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Theoretical Study on the Possibility of Using Frustrated Lewis Pairs as Bifunctional Metal-Free Dehydrogenation Catalysts of Ammonia−Borane

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Density functional theory calculations have been carried out to study the possibility of using "frustrated Lewis pairs" (FLPs) as bifunctional metal-free dehydrogenation catalysts of ammonia-borane, NH_3BH_3 (AB), according to the following points: (1) some FLPs react with H_2 at low temperature and the hydrogenated products release H_2 at high temperature; (2) some FLPs hydrogenate imines by taking the protic (N-bound) and hydridic (B-bound) H atoms of AB. In this work, the N/B pair (N-PMTN−$CH_2C_6H_4B(C_6F_5)_2$) is chosen to explore the possibility that FLPs release H_2 from AB. Two steps are involved in the proposed mechanism: first, AB is dehydrogenated by the N/B pair to form the NH/BH compound and NH_2BH_2 at low temperature, and then H_2 is released from the NH/BH compound at 110 °C and the N/B pair regenerates. Several competitive reaction channels have been considered. The calculational results show that the dehydrogenation of AB by the N/B pair has the lowest free-energy barrier. On the basis of the experimental N/B pair, a new dehydrogenation catalyst of AB has been designed, which can release H_2 from AB under milder conditions than the former. This work may be helpful for the experimental chemists to broaden the application of FLPs and to design new dehydrogenation catalysts of AB.

1. Introduction

It is well-known that Lewis acids (or bases) act as catalysts by activating the basic reactants (or acidic reactants) via Lewis acid−base interaction.[1] When this kind of interaction is very strong, acid and base can form a stable adduct.[2] Recently, Stephan et al. used this kind of interaction to activate small molecules, such as H_2,[3a,b] olefins,[3c] alkynes,[3d] N_2O,[3e] and CO_2.[3f] For example, the Lewis base center P and acid center B in $(C_6H_3Me_3)_2P(C_6F_4)B(C_6F_5)_2$ react with H_2 at room temperature to form $(C_6H_3Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$,[3a] which releases H_2 at 100 °C[3a] or adds the protic and hydridic H atoms (P−H and B−H) to the C=N bond.[4] As a new bond activation strategy, "frustrated Lewis pairs" (FLPs) have an increasing interest for experimental and theoretical scientists.[5−9]

As a very promising hydrogen storage material, ammonia−borane (NH_3BH_3, AB) has been one of the focuses of the experimental and theoretical studies because it contains 19.6 wt % H, larger than the target of 9 wt % H proposed by the U.S. Department of Energy.[10−12] It has been reported that some FLPs can react with H_2 at low temperature and the hydrogenated products release H_2 at high temperature.[3a,13,14] Stephan and Erker[15] have used FLPs to take the protic (N-bound) and hydridic (B-bound) H atoms of AB for hydrogenation of imines. Very recently, Tamm et al. found that a

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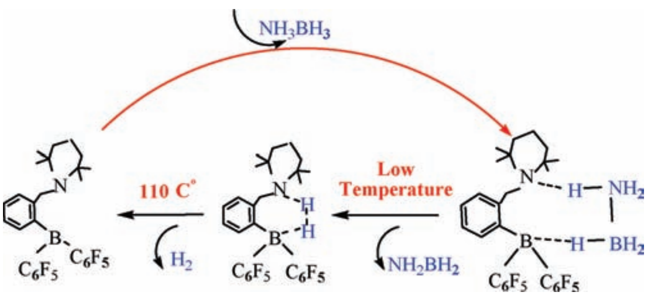
frustrated carbene−borane pair effects concerted dehydrogenation of the C−C bond into a C=C bond.[16] According to the Privalov report,[17] dehydrogenation of alcohols into ketones also proceeds through the bifunctional cooperation of Lewis acid center B and base center P of $(t\mathrm{Bu})_2\mathrm{P{=}B(C_6F_5)_2}$. So, it is very possible that FLPs may take the protic and hydridic H atoms of AB in a concerted manner and recombine them into H_2 under appropriate conditions. FLPs being used to release H_2 from AB should have the following two abilities: (1) taking the protic and hydridic H atoms from AB; (2) combining the protic and hydridic H atoms into H_2. Thus, these Lewis pairs that can reversibly activate H_2 are potential catalysts for H_2 release from AB. The P/B pairs[3a,13] and the N/B pair[14] can heterolytically cleave H_2 into protic and hydridic H atoms at room temperature and the hydrogenated products release H_2 at high temperature. Because the N−H bond is stronger than the P−H bond,[18,19] the N/B pair is more favorable in energy to release H_2 from AB than the P/B pair. Thus, the N/B pair (N-PMTN−$\mathrm{CH_2C_6H_4B(C_6F_5)_2}$) (**1**)[14] is chosen to explore the possibility that FLPs release H_2 from AB in this work.

Scheme 1. Possible Catalytic Cycle Using the N/B Pair **1** as a Bifunctional Dehydrogenation Catalyst of **2**



2. Computational Details

All calculations are performed with the B3LYP[20] method implemented in the *Gaussian 03* program.[21]

In these investigated reaction channels, H_2, AB, and NH_2BH_2 were applied with the 6-31G(d,p) basis set; for other species, the 6-31G(d,p) basis set was used for B, N, the phenyl group, and the atoms bound to B and P, while the 6-31G basis set was used for the rest of the atoms. Vibrational frequencies were obtained for all stationary points to check whether the optimized geometry corresponds to a minimum or transition state and to obtain Gibbs free energies at a temperature of 298 K.

To consider the effects of solvent polarity on the energies of all species, we employed the conductor-like polarizable continuum model (CPCM)[22] method with dichloromethane as the solvent to calculate the Gibbs free energy of solvation for all species using their gas-phase optimized geometries. In CPCM, the computed energies and properties depend on the cavity size. We have used the UAKS cavity in our calculations, as suggested by previous work.[23] The free energy for each species in solution is taken as the sum of the gas-phase free energy and the free energy of solvation.

3. Results and Discussion

3.1. N/B-Pair-Catalyzed Dehydrogenation of 2. A possible reaction mechanism has been proposed to illustrate how the N/B pair 1 takes the protic and hydridic H atoms from AB and recombines them into H_2, as shown in Scheme 1. First, **1** associates with **2** to form a transient species via N···H and B···H interactions; then, the protic and hydridic H atoms in **2** are taken by **1** to produce the hydrogenated species NH-PMTN−$\mathrm{CH_2C_6H_4BH(C_6F_5)_2}$; finally, H_2 is released from NH-PMTN−$\mathrm{CH_2C_6H_4BH(C_6F_5)_2}$ at 110 °C, and **1** regenerates for the next catalytic cycle.

In the first step, the N/B pair **1** first associates with **2** to form a transient complex **3** via N···H (1.81 Å) and B···H (1.35 Å) interactions (Figure 1). In **3**, the N−H and B−H bonds of **2** lengthen to 1.07 and 1.31 Å from 1.02 and 1.21 Å in **2**, while the N−B bond shortens to 1.59 Å from 1.67 Å in **2**, implying **2** in **3** has been strongly activated. **3** is 7.8 kcal/mol in free energy above **1** + **2** (Figure 2). Then, **4** and **5** are formed via **TS1**, in which the distances between the two H atoms of **2** and the B center as well as the N center shorten to 1.32 and 1.29 Å from 1.35 and 1.81 Å of **3**, while the N−H and B−H bonds of **2** lengthen to 1.35 and 1.35 Å from 1.07 and 1.31 Å of **3**, respectively. Obviously, the protic and hydridic H atoms of **2** are taken by N and B of **1** in a concerted way. In the gas phase, **TS1** is 13.4 kcal/mol above **1** + **2**. The solvent effect is also considered by using dichloromethane as the solvent. The free-energy barrier increases to 14.2 kcal/mol after inclusion of the solvent effect.

In the second step, H_2 is released from **4** via **TS2**. In **4**, the H···H distance is 1.68 Å, indicating a strong $H^-\cdots H^+$ interaction.[24] Most recently, Wu et al.[25] explored the role of the $\mathrm{B{-}H^-\cdots{}^+H{-}P}$ interaction in H_2 release from the hydrogenated FLPs. In **TS2**, the B−H and N−H distances lengthen to 1.78 and 1.91 Å from 1.21 and 1.02 Å in **4**, while the H−H distance shortens to 0.78 Å from 1.68 Å in **4** (Figures 1 and 3). **TS2** is 22.2 kcal/mol above **4**. The barrier increases to 27.6 kcal/mol after the solvent effect is included (Figure 2). The free energy of **1** + H_2 is 4.4 kcal/mol higher than that of **4** in the gas phase and 12.5 kcal/mol in the solvent phase, which is

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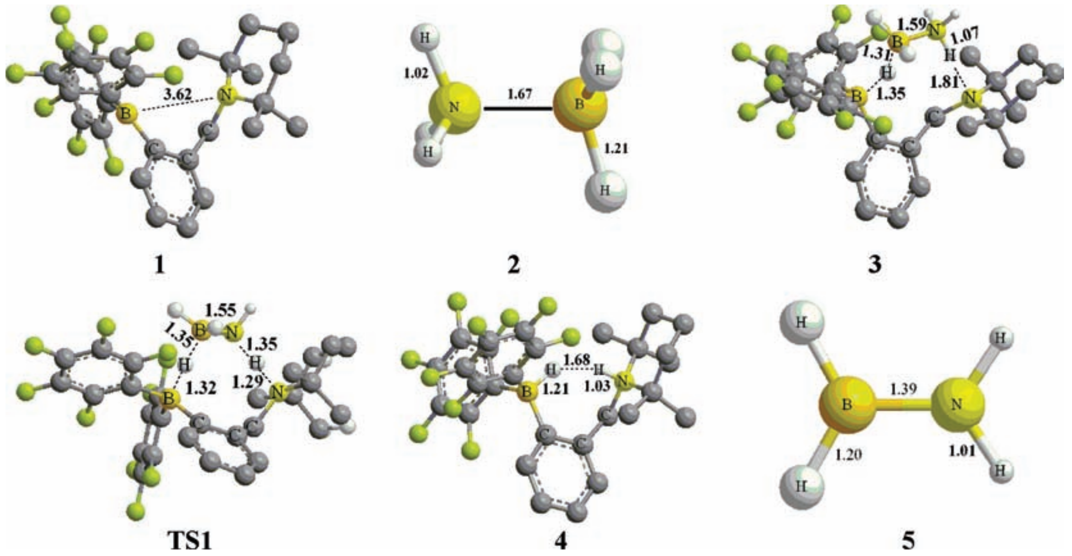
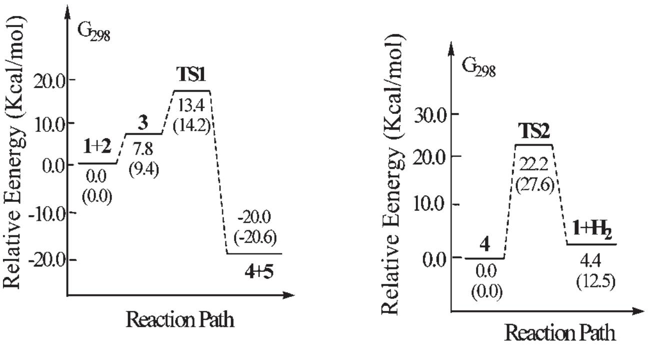


Figure 1. Optimized geometries of stationary points in the reaction channel to take the protic (N-bound) and hydridic H (B-bound) atoms of **2** by **1**. Just the N- and B-bound H atoms are shown for clarity.



(a) (b)

Figure 2. (a) Potential energy profile to take the protic and hydridic H atoms of **2** by **1**. (b) Potential energy profile of H_2 release from the hydrogenated product **4**. Free energies in the solvent are given in parentheses.

TS2

Figure 3. Optimized geometry of the transition state **TS2**. Just the N- and B-bound H atoms are shown for clarity.

consistent with the experimental observation that **1** reacts with H_2 at room temperature and the reverse reaction proceeds at 110 °C.[14] Although H_2 release from **4** is unfavorable in thermodynamics, the liberation of H_2 from the reaction system will shift the equilibrium and drive the reaction.[26]

3.2. N- and B-Catalyzed Dehydrogenation of 2. It has been reported that base[27] or acid[28] can catalyze the dehydrogenation of **2** by taking the protic or hydridic H atoms of **2**. Thus, the dehydrogenations of **2** catalyzed by N and B of **1** are also investigated. For the N-catalyzed one, the initiating step is to transfer the protic H atom of **2** to the N atom of **1**. The corresponding transition state **TS3** has been located. According to Figure 4, the distances between H and N of **2** and N of **1** are 1.80 and 1.08 Å, respectively, while the distance between N of **2** and B of **1** is 2.60 Å, implying that **TS3** is stabilized by the N···B interaction. Natural bond order (NBO) orbital analysis shows that the interaction between the lone-pair orbital of N in **2** and the empty orbital of B in **1** is 11.9 kcal/mol. **TS3** is 33.6 kcal/mol in free energy above **1** + **2**. After inclusion of the solvent effect, the barrier increases to 36.7 kcal/mol. For the B-catalyzed one, transferring the hydridic H atom of **2** to the B atom of **1** is the first step. **TS4** is the corresponding transition state, which is 38.8 kcal/mol above **1** + **2**. Similar to that in **TS3**, the N···B interaction stabilizes **TS4** as well (Figure4). After inclusion of the solvent effect, the barrier decreases to 38.3 kcal/mol. Thus, the N/B-pair-catalyzed H_2 release from **2** is more favorable in energy than the N- and B-catalyzed ones.

3.3. Dehydrogenation of 2 without a Catalyst. It is well-known that thermal dehydrogenation of **2** proceeds without a catalyst, which has been extensively investigated by experimental and theoretical scientists.[10,29,30] According to the report of Li et al.,[29] the intramolecular activation barrier of **2** is 32−33 kcal/mol. For a comparison of the

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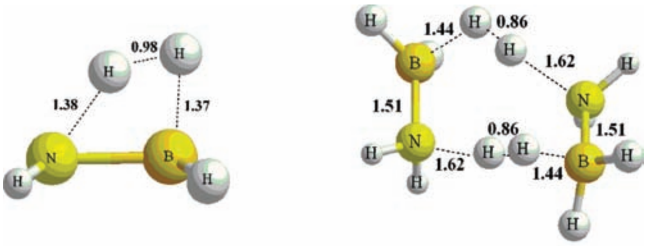
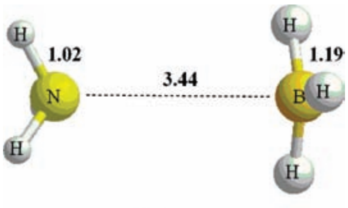
TS3 **TS4**

Figure 4. Optimized geometries of the transition states **TS3** and **TS4**. Just the N- and B-bound H atoms are shown for clarity.



TS5 **TS6**

Figure 5. Optimized geometries of the transition states **TS5** and **TS6**.



TS7

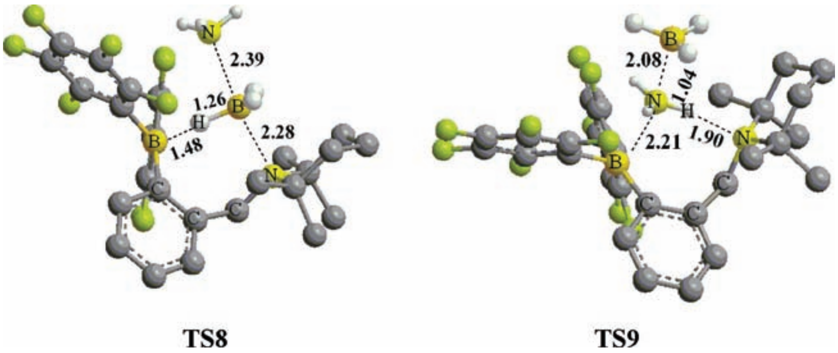
Figure 6. Optimized geometry of the transition state **TS7**.

barriers of all of the possible reaction channels, the intramolecular dehydrogenation mechanism is reinvestigated herein with the method mentioned above. In addition, the possibility of intermolecular dehydrogenation between two **2** molecules is considered as well. In the former, one H_2 molecule is released via the intramolecular dehydrogenation transition state **TS5** (Figure 5). **TS5** is 34.9 kcal/mol in the gas phase above **2** (40.6 kcal/mol after inclusion of the solvent effect), which is consistent with the reported 32−33 kcal/mol.[29] For the latter, two H_2 molecules are formed through the intermolecular dehydrogenation transition state **TS6** (Figure 5). **TS6** is 43.0 kcal/mol above **2** + **2**. After inclusion of the solvent effect, the barrier increases to 54.3 kcal/mol. Thus, dehydrogenation of **2** without a catalyst is less favorable in energy than that catalyzed by the N/B pair **1**.

3.4. Reaction To Break the N−B Bond of 2. BH_3 resulting from the breakage of the N−B bond can also catalyze the dehydrogenation of **2**.[30] Dixon and coworkers[30] have reported that the B−N bond dissociation barrier is 25.9 kcal/mol. The reaction to form BH_3 and NH_3 by breaking the N−B bond of **2** is reinvestigated as well. The corresponding transition state **TS7** has been located. The N···B distance in **TS7** is 3.44 Å, implying that it is a late transition state (Figure 6). **TS7** is 21.8 kcal/mol in the gas phase above **2**. The barrier increases to 29.0 kcal/mol after the solvent effect is considered. The N/B-pair-catalyzed dehydrogenation of **2** contains two consecutive steps: (1) taking the protic and hydridic H atoms of **2** by the N/B pair at low temperature; (2) releasing H_2 from the hydrogenated N/B pair at 110 °C. The free-energy barrier of cleaving the N−B bond is higher than that of the first step in the N/B-pair-catalyzed dehydrogenation of **2** (21.8 vs 13.4 kcal/mol), implying that **2** is negligible in the second step of the N/B-pair-catalyzed dehydrogenation of **2** because it will react with the N/B pair to produce the hydrogenated species in the first step. Therefore, the N/B-pair-catalyzed dehydrogenation is more likely to proceed than the cleavage of the N−B bond for **2**.

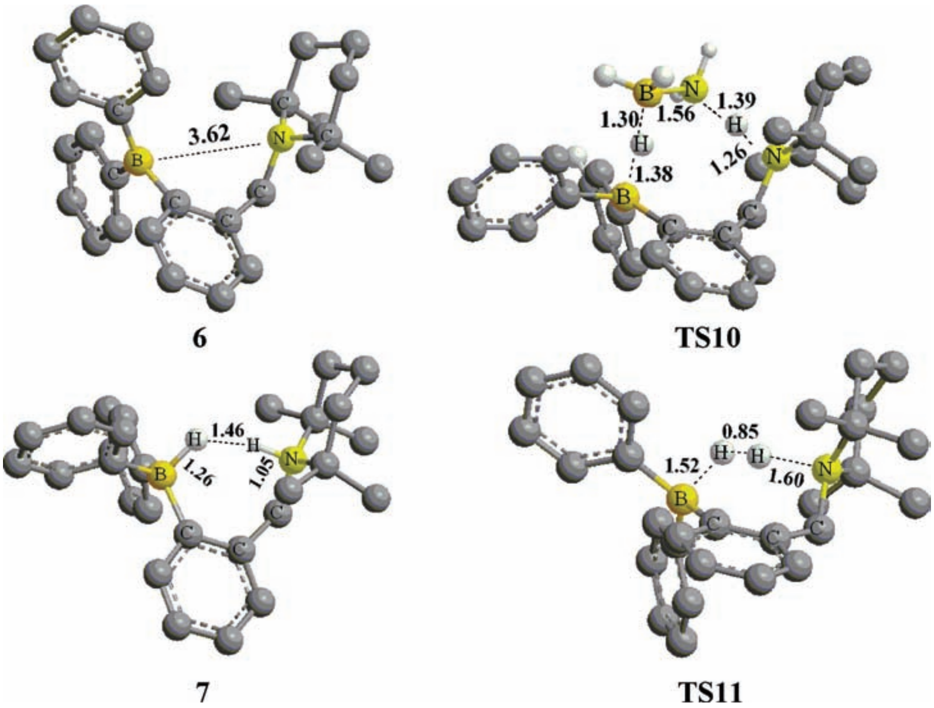
3.5. Reaction To Form 1−2 Adducts. Given that **2** is an adduct of NH_3 and BH_3 formed by the N−B interaction, it is also very possible that **1** can react with **2** to produce a **1**-BH_3 adduct and NH_3 (or a **1**-NH_3 adduct and BH_3). The corresponding transition states **TS8** and **TS9** have been located. The B···H (1.48 Å) and N···H (1.90 Å) interactions stabilize **TS8** and **TS9**, respectively (Figure 7). **TS8** is 36.2 kcal/mol above **1** + **2**, and the barrier increases to 39.9 kcal/mol after the solvent effect is included. **TS9** is 29.0 and 37.7 kcal/mol above **1** + **2** in the gas and solvent phases, respectively. The two reaction channels are thus less favorable than the dehydrogenation of **2** catalyzed by the N/B pair **1** because the former have higher free-energy barriers than the latter (36.2 and 29.0 kcal/mol vs 13.4 kcal/mol).

3.6. Design of a New Dehydrogenation Catalyst of 2 Based on the N/B Pair. The hydrogenated N/B pair releases H_2 at 110 °C,[14] whereas the acid- and transition-metal-catalyzed dehydrogenations of **2** proceed at mild temperature.[10] For decreasing the H_2 release temperature from the hydrogenated N/B pair, a new N/B pair **6** is designed by replacing the F atoms of the phenyl group in **1** with H atoms (Figure 8). **TS10** is the transition state through which **6** takes the protic and hydridic H atoms of **2**, which is 18.7 kcal/mol in free energy above **6** + **2**. After the solvent effect is considered, the barrier increases to 21.3 kcal/mol. Then, the hydrogenated species **7** releases H_2 via **TS11** with a free-energy barrier of 9.3 kcal/mol, which increases to 10.9 kcal/mol after inclusion of the solvent effect. Thus, **6** can release H_2 from **2** under milder conditions than **1** because the barrier of the rate-determining step is 27.6 kcal/mol in the **1**-catalyzed reaction and 21.3 kcal/mol in the **6**-catalyzed one. According to NBO orbital analysis, the electron occupancies in the empty orbital of B and the lone-pair orbital of N in **1** and **6**



TS8 **TS9**

Figure 7. Optimized geometries of the transition states **TS8** and **TS9**. Just the N- and B-bound H atoms are shown for clarity.



6 **TS10** **7** **TS11**

Figure 8. Optimized geometries of **6**, **TS10**, **7**, and **TS11**. Just the N- and B-bound H atoms are shown for clarity.

are 0.24 and 1.88 e and 0.23 and 1.88 e, respectively, implying that replacement of F atoms with H atoms has no obvious influence on the acidity of the Lewis acid center B and the basicity of the Lewis base center N.[2,31] From the activation strain model,[32] the influence of replacing F atoms with H atoms on the reactivity of **1** and **6** is due to the counterpoise of the following two factors: (1) the F···H interaction stabilizes the transition state; (2) the repulsion between F and the alkyl group is larger than that between H and the alkyl group. The calculation results show that the reduction of the repulsion between substituents on N and B by replacing F atoms with H atoms acts to decrease the barrier for H_2 release from the hydrogenated species but increases the barrier that takes the protic and hydridic H atoms from **2**. Thus, the N/B catalyst being used to release H_2 from **2** should have a strong interaction with H atoms and a weak repulsion between the substituents on N and B.

4. Conclusion

In this paper, we have presented a detailed density functional theory calculation to explore the possibility of applying FLPs as bifunctional metal-free dehydrogenation catalysts of AB. The proposed dehydrogenation mechanisms of AB by the N/B pair and the possible competitive reaction channels have been studied. The calculation results show that the dehydrogenation of AB by the N/B pair has the lowest free-energy barrier. Thus, it is very possible that FLPs can act as bifunctional catalysts to release H_2 from AB under appropriate conditions.

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Supporting Information Available: Total electronic energies, Gibbs free energies, and Cartesian coordinates of all stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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