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Review

Experimental and theoretical treatment of hydrogen splitting and storage in boron–nitrogen systems

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ABSTRACT

Hydrogen gas serves as a reducing agent and hydrogen atom source in numerous industrially important chemical processes and also has a great potential as a clean power source for fuel cells. In this respect, the reversible storage of hydrogen and the development of new metal-free hydrogenation catalysts are important tasks. Here, we review the recent literature, primarily on cases where the split H_2 forms an N–H···H–B dihydrogen bond. In these systems dihydrogen interaction was found to be the key actor in the hydrogen liberating process. Accordingly, the intramolecular *ansa*-aminoboranes (where B and N atoms are situated within each other's range) can reversibly activate hydrogen. Moreover, the theoretical studies of the hydrogen splitting by bulky Lewis acid–Lewis base systems are discussed.

Contents

1. Introduction

Hydrogen bonds are well-known interactions and considered to be very important in modern physics, chemistry and biology [1]. In the middle of the 90 s, a new kind of hydrogen bonding

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(M–$H^{\delta-}\cdots{}^{\delta+}$H–A) between metal or boron hydrides and classical proton donor groups, such as NH and OH, were discussed for the first time [2]. Later, the term "dihydrogen bond" (DHB) for these protic–hydridic interactions in the range 1.7–2.2 Å was suggested by Crabtree et al. [3]. Although a wide array of different organometallic systems contains dihydrogen bonds, non-metals with B–H···H–N interactions occupy a prominent role in this study. Furthermore, recent findings by our group highlight partially covalent DHBs in the *ansa*-ammonium-borate (1-*N*-TMPN-CH_2-2-[$B(C_6F_5)_2$]C_6H_4, where TMPNH is 2,2,6,6-tetramethylpiperidinium) with an extremely short H–H distance of the order of 1.6 Å [4]. The phenomenon occurs in the partially covalent DHB which can be treated as the intermediate stage of the hydrogen splitting, or inverse liberating process. Accordingly, understanding the mechanism of activation or formation of gaseous H_2 by non-metal compounds is essential for learning how to design metal-free systems for H_2 storage and new, metal-free hydrogenation catalysts. This implies understanding the role and the nature of the DHB interactions in these compounds [5].

2. Characterizing B–H···H–N dihydrogen bond systems with the Cambridge Structural Database

Significant interest in DHB interactions during the past 15 years has resulted in a couple of excellent reviews [3,6]. However, to the best of our knowledge, there are no recent systematic Cambridge Structural Database (CSD) searches incorporating all X-ray structures that have been published. We performed a search for B–H···H–N contacts in the CSD and 290 examples of intra- and intermolecular DHBs with short *d*(H···H) interactions, much smaller than twice the van der Waals radius of hydrogen (2.4 Å), were identified in 176 X-ray crystal structures (Fig. 1) [7].

The H···H distances are usually in the range of 1.7–2.2 Å, and the N–H···H angles are typically ranging from 130° to 170°, while the B–H···H angles tend to be strongly bent (in most cases 95–125°) (Fig. 2) [8]. The nature of these side-on bonds was explained by Crabtree and co-workers as an interaction between the electron donating σ B–H bond and the protonic N–H bond [3]. Thus, B–H···H–N systems are maximizing the attractive Coulomb interaction and their energies of interaction become substantial (12–29 kJ/mol). The simplest and best-studied compound, which contains DHBs and 19.6 wt% of hydrogen, the polar (5.2 D) ammonia–borane complex (NH_3*BH_3) has the strikingly high melting point of +104 °C relative to the isoelectronic substances ethane (−181 °C) or to the also polar fluoromethane (−141 °C, 1.8 D) mainly because of the DHB stabilization [9].

Although one of the most interesting DHB interactions with a length less than 1.65 Å was discussed only from a theoretical point of view [10], the shortest reliable intramolecular contact that we found in the CSD is close to 1.6 Å (⟨NHH = 154°, ⟨HHB = 125°,

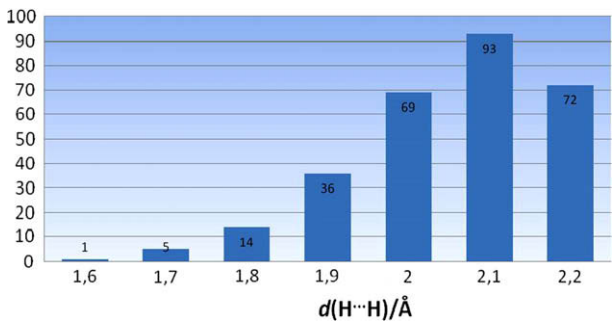


Fig. 1. Dependence of the numbers of the H···H contacts on the H···H distance in aminoboranes found in the Cambridge Structural Database.

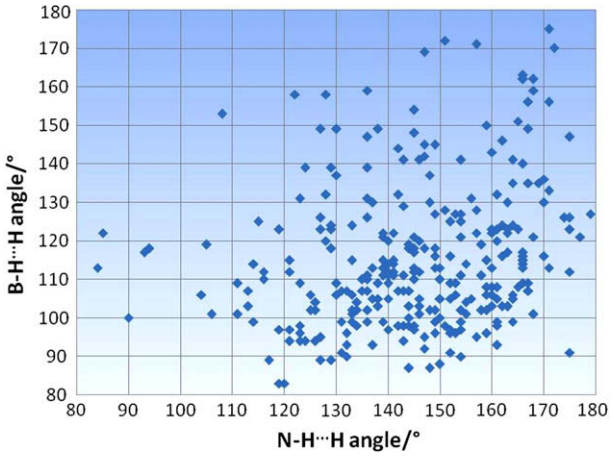
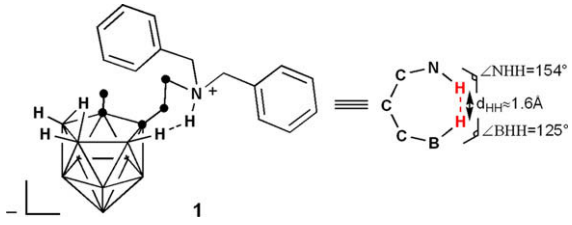


Fig. 2. The B–H···H angle versus the N–H···H angle of aminoboranes with H–H distances smaller than 2.2 Å.



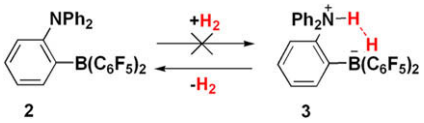
Scheme 1. ((Dibenzylamino)ethyl)dicarbollyl, [*nido*-7-$NHBn_2^+(CH_2)_2$-8-Me-7,8-$C_2B_9H_{10}^-$] [11] (where Bn is benzyl).

Scheme 1) [11]. Thus, this finding allowed us to analyze the geometry of the key "intermediate" of the reversible hydrogen activation process based on the "frozen" X-ray data. It should be noted that usually such compounds are not stable enough because of their tendency to the spontaneous liberation of hydrogen. Accordingly, the precursor to ammonia–borane – ammonium borohydride (NH_4BH_4) decomposes at temperatures above −40 °C to give H_2 and has a half-life of about 6 h at room temperature [12,13]. However, the given compound **1** is not able to form dihydrogen, because the negative charged hydride ion is not presented in the structure of DHB.

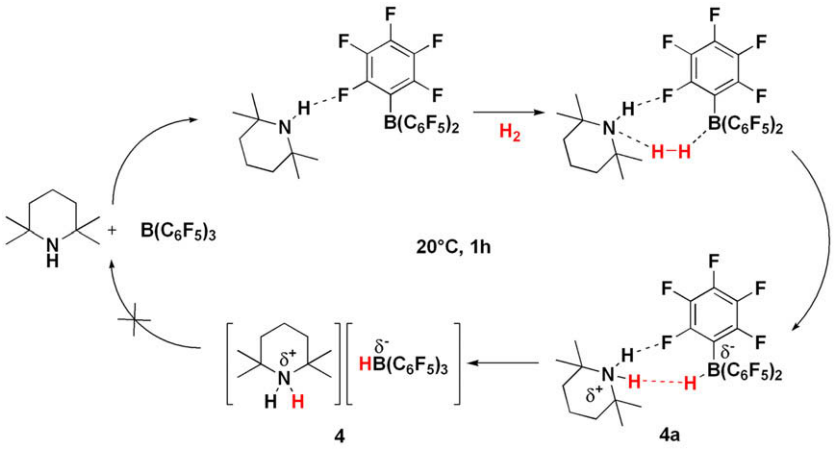
3. Hydrogen activation by amines in combination with $B(C_6F_5)_3$

In 2003 Roesler and Piers predicted that unusual non-metal systems based on 'separated Lewis acid–Lewis base' pairs would be suitable for reversibly activating H_2 (Scheme 2) [14]. Specifically, they not only speculated that compound **3** might be a "dihydrogen storage device, able to release H_2 upon heating or during a chemical reaction, regenerating **2**", but also suggested that strong DHB interactions would play a key role in this process. Unfortunately compound **2** was *not* able to cleave H_2 and the system **3** was never characterized. However, the *in situ* generated 1-Ph_2NH-2-[$HB(C_6F_5)_2$]C_6H_4 (**3**) spontaneously liberates hydrogen.

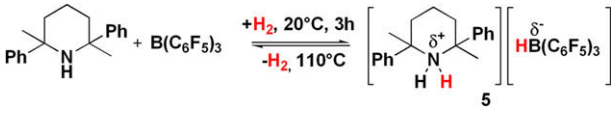
Despite the fact that the hydrogen–hydrogen bond is remarkably strong (432 kJ/mol) and non-polar, 3 years later, this approach was successfully applied for the reversible hydrogen activation by non-metal systems based on 'separated' phosphine–borane pairs



Scheme 2. Unsuccessful reversible hydrogen activation by Piers's aminoborane **3** [14].



Scheme 3. Proposed mechanism for the heterolytic cleavage of H_2 by TMPNH and $B(C_6F_5)_3$.



Scheme 4. Reversible hydrogen activation by *trans*-2,6-dimethyl-2,6-diphenylpiperidine and $B(C_6F_5)_3$.

[15,16]. Moreover, a number of theoretical papers and reviews on hydrogen storage in N···B systems have been published [17,18].

We reported the facile splitting of hydrogen by 2,2,6,6-tetramethylpiperidine (TMPNH) in combination with $B(C_6F_5)_3$ in 2008 [19]. Whereas this reaction gave the stable hydrogenated ionic product **4**, a remarkable intermediate **4a**, with a strong N–H···H–B interaction between ammonium and borate was observed by NMR spectroscopy (Scheme 3). Moreover, a recently reported concerted Lewis acid–Lewis base mechanism of heterolytic hydrogen splitting is quite consistent with the proposed mechanism [20], in which the bulky amine and borane are needed to prevent the formation of a classical Lewis donor–acceptor adduct. Instead of forming a favorable N–B bond, the N with its lone electron pair and the B with its 2pπ acceptor orbital remain at a certain distance. This makes it possible to use them as proton and hydride acceptors, respectively, upon the cleavage of dihydrogen. This situation was previously characterized as 'frustration' by Stephan and coworkers [21], and clear theoretical support for this idea was found by Rokob et al. [20a]. Thereby, for hydrogen activation by *t*-Bu_3P and $B(C_6F_5)_3$ the transition state (P–H···H–B) was almost linear, with H–H only slightly lengthened from 0.74 to 0.79 Å, and the activation energy was 43.5 kJ/mol. The H_2 was polarized and chemically activated by the totally frustrated system.

Later we examined the heterolytic splitting of hydrogen by *trans*-2,6-dimethyl-2,6-diphenylpiperidine and $B(C_6F_5)_3$. This reaction led to the formation of product **5** in quantitative yield after 3 h at room temperature. Interestingly, when a toluene solution of **5** (0.1 M) was refluxed at 110 °C in a closed system under reduced pressure for 36 h, a 50% conversion of **5** to the starting materials was observed (Scheme 4). This finding is in contrast to previous compounds $[TMPNH_2]^+[BH(C_6F_5)_3]^-$ (**4**) and $[t\text{-}BuNH_2Bn]^+[BH(C_6F_5)_3]^-$ (where Bn is benzyl) which are not able to liberate hydrogen upon heating [19,22].

To gain further insight into the mechanism of this reaction, we performed X-ray diffraction experiments (Fig. 3). While the X-ray crystallographic study of **4** showed isolated ions with the shortest NH···HB distance of 2.97 Å, connected only by a framework of NH···F (2.07 Å) hydrogen bonds [19], in the X-ray diffraction structure of **5** strong phenyl-perfluorophenyl π–π stacking and NH···F (2.34 Å), CH···F (2.52 Å) hydrogen bonding interactions were found. These non-covalent bonds between cation and anion resulted in the

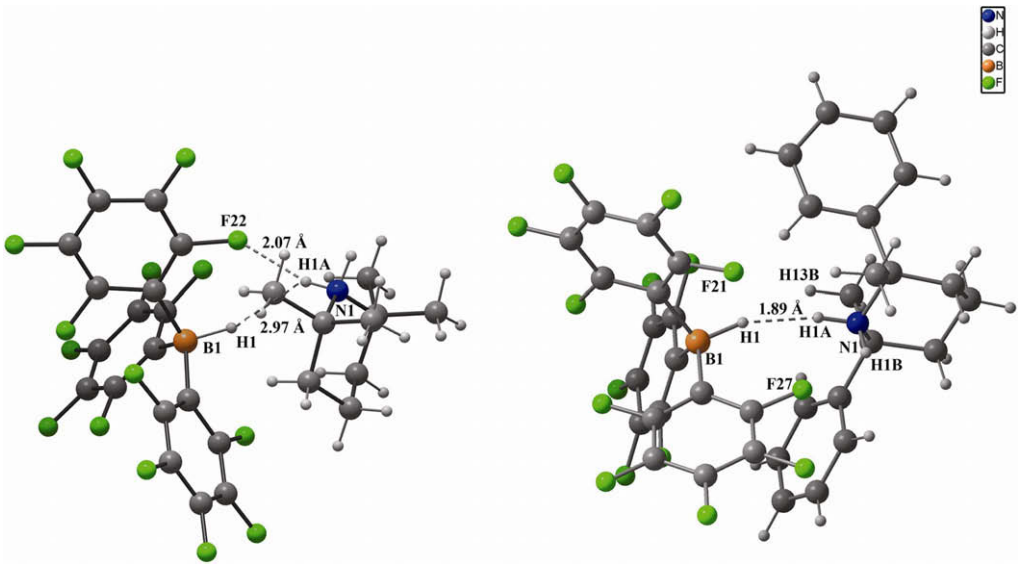
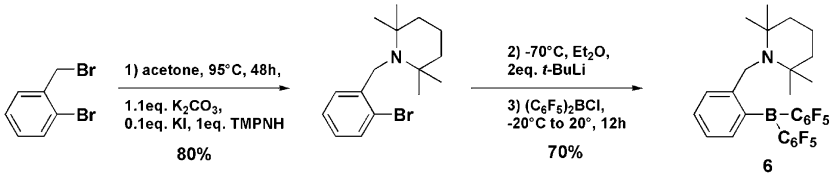


Fig. 3. X-ray structure of **4** and **5** [19,32].



Scheme 5. Synthesis of the *ansa*-aminoborane **6**.

short DHB interaction close to 1.89 Å (⟨NHH = 161°, ⟨HHB = 157°) [23]. According to these data binding together the 'separated Lewis acid–Lewis base' pairs has a greater effect on the properties of the whole system than reducing the Lewis basicity.

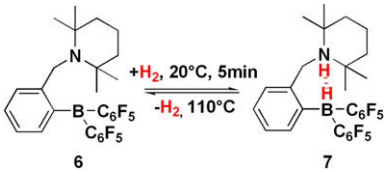
4. Reversible hydrogen activation by the *ansa*-aminoborane 1-*N*-TMPN-CH_2-2-[$B(C_6F_5)_2$]C_6H_4

The observation described above, the discovery of compound **1** with a partially covalent DHB and the previous work of Piers inspired us to attempt the synthesis of an intramolecular system with a pseudo five-membered NCCCB-ring [14]. In this respect we designed the *ansa*-aminoborane **6** and developed an effective and common procedure for the preparation of dual 'Lewis acid–Lewis base' systems (Scheme 5) [4].

1-(2-Bromobenzyl)-2,2,6,6-tetramethylpiperidine was synthesized through alkylation of TMPNH by 2-bromobenzylbromide in the presence of a base. It was then smoothly lithiated with *t*-BuLi at −70 °C and the lithiated derivative was transmetallated with $(C_6F_5)_2BCl$ to give the final product **6** in a total yield of 55%. Thus, the *ansa*-aminoborane **6** has been prepared on a gram scale (up to 5 g) by an efficient two-step synthesis from readily available precursors.

The compound **6** reacted rapidly with H_2 at 20 °C forming the air- and moisture stable 1-*N*-TMPNH-CH_2-2-[$HB(C_6F_5)_2$]C_6H_4 in quantitative yield (Scheme 6). Heating a toluene solution of **7** under vacuum at 110 °C (in analogy to **5**) up to 20 h resulted in the quantitative recovery of product **6** (Scheme 8). Accordingly, *ansa*-ammonium-borate **7** loses hydrogen much faster than the non-bridged system **5**.

In order to understand such a significant effect of the covalent bridge on the reactivity, the structure of **7** was determined by X-ray crystallography and studied theoretically (Fig. 4). While the X-ray data showed that the NH···HB distance is not as short as those found for compound **1** (1.78 Å, compared with 1.6 Å) [4], the theoretical investigations, including solvation, led to a H···H distance of 1.51 Å. Furthermore, preliminary neutron diffraction experiments also indicate an H–H distance of 1.58 Å [24]. The fact that they are shorter than the apparent X-ray value of 1.78 Å, may largely be because the X-ray technique detects electron-density distribution and locates the electron-density maxima of the atoms, while neutron scattering and calculations experiments locate the nuclei. Moreover, not only the short H···H contact indicates the presence of a strong DHB interaction, but also the experimental topological parameters such as the NHH (154°) and BHH (125°) angles are almost the same in compounds **1** and **7**. Accordingly, these results confirm the view that the formation of the stable, partially covalent DHB occurs only under a favorable geometry of the system and is one important prerequisite for the hydrogen liberation reaction. Further theoretical study of reaction path and energetic showed that the hydrogen splitting with system **6** occurs via a quasilinear (N–H···H–B) transition state at H–H of 0.78 Å, with the activation energy of 14 kJ/mol and the activation free energy of 62 kJ/mol [4,13,25]. The extra Coulomb attraction between the two ions at 3.32 Å (the calculated B–N distance for system **7**) would produce an attraction energy of 413 kJ/mol, and this would be comparable with the amount of energy required for the heterolytic cleavage of H_2, 432 kJ/mol [15]. According to this calculation, '*Coulomb pays for Heitler-London*' hypothesis was enounced [4], although this is only an order-of-magnitude estimate. The idea somewhat parallels the suggestion by Simons' group, that the Coulomb stabilization of Rydberg states by a nearby ion would play a role in the splitting of S–S bonds in proteins [26].



Scheme 6. Reversible hydrogen activation by the *ansa*-aminoborane **6**.

5. Catalytic reduction of imines by the *ansa*-ammonium-borate

To continue our investigations, we examined the *ansa*-ammonium-borate **7** in hydrogenations of non-sterically demanding imines and enamines under mild conditions (110 °C, 2 atm of H_2, Table 1).

While previous non-metal systems have shown only stoichiometric hydrogenation of the imine from benzaldehyde and benzylamine, employing *ansa*-ammonium-borate **7** as catalyst in this reaction resulted in 51% conversion of imine to amine (Table 1, entry 1) [22,27]. Continuing the reduction for up to the 48 h showed negligible influence on yield (60%, Table 1, entry 2). However, increasing the amount of catalyst from 4 to 8 mol% led to significantly enhanced conversion after 12 h (99%, Table 1, entry 3). The reduction of $C_6H_5CH_2N{=}CPh(CH_3)$ or $CH_3N{=}CPh(CH_3)$ gave *N*-benzyl-α-methylbenzylamine or *N*-methyl-α-methylbenzylamine, respectively, in almost quantitative conversions (Table 1, entries 4 and 5), while hydrogenation of less steric imines such as $CH_3N{=}CPh(H)$ and $CH_3N{=}CCH_2Ph(CH_3)$ provided only traces of the corresponding amines (4%, Table 1, entries 7 and 8).

These data support the standpoint that the rate-determining step of the hydrogenation mechanism is the suppression of the catalytic activity by amine–borane adduct formation **7a** and therefore the sum of the Lewis acidic and the steric factors of the catalyst and imine, respectively, play a decisive role (Scheme 7).

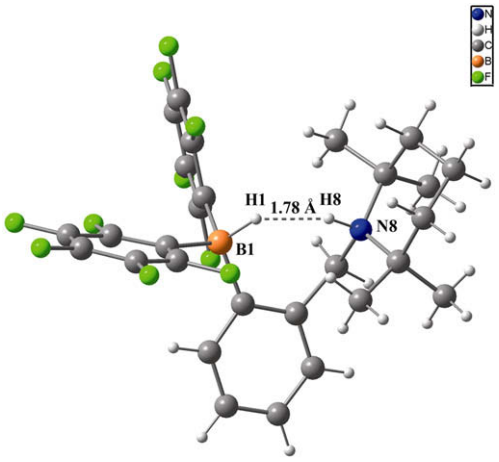
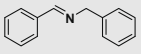
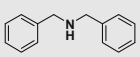
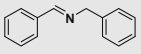
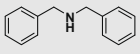
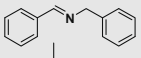
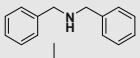
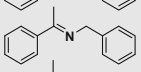
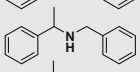
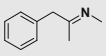
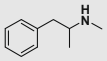


Fig. 4. X-ray structure of **7** [4].

Table 1
Catalytic reduction of imines by the *ansa*-ammonium-borate **7**.

Entry	Substrate	Time (h)	Amine	Yield (%)[a]
1		24		51[b]
2		48		60[b]
3		12		99[c]
4		6		99[b]
5		12		99[b]
6		‘		4[b]
7		24		4[b]

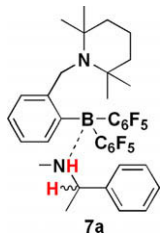
[a] Yield was determined by ^{1}H NMR spectroscopy.
[b] Catalyst **7** (4 mol%).
[c] Catalyst **7** (8 mol%).

6. Modification of the *ansa*-aminoborane system

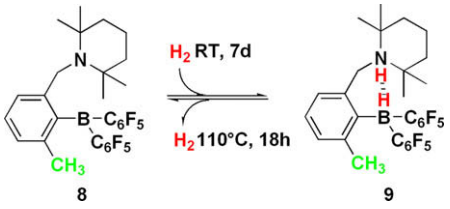
On the basis of the above results and the known chemistry of boranes, we proposed that the further reduction of Lewis acidity at the active boron center should not only lower the temperature needed for the hydrogen liberation process significantly, but should also lead to an increasing the activity of our catalyst in hydrogenation reactions [15c]. In this respect, the new *ansa*-aminoborane **8** with an electron donating group in *ortho*-position in relation to the boron was synthesized in the same manner as **6** (Scheme 5).

Interestingly, the electron donating group dramatically increases the time of the hydrogen splitting (1 week instead of a few minutes) as expected. It does not affect the molecular hydrogen formation reaction (Scheme 8). This phenomenon can only be explained by the steric or electronic influence of the CH_3 group on the structure of the *ansa*-ammonium-borate **9**. Although, the X-ray crystallographic study of **9** showed only insignificant changes in the rigid geometry (in comparison with **7**), the typical DHB interaction of 1.90 Å (⟨NHH = 133° and ⟨BHH = 126°) was detected instead of the partially covalent bond in system **7** (Fig. 5) [23].

Hence not only must the geometry of aminoboranes be appropriate to form strong DHB interactions, but the dual Lewis acidity/basicity must be correctly tuned in terms of combined efforts in order to obtain a partially covalent DHB interaction and a successful reversible hydrogen activation. Accordingly, the *ansa*-ammonium-borate **7** is able to split and form hydrogen in a facile way because: (1) the acidity and basicity of the active centers are sufficiently matched and (2) the favorable geometry for the formation of the partially covalent DHB interaction, which plays a key role in this process, is present.



Scheme 7. Adduct of catalyst **7** with *N*-methyl-1-phenylethanamine **7a**.



Scheme 8. Reversible hydrogen activation by the *ansa*-aminoborane **8**.

7. Conclusion

In summary, the short (less than 1.9 Å) and very short (less than 1.7 Å) dihydrogen bonds in boron–nitrogen systems are the key actors in the hydrogen liberating process. However, much of the energy, needed for splitting H_2, may come from the Coulomb attraction between the two counterions. Further, careful design of ‘Lewis acid–Lewis base’ systems, with appropriate geometry and matching of acidity and basicity, is essential for the synthesis of metal-free compounds for H_2 storage and hydrogenation catalysts. In fact this evolution is needed before any such applications can become practical and be effectively used.

8. Experimental

8.1. Physical methods

All experiments were performed on double-manifold H_2(Ar)/vacuum lines or in an argon glove box (MBraun Labmaster 130). Solvents were dried by an MBraun solvent purification system (MB SPS-800). Hydrogen gas was purchased from AGA Ab and passed through a drying unit prior to use. All organic reagents were purchased from Sigma–Aldrich and purified by conventional methods. HRMS (ESI$^+$-TOF) mass spectra were recorded on a Bruker micrOTOF mass spectrometer. NMR experiments were performed

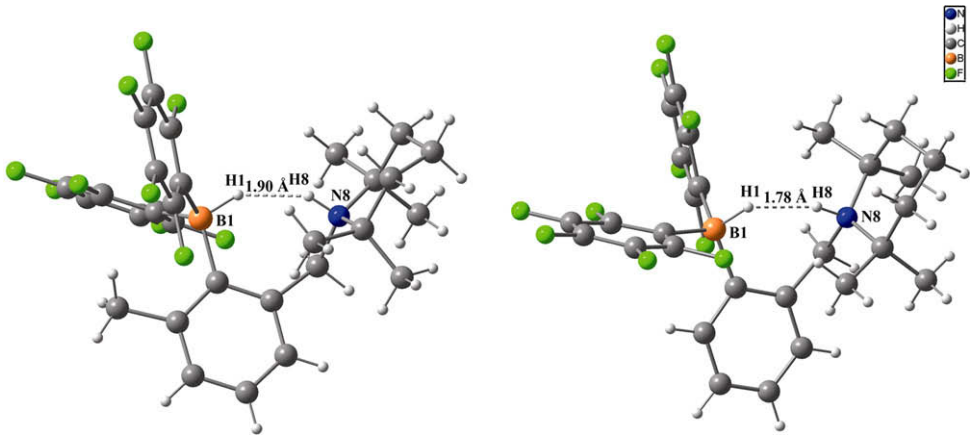


Fig. 5. X-ray structures of the *ansa*-ammonium-borates **9** (left) and **7** (right) [4,33].

on a Bruker ARX-300 spectrometer (^{1}H, ^{13}C, ^{19}F) or Bruker DPX-400 (^{11}B). ^{1}H and ^{13}C NMR spectra are referenced to Me_4Si by referencing the residual solvent peak. ^{11}B, ^{19}F NMR spectra were referenced externally to $BF_3^*Et_2O$ at 0 ppm and CF_3CO_2H at −78.5 ppm relative to $CFCl_3$ at 0 ppm, respectively. *trans*-2,6-Dimethyl-2,6-diphenylpiperidine, 2-bromo-3-methylbenzyl bromide and $(C_6F_5)_2BCl$ were prepared by the literature methods [28–30].

8.2. Synthetic methods

8.2.1. Trans-2,6-Dimethyl-2,6-diphenylpiperidinium hydrido[tris(pentafluorophenyl)]borate (**5**)

In a glove box, a 25-mL flame-dried Schlenk tube equipped with a stir bar, a Teflon stopcock and a cap (Glindemann®-sealing rings were used for conical joints instead of grease) was charged with $B(C_6F_5)_3$ (0.2 mmol, 102.4 mg), 1 mL dry toluene and *trans*-2,6-dimethyl-2,6-diphenylpiperidine (0.2 mmol, 53.1 mg). The reaction was degassed once with a freeze–pump–thaw cycle and refilled with H_2 (1 atm). The reaction was stirred at RT for 3 h. All volatiles were removed *in vacuo* to give the product **5** (155.9 mg, 100% yield) as a white solid. Crystals suitable for X-ray diffraction were grown from a C_6D_6 solution at 20 °C. Anal. Calc. for $C_{37}H_{25}BF_{15}N$: C, 57.02; H, 3.23; N, 1.80. Found: C, 57.30; H, 3.20; N, 1.85%. ^{1}H NMR (CD_2Cl_2, 300 MHz): *δ 7.50–7.42* (m, 10H, C_6H_5), δ 5.99 (br. t, 2H, $^1J_{NH}$ = 49 Hz, NH_2), δ 3.58 (br. q, 1H, $^1J_{BH}$ = 86 Hz), δ 2.69 (m, 2H, CH_2), δ 2.11 (m, 4H, CH_2), δ 1.44 (s, 6H, CH_3). ^{11}B NMR (CD_2Cl_2, 128 MHz): δ −24.48 (d, $^1J_{BH}$ = 86 Hz). ^{13}C NMR (C_6D_6, 75 MHz): δ 148.87 (dm, $^1J_{CF}$ = 241 Hz, *ortho*-C_6F_5), δ 138.81 (dm, $^1J_{CF}$ = 247 Hz, *para*-C_6F_5), δ 138.15 (s, Quaternary carbon of C_6H_5), δ 137.35 (dm, $^1J_{CF}$ = 255 Hz, *meta*-C_6F_5), δ 130.05 (s, *para*-C_6H_5), δ 129.83 (s, *meta*-C_6H_5), δ 124.35 (s, *ortho*-C_6H_5), δ 65.48 (s, $NC(CH_3)(Ph)CH_2$), δ 32.62 (s, $NC(CH_3)(Ph)CH_2$), δ 28.17 (s, CH_3), δ 16.18 (s, CH_2). Quaternary carbon of C_6F_5 ring was not observed. ^{19}F NMR (CD_2Cl_2, 282 MHz): δ −134.83 (d, 6F, $^3J_{FF}$ = 21 Hz, *ortho*-C_6F_5), δ −164.48 (t, 3F, $^3J_{FF}$ = 21 Hz, *para*-C_6F_5), δ −167.69 (m, 6F, *meta*-C_6F_5).

8.2.2. 1-(2-Bromo-3-methylbenzyl)-2,2,6,6-tetramethylpiperidine

A dry 25 mL Schlenk tube was charged with 1.413 g (10 mmol) 2,2,6,6-tetramethylpiperidine, 2.640 g (10 mmol) 2-bromo-3-methylbenzyl bromide, 1.6 g (11.6 mmol) K_2CO_3 and 0.166 g KI (1 mmol) in 18 mL of dry acetone. The mixture was heated at 95 °C for 48 h. The Schlenk tube was cooled and the contents filtered. The solvent present in the filtrate was removed under reduced pressure. The crude product was dissolved in 50 mL of Et_2O and extracted twice with 100 mL of 0.1 M HCl. The aqueous solution was basified to pH 12 with KOH and extracted twice with 50 mL of CH_2Cl_2. The resulting organic layer was dried over K_2CO_3, passed through a short column with silica gel and rotovaped to give 2.85 g of 1-(2-bromo-3-methylbenzyl)-2,2,6,6-tetramethylpiperidine (yield 88%) as white crystals. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.73 (d, 1H, $^3J_{HH}$ = 7.7 Hz, *ortho*-CH_3-C_6H_3), δ 7.17 (t, 1H, $^3J_{HH}$ = 7.5 Hz, *para*-Br-C_6H_3), δ 7.06 (d, 1H, $^3J_{HH}$ = 7.8 Hz, *ortho*-$TMPCH_2$-C_6H_3), δ 3.73 (s, 2H, $TMPCH_2$), δ 2.41 (s, 3H, $-C_6H_3CH_3$), δ 1.73 (br. s, 2H, $CH_2CH_2CH_2$), δ 1.54 (br. s, 4H, $CH_2CH_2CH_2$), δ 1.10 (br. s, 6H, CH_3), δ 0.86 (br. s, 6H, CH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 144.01 (s, quaternary carbon of $TMPCH_2C_6H_3$), δ 137.18 (s, quaternary carbon of $CH_3C_6H_3$), δ 128.15 (s, *ortho*-$CH_3C_6H_3$), δ 127.97 (s *ortho*-$TMPCH_2$-C_6H_3), δ 125.97 (m, quaternary carbon of Br-C_6H_3), δ 124.89 (s, *para*-Br-C_6H_3), δ 54.83 (s, $NC(CH_3)_2CH_2$), δ 49.50 (s, $TMPCH_2$), δ 41.30 (s, $CH_2CH_2CH_2$), δ 33.12 (br. s, CH_3), δ 23.30 (s, $C_6H_3CH_3$), δ 21.73 (br. s, CH_3), δ 17.89 (s, $CH_2CH_2CH_2$).

8.2.3. 1-{2-[Bis(pentafluorophenyl)boryl]-3-methylbenzyl}-2,2,6,6-tetramethylpiperidine (**8**)

1-(2-Bromo-3-methylbenzyl)-2,2,6,6-tetramethylpiperidine (0.973 g, 3 mmol) was lithiated at −70 °C in Et_2O (10 mL) using a 1.7 M solution of *t*-BuLi in pentane (3.6 mL, 6.1 mmol). The solution was allowed to warm up to room temperature and stirred over night. The solvent was removed *in vacuo* and the solid residue suspended in hexane (5 mL). Filtration yielded the lithium derivative as a fine pale yellow powder. Without further purification the crude lithium salt was dissolved in 17.5 mL of a 40:60 hexane/toluene mixture and cooled to −20 °C. A solution of $(C_6F_5)_2BCl$ (1.141 g, 3 mmol) in toluene (5 mL) was added dropwise over 5 min. Immediately, intense bright yellow coloration indicated formation of the product. The reaction mixture was stirred over night at room temperature and the solvent was removed *in vacuo*. The solid residue was suspended in hexane (15 mL), the contents filtered. The solvent present in the filtrate was removed to give 0.797 g of 1-{2-[bis(pentafluorophenyl)boryl]-3-methylbenzyl}-2,2,6,6-tetramethylpiperidine (yield 45%) as an orange oil. ^{1}H NMR (C_6D_6, 300 MHz): δ 7.90 (d, 1H, $^3J_{HH}$ = 8.0 Hz, *ortho*-$(C_6F_5)_2B$-C_6H_3), δ 7.26 (t, 1H, $^3J_{HH}$ = 7.3 Hz, *para*-$(C_6F_5)_2B$-C_6H_3), δ 6.91 (d, 1H, $^3J_{HH}$ = 7.3 Hz, *ortho*-$TMPCH_2$-C_6H_3), δ 3.70 (s, 2H, $TMPCH_2$), δ 2.05 (s, 3H, $C_6H_3CH_3$), δ 1.37 (br. s, 6H, $CH_2CH_2CH_2$), δ 0.81 (br. s, 12H, CH_3). ^{11}B NMR ($C_6D_5CD_3$, 128 MHz): δ 44.12 (br. s). ^{13}C NMR (C_6D_6, 75 MHz): δ 150.18 (s, quaternary carbon of $CH_3C_6H_3$), δ 148.64 (s, quaternary carbon of $TMPCH_2C_6H_3$), δ 147.09 (dm, $^1J_{CF}$ = 250 Hz, *ortho*-C_6F_5), δ 144.50 (dm, $^1J_{CF}$ = 260 Hz, *para*-C_6F_5), δ 138.61 (dm, $^1J_{CF}$ = 255 Hz, *meta*-C_6F_5), δ 130.64 (s, *para*-$(C_6F_5)_2B$-C_6H_3), δ 127.40 (s, *ortho*-CH_3-C_6H_3), δ 127.40 (s, *ortho*-$TMPCH_2$-C_6H_3), δ 64.90 (s, $NC(CH_3)_2CH_2$), δ 50.66 (s, $TMPCH_2$), δ 44.85 (s, $CH_2CH_2CH_2$), δ 30.54 (br. s, CH_3), δ 22.95 (s, $C_6H_3CH_3$), δ 22.70 (br. s, CH_3), δ 18.55 (s, $CH_2CH_2CH_2$). Quaternary carbons of C_6F_5 ring and $(C_6F_5)_2BC_6H_3$ were not observed. ^{19}F NMR (C_6D_6, 282 MHz): δ −129.40 (d, 6F, $^3J_{FF}$ = 21 Hz, *ortho*-C_6F_5), δ −145.25 (t, 3F, $^3J_{FF}$ = 20 Hz, *para*-C_6F_5), δ -161.11 (m, 6F, *meta*-C_6F_5). HRMS ESI^+-TOF: $C_{29}H_{26}BNF_{10}^*H^+$; Calc. 590.2077. Found: 590.2076.

8.2.4. Hydrido{2-methyl-6-[(2,2,6,6-tetramethylpiperidinium-1-yl)methyl]phenyl} bis(pentafluorophenyl)borate (**9**)

In a glove box, a 100-mL flame-dried Schlenk tube equipped with a stir bar, a Teflon stopcock and a glass stopper (Glindemann®-sealing rings were used for conical joints instead of grease) was charged with 1-{2-[bis(pentafluorophenyl)boryl]-3-methylbenzyl}-2,2,6,6-tetramethylpiperidine (**8**, 1.0 mmol, 0.589 g) and 10 mL dry toluene. The reaction was degassed once with a freeze–pump–thaw cycle and refilled with H_2 (1 atm). The reaction was stirred at 1000 rpm at room temperature for 7 days. All volatiles were removed *in vacuo*. The solid residue suspended in hexane (15 mL), the contents filtered to give 0.591 g of the product as a white solid (yield 100%). ^{1}H NMR (CD_2Cl_2, 300 MHz): *δ 7.07–6.95* (m, 3H, C_6H_3), δ 6.11 (br. s, 1H, N*H*), δ 4.57 (d, 2H, $^3J_{HH}$ = 5.5 Hz $TMPNHCH_2$), δ 3.67 (br. q, 1H, $^1J_{BH}$ = 76 Hz, B*H*), δ 2.05 (s, 3H, $C_6H_3CH_3$), δ 1.73 (m, 6H, $CH_2CH_2CH_2$), δ 1.53 (s, 6H, CH_3), δ 1.29 (s, 6H, CH_3). ^{11}B NMR (CD_2Cl_2, 128 MHz): δ −21.69 (d, $^1J_{BH}$ = 76 Hz). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 148.29 (dm, $^1J_{CF}$ = 230 Hz, *ortho*-C_6F_5), δ 146.55 (s, quaternary carbon of $CH_3C_6H_3$), δ 138.14 (dm, $^1J_{CF}$ = 245 Hz, *para*-C_6F_5), δ 136.82 (dm, $^1J_{CF}$ = 250 Hz, *meta*-C_6F_5), δ 134.95 (s, quaternary carbon of $TMPCH_2C_6H_3$), δ 131.14 (s, *para*-$(C_6F_5)_2BH$-C_6H_3), δ 125.28 (s, *ortho*-$CH_3C_6H_3$), δ 125.22 (s, *ortho*-$TMPCH_2$-C_6H_3), δ 67.60 (s, $NC(CH_3)_2CH_2$), δ 54.85 (s, $TMPNHCH_2$), δ 41.35 (s, $CH_2CH_2CH_2$), δ 31.62 (br. s, CH_3), δ 23.34 (s, $C_6H_3CH_3$), δ 21.57 (br. s, CH_3), δ 15.74 (s, $CH_2CH_2CH_2$). Quaternary carbons of C_6F_5 ring and $(C_6F_5)_2BC_6H_3$ were not observed. ^{19}F NMR (CD_2Cl_2, 282 MHz): δ −134.06 (d, 6F, $^3J_{FF}$ = 21 Hz, *ortho*-C_6F_5), δ −164.33 (t, 3F, $^3J_{FF}$ = 20 Hz, *para*-C_6F_5), δ −167.45 (m, 6F, *meta*-C_6F_5). HRMS ESI^+-TOF: $C_{29}H_{28}BNF_{10}^*Na^+$; Calc. 614.2052. Found: 614.2059.

8.2.5. Dehydrogenation of **5**

In a glove box, a 25-mL flame-dried Schlenk tube equipped with a stir bar, a Teflon stopcock and a glass stopper (Glindemann®-sealing rings were used for conical joints instead of grease) was

Table 2
Crystal data of compounds **5** and **9**.

	5	**9**
Formula	$C_{37}H_{25}BF_{15}N - C_6D_6$	$C_{29}H_{28}BF_{10}N$
Formula weight	863.53	591.33
T (K)	123(2)	123(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	16.612(1)	15.335(2)
b (Å)	9.962(1)	11.451(1)
c (Å)	22.626(2)	14.863(1)
β (°)	94.55(1)	90.59(1)
V (Å^3)	3732.5(5)	2609.8(4)
Z	4	4
D_{calc} (Mg m^{-3})	1.537	1.505
μ (mm^{-1})	0.141	0.137
F(000)	1744	1216
Crystal size (mm)	0.35 × 0.25 × 0.15	0.50 × 0.30 × 0.15 mm
Crystal color	Colorless crystals	Colorless crystals
θ_{max} (°)	27.5	27.5
Reflections collected	34901	40288
Independent reflections	8523	5979
R_{int}	0.0344	0.0029
Observed reflections	5963	4712
Goodness-of-fit on F^2	1.038	1.056
Parameters	550	377
Largest difference in peak and hole (e Å^{-3})	0.293/−0.245	0.321/−0.237
R_1 ($I > 2\sigma(I)$)	0.0448	0.0368
wR_2 (all data)	0.0919	0.0976

charged with **5** (0.1 mmol, 77.9 mg) and 1.0 mL of dry deuterated toluene (d^8). The reaction was degassed once with a freeze–pump–thaw cycle, stirred at 1000 rpm and at 110 °C for 36 h. NMR experiments (^{1}H, ^{11}B, ^{13}C and ^{19}F) of the solution showed a 50% conversion to *trans*-2,6-dimethyl-2,6-diphenylpiperidine and $B(C_6F_5)_3$. No side reactions were detected.

8.2.6. Dehydrogenation of **9**

In a glove box, a 25-mL flame-dried Schlenk tube equipped with a stir bar, a Teflon stopcock and a glass stopper (Glindemann®-sealing rings were used for conical joints instead of grease) was charged with **9** (0.1 mmol, 59.1 mg), 1.0 mL dry toluene. The reaction was degassed once with a freeze–pump–thaw cycle, stirred at 1000 rpm and at 110 °C for 20 h. All volatiles were removed *in vacuo* to give 58.9 mg of **8** (yield 100%) as an orange oil.

8.3. Crystallographic studies

The single-crystal X-ray diffraction studies of **5** and **9** were carried out on a Bruker-Nonius Kappa-CCD diffractometer at 123(2) K using Mo Kα radiation (λ = 0.71073 Å). Direct methods (SHELXS-97) were used for structure solution, and full-matrix least-squares refinement on F^2 (SHELXL-97) [31]. H atoms were localized by difference Fourier synthesis and refined using a riding model (H(N) and H(B) free) (see Table 2).

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