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Frustrated Lewis Pairs

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

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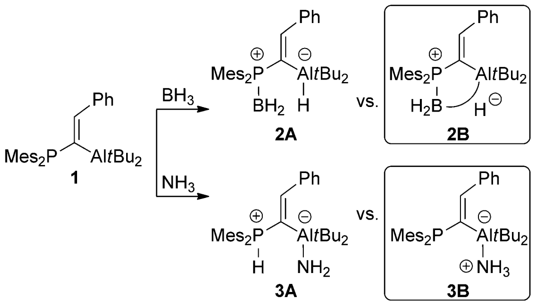
The discovery of single-bond activation at transition-metal centers has led to a plethora of catalytic transformations, which highlights the power of organometallic chemistry. Recently, main-group systems,[1] such as B/P-based frustrated Lewis pairs (FLPs)[2] and singlet carbenes,[3] possessing a lone 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 $BH_3{\cdot}THF$, ammonia (NH_3), and amine–boranes $H_3B{\cdot}NR_2H$[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]



Scheme 1. Reaction of FLP **1** with BH_3 and NH_3.

Treatment of **1** with a 1.0 M solution of $BH_3{\cdot}THF$ (1 equiv) in toluene at room temperature afforded, after work-up and crystallization, BH_3 adduct **2B** (80% yield, $\delta(^{31}P) = 3.0$, $\delta(^{11}B\{^1H\}) = -24.5$ ppm; Scheme 1). The borane moiety of **2B** displays dynamic behavior, as illustrated by the broad BH_3 resonance in the ^1H NMR spectrum at ambient temperature. At 330 K, the signal becomes a doublet ($\delta(^1H\{^{11}B\}) = 2.26$ ppm, $^2J(H,P) = 7.2$ 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 BH_3 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 NH_3 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

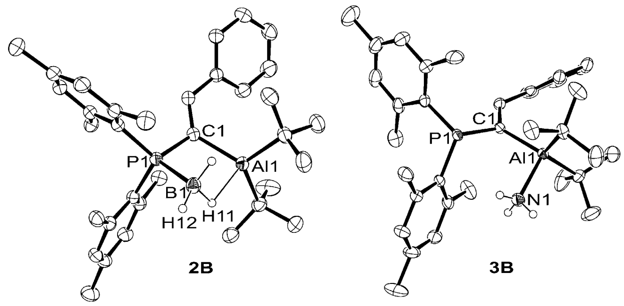


Figure 1. Molecular structures of **2B** and **3B**. Ellipsoids are set at 30% probability; hydrogen atoms, except at B1 (**2B**) and N1 (**3B**), are omitted for clarity. Selected average bond lengths [pm] for **2B**: P1–C1 180.7(2), C1–Al1 204.3(2), Al1–H11 192(2), H11–B1 124(2), B1–P1 196.7(2), B1–H12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

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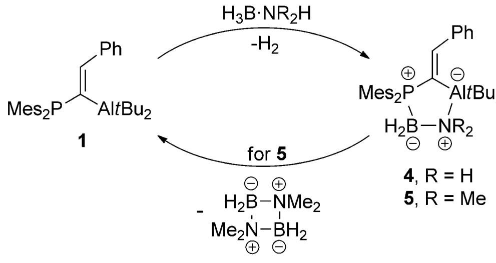
bond of its vinylic phenyl group. The relatively short B···Al distance of 253.0(2) pm of **2B** is in the upper range of related compounds containing Al-H-B bridges.[19] To provide insight into this mode of action, we resorted to M06-2X/6-31G(d) calculations.[20] In accord with the molecular structure, 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 ([D$_{14}$]*n*-hexane) seems to be low, and we did not observe a splitting of the B−H resonance in the ^{1}H{^{11}B} NMR spectrum even at −90 °C.

Next, NH_3 was bubbled through a solution of **1** in toluene at room temperature for 15 seconds to afford, after crystallization, the adduct **3B** (70 % yield; $\delta(^{31}P) = -6.6$ ppm; Scheme 1). A crystal structure determination established unequivocally the formation of a very rare ammonia–organoaluminum 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 NH_3 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 BH_3·THF (1 equiv) to NH_3 adduct **3B** at room temperature resulted in the elimination of ammonia and the formation of BH_3 adduct **2B** (65 % yield), together with small amounts of amine–borane $H_3B{\cdot}NH_3$. The inverse reaction of BH_3 adduct **2B** with ammonia yielded a complex mixture of which only ammonia adduct **3B** and $H_3B{\cdot}NH_3$ could be identified as minor components. Treatment of FLP **1** with $H_3B{\cdot}NH_3$ (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, $\delta^{31}P = 15.2$, $\delta(^{11}B\{^{1}H\}) = -12.0$ ppm; Scheme 2), which shows in the ^{1}H NMR spectrum both the BH and NH protons ($\delta(^{1}H) = 3.17$ and 1.31 ppm, respectively). Single-crystal X-ray diffraction analysis revealed that **4** is the P/Al adduct of the dehydrocoupling product $H_2B{=}NH_2$ (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 $H_3B{\cdot}NH_3$, 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 product ($\Delta G^{\ddagger} = 20.6$; $\Delta G = -7.7$ kcal mol^{-1}; Figure 3);[23] compound **6** bears short, intramolecular $P{-}H^{\delta+}\cdots{}^{\delta-}H{-}B$ 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 η^2-H_2 borane



Scheme 2. Dehydrocoupling of amine–boranes $H_3B{\cdot}NH_3$ and $H_3B{\cdot}NMe_2H$ with FLP **1**.

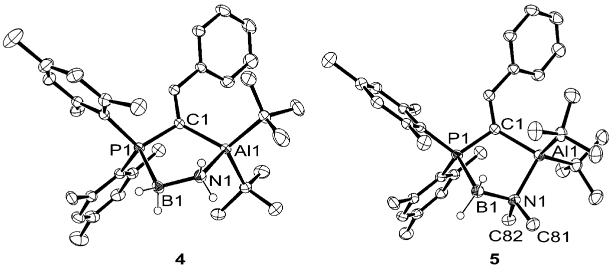


Figure 2. Molecular structures of **4** and **5**. Ellipsoids are set at 30 % probability; hydrogen atoms, except at B1 and N1, and *n*-hexane (**5**) solvent molecules are omitted for clarity. Selected average bond lengths [pm] for **4**: P1−C1 181.17(11), C1−Al1 204.74(12), Al1−N1 197.95(11), N1−B1 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-C-82 148.85(17), N1−B1 158.83(17), B1−P1 198.81(14).

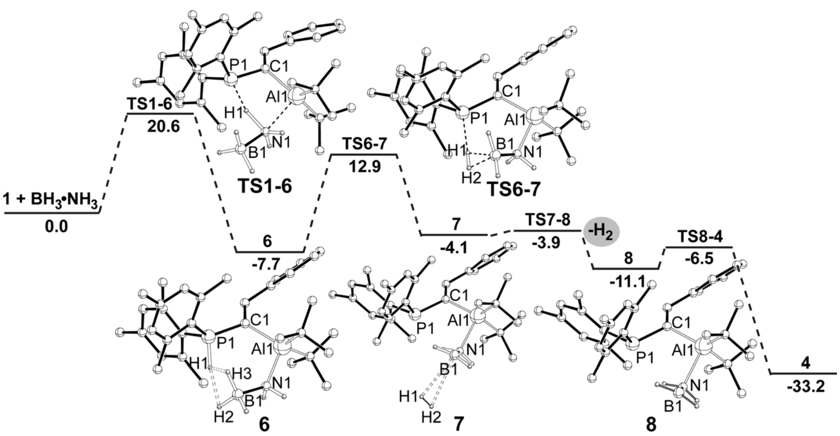


Figure 3. Relative M06-2X/6-31G(d) Gibbs free energies (in kcal mol^{-1}) for the dehydrogenation of $H_3B{\cdot}NH_3$ by FLP **1** and formation of aminoborane adduct **4**. Hydrogen atoms, except at B1 and N1, are omitted for clarity. Selected average bond lengths [pm] for **TS1–6**: P1−H1 167.3, H1−N1 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] ($\Delta\Delta G^{\neq} = 20.6$; $\Delta G = 3.6$ kcal mol^{-1}) that readily undergoes elimination of dihydrogen to afford aminoborane adduct **8** ($\Delta\Delta G^{\neq} = 0.2$; $\Delta G = -7.0$ kcal mol^{-1}). Finally, ring closure by P–B bond formation generates the experimentally ascertained heterocycle **4** ($\Delta\Delta G^{\neq} = 4.6$; $\Delta G = -22.1$ 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 $H_3B\cdot NMe_2H$ (1 equiv) affords the thermally unstable $H_2B{=}NMe_2$ adduct **5** (59 % yield, $\delta(^{31}P) = 12.5$, $\delta(^{11}B\{^{1}H\}) = -5.4$ 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 $[(H_2B{-}NMe_2)_2]$ (via transient $H_2B{=}NMe_2$)[28] and **1** ($\Delta G = -20.3$ kcal mol^{-1}).[20] Note that in accord with these findings, the formation of cyclodiborazane $[(H_2B{-}NH_2)_2]$ 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 $[(H_2B{-}NMe_2)_2]$ onto a cold finger (Scheme 2). Careful heating to 90 °C completes the reaction, affording cyclodiborazane $[(H_2B{-}NMe_2)_2]$ 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 $H_3B\cdot NMe_2H$ 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 $H_3B\cdot NMe_2H$ without FLP catalyst **1** at 90 °C (24 h) gave only traces (5 %) of $[(H_2B\text{-}NMe_2)_2]$, together with the linear dimer $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$ (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 BH_3, 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 $H_3B\cdot NMe_2H$, which proceeds by elimination of dihydrogen at the boron center and subsequent dimerization of the intermediate aminoborane $H_2B{=}NMe_2$.

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[29] The formation of the experimentally observed trimer $[(H_2B{-}NH_2)_3]$, see Ref. [28], is also endergonic ($\Delta G = 11.8\ \mathrm{kcal\,mol^{-1}}$).

[30] After analysis of the residual material that did not sublime, the total degree of dehydrogenation was estimated at 98% (9.3 mol% of **1**) and 89% (0.4 mol%), respectively.

Frustrated Lewis Pairs

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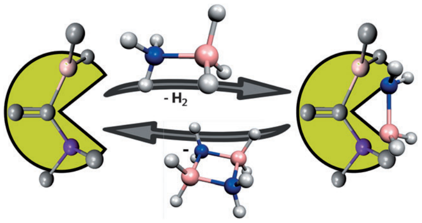
Reaction of a P/Al-Based Frustrated Lewis Pair with Ammonia, Borane, and Amine–Boranes: Adduct Formation and Catalytic Dehydrogenation



Open wide! The geminal P/Al-based frustrated Lewis pair (Mes$_2$P)(tBu$_2$Al)C=C(H)Ph forms stable Lewis adducts with BH$_3$ and NH$_3$. This compound facilitates the dehydrocoupling of the ammonia–borane adduct by unusual N–H bond activation and elimination of dihydrogen at the boron center, and it is a very active main-group-based FLP catalyst for the dehydrogenation of amine–borane H$_3$B·NMe$_2$H.