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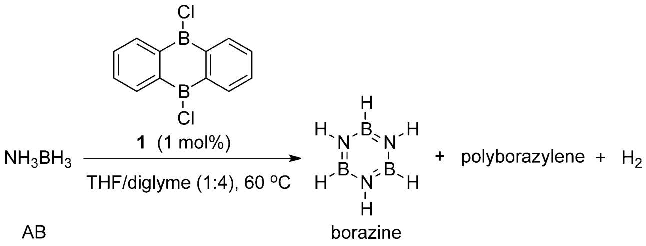
Metal-Free Ammonia–Borane Dehydrogenation Catalyzed by a Bis(borane) Lewis Acid

*Zhenpin Lu, Luca Schweighauser, Heike Hausmann, and Hermann A. Wegner**

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

Ammonia–borane ($AB = NH_3BH_3$) is an air- and moisture-stable solid with a gravimetric hydrogen content of 19.6%. Recently, it received rapidly increasing attention owing 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 (150°C 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 that promote the process at a lower temperature and at an efficient rate have been developed.[8–11] Most of these catalysts contain transition metals, which can be expensive or lead to environmental issues.[12–16] Surprisingly, only three examples of metal-free systems have been reported thus far. Baker and co-workers reported the dehydrogenation of AB using acids [$B(C_6F_5)_3$, $HOSO_2CF_3$] as catalysts.[17] Uhl et al. used a P/Al-based frustrated Lewis pair to achieve the dehydrogenation of AB and amine–boranes.[18] Furthermore, 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 co-workers, a 0.5 mol% catalyst loading resulted in the release of 1.3 equivalents H_2 per AB molecule, and with the method developed by Uhl et al., the dehydrogenation of AB cannot be achieved in catalytic fashion.

Because of our success with the diboraanthracene scaffold as a catalyst for the inverse-electron-demand Diels–Alder reaction,[20,21] we used 9,10-dichlorodiboraanthracene **1** for first experiments on the release of H_2 from AB. With its two Lewis acidic sites, it has a definite geometry and a rather high Lewis acidity owing 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°C, vigorous evolution of gas was observed immediately (Scheme 1). The solvent mixture is a compromise between the solubilities of catalyst **1** and AB and a suitable boiling point to run the reaction for longer periods of time 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 9,10-dichlorodibora-anthracene **1**.

The amount of H_2 generated from our catalytic system was quantified by the displacement of water in an inverted burette. After 7 h, 2.46 equivalents of H_2 per AB were obtained with 5 mol% of **1**. For comparison, the employment of 25 mol% of $B(C_6F_5)_3$ or $HOSO_2CF_3$ as the catalyst resulted in the formation of cyclotriborazane (CTB)[23] and *B*-(cyclodiborazanyl)aminoborohydride (BCDB)[24] and less than 1 equivalent of H_2.[17] To the best of our knowledge, this is the first metal-free catalyst that liberates more than 2 equivalents of H_2 per equivalent of AB. Guan et al. recently reported that within 24 h, 2.5 equivalents of H_2 were released with 5 mol% of iron pincer catalysts,[22] showing that our catalyst is competitive to transition-metal catalysts.

With this promising result in hand, the reaction conditions were optimized and other catalysts screened (Table 1). The catalyst loading influenced the reaction rate, but hardly the amount of H_2 generated (entries 1–4). When the reaction was conducted at room temperature, no H_2 evolution was observed (entry 5). Bromo bis(boron) catalyst **2**[25] effected the release of 1.82 equivalents of H_2 within 24 h (entry 6). When methyl-substituted bis(boron) catalysts **3**[26] and **5**[27] were used, less H_2 evolution was observed (entries 7 and 9). Furthermore, aryl bis(borohydride) **6**[28] was tested as a catalyst (entry 10). Under otherwise identical conditions, only

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[*] Z. Lu, L. Schweighauser, Dr. H. Hausmann, Prof. Dr. H. A. Wegner
Institut für Organische Chemie
Justus-Liebig-Universität Giessen
Heinrich-Buff-Ring 17, 35392 Gießen (Germany)
E-mail: hermann.a.wegner@org.chemie.uni-giessen.de

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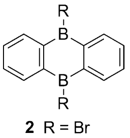
Table 1: Screening of catalysts and reaction conditions.

Entry[a]	Catalyst (mol %)	T [°C]	t [h]	H_2 [equiv][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	$B(C_6F_5)_3$ (5)	60	24	0.68
13	HCl (10)	60	24	0.94
14	–	60	24	0.30

[a] The reactions were performed in THF/diglyme (1:4) at 60 °C in a Schlenk tube. The starting material ammonia–borane was used as a crystalline solid. [b] The amount of H_2 was measured by displacing water from an inverted burette.



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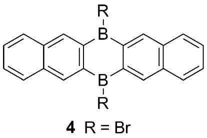
3 R = Me



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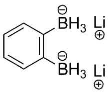
5 R = Me



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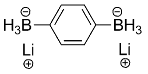

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0.67 equivalents of H_2 were obtained with 10 mol % of **6** as the catalyst. The ^{11}B NMR spectrum of the reaction solution showed a mixture of borazine, CTB, BCDB, polyborazylene, and $LiBH_4$. The lower efficiency of **6** could be due to the formation of $LiBH_4$, which influences the reactivity of the catalyst. With *para* derivative **7**,[29] similar results were achieved (entry 11). With 5 mol % of the monoboron Lewis acid $B(C_6F_5)_3$, only 0.68 equivalents of H_2 were formed (entry 12). Hydrochloric acid (HCl), which could be a decomposition product of **1**, generated only 0.94 equivalents H_2 (entry 13).

To confirm the superiority of the diboron catalyst, several analogous monoboron Lewis acids were tested (Table 2, entries 2–4). To achieve analogous conditions, the catalyst loading was doubled with respect to that of **1**. However, the catalytic efficiencies were not comparable to that of the diboron catalyst. Interestingly, the morphology of AB has a significant influence on the catalytic efficiency. For the initial screening experiments (Table 1, entry 1), crystalline AB was used. When powder-type AB was used in a second set of experiments, shorter reaction times were possible (Table 2, entry 1).

Table 2: Screening of boron chloride catalysts with a single boron atom.

Entry[a]	Catalyst (mol %)	T [°C]	t [h]	H_2 [equiv][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] The reactions were performed in THF/diglyme (1:4) at 60 °C in a Schlenk tube. The starting material ammonia–borane was used as a powder. [b] The amount of H_2 was measured by displacing water from an inverted burette.

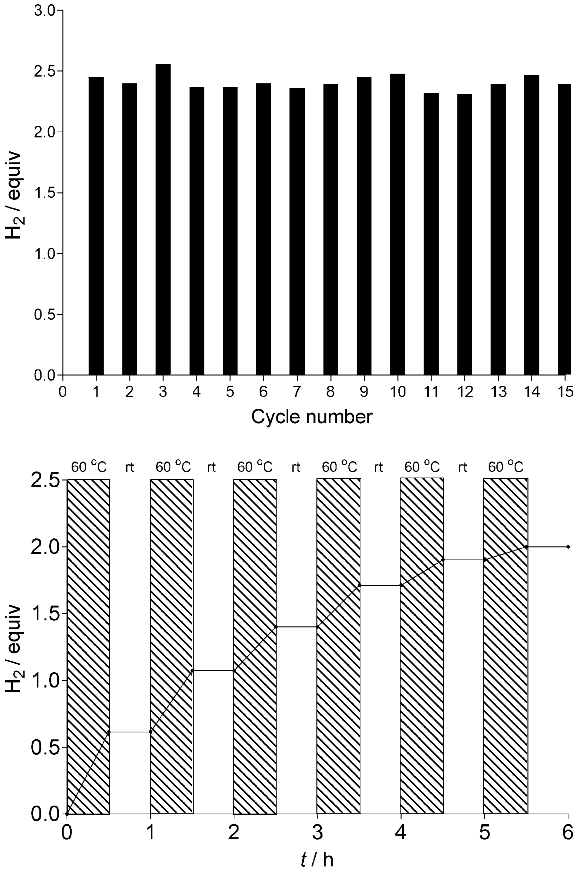


Figure 1. Multiple cycles using the same catalyst (top). Starting and stopping the hydrogen release reaction by temperature control (bottom, 0.25 M solution of AB).

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 15 times without any significant loss of catalyst activity. Although insoluble polyborazylene was 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 °C displays an advantage. The reaction can be efficiently stopped by cooling to room temperature and started by heating to 60 °C. The dehydrogenation can thus be reversibly started and stopped on demand until all the AB has been consumed (Figure 1, bottom). The reaction can also be run at different concentrations (0.13 M to 1.0 M AB solution, see the Supporting Information for details).

To gain insights into the mechanism, the AB dehydrogenation reaction was monitored by ^{1}H and ^{11}B NMR spectroscopy. A mixture of **1** (1 equiv) and AB (3 equiv) in [D_8]THF immediately formed ammonia–monochloroborane (NH_3BH_2Cl; see the Supporting Information for assignments).[30] The formation of NH_3BH_2Cl can be rationalized by a hydride attack of AB at 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 mol% **1** at 60 °C was monitored by ^{11}B NMR spectroscopy (Figure 2). The result of the individual KIEs $[(k_{NH_3BH_3}/k_{ND_3BH_3}) \times (k_{NH_3BH_3}/k_{NH_3BD_3}) = 1.76(3) \times 1.78(9) = 3.15(4)]$ is similar to the KIE observed for the doubly labeled substrate $[(k_{NH_3BH_3}/k_{ND_3BD_3}) = 2.88(5)]$, suggesting a mechanism where both B–H and N–H bonds are involved in the rate-determining step.

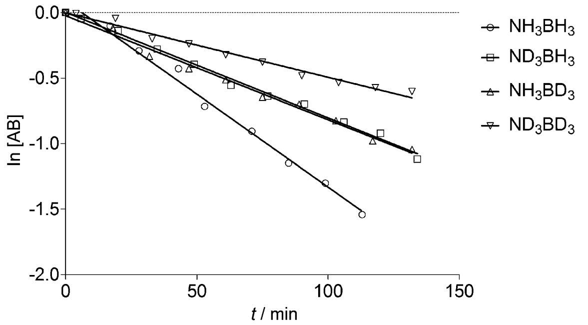
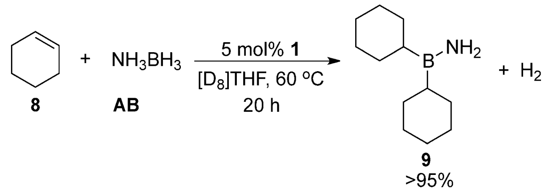


Figure 2. Kinetics of the dehydrogenation of NH_3BH_3 and its isotopologues (0.25 M in THF/diglyme) at 60 °C in the presence of **1** (5 mol%).

Cyclohexene (**8**) was added to the reaction to trap potential intermediates.[24] A mixture of cyclohexene (**8**), AB (1:1), and **1** (5 mol%) in [D$_8$]THF was heated at 60 °C for 20 h (Scheme 2). Cyclohexene (**8**) was fully converted into Cy_2BNH_2 (**9**), which was confirmed by a signal at 48 ppm in the ^{11}B NMR spectrum, supporting the formation of aminoborane (NH_2BH_2) as an intermediate. Similar observations have been made for transition-metal-based systems that enabled the formation of more than 2 equivalents of H_2.[24,31]



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

The reaction kinetics were 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 $[(3.7 \pm 0.1) \times 10^{-5}\,\mathrm{M\,s^{-1}}]$ is reduced after about 50% consumption of AB, as also reported by others.[21] Experiments with various concentrations of **1** and AB revealed that the catalytic dehydrogenation of AB is first order with respect to **1** and zero order in AB.

A mechanism is proposed in Figure 3. First, an exchange of chloride with hydrogen occurs on the boron atom in **1** to yield **A** as the formation of NH_3BH_2Cl was observed by NMR spectroscopy (see the Supporting Information). The interaction of **A** with AB leads to an AB-bound three-center-two-electron adduct **B** with ammonia–borane, which is responsible for the initiation of the dehydrogenation. Following a concerted mechanism, dihydrogen and NH_2BH_2 are released through transition state **C**, which should be the rate-determining step.[17a] This pathway is consistent with our kinetic studies, which had shown that both B–H and N–H bonds are involved in the rate-determining step (Figure 2). DFT computations[32] showed that the second B atom supports the coordination of AB (complex **B**) by stabilizing the negative charge on the catalytically active site. The computation of the isodesmic reaction revealed a 2.5 kcal mol^{-1} higher stabilization of the three-center-two-electron bond of AB to the catalytic species **A** compared to monoboron compounds, for example, BPh_2Cl. Simultaneous activation involving both B atoms resulted in a complex of much higher energy (see the 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] as the same intermediates were observed by NMR spectroscopy (see the Supporting Information).

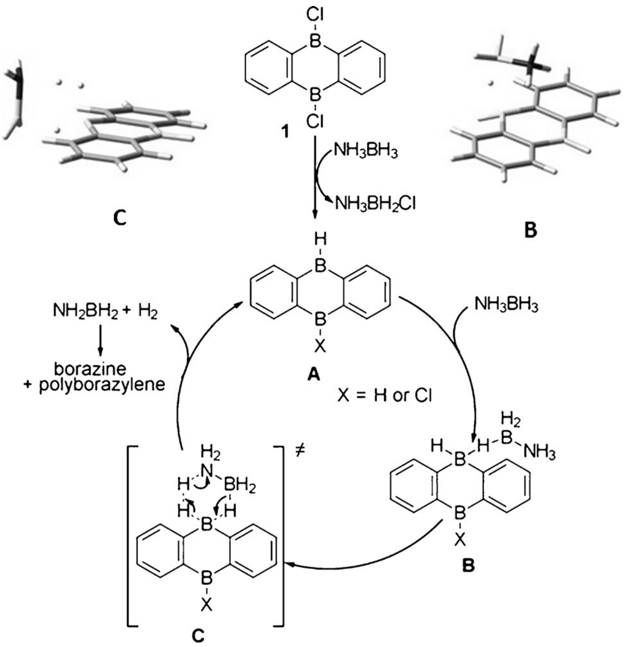


Figure 3. Proposed mechanism for the first step of the catalytic dehydrogenation of ammonia–borane. The shown geometry optimizations of **B** and **C** were computed at the B3LYP-D3 level of theory with a 6-31++G(d,p) basis set.[34,35]

In summary, we have developed a bis(borane) Lewis acid catalyst that enables the release of 2.46 equivalents of H_2 per AB molecule, which is the highest amount of H_2 that has been released from AB by using metal-free systems thus far. The catalytic system can be reused multiple times without loss of activity. The dehydrogenation can be initiated and stopped on demand simply by heating to 60 °C or cooling to room temperature. The high effectiveness of bis(borane) catalyst **1** is due to intramolecular stabilization of the initial three-center-two-electron complex with AB, which was supported by computations. The proposal is consistent with the kinetic data and the trapping experiments. Future work is directed to further studying the mechanism and applying the dehydrogenation of AB by a bis(borane) Lewis acid in energy-storage systems.

Experimental Section

Catalyst **1** (1.0 mg, 4.1 μmol, 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 room temperature in a Schlenk tube. The tube was sealed and heated at 60 °C for 24 h. The reaction mixture was analyzed by NMR spectroscopy, and the amount of H_2 evolved was determined by attachment to an inverse measuring burette with thin Tygon tubing.

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Keywords: ammonia–borane · dehydrogenation · homogeneous catalysis · hydrogen storage · Lewis acids

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