

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

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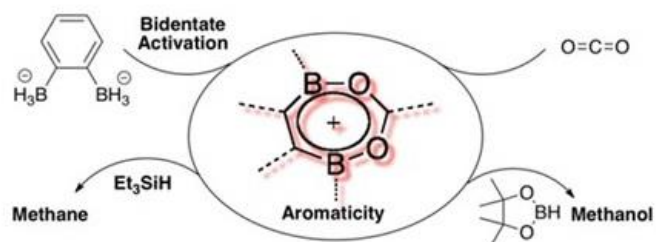
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Abstract:

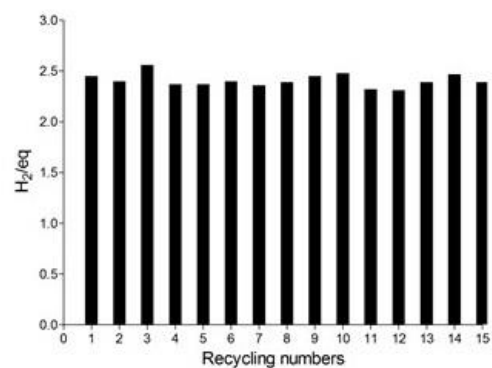
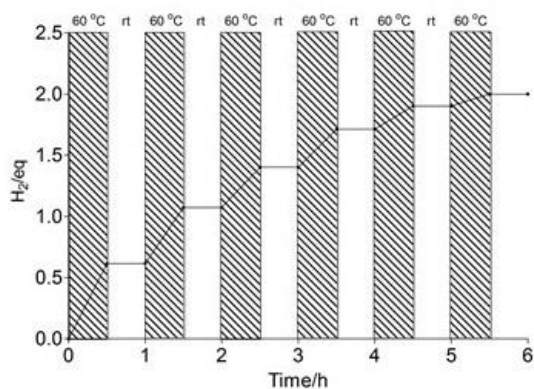
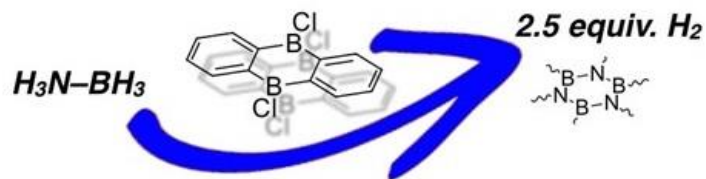
Bisboron chemistry in small molecule activation

The research on small molecules such as CO_2 , H_2 and NH_3BH_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 $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$. Treated with Et_3SiH / $\text{B}(\text{C}_6\text{F}_5)_3$, 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 ($\text{AB} = \text{NH}_3\text{BH}_3$) 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-dichlorodiboraanthracene) 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 CO_2 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 :

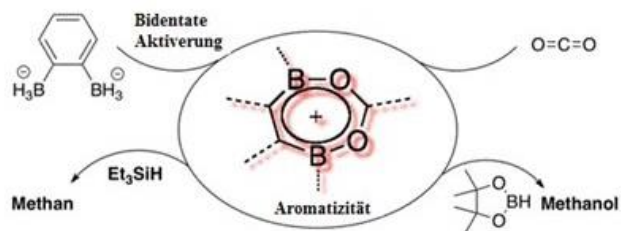
Bisborchemie zur Aktivierung niedermolekularer Verbindungen

Die Forschung zur Aktivierung niedermolekularer Verbindungen wie CO_2 , H_2 und NH_3BH_3 erfährt heutzutage große Aufmerksamkeit. CO_2 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 CO_2 aus der Luft als C1 Rohmaterial verwendet werden, welches weiter in industriell gefragte Produkte umgewandelt werden kann.

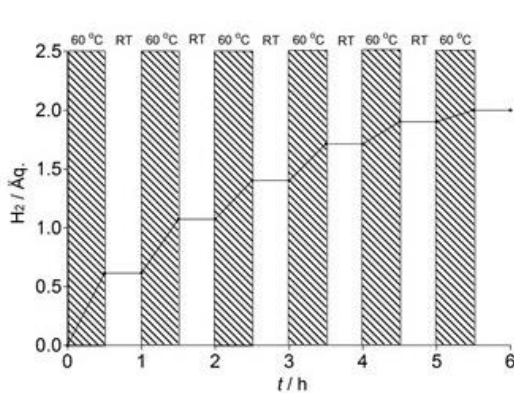
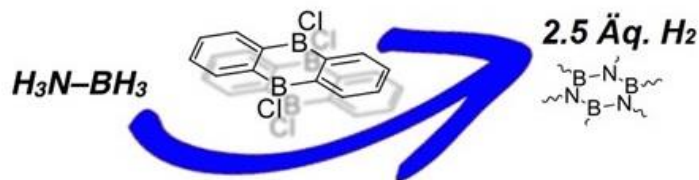
Im ersten Projekt habe ich das Prinzip der bidentaten Aktivierung auf eine neue katalytische Reduktion von Kohlenstoffdioxid angewendet (Abbildung I). In Abhängigkeit des Reduktionsmittels ist es möglich CO_2 mittels des bidentaten Borhydrid-Katalysators $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$ selektiv in Methan oder Methanol umzuwandeln. Unter Verwendung von Et_3SiH / $\text{B}(\text{C}_6\text{F}_5)_3$ wird CO_2 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 wird.

Weiterhin wird Wasserstoff als erneuerbare Energielieferant in Betracht gezogen, welcher insbesondere großes Potential für zukünftige Verwendungen als alternative Energiequelle aufweist. Dennoch bleibt es eine große Herausforderung Wasserstoff auf eine sichere und effiziente Art besonders für mobile Anwendungen zu speichern. Als vielversprechenden Kandidaten für ein Wasserstoff-Speichermaterial wurde Amminboran ($\text{AB} = \text{NH}_3\text{BH}_3$) vorgeschlagen. Bedauerlicherweise sind Katalysatoren nötig um effektiv Wasserstoff aus AB freizusetzen.

Im zweiten Projekt habe ich einen metallfreie Bis(boran) Lewis-säure-Katalysator entwickelt (9,10-Dichlordiboranthracen), welcher die Erzeugung von bis zu 2,5 Äquivalenten H_2 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 $60\text{ }^\circ\text{C}$ oder Kühlen auf Raumtemperatur gesteuert werden. Mechanistische Studien wurden mit DFT Rechnungen und kinetischen Experimenten gestützt.



1. Selektive Reduktion von CO_2 zu Methan bzw. Methanol mittels eines bidentaten Borat Katalysators.



2. Metallfreie Amminboran-Dehydrierung katalysiert durch eine Dibor-Lewis-Säure. Reaktionszyklen unter Verwendung desselben Katalysators (links). Temperaturkontrolliert Start/Stopp-Wasserstoff Freisetzungsexperimente (0.25 M Lösung von AB) (rechts).

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 Li₂[1,2-C₆H₄(BH₃)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.

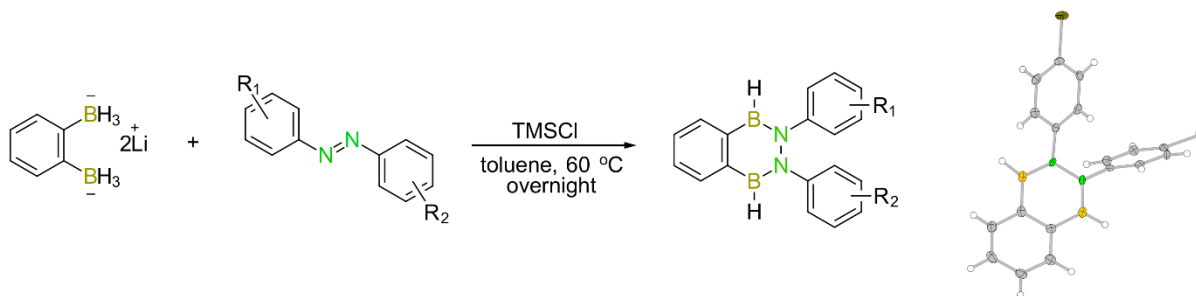


Figure II. One-pot synthesis of (B-N)₂-naphthalenes.

Zusammenfassung - Anhang:

Die Synthese neuer BN-Aromaten

In den letzten Jahrzehnten wurden moderne Technologien für das Design und die Darstellung neuer Materialien immer weiter verbessert. Durch wohlüberlegte Modellierung ist es möglich, neue Materialien zu entwickeln, welche die Anforderungen für verschiedenste Anwendungen erfüllen können. Aufgrund ihrer einzigartigen elektronischen Eigenschaften haben π -konjugierte organische Verbindungen Verwendung im Bereich der organischen Elektronik gefunden. Daher ist ein besonderes Forschungsinteresse an Kohlenstoff-basierten π -konjugierten organischen Systemen wie Acenen und polyzyklischen Kohlenwasserstoffen entstanden. Ein anderer möglicher Ansatz, um neuartige Materialien für derartige Anwendungen zu erzeugen besteht darin, Heteroatome in die π -konjugierten organischen Systeme einzufügen, was in einzigartigen optischen Eigenschaften resultiert.

Im Folgenden präsentiere ich die Darstellung verschieden substituierter (B–N)₂-Naphthaline *via* Eintopfreaktion von Li₂[1,2-C₆H₄(BH₃)₂] mit Azobenzol-Derivaten (Abbildung II). Untersuchungen der photophysikalischen Eigenschaften zeigten eine deutliche Blauverschiebung in den Absorptions-, sowie den Emissionsspektren im Vergleich zu den C-Analoga. Diese neuartigen B-N-dotierten Strukturen sind vielversprechende Kandidaten für den Einsatz als funktionelle Materialien im Bereich molekularen Elektronik.

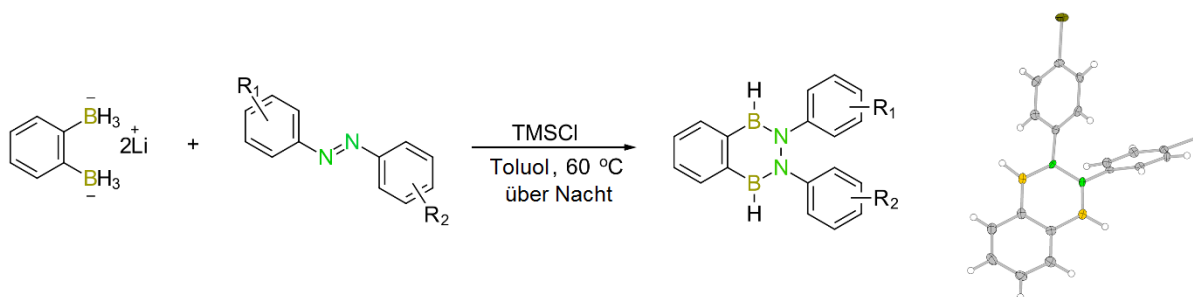


Abbildung II. Eintopfsynthese von (B–N)₂-Isosteren von Naphthalin.

Part 1

Bisboron chemistry in small molecule activation

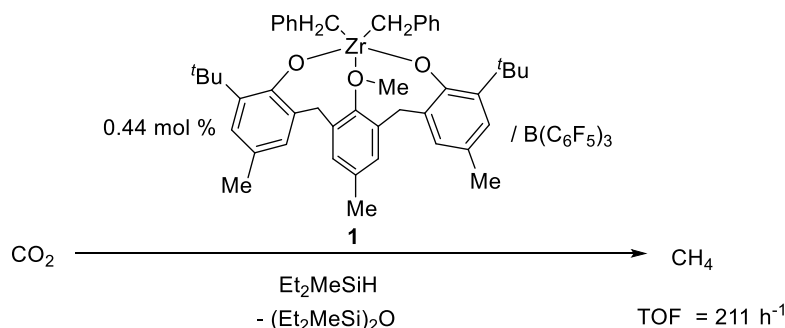
1.1 Introduction

Small molecules such as CO₂, H₂, N₂, O₂ and NH₃BH₃ 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.

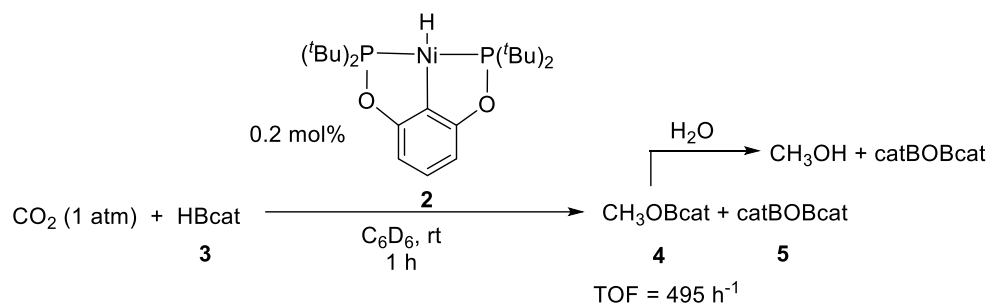
1.11 The recent progress of CO₂ activation

CO₂ 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 CO₂ appears as a highly attractive option as a C1 feedstock.^[1,2] Unfortunately, the high kinetic and thermodynamic stability of CO₂ 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 CO₂ 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 CO₂ into methane with hydrosilanes as reductant for the first time (Scheme 1).^[4] The Guan group achieved the reduction of CO₂ to methanol by a nickel catalyst **2** in the presence of catecholborane (HBcat) (Scheme 2).^[8]

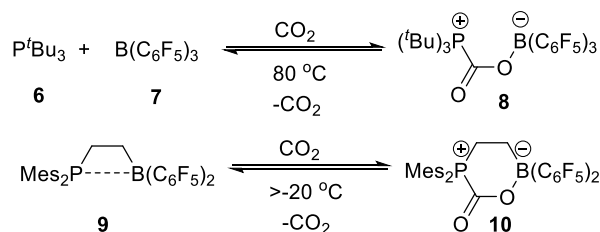


Scheme 1. Reduction of CO₂ with hydrosilanes catalyzed by zirconium-borane complexes **1**.

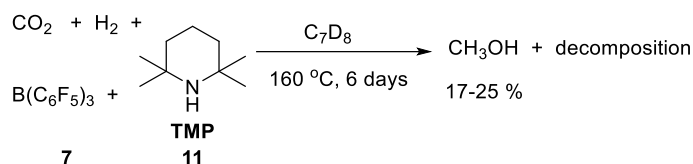


Scheme 2. Conversion of CO₂ to methanol by a nickel catalyst **2**.

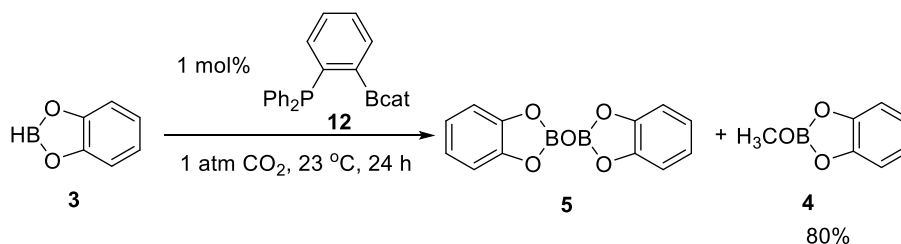
Despite of the important progress achieved by transition-metal-based catalysts on the topic of CO₂ reduction, it is necessary to develop other metal-free catalytic systems, as main-group elements are relatively cheaper and environmental friendly compared to most of the transition metals. In this regard, many transition-metal-free catalysts have been designed and developed to realize the transformation of CO₂ in the past few years. In 2009, Stephan, Erker and coworkers published the first study on the activation of CO₂ with the concept of Frustrated Lewis pairs (FLP)^[18] and the related carbonic acid derivatives were obtained (Scheme 3).^[19] Subsequently, the O'Hare group reported the first metal-free homogeneous hydrogenation of CO₂ to methanol relying on the FLP (B(C₆F₅)₃/TMP (2,2,6,6-tetramethylpiperidine)). However, the efficiency is still limited (Scheme 4).^[20] Furthermore, the Fontaine group synthesized a novel phosphine-borane organocatalyst **12** (1-Bcat-2-PPh₂-C₆H₄), which can efficiently achieve the reduction of CO₂ in the presence of hydraboranes (Scheme 5), and the related products could be hydrolysed to methanol.^[21]



Scheme 3. Reactions of FLP with CO₂.

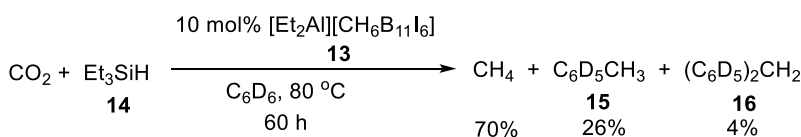


Scheme 4. Reduction of CO₂ to methanol by FLP.

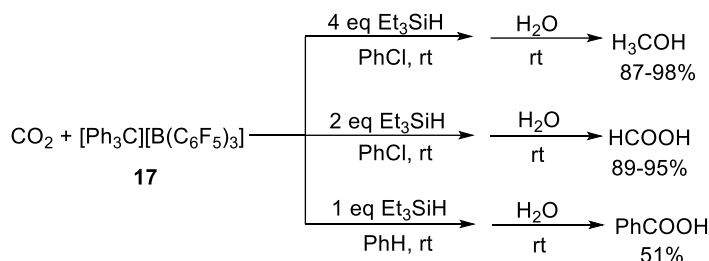


Scheme 5. Reduction of CO₂ by a FLP-based catalyst **12**.

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 [Et₂Al]⁺ **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]

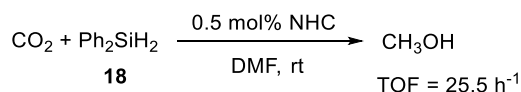


Scheme 6. Transformation of CO₂ to methane by a Lewis acid catalyst **13**.

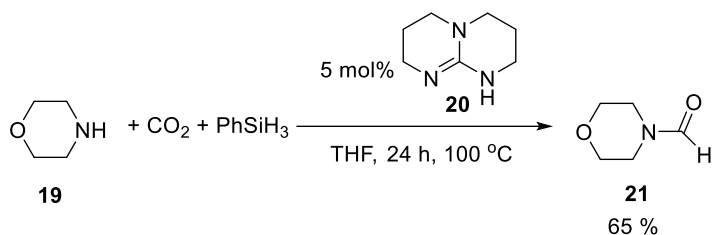


Scheme 7. Reduction of CO₂ to benzoic acid, formic acid and methanol by a silyl cation catalyst **17**.

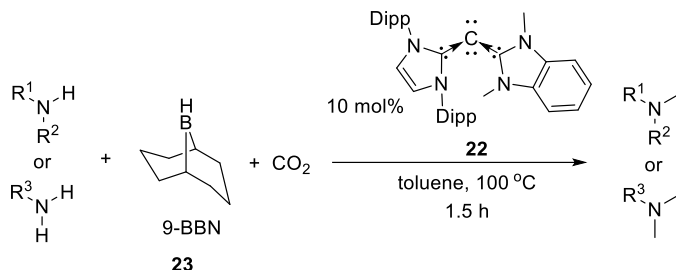
Also N-heterocyclic carbenes have been utilized by Ying and coworkers as catalysts for the conversion of CO₂ to methanol (Scheme 8).^[24] Furthermore, Cantat and coworkers have developed a nitrogen based catalytic system, which can achieve the recycling of CO₂ to formamides in the presence of amines 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 methanol catalyzed by N-heterocyclic carbenes.



Scheme 9. Methylation of amine with CO_2 by nitrogen-based catalytic system **20**.



Scheme 10. Methylation of amine with CO_2 by carbodicarbene **22**.

1.12 The recent progress of ammonia borane (NH_3BH_3) 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 = NH_3BH_3) 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 H_2 from AB (for over 1 equiv H_2 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 H_2 from AB (2.5 equiv H_2 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 H_2 per AB, rt, 1 mol% catalyst loading), and the catalyst **26** can be re-used for multiple times without loss of reactivity.^[38]

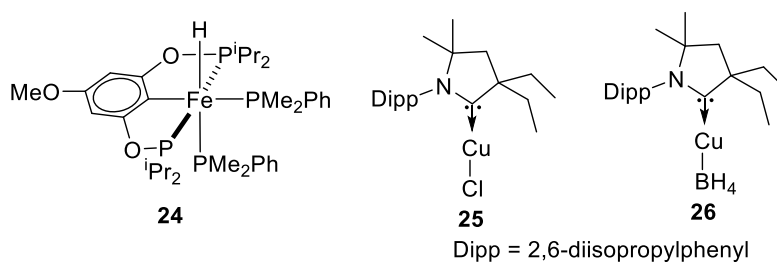


Figure 1. Transition-metal-based catalysts for the dehydrogenation of ammonia borane.

Examples for transition-metal-free catalysts are still limited. In 2007, Dixon, Baker and coworkers reported a study on Lewis acids [$\text{B}(\text{C}_6\text{F}_5)_3$, HOSO_2CF_3] catalyzed AB dehydrogenation, however, only with limited efficiency (1.1 equiv H_2 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 ($\sim 4 \text{ h}^{-1}$ for ammonia borane) is modest compared to the most reactive transition metal catalysts.^[42]

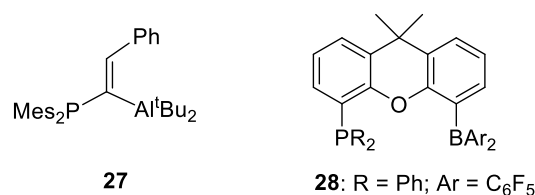


Figure 2. Main group FLP for ammonia borane dehydrogenation.

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.^[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.

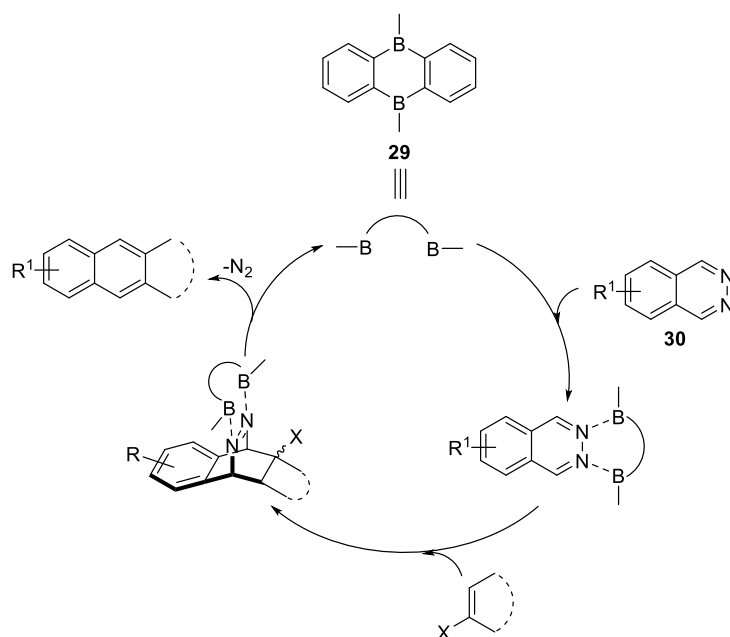
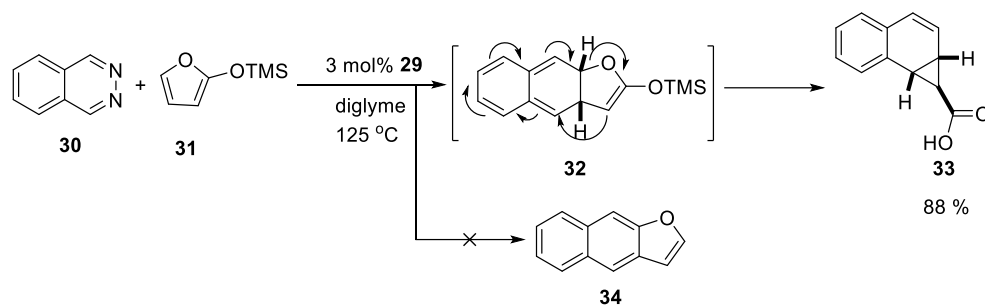


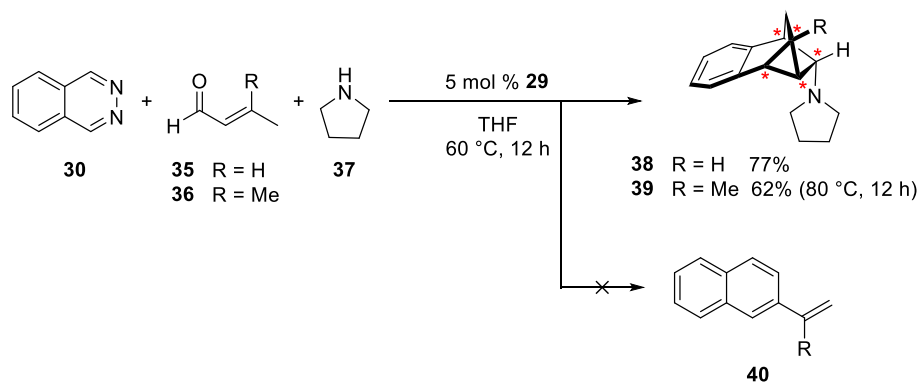
Figure 3. Catalytic principle of the bidentate Lewis acid catalyzed IEDDA reaction of 1,2-diazines.

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).^[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**.

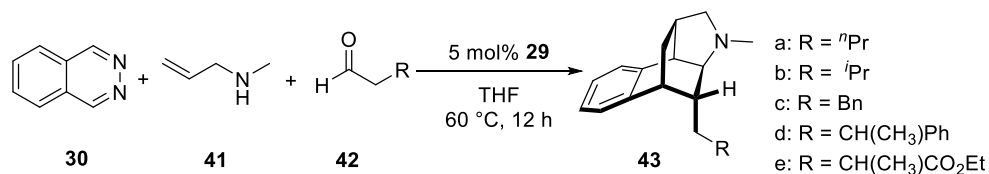


Scheme 11. Bidentate Lewis acid catalyzed cyclopropanation domino reaction with proposed mechanism.

Subsequently, the Wegner group further expanded the scope of the bidentate Lewis acid catalyzed IEDDA reaction. When the α,β -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 **29** was successfully applied in IEDDA reactions with high efficiency. In the bidentate Lewis acid catalysed IEDDA reaction the -N=N- in the substrate was eliminated due to the bidentate coordination. With phthalazines (bearing -N=N- unit) as dienes, the scope of the bidentate Lewis acid IEDDA has been expanded to different dienophile (enamine, furan *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 (CO₂) 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 CO₂ 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 CO₂ with catalytic methods before. Therefore, it would be of interest to investigate and develop bidentate catalysts for CO₂ activation.

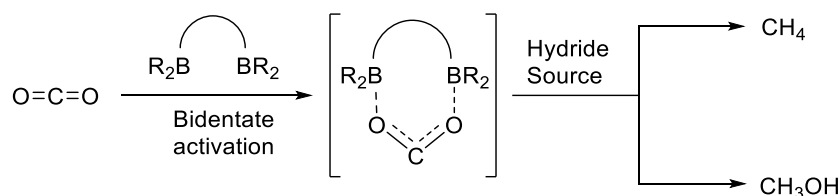


Figure 4. Transformation of CO₂ to methane or methanol with bidentate activation.

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 **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

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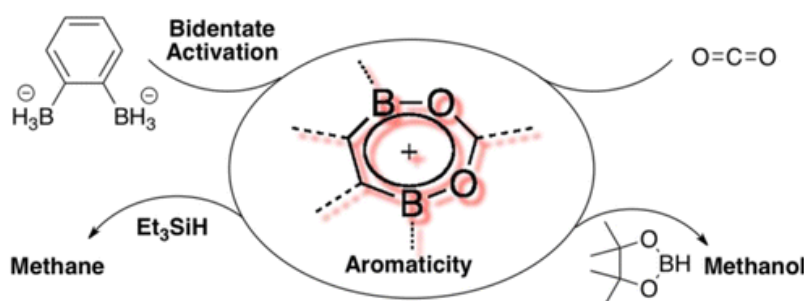
1.5 Contribution to the Literature

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

Reference: Z. Lu, H. Hausmann, S. Becker, H. A. Wegner. *J. Am. Chem. Soc.* **2015**, 137, 5332-5335.

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“A new transition-metal-free mode for the catalytic reduction of carbon dioxide via bidentate interaction has been developed. In the presence of $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$, 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

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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 $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$, 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.

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 (CO_2), with its two Lewis basic oxygen atoms, should also be an ideal target substrate for bidentate activation (Figure 1). CO_2 is highly attractive as a cheap and readily available C1 building block.⁴

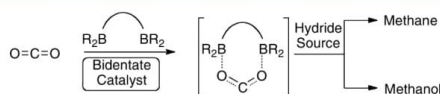


Figure 1. Activation of carbon dioxide by a bidentate catalyst for the conversion to methane or methanol.

The strong bidentate interaction will fixate the 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 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 CO_2 ,^{6–9} only a few non-transition-metal-based catalysts have been recently presented.¹⁰ These approaches are mainly based on the aforementioned FLP concept,^{11,12} strong Lewis acids,¹³ Lewis bases such as amines,¹⁴ or N-heterocyclic carbenes.¹⁵ Besides the different modes of interaction, all methods allow only the conversion of 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., **7** and **8**, which have been highly effective in the IEDDA of 1,2-diazenes, have been tested for the activation of CO_2 (Table 1). Triethylsilane (**2**, Et_3SiH) 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 (**9**, $\text{Li}_2[1,2\text{-C}_6\text{H}_4(\text{BH}_3)_2]$)¹⁷ was shown to be an effective candidate. When 10 mol% of **9** (relative to silane **2**) was reacted under an atmosphere of CO_2 (1 bar) in the presence of **2**, all the silane was consumed (Table 1, entry 1). $(\text{Et}_3\text{Si})_2\text{O}$ (**4**) was the main product, along with $(\text{Et}_3\text{SiO})_2\text{CH}_2$ (**5**) and Et_3SiOMe (**6**). The presence of **3** was indicated by a singlet at 0.14 ppm by ^1H NMR spectroscopy.¹⁸ Without **9** or $\text{B}(\text{C}_6\text{F}_5)_3$, no conversion of silane **2** was observed, proving the need for both catalysts. The solubility of **9** in $\text{C}_6\text{D}_5\text{Br}$ is poor; therefore, the reaction was carried out in $\text{THF-}d_8$ in order to increase the solubility. No transformation of silane **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 $\text{9/B}(\text{C}_6\text{F}_5)_3$ 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

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Table 1. Optimization of the Catalytic Reduction of CO₂^a

$$\text{O}=\text{C}=\text{O} + \text{Et}_3\text{SiH} \xrightarrow[\text{solvent, T, t}]{\text{cat./B(C}_6\text{F}_5)_3} \text{CH}_4 + (\text{Et}_3\text{Si})_2\text{O} + (\text{Et}_3\text{SiO})_2\text{CH}_2 + \text{Et}_3\text{SiOCH}_3$$

1
2
3
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7 R = Cl
8 R = Me
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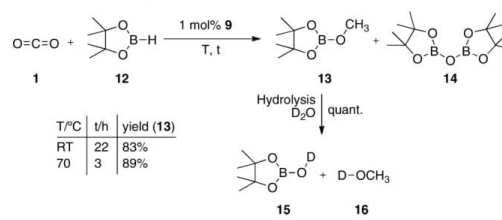
entry	cat.	cat. amt/mol%, ratio cat./B(C ₆ F ₅) ₃	solvent	T/°C	t/h	product ^b /%		
						4	5	6
1	9	10, 1:1	C ₆ D ₃ Br	RT	60	69	31	—
2	9	10, 1:1	THF- <i>d</i> ₈	RT	24	—	—	—
3	9	10, 1:1	C ₆ D ₃ Br	50	18	73	27	—
4	9	5, 1:1	C ₆ D ₃ Br	50	40	41	43	1
5 ^c	9	5, 1:1	C ₆ D ₃ Br	50	21	81	19	—
6 ^c	9	1, 1:1	C ₆ D ₃ Br	50	65	—	45	—
7 ^c	9	1, 1:3	C ₆ D ₃ Br	80	56	78	22	—
8 ^d	9	2, 1:1	—	80	5 days	58	42	—
9	10	10, 1:1	C ₆ D ₃ Br	50	41	18	54	3
10	11	10, 1:1	C ₆ D ₃ Br	50	24	4	91	—

^aThe reaction was performed with CO₂ (1 bar) in a Young NMR tube, unless noted otherwise. ^bBased on the consumption of 2; determined by ¹H NMR with toluene as an internal standard. ^cThe reaction was performed in a 25 mL Schlenk flask. ^dThe yield was determined by GC-MS.

7). In contrast to 9, B(C₆F₅)₃ is highly moisture and air sensitive. Therefore, if the amount of B(C₆F₅)₃ is too low, degradation might further reduce the amount and impede catalysis. The catalytic reduction of CO₂ to CH₄ using 9/B(C₆F₅)₃ 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 monoborate 10 (LiPhBH₃) was employed, which is the monodentate analogue to 9, significantly less conversion was observed (Table 1, entry 9). In particular, the amount of (Et₃Si)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 CO₂,²⁰ 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.⁷ With 12 there is no need to add B(C₆F₅)₃ as co-catalyst. Thus, a mixture of 9 (10 mol%) and 12 in THF-*d*₈ 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

Scheme 1. Reduction of CO₂ to Methanol Using the Bidentate Catalyst 9

LiPhBH₃, LiEtBH₃, 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 disilylacetate 5, which is the main side product. Ultimately, 5 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

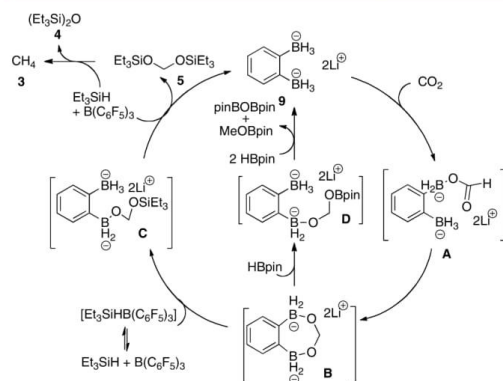
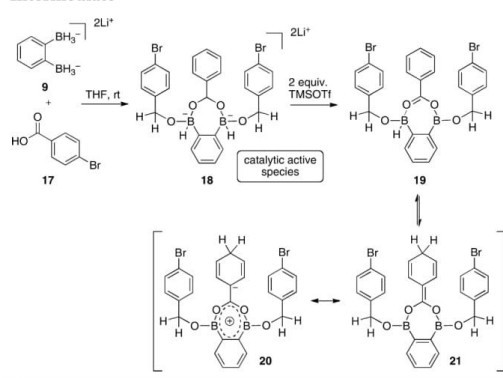


Figure 2. Proposed mechanism for catalytic reduction of CO₂ to methane and methanol.

C=O stretching vibration resulting from the addition of CO₂ to **9**. The stepwise reaction, first treating catalyst **9** with CO₂ and then adding HBpin, showed that three molecules of CO₂ are bound in the catalyst/substrate adduct. During the actual catalysis, the excess of reducing agent might already promote the reduction as soon as the CO₂ is activated by the catalyst, as shown in Figure 2. To increase solubility and enhance the crystallization ability, catalyst **9** was reacted with 1 equiv of 4-bromobenzoic acid (**17**) as CO₂ surrogate (Scheme 2).

Scheme 2. Isolation of a Surrogate of a Bidentate Intermediate



Interestingly, the bromine in the bound benzoic acid has been replaced by hydride, probably by a nucleophilic substitution reaction activated by the catalyst.²¹ The product of this transformation, **18**, was used as catalyst to CO₂ and Et₃SiH/B(C₆F₅)₃, resulting in full conversion of the silane and methane formation. After liberating LiH via the addition of TMSOTf, crystals suitable for X-ray analysis were obtained (Figure 3).²²

The structure clearly shows the bidentate activation of one benzoic acid molecule and the binding of two more equivalents, which have been reduced to the benzyl alcohol. These findings correspond to the experiments described for the CO₂ complex. Noteworthy is the dioxo-diborepine heterocycle, which has not

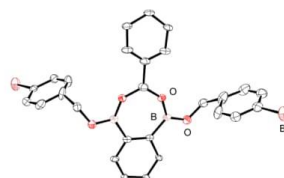
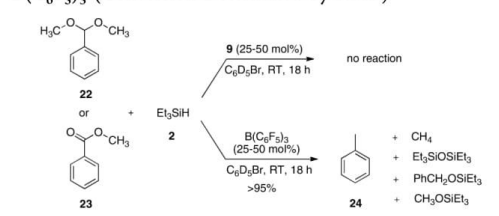


Figure 3. ORTEP plot of **20/21**. Thermal ellipsoids are set at the 50% probability level.

been described before. The entire ring is planar and is stabilized by aromaticity,²³ 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, support 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 bromobenzylic 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(C₆F₅)₃/silane system. Nevertheless, benzaldehyde dimethyl acetal (**22**) and methyl benzoate (**23**) have been tested as model structures for intermediates **A** and **B** in the catalytic cycle (Figure 2). In both cases, the mixture of B(C₆F₅)₃ and Et₃SiH induced the formation of toluene, methyl silyl ether, and benzyl silyl ether (Scheme 3). In contrast, no reaction took place when **9** was

Scheme 3. Support of the Role of the Catalytic System 9/B(C₆F₅)₃ (Conversion Determined by NMR)



added without the presence of B(C₆F₅)₃. This observation indicates that the bidentate borate catalyst **9** activates the CO₂, while the silane/B(C₆F₅)₃ is responsible for the final catalytic reduction to methane.

We also investigated the kinetics of the catalytic reaction with 9/B(C₆F₅)₃ as catalyst by NMR spectroscopy (see Supporting Information). In both cases, the consumption of Et₃SiH, respectively HBpin, showed a first-order reaction rate. In the beginning the data revealed an induction period of about 30 min.^{6d} 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 343 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-C₆H₄(BH₃)₂] efficiently promotes the selective reduction to either methane or methanol. The selectivity can be controlled by the reducing agent: In the presence of Et₃SiH/B(C₆F₅)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-diborepine heterocycle formed during the bidentate activation step is stabilized by aromaticity. The kinetics of both transformations have been studied, showing a first-order reaction rate after an initial induction period. For the reduction with Et₃SiH/B(C₆F₅)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>.

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Notes

The authors declare no competing financial interest.

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

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“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. ”





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

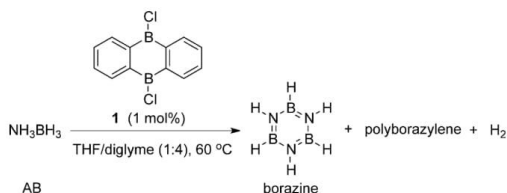
Zhenpin Lu, Luca Schweighauser, Heike Hausmann, and Hermann A. Wegner*

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 [$\text{B}(\text{C}_6\text{F}_5)_3$, 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



Scheme 1. Dehydrogenation of AB catalyzed by 9,10-dichlorodiboraanthracene **1**.

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.

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 $\text{B}(\text{C}_6\text{F}_5)_3$ or HOSO_2CF_3 as the catalyst resulted in the formation of cyclotriborazane (CTB)^[23] and *B*-(cyclo-diborazanyl)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

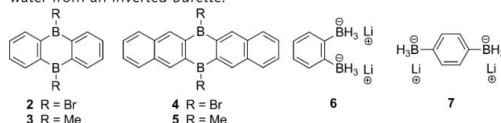
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Table 1: Screening of catalysts and reaction conditions.

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 ₆ F 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 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 ¹¹B 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 *para* derivative **7**,^[29] similar results were achieved (entry 11). With 5 mol % of the monoboron Lewis acid B(C₆F₅)₃, 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

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 ₂ Cl (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 H₂ was measured by displacing water from an inverted burette.

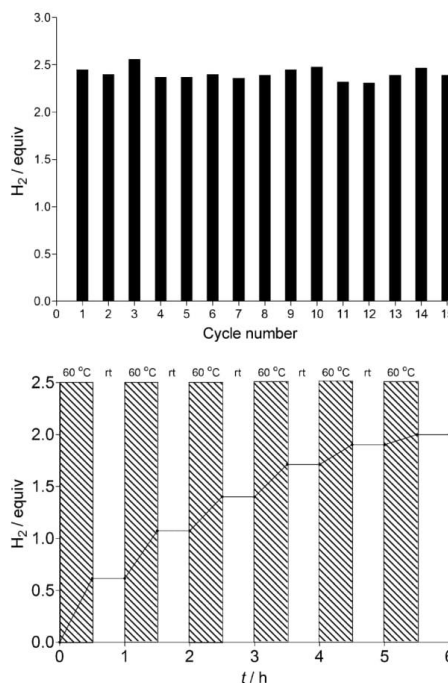


Figure 1. Multiple cycles using the same catalyst (top). Starting and stopping the hydrogen release reaction by temperature control (bottom, 0.25 M solution of AB).

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 ¹¹B NMR spectroscopy. A mixture of **1** (1 equiv) and AB (3 equiv) in [D₈]THF immediately formed ammonia–monochloroborane (NH₃BH₂Cl; see the Supporting Information for assignments).^[30] The formation of NH₃BH₂Cl 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 [$(k_{\text{NH}_3\text{BH}_3}/k_{\text{ND}_3\text{BH}_3}) \times (k_{\text{NH}_3\text{BD}_3}/k_{\text{ND}_3\text{BD}_3}) = 1.76(3) \times 1.78(9) = 3.15(4)$] is similar to the KIE observed for the doubly labeled substrate [$(k_{\text{NH}_3\text{BH}_3}/k_{\text{ND}_3\text{BD}_3}) = 2.88(5)$], suggesting a mechanism where both B–H and N–H bonds are involved in the rate-determining step.

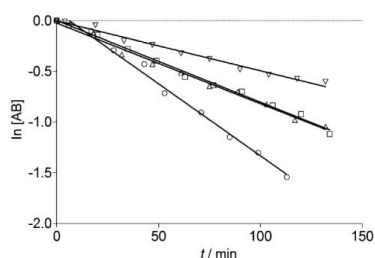
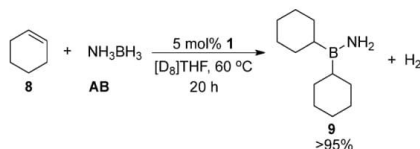


Figure 2. Kinetics of the dehydrogenation of NH_3BH_3 and its isotopologues (0.25 M in THF/diglyme) at 60 °C in the presence of **1** (5 mol %).

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 $[\text{D}_8]\text{THF}$ was heated at 60 °C for 20 h (Scheme 2). Cyclohexene (**8**) was fully converted into $\text{C}_6\text{H}_{11}\text{BNH}_2$ (**9**), which was confirmed by a signal at 48 ppm in



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

the ^{11}B NMR spectrum, supporting the formation of amino-borane (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]

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 [$(3.7 \pm 0.1) \times 10^{-5} \text{ M s}^{-1}$] 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 $\text{NH}_3\text{BH}_2\text{Cl}$ was observed by NMR

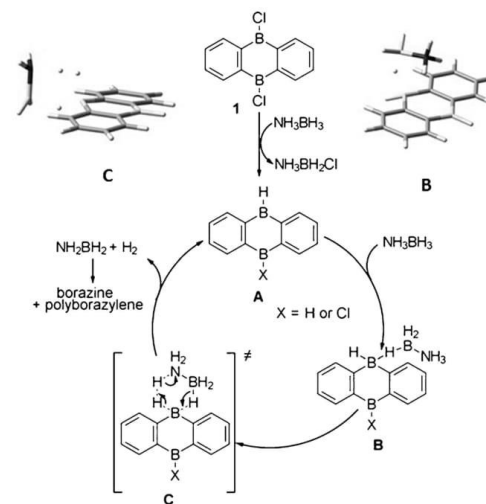


Figure 3. Proposed mechanism for the first step of the catalytic dehydrogenation of ammonia-borane. The shown geometry optimizations of **B** and **C** were computed at the B3LYP-D3 level of theory with a 6-31++G(d,p) basis set.^[34,35]

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).

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 H₂ 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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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

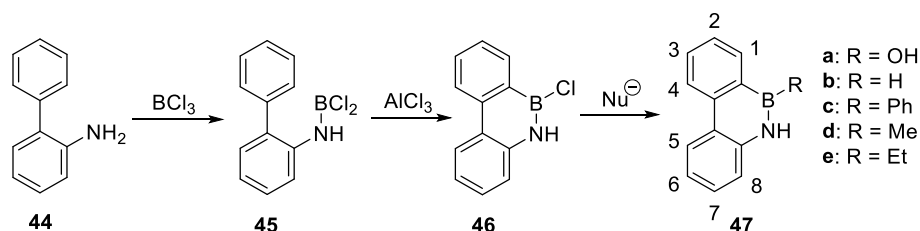
2.1 Introduction

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, π -conjugated organic compounds have gained a lot of interest due to their important applications in organic electronics.^[1-2] Among them many π -conjugated organic systems (such as acenes and polycyclic aromatic hydrocarbons with all-carbon π -skeletons) have been developed.^[3]

The incorporation of heteroatoms into π -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]

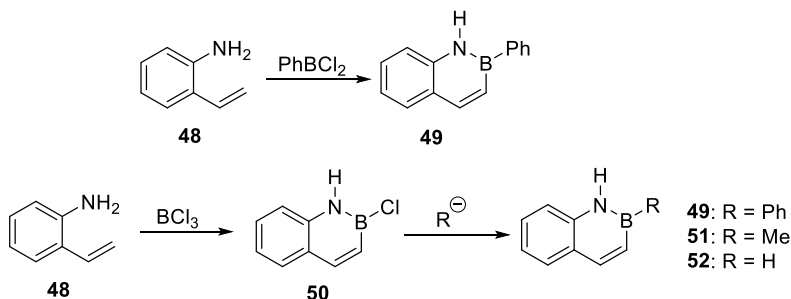
2.2 The recent progress of B, N aromatics

In 1958, Dewar and coworkers published the first synthesis of BN aromatics, 9,10-azabophenanthrenes **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-azabophenanthrene derivatives.

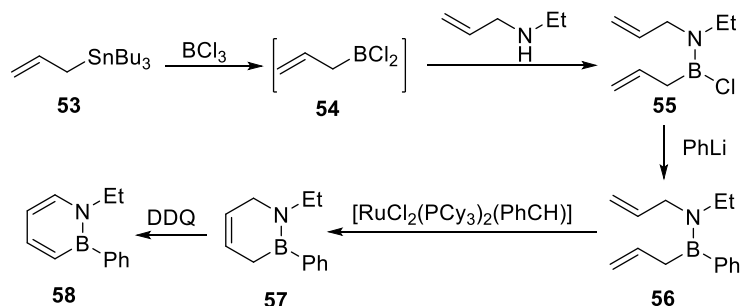
Subsequently, the Dewar group also reported the first synthesis of BN-naphthalene in 1959 (Scheme 15).^[11] The reaction of 2-aminostyrene (**48**) with phenylboron dichloride delivered the 2-phenyl-1,2-azaboranaphthalene (**49**). Surprisingly, BN-naphthalenes (**49**, **51** and **52**) show high stabilities and can remain intact in the presence of strong base or KMnO_4 .



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

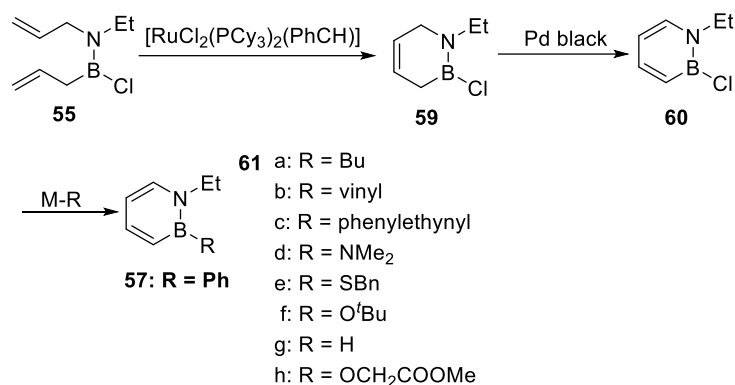
Afterwards, Polivaka,^[12-13] Goubeau^[14-15] and Gronowitz^[16-18] also reported their pioneering work on the synthesis of BN aromatics. However, encumbered by the material characterization capabilities of that time, most of these studies were still based on the synthesis of 1,2-azaborines derivatives, 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 BCl_3 . 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.



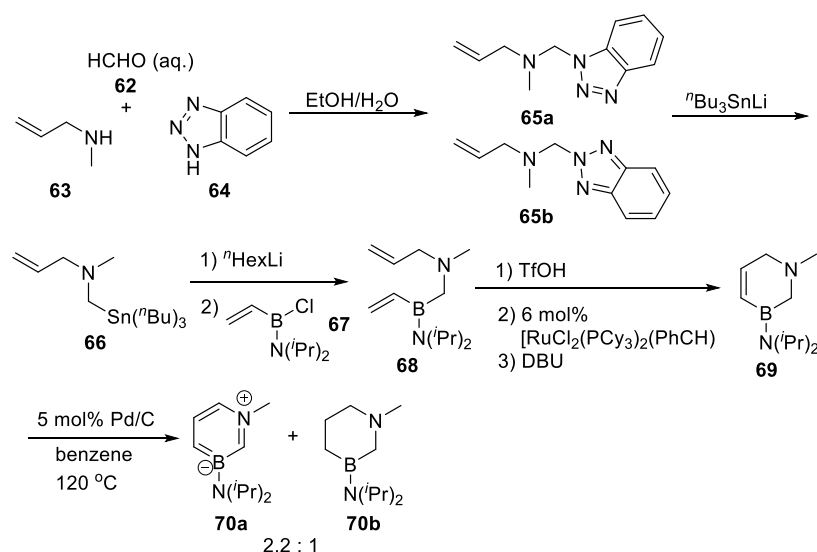
Scheme 16. Synthesis of 1,2-azaborine **58** by ring-closing metathesis.

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).^[20] Followed 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.



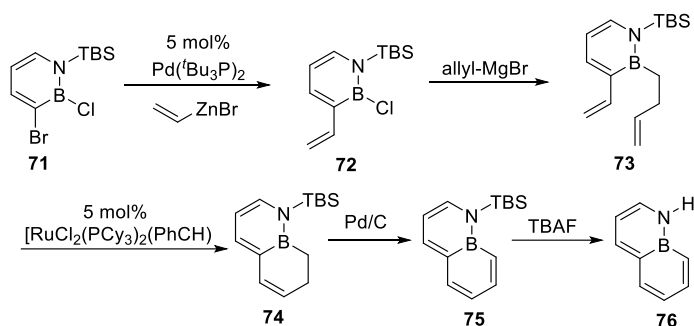
Scheme 17. Formation of boron-substituted 1,2-azaborines by nucleophilic substitution.

Inspired by the former results, the Liu group then created a first example of 1,3-azaborine (Scheme 18).^[21] The reaction of formaldehyde (**62**), allylmethylamine **63** and benzotriazole (**64**) gave a mixture of **65a**, **65b**, which were then treated with *n*Bu₃SnLi 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**.



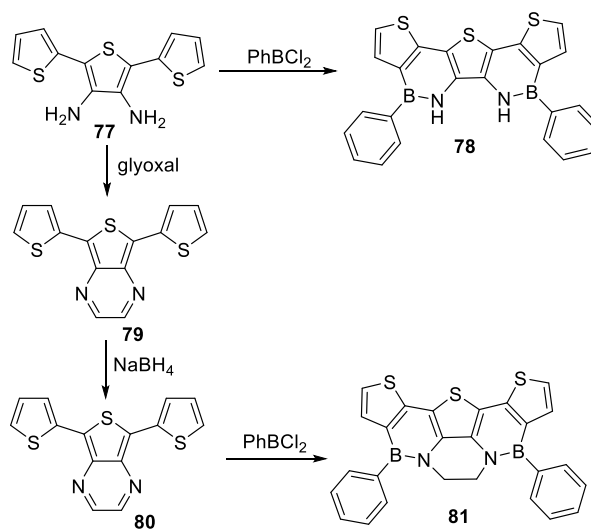
Scheme 18. Synthetic route to the first 1,3-azaborine **70a**.

Another interesting result from the Liu group was the synthesis of a new BN-naphthalene (Scheme 19).^[22] 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**.



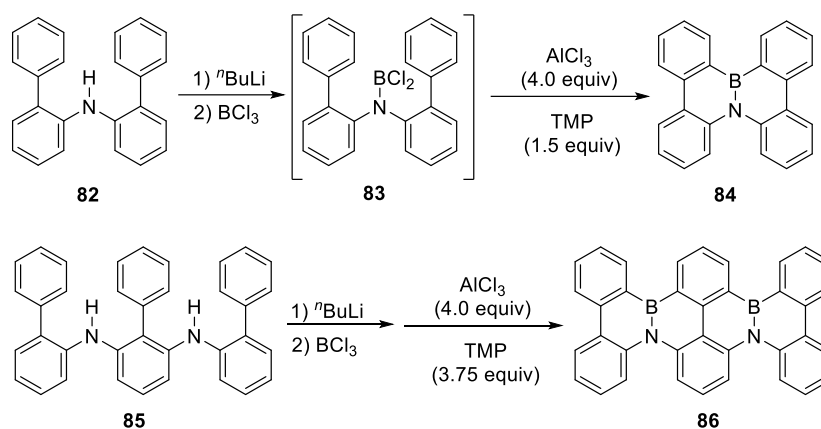
Scheme 19. Preparation of BN-naphthalene **76**.

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).^[23] Similar to Dewar's method,^[6] 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.



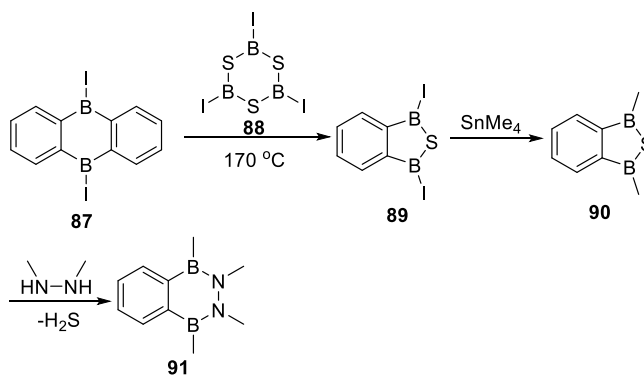
Scheme 20. Synthesis of 1,2-azaborine-fused oligothiophene **78**, **81**.

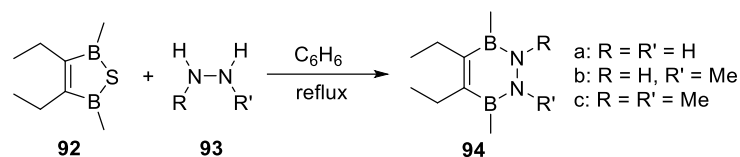
In 2011, Nakamura and coworkers reported a synthesis of BN-fused polycyclic aromatics through a tandem intramolecular electrophilic arene borylation procedure (Scheme 21).^[24] Dichloroboraneamine **83** was synthesized in situ from bis(biphenyl-2-yl)amine (**82**). After screening of a variety of Lewis acids and Brønsted bases, an addition of 4 equivalents of AlCl_3 and 1.5 equivalents of 2,2,6,6-tetramethyl-piperidine (TMP) to the starting material **83** was proved as the best condition for the generation of **84**, and it was found that the AlCl_3 /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**.



Scheme 21. Synthesis of BN-fused polycyclic aromatics.

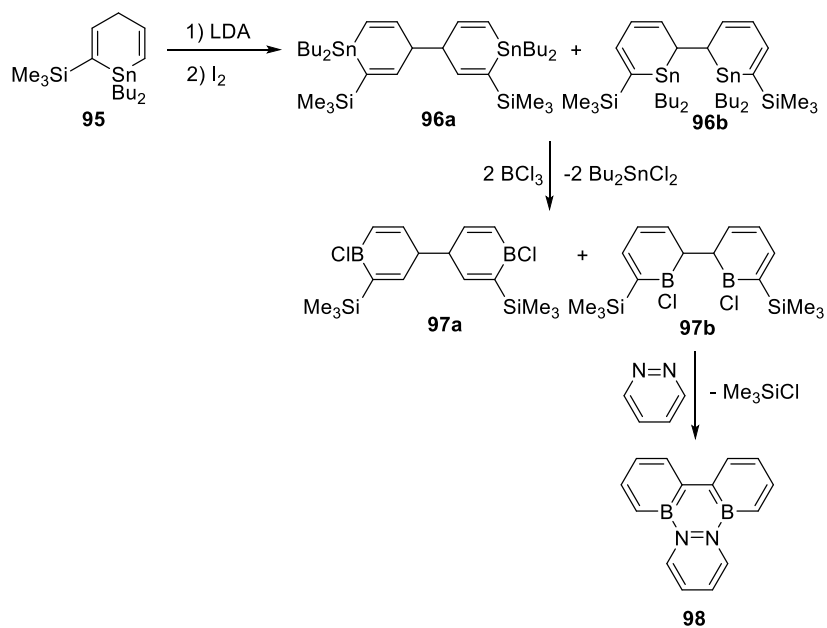
The before-mentioned studies were mainly on the chemistry of azaborine, which contains only one B-N unite in one aromatic ring. The incorporation of two B-N unites into the same aromatic ring was only scarcely reported in the literature. In 1974, Siebert and coworkers reported the first synthesis of BN aromatics with $\text{B}_2\text{C}_2\text{N}_2$ cores (Scheme 22).^[25] The reaction of bisboron compound **87** and triiodo borthiine (**88**) gave the thiadiborol compound **89**, which was then reacted with SnMe_4 to form a methyl substituted thiadiborol compound **90**. Treatment of **90** with 1,2-dimethylhydrazine delivered the B_2N_2 -aromatics **91**. Based on the similar procedure, the 1,2-diazas-3,6-diborin derivatives **94** were also synthesized.^[26]





Scheme 22. Synthetic method to B₂C₂N₂-aromatics.

In 2006, Piers and coworkers reported the synthesis of B₂N₂C₂-substituted triphenylene analogues (Scheme 23).^[27] According to their method, the treatment of stannacyclohexadiene (**95**) with LDA and I₂ afforded the coupling products **96a/96b** in a ratio of 60:40. Followed by the transmetalation with BCl₃, 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 B₂N₂C₂-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 B₂N₂C₂-heteroaromatic compounds have been reported in the literature. The syntheses of these B₂N₂C₂-heteroaromatic compounds often involve complicate 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 route to B₂N₂C₂-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 CO₂^[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 B₂N₂C₂-heteroaromatic compounds (Figure 5). Within this approach, I should be able to furnish the synthesis of novel B₂N₂C₂ heterocycles in one step.

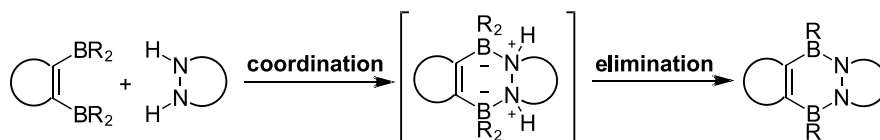


Figure 5. Proposed synthetic route to B₂N₂C₂ aromatic compounds.

2.4 References

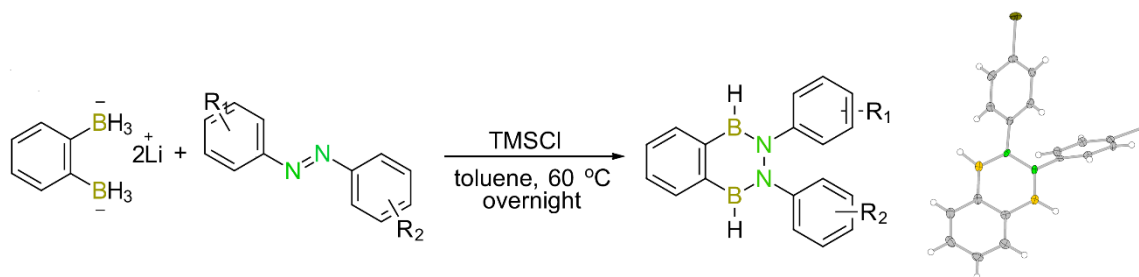
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2.5 Contribution to the Literature

Diazadiborines – (B–N)₂ Isosteres of Naphthalene

Z. Lu, C. Logemann, H. A. Wegner, manuscript in preparation.

“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 Li₂[1,2-C₆H₄(BH₃)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

Zhenpin Lu,^[a] Christian Logemann,^[b] Hermann A. Wegner^{[a]*}

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 various substituted (B–N)₂-naphthalenes via a one-pot reaction of Li₂[1,2-C₆H₄(BH₃)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-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 different electronic properties from their carbon isosteres.^[5] 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).^[6–12] Very recently, Liu and coworkers have developed a methodology for the synthesis of B–N-isosteres of naphthalene and indenyl.^[13] In these BN aromatic compounds only two carbon atoms in one aromatic unit have been replaced by heteroatoms (BNC₄ core). The introduction of even more heteroatoms into the aromatic structure promises further alteration of their physical properties (Figure 1). However, there are only a rare number of examples of B₂N₂C₂ heteroaromatic compounds so far.^[14–16] Piers and coworkers reported the syntheses of triphenylene analogues with B₂N₂C₂ cores, which show very interesting photophysical properties.^[14] Despite these important accomplishments, there is great potential to synthesize previously inaccessible B,N heterocycles, which particularly contain more than one B–N unit.

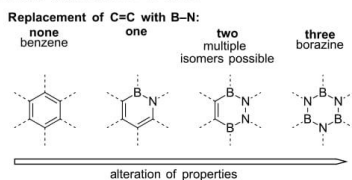


Figure 1. Systematic replacement of C=C with B–N units.

So far, synthetic methods to access B,N heteroaromatic compounds involve multiple steps and often have to rely on 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 B₂N₂C₂ 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*-phenylbisborate (**1**, Li₂[1,2-C₆H₄(BH₃)₂])^[20] with hydrazobenzenes should deliver novel B,N heterocycles containing the B₂N₂C₂-core in just one operation.

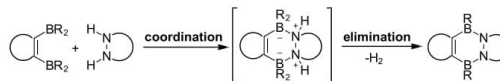
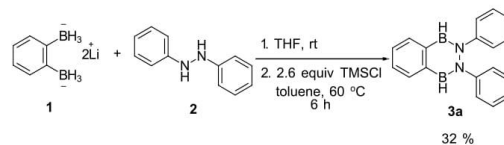


Figure 2. Proposed synthetic route to B₂N₂C₂ aromatic compounds

To prove the above-outline 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 24h 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 ¹¹B 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 hydrazobenzenes.

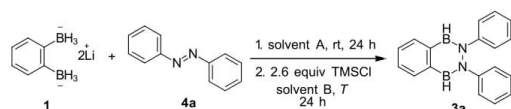
Hydrazobenzenes are not the ideal starting material, as they are air sensitive compounds and have to be prepared by reduction of either azobenzenes or nitrobenzenes often in low yields. Thus, we further investigated the possibility to use directly azobenzene **4a** as building block, which are air stable and can be easily prepared from various anilines.^[21] The bisborate **1** should also

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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**.

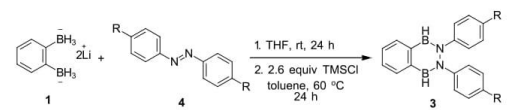


Entry ^[a]	Solvent A	Solvent B	T / °C	Yield of 3a [%] ^[b]
1	THF	toluene	60	34
2	toluene	toluene	60	-
3	CH ₂ Cl ₂	CH ₂ Cl ₂	rt	20
4	THF	THF	50	17
5	THF	toluene	rt	29
6	THF	CH ₂ Cl ₂	rt	23

^[a] Reaction condition: **1** (0.29 mmol), **4a** (0.27 mmol), TMSCl (0.75 mmol), solvent (4 mL), under N₂ in glovebox. ^[b] 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)₂-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)₂-naphthalenes from symmetric azobenzenes.

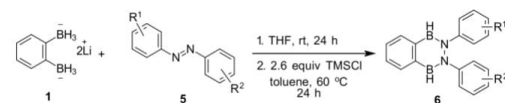


Entry ^[a]	R	Yield of 3 [%] ^[b]
1	H (4a)	34 (3a)
2	Me (4b)	63 (3b)
3	F (4c)	46 (3c)
4	Cl (4d)	56 (3d)
5	Br (4e)	30 (3e)
6	CH=CH ₂ (4f)	-

^[a] Standard condition: **1** (1.0 equiv), **4** (1.0 equiv), TMSCl (2.6 equiv). ^[b] 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)₂-naphthalenes from asymmetric azobenzenes.



Entry ^[a]	R ¹	R ²	Yield of 6 [%] ^[b]
1	4-Me	4-F (5a)	15 (6a)
2	4-OMe	4-F (5b)	17 (6b)
3	2-Br	2-F (5c)	31 (6c)
4	H	2-NO ₂ (5d)	-

^[a] Standard condition: **1** (1.0 equiv), **5** (1.0 equiv), TMSCl (2.6 equiv). ^[b] 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-B - 4.3(3)°, B-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],^[22] 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, 1.498(3) Å],^[10f,12] and B₂C₂N₂-substituted triphenylene [N-N bond, 1.422(4) Å] respectively.^[14]

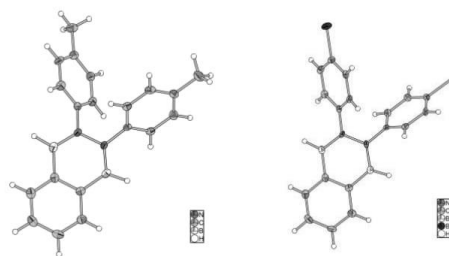


Figure 3. Molecular structure of **3b** and **3e**, anisotropic displacement ellipsoids are drawn at 50% probability.

B-N-doped aromatic compounds have been proposed as luminescent materials.^[23] 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-borazonaphthalene derivatives.^[24-26] They exhibited

almost the same absorption maxima at 310 nm independently of the substitution pattern on the phenyl rings.

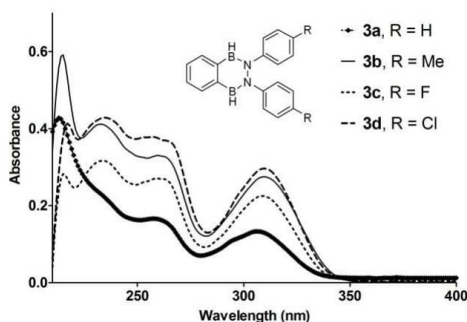


Figure 4. UV-vis spectra of selected (B-N)₂-naphthalene derivatives. All measurements were performed in cyclohexane at 10⁻⁵ M.

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-diphenylnaphthalene (**7**) exhibited values of λ_{abs} at 254 nm and λ_{em} at 373 nm respectively. The quantum yields of these (B-N)₂-naphthalenes were also measured. In accordance to the (B-N)₂-naphthalene reported by Liu,^[13] low values were obtained (less than 0.01, see Supporting Information).

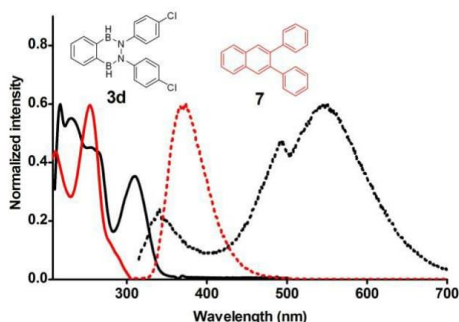


Figure 5. UV-vis absorption (solid black trace) and fluorescence emission spectra (dotted black trace) of **3d** and UV-vis absorption (solid red trace) and fluorescence emission spectra (dotted red trace) of **7** (all measured at 10⁻⁵ M in cyclohexane; all spectra have been normalized for comparison).

In summary, we developed an efficient method to access novel (B-N)₂-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. All the solvent was reduced under high vacuum. Then, TMSCl (94 μ L, 0.75 mmol, 2.60 equiv) in toluene (4 mL) was added to the mixture and the reaction was heated in a 60 °C oil bath overnight. All volatiles were removed under vacuum. The residue was submitted to sublimation at 160 °C (at <0.1 mbar). The target compound (26 mg, white solid, 34 %) was obtained as pure product. ¹H NMR (600 MHz, CDCl₃, 296.8 K): δ = 8.10 (dd, J_{HH} = 5.5, 3.2 Hz, 2H), 7.70 (dd, J_{HH} = 5.5, 3.2 Hz, 2H), 7.18 (m, 8H), 7.01 (m, 2H), 5.42 (br s, 2H, B/H) ppm. ¹³C NMR (100 MHz, CDCl₃, 296.8 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, 296.8 K): δ = 36.05 (br s) ppm. IR (neat) ν = 3049, 2531, 1597, 1490, 1426, 1320, 749, 690, 658, 507 cm⁻¹. HRMS (EI) calcd for C₁₈H₁₆B₂N₂ (M⁺) 282.14995, found 282.15044.

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

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2.6 Summary of the Results

In summary, I demonstrated a one-pot synthesis of novel (B-N)₂-aromatics by the reactions of Li₂[1,2-C₆H₄(BH₃)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.

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