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Dehydrogenation of Amine–Boranes Using p-Block Compounds

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Amine–boranes have gained a lot of attention due to their potential as hydrogen storage materials and their capacity to act as precursors for transfer hydrogenation. Therefore, a lot of effort has gone into the development of suitable transition- and main-group metal catalysts for the dehydrogenation of amine–boranes. During the past decade, new systems started to emerge solely based on p-block elements that promote the dehydrogenation of amine–boranes through hydrogen-transfer reactions, polymerization initiation, and main-group catalysis. In this review, we highlight the development of these p-block based systems for stoichiometric and catalytic amine–borane dehydrogenation and discuss the underlying mechanisms.

1. Introduction

In the search for renewable energy sources and clean energy, B–N compounds gained a lot of attention in recent years as promising lightweight materials for dihydrogen storage and on-demand release.\cite{1,2} From these materials, ammonia–borane $\text{NH}_3\text{BH}_3$ (AB) gained undoubtedly the most attention as a hydrogen storage material, because it contains a high weight percentage of dihydrogen (19.6\%).\cite{2,3} Due to the difference in electronegativity of boron and nitrogen, the B–H and N–H bonds of amine–boranes are polarized in opposite ways, resulting in hydric B–H (δ−) and protic N–H (δ+) hydrogen substituents. This characteristic feature enables the thermal release of dihydrogen and concomitant generation of aminoborane molecules that (often uncontrollably) oligomerize, resulting in a mixture of B–N products (Figure 1). Ammonia–borane is stable at room temperature, however, it undergoes thermolysis at temperatures above 120 °C;\cite{4–6} this process can be enhanced by cellulose embedding\cite{7} or by using ionic liquids as solvent.\cite{8,9} Additionally, N-substitution also proved to be an efficient method for lowering the decomposition temperature,\cite{10} because primary amine–borane adducts (RNH$_2$·BH$_3$) can release 1 equivalent of dihydrogen in solution at room temperature.\cite{11}

A great deal of interest has gone into the B–N containing products which are, depending on the amine–borane substate, B–N dimers (A, Figure 1), borazanes (B), borazines (C), and other oligomeric and polymeric B–N materials (D, E), with many potential applications, such as precursors to ceramic boron nitride materials.\cite{12} Note, for the sake of clarity, we have removed the formal charges from the majority of Lewis structures throughout this review, as is common practice in this area of chemistry.

Abstract: Amine–boranes have gained a lot of attention due to their potential as hydrogen storage materials and their capacity to act as precursors for transfer hydrogenation. Therefore, a lot of effort has gone into the development of suitable transition- and main-group metal catalysts for the dehydrogenation of amine–boranes. During the past decade, new systems started to emerge solely based on p-block elements that promote the dehydrogenation of amine–boranes through hydrogen-transfer reactions, polymerization initiation, and main-group catalysis. In this review, we highlight the development of these p-block based systems for stoichiometric and catalytic amine–borane dehydrogenation and discuss the underlying mechanisms.
2. Stoichiometric dehydrogenation

2.1. Dihydrogen transfer to inorganic N–B and P–B bonds

In 2011, Manners and co-workers investigated the redistribution of diborazines and found that these species were easily dehydrogenated by the stable aminoborane iPr$_2$N=BH$_2$.[19] Inspired by these findings, more simple amine–boranes were subjected to the same reaction conditions and they found that iPr$_2$N=BH$_2$ was able to dehydrogenate ammonia–borane (NH$_3$BH$_3$) quantitatively to form iPr$_2$NH·BH$_3$, along with dehydrogenation products [H$_2$B(μ-H)(μ-NH$_2$)BH$_3$]$_2$ and [NH$_2$=BH]$_2$, and a white precipitate, which was attributed to insoluble polyaminoborane species (Scheme 1).[20]

\[
\text{iPr}_2\text{N}=\text{BH}_2 \xrightarrow{20°C, \text{THF}} \text{iPr}_2\text{NH} \cdot \text{BH}_3 (100%) \]

Dehydrogenation products

Scheme 1. Reaction of iPr$_2$N=BH$_2$ with NH$_2$BH$_3$.

Broadening the scope of this reaction, Manners and co-workers also investigated the reaction of iPr$_2$N=BH$_2$ with MeNH$_2$BH$_3$ and found comparable reactivity after stirring the reaction mixture for 21 hours at 20°C (90% conversion to iPr$_2$NH·BH$_3$ along with various dehydrogenation products). The reaction of iPr$_2$N=BH$_2$ with the more sterically demanding Me$_2$NH·BH$_3$ resulted in a clean mixture of starting materials and products (iPr$_2$NH·BH$_3$ and [Me$_2$N=BBH]$_2$) even after a prolonged reaction time, suggesting the formation of an equilibrium mixture (Scheme 2).

\[
\text{iPr}_2\text{N}=\text{BH}_2 + \text{Me}_2\text{NH} \cdot \text{BH}_3 \xrightarrow{20°C, \text{THF}} \frac{1}{2} \text{iPr}_2\text{NH} \cdot \text{BH}_3 + \frac{1}{2} \text{[Me}_2\text{N=BBH]}_2
\]

Scheme 2. Equilibrium formation during the reaction of iPr$_2$N=BH$_2$ with Me$_2$NH·BH$_3$.

An in-depth computational study revealed that the reaction between iPr$_2$N=BH$_2$ and Me$_2$NH·BH$_3$ occurs in a bimolecular, concerted manner via a six-membered transition state (1) in which the protic and hydridic hydrogens of the N–H and the B–H moiety of Me$_2$NH·BH$_3$ are transferred simultaneously to, respectively, the nitrogen and boron atom of iPr$_2$N=BH$_2$ (Scheme 2).[21] This dehydrogenation step is endergonic and is driven by the exergonic dimerization of the simultaneously generated Me$_2$N=BBH$_2$.

The same methodology was applied to B-methylated amine–boranes, which are more thermally labile than the N-substituted amine–borane analogues and are prone to redistribution depending on their substitution pattern at the boron site.[22] The hydrogenation of iPr$_2$N=BH$_2$ with NH$_3$BH$_3$·Me, MeNH$_2$BH$_3$·Me, and Me$_2$NH·BH$_3$·Me was found to be very rapid and the dehydrogenation step was determined to be exergonic with a lower barrier compared with the N-substituted amine–boranes, which highlights the increased dihydrogen donating ability of the B-methylated amine–boranes.

In addition to iPr$_2$N=BH$_2$, Rivard and co-workers reported a zwitterionic aminoborane (2), which can be considered a donor–acceptor complex of the parent iminoborane HB$^+$(NH$_3$). This species is also able to abstract dihydrogen from Me$_2$NH·BH$_3$ (Scheme 3).[23] When 2 was reacted with Me$_2$NH·BH$_3$ for...
12 hours at room temperature, the hydrogenated product 3 formed along with the expected dehydrogenation by-products \([\text{Me}_2\text{N-BH}_3]_2\) and \(\text{Me}_2\text{NH-BH}_2-\text{Me}_2\text{N-BH}_4\), which were detected by NMR spectroscopy. To gain more insight into the mechanism, aminoborane 2 was reacted with \(\text{Me}_2\text{ND-BH}_3\), resulting in exclusive deuterium incorporation in the amine moiety, suggesting a similar mechanism as reported for \(i\text{Pr}_2\text{N}==\text{BH}_2\).[19,21]

As an alternative to aminoborane dihydrogen acceptors, the group of Stephan described a phosphinoborane while examining these compounds as frustrated Lewis pairs.[24–26] After establishing that these compounds are able to heterolytically cleave dihydrogen, phosphinoborane 4 was reacted with \(\text{Me}_2\text{NH·BH}_3\) and showed to be able to quantitatively abstract dihydrogen, while generating \([\text{Me}_2\text{N-BH}_2]_2\) (Scheme 4).[27] This resembles the greater affinity for \(\text{H}_2\) compared with the transient \(\text{Me}_2\text{N-BH}_4\), which was explained by the increase of Lewis acidity at the boron site by the perfluorinated aryl substituents.

Recently, Braunschweig and co-workers reported the first iminoborane that can rapidly dehydrogenate ammonia–borane at room temperature.[28] They showed that 1 equivalent of tert-butyl substituted iminoborane 5 (Scheme 5) rapidly reacts with 1 equivalent of AB, forming the expected aminoborane 6, along with borazine and other dehydrogenated products. The over-dehydrogenation of AB (and concomitant formation of other BN-cycles) was explained by subsequent dehydrogenation of the trimeric \(\text{B}(\text{cyclotriborazanyl})\text{amine–borane} \text{(BCTC)}\) intermediate by 5, as well as the capability of the formed \(\text{NH}_2\equiv\text{BH}_2\) to facilitate hydrogen release. Isotopic labelling experiments showed that the hydrogenation exclusively proceeds through \(\text{B}--\text{H}--\text{B}\) and \(\text{N}--\text{H}--\text{N}\) transfer. DFT calculations revealed that this exchange occurs via a low-lying six-membered transition state (7). This makes this process using iminoboranes much more facile than using aminoboranes, as reported by Manners and co-workers.[19] Additionally, 5 was also found to dehydrogenate the bulky \(N\text{-tBu-B-durylamine–borane},\) which could afford a new way of making bulky aminoboranes.

### 2.2. Dihydrogen transfer to organic C–C and C–E bonds (E = N, O, P)

While studying hydrogen transfer to organic moieties, Berke and co-workers reported on the transfer hydrogenation of imine substrates using amine–boranes.[29] The reaction of 1 equivalent of ammonia–borane with a broad variety of imine substrates resulted in transfer hydrogenation to yield the corresponding amines in excellent yields, along with the formation of AB dehydrogenation products (Scheme 6). Due to the mild reaction conditions, no side reactions were detected, which allowed the reaction conditions to be optimized in which 1 equivalent of ammonia–borane can hydrogenate 2 equivalents of imine quantitatively. Both kinetic isotope effect and Hammett correlation studies revealed that the reaction occurs through a concerted double-hydrogen-transfer step. Additionally, DFT studies confirmed that this reaction occurs via transition state 8 with concomitant \(\text{N}--\text{H}--\text{C}\) and \(\text{B}--\text{H}--\text{N}\) transfer, comparable to transfer hydrogenation to aminoboranes (Scheme 2).[19,21]

Expanding the scope of organic substrates, Berke and co-workers also studied the transfer hydrogenation of aldehydes and ketones with amine–boranes.[30] Although amine–boranes were already experimentally found to be able to reduce ke-
tones and aldehydes in the 1980’s, the underlying mechanism was never thoroughly studied. Unexpectedly, when a wide range of ketones and aldehydes were subjected to AB dehydrogenation in THF (ratio AB:substrate 2:1), the corresponding alcohol was not observed. Instead, in situ NMR studies revealed that an alkyl borate was formed, along with ammonia (Scheme 7). Low-temperature $^{11}$B NMR spectroscopy revealed that the expected AB dehydrogenation products were not present in the reaction mixture, which excluded the concerted hydrogen transfer mechanism. After in-depth NMR studies, the authors proposed that this reaction occurs through dissociation of the ammonia–borane Lewis pair, with subsequent facile hydroboration of the ketone or aldehyde by the in situ formed BH$_3$, leading to the formation of the corresponding alkyl borate. Interestingly, when the reaction was performed in methanol, the formation of the expected alcohol products was observed. This distinct difference was assumed to be the result of initial BH$_3$ exchange to form MeOH·BH$_3$, which then could undergo double hydrogen transfer to the substrate, forming the desired product.

This mechanism has been contested, however. The group of Zhou and Fan performed a theoretical study on the mechanism of ketone reduction by NH$_3$·BH$_3$, which suggested that ketones can also undergo a concerted double hydrogen transfer via transition state 10, similar to imines (Scheme 8). This process was found to be lower in energy compared with the initially proposed hydroboration mechanism by Berke. To explain the observed alkyl borate formation, alcoholysis of the in situ formed NH$_2$·BH$_3$ was proposed, resulting in the first B–O bond formation (11). Subsequent B–H bond additions to the ketone affords the alkyl borate as the final product.

To gain more insight into the transfer hydrogensation of aldehydes, Chen and co-workers studied the reaction of a variety of aldehydes in THF with ammonia–borane, which resulted in good to excellent conversion to the terminal alcohols and no formation of ammonia was observed (Scheme 9). In contrast to the findings of Berke and co-workers, note that there is a difference in reaction conditions. Although Berke used a ratio of 2:1 ratio of AB versus substrate, Chen used a 1:1 ratio of AB and aldehyde. Nevertheless, isotopic-labelling studies of Chen and co-workers with NH$_3$·BD$_3$ and ND$_3$·BH$_3$ strongly suggested that the main path for the reduction of aldehydes is through double hydrogen transfer, in which both the protic N–H and hydridic B–H hydrogens participate and are transferred to the O and C atom, respectively.

Subsequently, Berke and co-workers investigated the applicability of a range of polarized olefins bearing two electron withdrawing groups (EWG) on one side and H, aryl, or alkyl substituents on the other side of the C=C bond in the transfer-hydrogensation reaction with NH$_3$·BH$_3$. All substrates showed excellent conversion to the hydrogenated species under mild conditions. Interestingly, labelling studies using NH$_3$·BD$_3$ and ND$_3$·BH$_3$ revealed that the hydridic B–H hydrogen is transferred to the most nucleophilic carbon of the C=C double bond through hydroboration, which is in contrast to the expected...
concerted double hydrogen transfer and suggests that a different mechanism is operative.\textsuperscript{[21]} Kinetic isotope effect studies and intermediate trapping revealed that the olefin hydrogenation occurs in a two-step process, in which first the hydrogen is transferred by hydroboration, and then a rate-determining proton transfer from the amine takes place (13, Scheme 10).\textsuperscript{[38]} In addition, it was hypothesized that the generated (solvent-stabilized) aminoborane NH$_2$–BH$_2$ intermediate is capable of a second double hydrogen transfer to the olefin through transition state 15, which explains the formation of borazine and polyborazylene.

Another example of amine–borane dehydrogenation was provided by the Stephan group. Namely, the reaction between the Lewis adduct Mes$_3$P(AlX$_3$)$_2$ and CO$_2$ afforded species 16 (Scheme 11),\textsuperscript{[39]} which is prone to undergo reduction of the carbon center by dihydrogen transfer from NH$_3$·BH$_3$, resulting in various dehydrogenation products, like borazine, that were observed by $^{11}$B NMR spectroscopy. Subsequent quenching of the various methoxylaluminate species with water resulted in the formation of methanol, which could be extracted with yields of isolated materials ranging from 37 to 51%.

\[ \text{NH}_3\cdot\text{BH}_3 + \text{CH}_3\text{CO}_2\text{H} \rightarrow \text{MeO} + \text{H}_2 \]

\[ \text{Scheme 12. Formation and reactivity of aminodiborane 17.} \]

The second Lewis acid that was found to mediate amine–borane dehydrogenation is a gallium(III) complex, which was reported by the Wright group to react with stoichiometric amounts of ammonia–borane in a rather unexpected fashion.\textsuperscript{[41]} When Ga[N(SiMe$_3$)$_2$]$_3$ was treated with NH$_2$·BH$_3$, the galli-

\[ \text{NH}_2\cdot\text{BH}_3 + \text{THF-BH}_3 \rightarrow \text{H}_2\text{N-BH}_2 + \text{H}_2 + \text{THF} \]

\[ \text{Scheme 13. Proposed mechanism for the formation of aminodiborane from NH}_2\cdot\text{BH}_3 \text{and THF-BH}_3. \]
um-free product $[\text{B}(\text{NHBH})\text{N(SiMe$_3$)Si}(\text{Me$_3$})\text{N(SiMe$_3$)}$_2$]$ was isolated in low yield (3%). Clearly, 22 is obtained by the formation of several B–N and Si–N bonds as well as the formal release of dihydrogen (Scheme 14), yet the exact mechanism of the formation remains unclear.

$$\text{Ga}[\text{N(SiMe$_3$)}$_2$$_3] + \text{NH$_3$} \cdot \text{BH}_3 \rightarrow \text{GaN}[\text{N(SiMe$_3$)}$_2$$_3] + \text{Me$_3$} \cdot \text{BH}_3$$

Scheme 14. Reactivity of a gallium(III)-based complex with NH$_3$·BH$_3$.

### 2.4. Stoichiometric Lewis base-mediated dehydrogenation

Roessky and co-workers reported N-heterocyclic carbene (NHC) 23 (Scheme 15) to be inert towards molecular hydrogen. Nonetheless, 23 was found to be a very efficient reagent for the dehydrogenation of ammonia–borane, resulting in the formation of the NHC–H$_2$ adduct 24, whereas leaving the C–C double bond of the carbene unaffected $^{[42, 43]}$. In contrast, the reaction of N-heterocyclic germylene 25 with 1 equivalent of ammonia–borane led to the formation of germeylene 26 (Scheme 15), in which the N-heterocyclic germylene did abstract dihydrogen, but without oxidation of the germanium(II) center $^{[42]}$.

$$\begin{align*}
\text{NH$_3$} \cdot \text{BH}_3 + \text{EBN} &\rightarrow \text{EBN} + \text{NHMe} \cdot \text{BH}_3, \\
\text{NH$_3$} \cdot \text{BH}_3 + \text{C$_6$D$_6$} &\rightarrow \text{EBN} + \text{NHMe} \cdot \text{BH}_3
\end{align*}$$

Scheme 15. The reaction of an N-heterocyclic carbene and germylene with AB.

The group of Rivard extended the scope of this NHC chemistry and found that N-heterocyclic carbene 27 (Scheme 16) can dehydrogenate MeNH$_2$·BH$_3$ and PrNH$_2$·BH$_3$ forming the expected NHC–H$_2$ adduct 28 together with the carbene-bound B–N–B adduct NH$_3$·BH$_3$·NHR–BH$_3$ (29) in a 1:1 ratio $^{[24, 25, 26]}$. The formation of 29 was proposed to proceed through a sequence of events. First, the NHC dehydrogenates the amine–borane generating 28 and 1 equivalent of aminoborane RNH–BH$_2$, which is then trapped by a second equivalent of NHC giving rise to NH$_3$·BH$_3$·NHR(R)–BH$_3$ (29) in a 1:1 ratio. $^{[42]}$ The formation of 29 was proposed to proceed through a sequence of events. First, the NHC dehydrogenates the amine–borane generating 28 and 1 equivalent of aminoborane RNH–BH$_2$, which is then trapped by a second equivalent of NHC giving rise to NH$_3$·BH$_3$·NHR(R)–BH$_3$ (29) in a 1:1 ratio. $^{[42]}$

$$\begin{align*}
\text{NH$_3$} \cdot \text{BH}_3 + \text{MeNMe} &\rightarrow \text{MeNHMe} \cdot \text{BH}_3, \\
\text{NH$_3$} \cdot \text{BH}_3 + \text{C$_6$D$_6$} &\rightarrow \text{MeNHMe} \cdot \text{BH}_3
\end{align*}$$

Scheme 16. Dehydrogenation of RNH$_2$·BH$_3$ by an NHC.

Utilizing the sterically more demanding tBuNH$_2$·BH$_3$ still resulted in dehydrogenation by NHC 27, but now NHC·BH$_3$·NH(tBu)–BH$_3$ was isolated in only 10% yield. Multiple side products were detected by $^{11}$B NMR spectroscopy, indicating that carbene coupling to the transient tBuN–BH$_3$ is significantly suppressed by the increased steric bulk on the nitrogen atom. Interestingly, when DippNH$_2$·BH$_3$ (Dipp = 2,6-iPr$_2$C$_6$H$_3$) was reacted with 1 equivalent of NHC 27 a variety of products was detected such as NHC–H$_2$ (28), NHC·BH$_3$·NHDipp, NHC·BH$_3$·NH(Dipp)–BH$_2$ – dipp and NHC Me. This is caused by the lower nucophility of the nitrogen moiety in DippNH$_2$·BH$_3$, which reduces the degree of BH$_2$ exchange and makes isolation of NHC·BH$_3$·NHC(Dipp) possible. Instead of using 1 equivalent, Manns and co-workers described the reaction of 2 equivalents of NHC 27 with methylamine–borane, which afforded NHC–H$_2$ (28), whereas the in situ generated methylaminoborane was trapped by the second equivalent of NHC affording NHC·BH$_3$·NMe 30 (Scheme 17). $^{[42, 43]}

$$\begin{align*}
\text{NH$_3$} \cdot \text{BH}_3 + \text{MeNHMe} &\rightarrow \text{MeNHMe} \cdot \text{BH}_3, \\
\text{NH$_3$} \cdot \text{BH}_3 + \text{C$_6$D$_6$} &\rightarrow \text{NMeHMe} \cdot \text{BH}_3
\end{align*}$$

Scheme 17. 2:1 reaction of an NHC with MeNH$_2$·BH$_3$.

### 2.5. Stoichiometric frustrated Lewis pair-mediated dehydrogenation

Lewis acids and Lewis bases that do not form a classic Lewis acid/base adduct, due to steric hindrance, are called frustrated Lewis pairs (FLPs) $^{[24, 25, 26]}$, and these main-group species also exhibit reactivity towards amine–boranes. Miller and Bercaw showed that the addition of 1 equivalent of Me$_3$NH·BH$_3$ to a solution of PrBu$_3$ and B(C$_6$F$_5$)$_3$ resulted in the direct conversion (> 95%) to the ion pair [[tBu$_3$]PH][HB(C$_6$F$_5$)$_3$] and dimeric (Me$_3$NBH)$_2$ as major dehydrogenation product (Scheme 18). $^{[46]}

$$\begin{align*}
\text{R}_2\text{NH} \cdot \text{BH}_3 + \text{B(C$_6$F$_5$)$_3$} &\rightarrow [[\text{R}_2\text{NH}]\text{HB(C$_6$F$_5$)$_3$}] + (\text{R}_2\text{NBH})_2, \\
\text{MeCN} &\rightarrow \text{MeCN}
\end{align*}$$


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Keeping the reaction mixture one day at room temperature gave 97% conversion to (Me₂NBH₂)₂, with only trace amounts of (BH₃)₂NMe₂(µ-H) and H₂·NMe₂BH₃·NHMe₂. The order of addition appeared to be important. When B(C₆F₅)₃ was added a few minutes prior to the addition of PtBu₃, then only 50% of (Me₂NBH₂)₂ was obtained, whereas initial addition of the phosphine followed by B(C₆F₅)₃ led to almost quantitative formation of ([Bu₃PH][B(C₆F₅)₃]) and (Me₂NBH₂)₂. The authors hypothesized a stepwise mechanism might be operative in which B(C₆F₅)₃ abstracts hydride to form [R₂NBH₂]⁺, which is quickly deprotonated by the phosphine to generate R₂N=BH₂ that dimerizes to the final product. The PtBu₃/B(C₆F₅)₃ FLP was also able to dehydrogenate NH₂BH₃, however, lower conversions were obtained.

Alternatively, Manners and co-workers utilized combinations of different Group 14 triflates (Me₂SiOTf, Et₂SiOTf, and nBu₃SnOTf) with bulky nitrogen bases (2,6-di-tert-butylpyridine and 2,2,6,6-tetramethylpiperidine (TMP)) as frustrated Lewis pairs for the dehydrogenation of dimethylamine–borane. They found that the Me₂SiOTf/TMP combination converts Me₂NH·BH₃ rapidly (8 min) to the dimeric (Me₂NBH₂)₂ together with formation of the corresponding silane and piperidinium triflate (Scheme 19).

Switching to nBu₃SnOTf/TMP increased the rate of the reaction, whereas the Et₂SiOTf/TMP combination was found to be less reactive, which also resulted in more side products. The FLP combination of Me₂SiOT with the weaker base di-tert-butylpyridine also showed reduced reactivity and concomitant increased formation of side products. Control experiments showed that the separate components of the FLP system (the Lewis acid or Lewis base) were not able to dehydrogenate Me₂NH·BH₃, highlighting the potential of frustrated Lewis pairs as dehydrogenation agents.

### 3. Acid and base-initiated dehydrogenation

There are a number of examples in the literature of reactions in which a substoichiometric quantity of an acid or a base has been used for the dehydrogenation of ammonia–borane, but in which it has been shown that the mechanism goes through an initiation process instead of the acid or base acting formally as a catalyst.

#### 3.1. Brønsted and Lewis acid-initiated dehydrogenation

Dixon and co-workers described the liberation of dihydrogen from ammonia–borane by applying substoichiometric amounts of strong Brønsted and Lewis acids. It was found that these acids are not catalyzing the dehydrogenation of NH₂BH₃ but act as an initiator. The initiation step was proposed to go through either protonolysis of the B–H bond by a Brønsted acid or by hydride abstraction by a strong Lewis acid, forming borenium cation 31 (Scheme 20). Subsequently, the borenium intermediate 31 reacts with another equivalent of NH₂BH₃ followed by elimination of dihydrogen and formation of 33. DFT calculations indicated that 33 can further react with NH₂BH₃, which leads to chain transfer oligomerization. Following this strategy, loadings down to 0.5 mol% of acid (triflic acid (HOSO₂CF₃, HOTf), HCl, or B(C₆F₅)₃ as Lewis acid) were found to liberate over 1 equivalent of dihydrogen under mild conditions.

To gain more insight into the Brønsted acid-initiated dehydrogenation of ammonia–borane, the group of Paul performed an in-depth theoretical study on the underlying mechanism of NH₂BH₃ protonation using triflic acid in bis(2-methoxethyl) ether (diglyme). They found that the acid most likely protonates diglyme forming ion pair 34 (Scheme 21), which then reacts with ammonia–borane to form 35, in which the proton interacts with the hydrides of NH₂BH₃. Subsequently, the proton is transferred to the borane, forming the nonclassical pentacoordinate borane 36. This solvent-stabilized NH₂BH₄⁺ species can release dihydrogen with concomitant formation of NH₂BH₃–diglyme adduct 37, in which the boron atom is now strongly bound to diglyme through an oxygen atom. Important to note is that Dixon and co-workers did observe such a [NH₂BH₃(L)⁺] species experimentally, but proposed this species to form through direct protonolysis or hydride abstraction by the Lewis acid. Interestingly, the group of Paul found that 37 can react with another equivalent of NH₂BH₃ forming 38. Subsequent proton transfer (rate-determining step, RDS) followed...
by the release of H₂N=BH₂ regenerates the nonclassical pentacoordinate borane 36, and subsequently 37 after H₂ elimination. This rate-determining step with an energy barrier of 26.0 kcal mol⁻¹ correlates nicely with the experimental reaction temperature of 60 °C reported by the group of Dixon.⁴⁸ The regeneration of 37 was suggested to be responsible for excess H₂ release because it can react with other oligomeric BN species of H₂N=BH₂ producing more H₂, and not through a dehydrocoupling pathway suggested by Dixon and co-workers.⁴⁸

The group of Manners reported a stepwise method to generate dimeric (Me₂NBH₂)₂ utilizing a Brønsted acid and base.⁵¹ The dehydrogenation of dimethylamine–borane can be initiated by a protonation/H₂ elimination step with Brønsted acids such as HOTf and HCl,⁵² resulting in formation of H₂ and Me₂NH·BH₂X (X = OTf, Cl). Subsequently, these species can be rapidly converted to cyclic diborazane (Me₂NBH₂)₂ when reacted with an excess (10 equiv) of iPr₂EtN under ambient conditions (DCM, 25 °C, < 1 min).

### 3.2. Brønsted base-initiated dehydrogenation

Sneddon and co-workers reported on the use of a Brønsted base to initiate ammonia–borane dehydrogenation, namely 1,8-bis(dimethylamino)naphthalene, commonly known as proton sponge.⁵³ A substoichiometric loading of only 1 mol% of this strong base was shown to accelerate the dehydrogenation of NH₃BH₃ when the solid mixture was heated to 85 °C and approximately 1.1 equivalent of H₂ was released after 21 hours. Solid-state ¹¹B NMR spectroscopy of the final products revealed that a sp²-boron framework had formed, which is indicative for a product containing B–N unsaturated bonds. When ionic liquid 1-butyl-3-methylimidazolium chloride (bmmCl) was used as a solvent, the reaction rates significantly increased, and with loadings of 0.5 mol% of the proton sponge 2.1 equivalents of H₂ were evolved after 6 hours at 85 °C. The initial step in AB dehydrogenation utilizing a proton sponge is believed to be deprotonation of NH₃BH₃ forming the [NH₃–BH₃]⁻ anion (by analogy with 39 in Scheme 22, see below), which can react with AB and form anionic polymers with simultaneous release of dihydrogen.

Two years later, Sneddon and co-workers extended the Brønsted base-promoted dehydrogenation of ammonia–borane by applying Verkade's base (VB, Scheme 22) as polymerization initiator.⁵⁴ Although this Brønsted base did not perform as well as the proton sponge,⁵¹ liberation of 2 equivalents of H₂ from NH₃BH₃ was achieved with 5 mol% of Verkade's base in 24 hours. Similar to the proton sponge, the oligomerization was assumed to be initiated by deprotonation by the Brønsted base generating the reactive anion 39 (Scheme 22), which then reacts with another equivalent of NH₃BH₃, elongating the chain and liberating NH₃. Subsequent insertion of NH₃BH₃ leads to the formation of 40 and H₂.

To verify this mechanism, Verkade's base was reacted with 3 equivalents of NH₃BH₃ for 3 days at room temperature after which all the starting material was consumed. In good agreement with the proposed mechanism, product 40 was isolated in 74% yield (Scheme 23). When a 1:4 ratio was applied, two new salts, together with small amounts of 40, were isolated and characterized as the linear chain 41 and branched product 42. To gain further insight into the mechanism, 40 was reacted with 1 equivalent of NH₃BH₃ for 2 days at 50 °C, which also afforded a mixture of 41 and 42, supporting a stepwise, base-promoted oligomerization mechanism.
4. Acid and base-catalyzed dehydrogenation

4.1. Brønsted acid-catalyzed dehydrogenation

Recently, Yang and Du developed a new approach for the asymmetric transfer hydrogenation of imines and β-enamino esters utilizing chiral phosphoric acids.\(^{[55]}\) After a screening of potential chiral phosphoric acids (CPAs), they found that CPA 43 bearing bulky silyl substituents at the 3,3'-positions of the binaphthyl framework was an excellent catalyst for the benchmark reaction giving high conversion (94 %) and ee (93 %; Scheme 24). Under optimized conditions, a wide variety of imines and β-enamino esters were hydrogenated in high yields (55–96 %) with good to high enantioselectivity (66–94 % ee).

Stoichiometric reactions revealed that CPA 43 rapidly reacts with NH$_3$·BH$_3$ with concomitant release of H$_2$ and formation of a new chiral amine–borane 44 (Scheme 25). DFT calculations showed that 44 can transfer dihydrogen to the imine substrate through a six-membered transition state (45(S), Scheme 25) in which the H$_2$ transfer towards the (S)-isomer is preferred above the (R)-isomer (formation of the (S)-isomer in the final product was also confirmed by X-ray crystallography). This enantioselective transfer of H$_2$ led to the formation of the desired chiral amine and several [B@N] species (46), which were observed by $^{11}$B NMR spectroscopy. Additional DFT calculations revealed that 46 can then be hydrolyzed (via the four-membered transition state 47) to regenerate the chiral phosphoric acid 43 that can enter the catalytic cycle again.

4.2. Lewis acid-catalyzed dehydrogenation

A variety of Group 13 element Lewis acids were found to be active catalysts in the dehydrogenation of amine–boranes. Wright and co-workers utilized 8 mol % of Al(NMe$_2$)$_3$ for the dehydrogenation of Me$_2$NH·BH$_3$, which formed dimeric (Me$_2$NH)$_2$BH$_2$, together with small amounts of (Me$_2$N)BH and a new aluminum species [(Me$_2$N)$_2$BH$_2$AlH] (48; Scheme 26).\(^{[56]}\) Compound 48 was isolated and also showed catalytic activity towards Me$_2$NH·BH$_3$ dehydrogenation. DFT studies revealed that 48 is relatively unstable and can undergo a facile β-hydride transfer forming 49,\(^{[46]}\) which is another important potential catalyst for this reaction.

The related Al(NiPr$_2$)$_3$ is also catalytically active in the dehydrogenation of iPr$_2$NH·BH$_3$ in benzene at 60 °C.\(^{[57]}\) Given that a relatively long induction period was observed when using...
10 mol%, Al(NiPr₂)₃ was suspected to be a pre-catalyst in this reaction. A 1:2 stoichiometric reaction of Al(NiPr₂)₃ with iPr₂NH·BH₃ resulted in the formation of [H₃Al(µ-iPr)]₂ (50), which is structurally related to 49, and proved to be an efficient catalyst, even when catalyst loadings of 0.5 mol% were applied at 20 °C. The proposed mechanism of this reaction involves initial deprotonation of iPr₂NH·BH₃ to form 51 (Scheme 27), which is followed by β-hydride elimination to regenerate the active catalyst.

Additionally, the group of Wright reported several aluminum hydride species to be catalytically active in amine–borane dehydrogenation. For example, 10 mol% of LiAlH₄ converted Me₂NH·BH₃ almost quantitatively to dimeric (Me₂NBH)₂ when refluxed in toluene for 16 hours.[17] Similarly, neutral [(tBuO)₂AlHₓ] (x = 1 or 2) and lithium salts of [(tBuO)₂AlH]⁻ were found to catalyze the dehydrogenation of Me₂NH·BH₃ with [tBuO₂AlH]⁻ being superior compared with the other tert-butoxy-substituted aluminum catalysts.[56] Nonetheless, the underlying mechanism for dehydrogenation of amine–boranes is much more complicated and still needs further investigations.

The heavier analogue of Al(NMe₂)₃ Ga(NMe₂)₃ was successfully applied as catalyst for tBuNH·BH₃ dehydrogenation.[60] Under ambient conditions, 5 mol% of Ga(NMe₂)₃ slowly convert tBuNH·BH₃ to the borazine (tBuNHBH)₂ and also the formation of borazine was observed, which is the product of subsequent dehydrogenation.

Recently, Wegner and co-workers showed that 5 mol% of bis(borane) 52 can dehydrogenate ammonia–borane releasing up to 2.5 equivalents of dihydrogen per AB molecule, which is the first example of a metal-free catalyst capable of liberating more than 2 equivalents of H₂ (Scheme 28).[59, 60] Driven by this result, a series of other borane analogues were tested, however, none of them were superior to bis(borane) 52.[61] Interestingly, the evolution of H₂ can be switched on and off, because catalytic dehydrogenation occurs at 60 °C, which can be efficiently stopped by cooling to room temperature and started again by heating to 60 °C. More importantly, the catalyst did not decompose and could be reused multiple times by adding a new batch of NH₂BH₃ after the evolution of hydrogen was finished. This procedure was repeated 15 times without loss of catalytic activity.

Stoichiometric reactions revealed that the reaction starts by exchange of the chloride for a hydride from NH₂BH₃, forming ammonia–monochloroborane (NH₂BH₃·Cl) and 53 (Scheme 29). Kinetic-isotope studies suggested that during catalysis both B–H and N–H bonds are involved in the rate-determining step. The proposed mechanism, which is supported by DFT calculations, involves interaction of the Lewis acidic borane of 53 with NH₂BH₃, forming the three-center two-electron adduct 54, which releases both H₂ and H₂N·BH₃ via the rate-determining transition state 55 and regenerates the catalyst.

Paul and co-workers investigated the use of triarylboranes as catalysts for ammonia–borane dehydrogenation using DFT computational methods,[62] and they identified para-CF₃- and para-CN-substituted triphenylborane as promising synthetic targets with reaction barriers close to 20 kcal mol⁻¹. Additionally, they also predicted that these triarylboranes could be capable of liberating more than 2 equivalents of dihydrogen per AB moiety.

![Scheme 27. Mechanism for iPr₂NH·BH₃ dehydrogenation by 50.](image)

![Scheme 28. Catalytic dehydrogenation of NH₂BH₃ by 52.](image)

![Scheme 29. Mechanism of AB dehydrogenation by 53.](image)
Group 14 Lewis acids have also been explored. Waterman and co-workers investigated tin(IV) and tin(II) compounds in the catalytic dehydrogenation of amine–boranes\(^{[65, 66]}\) and found that 10 mol% of \(\text{Cp}^*\text{SnCl}_2\) (\(\text{Cp}^* = \text{C}_5\text{Me}_5\)) and \(\text{Ph}_2\text{SnCl}_2\) quantitatively converted \(\text{NH}_3\cdot\text{BH}_3\) to the corresponding dehydrogenation products (Table 1). SnCl\(_2\) showed the same excellent conversion, but with a much higher rate, and catalyst loadings down to 0.5 mol% remained efficient. Changing the substrate to \(\text{Me}_2\text{NH}\cdot\text{BH}_3\) drastically reduced the rate of the reactions, giving only 69, 47, and 23% of product at 65 °C using 10 mol% of \(\text{Cp}^*\text{SnCl}_2\), \(\text{Ph}_2\text{SnCl}_2\), and \(\text{SnCl}_2\), respectively. Precipitation of metallic tin was observed during these reactions and this was proposed to be the reductive termination step of the catalyst. The reactions are less selective towards the \(\text{(Me}_2\text{NH})_2\text{H}_2\) dimer, giving reaction mixtures containing \(\text{Me}_2\text{NH} \cdot \text{BH}_3\), \(\text{Me}_2\text{NH} \cdot \text{BH}_3\), \(\text{H}_2\text{BNMe}_2\cdot\text{BH}_3\), and other unidentified species.

Surprisingly, these tin catalysts showed much higher conversions when the bulky \(\text{tBuNH} \cdot \text{BH}_3\) was used as substrate, and after 4 to 5 days at 65 °C conversions of 95, 93, and 84% were obtained using 10 mol% of \(\text{Cp}^*\text{SnCl}_2\), \(\text{Ph}_2\text{SnCl}_2\), or 5 mol% \(\text{SnCl}_2\), respectively. Similar to \(\text{Me}_2\text{NH} \cdot \text{BH}_3\), these reactions were much less selective and a range of products were observed (Table 2) of which only small amounts of borazine, which is in contrast to the aluminum catalysts described above. The tin(IV) catalysts revealed a higher production of \(\text{tBuNH} \cdot \text{BH}_3\) (16–23%) compared with the tin(II) catalyst \(\text{SnCl}_2\) (<5%), which suggests a β-hydrogen elimination mechanism, resulting in a tin hydride and concomitant formation of the aminoborane. However, the overall mechanism as well as the nature of the active catalyst remains unresolved.

### Table 1. Dehydrogenation of amine–boranes by tin(IV) and tin(II) (pre)catalysts at 65 °C.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>RR'NH·BH(_3) Loading [mol%]</th>
<th>Conversion [%]</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp}^*\text{SnCl}_2)</td>
<td>R = R = H</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>(\text{Ph}_2\text{SnCl}_2)</td>
<td>R = R = H</td>
<td>10</td>
<td>100</td>
</tr>
<tr>
<td>(\text{SnCl}_2)</td>
<td>R = R = H</td>
<td>5</td>
<td>100</td>
</tr>
<tr>
<td>(\text{SnCl}_2)</td>
<td>R = R = H</td>
<td>0.5</td>
<td>100</td>
</tr>
<tr>
<td>(\text{Cp}^*\text{SnCl}_2)</td>
<td>R = R = Me</td>
<td>10</td>
<td>69</td>
</tr>
<tr>
<td>(\text{Ph}_2\text{SnCl}_2)</td>
<td>R = R = Me</td>
<td>10</td>
<td>47</td>
</tr>
<tr>
<td>(\text{SnCl}_2)</td>
<td>R = R = Me</td>
<td>10</td>
<td>23</td>
</tr>
<tr>
<td>(\text{Cp}^*\text{SnCl}_2)</td>
<td>R = (\text{tBu}, \text{R} = \text{H})</td>
<td>10</td>
<td>95</td>
</tr>
<tr>
<td>(\text{Ph}_2\text{SnCl}_2)</td>
<td>R = (\text{tBu}, \text{R} = \text{H})</td>
<td>10</td>
<td>93</td>
</tr>
<tr>
<td>(\text{SnCl}_2)</td>
<td>R = (\text{tBu}, \text{R} = \text{H})</td>
<td>5</td>
<td>84</td>
</tr>
</tbody>
</table>

4.3. Lewis base-catalyzed dehydrogenation

Radosevich and co-workers utilized a planar, trivalent phosphine for transfer hydrogenation with ammonia–borane as the hydrogen source.\(^{[62]}\) They found that in stoichiometric quantities, 56 can abstract 1 equivalent of dihydrogen from ammonia–borane to form dihydrophosphorane 57 (Scheme 30), which can subsequently transfer \(\text{H}_2\) quantitatively to azobenzene. Additionally, 56 is also catalytically active (10 mol%) and cleanly hydrogenates azobenzene to diphenylhydrazine with 94% conversion in 48 hours at 40 °C. During catalysis, dihydrophosphorane 57 was the only observable species by \(^{31}\)P NMR spectroscopy, indicating that 57 is the resting state of the catalytic cycle and, therefore, a two-electron redox mechanism cycling between P\(^{1}\) and P\(^{0}\) oxidation states was proposed (Scheme 30).

The group of Sakaki performed calculations to disclose the full mechanism of this catalytic reaction,\(^{[65, 66]}\) and they proposed that hydrogen abstraction from ammonia–borane does not occur solely at the P\(^{1}\) site.\(^{[62]}\) Instead, the reaction follows a concerted P–O cooperative mechanism, forming 58, which is also the active species for the hydrogen transfer to azobenzene (Scheme 31). This type of transfer hydrogenation is closely related to metal–ligand cooperativity in metal complexes bearing a pincer ligand.\(^{[81]}\) The isolation and catalytic activity of 57 was explained by its equilibrium with 58; 57 itself is not involved in the catalytic cycle.

Additional computational studies by Sakaki and co-workers led to the theoretical design of a new hydrogen transfer catalyst.\(^{[68]}\) They investigated the potential of a pincer-type phosphorus-containing compound 59 (Scheme 32) to transfer dihydrogen from ammonia–borane to carbon dioxide, as a promising metal-free approach for CO\(_2\) reduction. They found that replacing the oxygen atoms in the pincer ligand for nitrogen atoms drastically changed the mechanism from a concerted transfer of hydrogen to the substrate to a stepwise mechanism. Although the initial dehydrogenation step of ammonia–borane is similar to the original catalyst (Scheme 32), the next step involves hydride migration from the phosphorus atom to CO\(_2\) forming an unstable intermediate (60) which readily transforms to the more stable 61. Subsequently, the protic hydro-

### Table 2. Product distribution [%] of the dehydrogenation of tBuNH·BH\(_3\) by tin catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Polymers</th>
<th>tBuNH·BH(_3)</th>
<th>tBuNH·BH(_2)</th>
<th>tBuNH·BH(_3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Cp}^*\text{SnCl}_2)</td>
<td>20</td>
<td>0</td>
<td>16</td>
<td>26</td>
</tr>
<tr>
<td>(\text{Ph}_2\text{SnCl}_2)</td>
<td>41</td>
<td>8</td>
<td>23</td>
<td>23</td>
</tr>
<tr>
<td>(\text{SnCl}_2)</td>
<td>13</td>
<td>6</td>
<td>&lt;5</td>
<td>33</td>
</tr>
</tbody>
</table>

[Image 339x541 to 515x677]
gen is transferred to the coordinating formate group, which releases formic acid and regenerates the catalyst. The proposed increased rate of the reaction through the stepwise mechanism is due to differences in the HOMO levels of the ONO- (56) and NNN-type (59) pincer ligand, in which the pincer-type phosphorus ligand with the highest HOMO level is most active for CO₂ reduction by transfer hydrogenation.

Kinjo and co-workers found that N-heterocyclic phosphane 62 can quantitatively add to the N=N bond of an azobenzene to form N-heterocyclic phosphinohydrazine 63 (R=Ph, Scheme 33). Subsequently, the P–N bond can be cleaved by addition of NH₃·BH₃, giving diphenylhydrazine and regenerating the N-heterocyclic phosphane 62. Interestingly, when NH₃·BD₃ was applied, the deuterium was selectively transferred to the phosphorus center, demonstrating a regiospecific hydrogen transfer via a six-membered transition state (64), which was supported by DFT calculations. Compound 62 also functions as catalyst (5 mol%, 50 °C) and can hydrogenate a range of E-azo-compounds in good to excellent yields to the corresponding hydrazines using ammonia–borane as the hydrogen source.

4.4. FLP-catalyzed dehydrogenation

Utilizing the ability of frustrated Lewis pairs to activate small molecules, Slootweg as well as Uhl and co-workers reported on the reactivity of a phosphorus/aluminum-based FLP towards amine–boranes. Treatment of FLP 65 with 1 equivalent of NH₃·BH₃ liberates 1 equivalent of dihydrogen concomitant with the formation of the zwitterionic five-membered heterocycle 66 (Scheme 34). DFT calculations revealed that H₂ abstraction is initiated by the activation of the N@H bond of an amine–borane. Subsequent protonation of the B@H bond by the newly formed P–H moiety liberates dihydrogen, simultaneously generating an aminoborane adduct that can readily ring-close to form product 66. Increasing the steric bulk on the substrate destabilizes 67, which also allows catalytic dehydrogenation. The reaction of Me₂NH·BH₃ with 0.4 mol% of 65 afforded the four-membered cycloborazane 68 after 44 hours in 77%.
with turnover numbers and frequencies up to 198.3 and 4.5 h⁻¹, respectively.

Gallium analogue 69 showed similar reactivity towards Me₂NH·BH₃, yet in this case no aminoborane adduct intermediate (70) could be detected during the reaction and solely FLP 69 and cyclic diborazane 68 were observed. Treatment of FLP 69 with the sterically less hindered NH₃·BH₃ did afford the five-membered heterocycle 71, next to the evolution of dihydrogen gas (Scheme 34). This aminoborane adduct is not stable at elevated temperatures (75 °C) and full recovery of the P/Ga FLP 69 was observed together with the formation of dihydrogen, which prompted the question of whether 69 could act as a hydrogen transfer catalyst. Indeed, the reaction between NH₂BH₃, imine PhCH=NtBu and 4 mol % of the P/Ga-based FLP 69 resulted in the formation of the corresponding amine together with dehydrogenation products (Scheme 35).

The first linked phosphinoborane (i.e. one not containing a direct P–B bond) that dehydrogenates NH₂BH₃ catalytically was described by Stephan and Erker. Although FLP 72 is unreactive towards H₂, it rapidly reacts with ammonia–borane by abstracting H₂ to form dihydrogen adduct 73 (Scheme 36).

Moreover, 72 is active as a hydrogen transfer catalyst for the dehydrogenation of bulky imines. When 10 mol % catalyst loading was used, rapid formation of the corresponding amine and borazine was observed (Scheme 36). A few years later, the same groups reported a similar strategy for transfer hydrogenation of enamines using 72 as catalyst and ammonia–borane as the dihydrogen source.

Aldridge and co-workers reported dimethylxanthene-linked phosphinoborane FLP 74 to be active as catalyst for the dehydrogenation of several amine–boranes. FLP 74 was found to catalyze the liberation of dihydrogen from NH₂BH₃, MeNH₂BH₃, and Me₂NH·BH₃ at 55 °C using only 1 mol % catalyst loading, which is the first reported example of catalytic methyamine- and ammonia–borane dehydrogenation by a main-group-based frustrated Lewis pair without dihydrogen transfer. In order to probe the mechanism, stoichiometric reactions with 74 and Me₂NH·BH₃ revealed that the dehydrogenation of amine–boranes is initiated by activation of the B–H bond (Scheme 37), generating adducts 75–77, which are believed to be viable intermediates during the catalytic cycle.

Adducts 75, 76, and 77 were surprisingly stable and no release of hydrogen was observed when solutions were heated.
to 55 °C for 24 hours. Dehydrogenation of adduct 75 was achieved by the use of iPr₂P=N=BH₃ in a similar fashion to that reported by Manns and co-workers,[20,21] which resulted in the formation of aminoborane adduct 78. Isolated samples of this 9-membered heterocycle showed no further reactivity towards ammonia–borane, suggesting that this species is not involved in the catalytic cycle. Given that 75, 76, and 77 are thermally stable, their catalytic activity is dependent on the presence of additional amine–borane. Indeed, 76 can react with another equivalent of methylamine–borane to form oligomeric borane adduct 79 (Scheme 38), which can also be formed by reacting H₃B·NHMeBH₂·NH₂Me, and provides evidence for dehydrogenation through a chain-growth mechanism. Addition of a third equivalent of MeNH₂·BH₃ resulted in the formation of the cyclic trimer (NHMeBH₂)₃ and regeneration of the catalyst. In situ NMR measurements indicated that the addition of a methylamine–borane unit occurs through an end-growth dehydrogenative mechanism, instead of insertion of MeNH₂·BH₃ into the P–B bond of the adduct (79). Additionally, 74 can further dehydrogenate (NHMeBH₃)₃ under catalytic conditions (1 mol % of 74) producing trimethylborazine at 55 °C. A subsequent theoretical analysis of a related dimethylxanthene-bridged FLP explored this chain-growth mechanism in more detail, including the possible reversibility of each step that would lead to the regeneration of ammonia–borane.[73]

Recently, the group of Bourissou described a related orthophenylene-bridged phosphinoborane bearing the Fxyl substituent (Fxyl = 3,5-(F₃C)₂C₆H₃) on the boron site as an alternative to the frequently used C₆F₅ group.[74] This FLP (80) adopts a closed form at room temperature, that is, with an intramolecular P–B interaction, however the open form is still accessible. Treatment of 5 mol % of FLP 80 with methylamine–borane at 55 °C resulted in the formation of dihydrogen together with a mixture of the corresponding borazine and borazane ((MeNH₂BH₃)₃ and (MeNBH)₃, respectively). At 70 °C, dimethylamine–borane was completely converted to (Me₂NBH₂)₂. In only 30 minutes and using 1 mol %, this reaction takes 6 hours at 55 °C, indicating that 80 is more active than Aldridge’s xanthene-based FLP 74.[70] This dehydrogenation reaction can be further accelerated when 1 equivalent of a dihydrogen acceptor (PhHC=N=NBu) is present. Preorganization of the FLP appears to be important for the reaction rate.[76] Namely, when the Lewis pair combination of iPr₂PPh and B(Fxyl)₃ was used (5 mol %) for the dehydrogenation of Me₂NH·BH₃, only 35 % conversion was observed in 18 hours at 70 °C, whereas the reaction was complete in 30 minutes at 25 °C using the intramolecular catalyst 80.

FLP 80 was also found to catalyze the dehydrogenation of cyclic amine–boranes to the corresponding trimeric products under mild conditions with concomitant release of 2 equivalents of dihydrogen (Scheme 39). Additionally, using catalytic amounts of FLP 80 dimine–boranes were converted to the corresponding 1,3,2-diazaborolidines (Scheme 39). Good to excellent yields were obtained (80-99 %) under mild conditions (25–70 °C) and the use of PhHC=N=NBu as additive drastically reduced the reaction times.

In-depth NMR studies performed on the reaction of 80 with Me₂NH·BH₃ suggested that dihydrogen adduct 81 is a key intermediate in this reaction (Scheme 40). To support this, 81 was synthesized in a stepwise manner by reacting 80 with triflic acid and subsequently with triethylsilane; the molecular...
structure of 81 was confirmed by X-ray diffraction analysis (Scheme 40). Phosphonium–borate 81 was unstable at room temperature and rapid release of dihydrogen was observed upon warming up to room temperature (50% conversion after 10 min at 25°C), along with regeneration of 80, supporting that 81 is a viable intermediate in the catalytic dehydrogenation of amine–boranes.

An alternative system for the FLP-catalyzed transfer hydrogenation of imines was reported by Du and co-workers in 2016.[77] They found that under optimized conditions, catalytic amounts of Piers’ borane 82 (HB(C₆F₅)₂, 10 mol %) and chiral sulfanamide 83 (10 mol %) in toluene with 10 mol % of pyridine as additive can convert a variety of imines, containing both electron-withdrawing and -donating groups, to the corresponding chiral amines in 78–99% yield and 84–95% ee. NMR spectroscopic studies were carried out to probe the mechanism, and showed that Piers’ borane 82 and the chiral sulfanamide 83 initially form adduct 84 (Scheme 41), and only a trace amount of the dehydrogenation product 87 was observed. Additional DFT calculations showed that complex 84 can hydrogenate imines via an eight-membered transition state (85), leading to the formation of the chiral amine product and compound 86, which rearranges to the more stable conformation 87. Interestingly, ammonia–borane can act as a dihydrogen source to convert 87 to 89 (via the 6-membered transition state 88), which subsequently rearranges to regenerate the active catalyst 84.

The same group also applied this FLP (82 and 83) for the asymmetric transfer hydrogenation of 2,3-disubstituted quinoxalines using ammonia–borane as a dihydrogen source.[76] When 2-alkyl-3-arylquinoxalines were subjected to hydrogenation utilizing the combination of HB(C₆F₅)₂ and (R)-tert-butylsulfanamide (84) as catalyst, high yields were obtained (72–95%) with cis selectivity (94.6–97.3 dr) and 77–86% ee (Scheme 42). In contrast, the alkylated analogues, 2,3-dialkylquinoxalines, mostly favored formation of the trans products and a range of hydrogenated 2,3-dialkylquinoxalines were obtained in moderate to high yield (58–93%) with 28:72–75:25 dr (cis:trans) and 89–99% ee.

Du and co-workers also used a FLP strategy for the transfer hydrogenation of pyridines.[78] Inspired by Baker and Dixon,[48] they found that the combination of a 2,6-substituted pyridine with B(C₆F₅)₃ can abstract dihydrogen from ammonia–borane, giving piperidines with excellent cis-selectivity, along with the
formation of borazine, cyclotriborazane, and polyborazylenes as dehydrogenated products. After optimization, a variety of 2,6-diarylpyridines were successfully hydrogenated to the corresponding products in 63–88% yield with high cis-selectivity (97:3–99:1 dr; Scheme 43). It was also found that 2-aryl-6-methylpyridines can be applied for transfer hydrogenation and several substrates were successfully hydrogenated with moderate to good yields (56–88%) and good selectivity (86:14–99:1 dr).

Rivard and co-workers investigated the dehydrogenation abilities of N-heterocyclic iminoboranes IPr=N–BR₂ (IPr=([HCNDipp)₂C]; 90, 91, and 92 in Scheme 44) towards various amine–boranes. ⁹⁰ Stoichiometric reactions of 90 and 91 with NH₃BH₃ or MeNH₂BH₃ resulted in rapid conversions towards the corresponding H₂-adducts 93 and 94, respectively, along with the formation of aminoborane oligomers. IPr=N–BCl₂ (90) is also reactive towards sterically more demanding substrates and full conversion was achieved towards IPr=N(H)–B(H)Cl₂ (91) within 45 minutes when reacted with Me₂NH·BH₃. In contrast, the bulkier N-heterocyclic iminoborane IPr=N–BPhCl needed 6.5 hours for full conversion to IPr=N(H)–B(H)PhCl (94). Interestingly, the hydrogenated iminoboranes IPr=N(H)–B(H)Cl₂ (93) and IPr=N(H)–B(H)PhCl (94) are stable at room temperature and do not transfer dihydrogen to cyclohexene, PhHC≡NtBu or N-(1-styryl)piperidine. However, heating a solution of 94 in C₆D₆ at 70 °C for 3.5 days resulted in full dehydrogenation of 94 and regeneration of 91, demonstrating the potential of 91 as a potential catalyst for the dehydrogenation of methylamine–borane (Scheme 44).

Treatment of MeNH₂BH₃ with 2 mol% of IPr=N–BPhCl (91) at 70 °C for 17 hours resulted in the formation of dihydrogen as well as various dehydrogenation products, including (MeNH₂BH₃)₂ oligomers. After 17 hours, ¹¹B NMR spectroscopy revealed that 11% of MeNH₂BH₃ was still present, and the turnover number (TON) and turnover frequency (TOF) for the catalytic reaction were modest (43 and 2.5 h⁻¹, respectively). To elucidate the mechanism of the dehydrogenation step, IPr=N–BCl₂ (90) and IPr=N–BPhCl (91) were both reacted with Me₂NH·BD₃, which showed exclusive formation of IPr=N(H)–B(D)Cl₂ and IPr=N(H)–B(D)PhCl, respectively, suggesting a similar, concerted hydrogen transfer step as reported by Manners and co-workers. ¹⁹, ²¹ A computational analysis by Zou and co-workers suggested that FLP 95, bearing a strong Lewis acidic borane moiety (Scheme 45), ⁸¹ is able to dehydrogenate NH₃BH₃ through a low-energy barrier (97; ΔG* = 13.4 kcal mol⁻¹) forming dihydrogen adduct 99. However, the barrier for dihydrogen release is much higher (ΔG* = 22.2 or 27.6 kcal mol⁻¹ with solvent effect in DCM for 101) and endothermic. This is consistent with the experimental observation that the reverse reaction is operative because 95 activates H₂ at room temperature. ⁸² To overcome the high barrier for hydrogen release, Zou and co-workers designed the new B/N-based frustrated Lewis pair 96 in silico.
that bears the less electron-withdrawing phenyl substituents on boron (Scheme 45). Although hydrogen abstraction is now higher in energy ($\Delta G^* = 18.7 \text{ kcal mol}^{-1}$ for 98) and becomes the rate-determining step, the release of dihydrogen via 102 is facile ($\Delta G^* = 9.3 \text{ kcal mol}^{-1}$) and exothermic ($\Delta G = -14.6 \text{ kcal mol}^{-1}$), meaning that 96 could be a potent catalyst for ammonia–borane dehydrogenation.

Recently, the group of Li set out to theoretically design a preorganized frustrated Lewis pair that can liberate over two equivalents of $H_2$ from ammonia–borane.[83] They described three characteristics that an ideal catalyst should possess: 1) formation of a dative bond between the Lewis acid and base should be hindered; 2) the distance between the Lewis acid and base should be optimal in order to be able to dehydrogenate the substrate and to liberate $H_2$; 3) the formation of a stable adduct with dehydrogenation product $H_2N=\text{BH}_2$ should be disfavored, or the barrier should be higher than amineborane oligomerization. After screening over 300 intramolecular FLPs, they found that phenylene-bridged N/B-FLP $\text{iPr}_2\text{BC}_6\text{H}_{11}\text{BH}_2$ (103) meets all three requirements and can easily abstract 1 equivalent of dihydrogen from ammonia-borane ($\Delta G^* = 14.6 \text{ kcal mol}^{-1}$, Scheme 46) forming 104, and subsequently liberate dihydrogen ($\Delta G^* = 17.5 \text{ kcal mol}^{-1}$).

![Scheme 46. Energy barriers for 103 for ammonia–borane dehydrogenation.](image)

The first step for liberation of a second equivalent of dihydrogen is the dimerization of the formed $H_2N=\text{BH}_2$ through hydroboration, forming 104 (Scheme 47). Instead of additional chain-growth through a second hydroboration step ($\Delta G^* = 15.6 \text{ kcal mol}^{-1}$), FLP 103 is capable of dehydrogenating 105 to form the inorganic butadiene 106, which is slightly favored in energy and thus the preferred pathway ($\Delta G^* = 14.0 \text{ kcal mol}^{-1}$). Subsequently, 106 can hydroborate another equivalent of $H_2N=\text{BH}_2$ to give 107, which is followed again by a facile dehydrogenation step by FLP 103 to form 108 ($\Delta G^* = 13.6 \text{ kcal mol}^{-1}$). From this point, 108 can undergo dehydrogenative cyclization to borazine (BZ) or chain-growth to longer BN chains, which eventually leads to liberation of the second equivalent of $H_2$ from AB. Raising the temperature will finally transform the BZ or the long BN chains to polyborazylene, releasing overall more than two equivalents of $H_2$. It is important to note that this is a completely new pathway for AB dehydrogenation in which intermediates such as B-(cyclodiborazanyl)amine–borane (BCDB) or cycloborazole (CTB) (as shown in Scheme 6) are not formed.

5. Summary and Outlook

During the past decade, strategies for the dehydrogenation of amine–boranes utilizing solely p-block compounds have emerged, in which stoichiometric approaches based on hydrogen transfer to unsaturated (in)organic bonds were developed, as well as dehydrogenation reactions mediated by Lewis acids, Lewis bases, and frustrated Lewis pairs. Applied in substoichiometric amounts, Brønsted acids and bases were found to initiate dehydrogenative polymerization of amine–boranes, and to date only one Bransted acid has been reported to participate catalytically in transfer dehydrogenation. Additionally, several Lewis acids, Lewis bases, and frustrated Lewis pairs were found to act as catalysts during the dehydrogenation step, creating fully p-block-based catalytic systems for amine–borane dehydrogenation. The emergence of several P/B, P/Al, P/Ga, and B/N based frustrated Lewis pairs have led to new, active catalysts providing unique pathways for the liberation and transfer of $H_2$. Increased understanding of the diverse reaction mechanisms for the metal-free catalytic dehydrogenation is key for the development of new and robust p-block catalysts. This, combined with the ongoing research on spent-fuel regeneration, might offer more opportunities for the sustainable use of amine–boranes as a dihydrogen source for fuel or reductive chemistry, without the need for rare, expensive, and potentially toxic, transition metals.

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Conflict of interest

The authors declare no conflict of interest.

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