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A Novel Addition Mechanism for the Reaction of "Frustrated Lewis Pairs" with Olefins

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Density functional theory calculations have been carried out to investigate the addition mechanism for the reactions of "frustrated Lewis pairs" with olefins. Several reactions are studied in this work, which include a three-component reaction between a sterically demanding phosphane [P(*t*Bu)$_3$], borane [B(C$_6$F$_5$)$_3$], and ethylene, and a two-component reaction between an olefin derivative of phosphane [CH$_2$=CH–(CH$_2$)$_3$P(*t*Bu)$_2$] and B(C$_6$F$_5$)$_3$. For the two-component reaction, we find a concerted addition mechanism, in which the formation of the B–C and P–C bonds takes place simultaneously. For the three-component reaction, our calculations show that the reaction may be initiated by the weak association of B(C$_6$F$_5$)$_3$ with ethylene (to form a transient species) and then proceeds in a concerted transition state similar to that in the two-component reaction under study. The natural population analyses for the corresponding transition states indicate that the CH$_2$=CH group (in the two-component reaction) and C$_2$H$_4$ (in the three-component reaction) seem to act as a bridge for electron transfer from the Lewis base center P to the Lewis acid center B. We also investigate the reaction between P(*t*Bu)$_3$, propylene, and B(C$_6$F$_5$)$_3$. The results account well for the experimentally observed regioselectivity. In addition, our calculations also indicate that the presence of fluorine atoms in the borane is essential for stabilizing the addition product.

Introduction

The Lewis acid–base adduct is a very classical concept in chemistry. The interaction between Lewis acids and Lewis bases provides the guiding rule for many areas of chemistry.[1] It is generally accepted that the Lewis acid/Lewis base interaction is strong enough to form a Lewis acid–base adduct in many cases.[2] Recently, Stephan et al.[3] have found an unprecedented reactivity for the system containing sterically hindered phosphanes and boranes, in which the interaction between them is precluded by large substituents (such a pair of phosphanes and boranes was called a "frustrated Lewis pair"). For example, dihydrogen can be activated by a sterically demanding phosphane–borane compound[3a] or a combination of phosphanes and boranes.[3b] Very recently, it was reported that olefins can react with a combination of sterically demanding phosphane P(*t*Bu)$_3$ and borane [B(C$_6$F$_5$)$_3$] at room temperature.[4] Experiments also showed that olefin derivatives of phosphanes, CH$_2$=CH–(CH$_2$)$_3$PR$_2$ (R = *t*Bu, C$_6$H$_2$Me$_3$), can react with B(C$_6$F$_5$)$_3$ in CH$_2$Cl$_2$ at 25–45 °C to form cyclized phosphonium borates R$_2$PCH(C$_3$H$_6$)CH$_2$B(C$_6$F$_5$)$_3$. Interestingly, the formation of the complex B(C$_6$F$_5$)$_3$–C$_2$H$_4$ was not observed in the experiments with ^{19}F, ^{11}B, and ^{1}H NMR (183 K).[4] Nevertheless, previous experiments demonstrated that BF$_3$ and C$_2$H$_4$ may form a weakly bound complex in liquid argon (93–125 K).[5] MP2 calculations[6] revealed that the interaction between BF$_3$ and C$_2$H$_4$ in the BF$_3$–C$_2$H$_4$ complex is quite weak. Thus, the observed three-component reaction between olefins, phosphane, and borane is unprecedented, since neither tertiary phosphane nor tertiary borane exhibits significant reactivity with olefins, but a combination of them can react with olefins. Stephan et al.[4] have suggested that the first step of this reaction may still be the activation of the C=C bond by the borane, but phosphane should play a significant role in driving the addition reaction. Apparently, understanding the reactivity of such a "frustrated Lewis pair" is very important for extending the "frustrated Lewis pair" to other potential reactions.

Results and Discussion

Here, we report a detailed B3LYP density functional theory (DFT)[7] study to gain insight on the molecular mechanism of this type of reaction. The solvent effect is taken into account with the PCM method.[8] Two reactions are chosen in this work to study the possible addition mechanisms. One is the two-component reaction between B(C$_6$F$_5$)$_3$ and CH$_2$=CH–(CH$_2$)$_3$P(*t*Bu)$_2$, and the other is

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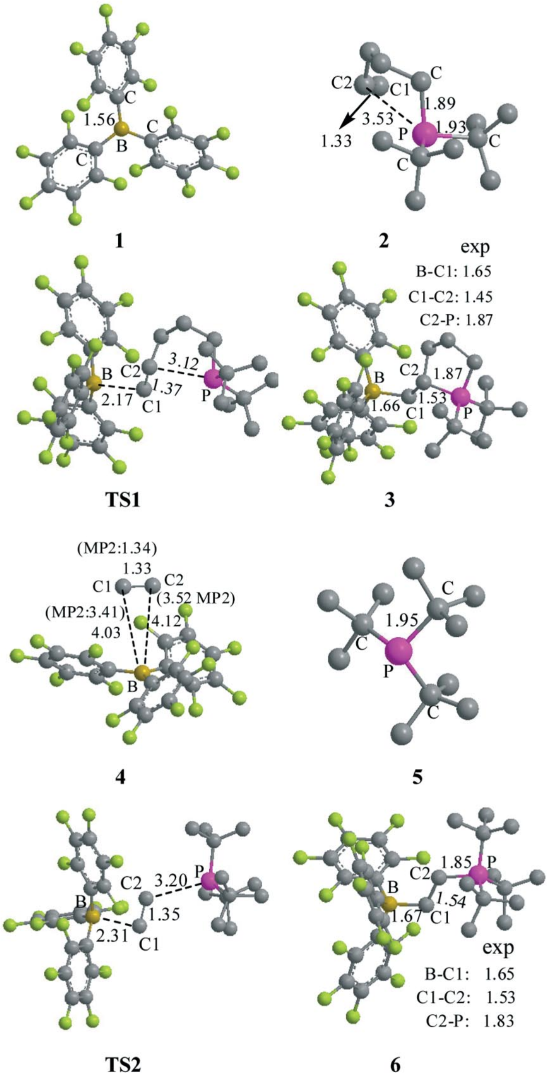
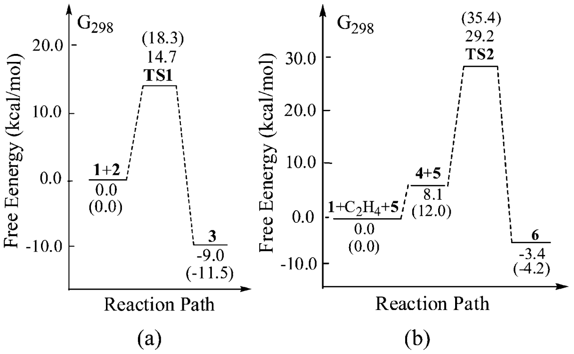
the three-component reaction between $B(C_6F_5)_3$, C_2H_4, and $P(tBu)_3$. For these two reactions, the optimized structures of some stationary points are shown in Figure 1, and the potential energy profiles are given in Figure 2.



1 **2** **TS1** **3** **4** **5** **TS2** **6**

Figure 1. The optimized geometries of stationary points in the two-component and three-component reactions investigated. All H atoms are omitted for clarity. For **3** and **6**, some bond lengths measured experimentally are given for comparison.



(a) (b)

Figure 2. (a) The free-energy profile of the two-component reaction. (b) The free-energy profile of the three-component reaction. Free energies in the solution phase are given in parentheses.

For the two-component reaction, we have explored the potential energy profile of the stepwise mechanism. The relaxed potential energy scan at various P–C2 distances shows that the energy of $CH_2{=}CH{-}(CH_2)_3P(tBu)_2$ will climb up to more than 52.0 kcal/mol (at d_{P-C2} = 1.90 Å). Thus, the formation of a hypothetical radical intermediate is energetically unfavorable. Instead, we found that the reaction may proceed in one step through a concerted transition state **TS1** to form the expected product **3**. The corresponding reactants are **1** and **2**, which is a higher-energy conformer of $CH_2{=}CH{-}(CH_2)_3P(tBu)_2$. This conformer can be readily reached through a series of rotations from the lowest-energy conformer (the details are given in Figure S1 in the Supporting Information). In **2**, the P–C2 distance is 3.53 Å. In **TS1**, the distance between the Lewis acid center B and C1 is 2.17 Å, the C=C bond of the $CH_2{=}CH$ group is elongated from 1.33 Å in **2** to 1.37 Å, and the distance between C2 and P is shortened from 3.53 Å in **2** to 3.12 Å. The transition vector clearly shows that the formation of the B–C1 and P–C2 bonds is concerted. For **3**, our optimized geometrical parameters are quite consistent with the data from the X-ray crystallographic study. **TS1** is 14.7 kcal/mol above the reactants **1**+**2**, and the process is exothermic by 9.0 kcal/mol (Figure 2). If the Lewis acid center B attacks the C2 atom of the $CH_2{=}CH$ group of **2**, another isomer of **3** will form (Figure S2). However, this process is less likely to take place, since the resulting species is 4.1 kcal/mol above **3** (Table S1). When the solvent effect is considered, the reaction barrier for the formation of **3** increases to 18.3 kcal/mol. Thus, the solvent has a significant influence on the potential energy surface. To conclude, a concerted addition mechanism is found for the observed reaction, which is different from the traditional stepwise addition mechanism.[9]

For the three-component reaction, we first consider the possible weakly bound complexes, which may be formed between any two of the reactants, C_2H_4, $B(C_6F_5)_3$ and $P(tBu)_3$. Our calculations show that the complex $B(C_6F_5)_3\cdots P(tBu)_3$ has the largest binding energy (8.3 kcal/mol), followed by the complex $B(C_6F_5)_3\cdots C_2H_4$ (4.9 kcal/mol), then the complex $P(tBu)_3\cdots C_2H_4$ (0.3 kcal/mol). Thus, the possibility of forming the encounter complex $P(tBu)_3\cdots C_2H_4$ is very low. The complex $B(C_6F_5)_3\cdots P(tBu)_3$ could be the transient species during the reaction, but this complex is unlikely to participate in the addition reaction, because it is difficult for olefins to insert into the narrow space between the $B(C_6F_5)_3$ moiety and the $P(tBu)_3$ moiety. Thus, we only consider the complex $B(C_6F_5)_3\cdots C_2H_4$ (**4**) as the potential intermediate in the addition reaction. Since B3LYP significantly underestimates the binding energy for weakly bonded systems,[10] we resort to the ab initio MP2 method for further evaluation of the interaction between C_2H_4 and $B(C_6F_5)_3$.[11] As expected, MP2 calculations with the same basis set lead to a stronger interaction between these two moieties (the corresponding structure is given in Figure S3). The binding energy in the encounter complex

4 is 10.8 kcal/mol at the MP2 level. After 50%BSSE (basis set superposition error)[12] is considered, the binding energy between $B(C_6F_5)_3$ and C_2H_4 reduces to 5.2 kcal/mol. Thus, the association of $B(C_6F_5)_3$ with C_2H_4 is likely to occur. However, we notice that the C=C bond in **4** is only 0.002 Å longer than that in free C_2H_4 even at the MP2 level, implying that the C=C bond is almost not activated in **4**. Assuming that **4** could be a possible transient species, we then explore possible reaction pathways between **4** and **5**. Our experience for the two-component reaction described above suggests that the reaction may also occur through a concerted process. As expected, our optimization results in a concerted transition state, **TS2**. As seen in Figure 1, **TS2** is structurally similar to **TS1**. In **TS2**, the P–C2 distance is 3.20 Å, the B–C1 distance is 2.31 Å, and the C=C bond is significantly activated, with a bond length of 1.35 Å. IRC (intrinsic reaction coordinate) calculations show that this transition state truly connects the reactants and the product **6**. The optimized structure of **6** is in good agreement with the experimental data. Energetically, the encounter complex **4** is 8.1 kcal/mol above the separate reactants $B(C_6F_5)_3$ and C_2H_4 (50%BSSE is considered) in free energy, being thermodynamically unstable at room temperature.[13] The free-energy barrier is 29.2 kcal/mol with respect to the reactants **1**+**5**+C_2H_4, and the product **6** is 3.4 kcal/mol lower in free energy than the reactants. When the free energies of solvation are added, the free-energy barrier increases to 35.4 kcal/mol.

To clarify the reactivity of the "frustrated Lewis pair", we have performed natural population analysis[14] for the reactants, transition states, and products in these two reactions. The natural charges on atoms (C1, C2, P, B) involved directly in the reactions are listed in Table 1. In the two-component reaction, the charge on the Lewis base center P varies from 0.86 *e* in **2** to 0.90 *e* in **TS1** and to 1.67 *e* in **3**. At the same time, the charge on the Lewis acid center B gradually decreases from 0.90 *e* in **1** to 0.71 *e* in **TS1** and to 0.43 *e* in **3**. During the process, the CH_2=CH group seems to act as a bridge for electron transfer from the Lewis base center P to the Lewis acid center B. In **TS1** the CH_2=CH group is of zwitterionic character. But in product **3**, the zwitterionic character of the CH_2=CH group disappears, because of the formation of the P–C2 and B–C1 bonds. For the three-component reaction, a similar trend is observed. However, the charge differences on the C1 and C2 atoms in **TS2** are smaller than those in **TS1**, because of the longer P–C2 and B–C1 distances in **TS2**.

Table 1. Natural charges (in a.u.) on C1, C2, P, and B atoms in **TS1**, **3**, **TS2**, and **6**.[a]

	TS1	**3**	**TS2**	**6**
B	0.71	0.43	0.78	0.43
P	0.90	1.67	0.93	1.72
C1	–0.57	–0.67	–0.48	–0.67
C2	0.09	–0.51	–0.19	–0.76

[a] Natural charges on C1, C2, P in **2** are –0.41, –0.14, 0.86 *e*. Natural charge on B in **1** is 0.90 *e*. Natural charges on C1, C2 in free C_2H_4 are –0.37, –0.37 *e*. Natural charge on P in **5** is 0.86 *e*.

It was also observed experimentally that the combination of $B(C_6F_5)_3$ and $P(tBu)_3$ could react with propylene or 1-hexene to give the corresponding addition products, in which the P atom adds to the secondary olefin carbon atom and the B atom adds to the terminal carbon atom of R–CH–CH_2 (R = CH_3 or C_4H_9). To interpret the regioselectivity observed in the experiment, we explored the potential energy profiles for the reaction between $CH_3CH=CH_2$, $B(C_6F_5)_3$, and $P(tBu)_3$. Depending on the carbon atom attacked by the B atom, two products, **7** or **8**, will form through **TS3** or **TS4** (Figure 3), respectively. Among the two products, species **7** is thermodynamically more stable than **8** by 3.2 kcal/mol. **TS3** is also 7.9 kcal/mol lower in free energy than **TS4**. Thus, the formation of **7** is more favorable than that of **8** from both thermodynamic and dynamic viewpoints. This result clearly accounts for the observed regioselectivity. Furthermore, the optimized structure of **7** is quite consistent with the data from the X-ray crystal structure of the experimental product, $(tBu)_3PCH(R)CH_2B(C_6F_5)_3$ (R = C_4H_9).[4]

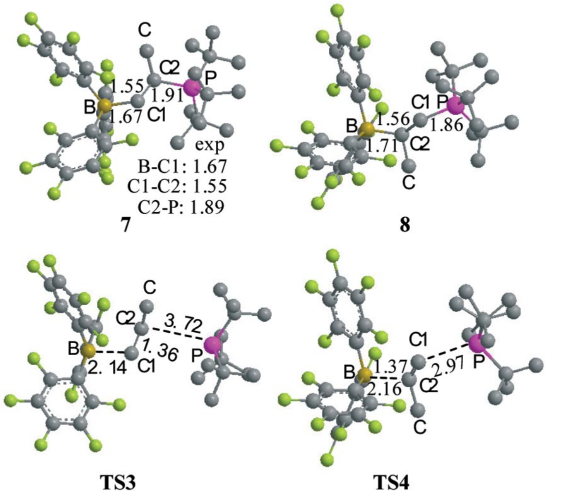


Figure 3. The optimized geometries of stationary points in the reaction of C_3H_6 with the combination of $B(C_6F_5)_3$ and $P(tBu)_3$. All H atoms are omitted for clarity. For **7**, some bond lengths in the experimental product, $(tBu)_3PCH(R)CH_2B(C_6F_5)_3$ (R = C_4H_9), are given for comparison.

In the reactions of olefins with "frustrated Lewis pairs", the experimentally used Lewis acid is always $B(C_6F_5)_3$. So one may ask what the role played by the F atoms in the borane moiety is. To address this issue, we replaced all F atoms in $B(C_6F_5)_3$ with H atoms and investigated the pathway of the three-component reaction, ethylene, $B(C_6H_5)_3$, and $P(tBu)_3$. The optimized structures are shown in Figure 4, together with the corresponding potential energy profile. Clearly, the corresponding product **10** is very unstable relative to the reactants. The free-energy barrier with respect to the reactants is also very high, 51.7 kcal/mol. The solvent has little effect on the stability of the product. By comparing the potential energy profiles of the reactions involving $B(C_6F_5)_3$ and $B(C_6H_5)_3$, one can conclude that strong electronegative F atoms may contribute to the reaction by: (1) forming C–H···F hydrogen bonds to stabilize the resulting product, (2) increasing the bond strength of the forming C–B bond by making the B center more electrophilic. Thus, the reaction of olefins with a combination of P(tBu)$_3$ and B(C_6H_5)$_3$ is unlikely to take place.

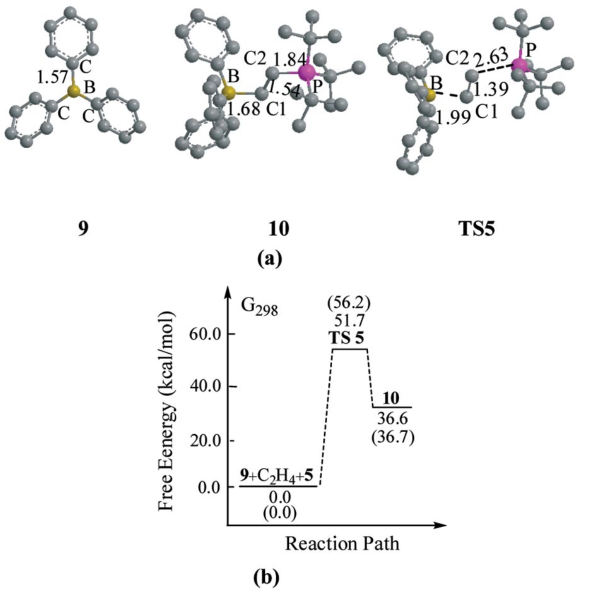


Figure 4. (a) The optimized geometries of stationary points in the reaction between C_2H_4, B(C_6H_5)$_3$, and P(tBu)$_3$. All H atoms are omitted for clarity. (b) The corresponding free-energy profile. Free energies in the solution are given in parentheses.

The present density functional study shows that the reactivity of the sterically frustrated Lewis pair of phosphanes and borane B(C_6F_5)$_3$ with olefins is quite different from the two-step electrophilic addition mechanism, in which a carbocation intermediate is usually involved. The similar reaction mechanism found for the two-component and three-component reactions indicates that the three-component reaction between phosphanes, a borane, and olefins is initiated by the association of C_2H_4 with B(C_6F_5)$_3$ and then proceeds through a concerted transition state, in which both the B–C and P–C bonds form simultaneously. We also investigated the reaction between P(tBu)$_3$, propylene, and B(C_6F_5)$_3$. The results account well for the experimentally observed regioselectivity. In addition, the role of F atoms in B(C_6F_5)$_3$ has also been analyzed by studying a three-component reaction between P(tBu)$_3$, C_2H_4, and B(C_6H_5)$_3$. The presence of fluorine atoms in the borane is found to be essential for stabilizing the addition product. We hope that the molecular mechanism suggested here can greatly boost the development of the "frustrated Lewis pair" in other areas of chemistry.

Methods

All calculations were performed with the B3LYP method implemented in the Gaussian03 program.[15] For the studied reactions, a full molecular model was adopted for all reactants. The 6-311++G(d,p) basis set was employed for C=C and H atoms bound to C=C, B, and P, and those carbon atoms bonded to B or P, while the 6-31G basis set was used for the rest of atoms. Vibrational frequencies were 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[16] calculations were performed to verify whether the reactant and the product are truly connected by the transition state. The natural population analysis was carried out with the NBO 3.1 program.[14]

To consider the bulk solvent effects on the energetics of all species, we employed the PCM method to calculate the Gibbs free energy of solvation by using the gas-phase optimized geometries of the solvents. For the three-molecular reactions of phosphane, boranes, and olefins, chlorobenzene instead of bromobenzene was used as the solvent, since the dielectric constant of bromobenzene is not given in the Gaussian03 program. For the two-component reaction, dichloromethane is employed as the solvent, as in related experiments. 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.

Supporting Information (see footnote on the first page of this article): Total electronic energies, Gibbs free energies, Cartesian coordinates of all stationary points, and structures of some species.

Acknowledgments

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