Project ID: ST104

DOE Hydrogen Program

Novel Carbon(C)-Boron(B)-Nitrogen(N)-Containing H_2 Storage Materials

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Department of Chemistry, Boston College
DOE Annual Merit Review and Peer Evaluations
Washington DC
June 10, 2015

Synthesis
Catalysis

Pacific Northwest NATIONAL LABORATORY
Characterization
COMSOL Modeling

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Theory

Protonex
Fuel Cell Operation

This presentation does not contain any confidential or otherwise restricted information

Overview

Timeline

Project start date: March 5, 2012
Relocation UO to BC:
June 2013 to September 2013
Project end date: August 14, 2015

Technical Barriers (Vehicular)

A. system weight and volume
C. efficiency
D. durability/operability
E. charging/discharging rates
J. thermal management
R. regeneration processes
S. by-product/spent material removal

Budget

Total funding spent (not including FFRDC funds)
: $1,437,558
Total DOE Project Value: $2,526,606
DOE share: $2,020,942 (includes
$862,000 in FFRDC funds)
cost share percentage: $505,321 (20%)

Project Team

Shih-Yuan Liu
Frank Tsung

Pacific Northwest NATIONAL LABORATORY

Tom Autrey
Abhi Karkamkar
Mark Bowden
Sean Whittemore
Adrian Houghton
Kriston Brooks

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David Dixon

Protonex

Paul Osenar
Jim Sisco

Outline

- Overview of proposed molecules
- Progress since the 2014 Annual Merit Review
  - Investigate endothermic desorption
  - Investigate coupled exo/endo desorption
  - Modeling (COMSOL) exo/endo desorption
- Summary of Overall Project Accomplishments
- Future Directions

Project Objectives

Develop novel chemical H_2 storage materials that have the potential to enable non-automotive applications and meet the 2020 DOE targets for vehicular applications with focus on three classes of materials:

1) liquid phase

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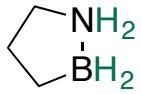
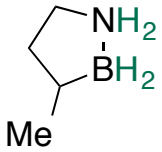


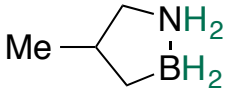
Mw = 71

B



Mw = 85

C



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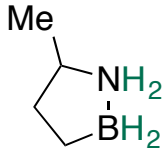
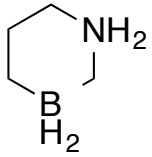


Mw = 85

2) potentially reversible

E



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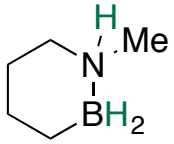

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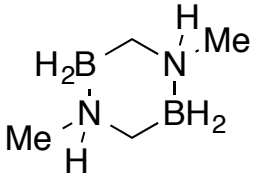
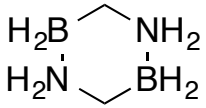


Mw = 114

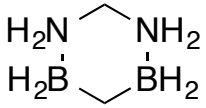
3) high capacity

H



Mw = 86

I



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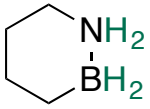
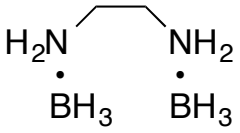


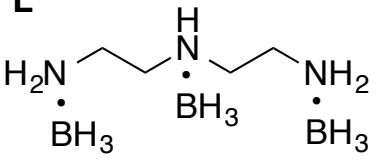
Mw = 85

K



Mw = 88

L



Mw = 145

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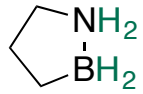

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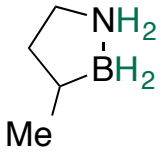

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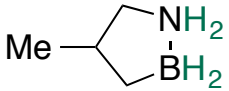

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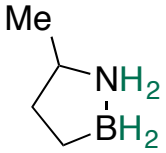

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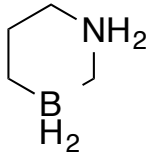

Mw = 85

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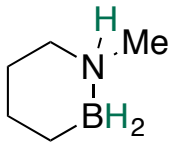

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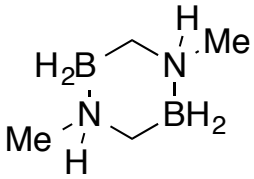

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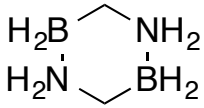

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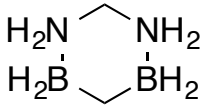

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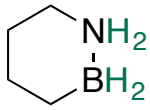

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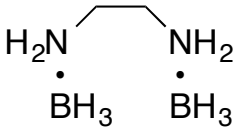

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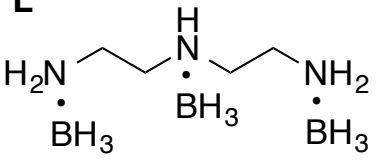

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Towards Vehicular Targets

From reverse engineering analysis (SSAWG 9/10/2014, Semelsberger)

Capacity: solutions: 9.8 – 10.6 wt%; slurries: 11.2 – 12.1 wt%
Density: > 70 g / L
Heat (exothermic): < l–6.4l kcal/mol
Heat (endothermic): < 4.0 kcal/mol
Ea (thermal activation): > 28 kcal/mol;
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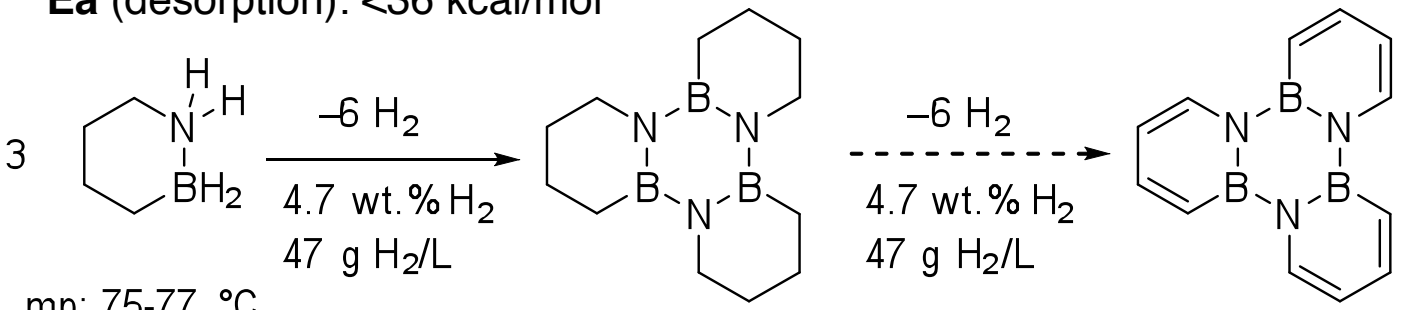

mp: 75-77 °C
d: 1.00 kg/L

Overall (–6 H_2)
ΔH(gas) = –83.1
ΔH(liquid) = –59.6
ΔG(gas) = –107.3

Per mol H_2:
ΔG(gas) = –17.8
ΔH(liquid) = –10.0
ΔG(THF) = –13.6

Overall (–6 H_2)
ΔH(gas) = +102.3
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ΔG(gas) = +49.4

overall potential:
9.4 wt.%; 94 g H_2/L,
potential **liquid phase** starting material at operating T

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Energies in kcal/mol @ 298K
Gas Phase: G3MP2
Liquid Phase: G3MP2 (gas) + BP*0.025 (Trouton's rule)

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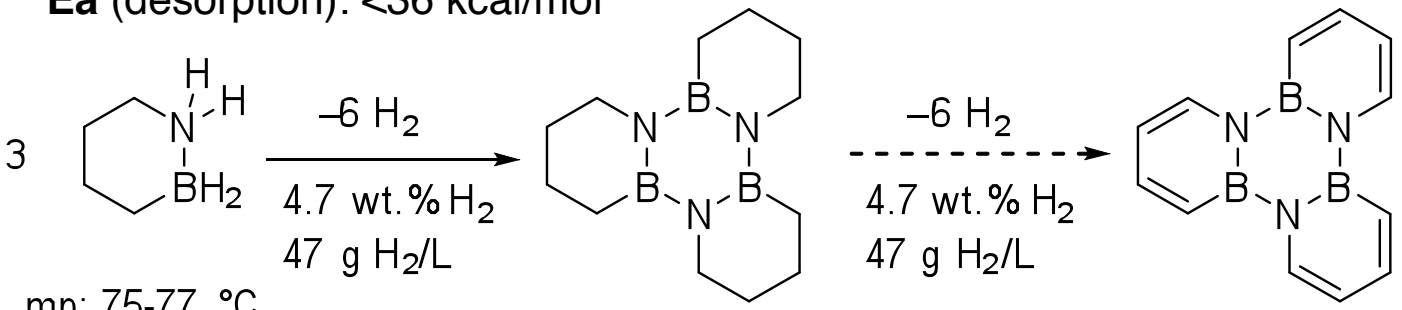
Need to develop H2 desorption from CC!



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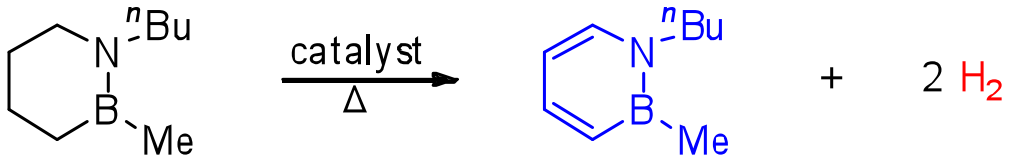
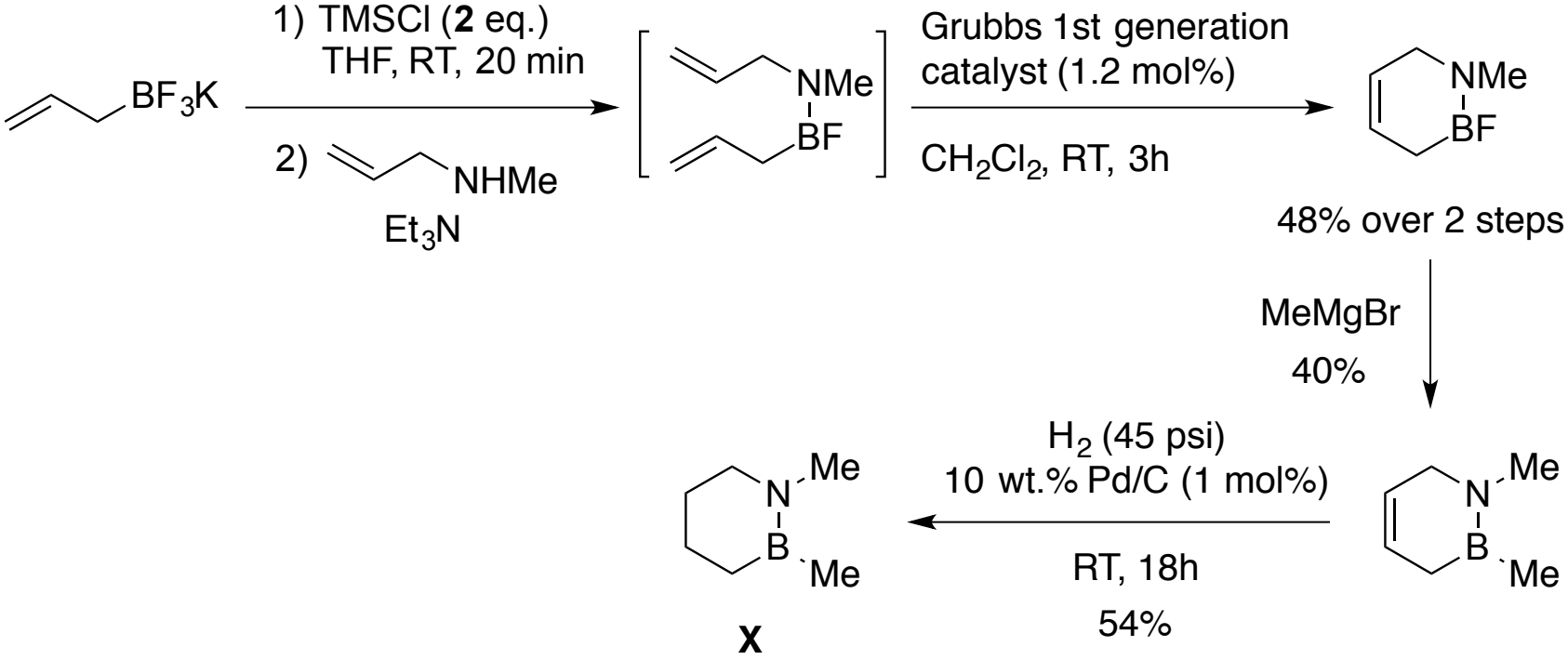
CC Dehydrogenation Catalyst Screen



Catalyst	Hydrogen Evolution	
	BN heterocycle	Cyclohexane
Pt/Al_2O_3 (0.5 wt%)	**No**	**Yes**
Pt/C (10 wt%)	**No**	**Yes**
Pd/Al_2O_3 (5 wt%)	**No**	**Yes**
Pd/C (10 wt%)	**Yes**	**Yes**
Pd/SiO_2 (5 wt%)	**No**	**Yes**

Synthesis of Compound X: A Model Compound for Endothermic Desorption



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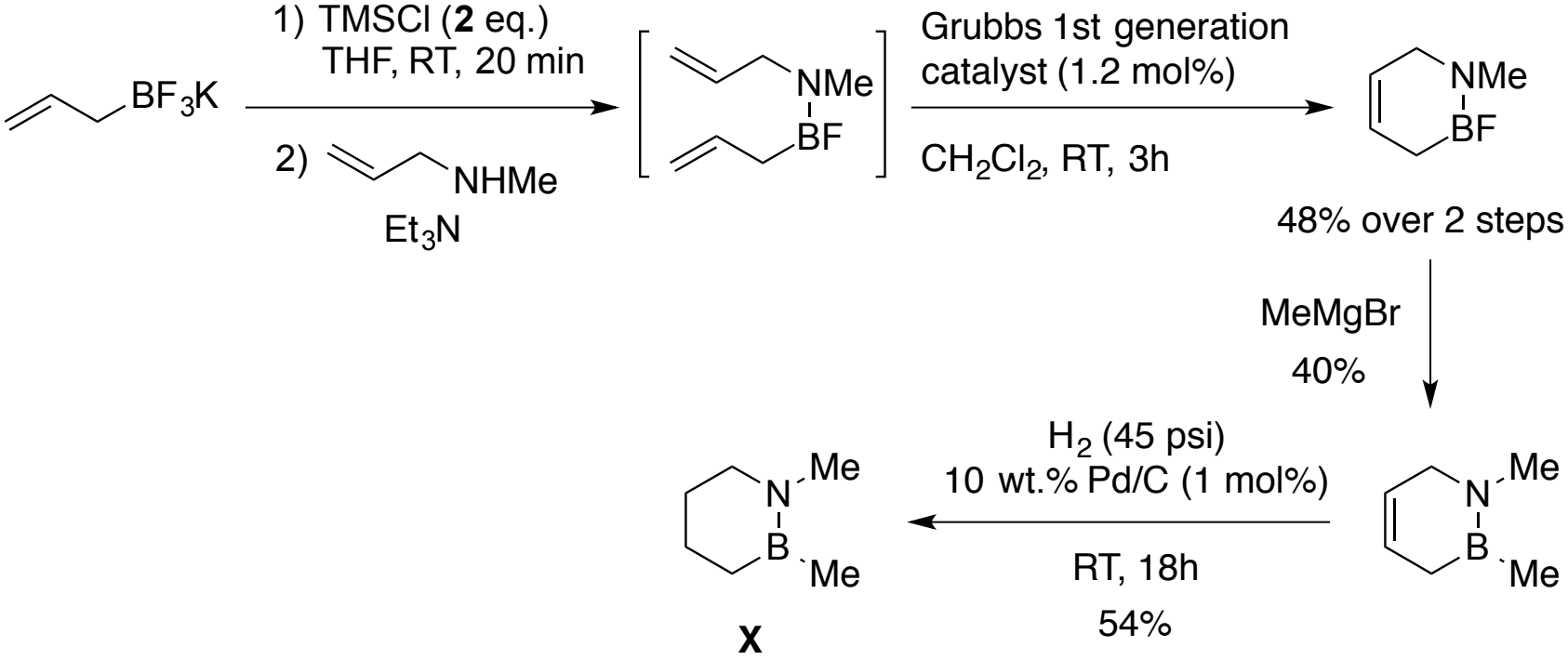

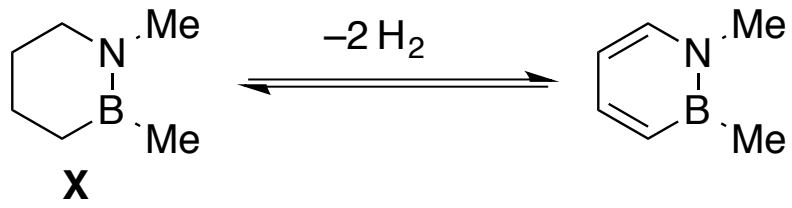

capacity	bp, mp (charged fuel)	bp,mp (spent fuel)	ΔH (kcal/mol)
3.6 %	bp: ~170 °C mp: < –35 °C	(bp: ~170 °C mp: < 0 °C)	**(30)** **[31]**

(): experimental values for the N-tBu derivative (at 333K, solution phase)
[]: predicted value at G3(MP2) level (298K, gas phase)

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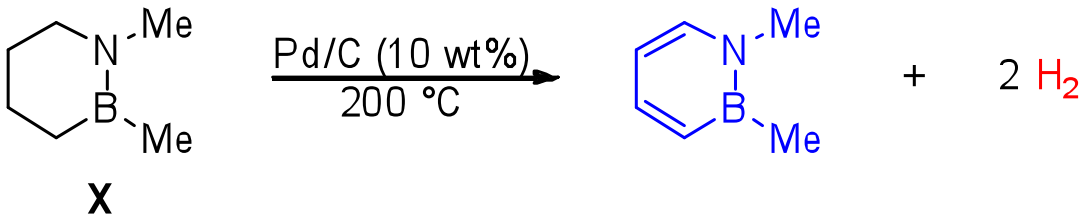
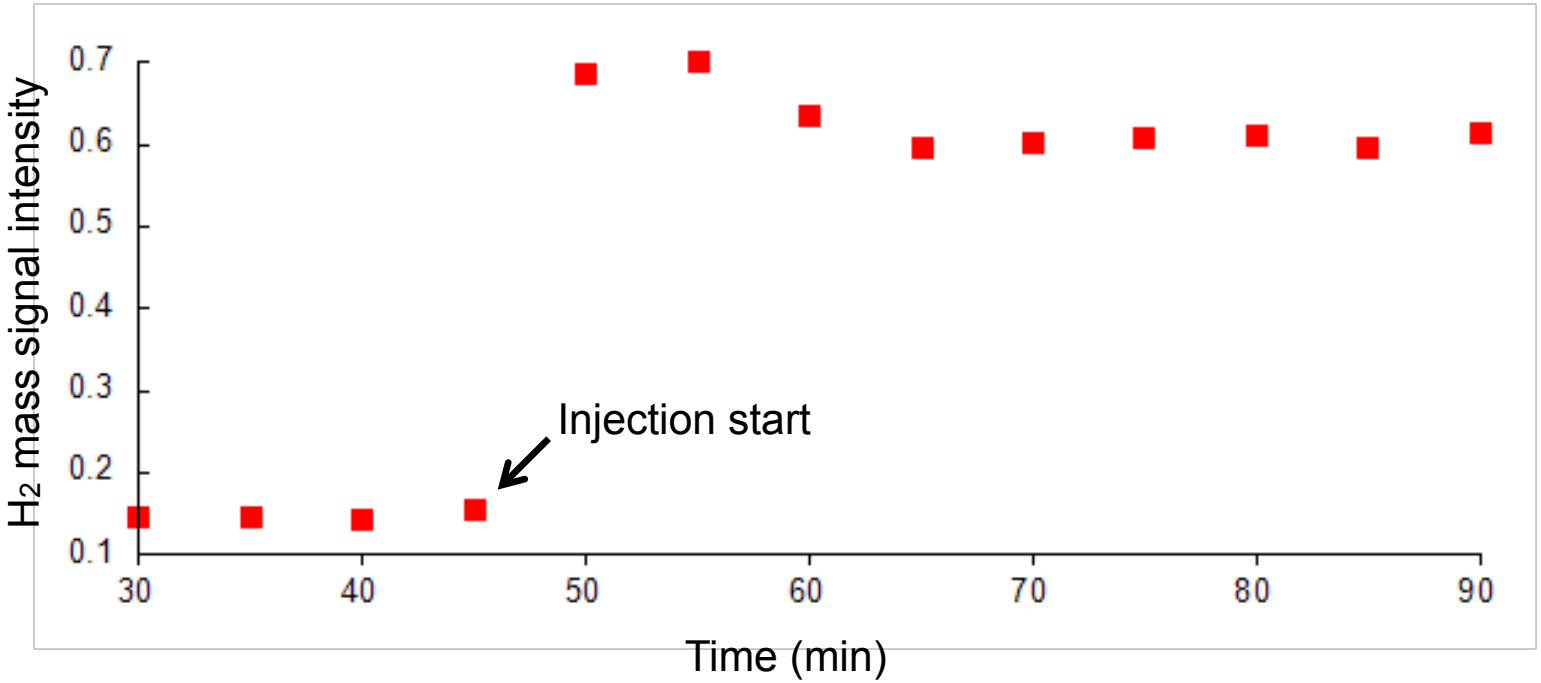
Continuous CC Dehydrogenation from Compound X

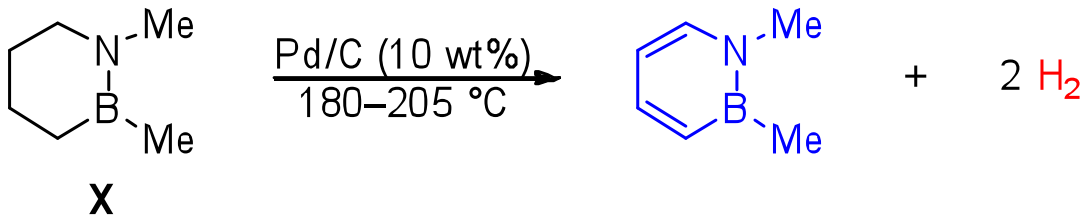


X

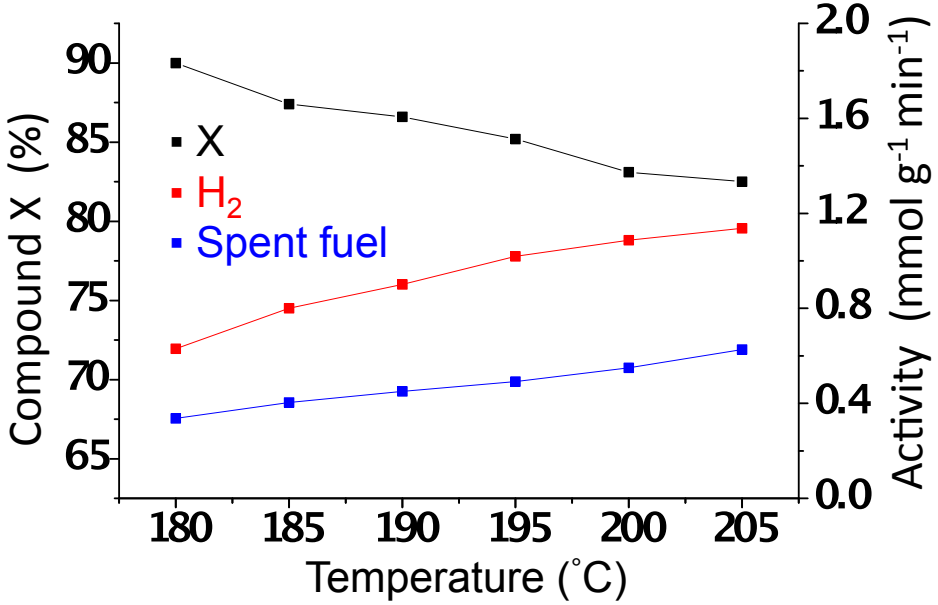


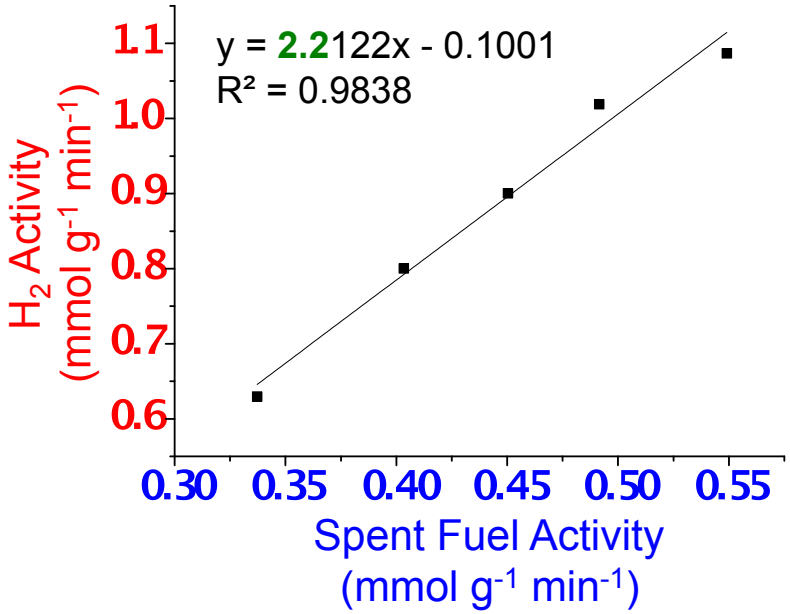
Catalyst loading optimization allows for continuous dehydrogenation

CC Dehydrogenation Temperature Screen



X





Catalytic activity observed at temperatures ~ 180 °C.
H_2:product ratio approximately 2:1 at all screened temperatures.

Dehydrogenation Activation Parameters

Substrate	E_a (kcal mol^{-1})	$\log_{10}$ A	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})
Compound X	+19.2±0.7	6.0±0.2	+18.3±0.7	–34±1
cyclohexene[a]	+10.2±0.4	4.7±0.2	+9.4±0.4	–40±1
cyclohexane[a]	+9.5±0.8	1.5±0.5	+8.6±0.8	–55±2

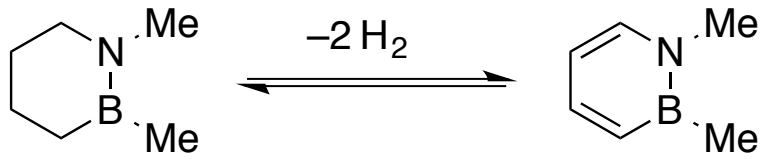
[a] Values determined experimentally using same reactor system as compound **X**

E_a and $\Delta H^{\ddagger}$ for compound X dehydrogenation are higher than either cyclohexene or cyclohexane.

Entropic parameters are similar to those of cyclohexene.

These activation parameters have been used for the modeling studies performed by the PNNL team.

Kinetic Coupling of Exothermic and Endothermic Reaction



X

3.6 wt%
29.9 g H_2/L

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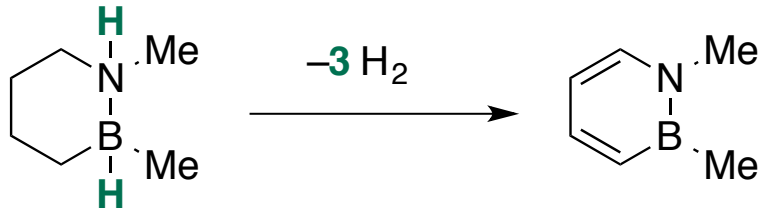
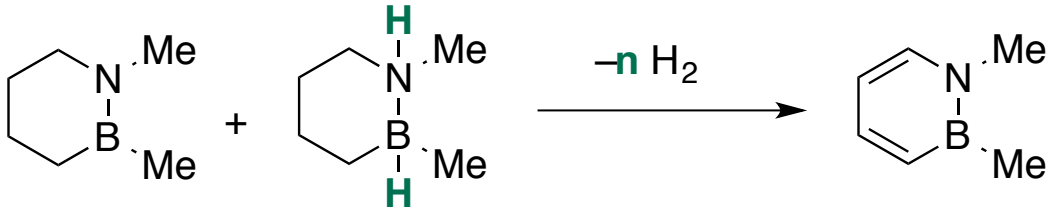


XH2

5.4 wt%
solid material at
room temperature

ΔH = +24.6 kcal/mol;
+8.2 kcal/mol H_2
ΔG = –2.2 kcal/mol



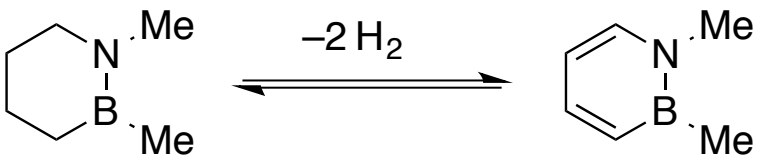
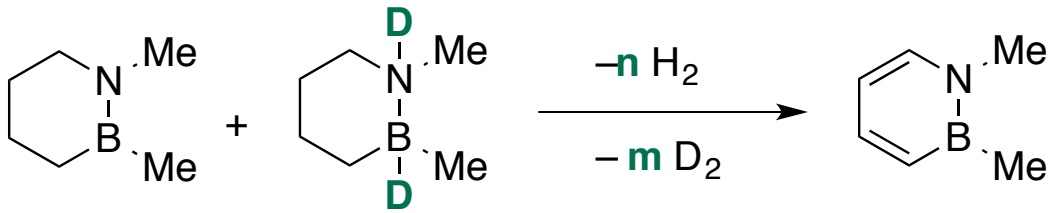
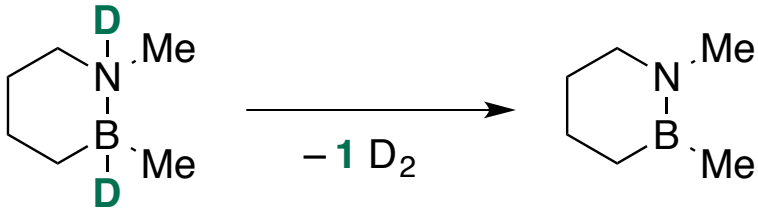
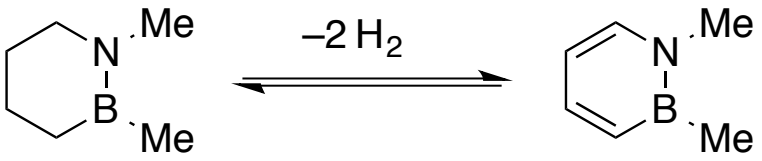
X **XH2**

1.0 : 2.5

4.9 wt%
liquid phase at
room temperature
41.2 g H_2/L

XH2 is a solid at room temperature (RT). On the other hand, the mixture of XH2 and X is a liquid phase material at RT and thus amenable to kinetic studies. Further more, the XH2+X mixture features higher storage capacities.

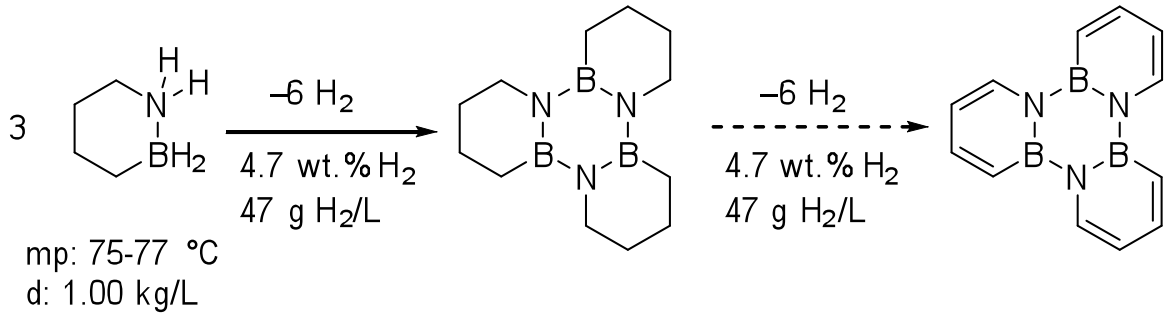
Preliminary Kinetic Studies

	Ea (kcal/mol)	$\log_{10}(A)$
 **X**	**19.2±0.7**	6.0±0.2
 **X** + **XD2**		
1.0 : 2.5		
 **XD2**	7.3	0.1
 **X**	**15.6**	4.8

The observed decrease in Ea for the exo/endo mixture is consistent with kinetic coupling.

Coupled Exothermic/Endothermic Reactions

- Rationale
  - Increase hydrogen capacity of CBN materials
    - Removal of H_2 from carbon backbone increases hydrogen capacity from 4.7 wt% to 9.4 wt%



  - Reduce energy required during endothermic dehydrogenation
    - RH_2**B-N**H_2R' → RH**B=N**HR' + H_2 Exothermic
    - RH_2**C-C**H_2R' → RH**C=C**HR' + H_2 Endothermic
  - Reduce maximum temperature associated with exotherm

Thermodynamic coupling can be beneficial to hydrogen capacity, on-board efficiency, and reactor design

Constraints for Effective Thermodynamic Coupling

- Parity between exothermic and endothermic reaction enthalpies
- Parity between exothermic and endothermic reaction rates
- Acceptable thermodynamic limitations on reaction equilibrium

  $\Delta G = -RT \ln(K_{eq}) = \Delta H - T\Delta S$

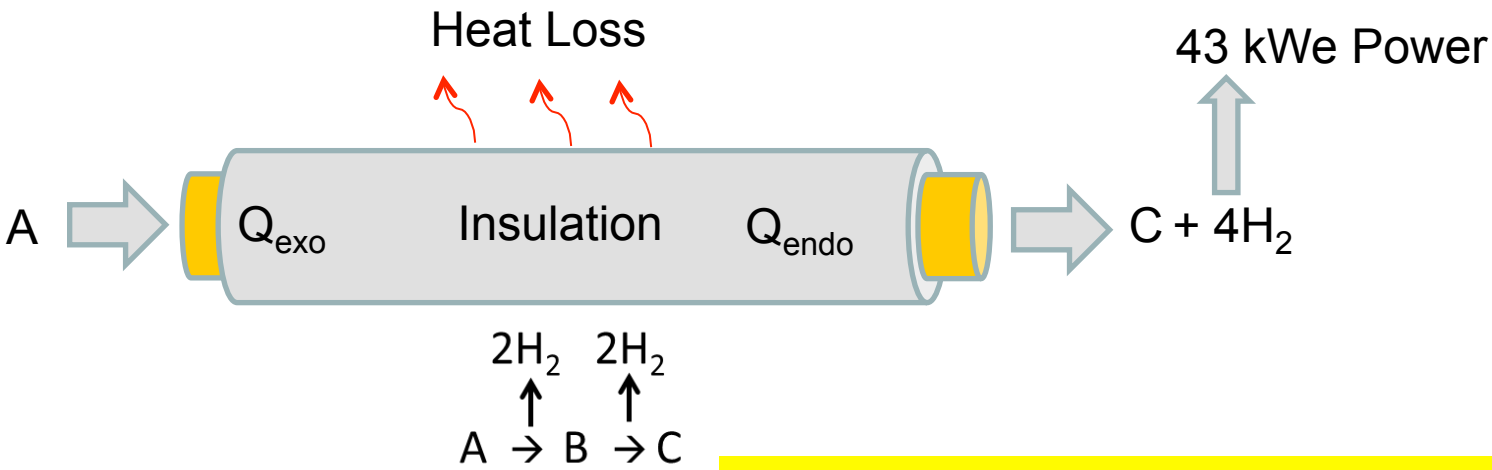
  Constraint on endothermic reaction only (< 50 kJ/mol)
- Reasonable energy requirements for regeneration

  Primarily a constraint on the exothermic reaction

To Be Effective Thermodynamic Coupling Requires Appropriate Thermodynamics and Kinetics

Approach to Modeling

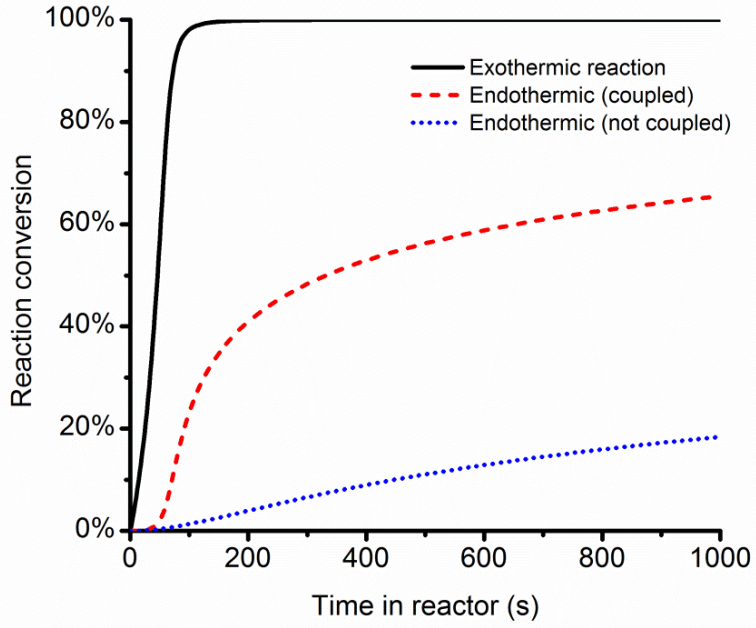
- Automotive Application
  - HSECoE assumes 43 kWe is required for 80 kWe auto
    - Ballast tank compensates for large transients
  - COMSOL Model Includes:
    - Reaction Enthalpy, Reaction Rate, Thermodynamic Equilibrium
    - Plug Flow Reactor with Axial/Radial Conduction
    - Heat Losses to Environment
  - Does not include H_2 production increasing velocity



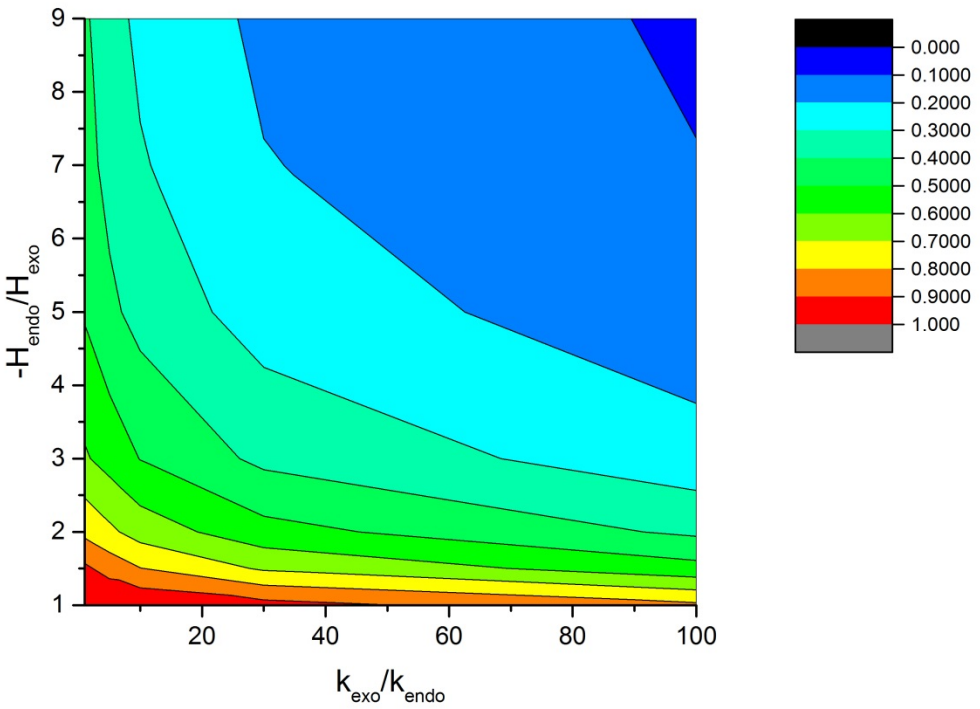
Model includes real reactor properties (e.g. heat and mass transfer) permitting first semi-quantitative evaluation of thermodynamic coupling

Modeling Results—Generic Reaction Parameters

Typical Results



Endothermic Reaction Conversion



Coupled reactions significantly improve endothermic reaction conversion

Reaction enthalpy ratio has larger impact on conversion than kinetic ratio

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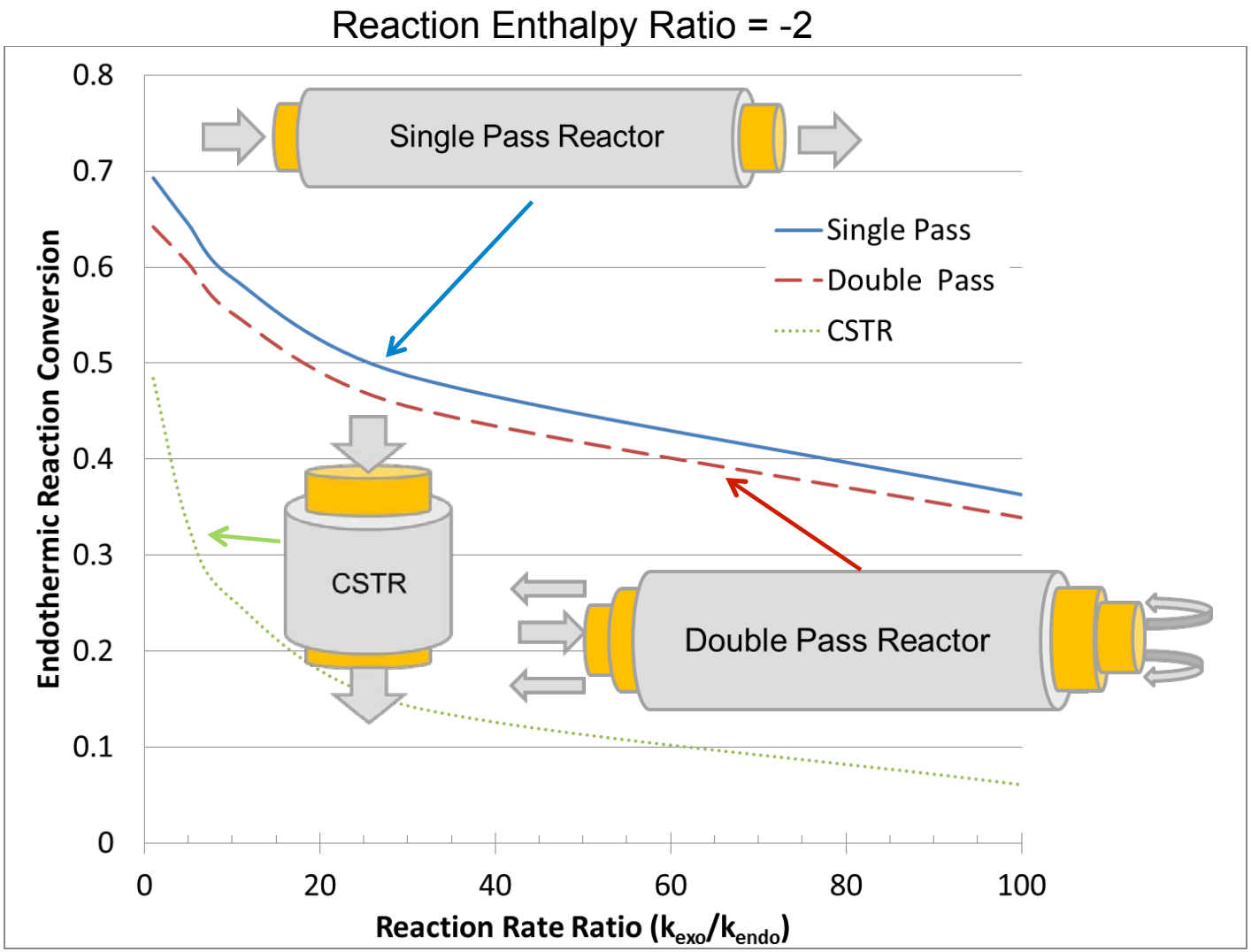
Impact of Reactor Configuration



Simple Single Pass Reactor Provides Highest Conversion

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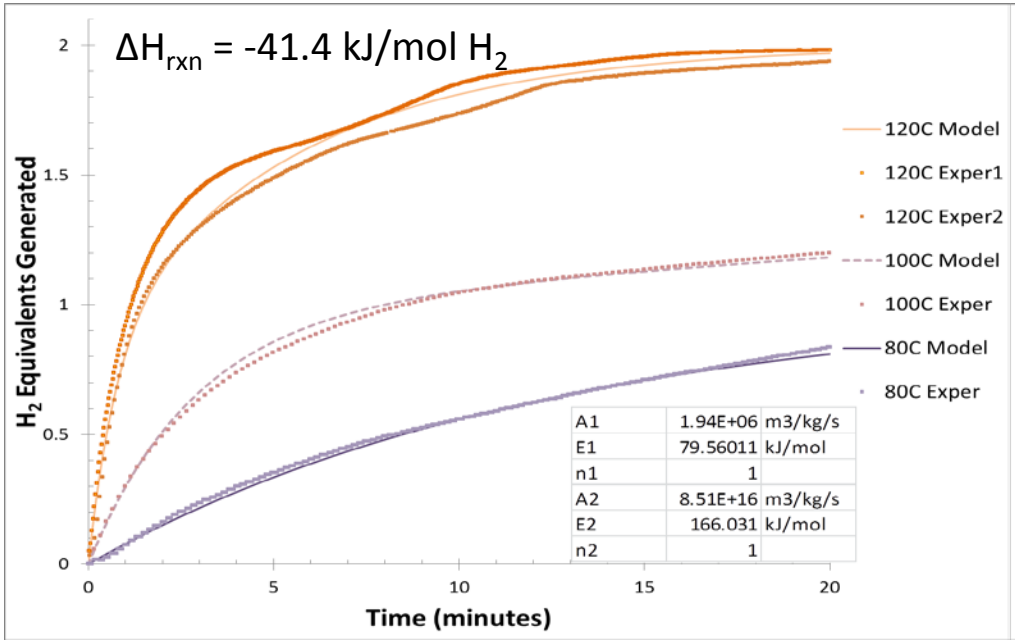
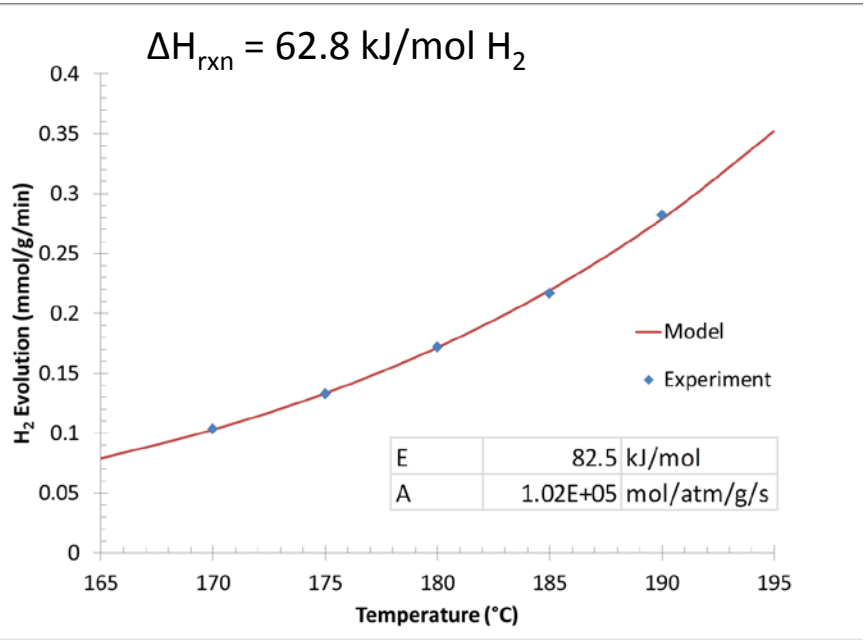
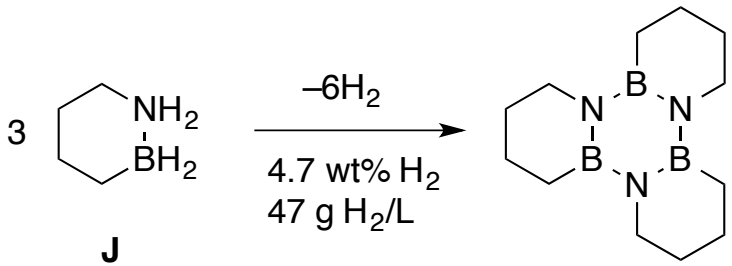
Reaction Parameters Based on Actual CBN Material Experiments

Exothermic Reaction



Endothermic Reaction





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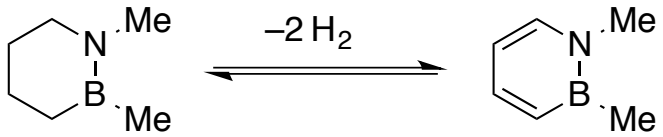

X

Thermodynamic Coupling Performed with Properties of Actual CBN Materials

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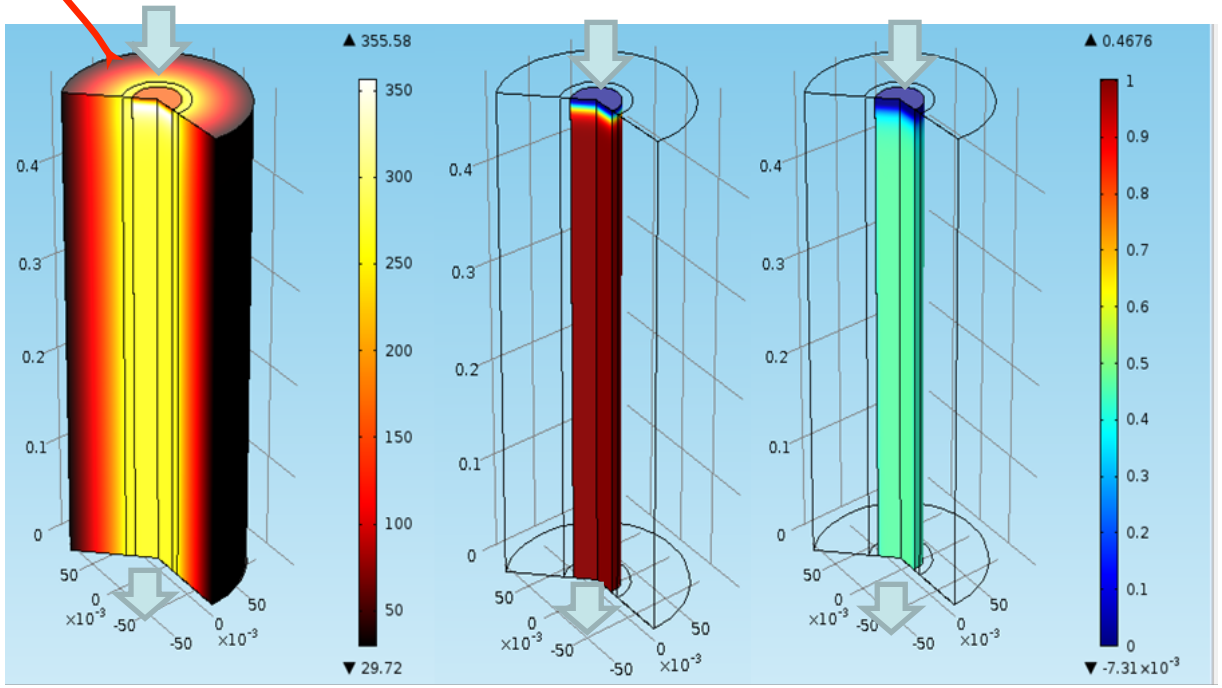
Modeling Results of Thermodynamically Coupled Reactions

Test Case	Active Reactions	Exothermic Conversion	Endothermic Conversion	Maximum Reactor Temperature
1	Exothermic and Endothermic	100%	46%	356°C
2	Exothermic Only	100%	N/A	508°C
3	Endothermic Only	N/A	3.2%	160°C



Temperature (°C) Exothermic & Endothermic Conversion

- **Large reduction in endothermic conversion without exothermic reaction**
- **High maximum temperature without endothermic reaction**

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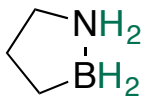
Summary

1) liquid phase

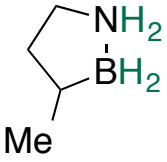
A



5.6 wt% H_2
52 g H_2/L
d: 0.92 g/mL
mp: 36-37 °C

Mw = 71

B



4.7 wt% H_2
42 g H_2/L
d: 0.89 g/mL
viscosity: 25 cP
mp: –16 to –18 °C
ΔH(exp) = –9.1 kcal / mol monomer

Mw = 85

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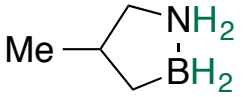
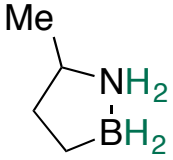


4.7 wt% H_2
42 g H_2/L
d: 0.89 g/mL
mp: 50 °C

Mw = 85

D

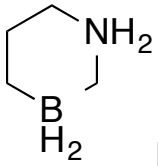


4.7 wt% H_2
mp: 25-27 °C

Mw = 85

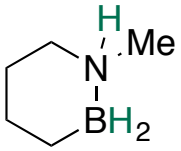
2) potentially reversible

E



Mw = 85

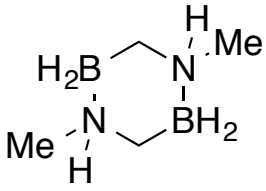
F



2.0 wt% (1 H_2)
17.4 g H_2/L
d: 0.87 g/mL
mp: 72-73 °C

Mw = 99

G

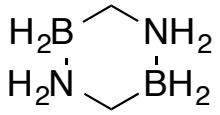


5.3 wt% (3 H_2)
mp: 65 °C
bp: 125 °C

Mw = 114

3) high capacity

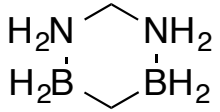
H



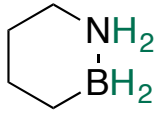
11.6 wt% (5 H_2)
mp: >150 °C
thermally stable

Mw = 86

I



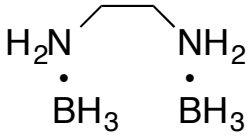
J



9.4 wt% (4 H_2)
94 g H_2/L
d: 1.00 g/mL
mp: 75 °C

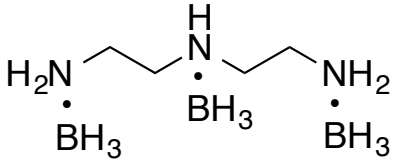
Mw = 85

K



~10 wt%
mp: 130 °C
decomp.
d: 0.82 g/mL
ΔH1(exp): –2.4
ΔH2(exp): –0.9

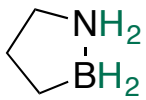
L



Summary: Materials not Made

1) liquid phase

A



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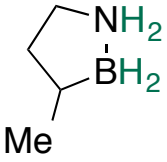
Mw = 71

B



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viscosity: 25 cP
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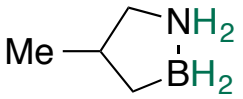
ΔH(exp) = –9.1 kcal / mol monomer

Mw = 85

C



4.7 wt% H_2
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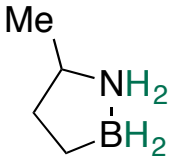
d: 0.89 g/mL
mp: 50 °C

Mw = 85

D

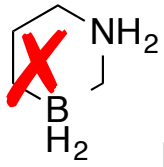


4.7 wt% H_2
mp: 25-27 °C

Mw = 85

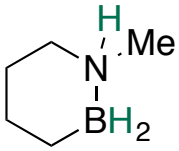
2) potentially reversible

E



Mw = 85

F



2.0 wt% (1 H_2)
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d: 0.87 g/mL
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Mw = 99

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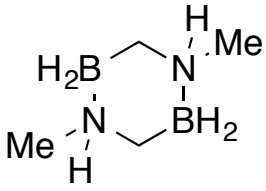


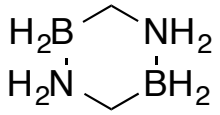
5.3 wt% (3 H_2)
mp: 65 °C
bp: 125 °C

Mw = 114

3 Compounds were not synthesized

3) high capacity

H

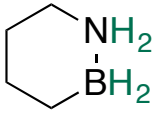


11.6 wt% (5 H_2)
mp: >150 °C
thermally stable

Mw = 86

I

J



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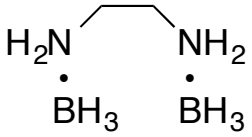

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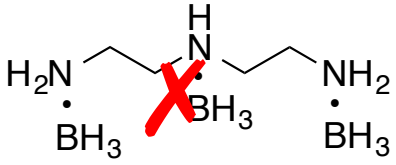
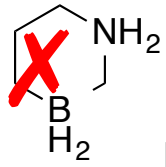


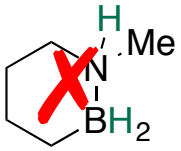
Summary: Potentially On-Board Reversible Materials

E



Mw = 85

F



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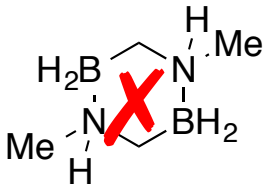


5.3 wt% (3 H_2)
mp: 65 °C
bp: 125 °C

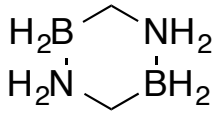
Mw = 114

Existence of thermodynamic sinks led to the down-selection of F and G.

Summary: High-Capacity Materials

- Compound **H** is a remarkably thermally stable material, yet it can be activated to release 4.7 wt% H_2 in the presence of a catalyst
- Investigation of **H** led to a better understanding of factors improving thermal stability, i.e., reduce the hydridic character of the B–H.
- Coupling of exothermic and endothermic reaction processes can lead to increased storage capacity and energy efficiency
- Compound **J** has the potential to meet the 2020 DOE system targets for vehicular applications

H



Mw = 86

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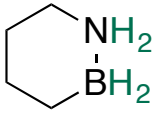

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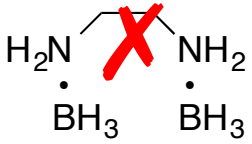

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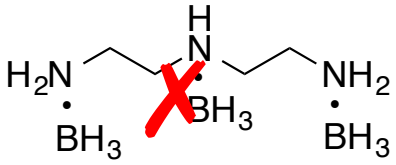
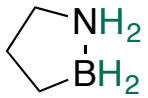


Summary: Liquid Phase Materials

A



Mw = 71

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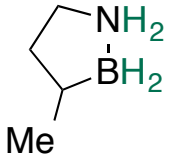
B



Mw = 85

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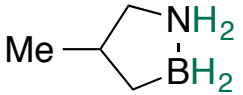
42 g H_2/L
d: 0.89 g/mL
viscosity: 25 cP
mp: –16 to –18 °C
ΔH(exp) = –9.1
kcal / mol monomer

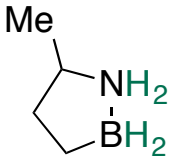
C



Mw = 85

4.7 wt% H_2
42 g H_2/L
d: 0.89 g/mL
mp: 50 °C

D



Mw = 85

4.7 wt% H_2
mp: 25-27 °C

- discovered a single-component liquid phase material
- demonstrated clean H_2 desorption both under thermal conditions and in the presence of a catalyst
- demonstrated use of compound **B** in the context of fuel cells in collaboration with Protonex, Inc.
- demonstrated that fuel blends of **B** with ammonia borane or **J** increase fuel capacity, decrease release of volatile detrimental impurities, and decreases the melting point of the mixture
- demonstrated that blends are conducive to tractable regeneration reactions

Summary: Liquid Phase Materials

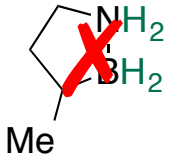
1) liquid phase

A

Mw = 71

5.6 wt% H_2
52 g H_2/L
d: 0.92 g/mL
mp: 36-37 °C

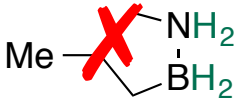
B



Mw = 85

4.7 wt% H_2
42 g H_2/L
d: 0.89 g/mL
viscosity: 25 cP
mp: –16 to –18 °C
$\Delta H(exp)$ = –9.1
kcal / mol monomer

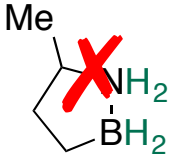
C



Mw = 85

4.7 wt% H_2
42 g H_2/L
d: 0.89 g/mL
mp: 50 °C

D



Mw = 85

4.7 wt% H_2
mp: 25-27 °C

Down-selected due to thermal stability issues
Ea (thermal decomposition) < 28 kcal/mol

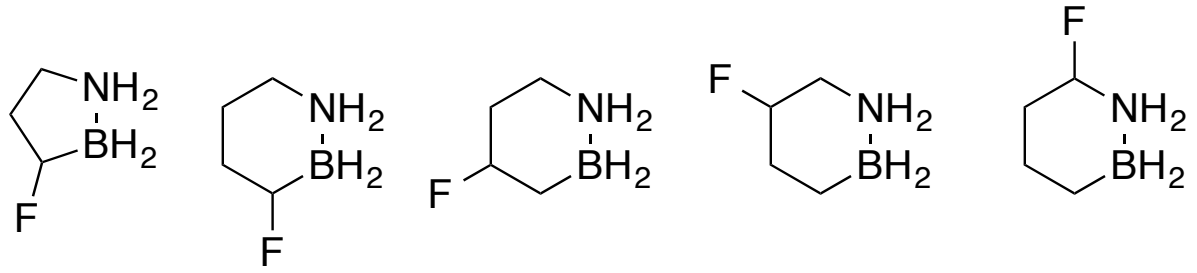
Liquid Phase Material Future Direction

Need to develop liquid-phase material that is thermally stable! These materials can be suitable for potential portable-power as well as H_2 delivery (to the forecourt) applications.

- Exothermic H_2 desorption will avoid problems with delivering the necessary H_2 pressures at the forecourt.

<u>How to make CBN compounds liquid phase and more stable:</u>

- Mechanistic studies are consistent with a second-order decomposition pathway that first involves a B–N bond dissociation.
- Six-membered CBN compounds are less prone to B–N bond dissociation consistent with their significantly improved thermal stability.
- Introduction of electron-withdrawing F substituents can reduce the hydridic character of the B–H, improving thermal stability.
- Use of mixtures can achieve melting depression
- Potential materials to be developed:



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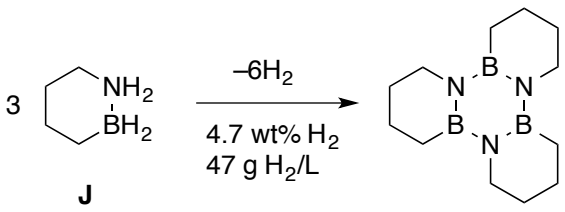
Jim Sisco

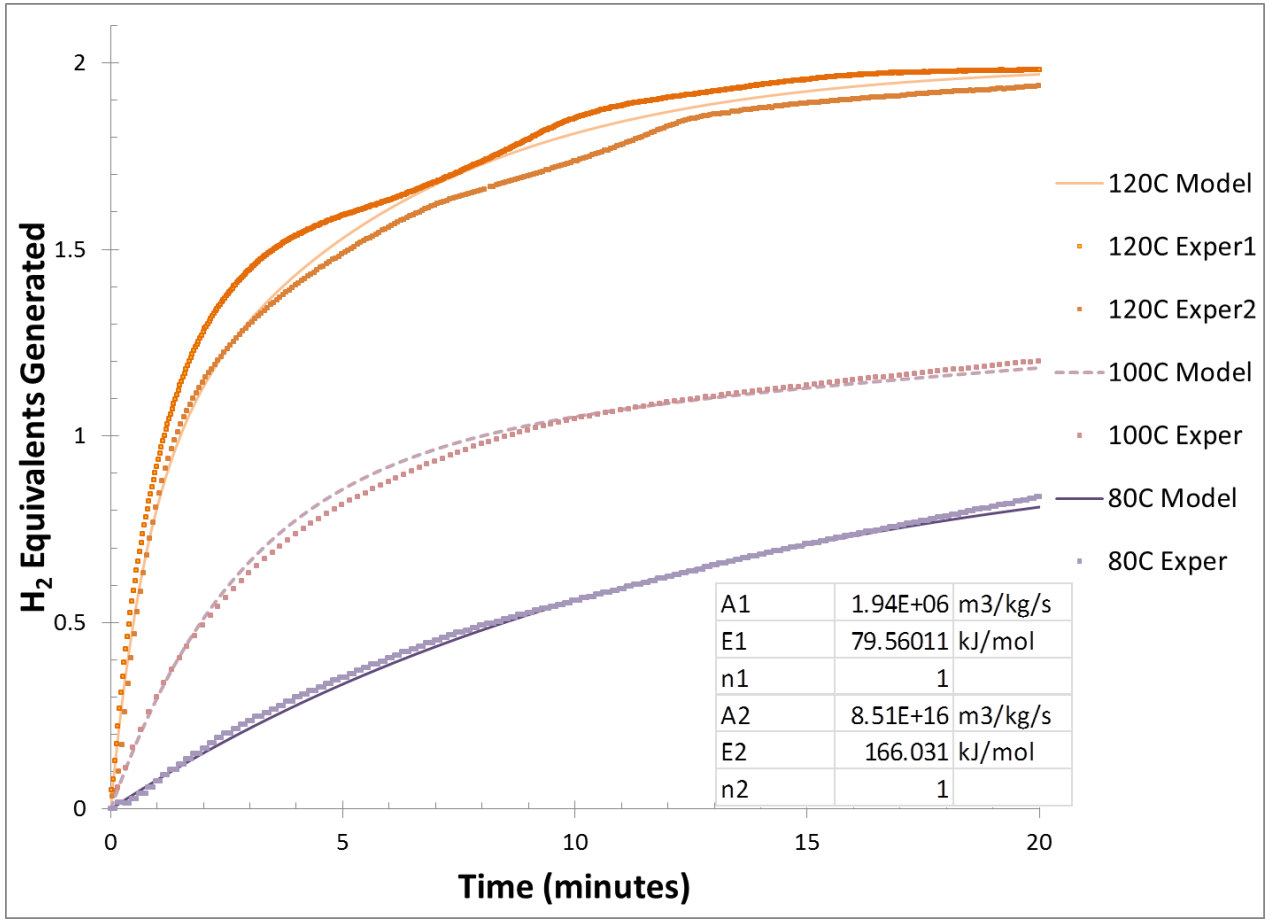
Technical Back-Up Slides

Compound J Exothermic Reaction

- Compound **J** reaction 80-120°C, 10% Pd on C, Batch Experiment
- Fit experimental data with two first order reactions in series

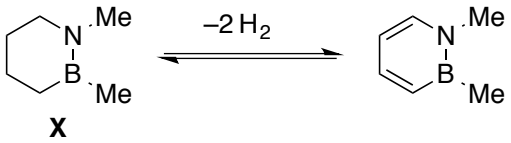


- Compound **J** and **J** trimer are both solid at room temperature
  - **J** cannot be used for the endothermic reaction kinetics
- ΔH_{rxn} = -41.4 kJ/mol H_2



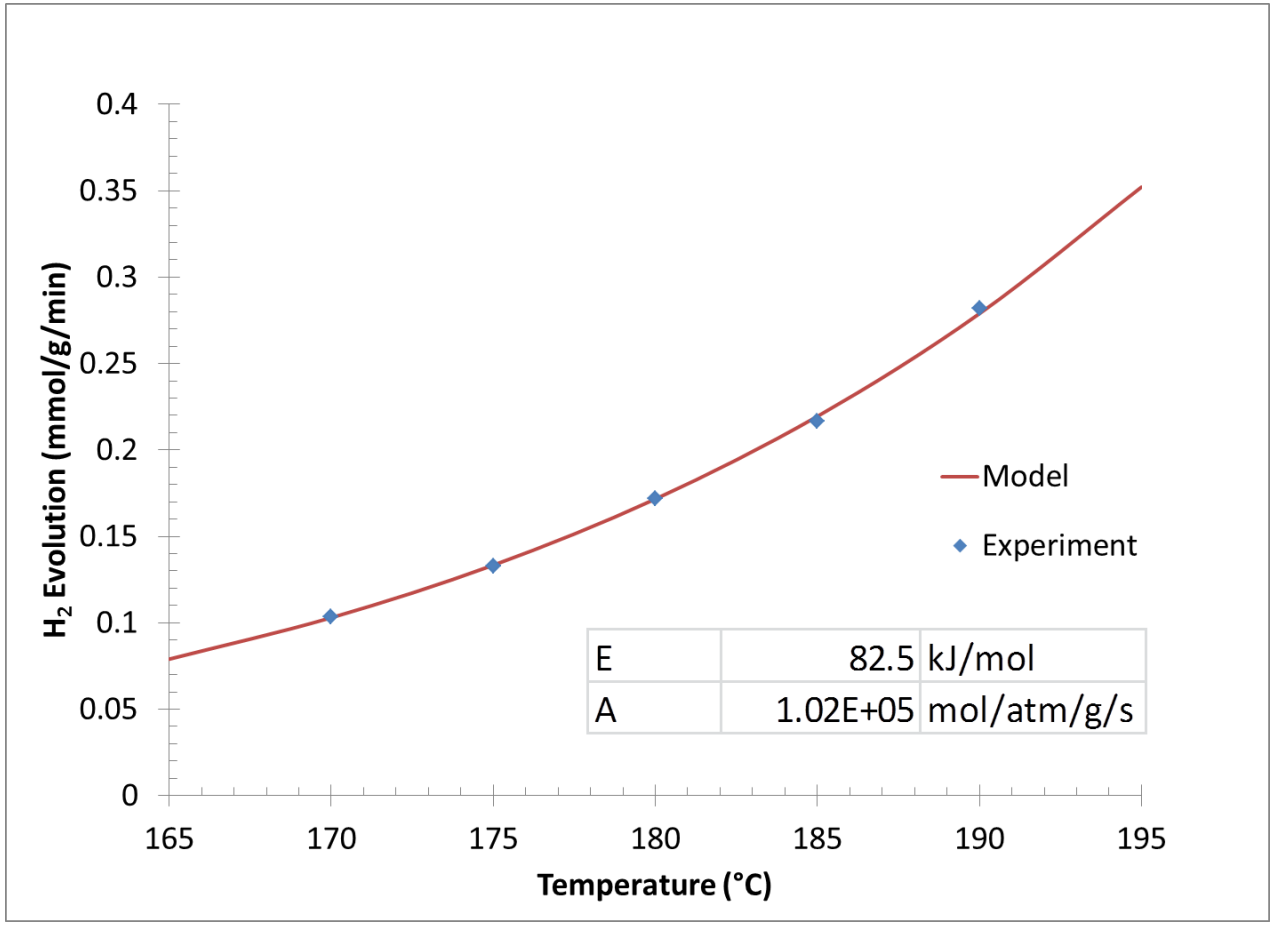
Compound X Endothermic Reaction Kinetics

- Compound **X** reaction 170-190°C, 10% Pd on C, Flow-Through Experiment
- Fit experimental data with one first order & equilibrium limited rxn

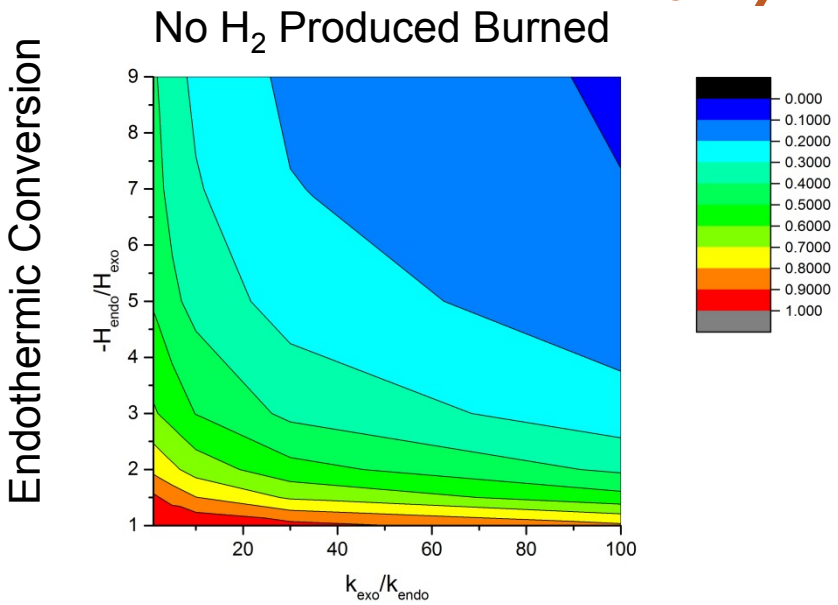


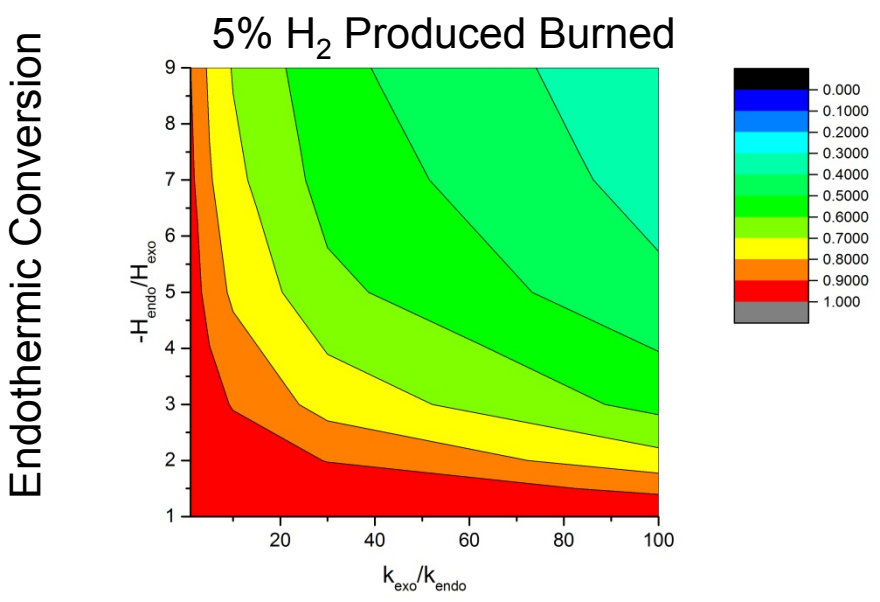
X

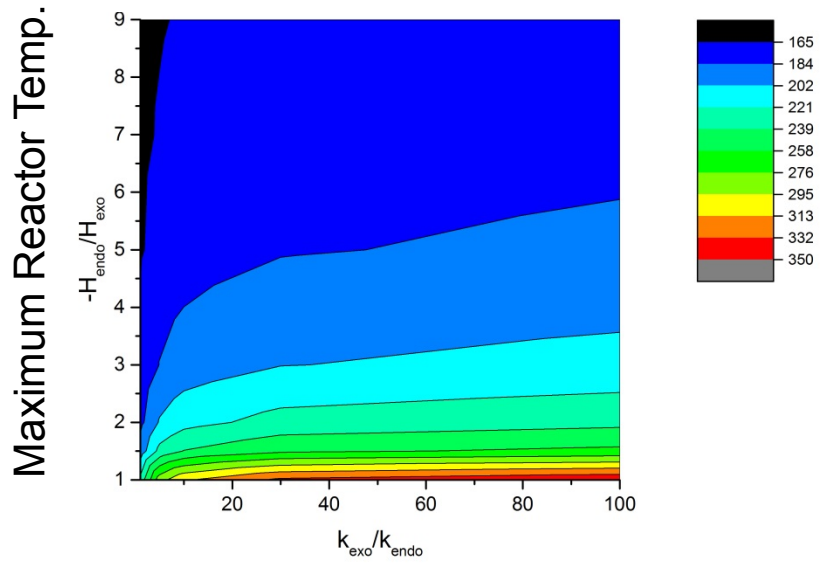
- Compound **X** is a liquid at room temperature, already has B-N hydrogen removed
  - **X** cannot be used for the exothermic reaction kinetics
- ΔH_{rxn} = 62.8 kJ/mol H_2

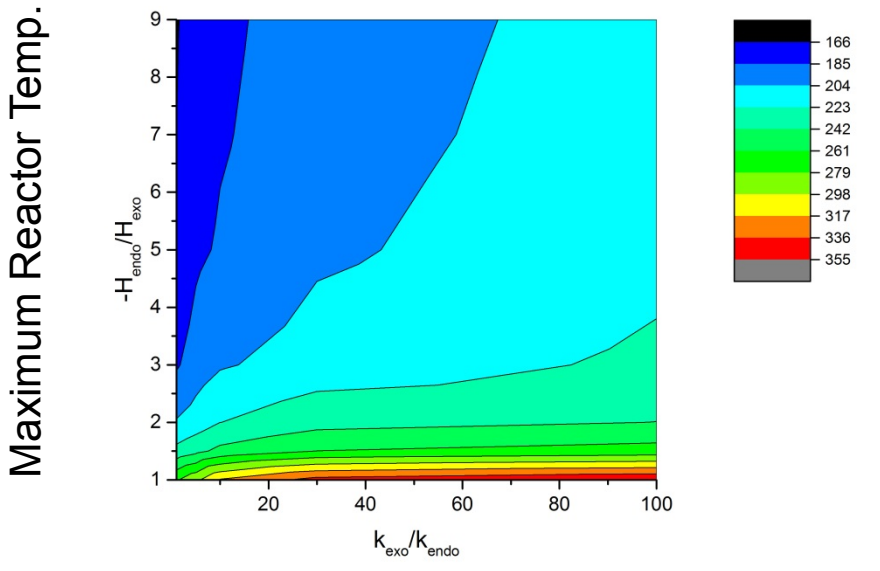


Impact of Burning Hydrogen on Thermodynamic Coupling



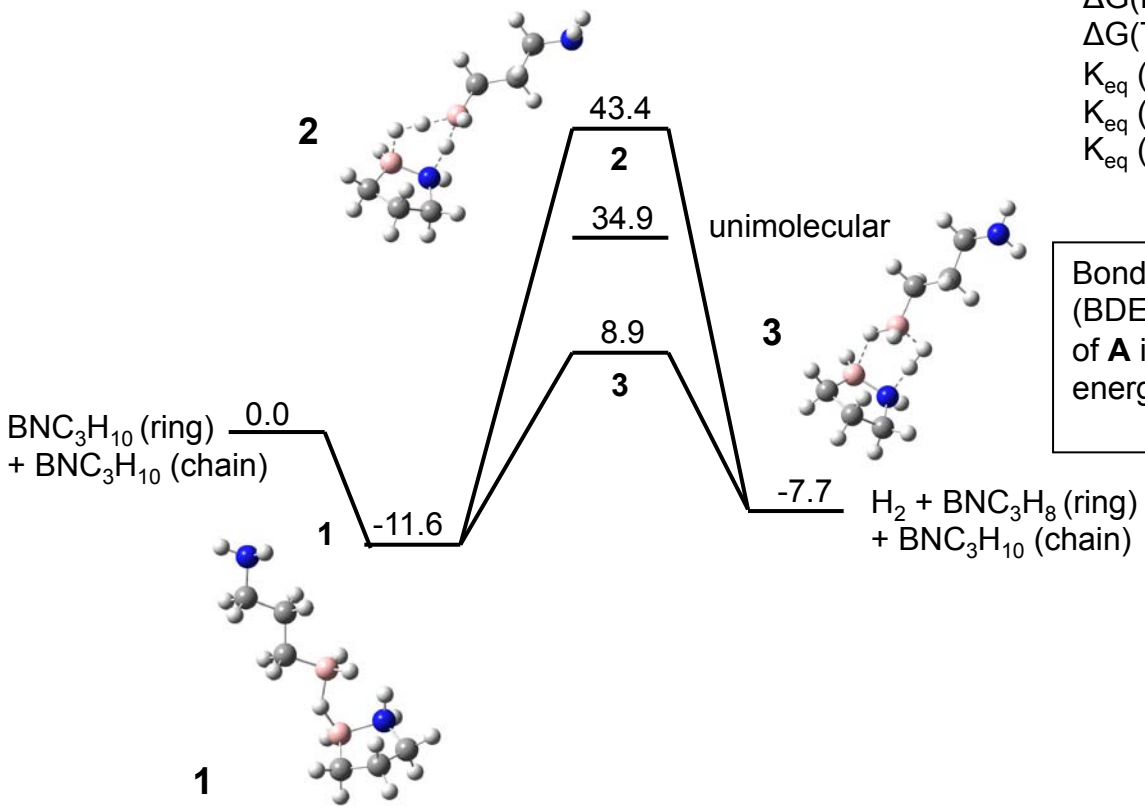


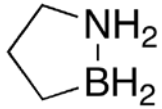




Bimolecular Mechanism of Thermal H_2 Desorption (CBN Cyclopentanes)

Potential energy surface for the catalyzed elimination of H_2 from A at 298 K in kcal/mol obtained at the B3LYP/DZVP2 level.



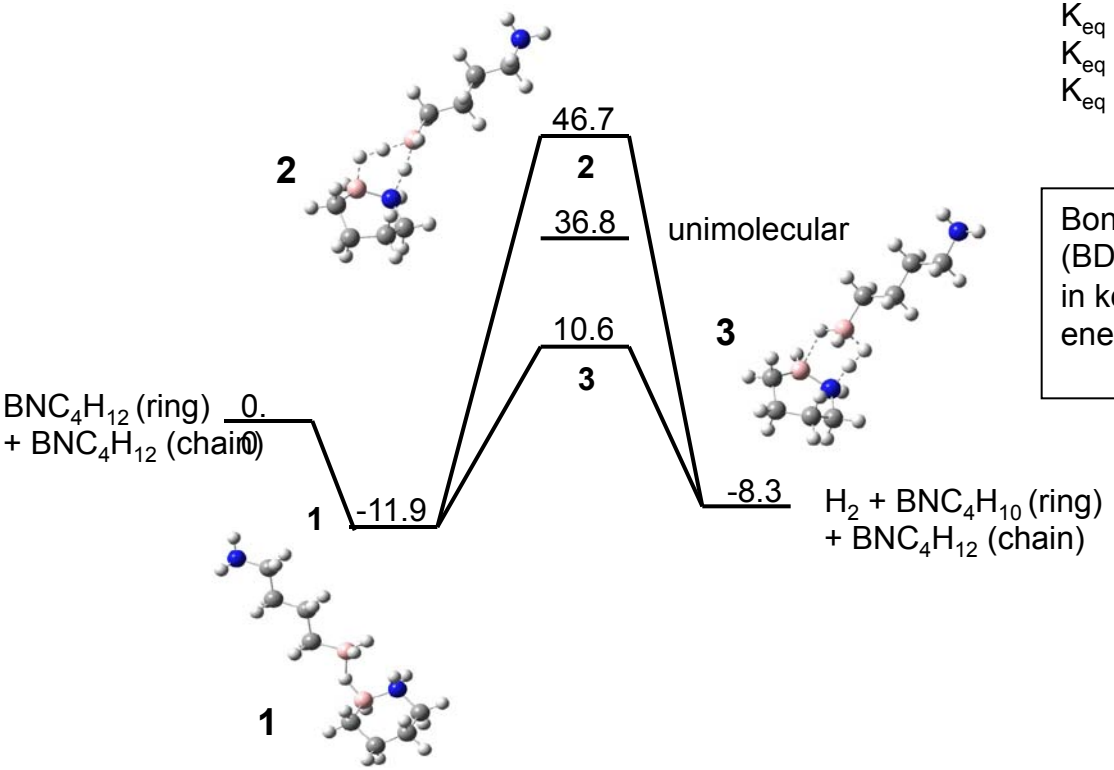


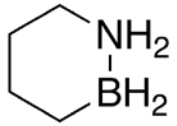
B-N BDE = 25.2
ΔG(gas) = 22.0
ΔG(Et_2O) = 25.6
ΔG(THF) = 29.9
K_{eq} (gas) =6.67×10^{-17}
K_{eq} (Et_2O) = 1.52×10^{-19}
K_{eq} (THF) = 1.14×10^{-22}

Bond dissociation energy (BDE) for the B-N bond of **A** in kcal/mol. Free energies at 298 K.

Bimolecular Mechanism of Thermal H_2 Desorption (CBN Cyclohexanes)

Potential energy surface for the catalyzed elimination of H2 from BNC_4H_{12} at 298 K in kcal/mol obtained at the B3LYP/DZVP2 level.





BDE = 28.6
$\Delta G(298) = 24.2$
$\Delta G(Et_2O) = 28.2$
$\Delta G(THF) = 32.8$
$K_{eq} = 1.62 \times 10^{-18}$
$K_{eq}\ (Et_2O) = 2.14 \times 10^{-21}$
$K_{eq}\ (THF) = 9.16 \times 10^{-25}$

Bond dissociation energy (BDE) for the B-N bond in kcal/mol. Free energies at 298 K.

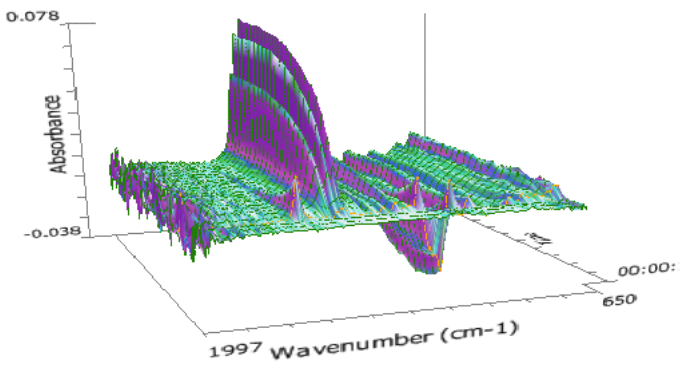
Kinetic ReactIR Experiments

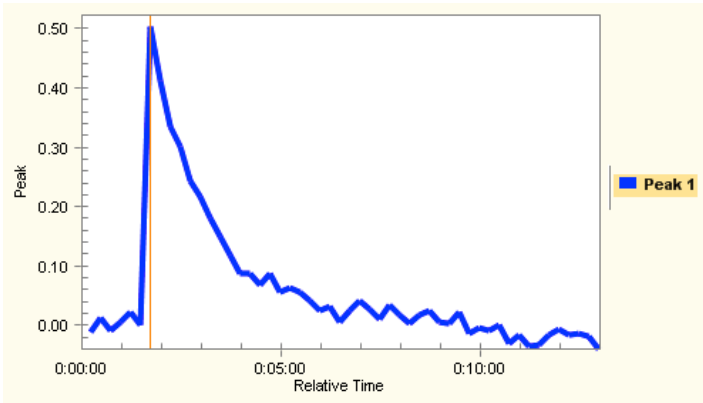
Experiment: Compound **B** in tetraglyme solution (kinetic studies)

Thermal decomposition is second order with respect to the substrate determined by initial rate kinetics → consistent with a bimolecular decomposition mechanism.

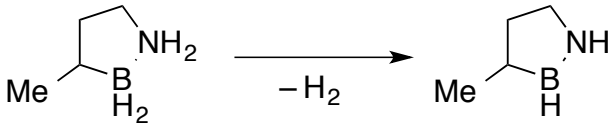
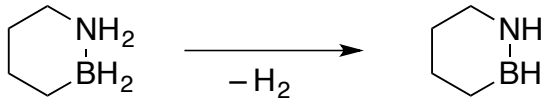
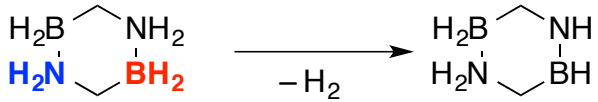
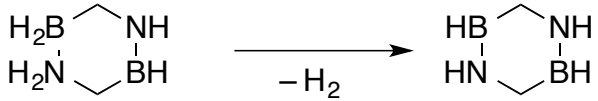
Activation parameters are also consistent with bimolecular decomposition mechanism:

E_a = 19 kcal/mol
A = 2.1 x 10^7 $M^{-1}s^{-1}$
$\Delta H^{\ddagger}$ = 18 kcal/mol
$\Delta S^{\ddagger}$ = –32 e.u.





New "Liquid-Phase" Materials Design with Increased Thermal Stability

entry	reaction	ΔH (kcal/mol)	ΔG (kcal/mol)
1	$NH_3–BH_3 \xrightarrow[-H_2]{} NH_2–BH_2$	–7.3[a] (5.1)[b]	–16.0
2		–5.9[a]	–14.3
3		–7.0[a]	–15.8
4 **H**		+4.6[a]	–4.4
5		–5.7[a]	–14.5

[a] G3MP2. [b] Feller-Peterson-Dixon composite correlated molecular orbital method.

Hypothesis:
The formally positively charged NH_2 group that is uniquely positioned in compound **H** is exerting an electron-withdrawing inductive effect that renders the B–H group less hydridic, thus reducing its propensity to release H_2.

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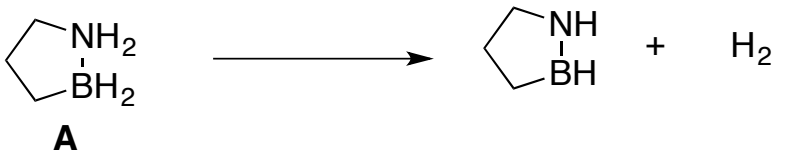
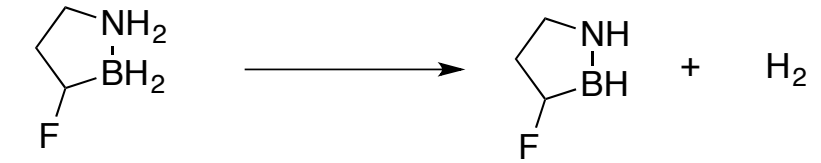
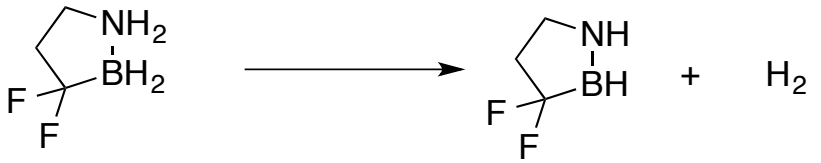
Potential New Targets For A Single-Component, Kinetically Stable, Liquid-Phase Material

reactions	ΔH (kcal/mol)	ΔG (kcal/mol)	materials H wt% (–2 H_2)
 **A**	–7.0	–15.3	5.6%
	**–0.7**	–9.0	4.5%
	–1.6	–10.1	3.7%

G3MP2 energies at 298K.

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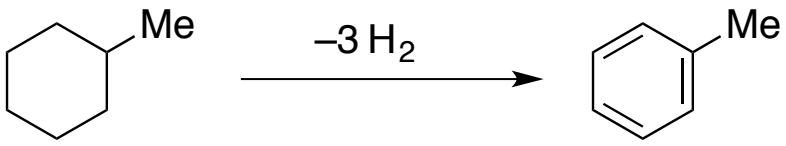
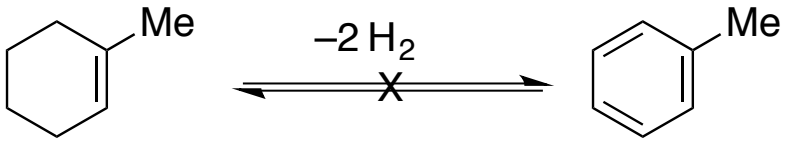
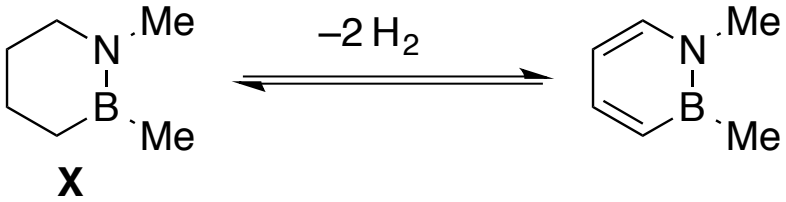
Model Compound X



capacity	bp, mp (charged fuel)	bp,mp (spent fuel)	ΔH (kcal/mol)
6.1 %	bp: +101 °C mp: –126 °C	bp: +111 °C, mp: –95 °C	**+49**



Recharging will lead to the fully saturated methylcyclohexane!



3.6 %	bp: ~170 °C mp: < –35 °C	(bp: ~170 °C mp: < 0 °C)	**(30)** **[31]**

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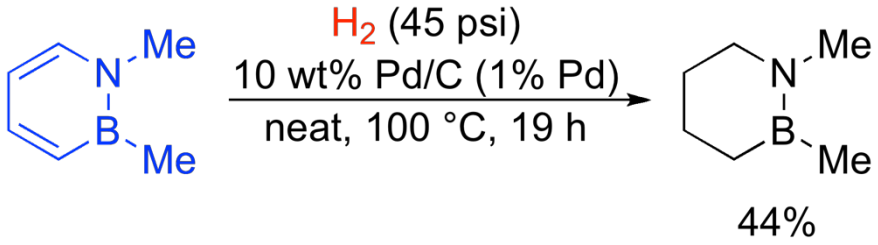
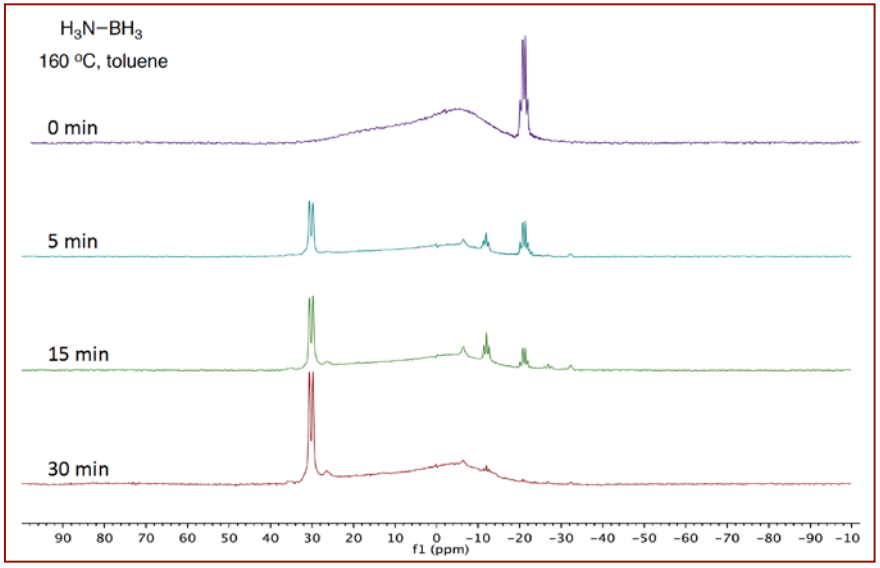
(): experimental values for the N-tBu derivative (at 333K, solution phase)
[]: predicted value at G3(MP2) level (298K, gas phase)

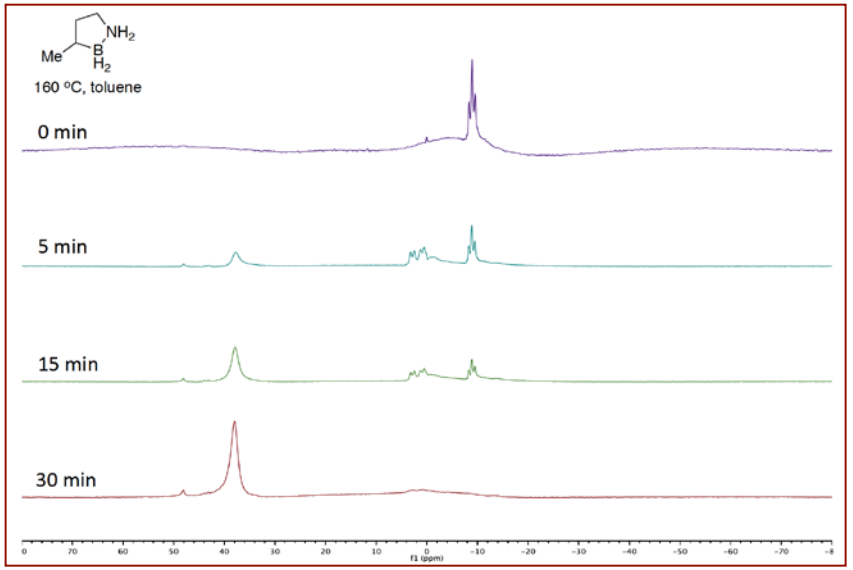
Unoptimized Regeneration of Compound X from Spent Fuel

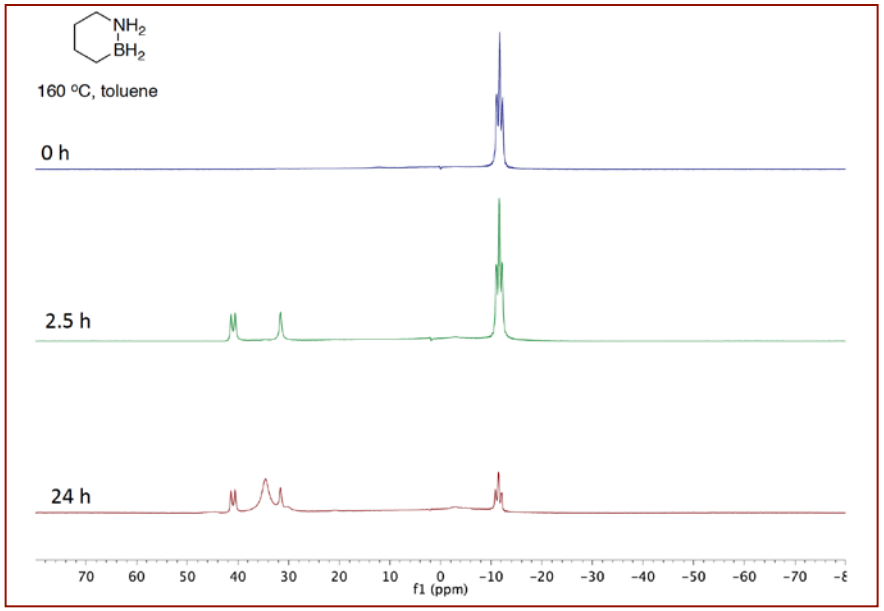


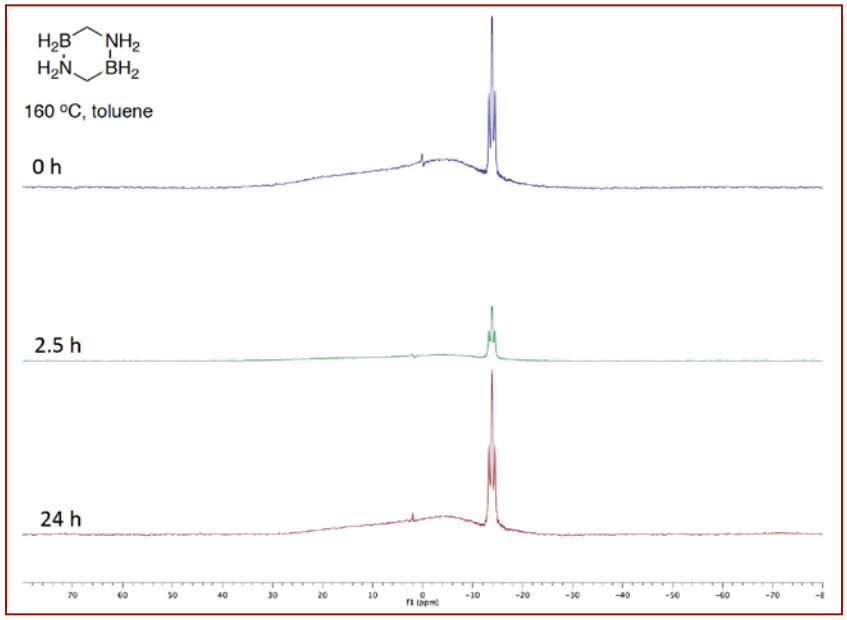
Regeneration with molecular H_2 needs further optimization.

Comparative Thermal Stability in Solution: AB ~ B < J < H

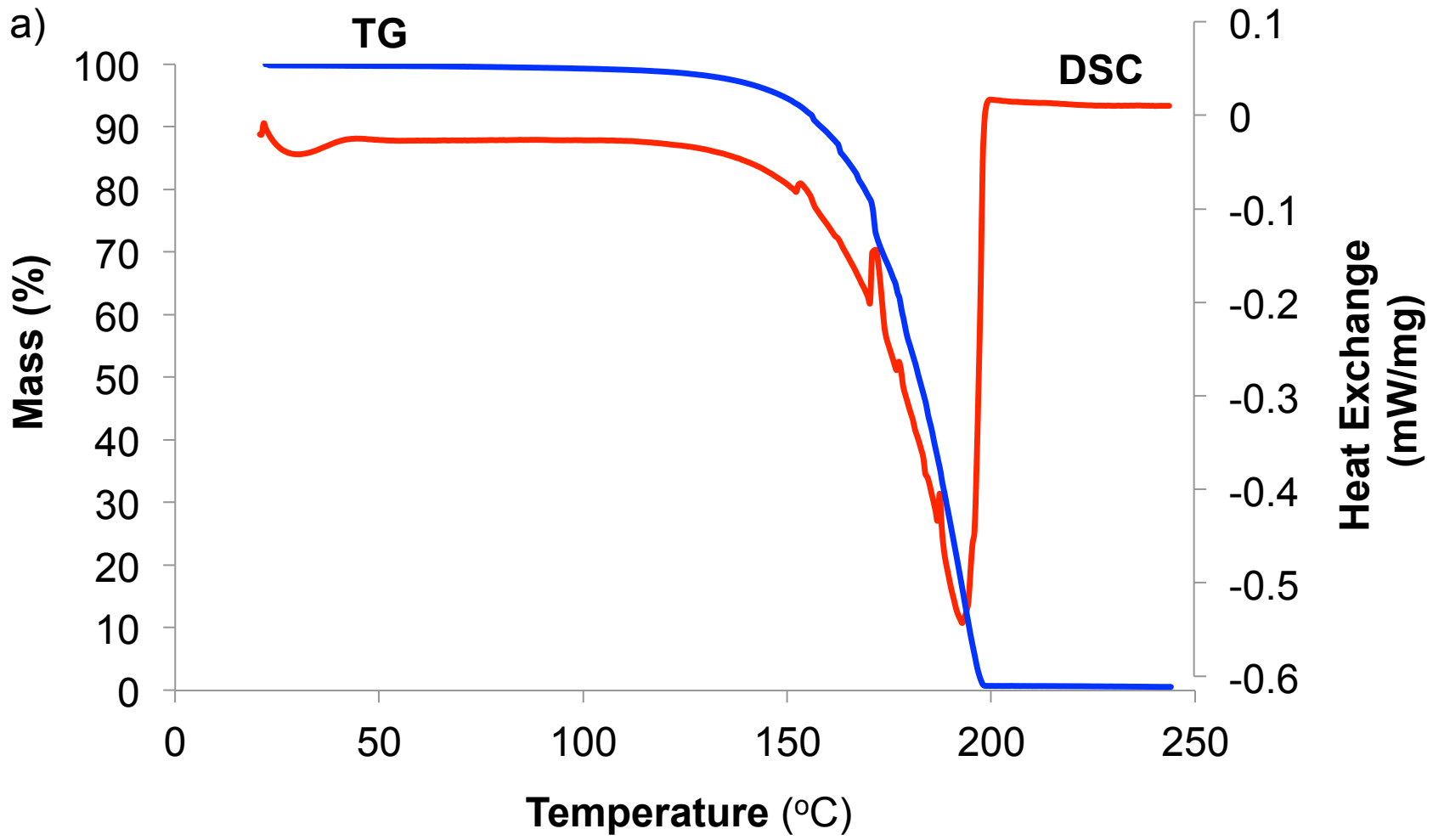






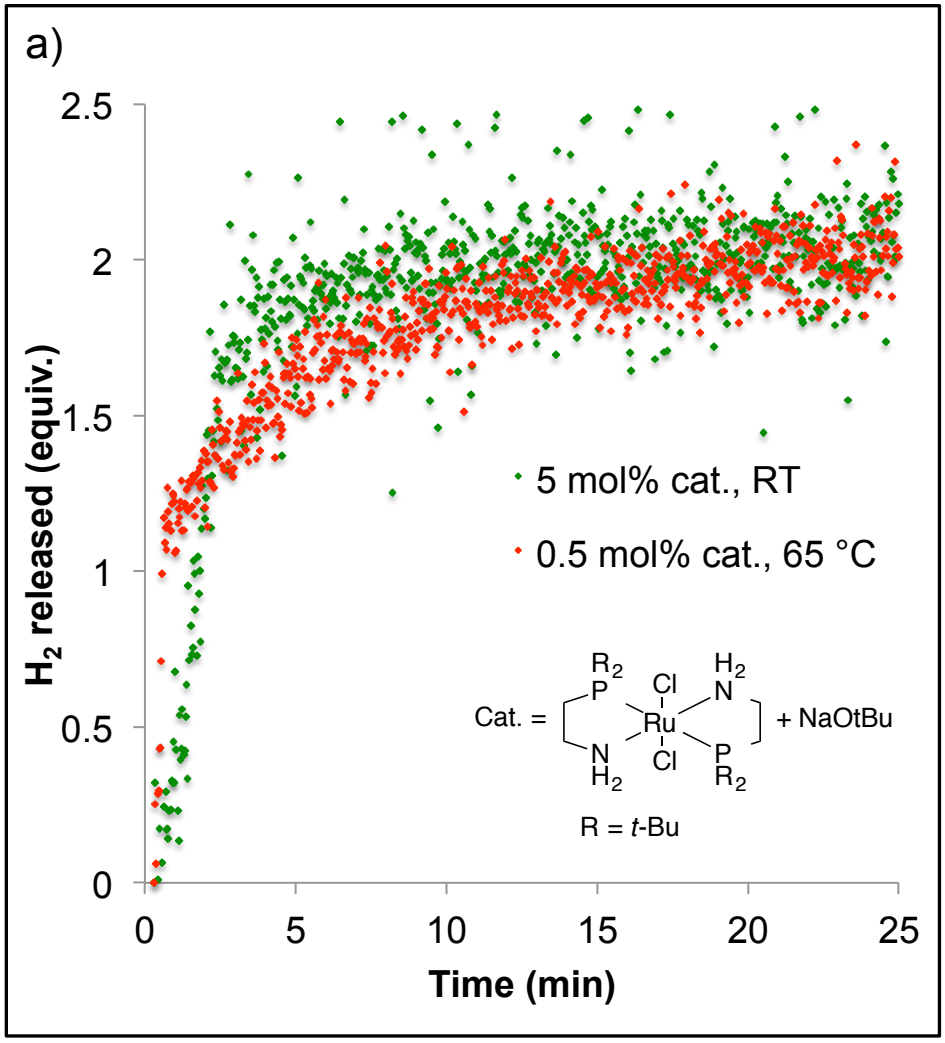


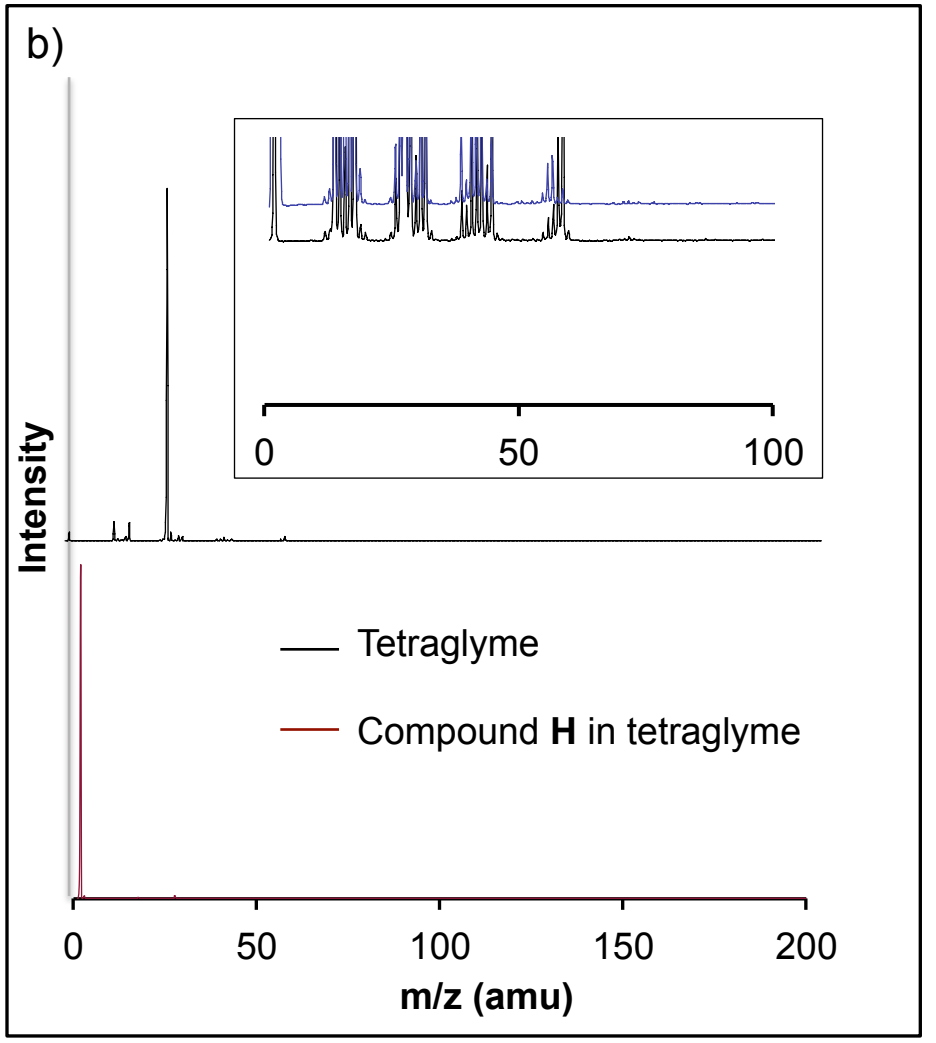
Thermal Stability of H as Neat Material: TGA-DSC



^{1}H and ^{11}B NMR indicated compound H is stable over the endothermic sublimation process.

Rapid Pure H_2 Release at Room Temperature





Compound H can be activated to release 4.7 wt% of analytically pure H_2 at room temperature in 15 min in the presence of a [Ru] catalyst.

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