

A Boron-Transfer Mechanism Mediating the Thermally Induced Revival of Frustrated Carbene–Borane Pairs from their Shelf-Stable Adducts

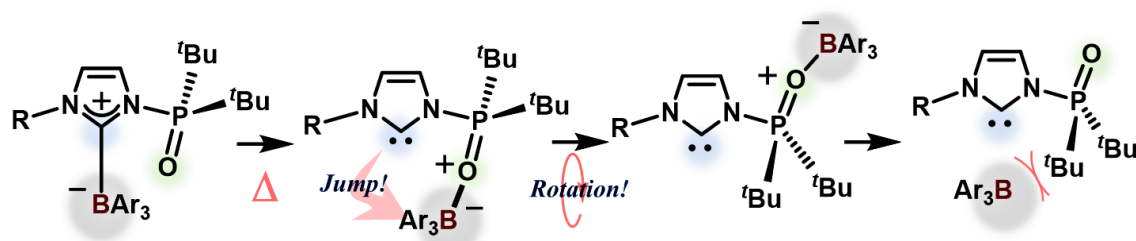
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Abstract: Combined experimental and theoretical studies allowed clarifying the reaction mechanism for the revival of frustrated carbene–borane pairs from external-stimuli-responsive classical Lewis adducts comprised of *N*-phosphine oxide-substituted imidazolylienes and triarylboranes. A borane-transfer process from the carbene carbon atom to the *N*-phosphinoyl oxygen atom was identified as the rate-determining event for the regeneration of the FLP species, eventually enabling the heterolytic cleavage of H₂.

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There have been many recent developments in the chemistry of frustrated Lewis pairs (FLPs) that have been of note, for example, the activation of H_2 mediated by main-group elements.^[1] In general, FLPs are transient and not shelf-stable species making their isolation challenging. Meanwhile, chemists have developed strategies that trigger the conformational isomerization of molecules in response to external-stimuli.^[2] These strategies can also be used to generate transient FLP species from classical Lewis adducts (CLAs) that act like their shelf-stable precursors.^[3,4] In 2015, we demonstrated a strategy to generate FLPs from shelf-stable CLAs ($\mathbf{1} \cdot \mathbf{B}^1$ in Figure 1) that are comprised of *N*-phosphine oxide-substituted imidazolyidenes (PoxIm; $\mathbf{1}$) and $\text{B}(\text{C}_6\text{F}_5)_3$ (\mathbf{B}^1). Here, the revival of the FLP from the CLA is closely controlled by a thermally induced conformational isomerization of the *N*-phosphinoyl moiety.^[4c,5] In 2018, Stephan et al. reported a system to control the generation of FLPs from CLAs via a light-induced *E/Z* isomerization of $(\text{C}_6\text{F}_5)_2\text{B}((p\text{-Tol})\text{S})\text{C}=\text{CCH}(t\text{Bu})$.^[6] Nevertheless, such FLP revival systems, including external-stimuli-responsive conformational isomerizations, are still underdeveloped. Thus, clarifying the relationship between external-stimuli-responsive conformational isomerizations and the interconversion that occurs between frustrated and quenched Lewis pairs is of great importance. This would allow a significant expansion of different strategies to design and apply FLP species.^[4e]

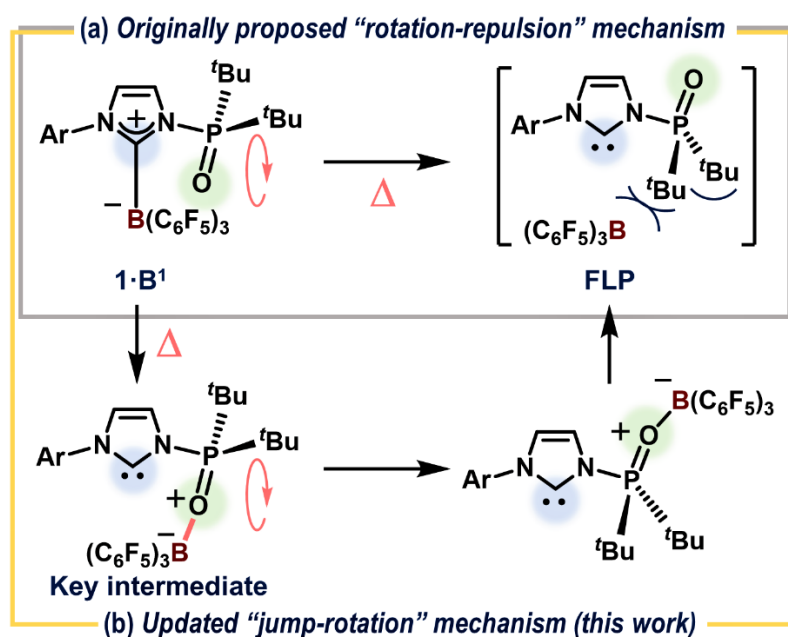
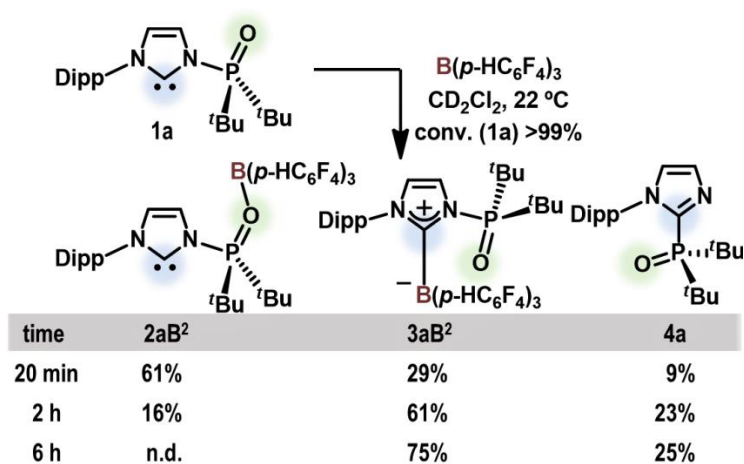


Figure 1. Revival of FLPs from $[\text{PoxIm}-\text{B}(\text{C}_6\text{F}_5)_3]$ adducts, induced by thermally responsive molecular motions. (a) A previously proposed mechanism. (b) The updated mechanism proposed based on the results of this work.

In our system that uses PoxImS, the revival mechanism has not been fully explained. A tentative mechanism in which a $\text{B}(\text{C}_6\text{F}_5)_3$ moiety is repelled by the *N*-phosphinoyl group via a thermally induced isomerization from the *syn* to *anti* conformation had been proposed. In this case the *syn/anti* conformation refers to the relative orientation of the carbene carbon atom and the *N*-phosphinoyl oxygen atom with respect to the N–P bond (Figure 1a).^[4c] Herein, we report the results of a combined experimental and theoretical mechanistic study that demonstrates the key role of a transfer step where the triarylborane (BAR_3) unit on the carbene carbon atom moves to the *N*-phosphinoyl oxygen atom (Figure 1b). In this study, PoxImS with 2,6-*i*Pr₂-C₆H₃, 2,4,6-Me₃-C₆H₂, and 3,5-*t*Bu₂-C₆H₃ groups were studied and are herein referred to as **1a**, **1b**, and **1c**, respectively.

To explore the impact of the Lewis acidity of BAR_3 on the formation and reactivity of the carbene–borane adducts, the reaction between **1a** and $\text{B}(p\text{-HC}_6\text{F}_4)_3$ (**B²**)^[7] was undertaken (Scheme 1). Full consumption of **1a** was confirmed after 20 minutes, resulting in the formation of two CLAs, i.e., **2aB²**, which contains a *N*-phosphinoyl oxygen–boron bond, and **3aB²**, which contains a carbene–boron bond, in 61% and 29% yield, respectively. Previously, we have reported that, even at –30 °C, **2aB¹** could be converted to **3aB¹** and that full identification of **2aB¹** could therefore be achieved using NMR analysis conducted at –90 °C.^[4c] In the present case, **2aB²** exhibited a longer life-time at room temperature than **2aB¹**, which enabled us to prepare single crystals of **2aB²** by recrystallization from the reaction mixture at –30 °C. The molecular structure of **2aB²** was unambiguously confirmed using single-crystal X-ray diffraction (SC-XRD) analysis. A set of (*R_a*) and (*S_a*) atropisomers of **2aB²** was identified in the asymmetric unit of the single crystal. The molecular structure of (*R_a*)-**2aB²** is shown in Figure 2a and demonstrates a rare example of complexation-induced N–P axial chirality.^[5c] As the reaction progressed, **2aB²** was converted to **3aB²** and **4a**; **2aB²** was fully consumed within 6 h to afford these compounds in 75% and 25% yield, respectively. It should be noted that **4a** is likely furnished via the migration of the *N*-phosphinoyl group from the nitrogen atom to the carbene carbon atom. However, in the absence of **B²**, this migration only proceeded to 9% at 100 °C, even after 25 h.^[5d] The formation of **4a** was therefore promoted by the enhancement of the electrophilicity of the P center via the coordination of the *N*-phosphinoyl moiety to **B²**. Regeneration of **B²** was observed along with the production of **4a**. The molecular structure of **3aB²** was also confirmed by SC-XRD analysis (Figure 2b). Comparison of the structural parameters between the solid-state structures of **3aB²** and **3aB¹** shows their similarity. For example, the C1–B distances in **3aB²** and in **3aB¹** are 1.710(3) Å and 1.696(3) Å, respectively. The interatomic distance of 3.257(3) Å between the O and B atoms in **3aB²** suggests the absence of a specific interaction between these atoms, similar to that in **3aB¹** (3.234(3) Å).



Scheme 1. Reaction between **1a** and $B(p\text{-HC}_6\text{F}_4)_3$ (**B²**). The reaction was monitored by NMR spectroscopy and the product yields were estimated based on ^{31}P NMR analyses.

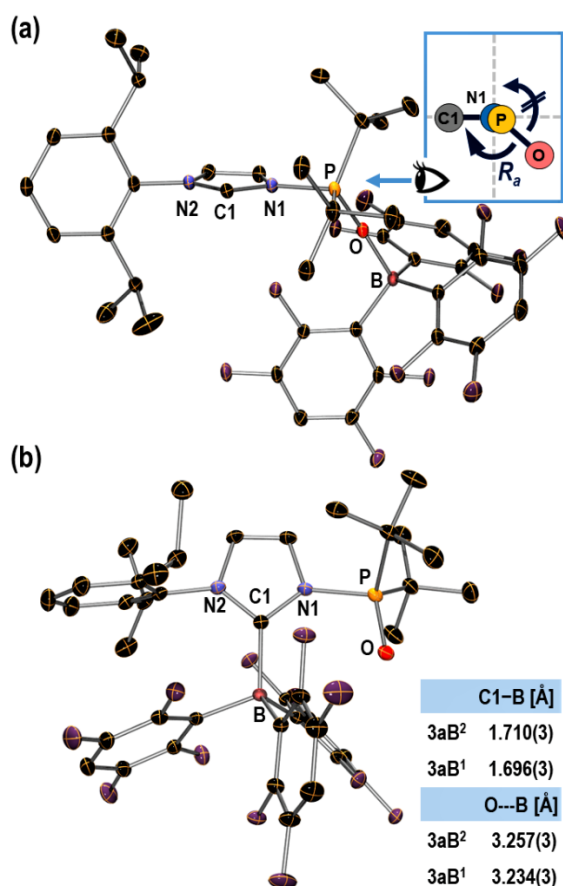
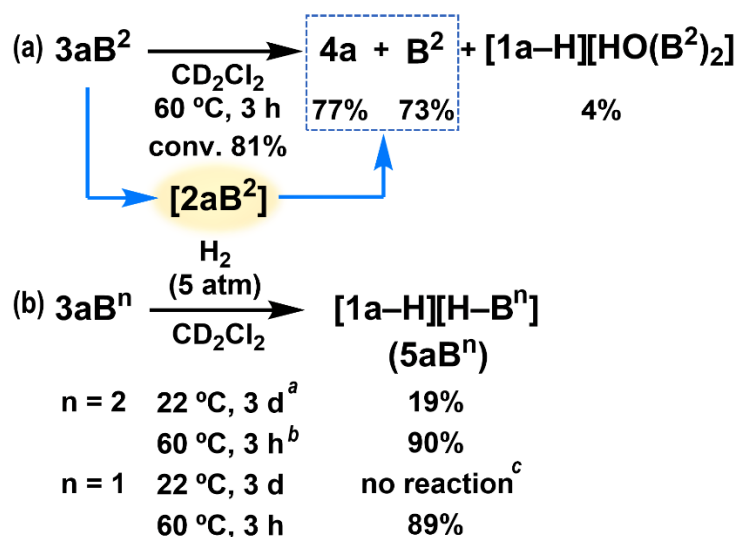


Figure 2. (a) Molecular structure of $(R_a)\text{-}2aB^2$ with thermal ellipsoids at 30% probability; H atoms and solvated C_7H_8 molecules are omitted for clarity. Selected bond lengths [\AA] and angles [$^\circ$]: O–B 1.556(2), N1–P 1.707(2), P–O 1.513(1); P–O–B 165.2(1), C1–N1–P–O 128.0(1). (b)

Molecular structure of **3aB²** with thermal ellipsoids at 30% probability; H atoms are omitted for clarity. A comparison of the carbene–boron bond lengths of **3aB²** and **3aB¹** (*cf.* ref 4c) is also shown; C1-N1-P-O: 15.3(2)°.

Thermolysis of **3aB²** at 60 °C for 3 h resulted in the generation of **4a** and **B²** in 77% and 73% yield, respectively, with concomitant formation of **[1a–H][HO(B²)₂]** in 4% yield (conversion of **3aB²** = 81%; Scheme 2a). Although **2aB²** was not observed via NMR analysis of this reaction at 60 °C, the formation of **4a** and **B²** indicates the *in-situ* regeneration of **2aB²** (*vide supra*). The formation of **[1a–H][HO(B²)₂]** can be rationalized in terms of a reaction between contaminated H₂O and the FLP species regenerated from **3aB²** via **2aB²**. The regeneration of the FLP species from **3aB²** was then clearly confirmed by treating **3aB²** with H₂ (5 atm) at 22 °C, resulting in the formation of **[1a–H][H–B²]** (**5aB²**) in a 19% yield with concomitant formation of **[1a–H][HO(B²)₂]** (8%) and **1a** (6%) (Scheme 2b). Under identical conditions, no reaction occurred when **3aB¹** was used.^[4c] At 60 °C, **5aB²** was generated in 90% yield after 3 h, which is almost comparable with the production of **5aB¹** (89%) from **3aB¹**.^[8] Thus, the lower Lewis acidity of **B²** relative to **B¹** allowed a more facile revival of the FLP species from **3aB²** than from **3aB¹**. However, the lower Lewis acidity did not affect the progress of the heterolytic cleavage of H₂ by FLPs at 60 °C.



Scheme 2. (a) Thermolysis of **3aB²** monitored via NMR spectroscopy. Product yields were calculated based on ³¹P and ¹⁹F NMR analyses. (b) Reaction between **3aB²** and H₂. Product yields were calculated based on ³¹P analysis. ^a**[1a–H][HO(B²)₂]** and **1a** were also observed in 8% and 6% yield, respectively. ^b**[1a–H][HO(B²)₂]** was also observed in 7% yield. ^cResults obtained using **3aB¹** are reproduced from ref. 4c.

To gain further insight into the reaction mechanism, the initial rate constants for the generation of **5aB**¹, k_{int} [10^{-5} s^{-1}], from the reaction between **3aB**¹ and H_2 in 1,2-dichloroethane- d_4 (DCE- d_4) at 60 °C were estimated by varying the H_2 pressure from 0.5 to 5.0 atm (Figure 3a). It should be noted here that when H_2 was pressurized at 5.0 atm, an excess of H_2 (ca. 0.3 mmol) with respect to **3aB**¹ (0.010 mmol) was added to the pressure-tight NMR tube. The concentration of H_2 clearly influenced the progress of the reaction, suggesting that the heterolytic cleavage of H_2 by the FLP species is involved in the rate-determining events. Next, the reaction between **3aB**¹ and H_2 at 5.0 atm of pressure was monitored in DCE- d_4 whilst the temperature was varied from 50 to 80 °C (Figure S27). Pseudo-first order rate constants, k_{obs} [10^{-5} s^{-1}], of 2.95(2), 11.2(8), 46.4(4) and 183(2) were estimated for the reactions at 50, 60, 70, and 80 °C, respectively. Thus, the activation energy and pre-exponential factor obtained from the plot based on the Arrhenius equation, $\ln k_{\text{obs}} = -(E_a/R)(1/T) + \ln A$, are $E_a = 31.2 \text{ [kcal mol}^{-1}\text{]}$ and $A = 3.3(36) \times 10^{16} \text{ [s}^{-1}\text{]}$ (Figure 3b). Given the close relation between E_a and ΔH^\ddagger , the values obtained for E_a suggest that the formation of **5aB**¹ via the reaction between **3aB**¹ and H_2 only occurs at temperatures higher than 25 °C.^[9]

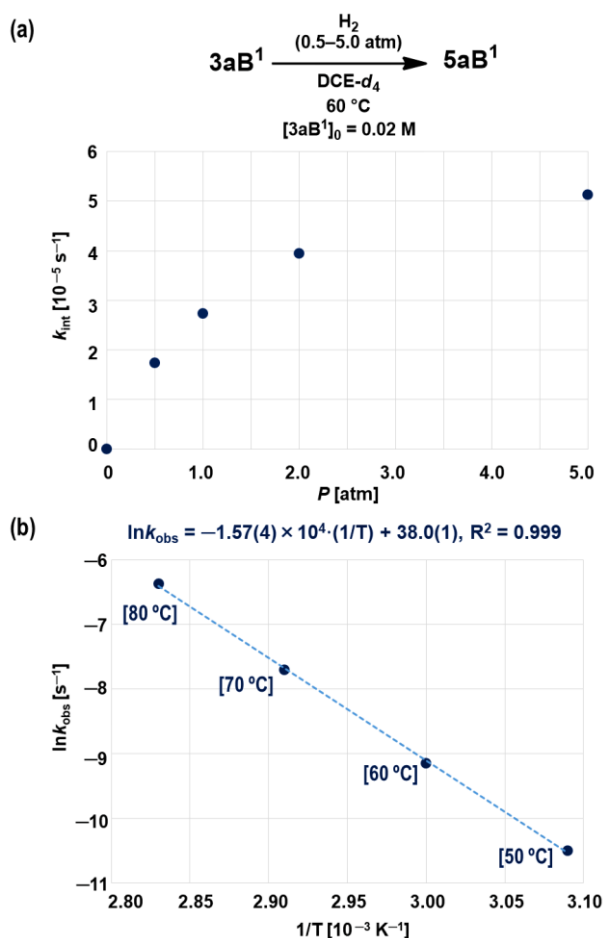


Figure 3. (a) Plot of the H₂ pressure, P [atm], as a function of the initial reaction rate constants, k_{int} [10^{-5} s^{-1}]. (b) Plot of $1/T$ [10^{-3} K^{-1}] as a function of $\ln k_{\text{obs}}$ [s^{-1}]. The k_{obs} values are the pseudo-first order rate constants for the formation of **5aB**¹ obtained from the reaction of **1a** ($2.0 \times 10^{-2} \text{ M}$ in DCE- d_4) and H₂ (5 atm).

Based on the results presented here and those previously reported,^[4c] the reaction between the carbene–borane adducts and H₂ to give [PoxIm–H][H–BAr₃] likely proceeds via the heterolytic cleavage of H₂ by the FLP species that are formed following the regeneration of the *N*-phosphinoyl oxygen–borane adducts. These steps are expected to be the rate-determining events because the concentration of H₂ (Figure 3a), the steric bulk of the *N*-aryl group^[4c] and the Lewis acidity of the BAr₃ moiety (Scheme 2b) influence the reaction rates and/or the temperature required to initiate the reaction between the carbene–borane adducts and H₂.

Density-functional theory (DFT) calculations were carried out for **3aB**¹ at the ω B97X-D/6-31G(d) level of theory (Figure 4a). The relative Gibbs free energies with respect to [**1a** + **B**¹] (0.0 kcal·mol^{−1}) are shown. During the transformation of **3aB**¹ (−18.0 kcal·mol^{−1}) to **2aB**¹ (−10.6 kcal·mol^{−1}), both of which were experimentally confirmed, the formation of an intermediate **2a'B**¹ (−7.4 kcal·mol^{−1}) was predicted via a C-to-O transfer of **B**¹ in **3aB**¹. This distinctive boron-transfer process takes place via activation complex **TS1a** (+6.9 kcal·mol^{−1}). The subsequent rotation of the *N*-phosphinoyl moiety via **TS2a** (+7.9 kcal·mol^{−1}) affords **2aB**¹. Next, the dissociation of the B–O bond occurs to regenerate [**1a** + **B**¹]. The optimized molecular structures of **TS1a** and **2a'B**¹ are shown in Figure 4c. In **TS1a**, the interatomic distances B···C1 and B···O are 4.24 and 3.34 Å, respectively, while **B**¹ adopts a planar geometry. Thus, **B**¹ is dissociated from both the carbene carbon and phosphinoyl oxygen atoms in **TS1a**, while the formation of the B–O bond (1.59 Å) is confirmed in **2a'B**¹. Based on the quantum theory of atoms in molecule (AIM) method, neither bond paths nor bond critical points were confirmed between the B and C1/O atoms in **TS1a** (Figure S30).^[10] This AIM analysis demonstrates that several non-covalent interactions, including π - π and H···F interactions, exist between the **1a** and **B**¹ moieties to stabilize **TS1a**.

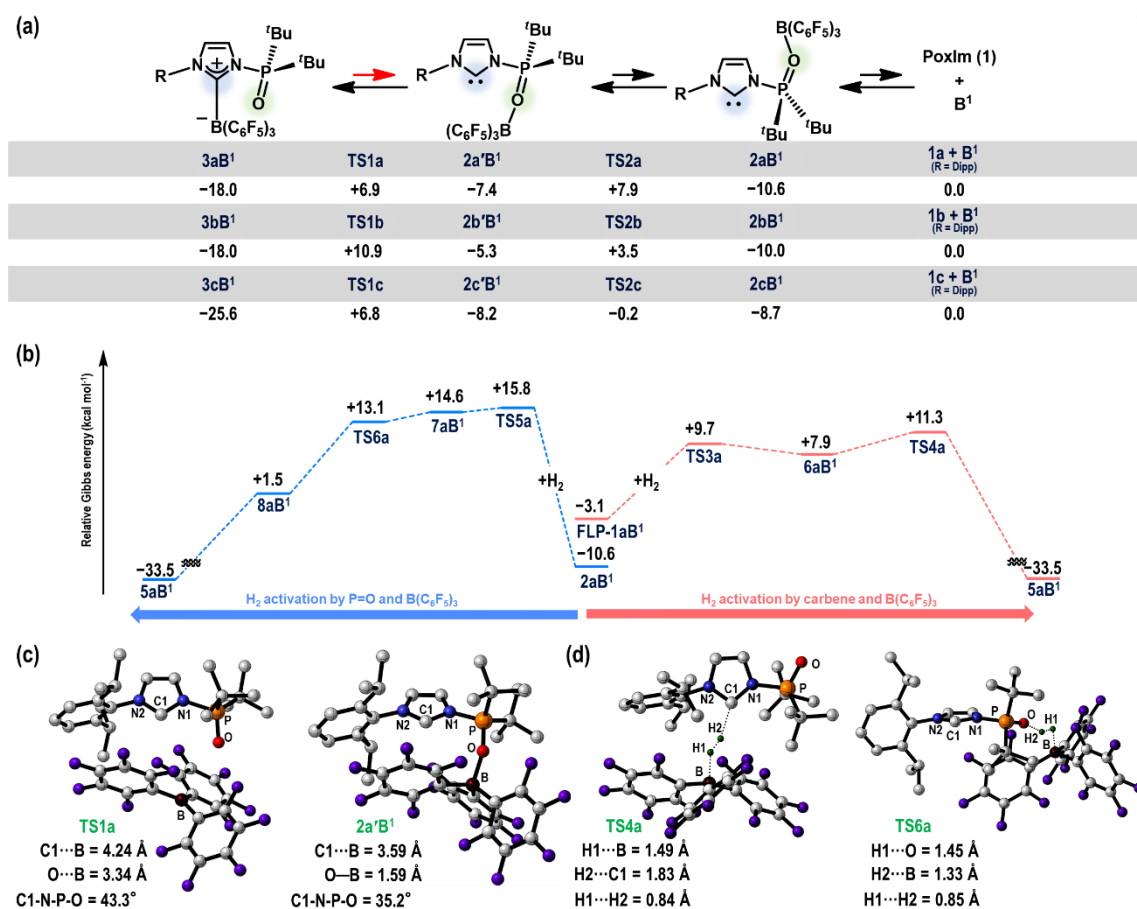


Figure 4. (a) Proposed mechanisms for the regeneration of $[1 + B^1]$ from the carbene–borane complexes $3aB^1$ – $3cB^1$. (b) Proposed mechanisms for the heterolytic cleavage of H_2 , enabled by the phosphinoyl oxygen and $B(C_6F_5)_3$ moieties (left) or by the carbene and $B(C_6F_5)_3$ moieties (right). (c) DFT-optimized molecular structures for **TS1a** and **2a'B¹**. (d) DFT-optimized molecular structures for **TS4a** and **TS6a**. The relative Gibbs energies [$kcal\ mol^{-1}$] are shown with respect to each $[1 + B^1]$, calculated at the $\omega B97X-D/6-31G(d)$ level of theory (298.15 K, 1 atm, see SI for details).

Two plausible mechanisms were evaluated for the FLP-mediated cleavage of H_2 on the basis that the Lewis-basic center reacts with H_2 via cooperation with B^1 (Figure 4b). One possibility is that the carbene carbon atom works as a Lewis base (path I; the right path in Figure 4b),^[1,11] while the other is that the *N*-phosphinoyl oxygen functions as a Lewis base (path II; the left path in Figure 4b).^[12] In path I, the heterolytic cleavage of H_2 takes places via **TS4a** (+11.3 $kcal\cdot mol^{-1}$), which arises from the insertion of H_2 into the reaction field around the carbene carbon and boron atoms in **FLP-1aB¹**, affording **5aB¹** (−33.5 $kcal\cdot mol^{-1}$), a species more thermodynamically stable than **3aB¹**. In the optimized structure of **TS4a** (Figure 4d), the dissociation of the H1–H2 bond (0.84 Å) occurs with the partial formation of the C1–H2/B–H1

bonds (1.83/1.49 Å). Based on these results, the overall path from **3aB**¹ to **5aB**¹ via **FLP-1aB**¹ is substantially exothermic ($\Delta G^\circ = -15.5 \text{ kcal}\cdot\text{mol}^{-1}$) and includes an overall activation energy barrier of +29.3 kcal·mol⁻¹ required to overcome **TS4a**. In path II, which takes place via **TS5a** (a transition state for the insertion of H₂ into the O–P bond) and **TS6a** (a transition state for the cleavage of H₂ between the O and P atoms), a higher activation energy barrier of +33.8 kcal·mol⁻¹ is predicted to yield intermediate **8aB**¹, which contains a P=O–H⁺ and B–H⁻ species. The subsequent transfer of H⁺ from the *N*-phosphinoyl oxygen atom to the carbene carbon atom furnishes **5aB**¹, although the details of this process remain unclear at this point. The molecular structure of **TS6a** shows that the cleavage of the H1–H2 bond (0.85 Å) by the *N*-phosphinoyl oxygen and boron atoms occurs in a cooperative fashion (Figure 4d). Given the experimental and theoretical results reported here, we conclude that path I is the more likely one.

The impact of the *N*-aryl substituents on the activation energy barriers for the regeneration of [**1** + **B**¹] was evaluated using calculations on **3bB**¹, which contains an *N*-Mes group, as well as **3cB**¹, which contains an *N*-Dtbp group. This afforded ΔG^\ddagger values of +28.9 and +32.4 kcal·mol⁻¹ for **3bB**¹ and **3cB**¹, respectively (Figure 4a). These results are consistent with the experimental observations, i.e. that **3aB**¹–**3cB**¹ did not react in the presence or absence of H₂ under ambient conditions, and that the temperature to induce the reaction between these CLAs and H₂ increases in the order **3aB**¹ (60 °C) < **3bB**¹ (80 °C) < **3cB**¹ (120 °C).^[4c]

In summary, the reaction mechanism for the revival of frustrated carbene–borane pairs from external-stimuli-responsive classical Lewis adducts (CLAs), comprised of *N*-phosphine oxide-substituted imidazolyliene (PoxIm) and triarylboranes (BAr₃), is reported based on a combination of experimental and theoretical studies. Remarkably, a transfer of the borane moiety from the carbene carbon atom to the *N*-phosphinoyl oxygen atom was identified as a key step in the heterolytic cleavage of H₂ by the regenerated FLP species. The optimized transition-state structure for this borane-transfer process was confirmed to include no bonding interactions between the carbene carbon/phosphinoyl oxygen and boron atoms, albeit that it is stabilized by intermolecular non-covalent interactions between the PoxIm and BAr₃ moieties. The heterolytic cleavage of H₂ takes place via the cooperation of the carbene carbon and the boron atoms, and exhibits a lower overall activation energy barrier than that of the path in which a combination of the *N*-phosphinoyl oxygen and boron atom mediates the H₂ cleavage. These results demonstrate the essential role of dynamic conformational isomerization in the regulation of the reactivity of shelf-stable but external-stimuli-responsive Lewis acid-base adducts by multifunctional Lewis bases.

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Keywords

Frustrated Lewis Pairs, *N*-Heterocyclic Carbenes, Hydrogen, Phosphine Oxide

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