Chapter 1

Dehydrogenation of Amine-Boranes using p-block Compounds

Abstract: Amine-boranes have gained a lot of attention because of their potential as hydrogen storage material. 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 via 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.

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1.1 Introduction

In the search for renewable energy sources and clean energy, B–N compounds gained a lot of attention in recent years as promising light-weight materials for dihydrogen storage and on-demand release.\[1] From these materials, ammonia-borane \( \text{NH}_3 \cdot \text{BH}_3 \) (AB) gained undoubtedly the most attention as hydrogen storage material, as it contains a high weight percentage of dihydrogen (19.6%).\[1-3] Because of the difference in electronegativity of boron and nitrogen, the B–H and N–H bonds of amine-boranes are polarized in an opposite way, resulting in hydric B–H (\( \delta^- \)) and protic N–H (\( \delta^+ \)) hydrogen substituents. This characteristic feature enables the thermal release of dihydrogen and concomitant generation of ammineborane molecules that (often uncontrollably) oligomerize, resulting in a mixture of B–N products. Ammonia-borane is stable at room temperature, however, it undergoes thermolysis at temperatures above 120 °C;\[4,5,6] this process can be enhanced by cellulose embedding\[7] or by using ionic liquids as solvent.\[8,9] Additionally, N-substitution also proved to be an efficient method for lowering the decomposition temperature,\[10] as primary arylamine-borane adducts (ArNH\(_2\)·BH\(_3\)) already release 1 equivalent of dihydrogen when kept in solution at room temperature.\[11] A great deal of interest has gone into the B–N containing products which are, depending on the amine-borane substrate, 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.\[12]

![Figure 1. BN containing products.](image-url)
In order to gain control over the selectivity in product distribution\textsuperscript{[13]} and to temper the reaction conditions, tremendous efforts have gone into the development of transition metal catalysts for amine-borane dehydrogenation.\textsuperscript{[14]} Complexes containing precious metals have proven to be excellent catalysts for this dehydrogenation step, while complexes utilizing the cheaper and abundant base metals, e.g., Fe and Ni, have also been explored.\textsuperscript{[15]} Even group 1 and 2 (main-group metal) based complexes were found to be active catalysts for amine-borane dehydrogenation.\textsuperscript{[16]} In addition, to maintain a sustainable use of amine-boranes as hydrogen storage material, several strategies have been developed to regenerate amine-boranes from the spent fuel material.\textsuperscript{[17]}

In this chapter, we provide an overview of all p-block based compounds that are reported to date that enable the dehydrogenation of amine-boranes. First, we treat stoichiometric dehydrogenation reactions, including dihydrogen transfer from amine-boranes to unsaturated (in)organic substrates, as well as Lewis acid, Lewis base, and frustrated Lewis pair mediated dehydrogenation reactions. Next, substoichiometric reactions are discussed, which involve Brønsted acid and Brønsted base initiated reactions and catalysis, Lewis acid and Lewis base catalysis, and lastly also frustrated Lewis pairs catalysis will be discussed.

1.2. Stoichiometric dehydrogenation

1.2.1 Dihydrogen transfer to inorganic N–B and P–B bonds

In 2011, Manners and co-workers investigated the redistribution of diborazanes and found that these species were easily dehydrogenated by the stable amino-borane \textit{i}Pr$_2$N=BH$_2$.\textsuperscript{[18]} Inspired by these findings, more simple amine-boranes were subjected to the same reaction conditions and they found that \textit{i}Pr$_2$N=BH$_2$ was able to dehydrogenate ammonia-borane (NH$_3$·BH$_3$) quantitatively to form \textit{i}Pr$_2$NH·BH$_3$ along with dehydrogenation products [H$_2$B(\textit{μ-H})(\textit{μ-NH$_2$})BH$_2$], [NH–BH]$_3$, and a white precipitate, which was attributed to insoluble polyamidoborane species (Scheme 1).\textsuperscript{[19]}
Broadening the scope of this reaction, Manners and co-workers also investigated the reaction of \( \text{iPr}_2\text{N}=\text{BH}_2 \) with MeNH\(_2\)·BH\(_3\) and found comparable reactivity after stirring the reaction mixture for 21h at 20 °C (90% conversion to \( \text{iPr}_2\text{NH}·\text{BH}_3 \) along with various dehydrogenation products). The reaction of \( \text{iPr}_2\text{N}=\text{BH}_2 \) with the sterically more demanding Me\(_2\text{NH}·\text{BH}_3\) resulted in a clean mixture of starting materials and products (\( \text{iPr}_2\text{NH}·\text{BH}_3 \) and \([\text{Me}_2\text{N}–\text{BH}_2]_2\)) even after a prolonged reaction time, suggesting the formation of an equilibrium mixture (Scheme 2).

An in-depth computational study revealed that the reaction between \( \text{iPr}_2\text{N}=\text{BH}_2 \) and Me\(_2\text{NH}·\text{BH}_3\) 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\(_2\text{NH}·\text{BH}_3\) are transferred simultaneously to, respectively, the nitrogen and boron atom of \( \text{iPr}_2\text{N}=\text{BH}_2 \) (Scheme 2).\(^{[20]}\) This dehydrogenation step is endergonic and is driven by the exergonic dimerization of the simultaneously generated Me\(_2\text{N}=\text{BH}_2\).
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.\textsuperscript{[21]} The hydrogenation of \(iPr_2N=BH_2\) with \(NH_3\cdotBH_2Me\), \(MeNH_2\cdotBH_2Me\) and \(Me_2NH\cdotBH_2Me\) was found to be very rapid and the dehydrogenation step was determined to be exergonic with a lower barrier compared to the N-substituted amine-boranes, which highlights the increased hydrogen donating ability of the B-methylated amine-boranes.

In addition to \(iPr_2N=BH_2\), Rivard and co-workers reported a donor-acceptor complex of imino-borane \(HB≡NH\) (2) that is also able to abstract dihydrogen from \(Me_2NH\cdotBH_3\) (Scheme 3).\textsuperscript{[22]} When 2 was reacted with \(Me_2NH\cdotBH_3\) for 12h at room temperature the hydrogenated product 3 formed along with the expected dehydrogenation by-products \([Me_2N–BH_2]_2\) and \(Me_2NH–BH_2–NMe_2–BH_3\), which were detected by NMR spectroscopy. To gain more insight into the mechanism, amino-borane 2 was reacted with \(Me_2ND\cdotBH_3\) resulting in exclusive H/D transfer from B to B and N to N, suggesting a similar mechanism as reported for \(iPr_2N=BH_2\).\textsuperscript{[18,20]}

\[\text{Scheme 3. Dihydrogen abstraction from } Me_2NH\cdotBH_3 \text{ with 2.}\]

As an alternative to amino-boranes as dihydrogen acceptor, the group of Stephan described a phosphino-borane while examining these compounds as frustrated Lewis pairs (see section 1.2.5 and 1.4.4).\textsuperscript{[23,24,25]} After establishing that these compounds are able to heterolytically cleave dihydrogen, phosphino-borane 4 was reacted with \(Me_2NH\cdotBH_3\) and showed to be able to quantitatively abstract dihydrogen, while generating \([Me_2N–BH_2]_2\) (Scheme 4).\textsuperscript{[26]} This resembles the greater affinity for \(H_2\) compared to the transient \(Me_2N=BH_2\), which was explained by the increase of Lewis acidity at the boron site by the perfluorinated aryl substituents.
Recently, Braunschweig and coworkers reported the first imino-borane that can rapidly dehydrogenate ammonia-borane at room temperature.\textsuperscript{[27]} They showed that 1 equivalent of tert-butyl substituted imino-borane 5 (Scheme 5) rapidly reacts with 1 equivalent of AB, forming the expected amino-borane 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 B-(cyclotriborazanyl)amine-borane (BCTC) intermediate by 5, as well as the capability of the formed NH\textsubscript{2}=BH\textsubscript{2} to facilitate hydrogen release. Isotopic labelling experiments showed that the hydrogenation exclusively proceeds through B–H⋯B and N–H⋯N transfer. DFT calculations revealed that this exchange occurs via a low-lying six-membered transition state (7), which makes this process using imino-boranes much more facile than the ones reported by Manners et al. for amino-boranes.\textsuperscript{[18]} Additionally, 5 was also found to dehydrogenate the bulky N-tBu-B-durylamine-borane, which could afford a new way of making bulky amino-boranes.
1.2.2 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.\[28] 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 condition, almost no side reactions were detected, which allowed the reaction conditions to be optimized in which 1 equivalent of ammonia-borane can hydrogenate nearly 2 equivalents of imine quantitatively. Both kinetic isotope effect and Hammet correlation studies revealed that the reaction occurs via a concerted double hydrogen transfer step. Additionally, DFT studies confirmed that this reaction occurs via transition state 8 with concomitant N–H→C and B–H→N transfer, comparable to transfer hydrogenation to amino-boranes (Scheme 2).\[18,20]

\[
\text{R, R'} = \text{alkyl, aryl}
\]

Scheme 6. Dihydrogen transfer from AB to imines.

Expanding the scope of organic substrates, Berke and co-workers also studied the transfer hydrogenation of aldehydes and ketones with amine-boranes.\[29] Although amine-boranes were already experimentally found to be able to reduce ketones and aldehydes in the 1980’s, the underlying mechanism was never thoroughly studied.\[30] Unexpectedly, when a wide range of ketones and aldehydes were subjected to AB dehydrogenation in THF (2:1
AB:substrate), the corresponding alcohol was not observed. Instead, \textit{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 to take place. After in-depth NMR studies, the authors proposed that this reaction occurs via dissociation of the ammonia-borane Lewis pair, with subsequent facile hydroboration of the ketone or aldehyde by the \textit{in situ} formed BH$_3$, leading to the formation of alkyl borates. 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. Thus far, it proved to be difficult to obtain definite proof for this proposed mechanism.

\begin{equation}
\text{NH}_3 \cdot \text{BH}_3 + 3 \text{O} = \text{NH}_3 \quad \text{THF} \quad \text{NH}_3 + \text{B}(\text{O} = \text{R})_{3} \\
\text{slow} \quad \text{fast}
\end{equation}

\begin{equation}
\text{NH}_3 + \text{BH}_3 \quad \text{fast}
\end{equation}

\begin{equation}
\begin{aligned}
\left[ \begin{array}{c}
\text{H-B-O} \\
\text{H} \\
\text{R} \\
\text{R'}
\end{array} \right] \quad \text{fast} \\
\begin{array}{c}
\text{R} \\
\text{R'}
\end{array} \\
\begin{array}{c}
\text{H-B-O} \\
\text{H} \\
\text{R} \\
\text{R'}
\end{array} \quad \text{fast}
\end{aligned}
\end{equation}

\begin{equation}
\begin{aligned}
\left[ \begin{array}{c}
\text{H-B-O} \\
\text{H} \\
\text{R} \\
\text{R'}
\end{array} \right] \quad \text{fast} \\
\begin{array}{c}
\text{R} \\
\text{R'}
\end{array} \\
\begin{array}{c}
\text{H-B-O} \\
\text{H} \\
\text{R} \\
\text{R'}
\end{array} \quad \text{fast}
\end{aligned}
\end{equation}

\textbf{Scheme 7}. Hydroboration of ketones and aldehydes.

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).\cite{31,32} This process was
found to be lower in energy compared to the initially proposed hydroboration mechanism by Berke.[29] To explain the observed alkyl borate formation, alcoholysis of the in situ formed \( \text{NH}_2=\text{BH}_2 \) 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.

\[
\text{NH}_3\cdot\text{BH}_3 + \overset{\text{R}}{\overset{\text{O}}{\overset{\text{R}}{\text{R}}}} \rightarrow \overset{\text{NH}_3}{\text{R}} + \overset{\text{B–O}}{\text{B}}\overset{\text{R}}{\text{R}}
\]

\[
\overset{\text{11}}{\overset{\text{H}_2\text{N}=\text{BH}_2}{\overset{\text{R}}{\overset{\text{O}}{\overset{\text{R}}{\text{R}}}}}} \stackrel{\text{alcoholysis}}{\longrightarrow} \overset{\text{H}_3\text{N}}{\overset{\text{R}}{\overset{\text{O}}{\overset{\text{R}}{\text{R}}}}}
\]

Scheme 8. Proposed mechanism by Zhou and Fan for alkyl borate formation.

To gain more insight into the transfer hydrogenation 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),[33] in contrast to the findings of Berke and co-workers.[29] Note that there is a difference in reaction conditions. While Berke used a 2:1 ratio of AB versus substrate, Chen used a 1:1 ratio of AB and aldehyde. Nevertheless, isotopic labelling studies of Chen et al. with \( \text{NH}_3\cdot\text{BD}_3 \) and \( \text{ND}_3\cdot\text{BH}_3 \) strongly suggested that the main path for the reduction of aldehydes is via double hydrogen transfer, where both the protic N–H and hydridic B–H hydrogens participate and are transferred to the O and C atom, respectively.
Scheme 9. Chen’s proposed mechanism for hydrogen transfer of AB to aldehydes.

Subsequently, Berke et al. investigated the applicability of a range of polarized olefins bearing two electron withdrawing groups (EWD) on one side and H, aryl or alkyl substituents on the other side of the C=C bond in the transfer hydrogenation reaction with NH₃·BH₃. All substrates showed excellent conversion to the hydrogenated species under mild conditions. Interestingly, labelling studies using NH₃·BD₃ and ND₃·BH₃ revealed that the hydric B–H hydrogen is transferred to the most nucleophilic carbon of the C=C double bond via hydroboration, which is in contrast to the expected concerted double hydrogen transfer and suggests that a different mechanism is operative. Kinetic isotope effect studies and intermediate trapping revealed that the olefin hydrogenation occurs in a two-step process, where first the hydrogen is transferred by hydroboration, and then a rate-determining proton transfer from the amine takes place (13, Scheme 10). In addition, it was hypothesized that the generated amino-borane NH₂=BH₂ intermediate (solvent stabilized) is capable of a second double hydrogen transfer to the olefin through transition state 15, which explains the formation of borazine and polyborazine.
Another example of amine-borane dehydrogenation was provided by the Stephan group. Namely, the reaction between the Lewis adduct Mes₃P(AlX)₃ and CO₂ afforded species 16 (Scheme 11), which is prone to undergo reduction of the carbon center by dihydrogen transfer from NH₃·BH₃, resulting in various dehydrogenation products, like borazine, that were observed by ¹ⁱB NMR spectroscopy. Subsequent quenching of the reaction mixture with water resulted in the formation of methanol, which could be extracted with isolated yields ranging from 37 to 51%.

Scheme 10. Reduction of C=C double bonds via hydrogen transfer of ammonia-borane.

Scheme 11. Metal-free conversion of CO₂ to methanol.
1.2.3 Lewis acid mediated dehydrogenation

Liberation of dihydrogen from ammonia-borane by Lewis acids is also feasible. In 2010, Shore and co-workers reported that one of the smallest Lewis acids (BH$_3$) enables the facile synthesis of amino-diborane 17 together with 1 equivalent of dihydrogen (Scheme 12). From amino-diborane 17 the inorganic butane analogue 18 was synthesized by the addition of ammonia, which highlights the applicability of 17 as inorganic building block.

\[
\text{NH}_3\cdot\text{BH}_3 + \text{THF} \cdot \text{BH}_3 \xrightarrow{\text{THF, rt}} \text{H}_2\text{B}_2\text{BH}_2 \cdot \text{NH}_3 + \text{H}_2 \cdot \text{THF} \\
\text{H}_2\text{B}_2\text{BH}_2 \cdot \text{H} + \text{NH}_3 \xrightarrow{\text{toluene, 0°C}} \text{H}_2\text{B}_2\text{NH}_3 \cdot \text{BH}_3
\]

Scheme 12. Formation and reactivity of amino-diborane 17.

In order to get a better understanding of the underlying mechanism, Chen and co-workers performed an in-depth study, including isotopic labelling, intermediate trapping and DFT calculations. They found that ammonia-diborane 19 (Scheme 13) and amino-borane 21 are key-intermediates in the formation of amino-diborane 17. 19, which is formed upon reacting NH$_3$·BH$_3$ with THF·BH$_3$, can transform into an ion pair that can reversibly form a BH$_5$-like intermediate (20). Subsequent loss of dihydrogen leads to the formation of 21, which reacts with BH$_3$ to ultimately form amino-diborane.
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. When Ga[N(SiMe$_3$)$_2$]$_3$ was treated with NH$_3$·BH$_3$, the gallium-free product [B{(NHBH)N(SiMe$_3$)Si(Me$_2$)N(SiMe$_3$)$_2$]}$_3$ 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.

**Scheme 13.** Proposed mechanism for the formation of amino-diborane from NH$_3$·BH$_3$ and THF·BH$_3$.

**Scheme 14.** Reactivity of a gallium(III)-based complex with NH$_3$·BH$_3$.
1.2.4 Lewis base mediated dehydrogenation

Roesky and co-workers reported N-heterocyclic carbene (NHC) 23 to be inert towards molecular hydrogen. Yet, 23 was found to be a very efficient reagent for the dehydrogenation of ammonia-borane (Scheme 15), resulting in the formation of the NHC-H₂ adduct 24, while leaving the C=C double bond of the carbene unaffected.⁴¹,⁴² In contrast, the reaction of N-heterocyclic germylene 25 with 1 equivalent of ammonia-borane led to the formation of germylene 26 (Scheme 15), in which the N-heterocyclic germylene did abstract dihydrogen, but without oxidation of the germanium(II) center.⁴¹

\[
\begin{align*}
\text{23} & \quad \quad \text{NH}_3\cdot\text{BH}_3 \\ & \quad \quad \text{toluene, rt} \\
\text{24} & \\
\text{25} & \quad \quad \text{NH}_3\cdot\text{BH}_3 \\
& \quad \quad \text{benzene-}d_6, \text{rt} \\
& \quad \quad \text{Ar} = 2,6-\text{iPr}_2\text{C}_6\text{H}_3 \\
\text{26} &
\end{align*}
\]

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 can dehydrogenate MeNH₂·BH₃ and iPrNH₂·BH₃ forming the expected dihydroaminal NHC-H₂ 28 together with the carbene-bound B–N–B adduct NHC·BH₂NH(R)–BH₃ (29) in a 1:1 ratio (Scheme 16).⁴³ The formation of 29 was proposed to proceed via a sequence of events. First, the NHC dehydrogenates the amine-borane generating the NHC-H₂ adduct and 1 equivalent of amino-borane RNH=BH₂, which is then trapped by a second equivalent of NHC giving rise to NHC·BH₂NH(R). Finally, NHC·BH₂NH(R) undergoes a BH₃ ligand exchange with the amine-borane starting material resulting in the formation of 29.
Utilizing the sterically more demanding tBuNH₂·BH₃ still resulted in dehydrogenation by NHC 27, but now NHC·BH₂NH(tBu)–BH₃ was isolated in only 10%. Multiple side-products were detected by ¹¹B NMR spectroscopy, indicating that carbene coupling to the transient tBuNH=BH₂ is significantly suppressed by the increased steric bulk on the nitrogen atom. Interestingly, when DippNH₂·BH₃ was reacted with 1 equivalent of NHC a variety of products could be detected such as NHC-H₂, NHC·BH₂NH(Dipp), NHC·BH₂NH(Dipp)–BH₃ and DippNH₂. This is caused by the lower nucleophilicity of the nitrogen moiety in DippNH₂·BH₃, which reduces the degree of BH₃ exchange and makes isolation of NHC·BH₂NH(Dipp) possible.

Furthermore, Manners and co-workers described the reaction of 2 equivalents of NHC 27 with methylamine-borane, which afforded NHC-H₂ 28, while the in situ generated methylamino-borane was trapped by the second equivalent of NHC affording NHC·BH₂NHMe 30 (Scheme 17).[^44]

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1.2.5 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),\textsuperscript{[23,24,25]} and these main-group species also exhibit reactivity towards amine-boranes. Miller and Bercaw showed that the addition of 1 equivalent of Me\textsubscript{2}NH·BH\textsubscript{3} to a solution of PrBu\textsubscript{3} and B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} resulted in the direct conversion (>95%) to the ion pair [tBu\textsubscript{3}PH][HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}] and dimeric (Me\textsubscript{2}NBH\textsubscript{2})\textsubscript{2} as major dehydrogenation product (Scheme 18).\textsuperscript{[45]} Keeping the reaction mixture one day at room temperature gave 97% conversion to (Me\textsubscript{2}NBH\textsubscript{2})\textsubscript{2}, with only trace amounts of (BH\textsubscript{2})\textsubscript{2}NMe\textsubscript{2}(μ-H) and H\textsubscript{3}B·NMe\textsubscript{2}BH\textsubscript{2}·NHMe\textsubscript{2}. The order of addition appeared to be important. When B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} was added a few minutes prior to the addition of PrBu\textsubscript{3} then only 50% of (Me\textsubscript{2}NBH\textsubscript{2})\textsubscript{2} was obtained, whereas first addition of the phosphine followed by B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} led to almost quantitative conversion of [tBu\textsubscript{3}PH][HB(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}] and (Me\textsubscript{2}NBH\textsubscript{2})\textsubscript{2}. The authors hypothesized a stepwise mechanism might be operative where B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} abstracts a hydride to form [R\textsubscript{2}NHBH\textsubscript{2}]\textsuperscript{+}, which is quickly deprotonated by the phosphine to generate R\textsubscript{2}N=BH\textsubscript{2} that dimerizes to the final product. The PrBu\textsubscript{3}/B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3} FLP was also able to dehydrogenate NH\textsubscript{3}·BH\textsubscript{3}, however, lower conversions were obtained.

\[
\begin{align*}
\text{tBu}_3\text{P} + \text{B}(\text{C}_6\text{F}_5)_3 & \xrightarrow{\text{R}_2\text{NH} \cdot \text{BH}_3, \text{C}_6\text{D}_5\text{Cl}} \text{[tBu}_3\text{PH}][\text{HB}(\text{C}_6\text{F}_5)_3] + (\text{R}_2\text{NBH}_2)_x \\
R &= \text{Me}, x = 2 \\
R &= \text{H}, x = n
\end{align*}
\]

Scheme 18. Dehydrogenation of amine-boranes utilizing PrBu\textsubscript{3}/B(C\textsubscript{6}F\textsubscript{5})\textsubscript{3}.

Alternatively, Manners and co-workers utilized combinations of different group 14 triflates (Me\textsubscript{3}SiOTf, Et\textsubscript{3}SiOTf and nBu\textsubscript{3}SnOTf) with bulky nitrogen bases (2,6-di-\textit{tert}-butylpyridine and 2,2,6,6-tetramethylpiperidine (TMP)) as frustrated Lewis pairs for the dehydrogenation of dimethylamine-borane.\textsuperscript{[46]} They found that the Me\textsubscript{3}SiOTf/TMP combination converts Me\textsubscript{3}NH·BH\textsubscript{3} rapidly (t\textsubscript{1/2} starting material = 10.3 minutes) to the dimeric (Me\textsubscript{2}NBH\textsubscript{2})\textsubscript{2}, together with formation of the corresponding silane and piperidinium triflate (Scheme 19).
Switching to \( nBu_3SnOTf/TMP \) increased the rate of the reaction, while the \( Et_3SiOTf/TMP \) combination was found to be less reactive, which also resulted in more side products. The same trend was observed for the combination of \( Me_3SiOTf \) with the weaker base di-\( tert \)-butylpyridine. Control experiments showed that the sole components of the FLP system were not able to dehydrogenate \( Me_2NH\cdotBH_3 \), highlighting the potential of frustrated Lewis pairs as dehydrogenation agents.

**1.3 Substoichiometric dehydrogenation**

**1.3.1 Brønsted 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\(^{[47]} \). It was found that these acids are not catalyzing the dehydrogenation of \( NH_3\cdotBH_3 \), but act as initiator. The initiation step was proposed to go via 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)\(^{[48]} \). Subsequently, the borenium intermediate \( 31 \) reacts with another equivalent of \( NH_3\cdotBH_3 \) followed by elimination of dihydrogen and formation of \( 33 \). DFT calculations indicate that \( 33 \) can further react with \( NH_3\cdotBH_3 \), which leads to chain transfer oligomerization. Following this strategy, loadings down to 0.5 mol% of acid (HOSO\(_2\)CF\(_3\), HCl, or B(C\(_6\)F\(_3\))\(_3\) as Lewis acid) were found to liberate over 1 equivalent of dihydrogen under mild conditions.
Scheme 20. Initiation step of AB dehydrogenation by Brønsted acids.

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 NH$_3$·BH$_3$ protonation using triflic acid in diglyme.$^{[49]}$ 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 NH$_3$·BH$_3$. Subsequently, the proton is transferred to the borane, forming the non-classical pentacoordinate borane (36). This solvent stabilized NH$_3$BH$_4^+$ species can release dihydrogen with concomitant formation of NH$_3$BH$_2^+$-diglyme adduct 37, in which the boron atom is now strongly bound to diglyme via an oxygen atom. Important to note is that Dixon and co-workers did observe such a [NH$_3$BH$_2$(L)]$^+$ species experimentally, but proposed this species to form via direct protonolysis or hydride abstraction by the Lewis acid.$^{[47]}$ Interestingly, the group of Paul found that 37 can react with another equivalent of NH$_3$·BH$_3$ forming 38. Subsequent proton transfer (RDS) followed by the release of H$_2$N=BH$_2$ regenerates the non-classical pentacoordinate borane 36, and subsequently 37 after H$_2$ elimination. This rate-determining step with an energy barrier of 26.0 kcal/mol correlates nicely with the experimental reaction temperature of 60 °C reported by the group of Dixon.$^{[47]}$ The regeneration of 37 was suggested to be responsible for excess H$_2$ release as it can react with other oligomeric BN species of H$_2$N=BH$_2$ producing more H$_2$, and not through a dehydrocoupling pathway suggested by Dixon and co-workers.$^{[47]}$
1.3.2 Bronsted acid catalyzed dehydrogenation

Recently, Yang and Du developed a new approach for asymmetric transfer hydrogenation of imines and β-enamino esters utilizing chiral phosphoric acids.\[^{50}\] After a screening of potential chiral phosphoric acids (CPAs), they found that CPA 39 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 22). Under optimized conditions, a wide variety of imines and β-enamino esters can be hydrogenated in high yields (55–96%) with good to high enantioselectivity (66–94% ee).
Stoichiometric reactions revealed that CPA 39 rapidly reacts with NH$_3$·BH$_3$ with concomitant release of H$_2$ and formation of a new chiral amine-borane 40 (Scheme 22). DFT calculations showed that 40 can transfer dihydrogen to the imine substrate through a six-membered transition state (41(S), Scheme 23) 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$_2$ leads to the formation of the desired chiral amine and several [B-N] species (42), which were observed by $^{11}$B NMR spectroscopy. Additional DFT calculations revealed that 42 can then be hydrolyzed (via four-membered transition state 43) to regenerate the chiral phosphoric acid 39 that can enter the catalytic cycle again.

**Scheme 22.** Imine reduction catalyzed by 39 with ammonia-borane as hydrogen source.
1.3.3 Brønsted base initiated dehydrogenation

Sneddon et al. reported on the use of a Brønsted base to initiate ammonia-borane dehydrogenation.[51] Using only 1 mol%, proton-sponge 1,8-bis(dimethylamino)naphthalene showed to accelerate the dehydrogenation of NH₃·BH₃ when the solid mixture was heated to 85 °C and approximately 1.1 equivalent of H₂ was released after 21 hours. Solid-sate 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 (bmimCl) 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 already evolved after 6 hours at 85 °C. The initial step in AB dehydrogenation utilizing a proton-sponge is believed to be deprotonation of NH₃·BH₃, forming the [NH₂–BH₃]⁻ anion 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) as polymerization initiator.[52] Although this Brønsted base did not perform as good as the proton-sponge,[51]
liberation of 2 equivalents of H₂ from NH₃·BH₃ 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 reactive species 44 (Scheme 24), which then reacts with another equivalent of NH₃·BH₃, elongating the chain and liberating NH₃. Subsequent insertion of NH₃·BH₃ leads to the formation of 45 and H₂.

\[
\text{NH}_3\cdot\text{BH}_3 + \text{VB} \rightarrow \text{VBH}^+ [\text{BH}_3\text{NH}_2]^+ \rightarrow \text{VBH}^+ [\text{BH}_3\text{NH}_2\text{BH}_3]^+ + \text{NH}_3
\]

\[
\text{H}_2 + \text{VBH}^+ [\text{BH}_3\text{NH}_2\text{BH}_2\text{NH}_2\text{BH}_3]^+ \rightarrow \text{VBH}^+ [\text{BH}_3\text{NH}_2\text{BH}_3]^+ + \text{NH}_3\cdot\text{BH}_3
\]

**Scheme 24.** Anionic polymerization of AB dehydrogenation initiated by a Brønsted base.

To verify this mechanism, Verkade’s base was reacted with 3 equivalents of NH₃·BH₃ for 3 days at room temperature after which all the starting material was consumed. In good agreement with the proposed mechanism, product 45 was isolated in 74% yield (Scheme 25). When a 1:4 ratio was applied, two new salts, together with small amounts of 45, were isolated and characterized as the linear chain 46 and branched product 47. To gain further insight into the mechanism, 45 was reacted with 1 equivalent of NH₃·BH₃ for 2 days at 50 °C, which also afforded a mixture of 46 and 47, supporting a stepwise, base-promoted oligomerization mechanism.
1.3.4 Lewis acid catalyzed dehydrogenation

1.3.4.1 Group 13 based Lewis acids

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(NMe₂)₃ for the dehydrogenation of Me₂NH·BH₃, which formed dimeric (Me₂NBH₂)₂ together with small amounts of (Me₂N₂)BH and a new aluminum species [{(Me₂N)₂BH₂}₂AlH] (48) (Scheme 26).{53} 48 was isolated and also showed catalytic activity towards Me₂NH·BH₃ dehydrogenation. DFT studies revealed that 48 is relatively unstable and can undergo a facile β-hydride transfer forming 49,{40} which is another important potential catalyst for this reaction.

Scheme 25. Formation and isolation of intermediates in the base-promoted AB polymerization.

Scheme 26. β-hydride transfer to form 49.
The related Al(NiPr₂)₃ is also catalytically active in the dehydrogenation of iPr₂NH·BH₃ in benzene at 60 °C. Since 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 [H₂Al(μ-NiPr₂)]₂ (50), which is structurally related to 48, 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 (Me₂NBH₂)₂ when refluxed in toluene for 16 hours. Similarly, [(tBuO)ₓAlH₃₋ₓ] (x = 1 or 2) and (L)Li[(tBuO)₂AlH₂] (L = THF or 1,4-dioxane) were found to catalyze the dehydrogenation of Me₂NH·BH₃, with tBuO₂AlH₂ being superior compared to the other tert-butoxy-substituted aluminum catalysts. 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 tBuNH₂·BH₃ dehydrogenation. Under ambient conditions, 5 mol% of Ga(NMe₂)₃ slowly converts tBuNH₂·BH₃ to the borazane (tBuNHBH₂)₃ 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). Driven by this result, a series of other borane analogues were tested, however, none of them were superior to bis(borane) 52. Interestingly, the evolution of H₂ can be switched on and off, as catalytic dehydrogenation occurs at 60 °C, which can be efficiently stopped by cooling to room temperature and again started by heating to 60 °C. More importantly, the catalyst did not decompose and could be reused multiple times by adding a new batch of NH₃·BH₃ after the evolution of hydrogen was finished. This procedure was repeated 15 times without loss of catalyst activity. Stoichiometric reactions revealed that the reaction starts by exchange of the chloride for a hydride from NH₃·BH₃, forming ammonia-monochloroborane (NH₃·BH₂Cl) 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 NH₃·BH₃, forming the three-center-two-electron adduct 54, which via rate-determining transition state 55, releases both H₂ and H₂N=BH₂ and regenerates the catalyst.
Paul and co-workers investigated the use of triarylboranes as catalysts for ammonia-borane dehydrogenation\cite{59} and they identified computationally para-CF$_3$- and para-CN-substituted triphenylborane to be promising hits with reaction barriers close to 20 kcal/mol. Additionally, they also predicted that these triarylboranes could be capable of liberating more than 2 equivalents of dihydrogen per AB moiety.

1.3.4.2 Group 14 based Lewis acids

Waterman and co-workers investigated tin(IV) and tin(II) compounds in the catalytic dehydrogenation of amine-boranes\cite{60} and found that 10 mol\% of Cp*$_2$SnCl$_2$ and Ph$_2$SnCl$_2$ quantitatively converted NH$_3$·BH$_3$ to the corresponding dehydrogenated 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 Me$_2$NH·BH$_3$
drastically influenced the rate of the reactions, giving only 69%, 47% and 23% of product at 65 °C using 10 mol% of Cp*₂SnCl₂, Ph₂SnCl₂ and SnCl₂, 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 (Me₂NBH₂)₂ dimer, giving reaction mixtures containing (Me₂NBH₂)₂, Me₂NHBH₂NMe₂, H₂BNMe₂BH₃, and other, unidentified species. Surprisingly, these tin catalysts showed much higher conversions when the bulky tBuNH₂·BH₃ 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 Cp*₂SnCl₂, Ph₂SnCl₂ or 5 mol% SnCl₂, respectively. Similar to Me₂NH·BH₃, 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 tBuNH=BH₂ (16–23%) compared to the tin(II) catalyst SnCl₂ (<5%), which suggests a β-hydrogen elimination mechanism, resulting in a tin hydride and concomitant formation of the amino-borane. 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·BH₃</th>
<th>Loading (mol %)</th>
<th>Conversion (%)</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp*₂SnCl₂</td>
<td>R = R’ = H</td>
<td>10</td>
<td>100</td>
<td>1 d</td>
</tr>
<tr>
<td>Ph₂SnCl₂</td>
<td>R = R’ = H</td>
<td>10</td>
<td>100</td>
<td>1 d</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>R = R’ = H</td>
<td>10</td>
<td>100</td>
<td>1 h</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>R = R’ = H</td>
<td>5</td>
<td>100</td>
<td>18 h</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>R = R’ = H</td>
<td>0.5</td>
<td>100</td>
<td>2 d</td>
</tr>
<tr>
<td>Cp*₂SnCl₂</td>
<td>R = R’ = Me</td>
<td>10</td>
<td>69</td>
<td>6 d</td>
</tr>
<tr>
<td>Ph₂SnCl₂</td>
<td>R = R’ = Me</td>
<td>10</td>
<td>47</td>
<td>4 d</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>R = R’ = Me</td>
<td>10</td>
<td>23</td>
<td>5 d</td>
</tr>
<tr>
<td>Cp*₂SnCl₂</td>
<td>R = tBu R’ = H</td>
<td>10</td>
<td>95</td>
<td>5 d</td>
</tr>
<tr>
<td>Ph₂SnCl₂</td>
<td>R = tBu R’ = H</td>
<td>10</td>
<td>93</td>
<td>4 d</td>
</tr>
<tr>
<td>SnCl₂</td>
<td>R = tBu R’ = H</td>
<td>5</td>
<td>84</td>
<td>5 d</td>
</tr>
</tbody>
</table>
Table 2. Product distribution (%) of the dehydrogenation of $t$BuNH$_2$BH$_3$ by tin catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Polymers</th>
<th>($t$BuBH)$_3$</th>
<th>$t$BuNH=BH$_2$</th>
<th>$t$BuNHB:H$_3$</th>
<th>Other</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cp*$_2$SnCl$_2$</td>
<td>20</td>
<td>0</td>
<td>16</td>
<td>26</td>
<td>30</td>
</tr>
<tr>
<td>Ph$_2$SnCl$_2$</td>
<td>41</td>
<td>8</td>
<td>23</td>
<td>23</td>
<td>30</td>
</tr>
<tr>
<td>SnCl$_2$</td>
<td>13</td>
<td>6</td>
<td>&lt;5</td>
<td>33</td>
<td>41</td>
</tr>
</tbody>
</table>

1.3.5 Lewis base catalyzed dehydrogenation

Radosevich and co-workers utilized a planar, trivalent phosphine for transfer hydrogenation with ammonia-borane as hydrogen source.$^{[61]}$ They found that in stoichiometric quantities, 56 can abstract 1 equivalent of dihydrogen from ammonia-borane to form dihydrophosphorane 57 (Scheme 30), which subsequently can transfer 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$^{\text{III}}$ and P$^{\text{V}}$ oxidation states was proposed (Scheme 30).

![Scheme 30. Proposed catalytic cycle for azobenzene hydrogenation.](image-url)
The group of Sakaki performed calculations to disclose the full mechanism of this catalytic reaction,\textsuperscript{[62,63]} which revealed that hydrogen abstraction from ammonia-borane does not solely occur at the P\textsuperscript{III} site.\textsuperscript{[61]} 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.\textsuperscript{[64]} The isolation and catalytic activity of 57 was explained by the 57 to 58 equilibrium; 57 itself is not involved in the catalytic cycle.

\begin{center}
\textbf{Scheme 31.} Calculated catalytic cycle for azobenzene transfer hydrogenation.
\end{center}

Additional computational studies by Sakaki and co-workers led to the theoretical design of a new hydrogen transfer catalyst.\textsuperscript{[65]} 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\textsubscript{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. While 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 hydrogen is transferred to the coordinating formate group, which releases formic acid and regenerates the catalyst. The proposed increased rate of the reaction via the stepwise mechanism is due to differences in the HOMO levels of the ONO-(56) and NNN-type (59) pincer ligand, where the pincer-type phosphorus ligand with the highest HOMO level is most active for CO$_2$ reduction by transfer hydrogenation.

![Scheme 32](image)

**Scheme 32.** Catalytic transfer hydrogenation by a pincer-type phosphorus compound.

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,
Subsequently, the P–N bond can be cleaved by addition of NH$_3$·BH$_3$, giving diphenylhydrazine and the N-heterocyclic phosphane 62 back. Interestingly, when NH$_3$·BD$_3$ was applied, the deuterium was selectively transferred to the phosphorus atom, demonstrating a regiospecific hydrogen transfer via a six-membered transition state (64), which was supported by DFT calculations. 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 hydrogen source.

Scheme 33. Proposed catalytic cycle for azobenzene hydrogenation catalyzed by 62.

1.3.6 FLP catalyzed dehydrogenation

Utilizing the ability of frustrated Lewis pairs to activate small molecules, Slootweg and Uhl et al. reported on the reactivity of a phosphorus/aluminum based FLP towards amine-boranes. Treatment of FLP 65 with 1 equivalent of NH$_3$·BH$_3$ liberates 1 equivalent of dihydrogen concomitant with the formation of five-membered heterocycle 66 (Scheme 34). DFT calculations revealed that H$_2$ abstraction is initiated by the activation of the N–H bond of ammonia-borane. Subsequent protonation of the B–H bond by the newly formed P–H moiety liberates dihydrogen, while generating an amino-borane adduct that can
readily ring-closes 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 cyclodiborazane 68 after 44 hours in 77% with turn-over numbers and frequencies up to 198.3 and 4.5 h⁻¹, respectively.

Scheme 34. Amine-borane dehydrogenation by a P/E (E = Al, Ga) FLP.

Gallium analogue 69 showed similar reactivity towards Me₂NH·BH₃, yet in this case no amino-borane adduct intermediate (70) could be detected during the reaction and solely FLP 69 and cyclic diborazane 68 were observed.[68] 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 amino-borane 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 whether 69 could act as a hydrogen
transfer catalyst. Indeed, the reaction between NH$_3$·BH$_3$, imine PhCH=NTBu and P/Ga-based FLP 69 resulted in the formation of the corresponding amine together with dehydrogenation products (Scheme 35).

\[
\text{NH}_3\cdot\text{BH}_3 + 2 \text{PhCH=NTBu} \xrightarrow{4 \text{ mol} \%} \text{rt} \quad 2 \text{HN-}t\text{Bu} + (\text{NBH})_n
\]

Scheme 35. FLP 69 as catalyst for imine hydrogenation.

The first phosphino-borane that dehydrogenates NH$_3$·BH$_3$ catalytically was described by Stephan and Erker.$^{69}$ Although FLP 72 is unreactive towards H$_2$, it rapidly reacts with ammonia-borane by abstracting H$_2$ to form dihydrogen adduct 73 (Scheme 36). Moreover, 72 is active as hydrogen transfer catalyst for the hydrogenation of bulky imines. When 10 mol\% catalyst loading was used, rapid formation of the corresponding amine and borazine (Scheme 36) was observed. A few years later, the same groups reported a similar strategy for transfer hydrogenation of enamines using 72 as catalyst and ammonia-borane as dihydrogen source.$^{70}$

Scheme 36. Phosphino-borane catalyzed transfer hydrogenation of imines.
Aldridge and co-workers reported a dimethylxanthene based phosphino-borane FLP 74 to be active as catalyst for dehydrogenation of several amine-boranes.\(^{[71]}\) 74 was found to catalyze the liberation of dihydrogen from NH\(_3\)·BH\(_3\), MeNH\(_2\)·BH\(_3\) and Me\(_2\)NH·BH\(_3\) at 55 °C using only 1 mol% catalyst loading, which is the first reported example of catalytic methylamine- and ammonia-borane dehydrogenation by a main group-based frustrated Lewis pair without dihydrogen transfer. Namely, stoichiometric reactions with 74 and Me\(_n\)NH\(_3\)·BH\(_3\) 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.

Scheme 37. Stoichiometric reactions of 74 with amine-boranes.

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 \(iPr_2N=BH_2\) in a similar fashion as reported by Manners and co-workers\(^{[18,20]}\) which resulted in the formation of amino-borane 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. Since 75, 76 and 77 are
thermally stable, their catalytic activity is depended 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 also forms by reacting 74 with $\text{H}_3\text{B} \cdot \text{NHMeBH}_2 \cdot \text{NH}_2\text{Me}$, and provides evidence for dehydrogenation via a chain-growing mechanism. Addition of a third equivalent of $\text{MeNH}_2 \cdot \text{BH}_3$ resulted in the formation of the cyclic trimer ($\text{NHMeBH}_2)_3$ and regeneration of the catalyst. *In situ* NMR measurements indicate that the addition of a methylamine-borane unit occurs via an end-growth dehydrogenative mechanism, instead of insertion of $\text{MeNH}_2 \cdot \text{BH}_3$ into the P–B bond of the adduct (79). Additionally, 74 can further dehydrogenate ($\text{NHMeBH}_2)_3$ under catalytic conditions (1 mol% of 74) producing trimethylborazine at 55 °C.

Scheme 38. Stoichiometric and catalytic reactions of 74 with methylamine-boranes.
Recently, the group of Bourissou described a related ortho-phenylene bridged phosphino-borane bearing the Fxyl substituent (Fxyl = 3,5-(F₃C)₂C₆H₃) on the boron site as alternative for the frequently used C₆F₆ group. This FLP adopts a closed form at room temperature, 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 borazane and borazine ((MeNH₂BH₂)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. This dehydrogenation reaction can be further accelerated when 1 equivalent of an dihydrogen acceptor (PhHC=NtBu) is present. Preorganization of the FLP appeared to be of high importance for the reaction rate. Namely, when the Lewis pair iPr₂PPh/B(Fxyl)₃ was used (5 mol%) for the dehydrogenation of Me₂NH·BH₃ only 35% conversion was observed in 18 hours at 70 °C, while the reaction was complete in 30 minutes at 25 °C using 80 as catalyst.

\[
\text{Scheme 39. Catalytic dehydrogenation of cyclic amine-boranes and diamine-boranes with 80.}
\]

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
diamine-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=NRtBu 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.[74]

![Scheme 40](image)

Scheme 40. Stepwise and catalytic generation of phosphonium-borate 81.

An alternative system for FLP catalyzed transfer hydrogenation of imines was reported by Du and coworkers in 2016.[75] They found that under optimized conditions, catalytic amounts of Piers’ borane 82 (10 mol%) and chiral sulfinamide 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 studies to reveal the underlying mechanism showed that Piers’ borane 82
and the chiral sulfinamide 83 initially form adduct 84 (Scheme 41), and only a trace amounts 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 regenerate the active species 84 by transfer hydrogenation of 87 to generate 89, which rearranges to 84 to close the catalytic cycle.

Scheme 41. FLP catalyzed asymmetric transfer hydrogenation of imines.

The same group also applied this FLP for the asymmetric transfer hydrogenation of 2,3-disubstituted quinoxalines using ammonia-borane as dihydrogen source. When 2-alkyl-3-
arylquinoxalines were subjected to hydrogenation utilizing HB(C₆F₅) and (R)-tert-butylsulfinamide 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.

![Scheme 42. FLP catalyzed reduction reactions of 2,3-disubstituted quinoxalines.](image)

Du and coworkers also used a FLP strategy for the transfer hydrogenation of pyridines.[77] Inspired by Baker and Dixon,[47] 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 borazine, cyclotriborazane, and polyborazines 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-selectivities (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 selectivities (86:14–99:1 dr).
Rivard et al. investigated the dehydrogenation abilities of N-heterocyclic iminoboranes (IPr=NR2) towards various amine-boranes (Scheme 44).\textsuperscript{[78]} Stoichiometric reactions of 90 and 91 with NH3·BH3 or MeNH2·BH3 resulted in rapid conversions towards the corresponding H2-adducts 93 and 94 along with the formation of amino-borane oligomers. IPr=NB–Cl2 (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. Yet, heating a solution of 94 in C6D6 at 70 °C for 3.5 days resulted in full dehydrogenation of 94 and regeneration of 91, which shows promise for 91 as potential catalyst for the dehydrogenation of methylamine-borane (Scheme 44).
Scheme 44. Reactivity of N-heterocyclic iminoboranes towards different amine-boranes.

Treatment of MeNH₂·BH₃ 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 (MeNH₂BH₂)ₙ oligomers. After 17 hours, ¹¹B NMR spectroscopy revealed that 11% of MeNH₂·BH₃ was still present, and the TON and 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.[¹⁸,²⁰]

A computational analysis by Zou and co-workers showed that FLP 95, bearing a strong Lewis acidic borane moiety (Scheme 45),[⁷⁹] is able to dehydrogenate NH₃·BH₃ via a low-energy barrier (97; ΔG° = 13.4 kcal/mol) forming dihydrogen adduct 99. However, the barrier
for dihydrogen release is much higher in energy ($\Delta G^\ddagger = 22.2$ kcal/mol, or $27.6$ kcal/mol with solvent-effect in DCM for 101) and endothermic. This confers with the experimental observation that the reverse reaction is operative as 95 activates H$_2$ at room temperature.$^{[80]}$

To overcome the high barrier for hydrogen release, Zou and co-workers theoretically designed the new B/N-based frustrated Lewis pair 96 that bears the less electron-withdrawing phenyl substituents on boron (Scheme 45). Although hydrogen abstraction is now higher in energy ($\Delta G^\ddagger = 18.7$ kcal/mol for 98) and becomes the rate-determining step, the release of dihydrogen via 102 is facile ($\Delta G^\ddagger = 9.3$ kcal/mol) and exothermic ($\Delta G = -14.6$ kcal/mol), meaning that 96 is a potent catalyst for ammonia-borane dehydrogenation.

Scheme 45. Calculated mechanism for ammonia-borane dehydrogenation.

Recently, the group of Li set out to theoretically design a preorganized frustrated Lewis pair that can liberate over two equivalent of H$_2$ from ammonia-borane.$^{[81]}$ 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$_2$N=BH$_2$ should be
disfavored, or the barrier should be higher than amino-borane oligomerization. After screening over 300 intramolecular FLPs, they found that phenylene-bridged N/B FLP \( iPr_2NC_6H_4BPh_2 (103) \) meets all these requirements and can easily abstract 1 equivalent of dihydrogen from ammonia-borane \( (\Delta G^\ddagger = 14.6 \text{ kcal/mol}, \text{ Scheme 46}) \) forming 104, and subsequently liberate dihydrogen \( (\Delta G^\ddagger = 17.5 \text{ kcal/mol}). \)

![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\(_2\)N=BH\(_2\) via hydroboration, forming 104 (Scheme 47). Instead of additional chain grown via a second hydroboration step \( (\Delta G^\ddagger = 15.6 \text{ kcal/mol}) \), FLP 103 is capable of dehydrogenating 105 forming the inorganic butadiene 106, which is slightly favored in energy and thus the preferred pathway \( (\Delta G^\ddagger = 14.0 \text{ kcal/mol}). \) Subsequently, 106 can hydroborate another equivalent of H\(_2\)N=BH\(_2\) giving 107, which is followed again by a facile dehydrogenation step by FLP 103 to form 108 \( (\Delta G^\ddagger = 13.6 \text{ kcal/mol}). \) From this point, 108 can undergo dehydrogenative cyclization to borazine (BZ) or chain grown 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 polyborazine, releasing overall more than two equivalents of H\(_2\). Important to note is that this is a completely new pathway for AB dehydrogenation in which intermediates such as B-(cyclodiborazanyl)amine-borane (BCDC) or cyclotriborazane (CTB) are not formed.
1.5 Summary and Outlook

During the past decade, dehydrogenation chemistry of amine-boranes utilizing solely p-block compounds have emerged, where 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 Bronsted acid has been reported to participate catalytically in transfer dehydrogenation. Additionally, several Lewis acids, Lewis bases and frustrated Lewis pairs were found to react as catalyst during the dehydrogenation step, creating a fully p-block based catalytic system for amine-borane dehydrogenation. The emergence of several P/B, P/Al, P/Ga and B/N based frustrated Lewis pairs led to new, active catalysts providing unique pathways for the liberation and transfer of H₂. 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 dihydrogen source for fuel or reductive chemistry, without the need for transition metals.
1.6 References


This same type of reactivity was also theoretically predicted by Musgrave and co-workers for a different NHC: P. M. Zimmerman, A. Paul, Z. Zhang, C. B. Musgrave, *Angew. Chem. Int. Ed.* 2009, **48**, 2201–2205.


