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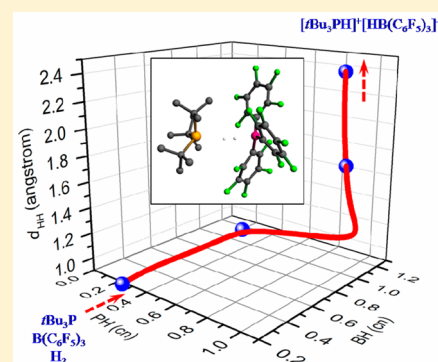
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Hydrogen Activation by Frustrated Lewis Pairs Revisited by Metadynamics Simulations

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Supporting Information

ABSTRACT: Frustrated Lewis pairs have great potential as metal-free catalysts, for example, for the activation of molecular hydrogen. However, rational design of improved catalysts is hampered because the catalytic reaction mechanisms still remain largely unclear. In this study, we present a density-functional-theory-based metadynamics study of the hydrogen activation by a typical frustrated Lewis pair, *t*Bu₃P/B(C₆F₅)₃. The computed free-energy landscape reveals a different reaction path compared with the ones in the literature. Importantly, we found different roles of the Lewis acid and base centers in the hydrogen activation. The rate-determining step is the hydride transfer to the Lewis acid, and the overall reaction is found to be exothermic once the proton transfer to the Lewis base step is accomplished.



INTRODUCTION

Several years ago, Stephan and coworkers introduced the concept of “frustrated Lewis pairs” (FLPs).¹ In these systems, the Lewis acid and base are sterically hindered by the presence of bulky organic substituents and hence are not neutralized. Instead, they form a complex, in which the reactivity of the Lewis acid and base remains. Interestingly, such FLPs were shown to be able to activate molecular hydrogen. The first example of such a catalytically active FLP was the covalently linked, sterically precluded, phosphinoborane (C₆H₂Me₃)₂-PC₆F₄B(C₆F₅)₂ (Me = methyl).¹ It was shown that this compound heterolytically activates and eliminates molecular hydrogen at a temperature of 150 °C. This remarkable finding represents the first known nonmetal system, which is able to both take up and release hydrogen molecules. A year later, stoichiometric mixtures of the Lewis acid B(C₆F₅)₃ with bulky phosphines R₃P (R = *t*Bu, C₆H₂Me₃) were shown to yield the corresponding hydrogenated ion-pair product, [R₃PH]⁺[HB(C₆F₅)₃]⁻, upon exposure to 1 atm of H₂ at 25 °C in toluene.² Around the same time, Erker et al. reported a remarkable four-membered heterocyclic phosphane-borane adduct, (C₆H₂Me₃)₂-PCH₂CH₂B(C₆F₅)₂, which was also demonstrated to activate hydrogen.³ When exposing a pentane solution of this compound to 1.5 atm of H₂ at 25 °C, the authors obtained a large amount of white phosphonium-borate salt [(C₆H₂Me₃)₂PH]⁺CH₂CH₂[BH(C₆F₅)₂]⁻ within 15 min. Later on, the FLP concept was

extended to include other Lewis systems, mainly consisting of the elements P/B or N/B combinations, and to activate other small molecules, such as CO₂, SO₂, and NO.^{4–9}

The hydrogen activation by FLPs has also attracted the interest of computational and theoretical chemists, which has so far lead to the proposal of two reaction mechanisms based on density functional theory (DFT) calculations. The first mechanism, a so-called electron-transfer (ET) model, was proposed by Pápai et al.¹⁰ Detailed molecular-orbital analysis indicates that a simultaneous ET from the lone pair of *t*Bu₃P to the σ*(H₂) orbital and from the σ(H₂) to the empty orbital of B(C₆F₅)₃ weakens the H–H bond and subsequently cleaves the hydrogen molecule heterolytically.¹¹ An alternative mechanism, the so-called electric-field (EF) model, was later proposed by Grimme et al.¹² This mechanism suggests that the hydrogen molecule is simply polarized by the EF, which is created by the acid–base pairs, and subsequently split without overcoming further energy barriers. Despite the considerable amount of studies on the hydrogen activation by FLPs, the actual mechanism is still under debate.¹³ It is commonly believed that the Lewis acid and base work in a cooperative way. However, their individual roles in the hydrogen activation remain unclear.

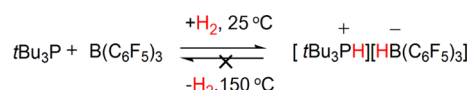
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In this study, we performed metadynamics and path-metadynamics¹⁴ simulations (which are based on the DFT-D level of theory) to compute the free-energy surface (FES) at finite temperature and to explore the lowest free-energy reaction path for the hydrogen activation by the prototypical FLP: $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ (Scheme 1). Probing the free-energy

Scheme 1. Hydrogen Activation by an Intermolecular FLP, $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$



landscape rather than the zero Kelvin potential energy surface allows us to incorporate entropic contributions due to flexible nature of the FLP complexes. By analyzing the FES, we aim to understand the detailed reaction path. More importantly, we intend to find out the individual roles of Lewis acid and base centers in the hydrogen activation.

RESULTS AND DISCUSSION

We started the ab initio, DFT-based, molecular dynamics (DFT-MD) simulations with the hydrogenated zwitterionic product, $[t\text{Bu}_3\text{PH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$, the structure of which was confirmed by X-ray crystallography.² As a result, we first see a hydrogen liberation process along the simulation instead of the reverse hydrogen activation process. The variance of the distances between phosphorus, boron, and hydrogen atoms versus the simulation time is depicted in Figure 1. We marked

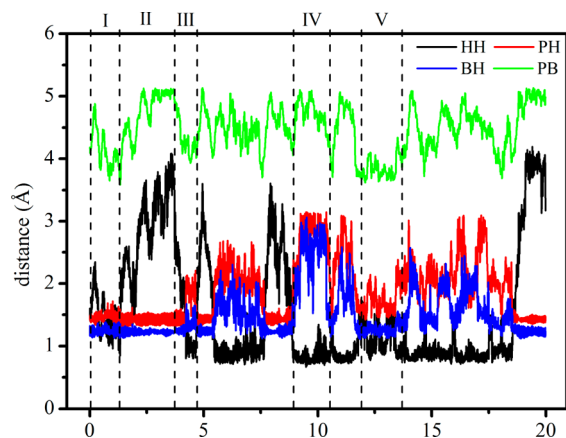


Figure 1. Illustration of the variation of $R(\text{H}-\text{H})$, $R(\text{P}-\text{H})$, $R(\text{B}-\text{H})$, and $R(\text{P}-\text{B})$ as functions of simulation time obtained from metadynamics simulations of hydrogen activation by $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ pair.

the trajectory with five representative regions, denoted as I, II, III, IV, and V, as shown in Figure 1, and we discuss hereafter each of the regions in chronological order. Region I: This region is basically the equilibration of the hydrogenated product at room temperature. The P–H and B–H bond lengths remained constant (<1.5 Å), whereas the P–B and H–H distances oscillated around their equilibrium values (4.0 Å for $R(\text{P}-\text{B})$ and 1.5 Å for $R(\text{H}-\text{H})$). This finding exposes the fact that the structure of the hydrogenated product is rather flexible due to the fact that the whole complex is bound via only weak van der Waals interactions and hydrogen bonds. Region II: Two charged fragments, $[t\text{Bu}_3\text{PH}]^+$ and $[\text{HB}(\text{C}_6\text{F}_5)_3]^-$ moved away from each other, and the distance between phosphorus

and boron atoms increased from 4.0 to 5.0 Å, while P–H and B–H bond lengths remained the same as that in region I, and the largest P–B distance is found in this region. The orientation of two charged fragments changed freely along the simulations, which is implied by the comparison of H–H and P–B distances. For example, the H–H distance varies from 1.5 to 4.0 Å. However, the P–B distance has a change of only 1 Å. This requires that the two hydrogen atoms (from the hydrogen molecule) have to point to different directions by changing the orientation of two fragments. Region III: The two fragments moved closer, and the P–B distance decreased from 5.0 to 4.0 Å. We found a dramatic change in the H–H distance in this region. The distance between the two hydrogen atoms decreases from 4.0 to 0.8 Å within <0.5 ps. This indicates that these two hydrogen atoms start to interact with each other and to form a hydrogen molecule. In this region, the P–H and B–H distances are, respectively, about 2.0 and 1.5 Å, indicating that the two hydrogen atoms still have certain interactions with both phosphorus and boron atoms. In short, region III in Figure 1 is a hydrogen molecule liberation preparation step, and it is an interface between the free hydrogen molecule and complete hydrogen split states. Region IV: The H–H distance decreased to 0.7 Å, B–H and the P–H distance increased to ~ 3 Å, and the P–B distance increased to ~ 4.5 Å. There are no interactions between hydrogen and phosphorus (or boron atoms) because both P–H and B–H distances are much longer than the typical P–H and B–H bond lengths. Therefore, a free hydrogen molecule is finally formed in this region. It is important to point out that P–B distance does not significantly change during the formation of a hydrogen molecule (i.e., the change is <0.5 Å). This finding is similar to that reported by Pu et al.¹⁵ Using AIMD simulations, the authors showed that the P–B distance remains almost frozen along the hydrogen cleavage process. Our finding is also in contrast with previous DFT calculations, in which the P–B distance changes almost 2 Å (i.e., from 5.8 to 4.0 Å) along the reaction path.¹⁶ Region V: the phosphorus and boron atoms have the shortest distance of 3.5 Å along the trajectory. The P–H is ~ 2 Å, whereas the B–H distance is ~ 1.2 Å. The distance between two hydrogen atoms is found to be from 1.0 to 1.5 Å. This indicates that in this region the hydrogen molecule is split into a proton and a hydride: The hydride is already captured by the boron atom, whereas the proton is still free.

On the ground of DFT calculations, two minima have been found on the potential energy surface, the hydrogenated product and the three component complex ($t\text{Bu}_3\text{P} + \text{B}(\text{C}_6\text{F}_5)_3 + \text{H}_2$).¹⁶ However, four minima have been found on the FES via metadynamics simulations, revealing a rather complicated reaction path. The geometries and the selected distances are depicted in Figure 2 (denoted as A, B, C, and D). In structure A, the hydrogen molecule is located almost perpendicular to the axis of phosphorus and boron atoms with a B–H–H angle of 70° , and the H–H distance is found to be 0.8 Å. According to previous studies,^{10,12,16,17} such a long H–H distance indicates that hydrogen molecule is starting to be polarized because the H–H bond length of the free hydrogen molecule is 0.74 Å. On the contrary, the hydrogen molecule is not completely split because the P–H and B–H distances are about 2.5 and 2.4 Å, respectively, which are larger than the typical P–H and B–H bond lengths (1.4 and 1.2 Å, respectively). It is interesting that the minimum A shows geometric features similar to that in the transition state, which has previously been identified by DFT calculations.^{10,12,16,17} In the structure of the TS, the hydrogen

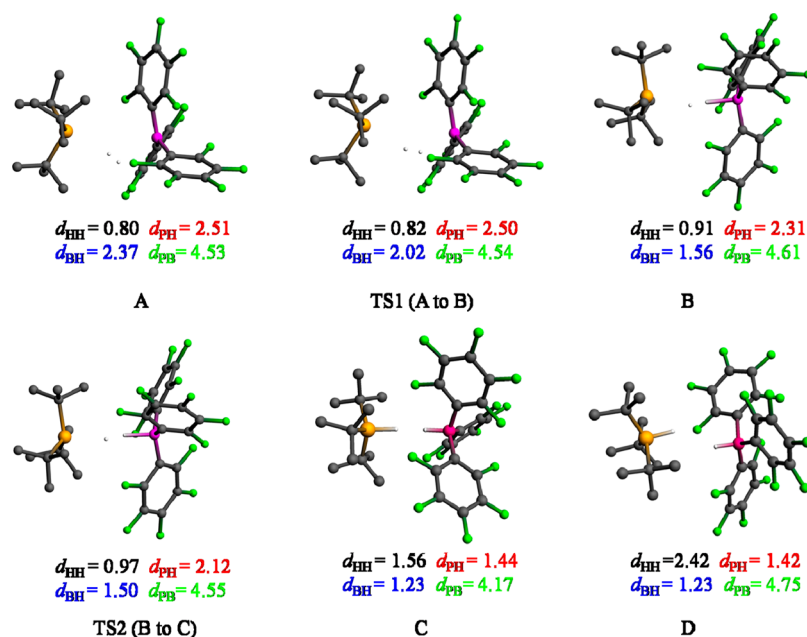


Figure 2. Representative structures of the four minima and two transition states obtained from metadynamics simulations with selected distances given in angstroms. Hydrogen atoms except in the hydrogen molecule are omitted for clarity. Color legend: P, yellow; B, pink; C, black; F, green; and H, white.

molecule is further polarized with the H–H distance varying from 0.78 to 0.89 Å, depending on the substitutes on the phosphorus and boron atoms, while the hydrogen has stronger interactions with phosphorus and boron atoms. The P–H distance varies from 1.78 to 2.28 Å, and the B–H distance varies from 1.38 to 1.94 Å in the TS.¹⁵ In structure B, the hydrogen molecule is split, and the distance between the two hydrogen atoms is 0.9 Å. The hydride is already attached to the boron atom, with a B–H distance of 1.6 Å, which is somewhat larger than the typical B–H bond length (~1.2 Å). However, the proton is still free, and the P–H bond is not formed; the P–H distance is 2.3 Å, which is much larger than the typical P–H bond length (~1.4 Å). The two hydrogen atoms move further into the pocket of the FLP complex with a P–H–H–B dihedral angle of 175°. The transition state connecting A and B (TS1) shows similar P–H and H–H distances to A, which are 2.5 and 0.82 Å, respectively. The B–H distance of 2.0 Å in TS1 is between that in states A and B. In structure TS2, which is the transition state of the proton-transfer step to the phosphorus atom, the H–H distance is found to be ~1.0 Å, as the proton moves closer to the phosphorus atom, which is at a P–H distance of 2.1 Å. We have found two conformers for the final hydrogenated product, $[\text{tBu}_3\text{PH}]^+[\text{HB}(\text{C}_6\text{F}_5)_3]^-$, denoted as C and D in Figure 2. In structure C, the hydrogen molecule is completely split, and both the proton and hydride are attached to the Lewis base (phosphorus) and acid (boron) centers. The distance between the two hydrogen atoms is 1.6 Å, and the P–H and B–H bond lengths are 1.4 and 1.2 Å, respectively. This configuration of the hydrogenated product is often found by the DFT calculations with similar geometric parameters, regardless of the computational level.^{10,12,16} Unlike the static DFT calculations, we have found a second configuration for the final hydrogenated product, denoted as structure D in Figure 2. The difference between C and D is the orientation of the two charged fragments. In structure C, the Lewis acid and base centers have a face-to-face orientation resulting in a shorter H–H distance (1.2 Å), and the three atoms (H⁺, B, and P)

have an almost linear arrangement with a P–H–H–B dihedral angle of 10°. In structure D, the two charged species are shifted with respect to each other, and the phosphorus atom points to one of the three C₆F₅ groups of B(C₆F₅)₃. The two dissociating hydrogen atoms point to different directions, resulting in a larger H–H distance (2.4 Å). In a previous study by Pu et al., two different conformers were found for the *t*Bu₃P/B(C₆F₅)₃ pair on the ground of conformational dynamics search.¹⁵ In one case, the phosphorus atom directly faces the boron atom, which is a face-to-face arrangement; however, in the other, the phosphorus atom faces one of the C₆F₅ groups of B(C₆F₅)₃.

The FES obtained from the metadynamics simulations is depicted in Figure 3. It is worth noting that often GGA functionals underestimate the energy barriers. However, the aim of this work is not to have a quantitative comparison with respect to the experimental findings. The relative energies between different elementary reaction steps follow, however, a similar trend at a different level of theory. In the following, we discuss the reaction mechanism for every elementary step:

(1) H₂ polarization: In this step, the hydrogen molecule moves freely into the pocket of the *t*Bu₃P/B(C₆F₅)₃ pair and becomes polarized through the interactions with the FLP complex. On the basis of DFT calculations, it was shown that hydrogen molecule needs to overcome a small energy barrier (<10 kcal mol⁻¹) to enter the pocket of the *t*Bu₃P/B(C₆F₅)₃ pair.¹² We do not observe this barrier because the starting point of our reaction path is state A, in which the hydrogen molecule is already in contact with the FLP. We take state A as the reference for our free-energy scale, which is ~10 kcal/mol higher in energy than the separated H₂ and FLP fragments often used as the reference in static DFT calculations.¹⁶

(2) Hydride transfer: After polarization of H₂, the hydride first attaches to the Lewis acid center (the boron atom), overcoming a free-energy barrier of 10 kcal mol⁻¹ and forming structure B (Figure 2).

(3) Proton transfer: The proton is subsequently transferred to the Lewis base center (the phosphorus atom). The energy

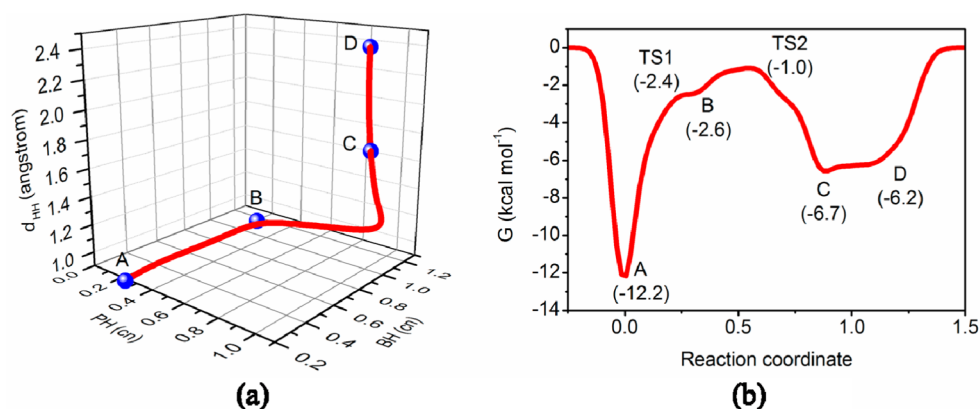


Figure 3. (a) Minimum free energy path in the space of collective variables. (b) Free-energy profile of the hydrogen activation by $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ pair obtained from the path-metadynamics simulation. The values of free energies are given in parentheses in kcal mol^{-1} .

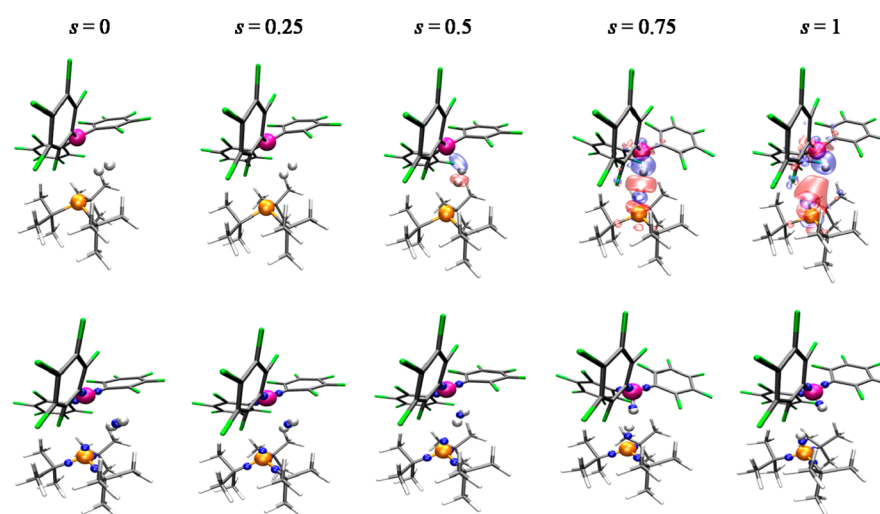


Figure 4. Top: electron density difference (isocontour value: $\pm 0.005 e$) upon H_2 dissociation. The difference is calculated via $\rho(\text{FLP}-\text{H}_2) - \rho(\text{FLP}) - \rho(\text{H}_2)$. Blue isosurface: gain of electron density; red isosurface: loss of electron density. Bottom: Wannier center displacement upon H_2 dissociation. Color legend: Wannier centers, blue; P, yellow; B, pink; C, black; F, green; and H, white.

barrier for this step is $\sim 2 \text{ kcal mol}^{-1}$, which is almost one-fifth of that for the hydride transfer step. Finally, two partially charged fragments, $[\text{tBu}_3\text{PH}]^-$ and $[\text{HB}(\text{C}_6\text{F}_5)_3]^+$, are formed. Importantly, we found that this step is exothermic with a free energy of -4 kcal mol^{-1} , which is downhill on the FES, as opposed to the hydride transfer step ($\sim +9 \text{ kcal mol}^{-1}$). The overall reaction is endothermic with a Gibbs free energy of $+6 \text{ kcal mol}^{-1}$. However, the endothermicity is largely due to the neglect of the solvation free energy, which contributes to about $-10 \text{ kcal mol}^{-1}$ in the case of hydrogen activation by FLPs.¹⁸ By including the solvation Gibbs free energies to the key states on the FES, we obtained a value of -3 kcal mol^{-1} as the overall reaction Gibbs free energies (see Table S1 in the Supporting Information). In recent studies, a common geometrical feature has been found in the structure of the TSs for the hydrogen activation by several intramolecular FLPs.^{19–21} The elongated hydrogen molecule shows a side-on arrangement to the boron atom and end-on arrangement to the phosphorus atom. The single imaginary vibrational mode of the TSs shows stronger interactions between the boron and the hydrogen atoms than that between the phosphorus and the hydrogen atoms.^{19–21} The computed covalent bond orders indicate that the B–H bond is formed earlier than the P–H bond in the TS for H_2 activation by an intermolecular FLP, $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$.¹²

These interesting geometrical features hint that the boron atom first interacts with the hydrogen molecule, capturing the hydride; subsequently, the remaining proton is captured by the phosphorus atom.

(4) Stabilization: Two charged fragments are then rearranged in a way that the Lewis acid and base centers have a face-to-face orientation (state C in Figure 3). The second conformer (state D) is found to be $0.5 \text{ kcal mol}^{-1}$ less stable in free energy, and the energy barrier to separate these two final states is almost zero. This indicates that both of the conformers (C and D) can exist as the final hydrogenated products, and they can transform to each other at room temperature. A similar situation has also been found in the case of hydrogen activation by an intramolecular FLPs, $\text{Mes}_2\text{PCH}_2\text{CH}_2\text{B}(\text{C}_6\text{F}_5)_2$. The final hydrogenated product can be in two states (trans and cis configurations by changing the dihedral angle of P–C–C–B chain), and the energy barriers between these two structures are $< 10 \text{ kcal mol}^{-1}$ based on DFT calculations.²² In the crystals, structure C was obtained. It might be that structure D was transferred into structure C during the crystallization process. It allows a perfect stacking to decrease the disorder of the system.

To gain deeper insight into the reaction mechanism, we have computed the electron density difference (that is the difference in the total electron density between the complex and the

noninteracting H₂ and FLP fragments with the same geometry) and the centers of maximally localized Wannier functions^{23,24} along the minimum free-energy path (MFEP). The results are displayed in Figure 4 for five equidistant snapshots along the path ($s = 0.0, 0.25, 0.5, 0.75,$ and 1.0 , which have geometric features similar to the structures presented in Figure 2). The results show that at $s = 0$ and 0.25 , in which the hydrogen molecule is still relatively far from the FLP reactive centers (average P–H and B–H distances are >2.5 Å), no noticeable charge transfer occurs between hydrogen and phosphorus or boron atoms. When the hydrogen molecule approaches the FLP active site, charge transfer is seen to take place from the H–H bond to the B–H bond ($s = 0.5$). Subsequently, polarization takes place at the phosphorus atom as its lone pair is stretched toward the now positively charged hydrogen atom ($s = 0.75$). Finally, the hydrogen molecule dissociates heterolytically as the proton binds to the phosphorus, leaving the hydride at the boron ($s = 1$). These findings are further confirmed by the plots of the centers of the Wannier orbitals along the MFEP (bottom panels in Figure 4). These Wannier centers typically localize at chemically intuitive electron pair positions, such as nuclei, chemical bonds, and lone pairs. We clearly see that one electron pair stays at the P atom, first as the P lone-pair and subsequently forming the P–H bond as the proton (without Wannier center) arrives. The electron pair forming the H–H bond transfers to the H atom closest to the boron and further to form the B–H bond. For further details, see the Figure S5 in the Supporting Information.

CONCLUSIONS

The reaction of hydrogen molecule with $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ FLP is revisited using DFT-based metadynamics simulations. The obtained lowest free-energy reaction path and the reaction mechanism are more eventful than previously suggested by static DFT calculations in the literature. Specifically, the hydrogen activation by $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ pair consists of multiple-elementary steps: polarization of hydrogen molecule, hydride transfer, and proton transfer. Interestingly, we have not obtained a minimum on the FES in which a regular hydrogen molecule is present. Once the hydrogen molecule moves inside the pocket of the FLPs, it becomes polarized by the interactions with FLP-complex. After H₂ polarization, the reaction continues in two more steps: hydride transfer to the boron atom and proton transfer to the phosphorus atom via the ET from the hydrogen (H[−]) to the boron atom and from the phosphorus atom to the hydrogen (H⁺). Previously, it was commonly believed that the roles of the Lewis acid and base centers are the same, supplying enough strength to cleave the H–H bond in a cooperative way. Instead, here we see different roles of the two reactive centers. Along the reaction path, the hydride transfer to the boron atom has the highest free-energy barrier, indicating that this step is the rate-determining step. The whole process is exothermic once the proton transfer to the phosphorus atom is achieved.

COMPUTATIONAL DETAILS

All DFT calculations (including geometry optimizations and ab initio molecular dynamics (AIMD) simulations) were performed using the CP2K program²⁵ with the Gaussian and plane-wave (GPW) method.²⁶ The valence orbitals were expanded in the DZVP-GTH Gaussian basis set, while an auxiliary plane-wave basis set up to the kinetic energy cutoff of 250 Ry was used to describe the valence electron density.

The core electrons were replaced by pseudopotentials. We used the PBE density functional²⁷ augmented with the Grimme D3 dispersion correction.²⁸ To avoid spurious interactions due to the periodicity of the planewave basis, we used the Martyna–Tuckermann technique²⁹ and a rather large $20 \times 20 \times 20$ Å unit cell. The AIMD simulations were done in the NVT ensemble, with the temperature controlled by a Nosé–Hoover chain thermostat of length 4, set at a temperature of 300 K, and a period of 500 fs. The MD time step was 0.5 fs.

In the metadynamics simulations, we used three collective variables (CVs) to bias the making and breaking of bonds between the phosphorus, boron, and hydrogen atoms, in particular: (1) the distance between the two hydrogen atoms in the hydrogen molecule ($R(\text{H–H})$), (2) the coordination number of the phosphorus atom by these hydrogen atoms (cn_{PH}), and (3) the coordination number of the boron atom by the hydrogen atoms (cn_{BH}). The advantage of coordination numbers as CVs is that those describe the unbounded states ($\text{cn} = 0$) and bound states ($\text{cn} = 1$) without specifying which hydrogen atom is involved in the reaction with phosphorus or boron atoms. The coordination number is functionalized as a sum of switch functions as follows

$$\text{cn} = \sum_j \frac{1 - \left(\frac{r_{ij}}{r_0}\right)^n}{1 - \left(\frac{r_{ij}}{r_0}\right)^m}$$

in which r_{ij} is the distance between the central atom i ($i = \text{P}, \text{B}$) and hydrogen atom j . The parameters were set to $n = 12$, $m = 24$, and $r_0 = 4.0$ au. Quadratic walls were used to avoid the sampling of uninteresting parts of the configuration space. In particular, the distance between phosphorus and boron atoms was limited to be <5.0 Å, and the PH and BH distances were restricted to be at most 3 Å. The Gaussian bias potentials were initially spawned every 25 time steps, with a height of $0.25 \text{ kcal mol}^{-1}$ and widths of 0.4 au along $R(\text{H–H})$ and 0.15 along cn_{PH} and cn_{BH} . After 10 ps of metadynamics simulation, the height was reduced to $0.10 \text{ kcal mol}^{-1}$ and the deposit interval was reduced to 50 MD steps. The path-metadynamics simulations¹⁴ were performed to further optimize the 1D free-energy profile along the MFEP. This path was obtained from the 3D metadynamics potential using the trace_irc program.³⁰ The path was expressed as a string of nodes in the space of the three metadynamics CVs, with 20 nodes in between the stable reactant and product minima and an additional 20 node extensions on either side. The Gaussian bias potentials were spawned every 100 time steps (50 fs), with a height of $0.5 \text{ kcal mol}^{-1}$ and a width of 0.05 au. The metadynamics and path-metadynamics simulations were carried out using the PLUMED plug-in³¹ in combination with CP2K.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.6b09991.

Additional information on path-metadynamics simulations and the Cartesian coordinates of the six structures depicted in Figure 2. (PDF)

Movie of molecular dynamics simulations at 300 K. (MPG)

Movie of electron density difference displacement upon H₂ dissociation. (MPG)

Movie of Wannier center displacement upon H₂ dissociation. (MPG)

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Notes

The authors declare no competing financial interest.

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