Hydrazine Borane and Hydrazinidoboranes as Chemical Hydrogen Storage Materials

Romain Moury, Umit Demirci

Review

Hydrazine Borane and Hydrazinidoboranes as Chemical Hydrogen Storage Materials

Romain Moury [1] and Umit B. Demirci [2],*

[1] Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1,
45470 Mülheim an der Ruhr, Germany; E-Mail: moury@mpi-muelheim.mpg.de

[2] IEM (Institut Europeen des Membranes), UMR 5635 (CNRS-ENSCM-UM2),
Universite Montpellier 2, Place E. Bataillon, F-34095 Montpellier, France

* Author to whom correspondence should be addressed; E-Mail: umit.demirci@um2.fr;
Tel.: +33-467-149-160; Fax: +33-467-149-119.

Abstract: Hydrazine borane $N_2H_4BH_3$ and alkali derivatives (*i.e.*, lithium, sodium and potassium hydrazinidoboranes $MN_2H_3BH_3$ with M = Li, Na and K) have been considered as potential chemical hydrogen storage materials. They belong to the family of boron- and nitrogen-based materials and the present article aims at providing a timely review while focusing on fundamentals so that their effective potential in the field could be appreciated. It stands out that, on the one hand, hydrazine borane, in aqueous solution, would be suitable for full dehydrogenation in hydrolytic conditions; the most attractive feature is the possibility to dehydrogenate, in addition to the BH_3 group, the N_2H_4 moiety in the presence of an active and selective metal-based catalyst but for which further improvements are still necessary. However, the thermolytic dehydrogenation of hydrazine borane should be avoided because of the evolution of significant amounts of hydrazine and the formation of a shock-sensitive solid residue upon heating at >300 °C. On the other hand, the alkali hydrazinidoboranes, obtained by reaction of hydrazine borane with alkali hydrides, would be more suitable to thermolytic dehydrogenation, with improved properties in comparison to the parent borane. All of these aspects are surveyed herein and put into perspective.

Keywords: chemical hydrogen storage; hydrazine borane; hydrazinidoborane; hydrolysis; thermolysis

1. Introduction

Access to energy has been one of the most important events in recent human history. The world entered into a new era with technological development related to widespread use of coal in the 19th century. With oil emerging in the 20th century, the world has entered into another era, characterized by faster technological progress, which has, unfortunately, negatively impacted the environment. Nowadays, and in light of past experience, a new era must begin. The 21st century could be that of the hydrogen century. Hydrogen is attractive owing to abundance via various sources, high mass energy density (120 MJ/kg) and oxidation into water. However, the transition C_xH_y (≤ 25 $wt\%$ H) $\rightarrow$ H_2 (100 $wt\%$ H), *i.e.*, the development of a near-future energy economy, is very challenging. Important technical/scientific issues touching production, storage and end-use have to be addressed [1–3].

Storage of hydrogen is particularly critical and problematic, mainly because molecular hydrogen is a gas, even the lightest one. Accordingly, it has a low volumetric energy density (10.7 kJ·L^{-1} at 27 °C and 1 bar). Solutions have been investigated in order to make safe and efficient technologies emerge. First, the conventional storage methods (*i.e.*, compressed gas up to 700 bars and cryogenic liquid at −253 °C) were considered while the efforts have been concentrated on storage system (*i.e.*, tank, pipes, and so on) in terms of safety and performance. Then, alternative methods, involving materials, which are generally called hydrogen storage materials, emerged [4–6].

Hydrogen storage materials enable a safer storage than the compressed and cryogenic technologies, and naturally carry 7–20 $wt\%$ H. Depending on their nature, there is distinction between physical storage (*i.e.*, cryo-adsorption) and chemical storage. With the former, porous materials store molecular hydrogen in conditions (−196 °C and 10–120 bars of H_2) that are milder than those for cryogenic liquid [4–7]. With respect to chemical hydrogen storage materials, atomic hydrogen is chemically bonded to a heteroatom and molecular hydrogen is released by solvolysis or thermolysis [4–6]. Borohydrides [8] and nitrogen-containing boranes (also called B–N–H compounds or boron- and nitrogen-based materials) [9] are typical examples.

Hydrazine borane $N_2H_4BH_3$ is one of the most recent boron- and nitrogen-based materials in the field of hydrogen storage. Though discovered and known since more than fifty years [10], the current energy context has been an opportunity to revive scientific interest on it, especially in view of the high gravimetric hydrogen density (15.4 $wt\%$ H). Hence, since 2009, hydrazine borane and new derivative compounds, the alkali hydrazinidoboranes $MN_2H_3BH_3$, have positioned themselves as being potential candidates for chemical hydrogen storage, then focusing more and more attention. This is the core topic of the present review, which for the first time aims at specifically focusing on these materials, giving a timely and detailed overview about fundamentals, and tentatively discussing application prospects on the basis of the recent achievements.

2. Brief Historical View of Hydrazine Borane

Hydrazine borane was first reported by Goubeau and Ricker in 1961, in an original paper written in German [10]. The article provides experimental details about the synthesis as well as useful data about the molecular and crystal structures. Interestingly, it is mentioned the formation of a shock-sensitive solid residue upon the release of 2 equivalents of H_2. Later, in 1967, Gunderloy stressed on the shock-sensitivity

and flammability of hydrazine borane but no further detail can be found in the report [11]. Yet, one year later, the same author wrote in a patent that hydrazine borane "is highly stable at room temperature (25 °C) and is neither impact nor friction sensitive" [12]. With hindsight, the contradiction does not appear to be so critical, since the borane-hydrazine compounds were demonstrated to be potential solid-state monopropellants for rocket devices [12–14] and fast hydrogen generating systems [15,16].

From an academic point of view, little research was carried out on hydrazine borane from 1961 to 2009. In 1971, the standard enthalpy was determined [17]. In 1997, hydrazine borane was used as precursor of porous boron nitride obtained by self-propagating high-temperature synthesis (Equation (1)) [18]. In 1999, the structure of hydrazine borane and that of its protonated analogue were calculated by the density functional theory method [19].
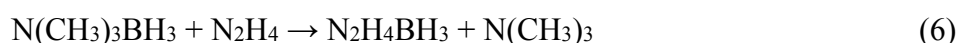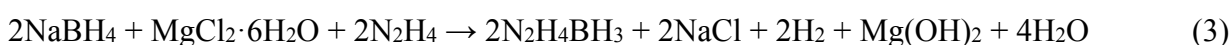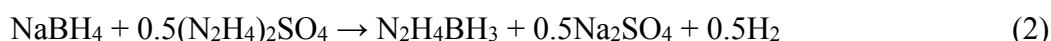
$$N_2H_4BH_3 \rightarrow BN + 0.5N_2 + 3.5H_2 \tag{1}$$
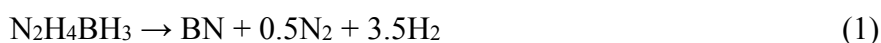
In the 2000s, ammonia borane NH_3BH_3 was the only boron- and nitrogen-based material under intense research for chemical hydrogen storage [20]. One of the strategies was to destabilize it by chemical modification (synthesis of derivatives) [21]. This is in this context that hydrazine borane, which can be seen as a derivative of ammonia borane, emerged in 2009. The same year, Hamilton *et al.* [22] dedicated very few lines to pristine hydrazine borane in a review paper about the boron- and nitrogen-based materials and, on the basis of the aforementioned 1960s' literature, suggested unsuitability for chemical hydrogen storage.

3. Hydrazine Borane

3.1. Synthesis

The original synthesis procedure of hydrazine borane (Equation (2)) is based on the reaction of sodium borohydride $NaBH_4$ with hydrazine sulfate $(N_2H_4)_2SO_4$ in dioxane at around 30 °C for 5–15 h [10]. It may be qualified as the classical procedure, reused by Hügle *et al.* in 2009 [23] and then, revisited and improved in terms of yield, purity and overall cost by Moury *et al.* in 2012 [24]. This is today the main procedure for the preparation of hydrazine borane at lab-scale.

Hydrazine borane can also be synthesized by reaction of sodium borohydride with magnesium chloride $MgCl_2$ either in hexahydrated form $MgCl_2 \cdot 6H_2O$ implying then the use of iced hydrazine N_2H_4 (Equation (3)) or in the form of a tetrahydrazinate $MgCl_2 \cdot 4N_2H_4$ (Equation (4)) with tetrahydrofuran C_4H_8O as solvent [12,25]. Instead of the chloride salt, a hydrazine salt $N_2H_4 \cdot HX$ with X = Cl or CH_3COO can be used (Equation (5)), the reaction taking place in tetrahydrofuran at temperatures between 50 and 100 °C [11,12,26]. The BH_3 source can be changed also. Trimethylamine borane $N(CH_3)_3BH_3$ can be reacted with hydrazine (Equation (6)) in benzene C_6H_6 at 50 °C for several hours [27].

$$NaBH_4 + 0.5(N_2H_4)_2SO_4 \rightarrow N_2H_4BH_3 + 0.5Na_2SO_4 + 0.5H_2 \tag{2}$$

$$2NaBH_4 + MgCl_2 \cdot 6H_2O + 2N_2H_4 \rightarrow 2N_2H_4BH_3 + 2NaCl + 2H_2 + Mg(OH)_2 + 4H_2O \tag{3}$$

$$2NaBH_4 + MgCl_2 \cdot 4N_2H_4 \rightarrow 2N_2H_4BH_3 + 2NaCl + Mg(N_2H_3)_2 + 2H_2 \tag{4}$$

$$NaBH_4 + N_2H_4 \cdot HCl \rightarrow N_2H_4BH_3 + NaCl + H_2 \tag{5}$$

$$N(CH_3)_3BH_3 + N_2H_4 \rightarrow N_2H_4BH_3 + N(CH_3)_3 \tag{6}$$

In chemistry, synthesis generally makes two or more reactants react in order to get the targeted molecule. This was the classical strategy for the reactions mentioned above. Often, the first attempts fail. Sometimes, a surprising result stands out, like the formation of hydrazine borane while trying to get ammonia borane. Sutton *et al.* [28,29] were widely involved in finding an efficient chemical route to form ammonia borane from one of its solid residue, polyborazylene. Hydrazine was tentatively used as reducing agent of polyborazylene in tetrahydrofuran. After 12 h of reaction under stirring in room conditions, hydrazine borane was found to form. This is somehow an alternative route for synthesizing hydrazine borane. This would be also a way of regeneration, provided the thermolysis of hydrazine borane mostly leads to polyborazylene.

The heat of formation of solid-state hydrazine borane was determined by pyrolysis in a bomb calorimeter under 29.6 bars of argon. Hydrazine borane decomposed into boron nitride BN (Equation (1)). The heat of formation of solid-state hydrazine borane was found to be 42.7 ± 0.4 kJ·mol^{-1} [17].

3.2. Molecular and Structural Analyses

The FTIR spectrum of hydrazine borane (Figure 1a) is typical of a boron- and nitrogen-based material, with numerous vibration bands, especially those ascribed to the N–H and B–H stretching regions (2600–3500 and 2100–2600 cm^{-1}). Compared to the spectrum of ammonia borane, it is roughly comparable, but shows several additional bands of different intensity [10]. Particularly, there are two small bands at 1915 and 2015 cm^{-1} (B–H stretching region), suggesting strong interactions between H of BH$_3$ and other elements. Another example is the band at 910 cm^{-1} in the BN–N asymmetric and N–N symmetric stretching region [24].

The solution-state ^{11}B NMR spectrum of hydrazine borane (Figure 1b) shows a signal at δ between -20 and -17.1 ppm, and the ^{11}B{^{1}H} spectrum a quartet (1:3:3:1) characteristic of the BH$_3$ group ($^{1}J_{BH}$ 94 ± 1 Hz) [23,24,30]. The presence of the N$_2$H$_4$ moiety can be verified in the ^{1}H NMR spectrum (Figure 1c) via two singlets at δ 3.44 ppm (NH$_2$–N) and δ 5.45 ppm (NH$_2$–B). The BH$_3$ group is also confirmed by a quartet (1:1.1:1.1:1) centered at δ 1.41 ppm due to the heteronuclear coupling between ^{11}B and ^{1}H and some small signals (three visible over the δ range 1.12–1.72 ppm and four overlapped) attributed to the heteronuclear coupling between ^{10}B and ^{1}H. The solid-state ^{11}B NMR spectrum (Figure 1d) shows two signals (due to quadrupolar coupling) centered at about δ -24 ppm and whose sharpness indicates high crystallinity.
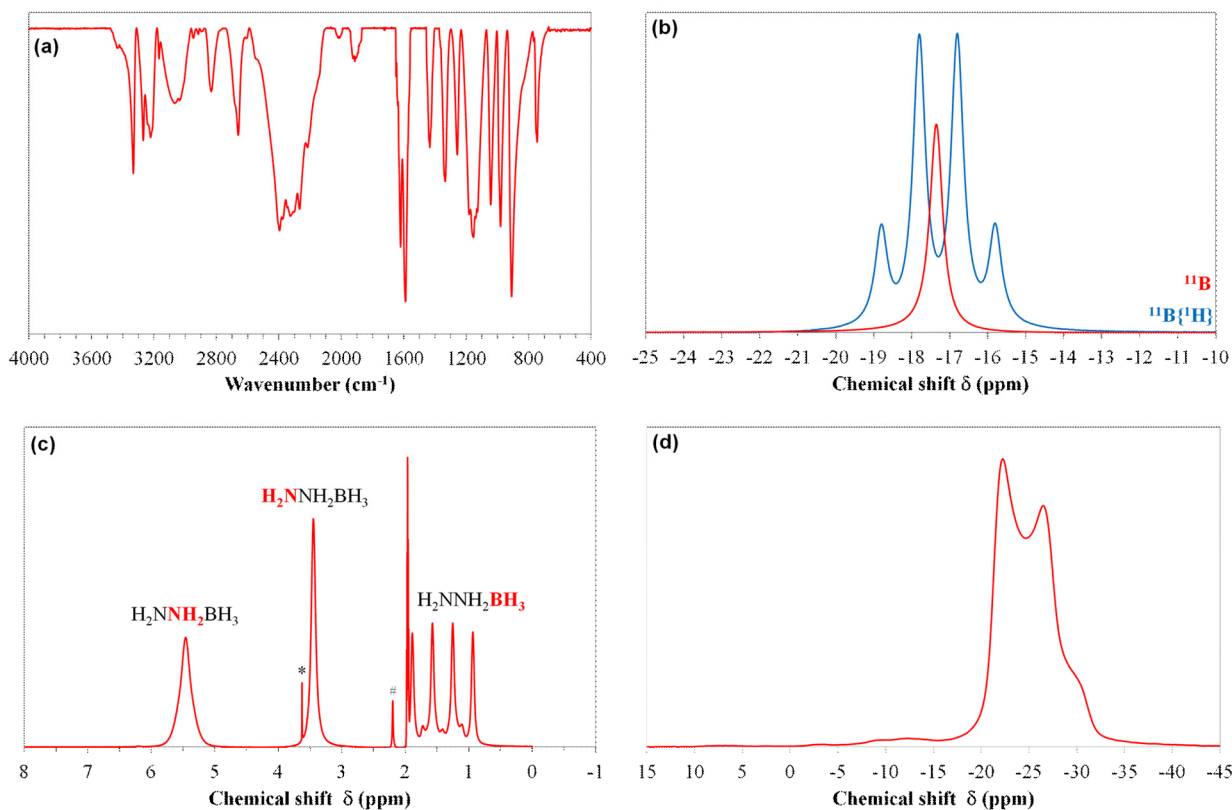
Figure 1. Molecular identification of hydrazine borane $N_2H_4BH_3$. (**a**) FTIR spectrum; (**b**) solution-state ^{11}B and $^{11}B\{^1H\}$ NMR spectra; (**c**) solution-state ^1H NMR spectrum; and (**d**) solid-state ^{11}B NMR spectrum. Adapted from [24]—Reproduced by permission of the Physical Chemistry Chemical Physics (PCCP) Owner Societies.

Hydrazine borane is a white crystalline solid and a Lewis acid-base adduct. By XRD of a single crystal, Goubeau and Ricker reported an orthorhombic *Pccn* (56) space group [10]. More recently, the structure was solved using an orthorhombic *Pbcn* (60) space group with all of the B, N and H atoms belonging to the 8 d sites; Further, the cell parameters were refined [24,31,32]. As shown in Table 1, the cell parameters *a*, *b* and *c* are in good agreement. Neutron diffraction experiment permitted to obtain correct coordinates of the H atoms [31]. The N–B, N–N, N–H and B–H bonds as well as the N–H···H–B and N–H···N interactions were described. The nature of the N–B coordinative (or dative) bond (1.596 Å) exhibits an electrostatic feature mainly, but with substantial contribution of covalence with a large electron population of ~2.1 electrons and a small donation of ~0.05 electron from the Lewis base (N) to the Lewis acid (B). With respect to the N–H···H–B intermolecular weak interaction (2.01(1)–2.41(1) Å) [31], it allows a head-to-tail network of the hydrazine borane molecules (Figure 2), which rationalizes the solid state of the material [24]. The N–H···N intermolecular interactions (2.114 Å) occur with the head-to-tail network, according to planes parallel to the *a*-axis. Of note is a dipole moment of 4.18 D determined by Goubeau and Ricker for hydrazine borane [10].

Table 1. Crystallographic data of hydrazine borane (HB) from various works (with ref. as reference and No. as number).

Feature	HB in ref. [10]	HB in ref. [31]	HB in ref. [24]	HB in ref. [32]
Analyzed sample	Single crystal	Single crystal	Single crystal	Powder
Crystal size (mm^3)	$2.5 \times 0.5 \times 0.5$	$0.3 \times 0.3 \times 0.2$	$0.45 \times 0.5 \times 0.5$	–
Temperature (K)	not given	95	173	Room
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Orthorhombic
Space group (No.)	*Pccn* (56)	*Pbcn* (60)	*Pbcn* (60)	*Pbcn* (60)
Z	8	8	8	8
a (Å)	13.05	12.974(2)	12.9788(5)	13.1227(11)
b (Å)	5.12	5.070(1)	5.0616(2)	5.1000(5)
c (Å)	9.55	9.507(1)	9.5087(4)	9.5807(9)
B–N bond (Å)	–	1.596	1.587	1.592
N–N bond (Å)	–	1.452	1.452	1.458
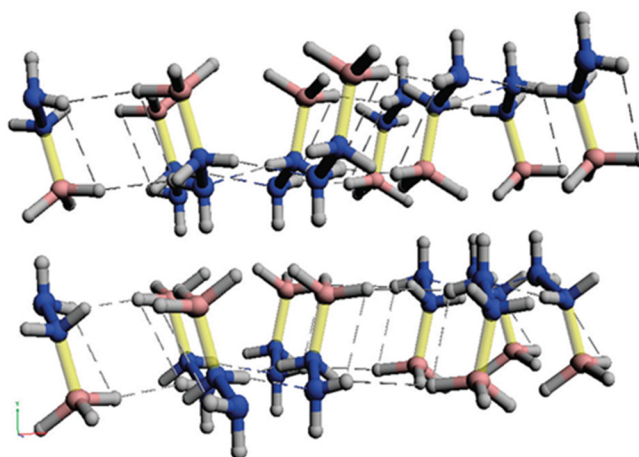
Figure 2. Head-to-tail network of the hydrazine borane molecules $N_2H_4BH_3$ determined from XRD data [24]—Reproduced by permission by the PCCP Owner Societies. The red arrow indicates the *x* axis and the green one the *y* axis. The intermolecular interactions are shown by the grey dashed lines.

3.3. Stability and Solubility

Moury *et al.* [24] analyzed hydrazine borane in solid state after storage for one month in an argon-filled glove box and room conditions. The XRD, ^{11}B NMR and FTIR spectroscopy techniques were used. No difference was observed between the results obtained after synthesis and those collected one month later. The authors emphasized the stability of hydrazine borane under inert and dry atmosphere. Data about long-term stability (e.g., up to one year) and stability under air are nevertheless missing.

Goubeau and Ricker [10] considered a large number of solvents to evaluate qualitatively the solubility of hydrazine borane. The solvents were classified into five categories such as: extremely soluble for e.g., water, methanol and pyridine; very soluble for e.g., ethanol, dioxane and tetrahydrofuran; soluble for dimethylaniline and acetyl acetate; moderately soluble for diethyl ether and *n*-butyl acetate; and insoluble for e.g., petroleum ether, benzole and chloroform. Elsewhere, the solubility of hydrazine borane in water was found to be low, *i.e.*, 6 g $N_2H_4BH_3$ in 100 g H_2O [30].By ^{11}B NMR analyses, hydrazine borane

solved in dioxane was found to be stable after one month in room conditions and under argon atmosphere [24]. Hydrazine borane could thus be kept solved in dioxane after the filtration following the synthesis. Moury *et al.* [24] also focused on the stability in water because hydrazine borane was intended to be dehydrogenated by hydrolysis in the presence of a catalyst. With deionized water at an initial pH of 6.8 and the same storage conditions than those used for dioxane, hydrazine borane hydrolyzed such that 99%, 98% and 93% of it remained unchanged after two days, one week, and one month, respectively. Karahan *et al.* [30] reported hydrolysis of <5% of hydrazine borane over four days of storage under air at room temperature. They also reported great stability in methanol but without further details. Moury *et al.* [24] envisaged stabilization of the aqueous solution by increasing the pH to 8 with the help of sodium hydroxide NaOH. Similar action has been efficient for hindering the spontaneous hydrolysis of sodium borohydride [9]. After one month, improved stability was noticed: 97% of hydrazine borane remained unchanged. The formation of a borate by-product by hydrolysis was evidenced by large signals at δ higher than 10 ppm. One can thus reasonably conclude that hydrogen evolution by spontaneous hydrolysis of hydrazine borane is negligible at the time scale of one catalytic hydrolysis experiment (<10 min), and long-term storage of aqueous alkaline solution of hydrazine borane may be satisfactorily.

4. Liquid-State Chemical Hydrogen Storage

4.1. Introductive Remark

Like sodium borohydride and ammonia borane [33], hydrazine borane in aqueous solution is a potential liquid-state chemical hydrogen storage material, which means that the main challenge is the catalytic dehydrogenation. Since 2011, mainly three groups, who were already much involved in hydrolyses of sodium borohydride and ammonia borane, have focused on catalytic dehydrogenation of hydrazine borane. This is discussed hereafter.

4.2. Hydrolysis of the BH3 Group of Hydrazine Borane

The Özkar's group (Middle East Technical University, Ankara, Turkey) have focused their efforts on the development of metal-based catalysts of different forms for hydrolysis of the BH_3 group of hydrazine borane (Equation (7)). Systematic works were performed where, in addition to the characterization of the catalyst (in fresh and/or used states), the hydrolysis reaction was analyzed in terms of turnovers, turnover frequency, power law and thermodynamic data (apparent activation energy, activation enthalpy and activation entropy). The lifetime and isolability/reusability of the catalysts were also systematically considered.
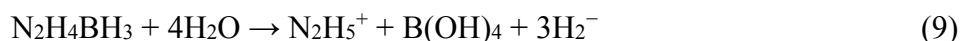
$$N_2H_4BH_3 + 2H_2O \rightarrow N_2H_5^+ + BO_2^- + 3H_2 \tag{7}$$
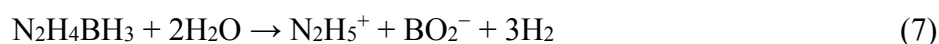
Some catalysts were *ex-situ* prepared: e.g., Rh/Al_2O_3, Ru/Al_2O_3, $Rh(0)$ or $Ru(0)$ nanoparticles supported on the zeolite Y [30]; $Rh(0)$ supported on hydroxyapatite $Ca_{10}(OH)_2(PO_4)_6$ [34]. Catalytic precursors were used to get some other catalysts by *in-situ* reduction owing to the reducing properties of hydrazine borane: e.g., $RhCl_3$ and $RuCl_3$ [30]; poly(4-styrenesulfonic acid-co-maleic-acid) stabilized Ni(II) [35]. With such catalytic materials, different results were obtained in terms of hydrogen generation rate and

catalytic lifetime. For the reason that will be evoked in the next sub-section and because focusing on the catalytic activity is off topic here, the reader is referred to the following review articles for more information about the catalysts, their performance and the kinetic parameters [32,36–38].

The hydrolysis reaction was reported to take place according to the reaction shown by Equation (6) However, the solution-state ^{11}B NMR spectrum reported by the authors shows a signal centered at 12.5 ppm, preceded by a shoulder at around 10 ppm. This is typical of the presence, in equilibrium, of the base tetrahydroxyborate anion $B(OH)_4^-$ and the acid counterpart boric acid $B(OH)_3$ [39]. Furthermore, in the hydrolysis conditions, the anhydrous borate anion BO_2^- cannot exist, the hydrated form $B(OH)_4^-$ being the thermodynamically stable phase [40]. Consequently, the hydrolysis more likely takes place according to the reactions described by Equation (8) ($\Delta_r H = -244.5$ kJ·mol^{-1}) and Equation (9) ($\Delta_r H = -208.7$ kJ·mol^{-1}). The theoretical gravimetric hydrogen storage capacity will thus be impacted (Figure 3): 7.3 w_t% for $N_2H_4BH_3$-$2H_2O$ in Equation (7); 6 w_t% for $N_2H_4BH_3$-$3H_2O$ in Equation (8); and 5.1 w_t% for $N_2H_4BH_3$-$4H_2O$ in Equation (9).

$$N_2H_4BH_3 + 3H_2O \rightarrow N_2H_4 + B(OH)_3 + 3H_2 \tag{8}$$

$$N_2H_4BH_3 + 4H_2O \rightarrow N_2H_5^+ + B(OH)_4 + 3H_2^- \tag{9}$$
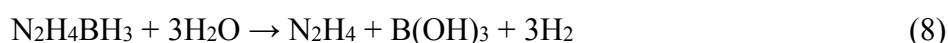
Karahan *et al.* [30] optimized the effective gravimetric hydrogen storage capacities. For a $H_2O/N_2H_4BH_3$ mole ratio of 6.6, 2.8 moles of H_2 per mole of $N_2H_4BH_3$ were released within 4 min at 25 °C. Taking into account the weight of the *in-situ* formed Rh(0) catalyst (from RhCl$_3$), this means an effective capacity of <3.4 w_t%. In harsher conditions, namely for a $H_2O/N_2H_4BH_3$ mole ratio of 2, complete hydrolysis was achieved within less than 6 h.
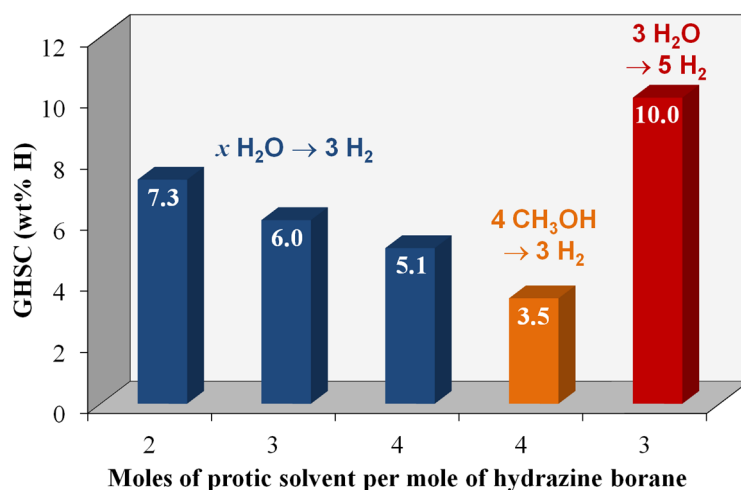
Figure 3. Theoretical gravimetric hydrogen storage capacity (denoted GHSC, in w_t% H) for the couples $N_2H_4BH_3$-xH_2O (with x equal to 2, 3 and 4) and $N_2H_4BH_3$-$4CH_3OH$. In blue and orange, the BH$_3$ group hydrolyzes only into 3 moles of H$_2$ (Equations (7)–(10)). In red, the BH$_3$ group and the N_2H_4 moiety generates 5 moles of H$_2$ (Equation (12)).

The absence of ammonia NH$_3$ as gaseous by-product was controlled with acid/base indicator or a trap of aqueous hydrochloric acid HCl placed upstream from the hydrolysis reactor [30,35]. In other words, this result suggests that either the N_2H_4 moiety is decomposed into NH$_3$ that remains solved in the aqueous medium kept at 25 °C or the catalyst is inactive towards the dehydrogenation of N_2H_4.

If the latter hypothesis is correct, the attractiveness of the catalyst would then be negatively affected; This is discussed hereafter.

It is worth mentioning that, like for sodium borohydride and ammonia borane, catalytic methanolysis of hydrazine borane (Equation (10)) was also investigated [41,42]. With the help of solution-state ^{11}B NMR and FTIR spectroscopic methods, the by-product hydrazinium tetramethoxyborate $N_2H_5B(OCH_3)_4$ was found to form. The advantage of this reaction over hydrolysis has not been demonstrated. Further, when water and methanol are put together, the hydrolysis reaction predominates [41]. The theoretical gravimetric hydrogen storage capacity of the couple $N_2H_4BH_3$-$4CH_3OH$ is low (3.5 $w_t\%$; Figure 3).

$$N_2H_4BH_3 + 4\ CH_3OH \rightarrow N_2H_5^+ + B(OCH_3)_4 + 3\ H_2^- \tag{10}$$

In the light of this overview, considering that ammonia borane is richer in hydrogen than hydrazine borane (19.5 $w_t\%$ *vs.* 15.4 $w_t\%$), and taking into account that the couple NH_3BH_3-$4H_2O$ (Equation (11)) is richer in hydrogen than the couple $N_2H_4BH_3$-$4H_2O$ (Equation (9); $\Delta_rH = -155.8$ kJ·mol^{-1}) with 5.8 $w_t\%$ *vs.* 5.1 $w_t\%$, that raises a question. What is the advantage of hydrazine borane over ammonia borane?

$$NH_3BH_3 + 4\ H_2O \rightarrow NH_4^+ + B(OH)_4 + 3\ H_2^- \tag{11}$$
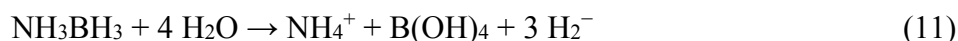
4.3. Hydrolysis of the BH₃ Group and Dehydrogenation of the N₂H₄ Moiety of Hydrazine Borane

The Demirci's group (University of Montpellier, France) in collaboration with the Xu's group (AIST, Osaka, Japan) joined their efforts to answer the question asked above. They demonstrated that the great advantage of hydrazine borane is that the N_2H_4 moiety can be dehydrogenated. In the case of the NH_3 group of ammonia borane, dehydrogenation is thermodynamically impossible in room conditions, limiting thus the theoretical gravimetric hydrogen storage capacity of NH_3BH_3-$3H_2O$ to 7.1 $w_t\%$. With $N_2H_4BH_3$-$3H_2O$ (Equation (12); $\Delta_rH = -193.9$ kJ·mol^{-1}), the gravimetric hydrogen storage capacity that could be ideally obtained is 10 $w_t\%$ (Figure 3).

$$N_2H_4BH_3 + 3H_2O \rightarrow B(OH)_3 + 5H_2 + N_2 \tag{12}$$
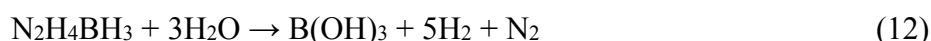
Every catalyst made of, e.g., nickel, cobalt, rhodium, ruthenium and platinum, is especially active in hydrolysis of the BH_3 group (and also of the BH_4^- anion), it is just a matter of rate [43,44]. The challenge is thus to find the metal-based catalyst that is active towards the dehydrogenation of the N_2H_4 moiety. Xu's group had developed active nickel-based alloyed nanoparticles for selective dehydrogenation of hydrous hydrazine $N_2H_4 \cdot H_2O$ at temperatures over the range 20–70 °C [45]. Indeed, the dehydrogenation of $N_2H_4 \cdot H_2O$ (Equation (13)) competes with the decomposition (Equation (14)).

$$N_2H_4 \cdot H_2O \rightarrow 2\ H_2 + N_2 + H_2O \tag{13}$$

$$N_2H_4 \cdot H_2O \rightarrow 4/3\ NH_3 + 1/3\ N_2 + H_2O \tag{14}$$
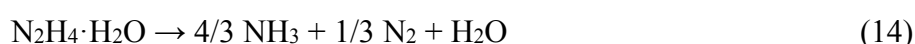
A first and successful attempt envisaged the use of nickel-platinum nanoparticles [46]. While the monometallic catalysts were found to be active in the hydrolysis of the BH_3 group only, the bimetallic alloy $Ni_{0.89}Pt_{0.11}$ showed to be active and 93% selective in the dehydrogenation of the N_2H_4 moiety, owing to geometric and electronic effects. However, the hydrogen evolution showed two regime of kinetics (Figure 4), with a fast first step attributed to the hydrolysis of BH_3 and a second one with slower kinetics due to the dehydrogenation of N_2H_4. The former reaction is at least 40 times faster. In fact,

during the first step, when the BH$_3$ groups are hydrolyzed, some of the N$_2$H$_4$ moieties interact with the catalytic surface and decompose [47,48]. The second regime of kinetics (*i.e.*, dehydrogenation of N$_2$H$_4$) determines the total time that the dehydrogenation of hydrazine borane really needs.

Other catalytic solutions were investigated: e.g., metal salts to form *in-situ* the catalytically active phase [49]; supported nickel [50]; Ni@NiPt core shell nanoparticles [51]. With respect to the nickel-based bimetallic alloy nanoparticles, several metals were tested: Pt, Rh, Ru, Ir, Fe, Co and Pd [52,53]. Though very active and almost-100% hydrogen selective, the Pt-, Rh- and Ir-containing systems were found not to be stable after the first cycle because of nickel surface enrichment, explained by borate-induced segregation [47,52]. Nickel, like cobalt, strongly adsorbs borates via M–O–B bonds, leading to the catalyst deactivation [54–56]. However, the presence of both Ni and the noble metal is essential and would be the optimum conditions to activate the bonds of the N$_2$H$_4$ moiety of hydrazine borane [52]. Recently, another group has contributed to the development of field. Li *et al.* [57] reported the synthesis and use of alumina supported Ni@(RhNi-alloy) nanocomposites that showed a H$_2$ selectivity of <95%.
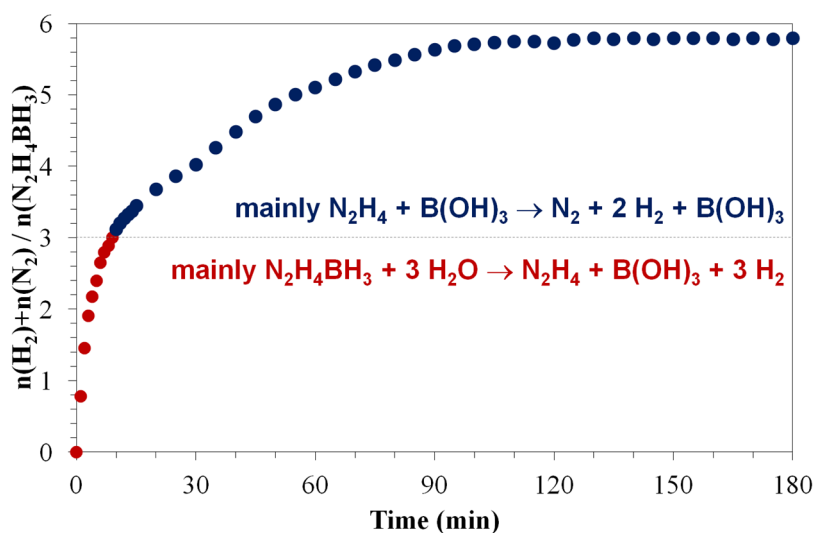
Figure 4. Stepwise catalytic dehydrogenation of aqueous hydrazine borane in near-room conditions and in the presence of Ni$_{0.89}$Pt$_{0.11}$ nanoparticles. The gas evolution is composed of a first step, *i.e.*, fast hydrolysis of the BH$_3$ group, followed by a second one, *i.e.*, slow dehydrogenation of the N$_2$H$_4$ moiety. Adapted from Ref. [46] with permission from The Royal Society of Chemistry.

Among the catalytic solutions investigated so far, the best performance was achieved with nanoporous carbon-supported Ni$_{0.6}$Pt$_{0.4}$ nanoalloys [58]. It is considered the best for the following three reasons: (*i*) It is 100% selective, generating five moles of H$_2$ and one mole of N$_2$ per mole of N$_2$H$_4$BH$_3$; (*ii*) It greatly improves the rates of the second regime of kinetics, making the reaction complete within <5 min at 30 °C; and (*iii*) It is stable in terms of activity and selectivity over five cycles.

Up to now, the catalytic activity and selectivity have been the major concerns. The heterogeneous catalysts were evaluated in favorable conditions, that is, using diluted aqueous hydrazine borane solutions. The effective gravimetric hydrogen storage capacities were therefore low (<0.5 *w*t%) and not realistic for practical applications. The highest capacity ever reported is 1.2 *w*t% for a H$_2$O/N$_2$H$_4$BH$_3$ molar ratio of 42, but in these conditions the selectivity of the Ni$_{0.89}$Pt$_{0.11}$ catalyst was negatively affected [47]. This

reveals another issue to overcome with the catalyst used in this reaction: it has to be selective whatever the concentration of the borane. This is the only way to get high effective gravimetric hydrogen storage capacities and to make aqueous hydrazine borane viable for liquid-state chemical hydrogen storage.

5. Solid-State Chemical Hydrogen Storage

5.1. Pristine Hydrazine Borane

The behavior of hydrazine borane under heating at constant temperature (70, 85, 100 and 200 °C) was first investigated by Goubeau and Ricker [10]. Melting at 61 °C was reported. Upon melting, the borane foamed because of its decomposition, which was then visually observed. Besides hydrogen, hydrazine in gaseous state was found to evolve whereas no gaseous boron-containing by-product (e.g., diborane B_2H_6) was detected. The solid residue forming upon the evolution of 1 mole of H_2 and 0.24–0.47 mole of N_2H_4 per mole of $N_2H_4BH_3$ (Equation (15)) was reported to be constituted by the structural unit $NHBH_2$. It was inert towards acidic and basic aqueous solutions. The evolution of the second mole of H_2 took place when the solid was kept at 200 °C for 10 h (Equation (16)). The as-obtained solid residue was found to be shock-sensitive and explosive.

$$n\text{N}_2\text{H}_4\text{BH}_3 \rightarrow [\text{NHBH}_2]_n + n/2\text{N}_2\text{H}_4 + n\text{H}_2 \tag{15}$$

$$[\text{NHBH}_2]_n \rightarrow [\text{NBH}]_n + n\text{H}_2 \tag{16}$$
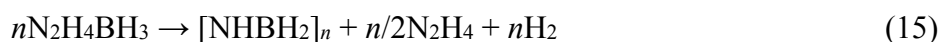
With the help of correlated molecular orbital theory, Vinh-Son *et al.* [59] concluded that the energy of the B–N dative bond of gas-phase hydrazine borane is larger than that of gas-phase ammonia borane ($\sim$130 *vs.* $\sim$110 kJ·mol^{-1}) and that such higher thermodynamic stability could be an advantageous feature for chemical hydrogen storage. However, experimental works performed by Hügle *et al.* [23] did not confirm: at 65 and 100 °C, less than one mole of H_2 per mole of $N_2H_4BH_3$ was liberated in 43 and 30 h, respectively. At higher temperatures, the hydrogen release was faster, with about 1.4 moles of H_2 per mole of $N_2H_4BH_3$ in less than 1 h at 140 °C. Slightly different results were reported by Moury *et al.* [24]. They found 1.8 moles of H_2 evolving at 140 °C, but with similar kinetics. Hence, both groups concluded that pristine hydrazine borane is not suitable for chemical hydrogen storage.

Moury *et al.* [24] analyzed the thermolytic decomposition of hydrazine in dynamic conditions (5 °C·min^{-1}), by TGA and DSC, and over the range 25–400 °C. It was confirmed that the melting occurs at around 60 °C with an enthalpy of 15 kJ·mol^{-1}. Together with melting, hydrazine borane dehydrogenated in small extent (1.2 w_t% H_2 at 95 °C). The main decomposition (mass loss of 28.7 w_t%) took place at 105–160 °C and had a heat of 20 kJ·mol^{-1}. The analysis of the evolving products revealed the presence of hydrogen and of the unwanted hydrazine, confirming the observations made by Goubeau and Ricker [10]. There was a third mass loss (4.3 w_t%), due to some dehydrogenation (14 kJ·mol^{-1}). Most importantly, it was reported that the solid residue forming upon this decomposition was shock-sensitive and made the authors strongly stress on the unsuitability of hydrazine borane for chemical hydrogen storage. In fact, hydrazine borane was recently proposed as being a possible hypergolic fuel for propellant systems [60,61].

Goubeau and Ricker [10] and, later, Moury *et al.* [24] proposed some likely structural units of the solid residue forming upon the release of the first equivalent of hydrogen (Figure 5). Any identification was found to be very difficult because of insolubility of the residue in organic solvents, reactivity in

water and alcohols (solvolysis), and amorphous state [23]. Furthermore, like for thermolysis of ammonia borane, the IR and solid-state NMR spectroscopy methods do not enable gaining insight about the exact nature of the solid residue [20–24]. For the solid residue forming upon the release of the second equivalent, none of the groups were able to recover it in safe conditions. Accordingly, there has been no mechanism proposed for the decomposition of hydrazine borane.

Like pristine hydrazine borane, neat ammonia borane is ineffective for chemical hydrogen storage. Hence, different strategies were envisaged to destabilize it: (*i*) Chemical doping; (*ii*) Dispersion in solvent (organic or ionic liquid) with/without the presence of a homogeneous metal-based catalyst; and (*iii*) Nanoconfinement into a porous host [22]. Strategies (*i*) and (*ii*) were also envisaged in the case of hydrazine borane. They are discussed hereafter. A fourth strategy (*iv*) was also considered: it consists in elaborating derivatives of the borane [22]. This was also applied to hydrazine borane. This is reported below.
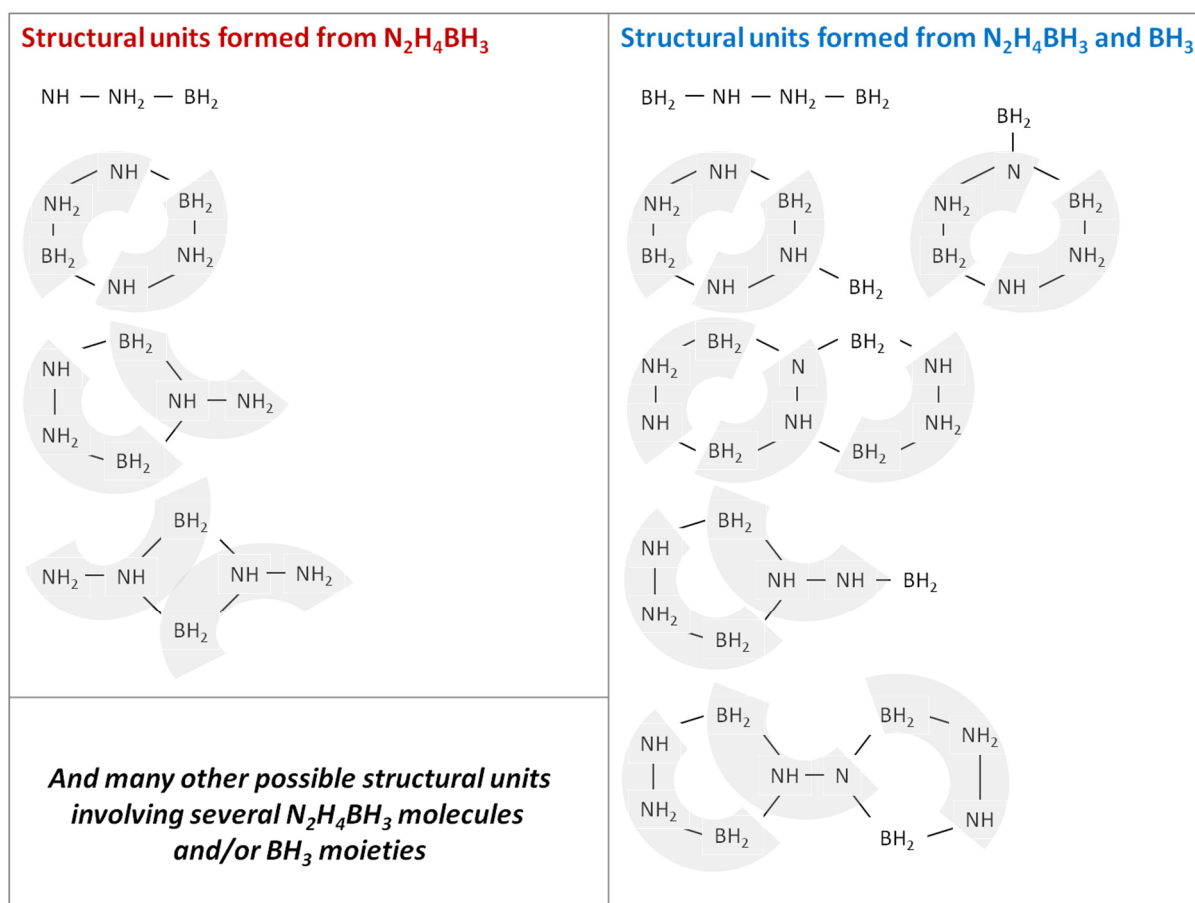
Figure 5. Examples of likely structural units of the solid by-products formed by the decomposition of hydrazine borane $N_2H_4BH_3$ over the range 25–200 °C [24]—reproduced by permission of the PCCP Owner Societies.

5.2. Chemical Doping of Hydrazine Borane

Hügle *et al.* [23] chose lithium hydride LiH to destabilize hydrazine borane. The 1:1 mixture (14.8 *w*t% H) was constituted of 4 $H^{\delta-}$ (from BH_3 of hydrazine borane and LiH) and 4 $H^{\delta+}$ (from N_2H_4 of hydrazine borane). In comparison to pristine hydrazine borane, better dehydrogenation

kinetics was reported. For example, at 150 °C more than three moles of H_2 per mole of the mixture were released within 4.5 h. The presence of lithium hydride improved not only the dehydrogenation extent, but also the dehydrogenation kinetics and the purity of the liberated hydrogen. Only traces of ammonia were detected.

Chemical doping was also studied by Toche *et al.* [62]. Borohydrides ($LiBH_4$ or $NaBH_4$) were added to hydrazine borane. The mixtures borane-borohydride had a molar ratio 4:1, namely with one $H^{\delta+}$ for one $H^{\delta-}$. They showed improved dehydrogenation properties in comparison to not only hydrazine borane but also to the borohydride. Indeed, the borane destabilized the borohydrides, making them dehydrogenate at temperatures much lower than the temperature 400 °C reported for the pristine borohydrides. The mixtures were capable of liberating hydrogen as soon as 50 °C. For example, the four moles of $N_2H_4BH_3$ and one mole of $LiBH_4$ released 12.1 moles of H_2 upon heating up to 300 °C (5 °C·min^{-1}), but 1.1 moles of N_2H_4 also evolved. It was proposed the formation of a solid residue of empirical formulae $LiB_5N_{5.8}H_{3.4}$ (Equation (17)), which consisted likely of polyborazylene- and/or boron nitride-like compounds. Interestingly, the presence of boron nitride was reported. It would have formed at <500 °C whereas the formation of such ceramic material generally occurs at >1000 °C [63].

$$4N_2H_4BH_3 + LiBH_4 \rightarrow LiB_5N_{5.8}H_{3.4} + 1.1N_2H_4 + 12.1H_2 \tag{17}$$
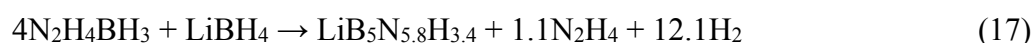
The formation of boron nitride from hydrazine borane at <300 °C was also reported in another contribution. Petit *et al.* [64] focused on the destabilization of hydrazine borane by ammonia borane, and *vice versa*, in equimolar amounts. The destabilization took place at 30 °C. The binary solid melted because one of the boranes disrupted the intermolecular $H^{\delta+}\cdots H^{\delta-}$ network of the other borane. At temperatures higher than 75 °C, the binary mixture explosively decomposed, liberating hydrogen and hydrazine. Alternatively, the sample was treated at 90 °C for 2 h so that a stable solid, *i.e.*, a mixture of oligomers from both boranes, was obtained. The stable solid was then investigated for chemical hydrogen storage. It was able to liberate *ca.* 11.4 *wt*% of almost pure H_2 from 75 to 300 °C according to a two-step process. Traces of ammonia were detected during the first decomposition step (75–150 °C). Very fast dehydrogenation was observed in the second step, which occurred at around 200 °C. The solid residue was found to be insoluble and stable in organic solvents as well as in water, and was analyzed by FTIR and XRD evidencing the formation of orthorhombic boron nitride. The presence of an amorphous phase of boron nitride could not be excluded.

The findings reported by Toche *et al.* [62] and Petit *et al.* [64] are very interesting from the point of view of ceramics chemistry. However, the formation of boron nitride is a drawback from the point of view of chemical hydrogen storage, since boron nitride cannot be recycled to close the hydrogen cycle with the aforementioned boron-based materials.

5.3. Dispersion and Catalysis of Hydrazine Borane

To date, just one paper reported the destabilization of hydrazine borane by dispersion in an organic solvent (tetrahydrofuran) and in the presence of a homogeneous catalyst (group 4 metallocene alkyne complexes of the type $Cp'_2M(L)(\eta^2\text{-}(CH_3)_3SiC_2Si(CH_3)_3)$ with Cp' as substituted or unsubstituted η^5-cyclopentadienyl and M as Ti (no L) or Zr (L = pyridine)) [65]. Up to four moles of H_2 and N_2 per mole of hydrazine borane evolved at 25 or 50 °C, in the best case within 32 h. The solid residue was

analyzed but the task was tough because of the reasons mentioned above. By elemental analysis, it was found a B/N ratio of 1:1.03, suggesting that 3.5 moles of H_2 and 0.5 mole of N_2 evolved. XRD and IR analyses were in line with the results reported by Moury *et al.* [24]. They were indicative of the formation of a mixture of cyclic $[H_2N–NH–BH_2]$ structures (Figure 5) and boron nitride species. Inspired from the process of Sutton *et al.* [28,29], the spent fuel was tentatively reduced by hydrazine in tetrahydrofuran at 50 °C. The attempt was successful in some extent. Further optimizations would be in progress (not reported yet in the open literature).

5.4. Chemical Modification of Hydrazine Borane

Chemical modification of hydrazine borane by reaction with an alkaline hydride was first introduced by Hügle *et al.* in 2009 [23]. However, the authors preferred to investigate the 1:1 mixture of lithium hydride and hydrazine borane (both in solid states; 14.8 *w*t% H) to avoid losing one equivalent of hydrogen (Equation (17)). In 2012, Wu *et al.* [32] reported the preparation of the first sample of lithium hydrazinidoborane $LiN_2H_3BH_3$ (11.6 *w*t% H) by ball-milling (200 rpm, 1 h) lithium hydride and hydrazine borane under inert atmosphere. The structure was solved using a monoclinic $P2_1/c$ (14) space group with all atoms in 4e sites. The adduct $LiN_2H_3BH_3\cdot2N_2H_4BH_3$ (13.9 *w*t% H) was obtained in a similar way by increasing the amount of hydrazine borane.

$$N_2H_4BH_3 + LiH \rightarrow LiN_2H_3BH_3 + H_2 \tag{18}$$

The formation of lithium hydrazinidoborane $LiN_2H_3BH_3$ can be explained by the reaction of the strong Lewis base H^- of lithium hydride with one of the protic hydrogen $H^{\delta+}$ on the middle NH_2 group of hydrazine borane and its replacement by the lithium cation Li^+ (Figure 6) [66]. Qian *et al.* [67] found by first-principles calculations that the most stable structure would be the one where the lithium cation Li^+ substitutes one of the hydrides $H^{\delta-}$ of the BH_3 group. No detail is provided on fate of the strong Lewis base H^- of lithium hydride and the substituted $H^{\delta-}$. This result is surprising, as even for amidoboranes, such an unexpected substitution has never been observed [21].
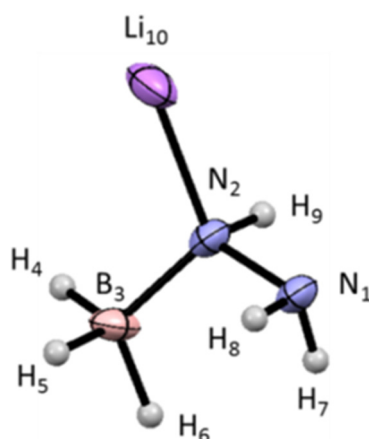
Figure 6. Asymmetric unit with labels of lithium hydrazinidoborane $LiN_2H_3BH_3$. Reprinted with permission from [66]. Copyright 2014 American Chemical Society.

Moury *et al.* [66] recently argued that they were also working on lithium hydrazinidoborane when Wu *et al.* [32] published their experimental report. However, the former researchers were not able to

compare favorably the structure of lithium hydrazinidoborane they mechano-synthesized to the compound proposed by later authors. Moury *et al.* [66] demonstrated that lithium hydrazinidoborane is a polymorphic material with a stable low-temperature phase with orthorhombic *Pbca* (61) space group, atoms standing in the 8c sites, and a metastable high-temperature phase as described by Wu *et al.* [32]. The former was called the β phase because discovered after the metastable phase, then called α. The crystallographic data for both phases are reported in Table 2. In their report, Moury *et al.* highlighted a phase transition from the β phase to the α phase at about 95 °C. The phase transition is of first order, the volume of the β phase (648.8 Å^3) being almost twice that of the α one (328.3 Å^3). The Li$\cdots$Li distance decreases from 3.49 Å for the β phase to 3.31 Å for the α one, explaining the better stability of the former phase.

Table 2. Crystallographic data of alkali hydrazinodoboranes at room temperature (No. as number).

MN$_2$H$_3$BH$_3$	α-LiN$_2$H$_3$BH$_3$	β-LiN$_2$H$_3$BH$_3$	NaN$_2$H$_3$BH$_3$	KN$_2$H$_3$BH$_3$
Reference	**[32,66]**	**[66]**	**[68]**	**[69]**
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic
Space group (No.)	*P2$_1$/c* (14)	*Pbca* (61)	*P2$_1$/n* (14)	*P2$_1$* (4)
a (Å)	5.8503(11)	10.25182(11)	4.97437(11)	6.72102(23)
b (Å)	7.4676(11)	8.47851(10)	7.95806(15)	5.89299(20)
c (Å)	8.8937(15)	7.46891(8)	9.29232(19)	5.77795(17)
β (°)	122.329(6)	–	93.8137(11)	108.2595(13)
B–N bond (Å)	1.539	1.549(2)	1.537(6)	1.541
N–N bond (Å)	1.469	1.495(2)	1.453(5)	1.463

The solid state of lithium hydrazinidoborane is explained by the presence of an intermolecular head-to-tail H$^{\delta+}\cdots$H$^{\delta-}$ interaction that form chains (*i.e.*, parallel plans on which the H$^{\delta+}\cdots$H$^{\delta-}$ network extends). In the β phase, the network was identified according to the definition of Klooster *et al.* [70], with a B–H$\cdots$H angle slightly bent (106.8°), a N–H$\cdots$H angle almost linear (171.2°) and a H$\cdots$H distance of 2.25 Å [66]. For both phases, the lithium is in tetrahedral environment (Figure 7). Two corners of the tetrahedron are occupied by the BH$_3$ moiety and interaction occurs through the BH$_2$ edges of the −BH$_3$ tetrahedron. Of the two remaining corners, one is occupied by the central N of the N$_2$H$_3$ moiety and the other by the terminal N through the lone electron pair. Thereby, these interactions induce a strong electronic modification in the [N$_2$H$_3$BH$_3$]$^-$ entities. Such coordination leads to modified B–H bond polarization, decreased electron density around the boron element, and, thus, increased reactivity of the hydridic H$^{\delta-}$ hydrogen. Further, compared to hydrazine borane, the B–N bond is shortened owing to strong electron donation from N to Li$^+$ and the N–N bond is stretched due to the interactions between Li$^+$ and the lone electrons pair of the terminal N (Tables 1 and 2). These results may rationalize the improved thermal dehydrogenation properties described hereafter [32].
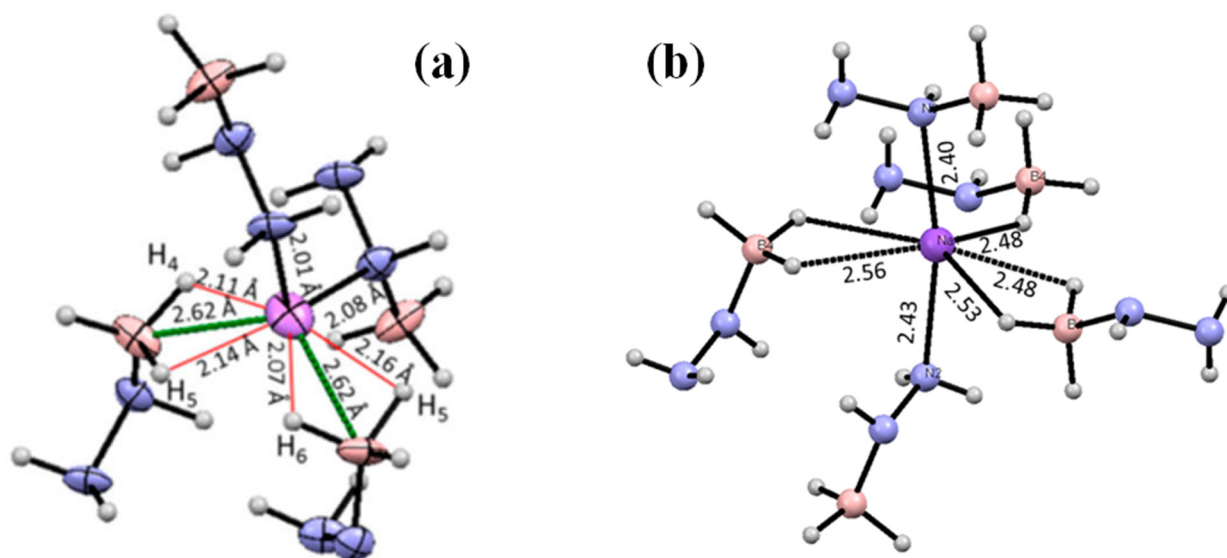
Figure 7. (**a**) Coordination of Li$^+$ in lithium hydrazinidoborane LiN$_2$H$_3$BH$_3$ (reprinted with permission from [66]; copyright 2014 American Chemical Society); (**b**) Coordination of Na$^+$ in sodium hydrazinidoborane NaN$_2$H$_3$BH$_3$ (reprinted with permission from [71]; copyright 2013 Wiley).

The thermal dehydrogenation of lithium hydrazinidoborane is indeed more attractive than that of hydrazine borane. By TGA, the α phase starts to generate hydrogen below 70 °C but most is liberated over the range 100–200 °C [32]. It was measured the release of 9.5 w_t% of H$_2$ at 200 °C. It was also detected the release of 0.7 w_t% of N$_2$ and 0.1 w_t% of NH$_3$. With respect to the β phase, the decomposition starts at 40 °C and follows a five-step process over the range 40–400 °C [66]. Up to 144 °C, a mass loss of 7.8 w_t% was observed due to the liberation of H$_2$ and a small amount of N$_2$ (<1 w_t%). The liberation of ammonia (along with H$_2$ and N$_2$) takes place at >144 °C. No traces of hydrazine, diborane or borazine were detected. In isothermal conditions, the β phase liberated 2.6 equivalents of H$_2$ in 1 h at 150 °C (*vs.* 1.4 equivalents for hydrazine borane) and without traces of ammonia. Apparent activation energy of 58 kJ·mol^{-1} was calculated [66]. With respect to the α phase, 2.4 equivalents of H$_2$ were released in 1 h at 130 °C [32].

Wu *et al.* [32] and then Moury *et al.* [66] suggested that the dehydrogenation of lithium hydrazinidoborane can be explained by the combination of protic H$^{\delta+}$ and hydridic H$^{\delta-}$ hydrogens that are in intermolecular interactions. The latter authors proposed a series of reaction mechanisms (Figure 8) and suggested the appearance of *bis*(lithium hydrazide) of diborane [(LiN$_2$H$_3$)$_2$BH$_2$]$^+$[BH$_4$]$^-$ as reaction intermediate. Nonetheless, a recent work on the isotopomer α-LiN$_2$H$_3$BD$_3$ gave evidence of the occurrence of homopolar pathways [72]. The initial dehydrogenation would be due to the reaction between two protic H$^{\delta+}$ hydrogens (homopolar N–H⋯H–N pathway) and it would be followed by the N–H⋯H–B and B–H⋯H–B pathways. It is generally admitted that the dehydrogenation of boranes is complex [71], and the reference [72] is further evidence of such complexity.
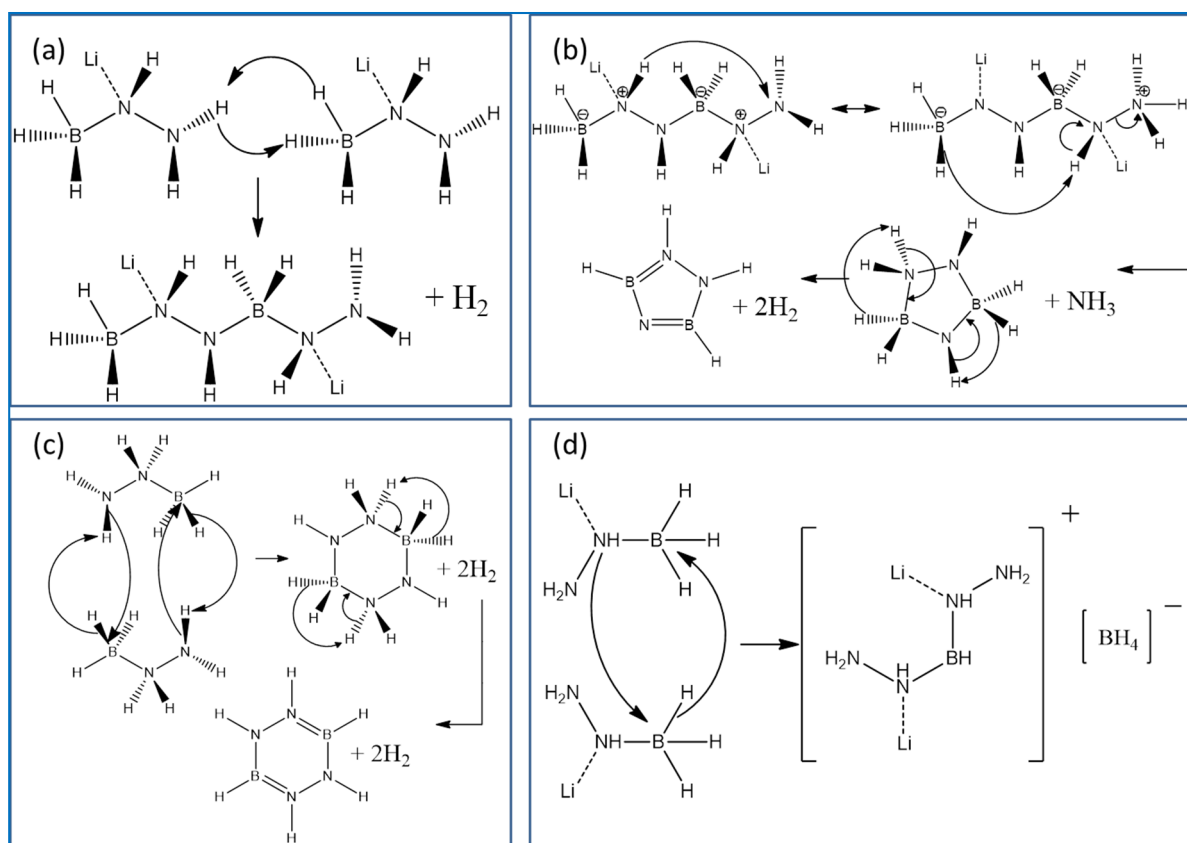
Figure 8. Proposition of mechanisms for the formation of monomeric units and *bis*(lithium hydrazide) of diborane $[(LiN_2H_3)_2BH_2]^+[BH_4]^-$. (**a**) Linear dimer with boron in sp^3 hybridization; (**b**) 5-Ring center monomer formed by proton exchange, then cyclization with NH$_3$ release and finally dehydrocyclization, where boron is in sp^2 hybridization; (**c**) 6-Ring center monomer formed by cyclization of two hydrazine borane monomers, followed by dehydrocyclization; and (**d**) Formation of *bis*(lithium hydrazide) of diborane $[(LiN_2H_3)_2BH_2]^+[BH_4]^-$. Reprinted with permission from [66]. Copyright 2014 American Chemical Society.

Moury *et al.* [68] investigated the sodium derivative. Sodium hydride NaH showed high reactivity towards hydrazine borane. An explosive reaction took place when the reactants were put into contact under inert atmosphere. The authors circumvented the problem by working in cold conditions (≤30 °C). Sodium hydrazinidoborane NaN$_2$H$_3$BH$_3$ (8.8 wt% H) was then successfully synthesized. The molecular structure was verified by the NMR and FTIR spectroscopy methods. The crystal structure was determined by powder XRD. A monoclinic structure with a space group *P2$_1$/n* (14) with all the atoms in the 4e sites (Table 2) was found. Like for lithium hydrazinidoborane, the sodium cation Na$^+$ replaces one of the protic H$^{\delta+}$ hydrogens of the middle NH$_2$, but unlike Li in LiN$_2$H$_3$BH$_3$, Na in NaN$_2$H$_3$BH$_3$ is surrounded by five hydrazinidoborane entities to fulfill the coordination sphere of Na (Figure 7). The coordination is obtained via the BH$_2$ edges, which activate the B–H bonds, as well as with the central and terminal nitrogen atoms in [N$_2$H$_3$BH$_3$]$^-$. Compared to the parent hydrazine borane, sodium hydrazinidoborane is destabilized. Like for lithium hydrazinidoborane, the DSC results suggested a complex reaction, involving at least four successive exothermic processes. Sodium hydrazinidoborane starts its dehydrogenation at around 60 °C. Below 100 °C, it is able to release 6 wt% of gases, mainly hydrogen. Nitrogen and traces of both ammonia and hydrazine were detected. At 150 °C, the overall

mass loss is 7.6 $w_t\%$. In a further work, Moury *et al.* [73] reported that the addition of an excess of 5 $w_t\%$ of sodium hydride leads to the formation of a sample of sodium hydrazinidoborane that is able to liberate *ca.* 8.8 $w_t\%$ of pure hydrogen at 160 °C.

The last hydrazinidoborane reported so far is the potassium one. In our laboratory, we found that the solid-state reaction between potassium hydride and hydrazine borane is extremely reactive in inert and room conditions, even more reactive than sodium hydride [74]. Such an issue was recently addressed by Chua *et al.* [69]. The preparations of sodium and potassium hydrazinidoboranes were performed in an autoclave while using tetrahydrofuran as dispersion medium. The synthesis of the potassium derivative $KN_2H_3BH_3$ (7.2 $w_t\%$ H) was confirmed by spectroscopy. The crystal structure was defined as being monoclinic with a space group $P2_1$ (4) (Table 2). Like the other hydrazinidoboranes, the substitution of one of the protic $H^{\delta+}$ hydrogens of the middle NH_2 by the potassium cation K^+ leads to a compound with changed bonding chemistry in comparison to hydrazine borane. Accordingly, potassium hydrazinidoborane showed improved dehydrogenation properties, with e.g., hydrogen evolution from ~50 °C and mass loss of 7.3 $w_t\%$ at 180 °C due to hydrogen and a small amount of ammonia. In isothermal conditions, at 88 °C, potassium hydrazinidoborane was able to liberate 1.8 equivalents of H_2 (60% of its theoretical H) within 1 h, whereas hydrazine borane released only 0.5 equivalent of H_2 (15% of its theoretical H). Chua *et al.* [69] emphasized the complexity of the dehydrogenation mechanisms. In particular, they suggested that the initial step would be characterized by the formation of dimers like $NH_2NH(M)BH_2$–$NHNH(M)BH_3$ and $NH_2NH(M)BH=NNH(M)BH_3$ (with M as Li, Na or K) obtained by intermolecular reactions between $H^{\delta+}$ in one molecule and $H^{\delta-}$ in another one. This is in agreement with the hypotheses reported by Moury *et al.* [66,68]. Also, Chua *et al.* [74] highlighted a clear correlation between the cation size and dehydrogenation properties of the metal hydrazinidoborane. In fact, the bigger the cation is, the lower the onset temperature of dehydrogenation.

The formation of an alkali derivative from hydrazine borane leads thus to a material more suitable for chemical hydrogen storage. Indeed, the dehydrogenation properties are improved in terms of onset temperature, kinetics and purity of hydrogen (*i.e.*, inhibition of the formation of the unwanted hydrazine and ammonia). Further, unlike for hydrazine borane, there is no mention of the formation of any shock-sensitive solid residue.

6. Conclusions and Outlook

Hydrazine borane $N_2H_4BH_3$ is under investigation for chemical hydrogen storage since the late 2010s when it was suggested as having a good potential in the field, especially as an alternative to ammonia borane NH_3BH_3. It was then studied for solid- and liquid-state chemical hydrogen storage, as was the case for ammonia borane. In fact, hydrazine borane faces the same challenges as ammonia borane.

Hydrazine borane is quite stable in water at neutral and basic pH, which is a first attractive feature for catalytic dehydrogenation in room conditions. Like for ammonia borane, the BH_3 group of hydrazine borane is easily hydrolyzed in the presence of a metal-based catalyst (homo- or heterogeneous), with almost three moles of hydrogen liberated with fast kinetics. Yet, in such a context, ammonia borane is more attractive in terms of gravimetric hydrogen storage capacities. In fact, interest on hydrazine borane does not arise unless the N_2H_4 moiety can be dehydrogenated. Nickel-based bimetallic nanoalloys showed to be efficient catalysts for both hydrolysis of BH_3 and selective dehydrogenation of N_2H_4.

Important achievements were reported in the recent years but more needs to be done for improving the kinetics of the latter reaction, which is still too slow in comparison to that of the former reaction. Also, more needs to be done to improve the catalysts stability in successive uses. The suitability of hydrazine borane for liquid-state chemical hydrogen storage has also to be evidenced by improving and optimizing the effective gravimetric hydrogen storage capacity, with the ideal target of 10 w_t%. This is in fact a critical issue as, beyond ammonia borane, sodium borohydride is also a candidate with high potential for liquid-state chemical hydrogen storage.

It could be undoubtedly stated that pristine hydrazine borane is not suitable for solid-state chemical hydrogen storage. Like ammonia borane, it decomposes under heating, mainly at >100 °C, and liberates substantial amounts of unwanted gaseous by-products along with hydrogen. The release of hydrazine is particularly problematic. Unlike ammonia borane, the extensive decomposition of hydrazine borane leads to the formation of a shock-sensitive and explosive solid residue. Such features serve hydrazine borane negatively. However, hydrazine borane should not be definitely discarded. Like ammonia borane, it may be destabilized with the help of a chemical additive. Also, it is an attractive reactant to get derivatives by reaction with alkaline hydrides. The preparation of the lithium, sodium and potassium hydrazinidoboranes $MN_2H_3BH_3$ (M as Li, Na and K) were reported to be successful by either ball-milling or solvent approach in autoclave. The as-obtained materials were fully characterized and then assessed for chemical hydrogen storage. By comparison to hydrazine borane, the derivatives showed improved dehydrogenation properties, in terms of release of almost pure hydrogen at low temperatures. However, the reaction mechanisms are still unknown and the solid residues not well identified. Like for ammonia borane, progresses on these aspects are likely to be limited because of the difficult characterization of the spent fuel. There is another grey area in relation to the solid residues, and one has to ensure that, unlike the solid residue of hydrazine borane, there is no risk with them. To date, there is no clear report about the stability, reactivity and sensitivity of the spent fuels stemming from the thermal dehydrogenation of the hydrazinidoboranes.

Last but not least, closing the hydrogen cycle with hydrazine borane is an important issue to address if future technological application is foreseen. Like in hydrolyses of sodium borohydride and ammonia borane, the by-products are boric acid $B(OH)_3$ and tetrahydroxyborate $B(OH)_4^-$. Their recyclability, via chemical recycling, has been considered over the past decade and mutual efforts could permit to develop efficient and cost-effective processes. It is important to note that the B–O bond is as strong as the C–O bond of carbon dioxide and a breakthrough should be expected to address the related cost issue. Recyclability into sodium borohydride would be a first important achievement as this compound is the main reactant for the synthesis of hydrazine borane. Otherwise, the development of aqueous hydrazine borane as hydrogen carrier could not be realized. Like in thermolysis of ammonia borane and derivatives, the recyclability of the solid residues forming upon thermal dehydrogenation of the hydrazinidoborane derivatives is much dependent on the identification of these solid residues. The difficult characterization of the solid residues is today the limiting factor. That is when the recyclability could be achievable by reduction, as that has been done for polyborazylene, a model residue of thermolyzed ammonia borane. In any case, the viability of hydrazine borane for chemical hydrogen storage will be closely related to closing the hydrogen cycle. In addition, even if the hydrogen cycle is closed, boranes could only be envisaged in off-board refueling systems due to the lack of direct rehydrogenation, but this is not essentially a drawback.

Up to here, hydrazine borane has been much compared to ammonia borane. So the question remains as to its interest compared to the latter. It would be premature to answer the question, mainly because of the discrepancy in the efforts dedicated to each borane. Ammonia borane has been under investigation for about ten years, whereas hydrazine borane has had focused attention since 2009. One may, however, state that hydrazine borane could be more attractive for liquid-state chemical hydrogen storage provided the aforementioned issues are addressed and that the derivatives of these boranes have a potential for solid-state chemical hydrogen storage. There is still room for improvement and the advances of the next years should help in shedding light on the real potential of hydrazine borane and derivatives.

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Author Contributions

Umit B. Demirci wrote the paper; Romain Moury contributed in writing the paper while specifically focusing on parts about crystallography and the hydrazinidoborane compounds.

Conflicts of Interest

The authors declare no conflict of interest.

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