IV.A.3 Lightweight Metal Hydrides for Hydrogen Storage

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Fiscal Year (FY) 2012 Objectives

- Develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE FreedomCAR targets.
- Synthesize and study aluminoborane compounds for hydrogen storage.
- Synthesize and study other lightweight, high-capacity boron hydride for hydrogen storage.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Multi-year Research, Development and Demonstration Plan.

(D) Durability/Operability
(E) Charging/Discharging Rates
(J) Thermal Management
(P) Lack of Understanding of Hydrogen Physisorption and Chemisorption

Technical Targets

This project is conducting synthesis and structure studies of the aluminoborane compounds. Insights gained from these studies will be applied towards the design and synthesis of hydrogen storage materials that may meet the following DOE 2010 hydrogen storage targets:

- Cost: $3-7/gasoline gallon equivalent at pump
- Specific energy: 1.5 kWh/kg (4.5 wt% H)
- Energy density: 0.9 kWh/L (0.028 kg/L)

FY 2012 Accomplishments

- In collaboration with both Northwestern University and National Institute of Standards and Technology (NIST), we have identified the structure of the aluminoborane, AlB_4H_{11}.
- We studied the formation mechanism of AlB_4H_{11}.
- We determined the formation mechanism of the diammoniate of diborane, DADB; and based on the mechanistic understanding we developed a convenient synthetic method for pure DADB.
- The stability of DADB in different solvents was investigated systematically.

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Introduction

The DOE defines onboard hydrogen storage for mobile vehicles as a "Grand Challenge". It is one of the biggest hurdles to the implementation of hydrogen-powered vehicles. Metal hydrides have the advantages of the highest volumetric density, relatively low working pressure, and reasonable working temperature range. The disadvantage of current reversible hydrides is a significant weight penalty. Metal borohydrides have among the highest gravimetric hydrogen storage capacities with the potential to meet the DOE gravimetric density targets and to offset the system weight penalties. However, desorption temperature, reversibility and formation of gaseous borane compounds during desorption are challenging issues for these materials. This project attempts to develop a high-capacity lightweight hydride for reversible vehicular hydrogen storage, capable of meeting or exceeding the 2010 DOE/FreedomCAR targets.

Approach

- Explore aluminoborane compounds such as AlB_4H_{11} and other high-capacity, lightweight boron hydrides for hydrogen storage.
- Study the structure and the formation mechanisms of AlB_4H_{11} using multiple techniques such as solution nuclear magnetic resonance (NMR), infrared (IR),

neutron vibrational analysis (NVS), and first-principles predictions.

Results

1. The Study of the Structure and Formation Mechanism of AlB_4H_{11}

The aluminoborane compound, AlB_4H_{11}, has shown attractive properties as potential hydrogen storage material [1], The properties of AlB_4H_{11} are quite different from other borane compounds, suggesting a potentially unique structure. The previous structure proposed by Himpsl and Bond [2] based on the analogue to pentaborane (B_5H_{11}) is inconsistent with the IR and ^{11}B NMR spectra of AlB_4H_{11} [1]. Hence, the determination of the AlB_4H_{11} structure is significant for the understanding of its stability and hydrogenation/dehydrogenation properties.

The amorphous nature of AlB_4H_{11} and its insolubility in organic solvents prevent us from determining its structure using X-ray diffraction (XRD), neutron diffraction, solution NMR, or mass spectrometry techniques. Solid-state NMR and vibrational spectra were found to be insufficient for even speculating on its structure. Instead, a novel combination of experimental measurements (NMR, IR, and NVS) with a theoretical prediction method (the Monte-Carlo based prototype electrostatic ground state (PEGS) search with density functional theory (DFT) calculations) are used to identify local structures of this amorphous AlB_4H_{11} phase. The structure identification is a closely coupled theoretical and experimental study involving the Ohio State University, Northwestern University, and NIST.

Among the predicted structures (Figure 1), Str-00 is the most stable one which has the best overall agreement with experimental observations. The AlB_4H_{11} structure contains distinct $[BH_4]$ and $[B_3H_7]$ units without any $[AlH_4]$ units. It forms a $-[B_3H_7]-Al(BH_4)-$ polymer chain with the $[BH_4]$ units twisted relative to each other perpendicular to the chain direction and bonded to Al, and a chain backbone consists of $[B_3H_7]$ and Al where the $[B_3H_7]$ unit exhibits a triangular boron configuration.

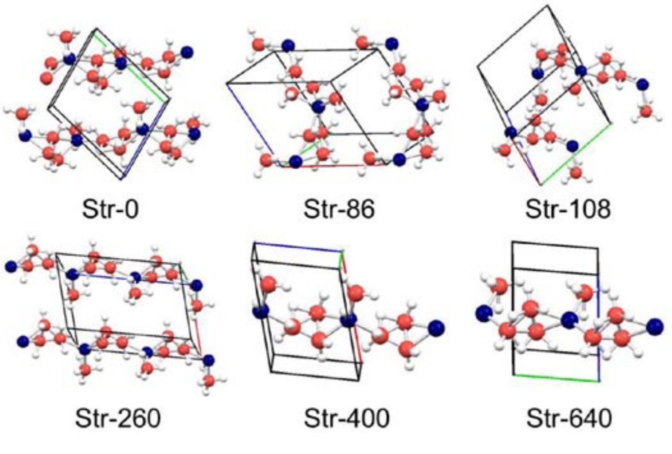

FIGURE 1. PEGS+DFT theoretically predicted AlB_4H_{11} crystal structures. The number in the nomenclature is the energy difference relative to the theoretically predicted lowest-energy AlB_4H_{11} structure. Al = blue, B = orange, H = white gray.

In order to further confirm the predicted structure, we compare the simulated ^{11}B NMR spectra of the predicted structures and the experimental solid state ^{11}B NMR spectrum [1]. The ^{11}B NMR spectra of the four predicted 2-fu structures (they are labeled as Str-0, Str-86, Str-108 and Str-260, respectively, in Figure 1) have been simulated using the Gauge Including Projector Augmented Waves method as implemented in the Quantum ESPRESSO package [3]. The simulated ^{11}B NMR indicates that two sets of signals are separately located at higher and lower fields, which is consistent with the solid ^{11}B NMR spectrum of AlB_4H_{11}. The simulated chemical shifts vary from structure to structure but are generally comparable with the experimental AlB_4H_{11} solid-state spectrum that has two broad signals located at around δ -38.8 and -51.0 ppm respectively at a roughly 2:1 ratio [1]. Three boron signals for the lowest energy structure (Str-0) are located at higher field (δ -58.48, -60.96, and -61.82 ppm) and five boron signals at lower field (δ -33.45, -41.29, -46.50, -46.61, and -47.61 ppm). The ratio of the two sets of signals (5:3) is close to the experimental value (2:1). Two broad peaks created by stacking together the two sets of the simulated NMR signals closely resemble the experimental solid-state ^{11}B NMR spectrum of AlB_4H_{11} with the peaks positions only differ by about 8~10 ppm (higher field) (Figure 2).

Two sets of boron signals are predicted for Str-86 with one set (two signals) located at δ -59.41 and -70.40 ppm and

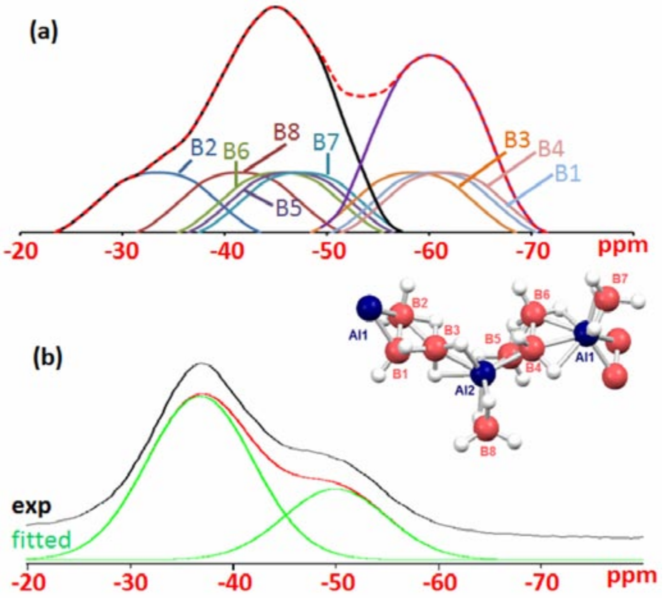

FIGURE 2. ^{11}B NMR spectra of AlB_4H_{11} (a) simulated based on the predicted Str-0 and (b) experiment

the other set (six boron signals) at δ -30.5 to 44.13 ppm. The intensity ratio of the two sets is 3:1. Both Str-108 and Str-260 have four boron signals at higher field and four boron signals at lower field with the integrated peak intensity ratio of 1:1.

As we discussed above, the comparison of the simulated ^{11}B NMR spectra of these structures with the solid-state ^{11}B NMR spectrum of AlB_4H_{14} indicates that the lowest-energy structure (Str-0) has the best merit in terms of both peak shapes and the peak intensity ratio, thus we believe Str-0 is the best representation of the AlB_4H_{11} structure.

We also studied the formation mechanism of AlB_4H_{11}. The reaction of $Al(BH_4)_3$ and diborane was monitored by ^{11}B and $^{11}B\{^1H\}$ NMR spectroscopy. The two starting materials, $Al(BH_4)_3$ and diborane, are each alone stable at 100°C in benzene solution. The ^{11}B and $^{11}B\{^1H\}$ NMR spectra of the mixture of $Al(BH_4)_3$ and diborane indicate that when reaction starts, two sets of small peaks simultaneously appear at nearly the signal of $Al(BH_4)_3$ (δ -33.4, -36.89 -38.1, -43.6, and -44.7 ppm) and at δ -52.6 and 53.8 ppm. The low-field peaks at around δ -33.4 to -44.7 ppm are related to an intermediate of $[HAl(BH_4)_2]_n$ with different states of aggregation [4], and the high-field peaks at δ -52.6 and -53.8 ppm might be related to a B_3H_7 group, which might not exist alone, but interacting with $[HAl(BH_4)_2]_n$ once it is formed. Therefore, the formation mechanism of AlB_4H_{11} is probably: 1) B_2H_6 initially pulls a BH_3 unit from $Al(BH_4)_3$ to form $[HAl(BH_4)_2]$ and B_3H_7 with one H_2 elimination; 2) two intermediates of $[HAl(BH_4)_2]$ and B_3H_7 interact in an unknown way once they are formed; and 3) a $-[B_3H_7]-Al(BH_4)-[B_3H_7]-$ polymer chain is formed as shown in Scheme 1.

$$Al(BH_4)_3 + B_2H_6 \rightarrow 1/n\ [HAl(BH_4)_2]_n + B_3H_9 \rightarrow 1/n\ [Al(B_3H_7)(BH_4)]_n + ½\ BH_3 + 2\ H_2$$

SCHEME 1. The formation mechanism of AlB_4H_{11}

The proposed mechanism is derived from both the ^{11}B NMR spectra and the literature work. It was reported that when $Al(BH_4)_3$ reacted with CO at ambient temperature, the CO molecule pulled a BH_3 moiety from $Al(BH_4)_3$ to form $[HAl(BH_4)_2]_n$ and $CO{\cdot}BH_3$ [4]. Comparing the reaction of $Al(BH_4)_3$ with CO at room temperature and with B_2H_6 at 100°C, it is reasonable to assume that B_2H_6 performed the same function as CO to pull a BH_3 group out from $Al(BH_4)_3$ to form a B_3H_9 unit and $[HAl(BH_4)_2]$. For the room-temperature reaction with CO, two signals of BH_{4-} were detected at δ -38.0 and -43.3 ppm, since two states of aggregation of $[HAl(BH_4)_2]_n$ (n = 1 or 2) were formed. This was supported by the formation of monomer and dimer compounds, $[HGa(BH_4)_2]$, and $[HGa(BH_4)_2]_2$, in a similar reaction of $Ga(BH_4)_3$ with CO. Thus, an elevated-temperature reaction with B_2H_6 could lead to higher oligomers of $[HAl(BH_4)_2]$; and the small peaks observed at δ -33.4 to -44.7 ppm are believed to represent polymeric $[HAl(BH_4)_2]_n$ with more than two different states of oligomers. These polymer species probably have limited solubility in the reaction media at this stage, so they were decreasingly detected in ^{11}B NMR spectroscopy as the reaction proceeded.

The reaction of B_2H_6 with a BH_3 unit to produce B_3H_9 followed by conversion to triborane, B_3H_7 with a H_2 molecule elimination has been extensively investigated both theoretically and experimentally [5]. The triborane could be stabilized by coordination with bases. Three boron atoms in B_3H_7 display one or two signals over a wide range when B_3H_7 is coordinated to different bases. In adducts of $CO{\cdot}B_3H_7$ and $PH_3{\cdot}B_3H_7$, one boron signal appeared at δ -51.2 ppm which is close to the small peaks observed in ^{11}B NMR in this experiment [6]. It is worthy to note that, although the existent format of B_3H_7 in the reaction system is unknown, it seems to interact with $[HAl(BH_4)_2]_n$. So we presumed the small peaks at δ -52.6 and -51.3 ppm were associated with a B_3H_7 group which interacted with $[HAl(BH_4)_2]_n$ in some way. At an initial stage, these species could be detected in ^{11}B NMR spectra. The assignment is confirmed by simulation B NMR spectra in which the chemical shifts of borons in the B_3H_7 group have a wide range from δ -30.5 ppm to -70.4 ppm. Another mechanism was also proposed [1].

2. Formation Mechanism and New Synthetic Method of DADB

DADB, an isomer of ammonia borane (AB) with 19.6 wt% hydrogen, has recently been studied as a potential hydrogen storage material. DADB was first observed in the 1920s in a mixture with ammonia borane (NH_3BH_3, AB) produced when ammonia reacted with diborane [7]. Though DADB has been known for almost a century, a convenient synthetic method for pure DADB has not been developed partly due to a lack of understanding of its formation mechanism. Many factors such as steric effects and solvent properties were considered and discussed in the literature, but were found to be insufficient to explain the formation mechanism of DADB [8]. Conflicting conclusions were drawn for different systems concerning different factors. To develop a more satisfactory explanation, we studied the formation mechanism of DADB and then employed the understanding to develop a convenient method to synthesize it.

We derived a new three-step mechanism for the formation of DADB in the reaction of ammonia with $THFBH_3$. Ammonia reacted with tetrahydrofuran $(THF){\cdot}BH_3$ first to produce AB and THF; then the formed AB reacts with another molecule of $THF{\cdot}BH_3$ to produce ammonia diborane ($NH_3BH_2(\mu\text{-}H)BH_3$, AaDB) – an intermediate; in the third step, another ammonia molecule reacts with AaDB to produce either AB or DADB. In step 3, dihydrogen bond, an attractive interaction between a protonic and a hydridic hydrogen, plays an important role in the formation of DADB, which was never recognized before for the formation of DADB. For the first time, we were able to catch the intermediate of AaDB by ^{11}B NMR (Figure 3) [9].

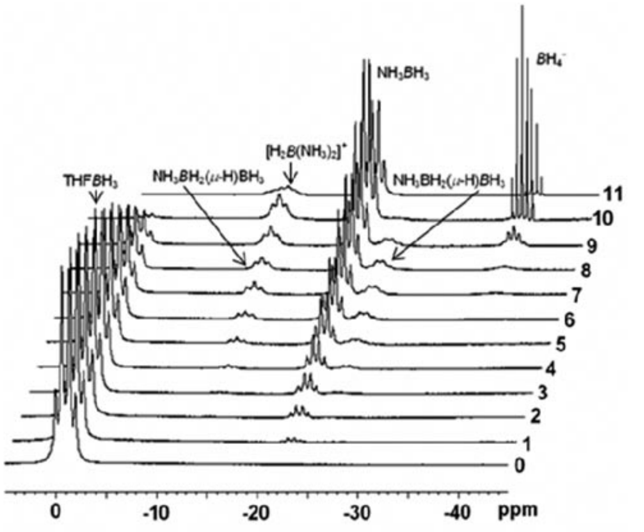

FIGURE 3. ^{11}B NMR spectra of the reaction of NH_3 with a THF·BH_3 solution at –78°C

$NH_3 + THFBH_3 \rightarrow NH_3BH_3$ (AB) + THF (1)

$NH_3BH_3 + THFBH_3 \rightarrow NH_3BH_2(\mu\text{-}H)BH_3$ (AaDB) + THF (2)

$NH_3BH_2(\mu\text{-}H)BH_3 + NH_3 \rightarrow [H_2B(NH_3)_2][BH_4]$ (DADB) + NH_3BH_3 (AB) (3)

The understanding of the formation mechanism of DADB leads to the conclusion that pure DADB could not be produced by the reaction between ammonia and THF·BH_3. DADB is consisted of an cation of $[H_2B(NH_3)_2]^+$ and an anion of $[BH_4]^-$. The ionic nature of DADB along with the mechanistic understanding prompted us to synthesize pure DADB through a metathesis reaction between $[H_2B(NH_3)_2]Cl$ and $NaBH_4$ in an appropriate solvent (reaction 4).

$[H_2B(NH_3)_2]Cl + Na[BH_4] \rightarrow [H_2B(NH_3)_2][BH_4]$ (DADB) + NaCl↓ (4)

After examining the reaction conditions especially by screening many solvents, we found that liquid ammonia is the best solvent for reaction 4. This convenient preparative method for DADB takes advantage of a modified synthesis of the cationic borane complex $[H_2B(NH_3)_2]Cl$ which was first synthesized by Shore and Parry in a reaction of DADB with NH_4Cl [10]. Cationic borane complexes can also be prepared by a reaction of amines with halogen substituted boranes. When ammonia monochloroborane (NH_3BH_2Cl), formed readily as gaseous HCl is added to a solution of AB in diethyl ether, is dissolved in liquid ammonia it is converted quantitatively to $[H_2B(NH_3)_2]Cl$. The formation of $[H_2B(NH_3)_2]Cl$ was verified by ^{11}B NMR and confirmed by XRD [11].

We also determined the stability of pure DADB. We found that DADB is stable in liquid ammonia but decomposes in organic solvents at room temperature. Its instability in THF was demonstrated using variable-temperature ^{11}B NMR experiments from –40°C to room temperature (Figure 4). DADB was stable at lower temperatures, slowly converting to AB as the temperature was raised (–10°C). Once AB was formed, it could not revert back to DADB when the temperature was lowered. This instability of the DADB in organic solvents at ambient temperature, not widely known, has led to confusion about the purity of the samples.

Conclusions and Future Directions

- In collaboration with Northwestern University and NIST, we have now identified the structure of AlB_4H_{11}, an amorphous chain compound containing both BH_4 and B_3H_7 units. This structure features were supported by the following observations: 1) both $[BH_4]^-$ and $[B_3H_8]^-$ ^{11}B NMR signals were observed in a liquid ammonia solution of AlB_4H_{11}, 2) good agreement between the simulated phonon density of states and the experimental IR and NVS results, and 3) good agreement between the predicted and simulated ^{11}B NMR spectra.

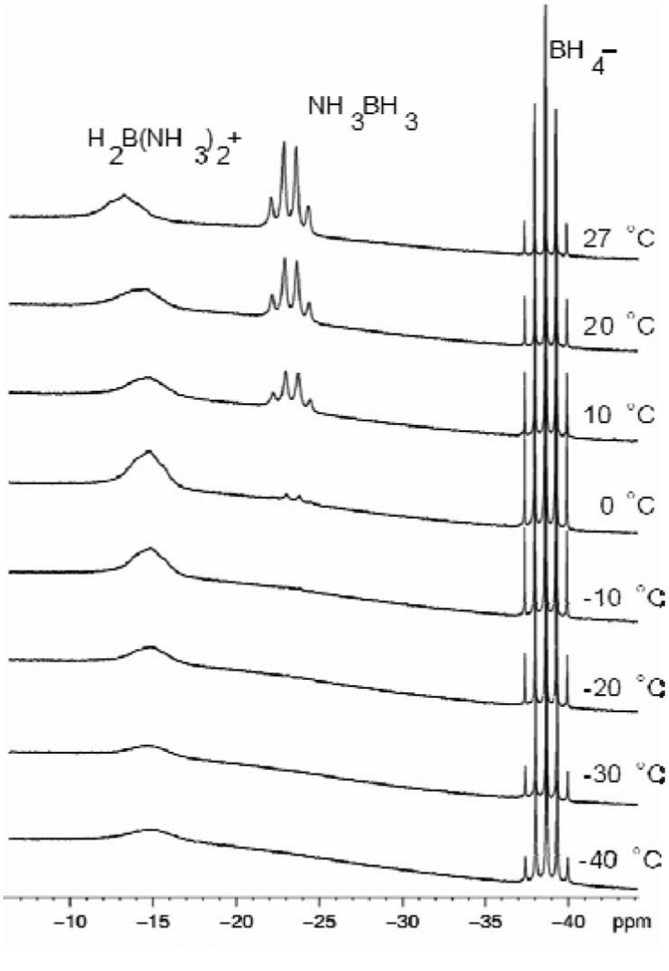

FIGURE 4. Variable temperature ^{11}B NMR spectra of DADB from –40°C to 27°C with 10°C intervals

- The formation mechanism of AlB_4H_{11} was studied by monitoring the reaction procedure using ^{11}B NMR spectroscopy and two plausible mechanisms were derived.
- Simple and efficient method for the preparation of the DADB was developed. The DADB was found to be unstable in organic solvents at room temperature.
- The formation mechanism of the DADB was determined to be a three step process.
- A final report of this entire project will be written at the end of 2012 as a conclusion of this project.

FY 2012 Publications/Presentations

1. X. Chen, Y. Zhang, Y. Wang, D.A. Knight, W. Zhou, T.B. Yisgedu, Z. Huang, H.K. Lingam, B. Billet, T.J. Udovic, G.M. Brown, S.G. Shore, C. Wolverton, and J.-C. Zhao "Structure determination of an amorphous compound AlB_4H_{11}" Chem. Sci., DOI: 10.1039/c2sc21100a (2012).

2. Z. Huang, M. Eagles, S. Porter, B. Billet, R.L. Corey, M.S. Conradi and J.-C. Zhao, "Thermolysis and solid state NMR studies of NaB_3H_8, $NH_3B_3H_7$ and $NH_4B_3H_8$" *Dalton Trans.* DOI:10.1039/C2DT31365K.

3. X. Chen, X. Bao, J.-C. Zhao, S.G. Shore "Experimental and computational study of the formation mechanism of the diammoniate of diborane: the role of dihydrogen bonds" *J. Am. Chem. Soc.* **2011**, 133, 14172-14175.

4. X. Chen, X. Bao, S.G. Shore, J.-C. Zhao "Large-scale and facile preparation of pure ammonia borane through displacement reactions" *Chem. Eur. J.* DOI: 10.1002/chem.201201342 (2012).

5. X. Chen, J. Gallucci, C. Campana, Z. Huang, H. Lingam, S.G. Shore, J.-C. Zhao "Anti and Gauche Conformers of an Inorganic Butane Analogue, $NH_3BH_2NH_2BH_3$" *Chem. Commun.* **2012**, *48*, 7943-7945.

6. H. Lingam, X. Chen*, J.-C. Zhao, S.G. Shore "A convenient synthesis and a NMR study of the diammoniate of diborane" *Chem. Eur. J.* **2012**, *18,* 3490-3492.

7. T.B. Yisgedu, Z. Huang, X. Chen, H.K. Lingam, G. King, A. Highley, S. Maharrey, P.M. Woodward, R. Behrens, S.G. Shore, J.-C. Zhao "The structural characterization of $(NH_4)_2B_{10}H_{10}$ and thermal decomposition studies of $(NH_4)_2B_{10}H_{10}$ and $(NH_4)_2B_{12}H_{12}$" *Inter. J. Hydrogen Energy* **2012**, *37,* 4267-4273.

8. T.B. Yisgedu, X. Chen, H. Lingam, , Z. Huang, A. Highley, S. Maharrey, P.M. Woodward, R. Behrens, S.G. Shore, J.-C. Zhao "Synthesis, Structural Characterization, and Thermal Decomposition Study of $Mg(H_2O)_6B_{10}H_{10}$•$4H_2O$" *J. Phys. Chem. C.* **2011**, *115,* 11793-11802.

9. Z. Huang, X. Chen, T.B. Yisgedu, E.A. Meyers, S.G. Shore, J.-C. Zhao "Ammonium octahydrotriborate ($NH_4B_3H_8$): new synthesis, structure, and hydrolytic hydrogen release" *Inorg. Chem.* **2011**, *50,* 3738-3742.

10. Z. Huang, X. Chen, T.B. Yisgedu, J.-C. Zhao, S.G. Shore "High-capacity hydrogen release through hydrolysis of NaB_3H_8" *Inter. J. Hydrogen Energy* **2011**, *36,* 7038-7042.

11. X. Chen*, H.K. Lingam, J.-C. Zhao, S.G. Shore"The roles of dihydrogen bonds in amine borane chemistry" Boron Americas XIII Meeting, Purdue University, USA, June 3–6, 2012.

12. X. Chen*, X. Bao, J.-C. Zhao, S.G. Shore "The formation mechanism of the diammoniate of diborane: the role of dihydrogen bonds" IME Boron XIV Conference, Niagara Falls, CA, September 15–19, 2011.

13. X. Chen*, X. Bao, J.-C. Zhao, S.G. Shore "Dihydrogen bond effects in amine borane chemistry"(INOR-1001) 241st ACS National Meeting, Anaheim, USA, March 27–31, 2011.

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