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Oligomerization and Autocatalysis of NH_2BH_2 with Ammonia−Borane

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The reactivity of NH_2BH_2 in the presence of ammonia−borane (**AB**) is investigated using ab initio CCSD(T) simulations to answer the following three questions: How do **AB** and NH_2BH_2 react? How do aminoborane species oligomerize apart from catalytic centers? Can the formation of experimentally observed products, especially cyclic $N_2B_2H_7$−NH_2BH_3, be explained through the kinetics of NH_2BH_2 oligomerization in the presence of **AB**? **AB** is shown to react with NH_2BH_2 by the addition of NH_3−BH_3 across the N═B double bond, generating linear $NH_3BH_2NH_2BH_3$. This species decomposes by surmounting a reasonable barrier to produce two NH_2BH_2 and H_2. The generation of additional NH_2BH_2 from NH_2BH_2 and **AB** provides a pathway for autocatalytic NH_2BH_2 production. The important intermediates along the oligomerization pathway include cyclic $(NH_2BH_2)_2$ and linear $NH_3BH_2NH_2BH_3$, both of which have been observed experimentally. Calculations show cyclic $N_2B_2H_7$−NH_2BH_3, an aminoborane analogue of ethylcyclobutane, to be the kinetically preferred stable intermediate resulting from oligomerization of free NH_2BH_2 over its isomers, cyclic $B_2N_2H_7$−BH_2NH_3 and cyclotriborazane, cyclic $(NH_2BH_2)_3$. Simulations show cyclotriborazane formation to be kinetically slower than cyclic $B_2N_2H_7$−NH_2BH_3 formation and imply that formation of the cyclic species cyclotriborazane and cyclopentaborazane may be catalyzed by binding of NH_2BH_2 to a catalytic metal center. Routes that may lead to larger noncyclic oligomers are suggested to be kinetically competitive. The highly reactive N═B double bonds of NH_2BH_2 are shown to be of central importance in understanding aminoborane oligomerization.

Introduction

The broad interest in using ammonia−borane (**AB**) for chemical storage of H_2 is demonstrated in the wide variety of techniques investigated for releasing H_2 from **AB**.[1] Besides thermolysis of **AB** in solid form or dissolved in solvent, acid catalysis and homogeneous catalysis have been attempted.[2,3] One key to utilizing **AB** as a H_2 storage medium is releasing as much of its 19.6 wt % of H_2 as possible, requiring that more than 1 equiv of H_2 be released from NH_3BH_3 to attain this goal. After release of the first 1 equiv of H_2 from **AB**, the resultant species generally have the empirical formula $(NH_2BH_2)_x$. While many species of this type have been proposed or observed, an understanding of their formation is key to completely explaining how **AB** can release multiple equivalents of H_2. Furthermore, an understanding of the transformation of the aminoborane species can aid in optimization for the release of multiple equivalents of H_2, for example, by avoiding species such as insoluble cyclopentaborazane, cyclic $(NH_2BH_2)_5$, which does not release H_2 through homogeneous catalysis.

The simplest product of a single H_2 removal from **AB** by homogeneous metal catalysts is NH_2BH_2. This species, however, is certainly short-lived and has only been isolated at low temperature.[3,4] The high reactivity of NH_2BH_2 can explain why many different products can be formed upon generation of NH_2BH_2. Numerous experiments have produced products resembling NH_2BH_2 oligomers, including cyclic dimers, trimers, pentamers, and other intermediates with the empirical formula $(NH_2BH_2)_x$. The questions then arise as to whether these intermediates are the result of

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NH_2BH_2 reacting with another NH_2BH_2 or with **AB** and whether they occur at catalytic metal centers or as free species in solution.

We have recently investigated **AB** dehydrogenation at nickel N-heterocyclic carbene catalysts and iridium pincer catalysts.[5,6] Our studies suggest that the dominant product of these catalytic dehydrogenations is NH_2BH_2. An open question regards whether NH_2BH_2 oligomerizes to cyclic species at the catalyst or as a free species in the solvent. Here, a knowledge of the reactivity of free **AB** and NH_2BH_2 in solvent can shed light on this process. In addition, the identity of the resultant oligomeric species determines whether the catalyst can release the second 1 equiv of H_2. While nickel N-heterocyclic carbene catalysts have been shown to release more than 2 equiv of H_2, [7] iridium pincer catalysts only release 1 equiv and form the insoluble cyclic pentamer $(NH_2BH_2)_5$. [8] Because the difference between these catalysts may lie in the location of oligomerization, this study examines the reactivity of unbound NH_2BH_2 to determine which oligomerizations can occur free of the catalyst. Our results show intermediates that are kinetically favorable and do not require a metal center for their oligomerization.

Dixon et al. investigated the reactivity of **AB** dimers using high-level CCSD(T) simulations to show that the ion-pair isomer, diammoniate of diborane (DADB), can explain the dehydrogenation of **AB** instead of direct **AB**−**AB** release of H_2.[9] Notable is that they found that the species formed from dehydrogenation of this $(\mathbf{AB})_2$ isomer is $NH_3BH_2NH_2BH_3$ (**sp3dimer**). We show below that **sp3dimer** can release two NH_2BH_2 and H_2, providing a source of NH_2BH_2 through uncatalyzed **AB** dehydrogenation. Additional pathways for NH_2BH_2 production have been described via assistance of BH_3.[10] The presence of BH_3 lowers the barrier for **AB** dehydrogenation and allows catalytic formation of NH_2BH_2 from **AB**.

Nutt and McKee have used density functional theory to study the reactivity of diborane and ammonia in pathways leading to borazine formation. [11] In Nutt and McKee's study, the reactivity of **AB** with NH_2BH_2 or resultant oligomers is not considered. Instead, most of their reactions consider NH_3, BH_3, and NH_2BH_2 to be present in the reaction media but without **AB**. This current study considers how **AB** reacts with NH_2BH_2 and resultant oligomers, which are mechanisms that are relevant for catalyzed and uncatalyzed **AB** dehydrogenation chemistry.

In this paper, we present the results of an ab initio study of the kinetics and thermodynamics of NH_2BH_2 reacting in the presence of **AB** based on energies obtained with the CCSD(T) couple-cluster method. Our focus is on the following three questions: How do **AB** and NH_2BH_2 react? How do aminoborane species oligomerize apart from catalytic centers? Can the formation of experimentally observed products, especially cyclic $N_2B_2H_7{-}NH_2BH_3$ (**ECB**), be explained through the kinetics of NH_2BH_2 oligomerization in the presence of **AB**? We limit the scope of this contribution to oligomers with at most three units of NH_2BH_2 because the initial products of **AB** dehydrogenation will be smaller oligomeric species. Furthermore, species with two or three units of NH_2BH_2 are often observed in experiment.[3,4,12−17] We do not consider ion-pair species because of their higher energy, where the lower-energy ion-pair isomer DADB is 10.6 kcal/mol higher in energy than the **AB** dimer and its formation proceeds over a 42 kcal/mol barrier. [9] All favored pathways presented herein have barriers considerably lower than 42 kcal/mol, implying an acceleration in **AB** dehydrogenation after NH_2BH_2 formation. The detailed mechanism determined by this study describes how **AB** and NH_2BH_2 react and suggests a straightforward pathway to the formation of an observed intermediate, cyclic $(B_2N_2H_7){-}NH_2BH_3$, an aminoborane analogue of ethylcyclobutane. This species has been identified by NMR and is an important intermediate in the conversion of **AB** to cyclotriborazane (**CTB**) and borazine[17] (see the Discussion section). We show that NH_2BH_2 and **AB** can react in the absence of catalytic centers to form **ECB** preferentially over its isomer cyclic $N_2B_2H_7{-}BH_2NH_3$ (**ECB2**) and **CTB**. Simulations showing that cyclic aminoborane species (larger than the cyclic dimer) form relatively slowly by the reaction of unbound **AB** and NH_2BH_2 suggest that cyclic aminoborane species are therefore more likely to form either while bound to a catalytic metal center or by slow isomerization of **ECB**.

In addition to showing that **ECB** formation is competitive, we also show that formation of the cyclic dimer, $(NH_2BH_2)_2$ (**cdimer**), and **sp3dimer** are kinetically and thermodynamically accessible. Because these species both react to form NH_2BH_2, they are key intermediates in the pathway from **AB** and NH_2BH_2 to larger oligomers. In addition to these two intermediates, $NH_2BHNH_2BH_3$ (**bh3int**) provides an avenue for further oligomerization. **bh3int** is short-lived because it reacts rapidly with both **AB** and NH_2BH_2 and is therefore unlikely to be identified in experiment. Another prominent feature of this chemistry is the autocatalysis of NH_2BH_2, which reacts in two steps with **AB** to release H_2 and generate additional NH_2BH_2 for oligomerization.

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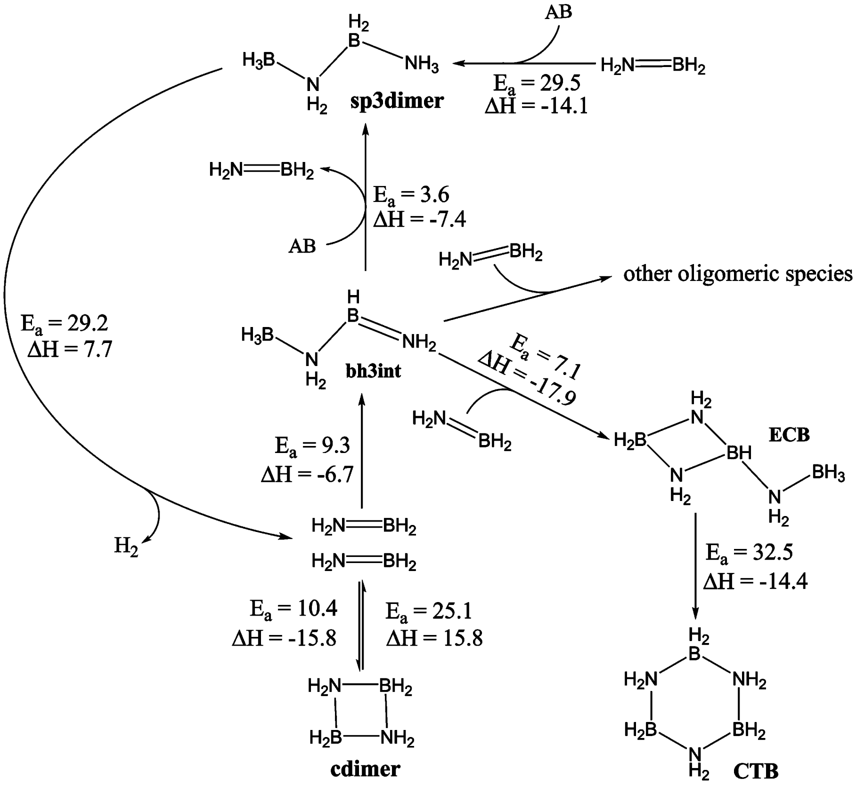
Scheme 1. Overall Scheme for the Reaction of NH_2BH_2 with **AB**[a]



[a] The reaction cycle may begin with NH_2BH_2 formed by dehydrogenation of **AB** by catalyst or assistance of BH_3, or by generation of **sp3dimer** by DADB transformation.

Computational Details

All geometries are optimized at the MP2 level of theory[18] with the correlation-consistent triple-ζ plus polarization basis set cc-pVTZ.[19] Frequency calculations are performed at the same level of theory for all stationary points, with zero imaginary frequencies at all intermediate structures and one imaginary frequency representing a saddle point for transition states. Single-point energies are then calculated using the robust coupled-cluster singles and doubles plus perturbative triples CCSD(T) method[20] with the cc-pVTZ basis set at the MP2 geometries. Furthermore, CCSD(T)//MP2 cc-pVTZ geometries and energies were compared to aug-cc-pVTZ[19] MP2 geometries and CCSD(T) energies to gauge whether diffuse functions are important. The MP2 geometries calculated using these two basis sets were very similar to each other, with bond distances and angles differing by less than 0.01 Å and 1.0°, respectively. Furthermore, the CCSD(T)//MP2 relative energies calculated using these two basis sets differed by less than 0.5 kcal/mol, showing that augmentation with diffuse functions is unnecessary to obtain accuracies of ~1 kcal/mol in this particular study. The core orbitals are frozen in all MP2 and CCSD(T) calculations. All energies reported herein are CCSD(T)/cc-pVTZ single-point energies calculated at MP2/cc-pVTZ geometries. Energies are zero-point-corrected using the MP2 zero-point energy. All calculations are performed using *Gaussian03*[21] and *NWCHEM*.[22]

Transition-state structures are verified to ensure that they connect their respective reactants and products using intrinsic reaction coordinate (IRC) calculations performed at the B3LYP/6-31G** level of theory.[23] We observed no qualitative differences between the MP2 structures at which the CCSD(T) energies were calculated and the B3LYP structures used for the IRC analysis. Gibbs free energies calculated at 25 °C are presented in the Supporting Information along with transition-state theory rate constants and Wigner tunneling corrections to these rate constants.[24]

Results

Thermodynamics of NH_2BH_2 Oligomerization. The active pathways that define the reactivity of **AB** with NH_2BH_2 are shown in Scheme 1. This scheme will be discussed in detail at the end of this Article. Before proceeding into a detailed discussion of each pathway connecting the intermediates of Scheme 1, we discuss the relative energies of the intermediates from a thermodynamic

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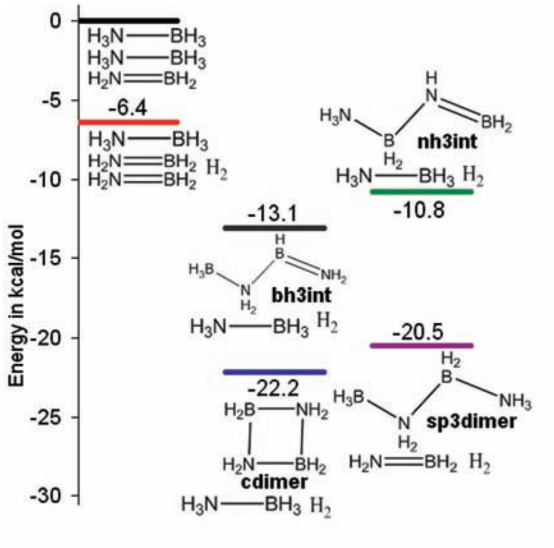

Figure 1. Thermodynamics of 2**AB** + NH_2BH_2 (0 K enthalpies in kcal/mol).

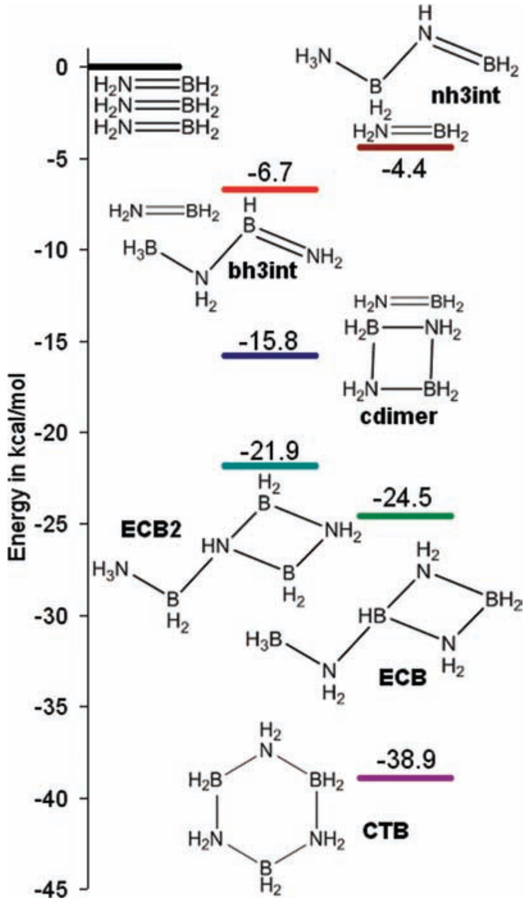

Figure 2. Thermodynamics of $3NH_2BH_2$ (0 K enthalpies in kcal/mol).

standpoint. Although many species aminoborane oligomers can be imagined, Figures 1 (with $x = 1$ or 2) and 2 (with $x = 1-3$) include the possible relevant species of this study. Figure 1 shows the thermodynamics of two **AB** reacting with one NH_2BH_2, and Figure 2 illustrates the thermodynamics of reactions of three NH_2BH_2. All represented reactions are clearly exothermic; although in certain cases the energetic difference between two isomers is small, all relative energies are easily within the resolution of CCSD(T)//MP2 (~1 kcal/mol). Consequently, the relative amounts of each intermediate are governed by kinetic considerations. In addition, we note that evolution of H_2 will cause certain reactions to be irreversible; once H_2 gas effuses from the system, the reaction cannot be reversed without adding H_2 to the system.

Generally, the energies of the intermediates can be gauged using only a few criteria. First, the removal of H_2 from **AB** to yield NH_2BH_2 is exothermic by 6.4 kcal/mol. Second, saturation of N=B double bonds in oligomeric species is favorable and can proceed through the addition of H_2 from **AB**, reaction involving hydrogen transfer from another NH_2BH_2 or the formation of a four-membered ring with NH_2BH_2. These considerations make the reactions that release H_2 from **AB** and oligomerize N=B double bonds exothermic. Regarding kinetic stability, NH_2BH_2 is very unlike ethylene because the π bond of NH_2BH_2 is polar and easily polarized to having a lone pair localized on N and an empty B orbital. [25] The polarities accessible to NH_2BH_2 create a marked contrast between the kinetic stability of carbon double bonds and the inherent reactive nature of N=B double bonds. For example, **AB** can transfer two H atoms to NH_2BH_2 through an identity reaction with a barrier of only 8.6 kcal/mol, while the analogous reaction between ethane and ethylene has a barrier of 48.1 kcal/mol.

Certain species shown in Figures 1 and 2 that have not been identified experimentally may be inferred to be short-lived intermediates. While NH_2BH_2 is only isolable at very low temperatures,[3,4] it has been proposed as a product of **AB** dehydrogenation through analogous dehydrogenation chemistry of Me_2NHBH_3.[16,26] Likewise, **cdimer** also has been suggested by analogy to dimers in Me_2NHBH_3 studies as well as being identified by NMR in **AB** thermolysis in both solvent[12] and the solid state.[13] Furthermore, observation of **cdimer** also provides evidence for the presence of NH_2BH_2 because it is the product of NH_2BH_2 dimerization. We are not aware of any experimental identification of **bh3int** but predict that it is thermodynamically unstable with respect to the formation of **cdimer** or **ECB** and reacts rapidly in the presence of **AB** or NH_2BH_2 (vide infra). In addition, **bh3int** is mechanistically reasonable because it is the hydroboration product of NH_2BH_2 + NH_2BH_2. Although hydroboration typically means the addition of B−H bonds to unsaturated organics, we use the term hydroboration for the addition of B−H bonds to unsaturated B−N bonds. **sp3dimer** has been identified in the solid-state decomposition of **AB**,[13] and we predict here that **sp3dimer** is a very relevant species. We show below that the formation of $BH_2NHBH_2NH_3$ (**nh3int**) and **ECB2** is kinetically unlikely even though they are thermodynamically favorable. We are unaware of any experimental identification of **nh3int** and **ECB2**. Finally, both **CTB**[4,12] and **ECB**[17] have been identified experimentally. Because **CTB** is significantly more thermodynamically stable than its isomer **ECB**, **CTB** likely does not transform into **ECB**. The reverse reaction of **ECB**

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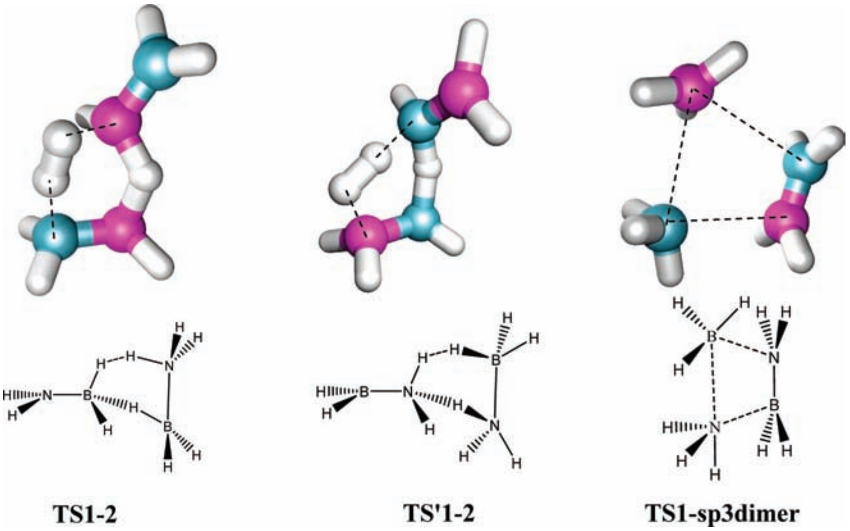

Figure 3. Transition states for reactions between **AB** and NH_2BH_2. From left to right: release of H_2, **TS1-2**; second release of H_2, **TS′1-2**; addition of NH_3BH_3 across the NH_2BH_2 double bond, **TS1-sp3dimer**. Blue, magenta, and white represent N, B, and H, respectively.

to **CTB**, however, is energetically reasonable because of its exothermicity. We note here that our thermodynamics are in agreement with values reported by Dixon et al.[27] In comparison to complete basis extrapolation CCSD(T) 0 K enthalpies, our reported thermodynamics for **AB** → NH_2BH_2 + H_2, 2**AB** → **cdimer** + $2H_2$, 2**AB** → **sp3dimer** + H_2, and 3**AB** → **CTB** + $3H_2$ differ by 0.4, −0.4, 0.5, and −0.1 kcal/mol, respectively, from Dixon et al.[27]

Reactivity of One NH_2BH_2 and One AB. When H_2 is formed from **AB** and NH_2BH_2, at least two bonds must be broken. The energetic difficulty lies in the breakage of an N−H or B−H bond of the sp^2-hybridized N or B of NH_2BH_2. We have identified three mechanisms through which this can proceed. Prior to reaction, **AB** favorably forms a hydrogen-bonded adduct (**1**) with NH_2BH_2, which is 5.4 kcal/mol lower in energy than the separated species. The first mechanism proceeds from **1** by protonation of an NH_2BH_2 borohydride along with replacement of that hydride with an **AB** hydride (**TS1-2**), as shown in Figure 3. This represents a concerted reaction where **AB** loses two H atoms to form H_2 and NH_2BH_2. One alternative mechanism is entirely analogous, except that the N−H hydrogen on NH_2BH_2 activates instead of the B−H hydrogen (**TS′1-2**), as shown in Figure 3. Similar to the first case, **AB** replaces the N−H hydrogen with a proton from its NH_3 acidic end. In both of these two cases, NH_2BH_2 is catalytic in dehydrogenating **AB** and no oligomeric species are formed directly from the reaction. Thus, the products of both **TS1-2** and **TS′1-2** are H_2 and two NH_2BH_2. The barriers relative to the hydrogen-bonded adduct, **1**, for **TS1-2** and **TS′1-2** are 34.9 and 39.9 kcal/mol, respectively.

In contrast to reaction through **TS1-2** or **TS′1-2**, **AB** can attack NH_2BH_2 in a fashion that leads to the oligomeric species. One reaction (via **TS1-bh3int**, shown in the Supporting Information) proceeds through protonation of an NH_2BH_2 borohydride, forming H_2 but without **AB** transferring a hydride to $BHNH_2$ as occurs in **TS1-2**. Instead, the N from **AB** associates its now-free N lone pair to the B of $BHNH_2$, and the reaction produces **bh3int**. This mechanism, however, involves a considerably high barrier of 50.4 kcal/mol above **AB**−NH_2BH_2 adduct **1**. Because the N−B bond in **AB** is weaker than the N−H and B−H bonds of **AB**, we also investigated the possibility of **AB** adding across the N═B double bond of NH_2BH_2 (**TS1-sp3dimer**). In this transition state, shown in Figure 3, the N−B bond of **AB** breaks, while the resulting NH_3 and BH_3 fragments attach to the B and N of NH_2BH_2, respectively. This reaction forms linear **sp3dimer** as the product and has a barrier of 29.5 kcal/mol above **1**. Because **TS1-sp3dimer** has a lower barrier than the other reactions of **AB** and NH_2BH_2, we predict that the reaction of **AB** with NH_2BH_2 will favorably generate the oligomeric **sp3dimer**. Figure 4 illustrates the schematic potential energy diagram for three reactions between NH_2BH_2 and **AB** showing **sp3dimer** formation to have the lowest barrier.

The relatively low barrier for the reaction of **AB** with NH_2BH_2 via **TS1-sp3dimer** is not completely unexpected because the N−B bond strength in **AB** is calculated to be only 27.2 kcal/mol at 0 K (close to the complete basis set extrapolation predicted value of 25.9 kcal/mol[28]). Here, opening of the N−B bond of **AB** and its addition across the N═B double bond of NH_2BH_2 can be described as NH_3 lone-pair transfer out of the BH_3 p orbital of **AB** into the NH_2BH_2 B p orbital. As the lone pair fills the B orbital of NH_2BH_2, the π bond of NH_2BH_2 breaks and two electrons are localized on the N of NH_2BH_2. This lone pair on the N can then transfer into the p orbital of BH_3, which is empty because NH_3 was donating its lone pair into NH_2BH_2. This orbital transformation is clearly seen in Figure 5, where the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of the transition state **TS1-sp3dimer** are visualized. The transition state is made accessible not only by the low-energy dissociation energy

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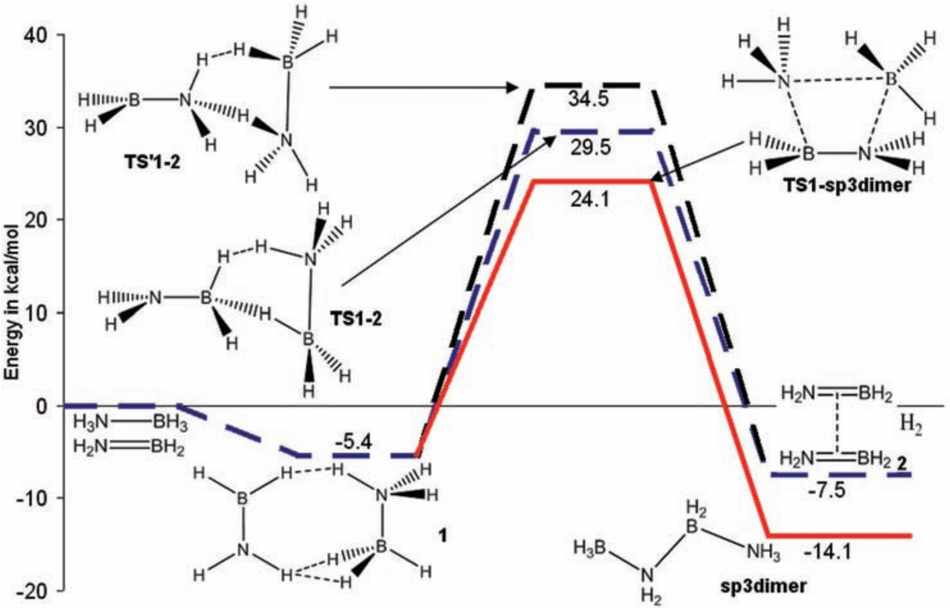

Figure 4. Reaction of **AB** with NH_2BH_2. The lowest barrier reaction proceeds through **TS1-sp3dimer**, which results in **sp3dimer** oligomer formation.

Figure 5. HOMO (left) and LUMO (right) for **TS1-sp3dimer**, showing the polarization of the π orbital of NH_2BH_2 onto the N and the empty p orbital of BH_3 ready to accept this pair of electrons.

of the N−B bond of **AB** but also by the polarization of the N=B π bond of NH_2BH_2.

Reactivity of One AB and Two NH_2BH_2. Because of the reactive nature of NH_2BH_2's double bond, the reaction of $NH_2BH_2 + NH_2BH_2$ proceeds faster than the reaction of **AB** with NH_2BH_2. The combination of two NH_2BH_2 and one **AB** can exhibit rapid formation of oligomeric species after **AB** dehydrogenation. The second NH_2BH_2 could be formed in experiment by decomposition of **sp3dimer** (vide infra), by **AB** dehydrogenation by BH_3,[10] or by dehydrogenation of **AB** by a catalyst metal center. At early reaction times, **AB** will greatly outnumber NH_2BH_2 and so the reaction of any intermediates of NH_2BH_2 oligomerization more likely occurs with **AB** than with a third NH_2BH_2. The energetic profile detailing the reactivity of two NH_2BH_2 and one **AB** is shown in Figure 6.

Prior to reaction, two NH_2BH_2 can associate by a weak $\pi-\pi$ interaction favorable by only 1.1 kcal/mol (**2**), which is unfavorable when free energy is included quantitatively (see the Supporting Information). Three possible reactions that can occur between two NH_2BH_2 include dimerization, hydroboration, and hydrogen transfer from one NH_2BH_2's N to the N on the second NH_2BH_2. Dimerization of N=B double bonds has been directly observed with methylated **AB** analogues.[16,26,29] The barrier for dimerization of NH_2BH_2 via NH_2BH_2 (**TS2-cdimer**) lies 10.4 kcal/mol above **2** and produces **cdimer**. Alternatively, the barrier for hydroboration via **TS2-bh3int** involves a similar barrier of 9.3 kcal/mol and generates **bh3int**. The hydrogen transfer from N to N (**TS2-nh3int**) yields **nh3int** and has a barrier of 27.7 kcal/mol above **2**, making it uncompetitive with the reaction through **TS2-cdimer** or **TS2-bh3int**. Because this reaction, which yields an NH_3 moiety from two NH_2BH_2, is kinetically prohibitive, species such as **ECB2** are less likely to form.

Because **cdimer** and **bh3int** are formed with very similar barriers, their generation from two NH_2BH_2 is roughly competitive. We thus investigate the reactivities of both **cdimer** and **bh3int** to further elucidate the most active pathways. Transformation of **cdimer**. which is the more thermodynamically stable of the two, via backreaction of the dimer to two **TS2-cdimer** followed by **TS2-bh3int** to yield **bh3int** involves a barrier of 25.1 kcal/mol above **cdimer**, so **cdimer** is able to transform into **bh3int**.

After the creation of **cdimer**, **AB** might react to form NH_2BH_2 and H_2 while reforming **cdimer** via **TS3-cdimer**. This reaction (shown in the Supporting Information because of its high barrier) is similar to **AB** attack of the B end of NH_2BH_2 that passes through **TS1-2**, where the hydride is protonated concomitantly with replacement of the protonated boron hydride with an **AB** hydride. The **TS3-cdimer** transition state therefore involves protonation of a **cdimer** hydride and **AB** replacement of the protonated hydride in **cdimer** with one of its own. Although **TS1-2** was the lowest barrier dehydrogenation of **AB** at NH_2BH_2, **TS3-cdimer** has a very high barrier, lying 57.8 kcal/mol above the lowest-energy hydrogen-bonded adduct (**3**) of **cdimer** and **AB**. This high barrier suggests that **cdimer** is a moderately stable species that can transform to **bh3int** but does not react with **AB**. Because **TS1-bh3int** has a significantly higher barrier

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(29) Gilbert, T. M. *Organometallics* **1998**, *17*, 5513–5520.

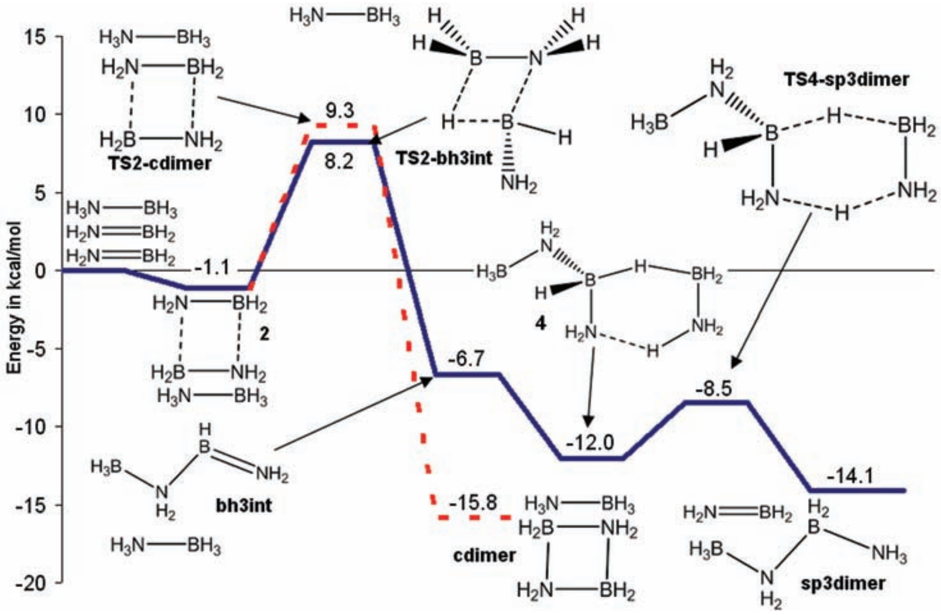


Figure 6. Energetic profile for the reaction of two NH_2BH_2 and **AB**, leading to the stable intermediates **cdimer** and **sp3dimer** through dimerization and hydroboration, respectively. Note that **TS2-nh3int**, which breaks an N−H bond of NH_2BH_2, is not shown because it has a barrier of 27.7 kcal/mol.

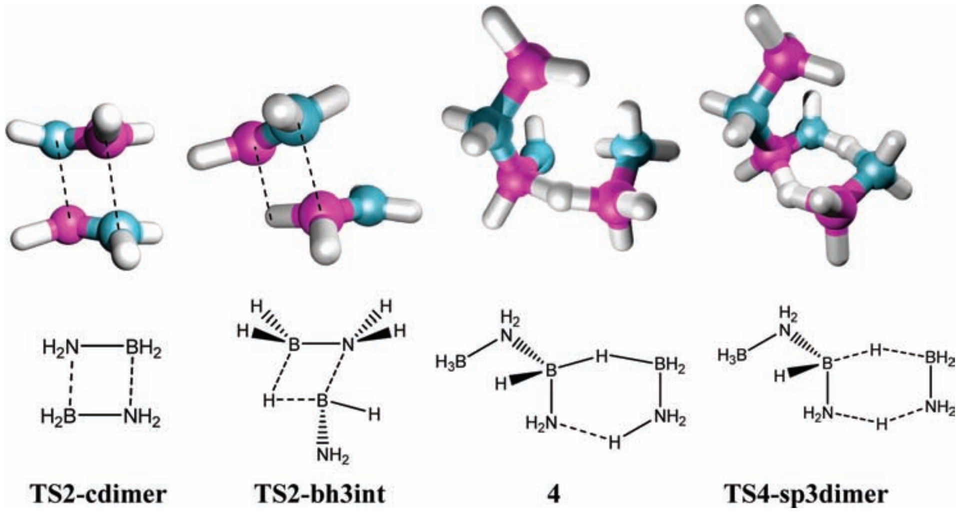


Figure 7. Transition states for reactions involving two NH_2BH_2 and **AB** that lead to **sp3dimer**. From left to right: NH_2BH_2 dimerization, **TS2-cdimer**; hydroboration, **TS2-bh3int**; **AB-bh3int** adduct **4**; **AB** addition of H to **bh3int** via **TS4-sp3dimer**.

than **TS1−2**, the reaction analogous to **TS1-bh3int** at **cdimer** to form **ECB** is not feasible. The stability of **cdimer** is not very surprising because the sp^3-attached H in **AB** has only been shown to react with other sp^3-attached H with barriers greater than 44 kcal/mol. [9]

The N═B double bond of **bh3int** makes it much more reactive than the relatively stable **cdimer**. Just as NH_2BH_2 is very reactive because of its double bond, hydroboration, cycloaddition, and hydrogenation by **AB** should also occur with **bh3int**. We will describe the reactivity of **bh3int** with NH_2BH_2 below but first address the reaction of **bh3int** with **AB** or by itself. Similarly to how **AB** can undergo a low barrier identity reaction with NH_2BH_2 that transfers two H atoms from **AB** to the double bond of NH_2BH_2, the double bond of **bh3int** can receive two H atoms from **AB** with a small barrier. First, **AB** associates two H atoms to the N═B double bond of **bh3int** to form **4**, as shown in Figure 7, which is favorable by 5.4 kcal/mol. The transition state between **4** and **sp3dimer** + NH_2BH_2 (**TS4-sp3dimer**) lies 3.6 kcal/mol above **4**. This reaction is exothermic by 7.4 kcal/mol with respect to separated **bh3int** and **AB** and is 2.1 kcal/mol below that of **4**. In addition to hydrogenation by **AB**, **bh3int** can release H_2 intramolecularly with a barrier of 29.6 kcal/mol to yield the aminoborane analogue of butadiene. Although a significant amount of this product might be generated in isolation, the presence of **AB** will far outcompete the formation of the butadiene analogue. In the presence of **AB**, **bh3int** will be immediately trapped by **TS4-sp3dimer** to form **sp3dimer**. Further, **TS4-sp3dimer** generates an additional NH_2BH_2, which propagates the oligomerization process. A full energetic profile for the pathway from two NH_2BH_2 and **AB** to **sp3dimer** and NH_2BH_2 is shown in Figure 6.

The pathway illustrated in Figure 6 shows that, with the participation of **AB**, two NH_2BH_2 react to form either the intermediate **cdimer** or **sp3dimer**. Although the intermedi-

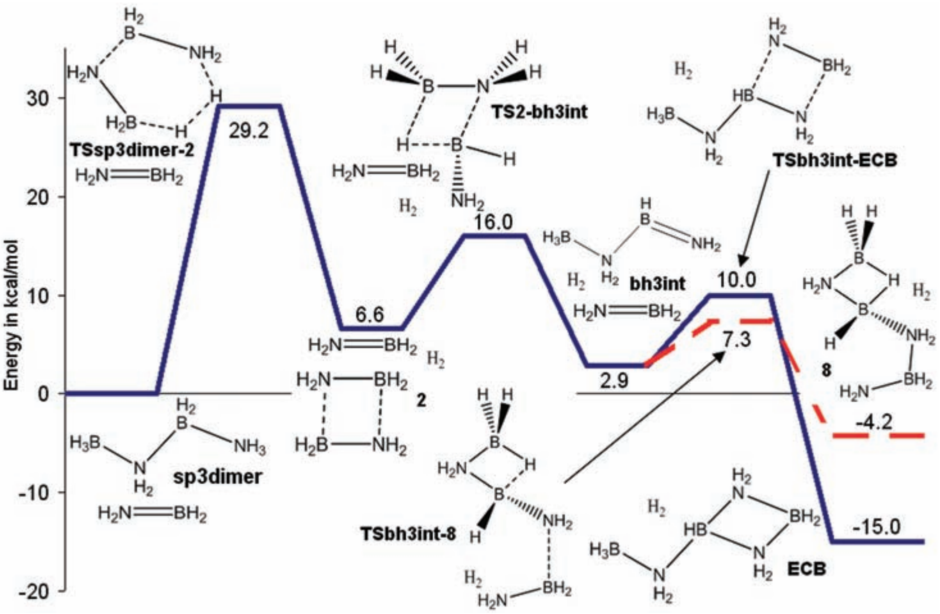


Figure 8. Energetic profile for transformation of **sp3dimer** and NH_2BH_2 to **ECB**. Release of H_2 via **TSsp3dimer-2** makes the first step of this pathway essentially irreversible and makes the formation of **ECB** even more favorable from a free-energy standpoint.

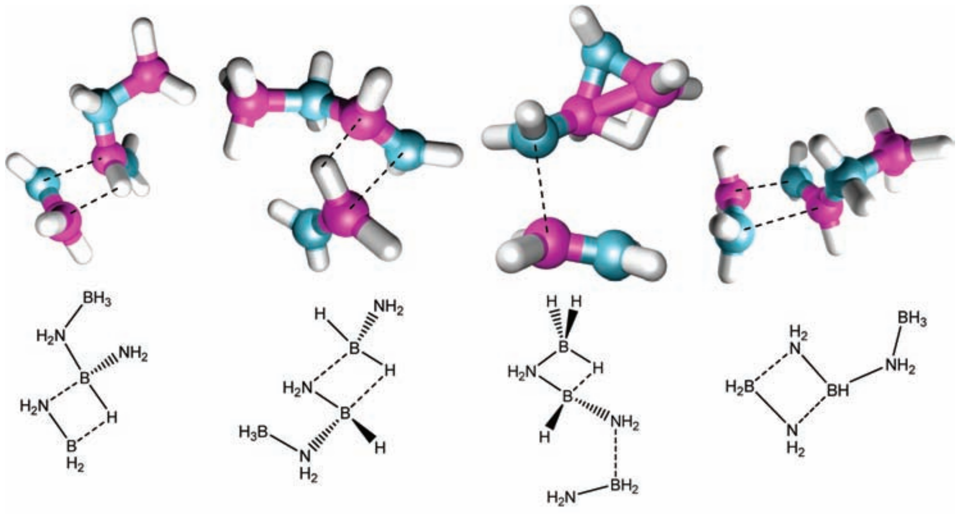
ates **cdimer** + **AB** and **sp3dimer** + NH_2BH_2 are close in energy, depletion of **sp3dimer** by the reaction described below (**TSsp3dimer-2**) allows the equilibrium to shift to produce more **sp3dimer**.

Reactivity of sp3dimer. The favored product of the reaction of **bh3int** and **AB** or of NH_2BH_2 and **AB**, **sp3dimer**, is also the product described by Dixon et al. resulting from activation of **AB** through DADB.[9] This linear dimer of **AB** can therefore be generated through multiple pathways and thus represents an important species in the pathway to further oligomerization of aminoborane. Two reasonable routes leading to decomposition of **sp3dimer** include dehydrogenation by a catalyst and intramolecular H_2 elimination. While the former is outside the scope of this study, the reaction likely proceeds through a mechanism similar to that which we have previously described for **AB**[5,6] because **sp3dimer** contains sp^3 N−H and B−H hydrogens that likely react similarly to **AB**. These catalytic reactions will yield either **bh3int** and H_2 or two NH_2BH_2 and H_2. In either case, the reaction will proceed to dehydrogenate additional **AB** or produce oligomers. On the other hand, intramolecular H_2 elimination (**TSsp3dimer-2**) can occur without a catalyst through a six-membered transition state, yielding two NH_2BH_2 and H_2. Although other eliminations of H_2 from **AB** dimers[9] or **cdimer** with **AB** had relatively high barriers, the simultaneous decomposition of **sp3dimer** into three molecules is more feasible. The energy of **TSsp3dimer-2** is 29.2 kcal/mol above its lowest energy internally hydrogen-bonded conformation. An alternative dehydrogenation, where two H atoms from adjacent N−B atoms at the BH_2NH_3 end of **sp3dimer** combine to form H_2 and **bh3int**, has a much higher barrier with a 44.9 kcal/mol transition-state energy. Similarly, elimination of H_2 from the NH_2BH_3 end of **sp3dimer** proceeds at a barrier of 47.6 kcal/mol.

Figure 8 shows the lowest barrier pathway from **sp3dimer** to **bh3int** and H_2. In this pathway, the forward reaction over **TSsp3dimer-2** is irreversible because the resultant H_2 will be released from the system. Furthermore, because **sp3dimer** is produced by the reaction of NH_2BH_2 and **AB**, reactions over the moderate barriers **TS1-sp3dimer** and **TSsp3dimer-2** together provide for the autocatalytic formation of NH_2BH_2. The reaction of **AB** with NH_2BH_2 is a feasible reaction at typical **AB** thermolysis conditions. This demonstrates how NH_2BH_2 production seeds **AB** dehydrogenation: once NH_2BH_2 is produced, **AB** dehydrogenation through NH_2BH_2 can proceed at a reasonable rate.

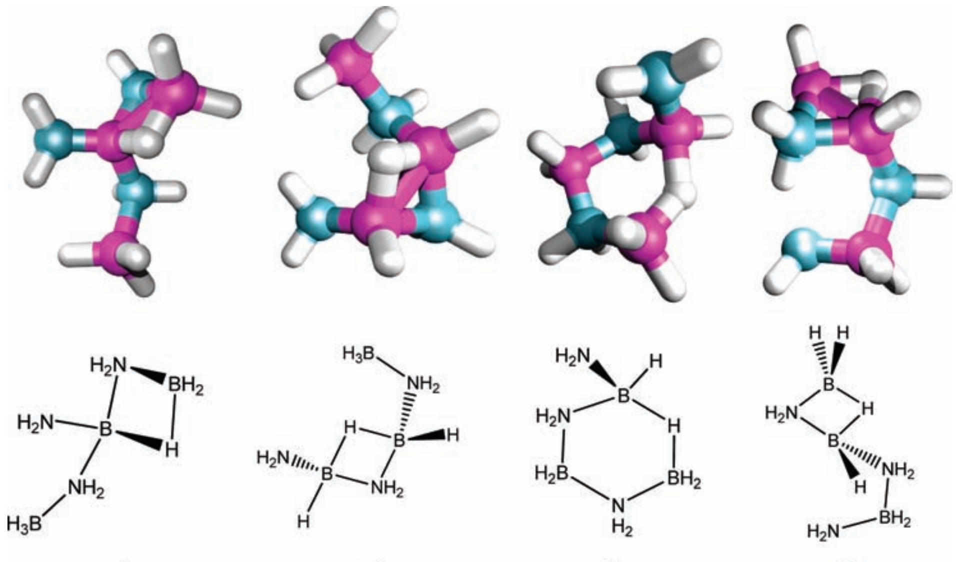
Oligomerization of Multiple NH_2BH_2. After intramolecular dehydrogenation of **sp3dimer** via **TSsp3dimer-2**, the two newly formed NH_2BH_2 molecules can react as described above. Because **cdimer** is relatively inert except in the transformation to **bh3int**, we consider here the pathways proceeding from **bh3int**. Having already addressed the reactivity of **bh3int** with **AB**, we now discuss the reactivity of **bh3int** with NH_2BH_2. Three reactions from this combination include hydroboration yielding longer-chain oligomers, dimerization to yield **ECB**, and a chain-extending reaction that could lead to longer oligomers. Amine hydrogen transfer analogous to that of **TS2-nh3int** is not considered because **TS2-nh3int** has a significantly higher barrier relative to alternative reactions of two N=B double bonds.

Hydroboration can occur at the B−H bond of **bh3int** similar to how it can occur at a B−H bond of NH_2BH_2 because both species have an N=B double bond available. These two reactions, shown in Figure 9, are of similar barrier, requiring 11.4 kcal/mol to activate the **bh3int** B−H bond (**TSbh3int-5**) and 10.1 kcal/mol to activate the NH_2BH_2 B−H bond (**TSbh3int-6**). Both products confirmed by the IRC calculation involve a bridged H between two B atoms, as shown in Figure 10. Both reactions are nearly thermoneutral because the products are −2.1 and 1.7 kcal/mol in energy compared to separated **bh3int** and NH_2BH_2 for the products of **TSbh3int-5** (**5**)



TSbh3int-5 **TSbh3int-6** **TSbh3int-8** **TSbh3int-ECB**

Figure 9. Transition states for reactions of NH_2BH_2 and **bh3int** yielding **5**, **6**, **8**, and **ECB**. From left to right: hydroboration of the B−H from **bh3int** via **TSbh3int-5**; hydroboration of the B−H bond from NH_2BH_2 via **TSbh3int-6**; attachment of B from NH_2BH_2 to the NH_2 end of **bh3int** via **TSbh3int-8**; formation of **ECB** via **TSbh3int-ECB**.



5 **6** **7** **8**

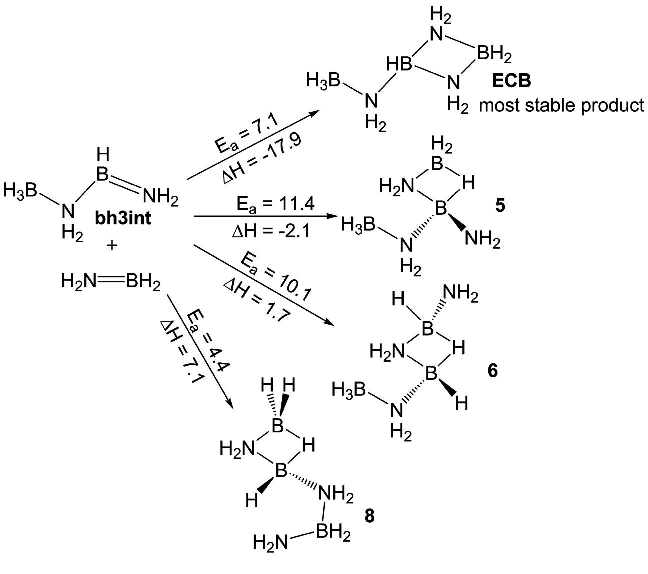
Figure 10. Intermediates involved in the reaction of **bh3int** + NH_2BH_2 and in the formation of **CTB**. From left to right: **5**, **6**, **7**, and **8**.

and **TSbh3int-6** (**6**), respectively. Isomerization of **6** to $NH_2BH_2NH_2BH_2NH_2BH_2$ with a hydride bridging the second and fifth B atoms (**7**) is shown in Figure 10. **TS6-7** has a low barrier of 1.3 kcal/mol, and intermediate **7** is 14.0 kcal/mol more stable than **6**.

Competing with hydroboration is 2 + 2 cycloaddition of NH_2BH_2 across the **bh3int** double bond. This competition is illustrated in Scheme 2. Figure 9 shows this cycloaddition reaction, which proceeds through **TSbh3int-ECB**, occurs with a barrier of only 7.1 kcal/mol, and directly produces **ECB**. **ECB** is 17.9 kcal/mol below **bh3int** and NH_2BH_2. Because the transition-state barrier for **ECB** formation is lower than the hydroboration barriers and the product is thermodynamically more stable, reaction through **TSbh3int-ECB** will be faster than hydroboration of **bh3int** with NH_2BH_2. The pathway leading through **TSbh3int-ECB** from three NH_2BH_2 is displayed in Figure 8.

In addition to hydroboration and dimerization, linear $NH_2BH_2NH_2BHNH_2BH_3$ (**8**) can be generated by the reaction of **bh3int** and NH_2BH_2 through **TSbh3int-8** with a barrier of 4.4 kcal/mol. In **TSbh3int-8**, shown in Figure 9, the B of NH_2BH_2 attaches to NH_2 of **bh3int**, causing a loss of the π bond. Because the π bond of **bh3int** is broken and a B becomes electron-deficient, a hydride from the BH_3 moiety donates into the empty p orbital of the electron-deficient B, forming the bridged hydride structure **8** shown in Figure 10. The product of this reaction (**8**) is 7.1 kcal/mol lower in energy than separated **bh3int** and NH_2BH_2. This low barrier reaction therefore competes kinetically with **TSbh3int-ECB**. **8**, however, is able to transform to **ECB**, which is thermodynamically more stable than **8** by 10.8 kcal/mol (see Figure 8). Although **ECB** is kinetically easily accessible from **8** and thermodynamically more stable than **8**, the kinetic favorability of **8** will provide an avenue for further oligomerization.

Scheme 2. Four Feasible Pathways for the Reaction of **bh3int** + NH_2BH_2[a]



[a] The reaction energetics for each path are shown in kilocalories per mole. See Figure 8 for a detailed comparison of the two more favorable reactions.

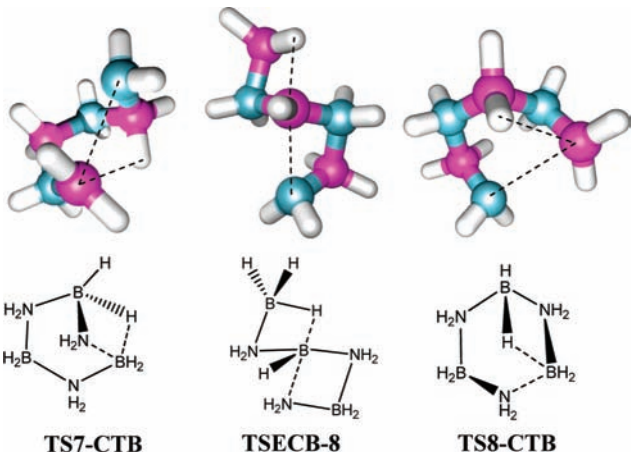


Figure 11. Transition states in pathways leading to the cyclic trimer, **CTB**. From left to right: **TS7-CTB**, **TSECB-8**, and **TS8-CTB**.

CTB Formation from ECB. While the above pathways detail the transformation of NH_2BH_2 to noncyclic products, the formation of **CTB** should also be considered. The transition states shown in Figure 11 lead to the **CTB** generation pathways shown in Figure 12: one involves hydroboration of **bh3int**, the second proceeds by the addition of NH_2BH_2 to the NH_2 end of **bh3int**, and the third is isomerization of **ECB**. Intermediate **7** is formed from **bh3int** and NH_2BH_2, and although the overall barrier from **bh3int** and NH_2BH_2 to form **7** is only 11.0 kcal/mol, the path through **TSbh3int-6** and **TS6-7** is not energetically preferred because it has a higher overall barrier than **TSbh3int-ECB** and **TSbh3int-8**. Nonetheless, **7** can transform into **CTB** (**TS7-CTB**) with a barrier of 29.0 kcal/mol above **7**. **TS7-CTB**, shown in Figure 11, involves donation of the dangling NH_2 lone pair of **7** into the empty p orbital of the B with the bridged hydride, allowing the bridged hydride to be displaced to yield **CTB**.

Conversion of **ECB** to **CTB** through the four steps with transition states **TSbh3int-ECB**, **TSbh3int-6**, **TS6-7**, and **TS7-CTB** is limited by the last step with a barrier of 34.6 kcal/mol above the entrance channel.

Alternatively, **CTB** can be formed from **8**, which has its BH_3 end group sharing a H atom with the nearby B, as shown in Figure 10. **ECB** can isomerize to **8** by coordinating its BH_3 end into the middle B of **ECB** rather than the previous NH_2 donation, which held the ring closed (**TSECB-8**). This transition state is shown in Figure 11 and lies 22.0 kcal/mol above **ECB**, with **8** being 10.8 kcal/mol higher in energy than **ECB**. Intermediate **8** can then transform to **CTB** in a single step (**TS8-CTB**) with a barrier of 32.5 kcal/mol above **ECB**. **TS8-CTB**, shown in Figure 11, is similar to **TS7-CTB** and occurs by attaching the NH_2 displaced by **TSECB-8** to the terminal B, while the B gives up its bridged hydride for the N lone pair. This step closes the ring and leaves two H atoms on each N and B. Because **8** can transform directly into **CTB**, **CTB** can also form from the reaction of **bh3int** and NH_2BH_2 without passing through **ECB**. This occurs with an overall barrier of 16.7 kcal/mol above **bh3int** and NH_2BH_2. We note that this is a significantly higher barrier than that of the formation of **ECB** from **bh3int** and NH_2BH_2. Overall, the formation of **CTB** can occur both from **ECB** and from **bh3int** and NH_2BH_2 with rate-limiting barriers of more than 32 kcal/mol when **ECB** is chosen as the reference energy because it is the most thermodynamically stable intermediate before **CTB** formation. **CTB** is thermodynamically 14.4 kcal/mol more stable than its isomer **ECB**, so the equilibrium of **CTB** to **ECB** will be strongly biased toward **CTB**.

Discussion

This study addresses three fundamental questions of particular interest: How do **AB** and NH_2BH_2 react? How do aminoborane species oligomerize apart from catalytic centers? Can the formation of experimentally observed products, especially **ECB**, be explained through the kinetics of NH_2BH_2 oligomerization in the presence of **AB**? These questions are answered by the results in Scheme 1, thermodynamic information from Figures 1 and 2, and the kinetic barriers shown in Table 1.

We answer the first question by showing that **AB** and NH_2BH_2 react to form oligomeric $NH_3BH_2NH_2BH_3$, or **sp3dimer**, directly. This reaction proceeding through **TS1-sp3dimer** has a barrier of 29.5 kcal/mol, so **AB** reacts at a reasonable rate with NH_2BH_2. It has been shown that BH_3 can catalyze **AB** dehydrogenation, producing NH_2BH_2.[10] This pathway is limited by the dissociation of **AB** into NH_3 and BH_3, which at this study's level of theory [CCSD(T)/cc-pVTZ] **AB** has an N−B bond strength of 27.2 kcal/mol. Therefore, activation of **AB** at NH_2BH_2 is competitive with activation at BH_3, and both pathways are likely to be simultaneously operating at sufficiently high temperatures.

As we have shown, **sp3dimer** releases H_2 while forming two NH_2BH_2 molecules with a barrier of 29.2 kcal/mol. This reaction (**TSsp3dimer-2**) produces additional NH_2BH_2 from

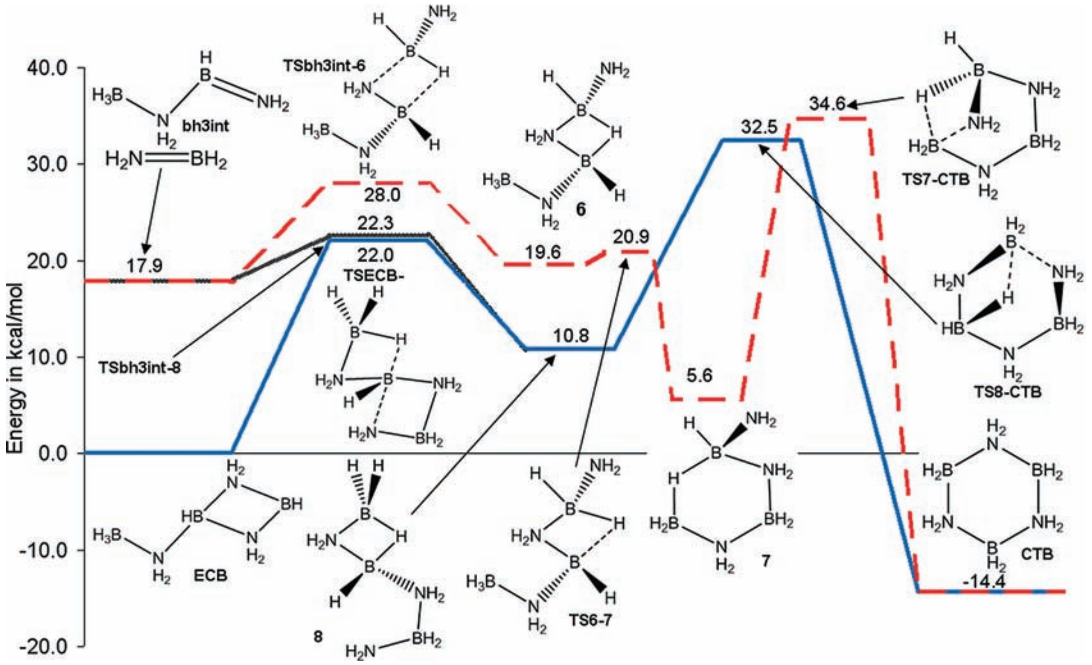


Figure 12. Energetic profiles for pathways to **CTB** formation from **ECB** or **bh3int** + **NH_2BH_2**.

Table 1. Activation Energetics and Frequencies for the Important Reactions in This Study

	transition-state barrier E_a(0 K) (kcal/mol)	transition-state mode frequency (cm^{-1})	reaction enthalpy ΔH(0 K)
TS1-2	34.9	−866.525	−2.1
TS′1-2	39.9	−1476.43	−2.1
TS1-bh3int	50.4	−1244.42	−7.7
TS1-sp3dimer	29.5	−168.835	−8.7
TS2-cdimer	10.4	−383.409	−14.7
TS2-bh3int	9.4	−360.764	−3.7
TS2-nh3int	27.7	−1370.83	−1.4
AB−NH_2BH_2 identity	8.6	−945.765	0.0
TS4-sp3dimer	3.6	−987.529	−2.1
TSbh3int-ECB	7.1	−305.224	−17.9
TSsp3dimer-2	29.2	−421.787	17.3
TSECB-8	22.0	−502.18	10.8
TS8-CTB	21.7	−277.371	−25.2
TSbh3int-5	11.4	−375.278	−2.1
TS7-CTB	29.0	−501.431	−20.0
TS6-7	1.3	−253.371	−14.0
TSbh3int-6	10.1	−304.769	1.7
TSbh3int-8	4.4	−120.418	7.1
TS3-cdimer	57.8	−1279.68	−6.4

AB, and NH_2BH_2 makes the reaction autocatalytic, with the autocatalysis only being stopped by oligomerization of NH_2BH_2. However, we note that because oligomerization of NH_2BH_2 is second order in NH_2BH_2 and proceeds with a very low barrier, NH_2BH_2 oligomerization will proceed much faster than reaction with **AB** once sufficient NH_2BH_2 is generated.

In response to the second question, the reaction of two NH_2BH_2 leads to the immediate formation of the products **cdimer** and **bh3int**. The key reactions of NH_2BH_2 with unsaturated aminoborane oligomers are the addition of NH_2BH_2 (by hydroboration or 2 + 2 cycloaddition) or the addition of H_2 from **AB** to an NH_2BHR moiety. Both types of reactions proceed with a very low barrier. Although other reactivities are possible, specifically the formation of H_2 by breakage of N−H and B−H bonds of any of the intermediates, alternative mechanisms except reactions at N═B double bonds are significantly slower. One key product then is the cyclic dimer of NH_2BH_2, **cdimer**, which forms with a low barrier and is relatively stable. The other key intermediate, **bh3int**, forms from hydroboration of two NH_2BH_2. The barrier for **bh3int** formation is only 1.0 kcal/mol lower than the **cdimer** formation barrier, so these reactions compete closely with each other. Although these two reactions are competitive, **cdimer** can decompose into two NH_2BH_2, which can then form **bh3int**. Once **bh3int** forms, it can be quickly trapped by **AB** or NH_2NH_2 to form the intermediates **sp3dimer**, **ECB**, or **8**. Overall, the favored products of **AB** + NH_2BH_2 are those produced through rapidly occurring reactions at the highly active N═B double bonds. sp^3 N−H and B−H bonds have been shown to be difficult to break in **AB**,[9] and similar results are obtained here: the barriers for H_2 evolution are all significantly higher than those for reactions at N═B double bonds.

Further oligomerization beyond three units of NH_2BH_2 is certainly possible and might proceed starting with **bh3int** through **TSbh3int-5**, **TSbh3int-6**, or **TSbh3int-8**. Therefore, **5**, **7** (from low-barrier isomerization of **6**), or **8** could further oligomerize with additional NH_2BH_2. Because **TSbh3int-5** and **TSbh3int-6** have higher barriers than **TSbh3int-ECB** and **TSbh3int-8**, further oligomerization will likely occur through **TSbh3int-8**. Because **TSbh3int-8** has a lower barrier than **TSbh3int-ECB**, the formation of **8** competes with the **ECB** formation. Furthermore, **8** is 10.8 kcal/mol higher in energy than **ECB**, so it can proceed through **TSECB-8** with a barrier of 11.3 kcal/mol to yield the thermodynamically more stable product, **ECB**. Considering the low barrier for **8** to isomerize exothermically to **ECB**, **ECB** likely is the major product from the reaction of **bh3int** and NH_2BH_2. The pathway from **bh3int** to **8**, however, does provide an avenue for further aminoborane oligomerization. If **5**, **7**, or **8** do form, however, **AB** might immediately add 2H in a manner similar to how **TS3-sp3dimer** or NH_2BH_2 might extend the N−B chain. These mechanisms, however, are beyond the scope of this study; we expect low barrier oligomerization to occur whenever there are N═B double bonds available.

The governing energetic barriers show that oligomerization can occur very rapidly whenever sufficient NH_2BH_2 is present (see Figures 6 and 8). The presence of **AB** near N═B double bonds of **bh3int**, however, generates additional NH_2BH_2 by transfer of 2H from **AB** to the oligomeric double bond of **bh3int**. We note that **sp3dimer** generated by this mechanism can intramolecularly generate two NH_2BH_2 molecules, which means the overall barrier to produce three NH_2BH_2 molecules from **bh3int** and **AB** is 29.2 kcal/mol. Furthermore, one NH_2BH_2 will react with an **AB** via **TS1-sp3dimer** with a barrier of 29.5 kcal/mol. Thus, the net reaction starting with just one NH_2BH_2 is NH_2BH_2 + **AB** → $2NH_2BH_2 + H_2$ with two rate-limiting steps of 29.5 and 29.2 kcal/mol. Alternatively, **sp3dimer** might be dehydrogenated by a catalyst yielding H_2 along with **bh3int** or two NH_2BH_2. From this, additional units of NH_2BH_2 will be produced along with the re-formation of **bh3int**. Because oligomerization of NH_2BH_2 is very fast, NH_2BH_2 rapidly transforms to **ECB** or **8** (which isomerizes to **ECB**). While the barriers for formation of cyclic species such as **CTB** are not unfeasibly high, **ECB** formation is favored because it has low kinetic barriers, leading to a thermodynamically stable intermediate. **CTB**, however, can be formed by the isomerization of **ECB**.

The third question is therefore answered by the results discussed above. The formation of **cdimer**,[12,13] **sp3dimer**,[13] and **ECB**[17] can reasonably be explained through kinetically preferred pathways of NH_2BH_2 oligomerization. **CTB**[12,17] is shown to form more slowly, likely by isomerization of **ECB**. Larger oligomeric products are also predicted to be possible from this study and have been experimentally observed.[8,30] We note that the key intermediate **bh3int** is shown to be very short-lived in the presence of NH_2BH_2 or **AB**, so experimental observation will be unlikely.

The reactions of NH_2BH_2 and **AB** can be categorized by their energetic barrier to elucidate which reactions occur at different temperatures. Metal-catalyzed reactions proceed at temperatures as low as room temperature,[8] while solid-state **AB** thermolysis can approach temperatures higher than 100 °C.[2] Because most reactions at N═B double bonds except direct **AB** + NH_2BH_2 reactions have a low barrier (∼12 kcal/mol or less), these reactions will be fast, even near room temperature. However, higher barrier reactions (∼29 kcal/mol or higher), such as **TS1-sp3dimer** and **TSsp3dimer-2**, have sufficiently high barriers that they may only occur slowly at lower temperature. Consequently, **bh3int**, **cdimer**, or **sp3dimer** might only form at lower temperatures after a catalyst has generated sufficient NH_2BH_2. Furthermore, **sp3dimer** likely only releases H_2 with the assistance of a metal catalyst at lower temperatures. At higher temperatures, however, the autocatalytic formation of NH_2BH_2 will proceed to generate extra NH_2BH_2, even without a metal catalyst. This mechanism is applicable to homogeneous catalysts at higher temperatures and also to uncatalyzed dehydrogenation of **AB**. The relative abundance of NH_2BH_2 is vital in understanding oligomerization of aminoboranes because oligomerization is competing with the addition of H_2 by **AB** (such as **TS4-sp3dimer**) across N═B bonds where oligomerization with NH_2BH_2 would otherwise occur.

During review of this publication, a new experimental study was published on the subject of this paper.[17] Shaw et al. showed that the thermal decomposition of **AB** in glyme at 50−95 °C proceeds through DADB formation (observed in small quantities at 50 °C). The most stable predicted intermediates from our study, **cdimer**, **ECB**, and **CTB**, were all identified in the experimental study by NMR. **sp3dimer** was not observed, indicating that **sp3dimer** decomposes at a faster rate than it forms. This is in agreement with our study because the initiation barrier of DADB formation from two **AB** is 42 kcal/mol;[9] therefore, **sp3dimer** will be readily dehydrogenated at similar conditions (with an intramolecular barrier of 29.2 kcal/mol) and will not accumulate in the reaction media. Instead, as H_2 continues to form, species of the empirical formula $(NH_2BH_2)_x$ will be thermodynamically favored (Figures 1 and 2).

Additionally, the order in which **cdimer**, **ECB**, and **CTB** appeared in Shaw et al.'s study is consistent with our theoretical study: first **cdimer**, then **ECB**, and finally **CTB**.[17] Although the authors suggested that **AB** reacts with **cdimer** to form **ECB**, we showed herein that **ECB** formation can be explained through NH_2BH_2 oligomerization. Because NH_2BH_2 has a very short lifetime, it is unobservable except at low temperatures[3,4] and its importance can only be explained through theoretical studies.

Conclusions

This study suggests that **AB** is able to react with NH_2BH_2 to directly form oligomeric aminoborane species. This species, linear **sp3dimer**, can decompose into additional NH_2BH_2 that reacts rapidly to form oligomeric species. These two reactions compose an autocatalytic cycle for dehydrogenation of **AB** by NH_2BH_2. We show through comparison of our predicted stable intermediates and experimental intermediates that our mechanistic study explains the oligomerization of two or three units of NH_2BH_2 and the formation of larger oligomers is expected to adhere to the principles described above. The potent reactivity of N═B double bonds in NH_2BH_2 and other aminoboranes is of utmost importance to understanding the oligomerization of **AB** + NH_2BH_2.

Cyclic aminoboranes can be formed by oligomerization of free NH_2BH_2 in solvent, but this study suggests that the formation of **ECB** is kinetically much faster and may be followed by slower **ECB** isomerization to **CTB**. The formation of cyclic species therefore likely occurs while NH_2BH_2 is bound to a metal center or by isomerization of free **ECB**. In addition, the iridium pincer catalyst[8] and nickel N-heterocyclic carbene catalyst[7] dehydrogenate oligomeric aminoboranes at unknown rates. Therefore, **ECB** will transform to cyclic species if catalytic dehydrogenation of **ECB** is slow.

This study establishes the link between releasing the first and second 1 equiv of H_2 from **AB**. The oligomeric species identified herein are key intermediates that form after the first H_2 is removed from **AB**. We are actively investigating the reactivities of these species with homogeneous catalysts to elucidate the differences between iridium pincer and nickel N-heterocyclic carbene chemistries, where only the latter releases the second 1 equiv of H_2 from **AB**.[7,8] The combined knowledge of oligomerization and catalyst reactivity will provide a more complete description of **AB** dehydrogenation. This description is vital to understanding why various catalytic systems release different equivalents of H_2 from **AB**.

Supporting Information Available: TS1-bh3int and **TS2-cdimer**, XYZ geometries and energies of all species, a comparison of Gibbs free energies with 0 K + ZPE energies for all transition states, calculated transition-state theory rate constants, and the full reference for *Gaussian03*. This material is available free of charge via the Internet at http://pubs.acs.org.

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