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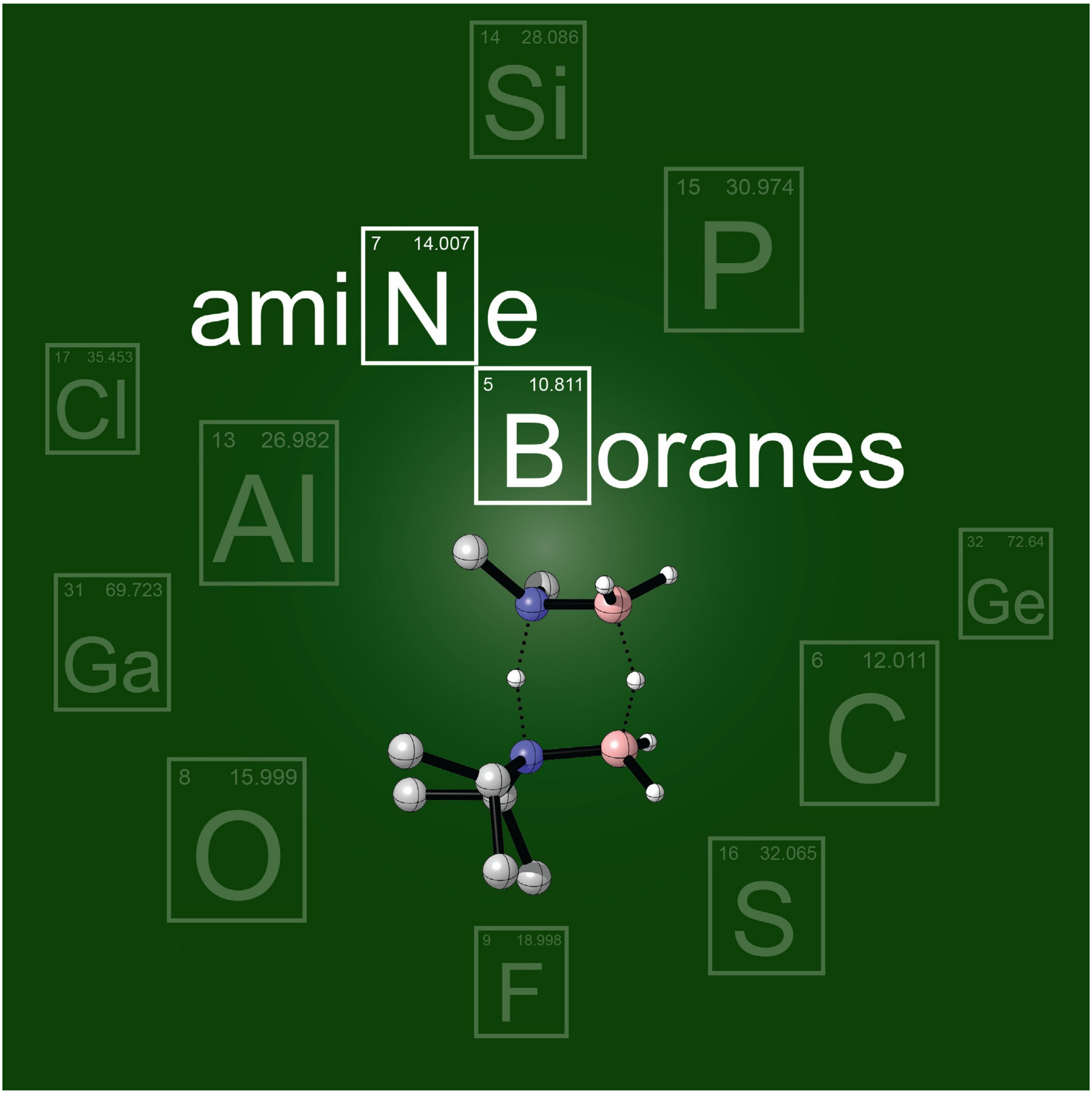
Dehydrogenation of Amine–Boranes Using p-Block Compounds

Devin H. A. Boom, Andrew R. Jupp, and J. Chris Slootweg*[a]



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.

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.[1] From these materials, ammonia–borane $NH_3{\cdot}BH_3$ (AB) gained undoubtedly the most attention as a hydrogen storage material, because it contains a high weight percentage of dihydrogen (19.6%).[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 ($\delta-$) and protic N–H ($\delta+$) 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;[4–6] 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] because primary amine–borane adducts ($RNH_2{\cdot}BH_3$) can release 1 equivalent of dihydrogen 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] 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.

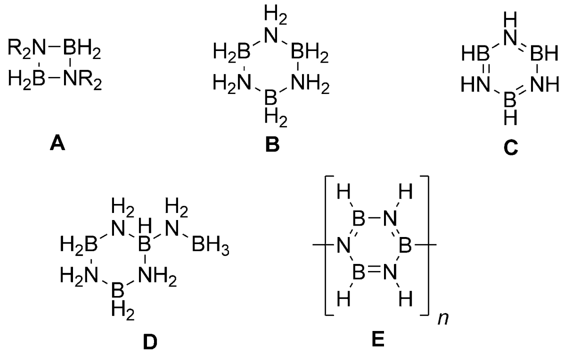


Figure 1. B–N-containing products.

In order to gain control over the selectivity in product distribution[13] and to temper the reaction conditions, tremendous efforts have gone into the development of transition-metal catalysts for amine–borane dehydrogenation.[14] Complexes containing precious metals have proven to be excellent catalysts for this dehydrogenation step, whereas complexes utilizing the cheaper and abundant base metals, for example Fe and Ni, have also been explored.[15] Even Group 1 and 2 (main-group metal) based complexes were found to be active catalysts for amine–borane dehydrogenation.[16] In addition, several strategies have been developed to regenerate amine–boranes from the spent fuel material, which provides a proof of concept for the use of amine–boranes as reusable hydrogen storage materials.[17]

In recent years there has been a huge growth in the chemistry of p-block species, and in particular their ability to effect reactivity that was previously thought to be exclusive to transition-metal complexes. This metallomimetic reactivity has been spearheaded by the development of frustrated Lewis pairs and low-coordinate main-group species, which between them are capable of activating a range of small molecules including dihydrogen, carbon dioxide, and even dinitrogen.[18] In this review, we provide an overview of the p-block-based compounds that have been reported to enable the dehydrogenation of amine–boranes. First, we explore stoichiometric dehydrogenation reactions, including dihydrogen transfer from amine–boranes to unsaturated (in)organic substrates, as well as stoichiometric Lewis acid, Lewis base, and frustrated Lewis pair mediated dehydrogenation reactions. Next, we examine systems in which Brønsted acids and bases initiate the dehydrogenation reactions, and finally discuss catalytic reactions involving Lewis acids, Lewis bases, and frustrated Lewis pairs.

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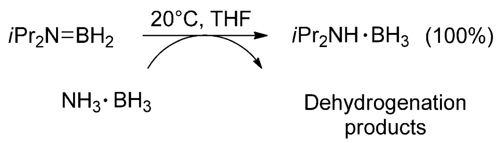
2. Stoichiometric dehydrogenation

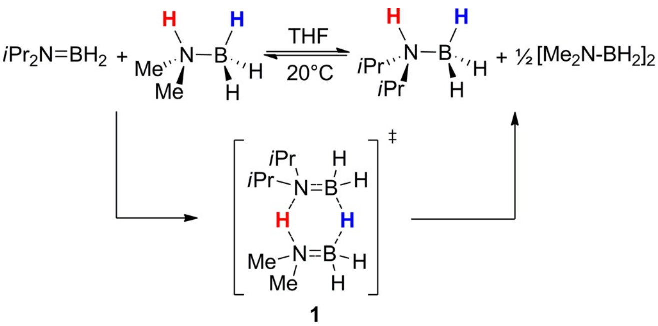
2.1. Dihydrogen transfer to inorganic N–B and P–B bonds

In 2011, Manners and co-workers investigated the redistribution of diborazanes and found that these species were easily dehydrogenated by the stable aminoborane *i*$Pr_2N{=}BH_2$.[19] Inspired by these findings, more simple amine–boranes were subjected to the same reaction conditions and they found that *i*$Pr_2N{=}BH_2$ was able to dehydrogenate ammonia–borane ($NH_3{\cdot}BH_3$) quantitatively to form *i*$Pr_2NH{\cdot}BH_3$ along with dehydrogenation products $[H_2B(\mu\text{-}H)(\mu\text{-}NH_2)BH_2]$, $[NH{=}BH]_3$, and a white precipitate, which was attributed to insoluble polyaminoborane species (Scheme 1).[20]



Scheme 1. Reaction of *i*$Pr_2N{=}BH_2$ with $NH_3{\cdot}BH_3$.

Broadening the scope of this reaction, Manners and co-workers also investigated the reaction of *i*$Pr_2N{=}BH_2$ with $MeNH_2{\cdot}BH_3$, and found comparable reactivity after stirring the reaction mixture for 21 hours at 20 °C (90 % conversion to *i*$Pr_2NH{\cdot}BH_3$ along with various dehydrogenation products). The reaction of *i*$Pr_2N{=}BH_2$ with the more sterically demanding $Me_2NH{\cdot}BH_3$ resulted in a clean mixture of starting materials and products (*i*$Pr_2NH{\cdot}BH_3$ and $[Me_2N{-}BH_2]_2$) even after a prolonged reaction time, suggesting the formation of an equilibrium mixture (Scheme 2).



Scheme 2. Equilibrium formation during the reaction of *i*$Pr_2N{=}BH_2$ with $Me_2NH{\cdot}BH_3$.

An in-depth computational study revealed that the reaction between *i*$Pr_2N{=}BH_2$ and $Me_2NH{\cdot}BH_3$ 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 $Me_2NH{\cdot}BH_3$ are transferred simultaneously to, respectively, the nitrogen and boron atom of *i*$Pr_2N{=}BH_2$ (Scheme 2).[21] This dehydrogenation step is endergonic and is driven by the exergonic dimerization of the simultaneously generated $Me_2N{=}BH_2$.

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.[22] The hydrogenation of *i*$Pr_2N{=}BH_2$ with $NH_3{\cdot}BH_2Me$, $MeNH_2{\cdot}BH_2Me$, and $Me_2NH{\cdot}BH_2Me$ 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 *i*$Pr_2N{=}BH_2$, Rivard and co-workers reported a zwitterionic aminoborane (**2**), which can be considered a donor–acceptor complex of the parent iminoborane $HB{\equiv}NH$, that is also able to abstract dihydrogen from $Me_2NH{\cdot}BH_3$ (Scheme 3).[23] When **2** was reacted with $Me_2NH{\cdot}BH_3$ for

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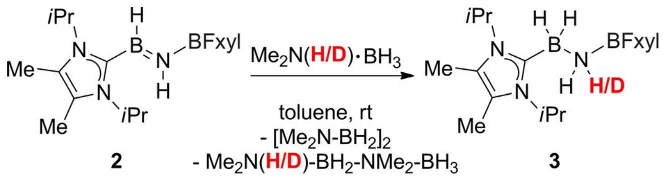
Andrew R. Jupp obtained his Ph.D. from the University of Oxford (2012–2016) under the supervision of Prof. Jose Goicoechea. He worked on phosphorus-containing analogues of the cyanate anion and urea, for which he was awarded the Reaxys Ph.D. Prize in Hong Kong in 2015. He subsequently carried out a Banting Postdoctoral Fellowship with Prof. Doug Stephan at the University of Toronto (2016–2018), working on the synthesis and reactivity of main-group Lewis acids and bases. He is currently a NWO-VENI laureate at the Van 't Hoff Institute for Molecular Sciences, University of Amsterdam, working with Assoc. Prof. Chris Slootweg on the activation of typically unreactive small molecules.

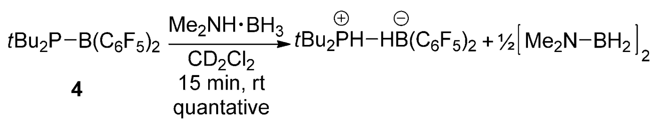
Chris Slootweg was born in Haarlem (The Netherlands) in 1978 and received his undergraduate education from Vrije Universiteit Amsterdam in 2001. After earning his Ph.D. in 2005 under the supervision of Prof. Koop Lammertsma, he pursued postdoctoral studies at the ETH Zürich with Peter Chen. In 2006, he returned to VU to initiate his independent career. He was promoted to Associate Professor in 2014, and moved to the University of Amsterdam in 2016. The mission of his laboratory is to educate students at the intersection of fundamental physical organic chemistry, main-group chemistry, and circular chemistry.



Scheme 3. Dihydrogen abstraction from $Me_2NH{\cdot}BH_3$ with **2** (Fxyl = 3,5-$(F_3C)_2C_6H_3$).

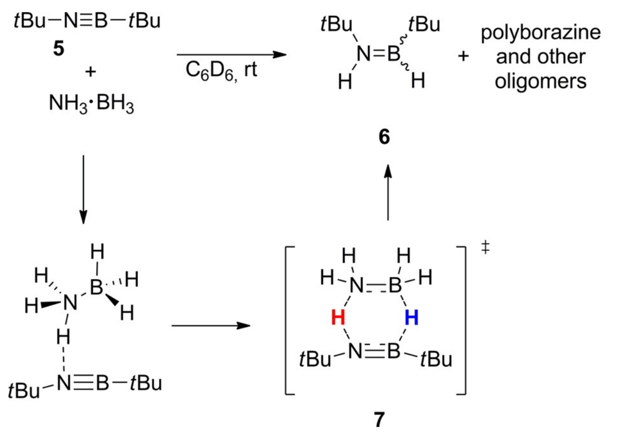
12 hours at room temperature, the hydrogenated product **3** formed along with the expected dehydrogenation by-products $[Me_2N{-}BH_2]_2$ and $Me_2NH{-}BH_2{-}NMe_2{-}BH_3$, which were detected by NMR spectroscopy. To gain more insight into the mechanism, aminoborane **2** was reacted with $Me_2ND{\cdot}BH_3$ resulting in exclusive deuterium incorporation in the amine moiety, suggesting a similar mechanism as reported for iPr$_2$N=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 $Me_2NH{\cdot}BH_3$ and showed to be able to quantitatively abstract dihydrogen, while generating $[Me_2N{-}BH_2]_2$ (Scheme 4).[27] This resembles the greater affinity for H_2 compared with the transient $Me_2N{=}BH_2$, which was explained by the increase of Lewis acidity at the boron site by the perfluorinated aryl substituents.



Scheme 4. H_2 abstraction by a phosphinoborane.

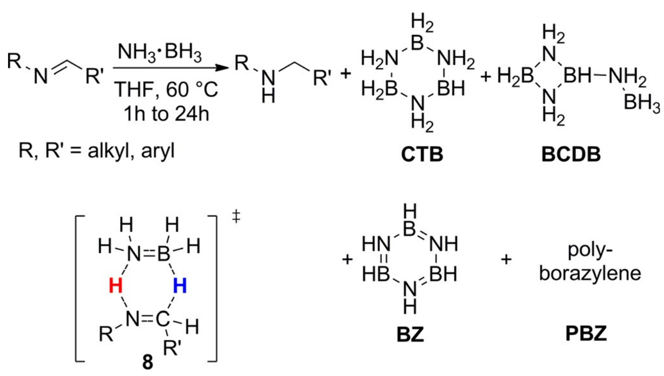
Recently, Braunschweig and co-workers reported the first iminoborane that can rapidly dehydrogenate ammonia–borane at room temperature.[28] They showed that 1 equivalent of *tert*-butyl substituted iminoborane **5** (Scheme 5) rapidly reacts with 1 equivalent of AB, forming the expected aminoborane **6**, 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 B-(cyclotriborazanyl)amine–borane (BCTC) intermediate by **5**, as well as the capability of the formed $NH_2{=}BH_2$ 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**). 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-tBu-B-durylamine–borane, which could afford a new way of making bulky aminoboranes.



Scheme 5. Computed mechanism for dihydrogen transfer from AB to iminoboranes.

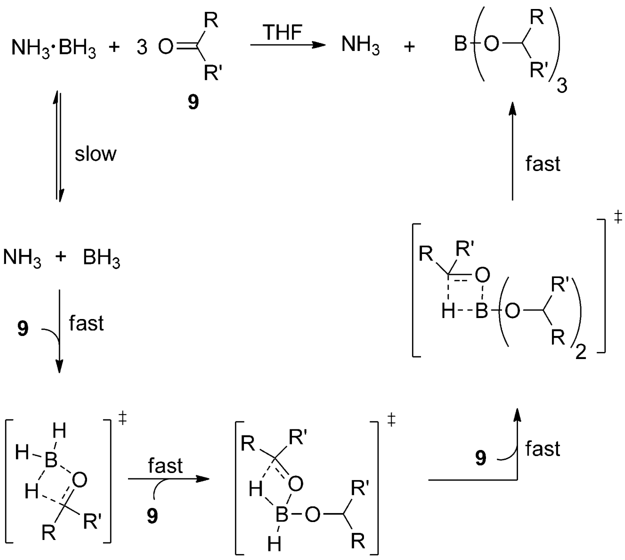
2.2. Dihydrogen transfer to organic C–C and C–E bonds (E = N, O, P)

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 N–H···C and B–H···N transfer, comparable to transfer hydrogenation to aminoboranes (Scheme 2).[19,21]



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.[30] 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.[31] 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

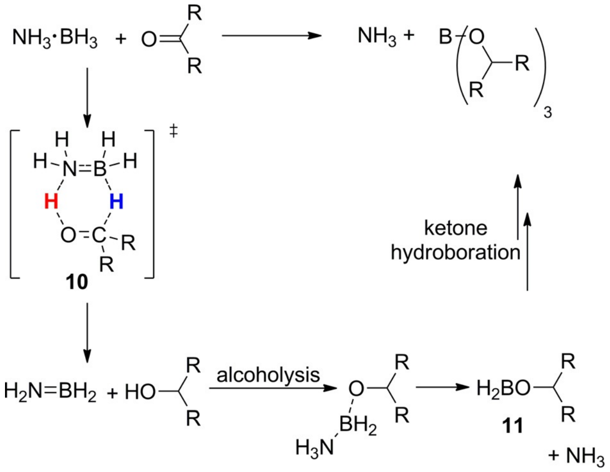


Scheme 7. Hydroboration of ketones and aldehydes.

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 $MeOH{\cdot}BH_3$, which then could undergo double hydrogen transfer to the substrate, forming the desired product.

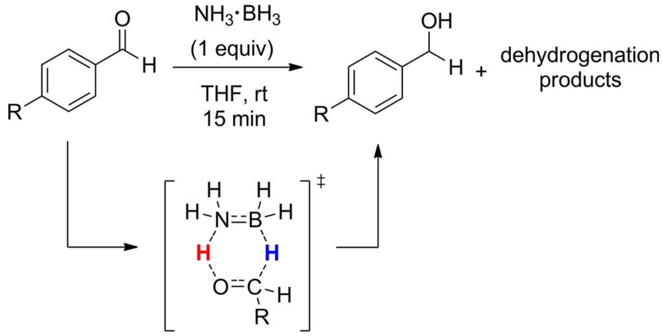
This mechanism has been contested, however. The group of Zhou and Fan performed a theoretical study on the mechanism of ketone reduction by $NH_3{\cdot}BH_3$, which suggested that ketones can also undergo a concerted double hydrogen transfer via transition state **10**, similar to imines (Scheme 8).[32,33] This process was found to be lower in energy compared with the initially proposed hydroboration mechanism by Berke.[30] To explain the observed alkyl borate formation, alcoholysis of the in situ formed $NH_2{=}BH_2$ 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.

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



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

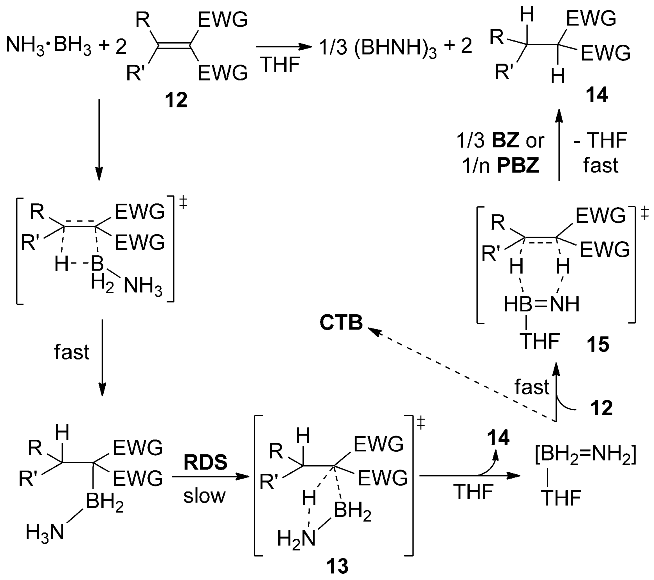
good to excellent conversion to the terminal alcohols and no formation of ammonia was observed (Scheme 9),[34] in contrast to the findings of Berke and co-workers.[30] Note that there is a difference in reaction conditions. Although Berke used a ratio of 2:1 ratio of AB versus substrate, Chen used a 1:1 ratio of AB



Scheme 9. Chen's proposed mechanism for hydrogen transfer of AB to aldehydes.

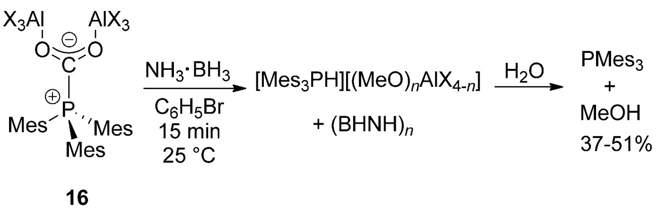
and aldehyde. Nevertheless, isotopic-labelling studies of Chen and co-workers with $NH_3{\cdot}BD_3$ and $ND_3{\cdot}BH_3$ strongly suggested that the main path for the reduction of aldehydes is through double hydrogen transfer, in which both the protic N–H and hydridic B–H hydrogens participate and 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-hydrogenation reaction with $NH_3{\cdot}BH_3$. All substrates showed excellent conversion to the hydrogenated species under mild conditions.[35] Interestingly, labelling studies using $NH_3{\cdot}BD_3$ and $ND_3{\cdot}BH_3$ revealed that the hydric 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.[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).[36] 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.



Scheme 10. Reduction of C=C double bonds through hydrogen transfer of ammonia–borane.

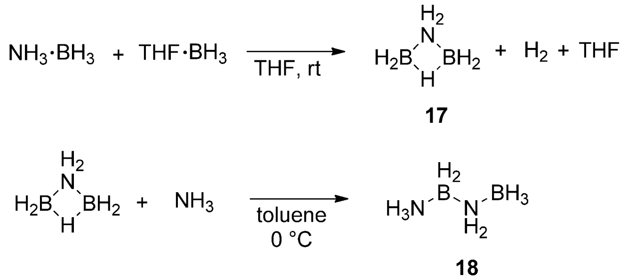
Another example of amine–borane dehydrogenation was provided by the Stephan group. Namely, the reaction between the Lewis adduct $Mes_3P(AlX_3)$ and CO_2 afforded species **16** (Scheme 11),[37] which is prone to undergo reduction of the carbon center by dihydrogen transfer from $NH_3{\cdot}BH_3$, resulting in various dehydrogenation products, like borazine, that were observed by ^{11}B NMR spectroscopy. Subsequent quenching of the various methoxyaluminate species with water resulted in the formation of methanol, which could be extracted with yields of isolated materials ranging from 37 to 51%.



Scheme 11. Transition-metal-free conversion of CO_2 to methanol.

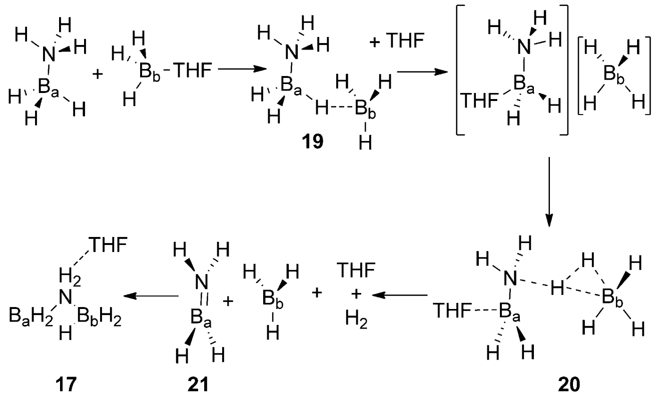
2.3. Stoichiometric Lewis acid-mediated dehydrogenation

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 aminodiborane **17** together with 1 equivalent of dihydrogen (Scheme 12).[38] From aminodiborane **17**, the inorganic butane analogue **18** was synthesized by the addition of ammonia, which highlights the applicability of **17** as an inorganic building block.[39]



Scheme 12. Formation and reactivity of aminodiborane **17**.

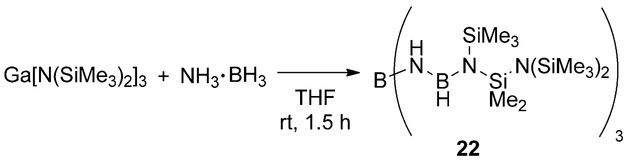
To get a better understanding of the underlying mechanism, Chen and co-workers performed an in-depth study, including isotopic labelling, intermediate trapping, and DFT calculations.[40] They found that ammonia–diborane **19** (Scheme 13)



Scheme 13. Proposed mechanism for the formation of aminodiborane from $NH_3{\cdot}BH_3$ and $THF{\cdot}BH_3$.

and aminoborane **21** are key intermediates in the formation of aminodiborane **17**. Compound **19**, which is formed upon reacting $NH_3{\cdot}BH_3$ with $THF{\cdot}BH_3$, 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 afford aminodiborane **17**.

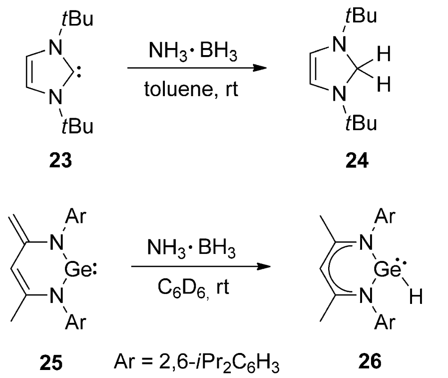
The second Lewis acid that was found to mediate amine–borane dehydrogenation is a gallium(III) complex, which was reported by the Wright group to react with stoichiometric amounts of ammonia–borane in a rather unexpected fashion.[41] When $Ga[N(SiMe_3)_2]_3$ was treated with $NH_3{\cdot}BH_3$, the gallium-free product [B{(NHBH)N(SiMe$_3$)Si(Me$_2$)N(SiMe$_3$)$_2$}$_3$] **22** 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 14. Reactivity of a gallium(III)-based complex with $NH_3{\cdot}BH_3$.

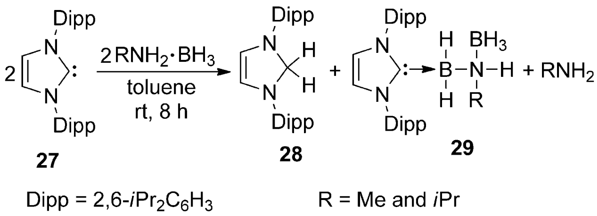
2.4. Stoichiometric Lewis base-mediated dehydrogenation

Roesky 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 germylene **26** (Scheme 15), in which the N-heterocyclic germylene did abstract dihydrogen, but without oxidation of the germanium(II) center.[42]



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

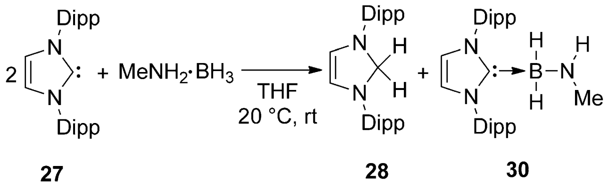
The group of Rivard extended the scope of this NHC chemistry and found that N-heterocyclic carbene **27** (Scheme 16) can dehydrogenate $MeNH_2{\cdot}BH_3$ and iPrNH$_2$·BH$_3$ forming the expected NHC–H_2 adduct **28** together with the carbene-bound B–N–B adduct NHC·BH$_2$NH(R)–BH$_3$ (**29**) in a 1:1 ratio.[44] 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 NHC·BH$_2$NH(R). Finally, NHC·BH$_2$NH(R) undergoes a BH$_3$ ligand exchange with the amine–borane starting material resulting in the formation of **29**.



Scheme 16. Dehydrogenation of $RNH_2{\cdot}BH_3$ by an NHC.

Utilizing the sterically more demanding tBuNH$_2$·BH$_3$ still resulted in dehydrogenation by NHC **27**, but now NHC·BH$_2$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 tBuNH=BH$_2$ 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$_2$NH(Dipp), NHC·BH$_2$NH(Dipp)–BH$_3$, and DippNH$_2$. This is caused by the lower nucleophilicity of the nitrogen moiety in DippNH$_2$·BH$_3$, which reduces the degree of BH$_3$ exchange and makes isolation of NHC·BH$_2$NH(Dipp) possible.

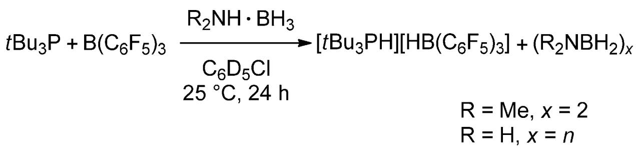
Instead of using 1 equivalent, Manners and co-workers described the reaction of 2 equivalents of NHC **27** with methylamine–borane, which afforded NHC–H$_2$ **28**, whereas the in situ generated methylaminoborane was trapped by the second equivalent of NHC affording NHC·BH$_2$NHMe **30** (Scheme 17).[45]



Scheme 17. 2:1 reaction of an NHC with $MeNH_2{\cdot}BH_3$.

2.5. Stoichiometric frustrated Lewis pair-mediated dehydrogenation

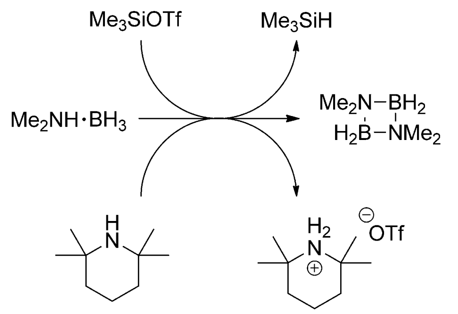
Lewis acids and Lewis bases that do not form a classic Lewis acid/base adduct, due to steric hindrance, are called frustrated Lewis pairs (FLPs),[24,25,26] and these main-group species also exhibit reactivity towards amine–boranes. Miller and Bercaw showed that the addition of 1 equivalent of Me$_2$NH·BH$_3$ to a solution of PtBu$_3$ 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$_2$NBH$_2$)$_2$ as major dehydrogenation product (Scheme 18).[46]



Scheme 18. Dehydrogenation of amine–boranes utilizing PtBu$_3$/B(C$_6$F$_5$)$_3$.

Keeping the reaction mixture one day at room temperature gave 97% conversion to $(Me_2NBH_2)_2$, with only trace amounts of $(BH_2)_2NMe_2(\mu\text{-}H)$ and $H_3B{\cdot}NMe_2BH_2{\cdot}NHMe_2$. The order of addition appeared to be important. When $B(C_6F_5)_3$ was added a few minutes prior to the addition of P*t*Bu$_3$ then only 50% of $(Me_2NBH_2)_2$ was obtained, whereas initial addition of the phosphine followed by $B(C_6F_5)_3$ led to almost quantitative formation of [*t*Bu$_3$PH][HB$(C_6F_5)_3$] and $(Me_2NBH_2)_2$. The authors hypothesized a stepwise mechanism might be operative in which $B(C_6F_5)_3$ abstracts a hydride to form $[R_2NHBH_2]^+$, which is quickly deprotonated by the phosphine to generate $R_2N{=}BH_2$ that dimerizes to the final product. The P*t*Bu$_3$/$B(C_6F_5)_3$ FLP was also able to dehydrogenate $NH_3{\cdot}BH_3$, however, lower conversions were obtained.

Alternatively, Manners and co-workers utilized combinations of different Group 14 triflates (Me_3SiOTf, Et_3SiOTf, and *n*Bu$_3$SnOTf) 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.[47] They found that the Me_3SiOTf/TMP combination converts $Me_2NH{\cdot}BH_3$ rapidly ($t_{1/2}$ starting material = 10.3 minutes) to the dimeric $(Me_2NBH_2)_2$, together with formation of the corresponding silane and piperidinium triflate (Scheme 19).



Scheme 19. Dehydrogenation of amine–boranes mediated by Me_3SiOTf/TMP.

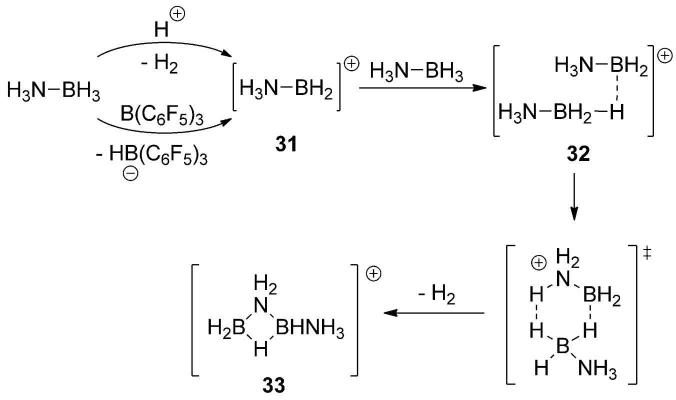
Switching to *n*Bu$_3$SnOTf/TMP increased the rate of the reaction, whereas the Et_3SiOTf/TMP combination was found to be less reactive, which also resulted in more side products. The FLP combination of Me_3SiOTf with the weaker base di-*tert*-butylpyridine also showed reduced reactivity and concomitant 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 $Me_2NH{\cdot}BH_3$, 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.

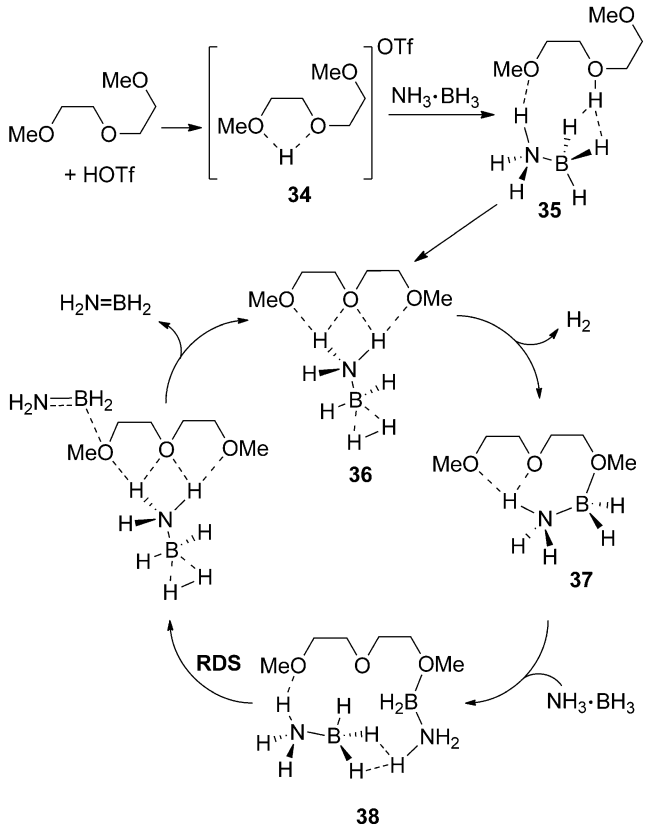
3.1. Brønsted and Lewis acid-initiated dehydrogenation

Dixon and co-workers described the liberation of dihydrogen from ammonia–borane by applying substoichiometric amounts of strong Brønsted and Lewis acids.[48] It was found that these acids are not catalyzing the dehydrogenation of $NH_3{\cdot}BH_3$, 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).[49] Subsequently, the borenium intermediate **31** reacts with another equivalent of $NH_3{\cdot}BH_3$ followed by elimination of dihydrogen and formation of **33**. DFT calculations indicated that **33** can further react with $NH_3{\cdot}BH_3$, which leads to chain transfer oligomerization. Following this strategy, loadings down to 0.5 mol% of acid (triflic acid ($HOSO_2CF_3$, HOTf), HCl, or $B(C_6F_5)_3$ as Lewis acid) were found to liberate over 1 equivalent of dihydrogen under mild conditions.



Scheme 20. Initiation step of AB dehydrogenation by Brønsted and Lewis 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 $NH_3{\cdot}BH_3$ protonation using triflic acid in bis(2-methoxyethyl) ether (diglyme).[50] 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 $NH_3{\cdot}BH_3$. Subsequently, the proton is transferred to the borane, forming the nonclassical pentacoordinate borane **36**. This solvent-stabilized $NH_3BH_4^+$ species can release dihydrogen with concomitant formation of $NH_3BH_2^+$–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 $[NH_3BH_2(L)]^+$ species experimentally, but proposed this species to form through direct protonolysis or hydride abstraction by the Lewis acid.[48] Interestingly, the group of Paul found that **37** can react with another equivalent of $NH_3{\cdot}BH_3$ forming **38**. Subsequent proton transfer (rate-determining step, **RDS**) followed



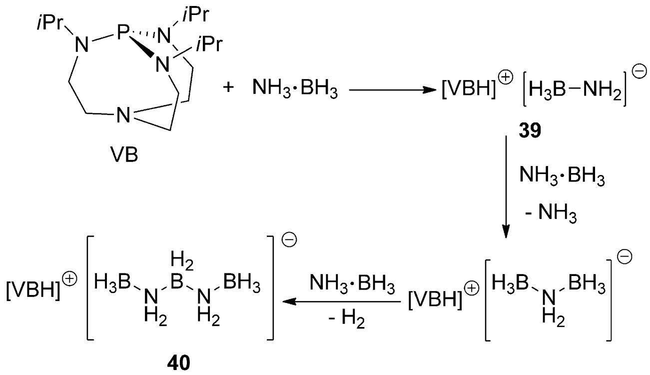
Scheme 21. Calculated mechanism for ammonia–borane dehydrogenation using triflic acid in diglyme.

by the release of $H_2N{=}BH_2$ regenerates the nonclassical pentacoordinate borane **36**, and subsequently **37** after H_2 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 H_2 release because it can react with other oligomeric BN species of $H_2N{=}BH_2$ producing more H_2, and not through a dehydrocoupling pathway suggested by Dixon and co-workers.[48]

The group of Manners reported a stepwise method to generate dimeric $(Me_2NBH_2)_2$ utilizing a Brønsted acid and base.[51] The dehydrogenation of dimethylamine–borane can be initiated by a protonation/H_2 elimination step with Brønsted acids such as HOTf and HCl,[52] resulting in formation of H_2 and $Me_2NH{\cdot}BH_2X$ (X = OTf, Cl). Subsequently, these species can be rapidly converted to cyclic diborazane $(Me_2NBH_2)_2$ when reacted with an excess (10 equiv) of iPr$_2$EtN under ambient conditions (DCM, 25 °C, < 1 min).

3.2. Brønsted base-initiated dehydrogenation

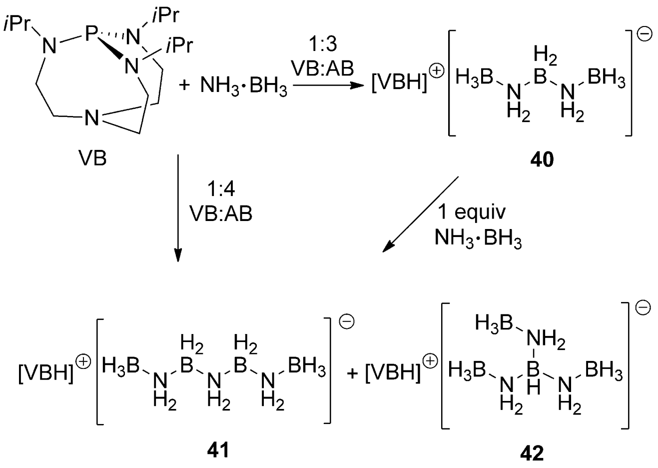
Sneddon and co-workers reported on the use of a Brønsted base to initiate ammonia–borane dehydrogenation, namely 1,8-bis(dimethylamino)naphthalene, commonly known as proton sponge.[53] A substoichiometric loading of only 1 mol % of this strong base was shown to accelerate the dehydrogenation of $NH_3{\cdot}BH_3$ when the solid mixture was heated to 85 °C and approximately 1.1 equivalent of H_2 was released after 21 hours. Solid-sate ^{11}B NMR spectroscopy of the final products revealed that a sp^2-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 H_2 were evolved after 6 hours at 85 °C. The initial step in AB dehydrogenation utilizing a proton sponge is believed to be deprotonation of $NH_3{\cdot}BH_3$, forming the $[NH_2{-}BH_3]^-$ anion (by analogy with **39** in Scheme 22, see below), which can react with AB and form anionic polymers with simultaneous release of dihydrogen.



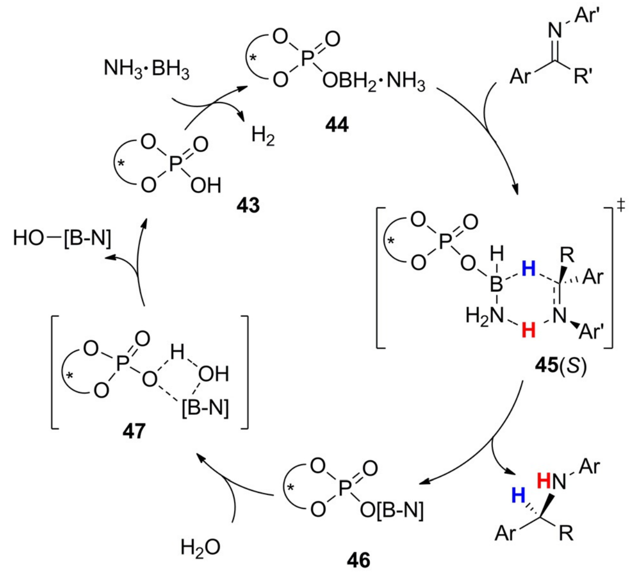
Scheme 22. Anionic polymerization of AB dehydrogenation initiated by a Brønsted base.

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 H_2 from $NH_3{\cdot}BH_3$ 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 $NH_3{\cdot}BH_3$, elongating the chain and liberating NH_3. Subsequent insertion of $NH_3{\cdot}BH_3$ leads to the formation of **40** and H_2.

To verify this mechanism, Verkade's base was reacted with 3 equivalents of $NH_3{\cdot}BH_3$ 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 $NH_3{\cdot}BH_3$ for 2 days at 50 °C, which also afforded a mixture of **41** and **42**, supporting a stepwise, base-promoted oligomerization mechanism.



Scheme 23. Formation and isolation of intermediates in the base-promoted polymerization of AB.



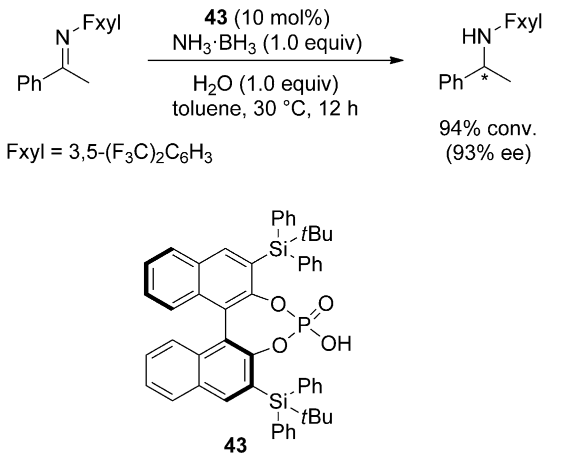
Scheme 25. Mechanism for transfer hydrogenation by **43** (shown schematically here).

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 $NH_3{\cdot}BH_3$ 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.

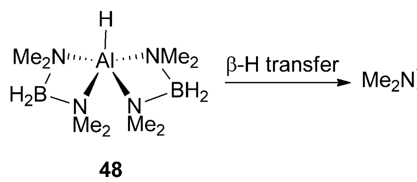


Scheme 24. Imine reduction catalyzed by **43** with ammonia–borane as hydrogen source.

4.2. Lewis acid-catalyzed dehydrogenation

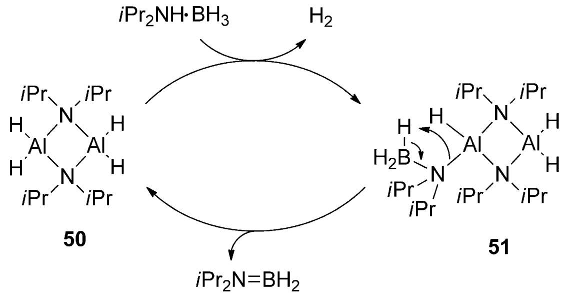
A variety of Group 13 element Lewis acids were found to be active catalysts in the dehydrogenation of amine–boranes. Wright and co-workers utilized 8 mol % of $Al(NMe_2)_3$ for the dehydrogenation of $Me_2NH{\cdot}BH_3$, which formed dimeric $(Me_2NBH_2)_2$ together with small amounts of $(Me_2N)_2BH$ and a new aluminum species $[\{(Me_2N)_2BH_2\}_2AlH]$ (**48**; Scheme 26).[56] Compound **48** was isolated and also showed catalytic activity towards $Me_2NH{\cdot}BH_3$ 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.

The related $Al(NiPr_2)_3$ is also catalytically active in the dehydrogenation of $iPr_2NH{\cdot}BH_3$ in benzene at 60 °C.[40] Given that a relatively long induction period was observed when using



Scheme 26. β-hydride transfer to form **49**.

10 mol %, $Al(NiPr_2)_3$ was suspected to be a pre-catalyst in this reaction. A 1:2 stoichiometric reaction of $Al(NiPr_2)_3$ with $iPr_2NH{\cdot}BH_3$ resulted in the formation of $[H_2Al(\mu\text{-}NiPr_2)]_2$ (**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 $iPr_2NH{\cdot}BH_3$ to form **51** (Scheme 27), which is followed by β-hydride elimination to regenerate the active catalyst.

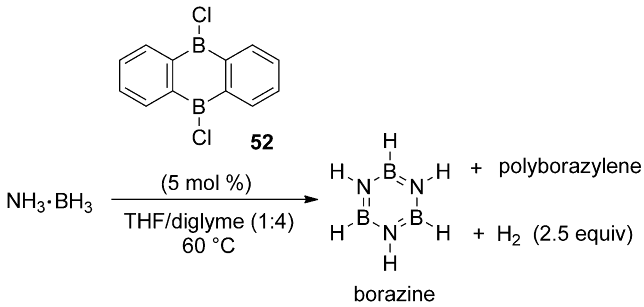


Scheme 27. Mechanism for $iPr_2NH{\cdot}BH_3$ dehydrogenation by **50**.

Additionally, the group of Wright reported several aluminum hydride species to be catalytically active in amine–borane dehydrogenation. For example, 10 mol % of $LiAlH_4$ converted $Me_2NH{\cdot}BH_3$ almost quantitatively to dimeric $(Me_2NBH_2)_2$ when refluxed in toluene for 16 hours.[57] Similarly, neutral $[(tBuO)_xAlH_{3-x}]$ ($x=1$ or 2) and lithium salts of $[(tBuO)_2AlH_2]^-$ were found to catalyze the dehydrogenation of $Me_2NH{\cdot}BH_3$, with $[tBuO_2AlH_2]^-$ being superior compared with the other *tert*-butoxy-substituted aluminum catalysts.[58] Nonetheless, the underlying mechanism for dehydrogenation of amine–boranes is much more complicated and still needs further investigations.

The heavier analogue of $Al(NMe_2)_3$, $Ga(NMe_2)_3$ was successfully applied as catalyst for $tBuNH_2{\cdot}BH_3$ dehydrogenation.[40] Under ambient conditions, 5 mol % of $Ga(NMe_2)_3$ slowly convert $tBuNH_2{\cdot}BH_3$ to the borazane $(tBuNHBH_2)_3$ and also the formation of borazine was observed, which is the product of subsequent dehydrogenation.

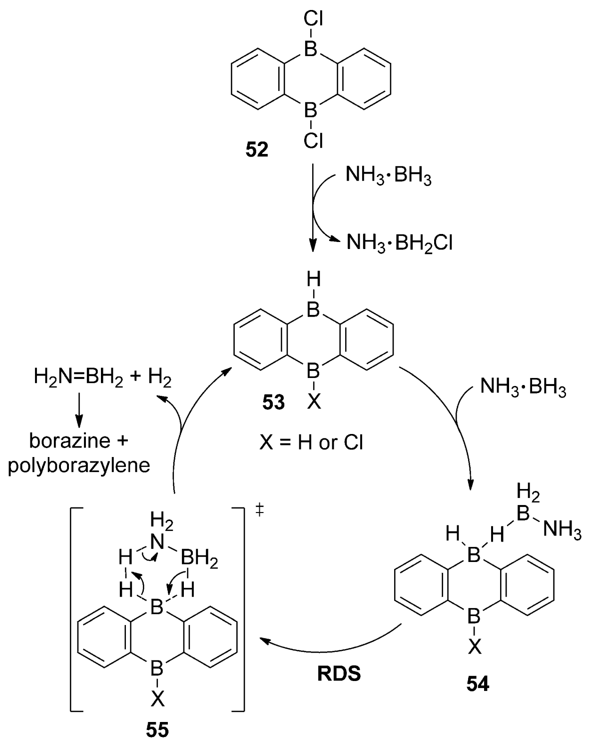
Recently, Wegner and co-workers showed that 5 mol % of bis(borane) **52** can dehydrogenate ammonia–borane releasing up to 2.5 equivalents of dihydrogen per AB molecule, which is the first example of a metal-free catalyst capable of liberating more than 2 equivalents of H_2 (Scheme 28).[59,60] Driven 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 H_2 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 $NH_3{\cdot}BH_3$ after the evolution of hydrogen was finished. This procedure was repeated 15 times without loss of catalytic activity.



Scheme 28. Catalytic dehydrogenation of $NH_3{\cdot}BH_3$ by **52**.

Stoichiometric reactions revealed that the reaction starts by exchange of the chloride for a hydride from $NH_3{\cdot}BH_3$, forming ammonia–monochloroborane ($NH_3{\cdot}BH_2Cl$) 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 $NH_3{\cdot}BH_3$, forming the three-center two-electron adduct **54**, which releases both H_2 and $H_2N{=}BH_2$ 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*-CF_3- 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 29. Mechanism of AB dehydrogenation by **53**.

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[63] and found that 10 mol% of $Cp^*_2SnCl_2$ ($Cp^* = C_5Me_5$) and Ph_2SnCl_2 quantitatively converted $NH_3{\cdot}BH_3$ 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 $Me_2NH{\cdot}BH_3$ drastically influenced the rate of the reactions, giving only 69, 47, and 23% of product at 65 °C using 10 mol% of $Cp^*_2SnCl_2$, Ph_2SnCl_2, and $SnCl_2$, 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 $(Me_2NBH_2)_2$ dimer, giving reaction mixtures containing $(Me_2NBH_2)_2$, $Me_2NHBH_2NMe_2$, $H_2BNMe_2BH_3$, and other unidentified species.

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

Catalyst	RR′NH·BH$_3$	Loading [mol%]	Conversion [%]	Time
$Cp^*_2SnCl_2$	R=R′=H	10	100	1 d
Ph_2SnCl_2	R=R′=H	10	100	1 d
$SnCl_2$	R=R′=H	10	100	1 h
$SnCl_2$	R=R′=H	5	100	18 h
$SnCl_2$	R=R′=H	0.5	100	2 d
$Cp^*_2SnCl_2$	R=R′=Me	10	69	6 d
Ph_2SnCl_2	R=R′=Me	10	47	4 d
$SnCl_2$	R=R′=Me	10	23	5 d
$Cp^*_2SnCl_2$	R=*t*Bu, R′=H	10	95	5 d
Ph_2SnCl_2	R=*t*Bu, R′=H	10	93	4 d
$SnCl_2$	R=*t*Bu, R′=H	5	84	5 d

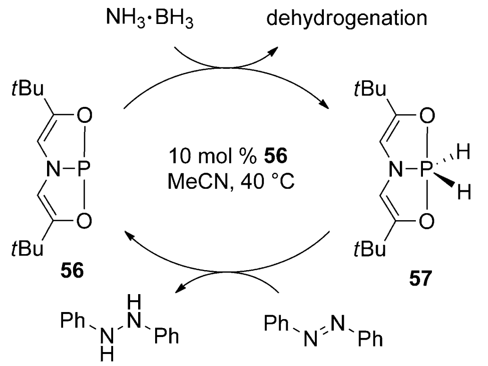
Surprisingly, these tin catalysts showed much higher conversions when the bulky $tBuNH_2{\cdot}BH_3$ was used as substrate, and after 4 to 5 days at 65 °C conversions of 95, 93, and 84% were obtained using 10 mol% of $Cp^*_2SnCl_2$, Ph_2SnCl_2, or 5 mol% $SnCl_2$, respectively. Similar to $Me_2NH{\cdot}BH_3$, 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 $tBuNH{=}BH_2$ (16–23%) compared with the tin(II) catalyst $SnCl_2$ (<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 2. Product distribution [%] of the dehydrogenation of $tBuNH_2{\cdot}BH_3$ by tin catalysts.

Catalyst	Polymers	$(tBuNBH)_3$	$tBuNH{=}BH_2$	$tBuNHB_2H_5$	Other
$Cp^*_2SnCl_2$	20	0	16	26	30
Ph_2SnCl_2	41	8	23	23	30
$SnCl_2$	13	6	<5	33	41

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.[64] They found that in stoichiometric quantities, **56** can abstract 1 equivalent of dihydrogen from ammonia–borane to form dihydrophosphorane **57** (Scheme 30),

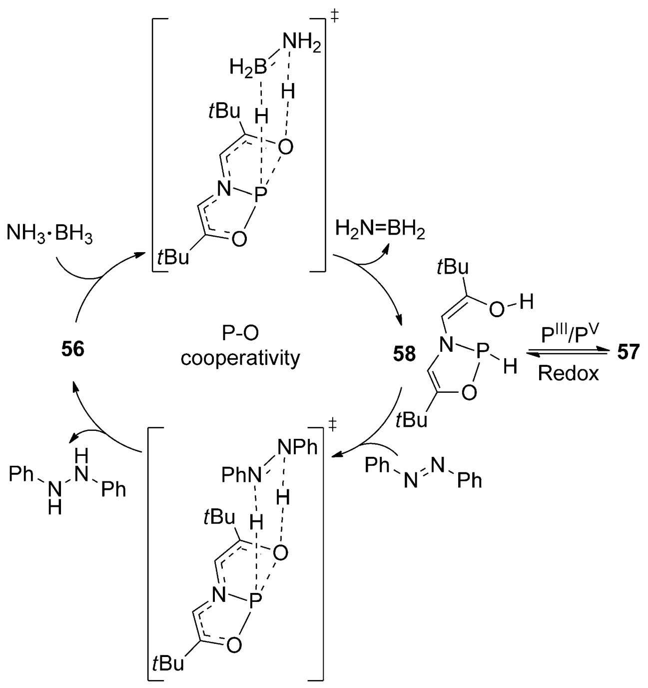


Scheme 30. Proposed catalytic cycle for azobenzene hydrogenation.

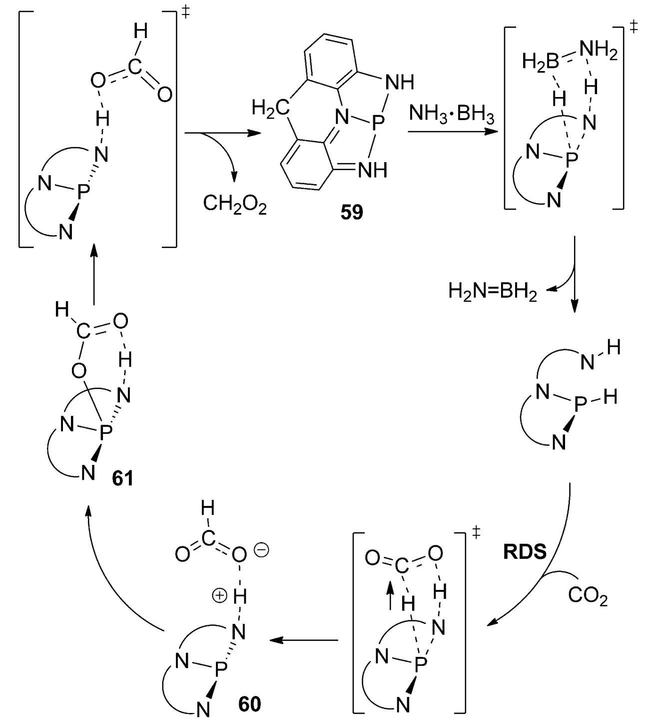
which can subsequently transfer H_2 quantitatively to azobenzene. Additionally, **56** is also catalytically active (10 mol%) and cleanly hydrogenates azobenzene to diphenylhydrazine with 94% conversion in 48 hours at 40 °C. During catalysis, dihydrophosphorane **57** was the only observable species 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^{III} and P^{V} 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^{III} 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.[67] 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-



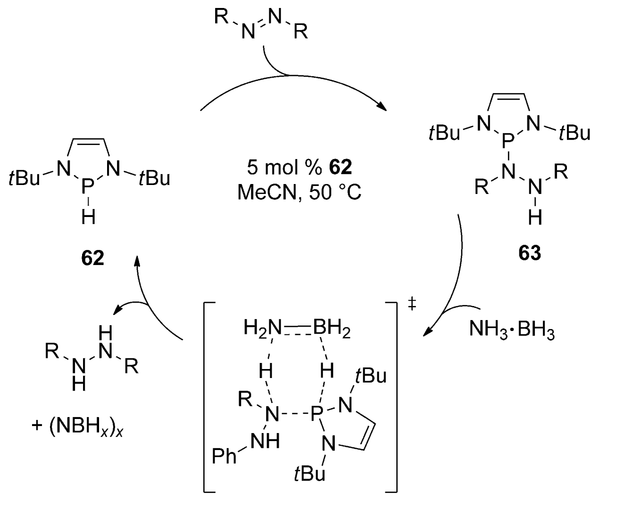
Scheme 31. Calculated catalytic cycle for azobenzene transfer hydrogenation.



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

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 CO_2 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).[69] Subsequently, the P–N bond can be cleaved by

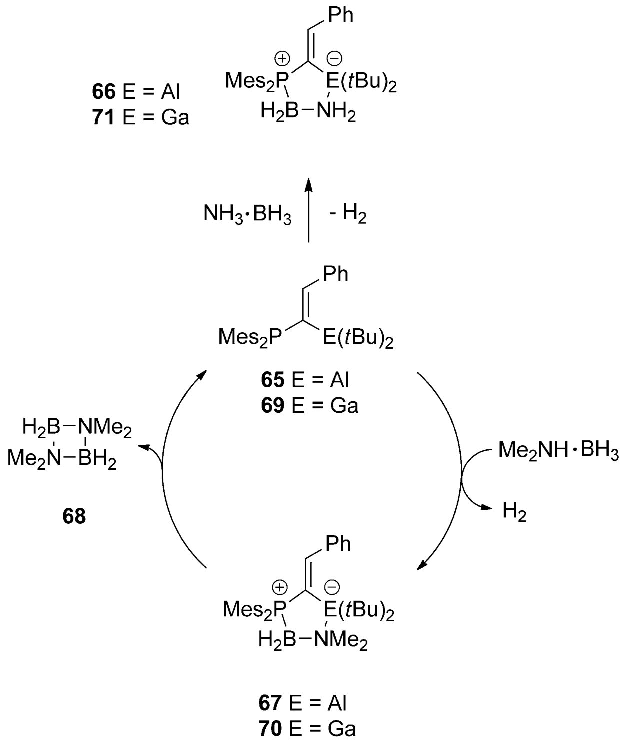


Scheme 33. Proposed catalytic cycle for azobenzene hydrogenation catalyzed by **62**.

addition of $NH_3{\cdot}BH_3$, giving diphenylhydrazine and regenerating the N-heterocyclic phosphane **62**. Interestingly, when $NH_3{\cdot}BD_3$ 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,[24–26] 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 $NH_3{\cdot}BH_3$ liberates 1 equivalent of dihydrogen concomitant with the formation of the zwitterionic five-membered heterocycle **66** (Scheme 34).[70] 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, 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 $Me_2NH{\cdot}BH_3$ with 0.4 mol % of **65** afforded the four-membered cyclodiborazane **68** after 44 hours in 77 %

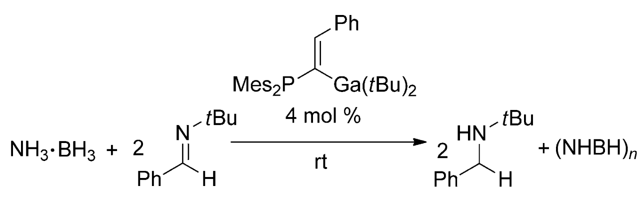


Scheme 34. Amine–borane dehydrogenation by a P/E (E=Al, Ga) FLP.

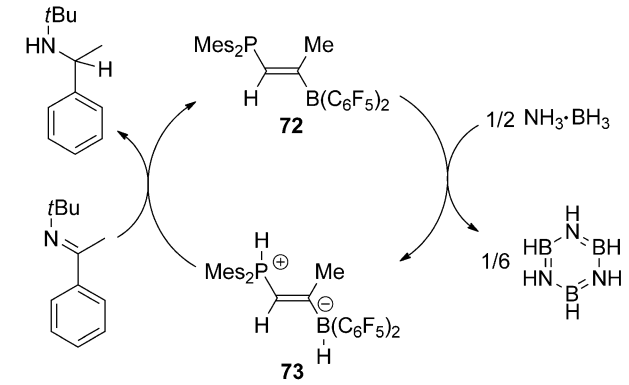
with turnover numbers and frequencies up to 198.3 and 4.5 h^{-1}, respectively.

Gallium analogue **69** showed similar reactivity towards $Me_2NH{\cdot}BH_3$, 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.[71] Treatment of FLP **69** with the sterically less hindered $NH_3{\cdot}BH_3$ 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 $NH_3{\cdot}BH_3$, imine PhCH=N*t*Bu 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 $NH_3{\cdot}BH_3$ catalytically was described by Stephan and Erker.[26a] 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).



Scheme 35. FLP **69** as catalyst for imine hydrogenation.

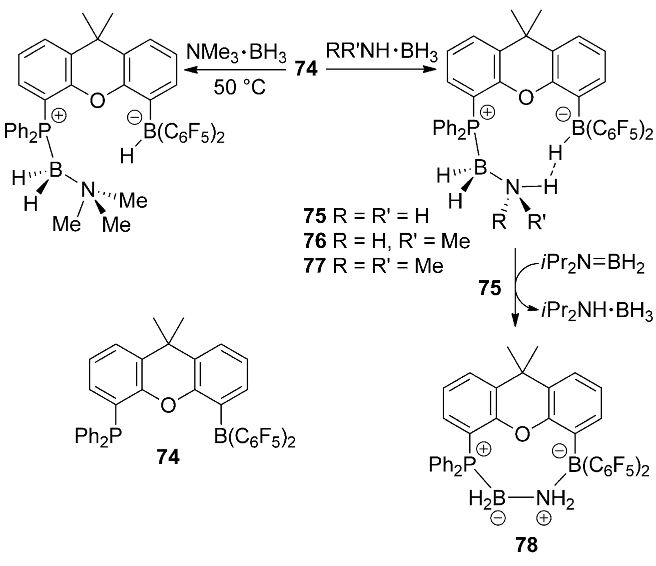


Scheme 36. Phosphinoborane-catalyzed transfer hydrogenation of imines.

Moreover, **72** is active as a hydrogen transfer catalyst for the hydrogenation 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.[26b]

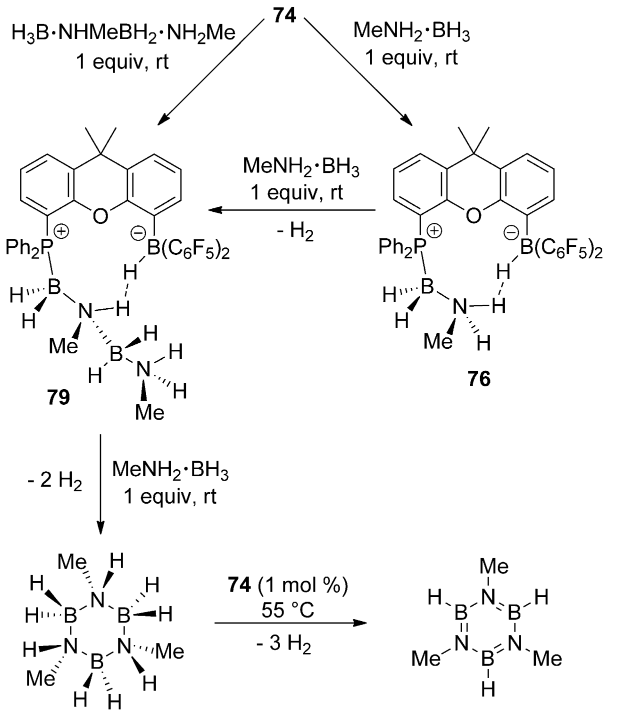
Aldridge and co-workers reported dimethylxanthene-linked phosphinoborane FLP **74** to be active as catalyst for the dehydrogenation of several amine–boranes.[72] FLP **74** was found to catalyze the liberation of dihydrogen from $NH_3{\cdot}BH_3$, $MeNH_2{\cdot}BH_3$, and $Me_2NH{\cdot}BH_3$ at 55 °C 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. In order to probe the mechanism, stoichiometric reactions with **74** and $Me_nNH_{3-n}{\cdot}BH_3$ 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.

Adducts **75**, **76**, and **77** were surprisingly stable and no release of hydrogen was observed when solutions were heated



Scheme 37. Stoichiometric reactions of **74** with amine–boranes.

to 55 °C for 24 hours. Dehydrogenation of adduct **75** was achieved by the use of $i\mathrm{Pr_2N{=}BH_2}$ in a similar fashion to that reported by Manners and co-workers,[19,21] 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



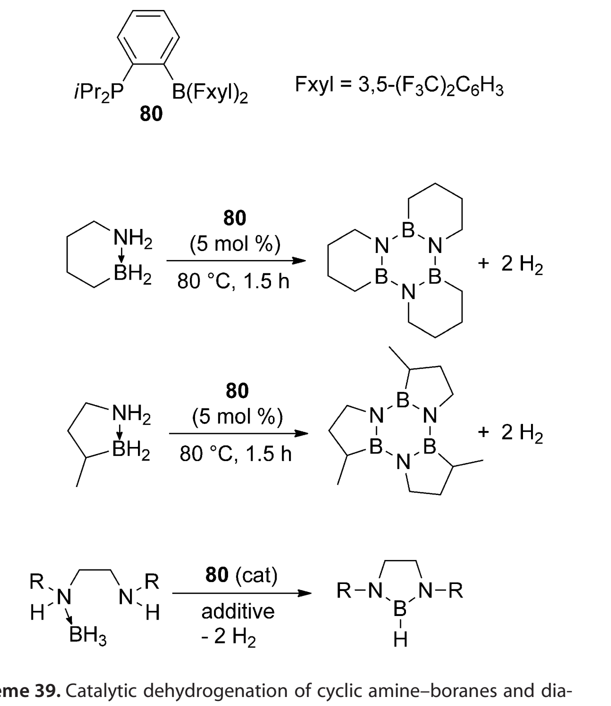
Scheme 38. Stoichiometric and catalytic reactions of **74** with methylamine–boranes.

74 with $H_3B{\cdot}NHMeBH_2{\cdot}NH_2Me$, and provides evidence for dehydrogenation through a chain-growth mechanism. Addition of a third equivalent of $MeNH_2{\cdot}BH_3$ resulted in the formation of the cyclic trimer $(NHMeBH_2)_3$ 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 $MeNH_2{\cdot}BH_3$ into the P–B bond of the adduct (**79**). Additionally, **74** can further dehydrogenate $(NHMeBH_2)_3$ 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]

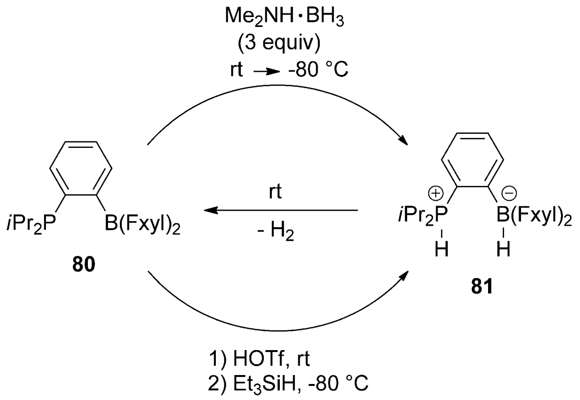
Recently, the group of Bourissou described a related *ortho*-phenylene-bridged phosphinoborane bearing the Fxyl substituent (Fxyl = 3,5-$(F_3C)_2C_6H_3$) on the boron site as an alternative to the frequently used C_6F_5 group.[74] This FLP (**80**) adopts a closed form at room temperature, that is, with 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 borazane and borazine ($(MeNHBH_2)_3$ and $(MeNBH)_3$, respectively). At 70 °C, dimethylamine–borane was completely converted to $(Me_2NBH_2)_2$. 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*t*Bu) is present. Preorganization of the FLP appears to be important for the reaction rate.[75] Namely, when the Lewis pair combination of $i\mathrm{Pr_2PPh}$ and $B(Fxyl)_3$ was used (5 mol%) for the dehydrogenation of $Me_2NH{\cdot}BH_3$, 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** 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=N*t*Bu as additive drastically reduced the reaction times.

In-depth NMR studies performed on the reaction of **80** with $Me_2NH{\cdot}BH_3$ 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



Scheme 39. Catalytic dehydrogenation of cyclic amine–boranes and diamine–boranes with **80**.



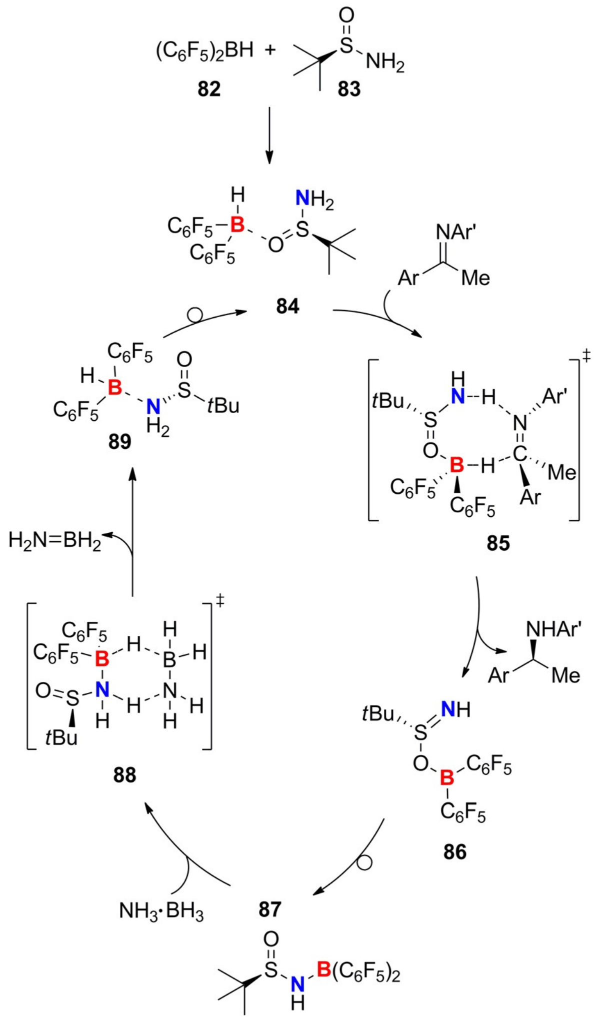
Scheme 40. Stepwise and catalytic generation of phosphonium–borate **81**.

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.[76]

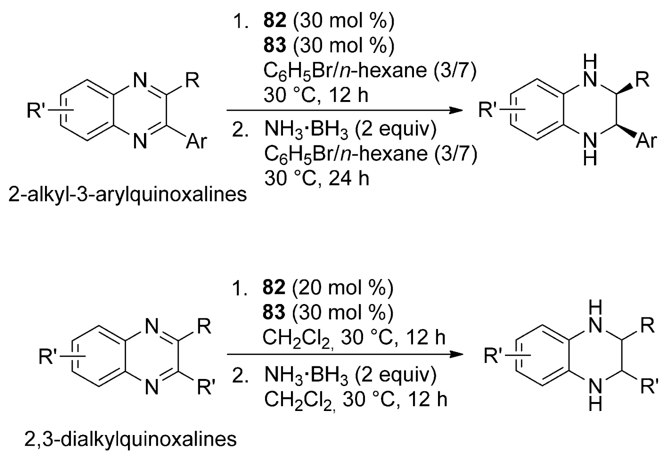
An alternative system for the FLP-catalyzed transfer hydrogenation of imines was reported by Du and co-workers in 2016.[77] They found that under optimized conditions, catalytic amounts of Piers' borane **82** ($HB(C_6F_5)_2$, 10 mol%) and chiral sulfinamide **83** (10 mol%) in toluene with 10 mol% of 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 spectroscopic studies were carried out to probe the mechanism, and showed that Piers' borane **82** and the chiral sulfinamide **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.[78] When 2-alkyl-3-arylquinoxalines were subjected to hydrogenation utilizing the combination of $HB(C_6F_5)_2$ and (*R*)-*tert*-butylsulfinamide (**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.[79] Inspired by Baker and Dixon,[48]

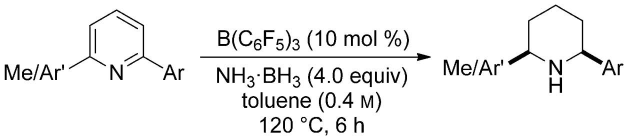


Scheme 41. FLP-catalyzed asymmetric transfer hydrogenation of imines.



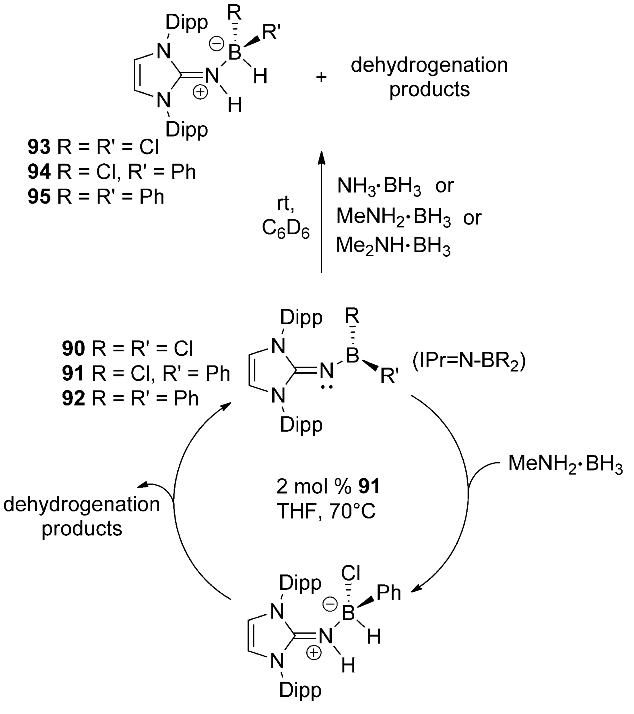
Scheme 42. FLP-catalyzed reduction reactions of 2,3-disubstituted quinoxalines.

they found that the combination of a 2,6-substituted pyridine with $B(C_6F_5)_3$ 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).



Scheme 43. FLP-catalyzed transfer hydrogenation of pyridines.

Rivard and co-workers investigated the dehydrogenation abilities of N-heterocyclic iminoboranes IPr=N–BR_2 (IPr= [$(HCNDipp)_2C$]; **90**, **91**, and **92** in Scheme 44) towards various amine–boranes.[80] Stoichiometric reactions of **90** and **91** with $NH_3{\cdot}BH_3$ or $MeNH_2{\cdot}BH_3$ resulted in rapid conversions towards the corresponding H_2-adducts **93** and **94**, respectively, along with the formation of aminoborane oligomers. IPr=N–BCl_2 (**90**) is also reactive towards sterically more demanding substrates and full conversion was achieved towards IPr=N(H)–B(H)Cl_2 (**91**) within 45 minutes when reacted with $Me_2NH{\cdot}BH_3$. 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)Cl_2 (**93**) and IPr=N(H)–B(H)PhCl (**94**) are stable at room temperature and do not transfer dihydrogen to cyclohexene, PhHC=N*t*Bu or N-(1-styryl)piperidine. However, heating a solution of **94** in C_6D_6 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).

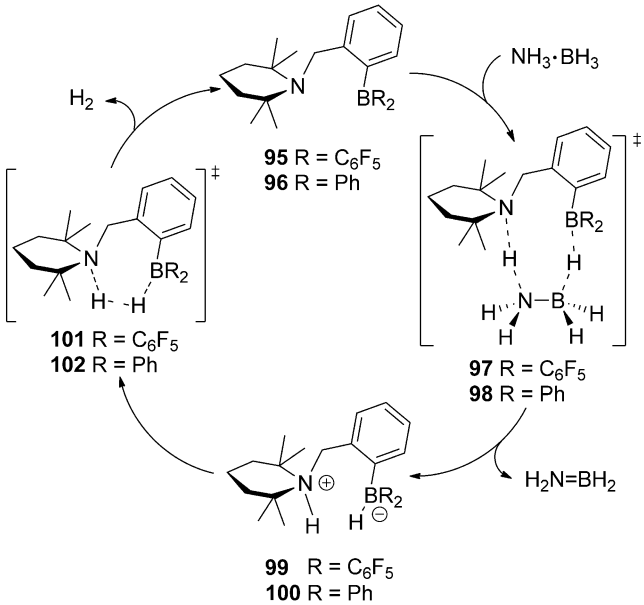


94

Scheme 44. Reactivity of N-heterocyclic iminoboranes towards different amine–boranes.

Treatment of $MeNH_2{\cdot}BH_3$ 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 $(MeNHBH_2)_x$ oligomers. After 17 hours, ^{11}B NMR spectroscopy revealed that 11% of $MeNH_2{\cdot}BH_3$ 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–BCl_2 (**90**) and IPr=N–BPhCl (**91**) were both reacted with $Me_2NH{\cdot}BD_3$, which showed exclusive formation of IPr=N(H)–B(D)Cl_2 and IPr=N(H)–B(D)PhCl, respectively, suggesting a similar, concerted hydrogen transfer step as reported by Manners and co-workers.[19,21]

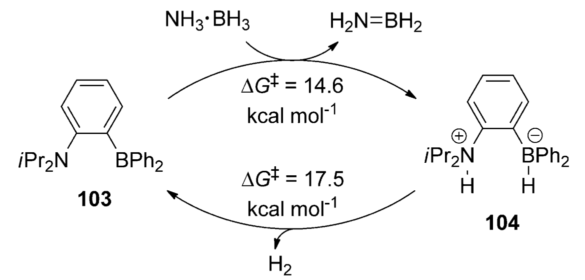
A computational analysis by Zou and co-workers suggested that FLP **95**, bearing a strong Lewis acidic borane moiety (Scheme 45),[81] is able to dehydrogenate $NH_3{\cdot}BH_3$ through a low-energy barrier (**97**; $\Delta G^{\ddagger} = 13.4$ kcal mol^{-1}) forming dihydrogen adduct **99**. However, the barrier for dihydrogen release is much higher ($\Delta G^{\ddagger} = 22.2$ 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 H_2 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



Scheme 45. Calculated mechanism for ammonia–borane dehydrogenation.

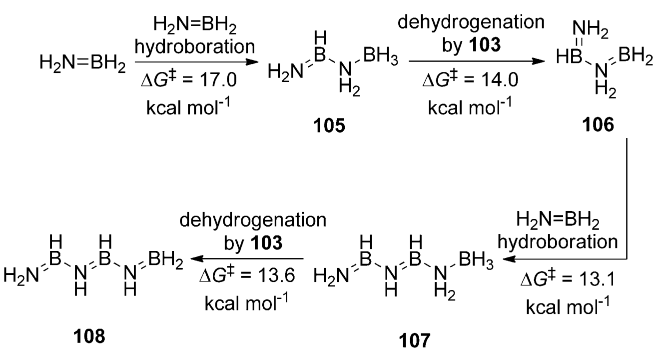
that bears the less electron-withdrawing phenyl substituents on boron (Scheme 45). Although hydrogen abstraction is now higher in energy ($\Delta G^{\neq}=18.7$ kcal mol^{-1} for **98**) and becomes the rate-determining step, the release of dihydrogen via **102** is facile ($\Delta G^{\neq}=9.3$ kcal mol^{-1}) and exothermic ($\Delta G=-14.6$ 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 $H_2N{=}BH_2$ should be disfavored, or the barrier should be higher than aminoborane oligomerization. After screening over 300 intramolecular FLPs, they found that phenylene-bridged N/B-FLP $i\mathrm{Pr_2BC_6H_4BPh_2}$ (**103**) meets all three requirements and can easily abstract 1 equivalent of dihydrogen from ammonia–borane ($\Delta G^{\neq}=14.6$ kcal mol^{-1}; Scheme 46) forming **104**, and subsequently liberate dihydrogen ($\Delta G^{\neq}=17.5$ kcal mol^{-1}).



Scheme 46. Energy barriers for **103** for ammonia–borane dehydrogenation.

The first step for liberation of a second equivalent of dihydrogen is the dimerization of the formed $H_2N{=}BH_2$ through hydroboration, forming **104** (Scheme 47). Instead of additional chain-growth through a second hydroboration step ($\Delta G^{\neq}=15.6$ 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 ($\Delta G^{\neq}=14.0$ kcal mol^{-1}). Subsequently, **106** can hydroborate another equivalent of $H_2N{=}BH_2$ to give **107**, which is followed again by a facile dehydrogenation step by FLP **103** to form **108** ($\Delta G^{\neq}=13.6$ 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 cyclotriborazane (CTB) (as shown in Scheme 6) are not formed.



Scheme 47. Oligomerization of aminoborane monomers assisted by **103**.

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 Brønsted 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.

Keywords: amine–boranes · ammonia–borane · dehydrogenation · hydrogen transfer · main-group catalysis

[1] For reviews about B–N compound as dihydrogen source, see: a) C. W. Hamilton, R. T. Baker, A. Staubitz, I. Manners, *Chem. Soc. Rev.* **2009**, *38*, 279–293; b) T. Umegaki, J.-M. Yan, X.-B. Zhang, H. Shioyama, N. Kuriyama, Q. Xu, *Int. J. Hydrogen Energy* **2009**, *34*, 2303–2311; c) Z. Huang, T. Autrey, *Energy Environ. Sci.* **2012**, *5*, 9257–9268; d) G. Moussa, R. Moury, U. B. Demirci, T. Şener, P. Miele, *Int. J. Energy Res.* **2013**, *37*, 825–842.
[2] For reviews about ammonia–borane as dihydrogen source, see: a) F. H. Stephens, V. Pons, R. T. Baker, *Dalton Trans.* **2007**, 2613–2626; b) B. Peng, J. Chen, *Energy Environ. Sci.* **2008**, *1*, 479–483; c) A. Staubitz, A. P. M. Robertson, M. E. Sloan, I. Manners, *Chem. Rev.* **2010**, *110*, 4023–4078; d) A. Staubitz, A. P. M. Robertson, I. Manners, *Chem. Rev.* **2010**, *110*, 4079–4124.
[3] T. B. Marder, *Angew. Chem. Int. Ed.* **2007**, *46*, 8116–8118; *Angew. Chem.* **2007**, *119*, 8262–8264.
[4] For in-depth studies on the thermolysis of ammonia–borane, see: a) G. Wolf, J. Baumann, F. Baitalow, F. P. Hoffmann, *Thermochim. Acta* **2000**, *343*, 19–25; b) F. Baitalow, J. Baumann, G. Wolf, K. Jaenicke-Rößler, G. Leitner, *Thermochim. Acta* **2002**, *391*, 159–168; c) J.-F. Petit, U. B. Demirci, *Inorg. Chem.* **2019**, *58*, 489–494.
[5] Related amine–boranes were also investigated for thermal decomposition, see: a) E. Framery, M. Vaultier, *Heteroat. Chem.* **2000**, *11*, 218–225; b) A. P. M. Robertson, G. R. Whittell, A. Staubitz, K. Lee, A. J. Lough, I. Manners, *Eur. J. Inorg. Chem.* **2011**, 5279–5287; c) A. P. M. Robertson, E. M. Leitao, T. Jurca, M. F. Haddow, H. Helten, G. C. Lloyd-Jones, I. Manners, *J. Am. Chem. Soc.* **2013**, *135*, 12670–12683.
[6] Thermally induced dihydrogen release from ammonia–borane and related amine–boranes were also investigated computationally: a) Q. S. Li, J. Zhang, S. Zhang, *Chem. Phys. Lett.* **2005**, *404*, 100–106; b) A. Staubitz, M. Besora, J. N. Harvey, I. Manners, *Inorg. Chem.* **2008**, *47*, 5910–5918; c) P. M. Zimmerman, Z. Zhang, C. B. Musgrave, *J. Phys. Chem. Lett.* **2011**, *2*, 276–281; d) T. Banu, K. Sen, D. Ghosh, T. Debnath, A. K. Das, *RSC Adv.* **2014**, *4*, 1352–1361; e) V. Rizzi, D. Polino, E. Sicilia, N. Russo, M. Parrinello, *Angew. Chem. Int. Ed.* **2019**, *58*, 3976–3980; *Angew. Chem.* *131*, 4016–4020.
[7] Y. J. Choi, E. C. E. Rönnebro, S. Rassat, A. Karkamkar, G. Maupin, J. Holladay, K. Simmonsa, K. Brooks, *Phys. Chem. Chem. Phys.* **2014**, *16*, 7959–7968.
[8] a) M. E. Bluhm, M. G. Bradley, R. Butterick, U. Kusari, L. G. Sneddon, *J. Am. Chem. Soc.* **2006**, *128*, 7748–7749; b) D. W. Himmelberger, L. R. Alden, M. E. Bluhm, L. G. Sneddon, *Inorg. Chem.* **2009**, *48*, 9883–9889.
[9] Enhanced dehydrogenation by ionic liquids was also found for *tert*-butylamine–borane, see: D. Kundu, S. Chakma, G. Pugazhenthi, T. Banerjee, *ACS Omega* **2018**, *3*, 2273–2281.
[10] L. Zhang, S. Li, Y. Tan, Z. Tang, Z. Guo, X. Yu, *J. Mater. Chem. A* **2014**, *2*, 10682–10687.
[11] H. Helten, A. P. M. Robertson, A. Staubitz, J. R. Vance, M. F. Haddow, I. Manners, *Chem. Eur. J.* **2012**, *18*, 4665–4680.
[12] a) D.-P. Kim, K.-T. Moon, J.-G. Kho, J. Economy, C. Gervais, F. Babonneau, *Polym. Adv. Technol.* **1999**, *10*, 702–712; b) E. M. Leitao, T. Jurca, I. Manners, *Nat. Chem.* **2013**, *5*, 817–829.
[13] a) A. Staubitz, A. P. Soto, I. Manners, *Angew. Chem. Int. Ed.* **2008**, *47*, 6212–6215; *Angew. Chem.* **2008**, *120*, 6308–6311; b) V. Pons, R. T. Baker, *Angew. Chem. Int. Ed.* **2008**, *47*, 9600–9602; *Angew. Chem.* **2008**, *120*, 9742–9744.
[14] For reviews about transition metal based amine–borane dehydrogenation catalysts, see: a) N. C. Smythe, J. C. Gordon, *Eur. J. Inorg. Chem.* **2010**, 509–521; b) N. E. Stubbs, A. P. M. Robertson, E. M. Leitao, I. Manners, *J. Organomet. Chem.* **2013**, *730*, 84–89; c) A. Rossin, M. Peruzzini, *Chem. Rev.* **2016**, *116*, 8848–8872; d) S. Bhunya, T. Malakar, G. Ganguly, A. Paul, *ACS Catal.* **2016**, *6*, 7907–7934; e) D. Han, F. Anke, M. Trose, T. Beweries, *Coord. Chem. Rev.* **2019**, *380*, 260–286; f) A. L. Colebatch, A. S. Weller, *Chem. Eur. J.* **2019**, *25*, 1379–1390.
[15] a) R. J. Keaton, J. M. Blacquiere, R. T. Baker, *J. Am. Chem. Soc.* **2007**, *129*, 1844–1845; b) R. T. Baker, J. C. Gordon, C. W. Hamilton, N. J. Henson, P.-H. Lin, S. Maguire, M. Murugesu, B. L. Scott, N. C. Smythe, *J. Am. Chem. Soc.* **2012**, *134*, 5598–5609; c) J. F. Sonnenberg, R. H. Morris, *ACS Catal.* **2013**, *3*, 1092–1102.
[16] For reviews on Group 1 and 2 metal-based amine–borane dehydrogenation catalysts, see: a) R. J. Less, R. L. Melen, D. S. Wright, *RSC Adv.* **2012**, *2*, 2191–2199; b) R. L. Melen, *Chem. Soc. Rev.* **2016**, *45*, 775–788.
[17] a) S. Hausdorf, F. Baitalow, G. Wolf, F. O. R. L. Mertens, *Int. J. Hydrogen Energy* **2008**, *33*, 608–614; b) B. L. Davis, D. A. Dixon, E. B. Garner, J. C. Gordon, M. H. Matus, B. Scott, F. H. Stephens, *Angew. Chem. Int. Ed.* **2009**, *48*, 6812–6816; *Angew. Chem.* **2009**, *121*, 6944–6948; c) A. D. Sutton, A. K. Burrell, D. A. Dixon, E. B. Garner III, J. C. Gordon, T. Nakagawa, K. C. Ott, J. P. Robinson, M. Vasiliu, *Science* **2011**, *331-334*, 1426–1429; d) C. Reller, F. O. R. L. Mertens, *Angew. Chem. Int. Ed.* **2012**, *51*, 11731–11735; *Angew. Chem.* **2012**, *124*, 11901–11905; e) Y. Tan, X. Yu, *RSC Adv.* **2013**, *3*, 23879–23894; f) E. Leitao, I. Manners, *Eur. J. Inorg. Chem.* **2015**, 2199–2205.
[18] a) D. W. Stephan, *Science* **2016**, *354*, aaf7229; b) P. P. Power, *Nature* **2010**, *463*, 171–177; c) M.-A. Légaré, C. Pranckevicius, H. Braunschweig, *Chem. Rev.* **2019**, https://doi.org/10.1021/acs.chemrev.8b00561; d) R. L. Melen, *Science* **2019**, *363*, 479–484.
[19] A. P. M. Robertson, E. M. Leitao, I. Manners, *J. Am. Chem. Soc.* **2011**, *133*, 19322–19325.
[20] As comparison, amino–borane $NH_2{=}BH_2$ was already addressed as non-innocent intermediate by computational studies: a) P. M. Zimmerman, A. Paul, Z. Zhang, C. B. Musgrave, *Inorg. Chem.* **2009**, *48*, 1069–1081; b) T. Malakar, L. Roy, A. Paul, *Chem. Eur. J.* **2013**, *19*, 5812–5817; c) S. Bhunya, P. M. Zimmerman, A. Paul, *ACS Catal.* **2015**, *5*, 3478–3493.
[21] E. M. Leitao, N. E. Stubbs, A. P. M. Robertson, H. Helten, R. J. Cox, G. C. Lloyd-Jones, I. Manners, *J. Am. Chem. Soc.* **2012**, *134*, 16805–16816.
[22] N. E. Stubbs, A. Schäfer, A. P. M. Robertson, E. M. Leitao, T. Jurca, H. A. Sparkes, C. H. Woodall, M. F. Haddow, I. Manners, *Inorg. Chem.* **2015**, *54*, 10878–10889.
[23] A. K. Swarnakar, C. Hering-Junghans, M. J. Ferguson, R. McDonald, E. Rivard, *Chem. Sci.* **2017**, *8*, 2337–2343.
[24] G. C. Welch, R. R. S. Juan, J. D. Masuda, D. W. Stephan, *Science* **2006**, *314*, 1124–1126.
[25] D. W. Stephan, *Acc. Chem. Res.* **2015**, *48*, 306–316.
[26] a) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2010**, *49*, 46–76; *Angew. Chem.* **2010**, *122*, 50–81; b) D. W. Stephan, G. Erker, *Angew. Chem. Int. Ed.* **2015**, *54*, 6400–6441; *Angew. Chem.* **2015**, *127*, 6498–6541.
[27] S. J. Geier, T. M. Gilbert, D. W. Stephan, *Inorg. Chem.* **2011**, *50*, 336–344.
[28] L. Winner, W. C. Ewing, K. Geetharani, T. Dellermann, B. Jouppi, T. Kupfer, M. Schäfer, H. Braunschweig, *Angew. Chem. Int. Ed.* **2018**, *57*, 12275–12279; *Angew. Chem.* **2018**, *130*, 12455–12459.
[29] X. Yang, L. Zhao, T. Fox, Z.-X. Wang, H. Berke, *Angew. Chem. Int. Ed.* **2010**, *49*, 2058–2062; *Angew. Chem.* **2010**, *122*, 2102–2106.
[30] X. Yang, T. Fox, H. Berke, *Tetrahedron* **2011**, *67*, 7121–7127.
[31] a) B. L. Allwood, H. Shahriari-Zavareh, J. F. Stoddart, D. J. Williams, *J. Chem. Soc. Chem. Commun.* **1984**, 1461–1464; b) B. Carboni, L. Monnier, *Tetrahedron* **1999**, *55*, 1197–1248, and references herein.
[32] X. Wang, W. Yao, D. Zhou, H. Fan, *Mol. Phys.* **2013**, *111*, 3014–3024.
[33] Another fully theoretical paper was published by Musgrave and co-workers on the reduction of CO_2 with ammonia–borane: P. M. Zimmerman, Z. Zhang, C. B. Musgrave, *Inorg. Chem.* **2010**, *49*, 8724–8728.
[34] W. Xu, H. Fan, G. Wu, P. Chen, *New J. Chem.* **2012**, *36*, 1496–1501.
[35] X. Yang, T. Fox, H. Berke, *Chem. Commun.* **2011**, *47*, 2053–2055.
[36] X. Yang, T. Fox, H. Berke, *Org. Biomol. Chem.* **2012**, *10*, 852–860.
[37] G. Ménard, D. W. Stephan, *J. Am. Chem. Soc.* **2010**, *132*, 1796–1797.
[38] X. Chen, J.-C. Zhao, S. G. Shore, *J. Am. Chem. Soc.* **2010**, *132*, 10658–10659.
[39] The interaction and reactivity of BH_3 with ammonia–borane was previously studied computationally: M. T. Nguyen, V. S. Nguyen, M. H. Matus, G. Gopakumar, D. A. Dixon, *J. Phys. Chem. A* **2007**, *111*, 679–690.
[40] H. Li, N. Ma, W. Meng, J. Gallucci, Y. Qiu, S. Li, Q. Zhao, J. Zhang, J.-C. Zhao, X. Chen, *J. Am. Chem. Soc.* **2015**, *137*, 12406–12414.
[41] M. M. Hansmann, R. L. Melen, D. S. Wright, *Chem. Sci.* **2011**, *2*, 1554–1559.
[42] A. Jana, C. Schulzke, H. W. Roesky, *J. Am. Chem. Soc.* **2009**, *131*, 4600–4601.
[43] The 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; *Angew. Chem.* **2009**, *121*, 2235–2239.
[44] K. J. Sabourin, A. C. Malcolm, R. McDonald, M. J. Ferguson, E. Rivard, *Dalton Trans.* **2013**, *42*, 4625–4632.

[45] N. E. Stubbs, T. Jurca, E. M. Leitao, C. H. Woodall, I. Manners, *Chem. Commun.* **2013**, *49*, 9098 – 9100.
[46] A. J. M. Miller, J. E. Bercaw, *Chem. Commun.* **2010**, *46*, 1709 – 1711.
[47] G. R. Whittell, E. I. Balmond, A. P. M. Robertson, S. K. Patra, M. F. Haddow, I. Manners, *Eur. J. Inorg. Chem.* **2010**, 3967 – 3975.
[48] F. H. Stephens, R. T. Baker, M. H. Matus, D. J. Grant, D. A. Dixon, *Angew. Chem. Int. Ed.* **2007**, *46*, 746 – 749; *Angew. Chem.* **2007**, *119*, 760 – 763.
[49] The borenium-cation intermediate has recently been trapped and characterized: R. J. Less, R. García-Rodríguez, H. R. Simmonds, L. K. Allen, A. D. Bond, D. S. Wright, *Chem. Commun.* **2016**, *52*, 3650 – 3652.
[50] S. Bhunya, A. Banerjee, R. Tripathi, N. N. Nair, A. Paul, *Chem. Eur. J.* **2013**, *19*, 17673 – 17678.
[51] O. J. Metters, A. M. Chapman, A. P. M. Robertson, C. H. Woodall, P. J. Gates, D. F. Wass, I. Manners, *Chem. Commun.* **2014**, *50*, 12146 – 12149.
[52] H. K. Lingam, C. Wang, J. C. Gallucci, X. Chen, S. G. Shore, *Inorg. Chem.* **2012**, *51*, 13430 – 13436.
[53] D. W. Himmelberger, C. W. Yoon, M. E. Bluhm, P. J. Carroll, L. G. Sneddon, *J. Am. Chem. Soc.* **2009**, *131*, 14101 – 14110.
[54] W. C. Ewing, A. Marchione, D. W. Himmelberger, P. J. Carroll, L. G. Sneddon, *J. Am. Chem. Soc.* **2011**, *133*, 17093 – 17099.
[55] Q. Zhou, W. Meng, J. Yang, H. Du, *Angew. Chem. Int. Ed.* **2018**, *57*, 12111 – 12115; *Angew. Chem.* **2018**, *130*, 12287 – 12291.
[56] H. J. Cowley, M. S. Holt, R. L. Melen, J. M. Rawson, D. S. Wright, *Chem. Commun.* **2011**, *47*, 2682 – 2684.
[57] R. J. Less, H. R. Simmonds, S. B. J. Dane, D. S. Wright, *Dalton Trans.* **2013**, *42*, 6337 – 6343.
[58] R. J. Less, H. R. Simmonds, D. S. Wright, *Dalton Trans.* **2014**, *43*, 5785 – 5792.
[59] Z. Lu, L. Schweighauser, H. Hausmann, H. A. Wegner, *Angew. Chem. Int. Ed.* **2015**, *54*, 15556 – 15559; *Angew. Chem.* **2015**, *127*, 15777 – 15780.
[60] L. Schweighauser, H. A. Wegner, *Chem. Eur. J.* **2016**, *22*, 14094 – 14103.
[61] The catalytic effect of borane (BH_3) was computationally investigated for dehydrogenation of cyclic amine–boranes: K. Sen, T. Banu, T. Debnath, D. Ghosh, A. K. Das, *RSC Adv.* **2014**, *4*, 21924 – 21938.
[62] S. Bhunya, A. Paul, *ChemCatChem* **2017**, *9*, 3870 – 3879.
[63] K. A. Erickson, D. S. Wright, R. Waterman, *J. Organomet. Chem.* **2014**, *751*, 541 – 545.
[64] N. L. Dunn, M. Ha, A. T. Radosevich, *J. Am. Chem. Soc.* **2012**, *134*, 11330 – 11333.
[65] G. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *Angew. Chem. Int. Ed.* **2014**, *53*, 4633 – 4637; *Angew. Chem.* **2014**, *126*, 4721 – 4725.
[66] G. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *ACS Catal.* **2016**, *6*, 4859 – 4870.
[67] J. R. Khusnutdinova, D. Milstein, *Angew. Chem. Int. Ed.* **2015**, *54*, 12236 – 12273; *Angew. Chem.* **2015**, *127*, 12406 – 12445.
[68] G. Zeng, S. Maeda, T. Taketsugu, S. Sakaki, *J. Am. Chem. Soc.* **2016**, *138*, 13481 – 13484.
[69] C. C. Chong, H. Hirao, R. Kinjo, *Angew. Chem. Int. Ed.* **2014**, *53*, 3342 – 3346; *Angew. Chem.* **2014**, *126*, 3410 – 3414.
[70] C. Appelt, J. C. Slootweg, K. Lammertsma, W. Uhl, *Angew. Chem. Int. Ed.* **2013**, *52*, 4256 – 4259; *Angew. Chem.* **2013**, *125*, 4350 – 4353.
[71] J. Possart, W. Uhl, *Organometallics* **2018**, *37*, 1314 – 1323.
[72] Z. Mo, A. Rit, J. Campos, E. L. Kolychev, S. Aldridge, *J. Am. Chem. Soc.* **2016**, *138*, 3306 – 3309.
[73] K. Wang, L.-J. Cheng, J.-G. Zhang, X.-B. Yu, *Int. J. Hydrogen Energy* **2018**, *43*, 4177 – 4185.
[74] M. Boudjelel, E. D. S. Carrizo, S. Mallet-Ladeira, S. Massou, K. Miqueu, G. Bouhadir, D. Bourissou, *ACS Catal.* **2018**, *8*, 4459 – 4464.
[75] F. Bertini, V. Lyaskovskyy, B. J. J. Timmer, F. J. J. de Kanter, M. Lutz, A. W. Ehlers, J. C. Slootweg, K. Lammertsma, *J. Am. Chem. Soc.* **2012**, *134*, 201 – 204.
[76] There are two other reports on P-based FLPs about catalytic dehydrogenation of amine–boranes. However, given that the Lewis acid is zirconium-based, this is not treated: a) A. M. Chapman, M. F. Haddow, D. F. Wass, *J. Am. Chem. Soc.* **2011**, *133*, 8826 – 8829; b) O. J. Metters, S. R. Flynn, C. K. Dowds, H. A. Sparkes, I. Manners, D. F. Wass, *ACS Catal.* **2016**, *6*, 6601 – 6611.
[77] S. Li, G. Li, W. Meng, H. Du, *J. Am. Chem. Soc.* **2016**, *138*, 12956 – 12962.
[78] S. Li, W. Meng, H. Du, *Org. Lett.* **2017**, *19*, 2604 – 2606.
[79] Q. Zhou, L. Zhang, W. Meng, X. Feng, J. Yang, H. Du, *Org. Lett.* **2016**, *18*, 5189 – 5191.
[80] M. W. Lui, N. R. Paisley, R. McDonald, M. J. Ferguson, E. Rivard, *Chem. Eur. J.* **2016**, *22*, 2134 – 2145.
[81] Y. Guo, X. He, Z. Li, Z. Zou, *Inorg. Chem.* **2010**, *49*, 3419 – 3423.
[82] V. Sumerin, F. Schulz, M. Atsumi, C. Wang, M. Nieger, M. Leskelä, T. Repo, P. Pyykkö, B. Rieger, *J. Am. Chem. Soc.* **2008**, *130*, 14117 – 14119.
[83] G. Ma, G. Song, Z. H. Li, *Chem. Eur. J.* **2018**, *24*, 13238 – 13245.

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