



Hydrogen Storage by Novel CBN Heterocycle Materials

Shih-Yuan Liu (lsy@uoregon.edu)

Department of Chemistry, University of Oregon

2009 Tech Team Review

Detroit, March 19, 2009

In partnership with the Chemical Hydrogen Storage Center of Excellence

STP_16_Liu

This presentation does not contain any confidential or otherwise restricted information

Overview

Timeline

start date: September 2008
end date: August 2011
percent complete: 22%

Budget

total project funding: \$930,855
DOE share: \$742,395
UO share: \$188,460

FY09 funding: \$275,000

Barriers

A. system weight and volume
C. efficiency
R. regeneration process

Project Collaborators



Prof. David Dixon



Dr. Tom Autrey

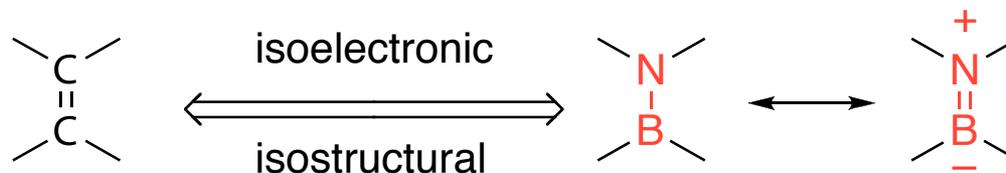


Prof. Karen Goldberg
Prof. Mike Heinekey

Executive Summary

- A new project as part of the CHSCoE
- Focus on cyclic H₂ storage materials containing C, B, and N
- New approach to H₂ storage that complements the materials currently under investigation
- These CBN materials can meet the DOE targets
- Couple *exothermic* H₂ desorption from *BN* with *endothermic* H₂ desorption from *CC* in a *cyclic* system to address reversibility
- Strong collaborative effort with feedback loops between theory, synthesis, catalysis, and charge/discharge characteristics measurements
- Progress: synthesized CBN materials, demonstrated facile H₂ absorption, received attention in general science news media

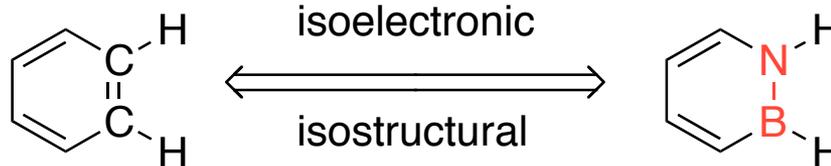
Research in the Liu Group - Relevance



benzene

1,2-dihydro-
1,2-azaborine

- important
- ubiquitous



Scientific Research:

synthesis

structure, bonding
aromaticity
catalysis, mechanism



Applications:

new synthetic methods
biomedical applications
optoelectronic materials
H₂ storage materials

Project Objectives - Relevance

Develop CBN heterocycles as novel hydrogen storage materials:

- liquid-phase
- gravimetric density (> 6 wt. %)
- volumetric density (> 4.5 vol. %)
- thermodynamics (H₂ absorption and desorption)
- regeneration (reversibility)
- 2010 DOE targets

Specific objectives – Phase I (9/1/2008 – 3/31/2010):

- calculate thermodynamic properties of CBN heterocycle materials
 - synthesize liquid phase CBN heterocycle materials
 - determine thermodynamic properties for CBN heterocycles via experiment
 - identify best theoretical model
-
- develop/identify catalysts for H₂ absorption and desorption to/from CBN heterocycles
 - demonstrate reversibility

Approach

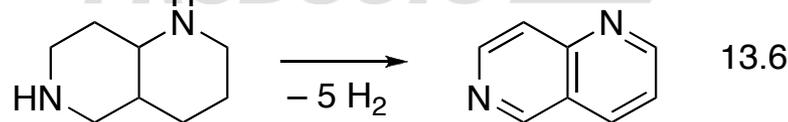
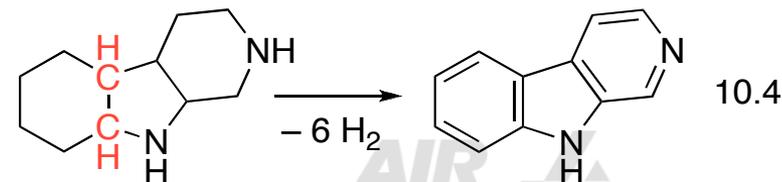
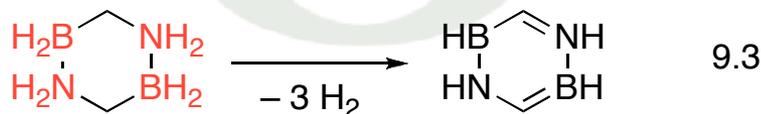
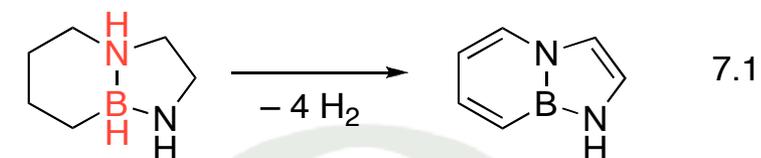
couple *exothermic* H₂ desorption from *BN* with *endothermic* H₂ desorption from *CC* in a *cyclic* system to achieve optimal thermodynamics for the overall H₂ absorption/desorption process

avg. ΔH
(kcal/mol H₂)

Goal: spent fuel can be directly regenerated on-board with H₂

Distinct from Air Products approach

- contains boron
- one CC is replaced by BN
- lower activation energy in some of the steps
- synergistically combines features of ammonia borane and cyclic systems



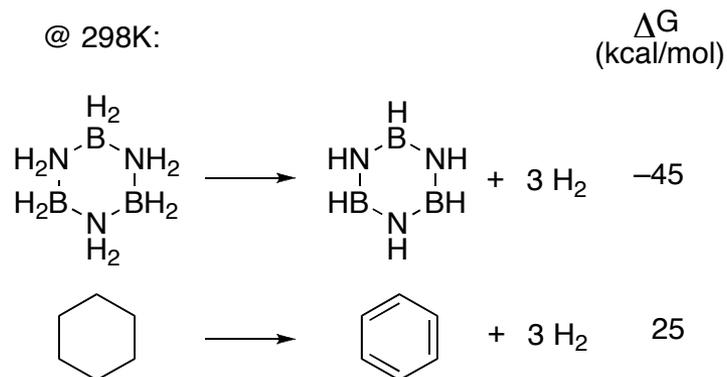
A Collaborative Approach

(calculate, synthesize, measure, optimize)



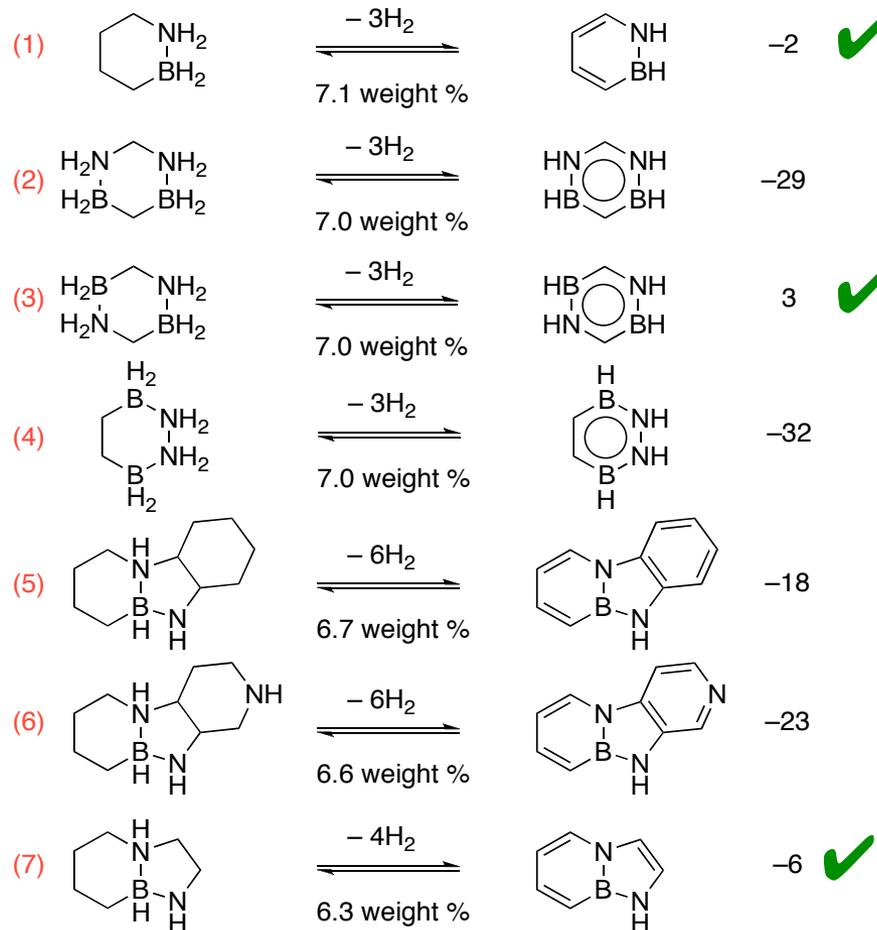
$$\Delta G = \Delta H - T\Delta S$$

reversible H₂ storage: $\Delta G \sim 0!$



Use theory to help select synthetic candidates

ΔG at 298K
(kcal/mol)



Approach - Summary

- distinct from ammonia borane and cyclic systems currently under investigation; complements the current approaches
- addresses technical barriers (system weight and volume, efficiency, regeneration)
- synergistic theoretical and experimental strategy (feedback loop for optimization)
- collaborative effort with CHSCoE partners (UA, PNNL, UW)

Milestones (Phase I)

- computational thermodynamic data of H₂ desorption of CBN heterocycle materials
- availability of CBN heterocycle materials for experimental investigation
- experimental thermodynamic data for CBN materials for comparison with theory
- selection of best theoretical models based on experiment

-
- identification of optimal catalysts/conditions for H₂ desorption from CBN materials and for regeneration of spent fuel

Go/no-go decisions (Phase I)

- go: if materials are synthetically readily available
no-go: if materials are synthetically not accessible
- go: if materials exhibit appropriate thermodynamic properties (theory + experiment)
no-go: if materials do not exhibit appropriate thermodynamic properties (theory + experiment)

Developing Synthetic Tools - Progress

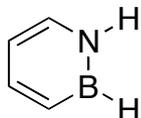
organic



benzene

Faraday
(1825)

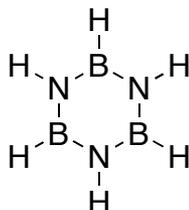
hybrid
organic/inorganic



1,2-dihydro-
1,2-azaborine

(2008)

inorganic



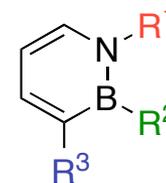
borazine

Stock
(1926)

 Adam Marwitz

 Myrna Matus

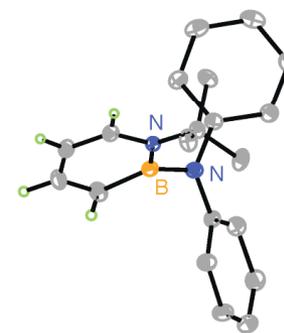
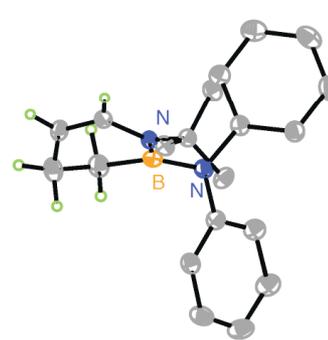
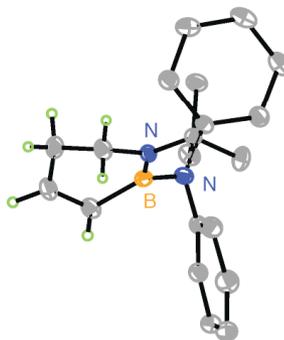
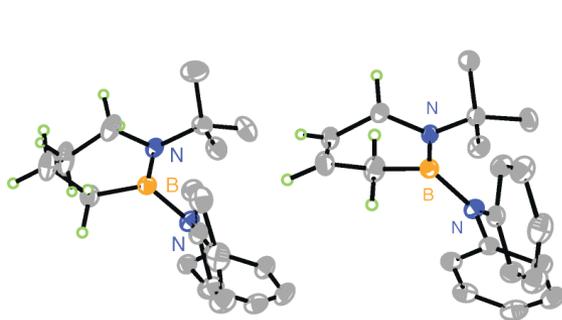
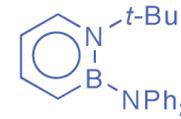
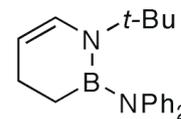
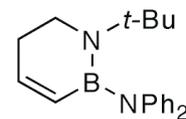
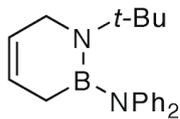
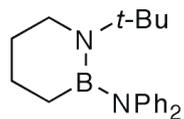
Angew. Chem. Int. Ed.
2009, 48, 973-7.



 Adam Marwitz
Org. Lett. **2007**, 9, 4905-8.

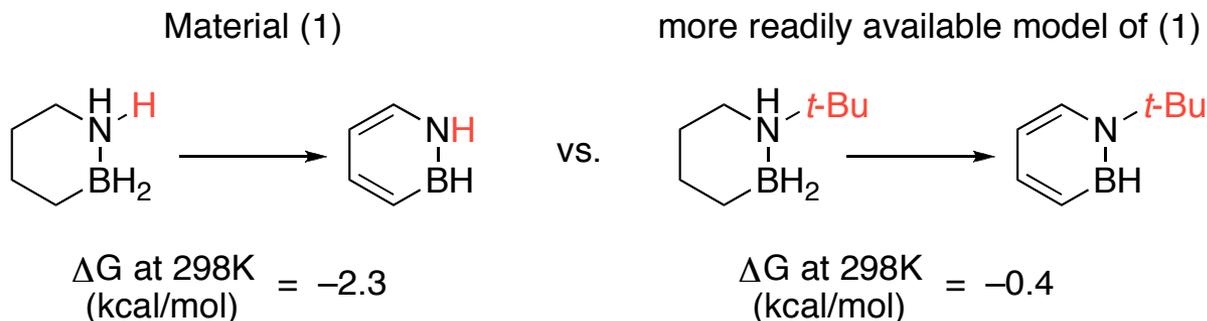
J. Am. Chem. Soc.
2008, 130, 7250-2.

 Eric Abbey



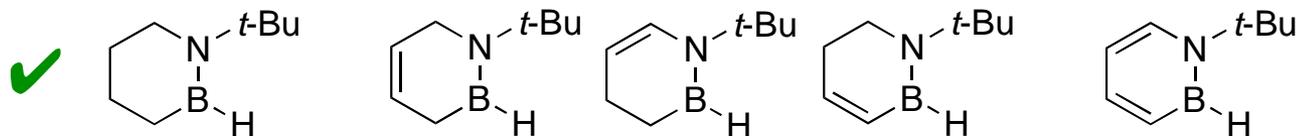
Several new materials have been prepared

Model for C₄BNH_x System - Progress



- similar thermodynamic properties, thus appropriate model

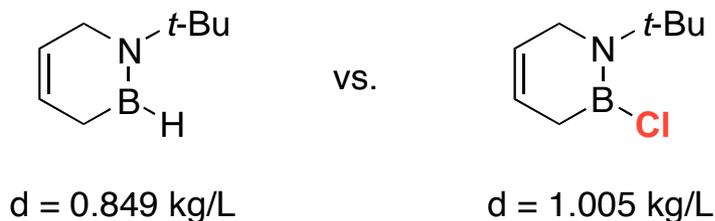
- **successfully prepared all five isomers of the model material**



- compounds delivered to UW for H₂ absorption/desorption studies
- compounds essential for obtaining experimental thermodynamic data at PNNL

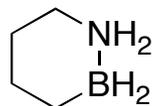
Assessing the Volumetric Density - Progress

- halogenated materials exhibit higher volumetric density



- CBN materials can meet the 2010 volumetric density targets**

Mw: 85
7.1 wt. %



assuming "d = 0.849"
0.060 kg H₂/L, i.e., 6.0 vol. %

Mw: 119
5.0 wt. %

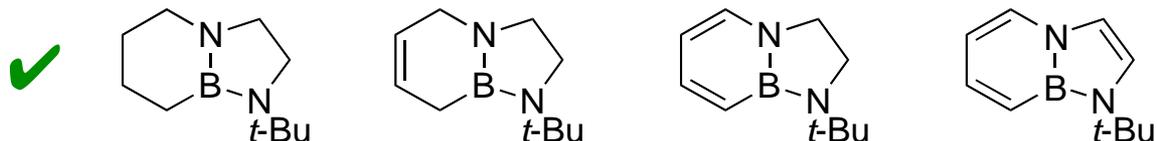


assuming "d = 1.005"
0.050 kg H₂/L, i.e., 5.0 vol. %

- boron substituents might be used to modulate thermodynamic properties without significant loss in volumetric density

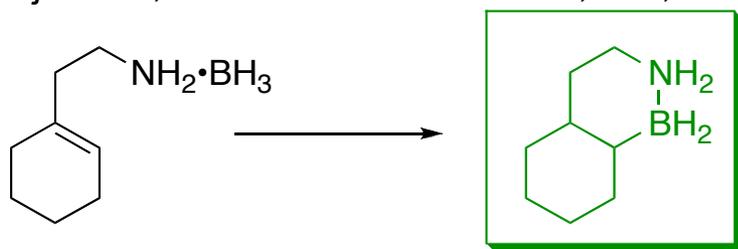
Toward CBN Material (1) and (7) - Progress

Eric Abbey: *N*-substituted model of CBN Material (7)

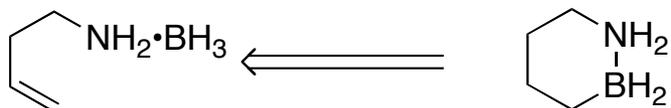


Kshitij Parab: unsubstituted CBN Material (1)

Vedejs et al., *J. Am. Chem. Soc.* **2003**, 125, 10502-3.



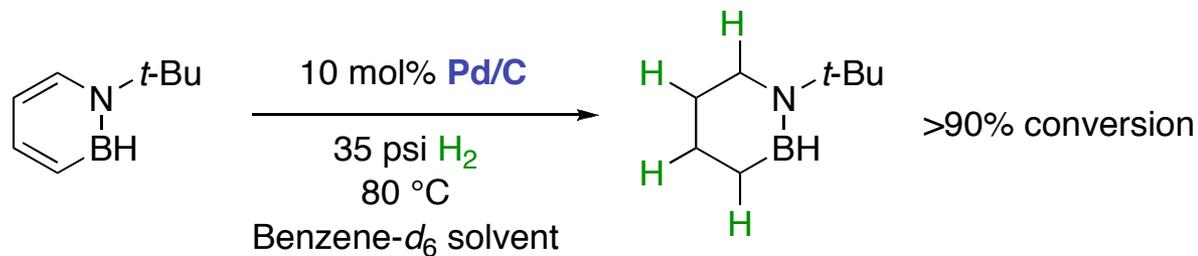
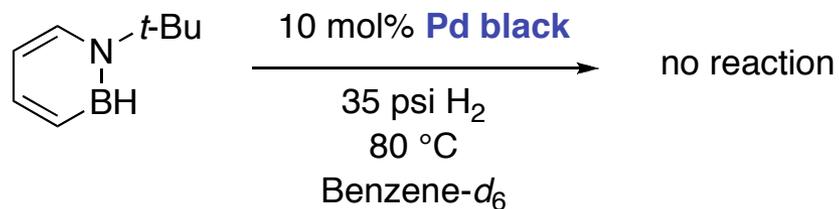
original published procedure not reproducible in our hands; successfully developed new conditions for the synthesis.



development of unsubstituted CBN Material (1) in progress

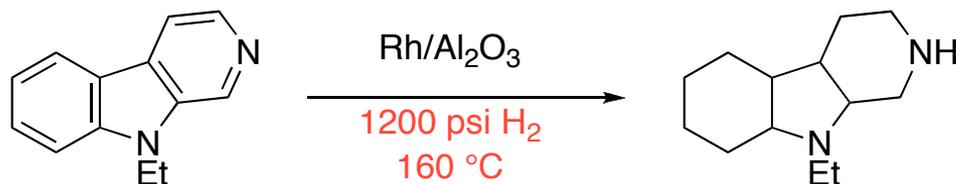
More materials are in route

Facile Hydrogen Uptake - Progress



Benzene- d_6 is not hydrogenated!

VS.



Hydrogen uptake has been observed

Collaborations

Project Collaborators



computational studies of H₂ desorption pathways of cyclic CBN materials, evaluation of thermodynamics and energetics



experimental mechanistic studies of H₂ absorption/desorption to/from cyclic CBN materials, thermodynamic measurements using reaction calorimetry, H₂ charge/discharge characteristics



development/discovery of efficient catalysts for H₂ desorption from CBN materials

Technology Transfer



obtained computed thermodynamic data and H₂ desorption reaction pathways for CBN heterocycle materials, will provide feedback with experimental data



obtained very preliminary thermodynamic data via reaction calorimetry



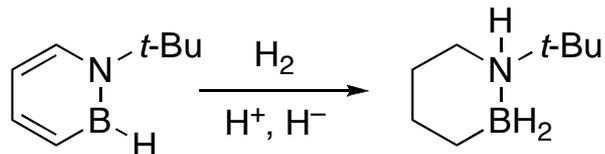
prepared CBN heterocycle materials and delivered to UW for further investigation

Proposed Future Work



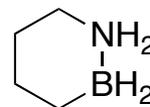
- determine charge/discharge characteristics

- demonstrate regeneration of spent fuel using the model system

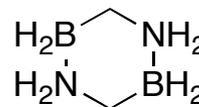


- experimental thermodynamic data for CBN heterocycle materials for comparison with theory, provide feedback loop to optimize theoretical modeling

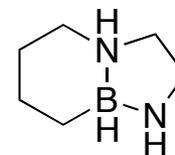
- focus on developing CBN Materials (1), (3), and (7)



(1)



(3)



(7)

- develop/identify efficient catalysts for H₂ desorption from these CBN materials

The proposed work will be carried out in collaboration with other center partners:

THE UNIVERSITY OF
ALABAMA

optimization of theory
thermodynamics
transition states


Pacific Northwest
NATIONAL LABORATORY

charge/discharge characteristics
mechanistic studies
thermodynamic data

 UNIVERSITY OF
WASHINGTON

catalyst development
couple exothermic H₂ desorption from BN
with endothermic H₂ desorption from CC

Project Summary

- Relevance:** development of novel liquid phase hydrogen storage materials with desirable storage capacity and thermodynamics for reversible H₂ absorption and desorption
- Approach:** coupling of exothermic H₂ desorption from BN with endothermic H₂ desorption from CC in a cyclic system to achieve optimal thermodynamics for H₂ absorption/desorption; distinct from amine-borane and cyclic materials currently under investigation
- Progress:**
- **developed synthetic tools for CBN heterocycle materials**
 - **prepared set of heterocycle CBN materials for H₂ absorption/desorption studies, delivered to partners within the CHSCoE**
 - **demonstrated facile H₂ absorption by CBN heterocycle materials**
- Collaborations:** active partnership with CHSCoE members (UA, PNNL, UW)
- Future Work:**
- further develop the synthesis of CBN Heterocycle Materials (1), (3), and (7)
 - obtain experimental thermodynamic data for CBN materials
 - determine/optimize H₂ charge/discharge characteristics