Carbene and N-phosphinoamidinate stabilized diboron derivatives for catalytic hydroboration

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**CARBENE AND N-PHOSPHINOAMIDINATE STABILIZED
DIBORON DERIVATIVES FOR CATALYTIC
HYDROBORATION**

FAN JUN

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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HYDROBORATION**

FAN JUN

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.

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Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journal(s) in which I am listed as an author.

Chapter **1** is published as J. Fan, M.-C. Yang, T. J. N. Hooper, M.-D. Su, and C.-W. So. Diboron-Carbene Complexes Derived from a Geminal Dianion. *Organometallics*, **40**, 1848-1853 (2021). DOI: 10.1021/acs.organomet.1c00108

The contributions of the co-authors are as follows:

- A/Prof So Cheuk Wai directed the project and edited the manuscript drafts.
- I designed and performed the experiment.
- Dr. Yang Ming-Chung and Prof. Su Ming-Der performed the computational theoretical study for the experiment.
- Dr. Thomas J. N. Hooper measured the solid state ^{11}B NMR for one of the compound.

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The contributions of the co-authors are as follows:

- A/Prof So Cheuk Wai directed the project and edited the manuscript drafts.
- I designed and performed the experiment.
- Mr. Mah Jian-Qiang assisted in portion of the catalysis laboratory work.
- Dr. Yang Ming-Chung and Prof Su Ming-Der performed the computational theoretical study for the experiment.

Chapter **3** is in the midst of peer reviewing.

The contributions of the co-authors are as follows:

- A/Prof So Cheuk Wai directed the project and edited the manuscript drafts.
- I designed and performed the experiment.
- Ms. Chia Pei Ting assisted in portion of the catalysis laboratory work.
- Dr. Yang Ming-Chung and Prof Su Ming-Der performed the computational theoretical study for the experiment.

Manuscript for Chapter 4 is in the midst of preparation.

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- A/Prof So Cheuk Wai directed the project and edited the manuscript drafts.
- I designed and performed the experiment.
- Dr. Yang Ming-Chung and Prof Su Ming-Der performed the computational theoretical study for the experiment.

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Fan Jun

List of Abbreviations and Symbols

Me	Methyl
Et	Ethyl
<i>i</i> Pr	Isopropyl
<i>t</i> Bu	<i>tert</i> -Butyl
Cy	Cyclohexyl
TMS	Trimethylsilyl (SiMe ₃)
Ph	Phenyl
Dipp	2, 6-Diisopropylphenyl
THF	Tetrahydrofuran
Tol	Toluene
Et ₂ O	Diethyl Ether
DCM	Dichloromethane
PhF	Fluorobenzene
ACN	Acetonitrile
C ₆ H ₆	Benzene
NMR	Nuclear Magnetic Resonance
δ	Chemical Shift
ppm	Parts Per Million
s	Singlet
d	Doublet
t	Triplet
q	Quartet
sept	Septet
m	Multiplet
br	Broad
Hz/MHz	Hertz/Megahertz
HRMS	High Resolution Mass Spectrometry
ESI	Electron Spray Ionization
calcd.	Calculated
EA	Elemental Analysis

M.p.	Melting Point
dec.	Decomposed
Å	Angstrom(S)
°	Degree
α	Alpha
β	Beta
γ	Gamma
DFT	Density Functional Theory
MO	Molecular Orbital
HOMO	Highest Occupied Molecular Orbital
LUMO	Lowest Unoccupied Molecular Orbital
WBI	Wiberg Bond Index
NBO	Natural Bond Orbital
NPA	Natural Population Analysis
NICS	Nucleus-Independent Chemical Shift
EDA	Energy Decomposition Analysis
NOCV	Natural Orbital For Chemical Valence
kcal	Kilocalories
<i>t</i> BuLi	<i>tert</i> -Butyllithium
<i>n</i> BuLi	<i>n</i> -Butyllithium
PhLi	Phenyllithium
KC ₈	Potassium Graphite
r.t.	Room Temperature
%	Percentage
M	Molar (Mol/dm ⁻³)
g	Gram(s)
h	Hour(s)
min	Minute(s)
mL	Millilitre(s)
°C	Degree Celsius
mmol	Millimole

atm	Atmosphere Pressure
eq.	Equivalent
R.t.p.	Room temperature

List of Synthesized Compounds

Formula	Numbering	Page	Structure
$C_{50}H_{40}B_2P_4S_4$	1.26	23
$C_{37}H_{39}NP_2S$	1.27	36
$C_{74}H_{74}B_2N_2P_4S_2$	1.29	25
$C_{74}H_{74}B_2N_2P_4S_2$	1.30	29
$C_{50}H_{52}B_4P_4$	1.32	32
$C_{27}H_{40}B_2Br_3N_2P$	2.35	76
$C_{34}H_{52}B_2BrN_4P$	2.36	76
$C_{34}H_{56}B_2BrN_4P$	2.37	80

Formula	Numbering	Page	Structure
$C_{35}H_{52}B_2BrN_4O_2P$	2.38	82	
$C_{53}H_{52}B_3BrF_{15}N_4O_2P$	2.39	82	
$C_{39}H_{57}B_2BrN_5P$	3.33	133	
$C_{39}H_{57}B_2BrN_5PS$	3.34	133	
$C_{39}H_{57}B_2BrN_5PSe$	3.35	133	
$C_{78}H_{114}B_4N_{10}P_2$	3.36	133	
$C_{39}H_{58}B_2N_5P$	3.37	133	
$C_{34}H_{58}B_2Br_4N_6Si_2$	4.34	176	

Formula	Numbering	Page	Structure
$C_{34}H_{58}B_2Br_2N_6Si_2$	4.35	176	
$C_{31}H_{32}B_2Br_3N_2P$	4.37	187	
$C_{48}H_{61}B_2BrN_5SiP$	4.38	187	

Abstract

This thesis describes the development of low-valent diboron species, such as diborane, diborene, diborene cation and borylborylene and the investigation of their small molecules activation and catalysis applications.

In **Chapter 1**, diboron-carbene complexes $[(\text{SPh}_2\text{P})_2\text{CB}]_2$ (**1.26**) derived from geminal dianions were synthesized from the reaction between bis(thiophosphinoyl) geminal dianion $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ with $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$. Unsymmetric geminal dianion $[\text{C}(\text{PPh}_2\text{NAr})(\text{PPh}_2\text{S})]^{2-}$ ($\text{Ar} = 2,6\text{-iPr}_2\text{C}_6\text{H}_3$) underwent a reaction with $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$, forming the diboron-carbene complex **1.29**, where one boron center bonds with two methanediides, leading to an allyl anionic-like $\text{C}=\text{B} \leftarrow \text{C}^{2-}$ electronic structure, while another boron center is stabilized by two imino substituents. This showed the lability of the boron-carbene bond. Diboron-carbene complex $[(\text{SPh}_2\text{P})(\text{ArNPh}_2\text{P})\text{CB}]_2$ (**1.30**) was obtained when complex **1.29** underwent isomerization via a 1,2-methanediide shift.

In **Chapter 2**, a stable *N*-phosphinoamidinato NHC-diborene **2.36** was synthesized and its catalytic capability toward hydroboration was investigated. The stable *N*-phosphinoamidinato NHC-diborene **2.36** was synthesized in a four-step reaction as shown in the figure below. Briefly, the *N*-phosphinoamidine ligand first

underwent lithiation, followed by a treatment with tetrabromodiborane-dimethylsulfide complex to generate complex **2.35**. It was then reacted with the N-heterocyclic carbene ^{Me}NHC and excess KC₈ to give complex **2.36**. Stoichiometrically activation is achievable in NH₃-BH₃ and CO₂ using complex **2.36**. Catalytic performance was shown using 2 mol % portion of **2.36** for hydroboration of carbon dioxide with HBpin to give methoxyborane [pinBOMe] as well as bis(boryl) oxide [(pinB)₂O]. Furthermore, N-formamides was obtained by using 5 mol % of **2.36** to catalyse the N-formylation of amines by CO₂ and pinacolborane. Chemoselective catalytic hydroboration of carbonyl compounds was also achieved.

Chapter 3 presents a pyridine-NHC-stabilized *N*-phosphinoamidinato diborene cation for activation of pyridine and episulfidation. Base-stabilized *N*-phosphinoamidinato diborene cation **3.33** having a ⁺B=B bond skeleton was obtained by the reaction of the *N*-phosphinoamidinato NHC-diborene **2.36** with excess pyridine. It underwent oxidation with elemental sulphur to form the diborathiirane cation **3.34**, as well as reduction with KC₈ to form the diaminodiborene **3.36**. In addition, compound **3.33** possesses catalytic capability. 20 mol% of **3.33** catalyzed the hydroboration of pyridine with pinacolborane and NaBPh₄ gave *N*-boryl-1,4-dihydropyridine. The

mechanistic studies show that the H-B bond of HBpin attacks the pyridine moiety in compound **3.33** to form the diaminodiborene **3.37**, which then reacts with Bpin⁺ to form N-boryl-1,4-dihydropyridine.

Lastly, **Chapter 4** documents an amidinato amidosilylene-diborene and borylborylene compounds for catalytic hydroboration of carbon dioxide. Bis(silylene)-dibromodiborene [L{Me₂N}Si]₂B₂Br₂ (**4.35**) was formed in a two steps reaction. The amidinato amidosilylene [LSiNMe₂] (**4.33**, L = PhC(N*t*Bu)₂) was first reacted with B₂Br₄(SMe₂)₂ to form bis(silylene)-tetrabromodiborane [L{Me₂N}Si]₂B₂Br₄ (**4.34**), followed by reacting with excess KC₈ to afford **4.35**. Furthermore, silylene-borylborylene **4.38** was obtained by the reaction of compound **4.33** with the *N*-phosphinoamidinate-bridged diborane **4.37** and KC₈. The lone pair electrons at the borylene center is stabilized by the phosphine and silylene donors and the boryl

substituent. It was capable of catalyzing hydroboration of CO₂ to form a methoxyborane [pinBOMe] (**4.39a**, yield: 93.7 %, TOF: 24.8 h⁻¹) and diborate ether [(pinB)₂O] (**4.39b**) in a 1:1 ratio.

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CHAPTER 1: A Zwitterionic Diboron-Carbene Complex by 1,2-

Methanediide Shift

1.1. Introduction

Stable N-heterocyclic carbenes (NHCs) were synthesized by Arduengo in 1991.^[1] They comprise a lone pair of electrons on the divalent carbon atoms. The vacant p orbital on the divalent carbon atom is stabilized by the lone pair electrons on the N substituents. They are nucleophilic and extremely powerful compounds in many aspects of chemistry, such as organometallic,^[2] material science,^[3] organic catalysis^[4] and main-group chemistry.^[5]

In diboron chemistry, NHCs were used to coordinate with the vacant p orbital on the boron atoms and alter the electronic property of the latter. The resulting complexes exhibit interesting photophysical property as well as reactivity in small molecules activation.^[6] In addition, they play important roles in borylation transformations,^[7] and their isolation provides a better understanding of related reaction mechanisms.

As an illustration, Marder and co-workers isolated a carbene-diboron complex **1.1** through the reaction of B₂pin₂ with one equivalent of ^{Cy}NHC (1,3-bis(cyclohexyl)imidazol-2-ylidene), which was viewed as an intermediate in the borylation of α,β -unsaturated substrates.^[8-9,11] However, the interaction between ^{Cy}NHC and B₂pin₂ was weak, resulting in a dynamic equilibrium in solution. To further investigate carbene-diboron complexes, the same research

team reported the synthesis of mono- and bis-carbene-diboron adducts (**1.2** and **1.3**) through the reaction of B₂Cat₂ with one or two equivalents of ^{Me}NHC (1,3,4,5-tetramethyl-imidazolin-2-ylidene).^[10] Unlike compound **1.1**, compound **1.2** and **1.3** were stable at r.t.p. in solution and no ^{Me}NHC dissociation was observed. Interestingly, compound **1.3** underwent rearrangement at 70 °C and formed a six-membered heterocycle product **1.4**, where the reaction involved the breaking of B-B bond and the insertion of a single BCat unit into one C-N bond of ^{Me}NHC.

Scheme 1.1. Syntheses of NHCs coordinated B₂pin₂ and B₂cat₂ adducts.

Braunschweig and co-workers isolated other class of NHC-diboron complexes containing a B-B double bond, that is, NHC-diborene.^[12] The salt metathesis reaction of lithiated 2-trimethylsilylthiophene **1.5** with diarylfluoroboranes in THF gave compound **1.6**. Compound **1.6** was reacted with boron tribromide in DCM to afford the borylated thiophene **1.7** the concomitant formation of side product trimethylbromosilane. The reductive coupling of carbene-borane complexes **1.8**, obtained from the reaction of **1.7** with one equivalent of ^{iPr}NHC, with excess potassium graphite (KC₈) generated

compound **1.9**. The combination of π -donating diborene cores and π -accepting diarylborane cores through a π conjugated thienyl group resulted in a highly conjugated quadrupolar chromophore with significantly small HOMO–LUMO gaps. This results in enhancing absorption and emission in the near-infrared region. The use of NHC stabilized diborenes as a superdonor provided a new method for the design and development of novel chromophores.

Scheme 1.2. Syntheses of quadrupolar chromophores based on NHC-diborenes.

Moreover, Braunschweig and co-workers reported the synthesis of ^{Dipp}NHC-diboron complex **1.11** containing a B-B triple bond.^[13] The reaction of two equivalents of ^{Dipp}NHC (^{Dipp}NHC = :{CN(Ar)CH}₂, Dipp = 2,6-*i*Pr₂C₆H₃) with tetrabromodiborane in pentane generated the bis(^{Dipp}NHC)-stabilized diborane complex **1.10**. Its subsequent reduction with four equivalents of sodium naphthalene (NaC₁₀H₈) in THF afforded the first bis(^{Dipp}NHC)-diboryne compound **1.11**. In comparison with NHCs, cyclic(alkyl)(amino) carbene (cAACs) are stronger σ donors and π acceptors with smaller HOMO and LUMO gap. This is owing to the replacement of one of the σ -withdrawing and π -donating amino groups adjacent to the carbene carbon of NHCs by a σ -

donating alkyl group. When DippNHC was replaced by cyclic (alkyl)(amino) carbene ($\text{Me}_c\text{AAC} = \text{:CN}(\text{Ar})\text{C}(\text{Me})_2\text{CH}_2\text{C}(\text{Me})_2$), the Me_cAAC -diboryne complex $[(\text{Me}_c\text{AAC})\text{B}]_2$ **1.13** was afforded by using the same synthetic strategy.^[14] Compound **1.13** possesses a cumulene skeleton, instead of a triply bonded structure. The different bonding nature between these two carbene-diboron complexes is mainly due to the stronger π -accepting capacity of Me_cAAC than that of DippNHC , leading to the delocalization of π electrons of B-B unit in **1.13** into the vacant p orbital of the carbene carbon.

Scheme 1.3. Syntheses of NHCs-supported diboryne and diboracumulene.

The different bonding nature and electronic properties between NHC-diboryne and Me_cAAC -diboracumulene were also elucidated by their reactivity in small molecules activation. For example, Me_cAAC -diboracumulene complex **1.13** can readily activate dihydrogen gas (H_2) at r.t.p. to form Me_cAAC -stabilized 1,2-dihydrodiborene **1.14** through the hydrogenation of B-B multiple bonds, whereas such reaction was not successful using DippNHC -diboryne **1.11** to get

the ^{Dipp}NHC analogue of **1.15** in a similar manner.^[15] This indicated that the feasibility of hydrogenation of B-B multiple bond relies on the electronic and steric properties of the carbene ligands. As compared to NHCs, the unique electronic properties of cAACs allowed them to stabilize a variety of reactive radical species.^[16] The reaction of **1.11** with disulfide or diselenide reagents led to the formation of a series of planar bis(^{Dipp}NHC)-diborenes (**16a-c**) through the S-S bond or Se-Se bond addition to the B-B multiple bond.^[17] In contrast, such reaction using **1.13** generated 90°-twisted diradical congeners (**17a-c**) without B-B multiple bonding feature, where the unpaired electrons at two boron centers are stabilized by the adjacent ^{Me}cAAC units.^[17] In addition, the reaction of **1.11** with excess carbon monoxide (CO) in benzene under mild reaction condition cleaved the B-B multiple bond and gave the resulting CO reductive coupling product **1.19**, where a planar bicyclic bis(boralactone) unit with a B=C-C=B skeleton was formed by the reduction coupling of four CO molecules with B₂ core and two ^{Dipp}NHCs still coordinated to the boron centres. Moreover, a CO-diboryne adduct **1.19** was isolated from this reaction under low temperature, which was considered as an intermediate of the CO reductive coupling reaction.^[18] In contrast, the same reaction using ^{Me}cAAC-diboracumulene **1.13** to react with excess CO afforded the bis(boraketene) **1.20**, in which two CO molecules was coordinated to the two boron centres.^[19]

Scheme 1.4. The reactivity of NHCs supported diboryne and diboracumulene.

Braunschweig and co-workers showed that an intermediate electronic structure between diboryne **1.11** and diboracumulene **1.13** was found in the ^{SDip}NHC-diboryne complex [(^{SDip}NHC)B]₂ **1.21** (^{SDip}NHC = imidazolidin-2-ylidene, :C{N(Ar)C(H)₂}₂).^[19] It was synthesized using similar method but employing a different carbene ligand ^{SDip}NHC, whose π-acidity is stronger than that of ^{Dip}NHC but weaker than that of ^{Me}cAAC. The intermediate electronic structure and properties of **1.21** in comparison to that of **1.11** and **1.13** were not only confirmed by spectroscopy data but also demonstrated by their reactivity. Similar to compound **1.13**, compound **1.21** could also activate dihydrogen gas (H₂) to form the hydrogenation product **1.22**.^[15] In addition, its reactivity towards CO displayed the differences among **1.11**, **1.13** and **1.21**. The reaction of **1.21** with 1 atm of CO at -30 °C allowed the isolation of the analogue of **1.20**, that is the bis(boraketene) compound **1.23**. It could then further react with additional

1 atm of CO to give bicyclic bis(boralactone) compound **1.24**, which is similar to **1.11**.^[19] The results have proven that the choice of different carbene ligands can significantly modulate the electronic structure, properties and reactivity of carbene-diboron complexes.

Scheme 1.5. Synthesis of **1.21** and its reactivity towards H₂ and CO.

The abovementioned results show that carbenes range from electrophilic to nucleophilic, directing diboron moieties to display different patterns of reactivity and catalysis. However, apart from NHC, other class of carbene-diboron complexes are still elusive possibly due to formidable synthetic challenge. It is imperative to find out more synthetic strategy to isolate carbene-diboron complexes not only for the fundamental bonding studies, but also for its possible application for small molecules activation, showing umpolung reactivity in comparison with that of NHC-diboron complexes. To tackle the challenge, we were interested in using geminal dianion^[20] to donate σ and π electrons into diboron orbitals of suitable symmetry and energy, leading to the formation of diboron complexes containing nucleophilic carbene.

In this chapter, carbene-diboron compounds derived from geminal dianions were synthesized, where the boron-carbene interaction is labile leading to a zwitterionic diboron carbene complex via 1,2-methanediide shift. The lability of

boron-carbene bond is important as it offers an opportunity to construct new diboron compound through rearrangement.

1.2. Results and Discussion

Geminal dianion compounds are highly reactive species that contain two lone pairs of electrons at a single carbon atom, which have attracted great research attention in the past 20 years owing to their unique electronic structure and properties. They have been shown to donate σ - and π - electrons into transition-metal, lanthanide, and actinide orbitals of suitable symmetry and energy, leading to the formation of metal-carbene complexes with nucleophilic character at the carbene center.^[20] This synthetic methodology can be applied to diboron chemistry.

To begin with, the bis(thiophosphinoyl) geminal dianion $[\text{C}(\text{PPh}_2\text{S})_2]^{2-}$ (**1.25**)^[21] was reacted with $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$ ^[22] in toluene at $-78\text{ }^\circ\text{C}$ (**Scheme 1.6**). The reaction mixture was warmed to r.t.p. for 10 minutes, which afforded the base-stabilized diboron carbene complex $[(\text{SPh}_2\text{P})_2\text{CB}]_2$ (**1.26**) as a yellow crystalline solid. No other byproducts were observed. Complex **1.26** is the first diboron-carbene complex comprising a base-stabilized $>\text{C}=\text{B}-\text{B}=\text{C}<$ skeleton with nucleophilic character at the carbene centers. The ^1H NMR spectroscopy shows one set of signals attributable to the ligand backbone. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy shows a signal at $\delta = 21.1$ ppm for the carbene center, which is shifted upfield in comparison with NHC, indicating its nucleophilic character. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy shows two doublets at $\delta = 37.9$ and 91.7 ppm, indicating that two thiophosphinoyl substituents are inequivalent in solution. The

$^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy shows one signal at $\delta = -4.3$ ppm, which is shifted upfield in comparison with that of the NHC-diboryne complexes **1.11**, **1.13** and **1.21** ($\delta = 39 - 80$ ppm).^[13-14] However, it is comparable with those of the NHC-bis(boraketene) $[(^{\text{SDip}}\text{NHC})(\text{OC})\text{B}]_2$ **1.23** ($\delta = -29$ ppm)^[18] and NHC-bis(boraketenimine) complex $[(^{\text{Me}}\text{cAAC})(t\text{BuNC})\text{B}]_2$ ($\delta = -8.9$ ppm),^[23] where the NHC-diboryne moiety is bonded with two additional donors, namely, carbon monoxide and tert-butylnocyanide.

Scheme 1.6. Synthesis of **1.26**.

The X-ray crystal structure of **1.26** shows that each boron center is bonded with the carbene and thiophosphinoyl substituent to form two coplanar five-membered rings (**Figure 1.1a**). The carbene center adopts a trigonal planar geometry (sum of the bond angles: 359.4°). The C-B bond lengths are $1.475(5)$ Å, which are intermediate between the C_{NHC} -boron bond lengths in the NHC-diboryne complexes, $[(^{\text{Me}}\text{cAAC})\text{B}]_2$ **1.13** ($1.459(2)$ Å) and $[(^{\text{Dip}}\text{NHC})\text{B}]_2$ **1.11** ($1.487(3)$ Å).^[13-14] The C-B bond lengths are also comparable with the OC-B bond length in the NHC-bis(boraketene) $[(^{\text{Me}}\text{cAAC})(\text{OC})\text{B}]_2$ **1.20** ($1.477(2)$ Å).^[19] These suggest that the C-B bond in **1.26** has some double bond character. The B-B bond length ($1.673(7)$ Å) is intermediate between B-B single bond

length in $[(^{\text{Me}}\text{cAAC})(\text{OC})\text{B}]_2$ **1.20** (1.760(4) Å)^[19] and B-B double bond length in the NHC stabilized dibromodiborene complex (1.562(4) Å).^[13] The short B-B bond supports the butadiene-like skeleton in complex **1.26**. The P-S bond lengths (2.0980(1), 1.959(4) Å) are longer, while the P-C bond lengths (1.748(3), 1.765(3) Å) are shorter in comparison with those of $[\text{CH}_2(\text{PPh}_2\text{S})_2]$ (P-S, average 1.945 Å; C-P, average 1.829 Å), indicating that the ligand backbone has a dipolar resonance structure. A similar observation was found in other metal-carbene complexes derived from geminal dianions.^[20]

Figure 1.1 (a) X-ray crystal structure of **1.26** with thermal ellipsoids at 50 % probability. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1-B1 1.475(5), B1-B1A 1.673(7), C1-P1 1.748(3), C1-P2 1.765(3), P1-S1 2.0980(1), P2-S2 1.959(4), S1-B1A 1.851(4), P1-C1-B1 109.9(2), P2-C1-B1 129.0(2), P1-C1-P2 120.53(18), C1-B1-B1A 118.7(3), B1-B1A-S1 111.2(3). (b) HOMO (-6.72 eV) (B: pink, P: orange, S: dark yellow, C: yellow, H: white). (c) HOMO-5 (-7.42 eV).

The electronic structure of **1.26** was further elucidated by DFT calculations (M06-2X/def2-TZVP). HOMO and HOMO-5 show the π orbital of the C-B double bond (**Figure 1.1b-c**). Accordingly, the Natural Bond Orbital analysis (NBO) of **1.26** (section 1.5.3.4) shows that the C1-B1 bond is composed of σ and π bond. The σ bond is formed by the overlapping of the C $\text{sp}^{1.17}$ and B $\text{sp}^{1.70}$

hybrids. The π bond is formed by the overlapping of p orbitals on the C and B atoms. The electron density of the C1-B1 σ and π bonds are polarized toward the C1 atom (σ bond: 70.1 %, π bond: 80.7 % of electron density), indicating a nucleophilic character at the methanediide atoms. This is consistent with the natural charges for the C and B centers of $-1.34e$ and $+0.25e$, respectively. The Wiberg bond indexes (WBIs) of the P–C (1.010) and P–S (0.982) show that the ligand backbone has a dipolar resonance structure. The B–B σ bond is formed by the overlapping of $sp^{1.60}$ hybrids on the boron atoms.

Scheme 1.7. Synthesis of **1.29**.

When the bis(thiophosphinoyl)methanediide in **1.26** was replaced by sterically hindered (thiophosphinoyl)(iminophosphoranyl)methanediide **1.28**, 1,2-methanediide shift was observed (**Scheme 1.7**). The dianion derivative $[Li_2C(PPh_2NAr)(PPh_2S)]$ (**1.28**, Ar = 2,6-*i*Pr₂C₆H₃), generated from the dilithiation of $H_2C(PPh_2NAr)(PPh_2S)$ **1.27**^[24] with *t*BuLi in diethyl ether, was reacted with $B_2Br_4(SMe_2)_2$ in toluene at $-78^\circ C$. The reaction mixture was warmed to r.t.p. for 15 minutes, which afforded the diboron carbene complex

1.29 as a yellow crystalline solid. In complex **1.29**, one carbene bonds with one boron atom of the diboron moiety similar to complex **1.26**. However, another one does not bond to the remaining boron center, resulting in the formation of zwitterionic carbon (C^{2-}) and boron (B^{2+}) skeleton. The former donates two electrons to the vacant p orbital on the carbene-bonded B atom, while the latter is stabilized by coordinating with two iminophosphoranyl moieties. The resulting $C=B \leftarrow C^{2-}$ skeleton is an analogue of allyl anion, where the C lone pair and $C=B$ π electrons delocalize along the skeleton, leading to canonical forms **A-C** as shown in **Scheme 1.7**. The additional dipolar resonance structure of the ligand backbone results in the canonical form **D**.

Complex **1.29** is the first example to show that a carbene-boron bond is labile, which can dissociate into C^{2-} and B^{2+} . Such lability is not observed in any NHC-diborane, -diborene and -diboryne complexes.^[25] In comparison with other Lewis base-diboron complexes, Braunschweig et al. showed that the phosphine-boron bonds in phosphine-diborene complexes are labile,^[26] where phosphine can undergo dissociation^[27] or 1,2-shift to form a novel borylborylene.^[28]

Complex **1.29** is stable in the solid, but is unstable in toluene and benzene, leading to low isolated yield (see below). The 1H NMR spectroscopy shows one set of signals attributable to the ligand backbone. The $^{13}C\{^1H\}$ NMR spectroscopy shows a signal at $\delta = 28.7$ ppm for the carbene center, which is comparable with that of **1.26**. The $^{31}P\{^1H\}$ NMR spectroscopy shows two signals

at $\delta = 37.2$ and 82.7 ppm. As complex **1.29** is unstable in solution, ^{11}B MAS NMR spectroscopy was performed, which shows two signals: a broad resonance at $\delta = 6.6$ ppm for the carbene-bonded B center and a narrow resonance at $\delta = 43.3$ ppm for the N-bonded B center due to its lower electron shielding.

Figure 1.2 (a) X-ray crystal structure of **1.29** with thermal ellipsoids at 50 % probability. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C25-B1 1.524(2), C62-B1 1.529(2), B1-B2 1.667(3), N1-B2 1.456(2), N2-B2 1.446(2), C25-P1 1.7276(16), P1-N1 1.7167(13), C62-P3 1.7437(16), P3-N2 1.7240(13), C25-B1-C62 143.68(15), C25-B1-B2 107.70(13), C62-B1-B2 108.57(13), N1-B2-N2 134.22(15), N1-B2-B1 113.05(14), N2-B2-B1 112.73(13), B1-C25-P1 106.82(11), C25-P1-N1 104.53(7), P1-N1-B2 106.07(10), C62-P3-N2 103.95(7), P3-N2-B2 106.96(11). **(b)** HOMO (-6.05 eV) (B: pink, P: orange, S: dark yellow, C: yellow, H: white). **(c)** HOMO-6 (-7.68 eV).

The X-ray crystal structure of **1.29** (**Figure 1.2a**) shows that two C atoms (C25, C62) coordinate with one boron center (B1), while the iminophosphoranyl groups coordinate with another one (B2). The thiophosphinoyl substituents are uncoordinated. The C25 and C62 atoms adopt a trigonal planar geometry (the sum of bond angles, C25: 359.7° , C62: 356.0°). The C25-B1 (1.524(2) Å) and C62-B1 bond lengths (1.529(2) Å) are equal. They are intermediate between

the C-B double bond length in **1.26** and the C-B single bond length (1.635(2) Å) in the B₂H₅⁺-methanediide complex [(BH₂)₂(μ-H){C(PPh₂S)₂Li(OEt₂)}].^[29] These indicate that the C23-B1-C62 skeleton possesses an allyl anionic electronic structure. In addition, the P–N bonds (1.7167(13), 1.7240(13) Å) are longer, while the P–C bonds (1.7276(16), 1.7437(16) Å) are shorter, in comparison with those of [H₂C(PPh₂NAr)(PPh₂S)] (P–N 1.537(6); C–P, 1.831(6), 1.844(6) Å), indicating a dipolar resonance of the ligand backbone.

Its electronic structure was further elucidated by DFT calculations (M06-2X/def2-TZVP). HOMO and HOMO-6 show allylic π-type molecular orbitals on the C=B←:C: skeleton (**Figure 1.2b-c**). The allyl anionic skeleton is further demonstrated by the WBI of C-B bonds (1.067 and 1.097). Accordingly, NBO analysis shows that the C25-B1 bond is composed of σ and π bond. The σ bond is formed by the overlapping of the C sp^{1.11} and B sp^{1.89} hybrids. The π bond is formed by the overlapping of p orbitals on the C and B atoms. The electron density of the C25-B1 σ and π bonds are polarized toward the C25 atom (69.4% electron density of σ bond and 85.5% electron density of π bond). The C62-B1 bond is composed of σ orbital due to the overlapping of C sp^{1.27} and B sp^{1.85} hybrids, mainly polarized toward the C62 atom (70.2 %). There is a lone pair orbital (p orbital) on the C62 atom, weakly π-interacting with the P atom. The NPA charge of B2 and B1 atoms are +0.86 and +0.33e, respectively. The WBIs of P–N bonds (0.778, 0.759) show that the ligand backbone has a dipolar resonance structure.

Upon heating complex **1.29** in toluene at 60 °C (**Scheme 1.8**), it intramolecularly underwent 1,2-methanediide shift to form the diboron carbene complex $[(\text{SPh}_2\text{P})(\text{ArNPh}_2\text{P})\text{CB}]_2$ (**1.30**), comprising two boron-carbene bond. The results show that the C-B interaction in complex **1.29** is weak. The ^1H NMR spectroscopy shows one set of signals attributable to the ligand backbone. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectroscopy shows a signal at $\delta = 28.2$ ppm for the carbene center, which is comparable with that of **1.29**. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy shows two signals at $\delta = 33.5$ and 63.9 ppm. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy shows one signal at $\delta = 18.9$ ppm. It is shifted downfield in comparison with that of **1.26**, indicating a weaker carbene-boron interaction.

Scheme 1.8. Synthesis of **1.30**.

Figure 1.3 (a) X-ray crystal structure of **1.30** with thermal ellipsoids at 50 % probability. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): C1-B1 1.549(4), C2-B2 1.534(4), B1-B2 1.712(4), B1-N1 1.501(4), B2-N2 1.513(3), C1-P1 1.714(3), P1-N1 1.683(2), C2-P3 1.724(2), P3-N2 1.672(2), C1-P2 1.738(3), P2-S1 1.9739(10), C2-P4 1.746(3), P4-S2 1.9692(9), P1-C1-P2 131.13(16), P1-C1-B1 86.29(17), P2-C1-B1 140.1(2), C1-B1-B2 132.6(2), C1-B1-N1 98.6(2), B2-B1-N1 128.8(2), B1-B2-N2 127.6(2), B1-C1-P1 86.29(17), C1-P1-N1 85.83(12), B2-C2-P3 86.74(16), C2-P3-N2 85.25(11). (b) HOMO (-6.46 eV) (B: pink, P: orange, S: dark yellow, C: yellow, H: white).

The NMR spectroscopy of **1.30** is consistent with the X-ray crystal structure (**Figure 1.3a**) that the C-B bond lengths (1.534(4), 1.549(4) Å) and B-B bond length (1.712(4) Å) are longer than those in complex **1.26**. It is because of the sterically hindered iminophosphoranyl groups weakening the B-C_{carbene} interaction. To support the hypothesis, more sterically hindered bis(iminophosphoranyl) geminal dianion^[20] [C(PPh₂NAr)₂]²⁻ was used instead of (thiophosphinoyl)(iminophosphoranyl) geminal dianion to prepare diboron-carbene complex, but no reaction between [C(PPh₂NAr)₂]²⁻ and B₂Br₄(SMe₂)₂ in toluene was found.

Its electronic structure was further elucidated by DFT calculations (M06-2X/def2-TZVP). The HOMO shows the C-B π orbital (**Figure 1.3b**). Accordingly, the NBO (section **1.5.3.10**) shows that the C1-B1 bond is composed of σ and π bond. The σ bond is formed by the overlapping of the C $sp^{1.55}$ and B $sp^{2.14}$ hybrids. The π bond is formed by the overlapping of p orbitals on the C and B atoms. The electron density of the C1-B1 σ and π bonds are polarized toward the C1 atom (71.1 % electron density of σ bond and 88.0 % electron density of π bond), indicating nucleophilic character at the carbene center. The π bond is more polarized than that of complex **1.26**. In this context, the higher polarization of C-B π bond and longer C-B bond length indicate that complex **1.30** possesses canonical forms **D – F** (**Scheme 1.8**).

BH₃ activation mediated via a diboron carbene complex was performed. Bis(phosphinoborane)methane [CH₂(PPh₂BH₃)₂]^[30] was reacted with two equivalents of *t*BuLi in toluene to form the geminal dianion [C(PPh₂BH₃)₂]²⁻ (**1.31**, **Scheme 1.9**). It was reacted with B₂Br₄(SMe₂)₂ in toluene at -78°C. The reaction mixture was warmed to r.t.p. and stirred for 30 minutes. It was filtered and the filtrate was concentrated to afford the B-H bond activation product [(H)(BH₂){C(PPh₂)(PPh₂BH₃)}]₂ (**1.32**) as a colorless crystalline solid. It is proposed that the reaction proceeds through the formation of a diboron carbene intermediate **A** (**Scheme 1.10**), where the carbene-boron double bonds attack the BH₃ moieties to form a zwitterionic intermediate **B**. Then, the B-H bonds attack the C_{methanediide} atom with the elimination of diboron to form a B-H bond

activated intermediate **C**. It subsequently undergoes dimerization to form compound **1.32**. The results evidence the C $\rightarrow$ B bond interaction in compounds **1.26** and **1.30**.

Scheme 1.9. Synthesis of **1.32**.

Compound **1.32** was analyzed by NMR spectroscopy. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy shows two signals at $\delta = 15.4$ and 25.4 ppm attributable to the inequivalent P nuclei. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy shows two signals at $\delta = -39.8$ and -32.01 ppm due to the four coordinate BH_3 and BH_2 moieties. X-ray crystallography shows that compound **1.32** is composed of a P and B-containing cyclohexyl ring (**Figure 1.4**). The C2 atom is bonded to H atom and BH_2 group, which suggests that BH_3 is transferred from one of the PPh_2 groups and then undergoes 1,1-addition on the carbene center. The endocyclic P-B bond length ($1.946(2)$ Å) is comparable with the exocyclic one ($1.923(3)$ Å), indicating that both are coordinative covalent bond.

Scheme 1.10. Proposed mechanism for the formation of **1.32**.

Figure 1.4. X-ray crystal structure of **1.32** with thermal ellipsoids at 50 % probability. H atoms of phenyl groups are omitted for clarity. Selected bond lengths (Å) and angles (deg): C2-B1 1.663(3), P2-B1 1.946(2), C2-P1 1.8350(18), P1-B2 1.923(2), P1-C2-P2A 123.08(11), P1-C2-B1 112.15(12), P2A-C2-B1 108.00(12).

1.3 Conclusion

In conclusion, the diboron carbene complex **1.26** derived from geminal dianion was isolated where σ and π electrons are donated from the carbene to the boron center. The lability of boron-carbene bond was found in the isolation of the zwitterionic diboron carbene complex **1.29**, where one boron center is bonded with two methanediides and another one is stabilized by the ligand backbone. Complex **1.29** underwent 1,2-methanediide shift to give the diboron carbene complex **1.30**. The lability of boron-carbene bond offers an opportunity to construct new diboron compound via zwitterionic carbon (C^{2-}) and boron (B^{2+}) centers.

1.4. Experimental

1.4.1. General procedure.

All operations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Chemicals were purchased from Sigma-Aldrich and used directly without further purification. All solvents were dried over K metal or CaH₂ prior to use. The ¹H, ¹¹B{¹H}, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a JEOL ECA 400 spectrometer. The solution NMR spectra were recorded in deuterated solvents and the chemical shifts are relative to SiMe₄ for ¹H and ¹³C; BF₃·Et₂O for ¹¹B; 85% H₃PO₄ for ³¹P, respectively. Solid state ¹¹B MAS NMR was recorded on a 14.1 T Bruker Advance III HD 600 MHz spectrometer with a Bruker 4mm HX MAS probe operating at an MAS frequency of 14 KHz. Due to the large ¹¹B background present in Bruker MAS NMR probes, a difference spectrum from a control acquisition is presented. The resulting spectrum was referenced to the unified scale using IUPAC recommended frequency ratios and processed using the Topspin software package.^[31] HRMS spectra were obtained at the Mass Spectrometry Laboratory in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System.

1.4.2. X-ray data collection.

The X-ray diffraction intensity data for compound **1.26**, **1.29**, **1.30** and **1.32** were measured at 100 K with a Bruker APEX II diffractometer equipped with a CCD detector, employing Mo K α radiation (λ = 0.71073 Å), with the SMART suite of programs.^[32] All data were processed and corrected for Lorentz and polarization effects with SAINT and for absorption effects with SADABS. Structural solution and refinement were carried out with the SHELXTL suite of programs.^[33] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light, non-hydrogen atoms. All non-hydrogen atoms were refined with anisotropic thermal parameters. A summary of selected crystallographic data is provided in section **1.5.1**.

1.4.3. The syntheses and characterization of procedures.

Synthesis of compound 1.26: The bis(thiophosphinoyl) geminal dianion [Li₂C(PPh₂S)₂] (**1.25**) (0.920 g, 2 mmol) was reacted with B₂Br₄(SMe₂)₂ (0.466 g, 1 mmol) in toluene at -78 °C. The reaction mixture was warmed to r.t.p. and

stirred for ten minutes. The resulting orange suspension was filtered and the filtrate was dried under vacuum to remove all volatiles to afford compound **1.26** as an orange solid in 54 % yield (0.48 g, 0.54 mmol). Yellow crystals were afforded by recrystallization from the saturated fluorobenzene solution of **1.26** at r.t.p. M.p.: 166 °C. ^1H NMR (399.5 MHz, C_6D_6 , 25 °C): δ 7.98-7.95 (m, 16 H ArH), 7.02-6.96 (m, 24 H ArH). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6 , 25 °C): δ -4.3 (s). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C): δ 91.7 (d, J_{PP} = 56.9 Hz), 37.9 (d, J_{PP} = 56.9 Hz). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 25 °C): 138.9 (C-Ar), 138.0 (C-Ar), 137.5 (C-Ar), 131.5 (C-Ar), 129.7 (C-Ar), 129.0 (C-Ar), 128.2 (C-Ar), 125.3 (C-Ar), 21.1 (PCP). HRMS (ESI): m/z calcd for $\text{C}_{50}\text{H}_{41}\text{B}_2\text{P}_4\text{S}_4$: 915.1228 $[(M + H)]^+$; found: 915.1210.

Synthesis of $\text{H}_2\text{C}(\text{PPh}_2\text{NAr})(\text{PPh}_2\text{S})$ **1.27:** The 2,6-diisopropylphenyl azide (10 mmol, 2.03 g) was added into the toluene solution of bis(diphenylphosphino)methane (10 mmol, 3.84 g) at r.t.p. and stirred for 12 hours, after which the sulfur powder (10 mmol, 0.32 g) was added into this brown solution and stirred for another 5 hours. The resulting yellow solution was filtered and the filtrate was concentrated to 5 mL to obtain **1.27** as colorless crystal in 81% (4.7 g, 8.07 mmol) yield. M.p.: 206 °C. ^1H NMR (399.5 MHz, C_6D_6 , 25 °C): 7.90-7.86 (m, 4 H, ArH), 7.74-7.70 (m, 4 H, ArH), 7.20 (d, 2 H, ArH, J_{HH} = 7.8 Hz), 7.06-7.02 (m, 1 H, ArH), 6.94-6.85 (m, 12 H, ArH), 3.96 (t, 2 H, PCH_2P , J_{PH} = 14.2 Hz), 3.61 (sept, 2 H, CHMe_2 , J_{HH} = 6.8 Hz), 1.16 (d, 12 H, CHMe_2 , J_{HH} = 6.8 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C): δ 33.0 (d, J_{PP} = 13.0), -14.2 (d, J_{PP} = 13.0). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8 , 25 °C): 143.4 (C-Ar), 141.6 (C-Ar), 134.8 (C-Ar), 134.0 (C-Ar), 133.4 (C-Ar), 132.3 (C-Ar), 132.2 (C-Ar), 131.0 (C-Ar), 130.8 (C-Ar), 130.7 (C-Ar), 128.1 (d, C-Ar, J = 12.5 Hz), 127.4 (d, C-Ar, J = 12.5 Hz), 122.1 (C-Ar), 118.6 (C-Ar), 34.6 (q, PCP, J = 40.5 Hz), 28.5 ($\text{CH}(\text{CH}_3)_2$), 23.2 ($\text{CH}(\text{CH}_3)_2$). HRMS (ESI): m/z calcd for $\text{C}_{37}\text{H}_{40}\text{NP}_2\text{S}$: 592.2357 $[(M + H)]^+$; found: 592.2366.

Synthesis of compound **1.28:** A solution of *t*-butyllithium (1.3 M, 3.3 mL, 4.3 mmol) in pentane was added into a Et_2O (40 mL) solution of $[\text{H}_2\text{C}(\text{PPh}_2\text{NAr})(\text{PPh}_2\text{S})]$ **1.27** (Ar = 2,6-*i*Pr $_2$ C $_6$ H $_3$, 1.18 g, 2 mmol) at -78 °C. The reaction mixture was warmed to r.t.p. and stirred for three hours. The resulting light yellow solution was dried under reduced pressure to remove all volatiles to afford compound **1.28** as a light yellow solid, which is very sensitive to air and moisture. M.p.: 104 °C. ^1H NMR (399.5 MHz, C_6D_6 , 25 °C): 8.18-8.14 (m, 4 H, ArH), 7.61-7.56 (m, 4 H, ArH), 7.11-7.07 (m, 3 H, ArH), 7.00-6.93 (m, 12 H, ArH), 3.74 (sept, 2 H, CHMe_2 , J_{HH} = 6.8 Hz), 3.20 (q, 6 H, CH_3CH_2 , J_{PH} = 6.8 Hz), 1.02 (t, 9 H, CH_3CH_2 , J_{PH} = 6.8 Hz), 0.90 (d, 12 H, CHMe_2 , J_{HH} = 6.8 Hz). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C): δ 34.8 (d, J_{PP} = 13.0), 15.1 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 25 °C): 145.1 (C-Ar), 144.8 (C-Ar), 141.5 (C-Ar),

140.7 (C-Ar), 139.0 (C-Ar), 138.1 (C-Ar), 132.2 (d, C-Ar, $J = 8.6$ Hz), 131.1 (d, C-Ar, $J = 10.6$ Hz), 129.5 (C-Ar), 127.3 (C-Ar), 123.4 (C-Ar), 121.2 (C-Ar), 65.5 (CH₃CH₂O), 27.9 (CH(CH₃)₂), 24.3 (CH(CH₃)₂), 14.6 (CH₃CH₂O). HRMS (ESI): m/z calcd for C₃₇H₃₈Li₂NP₂S: 604.2520 [($M + H$)]⁺; found: 604.2526.

Synthesis of compound 1.29: A solution of B₂Br₄(SMe₂)₂ (0.466 g, 1 mmol) in toluene (10 mL) was slowly added to the flask containing compound **1.28** at -78 °C. The reaction mixture was warmed to r.t.p. and stirred for 15 minutes. The resulting orange suspension was filtered and the filtrate was concentrated to 25 mL to afford compound **1.29**

as yellow crystals in 32 % yield (0.38 g, 0.316 mmol) at r.t.p. after two days. M.p.: 158 °C. ¹H NMR (399.5 MHz, THF-d₈, 25 °C): δ 8.20 (m, 1 H, ArH), 7.87 (m, 5 H, ArH), 7.59-7.36 (m, 10 H, ArH), 7.29 (m, 2 H, ArH), 7.08-7.03 (m, 4 H, ArH), 6.95-6.88 (m, 12 H, ArH), 6.78 (m, 3 H, ArH), 6.70 (m, 5 H, ArH), 6.38 (br, 2 H, ArH), 5.98 (br, 2 H, ArH), 3.14 (sept, 2 H, CHMe₂, $J_{HH} = 6.8$ Hz), 2.54 (sept, 2 H, CHMe₂, $J_{HH} = 6.8$ Hz), 1.24 (d, 6 H, CHMe₂, $J_{HH} = 6.4$ Hz), 0.07 (d, 6 H, CHMe₂, $J_{HH} = 6.8$ Hz), -0.18 (d, 6 H, CHMe₂, $J_{HH} = 6.4$ Hz), -0.43 (d, 6 H, CHMe₂, $J_{HH} = 6.4$ Hz). ¹¹B MAS NMR (192.55 MHz, 25 °C): δ 43.3, 6.6. ³¹P{¹H} NMR (162 MHz, THF-d₈, 25 °C): δ 82.7 (br), 37.2 (d, $J_{PP} = 13.0$). ¹³C{¹H} NMR (101 MHz, THF-d₈, 25 °C): 148.3 (C-Ar), 148.0 (C-Ar), 147.9 (C-Ar), 139.3 (C-Ar), 138.4 (C-Ar), 135.4 (C-Ar), 135.1 (C-Ar), 134.7 (C-Ar), 134.6 (C-Ar), 133.8 (C-Ar), 133.1 (C-Ar), 132.9 (C-Ar), 132.6 (C-Ar), 132.5 (C-Ar), 131.8 (C-Ar), 131.2 (C-Ar), 131.1 (C-Ar), 131.0 (C-Ar), 130.2 (C-Ar), 128.7 (C-Ar), 128.3 (C-Ar), 128.2 (C-Ar), 127.9 (C-Ar), 127.8 (C-Ar), 127.7 (C-Ar), 127.5 (C-Ar), 126.9 (C-Ar), 126.8 (C-Ar), 126.6 (C-Ar), 126.1 (C-Ar), 125.7 (C-Ar), 125.6 (C-Ar), 125.4 (C-Ar), 125.2 (C-Ar), 125.1 (C-Ar), 124.8 (C-Ar), 123.1 (C-Ar), 29.6 (CH(CH₃)₂), 29.2 (CH(CH₃)₂), 28.7 (d, PCP, $J = 33.2$ Hz), 23.3 (CH(CH₃)₂), 21.8 (CH(CH₃)₂), 21.4 (CH(CH₃)₂), 20.5 (CH(CH₃)₂). HRMS (ESI): m/z calcd for C₇₄H₇₅B₂N₂P₄S₂: 1201.4508 [($M + H$)]⁺; found: 1201.4517.

Synthesis of compound 1.30: A toluene solution of **1.29** (0.6 g, 0.5 mmol) was stirred overnight at 60 °C, after which, the resulting yellow solution was filtered and the filtrate was concentrated to 5 mL to afford compound **1.30** as yellow single crystals in 74 % yield (0.44 g, 0.37 mmol) at r.t.p. after one week.

M.p.: 208 °C. ¹H NMR (399.5 MHz, THF-d₈, 25 °C): δ 8.31 (m, 4 H, ArH), 7.52 (m, 6 H, ArH), 7.44 (m, 6 H, ArH), 7.34 (m, 6 H, ArH), 6.95-6.86 (m, 14 H, ArH), 6.80 (m, 2 H, ArH), 6.69 (m, 2 H, ArH), 6.63 (m, 6 H, ArH), 3.74 (sept, 2 H, CHMe₂, $J_{HH} = 6.8$ Hz), 2.86 (sept, 2 H, CHMe₂, $J_{HH} = 6.8$ Hz), 1.75 (d, 6 H, CHMe₂, $J_{HH} = 6.4$ Hz), 0.32 (d, 6 H, CHMe₂, $J_{HH} = 6.8$ Hz), -0.24 (d, 6 H, CHMe₂, $J_{HH} = 6.8$ Hz), -0.30 (d, 6 H, CHMe₂, $J_{HH} = 6.8$ Hz). ¹¹B{¹H} NMR (128 MHz, THF-d₈, 25 °C): δ 18.8 (br). ³¹P{¹H} NMR (162 MHz, THF-d₈, 25 °C): δ 63.9 (br),

33.5 (d, $J_{PP}=13.0$). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, THF- d_8 , 25 °C): 148.6 (C-Ar), 146.8 (C-Ar), 135.2 (C-Ar), 135.1 (C-Ar), 133.6 (C-Ar), 133.5 (C-Ar), 132.7 (C-Ar), 132.6 (C-Ar), 132.1 (C-Ar), 132.0 (C-Ar), 131.9 (C-Ar), 131.8 (C-Ar), 128.7 (C-Ar), 128.2 (C-Ar), 128.1 (C-Ar), 128.0 (C-Ar), 127.7 (C-Ar), 127.6 (C-Ar), 127.4 (C-Ar), 126.8 (C-Ar), 126.7 (C-Ar), 126.6 (C-Ar), 126.5 (C-Ar), 125.6 (C-Ar), 124.2 (C-Ar), 123.4 (C-Ar), 30.3 ($\text{CH}(\text{CH}_3)_2$), 28.2 (d, PCP, $J = 22.2$ Hz), 21.4 ($\text{CH}(\text{CH}_3)_2$). HRMS (ESI): m/z calcd for $\text{C}_{74}\text{H}_{75}\text{B}_2\text{N}_2\text{P}_4\text{S}_2$: 1201.4508 $[(M + H)]^+$; found: 1201.4540.

Synthesis of 1.32: The bis(boranophosphinoyl) geminal dianion $[\text{C}(\text{PPh}_2\text{BH}_3)_2]^{2-}$ (**1.31**) (0.848 g, 2 mmol) was reacted with $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$ (0.466 g, 1 mmol) in toluene at -78 °C. The reaction mixture was warmed up to r.t.p. and stirred for 0.5 h. The resulting yellow suspension was filtered and the filtrate was dried under reduced pressure to remove all volatiles, following which, the product was washed with pentane, obtained compound **1.32** as the white solid in 83 % yield (0.68 g, 0.83 mmol) Colourless

single crystals were obtained by recrystallization from a saturated dichloromethane solution at r.t.p.. M.p.: 135 °C. ^1H NMR (399.5 MHz, CDCl_3 , 25 °C): δ 7.65-7.61 (m, 10 H, ArH), 7.45-7.41 (m, 8 H, ArH), 7.36-7.32 (m, 12 H, ArH), 7.20-7.12 (m, 6 H, ArH), 7.03 (t, 2 H, ArH), 6.93 (t, 2 H, ArH), 3.25 (t, 2 H, PCHBH_2 , $J_{\text{PH}}=10.8$ Hz), 1.53-0.24 (br, 10 H, PBH_3 and PBH_2). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, CDCl_3 , 25 °C): δ -32.01(s), -39.80(s). $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3 , 25 °C): δ 25.41 (br), 15.38 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CDCl_3 , 25 °C): 132.14 (C-Ar), 132.04 (C-Ar), 130.97 (C-Ar), 128.21 (C-Ar), 128.11 (C-Ar), 127.84 (C-Ar), 29.39 (d, PCP, $J = 37.7$ Hz). HRMS (ESI): m/z calcd for $\text{C}_{50}\text{H}_{52}\text{B}_4\text{P}_4\text{Na}$: 843.3289 $[(M + \text{Na})]^+$; found: 843.3321.

1.5. Appendices

1.5.1. X-Ray crystallographic data for compounds 1.26, 1.29, 1.30 and 1.32.

	1.26 ·(Fluorobenzene) ₂	1.29 ·(Toluene) ₂	1.30 ·(Toluene) _{1.5}	1.32
Formula	C ₆₂ H ₅₀ B ₂ F ₂ P ₄ S ₄	C ₉₅ H ₉₉ B ₂ N ₂ P ₄ S ₂	C _{84.50} H ₈₆ B ₂ N ₂ P ₄ S ₂	C ₅₀ H ₅₂ P ₄ B ₄
Fw	1106.76	1478.38	1339.17	820.69
<i>T</i> /K	100(2)	100(2)	100(2)	100(2)
cryst system	triclinic	monoclinic	triclinic	triclinic
space group	<i>P</i> -1	<i>P</i> 1 21/ <i>c</i> 1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	9.0566(5)	12.7608(3)	17.2565(6)	8.9627(8)
<i>b</i> (Å)	12.6636(8)	21.9403(6)	20.1879(7)	11.9406(10)
<i>c</i> (Å)	13.8660(8)	28.9608(6)	21.0330(7)	16.4349(13)
<i>α</i> (deg)	63.8065(19)	90	84.2902(11)	78.653(2)
<i>β</i> (deg)	87.0006	97.9810(10)	85.1174(12)	74.639(2)
<i>γ</i> (deg)	74.813(2)	90	85.0595(11)	72.022(2)
<i>V</i> (Å ³)	1373.45(14)	8029.8(3)	7242.2(4)	1600.5(2)
<i>Z</i>	1	4	4	2
<i>d</i> _{calcd} (g cm ⁻³)	1.338	1.223	1.228	1.228
<i>μ</i> (mm ⁻¹)	0.337	0.195	0.209	0.228
<i>F</i> (000)	574	3140	2836	628
cryst size (mm)	0.100 x 0.120 x 0.260	0.080 x 0.120 x 0.200	0.120 x 0.200 x 0.220	0.010 x 0.018 x 0.080
2θ range (deg)	4.672 < 2θ < 52.06	4.992 < 2θ < 59.08	4.622 < 2θ < 58.89	4.704 < 2θ < 49.85
index range	-13 ≤ <i>h</i> ≤ 13, -18 ≤ <i>k</i> ≤ 18, -20 ≤ <i>l</i> ≤ 20	-17 ≤ <i>h</i> ≤ 16, -24 ≤ <i>k</i> ≤ 30, -38 ≤ <i>l</i> ≤ 40	-23 ≤ <i>h</i> ≤ 23, -27 ≤ <i>k</i> ≤ 27, -28 ≤ <i>l</i> ≤ 28	-10 ≤ <i>h</i> ≤ 10, - 14 ≤ <i>k</i> ≤ 14, -19 ≤ <i>l</i> ≤ 18
no. of rflns collected	53887	73804	167754	19935
no. of indep rflns	8809	22466	38220	5649
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0690/0.1185	0.0465/0.1005	0.0588/0.1218	0.0494/0.1018
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1551/0.1551	0.0731/0.1133	0.1130/0.1151	0.0784/0.1162
goodness of fit, <i>F</i> ²	1.013	1.03	1.017	1.022
no. of data/restraints/parameters	8809 / 2005 / 562	22466 / 612 / 1062	38220 / 894 / 1822	5649 / 0 / 374
largest diff peak and hole, eÅ ⁻³	0.444/-0.578	0.649/-0.924	0.607/-0.531	0.650/-0.460

1.5.2. NMR spectra of all new compounds (D-solvent and NMR frequency are shown in section 1.4.3)

1.26: ^1H

1.26: $^{11}\text{B}\{^1\text{H}\}$

1.26: $^{31}\text{P}\{^1\text{H}\}$

1.26: $^{13}\text{C}\{^1\text{H}\}$

1.27: ^1H

1.27: $^{31}\text{P}\{^1\text{H}\}$

1.27: $^{13}\text{C}\{^1\text{H}\}$

1.28: ^1H

1.28: $^{31}\text{P}\{^1\text{H}\}$

1.28: $^{13}\text{C}\{^1\text{H}\}$

1.29: ^1H

1.29: ^{11}B MAS

1.29: $^{31}\text{P}\{^1\text{H}\}$

1.29: $^{13}\text{C}\{^1\text{H}\}$

1.30: ^1H

1.30: $^{11}\text{B}\{^1\text{H}\}$

1.30: $^{31}\text{P}\{^1\text{H}\}$

1.30: $^{13}\text{C}\{^1\text{H}\}$

1.32: ^1H

1.32: $^{11}\text{B}\{^1\text{H}\}$

1.32: $^{31}\text{P}\{^1\text{H}\}$

1.32: $^{13}\text{C}\{^1\text{H}\}$

1.5.3. Theoretical Studies

All geometry optimizations and NBO analysis were computed using the M06-2X functional with def2-SVP basis set as implemented in the Gaussian 09 package of programs.^[34,35]

List of colour coded atom used in optimised structures

Abbreviation	Definition
Grey	Carbon
Blue	Nitrogen
Yellow	Sulfur
Pink	Boron
Orange	Phosphorus

1.5.3.1. Optimised geometries at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

Compound 1.26	Compound 1.29

Compound 1.30	

1.5.3.2. Optimized geometric parameters and Wiberg Bond Index of compound **1.26** at M06-2X/def2-SVP.

Bond No.	Bond Distance (Å)	Wiberg Bond Index
1(C-B)	1.481	1.224
2(C-P)	1.748	1.010
3(P-S)	2.110	0.982
4(S-B)	1.859	1.080
5(B-B)	1.690	0.967
6(C-B)	1.481	1.223
7(C-P)	1.748	1.010
8(P-S)	2.110	0.982

1.5.3.3. (a) Natural charge population of compound **1.26**. Natural charges on C, B were shown in red. (b) HOMO (-6.72 eV). (c) HOMO-1 (-6.91 eV). (d) HOMO-2 (-7.03 eV). (e) HOMO-3 (-7.03 eV). (f) HOMO-4 (-7.34 eV). (g) HOMO-5 (-7.42 eV). B: pink, P: orange, S: dark yellow, C: yellow, H: white.

1.5.3.4. NBO analysis of compound **1.26**.

	Orbital	Occupancy	Contribution	Atomic Orbitals
1(C-B, σ)		1.95	70.08% C + 29.92% B	C: 46.10% s + 53.96% p B: 36.96% s + 62.92% p
1(C-B, π)		1.82	80.68% C + 19.32% B	C: 99.93% p B: 99.86% p
2(C-P, σ)		1.96	59.36% C + 40.64% P	C: 24.29% s + 75.68% p P: 31.62% s + 67.83% p
3(P-S, σ)		1.96	45.31% P + 54.69% S	P: 18.89% s + 79.81% p S: 12.14% s + 87.32% p
4(S-B, σ)		1.97	67.34% S + 32.66% B	S: 32.45% s + 67.33% p B: 25.65% s + 74.11% p
5(B-B, σ)		1.93	50.00% B + 50.00% B	B: 38.48% s + 61.51% p B: 38.48% s + 61.51% p
6(C-B, σ)		1.95	70.08% C + 29.92% B	C: 46.10% s + 53.86% p B: 36.96% s + 62.97% p

6(C-B, π)		1.82	80.68% C + 19.32% B	C: 99.93% p B: 99.86% p
7(C-P, σ)		1.96	59.36% C + 40.64% P	C: 24.29% s + 75.68% p P: 31.62% s + 67.83% p
8(P-S, σ)		1.96	45.30% P + 54.70% S	P: 18.89% s + 79.81% p S: 12.14% s + 87.37% p
LP of S		1.97	100% S	S: 55.77% s + 44.17% p

1.5.3.5. Optimized geometric parameters and Wiberg Bond Index of compound **1.29** at M06-2X/def2-SVP.

Bond No.	Bond Distance (Å)	Wiberg Bond Index
1(B-C)	1.531	1.067
2(C-P)	1.734	1.068
3(P-N)	1.730	0.778
4(B-N)	1.451	0.849
5(B-B)	1.689	0.927
6(B-N)	1.445	0.867
7(P-N)	1.738	0.759
8(C-P)	1.749	1.058
9(C-B)	1.529	1.097

(a)	(b)	(c)

(d)	(e)	(f)

(g)	(h)	

1.5.3.7. NBO analysis of compound **1.29**.

	Orbital	Occupancy	Contribution	Atomic Orbitals
1(B-C, σ)		1.93	29.80% B + 70.20% C	B: 35.07% s + 64.87% p C: 44.04% s + 55.93% p
2(C-P, σ)		1.96	59.31% C + 40.69% P	C: 26.48% s + 73.42% p P: 30.07% s + 67.27% p
2(C-P, π)		1.64	93.97% C + 6.03% P	C: 99.94% p P: 49.88% p + 50.05% d
3(P-N, σ)		1.93	27.65% P + 72.35% N	P: 20.88% s + 78.03% p N: 38.98% s + 61.00% p
4(B-N, σ)		1.96	19.72% B + 80.28% N	B: 30.25% s + 69.52% p N: 42.41% s + 57.56% p
5(B-B, σ)		1.89	51.15% B + 48.85% B	B: 31.26% s + 68.72% p B: 35.09% s + 64.90% p
6(B-N, σ)		1.96	19.91% B + 80.09% N	B: 30.71% s + 69.07% p N: 42.37% s + 57.60% p

7(P-N, σ)		1.92	27.10% P + 72.90% N	P: 19.96% s + 78.92% p N: 40.48% s + 59.50% p
8(C-P, σ)		1.96	58.54% C + 41.46% P	C: 23.51% s + 76.45% p P: 31.36% s + 68.07% p
9(C-B, σ)		1.94	69.41% C + 30.59% B	C: 47.42% s + 52.56% p B: 34.54% s + 65.41% p
9(C-B, π)		1.78	85.47% C + 14.53% B	C: 99.29% p B: 99.82% p
LP of N(1)		1.76	100% N	N: 99.98% p
LP of N(2)		1.75	100% N	N: 99.98% p

1.5.3.8. Optimized geometric parameters and Wiberg Bond Index of compound **1.30** at M06-2X/def2-SVP.

Bond No.	Bond Distance (Å)	Wiberg Bond Index
1(B-N)	1.488	0.807
2(C-B)	1.547	1.037
3(C-P)	1.721	1.062
4(N-P)	1.696	0.781
5(B-B)	1.715	0.962

(a)	(b)	(c)

(d)	(e)	(f)

(g)		

1.5.3.10. NBO analysis of compound 1.30.

	Orbital	Occupancy	Contribution	Atomic Orbitals
1(B-N, σ)		1.95	19.99% B + 80.01% N	B: 25.93% s + 73.73% p N: 39.40% s + 60.56% p
2(C-B, σ)		1.92	71.08% C + 28.92% B	C: 39.20% s + 60.73% p B: 31.76% s + 68.09% p
2(C-B, π)		1.78	88.03% C + 11.97% B	C: 99.81% p B: 99.48% p
3(C-P, σ)		1.96	59.32% C + 40.68% P	C: 24.75% s + 75.15% p P: 31.10% s + 68.37% p
4(N-P, σ)		1.95	72.51% N + 27.49% P	N: 21.00% s + 78.93% p P: 19.88% s + 78.92% p
5(B-B, σ)		1.97	49.95% B + 50.05% B	B: 42.22% s + 57.76% p B: 42.27% s + 37.71% p
LP of N		1.77	100% N	N: 97.75% p

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CHAPTER 2: A *N*-Phosphinoamidinato NHC-Diborene Catalyst for

Hydroboration

2.1. Introduction

Multiply bonded main-group compounds containing an E=E double-bond (E = main-group element) or E≡E triple bond are of particular interest, as they exhibit transition-metal-like reactivity to activate and functionalize small molecules due to the possession of a HOMO and LUMO with a small energy difference.^[1-6]

B-B multiply bonded chemistry has made significant progress since the discovery of the first NHC-dihydrodiborene by Robinson group in 2008.^[7] A series of B-B multiply bonded species bearing different substituent groups and supporting ligands were isolated in the past decades.^[2] Besides dihydrogen (H₂)^[8] and carbon monoxide (CO)^[9] activation mentioned in Chapter 1, they also exhibited transition metal-like reactivity with other small molecules. For instance, treatment of diboracumulene **1.13** with 1 atm of propyne led to the formation of the triplet biradical **2.1** with a 2π-aromatic 1,3-diborete four-membered ring. When propyne was replaced by acetylene, a 6π-aromatic 1,4-diborabenzene six-membered ring **2.2** was formed through a spontaneous cycloaddition mechanism.^[10] In addition, the reaction of diboryne **1.21** with B₂Cat₂ yielded diboryldiborene **2.3** featuring π-conjugated B₄ core.^[11-12] Diboryne **1.21**

stepwise activated HBCat through hydroboration to form a hydro(boryl)diborene **2.4** and a neutral dihydrotetraborane **2.5**.^[13] Even though the reactivity of these B-B multiple bond species was well-established, they were limited to stoichiometric reactions. Multiply bonded boron compounds mediated catalytic reactions of small molecules has not been reported so far.

Scheme 2.1. Reactivity of diborynes towards small molecules.

As compared to the well-studied multiply bonded boron species, multiply bonded aluminium compounds are rare, which is mainly due to the synthetic challenges in isolating such reactive species. Recently, Inoue et al. accomplished remarkable achievement in synthesizing two stable dialumene compounds.^[14-15] The reaction of $i\text{PrNHC}$ -aluminum trihydride **2.6** with $\text{BX}_3 \cdot \text{SMe}_2$ ($\text{X}=\text{Br}, \text{I}$) formed $i\text{PrNHC}$ -aluminum trihalide adducts **2.7**, which were further reacted with di-*tert*-butyl(methyl)silyl sodium [$t\text{Bu}_2\text{MeSiNa}$] or 2,4,6-triisopropylphenyl lithium via salt metathesis mechanism to give aryl or silyl-substituted Al(III) precursors **2.8**. The subsequent reduction of **2.8** with KC_8

afforded dialumene compounds **2.9**, which exhibited a very small HOMO–LUMO gap. As such, dialumenes **2.9** showed potential to activate a variety of small molecules.

Scheme 2.2. Syntheses of Al-Al multiple bonding species.

As an illustration, aryl-substituted dialumene **2.9b** was capable of splitting H₂ to generate dialuminum dihydride complex **2.10**.^[15] In addition, dialumene **2.9b** could undergo [2+2] cycloaddition with unsaturated organic compounds, such as ethene and diphenylacetylene to form the corresponding four-membered ring products **2.11** and **2.12**.^[15] Moreover, stepwise activation of nitrous oxide (N₂O) with dialumene **2.9b** at low temperature formed the three-membered ring product **2.13**,^[15] which was further oxidized by additional equivalent of N₂O at r.t.p. to form compound **2.14**.

Scheme 2.3. Reactivity of dialumene **2.9b** towards small molecules.

Apart from the abovementioned boron and aluminium multiply bonded chemistry, isolation of heavier group 14 multiply bonded species and their reactivity were also explored. Ever since the isolation of the first example of disilene by West,^[16] a plethora of heavier group 14 elements multiply bonded compounds containing multiple bonds were reported.^[17] Recently, Inoue and coworkers demonstrated the isolation of a highly twisted disilene **2.16**^[18] from the reaction of bis(*tert*-butyl)imidazolin-2-iminotribromosilane *t*-BuNSiBr₃ **2.15** with two equivalents of KSiTMS₃, along with the formation of KBr and BrSiTMS₃ as side products. Owing to the presence of two imino groups as strong π -donors, disilene **2.16** has the longest Si=Si double bond reported to date, which indicates that the interaction between the two silicon atoms is relatively weak. The small HOMO-LUMO gap enabled disilene **2.16** to play an important role in small molecules activation.

Scheme 2.4. Synthesis of disilene **2.16**.

As expected, disilene **2.16** underwent *anti*-addition of H₂ under mild conditions to give dihydrodisilane compound **2.17**.^[18] DFT calculations indicate that the highly twisted and *trans*-bent geometry of disilene **2.16** was crucial for this transformation. Similar to dialumene **2.9b**, disilene **2.16** could also be oxidized by N₂O facilely to provide three-membered oxadisilirane ring **2.18**.^[19] In addition, disilene **2.16** could activate CO₂,^[19] and interestingly, the products of this reaction depended on the reaction temperature. At -78 °C, a [2+2] cycloaddition four-membered ring product **2.19** was isolated while at r.t.p., a five-membered silacycle **2.20** was isolated. Moreover, disilene **2.16** underwent 1,2-addition with ammonia (NH₃) at -78 °C to generate *trans*-hydroamination product **2.21**, which was similar to the case of H₂.^[19] When the reaction was carried out at r.t.p., the oxidative product **2.22** was observed. Despite the versatile reactivity of disilene **2.16** towards small molecules activation, these reactions were irreversible.

Scheme 2.5. Reactivity of disilene **2.16** towards small molecules.

Reversible small molecules activation based on multiply bonded main-group compounds was scarcely found. However, such reversibility is important in catalysis since this will allow the transfer and elimination of the functionalized product, as well as the regeneration of active catalyst.^[4] In 2009, Power and coworker illustrated that distannynes, containing a Sn-Sn triple bond, underwent the reversible reaction with ethylene under mild conditions to form the cycloaddition product **2.24**.^[20] Besides ethylene, the reaction of distannyne **2.23a** with H_2 at 80°C showed the presence of an equilibrium between distannyne **2.23a** and low-valent tin hydride complex **2.25**.^[21] These reversible small molecules activation provide considerable potential for the development of catalytic transformations based on main-group species.

Scheme 2.6. Reversible reactivity of distannynes towards ethylene and H₂.

A few examples of reversible small molecules activation indicate that small molecules have difficulty in dissociating from the main-group-element centers after activation. As such, catalytic organic transformations mediated by multiply bonded main-group compounds are rare, with only two examples being reported. The first example was the digermynes-catalyzed cyclotrimerization of terminal alkynes reported by Sasamori and co-workers in 2018, where the digermynes **2.26** [TbbGe≡GeTbb] (Tbb = 4-*t*Bu-2,6-[CH(TMS)₂]C₆H₂, TMS = SiMe₃) was a precatalyst that reacted with the alkyne to afford the digermabenzene **2.27**.^[22] It acted as the active catalyst to react with three more molecules of alkynes to form 1,2,4-triarylbenzene with high regioselectivity.

Scheme 2.7. Digermynes **2.26**-catalyzed cyclotrimerization of terminal alkynes.

The second example demonstrated by Inoue and co-workers in 2019 was CO_2 hydroboration catalyzed by a dialumene **2.9a** to form formoxyborane.^[23] Firstly, **2.9a** was able to activate CO_2 at low temperature to afford the [2+2] cycloaddition product **2.28**, which was thermally unstable and subsequently underwent rearrangement at 50 °C to give compound **2.29**. In addition, compound **2.28** was capable of reacting with two additional equivalents of CO_2 to form a $\text{Al}(\mu\text{-CO}_3)(\mu\text{-O})\text{Al}$ six-membered ring product **2.30**.

Scheme 2.8. Reactivity of dialumene **2.9a** towards CO_2 .

Based on these stoichiometric reaction results, the catalytic transformation

of CO₂ was performed. 5 mol% dialumene **2.9a** was able to catalyze the hydroboration of CO₂ with HBpin at 60 °C to generate the formic acid. Mechanistic studies showed that **2.9a** was a precatalyst, which reacted with CO₂ to form dialuminum carbonate compound **2.30**. This acted as the active catalyst to react with HBpin via **TS 2.31**. Subsequently, the hydride underwent 1,2-migration to form **Int 2.32**. After which, one equivalent of CO₂ inserted into the aluminum oxo skeleton to give **Int 2.34** via **TS 2.33**. Lastly, **Int 2.34** underwent the elimination of formoxyborane to regenerate compound **2.30**.

Scheme 2.9. Dialumene **2.9a** as a precatalyst for hydroboration of CO₂.

These results represent a fascinating area for main-group species containing multiple bonds and their use for catalytic organic transformations. However, in these catalyses, the Al=Al and Ge≡Ge multiple bonds were not able to be regenerated after the catalytic cycle. These gave rise to the question of whether main-group multiple bonds can be involved in a catalytic cycle.

Thus, in this chapter, a novel *N*-phosphinoamidinato *N*-heterocyclic carbene diborene species was synthesized and examined for its applications towards the catalytic hydroboration of carbon dioxide and catalytic *N*-formylation reactions of secondary and primary amines by carbon dioxide and pinacolborane, as well as the chemoselective catalytic hydroboration of carbonyl compounds. DFT calculations were also reported to rationalize our experimental findings.

2.2. Results and Discussion

To begin with, the *N*-phosphinoamidine^[24] was reacted with *n*BuLi in Et₂O for 3 h to afford the lithium derivative, which was then reacted with B₂Br₄(SMe₂)₂^[25] in toluene for 12 h (**Scheme 2.10**). The LiBr that formed in the reaction mixture was separated by filtration. After that, the filtrate was concentrated to afford the *N*-phosphinoamidinate-bridged diborane **2.35** as colorless crystals. The ¹¹B{¹H} NMR spectrum shows two signals at 55.5 and –11.9 ppm for sp² and sp³ boron centers, respectively. The ³¹P{¹H} NMR spectrum shows one signal at 35.9 ppm. X-ray crystallography of **2.35** shows that the ligand is bridging between two boron centers, where the length of the B1–B2 bond is 1.704(5) Å (**Figure 2.1a**). Moreover, the length of the N1–B1 bond is 1.428(5) Å, indicating that the N1 lone pair of electrons delocalize to the vacant p orbital of the B1 center more than to the amidinate N1–C13–N2 skeleton (C13–N2 1.279(4) Å, C13–N1 1.423(4) Å).

Scheme 2.10. Syntheses of **2.35** and **2.36**.

Compound **2.35** was reacted with MeNHC (:C{N(CH₃)C-(CH₃)₂}) at r.t.p. in toluene for 4 h to yield a red precipitate, which was then reacted with excess

KC₈ in toluene for 3 h at r.t.p. to yield a purple-red mixture (**Scheme 2.10**). The precipitate (graphite and KBr) that formed in the reaction mixture was removed by filtration. After that, the filtrate was concentrated to afford the phosphinoamidinato NHC-diborene compound **2.36** as a red crystalline solid. The ¹¹B{¹H} NMR spectroscopy displays two signals at 28.8 and 10.5 ppm, indicating that compound **2.36** is composed of a highly polarized B-B double bond. The signals are in the range of the ¹¹B NMR signals (12–32 ppm) of similar Lewis base-diborene complexes.^[7-8, 26-38] The ³¹P{¹H} NMR signal (45.9 ppm) is shifted downfield in comparison with that of **2.35**. The ¹³C{¹H} NMR signal at 152.9 ppm is attributable to the C_{carbene} center coordinating with the boron atom. The molecular structure of compound **2.36** obtained by X-ray crystallography is composed of a planar boron-containing six-membered ring with a N2–C1–N1–B2 torsion angle of –0.07° (**Figure 2.1b**). This indicates that there is six-π-electron delocalization along the N2–C1–N1–B1–B2 skeleton. The N1 lone pair electrons delocalize along the amidinate skeleton, as indicated by the length of the C1–N1 (1.366(4) Å) and C1–N2 (1.312(4) Å) bonds. This results in lengthening of the N–B bond (N1–B1 1.526(4) Å) in comparison with that of **2.35**. The length of the B2–B1 bond (1.562(5) Å) falls in the range of B–B double bond lengths (1.546–1.625 Å) in similar Lewis base-diborene complexes.^[7-8, 26-38] The NHC (B1–C20 1.590 Å) and phosphine (P1–B2 1.852(3) Å) of the phosphinoamidinate ligand are bonded with the B=B bond. Their bond lengths are similar to those of other NHC/phosphine-diborene

complexes (C–B 1.532–1.603 Å, P–B 1.863–1.929 Å). [7-8, 26-38]

Figure 2.1. (a) X-ray crystal structure of **2.35** with thermal ellipsoids at 50 % probability. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1-B2 1.704(5), B2-P1 1.940(4), B1-N1 1.428(5), N1-C13 1.423(4), N2-C13 1.279(4), P1-N2 1.673(3), N1-B1-B2 124.3(3), B1-B2-P1 103.9(2), B2-P1-N2 104.53(15), P1-N2-C13 127.8(2), N2-C13-N1 126.3(3), C13-N1-B1 120.8(3). (b) X-ray crystal structure of **2.36** with thermal ellipsoids at 50 % probability. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1-B2 1.562(4), B2-P1 1.851(4), B1-N1 1.526(4), P1-N2 1.641(2), N2-C1 1.312(4), N1-C1 1.366(4); N1-B1-B2 123.8(3), B1-B2-P1 112.5(2), B2-P1-N2 106.45(14), P1-N2-C1 129.8(2), N2-C1-N1 125.0(3).

DFT calculations (M06-2X/def2-TZVP, **2.5.3.2**) were performed to elucidate the electronic structure of **2.36**. The HOMO-1 shows the σ orbital of the B-B double bond (**Figure 2.2**). The HOMO exhibits the π orbital of the B=B bond, while the LUMO represents the N 2p orbital conjugated with the π system of the phenyl group. Accordingly, a natural bond orbital (NBO, **2.5.3.4.**) analysis illustrates that the B1–B2 σ bond arises from the mixing of sp hybrids on the boron atoms (B1, $sp^{1.31}$; B2, $sp^{1.41}$). The B1–B2 π bond is slightly polarized toward the B1 atom (54.2% B1 + 45.8% B2). It is generated by the mixing of B p orbitals. The WBI of 1.55 suggests that the B2–B1 bond is a double bond. In addition, natural population analysis (NPA) shows that the charges on the B1

and B2 atoms are -0.55 and 0.09 e, respectively. The dissected nucleus-independent chemical shift (NICS_{zz}(1), -4.6 ppm; **2.5.3.5**) shows that the diboron-containing six-membered ring in **2.36** is slightly aromatic.

Figure 2.2. Calculated frontier orbitals of compound **2.36** (B: pink, Br: brown, C: yellow, H: white, N: blue, P: orange).

The B-B double bond character in **2.36** was illustrated by its reactivity with NH_3BH_3 in toluene at $-78\text{ }^\circ\text{C}$ (**Scheme 2.11**). The reaction mixture was warmed to r.t.p. and stirred for 3 h. The precipitate that formed in the reaction mixture was discarded by filtration. After that, the borylboronium cation **2.37** was isolated as a colorless crystalline solid from the concentrated filtrate. It is proposed that the reaction proceeds through the addition of H^+ and H^- from NH_3BH_3 to the B-B double bond in **2.36** to form the diborane intermediate **I** and NH_2BH_2 . The second pair of H^+ and H^- from NH_2BH_2 attacks the *N*-phosphinoamidinate ligand and NHC-borane center, respectively, to form the *N*-phosphinoamidine ligand, which then displaces the Br^- moiety to form **2.37**. Its ^1H NMR spectrum exhibits signals for the *N*-phosphinoamidine and $^{\text{Me}}\text{NHC}$ backbone. The B-H signal cannot be found in the spectrum due to the

quadrupolar boron nucleus. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows a multiplet at 85.6 ppm due to the coupling with N–H and B–H protons. The $^{11}\text{B}\{^1\text{H}\}$ NMR spectrum shows two broad signals for the boronium cation (–14.2 ppm) and borane center (–36.2 ppm).

Scheme 2.11. Synthesis of **2.37**.

The molecular structure of **2.37** obtained by X-ray crystallography (**Figure 2.3**) illustrates that the *N*-phosphinoamidine chelates to the boronium B1 cation, while $^{\text{Me}}\text{NHC}$ coordinates to the borane B2 atom (C28–B2 1.603(3) Å). Both boron centers adopt a tetrahedral geometry. The B1...Br distance is 9.331 Å, indicating that there is no interaction between these atoms. The length of the B2–B1 bond is 1.749(4) Å. It is comparable to the B–B single-bond length in compound **2.35** (1.704(5) Å). The N1–B1 bond (1.617(3) Å) is considerably lengthened in comparison with the N–B single-bond length (1.428(5) Å) in compound **2.35**, indicating that the former is a coordinative covalent bond. In addition, the B1–P1 bond (1.970(2) Å) is comparable with the B–P coordinative covalent bond (1.940(4) Å) in compound **2.35**. These data support that the *N*-phosphinoamidine ligand chelates the boronium B1 cation.

Figure 2.3 X-ray crystal structure of **2.37** with thermal ellipsoids at 50 % probability. Partial H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1-B2 1.749(4), B2-C28 1.603(3), B1-N1 1.617(3), B1-P1 1.970(2), P1-N2 1.6987(19), N2-C13 1.360(3), N1-C13 1.313(3), N1-B1-P1 96.19(14), N1-B1-B2 120.62(19), P1-B1-B2 116.79(16), B1-B2-C28 114.2(2).

Compound **2.36** was capable of activating a small molecule, namely carbon dioxide (CO_2 , 1 atm), in toluene at r.t.p. (**Scheme 2.12**). The reaction mixture changed from reddish purple to colorless immediately. After the reaction mixture was filtered, compound **2.38** was isolated as a colorless crystalline solid from the concentrated filtrate. In the reaction, the B-B double bond in **2.36** undergoes a [2 + 2] cycloaddition with CO_2 to give compound **2.38**. Its ^1H NMR spectrum displays signals of the *N*-phosphinoamidinate and $^{\text{Me}}\text{NHC}$ ligand. The $^{11}\text{B}\{^1\text{H}\}$ NMR signals are at -5.5 and -17.9 ppm, which are shifted upfield in comparison with those of compound **2.36**, demonstrating that the boron centers are four-coordinate. Moreover, the $^{31}\text{P}\{^1\text{H}\}$ NMR signal (39.7 ppm), which is comparable with that of compound **2.35**, is shifted upfield in comparison to that of compound **2.36**. These spectroscopic data indicate that the B-B bond in compound **2.38** is a single bond. This is consistent with the

molecular structure of **2.38** (Figure 2.4a) obtained by X-ray crystallography, where the length of the B–B bond (1.770(3) Å) is comparable with that of the B–B single bond in compound **2.35**. The B₂CO four-membered ring is planar with the endocyclic O1–C28 bond (1.349(3) Å) being longer than the exocyclic O2–C28 bond (1.218(3) Å). In addition, the Br and ^{Me}NHC moieties are positioned in a *cis*-fashion in reference to the boron-containing four-membered ring. Compound **2.38** is stable in solution and the solid state and does not decompose in refluxing toluene. Recently, Braunschweig et al. reported that the treatment of the NHC-diborene [IPr(Br)BB(Br)IPr] (IPr = :C{N(2,6-iPr₂C₆H₃)CH}₂) with CO₂ formed a [2 + 2] cycloaddition product, which was thermally unstable and could not be isolated in quantity. It rearranged to form the 2,4-diboraoxetan-3-one containing oxo and carbonyl groups bridging between two boron centers.^[39]

Scheme 2.12. Syntheses of **2.38** and **2.39**.

It is anticipated that the activated CO₂ moiety in compound **2.38** can be further functionalized. As such, compound **2.36** was treated with CO₂ and tris(pentafluorophenyl)borane in toluene at r.t.p., where the reaction mixture

instantly changed from red-purple to colorless (**Scheme 2.12**). After it was stirred for 30 min, the solution was filtered. Compound **2.39** was isolated as colorless crystals from the concentrated filtrate. The reaction proceeds through the formation of compound **2.38**, where the exocyclic C=O double bond further coordinates to B(C₆F₅)₃ to form compound **2.39**. Its ¹¹B{¹H} NMR signals (−5.7, −20.3 ppm) are comparable with those of **2.38**, indicating the presence of a B₂CO four-membered ring. Moreover, the ¹¹B{¹H} NMR signal of −26.9 ppm is attributable to the four-coordinate B(C₆F₅)₃.

Figure 2.4 (a) X-ray crystal structure of **2.38** with thermal ellipsoids at 50 % probability. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1-B2 1.770(3), B2-C28 1.625(3), B1-O1 1.538(3), O1-C28 1.349(3), O2-C28 1.218(3), B2-P1 1.940(2), B1-N1 1.562(3), B1-C29 1.632(3), N1-B1-B2 118.67(17), B1-B2-P1 109.43(14), B1-B2-C28 78.73(15), B2-C28-O1 98.72(17), C28-O1-B1 96.48(15), O1-B1-B2 86.06(15). (b) X-ray crystal structure of **2.39** with thermal ellipsoids at 50 % probability. All H atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): B1-B2 1.791(6), B2-C28 1.593(5), B1-O1 1.625(5), O1-C28 1.292(4), O2-C28 1.280(4), O2-B3 1.551(5), B2-P1 1.950(4), B1-N1 1.544(5), B1-C29 1.619(6), N1-B1-B2 121.2(3), B1-B2-P1 106.6(2), O1-B1-B2 83.8(2), B1-B2-C28 77.6(2), B2-C28-

O1 104.2(3), C28-O1-B1 92.9(3), O1-C28-O2 122.7(3), B2-C28-O2 132.5(3), C28-O2-B3 128.1(3).

The molecular structure of **2.39** obtained by X-ray crystallography illustrates that the electronic structure of the B₂CO four-membered ring in **2.39** is different from that of **2.38** (**Figure 2.4b**). The O1–C28 (1.292(4) Å) and O2–C28 (1.280(4) Å) bond lengths are almost identical, indicating that the π electrons of double bond in the exocyclic C=O bond delocalizes along the O_{endo}–C–O_{exo} skeleton. The B2–C28 (1.593(5) Å) bond is shortened and the B1–O1 (1.625(5) Å) bond is lengthened in comparison with those in compound **2.38**. The experimental results show that **2.39** should be comprised of canonical forms, as illustrated in **Scheme 2.13**.

Scheme 2.13. Resonance structures of **2.39**.

It is anticipated that, if B(C₆F₅)₃ in **2.39** is replaced by HBpin, the B–H bond could attack the C=O bond to form the formoxyborane [pinBOC(O)H] and regenerate compound **2.36**. As such, compound **2.36** should show catalytic reactivity toward CO₂. To begin with, no reaction between carbon dioxide (CO₂) and pinacolborane (HBpin) in deuterated benzene (C₆D₆) at 110 °C was observed. A 2 mol % portion of **2.36** was then used to catalyze the reaction of

CO₂ with HBpin in C₆D₆ at r.t.p. (**2.4.4.1**). In the first 1 h, a mixture of the formoxyborane [pinBOC(O)H] (**2.40a**, reaction time 1 h, yield 7.5%) and bis(boryl)oxide [(pinB)₂O] (**2.40c**, reaction time 1 h, yield 8.2%) were formed. After 20 h, the conversion was still less than 30% and only **2.40c** was observed (reaction time 20 h, yield 26%). When the reaction temperature was increased to 110 °C (**Scheme 2.14**), the catalytic reaction was much more efficient and extremely clean (conversion >99%), forming a mixture of the methoxyborane [pinBOMe] (**2.40b**, yield 97.8%, TOF 33.3 h⁻¹) and **2.40c** in a 1:1 ratio. The activity of compound **2.36** is outstanding when the turnover frequency and product yield are considered. The turnover frequency (TOF) far surpasses those of main group-element hydride compounds (TOF (h⁻¹): Mg, 0.07; Ca, 0.1; Ge, 2.1; Sn, 14.5) for such catalysis.^[40] Our results are different from those for the NHC-dialumene-catalyzed hydroboration of CO₂ with HBpin, where 80% conversion of CO₂ to [pinBOC(O)H] was achieved at 80 °C for 3 h via the dialuminum carbonate active catalyst.^[23]

Scheme 2.14. Catalytic hydroboration of CO₂ with HBpin.

When the more sterically hindered 9-BBN (9-borabicyclo[3.3.1]nonane) was used instead of HBpin (**2.4.4.2**), 2 mol % of **2.36** catalyzed the

hydroboration of CO₂ in C₆D₆ at 110 °C to form small amounts of formoxyborane **2.41a** at time zero. When the reaction continued to proceed, bis(boryl)acetal (**2.41b**, reaction time 1 h, yield 27.5%) and methoxyborane (**2.41c**, reaction time 20 h, yield 92%) were sequentially observed. The chronological formation of hydroborated products suggest that the B-B double bond was recurrently restored in a catalytic cycle. Therefore, the B-B double bond in compound **2.36** is the active site in the catalytic hydroboration of CO₂.

Scheme 2.15. Catalytic hydroboration of CO₂ with 9-BBN.

To prove that compound **2.38** is an intermediate in the catalysis, 2 mol % of **2.38** was utilized to mediate the catalytic reaction of CO₂ and HBpin in deuterated benzene (C₆D₆) at 110 °C for 2 h to afford a mixture of **2.40b** (yield 92.7%, TOF 23.6 h⁻¹) and **2.40c** in a 1:1 ratio. This illustrates that compound **2.38** further reacts with HBpin to form a zwitterionic moiety in resemblance of compound **2.39**.

On the basis of these experimental studies, the catalytic cycle for the hydroboration of CO₂ with HBpin is proposed (**Scheme 2.16**) and has been studied by DFT calculations (M06-2X/def2-TZVP//M06-2X/def2-SVP/SMD(benzene)). The B-B double bond in **2.36** activates CO₂ with HBpin via **TS01** (ΔG = 20.7 kcal/mol). Subsequently, the H-B bond undergoes

nucleophilic attack to the C=O bond to form **Int01** ($\Delta G = -26.1$ kcal/mol). It appears as a [2 + 2] cycloaddition between **2.36** and the formoxyborane [HC(O)-OBpin]. The second HBpin then coordinates with the acetal oxygen atom in **Int01** via **TS02** ($\Delta G = -10.4$ kcal/mol) to give **Int02** ($\Delta G = -11.0$ kcal/mol). Its B-H bond attacks the acetal carbon atom via **TS03** ($\Delta G = -10.6$ kcal/mol), which induces nucleophilic attack of OBpin, leading to the formation of pinBOBpin coordinated to the formaldehyde oxygen atom in **Int03** ($\Delta G = -39.0$ kcal/mol). At this point, it is obvious that the first two C-H bond formations are kinetically facile processes. The steric effect between IMe and pinBOBpin leads to dissociation of the latter to form **Int04** ($\Delta G = -58.2$ kcal/mol). **Int04** is considered as a [2 + 2] cycloaddition product between **2.36** and a formaldehyde. The B-O bond in **Int04** reacts with the B-H bond of the third HBpin. It proceeds through σ -bond metathesis at **TS04** ($\Delta G^\ddagger = -30.2$ kcal/mol) to form **Int05** ($\Delta G = -71.9$ kcal/mol). The fourth HBpin then reacts with **Int05**. The B-H bond attacks the methylene carbon at **TS05** ($\Delta G^\ddagger = -46.7$ kcal/mol), which results in cleaving the B-C_{methylene} bond and forming the B-Bpin bond. These lead to the formation of **Int06** and MeOBpin ($\Delta G = -72.0$ kcal/mol). **Int06** undergoes 1,2-elimination of HBpin via **TS06** ($\Delta G^\ddagger = -41.1$ kcal/mol) to generate **2.36** and HBpin ($\Delta G = -73.2$ kcal/mol). The computed barriers of **Int04**→**TS04** (28.0 kcal/mol) and **Int06**→**TS06** (30.9 kcal/mol) are consistent with the catalysis requiring 110 °C to occur. The calculated results are in accordance with the experimental conditions and observations. A reaction temperature of 25 °C

resulted in **2.40c** with 26% yield (20 h), suggesting that the reaction ends at **Int04**. A reaction temperature of 110 °C provides sufficient energy to overcome the kinetic barrier (**TS04** and **TS06**), and hence a mixture of **2.40b** and **2.40c** was formed in a 1:1 ratio.

Scheme 2.16. DFT calculations of catalytic CO₂ hydroboration mechanism.

Then, the catalytic ability of **2.36** toward N-formylation of primary and secondary amines by carbon dioxide and pinacolborane was examined (**Table 2.2.1** and **2.4.4.3**). To begin with, compound **2.36** (5 mol %) cannot catalyze the reaction of **2.42e** and carbon dioxide (CO₂) at 90 °C without pinacolborane (HBpin, **2.4.4.4**). However, 5 mol % of **2.36** catalyzed the N-formylation of the primary aliphatic *n*butylamine **2.42b** and 3-methoxypropan-1-amine **2.42c** with CO₂ and HBpin in deuterated benzene (C₆D₆) at 90 °C to yield the corresponding N-formamides (yield (%)) (TOF (h⁻¹)): **2.43b**, 95 (40.0); **2.43c**, 96 (40.0), bis(boryl)oxide **2.40c**, and H₂. Second, a high yield and TOF were

accomplished for the N-formylation of aliphatic secondary diethylamine **2.42d** (yield 92%, TOF 50 h⁻¹), diisopropylamine **2.42a** (yield 98%, TOF 13.3 h⁻¹), and piperidine **2.42e** (yield 98%, TOF 33.3 h⁻¹). Third, aromatic *N*-methylaniline **2.42f** (yield 81%, TOF 3.1 h⁻¹) and indoline **2.42g** (yield 91%, TOF 1.4 h⁻¹) were less active in the catalyses.

Table 2.2.1. 2.36-catalyzed N-formylation^a

$\text{CO}_2 + \begin{array}{c} \text{R}^1 \text{N} \text{R}^2 \\ \\ \text{H} \\ \text{2.42} \end{array} \xrightarrow[\text{- H}_2, \text{- (pinB)}_2\text{O (2.40c)}]{\text{Catalyst 2.36 (5 mol \%), 2 equiv. HBpin, C}_6\text{D}_6, 90^\circ\text{C}}$				$\begin{array}{c} \text{R}^1 \text{N} \text{R}^2 \\ \\ \text{H} \text{C}=\text{O} \\ \text{2.43} \end{array}$

2.43a	2.43b	2.43c	2.43d	
>99 (98)%, 13.3 h ⁻¹	>99 (95)%, 40.0 h ⁻¹	>99 (96)%, 40.0 h ⁻¹	>99 (92)%, 50 h ⁻¹

2.43e	2.43f	2.43g		
>99 (98)%, 33.3 h ⁻¹	91 (81)%, 3.1 h ⁻¹	82 (81)%, 1.4 h ⁻¹		

^aReaction conditions: Amine (0.10 mmol), 2 equiv. of HBpin (0.20 mmol), catalyst **2.36** (5 mol%), C₆D₆ (0.50 mL), CO₂. Catalyst loading is relative to amine. Yields were determined by ¹H NMR spectroscopy using cyclohexane as an internal standard on the basis of the consumption of the amine. They were reported in parenthesis. The identity of the product was confirmed as R¹R²NC(=O)H. All the catalytic trials were reported in triplicate.

It is noteworthy that compound **2.36** is one of the rare main-group catalysts that mediate N-formylation using carbon dioxide and pinacolborane, including the NHC-silyliumylidene cation [(^{Me}NHC)₂SiH]I.^[41] Moreover, **2.36** exceeds the

latter in view of both reaction time and TOF (example of $[(^{\text{Me}}\text{NHC})_2\text{SiH}]^{\text{I}}$, **2.43a**: yield 68%, TOF 6.8 h^{-1}). Other main-group-element catalysts, namely proazaphosphatrane^[42] and carbodicarbene,^[43] can only use the potent 9-BBN for the N-methylation of amines with carbon dioxide.

To understand the catalytic mechanism, piperidine **2.42e** was reacted with HBpin in C_6D_6 at 90°C , resulting in the formation of the borylamine and H_2 . This suggests that the formation of H_2 in the above catalysis arose from the coupling reaction of amines and HBpin. In this context, a catalytic mechanism is proposed (**Scheme 2.17**). Compound **2.36** catalyzes the reaction of CO_2 and HBpin to form formoxyborane [pinBOC(O)H] (**2.40a**). This then undergoes a substitution reaction with borylamine, which is formed by the dehydrogenation reaction of amine and HBpin, to form N-formamide and pinBOBpin **2.40c**.

Scheme 2.17. Proposed mechanism for the N-formylation.

In addition to the catalytic hydroboration of carbon dioxide and N-

formylation, **2.36** (5 mol %) was able to catalyze the chemoselective hydroboration of aldehyde and ketone **2.44** in C₆D₆ at r.t.p. to form borate esters (**2.45**, 16 examples: aldehydes, yield = 99%, TOF = 4–120 h⁻¹; ketones, yield = 80–98%, TOF = 0.4–10 h⁻¹; **Scheme 2.18**, **Table 2.2.2** and **2.4.4.5**). The results further support that compound **2.36** is an active catalyst in >C=O hydroboration.

Scheme 2.18. Chemoselective hydroboration of carbonyl compounds.

The chemoselective ability of complex **2.36** toward hydroboration of carbonyl compounds was further examined. Firstly, complex **2.36** (5 mol %) was found to be capable of catalyzing hydroboration of aromatic aldehyde ArC(O)H (Ar = Ph, **2.44a**, Table 2) as well as its derivatives with electron donating (Ar = MeC₆H₄ **2.44b**, MeOC₆H₄ **2.44c**) and withdrawing substituents (MeCO₂C₆H₄ **2.44d**, FC₆H₄ **2.44e**), which quantitatively afforded the corresponding borate esters. Secondly, high yield was achieved for the hydroboration of non-aromatic aldehydes, namely cyclohexanecarboxaldehyde **2.44f** and 2,2-dimethylpropanal **2.44g**. The functionality in cinnamaldehyde **2.44h**, thiophene-2-carbaldehyde **2.44j**, 4-formylbenzonitrile **2.44k**, ferrocenecarboxaldehyde

2.44l and quinoline-2-carbaldehyde **2.44m** remains intact in these catalyses, showing that the **2.36**-catalyzed chemoselective hydroboration is possible. As expected, a higher reaction temperature and longer reaction time were required for the chemoselective hydroboration of ketones when compared to aldehydes due to their steric nature.

Table 2.2.2. Scope of Carbonyl Substrates^a

2.45a	2.45b	2.45c	2.45d	2.45e
>99 % (97 %), 19.8 h ⁻¹	>99 % (94 %), 9.6 h ⁻¹	>99 % (97 %), 13.3 h ⁻¹	>99 % (95 %), 13.3 h ⁻¹	>99 % (96 %), 4 h ⁻¹
2.45f	2.45g	2.45h	2.45j	2.45k
>99 % (82 %), 120 h ⁻¹	>99 % (81 %), 10 h ⁻¹	>99 % (92 %), 120 h ⁻¹	>99 % (96 %), 4.9 h ⁻¹	>99 % (82 %), 39.6 h ⁻¹
2.45l	2.45m	2.45n	2.45p	2.45q
>99 % (88 %), 120 h ⁻¹	>99 % (89 %), 120 h ⁻¹	>99 % (98 %), 3.3 h ⁻¹	90 % (85 %), 0.4 h ⁻¹	85 % (80 %), 0.4 h ⁻¹
2.45r				
>99 % (95 %), 10 h ⁻¹				

^aReaction conditions: carbonyl substrates (0.40 mmol), HBpin (0.41 mmol), C₆D₆ (0.5 mL), catalyst **2.36** (5 mol%). Yields are isolated yield, bracket one is the isolated yield, the other one is the conversion. All the catalytic trials were repeated in triplicate.

2.3. Conclusion

In conclusion, the *N*-phosphinoamidinato NHC-diborene compound **2.36** is a multiply bonded boron catalyst showing catalytic capability toward the hydroboration of CO₂ with HBpin and N-formylation of primary and secondary amines by CO₂ and HBpin, as well as chemoselective hydroboration of carbonyl compounds. In particular, compound **2.36** efficiently reduces CO₂ with HBpin to form MeOBpin and pinBOBpin. Its catalytic activity is superior to that of existing main-group-element catalysts employed for such reactions. In the mechanistic studies, compound **2.36** exhibits reactivity resembling that of a transition metal in the catalytic hydroboration of CO₂. Its B-B double bond activated CO₂ with HBpin, the initial intermediate of which was further reacted with two HBpin molecules to form MeOBpin and pinBOBpin, along with the regeneration of **2.36**.

2.4. Experimental

2.4.1. General procedure.

All operations were carried out under an inert atmosphere of argon gas by standard Schlenk techniques. Chemicals were purchased from Sigma-Aldrich and used directly without further purification. All solvents were dried over K metal or CaH₂ prior to use. The ¹H, ¹¹B{¹H}, ¹³C{¹H} and ³¹P{¹H} NMR spectra were recorded on a JEOL ECA 400 spectrometer. The solution NMR spectra were recorded in deuterated solvents and the chemical shifts are relative to SiMe₄ for ¹H and ¹³C; BF₃·Et₂O for ¹¹B; 85% H₃PO₄ for ³¹P, respectively. HRMS spectra were obtained at the Mass Spectrometry Laboratory in the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured with an OpticMelt Stanford Research System.

2.4.2. X-ray data collection.

The X-ray diffraction intensity data for compound **2.35**, **2.36**, **2.37**, **2.38** and **2.39** were using the same equipment and parameters as Chapter 1, section 1.4.2, page 35 of this thesis using the SMART suite of programs.^[44] Data processing, correction, structural solution and refinement were done similar with the SHELXTL suite of programs.^[45] Selected crystallographic data is provided in section 2.5.1.

2.4.3. The syntheses and characterization procedures.

Synthesis of 2.35. A solution of *n*BuLi (2.6 M, 0.4 mL, 1.05 mmol) in hexane was placed in a 100 mL Schlenk flask containing a stirred diethyl ether solution of *N*-phosphinoamidine (0.425 g, 1 mmol) at -78 °C, following which, the solution was warmed to r.t.p. and stirred for 3 h.

The resulting yellow solution was dried under vacuum to remove all volatiles. A solution of B₂Br₄(SMe₂)₂ (0.466 g, 1 mmol) in toluene was then slowly placed in the Schlenk flask at -78 °C. The reaction mixture was stirred at r.t.p. for 12 h and then was filtered. The filtrate was then concentrated and stored at 4 °C for 2 days to give **2.35** as a colorless crystalline solid (0.52 g, 0.76 mmol, 76% yield). M.p: 177 °C. ¹H NMR (399.5 MHz, 25 °C, C₆D₆): δ 7.33-7.30 (m, 2 H, ArH), 7.05-6.77 (m, 6 H, ArH), 3.38 (sept, 2 H, CHMe₂, J_{HH} = 6.8 Hz), 1.44 (d, 18 H, *t*Bu, J_{PH} = 14.2 Hz), 1.32 (d, 6 H, CHMe₂, J_{HH} = 6.8 Hz), 0.93 (d, 6 H, CHMe₂, J_{HH} = 6.8 Hz). ¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): δ 55.50 (s), -11.94 (s). ³¹P{¹H} NMR (162 MHz, 25 °C, C₆D₆): δ 35.72 (br). ¹³C{¹H}

NMR (101 MHz, 25 °C, C₆D₆): 168.14 (d, *J* = 11.6 Hz, NCN), 145.41 (CH-Ar), 140.05 (CH-Ar), 138.74 (d, *J* = 13.5 Hz, (C-Ar)), 129.44 (CH-Ar), 128.89 (CH-Ar), 128.78 (CH-Ar), 128.45 (CH-Ar), 127.62 (CH-Ar), 126.99 (C-Ar), 124.45 (C-Ar), 38.28 (d, *J* = 34.8 Hz, PC(CH₃)), 28.62 (CH(CH₃)₂), 27.77 (PC(CH₃)), 25.14 (CH(CH₃)₂), 23.34 (CH(CH₃)₂). HRMS (ESI): *m/z* calcd for C₂₇H₄₁B₂⁷⁹Br₃N₂P: 683.0744 [(*M* + *H*)⁺]; found: 683.0761.

Synthesis of 2.36 A toluene solution of 1,3,4,5-tetramethylimidazolin-2-ylidene (^{Me}NHC, 0.149 g, 1.2 mmol) was placed in a 100 mL Schlenk flask containing **2.35** (0.685 g, 1 mmol) at r.t.p.. After 10 min, the reaction mixture turned red with some precipitate. The resulting suspension was stirred for 4 h. Subsequently, it was filtered and the pale red residue was then dried under vacuum for 2 h. The red residue was the **2.35**·^{Me}NHC adduct and was used without further purification. A 30 mL portion of toluene was placed in a 100 mL Schlenk flask containing a mixture of **2.35**·^{Me}NHC (0.809 g, 1 mmol) and excess potassium graphite (0.54 g, 4 mmol) at r.t.p., causing the reaction mixture to turn purplish red immediately. The resulting suspension was stirred for 3 h and filtered. The filtrate was concentrated to 5 mL and stored at -20 °C for 1 day to give **2.36** as a red crystalline solid (0.24 g, 0.37 mmol, 37% yield). M.p.: 198 °C (dec.). ¹H NMR (399.5 MHz, 25 °C, C₆D₆): δ 7.66-7.64 (m, 2 H, ArH), 7.05-6.88 (m, 6 H, ArH), 3.37 (sept, 2 H, CHMe₂, *J*_{HH} = 7.2 Hz), 3.19 (s, 6 H, N-CH₃), 1.71 (d, 18 H, *t*Bu, *J*_{PH} = 12.8 Hz), 1.23 (s, 6 H, C-CH₃), 0.85 (d, 6 H, CHMe₂, *J*_{HH} = 6.4 Hz), 0.80 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz). ¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): δ 30.64 (s), 9.16 (s). ³¹P{¹H} NMR: (162 MHz, 25 °C, C₆D₆): δ 45.93 (br). ¹³C{¹H} NMR (101 MHz, 25 °C, C₆D₆): 152.85 (C-carbene), 145.37 (CH-Ar), 144.46 (CH-Ar), 141.05 (d, *J* = 16.4 Hz, C-Ar), 130.72 (CH-Ar), 129.01 (CH-Ar), 128.25 (CH-Ar), 127.62 (CH-Ar), 126.90 (CH-Ar), 126.70 (C-Ar), 126.65 (C-Ar), 124.13 (C-Ar), 123.04 (CCH₃), 38.65 (d, *J* = 42.5 Hz, PC(CH₃)), 33.13 (NCH₃), 28.47 (CH(CH₃)₂), 27.72 (d, *J* = 1.9 Hz, PC(CH₃)), 24.95 (CH(CH₃)₂), 23.55 (CH(CH₃)₂), 7.82 (CH₃). HRMS (ESI): *m/z* calcd for C₃₄H₅₃B₂⁷⁹BrN₄P: 649.3377 [(*M* + *H*)⁺]; found: 649.3395.

Synthesis of 2.37 A 20 mL portion of toluene was placed in a 100 mL Schlenk flask containing **2.36** (0.130 g, 0.2 mmol) and NH₃BH₃ (0.007 g, 0.2 mmol) at -78 °C. The resulting solution was warmed to r.t.p. and stirred for 3 h with the color changing from red-purple to pale red. The reaction solution was filtered. The filtrate was then concentrated and kept at r.t.p. to give **2.37** as a colorless crystalline solid (0.07 g, 0.11 mmol, 54% yield). M.p.: 147 °C. ¹H NMR (399.5 MHz, 25 °C, C₆D₆): δ 7.78-7.76 (m, 2 H, ArH), 6.87-7.04 (m, 4 H, ArH), 6.75-6.69 (m, 2 H, ArH), 3.29 (sept, 1 H, CHMe₂, *J*_{HH} = 7.2 Hz), 2.78 (sept, 1 H, CHMe₂, *J*_{HH} = 7.2 Hz), 2.61 (s, 6 H, N-CH₃), 1.78 (dd, 18 H, *t*Bu, *J*_{PH} = 12.8

Hz), 1.44 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.4$ Hz), 1.27 (s, 6 H, C-CH₃), 1.11 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz), 0.46 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz), 0.12 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz). ¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): δ -14.24 (br), -34.15 (br). ³¹P{¹H} NMR: (162 MHz, 25 °C, C₆D₆): δ 85.62 (br). ¹³C{¹H} NMR (101 MHz, 25 °C, C₆D₆): 167.13 (d, $J = 11.5$ Hz, NCN), 145.90 (C-carbene), 144.89 (CH-Ar), 143.81 (CH-Ar), 139.24 (d, $J = 8.6$ Hz, C-Ar), 132.17 (CH-Ar), 131.83 (CH-Ar), 130.23 (CH-Ar), 126.70 (CH-Ar), 126.11 (CH-Ar), 125.25 (C-Ar), 124.63 (C-Ar), 124.38 (C-Ar), 123.74 (CCH₃), 121.75 (CCH₃), 37.72 (d, $J = 23.1$ Hz, PC(CH₃)), 35.50 (d, $J = 25.1$ Hz, PC(CH₃)), 34.68 (NCH₃), 31.50 (NCH₃), 28.64 (CH(CH₃)₂), 28.08 (d, $J = 28.9$ Hz, PC(CH₃)), 27.74 (d, $J = 28.9$ Hz, PC(CH₃)), 25.48 (CH(CH₃)₂), 24.80 (CH(CH₃)₂), 23.94 (CH(CH₃)₂), 23.10 (CH(CH₃)₂), 22.67 (CH(CH₃)₂), 7.89 (CH₃), 7.58 (CH₃). HRMS (ESI): m/z calcd for C₃₄H₅₇B₂⁷⁹BrN₄P: 653.3690 [($M + H$)]⁺; found: 653.3705.

Synthesis of 2.38 A toluene solution of **2.36** (0.130 g, 0.2 mmol) in a Schlenk flask was degassed by a freeze–pump–thaw method. Then, CO₂ (1 bar) was filled. The resulting solution changed from reddish purple to colorless immediately. After 10 min of stirring, the solution was filtered. The filtrate was concentrated and kept at –20 °C

for 1 day to give **2.38** as a colorless crystalline solid (0.12 g, 0.178 mmol, 88% yield). M.p.: 193 °C. ¹H NMR (399.5 MHz, 25 °C, C₆D₆): δ 7.66–7.64 (m, 2 H, ArH), 7.14–7.02 (m, 2 H, ArH), 6.92–6.88 (m, 3 H, ArH), 6.79–6.75 (m, 1 H, ArH), 3.83 (sept, 1 H, CHMe₂, $J_{\text{HH}} = 7.2$ Hz), 3.63 (s, 3 H, N-CH₃), 2.83 (sept, 1 H, CHMe₂, $J_{\text{HH}} = 7.2$ Hz), 2.61 (s, 3 H, N-CH₃), 1.69 (d, 3 H, CHMe₂, $J_{\text{HH}} = 7.3$ Hz), 1.67 (dd, 18 H, *t*Bu, $J_{\text{PH}} = 12.8$ Hz), 1.37 (s, 3 H, C-CH₃), 0.92 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz), 0.87 (s, 3 H, C-CH₃), 0.74 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.4$ Hz), 0.09 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz). ¹¹B{¹H} NMR (128 MHz, 25 °C, C₆D₆): δ -5.47 (s), -17.86 (s). ³¹P{¹H} NMR (162 MHz, 25 °C, C₆D₆): δ 39.66 (br). ¹³C{¹H} NMR (101 MHz, 25 °C, C₆D₆): 168.72 (d, $J = 8.7$ Hz, NCN), 148.99 (C-carbene), 144.31 (CH-Ar), 142.42 (CH-Ar), 141.10 (d, $J = 15.4$ Hz, C-Ar), 130.53 (CH-Ar), 128.52 (CH-Ar), 127.28 (CH-Ar), 127.10 (CH-Ar), 126.76 (CH-Ar), 125.71 (C-Ar), 124.72 (C-Ar), 124.45 (C-Ar), 123.88 (CCH₃), 123.72 (CCH₃), 38.46 (d, $J = 44.3$ Hz, PC(CH₃)), 38.08 (d, $J = 44.3$ Hz, PC(CH₃)), 34.37 (NCH₃), 31.85 (NCH₃), 28.64 (CH(CH₃)₂), 27.88 (d, $J = 28.9$ Hz, PC(CH₃)), 26.71 (CH(CH₃)₂), 25.66 (CH(CH₃)₂), 25.09 (CH(CH₃)₂), 24.86 (CH(CH₃)₂), 22.87 (CH(CH₃)₂), 7.53 (CH₃), 7.31 (CH₃). HRMS (ESI): m/z calcd for C₃₅H₅₃B₂⁷⁹BrN₄O₂P: 693.3276 [($M + H$)]⁺; found: 693.3302.

Synthesis of 2.39 A toluene solution of **2.36** (0.130 g, 0.2 mmol) and tris(pentafluorophenyl)borane (0.110 g, 0.2 mmol) in a Schlenk flask was degassed by a freeze–pump–thaw method. Subsequently, CO₂ (1 bar) was filled. The resulting solution changed from red-purple to colorless immediately.

After 30 min of stirring, the solution was filtered. The filtrate was concentrated and kept at $-20\text{ }^{\circ}\text{C}$ for 1 day to afford **2.39** as a colorless crystalline solid (0.20 g, 0.168 mmol, 84% yield). M.p.: $161\text{ }^{\circ}\text{C}$. ^1H NMR (399.5 MHz, $25\text{ }^{\circ}\text{C}$, C_6D_6): δ 7.27-7.25 (m, 2 H, ArH), 7.08-6.90 (m, 2 H, ArH), 6.80-6.78 (m, 3 H, ArH), 6.64-6.61 (m, 1 H, ArH), 3.56 (s, 3 H, N-CH₃), 2.82 (sept, 1 H, CHMe₂, $J_{\text{HH}} = 7.2\text{ Hz}$), 2.49 (sept, 1 H, CHMe₂, $J_{\text{HH}} = 7.2\text{ Hz}$), 2.14 (s, 3 H, N-CH₃), 1.42 (dd, 18 H, *t*Bu, $J_{\text{PH}} = 12.8\text{ Hz}$), 1.42 (s, 3 H, C-CH₃), 1.13 (s, 3 H, C-CH₃), 0.95 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.4\text{ Hz}$), 0.81 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8\text{ Hz}$), 0.21 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8\text{ Hz}$), 0.10 (d, 3 H, CHMe₂, $J_{\text{HH}} = 6.8\text{ Hz}$). $^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, $25\text{ }^{\circ}\text{C}$, C_6D_6): δ -5.71, -20.32, -26.89. $^{19}\text{F}\{^1\text{H}\}$ NMR (376 MHz, $25\text{ }^{\circ}\text{C}$, C_6D_6): δ -131.31 (s, 1 F), -159.34 (t, 1 F, $J = 21.7\text{ Hz}$), -164.69 (dt, 1 F, $J = 21.7, 21.7\text{ Hz}$). $^{31}\text{P}\{^1\text{H}\}$ NMR: (162 MHz, $25\text{ }^{\circ}\text{C}$, C_6D_6): δ 37.44 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, $25\text{ }^{\circ}\text{C}$, C_6D_6): 168.48 (d, $J = 8.7\text{ Hz}$, NCN), 149.56 (C-F), 147.42 (C-carbene), 147.11 (C-F), 144.05 (CH-Ar), 141.74 (CH-Ar), 139.66 (d, $J = 16.3\text{ Hz}$, C-Ar), 138.33 (C-F), 137.58 (C-F), 135.73 (C-F), 130.89 (CH-Ar), 129.27 (CH-Ar), 129.01 (CH-Ar), 128.24 (CH-Ar), 127.61 (CH-Ar), 126.81 (C-Ar), 126.16 (C-Ar), 125.95 (C-Ar), 125.72 (C-Ar), 125.37 (CCH₃), 123.58 (CCH₃), 39.34 (d, $J = 45.7\text{ Hz}$, PC(CH₃)), 37.94 (d, $J = 39.5\text{ Hz}$, PC(CH₃)), 35.79 (NCH₃), 32.10 (NCH₃), 28.31 (d, $J = 38.5\text{ Hz}$, PC(CH₃)), 27.54 (CH(CH₃)₂), 26.82 (CH(CH₃)₂), 25.03 (CH(CH₃)₂), 24.21 (CH(CH₃)₂), 22.20 (CH(CH₃)₂), 21.11 (CH(CH₃)₂), 7.60 (CH₃), 7.53 (CH₃). HRMS (ESI): m/z calcd for $\text{C}_{53}\text{H}_{53}\text{B}_3^{79}\text{BrF}_{15}\text{N}_4\text{O}_2\text{P}$: 1205.3129 [(*M* + *H*)⁺]; found: 1205.3145.

2.4.4. Catalytic Studies

2.4.4.1. Synthesis of Compounds 2.40a–c. Catalyst **2.36** (0.026 g, 0.04 mmol), cyclohexane (internal standard, 0.168 g, 2 mmol, 50 equiv), and deuterated benzene (0.5 mL) were placed in a J. Young NMR tube. HBpin (0.256 g, 2 mmol, 50 equiv) was subsequently added. After that, the J. Young NMR tube was dipped in liquified nitrogen, which froze the reaction mixture. It was degassed using a freeze–pump–thaw method. Carbon dioxide (1 bar) was then filled. The reaction mixture was warmed from r.t.p. to 110 °C for 1.5 h. The catalysis was monitored using ¹H NMR spectroscopy. The yields were calculated on the basis of the integration of ¹H NMR signals of pinBOMe (**2.40b**) at 1.05 and 3.51 ppm and (pinB)₂O (**2.40c**) at 1.02 ppm relative to the –CH₂ signal of cyclohexane (internal standard) at 1.37 ppm. The chemical shifts of the products agree with the reported values in the literature and independent in situ NMR scale syntheses.^[46]

Entry	Substrate	Catalyst (X mol%)	Product	T (°C)	time (h)	Conversion (%)	Yield (%)	TOF (h ⁻¹)
1	CO ₂	0%	2.40a	110	12	0	0	0
			2.40b				0	
			2.40c				0	
2	CO ₂	2%	2.40a	25	1	17.8	7.5	8.8
			2.40b				0	
			2.40c				8.2	
3	CO ₂	2%	2.40a	60	2	31.4	0	7.8
			2.40b				30.1	
			2.40c				31	
4	CO ₂	2%	2.40a	60	12	99	0	4.1
			2.40b				97.6	
			2.40c				99	
5	CO ₂	2%	2.40a	90	3	86.7	0	14.4
			2.40b				82.9	
			2.40c				85.5	
6	CO ₂	2%	2.40a	90	5	99	0	9.9
			2.40b				98.6	
			2.40c				99	
7	CO ₂	2%	2.40a	110	1	84.0	0	42.0
			2.40b				82.1	
			2.40c				83.8	
8	CO ₂	2%	2.40a	110	1.5	99	0	33.3
			2.40b				97.8	
			2.40c				99	
9	CO ₂	1%	2.40a	110	7	99	0	14.3
			2.40b				96	
			2.40c				99	

2.4.4.2. Synthesis of Compounds 2.41a–d. Catalyst **2.36** (1.3 mg, 0.002 mmol), 9-BBN (0.012 g, 0.1 mmol, 50 equiv), and C₆D₆ (0.5 mL) were placed in a J. Young NMR tube. The solution was degassed by a freeze–pump–thaw method as described in the synthesis of **2.40a–c**. Carbon dioxide (1 bar) was then filled. After that, the resulting mixture was warmed from r.t.p. to 110 °C. The catalysis was checked by ¹H NMR spectroscopy at time intervals of 20 min,

$$\text{CO}_2 + 9\text{-BBN} \xrightarrow[\text{C}_6\text{D}_6, \text{ temp } ^\circ\text{C}]{\text{Catalyst } \mathbf{2.36} \text{ (2 mol\%)}} (\text{BBN})\text{OC(O)H} + \text{CH}_2(\text{BBN})_2 + \text{MeO}(\text{BBN}) + \text{O}(\text{BBN})_2$$

time h

2.41a **2.41b** **2.41c** **2.41d**

Entry	Substrate	Product	T (°C)	time (h)	Conversion (%)	Yield (%)	TOF (h ⁻¹)
1	CO ₂	2.41a	25	10min	12.8	1.8	38.4
		2.41b				6.4	
		2.41c				4.3	
2	CO ₂	2.41a	110	1	53	0	26.5
		2.41b				27.5	
		2.41c				24.3	
3	CO ₂	2.41a	110	20	99	0	2.5
		2.41b				0	
		2.41c				92	

CO_2 + $\text{R}^1\text{-N(R}^2\text{)-H}$ (2.42) $\xrightarrow[\text{C}_6\text{D}_6, \text{ T } ^\circ\text{C}]{\text{Catalyst 2.36 (X mol \%), 2 equiv. HBpin}}$ $\text{R}^1\text{-N(R}^2\text{)-C(=O)-H}$ (2.43)

Entry	Amines	Product	X	T (°C)	Time (h)	Conversion (%)	Yield (%)	TOF (h ⁻¹)
1	2.42a	2.43a	5	60	5	>99	-	4.4
2	2.42a	2.43a	5	90	1.5	>99	98	13.3
3	2.42a	2.43a	2	90	4	>99	-	12.5
4	ⁿ BuNH ₂ 2.42b	2.43b	5	90	0.5	>99	95	40.0

5	<chem>MeO(CH2)3NH2</chem> 2.42c	<chem>MeOCH2CH2CH2NHC=O</chem> 2.43c	5	90	0.5	>99	96	40.0
6	<chem>CCNCC</chem> 2.42d	<chem>CCN(CC)C=O</chem> 2.43d	5	90	0.4	>99	92	50.0
7	<chem>C1CCNCC1</chem> 2.42e	<chem>C1CCN(CC1)C=O</chem> 2.43e	5	90	0.6	>99	98	33.3
8	<chem>CN(C)Cc1ccccc1</chem> 2.42f	<chem>CN(C)Cc1ccccc1C=O</chem> 2.43f	5	90	6.0	91	81	3.1
9	<chem>C1CN2C=CC=CC=C2C1</chem> 2.42g	<chem>C1CN2C=CC=CC=C2C1C=O</chem> 2.43g	5	90	12	82	81	1.4

2.4.4.4. Control reactions for N-formylation of amines with CO₂ and HBpin.

Entry	2.36	HBpin	2.42e	CO ₂	T(°C)	Time(min)	Product / conversion
1	1 eq.	1 eq.	-	-	90	120	No reaction
2	1 eq.	-	1 eq.	-	25	120	No reaction
3	1 eq.	-	-	1 atm	0	1	2.38 / 99%
4	-	1 eq.	1 eq.	-	90	90	Boryl amine and H ₂ / 99%
5	-	1 eq.	1 eq.	1 atm	90	120	Boryl amine and H ₂ / 99%
6	5%	4 eq.	1 eq.	1 atm	90	120	No N-formylation product Mixture

2.4.4.5. Catalytic Reaction of Aldehydes and Ketones with HBpin: General Procedure. Catalyst **2.36** (0.013 g, 0.02 mmol) and C₆D₆ (0.5 mL) were mixed in a J. Young NMR tube. Pinacolborane (0.052 g, 0.41 mmol, 20.1 equiv) and carbonyl compounds (0.40 mmol, 20 equiv) were subsequently added. The catalytic settings are given (see below). The catalyses were checked by ¹H NMR spectroscopy to calculate their yields. The chemical shifts of the products are consistent with the reported values in the literature.^[46] All of the catalytic trials were performed three times.

Entry	Substrates	Product	X	T (°C)	Time (min)	Conversion (%)	Yield (%)	TOF (h ⁻¹)
1	<chem>O=Cc1ccccc1</chem> 2.44a	<chem>OCc1ccccc1OBpin</chem> 2.45a	0	24	120	3	-	-

2	2.44a	2.45a	2	24	90	98	-	32.7
3	2.44a	2.45a	5	24	30	99	97	39.6
4	2.44b	2.45b	5	24	60	96	94	19.2
5	2.44c	2.45c	5	24	60	96	95	19.2
6	2.44d	2.45d	5	24	45	>99	95	26.7
7	2.44e	2.45e	5	24	30	91	87	36.4
8	2.44f	2.45f	5	24	5	>99	82	240.0
9	2.44g	2.45g	5	24	5	88	81	211.2
10	2.44h	2.45h	5	24	5	>99	92	240.0
11	2.44j	2.45j	5	24	60	94	93	18.8
12	2.44k	2.45k	5	24	15	99	82	80.0
13	2.44l	2.45l	5	24	5	>99	88	240.0
14	2.44m	2.45m	5	24	5	>99	89	240.0
15	2.44n	2.45n	7	90	3h	>99	98	6.7
16	2.44p	2.45p	7	90	24h	87	85	0.8

17	2.44q	2.45q	7	90	24h	82	80	0.7
18	2.44r	2.45r	7	90	1h	>99	95	20.0

2.5. Appendices

2.5.1. X-Ray crystallographic data for compounds 2.35, 2.36 and 2.37.

	2.35	2.36·(Toluene)₂	2.37·(Toluene)₁
Formula	C ₂₇ H ₄₀ B ₂ Br ₃ N ₂ P	C ₄₁ H ₆₀ B ₂ BrN ₄ P	C _{37.50} H ₆₀ B ₂ BrN ₄ P
Fw	684.93	741.43	699.39
T/K	100(2)	100(2)	100(2)
cryst system	monoclinic	triclinic	triclinic
space group	<i>P</i> 1 21/ <i>n</i> 1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	11.6265(3)	11.2399(4)	11.2299(5)
<i>b</i> (Å)	14.0626(3)	12.4755(5)	12.7354(7)
<i>c</i> (Å)	36.8284(7)	16.2335(6)	15.0632(8)
α (deg)	90	70.7560(10)	87.2738(18)
β (deg)	93.6517(9)	70.8120(10)	80.4567(16)
γ (deg)	90	80.5830(10)	67.1822(17)
<i>V</i> (Å ³)	6009.2(2)	2025.82(13)	1957.90(17)
<i>Z</i>	8	2	2
<i>d</i> _{calcd} (g cm ⁻³)	1.514	1.215	1.186
μ (mm ⁻¹)	4.100	1.087	1.121
<i>F</i> (000)	2768	788	746
cryst size (mm)	0.06*0.10 x*0.12	0.04*0.20*0.22	0.04*0.06*0.10
2 θ range (deg)	4.737 < 2 θ < 59.46	5.044 < 2 θ < 58.64	5.188 < 2 θ < 57.52
index range	-17 ≤ <i>h</i> ≤ 17, - 20 ≤ <i>k</i> ≤ 20, - 54 ≤ <i>l</i> ≤ 46	-16 ≤ <i>h</i> ≤ 16, - 17 ≤ <i>k</i> ≤ 18, - 22 ≤ <i>l</i> ≤ 23	-12 ≤ <i>h</i> ≤ 16, - 18 ≤ <i>k</i> ≤ 18, - 22 ≤ <i>l</i> ≤ 22
no. of rflns collected	77157	46756	79469
no. of indep rflns	19841	12849	13043
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0500/0.0788	0.0616/0.1378	0.0558/0.0822
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1238/0.0997	0.1323/0.1696	0.1168/0.1018
goodness of fit, <i>F</i> ²	1.007	1.023	1.023
no. of data/restraints/params	19841 / 0 / 651	12849 / 224 / 497	13043 / 102 / 457
largest diff peak and hole, eÅ ⁻³	0.679/-0.690	0.782/-1.117	0.549/-0.612

2.5.1. X-Ray data for compounds 2.38 and 2.39.

	2.38 ·(Toluene) _{0.5}	2.39 ·(Toluene) ₁
Formula	C _{36.75} H ₅₄ B ₂ BrN ₄ O ₂ P	C ₆₀ H ₆₀ B ₃ BrF ₁₅ N ₄ O ₂ P
Fw	716.34	1297.43
T/K	100(2)	100(2)
cryst system	monoclinic	triclinic
space group	P 1 2/c 1	P -1
a (Å)	17.7337(5)	12.5052(4)
b (Å)	11.1930(3)	13.3489(4)
c (Å)	37.9253(9)	36.4456(11)
α (deg)	90	99.9302(11)
β (deg)	92.1900(12)	90.3086(11)
γ (deg)	90	102.3182(11)
V (Å ³)	7522.4(3)	5849.2(3)
Z	8	4
d _{calcd} (g cm ⁻³)	1.256	1.473
μ (mm ⁻¹)	1.172	0.826
F(000)	3028	2656
cryst size (mm)	0.14*0.20*0.22	0.02*0.03*0.20
2θ range (deg)	4.850 < 2θ < 58.32	4.864 < 2θ < 57.37
index range	-25<=h<=24, - 16<=k<=16, - 54<=l<=54	-16<=h<=16, - 18<=k<=17, - 49<=l<=49
no. of rflns collected	86206	124893
no. of indep rflns	23916	30117
R1, wR2 (I > 2σ(I))	0.0474/0.1003	0.0646/0.1122
R1, wR2 (all data)	0.0896/0.1169	0.1473/0.1473
goodness of fit, F ²	1.021	1.010
no. of data/restraints/params	23916 / 0 / 891	30117 / 327 / 1608
largest diff peak and hole, eÅ ⁻³	0.521 / -0.821	0.643 and -0.779

2.5.2. NMR Spectra of all new compounds (D-solvent and NMR frequency are shown in section 2.4.3)

2.35: ^1H

2.35: $^{11}\text{B}\{^1\text{H}\}$

2.35: $^{31}\text{P}\{^1\text{H}\}$

2.35: $^{13}\text{C}\{^1\text{H}\}$

2.36: ^1H

2.36: $^{11}\text{B}\{^1\text{H}\}$

2.36: $^{31}\text{P}\{^1\text{H}\}$

2.36: $^{13}\text{C}\{^1\text{H}\}$

2.37: ^1H

2.37: $^{11}\text{B}\{^1\text{H}\}$

2.37: $^{31}\text{P}\{^1\text{H}\}$

2.38: ^1H

2.38: $^{11}\text{B}\{^1\text{H}\}$

2.38: $^{31}\text{P}\{^1\text{H}\}$

2.38: $^{13}\text{C}\{^1\text{H}\}$

2.39: ^1H

2.39: $^{11}\text{B}\{^1\text{H}\}$

2.39: $^{19}\text{F}\{^1\text{H}\}$

2.39: $^{31}\text{P}\{^1\text{H}\}$

2.39: $^{13}\text{C}\{^1\text{H}\}$

2.5.3. Theoretical Studies

All geometry optimizations were computed using the M06-2X functional with def2-SVP basis set as implemented in the Gaussian 09 package of programs.^[47] The potential energy was refined by single point calculation with larger basis sets (def2-TZVP). The SMD model was used as the implicit solvent model with the dielectric constant of $\epsilon = 2.2706$ (benzene). The vibrational frequency calculations were performed to establish the nature of stationary points. The local minima were confirmed by zero imaginary frequencies, and transition states were characterized by an imaginary frequency. In the free energy profile, the Gibbs free energy (ΔG) was calculated at 298.15 K and 1 atm.

List of abbreviations used in theoretical studies.

Abbreviation	Definition
Cpd	Compound
HBpin	Pinacolborane
Int	Intermediate
TS	Transition state
MeOBpin	Methoxyborane

List of colour coded atoms used in optimised structures

Abbreviation	Definition
White	Hydrogen
Grey	Carbon
Blue	Nitrogen
Red	Oxygen
Pink	Boron
Yellow/Orange	Phosphorus
Brown	Bromine

2.5.3.1. Optimised geometries of the minimal and transition states at M06-2X/def2-TZVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

2.5.3.2. Molecular orbitals of compound 2.36.

2.5.3.3. Natural Localized Molecular Orbitals (NLMOs) of B=B bond of compound **2.36.**

2.5.3.4. Natural bond orbital (NBO) analysis of compound **2.36.^[48]**

Bond Length (Å)	WBI	Natural Charge (B ₁ , B ₂)	Bond Type	Occupancy	Polarization (B ₁ , B ₂)	Hybridization (B ₁ , B ₂)
1.561	1.55	(-0.55, 0.09)	σ	1.93	(50.2%, 49.8%)	(s ¹ p ^{1.31} , s ¹ p ^{1.41})
(1.561) ^a			π	1.69	(54.2%, 45.8%)	(s ¹ p ^{99.99} , s ¹ p ^{99.99})

^a Experimental value is adopted from crystal structure.

2.5.3.5. Nucleus - Independent Chemical Shifts (NICS) computations for **2.36^a.**

System	NICS _{zz} (1) (ppm)
Compound 2.36	-4.6
Benzene	-30.9

^a Calculated at the GIAO - MO6 - 2X/def2 – TZVP.

2.6. References

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CHAPTER 3: A Base stabilized Diborene Cation: Multifunctional Cationic

B=B⁺ Double Bond

3.1. Introduction

Boron(III) cations are electrophilic and well-known Lewis acidic reagents in stoichiometric and catalytic organic transformations,^[1] which have been widely studied. For example, one of the most significant boron(III) cationic compound is the diarylborinium ion **3.1**^[2] reported by Fukushima and co-workers, which showed versatile reactivity in stoichiometric reactions, including arylation-deoxygenation of CO₂,^[2] splitting of H₂,^[3] and activation of diphenylacetylene.^[4] In addition, Lewis bases (NHC or 2,6-lutidine) stabilized 9-BBN borenium ion (**3.2** and **3.3**) exhibited a variety of catalytic reactions, such as hydrogenation of imines^[5] and hydrosilylation of aryl ketones.^[6]

Scheme 3.1. Examples of boron(III) cation compounds.

In contrast, low-oxidation-state boron cations are extremely rare and their reactivity are unconventional in comparison with boron(III) cations. As an illustration, Wang and co-worker reported the synthesis of ^{Me}NHC-

borylborenium cation $[\text{MeNHC-B(Mes)-Bpin}]^+$ ($\text{MeNHC} = \text{:C}\{\text{N(Me)C(Me)}\}_2$), which composed of a B(II) cation and B-B single bond.^[7] MeNHC supported arylborane **3.4** was treated with iodine to give iodination product, which was further reacted with iPrNHC-CuBpin to give unsymmetric diboron compound **3.5**. The hydride abstraction of **3.5** with $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ produced borylborenium cation **3.6**. Owing to the presence of electrophilic boron centers, **3.6** was reacted with DMAP (4-dimethylaminopyridine) to form the corresponding Lewis base-acid adduct **3.7**. Interestingly, borylborenium cation **3.6** was capable of activating dihydrogen gas by the B(II) centre and the polarized B–B⁺ bond in a concurrent addition and elimination process to form complex **3.8**. The result of this study provided a better understanding of H_2 activation and offered a new approach for activating other element-element bonds involving low-valent cationic boron compounds.

Scheme 3.2. Synthesis and reactivity of NHC-borylborenium cation **3.6**.

Another important example of low-valent boron cations was the bis(silylene)-stabilized borylene cation-carbon monoxide complex **3.11**, which was reported by Xie group in 2017.^[8] Treatment of o-carborane based bis(silylene) ligand **3.9** with two equivalents of boron tribromide in toluene. The subsequent reduction with excess KC_8 in THF afforded the neutral bromoborylene complex **3.10** stabilized by bis(silylene). The reaction of neutral borylene **3.10** with $W(CO)_6$ in THF at 80 °C, forming the unprecedented borylene cation **3.11**. In this reaction, a carbon monoxide ligand in $W(CO)_6$ displaced the Br substituent in compound **3.10** to give **3.11** instead of forming donor-acceptor complex between the bromoborylene and $W(CO)_6$. Owing to the presence of a highly reactive B(I) cation centre, compound **3.11** showed potential reactivity towards small molecules activation. Treatment of **3.11** with dihydrogen gas (H_2 or D_2) in THF at 80 °C produced the borane cationic complex **3.12** through oxidative addition mechanism concomitant with the dissociation of CO. This study showed the syntheses and reactivity of unprecedented neutral and cationic borylene complexes, which served as valuable foundation for the further development of unusual low-valent boron compounds.

Scheme 3.3. Synthesis and H_2 activation of B(I) cation complex **3.11**.

In addition, Himmel and coworkers isolated a class of diboron(II) dicationic compounds using bicyclic guanidine 1,5,7-triazabicyclo[4.4.0]dec-5-ene (hppH) as a supporting ligand.^[9] These diboron(II) cations possess double reactivity pattern, acting as both electron acceptors and donors, which allow acceptance of the electrons from a Lewis base to the vacant B-B p orbital as well as transfer of the B-B σ bond electrons to the vacant orbital of a Lewis acid. To prove this concept, they systematically investigated the reactivity of guanidinato diboron(II) dications with different organic ligands.^[10]

Scheme 3.4. Synthesis of boron(II) cationic compounds.

Firstly, the reactions of doubly triflate-substituted diborane $[(\text{TfO})\text{B}(\text{hpp})]_2$ **3.13** with σ and π -donating 1,2-bis(tetramethylguanidino) benzene (btmgb) and 1,4,5,8-tetrakis(tetramethylguanidino) naphthalene (ttmgn) were carried out in CH_2Cl_2 . **3.13** was a good starting material to obtain boron(II) cationic compounds owing to the double readily exchangeable triflate substituents. After the reactions of **3.13** with ttmgn and btmgb, bis(diboron(II)) tetracationic compound **3.14** and diboron(II) dicationic compound **3.15** were isolated, respectively. Following which, π -acidic phenanthroline (phen) and pyrazino[2,3-f][1,10]phenanthroline (pzp) were used in a similar way to yield diboron(II) dicationic compounds **3.16** and **3.17**, respectively. The results showed that the

interaction between B-B σ orbital and vacant π orbital of ligands was not observed.

Scheme 3.5. The reaction of $[(\text{TfO})\text{B}(\text{hpp})]_2$ **3.13** with bq.

To show the feasibility of B-B σ bond as an electron donor, stronger π -acidic organic ligand was used to trigger this electron transfer. Treatment of diborane $[(\text{TfO})\text{B}(\text{hpp})]_2$ **3.13** with 3,5-bis-tert-butyl-1,2-benzoquinone (bq) in CH_2Cl_2 gave monocationic compound **3.20** as the product. The initial step of this reaction was the complexation to form dication **3.18**. The subsequent intramolecular electrons transfer from the B-B σ bond to the vacant π orbital of the ligand furnished **3.19** as an intermediate. As a result, the B-B σ bond was cleaved to form two B(III) centers and the bq ligand was reduced. Finally, one of triflate groups bonded with one B(III) cation to form complex **3.20**. Such dual properties of boron(II) dications as both electron acceptor and donor had opened a new perspective on low-valent boron cationic chemistry.

Scheme 3.6. The rearrangement of diboron(II) dication **3.21** to **3.22**.

Moreover, the same research group also demonstrated the rearrangement

of diboron(II) dication **3.21** to an unsymmetrical borylboron(II) dication **3.22**.^[11] Treatment of diboron compound $\text{B}_2\text{Cl}_2(\text{NMe}_2)_2$ with 1,2-bis(tetramethylguanidino) benzene ligand in the presence of halogen abstraction reagent OTfSiMe_3 at $-30\text{ }^\circ\text{C}$ furnished diboron(II) dication **3.21**. When the temperature increased to $25\text{ }^\circ\text{C}$, compound **3.21** was slowly isomerized to borylboron(II) dication **3.22** in a period of two hours. However, when catalytic amount of KF and [18]-crown-6 were added, this isomerization was completed within 15 minutes at $22\text{ }^\circ\text{C}$. This indicated that the nucleophilic F^- anion could catalyze the isomerization of diboron(II) dication. The experimental data showed that this isomerization was the first order reaction.

These new pattern of reactivity aroused our curiosity to discover a new class of low-oxidation-state boron cations that could possess catalytic capability toward small molecules. Among low-oxidation-state boron cations, base-stabilized diborene cation of composition $[\text{R}(\text{L})\text{B}=\text{B}(\text{L})]^+$ (R = substituent, L = Lewis base donor) composing of a Lewis acidic boron(I) cation and a reactive $\text{B}=\text{B}$ double bond has been our sought-after targets as the remarkable electronic structure could promote activating small molecules in a new fashion, leading to possible application in catalysis.

In this chapter, a pyridine-NHC-stabilized *N*-phosphinoamidinato diborene cation was synthesized and its dual functionality of the cationic boron-boron double bond was demonstrated in episulfidation and activation of pyridine. The

latter further showed that diborene cation and diaminodiborene played a vital role in the diborene-catalyzed hydroboration of pyridine derivatives.

3.2. Results and Discussion

To begin with, the *N*-phosphinoamidinato NHC-diborene **2.36**^[12] was used to react with excess pyridine in toluene at 90 °C for three days (**Scheme 3.7**). The colour of the reaction mixture was observed to turn from reddish purple to green. Following filtration and recrystallization in fluorobenzene, the pyridine-stabilized *N*-phosphinoamidinato NHC-diborene cation **3.33** was obtained as a black crystalline solid. Pyridine displaced a Br substituent in compound **2.36** to form a cationic $^+B=B$ bond skeleton in complex **3.33**. Such simple displacement reaction surprisingly were not reported in other Lewis base-dihalodiborene complexes.^[13-14] Recent report shows that displacement of the iodide substituent from the B-B double bond in a labile phosphine-diiododiborene complex $[(Cy_3P)B(I)=B(I)(PCy_3)]$ was not feasible.^[15] NMR was probed and X-ray crystallography was done to characterize compound **3.33**. The signal in 1H NMR spectroscopy shows the presence of *N*-phosphinoamidinate, NHC and pyridine backbone. The two signals at 16.7 and 33.3 ppm in the $^{11}B\{^1H\}$ NMR spectrum indicated that complex **3.33** has a polarized cationic $^+B=B$ bond. Accordingly, the resonances are downfield shifted as compared to those of **2.36** (10.5, 28.8 ppm) because of the presence of boron cation. The resonance at 44.6 ppm in the $^{31}P\{^1H\}$ NMR is close to that of **2.36** (45.9 ppm). Molecular structure of complex **3.33** is confirmed by X-ray crystallography, containing a planar six-membered ring skeleton with cationic boron-boron double bond

(**Figure 3.1a**). The length of B1-B2 bond (1.576(8) Å) is slightly elongated as compared to the length of B-B double bond in compound **2.36** (1.562(5) Å), owing to the presence of boron cation. Pyridine coordinates with the $^+B=B$ bond with the bond length of 1.545(6) Å (B2-N3), which is similar to the N-B coordinative covalent bond (1.559(9) Å) in the amidinato silylene-DMAP-boronium cation.^[16] In addition, the phosphine (P1-B2: 1.846(5) Å) and NHC (B1-C20: 1.583(7) Å) donors are bonded to the cationic boron-boron double bond in a *trans*-position. Their bond lengths are comparable with those of compound **2.36** (B-C_{NHC}: 1.590(4), B-P: 1.852(3) Å), respectively. The B2...Br1 distance (5.230(5) Å) suggests no interaction between the boron cation and bromide anion.

Scheme 3.7. Synthesis and reactivity of **3.33-3.37**.

To better understand the electronic structure of compound **3.33**, DFT calculations (M06-2X/def2-SVP) was carried out. HOMO exhibits B=B π orbital

(**Figure 3.1b**), while LUMO shows π^* orbital of the pyridine substituent (**Figure 3.1c**). Accordingly, the NBO analysis indicates that the B1-B2 σ bond is arisen from the mixing of $sp^{1.41}$ (B1) and $sp^{1.64}$ hybrids (B2) on the boron atoms. The mixing of B p orbitals with polarization toward the B2 atom (57.2% B2 + 42.9% B1) gave the B1-B2 π bond. B2-B1 bond has double bond character as suggested by the WBI of 1.48. Furthermore, the B2-N3 bond is highly polarized toward the N atom (19.7% B2 + 80.3% N3), which is formed by the overlapping of $sp^{1.59}$ hybrids on the N3 atom with the $sp^{2.44}$ hybrids on the B2 atom. Since the orbital terms of S-S is smaller than the one of T-T ($|\Delta E_{orb}(S-S)| = 158.2 < |\Delta E_{orb}(T-T)| = 302.7$), thus the EDA-NOCV calculations (BP86/TZP//M06-2X/def2-SVP) shows that pyridine forms a dative bond with the cationic boron-boron double bond in complex **3.33**.

Figure 3.1. (a) X-ray crystal structures of **3.33**. Thermal ellipsoids are illustrated at 50 % probability. For clarity, hydrogen atoms has been erased. Selected bond lengths (Å) and angles (deg): B1-B2 1.576(8), B1-C33 1.583(7), B2-N3 1.545(6), B2-P1 1.846(5), N1-B1 1.515(6), C33-B1-B2 115.0(4), B1-B2-N3 121.8(4), P1-B2-B1 112.4(4), B2-B1-N1 124.7(4). (b) HOMO. (c) LUMO.

The double bond character in the cationic diborene was illustrated in the episulfidation of compound **3.33** with elemental sulfur (**Scheme 3.7**). The

reaction turned from green to yellow. After which, it was left to stir at room temperature for 10 mins. Volatiles were then removed to afford the pyridine-NHC-stabilized *N*-phosphinoamidinato diborathiirane cation **3.34**. In a similar fashion, compound **3.33** was reacted with elemental selenium in toluene at -78°C for 10 min to form the diboraselenirane cation **3.35** (**Scheme 3.7**). In these reactions, compound **3.33** underwent two-electron oxidation of the cationic boron-boron double bond with a sulphur and selenium atom to form **3.34** and **3.35**, respectively. Compounds **3.34** and **3.35** are the first diborathiirane and diboraselenirane cations, respectively. They were isolated as a yellow crystalline solid from their concentrated fluorobenzene solution. The boron centers are four-coordinate as indicated by the upfield shifted signals in the $^{11}\text{B}\{^1\text{H}\}$ NMR spectroscopy (**3.34**: -8.5, -11.5; **3.35**: -5.1, -7.7 ppm) as compared to that of compound **3.33**. In addition, the resonance of **3.34** (43.7 ppm) in the $^{31}\text{P}\{^1\text{H}\}$ NMR is comparable with that of **3.35** (42.8 ppm). The $^{77}\text{Se}\{^1\text{H}\}$ NMR signal of **3.35** (-361.5 ppm, $J_{\text{P-Se}} = 96$ Hz) suggests the presence of bridging selenium. These spectroscopic data indicate a chalcogen atom bridged across the B-B single bond in compounds **3.34** and **3.35**. The conclusion is further confirmed by X-ray crystallographic structures composing of a B_2E three-membered cationic ring (**3.34**: E = S, **3.35**: E = Se; **Figure 3.2**). The B-B bond lengths (**3.34**: 1.708(5); **3.35**: 1.708(8) Å) show the presence of B-B single bond. The B-E bond lengths [**3.34**: E = S, 1.880(4), 1.925(3); **3.35**: E = Se, 2.039(6), 2.102(5) Å] are unequal, which are similar to the B-E_{bridging} bond in the

diborathiirane (1.873(3), 1.879(3)Å)^[17] and diboraselenirane (2.115(2) Å),^[18] respectively.

Figure 3.2. X-ray crystal structures of (a) **3.34** and (b) **3.35**. Thermal ellipsoids are illustrated at 50 % probability. For clarity, hydrogen atoms have been erased. (a) Selected bond lengths (Å) and angles (deg) of **3.34**: B1-B2 1.708(5), B1-C28 1.621(5), B2-N5 1.591(5), B2-P1 1.927(4), N1-B1 1.558(5), B1-S1 1.925(3), B2-S1 1.880(4), B1-S1-B2 53.33(16), B1-B2-S1 64.68(18), B2-B1-S1 61.99(17), N5-B2-B1 127.3(3), B2-B1-C28 116.7(3), P1-B2-B1 108.5(2), B2-B1-N1 122.7(3). (b) Selected bond lengths (Å) and angles (deg) of **3.35**: B1-B2 1.708(8), B1-C28 1.611(7), B2-N5 1.583(7), B2-P1 1.930(6), N1-B1 1.568(7), B1-Se1 2.102(5), B2-Se1 2.039(6), B1-Se1-B2 48.7(2), B1-B2-Se1 67.6(3), B2-B1-Se1 63.7(3), N5-B2-B1 127.8(4), B2-B1-C28 119.5(4), P1-B2-B1 108.5(3), B2-B1-N1 121.8(4).

In addition to the oxidation with elemental chalcogen, compound **3.3** underwent reduction with KC_8 in toluene at $-78\text{ }^\circ\text{C}$ (**Scheme 3.7**). The reaction colour immediately turned from green to dark blue. After which, it was stirred for 20 min at ambient temperature. Filtration was then done, followed by the concentration of the filtrate to obtain the *N*-phosphinoamidinato NHC-aminodiborene compound **3.36** as a dark red crystalline solid. It is considered

as a diaminodiborene derivative which was thought to be elusive in the reduction of aminoborane and diaminodiborane species.^[19-21] Its $^{11}\text{B}\{^1\text{H}\}$ NMR signals (19.9, 27.6 ppm) are comparable with that of compound **2.36**, suggesting the presence of boron-boron double bond, which corresponded to the X-ray crystal structure (**Figure 3.3**). The length of B1-B2 bond (1.591(5) Å) is comparable with that of B-B bond in **2.36**, while the length of B2-N5 bond (1.517(5) Å) is less than that of pyridine-diborene cation donor-acceptor interaction (1.545(6) Å) in **3.33**. The C30-C69 bond (1.567(4) Å) in compound **3.36** is a single bond.

Figure 3.3. X-ray crystal structures of (a) **3.37** and (b) **3.36**. Thermal ellipsoids are illustrated at 50 % probability. For clarity, all hydrogen atoms are erased. (a) Selected bond lengths (Å) and angles (deg): B1-B2 1.574(3), B1-C28 1.590(3), B2-N5 1.520(3), B2-P1 1.875(2), N1-B1 1.520(3), N5-B2-B1 124.71(19), B2-B1-C28 112.80(18), P1-B2-B1 109.39(16), B2-B1-N1 126.94(19). (b) Selected bond lengths (Å) and angles (deg): B1-B2 1.591(5), B1-C33 1.584(5), B2-N3 1.517(5), B2-P1 1.885(5), N1-B1 1.521(5), N3-B2-B1 125.4(5), B2-B1-C33 114.6(4), P1-B2-B1 109.3(3), B2-B1-N1 126.6(4).

Scheme 3.8. **3.33**-catalyzed hydroboration of pyridine and proposed catalytic mechanism.

The abovementioned reactivity suggests that compound **3.33** could have catalytic capability. To support the hypothesis, the catalytic hydroboration of pyridine was examined. First, there was no reaction between pyridine and HBpin in deuterated solvents (C_6D_6) at 110 °C. Second, 20 mol% of **3.33** was used to catalyze the hydroboration of pyridine **3.38a** with HBpin and $NaBPh_4$ (20 mol%) in C_6D_6 at 90 °C to form N-boryl-1,4-dihydropyridine (**3.39a**, Yield: 94%, TOF: 0.13 h^{-1} , **Scheme 3.8**). Third, $NaBPh_4$ was used to replace the Br^- counter-anion in compound **3.33** by BPh_4^- and facilitated the displacement of Br^- by pyridine in the catalysis (see below). It cannot catalyze the hydroboration

of pyridine. Fourth, it is proposed that the first step of catalysis involve the H-B bond of HBpin attacking the para position of pyridine in compound **3.33**. To support this, compound **3.33** was treated with a hydride reagent, namely $\text{KBH}(\text{sec-Bu})_3$ in toluene at $-78\text{ }^\circ\text{C}$ (**Scheme 3.7**). The reaction immediately turn from green to dark blue. It was left to stir for 30 min at ambient temperature. As a result, the *N*-phosphinoamidinato NHC-aminodiborene compound **3.37** was isolated. Its $^{11}\text{B}\{^1\text{H}\}$ NMR signals (18.2, 26.3 ppm) and X-ray crystallographic data (B1-B2: 1.574(3) Å, B2-N3: 1.520(3) Å; **Figure 3.3**) are comparable with those of **3.36**.

DFT calculations (M06-2X/def2-TZVP//M06-2X/def2-SVP) was done for the hydroboration of pyridine with HBpin. The catalytic cycle is proposed in **Scheme 3.8**. Pyridine coordinates with HBpin to form **PRC01** ($\Delta G = 2.5$ kcal/mol). The B-H bond in **PCR01** then attacks compound **3.33** through **TS01** ($\Delta G = 20.3$ kcal/mol) to obtain a mixture of **Int01** and **3.37** ($\Delta G = 14.8$ kcal/mol). The 1,4-dihydropyridine moiety in compound **3.37** barrierlessly attacks on the B cation in **Int01** to form **Int02**, while the Br^- counter-anion is bonded back to the boron-boron double bond to form compound **2.36** ($\Delta G = -6.2$ kcal/mol). Subsequently, the pyridine dissociates from N-boryl-1,4-dihydropyridine and displaces the Br substituent in compound **2.36** to form compound **3.39a** and regenerate compound **3.33** ($\Delta G = -11.4$ kcal/mol).

Experimental results and theoretical studies show that compound **3.33** is the first multiply bonded boron cation undergoing catalytic hydroboration of

pyridine. It is one of the very few non-metal main-group examples that catalyse such reaction, including the sterically hindered organoborane $\text{Ar}^{\text{F}}_2\text{BMe}$ ($\text{Ar}^{\text{F}} = 2,4,6\text{-tris(trifluoromethyl)phenyl}$),^[22] 1,3,2-diazaphosphenium triflate^[23] and NHC-silyliumylidene cation.^[24]

The catalysis can be extended to other pyridine derivatives using compound **2.36** as a pre-catalyst. 10 mol% of **2.36** alone was capable of catalyzing hydroboration of pyridazine **3.38b** and 3-cyanopyridine **3.38c** with HBpin at 90 °C in C_6D_6 (**Table 3.1**), which afforded the corresponding 1,4-hydroborated products as major products [**3.39b**, Yield: 94%, TOF: 1.18 h^{-1} and **3.39c**, Yield: 73%, TOF: 0.68 h^{-1}]. In case of **3.38c**, 1,2- (Yield: 5%) and 1,6-hydroborated products (Yield: 16%) were formed. Moreover, **2.36** displays less activity in the hydroboration of 3-bromopyridine **3.38d** with higher electron density of the aromatic ring, leading to a drop of the hydroboration yield (Yield of **3.39d**: 12%, TOF: 0.05 h^{-1}). It is proposed that the catalysis should proceed through an active diborene cation catalyst and a diamianodiborene intermediate similar to **Scheme 3.8**.

Table 3.1. Scope of Pyridine Substrates

	3.39b	3.39c	3.39d
	94%, 1.18 h ⁻¹	73%, 0.68 h ⁻¹	12%

Yields were derived from their ¹H NMR spectroscopy by monitoring the consumption of pyridine derivatives. Cyclohexane was used as an internal standard. The product was validated by the resonances in the ¹H NMR spectroscopy. Reaction conditions: pyridine substrates (0.10 mmol), HBpin (0.11 mmol), C₆D₆ (0.50 mL), catalyst **2.36** (10 mol%).

3.3. Conclusion

In conclusion, the pyridine-NHC-stabilized *N*-phosphinoamidinato diborene cation **3.33** was synthesized by the displacement of the Br substituent in the NHC-diborene compound **2.36** with pyridine. Compound **3.33** is a multiply bonded boron cation composing of a cationic $^+B=B$ bond. It underwent oxidation with elemental sulphur to form the diborathirane cation **3.34**, as well as reduction with KC_8 to form the diaminodiborene **3.36**. Compound **3.33** was capable of catalyzing the hydroboration of pyridine with HBpin to form N-boryl-1,4-dihydropyridine. The catalytic mechanism studies show that the H-B bond of HBpin attacks the para position of pyridine in compound **3.33** to form the diaminodiborene **3.37**, which then reacts with $Bpin^+$ to form N-boryl-1,4-dihydropyridine.

3.4. Experimental

3.4.1. General procedure.

All procedures follow Chapter 2, section 2.4.1, page 94 of this thesis.

3.4.2. X-ray data collection.

The X-ray diffraction intensity data for compound **3.33**, **3.34**, **3.35**, **3.36** and **3.37** were using the same equipment and parameters as Chapter 1, section 1.4.2, page 35 of this thesis using the SMART suite of programs.^[25] Data processing, correction, structural solution and refinement were done similar with the SHELXTL suite of programs.^[26] Selected crystallographic data is provided in section 3.5.1.

3.4.3. The syntheses and characterization procedures.

Synthesis of 3.33: The diborene **2.36**^[27] (0.33 g, 0.5 mmol) was reacted with excess pyridine (0.79 g, 10 mmol) in toluene at 90 °C for three days. The reaction solution was observed to turn from reddish purple to green. Volatiles were removed via vacuo to obtain compound **3.33** as a green solid in 87 % yield (0.31 g, 0.43 mmol).

Recrystallization from the saturated PhF solution gave black crystals of **3.33** at r.t.p. **M.p.:** 219 °C. **¹H NMR (399.53 MHz, CD₃CN, 25 °C):** δ 8.07 (d, 2 H, Pyridine *H*, *J*_{HH} = 5.9 Hz), 7.52 (m, 1 H, Ar*H*), 7.39 (d, 2H, Pyridine *H*, *J*_{HH} = 8.2 Hz), 7.23-7.20 (m, 3 H, Ar*H*), 7.14-7.12 (m, 1 H, Pyridine *H*), 7.07-7.03 (m, 4 H, Ar*H*), 3.16 (s, 6 H, N-CH₃), 2.97 (sept, 2 H, CHMe₂, *J*_{HH} = 7.2 Hz), 1.90 (s, 6 H, C-CH₃), 1.35 (d, 18 H, *t*Bu, *J*_{PH} = 13.8 Hz), 0.78 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz), 0.71 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz). **¹¹B{¹H} NMR (128 MHz, CD₃CN, 25 °C):** δ 33.3 (br), 16.7 (br). **³¹P{¹H} NMR (162 MHz, CD₃CN, 25 °C):** δ 44.6 (br). **¹³C{¹H} NMR (101 MHz, CD₃CN, 25 °C):** 157.5 (C-carbene), 144.7 (C-Ar), 143.0 (C-Ar), 134.4 (C-Ar), 130.5 (C-Ar), 128.2 (C-Ar), 127.9 (C-Ar), 126.8 (C=C), 125.9 (C-Ar), 124.9 (C-Ar), 38.7 (d, *J* = 43.3 Hz, PC(CH₃)), 33.3 (NCH₃), 27.9 (CH(CH₃)₂), 27.1 (d, *J* = 2.9 Hz, PC(CH₃)), 24.2 (CH(CH₃)₂), 23.1 (CH(CH₃)₂), 7.8 (CH₃). HRMS (ESI): *m/z* calcd for C₃₉H₅₈B₂⁷⁹BrN₅P: 728.3799 [(*M* + *H*)⁺]; found: 728.3813.

Synthesis of 3.34: Compound **3.33** (0.36 g, 0.5 mmol) was reacted with S powder (0.032 g, 1 mmol) in toluene at -78 °C. The reaction was observed to change immediately from green to yellow. The reaction mixture was then stirred for 10 min at room temperature. The yellow suspension was dried under vacuum to remove all volatiles to give

3.34 as a yellow solid in 91 % yield (0.34 g, 0.455 mmol). Yellow single crystals were then obtained via recrystallization from the saturated fluorobenzene solution of **3.34** at r.t.p.. **M.p.:** 212 °C. **¹H NMR (399.5 MHz, CD₃CN, 25 °C):** δ 8.62 (d, 2 H, Pyridine *H*, *J*_{HH} = 6.4 Hz), 8.10 (t, 1 H, Pyridine *H*, *J*_{HH} = 7.8 Hz), 7.60 (t, 2 H, Ar*H*, *J*_{HH} = 6.8 Hz), 7.42 (m, 2 H, Pyridine *H*), 7.21-7.12 (m, 2 H, Ar*H*), 7.05-7.00 (m, 4 H, Ar*H*), 3.21 (s, 3 H, N-CH₃), 3.04 (s, 3 H, N-CH₃), 2.97 (sept, 1 H, CHMe₂, *J*_{HH} = 7.2 Hz), 2.89 (sept, 1 H, CHMe₂, *J*_{HH} = 7.2 Hz), 1.92 (s, 3 H, C-CH₃), 1.85 (s, 3 H, C-CH₃), 1.57 (dd, 18 H, *t*Bu, *J*_{PH} = 14.2 Hz, *J*_{PH} = 14.2 Hz), 1.33 (d, 3 H, CHMe₂, *J*_{HH} = 6.4 Hz), 1.17 (d, 3 H, CHMe₂, *J*_{HH} = 6.4 Hz), 0.40 (d, 3 H, CHMe₂, *J*_{HH} = 6.4 Hz), 0.08 (d, 3 H, CHMe₂, *J*_{HH} = 6.4 Hz). **¹¹B{¹H} NMR (128 MHz, CD₃CN, 25 °C):** δ -8.5 (s), -11.5 (s). **³¹P{¹H} NMR: (162 MHz, CD₃CN, 25 °C):** δ 43.7 (br). **¹³C{¹H} NMR (101 MHz, CD₃CN, 25 °C):** 163.2 (d, *J* = 9.6 Hz, NCN), 146.3 (C-carbene), 145.5 (d, *J* = 3.8 Hz, C-Ar), 144.1 (C-Ar), 143.3 (C-Ar), 141.6 (C-Ar), 139.6 (d, *J* = 15.4 Hz, C-Ar), 130.7 (C-Ar), 128.8 (C-Ar), 127.7 (C-Ar), 126.7 (C=C), 126.5 (C=C), 126.2 (C-Ar), 126.1 (C-Ar), 124.8 (C-Ar), 124.1 (C-Ar), 41.1 (d, *J* = 41.4 Hz, PC(CH₃)), 39.6 (d, *J* = 41.4 Hz, PC(CH₃)), 33.1 (NCH₃), 33.0 (NCH₃), 28.8 (d, *J* = 1.9 Hz, PC(CH₃)), 28.7 (CH(CH₃)₂), 28.6 (d, *J* = 1.9 Hz, PC(CH₃)), 28.0 (CH(CH₃)₂), 26.0 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 23.7 (CH(CH₃)₂), 21.9 (CH(CH₃)₂), 8.1 (CH₃), 7.8 (CH₃). HRMS (ESI): *m/z* calcd for C₃₉H₅₈B₂⁷⁹BrN₅PS: 760.3520 [(*M* + *H*)⁺]; found: 760.3541.

Synthesis of 3.35: Compound **3.33** (0.36 g, 0.5 mmol) was reacted with Se powder (0.079 g, 1 mmol) in toluene for three hours at r.t.p.. The reaction solution gradually changed from green to yellow. The yellow suspension was then dried under vacuum to remove all volatiles. **3.35** was obtained as yellow solid in 88 % yield (0.36 g, 0.44 mmol).

Recrystallization in saturated fluorobenzene solution gave yellow crystals of **3.35** under r.t.p.. **M.p.:** 216 °C. **¹H NMR (399.5 MHz, CD₃CN, 25 °C):** δ 8.64 (d, 2 H, Pyridine *H*, *J*_{HH} = 6.0 Hz), 8.16-8.12 (m, 1 H, Pyridine *H*), 7.57 (t, 2 H, Ar*H*, *J*_{HH} = 6.8 Hz), 7.34 (m, 2 H, Pyridine *H*), 7.22 (t, 1 H, Ar*H*, *J*_{HH} = 6.4 Hz), 7.13 (m, 1 H, Ar*H*), 7.04-7.00 (m, 4 H, Ar*H*), 3.12 (s, 3 H, N-CH₃), 3.02 (s, 3 H, N-CH₃), 2.85 (sept, 2 H, CHMe₂, *J*_{HH} = 7.2 Hz), 1.95 (s, 3 H, C-CH₃), 1.88 (s, 3 H, C-CH₃), 1.68 (d, 9 H, *t*Bu, *J*_{PH} = 14.2 Hz), 1.55 (d, 9 H, *t*Bu, *J*_{PH} = 14.2 Hz), 1.33 (d, 3 H, CHMe₂, *J*_{HH} = 6.8 Hz), 1.20 (d, 3 H, CHMe₂, *J*_{HH} = 6.8 Hz), 0.47 (d, 3 H, CHMe₂, *J*_{HH} = 6.8 Hz), -0.07 (d, 3 H, CHMe₂, *J*_{HH} = 6.8 Hz). **¹¹B{¹H} NMR (128 MHz, CD₃CN, 25 °C):** δ -5.1 (s), -7.7 (s). **³¹P{¹H} NMR: (162 MHz, CD₃CN,**

25 °C): δ 42.8 (br). **$^{77}\text{Se}\{^1\text{H}\}$ NMR (71.9 MHz, CD_3CN , 25 °C):** δ -361.5 (d, $J_{\text{PSe}} = 96$ Hz). **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, CD_3CN , 25 °C):** 163.2 (d, $J = 9.6$ Hz, NCN), 146.2 (C-carbene), 146.1 (d, $J = 3.8$ Hz, C-Ar), 144.1 (C-Ar), 143.1 (C-Ar), 141.9 (C-Ar), 139.7 (d, $J = 15.4$ Hz, C-Ar), 130.7 (C-Ar), 128.8 (C-Ar), 127.9 (C-Ar), 127.2 (C-Ar), 126.7 (C=C), 126.3 (C=C), 124.9 (C-Ar), 123.9 (C-Ar), 41.6 (d, $J = 41.4$ Hz, PC(CH₃)), 40.7 (d, $J = 41.4$ Hz, PC(CH₃)), 33.9 (NCH₃), 33.3 (CH(CH₃)₂), 32.9 (NCH₃), 29.2 (d, $J = 1.9$ Hz, PC(CH₃)), 28.9 (d, $J = 1.9$ Hz, PC(CH₃)), 28.1 (CH(CH₃)₂), 26.4 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 23.4 (CH(CH₃)₂), 21.7 (CH(CH₃)₂), 8.3 (CH₃), 7.9 (CH₃). HRMS (ESI): m/z calcd for $\text{C}_{39}\text{H}_{58}\text{B}_2^{79}\text{BrN}_5\text{PSe}$: 808.2965 [($M + H$)]⁺; found: 808.2980.

Synthesis of 3.36: Compound **3.33** (0.36 g, 0.5 mmol) was reacted with potassium graphite (0.135 g, 1 mmol) in toluene at -78 °C. The reaction was observed to change immediately from green to dark blue. The reaction mixture was then left to stir for 20 min at room temperature. After which, a blue suspension was obtained. It was filtered and the filtrate was reduced to 5 mL by concentration. Dark red single crystals were obtained after two days at r.t.p. in 56 % yield (0.18 g, 0.28 mmol). The reduction of compound **3.33** with Li metal in 1,2-dimethoxyethan (DME) at r.t.p. for 4 hours could also give compound **3.36**. **M.p.:** 187 °C. **^1H NMR (399.5 MHz, C_6D_6 , 25 °C):** δ 7.74 (d, 4 H, ArH, $J_{\text{HH}} = 7.8$ Hz), 7.05-6.98 (m, 6 H, ArH), 6.09-6.87 (m, 6 H, ArH), 6.19 (d, 4 H, NCH=CH, $J_{\text{HH}} = 7.8$), 4.46 (d, 4 H, NCH=CH, $J_{\text{HH}} = 7.3$), 3.36 (sept, 4 H, CHMe₂, $J_{\text{HH}} = 7.2$ Hz), 3.17 (s, 12 H, N-CH₃), 2.58 (s, 2 H, CH-CH), 1.58 (d, 36 H, *t*Bu, $J_{\text{PH}} = 12.4$ Hz), 1.52 (s, 12 H, C-CH₃), 0.84 (d, 12 H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz), 0.80 (d, 12 H, CHMe₂, $J_{\text{HH}} = 6.8$ Hz). **$^{11}\text{B}\{^1\text{H}\}$ NMR (128 MHz, C_6D_6 , 25 °C):** δ 27.6 (br), 19.9 (br). **$^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, C_6D_6 , 25 °C):** δ 47.6 (br). **$^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 25 °C):** 149.5 (C-Ar), 145.3 (C-carbene), 144.9 (C-Ar), 140.7 (NC=C), 136.0 (NC=C), 130.5 (C-Ar), 126.6 (C=C), 126.5 (C-Ar), 126.1 (C-Ar), 124.2 (C-Ar), 123.3 (C-Ar), 97.4 (CH₂), 37.2 (d, $J = 34.6$ Hz, PC(CH₃)), 33.6 (NCH₃), 28.5 (d, $J = 3.8$ Hz, PC(CH₃)), 27.7 (CH(CH₃)₂), 24.6 (CH(CH₃)₂), 23.6 (CH(CH₃)₂), 8.3 (CH₃). HRMS (ESI): m/z calcd for $\text{C}_{78}\text{H}_{114}\text{B}_4\text{N}_{10}\text{P}_2\text{Na}$: 1319.8973 [($M + H$)]⁺; found: 1319.9023.

Synthesis of 3.37: $\text{KBH}^{\text{sec}}\text{Bu}_3$ (2.0 M, 0.25 mL, 0.5 mmol) in THF was added into a suspension of compound **3.33** (0.36 g, 0.5 mmol) in toluene (20 mL) at -78 °C. The reaction colour turned immediately from green to dark blue. After which, it was warmed to r.t.p. and stirred for 30 minutes. A blue suspension was then obtained. It was filtered and the filtrate was concentrated to 5 mL to give compound **3.37** as red

single crystals in 74 % yield (0.24 g, 0.37 mmol) after two days at r.t.p.. Compound **3.33** was reacted with LiAlH₄ in toluene for 3 hours at r.t.p. could also form compound **3.37**. **M.p.:** 173 °C. **¹H NMR (399.5 MHz, C₆D₆, 25 °C):** δ 7.73 (d, 2 H, ArH, *J*_{HH} = 7.8 Hz), 7.05-6.08 (m, 3 H, ArH), 6.91-6.86 (m, 3 H, ArH), 6.03 (d, 2 H, NCH=CH, *J*_{HH} = 7.8), 4.31 (d, 2 H, NCH=CH, *J*_{HH} = 8.2), 3.38 (sept, 2 H, CHMe₂, *J*_{HH} = 7.2 Hz), 3.33 (d, 2 H, CH₂, *J*_{HH} = 3.2), 3.18 (s, 6 H, N-CH₃), 1.57 (d, 18 H, *t*Bu, *J*_{PH} = 12.4 Hz), 1.42 (s, 6 H, C-CH₃), 0.84 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz), 0.81 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz). **¹¹B{¹H} NMR (128 MHz, C₆D₆, 25 °C):** δ 26.3 (br), 18.2 (br). **³¹P{¹H} NMR: (162 MHz, C₆D₆, 25 °C):** δ 47.9 (br). **¹³C{¹H} NMR (101 MHz, C₆D₆, 25 °C):** 149.5 (C-Ar), 145.3 (C-carbene), 144.9 (C-Ar), 140.7 (NC=C), 137.4 (NC=C), 130.6 (C-Ar), 126.6 (C=C), 126.5 (C-Ar), 126.1 (C-Ar), 124.2 (C-Ar), 123.2 (C-Ar), 94.2 (CH₂), 37.2 (d, *J* = 34.6 Hz, PC(CH₃)), 33.6 (NCH₃), 28.5 (d, *J* = 3.8 Hz, PC(CH₃)), 27.8 (CH(CH₃)₂), 24.7 (CH(CH₃)₂), 23.7 (CH(CH₃)₂), 8.1 (CH₃). HRMS (ESI): *m/z* calcd for C₃₉H₅₉B₂N₅P: 650.4694 [(*M* + *H*)⁺]; found: 650.4703.

3.4.4. Hydroboration of pyridine derivatives catalyzed by compound 2.36: compound **2.36** (6.5 mg, 0.01 mmol, 1 equiv.) was dissolved in 0.2 mL C₆D₆ in a J-Young NMR tube. Pyridine substrates (0.10 mmol, 10 equiv.), cyclohexane (internal standard, 10 equiv.) and HBpin (12.8 mg, 0.10 mmol, 10 equiv.) were subsequently added. The NMR tube was then rinsed with another 0.2 mL C₆D₆. The reaction was then heated at 90 °C. NMR spectroscopy was used to determine their yields. Upon completion of the catalyses, the resulting crude solutions were filtered and the filtrates were dried under vacuum. The dried residues were then further extracted with either pentane or hexane. The resultant N-boryl-1,4-dihydropyridine derivatives were isolated by removing volatiles under vacuum for a few hours. The products' chemical shifts corresponded to the literature values.^[24] Catalytic experiments were done in triplicates.

3.5. Appendices

3.5.1. X-Ray crystallographic data for compounds 3.33, 3.36 and 3.37.

	3.33 ·(Fluorobenzene) ₂	3.36	3.37 ·(Toluene) _{2.5}
Formula	C ₅₁ H ₆₇ B ₂ BrF ₂ N ₅ P	C ₃₉ H ₅₈ B ₂ N ₅ P	C ₉₉ H ₁₃₆ B ₄ N ₁₀ P ₂
Fw	920.59	649.49	1571.35
T/K	100(2)	100(2)	100(2)
cryst system	monoclinic	monoclinic	triclinic
space group	P 1 21/c 1	P 1 21/c 1	P -1
<i>a</i> (Å)	12.4683(14)	18.8594(12)	10.4304(3)
<i>b</i> (Å)	23.752(3)	8.4579(4)	10.8686(4)
<i>c</i> (Å)	17.3090(17)	23.4995(14)	21.1950(7)
α (deg)	90	90	84.5168(14)
β (deg)	104.047(3)	94.142(2)	76.5181(12)
γ (deg)	90	90	79.6352(14)
<i>V</i> (Å ³)	4972.7(9)	3738.6(4)	2294.80(13)
<i>Z</i>	4	4	1
<i>d</i> _{calcd} (g cm ⁻³)	1.230	1.154	1.137
μ (mm ⁻¹)	0.905	0.108	0.099
<i>F</i> (000)	1944	1408	850
cryst size (mm)	0.01 x 0.02 x 0.28	0.14 x 0.20 x 0.22	0.02 x 0.10 x 0.22
2 θ range (deg)	4.912 < 2 θ < 51.91	5.354 < 2 θ < 53.65	4.903 < 2 θ < 61.75
index range	-15 ≤ <i>h</i> ≤ 12, -28 ≤ <i>k</i> ≤ 28, -18 ≤ <i>l</i> ≤ 20	-22 ≤ <i>h</i> ≤ 24, -10 ≤ <i>k</i> ≤ 10, -30 ≤ <i>l</i> ≤ 29	-15 ≤ <i>h</i> ≤ 12, -15 ≤ <i>k</i> ≤ 15, -30 ≤ <i>l</i> ≤ 30
no. of rflns collected	46331	35887	34220
no. of indep rflns	9251	8249	14264
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2 σ (<i>I</i>))	0.0673/0.1191	0.0565/0.1075	0.0761/0.1777
<i>R</i> 1, <i>wR</i> 2 (all data)	0.1363/0.1463	0.0873/0.1188	0.1411/0.2234
goodness of fit, <i>F</i> ²	1.009	1.044	1.040
no. of data/restraints/params	9251 / 684 / 653	8249 / 0 / 438	14264 / 1994 / 946
largest diff peak and hole, eÅ ⁻³	0.482 / -0.536	0.349 / -0.426	1.211 / -1.041

3.5.1. X-Ray crystallographic data for compounds 3.34 and 3.35.

	3.34	3.35
Formula	C ₃₉ H ₅₇ B ₂ BrN ₅ PS	C ₃₉ H ₅₇ B ₂ BrN ₅ PSe
Fw	760.45	807.35
T/K	100(2)	100(2)
cryst system	monoclinic	triclinic
space group	P 1 2/c 1	P -1
a (Å)	20.5575(9)	12.1812(12)
b (Å)	12.3589(6)	16.4229(14)
c (Å)	16.1629(7)	20.205(2)
α (deg)	90	86.593(3)
β (deg)	92.1674(19)	85.018(3)
γ (deg)	90	88.255(2)
V (Å ³)	4103.5(3)	4018.3(7)
Z	4	4
<i>d</i> _{calcd} (g cm ⁻³)	1.231	1.335
μ (mm ⁻¹)	1.125	2.002
F(000)	1608	1680
cryst size (mm)	0.02 x 0.12 x 0.14	0.02 x 0.06 x 0.20
2θ range (deg)	5.156 < 2θ < 55.69	4.782 < 2θ < 55.72
index range	-27<=h<=27, -13<=k<=16, -21<=l<=21	
no. of rflns collected	38231	38342
no. of indep rflns	9798	38150
R1, wR2 (<i>I</i> > 2σ(<i>I</i>))	0.0605/0.1385	0.0785/0.1140
R1, wR2 (all data)	0.1075/0.1655	0.1429/0.1677
goodness of fit, <i>F</i> ²	1.031	1.026
no. of data/restraints/params	9798 / 563 / 555	38342 / 0 / 912
largest diff peak and hole, eÅ ⁻³	0.744 / -0.636	1.622 / -0.888

3.5.2. NMR Spectra of all new compounds (D-solvent and NMR frequency are shown in section 3.4.3)

3.33: ^1H

3.33: $^{11}\text{B}\{^1\text{H}\}$

3.33: $^{31}\text{P}\{^1\text{H}\}$

3.33: $^{13}\text{C}\{^1\text{H}\}$

3.34: ^1H

3.34: $^{11}\text{B}\{^1\text{H}\}$

3.34: $^{31}\text{P}\{^1\text{H}\}$

3.34: $^{13}\text{C}\{^1\text{H}\}$

3.35: ^1H

3.35: $^{11}\text{B}\{^1\text{H}\}$

3.35: $^{31}\text{P}\{^1\text{H}\}$

3.35: $^{13}\text{C}\{^1\text{H}\}$

Chemical structure of compound 1 is shown in the inset. The structure is a bis-phosphine complex. It features two phenylboronate groups (Ph-B(OH)2) and two phenylphosphine groups (Ph-PH2) linked by a central biphenyl moiety. The boron atoms are coordinated to the phosphorus atoms via their lone pairs, forming a six-membered ring. The phosphorus atoms are also coordinated to the boron atoms via their lone pairs, forming another six-membered ring. The central biphenyl moiety is linked to the boron atoms via its two phenyl rings.

¹H NMR spectrum (CDCl₃) of compound 1. The x-axis represents chemical shift (δ) in ppm, ranging from 0 to 8.0. The y-axis represents abundance. The spectrum shows several peaks with integration values. The peaks are labeled with their chemical shifts and integration values:

Chemical Shift (δ) [ppm]	Integration
7.75188	3.96
7.73242	
7.16000	
7.05353	6.12
7.03744	6.06
6.98713	
6.90885	
6.88753	
6.20177	3.87
6.18251	
4.57011	3.96
4.55779	
3.38205	4.01
3.36625	12.08
3.35047	
3.17941	
2.58181	2.15
1.59725	12.08
1.56634	
1.52399	
0.84883	
0.81075	
0.29072	

3.36: $^{11}\text{B}\{^1\text{H}\}$

3.36: $^{31}\text{P}\{^1\text{H}\}$

3.36: $^{13}\text{C}\{^1\text{H}\}$

3.37: ^1H

3.37: $^{11}\text{B}\{^1\text{H}\}$

3.37: $^{31}\text{P}\{^1\text{H}\}$

3.37: $^{13}\text{C}\{^1\text{H}\}$

3.5.3. Theoretical Studies

All geometry optimizations, MO and NBO analysis were computed using the M06-2X functional with def2-SVP basis set as implemented in the Gaussian 09 package of programs.^[28,29] EDA-NOCV (energy decomposition analysis–natural orbitals for chemical valence) were performed at BP86/TZP level of theory with ADF 2017.112 program. The potential energy was refined by single point calculation with larger basis sets (def2-TZVP). In the free energy profile, the Gibbs free energy (ΔG) was calculated at 298.15 K and 1 atm.

List of abbreviation used in theoretical studies.

Abbreviation	Definition
Cpd	Compound
HBpin	Pinacolborane
Int	Intermediate
TS	Transition state
Pyr	Pyridine

List of colour coded atom used in optimised structures

Abbreviation	Definition
Grey	Carbon
Blue	Nitrogen
Yellow	Bromine
Pink	Boron
Orange	Phosphorus
Red	Oxygen

3.5.3.1. Optimised geometries of the minimal and transition states at M06-2X/def2-SVP level of theory. Hydrogen atoms are omitted for clarity. The bond lengths displayed are measured in Angstroms (Å).

3.5.3.2. Natural Localized Molecular Orbitals (NLMOs) of B=B bond (a and b) and B-N bond (c) of compound 3.33.

3.5.3.3. Natural bond orbital (NBO) analysis of compound 3.33.

Bond Type	Occupancy	Polarization	Hybridization	Bond Length (Å)	WBI	Natural Charge
B ₁ B ₂ σ	1.92	49.3% B ₁ 50.7% B ₂	B ₁ : sp ^{1.41} B ₂ : sp ^{1.64}	1.600 (1.576) ^a	1.48	B ₁ : +0.24 B ₂ : -0.21
B ₁ B ₂ π	1.61	42.9% B ₁ 57.1% B ₂	B ₁ : sp ^{99.99} B ₂ : sp ^{99.99}			
B ₂ N ₃ σ	1.96	19.7% B ₂ 80.3% N ₃	B ₂ : sp ^{2.44} N ₃ : sp ^{1.59}	1.507 (1.545) ^a	0.7	N ₃ : -0.53

^a Experimental value is adopted from crystal structure.

3.5.3.4. EDA-NOCV results of compound 3.33 at the BP86/TZP//M06-2X/def2-SVP level. Fragments are pyridine (F₁) and B=B (F₂) in the singlet (S) and triplet (T) electronic states, respectively.^(a)

Fragments	B=B (S) and pyridine (S)	B=B (T) and pyridine (T)
$\Delta E_{\text{INT}}^{(b)}$	-69.5	-157.3
ΔE_{PAULI}	243.8	338.6
ΔE_{ELSTAT}	-155.1	-193.2
ΔE_{ORB}	-158.2	-302.7

^(a) All energy values are given in kcal/mol. ^(b) $\Delta E_{\text{INT}} = \Delta E_{\text{PAULI}} + \Delta E_{\text{ELSTAT}} + \Delta E_{\text{ORB}}$

It was said that the smallest ΔE_{orb} value indicates which fragment (S-S or T-T) is the best choice for describing the bonding situation, because the least alteration of the electronic charge distribution is required to yield the electronic structure of the molecule. Since the orbital terms of S-S is smaller than the one of T-T ($|\Delta E_{\text{orb}}(\text{S-S})| = 158.2 < |\Delta E_{\text{orb}}(\text{T-T})| = 302.7$), the B-N bonding in compound 3.33 is better described with S-S fragment (dative bond).

3.6. References

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CHAPTER 4. An Amidinato Amidosilylene-Diborene and –Borylborylene

Compound for Catalytic Hydroboration of Carbon Dioxide

4.1. Introduction

Silicon atoms in silylenes have a lone pair of electrons, which entails them nucleophilic characters as well as a vacant orbital that gives them their electrophilic characters.^[1] In 1994, the first stable N-heterocyclic silylene (NHSi) **4.1** was isolated by West and co-workers.^[2] This sparked interest in the field which led to the subsequent report of silylenes with different stabilization modes, including cyclic dialkylsilylene **4.2**,^[3] β -diketiminato silylene **4.3**,^[4] amidinato silylenes **4.4**,^[5-6] cyclic phosphalkene-substituted silylene **4.5**,^[8] cyclic(alkyl)(amino) silylene **4.6**,^[7] phosphine-amido silylene **4.7**,^[9-11] acyclic two coordinated silylenes (**4.8**, **4.9** and **4.10**),^[12-14] N-heterocyclic carbene dihalosilylenes complexes **4.11**.^[15]

Scheme 4.1. Examples of stable silylenes.

Their Lewis ambiphilicity leads to fruitful results in coordination chemistry^[16] and small molecules activation.^[17] As an illustration, boranes use their vacant p orbital to accept the lone pair of electrons from silylenes to form a series of silylene-borane complexes (**4.12** – **4.16**).^[18-22]

Scheme 4.2. Examples of isolated silylene-borane adducts.

Besides coordination, So and co-workers reported the silylene-BH₂OTf adducts (**4.18** and **4.21**) further underwent B-H and C-H bond activation induced by 4-dimethylaminopyridine and silylene **4.20**, respectively. The reaction of silylene **4.17** with BH₃·THF and MeOTf to form silylene-BH₂OTf adduct **4.18**, which was reacted with 4-dimethylaminopyridine to give the B-H bond activation product **4.19** coupled with the ring expansion.^[23] In contrast, the reaction of silylene-BH₂OTf adduct **4.21** with one additional equivalent of silylene **4.20** furnished the amidinato silylene-boronium ion **4.22** via the intramolecular C(sp³)-H borylation and H₂ elimination.^[24]

Scheme 4.3. The B-H and C-H bond activation of silylene-BH₂OTf adducts.

In the reaction of silylenes with haloboranes, silylenes were prone to undergo oxidative addition reaction with B-X bond instead of forming Lewis acid-base adducts,^[25-27] which are significantly different from similar reactions of haloboranes with carbenes or phosphines. As an illustration, Braunschweig et al. showed that a N-heterocyclic silylene [$\{(H)C(Xyl)N\}_2Si:$] (**4.23**, Xyl = 2,6-Me₂C₆H₃) underwent insertion with the B-Cl bond of PhBCl₂, followed by expansion of the NHSi ring to afford a six-membered silaborinine ring **4.24**. In case of bulkier 2,3,5,6-tetramethylphenyl dichloroborane, the stepwise B-Cl bond oxidative addition products **4.25** and **4.26** were obtained.^[28]

Scheme 4.4. The reaction of NHC **4.23** with aryl dihaloboranes.

Until now, only one example of stable silylene-haloborane complexes was isolated by Inoue group, where the reaction of NHC-hydridosilylene **4.27** with tribromoborane or phenyl dibromoborane formed the Lewis acid-base adducts **4.28**.^[22]

Scheme 4.5. The silylene stabilized haloborane adducts.

Moreover, the reactivity of silylenes toward boron compounds was extended to halodiboranes. Similar to haloboranes, no stable Lewis acid-base adduct between silylenes and tetrahalodiboranes was reported, which was a valuable precursor for the synthesis of silylene-multiply bonded boron complexes. For instance, Braunschweig and his team demonstrated that the N-heterocyclic silylene **4.17** reacted with 1,2-diaryl-1,2-dichlorodiborane to

produce NHSi adducts of 1-aryl-2-silyl-1,2-diboraindanes **4.29** via the functionalization of B-Cl and C-H bonds. In case of 1,1-diaryl-2,2-difluorodiborane, a similar product **4.30** was obtained.^[29]

Scheme 4.6. The reaction of NHSi with diaryldihalodiboranes.

The same group also isolated the neutral diboron radicals **4.31** from the reaction of the bis(amidinato)silylene **4.31** with 1,2-diaryl-1,2-dibromodiboranes via the reductive ligand transfer onto diaryldibromodiboranes and halides abstraction, along with the formation of amidinato bromosilane as a side product.^[30]

Scheme 4.7. The reaction of bis(amidinato)silylene with diaryldibromodiboranes.

Though silylenes exhibit diverse reactivity with boranes, they were seldom

used in the reaction with low-oxidation state boron complexes. To date, there has been only one example reported by Xie and co-workers, where a carborane-substituted bis(silylene)-bromoborylene and borylene cation were synthesized for dihydrogen activation.^[31] In case of multiply bonded boron compounds, their reactivity is still unknown so far.

Scheme 4.8. Bis(silylene) stabilized borylene and borylene cation.

Considering that the reactivity of multiply bonded boron derivatives toward small molecules interaction is governed by their Lewis base ligands, namely NHC and phosphine,^[32, 33] we were interested in exploring the effect of Lewis ambiphilic silylene on the electronic property of B-B multiple bond. We anticipated that the synergy interaction between Lewis ambiphilic silylene and B-B multiple bond could unlock catalytic capability of the latter.

Herein, we describe that an amidinato andiosilylene selectively mediated the reduction of tetrabromodiborane and *N*-phosphinoamidinate-bridged

tribromodiborane to form a silylene-diborene and –borylborylene, respectively. Their different extend of B-B multiple bond character and performance in catalytic hydroboration of carbon dioxide were studied by experimental and calculation methods.

4.2. Results and Discussion

The amidinato amidosilylene $[\text{LSiNMe}_2]$ (**4.33**, $\text{L} = \text{PhC}(\text{N}t\text{Bu})_2$)^[6] was reacted with 0.5 equivalents of $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$ to form the bis(silylene)-tetrabromodiborane $[\text{L}\{\text{Me}_2\text{N}\}\text{Si}]_2\text{B}_2\text{Br}_4$ (**4.34**). Compound **4.33** uses its lone pair of electrons to displace SMe_2 in $\text{B}_2\text{Br}_4(\text{SMe}_2)_2$ to form compound **4.34**. Other Lewis base adducts of tetrahalodiboranes(4) were reported by using phosphines and N-heterocyclic carbenes as electron donors, whereas silylenes were not used before.^[34]

Scheme 4.9. Synthesis of compound **4.34** and **4.35**.

The $^{11}\text{B}\{^1\text{H}\}$ NMR signal (-4.4 ppm) of complex **4.34** lies within the range of the $^{11}\text{B}\{^1\text{H}\}$ signals (-16.5 - -0.3 ppm) of other bis(Lewis base)-tetrabromodiborane compounds.^[34] The $^{29}\text{Si}\{^1\text{H}\}$ NMR (-5.1 ppm) is upfield shifted as compared to that of the amidinato amidosilylene-borane compound $[\text{L}\{(\text{Me}_3\text{Si})_2\text{N}\}\text{SiBH}_3]$ (22.1 ppm).^[23-24] The X-ray crystal structure of **4.34** indicates that the tetrahedral geometry was adopted by silicon and boron centers. The length of Si-B bond (2.029(2) Å) is slightly elongated as compared to the Si-B coordinative covalent bond in the amidinato amidosilylene-borane compound $[\text{L}\{(\text{Me}_3\text{Si})_2\text{N}\}\text{SiBH}_3]$ (1.974(3) Å).^[18]

Figure 4.1. X-ray crystal structures of **4.34**. Thermal ellipsoids are shown at 50 % probability. For clarity, all hydrogen atoms has been removed. Selected bond lengths (Å) and angles (deg): Si1-B1 2.029(2), B1-B1A 1.705(5), B1-Br1 2.084(2), B1-Br2 2.084(2), Si1-B1-Br1 105.13(11), Si1-B1-Br2 102.71(11), Si1-B1-B1A 122.16(19).

Compound **4.34** was then reacted with excess KC_8 in THF at ambient temperature for 12 hours to afford a red suspension. It was then filtered and concentrated to obtain the red crystalline solid of bis(silylene)-diborene compound $[\text{L}(\text{Me}_2\text{N})\text{SiB}(\text{Br})=\text{B}(\text{Br})\text{Si}(\text{NMe}_2)\text{L}]$ (**4.35**) with a yield of 58%. The $^{11}\text{B}\{^1\text{H}\}$ NMR signal (26.6 ppm) is downfield shifted as compared to that of **4.34**, which lies within the region of the $^{11}\text{B}\{^1\text{H}\}$ NMR resonances (12 – 32 ppm) of other Lewis base-diborene compounds.^[33, 35] On the other hand, the $^{29}\text{Si}\{^1\text{H}\}$ NMR resonance (1.7 ppm) is downfield shifted as compared to that of **4.34** (-5.1 ppm) due to the presence of a boron-boron multiply bond. Compound **4.35** has trans-configuration and the B centers adopt a trigonal planar geometry as shown using X-ray crystallography. The B1-B1A bond length (1.56(3) Å) lies within the region of boron-boron double bond length (1.546–1.625 Å) in other Lewis base-diborene compounds.^[33,35] The Si1-B1 bond (1.960(13) Å) is shorter than that of **4.34**.

The electronic structure of compound **4.35** was elucidated by DFT calculations. HOMO-1 shows a combination of the Si-B and B-B σ orbitals, while HOMO shows

similar characteristics to π orbital of the boron-boron double-bond. Accordingly, the NBO analysis shows that the mixing of sp hybrids on the B atoms results in the B1-B2 σ bond. On the other hand, overlapping of B p orbitals generates B1-B2 π bond. WBI of 1.66 further supports that B=B has double bond character. NPA indicates that a strong charge transfer from the silylene to diborene moieties with B and Si atoms having charges of -0.69 and 1.89 e, respectively. It is consistent with EDA-NOCV calculations that the Si-B bonds are better depicted as having an electron-sharing single bonds between charged fragments $\{L(Me_2N)Si\}^+$ (triplet, two molecules) and $\{B(Br)=B(Br)\}^{2-}$ (triplet). These attribute to the strong σ -donating property of the amidinato amidosilylene, leading to a more effective orbital overlap between the Si and B atoms in the Si-B σ bonds. Further support is found in the Laplacian distribution, where the electron density is concentrated in the middle of the Si-B bond.

Figure 4.2. (a) X-ray crystal structure of **4.35**. Thermal ellipsoids are shown at 50 % probability. For clarity, all hydrogen atoms are removed. Selected bond lengths (Å) and angles (deg): Si1-B1 1.961(13), B1-B1A 1.56(3), B1-Br1 2.060(13), Si1-B1-B1A 131.4(12), Br1-B1-B1A 120.4(11). (b) HOMO. (c) HOMO-1, (d) Contour plot of Laplacian distribution [$\nabla^2\rho(r)$] in the Si-B-B plane in **4.35**. Solid lines indicate the areas of the charge concentration ($\nabla^2\rho(r) < 0$) while dotted lines mean the charge depletion ($\nabla^2\rho(r) > 0$).

When $B_2Br_4(SMe_2)_2$ was replaced by the *N*-phosphinoamidinate-bridged diborane **4.37**, the reduction of **4.37** with excess KC_8 in the presence of **4.33** at r.t.p. gave a red suspension. After filtration and removal of volatiles, the *N*-phosphinoamidinato silylene-borylborylene **4.38** was afforded as a red crystalline solid with 42% yield. Red single crystals of **4.38** were isolated from its concentrated hexane solution. Base-stabilized borylborylene remains very much a novelty, with only two examples were reported by research groups of Braunschweig and Kinjo, which were synthesized by the rearrangement of a diborene or allenic diborene, respectively.^[36-37] Only signals for compound **4.38** were detected using NMR spectroscopy and the formation of diborene was not observed. The resonances in the 1H NMR spectroscopy of compound **4.38** indicate the presence of amidinate and *N*-phosphinoamidinate backbone. The $^{11}B\{^1H\}$ NMR spectrum showed a resonance at δ 39.5 ppm for the *BBr* center, an intermediate between the signals

for the three-coordinate boron center in **4.37** (52.0 ppm) and the diborene moiety in **4.35** (26.6 ppm). In addition, the $^{11}\text{B}\{^1\text{H}\}$ NMR signal for the *B*Si centre (-28.5 ppm) is comparable with that of the carborane-substituted bis(silylene)-bromoborylene **3.10** (-26.5 ppm).^[31] The large contrast of $^{11}\text{B}\{^1\text{H}\}$ NMR signals in **4.38** is also found in the 2-phosphinomethylphenyl phosphine-borylborylene (52.6 and -25.5 ppm).^[36-37] The $^{29}\text{Si}\{^1\text{H}\}$ NMR signal (20.9 ppm) is downfield shifted in contrast to that of the carborane-substituted bis(silylene)-bromoborylene **3.10** (18.2 ppm).^[31] The broad $^{31}\text{P}\{^1\text{H}\}$ NMR signal (47.5 ppm) indicates that the phosphine donor coordinates to the borylene centre in solution. Compound **4.38** has two trigonal planar boron atoms as shown by X-ray crystallography. The B2 atom is coordinated with the phosphine donor of the *N*-phosphinoamidinate ligand and the silylene ligand, while the B1 atom is bonded with the bromide substituent and the amidinate substituent of the *N*-phosphinoamidinate ligand. The B1-B2 bond length (1.559(12) Å) is comparable with that of **4.35** and the bis(phosphine)-borylborylene compounds (1.558(7) - 1.579(4) Å), indicating that the B1-B2 bond has some double bond character. The P1-B2 bond (1.828(8) Å) is shorter than that of the 2-phosphinomethylphenyl phosphine-borylborylene (1.853(4), 1.869(4) Å).^[36] In addition, the Si1-B2 bond (1.911(9) Å) is elongated, as compared to that of the carborane-substituted bis(silylene)-bromoborylene **3.10** (1.857(4) Å).^[31] Moreover, the N1-B1 bond length (1.48(1) Å) indicates that the N1 lone pair electrons largely delocalize to the vacant p orbital of the B1 center, as compared to the amidinate N1-C13-N2 skeleton. The analysis suggests that compound **4.38** is composed of resonance structures **A** – **C**.

Scheme 4.10. Synthesis of **4.38**.

DFT calculations were used to elucidate the electronic structure of compound **4.38**. HOMO-17 shows a combination of B-B and Si-B σ orbitals. HOMO shows π orbital centered on the B2 forming π -back-bonding with the Si1, P1 and B1 centers. Accordingly, the NBO shows that the B1-B2 π bond is polarized toward the B2 atom (68.9 % B2+ 31.1 % B1), which is a result of the mixing of B p orbitals. The B2-B1 bond has some double bond character as suggested from its WBI of 1.38, but the bond order is lower than that of **4.35**. The natural charge shows that the B-B bond is highly polarized and has a charge separation structure. These analyses favor that the B2 possesses a lone pair of electrons, which is stabilized by the vacant p orbital on the B1 atom, as well as the empty orbitals in the amidinato amidosilylene and phosphine donors. EDA-NOCV calculations show that the Si-B bond is a synergetic donor-acceptor interaction, where the main deformation density $\Delta\rho_1$ indicates the σ -donation from the Si1 to B2 atom and the second deformation density $\Delta\rho_2$ displays the π -donation from the B2 to Si1 atom.

Figure 4.3. (a) Molecular structure of **4.38** obtained by X-ray crystallography. Thermal ellipsoids are shown at 30 % probability. All hydrogen atoms are removed

for clarity. Selected bond lengths (Å) and angles (deg): B1-B2 1.559(12), B1-Br1 2.011(8), B1-N1 1.485(10), B2-Si1 1.911(9), B2-P1 1.828(8), N1-C13 1.386(8), N2-C13 1.298(8), N1-B1-Br1 110.3(5), N1-B1-B2 130.2(7), Br1-B1-B2 119.4(6), P1-B2-B1 106.1(6), P1-B2-Si1 130.4(5), Si1-B2-B1 123.2(6). (b) HOMO-17. (c) HOMO. (d) The deformation density $\Delta\rho_1$ of ΔE_{orb} (-121.6 kcal/mol, 78.1%) in EDA-NOCV calculations. (e) The deformation density $\Delta\rho_2$ of ΔE_{orb} (-15.3 kcal/mol, 9.8%) in EDA-NOCV calculations.

Scheme 4.11. Catalytic hydroboration of CO₂.

The presence of a B lone pair of electrons and vacant p orbital suggest that compound **4.38** should possess catalytic reactivity. In this context, compound **4.38** was used to catalyze hydroboration of CO₂. Firstly, CO₂ was not able to react with pinacolborane in C₆D₆ at 110 °C. 2 mol% of **4.38** was capable of mediating hydroboration of CO₂ with pinacolborane at the elevated temperature of 110°C in C₆D₆ to obtain methoxyborane [pinBOMe] (**4.39a**, yield: 93.7 %, TOF: 24.8 h⁻¹) and diborate ether [(pinB)₂O] (**4.39b**) in a 1:1 ratio. Compound **4.38** is the first borylene capable of catalyzing organic reaction. The activity of complex **4.38** in terms of TOF and product yield is outstanding. The TOF were greater than that of other Mg, Ca, Ge and Sn hydride compounds in the literature (TOF, Mg: 0.07, Ca: 0.1, Ge: 2.1, Sn: 14.5 h⁻¹) for the same catalysis,^[38] but it is less active than the *N*-phosphinoamidinato NHC-diborene complex (yield: 97.8 %, TOF: 33.3 h⁻¹).^[39]

Scheme 4.12. Proposed catalytic mechanism.

The catalytic mechanism is proposed. Lone pair of electrons on boron centre in compound **4.38** first attack CO_2 , while the O atom donates electrons back to the vacant orbital of another B centre to form a four-membered ring. Subsequently, the H-B bond of pinacolborane inserts into the C=O bond in **Int01** to generate **Int02**. The second pinacolborane coordinates to the O atom of the acetal and the H-B bond then attacks the acetal carbon atom. This leads to the nucleophilic attack of OBpin fragment to form diborate ether [pinBOBpin] and **Int03**. The subsequent σ -bond metathesis reaction occurred between the B-H bond of the third pinacolborane and the B-O bond in **Int03** to form **Int04**. The B-H bond of the fourth pinacolborane then attacks the methylene carbon of **Int04**, which results in the formation of MeOBpin and **Int05**. Finally, **Int05** undergoes 1,2-elimination of

pinacolborane to form back compound **4.38**.

4.3. Conclusion

In conclusion, the first bis(silylene)-dibormodiborene **4.35** and *N*-phosphinoamidinato silylene-borylborylene **4.38** were synthesized. The amidinato amidosilylene stabilizes the boron-boron double bond in compound **4.35** through the donation of the lone pair of electrons to the B vacant p orbital, while it forms a synergetic donor-acceptor interaction with the borylene center in compound **4.38**. Compound **4.38** exhibits catalytic capability because it possesses lone pair of electrons and vacant orbital on boron centers. It catalyzed hydroboration of CO₂ to form a mixture of methoxyborane [pinBOMe] and diborate ether [(pinB)₂O] in a 1:1 ratio. Its catalytic capability is much better than that of current main-group element catalysts employed. The B lone pair electrons and vacant p orbital in compound **4.38** activated CO₂ with HBpin as shown in the mechanistic studies. Further reaction of the intermediate with HBpin molecules forms compounds such as MeOBpin and pinBOBpin and **4.38** is regenerated.

4.4. Experimental

4.4.1. General procedure.

All procedures follow Chapter 2, section 2.4.1, page 94 of this thesis.

4.4.2. X-ray data collection.

The X-ray diffraction intensity data for compound **4.34**, **4.35**, **4.37**, and **4.38** were using the same equipment and parameters as Chapter 1, section 1.4.2, page 35 of this thesis using the SMART suite of programs.^[40] Data processing, correction, structural solution and refinement were done similar with the SHELXTL suite of programs.^[41] Selected crystallographic data is provided in section 4.5.1.

4.4.3. The syntheses and characterization procedures.

Synthesis of 4.34. 20 mL toluene was added into a 100 mL Schlenk flask containing amidinate stabilized silylene **4.33** (1 mmol, 0.304 g) and $B_2Br_4(SMe_2)_2$ (0.5 mmol, 0.233 g) at r.t.p., following which, the reaction mixture was stirred at r.t.p. for 6 h. The resulting light red solution was filtered and the filtrate was concentrated to 5 mL and stood for 2

days at 4 °C to obtain colourless block crystals in 93 % yield (0.87 g, 0.465 mmol). **M.p.:** 182 °C. **1H NMR** (399.5 MHz, $CDCl_3$, 25 °C): δ 7.94 (d, 1 H, ArH), 7.47 (d, 1 H, ArH), 7.41 (d, 3 H, ArH), 2.86 (s, 6 H, NMe_2), 1.32 (s, 18 H, tBu). **$^{11}B\{^1H\}$ NMR** (128 MHz, $CDCl_3$, 25 °C): δ -4.4 (s). **$^{13}C\{^1H\}$ NMR** (101 MHz, $CDCl_3$, 25 °C): 175.9 (NCN), 131.0 (C-Ar), 130.5 (C-Ar), 129.7 (C-Ar), 128.8 (C-Ar), 128.2 (C-Ar), 127.2 (C-Ar), 54.5 ($C(CH_3)_3$), 39.9 ($N(CH_3)_2$), 31.8 ($C(CH_3)_3$). **$^{29}Si\{^1H\}$ NMR** (79.4 MHz, $CDCl_3$, 25 °C): δ -5.1 (s). HRMS (ESI): m/z calcd for $C_{34}H_{59}B_2^{79}Br_4N_6Si_2$: 945.1259 [$(M + H)^+$]; found: 945.1277.

Synthesis of 4.35. 40 mL THF was added into a 100 mL Schlenk flask containing **4.34** (1 mmol, 0.95 g) and excess KC_8 (4 mmol, 0.54 g) at r.t.p., after 10 min the color of reaction mixture turned red. The resulting suspension was stirred at r.t.p. for 14 h, following which, the reaction mixture

was then filtered. After which, the filtrate was concentrated and stood for one week at 4 °C to obtain red single crystals in 58 % yield (0.45 g, 0.58 mmol). **M.p.:** 153 °C. **1H NMR** (399.5 MHz, C_6D_6 , 25 °C): δ 7.85 (d, 1 H, ArH), 6.93-

6.84 (m, 4 H, ArH), 3.09 (s, 6 H, NMe₂), 1.33 (s, 18 H, ^tBu). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 25 °C): δ 26.6 (s). ¹³C{¹H} NMR (101 MHz, [D₈]THF, 25 °C): 174.2 (NCN), 132.1 (C-Ar), 130.4 (C-Ar), 129.6 (C-Ar), 128.7 (C-Ar), 128.1 (C-Ar), 127.9 (C-Ar), 53.6 (C(CH₃)₃), 38.7 (N(CH₃)₂), 30.4 (C(CH₃)₃). ²⁹Si{¹H} NMR (79.4 MHz, [D₈]THF, 25 °C): δ 1.7 (s). HRMS (ESI): *m/z* calcd for C₃₄H₅₉B₂⁷⁹Br₂N₆Si₂: 787.2893 [(*M* + *H*)⁺]; found: 787.2905.

Synthesis of 4.37. Procedure was similar to the synthesis of **2.35** in chapter 2, section 2.4.3, page 94 of this thesis. Briefly, *n*BuLi (2.6 M, 0.4 mL, 1.05 mmol) in hexane was slowly added to a stirring *N*-phosphinoamidinate **4.36** (0.464 g, 1 mmol) in diethyl ether at -78 °C. The solution was then warmed to r.t.p. and stirred for additional 3 h. Volatiles were removed from resulting the yellow solution. After which, B₂Br₄(SMe₂)₂ (0.47 g, 1.01 mmol) in toluene was then slowly added at low temperature (-78 °C). The resulting reaction mixture was then stirred for 12 h at r.t.p.. The by-product LiBr was then removed by filtration. The solution was concentrated to 3 mL and then stood at 4 °C for one week to give **4.37** as a colourless single crystals (0.55 g, 0.77 mmol, 77 % yield). **M.p.:** 164 °C. ¹H NMR (399.5 MHz, CDCl₃, 25 °C): δ 8.09-8.04 (m, 4 H, ArH), 7.56-7.61 (m, 2 H, ArH), 7.57-7.53 (m, 4 H, ArH), 7.32-7.28 (m, 2 H, ArH), 7.13-7.10 (m, 2 H, ArH), 7.04-6.97 (m, 4 H, ArH), 2.61 (sept, 2 H, CHMe₂, *J*_{HH} = 6.8 Hz), 1.06 (d, 6 H, CHMe₂, *J*_{HH} = 6.4 Hz), 0.47 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz). ¹¹B{¹H} NMR (128 MHz, CDCl₃, 25 °C): δ 52.0 (br), -16.8 (br). ³¹P{¹H} NMR (162 MHz, CDCl₃, 25 °C): δ 9.3 (br). ¹³C{¹H} NMR (101 MHz, CDCl₃, 25 °C): δ 168.9 (NCN), 145.3 (C-Ar), 138.4 (C-Ar), 138.3 (C-Ar), 138.2 (C-Ar), 133.0 (C-Ar), 132.9 (C-Ar), 132.6 (C-Ar), 130.0 (C-Ar), 129.3 (C-Ar), 129.2 (C-Ar), 129.1 (C-Ar), 129.0 (C-Ar), 127.4 (C-Ar), 126.5 (C-Ar), 125.7 (C-Ar), 124.3 (C-Ar), 28.5 (CH(CH₃)₂), 24.5 (CH(CH₃)₂), 23.1 (CH(CH₃)₂). HRMS (ESI): *m/z* calcd for C₃₁H₃₃B₂⁷⁹Br₃N₂P: 723.0118 [(*M* + *H*)⁺]; found: 723.0136.

Synthesis of 4.38. Amidinato amidosilylene **4.33** (0.304 g, 1 mmol) in toluene was slowly added into a 100 mL Schlenk flask containing compound **4.37** (0.728 g, 1 mmol) and excess KC₈ (0.54 g, 4 mmol) at r.t.p.. It turned red immediately. After which, it was left to stir for 3 h at ambient temperature. It was then filtered and dried under reduced pressure to obtain the red solid (**4.38**, 0.36 g, 0.42 mmol, 42 % yield). The red single crystals of compounds **4.38** were obtained from their saturated hexane solution. **M.p.:** 143 °C. ¹H NMR (399.5 MHz, C₆D₆, 25 °C): δ 8.31-8.26 (m, 4 H, ArH), 7.37-7.34 (m, 2 H, ArH), 7.31-7.25 (m, 5 H, ArH), 7.12-7.10 (m, 2 H, ArH), 6.95-6.81 (m, 10 H, ArH), 3.51 (sept, 2 H, CHMe₂, *J*_{HH} = 6.8 Hz), 2.47 (s, 6 H, NMe₂), 1.56 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz), 1.22 (s, 18 H, ^tBu), 0.82 (d, 6 H, CHMe₂, *J*_{HH} = 6.8 Hz). ¹¹B{¹H} NMR (128 MHz, C₆D₆, 25 °C): δ 39.5 (br), -28.5 (br). ³¹P{¹H} NMR (162 MHz, C₆D₆, 25 °C):

δ 47.5 (br). $^{13}\text{C}\{^1\text{H}\}$ NMR (101 MHz, C_6D_6 , 25 °C): δ 174.3 (tBu-NCN-tBu), 159.2 (P-NCN-Dipp), 143.0 (C-Ar), 142.7 (C-Ar), 142.3 (C-Ar), 141.8 (C-Ar), 141.7 (C-Ar), 132.3 (C-Ar), 132.2 (C-Ar), 131.6 (C-Ar), 130.0 (C-Ar), 129.8 (C-Ar), 128.8 (C-Ar), 127.2 (C-Ar), 127.0 (C-Ar), 126.6 (C-Ar), 123.3 (C-Ar), 53.9 ($\text{C}(\text{CH}_3)_3$), 38.8 ($\text{N}(\text{CH}_3)_2$), 30.8 ($\text{C}(\text{CH}_3)_3$), 28.7 ($\text{CH}(\text{CH}_3)_2$), 24.6 ($\text{CH}(\text{CH}_3)_2$), 23.4 ($\text{CH}(\text{CH}_3)_2$). $^{29}\text{Si}\{^1\text{H}\}$ NMR (79.4 MHz, C_6D_6 , 25°C): δ 20.9 (s). HRMS (ESI): m/z calcd for $\text{C}_{48}\text{H}_{62}\text{B}_2^{79}\text{BrN}_5\text{SiP}$: 868.3822 [$(M + H)^+$]; found: 868.3888.

4.4.4. Catalytic Studies

Synthesis of Compounds 4.39a and 4.39b. The procedure was similar to Chapter 2, section 2.4.4.1, page 98 of this thesis for the synthesis of Compounds 2.40a–c. Instead of catalyst 2.36, catalyst 4.38 (0.035 g, 0.04 mmol) was used. Other chemicals and their amount were the same. The monitoring of the reaction was done using ^1H NMR spectroscopy. Yield was computed using integration of the ^1H NMR resonances of methoxyborane (4.39a) at 1.04 and 3.52 ppm and diborate ether (4.39b) at 1.01 ppm, taken with reference to the internal standard that is the $-\text{CH}_2$ signal of cyclohexane at 1.36 ppm. The products' chemical shifts corresponded with the literature values as well as other independent in situ NMR scale syntheses.^[39]

Entry	Substrate	Catalyst (X mol%)	Product	T (°C)	time (h)	Conversion (%)	Yield (%)	TOF (h ⁻¹)
1	CO ₂	0%	4.39a 4.39b	110	4	0	0 0	0
2	CO ₂	2%	4.39a 4.39b	110	1	58.4	55.0 57.3	29.2
3	CO ₂	2%	4.39a 4.39b	110	2.5	99	96.1 98.6	19.8
4	CO ₂	1%	4.39a 4.39b	110	2	74.2	70.4 75.2	37.1
5	CO ₂	1%	4.39a 4.39b	110	4	99	93.7 95.2	24.8
6	CO ₂	2%	4.39a 4.39b	90	4	31.6	27.8 30.4	3.9
7	CO ₂	2% Silylene 4.33	4.39a 4.39b	110	4	0	0 0	0
8	CO ₂	2% free ligand 4.36	PinBOC(O)H 4.39a 4.39b	110	4	27.8	8.1 18.8 19.4	3.5
9	CO ₂	2% 4.35	4.39a 4.39b	110	4	37.3	9.7 36.4	4.6

4.5. Appendices

4.5.1. X-Ray crystallographic data for compounds 4.34, 4.35, 4.37 4.38.

	4.34	4.35	4.37	4.38
Formula	C ₃₄ H ₅₈ B ₂ Br ₄ N ₆ Si ₂	C ₃₄ H ₅₈ B ₂ Br ₂ N ₆ Si ₂	C ₃₁ H ₃₂ B ₂ Br ₃ N ₂ P	C ₄₈ H ₆₁ B ₂ BrN ₅ PSi
Fw	948.30	788.48	724.90	868.60
T/K	100(2)	100(2)	100(2)	100(2)
cryst system	orthorhombic	monoclinic	orthorhombic	monoclinic
space group	P b c a	P 1 21/n 1	P b c a	C 1 2/c 1
a (Å)	17.2675(5)	12.738(4)	15.4999(8)	26.340(3)
b (Å)	13.0660(5)	12.142(4)	18.6696(5)	20.6612(13)
c (Å)	18.6398(6)	12.847(4)	21.3428(5)	20.3891(17)
α (deg)	90	90	90	90
β (deg)	90	94.568(10)	90	120.934(4)
γ (deg)	90	90	90	90
V (Å ³)	4205.5(2)	1980.7(11)	6176.1(4)	9517.8(14)
Z	4	2	8	8
<i>d</i> _{calcd} (g cm ⁻³)	1.498	1.322	1.559	1.212
μ (mm ⁻¹)	3.917	2.139	3.995	0.960
<i>F</i> (000)	1928	824	2896	3664
cryst size (mm)	0.03*0.20*0.24	0.06*0.12*0.32	0.06*0.10*0.12	0.02*0.10*0.12
2θ range (deg)	4.484 < 2θ < 57.91	4.622 < 2θ < 48.61	5.122 < 2θ < 60.91	5.061 < 2θ < 40.61
index range	-27<=h<=27, - 19<=k<=21, - 30<=l<=29	-15<=h<=15, - 14<=k<=14, - 15<=l<=15	-8<=h<=22, - 27<=k<=23, - 27<=l<=31	-24<=h<=31, - 24<=k<=20, - 24<=l<=24
no. of rflns collected	46322	34584	39401	33202
no. of indep rflns	9244	3545	10133	8435
<i>R</i> 1, <i>wR</i> 2 (<i>I</i> > 2σ(<i>I</i>))	0.0432/0.0889	0.0838/0.2059	0.0551/0.1158	0.0808/0.1441
<i>R</i> 1, <i>wR</i> 2 (all data)	0.0894/0.1025	0.1390/0.2455	0.1228/0.1433	0.2271/0.1961
goodness of fit, <i>F</i> ²	1.035	1.067	1.009	0.959
no. of data/restraints/params	9244 / 0 / 225	3545 / 0 / 206	10133 / 0 / 356	8435 / 0 / 535
largest diff peak and hole, eÅ ⁻³	0.808/-0.961	0.771/-1.035	1.007/-1.842	0.411/-0.644

4.5.2. NMR Spectra of all new compounds (D-solvent and NMR frequency are shown in section 4.4.3)

4.34: ^1H

4.34: $^{11}\text{B}\{^1\text{H}\}$

4.34: $^{13}\text{C}\{^1\text{H}\}$

4.34: $^{29}\text{Si}\{^1\text{H}\}$

4.35: ^1H

4.35: $^{11}\text{B}\{^1\text{H}\}$

4.35: $^{13}\text{C}\{^1\text{H}\}$

4.35: $^{29}\text{Si}\{^1\text{H}\}$

4.37: ^1H

4.37: $^{11}\text{B}\{^1\text{H}\}$

4.37: $^{31}\text{P}\{^1\text{H}\}$

4.37: $^{13}\text{C}\{^1\text{H}\}$

4.38: ^1H

4.38: $^{11}\text{B}\{^1\text{H}\}$

4.38: $^{31}\text{P}\{^1\text{H}\}$

4.38: $^{13}\text{C}\{^1\text{H}\}$

4.38: $^{29}\text{Si}\{^1\text{H}\}$

4.5.3. Theoretical Studies

All geometry optimizations, MO and NBO analysis were computed using the M06-2X functional with def2-SVP basis set as implemented in the Gaussian 09 package of programs.^[42,43] EDA-NOCV (energy decomposition analysis–natural orbitals for chemical valence) were performed at BP86/TZP level of theory with ADF 2017.112 program. The potential energy was refined by single point calculation with larger basis sets (def2-TZVP). In the free energy profile, the Gibbs free energy (ΔG) was calculated at 298.15 K and 1 atm.

4.5.3.1. Natural bond orbital (NBO) analysis of compound 4.35.

Bond Type	Occupancy	Polarization	Hybridization	Bond Length (Å)	WBI	Natural Charge
B ₁ B ₂ σ	1.95	50.0% B ₁ 50.0% B ₂	B ₁ : sp ^{1.07} B ₂ : sp ^{1.07}	1.568 (1.561) ^a	1.66	B ₁ : -0.69
B ₁ B ₂ π	1.77	50.0% B ₁ 50.0% B ₂	B ₁ : sp ^{99.99} B ₂ : sp ^{99.99}			B ₂ : -0.69
B ₁ Si ₃ σ	1.92	56.4% B ₁ 43.6% Si ₃	B ₁ : sp ^{2.16} Si ₃ : sp ^{1.21}	1.937 (1.961) ^a	1.02	Si ₃ : 1.89
B ₂ Si ₄ σ	1.92	56.4% B ₂ 43.6% Si ₄	B ₂ : sp ^{2.16} Si ₄ : sp ^{1.21}	1.937 (1.961) ^a	1.02	Si ₄ : 1.89

^a Experimental value is adopted from crystal structure.

4.5.3.2. EDA-NOCV results of compound 4.35 at the BP86/TZP//M06-2X/def2-SVP level. Fragments are B₂Br₂ (F₁) and silylene (F₂) in the singlet (S) and triplet (T) electronic states, respectively.^(a)

Fragments	B ₂ Br ₂ (S) and silylene (S)	B ₂ Br ₂ (T) and silylene (T)
ΔE _{INT} ^(b)	- 169.0	-231.4
ΔE _{PAULI}	716.9	391.1
ΔE _{EELSTAT}	-373.5	-272.2
ΔE _{ORB}	-483.2	-321.1
ΔE _{DISPE}	-29.3	-29.3

^(a) All energy values are given in kcal/mol. ^(b) ΔE_{INT} = ΔE_{PAULI} + ΔE_{EELSTAT} + ΔE_{ORB} + ΔE_{DISPE}

The present EDA-NOCV results (B3LYP-D3BJ/TZP//B3LYP/def2-SVP) suggest that the Si-B is more like a covalent bond because of smaller orbital term of T-T reference state (i.e., |ΔE_{orb}(T-T)| = 321.1 < |ΔE_{orb}(S-S)| = 483.2 kcal mol⁻¹).

4.5.3.3. Natural bond orbital (NBO) analysis of compound 4.38.

Bond Type	Occupancy	Polarization	Hybridization	Bond Length (Å)	WBI	Natural Charge
B ₁ B ₂ σ	1.93	44.0% B ₁ 56.0% B ₂	B ₁ : sp ^{1.18} B ₂ : sp ^{1.51}	1.594 (1.558) ^a	1.38	B ₁ : +0.45
B ₁ B ₂ π	1.64	31.1% B ₁ 68.9% B ₂	B ₁ : sp ^{99.99} B ₂ : sp ^{99.99}			B ₂ : -1.31
B ₂ Si σ	1.90	59.7% B ₂ 40.3% Si	B ₂ : sp ^{1.86} Si: sp ^{1.13}	1.893 (1.912) ^a	1.06	Si: 1.94
B ₂ P σ	1.95	43.4% B ₂ 56.6% P	B ₂ : sp ^{2.97} P: sp ^{1.58}	1.831 (1.827) ^a	1.07	P: 1.53

^a Experimental value is adopted from crystal structure.

4.5.3.4. EDA-NOCV results of compound **4.38** at the BP86/TZP//M06-2X/def2-SVP level. Fragments are silylene (F_1) and B_2 group (F_2) in the singlet (S) and triplet (T) electronic states, respectively.^(a)

Fragments	silylene (S) and B_2 group (S)	silylene (T) and B_2 group (T)
$\Delta E_{INT}^{(b)}$	- 120.3	-179.4
ΔE_{PAULI}	199.0	226.0
ΔE_{ELSTAT}	-137.8	-169.9
ΔE_{ORB}	-155.6	-209.7
ΔE_{DISPE}	-25.9	-25.9

^(a) All energy values are given in kcal/mol. ^(b) $\Delta E_{INT} = \Delta E_{PAULI} + \Delta E_{ELSTAT} + \Delta E_{ORB} + \Delta E_{DISPE}$

Because the smallest ΔE_{Orb} value means the least alteration of the electronic charge distribution, which is required to form the electronic structure of the molecule. The EDA-NOCV results suggest that the donor-acceptor interaction between two singlet states is more appropriate for Si-B bond.

4.6. References

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