

An amine-borane system featuring room temperature dehydrogenation and regeneration

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Abstract: Amine-borane complexes have been extensively studied as hydrogen storage materials. Herein, we report a new amine-borane system featuring a reversible dehydrogenation and regeneration at room temperature. In addition to high purity H₂, the reaction between ethylenediamine bisborane (EDAB) and ethylenediamine (ED) leads to unique boron-carbon-nitrogen 5-membered rings in the dehydrogenation product where one boron is tricoordinated by three nitrogen atoms. Due to the unique cyclic structure, the dehydrogenation product can be efficiently converted back to EDAB by NaBH₄ and H₂O at room temperature. This finding could lead to the discovery of new amine boranes with potential usage as hydrogen storage materials.

Hydrogen-rich compounds consisting of light elements such as B, N, and C have the potential to be used as hydrogen carriers due to their high volumetric and gravimetric density of hydrogen.^[1] Ammonia borane (NH₃BH₃, known as AB, 19.5 wt% hydrogen density) is one of the most studied hydrogen storage compounds.^[2] AB can release H₂ via catalytic hydrolysis, alcoholysis, and thermolysis.^[2a, 3] Under thermolytic conditions, H₂ is produced by the reactions between the Lewis basic H bound to B (H^{δ-}-B) and the Lewis acidic H bound to N (H^{δ+}-N),^[2a] and the decomposition products are typically highly stable BN polymers which are difficult to convert back to AB under mild conditions.^[4] During hydrolysis and alcoholysis, H₂ is produced via reactions between the H^{δ-}(-B) and H^{δ+}(-O).^[3] Conversion of the resultant B-O bond back to B-H is an energy-intensive process.^[4a]

For practical applications, the H-rich compounds need to form spent fuels that are regenerable under mild conditions for economic and operational reasons. To prevent the formation of extended solid polymers (as in the case of AB) while maintaining high hydrogen capacity, -H₂B-NH₂- units have been incorporated into 5-membered or 6-membered boron-carbon-nitrogen (BCN) heterocycles (Figure 1).^[5] Due to

both the steric confinement provided by the ring structures and H₂ formation being driven by B-H^{δ-}...H^{δ+}-N, the dehydrogenation product is a trimer species featuring -B-N- 6-membered rings (Figure 1). These trimers are advantageous as they can either exist in the liquid phase or are soluble in certain solvents, in contrast to the extended solid polymers produced in the dehydrogenation of AB. Remaining in the liquid phase throughout the process allows for high compatibility with the current infrastructure built to handle liquid hydrocarbon fuels.

On the one hand, these H-rich BCN compounds can be viewed as derivatives of NH₃BH₃ where one acidic and one basic hydrogen atoms are replaced by carbon-containing groups (Figure 1). This substitution modifies the chemical reactivities, as evidenced by different thermal stabilities of these BCN cyclic compounds compared with neat AB. On the other hand, BCN cyclic compounds are isoelectronic to their cyclic hydrocarbon counterparts such as methyl-cyclopentane and cyclohexane, where -CH₂-CH₂- is replaced by -H₂B-NH₂- (Figure 1).^[5] Compared with their isoelectronic hydrocarbons, BCN compounds can release H₂ at much lower temperatures.^[5] Hydrogenation converting CH=CH in BCN compound to -CH₂-CH₂- also occurs under milder conditions compared to its pure hydrocarbon counterpart, which are attributed to the disruption to the electronic structure by the heteroatoms.^[6]

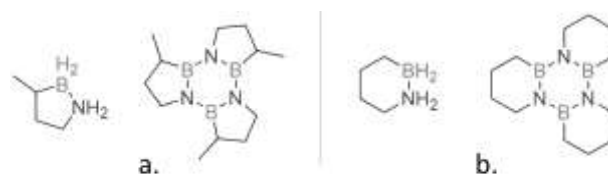
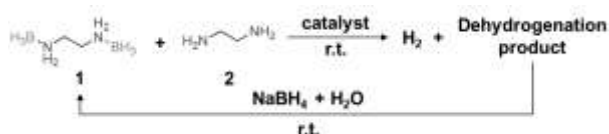


Figure 1. BCN heterocycles: a. Methyl-BN-cyclopentane (left) and its dehydrogenated form (right); b. BN cyclohexane (left) and its dehydrogenated form (right).^[5]

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Experimentally, studies on BCNs from a hydrogen storage perspective have been limited to replacement of $-\text{CH}_2-\text{CH}_2-$ units with $-\text{H}_2\text{B}-\text{NH}_2-$ in cyclopentane and cyclohexane. The ratio between the active B-N moieties and the carbon backbone should be maximised to achieve high hydrogen capacity. Geometrically there are numerous ways in which BH_2 and NH_2 can be substituted into these ring structures. For instance, the BH_2 and NH_2 groups can be separated by CH_2 units, or additional BH_2 or NH_2 groups can be included in the rings to form $-\text{B}-\text{N}-\text{B}-$ or $-\text{N}-\text{B}-\text{N}-$ moieties. Varying the number and relative positions of B, C, N will lead to compounds with different reactivities.^[7]



Scheme 1. The dehydrogenation and the regeneration reaction.

In this work, we report a new strategy for the formation of BCN cyclic dehydrogenation products between amine-borane and amine substrates (**Scheme 1**). To maximise the hydrogen capacity of the whole system, the primary amine must be both simple and contain multiple NH_2 groups. Thus, ethylenediamine bisborane (EDAB, **1**) and ethylenediamine (ED, **2**) were chosen for this study. Rapid hydrogen evolution takes place from the EDAB/ED mixture at room temperature in the presence of Pt/C, leading to the formation of 5-membered BCN rings containing $-\text{N}-\text{B}-\text{N}-$ linkages. EDAB can be reformed at room temperature from the dehydrogenation products by reacting with NaBH_4 and H_2O . The hydrogen storage system remains in the liquid phase throughout the hydrogen evolution and regeneration cycle, which could be compatible with the established technology and widespread infrastructure for handling liquid fuels.

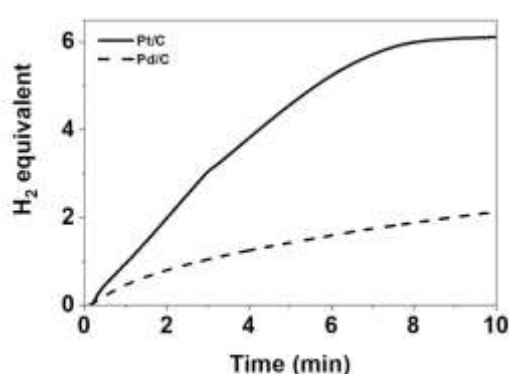


Figure 2. H_2 evolution from EDAB/ED mixture using Pt/C and Pd/C. Quantity of H_2 is represented relative to the quantity of EDAB.

EDAB was synthesised according to a published procedure.^[8] NMR spectra of EDAB are presented in **Figure S1-3**. To study the dehydrogenation performance, EDAB was mixed with a metal-based catalyst, and then ED was added quickly with vigorous stirring (**Scheme 1**). The gas evolution rate was

recorded *via* a flow meter, providing a molar ratio of H_2 produced per quantity of EDAB (**Figure 2**). In the gaseous product, only H_2 was detected in the MS analysis (**Figure S4**).

The dehydrogenation product in ED was collected after removing the catalyst by filtration. A series of chemical formulae are proposed based upon high-resolution mass spectrometry (HRMS) results: $\text{C}_4\text{H}_{13}\text{BN}_4$, $\text{C}_6\text{H}_{18}\text{B}_2\text{N}_6$, $\text{C}_6\text{H}_{15}\text{B}_3\text{N}_6$, $\text{C}_8\text{H}_{20}\text{B}_4\text{N}_8$, $\text{C}_{10}\text{H}_{25}\text{B}_5\text{N}_{10}$ (**Figure S5**). The proposed structures for these formulae are given in **Figure 3**. The core structure **3** (4,5-dihydro-1H-1,3,2-diazaborole) was not acquired by HRMS due to the mass range setting of the instrument (107-3000 a.u.); Compound **3** is unlikely to exist alone since the boron is dicoordinated, which will be very unstable in the absence of large stabilising groups. Compounds **6**, **7**, **8** are of extended structure based upon compound **3**, and their borons are coordinated and stabilised by nitrogens from the neighbouring unit. HRMS result indicates the presence of compounds **6**, **7**, **8**, but this can be caused by MS process. HRMS result indicates the presence of compound **4** and **5**. Triaminoborane tautomers (compound **4'** and **5'**) can also exist if **4** and **5** undergo hydrogen transfer transformation. At this stage, we have more evidence proving the presence of **4** and **5**, as shown in later discussions.

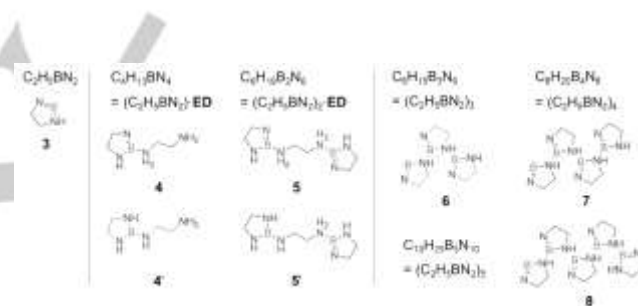


Figure 3. Proposed structures of the dehydrogenation products based on HRMS results.

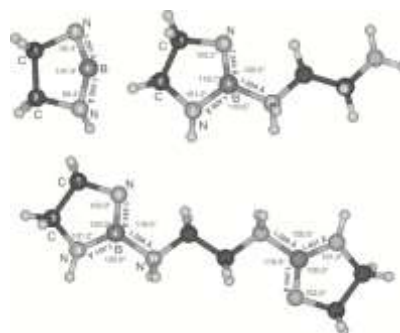


Figure 4. Key bond lengths and bond angles in the optimised structures.

Natural bond order (NBO) analyses^[9] were performed to investigate the bonding nature of the proposed structures after geometry optimisations with Gaussian16 at M062X/6-311++G(d,p). The optimised structures of compounds **3-5** are shown in **Figure 4**. The ring structure in compound **3** is distorted. Once coordinated by ED, the three $-\text{N}-\text{B}-\text{N}-$ angles become very close to 120° , indicating that ED stabilises the cyclic structure in **4** and **5**.

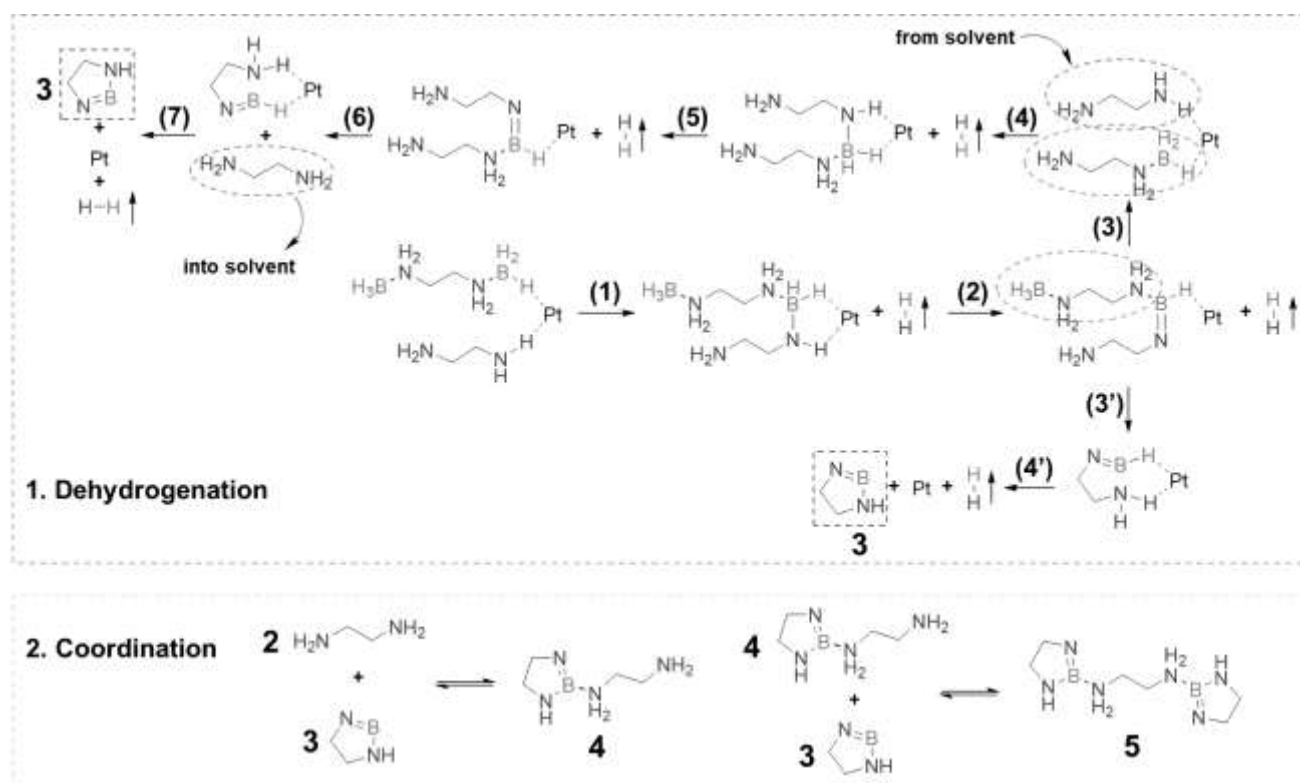


Figure 5. Proposed mechanism of the dehydrogenation and the coordination reactions of EDAB in ED.

Compound **4** is taken as the example discussing the bonding nature of the three boron-nitrogen bonds involving B4, N3 and N5. Analysis of optimised B-N bond lengths in compound **4** and **5** indicates that the 5-membered ring structure contains a bond with double-bond character (ranging from 1.297 to 1.344 Å amongst the structures) and a bond with single-bond character (range of 1.402 – 1.456 Å) (**Table S2**). Structures **4** and **5** also contain a B-N bond to the nominal ED moiety with bond lengths of 1.584 and 1.588 Å respectively, indicating a more dative-bond character (**Table S2**).

The dehydrogenation product displays strong fluorescence (**Figure S6**), while the starting materials show negligible fluorescence at 385 nm at the excitation of 310 nm, indicating the formation of a conjugated system in the dehydrogenation product. In our proposed structures (**Figure 3**), the combination of –N=B– double bonds and the electron pair on nitrogen likely provide the conjugation responsible for the fluorescence. The calculated emission from the first excited state of compound **4** sits around 443.9 nm, which is close to the experimental value. The difference between the calculated and experimental emission energies are likely due to the neglected solvent effects in the calculations and the potential limitation of the adopted models.^[10] This indicates the existence of –N=B– double bonds in the dehydrogenation product. The emission from the first excited state to the ground state for compound **4'** was at 258 nm, which is not detectable in our fluorescence measuring system.

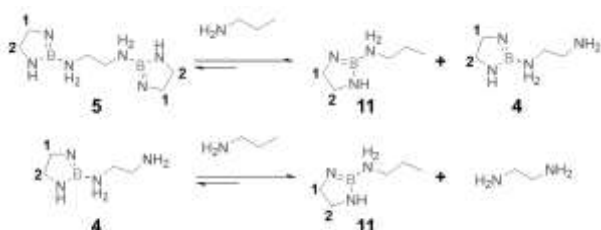
There are several key IR bands in the dehydrogenation product (**Figure S7**). The peak at 1491 cm⁻¹ is attributed to the stretch of –B=N– double bonds, which is consistent with the

literature^[11]. The signals at 1297 cm⁻¹ and 1329 cm⁻¹ are associated with –B–N– single bonds^[11a]. The intense peak at 697 cm⁻¹ belongs to the –B–N– dative bond, typically within the range between 650 cm⁻¹ and 800 cm⁻¹^[12]. All these results support the presence of –B=N–, –B–N–, and –B–N– bonds in the five-membered ring in compounds **4** and **5**. The –B–N– bond also indicates the possible existence of triaminoborane tautomers, compounds **4'** and **5'**.

Under the experimental conditions (room temperature and ambient pressure), the CH₂ group is unlikely to participate in the dehydrogenation reaction. This can be proven through the use of ethylenediamine-*d*₄ (NH₂CD₂CD₂NH₂, **9**). In the dehydrogenation product between EDAB-*d*₄ (**10**) and **9**, HRMS results demonstrate a C:D ratio of 1:2, proving the existence of CD₂ (**Figure S8**). We propose that the dehydrogenation of EDAB in ED occurs according to the following mechanism (**Figure 5**). Generally, the reaction involves dehydrogenation and coordination. The Pt catalyst activates both the B-bound H and the N-bound H, facilitating the formation of H₂.^[13] We have been unable to detect BH₂ and BH via ¹¹B NMR to confirm their formation likely due to the rapid nature of the reaction. The formation of BH likely weakens the B-N dative bond, which leads to the scission of this bond in steps 3 and 3' of the proposed dehydrogenation mechanism. Dative bonds have been observed by femtosecond technology, indicating that the reversible nature of a dative bond results from the fast electron transfer.^[14] With regard to the B-N dative bond in this study, the dissociation occurs by an S_N2 type mechanism.^[14] Brown and co-workers studied the dissociation enthalpies (in the gas phase) of several simple borane amine complexes.^[15] The

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values vary from 52 kJ mol⁻¹ to 152 kJ mol⁻¹. They are significantly lower than those of many bonds, such as B-N (typical σ bond, 389 kJ mol⁻¹), Al-H (285 kJ mol⁻¹), H-H (436 kJ mol⁻¹), CH₃-C₆H₅ (389 kJ mol⁻¹), etc.^[16] Thus, facile dissociation-association of the B-N dative bonds can occur during the dehydrogenation and also regeneration, which will be discussed hereafter.



Scheme 2. Propylamine exchange reaction of the dehydrogenation products.

Propylamine exchange reaction (**Scheme 2**) of the dehydrogenation products has provided further evidence for the 5-membered ring. NMR analysis of the propylamine exchanged product **11** (**Figure S9**) shows the chemical shifts of H1 and H2 to be 3.67 and 1.86 ppm, respectively. The difference in chemical shifts clearly indicates that C1 and C2 are non-equivalent, resulting from bonding to sp² N5 and sp³ N3. Signals at 2.67, 1.46 and 0.92 ppm are accounted for the presence of propylamine. The data confirm the structure of the exchanged product and indicate that it could only derive from either **4** or **5**, as shown in **Scheme 2**. We have not been able to grow single crystals of dehydrogenation products to obtain direct evidence of the 5-membered ring after numerous attempts.

Figure 6 shows ¹¹B NMR of dehydrogenation products. It reveals a boron nucleus that is less shielded than in EDAB. The two broad singlets at 25, and 28 ppm indicates that borons in the BCN 5-membered rings have two different chemical environments, likely caused by isomeric configuration. The NMR data are consistent with the reported ¹¹B NMR spectra of monocyclic diazaborolines exhibiting the chemical shifts from 15 to 45 ppm.^[17] The 5-membered ring has electron-deficient boron, which acts as a Lewis acid, which can be coordinated by the basic N from the NH₂ group of ED to produce complexes **4** and **5**. One equivalent of ED is consumed in step (3), and one equivalent of ED is released after step (6). For the mechanism illustrated in **Figure 5**, the overall net reaction is that one equivalent of EDAB reacts with one equivalent of ED to produce two equivalents of **3**. Considering this, the weight percent of hydrogen evolved in this reaction will be 8.2 wt% for the EDAB : ED ratio of 1:1. In reality, **4** and **5** form during the reaction where ED acts as a coordinating solvent and also as a reactant. The resultant hydrogen capacity is between 4.5 wt% (**4** only) and 5.8 wt% (**5** only).

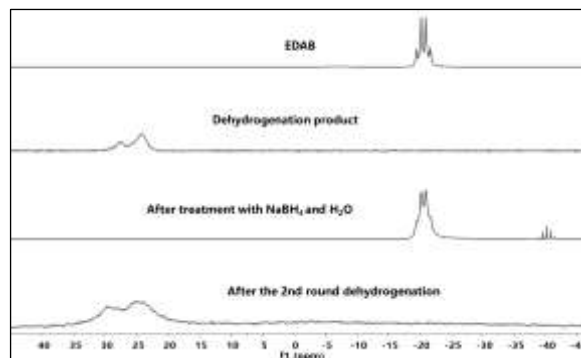


Figure 6. ¹¹B NMR spectra indicating success in regenerating EDAB.

After treatment with NaBH₄ and H₂O, the dehydrogenation product can be successfully converted to EDAB (**Figure 6**). A solution of NaBH₄ in ED is added to the dehydrogenation product followed by the addition of H₂O. Note that the dehydrogenation product of EDAB is unstable in air and undergoes hydrolysis to form boric acid. In this system, water has strong interactions with the ED, which suppresses its reaction with both NaBH₄ and the dehydrogenation product. A plausible regeneration first begins with dissociating the energetically labile B-N dative bond.^[18] In the reduction step, the N=B bond undergoes reduction with [BH₄]⁻ to form BH₃ and an intermediate which is protonated by water to form NH₂. Two moles of BH₃ interact with NH₂ *via* dative bond to form EDAB. Our one-pot reaction can be more favourable in terms of operation and cost than the two-step processes. For example, alcohol and LiAlH₄ were used sequentially to regenerate methyl-BN-cyclopentane from dehydrogenation products.^[5a] Efforts are underway to understand the detailed mechanism and improve the yield.

The efficiency of regeneration was estimated based upon the quantity of H₂ generated in the following cycle. As can be seen from the ¹¹B NMR spectra (**Figure 6**), all the B-containing species in the dehydrogenation product were successfully converted back to BH₃ containing species indicated by the quartet. EDAB was obtained after removing free (or non-coordinating) ED and residual NaBH₄. Around 5.1 equivalent amounts of H₂ was released in the second dehydrogenation, corresponding an efficiency of 84%. Note the efficiency can be improved if better purification process is developed.

In summary, we have successfully developed a BCN system featuring the rapid release of hydrogen gas and facile regeneration both at room temperature. The dehydrogenation leads to the formation of -N-B-N- units in 5-membered BCN rings. The exact bond nature (compound **4** vs **4'**) remains to be confirmed, ideally by single crystal structure analysis. This system allows for a degree of tunability through variation of the amine and borane complex substrates in order to achieve desirable properties dependent on specific applications. Compared with reported systems for hydrogen storage, this method requires neither high pressures nor high temperatures, which is beneficial for the net energy efficiency. This research sheds light on designing BCN-based hydrogen storage systems that could be applied for practical applications.

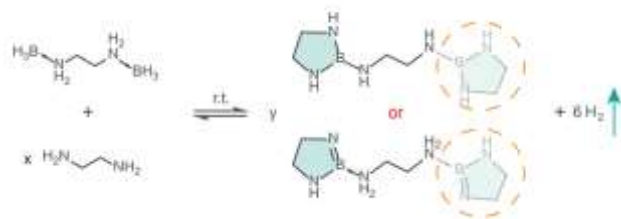
Acknowledgment

Z.H. acknowledges support under the Australian Research Council's Discovery Projects funding scheme (project number DP170101773) and Future Fellowship (project number: FT190100658), and support from the Alexander von Humboldt Foundation.

Keywords: amine-borane • hydrogen storage • regeneration • boron

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An amine-borane system has been discovered to deliver a reversible dehydrogenation/regeneration at room temperature. It provides a new way for hydrogen storage under mild conditions.