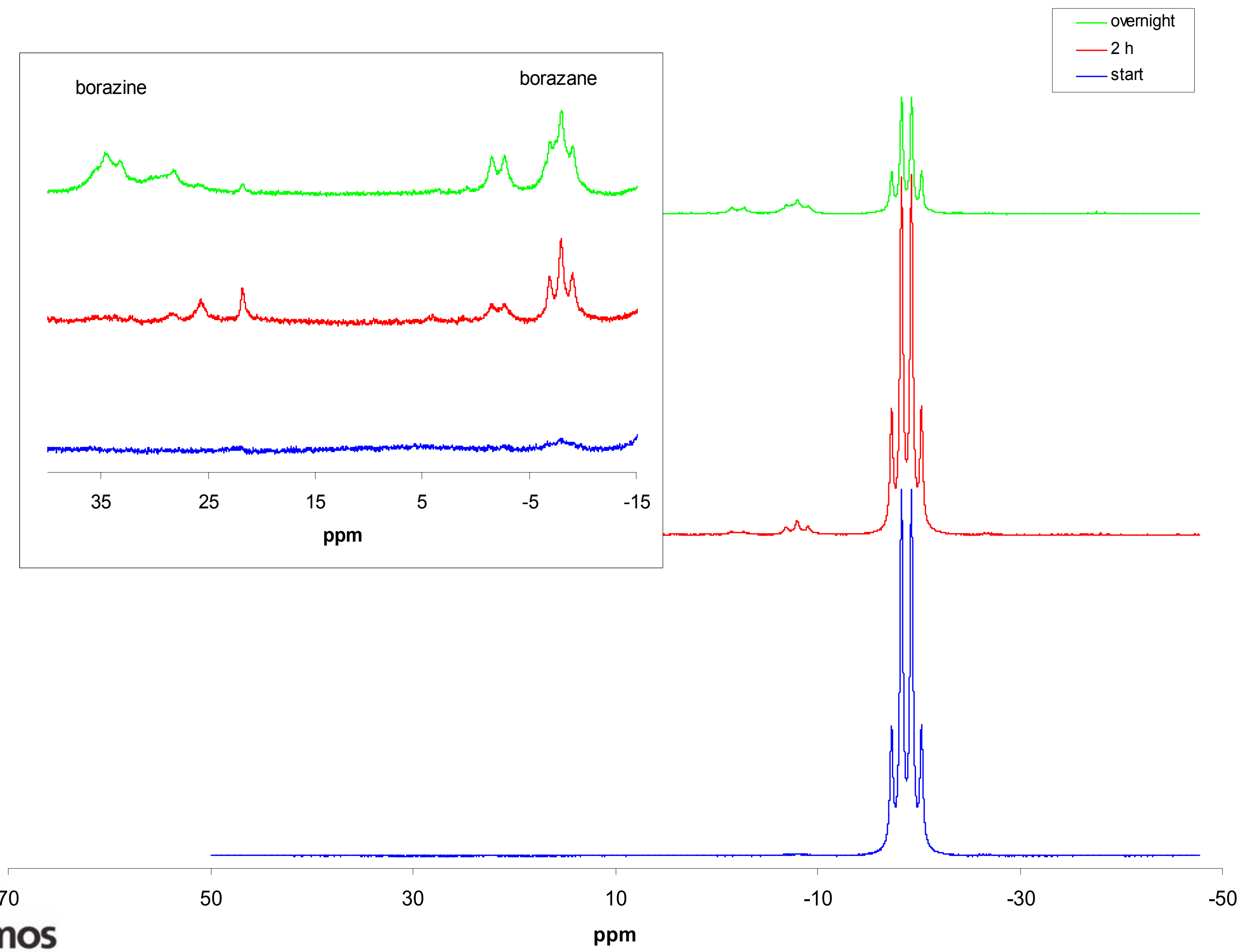
# Sample $^{11}B$ NMR Spectra: Uncatalyzed Thermolysis of $BH_3NH_3$ at 80 °C

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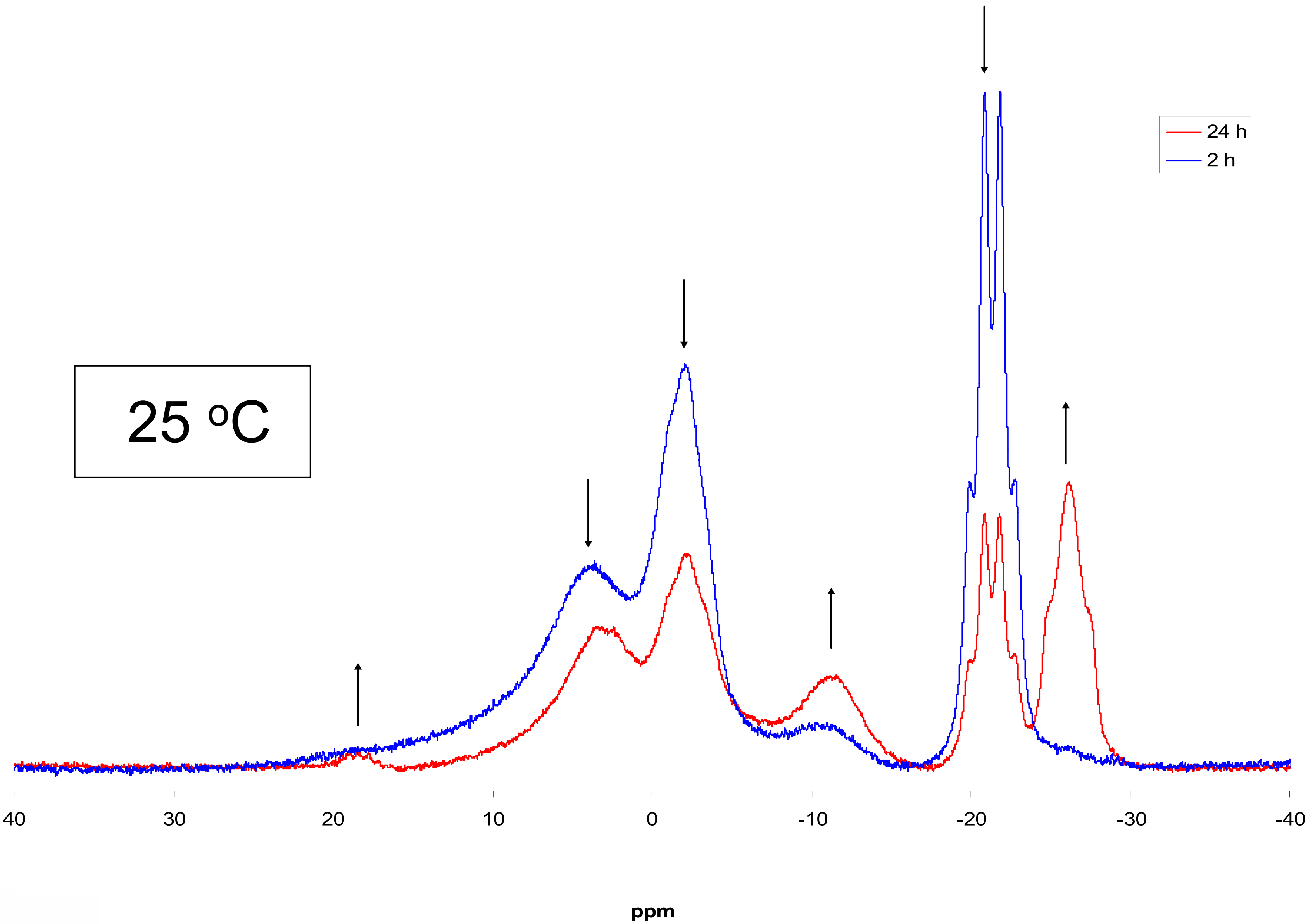
# Sample $^{11}B$ NMR Spectra: Catalyzed Dehydrogenation of $BH_3NH_3$

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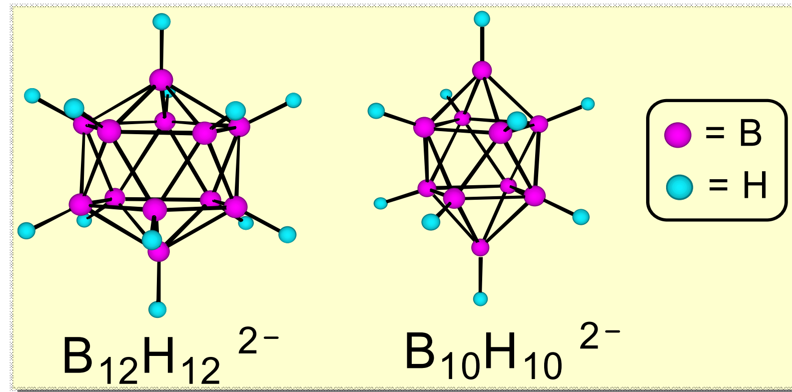
# First Year Milestones

- **Determine electrochemical behavior of polyhedral boranes.**
    - **with PSU, UCLA**
- **Assist in rapid throughput catalyst development on polyhedral borane hydrolysis/aminolysis**
    - **with PNNL, Intematix, UCLA**

- **Optimize reaction conditions for hydrogen evolution from $BH_3NH_3$**
- **Use alkyl-substituted, and $^2H$ and $^{15}N$ labeled amine-boranes to investigate dehydropolymerization mechanism w/ LANL catalysts**
- **Characterize solid $BNH_x$ products**
- **Extend dehydrogenation studies to triborane-amine compounds, B,N-substituted analogs, and polyhedral derivatives**
    - **with/ PNNL, Penn, NAU, UCLA**

# Polyhedral Boranes

Polyhedral boranes are more stable than borohydride and multiple electron sources




- Optimize catalysts for hydrolysis of polyhedral borane anions using rapid throughput heterogeneous catalyst synthesis and testing

$$Na_2B_{10}H_{10}\bullet 16H_2O \;\text{-->}\; 2\ NaBO_2 + 4\ B_2O_3 + 21\ H_2$$

- Other H2 generation routes
  - Aminolysis
  - Electrochemistry
- New regeneration routes from borate
  - with PNNL, Intematix, PSU, UCLA

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# Tier 2: Future Work

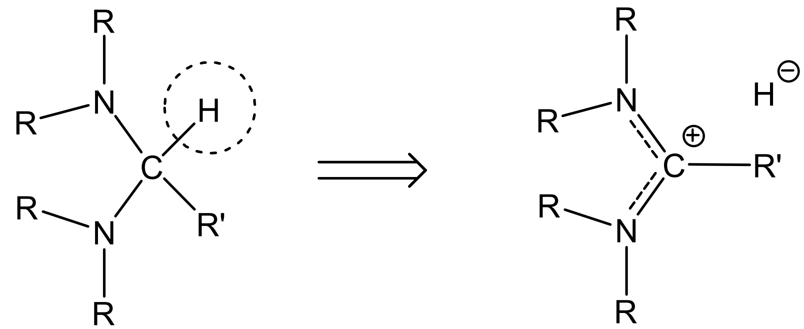
- **Polyhedral borane electrochemistry**
  - with PSU, UCLA
- **Catalyst development on polyhedral borane hydrolysis, aminolysis**
  - with Intematix, PNNL, UCLA
- **Mechanisms and catalyst development**
- **Regeneration of BN systems**
  - with PNNL, Penn, NAU, UCLA
- **Compare reactivity parameters with computation**
  - with PNNL, Alabama
- **Determine best practical routes to amine-boranes**
  - with ROH, US Borax, PNNL
- **Engage all relevant Center partners to optimize regeneration process and life-cycle for integrated B-N hydrogen storage system(s)**
  - Integrated amine-borane hydrogen storage system for engineering and economic assessment.

# Preliminary Results: Tier 3

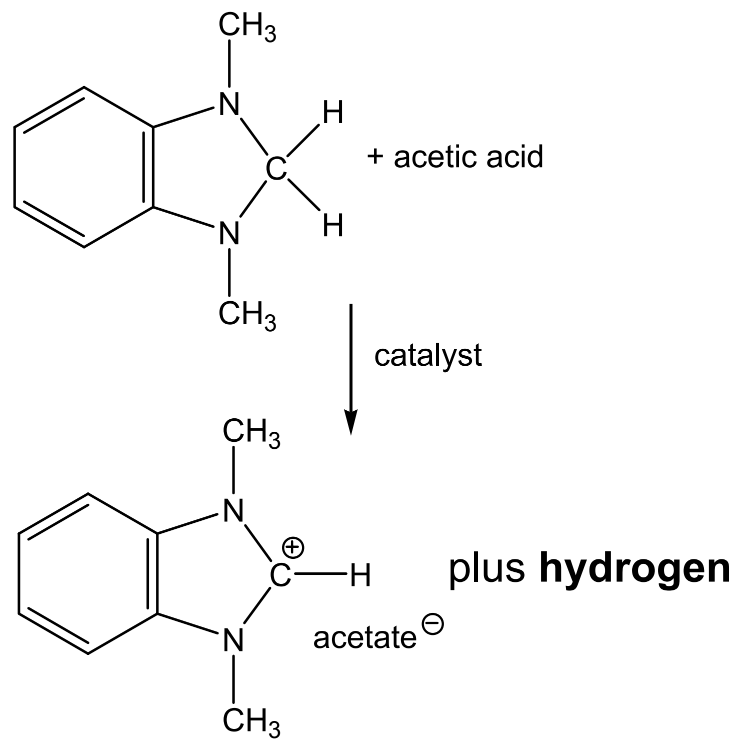
- Coupled reactions to drive hydrogen release
  - Have developed LANL-proprietary concepts for novel means of driving hydrogen-releasing reactions
  - Hypothetical hydrogen capacity > 6 wt%, >0.09 kg $H_2$/liter
  - Modeling, demonstration work begun
- Nanoparticles for hydrogen storage
  - Apparatus developed and demonstrated for preparing nanoparticles by "physical" means (ablation of target, gas-phase selection)
  - Installation of molecular hydrogen doser, atomic hydrogen doser, temperature-programmed-desorption nearing completion

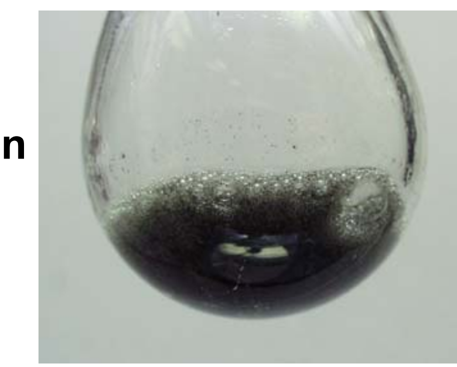
# Preliminary Results: Tier 3
## Heteroatom-Substituted Organic Compounds

- N-substituents make C-H bond act as “organic hydride”




- In laboratory test, mixture of “organic hydride” plus acid is unreactive …



- … until treated with catalyst
- Path forward: Improve capacity

# Future Work: Tier 3

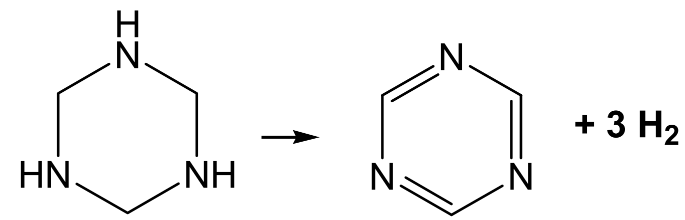
- **Heteroatom-substituted organic compounds:** Demonstrate principle (Y1), useful $H_2$ release rate (Y2)

  Remove "dead weight" and raise capacity (Y4-5)

- **Coupled reactions:** Prove hydrogen release (Y1), demonstrate useful $H_2$ release rate (Y2), using non-precious metals (Y3), pursue to demonstration (Y4-5)

- **Nanoparticles:** Demonstrate working apparatus (Y1), prepare nanoparticles rich in B, alloying metals, N (Y2); establish ability to hydrogenate, dehydrogenate (Y4-5)

Target:
Remove everything except N groups and "hydridic" CH

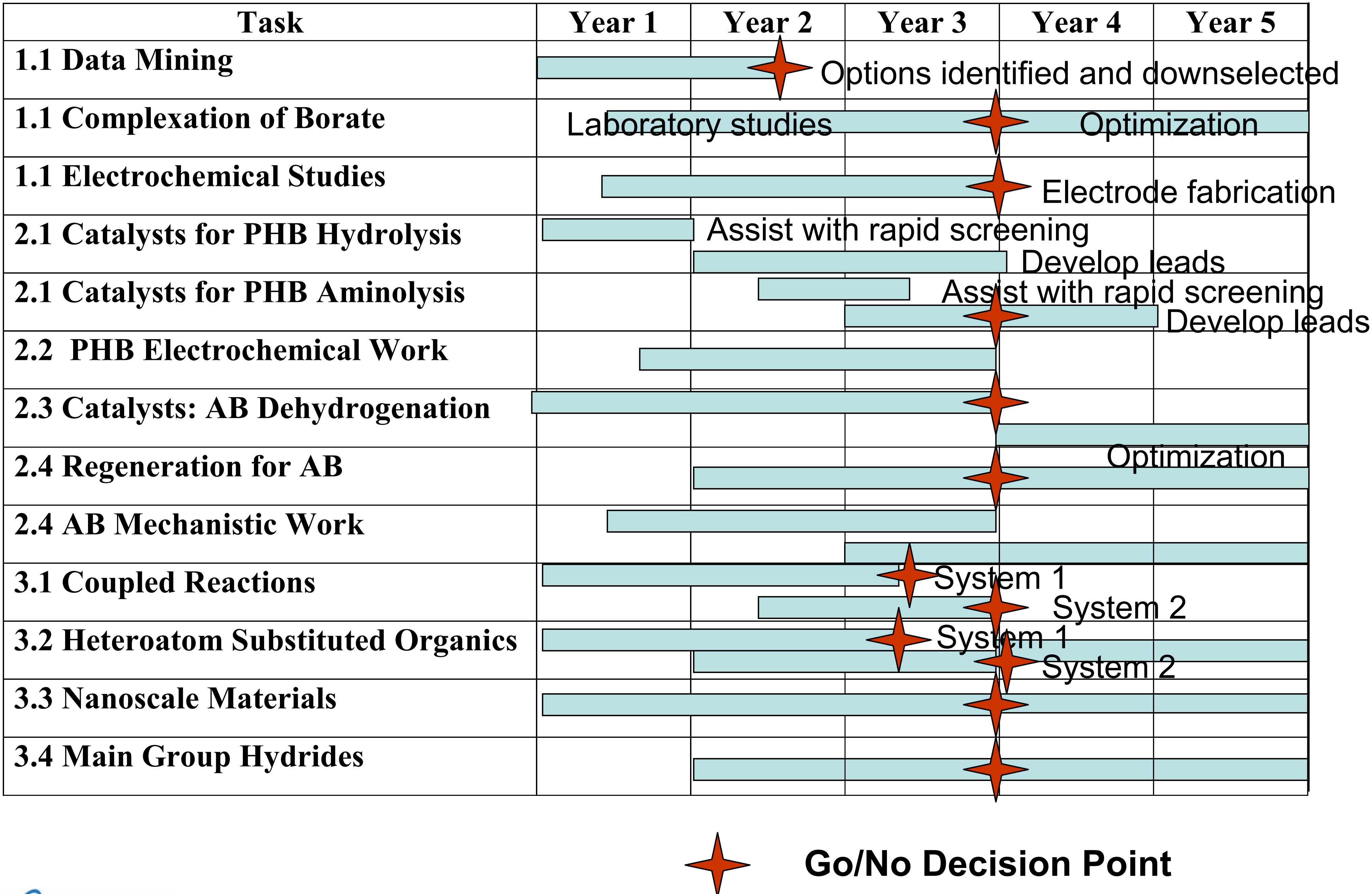



(material capacity > 6.9 wt% $H_2$)

U. Alabama has concepts to stabilize, immobilize these structural units

# Center Coordination

- Objectives
  - Real collaboration and information sharing within Tiers
  - Collaborative project structure
  - Share background information
  - Foster joint discovery/inventions
  - Reward and manage success
- Status
  - Joint development projects (Center projects) defined
  - Framework for IP management developed and being signed
    - **Defines management of joint inventions**
    - **Enables technology transfer**
  - Website developed
  - Center project meetings, conference calls
  - Monthly center-wide "newsletter"


Task
Year 1
Year 2
Year 3
Year 4
Year 5
1.1 Data Mining
Options identified and downselected
1.1 Complexation of Borate
Laboratory studies
Optimization
1.1 Electrochemical Studies
Electrode fabrication
2.1 Catalysts for PHB Hydrolysis
Assist with rapid screening
Develop leads
2.1 Catalysts for PHB Aminolysis
Assist with rapid screening
Develop leads
2.2 PHB Electrochemical Work
2.3 Catalysts: AB Dehydrogenation
Optimization
2.4 Regeneration for AB
2.4 AB Mechanistic Work
3.1 Coupled Reactions
System 1
System 2
3.2 Heteroatom Substituted Organics
System 1
System 2
3.3 Nanoscale Materials
3.4 Main Group Hydrides
Go/No Decision Point

# Hydrogen Safety

The most significant hydrogen hazard associated with this project is:

Inadvertant overpressurization of reaction or storage vessels with hydrogen

"Chemical Hydrogen Storage" requires working with chemicals and reactions that evolve hydrogen.  In closed vessels,evolved hydrogen may accumulate, resulting in explosion and fire hazards.

# Hydrogen Safety

Our approach to deal with this hazard is:

Do not close reaction or storage vessel until certain that the amount of hydrogen that could be evolved can be safely contained by the vessel. If necessary, maintain vent to inert atmosphere. Use relief valves.

# Publications and Presentations

- Patent disclosure submitted for new class of amine-borane dehydrogenation catalysts. Provisional patent to be submitted June '05
- Poster presentation, IPHE Hydrogen Storage, Lucca, Italy (June '05)
- Present poster at Inorganic Chemistry Gordon Research Conference (July '05, Newport, RI)
- Two abstracts submitted for American Chemical Society, FUEL Division Hydrogen Storage symposium (August '05, National ACS Meeting, Washington, D.C.)
- Present invited lecture FECHEM 16 (September '05, Budapest, Hungary).
- Paper submitted 3/05 "Hydrogen Evolution from Organic 'Hydrides' " by D. Schwarz et al.
- Provisional patents filed on heteroatom-substituted organic compounds