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

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

Prof. David Dixon

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

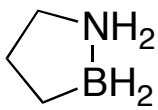
Tasks

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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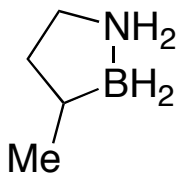

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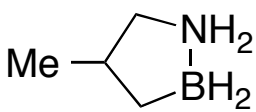

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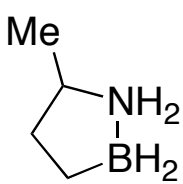
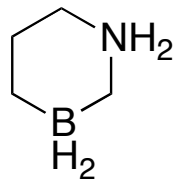


potential reversible systems

E



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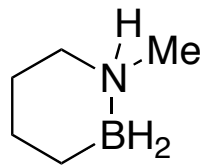

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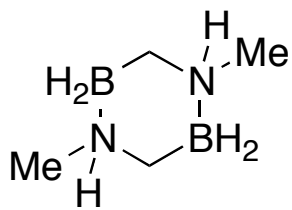
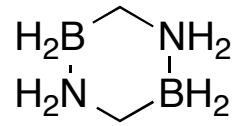
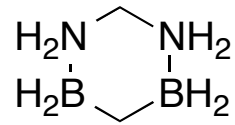


high capacity exothermic systems

H



I



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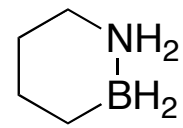

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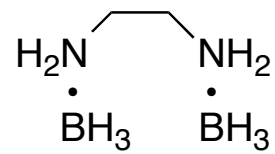

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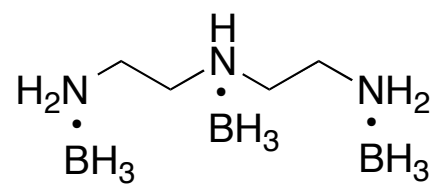


Phase I Deliverables & Go/No-Go Criteria

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

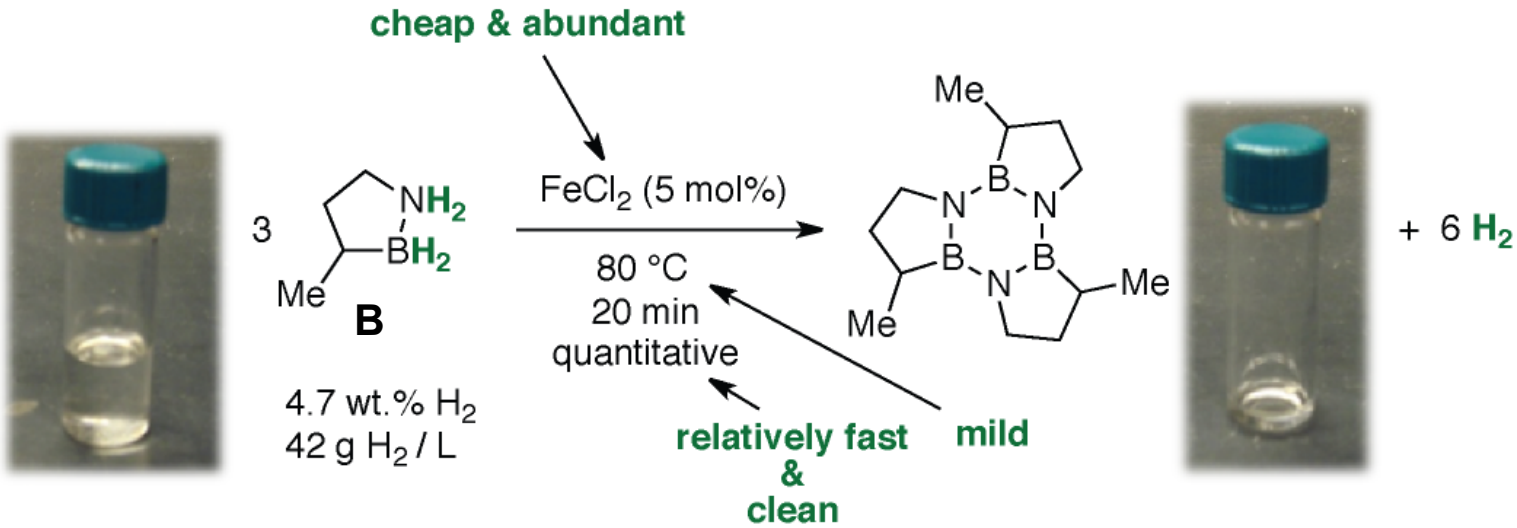
- $\Delta G \sim 0$ kcal/mol (overall)
- $\Delta H = +7$ to $+12$ kcal/mol H_2
- > 5.0 wt.%, > 40 g H_2/L
- T(release) < 200 °C

high-capacity systems

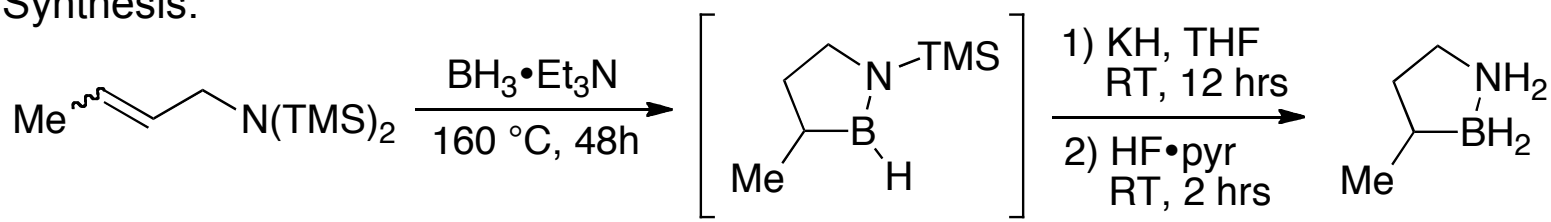
- > 8 wt.%
- T (release) < 150 °C

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

Preliminary Results: A Single-Component Liquid H_2 Storage Material



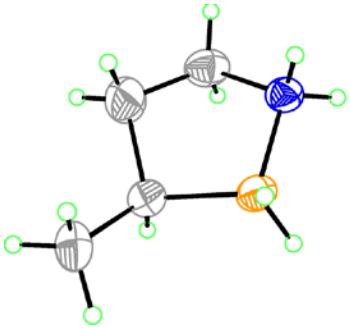
Synthesis:



Highlighted in:

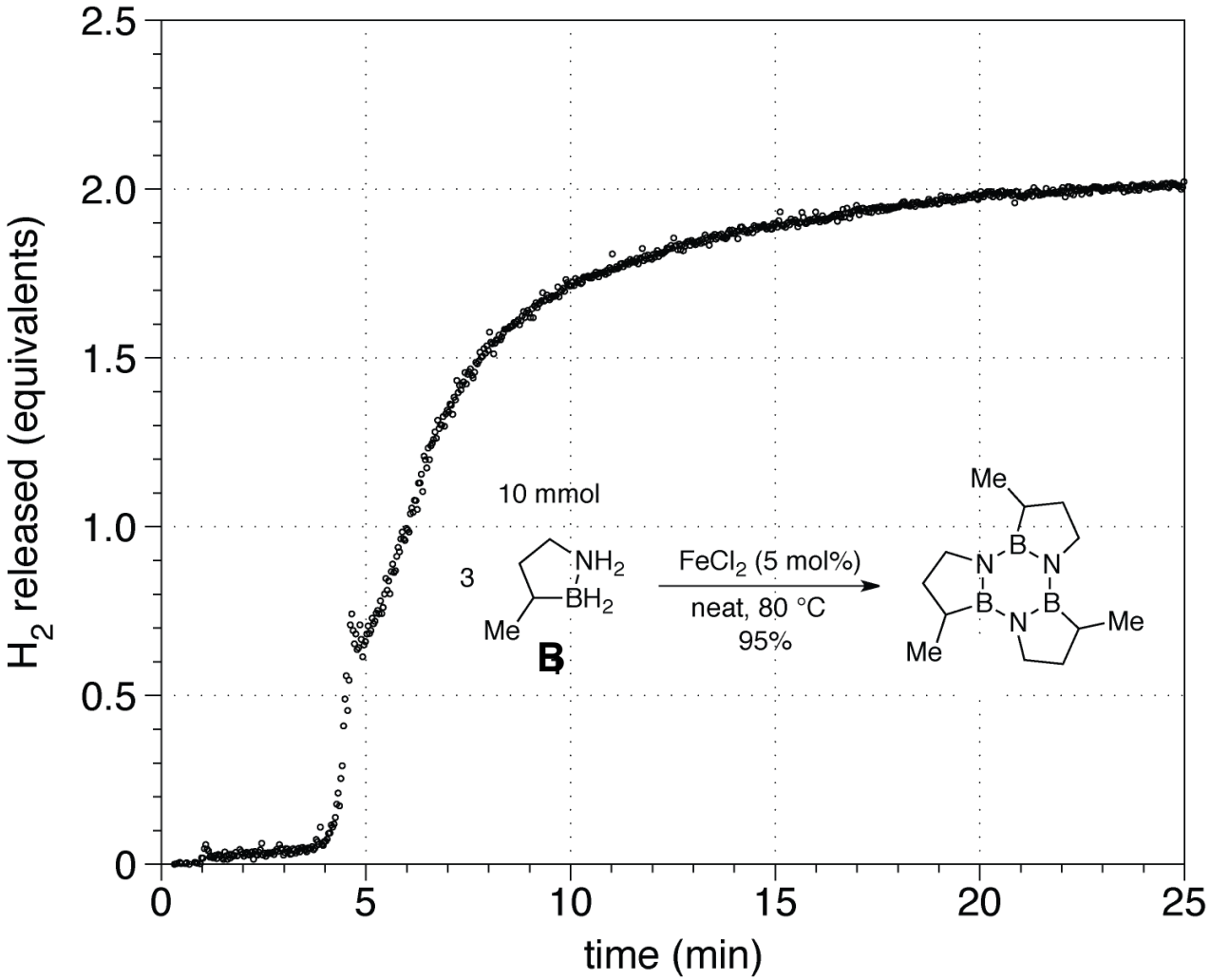
- *C&EN* **2011**, November 28, page 35.
- *Nature Chemistry* **2012**, *4*, page 5.
- *Nature Climate Change* **2012**, *2*, page 23.

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.

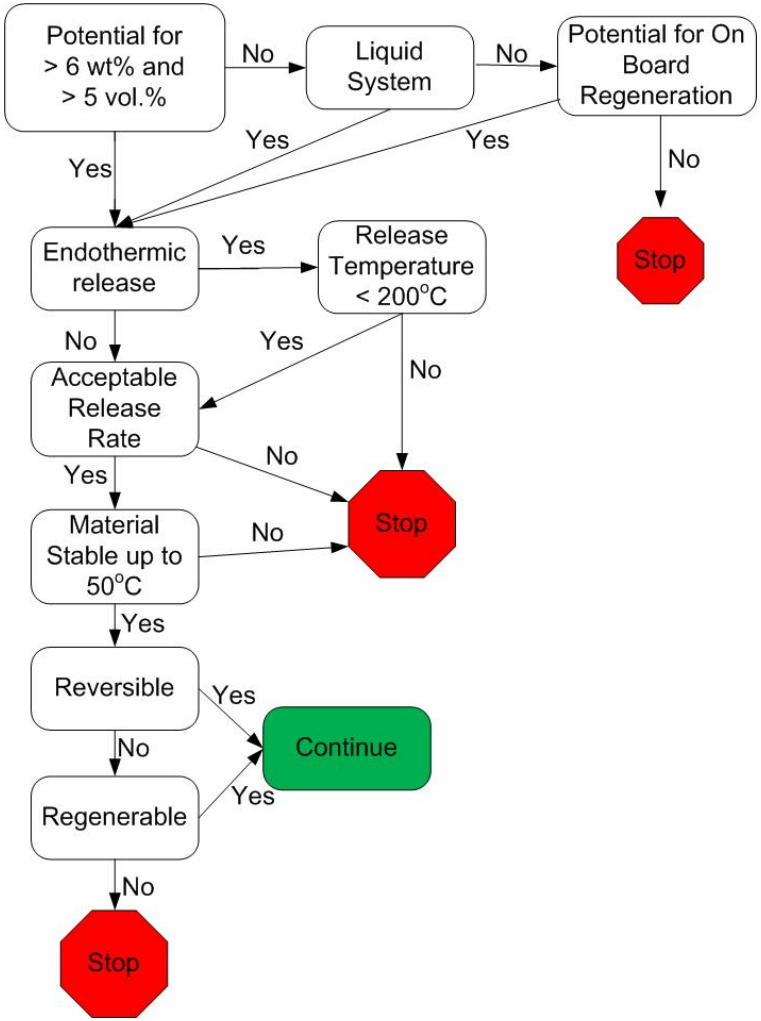
Dehydrogenation is feasible at larger scales as a neat liquid.

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



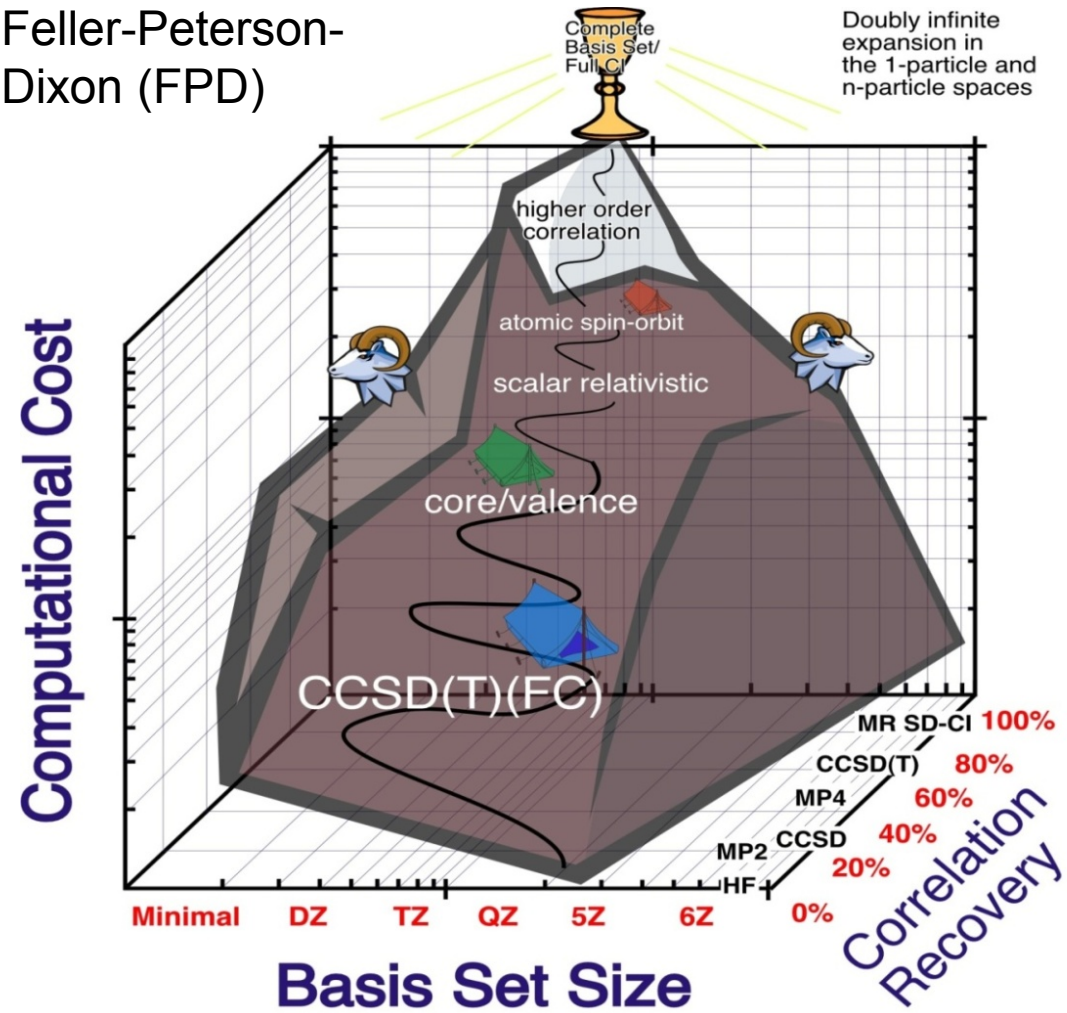
PNNL has the experience and unique capabilities needed to characterize H_2 storage materials. Characterization will provide the required insight to make rational decisions on the down-selection of materials to meet or exceed US DRIVE technical targets.

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

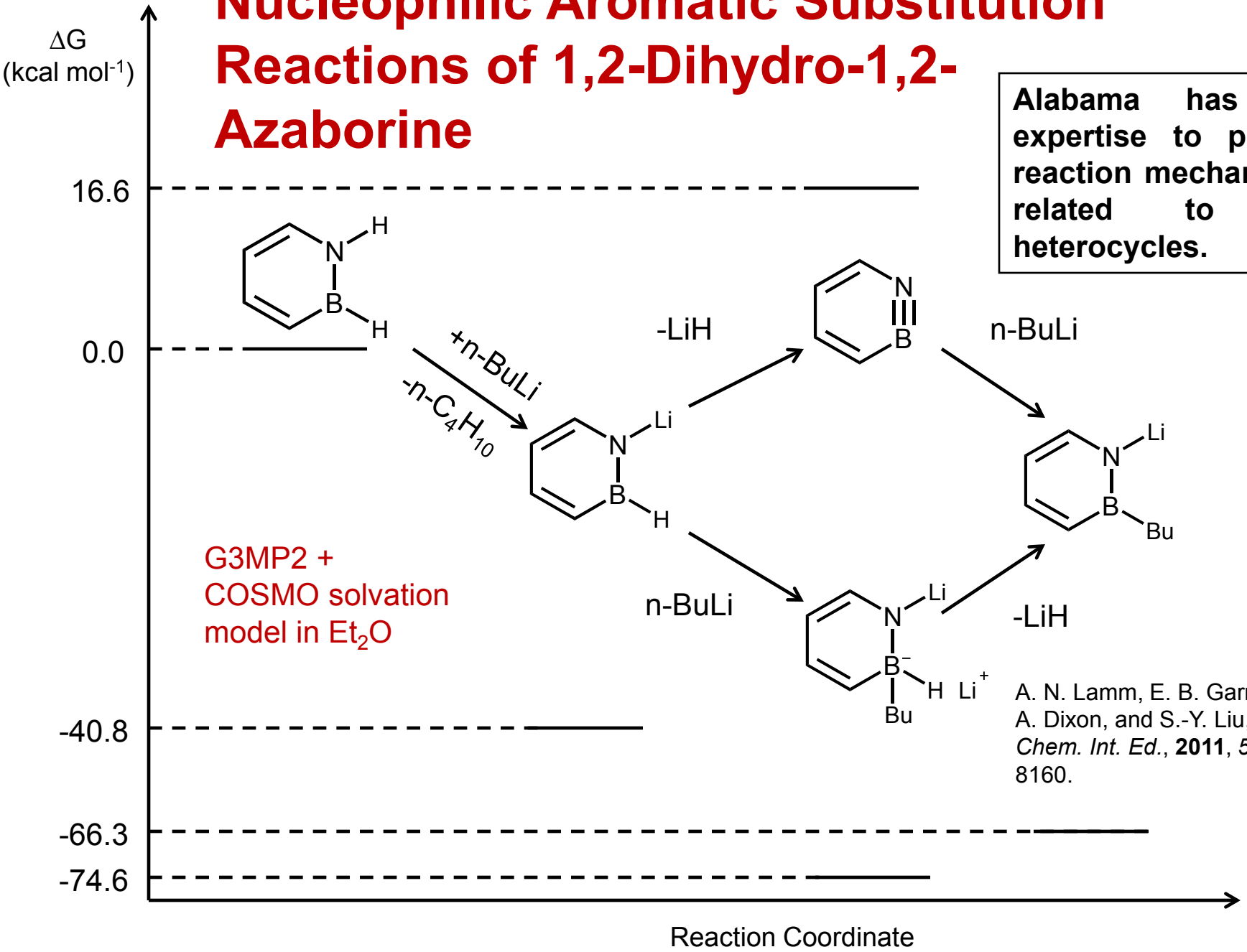
+ Thermal correction (0K → 298 K) – MP2/aug-cc-pVTZ level.

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

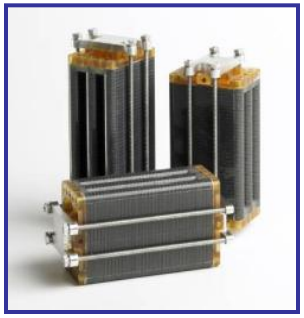
- Accelerating product revenue as products transition from trial to deployment
- 2011 product revenue projected growth at over 90%
- Major shareholders include Parker Hannifin, Goldman and Conduit Ventures

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

Government

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

Professional

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

Renewable

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

Current Targets