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Unusual Concerted Lewis Acid−Lewis Base Mechanism for Hydrogen Activation by a Phosphine−Borane Compound

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Density functional theory calculations have been carried out to investigate the possible reaction mechanisms for the reversible dihydrogen activation catalyzed by a phosphine−borane compound, $(C_6H_2Me_3)_2P(C_6F_4)B(C_6F_5)_2$ (Welch, G. C.; Juan, R. R. S; Masuda, J. D.; Stephan, D. W. *Science*. **2006**, *314*, 1124−1126). The present calculations show that an unusual concerted Lewis acid−Lewis base mechanism is more favorable than the proton transfer or hydride transfer mechanisms suggested previously. In the concerted Lewis acid−Lewis base mechanism, the H−H heterolytic cleavage is achieved through the simultaneous electron transfer from the lone-pair orbital of the Lewis base P center to the σ^* orbital of H_2 and from the σ orbital of H_2 to the empty orbital of the Lewis acid B center. The solvent is found to dramatically change the potential energy surface. The proposed mechanism can account well for the bimolecular H−D exchange process observed in deuteration experiments and the experimental fact that the H_2 activation is reversible at mild conditions.

1. Introduction

The activation of molecular hydrogen (H_2) has been an active field for two decades.[1] It is well known that dihydrogen can be activated on many transition-metal catalysts. On transition metal centers, dihydrogen is usually broken to form the metal-hydride complexes through an oxidative addition process (homolytic cleavage), or to form a metal hydride and a proton (heterolytic cleavage), which can easily transfer to a nearby metal-bound ligand.[1,2] However, some metal-free systems have been found to react with H_2 or liberate H_2 at mild conditions. For example, H_2 can be cleaved by substituted carbenes under room temperature, and the theoretical studies show the mechanism is most likely to be a hybrid between a homolytic and heterolytic cleavage.[3] Ge_2−alkyne compounds can also react with H_2 easily, and the highly reactive nature of these compounds is due to the possible singlet diradical character of the Ge−Ge bonding.[4] A mixture of phosphines and boranes is able to activate dihydrogen under room temperature as well.[5] Nevertheless, all of these metal-free H_2 activation reactions mentioned above are not reversible.

Recently, Stephan et al. reported the first nonmetal phosphonium−borate compound, $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$, that could liberate H_2 at temperatures above 100 °C, whereas the resulting phosphine−borane species, $(C_6H_2Me_3)_2P(C_6F_4)$-$B(C_6F_5)_2$, can add H_2 even at −25 °C to regenerate the original salt (Scheme 1).[6] Because this is the first example to achieve the reversible activation and liberation of H_2 on a nonmetal compound, understanding the mechanistic details of the related reaction is very crucial for further experimental searches for more-effective compounds used in hydrogen storage and activation. Stephan et al. have conducted some kinetic studies

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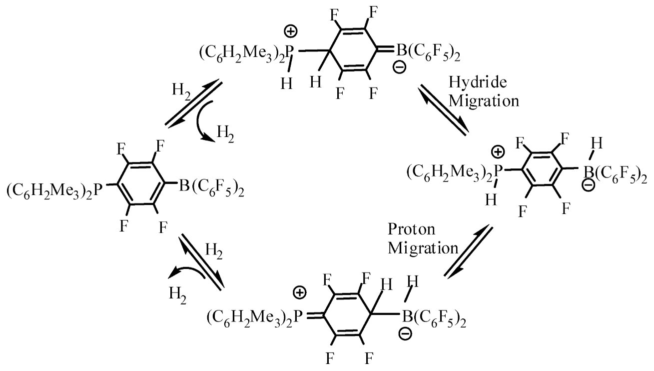
Scheme 1. Mechanisms Suggested by Stephan et al.



to probe the mechanism, and they proposed two possible reaction channels for the observed process.[6] One channel is the addition of H_2 to the C−B bond, followed by the intramolecular proton migration to the Lewis base center P; the other is the addition of H_2 to the C−P bond, followed by the hydride migration to the Lewis acid center B (Scheme 1). In this work, our purpose is to carry out density functional theory calculations to investigate the most probable mechanism for this reaction. We will explore the potential energy surfaces of two possible reaction channels suggested previously and a new mechanism presented in this work. Our calculations show that the concerted Lewis acid−Lewis base mechanism is most likely to be responsible for the observed H_2 activation.

2. Computational Details. All calculations are performed with the B3LYP[7a,b] method implemented in *Gaussian 03* program.[7c] For all of the stationary points involved in the reaction channels suggested by Stephan et al., a full molecular model is employed. We have used the 6−311++G(d,p) basis set for dihydrogen, B and P, those carbon atoms bonded to B or P and the central C_6F_4 group, and the 6−31G basis set for the rest of atoms (basis set I). For the proposed mechanism in this work, a full molecular model is adopted to explore the corresponding potential energy profile. A different basis set (basis set II) is used, in which the 6−311++G(d,p) basis set is employed for activated hydrogen atoms, B and P, and those carbon atoms bonded to B or P, and the 6−31G basis set is used for the rest of atoms. Vibrational frequencies are obtained for all stationary points to check whether the optimized geometry corresponds to a minimum or a transition state and to obtain Gibbs free energies at the temperature of 298 K. IRC[8] calculations are performed to verify whether the transition states are truly connected by the reactants and the products.

To consider the bulk solvent effects on the free energies of all species, we have employed the CPCM[9] method with toluene as the solvent to calculate the Gibbs free energy of solvation for some 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.[10] 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.

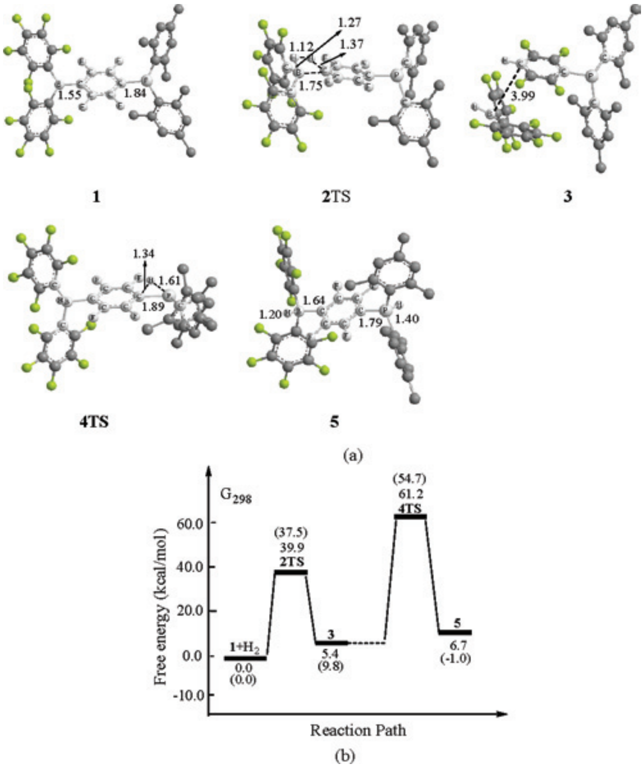


Figure 1. (a) The optimized geometries of the stationary points in the proton migration channel (with the basis set I). All hydrogen atoms (except activated hydrogen atoms) are omitted for clarity. (b) The free energy profile of the proton migration pathway. Free energies in the solvent are given in parentheses. The dotted line represents a series of proton transfer processes, which are omitted in this study.

3. Results and Discussion

3.1. Mechanisms Suggested by Stephan et al. Two reaction channels have been suggested by Stephan et al.[6] One channel is the addition of H_2 to the C−B bond, followed by the intramolecular proton migration to the Lewis base center P; the other is the addition of H_2 to the C−P bond, followed by the intramolecular hydride migration to the Lewis acid center B (Scheme 1). For these two channels, the optimized geometries of some stationary points and the corresponding potential energy profiles are shown in Figures 1 and 2, respectively, and their electronic energies (or Gibbs free energies) are listed in Tables S1 and S2 in the Supporting Information. In the following, we will discuss these two reaction channels separately.

3.1.1 Proton Migration Channel. Along this channel, H_2 is added to the $B-C_6F_4$ bond of the reactant **1** through **2TS**, heterolytically cleaving into a proton and a hydride. In **2TS**, the H−H distance is stretched to 1.12 Å, and the C−B distance is elongated from 1.55 Å in **1** to 1.75 Å. However, our optimization on the intermediate **3** ends up with two weakly bound fragments, with the C−B distance of 3.99 Å. This is understandable because the breakup of the C−B bond can allow the aromatic ring structure to be kept. **2TS** is 39.9 kcal/mol in free energy above the reactants **1**+H_2. If the reaction continues along this way, the C-bound proton shall transfer to the Lewis base center P via a series of successive migrations. The final product **5** is obtained through **4TS**, which is the transition state for the proton

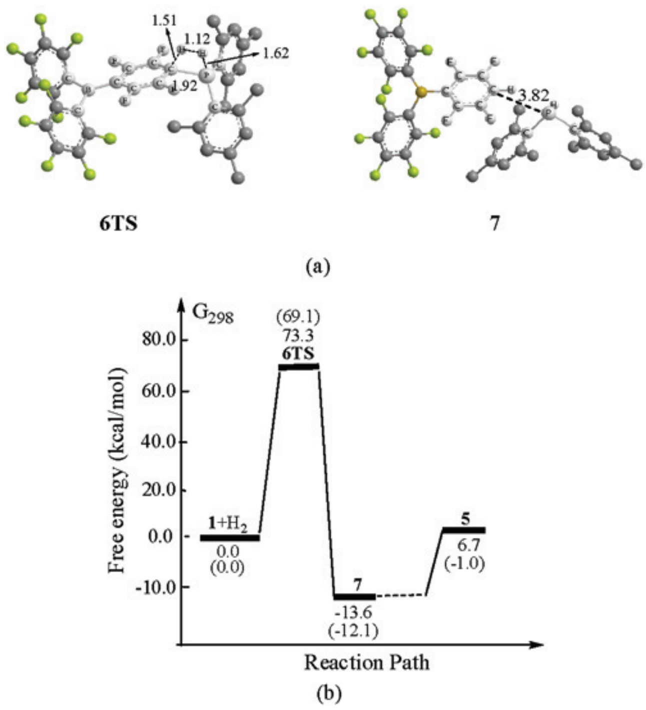


Figure 2. (a) The optimized geometries of some stationary points in the hydride migration channel (with the basis set I); (b) the free energy profile of the hydride migration pathway. Free energies in the solvent are given in parentheses. The dotted line represents a series of hydride transfer processes, which are omitted in this study.

transfer from C-bound to P-bound. In **4TS**, the H−P distance is 1.61 Å, and the C−H distance is 1.34 Å. **4TS** is 61.2 kcal/mol in free energy above **1**+H_2 in gas phase. After the solvent effect is considered, this barrier is reduced to 54.7 kcal/mol, which is not consistent with the experimental fact that the reaction of **1** with H_2 proceeds at the room temperature. Thus, this reaction channel can be excluded without further studies for other steps.

3.1.2 Hydride Migration Channel. According to this mechanism, H_2 is first heterolytically cleaved on the P−C_6F_4 bond of the reactant **1** to form the intermediate **7**. **6TS** is the corresponding transition state for the H_2 bond cleavage. In **6TS**, the H−H distance is 1.12 Å, and a C−P distance is 1.92 Å. The intermediate **7** also contains two weakly bound fragments, with a C−P distance of 3.82 Å. This H_2 cleavage transition state is 73.3 kcal/mol in free energy above **1**+H_2, but the intermediate **7** is 13.6 kcal/mol lower in free energy than **1**+H_2. The inclusion of the solvent effect would decrease the H_2 cleavage barrier to 69.1 kcal/mol. Because this barrier is also too high to reconcile with the experimental fact that **1** would readily react with H_2 at the 25 °C, we can conclude that this pathway is also unlikely, although details on the subsequent steps are not involved here.

It should be noted that the free energy of the product **5** is 6.7 kcal/mol higher than the reactants **1**+H_2 in gas phase. But when the solvent effect is added, the product **5** is 1.0 kcal/mol in free energy below the reactants **1**+H_2. The main reason is that product **5** has a significantly larger dipole moment (29.0 Debye) than the reactant **1** (6.9 Debye). Thus, the solvent plays a significant role in stabilizing the product **5**.

3.2. Concerted Lewis Acid−Lewis Base Mechanism. Here, we suggest a new mechanism to account for the studied reaction (Scheme 2). First, two phosphine−borane species may form an encounter complex through possible hydrogen bonds between two monomers. Then, a H_2 molecule may insert into the region between the Lewis acid B center and the Lewis base P center of the encounter complex to form an ion pair complex via a direct heterolytic cleavage of the H−H bond. It is expected that the cooperative interaction of the Lewis acid B center and Lewis base P center can promote the bond breaking. Subsequently, the ion-pair complex may dissociate into two ionic species (anion and cation) with the assistance of the solvent. The resulting ionic species still has an active B (or P) center. Thus, a cation species with an active B center may associate with another anion species with an active P center to form a similar encounter complex as described above. This encounter complex can also activate the H_2 molecule in a similar way as described in Scheme 2 to produce the final products.

To verify the suggested pathways, we first employ a full molecular model to explore the potential energy profiles. Because the full molecular model is quite large, we are not able to locate the structure of the direct heterolytic transition state. As a result, we resort to the relaxed potential energy scan by fixing the H−H distance at a series of values to determine the approximate transition state. To locate the structure of the direct H−H heterolytic transition state, we also employ a simplified model, in which the terminal C_6F_5 or $C_6H_2Me_3$ group connecting to the unreactive B (or P) center is replaced with a CH_3 group for simplicity. For the weakly bound complexes, BSSE corrections[11] should be included to obtain their accurate electronic energies (or the free energies). However, for large molecular clusters a recent review[12] shows that the 50% BSSE correction (computed

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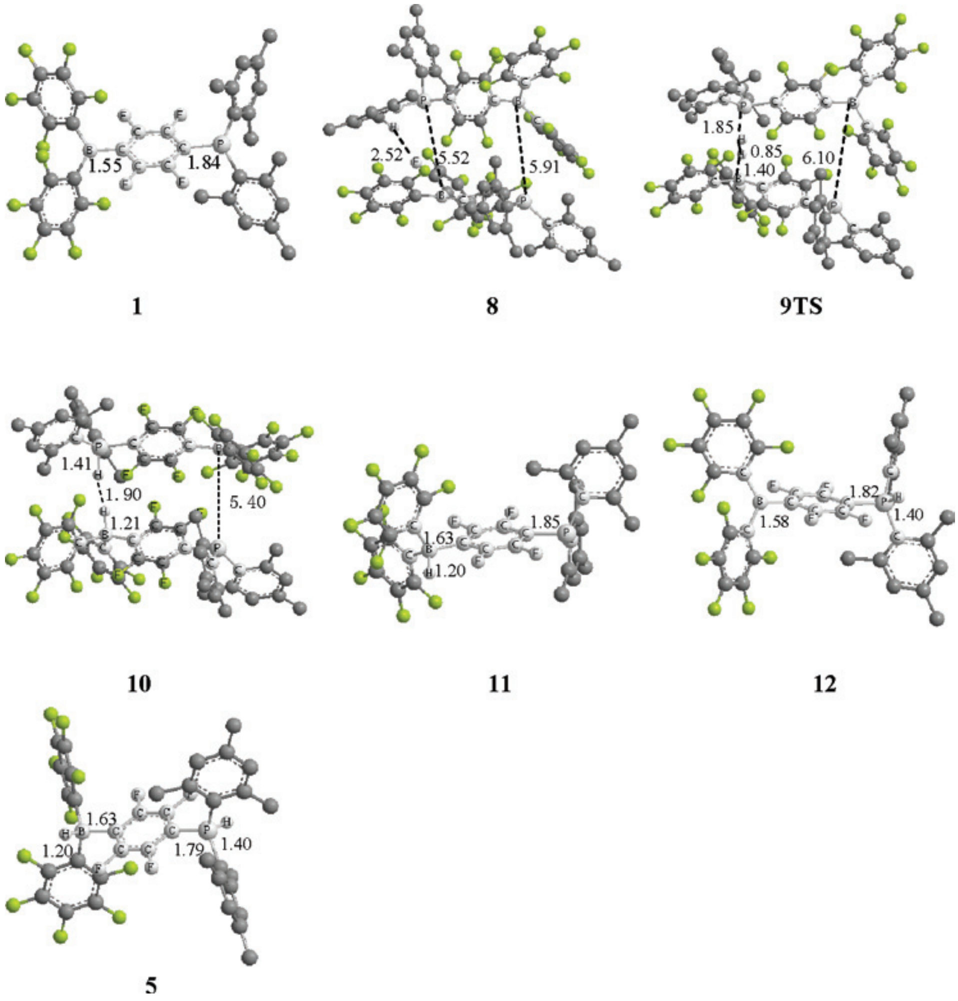
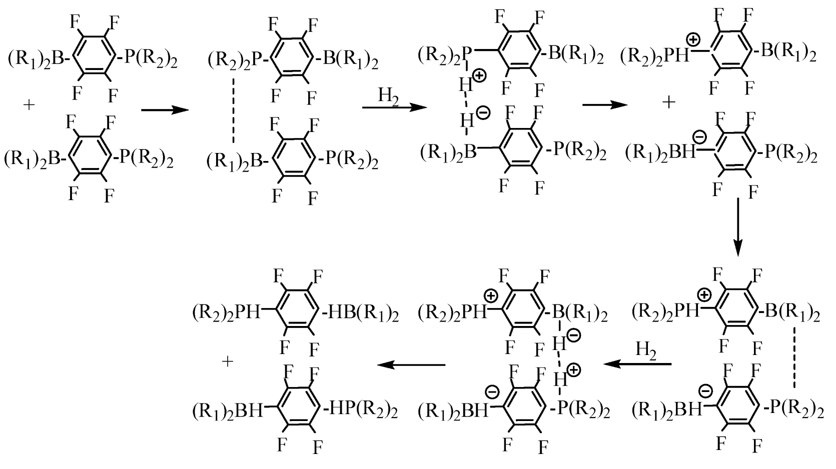


Figure 3. The optimized geometries of the stationary points in the concerted Lewis acid−Lewis base mechanism (with the basis set II). Only hydrogen atoms involved in C−H···F−C hydrogen bonds as well as in BH and PH groups are shown for clarity.

Scheme 2. Mechanism Proposed in This Work: $R_1{=}C_6F_5$, $R_2{=}C_6H_2Me_3$



with the counterpoise method) rather than the full BSSE correction gives more reasonable BSSE energies. Thus, the free energies of the loosely bounded complexes corrected with the 50% BSSE energies will be employed in our discussions.

3.2.1 Full Molecular Model. According to the proposed mechanism described above, reactant **1** will associate with another reactant in the head-to-tail manner to form a dimeric species **8** (Figure 3). In **8**, the distance between one B atom and its close P atom is 5.52 Å and 5.91 Å, respectively. There exist several C−H···F−C hydrogen bonds (the shortest is 2.52 Å) between two phosphine−borane monomers. The binding energy is 17.7 kcal/mol in **8**. After 50% BSSE is considered, the binding energy in **8** reduces to 7.6 kcal/mol. Clearly, the hydrogen bonds between two monomers may possibly lead to the formation of the encounter complex. In

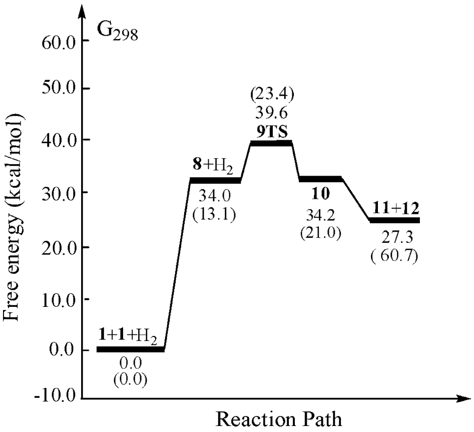


Figure 4. Free-energy profile of the concerted Lewis acid−Lewis base mechanism (with the basis set II). Free energies in the gas phase are given in parentheses. The free energies of loosely bounded species, **8**, **9TS**, and **10** are corrected by the 50% BSSE.

fact, the association of two reactants may lead to many dimeric species with a pair of reactive B and P centers like **8**. It should be mentioned that if one of these dimeric species, other than **8**, is employed as the intermediate, the qualitative picture described in the following steps would not change. On the other hand, one may want to know whether H_2 can bind to the B center or the P center of the reactant **1** to form the corresponding association complex (Figure S1 in the Supporting Information). Our calculations show that the (electronic) binding energy in the corresponding B−H_2 (or P−H_2) complex is only 1.1 (or 0.3 kcal/mol). So, these two association complexes are less likely to occur during the H_2 activation process.

Although the encountered **8** is 7.6 kcal/mol in electronic energy below the sum of two reactant molecules (**1** + **1**), it is 13.1 kcal/mol in free energy above two separated reactants **1** + **1** (Figure 4). Thus, the encountered **8** may be a transient and not necessarily a thermodynamically stable species. However, considering the fact that the DFT methods, like B3LYP, may significantly underestimate the complex binding energy[13] for the weakly bound complex, the encountered **8** may be, in fact, more stable than as expected from the present DFT calculation.

In the next step, an H_2 molecule may enter into the region between the electrophilic B center and the nucleophilic P center of **8** to split into one proton and one hydride with the assistance of the concerted interaction of the Lewis acid−Lewis base pair. Nevertheless, we were unable to locate the transition state for this H−H bond cleavage to form the ion pair **10** because the full molecular model is quite large, and the potential energy surface around this transition state is flat. Instead, we turn to a detailed relaxed potential energy scan by fixing the H−H distance at various values in the range of 0.744−1.90 Å (Figure 5) . Our starting point is to set the H−H distance to be 0.744 Å (which is the optimized bond distance for free H_2 at the B3LYP/6−311++G(d,p) level), and insert this H_2 into the region between one B center and its adjacent P center of **8** (the B−P distance of 5.52 Å is fixed). Then, we increase the H−H distance gradually from 0.744 to 1.90 Å and optimize all the other degrees of freedom. As seen from Figure 5, the potential energy climbs up first and then decreases monotonously with an exothermicity of 13.3 kcal/mol (from **9TS** to **10**). The highest point, which can be considered as an approximate transition state (called as **9TS**), corresponds to the structure with the H−H distance of 0.85 Å. **9TS** is calculated to be 10.3 kcal/mol above the isolated reactants **8** and H_2. In the ion pair **10**, the B−H and P−H bonds are of 1.41 and 1.21 Å, respectively, and the H−H bond is completely broken into one proton and one hydride (the distance is 1.90 Å). However, these two splitted hydrogen atoms still have significant electrostatic interaction ($P{-}H^{\delta+}\cdots{}^{-\delta}H{-}B$). The binding free energy between two monohydrogenated components in **10** is computed to be 39.7 kcal/mol. If two monohydrogenated components are dissociated from **10**, two intermediates **11** and **12** will be generated. **10** is 21.0 kcal/mol above the reactants but 39.7 kcal/mol below the **11** +**12**. Thus, ion pair **10** is very difficult to dissociate into **11** and **12** in gas phase.

However, the solvent will dramatically change the potential energy surface. Relative to the reactants **1**+**1**+H_2, the dimeric species **8**, **9TS**, and **10** are considerably destabilized by the solvent, but the anion intermediate **11** and cation intermediate **12** are strongly stabilized by the solvent. For example, the free energy of solvation is 52.3 kcal/mol for **8**, and 46.4 kcal/mol for **10** (detailed data are given in Table S3 in the Supporting Information). Because the free energy of solvation is almost zero for the charged intermediate **11** or **12** (the attractive electrostatic contribution is almost canceled by the repulsive non-electrostatic contribution), the intermediates **11** and **12** are more stable than ion pair **10** (by 6.9 kcal/mol) after the solvation free energies are added. Therefore, the dissociation of **10** into the monohydrogenated species **11** and **12** should be facile in the solvent. When the solvent effect is considered, the barrier height for the H−H heterolytic cleavage is about 39.6 kcal/mol (above the reactants **1**+**1**+H_2), the generation of two monohydrogenated species (**11** and **12**) is endothermic by 27.3 kcal/mol.

From the optimized lengths of the C−P bonds in **1** and **11**, one can see that the active Lewis base center P in **11** is slightly influenced by the addition of the hydride to the B center. Similarly, the active Lewis acid center B in **12** should have the similar ability to activate H_2 like that in **1**. Because the monohydrogenated species **11** (or **12**) still has an active Lewis base P center (or Lewis acid B center), it may associate with **1** (or **12**) to form an encounter complex, according to the mechanism shown in Scheme 2. If the species **11** associates with the reactant **1** to form an encounter complex, this encounter complex will activate H_2 to produce the products **5** and **11**, the whole process is exothermic by 0.8 kcal/mol. But if the species **11** and **12** form an encounter complex, this encounter complex will react with H_2 to yield two molecules of **5**, which is exothermic by 28.9 kcal/mol (the solvent effect is included). Therefore, the association of the species **11** and **12** is more likely to take place during

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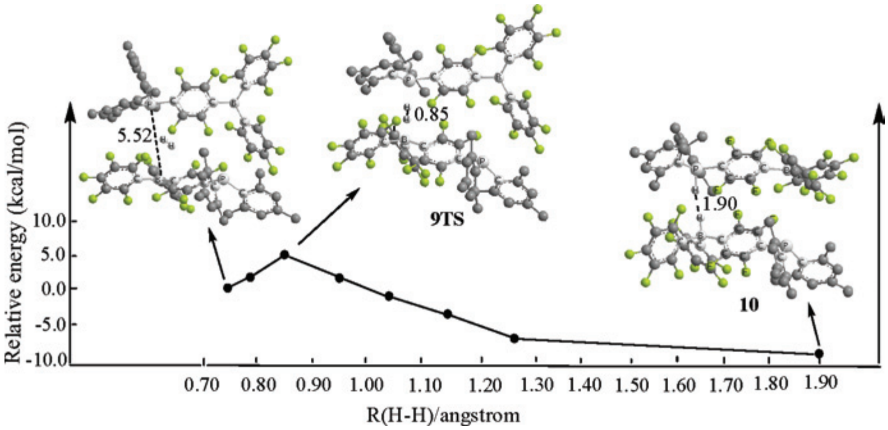

Figure 5. The relaxed potential energy scan for the H_2 cleavage step from **8**+H_2 to **10**. All hydrogen atoms (except in BH and PH) are omitted for clarity.

the reaction. The activation barrier for this second H−H cleavage by the corresponding encounter complex should be similar to that displayed in Figure 4. To conclude, two H_2 molecules are successively activated by the encounter complex with a pair of active B and P centers to produce two molecules of the fully hydrogenated product, **5**. The whole process from the reactants (**1**+**1**+2H_2) to the products (**5**+**5**) in the solvent is calculated to be exothermic by 1.6 kcal/mol (with the basis set II).

3.2.2 Simplified Molecular Model.

To better understand the H_2 activation step, we employ a simplified model to explore the potential energy surface for this step (Figure 6). The basis set II is used in all calculations. In this simplified model, the terminal C_6F_5 or $C_6H_2Me_3$ group connecting to the unreactive B (or P) center is replaced with a CH_3 group. So, the full molecular model of the reactant **1** can be simplified as **13** or **14**. Similarly, the species **15** is the simplified model to the encounter **8**. In **15**, the distance between a pair of active B and P atoms is 5.54 Å, and several C−H···F−C hydrogen bonds also exist between the monomer **13** and **14** (the shortest is 2.48 Å). A comparison of geometrical parameters in **15** with those in **8** indicates that **15** is a good approximation to the realistic dimeric species **8**. Energetically, **15** is 9.2 kcal/mol in free energy above the **13**+**14** (50% BSSE is considered). With **15** as the reactant, we have located the heterolytic H−H cleavage transition state **16TS**. In **16TS**, the P···H and B···H distances are 2.28 and 1.75 Å, respectively, and the H···H distance is elongated to 0.78 Å from 0.744 Å in free H_2. The transition vector clearly shows that the formation of both B−H and P−H bonds are concerted. The resulting ion pair **17** also has a similar structure as the realistic intermediate **10** in the active center. The H−H cleavage free energy barrier is 21.1 kcal/mol in the gas phase (relative to the reactants **13**+**14**+H_2) and 33.7 kcal/mol in the solvent. This barrier is slightly lower than that (39.6 kcal/mol) estimated with the relaxed potential energy scan in the preceding section.

To clarify the reactivity of the encounter complex with H_2, we have performed natural population analyses[14] for the reactant (**15**), transition state (**16TS**), and the product (**17**). The natural charges on atoms involved in the H−H cleavage step are listed in Table 1. The natural charge on the P atom increases from 0.89e in **15** to 0.96e in **16TS** and to 1.33e in **17**. At the same time, the natural charge on the B atom gradually decreases from 0.89e in **15** to 0.76e in **16TS**, and to 0.11e in **17**. It seems that H_2 acts as a bridge for electron transfer from the Lewis base P center to the Lewis acid B center. Natural charges on the P-bound and B-bound H atoms in **16TS** are 0.16e and −0.10e, respectively, implying a heterolytic cleavage process. Furthermore, the perturbation theory energy analysis[14] for **16TS** shows that the $n_P \rightarrow \sigma_{H-H}^*$ interaction is 22.0 kcal/mol and the $\sigma_{H-H} \rightarrow n_B^*$ interaction is 39.6 kcal/mol. This result clearly shows that the electron transfer from the lone pair orbital of the P atom to the σ^* orbital of H_2 and that from the σ orbital of H_2 to the empty p orbital of the B atom occur simultaneously, resulting in the breaking of the H−H bond. Thus, one can see that the H−H bond is heterolytically cleaved by the cooperation between a pair of active Lewis acid B and Lewis base P centers.

3.3. Comparisons with Experimental Results and Related Theoretical Studies.

According to our proposed mechanism, the dimeric encounter complex and the ion-pair complex should be the intermediates involved in the H_2 activation process. From the literature, we have found some indirect experimental evidence to support this viewpoint. In the crystal structure of $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ (**5**) reported previously,[6] there exist several C−H···F−C hydrogen bonds (the shortest H···F distance is 2.58Å) between two molecules of **5**, an indication that an encounter complex may form between two molecules of **1**. In a similar dihydrogen activation process, the crystal structure of the ion pair complex $(t\mathrm{Bu})_3P-H^{\delta+}\cdots{}^{-\delta}H-B(C_6F_5)_3$ was determined,[5] in which the H···H distance is 2.75 Å. In another study,[15] the molecule $(C_4H_9)_2PH(C_6F_4)BH(C_6F_5)_2$ was also crystallized, in which two monomers pack in a head-to-tail manner in the solid state, with significant $P-H^{\delta+}\cdots{}^{-\delta}H-B$

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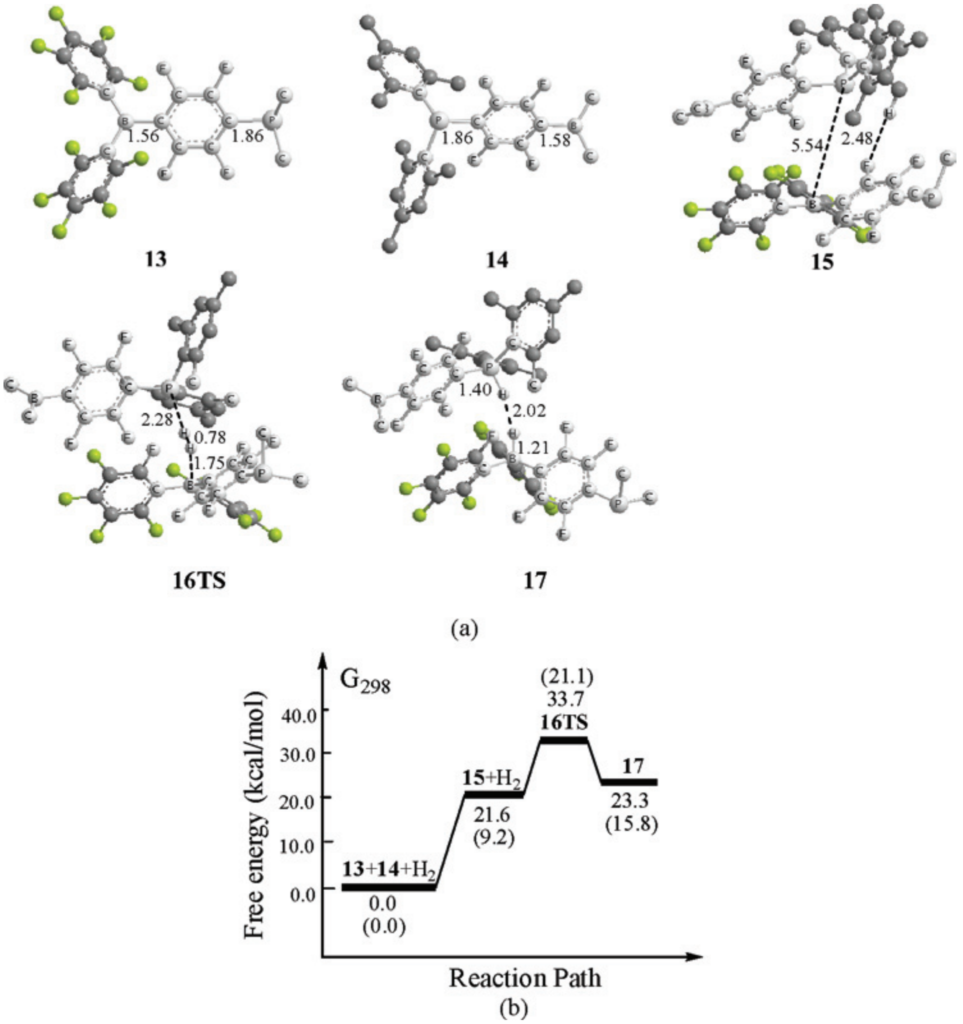

Figure 6. (a) Optimized geometries of some stationary points in the concerted Lewis acid−Lewis base mechanism (with the simplified molecular model); (b) and the corresponding free-energy profile. Free energies in the gas phase are given in parentheses. The free energies of loosely bounded species, **15** and **17**, are corrected by the 50% BSSE.

Table 1. Natural Charges (in a.u.) on P-bound H, B-bound H, B, and P atoms in **15**, **16TS** and **17**

	15	16TS	17
B	0.89	0.76	0.11
P	0.89	0.96	1.33
H (P−H)		0.16	0.09
H (B−H)		−0.10	−0.03

interactions (H···H = 2.602 Å). These results imply that the participation of the ion-pair intermediate **10** during the reaction process is highly possible.

In comparison with the proton transfer mechanism and hydride transfer mechanism, the concerted Lewis acid−Lewis base mechanism has a relatively lower free-energy barrier in the rate-limiting step (33.7 kcal/mol versus 54.7, 69.1 kcal/mol). This mechanism is reasonably consistent with the experimental facts that **1** can react rapidly with H_2 at 25 °C, but the reverse reaction takes place at temperatures above 100 °C because **1** is 1.0 kcal/mol higher above **5**. In the experiments, heating solutions of a 1:1 mixture of $(C_6H_2Me_3)_2PD(C_6F_4)BD(C_6F_5)_2$ and $(C_6H_2Me_3)_2PH(C_6F_4)BH(C_6F_5)_2$ to temperatures above 100 °C resulted in the release of H_2, D_2, and HD. The observation of HD implies a bimolecular exchange process involving the intermolecular approach of BD and PH fragments (or BH and PD fragments). Clearly, this experimental fact can be well accounted for by the mechanism proposed here. According to our mechanism, the release of H_2 (or HD, D_2) involves an intermolecular process, in which two molecules **5** (or deuterated **5**) should first form an association complex.

A recent theoretical work on the base-catalyzed hydrogenation of carbonyl compounds provides an implication for this mechanism, in which H_2 is activated by the electrophilic C atom of C═O and the nucleophilic O atom of $NaOCH_3$ via a six-membered-ring transition state.[16] Very recently, we found that the reaction of olefins with the sterically demanding phosphines and boranes[17] could also be explained by a similar concerted Lewis acid−Lewis base mechanism.[18] We also noted that, during the revision of this manuscript, a similar mechanism for the H_2 activation by a combination

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of $P(tBu)_3$ and $B(C_6F_5)_3$ was reported by Pápai et al.[19] In their theoretical study, H_2 activation was also suggested to be initiated by the association of $P(tBu)_3$ and $B(C_6F_5)_3$ to form a weakly bound complex, followed by the heterolytic cleavage of the H−H bond with the assistance of the phosphine-borane pair. This association complex $[P(tBu)_3\cdots B(C_6F_5)_3]$ (with a P···B distance of 4.2 Å) is also stabilized by a combination of multiple C−H···F−C hydrogen bonds and dispersion interactions. The association energy was calculated to be −11.5 kcal/mol, which is close to −12.6 kcal/mol (without BSSE correction) in species 15 calculated in this work. The transition state for the H−H bond cleavage located by Pápai et al.[19] is also similar to **16TS** we found here. To summarize from discussions above, we conclude that the concerted Lewis acid−Lewis base mechanism is most likely to be responsible for the observed H_2 activation.

4. Conclusions

In this article, we have presented a detailed density functional theory study to investigate the possible reaction mechanisms for the reversible H_2 activation catalyzed by a metal-free phosphonium−borate compound. Three possible pathways have been explored, which include: (1) the proton transfer mechanism; (2) the hydride transfer mechanism; (3) the concerted Lewis acid−Lewis base mechanism. The former two pathways suggested previously are found to be much less favorable than the concerted Lewis acid−Lewis base mechanism proposed in the present work. In the concerted Lewis acid−Lewis base mechanism, the H−H heterolytic cleavage is achieved through the simultaneous electron transfer from the lone pair orbital of the P atom to the σ^* orbital of H_2 and from the σ orbital of H_2 to the empty p orbital of the B atom. Our calculations also show that the solvent effect dramatically changes the potential energy surfaces. The present mechanism can account well for the bimolecular H−D exchange process observed in deuteration experiments and the experimental fact that the H_2 activation is reversible at mild conditions.

The present mechanism would be helpful for experimentalists to design more effective compounds that can catalyze the dihydrogen activation process. For example, the combination of other Lewis acids and Lewis bases is expected to be also applicable for H_2 activation. Of course, more experiments should be designed to validate the proposed mechanism.

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Supporting Information Available: 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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