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Catalytic Dehydrogenation of Amine-Boranes using Geminal Phosphino-Boranes


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

Abstract. The reaction of the intramolecular frustrated Lewis pair (FLP) tBu2PCH2BPh2 with the amine-boranes NH3·BH3 and Me2NH·BH3 leads to the formation of the corresponding FLP-H2 adducts as well as novel five-membered heterocycles that result from capturing the in situ formed amino-borane by a second equivalent of FLP. The sterically more demanding tBu2PCH2BMes2 does not form such a five-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

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, amine-boranes gained a lot of attention due to their potential application as dihydrogen storage material;[3] in particular ammonia-borane (AB) is of interest as it 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 materials science.[5] To date, a lot of research has been conducted on the catalytic dehydrogenation of amine-boranes 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 reported as efficient TM-free catalysts for amine-borane dehydrogenation.[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 catalyst loadings down to 1 mol-%.[12] Recently Uhl and co-workers found that the gallium analogue of II, phosphino-galane III, can be applied for ammonia- and dimethylamine-borane 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.\cite{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 two equivalents of tBu₃PCH₂BPPh₂ (1) with one equivalent of ammonia-borane (H₃N·BH₃, AB) in THF at room temperature resulted in immediate consumption of AB, along with formation of dihydrogen adduct 2 (δ₁¹¹B{¹H} = 59.0 ppm) and five-membered heterocycle 3 (δ₁³¹P{¹H} = 56.7 ppm) in a 1:1 ratio (Scheme 1). The products can be separated by extraction of 3 into n-pentane (leaving 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 doublet in the ¹³¹P NMR spectrum with a J_P,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.\cite{15a} In the solid state, the boron center in 2 is strongly pyramidalized [Σ(CB1C) 330.5°], which also resembles the upfield ¹¹B NMR shift (δ₁¹¹B{¹H} = 110.1 ppm). In contrast to the o-phenylene-bridged P/B FLP-H₂ adduct reported by Bourriou and co-workers,\cite{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 h at 80 °C).

The formation of the five-membered heterocycle 3 is believed to be the result of trapping of the highly polarized amine-borane intermediate H₂N=NH₂ by the second equivalent of FLP 1. In the ¹¹B{¹H} NMR spectrum, 3 displays a singlet resonance (δ = 1.95 ppm) for the FLP’s boron moiety together with a characteristic doublet (δ = 20.7 ppm, J_B,P = 85.5 Hz) that can be ascribed to the amino-borane fragment. The corresponding ¹³¹P{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.\cite{17} X-ray 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 five-membered heterocycle (Scheme 1, bottom right). Compared to the previously reported Al- and Ga-based five-membered heterocycles formed by H₂N=NH₂ trapping using the corresponding FLPs,\cite{10,13} 3 contains a shorter P₁–B₂ bond (1.9606(11) Å; cf. 1.9984(14) and 2.004(2) Å, respectively), suggesting that the trapped H₂N=NH₂ 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, H₂N·BD₃, which resulted in selective N–H to P and B–D to B transfer according to ¹³¹P 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.\cite{18} Analysis of the formation of 2 by density functional theory (DFT) calculations at the oB97X–D/6-311G** level of theory revealed that the interaction of ammonia-borane with FLP 1 leads to the formation of a three-center-two-electron adduct 4 as intermediate (Figure 2), which enables dihydrogen transfer from H₂N·BH₃ in a concerted manner via a seven-membered transition state, forming phosphonium-borate 2 and one equivalent of amino-borane H₂N=NH₂. The overall process is exergonic, and the low barrier (ΔG° = 13.1 kcal·mol⁻¹, ΔΔG° = 14.3 kcal·mol⁻¹) for TS₄₂,2 is in good agreement with the experimentally observed facile reaction (instantaneous at 0 °C). Additionally, trapping of the amino-borane H₂N=NH₂ fragment by a second equiva-
lent of FLP 1 makes the overall reaction even more exergonic ($\Delta E_{\text{trapping}} = -17.5 \text{ kcal mol}^{-1}$, $\Delta E_{\text{trapping}} = -34.7 \text{ kcal mol}^{-1}$).

Under the same conditions, the reaction of two equivalents of 1 with the bulkier dimethylamine-borane (Me$_2$NH·BH$_3$, DMAB) resulted in rapid formation of the known FLP-H$_2$ adduct 2 together with the methylated analogue of 3, compound 5 (Scheme 2). $^{31}$P{$^1$H} 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-H$_2$ adduct, and a broad resonance 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 $^{11}$B{$^1$H} NMR spectrum. DFT calculations at the $\omega$B97X-D/6-311G** level of theory suggest that the same mechanism takes place. With an overall barrier ($\Delta G$) 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 Supporting Information). Interestingly, when a sample of the reaction mixture was kept for a prolonged period at room temperature signals of the dimeric (Me$_2$NBH$_2$)$_2$ started to appear in the $^{11}$B{$^1$H} NMR spectrum due to release of the Me$_2$N=BH$_2$ fragment from 5 and subsequent dimerization. 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.

![Scheme 2. Reaction of 2 equivalents of FLP 1 with dimethylamine-borane.](image)

Encouraged by these findings, we set out to design a FLP system that disfavors amino-borane adduct formation. DFT calculations at the $\omega$B97X-D/6-311G** level of theory showed that only a slight change of the system could already prevent adduct formation. FLP $\text{Bu}_2\text{PCH}_2\text{BHMe}_2$ (6) bearing the bulkier mesityl substituents on boron was found to disfavor adduct formation with Me$_2$N=BH$_2$ ($\Delta G = 15.8$ 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,

![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 /\AA{} 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), $\Sigma$(CB1C) 359.8.](image)

Under similar conditions, FLP 6 (two equivalents) was reacted with one equivalent of ammonia-borane in 2-MeTHF (2-methylenetetrahydrofuran) at room temperature. After approximately 1 h at room temperature, the $^{11}$B{$^1$H} and $^{31}$P{$^1$H} NMR spectra of the reaction mixture revealed that 6 was fully converted into FLP-H$_2$ adduct 7 [$\delta^{31}$P{$^1$H} = 56.5 (s); $^{11}$B{$^1$H} = –15.0 (s)] and the five-membered heterocycle 8 [$\delta^{31}$P{$^1$H} = 58.1 (br. s); $^{11}$B{$^1$H} = 1.95 (s), –23.2 (s)], along with the formation of traces of dehydrogenation products such as borazine, cyclotriborazane (CTB) and $\text{B}-(\text{cyclodiborazanyl})$amino-borohydride (BCDB) and a few unidentified products (Scheme 4).

![Scheme 4. The reaction of 2 equivalents of 6 with dimethylamine-borane.](image)

Interestingly, heating the reaction mixture to 70 °C led to almost complete disappearance of H$_2$ adduct 7 and heterocycle 8, concomitant with an increase of dehydrogenation products together with the formation of degradation products, such as Me$_3$S$_2$B=NH$_2$ [$\delta^{31}$B{$^1$H} = 44.1 (br. s)]$^{119}$ and $\text{Bu}_2\text{PCH}_2\text{BH}_3$ [$\delta^{31}$P{$^1$H} = 39.9 (m); $^{11}$B{$^1$H} = 40.8 (d, $^1J_{B,P}$ = 57.8 Hz)], as was observed by $^{11}$B{$^1$H} and $^{31}$P{$^1$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 significant as only a few FLPs are reported to catalyze the dehydrogenation of AB.\[12\]–[14]

The labile character of both the FLP-H$_2$ adduct 7 and the five-membered 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 H$_3$N=BH$_3$ in 2-MeTHF, 6 was directly converted to H$_2$ 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 H$_2$ adduct 7 was still observable in both the $^{11}$B{$^{1}$H} and $^{31}$P{$^{1}$H} NMR spectrum, suggesting that this H$_2$ adduct is the resting state of the catalytic cycle. Prolonging the reaction time to 2 h at 70 °C resulted in an increase of dehydrogenation B–N products and full degradation of the catalyst to $t$Bu$_2$PCH$_2$BH$_3$ and Mes$_2$B=NH$_2$, and neither free FLP 6 nor the dihydrogen adduct 7 were observed by NMR spectroscopy.

DFT calculations at the oB97X–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 (Δ$^\ddagger$G = 25.1 kcal mol$^{-1}$, Δ$^\ddagger$E = 16.3 kcal mol$^{-1}$; Figure 3). This reaction step forming H$_2$ adduct 7 and H$_2$N=BH$_3$ was found to be exergonic by 6.13 kcal mol$^{-1}$ and 4.70 kcal mol$^{-1}$ (Δ$^\ddagger$G and Δ$^\ddagger$E). The energy barrier for dihydrogen release from 7 is the rate-determining step (Δ$^\ddagger$G = 27.3 kcal mol$^{-1}$, Δ$^\ddagger$E = 28.6 kcal mol$^{-1}$), which explains why H$_2$ 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.

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-H$_2$ adduct 7 was observed by $^{31}$P{$^{1}$H} NMR spectroscopy, while upon heating to 70 °C this species disappeared and the formation of dimeric (Me$_2$NBH$_2$)$_2$ was observed in the $^{11}$B 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 (Me$_2$NBH$_2$)$_2$ formation which was monitored by $^{11}$B NMR spectroscopy utilizing a seeded capillary filled with B(OMe)$_3$ as internal standard. Over time, FLP 6 continuously consumed the Me$_2$NH-BH$_3$ substrate, while producing the amino-borane dimer. Concomitant to the catalytic dehydrogenation, slow decomposition of the FLP catalyst to $t$Bu$_2$PCH$_2$BH$_3$ and several other unknown degradation products was observed. Eventually after 6 days at 70 °C, 6 was completely degraded and the production of (Me$_2$NBH$_2$)$_2$ stopped. Important to note is that in the absence of FLP 6, no dehydrogenation was observed under the same reaction conditions.

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 h.\[20\] 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 Traviesto-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 $t$Bu$_2$PCH$_2$BH$_2$ (1) affords $t$Bu$_2$PCH$_2$Mes$_2$ (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.

**Conclusions**

$t$Bu$_2$PCH$_2$BH$_2$ (1) conveniently dehydrogenates ammonia-borane and dimethylamine-borane to form the FLP-H$_2$ adduct...
and a new five-membered heterocycle 3. DFT calculations revealed that the underlying mechanism operates via formation of a three-center-two-electron adduct, which is followed by a concerted double hydrogen abstraction step involving a seven-membered transition state. The bulkier Bu₃PCH₂BMe₅ (6) was designed and subsequently synthesized in excellent yields, and shows catalytic activity towards ammonia-borane and dimethylamine-borane.

**Experimental Section**

**Materials and Methods:** All manipulations were carried out in an atmosphere of dry nitrogen, using standard Schlenk and drybox techniques. Solvents were purified, dried and degassed according to standard procedures and stored under 3 Å molecular sieves or a subdued sodium mirror. ¹H and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 400 or Bruker Avance 500 and internally referenced to the residual solvent resonances (CDCl₃): δ = 7.26, ¹³C{¹H} δ = 77.2; [D₆]THF: δ = 3.58, 1.72, ¹³C{¹H} δ = 67.2, 25.3; CD₂Cl₂: δ = 7.16, ¹³C{¹H} 128.1; Tol-d₅: δ = 7.09, 7.01, 6.97, 2.08, ¹³C{¹H} δ = 137.48, 128.77, 127.96, 125.13, 20.43. ³¹P{¹H}, ³¹P, ¹¹B{¹H} and ¹³C{¹H} NMR spectra were recorded on a Bruker Avance 400 or Bruker Avance 500 and internally referenced to 85.5 HPO₃, 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. Bu₃PCH₂Cl₂ and Bu₃PCH₂BPH₂ (1) (15 mmol) are synthesized following literature procedures. 2-MeTHF was purchased from Sigma Aldrich and subsequently degassed and dried with 3 Å molecular sieves. THF was stored at 4 °C.

**Preparation of Bu₃PCH₂BPH₂–NH₂BH₂ Adduct 2:** A solution of BCl₃ (1.0 equiv.) in THF (15 mL) was added to a solution of Bu₃PCH₂Cl₂ (1, 1.87 g, 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 pentane (3 × 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 in hot methanol (10 mmol⁻¹ g⁻¹ product) to afford colorless crystals upon cooling.

**Preparation of Bu₃PCH₂BPH₂–H₂ 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 Bu₃PCH₂BPH₂ (1, 1.87 g, 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 pentane (3 × 20 mL) and the solids were subsequently dried in vacuo to afford 3 as a colorless solid (0.754 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, [D₆]THF, 293 K): δ = 7.29 (d, 3JHH = 7.1 Hz, 4 H, o-PhH), 7.03 (t, 3JHH = 7.4 Hz, 4 H, m-PhH), 6.89 (t, 3JHH = 7.2 Hz, 2 H, p-PhH), 3.37 (br. s, 2 H, NH₂), 2.80–1.75 (br. m, 2 H, BH₂), 1.19–1.13 (m, 20 H, PCH₂B, C(CH₃)₃). ¹³C{¹H} NMR (100.62 MHz, [D₆]THF, 293 K): δ = 157.0 (br. s; ipso-PhC), 132.1 (s; o-PhC), 127.2 (s; m-PhC), 124.4 (s; p-PhC), 31.8 (d; 3JCP = 25.8 Hz; C(CH₃)₃), 28.1 (d; 3JCP = 1.2 Hz; C(CH₃)₃), 9.0 (s; PCH₂B). ³¹P{¹H} NMR (162.0 MHz, [D₆]THF, 293 K): δ = 56.7 (br. m). ¹¹B{¹H} NMR (128.4 MHz, [D₆]THF, 293 K): δ = –1.95 ppm (p; BPh₃). –20.7 (d; 3JBP = 85.5 Hz, BPh₃-N) ppm. HR-MS (ESI): 352.2554 [3H⁺].

**Preparation of Mes₂B(OMe)₃:** A solution of Mes₂B(OH)₃ (1.45 mL, 13 mmol, 1.0 equiv.) in THF (15 mL) was added dropwise to a solution of Mes₂B(OH)₂ (1.45 g, 13.3 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 5 h and subsequent stirring at room temperature, after which the volatiles were removed in vacuo and the mixture was extracted into n-pentane (40 + 18 mL). The combined extracts were washed in vacuo to yield a colorless solid (2.8 g, 82 %). Crystallization of this compound was possible from a solution in hot methanol (10 mL g⁻¹ product) to afford colorless crystals upon cooling.

**Preparation of Mes₂BCl:** A solution of BCl₃ (1.0 equiv.) in THF (27 mL, 27 mmol, 2.1 equiv.) was added dropwise to a solution of Mes₂ClBO (1.45 mL, 13.5 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 5 h and subsequent stirring at room temperature, after which the volatiles were removed in vacuo and the mixture was extracted into n-pentane (40 + 18 mL). The combined extracts were washed in vacuo to yield a colorless solid (2.8 g, 82 %). Crystallization of this compound was possible from a solution in hot methanol (10 mL g⁻¹ product) to afford colorless crystals upon cooling.
(100.62 MHz, C6D6, 293 K): δ = 143.4 (only observed in the HMBC spectrum, 1JCH coupling with MesH, o-MesCH3, and PCH2B; 1Jp-MesC), 139.1 (s; o-MesC), 138.3 (s; p-MesC), 129.2 (s; m-MesC), 31.5 [d, 1Jp,C = 25.1 Hz; C(CH3)3], 30.0 [d, 1Jp,C = 14.1 Hz; C(CH3)3], 28.1 (only observed in the HSQC spectrum, 1JCH coupling with PCH2B; PCH3B), 24.1 (2 x s; o-MesCH3), 21.2 (s; p-MesCH3).

31P{1H} NMR (161.97 MHz, [D6]toluene, 293 K): δ = 26.9 (s).

11B{1H} NMR (128.38 MHz, [D6]toluene, 293 K): δ = 82.0 (br. s) ppm.


Stability of tBu2PCH2BPh2:H2 Adduct (2) towards Heating: A NMR sample containing a solution of 2 in 2-MeTHF was heated to 50 °C for 3 h, after which 31P{1H} spectroscopy revealed no formation of tBu2PCH2Ph4 and only 2% decomposition to tBu2PCH3. Subsequent heating to 80 °C for 2 h resulted in liberation of dihydrogen and 17% conversion to tBu2PCH2Ph3 as well as 18% decomposition to tBu2PCH3.

Reaction of tBu2PCH2BMes2 (6) with 0.5 Equiv. of NH3BH3: A screw-cap NMR tube was charged with ammonia-borane (0.015 g, 0.075 mmol, 1.0 equiv.) and 2-MeTHF (6 mL). The reaction mixture was kept at room temperature and analyzed after 1 h with 31P{1H}, 11B{1H} and 11B NMR spectroscopy, showing a mixture of dehydrogenated amine-borane products [31P{1H}, 11B{1H} and 11B NMR spectroscopy, showing a mixture of dehydrogenated amine-borane products [31P{1H}, 11B{1H} and 11B NMR spectroscopy, showing a mixture of dehydrogenated amine-borane products [11B NMR: δ = 30.8 (borazine), –49.4 (BCDB), –11.2 (CTB), along with the formation of the H2 adduct 7 [11B NMR: δ = –15.0 (d, 1Jp,B = 81.1 Hz); 31P{1H} NMR: δ = 56.5 (s) and five-membered heterocycle 8 [11B NMR: δ = 1.92 (s), –23.3 (t, 1Jp,B = 72.9 Hz); 31P{1H} NMR: δ = 58.1 (br. s)]. Subsequently, the reaction mixture was heated to 70 °C over a white suspension was obtained (solids are postulated to be polyborazine) and 31P{1H}, 11B{1H} and 11B NMR spectroscopy revealed complete consumption of the H2 adduct 7 and heterocycle 8, as well as an increase in formation of borazine, polyborazine [11B NMR: δ = 24.8 (s)], formation of two unidentified products [11B NMR: δ = –23.4 (s) and –29.8 (s)], decomposition to Mes2B=NH [11B NMR: δ = 43.7 (s)] and tBu2PCH2BH3 [11B NMR: δ = –41.6 (dq, 1Jp,B = 96.4, 1Jp,P = 57.9 Hz; 31P{1H} NMR: δ = 39.9 (br. q)], and lastly also regeneration of FLP 6.

Reaction of tBu2PCH2BMes2 (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.) and 2-MeTHF (6 mL). The reaction mixture was kept at room temperature and directly analyzed by 31P{1H}, 11B{1H} and 11B NMR spectroscopy, which revealed formation of the H2 adduct 7 and the five-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-Nomius KappaCCD diffractometer at 123(2) K using Mo-Kα radiation (λ = 0.71073 Å) (2, 6) or Bruker D8 Venture diffractometer with Photon100 detector at 123(2) K using Mo-Kα radiation (λ = 0.71073 Å) (3). Direct Methods (SHELXS-97) were used for structure solution and refinement was carried out using SHELXL-2013/2014 (full-matrix least-squares on F2) [24]. 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, C5H12BP·0.5(C6H6), M w = 372.31, crystal size 0.50 × 0.30 × 0.20 mm, monoclinic, space group C2/c (no.15), a = 32.56(2) Å, b = 8.776(1) Å, c = 17.801(2) Å, β = 118.75(1)°, V = 459.8(10) Å3, Z = 8, p = 1.109 Mg·m–3, μ(Mo-Kα) = 0.13 mm–1, F(000) = 1604, 20 max = 55°, 25741 reflections, of which 5128 were independent (Rint = 0.039), 243 parameters, 38 restraints, R1 = 0.049 [for 4179 I > 2σ(I)], wR2 = 0.123 (all data), S = 1.03, largest diff. peak / hole = 0.88 / –0.44 e·Å–3.

3: Colorless crystals, C5H14BP·2H2, M w = 353.08, crystal size 0.48 × 0.48 × 0.36 mm, triclinic, space group P1 (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, p = 1.103 Mg·m–3, μ(Mo-Kα) = 0.13 mm–1, F(000) = 384, 20 max = 55°, 36356 reflections, of which 4902 were independent (Rint = 0.022), 239 parameters, 4 restraints, R1 = 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: Colorless crystals, C5H25BP·2H2, M w = 408.38, crystal size 0.60 × 0.45 × 0.40 mm, monoclinic, space group P21/c (no.14), a = 12.842(1) Å, b = 10.0331(1) Å, c = 20.5162(2) Å, β = 104.46(1)°, V = 2559.6(4) Å3, Z = 4, p = 1.060 Mg·m–3, μ(Mo-Kα) = 0.12 mm–1, F(000) = 896, 20 max = 55°, 24882 reflections, of which 5871 were independent (Rint = 0.054), 268 parameters, R1 = 0.050 [for 4666 I > 2σ(I)], wR2 = 0.135 (all data), S = 1.04, largest diff. peak / hole = 0.40 / –0.35 e·Å–3.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1967181 (2), CCDC-1967182 (3), and CCDC-1967183 (6). (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk)

Computational Details: All structures were optimized at the oB97X-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.

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