Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H_2 Storage Materials

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in collaboration with PNNL, University of Alabama, and Protonex

2012 Annual Merit Review
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ST104

This presentation does not contain any confidential or otherwise restricted information

Overview

Timeline

start date: April 1, 2012
end date: March 31, 2015
Phase I: 4/1/2012 – 9/30/2013
Phase II: 10/1/2013 – 3/31/2015
percentage complete: new project

Technical Barriers (Vehicular)

A. system weight and volume
C. efficiency
E. charging/discharging rates
R. regeneration process

Proposed Budget

total project funding: $2,526,606
DOE share: $2,020,942
cost share: $505,664

FY12: $540,000

Project Collaborators

Prof. Shih-Yuan Liu
Project Lead

Pacific Northwest National Laboratory

Dr. Jamie Holladay
Dr. Tom Autrey
Dr. Abhi Karkamkar
Dr. Doinita Neiner

The University of Alabama

Prof. David Dixon

Protonex

Dr. Paul Osenar

Project

Objectives:

- develop novel chemical H_2 storage materials that have the potential to meet 2017 DOE targets for vehicular applications and near-term market applications
- focus on three classes of materials: liquid-phase, high-capacity, reversible

Team Member Expertise:

University or Oregon (UO): synthesis and development of CBN H_2 storage materials
Pacific Northwest National Laboratory (PNNL):

- experimental characterization of materials (thermodynamics, kinetics, thermal stability, H_2 purity)
- scale up synthesis

University of Alabama (UA): computational chemistry
Protonex: fuel cell manufacturing expertise for near-term market applications

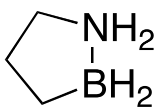
Tasks

1) Synthesis of proposed materials (UO, PNNL)
2) Characterization of synthesized materials (PNNL)
3) Theory (UA)
4) Scale-Up Synthesis (UO, PNNL),
5) Fuel Cell Testing (PNNL, Protonex)

Specific Synthetic Targets

well-defined liquid systems

A



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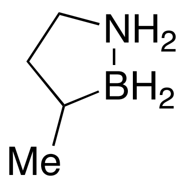

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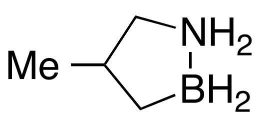

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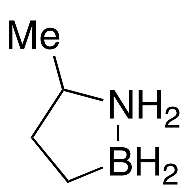
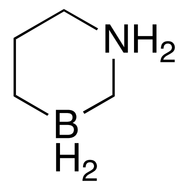


potential reversible systems

E



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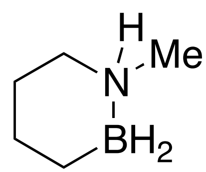

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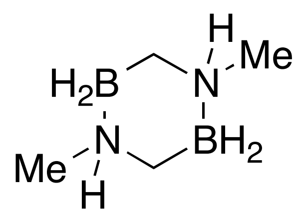
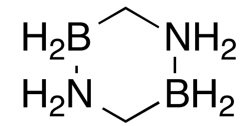


high capacity exothermic systems

H



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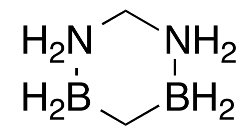

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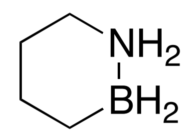

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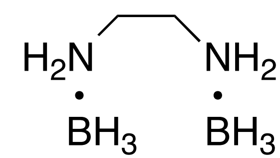

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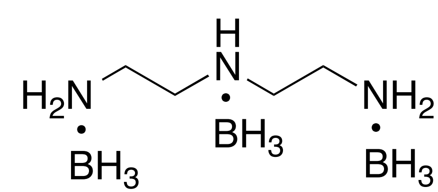


Phase I Deliverables & Go/No-Go Criteria

Task 1 (synthesis): > 6 CBN materials and > 3 blends made available for characterization
Task 2 (characterization): physical properties, thermodynamic & kinetic data, capacity measurements, catalyst structure, H_2 purity, DSC, TGA, MS, NMR, PCI
Task 3 (theory): thermodynamic, kinetic, spectroscopic properties of proposed materials

Phase II:
Task 4 (scale up): 10x to 100x increase in scale from initial methods (50-200 mg)
Task 5 (fuel cell testing): fuel cell testing data with best candidates

liquid systems

single component:
- liquid fuel at 0 °C
- > 4.5 wt.%, > 40 g H_2/L
- > 95% fuel purity
- T(release) < 110 °C
- regeneratable

multi component:
- liquid fuel at 0 °C
- > 5.5 wt.%, > 50 g H_2/L
- T(release) < 150 °C

reversible systems

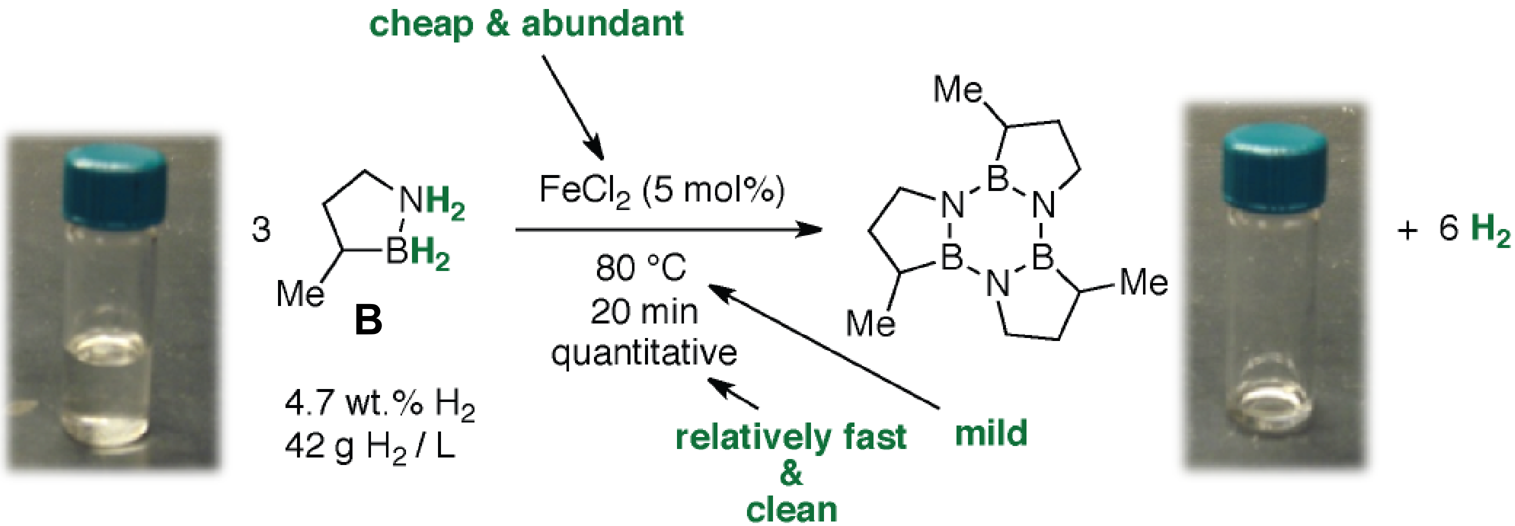
- ΔG ~ 0 kcal/mol (overall)
- ΔH = +7 to + 12 kcal/mol H_2
- > 5.0 wt.%, > 40 g H_2/L
- T(release) < 200 °C

high-capacity systems

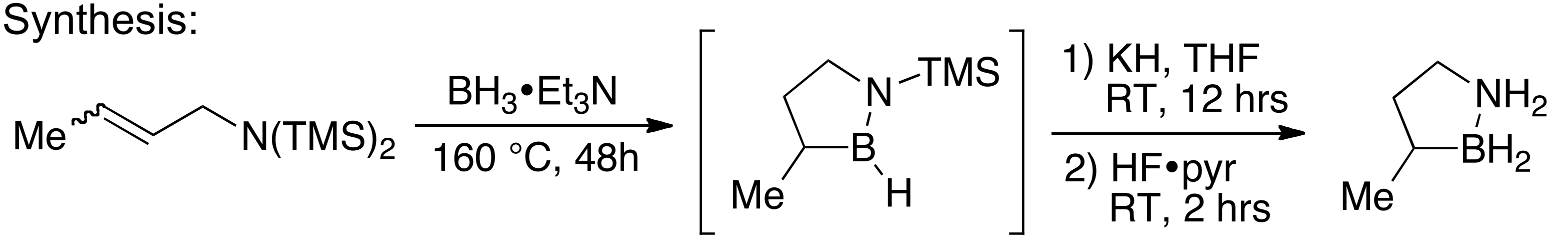
- > 8 wt.%
- T (release) < 150 °C

PNNL blends (K, L):
- > 8 wt.%
- T(release) < 150 °C

Preliminary Results: A Single-Component Liquid H_2 Storage Material



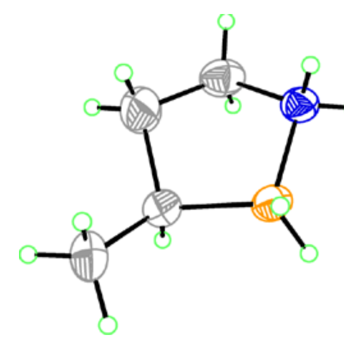
Synthesis:



Highlighted in:

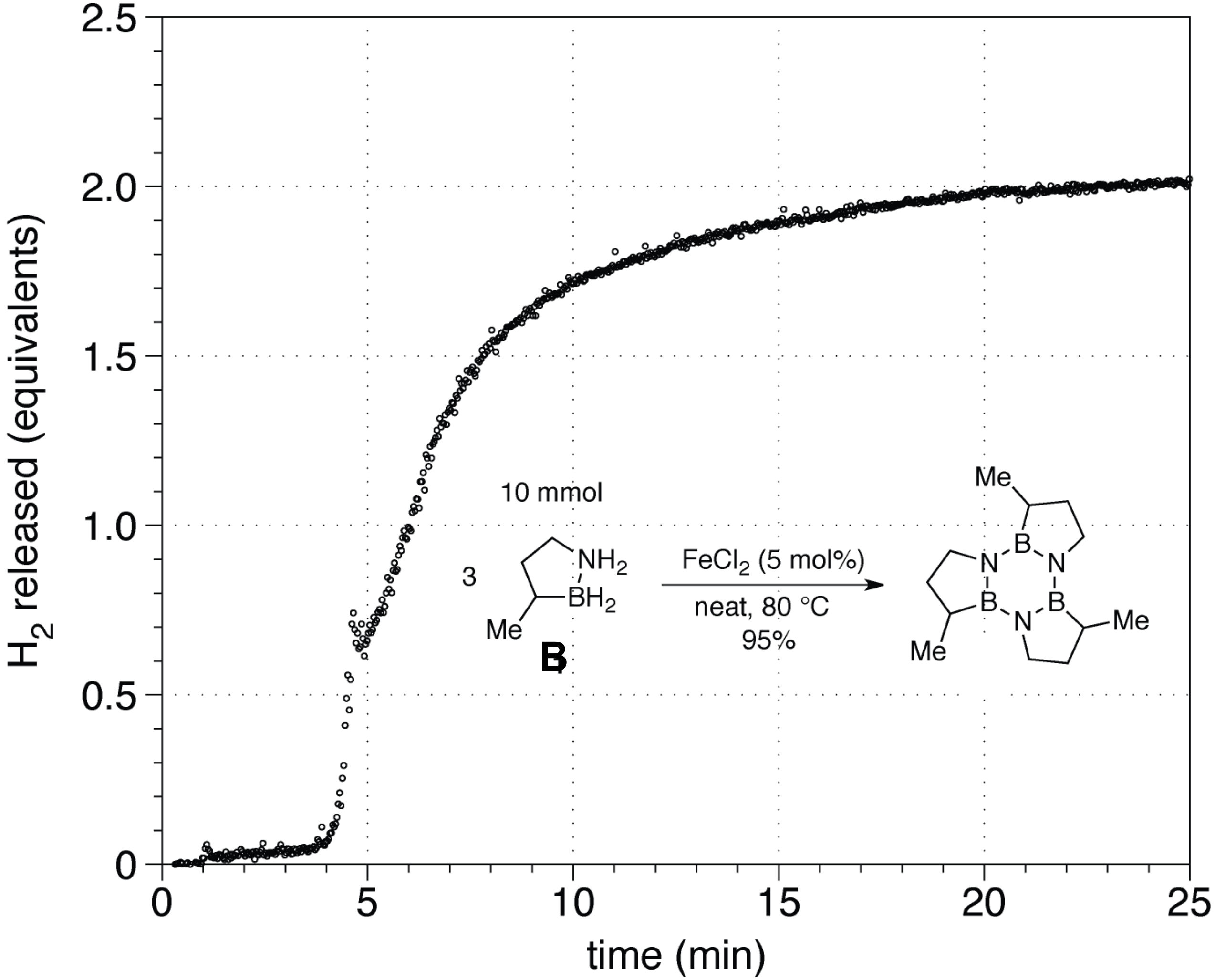
- *C&EN* **2011**, November 28, page 35.
- *Nature Chemistry* **2012**, *4*, page 5.
- *Nature Climate Change* **2012**, *2*, page 23.

Synthesis of Material B and its desorption was accomplished.



Wei Luo, Patrick Campbell *J. Am. Chem. Soc.* **2011**, *133*, 19326-9.

Fe-Catalyzed H_2 Release (Neat Liquid)



Catalyst particles (black) are on the surface of a magnetic stir bar.

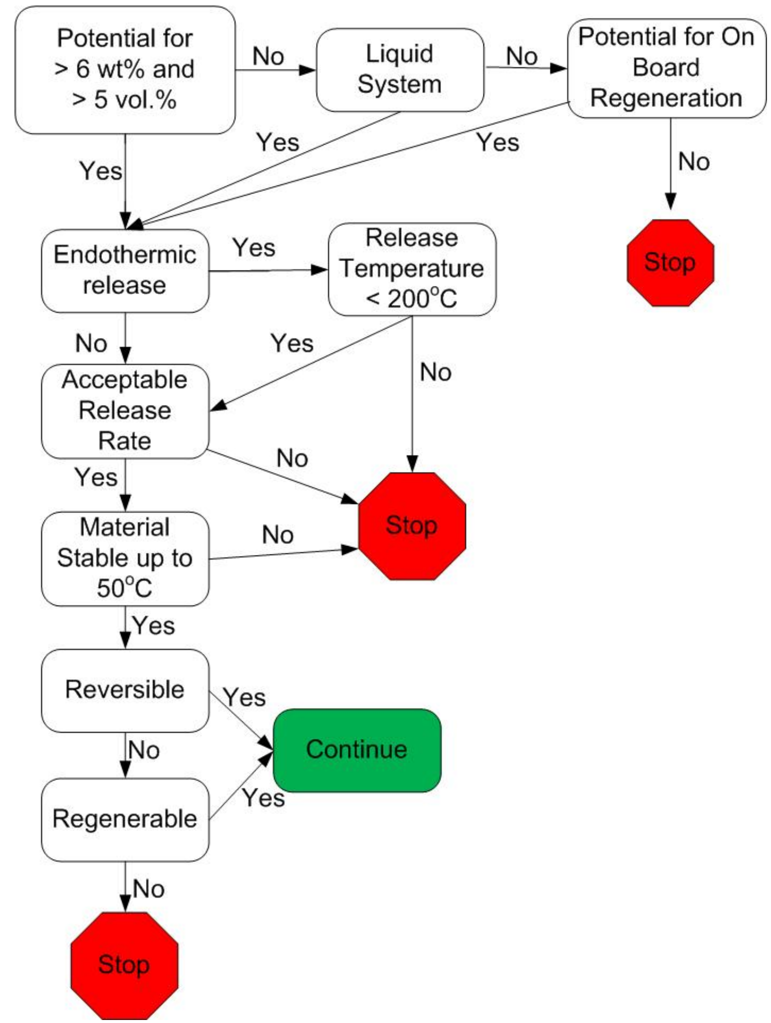
Dehydrogenation is feasible at larger scales as a neat liquid.

Wei Luo, Patrick Campbell *J. Am. Chem. Soc.* **2011**, *133*, 19326-9.

PNNL Expertise:

Our approach is to use multiple techniques to characterize materials to minimize errors in analysis

- Thermodynamics (enthalpies)
  - Reaction Calorimetry, PCI, NMR
- Kinetics (rates)
  - gas buret, PCI, in-situ NMR
- Thermal Stability
  - TGA, PCI, Volumetric gas burette
- Regeneration Process
  - NMR to identify structures in products. Required to enable a rational approach to regeneration
- Impurities (volatiles)
  - TGA/MS, TPD/IR,RGA



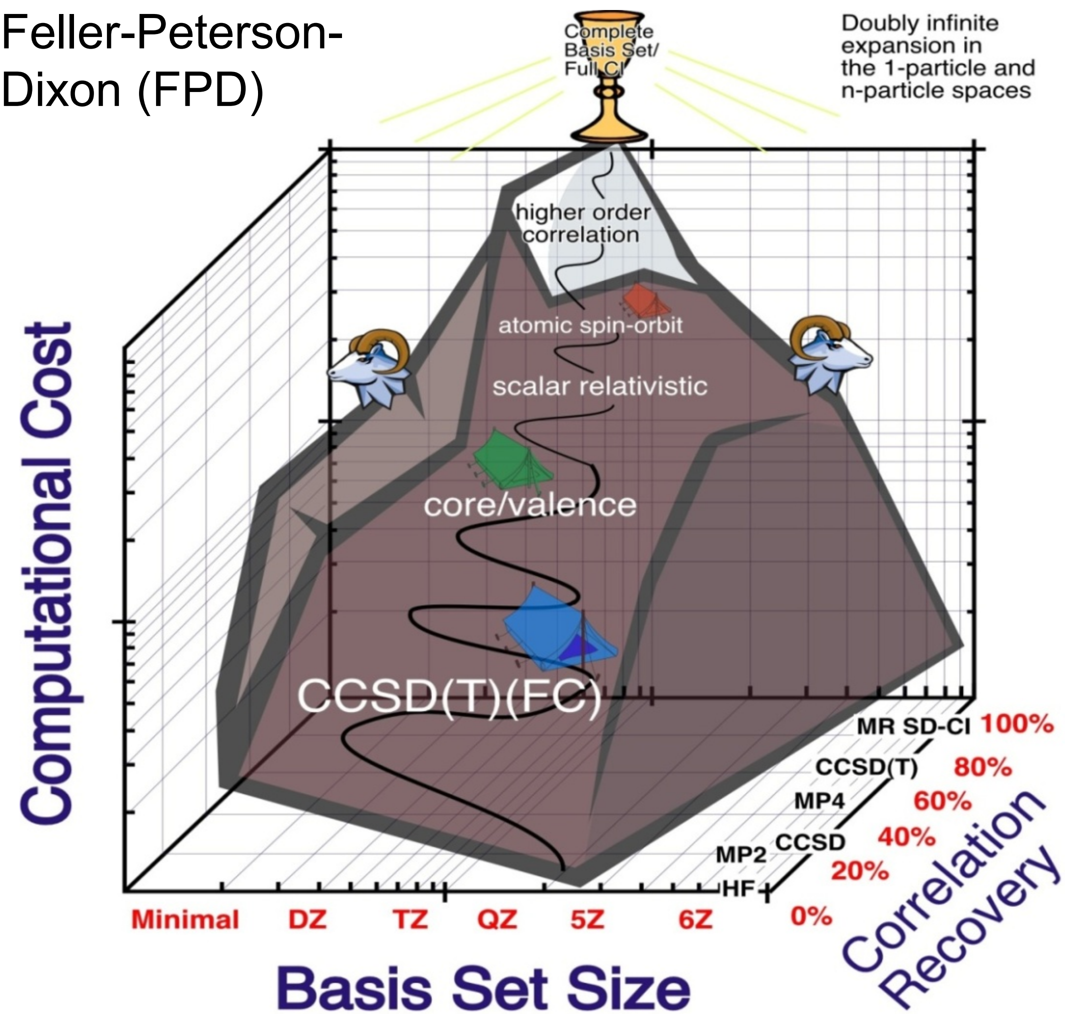
PNNL has the experience and unique capabilities needed to characterize H_2 storage materials. Characterization will provide the required insight to make rational decisions on the down-selection of materials to meet or exceed US DRIVE technical targets.

The University of Alabama: Objectives & Approaches

- Predict thermodynamic, kinetic, and spectroscopic properties of **A – L**
- Predict H_2 release mechanisms
- Predict regeneration mechanisms
- Help to develop potential catalysts
- Use correlated molecular orbital theory (Feller, Peterson, Dixon composite approach & G3MP2) and density functional theory with self-consistent reaction fields to predict reactions in the gas phase and in solution with different solvents

UA: High Level Computational Thermochemistry

Feller-Peterson-Dixon (FPD)



Gaussian09, MOLPRO, NWChem

$$E = E_{CBS} + E_{core} + E_{SR} + E_{SO} + E_{ZPE}$$

$$E_{atomization} = E_{atoms} - E_{molecule}$$

Total atomization energy (TAE) calculated at the CCSD(T) level extrapolated to the complete basis set limit (CBS) using the augmented-correlation consistent basis sets

+ Core corrections – CCSD(T)/cc-pwCVTZ level

+ Scalar relativistic correction – CI(SD)/cc-pVTZ (MVD) or MP2/cc-pVTZ DK (DKH)

+ Atomic/Molecular = Total spin orbit correction

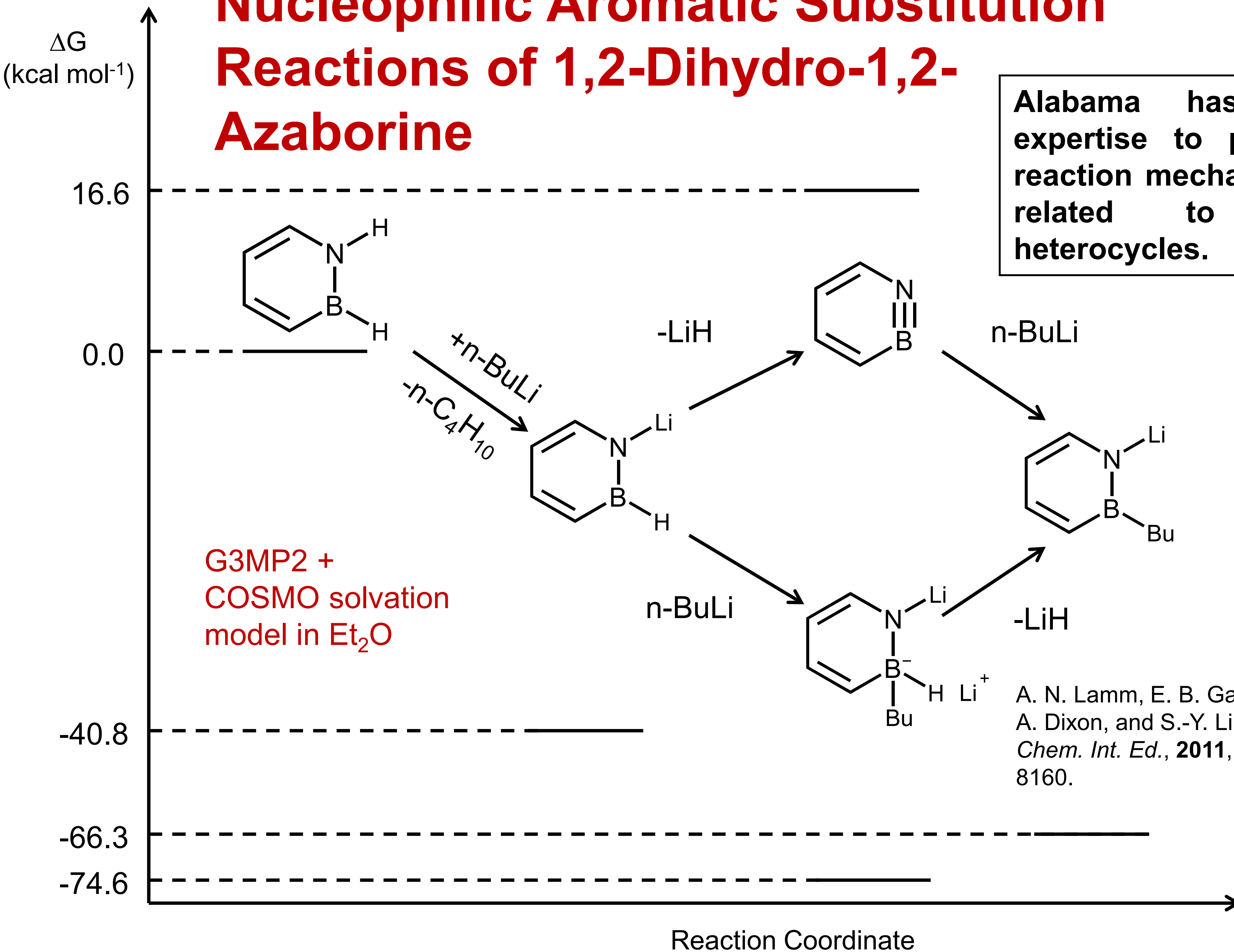
+ Zero point energy – MP2/aug-cc-pVTZ level

+ Thermal correction (0K → 298 K) – MP2/aug-cc-pVTZ level.

Atomic heats of formation ΔH_f to get molecular heats of formation ΔH_f

N^7 method

Nucleophilic Aromatic Substitution Reactions of 1,2-Dihydro-1,2-Azaborine



Alabama has the expertise to predict reaction mechanisms related to BN heterocycles.

A. N. Lamm, E. B. Garner, III, D. A. Dixon, and S.-Y. Liu, *Angew. Chem. Int. Ed.*, **2011**, *50*, 8157-8160.

Protonex: Perspective from Private Sector

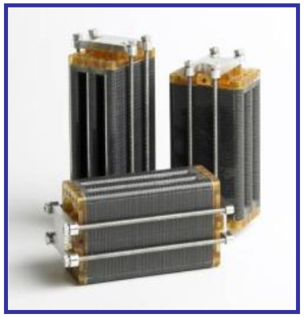
Organization	▪ Founded in 2000; headquartered in Southborough, MA with 48 employees ▪ Exceptional team with deep roots in fuel cell and high technology ▪ Listed on the AIM in July 2006; proactively delisted in June 2010
Solution Overview	▪ Leading provider of 100 - 1000 watt fuel cell power solutions ▪ Only fuel cell manufacturer to specialize in both PEM and SOFC designs ▪ Over 100 granted and pending patents on key technology
Value Proposition	▪ Clean, quiet, efficient and lightweight fuel cell power solutions ▪ High-performance and reliable fuel cells for military applications ▪ Runs on a range of fuels to deliver environmentally friendly energy
Customer and Partner Traction	▪ Targeted applications include: military battery charging, UAV power, APU, general portable, and others ▪ Key strategic partnerships with both military and commercial leaders
Financial Profile	▪ Accelerating product revenue as products transition from trial to deployment ▪ 2011 product revenue projected growth at over 90% ▪ Major shareholders include Parker Hannifin, Goldman and Conduit Ventures

Protonex Technology

- A leading provider of 100 - 1000 watt fuel cell power solutions
  - Focused on a broad range of applications under-served by batteries and generators
  - Providing clean, quiet, efficient, lightweight, high performance power solutions
  - Utilizing advanced PEM and SOFC technologies

Proton Exchange Membrane (PEM)

- Fuels
  - Methanol
  - Chemical Hydride
  - Hydrogen
- Operating temperature: 50˚C – 75˚C



Solid Oxide Fuel Cell (SOFC)

- Fuels
  - Propane
  - Gasoline, Diesel and JP-8
  - Bio and renewable fuels
- Operating temperature: 650˚C - 750˚C

PROVIDING FUEL FLEXIBILITY TO ADDRESS MULTIPLE APPLICATIONS. PROTONEX IS THE ONLY COMPANY WITH BOTH PEM AND SOFC

Potential Near-Term Application Opportunities

Military
- Generators/APUs
- Battery Chargers
- UAV/UGV/UUV Power
- Power Managers

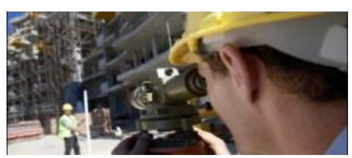
Backup Power
- Broadband / CATV
- Telecom Networks
- Critical Systems
- Traffic Systems

Recreation
- RV Power
- Marine Power
- Campsite/Cabins
- General Portable

Transport
- Truck Idling APU
- Personal Mobility
- Small EVs

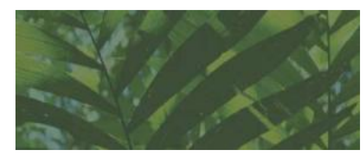
Protonex™

Emergency
- Homeowners
- Battery Chargers
- Comm. Equipment
- Security Systems



Professional
- Generators/APUs
- Battery Charging
- Scientific Equipment
- Video Equipment

Renewable
- Off Grid Homes
- Small Solar Systems
- Small Wind Systems
- Remote Monitoring



Government
- First Responders
- Generators/APUs
- Command Centers
- Remote Power

Current Targets