SCISPACE
formerly Typeset

Open access • Journal Article • DOI:10.1039/C2EE23039A

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

— Source link

Zhenguo Huang, Tom Autrey

Institutions: University of Wollongong, Pacific Northwest National Laboratory

Published on: 18 Oct 2012 - Energy and Environmental Science (The Royal Society of Chemistry)

Topics: Hydrogen storage

Related papers:

- Ammonia-borane and related compounds as dihydrogen sources.
- B–N compounds for chemical hydrogen storage
- Hydrogen-storage materials for mobile applications
- Ammonia-borane: the hydrogen source par excellence?
- Liquid-phase chemical hydrogen storage materials

Share this paper:

View more about this paper here: https://typeset.io/papers/boron-nitrogen-hydrogen-bnh-compounds-recent-developments-in-1z72qi3xdf

University of Wollongong

Research Online

Australian Institute for Innovative Materials - Papers

Australian Institute for Innovative Materials

2012

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

Zhenguo Huang
University of Wollongong, zhenguo@uow.edu.au

Tom Autrey
Pacific Northwest National Laboratories, tom.autrey@pnnl.gov

Follow this and additional works at: https://ro.uow.edu.au/aiimpapers

Part of the Engineering Commons, and the Physical Sciences and Mathematics Commons

Recommended Citation

Huang, Zhenguo and Autrey, Tom, "Boron-nitrogen-hydrogen (BNH) compounds: recent developments in hydrogen storage, applications in hydrogenation and catalysis, and new syntheses" (2012). *Australian Institute for Innovative Materials - Papers*. 321.
https://ro.uow.edu.au/aiimpapers/321

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

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

Abstract

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 NH_3BH_3, B_3H_8- 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-$H^{\delta+}$***$H^{\delta-}$-B dihydrogen interactions in molecule packing, thermal hydrogen evolution, and syntheses is also discussed within the review.

Keywords

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

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Huang, Z & Autrey, T (2012), Boron-nitrogen-hydrogen (BNH) compounds: recent developments in hydrogen storage, applications in hydrogenation and catalysis, and new syntheses, Energy and Environmental Science, 5(11), pp. 9257-9268.

This journal article is available at Research Online: https://ro.uow.edu.au/aiimpapers/321

Journal Name

Dynamic Article Links ►

Cite this: DOI: 10.1039/c0xx00000x

www.rsc.org/xxxxxx

ARTICLE TYPE

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

Zhenguo Huang[*a] **and Tom Autrey**[*b]

Received (in XXX, XXX) Xth XXXXXXXXX 20XX, Accepted Xth XXXXXXXXX 20XX
DOI: 10.1039/b000000x

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 NH_3BH_3, $B_3H_8^-$ 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 $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ 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 H_2 efficiently using the waste heat from a proton exchange membrane (PEM) fuel cell, ~ 80 °C, and simultaneously is

[a] *Institute for Superconducting and Electronic Materials, University of Wollongong, Innovation Campus, Squires Way, North Wollongong, NSW, 2522, Australia. Fax: 61 02 4221 5731; Tel: 61 02 4221 3220, E-mail: zhenguo@uow.edu.au*
[b] *Fundamental and Computational Sciences Directorate, Pacific Northwest National Laboratory, 908 Battelle Blvd K2-5, Richland, Washington 99352, USA. Fax: +01 (509) 375-3792; Tel: +01 (509) 375-3792. E-mail: tom.autrey@pnnl.gov.*

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 H_2/s below 60 °C and > 1 g H_2/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., $N{-}H^{\delta+}\cdots H^{\delta-}B$, defined as the "dihydrogen bond" by Richardon, 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 H_2 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 ($[(NH_3)_2BH_2][BH_4]$) (DADB), and octahydrotriborates ($B_3H_8^-$), as well as C, B, and N containing compounds (denoted as CBN in this review), such as ethane 1,2-di-amineborane ($BH_3NH_2CH_2CH_2NH_2BH_3$) (EDAB) and CBN heterocycles.

2.1 AB

2.1.1 Hydrogen evolution pathways

Several means have been regularly employed to extract H_2 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 with[55-58] 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 explanation[23])

Storage Parameter	Units	2017	Ultimate
System Gravimetric Capacity: Usable specific-energy from H_2 (net useful energy/max system mass)	kWh/kg (kg H_2/kg system)	1.8 (0.055)	2.5 (0.075)
System Volumetric Capacity: Usable energy density from H_2 (net useful energy/max system volume)	kWh/L (kg H_2/L system)	1.3 (0.040)	2.3 (0.070)
Storage System Cost:	$/kWh net ($/kg H_2)	TBD (TBD)	TBD (TBD)
• Fuel cost	$/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 (kg H_2/min)	3.3 (1.5)	2.5 (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	Scc/h		
• Toxicity	-	Meets or exceeds applicable standards	
• Safety	-		
• Loss of useable H_2	(g/h) kg H_2 stored	0.05	0.05

This journal is © The Royal Society of Chemistry [year]

AB is highly energy intensive and consequently an economic challenge. Solid state thermal decomposition is believed to proceed via the intermediate DADB and finally results in polymeric BNH compounds.[26] Decomposition of AB in ionic liquid (IL) follows the same pathway, but often with significantly enhanced rates most likely as a result of enhanced heat transfer and the stabilization of DADB in ionic liquids.[59]

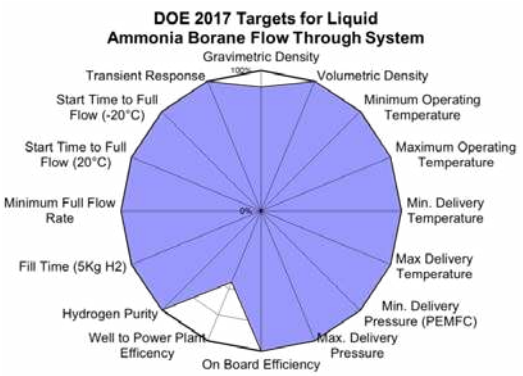
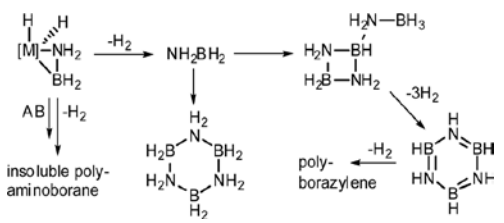


Fig. 1 Projections for exothermic AB release systems with 50% mass loaded fluids. Reprinted from 2012 U.S. DOE Annual Review.[62]

AB decomposition in organic solvents has not yet been well studied, but recent work by Mertens' group identified interesting concentration dependent dehydrogenation behavior.[60] DADB influences the rates of several dehydrogenation steps by interacting with various other intermediates. In highly concentrated solutions, a similar decomposition mechanism to that of solid AB was observed. Although the liquid medium adds a weight penalty to the system capacity, it affords easier transport of final decomposition products compared with the solid state. A recent study by a team of researchers in the Engineering Center of Excellence has shown that the performance of AB slurries can meet most of the U.S. DOE 2017 criteria (Fig. 1).[62]

Thermally induced AB dehydrogenation that is catalyzed by metal complexes in organic solutions tends to proceed via the formation of aminoborane (NH_2BH_2), which oligomerizes to cyclic intermediates or undergoes dehydropolymerization to polyborazylene (Scheme 1).[58,63,64] In addition to noble metals,[65-67,57] cost effective transition metal based catalysts have also proved very effective.[55,68] There exists a great variety of transition metal complexes and thus plenty of room for exploration and potential improvement with respect to efficacy and cost.

Thermal decomposition of neat AB suffers from the formation of traces of undesirable volatile products such as ammonia (NH_3) and borazine ($B_3N_3H_6$).[69-71] Many methods have been employed



Scheme 1 Proposed metal-catalyzed reaction pathways for AB dehydrogenation.[58]

to suppress the formation of these impurities, such as the introduction of metal catalysts[72-74] and additives.[53,54,75] Among these efforts, metal amidoboranes (MAB), such as $Li/Na/KNH_2BH_3$ and $Ca(NH_2BH_3)_2$, have shown improved hydrogen release performance in terms of purity and kinetics, and therefore have attracted broad attention.[76-80] Autrey's group found that H_2 release from MAB compounds proceeds through a bimolecular mechanism involving MH (M = Li, Na, or K) compounds as intermediates.[81] The decomposition products resulting from the release of 1 equivalent of H_2 from these MAB compounds indicate the presence of both BH_3 and sp^2 hybridized BH groups, which are significantly different from the products formed after H_2 release from AB. Theoretical work by Kim *et al.*,[82] and Lee and McKee[83] demonstrates a similar role for metals in facilitating the formation of H_2 by forming metal hydride intermediates during the decomposition. Recently, McGrady's group revealed new homopolar H···H interactions: viz. $B–H^{\delta-}\cdots^{\delta-}H–B$ and $N–H^{\delta+}\cdots^{\delta+}H–N$, in addition to $M^{\delta+}\cdots^{\delta-}H–B$ and $N–H^{\delta+}\cdots^{\delta-}H–B$ interactions (Fig. 2).[84] Upon heating, isotopomer $LiND_2BH_3$ gives off a significant quantity of H_2 along with HD, which can only arise from hydride-hydride interactions, either directly from $B–H^{\delta-}\cdots^{\delta-}H–B$ moieties or indirectly through the participation of Li-H intermediates. This finding indicates that the whole H_2 evolution process can be complex and can involve more than $N–H^{\delta+}\cdots^{\delta-}H–B$ interactions alone.

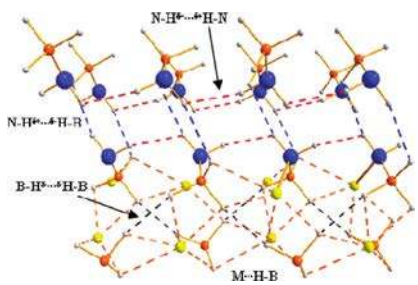


Fig. 2 Representation of the interactions in the extended structure of $Li/NaNH_2BH_3$ ($M^{\delta+}\cdots^{\delta-}H–B$: orange, $N–H^{\delta+}\cdots^{\delta-}H–B$: blue, $B–H^{\delta-}\cdots^{\delta-}H–B$: black, and $N–H^{\delta+}\cdots^{\delta+}H–N$: red dashed lines, respectively). Reprinted with permission from Ref. 84. Copyright (2011) American Chemical Society.

2.1.2 Regeneration of AB

To make AB a practical storage medium for large scale applications, its efficient and economic regeneration from spent fuel is critical. The spent fuel is believed to be a mixture of polyaminoborane (PAB) and polyiminoborane (PIB), with a general formulation that can be expressed as "BNH_x", with x varying between 0.5 and 1.[85]

Early efforts devoted to the regeneration of AB have been summarized.[39] These earlier efforts have demonstrated that the regeneration of AB is possible, but with high complexity and cost, and low efficiency.[86,87] It is known that the transition metals Rh, Co, and Ni can be used to activate molecular hydrogen to metal hydrides at moderate temperature and pressure.[88] A concerted effort was made to find metal hydrides with sufficient hydride donor ability to transfer a hydride to a borate ester that could be generated in the digestion of spent BNH fuels with a range of alcohols. This approach used a combination of

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]

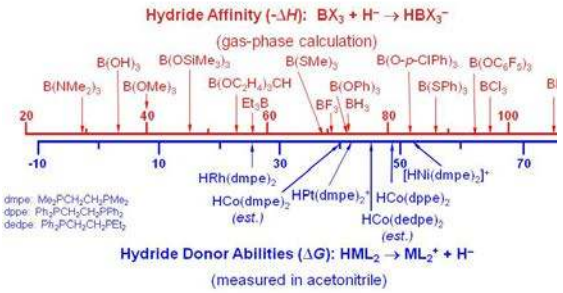


Fig. 3 Scales of experimentally determined hydride donor capabilities of selected transition-metal hydride complexes in acetonitrile (blue, bottom) and the calculated gas-phase hydride affinity values for selected BX_3 compounds (red, top). Reprinted with permission from Ref. 89. Copyright (2009) American 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
$BNH_n + 3\ HX \rightarrow {}^{n}/_{2}\ H_2\uparrow + NH_3\uparrow + BX_3$

Step 2: Transition Metal Hydride Formation
$3\ M^+ + 3\ H_2 \rightarrow 3\ MH_2^+\ [+\ 3\ base] \rightarrow 3\ MH + 3\ H^+\ base$

Step 3: Hydride Transfer/Ligand Redistribution
$3\ MH + 4\ BX_3 + Et_3N \rightarrow 3\ M^+ + 3BX_4^- + Et_3NBH_3$

Step 4: Recycling
$3\ BX_4^- + 3\ H^+base \rightleftharpoons 3\ HX\uparrow + 3\ base + 2\ BX_3$

Step 5: Ammoniation
$Et_3NBH_3 + NH_3 \rightarrow BH_3NH_3\downarrow + Et_3N$

Scheme 2 The 5 key steps of an overall process that regenerates AB from H_2 with recycling of other reagents and solvent.[91]

Scheme 2 shows the 5 key steps of an overall process that regenerates AB from H_2 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 (N_2H_4) in liquid NH_3 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 form borates. Using any material besides hydrogen, a metal hydride or hydrazine in stoichiometric amounts will be very difficult to accomplish economically at large scales.

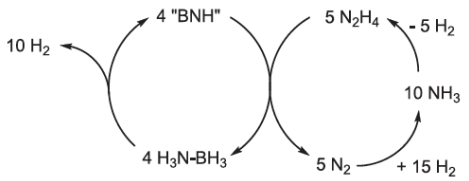


Fig. 4 Ideal overall reaction scheme for AB regeneration with hydrazine. Reprinted with permission from Ref. 93. Copyright (2011) The American Association for the Advancement of Science.

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 B_2H_6 and NH_3 at cryogenic temperatures.[96,97] These methods, however, do not afford high purity. In addition, B_2H_6 is highly flammable and thus very difficult to handle. Autrey's group recently developed a solid state synthesis of DADB by reacting ammonium borohydride (NH_4BH_4) with AB.[98] NH_4BH_4 was first synthesized by reacting NH_4F and $NaBH_4$ in liquid NH_3 at –78 °C. After a 1:1 molar mixture of AB and NH_4BH_4 was mechanically mixed in a SPEX mill for 10 minutes, phase pure DADB was obtained. The reaction mechanism can be expressed as:

$$NH_4BH_4 + NH_3BH_3 \rightarrow [(NH_3)_2BH_2][BH_4] + H_2 \qquad (1)$$

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 BH_4^- sites which coordinate with neighbouring $(NH_3)_2BH_2^+$ ions in different ways (Fig. 5). The nearest N–

This journal is © The Royal Society of Chemistry [year]

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

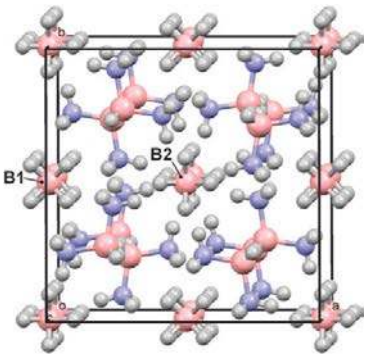


Fig. 5 Crystal structure of DADB viewed along the *c*-axis. The two crystallographically distinct BH_4^- sites are indicated.[98]

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.

$$2\ NaBH_4 + 2NH_4F \rightarrow 2\ NH_4BH_4 + 2NaF \quad (2)$$
$$NH_4BH_4 \rightarrow NH_3BH_3 + H_2 \quad (3)$$
$$NH_4BH_4 + NH_3BH_3 \rightarrow DADB + H_2 \quad (4)$$

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.

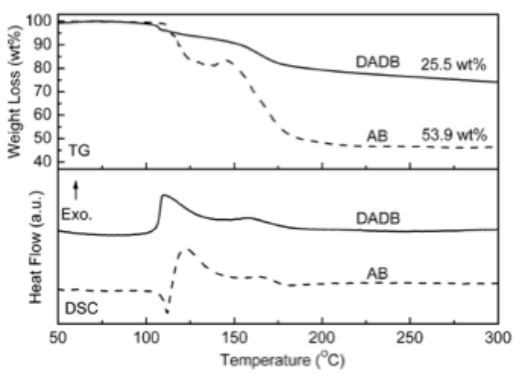


Fig. 6 Comparison of thermogravimetric analysis (TGA)/differential scanning calorimetry (DSC) profiles of DADB (solid lines) and AB (dashed lines). The heating rate was 5 °C/min. [99]

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 then 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]

$$2\ AB \Leftrightarrow DADB \quad (5)$$
$$AB + DADB \rightarrow PAB \quad (6)$$

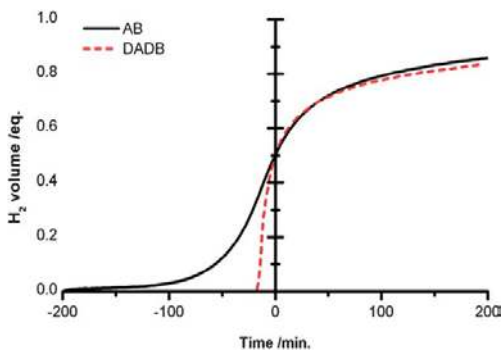


Fig. 7 Comparison of hydrogen release rates from AB and DADB at 85 °C measured in a gas buret normalized for τ(1/2)=0. Note that AB is slower than DADB in the first half-life; however, the rates are nearly equivalent for the second half-life.[31]

Sneddon's group has 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.

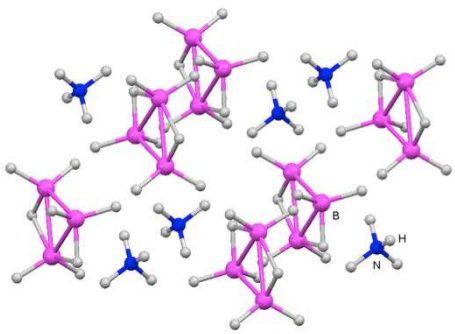


Fig. 8 Crystal structure of $NH_4B_3H_8$: B: pink, H: light grey, N: blue. Reprinted with permission from Ref. 116. Copyright (2011) American Chemical Society.

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 that 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.

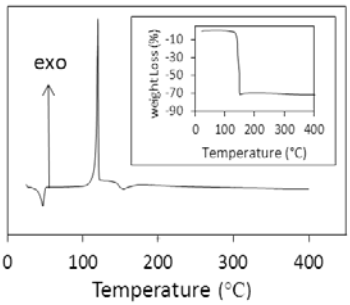


Fig. 9 DSC and TGA (inset) profiles of $NH_4B_3H_8$. The heating rate was 5 °C/min. Reprinted with permission from Ref. 116. Copyright (2011) American Chemical Society.

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_5H_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 %.

$$NH_4B_3H_8(s)+6H_2O(l) \xrightarrow{cat.} NH_4^+(aq)+3BO_2^-(aq)+2H^+(aq)+9H_2(g) \quad (7)$$

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, ^{11}B 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]

This journal is © The Royal Society of Chemistry [year]

By utilizing two well-known reactions: NH_3 reacting with $THF{\cdot}BH_3$ to form DADB and AB,[95,126] and DADB reacting with NH_4Cl to produce $(NH_3)_2BH_2Cl$,[11,127] Huang *et al.* obtained $(NH_3)_2BH_2B_3H_8$ via the metathesis between NaB_3H_8 and $(NH_3)_2BH_2Cl$. This procedure avoids flammable starting materials and produces high purity products, as evidenced by the NMR spectra (Fig. 10).

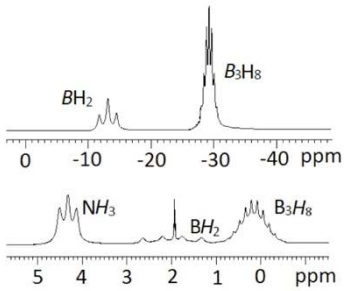


Fig. 10 ^{11}B NMR spectrum of $(NH_3)_2BH_2B_3H_8$ in THF (top), and ^1H NMR spectrum in CD_3CN (bottom).[125]

The DSC and TGA results indicate that melting and decomposition take place simultaneously at 100 °C and finish at around 160 °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 $B_3N_3H_6$.

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 $NH_4B_3H_8$ ($H^{\delta+} : H^{\delta-} = 3 : 6$), compared to the total 40 wt% weight loss and 15 wt% H_2 for $(NH_3)_2BH_2B_3H_8$ ($H^{\delta+} : H^{\delta-} = 3 : 5$).

2.4 CBN compounds

2.4.1 Ethane 1,2-di-amineborane ($BH_3NH_2CH_2CH_2NH_2BH_3$) (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 °C, indicating that storage at high temperature (> 60 °C) for a prolonged period is practical. Secondly, it releases hydrogen more rapidly than AB at temperatures higher than 120 °C, and this means that EDAB is 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 $B_3N_3H_6$, NH_3, or B_2H_6. The absence of $B_3N_3H_6$ 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.

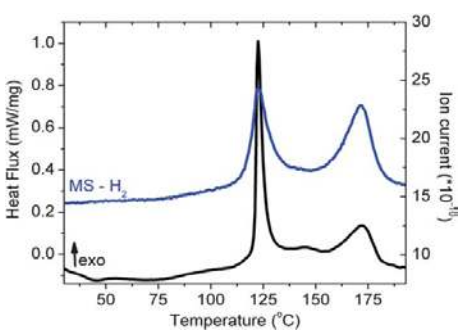


Fig. 11 DSC/mass spectroscopy (MS) data obtained by heating EDAB at 1 °C/min from 25 °C to 200 °C. Black curve is the heat flux; blue curve is the MS data.[128]

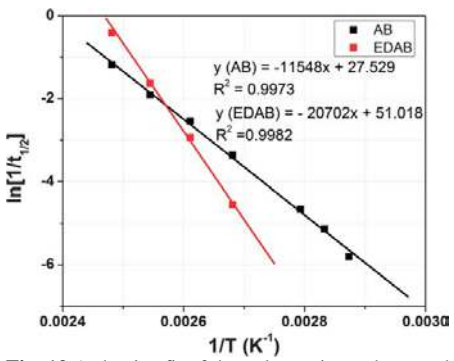


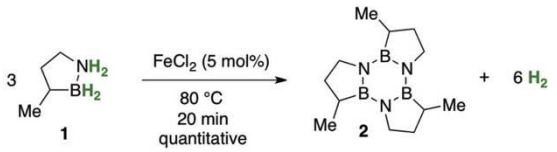
Fig. 12 Arrhenius fit of the volumetric gas burette data for EDAB and AB.[128]

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 °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

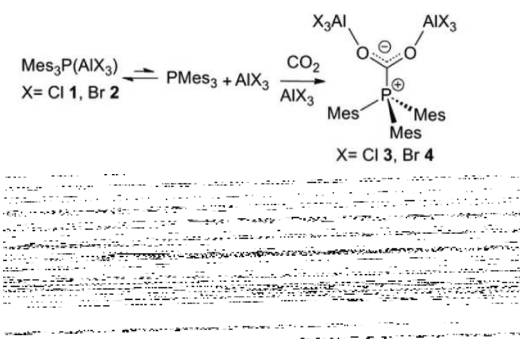
economical regeneration process needs to be developed.



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 alcohols[133-135] 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]



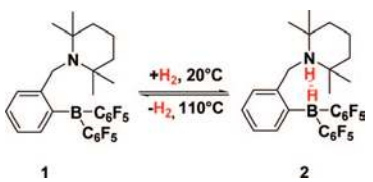
Scheme 4 Synthesis of $PMes_3/AlX_3$, $Mes_3P(CO_2)(AlX_3)_2$ (X = Cl, Br) (top) and the formation of CH_3OH upon adding AB followed by H_2O (bottom). Reprinted with permission from Ref. 142. Copyright (2010) American Chemical Society.

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, $PMes_3$ (Mes = 2,4,6-$C_6H_2Me_3$) and AlX_3 (X = Cl, 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-$CH_2C_6H_4B(C_6F_5)_2$ (where TMPNH is 2,2,6,6-tetramethylpiperidinyl). Reprinted with permission from Ref. 146. Copyright (2010) American Chemical Society.

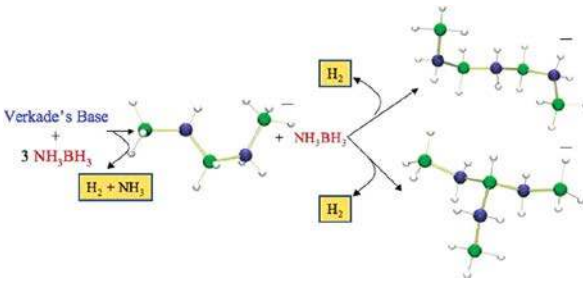
This was the first example of reversible 'hydrogen storage' in an amine borane complex. While the quantity of hydrogen is too low to be of practical significance for hydrogen storage applications, it is an important result because it shows that amine borane complexes can be used to activate hydrogen 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 $[C_{18}H_{39}N_4PH][H_3BNH_2BH_2NH_2BH_3]$,

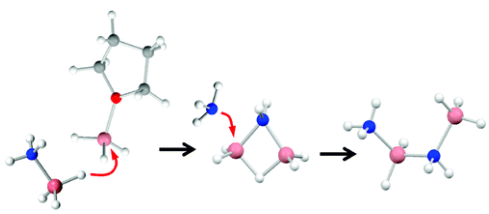
This journal is © The Royal Society of Chemistry [year]

$[C_{18}H_{39}N_4PH][HB(NH_2BH_3)_3]$, 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] 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 H_2 release reactions. Sequential H_2 elimination reactions lead to chain growth, which is likely facilitated by $N{-}H^{\delta+}\cdots H^{\delta-}{-}B$ 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. Reprinted with permission from Ref. 34. Copyright (2011) American Chemical Society.

Aminodiborane ($NH_2B_2H_5$) was first discovered 70 years ago through a tedious procedure using B_2H_6.[148] Little subsequent study has occurred because of its scarce availability. Recently, Chen *et al.* found that when AB and THF·BH_3 were mixed together at room temperature, $NH_2B_2H_5$ was formed via the formation of a dihydrogen bond and subsequent molecular hydrogen elimination (Scheme 7).[36] A concentrated $NH_2B_2H_5$·THF solution (1:1 ratio, based upon the integration of the hydrogen signals in the ^{1}H NMR spectrum) can be obtained with a yield of 70%. When NH_3 was bubbled into a solution of $NH_2B_2H_5$, an inorganic butane analogue, $NH_3BH_2NH_2BH_3$, was formed, a reaction which likely proceeded via the breaking of the bridge hydrogen bond in $NH_2B_2H_5$ (Scheme 7).



Scheme 7 Formation of $NH_2B_2H_5$ and $NH_3BH_2NH_2BH_3$. 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 $Na(H_3BNH_2BH_3)$ and its N-alkyl analogs.[35] $[NH_4][H_3BNH_2BH_3]$ was first proposed by Schlesinger and Berg to formulate DADB,[96] although later spectroscopic studies established that DADB is actually the borohydride salt $[(NH_3)_2BH_2][BH_4]$. 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 reflux, $Na(H_3BNH_2BH_3)$ is formed. This new compound displays a downfield ^{11}B NMR chemical shift compared with AB and $NaNH_2BH_3$ (Fig. 13).[35] Similar reactions with other amine-boranes afford $Na(H_3BNRR'BH_3)$. $Na(H_3BNH_2BH_3)$ can also be generated by reaction of 2 equivalent of AB with $NaNH_2$ in refluxing THF, which results in a better yield (50%).

$$4HNRR'\cdot BH_3 + 2Na \rightarrow 2\ Na(H_3BNRR'BH_3) + H_2 + 2\ HNRR' \quad (6)$$

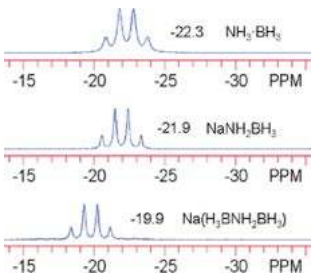


Fig. 13 ^{11}B NMR spectra of AB, $Na(NH_2BH_3)$, and $Na(H_3BNH_2BH_3)$. Reprinted with permission from Ref. 35. Copyright (2010) American Chemical Society.

6. Conclusion

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 $N{-}H^{\delta+}\cdots^{\delta-}H{-}B$ (dihydrogen bond) and the homopolar interactions, $B{-}H^{\delta-}\cdots^{\delta-}H{-}B$ and $N{-}H^{\delta+}\cdots^{\delta+}H{-}N$, in relation to crystal structure and H_2 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 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.

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 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, 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_3BH_3	19.4	144	108	-23	B_2H_6, $B_3N_3H_6$, NH_3	19,20
$LiNH_2BH_3$	10.9	52	92	-3−-5	NH_3	91
$NaNH_2BH_3$	7.6	43	89	-3−-5	NH_3	149
$[(NH_3)_2BH_2][BH_4]$	19.4	151	85	-34	B_2H_6, $B_3N_3H_6$, NH_3	29,98,99
$NH_4B_3H_8$	20.5	160	120	Not reported	$B_3N_3H_6$, B_2H_6, B_5H_9	116
$BH_3NH_2CH_2CH_2NH_2BH_3$	10	82	123	-10 (1st step), -4 (2nd step)	Not observed	128
$(NH_3)_2BH_2B_3H_8$	18.2	Not reported	100	Not reported	$B_3N_3H_6$, B_2H_6, B_5H_9	125
$C_4H_{12}BN$	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.

Acknowledgements

Z. H. is the recipient of a Discovery Early Career Research Award conferred by the Australian Research Council (Project No. DE120101496). T. A. acknowledges support from the U.S. Department of Energy's Basic Energy Sciences, Division of Chemical Sciences, Biosciences and Geosciences. Pacific Northwest National Laboratory is operated by Battelle.

References

1 H. C. Brown, *Boranes in Organic Chemistry*, Cornell University Press, Ithaca, NY, 1972, pp. 41-49.
2 A. Dequasie, *The Green Flame: Surviving Government Secrecy*, American Chemical Society, Washington DC, 1991.
3 H. C. Brown, H. I. Schlesinger, I. Sheft and D. M. Ritter, *J. Am. Chem. Soc.*, 1953, **75**, 192.
4 H. I. Schlesinger, H. C. Brown, J. R. Gilbreath and J. J. Katz, *J. Am. Chem. Soc.*, 1953, **75**, 195.
5 H. I. Schlesinger, H. C. Brown and A. E. Finholt, *J. Am. Chem. Soc.*, 1953, **75**, 205.
6 H. I. Schlesinger and H. C. Brown, *J. Am. Chem. Soc.*, 1953, **75**, 219.
7 H. I. Schlesinger, H. C. Brown and E. K. Hyde, *J. Am. Chem. Soc.*, 1953, **75**, 209.
8 H. I. Schlesinger, H. C. Brown, A. E. Finholt, J. R. Gilbreath, H. R. Hoekstra and E. K. Hyde, *J. Am. Chem. Soc.*, 1953, **75**, 215.
9 J. M. Abboud, B. Németh, J. -C. Guillemin, P. Burk, A. Adamson and E. R. Nerut, *Chem. Eur. J.*, 2012, **18**, 3981.
10 Z. T. Xiong, G. T. Wu, Y. S. Chua, J. J. Hu, T. He, W. L. Xu and P. Chen, *Energy Environ. Sci.*, 2008, **1**, 360.
11 D. J. Heldebrant, A. Karkamkar, J. C. Linehan and T. Autrey, *Energy Environ. Sci.*, 2008, **1**, 156.
12 T. He, H. Wu, G. Wu, J. Wang, W. Zhou, Z. Xiong, J. Chen, T. Zhang and P. Chen, *Energy Environ. Sci.*, 2012, **5**, 5686.
13 H. Wu, W. Zhou, F. E. Pinkerton, T. J. Udovic, T. Yildirim and J. J. Rush, *Energy Environ. Sci.*, 2012, **5**, 7531.
14 D. W. Himmelberger, C. W. Yoon, M. E. Bluhm, P. J. Carroll and L. G. Sneddon, *J. Am. Chem. Soc.*, 2009, **131**, 14101.
15 M. E. Bluhm, M. G. Bradley, R. Butterick III, U. Kusari and L. G. Sneddon, *J. Am. Chem. Soc.*, 2006, **128**, 7748.
16 J. Hannauer, O. Akdim, U. B. Demirci, C. Geantet, J. -M. Herrmann, P. Miele and Q. Xu, *Energy Environ. Sci.*, 2011, **4**, 3355.
17 U. B. Demirci and P. Miele, *Energy Environ. Sci.*, 2009, **2**, 627.
18 P. Wang and X. Kang, *Dalton Trans.*, 2008, **40**, 5400.
19 M. G. Hu, R. A. Geanangel and W. W. Wendlant, *Thermochim. Acta*, 1978, **23**, 249.
20 G. Wolf, J. Baumann, F. Baitalow and F. P. Hoffmann, *Thermochim. Acta*, 2000, **343**, 19.
21 K. R. Graham, T. Kemmitt and M. E. Bowden, *Energy Environ. Sci.*, 2009, **2**, 706.
22 K. C. Ott. Final Report for the DOE Chemical Hydrogen Storage Center of Excellence. http://www1.eere.energy.gov/hydrogenandfuelcells/pdfs/chemical_hydrogen_storage_coe_final_report.pdf
23 Targets for Onboard Hydrogen Storage Systems for Light-Duty Vehicles. US Department of Energy Office of Energy Efficiency and Renewable Energy and The FreedomCAR and Fuel Partnership. September 2009. http://www1.eere.energy.gov/hydrogenandfuelcells/storage/pdfs/targets_onboard_hydro_storage.pdf.
24 Peak power demands in a PEM fuel cell require approximately 0.02 g H_2/sec/kW.
25 S. D. Rassat, C. L. Aardahl, T. Autrey and R. S. Smith, *Energy Fuels*, 2010, **24**, 2596.
26 A. C. Stowe, W. J. Shaw, J. C. Linehan, B. Schmid and T. Autrey, *Phys. Chem. Chem. Phys.*, 2007, **9**, 1831.
27 M. Bowden, T. Autrey, I. Brown and M. Ryan, *Curr. Appl. Phys.*, 2008, **8**, 498.
28 W. J. Shaw, J. C. Linehan, N. K. Szymczak, D. J. Heldebrant, C. Yonker, D. M. Camaioni, R. T. Baker and T. Autrey, *Angew. Chem., Int. Ed.*, 2008, **47**, 7493.
29 M. Bowden and T. Autrey, *Current Opinion in Solid State & Materials Science*, 2011, **15**, 73.
30 G. R. Whittell and I. Manners, *Angew. Chem., Int. Ed.*, 2011, **50**, 10288.
31 T. Autrey, M. Bowden and A. Karkamkar, *Faraday Discuss.*, 2011, **151**, 157.
32 L. Roy, P. M. Zimmerman and A. Paul, *Chem. Eur. J.*, 2011, **17**, 435.
33 L. Song, L. Ci, H. Lu, P. B. Sorokin, C. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson and P. M. Ajayan, *Nano Lett.*, 2010, **10**, 3209.
34 W. C. Ewing, A. Marchione, D. W. Himmelberger, P. J. Carroll and L. G. Sneddon, *J. Am. Chem. Soc.*, 2011, **133**, 17093.
35 S. R. Daly, B. J. Bellott, D. Y. Kim and G. S. Girolami, *J. Am. Chem. Soc.*, 2010, **132**, 7254.
36 X. Chen, J. -C. Zhao and S. G. Shore, *J. Am. Chem. Soc.*, 2010, **132**, 10658.
37 C. W. Hamilton, R. T. Baker, A. Staubitz and I. Manners, *Chem. Soc. Rev.*, 2009, **38**, 279.
38 N. C. Smythe and J. C. Gordon, *Eur. J. Inorg. Chem.*, 2010, 509.
39 A. Staubitz, A. P. M. Robertson and I. Manners, *Chem. Rev.*, 2010, **110**, 4079.
40 P. Wang, *Dalton Trans.*, 2012, **41**, 4296.
41 F. H. Stephens, V. Pons and R. T. Baker, *Dalton Trans.*, 2007, **25**, 2613.
42 Y. Tan, Y. Guo, S. Li, W. Sun, Y. Zhu, Q. Li and X. Yu, *J. Mater. Chem.*, 2011, **21**, 14509.

This journal is © The Royal Society of Chemistry [year]

43 T. B. Richardson, S. Gala and R. H. Crabtree, *J. Am. Chem. Soc.*, 1995, **117**, 12875.
44 H. Wu, W. Zhou, F. E. Pinkerton, T. J. Udovic, T. Yildirimad and J. J. Rush, *Energy Environ. Sci.*, 2012, **5**, 7531.
45 W. J. Shaw, M. Bowden, A. Karkamkar, C. J. Howard, D. J. Heldebrant, N. J. Hess, J. C. Linehan and T. Autrey, *Energy Environ. Sci.*, 2010, **3**, 796.
46 H. Wu, W. Zhou, F. E. Pinkerton, M. S. Meyer, G. Srinivas, T. Yildirim, T. J. Udovic and J. J. Rush, *J. Mater. Chem.*, 2010, **20**, 6550.
47 Y. Li, F. Fang, Y. Song, Y. Li, Q. Zhang, L. Ouyang, M. Zhu and D. Sun, *Int. J. Hydrogen Energy*, 2012, **37**, 4274.
48 Y. Yamada, K. Yano and S. Fukuzumi, *Energy Environ. Sci.*, 2012, **5**, 5356.
49 P. -Z. Li, K. Aranishi and Q. Xu, *Chem. Commun.*, 2012, **48**, 3173.
50 D. Sun, V. Mazumder, Ö. Metin and S. Sun, *ACS Nano*, 2011, **5**, 6458.
51 D. Neiner, A. Luedtke, A. Karkamkar, W. Shaw, J. Wang, N. D. Browning, T. Autrey and S. M. Kauzlarich, *J. Phys. Chem. C*, 2010, **114**, 13935.
52 J. Luo, X. Kang, Z. Fang and P. Wang, *Dalton Trans.*, 2011, **40**, 6469.
53 Z. Tang, H. Chen, X. Chen, L. Wu and X. Yu, *J. Am. Chem. Soc.*, 2012, **134**, 5464.
54 Y. Zhao, J. Zhang, D. L. Akins and J. W. Lee, *Ind. Eng. Chem. Res.*, 2011, **50**, 10024.
55 R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P. -H. Lin, S. Maguire, M. Murugesu, B. L. Scott and N. C. Smythe, *J. Am. Chem. Soc.*, 2012, **134**, 5598.
56 B. L. Conley, D. Guess and T. J. Williams, *J. Am. Chem. Soc.*, 2011, **133**, 14212.
57 S. -K. Kim, W. -S. Han, T. -J. Kim, T. -Y. Kim, S. W. Nam, M. Mitoraj, Ł. Piekoś, A. Michalak, S. -J. Hwang and S. O. Kang, *J. Am. Chem. Soc.*, 2010, **132**, 9954.
58 W. R. H. Wright, E. R. Berkeley, L. R. Alden, R. T. Baker and L. G. Sneddon, *Chem. Commun.*, 2011, **47**, 3177.
59 D. W. Himmelberger, L. R. Alden, M. E. Bluhm, P. J. Carroll and L. G. Sneddon, *Inorg. Chem.*, 2009, **48**, 9883.
60 J. F. Kostka, R. Schellenberg, F. Baitalow, T. Smolinka and F. Mertens, *Eur. J. Inorg. Chem.*, 2012, 49.
61 A. McClaine, *Chemical Hydride Slurry for Hydrogen Production and Storage*, Final Report. DOI: 10.2172/940573
62 U. S. DOE, 2012 Annual Merit Review and Peer Evaluation Report, http://www.hydrogen.energy.gov/pdfs/review12/st000_stetson_2012_o.pdf
63 B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus and B. Scott, *Angew. Chem., Int. Ed.*, 2009, **48**, 6812.
64 A. Staubitz, M. E. Sloan, A. P. M. Robertson, A. Friedrich, S. Schneider, P. J. Gates, J. Schmedt auf der Günne and I. Manners, *J. Am. Chem. Soc.*, 2010, **132**, 13332.
65 M. Käß, A. Friedrich, M. Drees and S. Schneider, *Angew. Chem., Int. Ed.*, 2009, **48**, 905.
66 N. Blaquiere, S. Diallo-Garcia, S. I. Gorelsky, D. A. Black and K. Fagnou, *J. Am. Chem. Soc.*, 2008, **130**, 14034.
67 M. C. Denney, V. Pons, T. J. Hebden, D. M. Heinekey and K. I. Goldberg, *J. Am. Chem. Soc.*, 2006, **128**, 12048.
68 J. R. Vance, A. P. M. Robertson, K. Lee and I. Manners, *Chem. Eur. J.*, 2011, **17**, 4099.
69 D. J. Heldebrant, A. Karkamkar, N. J. Hess, M. Bowden, S. Rassat, F. Zheng, K. Rappe and T. Autrey, *Chem. Mater.*, 2008, **20**, 5332.
70 S. B. Kalidindi, J. Joseph and B. R. Jagirdar, *Energy Environ. Sci.*, 2009, **2**, 1274.
71 C. -H. Sun, X. –D. Yao, A. –J. Du, L. Li, S. Smith and G. –Q. Lu, *Phys. Chem. Chem. Phys.*, 2008, **10**, 6104.
72 T. He, Z. Xiong, G. Wu, H. Chu, C. Wu, T. Zhang and P. Chen, *Chem. Mater.*, 2009, **21**, 2315.
73 S. -K. Kim, T. -J. Kim, T. -Y. Kim, G. Lee, J. T. Park, S. W. Nam and S. O. Kang, *Chem. Commun.*, 2012, **48**, 2021.
74 S. Karahan, M. Zahmakıran and S. Özkar, *Chem. Commun.*, 2012, **48**, 1180.
75 Z. Tang, S. Li, Z. Yang and X. Yu, *J. Mater. Chem.*, 2011, **21**, 14616.
76 Z. Xiong, C. K. Yong, G. Wu, P. Chen, W. Shaw, A. Karkamkar, T. Autrey, M. O. Jones, S. R. Johnson, P. P. Edwards and W. I. F. David, *Nat. Mater.*, 2008, **7**, 138.
77 S. A. Shevlin, B. Kerkeni and Z. X. Guo, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7649.
78 K. J. Fijalkowski, R. V. Genova, Y. Filinchuk, A. Budzianowski, M. Derzsi, T. Jaroń, P. J. Leszczyński and W. Grochala, *Dalton Trans.*, 2011, **40**, 4407.
79 X. Kang, J. Luo, Q. Zhang and P. Wang, *Dalton Trans.*, 2011, **40**, 3799.
80 H. V. K. Diyabalanage, R. P. Shrestha, T. A. Semelsberger, B. L. Scott, M. E. Bowden, B. L. Davis and A. K. Burrell, *Angew. Chem., Int. Ed.*, 2007, **46**, 8995.
81 A. T. Luedtke and T. Autrey, *Inorg. Chem.*, 2010, **49**, 3905.
82 D. Y. Kim, H. M. Lee, J. Seo, S. K. Shin and K. S. Kim, *Phys. Chem. Chem. Phys.*, 2010, **12**, 5446.
83 T. B. Lee and M. L. McKee, *Inorg. Chem.*, 2009, **48**, 7564.
84 D. J. Wolstenholme, J. T. Titah, F.N. Che, K. T. Traboulsee, J. Flogeras and G. S. McGrady, *J. Am. Chem. Soc.*, 2011, **133**, 16598.
85 P. J. Fazen, E. E. Remsen, J. S. Beck, P. J. Carroll, A. R. McGhie and L. G. Sneddon, *Chem. Mater.*, 1995, **7**, 1942.
86 S. Hausdorf, F. Baitalow, G. Wolf and F. O. R. L. Mertens, *Int. J. Hydrogen Energy*, 2008, **33**, 608.
87 A. D. Sutton, B. L. Davis, K. X. Bhattacharyya, B. D. Ellis, J. C. Gordon and P. P. Power, *Chem. Commun.*, 2010, **46**, 148.
88 D. L. DuBois, D. M. Blake, A. Miedaner, C. J. Curtis, M. R. DuBois, J. A. Franz and J. C. Linehan, *Organometallics*, 2006, **25**, 4414.
89 M. T. Mock, R. G. Potter, D. M. Camaioni, J. Li, W. G. Dougherty, W. S. Kassel, B. Twamley and D. L. DuBois, *J. Am. Chem. Soc.*, 2009, **131**, 14454.
90 M.T. Mock, R. G. Potter, M.J. O'Hagan, D. M. Camaioni, W. G. Dougherty, W. S. Kassel and D. L. DuBois, *Inorg. Chem.*, 2011, **50**, 11914.
91 C. Aardahl, T. Autrey, D. Camaioni, D. Dubois, J. Linehan, A. Karkamkar, S. Rassat, R. Zheng, W. Shaw, J. Li, D. Heldebrant, R. Potter, M. Mock, A. Luedtke and T. Smurthwaite, "Chemical Hydrogen Storage Research at PNNL", U.S. DOE Annual Report, 2009.
92 R. G. Potter and D. M. Camaioni, M. Vasiliu and D. A. Dixon, *Inorg. Chem.*, 2010, **49**, 10512.
93 A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner III, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson and M. Vasiliu, *Science*, 2011, **331**, 1426.
94 E. Wiberg, *Z. Anorg. Allg. Chem.*, 1928, **173**, 199.
95 A. Stock and E. Pohland, *Ber. Dtsch. Chem. Ges.*, 1926, 59, 2215.
96 H. I. Schlesinger and A. B. Burg, *J. Am. Chem. Soc.*, 1938, **60**, 290.
97 S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, 1955, **77**, 6084.
98 M. Bowden, D. J. Heldebrant, A. Karkamkar, T. Proffen, G. K. Schenter and T. Autrey, *Chem. Commun.*, 2010, **46**, 8564.
99 Z. Fang, J. Luo, X. Kang, H. Xia, S. Wang, W. Wen, X. Zhou and P. Wang, *Phys. Chem. Chem. Phys.*, 2011, **13**, 7508.
100 H. K. Lingam, X. Chen, J. -C. Zhao and S. G. Shore, *Chem. Eur. J.*, 2012, **18**, 3490.
101 C. W. Yoon and L. G. Sneddon, *J. Am. Chem. Soc.*, 2006, **128**, 13992.
102 C. W. Yoon, P. J. Carroll and L. G. Sneddon, *J. Am. Chem. Soc.*, 2009, **131**, 855.
103 D. Gaines, R. Schaeffer and F. Tabbe, *Inorg. Chem.*, 1963, **2**, 526.
104 H. C. Miller, N. E. Miller and E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 1456.
105 L. V. Titov, E. R. Eremin and V. Y. Rosolovskii, *Russ. J. Inorg. Chem. (Engl. Transl.)*, 1982, **27**, 500.
106 C. Serrar and A. Ouassas, *Synth. React. Inorg. Met. -Org. Chem.*, 1996, **26**, 669.
107 L. V. Titov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 2003, **48**, 1471.
108 I. S. Antonov, M. A. Pchelkina, V. S. Nikitin, G. A. Egorenko, Z. F. Vinogradova and A. T. Kurekova, *Russ. J. Inorg. Chem.* (*Engl. Transl.*), 1973, **18**, 321.

109 W. V. Hough, L. J. Edwards and A. D. McElroy, *J. Am. Chem. Soc.*, 1956, **78**, 689.
110 D. M. Goedde, G. K. Windler and G. S. Girolami, *Inorg. Chem.*, 2007, **46**, 2814.
111 Z. Huang, G. King, X. Chen, J. Hoy, T. Yisgedu, H. K. Lingam, S. G. Shore, P. M. Woodward and J. -C. Zhao, *Inorg. Chem.*, 2010, **49**, 8185.
112 M. Chong, A. Karkamkar, T. Autrey, S.-i. Orimo, S. Jalisatgi and C. M. Jensen, *Chem. Commun.*, 2011, **47**, 1330.
113 W. V. Hough and J. M. Makhlouf, U.S. Patent No. 3,313,603, 1967.
114 D. A. L. Carvalho and N. W. Shust, U.S. Patent No. 3,564,561, 1971.
115 Y. Deng, D. Zhao, Z. Shan, Z. Peng and J. Song, Chinese Patent No. CN85100253A, 1986.
116 Z. Huang, X. Chen, T. Yisgedu, E. A. Meyers, S. G. Shore and J. -C. Zhao, *Inorg. Chem.*, 2011, **50**, 3738.
117 W. T. Klooster, T. F. Koetzle, P. E. M. Siegbahn, T. B. Richardson and R. H. Crabtree, *J. Am. Chem. Soc.*, 1999, **121**, 6337.
118 A. Brockman, Y. Zheng and J. Gore, *Int. J. Hydrogen Energy*, 2010, **35**, 7350.
119 Rohm and Haas: *The Sodium Borohydride Digest*, 2003, 8.
120 B. H. Liu and Z. P. Li, *J. Power Sources*, 2009, **187**, 527.
121 J. C. Walter, A. Zurawski, D. Montgomery, M. Thornburg and S. Revankar, *J. Power Sources*, 2008, **179**, 335.
122 G. Kodama and R. W. Parry, *J. Am. Chem. Soc.*, 1960, **82**, 6250.
123 S. G. Shore and H. D. Johnson II, *J. Am. Chem. Soc.,* 1970, **92**, 7586.
124 M. A. Toft, J. B. Leach, F. L. Himpsl and S. G. Shore, *Inorg. Chem.*, 1982, **21**, 1952.
125 Z. Huang, S. Porter, X. Chen, A. Du, H. K. Lingam, S. G. Shore and J.-C. Zhao, unpublished manuscript entitled: "Synthesis, structural analysis, and thermal decomposition studies of $(NH_3)_2BH_2B_3H_8$".
126 E. Mayer, *Inorg. Chem.*, 1972, **11**, 866.
127 S. G. Shore and R. W. Parry, *J. Am. Chem. Soc.*, 1958, **80**, 8.
128 D. Neiner, A. Karkamkar, M. Bowden, Y. J. Choi, A. Luedtke, J. Holladay, A. Fisher, N. Szymczak and T. Autrey, *Energy Environ. Sci.*, 2011, **4**, 4187.
129 P. G. Campbell, L. N. Zakharov, D. J. Grant, D. A. Dixon and S. -Y. Liu, *J. Am. Chem. Soc.*, 2010, **132**, 3289.
130 A. N. Lamm, E. B. Garner, D. A. Dixon and S. -Y. Liu, *Angew. Chem., Int. Ed.*, 2011, **50**, 8157.
131 W. Luo, L. N. Zakharov and S. -Y. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 13006.
132 W. Luo, P. G. Campbell, L. N. Zakharov and S. -Y. Liu, *J. Am. Chem. Soc.*, 2011, **133**, 19326.
133 G. C. Andrews, *Tetrahedron Lett.*, 1980, **21**, 697.
134 B. L. Allwood, H. Shahriarizavareh, J. F. Stoddart and D. J. Williams, *J. Chem. Soc.*, *Chem. Commun.*, 1984, **22**, 1461.
135 G. C. Andrews and T. C. Crawford, *Tetrahedron Lett.*, 1980, **21**, 693.
136 R. O. Hutchins, W. Y. Su, R. Sivakumar, F. Cistone and Y. P. Stercho, *J. Org. Chem.*, 1983, **48**, 3412.
137 X. H. Yang, L. L. Zhao, T. Fox, Z. X. Wang and H. Berke, *Angew. Chem., Int. Ed.*, 2010, **49**, 2058.
138 A. P. M. Robertson, E. M. Leitao and I. Manners, *J. Am. Chem. Soc.*, 2011, **133**, 19322.
139 W. Xu , H. Fan, G. Wu and P. Chen, *New J. Chem.*, 2012, **36**, 1496.
140 R. Angamuthu, P. Byers, M. Lutz, A. L. Spek and E. Bouwman, *Science*, 2010, **327**, 313.
141 S. Sato, T. Morikawa, S. Saeki, T. Kajino and T. Motohiro, *Angew. Chem.*, 2010, **122**, 5227.
142 G. Ménard and D. W. Stephan, *J. Am. Chem. Soc.*, 2010, **132**, 1796.
143 P. M. Zimmerman, Z. Zhang and C. B. Musgrave, *Inorg. Chem.*, 2010, **49**, 8724.
144 A. E. Ashley, A. L. Thompson and D. O'Hare, *Angew. Chem. Int. Ed.*, 2009, **48**, 9839.
145 G. C.Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* 2006, **314**, 1124.
146 V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskela, T. Repo, P. Pyykko and B. Rieger, *J. Am. Chem. Soc.*, 2008, **130**, 14117.
147 D. W. Stephan, S. Greenberg, T. W. Graham, P. Chase, J. J. Hastie, S. J. Geier, J. M. Farrell, C. C. Brown, Z. M. Heiden, G. C. Welch and M. Ullrich, *Inorg. Chem.*, 2011, **40**, 12338.
148 H. I. Schlesinger, D. M. Ritter and A. B. Burg, *J. Am. Chem. Soc.*, 1938, **60**, 2297.
149 K. J. Fijałkowski and W. Grochala, *J. Mater. Chem.*, 2009, **19**, 2043.
150 U.S. DOE has complied a publically available, searchable database on hydrogen storage materials. http://hydrogenmaterialssearch.govtools.us/.

This journal is © The Royal Society of Chemistry [year]