

Reaction of a P/Al-Based Frustrated Lewis Pair with Ammonia, Borane, and Amine–Boranes: Adduct Formation and Catalytic Dehydrogenation**

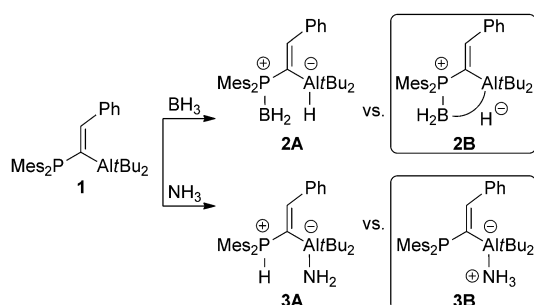
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The discovery of single-bond activation at transition-metal centers has led to a plethora of catalytic transformations, which highlights the power of organometallic chemistry. Recently, main-group systems,^[1] such as B/P-based frustrated Lewis pairs (FLPs)^[2] and singlet carbenes,^[3] possessing a lone pair of electrons and a vacant orbital were also shown to be able to split chemical bonds. Yet, despite this major advancement in main-group chemistry, the transfer of an activated fragment to a substrate remains challenging. The difficulty lies in regenerating the active species, which is a necessity for catalytic turnover. So far, FLP catalysis is only known with covalent H–H^[4] and Si–H^[5,6] bonds and sodium hydride.^[7] We were keen to extend this series.^[8]

Because the heterolytic B–H^[9] and N–H^[10] bond activation of boranes and amines by FLPs has received little attention, we investigated the formation of the activated species **2,3A** versus the adducts **2,3B** (Scheme 1). For this, we reacted the readily accessible geminal phosphorus/aluminum-based FLP **1**^[11] with BH₃·THF, ammonia (NH₃), and amine–boranes H₃B·NR₂H^[12] (R = H and Me). The potential of the B/N adduct as hydrogen carrier was revealed in the transition-

metal-catalyzed dehydrogenation.^[13] Remarkably, just two stoichiometric main-group-based FLP strategies have been reported to date.^[14,15] As FLP **1** is unreactive towards dihydrogen,^[11] we speculated that it might facilitate the dehydrogenation of amine–boranes bearing hydridic B–H and protic N–H bonds.^[16,17]

Treatment of **1** with a 1.0 M solution of BH₃·THF (1 equiv) in toluene at room temperature afforded, after work-up and crystallization, BH₃ adduct **2B** (80% yield, $\delta(^{31}\text{P}) = 3.0$, $\delta(^{1}\text{H}\{^{11}\text{B}\}) = -24.5$ ppm; Scheme 1). The borane moiety of **2B** displays dynamic behavior, as illustrated by the broad BH₃ resonance in the ¹H NMR spectrum at ambient temperature. At 330 K, the signal becomes a doublet ($\delta(^{1}\text{H}\{^{11}\text{B}\}) = 2.26$ ppm, $^2J(\text{H,P}) = 7.2$ Hz), indicating a direct interaction between the phosphorus and boron centers. Interestingly, the molecular structure of **2B**, obtained by a single-crystal X-ray structure determination (Figure 1, left),^[18] displays a BH₃



Scheme 1. Reaction of FLP **1** with BH₃ and NH₃.

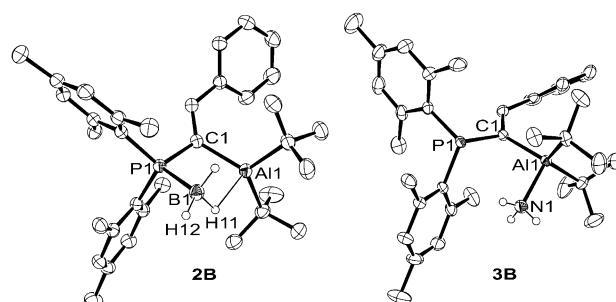


Figure 1. Molecular structures of **2B** and **3B**. Ellipsoids are set at 30% probability; hydrogen atoms, except at B1 (**2B**) and N1 (**3B**), are omitted for clarity. Selected average bond lengths [pm] for **2B**: P1–C1 180.7(2), C1–Al1 204.3(2), Al1–H11 192(2), H11–B1 124(2), B1–P1 196.7(2), B1–H12 110(2). **3B**: P1–C1 182.21(12), C1–Al1 203.68(13), Al1–N1 201.75(13).

fragment (B1–P1 196.7(2) pm) with an elongated B–H bond that participates in a B–H–Al three-center two-electron bond^[19] (B1–H11 124(2), Al1–H11 192(2) pm). This interaction and the concomitantly increased coordination number at aluminum are evident from a) the typical lengthening of the Al–C bonds from 199.1 in **1** to 202.4 pm in **2B** (202.6 pm in the NH₃ adduct **3B**, see below); and b) the larger elongation of the aluminum atom from the plane of its bonded carbon atoms than in FLP **1** (28.2 pm versus 12.5 pm; 35.0 pm in **3B**), causing the apex of the pyramid to point towards the bridging hydrogen atom. In contrast, the coordinatively unsaturated aluminum atom of **1** has only a weak interaction with a C–H

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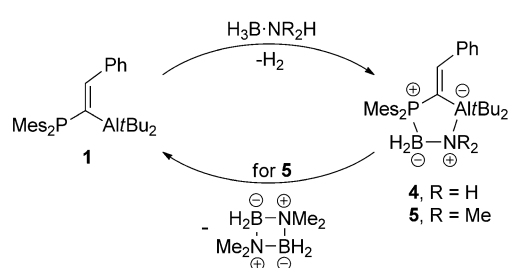
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bond of its vinylic phenyl group. The relatively short B...Al distance of 253.0(2) pm of **2B** is in the upper range of related compounds containing Al-H-B bridges.^[19] To provide insight into this mode of action, we resorted to M06-2X/6-31G(d) calculations.^[20] In accord with the molecular structure, adduct **2B** ($\Delta G = -16.0$ kcal mol⁻¹) features a BH...Al hydrogen bond and does not exist without this additional interaction. Furthermore, **2A** is not a stable minimum on the potential energy surface, indicating that FLP **1** is not prone to undergo B-H bond splitting. The rotational barrier in solution ([D₁₄]/*n*-hexane) seems to be low, and we did not observe a splitting of the B-H resonance in the ¹H{¹³B} NMR spectrum even at -90°C.

Next, NH₃ was bubbled through a solution of **1** in toluene at room temperature for 15 seconds to afford, after crystallization, the adduct **3B** (70% yield; $\delta(^{31}\text{P}) = -6.6$ ppm; Scheme 1). A crystal structure determination established unequivocally the formation of a very rare ammonia-organ-aluminum adduct (Al1-N1 201.75(13) pm; Figure 1, right).^[18,21] Lewis adduct **3B** features no NH...P interactions (also computationally) and is favored over N-H bond activation generating **3A** ($\Delta G = 19.9$ kcal mol⁻¹).^[20] To increase the potential for NH₃ splitting, the Lewis basicity of the donor site of FLP **1** can easily be enhanced,^[10,11] which is currently under investigation.

Interestingly, addition of BH₃·THF (1 equiv) to NH₃ adduct **3B** at room temperature resulted in the elimination of ammonia and the formation of BH₃ adduct **2B** (65% yield), together with small amounts of amine-borane H₃B·NH₃. The inverse reaction of BH₃ adduct **2B** with ammonia yielded a complex mixture of which only ammonia adduct **3B** and H₃B·NH₃ could be identified as minor components. Treatment of FLP **1** with H₃B·NH₃ (1 equiv) in toluene at room temperature did not afford the stable double P/B, Al/N adduct ($\Delta G = -14.5$ kcal mol⁻¹).^[20] Instead, this reaction resulted in evolution of dihydrogen to afford, after work-up and crystallization, adduct **4** (80% yield, $\delta(^{31}\text{P}) = 15.2$, $\delta(^{1}\text{H}\{^1\text{H}\}) = -12.0$ ppm; Scheme 2), which shows in the ¹H NMR spectrum both the BH and NH protons ($\delta(^1\text{H}) = 3.17$ and 1.31 ppm, respectively). Single-crystal X-ray diffraction analysis revealed that **4** is the P/Al adduct of the dehydrocoupling product H₂B=NH₂ (Figure 2, left),^[18,22] showing a unique five-membered heterocycle with a slightly distorted envelope conformation and a synclinal arrangement of the B/N-H bonds (HBNH torsion angles of 31 and 45°).

To gain insight into the underlying mechanism of the FLP-mediated dehydrogenation of H₃B·NH₃, we conducted M06-2X/6-31G(d) calculations^[20] on the full system. In contrast to the transition-metal-catalyzed dehydrogenation of amine-boranes that proceed by B-H bond activation,^[13] FLP **1** promotes the heterolytic N-H bond splitting to afford phosphonium aluminate **6** as initial prod-



Scheme 2. Dehydrocoupling of amine-boranes H₃B·NH₃ and H₃B·NMe₂H with FLP **1**.

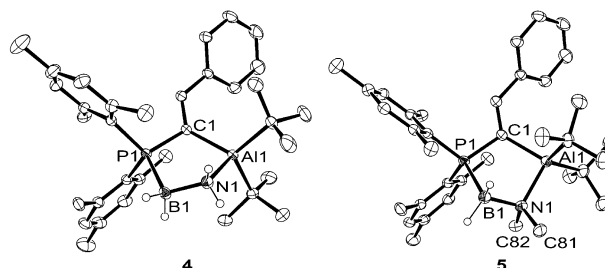


Figure 2. Molecular structures of **4** and **5**. Ellipsoids are set at 30% probability; hydrogen atoms, except at B1 and N1, and *n*-hexane (**5**) solvent molecules are omitted for clarity. Selected average bond lengths [pm] for **4**: P1-C1 181.17(11), C1-Al1 204.74(12), Al1-N1 197.95(11), N1-B1 157.01(17), B1-P1 199.84(14). **5**: P1-C1 182.51(11), C1-Al1 208.23(11), Al1-N1 202.16(11), N1-C81 149.06(16), N1-C82 148.85(17), N1-B1 158.83(17), B1-P1 198.81(14).

uct ($\Delta G^\ddagger = 20.6$; $\Delta G = -7.7$ kcal mol⁻¹; Figure 3),^[23] compound **6** bears short, intramolecular P-H^{δ+}...^{δ-}H-B contacts (for example, H1-H2 197.5 pm)^[24] and is much more stable than the corresponding B-H activated species ($\Delta\Delta G = 16.2$ kcal mol⁻¹). Next, protonation (by H1) of the hydridic H2-B1 bond^[25] yields the loosely bound η²-H₂ borane

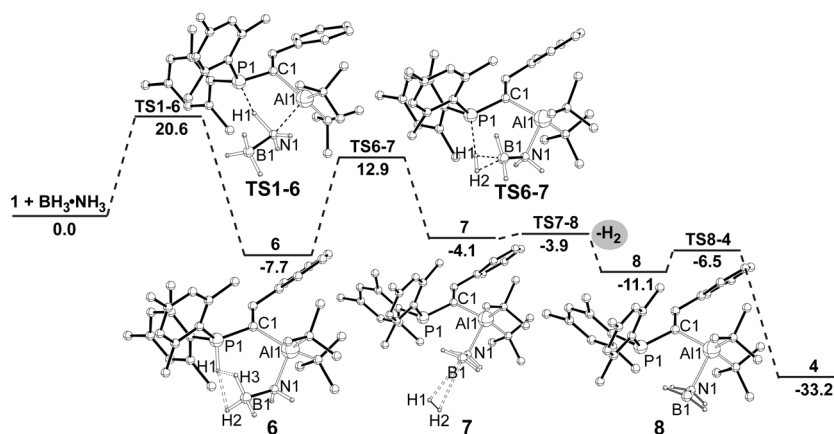


Figure 3. Relative M06-2X/6-31G(d) Gibbs free energies (in kcal mol⁻¹) for the dehydrogenation of H₃B·NH₃ by FLP **1** and formation of aminoborane adduct **4**. Hydrogen atoms, except at B1 and N1, are omitted for clarity. Selected average bond lengths [pm] for **TS1-6**: P1-H1 167.3, H1-N1 133.7, B1-N1 170.0, N1-Al1 233.3. **6**: P1-H1 139.2, H2-B1 123.0, H3-B1 122.1, H1-H2 197.5, H1-H3 216.2, B1-N1 163.3, N1-Al1 197.9. **TS6-7**: P1-H1 218.7, H1-B1 157.6, H2-B1 143.4, H1-H2 82.4, B1-N1 154.9. **7**: H1-B1 280.2, H2-B1 296.4, H1-H2 73.9, B1-N1 144.6. **8**: B1-N1 144.4.

complex **7**^[24a,26] ($\Delta\Delta G^\ddagger = 20.6$; $\Delta\Delta G = 3.6$ kcal mol⁻¹) that readily undergoes elimination of dihydrogen to afford amino-borane adduct **8** ($\Delta\Delta G^\ddagger = 0.2$; $\Delta\Delta G = -7.0$ kcal mol⁻¹). Finally, ring closure by P–B bond formation generates the experimentally ascertained heterocycle **4** ($\Delta\Delta G^\ddagger = 4.6$; $\Delta\Delta G = -22.1$ kcal mol⁻¹).

Whereas **4** is stable in solution and does not undergo further loss of dihydrogen in the presence of excess **1**, the reaction of FLP **1** with H₃B–NMe₂H (1 equiv) affords the thermally unstable H₂B=NMe₂ adduct **5** (59% yield, $\delta(^{31}\text{P}) = 12.5$, $\delta(^{11}\text{B}\{^1\text{H}\}) = -5.4$ ppm; Scheme 2), which only could be obtained when the reaction mixture was kept below –30 °C.^[27] Single-crystal X-ray analysis of crystals grown at –45 °C revealed that the molecular structure of **5** is similar to that of **4** except for the elongated Al1–N1 bond (**5**: 202.16(11), **4**: 197.95(11) pm; Figure 2).^[18] This elongated bond facilitates exergonic fragmentation at room temperature into dimeric [(H₂B–NMe₂)₂] (via transient H₂B=NMe₂)^[28] and **1** ($\Delta G = -20.3$ kcal mol⁻¹).^[20] Note that in accord with these findings, the formation of cyclodiborazane [(H₂B–NH₂)₂] from **4** is endergonic ($\Delta G = 15.0$ kcal mol⁻¹).^[20,29] Interestingly, the complete regeneration of FLP **1** from **5** suggests the feasibility of a catalytic dehydrocoupling. Indeed, heating neat dimethylamine–borane with 9.3 mol% of **1** in the melt at 45 °C resulted in vigorous gas evolution and the immediate sublimation of [(H₂B–NMe₂)₂] onto a cold finger (Scheme 2). Careful heating to 90 °C completes the reaction, affording cyclodiborazane [(H₂B–NMe₂)₂] in 71% yield of isolated product after just 45 min (TON = 7.6, TOF = 10.2 h⁻¹ based on isolated material). Lower catalyst loadings are also feasible. For example, treatment of H₃B–NMe₂H with only 0.4 mol% of **1** gave the four-membered cyclodiborazane in 77% yield of isolated product after 44 h (TON = 198.3, TOF = 4.5 h⁻¹).^[30] Heating H₃B–NMe₂H without FLP catalyst **1** at 90 °C (24 h) gave only traces (5%) of [(H₂B–NMe₂)₂], together with the linear dimer Me₂NH–BH₂–NMe₂–BH₃ (10%)^[28] and unreacted amine–borane (85%), which underscores the efficiency of FLP **1** in this catalytic dehydrogenation reaction.

In summary, FLP **1** readily forms adducts with ammonia and the borane BH₃, but reacts via N–H bond activation with amine–boranes. We demonstrated a new application of main-group-based FLPs, namely the catalytic dehydrocoupling of H₃B–NMe₂H, which proceeds by elimination of dihydrogen at the boron center and subsequent dimerization of the intermediate aminoborane H₂B=NMe₂.

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