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Metal-free ammonia borane dehydrogenation catalyzed by a bisborane Lewis acid

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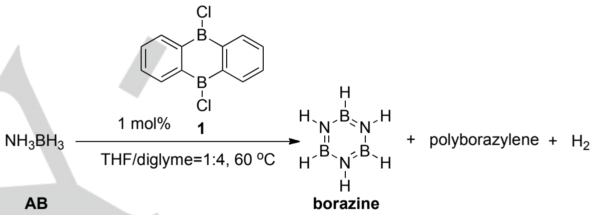
Dedication ((optional))

Abstract: The storage of energy in a safe and environmentally benign way is one of the challenges of today's society. Ammonia borane (AB = NH_3BH_3) has been proposed as a possible candidate for chemical storage of hydrogen. However, the efficient release is still an active field of research. Herein, we present a metal-free bisborane Lewis acid catalyst, which promotes the evolution of up to 2.5 equiv. of H_2/AB. The catalyst can be re-used multiple times without loss of activity. The moderate temperature of 60ºC required allows controlling the supply of H_2 on demand simply by heating and cooling. Mechanistic studies give preliminary insights into kinetics and mechanism of the catalytic reaction.

Ammonia borane (AB = NH_3BH_3) is an air- and moisture-stable solid of 19.6% gravimetric hydrogen content. Recently, it received rapidly expanding attention due to its potential applications in chemical hydrogen storage.[1-6] Although the release of H_2 from AB takes place thermally without any catalysts, the main drawbacks are high temperatures (150ºC for > 1 equiv. H_2)[2] and slow reaction rates which encumber the practical use of AB as a hydrogen-storage material.[7] Thus, a number of catalysts, which promote the process at a lower temperature and at an efficient rate, were developed.[8-11] Among these catalysts most contain transition-metals, which can be expensive or have environmental issues.[12-16] Surprisingly, only three examples of metal-free systems have been reported so far. Baker and coworkers reported the dehydrogenation of AB using acids [$B(C_6F_5)_3$, $HOSO_2CF_3$] as catalysts.[17] The Uhl group used a P/Al-based frustrated Lewis pair to achieve the dehydrogenation of AB and amine-boranes.[18] Also, a Lewis base catalyst has been shown to be effective.[19] However, the efficiency of these transition-metal-free systems is limited. In the approach by Baker and coworkers, a 0.5 % catalyst loading resulted in the release of 1.3 equiv. H_2 per AB, and the method presented by the group of Uhl cannot realize the dehydrogenation of AB in a catalytic fashion.

Our success with the bidentate diboranthrene scaffold as catalyst for the inverse electron-demand Diels-Alder reaction[20,21] led us to test 9,10-dichlorodiboranthrene **1** as the first candidate. With its two Lewis acidic sites it has a definite geometry and a rather high Lewis acidity due to the electron withdrawing effect of the Cl substituents. When 1 mol% of **1** was added to a solution of AB in THF/diglyme (1:4) at 60 ºC, vigorous evolution of gas was observed immediately (Scheme 1). The solvent mixture is a compromise between solubility of catalyst **1** and AB combined with a suitable boiling point to conduct the reaction at elongated times at the given temperature. The ^{11}B NMR spectrum of the soluble materials displayed a doublet at 30.5 ppm and a broad singlet at 25.5 ppm,[22] indicating that borazine and its BN-cross-linked oligomers (polyborazylene) were formed as the main by-products.



Scheme 1. Dehydrogenation of AB catalyzed by the bidentate catalyst 9,10-dichlorodiboranthrene **1**.

An inverted buret was introduced to quantify the amount of H_2 generated from our catalytic system by displacing water. After 7 h, 2.46 equiv. of H_2 per AB were obtained with 5 mol% of **1**. As comparison, the employment of 25 mol% $B(C_6F_5)_3$ or $HOSO_2CF_3$ as catalyst resulted in the formation of cyclotriborazane (CTB)[23] and *B*-(cyclodiborazanyl)-aminoborohydride (BCDB),[24] and less than 1 equiv. H_2 was generated in both situations.[17] To the best of our knowledge, this is the first example that a metal-free catalyst liberates over 2 equiv. of H_2 per equiv. of AB. For the transition-metal catalyzed system, Guan *et al.* recently reported that within 24 hours 2.5 eq H_2 was released with 5 mol% iron pincer catalysts,[22] showing that our catalyst is competitive to transition-metal catalysts.

With this promising result conditions were optimized and other catalysts screened (Table 1). The catalyst loading influenced the reaction rate, but only slightly the amount of H_2 generated (entry 1-4). If the reaction is conducted at rt no H_2 evolution was observed (entry 5). The bromo bisboron catalyst **2**[25] effected the release of 1.82 equiv. H_2 after 24 h (entry 6). When methyl-substituted bisboron **3**[26] and **5**[27] were introduced, less H_2 evolution was observed (entry 7, 9). Also, the arylbis(borohydride) compound **6**[28] was tested as catalyst (entry 10). Under the same conditions, only 0.67 eq H_2 was obtained with 10 mol% **6** as catalyst. The ^{11}B NMR of the reaction solution showed a mixture of borazine,

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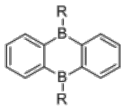
cyclotriborazane (CTB), *B*-(cyclodiborazanyl)-aminoborohydride (BCDB), polyborazylene and $LiBH_4$. The lower efficiency of **6** could be due to the formation of $LiBH_4$, which influenced the reactivity of the catalyst. With the *para* derivative **7**[29] similar results were obtained (entry 11). With 5 mol% of the monodentate Lewis acid $B(C_5F_5)_3$ only 0.68 eq H_2 were formed (entry 12). Hydrochloric acid (HCl), which could be a decomposition product of **1**, generated only 0.94 eq H_2 (entry 13).

Table 1. Optimization studies. Screening of catalysts and conditions.

Entry[a]	Catalyst (mol%)	T/ºC	t/h	H_2/eq[b]
1	**1** (5)	60	7	2.46
2	**1** (2)	60	24	2.20
3	**1** (1)	60	24	1.94
4	**1** (0.5)	60	24	1.82
5	**1** (5)	rt	7	–
6	**2** (5)	60	24	1.82
7	**3** (5)	60	24	1.43
8	**4** (1)	60	24	0.48
9	**5** (5)	60	24	1.02
10	**6** (10)	60	24	0.67
11	**7** (5)	60	24	0.32
12	$B(C_5F_5)_3$ (5)	60	24	0.68
13	HCl (10)	60	24	0.94
14	-	60	24	0.30

[a] Reaction conditions: The reaction was performed in THF/diglyme(1/4) at 60 ºC in a Schlenk tube. The starting material ammonia borane was a crystalline solid. [b] The amount of H_2 was measured by displacing water from an inverted buret.



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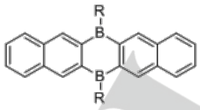

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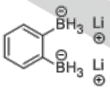

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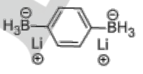

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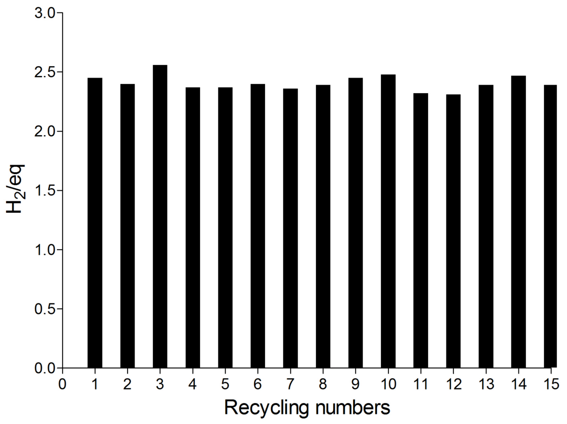
To prove the superiority of the bidentate nature, several analogous monodentate Lewis acid were tested (Table 2, entry 2-4). Under the same conditions, the catalyst loading was twice as for **1**. However, the catalytic efficiencies were not comparable to the bidentate catalyst. Interestingly, the morphology of the AB has a significant influence on the catalytic efficiency. For initial screening experiments (Table 1, entry 1) crystalline AB was used. When in a second batch a powder-type AB was introduced, a shorter reaction time was achieved (Table 2, entry 1).

Table 2. Screening of monodentate boronchlorid catalysts.

Entry [a]	Catalyst (mol%)	T/ºC	t/h	H_2/eq [b]
1	**1** (5)	60	4	2.36
2	BCl_3 (10)	60	24	1.85
3	$BPhCl_2$ (10)	60	10	2.07
4	BPh_2Cl (10)	60	14	2.11

[a] Reaction conditions: The reaction was performed in THF/diglyme (1/4) at 60 ºC in a Schlenk tube. The starting material ammonia borane was a powder. [b] The amount of H_2 was measured by displacing water from an inverted buret.

Catalyst **1** stayed active under the catalytic conditions and can be reused multiple times (Figure 1, top). After completion of the H_2 evolution, a new batch of AB was added. This procedure was repeated for 15 times without any significant loss of activity of the catalyst. Although insoluble polyborazylene built up during these multiple transformations no inhibition of the catalytic activity was observed. For practical applications it might be useful to be able to start and stop the evolution of H_2 on demand. Here, the necessity to heat the reaction to a moderate temperature of 60 ºC displays an advantage. The reaction can be efficiently stopped if kept at rt and started when heated to 60 ºC. This allows one to reversibly start and stop the dehydrogenation on demand until all the AB is consumed (Figure 1, bottom). The reaction can also be done at different concentrations (0.13 to 1.0 M AB solution, see Supporting Information for details).



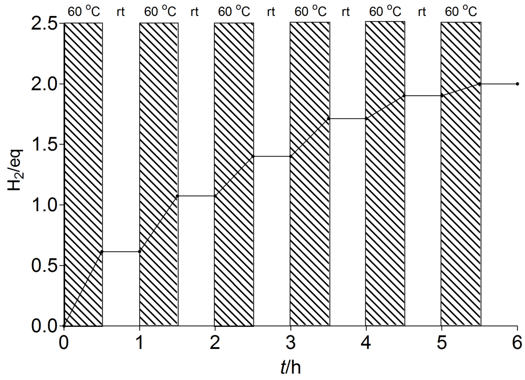


Figure 1. Multiple cycles using the same catalyst (top). Start/stop experiment of hydrogen release controlled by temperature (bottom, 0.25 M solution of AB).

To gain insights into the mechanism, the AB dehydrogenation reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy. A mixture of 1 equiv. **1** and 3 equiv. AB in THF-d_8 formed immediately ammonia monochloroborane (NH_3BH_2Cl) (see Supporting Information for assignment).[30] The formation of NH_3BH_2Cl can be rationalized by a hydride attack of AB to the boron center in **1** and subsequent addition of the chloride to the boron center of AB.

The consumption of ammonia borane and its isotopologues (ND_3BH_3, NH_3BD_3, ND_3BD_3) in the presence of 5% **1** at 60ºC were monitored by ^{11}B-NMR spectroscopy (Figure 2). The result of the individual KIEs [$(K_{NH3BH3}/K_{ND3BH3}) \times (K_{NH3BH3}/K_{NH3BD3})$] = 1.76(3) × 1.78(9) = 3.15(4) equals the KIE observed for the doubly labelled substrate [(K_{NH3BH3}/K_{ND3BD3})] = 2.88(5), suggesting a mechanism where B-H and N-H bonds are involved simultaneously in the rate-determining step.

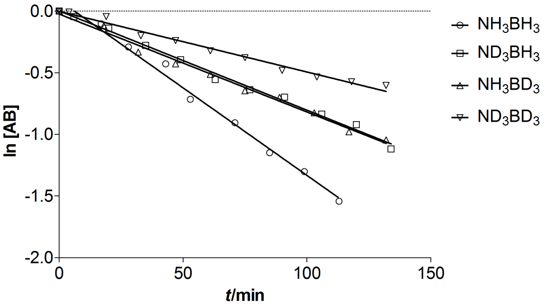
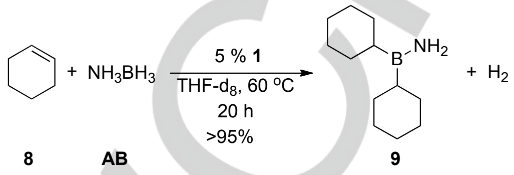


Figure 2. Dehydrogenation kinetics of NH_3BH_3 and its isotopomers (0.25 M in THF/diglyme) at 60°C in the presence of 5 mol% **1**.

Cyclohexene (**8**) was added to the reaction to trap potential intermediates.[24] A mixture of cyclohexene (**8**) and AB (1:1) with 5 mol% of **1** in THF-d_8 was heated at 60 ºC for 20 h (Scheme 2). All cyclohexene (**8**) was converted to Cy_2BNH_2 **9**, which is confirmed by a signal at 48 ppm in the ^{11}B-NMR spectrum, supporting the formation of aminoborane (NH_2BH_2) as intermediate. Similar observations have been made for transition metal based systems, in cases with more than 2 equiv. of H_2 production.[24,32]



Scheme 2. Trapping experiments with cyclohexene (**8**).

The kinetics have been investigated by monitoring the disappearance of AB by ^{11}B NMR spectroscopy. The reaction is faster in the beginning and slows down towards the end of the transformation. The depletion rate of AB [$(3.7 \pm 0.1) \times 10^{-5}$ M/s] is reduced after ~50% consumption of AB similar to others.[21] Experiments with variable concentrations of **1** and AB revealed that the catalytic dehydrogenation of AB is first order in **1** and zero order in AB. Interestingly, with progression of the reaction, the transformation seems to deviate from this reaction order.

A mechanism is proposed in Figure 3. First, an exchange of chloride with hydrogen occurs on the boron in **1** as NH_3BH_2Cl was observed by the NMR-studies (see Supporting Information). The interaction of **1** with AB forms an AB-bound three-center/two-electron adduct **B** with ammonia borane, which was responsible for the initiation of the dehydrogenation. Following a concerted mechanism, dihydrogen and NH_2BH_2 were released through transition state **C**, which should be the rate-determining step.[17a] This pathway is consistent with our kinetic studies that B-H and N-H bond are both involved in the rate-determining step (Figure 2). DFT computations[32] revealed that the second B-atom supports the coordination of AB (complex **B**) by stabilizing the negative charge on the catalytic active site. The computation of the isodesmic reaction revealed a 2.5 kcal mol^{-1} higher stabilization of the three-centre/two-electron bond of AB to catalyst **1** compared to e.g. BPh_2Cl. A simultaneous activation involving both B-atoms resulted in a much higher energy complex (see Supporting Information for details). The further dehydrogenation of NH_2BH_2 is thought to follow a similar mechanism as for transition-metal catalysts,[17b,33] since the same intermediates were traced by NMR studies (see Supporting Information).

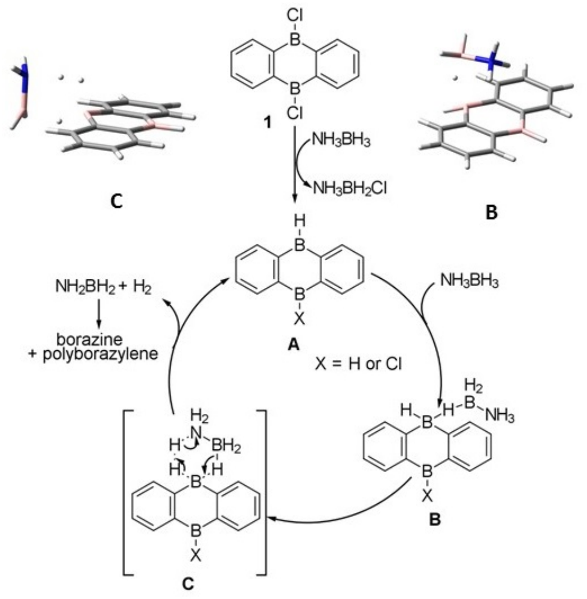


Figure 3. Proposed mechanism for the first step of the catalytic dehydrogenation of ammonia borane. The shown geometry optimizations of **B** and **C** were computed on a B3LYP-D3 level with a 6-31++G(d,p) basis set.[34,35]

In summary, we have developed a bisborane Lewis acid catalyst releasing 2.46 equiv. H_2 per AB, which is the highest amount of H_2 release from AB among all the metal-free systems reported. The catalytic system can be re-used multiple times without loss of activity. The dehydrogenation can be initiated and stopped on demand simply by heating to 60 ºC or cooling to rt. The high effectiveness of the bis-borane catalyst **1** originates from an intramolecular stabilization of an initial three-center/two-electron complex with AB, which is supported by computations. The proposal is consistent with the kinetic data and the trapping experiments. Future work is directed to further study the mechanism and to apply the dehydrogenation of AB by a bisborane Lewis acid in energy storage systems.

Experimental Section

Catalyst **1** (1.0 mg, 0.0041 mmol, 1.0 mol%) and ammonia borane (12.3 mg, 0.399 mmol, 1.00 equiv.) were mixed in solution of THF (0.4 mL) and diglyme (1.6 mL) at rt in a Schlenk tube. The tube was sealed and heated at 60 ºC for 24 h. The reaction can be analyzed by NMR spectroscopy and the amount of H_2 evolved by attachment to an inverse measuring buret with a thin Tygon® tubing.

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Keywords: Catalysis • Ammonia borane • Lewis acid • Dehydrogenation • Hydrogen storage

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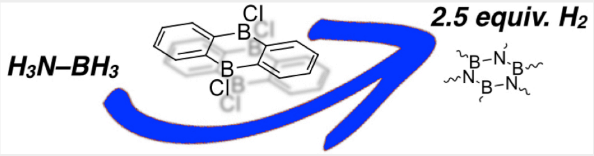

A highly efficient bisborane Lewis acid catalyst is presented releasing 2.46 equiv. H_2 per $H_3N–BH_3$ (AB) molecule. The catalytic system can be re-used multiple times without loss of activity. Furthermore, the dehydrogenation can be initiated and stopped on demand simply be heating to 60 °C or cooling to room temperature. Mechanistic studies have been done to elucidate the mode of action of the bisborane Lewis acid.

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