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Mechanism of B-H redistribution during reduction of Polyborazylene by Hydrazine

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Abstract: Density functional theory has been used to elucidate the mechanistic underpinnings of the regeneration of ammonia-borane (H_3B-NH_3, **AB**) from polyborazylene ($B_xN_xH_x$, **PBz**) in the presence of hydrazine (H_2N-NH_2, **Hz**). Herein, borazine ($B_3N_3H_6$, **Bz**) is used as the simplest relevant model of **PBz** for the regeneration process. Digestion of **Bz** using **Hz** was found to occur by a string of Lewis acid base adduct (between B atoms of **Bz** and **Hz** molecule) formation and **Hz** assisted proton transfer processes. Later, B-H bonds of $HB(NHNH_2)_2$, the **Bz** digested product, are redistributed to form hydrazine-borane (H_3B-NH_2NH_2, **HzB**) and $B(NHNH_2)_3$. Redistribution of B-H bonds occurs through hydroboration and concerted proton-hydride transfer. Another B-H redistributed product, $B(NHNH_2)_3$, produces **HzB** as a result of proton and hydride transfer from cis-diazene (**Dz**), the oxidized product of **Hz** in presence of O_2.

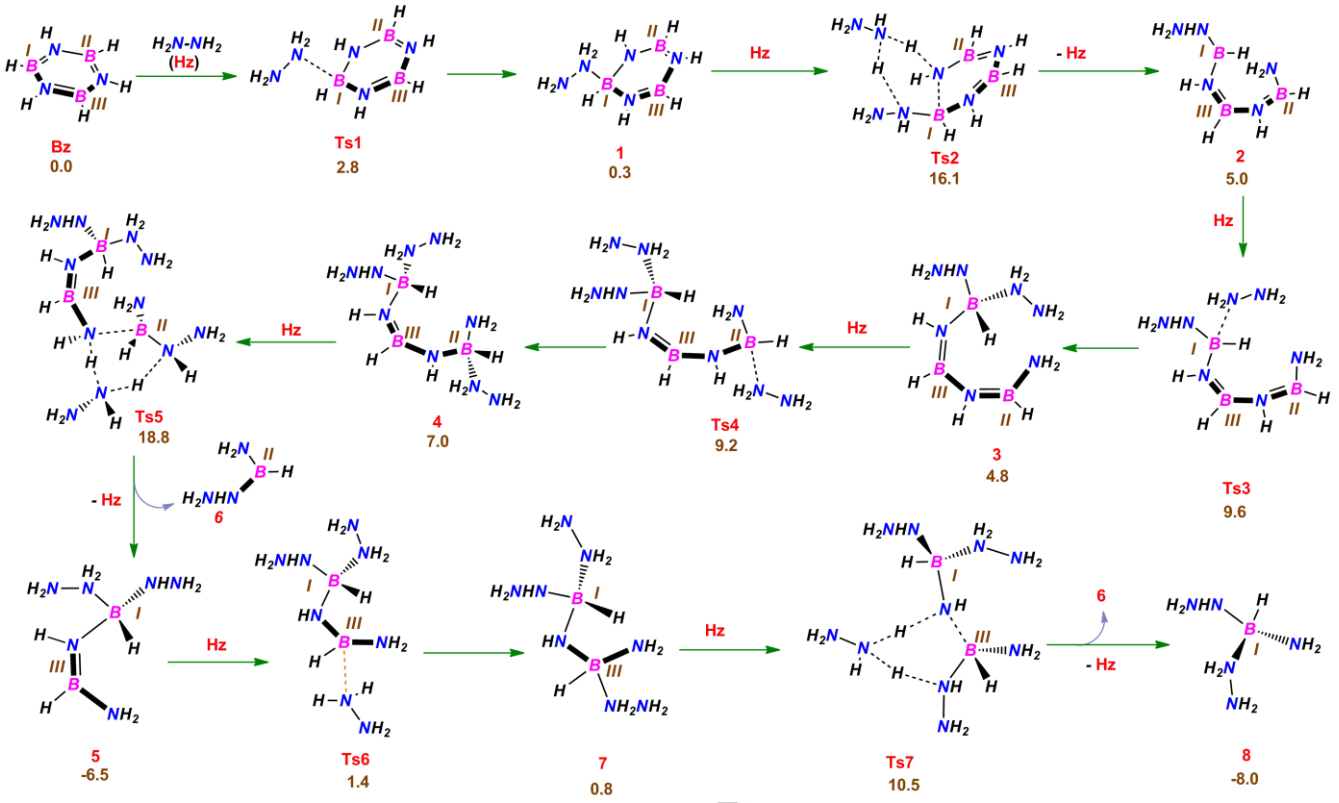
Introduction

In the last few decades, ammonia-borane (H_3B-NH_3, **AB**) has garnered a lot of attention as a potential chemical hydrogen storage material.[1] **AB**'s usefulness as a hydrogen storage material depends on the availability of an appropriate dehydrogenation catalyst and its regeneration from the spent fuel.[1i] A large variety of transition metal and metal-free catalysts have been designed in the past few years which are capable of releasing H_2 at a desirable rate and extent from **AB**.[1] However the regeneration of **AB** from spent fuel is the main obstacle for the development of a complete chemical hydrogen storage and delivery system using **AB**.[1h, 2]

After the release of more than two equivalents of hydrogen from **AB** by thermal or catalytic dehydrocoupling, polyborazylene ($B_xN_xH_x$, **PBz**) is usually formed as the main byproduct [1h] which is a BN-based graphene type of material. Regeneration of **AB** from **PBz** consists of two mains steps: (i) formation of a monomeric boron-containing unit by digestion of **PBz** and (ii) reduction of those boron fragments into BH_3.[2] In 2008, Mertens and coworkers developed a digestion method of **PBz** to yield BCl_3 and NH_4Cl with hydrochloric acid.[3] After obtaining BCl_3 they used another amine-borane (BH_3-NR_3, R is an alkyl group) to carry out Lewis base exchange with BCl_3. Subsequent to amine exchange, BH_3 and BCl_3-NR_3 is produced. BCl_3-NR_3 can be regenerated to BH_3-NR_3 by hydrodechlorination reaction. Later Gordon and coworkers reported an alternative **PBz** digestion process using benzenedithiol. The molecular fragments obtained after digestion, $(C_6H_4S_2)BH(NH_3)$, can be reduced to **AB** using Bu_2SnH_2.[4] Along with the hydrogenation of **PBz**, inorganic chemists have tried to attain the desired chemical reversibility of hydrogen storage for **AB** by hydrogenating aminoboranes, **Bz** which are the intermediates formed before **PBz** during the dehydrocoupling process. Recently, Manners and coworkers have reported hydrogenation of monomeric aminoborane, $NiPr_2{=}BH_2$ using H_2O, but it is not sustainable due to the highly exothermic formation of B-O bonds.[5] Szymczak and coworkers reported the regeneration of acetate derivatives of cyclotriborazane (**CTB**) from **Bz** using $Cr(CO)_3(CH_3CN)_3$, MeMgBr and acetic acid.[6] However, this regeneration process is also not sustainable as it requires sacrificial acid and Grignard reagent.

Compared to these approaches, a more effective regeneration scheme was achieved by Sutton and coworkers in 2011.[7] The authors showed that **PBz** can be converted back to **AB** in two steps: (i) addition of **Hz** with **PBz** in a sealed pressure vessel to produce **HzB**, and (ii) **HzB** is converted to **AB** in NH_3(l) at 60°C. They have proposed that **Hz** hydrogenates **PBz** to produce **HzB** with N_2 as the byproduct, but the mechanistic pathway of this process is not yet well understood. Deeper insight into this regeneration mechanism can provide details of the energy demand of the full process, and likely lead to improvements in conditions to better exploit this chemistry.

In recent years experimental and theoretical works have established that hydrogenation of B=N bond can occur via proton and hydride transfer to N and B atoms, respectively.[8] For instance, Zimmerman and co-workers have suggested the hydrogenation of B=N bond of amino-boranes can be achieved through concerted proton and hydride transfer from amine-boranes via a low barrier route.[8a] Manners and co-workers have experimentally demonstrated the hydrogenation of BN double bonds of $H_2B{=}N^iPr_2$ via metal-free hydrogen transfer using H_3B-NH_3 as the proton and hydride source.[8b-c] Additionally, theoretical calculations from our group suggested that B=N bonds of aminoboranes can be hydrogenated via dihydrogen transfer from hydrogenated BN nanotubes, and B=N bonds in BN fullerenes can be hydrogenated using suitable amine-boranes.[8d] Our recent study reveals that B=N double bond of aminoborane ($H_2B{=}NH_2$) is hydrogenated by the protons and hydrides present in thecyclotriborazane (**CTB**), B-(cyclodiborazanyl)-aminoborohydride (**BCDB**) and other in situ



Scheme 1. Reaction pathways for formation of single B-H containing units like $HB(NH_2)NHNH_2$ (**6**) and $HB(NH_2NH_2)(NHNH_2)NH_2$ (**8**) by **Bz** digestion in presence of **Hz** has been shown schematically. Relative free energies of each intermediate and transition state have been given in the scheme in unit of kcal/mol. Three B atoms of **Bz** molecule have been defined as B(I), B(II) and B(III) on the basis of their sequence of reactivity. Free energies are given at M05-2X(CPCM)/6-31++g(d,p)//M05-2X/6-31++g(d,p) level of theory.

generated B-N oligomers produced during ammonia-borane dehydrocoupling.[9] The exclusive characteristic which is common to these B=N hydrogenation reactions is that B and N accepts a hydride and a proton (respectively) during hydrogenation due to polarization at the B and N centers. In contrast, the hydrogenation of B=N bonds in polyborazylenes or aminoboranes by **Hz** stand apart as **Hz** bears only protic hydrogens. This peculiar facet of the **Hz**-facilitated hydrogenation certainly incites curiosity. Dixon and coworkers have shown that the transfer of N-H hydrogens of **Hz** to B=N bond (shown in equation1) is thermodynamically favorable when all the reactants are in solid state (ΔH = - 52.5 kcal/mol; ΔH = 5.7 kcal/mol when the reactants are in gas phase), but provided no

$$c\text{-}B_3N_3H_6 + 3\ N_2H_4 = 3\ H_3B\text{-}NH_3 + N_2 \quad \text{..... (1)}$$

mechanistic explanation for this reaction.[7] The protic nature of hydrogen atoms of **Hz**, however, suggests that the mechanistic paradigm of hydrogenation is likely to be quite different from B=N hydrogenation by amine-boranes. Hence, it is mechanistically intriguing how the protic hydrogens on **Hz** end up as hydrides and protons during the conversion of **PBz** to **AB**.

In recent times, Baker and coworkers have studied the reaction pathway of the **PBz** regeneration process,[10] using ^{11}B and ^{1}H NMR to elucidate the mechanistic details of the hydrogenation reaction. When **PBz** was treated with $NH_3(l)$, $HB(NH_2)_2$ and $B(NH_2)_3$ are produced in the reaction medium along with **AB**. During the course of the reaction, NMR signals for **AB** and $B(NH_2)_3$ grow in alongside decay of the signal corresponding to $HB(NH_2)_2$ units. From this observation they have concluded that a B-H bond redistribution process is operative.[10] However, their investigations did not shed light on the mechanistic intricacies of formation of the observed intermediates, $HB(NH_2)_2$, $B(NH_2)_3$ and the redistribution of B-H bonds. Recently several experimental and theoretical studies have reported that intermolecular redistribution of B-H and N-H hydrogen occurs between amine-borane and aminoborane by concerted dihydrogen transfer.[8] Our recent studies unravel that this redistribution process has a significant role in 2nd and 3rd equivalent hydrogen removal from **AB**.[9] The mechanistic aspect of B-H redistribution process which has a role to play in regeneration of **AB** from **PBz** is yet to be unearthed.

Herein, density functional theory simulations are used to elucidate the mechanism for redistribution of B-H hydrogens and for formation of B-H hydrides from **Bz** and **Hz**. Baker and coworkers have reported that the intermediates produced in the reaction path for **Bz** and **PBz** are similar in nature.[10] So for studying the reaction mechanism of redistribution of B-H hydrogens of **PBz**, we have used **Bz** as a model unit.

Results and Discussion

Our DFT study is directed towards unearthing the probable intermediates and transition states along the reaction path of hydrogenation of **Bz** by **Hz**. At first, we studied the disintegration of **Bz** molecule by the action of **Hz** to yield simplest B-H containing unit (details are provided in Scheme 1).

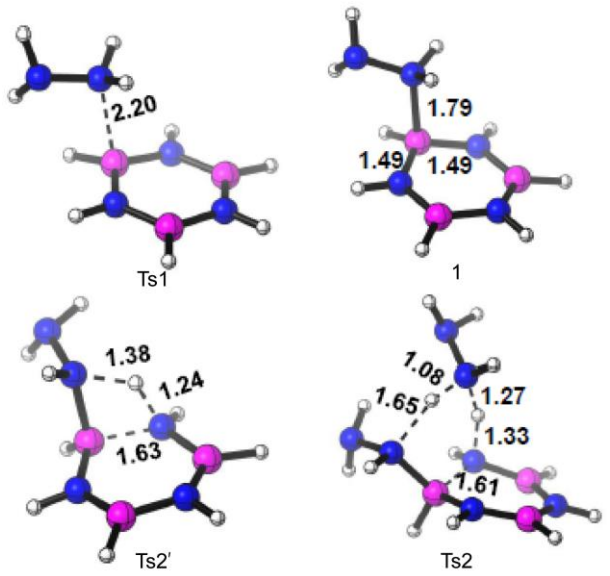
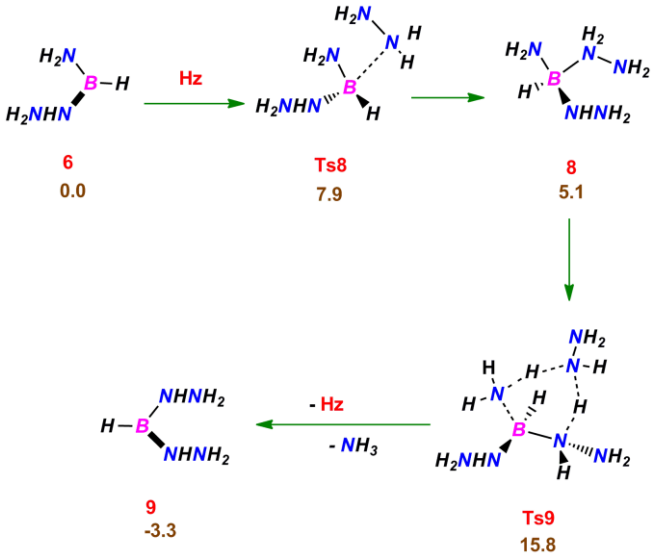


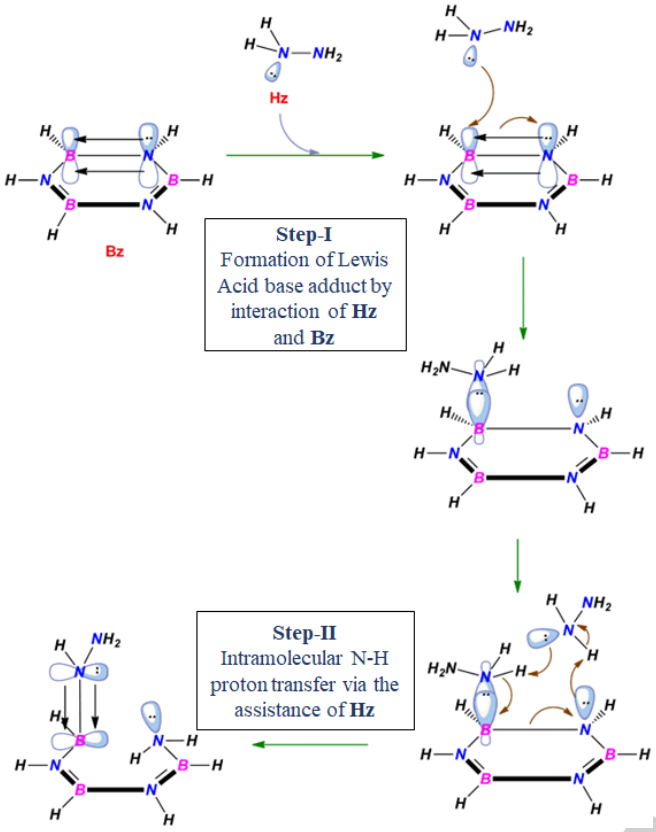
Figure 1. Optimized structure of a) **Ts1**, transition state for adduct formation between **Bz** and **Hz**; b) **1**, Lewis acid base adduct of **Bz** and **Hz**; c) **Ts2'**, intra-molecular proton transfer transition state without proton shuttle and d) **Ts2**, intra-molecular proton transfer transition state with hydrazine as proton shuttle. Bond distances are shown in Å. Color Code : Boron (Pink), Nitrogen (blue), Hydrogen (white). The dashed bonds indicate the bonds involved in the transition state.



Scheme 2. Formation of $HB(NHNH_2)_2$ (**9**), most stable single boron containing fragment, from $HB(NH_2)NHNH_2$ (**6**) and $HB(NH_2NH_2)(NHNH_2)NH_2$ (**8**) in presence of **Hz**. Relative free energy of each intermediate and transition states has been given in the scheme in unit of kcal/mol. Free energies are given at M05-2X(CPCM)/6-31++g(d,p)//M05-2X/6-31++g(d,p) level of theory.

(i) **Formation of single B-H containing unit [$HB(NHNH_2)_2$] from Bz**. Initially, we evaluated the possibility of coordination of **Hz** molecule to a boron atom of **Bz**. We found that a **Hz** molecule can bind to the B atom of **Bz** through **Ts1** (see Scheme 1 and Figure 1) by overcoming a very low free energy activation barrier of 2.8 kcal/mol. Adduct of **Bz** and **Hz**, $B_3N_3H_6$-NH_2NH_2 (**1**) (see Scheme 1 and Figure 1), is predicted to be unstable around 0.3 kcal/mol compared to the starting reactants, which means that binding of **Hz** and **Bz** is almost a thermoneutral process. **Hz** bound B atom of **1** is defined as B(I) and other boron atoms is defined accordingly for better understanding (see Scheme 1). After **Hz** binds to B(I) centre, the B-N bond distance involving B(I) and two neighboring N atoms increases from 1.43 Å to 1.49 Å. This indicates the weakening of B-N dative bonds on attachment of **Hz**. NBO analysis shows that the hydrogens present in the boron bound nitrogen atom of **Hz** are positively charged (0.416 and 0.440 au) and the neighboring N atoms of B(I) in **Bz** are negatively charged (-1.167 and -1.159 au). On binding to the B center the protic character of the N-H hydrogens on the coordinating N gets enhanced and one of them can be transferred to the nearest N atom from B(I). We found that this proton transfer can occur through two distinct pathways- (i) direct proton transfer (**Ts2'**), (ii) proton transfer using proton shuttle (**Ts2**) (see Scheme 1 and Figure 1). Both the cases of proton transfer are associated with a concomitant dissociation of B-N bond containing the N to which the proton is being transferred.

Our theoretical calculations show that the free energy activation barrier for the proton transfer using proton shuttle (through **Ts2**) is only 16.1 kcal/mol. In **Ts2**, one **Hz** molecule is acting as a proton shuttle (see Figure 1). Without this proton shuttle, the activation barrier of this proton transfer process(through **Ts2'**) is 30.1 kcal/mol in terms of free energy (see Figure 1). A comparison of the barriers associated with the two proton transfer pathways suggests that the shuttle mechanism is the preferred pathway for proton transfer. Proton transfer and concomitant B-N bond cleavage through **Ts2** lead to the formation of **2**, an open linear chain species (see Scheme 1). Open chain species (**2**) is transformed into $HB(NH_2)NHNH_2$ (**6**), a single B-H containing unit, and **5**, two B-H containing unit, by subsequent Lewis acid base adduct formation and B-N bond cleavage facilitated by **Hz** (see Scheme 1). The rate determining step of **5** and **6** formation from **2** is a B-N bond breaking step (**Ts5**) which involves an instantaneous proton shuttle by **Hz** and has free energy activation barrier of 18.8 kcal/mol (see Scheme 1). Similar Lewis acid base adduct formation and B-N bond cleavage promoted by **Hz** converts two boron containing open chain species (**5**) to $HB(NHNH_2)NH_2$ (**6**) and NH_2NH_2-$BH(NHNH_2)NH_2$ (**8**). The separation of two B-H containing unit happens at a free energy activation barrier height of 17.0 kcal/mol corresponding to the B-N bond rupture transition state (**Ts7**) (see Scheme 1). Till now our theoretical calculations suggest that digestion of each **Bz** molecule by **Hz** produces two units of **6** and one unit of **8** (see Scheme 1) and the overall chemical transformation is favored by 8.0 kcal/mol in terms of free energy. We have found that **6** can be easily transformed into **8** by forming a Lewis acid base adduct with **Hz** (see Scheme 2). The adduct formation occurs through **Ts8** (see Scheme 2) with a free energy activation barrier of 7.9 kcal/mol. Then **8** can generate $HB(NHNH_2)_2$ (**9**) and ammonia via an intra-molecular proton transfer and subsequent B-N bond rupture by the assistance of one **Hz** molecule (see Scheme 2). Formation of **9** and NH_3 from **6** and **Hz** is exothermic by 3.3 kcal/mol. Free energy activation barrier of **Ts9** (see Scheme 2) corresponding to the formation of **9** is 15.8 kcal/mol. **Hz** assisted adduct formation, proton transfer and subsequent B-N bond cleavage on **9** yielded the same unit. Followed by **Bz** digestion by **Hz**, **9** is formed which is the simplest and most stable unit. Similar to **6**, the intermediate **8** also transforms to **9** with the help of **Hz** by climbing the free energy activation barrier of 10.7 kcal/mol. So our detailed theoretical calculation shows that the most stable



Scheme 3. Schematic representation of the two most important steps in case of **Bz** digestion by **Hz**- a) Lewis acid base adduct formation and b) B-N bond cleavage by **Hz** assisted proton transfer.

form of B-H unit generated from **Bz** is **9**. We have found that formation of the most stable single B-H containing species (**9**) from **Bz** has rate determining barrier of 18.8 kcal/mol due to **Ts5** (see Scheme 1 and Scheme 2). Borazine digestion rate determining free energy barrier is 24.9 kcal/mol using DLPNO-CCSD(t)(CPCM)/aug-cc-pVTZ//M052x/6-31++g** level of theory. Using ^{11}B and ^{1}H NMR Baker and coworkers [10] reported that during regeneration of **AB** from **PBz** and liquid NH_3, $HB(NH_2)_2$ is formed. It is analogous to the single B-H containing unit $HB(NHNH_2)_2$ (**9**) obtained in our theoretical work after **Bz** digestion by the action of **Hz**. So our theoretical results for **Bz** digestion process combines well with the experimental results of Baker and coworkers [10].

Digestion of **Bz** by **Hz** involves reiteration of two main steps (see Scheme 3)-

(i) Lewis acid base adduct formation between the potential Lewis acidic centers (B-atoms) of **Bz** and Lewis basic centers (NH_2 ends) of **Hz**. Due to this adduct formation dative bond present between the B atom and neighboring N atoms of **Bz** is weakened.

(ii) Proton transfer from B bound **Hz** to one of the neighboring N atoms of **Bz** by the assistance of **Hz** resulted B-N bond rupture.

After gaining the mechanistic insight about the **Bz** digestion by **Hz** we have looked into the B-H redistribution process proposed by Baker and coworkers [10] which yielded **HzB** as a redistributed product. **9**, the simplest B-H containing unit obtained after **Bz** digestion by **Hz**, is one type of aminoborane. So we have checked the possibility of dimerization of **9**. We have found that the dimerization of **9** via **Ts_9_Dimer** (see Figure 2) involves

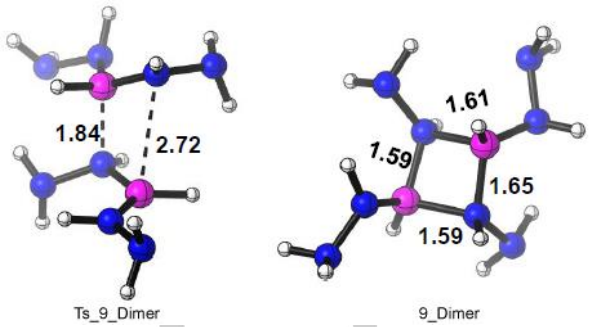
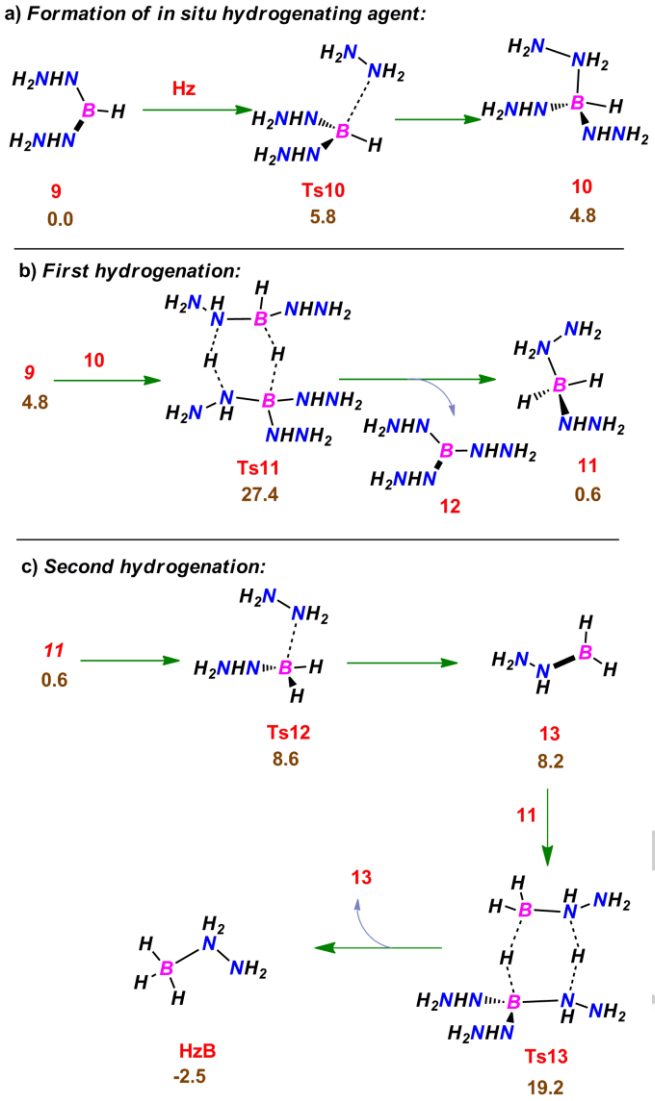


Figure 2. Optimized structure of a) **Ts_9_Dimer**, transition state for dimerization of **9**; b) **9_Dimer**, dimer of **9**. Bond distances are shown in Å. Color Code : Boron (Pink), Nitrogen (blue), Hydrogen (white). The dashed bonds indicate the bonds involved in the transition state.

free energy activation barrier of 19.8 kcal/mol, although formation of **9_Dimer** (see Figure 2) from two units of **9** is endoergic by 13.9 kcal/mol. This high endoergic nature of dimerization process suggests that **9** exists as a monomer in the solution. If we consider similar kind of reaction in case of **PBz** (anthracene type B-N framework) it can be found that the rate determining free energy activation barrier of the whole process is 22.8 kcal/mol which matches very well with that of **Bz** (ΔG= 18.8 kcal/mol). It clearly suggests that the **Bz** digestion process successfully mimics the digestion procedure of **PBz**. See Section 3 of Supporting Information for further details.

(ii) Redistribution of B-H bonds of $HB(NHNH_2)_2$. $HB(NHNH_2)_2$ (**9**) is the most crucial intermediate, which regenerates **HzB** by redistribution of B-H hydrides. We have found that there exists two channels for the B-H redistribution.

(a) **Redistribution via Concerted Dihydrogen Transfer.** **9** is capable of forming a Lewis acid base adduct with **Hz**. Formation of this Lewis acid base adduct NH_2NH_2-$BH(NHNH_2)_2$ (**10**) (see Scheme 4 and Figure 3a) is endoergic by 4.8 kcal/mol compared to separated reactants. Molecular electrostatic potential (MEP) analysis shows that **10** consists of two types of hydrogens- hydride and proton present on the boron center and the N atom of **Hz** adjacent to the B center respectively (see Figure 3b). So **10** can act as a hydrogenating agent like amine-boranes [1]. We have found that the dihydrogen transfer from **10** to another equivalent of **9** happens through **Ts11** (see Figure 3c) with a free energy activation barrier of 27.4 kcal/mol. As a result of this dihydrogen transfer process, **9** is converted to NH_2NH_2-$BH_2(NHNH_2)$ (**11**) and simultaneously $B(NHNH_2)_3$ (**12**) is formed from **10** (see Scheme 4). This entire dihydrogen transfer process is exoergic by 4.2 kcal/mol with respect to intermediate **9**. H_2B-$NHNH_2$ (**13**), which can be seen as aminoborane form of **HzB**, is produced from **11** by losing **Hz** molecule bound to the B atom via **Ts12** with the expense of 8.0 kcal/mol free energy activation barrier (see Scheme 4). Generation of **13** and **12** from two units **9** and one **Hz** molecule is endoergic by 8.2 kcal/mol. **13** can dimerize by overcoming a free energy activation barrier of 13.1 kcal/mol and the dimer is stabilized by 12.1 kcal/mol. So, one might expect that **13** exists as a dimer in the reaction medium. This endoergic formation of **13** via aforementioned route makes the rate determining free energy activation barrier 35.6 kcal/mol



Scheme 4. Redistribution of B-H hydrides present in **9** to form **HzB** with involvement of concerted dihydrogen transfer. a) Pathway for formation of **10**, the hydrogenating agent; b) first hydrogenation of **9** to form **Hz** bound adduct of **13**, aminoborane form of **HzB** and c) second hydrogenation to form **HzB.**

which is associated with the formation of second equivalent of **13**. Thus, dimer of **13** does not exist in solution. **13** can convert to **HzB** by dihydrogen transfer from another unit of hydrogenating agent (**10**). Dihydrogen transfer from **10** to **13** happens through **Ts13** (see Figure 3d) by overcoming a free energy activation barrier of 19.2 kcal/mol. The overall free energy change in formation of **HzB** and two equivalents of **12**, the dehydrogenated form of the hydrogenating agent, from three equivalents of **9** and **Hz** is exoergic by 2.5 kcal/mol. Rate determining free energy barrier of the whole redistribution process is 27.4 kcal/mol, which corresponds to the first dihydrogen transfer from hydrogenating agent **10** to the B-N dative bond of **9**.

Our aforementioned B-H redistribution pathway of **9** happens in two distinct steps – (i) generation of in situ hydrogenating agent from **9** and **Hz**, (ii) subsequent hydrogenation of two B-N bonds present in **9** (see Scheme 4).

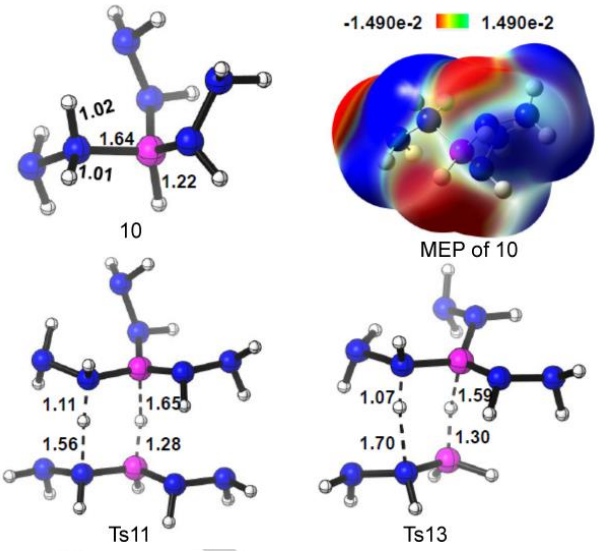
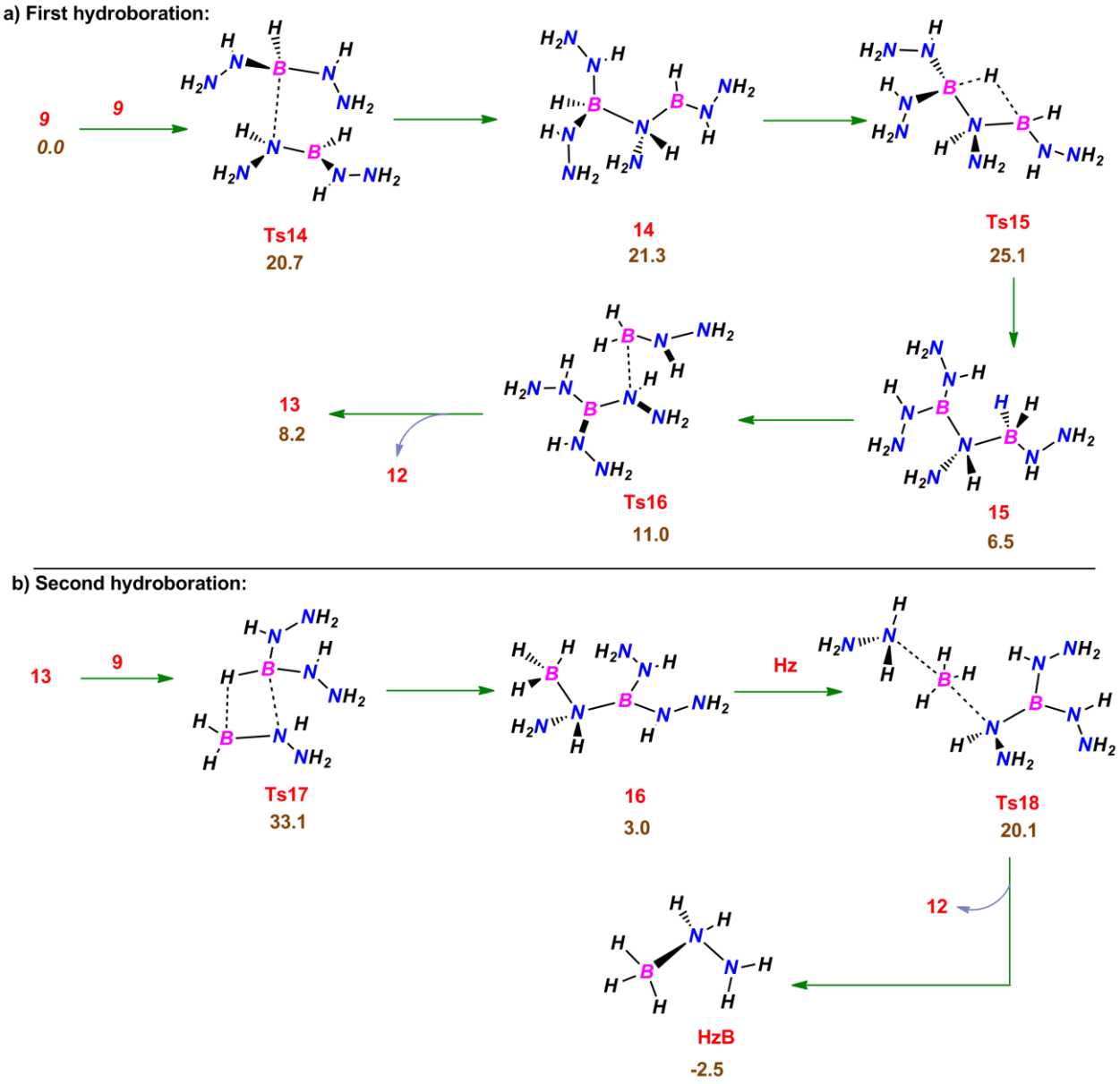


Figure 3. a) Optimized structure of hydrogenating agent **10**, b) MEP of **10**, c) first dihydrogen transfer transition state **Ts11** and d) second dihydrogen transfer transition state **Ts13**. Bond distances are shown in Å. Color Code : Boron (Pink), Nitrogen (blue), Hydrogen (white). The dashed bonds indicate the bonds involved in the transition state.

The rate determining barrier of this whole process by dihydrogen transfer is due to first B-N bond hydrogenation.

(b) **Redistribution via B-H Hydroboration. 9** consists of one B-H bond and two B-N dative bonds (B-$NHNH_2$ linkage) similar to aminoborane. It is a well-established fact that B-H bond of aminoborane can participate in hydroboration to the B-N dative bond of another aminoborane molecule.[11] So it is possible that B-H bonds of **9** can undergo a similar type of hydroboration reaction with another molecule of **9**. So we considered the possibility for rearrangement of B-H bonds through such hydroboration reactions (see Scheme 5).

Initially, two molecules of **9** form a Lewis acid base adduct (**14**) by donation of lone pair of N atom (of $NHNH_2$ ligand attached with the B center of each unit of **9**) to the B atom of another unit of **9**. This type of adduct formation before hydroboration is not possible for simple aminoborane. **14** is formed from two units of **9** by overcoming a free energy activation barrier of 20.7 kcal/mol via **Ts14** (see Figure 4) and the whole adduct formation process is endoergic by 21.3 kcal/mol. Optimized structure of **14** shows that one B atom is tetrahedral and another one is planar. After that hydride transfer occurs from tetrahedral B center to planar B center through **Ts15** which has an associated free energy activation barrier of 25.1 kcal/mol (see Figure 4). As a result of hydride transfer, **14** is converted to **15** (see Scheme 5) which later produces separated **12** and **13** via **Ts16** (see Figure 4) by overcoming a free energy activation barrier of 11.0 kcal/mol. Formation of **13** and **12** from **14** is an exoergic transformation by 13.1 kcal/mol. After that B-H bond of one unit of **9** undergoes hydroboration across B-N dative bond of **13** to yield BH_3 moiety. The hydroboration reaction happens between **13** and **9** via **Ts17** (see Figure 4) with free energy activation barrier of 33.1 kcal/mol leading to the formation of **16** (see Scheme 5)**,** which is a Lewis acid base adduct of BH_3 and **12**. **Hz** can facilitate the **HzB** formation from **16** through a nucleophilic substitution transition state, **Ts18**, by surmounting a free energy activation barrier of



Scheme 5. Redistribution of B-H hydrides of **9** to form **HzB** via the hydroboration pathway. Relative free energies of each intermediate and transition states are provided in kcal/mol. Free energies are given at the M05-2X(CPCM)/6-31++g(d,p)//M05-2X/6-31++g(d,p) level of theory.

20.1 kcal/mol (see Scheme 5). Rate limiting step of the whole B-H redistribution process by hydride transfer via hydroboration process is due to the second hydroboration step, where B-H bond of **9** undergoes addition across the B-N bond of **13**. Thus the rate determining free energy activation barrier of this B-H redistribution process is 33.1 kcal/mol which corresponds to the second hydroboration step.

The redistribution pathway consists of two B-H bond redistribution steps (see Schemes 4 and 5) –

(i) 1st B-H bond redistribution: Formation of **13**, aminoborane form of **HzB**, from **9**

$2\ HB(NHNH_2)_2 = BH_2\text{-}NHNH_2 + B(NHNH_2)_3$

(ii) 2nd B-H bond redistribution: Formation of **HzB** from its aminoborane form (**13**)

$HB(NHNH_2)_2 + H_2B\text{-}NHNH_2 + H_2N\text{-}NH_2 = H_3B\text{-}NH_2NH_2 + B(NHNH_2)_3$

The rate determining barriers associated with these two steps are compared here for determining the actual B-H

Table 1. Rate determining activation barriers and thermodynamics of the two B-H bond redistribution process during hydrazine-borane (**HzB**) formation from $HB(NHNH_2)_2$. All data are reported in terms of Gibbs free energy. Numbers in bracket are calculated using DLPNO-CCSD(t)(CPCM)/aug-cc-pVTZ//M052x/6-31++g** level of theory.

	1st B-H redistribution		2nd B-H redistribution	
	$\Delta G^{\ddagger}_{RDB}$ (kcal/mol)	ΔG (kcal/mol)	$\Delta G^{\ddagger}_{RDB}$ (kcal/mol)	ΔG (kcal/mol)
Concerted Pathway	27.4 (27.0)	8.2	19.2 (19.1)	- 2.5
Hydroboration Pathway	25.1(23.1)	8.2	33.1(32.4)	- 2.5

redistribution route. From Table 1, we can conclude that the 1st B-H bond redistribution occurs through hydroboration pathway and 2nd B-H redistribution follows the concerted dihydrogen transfer pathway. The free energy activation barrier for the second B-H redistribution process via concerted pathway increases to 24.0 kcal/mol due to the formation of endoergic hydrogenating agent (see Scheme 4a) after formation of **13**. So, the rate determining free energy activation barrier of the whole B-H redistribution process is 25.1 kcal/mol, which is associated with the first B-H redistribution process.

Our detailed theoretical investigation unravels the mechanistic aspects of the B-H redistribution process of **9** to yield **HzB**. During the redistribution process, $B(NHNH_2)_3$ (**12**) is formed as a result of hydride transfer from $HB(NHNH_2)_2$ (**9**). **12** is an analogous species of $B(NH_2)_3$, which was experimentally observed by Baker and coworkers [8] during the rearrangement of B-H hydrides of **Bz** in presence of liquid NH_3. So our proposed mechanistic pathway is in with the line of experimental

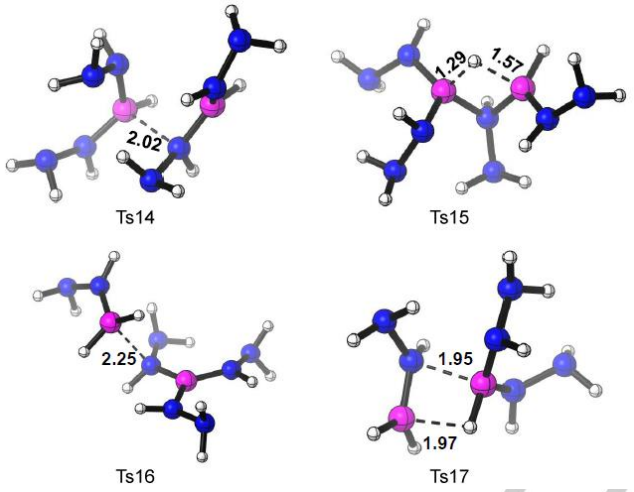


Figure 4. Optimized structures of important transition states corresponding to the B-H redistribution pathway via hydroboration of B-H bond across B-N dative bond- a) **Ts14**, b) **Ts15**, c) **Ts16** and d) **Ts17**. Bond distances are shown in Å. Color Code : Boron (Pink), Nitrogen (blue), Hydrogen (white). The dashed bonds indicate the bonds involved in the transition state.

results of Baker and coworkers. Our **Bz** digestion and B-H redistribution pathway can only explain the regeneration route for 1/3 of the total **HzB** formed from the **PBz** moiety. Hence, one needs to address the question how the remaining 2/3 of **HzB** obtained is formed.

(iii) Regeneration of HzB from $B(NHNH_2)_3$. Formation of **HzB** from $B(NHNH_2)_2$ (**12**) requires a hydride transfer from **Hz** to B center of **12**. In our theoretical calculations, we have looked intoseveral possibilities of hydride transfer from **Hz** to **12** (see SI section 4). Every possible B-H hydride formation step involves a large free energy activation barrier. It has been experimentally proposed long time ago that **Hz** in presence of aerial dioxygen produces cis-diazene (N_2H_2, **Dz**), which acts as a hydrogenating agent for a lot of organic substrates.[12] Recent theoretical studies of Paul's group explains the formation of **Dz** from **Hz** in the presence of dioxygen.[13] The estimated reaction kinetics of the **Dz** formation proposed by the theoretical analysis suggests that it is a slow process, which is in line with the kinetic study of Kappe and coworkers [14]. Sutton and coworkers [7] have also

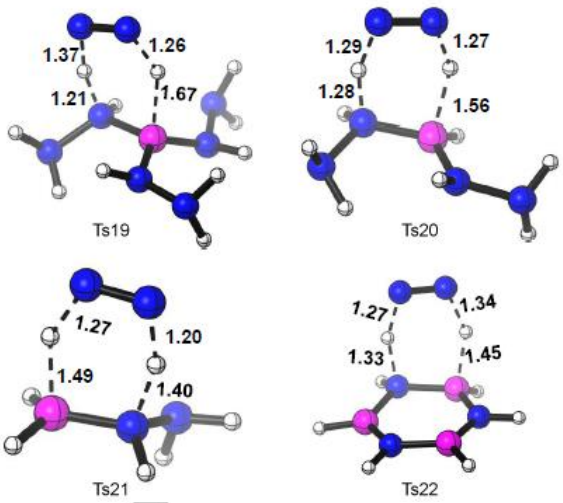


Figure 5. Optimized structures of a) **Ts19**, b) **Ts20**, c) **Ts2**1 and d) **Ts22** which are the transition states corresponding to regeneration of **HzB** from **12** and hydrogenation of **Bz** via dihydrogen transfer from cis-diazene (**Dz**). Bond distances are shown in Å. Color Code : Boron (Pink), Nitrogen (blue), Hydrogen (white). The dashed bonds indicate the bonds involved in the transition state.

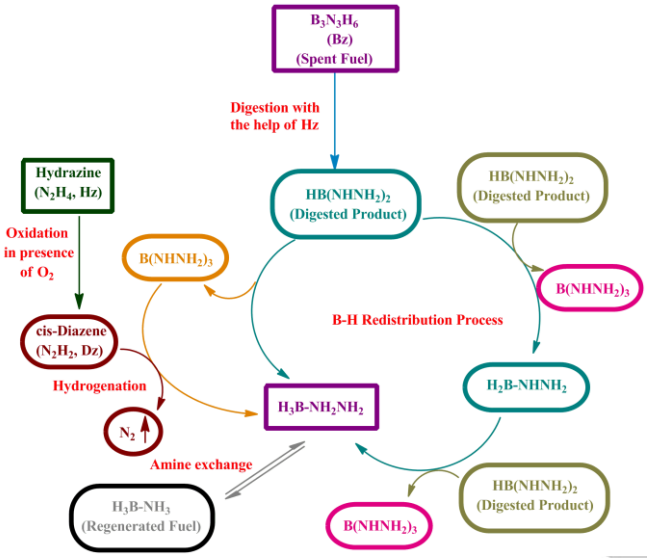
shown that high yield of **HzB** with minor amount of **AB** is obtained from **PBz** in presence of **Hz** in THF solvent after 12 hours. The reaction kinetics of **Bz** digestion by **Hz** and B-H redistribution process does not reflect the experimental observation of Sutton. The RDB of **Bz** digestion and B-H redistribution is 25.1 kcal/mol, which indicates that it would not be a slow reaction. So, we propose that the oxidation of **Hz** in presence of dioxygen is the rate determining step of the whole **AB** regeneration process from **PBz** by **Hz**. Formation of **Dz** from **Hz** in presence of dioxygen is the most crucial step. Sutton and coworkers have not reported whether hydrogen peroxide is formed after the completion of the reduction process.[7] We hereby propose that further experimental studies are required to identify the presence of hydrogen peroxide and such studies are expected to provide clues regarding the formation pathway of **Dz** in the medium. Plausibly, **Dz** has to be formed in this hydrogenation reaction by hydrazine where the final product is N_2. As suggested earlier, we suspect that in the presence of air, **Hz** is getting transformed to the more active **Dz** in the reaction vessel, which can more efficiently hydrogenate crucial intermediates.

Here, we have theoretically investigated the formation of **HzB** from $B(NHNH_2)_3$ (**12**) in presence of **Dz**. We have found that first dihydrogen transfer from **Dz** to **12** happens by overcoming a free energy activation barrier of 25.7 kcal/mol which is associated with the transition state **Ts19** (see Figure 5). Formation of **9**, **Hz** and N_2 from **12** and **Dz** is a highly exoergic process (ΔG= -35.1 kcal/mol). After that **9** is converted to **13**, aminoborane form of **HzB**, by concerted dihydrogen transfer from **Dz** via **Ts20** (see Figure 5) which involves free energy activation barrier of 26.4 kcal/mol. Similarly, **13** produces **HzB** by dihydrogen abstraction from **Dz** via **Ts21** (see Figure 5) by overcoming a free energy activation barrier of 17.0 kcal/mol. So our theoretical results suggest that three molecules of **Dz** convert **12** to **HzB** by subsequent three dihydrogen transfer with moderate free energy activation barriers.

The moderate free energy activation barriers of dihydrogen transfer from **Dz** to **12**, **9** and **13** raises a pertinent question- "Is cis-diimide (**Dz**) capable of hydrogenating polyborazylene (**PBz**) itself at a low activation barrier?" To answer this question, we have estimated the free energy activation barrier associated with the dihydrogen transfer from **Dz** to **Bz**. Hydrogenation of B-N bond of a simple **Bz** ring by **Dz** occurs at the expense of 31.7 kcal/mol free energy activation barrier via **Ts22** (see Figure 5), whereas rate determining free energy activation barrier associated with the hydrogenation of **12** by **Dz** is 25.7 kcal/mol. So, we can conclude that **Dz** will preferably hydrogenate **12**, the boron centers left after B-H redistribution, compared to the original **PBz** framework.

Conclusion

This detailed theoretical studies reveal a plausible mechanism for **HzB** formation from **Bz** by the action of **Hz** (see Scheme 6).



Scheme 6. Overview of the multistep regeneration process of spent fuel in presence of hydrazine (**Hz**).

The following concepts summarize the key mechanistic steps:
(i) A string of Lewis acid base adduct formation and subsequent proton transfer facilitates the digestion of **Bz** to yield single B-H containing units. **Hz** acts as a proton shuttle in all the proton transfer processes which occur in the reaction medium.
(ii) After digestion of **Bz**, redistribution of B-H hydrides takes place in the next step. Two single B-H containing units, which are **Bz** digested products, undergo hydroboration between them to yield a -BH_2 containing unit and a B-containing unit without any B-H hydride. Later, one single -BH containing unit forms a hydrogenating agent, which consists of two bipolar hydrogens (both protic and hydridic), after binding with one molecule of **Hz**. This hydrogenating agent transfers another B-H hydride to the -BH_2 containing unit and subsequently forms **HzB** and another equivalent of B-containing unit without any B-H hydride. So our theoretical investigation successfully explains the formation of one -BH_3 containing moiety from the three -BH containing moieties as a result of B-H redistribution. Also, two B-containing units are formed where no B-H hydride is present after the redistribution process.
(iii) These B-containing units formed as a result of B-H redistribution again regenerate **HzB** via two subsequent concerted proton and hydride transfer from cis-diazene (**Dz**), which is produced by the oxidation of **Hz** by dioxygen.
(iv) We have also checked the free energy activation barriers for hydrogenation of **Bz** by **Dz** and compared them with that of the B-containing units. Our theoretical results show that the hydrogenation of B-containing units is easier than **Bz** by cis-diazene (**Dz**). So, the **Dz** will only selectively hydrogenate the B-containing unit after digestion is complete.
Hence, our mechanistic investigation suggests that reduction of borazine (**Bz**) by hydrazine (**Hz**) is happening via a collective effort of three main steps, **Hz** assisted **Bz** digestion, redistribution of B-H hydrides of digested units and hydrogenation of hydride deficient B units (formed as a result of redistribution) by cis-diazene (**Dz**), oxidized product of **Hz**. Since **Bz** mimics the properties of polyborazylene (**PBz**), one can say that reduction of **PBz** will also follow similar steps. Our theoretical investigation also suggests that one may exploit the fact that cis diazene can also be used as a hydrogenating agent for polyborazylene which may lead to discovery of a more robust regeneration process for ammonia-borane.

Computational Details

All theoretical calculations were conducted using Gaussian09 package.[15] Geometries of all the intermediates and transition states were optimized using M05-2X functional [16] in conjunction with the Pople's 6-31++G(d,p) basis functions on each atom. All intermediates and transition states were characterized by all real normal modes (intermediates) and one imaginary normal mode (transition states). Initial guess geometries for transition states were generated using the growing string method.[17] We have included the effect of solvent in energy along the reaction pathways by performing single point calculations using the CPCM solvent model [18] and tetrahydrofuran (THF) (ε=7.4257) as solvent at M05-2X/6-31++g(d,p) level of theory. Decrease in translational entropy of each solute due to solvation has been accounted in our theoretical calculation by approximating 0.5 times of gas phase entropy as solution phase entropy. This approximation is based on experimental results of Wertz and have been generally used by the theoretical chemists for determination of free energies in case of predicting reaction pathways.[19] The working equation for determining solvent phase free energy is provided in supporting information (SI Section 1). Solvent phase free energies were estimated for 298.15 K and 1 atmospheric pressure. In the above text we discuss the relative stabilities and reaction barriers in terms of solvent phase free energies at the M05-2X(CPCM)/6-31++g(d,p)//M05-2X/6-31++g(d,p) level of theory. Moreover single point solvent phase calculations have been performed with gold standard CCSD(T) method[20] for the adduct formation reaction between **Hz** and **Bz** and we compared this result with those obtained in different level of theories (SI Section 2). The proper calibration justifies our choice of DLPNO-CCSD(t)[21](CPCM)/aug-cc-pVTZ//M052x/6-31++g** level of theory for further estimation of rate determining barriers involved in this reaction. For details see Section 2 in the supporting Information.

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Keywords: Ammonia-Borane Regeneration • Hydrazine • Polyborazylene • Diazene • Concerted Proton Hydride Transfer

[1] a) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023–4078; b) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079–4124. c) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626. d) N. C. Smythe, J. C. Gordon, *Eur. J. Inorg. Chem.* **2010**, 509–521. e) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279–293. f) B. Peng, J. Chen, *Energy Environ. Sci.* **2008**, *1*, 479–483. g) H. Li, Q. Yang, X. Chen, S. G. Shore, *J. Organomet. Chem.* **2014**, *751*, 60–66. h) S. Bhunya, T. Malakar, G. Ganguly, A. Paul, *ACS Catal.* **2016**, *6*, 7907–7934. i) A. Rossin, M. Peruzzini, *Chem. Rev.* **2016**, *116*, 8848−8872. j) T. B. Marder, *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118. K) I. Bhattacharjee, M. Sultana, S. Bhunya, A. Paul, *Chem. Commun.* **2022**, *58*, 1672-1684.

[2] O. T. Summerscales, J. C. Gordon, *Dalton Trans.* **2013**, *42*, 10075-10084.

[3] a) C. Reller, F. O. R. L. Mertens, *Angew. Chem. Int. Ed.* **2012**, *51*, 11731 –11735. b) S. Hausdorf, F. Baitalow, G. Wolf, F. O. R. L. Mertens, *Int. J. Hydrogen Energy* **2008**, *33*, 608-614.

[4] a) B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. Scott, F. H. Stephens, *Angew. Chem. Int. Ed.* **2009**, *48*, 6812–6816. b) A. D. Sutton, B. L. Davis, K. X. Bhattacharyya, B. D. Ellis, J. C. Gordon, P. P. Power, *Chem. Commun.* **2010**, *46*, 148–149.

[5] A. P. M. Robertson, G. R. Whittell, A. Staubitz, K. Lee, A. J. Lough, I. Manners, *Eur. J. Inorg. Chem.* **2011**, 5279–5287.

[6] a) T. J. Carter, J. W. Kampf, N. K. Szymczak, *Angew. Chem. Int. Ed.* **2012**, *51*, 13168 –13172. b) T. J. Carter, J. Y. Wang, N. K. Szymczak, *Organometallics* **2014**, *33*, 1540−1543. c) T. J. Carter, Z. M. Heiden, N. K. Szymczak, *Chem. Sci.* **2015**, *6*, 7258–7266.

[7] A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner III, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson, M. Vasiliu, *Science* **2011**, *331*, 1426-1429.

[8] a) P. M. Zimmerman, A. Paul, Z. Zhang, C. B. Musgrave, *Inorg. Chem.* **2009**, *48*, 1069−1081. b) A. P. M. Robertson, E. M. Leitao, I. Manners, *J. Am. Chem. Soc.* **2011**, *133*, 19322−19325. c) E. M. Leitao, E. N. Stubbs, A. Robertson, H. Helten, R. J. Cox, G. C. Lloyd-Jones, I. Manners, *J. Am. Chem. Soc.* **2012**, *134*, 16805−16816. d) L. Roy, S. Mittal, A. Paul, *Angew. Chem. Int. Ed.* **2012**, *51*, 4152−4156.

[9] S. Bhunya, P. M. Zimmerman, A. Paul, *ACS Catal.* **2015**, *5*, 3478−3493.

[10] B. L. Davis, B. D. Rekken, R. Michalczyk, E. B. Garner III, D. A. Dixon, H. Kalviri, R. T. Baker, D. L. Thorne, *Chem. Commun.* **2013**, *49*, 9095—9097.

[11] T. Malakar, L. Roy, A. Paul, *Chem. Eur. J.* **2013**, *19*, 5812–5817.

[12] a) S. Hünig, H. R. Müller, W. Thier, *Angew. Chem. Int. Ed.* **1965**, *4*, 271–280. b) D. J. Pasto, R. T. Taylor, *Org. React.***1991**, *40*, 91-155. c) M. P. Feth, K. Rossen, A. Burgard, *Org. Process Res. Dev.* **2013**, *17*, 282–293.

[13] A. Banerjee, G. Ganguly, L. Roy, S. Pathak, A. Paul, *Chem. Eur. J.* **2016**, *22*, 1216 – 1222.

[14] B. Pieber, T. S. Martinez, D. Cantillo, C. O. Kappe, Angew. Chem. Int. Ed. 2013, 52, 10241–10244.

[15] Gaussian 09, Revision A.02, Gaussian, Inc., Wallingford CT, **2009**. See supporting information for full citation.

[16] Y. Zhao, N. E. Schultz, D. G. Truhlar, *J. Chem. Theory Comput.* **2006**, *2*, 364-382.

[17] a) P. M. Zimmerman, *J. Chem. Phys.* **2013**, *138*, 184102. b) P. M. Zimmerman, *J. Chem. Theory Comput.* **2013**, *9*, 3043-3050. c) P. M. Zimmerman, *J. Comput. Chem.* **2015**, *36*, 601-611.

[18] a) V. Barone, M. Cossi, *J. Phys. Chem. A* **1998**, *102*, 1995-2001. b) M. Cossi, N. Rega, G. Scalmani, V. Barone, *J. Comp. Chem.* **2003**, *24*, 669-81.

[19] a) D. H. Wertz, J. *Am. Chem. Soc.* **1980**, *102*, 5316−5322. b) C. Spickermann, in Entropies of Condensed Phases and Complex Systems; Springer, Berlin, **2010**; Springer Theses, pp 76−80, and references therein. c) R. E. Plata, D. A. Singleton, *J. Am. Chem. Soc.* **2015**, *137*, 3811−3826.

[20] a) G. E. Scuseria, H. F. Schaefer III, *J. Chem. Phys.* **1989**, 90, 3700-3703. b) G. E. Scuseria, C. L. Janssen, H. F. Schaefer III, *J. Chem. Phys.* **1988**, 89, 7382-7387. c) G. D. Purvis III, R. J. Bartlett, *J. Chem. Phys.* **1982**, 76, 1910-1918.

[21] a) D. G. Liakos, Y. Guo, F. Neese, *J. Phys. Chem. A* **2020**, *124*, 90−100 b) J. Calbo, J. C. Sancho-García, E. Ortí, J. Aragó, *J. Comput. Chem.* **2017**, *38*, 1869–1878.

Entry for the Table of Contents

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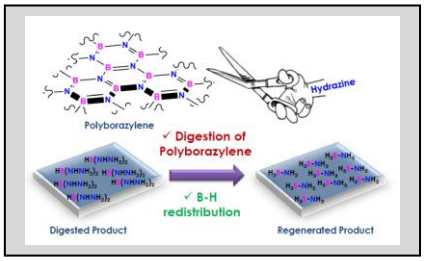

This work charts out the detailed mechanism of reduction of polyborazylene by hydrazine. Hydrazine initially helps to cleave the network of B-N bonds by acting as a Lewis base and proton shuttle. Later B-H redistribution between the B-H units formed after digestion of polyborazylene and further hydrogenation facilitated by diazene plays a vital role in regeneration of Ammonia-borane (H_3B-NH_3).