Bisboron Chemistry in Small Molecule Activation and
the Synthesis of Novel BN Aromatics

Inauguraldissertation
zur Erlangung des Doktorgrades der Naturwissenschaftlichen Fachbereiche im
Fachgebiet Organische Chemie der Justus-Liebig-Universität Gießen

vorgelegt von
Zhenpin Lu

aus
China

Betreuer: Prof. Dr. Hermann A. Wegner
Gießen 2016

Dekan:                  Prof. Dr. Volker Wissemann
Erstgutachter:       Prof. Dr. Hermann A. Wegner
Zweitgutachter:    Prof. Dr. Peter R. Schreiner, PhD
Versicherung nach § 17 der Promotionsordnung


Zhenpin Lu

Ort, Datum
Table of Contents

Abstract: ............................................................................................................................. 5
Zusammenfassung: .............................................................................................................. 7
Abstract - Appendix: .......................................................................................................... 9
Zusammenfassung - Anhang: .......................................................................................... 10

Part 1 .................................................................................................................................. 11
Bisboron chemistry in small molecule activation ......................................................... 11

1.1 Introduction .................................................................................................................. 11
   1.11 The recent progress of CO$_2$ activation ................................................................. 11
   1.12 The recent progress of ammonia borane (NH$_3$BH$_3$) dehydrogenation .......... 14
1.2 Previous research in the Wegner group ..................................................................... 16
1.3 Strategy and motivation .............................................................................................. 18
1.4 References .................................................................................................................... 19
1.5 Contribution to the Literature .................................................................................... 21
1.6 Summary of the Results ............................................................................................. 31

Part 2 .................................................................................................................................. 32
The synthesis of novel B, N aromatics ........................................................................... 32

2.1 Introduction .................................................................................................................. 32
2.2 The recent progress of B, N aromatics ....................................................................... 32
2.3 Strategy and motivation .............................................................................................. 38
2.4 References .................................................................................................................... 39
2.5 Contribution to the Literature .................................................................................... 40
2.6 Summary of the Results ............................................................................................. 45
Acknowledgement .......................................................................................................... 46
Abstract:

Bisboron chemistry in small molecule activation

The research on small molecules such as CO$_2$, H$_2$ and NH$_3$BH$_3$ receives currently a lot of attention. For instance, CO$_2$ is largely produced from industrial process and transportation, which leads to serious environmental issues. From the synthetic chemistry point of view, CO$_2$, which is cheaper and abundant in the air, could be utilized as C1 feedstock, by transferring into industrially valuable products. In the first project, I transfer the principle of bidentate activation to a new catalytic reduction of carbon dioxide (Figure I). Depending on the reducing agent selective transformation of CO$_2$ to either methane or methanol can be achieved efficiently in the presence of the bidentate borohydride catalyst Li$_2[1,2$-C$_6$H$_4$(BH$_3$)$_2$]. Treated with Et$_3$SiH / B(C$_6$F$_5$)$_3$, CO$_2$ will be converted to methane, while pinacolborane (HBpin) yields methanol. The reaction can also be conducted in a solvent-free manner. Mechanistic studies reveal a bidentate interaction supported by X-ray analysis of a possible intermediate, which is stabilized by aromatic character in a novel 1,3-dioxo-4,7-diborepine heterocycle.

Another small molecule, H$_2$, has been proposed in the context of green energy, which has great potential to be utilized as an alternative energy source in the future. However, the storage of dihydrogen in a safe, efficient way for on-board systems has been considered as a big challenge. Ammonia borane (AB = NH$_3$BH$_3$) appeared as a promising candidate for hydrogen-storage material due to its unique properties. Unfortunately, the efficient liberation of dihydrogen from AB needs to be facilitated by catalysts. In the second project, I developed a metal-free bis(borane) Lewis acid catalyst (9,10-dichlorodiborantracene) that promotes the generation of up to 2.5 equivalents of H$_2$ per AB molecule (Figure I). The catalyst can be reused for multiple times, and no loss of activity was observed in a fifteen-cycle experiment. The supply of H$_2$ can be controlled simply by heating to 60 °C or cooling to room temperature. Mechanistic studies have been supported by DFT computations and kinetic experiments.
1. Selective reduction of CO₂ to methane or methanol by a bidentate borate catalyst.

2. Catalytic dehydrogenation of ammonia borane by a bis(borane) Lewis acid. A fifteen-cycle experiment with the same catalyst (left). Control of the hydrogen release reaction by temperature (right, 0.25 M solution of ammonia borane).

**Figure I.** Small molecule activation by bisboron compounds.
**Zusammenfassung:**

**Bisborchemie zur Aktivierung niedermolekularer Verbindungen**

Die Forschung zur Aktivierung niedermolekularer Verbindungen wie CO₂, H₂ und NH₃BH₃ erfährt heutzutage große Aufmerksamkeit. CO₂ zum Beispiel fällt in großen Mengen bei industriellen Prozessen oder im Straßenverkehr an, was erhebliche Umweltprobleme nach sich zieht. Aus Sicht der synthetischen Chemie könnte das günstig verfügbare CO₂ aus der Luft als C₁ Rohmaterial verwendet werden, welches weiter in industriell gefragte Produkte umgewandelt werden kann.

Im ersten Projekt habe ich das Prinzip der bidentaten Aktivierung auf eine neue katalytische Reduktion von Kohlenstoffdioxid angewendet (Abbildung I). In Abhängigkeit des Reduktionsmittels ist es möglich CO₂ mittels des bidentaten Borhydrid-Katalysators Li₂[1,2-C₆H₄(BH₃)₂] selektiv in Methan oder Methanol umzuwandeln. Unter Verwendung von Et₃SiH / B(C₆F₅)₃ wird CO₂ zu Methan umgesetzt, während Pinakolboran (HBpin) zur Bildung von Methanol führt. Die Reaktion kann auch ohne Zugabe eines Lösungsmittels durchgeführt werden. Studien zum Mechanismus deuten auf eine bidentate Wechselwirkung hin, was auch durch Röntgenstrukturanalyse eines möglichen Intermediats gestützt wird. Dieses Intermediat wird durch den aromatischen Charakter in einem neuen 1,3-Dioxa-4,7-diborepin-Heterozyklus stabilisiert.


Im zweiten Projekt habe ich einen metallfreien Bis(boran) Lewis-säure-Katalysator entwickelt (9,10-Dichlordiboranthracen), welcher die Erzeugung von bis zu 2,5 Äquivalenten H₂ pro AB Molekül beschleunigt (Abbildung I). In einem 15 Zyklen umfassenden Experiment konnte der Katalysator ohne Aktivitätseinbußen wiederverwendet werden. Die Wasserstofffreisetzung kann durch einfaches Erhitzen auf 60 °C oder Kühlen auf Raumtemperatur gesteuert werden. Mechanistische Studien wurden mit DFT Rechnungen und kinetischen Experimenten gestützt.


Abbildung I. Bisborchemie zur Aktivierung niedermolekularer Verbindungen.
Abstract - Appendix:

The synthesis of novel BN aromatics

Modern technologies went through immense progress based on the design and preparation of novel materials in the past decades. Within rational design, new material can be developed to conform the requirements for different applications. Due to unique electronic properties, π-conjugated organic compounds have been applied in organic electronics. Thus, many carbon-based π-conjugated organic systems such as acenes and polycyclic aromatic hydrocarbons have been intensively investigated. Another possible approach to create novel materials for such applications is to incorporate heteroatoms into the π-conjugated organic system, which would bring remarkable optical as well as electronic properties. Herein, I present the preparation of different substituted (B–N)$_2$-naphthalenes via one-pot reactions of Li$_2$[1,2-C$_6$H$_4$(BH$_3$)$_2$] with azobenzene derivatives (Figure II). Investigation of their photophysical properties revealed a large blue shift in their absorption as well as emission spectra compared to their C-analogues. These new B-N-doped structures are promising candidates in the area of functional materials such as molecular electronics.

Figure II. One-pot synthesis of (B–N)$_2$-naphthalenes.
Zusammenfassung - Anhang:

Die Synthese neuer BN-Aromaten


Abbildung II. Eintopfsynthese von (B-N)$_2$-Isoteren von Naphthalin.
Part 1

Bisboron chemistry in small molecule activation

1.1 Introduction

Small molecules such as CO$_2$, H$_2$, N$_2$, O$_2$ and NH$_3$BH$_3$ have recently gained a lot of interests. There are several reasons involved for the popularity of this research area. Importantly, some of these small molecules are considered as critical players on the global climate change and other environmental issues. Another focus is to develop proper methods utilizing these small molecules as potential energy source for a more sustainable society. As on academic point of view, it remains challenging to achieve the transformation of these molecules into other valuable chemical feedstock due to their relatively stable physical properties.

1.1.1 The recent progress of CO$_2$ activation

CO$_2$ exists in the atmosphere and has been largely produced by industrial process, which is causing seriously environmental issues. Although it is still difficult to solve these problems, the dramatic increase in the amount of CO$_2$ appears as a highly attractive option as a C1 feedstock.$^{[1,2]}$ Unfortunately, the high kinetic and thermodynamic stability of CO$_2$ encumbered the efficient conversion into useful commodities. Therefore, efficient catalytic systems are required to overcome this obstacle.$^{[3]}$

Many transition-metal-based catalysts have been developed and play a dominant role in the reduction of CO$_2$ to methane,$^{[4-7]}$ methanol,$^{[8-10]}$ formaldehyde$^{[11]}$ or formic acid.$^{[12-17]}$ For example, in 2006 the Kawaguchi group developed an efficient zirconium-borane complex 1 as homogeneous catalyst, which could convert CO$_2$ into methane with hydrosilanes as reductant for the first time (Scheme 1).$^{[4]}$ The Guan group achieved the reduction of CO$_2$ to methanol by a nickel catalyst 2 in the presence of catecholborane (HBcat) (Scheme 2).$^{[8]}$

![Scheme 1. Reduction of CO$_2$ with hydrosilanes catalyzed by zirconium-borane complexes 1.](image-url)
Despite of the important progress achieved by transition-metal-based catalysts on the topic of CO$_2$ reduction, it is necessary to develop other metal-free catalytic systems, as main-group elements are relatively cheaper and environmental friendly compared to most of the transition metals. In this regard, many transition-metal-free catalysts have been designed and developed to realize the transformation of CO$_2$ in the past few years. In 2009, Stephan, Erker and coworkers published the first study on the activation of CO$_2$ with the concept of Frustrated Lewis pairs (FLP)\cite{18} and the related carbonic acid derivatives were obtained (Scheme 3).\cite{19}

Subsequently, the O’Hare group reported the first metal-free homogeneous hydrogenation of CO$_2$ to methanol relying on the FLP (B(C$_6$F$_5$)$_3$/TMP (2,2,6,6-tetramethylpiperidine)). However, the efficiency is still limited (Scheme 4).\cite{20} Furthermore, the Fontaine group synthesized a novel phosphine-borane organocatalyst 12 (1-Bcat-2-PPh$_2$-C$_6$H$_4$), which can efficiently achieve the reduction of CO$_2$ in the presence of hydraboranes (Scheme 5), and the related products could be hydrolysed to methanol.\cite{21}
Besides, strong Lewis acid catalysts have been developed and exploited for the research of CO₂ reduction. The Wehmschulte group reported the conversion of CO₂ to methane, toluene and diphenylmethane using \([\text{Et}_2\text{Al}]^+ 13\) as the Lewis acid catalyst with silane as the hydrogen source (Scheme 6).\(^{[22]}\) Based on the same principle, the Müller group can transform CO₂ into benzoic acid, formic acid and methanol catalyzed by a silyl cation compound 17 (Scheme 7).\(^{[23]}\)

**Scheme 6.** Transformation of CO₂ to methane by a Lewis acid catalyst 13.

**Scheme 7.** Reduction of CO₂ to benzoic acid, formic acid and methanol by a silyl cation catalyst 17.

Also N-heterocyclic carbenes have been utilized by Ying and coworkers as catalysts for the conversion of CO₂ to methanol (Scheme 8).\(^{[24]}\) Furthermore, Cantat and coworkers have developed a nitrogen based catalytic system, which can achieve the recycling of CO₂ to formamides in the presence of amines and silanes (Scheme 9).\(^{[25]}\) Very recently, the Ong group synthesized a novel carbodicarbene 22, which can catalyze the methylation of amines with CO₂ in the presence of 9-BBN (Scheme 10).\(^{[26]}\)

**Scheme 8.** Reduction of CO₂ to methane catalyzed by N-heterocyclic carbenes.
1.12 The recent progress of ammonia borane (NH₃BH₃) dehydrogenation

Nowadays we rely on petroleum based fuels for transportation, and the drawbacks of petroleum are their limited availability on earth and the large production of the greenhouse gases as side-products. Within this context, hydrogen appears as an ideal fuel, which generates only water as the oxidation product. For safety reasons, other proper hydrogen sources are needed instead of gas or liquid hydrogen. Ammonia borane (AB = NH₃BH₃) exists as an air- and moisture-stable solid with a content of hydrogen of about 19.6%, and these special natural properties make AB as a potential candidate for hydrogen storage.[27-32]

However, without any catalysts the release of H₂ from AB (for over 1 equiv H₂ per AB) occurs only at high temperature (150 °C) with slow reaction rates, which might be a problem during a practical use.[28] To overcome these issues, many transition-metal-based catalysts have been developed to promote the dehydrogenation of AB under mild conditions and with an efficient rate.[33-36] For example, Guan and coworkers reported a novel iron pincer compound 24 to facilitate the release of H₂ from AB (2.5 equiv H₂ per AB, 60 °C, 5 mol% catalyst loading) (Figure 1).[37] Bertrand and coworkers demonstrated two highly efficient copper complexes 25, 26 to promote the dehydrogenation of AB (2.8 equiv H₂ per AB, rt, 1 mol% catalyst loading), and the catalyst 26 can be re-used for multiple times without loss of reactivity.[38]
Examples for transition-metal-free catalysts are still limited. In 2007, Dixon, Baker and coworkers reported a study on Lewis acids [B(C₆F₅)₃, HOSO₂CF₃] catalyzed AB dehydrogenation, however, only with limited efficiency (1.1 equiv H₂ per AB, 60 °C, 0.5 mol% catalyst loading).[39,40] The Uhl group realized the dehydrogenation of AB and amine-boranes depending on a P/Al based frustrated Lewis pair 27 (Figure 2). The reaction could not be conducted in catalytic fashion.[41] Recently, the Aldridge group reported the first catalytic ammonia borane dehydrogenation by Frustrated Lewis pairs 28, the efficiency (~4 h⁻¹ for ammonia borane) is modest compared to the most reactive transition metal catalysts.[42]

**Figure 1.** Transition-metal-based catalysts for the dehydrogenation of ammonia borane.

**Figure 2.** Main group FLP for ammonia borane dehydrogenation.
1.2 Previous research in the Wegner group

In nature every living system achieves catalytic reactions relying on enzymes. With the effect of multidentate bindings, the enzymes can facilitate different transformations with high effectiveness and selectivity. Although it is difficult to reproduce such the high efficiency from nature in our modern chemistry research, the active mode of multiple interactions in enzymes is worth to be mimicked in new catalytic methods.

Recently, the Wegner group reported the use of a bidentate Lewis acid 29 as highly selective and effective catalyst for the inverse electron-demand Diels-Alder (IEDDA) reaction.\cite{43,44} The general idea is based on the following strategy (Figure 3): The coordination of the bidentate Lewis acid 29 to the 1,2-diazine moiety will lower the energy of the LUMO, which is crucial for the next cycloaddition step. Based on this method, the first Lewis acid catalysed IEDDA reactions have been successfully demonstrated with a variety of dienophiles, and phthalazine as a diene.

![Figure 3. Catalytic principle of the bidentate Lewis acid catalyzed IEDDA reaction of 1,2-diazines.](image)

Interestingly, when substituted furan 31 was selected as dienophile in the bidentate Lewis acid catalysed IEDDA reaction with phthalazines, a cyclopropane substituted dihydronaphthalene 33 formed as the final product (Scheme 11).\cite{45} Supported by DFT computations, a highly reactive \( o \)-quinodimethane like dihydronaphthalene 32 was proposed as intermediate, which goes through a [3,9]-sigmatropic rearrangement to generate the cyclopropane product 33. However, there is no evidence of the formation of naphthalene 34.
Scheme 11. Bidentate Lewis acid catalyzed cyclopropanation domino reaction with proposed mechanism.

Subsequently, the Wegner group further expanded the scope of the bidentate Lewis acid catalyzed IEDDA reaction. When the $\alpha,\beta$-unsaturated aldehydes 35/36 and pyrrolidine 37 were applied as in situ generated enamines in the reaction, an unexpected tricyclic 1,2,3,4-tetrahydronaphthalene 38/39 was obtained as the final product instead of the vinyl naphthalene 40 (Scheme 12).[^46] With allyl amine 41 and aldehyde 42 as starting material, a tricyclic product 43 was delivered in a highly selective manner (Scheme 13).

Scheme 12. Formation of 1,2,3,4-tetrahydronaphthalene from domino IEDDA-DA-reaction.

Scheme 13. Bidentate Lewis acid catalyzed domino IEDDA-DA-reactions.
1.3 Strategy and motivation

As mentioned above, a bidentate Lewis acid \(\text{29}\) was successfully applied in IEDDA reactions with high efficiency. In the bidententate Lewis acid catalysed IEDDA reaction the \(-\text{N}=\text{N}-\) in the substrate was eliminated due to the bidentate coordination. With phthalazines (bearing \(-\text{N}=\text{N}-\) unit) as dienes, the scope of the bidentate Lewis acid IEDDA has been expanded to different dienophile (enamine, furan \textit{et al}). Another approach to expand the concept of bidentate activation is to apply to other coordination substrates which should also have one or two Lewis basic active site, and to apply this bidentate activation in other type of reaction, for example small molecule activation. In this regard, carbon dioxide (\(\text{CO}_2\)) is a possible candidate which consists of two Lewis basic oxygen atoms as proper coordination sites. The activated carbon dioxide complexes are supposed to be further reduced to methane or methanol in the presence of a proper hydrogen source (Figure 3). Although, Stephan and coworkers have demonstrated the interaction of \(\text{CO}_2\) with a Frustrated Lewis pair (FLP), which consists of a bidentate Lewis acid and Lewis base,\(^{[47]}\) such bidentate activation has never been reported for the activation of \(\text{CO}_2\) with catalytic methods before. Therefore, it would be of interest to investigate and develop bidentate catalysts for \(\text{CO}_2\) activation.

![Figure 4. Transformation of \(\text{CO}_2\) to methane or methanol with bidentate activation.](image)

In the second project, I attempted the dehydrogenation of ammonia borane with bidentate Lewis acids as catalysts. Ammonia borane has been proposed as potential hydrogen source. However, the dehydrogenation of ammonia borane is challenging and requires the assist of efficient catalysts. During the former research, many highly efficient transition-metal-based catalysts have been developed for the dehydrogenation of ammonia borane. Very few examples of metal-free catalytic systems have been reported to promote the dehydrogenation of ammonia borane so far, and the efficiencies are not comparable to the transition-metal-based catalysts. The bidentate Lewis acid like \(\text{29}\) has two Lewis acidic sites and a definite geometry, which might have a higher reactivity compared to monodentate Lewis acids. These unique bidentate Lewis acids might bring a new catalytic mode in the dehydrogenation of ammonia borane.
1.4 References


1.5 Contribution to the Literature

Aromaticity as Stabilizing Element in the Bidentate Activation for the Catalytic Reduction of Carbon Dioxide


Copyright ©2015, with the permission from American Chemical Society

“A new transition-metal-free mode for the catalytic reduction of carbon dioxide via bidentate interaction has been developed. In the presence of Li$_2$[1,2-C$_6$H$_4$(BH$_3$)$_2$], CO$_2$ can be selectively transformed to either methane or methanol, depending on the reducing agent. The bidentate nature of binding is supported by X-ray analysis of an intermediate analogue, which experiences special stabilization due to aromatic character in the bidentate interaction. Kinetic studies revealed a first-order reaction rate. The transformation can be conducted without any solvent.”
Aromaticity as Stabilizing Element in the Bidentate Activation for the Catalytic Reduction of Carbon Dioxide

Zhenpin Lu,1 Heike Hausmann,1 Sabine Becker,8 and Hermann A. Wegner6,9

1 Institut für Organische Chemie and 2 Institut für Anorganische Chemie, Justus Liebig Universität, Heinrich-Buff-Ring 58, 35392 Giessen, Germany

Supporting Information

ABSTRACT: A new transition-metal-free mode for the catalytic reduction of carbon dioxide via bidentate interaction has been developed. In the presence of \( \text{Li}_{2}[\text{1,2-C}_6\text{H}_4\text{BH}_4]_2 \), \( \text{CO}_2 \) can be selectively transformed to either methane or methanol, depending on the reducing agent. The bidentate nature of binding is supported by X-ray analysis of an intermediate analogue, which experiences special stabilization due to aromatic character in the bidentate interaction. Kinetic studies revealed a first-order reaction rate. The transformation can be conducted without any solvent.

Catalysis has been—and still is—the basis for the success of efficient and sustainable chemical transformations.1 Although there have been tremendous developments over the past centuries, the need for new concepts for catalysis is as high as ever. Most catalytic processes are based on a monodentate interaction between catalyst and substrate. Nature, however, shows that multidentate interactions offer much higher specificity and selectivity.2 Recently, we showed that bidentate Lewis acids are highly selective and effective catalysts for the inverse electron demand Diels–Alder (IEDDA) reaction of 1,2-diazene.3 The usual complication in bidentate catalysis, product inhibition, was circumvented, as the coordinating functionality in the substrate (\( \text{N}=\text{N} \)) was eliminated during the transformation. Carbon dioxide (\( \text{CO}_2 \)), with its two Lewis basic oxygen atoms, should also be an ideal target substrate for bidentate activation (Figure 1). \( \text{CO}_2 \) is highly attractive as a cheap and readily available C1 building block.4

\[
\text{O=C=O} \quad \text{R}_\text{B} \quad \text{BR} \quad \text{R}_\text{B} \quad \text{BR} \quad \text{Hydride Source} \quad \text{Methane} \quad \text{Methanol}
\]

Figure 1. Activation of carbon dioxide by a bidentate catalyst for the conversion to methane or methanol.

The strong bidentate interaction will fixate the \( \text{CO}_2 \) molecule and enhance the electrophilicity of the carbon atom. The drastic change in structure due to the nucleophilic attack, e.g., by a hydride, should change the character of the bidentate interaction and allow regeneration of the catalyst. Stephan and co-workers showed the effective interaction of a bidentate Lewis acid in a frustrated Lewis pair (FLP) with \( \text{CO}_2 \).5 However, it was not possible to transform the complex further in a catalytic fashion to products such as methanol or methane due to its high stability. Besides transition-metal-catalyzed processes for the reduction of \( \text{CO}_2 \), only a few non-transition-metal-based catalysts have been recently presented.6–8 These approaches are mainly based on the aforementioned FLP concept,1,9 strong Lewis acids,10 Lewis bases such as amines,11 or \( \pi \)-heterocyclic carbene.12 Besides the different modes of interaction, all methods allow only the conversion of \( \text{CO}_2 \) to only one type of product, either methane or methanol.

In this report we show that, based on a new activation mode, a bidentate borohydride catalyst is highly effective for both transformations of the reaction to methane or to methanol.

To investigate the above-outlined rationale, different bidentate Lewis acid catalysts, e.g., \( \text{7} \) and \( \text{8} \), which have been highly effective in the IEDDA of 1,2-diazenes, have been tested for the activation of \( \text{CO}_2 \) (Table 1). Triethylsilane (\( \text{Et}_3\text{SiH} \)) was employed as reducing agent with \( \text{B}(\text{C}_6\text{F}_5)_3 \) as activator.16 However, none of the compounds showed catalytic activity.

After a thorough screening, lithium o-phenylbisborate (\( \text{9} \), \( \text{Li}_{2}[\text{1,2-C}_6\text{H}_4\text{BH}_4]_2 \))17 was shown to be an effective candidate. When 10 mol% of \( \text{9} \) (relative to silane \( \text{2} \)) was reacted under an atmosphere of \( \text{CO}_2 \) (1 bar) in the presence of \( \text{2} \), all the silane was consumed (Table 1, entry 1). (\( \text{Et}_3\text{Si} \))\( \text{O} \) (\( \text{4} \)) was the main product, along with (\( \text{Et}_3\text{SiO} \))\( \text{CH}_3 \) (\( \text{5} \)) and \( \text{Et}_3\text{SiOMe} \) (\( \text{6} \)). The presence of \( \text{3} \) was indicated by a singlet at 0.14 ppm by ‘\( \text{H} \) NMR spectroscopy.18 Without \( \text{9} \) or \( \text{B}(\text{C}_6\text{F}_5)_3 \), no conversion of silane \( \text{2} \) was observed, proving the need for both catalysts. The solubility of \( \text{9} \) in \( \text{C}_6\text{D}_6\text{Br} \) is poor; therefore, the reaction was carried out in THF-\( \text{d}_4 \) in order to increase the solubility. No transformation of silane \( \text{2} \) occurred under these conditions (Table 1, entry 2). Complexation of \( \text{B}(\text{C}_6\text{F}_5)_3 \) with THF might decrease the Lewis acidity of \( \text{B}(\text{C}_6\text{F}_5)_3 \), which is critical for the activation of 2. A reduction of the catalyst loading reduced the silane consumption (Table 1, entry 4). This effect could be attributed to the insufficient mixing of the solution and the gas phase, as all optimization reactions were carried out in a NMR tube. Consequently, a larger surface area (running the reaction in a round-bottom Schlenk flask) improved significantly the efficiency of the reaction (Table 1, entry 5). Reducing the loading of catalyst further to 1 mol% of \( \text{9}/\text{B}(\text{C}_6\text{F}_5)_3 \) led to a dramatic decrease of the catalytic efficiency (Table 1, entry 6). However, if the amount of \( \text{B}(\text{C}_6\text{F}_5)_3 \) was increased to 3 mol% and the reaction temperature elevated to 80 °C, the initial activity could be re-installed (Table 1, entry...
Table 1. Optimization of the Catalytic Reduction of CO₂

<table>
<thead>
<tr>
<th>entry</th>
<th>cat.</th>
<th>cat. atm/mol%, ratio cat.:B(C₆F₅)₂</th>
<th>solvent</th>
<th>T/°C</th>
<th>t/h</th>
<th>product/%</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>9</td>
<td>10:1:1</td>
<td>C₅D₅Br</td>
<td>RT</td>
<td>60</td>
<td>69:31: –</td>
</tr>
<tr>
<td>2</td>
<td>9</td>
<td>10:1:1</td>
<td>THF-d₈</td>
<td>RT</td>
<td>24</td>
<td>–:–:–</td>
</tr>
<tr>
<td>3</td>
<td>9</td>
<td>10:1:1</td>
<td>C₅D₅Br</td>
<td>50</td>
<td>18</td>
<td>73:27: –</td>
</tr>
<tr>
<td>4</td>
<td>9</td>
<td>5:1:1</td>
<td>C₅D₅Br</td>
<td>50</td>
<td>40</td>
<td>41:43:1</td>
</tr>
<tr>
<td>5ₕ</td>
<td>9</td>
<td>5:1:1</td>
<td>C₅D₅Br</td>
<td>50</td>
<td>21</td>
<td>81:19: –</td>
</tr>
<tr>
<td>6ₕ</td>
<td>9</td>
<td>1:1:1</td>
<td>C₅D₅Br</td>
<td>50</td>
<td>65</td>
<td>–:–:–</td>
</tr>
<tr>
<td>7</td>
<td>9</td>
<td>1:1:1</td>
<td>C₅D₅Br</td>
<td>80</td>
<td>56</td>
<td>78:22: –</td>
</tr>
<tr>
<td>8ₙ</td>
<td>9</td>
<td>2:1:1</td>
<td>–</td>
<td>80</td>
<td>5 d</td>
<td>58:42: –</td>
</tr>
<tr>
<td>9</td>
<td>10</td>
<td>10:1:1</td>
<td>C₅D₅Br</td>
<td>50</td>
<td>41</td>
<td>18:54:3</td>
</tr>
<tr>
<td>10</td>
<td>11</td>
<td>10:1:1</td>
<td>C₅D₅Br</td>
<td>50</td>
<td>24</td>
<td>4:91: –</td>
</tr>
</tbody>
</table>

*The reaction was performed with CO₂ (1 bar) in a Young NMR tube, unless noted otherwise. †Based on the consumption of 1, determined by ‘H NMR with toluene as an internal standard. ‡The reaction was performed in a 25 mL Schlenk flask. §The yield was determined by GC-MS.

In contrast to 9, B(C₆F₅)₂ is highly moist and air sensitive. Therefore, if the amount of B(C₆F₅)₂ is too low, degradation might further reduce the amount and impede catalysis. The catalytic reduction of CO₂ to CH₄ using 9/ B(C₆F₅)₂ as catalyst can also be done in a solvent-free manner (Table 1, entry 8). All the silane 2 was consumed within 5 days at 80 °C (analyzed by NMR spectroscopy).

The bidentate nature of the catalyst is essential for the high activity. When the monobidentate 10 (LiPPhB₃H) was employed, which is the monodentate analogue to 9, significantly less conversion was observed (Table 1, entry 9). In particular, the amount of (Et₃SiH)₂O (4) was greatly reduced compared to the reaction with the bidentate catalyst 9. Interestingly, when the reaction with 10 was conducted at room temperature (RT), after a rather long induction period, only one turnover was observed (see Supporting Information for details). Superhydride LiBH₄ (11) was also tested as catalyst (Table 1, entry 10). Although it is known that simple borohydrides can activate CO₂, only (Et₃SiO)₂CH₂ (5) was detected as the main product and not methane.

To prove the versatility of our catalyst, an alternative reducing agent, 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (12, HBPin) was tested, which has been applied in the reduction of CO₂ to methanol with transition metal catalysts. With 12 there is no need to add B(C₆F₅)₂ as co-catalyst. Thus, a mixture of 9 (10 mol%) and 12 in THF-d₈ was subjected to CO₂ (1 bar) at RT. After 2 h, MeOBpin 13 was the only CO₂-reduction product detectable. Hydrolysis with D₂O generates methanol, which was unambiguously confirmed by GC. Employment of only 1 mol% of 9 was also effective in the CO₂ reduction, and gave 83% of MeOBpin after 22 h at RT (Scheme 1). Since a higher reaction temperature might increase the efficiency of the catalytic system, the reaction was carried out with 1 mol% catalyst loading at 70 °C. Indeed, 51% conversion of MeOBpin was observed after only 30 min, and a yield of 89% was determined after 3 h by NMR. Simple borohydrides such as LiPPhB₃H, LiBeH₃, or NaBH₄ were less effective (see Supporting Information for details).

A proposed mechanism for the reduction of CO₂ to methane and methanol is shown in Figure 2. First, catalyst 9 forms an adduct with CO₂. Intramolecular hydride transfer generates the boron-bound formate adduct A, which may be further reduced by another hydride to form the acetal compound B. The bidentate nature of the catalyst seems to be important at this stage, in which the intramolecular hydride transfer is promoted as well as the stabilization of the intermediate. In the presence of Et₃SiH, the acetal moiety of intermediate B can be cleaved to give the disilylacetel S, which is the main side product. Ultimately, S is reduced to CH₄. In the presence of pinacol borane, the cyclic acetal is also opened and delivers D. In both cases a catalytically active hydride species is regenerated, closing the catalytic cycle.

The mechanistic proposal was supported by the following experiments. Treatment of 9 in THF–CO₂ solution (1 bar) at RT immediately led to the formation of a precipitate, indicating an interaction between CO₂ and 9. Unfortunately, the poor solubility of the CO₂ adducts even in THF encumbered further characterization by NMR spectroscopy. IR analysis of the CO₂ adduct showed an absorption at 1592 cm⁻¹ attributable to a
be described before. The entire ring is planar and is stabilized by aromaticity, as can be clearly seen in the X-ray structure. An additional hydride is positioned in the para position of the bound benzoic acid in the solid state (Scheme 2, 20 and 21). NMR studies, however, suggest a binding of the hydride at the boron atoms, as two broad signals in the B NMR have been observed. The refinement of the X-ray data shows one molecule in the independent unit of the elementary cell. The structure is disordered: 65% of the molecules are in an upright position, while the others are in the opposite position. Because of that, only the two central oxygen atoms and bromobenzyl residues are fully occupied and impede an exact location of the hydrogen atoms in the structure.

Structure 18 also proves that the bisborate catalyst 9 is capable of conducting the reduction to the alcoholate state, which is then further reduced by the B(C$_5$F$_4$)$_2$ /silane system. Nevertheless, benzaldehyde dimethyl acetal (22) and methyl benzoate (23) have been used as model structures for intermediates A and B in the catalytic cycle (Figure 2). In both cases, the mixture of B(C$_5$F$_4$)$_2$ and Et$_3$SiH induced the formation of toluene, methyl silyl ether, and benzyl silyl ether (Scheme 3). In contrast, no reaction took place when 9 was added without the presence of B(C$_5$F$_4$)$_2$. This observation indicates that the bidentate borate catalyst 9 activates the CO$_2$ while the silane/B(C$_5$F$_4$)$_2$ is responsible for the final catalytic reduction to methane.

We also investigated the kinetics of the catalytic reaction with 9/B(C$_5$F$_4$)$_2$ as catalyst by NMR spectroscopy (see Supporting Information). In both cases, the consumption of Et$_3$SiH, respectively HBPin, showed a first-order reaction rate. In the beginning, the data revealed an induction period of about 30 min. Interestingly, in the case of silane as reducing agent, two different temperature regimes can be observed. At 298 and 323 K, a similar rate is observed, however, with a much faster initiation rate. The same is true for 333 and 345 K, although with a faster reaction rate. At 328 K, a behavior in between can be seen. Therefore, it seems that, in this complex reaction, different steps are not equally accelerated with increasing
temperature, which also includes physical processes, such as gas absorption in the solvent.

In summary, a new transition-metal-free mode of activating CO₂ has been presented. The bidentate borohydride Li₂[1,2-C₆H₅(BH₂)₂] efficiently promotes the selective reduction to either methane or methanol. The selectivity can be controlled by the reducing agent: In the presence of Et₂SiH/B(C₆H₅)₃, CO₂ will be transformed to methane, while pinacolborane (HBpin) delivers methanol. The reaction can be conducted in a solvent-free manner. The bidentate interaction in the catalysis has been supported by X-ray analysis of a possible intermediate. The novel 1,3-dioxo-4,7-dihydroepine heterocycle formed during the bidentate activation step is stabilized by aromaticity. The kinetics of both transformations have been studied, showing a first-order rate law after an initial induction period. For the reduction with Et₂SiH/B(C₆H₅)₃, different rate-determining processes have been observed, depending on the reaction temperature in this highly complex reaction. Further studies to adopt this useful new catalytic metal-free transformation for practical applications are ongoing.

ASSOCIATED CONTENT

Supporting Information
Experimental data; crystallographic data, in CIF format, of 19. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author
*hermann.a.wegner@org.chemie.uni-giessen.de

Notes
The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors thank Peter Radgen and Helmut Rothe, E.ON Technologie & Innovation, for the useful discussions. Financial support by the Swiss National Science Foundation is gratefully acknowledged.

REFERENCES

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


Copyright ©2015, with the permission from John Wiley and Sons

“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$_3$BH$_3$) 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.”
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 = NH₃BH₃) 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 H₂ 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 H₂ on demand simply by heating and cooling. Mechanistic studies give preliminary insights into the kinetics and mechanism of the catalytic reaction.

Ammonia-borane (AB = NH₃BH₃) 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.[1-3] Although the release of H₂ from AB takes place thermally without any catalysts, the main drawbacks are high temperatures (150°C for >1 equiv H₂) and slow reaction rates, which encumber the practical use of AB as a hydrogen-storage material.[4] Thus a number of catalysts that promote the process at a lower temperature and at an efficient rate have been developed.[5-11] Most of these catalysts contain transition metals, which can be expensive or lead to environmental issues.[12-14] 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(CF₃)₄], HOSO₃CF₂ as catalysts.[15] Uhl et al. used a P/Al-based frustrated Lewis pair to achieve the dehydrogenation of AB and amine-boranes.[16] Furthermore, a Lewis base catalyst has been shown to be effective.[10] 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 of H₂ 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,[17,18] we used 9,10-dichlorodiboraanthracene I for first experiments on the release of H₂ 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 I 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 I and AB and a suitable boiling point to run the reaction for longer periods of time at the given temperature. The ¹⁹B NMR spectrum of the solution, materials displayed a doublet at 30.5 ppm and a broad singlet at 25.5 ppm, indicating that borazine and its BN-cross-linked oligomers (polyborazine) were formed as the main by-products.

The amount of H₂ generated from our catalytic system was quantified by the displacement of water in an inverted burette. After 7 h, 2.46 equivalents of H₂ per AB were obtained with 5 mol% of I. For comparison, the employment of 0.8 mol% of B(CF₃)₄ or HOSO₃CF₂ as the catalyst resulted in the formation of cyclostiborazane (CTB)[19] and B-(cyclodiborazanyl)aminoborohydride (BCDB)[20] and less than 1 equivalent of H₂. To the best of our knowledge, this is the first metal-free catalyst that liberates more than 2 equivalents of H₂ per equivalent of AB. Guan et al. recently reported that within 24 h, 2.5 equivalents of H₂ were released with 5 mol% of iron pincer catalysts[21] 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 H₂ generated (entries 1–4). When the reaction was conducted at room temperature, no H₂ evolution was observed (entry 5). Bromo bis(boron) catalyst 2[22] effected the release of 1.82 equivalents of H₂ within 24 h (entry 6). When methyl-substituted bis(boron) catalysts 3[23] and 5[24] were used, less H₂ evolution was observed (entries 7 and 9). Furthermore, aryl bis(borohydride) 6[25] was tested as a catalyst (entry 10). Under otherwise identical conditions, only
Table 1: Screening of catalysts and reaction conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol %)</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>H₂ [equiv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 (5)</td>
<td>60</td>
<td>7</td>
<td>2.46</td>
</tr>
<tr>
<td>2</td>
<td>1 (2)</td>
<td>60</td>
<td>24</td>
<td>2.20</td>
</tr>
<tr>
<td>3</td>
<td>1 (1)</td>
<td>60</td>
<td>24</td>
<td>1.94</td>
</tr>
<tr>
<td>4</td>
<td>0 (0.5)</td>
<td>60</td>
<td>24</td>
<td>1.82</td>
</tr>
<tr>
<td>5</td>
<td>1 (5)</td>
<td>RT</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>2 (5)</td>
<td>60</td>
<td>24</td>
<td>1.82</td>
</tr>
<tr>
<td>7</td>
<td>3 (5)</td>
<td>60</td>
<td>24</td>
<td>1.43</td>
</tr>
<tr>
<td>8</td>
<td>4 (1)</td>
<td>60</td>
<td>24</td>
<td>0.48</td>
</tr>
<tr>
<td>9</td>
<td>5 (5)</td>
<td>60</td>
<td>24</td>
<td>1.02</td>
</tr>
<tr>
<td>10</td>
<td>6 (10)</td>
<td>60</td>
<td>24</td>
<td>0.67</td>
</tr>
<tr>
<td>11</td>
<td>7 (5)</td>
<td>60</td>
<td>24</td>
<td>0.32</td>
</tr>
<tr>
<td>12</td>
<td>B(C₆F₅)₂ (5)</td>
<td>60</td>
<td>24</td>
<td>0.68</td>
</tr>
<tr>
<td>13</td>
<td>HCl (10)</td>
<td>60</td>
<td>24</td>
<td>0.94</td>
</tr>
<tr>
<td>14</td>
<td></td>
<td>60</td>
<td>24</td>
<td>0.30</td>
</tr>
</tbody>
</table>

[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 H₂ was measured by displacing water from an inverted burette.

0.67 equivalents of H₂ were obtained with 10 mol % of 6 as the catalyst. The ³¹B NMR spectrum of the reaction solution showed a mixture of borazine, CTB, BCDB, polyborazylene, and LiBH₄. The lower efficiency of 6 could be due to the formation of LiBH₄, which influences the reactivity of the catalyst. With pure derivative 7, similar results were achieved (entry 11). With 5 mol % of the monoboron Lewis acid B(C₆F₅)₂, only 0.68 equivalents of H₂ were formed (entry 12). Hydrochloric acid (HCl), which could be a decomposition product of 1, generated only 0.94 equivalents H₂ (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).

Catalyst 1 stayed active under the catalytic conditions and can be reused multiple times (Figure 1, top). After completion of the H₂ 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 H₂ 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 ¹H and ¹³B NMR spectroscopy. A mixture of 1 (1 equiv) and AB (3 equiv) in D₂O/THF immediately formed ammonia-monochloroborane (NH₃BH₂Cl; see the Supporting Information for assignments). The formation of NH₃BH₂Cl can be rationalized by a hydride attack of AB at the boron center in 1 and...

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

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst (mol %)</th>
<th>T [°C]</th>
<th>t [h]</th>
<th>H₂ [equiv]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1 (5)</td>
<td>60</td>
<td>4</td>
<td>2.36</td>
</tr>
<tr>
<td>2</td>
<td>BC₂H₂Cl (10)</td>
<td>60</td>
<td>24</td>
<td>0.67</td>
</tr>
<tr>
<td>3</td>
<td>BPK₂Cl (10)</td>
<td>60</td>
<td>10</td>
<td>2.07</td>
</tr>
<tr>
<td>4</td>
<td>BPK₂Cl (10)</td>
<td>60</td>
<td>14</td>
<td>2.11</td>
</tr>
</tbody>
</table>

[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 H₂ 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).
subsequent addition of the chloride to the boron center of AB.

The consumption of ammonia–borane and its isotopologues (ND, BH₃, NH₂BD₃, ND₂BD₃) in the presence of 5 mol% 1 at 60 °C was monitored by ¹¹B NMR spectroscopy (Figure 2). The result of the individual KIEs [(k_{NH3,BH3}/k_{ND2,BD3}) x (k_{NH2,BD3}/k_{ND,BH3}) = 1.76(3) x 1.78(9) = 3.15(4)] is similar to the KIE observed for the doubly labeled substrate [(k_{ND2,BD3}/k_{ND,BH3}) = 2.88(3)], hinting at a mechanism where both B–H and N–H bonds are involved in the rate-determining step.

Cyclohexene (8) was added to the reaction to trap potential intermediates. A mixture of cyclohexene (8), AB (1:1), and I (5 mol %) in D₂(THF) was heated at 60 °C for 20 h (Scheme 2). Cyclohexene (8) was fully converted into Cy₂NH₂B₃H₅ (9), which was confirmed by a signal at 48 ppm in the ¹¹B NMR spectrum, supporting the formation of amino-borane (NH₂BH₃) as an intermediate. Similar observations have been made for transition-metal-based systems that enabled the formation of more than 2 equivalents of H₂. The reaction kinetics were investigated by monitoring the disappearance of AB by ¹¹B NMR spectroscopy. The reaction is faster in the beginning and slows down towards the end of the transformation. The depletion rate of AB [13.7 ± 0.1 x 10⁻⁶ s⁻¹] is reduced after about 50% consumption of AB, as also reported by others. Experiments with various concentrations of 1 and AB revealed that the catalytic dehydrogenation of AB is first order with respect to I 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 NH₂BH₃Cl 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 NH₂BH₃ are released through transition state C, which should be the rate-determining step. 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 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 monoborane compounds, for example, BPh₃Cl. Simultaneous activation involving both B atoms resulted in a complex of much higher energy (see the Supporting Information for details). The further dehydrogenation of NH₂BH₃ is thought to follow a similar mechanism as for transition-metal catalysis as the same intermediates were observed by NMR spectroscopy (see the Supporting Information).

In summary, we have developed a bis(borane) Lewis acid catalyst that enables the release of 2.46 equivalents of H₂ per AB molecule, which is the highest amount of H₂ 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 I 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 I (1.0 mg, 4.1 μmol, 1.0 mol%) and ammonia-borane (12.3 mg, 0.399 mmol, 1.6 eq) 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 H₂ evolved was determined by attachment to an inverse measuring burette with thin Tygon tubing.

Acknowledgments

Funding was provided by the Swiss National Science Foundation.

Keywords: ammonia-borane - dehydrogenation - homogeneous catalysis - hydrogen storage - Lewis acids

How to cite: Angew. Chem. Int. Ed. 2015, 54, 15556–15559
Angew. Chem. 2015, 127, 15777–15780


Received: September 7, 2015
Published online: November 5, 2015
1.6 Summary of the Results

In the first project, I developed a new metal-free mode of CO₂ activation with the bidentate borohydride Li₂[1,2-C₆H₄(BH₃)₂] as catalyst, by which CO₂ can be selectively converted to methane or methanol depending on the reducing agents. When Et₃SiH/B(C₆F₅)₃ were chosen as reagents, CO₂ will be transformed into methane, while pinacolborane (HBpin) gives methanol. The reaction can also be achieved without the addition of any solvents. Mechanistic studies reveal a bidentate interaction supported by X-ray analysis of a possible intermediate, which is stabilized by aromatic character in a novel 1,3-dioxo-4,7-diborepine heterocycle.

The second project was about the dehydrogenation of ammonia borane catalysed by the bis(borane) Lewis acid 9,10-dichlorodiboraanthracene, which can facilitate the release of 2.46 equivalents of H₂ per AB molecule. The catalyst shows the best catalytic efficiency on ammonia borane dehydrogenation among all the other metal-free catalysts so far. Interestingly, the catalyst can be reused for multiple times, and no loss of activity was observed in a fifteen-cycle experiment. The supply of H₂ can be controlled simply by heating to 60 °C or cooling to room temperature. The intramolecular stabilization of an three-center-two-electron complex with AB is supposed to be responsible for the high effectiveness of the bis(borane) catalyst, which is further supported by DFT computations and kinetic experiments.
Part 2

The synthesis of novel BN aromatics

2.1 Introduction

Nowadays our world is facing some serious challenges such as global climate change and the shortage of natural resources. For chemists, to design and prepare novel materials with higher energy efficiency might be a possible solution addressing such challenges. Recently, \( \pi \)-conjugated organic compounds have gained a lot of interest due to their important applications in organic electronics.\(^{[1-2]} \) Among them many \( \pi \)-conjugated organic systems (such as acenes and polycyclic aromatic hydrocarbons with all-carbon \( \pi \)-skeletons) have been developed.\(^{[3]} \)

The incorporation of heteroatoms into \( \pi \)-conjugated organic systems is an efficient method to create novel compounds, which bring remarkable optical and electronic properties. Based on this strategy, many studies have been reported on the replacement of a pair of carbon atoms (C=C) in the aromatic compound with the corresponding B-N unite, due to the isoelectronic property of C=C and B-N bonds.\(^{[4]} \) Interestingly, the replacement of carbon atoms with boron and nitrogen brings distinct different electronic properties from their carbon isosteres.\(^{[5]} \) These boron-nitrogen heteroaromatic compounds have showed potential applications in biomedical studies as well as in material science.\(^{[4-5]} \)

2.2 The recent progress of B, N aromatics

In 1958, Dewar and coworkers published the first synthesis of BN aromatics, 9,10-azaboaphenanthrenes \( ^{47} \) (Scheme 14).\(^{[6]} \) The reaction of 2-aminobiphenyl \( ^{44} \) with BCl\(_3\) generated a proposed intermediate \( ^{45} \), which then proceeded through the Friedel-Crafts reaction to form the cyclic product \( ^{46} \) in the presence of AlCl\(_3\). Compound \( ^{46} \) can be further modified by various nucleophiles to deliver a series of BN-phenanthrene derivatives \( ^{47} \). After further explorations, compounds \( ^{47} \) were found to undergo electrophilic substitution reactions regioselectively at the 6 and 8 positions.\(^{[7-10]} \)

![Scheme 14. Synthesis of 9,10-azaboaphenanthrene derivatives.](image-url)
Subsequently, the Dewar group also reported the first synthesis of BN-naphthalene in 1959 (Scheme 15).\(^{[11]}\)

The reaction of 2-aminostyrene (48) with phenylboron dichloride delivered the 2-phenyl-1,2-azaboranaphthalene (49). Surprisingly, BN-naphthalenes (49, 51 and 52) show high stabilities and can remain intact in the presence of strong base or KMnO₄.

Scheme 15. Preparation of boron-substituted 1,2-azaboranaphthalenes.

Afterwards, Polivaka,\(^{[12-13]}\) Goubeau\(^{[14-15]}\) and Gronowitz\(^{[16-18]}\) also reported their pioneering work on the synthesis of BN aromatics. However, encumbered by the material characterization capabilities of that time, most of these studies were still based on the synthesis of 1,2-azaborines derivatives, and only with a few limited functional groups.

In 2000, Ashe and coworkers demonstrated a synthesis of monocyclic 1,2-azaborines via the ring closing metathesis (RCM) (Scheme 16),\(^{[19]}\) which is the start of a renewed interest of the BN aromatic chemistry. Firstly, allylboron dichloride 54 was synthesized through a transmetalation of allyltributyltin 53 with BCl₃. With the addition of allylethylamine compound 54 was converted to bis(allyl) aminoborane 55. Then, the chloride on the boron atom was substituted by the nucleophile PhLi to give compound 56. Followed by a ring closing metathesis, cyclic product 57 was generated. Finally, the target aromatic compound 58 was synthesized through the oxidation of 57 in the presence of DDQ.

Scheme 16. Synthesis of 1,2-azaborine 58 by ring-closing metathesis.
Based on Ashe’s synthetic method of 1,2-azaborines, the Liu group successfully synthesized a variety of 1,2-azaborine derivatives with various functional groups at the boron atom (Scheme 17). Following by the ring-closing metathesis and dehydrogenation procedure, aromatic product 60 was delivered. Several 1,2-azaborine derivatives 57, 61 were obtained by the reactions of compound 60 with various nucleophiles.

![Scheme 17. Formation of boron-substituted 1,2-azaborines by nucleophilic substitution.](image)

Inspired by the former results, the Liu group then created a first example of 1,3-azaborine (Scheme 18). The reaction of formaldehyde (62), allylmethelamine 63 and benzotriazole (64) gave a mixture of 65a, 65b, which were then treated with nBu3SnLi to afford the stannane reagent 66. With a lithium-tin transmetalation and the addition of electrophile 67, compound 66 was modified to the RCM precursor 68. A direct RCM reaction from 68 was not successful due to the decomposition of the catalyst attacked by the nucleophilic amine. The synthesis of cyclic product 69 was then achieved from the ammonium salt of 68 with triflic acid. A final dehydrogenation of 69 by Pd/C furnished the 1,3-azaborine 70a.

![Scheme 18. Synthetic route to the first 1,3-azaborine 70a.](image)
Another interesting result from the Liu group was the synthesis of a new BN-naphthalene (Scheme 19). Vinyl substituted 1,2-azaborine 72 was synthesized through a Negishi cross-coupling reaction, which is surprisingly compatible with the B-Cl unite. The reaction of 72 with the Grignard reagent gave the RCM precursor 73, which was then converted into the cyclic product 74 in the presence of Grubbs’ catalyst. The oxidation of 74 was achieved by Pd/C to form the N-TBS substituted BN-naphthalene 75. Treatment of compound 75 with TBAF furnished the BN-naphthalene 76.

**Scheme 19.** Preparation of BN-naphthalene 76.

Recently, many longer conjugated BN aromatics have been created concerning the potential application in material science. For instance, in 2010 Perepichka and coworkers demonstrated a synthesis of 1,2-azaborine-fused oligothiophene (Scheme 20). Similar to Dewar’s method, the reaction of diaminothiophene 77 with excess PhBCl₂ gave the bis(azaborine) 78. As the strong acidity of the N-H protons would be a problem for the further application, an ethylene-linked compound 81 was synthesized via a two-steps synthesis from 77. The molecular structures of 78 and 81 were confirmed by X-ray crystallography, which show both structure to be planar referred to the thiophene rings. However, the phenyl rings stay out of the plane, which limits their conjugation with the polycyclic moiety.

**Scheme 20.** Synthesis of 1,2-azaborine-fused oligothiophene 78, 81.
In 2011, Nakamura and coworkers reported a synthesis of BN-fused polycyclic aromatics through a tandem intramolecular electrophilic arene borylation procedure (Scheme 21). Dichloroboraneamine 83 was synthesized in situ from bis(biphenyl-2-yl)amine (82). After screening of a variety of Lewis acids and Brønsted bases, an addition of 4 equivalents of AlCl₃ and 1.5 equivalents of 2,2,6,6-tetramethylpiperidene (TMP) to the starting material 83 was proved as the best condition for the generation of 84, and it was found that the AlCl₃/TMP stoichiometry has a dramatic influence on the yields. The same optimized conditions could also be applied for the synthesis of the bis(BN)-fused PAH 86.


The before-mentioned studies were mainly on the chemistry of azaborine, which contains only one B-N unite in one aromatic ring. The incorporation of two B-N unites into the same aromatic ring was only scarcely reported in the literature. In 1974, Siebert and coworkers reported the first synthesis of BN aromatics with B₂C₂N₂ cores (Scheme 22). The reaction of bisboron compound 87 and triiodo borthiine (88) gave the thiadiborol compound 89, which was then reacted with SnMe₄ to form a methyl substituted thiadiborol compound 90. Treatment of 90 with 1,2-dimethylhydrazine delivered the B₂N₂-aromatics 91. Based on the similar procedure, the 1,2-diazas-3,6-diborin derivatives 94 were also synthesized.
Scheme 22. Synthetic method to $\text{B}_2\text{C}_2\text{N}_2$-aromatics.

In 2006, Piers and coworkers reported the synthesis of $\text{B}_2\text{N}_2\text{C}_2$-substituted triphenylene analogues (Scheme 23).\textsuperscript{[27]} According to their method, the treatment of stannacyclohexadiene (95) with LDA and I$_2$ afforded the coupling products 96a/96b in a ratio of 60:40. Followed by the transmetalation with BCl$_3$, the mixture can be converted to the related compounds 97a/97b (main product, 60%). The reaction of 97b with pyridazine gave the desired molecule 98. The X-ray crystallography of 98 shows a structure with a planar fused ring system. And the derivatives of 98 were found to have interesting photophysical properties from the UV-vis and fluorescence spectroscopy, which might have potential applications in organic-based devices.

Scheme 23. Synthesis of $\text{B}_2\text{N}_2\text{C}_2$-substituted triphenylene analogues.
2.3 Strategy and motivation

As afore introduced, a variety of BN aromatics have been nicely designed and created, and based on the elegant synthetic methods these novel aromatics could be further investigated in the field of material science.\[^5\] However, most of the studies on these BN aromatic compounds were still based on azaborines, which include only one B-N unit in one aromatic ring.\[^28\] Only a few examples of B\(_2\)N\(_2\)C\(_2\)-heteroaromatic compounds have been reported in the literature. The syntheses of these B\(_2\)N\(_2\)C\(_2\)-heteroaromatic compounds often involve complex transmetalation approaches,\[^{25-27}\] which require the addition of organolithium, -magnesium, -tin, and silicon compounds. Unfortunately, these organometallic reagents have to be synthesized by multiple steps and it can be difficult to synthesize the derivatives with various functional groups. Therefore, it would be of interest to develop new synthetic routes to B\(_2\)N\(_2\)C\(_2\)-heteroaromatic compounds with easy handlings.

Recently our group demonstrated the importance of bidentate activation by bisboron compounds, which I can successfully apply for the inverse electron-demand Diels-Alder (IEDDA) reaction of 1,2-diazene,\[^{29-30}\] the activation of CO\(_2\)\[^{31}\] as well as the dehydrogenation of ammonia borane.\[^{32}\] Inspired by these results, I proposed that the reaction of bisboron compounds with hydrazines would generate the related B\(_2\)N\(_2\)C\(_2\)-heteroaromatic compounds (Figure 5). Within this approach, I should be able to furnish the synthesis of novel B\(_2\)N\(_2\)C\(_2\) heterocycles in one step.

![Figure 5. Proposed synthetic route to B\(_2\)N\(_2\)C\(_2\) aromatic compounds.](image-url)
2.4 References

2.5 Contribution to the Literature

Diazadiborines – (B–N)$_2$ Isosteres of Naphthalene


“Polycyclic aromatic compounds doped with boron and nitrogen have attracted great attention due to their interesting alteration of properties. Herein, we present the preparation of various substituted (B–N)$_2$-naphthalenes via a one-pot reaction of Li$_2$[1,2-C$_6$H$_4$(BH$_3$)$_2$] with azobenzenes. Investigation of their photophysical properties revealed a large blue shift in their absorption as well as emission spectra compared to their C-analogues. These new B-N-doped structures are promising candidates in the area of functional materials such as molecular electronics.”

One pot synthesis of (B-N)$_2$-isosteres of naphthalene
Diazadiborines – (B–N)₂ Isosteres of Naphthalene


Dedication (optional)

Abstract: Polycyclic aromatic compounds doped with boron and nitrogen have attracted great attention due to their interesting alteration of properties. Herein, we present the preparation of a variety of substituted (B–N)₂-naphthalenes via a one-pot reaction of Li₄[1,2,3-C₆H₃(NH₂)] with azobenzenes. Investigation of their photophysical properties revealed a large blue shift in their absorption as well as emission spectra compared to their C-analogous. These new B-N-doped structures are promising candidates in the area of functional materials such as molecular electronics.

Boron-nitrogen heteroaromatic compounds have gained significant attention due to their potential applications in biomedical research as well as materials science.[1-4] The replacement of carbon atoms with boron and nitrogen brings distinct electronic properties to their carbon isotopes. Many studies have been reported on the exchange of a pair of carbon atoms (C=C) in the aromatic compound by boron and nitrogen atoms (B–N).[5-12] Very recently, Liu and coworkers have developed a methodology for the synthesis of B–N isosteres of naphthalene and indenyl,[13,14] the introduction of even more heteroatoms into the aromatic structure promulgates further alteration of their physical properties (Figure 1). However, there are only a rare number of examples of B₃N₃C₃ heteroaromatic compounds so far.[15-16] Piers and coworkers reported the syntheses of triphenylene analogues with B₃N₃C₃ cores, which show very interesting photophysical properties.[17] Despite these important accomplishments, there is great potential to synthesize previously inaccessible B–N heterocycles, which is particularly more than one B–N unit.

So far, synthetic methods to access B–N heteroaromatic compounds involve multiple steps and often require expensive transition metal catalysts or toxic metals such as stannanes. Thus, it remains a challenge to prepare novel B–N molecular structures efficiently including an easy and flexible introduction of substituents. We envisioned that the combination of bisboron compounds with hydrazines might afford the related B₃N₃C₃ compounds (Figure 2). Such an approach is inspired by our efforts in bidentate Lewis acid catalysis, which we applied for the inverse electron-demand Diels-Alder (IEDDA) reaction of 1,2-diazene,[17] the activation of CO₂,[18] as well as the release of H₂ from ammonia borane.[19] The bidentate interaction of lithium o-phenylenbisborate (1, Li₄[1,2-C₆H₃(NH₂)] with hydrazobenzenes should deliver novel B–N heterocycles containing the B₃N₃C₃ core in just one operation.

Figure 2. Proposed synthetic route to B₃N₃C₃ aromatic compounds

To prove the above-outlined proposal, we chose hydrazobenzene 2 as a test substrate (Scheme 1). A 1:1 mixture of 1 and 2 in THF-d₈ was monitored by ¹H NMR. However, no reaction occurred neither at rt nor at 60 °C. Then, an excess TMSCl was added to the mixture in order to abstract the boron-bound hydride ions. With this additive all the starting material was consumed within 24 h at rt. The reaction was optimised revealing toluene as solvent and a temperature of 60 °C for 6 h as the best conditions. The pure product 3 could be obtained through sublimation at 160 °C under high vacuum (< 0.5 mbar). 3a has been fully characterized by NMR as well as IR spectroscopy. The ¹B NMR spectrum of 3a shows a singlet at 36.0 ppm in CDCl₃. The IR spectrum exhibits a characteristic absorption at 2531 cm⁻¹ which is assigned to a B–H vibration.

Scheme 1. Synthesis of (B–N)₂-isosteres of naphthalene from hydrazobenzene.

Hydrazobenzenes are not the ideal starting material, as they are air sensitive compounds and have to be prepared by reduction of either azobenzenes or nitrobenzenes often in low yields. Thus, we further investigated the possibility to use directly azobenzene 4a as building block, which are air stable and can be easily prepared from various anilines.[20] The bisborate 1 should act also...
as a reducing agent. First experiments revealed, that solvent played a key role in the transformation (Table 1). Conducting the first step, the reduction, in polar solvents (THF, CH₂Cl₂) lead to better yields compared to toluene (entry 1, 2, 3). However, when THF was used in the second step a lower yield of 3a was observed (entry 4). After extensive screening a solvent combination of THF and toluene was established as the best choice.

**Table 1. Optimization of the generation of 3a.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent A</th>
<th>Solvent B</th>
<th>T / °C</th>
<th>Yield of 3a [%]11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>THF</td>
<td>toluene</td>
<td>60</td>
<td>34</td>
</tr>
<tr>
<td>2</td>
<td>toluene</td>
<td>toluene</td>
<td>60</td>
<td>-</td>
</tr>
<tr>
<td>3</td>
<td>CH₂Cl₂</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>20</td>
</tr>
<tr>
<td>4</td>
<td>THF</td>
<td>THF</td>
<td>50</td>
<td>17</td>
</tr>
<tr>
<td>5</td>
<td>THF</td>
<td>toluene</td>
<td></td>
<td>29</td>
</tr>
<tr>
<td>6</td>
<td>THF</td>
<td>CH₂Cl₂</td>
<td>rt</td>
<td>23</td>
</tr>
</tbody>
</table>

11 Reaction condition: 1 (0.29 mmol), 4a (0.27 mmol), TMSCl (0.75 mmol), solvent (4 ml), under N₂ in glovebox. Isolated product.

Different azo compounds were subjected to the optimized condition (Table 2). The results showed that our methodology has a good functional group tolerance. Both, electron-rich as well as electron-deficient azo compounds generated the corresponding (B-N)-naphthalenes in moderate to good yields (entry 1-5). Unfortunately, polymerization occurred in the presence of a vinyl group (entry 6).

**Table 2. Substrate scope in the syntheses of (B-N)-naphthalenes from symmetric azobenzenes.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R</th>
<th>Yield of 3 [%]11</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>H (4a)</td>
<td>34 (3a)</td>
</tr>
<tr>
<td>2</td>
<td>Me (4b)</td>
<td>63 (3b)</td>
</tr>
<tr>
<td>3</td>
<td>F (4c)</td>
<td>46 (3c)</td>
</tr>
<tr>
<td>4</td>
<td>Cl (4d)</td>
<td>56 (3d)</td>
</tr>
<tr>
<td>5</td>
<td>Br (4e)</td>
<td>30 (3e)</td>
</tr>
<tr>
<td>6</td>
<td>OCOH (4f)</td>
<td>-</td>
</tr>
</tbody>
</table>

11 Standard condition: 1 (1.0 equiv), 4 (1.0 equiv), TMSCl (2.6 equiv). Isolated product.

Unsymmetrically substituted azobenzenes were also tested (Table 3). However, compared to the symmetrically substituted starting materials lower yields (15-31 %) of the products were obtained. Because these B-N compounds were mostly liquid purification by sublimation was difficult. For nitro substituted 5d, no product could be obtained after sublimation.

**Table 3. Substrate scope in the syntheses of (B-N)-naphthalenes from asymmetric azobenzenes.**

<table>
<thead>
<tr>
<th>Entry</th>
<th>R¹</th>
<th>R²</th>
<th>Yield of 6 [%]10</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4-Me</td>
<td>4-F (5a)</td>
<td>15 (6a)</td>
</tr>
<tr>
<td>2</td>
<td>4-OMe</td>
<td>4-F (5b)</td>
<td>17 (6b)</td>
</tr>
<tr>
<td>3</td>
<td>2-Br</td>
<td>2-F (5c)</td>
<td>31 (6c)</td>
</tr>
<tr>
<td>4</td>
<td>H</td>
<td>2-NO₂ (5d)</td>
<td>-</td>
</tr>
</tbody>
</table>

10 Standard condition: 1 (1.0 equiv), 5 (1.0 equiv), TMSCl (2.6 equiv). Isolated product.

Single crystals of 3b as well as 3e were both grown from a concentrated solution in toluene at –20 °C, and the structures were unambiguously confirmed by X-ray diffraction (Figure 3). Both of these two structure were found to be nonplanar and slightly twisted, with small torsion angles [e.g. 3b, B–N–N–B : 4.3(3)°, B–C–C–B : 7.6(3)°] due to the steric repulsion of the two phenyl rings. For 3b, the B–N bond length [1.402(3) Å] is shorter than in other azaborines analogous, which corresponds to a localized B-N double bond [1.403(2) Å], strongly indicating its double-bond character (Figure 3). The lengths of the B–C bond [1.535(3) Å] and the N–N bond [1.430(2) Å] are close to the reported phenyl acetate azaborine [B–C bond, 1.488(3) Å] and B₂C₉N₂-substituted triphenylene [N–N bond, 1.422(4) Å] respectively.11

Figure 3. Molecular structure of 3b and 3e, anisotropic displacement ellipsoids are drawn at 50% probability.

B–N-doped aromatic compounds have been proposed as luminescent materials.12 Therefore, the optical properties of these novel B–N naphthalene derivatives have been investigated by UV-vis spectroscopy (Figure 4). Interestingly, the UV-vis spectra of these BN compounds in cyclohexane are close to the known 2,1-borazaronaphthalene derivatives.14-16 They exhibited
almost the same absorption maxima at 310 nm independently of the substitution pattern on the phenyl rings.

![Graph showing UV-vis spectra of selected (B-N)₃-naphthalene derivatives. All measurements were performed in cyclohexane at 10⁻¹ M.](image)

All the B,N compounds show two emission bands, one at 340 and one at 545 nm in the fluorescence emission spectra (Figure 5, see Figure S3 in the Supporting Information for details). In comparison, 2,3-diphenyl-naphthalene (7) exhibited values of λem at 254 nm and λex at 373 nm respectively. The quantum yields of these (B–N₃)-naphthalenes were also measured. In accordance to the (B–N₃)-naphthalene reported by Liu, [13] low values were obtained (less than 0.01, see Supporting Information).

![Graph showing UV-vis absorption (solid black trace) and fluorescence emission spectra (dotted black trace) of 3d and UV-vis absorption (solid red trace) and fluorescence emission spectra (dotted red trace) of 7 (all measured at 10⁻² M in cyclohexane; all spectra have been normalized for comparison).](image)

In summary, we developed an efficient method to access novel (B–N₃)-aromatics in one operation starting from a broad variety of azo compounds. Single-crystal XRD also confirmed the structure of these new B,N naphthalene isosteres. The UV-vis as well as the emission spectra of these compounds exhibited a large blue shift compared to the carbon analogue. The ease of preparation allows synthesizing large libraries of these new compounds. Such a collection of novel B,N heteroaromatics will be evaluated for applications in material science, such as molecular electronics in the future.

**Experimental Section**

Synthesis of 3a. General procedure: Bisborate 1 (55 mg, 0.29 mmol, 1.0 equiv) and azobenzene 4a (50 mg, 0.27 mmol, 0.93 equiv) were mixed in THF (5 mL) at rt and stirred overnight. After all the solvents were reduced under high vacuum, then DMF/MeCN (94 μL, 0.75 mmol, 2.60 equiv) in toluene (4 mL) was added to the mixture and the reaction was heated in a 50 °C oil bath overnight. After volatiles were removed under vacuum. The residue was submitted to sublimation at 160 °C (ca. 0.1 mbar). The target compound (28 mg, white solid, 34 %) was obtained as pure product. ¹H NMR (500 MHz, CDCl₃, 298.8 K): δ = 8.10 (d, J = 5.5, 3.2 Hz, 2H), 7.18 (m, J = 7.1), 3.24 (vs, 2H, 8H) ppm. ¹³C NMR (100 MHz, CDCl₃, 298.8 K): δ = 145.6, 136.8, 130.7, 128.3, 126.1, 125.3 ppm. The signal for the carbon adjacent to boron was not observed due to quadrupolar relaxation. ¹¹B NMR (128.42 MHz, CDCl₃, 298.6 K): δ = 36.65 (br s) ppm. IR (neat) ν ≈ 2549, 2531, 1597, 1490, 1436, 1320, 749, 696, 656, 507 cm⁻¹. HRMS (El) calc'd for C₁₂H₁₄Br₂N₂ (M⁺) 292.1495; found 292.1504.

**Acknowledgements**

Funding by the Swiss National Science Foundation is acknowledged. We thank Marcel A. Strauss for DFT computational support. We are indebted to Heike Hausmann for NMR and Erwin Röcker for HRMS measurements.

**Keywords:** boron • B,N heterocycles • azaborine • azobenzene • synthetic methods

2.6 Summary of the Results

In summary, I demonstrated a one-pot synthesis of novel (B-N)$_2$-aromatics by the reactions of Li$_2$[1,2-C$_6$H$_4$(BH$_3$)$_2$] with a variety of azobenzene derivatives. This synthetic approach allows for the preparation of large libraries of BN naphthalene isosteres. The structure of these new BN naphthalene isosteres were confirmed by NMR spectroscopy and single-crystal XRD. Compared to the carbon analogues, these BN aromatic compounds exhibited relatively large blue shifts both on the UV-vis and the emission spectra. The synthesis of these new BN heteroaromatics provides the possibility for further applications in material science, such as molecular electronics.
Acknowledgement

First and foremost I would like to express my sincere gratitude to my advisor Prof. Hermann A. Wegner for the continuous support of my Ph.D study. It is my honor to be part of the Wegner group. Thanks for giving me the opportunity working on such interesting, challenging projects. I appreciate all his contributions of time, ideas and funding, that I could have a great Ph.D experience in Giessen.

I also like to thank Prof. Dr. Peter R. Schreiner, PhD for the co-examination.

I greatly appreciate the support received from the Wegner group: Silas Götz, Dr. Luca Schweighauser, Sebastian Ahles, Dr. Silvia Bellotto, Sebastian Schmalisch, Marcel Strauß, Dr. Longcheng Hong, Andreas Heindl, Sebastian Beeck, Claudia Diehl, Kathrin Michel, Bruce McDonald, James Marsh, Andrey Petrov, Mi-Jung Song, Mirko Brodsky, André Blößer, Gastelle Tietcha, Julia Ruhl, Jan Griwatz and Oliver Haas, for the stimulating discussions, for the comfortable working atmosphere, and for all the fun that we have had in the past three years.

My sincere thanks goes to Dr. Luca Schweighauser, Marcel Strauß and Dr. Jan Philipp Wagner for DFT computations for my projects; Dr. Heike Hausmann for a lot of NMR measurements; Dr. Christian Logemann, Dr. Sabine Becker for X-ray single crystal measurements; Dr. Erwin Röker, Xuelu Ding, Dr. Stefanie Gerbig for HRMS measurements; Dr. Dennis Gerbig, Dr Olaf Burghaus (from Marburg) for the EPR measurement; Jonas Hofmann, Wenbo Zhang and Junpei Yue foFr the CV measurements; Edgar Reitz for the technical support; Doris Verch, Michaela Krekel for administrative assistance; and the other coworkers from our institute. Without their precious and professional support, it would not be possible to conduct my research.

I am grateful for the wonderful time spent with the friends that I met in Giessen: Zewei Bai, Dr. Junpei Yue, Tao Lei, Qingkui Jiang, PingPing Li, Lunwen Qian, Qing Wang, Qianhui Dai, Jiaqin Mei, Tao Peng, Beiqi Shao, Feng Zhang, Chengen Jiang, Kai Ni, Fei Song, Feng Wang, and Dr. Longcheng Hong.

Last but not least, I would like to thank all my family and friends for the continuous support throughout all my studies. For my parents who raised me up and supported me in all my pursuits. For my girlfriend Sun who gave me the faithful support and encouragement.