Synthesis and characterization of imide-based boranes and their cations

M.Sc. Research Thesis

BY

Sudipta Parua

(2203131009)



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of

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SUDIPTA PARUA



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CANDIDATE'S DECLARATION

I hereby certify that the work being presented in the thesis entitled "Synthesis and characterization of imide-based boranes and their cations" in the partial fulfillment of the requirements for the award of the degree of MASTER OF SCIENCE and submitted to the Department of Chemistry, Indian Institute of Technology Indore, is an authentic record of my work carried out during the period from July 2023 to May 2024 under the supervision of Dr. Dipak Kumar Roy, Department of Chemistry, Indian Institute of Technology Indore.

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

This is to certify that the above statement made by the candidate is correct to the best of my/our knowledge.

Giran Cur 14 15.05.2024

Dr. Dipak Kumar Roy

Sudipta Parua has successfully given his M.Sc. Oral Examination held on 09/05/2024.

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Signature of Supervisor of M.Sc. thesis Dr. Dipak Kumar Roy Date: $15.05 \cdot 1024$ Convener DPGC Dr. Umesh A Kshirsagar Date:

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Sudipta Parua

Department of Chemistry, IIT Indore

DEDICATED TO...

My beloved parents and sisters for their constant support in every way possible

ABSTRACT

Here, I have synthesized precursor for boron cations, which has been studied using mass spectrometry and NMR spectroscopy. The silicon boron exchange reaction is the most effective way to synthesize boron complexes among the other synthetic techniques investigated. Taking advantage of active hydrogen in a substrate, we investigated the reactivity of 9-BBN, which led to the formation of either a B-N bonded species or a four/six-membered B-N cyclic compound.

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NOMENCLATURE

δ	Delta (chemical shift)
nm	Nanometer
mL	Milliliter
mmol	milli mole
ppm	Parts per million
Hz	Hertz
g	Gram
mg	Milligram
Κ	Kelvin
°C	Degree Celsius

ACRONYMS

- Complex 1: 2-(trimethylsilyl)isoindoline-1,3 dione
- Complex 2: Ferrocene derivative of dibromoborane
- Complex 3: NHC adduct of Ferrocene derivative of dibromoborane
- Complex 4: 2-methylindole derivative of Ferrocene dibromoborane
- Complex 5: 2-methyl-1-(trimethylsilyl)-1*H*-indole
- Complex 6: 1-(bromo boraneyl)-2-methyl-1*H*-indole
- Complex 7: 1-bromo(phenyl)boraneyl-2-methyl-1*H*-indole
- Complex 8: 2-(1s, 5s)-9boracyclo[3.3.1]nonaneyl-1,3-dione
- CDCl₃: Deuterated Chloroform
- CHCl₃: Chloroform
- C_6D_6 : Benzene- d_6
- DCM: Dichloromethane
- DMSO: DimethylSulphoxide
- 9-BBN: 9-Borabicyclo[3.3.1]nonane
- BBr₃: Boron tribromide
- NEt₃: Triethylamine
- NHC: N-Heterocyclic Carbene
- n-BuLi: n-Butyllithium
- KOH: Potassium Hydroxide
- NaOH: Sodium Hydroxide
- THF: TetrahydroFuran

- TMSCI: Tetramethyl silyl chloride
- NMR: Nuclear Magnetic Resonance
- s: Singlet
- d: Doublet
- m: Multiplet
- *J*: Coupling constant

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Chapter 1

1.1 Introduction

Octet rule serves as a general principle in chemistry, elucidation the tendency of main group atoms to form compounds in a manner that ensures the enjoyment of eight valence electrons. Among the main group components of the second period, this principle is most attentively followed. The element boron, for example, is the third element of the second period and has six valences in its neutral three-coordination form. Consequently, it becomes advantageous for boron to accept an electron pair into its vacant 2p orbital to attain an octet configuration. This robust Lewis acidity, coupled with low electronegativity of boron, imparts distinctive properties to boron compounds, rendering them pivotal in diverse fields such as organic transformation, supramolecular complexation, and chemical bonding theory.

Because of their distinct bonding environments and electrical configurations, as well as their potential uses in bond activation and catalysis, boron cations are attracting a lot of attention to their study. Cationic boron compounds stand out as more prominent acceptors than their neutral counterparts, suggesting the possibility of a new class of catalysts and reagents with higher activity. In general, there are three classes of boron cations: borinium, borenium, and boronium (Figure 1.).^[3]



Figure 1. About the different classes of boron cations.

An interesting dimension is added by investigating two-coordinate cationic species, also referred to as "borinium ions," which have just four valence electrons. Because of their Lewis acidity, these ions exhibit exceptional reactivity and greatly depart from the Octet rule. Borinium ions are of particular interest since they are isoelectronic with the hypothesized two-coordinate carbon dication. While researchers have extensively studied three-coordinate and four-coordinate boron cations ^[2-5] but have also dedicated little effort to synthesizing two-coordinate borinium ions. ^[2,6]

The historical pursuit of synthesizing a borenium ion in solution dates back to 1958. During this time, it was documented that the reaction between chlorophenyl borane (Ph₂BCl) and AlCl₃ in nitrobenzene or methyl ethyl ketone resulted in a mixture that contained the diphenylborinium ion ^[7]. However, later it was determined that rather than forming borenium ions, this reaction produced boron cations with three or four coordination bonds to solvent molecules. ^[8,9]

Shifting the focus to imides, these functional groups are made up of two acyl groups attached to nitrogen and show enhanced resistance to hydrolysis. These are also high-strength polymer compounds called polyimides. ^[19] The imido group (=NH), which can function as a ligand, is another characteristic of inorganic imides, which can exist as gaseous or solid-state molecules. The majority of imides are cyclic compounds that have their names derived from dicarboxylic acids, such as phthalimide from phthalic acid. The N-substituent in imides made from amines is denoted by a prefix (for example, Ethylamine + Succinic acid = N-ethyl succinimide).

In 1982, Nöth and co-workers achieved a breakthrough by isolating a twocoordinate boron cation using dimethylamine and 2,2,6,6tetramethylpiperidino groups as substituents. ^[10] In 2022, Kong *et al.* reported a synthetic route of cationic iminoborane. ^[1] They demonstrate that incorporating an aryl group and NHC ligand in the cationic borane results in both boron-centered Lewis acidity and BN multiple bond reactivities. ^[1] In 2016, Singh *et al.* demonstrated a straightforward and well-thought synthetic approach for the production of hydride of borenium and chloroborenium cations, which are effectively stabilized by large bis(phosphinimino)amide ligands, regardless of whether a weakly coordinating, bulky anion is required or not. ^[11] These borenium ions strike a harmonious balance between stability and reactivity. ^[11] In 2022, Tan *et al.* reported recent advancements in borenium catalyzed reactions, their catalytic activity, methodology, and their plausible mechanism. ^[12]



Figure 2. Previously synthesized and characterized a few boron cations.

1.2 Objectives

Going through several literature studies, I devised a synthetic method to prepare different imide-based boranes and their cations to explore a potential role in Lewis acidity, organic transformation reaction, CO_2 reduction as well as H₂ activation, etc.



Figure 3. Aim of this Work.

In pursuing the potential imide-based boranes (Complex A), I have designed two possible pathways to furnish our desired product.



Figure 4. possible pathways to synthesized 2-(dibromoboraneyl)isoindoline-1,3-dione (complex A).

Path B, I have synthesized the Si-derivative of the phthalimide ligand (1). Afterward, the Silicon is replaced by boron using Lewis BBr₃ moiety to obtain complex, via a well-known trans-metalation reaction. In Path A, I initiate the reaction by directly combining phthalimide with BBr₃ in the presence of triethylamine as a base.

These boranes and their cations were further characterized by using different characterization techniques (NMR-spectroscopy, mass-spectrometry, XRD, etc.).

1. Experimental section

1.1. Instrumentation

All manipulations were carried out either in a dry argon atmosphere or under vacuum conditions using standard Schlenk line and glovebox techniques. Solvents, such as toluene, ether, benzene, and hexane were purified by distillation under dry argon and stored under the same inert gas atmosphere in the presence of molecular sieves of 4Å. Deuterated solvents were subjected to drying using molecular sieves and were degassed through three freeze-pump-thaw cycles before their utilization.

1.2. Materials

The solvents and reagents were purchased from commercially available sources like TCI, Spectro-chem, sigma-Aldrich-India (Meark), Loba-chem, Avra, SRL, Finer, BLD-pharm, SDFCL, Sisco-chem, and Euriisotope.

1.3. General Information

The course of reactions was monitored by Colour change, NMR, mass, etc. NMR chemical shifts are reported in ppm and coupling constants in Hz. ¹H and ¹³C NMR spectroscopy data were obtained at ambient temperature using a Bruker 500 NMR spectrometer (operating at 500 MHz for ¹H and 125 MHz for ¹³C). The NMR spectra of all intermediates and final compounds were analyzed by using MestReNova NMR software. The NMR samples were prepared in DMSO- d₆ and CDCl₃. solvent. The chemical shift was expressed in the form of ppm (δ) relative to surplus solvents protons as internal standards (CHCl₃: δ 7.26, DMSO: δ = 2.50 for ¹H NMR; and CHCl₃: δ 77.00, DMSO: δ 39.50 for ¹³C NMR).

2. Results and Discussion

Synthesis of Complexes

Part 1

In this context, I choose to pursue Path B for the synthesis complex A, as it is more efficient compared to Path A, which offers numerous possibilities, including the desired product. I employ techniques such as NMR-spectroscopy and mass-spectrometry to characterize the synthesized complexes.

2.1.1. Synthesis of Complex 1



Scheme 1. Synthesis of Complex 1.

Phthalimide (0.5 g, 3.39 mmol, 1.0 equiv.) was dissolved in THF (10 ml), then NEt₃ (0.447 g, 4.41 mmol, 1.3 equiv.) was added and stirred at r.t. for 30minutes under Argon atmosphere. After that TMSCl (0.479 g, 4.417 mmol, 1.3 equiv.) was added dropwise to the above solution at r.t. and the reaction mixture was stirred for 12 h. Following this reaction period, the mixture was filtered and dried the solvent under reduced pressure. A white solid of **1** (587 mg, yield 78%) was obtained. *Analytical data*. ¹**H NMR** (500 MHz, CDCl₃) δ 7.81 (dd, J = 5.5, 3.1 Hz, 2H), 7.70 (dd, J = 5.5, 3.1 Hz, 2H), 0.51 (s, 9H), ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 173.92, 134.55, 134.27, 123.40, ²⁹Si{¹H} NMR (99 MHz, CDCl₃) δ 13.46. LCMS M/Z calculated C₁₃H₁₆N₂O₂Si [M+CH₃CN] 260.0976 found 260.0926.

2.1.2. Reaction between Complex 1 and BBr₃



Scheme 2. Reaction between Complex 1 & BBr₃.

1 (0.315 g, 1.43 mmol, 1 equiv.) was dissolved in DCM (5 ml) and cooled to -78 °C and then BBr₃ (1.72 ml, in 1M heptane) was added dropwise and the reaction mixture was stirred for 2 h at -78 °C. Following this, the reaction mixture was allowed to warmed to room temperature and further stirred for 12 h. The reaction mixture was dried under reduced pressure to remove the solvent and extra BBr₃. Then the resulting residue was extracted with DCM (5 ml) , filtered over celite and dried under vacuum, an orange powder was obtained. *Analytical data*. ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 1.07, -24.73, ¹H NMR (500 MHz, CDCl₃) δ 8.42 – 7.67 (m, 4H). Here in ¹¹B NMR, we got two intense peaks at +1.07 ppm and -24.73 ppm, this negative is dedicated for [BBr₄]⁻. However, we are not sure that our desired complex was formed, because if the boron center is attached with one N-atom and two halogens, the ¹¹B NMR peak should be around +15 ppm to +25 ppm range. ^{[1] 11}B peak at +1.07 may be for the four coordinated boron complexes, there are two possibilities, which are given below.



2.1.3. Reaction between potassium salt of phthalimide with BBr₃



Scheme 3. Reaction between potassium salt of phthalimide with BBr₃.

I (0.3 g, 1.61 mmol, 1 equiv.) was taken in a schlenk tube and dissolved in toluene (8 ml), after a few minutes BBr₃ (1.94 ml in 1M heptane) was added dropwise over 30-minutes. Then the reaction mixture was warmed at 80 °C and stirred for 12 h (at 80 °C). After the reaction time, the mixture was filtered by using filter cannula, and the residue was dried under vacuum. We got brown powder. *Analytical data*: ¹¹**B NMR** (160 MHz, No locking) δ 1.11, -15.16, -24.67.

2.1.4. Reaction of phthalimide with BBr₃



Scheme 4. Reaction of phthalimide with BBr_{3.}

Phthalimide (0.250 g, 1.69 mmol, 1 equiv.) was taken in a schlenk tube and dissolved in toluene (10 ml) after a few minutes BBr₃ (2.03 ml in 1M heptane) was added dropwise over 30-minutes. Then the reaction mixture was warmed at 80 °C and stirred for 12 h (at 80 °C). After the reaction time, the mixture was filtered out by using a filter cannula, and the residue was dried under vacuum. We got brown powder. *Analytical data*: ¹¹B NMR (160 MHz, No locking) δ 0.62, -15.53, -25.01.

2.1.5. Reaction between Complex 1 and BBr3 under heating



Scheme 5. Reaction between Complex 1 & BBr₃ under heating conditions.

1 (0.5 g, 2.27 mmol, 1 equiv.) was taken in a schlenk tube and dissolved in toluene (15 ml) after a few minutes BBr₃ (2.73 ml in 1M heptane) was added dropwise over 30 minutes. Then after 10 minutes the reaction mixture was heated at 80 °C and stirred for 12 h (at 80 °C). After the reaction time, the mixture was filtered by using filter cannula, and the residue was dried under vacuum. We got brown powder. *Analytical data*: ¹¹B NMR (160 MHz, No locking) δ 20.69. In this case, from ¹¹B NMR, we got the related peak for the boron complex, in which the boron center is attached to one N-atom and two halogens. ^[5,8] We expect the formation of Complex A.

Part 2

Within this context, I described the synthetic procedure for the synthesis of complex B and its derivatives, by either trans-metalation or salt-metathesis procedure. I employ techniques such as NMR-spectroscopy and mass-spectrometry to characterize the synthesized complexes.

2.2.1 Synthesis of Complex B



Scheme 6. Synthesis of Complex B.

Complex **1** (0.250 g, 1.13 mmol, 1 equiv.) was dissolved in toluene (5 ml) in a schlenk tube and in another schlenk tube PhBCl₂ (0.181 g, 1.13 mmol, 1 equiv.) was also diluted in toluene (5 ml), then after few minutes the solution of PhBCl₂ was added to the solution of complex **1** at rt and the mixture was stirred, after 5 minutes the mixture was heated at 80 °C for 12 h. After the reaction time, the mixture was dried under vacuum, and the residue was washed with pentane. A brown solid product was obtained. *Analytical data*: ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 46.27, 29.01 and 20.31.

Part 3

2.3.1 Synthesis of Complex 2



Scheme 7. Synthesis of Complex 2.

Ferrocene (1.0 g, 5.37 mmol, 1 equiv.) was dissolved in hexane (40 ml) and then BBr₃ (5.37 ml, in 1M heptane) was added dropwise over 30 minutes and stirred the reaction mixture. After that, the mixture was refluxed at 80 °C for 5 h. After the reaction time, the mixture was filtered through filtering cannula, and the filtrate was kept in the refrigerator at -24 °C for crystallization. After one day we got the brown crystals of complex **2** (1.23 g, 65% yield). *Analytical data:* **¹H NMR** (500 MHz, CDCl₃) δ 4.93 (d, 2H), 4.54 (d, 2H), 4.25 (s, 5H). **¹³C{¹H} NMR** (126 MHz, CDCl₃) δ 71.68, 76.91, 77.42, 78.35. **¹¹B{¹H} NMR** (160 MHz, CDCl₃) δ 46.22.

2.3.2 Synthesis of Complex 3



Scheme 8. Synthesis of Complex 3.

In a J-Young NMR tube, 10 mg of complex **2** was taken and dissolved in CDCl₃, then 15 mg of NHC was added, and after 12 h reaction mixture was submitted for ¹¹B NMR. *Analytical data:* ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 7.36, 5.20. which is the signature peak for a four-coordinated boron complex.



Scheme 9. Reaction between Complex 2 and Complex 1.

To the solution of FcBBr₂ (0.250 g, 0.702 mmol, 1.0 equiv.) in toluene, a toluene solution of complex **1** (0.154 g, 0.702 mmol, 1.0 equiv.) was added at room temperature. After that the reaction mixture was stirred for 12 h at r.t. After the reaction time, the mixture was dried under vacuum, and washed with pentane. After drying we got a black powder as a product. *Analytical data:* ¹**H NMR** (500 MHz, CDCl₃) δ 7.41 (d, 1H), 7.16 (d, 1H), 6.70 (d, *J* = 45.9 Hz, 2H), 3.75 (s, 5H), 3.69 (d, 4H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 167.78, 134.63, 134.42, 123.63, 77.98, 77.40, 76.89, 68.81. ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 1.69. From the ¹¹B NMR data analysis, the compound may be a four-coordinated boron complex, in which phthalimide is coordinated with the boron center, which is given below.



2.3.4 Reaction between Complex 2 and potassium salt of phthalimide



Scheme 10. Reaction between Complex 2 and potassium salt of phthalimide.

To the solution of FcBBr₂ (0.250 g, 0.70 mmol, 1 equiv.) in toluene (5 ml), a solution of potassium salt of phthalimide (0.130 g, 0.70 mmol, 1 equiv.) in toluene (5 ml) was added at room temperature. The reaction mixture was allowed to be stirred for 12 h at room temperature and then filtered through a filter cannula. The obtained yellowish-orange filtrate was dried in vacuum to obtain the product as an orange powder. *Analytical data:* ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, *J* = 8.5 Hz, 2H), 7.77 (d, *J* = 5.2 Hz, 2H), 4.18 (s, 9H). ¹³C{¹H} NMR (126 MHz, CDCl₃) δ 167.93, 134.50, 132.77, 123.78, 68.93, 68.23. ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 19.09. From ¹¹B NMR, we confirm the formation of our desired complex, to support this statement we perform another reaction of complex 2 with the sodium salt of 2-methylindole, and in that case, we got ¹¹B NMR peak at 17.29 ppm.

2.3.5 Synthesis of Complex 4



Scheme 11. Synthesis of Complex 4.

To the solution of FcBBr₂ (0.1 g, 0.28 mmol, 1 equiv.) in toluene (3 ml), a solution of sodium salt of 2-methylindole (0.043 g, 0.28 mmol, 1 equiv.) in toluene (3 ml) was added at room temperature. The reaction mixture was allowed to be stirred for 12 h at room temperature and then filtered through a filter cannula. The obtained orange filtrate was dried in vacuum to get the product as a red powder. *Analytical data:* ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 17.29 ppm.

Part 4

2.4.1 Synthesis of Complex 5



Scheme 12. Synthesis of Complex 5.

A solution of indole (0.5 g, 3.81 mmol, 1 equiv.) in THF was cooled to -12 °C, *n*-butyllithium (1.52 ml, 1 equiv., in 2.5 M heptane) was added and the reaction mixture was allowed to warm to r.t. with stirring for 1 h. After that the solution was again cooled to -10 °C and a solution of trimethylchlorosilane (0.58 g, 4.95 mmol, 1.3 equiv.) in THF was added dropwise. The reaction mixture was stirred overnight at r.t. After the removal of a white precipitate by filtration, the solvent was evaporated and the residue was distilled to give a clear colorless liquid. *Analytical data:* ²⁹Si{¹H} NMR (99 MHz, CDCl₃) δ 6.58 ppm.

2.4.2 Synthesis of Complex 6



Scheme 13. Synthesis of Complex 6.

Complex 5 (1.8 g, 8.85 mmol, 1 equiv.) was dissolved in toluene (10 ml) and then BBr₃ (9.73 ml, 1.1 equiv., in 1M heptane) was added dropwise and the reaction mixture was stirred at room temperature, for 10 minutes. After 10 minutes, the reaction mixture was heated at 75 °C and stirred for 12 h. After being stirred for 12 h, the reaction mixture was filtered through filter cannula, and the filtrate was dried under vacuum. The product was obtained as an orange liquid. *Analytical data:* ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 17.99.

2.4.3 Synthesis of Complex 7



Scheme 14. Synthesis of Complex 7.

To the solution of Complex **6** (0.2 g, 0.66 mmol, 1 equiv.) in diethyl ether (3 ml), a solution of phenyl lithium (0.055 g, 0.66 mmol, 1 equiv.) in diethyl ether (3 ml) was added at room temperature. The reaction mixture was allowed to be stirred for 12 h at room temperature and then filtered through a filter cannula. The obtained white filtrate was dried in vacuum to get the product as a white oily liquid. *Analytical data*:¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 2.34, 7.21.

Part 5

2.5.1 Reaction between phthalimide and 9-BBN



Scheme 15. Reaction between phthalimide and 9-BBN.

Phthalimide (0.150 g, 1.01 mmol, 1.0 equiv.) was taken in a schlenk tube and dissolved in THF (5 ml), then 9-BBN (2.039 ml, in 0.5 M THF) was added to the above solution at 0 °C and stirred. The formation of H₂ gas bubbles was observed. After a few minutes, the reaction mixture was allowed to come to r.t. Then the mixture was stirred overnight at r.t. After the reaction time, the mixture was dried under vacuum. The greens-yellow solid was obtained. *Analytical data:* ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 58.93 (broad). The presence of an active hydrogen within the molecule facilitates the liberation of H₂ gas upon interaction with 9-BBN. ^[23, 24] Additionally, confirmation of the formation of the B-N bond was obtained from the ¹¹B NMR signals appeared in the same chemical shift region, further supporting the formation of the B-N. ^[23]

To confirm the liberation of H_2 gas and the establishment of B-N bond, we conducted a brief experiment in a J-Yong NMR tube. Within 30 minutes of introducing 9-BBN into phthalimide in CDCl₃, we analyzed the ¹H NMR and detected a singlet peak at 4.18 ppm, the characteristic peak for H_2 . ^[25] After drying the reaction mixture, we further recorded the ¹H NMR in CDCl₃ and there was no peak (singlet) at 4.18 ppm. So, from this analysis, we concluded that there is a formation of B-N bond via H_2 gas liberation.

2.5.2 Reaction between Ligand 1 and 9-BBN



Scheme 16. Reaction between Ligand 1 and 9-BBN.

Ligand **1** (0.150 g, 1.01 mmol, 1.0 equiv.) was taken in a schlenk tube and dissolved in THF (5 ml), then 9-BBN (2.039 ml, in 0.5 M THF) was added to the above solution at r.t. and stirred. The formation of H₂ gas bubbles was observed. The reaction mixture was stirred for 12 h at r.t. After the reaction time, the mixture was dried under vacuum. We got an off-white liquid product. *Analytical data:* ¹¹B{¹H} NMR (160 MHz, CDCl₃) δ 59.11. LCMS M/Z calculated C₂₁H₃₃ B₁N₂[M+nH] 325.2813 found 325.2911.

Chapter 3





6.

5.



7.



8.



20

Chapter 4



Figure 6. ¹H NMR of Complex **1.**



Figure 8. LCMS of Complex 1.





Figure 10. ¹H NMR of reaction between Complex **1** and BBr₃.

3. NMR data of reaction between potassium salt of phthalimide with





Figure 11. ¹¹B NMR of reaction between potassium salt of phthalimide with BBr_{3.}

4. NMR data of reaction between phthalimide with BBr₃



Figure 12. ¹¹B NMR of reaction between phthalimide and BBr₃.

5. NMR data of reaction between complex 1 and BBr3 under heating condition



Part 2

1. Characterization of Complex B

DIPAK-SP-P-GOFP.2.fid



Figure 14. ¹¹B{¹H} NMR of complex **B**.

Part 3



Figure 16. ¹H NMR of Complex 2.



Figure 17. $^{13}C{^{1}H}$ NMR of Complex 2.

∑7.36
∑5.20

2. Characterization of Complex 3

DIPAK-SP-P-30.2.fid





Figure 18. $^{11}B{}^{1}H{}$ NMR of Complex 3.

3. NMR data for reaction between Complex 2 and Complex 1



Figure 20. ¹H NMR of reaction between Complex **2** and Complex **1**.



Figure 21. $^{13}C{^{1}H}$ NMR of reaction between Complex **2** and Complex **1**.

4. NMR data for the reaction between Complex 2 and potassium salt of phthalimide



Figure 22. ¹¹B{¹H} NMR of reaction between Complex **2** and potassium salt of phthalimide.



Figure 23. ¹H NMR of reaction between Complex **2** and potassium salt of phthalimide.



Figure 24. ¹³C{¹H} NMR of reaction between Complex **2** and potassium salt of phthalimide.

5. Characterization of Complex 4



2. Characterization of Complex 6



Figure 27. ${}^{11}B{}^{1}H{}$ NMR of Complex 6.

3. Characterization of Complex 7

DIPAK-SP-P-66-ET.1.fid





Figure 28. ¹¹B{¹H} NMR of Complex **7**.

Part 5



Figure 29. ¹¹B{¹H} NMR of reaction between phthalimide and 9-BBN.

NMR data of a brief experiment of 9-BBN with phthalimide in a J-Yong NMR tube

1.2. 1H NMR of reaction mixture within 30 minutes



Figure 30. ¹H NMR of reaction between phthalimide and 9-BBN within 30 minutes.



Figure 32. ¹H NMR of phthalimide.

2. Characterization of reaction between Ligand 1 and 9-BBN



Figure 33. ¹¹B{¹H} NMR of reaction between Ligand 1 and 9-BBN.



Figure 34. LCMS of reaction between Ligand 1 and 9-BBN.

Chapter 5

Conclusion & Future Outlook

In conclusion, I have synthesized the precursor compounds for the boron cations. Complex **1** is the silicon-based compound which will help in isolating the silicon boron exchange compound. Following are the Complexes that were successfully synthesized.



Further characterization is required to confirm the identity of complexes A, B, and 8. The introduction of 9-BBN with the molecules containing an active hydrogen atom allowed us to investigate the formation of either a B-N bonded species or a four/six-membered B-N cyclic compound, via H₂ gas liberation. In the case ligand 1 reaction with 9-BBN can give two products one is a singly B-N bonded product and the other one is a 4-membered cyclic boron compound (similar to the cyclobutene), where the 2nd nitrogen atom forms a coordinate bond with the boron center. From this study, I would like to continue the following investigation.



Chapter 6

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