Final Report for the DOE-BES Program

Mechanistic Studies of Activated Hydrogen Release from Amine-Boranes

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NOTICE

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Summary

Effective storage of hydrogen presents one of the most significant technical gaps to successful implementation of the hydrogen economy, particularly for transportation applications. Amine boranes, such as ammonia borane H_3NBH_3 and ammonia triborane $H_3NB_3H_7$, have been identified as promising, high-capacity chemical hydrogen storage media containing potentially readily released protic (N-H) and hydridic (B-H) hydrogens. At the outset of our studies, dehydrogenation of ammonia borane had been studied primarily in the solid state, but our DOE sponsored work clearly demonstrated that ionic liquids, base-initiators and/or metal-catalysts can each significantly increase both the rate and extent of hydrogen release from amine boranes under moderate conditions. Our studies also showed that depending upon the activation method, hydrogen release from amine boranes can occur by very different mechanistic steps and yield different types of spent-fuel materials. The fundamental understanding that was developed during this grant of the pathways and controlling factors for each of these hydrogen-release mechanisms is now enabling continuing discovery and optimization of new chemical-hydride based hydrogen storage systems.

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Introduction

Effective storage of hydrogen presents one of the most significant technical gaps to successful implementation of the hydrogen economy, particularly for transportation applications.[1] Amine-boranes, such as ammonia borane (AB, H_3NBH_3, **1)** and ammonia triborane ($H_3NB_3H_7$, **2**) have been identified as promising, high-capacity chemical hydrogen storage media containing potentially readily released protic (N-H) and hydridic (B-H) hydrogens.[2] At the outset of our studies, dehydrogenation of ammonia borane had been studied primarily in the solid state,[3] but our DOE sponsored work that is summarized in this report clearly demonstrated that ionic liquids, base-initiators and/or metal-catalysts can each significantly increase both the rate and extent of hydrogen release from AB under moderate conditions. Our investigations also showed that, depending upon the activation method, hydrogen release from amine boranes can occur by very different mechanistic steps and yield different types of spent-fuel materials. The fundamental understanding that was developed during this grant of the pathways and controlling factors for each of these hydrogen-release mechanisms is now enabling continuing discovery and optimization of new chemical-hydride based hydrogen storage systems.

1) Ammonia Triborane

The high hydrogen release capacity that could potentially be achieved by ammonia triborane **2** oxidative-hydrolysis, (9.7 materials-wt% H_2) or thermolysis (17.7 materials-wt% H_2), has made it an attractive candidate for chemical hydrogen storage. Although $NH_3B_3H_7$ was first synthesized over 50 years ago,[4] owing to the lack of a suitable method for its efficient and safe synthesis, its reactivities and properties had not been intensively explored. Of the fewer than 30 previous publications on **2**, many were stimulated by the apparent contradiction between the computational studies that predict a symmetric single hydrogen-bridged C_S-symmetric structure, and the early single crystal X-ray determination of **2** that showed an asymmetric structure with perhaps two bridging-hydrogens. In this project, we demonstrated: (1) a new, efficient preparation of **2** that now makes this compound easily available; (2) a new crystallographic study of the solid-state structure of **2**, along with a structural determination of the **2**•18-crown-6 adduct, that resolves the contradictions with computational structural predictions; and (3) a description of the hydrolytic hydrogen release properties of **2**.[5,6]

Iodine oxidation of $B_3H_8^-$ in glyme solution to produce (glyme)B_3H_7, followed by displacement of the coordinated glyme by reaction with anhydrous ammonia was shown to provide a safe and convenient preparation of **2**. X-ray crystallographic determinations and DFT computational studies of both $NH_3B_3H_7$ and the $NH_3B_3H_7$•18-crown-6 adduct demonstrated that while computations predict a symmetric single bridging-hydrogen conformation, **2** has a highly asymmetric structure in the solid-state that results from intermolecular $N\text{-}H^{+}\text{--}H^{-}\text{-}B$ dihydrogen bonding interactions (**Figure 1**).

Studies of hydrolytic reactions showed that upon the addition of acid or an appropriate transition metal catalyst, aqueous solutions of **2** rapidly release hydrogen, with 6.1 material-wt% H_2-release being achieved from a 22.7-wt% aqueous solution of **2** at room temperature in the presence of 5wt%-Rh/Al_2O_3 (1.1 mol% Rh). The rate of H_2-release was controlled by both the catalyst loading and temperature. The hydrolysis reaction of a highly concentrated 22.7 wt% sample yielded 6.1 material-wt% H_2 [i.e., mat-wt% H_2 = H_2-wt/($NH_3B_3H_7$+H_2O+Rh/Al_2O_3-wts)] making an ammonia triborane-based hydrolytic system competitive with both the NH_3BH_3- and $NaBH_4$-based hydrolysis systems.

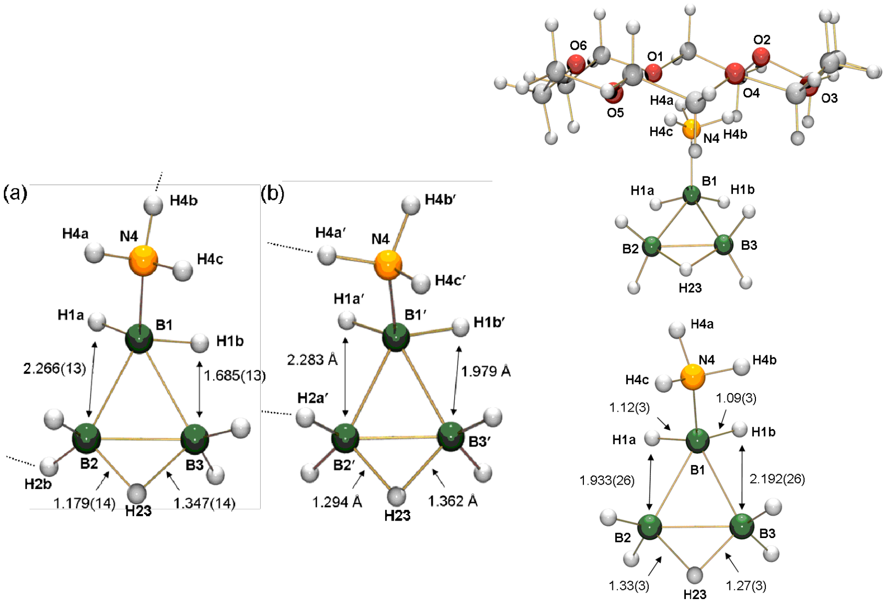


Figure 1. ***Left:*** Comparison of (a) the solid-state structure of **2** with (b) the DFT-optimized **2** structure. Dashed lines indicate the positions of the dihydrogen bonding interactions. ***Right:*** (*top*) X-ray crystal structure of **2**•18-crown-6; (*bottom*) selected distances in the ammonia triborane fragment of **2**•18-crown-6.

2) Ionic Liquid Activation of Ammonia Borane H_2-Release

One of the most significant findings of our DOE sponsored work was the discovery that ionic liquids provide advantageous media for ammonia borane dehydrogenation in which both the extent and rate of dehydrogenation are significantly increased over that which can be achieved by its solid-state reactions.[7-9] Furthermore, in contrast to solid-state reactions, ammonia borane dehydrogenations in ionic liquids do not exhibit any induction period. For example, AB reactions at 85 °C in 1-butyl-3-methylimidazolium chloride (bmimCl) (50:50-wt%) exhibited no induction period and released 1.0 H_2-equiv. in 67 min and 2.2 H_2-equiv. in 330 min at 85 °C, whereas comparable solid-state AB reactions had a 180 min induction period and required 360 min to release ~0.8 H_2-equiv. at 85 °C, with the release of only another ~0.1 H_2-equiv. at longer times. As shown in **Figure 2** below, more extensive studies demonstrated that both faster rates and a greatly increased extent of hydrogen release can be attained when other ionic liquids are employed.

It was also demonstrated that significant rate enhancements for the ionic-liquid mixtures could be obtained with only moderate increases in temperature, with, for example, a 50:50-wt% AB/bmimCl mixture releasing 1.0 H_2-equiv. in 5 min and 2.2 H_2-equiv. in only 20 min at 110 °C. Increasing the AB/bmimCl ratio to 80:20 still gave enhanced H_2-release rates compared to the solid-state, and produced a system that achieved 11.4 materials-weight percent H_2-release.

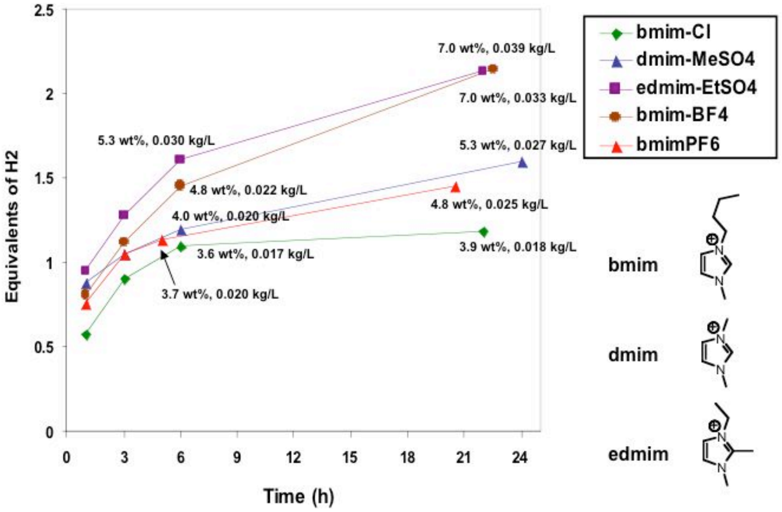


Figure 2. Summary of H_2 release in different ionic liquids at 85 ºC.

Solid-state and solution ^{11}B NMR studies of AB H_2-release reactions in progress strongly support the mechanistic pathway shown in **Figure 3** involving: (1) ionic-liquid promoted conversion of AB into its more reactive ionic diammoniate-of-diborane (DADB) form, (2) further intermolecular dehydrocoupling reactions between hydridic B-H hydrogens and protonic N-H hydrogens on DADB and/or AB to form neutral polyaminoborane polymers and (3) polyaminoborane dehydrogenation to unsaturated cross-linked polyborazylene materials.[10,11]

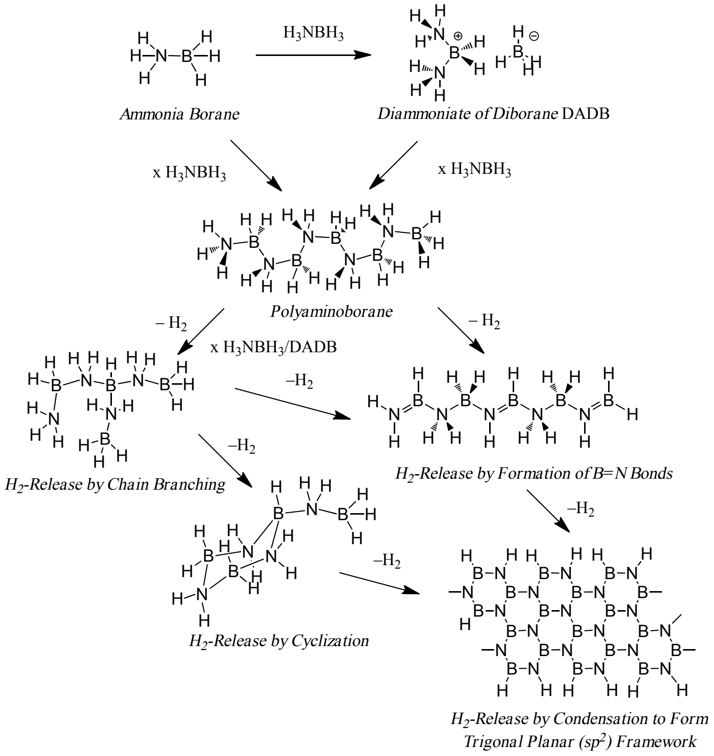


Figure 3. Proposed Pathway for Ionic Liquid Promoted H_2 Release from Ammonia Borane

3) Base-Initiated H_2 Release from AB

As shown in **Figure 4**, we also demonstrated that strong Bronsted bases, such as Proton Sponge, react with ammonia borane in either ionic-liquid or ethereal solvents to produce the $H_2NBH_3^-$ anion.[10-11] This anion then induces dehydropolymerization of ammonia borane to produce a growing polyaminoborane polymer with enhanced H_2-release rates. For example, AB reactions in 1-butyl-3-methylimidazolium chloride (bmimCl) containing 5.3 mol% PS released 2 equivalents of H_2 in 171 min at 85 °C and only 9 min at 110 °C, whereas comparable reactions without PS required 316 min at 85 °C and 20 min at 110 °C. Ionic liquid solvents proved more favorable than tetraglyme since they reduced the formation of undesirable products, such as borazine.

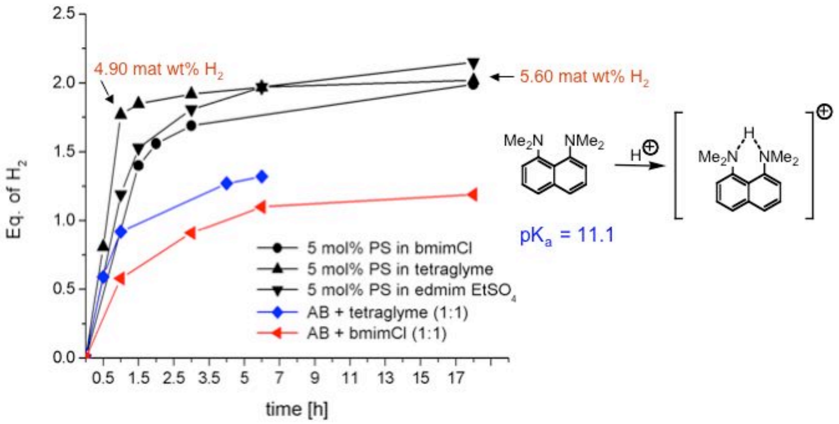


Figure 4. Proton Sponge promoted H_2-release in bmimCl ionic-liquid and tetraglyme solvents at 85 °C.

Based on extensive solid-state and solution ^{11}B NMR studies of PS-promoted reactions in progress, we proposed that the base-promoted AB H_2-release reactions precede via an anionic dehydropolymerization mechanism to produce growing anionic polyaminoborane polymers. Additional support for this mechanism was initially obtained through model studies of the reactions of the $Et_3BNH_2BH_3^-$ anion with AB.[11] This anion was synthesized by AB dehydrogenation with either lithium or potassium triethylborohydride. The crystallographically determined structure of the $[Et_3BNH_2BH_3]^- K^+ \bullet$18-crown-6 complex shown in **Figure 5** confirmed AB nitrogen-deprotonation by the triethylborohydride with the Lewis-acidic triethylborane group coordinated at the nitrogen. Subsequent reactions of $[Et_3BNH_2BH_3]^- Li^+$ with AB showed spectroscopic evidence of chain-growth products, providing further indirect support for a PS-promoted AB anionic dehydropolymerization H_2-release process.

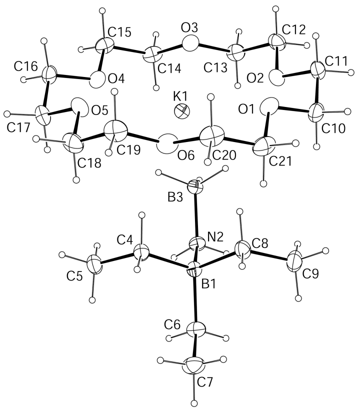
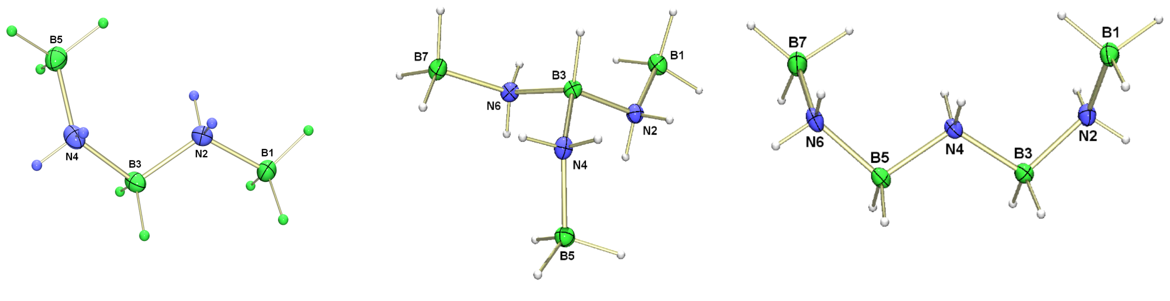


Figure 5. Crystallographically Determined Structure of $[Et_3BNH_2BH_3]^-K^+\bullet$18-crown-6.

Studies of the activating effect of the Verkade's base, 2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (VB), on the rate and extent of H_2-release from ammonia borane (AB) led to the syntheses and structural characterizations of three anionic aminoborane chain growth products that provided the first direct support for anionic dehydropolymerization mechanistic steps in the initial stages of base-promoted AB H_2-release reactions.[12] The $VBH^+[H_3BNH_2BH_2NH_2BH_3^-]$ (**3**) salt, containing a linear 5-membered anionic aminoborane chain, was produced in 74% yield via the room temperature reaction of a 3:1 AB:VB mixture in fluorobenzene solvent, while the branched and linear chain 7-membered anionic aminoborane oligomers $VBH^+[HB(NH_2BH_3)_3^-]$ **(4a)** and $VBH^+[H_3BNH_2BH_2NH_2BH_2NH_2BH_3^-]$ **(4b)** were obtained from VB/AB reactions carried out at 50 °C for 5 days when the ratio of AB to VB was increased to 4:1. X-ray crystal structure determinations confirmed that these compounds are the isoelectronic and isostructural analogs of the n-pentane, 3-ethylpentane and n-heptane hydrocarbons, respectively. The structural determinations also revealed significant interionic B-H--H-N hydrogen bonding interactions in these anions that could enhance dehydrocoupling chain-growth reactions.



3 **4a** **4b**

Figure 6. Crystallographically determined structures of structures of borane-capped aminoborane oligomers.

The isolation of these anionic chain-growth products provides strong direct evidence for the mechanistic sequence, illustrated in **Figure 7**, for base promoted AB H_2-release involving the initial formation of the previously known $[H_3BNH_2BH_3]^-$ anion,[13] followed by sequential dehydrocoupling of the B-H and H-N groups of AB with the growing borane-capped aminoborane anions. The H_2-eliminations are likely facilitated by N-H--H-B dihydrogen bonding interactions between the AB N-H protonic hydrogens and the hydridic B-H hydrogens of the growing anionic aminoborane chains. Thus, elimination of a protonic N-H on AB with one of the internal BH_2 hydridic hydrogens of **3** would yield **4a**, while the reaction of an AB with one of the **3** terminal BH_3 hydrides would give **4b**. Solid-state ^{11}B NMR studies showed that in the final stages of the AB H_2-release reactions, dehydrogenation of the initially formed sp^3-hybridized anionic-polyaminoboranes involves cyclization and formation of B=N unsaturation to ultimately yield polyborazylene-type sp^2-hybridized structures.

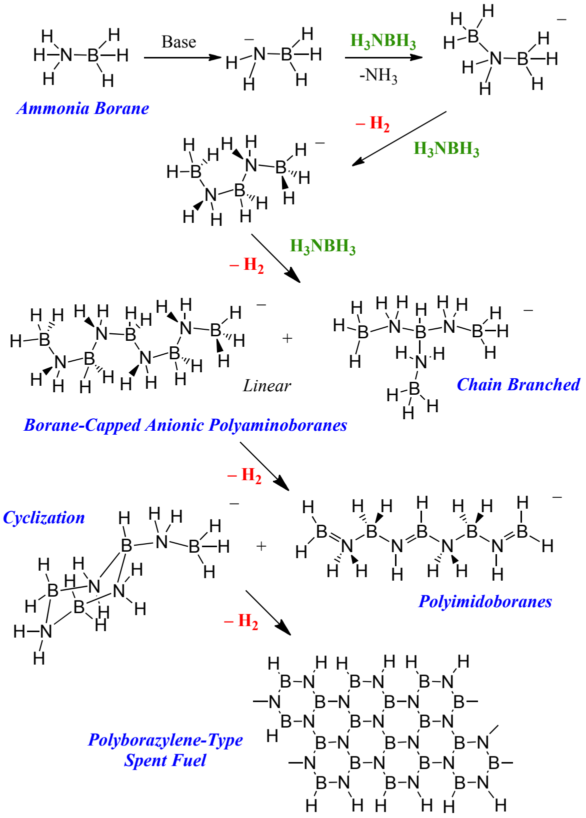
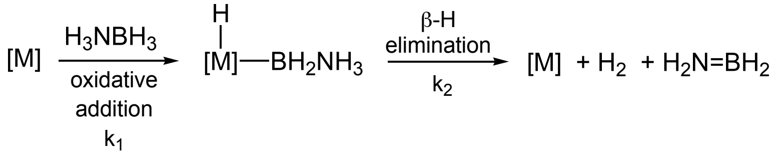


Figure 7. Proposed base-promoted anionic AB polymerization mechanism.

4) Homogenous Metal Complex-Catalyzed H_2 Release from AB

The variety of mechanisms by which metals and metal complexes effect hydrogen release from AB is manifested by the different dehydrogenation products that are formed. Using the [Rh(cod)(μ-Cl]$_2$ precatalyst (cod = 1,5-cyclooctadiene), the first detailed study by Manners and coworkers showed that AB dehydrogenation led eventually to borazine and B-N cross-linked borazine (polyborazylene).[14] It was later found, however, that some catalysts, such as the iridium ‘pincer’ bis(phosphine) complex used by Goldberg, Heinekey and coworkers,[15] rapidly release a single equivalent of hydrogen forming insoluble polyaminoborane. In evaluating the first order rate constants for disappearance of deuterated analogues of AB using Baker’s high extent Ni(NHC)$_2$ catalyst,[16] significant kinetic isotope effects were observed for dehydrogenation of H_3NBD_3 (1.7) and D_3NBH_3 (2.3). As expected, 1-d_6 gave the largest KIE (3.0). These results were taken to imply that the rate determining step(s) involve both B−H and N−H bond cleavage or that these two steps have similar rates (**Scheme 1**). While much more work has appeared over the period of our project on the pathways for metal-mediated AB activation,[17] we sought to address the origin of the striking selectivity difference discussed above.



$$[M] \xrightarrow[\text{oxidative addition } k_1]{H_3NBH_3} \overset{H}{\overset{|}{[M]}}\text{—}BH_2NH_3 \xrightarrow[k_2]{\beta\text{-H elimination}} [M] + H_2 + H_2N{=}BH_2$$

Scheme 1. Proposed reaction pathway for initial steps of metal-catalyzed AB dehydrogenation.

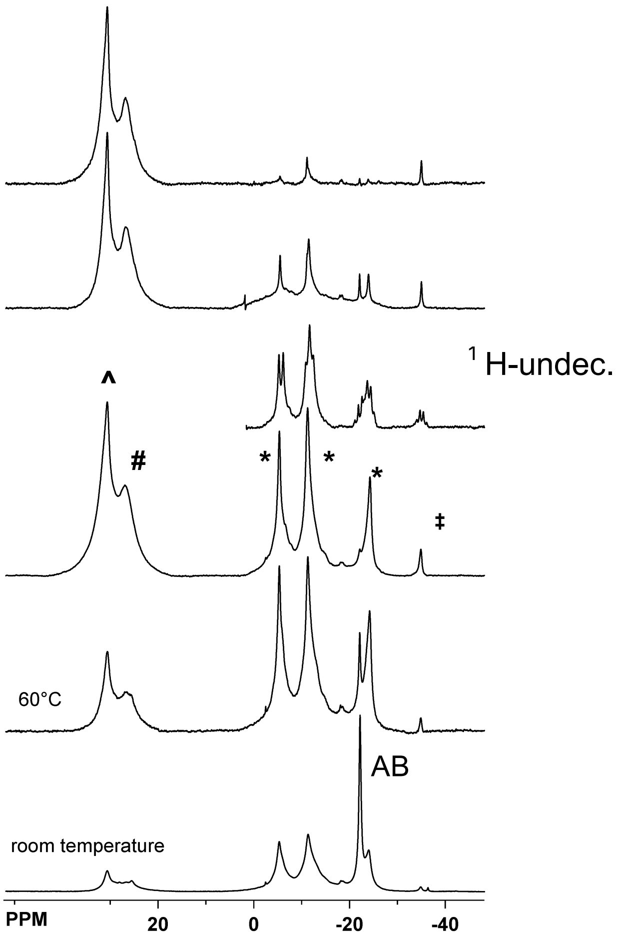
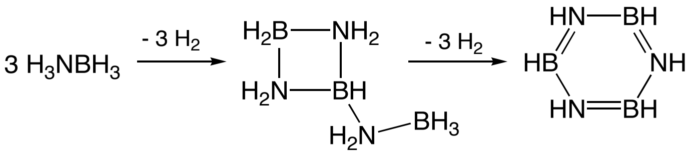


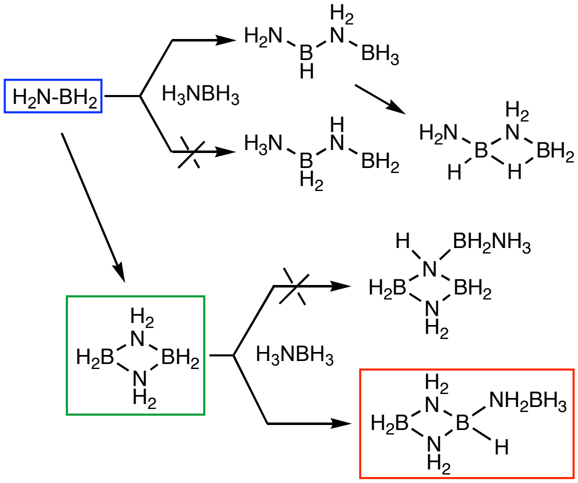
Figure 8. ^{1}H-decoupled ^{11}B NMR spectra of Ni(NHC)$_2$-catalyzed AB dehydrogenation in glyme. After 10 h at 25°C (bottom spectrum), the tube was placed in the NMR probe at 60°C and conversion of the intermediate (*) to borazine (^) and polyborazylene (#) monitored every 10 min. Minor products in top spectrum are $[H_2NBH_2]_3$ and $H_3B(NHC)$ (‡).

We began our studies by detailed monitoring of a variety of metal-catalyzed dehydrogenations in tetrahydrofuran (THF) and glyme (1,2-dimethoxyethane) solvents at different temperatures using multinuclear NMR spectroscopy. An unusual intermediate was identified by ^{11}B and ^{11}B-^{1}H NMR correlation experiments as the BN analog of ethylcyclobutane. More surprisingly, our Ni catalyst appeared to convert directly from AB to ECB to borazine (**Scheme 2, Figure 8**). The chemical shifts of ECB (BH: -5, BH_2: -12, BH_3: -23 ppm) matched well those predicted using DFT by Butterick and Sneddon (-4.4, -11.2, -23.8 ppm).



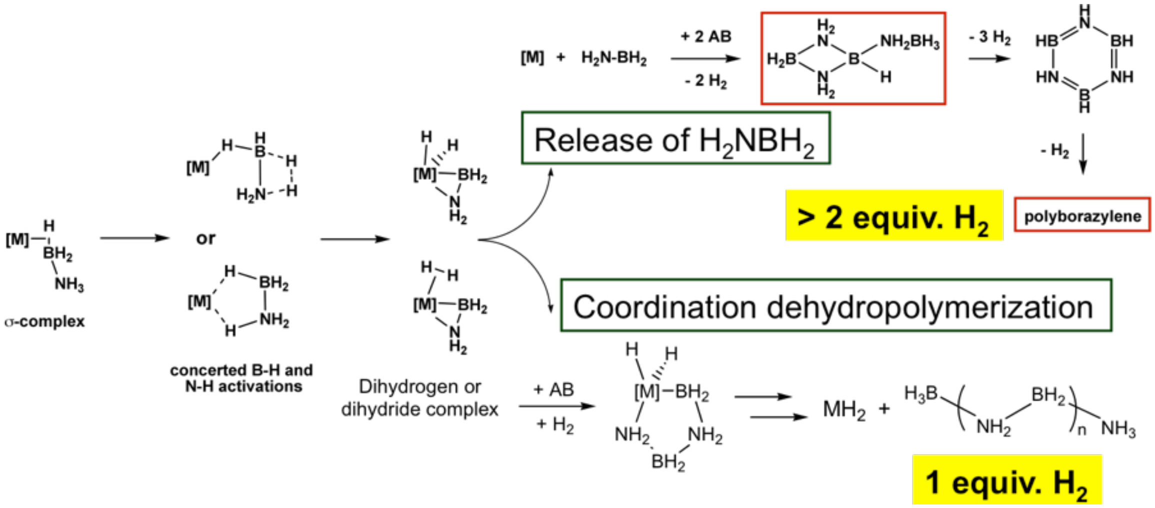
Scheme 2. AB Dehydrogenation reaction progression for one class of metal catalysts.

How is this unusual intermediate formed in such high yield? In previous experiments with N-substituted amine-boranes, we and others had observed initial formation of the monomeric aminoborane R_2NBH_2 that subsequently formed more stable cyclic dimers or trimers. The parent aminoborane, however, is much more reactive and has been shown previously in matrix studies to oligomerize rapidly above -120°C.[18] No examples of coordination of aminoborane to a transition metal had yet been reported either experimentally or theoretically. We reasoned that formation of this reactive compound in the presence of an excess of AB would likely result in reactive trapping by the latter (**Scheme 3**).[19]



Scheme 3. Trapping of aminoborane by AB.

In order to test our trapping hypothesis, we employed cyclohexene as an external trapping agent as aminoborane should be an excellent hydroboration agent. Indeed, addition of equal volumes of THF and cyclohexene using Manners' Rh catalyst gave complete trapping of the aminoborane as evidenced by formation of the doubly hydroborated product, Cy_2BNH_2. Even more interestingly, the same experiments using the Ir 'pincer' catalyst had no effect on the product distribution! It thus seems that the more productive Ni and Rh catalysts are able to eject the aminoborane from their coordination sphere whereas the Ir catalyst retains the aminoborane as a ligand that presumably reacts with additional equivalents of AB to build the polyaminoborane chain (**Scheme 4**). In keeping with this proposal, by performing the trapping experiments at 60°C, we now observe some hydroboration products even for the Ir catalyst, suggesting that at least some dissociation of the coordinated aminoborane ligand is occurring.



Scheme 4. Selectivity of H_2 release from AB depends on coordination of aminoborane, H_2NBH_2.

In our efforts to isolate the ECB intermediate so we could investigate catalysis of the second equivalent of H_2 from AB, we discovered that the Schwartz catalyst (Cp_2ZrHCl) can be used as an efficient precatalyst for the synthesis of this key intermediate. To our surprise, however, further studies suggest that this intermediate is actually the BN analog of *ethylcyclohexane*, an aminoborane *tetramer* (**Figure 9**). Additional DFT studies are in progress with David Dixon (Alabama) to understand the selective formation of ECH from AB and aminoborane.

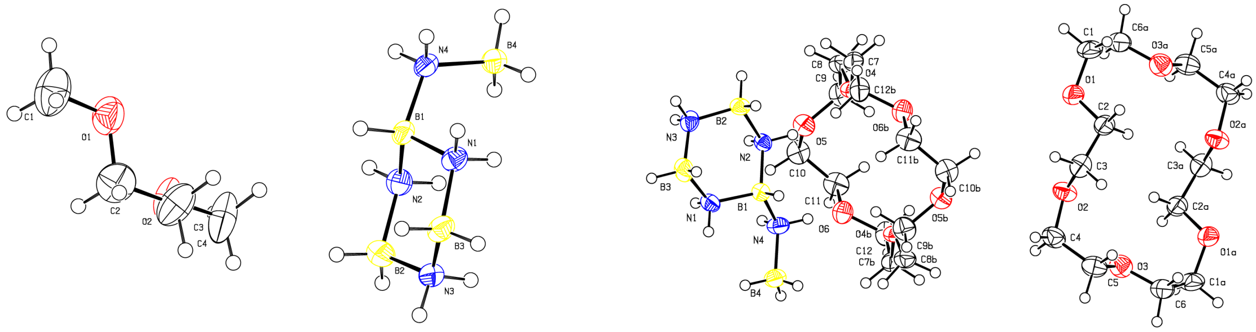


Figure 9. Crystal structures of ECH stabilized by hydrogen bonding with glyme (left) and 18-crown-6 (right).

5) Homogeneous Catalysis in Ionic Liquids

In our initial studies using $RuCl_2(PMe_3)_2$ complex, we showed that it was converted to a stable catalyst resting state, $RuH(BH_4)(PMe_3)_3$, under AB dehydrogenation conditions. Unfortunately, in ether solvents hydrogen release was slow (ca. 1 TO/min at 60°C) and the major product was insoluble polyaminoborane. Employing low concentrations of this catalyst in a variety of ionic liquids, however, we found that those with the stronger coordinating ethylsulfate anions effected hydrogen loss from AB *at 25° C without formation of insoluble polyaminoborane.* (**Figure 10**).[21]

In recent work we found that an iron dihydride complex containing phosphine supporting ligands is a robust homogeneous pre-catalyst for selective synthesis of polyaminoborane. Moreover, reaction of the corresponding hydrido-iron (II) cationic complex in imidazolium ionic liquids gives borazine and polyborazylene selectively. While ionic liquids necessarily increase the weight of the AB-based storage system, they may offer a more desirable fuel form with higher volumetric density relative to solid alternatives. Moreover, passing a liquid over a heterogeneous catalyst has already been demonstrated as a controllable hydrogen release method for transportation applications.[22]

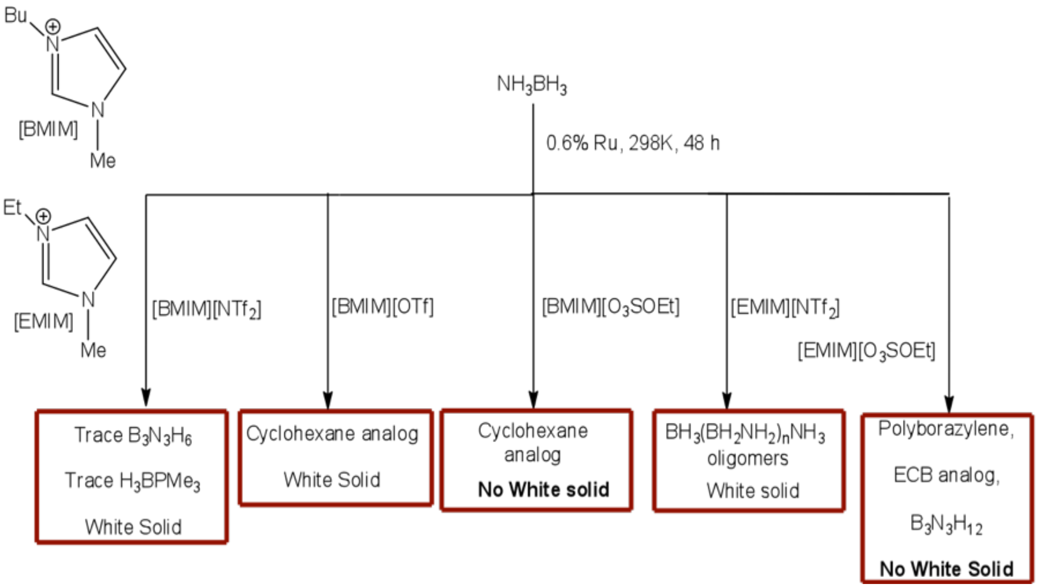


Figure 10. Ru complex-catalyzed AB release in ionic liquids

6) Heterogeneous Iron Catalysts

Catalyst robustness, selectivity and recyclability are the main challenges in this field that have not been completely solved. Looking to more practical catalysts, a heterogeneous iron catalyst made by *in situ* AB reduction of $FeCl_2$, shows excellent selectivity for borazine and PB (i.e. negligible insoluble polyaminoborane formation). Characterization of the catalyst by SEM, EDX and XPS suggests that it is has a novel Fe on Fe boride structure (**Figure 11**). The heterogeneous catalyst was recovered and reused several times with the same efficiency. This first long-lived, selective heterogeneous catalyst system[23] is most desirable for fuel cells from the engineering point of view, since hydrogen release can be controlled by flowing the ammonia-borane/IL solution over the catalyst bed.

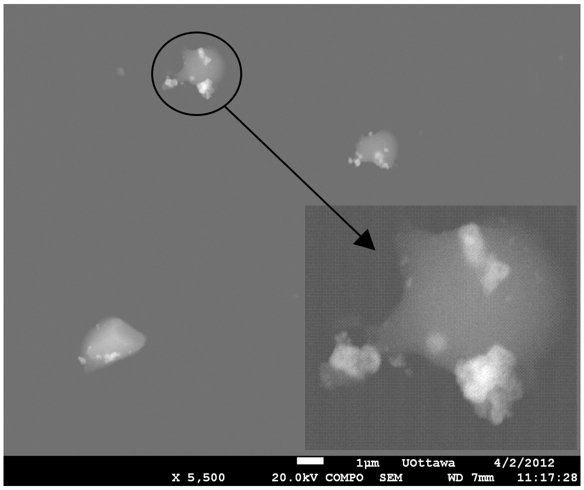


Figure 11. SEM images of the used heterogeneous iron catalyst. Iron particles (bright spots) are sitting on *in-situ* formed iron boride support (based on EDX analysis).

7) Conclusions and Future Outlook

Our completed DOE sponsored project has led to both the discovery and continued improvement of a variety of promising H_2-release systems based on amine boranes. These studies have also demonstrated that H_2-release from chemical hydrides can occur by a number of different mechanistic pathways and strongly suggest that optimal chemical-hydride based H_2-release systems may require the use of synergistic activation methods, including ionic-liquid, bases and/or transition metal catalysts, to induce H_2-loss from chemically different intermediates formed during release reactions.

8) Research Team

At Penn, Sneddon group co-workers included postdoctorals, Martin Bluhm and Laif Alden, graduate students Dan Himmelberger, William Ewing, Emily Berkeley and Chang Won Yoon and undergraduate student Allegra Marchione. At Los Alamos National Lab, Baker co-workers included Drs. Frances Stephens and Vincent Pons, while at uOttawa Drs. Giovanni Rachiero, Will Wright, Richard Burchell, Matthew Rankin and Hassan Kalviri were joined by visiting graduate students Felix Gaertner and Johannes Thomas from the LIKAT catalysis center in Rostock, Germany and Morgane LeFur from ENSICAEN in France.

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10) Publications and Presentations

Publications

1. Bluhm, M.; Bradley, M. G.; Butterick, III, R.; Kusari, U.; Sneddon, L. G. Amine Borane-based Chemical Hydrogen Storage: Enhanced Ammonia-Borane Dehydrogenation in Ionic Liquids," *J. Am. Chem. Soc.* **2006**, *128*, 7748-7749.
2. Yoon, C. W.; Sneddon, L. G. "Ammonia Triborane: A Promising New Candidate for Amine Borane-Based Chemical Hydrogen Storage," *J. Am. Chem. Soc.* **2006**, *128*, 13992-13993.
3. Stephens, F. H.; Pons, V.; Baker, R. T. "Ammonia-Borane: The Hydrogen Storage Material *Par Excellence*?" *Dalton Trans.* **2007**, 2613-2626.
4. Alden, L. R.; Griffin, C. P.; Sneddon, L. G. "Metal-Catalyzed Hydrogen Release from Ammonia Borane in Ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, *53*, 670-671.
5. Himmelberger, D.; Bluhm, M.; Sneddon, L. G. "Proton Sponge Induced Release from Ammonia Borane in Ionic Liquids" *Prepr. Sym., ACS Div. Fuel Chem.* **2008**, *53*, 666-667.

6. Pons, V.; Baker, R. T. “Taking the High Road: Soluble B-N High Polymers from Metal Complex-Catalyzed Amine Borane Dehydrogenation,” *Angew. Chem. Int. Ed.* **2008**, 47, 9600-9602.
7. Shaw, W. J.; Linehan, J. C.; Szymczak, N. K.; Heldebrant, D. J.; Yonker, C.; Camaioni, D. M.; Baker, R. T.; Autrey, T. “*In Situ* Multinuclear NMR Studies of the Thermal Decomposition of Ammonia Borane in Solution,” *Angew. Chem., Int. Ed.* **2008**, *47*, 7493-7497.
8. Yoon, C. W.; Carroll, P. J.; Sneddon, L. G. "Ammonia Triborane: A New Synthesis, Structural Determinations and Hydrolytic Hydrogen-Release Properties" *J. Am. Chem. Soc.* **2009**, *131*, 855-864.
9. Himmelberger, D.; Chang, W. Y.; Bluhm, M.; Carroll, P. J.; Sneddon, L. G. “Base-promoted Ammonia Borane Hydrogen Release,” *J. Am. Chem. Soc.* **2009**, *131*, 14101-14110.
10. D. W. Himmelberger, L. R. Alden, M. E. Bluhm, P. J. Carroll and L. G. Sneddon ”Ammonia Borane Hydrogen Release in Ionic Liquids” *Inorg. Chem.* **2009**, *48*, 9883-9889.
11. Ewing, W. C.; Marchione, A.; Himmelberger, D.; Carroll, P. J.; Sneddon, L. G. “Syntheses and Structural Characterizations of Anionic Borane-Capped Ammonia-Borane Oligomers: Evidence for Ammonia Borane H_2-Release via a Base-Promoted Anionic Dehydropolymerization Mechanism” *J. Am. Chem. Soc.* **2011**, *133*, 17093-17099.
12. Wright, W. R. H.; Berkeley, E. R.; Alden, L. R.; Baker, R. T.; Sneddon, L. G. “Transition Metal-Catalyzed Ammonia-Borane Dehydrogenation in Ionic Liquids,” *Chem. Commun.* **2011**, *47*, 3177-3179.
13. Wright, W. R. H.; Menant, C. L.; Baker, R. T. “Tuning the Selectivity of Transition-Metal-Catalyzed Ammonia-Borane Dehydrogenation in Ionic Liquids,” submitted for publication.
14. Kalviri, H.; Gaertner, F.; Korobkov, I.; Baker, R. T. “Metal-Catalyzed Ammonia-Borane Dehydrogenation: Addressing the Second Equivalent,” submitted for publication.
15. Kalviri, H.; LeFur, M.; Baker, R. T. “Robust Iron Heterogeneous Catalyst for Ammonia Borane Dehydrogenation,” submitted for publication.

Three additional project publications from uOttawa are in preparation.

Presentations

1. L. G. Sneddon, M. E. Bluhm, L. Alden, D. Himmelberger and M. G. Bradley “Amineborane Based Chemical Hydrogen Storage” invited lecture in the Sheldon Shore Award Symposium at the National American Chemical Society Meeting, Chicago, March, 2007.
2. L. G. Sneddon, M. E. Bluhm, L. Alden, D. Himmelberger and M. G. Bradley “Amineborane Based Chemical Hydrogen Storage" invited lecture at the Symposium on Hydrogen Storage at the Materials Science and Technology Conference, Detroit, September, 2007.
3. L. G. Sneddon “Amineborane Based Chemical Hydrogen Storage” invited lecture at the DOE Tech Team Meeting, Detroit, Michigan, January 2008.
4. L. R. Alden, M. E. Bluhm, C. P. Griffin, L. G. Sneddon "Improved Hydrogen Release from Ammonia Borane in Ionic Liquids" Materials Research Meeting, San Francisco, March, 2008.

5. B. Ewing and L. G. Sneddon "Progress Towards Ammonia Borane Regeneration" Materials Research Meeting, San Franciso, March, 2008.
6. L. G. Sneddon "Borane-Based Chemical Hydrogen Storage" Boron Americas Meeting, St. Louis, May, 2008.
7. Laif Alden, C. P. Griffin, and L. G. Sneddon "Metal Catalyzed Hydrogen Release from Ammonia Borane in Ionic Liquids " National American Chemical Society Meeting, Philadelphia, August, 2008.
8. D. Himmelberger, M. Bluhm and L. G. Sneddon "Proton Sponge Induced Hydrogen Release in Ionic Liquids" National American Chemical Society Meeting, Philadelphia, August, 2008
9. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" invited lecture at the International Meeting on Boron Chemistry Barcelona, Spain, September 2008.
10. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" invited lecture at the DOE Tech Team Meeting, Detroit, Michigan, March, 2009.
11. E. Berkeley, L. Alden, P. Carroll and L. G. Sneddon "Ammonia borane dehydrogenation using metal catalysts in ionic liquids" poster at the National American Chemical Society Meeting, Washington D.C., August 2009.
12. D. Himmelberger, L. Alden, M. Bluhm and L. G. Sneddon "Activated hydrogen release from ammonia borane in ionic liquids" National American Chemical Society Meeting, Washington D.C., August 2009.
13. D. Himmelberger, M. E. Bluhm, L. R. Alden, C. W. Yoon, B. Ewing, E. Berkeley, M. G. Bradley and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" invited lecture at Indiana University, November 2009.
14. D. Himmelberger, M. E. Bluhm, L. R. Alden, C. W. Yoon, B. Ewing, E. Berkeley, M. G. Bradley and L. G. Sneddon "Amineborane Chemical Hydrogen Storage" Riley O. Schaeffer Lecturer at the University of New Mexico, November 2009.
15. E. R. Berkeley, L. R. Alden, D. W. Himmelberger, M. E. Blum,and L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" Boron Americas Meeting, East Lansing, Michigan, June, 2010.
16. L. G. Sneddon, D. W. Himmelberger, M. E. Bluhm, L. R. Alden, E. Berkeley, W. R. H. Wright, G. P. Rachiero and R. T. Baker "Amine Borane Based Chemical Hydrogen Storage" International Meeting on Coordination chemistry, Adelaide, Australia, July, 2110.
17. E. R. Berkeley, L. R. Alden, L. G. Sneddon "Metal catalysed hydrogen release from ammonia borane in ionic liquids" International Meeting on Boron Chemistry, Niagara Falls, Canada, September 2011.
18. L. G. Sneddon "Amineborane Based Chemical Hydrogen Storage" American Chemical Society Philadelphia Section Award Lecture, Philadelphia, October 20 2011.
19. Pons, V.; Baker, R. T.; Camaioni, D. M.; Li, J., "Spit it out, already! Mechanistic Studies of Metal-Catalyzed Dehydrogenation of Ammonia-Borane," presented at the Spring ACS Meeting, New Orleans, LA, March, 2008.
20. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," McElwain Lecture, invited lecture at University of Wisconsin, April, 2008.
21. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at University of Zurich, ETH, Lausanne University, Switzerland and Toulouse University, France, April, 2008.
22. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Canadian Chemistry

Conference, Edmonton, Canada, May, 2008.

23. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Inorganic Chemistry Gordon Research Conference, Newport, RI, July, 2008.
24. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at SACIQ Conference, Quebec City, Canada, August, 2008.
25. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at International Boron Conference, Platja D'Aro, Spain, September, 2008.
26. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Humphrey Symposium, University of Vermont, September, 2008.
27. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Celebration of Nanomedicine and Materials, University of Missouri, October, 2008.
28. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Materials Science Institute Retreat, University of Oregon, December, 2008.
29. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Hydrogen and Hydrogen Storage Materials, Bangalore, India, January, 2009.
30. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Technical University Berlin, February, 2009.
31. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at University of Texas, April, 2009.
32. Baker, R. T. "Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation: a Promising Material for Chemical Hydrogen Storage," invited lecture at Korea University, Korea Institute for Science and Technology, 10th Asian Hydrogen Energy Conference, April, 2009.
33. Rachiero, G. P.; Kivi, C. E.; Baker, R. T., "Mechanistic Insights into the Role of Lewis Acidic Metal Complexes as Amine-Borane Dehydrogenation Catalysts," oral presentation at Inorganic Chemistry Discussion Weekend, Guelph University, Ontario, Canada, November, 2009.
34. Baker, R. T. "Pulling the Weight: Base Metal-Catalyzed Dehydrogenation of Amine-Borane Fuel Blends," invited IGERT lecture at UMass Amherst, April 2009.
35. Baker, R. T. "Hydrogen storage options for long-haul transportation: Can amine-boranes pull their own weight?" invited Sigma Xi lecturer, McGill University, Montreal, Quebec, Canada, February, 2010.
36. Baker, R. T. "Catalyzed Dehydrogenation of Amine-Borane Fuel Blends," invited lecture at NRC Hydrogen Storage Materials Workshop, Ottawa, Canada, April, 2010.
37. Baker, R. T. "Catalyzed Dehydrogenation of Amine-Borane Fuel Blends," invited lecture at Canadian Catalysis Symposium, Banff, Alberta, May, 2010.

38. Baker, R. T. “Mechanistic Studies of Metal-Catalyzed Amine-Borane Dehydrogenation,” invited lecture at Canadian Society of Chemistry National meeting, Toronto, Canada, May, 2010.
39. Burchell, R.; Rachiero, G. P.; Kivi, C. E.; Baker, R. T., Cationic Manganese Phosphine Catalysts for Amine-Borane Dehydrogenation, oral presentation at Canadian Society of Chemistry national meeting, Toronto, Canada, June, 2010.
40. Wright, W. R. H.; Baker, R. T.; Sneddon, L. G. Transition Metal Complex-Catalyzed Dehydrogenation of Amine-Boranes in Ionic Liquids, oral presentation at Canadian Society of Chemistry national meeting, Toronto, Canada, June, 2010.
41. Baker, R. T. “Catalyzed Dehydrogenation of Amine-Borane Fuel Blends,” invited lecture at Materials Forum, Montecatini Terme, Italy, June, 2010.
42. Baker, R. T. “Catalyzed Dehydrogenation of Amine-Borane Fuel Blends,” Catalysis and Photochemistry Symposium, Rostock, Germany, June, 2010.
43. Baker, R. T. “Mechanistic Studies of Catalyzed Amine-Borane Dehydrogenation for H_2 Storage,” University of Kentucky, October, 2010.
44. Baker, R. T. “Mechanistic Studies of Catalyzed Dehydrogenation of Ammonia-Borane for Hydrogen Storage,” Entretiens Jacques Cartier Catalysis Colloquium, Lyon, France, November, 2010.
45. Baker, R. T. and Sneddon, L. G. “Metal-Catalyzed Dehydrogenation of Amine-Borane Fuel Blends,” Symposium on Advances in Chemistry and Materials for Hydrogen Storage, Pacifichem, Honolulu, HI, December, 2010.
46. Baker, R. T. “Metal Complex-Catalyzed Dehydrogenation of Early Main Group BN Compounds,” Symposium on Early Main Group Chemistry, Pacifichem, Honolulu, HI, December, 2010.
47. Baker, R. T. “Controlling Amine-Borane Dehydrogenation with Homogeneous Catalysis,” Symposium on Organoboron, Organosilicon and Organophosphorus Compounds as Optoelectronic and Energy-related Materials, Pacifichem, Honolulu, HI, December, 2010.
48. Baker, R. T. “Drop-In’ Liquid Fuels: Catalyzed Ammonia-Borane Dehydrogenation in Ionic Liquids,” Swiss Chemical Society Spring meeting, Zurich, Switzerland, February, 2011.
49. Baker, R. T. “Mechanistic Studies of Catalyzed Amine-Borane Dehydrogenation for H_2 Storage,” Wolczanski Organometallic Chemistry Award Symposium, Spring ACS meeting, Anaheim, CA, March, 2011.
50. Baker, R. T. “Mechanistic Studies of Catalyzed Amine-Borane Dehydrogenation for H_2 Storage,” Coates lecture, University of Wyoming, April, 2011.
51. Baker, R. T. “’Drop-In’ Liquid Fuels: Catalyzed Ammonia-Borane Dehydrogenation in Ionic Liquids,” Symposium on Hydrogen Storage, Canadian Society of Chemistry national meeting, Montreal, Canada, June, 2011.
52. Baker, R. T. “Materials Requirements for Transportation Applications using Ammonia-Borane Dehydrogenation,” Symposium on 21st Century Materials, Canadian Society of Chemistry national meeting, Montreal, Canada, June, 2011.

11) Statement of Unexpended Funds

No funds remained unexpended or uncommitted at the end of the final budget period.