Studies on the chemistry of diazadiborinines

Goh, Gillian Kor Hwee

2021

Goh, G. K. H. (2021). Studies on the chemistry of diazadiborinines. Doctoral thesis, Nanyang Technological University, Singapore.

<https://hdl.handle.net/10356/145962>

<https://doi.org/10.32657/10356/145962>

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

Downloaded on 26 Apr 2023 11:28:23 SGT

**NANYANG
TECHNOLOGICAL
UNIVERSITY**

SINGAPORE

**[STUDIES ON THE CHEMISTRY OF
DIAZADIBORININES]**

[GILLIAN GOH KOR HWEE]

**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

[2021]

**[STUDIES ON THE CHEMISTRY OF
DIAZADIBORININES]**

[GILLIAN GOH KOR HWEE]

**SCHOOL OF PHYSICAL AND MATHEMATICAL
SCIENCES**

A thesis submitted to the Nanyang
Technological University in partial fulfilment of
the requirement for the degree of Doctor of
Philosophy

2021

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research done by me except where otherwise stated in this thesis. The thesis work has not been submitted for a degree or professional qualification to any other university or institution. I declare that this thesis is written by myself and is free of plagiarism and of sufficient grammatical clarity to be examined. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

[15/1/2021]

.....
Date

[Gillian Goh Kor Hwee]

.....
gillian goh
[Gillian Goh Kor Hwee]

Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it of sufficient grammatical clarity to be examined. To the best of my knowledge, the thesis is free of plagiarism and the research and writing are those of the candidate's except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

[Input Supervisor Signature Here]

15/1/21

.....
Date

.....
[

Professor Rei Kinjo]

Authorship Attribution Statement

*(B) This thesis contains material from [4] paper(s) published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter 2 is published as G. K. H. Goh; R. Kinjo, 1,3,2,5 diazadiborinine with a Mes group, *Journal Title*, **2020**, XX, XXXX.

Chapter 3 is published as G. K. H. Goh; R. Kinjo, Oxidative Addition of Elemental Selenium to 1,4,2,5-Diazadiborinine, *Dalton. Trans.*, **2019**, 48, 7514.

*(Selected as a HOT Article)

Chapter 4 is published as G. K. H. Goh; R. Kinjo, Metal-free C(*sp*³)-H borylation by a 1,4,2,5-Diazadiborinine, *Journal Title*, **2020**, XX, XXXX.

Chapter 5 is published as G. K. H. Goh; R. Kinjo, Skeletal isomerization of diselenadiazadiborabicyclo[2.2.2]octane, *Journal Title*, **2020**, XX, XXXX.

[15/1/2021]

[Gillian Goh Kor Hwee]

.....
Date

.....
gillian goh
[Gillian Goh Kor Hwee]

Abstract

Transition metal catalysts had long been well known for its generation of toxic side products in many reactions. In addition, transition metal catalysts are often expensive, increasing the disadvantages of the utilization of such catalysts. At such, many researchers had since turned their focus on to utilizing main group catalysts which promotes a greener and lower cost alternative.

Among various classes of the main group catalysts, most research had been completed on Phosphorous, Germanium, Silicon, Aluminum compounds as well as azaborinines. However, the scope of diazadiborinines successfully synthesized remained limited to date. As such, the reported catalytic ability of diazadiborinines remained scarce. Nevertheless, previously reported catalytic activity of diazadiborinines had displayed vast potential to be investigated based on its prior ability to activate many small molecules including enthalpically strong σ -bonds as well as non-activated unsaturated bonds with mild reaction conditions.

With that, we are interested to pursue the novel chemistry of diazadiborinines in this thesis. We attempt to synthesize new diazadiborinines with more efficient reaction pathways and explore unprecedented reactivity as well as to understand the mechanism of these catalytic systems. This thesis will focus mainly on the utilization of the novel 1,4,2,5 diazadiborinine as an efficient catalyst in C-H bonds and dichalcogenide Se-Se bond activation reactions. The novel chemical transformation of the skeletal isomerization process observed

experimentally will also be analyzed. All mechanisms proposed in this thesis were investigated using experimental and DFT calculations. Understanding these catalytic systems and their ability to perform chemical transformations will allow the development of a platform to generate more effective and green catalysts of practical applications in the future.

Acknowledgements

I would first like to thank Nanyang Technological University, School of Physical and Mathematical Sciences, Division of Chemistry and Biological Chemistry for giving me the opportunity to pursue my passion in research as a Ph.D. candidate. Next, I would like to thank my supervisor, Assoc Professor Rei Kinjo for all his advice, guidance, and assistance throughout the four years of Ph.D. candidature. I would also like to express my gratitude to my TAC committee members, Professor Leung Pak Hing and Assistant Professor Rowan Dury Young for all their guidance and encouragement. I am thankful to Dr Rakesh Ganguly, Dr Li Yongxin, Ms. Goh Ee Ling and Ms. Zhu Wen Wei for their kind advice and assistance on crystallography analysis, NMR and HRMS operations, respectively. Next, I would like to thank my past team members (Dr ChongChe Chang, Dr Lu Wei, Dr Rao Bin, Dr Su Yuan Ting, Dr Wang Bao Lin, Dr Su Bo Chao, Dr Wu Di, Dr Wang Li Liang and Dr Soichiro Natsuka) and present team members (Dr Do Dinh Cao Huan, Ms. Ota Kei and Mr. Kota Koshino) for all their teachings and support in these 4 years. Finally, I want to thank all the CBC staff who had provided administrative assistance and my fellow CBC peers who were always there to lend a helping hand in times of need.

On the personal side, I would like to thank my family for being my pillar of strength, especially my parents who always gave me unwavering support and unconditional love. Also, not to miss out my beloved brother and my sister-in-law who never fails to brighten up my life with funny posts and comments. I want to express my gratitude to all my friends (Wendy, CCHMS coolest friends ever,

SAJC CLSF) for all the kind understanding when I am always missing in action and the kind arrangements to accommodate me for meetups when all of them have their own schedules and work. Lastly, I want to credit my religion and express my utmost gratitude to the Buddha for giving me faith and courage to persevere in all times of challenges and obstacles.

Table of Contents

Abstract	1
Acknowledgements	2
Table of Contents	3
Chapter 1 Introduction.....	8
1.1 General properties and practical applications of boron compounds	8
1.2 BN/CC isosterism	12
1.3 Synthesis, reactivity, and applications of Borazine, Azaborinine and BN fullerenes	14
1.4 Recent development of Diazadiborinines	32
1.5 Main objectives of the thesis	34
1.6 References.....	35
 Chapter 2 Synthesis and characterization of novel 1,3,2,5 and 1,4,2,5-diazadiborinines	 39
2.1 Introduction.....	39
2.2 Results and Discussion:1,3,2,5-diazadiborinine with Mes and Ph on boron centers respectively	55
2.3 Results and Discussion:1,3,2,5-diazadiborinine with Ph and Cl on boron centers respectively	65
2.4 Results and Discussion: Annulated 1,4,2,5-diazadiborinine with Ph on boron centers	77

2.5	Conclusion	90
2.6	Experimental Section.....	92
2.7	References.....	139
Chapter 3 Oxidative Addition of Elemental Selenium to 1,4,2,5-Diazadiborinine		142
3.1	Introduction.....	142
3.2	Results and Discussion.....	157
3.3	Conclusion	167
3.4	Experimental Section.....	169
3.4	References.....	183
Chapter 4 Metal-free C(sp³)-H borylation by a 1,4,2,5-Diazadiborinine		186
4.1	Introduction.....	186
4.2	Results and Discussion.....	198
4.3	The proposed mechanistic pathway for reaction between 12 and toluene.....	212
4.4	Kinetic Studies	215
4.5	Conclusion	232
4.6	Experimental Section.....	234
4.7	References.....	306
Chapter 5 Skeletal isomerization of diselenadiazadiborabicyclo[2.2.2]octane		308
5.1	Introduction.....	308
5.2	Results and Discussion.....	315

5.3	The proposed mechanistic pathway for the skeletal isomerization from 13 to 26	324
5.4	Kinetic Studies	326
5.5	Conclusion	331
5.6	Experimental Section.....	333
5.7	References.....	353
Chapter 6	Conclusion	356

Chapter 1 Introduction

1.1 General Properties and applications of boron compounds

Discovering the unique properties of elements and applying them to benefit mankind are always the key force to propel developments in scientific research. Since the identification of Boron as an element in 1824¹, many researchers had subsequently, uncovered unique physiochemical properties of boron that make its compounds an attractive addition to the field of organic synthesis, biomedical, organic photovoltaics (OVPs), Li-ion batteries, dye-sensitized solar cells (DSSCs), light emitting diodes (OLEDs) and organic transistors (OFETs) applications.² Boron contributes to the synthesis of fine chemicals as exemplified by the use of aryl boronic ester for Suzuki coupling (Scheme 1) in 2010 Nobel Prize in Chemistry.² Tricoordinate borane is able to form dative bonds with nucleophiles readily to generate an anionic, tetrahedral structure from a trigonal-planar structure. This property increases the binding affinity of boron derived pharmaceutical drugs to nucleophiles at enzyme active sites in the human body, giving rise to enhanced selectivity and potency. A well demonstrated example would be Bortezomib, an anti-cancer drug which is generally marketed as Velcade (Fig 1). Boron is electron deficient as it contains four valance orbitals but only has three valance electrons. The empty p-orbital makes Boron strong electrophiles and Lewis acids that are susceptible towards electron donation from Lewis bases as reported by Gay-Lussac and co-workers.^{2c}

Other than boron, boranes are also known to contain electrophilic boron centers that are electron deficient. In the classic example of diboranes, two electrons from each boron atom were utilized for the bonding with two terminal hydrogen atoms, respectively. The bridging hydrogen atom then provides one electron for bonding with the last remaining valance electron at boron. The B_2H_2 ring formed is thus held together by four electrons, demonstrating the electron deficient three-center two-electron bonding (Fig 2).² A more commonly known application of such electron deficient boranes (Fig2) is the organic light-emitting diode (OLEDs). The electron deficient boranes in OLEDs can become powerful electron acceptors to modulate bright charge-transfer luminescence with the combination of electron donors in p-conjugated materials.³ Other examples include amine-boranes utilized for storage of hydrogen gas and Frustrated Lewis Pairs (FLPs) for the activation of small molecules such as H_2 (Scheme 2).⁴

Scheme 1 General Scheme for Suzuki reaction

Figure 1 Structure of Velcade

Figure 2 Structure of Diborane and selected examples of triaryl boron compounds in optoelectronic applications

Amino-boranes for storage of H₂

Frustrated Lewis Pairs (Activation of small molecules)

Scheme 2 General scheme depicting applications of electron deficient boranes

1.2 BN/CC isosterism

Due to the boron's ability to form covalent bonds with carbon, the inclusion of boron in organic structures has garnered much attention from the researchers. This brings about the emergence of an isoelectronic relationship between BN and CC units which can be attributed to the same number of total valence electrons possessed by both units. Boron contains three valence electrons whereas nitrogen contains five valence electrons. Each carbon atom in the CC unit contributes four valence electrons, giving rise to a total of eight valence electrons in both BN and CC units, respectively.

Three variants featuring the sp , sp^2 and sp^3 BN/CC isoelectronic relationships are feasible (Fig 3).⁵In spite of a same number of valence electrons, the molecular and electronic properties of a compound vary when the CC unit is substituted with a BN unit. An example would be ammonia borane (AB) and ethane. Both of which contains the same number of valence electrons. However, ammonia borane exists as a solid while ethane exists as a gas at room temperature. Ammonia borane has a high melting point of 104 °C whereas ethane only has a low boiling point of -89 °C. A significantly larger amount of heat energy is needed to overcome the strong dihydrogen bonding between ammonia borane molecules than the weak dispersion forces between ethane molecules. Furthermore, the nitrogen atom in ammonia borane carries a positive formal charge and the boron atom carries a negative formal charge. The allocation of charge is due to the π bonding in its resonance structure. The difference in the electric charges at the BN ends will generate a net polarity whereby ammonia

borane has a strong dipole moment of 5.2D (Fig 3).⁶ Owing to symmetry in the structure of ethane, ethane has no effective dipole moment.⁷ The distinctions among ammonia borane and ethane displayed above clearly illustrates the difference in the molecular and electronic properties of the isosteres. The BN/CC isosterism presented a possibility to tune molecular and electronic properties in isosteres to allow development of novel compounds with diversity. The sp^2 type of BN isosteres are generally more stable than the sp^3 BN isosteres. Therefore, more efforts were aimed at developing effective synthetic routes for the sp^2 BN isosteres. In the rest of the chapter, formal charges had been omitted or partially omitted in most of the structures discussed.

Figure 3 Diagram illustrating the sp , sp^2 and sp^3 BN/CC isoelectronic relationship

1.3 Synthesis, reactivity, and applications of Borazine, Azaborinines and

BN fullerenes

1.3.1 Borazine

Out of the three types of isosterism, the sp^2 BN/CC isosterism incorporating conjugated aromatic structures has been the focus of many researchers. This is due to the diverse functionality achieved by the sp^2 arene isosteres through the tuning of its electronic properties. In 1926, Stock and Pohland had first reported the synthesis of borazine ($B_3H_6N_3$) by diborane and ammonia (Scheme 3).⁸ Borazine is classified as the inorganic benzene whereby all the carbon atoms of benzene are replaced by boron and nitrogen atoms. Despite being the first example of the BN/CC isosterism involving a benzene ring, the aromaticity of borazine remains unestablished.⁹ Borazine has equal B–N bond length⁹ and a same number of π electrons as benzene¹⁰, giving it considerable aromatic properties. However, borazine's inclination towards addition reactions with HCl, $NaBH_4$ or bromine⁹ refutes the previous consideration, making its aromaticity largely debatable to date.

Scheme 3 Synthesis of Borazine by Stock and Pohland

1.3.2 1,2-Azaborinine

Following Stock and Pohland's synthesis of borazine, Dewar and co-workers pioneered the synthetic work of a mono BN substituted aromatic system in 1958. The 9-carbon atom in phenanthrene was replaced with nitrogen by reacting 2-phenylaniline with BCl_3 . Friedel–Crafts cyclization upon the addition of AlCl_3 would further substitute the 10-carbon atom with boron. Subsequent nucleophilic substitution at the B–Cl bond would afford derivatives of the 9 aza-10-boraphnenathrene (Scheme 4).¹¹ The sixth and eighth carbon positions in the 9 aza-10-boraphnenathrene derivatives were discovered to be susceptible to electrophilic aromatic substitution.¹² The specificity of the location for electrophilic substitution were much dependent on the electrophiles utilized.¹² It was also observed that deprotonation was plausible at the position of the nitrogen.

Scheme 4 Synthesis of 9-aza-10-boraphnenathrene by Dewar and co-workers

Following in 1962, Dewar and co-workers reported the first 1,2-azaborinine species by desulfurization of BN-benzothiophene using Raney nickel (Scheme 5).¹³ The 1,2-azaborinine species were investigated for its acid and base stability whereby it remained unaffected when subjected to acid and base for long periods of time. In addition, the double bonds present in the ring were not reduced by Raney nickel, demonstrating signs of aromatic stability.¹⁴ In 1963, White

synthesized the phenyl-substituted 1,2-azaborinine species by means of a palladium-catalyzed dehydrogenation of the azaboracyclohexane (Scheme 6).¹⁵ Next, Dewar and co-workers synthesized the parent 1,2-azaborinine ring in 1967.¹⁵ They attempted to utilize a hydroboration-oxidation strategy but failed to generate the borazarene due to its rapid polymerization in which BN-triphenylene was obtained instead (Scheme 7). The borazarene was therefore observed to be a chemically unstable system with its sole characterization being conducted via mass spectrometry.¹⁵

Scheme 5 Synthesis of 1,2-azaborinine species by Dewar and co-workers

Scheme 6 Synthesis of 2-phenyl-1,2-azaborinine species by White

Scheme 7 Failed hydroboration-oxidation pathway of borazarene by Dewar and co-workers

In 1980, Gronowitz and co-workers reported the first synthesis of monocyclic 1,2-azaborinines with aliphatic substitutions at the fourth and fifth carbon positions (Scheme 8).¹⁶ The inclusion of the thiophene group at the α position to boron leads to the sole desulfurization of thiophene at the fourth carbon position with a substitution of an ethyl group in place. The further reaction allows for an aliphatic butyl group to replace the previous aromatic group at the α position.

Scheme 8 Synthesis of 4,5 substituted 1,2-azaborinines by Gronowitz and co-workers

The Ashe group discovered a ring closing metathesis and oxidation synthetic pathway to afford 1,2 monocyclic azaborinines in 2000. The prior synthesis developed by Dewar et al. required high temperatures for the

desulfurization or dehydrogenation processes whereas the Ashe reaction route afforded a higher yield under the milder conditions (Scheme 9).¹⁷ Allyltributyltin was reacted with BCl_3 to generate an allylboron dichloride. Condensation subsequently proceeded with the addition of an ethylallylamine. A phenyl group was inserted to the boron with the removal of the chloride which ring closing metathesis next occurred with Grubbs' first-generation catalyst. The 1,2-azaborinine precursor was further oxidized with DDQ to afford the final monocyclic 1,2-azaborinine.

Subsequently in 2001, Ashe and co-workers reported the first crystallographic characterization of the azaborinine generated by a ring expansion pathway of 1,2-azaborinine with dichloromethane and a lithium base (Scheme 10).¹⁸ This ring expansion strategy gave a higher yield of 35% as compared to the ring closing metathesis method of 25% previously developed in 2000.

Scheme 9 Synthesis of 1,2-azaborinines with ring closing metathesis by Ashe and co-workers

Scheme 10 Synthesis of 1,2-azaborinines with ring expansion by Ashe and co-workers

Next, the Ashe group communicated the reactivity of the monocyclic 1,2-azaborinines towards electrophiles in 2007.¹⁹ They reported the first aromatic substitution of the 1,2-azaborinine species indicating the ortho (α) and para (γ) positions to boron were more likely to encounter electrophilic substitution (Scheme 11). In the same year, the group of Liu reported the nucleophilic substitution reactions of the monocyclic 1,2-azaborinine (Scheme 12).²⁰ The chloro 1,2-azaborinine species were utilized for the nucleophilic substitution investigations. Liu and co-workers subsequently investigated and described the 1,2-azaborinine structure as a potential hydrogen storage system with suitability to be utilized as hydrogen storage materials.

Scheme 11 Electrophilic substitution of monocyclic 1,2-azaborinines by Ashe and co-workers

Nu = BuLi, Li-vinyl, PhMgBr, LiNMe₂, K-SBn,
K-OfBu, LiBEt₃-H, BrMg—≡—Ph

Scheme 12 Nucleophilic substitution of monocyclic 1,2-azaborinines by Liu and co-workers

1.3.3 1,3-Azaborinine

The developments in the 1,2-azaborinines had renewed interest in the synthesis of 1,3 and 1,4-azaborinines. The synthesis of 1,3-azaborinines was greatly pursued due to its difficulty to be generated. Computational calculations had predicted that the low thermodynamic stability of the 1,3-azaborinine ring structure has resulted in its synthetic challenge.²¹ Despite so, the first isolation of the 1,3-azaborinine ring was reported in 2011 by Liu and co-workers (Scheme 13).²² The 1,3-azaborinine derivative is observed to be of a stable structural motif with considerable aromatic properties.

Scheme 13 General synthetic pathway of monocyclic 1,3-azaborinines by Liu and co-workers

The group of Liu employed a substrate bearing a methyl group (R) and a N(*i*Pr)₂ group (R') to facilitate a Lewis acid and Lewis base interaction between boron and nitrogen lone pair (Scheme 13). They first attempted to react stannane nucleophile and vinyl boron chloride through direct trans metalation but failed to obtain their desired precursor for the ring closing metathesis. However, the lithium-tin exchange of the stannane nucleophile **a** with *n*-hexyl lithium following an addition of the vinyl boron chloride electrophile **b** could afford the desired precursor **c**. Triflic acid was subsequently added to protect the nucleophilic amine group on **c** from degrading the catalysts of the ring closing metathesis pathway. Deprotonation with DBU occurs after ring closing metathesis, giving the precursor **c**. The 1,3-azaborinine **d** was then obtained via dehydrogenation at the optimized conditions of 5mol% catalyst loading at 120 °C in benzene. The selectivity of the desired azaborinine to the reduced byproduct was the highest at a ratio of 2.2:1 (Scheme 14). The 1,3-azaborinine was found to react with Cr (CO)₃(MeCN)₃ to afford a piano-stool complex (Scheme 15). The 1,3-azaborinine can also undergo electrophilic aromatic substitution with dimethyl(methylene) ammonium chloride (Scheme 16).²²

Scheme 14 Optimized synthetic pathway of monocyclic 1,3-azaborinines by

Liu and co-workers

Scheme 15 Reaction scheme of 1,3-azaborinines with $\text{Cr}(\text{CO})_3(\text{MeCN})_3$ by Liu

and co-workers

Scheme 16 Electrophilic aromatic substitution of 1,3-azaborinines by Liu and co-workers

The reactivity of the 1,3-azaborinines towards various nucleophiles such as vinyl magnesium bromide, CsF, LiAlH₄, LiOAc and MeOH were also investigated. However, the N(*i*Pr)₂ group seems too strong to act as a leaving group and there was lack of reactivity towards the nucleophiles. It was discovered acetic acid reacted readily with boron of the 1,3-azaborinine ring to generate a B-OAc 1,3-azaborinine product (Scheme 17).²² The acidic conditions might have caused protonation of the nitrogen lone pair to make the N(*i*Pr)₂ a better leaving group for nucleophilic substitution to occur. Therefore, Liu and co-workers subsequently incorporated acidic conditions to propel nucleophilic substitution. Various successful reports of nucleophilic reactivity such as MeOH, HCl, TMSCN and HF.Py then emerged (Scheme 17).²³ The leaving group was then changed to *t*BuCO₂ to facilitate nucleophilic substitution at the boron under neutral or basic conditions (Scheme 18).²³

Scheme 17 Nucleophilic substitution of 1,3-azaborinines under acidic conditions by Liu and co-workers

Scheme 18 Nucleophilic substitution of 1,3-azaborinines under basic/neutral conditions by Liu and co-workers

1.3.4 1,4-Azaborinine

Although quantum chemical calculations had predicted the 1,4-azaborinine to be more thermodynamically stable than its 1,3 counterpart,²¹ the similar synthetic challenge persisted for monocyclic 1,4-azaborinines.²⁴ In 1961, Maitlis reported the substitution of boron and nitrogen at the 1,4 positions in heterocyclic acenes (Fig 4).²⁵ In 1992, Clark and co-workers also synthesized the same anthracene ring by utilizing 2,2'-dilithiodiphenylmethanamine and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ followed by the addition of mesityl lithium (Scheme 19).²⁵ Following in 2006 to 2010, the group of Kawashima subsequently reported several 1,4 BN substituted structures (Fig 5).²⁵ It was until 2012 when the first monocyclic 1,4-azaborinine was successfully synthesized by Braunschweig and co-workers.²⁶ They selected acetylene, iminoborane and $[(\text{iPr}_3\text{P})_2\text{RhCl}]_2$ for the synthesis of the desired azaborinine (Scheme 20).

Figure 4 Structure of 10,9-borazaroanthracene by Maitlis

Scheme 19 Synthesis of 10,9-borazaroanthracene by Clark and co-workers

Figure 5 Structures of polycyclic dibenzo-fused 1,4-azaborines by Kawashima and co-workers

Scheme 20 Synthesis of first 1,4-azaborinine by Braunschweig and co-workers

In 2014, the group of Liu attempted to generate non-dibenzo-fused 1,4-azaborinine compounds (Scheme 21).²⁸ In order to incorporate a better leaving group (OMe), MeOH was added whereby OMe is replaces the N(*i*Pr)₂ group at boron. Several nucleophiles were screened for the investigation of the mono-benzofused 1,4-azaborinine towards nucleophilic substitution (Scheme 22).

Scheme 21 Proposed mechanism for the formation of mono-benzo-fused 1,4-azaborinine by Liu and co-workers

Scheme 22 Nucleophilic substitution of mono-benzofused 1,4-azaborinine by Liu and co-workers

In 2016, the group of Liu reported a novel synthetic route to monocyclic 1,4-azaborinines (Scheme 23),²⁹ which allowed accessing to monocyclic 1,4-azaborinines bearing various substituents on the B atom. The *i*Pr₂N-substituted 1,4-azaborinine was converted to as the derivatives bearing OMe, Cl or pivalate group on the B atom. Utilizing the precursors with OMe or Cl at the boron center, nucleophilic substitution with various nucleophiles (Scheme 24) directly afforded a variety of 1,4-azaborinines.

Scheme 23 Synthesis of monocyclic 1,4-azaborinines by Liu and co-workers

Scheme 24 Nucleophilic substitution of 1,4-azaborinines by Liu and co-workers

The 1,4-azaborinine derivatives bearing the donor and acceptor-substituted para-terphenyls are found to exhibit photophysical properties (Fig 6).²⁹ Compound **i** consists of a boron atom acting as an acceptor while the nitrogen atom in the 1,4-azaborinine ring acts as the donor. Compound **k** exhibits the opposite polarity from **i**. The boron atom in the 1,4-azaborinine ring of **k** acts as a donor whereas the nitrogen atom acts as an acceptor. Compounds **j** and **l** are carbon counterparts of compounds **i** and **k**, respectively with the benzene ring in place of the 1,4-azaborinine ring. Compounds **j** and **l** display relatively similar absorption and emission wavelengths whereas compounds **i** and **k** show significantly distinct absorption and emission wavelengths (Table 1). The observed results show that the incorporation of different donor/acceptor groups at the boron/nitrogen atoms in the 1,4-azaborinine ring results in vast differences in the optical properties of compounds **i** and **k**. Such differences in optical

properties are particularly useful in the optoelectronic industries for the organic light emitting diodes (OLEDs).²⁹

Figure 6 Structures of the donor and acceptor-substituted para-terphenyls by Liu and co-workers

	i	j	k	l
λ_{abs} (nm)	296	272	313	270
λ_{em} (nm)	482	365	359	370

Table 1 Table of absorption and emission wavelengths for compounds **i - l**

1.3.5 Boron-Nitride Fullerenes

Since the discovery of fullerenes by Kroto and co-workers in 1985,³⁰ Boron-Nitride fullerenes like structures have been of interest to many researchers.

Boron-Nitride structures are chemically stable, heat resistant and they contain semiconducting properties.³⁰ This propelled many to investigate the BN/CC isosterism concept in graphene allotropes. Computational investigations by Kar and co-workers show that the substitution of a contiguous Boron-Nitride unit is thermodynamically more stable than incorporating a boron and nitrogen atom separately into the system.^{31,32} To obtain the BN fullerene, the first BN bond should be substituted at the adjoining site between two six-membered rings. The second BN unit should be placed at the adjacent position to nitrogen atom in an alternate fashion within one hexagonal ring (Fig 7).³³ The third BN replacement will complete the B_3N_3 six-membered ring to afford an encapsulated borazine (Fig 7).³¹

Figure 7 BN substitution in BN fullerenes

In 2015, Kim and co-workers successfully synthesized *h*-BN fullerenes by employing a one pot synthetic method,³⁴ in which heating a mixture of graphene oxide (GO) and B_2O_3 in the presence of NH_3 gas generated the BN fullerene (Scheme 25). Application of BN fullerenes include their utilities as high heat resistant semiconductors, insulator lubricants and storage materials for gases.

$h=17$
which $h=7,8,$
 $9...,24$

Scheme 25 Synthesis of h -BN fullerenes by Kim and co-workers

1.4 Recent development of Diazadiborinines

There had been significant progress in the chemistry of B, N-containing aromatic molecules in the last decade. The synthesis of azaborinines and its chemical reactivity at the boron center had been extensively reported and studied, which brings a shift in focus towards the unexplored field of diazadiborinines with $B_2C_2N_2$ ring system.

Various permutations of the $B_2C_2N_2$ ring exists in the computational investigations but only a limited number of diazadiborinine have been successfully synthesized over the past few years. The successfully isolated structures consist of the 1,3,2,4; 1,3,2,5; 1,4,2,3; 1,4,2,5; 1,5,2,4 and 1,2,3,6-diazadiborinines.^{24,35} Examples of successfully isolated and structurally characterized diazadiborinines are presented in Fig 8. A more detailed description of the various diazadiborinines is further elaborated in the following chapters of the thesis.

Figure 8 Reported diazadiborinine structures

1.5 Main Objectives of the thesis

Given the diverse uses of the BN/CC-substituted compounds, the limited amount of isolated diazadiborinines propels researchers to continuously pursue its synthesis. Challenged by this limited scope, we were interested to develop efficient synthetic routes to novel diazadiborinines. Investigation of the chemical reactivity of the newly developed diazadiborinines is of immense significance from a viewpoint of the potential application. With these two objectives in mind, we have designed, synthesized, and fully characterized novel diazadiborinine derivatives and investigated their reactivity.

The newly developed synthetic route allows accessing to the diazadiborinines in a straightforward and highly efficient manner. The emerged diazadiborinines and its reacted species stemming from this thesis paves a way for the further development of the chemistry of B, N-aromatic molecules and relevant material sciences.

1.6 References

1. J. Berzelius, *Investigation of hydrofluoric acid and of its most noteworthy compounds*, **1824**, 12, 46.
2. (a) Z. M. Hudson; S. Wang, *Dalton Trans.*, **2011**, 40, 7805; (b) A. Suzuki, *Angew. Chem.*, **2011**, 123, 6854; (c) J. L. G. Lussac, L. J. Thénard, "Sur l'acide fluorique". *Annales de Chimie.*, **1809**, 69, 204; (d) F. A. Cotton; G. Wilkinson; P. L. Gaus, *Basic Inorganic Chemistry*, 2nd ed. Wiley, **1987**, 113.
3. (a) T. Noda; Y. Shirota, *J. Am. Chem. Soc.*, **1998**, 120, 9714; (b) T. Noda; H. Ogawa; Y. Shirota, *Adv. Mater.*, **1999**, 11, 283; (c) Y. Shirota; M. Kinoshita; T. Noda; K. Okumoto; T. Ohara, *J. Am. Chem. Soc.*, **2000**, 122, 11021; (d) H. Doi; M. Kinoshita; K. Okumoto; Y. Shirota, *Chem. Mater.*, **2003**, 15, 1080; (e) Y. Shirota; *J. Mater. Chem.*, **2005**, 15, 75; (f) W. L. Jia; D. R. Bai; T. McCormick; Q. D. Liu; M. Motala; R. Wang; C. Seward; Y. Tao; S. Wang, *Chem.–Eur. J.*, **2004**, 10, 994; (g) W. L. Jia; X. D. Feng; D. R. Bai; Z. H. Lu; S. Wang; G. Vamvounis, *Chem. Mater.*, **2005**, 17, 164; (h) F. H. Li; W. L. Jia; S. Wang; Y. Q. Zhao; Z. H. Lu, *J. Appl. Phys.*, **2008**, 103, 034509/1; (i) D. Tanaka; T. Takeda; T. Chiba; S. Watanabe; J. Kido, *Chem. Lett.*, **2007**, 36, 262; (j) L. X. Xiao; Z. J. Chen; B. Qu; J. X. Luo; S. Kong; Q. H. Gong; J. Kido, *Adv. Mater.*, **2011**, 23, 926.
4. G. C. Welch; R. San Juan; J. D. Matsuda; D. W. Stephan, *Science.*, **2006**, 314, 1124.
5. R. H. Pritchard; C. W. Kern, *J. Am. Chem. Soc.*, **1969**, 91, 1631.

6. P. G. Campbell; A. V. J. Marwitz; S. Y. Liu, *Angew. Chem. Int. Ed.*, **2012**, *51*, 6074.
7. L. R. Thorne; R. D. Suenram; F. J. Lovas, *J. Chem. Phys.*, **1983**, *78*, 167.
8. A. Stock; E. Pohland, *Ber. Dtsch. Chem. Ges.*, **1926**, *59*, 2210.
9. (a) R. Islas; E. Chamorro; J. Robles; T. Heine; J. C. Santos; G. Merino, *Struct. Chem.* **2007**, *18*, 833; (b) D. E. Bean; P. W. Fowler, *J. Phys. Chem. A*, **2011**, *115*, 13649; (c) A. Soncini; C. Domene; J. J. Engelberts; P. W. Fowler; A. Rassat; J. H. van Lenthe; R. W. A. Havenith; L. W. Jenneskens, *Chem. Eur. J.*, **2005**, *11*, 1257; (d) A. K. Phukan; A. K. Guha; B. Silvi, *Dalton Trans.*, **2010**, *39*, 4126.
10. E. Wiberg, *Naturwiss.*, **1948**, *35*, 82.
11. M. J. S. Dewar; V. P. Kubba; R. Pettit, *J. Chem. Soc.*, **1958**, 3073.
12. (a) M. J. S. Dewar, *Tetrahedron*, **1959**, *7*, 213; (b) M. J. S. Dewar; V. P. Kubba, *J. Org. Chem.*, **1960**, *25*, 1722; (c) M. J. S. Dewar, V. P. Kubba, *J. Am. Chem. Soc.*, **1961**, *83*, 1757; (d) M. J. S. Dewar; P. M. Maitlis, *J. Am. Chem. Soc.*, **1961**, *83*, 187.
13. M. J. S. Dewar; P. A. Marr, *J. Am. Chem. Soc.*, **1962**, *84*, 3782.
14. D. G. White, *J. Am. Chem. Soc.*, **1963**, *85*, 3634.
15. K. M. Davies; M. J. S. Dewar; P. Rona, *J. Am. Chem. Soc.*, **1967**, *89*, 6294.
16. S. Gronowitz; I. Ander, *Chem. Scr.*, **1980**, *15*, 23.
17. A. J. Ashe; X. D. Fang, *Org. Lett.*, **2000**, *2*, 2089.
18. A. J. Ashe; X. Fang; J. W. Kampf, *Organometallics*, **2001**, *20*, 5413.

19. J. Pan; J. W. Kampf; A. J. Ashe, *Org. Lett.*, **2007**, *9*, 679.
20. A. J. V. Marwitz; E.R. Abbey; J.T. Jenkins; L.N. Zakharov; S.Y. Liu, *Org. Lett.*, **2007**, *9*, 4905.
21. a) M. H. Matus; S.Y. Liu; D. A. Dixon, *J. Phys. Chem. A*, **2010**, *114*, 2644;
b) M. Kranz; T. Clark, *J. Org. Chem.*, **1992**, *57*, 5492.
22. S. Xu; L. N. Zakharov; S.Y. Liu, *J. Am. Chem. Soc.*, **2011**, *133*, 20152.
23. S. Xu; T. C. Mikulas; L. N. Zakharov; D. A. Dixon; S. Y. Liu, *Angew. Chem. Int. Ed.*, **2013**, *52*, 7527.
24. M. J. D. Bosdet; W. E. Piers, *Can. J. Chem.*, **2008**, *86*, 8.
25. (a) P. M. Maitlis, *J. Chem. Soc.*, **1961**, 425; (b) M. Kranz; F. Hampel; T. Clark, *J. Chem. Soc., Chem. Commun.*, **1992**, 1247; (c) T. Agou; J. Kobayashi; T. Kawashima, *Org. Lett.*, **2006**, *8*, 2241; (d) T. Agou; J. Kobayashi; T. Kawashima, *Chem. Commun.*, **2007**, 177, 3204 (e) T. Agou; J. Kobayashi; T. Kawashima, *Chem. Eur. J.*, **2007**, *13*, 8051.
26. H. Braunschweig; A. Damme; J. O. C. Jimenez-Halla; B. Pfaffinger; K. Radacki; J. Wolf, *Angew. Chem. Int. Ed.*, **2012**, *51*, 10034.
27. P. R. P. Barreto; A. F. A. Vilela; R. Gargano, *Int. J. Quantum Chem.*, **2005**, *103*, 659.
28. S. Xu; F. Haeffner; B. Li; L. N. Zakharov; S. Y. Liu, *Angew. Chem. Int. Ed.*, **2014**, *53*, 6795; *Angew. Chem.*, **2014**, *126*, 6913.
29. X. Liu; Y. Zhang; B. Li; L. N. Zakharov; M. Vasiliu; D. A. Dixon; S.Y. Liu, *Angew. Chem. Int. Ed.*, **2016**, *55*, 8333.

30. H. Kroto; J. Heath; S. O'Brien; R. Curl; R. Smalley, *Nature*, **1985**, *318*, 162.
31. J. Pattanayak; T. Kar; S. Scheiner, *J. Phys. Chem. A*, **2001**, *105*, 8376.
32. Z. Chen; K. Ma; H. Zhao; Y. Pan; X. Zhao; A. Tang; J. Feng, *J. Mol. Struct. (Theochem)*, **1999**, *466*, 127.
33. (a) Z. Chen; K. Ma; H. Zhao; Y. Pan; X. Zhao; A. Tang; J. Feng, *J. Mol. Struct. (Theochem)*, **1998**, *452*, 219; (b) K. A. Yee; H. Yi; S. Lee; S. K. Kang; J. S. Song; S. Seong, *Bull. Korean Chem. Soc.*, **2003**, *24*, 494.
34. S. S. Kim; T. V. Khai; Y. J. Kwon; A. Katoch; P. Wu; H. W. Kim, *Met. Mater. Int.*, **2015**, *21*, 950.
35. (a) B. Wang; R. Kinjo, *Chem. Sci*, **2019**, *10*, 2088; (b) B. Wang; Y. Li; R. Ganguly; H. Hirao; R. Kinjo, *Nat. Commun.*, **2016**, *7*, 11871; (c) B. Wang; Y. Li; R. Ganguly; R. Webster; R. Kinjo, *Angew. Chem. Int. Ed.*, **2018**, *56*, 7826; (d) D. Wu; L. Kong; Y. Li; R. Ganguly; R. Kinjo, *Nat. Commun.*, **2015**, *6*, 7340; (e) D. Wu; L. Kong; Y. Li; R. Ganguly; H. Hirao; R. Kinjo, *Chem. Sci.*, **2015**, *6*, 7150; (f) D. Wu; Y. Li; R. Ganguly; R. Kinjo, *Chem. Commun.*, **2017**, *53*, 12734; (g) Y. Su; Y. Li; R. Ganguly; R. Kinjo, *Angew. Chem. Int. Ed.*, **2018**, *57*; (h) G. K. H. Goh; Y. Li; R. Kinjo, *Dalton Trans.*, **2019**, *48*, 7514.

Chapter 2 Synthesis and Characterization of novel 1,3,2,5 and 1,4,2,5-Diazadiborinines

2.1 Introduction

2.1.1 1,3,2,4-Diazadiborinines

Computational calculations predicted the 1,3,2,4-diazadiborinine structure to be the most thermodynamically stable among all permutations of the $B_2C_2N_2$ rings.^{1,2} In 1964, Köster and Iwasaki first reported a synthetic route involving the dimerization of aromatic amine-borane adducts to generate the 1,3,2,4-diazadiborinine ring (Scheme 1).³ The 1,3,2,4-diazadiborinine structure was observed to be susceptible to hydrolysis. In 1988, Paetzold and co-workers reported the synthesis of a 1,3,2,4-diazadiborinine analogue by the [4+2] cycloaddition reaction of dimethylacetylenedicarboxylate with diazadiboretidine (Scheme 2).⁴ The crystallographic analysis revealed that the 1,3,2,4-diazadiborinine ring is twisted, probably due to the steric hindrance of the bulky *t*Bu substituents.

Scheme 1 Synthesis of the first 1,3,2,4-diazadiborinine by Köster and Iwasaki

Scheme 2 Synthesis of the 1,3,2,4-diazadiborinine by Paetzold and co-workers

Frangé and co-workers subsequently investigated the reactivity of the first 1,3,2,4-diazadiborinine developed by Köster and Iwasaki towards electrophilic metal centers.⁵ $\text{Cr}(\text{CO})_6$ was found to react with the 1,3,2,4-diazadiborinine. The $\text{Cr}(\text{CO})_3$ moiety would attach to the annulated phenyl ring with three possibilities of coordination sites (Scheme 3) whereby a mixture of isomers was obtained.

Scheme 3 Reactivity of the 1,3,2,4-diazadiborinine with $\text{Cr}(\text{CO})_6$ by Frangé and co-workers

2.1.2 1,3,2,5-Diazadiborinines

Kinjo and co-workers reported the first synthesis of a 1,3,2,5-diazadiborinine featuring both electrophilic and nucleophilic boron centers in 2015 (Fig. 1).⁶

Synthetic route to 1,3,2,5-diazadiborinine is shown in Scheme 4. Two equivalents of oxazoline were first added to a solution of *n*BuLi in THF. Subsequent addition of one equivalent of dichlorophenylborane generated the intermediate **a**, which was treated with another equivalent of dichlorophenylborane to generate compound **b**. Reduction of compound **b** with six folds of KC₈ afforded 1,3,2,5-diazadiborinine with phenyl groups at two respective boron centers as a white powder in a 32% yield. The 1,3,2,5-diazadiborinine comprises of a formal B(+I)/B(+III) mixed valance system in the aromatic six-membered ring with two spectroscopically inequivalent boron atoms (Fig 1). The nucleophilic boron center is tricoordinate and surrounded by eight electrons involving a lone pair of electrons whereas the electrophilic boron center consists of a vacant orbital. Indeed, it has been demonstrated that the 1,3,2,5-diazadiborinine reacts with MeOTf, phenylacetylene, CO₂, ethylene, styrene derivatives, norbornene and PhLi.^{6,7,8}

Figure 1 B(+I)/B(+III) mixed valance system of the 1,3,2,5-diazadiborinine synthesized by Kinjo and co-workers

Scheme 4 Synthesis of the 1,3,2,5-diazadiborinine with Ph groups at respective boron by Kinjo and co-workers

In 2018, Kinjo and co-workers subsequently developed an annulated 1,3,2,5-diazadiborinine with 14π electrons.⁹ The synthetic procedure is like that for the first 1,3,2,5-diazadiborinine (Scheme 4), and the annulated 1,3,2,5-diazadiborinine was obtained as an orange powder in a yield of 58% (Scheme 5).

Scheme 5 Synthesis of the annulated 1,3,2,5-diazadiborinine by Kinjo and co-workers

The annulated 1,3,2,5-diazadiborinine was computed to feature a small HOMO–LUMO gap (2.84 eV), which enhances the reactivity towards small molecules. The annulated 1,3,2,5-diazadiborinine readily reacts with H_2 and NH_3 gas under mild conditions. 2,6-dimethylphenylisonitrile also readily reacts with the annulated diazadiborinine at room temperature.⁹

2.1.3 1,4,2,3-Diazadiborinines

Computational calculations indicate the 1,4,2,3-diazadiborinine structure to be more stable than the 2,3,1,4-diazadiborinine structure. However, there were only few examples of the successful isolation of the 1,4,2,3-diazadiborinine species.^{1,2} In 1963, Nöth and co-workers successfully synthesized three 1,4,2,3-diazadiborinines (Fig 2).¹⁰ These 1,4,2,3-diazadiborinines have been generated by the condensation of a dialkyl diborabis(dimethylamide) with an *ortho* diamino-substituted aromatic precursor. Nöth and co-workers subsequently reported the reaction of 1,4,2,3-diazadiborinine analogue **e2** with $\text{Cr}(\text{CO})_6$ (Scheme 6) at the aromatic ring adjacent to the 1,4,2,3-diazadiborinine ring in 1978.¹¹

Figure 2 Structures of 1,4,2,3-diazadiborinines synthesized by Nöth and co-workers

Scheme 6 Reaction of 1,4,2,3-diazadiborinine with $\text{Cr}(\text{CO})_6$ synthesized by Nöth and co-workers

In 1997, Cowley, Marder and Norman reported the isolation of a 1,4,2,3-diazadiborinine consisting of the B₄O₂ ring (Scheme 7).¹² Treatment of two equivalents of B₂(OMe)₄ with two equivalents of Li₂[dab] generated the desired colorless compound. In 2015, Sahin and co-workers synthesized the first monocyclic 1,4,2,3-diazadiborinine (Scheme 8).¹³ The anion **f** was added to dichloro-diborane **g** to generate the 1,4,2,3-diazadiborinines **h** in which the possible monocyclic species are presented in scheme 7. The bicyclic 1,4,2,3-diazadiborinine was generated when the anion **f** was added to dichloro-diborolane (Scheme 9). In 2017, Braunschweig and co-workers successfully synthesized the 1,4,2,3-diazadiborinine-2,3-diamine **j** from diamino dilithium salt **i** and B₂Cl₂(NMe₂)₂ (Scheme 10). Subsequent addition of two equivalents of BH₃SMe₂ to precursor **j** generated the 1,4-dimesityl-1,2,3,4-tetrahydro-1,4,2,3-diazadiborinine **i**. Compound **k** was generated when only one equivalent of BH₃SMe₂ was added to precursor **j**. 1,4-dimesityl-1,2,3,4-tetrahydro-1,4,2,3-diazadiborinine **i** was obtained with another additional fold of BH₃SMe₂.¹⁴

Scheme 7 Synthesis of the 1,4,2,3-diazadiborinine with B₄O₂ ring by Cowley, Marder and Norman

Monocyclic species:

Scheme 8 Synthesis of the monocyclic 1,4,2,3-diazadiborinines by Sahin and co-workers

Scheme 9 Synthesis of the bicyclic 1,4,2,3-diazadiborinines by Sahin and co-workers

Scheme 10 Synthesis of the 1,4-dimesityl-1,2,3,4-tetrahydro-1,4,2,3-diazadiborinine by Braunschweig and co-workers

2.1.4 1,4,2,5-Diazadiborinines

In 2016, Kinjo and co-workers synthesized the first 1,4,2,5-diazadiborinine with spectroscopically equivalent boron centers that display both Lewis acidic and basic properties.¹⁵ The boron centers act as both nucleophilic and electrophilic centers indicating the amphiphilic nature (Scheme 11).

Scheme 11 Resonance structures of the 1,4,2,5-diazadiborinine synthesized by Kinjo and co-workers

Two equivalents of 1-methyl-1H-imidazole were first added to a solution of *n*BuLi in THF. Subsequent addition of dimethyl phenylboronate and TMSCl generated the intermediate **m**. The resulting mixture was treated with BCl₃ to generate precursor **n**, which was further reacted with an excess amount of KC₈ to afford the 1,4,2,5-diazadiborinine (Scheme 12). The 1,4,2,5-diazadiborinine was obtained as an orange powder in 52% yield. The 1,4,2,5-diazadiborinine was found to react with MeOTf, pinacolborane, diphenylsilane, phenylsilane, bis(4-fluorophenyl) phosphine, styrene, 1,1-diphenylpropa-1,2-diene, bromo-4-ethynylbenzene, benzonitrile, 4-chloro benzonitrile, CO₂, O₂ and H₂ gas.^{15,16,17}

Scheme 12 Synthesis of the 1,4,2,5-diazadiborinine with Ph group attached to boron by Kinjo and co-workers

In 2018, Kinjo and co-workers synthesized the same 1,4,2,5-diazadiborinine ring with bulky mesityl groups attached to boron atoms (Scheme 13).¹⁸ The synthetic procedure is similar to that in scheme 12 with the exception

of the addition of dimethyl 2,4,6-trimethylphenylboronate and trimethylsilyl trifluoromethane sulfonate to generate the precursor **o**. Precursor **o** was then reduced by eight folds of KC_8 to yield the 1,4,2,5-diazadiborinine with mesityl group on the boron atoms. The 1,4,2,5-diazadiborinine with mesityl group on the boron atoms was obtained as a light orange powder in 57% yield.

Scheme 13 Synthesis of the 1,4,2,5-diazadiborinine with Mes group attached to boron by Kinjo and co-workers

While the reaction of the 1,4,2,5-diazadiborinine with Ph groups attached to the boron atoms with $\text{AgAl}\{\text{OC}(\text{CF}_3)_3\}_4$ afforded a complex mixture, the same reaction with Mes-substituted derivative yielded the isolable cation radical species **p** which was isolated as a deep red powder in 52% yield (Scheme 14).¹⁸

Scheme 14 Synthesis of the 1,4,2,5-diazadiborinine radical cation by Kinjo and co-workers

The radical species **p** was able to further react with *p*-benzoquinone to generate the light yellow dicationic species **q** in a yield of 59% (Scheme 15). When one equivalent of Ph_3SnH was added to the radical species **p**, one of the boron atoms in **p** abstracted a hydrogen radical from Ph_3SnH to generate the intermediate **r** (Scheme 16). One equivalent of pyridine was subsequently added to generate the colorless monocationic species **s** in a yield of 13% (Scheme 16).

18

Scheme 15 Synthesis of dicationic species **q** by Kinjo and co-workers

Scheme 16 Synthesis of dicationic species **q** by Kinjo and co-workers

2.1.5 1,5,2,4-Diazadiborinines

In 2006, Roesler and co-workers synthesized the first 1,5,2,4-diazadiborinine derivative (Scheme 17).¹⁹ The 1,5,2,4-diazadiborinine ring was observed to be a six π electrons system with the charge localized on the ring framework. One equivalent of (*E*)-*N*, *N'*-bis(2,6-diisopropylphenyl)-*N*-(trimethylsilyl) formimidamide was first added to one equivalent of 1,1-bis(methylchloroboryl)ethane in the presence of trimethylsilyl triflate to generate the zwitterionic ring species **t**. Subsequently, one equivalent of $\text{K}[\text{N}(\text{SiMe}_3)_2]$ was added to the compound **t** for deprotonation to afford 1,5,2,4-diazadiborinine **u**. Compound **u** was further deprotonated with *n*BuLi to generate the lithium salt of the 1,5,2,4-diazadiborinine.

Scheme 17 Synthesis of 1,5,2,4-diazadiborinine ring by Roesler and co-workers

2.1.6 1,2,3,6-Diazadiborinines

Out of all $B_2C_2N_2$ diazadiborinines, the 1,2,3,6-diazadiborinine was the first structure to be isolated despite computational calculations predicting it to be less stable than the 1,3,2,4-diazadiborinine ring by over 50 kcal/mol.^{1,2} Siebert and co-workers successfully isolated the 1,2,3,6-diazadiborinine structure in 1976.^{21,22} One equivalent of 3,4-diethyl-2,5-dimethyl-2,5-dihydro-1,2,5-thiadiborole was added to one equivalent of hydrazine to generate the 1,2,3,6-diazadiborinine compound (Scheme 18). The 1,2,3,6-diazadiborinine was found to react with $(MeCN)_3Cr(CO)_3$ to generate $\eta^6-Cr(CO)_3$ compounds (Scheme 19).

Scheme 18 Synthesis of 1,2,3,6-diazadiborinine ring by Siebert and co-workers

Scheme 19 Synthesis of $\eta^6-Cr(CO)_3$ compounds by Siebert and co-workers

Piers and co-workers synthesized the first polycyclic 1,2,3,6-diazadiborinine in 2003 and 2006 (Scheme 20).^{23,24} One equivalent of 2,2'-

diborabiphenyl precursor was added to one equivalent of pyridazine Lewis bases to generate the polycyclic 1,2,3,6-diazadiborinine species **v**, **w** and **x**.

Scheme 20 Synthesis of polycyclic 1,2,3,6-diazadiborinine compounds by Piers and co-workers

2.2 Results and Discussion: 1,3,2,5-diazadiborinine with Mes and Ph on boron centers respectively

2.2.1 Objective to synthesize the 1,3,2,5-diazadiborinine with Mes and Ph on boron centers

Figure 3 Present work

Our initial attempt to react **1,3,2,5 b** with small molecules such as hydrogen (H₂), selenium (Se), sulfur (S) did not yield any crystals of the products suitable for x-ray diffraction studies, which hampered the investigation of the reactivity of **1,3,2,5 b**. To circumvent the issue, we designed a 1,3,2,5-diazadiborinine featuring a bulkier mesityl group at one of the boron centers in the aim to increase the kinetic stability and crystalline property of the products after small molecule activation (Fig 3). In chapter 2.2, we present the synthesis, isolation, and characterization of compound **4**.

2.2.2 Synthesis and Discussion of the 1,3,2,5-diazadiborinine with Mes and Ph on boron centers respectively

Two equivalents of 4,4-dimethyl-2-oxazoline **1** were added to a stoichiometric amount of *n*BuLi in THF at -78°C . Another one equivalent of dichlorophenylborane was subsequently added to the mixture. The crude compound **2** was used directly for the next step without any purification, which one equivalent of dichloro(mesityl)borane was further added and stirred for one hour at -78°C . After workup, compound **3** was gained as a pale-yellow powder in 57% yield. Compound **3** was fully characterized by the standard spectroscopic means and X-ray crystallography (Fig 4). An addition of six-fold excess of potassium graphite to compound **3** in anhydrous toluene generated the 1,3,2,5-diazadiborinine **4** (Fig 5) as a white powder in 62% yield (Scheme 21).

Scheme 21 Synthesis of the 1,3,2,5-diazadiborinine **4**

Figure 4 The solid-state structure of **3**. Thermal ellipsoids are set at the 50% probability level. All H atoms and solvent molecules are omitted for clarity.

Figure 5 The solid-state structure of **4**. Thermal ellipsoids are set at the 50% probability level. All H atoms and solvent molecules are omitted for clarity.

The ^{11}B NMR spectrum of **4** in C_6D_6 displayed a singlet at 7.3 ppm and 25.2 ppm, which are shifted downfield compared with those (−11.0 ppm and 4.15 ppm) of **3**. The calculated ^{11}B NMR chemical shift (25.5 ppm and 7.10 ppm) of **4** by the gauge-independent atomic orbital (GIAO) method at the B3LYP/6-311G(d,p) level of theory reasonably agrees with the experimental value (Table 1).

		Isotropic Values	Calculated $\delta (^{11}\text{B})[\text{ppm}]$	Experimental $\delta (^{11}\text{B})[\text{ppm}]$
3	B1	98.2190	5.1989	4.15
	B2	114.9542	−11.5363	−11.0
4	B1	77.9557	25.4622	25.2
	B2	96.3155	7.1024	7.31
BF₃.Et₂O (Reference)		103.4179	-	-

Table 1 Experimental and calculated ^{11}B NMR chemical shifts of compounds **3** and **4**.

Crystallographic studies revealed that the $\text{B}_2\text{C}_2\text{N}_2$ six membered ring of compound **4** is essentially planar, in which the boron atoms display trigonal-planar geometry with the N2-B1-N1 bond angle of $114.92(12)^\circ$ and the C6-B2-C1 bond angle of $108.58(11)^\circ$. The B1–N1 [$1.4415(18) \text{ \AA}$], B1–N2 [$1.4352(18) \text{ \AA}$], B2–C1 [$1.4936(19) \text{ \AA}$] and B2–C6 [$1.4947(19) \text{ \AA}$] distances in **4** are shorter than $1.588\text{--}1.590(6) \text{ \AA}$ and $1.602(7)\text{--}1.612(6) \text{ \AA}$ in compound **3**, respectively (Table 2). The B–C and B–N bonds also lie between values of $1.47\text{--}1.50 \text{ \AA}$ and

1.43-1.46 Å, respectively.^{6-9,15-17} The N–C bonds in **4** (N1–C6: 1.3758(16) Å, N2–C1: 1.3813(16) Å) are only slightly elongated when compared to those (N–C: 1.288(6) Å and 1.293(6) Å) in **3**. These structural properties suggest the delocalization of 6 π electrons over the B₂C₂N₂ 6-membered ring.

Bond (Å)	X-ray data	Optimized structure	WBI Value
B1-N1	1.4415(18)	1.4414	0.9285
B1-N2	1.4352(18)	1.4350	0.9284
B2-C1	1.4936(19)	1.4936	1.2142
B2-C6	1.4947(19)	1.4948	1.2144
N1-C6	1.3758(16)	1.3759	1.1320
N2-C1	1.3813(16)	1.3814	1.1321

Table 2 Selected bond lengths and Wiberg Bond Index (WBI) for the optimized geometries of compound **4**. To gain insight into the electronic property

of compound **4**, theoretical calculations were carried out using a DFT method at the B3LYP/6-311G(d,p) level of theory. The HOMO of **4** is mainly dominated by the π system over the $B_2C_2N_2$ six-membered ring with a node between the NBN and CBC π units and encompasses some contribution from the N lone pairs of the oxazoline components (Fig 6). The LUMO of **4** consists of N–C π bonding interactions with the contribution from the O lone pairs and the π orbitals of the Mes ring (Fig 7).

Figure 6 Top view (left) and side view (right) of the HOMO of **4**

Figure 7 Top view (left) and side view (right) of the LUMO of **4**

The Wiberg bond index (WBI) values of B2–C1 (1.21), B2–C6 (1.21), C6–N1 (1.13), C1–N2 (1.13) suggest the partial multiple-bond nature of these bonds (Table 2), supporting the delocalization of π electrons over the central ring. Natural population analysis shows that B1 has a charge of +0.98 while B2 has a charge of +0.18.

The nucleus-independent chemical shift (NICS) values of **4** (NICS (0): –5.9, NICS (1): –5.0) are less negative than those of **1,4,2,5 n** (NICS (0): –8.2, NICS(1): –8.0) and benzene (NICS(0): –8.0, NICS(1): –10.2) but comparable to the **1,3,2,5 d** (NICS(0): –6.8, NICS(1): –6.4). This suggests that compound **4** features weaker aromatic character compared to **1,4,2,5 n**, but comparable to that of **1,3,2,5 d**. While the NICS values in general allow the comparison among

similar compounds, it would not be conclusive to characterize the aromaticity of 1,3,2,5-diazadiborinine ring,²⁵ because the oxazoline rings adjacent to the central B₂C₂N₂ ring in compound **4** will contribute to the global induced ring current. Therefore, we employed the anisotropy of the current (induced) density (ACID) method in addition to the NICS method to evaluate the aromaticity of the 1,3,2,5-diazadiborinine ring in compound **4**.²⁶

The ACID isosurfaces of **4** were further separated into σ and π contribution. The ACID plot concentrating on the π molecular orbital interactions of **4** demonstrates a 6π conjugation (Fig 8), which indicates an aromatic character

Figure 8 (a)The ACID plot of compound **4**, (b) The selected π MOs (MO 111, 109 and 106) used for the ACID plot.

The natural resonance theory (NRT) calculations demonstrate the percentage composition of each possible Lewis structure of the parent 1,3,2,5-

diazadiborinine ring. Among the various calculated Lewis structures, Table 3 presents the Lewis structures that are most relevant for the analysis of the reactivity towards the boron centers of the 1,3,2,5-diazadiborinine ring. The natural resonance theory (NRT) calculations of **4** demonstrates that the two spectroscopically inequivalent boron atoms in the 1,3,2,5 diazadiborinine ring can act as nucleophilic or electrophilic centers, respectively (Table 3). Therefore compound **4** possess independent boron active sites which one boron behaves as a Lewis acid center and the other boron as the Lewis base center.

Table 3 Natural Resonance Theory structures and the percentage composition

NRT Structures	Percentage composition	NRT Structures	Percentage composition
	2.08%		0.31%
	7.52%		0.20%
	0.31%		0.20%
	0.31%		0.20%
	0.31%		0.20%

2.3 Results and Discussion: 1,3,2,5-diazadiborinine with Ph and Cl on boron centers respectively

2.3.1 Objective to synthesize the 1,3,2,5-diazadiborinine with Ph and Cl on boron centers

Figure 9 Present work

Our initial attempt to react **1,3,2,5 d** with white phosphorus (P_4) did not yield any crystals of the product suitable for x-ray diffraction studies, which hampered the investigation of the reactivity of **1,3,2,5 d**. To circumvent the issue, we designed a derivative with methyl groups at the annulated rings to tune the physical properties of the $B_2C_2N_2$ six membered ring in the aim to increase the solubility and crystalline property of the products after activation with white phosphorus (Fig 9). In chapter 2.3, we present the synthesis, isolation, and characterization of compound **9**.

2.3.2 Synthesis and Discussion of the 1,3,2,5-diazadiborinine with Ph and Cl on boron centers

Two equivalents of 1-mesityl-4,5-dimethyl-1H-imidazole **5** were added to a stoichiometric amount of *n*BuLi in toluene (Scheme 22). The subsequent addition of 1.05 equivalents of N(*i*Pr)₂BCl₂ in ether yielded compound **6**. The mixture was filtered to remove LiCl salts and subjected to vacuum to remove the solvents present. One equivalent of dichlorophenylborane was then added to the solution of compound **6** in DCM. Without any further purification, two equivalents of HCl in ether were added to the crude mixture of compound **7** to generate compound **8**. Reduction of compound **8** with two equivalents of potassium graphite (KC₈) in THF proceeded slowly over 24 hours to obtain 1,3,2,5-diazadiborinine **9**, which was further confirmed by x-ray diffraction studies (Fig 10).

Scheme 22 Synthesis of the 1,3,2,5-diazadiborinine **9**

The ^{11}B NMR spectrum of **9** in THF displayed a singlet at 9.66 ppm (B2) and 23.21 ppm (B1), which are shifted downfield compared with that of **8** (−6.59 ppm and 3.71 ppm). (Table 4).

Figure 10 The solid-state structure of **9**. Thermal ellipsoids are set at the 50% probability level. All H atoms and solvent molecules are omitted for clarity

		Isotropic Values	Calculated δ (^{11}B)[ppm]	Experimental δ (^{11}B)[ppm]
9	B1	92.1102	11.31	9.66
	B2	80.1171	23.30	23.21
BF₃.Et₂O (Reference)		103.4179	-	-

Table 4 Experimental and calculated ^{11}B NMR chemical shifts of compound **9**. In the solid-state structure, compound **9** exhibits a nearly planar

B₂C₂N₂ six-membered ring. Two boron centers are inequivalent and adopt a trigonal planar geometry (the sum of the bond angles: B1 = 359.9° and B2 = 360.0°). The B–C bond (B1–C1: 1.477 Å, B1–C2: 1.477 Å) and B–N bond (B2–N1: 1.440 Å, B2–N2: 1.445 Å) distances in **9** lie between the ranges of 1.47-1.50 Å for B-C bonds and 1.43-1.46 Å for B-N bonds.^{6-9,15-17} The N–C bonds in **9** are (N2–C2: 1.415 Å, N1–C1: 1.410 Å). Wiberg bond index (WBI) values of B1–C1 (1.20), B1–C4 (1.20), B2–N1 (0.949), B2–N2 (0.949), C1–N1 (1.10), C2–N2 (1.10) suggest the partial multiple-bond nature of these bonds. These metric data indicate a delocalization of π electrons over the central six-membered ring.

Bond (Å)	X-ray data	Optimized structure	WBI Value
B1-C1	1.4774	1.48803	1.1995
B1-C2	1.4766	1.48810	1.1994
B2-N1	1.4395	1.44680	0.9492
B2-N2	1.4451	1.44679	0.9492

N1-C1	1.4097	1.40806	1.0957
N2-C2	1.4147	1.40797	1.0957

Table 5 Selected bond lengths and Wiberg Bond Index (WBI) for the optimized geometries of compound **9**.

The UV/Vis absorption spectrum of **9** exhibits the maximum absorption band at a wavelength of 405 nm, which is hypsochromically shifted in comparison with those of **1,4,2,5 n** (496 nm) and **1,3,2,5 d** (420 nm).^{9,15} The experimental maximum absorption band (Fig 11) is in reasonable agreement with the computed UV/Vis absorption spectroscopy with the time dependent DFT (TD-DFT) method at the B3LYP/6-311G(d,p) level. The computed maximum absorption band appears at 337 nm (Fig 12), in line with the experimental value at 405 nm.

Figure 11 UV Vis absorption spectrum of **9** in benzene

Figure 12 Calculated UV Vis absorption spectrum of **9** by TD-DFT at B3LYP/6-311G(d,p) level of theory

To gain insight into the electronic property of compound **9**, theoretical calculations were carried out using a DFT method at the B3LYP/6-311G(d,p) level of theory. The HOMO of **9** is mainly dominated by the π system over the $B_2C_2N_2$ six membered ring with a node between the NBN and CBC π units and encompasses some contribution from the N lone pairs and the C=C moieties of the annulated rings (Fig 13). The LUMO of **9** consists of π -orbitals of the phenyl ring (Fig 14).

Figure 13 Side view (left) and top view (right) of the HOMO of **9**

Figure 14 Side view (left) and top view (right) of the LUMO of **9**

The HOMO–LUMO energy gap (3.18 eV) of **9** is slightly larger than that (2.84 eV) of **1,4,2,5 n**. Natural population analysis shows that the two boron atoms are inequivalent with a different charge of + 0.21 and + 0.88 for B1 and B2, respectively. The nucleus-independent chemical shift (NICS) values of **9** (NICS (0): –6.1, NICS (1): –6.6) are comparable to those of **1,4,2,5 n** (NICS(0): –8.2, NICS(1): –8.0) but less negative than those of **1,3,2,5 d** (NICS(0): –6.8, NICS(1): –6.4) and benzene (NICS(0): –8.0, NICS(1): –10.2).

The ACID isosurfaces of **9** were separated into σ and π contribution. The current density vectors on the ACID isosurfaces indicates a strong diatropic ring current in the π system of the 5,6,5 ring. The ACID plot also demonstrates a 12π conjugation (Fig 15) which indicates an anti-aromatic character in **9**. The anti-aromaticity is further supported by the less than unity WBIs of the B–N bonds in compound **9** as compared to other aromatic BN compounds. The WBI of the B–N bond in compound **9** has a value of 0.9492 which is lesser than that of 1.443 in **1,3,2,5 b** and 1.458 in **1,4,2,5 n**.^{6,15}

MO 149

MO 148

MO 146

MO 143

MO 139

MO 137

MO 134

MO 92

MO 90

Figure 15 (a) The ACID plot of compound **9**, (b) The selected π -MOs (MO 149, 148, 146, 143, 139, 137, 114, 92 and 90) used for the ACID plot.

2.4 Results and Discussion: Annulated 1,4,2,5-diazadiborinine with Ph on boron centers

2.4.1 Objective to synthesize the annulated 1,4,2,5-diazadiborinine with Ph on boron centers

Present work :

Figure 16 Present work

The initial attempt to react **1,4,2,5 n** with selenium (Se) did not yield any crystals suitable for x-ray diffraction studies. This hampered the investigation of the reactivity of **1,4,2,5 n**. To circumvent the issue, we designed a new 1,4,2,5-diazadiborinine derivative bearing bulky aryl groups on the annulated diazadiborinine skeleton (Fig 16), to increase the selectivity of the reaction as well as the stability of the product. Given that the previous reaction pathway to generate **1,4,2,5 n** is complicated and involves several steps (Scheme 12), we explored a more efficient and straightforward synthetic pathway to 1,4,2,5-diazadiborinines. In chapter 2.4, we present the synthesis, isolation, and characterization of compound **12**.

2.4.2 Synthesis and Discussion of the annulated 1,4,2,5-diazadiborinine with Ph on boron centers

After vast investigation of the synthetic strategy, the most efficient route to 1,4,2,5-diazadiborinines has been established (Scheme 23). Two equivalents of 1-mesityl-4,5-diphenylimidazol **10** were added to a stoichiometric amount of *n*BuLi in toluene. The subsequent addition of two equivalents of dichlorophenylborane in ether yielded a mixture involving a major product and a minor product (Fig 55), from which 2,5-dichloro-1,4,2,5-diazadiborinine derivative **11** was obtained in 68% yield. Compound **11** was fully characterized by the standard spectroscopic means and X-ray crystallography (Fig 17). Reduction of **11** with an excess amount of potassium graphite (KC₈) in toluene proceeded slowly over 24 hours. After workup, 1,4,2,5-diazadiborinine **12** was obtained as a red powder in 61% isolated yield.²⁴

Scheme 23 Synthesis of the annulated 1,4,2,5-diazadiborinine with Ph on boron centers

The ^{11}B NMR spectrum of **12** in C_6D_6 displayed a singlet at 10.28 ppm, which is shifted downfield compared with that (-0.89 ppm) of **11**. The calculated ^{11}B NMR chemical shift (19.9 ppm) of **11** by the gauge-independent atomic orbital (GIAO) method at the B3LYP/6-311G(d,p) level of theory reasonably agrees with the experimental value (Table 6). In the ^1H NMR of **11**, only two signals for the methyl groups of the mesityl groups were observed at 1.89 ppm and 2.22 ppm, indicative of the symmetric feature of **12**, which was further confirmed by the X-ray diffraction study (Fig 18).

Figure 17 The solid-state structure of **11**. Thermal ellipsoids are set at the 50% probability level. All H atoms and solvent molecules are omitted for clarity.

Figure 18 The solid-state structure of **12**. Thermal ellipsoids are set at the 50% probability level. All H atoms and solvent molecules are omitted for clarity

	Isotropic Values	Calculated δ (^{11}B) [ppm]	Experimental δ (^{11}B) [ppm]
11	104.0800	-0.6621	-0.89
	104.0803	-0.6624	
12	83.4751	19.9	10.28
	83.4775	19.9	
BF₃.Et₂O (Reference)	103.4179	-	-

Table 6 Experimental and calculated ^{11}B NMR chemical shifts of compounds **11** and **12**

In the solid-state structure, compound **12** exhibits pseudo C_2 -symmetry involving the nearly planar $\text{B}_2\text{C}_2\text{N}_2$ six-membered ring. Two boron centers are formally equivalent and adopt a trigonal planar geometry (the sum of the bond angles: $\text{B1} = 359.2^\circ$ and $\text{B2} = 359.5^\circ$). Both the B–N bond (B1–N1 : $1.457(4)$ Å,

B2–N3: 1.462(4) Å) and B–C bond (B1–C1: 1.496(4) Å, B2–C2: 1.494(4) Å) distances in **12** are shorter than those of **11** (B–N: 1.566(2) Å, B–C: 1.620(2) Å) and lie between the ranges of 1.47-1.50 Å for B-C bonds and 1.43-1.46 Å for B-N bonds.^{6-9,15-17} The N–C bonds in **12** (N3–C1: 1.407(3) Å, N1–C2: 1.406(3) Å) are only slightly elongated when compared to those (N–C: 1.346(2) Å) in **11** (Table 7). Wiberg bond index (WBI) values of B1–C1 (1.19), B2–C2 (1.19), C2–N1 (1.12), C1–N3 (1.12) suggest the partial multiple-bond nature of these bonds. These metric data indicate a delocalization of π electrons over the central six-membered ring.

Bond (Å)	X-ray data	Optimized structure	WBI Value
B1-N1	1.457(4)	1.4574	0.9144
B1-C1	1.496(4)	1.4960	1.1868
B2-N3	1.462(4)	1.4624	0.9144
B2-C2	1.494(4)	1.4942	1.1867
N3-C1	1.407(3)	1.4073	1.1223
N1-C2	1.406(3)	1.4058	1.1223

Table 7 Selected Bond Lengths and Wiberg Bond Index (WBI) for the optimized geometries of compound **12**.

The UV/Vis absorption spectrum of **12** exhibits the maximum absorption band at a wavelength of 533 nm, which is bathochromically shifted in comparison with those of (496 nm) of **1,4,2,5 n** and (420 nm) of **1,3,2,5 d**.^{9,15} The experimental maximum absorption band (Fig 19) is in reasonable agreement with the computed UV/Vis absorption spectroscopy with the time dependent DFT (TD-DFT) method at the B3LYP/6-311G(d,p) level. The computed maximum absorption band appears at 528 nm (Fig 20). This is in line with the experimental value at 533 nm.

Figure 19 UV Vis absorption spectrum of **12** in toluene

Figure 20 Calculated UV Vis absorption spectrum of **12** by TD-DFT at B3LYP/6-311G(d,p) level of theory

To gain insight into the electronic property of compound **12**, theoretical calculations were carried out using a DFT method at the B3LYP/6-311G(d,p) level of theory. The HOMO of **12** is mainly dominated by the π system over the $B_2C_2N_2$ six membered ring with a node between the two CBN π units and encompasses some contribution from the N lone pairs and the C=C moieties of the annulated rings (Fig 21). The LUMO of **12** is a π -type orbital that consists of C–B and N–C π bonding interactions with the contribution from the N lone pairs and the π orbitals of the phenyl rings (Fig 22).

Figure 21 Side view (left) and top view (right) of the HOMO of **12**

Figure 22 Side view (left) and front view (right) of the LUMO of **12**.

The HOMO–LUMO energy gap (2.60 eV) of **12** is slightly smaller than that (2.84 eV) of **1,4,2,5 n**. Natural population analysis shows that the two boron atoms possess the same charge of +0.57.

The nucleus-independent chemical shift (NICS) values of **12** (NICS (0): –6.2, NICS (1): –6.7) are comparable to those of **1,4,2,5 n** (NICS(0): –8.2, NICS(1): –8.0) but less negative than those of **1,3,2,5 d** (NICS(0): –6.8, NICS(1): –6.4) and benzene (NICS(0): –8.0, NICS(1): –10.2). While the NICS values in general allow the comparison among similar compounds, it would not be conclusive to characterize the aromaticity of 1,4,2,5-diazadiborinine ring,²⁵ because the annulated aromatic rings adjacent to the central B₂C₂N₂ ring in compound **12** will contribute to the global induced ring current. Therefore, we employed the anisotropy of the current (induced) density (ACID) method in addition to the NICS method to evaluate the aromaticity of the 1,4,2,5-diazadiborinine ring in compound **12**.²⁶ The ACID isosurfaces of **12** were separated into σ and π contribution. The current density vectors on the ACID isosurfaces demonstrate a strong diatropic ring current in the π system of the 5,6,5 ring. The ACID plot also demonstrates a 12π conjugation (Fig 23) which indicates an anti-aromatic character in **12**. The anti-aromaticity is further supported by the less than unity WBIs of the B–N bonds in compound **12** as compared to other aromatic BN compounds. The WBI of the B–N bond in compound **12** has a value of 0.9144 which is lesser than that of 1.443 in **1,3,2,5 b** and 1.458 in **1,4,2,5 n**.^{6,15}

The natural resonance theory (NRT) calculations of **12** demonstrates that each of the two boron atoms in the 1,4,2,5 diazadiborinine ring can act as both nucleophilic and electrophilic centers (Table 8). This results in the presence of a single boron active site with ambiphilic nature, which could be useful to investigate novel reactivity.

Figure 23 (a) The ACID Plot of **12** (b) The selected π MOs (MO 225, 224, 222, 208, 207, 205 and 203) used for the ACID plot.

NRT Structures

Percentage composition

3.29%

3.29%

3.29%

3.29%

Table 8 Natural Resonance Theory structures and the percentage composition

2.5 Conclusion

In conclusion, we have successfully developed three novel diazadiborinine derivatives (compound **4**: 1,3,2,5-diazadiborinine with Mes and Ph groups on boron atoms, compound **9**: 1,3,2,5-diazadiborinine with Ph and Cl groups on boron atoms, compound **12**: 1,4,2,5-diazadiborinine with Ph group on boron atoms).

Compounds **4**, **9** and **12** were fully characterized by NMR spectroscopic and x-ray diffraction studies. NMR shielding tensors for compounds **4**, **9** and **12** were computed with the Gauge-Independent Atomic Orbital (GIAO) method at the B3LYP/6-311G(d,p) level for the comparison of the experimental and computed boron spectroscopic values. The computed NMR values agreed well with those of the experimental values. This supports the feasibility of the reaction route developed to synthesize the diazadiborinines and will be useful to widen the scope of the diazadiborinines for future reactivity studies.

The molecular orbital analysis for compound **4**, **9** and **12** was conducted, which indicated that the six π electrons are delocalized over the 1,3,2,5 and 1,4,2,5-diazadiborinine ring, respectively. DFT calculations were subsequently performed at the B3LYP/6-311G(d,p) level of theory to gain insight into the electronic features of compound **4**, **9** and **12**. The nucleus independent chemical shifts (NICS) was conducted and the relatively moderate negative NICS values show that the aromaticity of the B₂C₂N₂ ring in compounds **4**, **9** and **12** are moderate as compared to that of benzene. Taking into consideration the effects of the annulated rings beside the central B₂C₂N₂ ring, the anisotropy of the

induced current density (ACID) method was further utilized for the analysis of the aromatic features of the $B_2C_2N_2$ ring in compounds **4**, **9** and **12**. The ACID plots indicate the aromatic character of compounds **4**, **9** and **12**. Strong aromatic character is known to stabilize compounds and provide biochemical or industrial uses. Thus, the aromaticity in compounds **4**, **9** and **12** could possibly enhance its stability for experimental deductions in the later part of the reactivity investigations.

The Natural resonance theory (NRT) studies was performed and various structures with its percentage composition were generated. With respect to compounds **4** and **9**, it is likely when one boron behaves as a Lewis acid, the other boron takes up a Lewis base character through the interaction of the π system. Whereas for compound **12**, a single boron active site with ambiphilic nature exists. With the electronic properties in mind, we seek to further explore novel reactivity reactions.

All DFT calculations had been performed by the Ph.D. candidate Gillian Goh Kor Hwee.

2.6 Experimental Section

2.6.1 Synthesis, physical and spectroscopic data for all new compounds

Materials and Method: All reactions were performed in an atmosphere of nitrogen or argon by using standard Schlenk or dry box techniques; solvents were dried with Na metal and K metal. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra were obtained with either Bruker Avance 300 MHz AV300, AV 500 or AVIII 400 MHz BBFO1, BBFO2 and ECA400 spectrometers at 298 K. Coupling constants J are given in Hz. Chemical shifts (δ) are given in p.p.m. 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. Ultraviolet spectra were recorded on Cary 100 UV-Vis spectrometer.

Synthesis of **3**:

To a solution of 4,4 dimethyl-2oxazoline **1** (1.00 ml, 9.48 mol) in THF (50 ml) was added $n\text{BuLi}$ (2.5M in hexane, 4.00 mL, 10 mmol) in a dropwise manner at -78°C . The mixture was then stirred at -78°C for one hour before the dropwise addition of dichlorophenylborane (0.62 ml, 4.78 mmol). The mixture was subsequently stirred at -78°C for another one hour before slowly raising it to

room temperature. It was left to stir overnight at room temperature to obtain compound **2**. The mixture was filtered to remove all the insoluble material before evaporating the THF to dryness. Dichloro(mesityl)borane (0.95g, 4.73 mmol) was added dropwise to compound **2** in toluene (50 ml) at -78°C . The mixture was stirred for one hour before rising slowly to room temperature and allowing it to stir for another 48 hours. The crude mixture **3** was subjected to filtration before evaporating the solvent to dryness. The residue was washed with hexanes (20 mL), and then dried under vacuum to afford **3** (2.62 g, 5.40 mmol) as a light-yellow powder (57%). Colorless single crystals of **3** were obtained by recrystallization from a toluene solution at ambient temperature.

M.p.: 213°C . ^1H NMR (400 MHz, C_6D_6): δ = 8.25 (d, $J=7.2$ Hz, 1H), 7.43 (t, $J=7.6$ Hz, 1H), 7.04-7.00 (m, 3H), 6.82 (s, 1H), 6.66 (s, 1H), 3.28 (d, $J=8.8$ Hz, 2H), 3.20 (d, $J=8.8$ Hz, 2H), 3.01 (s, 3H), 2.11 (s, 6H), 1.22 (s, 6H), 0.48 (s, 6H) ppm; ^{11}B NMR (400 MHz, C_6D_6): δ -11.1, 4.10 ppm; ^{13}C NMR (300 MHz, C_6D_6): 137.64 (CH-Ar), 137.44 (CH-Ar), 132.95 (C-Ar), 132.25 (C-Ar), 130.50 (C-Ar), 125.44 (C-Ar), 81.63 (CH-Ar), 68.30 (C-Ar), 27.47 (CH-Ar), 26.58 (CH-Ar), 24.81 (CH-Ar), 24.74 (CH-Ar).

Synthesis of **4**:

A mixture of **3** (1.00 g, 2.06 mmol) and KC_8 (1.67 g, 12.4 mmol) in toluene (15 mL) was stirred at room temperature overnight. After filtration, all volatiles were removed under vacuum to afford **4** (0.53 g, 1.28 mmol) as a light-yellow powder (62%). Light yellow single crystals of **4** were obtained by recrystallization from a toluene solution at ambient temperature.

M.p.: 155 °C. ^1H NMR (300 MHz, C_6D_6): δ = 8.85 (d, J =7.0 Hz, 2H), 7.64 (t, J =6.6 Hz, 2H), 7.34 (s, 1H), 6.72 (s, 2H), 3.65 (s, 4H), 2.15 (s, 3H), 2.03 (s, 6H), 0.85 (s, 12H) ppm; ^{11}B NMR (400 MHz, C_6D_6): δ 25.2, 7.31 ppm; ^{13}C NMR (300 MHz, C_6D_6): 140.87 (C-Ar), 134.69 (CH-Ar), 127.92 (CH-Ar), 127.68 (CH-Ar), 127.44 (CH-Ar), 124.92 (CH-Ar), 80.67 (CH-Ar), 62.93 (C-Ar), 25.67 (CH-Ar), 24.64 (CH-Ar), 20.88 (CH-Ar). HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{32}\text{B}_2\text{N}_2\text{O}_2$: 415.2726 [$(M + H)$] $^+$; found: 415.2728.

Synthesis of **6**:

To a toluene (10 mL) solution of 1-mesityl-4,5-dimethyl-1H-imidazole **5** (1.0 g, 4.67 mmol), $n\text{BuLi}$ (2.0M in hexane, 2.32 mL, 4.64 mmol) was added dropwise at -78 °C. The solution was stirred at -78 °C for five hours, and then $\text{N}(\text{iPr})_2\text{BCl}_2$ (0.42 mL, 2.34 mmol) in ether (1.76 mL) was added to the reaction mixture. The solution was gradually warmed up to -20 °C over 3 hours. After the insoluble residue was filtered off, all volatiles were removed under vacuum to afford a

yellowish green powder. The residue was washed with hexanes (20 mL), and then dried under vacuum to afford **6** (0.88 g, 1.64 mmol) as a yellow powder (69%).

M.p.: 141 °C. ^1H NMR (400 MHz, C_6D_6): δ = 6.80 (s, 4H), 4.13 (t, J =6.8 Hz, 2H), 2.30 (s, 6H), 2.13 (s, 6H), 1.79 (s, 12H), 1.71 (s, 6H), 1.17 (d, J =7.2 Hz, 12H) ppm; ^{11}B NMR (400 MHz, CDCl_3): δ 30.1 ppm; ^{13}C NMR (400 MHz, C_6D_6): 137.09 (C-Ar), 136.17 (C-Ar), 134.48 (C-Ar), 133.89 (C-Ar), 128.88 (CH-Ar), 122.94 (C-Ar), 50.94 (CH-Ar), 24.45 (CH-Ar), 20.72 (CH-Ar), 17.95 (CH-Ar), 13.23 (CH-Ar), 8.43 (CH-Ar).

Synthesis of **7**:

To a DCM (10 mL) solution of **6** (0.88 g, 1.64 mmol), dichlorophenylborane (0.34 mL, 2.62 mmol) was added to the reaction mixture at -60 °C. The solution was gradually warmed up to room temperature over 4 hours. After the insoluble residue was filtered off, all volatiles were removed under vacuum to afford a light-yellow powder **7** (0.72 g, 1.03 mmol) (63%).

M.p.: 189 °C. ^1H NMR (400 MHz, C_6D_6): δ = 7.63 (t, J =7.4 Hz, 3H), 7.47 (t, J =7.6 Hz, 4H), 7.12 (d, J =2.8 Hz, 2H), 3.76 (quin, 2H), 2.34 (s, 6H), 2.09 (s, 6H), 1.90 (s, 6H), 1.82 (s, 6H), 1.54 (s, 6H), 1.18 (d, J =7.2 Hz, 6H), 0.44 (d, J =7.2

Hz, 6H) ppm; ^{11}B NMR (400 MHz, CDCl_3): δ 29.88, c3.17 ppm; ^{13}C NMR (400 MHz, C_6D_6): 141.25 (C-Ar), 134.73 (C-Ar), 134.47 (C-Ar), 133.68 (C-Ar), 133.31 (C-Ar), 131.18 (C-Ar), 130.99 (CH-Ar), 130.69 (CH-Ar), 130.48 (C-Ar), 128.49 (CH-Ar), 128.35 (CH-Ar), 53.58 (CH-Ar), 24.06 (CH-Ar), 18.58 (CH-Ar), 18.09 (CH-Ar), 12.59 (CH-Ar), 9.18 (CH-Ar).

Synthesis of **8**:

To a DCM (10 mL) solution of **7** (0.72 g, 1.03 mmol), HCl in ether (2.0M, 1.03 mL, 2.06 mmol) was added to the reaction mixture at $-60\text{ }^{\circ}\text{C}$. The solution was gradually warmed up to room temperature over 12 hours. All volatiles were removed under vacuum to afford a white powder **8** (0.48 g, 0.77 mmol) (75%).

M.p.: $185\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, C_6D_6): δ = 8.12 (d, $J=6.8\text{ Hz}$, 2H), 7.34 (t, $J=7.6\text{ Hz}$, 2H), 7.20 – 7.18 (m, 1H), 6.68 (d, $J=3.6\text{ Hz}$, 4H), 2.10 (s, 6H), 2.06 (s, 6H), 2.05 (s, 6H), 2.00 (s, 6H), 1.23 (s, 6H) ppm; ^{11}B NMR (400 MHz, CDCl_3): δ 3.71, -6.59 ppm; ^{13}C NMR (400 MHz, C_6D_6): 138.66 (C-Ar), 136.59 (C-Ar), 136.03 (C-Ar), 133.26 (CH-Ar), 132.00 (C-Ar), 20.71 (CH-Ar), 18.53 (CH-Ar), 11.52 (CH-Ar), 7.38 (CH-Ar).

Synthesis of **9**:

A mixture of **8** (0.08 g, 0.13 mmol) and KC_8 (0.035 g, 0.26 mmol) in THF (3 mL) was stirred at $-10\text{ }^\circ\text{C}$ for 5 hours before raising the mixture to room temperature overnight. After filtration, all volatiles were removed under vacuum to afford **9** (0.044 g, 0.078 mmol) as an orange powder (60%).

M.p.: $168\text{ }^\circ\text{C}$. ^1H NMR (400 MHz, C_6D_6): $\delta = 7.25$ (d, $J=8.0$ Hz, 2H), 7.20 (d, $J=8.0$ Hz, 1H), 7.07 (t, $J=8.0$ Hz, 2H), 6.77 (s, 4H), 2.10 (s, 6H), 2.13 (s, 18H), 1.72 (s, 6H), 1.60 (s, 6H) ppm; ^{11}B NMR (400 MHz, C_6D_6): δ 9.66, 23.21 ppm; ^{13}C NMR (400 MHz, C_6D_6): 137.89 (C-Ar), 137.61 (C-Ar), 135.16 (C-Ar), 135.00 (CH-Ar), 128.30 (CH-Ar), 128.06 (CH-Ar), 127.82 (CH-Ar), 118.85 (CH-Ar), 21.16 (CH-Ar), 18.23 (CH-Ar), 13.97 (CH-Ar), 8.87 (CH-Ar).

Synthesis of **11**:

To a toluene (10 mL) solution of 1-Mesityl-4,5-diphenyl-2-imidazole (1.0 g, 0.282 mmol), $n\text{BuLi}$ (2.5M in hexane, 1.29 mL, 0.322 mmol) was added

dropwise at $-78\text{ }^{\circ}\text{C}$. The solution was stirred at $-78\text{ }^{\circ}\text{C}$ for five hours, and then dichlorophenylborane (0.19 mL, 0.282 mmol) in ether (1.76 mL) was added to the reaction mixture. The solution was gradually warmed up to room temperature over 14 hours. After the insoluble residue was filtered off, all volatiles were removed under vacuum to afford a yellowish green powder. The residue was washed with hexanes (20 mL), and then dried under vacuum to afford **11** (0.68 g, 0.738 mmol) as a white powder (68%). Colorless single crystals of **11** were obtained by recrystallization from a toluene solution at ambient temperature.

M.p.: $159\text{ }^{\circ}\text{C}$. ^1H NMR (400 MHz, CD_2Cl_2): 7.08 – 7.05 (m, 4H, ArH), 7.01 – 6.97 (m, 4H, ArH), 6.95 – 6.92 (m, 12H, ArH), 6.89 (s, 2H, ArH), 6.85 (d, 4H, , $J = 0.9\text{ Hz}$, ArH), 6.30 (s, 2H, ArH), 2.26 (s, 6H, CH_3), 2.16 (s, 6H, CH_3), 0.94 (s, 6H, CH_3). ^{11}B NMR (128 MHz, CD_2Cl_2): -0.89 (s). ^{13}C NMR (100 MHz, C_6D_6): 138.32 (C-Ar), 137.45 (C-Ar), 136.24 (C-Ar), 134.98 (C-Ar), 134.86 (C-Ar), 134.14 (CH-Ar), 132.65 (CH-Ar), 132.42 (CH-Ar), 132.22 (CH-Ar), 130.12 (C-Ar), 132.08 (CH-Ar), 128.22 (CH-Ar), 128.19 (CH-Ar), 128.03 (CH-Ar), 127.37 (CH-Ar), 127.14 (CH-Ar), 126.63 (C-Ar), 126.39 (C-Ar), 125.92 (CH-Ar), 125.50 (CH-Ar), 20.60 (CH_3 -Ar), 19.83 (CH_3 -Ar), 16.86 (CH_3 -Ar). HRMS (ESI): m/z calcd for $\text{C}_{60}\text{H}_{52}\text{B}_2\text{Cl}_2\text{N}_4$: 921.3833 [$(M + H)^+$]; found: 921.3864.

Synthesis of **12**:

A mixture of **11** (0.20 g, 0.022 mmol) and KC_8 (0.018 g, 0.132 mmol) in toluene (15 mL) was stirred at room temperature overnight. After filtration, all volatiles were removed under vacuum to afford **12** (0.12 g, 0.14 mmol) as a red powder (61%). Red single crystals of **12** were obtained by recrystallization from a benzene solution at ambient temperature.

M.p.: 150 °C. ^1H NMR (400 MHz, C_6D_6) δ 7.10 (d, 5H, $J = 7.5\text{Hz}$ ArH), 7.05 (d, 2H, $J = 7.0\text{Hz}$, ArH), 6.92 – 6.90 (m, 4H, ArH), 6.73 (d, 6H, $J = 7.8\text{Hz}$ ArH), 6.96 – 6.57 (m, 5H, ArH), 6.74 (d, 3H, $J = 7.6\text{Hz}$, ArH), 6.58 (d, 3H, $J = 6.8\text{Hz}$, ArH), 6.26 (s, 4H, ArH), 2.22 (s, 12H, CH_3), 1.89 (s, 6H, CH_3). ^{11}B NMR (128 MHz, C_6D_6): 10.28 (s). ^{13}C NMR (100 MHz, C_6D_6): 136.86 (C-Ar), 136.26 (C-Ar), 134.85 (C-Ar), 134.55 (CH-Ar), 134.07 (CH-Ar), 133.97 (C-Ar), 133.06 (C-Ar), 132.08 (CH-Ar), 130.32 (CH-Ar), 128.57 (CH-Ar), 128.19 (C-Ar), 127.56 (C-Ar), 127.32 (CH-Ar), 127.23 (CH-Ar), 126.94 (CH-Ar), 126.09 (CH-Ar), 126.65 (C-Ar), 125.50 (C-Ar), 124.42 (CH-Ar), 121.95 (C-Ar), 20.47 (CH_3 -Ar), 18.59 (CH_3 -Ar). HRMS (ESI): m/z calcd for $\text{C}_{60}\text{H}_{52}\text{B}_2\text{N}_4$: 851.4435 [$(M + H)^+$]; found: 851.4456. UV-vis (ϵ , in toluene): $\lambda = 533\text{ nm}$ (7490), 311 nm (4370).

Figure 24 Electrospray ionization (ESI) mass spectrum of compound **4**

Figure 25 Electrospray ionization (ESI) mass spectrum of compound **11**.

Figure 26 Electrospray ionization (ESI) mass spectrum of compound **12**.

2.6.2 NMR spectra for all new compounds

Figure 27 ¹H NMR spectrum of **3**

Figure 28 ¹¹B NMR spectrum of **3**

Figure 29 ^{13}C NMR spectrum of **3**

Figure 30 ^{13}C NMR (DEPT 135) NMR spectrum of **3**

Figure 31 ¹H NMR spectrum of **4**

Figure 32 ¹¹B NMR spectrum of **4**

Figure 33 ^{13}C NMR spectrum of **4**

Figure 34 ^{13}C NMR (DEPT 135) NMR spectrum of **4**

Figure 35 ¹H NMR spectrum of **6**

Figure 36 ¹¹B NMR spectrum of **6**

Figure 37 ^{13}C NMR spectrum of **6**

Figure 38 ^{13}C (DEPT 135) NMR spectrum of **6**

Figure 39 ¹H NMR spectrum of 7

Figure 40 ¹¹B NMR spectrum of 7

Figure 41 ^{13}C NMR spectrum of **7**

Figure 42 ^{13}C (DEPT 135) NMR spectrum of **7**

Figure 43 ¹H NMR spectrum of **8**

Figure 44 ¹¹B NMR spectrum of **8**

Figure 45 ^{13}C NMR spectrum of **8**

Figure 46 ^{13}C (DEPT 135) NMR spectrum of **8**

Figure 47 ¹H NMR spectrum of **9**

Figure 48 ¹¹B NMR spectrum of **9**

Figure 49 ^{13}C NMR spectrum of **9**

Figure 50 ^{13}C (DEPT 135) NMR spectrum of **9**

Figure 51 ^1H NMR spectrum of **11**

Figure 52 ^{11}B NMR spectrum of **11**

Figure 53 ^{13}C NMR spectrum of **11**

Figure 54 ^{13}C (DEPT 135) NMR spectrum of **11**

Figure 55 ^1H NMR spectrum of crude mixture containing of **11** and a minor product **m** in C_6D_6

Figure 56 ^1H NMR spectrum of **12**

Figure 57 ^{11}B NMR spectrum of **12**

Figure 58 ^{13}C NMR spectrum of **12**

Figure 59 ^{13}C (DEPT 135) NMR spectrum of **12**

2.6.3 Crystallographic data

X-ray data collection and structural refinement. Intensity data for compounds **3**, **4**, **9**, **11** and **12** were collected at 100 K using a Bruker D8 Quest diffractometer. The structures were solved by Intrinsic Phasing (SHELXTL XT-2014)²⁷ and refined for all data by full-matrix least squares methods on F^2 .²⁸ 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: 1902297-1902299 contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif.

Table 9 Summary of Data collection and structure refinement for compounds **3**, **4**, **9**, **11** and **12**

	3	4	9	11	12
Formula	C ₃₂ H ₄₀ B ₂ Cl ₂ N ₂ O ₂	C ₂₅ H ₃₂ B ₂ N ₂ O ₂	C ₃₄ H ₃₉ B ₂ ClN ₄	C ₆₆ H ₅₈ B ₂ Cl ₂ N ₄	C ₆₀ H ₅₂ B ₂ N ₄
Fw	577.18	414.14	560.76	999.68	850.67
Cryst syst	triclinic	orthorhombic	monoclinic	triclinic	triclinic
Space group	P -1	P b c a	P 1 21/n 1	P -1	P -1
Size (mm ³)	0.010 x 0.040 x 0.220	0.060 x 0.080 x 0.120	0.3660 x 2.2370 x 1.2212	0.100 x 0.140 x 0.160	0.040 x 0.220 x 0.240
T/K	103(2)	100(2)	100(2)	100(2)	100(2)
a, Å	9.0850(8)	14.0457(5)	12.3062(2)	8.0320(2)	12.2084(6)
b, Å	11.8106(9)	13.6743(6)	33.6195(5)	12.9483(3)	14.2682(8)
c, Å	15.4649(16)	23.3662(9)	15.0286(3)	13.2734(3)	15.0075(8)
α, deg	87.817(7)	90	90	93.7410(9)	114.4228(17)
β, deg	77.102(8)	90	92.985(1)	92.4577(8)	98.0538(17)
γ, deg	68.485(6)	90	90	104.6101(9)	90.2251(18)
V, Å ³	1503.0(2)	4487.8(3)	6209.32(18)	1330.44(5)	2351.2(2)
Z	2	8	8	1	2
d calcd g.cm ⁻³	1.275	1.226	1.200	1.248	1.202
μ, mm ⁻¹	2.185	0.076	0.153	0.169	0.069
Refl collected	19638	102958	11842	55990	26578
T _{max} /T _{min}	0.9780/0.6450	0.9950/0.9910	0.980/0.880	0.9830/0.9740	0.9970/0.9840
N _{measd}	5270	6038	8839	8530	10210
[R _{int}]	0.1461	0.1110		0.0564	0.1030
R [I>2sigma(I)]	0.0736	0.0444	0.0440	0.0468	0.0665
Rw [I>2sigma(I)]	0.1169	0.0681	0.1086	0.0702	0.1403
	0.959		1.060		1.035
GOF		1.040		1.026	
Largest diff peak /hole[e ⁻ Å ⁻³]	0.472/-0.533	0.304/-0.231	0.273/-0.251	0.363/-0.260	0.258/-0.301

Table 10 The coordinates (XYZ) for various optimized structures **3**,**4**,**9**,**11** and **12**

3

B	0.71607600	0.05431500	0.59962100
B	-2.07041800	-0.21415000	-0.90328400
C	-1.17587700	-1.41275300	-0.31538400
C	-0.73408200	-3.49945300	0.38295500
H	-0.67655500	-4.45194100	-0.14025300
H	-1.14392800	-3.64367200	1.38580100
C	0.58836300	-2.71741400	0.38973200
C	1.45876300	-3.12864100	-0.80823000
H	2.35235700	-2.51079800	-0.87823800
H	0.90286700	-3.05188900	-1.74545000
H	1.76990700	-4.16935600	-0.68054700
C	1.34221600	-2.91141200	1.70323700
H	0.75438500	-2.58174400	2.55853800
H	2.28866600	-2.37225000	1.69724700
H	1.56637200	-3.97620400	1.81845600
C	-1.20734100	1.12874500	-0.71023300
C	-0.67573900	3.28576500	-1.02323300
H	-1.18689300	4.21426400	-0.77726400
H	-0.13457200	3.39444100	-1.96710900
C	0.20738200	2.74937100	0.11301400
C	-0.32258100	3.24676300	1.46881300
H	0.25058300	2.83866500	2.29789700

H	-1.36911300	2.96897200	1.61055000
H	-0.24622800	4.33785700	1.49429400
C	1.66651100	3.15586900	-0.07792300
H	2.29468900	2.79631400	0.73523200
H	1.71939700	4.24903300	-0.08492600
H	2.07896800	2.78710900	-1.01654300
C	2.30883700	0.09839200	0.22418000
C	2.65054300	0.05753700	-1.16228600
C	1.63540000	0.05108100	-2.29144000
H	1.24157500	1.05338600	-2.48509400
H	0.77702500	-0.59075400	-2.11715900
H	2.10783300	-0.28477900	-3.21641800
C	3.98481200	0.05832100	-1.57793400
H	4.19632400	0.02182200	-2.64289500
C	5.04413500	0.10561400	-0.67886400
C	6.47793000	0.06877300	-1.14688300
H	6.80092000	-0.95967300	-1.34261500
H	7.15287100	0.48695400	-0.39685300
H	6.60939200	0.63163100	-2.07457500
C	4.71830300	0.17164600	0.66928200
H	5.52230600	0.22841000	1.39671600
C	3.39722300	0.17591700	1.13970700
C	3.27761200	0.30110200	2.64911600
H	4.27500000	0.38009500	3.08596000
H	2.77683500	-0.55030500	3.10982400
H	2.71198400	1.18439900	2.94831200
C	-3.50181900	-0.07741700	-0.17201100
C	-3.56470700	0.00537500	1.22997900

H	-2.65113500	-0.03220300	1.81684100
C	-4.78040200	0.13738300	1.89796900
H	-4.79723200	0.19542700	2.98135600
C	-5.97049500	0.19266500	1.17574500
H	-6.91947600	0.29380500	1.69137700
C	-5.93003300	0.11572200	-0.21423300
H	-6.85087800	0.15682100	-0.78673100
C	-4.71054300	-0.01605500	-0.87690000
H	-4.69641800	-0.07794800	-1.95849000
Cl	0.23867000	0.15034000	2.48147300
Cl	-2.16855000	-0.54716100	-2.78041100
N	0.03678600	-1.31324900	0.16446300
N	-0.08237700	1.25805600	-0.05310600
O	-1.65584300	-2.64564200	-0.34130400
O	-1.67984500	2.25917100	-1.21188700

4

B	0.70426000	-0.00085500	0.00414500
B	-2.33272700	0.00098100	0.00130500
C	-1.46059200	1.20926100	0.08971400
C	-0.87464400	3.34503300	0.55781000
H	-0.88130200	3.43956100	1.65031100
H	-1.03390000	4.32401600	0.10613600
C	0.40019400	2.64770400	0.06385200

C	0.71420600	3.05919600	-1.38219500
H	1.57649700	2.51326700	-1.76260600
H	0.94581900	4.12752800	-1.42303100
H	-0.13999300	2.86706900	-2.03534300
C	1.56642000	2.97643700	0.99506200
H	1.37670600	2.61224000	2.00580800
H	1.67587800	4.06444200	1.04528700
H	2.50759300	2.56126400	0.64030000
C	-1.46188400	-1.20841900	-0.08383200
C	-0.87740400	-3.34491800	-0.54991400
H	-0.88085500	-3.43853000	-1.64252500
H	-1.03933900	-4.32399800	-0.09943100
C	0.39662000	-2.64951500	-0.05155000
C	0.70324900	-3.06015500	1.39637400
H	1.56493900	-2.51575300	1.78026000
H	0.93246700	-4.12892000	1.43921200
H	-0.15345900	-2.86572400	2.04554600
C	1.56649400	-2.98182900	-0.97682500
H	1.38247600	-2.61858700	-1.98892700
H	1.67366700	-4.07015500	-1.02504900
H	2.50704700	-2.56852400	-0.61821800
C	2.29147000	-0.00090600	-0.00008700
C	3.01488200	0.04297500	-1.21452000
C	2.32700400	0.05574400	-2.56544000
H	2.65425900	0.90853900	-3.16806300
H	1.24071000	0.10323500	-2.48253200
H	2.57587400	-0.84528300	-3.13501800
C	4.41163900	0.04482400	-1.20040600

H	4.94739800	0.07812600	-2.14570100
C	5.13689800	-0.00746900	-0.01056900
C	6.64645100	0.01980300	-0.01612600
H	7.05771500	-0.47152200	0.86858200
H	7.01997400	1.04971900	-0.02212500
H	7.05132400	-0.47793600	-0.90052800
C	4.42041300	-0.06003000	1.18400000
H	4.96289300	-0.10489200	2.12488700
C	3.02333700	-0.04967100	1.20843300
C	2.34567900	-0.06554100	2.56433900
H	2.67910100	-0.91849400	3.16335800
H	1.25887900	-0.11473500	2.48932100
H	2.59708300	0.83520900	3.13327800
C	-3.90737200	0.00218900	-0.00198000
C	-4.65363100	-1.14360400	0.34229400
H	-4.13208000	-2.05290000	0.61371000
C	-6.04621400	-1.14492700	0.34131600
H	-6.58302100	-2.04791700	0.61558100
C	-6.75165100	0.00447100	-0.00874800
H	-7.83665200	0.00533400	-0.01134300
C	-6.04272500	1.15275200	-0.35542100
H	-6.57676900	2.05659800	-0.63225600
C	-4.65016700	1.14919200	-0.34974900
H	-4.12587200	2.05764800	-0.61870400
N	-0.07539200	-1.21481400	-0.09013700
N	-0.07420300	1.21383800	0.09920600
O	-1.93912400	2.48112400	0.16252300
O	-1.94182400	-2.47978500	-0.15701200

B	0.49297800	0.00534500	0.00102500
B	-2.49505200	-0.01895200	-0.00012300
C	-0.30980500	-1.24755300	-0.00418300
C	-0.33004300	1.24512700	0.00544500
C	-2.16455500	-2.59605300	-0.01265700
C	-1.06777700	-3.39161600	-0.01462000
C	-3.59168200	-3.03407700	-0.01821500
H	-3.63160500	-4.12400900	-0.02299600
H	-4.13545100	-2.67676000	-0.89538800
H	-4.14009900	-2.68429700	0.85902900
C	-0.95427400	-4.87988100	-0.02311600
H	-1.94011400	-5.34287100	-0.02487000
H	-0.40984600	-5.24427600	0.85287300
H	-0.41168700	-5.23397400	-0.90453300
C	1.40607900	-3.10349900	-0.00246200
C	2.02795900	-3.37582600	1.22261100
C	3.30908800	-3.93024700	1.20432500
H	3.80278100	-4.13754000	2.14884400
C	3.97315600	-4.20944400	0.01007500
C	3.32791500	-3.91146100	-1.19182200
H	3.83731200	-4.10426400	-2.13129800
C	2.04858300	-3.35760700	-1.22255800
C	1.35133400	-3.04148700	2.52825900

H	1.15962200	-1.96723000	2.59866400
H	1.97702900	-3.33337400	3.37339800
H	0.38575500	-3.54521900	2.63051300
C	5.34856700	-4.83233700	0.01174000
H	5.84756900	-4.69372500	0.97312200
H	5.98285300	-4.39698200	-0.76459500
H	5.29302200	-5.90976800	-0.17916700
C	1.39297700	-3.00172000	-2.53307700
H	0.42083500	-3.48894200	-2.65104900
H	2.02432600	-3.29566100	-3.37330900
H	1.21921300	-1.92384300	-2.59572200
C	-2.20657800	2.56324400	0.01206000
C	-1.12285400	3.37653600	0.01454600
C	-3.64056800	2.97832100	0.01597000
H	-3.69784700	4.06746300	0.02110300
H	-4.17971900	2.61205700	0.89225000
H	-4.18215100	2.62022600	-0.86218400
C	-1.03344300	4.86647400	0.02240900
H	-2.02664600	5.31338100	0.02393600
H	-0.49497400	5.23927000	-0.85373300
H	-0.49663100	5.22965400	0.90364500
C	1.35577200	3.12744200	0.00380900
C	1.99200200	3.39599800	1.22321900
C	3.26235700	3.97206600	1.19216300
H	3.76492200	4.18189500	2.13155500
C	3.90492200	4.27371200	-0.00930200
C	3.24379700	3.98637900	-1.20406300
H	3.73170500	4.20733600	-2.14859400

C	1.97288200	3.41070900	-1.22204100
C	1.33892100	3.03914000	2.53474500
H	1.96568500	3.34490100	3.37418500
H	1.17823000	1.95955900	2.60282800
H	0.36076800	3.51502300	2.64935200
C	5.29587600	4.86129100	-0.01626800
H	5.47091600	5.48408100	0.86420600
H	5.46657200	5.47344100	-0.90492800
H	6.05331000	4.06988100	-0.01316200
C	1.29841600	3.07119500	-2.52746600
H	1.11917500	1.99491800	-2.59972400
H	1.91970300	3.37190500	-3.37276700
H	0.32684500	3.56372400	-2.62775900
C	-4.07768300	-0.03171300	-0.00032400
C	-4.80922500	-0.04313800	1.19811600
H	-4.27995300	-0.04334000	2.14640900
C	-6.20326200	-0.05424200	1.20315100
H	-6.74120800	-0.06290300	2.14525900
C	-6.90534700	-0.05426000	-0.00043500
H	-7.98981300	-0.06282800	-0.00048000
C	-6.20325000	-0.04312100	-1.20396200
H	-6.74119400	-0.04304200	-2.14611300
C	-4.80921900	-0.03194900	-1.19881700
H	-4.27995400	-0.02317500	-2.14707200
Cl	2.32292300	0.01954300	0.00182700
N	-1.71774700	-1.23918800	-0.00571100
N	-1.73775200	1.21380900	0.00587100
N	0.06776100	-2.58258600	-0.00934000

N	0.02562700	2.58606200	0.01049200
---	------------	------------	------------

C	-2.44374100	6.04444400	-1.14257100
H	-2.53937300	7.10123400	-1.36643100
H	-2.27895100	6.34159600	0.98311400
C	-2.46303300	5.10678900	-2.17278600
C	-2.29998500	5.61883700	0.17545600
C	-2.34090500	3.75110600	-1.88486500
H	-2.57250300	5.42964300	-3.20195900
C	-2.17546000	4.26243100	0.46350600
C	-2.19263400	3.31391200	-0.56372700
H	-2.34943500	3.02319400	-2.68651400
H	-2.04818500	3.93893900	1.48902200
C	-2.16885400	1.85585100	-0.27363600
C	-3.27018500	1.05869600	-0.14790400
N	-1.04265500	1.02883000	-0.16347300
C	-4.69902700	1.44113300	-0.16496800
N	-2.80352400	-0.24927700	0.02528400
B	0.45315700	1.52314600	-0.21161300
C	-1.43873400	-0.24310500	0.02002600
C	-5.19107400	2.33126900	0.79894300
C	-5.57717900	0.96409300	-1.14613900

C	-3.68489400	-1.37413600	0.27035900
C	1.43873500	0.24313000	-0.02002200
C	0.67095800	2.65435200	0.92349400
Cl	0.73421500	2.17858500	-1.99610100
B	-0.45315600	-1.52312000	0.21161900
H	-4.52195400	2.71397900	1.55922700
C	-6.52539700	2.72742200	0.78628300
C	-6.91156800	1.35832500	-1.15607800
H	-5.21193600	0.29686400	-1.91485100
C	-4.11958200	-2.16421500	-0.79951200
C	-4.15258100	-1.58438200	1.58099300
N	1.04265000	-1.02880100	0.16348600
N	2.80352600	0.24928400	-0.02529700
C	0.27329400	2.36775500	2.24151500
C	1.20859500	3.92338400	0.67877800
H	2.74086800	0.39332100	-2.71164200
H	1.51820700	4.18006100	-0.32702200
C	-0.67092900	-2.65433200	-0.92348600
Cl	-0.73421000	-2.17856100	1.99610600
H	-6.88708300	3.41781500	1.53983800
C	-7.39084700	2.23917400	-0.18927200
H	-7.57585500	0.98059200	-1.92511800
C	-3.72243300	-1.91972500	-2.23414000
C	-4.98922900	-3.22412700	-0.51939400
C	-5.01285100	-2.65578700	1.80343200
C	-3.79640200	-0.66175000	2.71895500
C	2.16883600	-1.85582900	0.27368500
C	3.27017400	-1.05869400	0.14788600

C	3.68490900	1.37412500	-0.27039800
H	-0.14221200	1.39160400	2.47663500
C	0.38944000	3.30722500	3.26409900
C	1.33334300	4.86920500	1.69584600
C	3.79637400	0.66168400	-2.71898000
C	-0.27320900	-2.36775100	-2.24149300
C	-1.20857400	-3.92336300	-0.67877700
H	-2.74088100	-0.39344200	2.71168900
H	-1.51822500	-4.18002900	0.32701300
H	-8.43046900	2.54655300	-0.19925000
H	-3.13664800	-1.01122300	-2.36271600
H	-4.61598800	-1.84408900	-2.86176700
H	-3.12623800	-2.75098400	-2.61422100
H	-5.32497000	-3.84792000	-1.34225900
C	-5.43426700	-3.49611500	0.76942500
H	-5.36942100	-2.83427100	2.81307500
H	-4.38469400	0.25977400	2.66373600
H	-4.01425500	-1.13866100	3.67582900
C	2.19257800	-3.31387800	0.56383500
C	4.69901400	-1.44114000	0.16491900
C	4.11963600	2.16420900	0.79945400
C	4.15258400	1.58433400	-1.58104200
H	0.06962500	3.05565000	4.27010900
C	0.91999500	4.56824900	2.99224900
H	1.74584700	5.84750900	1.47205400
H	4.38471900	-0.25980900	-2.66380100
H	4.01413500	1.13860500	-3.67586800
H	0.14231200	-1.39160300	-2.47660400

C	-0.38931500	-3.30723100	-3.26407300
C	-1.33328000	-4.86919300	-1.69584100
C	-6.34377000	-4.66673200	1.05331800
C	2.34076500	-3.75103000	1.88499700
C	2.17540200	-4.26243400	-0.46336400
C	5.19105500	-2.33123500	-0.79903200
C	5.57717300	-0.96413800	1.14610200
C	3.72252500	1.91974300	2.23409700
C	4.98930200	3.22409700	0.51930300
C	5.01287800	2.65571200	-1.80351300
H	1.01098500	5.30604500	3.78244100
H	-0.06945800	-3.05566600	-4.27007200
C	-0.91988200	-4.56825100	-2.99223000
H	-1.74579400	-5.84749500	-1.47205500
H	-6.79691100	-5.05147400	0.13748100
H	-7.14783400	-4.38851000	1.73978700
H	-5.78851700	-5.48770100	1.51928100
H	2.34928200	-3.02308900	2.68662000
C	2.46283400	-5.10670700	2.17297100
C	2.29986600	-5.61883300	-0.17526000
H	2.04816500	-3.93897400	-1.48889400
H	4.52193100	-2.71391200	-1.55933000
C	6.52537900	-2.72738800	-0.78639900
C	6.91156300	-1.35837000	1.15601700
H	5.21193400	-0.29694100	1.91484400
H	3.13662800	1.01131600	2.36268500
H	4.61610000	1.84397900	2.86168100
H	3.12645800	2.75107500	2.61422100

H	5.32507000	3.84789700	1.34215300
C	5.43432600	3.49605100	-0.76952800
H	5.36944000	2.83416900	-2.81316400
H	-1.01084000	-5.30605500	-3.78241700
H	2.57224500	-5.42952900	3.20216100
C	2.44355500	-6.04439800	1.14278800
H	2.27883300	-6.34162200	-0.98289200
H	6.88706100	-3.41774800	-1.53998400
C	7.39083500	-2.23918000	0.18917100
H	7.57585500	-0.98066800	1.92506700
C	6.34385800	4.66663900	-1.05345500
H	2.53913600	-7.10118300	1.36669100
H	8.43045700	-2.54655900	0.19912900
H	6.79700700	5.05139700	-0.13762900
H	7.14791600	4.38837600	-1.73991400
H	5.78862400	5.48760600	-1.51944400

B	-0.56492000	-1.40582300	0.10668500
B	0.56495500	1.40598200	0.10654600
C	-1.05816300	-2.86091100	0.48839300
C	-1.87079000	-3.67491000	-0.31590100
H	-2.16702600	-3.32608700	-1.29863200
C	-2.30600400	-4.92787500	0.10890900
H	-2.93106200	-5.53003700	-0.54218700

C	-1.93826900	-5.41043400	1.36291200
H	-2.27571500	-6.38623200	1.69566100
C	-1.12568400	-4.62978600	2.18198500
H	-0.82638400	-4.99530500	3.15903200
C	-0.69318100	-3.37957600	1.74494900
H	-0.05435900	-2.78943900	2.39607900
C	1.41046400	0.16602500	0.06857500
C	3.10528900	-1.34656800	-0.06299700
C	1.93136400	-2.04083400	-0.17410900
C	1.80371200	-3.46115400	-0.55837000
C	1.19286300	-3.81151500	-1.77108400
H	0.73723000	-3.03777700	-2.37879900
C	1.17628300	-5.13253700	-2.20303900
H	0.70180900	-5.38409200	-3.14525000
C	1.76942300	-6.13097900	-1.43096300
H	1.75505200	-7.16161300	-1.76742600
C	2.37393300	-5.79588400	-0.22237200
H	2.83131300	-6.56596500	0.38886400
C	2.38919300	-4.47293400	0.21128200
H	2.85925800	-4.21747400	1.15337000
C	4.48815900	-1.86239900	-0.17041500
C	4.87092000	-2.61526700	-1.28986200
H	4.14926800	-2.80691900	-2.07407500
C	6.16175600	-3.12371000	-1.39755700
H	6.43726700	-3.70431200	-2.27077100
C	7.09487600	-2.88829700	-0.39038700
H	8.10085000	-3.28382700	-0.47468400
C	6.72620200	-2.14246200	0.72664800

H	7.44371600	-1.95611500	1.51785200
C	5.43524300	-1.63415200	0.83678100
H	5.16039600	-1.06502500	1.71491700
C	3.78330100	1.04103000	0.16642500
C	4.15866700	1.57093200	1.41071500
C	5.14986600	2.55151300	1.43664600
H	5.44660500	2.96694500	2.39498300
C	5.76354500	3.01395400	0.27209000
C	5.36434800	2.46619300	-0.94621900
H	5.82953200	2.81324500	-1.86391900
C	4.37769200	1.48177700	-1.02448600
C	3.97177300	0.91918400	-2.36432000
H	4.43273200	-0.05766000	-2.53952600
H	4.28884400	1.58390400	-3.17022100
H	2.88966800	0.78652400	-2.43224600
C	6.81034200	4.09986200	0.33347300
H	7.39277500	4.14658400	-0.58905100
H	7.50286400	3.93937300	1.16398800
H	6.34540700	5.08021300	0.48299100
C	3.50824300	1.12296500	2.69527300
H	3.25701700	0.06071700	2.68195100
H	2.57738300	1.67277700	2.86066100
H	4.16490000	1.31472000	3.54651400
C	1.05833900	2.86109900	0.48792300
C	0.69335100	3.38022000	1.74428400
H	0.05435700	2.79041200	2.39554300
C	1.12606600	4.63047500	2.18098000
H	0.82674700	4.99634800	3.15788800

C	1.93887800	5.41071800	1.36174800
H	2.27649100	6.38654700	1.69423400
C	2.30662200	4.92771200	0.10791800
H	2.93185700	5.52955200	-0.54330500
C	1.87119200	3.67470600	-0.31654900
H	2.16743700	3.32553100	-1.29915500
C	-1.41041400	-0.16587800	0.06868100
C	-3.10531500	1.34660600	-0.06282200
C	-1.93143200	2.04095400	-0.17400400
C	-1.80403600	3.46133600	-0.55805300
C	-2.39036600	4.47275900	0.21145700
H	-2.86083400	4.21693800	1.15324500
C	-2.37546000	5.79577900	-0.22197300
H	-2.83350500	6.56556300	0.38913900
C	-1.77044900	6.13133000	-1.43019300
H	-1.75634200	7.16202400	-1.76648600
C	-1.17644800	5.13327000	-2.20209400
H	-0.70155800	5.38518300	-3.14400000
C	-1.19267900	3.81216700	-1.77037000
H	-0.73637600	3.03874100	-2.37797100
C	-4.48824500	1.86226400	-0.17037000
C	-5.43532700	1.63411100	0.83684300
H	-5.16041500	1.06524200	1.71512700
C	-6.72636200	2.14219600	0.72654100
H	-7.44388200	1.95592900	1.51775900
C	-7.09510200	2.88770900	-0.39068600
H	-8.10113400	3.28306300	-0.47511800
C	-6.16197700	3.12303400	-1.39787500

H	-6.43754700	3.70339200	-2.27123200
C	-4.87106800	2.61481800	-1.29000500
H	-4.14939400	2.80641500	-2.07421500
C	-3.78315400	-1.04106200	0.16642700
C	-4.15872700	-1.57095600	1.41064800
C	-5.14981700	-2.55166000	1.43640000
H	-5.44670900	-2.96708500	2.39469300
C	-5.76316200	-3.01423400	0.27172800
C	-5.36376000	-2.46647200	-0.94651900
H	-5.82870200	-2.81362500	-1.86430100
C	-4.37721900	-1.48193200	-1.02460600
C	-3.97107500	-0.91932000	-2.36436300
H	-4.43208300	0.05748100	-2.53967200
H	-4.28792700	-1.58407600	-3.17032200
H	-2.88896800	-0.78657500	-2.43206900
C	-6.80982800	-4.10028000	0.33293200
H	-6.34481900	-5.08048100	0.48320200
H	-7.39166600	-4.14751100	-0.58993700
H	-7.50290900	-3.93953100	1.16293700
C	-3.50862200	-1.12290500	2.69534000
H	-2.57785500	-1.67278800	2.86104200
H	-4.16552600	-1.31451900	3.54641900
H	-3.25729500	-0.06068600	2.68198500
N	0.86510800	-1.12065700	-0.03759700
N	2.79952200	-0.00510200	0.11351300
N	-0.86510100	1.12082800	-0.03757000
N	-2.79946800	0.00517500	0.11369600

2.7 References

1. R. J. Doerksen; A. J. Thakkar, *J. Phys. Chem. A*, **1998**, *102*, 4679.
2. S. T. Massey; R. W. Zoellner, *Inorg. Chem.*, **1991**, *30*, 1063.
3. R. Köster; K. Iwasaki, *Adv. Chem. Ser.*, **1964**, *42*, 157.
4. P. Schreyer; P. Paetzold; R. Boese, *Chem. Ber.*, **1988** *121*, 195.
5. (a) S. Allaoud; A. Karim; A. Mortreux; F. Petit; B. Frange, *J. Organomet. Chem.*, **1989**, *379*, 89; (b) S. Allaoud; S. Conté; B. Fenet; B. Frange; F. Robert; F. Sécheresse; A. Karim, *J. Organomet. Chem.*, **1994**, *469*, 59; (c) B. Abouhamza; M. A. Ali; S. Allaoud; O. Blacque; B. Frange; A. Karim, *Acta Cryst.*, **2001**, *57*, 796.
6. D. Wu; L. Kong; Y. Li; R. Ganguly; R. Kinjo, *Nat. Commun.*, **2015**, *6*, 7340.
7. D. Wu; L. Kong; Y. Li; R. Ganguly; H. Hirao; R. Kinjo, *Chem. Sci.*, **2015**, *6*, 7150.
8. D. Wu; Y. Li; R. Ganguly; R. Kinjo, *Chem. Commun.*, **2017**, *53*, 12734.
9. Y. Su; Y. Li; R. Ganguly; R. Kinjo, *Angew. Chem. Int. Ed.*, **2018**, *57*, 7846.
10. H. Nöth; P. Fritz, *Z. Anorg. Allg. Chem.*, **1963**, *324*, 129.
11. R. Goetze; H. Nöth, *J. Organomet. Chem.*, **1978**, *145*, 151.
12. C. J. Carmalt; W. Clegg; A. H. Cowley; F. J. Lawlor; T. B. Marder; N. C. Norman; C. R. Rice; O. J. Sandoval; A. J. Scott, *Polyhedron*, **1997**, *16*, 2325.

13. H. C. Söyleyici; S. Uyanik; R. Sevincek; E. Firinci; B. Bursali; O. Burgaz; M. Aygün; Y. Şahin, *Inorg. Chem. Commun.*, **2015**, *61*, 214.
14. M. Arrowsmith; H. Braunschweig; K. Radacki; T. Thiess; A. Turkin, *Chem. Eur. J.*, **2017**, *23*, 2179.
15. B. Wang; Y. Li; R. Ganguly; H. Hirao; R. Kinjo, *Nat. Commun.*, **2016**, *7*, 11871.
16. B. Wang; R. Kinjo, *Chem. Sci.*, **2019**, *10*, 2088.
17. B. Wang; R. Kinjo, *Tetrahedron*, **2018**, *74*, 7273.
18. B. Wang; Y. Li; R. Ganguly; R. Webster; R. Kinjo, *Angew. Chem. Int. Ed.*, **2018**, *56*, 7826.
19. T. D. Forster; K. E. Krahulic; H. M. Tuononen; R. McDonald; M. Parvez; R. Roesler, *Angew. Chem., Int. Ed.*, **2006**, *45*, 6356.
20. W. Siebert; R. Full, *Angew. Chem., Int. Ed.*, **1976**, *15*, 45.
21. W. Siebert; R. Full; H. Schmidt; J. von Seyerl; M. Halstenberg; G. Huttner, *J. Organomet. Chem.*, **1980**, *191*, 15.
22. D. J. H. Emslie; W. E. Piers; M. Parvez, *Angew. Chem., Int. Ed.*, **2003**.
23. C. A. Jaska; D. J. H. Emslie; M. J. D. Bosdet; W. E. Piers; T. S. Sorensen; M. Parvez, *J. Am. Chem. Soc.*, **2006**, *128*, 10885.
24. G. K. H. Goh; Y. Li; R. Kinjo, *Dalton Trans.*, **2019**, *48*, 7514.
25. A. Stanger, *Chem. Commun.*, **2009**, 1939.
26. D. Geuenich; K. Hess; F. Köhler; R. Herges, *Chem. Rev.*, **2005**, *105*, 3758.
27. G. M. Sheldrick, *Acta Cryst.*, **2015**, *A71*, 3.

28. G. M. Sheldrick, *Acta Cryst.*, **2015**, *C71*, 3.

Chapter 3 Oxidative addition of elemental Selenium to 1,4,2,5-Diazadiborinine

3.1 Introduction

3.1.1 O–O bond activation

Recently, Wagner and co-workers synthesized the 9,10-diborananthracene salt **a** that reacted with the dichalcogen $\text{O}_2(t\text{Bu})_2$.¹ Upon the reductive cleavage of the O–O bond, compound **b** and **a** were generated (Scheme 1). The two bulky $[\text{O}(t\text{Bu})]$ groups were inserted in a syn fashion at the axial positions of the boron atoms.

Scheme 1 Reaction of 9,10-diborananthracene **a** with $\text{O}_2(t\text{Bu})_2$ to obtain compound **b** by Wagner and co-workers

3.1.2 S–S bond activation

In 2016, Martin and co-workers reported the reaction of sulfur with the pentaarylboroles **c** and **e** to generate the 1,2-thiaborine **d** and **f**, respectively (Scheme 2).² These reactions proceeded at 65 °C in benzene for sixteen hours. Compound **d** was isolated in a yield of 44% and compound **e** was isolated in a yield of 42%. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **d** displays a singlet at 50.8 ppm

which is shifted up field from that (65.0 ppm) of compound **c**, and compound **f** displays a peak at 51.1 ppm.

Scheme 2 Reaction of pentaarylboroles **c** and **e** with S_8 by Martin and co-workers

In 2018, Braunschweig and co-workers reported the first example of the insertion of the monomeric borylene into the S–S bond to generate the cAAC-supported cyanoboron dichalcogenide.³ A tetrameric borylene **g** was reacted with four equivalents of PhS–SPh to generate compound **h** (Scheme 3). The ^{11}B NMR spectrum of compound **h** shows a singlet at -9.6 ppm, which is shifted up field with respect to that (-4.2 ppm) of compound **g**,⁴ indicating the presence of a sp^3 hybridized boron center in compound **h**.

Scheme 3 Reaction of compound **g** with PhS–SPh by Braunschweig and co-workers

Next, one equivalent of tetrameric borylene **g** was reacted with 0.5 equivalents of elemental sulfur to generate two equivalents of compound **i** in 88% yield (Scheme 4). The ¹¹B NMR chemical shift of compound **i** was observed at –17.9 ppm while that of compound **g** is –4.2 ppm. When one equivalent of compound **g** was reacted with 0.75 equivalents of sulfur, compound **j** was generated in a 71% yield. The ¹¹B NMR chemical shift of compound **j** was observed at –8.5 and –9.1 ppm. When one equivalent of compound **g** was treated with one equivalent of sulfur, compound **k** was generated in 53% yield (Scheme 4). The ¹¹B NMR chemical shift of compound **k** was observed at –11.2 ppm.

Scheme 4 Reaction of compound **g** with 0.5, 0.75 and 1 eq of S_8 by Braunschweig and co-workers

In 2019, Wagner and co-workers reported the reductive cleavage of the S–S bond of S_2Me_2 and $S_2(pTol)_2$ by compound **a** to generate compound **l** and **m**, respectively (Scheme 5).¹ When compound **a** was reacted with a smaller S_2Me_2 , the two boron atoms were connected to a mono MeS ligand in compound **l**. However, when a bulkier $S_2(pTol)_2$ was reacted with compound **a**, a tetracoordinate boron atom connected to STol and a tricoordinate boron atom were resulted in compound **m**.

Scheme 5 Reaction of compound **a** with S_2Me_2 and $\text{S}_2(p\text{Tol})_2$ by Wagner and co-workers

3.1.3 Se–Se bond activation

In 2018, Braunschweig and co-workers reported the S–S bond activation by compound **g** to generate the cAAC-supported cyanoboron dichalcogenide (Scheme 3).³ In the same report, compound **g** was also found to react with RSe–SeR ($\text{R} = \text{Me}$ or Ph) at room temperature to furnish compounds **n** and **o** (Scheme 6).³ Similar to the reactions shown in scheme 4, different equivalents of elemental selenium added to compound **g** generated different products **p** and **q** (Scheme 7). Compound **q** could also be generated with the reaction of compound **r** with two equivalents of selenium at room temperature in benzene (Scheme 8). Compound **p** was generated when compound **r** was treated with one equivalent of selenium at 60 °C (Scheme 9). Compound **r** could be regenerated from the reversible reaction, in which one equivalent of selenium was eliminated at room temperature over a period of three days from compound **p** (Scheme 9).

Compound **p** could also be generated by the removal of one equivalent of selenium from compound **q** over a period of four days (Scheme 10). In 2019, Wagner and co-workers reported 9,10-diborananthracene **a** undergoes the reductive cleavage of the Se–Se bond at room temperature to generate compound **s** (Scheme 11).¹

Scheme 6 Reaction of compound **g** with RSe–SeR by Braunschweig and co-workers

Scheme 7 Reaction of compound **g** with 4 and 6 eq of Se by Braunschweig and co-workers

Scheme 8 Reaction of compound **r** with 2 eq of Se with by Braunschweig and co-workers

Scheme 9 Reversible reaction of compound **r** and **p** with 1 eq of Se with by Braunschweig and co-workers

Scheme 10 Generation of compound **p** by the elimination of Se from **q** by Braunschweig and co-workers

Scheme 11 Reactivity of compound **a** with PhSe-SePh by Wagner and co-workers

3.1.4 Te–Te bond activation

In 2019, Wagner and co-workers synthesized compound **t** from the reaction of 9,10-diborananthracene **a** at room temperature by the reductive cleavage of the Te–Te bond (Scheme 12).¹

Scheme 12 Reactivity of compound **a** with PhTe-TePh by Wagner and co-workers

3.1.5 O=O bond activation

In 2009, Piers and co-workers reported the O=O bond activation by N-heterocyclic carbene-stabilized 9-boraaanthracene compounds **u** and **w**.⁵ Compounds **u** and **w** were exposed to O_2 gas in DCM to generate compounds **v** and **x**, respectively (Scheme 13). A bicyclo[2,2,2] geometry which involve an O_2 unit between the boron atom and the carbon atom at the 10-position was observed in compounds **v** and **x** as confirmed by the crystallographic structures.

In 2011, Bourissou and co-workers reported the spontaneous activation of the singlet O_2 by the phosphine–boronate compound **y** to generate the first B–O–O skeleton in a peroxoboronate moiety **z** as a moisture sensitive white solid (Scheme 14). Compound **z** was then reacted with another equivalent of compound **y** at room temperature over a period of three hours to generate

compound **aa** (Scheme 14). Compound **bb** also reacted with singlet O_2 spontaneously at room temperature to generate compound **cc** which an additional equivalent of **bb** would generate compound **dd** (Scheme 15).⁶

Scheme 13 Reaction of compound **u** and **w** with O_2 by Piers and co-workers

Scheme 14 Reaction of compound **y** with O_2 by Bourissou and co-workers

Scheme 15 Reaction of compound **bb** with O₂ by Bourissou and co-workers

In 2014, Agapie and Henthorn reported the reduction of dioxygen by two equivalents of ferrocenes with the boron Lewis acid **ee** to generate the bis(ferrocenium) bis(borane)peroxides **ff** (Scheme 16).⁷ In 2017, Erker and co-workers reported the reduction of the triplet O₂ by TEMPO with two equivalents of the boron Lewis acids **gg** and **ii** at 1.5 bar in DCM to generate the bis(borane)peroxide/-superoxide compounds **hh** and **jj**, respectively (Scheme 17).⁸

Scheme 16 Reaction of compound **ee** with O₂ by Agapie and Henthorn

room temperature to generate compound **o** (Scheme 19).¹⁰ The crystallographic structure of compound **oo** displayed an endoperoxide core.

Scheme 19 Reaction of compound **nn** with O₂ by Harman and co-workers

In 2016, Kinjo and co-workers reported the activation of triplet O₂ by the azaborabutadiene **pp** at a low temperature of $-78\text{ }^{\circ}\text{C}$ to generate the boron peroxide compound **q** which featured a BC₂NO₂ six-membered ring (Scheme 20).¹¹ The mechanism was hypothesized to involve radical coupling between the azaborabutadiene **pp** and triplet O₂. An alternative hypothesis would be the transfer of electron from the azaborabutadiene **pp** to the triplet O₂. Subsequently, a B–O bond formation could occur for the generation of compound **qq**. Compound **pp** was also reacted with elemental sulfur and selenium at room temperature to generate compound **rr** and **ss** respectively (Scheme 20).¹¹ Compound **rr** contained a BC₂NS five-membered ring while compound **s** contained a BC₂NSe five-membered ring.¹²

Scheme 20 Reaction of compound **pp** with O_2 , S_8 and Se by Kinjo and co-workers

In 2018, Kinjo and co-workers reported the stepwise O_2 activation by compound **tt**.¹³ Compound **tt** was subjected to O_2 gas at 1 atm in benzene over a period of five minutes to generate compound **uu** (Scheme 21). The crystallographic structure of compound **uu** showed a bicycle [2.2.2] structure with an endocyclic O–O bond between two boron atoms. Compound **uu** was added to another one equivalent of **tt** at 80 °C for ten hours to generate the $B_4C_2N_2O_2$ ten-membered ring compound **vv** (Scheme 21).

Scheme 21 Reaction of compound **tt** with O_2 by Kinjo and co-workers

3.2 Results and Discussion:

3.2.1 Objective

Since the emergence of Frustrated Lewis pairs (FLP) in 2006,¹⁴ the element-element bond activation no longer solely belongs to the domain of the transition metal complexes. Following, the FLP concept further developed to encompass the main-group ambiphiles (MGA).¹⁵ Among them, the boron-based systems have gained considerable focus due to their low toxicity, which is one of the main disadvantage of utilizing transition metals in reactions.¹⁶⁻²⁰ Very recently, the group of Wagner has demonstrated that 9,10-diboraanthracene dianion cleaves the chalcogen-chalcogen bonds of various dichalcogenides E_2R_2 ($E = O, S, Se, Te$).¹ Albeit this area has significantly advanced in recent years, no investigation on the reactivity of aromatic boron heterocycles toward elemental selenium (Se) has been described thus far, which prompted us to study the chemical behavior of diazadiborinine in this respect.

Here, we report the reactivity of 1,4,2,5-diazadiborinine **12** towards selenium.²¹

3.2.2 Reaction of 1,4,2,5-diazadiborinine with Selenium

Two equivalents of grey selenium were added to one equivalent of **12** in C₆D₆ (Scheme 22). The reaction mixture was heated at 80 °C for 14 hours and monitored by NMR spectroscopy. During the reaction, the red color of the solution gradually turned yellow. After workup, compound **13** was obtained as a yellow powder in 60% yield.

Scheme 22 Reaction of compound **12** with Selenium

The ¹¹B NMR spectrum of **13** exhibits a characteristic signal at 1.04 ppm, indicating the formation of the tetracoordinate boron center, which is shifted up field compared to that (10.28 ppm) of **12**. The calculated ¹¹B NMR chemical shift (−1.42 ppm) on **13** using the gauge-independent atomic orbital (GIAO) method at the B3LYP/6-311G(d,p) level of theory reasonably agrees with the experimental value (Table 1). In the ¹H NMR of **13**, three signals for the methyl groups of the mesityl groups were observed at 1.78 ppm, 2.10 ppm and 2.20 ppm. The ¹³C and DEPT135 NMR also display three signals at 17.97, 19.47 and 20.31 ppm. The ⁷⁷Se{¹H} NMR spectrum exhibits two ⁷⁷Se signals at 147.05 ppm and 142.27 ppm (Fig 10). No obvious information was collected regarding why the

molecular motion in the solution may allow for detecting the ^1H and ^{13}C NMR signals of compound **13** as if a C_2 symmetry molecule, whereas those two inequivalent Se atoms could still be observed as two different signals in the $^{77}\text{Se}\{^1\text{H}\}$ NMR time scale.

	Isotropic Values	Calculated $\delta (^{11}\text{B})$ [ppm]	Experimental $\delta (^{11}\text{B})$ [ppm]
4	104.8418	-1.4239	1.04
	104.8409	-1.4230	
BF₃.Et₂O (Reference)	103.4179	-	-

Table 1 Experimental and calculated ^{11}B NMR chemical shifts of compound

13.

The solid-state structure of **13** was confirmed by the X-ray diffraction study (Fig 1). Compound **13** bears a bicyclo[2.2.2] skeleton involving a B–Se–Se–B unit, a rare example of a heavier analogue of diboraperoxide.²¹ The boron centers in **13** adopt a tetrahedral geometry and the B1, B2, Se1 and Se2 atoms are nearly coplanar (the B–Se–Se–B torsion angle = 3.2°). The Se1–Se2 bond distance (2.354(2) Å) is close to the range reported for Se–Se single bonds (2.34 to 2.98 Å).²² The B1–Se1 bond (2.114(13) Å) and B2–Se2 bond (2.114(12) Å) distances

are in the range of those reported for B–Se single bonds as observed for related compounds (1.94 to 2.15 Å).^{3,23,24} Both the B–N bond (B1–N3: 1.577(13) Å, B2–N1: 1.566(13) Å) and the B–C bond (B1–C2: 1.588(15) Å, B2–C1: 1.600(15) Å) distances in **13** are longer than those in **12**, whereas the N–C bond distances (N1–C2: 1.334(11) Å, N3–C1: 1.357(12) Å) in **13** are slightly shorter in comparison with those in **12** (Table 4). To the best of our knowledge, the formation of **13** represents the first example of the oxidative addition of selenium to a diazadiborinine.²¹

Figure 1 The solid-state structure of **13**. Thermal ellipsoids are set at the 50% probability level. All H atoms are omitted for clarity.

B–N (Å)	1.4574(4)	1.577(13)
	1.4624(4)	1.566(13)
N–C (Å)	1.4073(3)	1.334(11)
	1.4058(3)	1.357(12)
C–B (Å)	1.4960(4)	1.588(15)
	1.4942(4)	1.600(15)

Table 4 BN, NC, and CB Bond Lengths of compounds **12** and **13**

We compared the experimentally determined structure with the computationally optimized structure. The data showed that compound **13** was not in a perfect C₂ symmetry. Instead, compound **13** has a slightly distorted symmetry (Table 2), which could be due to the rigid and annulated skeletal framework bearing the bulky Ph and Mes substituents. It seemed that the two Se atoms were at least essentially inequivalent in the solid state. We assumed that the molecular motion in the solution might allow for the detection of compound **13** as if as a C₂ symmetry molecule in the ¹H and ¹³C NMR spectra, whereas the two inequivalent Se atoms could still be observed as two different signals in the ⁷⁷Se{¹H} NMR time scale. The time scale of the ¹H NMR is 3.9s, ¹³C NMR (1.3s) and ⁷⁷Se{¹H} NMR is 0.2s. The distorted geometry seems to be only captured within the short acquisition time of the ⁷⁷Se{¹H} NMR.

Figure 3 Optimized structure of compound **13**.

Bond (Å)	X-ray data	Optimized structure	WBI Value
B1–N3	1.577(13)	1.5775	0.6503
B1–C2	1.588(15)	1.5876	0.8489
B2–N1	1.566(13)	1.5656	0.6503
B2–C1	1.600(15)	1.6004	0.8489
N1–C2	1.334(11)	1.3342	1.2873
N3–C1	1.357(12)	1.3573	1.2873
B1–Se1	2.114(12)	2.1139	0.8674
B2–Se2	2.114(13)	2.1144	0.8674
Se1–Se2	2.3543(18)	2.3543	0.5955

Table 2 Selected Bond Lengths and Wilberg Bond Index (WBI) for the optimized geometries of compound **13**.

In addition, we performed DFT calculations at the B3LYP/6-311G(d,p), HCTH/6-311G(d,p) and OLYP/6-311G(d,p) levels of theory to estimate the spin-spin coupling constant between the B–Se and the Se–Se moieties in compound **13**. The results are summarized in the Table 3: the Se–Se coupling constants = 157 Hz ~186 Hz; Se–B coupling constants = 21 Hz ~ 23 Hz. These coupling constants were too small to be detected by the $^{77}\text{Se}\{^1\text{H}\}$ NMR spectroscopy (76.19674 Hz). Considering the nuclear spin and natural abundance of B [^{10}B : $I = 3$ (20%); ^{11}B : $I = 3/2$ (80%)] and ^{77}Se [$I = 1/2$ (7.6%)], neither B–Se coupling nor Se–Se coupling would give rise to two signals as if a doublet.

Method	Se1–Se2	B1–Se1	B2–Se2
B3LYP	186.739 Hz	21.0163 Hz	21.0177 Hz
HCTH	157.446 Hz	23.6318 Hz	23.6335 Hz
OLYP	158.218 Hz	23.8291 Hz	23.8306 Hz

Table 3 Se–Se and B–Se coupling constants of compound **13**

The HOMO of **13** mainly corresponds to the lone pairs of the selenium atoms (Fig 4), implying the Se–Se unit in **13** could be one of the most reactive moieties. Therefore, we briefly examined the reactivity of **13**. As a preliminary reactivity investigation, compound **13** was treated with two equivalents of PPh₃ (Scheme 23) and monitored the reaction by ¹H NMR spectroscopy (Fig 11). Even with heating at 75 °C for 24 hours, no reaction was observed. The ⁷⁷Se{¹H} spectra of the reaction mixture still indicated two signals corresponding to compound **13**, confirming neither the formation of the mono bridged species nor the regeneration of starting material **12** occurred.

Scheme 23 Reaction of **13** with PPh₃

Figure 4 Side view (left) and top view (right) of the HOMO of **13**

The reactivity of low-valent boron species and Se has reported by Tokitoh et al.²³ and Braunschweig et al.³, provide insight into our mechanistic study.

In 1999, the group of Tokitoh reported the formation of compound **aaa** from compound **bbb** (Scheme 24). The borylene intermediate **xx** was first generated which subsequently dimerized to form compound **yy**. Path a suggests that compound **yy** will undergo reductive insertion of three selenium atoms to generate compound **aaa** with the cleavage of B=B bond. Path b suggests that a monomeric compound **zz** dimerizes to compound **bbb** before the insertion of one selenium atom to afford compound **aaa**. In 2018, the group of Braunschweig presented the proposed mechanistic pathway for formation of compound **p**. The formation of compound **p** was predicted to follow pathway b proposed by Tokitoh and co-workers. The association of selenium with the tetramer **g** will cause compound **g** to disaggregate and form the possible intermediates **ccc** and **ddd**(Scheme 25). Intermediate **ccc** subsequently dimerizes via bridging selenium

atoms to afford compound **p**. Intermediate **ccc** and intermediate **ddd** will combine to generate compound **q**.

Scheme 24 Mechanistic pathway proposed by the group of Tokitoh for the formation of compounds **aaa** and **bbb**.

Scheme 25 Possible intermediates for the mechanistic pathway of formation for compounds **p** and **q**.

Since selenium is more electronegative than boron, Se would remove electrons from the boron atoms and oxidize the boron atoms in compound **12** to generate compound **13**. We hypothesized two possible ways which selenium could be added to the boron atoms. The first method could proceed by the sequential Se atom transfers to the boron atoms in compound **12**. We had investigated with 2 equivalents of PPh₃ to find out if a formation of a monobridged ligand is possible. The successful reaction with compound **13** should generate a monobridged Se intermediate and finally generate the starting material **12**. However, no reaction was observed even when temperature was raised to 75°C for 24h. Thus, a one selenium transfer is not observed in this instance. The second method involves that compound **12** selectively extracts a Se₂ unit from the bulk Se chains and associated with **12** to form intermediate **eee** and subsequently compound **13** (Scheme 26). We had attempted to predict the mechanism however no obvious information regarding its transition intermediates were observed for any conclusion to be made.

Scheme 26 A one Selenium transfer mechanism (top) and proposed mechanism for formation of compound **13** (bottom)

3.3 Conclusion

Under the heating condition, compound **12** reacts with elemental selenium to afford a bicyclo[2.2.2] molecule **13** involving a B–Se–Se–B unit, a heavier analogue of dibora-peroxide. While the investigations for the transition states gave no conclusive results, the proposed mechanistic pathway seems feasible, in which the proposed intermediate might be too unstable to be retained

in the solution long enough to be captured by the NMR monitoring. This agrees with the potential energy surface (pes) scans conducted for the investigations of the transition states which no obvious local maxima points were detected, indicating that the formation of **13** and the transition states could be simultaneous.

With this reactivity results, we have broadened the scope of diazadiborinines for small molecule activation to include the oxidative addition of selenium. Its undeniable potential to access to the heavy analogues of diboraperoxide may stimulate the research into this area (more details are discussed in the chapter 5).

All DFT calculations had been performed by the Ph.D. candidate Gillian Goh Kor Hwee.

3.4 Experimental Section

3.4.1 Synthesis, physical and spectroscopic data for all new compounds

Materials and Method: All reactions were performed in an atmosphere of nitrogen or argon by using standard Schlenk or dry box techniques; solvents were dried with Na metal and K metal. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B and $^{77}\text{Se}\{^1\text{H}\}$ NMR spectra were obtained with either Bruker Avance 300, MHz AV300, AV 500 or AVIII 400 MHz BBFO1, BBFO2 and ECA400 spectrometers at 298 K. Coupling constants J are given in Hz. Chemical shifts (δ) are given in p.p.m. 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. Ultraviolet spectra were recorded on Cary 100 UV-Vis spectrometer.

Synthesis of **13**:

C_6D_6 (6 mL) was added to a mixture of **12** (0.20 g, 0.235 mmol) and grey selenium (0.0371 g, 0.470 mmol). The reaction mixture was heated at 80 $^\circ\text{C}$ for 14 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was

washed with hexanes (10 mL) and dried under vacuum to afford **13** (0.142 g, 0.141 mmol) as a pale-yellow powder (60%). Yellow single crystals of **13** were obtained by recrystallization from a benzene solution at ambient temperature.

M.p.: 165 °C. ^1H NMR (400 MHz, C_6D_6) δ 7.95 (d, 2H, $J = 6.1\text{Hz}$, ArH), 7.59 (d, 1H, $J = 5.6\text{Hz}$, ArH), 7.26 (s, 2H, $J = 5.9\text{Hz}$, ArH), 6.92 – 6.90 (m, 4H, ArH), 6.84 – 6.77 (m, 5H, ArH), 6.71 – 6.66 (m, 5H, ArH), 6.61 (t, 6H, $J = 5.8, 6.2\text{Hz}$, ArH), 6.53 (d, 4H, $J = 5.9\text{Hz}$, ArH), 6.48 (t, 1H, $J = 5.9, 5.8\text{Hz}$, ArH), 6.28 (s, 2H, ArH), 5.95 (s, 2H, ArH), 2.19 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 1.78 (s, 6H, CH_3). ^{11}B NMR (128 MHz, C_6D_6): 1.04 (s). ^{13}C NMR (100 MHz, C_6D_6): 137.6 (C-Ar), 134.4 (C-Ar), 132.0 (CH-Ar), 131.6 (CH-Ar), 130.3 (C-Ar), 129.0 (C-Ar), 128.8 (C-Ar), 128.0 (CH-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 127.7 (CH-Ar), 127.4 (CH-Ar), 127.3 (C-Ar), 127.2 (CH-Ar), 126.9 (CH-Ar), 126.7 (C-Ar), 126.4 (CH-Ar), 126.1 (C-Ar), 126.0 (CH-Ar), 123.4 (C-Ar), 20.3 (CH_3 -Ar), 19.5 (CH_3 -Ar), 18.0 (CH_3 -Ar). $^{77}\text{Se}\{^1\text{H}\}$ NMR (71.9 MHz, C_6D_6): 148.17, 142.73. HRMS (ESI): m/z calcd for $\text{C}_{60}\text{H}_{52}\text{B}_2\text{N}_4\text{Se}_2$: 1009.2815 [$(M + H)^+$]; found: 1009.2832.

Experimental Mass

Figure 5 Electrospray ionization (ESI) mass spectra of compound **13** with isotopic distributions.

3.4.2 NMR spectra for all new compounds

Figure 6 ^1H NMR spectrum of **13**.

Figure 7 ^{11}B NMR spectrum of **13**.

Figure 8 ^{13}C NMR spectrum of **13**.

Figure 9 ^{13}C NMR (DEPT 135) spectrum of **13**.

Figure 10 $^{77}\text{Se}\{^1\text{H}\}$ NMR spectrum of **13** (*presence of two peaks is putatively due to inequivalent selenium atoms in Se NMR time scale, as predicted by X-ray diffractometry and DFT studies: see *Table 2*).

Figure 11 ^1H NMR spectrum in monitoring the formation of **13** during the reaction of **12** with Se at 80 °C.

Figure 12 ¹H NMR spectrum in monitoring of reaction of **13** with PPh₃ (2 eq).

Figure 13 ⁷⁷Se{¹H} NMR spectrum of a mixture of **13** and PPh₃ after heating at 75 °C for 24h.

3.4.3 Crystallographic Data

X-ray data collection and structural refinement. Intensity data for compound **13** was collected at 100 K using a Bruker D8 Quest diffractometer. The structure was solved by Intrinsic Phasing (SHELXTL XT-2014)²⁵ and refined for all data by full-matrix least squares methods on F^2 .²⁶ 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. The restraint RIGU for the whole molecule was used in the refinement of rei1167m cif. CCDC: 1902297-1902299 contains the supplementary crystallographic data for this paper. 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 Summary of Data collection and structure refinement for compound **13**.

13	
Formula	C ₆₀ H ₅₂ B ₂ N ₄ Se ₂
Fw	1008.59
Cryst syst	triclinic
Space group	P -1
Size (mm ³)	0.020 x 0.100 x 0.120
T/K	100(2)
<i>a</i> , Å	13.734(6)
<i>b</i> , Å	14.180(5)
<i>c</i> , Å	15.375(6)
α , deg	65.974(7)
β , deg	75.771(9)
γ , deg	62.708(8)
V, Å ³	2423.9(17)
<i>Z</i>	2
<i>d</i> calcd g.cm ⁻³	2423.9(17)
μ , mm ⁻¹	1.571
Refl collected	18578
T _{max} /T _{min}	0.9690/0.8340
N _{meas}	8527
[R int]	0.1418
R [I>2sigma(I)]	0.0959
Rw[I>2sigma(I)]	0.2213
GOF	1.026
Largest diff peak/hole[e·Å ⁻³]	0.812/-0.873

Table 6 The coordinates (XYZ) for various optimized structure **13**

B	0.50740000	1.39855600	0.45301000
B	-0.50730800	-1.39859100	0.45303400
C	1.04333400	2.87093600	0.09877500
C	0.78056000	3.43331800	-1.16090000
H	0.19111900	2.87523000	-1.88172900
C	1.22372500	4.70558900	-1.51118400
H	0.98958100	5.10884000	-2.49082600
C	1.95306700	5.46477200	-0.59940000
H	2.29330900	6.46057600	-0.86237600
C	2.23220800	4.93291900	0.65645600
H	2.79577800	5.51310400	1.37958000
C	1.78276300	3.65790400	0.99324800
H	2.01364300	3.27505300	1.98204500
C	1.41686300	0.15444100	-0.04497300
C	2.06720100	-1.99552700	-0.08279600
C	3.17266300	-1.22879500	-0.33805200
C	3.65474600	1.19976000	-0.60952600
C	3.71223700	1.70303100	-1.91786900
C	4.64395000	2.70182100	-2.19488800
H	4.69453700	3.10342300	-3.20216300
C	5.50826800	3.19578800	-1.21639800
C	5.43247400	2.65417600	0.06500600

H	6.10185900	3.01976500	0.83742700
C	4.51849500	1.65135200	0.39542400
C	4.49571800	1.07655000	1.78875100
H	4.96967500	1.76465700	2.49125500
H	5.04865300	0.13260300	1.82671900
H	3.48004800	0.87766100	2.13659200
C	6.47473800	4.31013900	-1.53399600
H	5.97913700	5.28401200	-1.45603200
H	6.86528200	4.22361900	-2.55102200
H	7.32099200	4.31500000	-0.84370800
C	2.80727900	1.18642500	-3.00860400
H	3.13861300	1.54809800	-3.98347800
H	1.77921900	1.52492200	-2.85984200
H	2.78260800	0.09374100	-3.04080700
C	4.57841700	-1.65864200	-0.50813800
C	5.32186500	-1.35285300	-1.65542900
H	4.87417400	-0.77265000	-2.45109500
C	6.63516000	-1.79458700	-1.78899900
H	7.19409600	-1.54730800	-2.68451800
C	7.22746800	-2.55293200	-0.78220200
H	8.24992800	-2.89743500	-0.88875800
C	6.49743900	-2.86623700	0.36222900
H	6.94834000	-3.45614000	1.15215600
C	5.18639200	-2.42162200	0.49957900
H	4.62273000	-2.66800000	1.39082800
C	2.08865500	-3.46573700	0.08869700
C	2.60015200	-4.27657900	-0.93199000
H	2.89482300	-3.82612400	-1.87255000

C	2.73331900	-5.64931300	-0.74908200
H	3.12862500	-6.26288800	-1.55095300
C	2.35861200	-6.23165500	0.45930100
H	2.45946300	-7.30163400	0.60350600
C	1.85180900	-5.43178100	1.48184400
H	1.55856800	-5.87748300	2.42572500
C	1.71952800	-4.05853900	1.30230400
H	1.33136500	-3.43760700	2.10113800
C	-1.04332100	-2.87094200	0.09882400
C	-0.78073400	-3.43324700	-1.16092400
H	-0.19137300	-2.87509500	-1.88177100
C	-1.22396900	-4.70548800	-1.51123100
H	-0.98998300	-5.10867500	-2.49093700
C	-1.95317800	-5.46472400	-0.59938400
H	-2.29348100	-6.46050100	-0.86238000
C	-2.23210100	-4.93296000	0.65655800
H	-2.79554400	-5.51320200	1.37973800
C	-1.78259500	-3.65797000	0.99336900
H	-2.01329800	-3.27520400	1.98224000
C	-1.41680200	-0.15448400	-0.04490400
C	-2.06712800	1.99550000	-0.08266900
C	-3.17258800	1.22876800	-0.33790100
C	-3.65476500	-1.19970900	-0.60954200
C	-4.51832900	-1.65156300	0.39555600
C	-5.43237200	-2.65423300	0.06515400
H	-6.10160100	-3.01995900	0.83765200
C	-5.50856100	-3.19550300	-1.21644200
C	-4.64458900	-2.70126900	-2.19500000

H	-4.69560100	-3.10246600	-3.20240900
C	-3.71267600	-1.70257100	-1.91795600
C	-2.80784200	-1.18612700	-3.00886700
H	-2.77824700	-0.09350700	-3.03738200
H	-3.14280700	-1.54303900	-3.98426800
H	-1.78102500	-1.52989200	-2.86339400
C	-6.47504300	-4.30993800	-1.53368400
H	-5.98223500	-5.28432000	-1.44475500
H	-6.85737700	-4.22987500	-2.55430200
H	-7.32668300	-4.30808300	-0.84999600
C	-4.49519800	-1.07701600	1.78898400
H	-3.47943200	-0.87842100	2.13671200
H	-4.96923200	-1.76511800	2.49143600
H	-5.04788100	-0.13293400	1.82719300
C	-4.57834500	1.65861300	-0.50804200
C	-5.18665500	2.42085400	0.50001300
H	-4.62325000	2.66667900	1.39158100
C	-6.49769600	2.86547600	0.36256600
H	-6.94888900	3.45481000	1.15275100
C	-7.22732900	2.55293000	-0.78232100
H	-8.24977800	2.89744300	-0.88896100
C	-6.63464900	1.79536300	-1.78949300
H	-7.19328600	1.54871800	-2.68537300
C	-5.32137200	1.35361500	-1.65581500
H	-4.87331800	0.77405200	-2.45175100
C	-2.08867600	3.46569000	0.08897400
C	-2.60042300	4.27658600	-0.93154800
H	-2.89519100	3.82620600	-1.87211200

C	-2.73370600	5.64928800	-0.74848300
H	-3.12920600	6.26289700	-1.55023200
C	-2.35886300	6.23155200	0.45989600
H	-2.45980700	7.30150500	0.60422500
C	-1.85181200	5.43162500	1.48227300
H	-1.55846300	5.87726000	2.42615300
C	-1.71941600	4.05841500	1.30257800
H	-1.33106900	3.43745500	2.10129900
N	0.97791000	-1.12348400	0.05203600
N	2.75164400	0.10548500	-0.32920200
N	-0.97784400	1.12343900	0.05214400
N	-2.75159900	-0.10551400	-0.32907100
Se	0.52031400	1.07565100	2.60622500
Se	-0.52000700	-1.07573900	2.60624500

3.5 References

1. E. V. Grotthuss, F. Nawa, M. Bolte, H. W. Lerner, M. Wagner, *Tetrahedron*, **2019**, 75, 26.
2. S. Yruegas, C. D. Martin, *Chem. Eur. J.*, **2016**, 22, 18358.
3. D. Auerhammer, M. Arrowsmith, R. D. Dewhurst, T. Kupfer, J. Böhnke, H. Braunschweig, *Chem. Sci.*, **2018**, 9, 2252.
4. M. Arrowsmith, D. Auerhammer, R. Bertermann, H. Braunschweig, G. Bringmann, M. A. Celik, R. D. Dewhurst, M. Finze, M. Grüne, M. Hailmann, T. Hertle, I. Krummenacher, *Angew. Chem., Int. Ed.*, **2016**, 55, 14464.
5. T. K. Wood, W. E. Piers, B. A. Keay, M. Parvez, *Angew. Chem., Int. Ed.*, **2009**, 48, 4009.
6. S. Porcel, G. Bouhadir, N. Saffon, L. Maron, D. Bourissou, *Angew. Chem., Int. Ed.*, **2010**, 49, 6186.
7. a) J. T. Henthorn, T. Agapie, *Angew. Chem., Int. Ed.*, **2014**, 53, 12893; b) J. T. Henthorn, S. Lin, T. Agapie, *J. Am. Chem. Soc.*, **2015**, 137, 1458; c) L. Liu, L. L. Cao, Y. Shao, D. W. Stephan, *J. Am. Chem. Soc.*, **2017**, 139, 10062.
8. X. Tao, C. G. Daniliuc, O. Janka, R. Pçttgen, R. Knitsch, M. R. Hansen, H. Eckert, M. Lgbbesmeyer, A. Studer, G. Kehr, G. Erker, *Angew. Chem., Int. Ed.*, **2017**, 56, 16641.
9. E. Tsurumaki, J. Sung, D. Kim, A. Osuka, *Angew Chem., Int Ed.*, **2016**, 55, 2596.

10. J. W. Taylor, A. McSkimming, C. F. Guzman, W. H. Harman, *J. Am. Chem. Soc.*, **2017**, *139*, 11032.
11. L. Kong, W. Lu, Y. Li, R. Ganguly, R. Kinjo, *Angew. Chem., Int. Ed.*, **2016**, *55*, 14718.
12. A. Z. Rys, E. K. V. Schultz, D. N. Harpp, *J. Sulfur Chem.*, **2010**, *31*, 351.
13. B. Wang, R. Kinjo, *Chem. Sci.*, **2019**, *10*, 2088.
14. G. C. Welch, R. R. San Juan, J. D. Masuda, D. W. Stephan, *Science*, **2006**, *314*, 1124.
15. a) D. Wu, R. Ganguly, Y. Li, S. N. Hoo, H. Hirao, R. Kinjo, *Chem. Sci.*, **2015**, *6*, 7150; b) D. Wu, L. Kong, Y. Li, R. Ganguly, R. Kinjo, *Nat. Commun.*, **2015**, *6*, 7340; c) B. Wang, Y. Li, R. Ganguly, H. Hirao, R. Kinjo, *Nat. Commun.*, **2016**, *6*, 11871; d) E. V. Grotthuss, E. Diefenbach, M. Bolte, H. W. Lerner, M. C. Holthausen, M. Wagner, *Angew. Chem., Int. Ed.*, **2016**, *55*, 14067.
16. M. Arrowsmith, H. Braunschweig, T. E. Stennett, *Angew. Chem., Int. Ed.*, **2017**, *56*, 96.
17. M. A. Le´gare, C. Prankevicius, H. Braunschweig, *Chem. Rev.*, **2019**, *119*, *14*, 8261.
18. H. Braunschweig, T. Kupfer, *Chem. Commun.*, **2011**, *47*, 10903.
19. H. Braunschweig, I. Krummenacher, J. Wahler, in *Adv. Organomet. Chem.*, ed. A. F. Hill and M. J. Fink, Academic Press, **2013**, *61*, 1.
20. J. H. Barnard, S. Yruegas, K. Huang, C. D. Martin, *Chem. Commun.*, **2016**, *52*, 9985.

21. G. K. H. Goh, Y. Li, R. Kinjo, *Dalton Trans.*, **2019**, 48, 7514.
22. a) S. Zhang, X. Wang, Y. Su, Y. Qiu, Z. Zhang, X. Wang, *Nat. Commun.*, **2014**, 5, 4127; b) M. Majid, S. Bénazeth, C. Souleau, J. Purans., *Phys. Rev. B.*, **1998**, 58, 6104.
23. a) H. Braunschweig, T. Dellermann, W. C. Ewing, T. Kramer, C. Schneider, S. Ullrich, *Angew. Chem., Int. Ed.*, **2015**, 54, 10271; b) M. Ito, N. Tokitoh, T. Kawashima, R. Okazaki, *Tetrahedron Lett.*, **1999**, 40, 5557.
24. a) W. Clegg, C. Dai, F. J. Lawlor, T. B. Marder, P. Nguyen, N. C. Norman, N. L. Pickett, W. P. Power, A. J. Scott, *J. Chem. Soc., Dalton Trans.*, **1997**, 0, 839; b) B. Wrackmeyer, E. V. Klimkina, W. Milius, *Eur. J. Inorg. Chem.*, **2011**, 4481; c) B. Wrackmeyer, E. V. Klimkina, W. Milius, *Polyhedron*, **2010**, 29, 2324; d) H. Braunschweig, P. Constantinidis, T. Dellermann, W. C. Ewing, I. Fischer, M. Hess, F. R. Knight, A. Rempel, C. Schneider, S. Ullrich, A. Vargas, J. D. Woollins, *Angew. Chem., Int. Ed.*, **2016**, 55, 5606.
25. G. M. Sheldrick, *Acta Cryst.*, **2015**, A71, 3.
26. G. M. Sheldrick, *Acta Cryst.*, **2015**, C71, 3.

Chapter 4 Metal-free C(sp³)-H borylation by a 1,4,2,5-Diazadiborinine

4.1 Introduction

4.1.1 sp² C–H borylation

In 2006, the group of Aldridge presented the first example of migratory insertion into a C–H bond for an isolated transition metal boryl complex (Scheme 1).¹ The driving force for the insertion of the [B(C₆F₅)₂] moiety into a C–H bond of the Cp ring is the coordination of the CO ligand to the Fe metal center. It is proposed that [B(C₆F₅)₂][–] migrates as a unit to the Cp ring however the mechanistic pathway was not discussed in detail by Aldridge et al. The ¹¹B NMR spectrum for compound **b** shows a doublet at –24.8 ppm with a coupling constant of 90 Hz indicative of the B–H coupling.

Scheme 1 The sp² C–H activation of compound **a** by the group of Aldridge

In 2008, Braunschweig and co-workers presented the reaction between chromium borylene compound **c** and excess amount of 3,3-dimethylbutene at room temperature in THF for 40 hours.² The borylene in compound **c** inserts into an sp² C–H bond of the 3,3-dimethylbutene to afford compound **d** and **e** (Scheme

2). Compound **d** and **e** were generated in the ratio of 1:3 as observed in the ^1H NMR spectroscopy analysis of the red crude oil obtained after workup. There were multiple attempts made at crystallization of the crude red oil in hexane at -60°C with the removal of the starting material compound **c** before the red crystals of **e** were successfully isolated. The ^{11}B NMR spectroscopy of compound **e** displayed a signal at 43.5 ppm. The non-coordinated compound **d** could be isolated from the crude mixture by the addition of two equivalents of PCy_3 (Scheme 3). Compound **d** was isolated as a colourless liquid.

Scheme 2 The sp^2 C–H activation of compound **c** by the group of Braunschweig

Scheme 3 The generation of the pure compound **d** by the group of Braunschweig

In 2015, the group of Braunschweig reported an unexpected C–H activation of the generally inert Cp ligand by compound **f** (Scheme 4).³ Compound **f** first undergoes isomerization which the former borylene moiety migrates to the cyclopentadienyl (Cp) ligand and subsequently inserts into a C–H bond to afford compound **g** in DCM at room temperature. The initial red solution containing compound **f** gradually turned yellow. The generation of compound **g** is also feasible with the use of non-polar hydrocarbon solvents such as benzene or hexane at a slower rate. Compound **g** contains an 18-valence electron metal center and a tetracoordinate boron center. The ¹¹B NMR spectrum of compound **g** shows a doublet at 2.79 ppm with a coupling constant of 64 Hz indicative of the B–H coupling.

Scheme 4 The sp^2 C–H activation of compound **f** by the group of Braunschweig

In 2019, Kinjo et al. had described the first selective activation of a C–H bond of benzene (C_6H_6) and the 1,3-di(trifluoromethyl)benzene by an annulated 5-chlorinated 1,3,2,5-diazadiborinine derivative **h** (Scheme 5).^{4,30} Compound **h** was heated at 90 °C for 30 hours in a benzene solution which the red solution gradually turned into a colorless solution. Compound **i** was isolated as a white powder in 76% yield after the workup. Compound **j** was generated at 120 °C over 18 hours as a white powder in 72% yield. Compound **i** and **j** were confirmed by crystallographic studies which present both the aryl group and the H atom connected on the boron centers to be on the same side with respect to the $\text{B}_2\text{C}_2\text{N}_2$ six-membered ring. This indicates that the C–H activation proceeds regio- and stereo selectively.

Scheme 5 The sp^2 C–H activation of compound **h** by the group of Kinjo

4.1.2 sp^3 C–H activation by phosphinidene complexes

In 1993, the group of Stephan had presented the sp^2 Cp–H activation by a terminal phosphinidene complex **k**.⁵ The hydrogen of the Cp ring was transferred to the phosphinidene ligand to afford compound **l** (Scheme 6). The driving force of the reaction was proposed to be the absence of alternative ligands available to the metal center, therefore the hydrogen atom had limited choice but to coordinate with the phosphinidene ligand instead of engaging in a reversed migratory insertion.

Scheme 6 The sp^2 C–H activation of compound **k** by the group of Stephan

4.1.3 sp^3 C–H borylation

In 2001, the group of Weber reported the treatment of compound **m** with potassium–sodium alloy in toluene solution in the presence of [15] crown-5 at room temperature for 2 hours.⁶ This reaction yielded a 1: 1 mixture of compound **n** and **o** (Scheme 7). Compound **o** was subsequently isolated in an 88% yield. The same reaction was conducted in $[D_8]$ toluene and the reaction yielded compound **p** and **q** in a 1: 1 ratio. It is noteworthy that the similar reaction conducted in C_6D_6 only led to the selective production of compound **n**. This indicates that C_6D_6 did not contribute the source of deuterium or the phenyl substituent, differing from that in the case of toluene. A reasonable mechanistic pathway was proposed (Scheme 8). Compound **m** was initially reduced to radical **s** via radical anion **r**. Radical **s** could be further reduced to compound **t**. Compound **t** acts as a strong Brønsted base to abstract a deuteron from $[D_8]$ toluene to give compound **p** and $C_6D_5CD_2^-$. Compound **q** was generated with the addition of another equivalent of compound **m**.

Scheme 7 The sp^3 C–H, C–D activation of compound **m** by the group of Weber

Scheme 8 The mechanistic pathway for the sp^3 C–D activation of compound **m** by the group of Weber

In 2011, the group of Braunschweig reported the reaction between compound **u** and vinylidenerhodium compound **v** to generate compound **w** at 40°C in C_6D_6 for 16 hours (Scheme 9).⁷ After coupling to the vinylidene ligand,

the borylene ligand was inserted into a sp^3 C–H bond of an adjacent cyclohexyl group to afford compound **x** at 85 °C in C_6D_6 for 14 days (Scheme 10). Compound **x** was subsequently isolated as pale-yellow crystals by crystallization from hexane at room temperature. The $^{11}B\{^1H\}$ NMR spectrum of compound **x** showed a signal at 68.7 ppm. This was presented as the first example of a thermally induced B–C to C–C coordination shift with a subsequent sp^3 C–H activation by the B=C bond.

Scheme 9 The generation of compound **w** by the group of Braunschweig

Scheme 10 The sp^3 C–H activation of compound **w** by the group of Braunschweig

In 2014, Yamashita, Nozaki and Anwender et al. reported the treatment of toluene and *p*-xylene with the diaminoboryllithium **y**.⁸ Compound **y** was treated with 1.6 equivalents of toluene at room temperature in a [D₁₂] cyclohexane solution for 4 days to generate compound **z** and a white precipitate, LiH (Scheme 11). Compound **y** was also treated with *p*-xylene in *n*-hexane for three days at room temperature to afford compound **aa**, **bb**, **cc** and LiH (Scheme 12). Compound **aa** and **bb** were subsequently isolated in yields of 19% and 15% respectively. The mechanistic pathway was proposed which compound **y** deprotonates the methyl group of toluene to generate compound **cc** and benzyllithium. A nucleophilic attack then occurs at the anionic phenyl carbon at the boron center which gives compound **dd**. LiH is then precipitated with the elimination of the hydride to generate compound **z** (Scheme 13).

Scheme 11 The sp^3 C–H activation of compound **y** with toluene by Yamashita, Nozaki, Anwender and co-workers

Scheme 12 The sp^3 C–H activation of compound **y** with *p*-xylene by Yamashita, Nozaki, Anwender and co-workers

Scheme 13 The mechanistic pathway for the sp^3 C–H activation of compound **y** with toluene by Yamashita, Nozaki, Anwender and co-workers

In 2017, the group of Wang reported the two electron reduction of the 2,6-bis(BMes₂)mesitylene with elemental potassium to generate the C–H activation product which bears a BC₃ four-membered ring (Scheme 14).⁹ The diradical **ee** undergoes C–H activation with the methyl group of the central aromatic ring at -30°C over a period of three days to afford the dianion salt, compound **ff**. Compound **ff** was isolated as colorless crystals. Two signals at -7.5 and -14.9 ppm were observed in the ^{11}B NMR spectrum. The latter signal was observed as a doublet with a coupling constant of 76.4 Hz due to its coupling with the hydrogen atom.

Scheme 14 The sp^3 C–H activation of compound **ee** by the group of Wang

4.2 Results and Discussion:

4.2.1 Objective

There had been significant progress made towards the development of systems that catalyzes borylation reactions of C–H bonds in alkanes, alkenes, and arenes over the past several decades.¹⁻⁹ The advantage of such sp^2/sp^3 C–H activations lies in the ability to shortcut synthetic routes, provide possibility for late-stage diversification and regioselective modification of aromatic compounds.³ The investigations had developed from stoichiometric reactions to synthetic methods currently being studied by several groups and utilized by synthetic chemists in materials sciences, synthesis of fine chemicals and natural product synthesis for drug development. In addition, many of such sp^2/sp^3 C–H activations reported utilized transition metals as a catalyst which tends to produce side products that are harmful to the environment.⁴ As such, metal-free sp^2/sp^3 C–H activations appear as the solution highly sought by researchers in various chemical fields.

With this goal in mind, we seek to discover the possibilities of metal-free C–H borylation by diazadiborinines ($B_2C_2N_2$ six-membered rings) which remains extremely challenging to date. Herein, we report the synthesis, single crystal X-ray diffraction analysis and computational studies of the first metal-free sp^3 C–H borylation by a 1,4,2,5-Diazadiborinine.

4.2.2 Reaction of 1,4,2,5-diazadiborinine with Toluene and [D₈] toluene

Ten equivalents of toluene were added to one equivalent of **12** (Scheme 15) in a NMR tube. The reaction mixture was heated at 50 °C for 100 hours and monitored by NMR spectroscopy. During the reaction, the red color of the solution gradually turned yellow. A crude mixture involving a major product and a minor product (Fig. 37) was generated and subjected to work up, from which compound **14** was obtained as a yellow powder in 42% isolated yield. Compound **14** was fully characterized by standard spectroscopic techniques and X-ray crystallography (Fig. 1).

Scheme 15 Reactivity of compound **12** with Toluene

Figure 1 The solid-state structure of **14**. Thermal ellipsoids are set at the 50% probability level. All H atoms and solvent molecules are omitted for clarity

Crystallographic studies revealed that compound **14** bears a 1,3,2,5 B₂C₂N₂ six-membered skeleton involving a CH₂Ph unit attached on the boron center between two nitrogen atoms while the H atom forms a B–H unit with the boron center between two carbon atoms. This represents a rare example of a metal-free C(*sp*³)–H borylation by an aromatic diazadiborinine involving the skeletal isomerization of the diazadiborinine ring. The CH₂–Ph unit and the H atom on the boron centers are on different sides with respect to the 1,3,2,5 B₂C₂N₂ six-membered ring. Note that the formation of compound **14** represents the first example of *sp*³C–H activation by a diazadiborinine in addition to the skeletal isomerization from a 1,4,2,5 B₂C₂N₂ ring to a 1,3,2,5 activated product.

In the solid state structure, the boron centers in **14** adopt a tetrahedral geometry with the N1–B1–N3 bond angle of 106.7(2) ° and the C1–B2–C25 bond angle of 105.5(2)°. The B1–N1 [1.586(4) Å], B1–N3 [1.591(4) Å], B2–C1 [1.608(4) Å] and B2–C25 [1.598(4) Å] distances in **14** are longer than 1.457–1.462(4) Å and 1.494–1.496(4) Å in compound **12**, respectively (Table 1). The N–C bonds in **14** (N1–C1: 1.335(3) Å, N3–C25: 1.341(3) Å) are shorter when compared to those (N–C: 1.406(3) Å and 1.407(3) Å) in **12**. The B1–C55 bond (1.629(4) Å) and B2–H1B bond (1.15(3) Å) distances are in the range of those reported for B–C (1.55–1.65 Å) and B–H single bonds as observed for related compounds (1.14 to 1.20 Å).^{3,4,7}

	12	14
B–N (Å)	1.457(4) 1.462(4)	1.586(4) 1.591(4)
N–C (Å)	1.407(3) 1.406(3)	1.335(3) 1.341(3)
C–B (Å)	1.496(4) 1.494(4)	1.608(4) 1.598(4)

Table 1 BN, NC, and CB Bond Lengths of compounds **12** and **14**

To gain insight into the electronic properties of compound **14**, theoretical calculations were carried out using a DFT method at the B3LYP/6-311G(d,p) level of theory. The HOMO of **14** is mainly dominated by the π system interactions over the CBC π unit in the $B_2C_2N_2$ ring with the phenyl ring attached to the boron center, the NBN π unit in the $B_2C_2N_2$ ring with the CH_2Ph unit attached to the boron atom. There is also significant contribution from the annulated imidazole ring consisting of the N lone pairs and the C=C moieties π interactions with the π system of the phenyl substituents (Fig. 2). The LUMO of **14** consists of the π bonding interactions of the annulated imidazole rings with contribution from the N lone pairs and the C=C moieties with the π orbitals of the phenyl substituents (Fig. 3). The HOMO–LUMO energy gap (5.02 eV) of **14** is larger than that (2.56 eV) of **12**.

Figure 2 Side view (left) and top view (right) of the HOMO of **14**. All H atoms are omitted for clarity

Figure 3 Side view (left) and top view (right) of the LUMO of **14**. All H atoms are omitted for clarity

The Wiberg bond index (WBI) values of B1–N1 (0.62), B1–N3 (0.62), B2–C1 (0.89) and B2–C25 (0.89) in **14** suggest the single bond nature around boron atoms in the B₂C₂N₂ ring as compared to the Wiberg bond index (WBI) values of B1–C1 (1.19), B2–C2 (1.19), C2–N1 (1.12), C1–N3 (1.12) in **12** which features the partial multiple-bond nature of the bonds in the B₂C₂N₂ ring. **14** adopts a tetrahedral geometry at the boron centers which agrees with the crystallographic structure.

Bond (Å)	X-ray data	Optimized structure	WBI Value
B1–N1	1.586(4)	1.60740	0.6212
B1–N3	1.591(4)	1.60609	0.6212
B2–C1	1.608(4)	1.61308	0.8850
B2–C25	1.598(4)	1.61270	0.8851
N1–C1	1.335(3)	1.34569	1.3392
N3–C25	1.341(3)	1.34558	0.7780
B1–C55	1.629(4)	1.64191	0.8285
B2–H1B	1.15(3)	1.21316	0.9113

Table 2 Selected Bond Lengths and Wilberg Bond Index (WBI) for the optimized geometries of compound **14**

The ^{11}B NMR spectrum of **14** exhibits a characteristic signal at 1.08 and -19.8 ppm, indicating the formation of two tetracoordinate boron centers. Both

boron centers are shifted up field compared to that (10.28 ppm) of **12**. The calculated ^{11}B NMR chemical shift (0.32 and -21.1 ppm) on **14** using the gauge-independent atomic orbital (GIAO) method at the B3LYP/6-311G(d,p) level of theory reasonably agrees with the experimental value (Table 3). The boron center connected to the CH_2Ph unit, in between two nitrogen atoms is assigned to 1.08 ppm while the other boron center connected to a H atom, in between two carbon atoms, is assigned to -19.8 ppm (Fig. 28). The coupling of the signal at -19.8 ppm in the ^{11}B NMR indicates the presence of a B–H unit (Fig. 29). The value of the coupling constant of the B–H unit is 75.8 Hz which is in the range of those reported for B–H single bonds as observed for related compounds (64 to 90 Hz).^{3,4,7} In the ^1H NMR of **14**, three signals for the methyl groups of the mesityl groups were observed at 1.31 ppm, 1.85 ppm and 2.45 ppm indicative that compound **12** had reacted with toluene to generate compound **14** (Fig. 27). In the HMQC NMR, the CH_2 of the B– CH_2Ph unit in compound **14** is assigned at 29.9 ppm in the ^{13}C (DEPT135) NMR spectrum and 3.08 ppm in the ^1H NMR spectrum, respectively (Fig. 31).

	Isotropic Values	Calculated $\delta (^{11}\text{B})[\text{ppm}]$	Experimental $\delta (^{11}\text{B})[\text{ppm}]$
14	103.0923	0.3256	1.08
	124.5490	-21.1311	-19.8
BF₃.Et₂O (Reference)	103.4179	-	-

Table 3 Experimental and calculated ^{11}B NMR chemical shifts of compound **14**.

Our initial attempt to monitor the reaction of **12** with ten equivalents of toluene in C_6D_6 did not yield any conclusive results, which was probably due to the presence of excess C_6D_6 which hindered the generation of **14**. In order to circumvent the issue, one equivalent of **12** was treated with ten equivalents of $[D_8]$ toluene solution at $50^\circ C$ for 70 hours in aims to monitor the progress of reaction by 1H NMR (Fig. 37). In the 1H NMR monitoring of **14**, three signals for the methyl groups of the mesityl groups were observed at 1.24 ppm, 1.84 ppm and 2.43 ppm indicative that compound **12** had reacted with $[D_8]$ toluene to generate compound **14**. The crystals isolated from the reaction of **12** and toluene were dissolved in $[D_8]$ toluene to act as a point of reference to the monitoring 1H spectrum (Fig. 38). The two protons corresponding to the CH_2Ph unit signaled at 2.99 ppm are not observed in the 1H NMR monitoring with $C_6D_5CD_2^-$ unit in place. The proton corresponding to the B–H unit at 5.61 ppm is not observed with B–D unit in place and the signals observed from 7.32-7.54 ppm corresponding to the aromatic protons of phenyl group in CH_2Ph unit are also not observed with the aromatic deuterated protons in place. Note that there is presence of various peaks at up field region of 1-3 ppm which could correspond to a 1,4,2,5 toluene activated product with the D and $C_6D_5CD_2^-$ being in cis conformation with respect to the $B_2C_2N_2$ ring. This will be discussed in detail in the mechanism section of this chapter.

The boron center connected to the $C_6D_5CD_2^-$ unit, in between two nitrogen atoms is assigned to 1.47 ppm while the other boron center connected to a D atom, in between two carbon atoms, is assigned to -19.8 ppm (Table 4). These boron

chemical shifts reasonably agree with that of **14** signaled at 2.01, –19.7 ppm in [D₈] toluene and 1.08, –19.8 ppm in C₆D₆. (Table 4).

Experimental δ (¹¹ B) [ppm]	14 in C ₆ D ₆	14 in [D ₈] toluene	15 in [D ₈] toluene
B1	1.08	2.01	1.47
B2	–19.8	–19.7	–19.8

Table 4 Experimental ¹¹B NMR chemical shifts of compound **14** in C₆D₆, [D₈] toluene and compound **15** in [D₈] toluene .

4.2.3 Reaction of 1,4,2,5-diazadiborinine with the halogenated methylbenzenes (x= I, Cl, F) and the trifluoromethyl benzenes (x= CF₃).

As the previous reaction with toluene and [D₈] toluene proceeded at 50 °C, the scope of the activation of the *sp*³ C–H bond was examined at 50 °C with various halogenated methylbenzenes (x= I, Cl, F) and trifluoromethyl benzenes (x= CF₃). Meta and para substituents were investigated for their effects on the reaction yield and reaction rates.

Scheme 16 The *sp*³ C–H activation of the electron-withdrawing methylbenzenes by **12**

In an NMR tube, ten equivalents of electron-withdrawing methylbenzenes (x=CF₃, F, Cl and I) were added to one equivalent of **12** in C₆D₆(Scheme 16). The reaction mixture was heated at 50 °C and monitored by NMR spectroscopy. During the reaction, the red color of the solution gradually turned yellow for the reactions investigated. A crude mixture involving a major product and a minor product (Fig. 41,53,54,60,66,67,73) was generated and subjected to work up, from which compounds **16-21** were obtained as a yellow powder. Compound **16-21** were subsequently generated in large scale and fully characterized by standard spectroscopic techniques.

The electron-withdrawing methylbenzenes **16- 21** afforded a moderate yield of 43-52 %. The moderate yield could be due to slight presence of the starting material **12** when the reactions were halted due to insignificant reaction progress with time. In addition, some of the product may exist as the 1,4,2,5 activated isomer which is not thermodynamically stable enough to exist in the solid state (Table 5).

Electron-withdrawing methylbenzenes	Product	T [°C]	Time/ hours	Yield [%]
16	50	16	52
17	50	20	50
18	50	22	51
19	50	24	53
20	50	18	45
21	50	30	43

Table 5 Substrate scope of electron-withdrawing methylbenzenes and the respective reaction conditions and yields for compound **16-21**.

The para substituents giving rise to compound **16-19** generated a yield of 50-53% while the meta substituents (compound **20,21**) generated a yield of 43-45%. The meta electron-withdrawing substituents gave a lower yield as compared to the para substituents. The experimental yields agree with the hypothesis that para electron-withdrawing substituents contribute more resonance effect to stabilize the negative charge of the conjugate base, therefore increasing acidity of the sp^3 C–H bond for a greater rate of reaction and reaction yield.

4.2.4 Reaction of 1,4,2,5-diazadiborinine with the *m/p*-xylenes ($x = \text{CH}_3$), methoxy methylbenzene ($x = \text{OMe}$) and N, N,4-trimethylaniline ($x = \text{N}(\text{CH}_3)_2$).

The previous reaction with toluene, [D₈] toluene and the various electron-withdrawing substituents proceeded at 50 °C, thus the scope of the activation of sp^3 C–H bond for the electron donating substituents ($x = \text{CH}_3$, OMe and $\text{N}(\text{CH}_3)_2$) were initially examined at 50 °C. Both meta and para substituents were investigated for their effects on the reaction yield and reaction rates. However, the reactions did not seem to proceed well with little changes observed via NMR spectroscopy or the physical color of the solution. The investigations were then conducted at a higher temperature of 80 °C to determine the effects of electron donating substituents on the sp^3 C–H bond activation by **12**.

Scheme 17 The sp^3 C–H activation of the electron donating methylbenzenes by

12

In an NMR tube, ten equivalents of various electron donating methylbenzenes ($x = \text{CH}_3$, OMe and $\text{N}(\text{CH}_3)_2$) were added to one equivalent of **12** (Scheme 17) in C_6D_6 . The reaction mixture was heated at 80°C and monitored by NMR spectroscopy. During the reaction, the red color of the solution gradually turned yellow for the reactions investigated. A crude mixture involving a major product and a minor product (Fig. 79,90) was generated and subjected to work up, from which compounds **22-25** were obtained as a yellow powder. Compound **22-25** were subsequently generated in large scale and fully characterized by standard spectroscopic techniques.

Electron donating methylbenzenes	Product	T [$^\circ\text{C}$]	Time/ hours	Yield [%]
	22	80	70	35
	23	80	70	40

24	80	70	40
25	80	72	34

Table 6 Substrate scope of electron donating methylbenzenes and the respective reaction conditions and yields for compound **22-25**.

The electron donating methylbenzenes **22-25** afforded a slightly lower yield of 34-40% (Table 6). The lower yield could be attributed to the electron donating nature of the substituents via resonance effect which increases the negative charge of the conjugate base. This in turn reduces the stability of the conjugate base and decreases the acidity of the sp^3 C–H bond as compared to that of the electron-withdrawing substituents. Therefore, a slightly lower yield and harsher reaction conditions were observed for the electron donating substituents with respect to the electron-withdrawing substituents.

4.3 The Proposed mechanistic pathway for reaction between **12** and toluene:

To gain insight into the reaction mechanism, the pathways for the reaction of **12** with toluene were explored theoretically using pbe1pbe/Def2SVP Empirical Dispersion=GD3BJ SCRF= (PCM, solvent=Toluene) functional. Based on the experimental data of the ^1H monitoring spectra of the generation of compound **14** and the minor product (Fig. 37) with the stability of compound **14** in C_6D_6 at 50°C (Fig. 101), compound **14** and its minor product does not seem to be in equilibrium which no reversible formation of **14** with its minor product was observed. Therefore, we proposed the possibility of two different mechanistic pathways which exists to generate compound **14** and its minor product from compound **12** and toluene, respectively.

Despite multiple attempts to isolate and characterize the minor product, we had not been successful to confirm the identity of the minor product by crystallography studies. However, we had utilized computational studies to propose the identity of the minor product to be the cis C–H activated 1,4,2,5 adduct as shown in the first proposed mechanistic pathway below (Fig. 4). Compound **12** and toluene reacted at 50°C in a concerted fashion to overcome an activation barrier of 40.9 kcal/mol. The reaction pathway subsequently passed through the transition state structure **TS1** before generating the minor product **Int1a** at the energy level of -20.8 kcal/mol.

The second proposed mechanistic pathway (Fig. 5). involved compound **12** first reacting with toluene at 50°C to overcome a similar activation energy barrier of 40.9 kcal/mol to generate a concerted C–H activated transition state

structure **TS1** before affording the **Int1b** structure at 36.1kcal/mol. It is noteworthy that **Int1b** is the incomplete structure of **Int1a** which the B–C bond between one of the boron of the B₂C₂N₂ ring and the carbon atom of the annulated imidazole is cleaved. **Int1b** subsequently passed through **TS2** by overcoming an activation barrier of 9.3kcal/mol to generate **Int2** at the energy level of 44.7kcal/mol. At the current stage, the adjacent annulated imidazole was completely cleaved from the two boron atoms which both the B–C and B–N bond were cleaved in attempt to form the BNN unit. **Int2** further overcomes an activated barrier of 4.7kcal/mol to bypass **TS3** to generate **Int3** at the energy level of –16.4 kcal/mol with the formation of a BCC unit. It is noteworthy that **Int3** resembles a disoriented structure of the cis C–H activated 1,3,2,5 adduct which the skeletal isomerization from the initial 1,4,2,5 B₂C₂N₂ skeletal ring in compound **12** had occurred. A subsequent cis trans isomerism then takes place with **Int3** to generate the final compound **14** at the energy level of –25.9 kcal/mol as a trans C–H activated 1,3,2,5 adduct, confirmed by the xray crystallography studies. The driving force of the generation of compound **14** is believed to be the stability of compound **14** which is the lower energy and more stable structure as compared to the cis C–H activated 1,4,2,5 adduct, **Int1a**.

Figure 4 Concerted C-H bond activation of toluene by **12** to generate minor product.

Figure 5 Concerted C-H bond activation of toluene by **12** to generate compound **14**.

4.4 Kinetic Studies:

4.4.1 The Kinetic Isotope Effect of Toluene and [D₈] toluene

To gain insight into the sp^3 C–H activation mechanism, we carried out further analysis of the reaction using deuterated [D₈] toluene to examine the deuterium kinetic isotope effects (DKIE) on the reaction. A solution of 4.7×10^{-5} mol of **12** in 0.6 mL of [D₈] toluene was prepared in a sealed NMR tube and heated at 50°C for 100 hours. The reaction was monitored by NMR spectroscopy. The DKIE value was generated based on the rate constants obtained from the concentration time graph of toluene and [D₈] toluene determined experimentally (Fig.4,5).

Figure 6 Plot of the rate of reaction of **12** with toluene at 50 °C over 100 hours

Figure 7 Plot of the rate of reaction of **12** with [D₈] toluene at 50°C over 100 hours

The experimental DKIE of toluene and [D₈] toluene showed a value of 2.31 (Table 7). The value implies that a larger energetic input is needed for [D₈] toluene to reach the transition state. This is due to deuterium being a heavier isotope of the hydrogen atom which lowers its vibration frequencies and thus [D₈] toluene possesses a lower zero-point energy than toluene.^{10,11} Geometry optimization calculations of [D₈] toluene and toluene were performed at the pbe1pbe/Def2SVP level of theory with the dispersion forces Empirical Dispersion=GD3BJ and the solvent effects SCRF= (PCM, solvent=Toluene) taken into consideration. The calculated zero-point vibrational energy of [D₈] toluene is 64.4 kcal/mol while that of toluene is 80.6 kcal/mol. With a lower zero-point energy, more energy is required to cleave the *sp*³ C–D bond. This results in a higher activation energy needed for the bond cleavage which lowers the rate of reaction between **12** and [D₈] toluene as compared to that of **12** with toluene. The

activation energy estimated from the computational calculations for toluene is 40.9 kcal/mol while that of [D₈] toluene is 41.8 kcal/mol. The values agree reasonably well with the experimental DKIE value which indicates a supposedly higher activation energy required for the reaction of **12** and [D₈] toluene (Fig. 6,7). The large DKIE value obtained indicates that the *sp*³ C–H bond cleavage occurs at the rate-determining step.¹⁰⁻¹³

Substituent (x)	Rate constant (k)	DKIE (k _H /k _D)
H	0.019	2.31
D	0.008	

Table 7 Rate constant of **12** with toluene and [D₈] toluene and the DKIE value

Figure 8 Plausible reaction pathway of **12** with toluene at 50 °C for the formation of Int 1

Figure 9 Plausible reaction pathway of **12** with [D₈] toluene at 50 °C for the formation of Int 1D.

4.4.2 Hammett Plot of the halogenated methylbenzenes (x= I, Cl, F) and the trifluoromethyl methylbenzenes (x= CF₃)

The reaction of **12** with toluene and [D₈] toluene was monitored at 50 °C over a period of 100 hours previously. To gain further insight into the effect of various electron withdrawing substituents of the halogenated benzenes (x= I, Cl, F) and the trifluoromethyl benzenes (x= CF₃) on the reaction rate and the mechanistic pathway, a Hammett plot was constructed based on the Hammett equation. The Hammett equation holds for reaction rates k of a series of reactions with substituted benzene derivatives depicted as, $\log(k/k_0) = \sigma\rho$. In this equation, k represents the rate constant of the substituted reactant (x= I, Cl, F and CF₃)

while k_0 represents the rate constant of the unsubstituted reactant, toluene ($x=H$). The symbol, σ , represents the substituent constant which is specific for each substituent x and the σ values are obtained directly from the literature.^{14,15} σ is a measure of the total polar effect exerted by substituent, x , on the reaction center with respect to the unsubstituted reactant. It can be determined using the equation $\sigma = -(\text{p}K_a - \text{p}K_a(H))$. However, we had also utilized meta and para variations of the substituents and therefore the resonance effects of the substituents at the para positions had to be taken into consideration. It is noteworthy that the substituents at the meta positions exhibit little or no resonance effects and no modifications will be required for the σ values of the meta substituents, 1-iodo-4-methylbenzene ($x=I$) and 1-methyl-4-(trifluoromethyl)benzene ($x=CF_3$). The modified substituent constant for para substituents, σ_p^- , is defined as $\frac{1}{2.11} \log_{10} \left(\frac{k}{k_0} \right)$ which k represents the reaction rate of the substituted reactant ($x=I, Cl, F$ and CF_3) while k_0 represents the reaction rate of the unsubstituted reactant, toluene ($x=H$).

The symbol, ρ , represents the reaction constant which is equivalent to the gradient of the Hammett plot.^{14,15} In this thesis, $\log(k/k_0)$ is plotted against the modified σ_p^- for the Hammett plot of the halogenated ($x=I, Cl, F$) benzenes and the trifluoromethyl benzenes ($x=CF_3$) (Fig.8). The reaction rate graphs of 1-iodo-4-methylbenzene, 1-iodo-3-methylbenzene ($x=I$), 1-chloro-4-methylbenzene ($x=Cl$), 1-fluoro-4-methylbenzene ($x=F$), 1-methyl-4-(trifluoromethyl)benzene and 1-methyl-3-(trifluoromethyl)benzene ($x=CF_3$) can be found in the kinetic data section of this chapter.

modified σ_{p-}	$\log(k/k_0)$
0	0
0.140099	0.29561
0.182238	0.384521
0.348101	0.734493
0.353	0.27985
0.43	1.011005
0.495624	1.045766

Figure 10 Hammett Plot of the halogenated ($x=H, I, Cl, F$) benzenes and the trifluoromethyl benzenes ($x=CF_3$).

From the Hammett plot (Fig.8), the positive ρ is denoted by the gradient which indicates that the rate of the sp^3 C-H bond cleavage is accelerated by electron-withdrawing substituents. The Hammett plot shows that the rate of sp^3 C-H bond cleavage follows as $4-CF_3 > 4-F > 4-Cl > 4-I > H$. This result

reasonably agrees with the value of the rate constants obtained experimentally (Table 8). The experimental results agree with the electronegativities of the halogens which follows the trend $F > Cl > I$.¹⁶⁻¹⁸ A more electronegative fluorine in 1-fluoro-4-methylbenzene has a greater tendency to attract electrons towards itself than chlorine or iodine via the resonance effect. This results in a delocalization of the negative charge on the sp^3 carbon and stabilizes the conjugate base for the generation of a more acidic sp^3 C–H bond in 1-fluoro-4-methylbenzene. A greater rate of sp^3 C–H bond cleavage will be observed for 1-fluoro-4-methylbenzene, followed by 1-chloro-4-methylbenzene and 1-iodo-4-methylbenzene respectively. The rate of sp^3 C–H bond cleavage for 1-methyl-4-(trifluoromethyl) benzene and 1-methyl-3-(trifluoromethyl) benzene are greater than that of 1-fluoro-4-methylbenzene. The CF_3 group is more electron withdrawing than fluorine, therefore a more acidic sp^3 C–H bond is generated leading to a faster rate of C–H bond cleavage.

From the Hammett plot, deviations from the linear trendline of 1-methyl-3-(trifluoromethyl) benzene ($x = CF_3$) and 1-iodo-3-methylbenzene ($x = I$) were observed. There were no modifications made to the σ values of the meta substituents due to its low contribution to the resonance effect. This could have resulted in these slight deviations from the trendline and generated a lower R^2 value of 0.78. The positive ρ also indicates the development of a negative charge on the reaction center in the transition state of the rate limiting step.^{14,15} This reasonably agrees with the structures of the transition state of the reaction between **12** and the halogenated benzenes ($x = I, Cl, F$) and the trifluoromethyl

benzenes ($x = \text{CF}_3$). The energy level diagrams will be further discussed in the section 4.4.5 of this chapter.

Substituent (x)	Rate constant (k)
4- CF_3	-0.213
3- CF_3	-0.196
4-F	-0.104
4-Cl	-0.046
4-I	-0.038
3-I	-0.033
H	-0.019

Table 8 Experimental rate constant of **12** with halogenated benzenes ($x = \text{H}$, I, Cl, F) and the trifluoromethyl benzenes ($x = \text{CF}_3$) at 50 °C

4.4.3 Hammett Plot of the *m/p*-xylenes ($x = \text{CH}_3$), methoxy methylbenzene ($x = \text{OMe}$) and N, N,4-trimethylaniline ($x = \text{N}(\text{CH}_3)_2$).

To gain further insight into the effect of various electron donating substituents of the methylated benzenes ($x = \text{CH}_3$), methoxy benzene ($x = \text{OMe}$) and N, N,4-trimethylaniline ($x = \text{N}(\text{CH}_3)_2$) on the reaction rate and the mechanistic pathway, a Hammett plot was constructed based on the Hammett equation $\log(k/k_0) = \sigma\rho$. It is noteworthy that even though electron donating substituents were utilized in this Hammett plot, the electron donation was transmitted via resonance effect. Therefore, the modified substituent constant for para substituents, σ_p^- , follows as $\frac{1}{2.11} \log_{10}(\frac{k}{k_0})$ which k represents the reaction rate of the substituted reactant ($x = \text{CH}_3$, OMe and $\text{N}(\text{CH}_3)_2$) while k_0 represents the reaction rate of the unsubstituted reactant, toluene ($x = \text{H}$). The reaction rate graphs of *p*-xylene, *m*-xylene ($x = \text{CH}_3$), 1-methoxy-4-methylbenzene ($x = 4\text{-OMe}$) and N, N,4-trimethylaniline ($x = 4\text{-N}(\text{CH}_3)_2$) can be found in the kinetic data section of this chapter.

From the Hammett plot (Fig.9), the ρ value of 1.43 is lesser than the ρ value of the electron-withdrawing substituents 2.01. This indicates that the rate of the $sp^3\text{C-H}$ bond cleavage is accelerated by electron-withdrawing substituents rather than the electron donating groups. This observation agrees with the electron donating nature of the substituents which increases the electron density on the aromatic ring through the resonance donating effect.¹⁵⁻¹⁷ This in turn increases the negative charge on the sp^3 carbon of the conjugate base and destabilization occurs to reduce the acidity of the $sp^3\text{C-H}$ bond. A lower rate of

sp^3 C–H bond cleavage is thus observed for the electron donating substituents with respect to the electron-withdrawing substituents. The Hammett plot shows that the rate of sp^3 C–H bond cleavage follows as 4–OMe > 4–N(CH₃)₂ > 4–CH₃. This result reasonably agrees with the value of the rate constants obtained experimentally (Table 9).

modified σ_{p-}	$\log(k/k_0)$
0	0
-0.25335	-0.53459
-0.23527	-0.49642
-0.069	-0.55097
-0.22615	-0.47717

Figure 11 Hammett Plot of the methylated benzenes ($x = \text{CH}_3$), methoxy benzene ($x = 4\text{-OMe}$) and N, N,4-trimethylaniline ($x = 4\text{-N(CH}_3)_2$).

From the Hammett plot, deviation from the linear trendline of *m*-xylene ($x = \text{CH}_3$) was observed. There were no modifications made to the σ value of the *m*-xylene due to its low contribution to the resonance effect. This could have resulted in the deviation from the trendline and generated a low R^2 value of 0.50. However, if the focus is brought to the remaining electron donating substituents excluding *m*-xylene, the points fall directly on the trendline to give a R^2 value of 1.00. We can reasonably conclude that the low R^2 value is due to the *m*-xylene whose mesomeric effects are not taken into consideration.^{14,15}

The positive ρ also indicates the development of a negative charge on the reaction center in the transition state of the rate limiting step. This reasonably agrees with the structures of the transition state of the reaction between **12** and *p*-xylene ($x = \text{CH}_3$). The energy level diagrams will be further discussed in the section 4.4.5 of this chapter.

Substituent (x)	Rate constant (k)
4-OMe	-0.0064
4-N(CH ₃) ₂	-0.0061
4-CH ₃	-0.0056
3-CH ₃	-0.0054

Table 9 Experimental rate constant of **12** with methylated benzenes ($x = \text{CH}_3$), methoxy benzene ($x = \text{OMe}$) and N, N,4-trimethylaniline ($x = \text{N}(\text{CH}_3)_2$) at 80 °C

4.4.4 The energy level diagrams of **12** with toluene, [D₈] toluene, 1-methyl-4-(trifluoromethyl) benzene (x=F) and *p*-xylene (x=CH₃).

To gain insight into the reaction mechanism of **12** with toluene, [D₈] toluene, halogenated benzenes (x= I, Cl, F), trifluoromethyl benzenes (x= CF₃), methylated benzenes (x= CH₃), methoxy benzene (x= 4-OMe) and N,N,4-trimethylaniline (x= 4-N(CH₃)₂), the energy level diagram of **12** with toluene(Fig.10), [D₈] toluene(Fig.11), 1-methyl-4-(trifluoromethyl)benzene(x= F) (Fig.12) and *p*-xylene (x=CH₃) (Fig.13) will be discussed. The plausible pathways were explored theoretically using the pbe1pbe/Def2SVP functional. The dispersion forces were taken into consideration with Empirical Dispersion=GD3BJ and the solvent effects were accounted for by SCRF=(PCM, solvent=Toluene).The respective values of the sum of electronic and thermal free energies of the transition state, intermediate and product of the various substituents are displayed in the table below(Table 10). The activation barriers for the various substituents are also provided in the table.

The activation barrier for the activation of the *sp*³ C–H bond in toluene is found to be 40.9 kcal/mol. This value is slightly lower than the activation barrier of [D₈] toluene which is 41.8 kcal/mol. The calculated results is in agreement with the experimental rate of reaction as mentioned in section 4.4.1 which the rate constant of the reaction of **12** with [D₈] toluene is smaller than that of toluene (Table 7). The smaller rate constant implies a slower rate of reaction which a supposedly higher activation energy is required for the reaction of **12** and [D₈] toluene as compared to toluene. From the Hammett plot in section 4.4.3, the

positive ρ denoted by the gradient indicates that the rate of the sp^3 C–H bond cleavage is accelerated by electron-withdrawing substituents. This is supported by the slightly lower activation barrier of the reaction between **12** and 1-methyl-4-(trifluoromethyl) benzene ($x=F$) at 40.8 kcal/mol as compared to the activation barrier of 40.9 and 41.8 kcal/mol with respect to toluene and $[D_8]$ toluene. This observation is also consistent with the trend of the rate constants which follows as 4–F > 4–H > 4–D (Table 8). The gradient of the Hammett plot of the electron donating substituents in section 4.4.4 indicates that the rate of the sp^3 C–H bond cleavage is accelerated by electron-withdrawing substituents rather than the electron donating groups. This observation reasonably agrees with the computed activation barrier of 41.4 kcal/mol for that of **12** and *p*-xylene ($x=CH_3$) as compared to 40.8 kcal/mol for **12** and 1-methyl-4-(trifluoromethyl) benzene ($x=F$) (Table 10).

In addition, both Hammett plots in section 4.4.3 and 4.4.4 had a positive ρ value. This indicates the development of a negative charge on the reaction center in the transition state of the rate limiting step. In section 4.4.1, we had raised the possibility of the sp^3 C–H bond cleavage to be involved in the rate determining step as seen from the large DKIE value obtained. This hypothesis is consistent with the computed transition state structures. In all the energy level diagrams, the TS displays a $xPh-CH_2$ conjugate base structure with an adjacent proton

Figure 11 The energy level diagram of **12** with toluene

Figure 12 The energy level diagram of **12** with $[D_8]$ toluene

Figure 13 The energy level diagram of **12** with 4 fluorobenzene ($x=F$)

Figure 14 The energy level diagram of **12** with *p*-xylene ($x=CH_3$)

	(x=4-H)	(x=4-D)	(x=4-F)	(x=4-CH ₃)
TS (Hartrees)	-2851.908	-2851.936	-2950.989	-2891.127
Int (Hartrees)	-2852.006	-2852.030	-2951.090	-2891.227
Product (Hartrees)	-2852.014	-2852.041	-2951.098	-2891.233
Activation energy barrier (kcal/mol)	40.9	41.8	40.8	41.4

Table 10 The sum of electronic and thermal free energies for the transition states, intermediate, product of substituents (x=H, D, F, CH₃) and the respective activation barriers

4.5 Conclusion

In summary, we had discovered a metal-free $C(sp^3)$ -H borylation pathway by a 1,4,2,5-Diazadiborinine under mild reaction conditions. We had successfully isolated the $C(sp^3)$ -H activated structures **14-25** and confirmed the structures by NMR and HRMS characterization results. Compound **14** was successfully identified by crystallographic studies. DFT calculations revealed a plausible mechanistic pathway which involved the possibility of two different pathways. The first pathway is the facile addition of the C-H bond of 1,4,2,5 diazadiborinine **12**, leading to the possible formation of the cis C-H activated 1,4,2,5 adduct as supported by NMR monitoring results. The second pathway involved the initial generation of a concerted C-H activated transition state structure before the cleavage of the B-C bond between one of the boron of the $B_2C_2N_2$ ring and the carbon atom of the annulated imidazole. The adjacent annulated imidazole was subsequently completely cleaved from the two boron atoms in attempt to form the BNN unit followed by the BCC unit. A subsequent cis trans isomerism then occurred to generate the final compound **14** as a trans C-H activated 1,3,2,5 adduct. The DKIE results demonstrated the $C(sp^3)$ -H activation step to be the rate-determining step, which is consistent with the DFT proposed mechanism with the highest activation barrier of 40.9kcal/mol. It is noteworthy that the proposed mechanism is a plausible one however it might not be the sole definite mechanism that exists. The vast possibilities of B-C, B-N bond breakage and connection with cis-trans isomerism remains fascinating and studies are still ongoing for further novel break throughs in the future. The

Hammett studies gave further insight into the effect of various electron withdrawing substituents of the halogenated benzenes ($x = \text{I}, \text{Cl}, \text{F}$), the trifluoromethyl benzenes ($x = \text{CF}_3$), various electron donating substituents of the methylated benzenes ($x = \text{CH}_3$), methoxy benzene ($x = \text{OMe}$) and *N,N*,4-trimethylaniline ($x = \text{N}(\text{CH}_3)_2$) on the reaction rate and the mechanistic pathway. Both Hammett plots in section 4.4.3 and 4.4.4 had a positive ρ value which indicates the development of a negative charge on the reaction center in the transition state of the rate limiting step. The possibility of the sp^3 C–H bond cleavage to be involved in the rate determining step was further supported by the large DKIE value obtained. This result is consistent with the computed transition state structures which all transition state structures displayed a $x\text{Ph}-\text{CH}_2$ conjugate base structure with an adjacent proton.

The above work done represents the first sp^3 C–H activation by a diazadiborinine in a transition metal free environment. The possibility of the green and efficient pathway discovered poses a valuable toolkit for further venture into novel aromatic structures and practical applications.

All DFT calculations had been performed by the Ph.D. candidate Gillian Goh Kor Hwee.

4.6 Experimental Section

4.6.1 Synthesis, physical and spectroscopic data for all new compounds

Materials and Method: All reactions were performed in an atmosphere of nitrogen or argon by using standard Schlenk or dry box techniques; solvents were dried with Na metal and K metal. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were obtained with either Bruker Avance 300, MHz AV300, AV 500 or AVIII 400 MHz BBFO1, BBFO2 and ECA400 spectrometers at 298 K. Coupling constants J are given in Hz. Chemical shifts (δ) are given in p.p.m. 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. Ultraviolet spectra were recorded on Cary 100 UV-Vis spectrometer.

Synthesis of **14**:

Toluene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 50 °C for 100 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **14** (0.336 g, 0.141 mmol) as a pale-

yellow powder (42%). Colourless single crystals of **14** were obtained by recrystallization from a toluene solution at ambient temperature.

M.p.: 179 °C . ^1H NMR (400 MHz, C_6D_6) δ 7.65 (d, 2H, $J = 7.12\text{Hz}$, ArH), 7.48 (t, 3H, $J = 7.32, 7.68\text{Hz}$, ArH), 7.38 (t, 2H, $J = 7.4, 7.28\text{Hz}$, ArH), 7.17 (s, 5H, ArH), 6.93 (d, 3H, $J = 1.32\text{Hz}$, ArH), 6.87 (t, 5H, $J = 7.16, 7.28\text{Hz}$, ArH), 7.03 – 7.01 (m, 4H, ArH), 6.67 – 6.64 (m, 6H, ArH), 6.59 – 6.57 (m, 6H, ArH), 6.49 (s, 1H, ArH), 6.12 (s, 2H, ArH), 5.74 (s, 1H, ArH), 3.08 (s, 2H, CH_2), 2.47 (s, 6H, CH_3), 1.85 (s, 6H, CH_3), 1.31 (s, 6H, CH_3). ^{11}B {1H} NMR (128 MHz, C_6D_6): 1.08 (s), –19.8. ^{11}B NMR (128 MHz, C_6D_6): 1.04 (s), –19.4, –20.0 (d). ^{13}C NMR (100 MHz, C_6D_6): 146.6 (C-Ar), 137.6 (C-Ar), 136.3 (C-Ar), 135.9 (CH-Ar), 134.0 (C-Ar), 133.0 (C-Ar), 132.9 (CH-Ar), 132.3 (CH-Ar), 132.0 (CH-Ar), 129.9 (CH-Ar), 129.2 (CH-Ar), 128.8 (CH-Ar), 128.6 (CH-Ar), 128.5 (CH-Ar), 128.4 (CH-Ar), 128.3 (CH-Ar), 127.2 (CH-Ar), 127.0 (CH-Ar), 126.6 (CH-Ar), 125.4 (CH-Ar), 125.1 (CH-Ar), 124.1 (CH-Ar) , 123.5 (CH-Ar), 29.8 (CH_2 -Ar), 20.5 (CH_3 -Ar), 18.5 (CH_3 -Ar), 17.6 (CH_3 -Ar). HRMS (ESI): m/z calcd for $\text{C}_{67}\text{H}_{60}\text{B}_2\text{N}_4$: 942.5119 [$(M + H)$] $^+$; found: 942.5129.

^{13}C NMR (100 MHz, CDCl_3): 146.6 (C-Ar), 137.5 (C-Ar), 136.2 (C-Ar), 135.5 (CH-Ar), 135.4 (C-Ar), 133.6 (C-Ar), 132.7 (CH-Ar), 132.6 (C-Ar), 132.4 (C-Ar), 131.5 (C-Ar), 129.9 (CH-Ar), 128.9 (CH-Ar), 128.7 (C-Ar), 128.5 (CH-Ar), 128.2 (CH-Ar), 128.1 (CH-Ar), 127.4 (CH-Ar), 127.1 (CH-Ar), 126.8 (CH-Ar), 125.0 (CH-Ar), 124.9 (C-Ar), 123.9 (CH-Ar) , 122.9 (CH-Ar), 31.7 (CH_2 -Ar), 21.0 (CH_3 -Ar), 18.6 (CH_3 -Ar), 17.5 (CH_3 -Ar).

^1H NMR (400 MHz, $\text{C}_6\text{D}_5\text{CD}_3$) δ 7.55 (d, 2H, $J = 7.2\text{Hz}$, ArH), 7.41 (t, 2H, $J = 7.2, 7.6\text{Hz}$, ArH), 7.33 (d, 1H, $J = 7.2\text{Hz}$, ArH), 7.10 (s, 2H, ArH), 7.04 (d, 2H, $J = 4.8\text{Hz}$, ArH), 6.97 (d, 11H, $J = 7.2\text{Hz}$, ArH), 6.84 (t, 5H, $J = 7.6, 7.6\text{Hz}$, ArH), 6.63 (t, 7H, $J = 7.2, 7.6\text{Hz}$, ArH), 6.58 – 6.54 (m, 5H, ArH), 6.05 (s, 2H, ArH), 5.61 (s, 1H, ArH), 2.99 (s, 2H, CH_2), 2.43 (s, 6H, CH_3), 1.84 (s, 6H, CH_3), 1.24 (s, 6H, CH_3). ^{11}B NMR (128 MHz, C_6D_6): 2.01 (s), $-19.5, -20.0$ (d).

Synthesis of **15**:

[D₈] toluene (5 mL) was added to **12** (0.400 g, 0.470 mmol) in a Schlenk flask. The reaction mixture was heated at 50 °C for 100 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (10 mL) and dried under vacuum to afford **15** (0.160 g, 0.168 mmol) as a pale-yellow powder (40%).

M.p.: 181 °C. ¹¹B {¹H} NMR (128 MHz, C₆D₆): 1.47 (s), −19.8 (s). ²H NMR (100 MHz, CDCl₃): 4.33, 2.19. HRMS (ESI): *m/z* calcd for C₆₇H₅₂B₂N₄D₈: 951.5584 [(*M* + *H*)]⁺; found: 951.5623.

Synthesis of **16**:

1-methyl-4-(trifluoromethyl) benzene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 50 °C

for 16 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **16** (0.416 g, 0.412 mmol) as a pale-yellow powder (52%).

M.p.: 175 °C. ^1H NMR (400 MHz, C_6D_6) δ 7.49 (d, 4H, $J = 7.6\text{Hz}$, ArH), 7.37 (t, 6H, $J = 7.2, 7.6\text{Hz}$, ArH), 7.29 (t, 5H, $J = 7.2, 5.2\text{Hz}$, ArH), 7.20 – 7.14 (m, 7H, ArH), 7.08 (d, 5H, $J = 6.8$, ArH), 6.89 (s, 1H, ArH), 6.83 (s, 3H, ArH), 6.79 (t, 4H, $J = 7.2, 6.4\text{Hz}$, ArH), 6.54 (d, 2H, $J = 6.8\text{Hz}$, ArH), 6.37 (s, 2H, ArH), 2.20 (s, 6H, CH_3), 2.17 (s, 6H, CH_3), 2.02 (s, 2H, CH_2), 0.90 (s, 6H, CH_3). ^{11}B {1H} NMR (128 MHz, CDCl_3): –13.5 (s), –20.0. ^{11}B NMR (128 MHz, CDCl_3): –13.5 (s), –19.8, –20.4 (d). ^{13}C NMR (100 MHz, CDCl_3): 137.8 (C-Ar), 137.5 (C-Ar), 137.4 (CH-Ar), 136.6 (C-Ar), 135.9 (C-Ar), 135.6 (C-Ar), 135.4 (CH-Ar), 132.8 (CH-Ar), 131.4 (C-Ar), 130.4 (C-Ar), 130.1 (CH-Ar), 129.8 (CH-Ar), 129.3 (CH-Ar), 129.0 (CH-Ar), 128.9 (C-Ar), 128.5 (CH-Ar), 128.2 (CH-Ar), 127.9 (CH-Ar), 127.3 (CH-Ar), 126.9 (CH-Ar), 126.6 (CH-Ar), 126.1 (CH-Ar), 125.2 (C-Ar), 125.1 (C-Ar), 123.7 (CH-Ar), 29.7 (CH_2 -Ar), 18.5 (CH_3 -Ar), 17.9 (CH_3 -Ar), 16.8 (CH_3 -Ar). HRMS (ESI): m/z calcd for $\text{C}_{68}\text{H}_{59}\text{B}_2\text{N}_4\text{F}_3$: 1011.4956 [$(M + H)^+$]; found: 1011.4960.

Synthesis of **17**:

1-fluoro-4-methylbenzene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 50 °C for 20 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **17** (0.400 g, 0.416 mmol) as a pale-yellow powder (50%).

M.p.: 170 °C. ¹H NMR (400 MHz, CDCl₃) ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, 2H, *J* = 8.56Hz, *ArH*), 7.62 (d, 3H, *J* = 8.16Hz, *ArH*), 7.53 (s, 2H, *ArH*), 7.38(t, 1H, *J* = 7.2,7.72Hz *ArH*), 7.31(d, 1H, *J* = 0.92Hz, *ArH*), 7.28(s, 1H, *ArH*), 7.24 (s, 1H, *ArH*), 7.22 (s, 2H, *ArH*), 7.18 (d, 2H, *J* = 2.64Hz, *ArH*), 7.16 (s, 2H, *ArH*), 7.14 (d, 2H, *J* = 1.48Hz, *ArH*), 7.12 (d, 2H, *J* = 1.8Hz, *ArH*), 7.10 (d, 1H, *J* = 1.4Hz, *ArH*), 7.08 (d, 2H, *J* = 1.76Hz, *ArH*), 6.91 (s, 2H, *ArH*), 6.84 (d, 2H, *J* = 2.2Hz, *ArH*), 6.79 (s, 2H, *ArH*), 6.65 (d, 4H, *J* = 6.56Hz, *ArH*), 6.38 (s, 2H, *ArH*), 2.31 (s, 6H, CH₃), 2.21 (s, 6H, CH₃), 2.17 (s, 2H, CH₂), 2.02 (s, 6H, CH₃). ¹¹B {¹H} NMR (128 MHz, CDCl₃): 2.26 (s), -20.1. ¹¹B NMR (128 MHz, CDCl₃): 2.27 (s), -19.9, -20.6 (d). ¹³C NMR (100 MHz, CDCl₃): 137.7 (C-Ar), 137.4 (C-

Ar), 136.2 (CH-Ar), 135.4 (CH-Ar), 134.7 (C-Ar), 134.4 (C-Ar), 134.2 (CH-Ar), 133.6 (C-Ar), 131.5 (C-Ar), 131.0 (C-Ar), 129.2 (C-Ar), 129.1 (C-Ar), 128.9 (CH-Ar), 128.6 (CH-Ar), 127.8 (CH-Ar), 127.6 (CH-Ar), 127.3 (CH-Ar), 127.2 (CH-Ar), 127.0 (C-Ar), 126.8 (CH-Ar), 126.0 (CH-Ar), 125.7 (CH-Ar), 125.4 (CH-Ar), 124.9 (CH-Ar), 28.6 (CH₂-Ar), 19.9 (CH₃-Ar), 16.7 (CH₃-Ar), 15.6 (CH₃-Ar). HRMS (ESI): m/z calcd for C₆₇H₅₉B₂N₄F: 961.4988 [(*M* + *H*)⁺]; found: 961.5018.

Synthesis of **18**:

1-chloro-4-methylbenzene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 50 °C for 22 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **18** (0.408 g, 0.418 mmol) as a pale-yellow powder (51%).

M.p.: 178 °C. ¹H NMR (400 MHz, C₆D₆) δ 8.10 (d, 3H, *J* = 7.2Hz, *ArH*), 7.73 (d, 2H, *J* = 8.0Hz, *ArH*), 7.33 (d, 3H, *J* = 7.2Hz, *ArH*), 7.21 (s, 2H, *ArH*), 7.10 – 7.03 (m, 8H, *ArH*), 6.98 – 6.90 (m, 7H, *ArH*), 6.89 – 6.85 (m,

hexanes (15 mL) and dried under vacuum to afford **19** (0.424 g, 0.397 mmol) as a pale-yellow powder (53%).

M.p.: 173 °C. ^1H NMR (400 MHz, C_6D_6) δ 7.87 (d, 5H, $J = 7.2\text{Hz}$, ArH), 7.38 (d, 5H, $J = 8.4\text{Hz}$, ArH), 7.14 (t, 7H, $J = 7.3, 7.0\text{Hz}$, ArH), 7.10 (s, 4H, ArH), 7.03 (d, 4H, $J = 7.8\text{Hz}$, ArH), 6.90 (d, 2H, $J = 6.6\text{Hz}$, ArH), 6.87 (d, 2H, $J = 3.7\text{Hz}$, ArH), 6.85 (s, 1H, ArH), 6.50 (d, 7H, $J = 2.6\text{Hz}$, ArH), 6.48 (s, 2H, ArH), 2.37 (s, 2H, CH_2), 1.94 (s, 6H, CH_3), 1.87 (s, 6H, CH_3), 1.77 (s, 6H, CH_3). ^{11}B { 1H } NMR (128 MHz, CDCl_3): 3.41 (s), -18.6 . ^{11}B NMR (128 MHz, CDCl_3): 3.30 (s), -18.5 , -18.9 (d). ^{13}C NMR (100 MHz, CDCl_3): 143.6 (C-Ar), 138.8 (C-Ar), 138.5 (C-Ar), 138.2 (CH-Ar), 137.3 (CH-Ar), 129.0 (C-Ar), 135.8 (C-Ar), 135.7 (CH-Ar), 134.7 (C-Ar), 132.6 (C-Ar), 132.2 (C-Ar), 131.4 (C-Ar), 130.5 (CH-Ar), 130.1 (CH-Ar), 129.8 (CH-Ar), 129.0 (CH-Ar), 128.4 (CH-Ar), 128.2 (CH-Ar), 128.0 (CH-Ar), 127.2 (CH-Ar), 126.9 (CH-Ar), 126.6 (CH-Ar), 125.7 (C-Ar), 125.4 (C-Ar), 124.9 (C-Ar), 29.8 (CH_2 -Ar), 22.8 (CH_3 -Ar), 17.9 (CH_3 -Ar), 14.2 (CH_3 -Ar). HRMS (ESI): m/z calcd for $\text{C}_{67}\text{H}_{59}\text{B}_2\text{N}_4\text{I}$: 1069.4049 [$(M + H)^+$]; found: 1069.4083.

Synthesis of **20**:

1-methyl-3-(trifluoromethyl) benzene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 50 °C for 18 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **20** (0.360 g, 0.356 mmol) as a pale-yellow powder (45%).

M.p.: 178 °C. ¹H NMR (400 MHz, C₆D₆) δ 7.58 (d, 2H, *J* = 7.6Hz, Ar*H*), 7.25 (d, 1H, *J* = 5.6Hz, Ar*H*), 6.90 (d, 6H, *J* = 7.2Hz, Ar*H*), 6.84 – 6.78 (m, 5H, Ar*H*), 6.70 – 6.65 (m, 5H, Ar*H*), 6.60 (t, 8H, *J* = 7.08, 7.6Hz Ar*H*), 6.55 (d, 4H, *J* = 7.2Hz, Ar*H*), 6.48 (s, 2H, Ar*H*), 6.28 (s, 2H, Ar*H*), 5.95 (s, 2H, Ar*H*), 2.19 (s, 6H, CH₃), 2.10 (s, 6H, CH₃), 1.92 (s, 2H, CH₂), 1.78 (s, 6H, CH₃). ¹¹B {¹H} NMR (128 MHz, CDCl₃): –13.3 (s), –20.0. ¹¹B NMR (128 MHz, CDCl₃): –13.3 (s), –19.8, –20.4 (d). ¹³C NMR (100 MHz, CDCl₃): 138.8 (C-Ar), 137.4 (C-Ar), 136.6 (C-Ar), 135.8 (C-Ar), 135.6 (C-Ar), 135.4 (CH-Ar), 132.8 (C-Ar), 131.3 (C-Ar), 130.2 (C-Ar), 130.1 (CH-Ar), 129.8 (CH-Ar), 129.0 (C-Ar), 128.9 (CH-Ar), 128.8 (C-Ar), 128.6

(CH-Ar), 128.4 (CH-Ar), 128.3 (CH-Ar), 128.2 (CH-Ar), 127.9 (CH-Ar) ,
 127.4 (C-Ar), 126.9 (CH-Ar), 126.8 (CH-Ar), 126.1 (CH-Ar), 123.6 (CH-Ar),
 122.2 (C-Ar), 29.7 (CH₂-Ar), 18.5 (CH₃-Ar), 17.8 (CH₃-Ar), 16.8
 (CH₃-Ar). HRMS (ESI): *m/z* calcd for C₆₈H₅₉B₂N₄F₃: 1011.4956 [(*M* + *H*)]
⁺; found: 1011.4946.

Synthesis of **21**:

1-iodo-3-methylbenzene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 50 °C for 30 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **21** (0.344 g, 0.322 mmol) as a pale-yellow powder (43%).

M.p.: 173 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, 2H, *J* = 7.2Hz, Ar*H*), 7.60 (d, 3H, *J* = 8.0Hz, Ar*H*), 7.52 (t, 2H, *J* = 8.0, 6.0Hz, Ar*H*), 7.37 (t, 3H, *J* = 7.24, 7.68Hz, Ar*H*), 7.26 – 7.17 (m, 9H, Ar*H*), 7.15 – 7.07 (m, 9H, Ar*H*), 7.01 (t, 4H, *J* = 7.72, 7.72Hz, Ar*H*), 6.89 (s, 4H, Ar*H*), 6.83 (s, 2H, Ar*H*), 6.37 (s, 1H, Ar*H*), 2.33 (s, 6H, CH₃), 2.31 (s, 6H, CH₃), 2.20 (s, 2H,

CH₂), 2.01 (s, 6H, CH₃) . ¹¹B {¹H} NMR (128 MHz, CDCl₃): 0.26 (s), -17.9. ¹¹B NMR (128 MHz, CDCl₃): 0.26 (s), -17.8, -18.3 (d). ¹³C NMR (100 MHz, CDCl₃): 140.3 (C-Ar), 138.8 (C-Ar), 138.5 (C-Ar), 138.0 (CH-Ar), 137.4 (CH-Ar), 136.5 (C-Ar), 135.7 (C-Ar), 135.6 (C-Ar), 135.4 (CH-Ar), 134.4 (C-Ar), 132.7 (C-Ar), 131.9 (CH-Ar), 130.2 (CH-Ar), 130.0 (C-Ar), 129.9 (C-Ar), 129.7 (CH-Ar), 129.0 (CH-Ar), 128.4 (CH-Ar), 128.1 (CH-Ar), 127.9 (CH-Ar), 127.3 (CH-Ar), 126.8 (CH-Ar), 126.6 (CH-Ar), 126.0 (C-Ar), 29.8 (CH₂-Ar), 18.5 (CH₃-Ar), 16.7 (CH₃-Ar), 14.1 (CH₃-Ar). HRMS (ESI): *m/z* calcd for C₆₇H₅₉B₂N₄I: 1069.4049 [(*M* + *H*)⁺]; found: 1069.4052.

Synthesis of **22**:

p-xylene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 80 °C for 70 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **22** (0.280 g, 0.293 mmol) as a pale-yellow powder (35%).

1-methoxy-4-methylbenzene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 80 °C for 70 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **23** (0.320 g, 0.329 mmol) as a pale-yellow powder (40%).

M.p.: 177 °C. ^1H NMR (400 MHz, C_6D_6) ^1H NMR (400 MHz, C_6D_6) δ 8.05 (d, 3H, $J = 7.2\text{Hz}$, ArH), 7.93 (d, 2H, $J = 7.28\text{Hz}$, ArH), 7.19 (s, 5H, ArH), 7.08 – 7.02 (m, 6H, ArH), 6.92 – 6.08 (m, 15H, ArH), 6.60 (s, 2H, ArH), 6.53 (s, 2H, ArH), 6.48 (s, 2H, ArH), 6.28 (s, 1H, ArH), 2.31 (s, 2H, CH_2), 1.92 (s, 6H, CH_3), 1.82 (s, 6H, CH_3), 1.76 (s, 9H, CH_3). ^{11}B {1H} NMR (128 MHz, CDCl_3): –13.5 (s), –20.0. ^{11}B NMR (128 MHz, CDCl_3): –13.8 (s), –19.8, –20.5 (d). ^{13}C NMR (100 MHz, CDCl_3): 138.9 (C-Ar), 137.5 (C-Ar), 136.6 (C-Ar), 135.8 (C-Ar), 135.1 (CH-Ar), 133.7 (CH-Ar), 132.2 (C-Ar), 130.5 (CH-Ar), 130.1 (CH-Ar), 129.9 (CH-Ar), 129.8 (CH-Ar), 129.2 (C-Ar), 129.0 (CH-Ar), 128.5 (CH-Ar), 128.4 (C-Ar), 128.3 (CH-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.0 (CH-Ar), 127.3 (C-Ar), 126.9 (CH-Ar), 126.7 (C-Ar), 126.1 (CH-Ar), 122.5 (CH-Ar), 31.7 (CH_2 -Ar), 21.1 (CH_3 -Ar), 20.6 (CH_3 -Ar), 18.6 (CH_3 -Ar), 17.9 (CH_3 -Ar). HRMS (ESI): m/z calcd for $\text{C}_{68}\text{H}_{62}\text{B}_2\text{N}_4\text{O}$: 973.5188 [$(M + H)^+$]; found: 973.5200.

Synthesis of **24**:

N,N,4-trimethylaniline (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 80 °C for 70 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **24** (0.320 g, 0.325 mmol) as a pale-yellow powder (40%).

M.p.: 179 °C . ^1H NMR (400 MHz, C_6D_6) δ 7.72 (d, 2H, $J = 8.56\text{Hz}$, *ArH*), 7.62 (d, 4H, $J = 8.16\text{Hz}$, *ArH*), 7.53 (s, 2H, *ArH*), 7.38(t, 4H, $J = 7.2, 7.72\text{Hz}$, *ArH*), 7.31(d, 1H, $J = 0.92\text{Hz}$, *ArH*), 7.28(s, 2H, *ArH*), 7.24 (s, 1H, *ArH*), 7.22 (s, 2H, *ArH*), 7.18 (d, 2H, $J = 2.64\text{Hz}$, *ArH*), 7.16 (s, 1H, *ArH*), 7.14 (d, 2H, $J = 1.48\text{Hz}$, *ArH*), 7.12 (d, 2H, $J = 1.8\text{Hz}$, *ArH*), 7.10 (d, 2H, $J = 1.4\text{Hz}$, *ArH*), 7.08 (d, 2H, $J = 1.76\text{Hz}$, *ArH*), 6.91 (s, 4H, *ArH*), 6.84 (d, 2H, $J = 2.2\text{Hz}$, *ArH*), 6.79 (s, 1H, *ArH*), 6.65 (d, 1H, $J = 6.56\text{Hz}$, *ArH*), 6.38 (s, 1H, *ArH*), 2.31 (s, 6H, CH_3), 2.21 (s, 6H, CH_3), 2.17 (s, 2H, CH_2), 2.02 (s, 12H, CH_3) . ^{11}B {1H} NMR (128 MHz, CDCl_3): -14.3 (s), -20.1. ^{11}B NMR (128 MHz, CDCl_3): -14.1 (s), -19.9, -20.7 (d). ^{13}C NMR (100 MHz,

CDCl₃): 137.4 (C-Ar), 135.8 (CH-Ar), 134.3 (C-Ar), 134.2 (C-Ar), 133.4 (C-Ar), 133.3 (C-Ar), 133.2 (C-Ar), 130.0 (CH-Ar), 129.8 (CH-Ar), 129.6 (CH-Ar), 129.1 (CH-Ar), 128.8 (C-Ar), 128.7 (C-Ar), 128.5 (CH-Ar), 128.2 (CH-Ar), 128.0 (CH-Ar), 127.9 (CH-Ar), 127.4 (CH-Ar), 127.2 (C-Ar), 126.3 (C-Ar), 125.5 (CH-Ar), 124.6 (C-Ar), 119.6 (CH-Ar), 113.7 (CH-Ar), 31.6 (CH₃-Ar), 29.1 (CH₂-Ar), 22.7 (CH₃-Ar), 17.8 (CH₃-Ar), 14.2 (CH₃-Ar). HRMS (ESI): *m/z* calcd for C₆₉H₆₅B₂N₅: 986.5504 [(*M* + *H*)]⁺; found: 986.5502.

Synthesis of **25**:

m-xylene (10 mL) was added to **12** (0.800 g, 0.941 mmol) in a Schlenk flask. The reaction mixture was heated at 80 °C for 72 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to afford **25** (0.272 g, 0.284 mmol) as a pale-yellow powder (34%).

M.p.: 180 °C. ¹H NMR (400 MHz, C₆D₆) δ 7.73 (d, 3H, *J* = 10.7Hz, *ArH*), 7.63 (d, 3H, *J* = 10.56Hz, *ArH*), 7.38 (t, 5H, *J* = 9.12, 10.04Hz, *ArH*), 7.24

(d, 4H, $J = 8.88\text{Hz}$, ArH), 7.19 (s, 4H, ArH), 7.16(d, 4H, $J = 5.16\text{Hz}$, ArH), 7.10 (d, 4H, $J = 9.08\text{Hz}$, ArH), 6.91 (s, 3H, ArH), 6.85 (s, 3H, ArH), 6.66 (d, 1H, $J = 9.36\text{Hz}$, ArH), 6.38 (s, 2H, ArH), 3.82(s, 1H, ArH), 2.32 (s, 2H, CH₂), 2.22 (s, 6H, CH₃), 2.18 (s, 6H, CH₃), 2.03 (s, 9H, CH₃). ¹¹B {1H} NMR (128 MHz, CDCl₃): -13.6 (s), -18.6. ¹¹B NMR (128 MHz, CDCl₃): -13.1 (s), -18.3, -19.1 (d). ¹³C NMR (100 MHz, CDCl₃): 137.5 (C-Ar), 137.4 (C-Ar), 136.6 (C-Ar), 135.9 (C-Ar), 135.6 (CH-Ar), 134.8 (C-Ar), 132.7 (C-Ar), 131.3 (C-Ar), 130.1 (CH-Ar), 129.8 (CH-Ar), 129.0 (CH-Ar), 128.5 (CH-Ar), 128.4 (CH-Ar), 128.2 (CH-Ar), 128.1 (C-Ar), 127.9 (CH-Ar), 127.8 (C-Ar), 127.6 (C-Ar), 127.2 (CH-Ar), 126.9 (CH-Ar), 126.6 (CH-Ar), 126.0 (CH-Ar), 123.6 (CH-Ar), 29.7 (CH₂-Ar), 21.3 (CH₃-Ar), 18.5 (CH₃-Ar), 17.9 (CH₃-Ar), 16.8 (CH₃-Ar). HRMS (ESI): m/z calcd for C₆₈H₆₂B₂N₄: 957.5239 [($M + H$)]⁺; found: 957.5254.

Figure 15 Electrospray ionization (ESI) mass spectra of compound **14**.

Figure 16 Electrospray ionization (ESI) mass spectra of compound **15**.

Figure 17 Electrospray ionization (ESI) mass spectra of compound **16**.

Figure 18 Electrospray ionization (ESI) mass spectra of compound **17**.

Figure 19 Electrospray ionization (ESI) mass spectra of compound **18**.

Figure 20 Electrospray ionization (ESI) mass spectra of compound **19**

Figure 21 Electrospray ionization (ESI) mass spectra of compound **20**.

Figure 22 Electrospray ionization (ESI) mass spectra of compound **21**.

Figure 23 Electrospray ionization (ESI) mass spectra of compound **22**.

Figure 24 Electrospray ionization (ESI) mass spectra of compound **23**

Figure 25 Electrospray ionization (ESI) mass spectra of compound **24**

Figure 26 Electrospray ionization (ESI) mass spectra of compound **25**

4.6.2 NMR spectra for all new compounds

Figure 27. ¹H NMR spectrum of **14** in C₆D₆

Figure 28. ¹¹B {¹H} NMR spectrum of **14** in C₆D₆

Figure 29. ¹¹B NMR spectrum of **14** in C₆D₆

Figure 30. ¹³C NMR spectrum of **14** in C₆D₆

Figure 31. ^{13}C NMR (DEPT 135) spectrum of **14** in C_6D_6

Figure 32. ^2D (HMQC) NMR monitoring spectrum of **14** in C_6D_6 .

Figure 33. ^{13}C NMR spectrum of **14** in CDCl_3

Figure 34. ^{13}C NMR (DEPT 135) spectrum of **14** in CDCl_3

Figure 35. ¹H NMR spectrum of **14** in [D₈] toluene

Figure 36. ¹¹B NMR spectrum of **14** in [D₈] toluene

Figure 37. ^1H NMR monitoring spectrum of **15** at 50°C in $[\text{D}_8]$ toluene for 100 hours.

Figure 38. ^1H NMR monitoring spectrum of **15** at 50°C in $[\text{D}_8]$ toluene

Figure 39. ^{11}B NMR spectrum of **15** in $[\text{D}_8]$ toluene.

Figure 40. ^2H NMR spectrum of **15** in CDCl_3 .

Figure 41. ^{11}B monitoring NMR of **16** in C_6D_6

Figure 42. ^1H NMR of **16** in CDCl_3 .

Figure 43. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **16** in CDCl_3 .

Figure 44. ^{11}B NMR spectrum of **16** in CDCl_3 .

Figure 45. ^{13}C NMR spectrum of **16** in CDCl_3

Figure 46. ^{13}C NMR (DEPT 135) spectrum of **16** in CDCl_3 .

Figure 47. ¹H NMR of **17** in CDCl₃.

Figure 48. ¹¹B{¹H} NMR spectrum of **17** in CDCl₃.

Figure 49. ^{11}B NMR spectrum of **17** in CDCl_3 .

Figure 50. ^{13}C NMR spectrum of **17** in CDCl_3 .

Figure 51. ^{13}C NMR (DEPT 135) spectrum of **17** in CDCl_3

Figure 52. ^2D (HMQC) NMR monitoring spectrum of **17** in CDCl_3 .

Figure 53. ^1H monitoring NMR of **18** in C_6D_6 at $50\text{ }^\circ\text{C}$.

Figure 54. ^1H (upfield) monitoring NMR of **18** in C_6D_6 at $50\text{ }^\circ\text{C}$

Figure 55. ¹H NMR of **18** in C₆D₆

Figure 56. ¹¹B {¹H} NMR of **18** in CDCl₃

Figure 57. ^{11}B NMR of **18** in CDCl_3

Figure 58. ^{13}C NMR spectrum of **18** in CDCl_3

Figure 59. ^{13}C NMR (DEPT 135) spectrum of **18** in CDCl_3

Figure 60. ^1H monitoring NMR of **19** in C_6D_6 at 50 °C.

Figure 61. ^1H NMR of **19** in C_6D_6 at 50°C .

Figure 62. ^{11}B NMR spectrum of **19** in CDCl_3 .

Figure 63. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **19** in CDCl_3 .

Figure 64. ^{13}C NMR spectrum of **19** in CDCl_3 .

Figure 65. ^{13}C NMR (DEPT 135) spectrum of **19** in CDCl_3

Figure 66. $^{11}\text{B}\{^1\text{H}\}$ monitoring NMR spectrum of **20** in C_6D_6 in 50°C .

Figure 67. ^1H monitoring NMR spectrum of **20** in C_6D_6 in 50 °C.

Figure 68. ^1H NMR spectrum of **20** in C_6D_6

Figure 69. $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum of **20** in CDCl_3 .

Figure 70. ^{11}B NMR spectrum of **20** in CDCl_3 .

Figure 71. ^{13}C NMR spectrum of **20** in CDCl_3

Figure 72. ^{13}C NMR (DEPT 135) spectrum of **20** in CDCl_3

Figure 73. ^1H monitoring NMR of **21** in C_6D_6 at 50 °C.

Figure 74. ^1H NMR of **21** in CDCl_3 at 50 °C.

Figure 75. ^{11}B NMR spectrum of **21** in C_6D_6 .

Figure 76. ^{11}B $\{^1\text{H}\}$ NMR spectrum of **21** in C_6D_6

Figure 77. ¹³C NMR spectrum of **21** in CDCl₃

Figure 78. ¹³C NMR (DEPT 135) spectrum of **21** in CDCl₃

Figure 79. ^{11}B monitoring NMR of **22** in C_6D_6

Figure 80. ^1H NMR of **22** in CDCl_3 .

Figure 81. ^{11}B NMR of **22** in CDCl_3

Figure 82. ^{11}B $\{^1\text{H}\}$ NMR spectrum of **22** in CDCl_3

Figure 83. ^{13}C NMR spectrum of **22** in CDCl_3

Figure 84. ^{13}C NMR (DEPT 135) spectrum of **22** in CDCl_3

Figure 85. ^1H NMR spectrum of **23** in C_6D_6

Figure 86. ^{11}B { ^1H } NMR spectrum of **23** in C_6D_6

Figure 88. ^{13}C NMR spectrum of **23** in CDCl_3

Figure 89. ^{13}C NMR (DEPT 135) spectrum of **23** in CDCl_3

Figure 90. ^{11}B { ^1H } monitoring NMR spectrum of **24** in C_6D_6

Figure 91. ^1H NMR spectrum of **24** in CDCl_3

Figure 92. ^{11}B $\{^1\text{H}\}$ NMR spectrum of **24** in CDCl_3

Figure 93. ^{11}B NMR spectrum of **24** in CDCl_3

Figure 94. ^{13}C NMR spectrum of **24** in CDCl_3

Figure 95. ^{13}C NMR (DEPT 135) spectrum of **24** in CDCl_3

Figure 96. ^1H NMR spectrum of **25** in C_6D_6

Figure 97. ^{11}B NMR spectrum of **25** in CDCl_3

Figure 98. ^{11}B $\{^1\text{H}\}$ NMR spectrum of **25** in CDCl_3

Figure 99. ¹³C NMR spectrum of **25** in CDCl₃

Figure 100. ¹³C NMR (DEPT 135) spectrum of **25** in CDCl₃

Figure 101. ^1H monitoring NMR of **14** in C_6D_6 at 50°C .

4.6.3 Crystallographic Data

X-ray data collection and structural refinement. Intensity data for compound **14** was collected at 100 K using a Bruker D8 Quest diffractometer. The structure was solved by Intrinsic Phasing (SHELXTL XT-2014)²⁵ and refined for all data by full-matrix least squares methods on F^2 .²⁶ 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. The restraint RIGU for the whole molecule was used in the refinement of rei1246m.cif. CCDC: contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif

Table 11. Summary of Data collection and structure refinement for compound **14**.

14	
Formula	C ₇₃ H ₆₆ B ₂ N ₄
Fw	1020.91
Cryst syst	triclinic
Space group	P -1
Size (mm ³)	0.040 x 0.120 x 0.260
T/K	100(2)
<i>a</i> , Å	13.8619(10)
<i>b</i> , Å	14.1078(9)
<i>c</i> , Å	17.3179(11)
α , deg	68.127(2)
β , deg	73.422(2)
γ , deg	66.341(2)
<i>V</i> , Å ³	2841.8(3)
<i>Z</i>	2
<i>d</i> calcd g.cm ⁻³	1.193
μ , mm ⁻¹	0.068
Refl collected	37014
T _{max} /T _{min}	0.9970/0.9820
N _{measd}	11597
[R int]	0.1530
R [I>2sigma(I)]	0.0684
Rw[I>2sigma(I)]	0.1716
GOF	0.997
Largest diff peak/hole[e·Å ⁻³]	0.256/-0.275

4.6.4 Reaction time graphs for electron-withdrawing and electron donating substituents

Figure 102 Reaction time graph of **12** with 1-methyl-4-(trifluoromethyl) benzene(x= CF₃).

Figure 103 Reaction time graph of **12** with 1-fluoro-4-methylbenzene (x=F).

Figure 104 Reaction time graph of **12** with 1-chloro-4-methylbenzene (x=Cl).

Figure 105 Reaction time graph of **12** with 1-iodo-4-methylbenzene (x=I).

Figure 106 Reaction time graph of **12** with 1-methyl-3-(trifluoromethyl)benzene ($x = \text{CF}_3$).

Figure 107 Reaction time graph of **12** with 1-iodo-3-methylbenzene ($x = \text{I}$).

Figure 108 Reaction time graph of **12** with *p*-xylene (x= CH₃).

Figure 109 Reaction time graph of **12** with 1-methoxy-4-methylbenzene (x= OMe).

Figure 110 Reaction time graph of **12** with *N,N*,4-trimethylaniline ($x = \text{N}(\text{CH}_3)_2$).

Figure 111 Reaction time graph of **12** with *m*-xylene ($x = \text{CH}_3$).

Table 12 The coordinates (XYZ) for various optimized structure **14**

B	-0.01240100	-1.86919000	0.25233800
B	0.00145000	1.35334400	-0.20726300
C	-1.29511200	0.39547600	-0.14851300
C	-3.43434000	-0.31357900	-0.26352200
C	-2.63094300	-1.39522800	-0.02026500
C	-3.10110800	-2.80782600	0.01349500
C	-3.36414400	-3.48473900	1.20980500
H	-3.17390200	-2.99774300	2.15762900
C	-3.88227600	-4.77754500	1.20014800
H	-4.07738500	-5.28445400	2.13862900
C	-4.15638900	-5.41176300	-0.00874000
H	-4.56022400	-6.41803400	-0.01703200
C	-3.91345600	-4.74346100	-1.20624400
H	-4.12454000	-5.22720900	-2.15303400
C	-3.39218900	-3.45394600	-1.19416900
H	-3.19427000	-2.94254600	-2.12768000
C	-4.90490700	-0.25270200	-0.38993700
C	-5.71015600	-0.81308100	0.61286300
H	-5.24238200	-1.26533000	1.47781300
C	-7.09766900	-0.79133800	0.51128600
H	-7.69931400	-1.23251600	1.29797600

C	-7.71027100	-0.20057200	-0.59107400
H	-8.79138300	-0.18007200	-0.66968700
C	-6.92321900	0.36351800	-1.59215900
H	-7.38926700	0.82306600	-2.45652600
C	-5.53530900	0.33595500	-1.49555900
H	-4.94175700	0.76961100	-2.28859100
C	-3.00418100	2.13840900	-0.66602200
C	-2.89913300	2.59342800	-1.98839200
C	-3.32738200	3.89227800	-2.27042900
H	-3.25233900	4.25559500	-3.29075700
C	-3.85365200	4.72604600	-1.28421000
C	-3.96120400	4.22725100	0.01411300
H	-4.37508200	4.85847900	0.79405800
C	-3.54648300	2.93865900	0.34958100
C	-3.69259600	2.43361400	1.76142700
H	-3.99401300	3.24425300	2.42622800
H	-2.75242800	2.02367900	2.13415600
H	-4.45119100	1.64746000	1.82193100
C	-4.27794200	6.13889400	-1.60510000
H	-5.18167700	6.41811000	-1.05766200
H	-4.47443900	6.26482900	-2.67202200
H	-3.49535700	6.85310500	-1.32719900
C	-2.35337400	1.72317900	-3.09391500
H	-1.26866800	1.62167200	-3.00851200
H	-2.58028700	2.15683300	-4.06950800
H	-2.76833400	0.71230100	-3.06557100
C	1.28945100	0.38450500	-0.15058600
C	3.41949500	-0.34658800	-0.28909200

C	2.60611600	-1.42266300	-0.05610700
C	3.06092700	-2.84076900	-0.04690300
C	3.33304700	-3.53539900	1.13718500
H	3.16020800	-3.05943800	2.09394400
C	3.83728900	-4.83331300	1.10390800
H	4.03983600	-5.35409500	2.03317700
C	4.08811700	-5.45505000	-0.11643300
H	4.48129100	-6.46522300	-0.14285800
C	3.83538700	-4.76936300	-1.30204300
H	4.02798100	-5.24333300	-2.25768300
C	3.32799500	-3.47475200	-1.26648000
H	3.12253400	-2.94958300	-2.19066800
C	4.88845100	-0.30192100	-0.43856300
C	5.70549400	-0.86920100	0.55024900
H	5.24873300	-1.31472100	1.42470900
C	7.09107500	-0.86412100	0.42173500
H	7.70282600	-1.31027100	1.19774300
C	7.68890200	-0.28421500	-0.69437400
H	8.76845000	-0.27695900	-0.79401600
C	6.88950200	0.28545100	-1.68261900
H	7.34434800	0.73557300	-2.55784900
C	5.50361700	0.27480700	-1.55878900
H	4.89834500	0.70938300	-2.34263700
C	3.02235700	2.12001200	-0.62073400
C	3.57139300	2.87352000	0.42851300
C	4.01216500	4.16490300	0.14553400
H	4.43125000	4.75872000	0.95166800
C	3.92419000	4.71410500	-1.13463700

C	3.38954800	3.92846800	-2.15357800
H	3.32918100	4.33099500	-3.16019700
C	2.93383300	2.62757200	-1.92398700
C	2.37019200	1.82293900	-3.06965600
H	2.60397900	0.75987000	-2.98525000
H	2.76246500	2.18666400	-4.02161400
H	1.28046900	1.90642000	-3.09870800
C	4.38132400	6.12839700	-1.39867400
H	4.51919800	6.31110100	-2.46642000
H	5.32614800	6.34330100	-0.89257000
H	3.64455000	6.85073700	-1.03141800
C	3.69390300	2.31529800	1.82260200
H	4.43399900	1.51043600	1.86218500
H	2.74124500	1.91465300	2.17330000
H	4.00761500	3.09499600	2.51809200
C	-0.02850000	-2.98347000	-0.94039200
C	-0.03234000	-4.36559900	-0.71456400
H	-0.02500600	-4.74440700	0.30104800
C	-0.04529200	-5.28395100	-1.76381700
H	-0.04780200	-6.34761500	-1.54919100
C	-0.05508600	-4.84055800	-3.08334600
H	-0.06513800	-5.55231000	-3.90217900
C	-0.05170500	-3.46956400	-3.34085100
H	-0.05929000	-3.10910600	-4.36496600
C	-0.03860700	-2.56424800	-2.28218500
H	-0.03623100	-1.50055100	-2.50641500
C	-0.00137800	-2.51132000	1.76343200
H	-0.87519900	-3.16177000	1.84648900

H	0.85823800	-3.18317200	1.82308700
C	0.02664600	-1.59882100	2.96666200
C	1.23562700	-1.16684600	3.53356000
H	2.17200900	-1.45104100	3.06785300
C	1.26767200	-0.38860100	4.68850200
H	2.22243600	-0.08196900	5.10245000
C	0.08240000	-0.00867200	5.31393700
H	0.10422700	0.58830400	6.21869900
C	-1.13109700	-0.40626000	4.75773300
H	-2.06498000	-0.11422700	5.22627400
C	-1.15366600	-1.18481800	3.60251800
H	-2.11075400	-1.48507600	3.19230700
C	0.00392500	2.54233200	0.90751500
C	0.01179000	3.89143100	0.51845800
H	0.01701900	4.13163500	-0.53963600
C	0.01300500	4.92960900	1.44875600
H	0.01912000	5.96047300	1.10826900
C	0.00675800	4.64638300	2.81352700
H	0.00804400	5.45089900	3.54184300
C	-0.00138100	3.31717900	3.23056600
H	-0.00636500	3.07650400	4.28863200
C	-0.00315900	2.28712700	2.28909800
H	-0.00997500	1.26320300	2.64493600
N	-1.30512500	-0.93521100	0.05160700
N	-2.58296400	0.79275600	-0.35455300
N	1.28608800	-0.94867700	0.03162000
N	2.58060800	0.77074400	-0.35710800
H	0.00607600	1.87259100	-1.30367400

4.6.5 References

1. Sheldrick, G. M. (2015). *Acta Cryst. A* **71**, 3–8.
2. Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
3. Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.
4. Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926.

4.7 References

27. S. Aldridge, D. L. Kays, A. Al-Fawaz, K. M. Jones, P. N. Horton, M. B. Hursthouse, R. W. Harrington, W. Clegg, *Chem. Commun.*, **2006**, 2578.
28. H. Braunschweig, R. D. Dewhurst, T. Herbst, K. Radacki, *Angew. Chem. Int. Ed.*, **2008**, 47, 5978.
29. H. Braunschweig, J. O. C. Jimenez-Halla, K. Radacki, R. Shang, *Chem. Commun.*, **2015**, 51, 16569.
30. Y. Su, D. C. H. Do, Y. Li, R. Kinjo, *J. Am. Chem. Soc.*, **2019**, 141, 13729.
31. J. Ho, Z. Hou, R. J. Drake, D. W. Stephan, *Organometallics*, **1993**, 12, 3145.
32. L. Weber, M. Schnieder, P. Lönnecke, *J. Chem. Soc., Dalton Trans.*, **2001**, 3459.
33. H. Braunschweig, Q. Ye, A. Damme, T. Kupfer, K. Radacki, J. Wolf, *Angew. Chem. Int. Ed.*, **2011**, 50, 9462.
34. N. Dettenrieder, Y. Aramaki, B. M. Wolf, C. Maichle-Mcßmer, X. Zhao, M. Yamashita, K. Nozaki, R. Anwender, *Angew. Chem. Int. Ed.*, **2014**, 53, 6259.
35. L. Wang, Y. Fang, H. Mao, Y. Qu, J. Zuo, Z. Zhang, G. Tan, X. Wang, *Chem. Eur. J.*, **2017**, 23, 6930.
36. P. Atkins, *Atkins' Physical Chemistry (8th ed.)*. Oxford University Press., **2006**, 286, 816.
37. K. J. Laidler, *Chemical Kinetics (3rd ed.)*. Harper & Row., **1987**, 978.
38. E. M. Simmons, J. F. Hartwig, *Angew. Chem. Int. Ed.*, **2012**, 51, 3066.

39. K. B. Wiberg, L. H. Slaugh, *J. Am. Chem. Soc.*, **1958**, 80, 3033.
40. IUPAC, *Compendium of Chemical Terminology 2nd ed. (the "Gold Book")*, **1997**, 27, 32.
41. L. S. Keenan, P. K. Peterson, K. Peterson, K. Jacobson, *J. Chem. Educ.*, **2008**, 85, 558.
42. IUPAC, *Compendium of Chemical Terminology 2nd ed. (the "Gold Book")*, **1997**, 19, 90.
43. W. B. Jensen, *J. Chem. Educ.*, **1996**, 73, 11.
44. L. Pauling, *J. Am. Chem. Soc.*, **1932**, 54, 3570.

Chapter 5 Skeletal Isomerization of diselenadiazadiborabicyclo[2.2.2]octane

5.1 Introduction

Over the past decade, many selenium compounds were discovered to be useful reagents and catalysts for organic synthesis to generate various compounds with different functional groups.¹ Such selenium catalyzed reactions are often green and environmentally friendly, which further adds on to its attractiveness in the synthetic field.

In 1972, Sharpless and Lauer explained the selective oxidation of alkene **a** due to a two-step process. The first process occurred with an ene reaction to generate compound **b**. The subsequent process involved a sigma tropic [2,3]-rearrangement of compound **b** that generated compound **c** with the double bond returning to its prior location to finally afford compound **d** after eliminating a H₂O molecule (Scheme 1).² In 2011, the group of Argade (Scheme 2) reacted compound **e** with SeO₂ and discovered that the allylic oxidation reaction was regioselective and generated compound **f**. They suggested that the SeO₂ had induced the transformation of compound **e** to compound **f**.³

Scheme 1 The allylic oxidation of compound **a** with SeO_2 by Sharpless and Lauer

Scheme 2 The allylic oxidation of compound **e** with SeO_2 by the group of Argade

In 2003, Remias and Sen reported the oxidation of toluene to benzaldehyde by an active oxidant generated from the reaction of SeO_2 or selenium with nitrogen oxides (Scheme 3). Nitric oxide (NO) is first oxidized to nitrogen dioxide (NO_2). Nitrogen dioxide then abstracts one of the benzylic hydrogens to form the benzyl radical **g**. Radical **g** subsequently oxidizes selenium to SeO_2 which oxidizes the benzyl radical **g** to generate the aldehyde and the final acid product **h**.⁴ In 2001, the group of Gupta reported the aromatization of compound **i** to compound **j**

utilizing SeO_2 as the stoichiometric oxidant (Scheme 4). A high yield of 75-92% was obtained for compound **i** via this SeO_2 mediated aromatization.⁵

Scheme 3 The benzylic oxidation by SeO_2/Se to generate compound **h** reported by Remias and Sen

Scheme 4 The aromatization of compound **i** with SeO_2 by the group of Gupta

In 2011, Kakiuchi and co-workers reported the synthesis of compound **l** through an intramolecular Friedel-Crafts reaction-oxidation of compound **k** mediated by SeO_2 at 150°C . SeO_2 first proceeds to oxidize the methyl group in compound **k** to form the formyl group in compound **l**. The formyl group in **l** subsequently acylates the adjacent benzene ring to afford the cyclopentanone ring in **l** (Scheme 5).⁶ In the same year, Goncalves and co-workers discovered the one pot synthesis of tetraphenylporphyrin **n** (Scheme 6) with SeO_2 as the oxidant in dichloromethane at room temperature for thirty minutes. The first step involved the condensation of the pyrrole and benzaldehyde in **m** before the subsequent

oxidation by SeO_2 to afford **n**. The mild reaction conditions required coupled with the efficient reaction pathway for the generation of **n** had resulted in a good yield of 65% being obtained.⁷

Scheme 5 The Intramolecular Friedel-Crafts reaction-oxidation of compound **k** with SeO_2 by Kakiuchi and co-workers

Scheme 6 The Synthesis of compound **n** with SeO_2 by Goncalves and co-workers

Selenides are well known mild reagents and catalysts for oxidation of various compounds such as alkenes, alcohols, thiols, sulfides, phosphines, hydrazide and amines.⁸⁻¹² In 2002, Sheldon and co-workers reported the oxidation of aldehydes and ketone **o** with selenide **q** to afford carboxylic acids and carboxy esters respectively. The bis(perfluorooctyl) benzeneperoxyseleninic acid **p** was generated as the intermediate in the oxidation process (Scheme 7).¹³ Another

well-known catalyst for oxidation reactions are diselenides, $RSeSeR$. Diselenides can act as catalysts for the oxidation of different compounds with hydrogen peroxide. In 1987, the group of Młochowski proposed the oxidation of diselenide **t** with hydrogen peroxide to generate compound **s** and finally compound **r** (Scheme 8). Młochowski and co-workers suggested that the effectiveness of the selenium catalysts was largely dependent on the type of substrate used. It was observed that ortho-substituted diphenyl diselenides was the best choice of catalyst for the oxidation of sulfides into sulfoxides in the presence of hydrogen peroxide.¹⁴ In 2007, Johansson and co-workers reported the generation of nitroso compound **v** from the oxidation of compound **u** by hydrogen peroxide utilizing diphenyl diselenide as a catalyst (Scheme 9).¹⁵ Various nitroso compounds with different R groups can be generated through this pathway in $CHCl_3$ at room temperature in two hours.

Scheme 7 The oxidation of compound **o** with Se and hydrogen peroxide by Sheldon and co-workers

Scheme 8 The oxidation of compound **r** catalyzed by diaryl diselenide **t** reported by Młochowski.

Scheme 9 The oxidation of compound **u** catalysed with PhSeSePh reported by Johansson and co-workers.

In 1993, Piasecki and co-workers reported the synthesis of compound **w** and aniline to generate the diselenide compound **x** in the presence of Na₂Se₂ or Li₂Se₂(Scheme 10).¹⁶ Through the utilization of various amines with primary amino groups and different substituted diphenyl diselenides, many varying compounds can be obtained.¹⁷

Scheme 10 The generation of compound **x** reported by Piasecki and co-workers.

5.2 Results and Discussion:

5.2.1 Objective

Selenium containing compounds had long been exploited as oxidants, oxygen-transfer agents and catalysts to mediate various reactions to generate different functional groups.¹⁻¹⁷ A few of such examples are SeO₂, selenide and diselenides. Over the past decade, these selenium containing compounds had aided in the completion of multiple reactions such as the oxidation of methyl groups in arenes, heteroarenes, dehydrogenation, oxidative C-O and C-C cleavage, oxidative ring closure and ring transformations.¹ These interesting reactions had propelled our curiosity to further investigate effects of selenium or selenium containing compounds on novel chemical transformations of compounds. As previously mentioned in chapter 3 of the thesis, compound **13** was generated by the oxidative addition of selenium to the 1,4,2,5 diazadiborinine ring. We were very interested to discover further possibilities that compound **13** and selenium can bring to the world of chemical transformations. Thereby, we report the first skeletal isomerization of diselenadiazadiborabicyclo[2.2.2]octane to generate compound **26** in this chapter 5 of thesis.

5.2.2 Skeletal Isomerization of 1,4,2,5-diazadiborinine Selenium adduct to the 1,3,2,5- diazadiborinine Selenium adduct

Ten equivalents of selenium were added to one equivalent of **12** (Scheme 11) in a NMR tube. The reaction mixture was heated at 80 °C for 70 hours and monitored by NMR spectroscopy. During the reaction, the red color of the solution gradually turned orange. A crude mixture involving a major product and a minor product (Fig. 16) was generated and subjected to work up, from which compound **26** was obtained as a orange powder in 30% isolated yield. Compound **26** was fully characterized by standard spectroscopic techniques and X-ray crystallography (Fig. 1).

Scheme 11 Reactivity of compound **12** with Selenium at 80 °C for 70 hours to generate compound **26**

The ¹¹B NMR spectrum of **26** exhibits a characteristic signal at 2.28 and −9.47 ppm, indicating the formation of two tetracoordinate boron centers, which are shifted up field compared to that (10.28 ppm) of **12**. The calculated ¹¹B NMR chemical shift (2.66, −6.90 ppm) on **26** using the gauge-independent atomic orbital (GIAO) method at the B3LYP/6-311G(d,p) level of theory reasonably agrees with the experimental value (Table 1). In the ¹¹B NMR monitoring spectrum, the formation of compound **13** was observed at t=15 h before the initial observation of the formation of compound **26** at t=48 h (Fig. 18). This observation

is consistent with the ^1H NMR monitoring spectrum which three signals for the methyl groups of the mesityl groups were observed at 1.75 ppm, 2.07 ppm and 2.16 ppm at $t=24$ h to $t=70$ h indicative that compound **26** had been successfully generated. The three signals observed differs from that of compound **13** (Fig. 17) which the methyl groups of the mesityl groups were signaled at 1.78 ppm, 2.10 ppm and 2.20 ppm at $t=24$ h to $t=70$ h. These observations indicates that the formation of compound **26** represents the first example of the skeletal isomerization from a 1,4,2,5 bicyclo[2.2.2] molecule **13** involving a B–Se–Se–B unit ring to a 1,3,2,5 B–Se–Se–B activated product.

	Isotropic Values	Calculated δ (^{11}B)[ppm]	Experimental δ (^{11}B)[ppm]
13	104.8418	–1.4239	1.04
	104.8409	–1.4230	
26	100.7562	2.661	2.28
	110.3170	–6.899	–9.47
BF₃.Et₂O (Reference)	103.4179	-	-

Table 1 Experimental and calculated ^{11}B NMR chemical shifts of compound **13** and **26**.

Scheme 12 Reactivity of compound **12** with Selenium at 80 °C for 14 hours to generate compound **13**

The solid-state structure of **26** was confirmed by the X-ray diffraction study (Fig 1). Compound **26** bears a bicyclo[2.2.2] skeleton involving a B–Se–Se–B unit with 1,3,2,5 diazadiborinine, a rare example of a heavier analogue of diboraperoxide.¹⁸ The boron centers in **26** adopt a tetrahedral geometry and the B1, B2, Se1 and Se2 atoms are nearly coplanar (the B–Se–Se–B torsion angle = 5.7°). The Se1–Se2 bond distance (2.3626(4) Å) is close to the range reported for Se–Se single bonds (2.34 to 2.98 Å).²² The B1–Se1 bond (2.107(3) Å) and B2–Se2 bond (2.181(3) Å) distances are in the range of those reported for B–Se single bonds as observed for related compounds (1.94 to 2.15 Å).^{3,23,24} Both the B–N bond (B1–N1: 1.556(4) Å, B1–N3: 1.550(4) Å) and the B–C bond (B2–C1: 1.608(4) Å, B2–C25: 1.590(4) Å) distances in **26** are longer than those in **12**, whereas the N–C bond distances (N1–C1: 1.347(3) Å, N3–C25: 1.355(4) Å) in **26** are slightly shorter in comparison with those in **12** (Table 2). To the best of our knowledge, the formation of **26** represents the first example of the skeletal isomerization from a 1,4,2,5 bicyclo[2.2.2] molecule **13** involving a B–Se–Se–B unit ring to a 1,3,2,5 B–Se–Se–B activated product.¹⁸ The UV/Vis absorption spectrum of **26** exhibits the maximum absorption band at a wavelength of 308 nm (Fig. 2). This is in the acceptable range as compared the computed UV Vis absorption spectra of **26** by TD-DFT at B3LYP/6-311G(d,p) level of theory which displayed a absorption band at a wavelength of 255 nm (Fig. 3).

Figure 1 The solid-state structure of **26**. Thermal ellipsoids are set at the 50% probability level. All H atoms are omitted for clarity.

B–N (Å)	1.4574(4)	1.556(4)
	1.4624(4)	1.550(4)
N–C (Å)	1.4073(3)	1.347(3)
	1.4058(3)	1.355(4)
C–B (Å)	1.4960(4)	1.608(4)
	1.4942(4)	1.590(4)

Table 2 BN, NC and CB Bond Lengths of compounds **12** and **26**

Figure 2. UV Vis absorption spectrum of **26** in toluene.

Figure 3. Calculated UV Vis absorption spectra of **26** by TD-DFT at B3LYP/6-311G(d,p) level of theory

To gain insight into the electronic properties of compound **26**, theoretical calculations were carried out using a DFT method at the B3LYP/6-311G(d,p) level of theory. Like compound **13**, the HOMO of **26** mainly corresponds to the lone pairs of the selenium atoms (Fig 4), implying the Se-Se unit in **26** could be one of the most reactive moieties. The LUMO of **26** consists of the π bonding interactions of the annulated imidazole rings with contribution from the N lone pairs and the C=C moieties with the π orbitals of the phenyl substituents, predominantly the phenyl ring coplanar to the imidazole (Fig.5). The LUMO also involves the π system interactions over the BCC π unit in the $B_2C_2N_2$ ring and the selenium atoms. The HOMO– LUMO energy gap (3.53 eV) of **26** is rather similar to that of **13** (3.55 eV) but larger than that (2.56 eV) of **12**.

Figure 4. Side view (left) and front view (right) of the HOMO of **26**.

Figure 5. Side view (left) and front view (right) of the LUMO of **26**.

The Wiberg bond index (WBI) values of B1–N1 (0.63), B1–N3 (0.62), B2–C1 (0.87) and B2–C25 (0.87) in **26** suggest the single bond nature around boron atoms in the B₂C₂N₂ ring as compared to the Wiberg bond index (WBI) values of B1–C1 (1.19), B2–C2 (1.19), C2–N1 (1.12), C1–N3 (1.12) in **12** (Table 3) which features the partial multiple-bond nature of the bonds in the B₂C₂N₂ ring. **26** adopts a tetrahedral geometry at the boron centers which agrees with the crystallographic structure.

Bond (Å)	X-ray data	Optimized structure	WBI Value
B1-N1	1.556(4)	1.56601	0.6280
B1-N3	1.550(4)	1.57103	0.6241
B1-Se1	2.107(3)	2.13657	0.9329
B2-C1	1.608(4)	1.60568	0.8678
B2-C25	1.590(4)	1.60493	0.8740
B2-Se2	2.181(3)	2.2944	0.8045
N1-C1	1.347(3)	1.35295	1.2864
N3-C25	1.355(4)	1.35402	1.2896
Se1-Se2	2.3626(4)	2.39203	0.7439

Table 3. Selected Bond Lengths and Wiberg Bond Index (WBI) for the optimized geometries of compound **26**.

5.3 The Proposed mechanistic pathway for the skeletal isomerization from compound **13** to **26**:

After the formation of compound **13** at 80°C, experimental data had demonstrated that prolonged heating at the same temperature for another two days was discovered to result in the skeletal isomerization of the B₂C₂N₂ ring in **13** to generate the 1,3,2,5 selenium adduct, compound **26**(Fig.16). To gain insight into its mechanism, the pathway for the skeletal isomerization of **13** to **26** was explored theoretically using B3LYP/6-31G(d,p) functional using simplified model structures **13'** and **26'** which the phenyl groups on the annulated imidazoles were replaced with hydrogen atoms and the mesityl groups were replaced with methyl groups.

Compound **13'** first passed through the transition state structure **TS1** by overcoming an activation barrier of 56.1kcal/mol to afford **Int1** at the energy level of 43.2kcal/mol. At the current stage, one of the B–C bonds in the B₂C₂N₂ ring was cleaved and the annulated imidazole was oriented in the position such that the nitrogen atom was placed in a close proximity to the boron atom to form the BNN unit. **Int1** subsequently passed through **TS2** by overcoming an activation barrier of 12.5kcal/mol to afford the 1,3,2,5 selenium adduct, compound **26'** at the energy level of 0.06kcal/mol with the formation of a BCC unit(Fig.6). The structure of compound **26** was successfully confirmed through xray crystallography studies. It is noteworthy that we were able to obtain the crystal structures of both the 1,4,2,5 selenium adduct, compound **13** and the 1,3,2,5 selenium adduct, compound **26** even though we were unsuccessful in

attempts to obtain the cis activated C–H 1,4,2,5 structure mentioned in the previous chapter 4. This is probably due to the relatively close energies of both compound **13** and **26** which are lower in energy and more stable than the cis activated C–H 1,4,2,5 structure in chapter 4.

Figure 6. Proposed mechanistic pathway for the generation of **26'** from **13'**.

5.4 Kinetic Studies:

The computationally estimated activation parameters for the skeletal isomerization process ($\Delta H^\ddagger = 1.04 \text{ kcalmol}^{-1}$, $\Delta G^\ddagger_{(298)} = 0.33 \text{ kcalmol}^{-1}$) agreed well with the experimental results ($\Delta H^\ddagger = 2.98 \pm 2.0 \text{ kcalmol}^{-1}$, $\Delta G^\ddagger_{(298)} = 5.90 \pm 5.6 \text{ kcalmol}^{-1}$). The slightly positive Gibbs-free energy value suggests that the skeletal isomerization from compound **13** to **26** is a slightly endergonic process. This implies that the formation of compound **26** is slightly less favorable than the formation of compound **13**, which aligns with our experimental monitoring of the skeletal isomerization (Fig. 16, 20, 21) that compound **13** was generally present in a larger ratio than compound **26** throughout the entire 70h. In comparison to the monitoring spectra of the reversed reaction of compound **26** to compound **13** at 80°C (Fig. 19), the ratio of compound **13** regenerated in the reverse reaction was larger than that of compound **26** regenerated in the forward reaction (Fig. 16, 20, 21). The driving force of the skeletal isomerization of **13** to **26** could be most possibly due to the prolonged heating of the reaction at a high temperature of 80°C at 70h. It is noteworthy that compound **13** can be generated at 80°C with a reaction time of 14-16h. Therefore, the continuous heating at 80°C could have provided the excess amount of energy to the reaction system to overcome the activation barrier of 56.1 kcal/mol to bypass **TS1** from **13'** to generate **Int1** and subsequently compound **26'** (Fig. 6). In addition, free energy of the system will be further lowered throughout the reaction pathway to generate compound **26'**. The Gibbs free energy of **13'** to **Int1** gives a $\Delta G^\ddagger$ value of +43.2 kcal/mol where the $\Delta G^\ddagger$ value of **Int1** to **26'** is -96.3 kcal/mol. This drives

the reaction to proceed forward to finally afford **26'**. The excess amount of selenium present in the reaction may also be a factor in driving the slightly endergonic skeletal isomerization from **13'** to **26'**. It is generally known that selenium tends to form cationic clusters in solution. The excess selenium may cluster to form homopolyatomic radical cations to stabilize the negative charges on the boron atoms in the transition state structures and the intermediate.^{19,20} This act of stabilization might help to propel the slightly endogenic pathway to obtain **26**.

Figure 7. Plot of $\ln [^{1425}\text{Se}]$ against time to determine rate constant (k) at 70°C .

Figure 10. Plot of $\ln [^{1425}\text{Se}]$ against time to determine rate constant (k) at 100°C .

T/K	1/(T/K ⁻¹)	k/s ⁻¹	ln(K/T)
343.15	0.002914	0.0179	-9.86112
353.15	0.002832	0.0212	-9.72065
363.15	0.002754	0.0222	-9.70248
373.15	0.00268	0.0284	-9.48335

Figure 11. Eyring plot for the formation of **26**.

5.5 Conclusion

In summary, we had successfully synthesized compound **26** which is the skeletal isomer of **13**. Through experimental monitoring of the NMR spectra, we were able to observe the skeletal isomerization from **13** to **26** under prolonged heating conditions at 80°C. It is noteworthy that the skeletal isomerization process was observed to be reversible under the addition of excess selenium. The excess selenium was hypothesized to form cationic clusters to stabilize the negative charges on the boron atoms in the transition states which helped to propel the slightly endogenic reaction from **13** to **26**. DFT calculations had provided the Gibbs free energy value of the slightly endogenic reaction to be 0.33kcal/mol which is still considered highly feasible for the reaction to proceed under prolonged heating conditions. We had proposed a plausible mechanism supported by DFT calculations in the formation of **13** to **26**. The various computed Gibbs free energy levels of the starting compound, transition states, intermediates and final product were within an acceptable range of values. In addition, kinetic studies on the Eyring plot were conducted to gauge the experimentally determined $\Delta G^\ddagger$ and $\Delta H^\ddagger$ values of the skeletal isomerization process. The experimentally determined values were in an acceptable range as the computed values, further confirming the existence of the skeletal isomerization of **13** to **26**. With that, we report the first skeletal isomerization of diselenadiazadiborabicyclo[2.2.2]octane to add on to the various interesting chemical transformations of selenium and selenium containing compounds.

All DFT calculations had been performed by the Ph.D. candidate Gillian Goh Kor Hwee.

5.6 Experimental Section

5.6.1 Synthesis, physical and spectroscopic data for all new compounds

Materials and Method: All reactions were performed in an atmosphere of nitrogen or argon by using standard Schlenk or dry box techniques; solvents were dried with Na metal and K metal. ^1H , $^{13}\text{C}\{^1\text{H}\}$, ^{11}B and $^{11}\text{B}\{^1\text{H}\}$ NMR spectra were obtained with either Bruker Avance 300, MHz AV300, AV 500 or AVIII 400 MHz BBFO1, BBFO2 and ECA400 spectrometers at 298 K. Coupling constants J are given in Hz. Chemical shifts (δ) are given in p.p.m. 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. Ultraviolet spectra was recorded on Cary 100 UV-Vis spectrometer.

Synthesis of **26**:

C_6D_6 (10 mL) was added to a mixture of **12** (0.40 g, 0.470 mmol) and excess grey selenium (0.38 g, 4.70 mmol). The reaction mixture was heated at 80 °C for 70 hours and monitored by NMR spectroscopy. After completion of the reaction, all volatiles were removed under vacuum. The residue was washed with hexanes (15 mL) and dried under vacuum to

afford **26** (0.12 g, 0.119 mmol) as a pale orange powder (30%). Orange single crystals of **26** were obtained by recrystallization from a benzene solution at ambient temperature.

M.p.: 168 °C. ^1H NMR (400 MHz, C_6D_6) δ 7.92 (d, 2H, $J = 4.88\text{Hz}$, ArH), 7.56 (d, 1H, $J = 5.64\text{Hz}$, ArH), 7.26 (s, 2H, $J = 5.92\text{Hz}$, ArH), 6.87 (d, 5H, $J = 5.84\text{Hz}$, ArH), 6.81 – 6.74 (m, 6H, ArH), 6.68 – 6.63 (m, 5H, ArH), 6.58 (t, 6H, $J = 5.84$, 4.24Hz, ArH), 6.52 (d, 3H, $J = 5.88\text{Hz}$, ArH), 6.45 (t, 1H, $J = 5.88$, 6.28Hz, ArH), 6.25 (s, 2H, ArH), 5.92 (s, 2H, ArH), 2.17 (s, 6H, CH_3), 2.07 (s, 6H, CH_3), 1.75 (s, 6H, CH_3). ^{11}B NMR (128 MHz, C_6D_6): 2.28, -9.47(s). ^{13}C NMR (100 MHz, C_6D_6): 138.2 (C-Ar), 137.9 (CH-Ar), 137.1 (C-Ar), 134.9 (CH-Ar), 134.7 (C-Ar), 134.2 (C-Ar), 133.2 (C-Ar), 132.3 (CH-Ar), 132.0 (CH-Ar), 131.6 (CH-Ar), 130.7 (CH-Ar), 130.5 (C-Ar), 130.2 (CH-Ar), 129.4 (CH-Ar), 128.7 (CH-Ar), 127.1 (CH-Ar), 126.5 (CH-Ar), 123.8 (CH-Ar), 20.7 (CH_3 -Ar), 19.8(CH_3 -Ar), 18.3(CH_3 -Ar). HRMS (ESI): m/z calcd for $\text{C}_{60}\text{H}_{52}\text{B}_2\text{N}_4\text{Se}_2$: 1009.2815 [$(M + H)^+$]; found: 1009.2832. UV-vis (ϵ , in toluene): $\lambda = 308\text{ nm}$ (4328), 285 nm (4005).

5.6.2 NMR spectra for all new compounds

Figure 12. ^1H NMR spectrum of 26

Figure 13. ^{11}B NMR spectrum of 26

Figure 14. ^{13}C NMR spectrum of **26**

Figure 15. ^{13}C DEPT 135 NMR spectrum of **26**

Figure 16. ^1H NMR spectrum in monitoring the formation of **13** and **26** during the reaction of **12** with Se at 80 °C.

Figure 17. ^1H NMR spectrum of formation of **13** and **26** at 80°C, 70h.

Figure 18. ^{11}B NMR spectrum in monitoring the formation of **13** and **26** during the reaction of **12** with Se at 80°C .

Figure 19. ^1H NMR spectrum in monitoring the formation of **26** from **13** at 80°C .

Figure 20. ^1H NMR spectrum in monitoring the formation of **13** from **26** at 80 °C.

Figure 21. ^1H NMR downfield spectrum in monitoring the formation of **13** from **26** at 80 °C.

Figure 22. Electrospray ionization (ESI) mass spectra of compound **26**.

5.6.3 Crystallographic Data

X-ray data collection and structural refinement. Intensity data for compound **26** was collected at 100 K using a Bruker D8 Quest diffractometer. The structure was solved by Intrinsic Phasing (SHELXTL XT-2014)¹ and refined for all data by full-matrix least squares methods on F^2 .² 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. The restraint RIGU for the whole molecule was used in the refinement of rei1299m.cif. CCDC: contains the supplementary crystallographic data for this paper. The data can be obtained free of charge from the Cambridge Crystallography Data Center via www.ccdc.cam.ac.uk/data_request/cif

Table 4. Summary of Data collection and structure refinement for compound **26**.

26	
Formula	C ₆₀ H ₅₂ B ₂ N ₄ Se ₂
Fw	1008.59
Cryst syst	monoclinic
Space group	P 1 21/n 1
Size (mm ³)	0.060 x 0.120 x 0.280
T/K	100(2)
<i>a</i> , Å	16.3515(6)
<i>b</i> , Å	17.5727(6)
<i>c</i> , Å	17.2343(8)
α , deg	90
β , deg	91.8522(16)
γ , deg	90
<i>V</i> , Å ³	4949.5(3)
<i>Z</i>	4
<i>d</i> calcd g.cm ⁻³	1.354
μ , mm ⁻¹	1.538
Refl collected	47201
<i>T</i> _{max} / <i>T</i> _{min}	0.9130/0.6730
<i>N</i> _{meas}	13781
[<i>R</i> int]	0.0930
<i>R</i> [<i>I</i> >2sigma(<i>I</i>)]	0.0507
<i>R</i> _w [<i>I</i> >2sigma(<i>I</i>)]	0.1033
GOF	1.014
Largest diff peak/hole[e ⁻ Å ⁻³]	0.653/-0.638

5.6.4 Computational details

Gaussian 09E was used for the density functional theory (DFT) calculations.³ Geometry optimization and frequency calculations of compound **13** and **26** were performed at the B3LYP/6-311G(d,p) level of theory. Geometry optimization and frequency calculations of compound **13'**, **TS1**, **Int1**, **TS2** and **26'** were performed at the B3LYP/6-31G(d,p) level of theory. NBO calculations for compound **26** were performed at B3LYP/6-311G(d,p) level.⁴ NMR shielding tensors for compound **26** were computed with the Gauge-Independent Atomic Orbital (GIAO) method at the B3LYP/6-311G(d,p) level. The calculated boron chemical shifts were derived with reference to that of BF₃·Et₂O.

Figure 25. The optimized structure of **26**.

Table 5: The coordinates (XYZ) for various optimized structure **26**

B	0.01700600	-1.81825400	0.30770800
B	-0.00815600	1.15826000	0.56869900
C	1.28028000	0.38127400	0.00796500
C	3.38687700	-0.30940500	-0.39822400
C	2.59650300	-1.41654100	-0.25473500
C	3.10028900	-2.81162100	-0.22457300
C	3.15384400	-3.52086400	0.98200700
H	2.71925600	-3.08267200	1.87300000
C	3.75237700	-4.77562300	1.03461400
H	3.78748600	-5.31288500	1.97592300
C	4.30557400	-5.33944800	-0.11364500
H	4.77215500	-6.31738600	-0.07050600
C	4.25439300	-4.64143300	-1.31741000
H	4.67887800	-5.07397000	-2.21647100
C	3.65856800	-3.38445800	-1.37145900
H	3.62486300	-2.84095900	-2.30826500
C	4.85452200	-0.23409700	-0.57365900
C	5.68830200	-0.85006100	0.37107400
H	5.24525600	-1.35879300	1.21791100

C	7.07209800	-0.81705100	0.22878500
H	7.69800400	-1.30120200	0.96985600
C	7.64972500	-0.16333400	-0.85704300
H	8.72794400	-0.13550200	-0.96720700
C	6.83249000	0.45257400	-1.80168200
H	7.27167000	0.96065000	-2.65286500
C	5.44803100	0.41590900	-1.66366600
H	4.82898200	0.89089600	-2.41251300
C	3.02085600	2.16346600	-0.39651600
C	2.93684800	2.77335000	-1.65582900
C	3.46419300	4.05652900	-1.79908100
H	3.40530500	4.54061800	-2.76906100
C	4.06130600	4.73028700	-0.73346800
C	4.13636800	4.08273900	0.49905300
H	4.60325100	4.58905000	1.33808800
C	3.62882200	2.79741800	0.69444300
C	3.75584800	2.12110900	2.03501400
H	2.82838100	1.62786200	2.33512400
H	4.02262100	2.84802900	2.80407600
H	4.54004300	1.35765600	2.01315400
C	4.58301800	6.13634700	-0.90077200
H	5.43731400	6.32602500	-0.24689100
H	3.80770100	6.86793100	-0.64812600
H	4.89271700	6.32882300	-1.93054900
C	2.29415100	2.08505700	-2.83523300
H	2.58816100	1.03597300	-2.91619800
H	2.56451200	2.58780800	-3.76559200
H	1.20391300	2.10287600	-2.75480600
C	-1.30601800	0.36411500	0.05812600
C	-3.39888200	-0.38964600	-0.31406500
C	-2.56496700	-1.46974000	-0.24844800
C	-3.01529600	-2.88505700	-0.19421900
C	-3.35470100	-3.43634200	1.04716000
H	-3.19142300	-2.85406100	1.94586300
C	-3.88033300	-4.72259000	1.12791900
H	-4.13968000	-5.13666700	2.09591300
C	-4.07555800	-5.47235100	-0.02962700
H	-4.48645300	-6.47399300	0.03271800
C	-3.73831500	-4.93171100	-1.26817000
H	-3.88010300	-5.51251300	-2.17252600
C	-3.21351200	-3.64539900	-1.34986300
H	-2.93979400	-3.23396000	-2.31349100
C	-4.86399700	-0.35269700	-0.49871200
C	-5.70112600	0.23732800	0.45847400
H	-5.27079800	0.67468700	1.34954100

C	-7.08143200	0.24362700	0.28694800
H	-7.71245300	0.70152000	1.04031900
C	-7.65237100	-0.34381000	-0.84020100
H	-8.72858600	-0.34002300	-0.97117600
C	-6.83259900	-0.94139100	-1.79380200
H	-7.26698200	-1.40613800	-2.67172900
C	-5.45069800	-0.94400900	-1.62551100
H	-4.81917500	-1.40985300	-2.37126900
C	-3.12229200	2.08897400	-0.30535400
C	-3.31659900	2.54425500	-1.62196000
C	-3.85847400	3.81268000	-1.80747200
H	-4.00181800	4.17629300	-2.82048600
C	-4.21468500	4.62775400	-0.72995600
C	-4.01227000	4.13940200	0.55638700
H	-4.27755000	4.75816800	1.40823100
C	-3.47249600	2.87193100	0.79916500
C	-3.28748600	2.41835800	2.22496800
H	-2.48695200	2.99109000	2.70041100
H	-3.01183100	1.36878700	2.30653700
H	-4.20126100	2.59041000	2.80149100
C	-4.82449200	5.98910800	-0.96051400
H	-4.38861400	6.47732800	-1.83564500
H	-4.67608000	6.64241000	-0.09831900
H	-5.90326800	5.91078600	-1.13448100
C	-2.94803100	1.70138000	-2.81844500
H	-3.68164700	0.90732500	-2.98497000
H	-1.97460200	1.22006100	-2.69622600
H	-2.91420300	2.31481500	-3.72049100
C	0.03256200	-3.24109700	-0.43349300
C	0.13377600	-3.25003900	-1.83489500
H	0.20619900	-2.30653700	-2.36922900
C	0.14989500	-4.43593400	-2.56313600
H	0.23370700	-4.40854700	-3.64494600
C	0.06396200	-5.65806600	-1.89965000
H	0.07895400	-6.58738900	-2.45894900
C	-0.03830800	-5.67587500	-0.51105700
H	-0.10630200	-6.62170000	0.01556100
C	-0.05276600	-4.48183600	0.20678100
H	-0.13665300	-4.52443900	1.28769300
C	-0.00877700	2.76863700	0.55077600
C	-0.26400800	3.46630500	-0.64122500
H	-0.47598100	2.91032300	-1.54761600
C	-0.27168500	4.85646000	-0.70517800
H	-0.47872300	5.35188400	-1.64780300
C	-0.02232800	5.60883500	0.44026500

H	-0.03192400	6.69275200	0.39892700
C	0.23604900	4.95010200	1.63838400
H	0.43467500	5.51882800	2.54088600
C	0.24317400	3.55639800	1.68574000
H	0.46030800	3.07962100	2.63571000
N	1.28479600	-0.97051900	-0.04789600
N	2.54978000	0.80513700	-0.25201000
N	-1.26564400	-0.98491500	-0.05076800
N	-2.60473900	0.74970500	-0.12550900
Se	0.00540100	-1.88645600	2.44315600
Se	0.02829900	0.49207100	2.69596500

Zero-point correction=	0.376496 (Hartree/Particle)
Thermal correction to Energy=	0.401679
Thermal correction to Enthalpy=	0.402623
Thermal correction to Gibbs Free Energy=	0.319852
Sum of electronic and zero-point Energies=	-5841.494020
Sum of electronic and thermal Energies=	-5841.468837
Sum of electronic and thermal Enthalpies=	-5841.467893
Sum of electronic and thermal Free Energies=	-5841.550664

Table 6. Free energy difference (ΔG in kcal mol⁻¹) of **13'**.

Zero-point correction=	0.372732 (Hartree/Particle)
Thermal correction to Energy=	0.398096
Thermal correction to Enthalpy=	0.399041
Thermal correction to Gibbs Free Energy=	0.315880
Sum of electronic and zero-point Energies=	-5841.404481
Sum of electronic and thermal Energies=	-5841.379116
Sum of electronic and thermal Enthalpies=	-5841.378172
Sum of electronic and thermal Free Energies=	-5841.461333

Table 7. Free energy difference (ΔG in kcal mol⁻¹) of **TS1**.

Zero-point correction=	0.374086 (Hartree/Particle)
Thermal correction to Energy=	0.399835
Thermal correction to Enthalpy=	0.400779
Thermal correction to Gibbs Free Energy=	0.316052
Sum of electronic and zero-point Energies=	-5841.423816
Sum of electronic and thermal Energies=	-5841.398067
Sum of electronic and thermal Enthalpies=	-5841.397122
Sum of electronic and thermal Free Energies=	-5841.481850

Table 8. Free energy difference (ΔG in kcal mol⁻¹) of **Int1**.

Zero-point correction=	0.372810 (Hartree/Particle)
Thermal correction to Energy=	0.398181
Thermal correction to Enthalpy=	0.399125
Thermal correction to Gibbs Free Energy=	0.315926
Sum of electronic and zero-point Energies=	-5841.404952
Sum of electronic and thermal Energies=	-5841.379581
Sum of electronic and thermal Enthalpies=	-5841.378637

Sum of electronic and thermal Free Energies= -5841.461836

Table 9. Free energy difference (ΔG in kcal mol⁻¹) of **TS2**.

Zero-point correction=	0.376622 (Hartree/Particle)
Thermal correction to Energy=	0.401771
Thermal correction to Enthalpy=	0.402716
Thermal correction to Gibbs Free Energy=	0.320091
Sum of electronic and zero-point Energies=	-5841.494036
Sum of electronic and thermal Energies=	-5841.468887
Sum of electronic and thermal Enthalpies=	-5841.467942
Sum of electronic and thermal Free Energies=	-5841.550567

Table 10. Free energy difference (ΔG in kcal mol⁻¹) of **26'**.

Zero-point correction=	0.963895 (Hartree/Particle)
Thermal correction to Energy=	1.025174
Thermal correction to Enthalpy=	1.026119
Thermal correction to Gibbs Free Energy=	0.863189
Sum of electronic and zero-point Energies=	-7389.364049

Sum of electronic and thermal Energies=	-7389.302770
Sum of electronic and thermal Enthalpies=	-7389.301826
Sum of electronic and thermal Free Energies=	-7389.464755

Table 11. Free energy difference (ΔG in kcal mol⁻¹) of **13**.

Zero-point correction=	0.963642 (Hartree/Particle)
Thermal correction to Energy=	1.025145
Thermal correction to Enthalpy=	1.026089
Thermal correction to Gibbs Free Energy=	0.862029
Sum of electronic and zero-point Energies=	-7389.362615
Sum of electronic and thermal Energies=	-7389.301112
Sum of electronic and thermal Enthalpies=	-7389.300168
Sum of electronic and thermal Free Energies=	-7389.464228

Table 12. Free energy difference (ΔG in kcal mol⁻¹) of **26**.

5.6.5 References

5. Sheldrick, G. M. (2015). *Acta Cryst. A* **71**, 3–8.
6. Sheldrick, G. M. (2015). *Acta Cryst. C* **71**, 3–8.
7. Gaussian 09, Revision B.01, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian, Inc., Wallingford CT, 2013.
8. Reed, A. E.; Curtis, L. A.; Weinhold, F. *Chem. Rev.* **1988**, 88, 899–926.

5.7 References

1. J. Młochowski; H. W. Młochowska, *Molecules*, **2015**, *20*, 10205.
2. K. B. Sharpless; R. F. Lauer, *J. Am. Chem. Soc.*, **1972**, *94*, 7154.
3. R. M. Patel; V. G. Puranik; N. P. Argade, *Org. Biomol. Chem.*, **2011**, *9*, 6312.
4. J. E. Remias; A. Sen, *J. Mol. Cat. A Chem.*, **2003**, *201*, 63.
5. S. Paul; S. Shivani; M. Gupta; D. Choudhary; R. Gupta, *Bull. Korean Chem. Soc.*, **2007**, *28*, 336.
6. Y. Zhang; H. Tanimoto; Y. Nishiyama; T. Morimoto; K. Kakiuchi, *Heterocycles*, **2011**, *83*, 2337.
7. S. M. S. Ló; D. R. B. Ducatti; M. E. R. Duarte; S. M. W. Barreira; M. D. Nosedá; A. G. Gonçalves, *Tetrahedron Lett.*, **2011**, *52*, 1441.
8. F. Ogura; T. Otsubo; T. Wirth; Z. Ali Khan, *EROS Encyclopedia of Reagents for Organic Synthesis*; Fuchs, P.L., Ed.; Wiley & Sons: Chichester, UK, **2007**.
9. T. G. Back, *Oxford University Press: Oxford, UK*, **1999**, 93.
10. J. Młochowski; M. Brząszcz; M. Giurg; J. Palus; H. Wójtowicz, *Eur. J. Org. Chem.*, **2003**, *2003*, 4329.
11. J. Młochowski; R. Lisiak; H. Wójtowicz-Młochowska; S. Patai; Z. Rappoport; J. F. Liebman; Marek; I. Eds, *Wiley: Chichester, UK*, **2012**, *3*, 1083.
12. J. Młochowski; W. Peczyńska-Czoch; M. Piętka-Ottlik; H. Wójtowicz-Młochowska, *Open Catal. J.*, **2011**, *4*, 54.

13. G. J. Ten Brink; J. M. Vis; I. W. C. E. Arends; R. A. Sheldon, *Tetrahedron*, **2002**, 58, 3977.
14. L. Syper; J. Młochowski, *Tetrahedron*, **1987**, 43, 207.
15. D. Zhao; M. Johansson; J. E. Bäckvall, *Eur. J. Org. Chem.*, **2007**, 26, 4431.
16. J. Młochowski; K. Kloc; L. Syper; A. D. Inglot, *Liebigs Ann. Chem.*, **1993**, 1239.
17. W. D. Pfeiffer, *Sci. Synth.*, **2001**, 11, 931.
18. G. K. H. Goh; Y. Li; R. Kinjo, *Dalton Trans.*, **2019**, 48, 7514.
19. J. Carsten; M. C. Nierstenhöfer, *Eur. J. Inorg. Chem.*, **2020**, 200.
20. (a) J. Beck, *Coord. Chem. Rev.*, **1997**, 163, 55; (b) I. Krossing, *Royal Society of Chemistry, Cambridge*, **2007**, 381; (c) S. Brownridge; I. Krossing; J. Passmore; H. D. B. Jenkins; H. K. Roobottom, *Coord. Chem. Rev.*, **2000**, 197, 397; (d) E. Ahmed; M. Ruck, *Coord. Chem. Rev.*, **2011**, 255, 2892; (e) R. D. Burbank, *Acta Crystallogr.*, **1951**, 4, 140; (f) T. Maaninen; J. Konu; R. S. Laitinen, *Acta Crystallogr.*, **2004**, 60, 2235; (f) Z. Cernosek; A. Růžicka; J. Holubová; E. Cernosková, *Main Group Met. Chem.*, **2007**, 30, 231; (g) W. C. Cooper; R. A. Westbury, *In Selenium New York*, **1974**, 87; (h) A. Benamar; D. Rayane; P. Melinon; B. Tribollet; M. Broyer; *Z. Phys. D: At. Mol. Clusters*, **1991**, 19, 237; (i) K. Kooser; D. T. Ha; E. Itälä; J. Laksman; S. Urpelainen; E. Kukk, *J. Chem. Phys.*, **2012**, 137, 44304. (j) R. Minkwitz; H. Borrmann; J. Nowicki, *Z. Naturforsch.*, **1991**, 46, 629; (k) R. K. McMullan; D. J. Prince; J. D.

Corbett, *J. Chem. Soc.*, **1969**, 23, 1438; (l) J. Beck; T. Hilbert, *Z. Anorg. Allg. Chem.*, **2000**, 626, 837; (m) J. Beck; J. Wetterau, *Inorg. Chem.*, **1995**, 34, 6202.

Chapter 6 Conclusion

In conclusion, we had successfully developed three novel diazadiborinine derivatives compound **4**: 1,3,2,5-diazadiborinine with Mes and Ph groups on boron atoms, compound **9**: 1,3,2,5-diazadiborinine with Ph and Cl groups on boron atoms and compound **12**: 1,4,2,5-diazadiborinine with Ph group on boron atoms. The AICD calculations had demonstrated that compound **4** is an aromatic compound while compound **9** and **12** are anti aromatic compounds. We had discovered a more efficient synthetic method to afford diazadiborinines in a higher yield as compared to the complicated reaction pathways previously reported. We had successfully broadened the scope of reactivity of diazadiborinines with Selenium-Selenium and sp^3 C-H bond activations under metal free and mild conditions. We had also discovered the possibility of skeletal isomerization of the 1,4,2,5 diazadiborinine to a 1,3,2,5 activated product and attempted to propose a suitable mechanism via DFT calculations. It is noteworthy that the proposed mechanism is a plausible one however it might not be the sole definite mechanism that exists. The vast possibilities of B-C, B-N bond breakage and connection with cis-trans isomerism remains fascinating and studies are still ongoing for further novel break throughs in the future. The Hammett Plot for the electron donating and withdrawing substituents were plotted to investigate the effects on the sp^3 C-H activations by compound **12**. The

Eyring Plot was also plotted to find out the changes on the rate or reaction against temperature for compound **13** to **26**.

In terms of the scientific implications, the results presented by this thesis are expected to create a platform to generate novel aromatic and anti-aromatic green catalysts which serves under metal free and mild conditions. It serves as a chemical toolkit for other researchers to develop and expand the limited scope and reactivities of the diazadiborinines currently. Also, the mild conditions would require less monetary cost to conduct the reactions and less toxic side products are generated under the metal free conditions.

In terms of the impact to the society at large, the results presented in this thesis could serve as a platform for blue sky research to develop potential drugs. C-H activations are commonly present in the production of pharmaceuticals. The possibility of diazadiborinines being able to activate sp^3 C-H bonds under mild conditions could serve to propel more break throughs in the production of useful drugs whose production might only be possible under harsh conditions previously. The presence of excess selenium in the body results in carcinogenic conditions and impact the development of fetuses. The possibility of diazadiborinines being able to activate selenium could serve to combat this situation and stimulate research towards the anti-cancer drug development.