

## IV.B.1 Hydrogen Storage by Novel CBN Heterocycle Materials

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### Technical Targets

This project is developing new liquid phase materials for hydrogen storage that can be readily regenerated. Insights gained from these studies will be applied toward the design and synthesis of hydrogen storage materials that meet the following DOE 2015 hydrogen storage targets:

- Specific energy: 1.8 kWh/kg (5.5 wt%)
- Energy density: 1.3 kWh/L (4.0 vol%)

### FY 2011 Accomplishments

- Synthesized the parent six-membered fully charged fuel of Material System (1) and partially charged parent BN-indole Material System (7).
- Formulated N-H (1), N-tBu (1'), and N-Me (1'') materials as liquids.
- Experimentally determined the energetic landscape of Material System (1) and provided a direct comparison with the computationally predicted values.
- Developed catalysts and conditions to optimize release of H<sub>2</sub> from Materials System (1).



### Fiscal Year (FY) 2011 Objectives

The objective of this project is to develop novel boron-nitrogen heterocycles as liquid-phase hydrogen storage materials with storage capacities and thermodynamic properties that have the potential to lead to rechargeable systems capable of meeting DOE targets. We seek to:

- Develop new materials that:
  - are structurally well-defined along the desorption/absorption processes
  - exhibit appropriate enthalpy of H<sub>2</sub> desorption
  - are liquids at operating temperatures
  - possess high H<sub>2</sub> storage capacities
- Identify catalysts that will release hydrogen from these materials at temperatures <200°C.
- Develop conditions that will readily recharge the spent fuel.

### Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

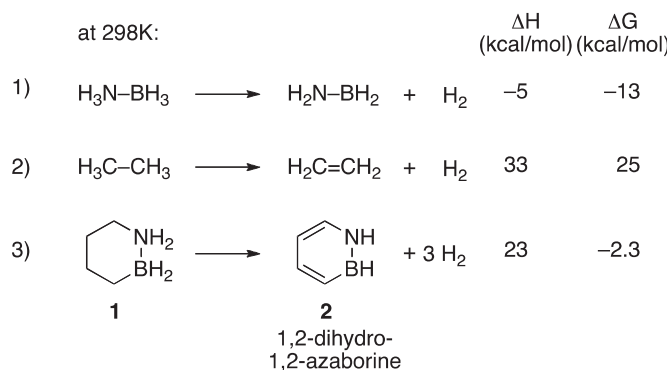
- (A) System Weight and Volume
- (C) Efficiency
- (E) Charging/Discharging Rates
- (R) Regeneration Process

### Introduction

Hydrogen storage is a vital component in the development of a hydrogen-based energy infrastructure. Boron nitrogen containing compounds, e.g., ammonia borane (H<sub>3</sub>N-BH<sub>3</sub> or AB), have attracted much attention as chemical H<sub>2</sub> storage materials because of their high gravimetric hydrogen densities and fast kinetics of H<sub>2</sub> release. This project is developing structurally well-defined liquid carbon-boron-nitrogen (CBN) hydrogen storage materials (i.e., heterocycles containing carbon, boron, and nitrogen) that have the potential to be reversibly regenerated using molecular hydrogen. A liquid phase, hydrogen storage system that can be regenerated using molecular hydrogen is highly desired for many reasons, including versatility, lower cost and improved efficiency, and durability. Such a storage material will allow on-board hydrogen storage. It can also be applied as an off-board energy carrier for vehicle and stationary applications that takes advantage of the existing liquid fuels infrastructure.

### Approach

In order to accomplish reversibility, neutrality in free energy of the hydrogen release process (i.e.,  $\Delta G \sim 0$  kcal/mol) at the operating temperature is pivotal. The dehydrogenation of AB is exergonic by -13 kcal/mol at 298 K (eq 1). In contrast to AB, the dehydrogenation of



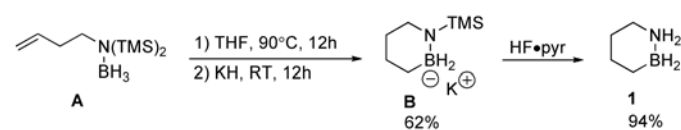
its isoelectronic organic counterpart, ethane ( $CH_3-CH_3$ ), is endergonic by +25 kcal/mol (eq 2). The coupling of endothermic dehydrogenation from CC with exothermic dehydrogenation from BN in a cyclic six-membered framework could lead to a reversible  $H_2$  storage system. Indeed, high-level computational analysis indicates that the release of  $H_2$  from CBN heterocycles such as **1** has favorable overall thermodynamics conducive to reversibility, (e.g., see eq 3). The potential for reversible hydrogen release/uptake and the relatively high gravimetric hydrogen density of CBN heterocycle materials (e.g. 7.1 wt% for **1**) render their preparation and development an important goal. This project is investigating several CBN heterocycle materials for  $H_2$  storage applications using a synergistic theoretical and experimental approach. Synthesis will be a crucial component of this project given the relatively unexplored nature of these CBN heterocycles. The structurally well-defined nature of these CBN heterocycle materials will facilitate their characterization and mechanistic investigation of the proposed desorption/absorption processes.

## Results

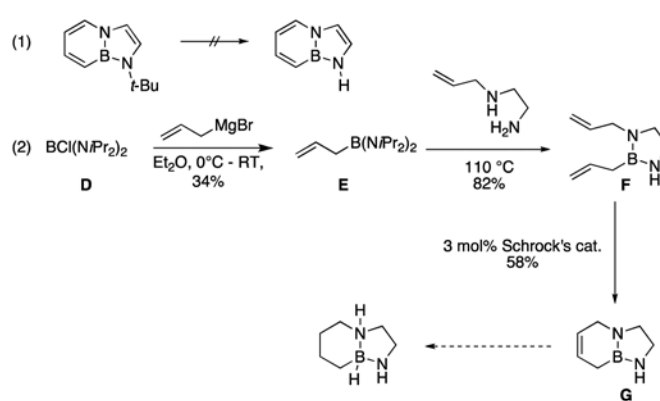
### Synthesis of Parent CBN Heterocycle Materials

We have successfully synthesized the parent charged fuel, **1**, illustrated in Scheme 1. From the *N*-bis-protected homoallylic amine  $BH_3$  adduct **A**, refluxing in tetrahydrofuran (THF) followed by treatment of the crude product with KH furnished the potassium salt **B** in 62% yield. Subsequent treatment with 2 equivalents of HF-pyridine afforded **1** in 94% yield.

In Phase I of this project we developed a synthesis of the *N*-*t*-Bu derivative of the spent fuel of Material (7). However, we found that it was challenging to remove



**SCHEME 1.** Synthesis of Parent Fuel Material System (1)



**SCHEME 2.** Progress toward the Synthesis of the Parent CBN Material System (7)

the *t*-Bu group from nitrogen to generate the parent unsubstituted fuel system (Scheme 2, eq 1). In Phase II, we developed a new synthetic route to (7) without the use of protecting group strategies (Scheme 2, eq 2). Treatment of chloroborane **D** with allyl magnesium bromide produced allylborane **E**. Condensation of **E** with *N*-allylethylene diamine furnished intermediate **F**, which upon ring closing metathesis produced the bicyclic material **G** without a protecting group on nitrogen. Intermediate **G** is a partially spent fuel intermediate of System (7), and we envision that it will serve as a very useful compound for the preparation of the fully charged fuel and other partially spent fuel of this system. Based on preliminary thermodynamic analysis, we believe that the challenges associated with System (7) are similar to those of System (1). Thus, we conclude that it would be most prudent to focus on System (1).

### Formulation of CBN Heterocycles as Liquids

We formulated the parent fully charged fuel **1** and the *N*-substituted fuels **1'** and **1''** as liquids. Melting points and liquid densities were also determined for **1**, **1'** and **1''** (Table 1). Compounds **1** and **1''** are liquids at an

**TABLE 1.** Formulation of CBN Heterocycles as Liquids

entry	neat material	THF solution	Et <sub>2</sub> O solution
	mp: 63-63 °C d (kg/L): 0.99 ± 0.05 vol (g H <sub>2</sub> /L): <b>70</b> wt (%): <b>7.1</b>	sol (g/L): 434 ± 20 d (kg/L): 0.8992 vol (g H <sub>2</sub> /L): 30.7 wt (%): 3.4	sol (g/L): 346 ± 30 d (kg/L): 0.781 ± 0.02 vol (g H <sub>2</sub> /L): 24.5 wt (%): 2.2
	mp: 96-98 °C d (kg/L): 0.61 ± 0.07 vol (g H <sub>2</sub> /L): 25 wt (%): 4.3	sol (g/L): 284 ± 28 d (kg/L): 0.8892 vol (g H <sub>2</sub> /L): 11.7 wt (%): 1.3	sol (g/L): 84.4 ± 4 d (kg/L): 0.7134 vol (g H <sub>2</sub> /L): 3.47 wt (%): 0.4
	mp: 72-73 °C d (kg/L): 0.87 ± 0.08 vol (g H <sub>2</sub> /L): <b>53</b> wt (%): <b>6.1</b>	sol (g/L): 292 ± 5 d (kg/L): 0.8992 vol (g H <sub>2</sub> /L): 17.8 wt (%): 2.0	sol (g/L): 106 ± 18 d (kg/L): 0.7134 vol (g H <sub>2</sub> /L): 6.5 wt (%): 0.73

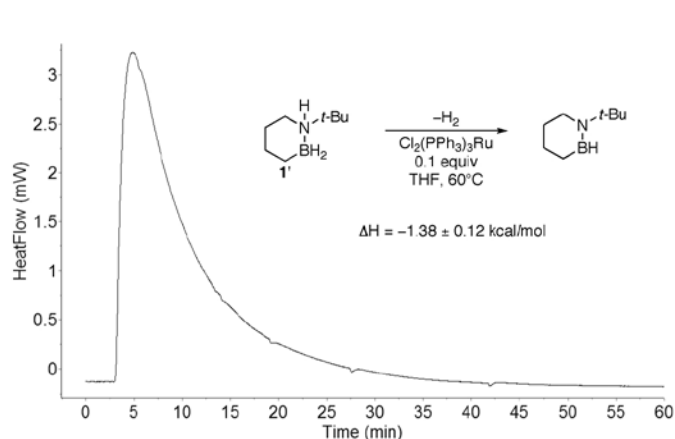
operating temperature of 80°C. Assuming the release of 3 equivalents of H<sub>2</sub>, **1** and **1'** exhibit reasonable volumetric and gravimetric capacities (**1**: 7.1 wt%, 70 g H<sub>2</sub>/L; **1'**: 6.1 wt%, 53 g H<sub>2</sub>/L). At ambient temperatures **1** and **1'** are solids. When solubilizing additives are added to these materials at ambient temperature, the storage capacities are significantly reduced (e.g., see THF solution column). A slurry formulation will result in storage capacities that are between the limiting scenarios (i.e., values between the “neat material” and “THF solution” columns) at ambient temperatures.

### Thermodynamics of Hydrogen Uptake and Release

We determined the enthalpy of hydrogenation uptake of the spent fuel material **2'** and the partially spent materials **3'**, **4'**, and **6'** *experimentally* via reaction calorimetry. As part of this process, we determined a lower resonance stabilization energy (RSE = 16.6 ± 1.3 kcal/mol) of our CBN heterocyclic system vs. the corresponding non-BN-containing carbocyclic system (~32 kcal/mol). This is consistent with the observed improved H<sub>2</sub> adsorption ability of CBN materials compared to the carbocyclic system. We were also able to determine the enthalpy of the dehydrogenation from the *N*-*t*Bu model fuel **1'**, catalyzed by 10 mol% Cl<sub>2</sub>(PPh<sub>3</sub>)<sub>3</sub>Ru. A representative heat flow trace is illustrated in Scheme 3 (left). Thus, we have completed the experimental thermodynamic analysis (values in parenthesis) of this material system shown in Scheme 3 (right), which agree reasonably with computationally predicted values (values in brackets).

### Development of Catalysts and Conditions to Optimize H<sub>2</sub> Release from **1**

During the course of our investigations of heterocycle **1**, we determined that it readily released two equivalents of H<sub>2</sub> to form trimer **T** in quantitative yield with virtually no formation of potential fuel cell poisons encountered in AB decomposition (e.g., no formation of ammonia or borazine).



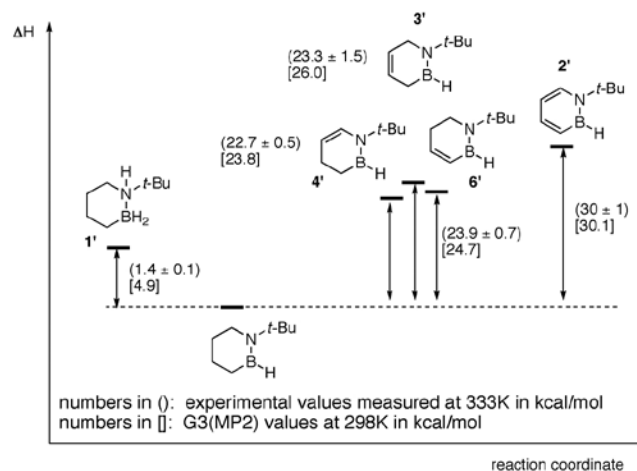
**SCHEME 3.** Thermodynamics of Hydrogen Release from CBN Material System (**1**)

We screened a variety of hetero- and homogeneous catalysts and conditions to release up to two equivalents of H<sub>2</sub> from **1**. We focused on three main factors: 1) cost of catalyst; 2) catalyst loading; 3) reaction time. In a general procedure, we added a solution of **1** and the catalyst to a J-Young tube, which we sealed and immersed in an 80°C oil bath; reaction progress was monitored by <sup>11</sup>B nuclear magnetic resonance. Selected results are listed in Table 2. At 80°C in toluene, many catalysts enabled complete release of two equivalents of H<sub>2</sub> within 60 minutes. The most active catalysts were the rhodium dimers [Cl(cod)Rh]<sub>2</sub> and [(nbd)ClRh]<sub>2</sub> (entries 7 and 8, respectively) which achieved complete trimer formation in 15 minutes at 5 mol% catalyst loading. The low cost, heterogeneous catalyst CoCl<sub>2</sub> (entry 5) enabled the complete release of two equivalents H<sub>2</sub> in 30 minutes at 10 mol% catalyst loading. As a control, we heated a sample of **1** at 80°C in toluene with no catalyst; only starting material was observed after 3 hours.

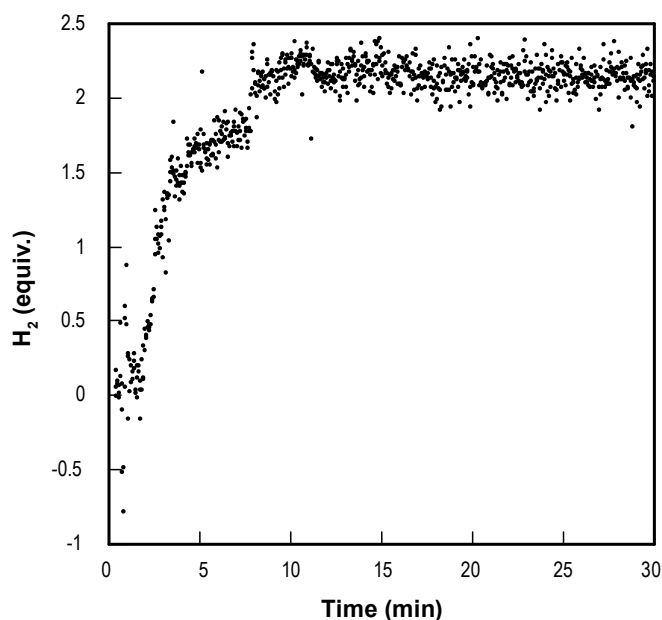
We measured the amount and rate of H<sub>2</sub> release from **1** with 5 mol% CoCl<sub>2</sub> in toluene using an automated gas burette system. As can be seen from Figure 1, release of

**TABLE 2.** Optimization Survey of Catalysts and Conditions to Release Two Equivalents of H<sub>2</sub> from the Parent of Material System (**1**)

Entry	Catalyst	Loading (mol%)	Time(min)	% Yield <b>T</b>
1	(dppe)NiCl <sub>2</sub>	10	60	100
2	[Cl(cod)Ir] <sub>2</sub>	10	60	100
3	[(C <sub>2</sub> H <sub>2</sub> ) <sub>2</sub> ClRh] <sub>2</sub>	10	60	100
4	(PPh <sub>3</sub> ) <sub>2</sub> NiCl <sub>2</sub>	5	60	100
5	CoCl <sub>2</sub>	10	30	100
6	Cp*RuCl <sub>2</sub>	5	30	100
7	[Cl(cod)Rh] <sub>2</sub>	5	15	100
8	[(nbd)ClRh] <sub>2</sub>	5	15	100



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



**FIGURE 1.** Automated Burette Measurement of H<sub>2</sub> Release from **1**

the first equivalent of H<sub>2</sub> from **1** takes place in less than 5 minutes from the instant the reaction flask is submerged in an 90°C oil bath. Trimer formation (coinciding with the release of an additional equivalent of H<sub>2</sub>) is complete within 15 minutes of start of the reaction.

## Conclusions and Future Directions

In summary, we expanded our synthetic toolbox for the preparation of CBN heterocycles to achieve the synthesis of the parent charged fuel **1**, and N-substituted derivatives **1'** and **1''**. The synthetic availability of CBN heterocycle materials enabled us to experimentally determine thermodynamic data for hydrogen uptake and release from these materials, and optimize conditions for release of H<sub>2</sub> from **1**. We determined that the parent charged fuel **1** readily releases two equivalents of H<sub>2</sub> in a clean and quantitative process to form a well-defined trimer product under mild conditions using a relatively cheap CoCl<sub>2</sub> catalyst. We also demonstrated that compound **1** is thermally stable up to its melting point, and that decomposition with concomitant H<sub>2</sub> release requires a catalyst.

In FY 2012, we will:

- Optimize our current synthesis with regard to scale up of Material System (1).
- Develop/optimize conditions/catalysts for H<sub>2</sub> desorption for Material System (1).
- Improve energy efficiency for recharging the spent fuel of Material System (1).

## Selected FY 2011 Publications/Presentations

1. “Resonance Stabilization Energy of 1,2-Azaborines: A Quantitative Experimental Study by Reaction Calorimetry”; Patrick G. Campbell, Eric R. Abbey, Doinita Neiner, Daniel J. Grant, David A. Dixon, and Shih-Yuan Liu; *J. Am. Chem. Soc.* **2010**, *132*, 18048-18050.
2. “Hydrogen Storage by Carbon(C) Boron(B) Nitrogen(N) Heterocycles”; Patrick G. Campbell, Kshitij Parab, David A. Dixon, Shih-Yuan Liu; *24<sup>th</sup> International Conference on Organometallic Chemistry* (PS2-144), Taipei, Taiwan, July 2010.
3. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; Shih-Yuan Liu; *Seminar*, National Taiwan University, Taipei, Taiwan, July 2010.
4. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; Shih-Yuan Liu; *Seminar*, University of St. Andrews, St. Andrews, UK, September 2010.
5. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; University of Calgary, Calgary, Alberta, Canada, *Seminar*, November 5, 2011.
6. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; University of Pennsylvania, Philadelphia, PA, *Seminar*, November 9, 2011.
7. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; University of California, Berkeley, Berkeley, CA, *Seminar*, December 2, 2010.
8. “Hydrogen Storage by Carbon(C) Boron(B) Nitrogen(N) Heterocycles”; Honolulu, Hawaii, *Pacificchem 2010 Symposium #69 “Advances in Chemistry and Materials for Hydrogen Storage”*; *invited lecture*, December 17, 2010.
9. “Resonance Stabilization Energy of 1,2-Azaborines: A Quantitative Experimental Study by Reaction Calorimetry”; Patrick G. Campbell, Shih-Yuan Liu; *Materials Science Institute Conference*, Gleneden Beach, OR (2010), *Poster Presentation*, December 12, 2010.
10. “Hydrogen Storage by Novel CBN Heterocycle Materials”; USCAR, Detroit MI. *Department of Energy TechTeam Review*, March 17, 2011.
11. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; Ohio State University, Columbus, OH, *Seminar*, April 8, 2011.
12. “Hydrogen Storage by Novel CBN Heterocycle Materials”; Washington DC, DOE Annual Merit Review, May 13, 2011.
13. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; ETH Zürich, Zürich, Switzerland, *Seminar*, June 6, 2011.
14. “Developing the Basic Science and Applications of Boron(B)-Nitrogen(N)-Containing Heterocycles”; University of Würzburg, Würzburg, Germany, *Seminar*, June 8, 2011.