



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%

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

Barriers

A. system weight and volume

C. efficiency

E. charging/discharging rates

R. regeneration process

Project Collaborators



Prof. David Dixon

Project Objectives - Relevance

Develop CBN heterocycles as novel hydrogen storage materials:

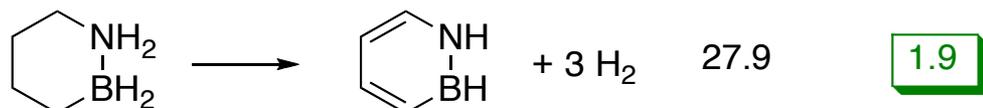
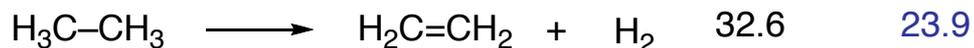
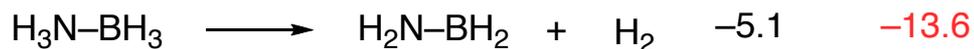
- liquid-phase
- gravimetric density (> 5.5 wt. %)
- volumetric density (> 40 g H₂/L system)
- thermodynamics (H₂ absorption and desorption)
- regeneration (reversibility)
- 2017 DOE targets for vehicular applications + near-term market applications

Specific Phase II Tasks

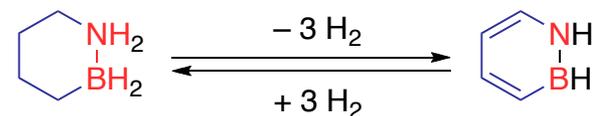
- 1) synthesize parent charged fuel of CBN heterocycle material (1); **completed** 1/22/2011
- * 2) optimize CBN heterocycle materials synthesis; **completed** 10/20/2011
- * 3) obtain experimental thermodynamic data for model CBN heterocycles; **completed** 7/21/2011
- 4) formulate materials as liquids; **completed** 1/22/2011
- * 5) develop/identify conditions to optimize H₂ 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):



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.

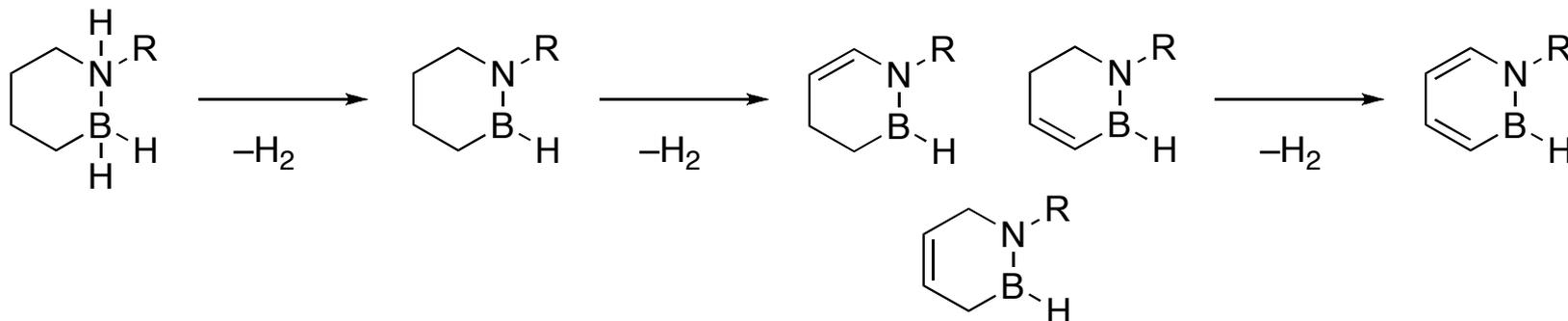


charged fuel

spent fuel

Overall thermodynamics is conducive to reversibility.

A Well-Defined Molecular Approach



charged fuel

potential intermediates

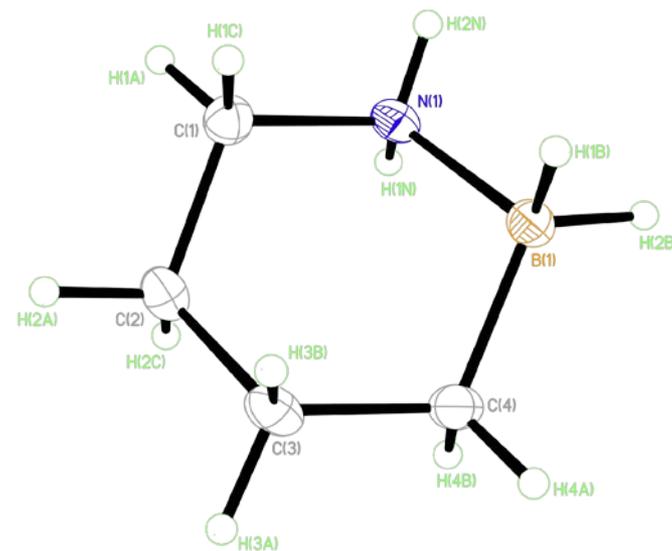
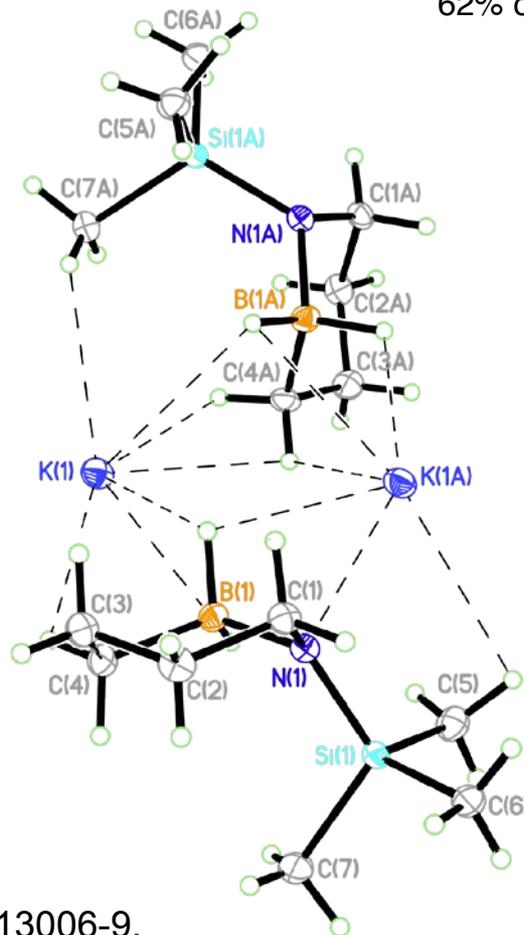
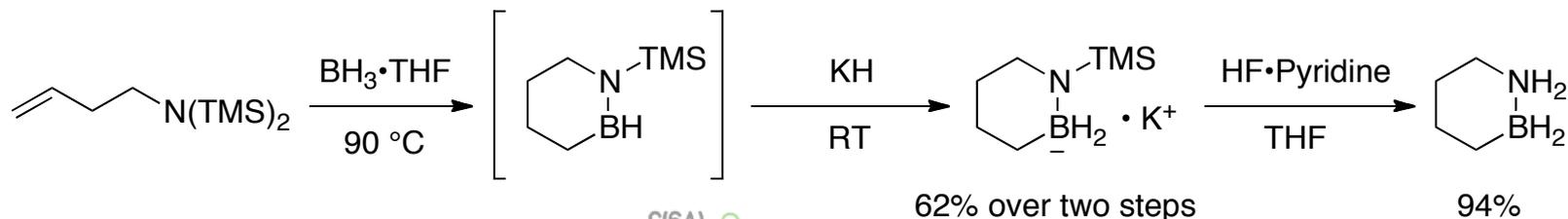
spent fuel

- 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
 - for single-component systems:
 - formation of polymers or larger networks \rightarrow 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



Synthesis of the parent molecule was successful.

 Wei Luo

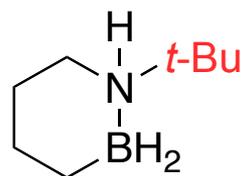
J. Am. Chem. Soc. **2011**, *133*, 13006-9.

Previous Progress (Task 4, Completed)

Formulate Materials as Liquids

7

Potential capacities, assuming 3 equivalent H₂ release:



neat material

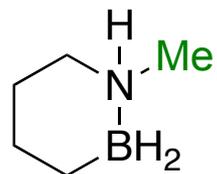
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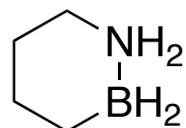
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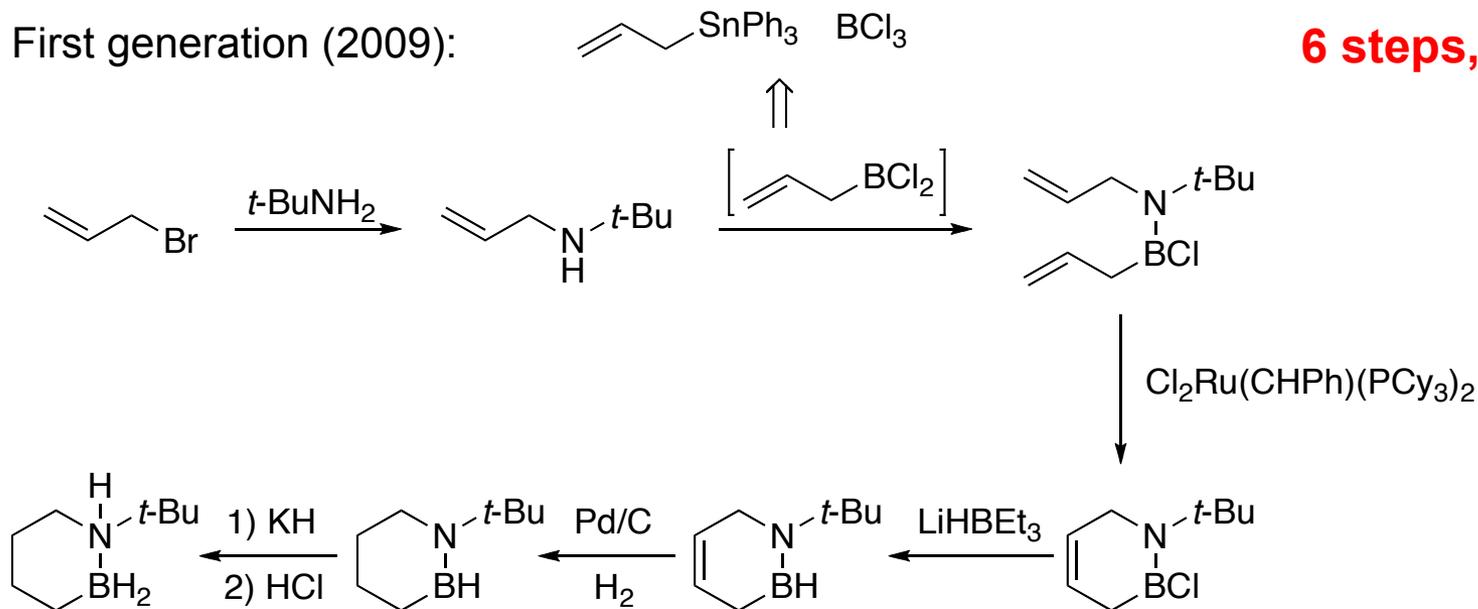
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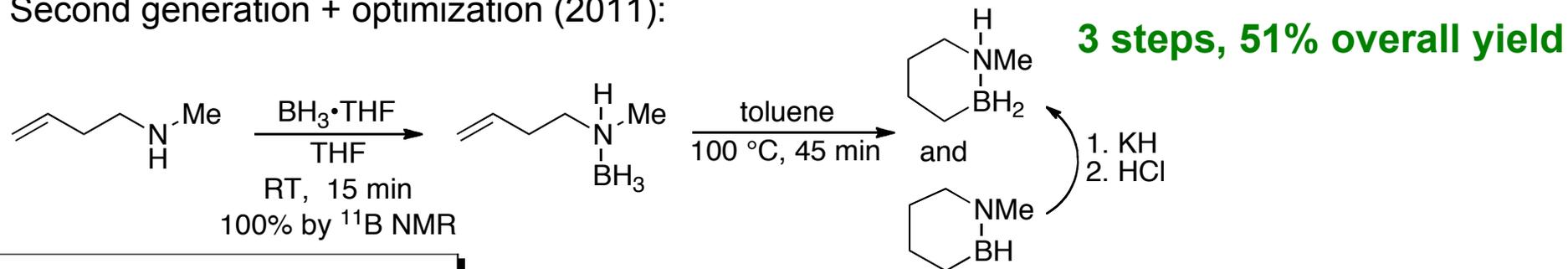
New Progress (Task 2, Completed)

Optimize Materials Synthesis

First generation (2009):



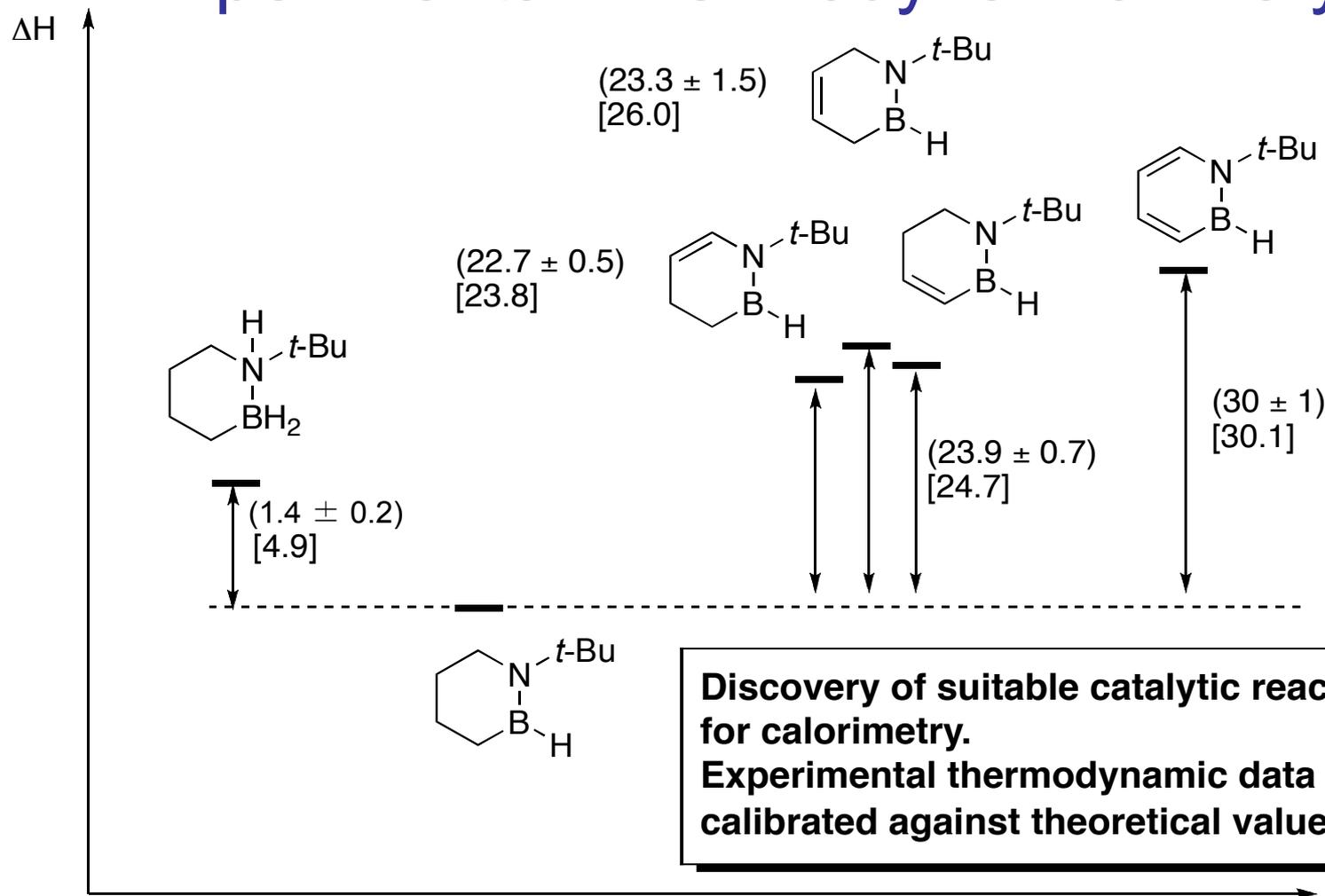
Second generation + optimization (2011):



First-fill synthesis was improved.

New Progress (Task 3, Completed)

Experimental Thermodynamic Analysis –

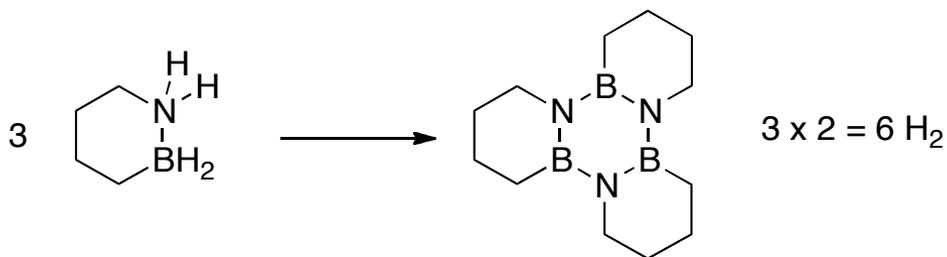
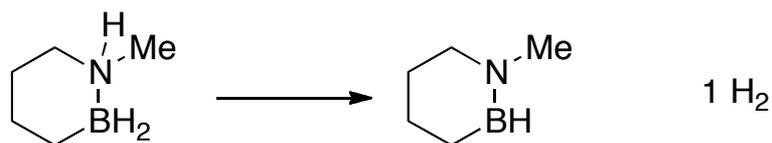
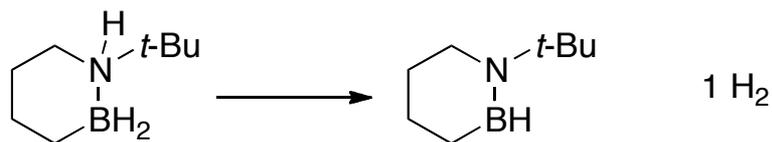


numbers in (): experimental values measured at 333K in kcal/mol
 numbers in []: G3(MP2) values at 298K in kcal/mol

reaction coordinate

New Progress (Task 5)

H₂ Desorption from BN is Facile



H₂ 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 H₂

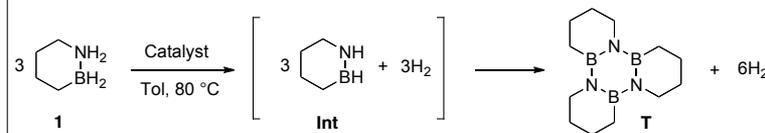


New Progress (Task 5)

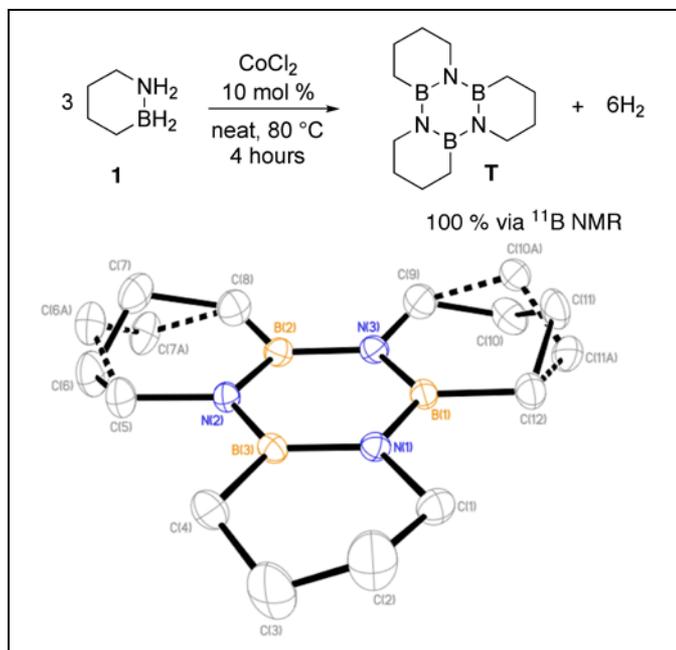
Screening of Catalysts for Trimerization

- 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 .

Table 1: Catalyst and condition screening for dehydrogenation of 1



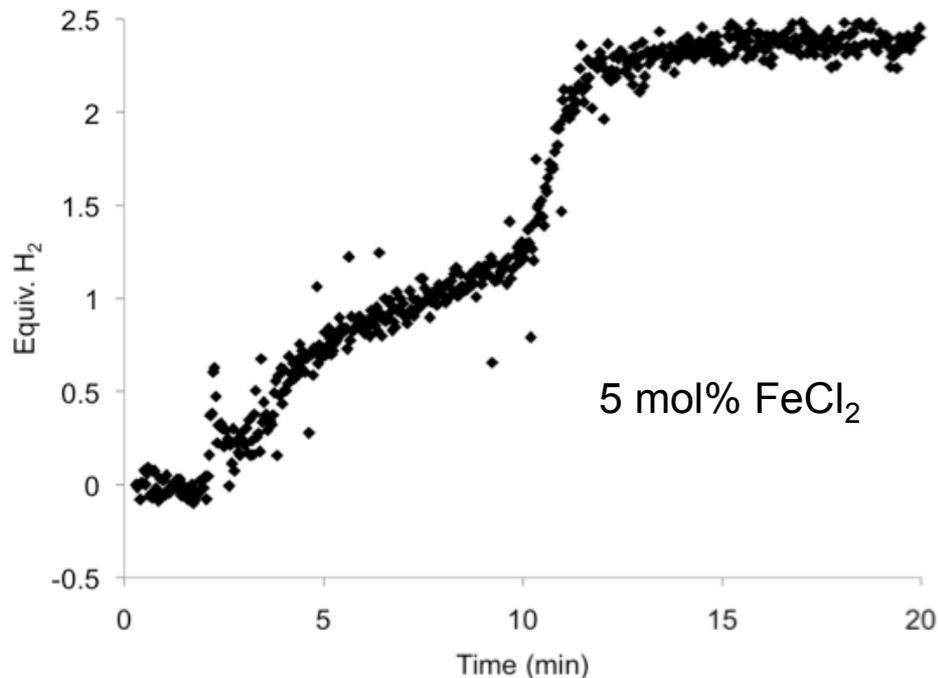
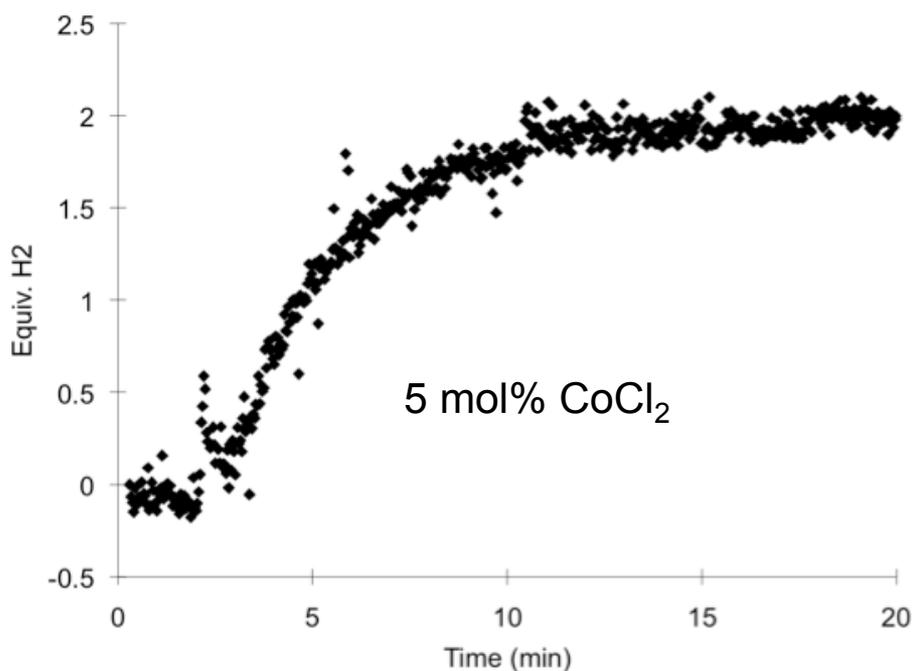
Entry	Catalyst	Loading (mol%)	Time(min)	% Yield Int	% Yield T
1	CoCl_2	10	60		100
2	(dppe) NiCl_2	10	60		100
3	$\text{Cr}(\text{MeCN})_3(\text{CO})_3$	10	60		N/R*
4	$[\text{Cl}(\text{cod})\text{Ir}]_2$	10	60		100
5	$[\text{Cl}(\text{cod})\text{Rh}]_2$	10	60		100
6	$[(\text{C}_2\text{H}_2)_2\text{ClRh}]_2$	10	60		100
7	Cp^*RuCl_2	10	60		100
8	$(\text{cod})_2\text{RhBF}_4$	10	60		N/R*
9	$(\text{PPh}_3)_2\text{NiCl}_2$	5	60		100
10	$[(\text{nbd})\text{ClRh}]_2$	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	$[\text{Cl}(\text{cod})\text{Ir}]_2$	5	30	20	80
15	$[\text{Cl}(\text{cod})\text{Rh}]_2$	5	30		100
16	Cp^*RuCl_2	5	30		100
17	$(\text{PPh}_3)_2\text{NiCl}_2$	5	30	40	60
18	$[(\text{nbd})\text{ClRh}]_2$	5	30		100
19	CoCl_2	10	15	50	50
20	$[\text{Cl}(\text{cod})\text{Rh}]_2$	5	15		100
21	Cp^*RuCl_2	5	15	60	40
22	$[(\text{nbd})\text{ClRh}]_2$	5	15		100



New Progress (Task 5)

FeCl₂ Acts as Catalyst for Trimerization

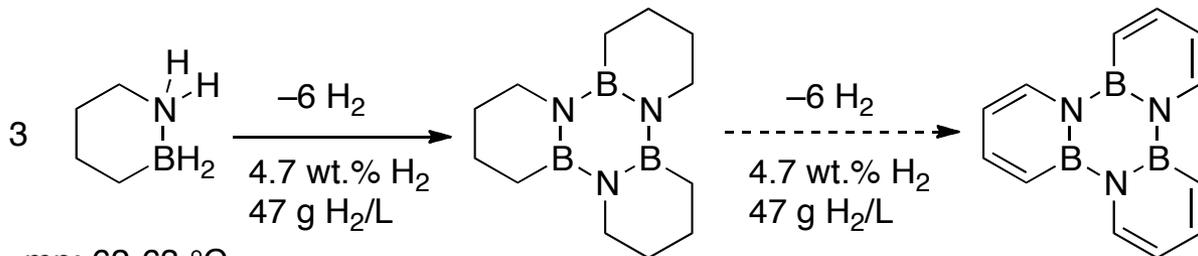
- Conditions: 80 °C in toluene solution.
- Release of 2 equiv. H₂ corresponds to complete conversion.



- FeCl₂ is cheap (\$0.30 / kg)
- H₂ desorption behavior is catalyst dependent.
- Mechanistic details still under investigation.

New Progress (Task 5)

Progress toward Removing H₂ 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 H₂/L

G3(MP2), 298K:

$\Delta H = +5.9$ kcal/mol monomer

$\Delta G = -19.3$ kcal/mol monomer

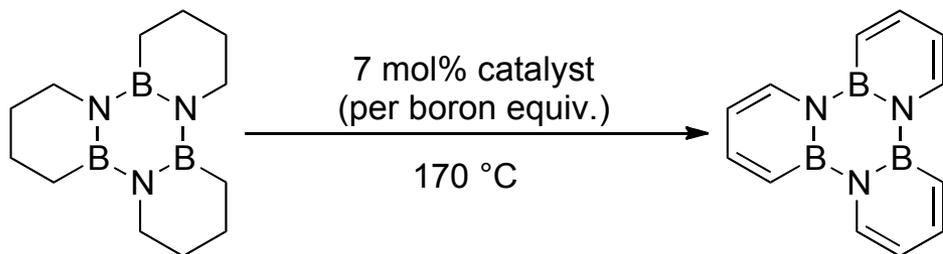
$\Delta H = +1.5$ kcal/mol H₂

$\Delta G = -4.8$ kcal/mol H₂

solid phase (single component)

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Preliminary attempts using transition metal catalysts:



Keep in mind that this reaction is endothermic:
 $\Delta H \sim 3 \times 30$ kcal/mol product.

starting material

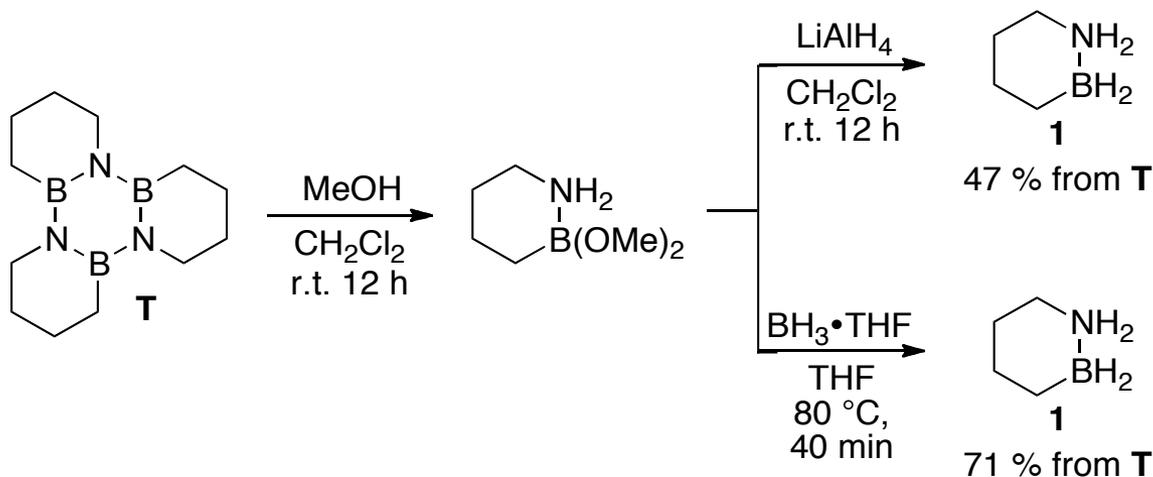
product

by GC analysis:

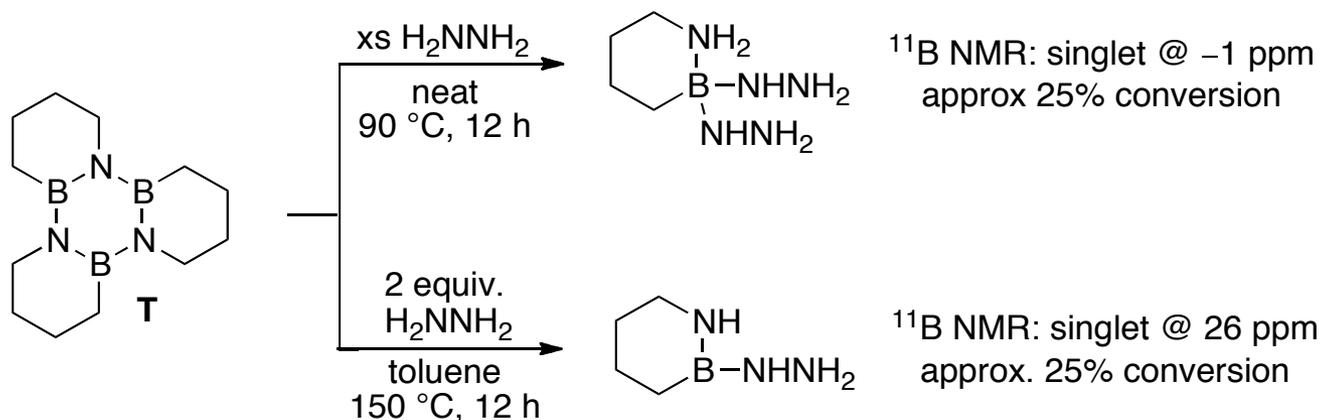
- complete conversion of the starting material
- significant formation of the desired product

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.

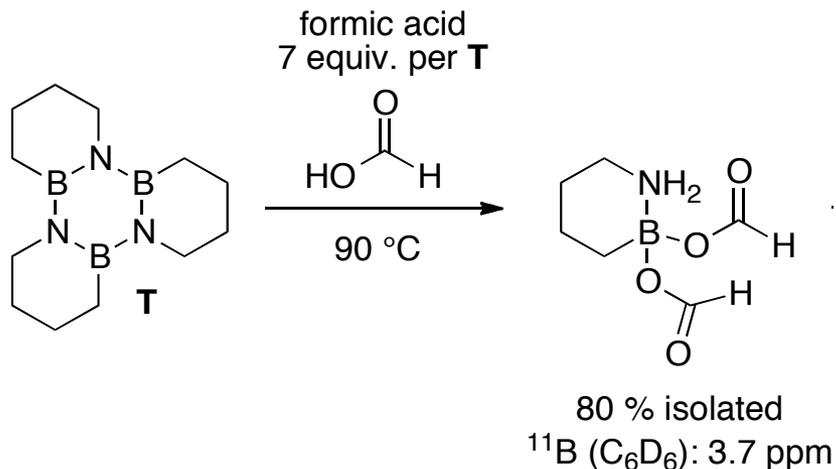
New Progress (Task 6)

Formic Acid as Potential H₂ Source

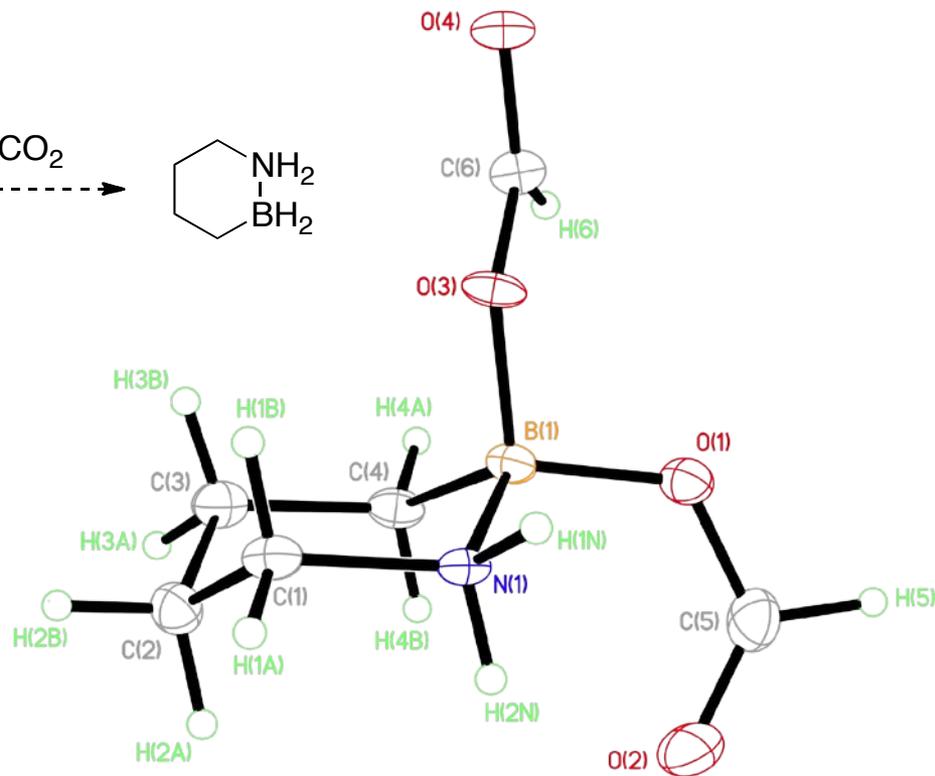
Formic acid:

- 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.

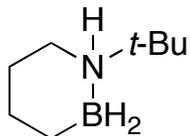


NMR indicates clean reaction. Loss in yield may be due to isolation procedures.

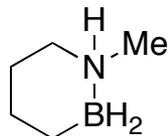


Summary of Accomplishments: Material Synthesis and Properties

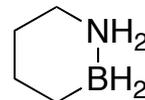
1. Synthesized family of novel CBN-heterocyclic materials, including parent:



4.3 wt% H₂

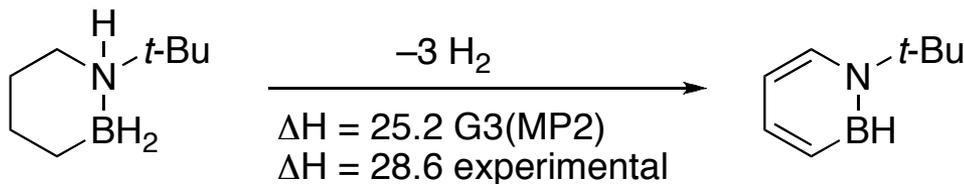


6.1 wt% H₂



7.1 wt% H₂ 3 equiv. release
9.5 wt% H₂ 4 equiv. release

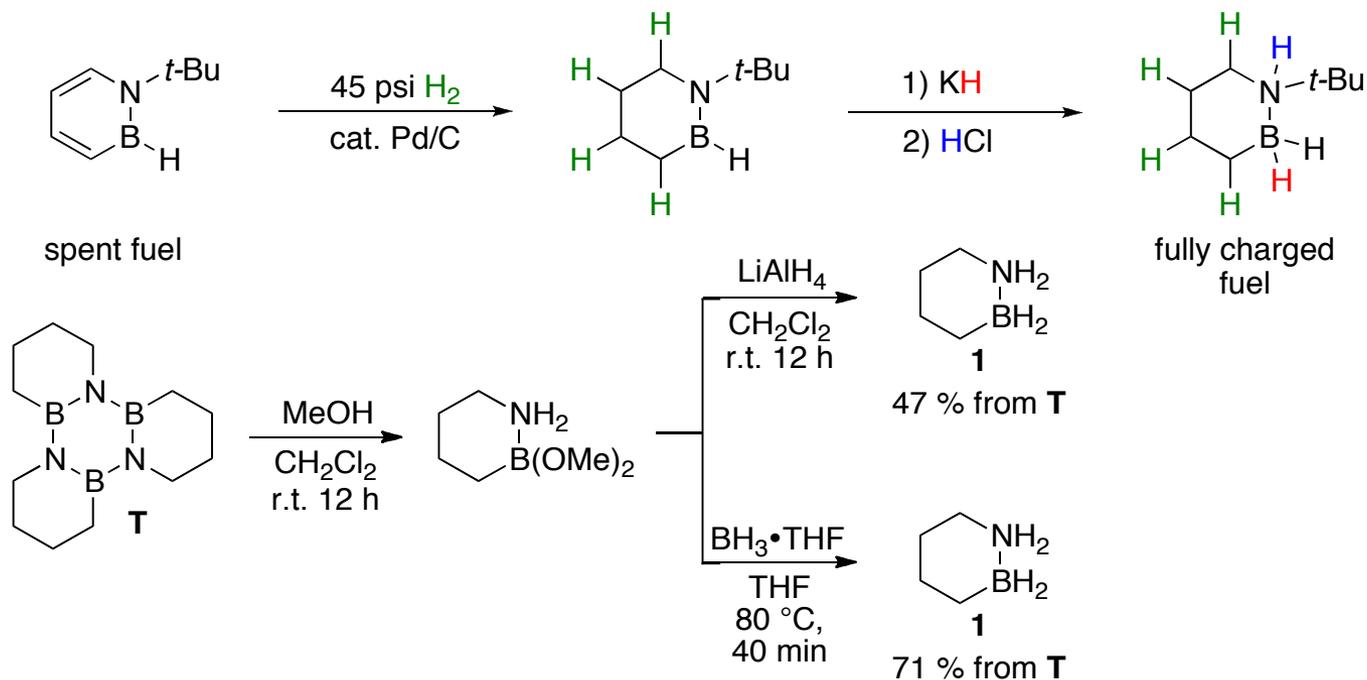
1. Improved material synthesis: all 3 steps, > 50% overall yield from commercially available starting materials
2. Completed experimental thermodynamic measurements to corroborate computational results (in kcal/mol):



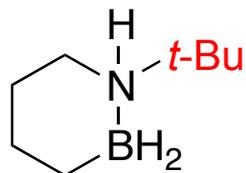
3. Formulated materials as liquids, determined H₂ capacity in solution

Summary of Accomplishments: H₂ Release and Regeneration

5. Hydrogen release (materials are thermally stable beyond their melting points):
- Loss of H₂ from B–N is facile, numerous hetero- and homogeneous catalysts promote loss of H₂ at $\leq 80^\circ\text{C}$
 - Trimerization of parent molecule occurs, releasing 2 equiv. H₂ per monomer
 - Proof-of-concept success for H₂ desorption from C–C
6. Regeneration of spent fuel material has been demonstrated:



Toward a Liquid Fuel



neat material

mp: 96-98 °C
 d (kg/L): 0.61 ± 0.07
 vol. (g H₂/L): 25
 wt.(%): 4.3

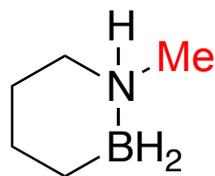
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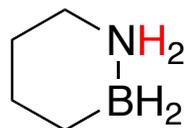
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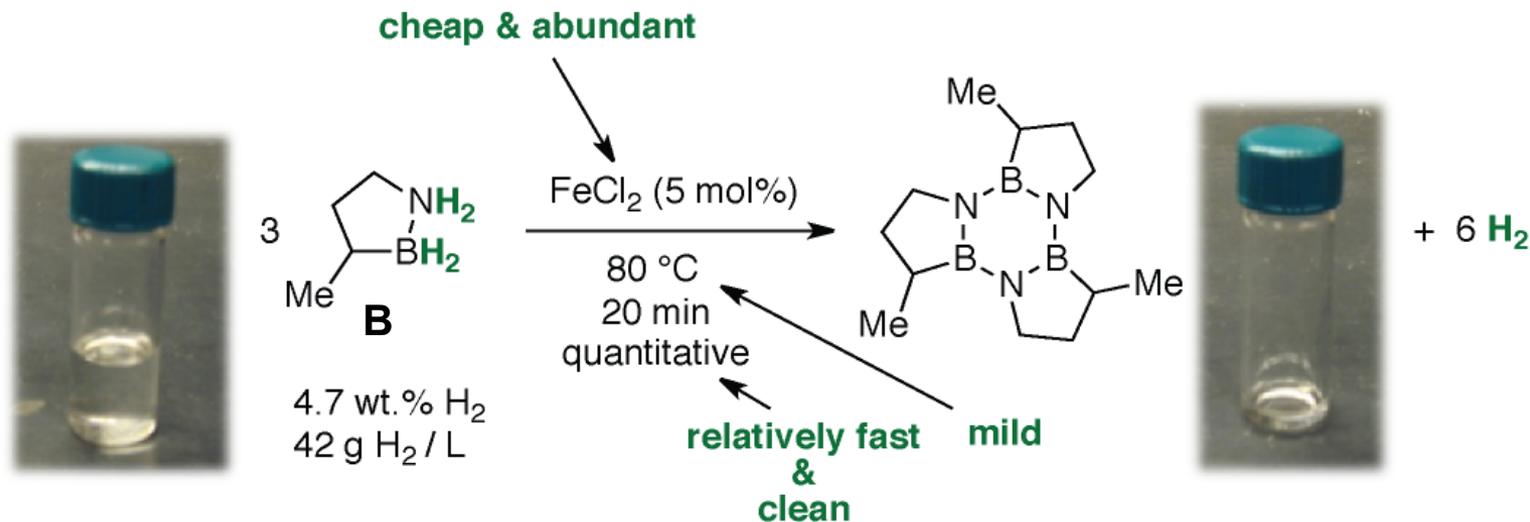
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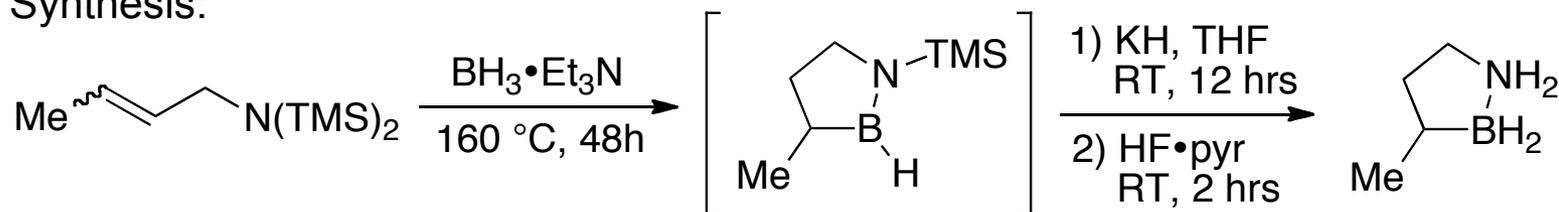
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It appears the smaller the molecule the lower the melting point.

A Single-Component Liquid H₂ Storage Material



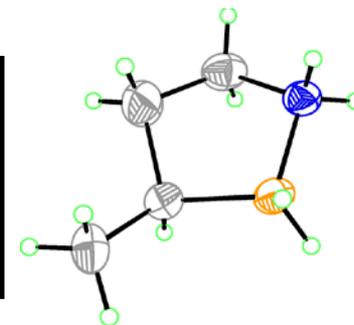
Synthesis:



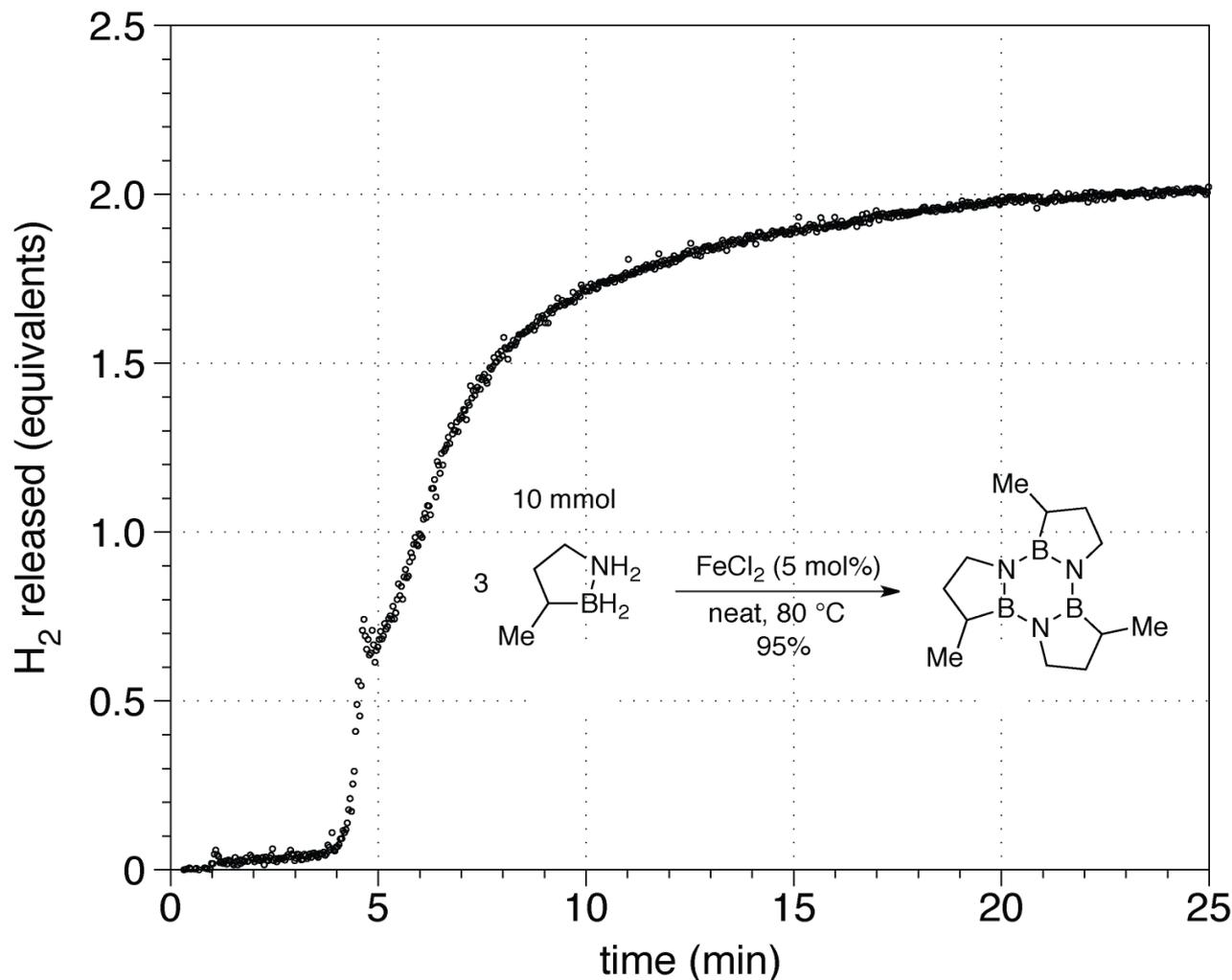
Highlighted in:

- *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.



Fe-Catalyzed H₂ 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.

Collaborations

Project Collaborators

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


Pacific Northwest
NATIONAL LABORATORY

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

Project Summary

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

Progress:

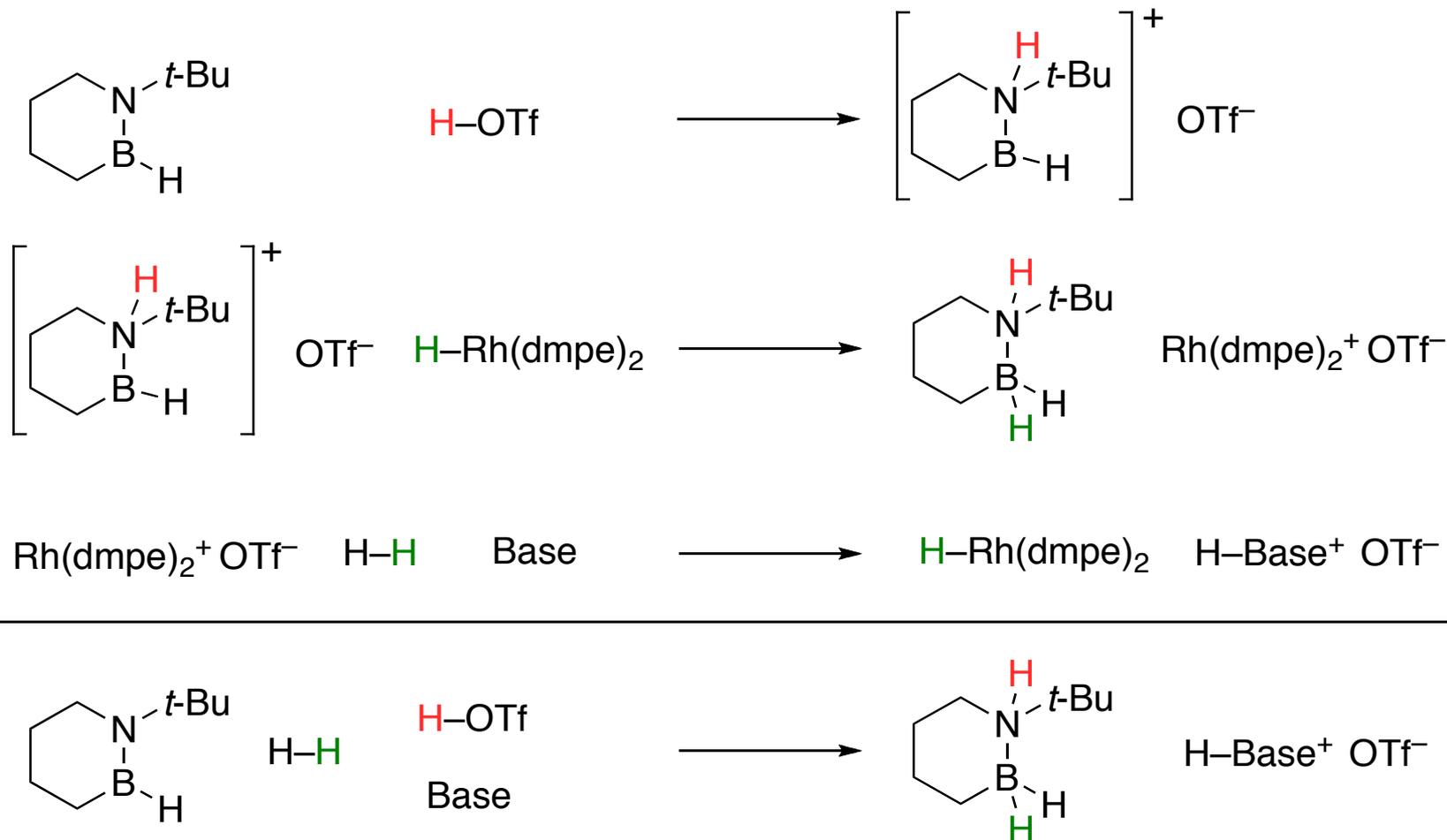
- **completed synthetic optimizations (Task 2)**
- **completed experimental thermodynamic analysis (Task 3)**
- **discovered FeCl₂ as effective catalyst for H₂ desorption from BN (Task 5)**
- **preliminary discovery of dehydrogenation from CC (Task 5)**
- **completed regeneration of trimer spent fuel (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