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Catalytic Dehydrogenation of Amine-Boranes using Geminal Phosphino-Boranes

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Dedicated to Professor Manfred Scheer on the Occasion of his 65th Birthday

Abstract: The reaction of the intramolecular frustrated Lewis pair (FLP) $tBu_2PCH_2BPh_2$ with the amine-boranes NH₃·BH₃ and Me₂NH·BH₃ leads to the formation of the corresponding FLP-H₂ adducts as well as novel 5-membered heterocycles that result from capturing the *in situ* formed amino-borane by a second equivalent of FLP. The sterically more demanding $tBu_2PCH_2BMes_2$ does not form such a 5-membered heterocycle when reacted with Me₂NH·BH₃ and its H₂ adduct liberates dihydrogen at elevated temperatures, promoting the metal-free catalytic dehydrogenation of amine-boranes.

Introduction

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During the past decades tremendous breakthroughs were made in main-group mediated chemical transformations and new strategies for single bond activations were discovered. The notion that frustrated Lewis pairs (FLPs) can heterolytically cleave dihydrogen^[1] spawned a new research field for metal-free stoichiometric and catalytic chemical transformations, such as hydrogenation and dehydrogenation reactions.^[2]

As a substrate for catalytic dehydrogenation, amineboranes gained a lot of attention due to their potential application as dihydrogen storage material;^[3] in particular ammonia-borane (AB) is of interest as is contains a high weight percentage of dihydrogen (19.6%).^[4] Furthermore, the products resulting of amine-borane dehydrogenation are valuable, with many potential applications in material science.^[5] To date, a lot of research has been conducted on the catalytic dehydrogenation of amineboranes by transition metal (TM) complexes.^[6] Alternatively, efforts have been made in the development of group 1 and 2 catalysts,^[7] and recently frustrated Lewis pairs have been

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reported as efficient TM-free catalysts for amine-borane dehydrogenation. $\ensuremath{^{[8]}}$

The first FLP catalyst for ammonia-borane dehydrogenation was reported by Stephan and Erker (I, Figure 1) utilizing a transfer hydrogenation step for catalyst regeneration.^[9] After this, Uhl and co-workers and some of us reported on the catalytic dehydrogenation of dimethylamine-borane (DMAB) by phosphino-alane II.^[10] In 2016, Rivard and co-workers extended the field and showed that iminoborane IV can dehydrogenate methylamine-borane (MAB) at 70 °C, utilizing 2 mol% of IV.[11] In the same year, Aldridge et al. reported that the xanthene-based phosphino-borane V is capable of dehydrogenating AB, MAB and DMAB with catalysts loadings down to 1 mol%.[12] Recently Uhl and co-workers found that the gallium analogue of II, phosphinogalane III, can be applied for ammonia- and dimethylamineborane dehydrogenation too.^[13] At the same time, the group of Bourissou showed that phosphino-borane VI rapidly converts a variety of amine-borane substrates to the corresponding dehydrogenated products.[14]



Figure 1. FLP catalysts for amine-borane dehydrogenation.

We developed geminal phosphino-borane FLP **VII** (R = tBu, R' = Ph; **1**) bearing a methylene linker, which shows reactivity towards a variety of small molecules and metal complexes.^[15 , 16] Herein, we describe the (catalytic) dehydrogenation of amine-boranes by such geminal frustrated Lewis pairs using a rational catalyst design approach targeting increased reactivity.

Results and Discussion

Treatment of 2 equivalents of $tBu_2PCH_2BPh_2$ (1) with 1 equivalent of ammonia-borane (H₃N·BH₃, AB) in THF at room

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temperature resulted in immediate consumption of AB, along with formation of dihydrogen adduct 2 ($\delta^{31}P\{^{1}H\}$ = 59.0 ppm) and 5membered heterocycle **3** ($\delta^{31}P{^1H} = 56.7$ ppm) in a 1:1 ratio. The products can be separated by extraction of 3 into n-pentane (leaving pure 2 as residue in 57% yield) and subsequent filtration of the combined extracts over alumina to remove trace amounts of 2 from the extract, giving 3 as colorless solid in 74% yield. H₂ adduct 2 displays a double multiplet in the ³¹P NMR spectrum with a ${}^{1}J_{P,H}$ coupling of 453.2 Hz, and a doublet in the ${}^{11}B$ NMR spectrum (${}^{1}J_{B,H}$ = 83.5 Hz), which is characteristic for a P–H and B-H bond, respectively. Single crystals suitable for X-ray diffraction analysis of 2 were obtained from *n*-pentane at 4 °C, which confirmed the formation of the FLP-H₂ adduct that was previously obtained from the reaction of 1 with dihydrogen.^[15a] In the solid state, the boron center in 2 is strongly pyramidalyzed (Σ (CB1C) 330.5°), which also resembles the upfield ¹¹B NMR shift $(\delta^{11}B^{1}H) = -10.1$ ppm). In contrast to the o-phenylene-bridged P/B FLP-H₂ adduct reported by Bourissou and co-workers,^[14] dihydrogen adduct 2 is stable at room temperature in the solid state and in solution, and only slowly released dihydrogen at elevated temperatures (2 hours at 80 °C).



Scheme 1. Reaction of 2 equivalents of FLP 1 with 1 equivalent of ammoniaborane (top) and the molecular structures (bottom) of 2 (left) and 3 (right) (ellipsoids at 50% probability, FLP-hydrogens, and a toluene molecule for 2 are omitted for clarity). Selected bond lengths (Å) and angles (°) for 2: P1-C1 1.7759(16), B1-C1 1.683(2), P1-C1-B1 113.48(11), Σ (CB1C) 330.5 3: P1-C1 1.8155(10), C1-B1 1.6626(14), B1-N1 1.6321(13), N1-B2 1.5898(14), B2-P1 1.9606(11).

The formation of the 5-membered heterocycle 3 is believed to be the result of trapping of the highly polarized amino-borane intermediate H₂N=BH₂ by the second equivalent of FLP 1. In the ¹¹B{¹H} NMR spectrum, **3** displays a singlet resonance ($\delta = -1.95$ ppm) for the FLP's boron moiety together with a characteristic doublet ($\delta = -20.7$ ppm, ¹J_{B,P} = 85.5 Hz) that can be ascribed to the amino-borane fragment. The corresponding ³¹P{¹H} NMR spectrum supports this notion as a broad signal was observed at δ = 56.7 ppm, which is common for such B–P interactions.^[17] Xray diffraction analysis of suitable single crystals of 3, obtained by layering a solution of 3 in DCM with pentane, unambiguously established the formation of the P-C-B-N-B based 5-membered heterocycle (Scheme 1, bottom right). Compared to the previously reported AI- and Ga-based 5-membered heterocycles formed by H₂N=BH₂ trapping using the corresponding FLPs,^[10,13] 3 contains a shorter P1-B2 bond (1.9606(11) Å; c.f. 1.9984(14) and 2.004(2) Å, respectively), suggesting that the trapped $H_2N=BH_2$ fragment is more tightly bound to the FLP in **3**.

In order to gain more insight into the mechanism of this dehydrogenation reaction, FLP 1 was reacted with the deuterated analogue of AB, H₃N·BD₃, which resulted in selective N-H to P and B–D to B transfer according to ³¹P and ¹¹B NMR spectroscopy. This suggests a similar double hydrogen transfer mechanism being operative as was observed previously by Manners et al. for dihydrogen transfer from ammonia-borane to sterically encumbered amino-boranes.^[18] Analysis of the formation of 2 by density functional theory (DFT) calculations at the wB97X-D/6-311G** level of theory revealed that the interaction of ammoniaborane with FLP 1 leads to the formation of a three-center-twoelectron adduct 4 as intermediate (Figure 2), which enables dihydrogen transfer from H₃N·BH₃ in a concerted manner via a 7membered transition state, forming phosphonium-borate 2 and one equivalent of amino-borane H₂N=BH₂. The overall process is exergonic, and the low barrier ($\Delta G^{\ddagger} = 13.1 \text{ kcal} \cdot \text{mol}^{-1}$, $\Delta E^{\ddagger} = 14.3$ kcal mol⁻¹) for **TS**₄₋₂ is in good agreement with the experimentally observed facile reaction (instantaneous at 0 °C). Additionally, trapping of the amino-borane H₂N=BH₂ fragment by a second equivalent of FLP 1 makes the overall reaction even more exergonic ($\Delta G_{\text{trapping}} = -17.5 \text{ kcal} \cdot \text{mol}^{-1}$, $\Delta E_{\text{trapping}} = -34.7$ kcal·mol⁻¹).



Figure 2. Gibbs free energy and (energy) profile calculated for dehydrogenation of ammonia-borane by FLP 1 in kcal·mol⁻¹.

Under the same conditions, the reaction of 2 equivalents of 1 with the bulkier dimethylamine-borane (Me₂NH·BH₃, DMAB) resulted in rapid formation of the known FLP-H₂ adduct 2 together with the methylated analogue of 3, compound 5 (Scheme 2). ³¹P{¹H} NMR spectroscopy of the reaction mixture revealed comparable resonance signals as for the reaction of 1 with AB ($\delta^{31}P{^{1}H} = 59.0$ ppm for the FLP-H₂ adduct, and a broad resonance signal for the methylated heterocycle; $\delta^{31}P{^{1}H} = 43.0$ ppm). In contrast to 3, the ¹J_{B,P} coupling in 5 is significantly smaller and no clear doublet was observed in the ¹¹B{¹H} NMR spectrum. DFT calculations at the ω B97X–D/6-311G^{**} level of theory suggest that the same mechanism takes place. With an overall

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barrier (ΔG) of only 14.1 kcal·mol⁻¹ ($\Delta E^{\ddagger} = 14.5$ kcal·mol⁻¹), the experimentally observed reaction rate is in good agreement with the DFT calculations (see ESI). Interestingly, when a sample of the reaction mixture was kept for a prolonged period at room temperature signals of the dimeric (Me₂NBH₂)₂ started to appear in the ¹¹B{¹H} NMR spectrum due to release of the Me₂N=BH₂ fragment from **5** and subsequent dimerisation. This indicates that increasing the steric bulk of the substrate reduces the bond strength of the amino-borane fragment to FLP **1**, which suggests that increasing the steric bulk of the FLP's substituents should also prevent adduct formation.

$$2 \ tBu_2P BPh_2 + Me_2NH \cdot BH_3 \xrightarrow{THF, rt} tBu_2P BPh_2 + tBu_2$$

Scheme 2. Reaction of 2 equivalents of FLP 1 with dimethylamine-borane.

Encouraged by these findings, we set out to design a FLP system that disfavors amino-borane adduct formation. DFT calculations at the ω B97X-D/6-311G** level of theory showed that only a slight change of the system could already prevent adduct formation. FLP tBu2PCH2BMes2 (6) bearing the bulkier mesityl substituents on boron was found to disfavor adduct formation with Me₂N=BH₂ (ΔG = 15.8 kcal·mol⁻¹), which makes 6 an interesting synthetic target for catalytic dehydrogenation. Following the same synthetic strategy used for our previously reported FLP 1,^[15a] the reaction of tBu₂PCH₂Li with 1 equivalent of CIBMes₂ cleanly afforded 6 that after work up was isolated as an orange solid in 99% yield. The $^{31}\text{P}\{^1\text{H}\}$ and $^{11}\text{B}\{^1\text{H}\}$ NMR resonances of 6 are rather similar compared to 1, namely a sharp singlet at 26.9 ppm and a broad singlet at 82.5 ppm, respectively. X-ray diffraction analysis of orange crystals obtained by cooling a saturated heptane solution of 6 to -20 °C showed that the boron empty p-orbital is rotated away from the phosphorus lone-pair (torsion angle P1-C1-B1-C11 = 168.9°) and that the boron center bears a planar geometry (\sum (CB1C) = 359.8°), making any LA…LB type of interaction negligible in the solid state (Scheme 3). The physical appearance of FLP 6 is noteworthy; whereas phenyl-substituted FLP 1 is an oil at room temperature, the mesityl-substituted analogue 6 is a solid, which facilitates the handling of the compound.





Scheme 3. Synthesis of FLP 6 (top) and its molecular structure (bottom; ellipsoids at 50% probability, hydrogen atoms are omitted for clarity). Selected bond lengths (Å) and angles (°) for 6: P1-C1 1.8605(17), C1-B1 1.582(3), P1-C1-B1 124.21(12), P1-C1-B1-C11 168.94(12), Σ (CB1C) 359.8.

Under similar conditions, FLP **6** (2 equivalents) was reacted with 1 equivalent of ammonia-borane in 2-MeTHF (2methyltetrahydrofuran) at room temperature. After approximately 1 hour at room temperature, the ¹¹B{¹H} and ³¹P{¹H} NMR spectra of the reaction mixture revealed that **6** was fully converted into FLP-H₂ adduct **7** (δ^{31} P{¹H} = 56.5 (s); ¹¹B{¹H} = -15.0 (s)) and the 5-membered heterocycle **8** (δ^{31} P{¹H} = 58.1 (br. s); ¹¹B{¹H} = 1.95 (s), -23.2 (s)), along with the formation of traces of dehydrogenation products such as borazine, cyclotriborazane (CTB) and *B*-(cyclodiborazanyl)aminoborohydride (BCDB) and a few unidentified products (Scheme 4).



Scheme 4. The reaction of 2 equivalents of 6 with dimethylamine-borane.

Interestingly, heating the reaction mixture to 70 °C led to almost complete disappearance of H₂-adduct **7** and heterocycle **8**, concomitant with an increase of dehydrogenation products together with the formation of degradation products, such as Mes₂B=NH₂ ($\delta^{11}B{^{1}H}$ = 44.1 (br. s))^[19] and *t*Bu₂PCH₃·BH₃ ($\delta^{31}P{^{1}H}$ = 39.9 (m); ¹¹B{^{1}H} = -40.8 (d, ¹J_{B,P} = 57.8 Hz)), as was observed by ¹¹B{^{1}H} and ³¹P{^{1}H} NMR spectroscopy. In addition, regeneration of FLP **6** was observed, suggesting that **6** could play a role in catalytic amine-borane dehydrogenation, which is

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significant as only a few FLPs are reported to catalyze the dehydrogenation of AB.^[12,13,14]

The labile character of both the FLP-H₂ adduct 7 and the 5membered heterocycle 8 inspired us to investigate the possibility to apply 6 as a catalyst for ammonia-borane dehydrogenation. When 4 mol% of 6 was added to a suspension of H₃N·BH₃ in 2-MeTHF, 6 was directly converted to H₂-adduct 7 and heterocycle **8** according to ${}^{11}B{}^{1}H{}$ and ${}^{31}P{}^{1}H{}$ NMR spectroscopy. When the reaction mixture was heated to 70 °C, a modest evolution of dihydrogen gas was visually observed as bubbles appeared from the reaction mixture. After 20 minutes at 70 °C, a mixture of dehydrogenation products was formed, yet the H₂-adduct 7 was still observable in both the ${}^{11}B{}^{1}H{}$ and ${}^{31}P{}^{1}H{}$ NMR spectrum, suggesting that this H₂-adduct is the resting state of the catalytic cycle. Prolonging the reaction time to 2 hours at 70 °C resulted in an increase of dehydrogenation B-N products and full degradation of the catalyst to $tBu_2PCH_3 \cdot BH_3$ and $Mes_2B=NH_2$, and neither free FLP 6 nor the dihydrogen adduct 7 were observed by NMR spectroscopy.

DFT calculations at the ω B97X–D/6-311G** level of theory confirm that dihydrogen adduct **7** is a plausible resting state in the catalytic dehydrogenation of AB. Similar to **1**, the calculations suggest that the initial interaction via a three-center-two-electron adduct is followed by a concerted double hydrogen abstraction step ($\Delta G^{\ddagger} = 25.1 \text{ kcal·mol}^{-1}, \Delta E^{\ddagger} = 16.3 \text{ kcal·mol}^{-1}$; Figure 3). This reaction step forming H₂-adduct **7** and H₂N=BH₂ was found to be exergonic by 6.13 kcal·mol⁻¹ (ΔG) and 4.70 kcal·mol⁻¹ (ΔE). The energy barrier for dihydrogen release from **7** is the rate-determining step ($\Delta G^{\ddagger} = 27.3 \text{ kcal·mol}^{-1}, \Delta E^{\ddagger} = 28.6 \text{ kcal·mol}^{-1}$), which explains why H₂-adduct **7** can be observed by NMR spectroscopy during the reaction and why release of dihydrogen is observed after the reaction mixture is heated to elevated temperatures.



Figure 3. Gibbs free energy and (energy) profile calculated for AB dehydrogenation by 6 in kcal-mol⁻¹.

Under our standard catalytic conditions (4 mol% of 6, 70 °C, 2.1 M DMAB, in 2-MeTHF) dimethylamine-borane was set for dehydrogenation (Scheme 5). Initial formation of the FLP-H₂ adduct 7 was observed by ³¹P{¹H} NMR spectroscopy, while upon heating to 70 °C this species disappeared and the formation of dimeric (Me₂NBH₂)₂ was observed in the ¹¹B NMR spectrum, along with traces of other dehydrogenation products as well as the evolution of dihydrogen gas. Prolonging the reaction time resulted in an increase of (Me2NBH2)2 formation which was monitored by ¹¹B NMR spectroscopy utilizing a sealed capillary filled with B(OMe)₃ as internal standard. Over time, FLP 6 continuously consumed the Me₂NH·BH₃ substrate, while producing the amino-borane dimer. Concomitant to the catalytic dehydrogenation, slow decomposition of the FLP catalyst 6 to tBu₂PCH₃·BH₃ and several other unknown degradation products was observed. Eventually after 6 days at 70 °C, 6 was completely degraded and the production of (Me₂NBH₂)₂ stopped. Important to note is that in the absence of FLP 6, no dehydrogenation was observed under the same reaction conditions.



Scheme 5. Catalytic dehydrogenation of dimethylamine-borane by FLP 6.

The highest turnover number (TON) was obtained with 4 mol% catalyst loading at 70 °C, reaching 23 turnovers after 6 days. For comparison, a range of Ru pincer complexes performed the same reaction with TONs of between 2 and 99 after 24 hours.^[20] The turnover frequency (TOF) after approximately 10% conversion of the dimethylamine-borane substrate at 50 °C was found to be 0.62 h⁻¹, which is not high, but is comparable with several transition metal complexes reported by Travieso-Puente and co-workers.^[21] As expected, higher TOFs were obtained at higher temperatures and after approximately 10% conversion at 60, 70 and 80 °C TOFs of 1.89, 2.65 and 4.36 h⁻¹ were obtained, respectively. At these elevated temperatures faster catalyst decomposition was observed resulting in lower turnover frequencies as the conversion increases.

Since a minor modification of our original FLP $tBu_2PCH_2BPh_2$ (1) affords $tBu_2PCH_2BMes_2$ (6) that changed the reactivity towards dimethylamine-borane from stoichiometric to catalytic dehydrogenation, we envision that additional changes of the P- and B-substituents might further increase the activity of the FLP catalyst, which is an ongoing endeavor in our laboratories.

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Conclusions

 $tBu_2PCH_2BPh_2$ (1) conveniently dehydrogenates ammoniaborane and dimethylamine-borane to form the FLP-H₂ adduct **2** and a new 5-membered heterocycle **3**. DFT calculations revealed that the underlying mechanism operates via formation of a threecenter-two-electron adduct, which is followed by a concerted double hydrogen abstraction step involving a 7-membered transition state. The bulkier $tBu_2PCH_2BMes_2$ (**6**) was designed and subsequently synthesized in excellent yields, and shows catalytic activity towards ammonia-borane and dimethylamineborane.

Experimental Section

Materials and Methods: All manipulations were carried out under an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures and stored under 3Å molecular sieves or a sublimed sodium mirror. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 400 or Brucker Avance 500 and internally referenced to the residual solvent resonances (CDCl₃: ¹H δ 7.26, ¹³C{¹H} δ 77.2; THF-d₈: ¹H δ 3.58, 1.72, ¹³C{¹H} δ 67.2, 25.3; C₆D₆: ¹H δ 7.16, ¹³C{¹H} 128.1; Tol-*d*₈: 1 H δ 7.09, 7.01, 6.97, 2.08, 13 C{ 1 H} δ 137.48, 128.87, 127.96, 125.13, 20.43). $^{31}P\{^{1}H\},~^{31}P,~^{11}B\{^{1}H\}$ and ^{11}B NMR spectra were recorded on a Bruker Avance 400 and externally referenced (85% H₃PO₄, BF₃·OEt₂, respectively). High resolution mass spectra were recorded on a Bruker MicroTOF with ESI nebulizer (ESI). Melting points were measured in sealed capillaries and are uncorrected. tBu2PCH2Li,[22] and tBu2PCH2BPh2 (1)^[15a] were synthesized following literature procedures. 2-MeTHF was purchased from Sigma Aldrich and subsequently degassed and dried with 3Å molecular sieves. NH₃·BH₃, NHMe₂·BH₃, PBr₃, MesMgBr (1M in THF), LiAIH₄, *n*-BuLi (1.6M in hexane), *t*-BuLi (1.7M in pentane), MeLi (1.6M in Et₂O), BCl₃ (1 M in heptane) and B(OMe)₃ were purchased from Sigma Aldrich, and all were used without any further purification.

Preparation of *t***Bu**₂**PCH**₂**BPh**₂**-H**₂ **adduct** 2:^[15a] A THF stock solution of ammonia-borane (28.84 mL, 0.1 M, 2.88 mmol, 1.0 equiv.) was added to a solution of *t*Bu₂PCH₂BPh₂ (1, 1.87 gr, 5.77 mmol, 2.0 equiv.) in THF (15 mL) at 0 °C. After addition, the reaction mixture was warmed to room temperature and all volatiles were removed *in vacuo*. The obtained colorless solid was thoroughly washed with *n*-pentane (3 x 20 mL) and the solids were subsequently dried *in vacuo* to afford **2** as a colorless solid (0.536 g, 57%). Colorless X-ray quality crystals were obtained from a solution of **2** in *n*-pentane which was stored at 4 °C. ¹H NMR (400.13 MHz, THF-*d*₈, 293 K): δ 7.32 (d, ³*J*_{H,H} = 7.1 Hz, 4H; *o*-Ph*H*), 6.97 (t, ³*J*_{H,H} = 7.4 Hz, 4H; *m*-Ph*H*), 6.82 (t, ³*J*_{H,H} = 7.3 Hz, 2H; *p*-Ph*H*), 4.96 (dt, ¹*J*_{H,P} = 453.2 Hz, ³*J*_{H,H} = 4.8 Hz, 1H; P*H*), 3.12–2.29 (br. m, 1H; B*H*), 1.26 (d, ³*J*_{H,P} = 14.8 Hz, 18H; C(C*H*₃)₃), 1.19–1.10 (br. m, 2H; PC*H*₂B). ³¹**P**(¹**H**) NMR (162.0 MHz, THF-*d*₈, 293 K): δ -10.1 (s). ¹¹**B**(¹**H**) NMR (128.4 MHz, THF-*d*₈, 293 K): δ 59.0 (s).

Preparation of $tBu_2PCH_2BPh_2-NH_2BH_2$ adduct 3: A THF stock solution of ammonia-borane (28.84 mL, 0.1 M, 2.88 mmol, 1.0 equiv.) was added to a solution of $tBu_2PCH_2BPh_2$ (1, 1.87 gr, 5.77 mmol, 2.0 equiv.) in THF (15 mL) at 0 °C. After addition, the reaction mixture was warmed to room temperature and all volatiles were removed *in vacuo*. The obtained white solid was thoroughly extracted in *n*-pentane (3 x 20 mL). The combined extracts were filtered over a pad of alumina, which was subsequently flushed with 250 mL eluent (cyclohexane/ethyl acetate 20:1, resp.). The collected filtrate was dried *in vacuo* to afford **3** as a colorless solid (0.754).

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g, 74%). X-ray quality crystals were obtained from a solution of **3** (289 mg) in a pentane/DCM mixture (7.5 mL : 0.54 mL) which was stored at 4 °C. Mp. (nitrogen, sealed capillary): 128 °C. ¹H NMR (400.13 MHz, THF-*d*₈, 293 K): δ 7.29 (d, ³*J*_{H,H} = 7.1 Hz, 4H; *o*-Ph*H*), 7.03, (t, ³*J*_{H,H} = 7.4 Hz, 4H; *m*-Ph*H*), 6.89 (t, ³*J*_{H,H} = 7.2 Hz, 2H, *p*-Ph*H*), 3.37 (br. s, 2H; N*H*₂), 2.80–1.75 (br. m, 2H; B*H*₂), 1.19–1.13 (m, 20H; PC*H*₂B, C(C*H*₃)₃).¹³C{¹H} NMR (100.62 MHz, THF-*d*₈, 293 K): δ 157.0 (br. s; *ipso*-Ph*C*), 132.1 (s; *o*-Ph*C*), 127.2 (s; *m*-Ph*C*), 124.4 (s; *p*-Ph*C*), 31.8 (d; ¹*J*_{C,P} = 25.8 Hz; *C*(CH₃)₃), 28.1 (d; ²*J*_{C,P} = 1.2 Hz; C(CH₃)₃), 9.0 (s; PC*H*₂B). ³¹P{¹H} NMR (162.0 MHz, THF-*d*₈, 293 K): δ 56.7 (br. m). ¹¹B{¹H} NMR (128.4 MHz, THF-*d*₈, 293 K): δ -1.95 (s; *B*Ph₂), -20.7 (d, ¹*J*_{B,P} = 85.5 Hz; P*B*H₂N). HR-MS (ESI): 352.2554 [**3**–H]⁺, calcd for: C₂₁H₃₃B₂NP⁺ 352.25312.

Preparation of Mes₂BOMe:^[23] A solution of MesMgBr (1 M in THF, 27 mL, 27 mmol, 2.1 equiv.) was added dropwise to a solution of B(OMe)₃ (1.45 mL, 1.35 g, 13 mmol, 1.0 equiv.) in THF (15 mL), which resulted in a grey suspension that turned into a brown solution after heating to 55 °C for 5h and subsequent stirring at room temperature overnight. The volatiles were removed *in vacuo* and the mixture was extracted into *n*-pentane (40 + 18 mL). The combined extracts were dried *in vacuo* to yield a colorless solid (2.98 g, 82%). Crystallization of this compound was possible from a solution in hot methanol (10 mL/g product) to afford colorless crystals upon cooling. ¹H NMR (500.23 MHz, CDCl₃, 293 K): δ 6.79 (s, 4H; Mes/H), 3.75 (s, 3H; OCH₃), 2.27 (s, 6H; *p*-MesCH₃), 2.22 (s, 12H; *o*-MesCH₃). ¹³C{¹H} NMR (125.80 MHz, CDCl₃, 293 K): δ 128.3 (br. s; *m*-MesC), 54.3 (s; OCH₃), 22.4 (s; *o*-MesCH₃), 21.3 (s; *p*-MesCH₃), the signals for *ipso*-MesC, *o*-MesC and *p*-MesC are unresolved. ¹¹B{¹H} NMR (128.38 MHz, CDCl₃, 293 K): δ 45.0 (br. s).

Preparation of Mes₂BCI:^[24] A solution of BCI₃ (1 M in heptane, 19 mL, 19 mmol, 1.3 equiv.) was added dropwise to a solution of Mes₂BOMe (4.13 g, 14.8 mmol, 1.0 equiv.) in heptane (20 mL) at room temperature, after which the mixture was heated overnight at 60 °C. The reaction mixture was cooled to room temperature and the volatiles were removed in vacuo to offer pinkish solids that were extracted into *n*-pentane (12 + 20 mL). The combined extracts were dried in vacuo, which afforded a colorless solid (3.86 g, 92%). X-ray quality crystals were obtained by recrystallization from hot pentane (2.6 mL/g crude Mes₂BCI) and subsequent washing with pentane (0.5 mL/g crude) at -80 °C to afford colorless crystals. Mp. (nitrogen, sealed capillary): 80-84 °C (trajectory). ¹H NMR (500.23 MHz, CDCl₃, 293 K): δ 6.83 (s, 4H; Mes-H), 2.30 (s, 12H; o-MesCH₃), 2.28 (s, 6H; p-MesCH₃). ¹³C{¹H} NMR (125.80 MHz, CDCI₃, 293 K): δ 140.9 (s; o-MesC), 140.5 (s; p-MesC), 129.0 (s; m-MesC), 23.4 (s; o-MesCH₃), 21.4 (s; p-MesCH₃), the signal for ipso-MesC is unresolved. ¹¹B{¹H} NMR (128.38 MHz, CDCl₃, 293 K): δ 69.9 (br. s).

Preparation of tBu2PCH2BMes2 (6): A solution of Mes2BCI (3.47 g, 12.2 mmol, 1.0 equiv.) in Et₂O (15 mL) was added dropwise to a suspension of tBu₂PCH₂Li (2.72 g, 16.4 mmol, 1.3 equiv.) in Et₂O (15 mL) at -80 °C and after addition the reaction mixture was warmed to room temperature. After 2.5 days of stirring at room temperature, the suspension was concentrated in vacuo which afforded an orange foam. The foam was extracted into npentane (25 mL) and filtered over a Schlenk filter packed with Celite. Subsequently, the Celite layer was extracted into pentane (3 x 10 mL) and the combined extracts were concentrated in vacuo, which afforded an orange solid (4.94 g, 99%). X-ray quality crystals were obtained from a solution of 0.45 g of 6 in 1 mL of hot heptane (80-85 °C) and subsequent slow cooling to -20 °C. Mp. (nitrogen, sealed capillary): 79-87 °C (trajectory). ¹H NMR (400.13 MHz, C₆D₆, 293 K): δ 6.77 (s, 4H; MesH), 2.43 (s, 12H; o-MesCH₃), 2.15 (s, 6H; p-MesCH₃), 2.09 (d, ²J_{H,P} = 4.7 Hz, 2H; PCH₂B), 1.08 (d, ²J_{H,P} = 10.5 Hz, 18H; C(CH₃)₃). ¹³C{¹H} NMR (100.62 MHz, C₆D₆, 293 K): δ 143.4 (only observed in the HMBC spectrum, ³J_{C,H} coupling with MesH, o-MesCH₃, and PCH₂B; ipso-MesC), 139.1 (s; o-MesC), 138.3 (s; p-MesC), 129.2 (s; m-MesC), 31.5 (d, ¹J_{C,P} = 25.1 Hz;

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C(CH₃)₃), 30.0 (d, ¹*J*_{C,P} = 14.1 Hz; C(CH₃)₃), 28.1 (only observed in the HSQC spectrum, ¹*J*_{C,H} coupling with PC*H*₂B; PCH₂B), 24.1 (2 x s; *o*-MesCH₃), 21.2 (s; *p*-MesCH₃). ³¹P{¹H} NMR (161.97 MHz, toluene-*d*₈, 293 K): δ 26.9 (s). ¹¹B{¹H} NMR (128.38 MHz, toluene-*d*₈, 293 K): δ 82.0 (br. s). HR-MS (ESI): 409.3200 [6+H]⁺, calcd for C₂₇H₄₃BP⁺ 409.3190.

Stability of $tBu_2PCH_2BPh_2-H_2$ adduct (2) towards heating: A NMR sample containing a solution of 2 in 2-MeTHF was heated to 50 °C for 3 hours, after which ³¹P{¹H} spectroscopy revealed no formation of $tBu_2PCH_2Ph_2$ and only 2% decomposition to tBu_2PCH_3 . Subsequent heating to 80 °C for 2 hours resulted in liberation of dihydrogen and 17% conversion to $tBu_2PCH_2Ph_2$ as well as 18% decomposition to tBu_2PCH_3 .

Reaction of tBu2PCH2BMes2 (6) with 0.5 equiv. of NH3BH3: A screwcap NMR tube was charged with ammonia-borane (0.0054 g, 0.175 mmol, 1.0 equiv.), tBu2PCH2BMes2 (6, 0.1428 g, 0.350 mmol, 2.0 equiv.) and 2-MeTHF (6 mL). The reaction mixture was kept at room temperature and analyzed after 1 hour with ³¹P{¹H}, ¹¹B{¹H} and ¹¹B NMR spectroscopy, showing a mixture of dehydrogenated ammonia-borane products (11B{1H} NMR: δ 30.8 (borazine), -4.94 (BCDB), -11.2 (CTB)), along with the formation of the H₂-adduct **7** (^{11}B NMR: δ –15.0 (d, $^{1}J_{B,H}$ = 81.1 Hz); $^{31}P{^{1}H}$ NMR: δ 56.5 (s)) and 5-membered heterocycle 8 (11B NMR: δ 1.92 (s), -23.3 (t, ${}^{1}J_{B,H}$ = 72.9 Hz); ${}^{31}P{}^{1}H$ NMR: δ 58.1 (br. s)). Subsequently, the reaction mixture was heated to 70 °C overnight and a white suspension was obtained (solids are postulated to be polyborazine) and ³¹P{¹H}, ¹¹B and ¹¹B{¹H} NMR spectroscopy revealed complete consumption of the H₂adduct ${\bf 7}$ and heterocycle ${\bf 8},$ as well as an increase in formation of borazine, polyborazine (^{11}B NMR: δ 24.8 (s)), formation of two unidentified products (¹¹B NMR: δ –23.4 (s) and –29.8 (s)), decomposition to Mes₂B=NH₂ (¹¹B NMR: δ 43.7 (s)) and tBu₂PCH₃·BH₃ (¹¹B NMR: δ –41.6 (dq, ¹J_{B,H} = 96.4 Hz, ${}^{1}J_{B,P} = 57.9$ Hz; ${}^{31}P{}^{1}H{}$ NMR: δ 39.9 (br. q), and lastly also regeneration of FLP 6.

Reaction of tBu_2PCH_2BMes_2(6) with 25 equiv. of NH₃BH₃: A screw-cap NMR tube was charged with ammonia-borane (0.031 g, 1.357 mmol, 25.0 equiv.), tBu_2PCH_2BMes_2(6, 0.022 g, 0.054 mmol, 1.0 equiv.) and 2-MeTHF (6 mL). The reaction mixture was mixed at room temperature and directly analyzed by {}^{31}P{}^{1}H{}, {}^{11}B{}^{1}H{} and {}^{11}B NMR spectroscopy, which revealed formation of the H₂-adduct 7 and the 5-membered heterocycle 8. Subsequently, the NMR tube was heated to 70 °C and analyzed by NMR spectroscopy after 20 and 120 minutes, after which complete consumption of FLP 6 and H₂-adduct 7 was observed, along with the formation of dehydrogenation products and dihydrogen gas.

X-ray Crystallography: The single-crystal X-ray diffraction studies were carried out on a Bruker-Nonius KappaCCD diffractometer at 123(2) K using Mo-K α radiation ($\lambda = 0.71073$ Å) (**2**, **6**) or Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo-K α radiation ($\lambda = 0.71073$ Å) (**3**). Direct Methods (SHELXS-97)^[25] were used for structure solution and refinement was carried out using SHELXL-2013/2014 (full-matrix least-squares on P^2).^[26] Hydrogen atoms were localized by difference electron density determination and refined using a riding model (H(B, N, P) free). Semi-empirical absorption corrections were applied. For **3** an extinction correction was applied.

2: colorless crystals, $C_{21}H_{32}BP \cdot 0.5(C_7H_8)$, $M_r = 372.31$, crystal size 0.50 x 0.30 x 0.20 mm, monoclinic, space group C2/c (no.15), a = 32.562(4) Å,

b = 8.776(1) Å, *c* = 17.801(2) Å, β = 118.75(1)°, *V* = 4459.8(10) Å³, *Z* = 8, *ρ* =1.109 Mg/m⁻³, μ(Mo-K₀) = 0.13 mm⁻¹, *F*(000) = 1624, 2θ_{max} = 55°, 25741 reflections, of which 5128 were independent (*R*_{nt} = 0.039), 243 parameters, 38 restraints, *R*₁ = 0.049 (for 4179 I > 2σ(I)), w*R*₂ = 0.123 (all data), *S* = 1.03, largest diff. peak / hole = 0.88 / -0.44 e Å⁻³.

3: colorless crystals, C₂₁H₃₄B₂NP, M_r = 353.08, crystal size 0.48 x 0.48 x 0.36 mm, triclinic, space group *P*-1 (no.2), *a* = 9.0523(5) Å, *b* = 10.2844(6) Å, *c* = 13.0205(8) Å, α = 100.971(2)°, β = 108.436(2)°, γ = 104.693(2)°, V = 1062.92(11) Å³, Z = 2, ρ = 1.103 Mg/m⁻³, μ(Mo-K_a) = 0.13 mm⁻¹, *F*(000) = 384, 2θ_{max} = 55°, 36356 reflections, of which 4902 were independent ($R_{int} = 0.022$), 239 parameters, 4 restraints, $R_1 = 0.032$ (for 4554 I > 2σ(I)), wR₂ = 0.085 (all data), *S* = 1.05, largest diff. peak / hole = 0.35 / -0.28 e Å⁻³.

6: orange crystals, $C_{27}H_{42}BP$, $M_r = 408.38$, crystal size $0.60 \times 0.45 \times 0.40$ mm, monoclinic, space group $P_{21/c}$ (no.14), a = 12.842(1) Å, b = 10.033(1) Å, c = 20.516(2) Å, $\beta = 104.46(1)^{\circ}$, V = 2559.6(4) Å³, Z = 4, $\rho = 1.060$ Mg/m⁻³, μ (Mo-K_a) = 0.12 mm⁻¹, F(000) = 896, $2\theta_{max} = 55^{\circ}$, 24882 reflections, of which 5871 were independent ($R_{int} = 0.054$), 268 parameters, $R_1 = 0.050$ (for 4666 I > $2\sigma(I)$), $wR_2 = 0.135$ (all data), S = 1.04, largest diff. peak / hole = 0.40 / -0.35 e Å⁻³.

CCDC-1967181 (2), CCDC-1967182 (3), and CCDC-1967183 (6) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: All structures were optimized at the ω B97X–D level of theory,^[27] using Gaussian 09, Revision D01.^[28] Geometry optimizations were performed using the 6-311G(d,p) basis set,^[29,30] and the nature of each stationary point was confirmed by frequency calculations.

Supporting Information (see footnote on the first page of this article): Cartesian coordinates for all computed structures and a video of the catalytic dehydrogenation of DMAB with **6** are given as Supporting Information available online.

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Keywords: frustrated Lewis pairs • amine-boranes • dehydrogenation • main-group catalysis • density functional calculations

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