Synthesis, structural characterization, and reactivity of 1,3,2,5-diazadiborinine

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**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**Synthesis, Structural Characterization, and Reactivity of
1,3,2,5-Diazadiborinine**

WU DI

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

2018

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1,3,2,5-Diazadiborinine**

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School of Physical and Mathematical Sciences

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Abstract

Because of the isoelectronic and isostructural relationships between a carbon-carbon double bond (C=C) and a boron-nitrogen single bond (B-N), the substitution a B-N unit for a C=C unit is considered to be one of the important strategies, and this method will form and expand the diversity of aromatic molecules. My thesis mainly focused on the isolation, characterization and relative reactivity of 1,3,2,5-diazadiborinine **C**. Because compound **C** possess both a nucleophilic (Lewis base) and an electrophilic (Lewis acid) boron centre in the B₂N₂C₂ six-membered ring, it can activate MeOTf, PhC≡CH, CO₂ and alkene derivatives without any catalysts. Notably, the reaction between **C** and CO₂ or alkene derivatives underwent reversible [4+2] cycloaddition reactions to afford the corresponding compounds. The addition reaction of a series of sp, sp² and sp³ hybridized carbanions to **C** affords isolable ionic species, which can be regarded as Janovsky-type complexes. Moreover, **C** can also serve as a pre-catalyst to promote hydroboration of carbonyl compounds as well as carbon dioxide, in which the actual active catalyst is the adduct of **C** with carbonyls or CO₂, respectively.

Chapter 1

General Introduction

1.1 Benzene

Since the identification and isolation of benzene by Faraday in 1825,^[1] it has been a very important compounds in chemistry due to its wide application.^[2] Soon after its isolation, Kekulé suggested that benzene was a six-membered ring featuring alternating carbon-carbon single (C-C) and carbon-carbon double (C=C) bonds.^[3] In 1928, Lonsdale confirmed the structure of benzene and demonstrated that all six carbon-carbon bond distances are equal (1.40 Å).^[4] The peculiarity of the structure of benzene as well as its relatively unreactive nature, prompted many chemists to come up with various theories to describe the electronic properties of benzene.^[5] One of the most prominent theories was the work of Hückel, which introduced both valence bond theory and molecular orbital theory to describe benzene and other unsaturated hydrocarbons.^[5a] Hückel's explanations made a substantial contribution to the field's understanding of aromaticity and electron delocalization in many organic molecules.^[6]

1.2 Borazine

Boron, with atomic number of five, has a total of five electrons revolving around the nucleus, and its outermost shell contains three electrons. Due to the octet rule, trivalent boron compounds featuring six electrons in their outermost shell and an unoccupied 2p orbital can accept a lone pair of electrons. In the case of ammonia-borane, the lone pair on the nitrogen coordinates to the unoccupied 2p orbital of the boron atom. Consequently, because the total number of valence electrons is fourteen, ammonia-borane is isoelectronic with ethane which consists of an sp³-hybridized carbon-carbon (C-C) single bond (Scheme 1.1). Due to the difference in polarity between ammonia borane and ethane,^[7] the highly polar ammonia-borane, with its stronger inter-molecular forces, is solid, while non-polar ethane is a gas at room temperature.^[8] In addition,

aminoborane and imidoborane are very unstable and are much more prone to polymerize than ethylene and acetylene. Substitution of carbon-carbon double bonds (C=C) with boron-nitrogen bonds (B-N) gives rise to another important class of aromatic compounds with altered electronic properties. Borazine **1**, which was isolated in 1926, is commonly referred as the “inorganic benzene”, because of its isoelectronic and isostructural relationships with benzene (Scheme 1.2).^[9] Compared with benzene, borazine **1** displays weaker aromaticity and less stability, and readily decomposes on exposure to moisture. Compared to non-polar C=C bonds in an aromatic ring, polar B-N bonds lead to poor delocalization around the aromatic ring.^[9b,9c] The method of formal replacement of a C=C double bond unit by a B-N bond unit enriches electronic systems and alters the properties of aromatic molecules.^[10] Assembling a boron-nitrogen (B-N) moiety within a heterocyclic compound has attracted great interest especially in the fields of materials chemistry and biological chemistry.^[11]

Scheme 1.1 The isoelectronic relationships between CC and BN units.

Scheme 1.2 Structure of borazine **1**.

1.3 General routes to synthesize 1,2-azaborinine derivatives

1,2-Azaborinine derivatives can be prepared by several methods including Friedel-Crafts reaction^[12], hydroboration^[16] followed by dehydrogenation^[17], ring-closing metathesis^[23] followed by ring-expansion^[24], ring-closing metathesis followed by oxidation and [2+2+2] cycloadditions^[32].

1.3.1 Friedel-Crafts method^[12]

In 1958, Dewar group reported the isolation of 9,10-azaboraphenanthrenes, which were the first examples of 1,2-azaborinine derivatives (Scheme 1.3).^[13] Treatment of boron trichloride (BCl₃) with 2-aminodiphenyl **2** in benzene generated 2-diphenylaminoboron dichloride **3**. Treatment of **3** with a catalytic amount of AlCl₃ led to the formation of 10-chloro-9-aza-10-boraphanthrene **4** via Friedel-Crafts cyclization. **4** was reacted with several nucleophiles (R) to afford the corresponding substitution products **5-8**. Based on UV/Vis spectroscopy, **5** shows similar absorption bands with that of phenanthrene.

Scheme 1.3 Synthetic route to 9,10-azaboraphenanthrenes.

Dewar et al. also reported that a mixture of 2-aminostyrene **9** with BCl_3 afforded 1,2-azaboranaphthalens derivatives via direct cyclization, which are BN analogs of naphthalene (Scheme 1.4).^[14] Interestingly, compounds **11-14** were synthesized by nucleophilic substitution reactions and were stable in strong base. Moreover, compound **14** was inert toward strong acids. Halogenation of compound **12** was reported by the Dewar group (Scheme 1.5).^[15] The proposed mechanism suggests that the first step involves the formation of a π -complex as an intermediate, and the aromatic substitution products **15** and **17** and the ring-opened by-products **16** and **18** were generated from this intermediate. The addition of one equivalent of Cl_2 to compound **12** resulted in the ring-opened compound **16** in 67% yield. In contrast, the reaction of compound **12** with Br_2 gave an aromatic substitution product **17** as the major product.

Scheme 1.4 Preparation of 1,2-azaboranaphthalene derivatives.

Scheme 1.5 Halogenation of **12**.

1.3.2 Hydroboration^[16] and dehydrogenation^[17]

In addition to the Friedel-Crafts-type reactions, hydroboration to cyclize the six-membered ring followed by dehydrogenation to generate the aromatic ring have also been used to synthesize 1,2-azaborinine derivatives.^{[18][20][21][22]} In 1964, the Dewar group first synthesized 9,10-azaboranonaphthalene **21** (Scheme 1.6).^[13] Hydroboration of **19** with BH_3NMe_3 in toluene generated octahydro-9,10-azaboranonaphthalene **20**. Subsequently, dehydrogenation of **20** by Pd/C gave compound **21** as colorless plates,

which has the same odor as naphthalene. In addition, the Dewar group also examined the substitution reaction with an electrophilic reagent. When compound **22** was reacted with malonaldehyde bis(diethylacetal) in the presence of $\text{CF}_3\text{CO}_2\text{H}$, the tricyclic 11,12-azaborarophenalenium cation **23** was formed (Scheme 1.7).^[19]

Scheme 1.6 Synthetic route to 9,10-azaboraronaphthalene **21**.

Scheme 1.7 Synthetic route to tricyclic 11,12-azaborarophenalenium cation **23**.

The Dewar group has expanded the hydroboration-dehydrogenation methodology for the synthesis of monocyclic 1,2-azaborinine. Hydroboration of 4-amino-1-hexene **24** under heating generated tristetramethyleneborazine **25**. Dehydrogenation of **25** by Pd/C gave compound **26**, which was characterized by elemental analysis (Scheme 1.8).^[20] Eight years later, the synthesis of monocyclic 1,2-azaborinine was achieved by the Goubeau group by a similar method (Scheme 1.9).^[21] Hydroboration of 4-amino-1-hexene **27** with BH_3NMe_3 gave compound **28**, and subsequent dehydrogenation of **28** by $\text{Pd}/\text{Al}_2\text{O}_3$ afforded monocyclic compound **29**.

Scheme 1.8 Synthetic route to **26**.

Scheme 1.9 Synthetic route to N-methyl-tetrahydro-1,2-azaborinine **29**.

1.3.3 Ring-closing metathesis^[23] and ring-expansion reaction^[24]

In 2004, the Braunschweig group reported the reaction of anti-aromatic boroles with various azides to generate aromatic 1,2-azaborinines **30-33** via a ring-expansion reaction (Scheme 1.10).^[25] Depending on the substituent on the azide, BN isosteres of azo dyes **34-36** could be synthesized through the same ring-expansion reaction (Scheme 1.11), and it has been demonstrated that these compounds show the same UV/Vis absorption spectra as the corresponding azo dye products.^[26]

Scheme 1.10 Synthetic routes to aromatic 1,2-azaborinine derivatives **30-33** by ring-expansion reactions.

Scheme 1.11 Synthetic routes to BN isosteres of azo dyes **34-36**.

The combination of ring-closing metathesis and ring-expansion reaction for the synthesis of 1,2-azaborinine derivatives has been reported. In 2001, Ashe group reported that ring-closing metathesis reactions combined with subsequent ring-expansion reactions afforded 1,2-azaborinine derivatives **40-42** (Scheme 1.12).^[27] Treatment of **37** with Grubbs catalyst afforded **38**. Deprotonation of **38** by LDA gave lithium 1,2-azaborolides **39**. Mixture of **39** and base in dichloromethane (DCM) solution generated 1,2-azaborinine derivatives **40-42**.

Scheme 1.12 Synthetic routes to 1,2-azaborinine derivatives **40-42**.

1.3.4 Ring-closing metathesis and oxidation reactions

Compared with ring-closing metathesis and ring-expansion reaction, the direct formation of a six-membered C₄BN ring followed by dehydrogenation has been found to be more convenient for the synthesis of 1,2-azaborinine.^{[28][29][30]} In 2000, Ashe group

first synthesized compound **45** by a ring-closing metathesis-oxidation reaction (Scheme 1.13).^[28] Treatment of **43** with Grubbs catalyst at room temperature afforded the ring-closed product **44**. The reaction of **44** with 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) gave compound **45**. In 2007, the Liu group also reported the synthesis of **46**, which was further reacted with various nucleophiles to afford functionalized 1,2-azaborinine products **47-55** (Scheme 1.14).^[29]

Scheme 1.13 Synthetic route to 1-ethyl-2-phenyl-1,2-azaborinine **45**.

Scheme 1.14 Synthetic routes to boron-substituted 1,2-azaborinine derivatives **47-55**.

While the synthesis of 1,2-azaborinine derivatives has been well documented, the synthesis and isolation of 1,2-dihydro-1,2-azaborinine, which can be viewed as a hybrid organic/inorganic benzene, was not reported until 2008 when the Liu group reported its synthesis and characterization (Scheme 1.15).^[31] **56** was prepared through ring-closing metathesis followed by dehydrogenation. Complexation of **56** with Cr(CO)₃(MeCN)₃ afforded complex **57**. Treatment of **57** with HF generated compound **58** via the cleavage

of the TBS group on the nitrogen atom. Removal of the $\text{Cr}(\text{CO})_3$ moiety in **58** by PPh_3 afforded the final product **59**.

Scheme 1.15 Synthetic route to **59**.

1.3.5 [2+2+2] Cycloaddition reactions^[32]

In 2014, the Braunschweig group reported a new method to synthesize 1,2-azaborinine derivatives. [2+2+2] cycloadditions are used in their strategy (Scheme 1.16).^[33] Reaction of symmetrical iminoborane **60** with two equivalents of ethynylferrocene in the presence of a catalytic amount of $[(^i\text{Pr}_3\text{P})_2\text{RhCl}]_2$ produced **61**, which features ferrocenyl units that make it potentially applicable in materials chemistry. Treatment of **60** with a stoichiometric amount of $[(^i\text{Pr}_3\text{P})_2\text{RhCl}]_2$ in the presence of ethynylferrocene gave η^4 complex **62**. Subsequent [4+2] cycloaddition of **62** with $[\text{D}_1]$ ethynylferrocene gave product **63** and confirmed the [2+2+2] mechanism. Braunschweig group and Lambert group demonstrated that functionalization of 1,2-azaborinines at the C4 and C6 positions could be achieved by using unsymmetrical iminoborane **64** (Scheme 1.17).^[34] A mixture of **64**, the appropriate alkyne, and $[(^i\text{Pr}_3\text{P})_2\text{RhCl}]_2$ afforded η^4 complexes **65-66**. Subsequent reaction with either phenylacetylene or acetylene generated functionalized 1,2-azaborinines **67-72**.

Scheme 1.16 Synthetic routes to 1,2-azabroinine derivatives **61** and **63** by [2+2+2] cycloaddition reaction.

Scheme 1.17 Synthetic routes to 1,2-azabroinine derivatives **67-72**.

1.4 General route to synthesis of 1,3-azaborinine derivatives

Compared to the well-documented 1,2-azaborinine derivatives, there are limited synthetic procedures for the preparation of 1,3-azaborinine derivatives, because of their poor thermal stability.^[35] In 2011, a ring-closing metathesis-dehydrogenation method has been used to synthesize 1,3-azaborinine derivatives.

1.4.1 Ring-closing metathesis and dehydrogenation

In 2011, the Liu group developed the first synthetic route to synthesize 1,3-azaborinine derivatives (Scheme 1.18).^[35] Treatment of a mixture of N-methylallylamine, formaldehyde and benzotriazole at room temperature gave products **73** and **74**. Subsequent addition of $n\text{Bu}_3\text{SnLi}$ to **73** and **74** generated compound **75**. Lithium-tin exchange of **75** with $n\text{hexyllithium}$ followed by electrophilic addition with **76** produced **77**. After protecting the nitrogen atoms with triflic acid, ring-closing metathesis and subsequent deprotonation by DBU, afforded heterocycle **78**. 1,3-Azaborinine **79** was then synthesized by dehydrogenation of **78**. Compound **79** reacted with acetic acid to afford the B-OAc substituted **80** and an iminium cation to give C6-substituted **81** (Scheme 1.19).

Scheme 1.18 Synthetic route to 1,3-azaborinine derivative **79**.

Scheme 1.19 Derivatization of 1,3-azaborinine **79**.

1.5 General routes for the synthesis of 1,4-azaborinine derivatives

Several routes have also been employed for the synthesis of 1,4-azaborinine derivatives. Dilithium species, [2+2+2] cycloaddition reactions and Ring-closing metathesis have all been used in these synthesis.

1.5.1 Conversion of dilithium species to cyclized products

In 1961, Maitlis first reported the synthesis of 10,9-borazaroanthracene derivative **82** (Scheme 1.20).^[36] The Clark group reported the first structure of a 1,4-azaborinine derivative in 1992 (Scheme 1.21).^[37] The reaction of dilithiodiphenylmethanamine **83** with $\text{BF}_3 \cdot \text{Et}_2\text{O}$ followed by the addition of mesityl lithium gave product **84**. The Liu group also reported a new synthetic route for the preparation of N- and B-substituted monocyclic 1,4-azaborinine **87** (Scheme 1.22).^[38] The reaction of **85** with $t\text{BuLi}$ followed by quenching with $i\text{Pr}_2\text{NBCl}_2$ generated heterocycle **86**. Treatment of **86** with a catalytic amount of $\text{HRuCl}(\text{CO})(\text{PPh}_3)_3$ induced isomerization to **87**.

Scheme 1.20 Structure of **82**.

Scheme 1.21 Synthetic route to **84**.

Scheme 1.22 Synthetic route to **87**.

1.5.2 [2+2+2] cycloaddition reaction

In 2012, the Braunschweig group reported the preparation of the first non-benzannulated 1,4-azaborinine through a [2+2+2] cyclotrimerization reaction (Scheme 1.23).^[39] The reaction of iminoborane $^t\text{Bu-B}\equiv\text{N-}^t\text{Bu}$ with a catalytic amount of $[(^i\text{Pr}_3\text{P})_2\text{RhCl}]_2$ under acetylene atmosphere afforded **88**. Stable intermediate **89** was isolated, which confirmed the tandem [2+2]/[2+4] cycloaddition process. To demonstrate the synthetic utility of the functionalized 1,4-azaborinine derivative, they also reported the isolation of bis- and tris-1,4-azaborinines by varying the alkyne (Scheme 1.24).^[40] The reaction of iminoborane $^t\text{Bu-B}\equiv\text{N-}^t\text{Bu}$ with $[(^i\text{Pr}_3\text{P})_2\text{RhCl}]_2$ in the presence of bis-alkynes produced η^4 complexes **90-91**. Subsequent reactions under an acetylene atmosphere afforded bis-1,4-azaborinines **92-93**. By employing a tris-alkyne with the same methodology, **94** could be obtained.

Scheme 1.23 Synthetic routes to **88** and **89** by [2+2] or [2+4] cycloaddition reactions.

Scheme 1.24 Synthetic routes to **92-94**.

1.5.3 Ring-closing metathesis

In 2014, the Liu group synthesized a monobenzofused 1,4-azaborinine by ring-closing metathesis (Scheme 1.25).^{[41][42]} N-Substitution of 2-bromoaniline gave

compound **95**. The reaction of **95** with a catalytic amount of $(\text{PPh}_3)_3(\text{CO})(\text{Cl})\text{RuH}$ afforded **96**. **96** was reacted with $n\text{BuLi}$ followed by vinylboron chloride to yield compound **97**. Finally, **97** was treated with a catalytic amount of Grubbs catalyst to generate the designed product **98** via ring-closing metathesis.

Scheme 1.25 Synthetic route to monobenzofused 1,4-azaborinine derivative **98** by ring-closing metathesis.

1.6 Application of 1,2- and 1,4-azaborinine derivatives

In addition to well-documented methodologies for the preparation of azaborinine derivatives, applications of 1,2- and 1,4-azaborinine derivatives have also been explored. Functionalized azaborinine derivatives can be used as ligands, hydrogen storage materials, π -conjugated materials and biomedical applications^[43].

1.6.1 Functionalization of 1,2-azaborinine derivatives

1,2-Azaborinine derivatives can be functionalized via several methods including Diels-Alder and cross-coupling reactions.^[10]

1.6.1.1 Diels-Alder reactions

In 2015, the Liu group first reported the synthesis of compound **99** by [4+2] cycloadditions of 1,2-azaborinine derivatives with dienophiles in the presence of AlCl_3 . In the reaction, 1,2-azaborinine derivatives can be regarded as 4C+1N synthons for the preparation of functionalized 6-membered rings **99'** (Scheme 1.26).^[44]

Scheme 1.26 Synthesis of **99** by Diels-Alder reactions.

1.6.1.2 Cross-coupling reactions

In 2015, the Liu group synthesized various 1,2-azaborinine derivatives bearing a B-Cl bond by Negishi cross-coupling reactions^[45] (Scheme 1.27).^[46] The reaction of compound **100** with various zinc reagents in the presence of 5.0 mol% $\text{Pd}(\text{P-}^t\text{Bu}_3)_2$ gave the corresponding products **101-106**. Thus, the B-Cl bond in **100** was tolerated under the reaction conditions. Meanwhile, the reaction of compound **103** with allyl-MgBr gave **107**. Treatment of **107** with a catalytic amount of Grubbs catalyst formed **108** via a classical ring-closing metathesis. Subsequent deprotonation of **108** generated the anionic 10- π -electron product **109**, which could be regarded as an isostere of indole (Scheme 1.28). Similarly, starting from compound **103**, a nucleophilic reaction with 3-butenylmagnesium bromide, ring-closing metathesis, oxidation and deprotection, led to the formation of **113** (Scheme 1.29).

Scheme 1.27 Synthetic routes to 1,2-azaborinine derivatives by Negishi cross-coupling reaction.

Scheme 1.28 Synthetic route to product **109**.

Scheme 1.29 Synthetic route to **113**.

The Liu group synthesized B-substituted 1,2-azaborinines via the selective functionalization of the C6 substituent with Ir-catalyzed C-H borylation (Scheme 1.30).^[47] After screening the reaction conditions, the formation of B-substituted 1,2-

azaborinines **114** was achieved by the C-H borylation of 1,2-azaborinines with bis(pinacolato)diboron (B_2pin_2) in the presence of 1.5 mol% $[Ir(OMe)(cod)]_2$. Subsequent Suzuki cross-coupling reactions furnished C6-substituted 1,2-azaborinines, one of which 6-[pyrid-2-yl]-1,2-azaborinine **115**, could be used as an N,N-bidentate ligand.

Scheme 1.30 Synthetic route to C6-substituted 1,2-azaborinine derivatives **115**.

1.6.2 Ligands application enabling regio- and diastereoselective reactions

Utilization of a 1,4-azaborinine derivative as a ligand in a catalytic reaction was reported. In 2014, the Liu group reported a palladium-catalyzed hydroboration using 1,4-azaborinine **116** as a ligand (Scheme 1.31).^[41] While the use of carbonaceous ligand **116-C** led to the formation of **C** as a major product, the cis-hydroboration product **B** was obtained selectively when **116** was employed as the ligand.

Scheme 1.31 **116** and **116-C** as ligands in Pd-catalyzed hydroboration.

1.6.3 Hydrogen storage

Hydrogen, a flammable gas, is regarded as a clean energy source, but how to store hydrogen is a big challenge. Therefore, the development of efficient and safe hydrogen storage approaches is viewed as a very important topic.^[48] Ammonia borane (H_3NBH_3) has a gravimetric density of 19.6 wt % H_2 ^[49] and is considered as a potential hydrogen source.^[50] In addition to H_3NBH_3 , BN heterocycles can release H_2 via dehydrogenation using a catalytic amount of Pd/C. In 2010, the Liu group and Dixon group reported the application of BN heterocycles as a potential hydrogen storage platform.^[51] In the proposed fuel cycle, 1,2-azaborinine derivatives **120** could refuel three equivalents of H_2 to obtain the charged fuel **117** (Scheme 1.32). Charged fuel **117** could release H_2 stepwise to form **118**, **119** and **120** via dehydrogenation. Based on the calculated results, dehydrogenation of charged fuel **117** almost forms a reversible H_2 storage system ($\Delta G \approx 0$ kcal/mol) because of the production of the aromatic 1,2-azaborinine derivatives **120** (Scheme 1.33). 1,2-Dihydro-1,2-azaborinine **59** (Scheme 1.15) as a hydrogen-based compound exhibits a gravimetric density of 7.1 wt % H_2 .

Scheme 1.32 Storage and release of hydrogen by 1,2-azaborinine derivatives.

R = H; $\Delta H = 23.5$ kcal/mol; $\Delta G = -2.3$ kcal/mol

R = Me; $\Delta H = 26.0$ kcal/mol; $\Delta G = -0.3$ kcal/mol

R = *t*Bu; $\Delta H = 25.2$ kcal/mol; $\Delta G = -0.4$ kcal/mol

Scheme 1.33 Charge fuel to spent fuel for hydrogen release.

1.6.4 π -Conjugated materials

Although the synthesis of monocyclic 1,2-azaborinine units has been well documented, installation of 1,2-azaborinine units into conjugated oligomers and polymers remains unexplored. In 2015, the Liu group and Jäkle group reported the synthesis of 1,2-azaborinine oligomers and polymers by Suzuki-Miyaura cross-coupling methods (Scheme 1.34-1.35).^[52] They first synthesized compounds **122** and **121**,

respectively. The cross-coupling reaction between **121** and **122** generated 1,2-azaborinine dimer **123**. After borylation of **123** to afford **124**, the cross-coupling reaction between **124** and **122** produced trimer **125** (Scheme 1.34). The C-H borylation of **122** generated **126**. Polymerization of **126** afforded the 1,2-azaborinine polymer **127** (Scheme 1.35).

Scheme 1.34 Synthetic routes to 1,2-azaborinine dimer **123** and trimer **125**.

Scheme 1.35 Synthetic route to 1,2-azaborinine polymer **127** by Suzuki-Miyaura cross-coupling reaction.

1.7 Objectives and aims

Figure 1.1 Target core structure of 1,3,2,5-diazadiborinine derivatives.

The replacement of a C=C unit by a B-N unit to form azaborinine derivatives is very promising and this method can be used to modify the intrinsic electronic properties of the six-membered aromatic heterocyclic compounds. However, installation of two B-N units into aromatic scaffolds furnishing an aromatic $C_2B_2N_2$ six-membered ring has limited cases.^[10] Compared to azaborinine derivatives, diazadiborinine derivatives are not well developed. Compounds 1,3-diaza-2,4-diborinine, 1,2-diaza-3,6-diborinine, 1,4-diaza-2,3-diborinine and 1,5-diaza-2,4-diborinine have been reported and their limited reactivity and applicability studies have been reported. This has inspired us to design and synthesize a 1,3,2,5-diazadiborinine derivative, as it may possess interesting properties, for example, unusual photochemical characteristics and ability to activate small molecules. This project mainly focuses on the synthesis of 1,3,2,5-diazadiborinine and investigation of its reactivity towards small molecules (Figure 1.1).

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Chapter 2

Synthesis and Structural Characterization of 1,3,2,5- Diazadiborinine

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2.1 Introduction

Compounds involving one B-N unit in the six-membered heterocycle, namely azaborinines, have been extensively studied. However, synthetic routes of the heterocyclic aromatic ring with two B-N units, namely diazadiborinines, is relatively limited.^[1] Synthetic routes to 1,4-diaza-2,3-diborinine **I**, 1,3-diaza-2,4-diborinine **IV**, 1,3-diaza-4,6-diborinine **V** and 1,2-diaza-3,6-diborinine **VIII** have been reported, but only elimination, dimerization and deprotonation reactions have been used to construct those aromatic compounds (Figure 2.1).^[2-9] Moreover, synthetic methods for the preparation of 1,3-diaza-5,6-diborinine **II**, 1,2-diaza-3,4-diborinine **III**, 1,4-diaza-3,5-diborinine **VI**, 1,2-diaza-3,5-diborinine **VII**, 1,3-diaza-2,5-diborinine **IX** and 1,4-diaza-2,5-diborinine **X** have not been explored (Figure 2.1).^[1]

Figure 2.1 Possible structures of diazadiborinine derivatives.

2.1.1 1,3-Diaza-2,4-diborinines

A general synthetic method for the preparation of 1,3-diaza-2,4-diborinine involves the dimerization of an amine-borane adduct. In 1964, Köster and Iwasaki first reported the synthesis of 1,3-diaza-2,4-diborinine derivatives **1** (Scheme 2.1).^[2] Later, Frange group used the same methodology to construct 1,3-diaza-2,4-diborinine **2** and **3** (Scheme 2.2 and Scheme 2.3).^[3] In addition, 1,3-diaza-2,4-diborinine derivatives **4** could react with chromium hexacarbonyl ($\text{Cr}(\text{CO})_6$) to form a π -coordinated η^6 -chromium complex **5** (Scheme 2.4).^[4]

Scheme 2.1 Synthesis of 1,3-diaza-2,4-diborinine **1**.

Scheme 2.2 Synthesis of 1,3-diaza-2,4-diborinine **2**.

Scheme 2.3 Synthesis of 1,3-diaza-2,4-diborinine **3**.

Scheme 2.4 Synthesis of a π -coordinated η^6 -chromium complex **5**.

2.1.2 1,2-Diaza-3,6-diborinines

In 1976, the Full group isolated 1,2-diaza-3,6-diborinine **6** from the reaction of a thiadiborolene with a hydrazine (Scheme 2.5).^[5] Compound **6** reacted with $(\text{MeCN})_3\text{Cr}(\text{CO})_3$ to afford the corresponding η^6 -complex **7**. Recently, a new synthetic route for the synthesis of 1,2-diaza-3,6-diborinines **11-13** has been developed by the Piers group. Compounds **11-13** were obtained by the reaction of diborabiphenyl precursors **8-10** with pyridazine (Scheme 2.6).^[6] Compared with the related aromatic hydrocarbon triphenylene, compound **13** has unique optical properties. For example, it has a deep red color and lower-energy charge-transfer absorption bands ($\lambda_{\text{max}}(\text{CH}_2\text{Cl}_2) = 509$ and 545 nm).

In 1997, the Cowley group and the Marder group prepared an *oxo*-bridged dimer of 1,4-diaza-2,3-diborinine **14** by the reaction of 1,4-diaza-2,3-diene dianion with $\text{B}_2(\text{OMe})_4$ (Scheme 2.7).^[7] Recently, monocyclic and bicyclic 1,4-diaza-2,3-diborinine derivatives **15-17** were isolated by the Şahin group (Scheme 2.8).^[8] 1,4-Diaza-2,3-diene dianion can react with 1,2-dichlorodiborane or 1,2-dichloro-1,2-diborolane to afford **15-17** or **18**, respectively. In contrast with the half-chair conformation observed in **17**, the crystal structure of **15** displays that the diazadiborinine ring is almost planar, which implies the enhanced aromaticity in **15**. In addition, the Braunschweig group synthesized 2,3-bis(dimethylamino)-substituted 1,4-diaza-2,3-diborinine **19** and selective reduction of **19** by BH_3SMe_2 gave dihydro-1,4-diaza-2,3-diborinine **20** and monohydro-1,4-diaza-2,3-diborinine **21** (Scheme 2.9).^[9]

Scheme 2.7 Synthesis of 1,4-diaza-2,3-diborinine derivative **14**.

Scheme 2.8 Synthesis of 1,4-diaza-2,3-diborinine derivatives **15-18**.

Scheme 2.9 Synthesis of 1,4-diaza-2,3-diborinine derivatives **19-21**.

2.1.4 1,5-Diaza-2,4-diborinines

1,5-Diaza-2,4-diborinines derivatives featuring two B-N units have only been reported by the Roesler group (Scheme 2.10).^[10] The reaction of trimethylsilyl formamidinate with 1,1-bis(methylchloroboyl)ethane gave zwitterionic ring **22**. Deprotonation of compound **22** by KHMDS in benzene afforded 1,5-diaza-2,4-diborinine **23**. Interestingly, further deprotonation of **23** by $n\text{BuLi}$ in THF afforded the anionic carbene **24**.

Scheme 2.10 Synthesis of 1,5-diaza-2,4-diborinines **23-24**.

2.2 Objective

Because synthetic routes for the preparation of diazadiborinine derivatives are limited,^[1] it prompts us to develop new methods for the synthesis of unknown diazadiborinine compounds, especially 1,3-diaza-2,5-diborinine **IX** (Figure 2.1). **IX** has several resonance structures, **IX-a**, **IX-b** and **IX-c**, which features nucleophilic and electrophilic boron centers, and has the potential to activate small molecules as frustrated Lewis pairs^[11] (Figure 2.2).

Figure 2.2 Resonance structures of **IX**.

2.3 Results and Discussion

Treatment of 4,4'-dimethyl-2-oxazoline with n BuLi in THF gave the 2-lithio-4,4'-dimethyl-2-oxazolidine intermediate, and the addition of dichlorophenylborane (PhBCl_2) to that intermediate gave a crude THF solution of compound **A**. Crude **A** was combined with one equivalent of PhBCl_2 in toluene to afford product **B** in 29% yield (Scheme 2.11). Compound **B** was fully characterized by NMR spectroscopy. The ^{11}B NMR spectrum of **B** display two peaks, one signal appeared at 3.5 parts per million (ppm) corresponds to the boron between two nitrogen atoms, and the other signal (-11.4 ppm) can be attributed to the boron atom adjacent to two carbon atoms. The solid-state structure of **B** was confirmed by X-ray diffraction analysis (Figure 2.3), which revealed the tetrahedral geometry around the B1 and B2 atoms, indicative of a characteristic sp^3 hybridization. Both the B1-N1 (1.563(4) Å) and B1-N2 (1.573(4) Å) distances are typical of boron-nitrogen single bonds (1.51–1.58 Å).^[12] Compared with the B2-C11 distance (1.589(5) Å), the B2-C12 (1.575(5) Å) distance is shorter, which shows the unsymmetrical geometry of **B**. The N1-C11 (1.292(4) Å) and N2-C12 (1.287(4) Å) distances are typical of nitrogen-carbon double bonds (1.27–1.30 Å).^[13]

Scheme 2.11 Synthesis of compound **B**.

Figure 2.3 Solid-state structure of **B** (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

The reduction of **B** using six equivalents of potassium graphite (KC_8) in toluene afforded the desired product **C** as a white powder in 32% yield (Scheme 2.12). In the ^{11}B NMR spectrum of **C**, two signals were observed, a broad peak for the boron atom between two nitrogen atoms was observed at 24.9 ppm, and a sharp peak for the boron atom between two carbon atoms appeared at 7.3 ppm. Both signals are shifted downfield compared with those (3.5 ppm and -11.4 ppm) of **B**. Compound **C** displayed good thermal stability, since no decomposition was observed even when **C** was heated at 150 °C in a sealed Young NMR tube for several hours in C_6D_6 . Single crystals of **C** were obtained from a saturated benzene solution at room temperature, and the X-ray diffraction analysis revealed the 1,3,2,5-diazadiborinine structure of **C**, in which the central six-membered $\text{B}_2\text{C}_2\text{N}_2$ ring is planar (Figure 2.4). The two boron atoms exhibit trigonal-planar geometries (the sum of the boron angles: B1: 359.93° and B2: 359.96°), which are characteristic sp^2 hybridization. The phenyl ring at B1 is almost perpendicular to the $\text{B}_2\text{C}_2\text{N}_2$ six-membered ring, whereas the phenyl ring at B2 is slightly twisted by 11.9° relative to the $\text{B}_2\text{C}_2\text{N}_2$ ring. The B2-C5 (1.483(3) Å) and B1-N1 (1.443(3) Å)

distances are significantly shorter than those of the corresponding bonds in **B** (1.589(5) Å and 1.876(5) Å) and 1.573(4)-1.873(4) Å) and lie between typical single (boron-carbon: 1.58–1.62 Å; boron-nitrogen: 1.51–1.58 Å) and double bonds (boron-carbon: 1.42–1.45 Å; boron-nitrogen: 1.27–1.30 Å) of boron-carbon and boron-nitrogen, respectively.^{[12][14]} On the other hand, the N1-C5 (1.374 (3) Å) distance is longer than that of the corresponding bond in **B** (1.287(4) Å and 1.292(4) Å). This unique geometrical property demonstrates the delocalization of the 6 π -electrons over the B₂C₂N₂ ring, suggesting the aromatic property. Accordingly, several resonance structures involving **C1-C3** can be considered for the actual electronic structure of **C** (Scheme 2.13).

Scheme 2.12 Synthesis of 1,3,2,5-diazadiborinine derivative **C**.

Scheme 2.13 Selected resonance structures of **C**.

Figure 2.4 Solid-state structure of **C** (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

To gain further insight into the electronic properties of **C**, we performed quantum chemical density functional theory calculations on **C** at the B3LYP/6-311G+(d,p) level of theory, which involved geometry optimization, natural bond orbital (NBO) analysis and natural population analysis (NPA). The optimized geometry of **C** is in good agreement with the experimental structural parameters. The Wiberg bond index (WBI) values for the B2-C5 (1.21), C5-N1 (1.14) and N1-B1 (0.96) bonds suggest these bonds have some partial double-bond character. Natural population analysis shows the B2 atoms (+0.19) are more electronegative than the B1 atoms (+0.94), but the B2 atoms are more electropositive than reported neutral tri-coordinate nucleophilic boron atoms.^[15] The HOMO of **C** shows a π -system over the six-membered B₂C₂N₂ ring featuring a node between the NBN and CBC π -units, and the phenyl ring on the B2 atom displays anti-bonding conjugation with the π -electrons of the B₂N₂C₂ ring (Figure 2.5a). The HOMO-4 and HOMO-5 of **C** correspond to π -bonding interactions between the N1 and C5 atoms (Figure 2.5b). In the ultraviolet-visible absorption spectrum of **C**, the maximum absorption band appears at the wavelength (λ) of 275 nm, which is

comparable to that of *para*-terphenyl ($\lambda = 277\text{nm}$), an isoelectronic species with **C**.^[16]

The solid state of **C** showed light blue-fluorescence under an ultraviolet lamp (Figure 2.5c), while *para*-terphenyl shows purple fluorescence.^[17]

Figure 2.5 (a) Plot of the HOMO of **C**. (b) Plots of the HOMO–4 (left) and HOMO–5 (right) of **C**. (c) Photographic image of the fluorescence of **C** in its solid state under ultraviolet irradiation.

The nucleus-independent chemical-shift values NICS(0) and NICS(1) were calculated at the same level of theory to evaluate the aromaticity of **C**. The NICS values of benzene, 1,2-azaborinine, 1,3-azaborinine and borazine were compared with that of 1,3,2,5-diazadiborinine **C'** (Figure 2.6). Although the NICS values of **C'** are less negative than those of benzene, 1,2-azaborinine and 1,3-azaborinine, the values are more negative than that of borazine, which indicates **C'** is aromatic. In addition, the resonance stabilization energy (RSE) was also determined to estimate the aromaticity of **C'** (Table 2.1). The RSE value of **C'** is $\sim 22.4 \text{ kcal mol}^{-1}$ less than of benzene ($\text{RSE} = 34.1 \text{ kcal mol}^{-1}$), thus it can be estimated to be $11.7 \text{ kcal mol}^{-1}$, which is smaller than those of 1,3-azaborinine ($\text{RSE} = 29 \text{ kcal mol}^{-1}$)^[18a] and 1,2-azaborinine ($\text{RSE} = 21 \text{ kcal mol}^{-1}$)^[18b].

NICS(0)	-4.3	-8.0	-4.9	-6.2	-1.6
NICS(1)	-6.5	-10.2	-7.1	-8.6	-2.7

Figure 2.6 Calculated NICS(0) and NICS(1) values for **C'** benzene, 1,2-azaborinine, 1,3-azaborinine, and borazine. Calculated at the B3LYP/6-311+G(d,p) level of theory.

Table 2.1 Raw energy data from the RSE calculations.

	total energy (au)	ZPE	H _{corr}	G _{corr}	E + ZPE	E + H _{corr}	E + G _{corr}
C'	-239.1673577	0.09486	0.10072	0.06701	-239.072496	-239.066641	-239.100351
C' + 2H	-240.3757176	0.11428	0.12147	0.08495	-240.261436	-240.254245	-240.290766
C₆H₆	-232.3112711	0.10018	0.10552	0.07272	-232.211091	-232.205750	-232.238555
C₆H₈	-233.4838985	0.12182	0.12794	0.09359	-233.362082	-233.355957	-233.390311
[(C' + 2H) + C₆H₆] - (C' + C₆H₈) [au]	-0.03573264				-0.03794864	-0.03739664	-0.03865864
[kcal mol⁻¹]	-22.42257285				-23.813134	-23.4667487	-24.2586658

H_{corr} = Enthalpy correction. G_{corr} = Free energy correction.

2.4 Conclusion

In conclusion, the six-membered 1,3,2,5-diazadiborinine **C** featuring a $C_2B_2N_2$ ring was synthesized and successfully isolated. An X-ray diffraction study and molecular orbital analysis indicated the 6π electrons were delocalized over the central $B_2N_2C_2$ six-membered ring of compound **C**, which was further evaluated using DFT calculations and resonance structures of **C2** possesses both potentially nucleophilic and electrophilic boron centres on the aromatic six-membered ring. In addition to its unique optical property, which displays distinct light blue-fluorescence emission in the solid state, the relatively small negative NICS values as well as the small RSE values of **C** indicated that its aromaticity is moderated compared to those of benzene and other azaborinines.

2.5 Experimental section

2.5.1 Synthesis, physical and spectroscopic data for all new compounds

General synthetic procedures: All reactions were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂, and were distilled under nitrogen. Reagents were of analytical grade, obtained from commercial suppliers and were used without further purification. ¹H, ¹³C and ¹¹B NMR spectra were recorded on a Bruker AVIII 400MHz spectrometers at 298 K. In the ¹³C NMR spectra of compounds **B-C**, presumably owing to the coupling with boron atoms, signals for the carbon atoms directly bonding to boron atoms could not be observed. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with OptiMelt apparatus (Stanford Research System). Fourier transform infrared (FT-IR) spectra were recorded on a SHIMADZU IR Prestige-21 spectrometer using solid compound. Ultraviolet and fluorescence spectra were recorded on Cary 100 UV-Vis and SHIMADZU RF-5301PC Spectrofluorophotometer, respectively.

Compound B: A hexane solution (1.6 M) of ⁿBuLi (6.25 mL, 10.00 mmol) was added dropwise into a THF solution (50 mL) of 4,4-dimethyl-2-oxazoline (1.00 mL, 9.48 mmol) at -78 °C. After stirring for 1 hour at -78 °C, dichlorophenylborane (0.62 mL, 4.72 mmol) was added into the solution. The reaction mixture was warmed to room temperature and stirred overnight. After the solvent was removed under vacuum, toluene (60 mL) was added and salts were filtered off, which was used directly for next step without further purification. Dichlorophenylborane (0.62 mL, 4.72 mmol) was added

dropwise into the solution at $-78\text{ }^{\circ}\text{C}$. The reaction mixture was left to stir for 1 hour at $-78\text{ }^{\circ}\text{C}$, and slowly warmed to room temperature and stirred overnight. The solvent was removed under vacuum, and the solid residue was recrystallized from benzene to afford colorless crystals of **B** (0.61 g, 29%). Mp: $207\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, C_6D_6): δ = 0.52 (s, 6 H, CH_3), 1.21 (s, 6 H, CH_3), 3.06 (d, 2H, J = 9.2 Hz, CH_2), 3.13 (d, 2 H, J = 8.8 Hz, CH_2), 7.21 - 8.29 (m, 10 H, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.2 (CH_3), 27.5 (CH_3), 68.3 ($\text{C}(\text{CH}_3)_2$), 81.8 (CH_2), 127.6 (CH), 132.4 (CH), 133.1 (CH), 136.0 (CH); DEPT - 135 NMR (100 MHz, C_6D_6): δ = 24.2 (CH_3), 27.5 (CH_3), 127.6 (CH), 128.0 (CH), 128.3 (CH), 132.4 (CH), 133.1 (CH), 136.0 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): δ = -11.4 (s), 3.5 (s); HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{26}\text{B}_2\text{N}_2\text{O}_2\text{Cl}$: 407.1869 [(M)] $^{+}$; found: 407.1866.

Compound C: Potassium graphite (1.49 g, 11.04 mmol) was slowly added to a solution of **B** (0.82 g, 1.84 mmol) in toluene (50 mL) and stirred overnight at room temperature. After filtration, the solvent was concentrated to 5 mL under vacuum. The solid residue was filtered off and washed with hexane (15 mL), and then dried under vacuum to afford **C** as a white powder (0.22 g, 32 %). Mp: $133\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, C_6D_6) δ = 0.79 (s, 12 H, CH_3), 3.63 (s, 4 H, CH_2), 7.09 - 8.84 (m, 10 H, ArH); ^{13}C NMR (100 MHz, C_6D_6) δ = 27.5 (CH_3), 62.8 ($\text{C}(\text{CH}_3)_2$), 80.9 (CH_2), 125.4 (CH), 127.1 (CH), 127.7 (CH), 134.7 (CH), 135.1 (CH); DEPT - 135 NMR (100 MHz, C_6D_6): δ = 27.5 (CH_3), 125.4 (CH), 127.1 (CH), 127.7 (CH), 128.4 (CH), 134.7 (CH), 135.1 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): δ = 7.3 (s), 24.9 (s); UV-Vis (THF): λ = 275 nm (ϵ : 5740); HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{27}\text{B}_2\text{N}_2\text{O}_2$: 373.2259 [$(M+H)$] $^{+}$; found: 373.2271; IR (KBr, cm^{-1}):

1591.3, 1475.5, 1444.7, 1421.5, 1392.6, 1375.3, 1303.9, 1253.7, 1205.5, 1103.3, 1074.4, 1033.9, 1016.5, 954.8, 939.3.

Figure 2.7 The normalized absorption in THF (black line) and fluorescence spectra in THF (red line) and in the solid-state (blue line) of **C**.

Figure 2.8 The image of **C** (right) and para-terphenyl ($\text{PhC}_6\text{H}_4\text{Ph}$) (left, for comparison) under UV irradiation.

Figure 2.9 The solid-state IR spectrum of **C**.

2.5.2 NMR Spectra

Figure 2.10 ¹H NMR spectrum of **B**.

Figure 2.11 ¹¹B NMR spectrum of **B**.

Figure 2.12 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **B**.

Figure 2.13 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **B**.

Figure 2.14 ^1H NMR spectrum of C.

Figure 2.15 ^{11}B NMR spectrum of C.

Figure 2.16 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **C**.

Figure 2.17 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **C**.

2.5.3 Crystal structure determination of compounds **B-C**

X-ray data collection and structural refinement. Intensity data for compounds **B** and **C** were collected using a Bruker APEX II diffractometer. The crystals of **C** was measured at 103(2) K and the crystals of **B** were measured at 296(2) K. The structure was solved by direct phase determination (SHELXS-97)^[19] and refined for all data by full-matrix least squares methods on F^2 .^[20] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1049275-1049276 contains the supplementary crystallographic data for this thesis. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 2.2 Summary of Data Collection and Structure Refinement.

	B (C ₆ H ₆) _{0.5}	C
Formula	C ₂₅ H ₂₉ B ₂ Cl ₂ N ₂ O ₂	C ₂₂ H ₂₆ B ₂ N ₂ O ₂
Fw	482.02	372.07
cryst syst	triclinic	orthorhombic
space group	P-1	P b c n
Size (mm ³)	0.140 x 0.160 x 0.240	0.040 x 0.400 x 0.420
T, K	296(2)	103(2)
a, Å	9.205(3)	9.3775(15)
b, Å	10.740(3)	22.196(4)
c, Å	13.922(4)	9.4320(15)
α, deg	82.772(9) °	90°
β, deg	76.229(9)°	90°

γ , deg	74.293(9) °	90°
V, Å ³	1284.1(6)	1963.2(5)
Z	2	4
$d_{\text{calcdg}} \cdot \text{cm}^{-3}$	1.247	1.259
μ , mm ⁻¹	0.277	0.079
Refl collected	15505	2451
T _{min} / T _{max}	0.9360/0.9620	0.9680/0.9970
N _{measd}	4454	2451
[R _{int}]	0.0528	0.0939
R [I>2sigma(I)]	0.0629	0.0672
R _w [I>2sigma(I)]	0.2089	0.2035
GOF	1.034	0.848
Largest diff peak/hole[e·Å ⁻³]	0.262/-0.268	0.323/-0.237

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Chapter 3

Reactivity of 1,3,2,5-

Diazadiborinine:

Bond/Small molecule

activation

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3.1 Introduction

In 1942, the Brown group first reported the preferential interaction of 2,6-lutidine with trifluoride boron (BF_3) rather than trimethyl boron (BMe_3) (Scheme 3.1).^[1] This observation implies that the formation of classical Lewis acid-base adducts is hampered by the presence of bulky substituents, because of steric hindrance. These uncombined Lewis acid-base adducts are referred to as frustrated Lewis pairs (FLPs).^[2] Beginning in 2006, the Stephan group comprehensively and extensively developed the chemistry of frustrated Lewis pairs.^[3] In their work, they prepared compound **2** and demonstrated its ability to reversibly activate H_2 (Scheme 3.2).^[4]

Scheme 3.1 Treatment of 2,6-lutidine with BF_3 and BMe_3 .

Scheme 3.2 Reversible activation of H_2 by compound **2**.

In 2007, they also discovered that H_2 could be activated by boranes and phosphines via a facile heterolytic cleavage (Scheme 3.3). The introduction of H_2 (1 atm) into a solution of boranes and phosphines afforded the corresponding phosphonium borates **3** and **4** at room temperature.^[5] Compared to the ability of compound **2** to reversibly activate H_2 , phosphonium borates **3** and **4** did not regenerate the starting materials under the heating condition.

Scheme 3.3 Activation of H₂ by phosphine and borane.

In addition to the activation of H₂,^[6] Stephan group expanded the reactivity of FLPs to the activation of olefins (Scheme 3.4).^[7] Three component-based olefin activations have been demonstrated. Treatment of P^tBu₃ with tri(pentafluorophenyl)borane (B(C₆F₅)₃) under an ethylene atmosphere at room temperature afforded product **5**. Both CH₂=CH-CH₃ and CH₂=CH-(CH₂)₃CH₃ also underwent bond activation by FLPs to yield **6** and **7**, respectively. In addition to these intermolecular activation of olefins, semi-intramolecular activation was examined with (pentenyl)PR (R = ^tBu or Mes) and (B(C₆F₅)₃), which afforded products **8-9**. Mechanistic studies indicate that the initial step of the reaction is the interaction between B(C₆F₅)₃ and the olefins, which is followed by the attack of phosphines.

Scheme 3.4 Activation of olefin by FLPs.

In 2009, the Stephan group reported the activation of phenylacetylene by phosphine with borane or alane.^{[8][9]} Two different reaction pathways have been described for the formation of alkynylborate(aluminate) salts and deprotonation products (Scheme 3.5).^[9]

Phenylacetylene was introduced into the solution of $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{Al}(\text{C}_6\text{F}_5)_3$ with tBu_3P to form C-H activated compounds **10** and **11**, respectively. In contrast, the mixture of phenylacetylene, and $(o\text{-C}_6\text{H}_4\text{Me})_3\text{P}$ with either $\text{B}(\text{C}_6\text{F}_5)_3$ or $\text{Al}(\text{C}_6\text{F}_5)_3$ produced the corresponding addition products **12** and **13**, respectively. In addition, the classical Lewis acid-base adducts **14** also reacted with phenylacetylene to give addition product **15**, due to dissociation of **14** in solution.

Scheme 3.5 Activation of phenylacetylene by FLPs or classic Lewis acid-base adducts.

It has been reported the activation of CO_2 , which is the most oxidized form of carbon, can be achieved by using FLPs.^{[10][11]} The Stephan group, Erker group and Grimme group explored FLPs for the reversible activation of carbon dioxide under mild conditions (Scheme 3.6).^[11] Treatment of $\text{B}(\text{C}_6\text{F}_5)_3$ with P^tBu_3 under an atmosphere of carbon dioxide (CO_2) afforded product **16**. Upon heating under vacuum, CO_2 was released from **16** to re-form $\text{B}(\text{C}_6\text{F}_5)_3$ and P^tBu_3 . Intramolecular FLP **17** was also used to activate CO_2 and afforded **18**. Similar to the reaction of **16**, **18** also could release CO_2 under the heating condition.

Scheme 3.6 Reversible activation CO₂ by FLPs.

The activation of small molecules by FLPs involving highly Lewis acidic B(C₆F₅)₃ and a bulky phosphine has been well documented. In contrast, hydrogen activation using aromatic heterocycles, namely catalyst-free hydrogenative dearomatization, has rarely been reported (Scheme 3.7).^[12] In 2014, the Stephan group discovered that the aromatic heterocycle 2,4,6-tri-*tert*-butyl-1,3,5-triphospha^{benzene} **19** reacted with H₂ (4 atm) at 100 °C to afford the bicyclic species **21** via H₂ activation and hydride transfer reaction. Both the experimental results and theoretical calculations suggested that the initial step in the mechanism involves isomerization of **19** to boat-shaped conformation **19'**, which features a nucleophilic carbon and an electrophilic phosphorus. This conformation allowed the orbital interaction between **19'** and H₂, thus allowing the formation of 1,4-addition product **20**. Subsequently, **20** underwent an irreversible suprafacial hydride shift to afford **21**.

Scheme 3.7 Activation of H₂ by **19**.

3.2 Results and Discussions

As mentioned in the chapter 2, compound **C** exhibits the aromatic property with the delocalization of 6π -electrons over the central $B_2C_2N_2$ ring. One of the resonance structures **C2** (Scheme 3.8) implies the potential unique nature of the two boron atoms: one as a nucleophilic center and the other as an electrophilic center. To investigate the reactivity of **C**, we tested the reaction of **C** with methyl trifluoromethanesulfonate (MeOTf), which features an electrophilic methyl cation (Me^+) and a nucleophilic trifluoromethanesulfonate (TfO^-). Addition of one equivalent of MeOTf to a solution of **C** in acetonitrile at room temperature generated compound **D**. After 1 hour and removal of the solvent under vacuum, **D** was obtained in 75% yield (Scheme 3.8), and it was fully characterized by NMR spectroscopy and single-crystal X-ray diffraction. In the ^{11}B NMR spectrum of **D**, a broad peak for the boron atom between two nitrogen atoms was observed at 4.2 ppm and a sharp peak for the boron atom between two carbon atoms appeared at -19.7 ppm. Compared to the corresponding peaks of **C** (7.3 ppm and 24.9 ppm), both signals were shifted upfield. The X-ray structure of **D** was in good agreement with the expected results; the boron between two nitrogen atoms bonds with TfO^- , whereas Me^+ is attached to the boron between two carbon atoms (Figure 3.1). Based on the reactivity of **C** with MeOTf, two boron centers in compound **C** can act as Lewis-acidic and Lewis-basic centers much like what is seen in FLPs' systems.^{[2][3]}

Scheme 3.8 Reaction of **C** with MeOTf.

Figure 3.1 Solid-state structure of **D** (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

To further examine the reactivity of **C**, carbon dioxide (CO_2) was used to react with **C** (Scheme 3.9). CO_2 gas (1 atm) was introduced to a solution of **C** in benzene, and the reaction mixture was heated at 70 °C for two hours. After filtration and drying under vacuum, compound **E** was isolated in 72% yield. In the ^{11}B NMR spectrum of **E**, two signals appeared at -16.7 ppm and 3.1 ppm. Compared to the corresponding signals of **C** (7.3 ppm and 24.9 ppm), both signals of **E** were shifted upfield, which implies the boron atoms were tetrahedral. We also performed the same reaction with ^{13}C -labelled

carbon dioxide, and a new signal appeared in the ^{11}B NMR spectrum at -16.7 ppm (broad doublet, $^1J_{\text{B-C}} = 42.4$ Hz) due to the coupling with the ^{13}C -carbon atom. In the ^{13}C NMR spectrum, the broad signal from the ^{13}C -carbon was observed at 191.1 ppm. The structure of **E** was confirmed by X-ray diffractometry, which revealed the formation of new B1-O1 and B2-C1 bonds via a regioselective [4+2] cycloaddition reaction between **C** and CO_2 (Figure 3.2). The B1 and B2 atoms in **C** have positive and negative charges, respectively, which is in agreement with the electronegative O1 atom and the electropositive C1 atom of CO_2 forming B1-O1 and B2-C1 bonds, respectively. Compared to the B1-N1 ($1.443(3)$ Å) and the B2-C5 ($1.483(3)$ Å) bonds of **C**, the B1-N2 ($1.594(7)$ Å) and B1-N1 ($1.598(6)$ Å) and the B2-C12 ($1.596(7)$ Å) and B2-C11 ($1.602(7)$ Å) bonds of **E** are significantly longer. The N1-C11 ($1.306(5)$ Å) and N2-C12 ($1.310(5)$ Å) distances are shorter than those of **C** ($1.374(3)$ Å). The B1-O3 ($1.509(6)$ Å) and B2-C17 ($1.673(7)$ Å) distances are longer than typical boron-oxygen ($1.28\text{--}1.43$ Å)^[13] and boron-carbon ($1.58\text{--}1.62$ Å)^[14] single bonds. Moreover, we observed the reversible nature of the CO_2 addition by **C**. **E** released the carbon dioxide under heating condition (90 °C), and after 50 minutes, **C** was quantitatively reformed.

Scheme 3.9 Reversible activation of CO_2 by compound **C**.

Figure 3.2 Solid-state structure of **E** (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

Next, the activation of alkyne was examined with phenylacetylene ($\text{PhC}\equiv\text{CH}$). Treatment of **C** with one equivalent of $\text{PhC}\equiv\text{CH}$ in benzene at 70 °C for two hours afforded product **F**, which was isolated as a colorless solid in 91% yield (Scheme 3.10). In the ^{11}B NMR spectrum of **F**, signals appeared at -13.6 ppm and 0.1 ppm, both of which are shifted upfield relative to those of **C** (7.3 ppm and 24.9 ppm). Single crystals of **F** were obtained from a saturated THF/hexane solution at -25 °C, and X-ray diffraction analysis revealed that **F** was formed by B/B addition to $\text{PhC}\equiv\text{CH}$ (Figure 3.3). The positive B1 atom and the negative B2 atom in **C** bond to the terminal carbon C1 atom and the internal carbon C2 atom in $\text{PhC}\equiv\text{CH}$, respectively, because C1 atom is more electronegative than C2 atom.^[15] The C1-C2 distance ($1.334(4)$ Å) is typical of a carbon double bond (1.34 Å).^[16] The B2-C3 ($1.621(4)$ Å) distance is a slightly longer than the B2-C8 distance ($1.616(4)$ Å).

Scheme 3.10 Reversible activation of $\text{PhC}\equiv\text{CH}$ by compound **C**.

Figure 3.3 Solid-state structure of **F** (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

In addition, alkene was also used to test the reactivity of **C**. Ethylene gas ($\text{CH}_2=\text{CH}_2$) (1 atm) was introduced to a benzene solution of **C**, and the reaction mixture was stirred at room temperature for three hours (Scheme 3.11). After removal of benzene under vacuum, product **G** was obtained in 97% yield. In the ^{11}B NMR spectrum, two new signals appeared at -16.0 ppm and 1.6 ppm, both of which are shifted upfield relative to those of **C** (7.3 ppm and 24.9 ppm). Single crystals suitable for X-ray diffraction analysis were obtained by recrystallization from a saturated benzene solution at room

temperature. The solid-state structure (Figure 3.4) of **G** revealed that the two boron centers are tetrahedral, which is characteristic of sp^3 hybridized atoms. The B1-C1 (1.653(5) Å) and B2-C2 (1.671(5) Å) distances are significantly longer than typical B-C single bond distances (1.50–1.59 Å).^[14] The B1-N1 (1.588(5) Å) and B1-N2 (1.611(5) Å) and B2-C3 (1.593(5) Å) and B2-C8 (1.594(5) Å) distances of **G** are longer than those of **C** (1.443(3) Å) and (1.483(3) Å), but the C3-N1 (1.302(4) Å) and C8-N2 (1.304(4) Å) distances are shorter relative to those of **C** (1.374(3) Å). The C1-C2 distance (1.550(4) Å) shows that bond has substantial C-C single bond character (1.54 Å).^[17] These structural studies demonstrated that the [4+2] cycloaddition reaction occurred on the two boron centers in **C**. Interestingly, when a benzene solution of **G** was heated at 150 °C for six hours, $CH_2=CH_2$ was released and **C** was quantitatively regenerated.

Scheme 3.11 Reversible activation of ethylene by compound **C**.

Figure 3.4 Solid-state structure of **G** (All hydrogen atoms except for those on the C1 and C2 atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

To examine the scope of alkenes activation, we also tested the reactions of **C** with styrene derivatives. Two equivalents of styrene were added to a C_6D_6 solution of **C** in a J. Young NMR tube at ambient temperature, and the reaction mixture was monitored by NMR spectroscopy. After 12 hours, **C** was fully consumed, and product **H1** had been generated in 90% yield. In the ^{11}B NMR spectrum, two new signals were detected at -14.3 ppm and 0.8 ppm, both of which were shifted upfield compared with those of **C** (7.3 ppm and 24.9 ppm). Single crystals of **H1** were obtained by recrystallization from a mixed benzene/hexane solution at room temperature. X-ray diffraction analysis of **H1** revealed that the C1 and C2 moieties of styrene selectively bonded to B1 and B2, respectively, via a [4+2] cycloaddition reaction (Figure 3.5a). Heating a C_6D_6 solution of **H1** at 110 °C released styrene concomitant with the regeneration of **C** via a retro-[4+2] cycloaddition reaction. Because the para-substituent on the styrene derivatives has an effect on the rate of the [4+2] cycloaddition reaction,^[18] 4-methylstyrene, 4-

methoxystyrene, 4-bromostyrene and 4-(trifluoromethyl)styrene were employed for the reaction with **C**, and afforded products **H2**, **H3**, **H4** and **H5**, respectively. We also studied the X-ray diffraction of **H2** (Figure 3.5b) and **H4** (Figure 3.5c), both of which show similar structure as **H1** via regio-selective [4+2] cycloaddition. Heating **H2-H5** also regenerated **C** and the corresponding styrene derivatives via retro-[4+2] cycloaddition reactions. The rate constant k was obtained from the conversion of **C** to the corresponding cycloaddition product based on their integrals in the ^1H NMR spectrum. Reaction times longer than 12 hours are required to fully convert **C** and the styrene derivatives to the corresponding cycloadducts **H1-H3**. In contrast, the reaction times for the formation of cycloadducts **H4** and **H5** are less than 6 hours and 3 hours, respectively, probably due to electronic effects. The para-substituents of the styrene derivatives also influence the equilibrium constant of the reversible cycloaddition (Table 3.1 and Table 3.2). Cycloadducts **H4** and **H5** can regenerate **C** and the corresponding styrene derivatives at ambient temperature, more easily than **H1-H3**. To evaluate the substituent effect on the cycloaddition reaction, the Hammett correlation was determined for the reaction of **C** with styrene derivatives.^[19] The Hammett correlation for the reaction of **C** with styrene derivatives shows a linear correlation between $\lg k$ and the substituent constants with ρ of 1.43, which implied the cycloaddition reaction is reasonably sensitive to substituent effects (Figure 3.6).

Scheme 3.12 Reversible activation of styrene by compound **C**.

Figure 3.5 Solid-state structures of **H1** (a), **H2** (b) and **H4** (c) (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

<i>para</i> -substituents of styrene derivatives	Substituent constant	lg <i>k</i>
R = -OMe	-0.27	-4.113509275
R = -Me	-0.17	-4.070581074
R = -H	0.00	-3.920818754
R = -Br	0.23	-3.465973894
R = -CF ₃	0.54	-3.009661145

Figure 3.6 Hammett plot for the reactions of **C** with styrene derivatives.

Table 3.1 Reaction time (h) vs the conversion (%) of **H** to **C** and the corresponding styrene derivatives at ambient temperature.

	12 h	36 h	60 h	84 h	108 h
H1	7.60%	14.60%	16.90%	18.00%	18.00%
H2	12.00%	18.40%	21.00%	21.60%	21.60%
H3	14.70%	21.60%	24.20%	25.10%	25.10%
H4	5.30%	6.70%	7.10%	7.10%	7.10%
H5	4.00%	4.30%	4.60%	4.60%	4.60%

Table 3.2 The concentration (M) of [**H**] and [styrene derivatives] (= [**C**]) at equilibrium.

Concentrations of H and styrene derivatives in equilibrium			
<i>para</i> -substituents	[H]	[styrene derivative]	equilibrium constants (K) at r.t.
R = -H	0.01764	0.00392	1.148×10^3
R = -Me	0.02050	0.00584	0.601×10^3
R = -OMe	0.01890	0.00643	0.457×10^3
R = -Br	0.01993	0.00151	8.741×10^3
R = -CF ₃	0.01931	0.00098	2.011×10^4

To gain insight into the reaction mechanism, pathways for the cycloaddition reaction between **C** and styrene were explored theoretically using DFT calculations at the M06-2X(SCRF, solvent = benzene)/def2-TZVP//M06-2X/6-31G* level of theory, where the M06-2X functional accounts for the dispersion effect. While concerted and stepwise mechanisms are plausible pathways for cycloaddition reaction, only a concerted pathway could be confirmed by the calculations (Figure 3.7a). Two possible pathways for the concerted mechanism were obtained. Compared to the less favored pathway B, favored pathway A not only produced the experimentally observed product but also had a lower energy barrier. The computationally estimated activation

parameters for the [4+2] cycloaddition process in pathway A ($\Delta H^\ddagger = 4.2 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -48.9 \text{ e.u.}$, $\Delta G^\ddagger(298) = 18.8 \text{ kcal mol}^{-1}$) agreed reasonably well with the experimental values ($\Delta H^\ddagger = 11.6 \pm 0.9 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -37.6 \pm 3.0 \text{ e.u.}$, $\Delta G^\ddagger(298) = 22.8 \pm 1.8 \text{ kcal mol}^{-1}$) (Figure 3.8 and Figure 3.9). Interestingly, the transition state (TS) geometries indicate that the reaction is highly asynchronous (Figure 3.7b). Because the HOMO of styrene is centered over the terminal carbon and has good orbital overlap with the LUMO+3 of **C**, the distance between terminal carbon atom of styrene and boron atom of the N-B-N moiety in **C** is short (2.18 Å) (Figure 3.10). In addition to orbital interactions, charges on the boron atoms in **C** and terminal/internal carbon atoms of the styrene also play important roles in determining regioselectivity of the reaction. Based on analysis of the Müliken charges, the boron atoms of the N-B-N and C-B-C moieties of **C** have positive and negative charges, respectively (Figure 3.11). The internal carbon in styrene is more positive than the terminal carbon, so the TS for path B has a larger electrostatic repulsion. These results are in line with the experimentally observed selective formation of cycloadducts **H**.

a)

b)

Figure 3.7 a) DFT-calculated free energy profiles (kcal mol^{-1}) for the proposed mechanism of the [4+2] cycloaddition reaction between **C** and styrene. The optimized structures were obtained at the M06-2X/6-31G* level of theory. The ΔG values in C_6H_6 at 298 K were obtained from the M06-2X/6-31G* gas-phase harmonic frequencies and the energy in C_6H_6 was calculated with the 6-311+G(d,p) basis set. b) Transition-state geometries.

Figure 3.8 Plots of $\ln [C]$ against time to determine the rate constant (k) at various temperatures.

T/K	1/(T/K ⁻¹)	k/s ⁻¹	(k/s ⁻¹)/(T/K)	Ln(k/T)
300.15	0.003331667	0.000133	4.43112E-07	-14.62944378
313.15	0.003193358	0.000361	1.1528E-06	-13.67331491
328.15	0.003047387	0.000690	2.1027E-06	-13.07228978
338.15	0.002957267	0.001467	4.33831E-06	-12.34802536

$$\Delta H^\ddagger = 11.6 \pm 0.9 \text{ kcal/mol}$$

$$\Delta S^\ddagger = -37.6 \pm 3.0 \text{ e.u.}$$

$$\Delta G^\ddagger = 22.8 \pm 1.8$$

Figure 3.9 Eyring plot for the cycloaddition reaction between **C** and styrene.

a)

b)

Figure 3.10 Key frontier orbitals of **C** (a) and styrene (b) (M06/6-31G*). Orbital energies (in Hartrees) are shown in parentheses. Hydrogen atoms are omitted for clarity.

a)

b)

Figure 3.11 a) Key Mulliken charges of **C** (a) and styrene (b) (M06/6-31G*). Hydrogen atoms are omitted for clarity.

To expand the substrate scope, 1,1-bis(trimethylsilyl)ethene, trans-diphenylethene, cyclohexene and cyclohexadiene were used to react with **C**. However, those substrates did not react with **C** even under heating condition (RT~150 °C), probably due to the steric hindrance. In contrast, norbornene with its strained bicyclic framework, reacted with **C** at 90 °C to afford **I** in 83% yield (Scheme 3.13). The ¹¹B NMR spectrum of **I** showed two new signals at -15.8 ppm and 1.3 ppm, both of which were shifted upfield relative to those of **C** (7.3 ppm and 24.9 ppm). The solid-state structure (Figure 3.12) of **I** revealed that the [4+2] cycloaddition reaction occurred on the two boron centers in **C** and the two boron centers are tetrahedral, indicative characteristic of the sp³ hybridization. The stereoselectivity of the reaction originated probably from the fact that the steric hindrance of the CH₂ moiety is smaller than that of the CH₂CH₂ part of norbornene. The B1-C23 (1.643(3) Å) and B2-C24 (1.680(3) Å) distances are significantly longer than typical B-C single bonds (1.50–1.59 Å).^[14] Heating a benzene

solution of **I** at 150 °C for ten hours quantitatively regenerated norbornene and **C** via a retro-[4 + 2] cycloaddition.

Scheme 3.13 Reversible activation of norbornene by compound **C**.

Figure 3.12 Solid-state structure of **I** (all hydrogen atoms are omitted for clarity).

Thermal ellipsoids are set at the 50% probability level.

3.3 Conclusion

In conclusion, we have shown that 1,3,2,5-diazadiborinine **C** reacts with methyl trifluoromethanesulfonate, CO₂ and phenylacetylene to produce [4+2] cycloadducts **D**, **E**, and **F**, respectively. Notably, these reactions proceeded regioselectively and adduct **E** can be dissociated to carbon dioxide and **C** under the heating condition. Moreover, we demonstrated that **C** and alkene derivatives, such as ethylene, styrene derivatives and norbornene, underwent [4+2] cycloaddition reactions to afford the corresponding bicyclo[2.2.2] compounds. All products could regenerate **C** and the corresponding alkenes under the heating condition via retro-[4+2] cycloaddition reactions. DFT calculations showed that the cycloaddition reaction of **C** with styrene proceeded via a concerted pathway. The steric factor in the transition state as well as the polarity of the respective unsaturated bonds in the substrates may rationalize the regioselectivity of the cycloaddition reactions.

3.4 Experimental section

3.4.1 Synthesis, physical and spectroscopic data for all new compounds

General synthetic procedures: All reactions were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH_2 , and were distilled under nitrogen. Reagents were of analytical grade, obtained from commercial suppliers and were used without further purification. ^1H , ^{13}C , ^{11}B and ^{19}F NMR spectra were recorded on a Bruker AVIII 400MHz or Bruker Avance 500 MHz AV500 spectrometers at 298 K. In the ^{13}C NMR spectra of compounds **D**, **E**, **F**, **G**, **H1-H5**, **I**, signals for the carbon atoms directly bonding to boron atoms could not be observed. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with OptiMelt (Stanford Research System).

Compound D: Methyl trifluoromethanesulfonate (7.42 μL , 0.068 mmol) was added into an acetonitrile (6 mL) solution of **C** (0.021 g, 0.056 mmol) and stirred for 1 hour at room temperature. After the solvent was removed under vacuum, the solid residue was recrystallized from a 2:1 mixture of fluorobenzene/hexane to afford colorless crystals of **D** (0.022g, 75%).

Mp: 151 $^{\circ}\text{C}$ (dec). ^1H NMR (400 MHz, THF-d_8): δ = 0.34 (s, 3 H, BCH_3), 0.87 (s, 6 H, CH_3), 1.38 (s, 6 H, CH_3), 4.14 (d, 2 H, J = 8.8 Hz, CH_2), 4.26 (d, 2 H, J = 8.4 Hz, CH_2), 7.06 - 7.66 (m, 10 H, ArH); ^{13}C NMR (100 MHz, THF-d_8): δ = 22.4 (CH_3), 29.0 (CH_3), 67.3 ($\text{C}(\text{CH}_3)$), 83.2 (CH_2), 126.1 (CH), 127.7 (CH), 128.1 (CH), 129.6 (CH), 130.8 (CH), 132.4 (CH); ^{11}B NMR (76.8 MHz, THF-d_8): δ = -19.7 (s), 4.2 (s); ^{19}F NMR (225.6

MHz, THF- d_8): $\delta = -81.2$ (s); HRMS (ESI): m/z calcd for $C_{24}H_{30}B_2N_2O_5SF_3$: 537.2014 [(M+H)]⁺; found: 537.2006.

Compound **E**: A benzene (15 mL) solution of compound **C** (0.061 g, 0.040 mmol) was degassed using a freeze-pump-thaw method, and then CO₂ (1 bar) was introduced into the schlenk tube at room temperature. After 2 hours at 70 °C, a white precipitate was collected by filtration and dried under vacuum to afford **E** (0.049 g, 72%).

Mp: 158 °C (dec). ¹H NMR (400 MHz, CD₂Cl₂): $\delta = 0.90$ (s, 6 H, CH₃), 1.50 (s, 6 H, CH₃), 4.36 (d, 2 H, $J = 9.2$ Hz, CH₂), 4.39 (d, 2 H, $J = 9.2$ Hz, CH₂), 7.22 - 7.95 (m, 10 H, ArH); ¹³C NMR (100 MHz, CD₂Cl₂) $\delta = 25.9$ (CH₃), 27.7 (CH₃), 66.5 (C(CH₃)₂), 86.4 (CH₂), 126.9 (CH), 127.5 (CH), 129.1 (CH), 134.97 (CH), 134.99 (CH), 135.1 (CH); ¹¹B NMR (76.8 MHz, CD₂Cl₂): $\delta = -16.7$ (s), 3.1 (s); HRMS (ESI): m/z calcd for $C_{23}H_{27}B_2N_2O_4$: 417.2157 [(M+H)]⁺; found: 417.2161.

Compound **E**-¹³C: Compound **C** (0.015 g, 0.040 mmol) was added to a sealable J-Young NMR tube and dissolved in C₆D₆ (0.35 mL). The sample was degassed using a freeze-pump-thaw method. Labile ¹³CO₂ was condensed into the NMR tube at 77 K, followed by warming to room temperature, and reacted for 2 hours at 70 °C. Cool down to room temperature, filtered off the solution and afford white solid of **E**-¹³C (0.013 g, 80%).

¹³C NMR (100 MHz, CD₂Cl₂): $\delta = 25.9$ (CH₃), 27.7 (CH₃), 66.5 (C(CH₃)₂), 86.4 (CH₂), 126.9 (CH), 127.5 (CH), 129.1 (CH), 134.97 (CH), 134.99 (CH), 135.1 (CH), 191.1 (br d, $J_{CB} = 42.4$ Hz, ¹³C-B); ¹¹B NMR (76.8 MHz, CD₂Cl₂): $\delta = -16.7$ (br d, $J_{BC} = 42.4$ Hz, ¹³C-B), 3.1 (s).

Regeneration of **C** from **E**: Compound **E** was dissolved in a 1:1 mixture of CD₃CN/THF-d₈, and heated at 90 °C. Reaction was monitored by ¹H and ¹¹B NMR spectroscopy and after 50 min, a quantitative regeneration of **C** was confirmed.

Compound **F**: Phenylacetylene (9.2 μL, 0.087 mmol) was added into a C₆D₆ (0.5 mL) solution of **C** (0.031 g, 0.083 mmol) and heated at 70 °C. The reaction was monitored by NMR spectroscopy. After 2 hours, the solvent was removed under vacuum, and the solid residue was recrystallized from THF/hexane to afford colorless crystals of **F** (0.036 g, 91%).

Mp: 120 °C. ¹H NMR (400 MHz, C₆D₆) δ = 0.52 (s, 6 H, CH₃), 0.87 (s, 6 H, CH₃), 3.44 (d, 2H, *J* = 8.4 Hz, CH₂), 3.51 (d, 2 H, *J* = 8.4 Hz, CH₂), 7.01 - 8.04 (m, 16 H, ArH); ¹³C NMR (125 MHz, CDCl₃): δ = 25.0 (CH₃), 27.4 (CH₃), 65.9 (C(CH₃)₂), 84.9 (CH₂), 124.7 (CH), 125.3 (CH), 126.7 (CH), 127.2 (CH), 127.6 (CH), 127.9 (CH), 128.5 (CH), 132.3 (CH), 135.2 (C_q); ¹¹B NMR (76.8 MHz, C₆D₆): δ = -13.6 (s), 0.1 (s); HRMS (ESI): *m/z* calcd for C₃₀H₃₃B₂N₂O₂: 475.2728 [(M+H)]⁺; found: 475.2733.

Compound G: A C₆D₆ (0.35 mL) solution of **C** (0.010 g, 0.027 mmol) was added to a J-Young NMR tube. The sample was degassed using a freeze-pump-thaw method. Ethylene (1 bar) was introduced into the NMR tube at room temperature, and the reaction was monitored by NMR spectroscopy. After 3 hours, all volatiles were removed under vacuum, which afforded a white powder of **G** (0.011 g, 97%).

Mp: 156 °C. ¹H NMR (500 MHz, C₆D₆): δ = 0.51 (s, 6 H, CH₃), 0.91 (s, 6 H, CH₃), 1.05-1.08 (m, 2 H, BCH₂), 1.25-1.28 (m, 2 H, BCH₂), 3.35 (d, *J* = 8.5 Hz, 2 H, CH₂), 3.41 (d, *J* = 9.0 Hz, 2 H, CH₂), 7.25 - 8.14 (m, 10 H, ArH); ¹³C NMR (125 MHz, C₆D₆): δ = 26.1 (CH₃), 28.0 (CH₃), 65.3 (C(CH₃)₂), 83.3 (CH₂), 126.0 (CH), 127.5 (CH), 127.8

(CH), 134.8 (CH); ^{13}C NMR (DEPT-135, 125 MHz, C_6D_6): δ = 26.1 (CH_3), 28.0 (CH_3), 126.0 (CH), 127.5 (CH), 127.8 (CH), 128.0 (CH), 128.4 (CH), 134.8 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): δ = -16.0 (s), 1.6 (s). HRMS (ESI): m/z calcd for $\text{C}_{24}\text{H}_{31}\text{B}_2\text{N}_2\text{O}_2$: 401.2572 $[(M+H)]^+$; found: 401.2581.

Compound H1: Styrene (6.2 μL , 0.054 mmol) was added into a C_6D_6 (0.6 mL) solution of **C** (0.010 g, 0.027 mmol) in a J-Young NMR tube at room temperature. The reaction was monitored by NMR spectroscopy. After 12 hours, all volatiles were removed under vacuum. The residue was washed with hexane and dried under vacuum to afford a colorless solid of **H1** (0.012g, 90%).

Mp: 132 $^\circ\text{C}$. ^1H NMR (400 MHz, C_6D_6) δ = 0.57 (s, 3 H, CH_3), 0.59 (s, 3 H, CH_3), 0.91 (s, 3 H, CH_3), 1.1 (s, 3 H, CH_3), 1.29 (dd, J = 5.0 Hz, J = 13.6 Hz, 1 H, CH_2), 1.84 (dd, J = 10 Hz, J = 13.6 Hz, 1 H, CH_2), 2.72 (dd, J = 5.0 Hz, J = 10 Hz, 1 H, CH_2), 3.37 (d, J = 8.8 Hz, 1 H, CH_2), 3.48 (d, J = 8.8 Hz, 1 H, CH_2), 3.61 (d, J = 8.8 Hz, 1 H, CH_2), 3.70 (d, J = 8.8 Hz, 1 H, CH_2), 6.99 - 8.02 (m, 15 H, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 25.4 (CH_3), 25.8 (CH_3), 27.8 (CH_3), 29.0 (CH_3), 65.0 ($\text{C}(\text{CH}_3)_2$), 65.4 ($\text{C}(\text{CH}_3)_2$), 83.4 (CH_2), 83.8 (CH_2), 123.9 (CH), 125.5 (CH), 127.1 (CH x2), 127.9 (CH x5), 128.2 (CH), 135.1 (CH), 151.9 (CH); ^{13}C NMR (DEPT-135, 100 MHz, C_6D_6): δ = 25.4 (CH_3), 25.8 (CH_3), 27.8 (CH_3), 29.0 (CH_3), 123.9 (CH), 125.5 (CH), 127.1 (CH), 127.9 (CH), 128.2 (CH), 135.1 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): δ = -14.3 (s), 0.8 (s); HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{35}\text{B}_2\text{N}_2\text{O}_2$: 477.2885 $[(M+H)]^+$; found: 477.2899.

Compound H2: By following the procedure for the synthesis of **H1**, the reaction of **C** and 4-methylstyrene afforded **H2** as a colorless solid (83%).

Mp: 116 °C. ¹H NMR (400 MHz, C₆D₆): δ = 0.56 (s, 3 H, CH₃), 0.60 (s, 3 H, CH₃), 0.89 (s, 3 H, CH₃), 1.07 (s, 3H, CH₃), 1.28 (dd, *J* = 5.0 Hz, *J* = 13.5 Hz, 1 H, BCH₂), 1.84 (dd, *J* = 9.9 Hz, *J* = 13.5 Hz, 1 H, BCH₂), 2.13(s, 3 H, CH₃), 2.73 (dd, *J* = 5.0 Hz, *J* = 9.9 Hz, 1 H, BCH₂), 3.34 (d, *J* = 8.8 Hz, 1 H, CH₂), 3.45 (d, *J* = 8.8 Hz, 1 H, CH₂), 3.61 (d, *J* = 8.8 Hz, 1 H, CH₂), 3.72 (d, *J* = 8.8 Hz, 1 H, CH₂), 6.95 - 8.04 (m, 14 H, ArH); ¹³C NMR (100 MHz, C₆D₆): δ = 21.1 (CH₃), 25.5 (CH₃), 25.8 (CH₃), 27.8 (CH₃), 29.0 (CH₃), 65.0 (C(CH₃)₂), 65.4 (C(CH₃)₂), 83.4 (CH₂), 83.8 (CH₂), 125.5 (CH), 127.1 (CH), 128.7 (CH), 132.6 (CH), 135.2 (CH), 148.7 (CH); ¹³C NMR (DEPT-135, 100 MHz, C₆D₆): δ = 21.1 (CH₃), 25.5 (CH₃), 25.8 (CH₃), 27.8 (CH₃), 29.0 (CH₃), 125.5 (CH), 127.1 (CH), 127.9 (CH), 128.1 (CH), 128.4 (CH), 128.7 (CH), 135.2 (CH); ¹¹B NMR (76.8 MHz, C₆D₆): δ = -14.3 (s), 0.9 (s) ; HRMS (ESI): *m/z* calcd for C₃₁H₃₇B₂N₂O₂: 491.3041 [(*M*+*H*)]⁺; found: 491.3050.

Compound H3: By following the procedure for the synthesis of **H1**, the reaction of **C** and 4-methoxystyrene afforded **H3** as a colorless solid (85%).

Mp: 117 °C. ¹H NMR (400 MHz, C₆D₆): δ = 0.57 (s, 3 H, CH₃), 0.58 (s, 3 H, CH₃), 0.89 (s, 3 H, CH₃), 1.06 (s, 3 H, CH₃), 1.25 (dd, *J* = 5.0 Hz, *J* = 13.6 Hz, 1 H, BCH₂), 1.85 (dd, *J* = 10 Hz, *J* = 13.6 Hz, 1 H, BCH₂), 2.73 (dd, *J* = 5.0 Hz, *J* = 10 Hz, 1 H, BCH), 3.32 (s, 3 H, OCH₃), 3.34 (d, *J* = 8.8 Hz, 1 H, CH₂), 3.46 (d, *J* = 8.8 Hz, 1 H, CH₂), 3.60 (d, *J* = 8.8 Hz, 1 H, CH₂), 3.68 (d, *J* = 8.8 Hz, 1 H, CH₂), 6.76 - 8.05 (m, 14 H, ArH); ¹³C NMR (100 MHz, C₆D₆): δ = 25.5 (CH₃), 25.8 (CH₃), 27.8 (CH₃), 28.9 (CH₃), 54.7 (OCH₃), 65.0 (C(CH₃)₂), 65.4 (C(CH₃)₂), 83.4 (CH₂), 83.8 (CH₂), 113.6 (CH), 125.6 (CH), 127.1 (CH), 127.9 (CH), 128.9 (CH), 135.2 (CH), 143.6 (CH), 157.0 (CH); ¹³C NMR (DEPT-135, 100 MHz, C₆D₆): δ = 25.5 (CH₃), 25.8 (CH₃), 27.8 (CH₃), 28.9 (CH₃), 54.7 (OCH₃), 113.6 (CH), 125.6 (CH), 127.1 (CH), 127.9 (CH), 128.4 (CH), 128.9 (CH),

135.2 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): $\delta = -14.3$ (s), 1.1 (s); HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{37}\text{B}_2\text{N}_2\text{O}_3$: 507.2990 $[(M+H)]^+$; found: 507.3000.

Compound H4: By following the procedure for the synthesis of **H1**, the reaction of **C** and 4-bromostyrene afforded **H4** as a colorless solid (89%).

Mp: 273 °C. ^1H NMR (400 MHz, C_6D_6): $\delta = 0.51$ (s, 3 H, CH_3), 0.53 (s, 3 H, CH_3), 0.87 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3), 1.13 (dd, $J = 5.0$ Hz, $J = 13.6$ Hz, 1 H, BCH_2), 1.73 (dd, $J = 9.8$ Hz, $J = 13.6$ Hz, 1 H, BCH_2), 2.56 (dd, $J = 5.0$ Hz, $J = 9.8$ Hz, 1 H, BCH), 3.32 (d, $J = 8.8$ Hz, 1 H, CH_2), 3.44 (d, $J = 8.8$ Hz, 1 H, CH_2), 3.56 (s, 2 H, CH_2), 6.82 - 7.95 (m, 14 H, ArH); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.4$ (CH_3), 25.8 (CH_3), 27.8 (CH_3), 28.9 (CH_3), 65.0 ($\text{C}(\text{CH}_3)_2$), 65.5 ($\text{C}(\text{CH}_3)_2$), 83.4 (CH_2), 83.8 (CH_2), 117.4 (CH), 125.8 (CH), 127.2 (CH), 128.0 (CH), 129.8 (CH), 130.8 (CH), 135.0 (CH), 151.0 (CH); ^{13}C NMR (DEPT-135, 100 MHz, C_6D_6): $\delta = 25.4$ (CH_3), 25.8 (CH_3), 27.8 (CH_3), 28.9 (CH_3), 125.8 (CH), 127.2 (CH), 128.0 (CH), 128.4 (CH), 129.8 (CH), 130.8 (CH), 135.0 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): $\delta = -14.4$ (s), 1.0 (s); HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{34}\text{B}_2\text{N}_2\text{O}_2\text{Br}$: 555.1990 $[(M+H)]^+$; found: 555.2003.

Compound H5: By following the procedure for the synthesis of **H1**, the reaction of **C** and 4-(trifluoromethyl)styrene afforded **H5** as a colorless solid (86%).

Mp: 150 °C. ^1H NMR (400 MHz, C_6D_6): $\delta = 0.53$ (s, 3 H, CH_3), 0.54 (s, 3 H, CH_3) 0.88 (s, 3 H, CH_3), 1.04 (s, 3 H, CH_3), 1.16 (dd, $J = 4.9$ Hz, $J = 13.7$ Hz, 1 H, BCH_2), 1.73 (dd, $J = 9.8$ Hz, $J = 13.7$ Hz, 1 H, BCH_2), 2.60 (dd, $J = 4.9$ Hz, $J = 9.8$ Hz, 1 H, BCH), 3.34 (d, $J = 8.8$ Hz, 1 H, CH_2), 3.46 (d, $J = 8.8$ Hz, 1 H, CH_2), 3.56 (d, $J = 9.0$ Hz, 1 H, CH_2), 3.59 (d, $J = 9.0$ Hz, 1 H, CH_2), 6.97 - 7.90 (m, 14 H, ArH); ^{13}C NMR (100 MHz, C_6D_6): $\delta = 25.4$ (CH_3), 25.8 (CH_3), 27.8 (CH_3), 29.0 (CH_3), 65.1 ($\text{C}(\text{CH}_3)_2$), 65.5

($\underline{\text{C}}(\text{CH}_3)_2$), 83.5 (CH₂), 83.9 (CH₂), 124.67 (CH), 124.70 (CH), 124.74 (CH), 125.9 (CH), 127.2 (CH), 134.9 (CH), 156.7 (CH); ¹³C NMR (DEPT-135, 100 MHz, C₆D₆): δ = 25.4 (CH₃), 25.8 (CH₃), 27.8 (CH₃), 29.0 (CH₃), 124.67 (CH), 124.70 (CH), 124.74 (CH), 125.9 (CH), 127.2 (CH), 128.1 (CH), 128.4 (CH), 134.9 (CH); ¹¹B NMR (76.8 MHz, C₆D₆): δ = -14.4 (s), 1.0 (s); ¹⁹F NMR (225.6 MHz, C₆D₆): δ = -61.4; HRMS (ESI): m/z calcd for C₃₁H₃₄B₂N₂O₂F₃: 545.2758 [($M+H$)]⁺; found: 545.2769.

Compound I: Norbornene (0.006 g, 0.065 mmol) was added into a C₆D₆ (0.5 mL) solution of **C** (0.020 g, 0.054 mmol) in a J-Young NMR tube. The reaction was monitored by NMR spectroscopy. After heating at 90 °C for 12 hours, the solvent was removed under vacuum. The resulting residue was recrystallized from benzene/hexane to afford colorless crystals of **I** (0.021g, 83%).

Mp: 250 °C. ¹H NMR (400 MHz, C₆D₆): δ = 0.49 (s, 3 H, CH₃), 0.55 (s, 3 H, CH₃), 0.75 (d, J = 9.6 Hz, 1 H), 0.82 (s, 3 H, CH₃), 0.90 (d, J = 9.6 Hz, 1 H), 1.19 (s, 3 H, CH₃), 1.30 - 2.65 (m, 8 H), 3.32 (d, J = 8.8 Hz, 1 H, CH₂), 3.37 (d, J = 8.8 Hz, 1 H, CH₂), 3.52 (d, J = 8.8 Hz, 1 H, CH₂), 3.64 (d, J = 8.8 Hz, 1 H, CH₂), 7.24 - 8.27 (m, 10 H, ArH); ¹³C NMR (100 MHz, C₆D₆): δ = 23.9 (CH₃), 25.8 (CH₃), 28.2 (CH₃), 30.4 (CH₃), 34.3 (CH₂), 34.5 (CH₂), 35.3 (CH₂), 40.3 (CH₃), 41.2 (CH₃), 64.3 ($\underline{\text{C}}(\text{CH}_3)_2$), 64.9 ($\underline{\text{C}}(\text{CH}_3)_2$), 83.8 (CH₂), 84.7 (CH₂), 125.7 (CH), 127.5 (CH), 127.7 (CH), 135.2 (CH); ¹³C NMR (DEPT-135, 100 MHz, C₆D₆): δ = 23.9 (CH₃), 25.8 (CH₃), 28.2 (CH₃), 30.4 (CH₃), 40.3(CH₃), 41.2 (CH₃), 125.7 (CH), 127.5 (CH), 127.7 (CH), 128.4 (CH), 135.2 (CH); ¹¹B NMR (76.8 MHz, C₆D₆): δ = -15.8 (s), 1.3 (s); HRMS (ESI): m/z calcd for C₂₉H₃₇B₂N₂O₂: 467.3041 [($M+H$)]⁺; found: 467.3051.

3.4.2 NMR Spectrums

Figure 3.13 ¹H NMR spectrum of **D**.

Figure 3.14 ¹¹B NMR spectrum of **D**.

Figure 3.15 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **D**.

Figure 3.16 ^{19}F NMR spectrum of **D**.

Figure 3.17 ^1H NMR spectrum of **E**.

Figure 3.18 ^{11}B NMR spectrum of **E**.

Figure 3.19 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **E**.

Figure 3.20 ^{11}B NMR spectrum of **E- ^{13}C** .

Figure 3.21 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **E**- ^{13}C .

Figure 3.22 ^1H spectrum showing the regeneration of **C** from **E**.

Figure 3.23 ^{11}B spectrum showing the regeneration of C from E.

Figure 3.24 ^1H NMR spectrum of F.

Figure 3.25 ^{11}B NMR spectrum of F.

Figure 3.26 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of F.

Figure 3.27 ^1H NMR spectrum of G.

Figure 3.28 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of G.

Figure 3.29 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **G**.

Figure 3.30 ^{11}B NMR spectrum of **G**.

Figure 3.31 ^1H NMR spectrum of **H1**.

Figure 3.32 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **H1**.

Figure 3.33 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **H1**.

Figure 3.34 ^{11}B NMR spectrum of **H1**.

Figure 3.35 ¹H NMR spectrum of H2.

Figure 3.36 ¹³C{¹H} NMR spectrum of H2.

Figure 3.37 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **H2**.

Figure 3.38 ^{11}B NMR spectrum of **H2**.

Figure 3.39 ^1H NMR spectrum of H3.

Figure 3.40 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of H3.

Figure 3.41 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **H3**.

Figure 3.42 ^{11}B NMR spectrum of **H3**.

Figure 3.43 ^1H NMR spectrum of H4.

Figure 3.44 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of H4.

Figure 3.45 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **H4**.

Figure 3.46 ^{11}B NMR spectrum of **H4**.

Figure 3.47 ¹H NMR spectrum of **H5**.

Figure 3.48 ¹³C {¹H} NMR spectrum of **H5**.

Figure 3.49 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **H5**.

Figure 3.50 ^{11}B NMR spectrum of **H5**.

Figure 3.51 ^{19}F NMR spectrum of **H5**.

Figure 3.52 ^1H NMR spectrum of **I**.

Figure 3.53 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **I**.

Figure 3.54 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **I**.

Figure 3.55 ^{11}B NMR spectrum of **I**.

3.4.3 Crystal Structure Determination of Compounds **D**, **E**, **F**, **G**, **H1**, **H2**, **H4** and **I**

X-ray data collection and structural refinement. Intensity data for compounds **D**, **E**, **F**, **G**, **H1**, **H2**, **H4** and **I** were collected using a Bruker APEX II diffractometer. The crystals of **D**, **E**, **F** and **H2** were measured at 103(2) K and the crystals of **G**, **H1**, **H4** and **I** were measured at 153(2) K. The structure was solved by direct phase determination (SHELXS-97)^[20] and refined for all data by full-matrix least squares methods on F^2 .^[21] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1049277-1049279 and 1418724-1418728 contain the supplementary crystallographic data for this thesis. The data can be obtained free of

charge from the Cambridge Crystallography Data Center via
www.ccdc.cam.ac.uk/data_request/cif.

Table 3.3 Summary of Data Collection and Structure Refinement.

	D₂ (C₆H₅F)₅	E (CH₂Cl₂)_{0.5}	F (thf)_{0.75} (C₆H₆)_{0.25}
Formula	C ₇₈ H ₈₃ B ₄ F ₁₁ N ₄ O ₁₀ S ₂	C _{23.50} H ₂₇ B ₂ ClN ₂ O ₄	C _{34.50} H _{39.50} B ₂ N ₂ O _{2.75}
Fw	1552.84	458.54	547.80
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> 1 21/ <i>n</i> 1
Size (mm ³)	0.060 x 0.100 x 0.420	0.020 x 0.100 x 0.280	0.040 x 0.320 x 0.380
T, K	103(2)	103(2)	103(2)
a, Å	10.8994(10)	13.0170(16)	11.3572(9)
b, Å	13.3303(14)	6.3932(8)	9.8183(8)
c, Å	14.0182(13)	27.756(3)	27.031(2)
α, deg	98.334(4)°	90°	90
β, deg	90.656(4)°	99.795(4)°	96.547(4)
γ, deg	109.608(4)°	90°	90
V, Å ³	1894.4(3)	2276.2(5)	2994.5(4)
Z	1	4	4
d _{calcd} g·cm ⁻³	1.361	1.338	1.215
μ, mm ⁻¹	0.159	0.202	0.075
Refl collected	27307	17919	25342
T _{min} / T _{max}	0.9360/0.9910	0.9460/0.9960	0.9720/0.9970
N _{measd}	9409	4020	5884
[R _{int}]	0.1022	0.1490	0.0863
R [I>2sigma(I)]	0.0790	0.0730	0.0689
R _w [I>2sigma(I)]	0.2145	0.2232	0.2237

GOF	1.017	1.053	1.007
Largest diff peak/hole[e·Å ⁻³]	1.084/-0.466	0.424/-0.480	0.553 /-0.441

	G (C₆D₆)1/2	H1	H2
Formula	C ₂₇ H ₃₀ B ₂ D ₃ N ₂ O ₂	C ₃₀ H ₃₄ B ₂ N ₂ O ₂	C ₃₁ H ₃₆ B ₂ N ₂ O ₂
Fw	422.19	476.21	490.24
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 1 21/ <i>n</i> 1
Size (mm ³)	0.200 x 0.180 x 0.020	0.040 x 0.100 x 0.180	0.360 x 0.400 x 0.420
T, K	153(2)	153(2)	103(2)
a, Å	6.2435(5)	12.0335(18)	9.498(2)
b, Å	13.8921(9)	13.357(2)	9.090(2)
c, Å	14.2338(10)	17.045(3)	30.647(7)
α, deg	100.533(4) °	73.663(4)°	90°
β, deg	92.139(5)°	81.968(4)°	94.119(3)°
γ, deg	100.164(5) °	79.686(4)°	90°
V, Å ³	1191.63(15)	2575.0(7)	2639.1(11)
Z	2	4	4
d _{calc} g·cm ⁻³	1.232	1.228	1.234
μ, mm ⁻¹	0.075	0.075	0.075
Refl collected	4727	9199	4811
T _{min} / T _{max}	0.79/1.00	0.9870/0.9970	0.9690/0.9730
N _{meas}	4727	9199	4811
[R _{int}]	0.1367	0.0814	0.0862
R [I>2σ(I)]	0.0771	0.0858	0.0595
R _w [I>2σ(I)]	0.1726	0.2381	0.1579
GOF	0.928	1.046	1.013
Largest diff peak/hole[e·Å ⁻³]	0.377/-0.238	0.555/-0.376	0.280/-0.365

	H4	I (C₆H₆)1/2
Formula	C ₃₀ H ₃₃ B ₂ BrN ₂ O ₂	C ₃₂ H ₃₉ B ₂ N ₂ O ₂
Fw	555.11	505.27
cryst syst	monoclinic	monoclinic
space group	<i>P 1 21/n 1</i>	<i>P 1 21/n 1</i>
Size (mm ³)	0.110 x 0.120 x 0.420	0.180 x 0.220 x 0.300
T, K	153(2)	153(2)
a, Å	9.5066(6)	8.8862(4)
b, Å	9.2480(5)	21.9850(11)
c, Å	30.632(2)	14.0495(7)
α, deg	90°	90°
β, deg	94.399(3)°	96.2349(19)°
γ, deg	90°	90°
V, Å ³	2685.1(3)	2728.5(2)
Z	4	4
dcalcdg·cm ⁻³	1.373	1.230
μ, mm ⁻¹	1.562	0.075
Refl collected	17487	44526
T _{min} / T _{max}	0.5600/0.8470	0.9780/0.9870
N _{measd}	7720	6540
[R _{int}]	0.0636	0.0827
R [I>2sigma(I)]	0.0583	0.0502
R _w [I>2sigma(I)]	0.1268	0.1777
GOF	0.986	1.093
Largest diff peak/hole[e·Å ⁻³]	0.442 /-0.702	0.456/-0.504

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Chapter 4

Formylation of Amine with CO_2

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4.1 Introduction

4.1.1 Main group catalysts for N-formylation reaction

Carbon dioxide (CO₂) is one of the major contributors to greenhouse gas on Earth, thus, reducing CO₂ has attracted much attention in recent years. There are growing interests in the utilization of CO₂ for producing useful chemicals.^[1] Many organometallic catalysts effectively promote the *N*-formylation of amines using CO₂.^[2] Whereas transition metals pollute the environment, the metal-free catalytic method is regarded as a more environmentally friendly process to this reaction. Several reports have revealed that main group species also can be good catalyst for the transformation of CO₂ as a C1 source to form formamides (Scheme 4.1).^[3]

Figure 4.1 Main group species for *N*-formylation of amine using CO₂.

Because of the important applications of amides,^[4] several methods for synthesizing amides using CO₂ under ambient conditions have been explored.^{[2][3]} Following the discovery of the adduct of 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD) **I** with CO₂,^[5] the Cantat group disclosed that **I** promoted the *N*-formylation of amines using CO₂ and phenylsilane at 100 °C.^[3h] The stoichiometric reaction of TBD-CO₂

adduct **1** with amines afforded **2** and **3** (Scheme 4.2). The subsequent reductions of **2** and **3** with triethoxysilane ((EtO)₃SiH) quantitatively generated the reductive products **4** and **5** concomitant with siloxane as the oxidation side-product (Scheme 4.2). The same group reported that *N*-heterocyclic carbenes **II** could also promote the *N*-formylation of various amines, anilines, imines, hydrazines, hydrazones and *N*-heterocycles using CO₂ and polymethylhydrosiloxane (Scheme 4.2). This catalytic reaction can be performed under milder conditions and has a broader substrate scope, compared with **I**.^[3i]

Scheme 4.1 Reaction of **1** with amines and subsequent reduction by (EtO)₃SiH.

Scheme 4.2 Catalytic *N*-formylation of amines by **II**.

A catalytic amount of 1,3,2-diazaphospholene **IV** featuring a highly polarized P-H bond promotes the *N*-formylation of amines using CO₂ and diphenylsilane (Ph₂SiH₂) via hydrophosphination of CO₂ and the subsequent formate transfer reaction (Scheme 4.3).^[3d] Mechanistic studies suggest that the P-H bond of **IV** first inserts into the C=O bond of CO₂ to form **IV-CO₂** at room temperature. Next, formate transfer from **IV-CO₂** to Ph₂SiH₂ affords Ph₂Si(OCHO)₂ with concomitant regeneration of catalyst **IV**.

Finally, $\text{Ph}_2\text{Si}(\text{OCHO})_2$ reacts with amines to produce *N*-formylated products via an addition reaction. Various primary and secondary amines bearing electron-withdrawing as well as electron-donating groups are well tolerated. Glycine betaine **VII** also catalyzes the reductive functionalization of CO_2 with amines and Ph_2SiH_2 , in which formamides, amins or methylamines can be selectively formed by tuning the reaction conditions (Scheme 4.4).^[3a] The proposed reaction pathway for the reductive functionalization of CO_2 involves activation of Ph_2SiH_2 by **VII** and subsequent addition of CO_2 to afford $\text{Ph}_2\text{HSiOCHO}$ concomitant with the regeneration of **VII**. $\text{Ph}_2\text{HSiOCHO}$ not only reacts with amines to form formamides, but is also further reduced by Ph_2SiH_2 to afford $(\text{Ph}_2\text{HSiO})_2\text{CH}_2$. Subsequent reaction of $(\text{Ph}_2\text{HSiO})_2\text{CH}_2$ with amines generates methylamines. In the presence of **VII**, methylamines can be converted to amins (Scheme 4.5).

Scheme 4.3 Proposed mechanism for the *N*-formylation of amines catalyzed by **IV**.

Scheme 4.4 Reductive functionalization of CO_2 with amines by **VII**.

Scheme 4.5 Proposed reaction pathway for the reductive functionalization of CO_2 by **VII**.

4.2 Results and Discussions

In chapter 3, we have shown that 1,3,2,5-diazadiborinine **C** exhibits unique reactivity including the reversible cycloaddition with unactivated unsaturated bonds. Because **C** could not only activate CO₂ to form 1,3,2,5-diazadiborinine-CO₂ adduct **E**, but also CO₂ was released from **E** upon heating concomitant with the regeneration of **C**, we envisaged that **C** could promote reduction and functionalization of CO₂ in a catalytic manner. In this chapter, we demonstrate that **C** can indeed serve as an effective catalyst for CO₂ valorization.

Scheme 4.6 The structures of **C** and **E**.

4.2.1 *N*-formylation of amines using CO₂ catalyzed by **C**

We began our study by investigating catalytic *N*-formylation of *N*-methylaniline **6a** (Table 4.1). In the absence of catalyst **C**, only 5% yield of **7a** was observed (Table 4.1, entry 1). With 5 mol % of catalyst **C** in CD₃CN, compound **7a** was formed in 95% yield after 4.8 hours (Table 4.1, entry 2). When the catalyst loading was decreased to 2 mol %, a similar yield and reaction time were observed (Table 4.1, entry 3). Further reducing of the catalyst loading to 1 mol % required longer-reaction times (Table 4.1, entry 4). In our brief screening of reaction conditions, we found that 2 mol % catalyst loading was the best ratio for *N*-formylation of *N*-methylaniline.

Table 4.1 Optimization of the *N*-formylation reaction conditions.^[a]

Entry	cat. C [mol%]	solvent	Time [h]	Yield [%] ^[b]
1	1 (0 mol%)	CD ₃ CN	20 h	5%
2	1 (5 mol%)	CD ₃ CN	4.8 h	95%
3	1 (2 mol%)	CD₃CN	5.5 h	95%
4	1 (1 mol%)	CD ₃ CN	9 h	95%

[a] Reaction conditions: *N*-methylaniline (0.215 mmol), HBpin (0.645 mmol), CO₂ (45 mg), CD₃CN (0.4 ml). Catalyst loading relative to *N*-methylaniline. [b] Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

With the optimized reaction conditions in hand, the scope of the catalytic *N*-formylation of various aldehydes was briefly examined (Table 4.2). Primary aryl amines were investigated and the corresponding *N*-formylated products were generated in excellent yields (**7b-7d**, 81%-95%). Substrates featuring electron-withdrawing as well as electron-donating groups on the aryl substituent also provided the corresponding formamides in good yields (**7e-7g**, 76%-94%). Dialkylamines, such as diethylamine and diisopropylamine, gave the B-N coupling products with HBpin,^[6] and the desired *N*-formamide products were not observed. We also tested various secondary amines and all of them were well tolerated in this reaction (**7h-7n**, 80%-98%).

Table 4.2 Scope of catalytic *N*-formylation of amines with CO₂.

$\text{R}-\text{N}(\text{H})-\text{R}'$ 6b-6n		$\xrightarrow[\text{CD}_3\text{CN / RT}]{\text{cat. } \mathbf{C} \text{ (2mol\%)} \atop \text{CO}_2 \atop \text{HBpin (3 equiv)}}$		$\text{R}-\text{N}(\text{H})-\text{C}(=\text{O})-\text{H} + \text{O}(\text{Bpin})_2$ 7b-7n	
6		Time [h]	Yield [%] ^[b]	TON	TOF [hr ⁻¹]
6b		10 h	95%	48	5
6c		23 h	81%	41	2
6d		16 h	87%	44	3
6e		20 h	94%	47	2
6f		12 h	87%	44	4
6g		22 h	76%	38	2
6h		11 h	85%	43	4
6i		5.5 h	98%	49	9
6j		4 h	93%	47	12
6k		21 h	80%	40	2
6l		8 h	94%	47	6
6m		21 h	80%	40	2
6n		5 h	83%	42	8

[a] Reaction conditions: **C** (0.0043 mmol), *N*-methylaniline (0.215 mmol), HBpin (0.645 mmol), CO₂ (45 mg), CD₃CN (0.4 ml). [b] Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

4.2.2 Mechanistic Study

To gain insight into the reaction mechanism, we performed several control reactions. Compound **C** did not react with *N*-methylaniline **6a** or HBpin. Formation of **E** initially occurred via a [4+2] cycloaddition of **C** with CO₂. Although **E** did not react with **6a**, a mixture of **E** with HBpin (3.0 eq) afforded the major product of HCOOBpin **8** and the side-product of O(Bpin)₂, and no compound **C** was observed (Scheme 4.7a). Because **E** does not regenerate **C** in this reaction, the dissociation of CO₂ from **E** in the formation of **8** is not involved in the main catalytic cycle. Treatment of **6a** with HBpin (3.0 eq) in the presence of **E**-(¹³CO₂) (1.0 eq) under CO₂ atmosphere afforded **7a** in 95% (Scheme 4.7b). In the ¹³C NMR spectrum of **7a**, no signal for the ¹³C atom was observed, which suggested that the CO₂ moiety of **E** does not transfer to **6a** in the catalytic cycle.

Without CO₂, the mixture of **6a** (1.0 eq) with HBpin (3.0 eq) in the presence of **E** only formed the dehydrocoupling product **9** (Scheme 4.7c).^[7] To prove whether **9** was the key intermediate, we tested the reaction between **9** and HBpin with and without **C** (Scheme 4.8a). In the absence of compound **C**, no reaction between **9** and HBpin (2.0 eq) under CO₂ atmosphere was observed. With 2 mol % of **C**, **7a** was obtained in 15% yield after 7 hours. Although **7a** was formed, this reaction was too slow to be involved in the main catalytic cycle. Interestingly, HBpin under CO₂ in the presence of 2 mol % or 9 mol % **C** generated **8** in 48% or 70% yield, respectively (Scheme 4.8b). The reaction of the mixture of **8** and **6a** (1.0 eq) with HBpin (2.5 eq) quantitatively afforded *N*-formyl-*N*-methylaniline **7a**, implying this process did not involve the catalyst (Scheme 4.8c).

Scheme 4.7 Control reactions: a) reaction of **E** with **6a** (top) and HBpin (bottom); b) reaction of **E-(^{13}C)** with **6a** under CO_2 ; c) reaction of **E** with **6a** in the absence of CO_2 .

Scheme 4.8 Control reactions: a) reactions of **9** and HBpin, with and without **C** under CO₂; b) catalytic hydroboration of CO₂ using **C**; c) synthesis of **7a** from **8** and **6a**; d) catalytic hydroboration of CO₂ using **G**.

Based on these control experiments, we proposed that **E** could be the active catalyst in the *N*-formylation reaction. The similar reaction pathway is also reported for frustrated Lewis pairs (**FLPs**) promoted *N*-formylation reactions, in which the CO₂ adduct **FLPs** CH₂O remains in the catalytic cycle as the active catalyst (Scheme 4.9).^[8] Density functional theory (DFT) calculations at the M06-2X(SCRF)/def2-TZVP//M06-2X(SCRF)/6-31G*^[9] level of the theory suggest a catalytic cycle in which compound **E** serves as a Lewis basic catalyst (Scheme 4.10). The activation of the B-H bond of HBpin

by **E** is followed by a hydride transfer to CO₂, which produces key intermediate HCOOBpin **8** via **TS'**. Subsequently, **8** reacts with amines in the presence of HBpin to furnish formamides and HOBpin, which undergoes dehydrogenative coupling with HBpin to form O(Bpin)₂. Compared to the **TS** pathway (40.1 kcal mol⁻¹), which involves a transition state stabilized mainly by an electrostatic interaction between **E** and the negatively charged hydride of HBpin, the **TS'** pathway has a lower activation barrier (18.8 kcal mol⁻¹) (Scheme 4.11).

Scheme 4.9 Catalytic hydroboration of CO₂ by the active catalyst **FLPs CH₂O**.

To examine the effect of O-C=O moiety in **E**, we replaced O-C=O moiety with a CH₂-CH₂ moiety in **G**, and tested the *N*-formylation reaction using ethylene-adduct **G** as the catalyst (Scheme 4.8d). With 2 mol % of **G**, the reactions of **6a** and **6i** with HBpin under CO₂ atmosphere gradually afford the corresponding formamides **7a** and **7i**, respectively. These reactions also confirm that **G** serves as the active catalyst and promotes the *N*-formylation reaction despite the lack of the Lewis basic O-C=O moiety. Very recently, the catalyst-free *N*-formylation of amines using CO₂ and ammonia-borane (H₃N-BH₃) was also reported.^[10]

Scheme 4.10 Proposed reaction mechanism for the **E**-catalyzed *N*-formylation of amines.

Scheme 4.11 Free-energy profile (in kcal mol^{-1}) for the reaction between **E** and HBpin under CO_2 in CH_3CN at 298 K as determined at the M06-2X(SCRF)/def2-TZVP//M06-2X(SCRF)/6-31G* level of theory.

4.3 Conclusion

The inorganic/organic hybrid benzene ($B_2C_2N_2$) **C** effectively promotes the *N*-formylation of amines using CO_2 and HBpin under ambient conditions. Various primary and secondary amines bearing electron-withdrawing as well as electron-donating groups were well tolerated. Experimental and theoretical mechanistic studies revealed that the actual active catalyst is the adduct **E**, which serves as a Lewis base to catalyze the hydroboration of CO_2 , which is in contrast with the proposed mechanisms for other main-group compound-catalyzed reduction of CO_2 .^{[1][3][11]} The hydroboration of CO_2 with HBpin affords HCOOBpin **8** as the intermediate via the activation of the B-H bond of HBpin by **E**. The subsequent non-catalytic reaction of **8** with amines affords amides under ambient conditions.

4.4 Experimental section

4.4.1 Synthesis, physical and spectroscopic data for all new compounds

General considerations: All reactions were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂, and distilled under nitrogen. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ¹H, ¹³C and ¹¹B NMR spectra were recorded on a Bruker AVIII 400MHz spectrometers at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet. Coupling constants *J* are given in Hz. In the ¹³C NMR spectra, due to the coupling with boron atoms, signals for the carbon atoms directly bonding to boron atoms could not be observed. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with OptiMelt apparatus (Stanford Research System).

Reaction between E and HBpin: Compound E (0.025 g, 0.060 mmol), HBpin (26 μL, 0.180 mmol), and CD₃CN (0.45 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 2h, a formation of product **8** concomitant with O(Bpin)₂ was confirmed.

Figure 4.2 ^1H NMR (C_6D_6) spectrum of a reaction mixture of **E** and HBpin (3 eq) after 2h at ambient temperature, indicating a formation of **8**.

Figure 4.3 ^{11}B NMR (C_6D_6) spectrum of a reaction mixture of **E** and HBpin (3 eq) after 2h at ambient temperature, indicating a formation of **8**.

Catalytic hydroboration of CO₂ with 2 mol % of C: Compound **C** (0.002 g, 0.00537 mmol), HBpin (39 μ L, 0.269 mmol) and CD₃CN (0.4 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The sample was degassed using a freeze-pump-thaw method, and CO₂ (approximately 45 mg) was introduced into the NMR tube at -196 °C. The reaction was monitored by NMR spectroscopy. After 34 h, the formation of product **8** (48% yield) was confirmed.^[S1]

Figure 4.4 ¹H NMR (CD₃CN) spectrum after 34 h.

Figure 4.5 ^{11}B NMR (CD_3CN) spectrum after 34 h.

Catalytic hydroboration of CO_2 with 9 mol % of C: Compound **C** (0.009 g, 0.0242 mmol), HBpin (39 μL , 0.269 mmol) and CD_3CN (0.4 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The sample was degassed using a freeze-pump-thaw method, and CO_2 (approximately 45 mg) was introduced into the NMR tube at -196°C . The reaction was monitored by NMR spectroscopy. After 24 h, the formation of product **8** (70% yield) was confirmed.

Figure 4.6 ^1H NMR (CD_3CN) spectrum after 24 h.

Figure 4.7 ^{11}B NMR (CD_3CN) spectrum after 24 h.

Stoichiometric reaction between 8 and *N*-methylaniline 6a: Compound **8** (0.318 mmol), *N*-methylaniline **6a** (34 μ L, 0.318 mmol) and C₆D₆ (0.5 mL) were loaded in a dried J-Young Tube under argon atmosphere. The tube was sealed, shaken and the reaction was monitored by NMR spectroscopy. After 3 h, the formation of product **7a** (66% yield) was confirmed. By adding 2.5 equivalents of HBpin (115 μ L, 0.795 mmol) to the reaction solution, compound **7a** was obtained in >95% yield.

Figure 4.8 ¹H NMR (C₆D₆) spectrum after 3 h.

Figure 4.9 ^1H NMR (C_6D_6) spectrum after addition of HBpin (2.5 eq).

Stoichiometric reaction between E, 6a and HBpin: Compound **E** (0.023 g, 0.055 mmol), *N*-methylaniline **6a** (6 μL , 0.055 mmol), HBpin (24 μL , 0.166 mmol), and CD_3CN (0.4 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction was monitored by NMR spectroscopy. After 20h, a clean formation of product pinB-NMePh **9** was confirmed.

Figure 4.10 ^1H NMR (CD_3CN) spectrum after 20h.

Figure 4.11 ^{11}B NMR (CD_3CN) spectrum after 20h.

Examination of a catalytic reaction using 9 as a starting material: Compound **C** (0.0016g, 0.0043 mmol), HBpin (62 μ L, 0.430 mmol), **9** (0.050g, 0.215mmol), the internal standard 1,3,5-trimethoxybenzene (10 mg), and CD_3CN (0.4 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The sample was degassed using a freeze-pump-thaw method, and CO_2 (approximately 45 mg) was introduced into the NMR tube at -196°C . The reaction was monitored by NMR spectroscopy. After 7 h, the formation of product **7a** (15% yield) was confirmed.

Figure 4.12 ^1H NMR (CD_3CN) spectrum after 7 h.

Stoichiometric reaction between E-($^{13}\text{CO}_2$), **6a and HBpin with CO_2 :** Compound **E**-($^{13}\text{CO}_2$) (0.026 g, 0.062 mmol), HBpin (45 μL , 0.31 mmol), *N*-methylaniline **6a** (6.7 μL , 0.062 mmol) and CD_3CN (0.4 mL) were loaded in a dried J-Young Tube under argon atmosphere. The sample was degassed using a freeze-pump-thaw method, and CO_2 (approximately 45 mg) was introduced into the NMR tube at $-196\text{ }^\circ\text{C}$. The reaction was monitored by NMR spectroscopy. After 7 h, the formation of product **7a** (>95% yield) was confirmed.

Figure 4.13 ^1H NMR (CD_3CN) spectrum after 7 h.

Figure 4.14 ^{11}B NMR (CD₃CN) spectrum after 7 h.

Figure 4.15 $^{13}\text{C}\{^1\text{H}\}$ NMR (CD₃CN) spectrum after 7 h.

General catalytic procedures for the *N*-formylation of amines: Compound **C** (0.0016g, 0.0043 mmol), HBpin (94 μ L, 0.645 mmol), *N*-methylaniline (23 μ L, 0.215mmol), the internal standard 1,3,5-trimethoxybenzene (10 mg) and CD₃CN (0.4 mL) were loaded in a dried J-Young Tube under argon atmosphere. The sample was degassed using a freeze-pump-thaw method, and CO₂ (approximately 45 mg) was introduced into the NMR tube at –196 °C. The reaction was monitored by NMR spectroscopy. PhMeN(CHO) **7a** was purified by preparative TLC using ethyl acetate/hexane/triethylamine as the eluent. Spectral data of all products are in accordance with those reported in the literature.

7a: as a mixture of rotamers (5:95), Major rotamer: ¹H NMR (400 MHz, CDCl₃) δ = 3.32 (s, 3 H, CH₃), 7.16-7.19 (m, 2 H, ArH), 7.26-7.30 (m, 1 H, ArH), 7.39-7.43 (m, 2 H, ArH), 8.48 (s, 1 H, CHO); ¹³C NMR (100 MHz, C₆D₆): δ = 32.2 (CH₃), 122.5 (CH), 126.6 (CH), 129.8 (CH), 142.4 (^{Ar}C-N), 162.5 (CHO).

7b: as a mixture of rotamers (49:51), ¹H NMR (400 MHz, CDCl₃) δ = 2.26 (m, 9 H, CH₃), 6.90-6.93 (m, 2 H, ArH), 8.03-8.37 (m, 1 H, CHO); ¹³C NMR (100 MHz, C₆D₆): δ = 18.6 (CH₃), 18.7 (CH₃), 21.00 (CH₃), 21.03 (CH₃), 129.1 (CH), 129.4 (CH), 129.9 (CH), 130.6 (CH), 135.1 (^{Ar}C-N), 135.3 (^{Ar}C-N), 137.6 (^{Ar}C-C), 137.7 (^{Ar}C-C), 159.7 (CHO), 165.2 (CHO).

7c: as a mixture of rotamers (42:58), Major rotamer: ¹H NMR (400 MHz, CDCl₃) δ = 1.18-1.22 (m, 6 H, CH₃), 2.59-2.69 (m, 4 H, CH₂), 7.13-7.28 (m, 3 H, ArH), 8.06 (d, 0.55 H, *J* = 12 Hz, CHO), 8.42 (d, 0.39 H, *J* = 1.2 Hz, CHO); ¹³C NMR (100 MHz, C₆D₆): δ = 14.6 (CH₃), 14.9 (CH₃), 25.0 (CH₂), 25.1 (CH₂), 126.6 (CH), 127.1 (CH), 128.5 (CH), 128.6 (CH), 131.2 (^{Ar}C-N), 131.7 (^{Ar}C-N), 141.5 (^{Ar}C-C), 142.1 (^{Ar}C-C), 160.2 (CHO), 165.2 (CHO).

7d: as a mixture of rotamers (38:62), ^1H NMR (400 MHz, CDCl_3) δ = 1.22 (d, 12 H, J = 6.8 Hz, CH_3), 3.12 (sept, 0.8 H, J = 6.8 Hz, CH), 3.22 (sept, 1.31 H, J = 6.8 Hz, CH), 6.75 (s, 0.35 H, NH), 7.03 (d, 0.62 H, J = 11.6 Hz, NH), 7.19-7.22 (m, 2 H, ArH), 7.30-7.36 (m, 1 H, ArH), 8.03 (d, 0.63 H, J = 12 Hz, CHO), 8.48 (d, 0.38 H, J = 1.6 Hz, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.8 (CH_3), 28.6 (CH), 29.0 (CH), 123.7 (CH), 124.0 (CH), 129.0 (CH), 129.1 (CH), 129.6 ($^{\text{Ar}}\text{C-N}$), 130.0 ($^{\text{Ar}}\text{C-N}$), 146.3 ($^{\text{Ar}}\text{C-C}$), 147.0 ($^{\text{Ar}}\text{C-C}$), 160.6 (CHO), 165.2 (CHO).

7e: as a mixture of rotamers (32:68), ^1H NMR (400 MHz, CDCl_3) δ = 3.87 (s, 0.95 H, OCH_3), 3.89 (s, 2.11 H, OCH_3), 6.88-6.99 (m, 2 H, ArH), 7.06-7.21 (m, 1.37 H, ArH), 7.67 (br, 0.32 H, NH), 7.79 (br, 0.68 H, NH), 8.36 (dd, 0.7 H, J = 1.2 Hz, J = 8 Hz, ArH), 8.46 (d, 0.68 H, J = 1.2 Hz, CHO), 8.74 (d, 0.32 H, J = 11.6 Hz, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 55.9 (CH_3), 110.1 (CH), 111.4 (CH), 116.7 (CH), 120.7 (CH), 121.2 (CH), 121.3 (CH), 124.4 (CH), 126.9 ($^{\text{Ar}}\text{C-N}$), 147.9 ($^{\text{Ar}}\text{C-O}$), 158.8 (CHO), 161.5 (CHO).

7f: as a mixture of rotamers (31:69), ^1H NMR (500 MHz, CDCl_3) δ = 7.06-7.45 (m, 4 H, ArH), 7.67 (br, 0.74 H, NH), 8.42 (d, 0.68 H, J = 8.5 Hz, NH), 8.51 (s, 0.69 H, CHO), 8.73 (d, 0.31 H, J = 11.5 Hz, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 118.6 (CH), 120.1 (CH), 122.1 (CH), 122.6 (CH), 125.3 ($^{\text{Ar}}\text{C-N}$), 128.0 ($^{\text{Ar}}\text{C-N}$), 129.3 ($^{\text{Ar}}\text{C-Cl}$), 133.8 ($^{\text{Ar}}\text{C-Cl}$), 158.9 (CHO), 161.5 (CHO).

7g: as a mixture of rotamers (50:50), ^1H NMR (400 MHz, CDCl_3) δ = 3.79 (s, 1.5 H, CH_3), 3.80 (s, 1.5 H, CH_3), 6.85-6.90 (m, 2 H, ArH), 7.02-7.05 (m, 1 H, ArH), 7.35 (br, 0.5 H, NH), 7.43-7.45 (m, 1 H, CHO), 8.00 (br, 0.5 H, NH), 8.50 (d, 0.5 H, J = 11.6 Hz, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 55.6 (CH_3), 55.7 (CH_3), 114.4 (CH), 115.0 (CH), 121.8 (CH), 121.9 (CH), 129.6 ($^{\text{Ar}}\text{C-N}$), 130.0 ($^{\text{Ar}}\text{C-N}$), 156.9 ($^{\text{Ar}}\text{C-O}$), 157.8 ($^{\text{Ar}}\text{C-O}$), 159.0 (CHO), 163.2 (CHO).

7h: as a mixture of rotamers (3:97), ^1H NMR (400 MHz, CDCl_3) δ = 1.16 (t, 3 H, J = 7.2 Hz, CH_3), 3.86 (q, 2 H, J = 7 Hz, CH_2), 7.16-7.43 (m, 5 H, ArH), 8.36 (s, 1 H, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 13.2 (CH_3), 40.2 (CH_2), 124.4 (CH), 127.0 (CH), 129.8 (CH), 141.0 ($^{\text{Ar}}\text{C-N}$), 162.2 (CHO).

7i: as a mixture of rotamers (6:94), Major rotamer: ^1H NMR (400 MHz, CDCl_3) δ = 3.18 (s, 3 H, CH_3), 3.83 (s, 3 H, OCH_3), 6.94-6.98 (m, 2 H, ArH), 7.09-7.11 (m, 1 H, ArH), 7.28-7.30 (m, 1 H, ArH), 8.15 (s, 1 H, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 32.8 (CH_3), 55.7 (OCH_3), 112.1 (CH), 121.0 (CH), 127.9 (CH), 129.1 (CH), 130.8 ($^{\text{Ar}}\text{C-N}$), 155.1 ($^{\text{Ar}}\text{C-OMe}$), 163.6 (CHO).

7j: as a mixture of rotamers (6:94), Major rotamer: ^1H NMR (400 MHz, CDCl_3) δ = 3.26 (s, 3 H, CH_3), 3.81 (s, 3 H, OCH_3), 6.92 (d, 2 H, J = 8.8 Hz, ArH), 7.09 (d, 2 H, J = 9.2 Hz, ArH), 8.33 (s, 1 H, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 32.8 (CH_3), 55.7 (OCH_3), 114.9 (CH), 124.8 (CH), 135.4 ($^{\text{Ar}}\text{C-N}$), 158.4 ($^{\text{Ar}}\text{C-OMe}$), 162.6 (CHO).

7k: as a mixture of rotamers (12:88), Major rotamer: ^1H NMR (400 MHz, CDCl_3) δ = 3.36 (s, 3 H, CH_3), 7.28 (d, 2 H, J = 8.8 Hz, ArH), 7.72 (d, 2 H, J = 8.8 Hz, ArH), 8.65 (s, 1 H, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 31.5 (CH_3), 109.6 (C-CN), 118.3 (CN), 121.2 (CH), 133.9 (CH), 146.0 ($^{\text{Ar}}\text{C-N}$), 161.7 (CHO).

7l: as a mixture of rotamers (6:94), Major rotamer: ^1H NMR (400 MHz, CDCl_3) δ = 3.29 (s, 3 H, CH_3), 7.05 (d, 2 H, J = 8.4 Hz, ArH), 7.52 (d, 2 H, J = 8.8 Hz, ArH), 8.45 (s, 1 H, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 32.1 (CH_3), 119.8 (C-Br), 123.9 (CH), 132.9 (CH), 141.4 ($^{\text{Ar}}\text{C-N}$), 162.0 (CHO).

7m: as a mixture of rotamers (7:93), Major rotamer: ^1H NMR (400 MHz, CDCl_3) δ = 3.35 (s, 3 H, CH_3), 7.29 (d, 2 H, J = 8.4 Hz, ArH), 7.68 (d, 2 H, J = 8.4 Hz, ArH), 8.59 (s, 1 H, CHO); ^{13}C NMR (100 MHz, C_6D_6): δ = 31.8 (CH_3), 121.6 (CH), 127.0 (CH),

127.1 (CF₃), 128.5 (^{Ar}C-CF₃), 145.3 (^{Ar}C-N), 162.0 (CHO); ¹⁹F NMR (376 MHz, CDCl₃): δ = -62.4 (s).

7n: as a mixture of rotamers (8:92), Major rotamer: ¹H NMR (400 MHz, CDCl₃) δ = 1.96 (quint, 2 H, J = 6.2 Hz, CH₂), 2.82 (t, 2 H, J = 6.4 Hz, CH₂), 3.81 (t, 2 H, J = 6 Hz, CH₂), 7.09-7.22 (m, 4 H, ArH), 8.79 (s, 1 H, CHO); ¹³C NMR (100 MHz, C₆D₆): δ = 22.4 (CH₃), 27.3 (CH₂), 40.5 (CH₂), 117.2 (CH), 124.7 (CH), 127.3 (CH), 129.1 (^{Ar}C-C), 129.8 (CH), 137.4 (^{Ar}C-N), 161.3 (CHO).

Catalytic *N*-formylation of *N*-methylaniline **7a with 2 mol % of **G**:** Compound **G** (0.0017g, 0.0043 mmol), HBpin (94 μL, 0.645 mmol), *N*-methylaniline **6a** (23 μL, 0.215mmol) and CD₃CN (0.4 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The sample was degassed using a freeze-pump-thaw method, and CO₂ (approximately 45 mg) was introduced into the NMR tube at -196 °C. The reaction was monitored by NMR spectroscopy. After 10 hours at room temperature, the formation of **7a** (95% yield) was confirmed.

Figure 4.16 ¹H NMR (CD₃CN) spectrum after 10 h.

Catalytic N-formylation of 2-methoxy-*N*-methylaniline **6i with 2 mol % of **G**:**

Compound **G** (0.0017g, 0.0043 mmol), HBpin (94 μ L, 0.645 mmol), 2-methoxy-*N*-methylaniline **7i** (28 μ L, 0.215mmol) and CD₃CN (0.4 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The sample was degassed using a freeze-pump-thaw method, and CO₂ (approximately 45 mg) was introduced into the NMR tube at -196°C . The reaction was monitored by NMR spectroscopy. After 13 hours at room temperature, the formation of **7i** (98% yield) was confirmed.

Figure 4.17 ¹H NMR (CD₃CN) spectrum after 13 h.

Reaction between G and CO₂: Compound **G** (0.020 g, 0.0500 mmol) and C₆D₆ (0.5 mL) were loaded in a dried J-Young Tube under argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. The sample was degassed using a freeze-pump-thaw method, and CO₂ (approximately 45 mg) was introduced into the NMR tube at −196 °C. After 12 hours at room temperature, no reaction was confirmed.

Figure 4.18 ¹H NMR (C₆D₆) spectrum of a reaction mixture of **1c** (1eq) and CO₂ after 12 hours at ambient temperature.

Figure 4.19 $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6) spectrum of a reaction mixture of **G** (1eq) and CO_2 after 12 hours at ambient temperature.

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Chapter 5

Electrostatic Catalysis for hydroboration

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5.1 Introduction

5.1.1 Main group catalysts for hydroboration reaction

The hydrogenation of carbonyl compounds to form alcohols is a very important process in many fields such as pharmaceutical chemistry.^{[1][2]} Because hydrogenation usually requires the use of highly flammable H₂ gas, hydroboration has attracted considerable attention as a potential alternative for the conversion of carbonyl species to boric acid derivatives, which can then be converted to the corresponding alcohol by hydrolysis.^[1] Transition metals are commonly employed as effective and convenient catalysts for the hydroboration of carbonyl compounds.^[3] Main group compounds are increasingly used as alternatives to transition metal complexes,^[4] since it has been reported that some main group compounds can mimic transition metals in the activation of small molecules as well as in the reduction of unsaturated bonds.^{[4][5]}

In 1984, Noyori group isolated lithium aluminum hydride **1**, which features a binaphthol ligand and is derived from the reaction of lithium aluminum hydride with 2,2'-dihydroxy-1,1'-binaphthyl (Scheme 5.1).^[5g] Compound **1** catalyzed the reduction of prochiral carbonyl compounds in a highly enantioselective manner. Although **1** demonstrated excellent enantioselectivity, stoichiometric amounts of **1** were required to reduce the carbonyl compounds. Woodward group designed and synthesized compound **2** as a catalyst to promote the hydroboration reaction of carbonyl compounds using catecholborane.^[5f] Based on the combination of the "soft" catalyst **2** and catecholborane as the "hard" terminal hydride source, they successfully utilized **2** as an effective catalyst to promote removal of the alkoxide substituent on in **2'** to form the hydroboration product and regenerate **2** (Scheme 5.2).

Scheme 5.1 Main-group species for the hydroboration of carbonyl compounds.

Scheme 5.2 Hydroboration of carbonyl compounds by **2**.

Hill's group and Stasch's group independently reported that alkyl magnesium complex **3** and **9** could be used as catalysts for the hydroboration of carbonyl compounds with pinacolborane (HBpin) at ambient temperature.^{[5d][5h]} Experimental and mechanistic studies have revealed that the actual active catalyst is magnesium hydride species **3'**, which is formed via B-H/C-Mg metathesis between **3** and HBpin (Scheme 5.3). Notably, a wide range of aliphatic and aromatic aldehydes and ketones are well tolerated, and catalyst loadings of **3** and **9** can be as low as 0.05 mol %.

Scheme 5.3 Synthesis of **3'** via B-H/C-Mg metathesis of **3** and HBpin.

Other than magnesium complexes **3** and **9**, Jones group first demonstrated that low-valent p-block metal hydrides **4** with HBpin could efficiently and selectively promote the hydroboration of carbonyl compounds.^[5c] **4** could not only selectively reduce the ketone fragment of 2-cyclohexen-1-one but also could catalyze the hydroboration of aliphatic and aromatic aldehydes. Reactions with bulky ketone substrates require higher catalyst loadings and longer reaction times to reach completion. In addition, low-valent metals **11** and **12** were also explored as catalysts for hydroboration.^{[5i][5j]}

Recently, our group reported that 1,3,2-diazaphospholene **5** effectively catalyzed the hydroboration of carbonyl compounds with HBpin, which is regarded as the first example of a metal-free catalytic hydroboration.^[5b] With this system, the hydroboration of aldehydes proceeds well at ambient temperature, whereas the same reaction with ketone substrates proceeds at 90 °C. An experimental mechanistic study and calculations revealed that the rate-determining step involves the bond dissociation and formation of

the P-O and B-H bonds via a σ -bond metathesis in a step-wise but nearly concerted pathway.

Organoaluminum hydrides **6** and **10**, which feature triflate substituents at their aluminum centers, both promoted the catalytic hydroboration of carbonyl compounds. The catalytic addition of trimethylsilyl cyanide (TMSCN) to carbonyl compounds was promoted by **6**, and the catalytic hydroboration of terminal arylalkynes was promoted by **10**.^{[5a][5k]} Moreover, Okuda group reported that an alkali metal and hydridic borate catalytic system (**7** and **8**) could be used to promote hydroboration.^{[5l][5m]}

In general, most main-group elements promote hydroboration reactions via an insertion-metathesis mechanism (Scheme 5.4).^[1a] The initial step is the insertion of the E-H (E = Al, P, Ge or Sn) bond of **I** into the C=O bond of carbonyl in **II** to afford **III**. Subsequent σ -bond metathesis between the E-O moiety of **III** and HBpin leads to the formation of pinacolborate ester **IV** concomitant with the regeneration of the catalyst.

Scheme 5.4 Hydroboration of carbonyl compounds via a σ -bond metathesis mechanism.

5.2 Results and discussion

5.2.1 Stoichiometric reactions of **C** with acetophenone and HBpin

In chapter 4, we presented that 1,3,2,5-diazadiborinine **C** is an effective pre-catalyst for the *N*-formylation of various amines using carbon dioxide (CO₂) and pinacolborane (HBpin) under mild conditions via a Lewis-base activation mechanism. This prompted us to investigate hydroboration reaction of carbonyl compounds with **C** as the catalyst. To begin our study, we performed several stoichiometric reactions.

When one equivalent of acetophenone **7a** was added to a deuterated benzene solution of **C**, compound **J** was quantitatively formed (Scheme 5.5a). In the ¹¹B NMR spectrum of **J**, new signals were detected at 2.8 ppm and –13.6 ppm, both of which are shifted upfield relative to those of **C** (7.3 and 24.9 ppm). After the removal of the all volatiles, **J** was isolated as a white powder in 95% yield. The solid-state structure of **J** was confirmed by X-ray diffraction analysis (Figure 5.1), which revealed that compound **J** was formed via a regioselective [4+2] cycloaddition. This selectivity was because of the Lewis basic boron atom between two carbon atoms and the Lewis acidic boron atom between two nitrogen atoms in **C**. Both the boron centers in **J** are tetrahedral, indicative of typical characteristic sp³ hybridization. The B1-O1 bond (1.450(2) Å) is a slightly longer than typical B-O single bonds (1.28–1.43 Å),^[6a] and the B2-C7 bond (1.729(2) Å) is significantly longer than typical B-C single bonds (1.50–1.59 Å).^[6b]

a)

b)

c)

Scheme 5.5 (a) Reaction of **C** with acetophenone **7a**. (b) Reaction of **J** with HBpin and **7a**. (c) Reaction of **7g** and HBpin in the presence of **J**.

Figure 5.1 Solid-state structure of **J** (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

Subsequently, one equivalent of HBpin was added to the C₆D₆ solution of compound **J**, and no corresponding hydroboration product was observed (Scheme 5.5b). Upon addition of one equivalent of acetophenone **7a** to the solution, the desired product PhCHMeOBpin **8a** was obtained along with unreacted **J** (Scheme 5.5b). Meanwhile, treatment of **J** with 4'-methoxyacetophenone **7g** (1.5 eq) and HBpin (3 eq) in CD₃CN at room temperature quantitatively generated 4'-MeO-PhCHMeOBpin **8g** (Scheme 5.5c). The formation of product **8g** rather than **8a** indicates the carbonyl moiety is not dissociated from **J**.

5.2.2 Hydroboration of ketones and aldehydes catalyzed by **C**

Next, we moved from stoichiometric reactions to catalytic reactions. In the absence of catalyst **C**, no product was observed (Table 5.1, entry 1). With 5 mol % of catalyst **C** in C₆D₆, compound **8a** was formed in 98% yield after 2 h (Table 5.1, entry 2). When the catalyst loading was decreased to 2 mol %, the similar yield and reaction time were

observed (Table 5.1, entry 3). Further reduction of the catalyst loading to 1 mol % resulted in longer reaction time (Table 5.1, entry 4). Interestingly, when we used CD₃CN as the solvent, the reaction was completed in much less time (Table 5.1, entry 5 and 6). Changing the HBpin to 9-borabicyclo(3.3.1)nonane (9-BBN) could also give hydroboration product **8a'** in good yields but longer time (Table 5.1, entry 7).

Table 5.1 Optimization of the hydroboration reaction conditions.^[a]

7a **8a** ([B] = Bpin)
8a' ([B] =)

Entry	cat. [mol%]	reagent [1.0 equiv]	solvent	Time [h]	Yield [%] ^[b]
1	0	HBpin	C ₆ D ₆	2	0%
2	5	HBpin	C ₆ D ₆	2<	95%
3	2	HBpin	C ₆ D ₆	2	98%
4	1	HBpin	C ₆ D ₆	8	98%
5	2	HBpin	CD₃CN	0.5	98%
6	1	HBpin	CD ₃ CN	5	98%
7	2	9-BBN	C ₆ D ₆	6.5	98%

[a] Reaction conditions: acetophenone (0.269 mmol), H-source (0.269 mmol), solvent (0.5 ml). [b] Yields were determined by ¹H-NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard.

With the optimized reaction conditions in hand, the scope of the catalytic reaction with a variety of carbonyl compounds was briefly examined (Table 5.2 and Table 5.3). The reaction yields of the hydroboration of aliphatic ketones (**7b-7e**) and aldehydes (**9a-9b**) were high. In the case of aryl substituents, various carbonyl compounds bearing both electron-withdrawing (**7f**, **7i**; **9d-9f**) and electron-donating (**7g**, **7j**; **9g**, **9h**) group also gave the corresponding products in good yields. Hydroboration of α,β-unsaturated carbonyl compounds (**7k**, **7l**) proceeded selectively to give the corresponding products in good yields (**8k**: 98%; **8l**: 98%). Benzoquinone (**7m**) could also generate the borate

ester in very good yield (**8m**: 98%). Moreover, hydroboration of terephthalaldehyde (**9i**) in the presence of two equivalent of HBpin afforded the bis(hydroborated) derivative in excellent yield (**10i**: 98%). Similarly, hydroboration of bis(hydroborated) derivative (**9j**) generated 4-acetylbenzaldehyde (**10j**: 57%).

Table 5.2 Scope of catalytic hydroboration of ketone substrates.

	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{R}' \\ \text{7b-7m} \end{array}$	$\xrightarrow[\text{CD}_3\text{CN / RT}]{\begin{array}{c} \text{C (2 mol\%)} \\ \text{HBpin (1 eq)} \end{array}}$		$\begin{array}{c} \text{R}' \\ \\ \text{R}-\text{C}-\text{O}-\text{Bpin} \\ \text{8b-8m} \end{array}$	
		Time [h]	Yield [%] ^[a]	TON	TOF [hr ⁻¹] ^[b]
7b		2.75 h	98%	49	18
7c		168 h	85%	43	0.3
7d		0.17 h<	98%	49	>288 ^[c]
7e	2-adamantanone	0.17 h<	98%	49	>288 ^[c]
7f		2 h	98%	49	25
7g		48 h	95%	48	1
7h		2.5 h	98%	49	20
7i ^[d]		3 h	98%	49	16
7j ^[d]		7.5 h	96%	48	6
7k		10 h	98%	49	5
7l		3 h	98%	49	16
7m ^[e]		0.17 h<	98%	49	>288 ^[c]

[a] Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b] Turnover frequency (TOF) = turnover number (TON) / average reaction time. [c] TOF lower limit. [d] Reaction conducted using C₆D₆ as solvent. [e] HBpin (2 eq) was employed in this reaction.

Table 5.3 Scope of the catalytic hydroboration of aldehyde substrates.

$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{H} \\ \text{9a-9j} \end{array}$		$\xrightarrow[\text{CD}_3\text{CN / RT}]{\begin{array}{c} \text{C (2 mol\%)} \\ \text{HBpin (1 eq)} \end{array}}$		$\begin{array}{c} \text{R}-\text{CH}_2-\text{O}-\text{Bpin} \\ \text{10a-10j} \end{array}$	
9		Time [h]	Yield [%] ^[a]	TON	TOF [hr ⁻¹] ^[b]
9a		1.83 h	98%	49	27
9b		0.17 h<	98%	49	>288 ^[c]
9c		0.25 h	98%	49	196
9d		0.17 h<	98%	49	>288 ^[c]
9e		0.17 h<	98%	49	>288 ^[c]
9f		0.33 h	98%	49	148
9g		0.83 h	98%	49	59
9h		7 h	98%	49	7
9i ^[d]		1 h	98%	49	49
9j ^[d]		168 h	57%	29	0.2

[a] Yields were determined by ¹H NMR spectroscopy using 1,3,5-trimethoxybenzene as an internal standard. [b] Turnover frequency (TOF) = turnover number (TON) / average reaction time. [c] TOF lower limit. [d] HBpin (2 eq) was employed in this reaction.

5.2.3 Kinetic Study

To gain insight into the hydroboration mechanism, we carried out further analysis of the catalytic reaction. To determine the order of the catalytic hydroboration reaction, C₆D₆ solutions of different concentrations of **C**, HBpin, and diisopropyl ketone **7c** were prepared in sealed NMR tubes, and the reactions were monitored by ¹H NMR at 2-min intervals at ambient temperature. Based on the rate constants K_{obs} simulated from the kinetic conversion charts (Figure 5.2–5.7), we confirmed the rate law ($K_{\text{obs}} = k[\text{C}]^1[\text{HBpin}]^1[\text{7c}]^1$). The Eyring analysis revealed activation parameters including $\Delta H^\ddagger = 8.6 \pm 1.0 \text{ kcal mol}^{-1}$, $\Delta S^\ddagger = -50.7 \pm 3.1 \text{ e.u.}$, $\Delta G^\ddagger(298) = 23.7 \pm 1.9 \text{ kcal mol}^{-1}$ (Figure 5.8 and Figure 5.9). In addition, deuterated pinacolborane (DBpin) was used to examine deuterated kinetic isotope effects (DKIEs) on the reactions with **7c** (Scheme 5.6; Figure 5.10). A CD₃CN solution of **7c** with excess DBpin (5.1 eq) in the presence of **C** (3 mol %) was prepared in a sealed NMR tube, and the reaction was monitored by ¹H NMR at 10-min intervals. Based on the rate constants simulated from the kinetic conversion chart, a normal DKIE value of 3.65 was determined for the reactions. We also performed the same reaction employing ¹⁸O-labelled diisopropyl ketone **7c-¹⁸O**, which provided a ¹⁶O/¹⁸O KIE value of 1.83 (Figure 5.10).^{[5b][7]} The double KIE reaction with DBpin and ¹⁸O-labelled diisopropyl ketone showed the largest DKIE value 5.97, and these results suggested that the dissociation of the B-H bond in HBpin and the C=O bond in **7c** and/or the formation of the B-O bond and the C-H bond, are all involved in the rate-determining step.

Figure 5.2 Plot of $[i\text{Pr}_2\text{COHBpin } 8\text{c}]$ against time for varying concentration of C. $[i\text{Pr}_2\text{CO } 7\text{c}] = 0.2307 \text{ M}$, $[\text{HBpin}] = 1.2091 \text{ M}$.

Figure 5.3 Plot of k against different concentrations of C indicating 1st order dependence on $[\text{C}]$.

Figure 5.4 Plot of $[i\text{Pr}_2\text{HCOBpin } \mathbf{8c}]$ against time for varying concentrations of $i\text{Pr}_2\text{CO}$ **7c**. $[C] = 0.009430 \text{ M}$, $[\text{HBpin}] = 1.2091 \text{ M}$.

Figure 5.5 Plot of k against different concentrations of $i\text{Pr}_2\text{CO } \mathbf{7c}$ indicating 1st order dependence on $[i\text{Pr}_2\text{CO } \mathbf{7c}]$.

Figure 5.6 Plot of $[^iPr_2HCOBpin\ 8c]$ against time for varying concentrations of HBpin. $[^iPr_2CO\ 7c] = 0.2307\ M$, $[C] = 0.009430\ M$.

Figure 5.7 Plot of k against different concentrations of HBpin indicates 1st order dependence on $[HBpin]$.

Figure 5.8 Plot of $\ln[{}^i\text{Pr}_2\text{CO } 7\text{c}]$ against time at different temperatures.

T / K	1 / (T / K ⁻¹)	k / s ⁻¹	(k / s ⁻¹) / (T / K)	ln (k / T)
308.15	0.003245173	0.0000427	1.38569E-07	-15.79189832
318.15	0.003143171	0.0000753	2.36681E-07	-15.25655339
328.15	0.003047387	0.0000966	2.94378E-07	-15.03840264
338.15	0.002957267	0.0001737	5.13677E-07	-14.48167047

$$\Delta H^\ddagger = 8.6 \pm 1.0 \text{ kcal/mol}$$

$$\Delta S^\ddagger = -50.7 \pm 3.1 \text{ e.u.}$$

$$\Delta G^\ddagger_{298} = 23.7 \pm 1.9 \text{ kcal/mol}$$

Figure 5.9 Eyring plot of the catalytic reaction of **C**, HBpin and ¹Pr₂CO **7c**.

Scheme 5.6 Deuterated kinetic isotope effects (DKIEs) on the reactions of **7c**/**7c-¹⁸O**, HBpin/DBpin and **C**.

$$k(7\text{c, HBpin})/k(7\text{c-}^{18}\text{O, HBpin}) = 1.8272$$

$$k(7\text{c, HBpin})/k(7\text{c, DBpin}) = 3.6544$$

$$k(7\text{c, HBpin})/k(7\text{c-}^{18}\text{O, DBpin}) = 5.9658$$

Figure 5.10 Plot of $\ln[{}^i\text{Pr}_2\text{CO } 7\text{c}/7\text{c-}^{18}\text{O}]$ against time for (7c, HBpin), (7c- ^{18}O , HBpin), (7c, DBpin) and (7c- ^{18}O , DBpin). Simulated reaction constants: $k(7\text{c, HBpin}) = 0.0000698 \text{ s}^{-1}$, $k(7\text{c-}^{18}\text{O, HBpin}) = 0.0000382 \text{ s}^{-1}$, $k(7\text{c, DBpin}) = 0.0000191 \text{ s}^{-1}$, $k(7\text{c-}^{18}\text{O, DBpin}) = 0.0000117 \text{ s}^{-1}$.

5.2.4 Density functional theory (DFT) study of the hydroboration reaction

To gain insight into the reaction mechanism, pathways for the hydroboration of acetophenone **7a** with pinacolborane (HBpin) catalyzed by **C** were explored theoretically using DFT calculations at the M06-2X(SCRf)/def2-TZVP//M06-2X(SCRf)/6-31G*[⁸] level of theory. The solvent effect of acetonitrile (CD₃CN) was described by the SCRf (IEFPCM) solvent model. The activation barriers for hydroboration are estimated to be 27.1 kcal mol⁻¹, which is reasonably low and the lowest of all the barriers obtained (Figure 5.11 and Figure 5.12). Interestingly, no intramolecular bond dissociation/recombination of **J** is involved in this path (Figure 5.12a). Instead, the interaction between compound **J** and the migrating hydride of HBpin involved in the transition state to promote an insertion of B-H bond of HBpin into the C=O moiety of **7a**. The electrostatic potential map shows that the electrostatically positive and hole-shaped site of **J** interacts with the negatively charged hydride of HBpin (Figure 5.12b, left and middle). The hydrogen atoms of **J** (Figure 5.12b, right, highlighted in yellow), which feature partial positive charges, encircle the hydride of HBpin. Thus, compound **J** serves as an electrostatic catalyst to lower the activation barrier for the transition state, which involves cleavage of the B-H and C=O bonds and the formation of the B-O and C-H bonds. This result agrees reasonably well with the results of the D-KIE analysis. The similar transition state was identified for hydroboration reaction with 9-BBN as the hydride source (Figure 5.13).

Figure 5.11 Free energy profiles (in kcal/mol) for other paths: free-energy profile (in kcal mol⁻¹) for the reaction between **7a** and HBpin catalyzed by **J** in CH₃CN at 298 K, as determined at the M06-2X(SCRF)/def2-TZVP//M06-2X(SCRF)/6-31G* level of theory.

a)

b)

Figure 5.12 DFT-calculated free-energy profile of a plausible mechanism: a) free-energy profile (in kcal mol⁻¹) for the reaction between **7a** and HBpin catalyzed by **J** in CH₃CN at 298 K, as determined at the M06-2X(SCRF)/def2-TZVP//M06-2X(SCRF)/6-31G* level of theory; b) electrostatic potential map of the transition state.

Figure 5.13 Free energy profile (in kcal/mol) for the reaction between **7a** and 9-BBN catalyzed by **J** in CH₃CN at 298 K, as determined at the M06-2X(SCRF)/def2-TZVP//M06-2X(SCRF)/6-31G* level of theory. The relatively low barrier obtained for this reaction is likely associated with the fact that 9-BBN tends to form a stable dimer.

5.2.5 Hydroboration reactions with related molecules

Further experiments to confirm the reaction mechanism were performed. To confirm the innocence of the B-C-O-B moiety of **J**, compound **G** bearing the B-C-C-B framework was employed as the catalyst for the catalytic hydroboration reaction. No reaction between **G** and **7a** (1.0 eq) was observed under the tested reaction conditions. With 2 mol % of **G**, **7a** was fully converted to **8a** after 10 h (Table 5.4, entry 1). When **7h** was used as the substrate, it was converted to **8h** in 93% yield after 21 h. These results indicate that the B-C-O-B moiety of **J** is not an active site for the hydroboration reaction. Compared with **G**, the observed faster reaction rate observed with **J** implies that the polar catalyst promotes hydroboration more effectively. The calculations, in which the sums of the natural population analysis charge of the C fragments in **J** and **G**

are +0.65 and +0.39, respectively, agree reasonably well with the experimental result. Using triphenyl borane (BPh₃) and tris(pentafluorophenyl)borane (B(C₆F₅)₃) as strong Lewis acids did not promote the hydroboration reaction at ambient temperature (Table 5.4, entry 2 and 3). 1-Methylindole-2-boronic acid MIDA ester **MIDA** involving a dative N-B bond also did not catalyze the hydroboration (Table 5.4, entry 4). The catalytic activities of **[2-Ph-N-MeOx]OTf**, **2-PhOx** and *N*-MeOx BPh₃ were also tested. With 2 mol % or a stoichiometric amount of **[2-Ph-N-MeOx]OTf**, no product **8a** was observed (Table 5.4, entry 5). **2-PhOx** with BPh₃ promotes hydroboration of **2-PhOx** instead of hydroboration of **7a** (Table 5.4, entry 6). With 2 mol % or 100 mol % of *N*-MeOx BPh₃, **8a** was obtained in 6% or 12% yield, respectively (Table 5.4, entry 7). Interestingly, compound **K**, which features the polarized B₂N₂C₂ moiety, promoted the hydroboration reaction, and the product was obtained in an excellent yield, implying that the polarized B₂N₂C₂ structure seems the key factor for the catalytic activity (Table 5.4, entry 8). We confirmed that a π -acidic naphthalene diimide **NDI**,^[9] which can be used as a noncovalent electrophilic catalyst, does not catalyze the hydroboration reaction (Table 5.4, entry 9).

Table 5.4 Examination of the catalytic activities of the related compounds

<div style="text-align: center;"> <p>7a cat. HBpin (1 eq) solvent / RT 8a</p> </div>				
Entry	Catalyst (mol %)	Solvent	Time (hr)	Yield of 3a (%) ^[a]
1	<p>G (2)</p>	CD ₃ CN	10	95
2	BPh ₃ (100)	CD ₃ CN	12	0
3	B(C ₆ F ₅) ₃ (100)	CD ₃ CN	12	0
4	<p>MIDA (2 or 100)</p>	CD ₃ CN	12	0
5	<p>[2-Ph-N-MeOx]OTf (2 or 100)</p>	CD ₃ CN	12	0
6	<p>2-PhOx (100)</p>	CD ₃ CN	5	<div style="text-align: center;"> <p>2-PhOx-HBpin</p> <p>89%</p> </div>
7	N-MeOx•BPh₃ (2 or 100)	CDCl ₃ ^[b]	48	12 (100 mol % of catalyst)
		CD ₃ CN	12	6 (2 mol % of catalyst)
8	<p>K (2)</p>	CD ₃ CN	0.5	97
9	<p>NDI (2 or 100)</p>	CDCl ₃ ^[b]	12	0

Reaction conditions: acetophenone (0.269 mmol), HBpin (0.269 mmol), solvent (0.5 ml). [a] Yields were determined by ¹H-NMR spectroscopy. [b] Due to the poor solubility of **N-MeOx•BPh₃** and **NDI** in CD₃CN, the reactions were performed in CDCl₃.

5.3 Conclusion

In summary, we have demonstrated that 1,3,2,4-diazadiborinine **C** is an effective pre-catalyst for the promotion of the hydroboration of carbonyl compounds under mild conditions. Electron-withdrawing as well as electron-donating carbonyl compounds are well tolerated. Experimental and theoretical mechanistic studies confirmed that the actual catalyst is adduct of **C** with the carbonyl, and an electrostatic interaction between the **C**-carbonyl adduct and the hydride of HBpin is involved in the transition state. The partial positive hole-shaped structure of the adduct stabilizes the transition state via the electrostatic interactions. Thus, the reaction mechanism discovered here is totally different from an insertion-metathesis mechanism reported for the hydroboration of carbonyls catalyzed by other main-group species.

5.4 Experimental section

5.4.1 Synthesis, physical and spectroscopic data for all new compounds

General considerations: All reactions were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂, and distilled under nitrogen. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ¹H, ¹³C and ¹¹B NMR spectra were recorded on a Bruker AVIII 400MHz spectrometers at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, dd = doublet of doublets, m = multiplet. Coupling constants *J* are given in Hz. In the ¹³C NMR spectra, due to the coupling with boron atoms, signals for the carbon atoms directly bonding to boron atoms could not be observed. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with OptiMelt apparatus (Stanford Research System).

General catalytic procedures for the hydroboration of carbonyl compounds:

Compound **C** (0.00538 mmol: 2 mol %), aldehyde or ketone (0.269 mmol), HBpin (39 μL, 0.269 mmol), the internal standard 1,3,5-trimethoxybenzene (10 mg) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and monitored by NMR spectroscopy. Products were isolated by removing volatiles under vacuum for several hours.

8a: ¹H NMR (400 MHz, CDCl₃) δ = 1.26 (s, 6 H, CH₃), 1.29 (s, 6 H, CH₃), 1.54 (d, 3 H, *J* = 6.4 Hz, CH₃), 5.29 (q, 1 H, *J* = 6.4 Hz, CH), 7.28-7.42 (m, 5 H, ArH); ¹³C NMR

(100 MHz, C₆D₆): δ = 24.6 (CH₃), 24.7 (CH₃), 25.5 (CH₃), 72.7 (CH), 82.8 (C(CH₃)₂), 125.4 (CH), 127.2 (CH), 128.3 (CH), 144.7 (C_q); ¹¹B NMR (128 MHz, CDCl₃): δ = 22.1. **8a'**: ¹H NMR (400 MHz, CDCl₃) δ = 1.27 (br, 2 H, CH), 1.43 (d, 3 H, J = 6.8 Hz, CH₃), 1.64-1.81 (m, 12 H, CH₂), 5.19 (q, 1 H, J = 6.4 Hz, CH), 7.03-7.29 (m, 5 H, ArH); ¹³C NMR (100 MHz, C₆D₆): δ = 23.6 (CH₂), 26.3 (CH₃), 33.4 (CH₂), 33.7 (CH₂), 73.9 (CH), 125.8 (CH), 127.4 (CH), 128.7 (CH), 145.9 (C^q); DEPT - 135 NMR (100 MHz, C₆D₆): δ = 26.0 (CH₃), 73.5 (CH), 125.4 (CH), 127.1 (CH), 128.3 (CH); ¹¹B NMR (128 MHz, CDCl₃): δ = 57.16. HRMS (ESI): m/z for C₁₆H₂₄BO: 243.1920 [(M+H)]⁺; found: 243.1919.

8b: ¹H NMR (400 MHz, CDCl₃) δ = 0.85 (s, 9 H, CH₃), 1.10 (d, 3 H, J = 6.4 Hz, CH₃), 1.23 (s, 12 H, CH₃), 3.85 (q, 1 H, J = 6.4 Hz, CH); ¹³C NMR (100 MHz, C₆D₆): δ = 17.4 (CH₃), 24.5 (CH₃), 24.7 (CH₃), 25.6 (CH₃), 34.9 (C(CH₃)₃), 78.3 (CH), 82.5 (C(CH₃)₂); ¹¹B NMR (128 MHz, CDCl₃): δ = 22.0.

8c: ¹H NMR (400 MHz, CDCl₃) δ = 0.85 (t, 12 H, J = 7.2 Hz, CH₃), 1.21 (s, 12 H, CH₃), 1.78 (oct, 2 H, J = 6.8 Hz, CH(CH₃)₂), 3.46 (t, 1 H, J = 6 Hz, CH); ¹³C NMR (100 MHz, C₆D₆): δ = 17.4 (CH₃), 19.9 (CH₃), 24.8 (CH₃), 30.8 (CH(CH₃)₂), 83.2 (CH(CH₃)₂), 85.0 (CH); ¹¹B NMR (128 MHz, CDCl₃): δ = 22.2.

8d: ¹H NMR (400 MHz, CDCl₃) δ = 1.15-1.18 (m, 1 H, CH₂), 1.22 (s, 12 H, CH₃), 1.24-1.82 (m, 9 H, CH₂), 3.96 (sept, 1 H, J = 3.8 Hz, CH); ¹³C NMR (100 MHz, C₆D₆): δ = 23.9 (CH₂), 24.6 (CH₃), 25.5 (CH₂), 34.3 (CH₂), 72.7 (CH), 82.5 (CH(CH₃)₂); ¹¹B NMR (128 MHz, CDCl₃): δ = 21.9.

8e: ¹H NMR (400 MHz, CDCl₃) δ = 1.23 (s, 12 H, CH₃), 1.43 (d, 2 H, J = 11.6 Hz, adamantly-H), 1.68-1.89 (m, 10 H, adamantly-H), 2.12 (d, 2 H, J = 12 Hz, adamantly-H), 4.17 (t, 1 H, J = 3.2 Hz, CH); ¹³C NMR (100 MHz, C₆D₆): δ = 24.7 (CH₃), 27.2

(adamantly-C), 31.2 (adamantly-C), 34.1 (adamantly-C), 36.5 (adamantly-C), 37.8 (adamantly-C), 77.0 (CH), 82.4 ($\underline{\text{C}}(\text{CH}_3)_2$); ^{11}B NMR (128 MHz, CDCl_3): δ = 21.8.

8f: ^1H NMR (400 MHz, CDCl_3) δ = 1.26 (s, 6 H, CH_3), 1.29 (s, 6 H, CH_3), 1.53 (d, 3 H, J = 6.4 Hz, CH_3), 5.64 (q, 1 H, J = 6.4 Hz, CH), 7.19-7.23 (m, 1 H, ArH), 7.29-7.35 (m, 2 H, ArH), 7.66-7.69 (m, 1 H, 1 H, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.9 (CH_3), 24.6 (CH_3), 69.6 (CH), 82.9 ($\underline{\text{C}}(\text{CH}_3)_2$), 126.7 (CH), 127.1 (CH), 128.2 (CH), 129.2 (CH), 131.1 (C^q), 142.3 (C-Cl); ^{11}B NMR (128 MHz, CDCl_3): δ = 16.8.

8g: ^1H NMR (400 MHz, CDCl_3) δ = 1.21 (s, 6 H, CH_3), 1.24 (s, 6 H, CH_3), 1.48 (d, 3 H, J = 6.4 Hz, CH_3), 3.78 (s, 3 H, CH_3), 5.21 (q, 1 H, J = 6.4 Hz, CH), 6.85 (d, 2 H, J = 8.8 Hz, ArH), 7.29 (d, 2 H, J = 8.8 Hz, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.6 (CH_3), 24.7 (CH_3), 25.4 (CH_3), 55.3 (CH_3), 72.3 (CH), 82.7 ($\underline{\text{C}}(\text{CH}_3)_2$), 113.6 (CH), 126.7 (CH), 136.9 (C^q), 158.83 (C-O); ^{11}B NMR (128 MHz, CDCl_3): δ = 22.0.

8h: ^1H NMR (400 MHz, CDCl_3) δ = 1.26 (s, 12 H, CH_3), 6.26 (s, 1 H, CH), 7.25-7.47 (m, 10 H, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.6 (CH_3), 78.0 (CH), 83.0 ($\underline{\text{C}}(\text{CH}_3)_2$), 126.6 (CH), 127.4 (CH), 128.3 (CH), 143.2 (C^q); ^{11}B NMR (128 MHz, CDCl_3): δ = 22.5.

8i: ^1H NMR (400 MHz, CDCl_3) δ = 1.20 (s, 12 H, CH_3), 6.12 (s, 1 H, CH), 7.28 (s, 8 H, CH); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.6 (CH_3), 76.7 (CH), 83.3 ($\underline{\text{C}}(\text{CH}_3)_2$), 128.0 (CH), 128.6 (CH), 133.4 (C^q), 141.3 (C-Cl); ^{11}B NMR (128 MHz, CDCl_3): δ = 22.5.

8j: ^1H NMR (400 MHz, CDCl_3) δ = 1.25 (s, 12 H, CH_3), 2.35 (s, 6 H, CH_3), 6.19 (s, 1 H, CH), 7.15 (d, 4 H, J = 8 Hz, ArH), 7.31 (d, 4 H, J = 8 Hz, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 21.2 (CH_3), 24.6 (CH_3), 77.7 (CH), 83.0 ($\underline{\text{C}}(\text{CH}_3)_2$), 126.5 (CH), 129.0 (CH), 136.9 (C^q), 140.6 (C-Me); ^{11}B NMR (128 MHz, CDCl_3): δ = 22.4.

8k: ^1H NMR (400 MHz, CDCl_3) δ = 1.26 (s, 12 H, CH_3), 4.53 (q, 2 H, J = 1.4 Hz, CH_2), 6.24-6.31 (m, 1 H, CHCH), 6.61 (d, 1 H, J = 16 Hz, ArCH), 7.19-7.37 (m, 5 H, ArH);

^{13}C NMR (100 MHz, C_6D_6): δ = 24.7 (CH_3), 65.3 (CH_2), 83.0 ($\underline{\text{C}}(\text{CH}_3)_2$), 126.5 (CH), 126.9 (CH), 127.6 (CH), 128.6 (C^q), 130.7 ($\text{Ar}-\underline{\text{CH}}$), 136.9 ($\text{Ar}-\text{CH}\underline{\text{CH}}$); ^{11}B NMR (128 MHz, CDCl_3): δ = 22.3.

8l: ^1H NMR (400 MHz, CDCl_3) δ = 1.07 (s, 12 H, CH_3), 1.29-1.38 (m, 1 H, CH_2), 1.61-1.83 (m, 5 H, CH_2), 4.77-4.79 (m, 1 H, CH), 5.64-5.68 (m, 1 H, CH), 5.90-5.93 (m, 1 H, CH); ^{13}C NMR (100 MHz, C_6D_6): δ = 19.4 (CH_2), 24.7 (CH_3), 25.2 (CH_2), 31.4 (CH_2), 68.4 (CH), 82.4 ($\underline{\text{C}}(\text{CH}_3)_2$), 129.8 (CH), 130.1 (CH); ^{11}B NMR (128 MHz, CDCl_3): δ = 22.5.

8m: Mp: 140 °C. ^1H NMR (400 MHz, CDCl_3) δ = 1.29 (s, 24 H, CH_3), 6.98 (s, 4 H, CH); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.6 (CH_3), 83.5 ($\underline{\text{C}}(\text{CH}_3)_2$), 120.0 (CH), 149.0 ($\text{C}-\text{O}$); ^{11}B NMR (128 MHz, CDCl_3): δ = 21.7; HRMS (ESI): m/z calcd for $\text{C}_{18}\text{H}_{29}\text{B}_2\text{O}_6$: 363.2150 $[(M+H)]^+$; found: 363.2167.

10a: ^1H NMR (400 MHz, CDCl_3) δ = 0.88 (d, 6 H, J = 6.4 Hz, CH_3), 1.23 (s, 12 H, CH_3), 1.43 (q, 2 H, J = 6.6 Hz, CH_2), 1.69 (sept, 1 H, J = 6.8 Hz, CH), 3.85 (t, 2 H, J = 6.8 Hz, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 22.6 (CH_3), 24.6 (CH_3), 24.7 (CH), 40.4 (CH_2), 63.4 (CH_2), 82.7 ($\underline{\text{C}}(\text{CH}_3)_2$); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.1 (s).

10b: ^1H NMR (400 MHz, CDCl_3) δ = 0.89 (d, 6 H, J = 6.8 Hz, CH_3), 1.24 (s, 12 H, CH_3), 1.80 (sept, 1 H, J = 6.8 Hz, CH), 3.61 (d, 2 H, J = 6.4 Hz, CH_2); ^{13}C NMR (100 MHz, CDCl_3): δ = 18.9 (CH_3), 24.7 (CH_3), 29.9 (CH), 71.5 (CH_2), 82.7 ($\underline{\text{C}}(\text{CH}_3)_2$); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.0 (s).

10c: ^1H NMR (400 MHz, CDCl_3) δ = 1.25 (s, 12 H, CH_3), 4.92 (s, 2 H, CH_2), 7.22-7.33 (m, 5 H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.7 (CH_3), 66.7 (CH_2), 83.0 ($\underline{\text{C}}(\text{CH}_3)_2$), 126.8 (CH), 127.4 (CH), 128.3 (CH), 139.3 (C^q); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.4 (s).

10d: ^1H NMR (400 MHz, CDCl_3) δ = 1.22 (s, 12 H, CH_3), 4.93 (s, 2 H, CH_2), 7.40 (d, 2 H, J = 8.8 Hz, CH), 7.57 (d, 2 H, J = 8.4 Hz, CH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.5 (CH_3), 65.7 (CH_2), 83.2 ($\text{C}(\text{CH}_3)_2$), 111.1 ($\text{C}(\text{CN})$), 118.8 (CN), 126.8 (CH), 132.1 (CH), 144.6 (C^q); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.4 (s).

10e: ^1H NMR (400 MHz, CDCl_3) δ = 1.22 (s, 12 H, CH_3), 4.97 (s, 2 H, CH_2), 7.12-7.47 (m, 4 H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.7 (CH_3), 64.2 (CH_2), 83.2 ($\text{C}(\text{CH}_3)_2$), 126.8 (CH), 127.8 (CH), 128.4 (CH), 129.1 (CH), 132.0 (C^q), 136.9 (C-Cl); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.4 (s).

10f: ^1H NMR (400 MHz, CDCl_3) δ = 1.21 (s, 12 H, CH_3), 4.83 (s, 2 H, CH_2), 7.15-7.30 (m, 4 H, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.7 (CH_3), 66.0 (CH_2), 83.2 ($\text{C}(\text{CH}_3)_2$), 124.7 (CH), 126.9 (CH), 127.5 (CH), 129.6 (CH), 134.3 (C^q), 141.4 (C-Cl); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.4 (s).

10g: ^1H NMR (400 MHz, CDCl_3) δ = 1.20 (s, 12 H, CH_3), 2.86 (s, 6 H, $\text{N}(\text{CH}_3)_2$), 4.76 (s, 2 H, CH_2), 6.64 (d, 2 H, J = 8.4 Hz, ArH), 7.18 (d, 2 H, J = 8 Hz, ArH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.7 (CH_3), 40.7 (CH_3), 66.8 (CH_2), 82.7 ($\text{C}(\text{CH}_3)_2$), 112.4 (CH), 127.3 (C^q), 128.5 (CH), 150.2 (C-N); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.4 (s).

10h: ^1H NMR (400 MHz, CDCl_3) δ = 1.25 (s, 12 H, CH_3), 3.77 (s, 3 H, CH_3), 4.84 (s, 2 H, CH_2), 6.85 (d, 2 H, J = 8.8 Hz, CH), 7.27 (d, 2 H, J = 8.8 Hz, CH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.7 (CH_3), 66.5 (CH_2), 82.9 ($\text{C}(\text{CH}_3)_2$), 113.8 (CH), 128.6 (CH), 131.6 (C^q), 159.1 (C-O); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.3 (s).

10i: ^1H NMR (400 MHz, CDCl_3) δ = 1.25 (s, 24 H, CH_3), 4.91 (s, 4 H, CH_2), 7.31 (s, 4 H, CH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.6 (CH_3), 66.5 (CH_2), 82.9 ($\text{C}(\text{CH}_3)_2$), 126.7 (CH), 138.4 (C^q); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.4 (s).

10j: ^1H NMR (400 MHz, CDCl_3) δ = 1.20 (s, 6 H, CH_3), 1.23 (s, 6 H, CH_3), 1.25 (s, 12 H, CH_3), 1.47 (d, 3 H, J = 6.4 Hz, CH_3), 4.90 (s, 2 H, CH_2), 5.23 (q, 1 H, J = 6.4 Hz, CH), 7.29 (d, 2 H, J = 8.8 Hz, CH), 7.33 (d, 2 H, J = 8.4 Hz, CH); ^{13}C NMR (100 MHz, CDCl_3): δ = 24.54 (CH_3), 24.58 (CH_3), 25.4 (CH_3), 66.1 (CH_2), 72.4 (CH), 82.7 ($\text{C}(\text{CH}_3)_2$), 82.9 ($\text{C}(\text{CH}_3)_2$), 125.3 (CH), 126.7 (CH), 138.1 (C^q), 143.8 (C-O); ^{11}B NMR (128 MHz, C_6D_6): δ = 22.3 (s); HRMS (ESI): m/z calcd for $\text{C}_{21}\text{H}_{35}\text{B}_2\text{O}_6$: 405.2620 $[(M+H)]^+$; found: 405.2655.

Synthesis of compound J: Acetophenone **7a** (6.3 μL , 0.054 mmol) was added into a C_6D_6 (0.5 mL) solution of 1,3,2,5-diazadiborinine **C** (0.020 g, 0.054 mmol) at room temperature. The reaction occurred immediately as monitored by NMR spectroscopy. After removal of all volatiles, the solid residue was recrystallized from a benzene/hexane mixed solution to afford colorless crystals of **J** (0.025 g, 95%).

Mp: 212 $^\circ\text{C}$. ^1H NMR (400 MHz, C_6D_6): δ = 0.67 (s, 3 H, CH_3), 0.73 (s, 3 H, CH_3), 0.95 (s, 3 H, CH_3), 0.99 (s, 3 H, CH_3), 1.80 (s, 3 H, CH_3), 3.22 (d, 1 H, J = 8.4 Hz, CH_2), 3.35 (d, 1 H, J = 8.4 Hz, CH_2), 3.44 (d, 1 H, J = 8.8 Hz, CH_2), 3.62 (d, 1 H, J = 8.8 Hz, CH_2), 7.04 - 8.8.31 (m, 15 H, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 25.0 (CH_3), 26.2 (CH_3), 28.0 (CH_3), 28.5 (CH_3), 29.9 (CH_3), 64.0 ($\text{C}(\text{CH}_3)_2$), 65.0 ($\text{C}(\text{CH}_3)_2$), 83.95 (CH_2), 84.02 (CH_2), 124.9 (CH), 126.2 (CH), 126.6 (CH), 126.98 (CH), 127.02 (CH), 127.9 (C_q), 128.1 (CH), 135.9 (CH), 152.3 (B-C-O); DEPT - 135 NMR (100 MHz, C_6D_6): δ = 25.0 (CH_3), 26.2 (CH_3), 28.0 (CH_3), 28.5 (CH_3), 29.9 (CH_3), 124.9 (CH), 126.2 (CH), 126.6 (CH), 126.98 (CH), 127.03 (CH), 128.2 (CH), 128.4 (CH), 135.9 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): δ = -13.6 (s), 2.8 (s). HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{35}\text{B}_2\text{N}_2\text{O}_3$: 493.2834 $[(M+H)]^+$; found: 493.2850.

2-PhOx-HBpin: Mp: 63 °C. ^1H NMR (400 MHz, C_6D_6): δ = 0.98 (s, 6 H, CH_3), 1.02 (s, 6 H, CH_3), 1.41 (s, 3 H, CH_3), 1.44 (s, 3 H, CH_3), 3.50-3.55 (m, 2 H, CH_2), 6.31 (s, 1 H, CH), 7.13 (m, 1 H, ArH), 7.23 (t, 2 H, J = 7.6 Hz, ArH), 7.64 (d, 2 H, J = 7.6 Hz, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 24.1 (CH_3), 24.9 (CH_3), 26.7 (CH_3), 27.4 (CH_3), 59.1 ($\text{C}(\text{CH}_3)_2$), 78.4 (CH_2), 81.9 ($\text{C}(\text{CH}_3)_2$), 92.1 (CH), 127.4 (CH), 143.2 (CH); DEPT - 135 NMR (100 MHz, C_6D_6): δ = 24.1 (CH_3), 24.9 (CH_3), 26.7 (CH_3), 27.4 (CH_3), 92.1 (CH), 127.4 (CH), 128.05 (CH), 128.14 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): δ = 23.5 (s); HRMS (ESI): m/z calcd for $\text{C}_{17}\text{H}_{27}\text{BNO}_3$: 304.2084 $[(M+H)]^+$; found: 304.2081.

Synthesis of *N*-MeOx BPh₃: A hexane solution (2.5 M) of $n\text{BuLi}$ (2 ml, 5.00 mmol) was added dropwise into a THF solution (50 ml) of 4,4-dimethyl-2-oxazoline (0.50 ml, 4.74 mmol) at -78°C . After stirring for 1 h at -78°C , triphenyl borane (1.15g, 4.74 mmol) was added into the solution. The reaction mixture was warmed to room temperature and stirred overnight. After the solvent was removed under vacuum, toluene (60 ml) was added and salts were filtered off, which was used directly for next step without further purification. Methyl trifluoromethanesulfonate (0.52 ml, 4.74 mmol) was added dropwise into the solution at room temperature and stirred overnight. The solvent was removed under vacuum, and the solid residue was washed with toluene and hexane to afford colorless powder of *N*-MeOx BPh₃ (0.89 g, 53%). Melting point (Mp): 192°C . ^1H NMR (400 MHz, C_6D_6): δ = 0.25 (s, 6 H, CH_3), 2.10 (s, 3 H, NCH_3), 3.19 (s, 2 H, CH_2), 7.23 (t, 3 H, J = 7.4 Hz, ArH), 7.38 (t, 6 H, J = 7.4 Hz, ArH), 7.64 (d, 6 H, J = 7.2 Hz, ArH); ^{13}C NMR (100 MHz, C_6D_6): δ = 23.2 (CH_3), 29.4 (NCH_3), 63.8 ($\text{C}(\text{CH}_3)_2$), 79.9 (CH_2), 124.9 (CH), 127.5 (CH), 135.3 (CH); ^{11}B NMR (76.8 MHz, C_6D_6): δ = -8.9 (s); HRMS (ESI): m/z calculated for $\text{C}_{24}\text{H}_{27}\text{BNO}$: 356.2186 $[(M+H)]^+$; found: 356.2198.

K: Mp: 173°C . ^1H NMR (400 MHz, D-THF): δ = 0.35 (s, 3 H, BCH_3), 0.61 (s, 12 H, CH_3), 3.93 (d, 2 H, J = 8.8 Hz, CH_2), 3.95 (d, 2 H, J = 8.4 Hz, CH_2), 7.01-7.91 (m, 15

H, ArH); ^{13}C NMR (100 MHz, D-THF): δ = 25.6 (CH_3), 25.7 (CH_3), 68.0 ($\text{C}(\text{CH}_3)_2$), 81.8 (CH_2), 125.4 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.9 (CH), 128.0 (CH), 133.4 (CH), 135.2 (CH), 135.4 (CH); DEPT - 135 NMR (100 MHz, D-THF): δ = 25.6 (CH_3), 25.7 (CH_3), 125.4 (CH), 127.3 (CH), 127.4 (CH), 127.5 (CH), 127.9 (CH), 128.0 (CH), 133.4 (CH), 135.2 (CH), 135.4 (CH); ^{11}B NMR (76.8 MHz, D-THF): = -19.29 (s), -0.78 (s). HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{B}_2\text{N}_2\text{O}_2$: 465.2885 $[(\text{M}+\text{H})]^+$; found: 465.2896.

Attempt of catalytic hydrosilylation of acetophenone **7a:** 1,3,2,5-Diazadiborinine **C** (0.00538 mmol: 2 mol %), acetophenone **7a** (31 μ L, 0.269 mmol), triethoxysilane (50 μ L, 0.269 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. However, after 2 hours, no reaction was confirmed.

Figure 5.14. ¹H NMR (CD₃CN) spectrum of a mixture of acetophenone **7a** and (EtO)₃SiH after 2 hours at ambient temperature.

Stoichiometric reaction between J and pinacolborane (HBpin): Compound **J** (0.026 g, 0.0538 mmol), HBpin (8 μ L, 0.0538 mmol) and C₆D₆ (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 3 hours at room temperature, no reaction was confirmed.

Figure 5.15 ¹H NMR (C₆D₆) spectrum of a mixture of **J** and HBpin (1.0 eq) after 3 hours at ambient temperature.

Reaction of J, HBpin and acetophenone: Acetophenone **7a** (6 μ L, 0.0538 mmol) was added to a C_6D_6 (0.5 mL) solution of compound **J** (0.026 g, 0.0538 mmol) and HBpin (16 μ L, 0.108 mmol in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 60 minutes, a quantitative formation of product **8a** was confirmed while **J** was unchanged.

Figure 5.16 1H NMR (C_6D_6) spectrum of a reaction mixture of **J**, **7a** (1 eq) and HBpin (2 eq) after 60 minutes at ambient temperature, indicating a quantitative formation of **8a**.

Reaction among J, HBpin and 4'-methoxyacetophenone 7g: Compound **J** (0.013 g, 0.0269 mmol), HBpin (12 μ L, 0.0807 mmol), 4'-methoxyacetophenone **7g** (5.5 μ L, 0.0404 mmol) and C₆D₆ (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 50 minutes at room temperature, a quantitative formation of **8g** was confirmed.

Figure 5.17 ¹H NMR (C₆D₆) spectrum of a reaction mixture of **J**, **7g** (1 eq) and HBpin (2 eq) after 50 minutes at ambient temperature, indicating a quantitative formation of **8g**.

Reaction among triphenyl borane (Ph₃B), HBpin and acetophenone **7a:** Triphenyl borane (Ph₃B) (0.032 g, 0.134 mmol), HBpin (19.4 μ L, 0.134 mmol), acetophenone **7a** (15.7 μ L, 0.134 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 12 hours at room temperature, no formation of **8a** was observed.

Figure 5.18 ¹H NMR (CD₃CN) spectrum of a reaction mixture of Ph₃B (1 eq), **7a** (1 eq) and HBpin (1 eq) after 12 hours at ambient temperature.

Reaction among tris(pentafluorophenyl)borane, HBpin and acetophenone 7a:

Tris(pentafluorophenyl)borane (0.068 g, 0.134 mmol), HBpin (19.4 μ L, 0.134 mmol), acetophenone **7a** (15.7 μ L, 0.134 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 12 hours at room temperature, no formation of **8a** was observed.

Figure 5.19 ¹H NMR (CD₃CN) spectrum of a reaction mixture of tris(pentafluorophenyl)borane (1 eq), **7a** (1 eq) and HBpin (1 eq) after 12 hours at ambient temperature.

Reaction among 1-Methylindole-2-boronic acid MIDA ester (MIDA), HBpin and acetophenone 7a: 1-Methylindole-2-boronic acid MIDA ester (**MIDA**) (0.0192 g, 0.0670 mmol), HBpin (9.7 μ L, 0.0670 mmol), acetophenone **7a** (7.8 μ L, 0.0670 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 12 hours at room temperature, no formation of **8a** was observed.

Figure 5.20 ¹H NMR (CD₃CN) spectrum of a reaction mixture of **MIDA** (1 eq), **7a** (1 eq) and HBpin (1 eq) after 12 hours at ambient temperature.

Reaction among [2-Ph-*N*-MeOx]OTf, HBpin and acetophenone **7a:** [2-Ph-*N*-MeOx]OTf (0.045 g, 0.134 mmol), HBpin (19.4 μ L, 0.134 mmol), acetophenone **7a** (15.7 μ L, 0.134 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 12 hours at room temperature, no formation of **8a** was observed.

Figure 5.21 ¹H NMR (CD₃CN) spectrum of a reaction mixture of [2-Ph-*N*-MeOx]OTf (1 eq), **7a** (1 eq) and HBpin (1 eq) after 12 hours at ambient temperature.

Reaction among 2-PhOx, triphenyl borane (Ph₃B), HBpin and acetophenone 7a: 2-PhOx (11.3 μ L, 0.067 mmol), triphenyl borane (Ph₃B) (16.2 mg, 0.067 mmol), HBpin (9.7 μ L, 0.067 mmol), acetophenone **7a** (7.8 μ L, 0.067 mmol) and CDCl₃ (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 5 hours at room temperature, the formation of **2-PhOx-HBpin** was confirmed.

Figure 5.22 ¹H NMR (CD₃CN) spectrum of a reaction mixture of **2-PhOx** (1eq), Ph₃B (1eq), **7a** (1eq) and HBpin (1eq) after 5 hours at ambient temperature.

Reaction among *N*-MeOx-BPh₃, HBpin and acetophenone **7a:** *N*-MeOx-BPh₃ (0.0476 g, 0.134 mmol), HBpin (19.4 μ L, 0.134 mmol), acetophenone **7a** (15.7 μ L, 0.134 mmol) and CDCl₃ (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 48 hours at room temperature, the formation of **8a** (12% yield) was confirmed.

Figure 5.23 ¹H NMR (CDCl₃) spectrum of a reaction mixture of *N*-MeOx-BPh₃ (1 eq), **7a** (1 eq) and HBpin (1 eq) after 48 hours at ambient temperature.

Catalytic hydroboration of acetophenone **7a and HBpin with 2 mol % of *N*-MeOx-BPh₃:** *N*-MeOx-BPh₃ (0.0019 g, 0.00538 mmol), HBpin (39 μ L, 0.269 mmol), acetophenone **7a** (31.4 μ L, 0.269 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 12 hours at room temperature, the formation of **8a** (6% yield) was confirmed.

Figure 5.24 ¹H NMR (CD₃CN) spectrum of a reaction mixture of *N*-MeOx-BPh₃ (2 mol %), **7a** (1 eq) and HBpin (1 eq) after 12 hours at ambient temperature.

Catalytic hydroboration of acetophenone **7a and HBpin with 2 mol % of **K**:**
 Compound **K** (0.0025 g, 0.00538 mmol), HBpin (39 μ L, 0.269 mmol), acetophenone **7a** (31.4 μ L, 0.269 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 30 minutes at room temperature, the formation of **8a** (97% yield) was confirmed.

Figure 5.25 ¹H NMR (CD₃CN) spectrum of a reaction mixture of **K** (2 mol %), **7a** (1 eq) and HBpin (1 eq) after 30 minutes at ambient temperature.

Reaction among NDI, HBpin and acetophenone 7a: Compound **NDI** (0.005 g, 0.012 mmol), HBpin (1.8 μ L, 0.012 mmol), acetophenone **7a** (1.4 μ L, 0.012 mmol) and CDCl_3 (2.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 12 hours at room temperature, no formation of **8a** was observed.

Figure 5.26 ^1H NMR (CDCl_3) spectrum of a reaction mixture of **NDI** (1 eq), **7a** (1 eq) and HBpin (1 eq) after 12 hours at ambient temperature.

Reaction between G and acetophenone 7a: Compound **G** (0.020 g, 0.050 mmol), acetophenone **7a** (5.8 μ L, 0.050 mmol) and C₆D₆ (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction is monitored by NMR spectroscopy. After 12 hours at room temperature, no reaction was observed.

Figure 5.27 ¹H NMR (C₆D₆) spectrum of a reaction mixture of **G** (1 eq) and **7a** (1 eq) after 12 hours at ambient temperature.

Catalytic hydroboration of acetophenone **7a with 2 mol % of **G**:** Compound **G** (0.0022 g, 0.00538 mmol), HBpin (39 μ L, 0.269 mmol), acetophenone **7a** (31 μ L, 0.269 mmol) and CD₃CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction was monitored by NMR spectroscopy. After 10 hours at room temperature, the formation of **8a** (95% yield) was confirmed.

Figure 5.28 ¹H NMR (CD₃CN) spectrum after 10 hours.

Figure 5.29 ^{11}B NMR (CD_3CN) spectrum after 10 hours.

Catalytic hydroboration of benzophenone **7h with 2 mol % of **G**:** Compound **G** (0.0022 g, 0.00538 mmol), HBpin (39 μL , 0.269 mmol), benzophenone **7h** (0.049 g, 0.269 mmol) and CD_3CN (0.5 mL) were loaded in a dried J-Young Tube under an argon atmosphere. The tube was sealed, shaken and the reaction was monitored by NMR spectroscopy. After 21 hours at room temperature, the formation of **8h** (93% yield) was confirmed.

Figure 5.30 ^1H NMR (CD_3CN) spectrum after 21 hours.

Figure 5.31 ^{11}B NMR (CD_3CN) spectrum after 21 hours.

7.4.2 NMR Spectra

Figure 5.32 ¹H NMR spectrum of **J**.

Figure 5.33 ¹¹B NMR spectrum of **J**.

Figure 5.34 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **J**.

Figure 5.35 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **J**.

Figure 5.36 ¹H NMR spectrum of **8a'**.

Figure 5.37 ¹¹B NMR spectrum of **8a'**.

Figure 5.38 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8a'**.

Figure 5.39 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **8a'**.

Figure 5.40 ^1H NMR spectrum of **8m**.

Figure 5.41 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **8m**.

Figure 5.42 ^{11}B NMR spectrum of **8m**.

Figure 5.43 ^1H NMR spectrum of **10j**.

Figure 5.44 ^{11}B NMR spectrum of **10j**.

Figure 5.45 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **10j**.

Figure 5.46 ¹H NMR spectrum of 2-PhOx-HBpin.

Figure 5.47 ¹¹B NMR spectrum of 2-PhOx-HBpin.

Figure 5.48 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **2-PhOx-HBpin**.

Figure 5.49 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **2-PhOx-HBpin**.

Figure 5.50 ¹H NMR spectrum of N-MeOxBPh₃.

Figure 5.51 ¹¹B NMR spectrum of N-MeOxBPh₃.

Figure 5.52 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of N-MeOxBPh₃.

Figure 5.53 ^1H NMR spectrum of K.

Figure 5.54 ^{11}B NMR spectrum of K.

Figure 5.55 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of K.

Figure 5.56 $^{13}\text{C}\{^1\text{H}\}$ NMR (DEPT-135) spectrum of **K**.

5.4.3 Crystal Structure Determination of Compound **J**

X-ray data collection and structural refinement. Intensity data for compound **J** was collected using a Bruker APEX II diffractometer. The crystal of **J** was measured at 103(2) K. The structure was solved by direct phase determination (SHELXS-97)^[10] and refined for all data by full-matrix least squares methods on F^2 .^[11] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1523108 contains the supplementary crystallographic data for this thesis. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 5.5 Summary of Data Collection and Structure Refinement.

	J
Formula	C ₃₀ H ₃₄ B ₂ N ₂ O ₃
Fw	492.21
cryst syst	monoclinic
space group	<i>P 1 2/n 1</i>
Size (mm ³)	0.200 x 0.220 x 0.420
T, K	103(2)
<i>a</i> , Å	16.4107(13)
<i>b</i> , Å	8.5374(7)
<i>c</i> , Å	19.6484(15)
<i>a</i> , deg	90°
<i>b</i> , deg	111.541(2)°
<i>g</i> , deg	90°
<i>V</i> , Å ³	2560.6(4)
<i>Z</i>	4
<i>d</i> _{calcd} g·cm ⁻³	1.277
<i>m</i> , mm ⁻¹	0.081
Refl collected	37706
<i>T</i> _{min} / <i>T</i> _{max}	0.9670/0.9840
<i>N</i> _{measd}	6629
[<i>R</i> _{int}]	0.0970
<i>R</i> [<i>I</i> >2sigma(<i>I</i>)]	0.0536
<i>R</i> _w [<i>I</i> >2sigma(<i>I</i>)]	0.1326

GOF	1.028
Largest diff peak/hole[e·Å ⁻³]	0.364/-0.305

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Chapter 6

Generation of a Nucleophilic Boron

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6.1 Introduction

Owing to the vacant p orbital on the central boron atom, trivalent boron compounds are well regarded as electrophiles.^[1] Synthesis of nucleophilic organoboron compounds is highly challenging due to its poor stability and limited synthetic methods (Figure 6.1).^[2-10] To date, only three methods have been used for the synthesis of the nucleophilic organoboron anions: (i) two-electron B-X bond reduction of haloboranes, (ii) deprotonation of four-coordinated borate species, (iii) heterolytic B-B bond.^[2-9]

Figure 6.1 Anionic boron nucleophiles.

In 2006, the Nozaki and Yamashita group first isolated boryllithium **1**, which created a new prospect on nucleophilic organoboron chemistry.^[2] Reduction of

bromoborane **10** by a combination of lithium powder and naphthalene in THF at $-45\text{ }^{\circ}\text{C}$ afforded the boryllithium **1** (Scheme 6.1). **1** could be used as a nucleophilic boron species, which allows the formation of new boron-element bonds.^[11] The same method was also employed to prepare boryllithium **7** by the Kinjo group.^[7] Later, the Braunschweig group reported that the reduction of a transition-metal-bound B-X moiety in **11** generated the corresponding linear anionic dimetalloborylene complex **2** (Scheme 6.2).^[3a]

Scheme 6.1 Synthesis of boryllithium **1**.

Scheme 6.2 Synthesis of the linear anionic dimetalloborylene complex **2**.

Taking advantage of the ability of N-heterocyclic carbenes (NHCs) to stabilize low-valent boron-containing species,^[12] the Braunschweig group introduced NHCs to stabilize low-valent boryl anion **3**. Treatment of **12** with an excess of KC_8 in Et_2O gave the NHCs stabilized borole anion **3** (Scheme 6.3).^[3b] Similarly, NHCs supported boryl anion **4** was generated and trapped by electrophiles.^[4] The Willner group and Finze group independently reported the synthesis of boryl dianion **5** by reduction of $\text{K}[\text{B}(\text{CN})_4]$ or deprotonation of $\text{K}[\text{HB}(\text{CN})_3]$, respectively (Scheme 6.4).^[5]

Scheme 6.3 Synthesis of NHCs stabilized borole anion **3**.

Scheme 6.4 Synthesis of dianion **5**.

Compared with NHCs, cyclic (alkyl)(amino)carbenes (CAACs) are more nucleophilic (σ donating) and electrophilic (π accepting).^[13] The synthesis of CAAC-supported boryl anion was achieved by deprotonation of a neutral borohydride. Treatment of **15** with KHMDS in THF led to boryl anion **6** (Scheme 6.5).^[6] Employed with the same method, deprotonation of **16** with n BuLi at -78 °C afforded boryl anion **9** (Scheme 6.6).^[9] Besides reduction and deprotonation reactions, heterolytic cleavage of the B-B bond in $B_2(\text{pin})_2$ has also been developed recently for the synthesis of isolable nucleophilic boron species (Scheme 6.7).^[8] Treatment of β -diketiminato magnesium n butyl derivative **17** with $B_2\text{pin}_2$ furnished compound **18**. Subsequent addition of 4-(dimethylamino)pyridine (DMAP) to the solution of **18** afforded magnesium-bound boryl anion **8**. Until now, only those three methods for the synthesis of nucleophilic organoboron anions are known and thus limited. Another methodology, which is used to synthesize anionic boron, can be developed.

Scheme 6.5 Synthesis of boryl anion **6**.

Scheme 6.6 Synthesis of boryl anion **9**.

Scheme 6.7 Synthesis of magnesium-bound boryl anion **8**.

6.2 Results and discussions

In chapter 3, we have shown that 1,3,2,5-diazadiborinine **C** features both nucleophilic (between two carbon atoms) and electrophilic (between two nitrogen atoms) boron centers, which can cooperatively activate carbon dioxide, alkenes and alkyne without any catalysts. It prompted us to investigate the reaction between **C** and nucleophiles, as the electrophilic boron center in **C** could be attacked by nucleophiles.

Due to the isoelectronic and isosteric relationship between the C=C and B-N units, azaborinine (BNC₄) and diazadiborinine (B₂N₂C₂) are regarded as hybrid organic/inorganic benzenes.^[14] If the boron atom in the aromatic azaborinine or diazadiborinine has a good leaving group, functionalization of azaborinine and diazadiborinine by nucleophilic substitution reaction at the boron atom can be easily achieved.^[14] While the absence of a leaving group at the boron atom, it leads to form an ionic species, which is regarded as a Janovsky complex analogs (Scheme 6.8).^[15] In this chapter, we present the synthesis of the nucleophilic organoboron anions by the nucleophilic reactions (Scheme 6.9).

Scheme 6.8 The isoelectronic relationship between inorganic Janovsky complex and Janovsky complex.

Scheme 6.9 Synthesis of the nucleophilic organoboron anions by the nucleophilic reaction.

Treatment of **C** with phenyl lithium (PhLi) in a deuterated tetrahydrofuran (THF- d_8) afforded a red solution of **K** immediately (Scheme 6.10). In the ^{11}B NMR spectrum, two new signals were detected at -0.5 ppm and -3.2 ppm, both of which were shifted upfield compared with those of **C** (7.3 ppm and 24.9 ppm). After the removal of solvent, **K** was isolated as a red powder in 72% yield. Single crystals of **K** were obtained from a concentrated solution of THF at -10 °C, and the solid-state structure was confirmed by X-ray diffraction analysis (Figure 6.2a). **K** exhibits an ionic structure with a cationic lithium coordinated by four THF molecules, in which the closest distance between the cationic and anionic fragments is 5.471 Å, indicating no interaction between them. The central $\text{B}_2\text{C}_2\text{N}_2$ six-membered ring in the anionic moiety of **K** displays nearly co-planar geometry. Upon nucleophilic attack of PhLi to the Lewis acidic B1 atom in **C**, the B1 atom in **K** is tetra-coordinated with two nitrogen atoms (N1, N2) and two Ph groups. The B2 atom is tri-coordinated with C2, C3 and C4 atoms with the sum of the bond angles of 359.9° , indicative of a characteristic sp^2 hybridization.

Scheme 6.10 Synthesis of **K/K'**.

Both B1-N2 (1.564(5) Å) and B1-N1 (1.574(6) Å) distances are longer than that (1.443(3) Å) in **C**, whereas the distances of N1-C17 (1.358(5) Å) and N2-C18 (1.356(5) Å) bonds are shorter than (1.374(3) Å) in **C**. Significantly, the B2-C18 (1.485(7) Å) and B2-C17 (1.492(6) Å) distances are close to the corresponding bonds of **C** (1.483(3) Å) and lie between typical boron-carbon single and double bonds,^[16] which suggests the delocalization of π -electron over the C2-B2-C4 moiety in **K**. The optimized geometry of **K** at the B3LYP/6-311+(d,p) level of theory is in good agreement with experimental structural parameters. The HOMO of **K** is mainly a π -type orbital over the C17-B2-C18 moiety with some contribution from the N and O lone pairs (Figure 6.2b). Wiberg bond index values of the B2-C17 bonds (1.21) and the B2-C18 bonds (1.21) are large than 1, indicative of the partial double-bond character of these bonds. To the best of our knowledge, **K** is the first isolated Janovsky complex analogue derived from diazadiborinine.^[17]

a)

b)

Figure 6.2 (a) The solid-state structure of **K** (all hydrogen atoms and the counterion are omitted for clarity). (b) The plot of the HOMO of **K**.

With isolable ionic species **K** in hand, we examined its nucleophilic ability, because the electronic property of the C2-B2-C4 moiety in **K** was similar to that in recently reported borylene species,^[10] many of which exhibit nucleophilic nature owing to its electron richness.^{[10a][10b][10h][10i]} To confirm the reactivity of **K** as a boron-centered nucleophile, we carried out the reaction of **K** with methyl iodide (MeI). Treatment of **K** with a slight excess amount of MeI in THF-*d*₈ solution afforded **L** in 76% yield (Scheme 6.11). X-ray diffraction study of **L** confirmed that the methyl group was bound to the B2 atom in **L**, demonstrating the nucleophilic nature of **K** (Figure 6.3). Note an electron-transfer mechanism involving the radical intermediate can not be ruled out for the formation of **L**.^[18]

A mixture of one equivalent of Cy₃PAuCl with **K** in THF-*d*₈ at room temperature gave **M** in 65% yield after work up (Scheme 6.11). The ¹¹B NMR spectrum of **M** displays two singlets at –0.4 ppm and –11.6 ppm, which are assigned to the boron atom between two nitrogen atoms and the boron atom bound to the Au atom, respectively. The X-ray diffraction analysis of **M** reveals the formation of a B2-Au1 bond with the bond distance of 2.204(5) Å, which is nearly similar to that 2.166(14) Å in L₂PhB:→AuCl (L = oxazol-2-ylidene) (Figure 6.4).^{[19][20]} The P1-Au1-B2 angle is 175.9° and the P1-Au1 distance is 2.3287(13) Å, which is a slightly longer than typical P-Au bonds (2.23–2.30 Å).^[21]

Scheme 6.11 Reactions of **K** with MeI and Cy₃PAuCl.

Figure 6.3 Solid-state structure of **L** (all hydrogen atoms except for those on C3 are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

Figure 6.4 Solid-state structure of **M** (all hydrogen atoms are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

To examine the scope of nucleophiles, we further explored the nucleophilic reaction of **K** with sp and sp^3 hybridized carbanions (Scheme 6.12). Treatment of **K** with a slight excess amount of methyl lithium (MeLi) in THF- d_8 afforded a red solution immediately. Subsequent addition of two equivalents of 12-crown-4 ether afforded **N** as red crystals in 77% yield, which displayed two signals at 0.5 ppm and -1.3 ppm in the ^{11}B NMR spectrum. The solid-state structure of **N** reveals an ionic structure involving a cationic lithium coordinated by two 12-crown-4 ether molecules. The B1 atom is tetra-coordinated with two nitrogen atoms (N1, N2), one Ph group and one Me group. By using the same synthetic method with (phenylethynyl)lithium ($\text{PhC}\equiv\text{CLi}$), **O** was isolated in 80% yield, which displays two signals at -0.4 ppm and -3.9 ppm in the ^{11}B NMR spectrum (Scheme 6.12). The $\text{PhC}\equiv\text{C}$ moiety coordinates to the B1 atom, which is confirmed by the solid-state structure (Figure 5.6). Moreover, 2-lithio-1-methylimidazolidine was introduced to **C**, and the corresponding **P** was obtained in 82%

yield (Scheme 6.12), which was confirmed by X-ray diffraction analysis (Figure 6.7). Although sp , sp^2 or sp^3 hybridized carbanions reacted with **C**, the reactions of **C** with MeMgI, Me₂NLi, NaN₃, CsF, ^tBuLi, ^tBuONa did not produce the corresponding anionic species. This may be due to a combination of factors such as steric (for ^tBu groups), stability of cationic species (for those involving Mg²⁺, Cs⁺) and poor nucleophilicity (NaN₃, Me₂NLi).

Scheme 6.12 Synthesis of **N**, **O** and **P**.

Figure 6.5 Solid-state structure of **N** (all hydrogen atoms except for those on C1 and counterions are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

Figure 6.6 Solid-state structure of **O** (all hydrogen atoms and counterions are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

Figure 6.7 Solid-state structure of **P** (all hydrogen atoms and counterions are omitted for clarity). Thermal ellipsoids are set at the 50% probability level.

6.3 Conclusion

In summary, the addition reaction of a series of sp , sp^2 and sp^3 hybridized carbanions (PhLi, MeLi, PhC $\equiv$ CLi and 2-lithio-1-methylimidazolidine) to diazadiborinine **C** affords isolable ionic species **K**, **N-P**, which can be regarded as Janovsky-type complexes. X-ray diffraction and computational studies of **K** reveals the delocalization of π -electrons over the C-B-C moiety in the central B₂N₂C₂ six-membered ring. **K** as a boron-center nucleophile could react with MeI and Cy₃PAuCl to generate **L** and **M**, respectively.

6.4 Experimental section

6.4.1 Synthesis, physical and spectroscopic data for all new compounds

General considerations: All reactions were performed under an atmosphere of dry argon using standard Schlenk or dry box techniques; solvents were dried over Na metal, K metal or CaH₂, and distilled under nitrogen. Reagents were of analytical grade, obtained from commercial suppliers and used without further purification. ¹H, ¹³C, ¹¹B and ³¹P NMR spectra were recorded on a Bruker AVIII 400 MHz or Bruker AV 400 MHz, spectrometers at 298 K. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, m = multiplet. Coupling constants *J* are given in Hz. In the ¹³C NMR spectra of compounds **K**, **L**, **M**, **N**, **O**, **P** signals for the carbon atoms directly bonding to the boron atom could not be observed, presumable due to the coupling with the boron atom. Electrospray ionization (ESI) mass spectra were obtained at the Mass Spectrometry Laboratory at the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with OptiMelt apparatus (Stanford Research System).

Compound K/K': Phenyl lithium (0.007 g, 0.081 mmol) was added into a THF-*d*₈ (0.45 mL) solution of 1,3,2,5-diazadiborinine **C** (0.025 g, 0.067 mmol) in a J-Young NMR tube at room temperature. The tube was sealed, shaken and the reaction was monitored by NMR spectroscopy, which indicated the formation of **K** (0.036 g, 72% yield) (Figure 5.8).^{*} Subsequently, 12-crown-4 ether (22 μL, 0.134 mmol) was added into the solution. After 2 hours, the red crystal generated was filtered off, washed with THF (5 mL), and then dried under vacuum to afford **K'** as a red powder (0.038 g, 70% yield).

(*Single crystals of **K** suitable for X-ray diffraction analysis were obtained from a concentrated solution of THF at $-10\text{ }^{\circ}\text{C}$ without addition of 12-crown-4.)

M.p.: $125\text{ }^{\circ}\text{C}$ (dec.); ^1H NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 0.87$ (s, 12 H, CH_3), 3.67 (s, 32 H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.94 (s, 4 H, CH_2), 6.85-8.92 (m, 15 H, ArH); ^{13}C NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 26.1$ (CH_3), 62.1 ($\text{C}(\text{CH}_3)_2$), 70.6 ($\text{OCH}_2\text{CH}_2\text{O}$), 81.9 (CH_2), 125.3 ($\text{CH} \times 2$), 126.9 ($\text{CH} \times 4$), 127.2 ($\text{CH} \times 3$), 133.2 ($\text{CH} \times 2$); ^{13}C NMR (DEPT-135, 100 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 26.1$ (CH_3), 125.3 ($\text{CH} \times 2$), 126.9 ($\text{CH} \times 4$), 127.2 ($\text{CH} \times 3$), 133.2 ($\text{CH} \times 2$); 136.3 ($\text{CH} \times 4$); ^{11}B NMR (76.8 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = -0.9$ (s), 1.4 (s); HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{31}\text{B}_2\text{N}_2\text{O}_2$: 449.2572 [M] $^-$; found: 449.2589.

Figure 6.8 ^{11}B NMR ($\text{THF}-d_8$) spectrum of a mixture of **C** and **Phenyl lithium** after 2 hours at ambient temperature.

Compound L: Methyl iodide ($5\text{ }\mu\text{L}$, 0.081 mmol) was added into a $\text{THF}-d_8$ (0.45 mL) solution of **K** (0.031 g, 0.067 mmol) in a J-Young NMR tube at room temperature. The reaction occurred immediately as confirmed by NMR spectroscopy. After removal of all volatiles, the solid residue was recrystallized from a THF/hexane mixed solution to afford colorless crystals of **L** (0.024 g, 76% yield).

Mp: 173 °C. ^1H NMR (400 MHz, THF- d_8): δ = 0.35 (s, 3 H, BCH_3), 0.61 (s, 12 H, CH_3), 3.92-3.97 (m, 4 H, CH_2), 7.00-7.91 (m, 15 H, ArH); ^{13}C NMR (100 MHz, THF- d_8): δ = 25.6 (CH_3), 25.7 (CH_3), 68.0 ($\text{C}(\text{CH}_3)_2$), 81.8 (CH_2), 125.4 (CH x1), 127.3 (CH x1), 127.4 (CH x1), 127.5 (CH x2), 127.9 (CH x2), 128.0 (CH x2), 133.4 (CH x2), 135.2 (CH x2), 135.4 (CH x2); ^{13}C NMR (DEPT-135, 100 MHz, THF- d_8): δ = 25.6 (CH_3), 25.7 (CH_3), 125.4 (CH x1), 127.3 (CH x1), 127.4 (CH x1), 127.5 (CH x2), 127.9 (CH x2), 128.0 (CH x2), 133.4 (CH x2), 135.2 (CH x2), 135.4 (CH x2); ^{11}B NMR (76.8 MHz, THF- d_8): δ = -19.3 (s), -0.8 (s). HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{35}\text{B}_2\text{N}_2\text{O}_2$: 465.2885 $[(\text{M}+\text{H})]^+$; found: 465.2896.

Compound M: Cy_3PAuCl (0.034 g, 0.067 mmol) was added into a THF- d_8 (0.45 mL) solution of **K** (0.031 g, 0.067 mmol) in a J-Young NMR tube at room temperature. The reaction occurred immediately as confirmed by NMR spectroscopy. After removal of all volatiles, the solid residue was recrystallized from a THF/hexane mixed solution to afford colorless crystals of **M** (0.040 g, 65% yield).

M.p.: 175 °C (dec.); ^1H NMR (400 MHz, THF- d_8): δ = 0.64 (s, 6 H, CH_3), 0.66 (s, 6 H, CH_3), 1.26-2.11 (m, 33 H), 4.01-4.07 (m, 4 H, CH_2), 7.12-7.95 (m, 15 H, ArH); ^{13}C NMR (100 MHz, THF- d_8): δ = 25.2 (CH_3), 25.5 (CH_3), 26.7 (CH_2), 27.7 (CH_2), 27.8 (CH_2), 31.4 (CH_2), 33.4 (CH), 33.7 (CH), 69.0 ($\text{C}(\text{CH}_3)_2$), 82.1 (CH_2), 126.9 (CH x1), 127.6 (CH x2), 127.67 (CH x1), 127.70 (CH x1), 128.18 (CH x2), 128.20 (CH x2), 133.3 (CH x2), 135.1 (CH x2), 135.3 (CH x2); ^{13}C NMR (DEPT-135, 100 MHz, THF- d_8): δ = 25.2 (CH_3), 25.5 (CH_3), 33.4 (CH), 33.7 (CH), 126.9 (CH x1), 127.6 (CH x2), 127.68 (CH x1), 127.70 (CH x1), 128.19 (CH x2), 128.21 (CH x2), 133.3 (CH x2), 135.1 (CH x2), 135.3 (CH x2); ^{11}B NMR (76.8 MHz, THF- d_8): δ = -11.6 (s), -0.4 (s);

^{31}P NMR (162 MHz, CDCl_3): $\delta = 53.3$ (s); HRMS (ESI): m/z calcd for $\text{C}_{46}\text{H}_{65}\text{AuB}_2\text{N}_2\text{O}_2\text{P}$: 927.4635 $[(M+H)]^+$; found: 927.4644.

Compound N: By following the procedure for the synthesis of **K'**, the reaction of **C** with the **methyl lithium** solution afforded **N** as a red powder (0.039 g, 77 % yield).

M.p.: 110 °C (dec.); ^1H NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$) $\delta = 0.96$ (s, 3 H, BCH_3), 1.17 (s, 6 H, CH_3), 1.47 (s, 6 H, CH_3), 3.67 (s, 32 H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.87 (d, $J = 7.2$ Hz, 2 H, CH_2), 3.97 (d, $J = 7.2$ Hz, 2 H, CH_2), 6.80-8.84 (m, 10 H, ArH); ^{13}C NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 26.6$ (CH_3), 29.0 (CH_3), 61.3 ($\underline{\text{C}}(\text{CH}_3)_2$), 70.8 ($\text{OCH}_2\text{CH}_2\text{O}$), 82.0 (CH_2), 117.5 (CH x1), 124.8 (CH x1), 126.8 (CH x2), 127.2 (CH x2), 133.0 (CH x2), 133.8 (CH x2); ^{13}C NMR (DEPT-135, 100 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 26.6$ (CH_3), 29.0 (CH_3), 117.5 (CH x1), 124.8 (CH x1), 126.9 (CH x2), 127.2 (CH x2), 133.1 (CH x2), 133.8 (CH x2); ^{11}B NMR (76.8 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = -1.3$ (s), 0.5 (s); HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{29}\text{B}_2\text{N}_2\text{O}_2$: 387.2415 $[(M)]^-$; found: 387.2431.

Compound O: By following the procedure for the synthesis of **K'**, the reaction of **C** with **(phenylethynyl)lithium** afforded **O** as a red powder (0.045 g, 80 % yield).

M.p.: 166 °C (dec.); ^1H NMR (400 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 1.51$ (s, 6 H, CH_3), 1.86 (s, 6 H, CH_3), 3.67 (s, 32 H, $\text{OCH}_2\text{CH}_2\text{O}$), 3.93 (d, $J = 7.2$ Hz, 2 H, CH_2), 4.06 (d, $J = 7.2$ Hz, 2 H, CH_2), 6.85-8.84 (m, 15 H, ArH); ^{13}C NMR (100 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 26.3$ (CH_3), 27.5 (CH_3), 61.3 ($\underline{\text{C}}(\text{CH}_3)_2$), 70.8 ($\text{OCH}_2\text{CH}_2\text{O}$), 81.9 (CH_2), 118.2 (CH x1), 125.3 (CH x1), 127.0 (CH x1), 127.1 (CH x2), 127.3 (CH x2), 128.7 (C_q), 129.2 (CH x2), 131.7 (CH x2), 132.0 (C_q), 133.1 (CH x2), 133.8 (CH x2); ^{13}C NMR (DEPT-135, 100 MHz, $\text{C}_5\text{D}_5\text{N}$): $\delta = 26.3$ (CH_3), 27.5 (CH_3), 118.2 (CH x1), 125.3 (CH x1), 127.0 (CH x1), 127.1 (CH x2), 127.3 (CH x2), 129.2 (CH x2), 131.7 (CH x2), 133.1 (CH x2), 133.8

(CH x2); B NMR (76.8 MHz, C₅D₅N): $\delta = -3.9$ (s), -0.4 (s); HRMS (ESI): m/z calcd for C₃₀H₃₁B₂N₂O₂: 473.2572 [(*M*)]⁻; found: 473.2580.

Compound P: By following the procedure for the synthesis of **K'**, the reaction of **C** and **1-lithio-1-methylimidazolid** afforded **P** as a red powder (0.045 g, 82 % yield).

M.p.: 98 °C (dec.); ¹H NMR (400 MHz, C₅D₅N): $\delta = 0.85$ (s, 6 H, CH₃), 0.93 (s, 6 H, CH₃), 3.68 (s, 32 H, OCH₂CH₂O), 3.92-3.96 (m, 4 H, CH₂), 4.01 (s, 3 H, NCH₃), 6.88-8.93 (m, 12 H); ¹³C NMR (100 MHz, C₅D₅N): $\delta = 24.4$ (CH₃), 27.1 (CH₃), 36.6 (NCH₃), 62.1 (C(CH₃)₂), 70.6 (OCH₂CH₂O), 81.7 (CH₂), 118.3 (CH x1), 121.0 (CH x1), 125.2 (CH x1), 126.6 (CH x1), 126.7 (CH x1), 127.2 (CH x3), 128.3 (CH x1), 133.3 (CH x3); ¹³C NMR (DEPT-135, 100 MHz, C₅D₅N): $\delta = 24.4$ (CH₃), 27.1 (CH₃), 36.6 (NCH₃), 118.3 (CH x1), 121.0 (CH x1), 125.2 (CH x1), 126.6 (CH x1), 126.7 (CH x1), 127.3 (CH x3), 128.3 (CH x1), 133.3 (CH x3); ¹¹B NMR (76.8 MHz, C₅D₅N): $\delta = -1.8$ (s), -1.1 (s); HRMS (ESI): m/z calcd for C₂₆H₃₁B₂N₄O₂: 453.2633 [(*M*)]⁻; found: 453.2639.

6.4.2 NMR Spectrums

Figure 6.9 ¹H NMR spectrum of K.

Figure 6.10 ¹¹B NMR spectrum of K.

Figure 6.11 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of K.

Figure 6.12 DEPT-135 $\{^1\text{H}\}$ NMR spectrum of K.

Figure 6.13 ¹H NMR spectrum of L.

Figure 6.14 ¹¹B NMR spectrum of L.

Figure 6.15 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **L**.

Figure 6.16 DEPT-135 $\{^1\text{H}\}$ NMR spectrum of **L**.

Figure 6.17 ^1H NMR spectrum of **M**.

Figure 6.18 ^{11}B NMR spectrum of **M**.

Figure 6.19 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **M**.

Figure 6.20 DEPT-135 $\{^1\text{H}\}$ NMR spectrum of **M**.

Figure 6.21 ^{31}P NMR spectrum of **M**.

Figure 6.22 ^1H NMR spectrum of **N**.

Figure 6.23 ^{11}B NMR spectrum of N.

Figure 6.24 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of N.

Figure 6.25 DEPT-135 $\{^1\text{H}\}$ NMR spectrum of N.

Figure 6.26 ^1H NMR spectrum of O.

Figure 6.27 ^{11}B NMR spectrum of **O**.

Figure 6.28 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **O**.

Figure 6.29 DEPT-135 NMR { ^1H }NMR spectrum of O.

Figure 6.30 ^1H NMR spectrum of P.

Figure 6.31 ^{11}B NMR spectrum of **P**.

Figure 6.32 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **P**.

Figure 6.33 DEPT-135 NMR{¹H} NMR spectrum of **P**.

6.4.3 Crystal Structure Determination of Compounds **K**, **L**, **M**, **N**, **O** and **P**

X-ray data collection and structural refinement. Intensity data for compounds **K**, **L**, **M**, **N**, **O** and **P** were collected using a Bruker APEX II diffractometer. The crystals of **L**, **M**, **N**, **O** and **P** were measured at 100(2) K and the crystal of **K** was measured at 103(2). The structure was solved by direct phase determination (SHELXS-97)^[22] and refined for all data by full-matrix least squares methods on F^2 .^[23] All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotropic thermal parameters and included in the structure-factor calculations. CCDC: 1569030-1569035 contains the supplementary crystallographic data for this thesis. The

data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 6.1 Summary of Data Collection and Structure Refinement.

	K	L (toluene)_{0.5}	M
Formula	C ₄₄ H ₆₃ B ₂ LiN ₂ O ₆	C _{32.50} H ₃₈ B ₂ N ₂ O ₂	C ₄₆ H ₆₄ AuB ₂ N ₂ O ₂ P
Fw	744.52	510.27	926.54
cryst syst	triclinic	triclinic	monoclinic
space group	<i>P</i> -1	<i>P</i> -1	<i>P</i> 1 21/ <i>c</i> 1
Size (mm ³)	0.100 x 0.240 x 0.320	0.140 x 0.220 x 0.320	0.100 x 0.220 x 0.320
T, K	103(2)	100(2)	100(2)
<i>a</i> , Å	17.0101(4)	13.8934(5)	21.6138(7)
<i>b</i> , Å	17.8543(5)	14.2385(4)	11.4783(3)
<i>c</i> , Å	28.3178(7)	16.4845(5)	18.9214(5)
α , deg	79.6457(17) °	107.9003(9)°	90°
β , deg	87.6737(15)°	98.7434(11)°	114.5269(10)°
γ , deg	88.4679(17) °	106.7165(9)°	90°
V, Å ³	8451.5(4)	2866.72(16)	4270.6(2)
Z	8	4	4
<i>d</i> _{calcd} g·cm ⁻³	1.170	1.182	1.441
μ , mm ⁻¹	0.592	0.072	3.521
Refl collected	29269	130017	71330
<i>T</i> _{min} / <i>T</i> _{max}	0.8330/0.9430	0.9770/0.9900	0.3990/0.7200

N _{measd}	29269	13661	8075
[R _{int}]	0.1677	0.1284	0.0613
R [I>2sigma(I)]	0.0956	0.0724	0.0379
R _w [I>2sigma(I)]	0.2796	0.1369	0.0819
GOF	1.022	1.115	1.182
Largest diff peak/hole[e·Å ⁻³]	0.557/-0.500	0.409/-0.267	2.166/-1.183

	N (THF)	O (THF)_{1.5}	P (THF)₂
Formula	C ₄₃ H ₆₉ B ₂ LiN ₂ O ₁₁	C ₅₂ H ₇₅ B ₂ LiN ₂ O _{11.50}	C ₅₀ H ₇₉ B ₂ LiN ₄ O ₁₂
Fw	818.56	940.70	956.73
cryst syst	triclinic	monoclinic	monoclinic
space group	<i>P</i> - <i>I</i>	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> 1 21/ <i>c</i> 1
Size (mm ³)	0.142 x 0.206 x 0.217	0.060 x 0.300 x 0.320	0.179 x 0.186 x 0.236
T, K	100(2)	100(2)	100(2)
<i>a</i> , Å	11.8344(4)	12.1544(3)	11.7547(3)
<i>b</i> , Å	12.2694(4)	23.3935(6)	28.7561(8)
<i>c</i> , Å	15.7797(5)	17.8383(5)	15.7165(4)
α, deg	92.1118(10)°	90°	90°
β, deg	103.9532(11)°	96.1514(10)°	108.0772(12)°
γ, deg	93.1230(10)°	90°	90°
V, Å ³	2217.36(13)	5042.8(2)	5050.3(2)
Z	2	4	4
<i>d</i> _{calcd} g·cm ⁻³	1.226	1.239	1.258

μ, mm^{-1}	0.086	0.085	0.088
Refl collected	44237	62962	48424
T_{min}/T_{max}	0.9820/0.9880	0.9730/0.9950	0.9800/0.9840
N_{measd}	9013	11104	8908
$[R_{\text{int}}]$	0.0828	0.1118	0.0562
$R [I > 2\sigma(I)]$	0.0635	0.0596	0.0725
$R_w [I > 2\sigma(I)]$	0.1598	0.1644	0.1614
GOF	1.032	1.018	1.191
Largest diff	0.532/-0.430	0.430/-0.519	0.503 /-0.344
peak/hole[e·Å ⁻³]			

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Conclusion

Chapter 1 describes general routes to synthesize 1,2-azaborinines, 1,3-azaborinines and 1,4-azaborinines and their applications. Compared to azaborinine derivatives, diazadiborinine derivatives are not well developed. This has inspired us to design and synthesize a 1,3,2,5-diazadiborinine derivative.

Chapter 2 shows the six-membered 1,3,2,5-diazadiborinine **C** featuring a $C_2B_2N_2$ ring was synthesized and successfully isolated. An X-ray diffraction study and molecular orbital analysis indicated the 6π electrons were delocalized over the central $B_2N_2C_2$ six-membered ring of compound **C**. In addition to its unique optical property, the relatively small negative NICS values as well as the small RSE values of **C** indicated that its aromaticity is moderated compared to those of benzene and other azaborinines.

Chapter 3 demonstrates that **C** reacts with methyl trifluoromethanesulfonate, CO_2 and phenylacetylene to produce [4+2] cycloadducts **D**, **E**, and **F**, respectively. Notably, these reactions proceeded regioselectively and adduct **E** can be dissociated to carbon dioxide and **C** under the heating condition. Moreover, we demonstrated that **C** and alkene derivatives, such as ethylene, styrene derivatives and norbornene, underwent reversible [4+2] cycloaddition reactions to afford the corresponding compounds.

In Chapter 4, compound **C** effectively promotes the *N*-formylation of various amines using CO_2 and HBpin. The mechanism of hydroboration of CO_2 with HBpin involves the activation of the B-H bond of HBpin by the adduct of **C** with CO_2 , which allows for the facile transfer of the hydride from the boron center to the carbon in second CO_2 to afford a boric ester (HCOOBpin). This reaction has been further applied to *N*-formylation reaction of amines, and various primary and secondary amines.

Chapter 5 demonstrates that compound **C** effectively promotes the hydroboration reaction of ketones and aldehydes with pinacol borane (H-Bpin) at ambient condition.

Joint experimental and theoretical mechanistic studies have disclosed that the actual active catalyst is the adduct of **C** with carbonyls. This reaction proceeds via a hitherto unknown pathway: thus far, conventional hydroboration by main group-based catalysts proceeds via an insertion-metathesis mechanism whereas the mechanism presented herein involves a transition state stabilized mainly by an electrostatic interaction between the adduct and H-Bpin.

Chapter 6 shows the addition reactions of a series of sp , sp^2 and sp^3 hybridized carbanions to afford isolable ionic species **K**, **N-P**, which can be regarded as Janovsky-type complexes. π -Electrons delocalize over the C-B-C moiety in the $B_2N_2C_2$ six-membered ring of **K**, which is determined by X-ray diffraction and computational studies. **K** as a boron-center nucleophile could react with MeI and Cy_3PAuCl to generate **L** and **M**, respectively.

List of Publications related to this Thesis

1. **Di Wu**, Yongxin Li, Rakesh Ganguly, Rei Kinjo* “Snapshot of Inorganic Janovsky Complex Analogues featuring a Nucleophilic Boron Center” *Chem. Commun.* **2017**, 53, 12734.
2. **Di Wu**, Ruixing Wang, Yongxin Li, Rakesh Ganguly, Hajime Hirao*, Rei Kinjo* “Electrostatic Catalyst Generated from Diazadiborinine for Carbonyl Reduction” *Chem* **2017**, 3, 134.
3. **Di Wu**, Rakesh Ganguly, Yongxin Li, Sin Ni Hoo, Hajime Hirao*, Rei Kinjo* “Reversible [4+2] Cycloaddition Reaction of 1,3,2,5-Diazadiborinine with Ethylene” *Chem. Sci.* **2015**, 6, 7150.
4. **Di Wu**, Lingbing Kong, Yongxin Li, Rakesh Ganguly, Rei Kinjo* “1,3,2,5-Diazadiborinine Featuring Nucleophilic and Electrophilic Boron Centres” *Nat. Commun.* **2015**, 6, 7340.