Hydrogen Storage by Novel CBN Heterocycle Materials

Shih-Yuan Liu (lsy@uoregon.edu)
Department of Chemistry, University of Oregon
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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%

Barriers

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

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

Project Collaborators

THE UNIVERSITY OF ALABAMA Prof. David Dixon

Project Objectives - Relevance

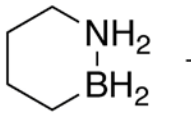
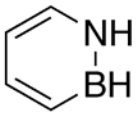
Develop CBN heterocycles as novel hydrogen storage materials:

- liquid-phase
- gravimetric density (> 5.5 wt. %)
- volumetric density (> 40 g H_2/L system)
- thermodynamics (H_2 absorption and desorption)
- regeneration (reversibility)
- 2015 DOE targets

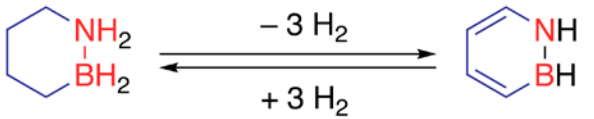
Specific objectives

- 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 H_2 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):			ΔH (kcal/mol)	ΔG (kcal/mol)
$H_3N–BH_3$	$\longrightarrow$	$H_2N–BH_2 + H_2$	–5.1	–13.6
$H_3C–CH_3$	$\longrightarrow$	$H_2C=CH_2 + H_2$	32.6	23.9
	$\longrightarrow$	 $+ 3\ H_2$	27.9	1.9

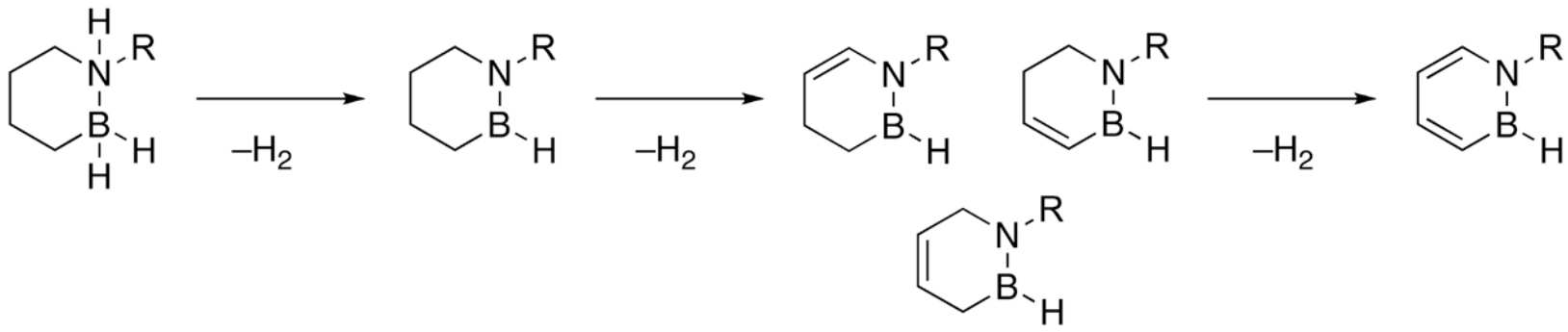
couple *exothermic* H_2 desorption from *BN* with *endothermic* H_2 desorption from *CC* in a *cyclic* system to achieve optimal thermodynamics for the overall H_2 absorption/ desorption process.



charged fuel spent fuel

According to calculations:
ΔH IS in the 7-12 kcal/mol H_2 range,
i.e., 27.9 / 3 = 9.3 kcal/mol H_2 released.

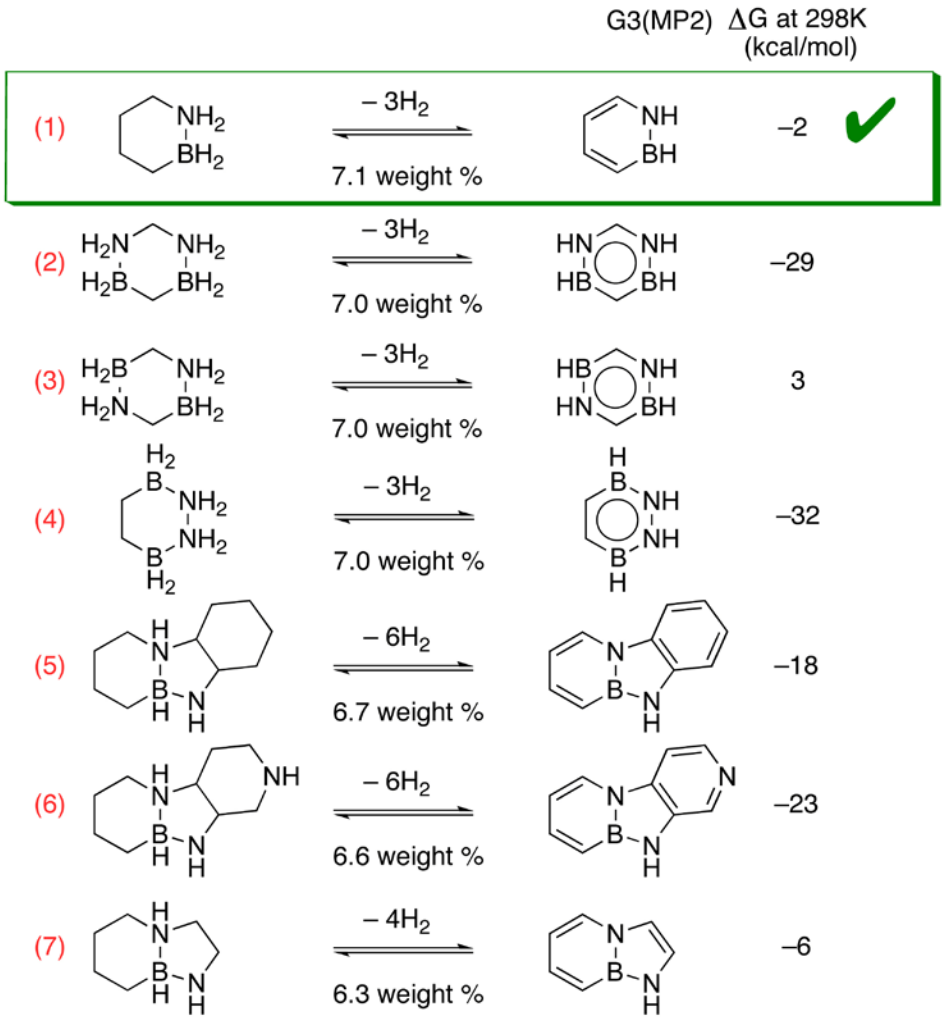
A Well-Defined Molecular Approach



- 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

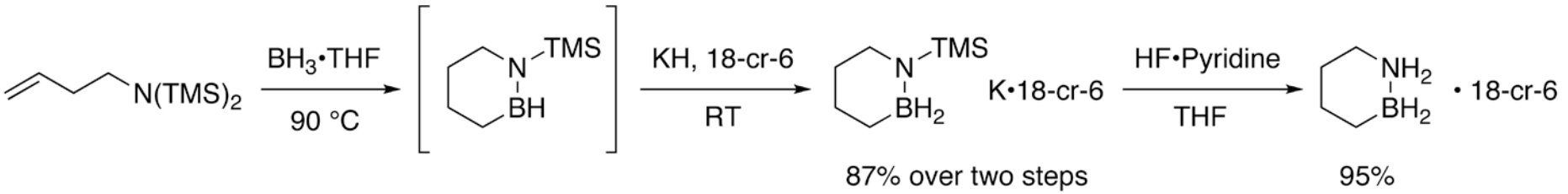
Unlike ammonia borane (AB), which is commercially available and a known compound (Shore et al. 1958), the proposed materials are unknown (as of 2008), nor are the methods to prepare them.

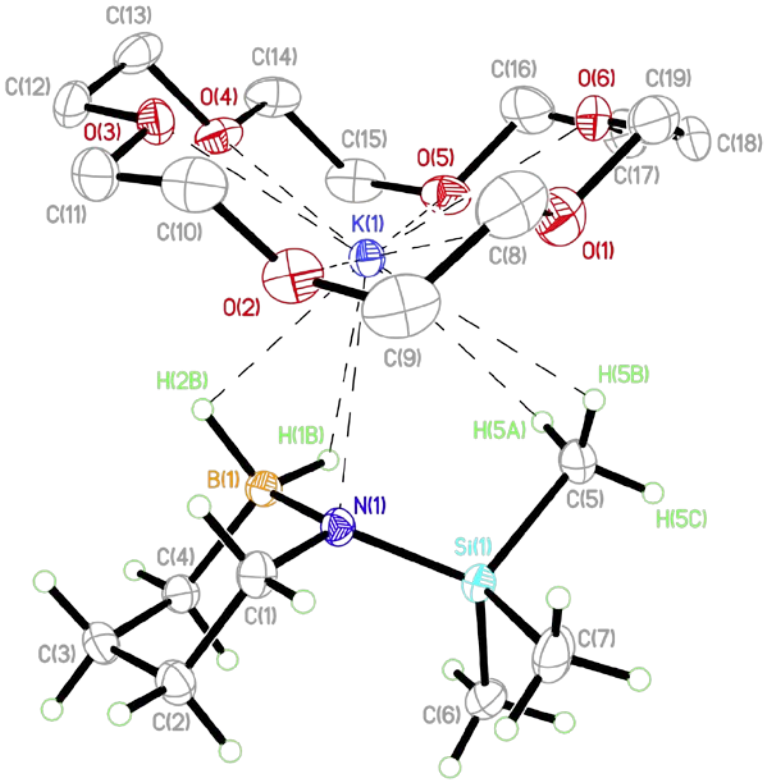
Since project began in September of 2008, we have:

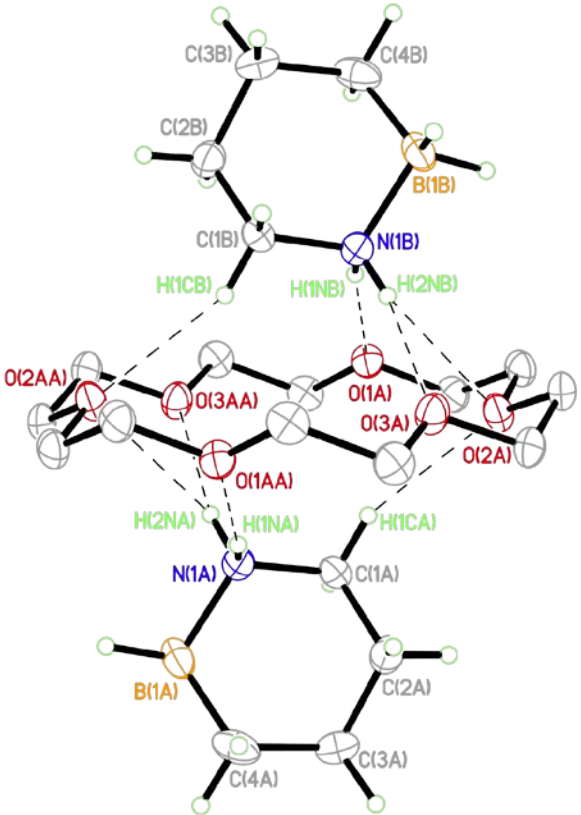
- developed the necessary synthetic tools to prepare the CBN heterocycle materials
- developed a First-Fill synthesis for the proposed materials.
- developed a simple route for regeneration of the spent fuel
- investigated the relevance of aromaticity on the hydrogen uptake process

Previous work focused on SYNTHESIS

Synthesis of the Parent – New Progress



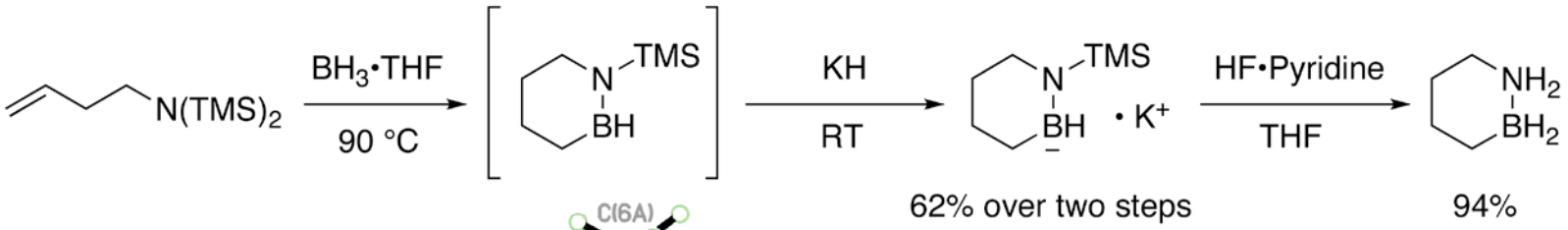


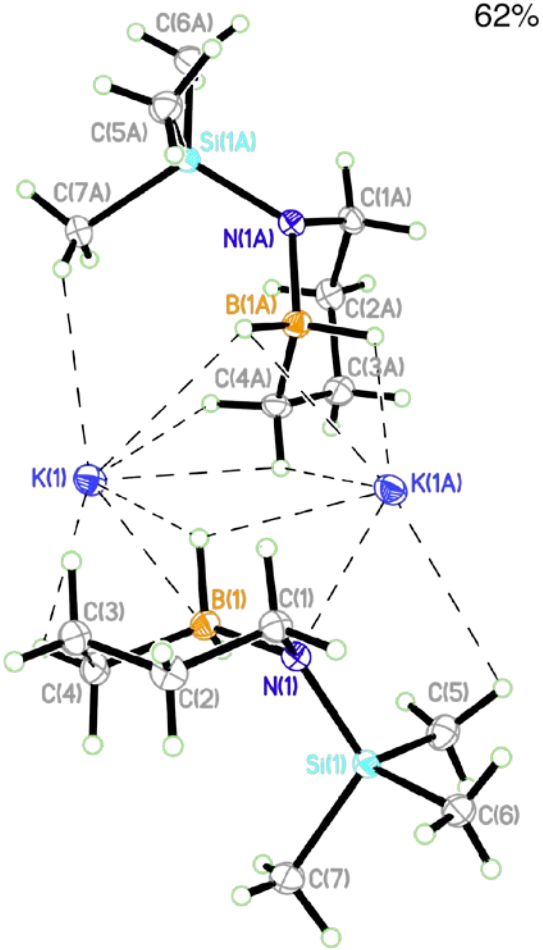


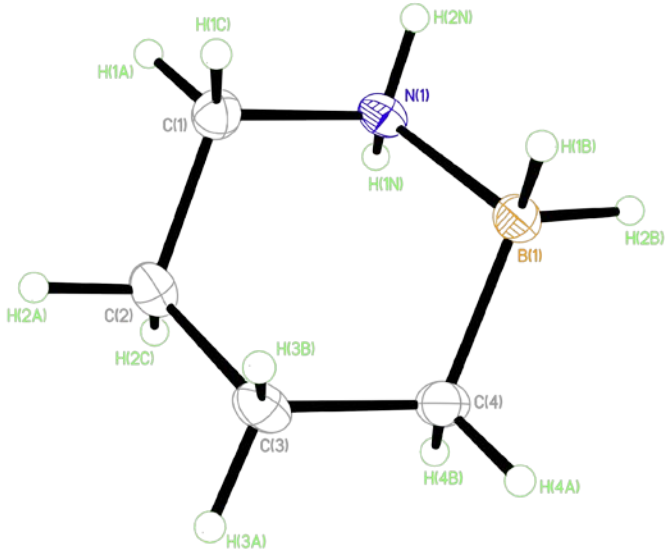
Toward the parent material

Wei Luo

Parent Material was successfully prepared – New Progress

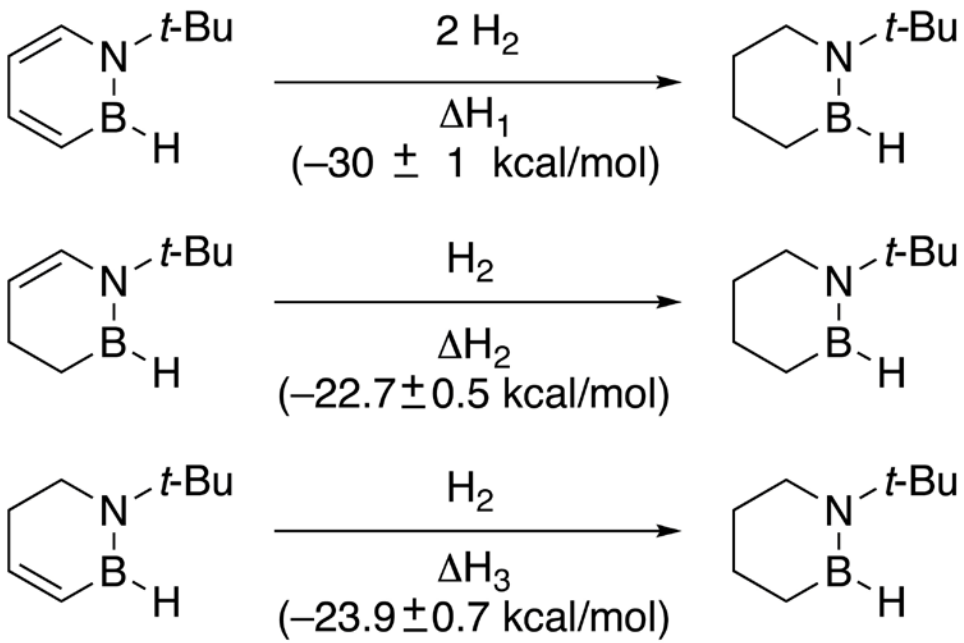




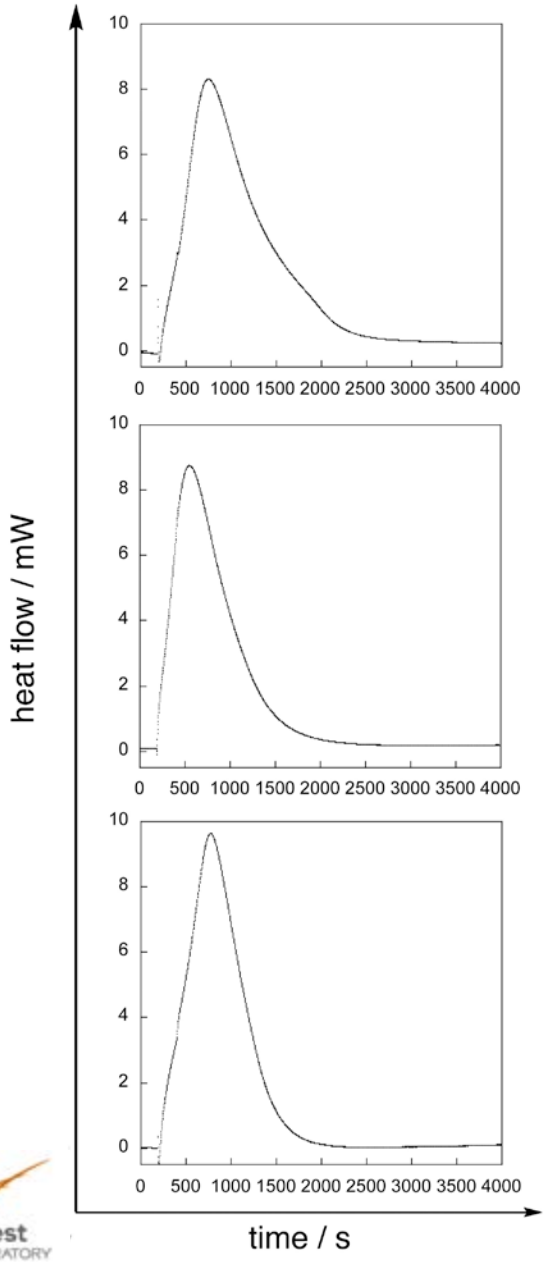


Wei Luo

Experimental Thermodynamic Analysis – New Progress



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



Discovery of suitable catalytic "homogeneous" reaction conditions for calorimetry.

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

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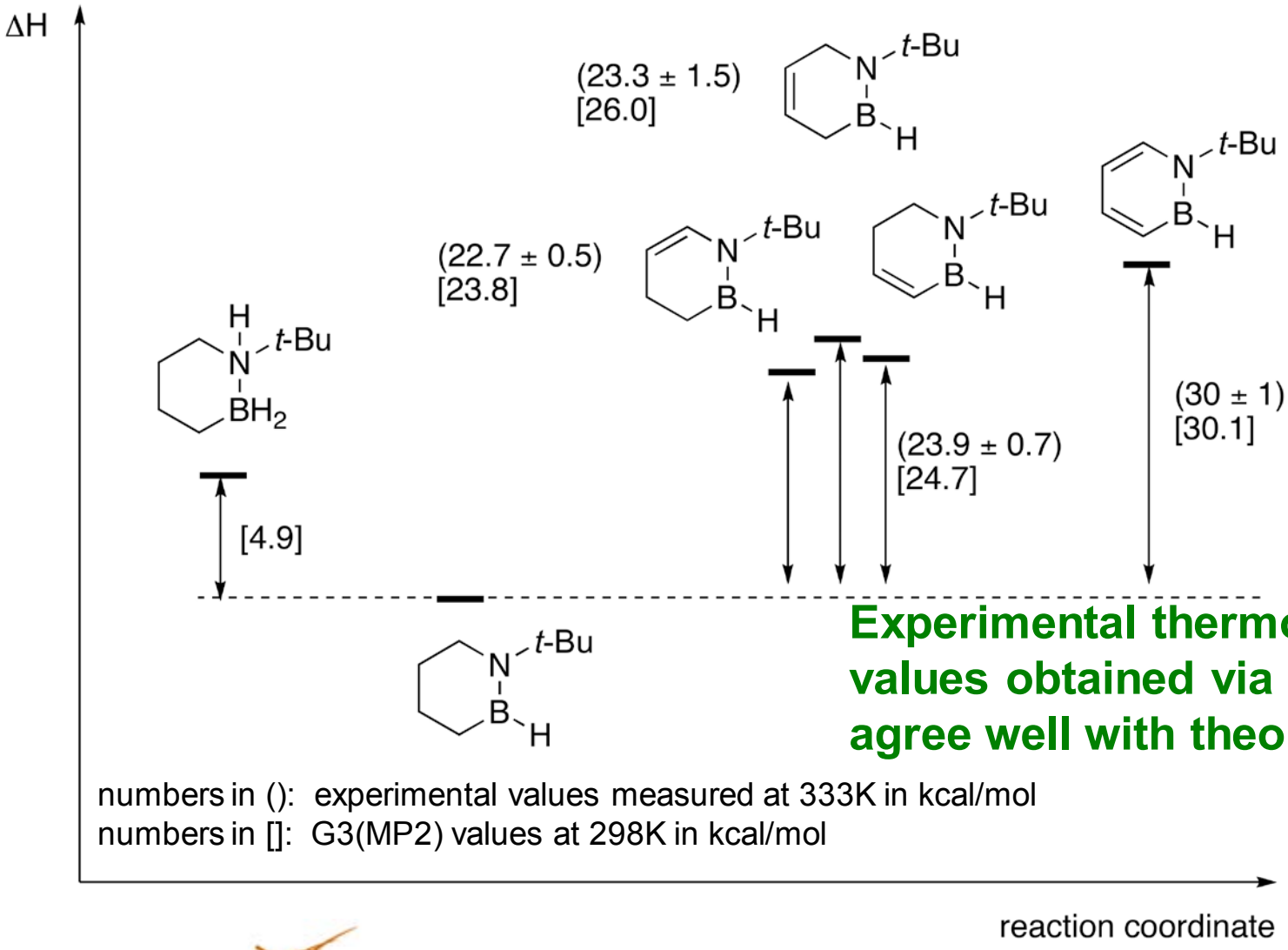
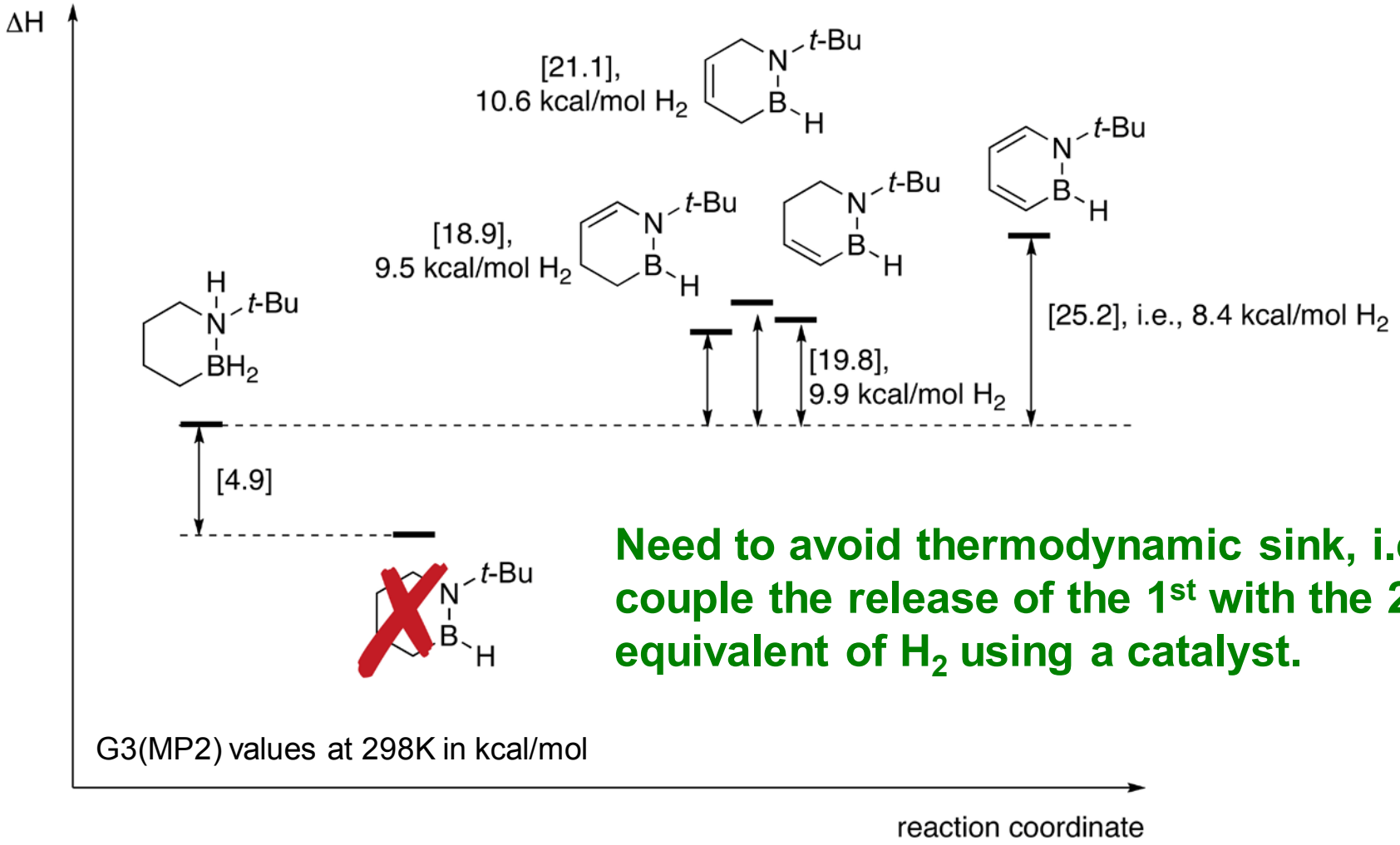
Enthalpy: Experiment and Theory – New Progress



Experimental thermodynamic values obtained via calorimetry agree well with theory.

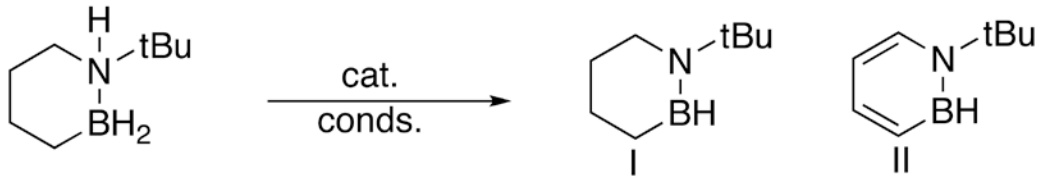
numbers in (): experimental values measured at 333K in kcal/mol
numbers in []: G3(MP2) values at 298K in kcal/mol

Enthalpy: Experiment and Theory New Progress



Need to avoid thermodynamic sink, i.e., couple the release of the 1st with the 2nd equivalent of H_2 using a catalyst.

Efforts Toward Coupled Release of H_2

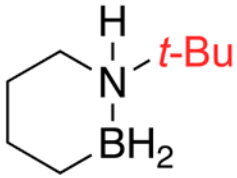


entry	catalyst	mol %	solvent	temp °C	% yield I	% yield II
1	$Pd[P(tBu)_3]_2$	10	THF	65	75, 24h	0
2	$[(cod)(PCy_3)PyIr]^+PF_6^-$	10	THF	65	90, 24h	0
3	$Cl_2(PPh_3)_3Ru$	10	THF	65	>95, 3h	0
4	$Cl(PPh_3)_3Rh$	10	THF	65	>95, 3h	0
5	$[Cl_2Cp^*Ir]_2$	10	THF	65	>95, 24h	0
6	$Pd(OAc)_2$	10	THF	65	50, 3h	0
7	$PtCl_2(PPh_3)_2$	10	THF	65	50, 19h	0
8	$[(cod)(PCy_3)PyIr]^+PF_6^-$	20	C_6D_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

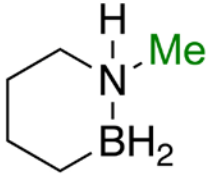
Catalysts/conditions screened thus far do not lead to coupled release of H_2. Will explore Ta and Nb catalysts, Rothwell et al. *JACS* 1997.

Formulation of Materials as Liquids New Progress

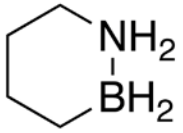
Potential capacities, assuming 3 equivalent H_2 release:



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



neat material	THF solution	Et_2O solution
mp: 72-73 °C	sol. (g/L): 292 ± 5	sol. (g/L): 106 ± 18
d (kg/L): 0.87 ± 0.08	d (kg/L): "0.89"	d (kg/L): "0.71"
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

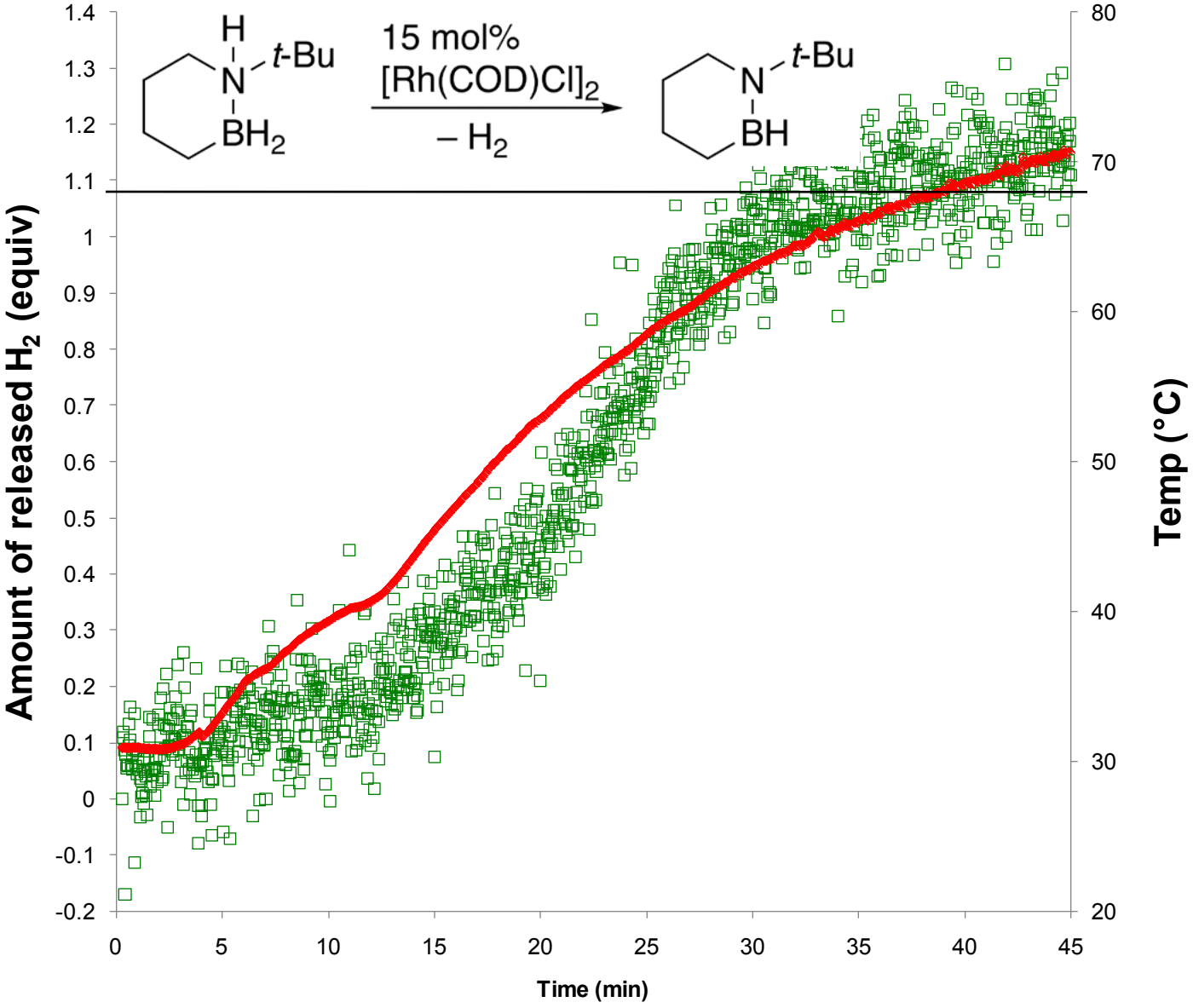


neat material	THF solution	Et_2O solution
mp: 62-63 °C	sol. (g/L): 434 ± 20	sol. (g/L): 347 ± 30
d (kg/L): 1.00 ± 0.05	d (kg/L): "0.89"	d (kg/L): "0.71"
vol. (g H_2/L): 70	vol. (g H_2/L): 30.7	vol. (g H_2/L): 25
wt.(%): 7.1	wt.(%): 3.4	wt.(%): 3.1

DOE 2015 target: 5.5 wt%, 40 g H_2/L

Patrick Campbell, Wei Luo

H_2 Desorption – New Progress



N_H2 (equiv)

T_rxn

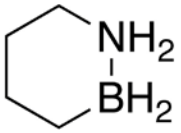
Conditions:
100 mg substrate
15 mol% catalyst
pentadecane as solvent (2 mL)

1 equiv. of H_2 is readily released

Patrick Campbell

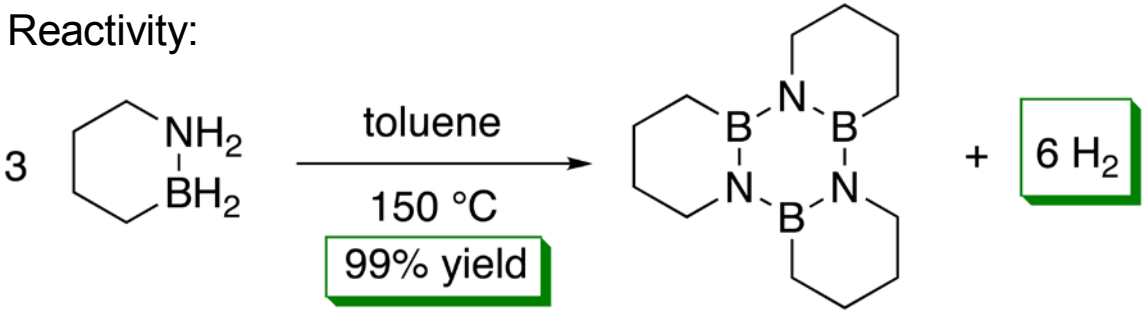
Properties and Reactivity of the Parent – New Progress

Stability:



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

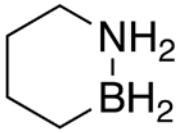
Reactivity:



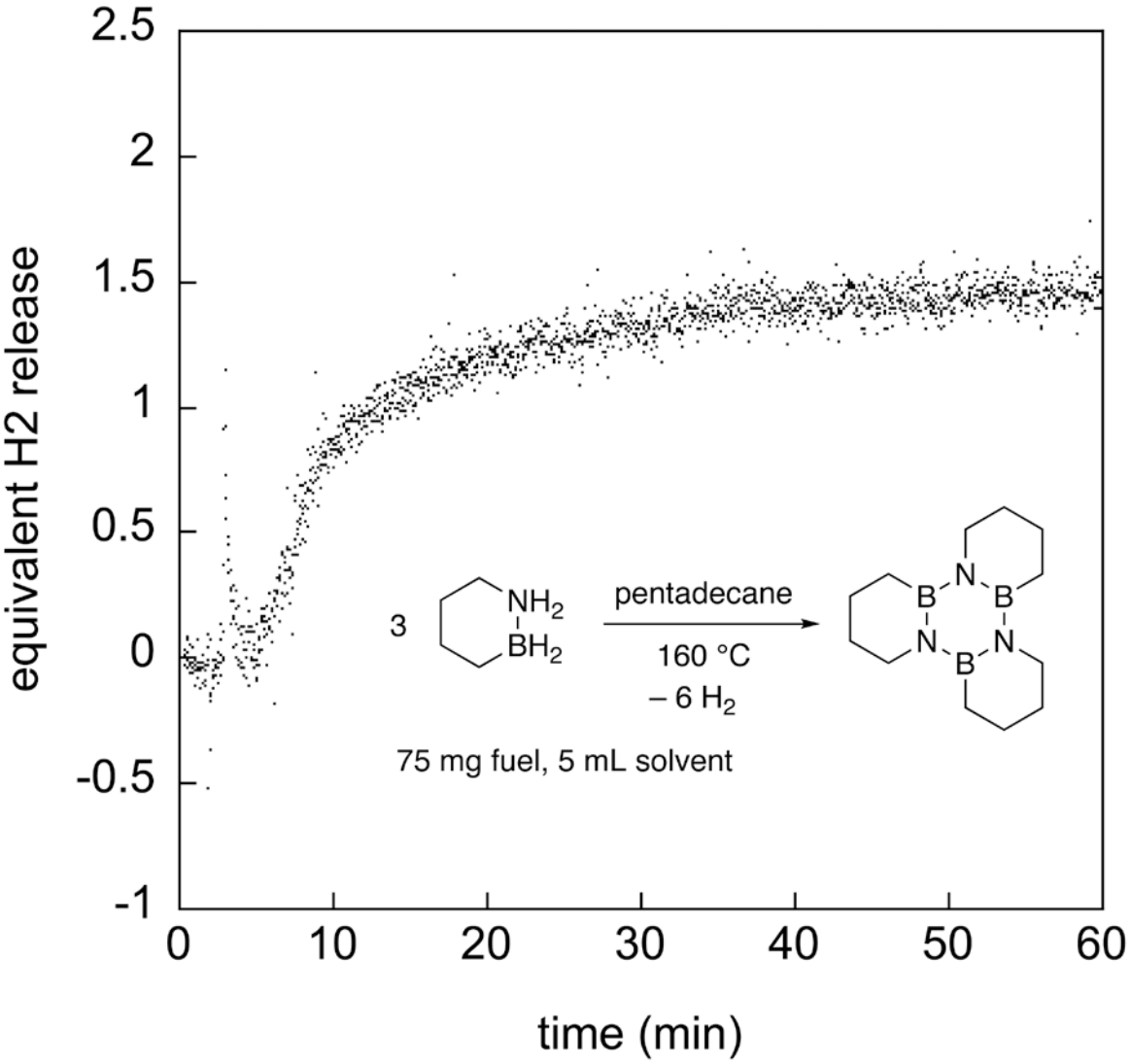
A viable ammonia borane alternative?

- **clean reaction**
- **well-defined**
- **"no NH_3"**
- **"no $B_3N_3H_6$"**
- **reasonable capacities**

assuming 2 equivalent H_2 release:

	neat material	THF solution	Et_2O solution
	mp: 62-63 °C d (kg/L): 1.00 ± 0.05 vol. (g H_2/L): 47 wt.(%): 4.7	sol. (g/L): 434 ± 20 d (kg/L): "0.89" vol. (g H_2/L): 20 wt.(%): 2.3	sol. (g/L): 347 ± 30 d (kg/L): "0.71" vol. (g H_2/L): 17 wt.(%): 2.1

H_2 Desorption 2 Equivalent Release from the Parent – New Progress



Preliminary studies indicate that up to 1.5 equiv. H_2 is released.

Collaborations

Project Collaborators

THE UNIVERSITY OF ALABAMA

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

Technology Transfer

THE UNIVERSITY OF ALABAMA

obtained computed thermodynamic data and H_2 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 H_2 desorption from these CBN materials for both the 3 equiv. and 2 equiv. release systems
- catalyst screening, development for coupled H_2 desorption from CBN materials
- determine/optimize charge/discharge characteristics
- develop more efficient regeneration of spent fuel (formic acid, PNNL M-H route)

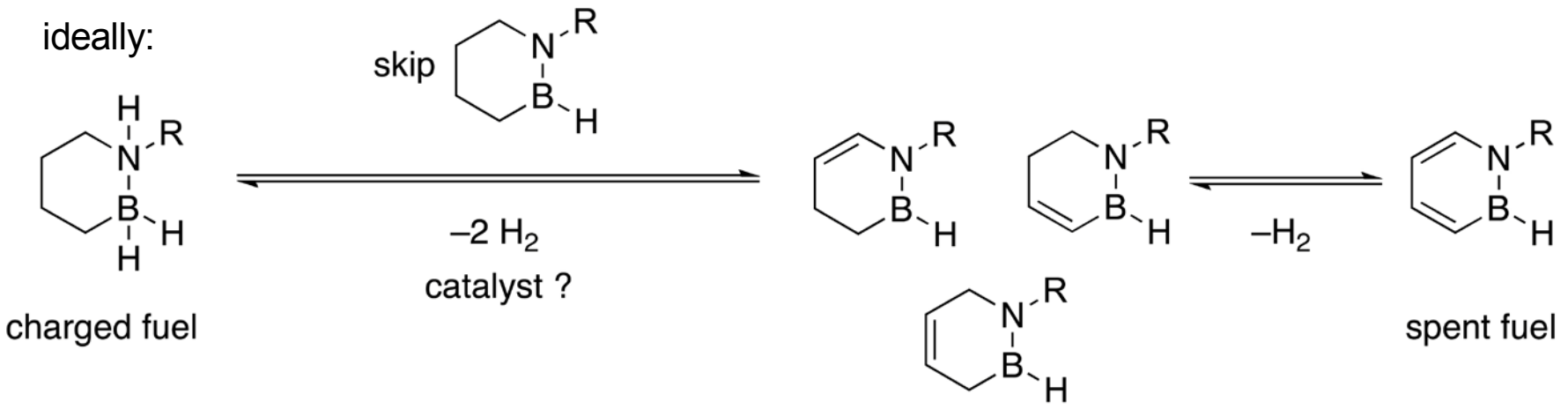
Project Summary

Relevance:	development of novel liquid phase hydrogen storage materials with desirable storage capacity and thermodynamics for reversible 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:	**• 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 H_2 for non-parent substrates** **• investigated the properties of the parent,** **• discovered clean and efficient release of 2 equiv. of H_2 from parent material**
Collaborations:	active partnership with UA and PNNL
Future Work:	• complete remaining experimental thermodynamic data point • determine/optimize H_2 charge/discharge characteristics • develop better conditions for regeneration

Technical Back-Up Slides

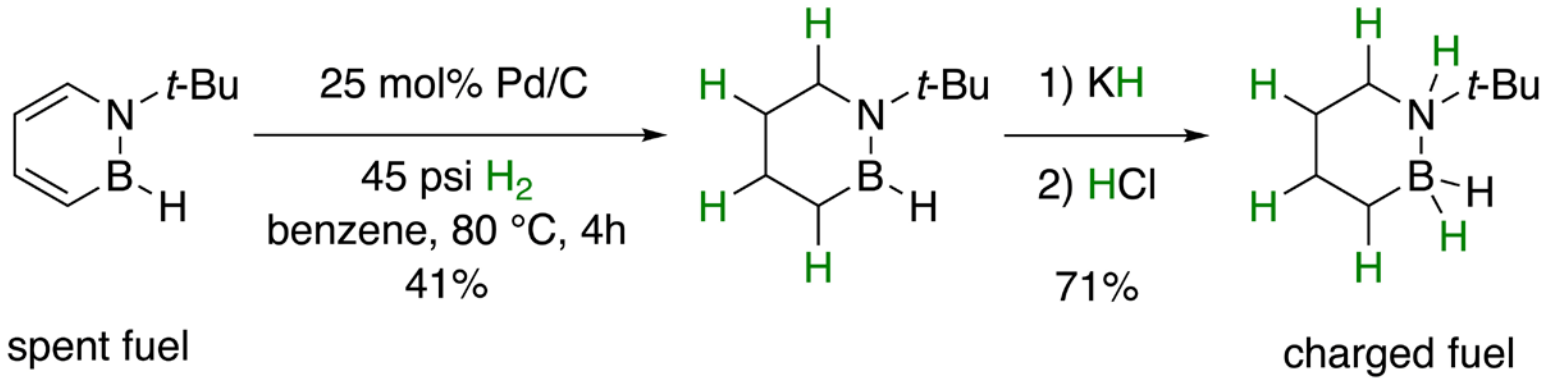
Technical Back-Up Slide: The Issue of Regeneration

ideally:



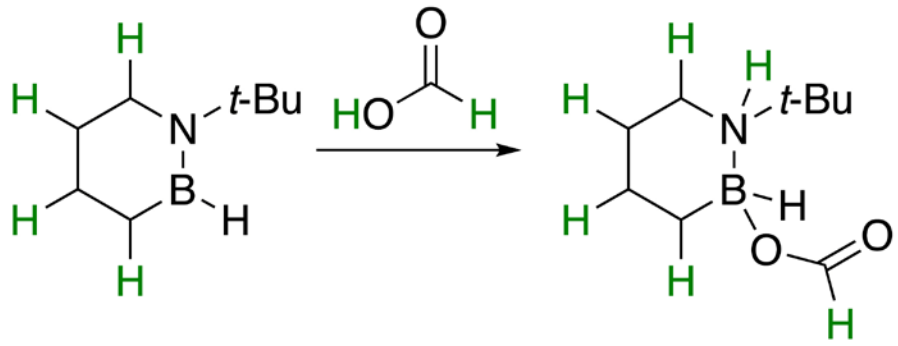
benefit: facilitates regeneration, potentially using molecular H_2
challenge: requires catalyst screening, discovery, development

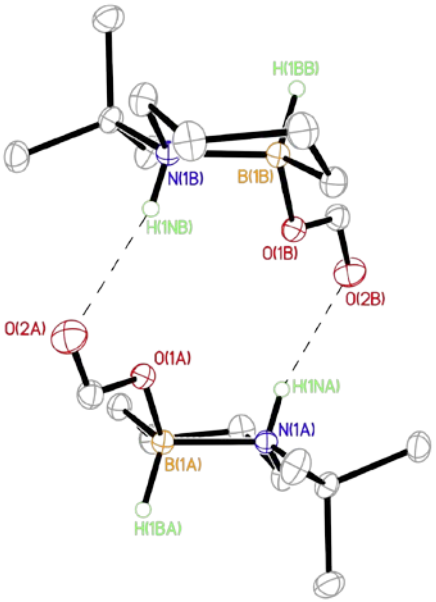
thus far accomplished:

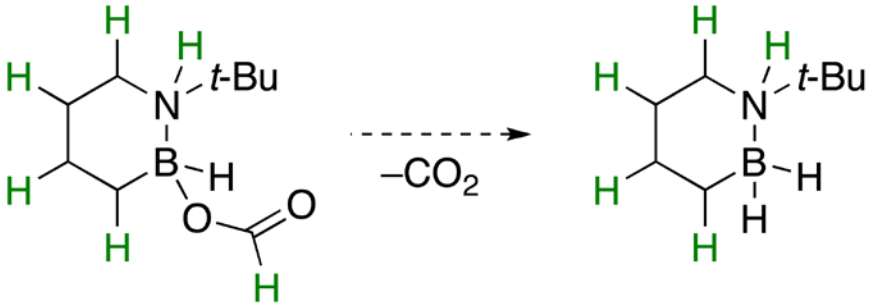


Technical Back-Up Slide: Regeneration

formic acid pathway:



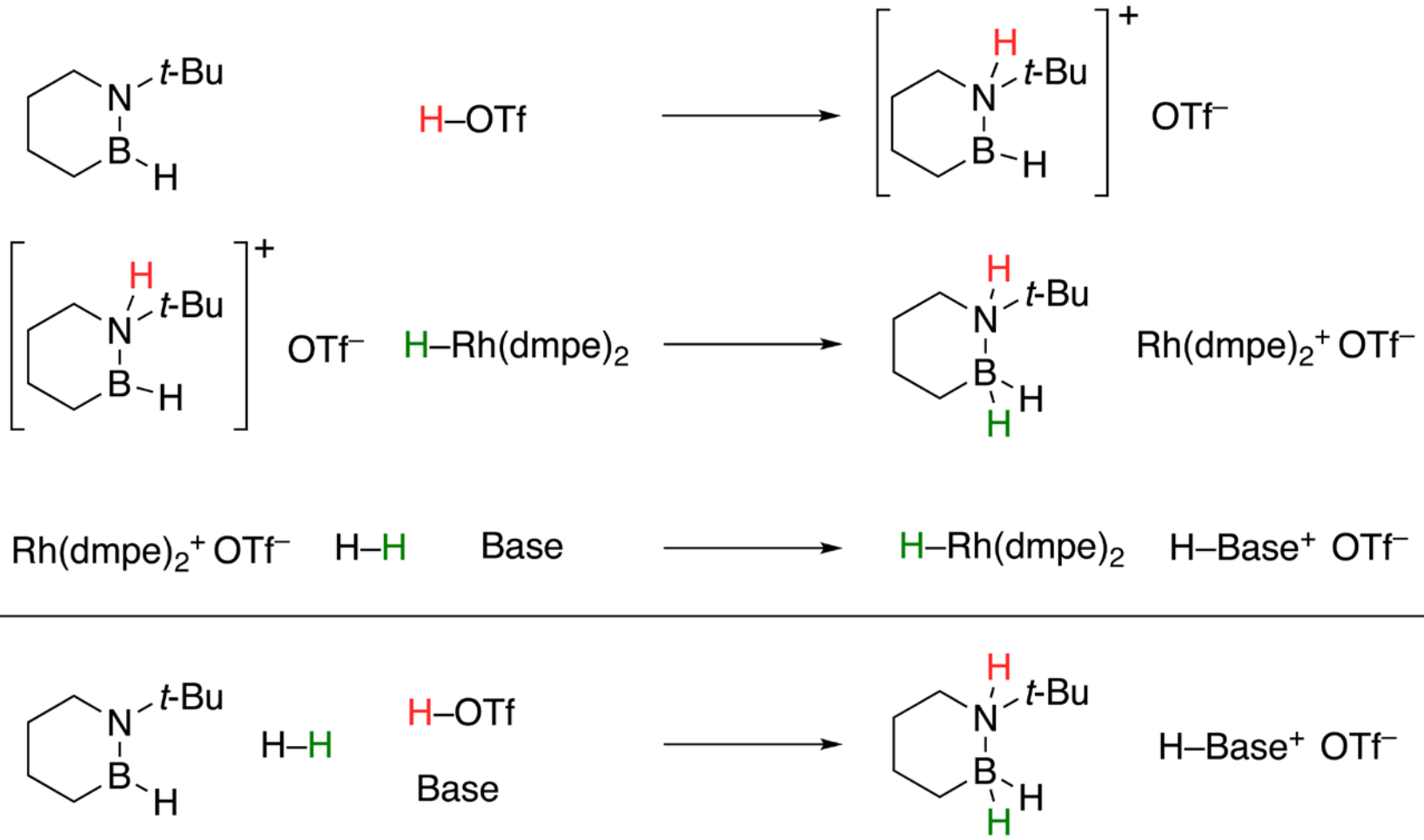




ΔG = 5.7 kcal/mol
ΔH = 16.1 kcal/mol
G3MP2 at 298 K

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