

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

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Recent developments on chemistry of frustrated Lewis pairs (FLPs) are noteworthy, as illustrated by the heterolytic cleavage of H₂ mediated by the main-group elements.¹⁾ In 2015, we demonstrated a strategy to generate FLPs from shelf-stable classical Lewis adducts (CLAs) comprising *N*-phosphine-oxide-substituted imidazolylidenes (PoxIm)s and B(C₆F₅)₃,²⁾ however, the revival mechanism was not fully clarified. Herein, we report the reaction mechanism on this revival process based on a combination of experimental and theoretical studies.³⁾

Treatment of CLA **1** with H₂ resulted in the formation of **4** via the regeneration of FLP species (Figure 1). A transfer of the borane moiety from the carbene carbon atom to the *N*-phosphinoyl oxygen atom (from **1** to **2**) was identified as a key step for the heterolytic cleavage of H₂ by the regenerated FLP species. The molecular structure of **3** including the *N*-phosphinoyl oxygen–boron bond was confirmed by the single-crystal X-ray diffraction analysis. The mechanism showed in Figure 1 was also supported by kinetics and DFT studies.

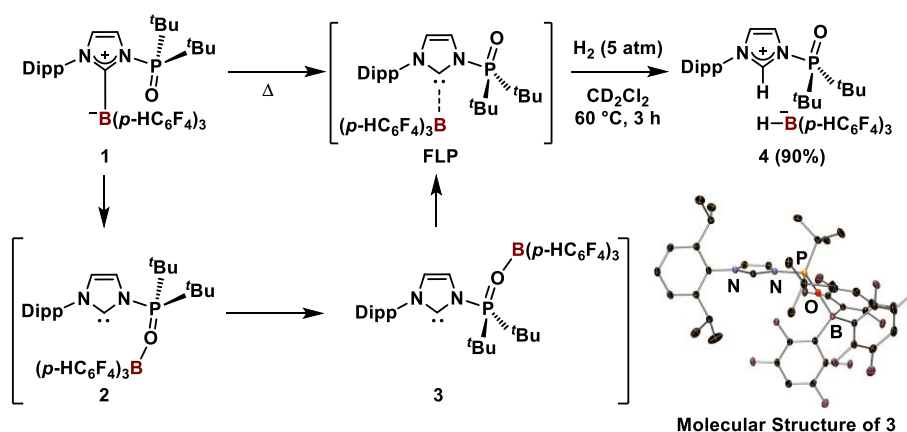


Figure 1. Revival of FLP from **1** and its reaction with H₂.

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