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Boron-nitrogen-hydrogen (BNH) compounds: recent developments in hydrogen storage, applications in hydrogenation and catalysis, and new syntheses

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Abstract

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Keywords

hydrogenation, applications, storage, developments, nitrogen, recent, hydrogen, boron, compounds, catalysis, bnh, syntheses

Disciplines

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ARTICLE TYPE

Boron-nitrogen-hydrogen (BNH) compounds: recent developments in hydrogen storage, applications in hydrogenation and catalysis, and new syntheses

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The strong efforts devoted to the exploration of BNH compounds for hydrogen storage have led to impressive advances in the field of boron chemistry. This review summarizes progress in this field from three aspects. It starts with the most recent developments in using BNH compounds for hydrogen storage, covering NH₃BH₃, B₃H₈⁻ containing compounds, and CBN compounds. The following section then highlights interesting applications of BNH compounds in hydrogenation and catalysis. The last part is focused on breakthroughs in the syntheses and discovery of new BNH organic analogues. The role of N–H^{δ+}...H^{δ-}–B dihydrogen interactions in molecule packing, thermal hydrogen evolution, and syntheses is also discussed within the review.

1. Introduction

Boranes and boron-nitrogen-hydrogen (denoted as BNH in this review) compounds attracted intense study in the 1950s, almost exclusively for military applications.^{1,2} Although the goal of using these compounds as high energy fuels for jets was never achieved, the concerted effort did result in a wealth of technical information on boron chemistry.^{3–8} Half a century of dormancy then followed, with only scattered research carried out. Most recently, BNH compounds have regained intense attention due to

their potential application as hydrogen storage materials.^{9–18}

Among these compounds, ammonia borane (AB) has been studied the most, since it 1) has a high hydrogen content of 19.4 wt% and 2) releases 12 wt% hydrogen at moderate temperatures (< 120 °C).^{19–21} AB is arguably one of the most promising candidates to meet many of the criteria set by the U.S. Department of Energy (DOE) for automotive applications.²²

Two main DOE criteria relate to gravimetric and volumetric densities (Table 1).²³ These numbers refer to the whole system, including the container, heater, piping, materials, etc. Therefore, a compound with 5.5 wt% hydrogen fails to meet the 2017 target. There are other critical parameters, such as stability at high temperatures under long dormancy and sufficient kinetics within appropriate temperature and pressure ranges. One of the challenges is to have a hydrogen storage material that can release H₂ efficiently using the waste heat from a proton exchange membrane (PEM) fuel cell, ~ 80 °C, and simultaneously is

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Broader context

Hydrogen is believed to be an ideal synthetic fuel for the future. It can be a highly effective medium to store and transfer energy produced by renewable resources such as wind and solar, whose intermittent nature has limited their wide deployment. Its chemical energy can be extracted using a fuel cell to power an electrical engine at very high efficiency, and this process produces virtually no pollution. One key technological challenge for the transformation to hydrogen-based energy is to find a safe and efficient way to store hydrogen. A hydrogen storage system for both stationary and mobile applications must possess a number of characteristics, such as high storage capacity, fast kinetics, long cycle life, and safety under normal use. Solid state hydrogen storage has attracted substantial research and development around the world, since it offers higher volumetric and gravimetric capacities than traditional compression and liquefaction. Intense efforts have been directed towards research on boron-nitrogen-hydrogen (BNH) compounds, among which, ammonia borane is the outstanding example. The strong investment in BNH by government agencies, universities, and companies has led to a much improved understanding of boron chemistry, which provides essential guidance in the search for ideal hydrogen storage candidates, as well as interesting applications in other fields.

indefinitely stable at 60 °C. This represents an enormous change in reactivity over a narrow temperature range, i.e., 0 g H₂/s below 60 °C and > 1 g H₂/s at 80 °C.²⁴ To make AB suitable for practical applications, it is not necessary to destabilize it to afford a faster rate at 80 °C, but it is necessary to maintain control of thermal management of the exothermic reaction to keep the temperature from going too high. Therefore, approaches to enhance stability at 60 °C are much more important than approaches to destabilize AB to get faster rates at 80 °C.²⁵

As with any strong effort devoted to a certain field, the research carried out by national laboratories, academic institutions and their industry partners around the world has further enriched the field of boron chemistry. This includes, but is not limited to, a much improved understanding of reaction mechanisms,²⁶⁻²⁹ promising new applications,³⁰⁻³³ and the discovery of new BNH compounds.³⁴⁻³⁶ Several excellent reviews on BNH compounds have been published with a focus on hydrogen storage.³⁷⁻⁴⁰ In contrast with these surveys, the present review highlights not only the most recent progress (largely from 2010 onwards) in hydrogen storage, but also includes studies of catalysis and reduction reactions (i.e. hydrogenation) and syntheses of new BNH compounds. This work is accordingly broken down into these areas, with an emphasis on important breakthroughs that may provide guidance for further research.

In BNH compounds, the H bound to the more electronegative N is protic and the H bound to the less electronegative B is

hydridic.⁴¹⁻⁴³ These two types of H atoms are commonly found to form a special interaction, i.e., N-H^{δ+}...H^{δ-}B, defined as the “dihydrogen bond” by Richardson, Gala, and Crabtree,⁴³ a term which is widely used these days in most of the literature.⁴⁴⁻⁴⁷ As will be seen from this present review, the dihydrogen interaction plays an important role in molecule packing in crystals and H₂ evolution. Several chemical reactions have been designed and carried out successfully based on this unique interaction.

2. Hydrogen storage

This section summarizes the latest developments in this field, focusing on AB, alkali metal aminoboranes, diammoniate of diborane ((NH₃)₂BH₂][BH₄]) (DADB), and octahydrotriborates (B₃H₈⁻), as well as C, B, and N containing compounds (denoted as CBN in this review), such as ethane 1,2-di-amineborane (BH₃NH₂CH₂CH₂NH₂BH₃) (EDAB) and CBN heterocycles.

2.1 AB

2.1.1 Hydrogen evolution pathways

Several means have been regularly employed to extract H₂ from AB, i.e., hydrolysis,⁴⁸⁻⁵⁰ solid state thermal decomposition with/without the aid of additives and metal catalysts,⁵¹⁻⁵⁴ decomposition of AB in liquids with⁵⁵⁻⁵⁸ or without catalysts,^{59,60,28} and more recently using AB in pumpable slurries similar to the approach of Safe Hydrogen.^{23,61} Since the hydrolytic reaction affords stable B-O bonds, the reformation of

Table 1 U.S. DOE Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles. (Please refer to U.S. DOE website for detailed technical explanation²³)

Storage Parameter	Units	2017	Ultimate
System Gravimetric Capacity:	kWh/kg	1.8	2.5
Usable specific-energy from H ₂ (net useful energy/max system mass)	(kg H ₂ /kg system)	(0.055)	(0.075)
System Volumetric Capacity:	kWh/L	1.3	2.3
Usable energy density from H ₂ (net useful energy/max system volume)	(kg H ₂ /L system)	(0.040)	(0.070)
Storage System Cost:	\$/kWh net	TBD	TBD
• Fuel cost	(\$/kg H ₂)	(TBD)	(TBD)
	\$/gge at pump	2-4	2-4
Durability/Operability:			
• Operating ambient temperature	°C	-40/60 (sun)	-40/60 (sun)
• Min/max delivery temperature	°C	-40/85	-40/85
• Operational cycle life (1/4 tank to full)	cycles	1500	1500
• Min delivery pressure from storage system; FC= fuel cell, ICE= internal combustion engine	bar (abs)	5 FC/35 ICE	3 FC/35 ICE
• Max delivery pressure from storage system	bar (abs)	12 FC/100ICE	12 FC/100 ICE
• Onboard efficiency	%	90	90
• “Well” to powerplant efficiency	%	60	60
Charging / Discharging Rates:			
• System fill time (5 kg)	min	3.3	2.5
	(kg H ₂ /min)	(1.5)	(2.0)
• Minimum full flow rate	(g/s)/kW	0.02	0.02
• Start time to full flow (20°C)	s	5	5
• Start time to full flow (-20°C)	s	15	15
• Transient response 10%-90% and 90% - 0%	s	0.75	0.75
Fuel Purity (H ₂ from storage)	% H ₂	SAE J2719 and ISO/PDTS 14687-2 (99.97% dry basis)	
Environmental Health & Safety:			
• Permeation & leakage	Scch/h		
• Toxicity	-	Meets or exceeds applicable standards	
• Safety	-		
• Loss of useable H ₂	(g/h) kg H ₂ stored	0.05	0.05

experiment and theory to match the H^- affinity of the borate ester with the H^- donor capability of the metal hydride to maximize efficiency and minimize energy steps.^{89,90}

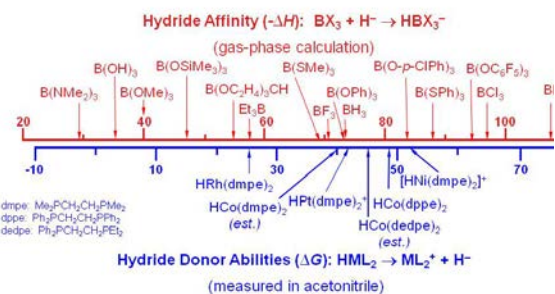
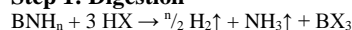


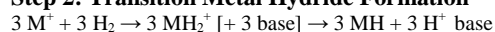
Fig. 3 Scales of experimentally determined hydride donor capabilities of selected transition-metal hydride complexes in acetonitrile (blue, bottom) and the calculated gas-phase hydride affinity values for selected BX₃ compounds (red, top). Reprinted with permission from Ref. 89. Copyright (2009) American Chemical Society.

Fig. 3 shows that not all borate esters are the same, and there is a wide range of H^- affinity, depending on the structural and electronic properties of the borate ester. An important outcome of this work was to show that borate esters are not a thermodynamic dead end: in fact, there are a range of borate esters that can be reduced by metal hydrides. On a parallel scale, Fig. 3 shows that the hydride donating capability of the metal hydride can be tuned by changing either the metal or the ligands attached to the metal.

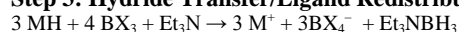
Step 1: Digestion



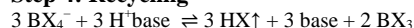
Step 2: Transition Metal Hydride Formation



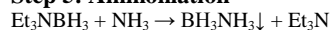
Step 3: Hydride Transfer/Ligand Redistribution



Step 4: Recycling



Step 5: Ammoniation



Scheme 2 The 5 key steps of an overall process that regenerates AB from H₂ with recycling of other reagents and solvent.⁹¹

Scheme 2 shows the 5 key steps of an overall process that regenerates AB from H₂ with recycling of other reagents and the solvent. Each step of the process has been studied in detail to gain insight into the factors that affect reactivity and efficiency.⁹² While each key step has been demonstrated, further work is needed to optimize the process and make the activation of hydrogen catalytic.

Very recently, a surprising, and efficient one pot regeneration method has been reported.⁹³ In all previous cases, metal hydrides were used to regenerate the hydridic B–H bonds, however, in this

new method, anhydrous hydrazine, not typically considered to provide hydridic hydrogen, almost completely converts polyborazylene back to AB via treatment with hydrazine (N₂H₄) in liquid NH₃ at 40 °C in a sealed pressure vessel. This process involves neither noble metal nor transition metal catalysts, and while the mechanism of B–H bond formation is not understood the process is simple and efficient (up to 95% yield). Fig. 4 illustrates the closed cycle for the usage and reformation of AB. Hydrazine, however, is in limited production worldwide. Large-scale economical production is thus needed to make this method a practical industrial process.

The optimum regeneration process for BNH hydrogen storage materials will require catalysts to activate hydrogen, e.g., to make hydrazine from nitrogen or boranes from borates. Using any material besides hydrogen, a metal hydride or hydrazine in stoichiometric amounts will be very difficult to accomplish economically at large scales.

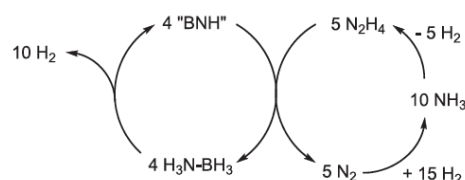


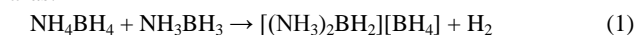
Fig. 4 Ideal overall reaction scheme for AB regeneration with hydrazine. Reprinted with permission from Ref. 93. Copyright (2011) The American Association for the Advancement of Science.

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2.2 Diammoniate of diborane (DADB)

In contrast to the intensive attention devoted to AB as a potential hydrogen storage material, much less is known about the isomer, DADB, in spite of its discovery predating that of AB.^{94,95} DADB has been experimentally proven to be an intermediate during the thermal decomposition of AB and AB/IL blends,^{26,58} but its synthesis and isolation have always been challenging until very recently. Here, we summarize the most recent progress on this compound, with a focus on its preparation.

The earlier syntheses of DADB used direct reaction of B₂H₆ and NH₃ at cryogenic temperatures.^{96,97} These methods, however, do not afford high purity. In addition, B₂H₆ is highly flammable and thus very difficult to handle. Autrey's group recently developed a solid state synthesis of DADB by reacting ammonium borohydride (NH₄BH₄) with AB.⁹⁸ NH₄BH₄ was first synthesized by reacting NH₄F and NaBH₄ in liquid NH₃ at -78 °C. After a 1:1 molar mixture of AB and NH₄BH₄ was mechanically mixed in a SPEX mill for 10 minutes, phase pure DADB was obtained. The reaction mechanism can be expressed



The authors solved the crystal structure of DADB from a combination of X-ray and neutron powder diffraction analysis using Rietveld refinement. There are two crystallographically distinct BH₄⁻ sites which coordinate with neighbouring (NH₃)₂BH₂⁺ ions in different ways (Fig. 5). The nearest N–

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$H^{\delta+} \dots \delta^- H-N$ distances range from 1.8 to 2.1 Å, indicating the presence of dihydrogen interactions.

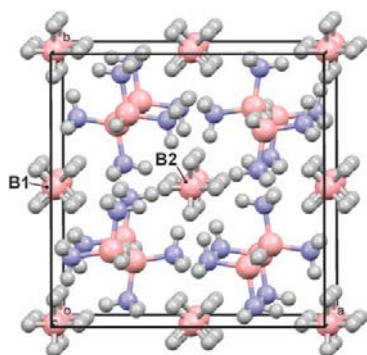
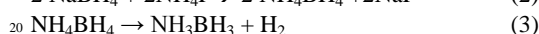


Fig. 5 Crystal structure of DADB viewed along the c -axis. The two crystallographically distinct BH_4^- sites are indicated.⁹⁸

A modified synthetic route has been developed by Fang *et al.*⁹⁹ Instead of isolating pure NH_4BH_4 , they ball milled $NaBH_4$ together with NH_4F using a low energy Fritsch 7 planetary mill. The X-ray diffraction pattern indicates the formation of DADB and NaF. About 1 mole H_2 per mole of $NaBH_4$ (or NH_4F) was observed after 3 h milling. The reaction seems to follow the same pathways as those of Autrey's method.⁹⁸ Initially, NH_4BH_4 was formed during the ball milling (Eq. (2)), and then part of it decomposed into NH_3BH_3 and H_2 upon further milling (Eq. (3)). The newly formed NH_3BH_3 was then reacted with NH_4BH_4 and produced DADB (Eq. (4)). This modified method simplifies manipulation of the reaction and is feasible for bench-top scale synthesis in a typical laboratory.



Another quite different method has also been developed.¹⁰⁰

This synthesis, however, involves more steps and has a complex set-up associated with handling gaseous HCl and liquid NH_3 .

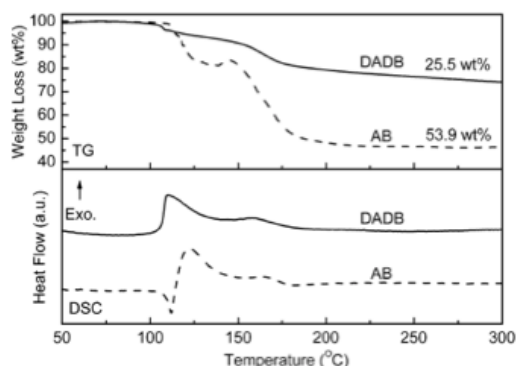


Fig. 6 Comparison of thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) profiles of DADB (solid lines) and AB (dashed lines). The heating rate was 5 °C/min.⁹⁹

Although DADB remains stable in the solid state if stored in an

inert atmosphere, it undergoes quick decomposition in solvents at room temperature with partial conversion to AB.¹⁰⁰

Upon heating, DADB undergoes decomposition in two steps, similar to those of AB (Fig. 6).⁹⁹ The onset temperature for the first step, however, is lower for DADB than for AB. DADB exhibits no appreciable induction period, even at moderate temperatures, while AB suffers from a long induction period prior to H_2 release. This is consistent with the finding that DADB is an intermediate during the decomposition of AB. It has also been noted that AB is an intermediate in the decomposition of DADB and that the mixture of the two are more reactive than either species independently. Evidence for this arises from the observation that the ^{11}B NMR of the product, PAB, is identical no matter the starting material,³¹ AB or DADB, and the observation that the rate of H_2 release from AB or DADB is identical during the 'second half-life' consistent with a similar decomposition pathway after the establishment of an equilibrium, Eq. (5) and (6) (Fig. 7).³¹

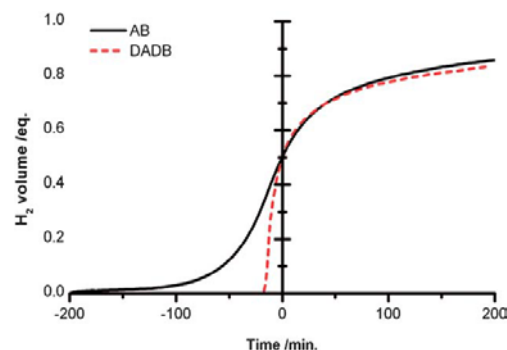
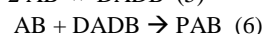


Fig. 7 Comparison of hydrogen release rates from AB and DADB at 85 °C measured in a gas buret normalized for $\tau(1/2)=0$. Note that AB is slower than DADB in the first half-life; however, the rates are nearly equivalent for the second half-life.³¹

Sneddon's group also reported the superior performance of DADB over AB in terms of decomposition in ionic liquid, where a faster release rate from DADB has been observed.⁵⁹

2.3 Octahydrotriborate

There exist a variety of B_mH_n moieties that are either neutral, such as B_2H_6 and B_4H_{10} , or carry one or two negative charges, BH_4^- and $B_{12}H_{12}^{2-}$ for instance. So far, NH_3BH_3 and $NaBH_4$ have been intensively studied. One BH condensation up on the ladder from these is B_2H_6 , however, its explosive and toxic nature virtually eliminates it from any significant attention. Another BH condensation up is B_3H_7 (best known in the form of $NH_3B_3H_7$) and $B_3H_8^-$, both of which have high hydrogen content. Sneddon's group have carried out outstanding work on $NH_3B_3H_7$, from synthesis and the structure solution to hydrogen release.^{101,102} Beyond these initial reports, little follow-up work on $NH_3B_3H_7$ has been done, so this review is focused on $B_3H_8^-$ compounds.

2.3.1 $NH_4B_3H_8$

Although NaB_3H_8 does not contain N, it will be briefly discussed

because of its importance as a precursor to other $B_3H_8^-$ compounds. NaB_3H_8 has a higher hydrogen capacity (12.6 wt% H) compared with the intensively studied $NaBH_4$ (10.8 wt%). Historically, NaB_3H_8 was obtained in a solvated form and then used as a precursor for further syntheses of other $B_3H_8^-/B_3H_7$ compounds.¹⁰³⁻¹⁰⁸ From a hydrogen storage point of view, the unsolvated form of NaB_3H_8 is necessary because solvents add penalty weight. The synthesis of unsolvated NaB_3H_8 , however, traditionally requires B_2H_6 .^{109,110} Recently, Huang *et al.* developed a B_2H_6 -free method to synthesize unsolvated NaB_3H_8 with a yield close to 70%.¹¹¹ There is concern over this route, however, since mercury is used, although it can be recycled. Chong *et al.* have reported an alternative solvent free synthesis of $Mg(B_3H_8)_2$ with about 12% yield in the thermal decomposition of $Mg(BH_4)_2$ at 300 °C.¹¹² Heating at lower temperatures for longer periods of time, 250 °C for 5 weeks, did lead to higher yields however further work is required to optimize this synthetic pathway.

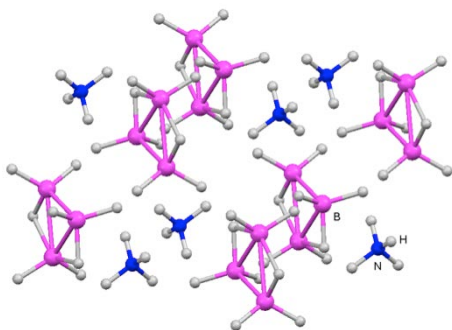


Fig. 8 Crystal structure of $NH_4B_3H_8$: B: pink, H: light grey, N: blue. Reprinted with permission from Ref. 116. Copyright (2011) American Chemical Society.

Ammonium octahydrotriborate ($NH_4B_3H_8$) has a very high hydrogen content of 20.5 wt%. The original synthesis reported 40 years ago involved pentaborane (B_5H_9), which is highly volatile and inflames violently upon contact with air.^{113,114} Pentaborane-free patents were later developed, but the procedures are complicated, requiring intermediate compounds and large amounts of solvents.¹¹⁵ Huang *et al.* recently found that by reacting unsolvated NaB_3H_8 with NH_4Cl in liquid NH_3 at -78 °C, $NH_4B_3H_8$ was formed and could be extracted using dry tetrahydrofuran (THF).¹¹⁶ This process can also be carried out with solvated NaB_3H_8 , since 1) solvents coordinated to NaB_3H_8 will not change the course of the reaction; 2) $NH_4B_3H_8$ can be easily isolated using THF; and 3) the $NaCl$ side product is insoluble in most organic solvents. In this case, different synthetic routes to solvated NaB_3H_8 can be employed, and thus mercury can be avoided.¹⁰³⁻¹⁰⁵

A separate ion pair structure exists in $NH_4B_3H_8$ (Fig. 8), with the shortest $N-H^{\delta+} \cdots H^{\delta-}-B$ distance being 2.37 Å, very close to the sum of the van der Waals radii between two hydrogen atoms, 2.4 Å. All other $N-H^{\delta+} \cdots H^{\delta-}-B$ distances are more than 2.47 Å. These dihydrogen distances are longer than those observed in $NH_3B_3H_7$ ¹⁰² and NH_3BH_3 ¹¹⁷. $NH_4B_3H_8$ in pure and solid form is stable at room temperature, with no detectable signs of decomposition within one month.

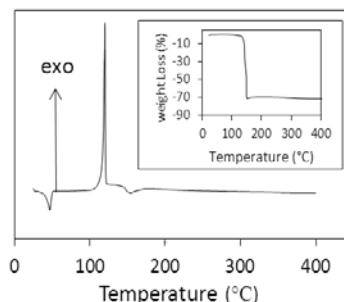
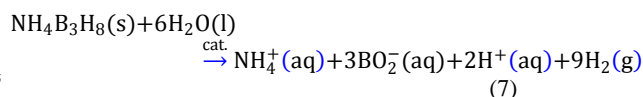


Fig. 9 DSC and TGA (inset) profiles of $NH_4B_3H_8$. The heating rate was 5 °C/min. Reprinted with permission from Ref. 116. Copyright (2011) American Chemical Society.

DSC and TGA results collectively indicate that melting and decomposition take place simultaneously at 120 °C, with a substantial weight loss at this temperature (Fig. 9).¹¹⁶ However, only 10 wt % of the weight loss is associated with H_2 , while the rest is due to the formation of B_2H_6 , B_3H_9 , and $B_3N_3H_6$. Thus, $NH_4B_3H_8$ is not a suitable candidate for hydrogen storage through thermal decomposition without additional work.

Hydrolytic studies, however, have demonstrated that $NH_4B_3H_8$ has advantages over $NaBH_4$ and NH_3BH_3 , the most studied chemical hydrides for hydrogen storage via hydrolysis. $NH_4B_3H_8$ is more soluble in water (> 45 wt %) than NH_3BH_3 (26 wt %)¹¹⁸ and $NaBH_4$ (35 wt %)¹¹⁹. The lower solubility limits the theoretical hydrogen density of the respective systems to 5.1 wt % for NH_3BH_3 and 7.5 wt % for $NaBH_4$. Hydrolysis showed that 1 mmol $NH_4B_3H_8$ releases a near theoretical value of 8.80 mmol H_2 . Based on Eq. (7), therefore, this system has a high theoretical hydrogen weight density (wt % = $H_2 / (NH_4B_3H_8 + H_2O)$) of 10.8 wt %.



Unlike $NaBH_4$, which is stable only in strong alkaline solutions,^{120,121} an aqueous $NH_4B_3H_8$ solution is reasonably stable. At 28 °C, for the same molar concentration, i.e., 2 M, ¹¹B nuclear magnetic resonance (NMR) studies showed that more than 50% of $NaBH_4$ decomposed over one day, while less than 10% of $NH_4B_3H_8$ decomposed over a week.¹¹⁶ Calculations indicate that H_2 release from $NH_4B_3H_8$ is much less exothermic than from $NaBH_4$, NH_3BH_3 , or $NH_3B_3H_7$. Its less exothermic nature favors $NH_4B_3H_8$ over the other candidates from the standpoint of heat management and system design.

2.3.2 Diammoniate of tetraborane ($(NH_3)_2BH_2B_3H_8$)

This compound has a high hydrogen content of 18.2 wt%, however, the only available syntheses involve tetraborane (B_4H_{10}), which is highly volatile and combusts violently upon contact with air.^{122,123} Furthermore, B_4H_{10} is not commercially available, and its synthesis remains complex and challenging.¹²⁴ There have been few studies on this compound since its discovery 50 years ago. Huang *et al.* recently developed a safe and efficient synthesis method for this compound and studied its thermal decomposition properties.¹²⁵

By utilizing two well-known reactions: NH_3 reacting with $\text{THF}\cdot\text{BH}_3$ to form DADB and AB,^{95,126} and DADB reacting with NH_4Cl to produce $(\text{NH}_3)_2\text{BH}_2\text{Cl}$,^{11,127} Huang *et al.* obtained $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$ via the metathesis between NaB_3H_8 and $(\text{NH}_3)_2\text{BH}_2\text{Cl}$. This procedure avoids flammable starting materials and produces high purity products, as evidenced by the NMR spectra (Fig. 10).

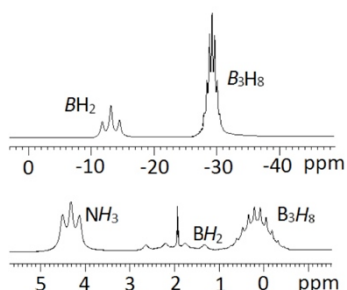


Fig. 10 ^{11}B NMR spectrum of $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$ in THF (top), and ^1H NMR spectrum in CD_3CN (bottom).¹²⁵

The DSC and TGA results indicate that melting and decomposition take place simultaneously at $100\text{ }^\circ\text{C}$ and finish at around $160\text{ }^\circ\text{C}$, with a total weight loss of 40 wt%. Approximately 15 wt% of the weight loss is due to H_2 evolution, while the rest is associated with B_2H_6 , B_5H_9 , and $\text{B}_3\text{N}_3\text{H}_6$.

It is well known that thermal decomposition of B_3H_8 containing compounds tends to generate B_5H_9 and/or B_2H_6 .^{105,107} The presence of the protonic NH groups seems to suppress the formation of these boranes and facilitates the formation of H_2 , considering the total 70 wt% weight loss and the 10 wt% H_2 for $\text{NH}_4\text{B}_3\text{H}_8$ ($\text{H}^{\delta+} : \text{H}^{\delta-} = 3 : 6$), compared to the total 40 wt% weight loss and 15 wt% H_2 for $(\text{NH}_3)_2\text{BH}_2\text{B}_3\text{H}_8$ ($\text{H}^{\delta+} : \text{H}^{\delta-} = 3 : 5$).

2.4 CBN compounds

2.4.1 Ethane 1,2-di-amineborane ($\text{BH}_3\text{NH}_2\text{CH}_2\text{CH}_2\text{NH}_2\text{BH}_3$) (EDAB)

EDAB has recently been studied as a promising hydrogen storage candidate (Fig. 11).¹²⁸ EDAB possesses a number of distinct advantages compared with AB. First of all, it is more stable than AB at temperatures lower than $100\text{ }^\circ\text{C}$, indicating that storage at high temperature ($> 60\text{ }^\circ\text{C}$) for a prolonged period is practical. Secondly, it releases hydrogen more rapidly than AB at temperatures higher than $120\text{ }^\circ\text{C}$, and this means that EDAB is

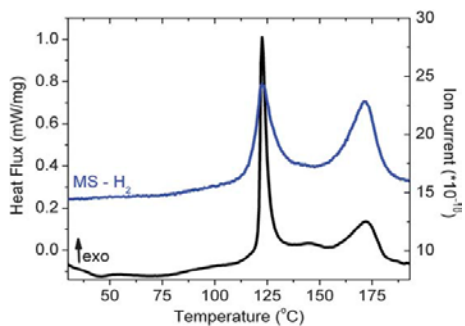


Fig. 11 DSC/mass spectroscopy (MS) data obtained by heating EDAB at $1\text{ }^\circ\text{C}/\text{min}$ from $25\text{ }^\circ\text{C}$ to $200\text{ }^\circ\text{C}$. Black curve is the heat flux; blue curve is the MS data.¹²⁸

more effective at providing H_2 when needed, especially during acceleration (Fig. 12). A fast rate at the release temperatures coupled with stability at high storage temperatures is a significant concern for practical storage, but this has so far been elusive for approaches aimed at enhancing the rate of hydrogen release from solid AB. The enthalpy of H_2 release is less exothermic than for AB, amounting to approximately -10 kJ/mol H_2 and -4 kJ/mol H_2 for the first and second steps, respectively, which will simplify heat management in practical devices. Furthermore, there are no detectable impurities, and in particular, no $\text{B}_3\text{N}_3\text{H}_6$, NH_3 , or B_2H_6 . The absence of $\text{B}_3\text{N}_3\text{H}_6$ and NH_3 is not a surprise as it is difficult to provide a mechanism to show how they would be formed from EDAB, however, the absence of B_2H_6 needs further study as it is difficult to detect given the high reactivity.

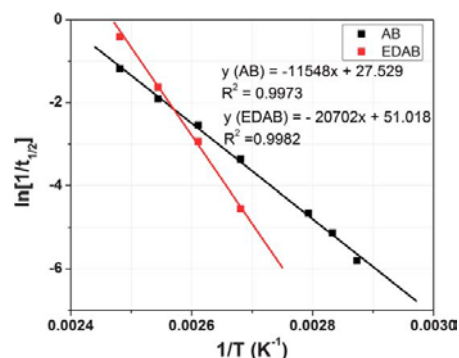


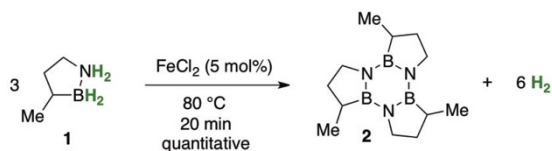
Fig. 12 Arrhenius fit of the volumetric gas burette data for EDAB and AB.¹²⁸

2.4.2 Heterocycles

This class of compounds (i.e., cyclic molecules containing C, B, and N) for hydrogen storage has recently been investigated by Liu's group from the University of Oregon.¹²⁹⁻¹³¹ The aim of this research is to develop liquid hydrogen storage materials to make use of the existing liquid fuel distribution channels such as pipelines and tankers, which would be more cost-effective compared with transporting solid hydrogen storage materials. Liu's group has carried out elaborate work on the synthesis, catalytic dehydrogenation, and regeneration of several CBN heterocycles. One sample of particular interest is BN-methylcyclopentane (Scheme 3),¹³² which is in liquid form under ambient conditions. Upon adding cheap catalysts such as FeCl_2 and NiCl_2 , this compound can give off H_2 at temperatures below or at $80\text{ }^\circ\text{C}$, with the formation of a single dehydrogenation product that is also a liquid at room temperature. The authors have also demonstrated the conversion of the dehydrogenated product back to the charged fuel with a 92% yield under relatively mild conditions. Although the material capacity (4.7 wt%) falls short of the 2017 target for automobile applications (5.5 wt% system),²³ this research demonstrates a viable H_2 storage option for portable and carrier applications.

As the complex decomposes to a liquid product, this approach enables a much simpler system design with respect to fuel feed and recovery. In addition, the low dehydrogenation temperature indicates that waste heat from a proton exchange membrane fuel cell can be used, which allows a highly efficient use of energy. As noted by the authors, to make the process cost-effective, an

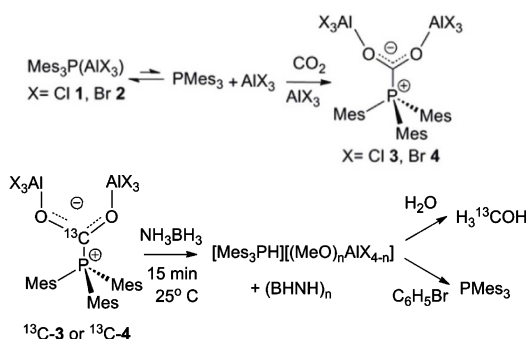
economical regeneration process needs to be developed.



Scheme 3 A single-component liquid-phase hydrogen storage material. Reprinted with permission from Ref. 132. Copyright (2011) American Chemical Society.

3. Applications in hydrogenation

Due to its high hydrogen content and reducing capability, AB has also been studied as a hydrogenating agent in organic syntheses, such as converting aldehydes to alcohols¹³³⁻¹³⁵ and reducing cyclohexyl imines and iminium salts.¹³⁶ In those studies, AB was thought to transfer hydridic H on boron to unsaturated functional groups. Recent work, however, reveals a different mechanism. Berke and co-workers found that AB reduces imine through a concerted double hydrogen transfer process, where the protic H(N) and hydridic H(B) are transferred to the nitrogen and carbon ends of the imine group, respectively.¹³⁷ This double-hydrogen transfer process was also observed by Manner *et al.* in the case of N=B double bond reduction,¹³⁸ and by Chen during the hydrogenation of aromatic aldehydes by AB.¹³⁹



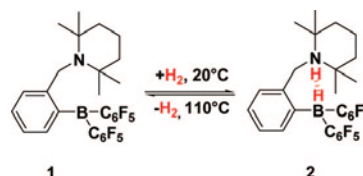
Scheme 4 Synthesis of $\text{PMes}_3/\text{AIX}_3$, $\text{Mes}_3\text{P}(\text{CO}_2)(\text{AIX}_3)_2$ ($\text{X} = \text{Cl}, \text{Br}$) (top) and the formation of CH_3OH upon adding AB followed by H_2O (bottom). Reprinted with permission from Ref. 142. Copyright (2010) American Chemical Society.

This double-electron transfer process also renders AB applicable in renewable energy research from a different perspective. It is well known that CO_2 is the main contributing factor to global warming and climate change. Reduction of CO_2 to a useful fuel such as methanol has surfaced as a chemical challenge of great interest. Due to its limited reactivity, CO_2 reduction is currently achieved by using electrocatalysts or heterogeneous photocatalysts that involve transition-metal containing complexes and materials.^{140,141} Recently, Stephan *et al.* described a rapid, room temperature conversion of frustrated Lewis pair (FLP)-activated CO_2 to CH_3OH using AB as the hydrogen source, without the assistance of a transition metal (Scheme 4).¹⁴² First, PMes_3 ($\text{Mes} = 2,4,6\text{-C}_6\text{H}_2\text{Me}_3$) and AIX_3 ($\text{X} = \text{Cl}, \text{Br}$) react to form weak Lewis adducts, which then can react irreversibly with CO_2 . After the solution reacts with AB, H_2O is introduced to produce CH_3OH , which can be extracted with a decent yield of 37-51%. Theoretical investigations by Zimmerman *et al.* suggested that AB reduces CO_2 through the two-hydrogen transfer process.^{32,143} This pioneering research is expected to provide valuable insights for developing strategies for CO_2 reduction using AB as an efficient reducing agent, although regeneration of AB from the end products will be challenging, since B-O bonds tend to form upon adding H_2O . The ultimate economic impact is likely to be dependent on the energy output from consuming CH_3OH versus the energy input from converting B-O to B-H in a catalytic regeneration reaction.

In a related report Ashley and co-workers demonstrated that an amine borane complex could be used to activate both hydrogen and CO_2 to make CH_3OH in a stoichiometric reaction.¹⁴⁴

4. Catalysis

Prior to Welch and Stephan's observation that H_2 could be added reversibly across a frustrated Lewis pair of phosphine and borane,¹⁴⁵ the common dogma was that metals were required to activate hydrogen. Sumerin and co-workers, however, demonstrated reversible hydrogen addition to a structurally linked amine borane complex (Scheme 5).¹⁴⁶



Scheme 5 Reversible H_2 activation by N-TMPN- $\text{CH}_2\text{C}_6\text{H}_4\text{B}(\text{C}_6\text{F}_5)_2$ (where TMPNH is 2,2,6,6-tetramethylpiperidiny). Reprinted with permission from Ref. 146. Copyright (2010) American Chemical Society.

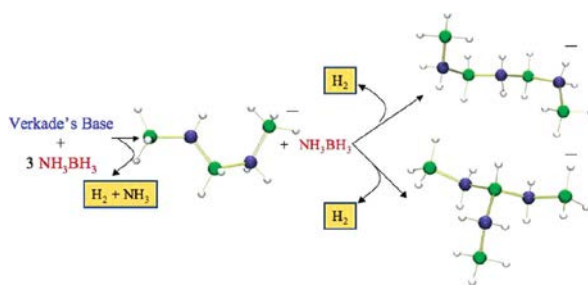
This was the first example of reversible 'hydrogen storage' in an amine borane complex. While the quantity of hydrogen is too low to be of practical significance for hydrogen storage applications, it is an important result because it shows that amine borane complexes can be used to activate hydrogen at moderate temperature and pressure to be used in catalytic reduction reactions. Since these pioneering studies, there have been several examples demonstrating the catalytic reduction of unsaturated polar molecules by a wide range of amine-borane frustrated Lewis pairs.¹⁴⁷ This is an exciting new area of research using amine boranes for applications beyond hydrogen storage, and the field is rapidly growing with new examples of hydrogen activation for catalysis being reported.

5. Synthesis of new inorganic analogues

Serendipity has again made an amazingly good appearance with the reports of new BNH compounds during these extensive studies, which further enriches the chemistry of boron. Studying the activating effects of Verkade's base (VB), 2,8,9-triisobutyl-2,5,8,9-tetraaza-1-phosphabicyclo [3.3.3] undecane, on the rate and extent of H_2 release from AB, Sneddon's group discovered the formation of $[\text{C}_{18}\text{H}_{39}\text{N}_4\text{PH}][\text{H}_3\text{BNH}_2\text{BH}_2\text{NH}_2\text{BH}_3]$,

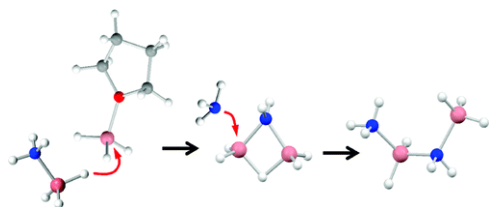
$[C_{18}H_{39}N_4PH][HB(NH_2BH_3)_3]$, and
 $[C_{18}H_{39}N_4PH][H_3BNH_2BH_2NH_2BH_2NH_2BH_3]$ (Scheme 6), which
 are isoelectronic and isostructural analogues of the hydrocarbons
 n-pentane, 3-ethylpentane, and n-heptane, respectively.³⁴

5 Considering the synthesis conditions (room-temperature for the
 five-membered and 50 °C for the seven-membered compounds),
 these anionic aminoborane oligomers are likely to be early
 intermediates in base-promoted AB H₂ release reactions.
 Sequential H₂ elimination reactions lead to chain growth, which
 10 is likely facilitated by N–H^{δ+}...H^{δ-}–B dihydrogen-bonding
 interactions in these anionic aminoborane chains.



Scheme 6 Synthesis of $[C_{18}H_{39}N_4PH][H_3BNH_2BH_2NH_2BH_3]$,
 $[C_{18}H_{39}N_4PH][HB(NH_2BH_3)_3]$, and
 $[C_{18}H_{39}N_4PH][H_3BNH_2BH_2NH_2BH_2NH_2BH_3]$ via reactions
 between Verkade's base and AB. B: green; N: navy; H: light grey.
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 American Chemical Society.

Aminodiborane (NH₂B₂H₅) was first discovered 70 years ago
 through a tedious procedure using B₂H₆.¹⁴⁸ Little subsequent
 15 study has occurred because of its scarce availability. Recently,
 Chen *et al.* found that when AB and THF·BH₃ were mixed
 together at room temperature, NH₂B₂H₅ was formed via the
 formation of a dihydrogen bond and subsequent molecular
 hydrogen elimination (Scheme 7).³⁶ A concentrated
 20 NH₂B₂H₅·THF solution (1:1 ratio, based upon the integration of
 the hydrogen signals in the ¹H NMR spectrum) can be obtained
 with a yield of 70%. When NH₃ was bubbled into a solution of
 NH₂B₂H₅, an inorganic butane analogue, NH₃BH₂NH₂BH₃, was
 25 formed, a reaction which likely proceeded via the breaking of the
 bridge hydrogen bond in NH₂B₂H₅ (Scheme 7).



Scheme 7 Formation of NH₂B₂H₅ and NH₃BH₂NH₂BH₃. B:
 purple, N: blue, H: light grey. Reprinted with permission from
 Ref. 36. Copyright (2010) American Chemical Society.

Another breakthrough occurred in the syntheses of the long-
 sought unsubstituted aminodiboranate Na(H₃BNH₂BH₃) and its
 N-alkyl analogs.³⁵ [NH₄][H₃BNH₂BH₃] was first proposed by
 30 Schlesinger and Berg to formulate DADB,⁹⁶ although later
 spectroscopic studies established that DADB is actually the

borohydride salt [(NH₃)₂BH₂][BH₄]. After being neglected for
 about 80 years, this anion was proved to exist by Girolami *et al.*,
 who found that when AB with excess Na in THF was subject to
 35 reflux, Na(H₃BNH₂BH₃) is formed. This new compound displays
 a downfield ¹¹B NMR chemical shift compared with AB and
 NaNH₂BH₃ (Fig. 13).³⁵ Similar reactions with other amine-
 boranes afford Na(H₃BNRR'BH₃). Na(H₃BNH₂BH₃) can also be
 generated by reaction of 2 equivalent of AB with NaNH₂ in
 40 refluxing THF, which results in a better yield (50%).

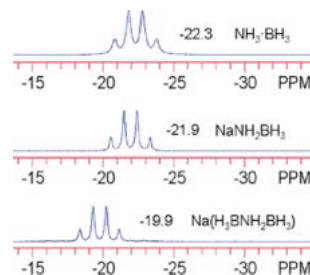


Fig. 13 ¹¹B NMR spectra of AB, Na(NH₂BH₃), and
 Na(H₃BNH₂BH₃). Reprinted with permission from Ref. 35.
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6. Conclusion

45 Whether BNH compounds hold the key to hydrogen storage
 remains uncertain, but the current renewed interest and strong
 efforts have so far resulted in a much improved understanding of
 boron chemistry. There has been enhanced recognition of the H–
 H interactions, including both N–H^{δ+}...^{δ-}H–B (dihydrogen bond)
 50 and the homopolar interactions, B–H^{δ-}...^{δ+}H–B and N–H^{δ+}...^{δ+}H–
 N, in relation to crystal structure and H₂ evolution. The
 development of safe and efficient syntheses of existing
 compounds will enable further studies of their applications. The
 discovery of new compounds certainly enriches the field of boron
 55 chemistry by opening up room for new syntheses and new
 applications. The catalysis and hydrogenation work using
 ammine borane complexes is exciting; few chemists would have
 suggested just over 6 years ago that hydrogen could be activated
 at low temperature and pressure without using transition metals.

60 The employment of modern advanced techniques, such as high
 field solid state NMR spectrometers and high level density
 functional theory (DFT) calculation tools, together with
 worldwide collaborations, offers a very strong edge over the
 studies in the 1950s. It has to be acknowledged, however, that the
 65 pioneering work carried out by A. Stock, H. I. Schlesinger, D. M.
 Ritter, A. B. Burg, P. W. Parry, M. F. Hawthorne, H. C. Brown,
 S. G. Shore, etc. has laid a solid foundation for the work of today.
 Their earlier experimental findings and speculations are often
 referred to and provide guidance for today's research. Likewise,
 70 today's outcomes will also shed light on future research in this
 field.

Table 2 Reviewed compounds for hydrogen storage.

Compounds	Density		Onset release temperature (°C)	Enthalpy (kJ/mol)	Impurities	References
	wt % H ₂	g H ₂ /L				
NH ₃ BH ₃	19.4	144	108	-23	B ₂ H ₆ , B ₃ N ₃ H ₆ , NH ₃	19,20
LiNH ₂ BH ₃	10.9	52	92	-3--5	NH ₃	91
NaNH ₂ BH ₃	7.6	43	89	-3--5	NH ₃	149
[(NH ₃) ₂ BH ₂][BH ₄]	19.4	151	85	-34	B ₂ H ₆ , B ₃ N ₃ H ₆ , NH ₃	29,98,99
NH ₄ B ₃ H ₈	20.5	160	120	Not reported	B ₃ N ₃ H ₆ , B ₂ H ₆ , B ₅ H ₉	116
BH ₃ NH ₂ CH ₂ CH ₂ NH ₂ BH ₃	10	82	123	-10 (1 st step), -4 (2 nd step)	Not observed	128
(NH ₃) ₂ BH ₂ B ₃ H ₈	18.2	Not reported	100	Not reported	B ₃ N ₃ H ₆ , B ₂ H ₆ , B ₅ H ₉	125
C ₄ H ₁₂ BN	4.7	42	150	Not reported	Not observed	132

Note: U.S. DOE has recently compiled a database on hydrogen storage materials.¹⁵⁰ Variation in desorption temperatures and enthalpy has been observed. Please refer to the specific experimental conditions.

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