



Hydrogen Storage by Novel CBN Heterocycle Materials

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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: 70%

Budget

total project funding: \$1,436,356

DOE share: \$1,149,085

UO share: \$291,529

Fed. funding FY10 (Actual): \$300,000

Fed. funding FY11 (Planned): \$300,000

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:

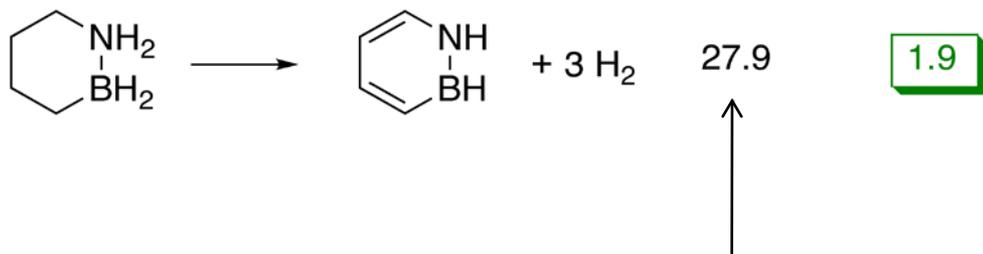
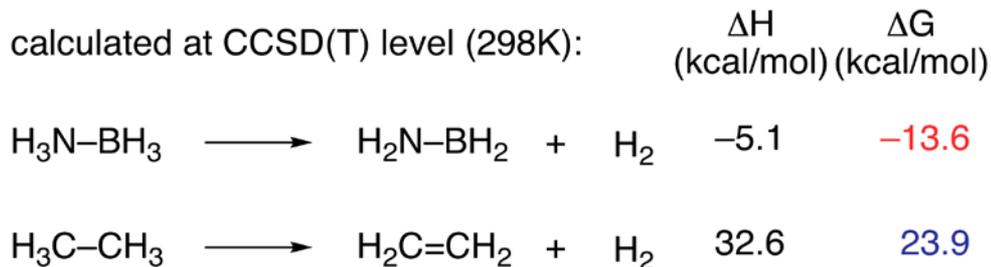
- liquid-phase
- gravimetric density (> 5.5 wt. %)
- volumetric density (> 40 g H₂/L system)
- thermodynamics (H₂ absorption and desorption)
- regeneration (reversibility)
- 2015 DOE targets

Specific objectives

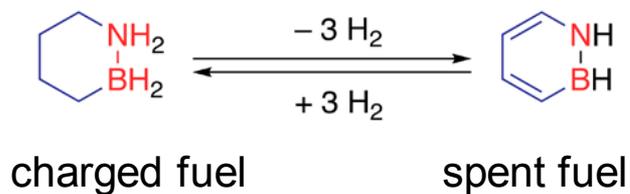
- synthesize novel CBN heterocycle materials (First-Fill synthesis)
- provide a thermodynamic analysis of materials (experiment and theory)
- formulate materials as liquids
- develop/identify conditions for H₂ desorption (release) with the potential to meet DOE targets
- develop/identify conditions for regeneration from spent fuel

The CBN Heterocycle Approach

calculated at CCSD(T) level (298K):

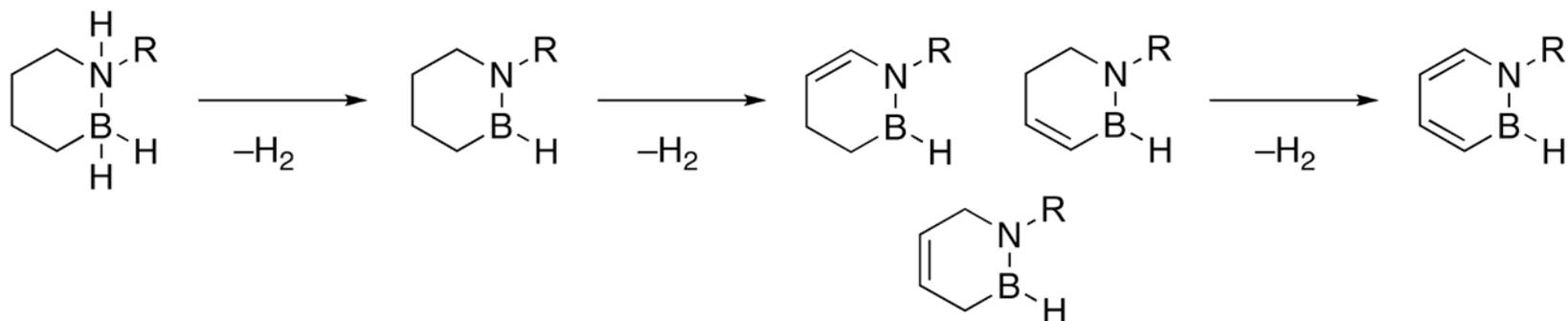


couple *exothermic* H₂ desorption from *BN* with *endothermic* H₂ desorption from *CC* in a *cyclic* system to achieve optimal thermodynamics for the overall H₂ absorption/desorption process.



**According to calculations:
 ΔH IS in the 7-12 kcal/mol H₂ range,
 i.e., $27.9 / 3 = 9.3$ kcal/mol H₂ released.**

A Well-Defined Molecular Approach



charged fuel

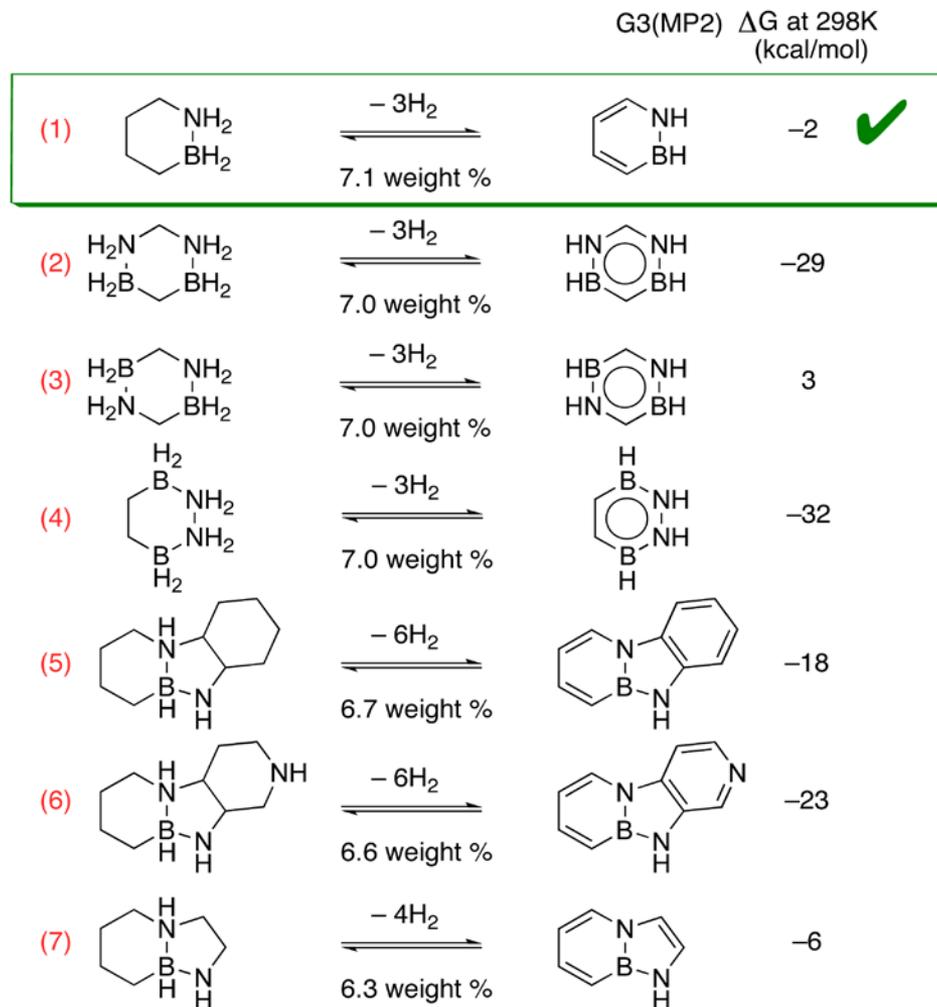
potential intermediates

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

Previous Progress

Down-selection to one material system based on theory and synthetic accessibility



Myrna Matus

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

Previous Progress – Summary

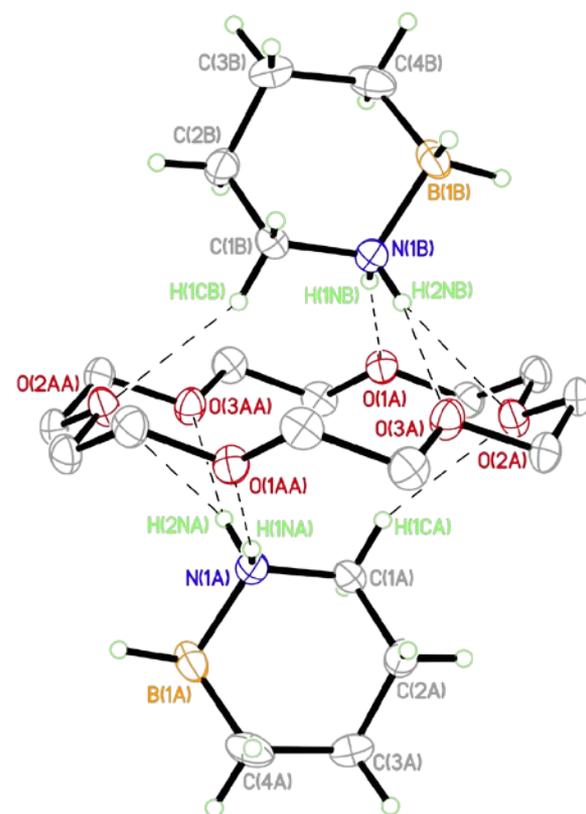
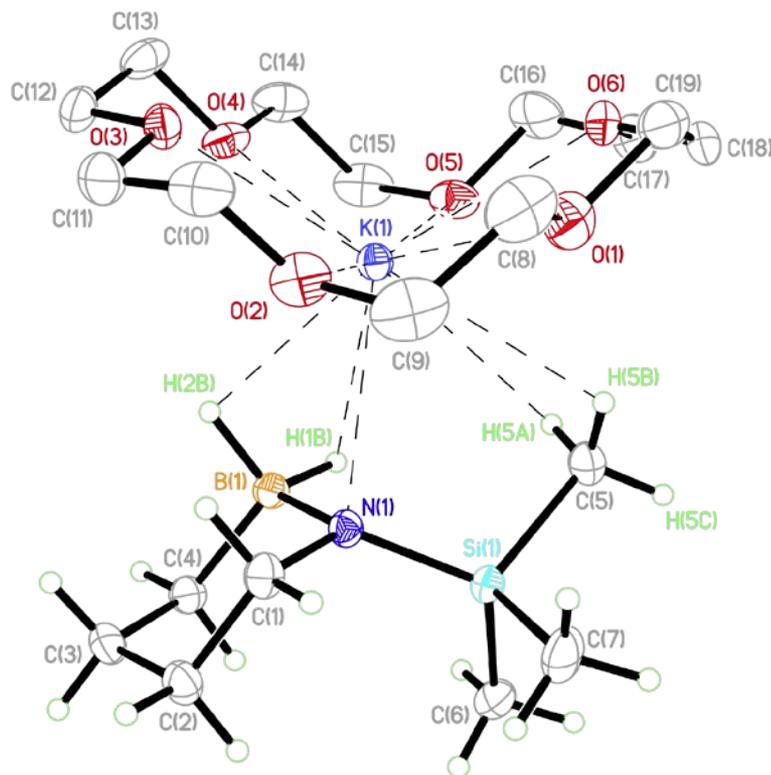
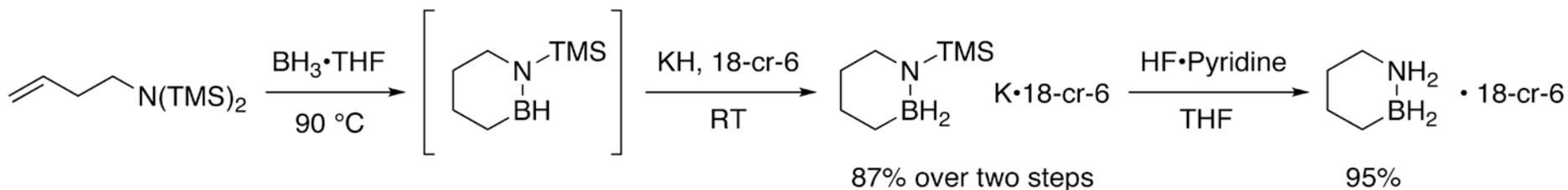
Unlike ammonia borane (AB), which is commercially available and a known compound (Shore et al. 1958), the proposed materials are unknown (as of 2008), nor are the methods to prepare them.

Since project began in September of 2008, we have:

- developed the necessary synthetic tools to prepare the CBN heterocycle materials
- developed a First-Fill synthesis for the proposed materials.
- developed a simple route for regeneration of the spent fuel
- investigated the relevance of aromaticity on the hydrogen uptake process

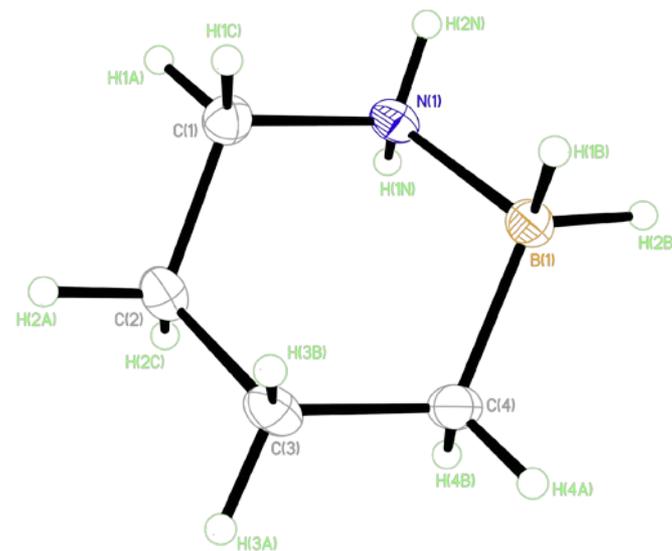
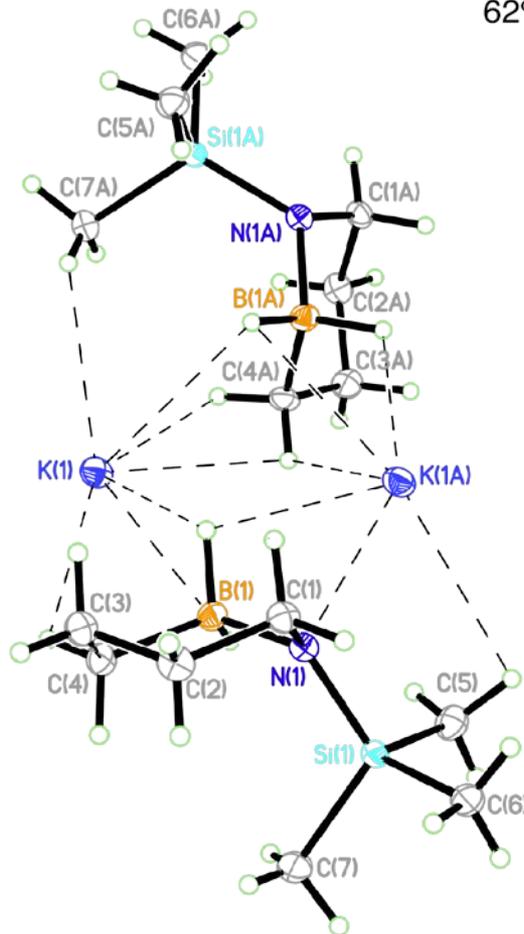
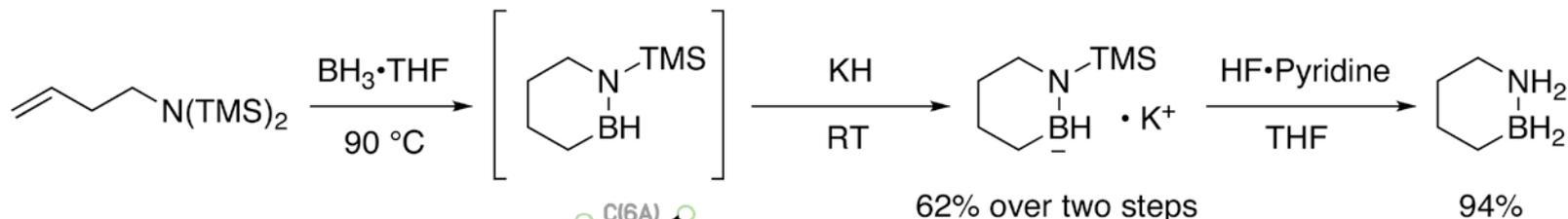
Previous work focused on SYNTHESIS

Synthesis of the Parent – New Progress

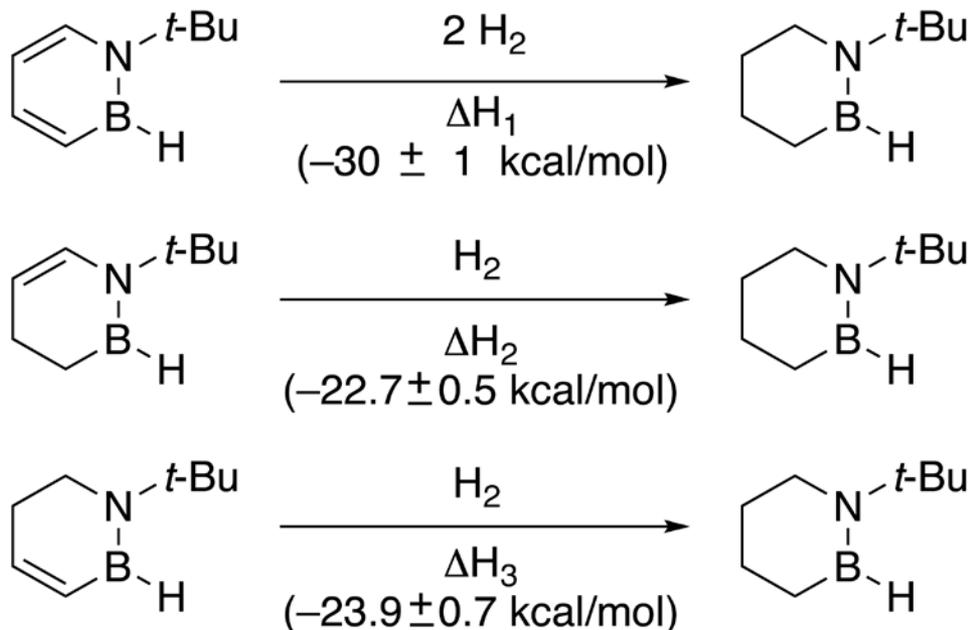


Toward the parent material

Parent Material was successfully prepared – New Progress

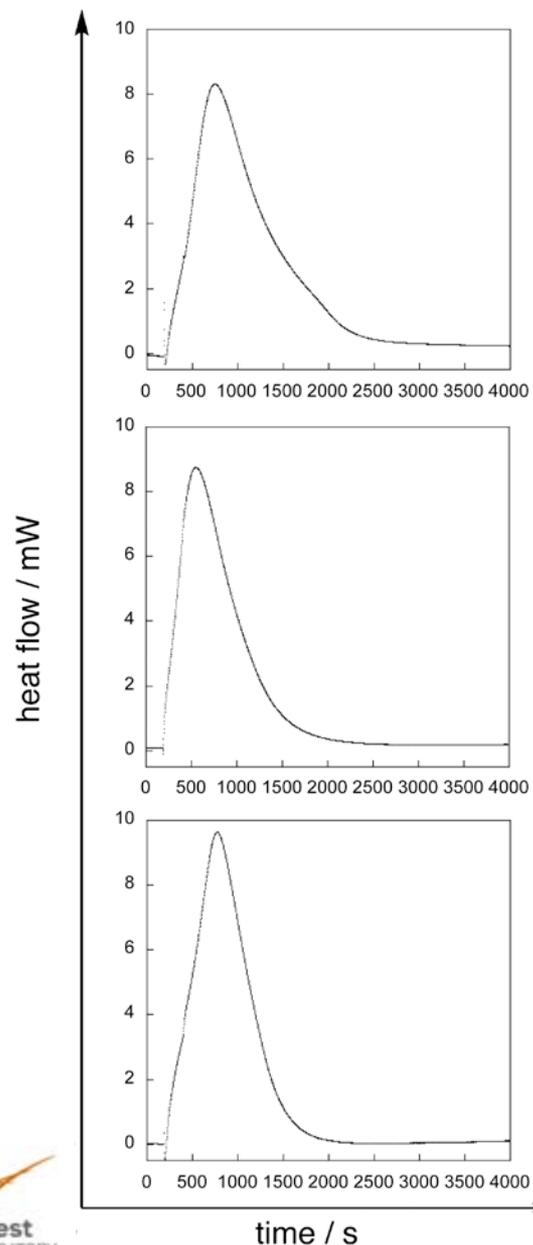


Experimental Thermodynamic Analysis – New Progress

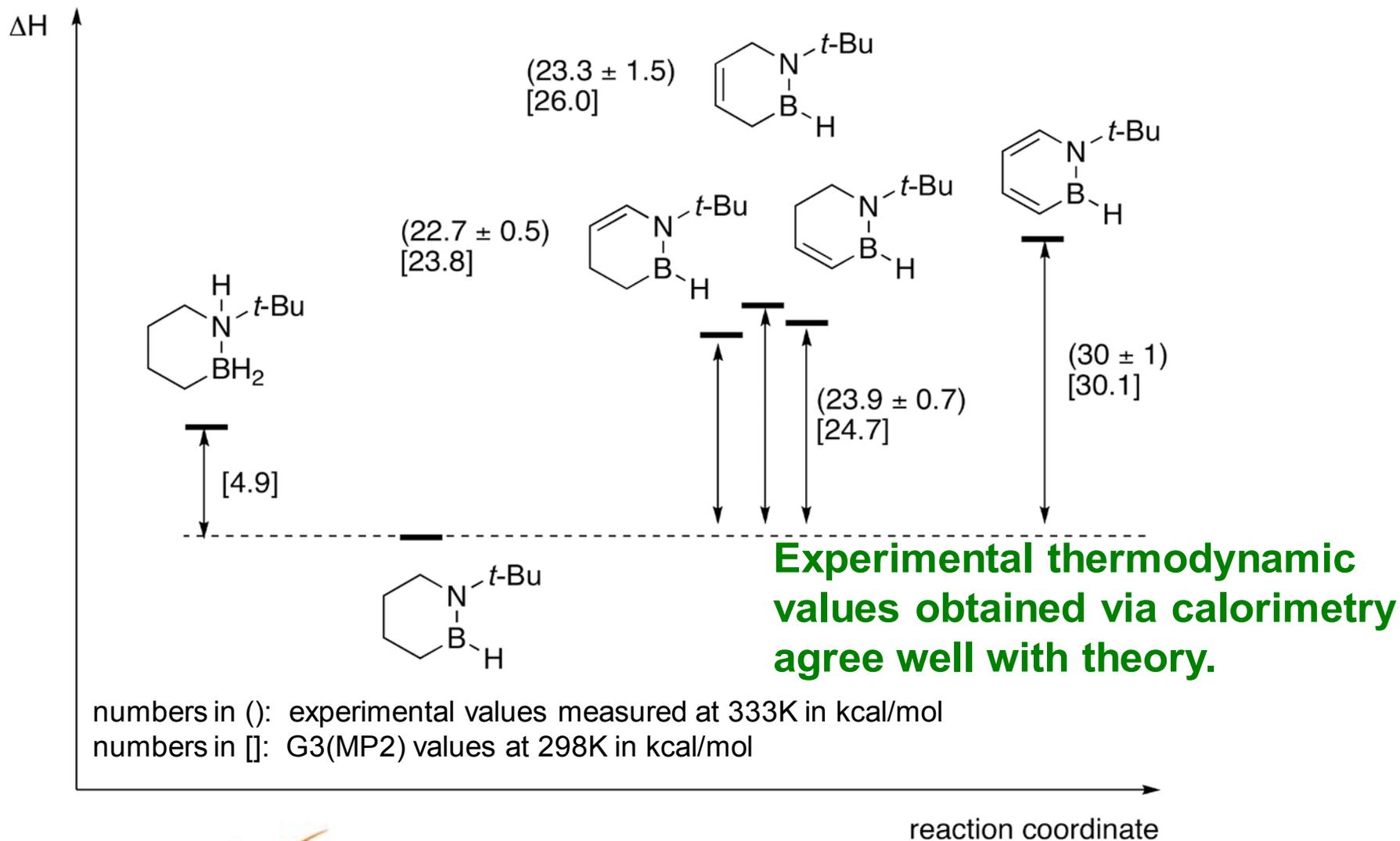


Conditions:
 10 mol% Muetterties' catalyst
 $(\eta^3\text{-allyl})\text{Co}[\text{P}(\text{OMe})_3]_3$,
 50 psi H_2 , hexanes, 60 °C

**Discovery of suitable catalytic “homogeneous”
 reaction conditions for calorimetry.**

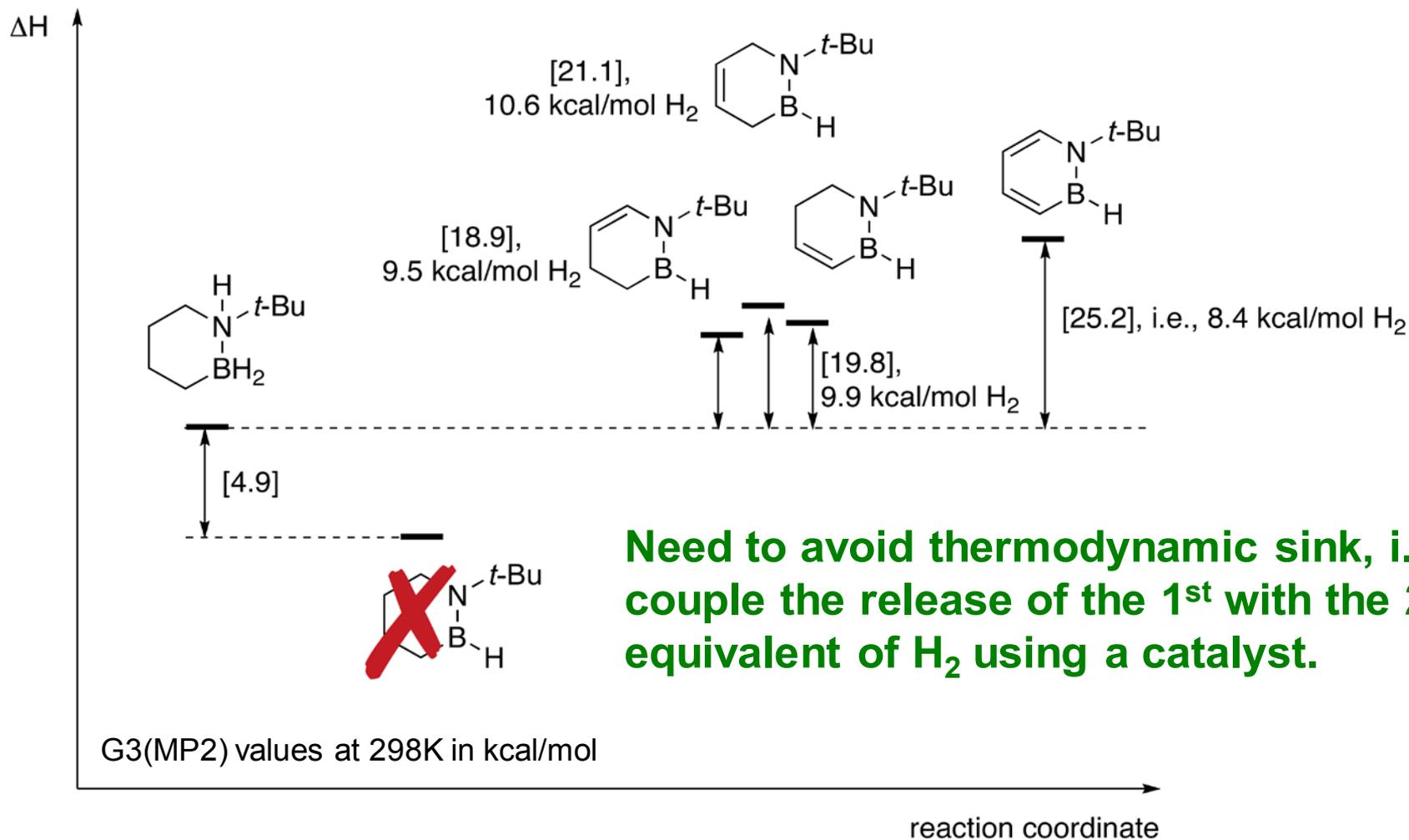


Enthalpy: Experiment and Theory – New Progress

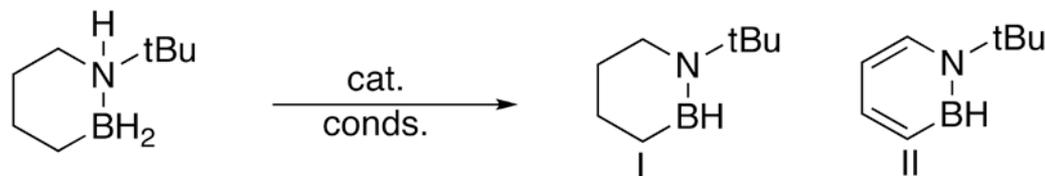


Enthalpy: Experiment and Theory

New Progress



Efforts Toward Coupled Release of H₂



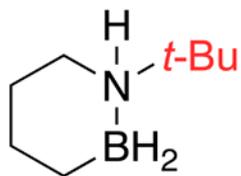
entry	catalyst	mol %	solvent	temp °C	% yield I	% yield II
1	Pd[P(tBu) ₃] ₂	10	THF	65	75, 24h	0
2	[(cod)(PCy ₃)PyIr] ⁺ PF ₆ ⁻	10	THF	65	90, 24h	0
3	Cl ₂ (PPh ₃) ₃ Ru	10	THF	65	>95, 3h	0
4	Cl(PPh ₃) ₃ Rh	10	THF	65	>95, 3h	0
5	[Cl ₂ Cp*Ir] ₂	10	THF	65	>95, 24h	0
6	Pd(OAc) ₂	10	THF	65	50, 3h	0
7	PtCl ₂ (PPh ₃) ₂	10	THF	65	50, 19h	0
8	[(cod)(PCy ₃)PyIr] ⁺ PF ₆ ⁻	20	C ₆ D ₆	80	90, 30m	0
9	Pd/C	g. wool	neat	140	0	0
10	Pd ⁰	10	neat	300	0	0
11	Pd ⁰	20	cyclohexene	300	0	0
12	η ³ -allylCo[P(OMe) ₃] ₄	25	pentadec./H ₂	150	90, 1h	0
13	Ru/C	10	pentadec.	300	0	0

Catalysts/conditions screened thus far do not lead to coupled release of H₂. Will explore Ta and Nb catalysts, Rothwell et al. JACS 1997.

Formulation of Materials as Liquids

New Progress

Potential capacities, assuming 3 equivalent H₂ release:



neat material

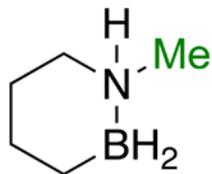
mp: 96-98 °C
d (kg/L): 0.61 ± 0.07
vol. (g H₂/L): 25
wt.(%): 4.3

THF solution

sol. (g/L): 284 ± 28
d (kg/L): "0.89"
vol. (g H₂/L): 11.7 g
wt.(%): 1.3

Et₂O solution

sol. (g/L): 84.4 ± 4
d (kg/L): "0.71"
vol. (g H₂/L): 3.47
wt.(%): 0.4



neat material

mp: 72-73 °C
d (kg/L): 0.87 ± 0.08
vol. (g H₂/L): 53
wt.(%): 6.1

THF solution

sol. (g/L): 292 ± 5
d (kg/L): "0.89"
vol. (g H₂/L): 17.8
wt.(%): 2.0

Et₂O solution

sol. (g/L): 106 ± 18
d (kg/L): "0.71"
vol. (g H₂/L): 6.5
wt.(%): 0.73



neat material

mp: 62-63 °C
d (kg/L): 1.00 ± 0.05
vol. (g H₂/L): 70
wt.(%): 7.1

THF solution

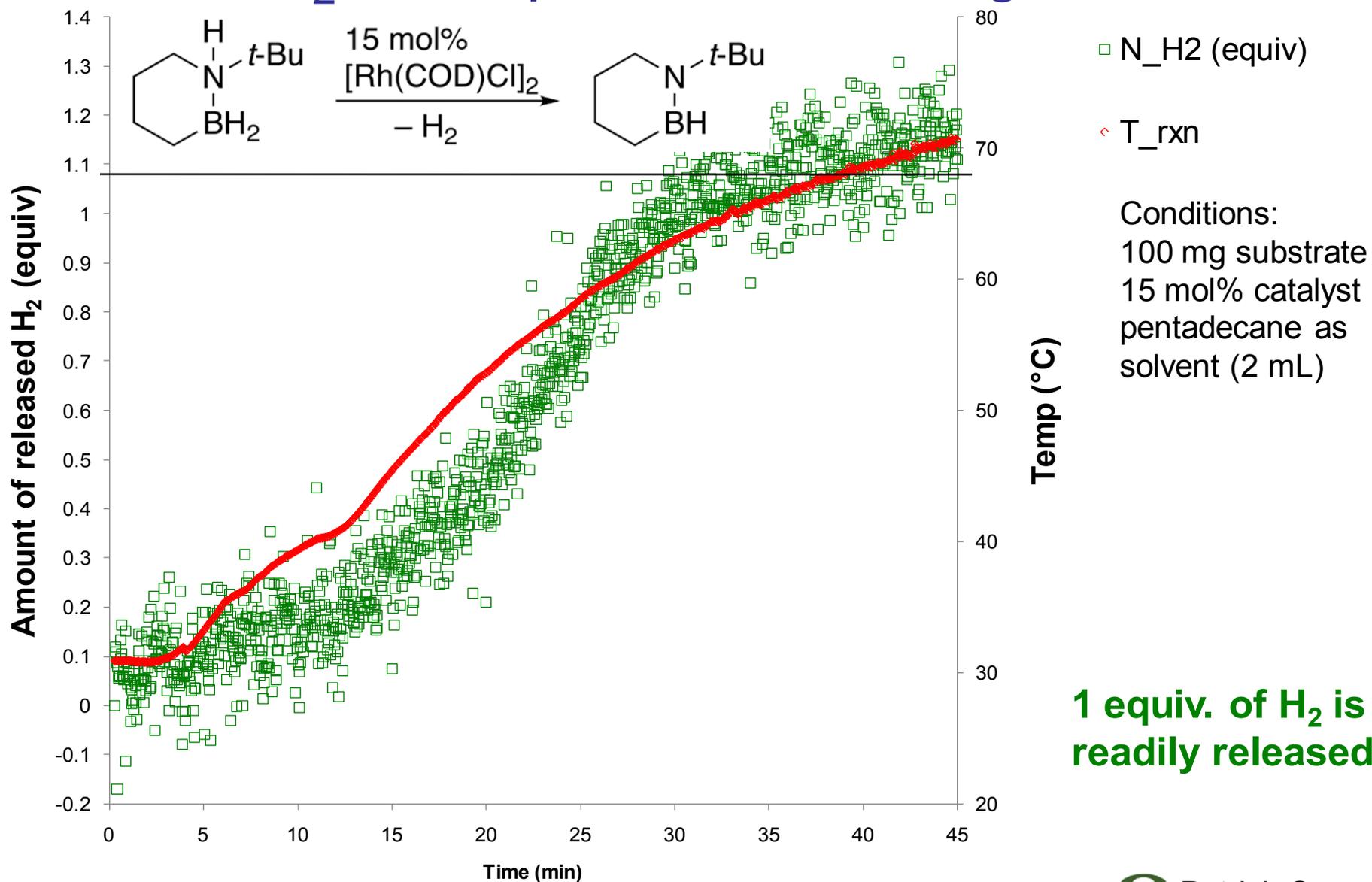
sol. (g/L): 434 ± 20
d (kg/L): "0.89"
vol. (g H₂/L): 30.7
wt.(%): 3.4

Et₂O solution

sol. (g/L): 347 ± 30
d (kg/L): "0.71"
vol. (g H₂/L): 25
wt.(%): 3.1

DOE 2015 target: 5.5 wt%, 40 g H₂/L

H₂ Desorption – New Progress



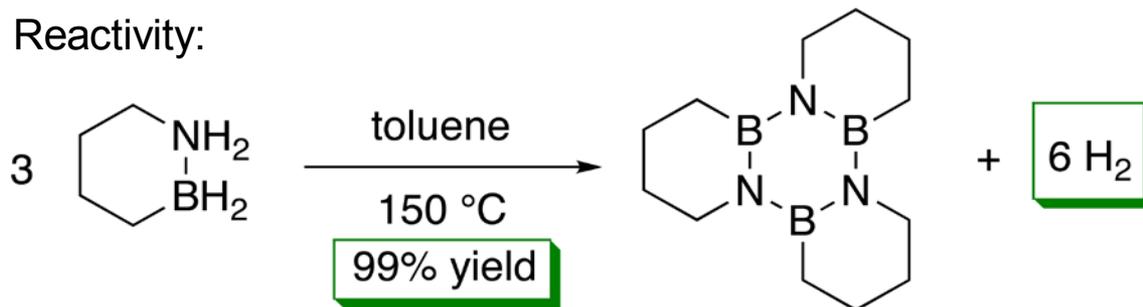
Properties and Reactivity of the Parent – New Progress

Stability:



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

Reactivity:



assuming 2 equivalent H₂ release:



neat material

mp: 62-63 °C
d (kg/L): 1.00 ± 0.05
vol. (g H₂/L): 47
wt.(%): 4.7

THF solution

sol. (g/L): 434 ± 20
d (kg/L): "0.89"
vol. (g H₂/L): 20
wt.(%): 2.3

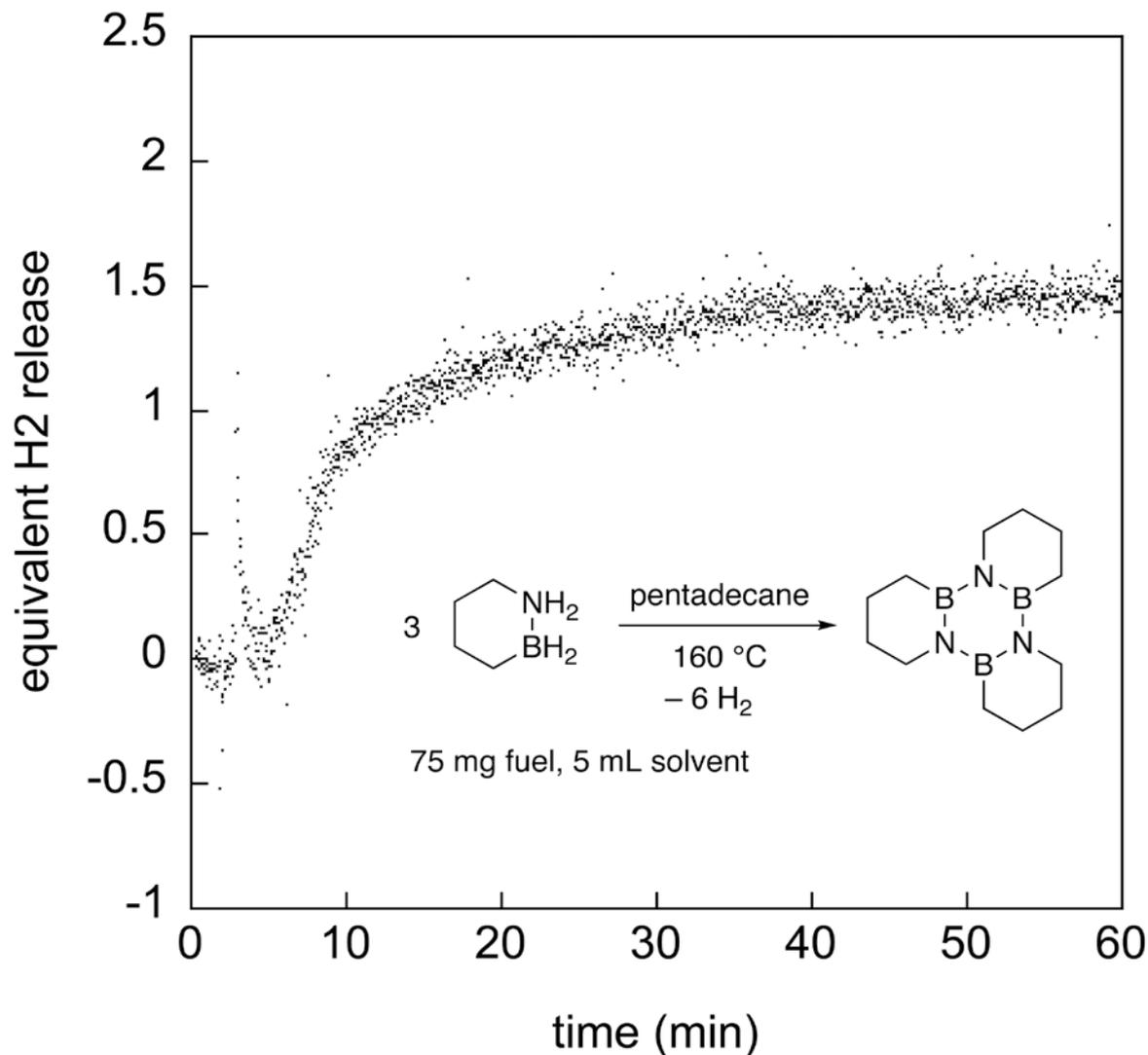
Et₂O solution

sol. (g/L): 347 ± 30
d (kg/L): "0.71"
vol. (g H₂/L): 17
wt.(%): 2.1

**A viable ammonia
borane alternative?**

- **clean reaction**
- **well-defined**
- **“no NH₃”**
- **“no B₃N₃H₆”**
- **reasonable capacities**

H₂ Desorption 2 Equivalent Release from the Parent – New Progress



Preliminary studies indicate that up to 1.5 equiv. H₂ is released.

Collaborations

Project Collaborators

THE UNIVERSITY OF
ALABAMA

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

Technology Transfer

THE UNIVERSITY OF
ALABAMA

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


Pacific Northwest
NATIONAL LABORATORY

obtained thermodynamic data via reaction calorimetry

Proposed Future Work

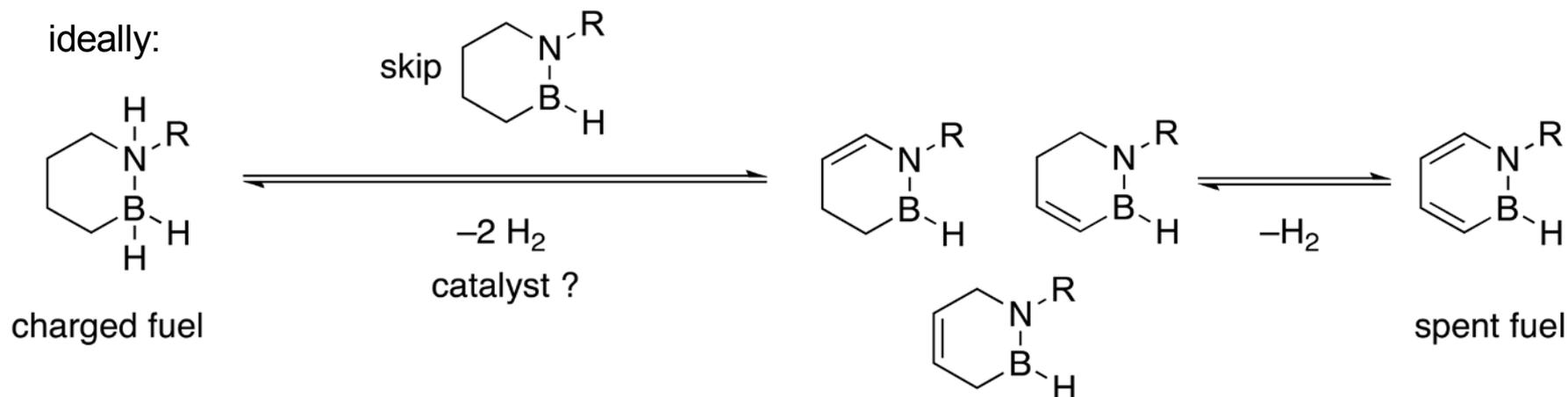
- focus on developing CBN Materials (1)
- complete experimental thermodynamic data for CBN heterocycle materials for comparison with theory (one data point left)
- develop/identify/optimize conditions for H₂ desorption from these CBN materials for both the 3 equiv. and 2 equiv. release systems
- catalyst screening, development for coupled H₂ desorption from CBN materials
- determine/optimize charge/discharge characteristics
- develop more efficient regeneration of spent fuel (formic acid, PNNL M-H route)

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:**
- **synthesized the parent CBN heterocycle material**
 - **determined 4 out of 5 experimental thermodynamic data points**
 - **formulated CBN materials as liquid fuels and determined their potential capacities**
 - **developed conditions for release of 1 equiv. of H₂ for non-parent substrates**
 - **investigated the properties of the parent,**
 - **discovered clean and efficient release of 2 equiv. of H₂ from parent material**
- Collaborations: active partnership with UA and PNNL
- Future Work:
- complete remaining experimental thermodynamic data point
 - determine/optimize H₂ charge/discharge characteristics
 - develop better conditions for regeneration

Technical Back-Up Slides

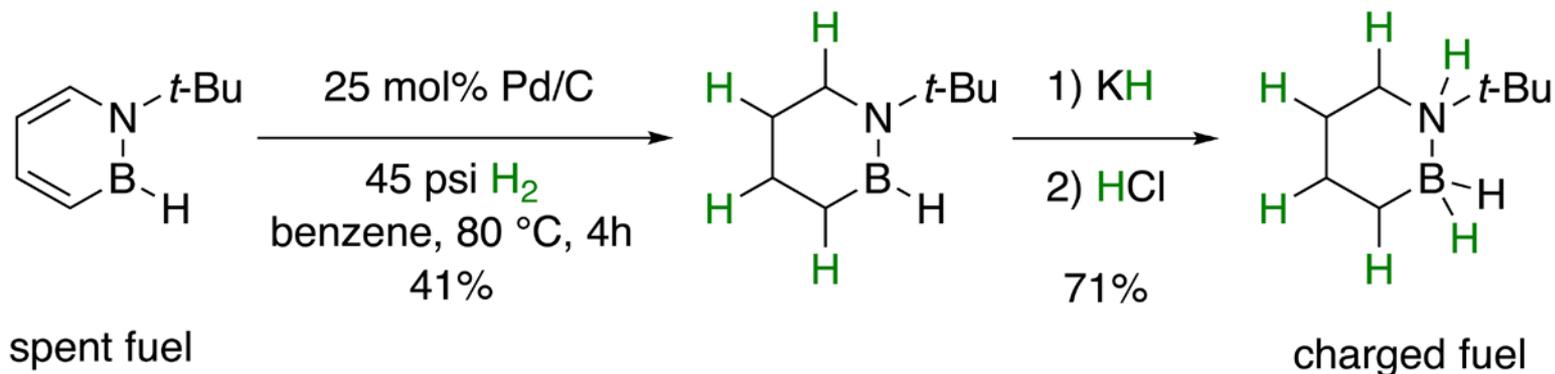
Technical Back-Up Slide: The Issue of Regeneration



benefit: facilitates regeneration, potentially using molecular H_2

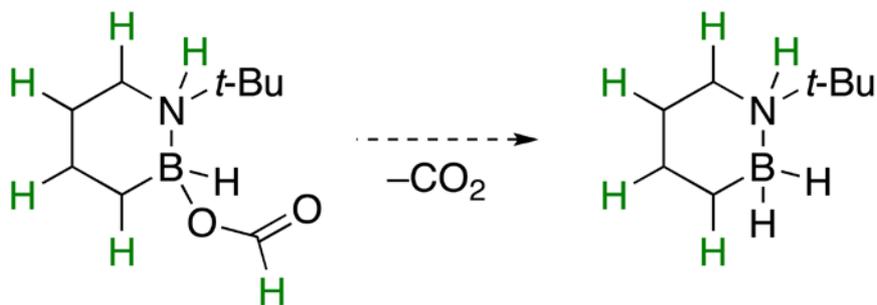
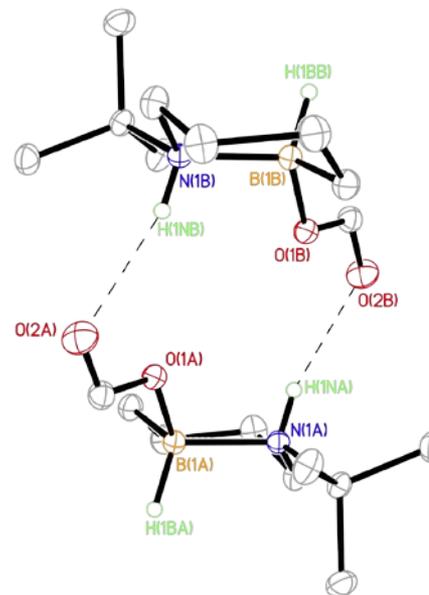
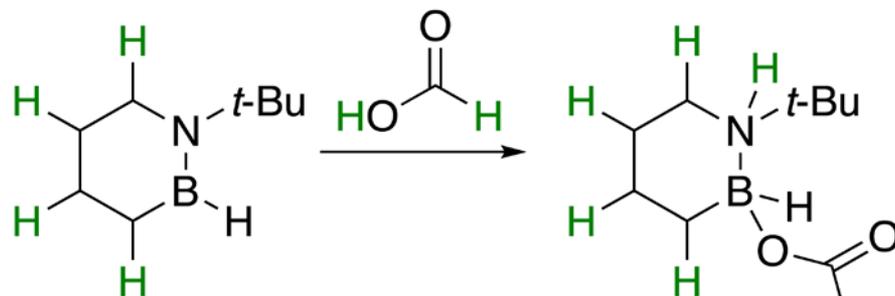
challenge: requires catalyst screening, discovery, development

thus far accomplished:



Technical Back-Up Slide: Regeneration

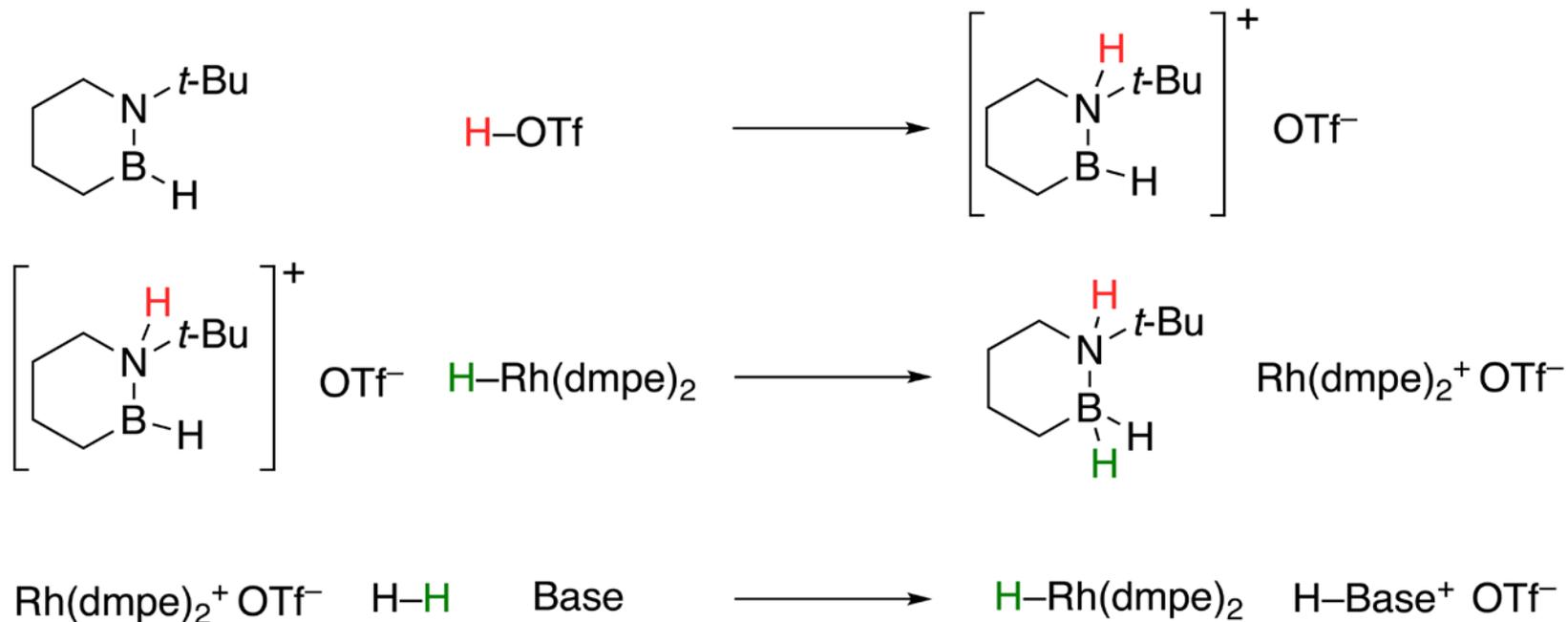
formic acid pathway:



$\Delta G = 5.7 \text{ kcal/mol}$
 $\Delta H = 16.1 \text{ kcal/mol}$
 G3MP2 at 298 K

Technical Back-Up Slide: Regeneration

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



Use acid-base chemistry to drive an uphill process