Hydrogen Storage by Novel CBN Heterocycle Materials

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Department of Chemistry, University of Oregon
2010 Annual Merit Review
Washington DC, June 10, 2010
In partnership with the Chemical Hydrogen Storage Center of Excellence

Project ID: ST038

This presentation does not contain any confidential or otherwise restricted information

Overview

Timeline

start date: September 2008
end date: March 2012
percent complete: 40%

Barriers

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

Budget

total project funding: $1,440,614
DOE share: $1,149,085
UO share: $291,529

funding received: $403,432
funding for FY10: $200,000

Project Collaborators

THE UNIVERSITY OF ALABAMA — Prof. David Dixon

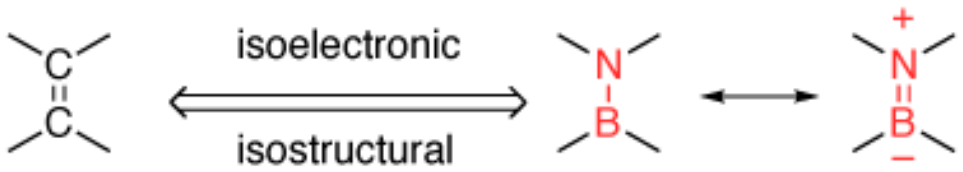
Pacific Northwest NATIONAL LABORATORY — Dr. Tom Autrey

UNIVERSITY OF WASHINGTON — Prof. Karen Goldberg, Prof. Mike Heinekey

Key Summary

- A relatively new project as part of the CHSCoE.
- Focus on cyclic H_2 storage materials containing C, B, and N.
- New approach to H_2 storage that complements the materials currently under investigation.
- Couple *exothermic* H_2 desorption from *BN* with *endothermic* H_2 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 heterocycle materials, demonstrated a pathway for regeneration of the spent fuel that includes using molecular H_2, developed a First-Fill synthesis, measured thermodynamic parameters that corroborate computational predictions, performed preliminary desorption studies.

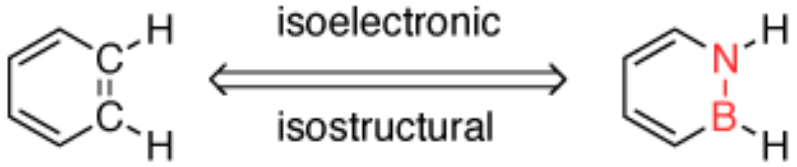
Research in the Liu Group - Relevance



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
H_2 storage materials

Project Objectives - Relevance

Develop CBN heterocycles as novel hydrogen storage materials:

- liquid-phase storage system
- gravimetric density
- volumetric density
- thermodynamics (H_2 absorption and desorption)
- cost effective and energy efficient regeneration (reversibility)

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

- calculate thermodynamic properties of CBN heterocycle materials
- synthesize novel CBN heterocycle materials
- determine thermodynamic properties for CBN heterocycles via experiment

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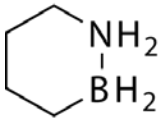
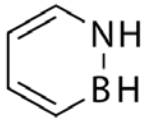
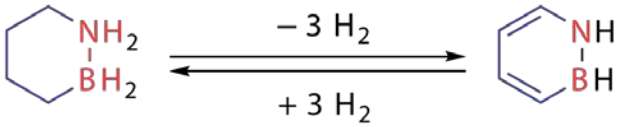
Phase II objectives (4/1/2010 – 3/31/2012)

- optimize the gravimetric density of materials
- develop a First-Fill synthesis
- develop/identify/optimize conditions for H_2 absorption (regeneration)
- develop/identify/optimize conditions for H_2 desorption (release)

The CBN Heterocycle Approach

calculated at CCSD(T) level (298K):				ΔH (kcal/mol)	ΔG (kcal/mol)
$H_3N–BH_3$	⟶	$H_2N–BH_2$ +	H_2	−5.1	−13.6
$H_3C–CH_3$	⟶	$H_2C=CH_2$ +	H_2	32.6	23.9
	⟶		+ 3 H_2	27.9	1.9

couple *exothermic* H_2 desorption from *BN* with *endothermic* H_2 desorption from *CC* in a *cyclic* system to achieve optimal thermodynamics for the overall H_2 absorption/ desorption process.



charged fuel spent fuel

- **Spent fuel can potentially be directly regenerated with H_2.**

Patrick Campbell *J. Am. Chem. Soc.* **2010**, *132*, 3289-3291.

A Collaborative Approach

(calculate, synthesize, measure, optimize)$_n$

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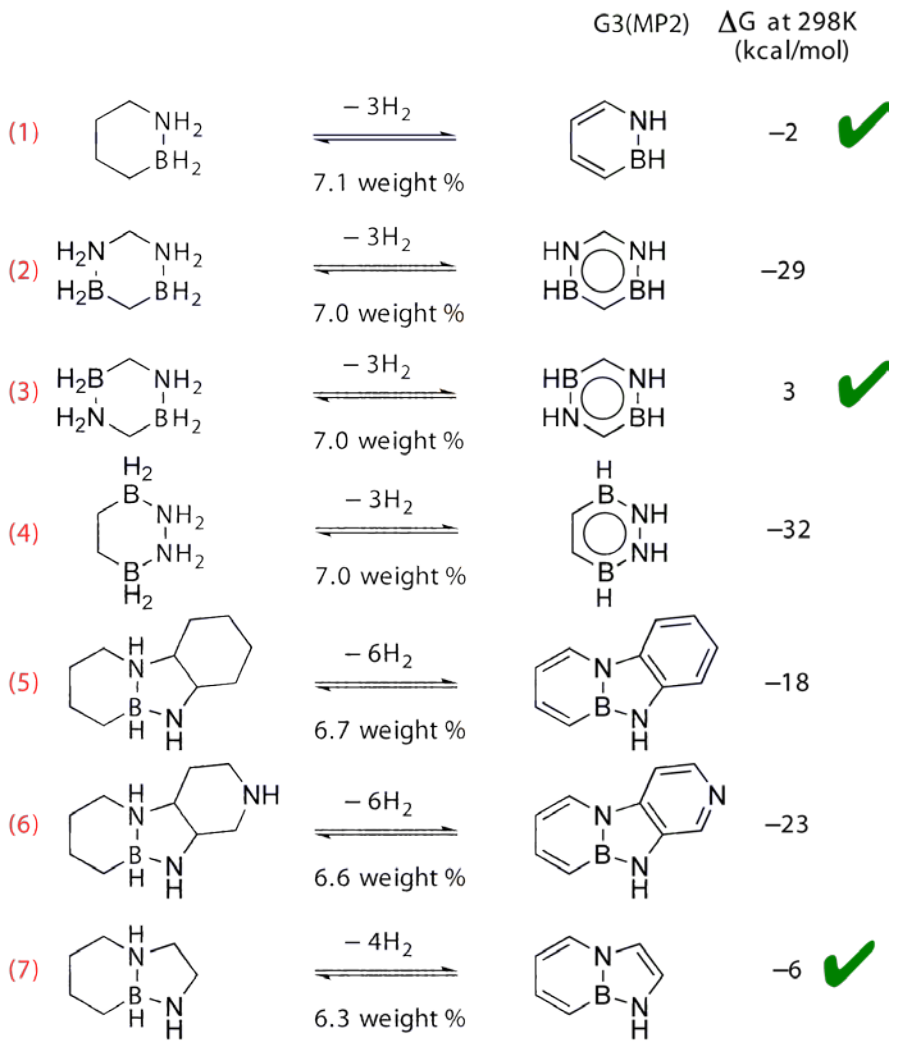
$$\Delta G = \Delta H - T\Delta S$$

reversible H_2 storage: $\Delta G \sim 0$!

- **use theory to help select synthetic candidates**



Myrna Matus

J. Phys. Chem. A **2010**, *114*, 2644-54.

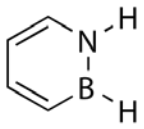
Progress - Developing Synthetic Tools

organic

benzene

Faraday
(1825)

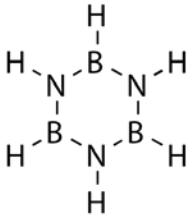
hybrid
organic/inorganic



1,2-dihydro-
1,2-azaborine

(2008)

inorganic



borazine

Stock
(1926)

Adam Marwitz

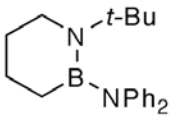
Myrna Matus

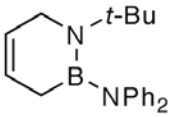
Angew. Chem. Int. Ed.
2009, *48*, 973-7.

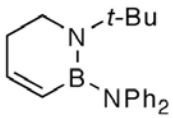
Adam Marwitz

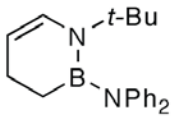
Org. Lett. **2007**, *9*, 4905-8.

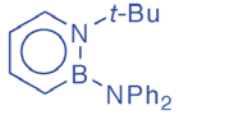
- **The proposed CBN heterocycle materials are new and not commercially available. New synthetic tools have been developed to address the synthetic challenge.**

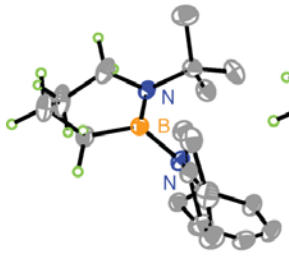


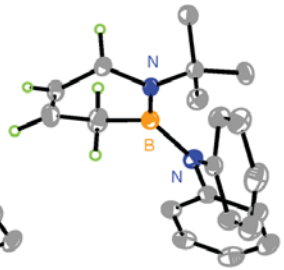


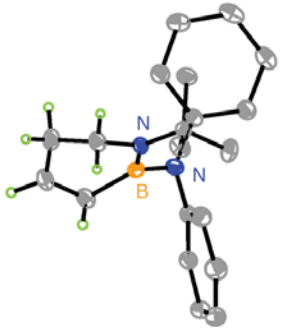


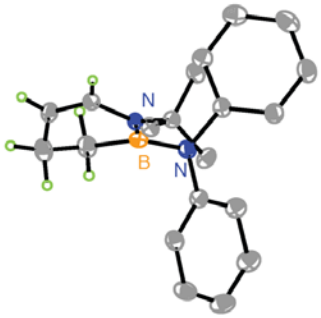


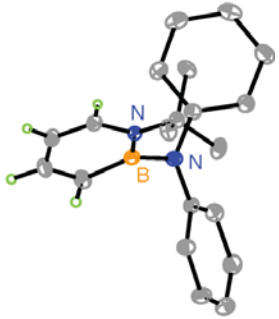












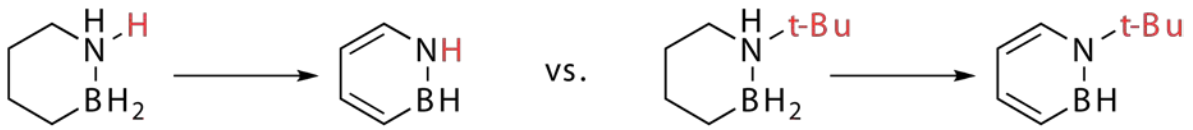
J. Am. Chem. Soc.
2008, *130*, 7250-2.

Eric Abbey

Progress – Model for C_4BNH_x System

- **Model and parent materials have similar thermodynamic properties.**

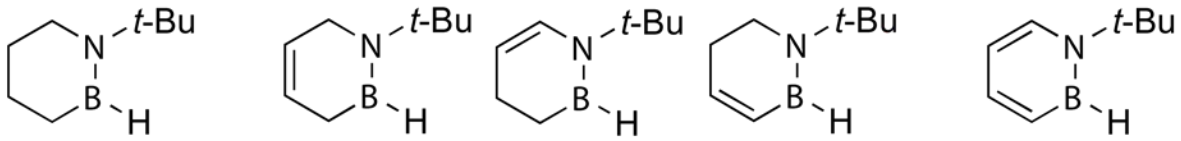
Material (1) vs. more readily available model of (1)



ΔG at 298K (kcal/mol) = –2.3

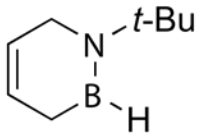
ΔG at 298K (kcal/mol) = –0.4

- **successfully prepared several compounds related to the model material**



- low-melting liquids mp < –30 °C

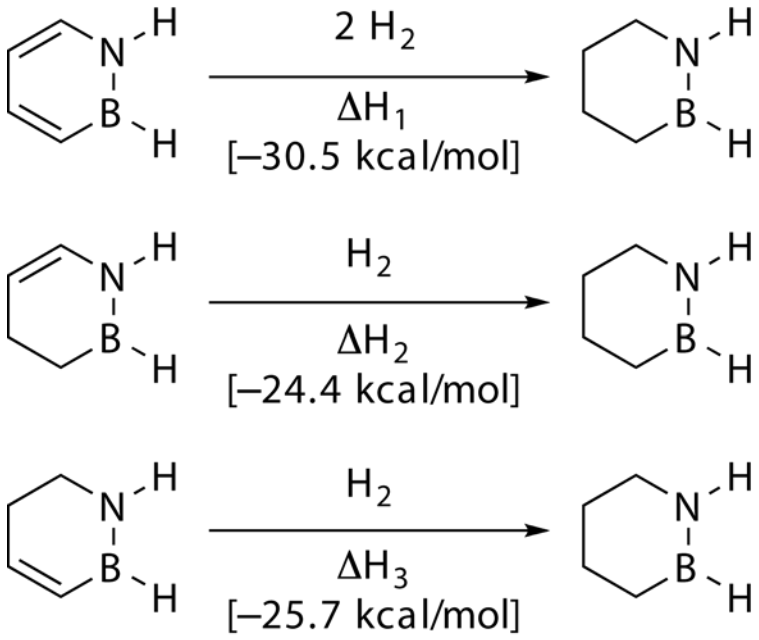
- **determined density of select model material**



d = 0.849 kg/L

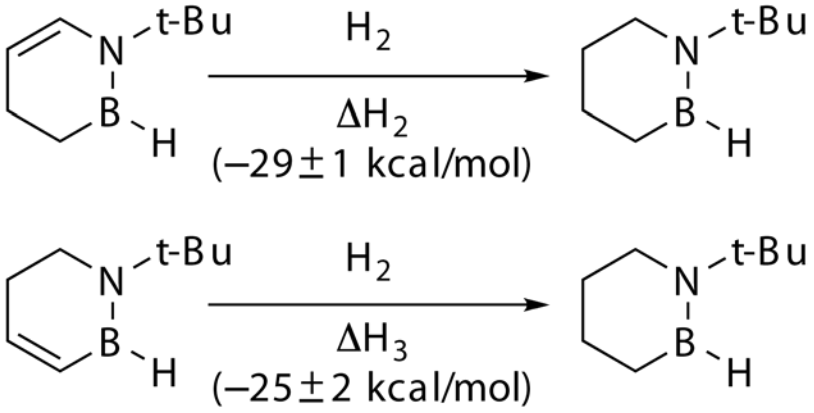
Progress – Hydrogenation Enthalpies: Theory vs. Experiment

theory



experiment

?



$RuCl_2(PPh_3)_3$ catalyst (homogeneous)

Pacific Northwest NATIONAL LABORATORY — Dr. Tom Autrey

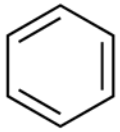
THE UNIVERSITY OF ALABAMA — Prof. David Dixon

- **Experimental data are consistent with theory.**

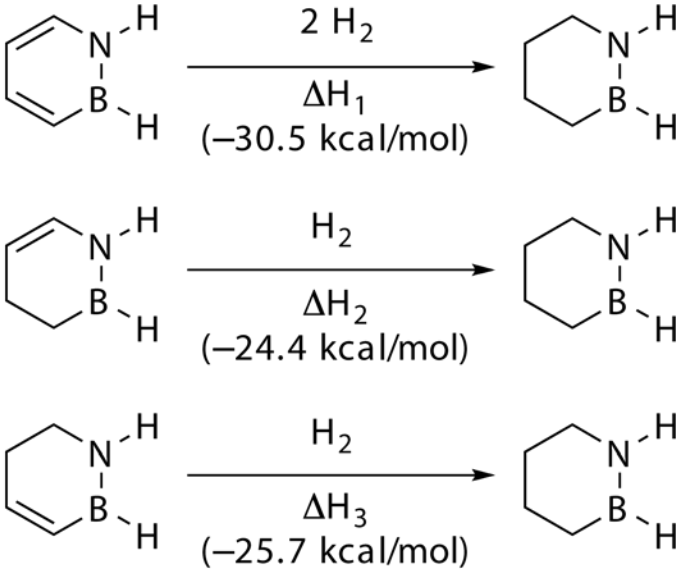
Patrick Campbell

Progress – Relevance of Aromaticity

benzene
highly aromatic

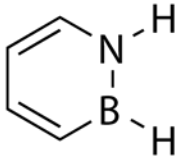


more difficult to hydrogenate



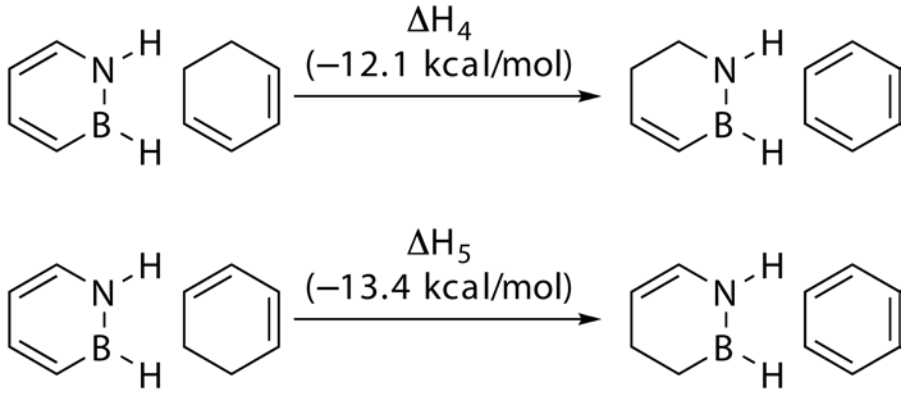
$ASE = \Delta H_1 - (\Delta H_2 + \Delta H_3) = 19.6$ kcal/mol

vs.



1,2-azaborine
less aromatic

easier to hydrogenate
= regenerate



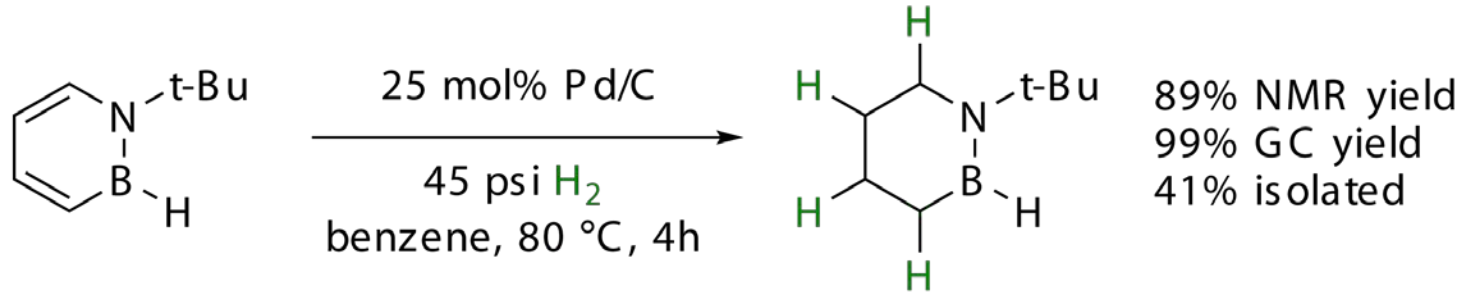
$ASE = 32.2 - |(\Delta H_4 + \Delta H_5)/2| = 19.5$ kcal/mol

- **Regeneration of CBN heterocycle materials with H_2 should be facile due to reduced aromaticity compared to the all-carbon system.**

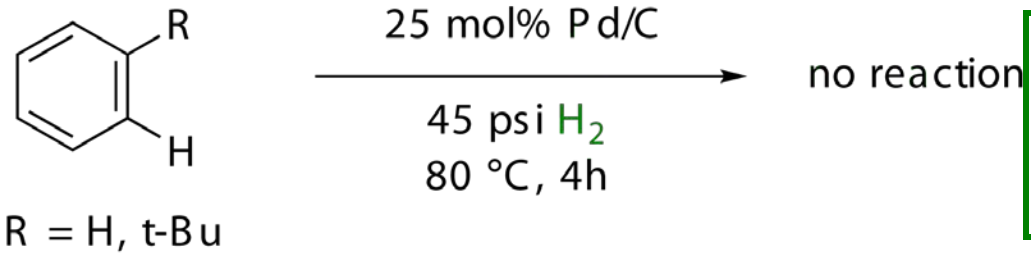
THE UNIVERSITY OF ALABAMA
Prof. David Dixon

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

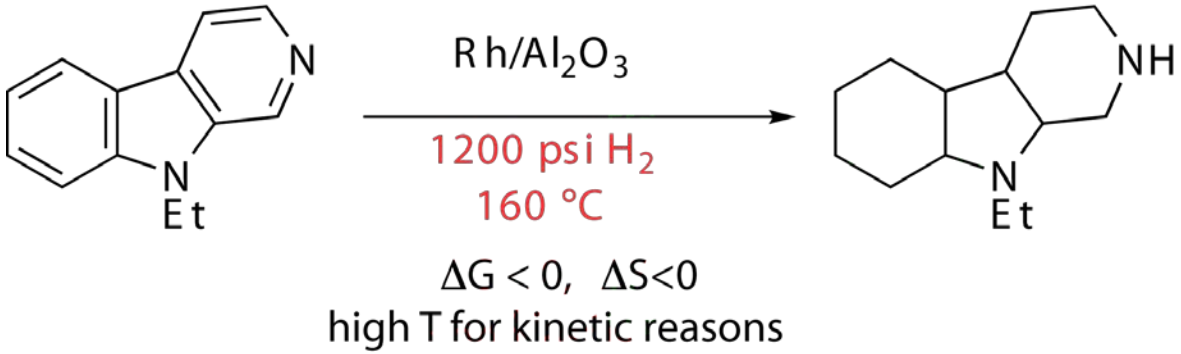
Progress – Facile Hydrogen Uptake



vs.



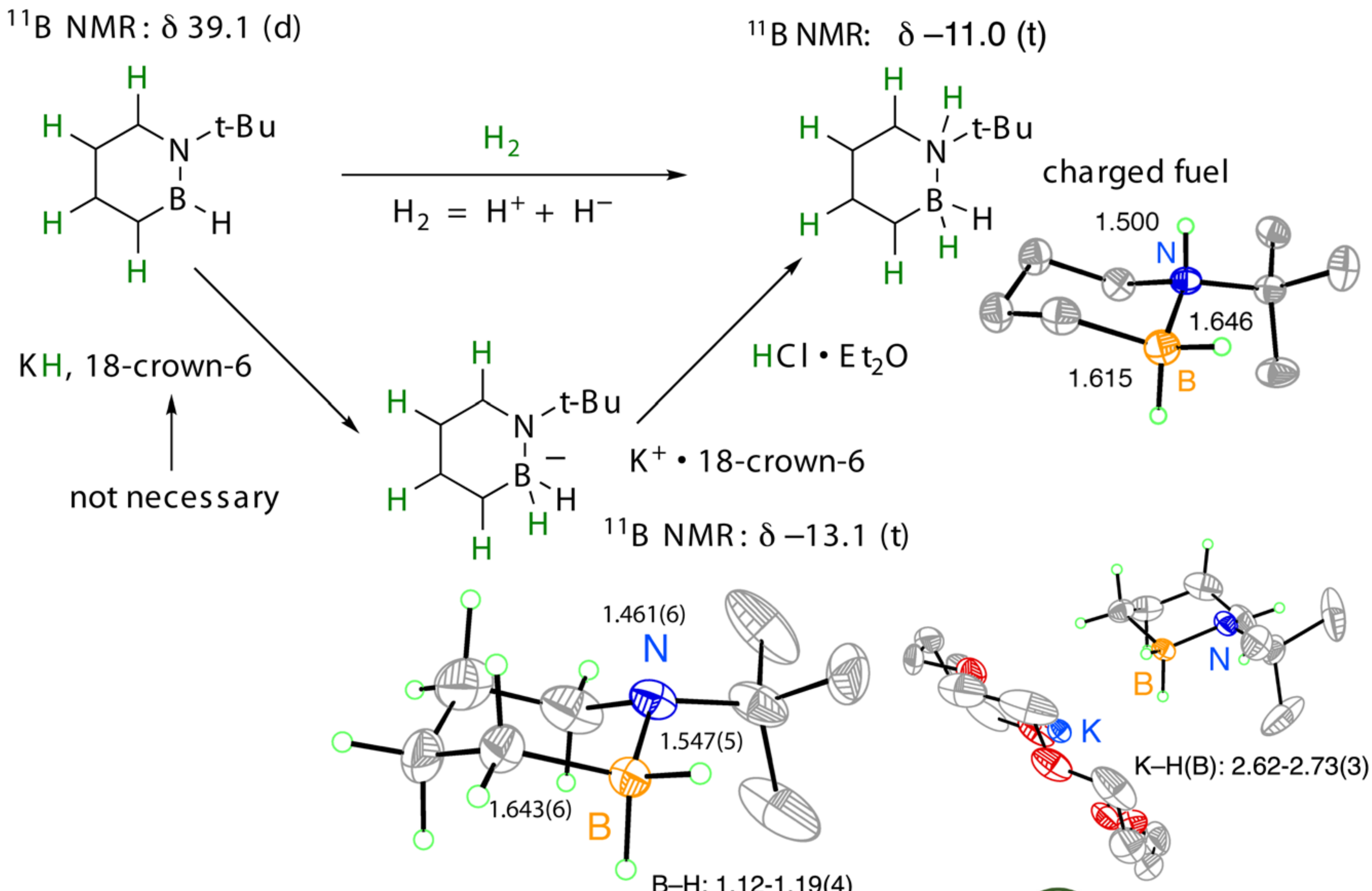
- **CBN heterocycle materials ARE easier to regenerate with H_2 compared to the all-carbon system.**



$\Delta G < 0$, $\Delta S < 0$
high T for kinetic reasons

 J. Am. Chem. Soc. **2010**, *132*, 3289-3291.

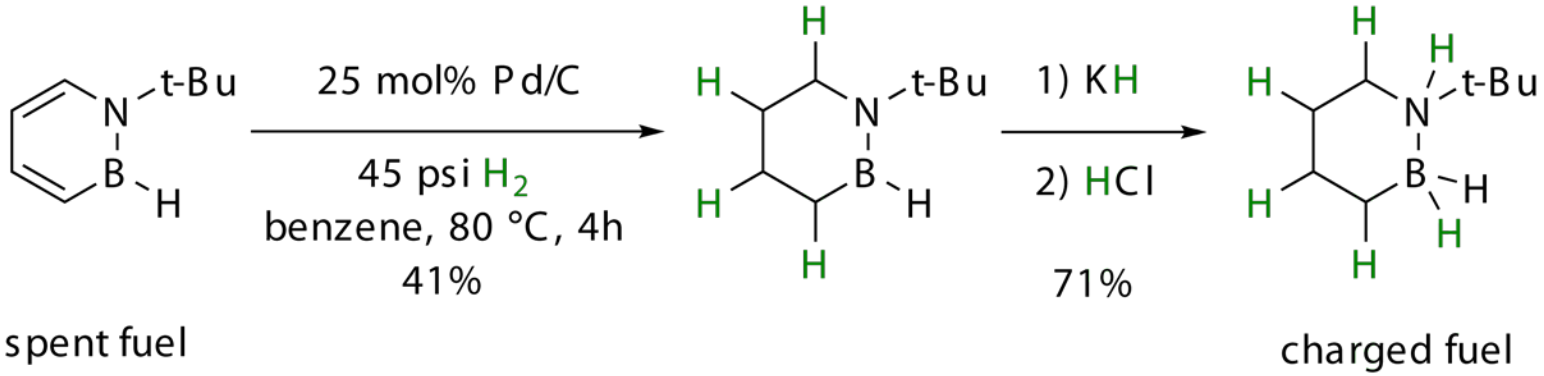
Progress – Regeneration Completed



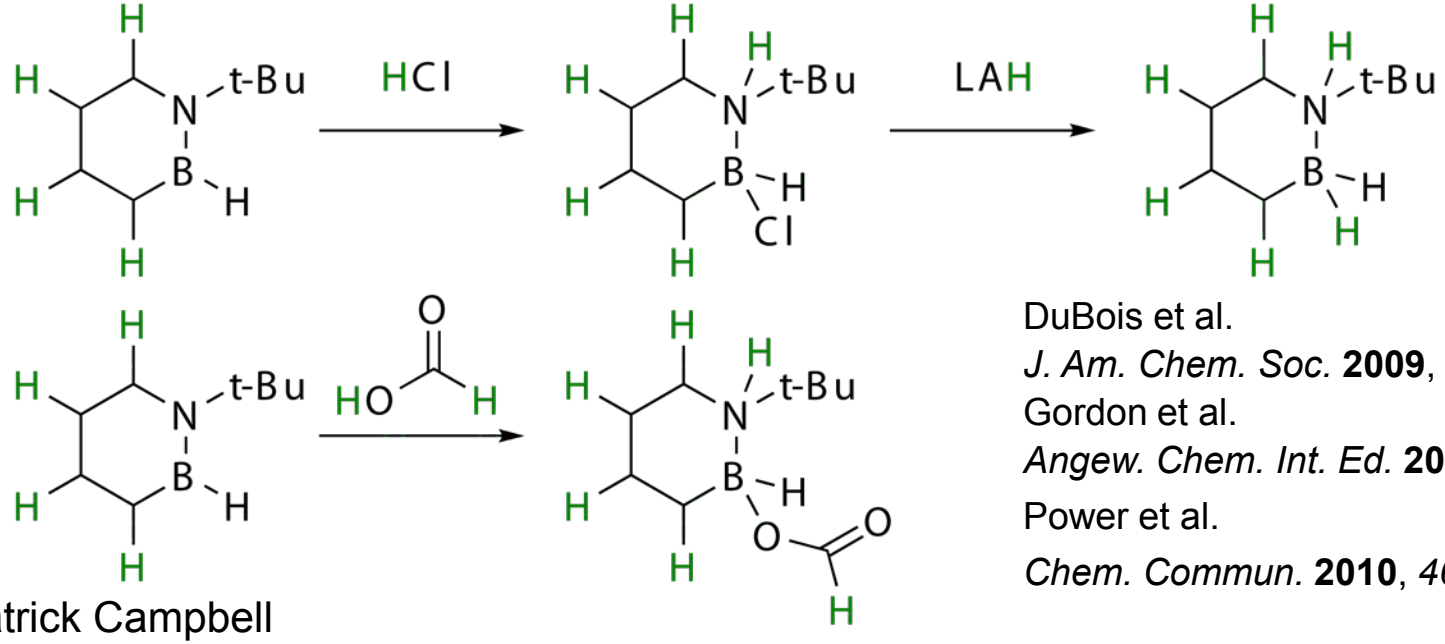
Patrick Campbell

Progress – Simple Regeneration using H_2, H^-, H^+

- **developed a simple three-step procedure for regeneration of spent fuel**
- **first synthetic access to the charged CBN fuel (Material (1))**

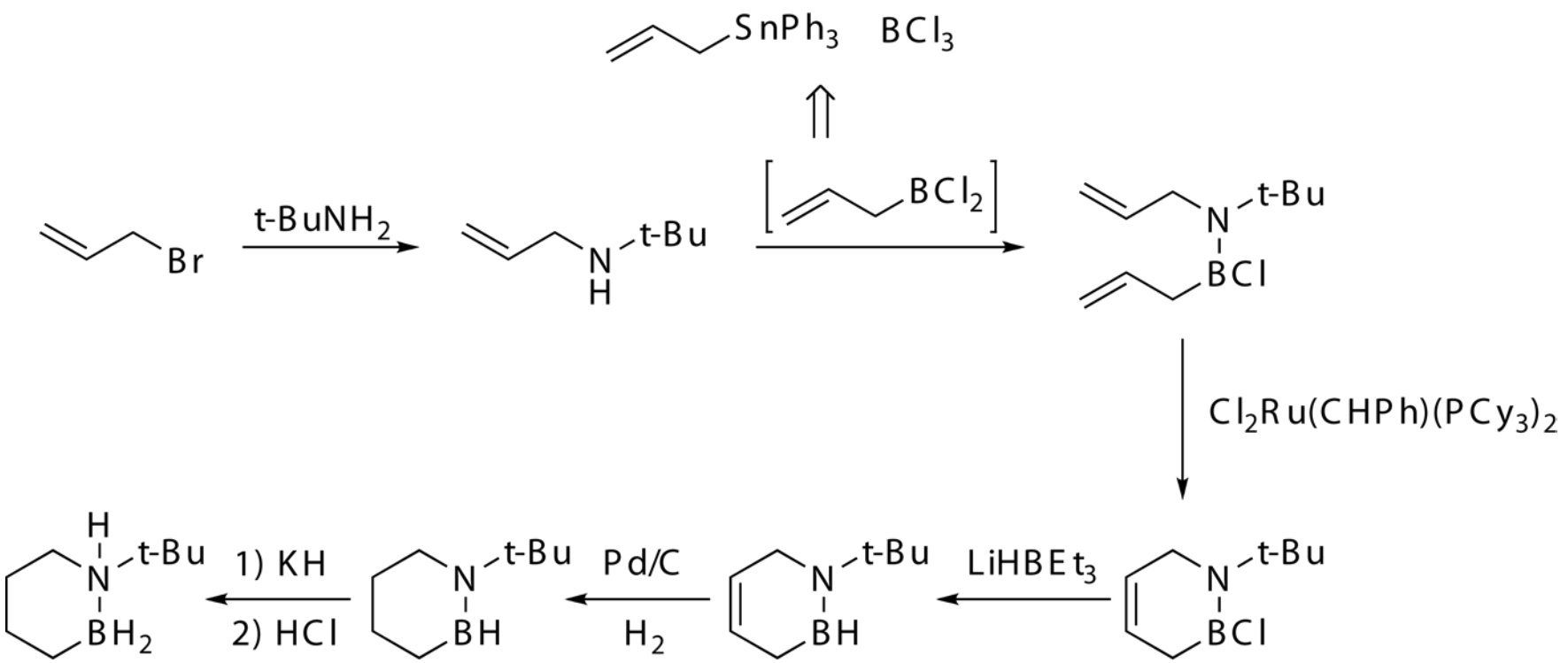


- **need to screen for milder reductants, e.g., transition metal hydrides, formic acid**



DuBois et al.
J. Am. Chem. Soc. **2009**, *131*, 14454-65.
Gordon et al.
Angew. Chem. Int. Ed. **2009**, *48*, 6812-6.
Power et al.
Chem. Commun. **2010**, *46*, 148-9.

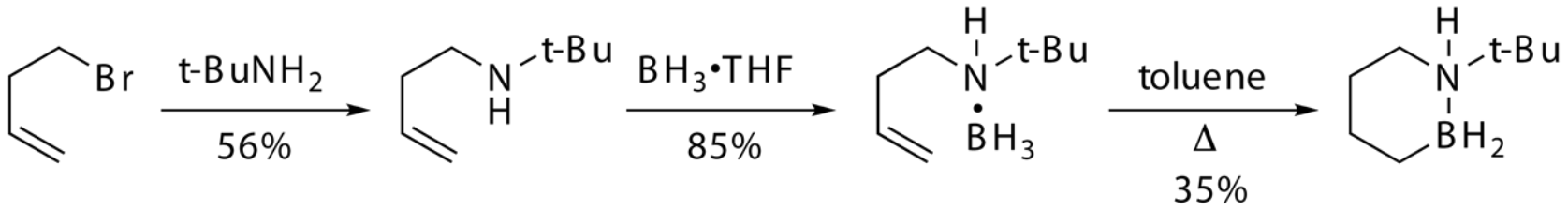
Progress – First Fill Synthesis



7 steps, 9% overall yield

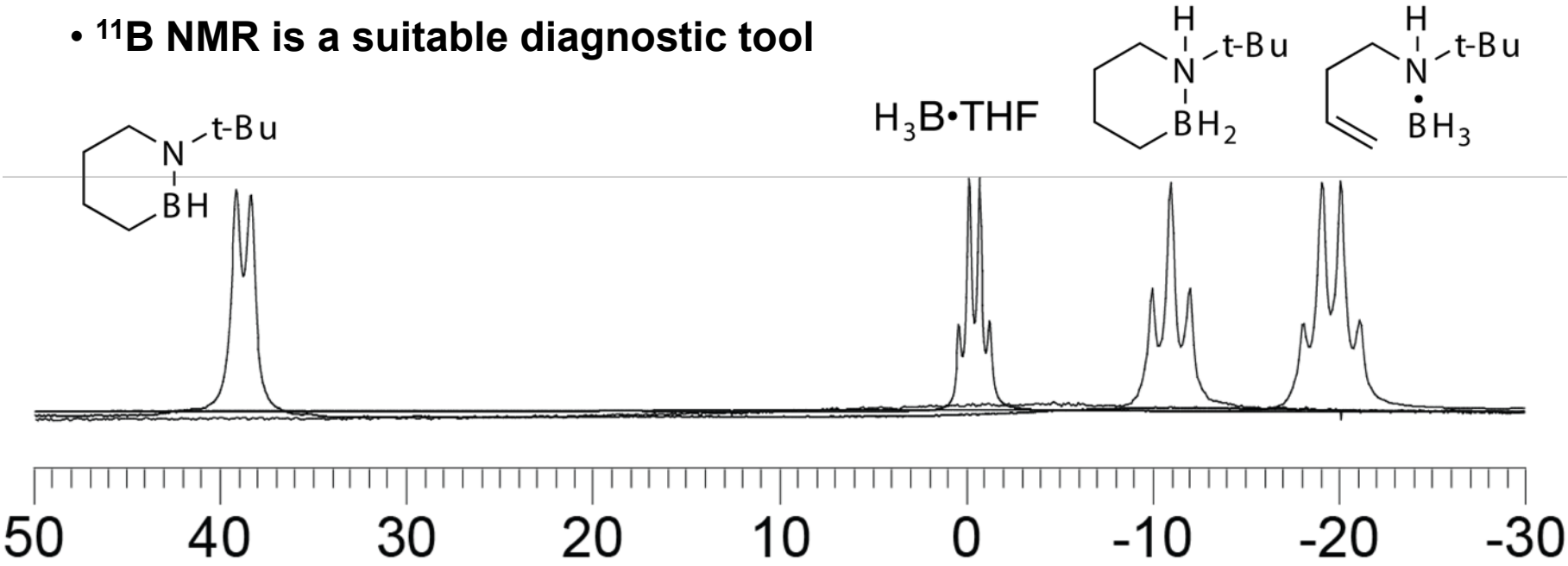
There is a need for a simple First-Fill synthesis!

Progress – First Fill Synthesis



3 steps, 17% overall yield

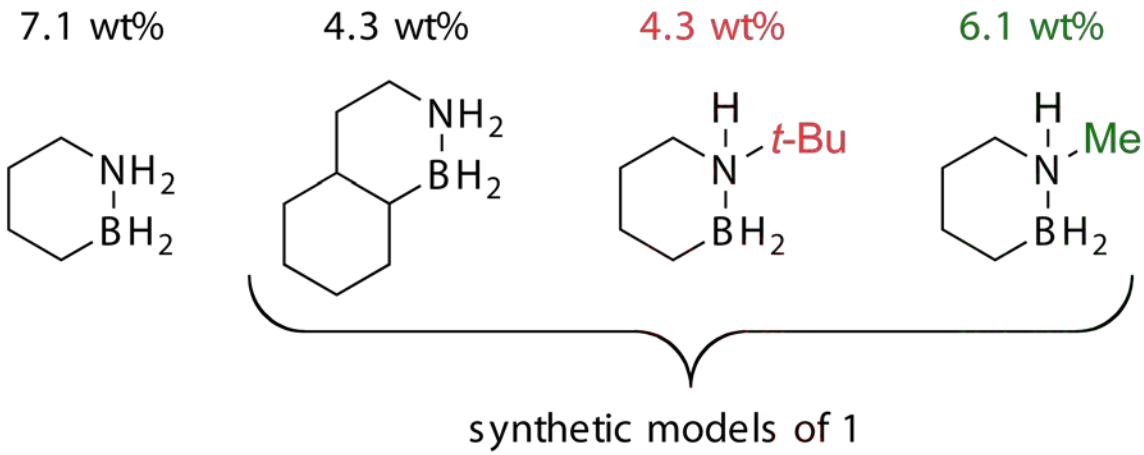
- **^{11}B NMR is a suitable diagnostic tool**

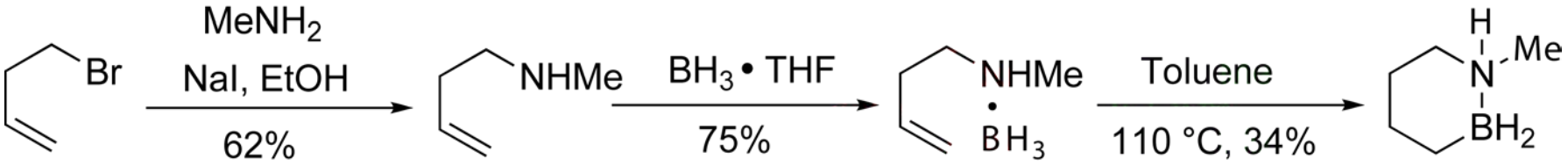


- **accomplished a simplified First-Fill synthesis**
- **need to improve each individual steps**
- **need to improve gravimetric density**

Kshitij Parab

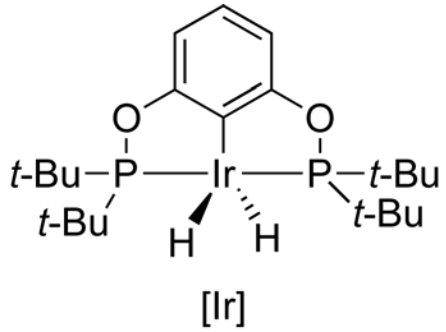
Progress – Improving the Gravimetric Density of CBN Materials



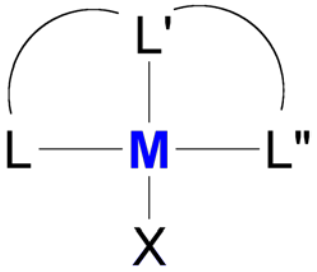


• synthesized a material with significantly improved storage capacity

UW - Progress



Highly active catalyst



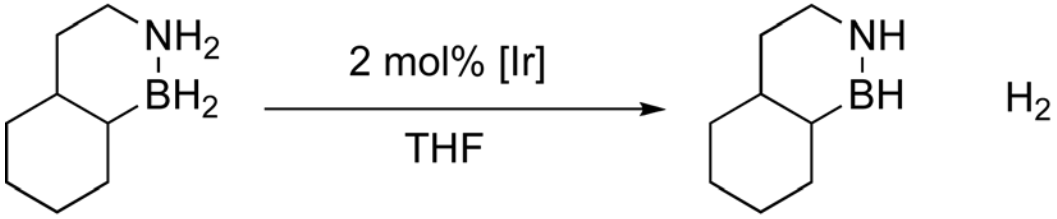
Basic Tridentate Ligand Motif

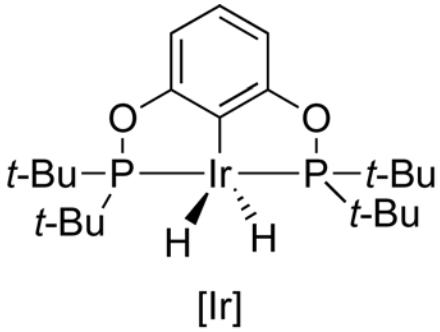
synthesis of new metal catalysts based on the tridentate ligand motif

- Replace Ir with inexpensive metal
- Tune L, L', L'' and X to achieve high activity and catalyst stability

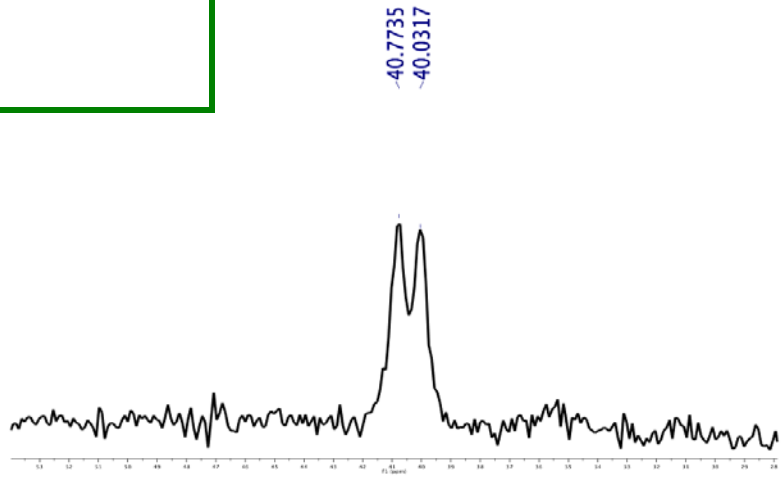
Heinekey and Goldberg et al.
J. Am. Chem. Soc. **2006**, *128*, 12048-9.
J. Am. Chem. Soc. **2008**, *130*, 10812-20.
Inorg. Chem. **2010**, *49*, 1733-42.

UW - Progress
Dehydrogenation of CBN Heterocycles





- **At RT release of 1 eq. H_2 is observed.**
- **^{11}B NMR is consistent with formation of BHNH product.**
- **Product characterization is in progress.**



UNIVERSITY OF WASHINGTON
Tony St. John

Collaborations

Project Collaborators

THE UNIVERSITY OF ALABAMA

computational studies of H_2 desorption pathways of cyclic CBN materials, evaluation of thermodynamics and energetics

Pacific Northwest NATIONAL LABORATORY

experimental mechanistic studies of H_2 absorption/desorption to/from cyclic CBN materials, thermodynamic measurements using reaction calorimetry, H_2 charge/discharge characteristics

UNIVERSITY OF WASHINGTON

development/discovery of efficient catalysts for H_2 desorption from CBN materials

Technology Transfer

THE UNIVERSITY OF ALABAMA

obtained computed thermodynamic data and H_2 desorption reaction pathways for CBN heterocycle materials, will continue provide feedback with experimental data

Pacific Northwest NATIONAL LABORATORY

obtained thermodynamic data via reaction calorimetry

UNIVERSITY OF WASHINGTON

prepared CBN heterocycle materials and delivered to UW for further investigation
obtained preliminary H_2 desorption data

Proposed Future Work

- focus on developing CBN Materials (1) and (7)
- complete experimental thermodynamic data for CBN heterocycle materials for comparison with theory
- develop/identify/optimize conditions for H_2 desorption from these CBN materials
- determine charge/discharge characteristics
- develop more efficient regeneration of spent fuel
- formulate the charged fuel as liquids

Project Summary

Relevance:	development of novel hydrogen storage materials with desirable storage parameters and thermodynamics for reversible H_2 absorption and desorption
Approach:	coupling of exothermic H_2 desorption from BN with endothermic H_2 desorption from CC in a cyclic system to achieve optimal thermodynamics for H_2 absorption/desorption; distinct from amine-borane and cyclic materials currently under investigation
Progress:	**• developed synthetic tools for CBN heterocycle materials** **• measured experimental thermodynamic data that corroborate the values predicted by theory** **• demonstrated regeneration of spent fuel material using H_2, H^-, and H^+ sources** **• developed a First-Fill synthesis of charged fuel** **• performed preliminary H_2 release studies**
Collaborations:	active partnership with CHSCoE members (UA, PNNL, UW)
Future Work:	• further develop the synthesis of CBN Heterocycle Materials (1) and (7) • complete experimental thermodynamic data for CBN materials • determine/optimize H_2 charge/discharge characteristics • develop more efficient regeneration of spent fuel