Hydrogen Storage by Novel CBN Heterocycle Materials

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in collaboration with the University of Alabama

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ST038

This presentation does not contain any confidential or otherwise restricted information

Overview

Timeline

start date: September 2008
end date: March 2012
percent complete: 95%

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
FY 2011 funding: $300,000
Planned FY 2012 funding: $145,653

Project Collaborators

THE UNIVERSITY OF ALABAMA Prof. David Dixon

Project Objectives - Relevance

Develop CBN heterocycles as novel hydrogen storage materials:

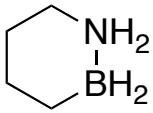
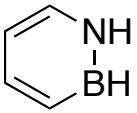
- liquid-phase
- gravimetric density (> 5.5 wt. %)
- volumetric density (> 40 g H_2/L system)
- thermodynamics (H_2 absorption and desorption)
- regeneration (reversibility)
- 2017 DOE targets for vehicular applications + near-term market applications

Specific Phase II Tasks

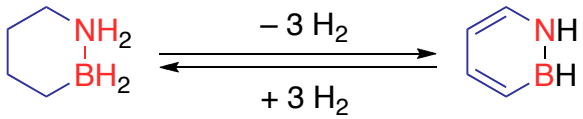
1) synthesize parent charged fuel of CBN heterocycle material (1); **completed** 1/22/2011
* 2) optimize CBN heterocycle materials synthesis; **completed** 10/20/2011
* 3) obtain experimental thermodynamic data for model CBN heterocycles; **completed** 7/21/2011
4) formulate materials as liquids; **completed** 1/22/2011
* 5) develop/identify conditions to optimize H_2 desorption from CBN materials; 90% complete
* 6) develop/identify conditions for regeneration of the spent fuels; 90% complete

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

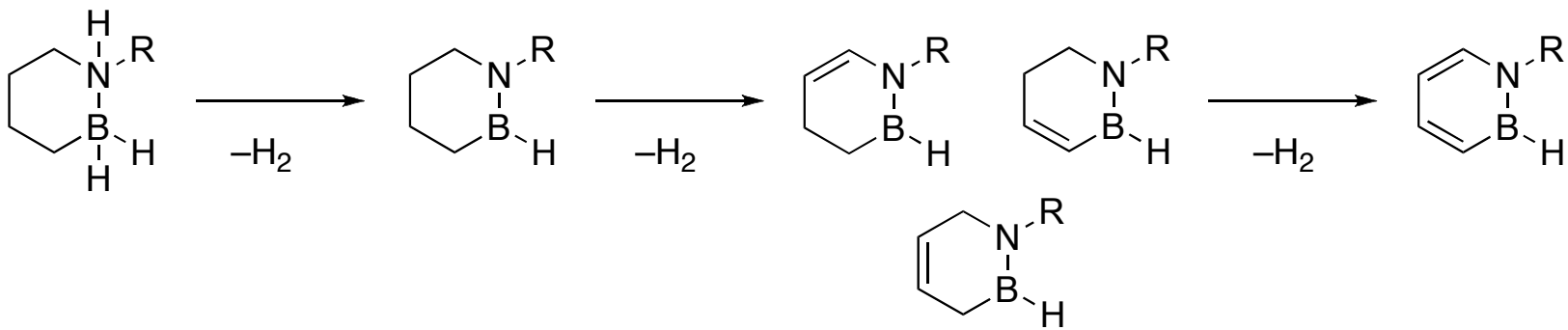
couple *exothermic* H_2 desorption from *BN* with *endothermic* H_2 desorption from *CC* in a *cyclic* system to achieve optimal thermodynamics for the overall H_2 absorption/ desorption process.



charged fuel spent fuel

Overall thermodynamics is conducive to reversibility.

A Well-Defined Molecular Approach

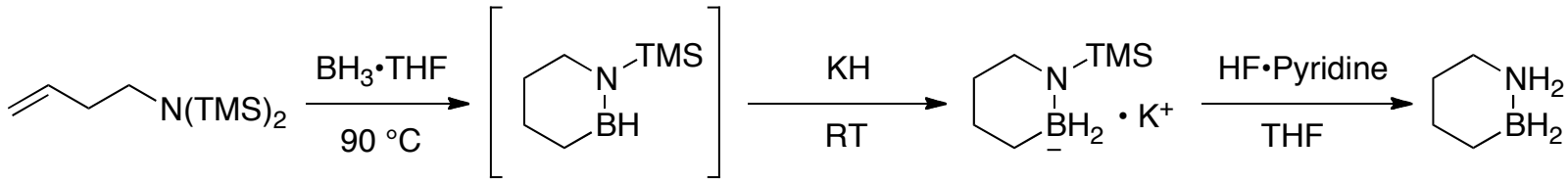


charged fuel potential intermediates spent fuel

- The materials remain well-defined molecular species throughout the lifecycle, from fully charged fuel to the spent fuel.
- Potential **advantages** of well-defined nature include:
  - no involvement of insoluble polymeric materials
  - better characterization of reaction products and reaction processes
  - facilitates computational and mechanistic studies
  - facilitates formulation as liquids
- Potential **disadvantages** of well-defined molecular approach include:
  - lower storage capacity
  - <u>for single-component systems:</u>
  - formation of polymers or larger networks → higher capacity (e.g., AB), solids

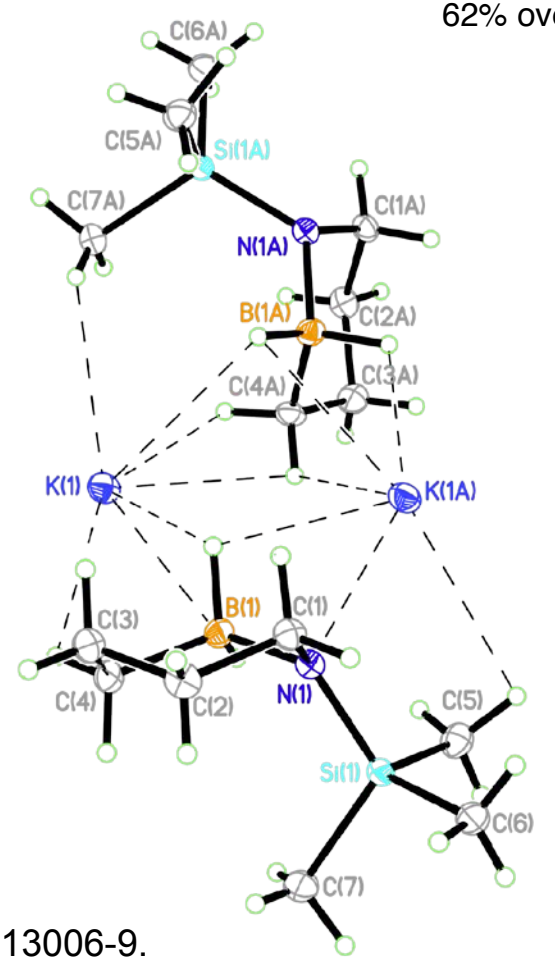
trade off between capacity, solid phase vs. liquid phase, well-defined species

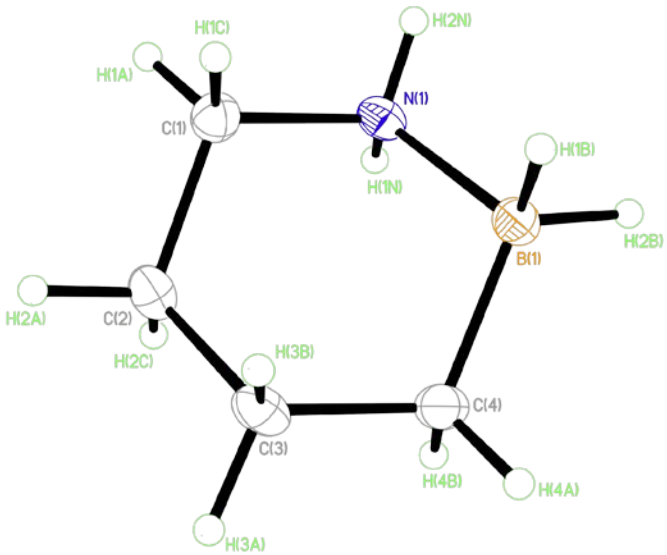
Previous Progress (Task 1, Completed) Synthesis of Parent



62% over two steps

94%





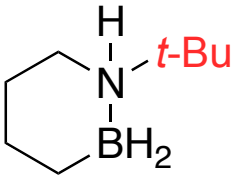
Synthesis of the parent molecule was successful.

Wei Luo

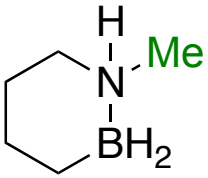
J. Am. Chem. Soc. **2011**, *133*, 13006-9.

Previous Progress (Task 4, Completed) Formulate Materials as Liquids

Potential capacities, assuming 3 equivalent H_2 release:



neat material	THF solution	Et_2O solution
mp: 96-98 °C	sol. (g/L): 284 ± 28	sol. (g/L): 84.4 ± 4
d (kg/L): 0.61 ± 0.07	d (kg/L): "0.89"	d (kg/L): "0.71"
vol. (g H_2/L): 25	vol. (g H_2/L): 11.7 g	vol. (g H_2/L): 3.47
wt.(%): 4.3	wt(%): 1.3	wt(%): 0.4



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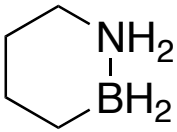
vol. (g H_2/L): 53	vol. (g H_2/L): 17.8	vol. (g H_2/L): 6.5
wt.(%): 6.1	wt.(%): 2.0	wt.(%): 0.73



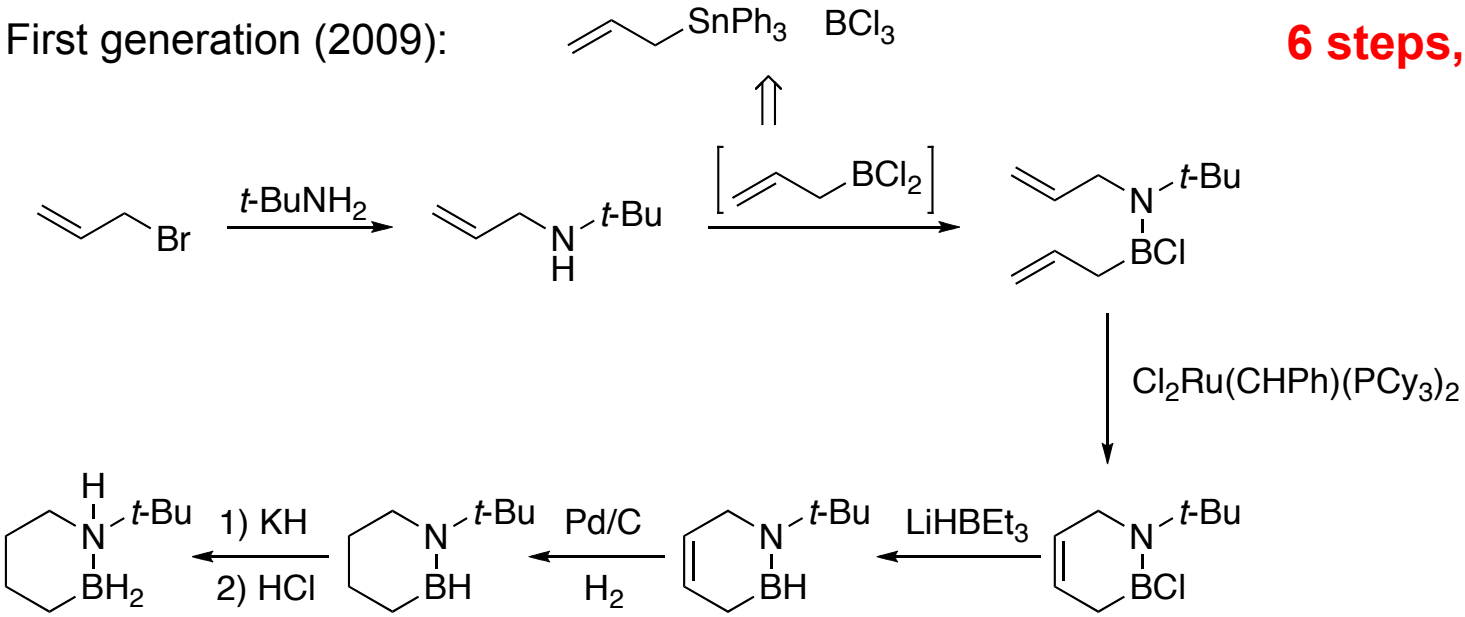
neat material	THF solution	Et_2O solution
mp: 62-63 °C	sol. (g/L): 434 ± 20	sol. (g/L): 347 ± 30
d (kg/L): 1.00 ± 0.05	d (kg/L): "0.89"	d (kg/L): "0.71"
vol. (g H_2/L): 70	vol. (g H_2/L): 30.7	vol. (g H_2/L): 25
wt.(%): 7.1	wt.(%): 3.4	wt.(%): 3.1

Patrick Campbell, Wei Luo

New Progress (Task 2, Completed)
Optimize Materials Synthesis

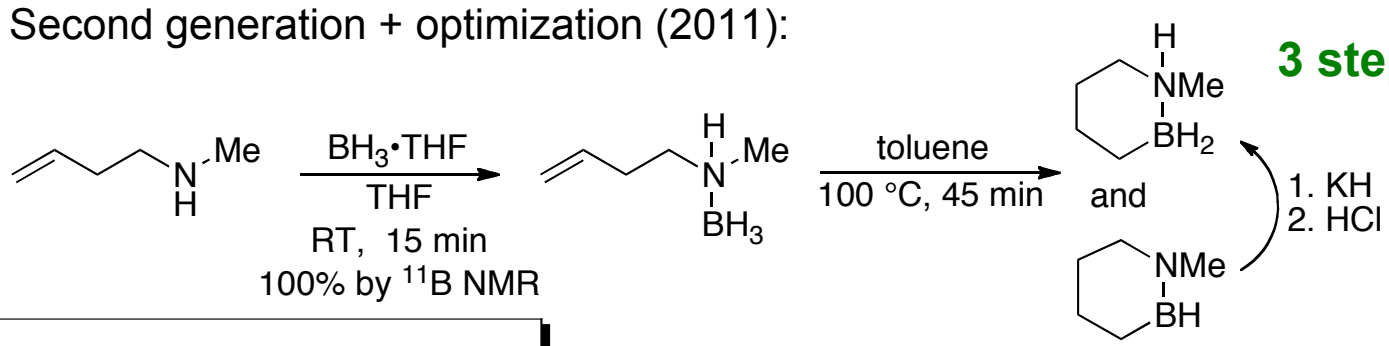
First generation (2009):

6 steps, 9% overall yield



Second generation + optimization (2011):

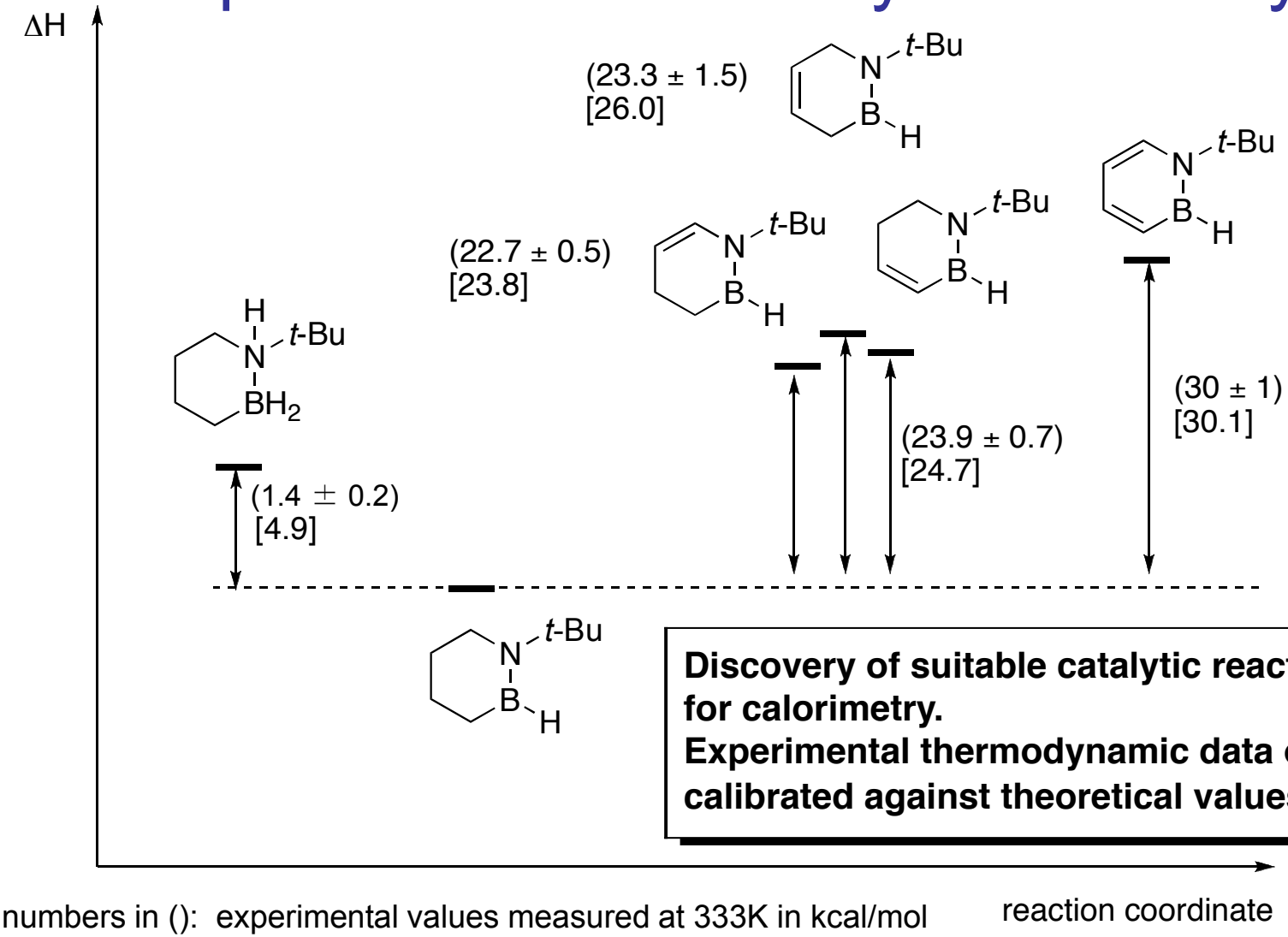
3 steps, 51% overall yield



First-fill synthesis was improved.

Wei Luo, Kshitij Parab, Patrick Campbell

New Progress (Task 3, Completed) Experimental Thermodynamic Analysis –



Discovery of suitable catalytic reaction conditions for calorimetry.
Experimental thermodynamic data obtained and calibrated against theoretical values.

numbers in (): experimental values measured at 333K in kcal/mol
numbers in []: G3(MP2) values at 298K in kcal/mol

Patrick Campbell *J. Am. Chem. Soc.* **2010**, *132*, 18048-50.

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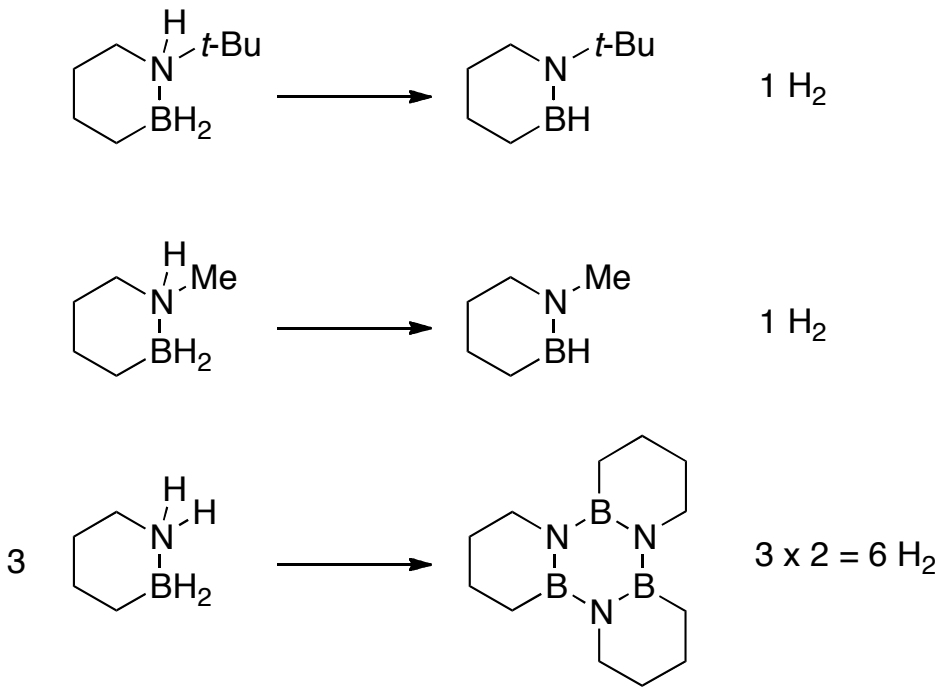
New Progress (Task 5)
H_2 Desorption from BN is Facile



H_2 desorption occurs thermally at ~150 °C, catalytically at < 80 °C for all three reactions.

Reviewer 3 is right! Trimerization occurs and needs to be considered.

G3(MP2), 298K:
$\Delta H = -83.1$; $\Delta G = -107.3$ kcal/mol trimer
$\Delta H = -27.7$; $\Delta G = -35.8$ kcal/mol monomer
$\Delta H = -13.9$; $\Delta G = -17.9$ kcal/mol H_2

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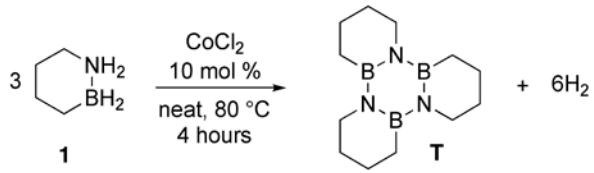
New Progress (Task 5)
Screening of Catalysts for Trimerization

- **Neutral Rh(I) catalyst are most active (5 mol%, 15 min); entries 20 and 22.**
- **$CoCl_2$ is the most active (10 mol%, 30 min) among first-row transition metals that we screened in Table 1 (Entry 13).**
- **Most catalysts effect the trimerization.**
- **Without a catalyst, no reaction occurs after 3 hrs at 80 °C.**



100 % via ^{11}B NMR

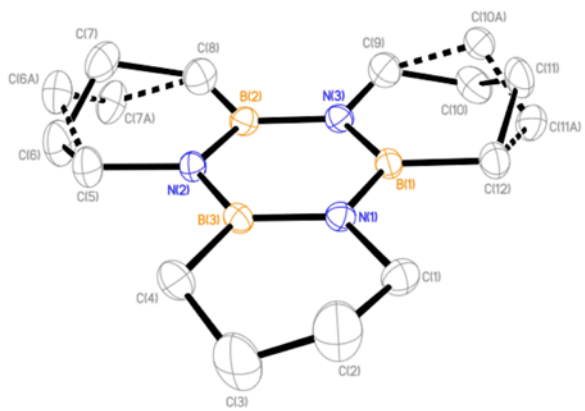
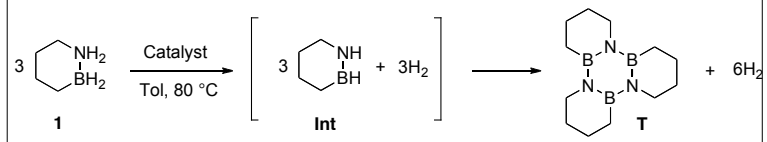


Table 1: Catalyst and condition screening for dehydrogenation of **1**



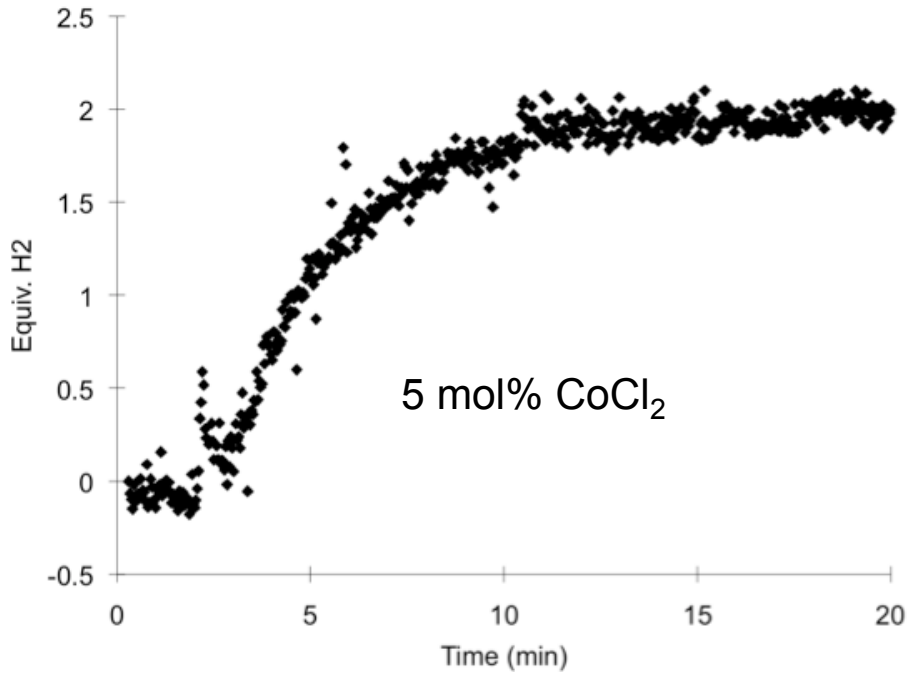
Entry	Catalyst	Loading (mol%)	Time(min)	% Yield **Int**	% Yield **T**
1	$CoCl_2$	10	60		100
2	$(dppe)NiCl_2$	10	60		100
3	$Cr(MeCN)_3(CO)3$	10	60		N/R*
4	$[Cl(cod)Ir]_2$	10	60		100
5	$[Cl(cod)Rh]_2$	10	60		100
6	$[(C_2H_2)_2ClRh]_2$	10	60		100
7	Cp^*RuCl_2	10	60		100
8	$(cod)_2RhBF_4$	10	60		N/R*
9	$(PPh_3)_2NiCl_2$	5	60		100
10	$[(nbd)ClRh]_2$	5	60		100
11	$RuCl_3$	10	60		N/R*
12	$(dppe)NiCl_2$	5	30	50	50
13	$CoCl_2$	10	30		100
14	$[Cl(cod)Ir]_2$	5	30	20	80
15	$[Cl(cod)Rh]_2$	5	30		100
16	Cp^*RuCl_2	5	30		100
17	$(PPh_3)_2NiCl_2$	5	30	40	60
18	$[(nbd)ClRh]_2$	5	30		100
19	$CoCl_2$	10	15	50	50
20	$[Cl(cod)Rh]_2$	5	15		100
21	Cp^*RuCl_2	5	15	60	40
22	$[(nbd)ClRh]_2$	5	15		100

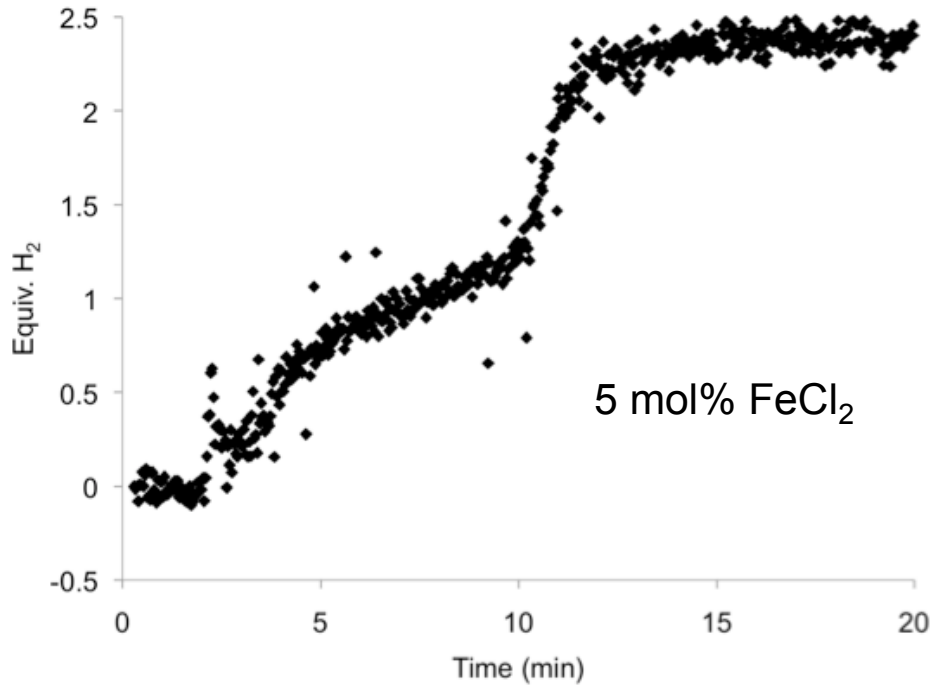
*N/R means no reaction or mix of undesired products

Wei Luo

New Progress (Task 5)
$FeCl_2$ Acts as Catalyst for Trimerization

- Conditions: 80 °C in toluene solution.
- Release of 2 equiv. H_2 corresponds to complete conversion.





- **$FeCl_2$ is cheap ($0.30 / kg)**
- **H_2 desorption behavior is catalyst dependent.**
- **Mechanistic details still under investigation.**

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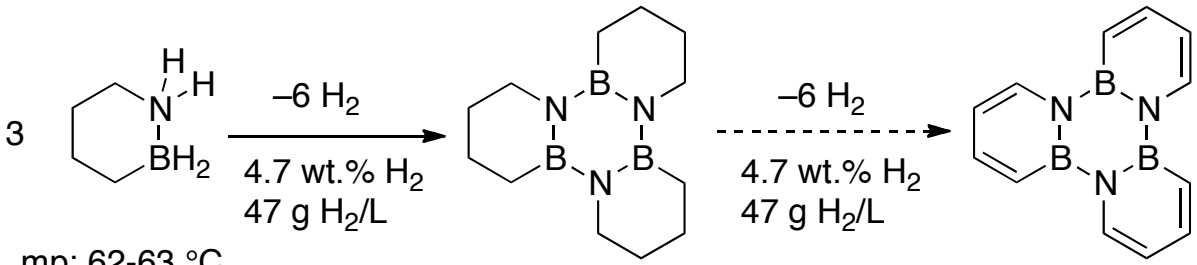
New Progress (Task 5)
Progress toward Removing H_2 from CC



mp: 62-63 °C
d: 1.00 kg/L

air stable (neat and in solution)
moisture stable (neat and in solution)
thermally stable up to its melting point

Overall potential:
9.4 wt.%; 94 g H_2/L
G3(MP2), 298K:
ΔH = +5.9 kcal/mol monomer
ΔG = –19.3 kcal/mol monomer
ΔH = +1.5 kcal/mol H_2
ΔG = –4.8 kcal/mol H_2
solid phase (single component)

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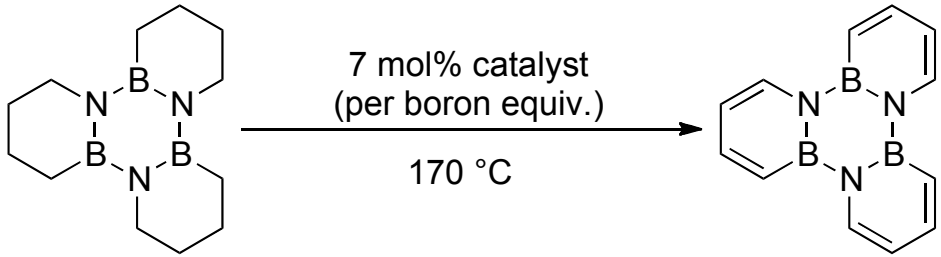
Preliminary attempts using transition metal catalysts:



starting material

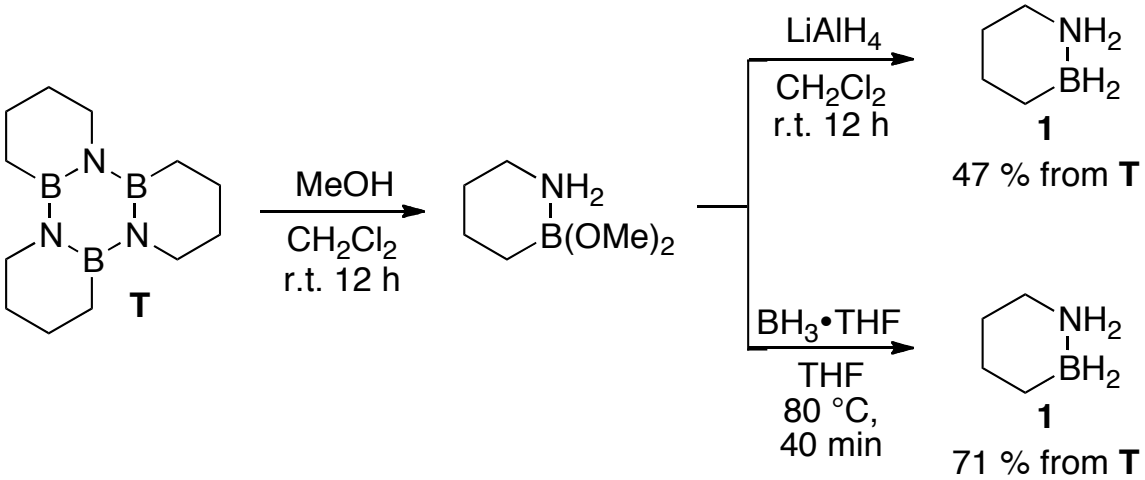
product

Keep in mind that this reaction is endothermic:
ΔH ~ 3 x 30 kcal/mol product.

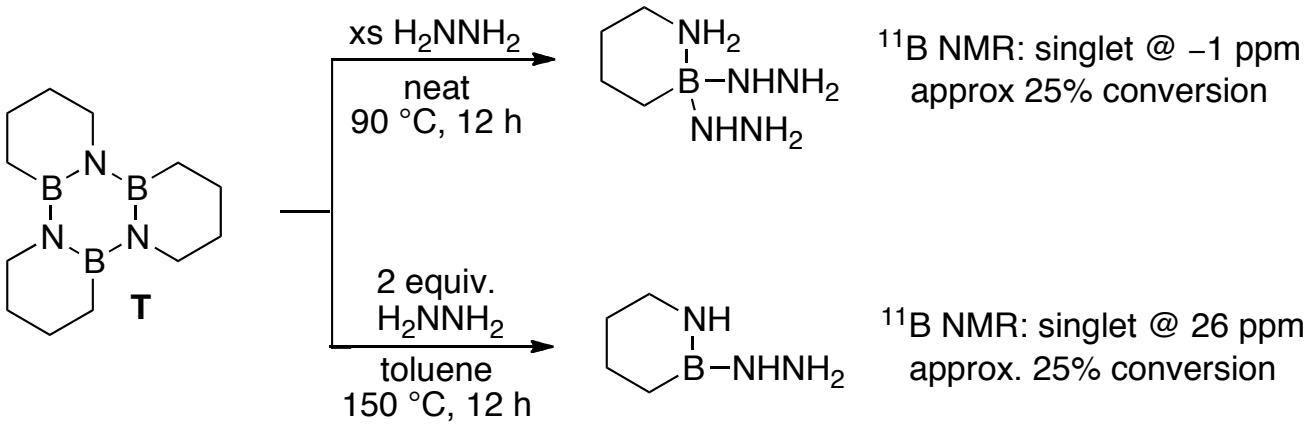
by GC analysis:
- complete conversion of the starting material
- significant formation of the desired product

Jacob Ishibashi

New Progress (Task 6)
Progress toward Regeneration



Conversion of the spent fuel trimer T back to the charged fuel 1 was accomplished.

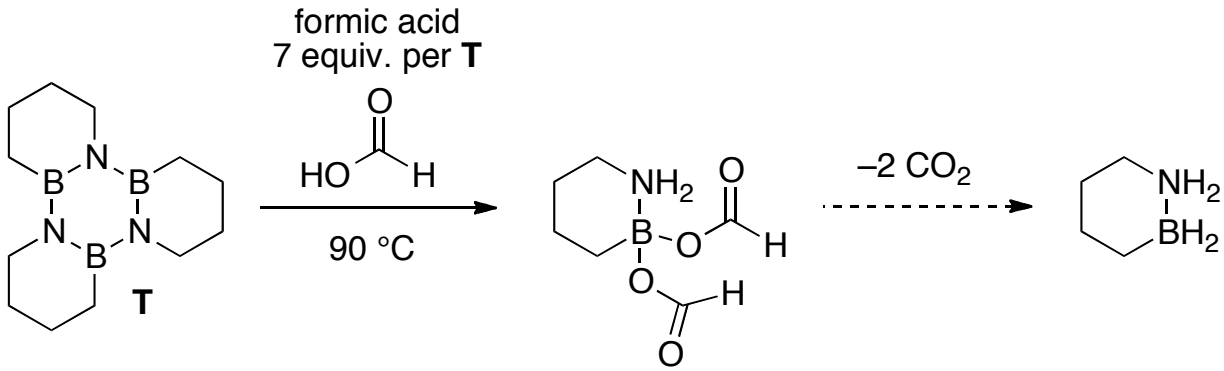


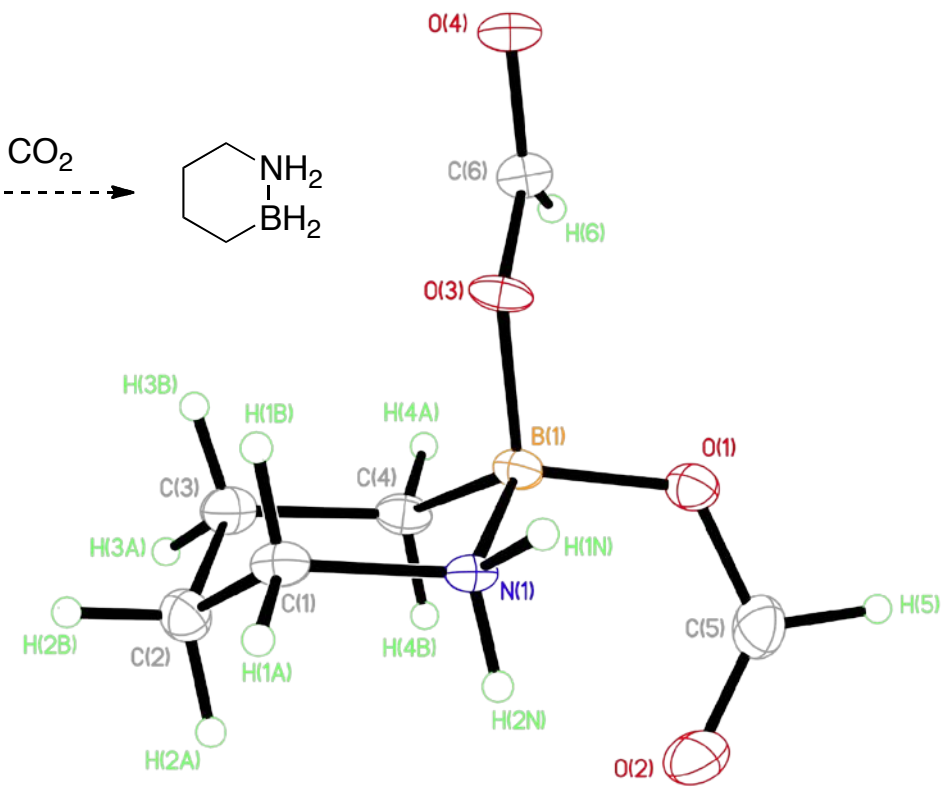
Preliminary investigation using hydrazine did not lead to regeneration.

New Progress (Task 6)
Formic Acid as Potential H_2 Source

Formic acid:
- produced ~700,000 tons / year (commodity chemical)
- relatively cheap at $0.8-1.2 / kg
- potential for use as near-term solution for regeneration

Formic acid serves as a digestion agent and proton source to break up the trimer.

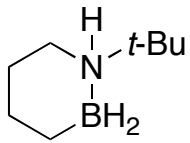




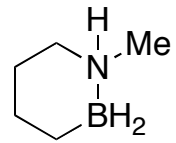
NMR indicates clean reaction. Loss in yield may be due to isolation procedures.

Summary of Accomplishments: Material Synthesis and Properties

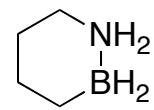
1. Synthesized family of novel CBN-heterocyclic materials, including parent:



4.3 wt% H_2



6.1 wt% H_2

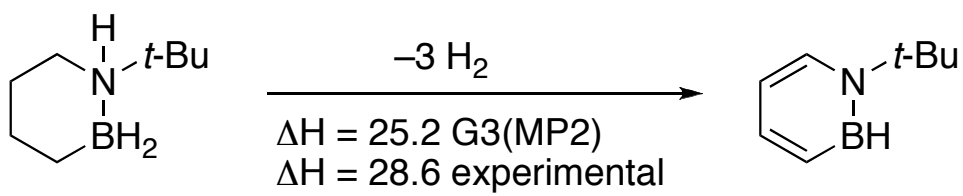


7.1 wt% H_2 3 equiv. release

9.5 wt% H_2 4 equiv. release

1. Improved material synthesis: all 3 steps, > 50% overall yield from commercially available starting materials

2. Completed experimental thermodynamic measurements to corroborate computational results (in kcal/mol):

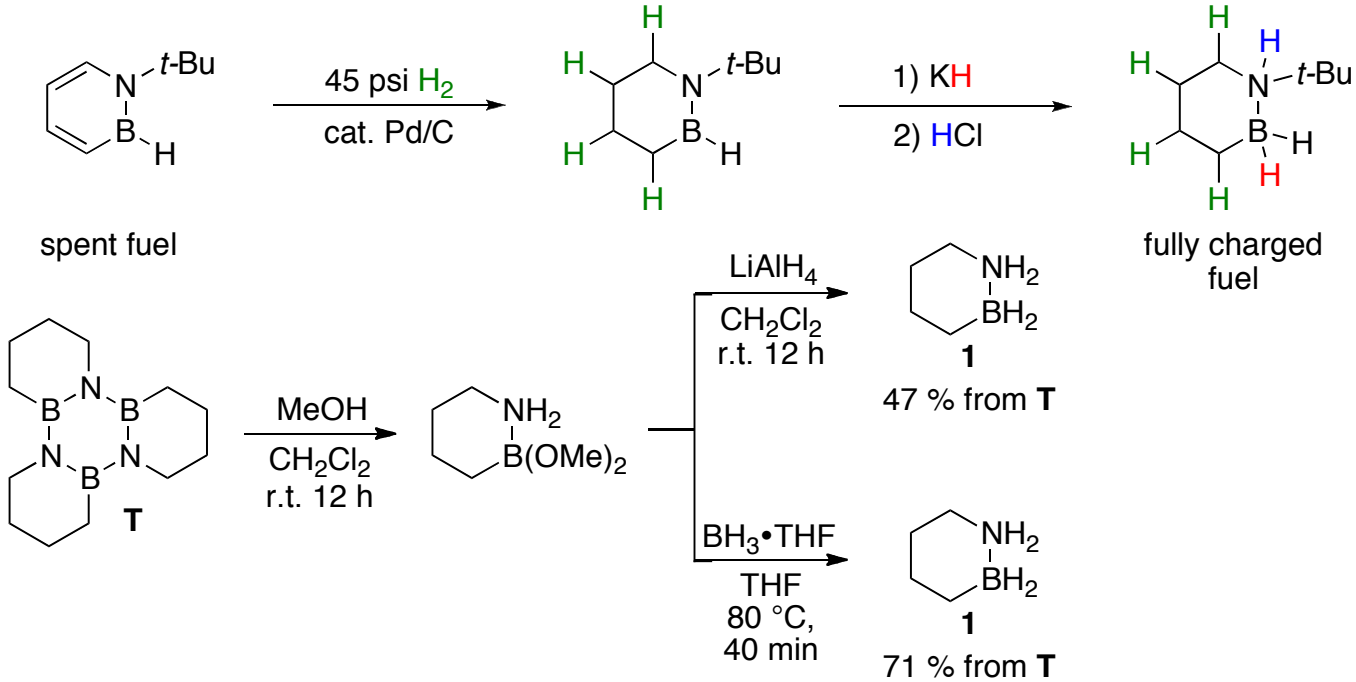


3. Formulated materials as liquids, determined H_2 capacity in solution

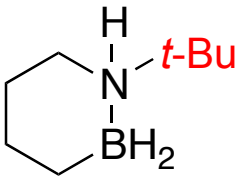
Summary of Accomplishments: H_2 Release and Regeneration

5. Hydrogen release (materials are thermally stable beyond their melting points):
   a. Loss of H_2 from B–N is facile, numerous hetero- and homogeneous catalysts promote loss of H_2 at ≤ 80 °C
   b. Trimerization of parent molecule occurs, releasing 2 equiv. H_2 per monomer
   c. Proof-of-concept success for H_2 desorption from C–C

6. Regeneration of spent fuel material has been demonstrated:



Toward a Liquid Fuel



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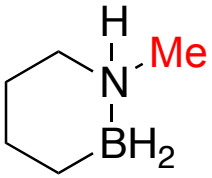

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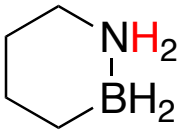

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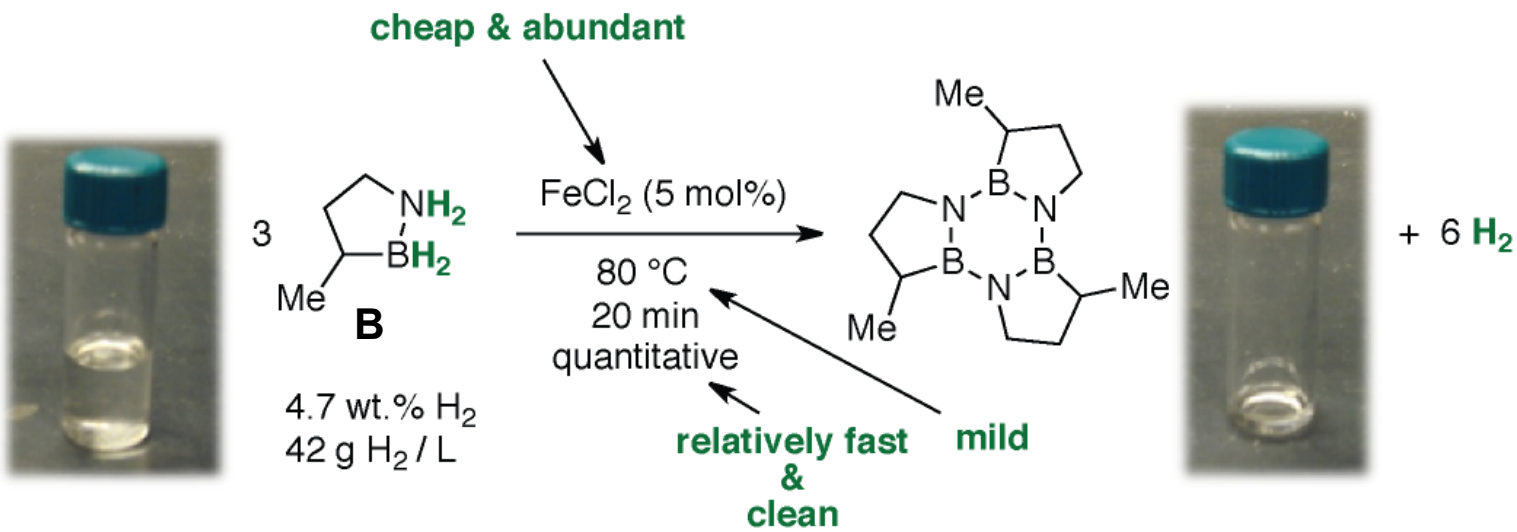
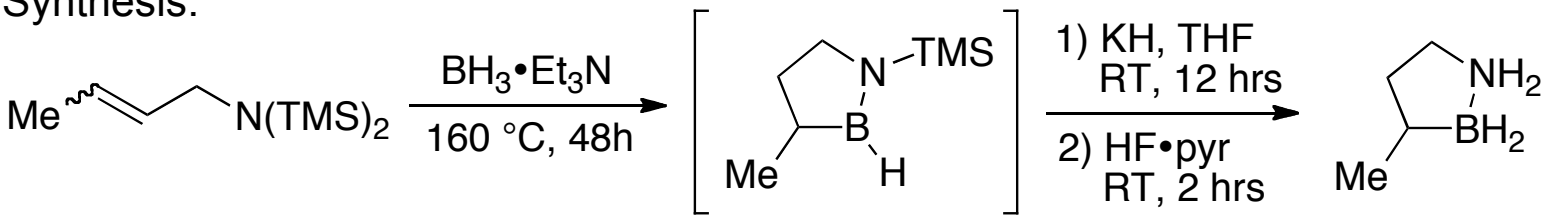
wt.(%): 7.1	wt.(%): 3.4	wt.(%): 3.1

It appears the smaller the molecule the lower the melting point.

A Single-Component Liquid H_2 Storage Material



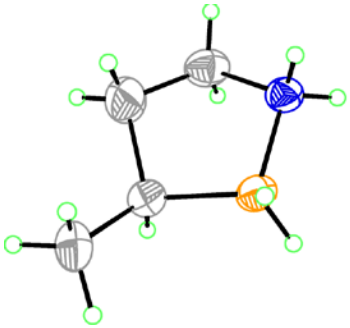
Synthesis:



Highlighted in:

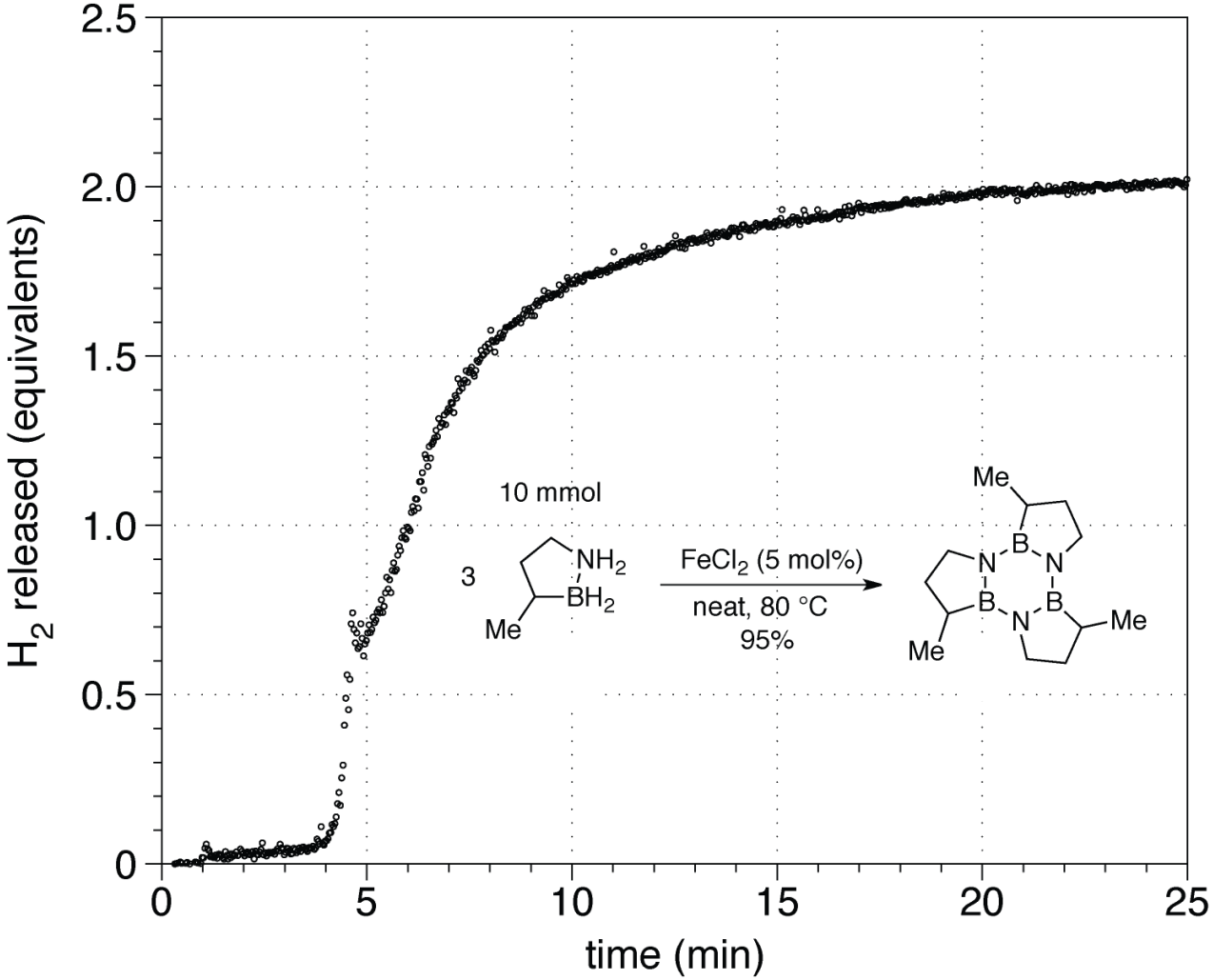
- *C&EN* **2011**, November 28, page 35.
- *Nature Chemistry* **2012**, *4*, page 5.
- *Nature Climate Change* **2012**, *2*, page 23.

Synthesis of a liquid material without phase change 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.

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

Project Summary

Relevance: development of novel hydrogen storage materials with desirable storage capacity and thermodynamics for potential 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 organic materials

Progress:

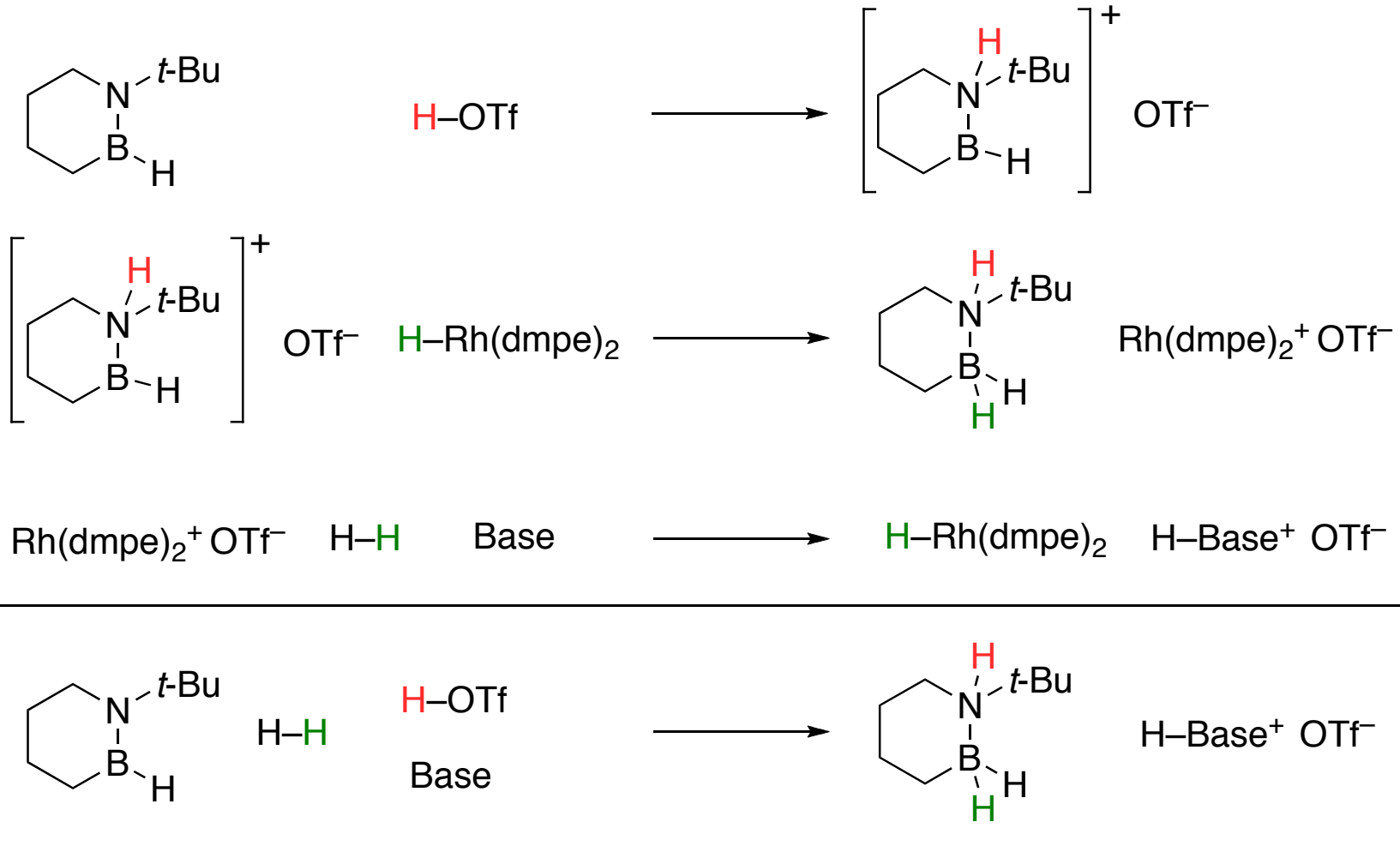
- **completed synthetic optimizations (Task 2)**
- **completed experimental thermodynamic analysis (Task 3)**
- **discovered $FeCl_2$ as effective catalyst for H_2 desorption from BN (Task 5)**
- **preliminary discovery of dehydrogenation from CC (Task 5)**
- **completed regeneration of trimer spent fuel (Task 6)**
- **discovered formic acid as a digestion agent (Task 6)**
- **discovered a single-component liquid-phase storage material**

Collaborations: active partnership with UA and PNNL

Technical Backup Slides

PNNL M-H Regeneration Route

metal hydride pathway: Mock et al. *J. Am. Chem. Soc.* **2009**, *131*, 14454-65.



Use acid-base chemistry to drive an uphill process