

# Computational Design of Frustrated Lewis Pairs as a Strategy for Catalytic Hydrogen Activation and Hydrogenation Catalyst

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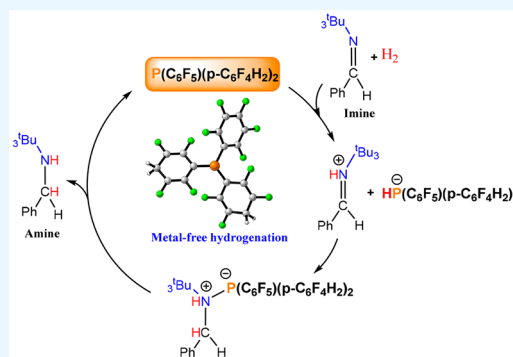


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**ABSTRACT:** Catalytic hydrogenation is one of the most important reaction types commonly used in chemistry and chemical industry. Recently, there has been significant interest in developing a metal-free hydrogenation catalyst to avoid the problems caused by using heavy transition metal catalysts. On the basis of the advances of metal-free hydrogen activation with frustrated Lewis pairs (FLPs, e.g.  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ ) which often uses boron as a Lewis acid center, we computationally explored the prospect for phosphorus(V) and sulfur(VI) as Lewis acid centers to construct FLPs for hydrogen activation and hydrogenation. We found out that the proposed FLPs with P(V)- or S(VI)-centered Lewis acid can also activate  $\text{H}_2$  with a mechanism similar to that used by the conventional FLPs. A heterolytic cleavage of H–H is achieved when electrons are donated simultaneously from the  $\sigma$  orbital of  $\text{H}_2$  to the empty orbital of the Lewis acid center and from the lone-pair orbital of the Lewis base center to the  $\sigma^*$  orbital of  $\text{H}_2$ . The multiple C–H...F hydrogen bonds further aid the association of the pairs for  $\text{H}_2$  activation. Some of our designed FLPs possess kinetics and thermodynamics for developing hydrogenation catalysts. This computational exploration could inspire experimental development of a new type of FLPs with P(V) or S(VI) or a Lewis acid partner for FLPs for reversible  $\text{H}_2$  activation.



## 1. INTRODUCTION

Catalytic hydrogenation reactions are important chemical transformations that are widely used in both laboratory synthesis and chemical industry.<sup>1</sup> Molecular hydrogen ( $\text{H}_2$ ) activation is the preliminary step in the direct hydrogenation (i.e., using hydrogen molecule as a hydrogen source, because of the low polarizability and strong covalent bond of the  $\text{H}_2$  molecule).<sup>1,2,86</sup> While the activation step is commonly achieved by using heavy precious transition metal (TM) compounds, these are not ideal because of the cost and contaminations of heavy precious TMs.<sup>1</sup> Recently, there have been significant efforts to replace the heavy transition metal catalysts with the metal-free catalyst for hydrogen activation or hydrogenation reaction, due to their great economic and environmental advantages.<sup>3–9</sup>

In 2006, Stephan and co-workers made a breakthrough discovery in the main group reversible metal-free hydrogen activation.<sup>10–14</sup> In their study, a covalently linked, phosphino borane  $\text{R}_2\text{P}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2$  ( $\text{R} = \text{Mes}, t\text{Bu}$ )<sup>10–14</sup> and a simple combination of bulky Lewis pairs of phosphines and boranes ( $\text{R}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ ,  $\text{R} = t\text{Bu}, \text{Mes}$ ) also activated  $\text{H}_2$  easily. These bulky Lewis pairs have been termed “frustrated Lewis pairs” (FLPs)<sup>15</sup> and show high reactivity to hydrogen.<sup>16–34</sup> Besides  $\text{H}_2$ , they also activate a series of small molecules such as  $\text{CO}_2$ ,<sup>35–37</sup>  $\text{NH}_3$ ,<sup>38</sup> and  $\text{CH}_4$ <sup>39</sup> and to hydrogenate imines<sup>40–44</sup> and ketones.<sup>44</sup>

Nowadays, the rapid development of FLPs has further inspired both experimental<sup>10–14,45–51</sup> and computational

chemists<sup>16–34</sup> to study the actual mechanism of metal-free hydrogen activation and hydrogenation reaction.<sup>10–14,52–55</sup> Similarly, the vast advancement of frustrated Lewis pairs (FLPs, e.g.  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ ) has been exploited on a boron-based Lewis acid center.<sup>56</sup> However, this chemistry has raised concerns about the potential reactivity and utility of other main group elements. For an alternative catalyst, the concept of an “umpolung” (i.e., tuning the Lewis acids and bases) concept that has been applied to modify FLPs chemistry.<sup>57–61</sup> Inspired by the FLP principle, we relied on DFT computations to design metal-free catalysts, for molecular hydrogen activation reaction and hydrogenation reactions. Herein, we computationally explored whether phosphorus(V) or sulfur(VI) could be used as a Lewis acid center to construct FLPs with different substituents for hydrogen activation and hydrogenation (Figure 1(a)) and identified a metal-free strategy for reversible hydrogen activation and for a catalyst for direct hydrogenation reactions. Indeed, we compared the results with the common frustrated Lewis pairs ( $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ ).<sup>15</sup>

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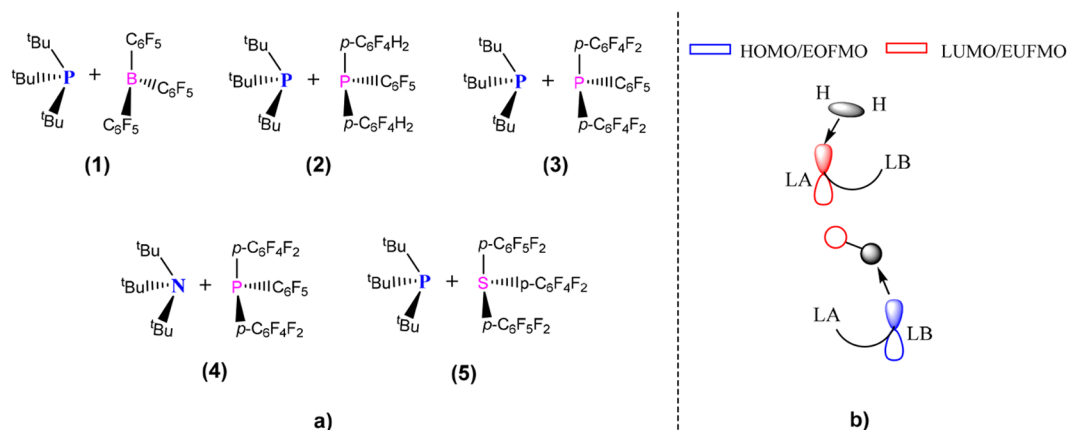


Figure 1. (a) The investigated intermolecular Frustrated Lewis Pairs. (b) The orbital interactions for heterolytic  $\text{H}_2$  activation.

Table 1. Relative Enthalpies and Free Energies (kcal/mol) of the Designed Complexes 1–5 in THF<sup>a</sup>

Complex	Transition state		Product		Properties of the Complexes				
	$\Delta H^\ddagger$	$\Delta G^\ddagger$	$\Delta H$	$\Delta G$	LB–LA bond (Å)	Binding Energy	$W_{\text{LB-LA}}$	$q_{\text{LA}}$	$q_{\text{LB}}$
1	−5.5	16.2	−39.7	−17.9	3.66	4.3	0.0827	0.88	−0.93
2	0.8	23.3	−33.4	−10.7	3.52	1.2	0.0524	1.42	−0.93
3	−7.5	15.9 <sup>b</sup>	−63.7	−40.5	3.28	−2.0	0.2070	1.49	1.07
4	−4.2	19.3	−67.9	−44.7	4.33	1.8	0.0073	1.48	−0.62
5	0.7	21.8	−34.8	−13.1	3.41	4.9	0.0728	0.99	−1.25

<sup>a</sup>All values are relative to the separated reactants (Lewis acid, Lewis base, and an isolated  $\text{H}_2$  molecules). The Lewis pair center bond lengths are in Å. The Wiberg bond order of the LB–LA bond center is  $W_{\text{LB-LA}}$ . NBO charges (in a.u.) on the two Lewis pair center are  $q_{\text{LA}}$  and  $q_{\text{LB}}$ . Binding energies are in kcal/mol. <sup>b</sup>Except for those of TS3 which are relative to complex 3 +  $\text{H}_2$ .

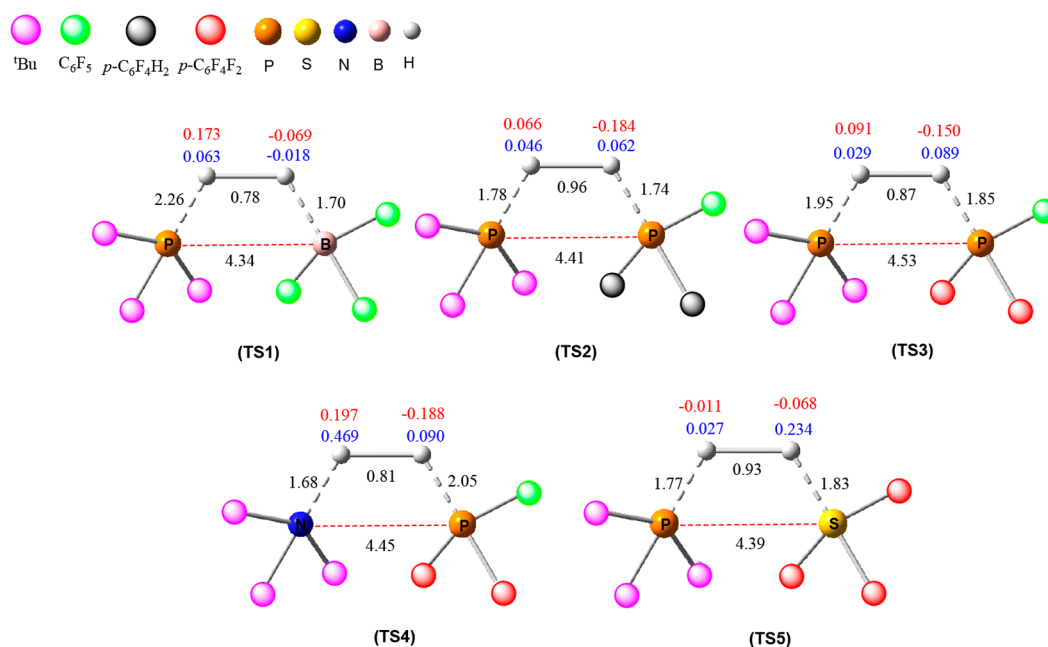


Figure 2.  $\text{H}_2$  activation together with the key bond lengths in Å (black) and the NBO charges (in  $e$ ) on the two H atoms in the transition states (red) and products (blue) of the studied FLPs.

## 2. COMPUTATIONAL DETAILS

In this study, all structures were optimized and characterized in the gas phase at the M06-2X<sup>62–67</sup>/6-31G(d,p)<sup>68–71</sup> level. Harmonic frequency analysis calculations were subsequently performed to verify the optimized structures to be minimal (no imaginary frequency) or transition states (TSs, having a unique

one imaginary frequency). The energies were then improved by M06-2X/6-311++G(d,p)<sup>72–77</sup> single-point calculations with solvent effects accounted for by the SMD<sup>78,79</sup> solvent model, using the most common solvent in FLP chemistry (THF). In addition, the ideal gas-phase thermal corrections cannot properly take into account the entropy contributions when the

number of molecules changes, because it ignores the solvent suppression on the rotational and translational freedoms of substrates, resulting in an overestimation of entropy contributions to the reaction free energies in solution.<sup>80–82</sup> Since no standard quantum mechanics-based approach is available for accurate prediction of the entropy in solution, we adopted a correction of  $(m - n) \times 1.9$  kcal/mol for a reaction from  $m$  to  $n$  components.<sup>83</sup> Atomic partial charges were calculated at the M06-2X/6-311++G(d,p) level according to the natural bond orbital (NBO) method.<sup>80–82</sup> All standard DFT calculations were carried out by using the Gaussian 09 program.<sup>84</sup> Selected optimized structures are illustrated using the CYL view.<sup>85</sup> Total energies and Cartesian coordinates of all optimized structures are given in the Supporting Information (SI).

### 3. RESULTS AND DISCUSSION

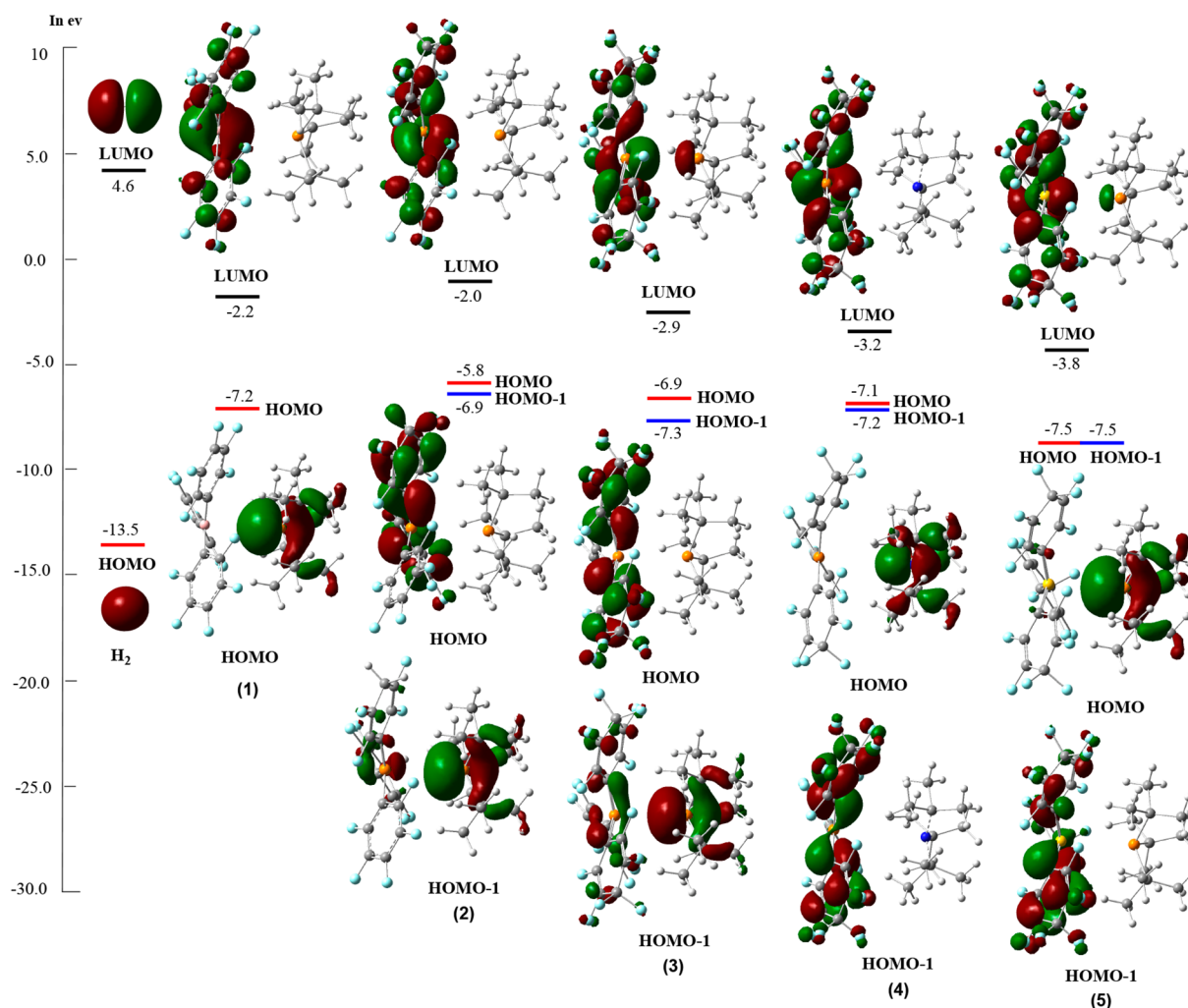
**Investigated Frustrated Lewis Pair System.** As shown in Figure 1(a), the hydrogen activation was carried out by using the five FLPs catalysts. Among these, a well-known mechanism has been discovered for complex 1 ( $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ ),<sup>17,18</sup> while the other four pairs are our computationally designed catalysts. The selecting criteria for the FLPs are: for complexes 1, 2, 3, and 5, we selected the same base ( $t\text{Bu}_3\text{P}$ ), and varied the acid ( $\text{B}(\text{C}_6\text{F}_5)_3$ ,  $\text{P}(\text{C}_6\text{F}_5)(p\text{-C}_6\text{F}_4\text{H}_2)_2$ ,  $\text{P}(\text{C}_6\text{F}_5)(p\text{-C}_6\text{F}_4\text{F}_2)_2$ , and  $\text{S}(p\text{-C}_6\text{F}_4\text{F}_2)_3$ ) respectively, while for complexes 3 and 4, we selected the same acid ( $\text{P}(\text{C}_6\text{F}_5)(p\text{-C}_6\text{F}_4\text{F}_2)_2$ ) but varied the base ( $t\text{Bu}_3\text{P}$  and  $t\text{Bu}_3\text{N}$ ). Table 1 summarized the computational properties of the studied complexes. As shown in Table 1, the small Wiberg bond indices ( $<0.20$ ) and long bond distances (3.28–4.33 Å) showed that no dative bonds were formed between the reactive Lewis centers, which implied that the combinations of complexes 1–5 can be considered as FLPs to accommodate and activate the guest  $\text{H}_2$  molecules without affecting the kinetics of the reaction.

All the studied FLP complexes are mainly stabilized by nonbonding interactions (i.e., multiple C–H...F hydrogen bonding and dispersion interactions) between the bulky Lewis base and their complementary Lewis acid. Figure 2 displays the key bond lengths and charge transfer between the selected atoms of interest, i.e., H, N, B, P, and S; we performed Natural Bond Orbital (NBO) analyses of TSs and products. In all TSs, the two hydrogen atoms that make up the dihydrogen moiety bear different bond lengths and charges with the Lewis pair center revealing that the  $\text{H}_2$  activation is strictly heterolytic. Moreover, the FMOs for the transition states shown in Figure S1 resulted in the partial charge transfer from the dihydrogen moiety to the Lewis base and acid, and vice versa. Furthermore, the electron occupancies in the empty orbital of P in complexes 2 and 3 are 1.42e and 1.49e, respectively, which explains the replacement of *para*-H atoms ( $\text{P}(\text{C}_6\text{F}_5)(p\text{-C}_6\text{F}_4\text{H}_2)_2$ ) with F atoms which lead to a slightly increased acidity of the Lewis acid center and, similarly, the F...H interaction which stabilizes the transition state and increases the acidic center. Indeed, replacing H atoms with F atoms decreased the barrier by 7.4 kcal/mol for  $\text{H}_2$  activation.

**Reaction Barriers for the Activation of  $\text{H}_2$  by FLPs.** As shown in Table 1, except for complex 3, the activation free energies of all studied FLPs are significantly higher than those of well-known pairs (i.e.,  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  ( $\Delta G = 16.2$  kcal/mol), due to an excellent acidity of borane which can improve the  $\text{H}_2$  activation. The activation barrier of complex 1  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  is substantially lower, but the reaction is highly exergonic by 17.9 kcal/mol, which is not ideal for developing (nearly) reversible

$\text{H}_2$  activation and catalytic hydrogenation reactions. Upon comparing the activation barriers of the well-known pairs (i.e.,  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  with our designed molecules, the designed molecules are accessible under the experimental condition for developing reversible  $\text{H}_2$  activation. Therefore, our designed FLPs can develop reversible  $\text{H}_2$  activation and hydrogenation reactions. In line with the energy barriers, the dihydrogen moieties in all TSs are only stretched slightly: the dihydrogen bond lengths, 0.78 Å (TS1), 0.96 Å (TS2), 0.87 Å (TS3), 0.81 Å (TS4), and 0.93 Å (TS5), are compared with the 0.73 Å of free  $\text{H}_2$ . Further, the binding energies of the studied complexes 1, 2, 4, and 5 are 4.3, 1.2, 1.8, and 4.9 kcal/mol, respectively, indicated that the process is entropically favored. In complex 3, the nonbonding interaction (i.e., multiple C–H...F hydrogen bonding) is responsible for the association and gives rise to the binding energy of  $-2.0$  kcal/mol, which reacts rapidly with  $\text{H}_2$  via TS3, representing only a small energy barrier of 15.9 kcal/mol (see Table 1). However, the heterolytic cleavage of the H–H bond is a highly exothermic process (40.5 kcal/mol) which forms irreversible hydrogen activation and yields the ion pair 3PR (see Figures S2 and S3 for more details). From the energy results of the designed complexes 3 and 4, we rationalized the following aspects: (i) the electrostatic interaction between the  $\text{H}_{\text{app}}$  ( $\text{H}_{\text{app}}$  hereafter represents the approaching H atoms) and Lewis basic center can play a different role in the hydrogen activations, the N-center in 4 with a negative charge  $-0.62e$  while the P-center in 3 bears a positive charge of  $1.07e$ . With the  $\text{H}_{\text{app}}$  having a positive charge, the repulsive electrostatic interaction between the P-center and  $\text{H}_{\text{app}}$  disfavors the hydrogen activation by complex 3, but the attractive interaction favors the hydrogen activation by complex 4. However, due to the soft P(V)-Lewis base center in complex 3 with a hard Lewis base center N in complex 4, the activation barriers and endergonicities are comparable with those of complex 4 for  $\text{H}_2$  activations (see Table 1). (ii) All the studied molecules showed face-to-face orientations of the two orbitals which look ideal for hydrogen activation; see Figure S1 for more details. All these features bear a close resemblance to those obtained for the  $t\text{Bu}_3\text{P} + \text{B}(\text{C}_6\text{F}_5)_3 + \text{H}_2$  reaction<sup>18</sup> indicating that a heterolytic cleavage of H–H is achieved when electrons are donated simultaneously from the  $\sigma$  orbital of  $\text{H}_2$  to the empty orbital of the Lewis acid center and from the lone-pair orbital of the Lewis base center to the  $\sigma^*$  orbital of  $\text{H}_2$ . Similarly, in complex 1 ( $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$  pair), the H–H heterolytic cleavage is done via the interaction between H–H bonding electrons and the empty orbital of the B-center as well as the phosphorus lone pair and the H–H  $\sigma^*$  orbital along the reaction pathway.

**Comparison of the Reversible  $\text{H}_2$  Activation by Complexes 2 and 5.** For reversible  $\text{H}_2$  activation, we selected P(V)- and S(VI)-centered Lewis acids (i.e., complex 2 and 5) as representatives, and both molecules improved the endergonicity of 10.7 and 13.1 kcal/mol with a comparable energy barrier of 23.3 and 21.8 kcal/mol respectively. Furthermore, they have quite long H–H bonds (0.96 and 0.93 Å, respectively) in their TSs as compared to complex 1 (i.e.,  $t\text{Bu}_3\text{P}/\text{B}(\text{C}_6\text{F}_5)_3$ ) (0.78 Å) (see Table 1). According to Hammond's postulate, transition states with longer H–H bonds typically have higher barriers and endergonic activations.<sup>83</sup> Previously, Papi and co-workers had studied the thermodynamics and kinetics of different FLP hydrogen activations. In agreement with experimental evidence, they found that the reversible FLP hydrogen activation systems are slightly exergonic.<sup>19</sup> For example, the expected  $\Delta G$  values of  $\text{Mes}_2\text{P}-\text{C}_6\text{F}_4-\text{B}(\text{C}_6\text{F}_5)_2$ ,<sup>10</sup> 1,8-bis(diphenylphosphino) naphtha-



**Figure 3.** Frontier molecular orbitals of H<sub>2</sub> with those of studied FLPs (1–5) in Figure 2.

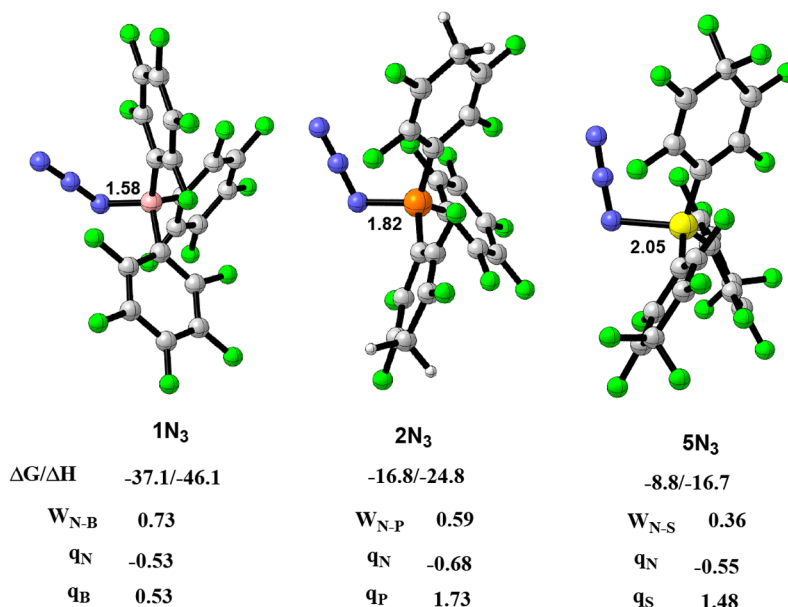
lene/B-(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>,<sup>41</sup> and (*o*-C<sub>6</sub>H<sub>4</sub>Me)<sub>3</sub>-P/B(*p*-C<sub>6</sub>F<sub>4</sub>H)<sub>3</sub><sup>13</sup> are −2.5, −2.1, and −0.1 kcal/mol at the M05-2X/6-311++G(d,p)//M05-2X/6-31G(d) level in toluene, respectively. However, in our designed complex the Δ*G* values of complex 2 (−10.7 kcal/mol) and complex 5 (−13.1 kcal/mol) seemed to be relatively too large for reversible hydrogen activations (see Table 1). However, the experimentally reversible intramolecular linked TMPN-CH<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>-B(C<sub>6</sub>F<sub>6</sub>)<sub>2</sub><sup>47</sup> system has a free energy of −12.5 kcal/mol at the M05-2X/6-311++G\*\*//M05-2X/6-31G\* level in toluene<sup>19</sup> and −7.3 kcal/mol at the PBE/6-31G\* level in benzene.<sup>47</sup> Indeed, the previous computed free energy was −12.7 kcal/mol at the M05-2X/6-311++G\*\*//M05-2X/6-31G\* level for (3-borabicyclo[3.3.1]nonane(3-BBN) molecules in toluene.<sup>20</sup> Therefore, we speculate that our designed complexes 2 and 5 could be promising metal-free hydrogenation catalysts for a (nearly) reversible hydrogen activation reaction. In short, when the bond length between the reactive Lewis centers of studied FLPs increases, the guest H<sub>2</sub> molecule can be accommodated easily, with a lowering of the activation energy except for that of complex 4.

Figure 3 displays the calculated HOMO and LUMO orbitals of the studied frustrated complexes and the effect of replacing the Lewis acid and base combinations (see Figure S1 for details). As shown in Figure 3, the FMOs of complex 1 (*t*Bu<sub>3</sub>P/B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>) showed that the HOMO is localized on the

phosphine fragment, and its main constituent is the sp<sup>3</sup> hybrid lone pair of the phosphorus atom. Similarly, the LUMO of the complex is composed of mainly the boron vacant orbital, which showed the steric congestion of the FLP members to prevent the efficient overlap between the frontier orbitals of the acid and base for dative bond formation. Based on our computed result, all studied complexes have similar LUMOs, which originate from the empty orbitals of the Lewis acid and serve as EUFMOs, but their HOMOs differ significantly. However, complexes 2 and 3 have one occupied orbital with the correct symmetry to interact with the σ\* orbital of H<sub>2</sub> called the EOFMO (i.e., HOMO − 1) which comes from the lone pairs of these molecules. Note that the HOMOs of these molecules do not have the right symmetry to interact with the σ\* orbital of H<sub>2</sub>, which does not contribute to H<sub>2</sub> activation. For complexes 1, 4, and 5, the HOMOs are dominated by the lone pairs of the Lewis base center.

As shown in Figure 3, the more effective orbital interactions (i.e., the gap) between the EOFMO/LUMOs in complex 2 and HOMO/LUMO of complex 5 showed that it is somewhat difficult to accommodate the guest hydrogen molecule in the cavity between the two active centers which results in an increased barrier of 23.3 and 21.8 kcal/mol respectively (see Table 1), as compared to complex 1 (16.2 kcal/mol). Therefore, the more favorable energy of complex 1 can be attributed to the





**Figure 4.** Optimized structures for the complexes of N<sub>3</sub> with Lewis acid analogs in Figure 1: the binding energies and enthalpies (in kcal/mol) of the designed FLPs pair; Wiberg bond order of the N-Lewis acid bond center bond ( $W_{N-LA}$ ); NBO charges (in a.u.) on the two Lewis pair center; the values are the key bond lengths in Å.

effective orbital interactions shown in Figure 1b, as compared to complexes 2 and 5. However, in complexes 2 and 5, the nonbonding interactions stabilize hydrogen molecule activation.

To gain insight into the complexation energies of the designed FLPs, we chose complexes 2 and 5 with the azide N<sub>3</sub> with a Lewis base probe as a representative to eliminate the effect of possible hydrogen bonds between LA and LB. Similarly, we also use NH<sub>3</sub> and CN Lewis base probes (see Table 4 in SI for more details). Figure 4 shows the complexes of N<sub>3</sub> with Lewis acid analogs and compared the association ability of the predecessor Lewis acids (i.e., B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>). The association energy of the B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> moiety with N<sub>3</sub> tends to form a moderately strong adduct with association free energy of  $\Delta G = -37.1$  kcal/mol. Indeed, the short N–B bond distance found in this adduct indicated a strong N–B bonding interaction between the Lewis acid center and the N<sub>3</sub> molecule which provided significant stabilization. Similarly, the designed Lewis acid center of complexes 2 and 5 formed relatively weak adducts with an association free energy of  $\Delta G = -16.8$  and  $-8.8$  kcal/mol. However, due to the noncovalent interactions between the Lewis base and Lewis acid nonbonding interactions, the complexes are stable.

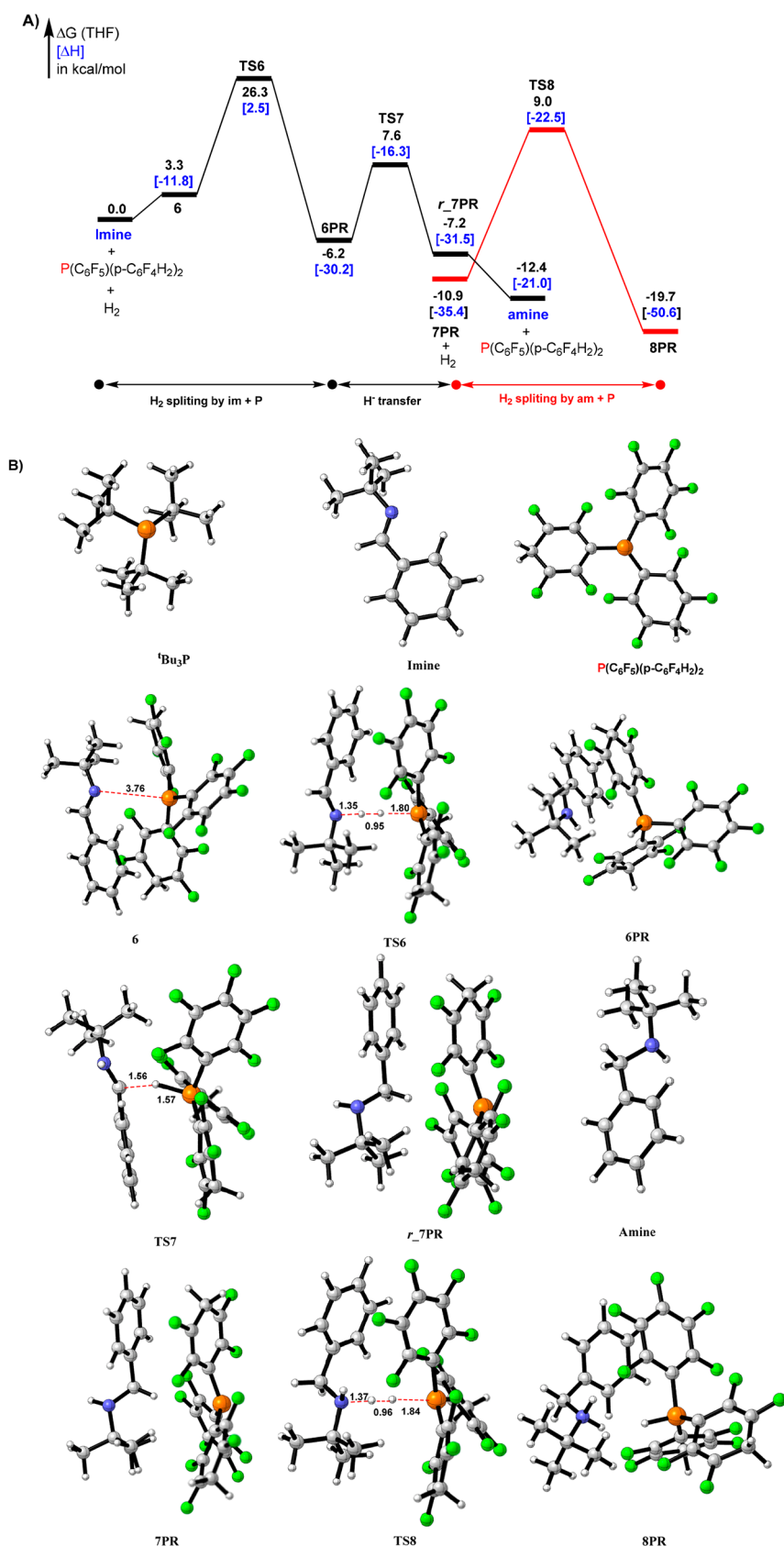
#### Reduction of Imine by P(C<sub>6</sub>F<sub>5</sub>)(*p*-C<sub>6</sub>F<sub>4</sub>H<sub>2</sub>)<sub>2</sub> and H<sub>2</sub>.

Finally, we investigated whether the designed complexes can perform a direct hydrogenation reaction with the sterically encumbered and electron-rich imine *t*BuN=CPh(H) molecule and discussed their potential energy surface. Previously, Papai and co-workers have reported the reaction mechanism for the transition metal-free direct hydrogenation of bulky imines catalyzed by the Lewis acid B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>.<sup>17</sup> For the present analysis, we chose the LA part of complex 2 as a representative, and it can perform the full catalytic cycle. Figure 5A presents our computed energy profile for the reduction of imine *t*BuN=CPh(H) with the LA part of complex 2, and Figure 5B displays the optimized structures of all stationary points labeled in Figure 5A. Alternatively, we calculate the direct hydrogenation reaction at the experimental temperature ( $T = 353.15$  K) presented by Papai

and co-workers (see Figure S4 in SI for more details).<sup>17</sup> The reaction takes place in the three-step mechanism, namely, hydrogen activation (6-TS6-6PR), hydrogen transfer, and the product release. First, the donor P and acceptor P(V) center of complex 2 activate the H–H bond *via* crossing TS6, giving a stable iminiumhydridophosphate ion pair (6PR). Subsequently, hydride transfer to the carbon center of the iminium ion by the hydridophosphate results in the neutral amine-phosphine adduct *r*<sub>7</sub>PR bound by electrostatic interaction *via* crossing a barrier of 13.8 kcal/mol (TS7) and is exergonic by 7.2 kcal/mol. Finally, the dissociation of amine from *r*<sub>7</sub>PR generates the catalyst with the energy costs only 5.2 kcal/mol. Parallel to the imine-phosphane pair, a preorganized amine-phosphane frustrated complex can be identified on the catalytic cycle (7PR, see Figure 5). An internal rearrangement of the *r*<sub>7</sub>PR ion pair gives more stable isomer 7PR. The H–H bond activation in 7PR occurs *via* TS8 with the free-energy barrier of 19.9 kcal/mol related to the near intermediate and is exergonic by 19.7 kcal/mol, yielding stable iminiumhydridophosphate ion pair 8PR. Overall, relative to the separated reactant, the hydrogen activation catalytic cycle has a rate-determining step barrier of 26.3 kcal/mol (TS6), with exergonicity of 6.2 kcal/mol.

## 4. CONCLUSIONS

In summary, we have proposed a strategy to design a metal-free hydrogen activation site for metal-free hydrogenation catalysts. For all designed catalysts, the hydrogenation reaction mechanism bears a close resemblance to the often-used FLPs *t*Bu<sub>3</sub>P + B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>. Among the reported molecules, the potential energy surfaces of complexes 2 and 5 are comparable with that of complex 1 for hydrogen activation. Even if the more effective orbital interactions are in complexes 2 and 5 (i.e., EOFMO/LUMOs and HOMO/LUMO), the nonbonding interactions (i.e., multiple C–H⋯F hydrogen bonding and noncovalent interactions between the FLPs pairs) stabilize hydrogen molecule activation. Therefore, we speculate that these molecules could be a promising metal-free hydrogenation



**Figure 5.** (A) Free-energy profile (in kcal/mol) for  $H_2$  splitting by im+P and am+P. (B) Optimized structures of all the stationary points, with values in black being bond lengths in angstroms (Å). Energies are relative to imine, and  $P(C_6F_5)(p-C_6F_4H_2)_2$  and  $H_2$  are mass balanced.

catalyst. The frontier molecular orbitals (MOs) analysis of all the studied molecules showed ideal molecules for hydrogen activation. In the phosphine-catalyzed imine hydrogenation, the LA part of complex **2** achieved catalytic direct hydrogenation of the sterically encumbered and electron-rich imine *t*BuN=CPh(H), with a rate-determining step barrier of 26.3 kcal/mol (TS6), and the H transfer, measured from the near intermediate, is 13.8 kcal/mol. These results predict that the reactions are experimentally achievable under mild reaction conditions. Besides that, the reduced product amine can take part in the hydrogen activation process and, therefore, opens an autocatalytic pathway. Finally, this computational exploration could inspire the experimental development of a new type of FLPs with P(V) or S(VI) or a Lewis acid partner for FLPs.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c07442>.

Additional computational results and optimized Cartesian coordinates for DFT-optimized structures (PDF)

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Complete contact information is available at: <https://pubs.acs.org/doi/10.1021/acsomega.2c07442>

### Notes

The authors declare no competing financial interest.

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## ■ REFERENCES

- (1) Kubas, G. J. Fundamentals of H<sub>2</sub> binding and reactivity on transition metals underlying hydrogenase function and H<sub>2</sub> production and storage. *Chem. Rev.* **2007**, *107*, 4152–4205.
- (2) Stephan, D. W.; Erker, G. Frustrated Lewis pairs: metal-free hydrogen activation and more. *Angew. Chem., Int. Ed. Engl.* **2010**, *49*, 46–76.
- (3) Spikes, G. H.; Fettinger, J. C.; Power, P. P. Facile activation of dihydrogen by an unsaturated heavier main group compound. *J. Am. Chem. Soc.* **2005**, *127*, 12232–12233.
- (4) Bettinger, H. F.; Filthaus, M.; Neuhaus, P. Insertion into dihydrogen employing the nitrogen centre of a borylnitrene. *Chem. Commun.* **2009**, *16*, 2186–2188.
- (5) Moc, J. Interaction of Ga<sub>3</sub> cluster with molecular hydrogen: combined DFT and CCSD(T) theoretical study. *Eur. Phys. J. D.* **2009**, *53*, 309–317.
- (6) Zhong, G.; Chan, B.; Radom, L. Low barrier hydrogenolysis of the carbon-heteroatom bond as catalyzed by HALF(4). *Org. Lett.* **2009**, *11*, 749–751.
- (7) Hoshimoto, Y.; Kinoshita, T.; Hazra, S.; Ohashi, M.; Ogoshi, S. Main-group-catalyzed reductive alkylation of multiply substituted amines with aldehydes using H<sub>2</sub>. *J. Am. Chem. Soc.* **2018**, *140*, 7292–7300.
- (8) Ito, S.; Miura, J.; Morita, N.; Yoshifuji, M.; Arduengo, A. J. Modeling the direct activation of dihydrogen by a P2C2 cyclic biradical: formation of a cyclic bis(P-H λ<sup>5</sup>-phosphorane). *Inorg. Chem.* **2009**, *48*, 8063–8065.
- (9) Wang, Y.; Ma, J. Silylenes and germylenes: The activation of H-H bond in hydrogen molecule. *J. Organomet. Chem.* **2009**, *694*, 2567–2575.
- (10) Welch, G. C.; Juan, R. R. S.; Masuda, J. D.; Stephan, D. W. Reversible, metal-free hydrogen activation. *Science* **2006**, *314*, 1124–1126.
- (11) Stephan, D. W. “Frustrated Lewis pairs”: a concept for new reactivity and catalysis. *Org. Biomol. Chem.* **2008**, *6*, 1535–1539.
- (12) Welch, G. C.; Cabrera, L.; Chase, P. A.; Hollink, E.; Masuda, J. D.; Wei, P.; Stephan, D. W. Tuning Lewis acidity using the reactivity of “frustrated Lewis pairs”: facile formation of phosphine-boranes and cationic phosphonium-boranes. *Dalton Trans.* **2007**, 3407–3414.
- (13) Ullrich, M.; Lough, A. J.; Stephan, D. W. Reversible, Metal-Free, Heterolytic Activation of H<sub>2</sub> at Room Temperature. *J. Am. Chem. Soc.* **2009**, *131*, 52–53.
- (14) Wang, S.; Sherbow, T. J.; Berben, L. A.; Power, P. P. Reversible Coordination of H<sub>2</sub> by a Distannyne. *J. Am. Chem. Soc.* **2018**, *140*, 590–593.
- (15) Welch, G. C.; Stephan, D. W. Facile heterolytic cleavage of dihydrogen by phosphines and boranes. *J. Am. Chem. Soc.* **2007**, *129*, 1880–1881.
- (16) Hamza, A.; Stirling, A.; Andras Rokob, T.; Papai, I. Mechanism of hydrogen activation by frustrated Lewis pairs: A molecular orbital approach. *Int. J. Quantum Chem.* **2009**, *109*, 2416–2425.
- (17) Rokob, T. A.; Hamza, A.; Stirling, A.; Pápai, I. On the mechanism of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>-catalyzed direct hydrogenation of imines: inherent and thermally induced frustration. *J. Am. Chem. Soc.* **2009**, *131*, 2029–2036.
- (18) Rokob, T. A.; Hamza, A.; Stirling, A.; Soos, T.; Papai, I. Turning frustration into Bond activation: A theoretical mechanistic study on heterolytic hydrogen splitting by frustrated Lewis Pairs. *Angew. Chem.* **2008**, *120*, 2469–2472.
- (19) Rokob, T. A.; Hamza, A.; Pápai, I. Rationalizing the reactivity of frustrated Lewis Pairs: thermodynamics of H<sub>2</sub> activation and the role of acid-base Properties. *J. Am. Chem. Soc.* **2009**, *131*, 10701–10710.
- (20) Lu, G.; Li, H.; Zhao, L.; Huang, F.; Wang, Z. X. Computationally designed metal-free hydrogen activation site: reaching the reactivity of metal-ligand bifunctional hydrogenation catalysts. *Inorg. Chem.* **2010**, *49*, 295–301.
- (21) Privalov, T. Hydrogenation of imines by phosphonium borate zwitterions: a theoretical study. *Dalton Trans.* **2009**, 1321–1327.
- (22) Stirling, A.; Hamza, A.; Rokob, T. A.; Papai, I. Concerted attack of frustrated Lewis acid-base pairs on olefinic double bonds: a theoretical study. *Chem. Commun.* **2008**, 3148–3150.
- (23) Lu, G.; Li, H.; Zhao, L.; Huang, F.; Schleyer, P. v. R.; Wang, Z.-X. Designing Metal-Free Catalysts by Mimicking Transition-Metal Pincer Templates. *Chem. Eur. J.* **2011**, *17*, 2038–2043.
- (24) Guo, Y.; Li, S. A Novel Addition Mechanism for the Reaction of “Frustrated Lewis Pairs” with Olefins. *Eur. J. Inorg. Chem.* **2008**, *2008*, 2501–2505.
- (25) Wang, Z.; Lu, G.; Li, H.; Zhao, L. Encumbering the intramolecular π donation by using a bridge: A strategy for designing metal-free compounds to hydrogen activation. *Sci. Bull.* **2010**, *55*, 239–245.
- (26) Nyhlen, J.; Privalov, T. “Frustration” of Orbital Interactions in Lewis Base/Lewis Acid Adducts: A Computational Study of H<sub>2</sub> Uptake



by Phosphanlyboranes  $R_2P = BR'_2$ . *Eur. J. Inorg. Chem.* **2009**, 2009, 2759–2764.

(27) Lu, G.; Zhang, P.; Sun, D.; Wang, L.; Zhou, K.; Wang, Z. X.; Guo, G. C. Gold catalyzed hydrogenations of small imines and nitriles: enhanced reactivity of Au surface toward  $H_2$  via collaboration with a Lewis base. *Chem. Sci.* **2014**, 5, 1082–1090.

(28) Zhang, C.; Lv, X.; Lu, G.; Wang, Z. X. Metal-free homolytic hydrogen activation: a quest through density functional theory computations. *New J. Chem.* **2016**, 40, 8141–8148.

(29) Zeonjuk, L. L.; Vankova, N.; Mavrandonakis, A.; Heine, T.; Roschenthaler, G.-V.; Eicher, J. On the mechanism of hydrogen activation by frustrated lewis pairs. *Chem. Eur. J.* **2013**, 19, 17413–17424.

(30) Nyhlen, J.; Privalov, T. On the possibility of catalytic reduction of carbonyl moieties with tris(pentafluorophenyl)borane and  $H_2$ : a computational study. *Dalton Trans.* **2009**, 5780–5786.

(31) Privalov, T. On the Possibility of Conversion of Alcohols to Ketones and Aldehydes by Phosphinoboranes  $R_2PBR'R''$ : A Computational Study. *Chem. Eur. J.* **2009**, 15, 1825–1829.

(32) Rokob, T. A.; Bakó, L.; Stirling, A.; Hamza, A.; Pápai, I. Reactivity Models of Hydrogen Activation by Frustrated Lewis Pairs: Synergistic Electron Transfers or Polarization by Electric Field? *J. Am. Chem. Soc.* **2013**, 135, 4425–4437.

(33) Privalov, T. The Role of Amine- $B(C_6F_5)_3$  Adducts in the Catalytic Reduction of Imines with  $H_2$ : A Computational Study. *Eur. J. Inorg. Chem.* **2009**, 2009, 2229–2237.

(34) Guo, Y.; Li, S. Unusual Concerted Lewis Acid-Lewis Base Mechanism for Hydrogen Activation by a Phosphine-Borane Compound. *Inorg. Chem.* **2008**, 47, 6212–6219.

(35) Liu, L.; Vankova, N.; Heine, T. A kinetic study on the reduction of  $CO_2$  by frustrated Lewis pairs: from understanding to rational design. *Phys. Chem. Chem. Phys.* **2016**, 18, 3567–3574.

(36) Mommig, C. M.; Otten, E.; Kehr, G.; Fröhlich, R.; Grimme, S.; Stephan, D. W.; Erker, G. Reversible metal-free carbon dioxide binding by frustrated lewis pairs. *Angew. Chem., Int. Ed.* **2009**, 48, 6643–6646.

(37) Jiang, B.; Zhang, Q.; Dang, L. Theoretical studies on bridged frustrated Lewis pair (FLP) mediated  $H_2$  activation and  $CO_2$  hydrogenation. *Org. Chem. Front.* **2018**, 5, 1905–1915.

(38) Li, H.; Wen, M.; Lu, G.; Wang, Z. X. Catalytic metal-free intramolecular hydroaminations of non-activated aminoalkenes: A computational exploration. *Dalton Trans.* **2012**, 41, 9091–9100.

(39) Lu, G.; Zhao, L.; Li, H.; Huang, F.; Wang, Z.-X. Reversible Heterolytic Methane Activation of Metal-Free Closed-Shell Molecules: A Computational Proof-of-Principle Study. *Eur. J. Inorg. Chem.* **2010**, 2010, 2254–2260.

(40) Chase, P. A.; Welch, G. C.; Jurca, T.; Stephan, D. W. Metal-free catalytic hydrogenation. *Angew. Chem., Int. Ed.* **2007**, 46, 8050–8053.

(41) Jiang, C.; Blacque, O.; Berke, H. Metal-free hydrogenation and hydrogenation of imines by 1,8-bis(dipentafluorophenylboronyl)naphthalene. *Chem. Commun.* **2009**, 5518–5520.

(42) Zhao, L.; Li, H.; Lu, G.; Wang, Z. X. Computational design of metal-free catalysts for catalytic hydrogenation of imines. *Dalton Trans.* **2010**, 39, 4038–4047.

(43) Zhao, L.; Li, H.; Lu, G.; Huang, F.; Zhang, C.; Wang, Z. X. Metal-free catalysts for hydrogenation of both small and large imines: a computational experiment. *Dalton Trans.* **2011**, 40, 1929–1937.

(44) Li, H.; Zhao, L.; Lu, G.; Huang, F.; Wang, Z. X. Catalytic metal-free ketone hydrogenation: a computational experiment. *Dalton Trans.* **2010**, 39, 5519–5526.

(45) Wang, H.; Fröhlich, R.; Kehr, G.; Erker, G. Heterolytic dihydrogen activation with the 1,8-bis(diphenylphosphino)naphthalene/ $B(C_6F_5)_3$  pair and its application for metal-free catalytic hydrogenation of silyl enol ethers. *Chem. Commun.* **2008**, 5966–5968.

(46) Geier, S. J.; Stephan, D. W. Lutidine/ $B(C_6F_5)_3$ : at the boundary of classical and frustrated lewis pair reactivity. *J. Am. Chem. Soc.* **2009**, 131, 3476–3477.

(47) Sumerin, V.; Schulz, F.; Atsumi, M.; Wang, C.; Nieger, M.; Leskelä, M.; Repo, T.; Pykkö, P.; Rieger, B. Molecular Tweezers for

Hydrogen: Synthesis, Characterization, and Reactivity. *J. Am. Chem. Soc.* **2008**, 130, 14117–14119.

(48) Sumerin, V.; Schulz, F.; Nieger, M.; Leskela, M.; Repo, T.; Rieger, B. Facile heterolytic  $H_2$  activation by amines and  $B(C_6F_5)_3$ . *Angew. Chem., Int. Ed.* **2008**, 47, 6001–6003.

(49) Geier, S. J.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. From Classical Adducts to Frustrated Lewis Pairs: Steric Effects in the Interactions of Pyridines and  $B(C_6F_5)_3$ . *Inorg. Chem.* **2009**, 48, 10466–10474.

(50) Chase, P. A.; Jurca, T.; Stephan, D. W. Lewis acid-catalyzed hydrogenation:  $B(C_6F_5)_3$ -mediated reduction of imines and nitriles with  $H_2$ . *Chem. Commun.* **2008**, 1701–1703.

(51) Spies, P.; Schwendemann, S.; Lange, S.; Kehr, G.; Fröhlich, R.; Erker, G. Metal-Free Catalytic Hydrogenation of Enamines, Imines, and Conjugated Phosphinoalkenylboranes. *Angew. Chem., Int. Ed.* **2008**, 47, 7543–7546.

(52) Ramos, A.; Lough, A. J.; Stephan, D. W. Activation of  $H_2$  by frustrated Lewis pairs derived from mono- and bis-phosphinoferrrocenes and  $B(C_6F_5)_3$ . *Chem. Commun.* **2009**, 1118–1120.

(53) Holschumacher, D.; Taouss, C.; Bannenberg, T.; Hrib, C. G.; Daniliuc, C. G.; Jones, P. G.; Tamm, M. Dehydrogenation reactivity of a frustrated carbene-borane Lewis pair. *Dalton Trans.* **2009**, 6927–6929.

(54) Chase, P. A.; Gille, A. L.; Gilbert, T. M.; Stephan, D. W. Frustrated Lewis pairs derived from N-heterocyclic carbenes and Lewis acids. *Dalton Trans.* **2009**, 7179–7188.

(55) Mömning, C. M.; Frömel, S.; Kehr, G.; Fröhlich, R.; Grimme, S.; Erker, G. Reactions of an Intramolecular Frustrated Lewis Pair with Unsaturated Substrates: Evidence for a Concerted Olefin Addition Reaction. *J. Am. Chem. Soc.* **2009**, 131, 12280–12289.

(56) Mobus, J.; vom Stein, T.; Stephan, D. W. Cooperative Lewis acidity in borane-substituted fluorophosphonium cations. *Chem. Commun.* **2016**, 52, 6387–6390.

(57) Zhou, J.; Liu, L. L.; Cao, L. L.; Stephan, D. W. An umpolung of Lewis acidity/basicity at nitrogen by deprotonation of a cyclic (amino)(aryl)nitrenium cation. *Chem. Commun.* **2018**, 54, 4390–4393.

(58) Stephan, D. W. A Tale of Two Elements: The Lewis Acidity/Basicity Umpolung of Boron and Phosphorus. *Angew. Chem., Int. Ed.* **2017**, 56, 5984–5992.

(59) Bayne, J. M.; Stephan, D. W. Phosphorus Lewis acids: emerging reactivity and applications in catalysis. *Chem. Soc. Rev.* **2016**, 45, 765–774.

(60) Burford, N.; Ragogna, P. J.; Robertson, K. N.; Cameron, T. S.; Hardman, N. J.; Power, P. P. Coordination Chemistry Umpolung: A Gallane Ligand on a Phosphine Lewis Acceptor. *J. Am. Chem. Soc.* **2002**, 124, 382–383.

(61) Scott, D. J.; Fuchter, M. J.; Ashley, A. E. Designing effective 'frustrated Lewis pair' hydrogenation catalysts. *Chem. Soc. Rev.* **2017**, 46, 5689–5700.

(62) Xu, H.; Zhu, Z.; Guo, Y.; Liu, C.; Zhang, W.; Zhu, Y.; Wang, Y.; Tang, M. A DFT study on N-heterocyclic carbene catalyzed [4 + 2] annulation reaction with in situ generated heterocyclic orthoquinodimethane: Mechanism, origin of enantioselectivity and role of catalyst. *Tetrahedron.* **2018**, 74, 1009–1015.

(63) Ma, G.; Li, Z. H. Methane activation by metal-free Lewis acid centers only—a computational design and mechanism study. *Phys. Chem. Chem. Phys.* **2016**, 18, 11539–11549.

(64) Zhao, Y.; Truhlar, D. G. Density Functional Theory for Reaction Energies: Test of Meta and Hybrid Meta Functionals, Range-Separated Functionals, and Other High-Performance Functionals. *J. Chem. Theory Comput.* **2011**, 7, 669–676.

(65) Walker, M.; Harvey, J. A. A.; Sen, A.; Dessent, C. E. H. Performance of M06, M06–2X, and M06–HF density functionals for conformationally flexible anionic clusters: M06 functionals perform better than B3LYP for a model system with dispersion and ionic hydrogen-bonding interactions. *J. Phys. Chem. A.* **2013**, 117, 12590–12600.

(66) Valero, R.; Costa, R.; de P. R. Moreira, I.; Truhlar, D. G.; Illas, F. Performance of the M06 family of exchange-correlation functionals for



- predicting magnetic coupling in organic and inorganic molecules. *J. Chem. Phys.* **2008**, *128*, 114103.
- (67) Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241.
- (68) Zhao, Y.; Truhlar, D. G. Density Functionals with Broad Applicability in Chemistry. *Acc. Chem. Res.* **2008**, *41*, 157–167.
- (69) Hariharan, P. C.; Pople, J. A. The influence of polarization functions on molecular orbital hydrogenation energies. *Theor. Chim. Acta* **1973**, *28*, 213–222.
- (70) Hehre, W. J.; Ditchfield, R.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XII. Further Extensions of Gaussian-Type Basis Sets for Use in Molecular Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1972**, *56*, 2257–2261.
- (71) Ditchfield, R.; Hehre, W. J.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. IX. An Extended Gaussian-Type Basis for Molecular-Orbital Studies of Organic Molecules. *J. Chem. Phys.* **1971**, *54*, 724–728.
- (72) Hay, P. J. Gaussian basis sets for molecular calculations. The representation of 3d orbitals in transition-metal atoms. *J. Chem. Phys.* **1977**, *66*, 4377–4384.
- (73) Binning, R. C.; Curtiss, L. A. Compact contracted basis sets for third-row atoms: Ga–Kr. *J. Comput. Chem.* **1990**, *11*, 1206–1216.
- (74) Raghavachari, K.; Trucks, G. W. Highly correlated systems. Excitation energies of first row transition metals Sc–Cu. *J. Chem. Phys.* **1989**, *91*, 1062–1065.
- (75) Frisch, M. J.; Pople, J. A.; Binkley, J. S. Self-consistent molecular orbital methods 25. Supplementary functions for Gaussian basis sets. *J. Chem. Phys.* **1984**, *80*, 3265–3269.
- (76) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; Schleyer, P. V. R. Efficient diffuse function-augmented basis sets for anion calculations. III. The 3–21+G basis set for first-row elements, Li–F. *J. Comput. Chem.* **1983**, *4*, 294–301.
- (77) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. Self-consistent molecular orbital methods. XX. A basis set for correlated wave functions. *J. Chem. Phys.* **1980**, *72*, 650–654.
- (78) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. Universal Solvation Model Based on Solute Electron Density and on a Continuum Model of the Solvent Defined by the Bulk Dielectric Constant and Atomic Surface Tensions. *J. Chem. Phys.* **2009**, *113*, 6378–6396.
- (79) Domańska, U.; Laskowska, M.; Pobudkowska, A. Phase equilibria study of the binary systems (1-butyl-3-methylimidazolium thiocyanate ionic liquid + organic solvent or water). *J. Phys. Chem. B.* **2009**, *113*, 6397–6404.
- (80) Reed, A. E.; Curtiss, L. A.; Weinhold, F. Intermolecular interactions from a natural bond orbital, donor-acceptor viewpoint. *Chem. Rev.* **1988**, *88*, 899–926.
- (81) Reed, A. E.; Weinstock, R. B.; Weinhold, F. Natural population analysis. *J. Chem. Phys.* **1985**, *83*, 735–746.
- (82) Foster, J. P.; Weinhold, F. Natural hybrid orbitals. *J. Am. Chem. Soc.* **1980**, *102*, 7211–7218.
- (83) Hammond, G. S. A Correlation of Reaction Rates. *J. Am. Chem. Soc.* **1955**, *77*, 334–338.
- (84) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.;
- Cioslowski, J.; Fox, D. J. *Gaussian 09; Gaussian, Inc.*; Wallingford, CT, 2009.
- (85) Legault, C. Y. *CYLVView, version 1.0 b*; Université de Sherbrooke: Sherbrooke, Quebec, Canada, 2009.
- (86) Das, U. K.; Chakraborty, S.; Diskin-Posner, Y.; Milstein, D. Direct conversion of alcohols into alkenes by dehydrogenative coupling with hydrazine/hydrazone catalyzed by manganese. *Angew. Chem., Int. Ed.* **2018**, *57*, 13444–13448.