

**Hydroboration Studies of Olefins with Heterocyclic Hydroborating Reagents
with Various Transition Metal Complexes: Attempted Diastereoselective
Synthesis of Homoallylic Alcohols *via* Hydroboration.**

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Declaration

The experimental work described in this dissertation was carried out in the School of Chemistry, College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Pietermaritzburg, under the supervision of Professor Ross S. Robinson.

I hereby declare that these studies represent original work by the author and have not otherwise been submitted in any form for any degree or diploma to any tertiary institution. Where the use of published information from other authors has been made and it is duly acknowledged in the text.

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Professor Ross S. Robinson (Supervisor)

Abstract

Hydroboration is one of the key routes to afford organoborane esters which are versatile intermediate in organic synthesis. Investigations of different hydroborating reagents and catalysts toward hydroboration present alternative to achieve organoborane ester with different stability, selectivity, and yield. Hence, a part of this study was focused on the preparation of heterocyclic hydroborating reagents with a single site available for hydroboration. Four reagents were prepared which included the well-known catecholborane (**23**) and pinacolborane (**24**) and the hardly studied 2,3-dihydro-1,3,2-benzodiazaborole (**31**) and 2,3-dihydro-1,3,2-benzoxazaborole (**34**).

A study to utilize hydroboration to prepare allylic boronic esters using the four hydroborating reagent above was also undertaken. These esters were to be further employed for diastereoselective synthesis of homoallyl alcohols. Unfortunately, study failed after attempts to preparation and extraction these esters such as (*Z*)-4,4,5,5-tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (**104**) were unsuccessful. The ^{11}B -NMR spectroscopy results indicated the formation of a new signal of boron compound which was assumed as the corresponding esters, however, was never isolated for further evidence.

The four hydroboration reagents mentioned above were further investigated for hydroboration with different transition metal catalysts namely Wilkinson's catalyst (**58**), dimethyltitanocene 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron(II) chloride ($(^{i\text{Pr}}\text{BIP})\text{FeCl}_2$) (**79**) and 2,6-bis-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine iron(II) chloride ($(^{\text{Mes}}\text{BIP})\text{FeCl}_2$) (**80**). These study indicated the better hydroboration efficiency of the $(^{i\text{Pr}}\text{BIP})\text{FeCl}_2$ (**79**) and $(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (**80**) for the hydroboration with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) and 2,3-dihydro-1,3,2-benzoxazaborole (**34**) compared to the Wilkinson's catalyst (**58**). Poor reactivity of dimethyltitanocene toward hydroboration was also observed. Furthermore, within this study two boronic esters 2-octyl-1,3,2-benzoxazaborolane (**53**) and 2-(2-phenylpropyl)-1,3,2-benzoxazaborolane (**116**) were isolated for the first time.

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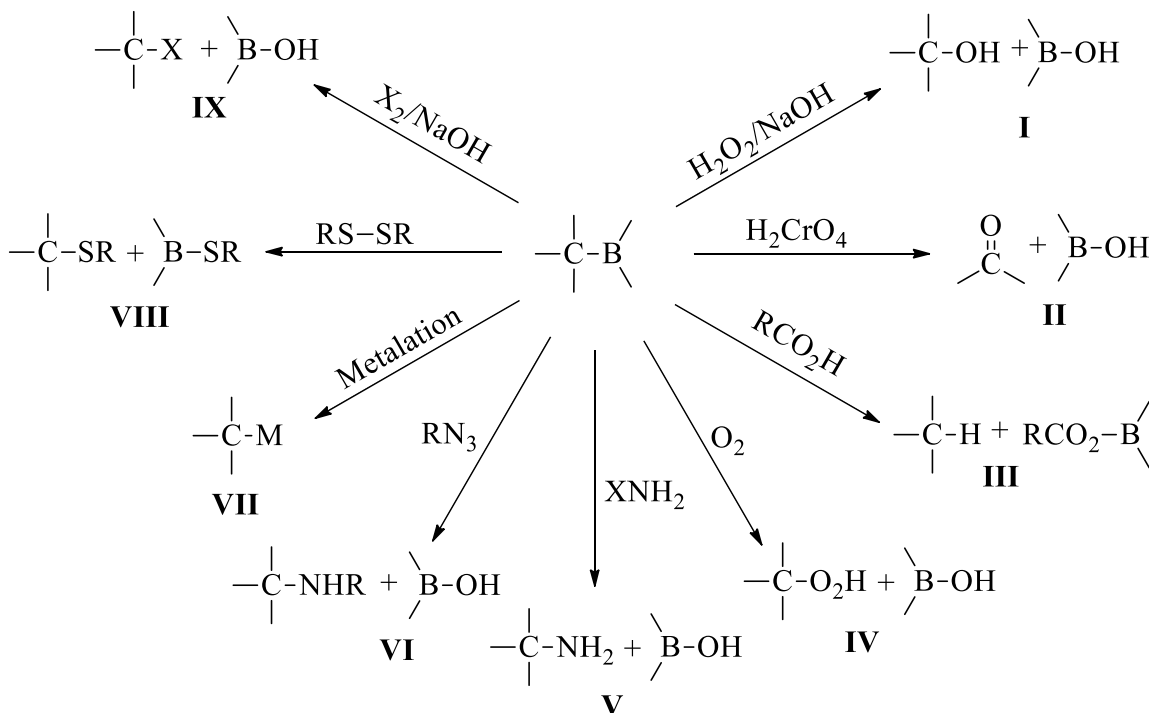
Abbreviations

atm	Atmosphere
¹¹ B	Boron-11
BH ₃	Borane
B ₂ H ₆	Diborane
BMS	Borane dimethyl sulfide
°C	Degrees Celsius
¹³ C	Carbon-13
COSY	Correlation spectroscopy
DCM	Dichloromethane
DEPT	Distortionless enhancement by polarisation transfer
Et ₂ O	Diethyl ether
ee.	Enantiomeric excess
hrs	Hour(s)
¹ H	Proton
HMBC	Heteronuclear multiple-bond correlation
HR-APIMS	High-resolution atmospheric pressure ionisation mass spectrometry
HPLC	High-performance liquid chromatography
HSQC	Heteronuclear single-quantum correlation
Hz	Hertz
<i>i</i> Pr	Isopropyl
MeOH	Methanol
Mes	Mesityl
min	Minutes
NMR	Nuclear Magnetic Resonance
ppm	Parts per million
PPh ₃	Triphenylphosphine
THF	Tetrahydrofuran
TS	Transition state

1. Introduction

1.1. Organoboranes and their importance: Direct focus on boronic esters

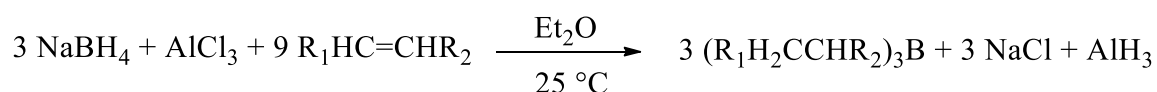
Organoboranes are versatile intermediates in organic synthesis due to their ability to induce a vast range of transformations such as oxidation (**I**, **II** and **IV**), protonation (**III**), amination (**V** and **VI**), metalation (**VII**) sulfurization (**VIII**) and halogenation (**IX**) (Scheme 1.1).¹ Organoboranes, especially boronic esters incorporate unique properties which include mild Lewis acidity (due to vacant *p*-orbital), stability towards atmospheric oxidation, highly selective and low toxicity to humans.² Therefore, the manner in which these organoboranes are afforded is of importance as they are often the key intermediates for organic synthetic routes.



Scheme 1.1: Organoboranes and their possible range of transformations.

Boronic esters are commonly prepared through alkylhalides conversion to Li or Grignard reagents thereafter the reagents are reacted with boron compounds.¹ Recently there have been some reports of boronic esters obtained from borylation of saturated hydrocarbons and alkylhalides in the presence of a rhodium and copper catalyst respectively.^{3, 4} This report has been focused on a discussion of boronic esters achieved *via* hydroboration.

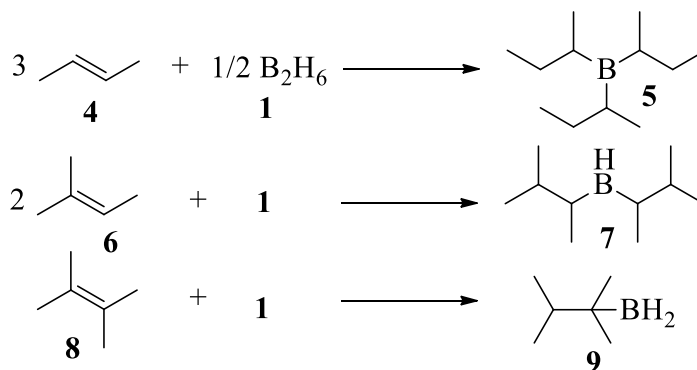
Brown and Rao⁷ made the most important developments in the area of hydroboration in 1956. These authors noticed that the reducing power of sodium borohydride (NaBH₄) was enhanced in the presence of aluminium chloride and hydroboration with this reagent afford the trialkylboranes at room temperature in a high yield. The same authors⁸ further reported that hydroboration proceeds efficiently in the presence of ethereal solvents and less readily in solvent free condition or hydrocarbon solvents. In the above studies,^{7,8} ethylene, 1-pentene and 2-pentene, styrene (**10**), and cyclohexane (**17**) were reacted with NaBH₄ in an ethereal solvent and the presence of aluminium chloride (AlCl₃) at room temperature to form the corresponding trialkyl boranes (Scheme 1.4). Often in literature, Brown and Rao have been recognized as the founders of hydroboration although it's untrue since Hurd⁵ was the first to report the reaction. The misunderstanding most probably because a clear descriptive of hydroboration was first reported by Brown and Rao.⁷



Scheme 1.4: Hydroboration of olefins with sodium borohydride in the presences of aluminium chloride.

1.3. Stoichiometry and Regioselectivity

The stoichiometry for hydroboration of olefins with borane proceeds to form trialkylboranes.⁷⁻¹⁰ However, steric requirements of the olefin could result in a change of stoichiometry of the reaction to afford either of dialkylboranes or monoalkylboranes. This effect was first demonstrated by Brown and Klender in 1962 when they observed that hydroboration of 2-butene (**4**) with borane (**1**) to afford tributylborane (**7**).¹⁰ Although when a sterically more demanding olefin such as 2-methyl-2-butene (**6**) was used a afforded dialkylborane (**7**) and a further increase in the steric requirements of the olefin to 2,3-dimethyl-2-butene (**8**) afforded a monoalkylborane (**9**), irrespective of the reactant amount ratio (Scheme 1.5).



Scheme 1.5: Effect of steric for hydroboration of olefins with diborane (**1**).

Brown and Zweifel studied the directive influence for hydroboration of olefins with borane (**1**).¹¹ In this study, simple terminal alkenes such as 1-butene (**2**), 1-pentene, 1-hexene (**38**) resulted in 94% boron being located at the terminal position, branching of the alkyl groups of the alkenes such as 3-methyl-1-butene, 3,3-methyl-1-pentene, and 4,4-dimethyl-1-hexene had no significant influence on the distribution of boron with the exception of the case of a phenyl group on styrene in which 80% of boron was found being located at the terminal position (Figure 1.1).¹¹ These authors further investigated the influence alkyl substitution on the 2-position using 2-methyl-1-butene, 2,4,4-trimethyl-1-pentene and α -methylstyrene (**74**) were investigated and in all cases, 99% or more of the boron was found to be located at the terminal position. Furthermore when trisubstituted alkenes were investigated 98% of the boron was located at the less substituted position and when acyclic internal alkenes were studied they resulted with an even boron distribution.¹¹ The above authors concluded from this study that regioselectivity of hydroboration was influenced by steric interactions.

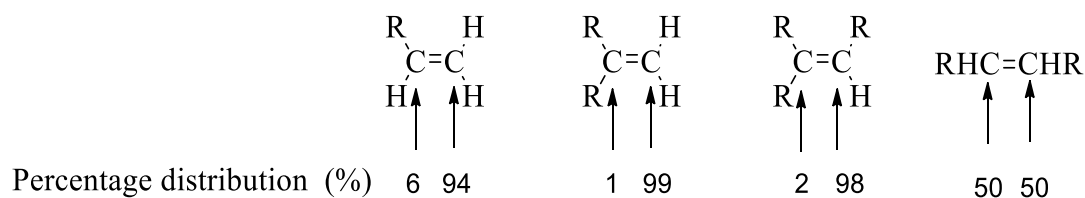


Figure 1.1: The regioselectivity observed for the hydroboration of different types of olefins with borane (**1**)

The steric effect of hydroborating reagents on the regioselectivity for hydroboration have been demonstrated in a series of different studies.¹²⁻¹⁴ Brown and Zweifel¹² reported on the hydroboration of 1-hexene (**38**) and styrene (**10**) to afford 99% and 98% of the boron being located at the terminal position using the sterically demanding hydroborating reagent disiamylborane (Sia₂BH) (**11**) respectively.¹² Similar results were reported by Knights and Brown¹³ when borabicyclo[3.3.1]nonane (9-BBN) (**12**) was studied with the same olefins (a representation of these studies is depicted by Figure 1.2). The study demonstrated that high steric requirement of alkyl hydroborating reagents results in the boron being attached to the less hindered carbon of the double bond. Further support was reported by Zweifel *at al.*,¹⁴ that indicated the hydroboration of styrene (**10**) with dicyclohexylborane (**18**), bis-(trans-2-methylcyclohexyl)-borane, or diisopinocampheylborane (**21**) afforded similar results.

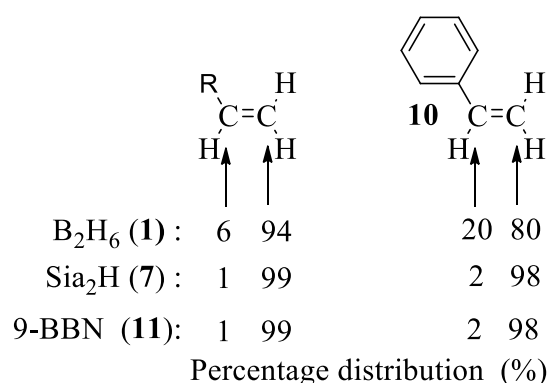


Figure 1.2: The regioselectivity observed for the hydroboration of terminal alkenes and styrene with the various hydroborating reagent.

From the above studies, it was noted from the results for the hydroboration of styrene (**10**) were incompatible with the other terminal alkenes and Brown and Zweifel made numerous attempts to find an explanation for the observed directive influence of phenyl group using styrene (**10**).¹¹

They attempted to change the boron distribution by using different boron-hydride sources, solvents and reaction temperature for hydroboration, however, no significant change was observed. It was only upon the addition of *para*-substituents on styrene (**10**) that a change was noted. When 4-methoxystyrene, 4-methylstyrene, styrene (**10**) and 4-chlorostyrene were investigated and they afforded 9%, 18%, 20% and 35% of boron addition at the alpha-carbon respectively (Figure 1.3).¹¹ These authors concluded that both steric and electronic factors influence the regioselectivity of the hydroboration reaction.

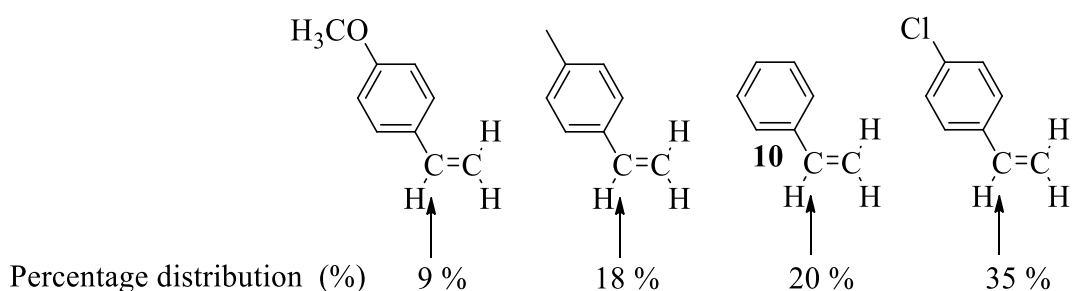
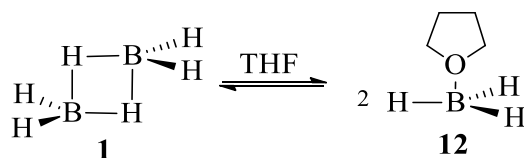


Figure 1.3: The regioselectivity observed for the hydroboration of styrene (**10**) analogues with different *para*-substituents hydroborated with borane (**1**).

1.4. Mechanism of Hydroboration

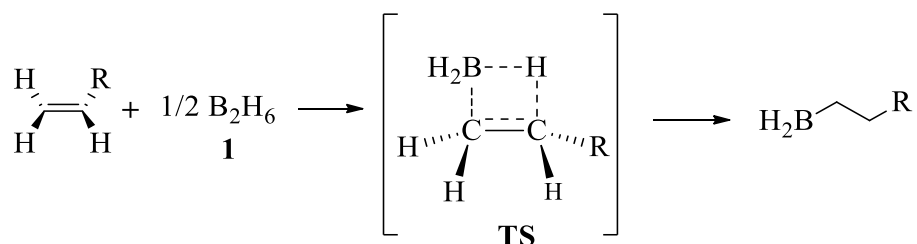
In 1956, Brown⁷ reported that hydroboration of simple olefins proceeds efficiently in an ethereal solvent and this discovery of the reaction was attributed to the formation of a borane-solvent complex such as *borane-tetrahydrofuran complex* (**12**) as depicted in Scheme 1.6. The formation of this complex (**12**) resulted in an increased concentration of borane (**1**) in solution available for hydroboration and, therefore, the reactions proceeded faster and more efficiently compared to early reports.^{5,6}



Scheme 1.6: Diborane and tetrahydrofuran interactions.

Brown and Zweifel¹¹ reported that using different ethereal solvents such as ether, tetrahydrofuran and glycine had no significant influence on the regioselectivity for hydroboration of styrene (**4**). It

was then suggested that solvent participation in the transition state that controls the direction of the addition of boron was minimal. Hydroboration had been reported to proceed by a Markovnikov addition boron-hydrogen moiety (B–H) and by a *cis*-addition of B–H observed from hydroboration of cyclic olefins.^{7, 15} Further evidence for a *cis*-addition of B–H was reported by Brown and Ravindrab.^{16, 17} These authors reported the hydroboration of alkyne with a *cis*-addition of B–H to afford *trans*-alkenylboranes. After careful analysis of these studies, Brown and Zweifel¹¹ proposed a four-coordinate transition state (TS) depicted in Scheme 1.7.



Scheme 1.7: Four coordinate transition state for hydroboration.

The four-coordinate transition state for hydroboration then would proceed *via* two possible pathways which determine the regioselectivity of the reaction (Figure 1.4).¹¹ The thermodynamically favourable transition state would be obtained when the larger group boron (compared to hydrogen) adds to the less hindered side of the alkene double bond upon hydroboration to avoid steric repulsion forces depicted in Figure 1.4.

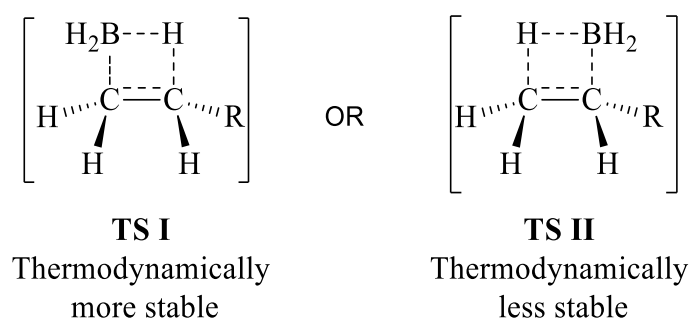
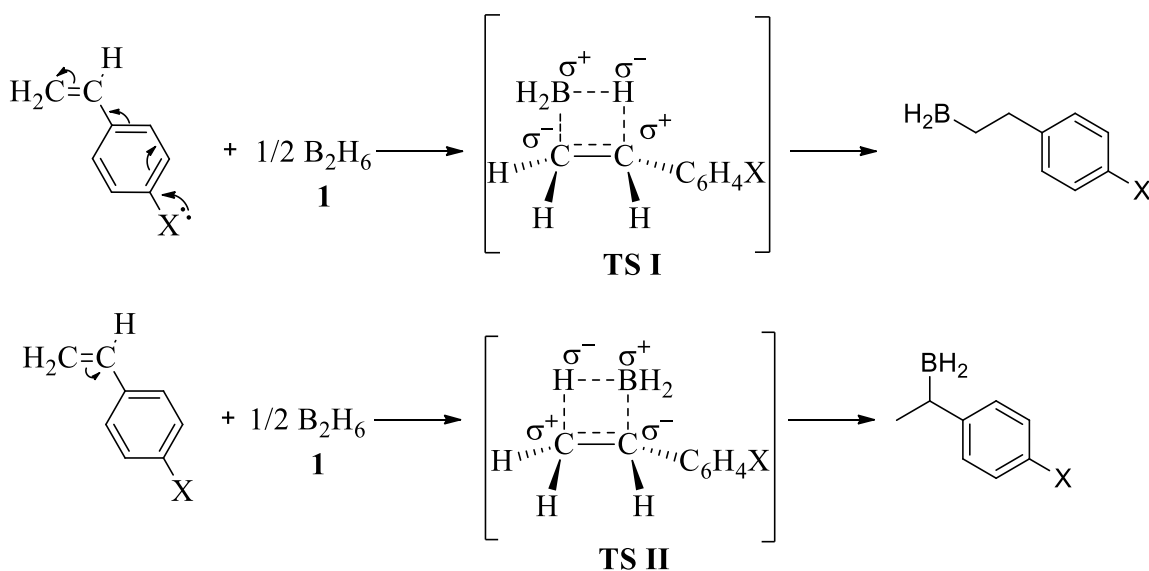


Figure 1.4: The two possible four-coordinate transition state that determines the regioselectivity of the hydroboration.

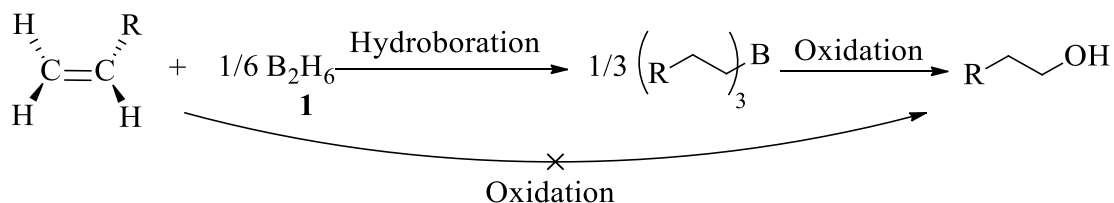
The four-coordinate transition state mechanism could be also used to account for the electronic influences of *para*-substituents on styrene (**10**) (Figure 1.3).^{11, 18} It was assumed that boron-

hydrogen bond was polarized with hydrogen possessing a hydridic character. An electronic shift on the carbon-carbon double bond would afford opposite partial charge in each of the double bond carbons therefore upon hydroboration electrostatic interaction would influence transition state stability and the tendency of *para*-substituents to influence the regioselectivity. Electron donating *para*-substituents on styrene (**10**) would increase partial charge at the β -position thereby destabilization of transition state II and favour transition state I while opposite effect would be observed for an electron withdrawing *para*-substituents (Scheme 1.8).



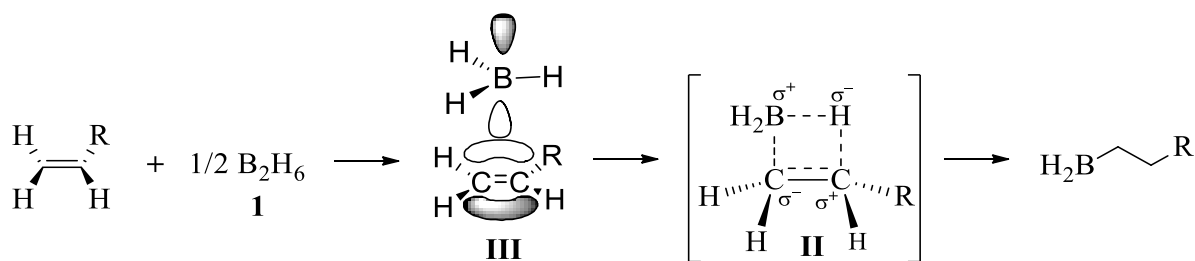
*Scheme 1.8: Transition state for hydroboration styrene (**10**) derivatives and their associated electronic shift for donating and withdrawing substituent.*

It must be noted that in all these hydroboration studies that analysis and conclusions were drawn using results obtained from the hydroboration-oxidation reaction alcohol final product. Therefore, it was always assumed that the reaction proceeds with a retention of configuration and no direct oxidation of the olefin as depicted in Scheme 1.9.



Scheme 1.9: The hydroboration-oxidation reaction of olefins to afford alcohols.

Klein and Wolff¹⁹ made further developments to the mechanism proposed by Brown and Zweifel depicted in Scheme 1.7. These authors reviewed the results reported by Brown and Zweifel,²⁰ thereafter, calculated relative reactivity of tertiary carbons on 2-methylbutene and it was found to be eight times more reactive than the same carbon on 1-butene (**2**) and that of 2-methylpentene to be seven times more reactive than the same carbon on 1-pentene. They concluded that these results could not be explained solely using the four-center transition state mechanism depicted in Scheme 1.7. To justify the above observations these authors proposed a three-centered pre-transition state complex of the alkene-borane complex (**III**) added to the initially proposed mechanism (Scheme 1.10). This complex (**III**) activation energy was relatively small therefore the formation of the complex would be insensitive of the olefin. Thereafter this complex rearranges to four-center transition state (**II**) indicating most hydroboration reactions would proceed at comparable rates.¹⁹



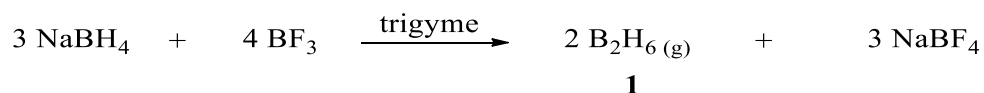
Scheme 1.10: The pre-transition state hydroboration complex.

1.5. Hydroborating Reagents

Since the interesting hydroboration report by Brown and Rao in 1956,⁷ many studies have been conducted to develop the reaction. Several studies have focused on the development of the hydroborating reagent to achieve better selectivity, stability, and hydroboration efficiency.^{10, 12-15.}²¹ In the past six decades a number of hydroborating reagents have been discovered and in this section, selected hydroborating reagents are discussed with the primary focus on their synthesis, stability, and hydroboration efficiency.

1.5.1. Borane and its Adducts

The first efficient method to prepare the diborane (**1**) was reported Schlesinger in 1931 when boron chloride was reacted with hydrogen to afford diborane (**1**) in a 90% yield.²² Synthesis of diborane/borane (**1**) has been improved over the years and in 2000, Kanth and Brown reported the most convenient route towards the synthesis of diborane (**1**). In this study sodium borohydride (NaBH₄) and boron trifluoride (BF₃) both dissolve separately in triglyme or tetraglyme thereafter reacted to afford the diborane in a 94% yield (Scheme 1.11).²³



Scheme 1.11: Preparation of borane from boron chloride and sodium borohydride.

The first hydroborating reagent was diborane (**1**) and hydroboration with this reagent was reported to require high reaction temperature and poor yields. When the diborane (**1**) was coupled with Lewis base to afford monomeric borane adduct, a significant enhancement was observed, and the reaction could proceed efficiently with excellent yields at room temperature.⁷ These type of adducts present better stability than diborane and over the years a number of these adducts have been discovered.

Borane adducts are usually prepared by passing of the borane gas through the corresponding solvent. *Tetrahydrofuran-Borane complex* (**12**) is the most stable and used ethereal borane adducts but the setbacks with this reagent are it isolated use in ethereal solvents and low commercially available in low concentration (1 M). The stability trend for ethereal adducts observed is $\text{THF}\cdot\text{BH}_3 > \text{Me}_2\text{O}\cdot\text{BH}_3 \gg \text{Et}_2\text{O}\cdot\text{BH}_3$.¹⁵ The more stable borane adduct reagent can be prepared from the least one through and exchange reaction such as phosphine- and amine-borane adducts which are prepared from $\text{THF}\cdot\text{BH}_3$ (**12**).²⁴

Dimethyl sulfide-borane complex, $\text{BH}_3\cdot\text{SMe}_2$ (BMS) (**16**) is the most used of all available borane adduct.²⁵⁻²⁷ The reagent was first prepared by Burg and Wagner²⁸ by the condensation of borane gas and dimethyl sulfide. It presents numerous advantages over other adducts, for example, increased stability and commercially available in concentration ten times higher than that of $\text{THF}\cdot\text{BH}_3$ (**12**) and can be utilized in a wide range of solvents.²⁹ Furthermore, dimethyl sulfide is insolubility in water, therefore, simple ether-water extraction of the organic product can be performed. This reagent was chosen for the preparation of all hydroborating reagents for this project. The setbacks for using BMS (**16**) is that dimethyl sulfide from the reagent has a pungent odour. Recently Smith *et al.*,²⁵ reported that replacing BMS (**16**) with poly(propyl sulfide)-borane (**13**) (Figure 1.5) reactivity and paralleled the properties of BMS (**16**) without the disadvantage of the odour.

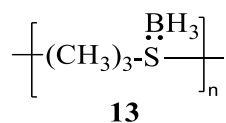
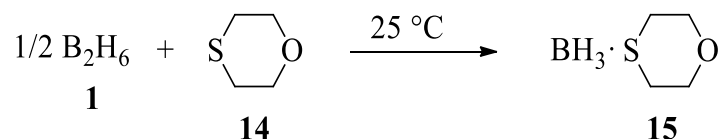


Figure 1.5: Poly(propyl sulfide)-borane.

Brown and Mandal³⁰ discovered that borane-1,4-thioxane (**15**) can be prepared by passing diborane (**1**) gas through 1,4-thioxane (**14**) at 25 °C (Scheme 1.12). In this studies, the reagent was reported to be stable at 25 °C, miscible with standard solvents used for hydroboration, and could be presented in high concentration (8 M). Thereafter, the reagent was used to perform a range of hydroboration reactions and demonstrated properties similarly to BMS (**16**).



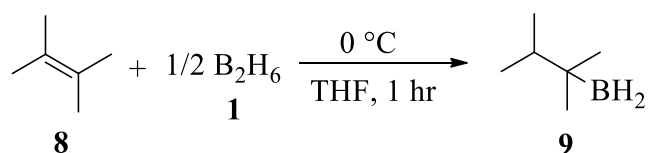
Scheme 1.12: Preparation of borane-1,4-thioxane (**15**) from diborane and 1,4-thioxane (**14**).

1.5.2. Alkylborane Hydroborating Reagents

Alkylborane hydroborating reagents are usually a product of the hydroboration of sterically demanding alkenes which afford monoalkylboranes or dialkylboranes and most of these reagents exist as dimers but for convenient they are treated as monomers (brief discussions of some of these reagents were highlighted previously in section 1.3 and 1.4). Organoboranes are a key intermediate to many organic syntheses and often an alternative hydroborating reagents to diborane are typically required to afford these intermediate with different selectivity, yield, stability. This section is focused on the discussion of some common alkylborane.

1.5.2.1. *Thexylborane* (**9**)

Thexylborane (**9**) can be obtained from the controlled hydroboration of 1,2-dimethyl-2-butene (**8**) with borane-tetrahydrofuran adduct (**12**) (Scheme 1.13).¹⁰ Negishi *et al.*³¹ reported that when this reaction was conducted in the presence of a large excess of the olefin the reaction can afford dithexylborane. Furthermore, Rice and Okamoto³² reported that when this reaction was done at high pressure (500 - 600 atm) it affords trithexylborane, however, dithexylborane and trithexylborane tend to isomerize with the boron atom migration to the terminal position of the alkyl groups to relieve steric strains. Thexylborane (**9**) was reported to be stable for at least a week when stored in THF at 0 °C after that time the migration of the boron to the terminal position becomes significant (3% in 8 days to 9% in 16 days).³³

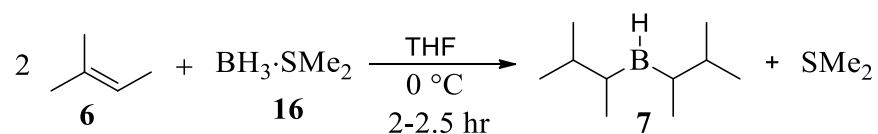


Scheme 1.13: Synthesis of thexylborane (**9**).

Thexylborane (**9**) has demonstrated a similar or minimal increase of regioselectivity towards olefin hydroboration to that observed with diborane (**1**), for example, the hydroboration of 1-hexene (**38**) afforded 95% of the boron being located at the terminal position and similar results were obtained with diborane (**1**).³⁴

1.5.2.2. *Bis(3-methyl-2-butyl)borane (7)*

Brown *et al.*,^{7, 9, 10} reported that the hydroboration of 2-methyl-2-butene (**6**) with diborane (**1**) in diglyme at 0 °C affords bis(3-methyl-2-butyl)borane (**7**) also known as disiamylborane (Sia₂BH), and a further reaction to afford the corresponding trialkylate borane being slowly or negligible. An improved synthetic route was reported Brown and Moerikofer²⁶, the new route utilized *borane-dimethyl sulfide complex (16)* as a hydroborating reagent and THF solvent as illustrated in Scheme 1.14.



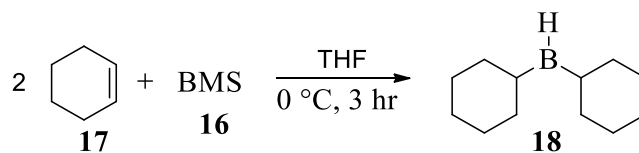
Scheme 1.14: Synthesis of bis(3-methyl-2-butyl)borane (7).

The large steric requirements of Sia₂BH (**7**) provide some steric control over the regioselectivity of hydroboration hence hydroboration with the reagent predominately favoured the formation of less sterically demanding product (some examples were discussed in section 2.3). Brown and Moerilkofer³⁵ reported that Sia₂BH (**7**) was more selective to the structure of the olefin than diborane (**1**), in this study it was illustrated that difference in reactivity of the most and least reactive olefin was about a factor of 30 with borane (**1**) while 10 000 with Sia₂BH (**7**).

The high selectivity of Sia₂BH (**7**) enables possible selective hydroboration of more reactive olefin in the presence of least reactive ones, for example, the hydroboration of 1-hexene (**38**) in the presence of 2-hexene, cyclopentene in the presence of cyclohexene (**17**).^{12, 36, 37} Most remarkably, the reagent can discriminate between *cis*- and *trans*-isomers, for example, Brown and Zweifel¹² demonstrated that *cis*-2-pentene can be separated from *trans*-2-hexene with this reagent.

1.5.2.3. *Dicyclohexylborane (18)*.

Brown and Moerikofer³⁸ discovered that dicyclohexylborane (**18**) can be synthesized from the hydroboration of cyclohexene (**17**) with borane in diglyme at 0 °C. A more convenient synthetic route to afford the reagent was reported in 1977 by Brown *et al.*²⁶, cyclohexene (**17**) was hydroborated with BMS (**16**) in THF, Et₂O or DCM at 0 °C as illustrated in Scheme 1.15. In 2012, Smith *et al.*,²⁵ reported that this reagent can also be prepared with a similar protocol using poly(propylene sulfide)-borane (**13**) as borane source and afford a moderate yield of 77%.

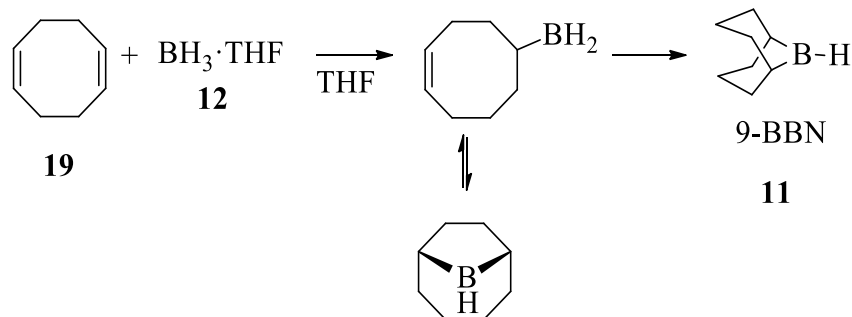


Scheme 1.15: Synthesis of dicyclohexylborane (18).

Dicyclohexylborane (**18**) was reported to be less prone to isomerization degradation than Sia₂BH **7** while their regioselectivity toward hydroboration of olefin parallels each other.^{14, 39} The reagent is less bulky than other regioselective alkylborane reagents such as bis(3-methyl-2-butyl)borane (**7**) and diisopinocampheylborane (**21**) which may be used to an advantage for the hydroboration of hindered olefins whereby the bulky reagents suffer from significant dehydroboration.

1.5.2.4. *9-borabicyclo[3.3.1]nonane (11)*.

Knight and Brown²⁷ reported that 9-borabicyclo[3.3.1]nonane (**11**) was conveniently synthesized from controlled hydroboration of 1,5-cyclooctadiene (**19**) with *borane-tetrahydrofuran complex* (**12**) to afford the corresponding reagent in an excellent yield of 99% (Scheme 1.16). In this study, the reagent was reported to possess extraordinary thermal stability and resistance toward atmospheric oxidation, these properties are uncommon for dialkylboranes such as Sia₂BH (**7**) and dicyclohexylborane (**18**) as discussed above.

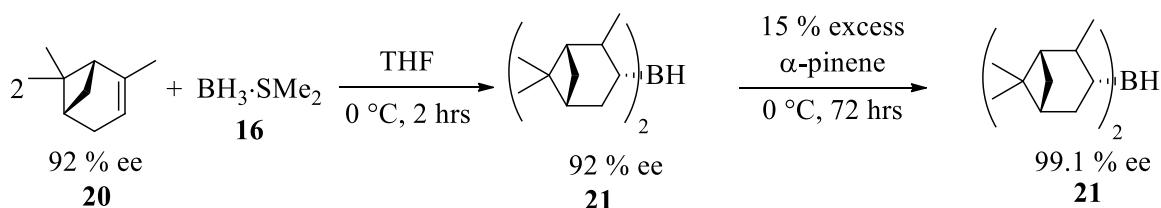


Scheme 1.16: Synthesis of 9-borabicyclo[3.3.1]nonane (**11**).

Knight and Brown¹³ also reported that the regioselectivity of hydroboration with 9-BBN (**11**) is highly similar to that of Sia₂BH (**7**) and that hydroboration with this reagent proceed more rapidly, for example, the hydroboration of 2-methyl-2-butene (**6**) and *cis*-4-methyl-2-pentene require six and five hours, respectively complete with Sia₂BH (**7**) whereas both reactions require 5 minutes with 9-BBN (**11**).

1.5.2.5. *Diisopinocampheylborane (21)*.

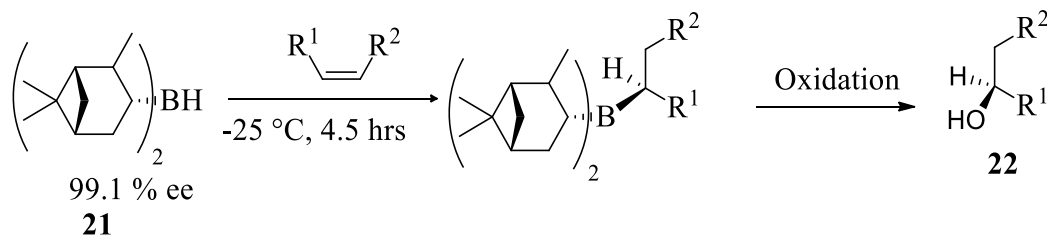
Brown *et al.*,⁴⁰ reported that diisopinocampheylborane (**21**) can be conveniently prepared in high enantiomeric excess (ee) from BMS (**16**) and 92% ee α -pinene. The reaction proceeds at 0 °C in THF for two hours to afford diisopinocampheylborane (**21**) in a 92% ee thereafter 15% excess α -pinene was added thereafter allowed to equilibrate for 3 days at the same temperature which afforded a 99.1% ee of the reagent (Scheme 1.17).



Scheme 1.17: Synthesis of diisopinocampheylborane (**21**).

This reagent demonstrated the high stereoselectivity upon hydroboration when Zweifel *et al.*,¹⁴ conducted a clean extraction of 2-*trans*-hexene (99% pure) from an equimolar *trans*- and *cis*-isomers. This reagent was also used for asymmetric hydroboration of disubstituted

cis-alkenes such as *cis*-2-butene, *cis*-2-pentene, *cis*-2-hexene or *cis*-4,4-dimethyl-2-pentene and after oxidation afford the corresponding chiral alcohols (**22**) with 60 – 98.1% ee (Scheme 1.18).



Scheme 1.18: Hydroboration of prochiral *cis*-2-alkene with diisopinocampheylborane (**21**).

1.5.3. Heterocyclic Hydroborating Reagents.

Since the first report of a potential heterocyclic hydroborating reagent reported by Rose and Shore⁴¹ in 1962, a number of heterocyclic hydroborating reagents have been discovered to date. These reagents have demonstrated high regio-, chemo- and stereoselectivity with high reaction yields upon hydroboration in the presence of some metal catalysts.^{42, 43} The shortcomings of using these reagents is that they tend to disproportionate and afford symmetrical products. Upon hydroboration, the disproportionation of the hydroborating reagents result in reduced reaction yields and in some cases it prohibits hydroboration to take place.^{41, 44-46}

Uncatalyzed hydroboration with heterocyclic boranes often requires harsh conditions and are not as highly selective as the alkylboranes type hydroborating reagents discussed in section 1.5.2.³⁷⁻³⁹ The reduced reactivity and selectivity of heterocyclic hydroborating reagents compared to diborane and dialkylborane can attribute the reduced Lewis acidity of the reagent due to π -back bonding from hetero-atom to boron atom as depicted in Figure 1.6.⁴⁴

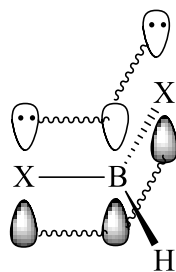


Figure 1.6: Orbitals interaction upon π -back bonding.

In this section selected heterocyclic hydroborating reagents shown in Figure 1.7 will be discussed in more details.

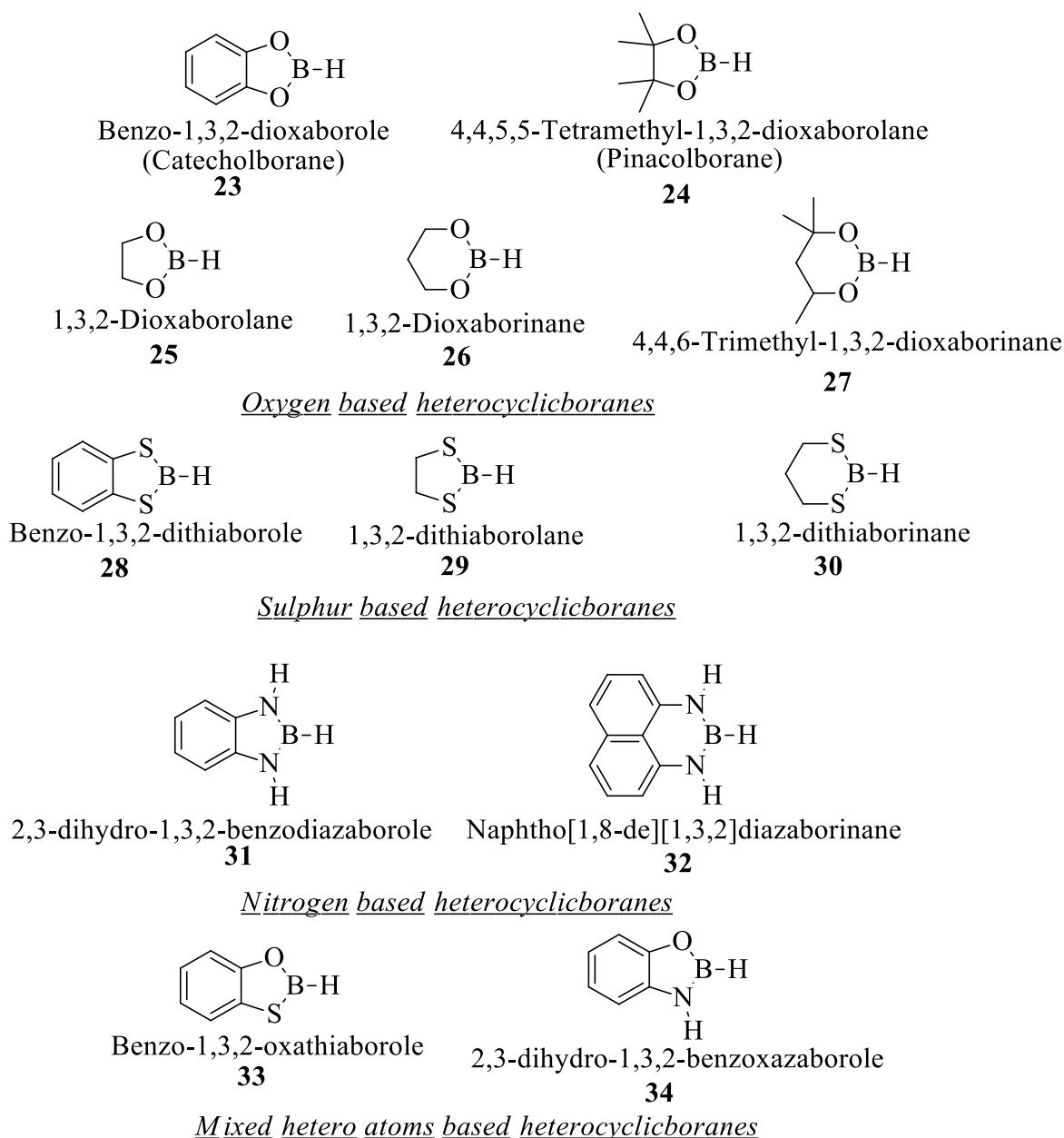
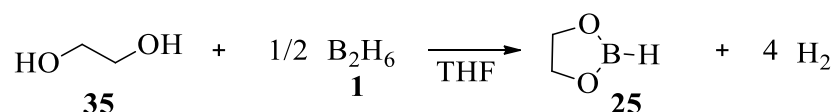


Figure 1.7: Section selected heterocyclic hydroborating reagents for review.

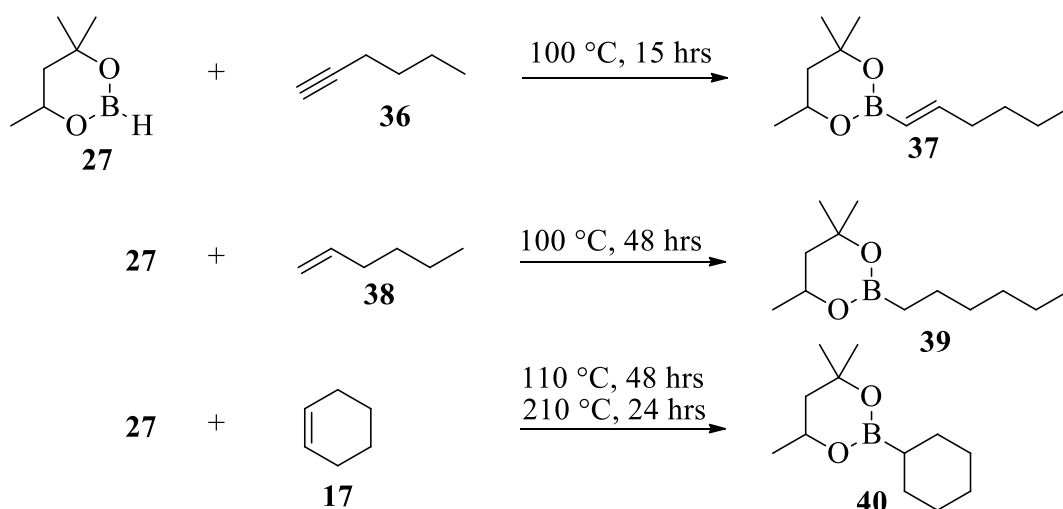
1.5.3.1. *Oxygen based heterocyclic hydroborating reagents*

The parent structure of five-membered oxygen based boroles 1,3,2-dioxaboralane (**25**) was first reported briefly by Schlesinger and Burg.⁴⁷ A more detailed study of this reagent was investigated by Rose and Shore⁴¹ in which 1,3,2-dioxaboralane (**25**) was prepared from ethylene glycol (**35**) and diborane (**1**) with a 60% yield as illustrated in Scheme 1.19. In this study, the stability of the reagent was investigated and it was observed that the reagent suffered from excessive disproportionation. The author noted in the presence of high impurity the initial rate of disproportionation was about 1% /min. Probably due to high instability of this reagent (**25**) was the reason for the lack of hydroboration reports with it and similar with 1,3,2-dioxaborinane (**26**).



Scheme 1.19: Synthesis of 1,3,2-dioxaboralane (25).

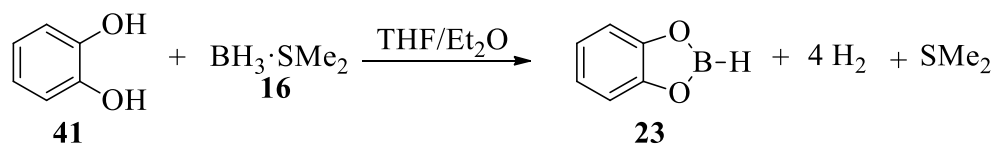
The initial success in the area of hydroboration with heterocyclic hydroborating reagents was reported by Woods and Strong⁴⁴ in 1966. These authors reported that 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**) demonstrated extraordinary stability towards disproportionation compared to the heterocyclic boranes which have been discussed above. This reagent was reported to be stable upon distillation at 50 °C (50 mm) and with slight disproportionation at 112 °C and can be stored for a month at 25 °C without any detectable degradation. In this study 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**) was reported to hydroborate terminal alkynes, terminal alkenes, and cyclic alkenes to afford exclusively the less sterically demanding product in yields ranging from 27 – 58%, however, harsh reaction conditions were required (Scheme 1.20).



*Scheme 1.20: Hydroboration of 1-hexyne (**36**), 1-hexene (**38**) and cyclohexene (**17**) with 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**).*

The reduced reactivity of 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**) compared to diborane (**1**) and dialkylboranes hydroborating reagents (discussed above in section 12.4.2) were attributed to the reduced Lewis acidity of the reagent due to π -back bonding from the oxygen to the boron atom.⁴⁴ Furthermore, the high selectivity for terminal preference of the reagent was expected due its large steric requirements as that observed with 9-BBN (**11**).^{12, 36, 37}

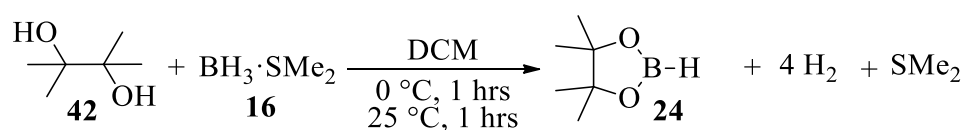
In 1971, Brown and Gupta⁴⁵ reported that catecholborane (**23**) could be prepared from 1,2-dihydroxybenzene (**41**) and borane-tetrahydrofuran complex (**12**) in THF at 0 °C. Brown *et al.*,²⁶ reported an alternative synthetic route which BMS (**16**) is utilized as the hydroborating reagent (Scheme 1.21).



*Scheme 1.21: Synthesis of catecholborane (**23**).*

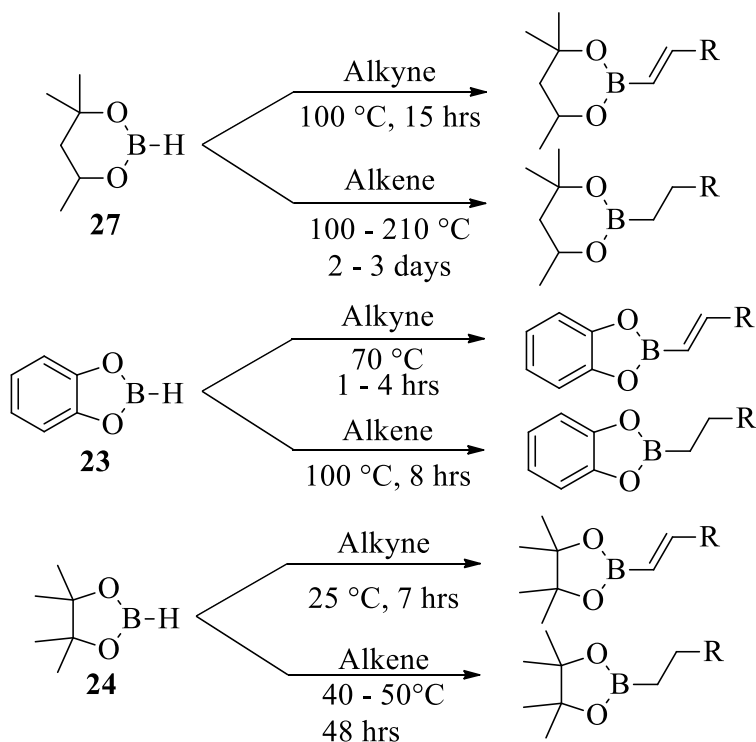
When catecholborane (**23**) was used for the hydroboration of alkenes⁴⁵ and alkynes⁴⁸, it demonstrated better regioselectivity than diborane (**1**) but as the case of 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**), harsh reaction conditions were also required. In these studies, it was illustrated that to perform hydroboration of alkenes required a temperature of 100 °C and the hydroboration of alkynes required a temperature of 70 °C.

In 1992, Tucker *et al.*,⁴⁹ reported that pinacolborane (**24**) could be easily prepared from pinacol (**42**) and BMS (**16**) at 0 °C – 25 °C as depicted in Scheme 1.22. This reagent demonstrated better stability than catecholborane (**23**).



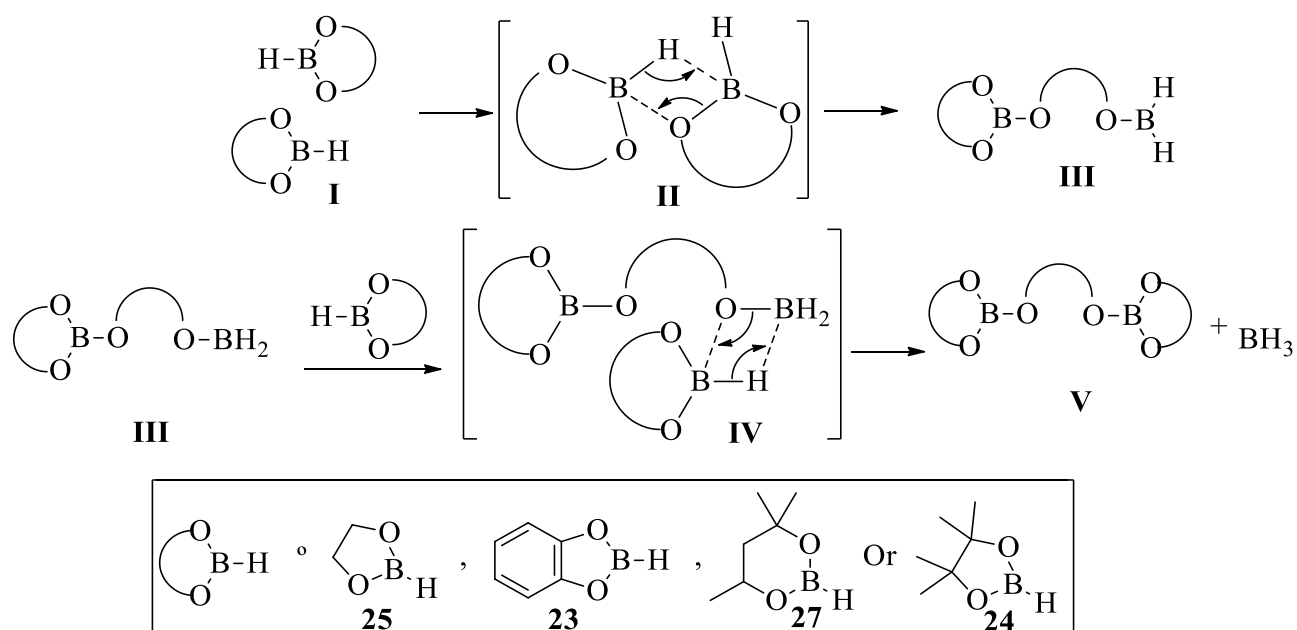
Scheme 1.22: Synthesis of pinacolborane.

Pinacolborane (**24**) was used for the hydroboration of alkynes at 25 °C and alkenes at 50 °C to afford the corresponding alkylboronic acid pinacol esters and alkeylboronic acid pinacol esters under mild condition compared to the other oxygen based heterocyclic boranes (Scheme 1.23).⁴⁹ The hydroboration with this reagent afforded better regioselectivity than catecholborane (**23**), for example, hydroboration of styrene (**10**) and 2-hexyne afforded 96% and 93% of the less sterically demanding product with pinacolborane (**24**) whereas 91% and 60% was observed with catecholborane (**23**), respectively.^{45, 48, 49} Furthermore, advantages of using pinacolborane (**24**) over the other hydroborating reagents were that alkylboronic acid pinacol esters and alkeylboronic acid pinacol esters could be purified by flash chromatography without notable decomposition.



Scheme 1.23: Hydroboration of alkyne and alkene with oxygen-based heterocyclic hydroborating reagents.

The disproportionation of dialkoxyborane reagents such as 1,3,2-dioxaborolane (**25**),⁴¹ dimethoxyborane,^{50, 51} 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**),⁴⁴ and catecholborane (**23**)⁵² have been documented. In all these studies the alkoxyboranes were reported to undergo a similar disproportionation mechanism as illustrated in Scheme 1.24.



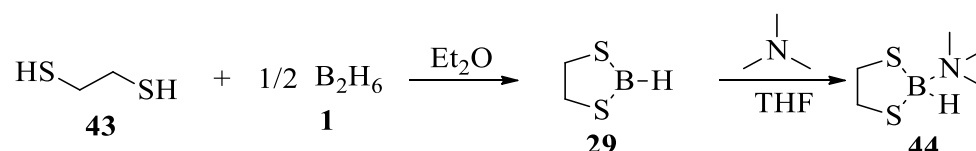
Scheme 1.24: Disproportionation path for oxygen-based heterocyclic hydroborating reagents.

The mechanism for the disproportionation of alkoxyboranes (Scheme 1.24) has two major steps:

- ❖ The first step (**I** → **II** → **III**) involves the interaction of two alkoxyborane compounds (**I**) and thereby formation of the bridge four-center activated complex **II** which then undergoes rearrangement to afford intermediate **III**. The kinetic studies conducted by Uchida *et al.*,⁵¹ for the disproportionation of dimethoxyborane indicated that the reaction was second order and the formation of **II** was the rate determining step.
- ❖ The second step (**III** → **IV** → **V**) involves the intermediate **III** interacting with another alkoxyborane thereby affording complex **IV** similar to **II** and also undergo similar rearrangements to afford the disproportionation products **V**. The second step has been assumed to be rapid and has been supported by the presence of intermediate **III** in low or undetectable concentrations in a number of studies such as 1,3,2-dioxaborolane (**25**),⁴¹ catecholboranes (**23**),²¹ and 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**)⁴⁴ studies.

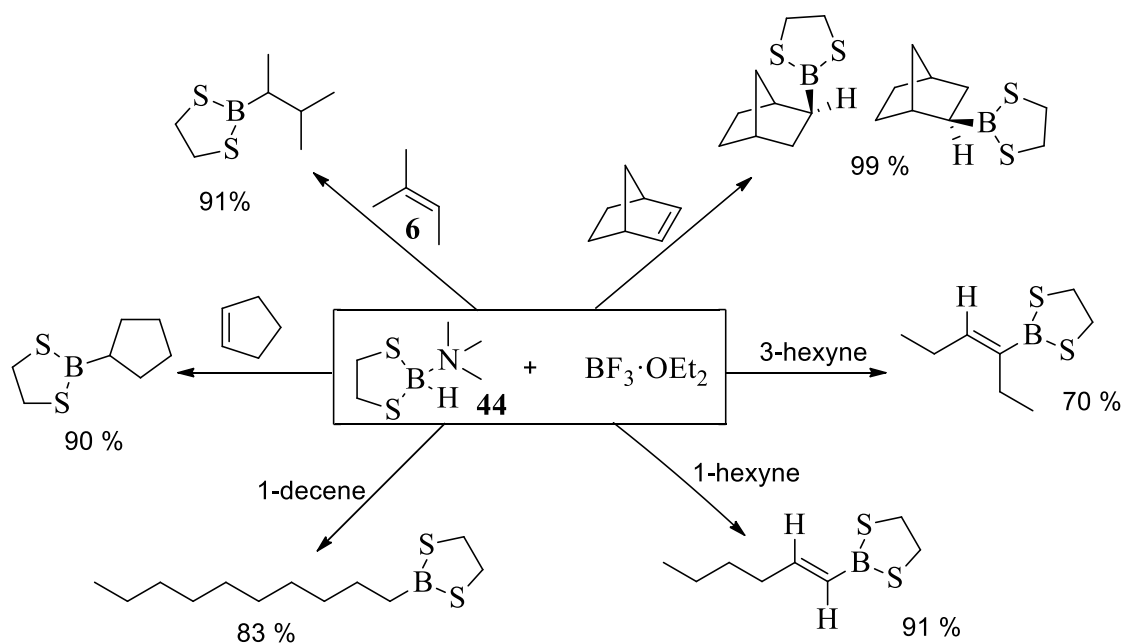
1.5.3.2. Sulphur based heterocyclic hydroborating reagents.

Egan *et al.*,⁵³ (in 1964) first report the synthesis of 1,3,2-dithiabolane (**29**) from diborane and ethane-1,2-dithiol in ether solvent thereafter used to prepare the corresponding highly stable trimethylamine adduct (**44**) in THF as illustrated in Scheme 1.25. Unfortunately, the yield for the reaction was never mentioned in this report.



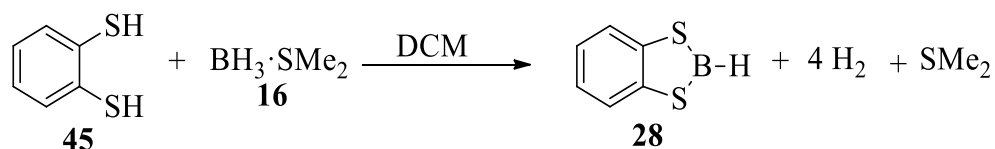
Scheme 1.25: Synthesis of 1,3,2-dithiabolane (**29**).

Thaisrivongs and Wuest⁴⁶ discovered that hydroboration of alkenes with 1,3,2-dithiabolane (**29**) afforded the desired boronic ester but with a significant amount of disproportionation of the hydroborating reagent (similar mechanism of disproportionation to that observed with oxygen based heterocyclic hydroborating reagents discussed above). Hadebe *et al.*,^{54, 55} reported similar results when working with 1,3,2-dithiabolane (**29**) and 1,3,2-dithiaborinane (**30**). In these reports, DFT studies were conducted for hydroboration and disproportionation of these reagents. The DFT studies indicated that the activation energy for the transition state for the disproportionation of the reagent was lower than the respective activation energy for the hydroboration pathway. However, Thaisrivongs and Wuest,⁴⁶ reported that when 1,3,2-dithiabolane (**29**) was generated *in-situ* from its trimethylamine adduct (**44**) and BF₃·OEt₂, the disproportionation of the reagent was minimized and hydroboration of the alkene could proceed with high yields for a number of olefins (Scheme 1.26). However, the regioselectivity of the reaction was never discussed.



Scheme 1.26: Hydroboration with 1,3,2-dithiaborole (**29**) generated from its trimethylamine (**44**).

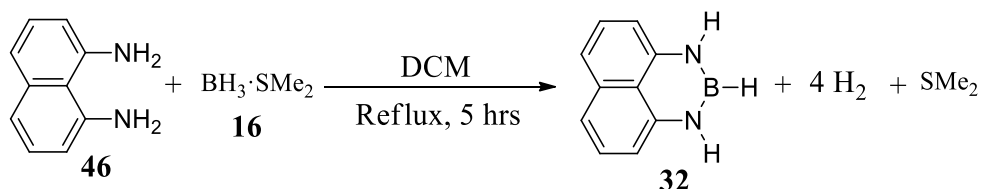
Hadebe and Robinson²¹ prepared 1,3,2-benzodithiaborole (**28**) from 1,2-benzenethiol (**45**) and BMS (**16**) in dichloromethane with an excellent yield of >99% (Scheme 1.27). In this study 1,3,2-benzodithiaborole (**28**) was used for the uncatalyzed-hydroboration of 1-octene (**52**) and 4-*trans*-octene at elevated temperatures (150 °C) to afford corresponding boronic esters in 65% and 15%, respectively. An advantage of using 1,3,2-benzodithiaborole for hydroboration was that the corresponding alkylboronic esters obtained could be isolated using flash chromatography as in the case of pinacolborane (**24**).²¹



Scheme 1.27: Synthesis of 1,3,2-benzodithiaborole (**28**).

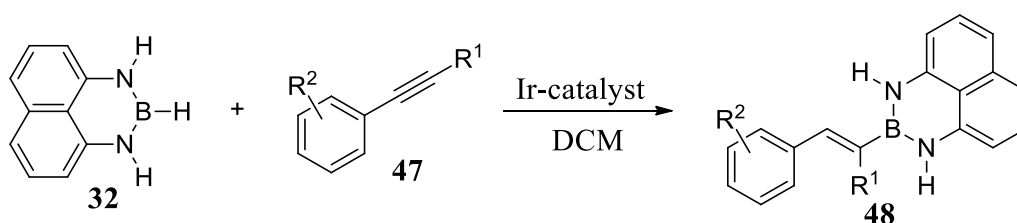
1.5.3.3. Nitrogen based heterocyclic hydroborating reagents

Slabber⁵⁶ reported that 2,3-dihydro-naphtho[1,8-*de*][1,3,2]diazaborinane (**32**) could be achieved by the reaction of naphthalene-1,8-diamine (**46**) with BMS (**16**) in dichloromethane with a yield of 95% (Scheme 1.28).



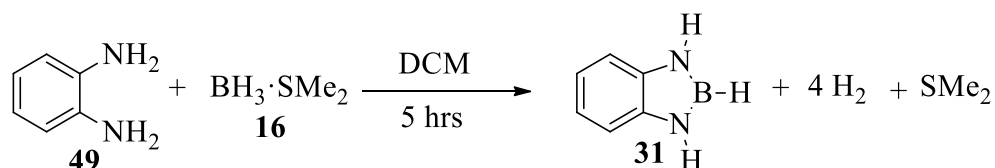
*Scheme 1.28: Synthesis of 2,3-dihydro-naphtho[1,8-*de*][1,3,2]diazaborinane (**32**).*

In this study, slabber⁵⁶ reported the hydroboration of selected olefins with two rhodium catalysts that resulted in yields ranging from 10% to 94%. Iwate and Suginome⁵⁷ reported iridium-catalyzed hydroboration of aromatic and aliphatic alkynes with this reagent which afforded the corresponding alkenyl-naphtho[1,8-*de*][1,3,2]diazaborinane esters (**48**) in good yields ranging from 63% to 84% (Scheme 1.29). Thereafter, the corresponding esters were utilized for iterative Suzuki-Miyaura coupling reaction for the synthesis of oligo(phenylenevinykene)s. The naphtho[1,8-*de*][1,3,2]diazaborinane analogue (**32**) on the ester serves as a protecting group for the boronyl group (B(OH)₂) for the reaction. Hydroboration products achieved from this reagent were stable and could be isolated in the atmosphere without any decomposition.^{56, 57}



*Scheme 1.29: Iridium-catalyzed hydroboration of alkynes with 2,3-dihydro-naphtho[1,8-*de*][1,3,2]diazaborinane (**32**).*

Hadebe *et al.*,⁵⁸ reported the rhodium catalyzed hydroboration of 1-octene, styrene (**10**), 1-hexyne and 4-vynylanisole with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) which afforded the corresponding boronic esters in 78 - 92% yields. In this study, 2,3-dihydro-1,3,2-benzodiazaborole (**31**) was prepared from *o*-phenylenediamine (**49**) and BMS (**16**) under reflux in DCM which afforded 95% yield after 5 hours.



Scheme 1.30: Preparation of 2,3-dihydro-1,3,2-benzodiazaborole (31).

Hadebe and Robinson²¹ compared the reactivity of 2,3-dihydro-1,3,2-benzodiazaborole (**31**) with that of catecholborane (**23**) and 1,3,2-benzodithiaborole (**28**) for the hydroboration of alkenes. The time and temperature required to afford hydroboration of alkenes for each reagent have being depicted in Figure 1.8. The stability trend for the observed hydroboration of alkenes with heterocyclic hydroborating reagents in decreasing order was: O > S > N and this trend were attributed to the reduced Lewis acidity of the reagents due to their magnitude of π -back bonding from the hetero-atom to boron.

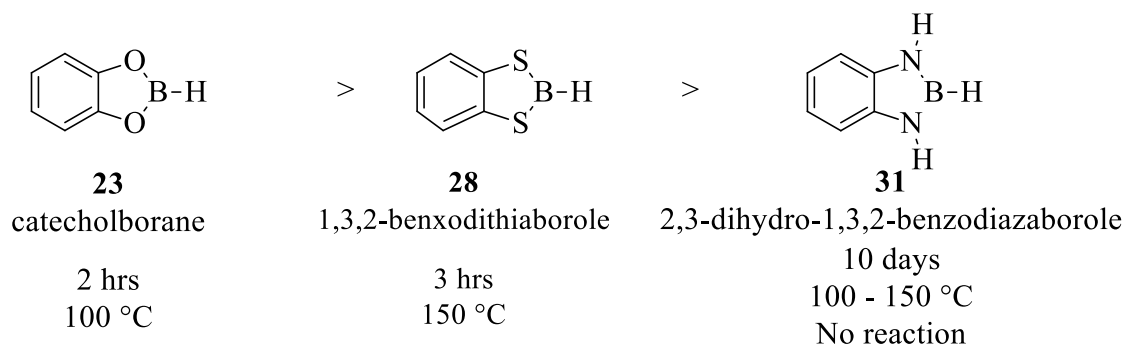


Figure 1.8: Relative reactivity of catecholborane analogues towards hydroboration.

Although a catalyst could be used to activate these heterocyclic hydroborating reagents, Männig and Nöth⁴² noted that only sufficiently acidic boron compounds could be activated. For instance, 1,3-dimethyl-1,3,2-diazaborolidine (Figure 1.9) could not be activated for hydroboration due to low Lewis acidity from the strong π -back bonding of the nitrogen (secondary amine) to boron.

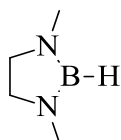
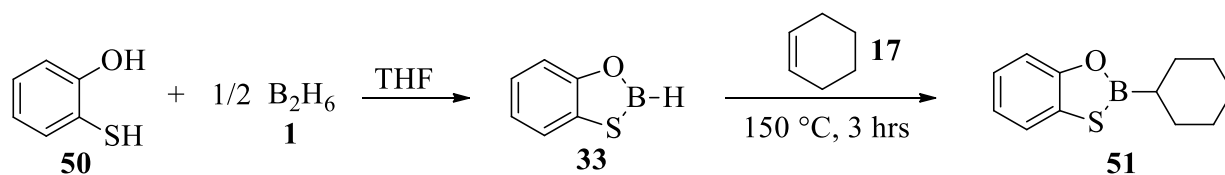


Figure 1.9: 1,3-dimethyl-1,3,2-diazaborolidine.

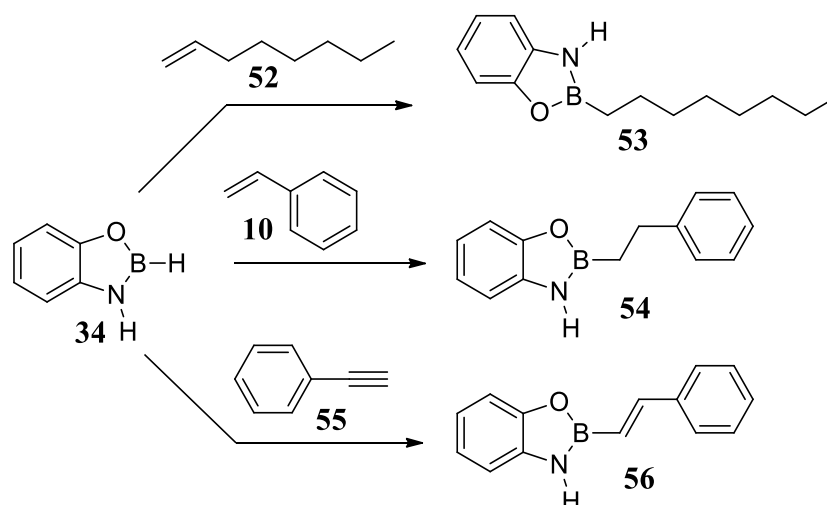
1.5.3.4. *Mixed Based Heterocyclicboranes*

Cabiddu *et al.*,⁵⁹(1975) reported that 2-hydroxythiophenol (**50**) can be reacted with diborane to afford benzo-1,3,2-oxathiaborole (**33**) in a 78% yield. Subsequently, the reagent was tested for hydroborating potential through the hydroboration of cyclohexene which afforded the corresponding ester in 56% yield (Scheme 1.31). This was the first report of a five-membered heterocyclic hydroborating reagent which contained the O–B–S linkage. However, the reagent was never utilized again for hydroboration after this report.



Scheme 1.31: Preparation of benzo-1,3,2-oxathiaborole (**33**) and its subsequent potential toward hydroboration.

Slabber⁵⁶ reported when 1,2-aminophenol (**102**) reacts with BMS to afford 2,3-hydro-1,3,2-benzooxazaborole (**34**) with 85% yield in THF at 25 °C. In this study, the reagent was used for hydroboration reactions of selected olefins catalyzed by two rhodium catalysts which afforded the corresponding boronic esters with yields ranging from 18% to 89% (Scheme 1.32).



Scheme 1.32: Hydroboration of 1-octene (**52**), styrene (**10**) and ethynylbenzene (**55**) with 2,3-dihydro-1,3,2-benzooxazaborole (**34**).

2,3-Dihydro-1,3,2-benzooxazaborole (**34**) was reported to also undergo disproportion upon hydroboration and afforded the borazine analogue shown in Figure 1.10.⁵⁶

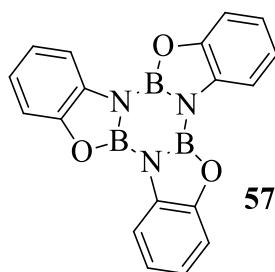
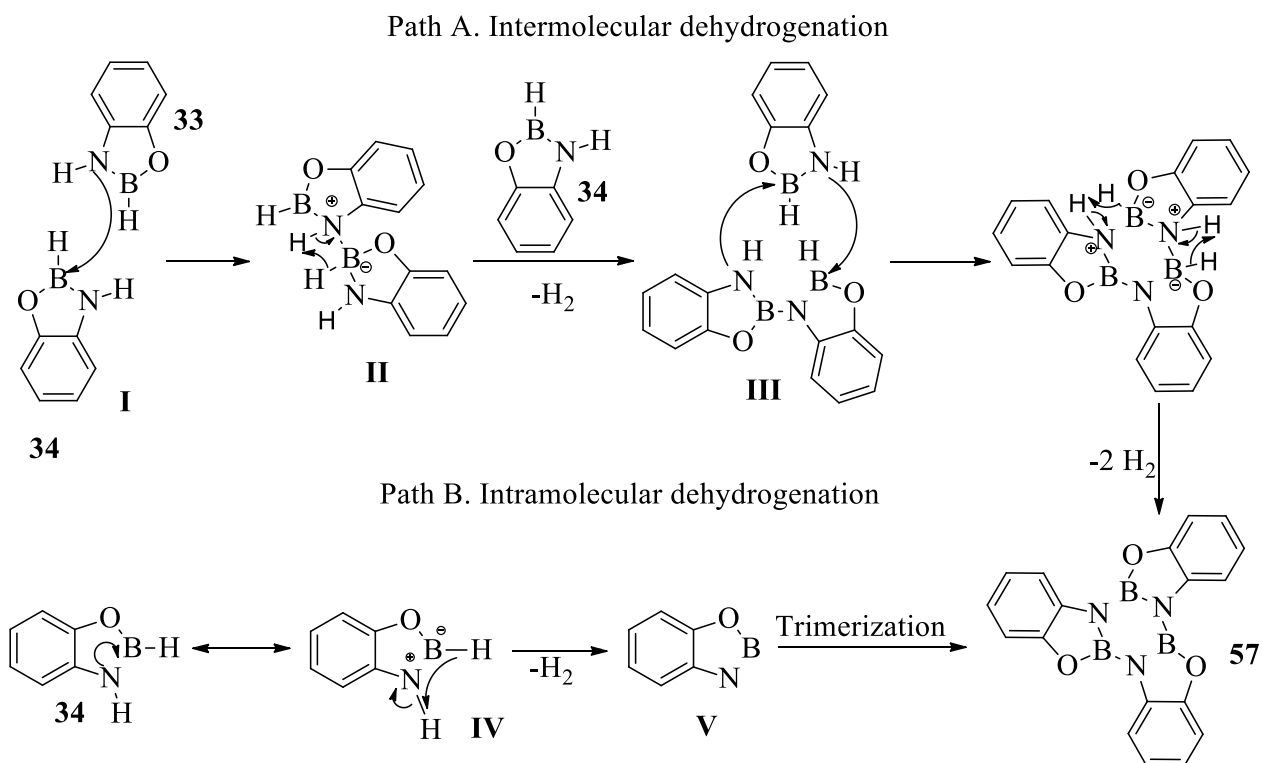


Figure 1.10: Borazine derivative of 2,3-dihydro-1,3,2-benzooxazaborole (**34**).

Stepanenko *et al.*,⁶⁰ demonstrated that when 1,3,2-oxazaborolidines (**34**) were heated above 120 °C they afforded borazine analogues (**57**) in high yields. In this study, it was proposed that the mechanism toward the observed borazines was either from intermolecular dehydrogenation or intramolecular dehydrogenation and an illustration of the mechanisms using 2,3-dihydro-1,3,2-benzooxazaborole (**34**) is shown in Scheme 1.33.



Scheme 1.33: Disproportionation of 2,3-hydro-1,3,2-benzooxazaborole (34).

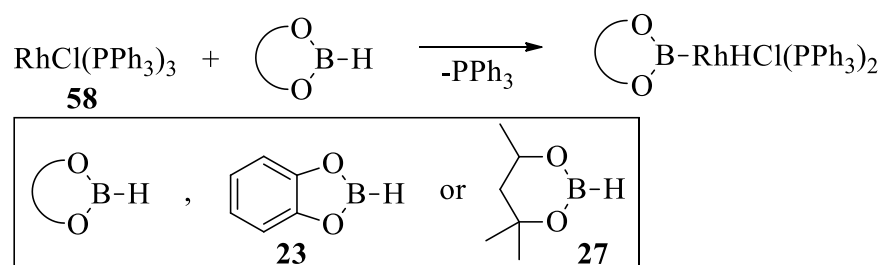
- ❖ Path A indicated the formation of the borazine analogue (**57**) via the intermolecular dehydrogenation pathway. A nucleophilic attack of nitrogen on boron atom accompanied by the elimination of hydrogen (Step **I** → **II**). This is followed by another hydroborating reagent (**34**) which attack and get attacked by intermediate **II** in a similar manner as the Step **I** → **II** forming a ring-closure to afford borazine analogue (**57**).
- ❖ Path B indicated the formation of the borazine analogue (**57**) via intramolecular dehydrogenation in which the oxazaborolane (**34**) afforded the dehydrogenated borole with a nitrogen-boron double bond (**V**). Subsequently, **V** undergoes trimerization to afford borazine analogue (**57**).

1.6. Metal-catalyzed hydroboration

Hydroboration can proceed easily with most boranes and alkylboranes without a catalyst. The vast application of hydroboration products often demands that organoboranes with different reactivity and stability. In most instances, it may be required to prepare organoboranes from the hydroboration with less reactive olefins or hydroborating reagents which may afford poor selectivity and yield. Fortunately, metal-catalyzed hydroboration provides an alternative for conducting hydroboration these type of reagents to achieve better selectivity and yields.

1.6.1. Wilkinson's catalysts (58)

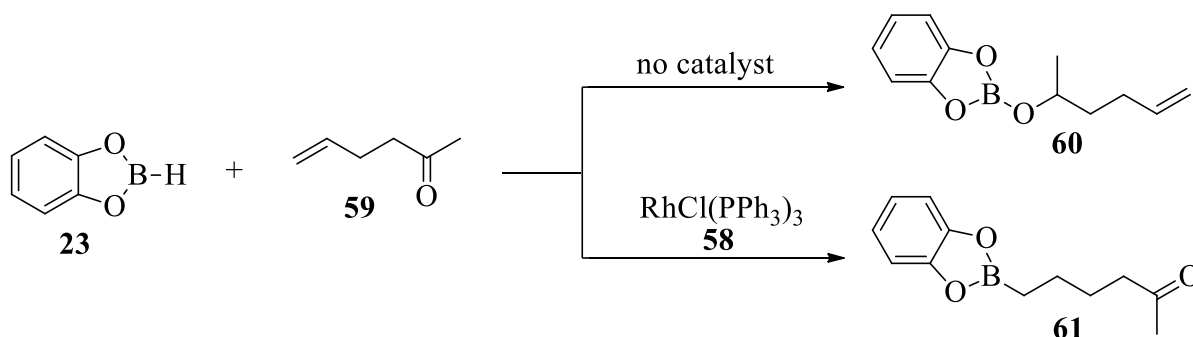
In 1975, Kono *et al.*,⁶¹ discovered that tris(triphenylphosphine)rhodium(I) chloride ($\text{RhCl}(\text{PPh}_3)_3$) (**58**) also known as the Wilkinson's catalyst undergoes oxidative addition when treated with either catecholborane (**23**) or 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**) as illustrated in Scheme 1.34. At the time of this report, it had already been reported that uncatalyzed hydroboration of olefins with catecholborane (**23**)^{45, 48} and 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**)⁴⁴ required elevated temperatures to proceed. Furthermore, the Wilkinson's catalyst, as well as other rhodium catalysts, were capable of catalyzing olefins addition hydrometallation reactions such as hydrogenation, hydrosilylation, hydrocyanation and hydroformylation had also been demonstrated.⁶² The juxtaposition of these facts presented an opportunity to employ rhodium complexes in an attempt to improve the hydroboration of olefins.



Scheme 1.34: Oxidative addition of the Wilkinson's catalyst with oxygen heterocyclic reagents

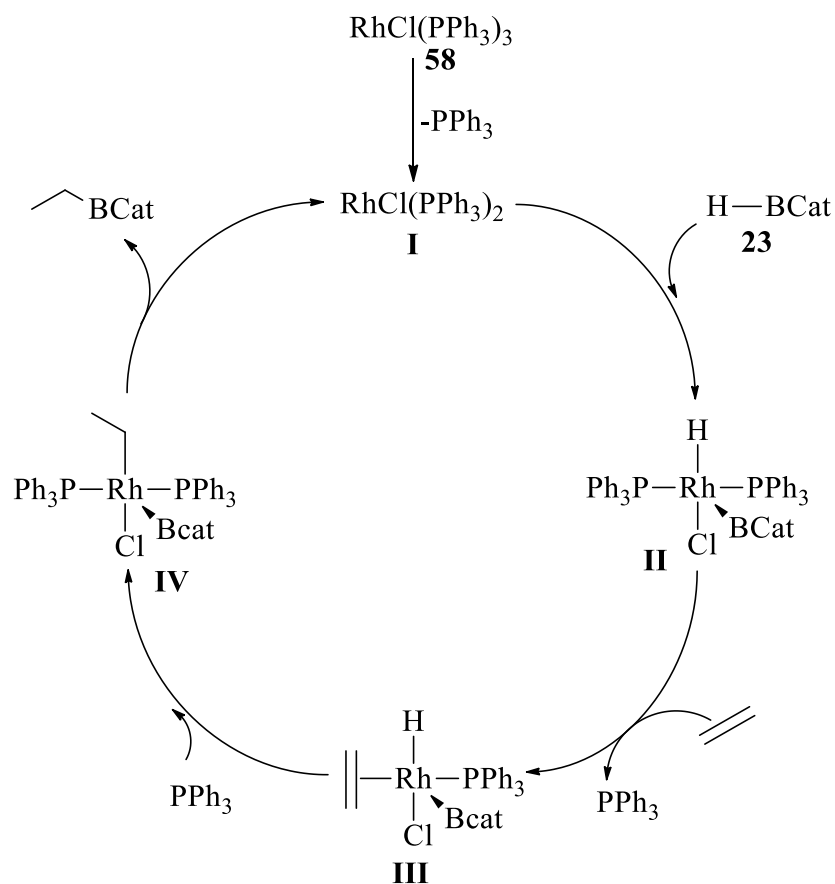
A decade after the report published by Kono *et al.*,⁶¹ Männig and Nöth⁴² reported the first examples of metal catalyzed hydroboration. In this study, the hydroboration of alkynes and alkenes with catecholborane (**23**) in the presence of catalytic amount of Wilkinson's catalysts were reported to proceed efficiently without difficulty at room temperature. Hydroboration of olefins such as 1-octene (**52**), cyclopentene, cyclohexene (**17**) and 1-hexyne with catecholborane (**23**) was reported with yields ranging from 21.5% to 83.3%. Hydroboration of olefins with 4,4,6-trimethyl-1,3,2-dioxaborinane (**27**) was also enhanced by the addition of a catalytic amount of Wilkinson's catalyst although less efficient as compared to catecholborane (**23**).

Männig and Nöth⁴² also discovered that it was possible to activate a carbon-carbon double bond strongly such that it was preferentially hydroborated in the presence of a keto-group, for example, 5-hexen-2-one (**59**) reacts rapidly with catecholborane (**23**) to exclusively provide 2-(hex-5-en-2-yloxy)benzo-1,3,2-dioxaborole (**60**) (Scheme 1.35). However, compound (**61**) was the major product when the reaction was done in the presence of a catalytic amount of Wilkinson's catalyst. In this study, it was reported that the double bond could not be activated sufficiently to compete with a more reactive group such as aldehydes.



*Scheme 1.35: Hydroboration 5-hexen-2-one (**59**) by catecholborane (**23**) with and without Wilkinson's catalyst (**58**).*

Männig and Nöth⁴² initially proposed the mechanism for the Wilkinson's catalyzed hydroboration of olefins (Scheme 1.36). In this report, the authors reported that adduct **II** which was first isolated by Kono *et al.*,⁶¹ reacts with olefins to afford the corresponding alkylboronate esters which supported the preliminary steps of the proposed mechanism (Scheme 1.36).

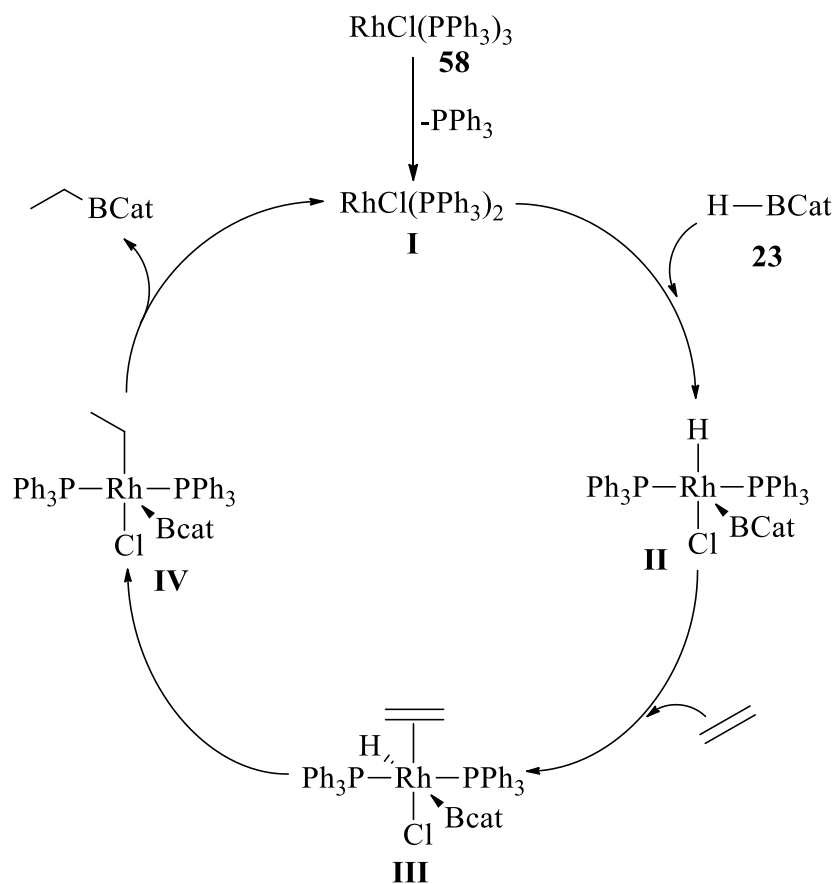


Scheme 1.36: Dissociative Wilkinson's catalyst hydroboration catalytic cycle.

The mechanism proposed by Männig and Nöth⁴² for the hydroboration of olefins with Wilkinson's catalyst entails the loss of triphenylphosphine (PPh_3) affording the transient species **I** which enters the catalytic cycle thereafter followed by (Scheme 1.36):

- ❖ (**I** → **II**) Oxidative addition of catecholborane, CatBH (**23**) to afford intermediate adduct **II**. Evidence of this adduct **II** was first reported by Kono *et al.*,⁶¹ and when olefins were added to a solution of the isolated adduct **II** the corresponding boronic esters were formed which supported the preliminary steps of the proposed mechanism or formation of adduct **II**.
- ❖ (**II** → **III**) PPh_3 elimination accompanied by olefin binding at the vacant site.
- ❖ (**III** → **IV**) Migratory insertion of the olefin to the hydride accompanied by re-binding of PPh_3 .
- ❖ (**III** → **IV**) Reductive elimination of the ester product and regeneration of species **I**.

Burgers *et al.*,⁶³ proposed an alternative mechanism for the Wilkinson's catalyzed (**58**) hydroboration of olefins (Scheme 1.37) which was an analog for the well-studied rhodium-catalysed hydrometallation reactions such as hydrogenation, hydrocyanation and hydrosilation.⁶² The preliminary steps in mechanisms are identical, only upon step (**II** → **III**→**IV**) mechanism differs. According to Burgers *et al.*,⁶³ (**II** → **III**→**IV**) olefin binding occurs without dissociation to afford the octahedral adduct **III** which is followed by hydride migration (Scheme 1.37).

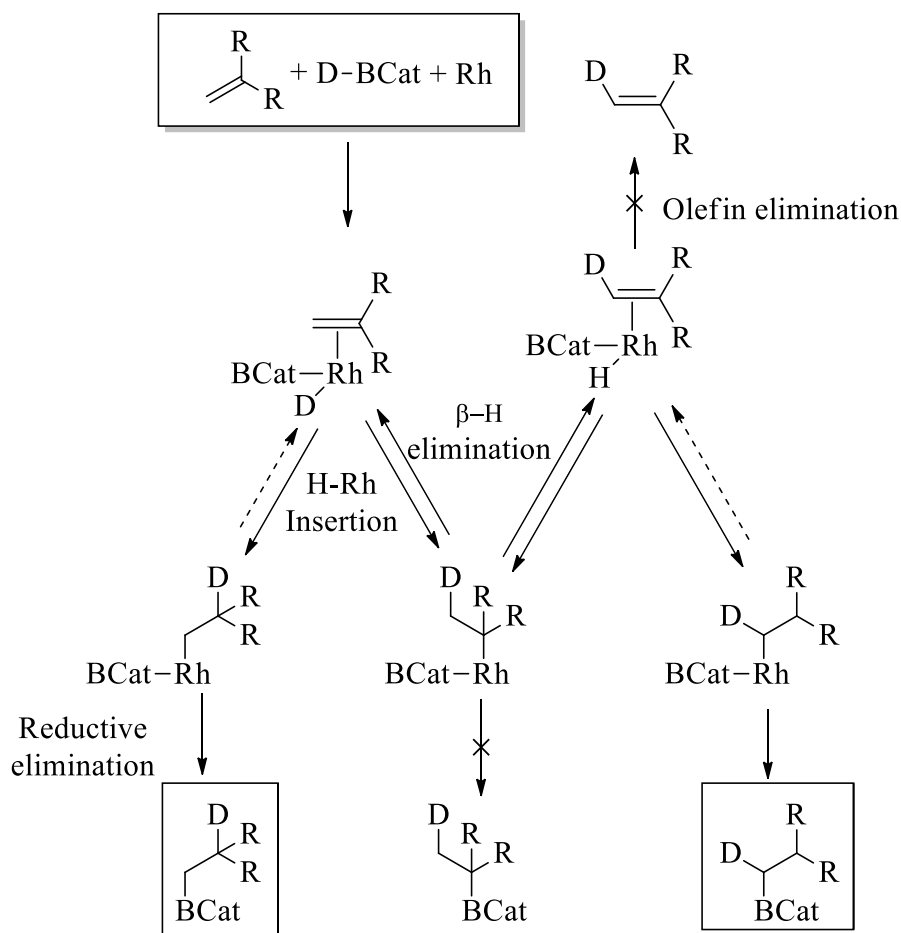


Scheme 1.37: Associative Wilkinson's catalyst hydroboration catalytic cycle.

The differences in both mechanisms presented are based on assumptions with no experimental evidence had been presented to date which refutes one mechanism over the other. The lack of evidence has raised a few of important questions such as what is the exact geometry of adduct **III** and whether mechanism pathway proceeds by H–M insertion or B–M insertion.

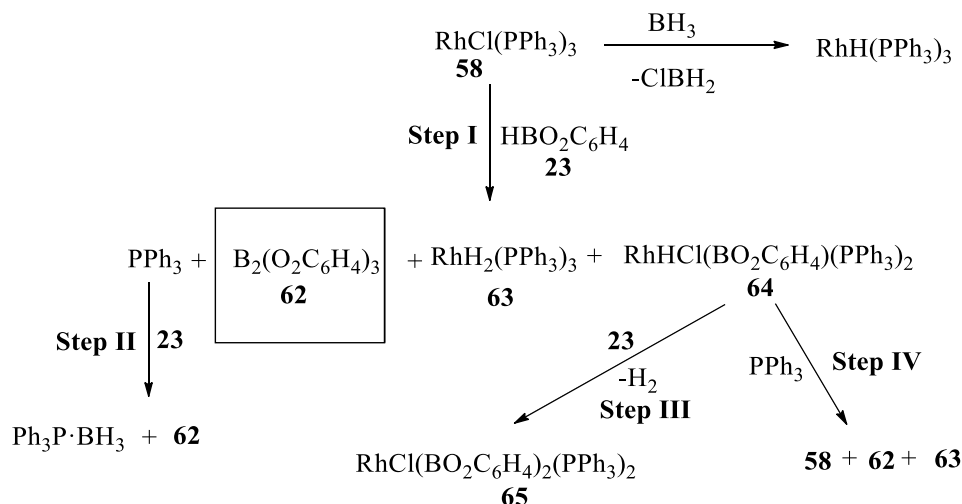
A number of computational studies had been conducted to address this problem. For example, Musaev *et al.*,⁶⁴ reported Ab initio molecular orbital calculations for possible pathway and geometry of the mechanism presented by Burgers *et al.*,⁶³ and the result supported the proposed catalytic cycle (Scheme 1.37) but also indicated B–M insertion was also possible. Furthermore, Widauer *et al.*,⁶⁵ conducted DFT studies on two proposed mechanisms and came to the similar conclusion that the mechanism proposed by Burgers⁶³ was favored. However, caution must be made when drawing a conclusion from these computation studies reports as calculations were conducted with several assumptions. For example, calculation conducted using small group PH₃ instead of PPh₃ (usually to simplify algorithms). In this case, PH₃ would be expected to behave similarly to PPh₃. However steric strains would be reduced on the intermediate adducts and the associative mechanism by Burgers⁶³ would be more favoured against Männig and Nöth's⁴² dissociative mechanism.

Evans *et al.*,^{66, 67} reported a number of studies on the Wilkinson's catalyzed hydroboration of olefins which shed light in the degree of reversibility of elementary steps of the mechanism (Scheme 1.38). In this study deuterium labelling was performed using a limited amount of deuteriocatecholborane (CatB–D), to explain the incorporation of deuterium on recovered olefins. These authors suggested that it would mean H–Rh insertion and olefin binding steps occur reversibly under the reaction conditions. To explain incorporation of deuterium alpha-to boron in the product ester would imply that H–Rh insertion occurs reversibly. It was concluded from this study that the degree of reversibility of steps in the mechanism was substrate dependent. Therefore, extending finding a substrate to a group of substrates must be done with caution, for example, 1,1-disubstituted alkenes high region selectivity was attributed to the reversibility of H–Rh insertion step coupled high preference of primary alkyl-rhodium reductive elimination. However, different observations were reported, styrene and 1-decane such as secondary alkyl-rhodium reductive elimination were observed.



Scheme 1.38: Reversibility of steps for Wilkinson's catalyst (58) catalyzed hydroboration.

Burgers *et al.*,⁶⁸ criticized most of the findings by Evans and co-workers^{66, 67} and suggested that the mechanism proceeded to afford predominately terminal or less sterically demanding product. However, it was also suggested that different results could be due to that Wilkinson's catalyst and catecholborane do not react to form a single species and competing processes would influence the observed differences in the results. Shortly after these authors⁶³ demonstrated that the Wilkinson's catalyst and catecholborane reaction involve a number of competing parallel reactions, among those reactions, was the disproportionation of the hydroborating reagent reaction to afford B₂(O₂C₆H₄)₃ (**62**) (Scheme 1.39).



Scheme 1.39: A chain of reaction which may occur in the presences of Wilkinson's catalyst (**58**) and catecholborane (**23**).

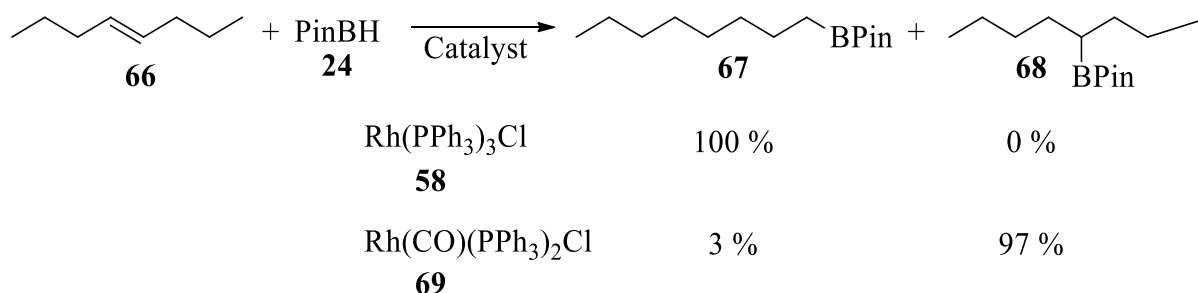
Burgers *et al.*,⁶³ reported that the disproportionation of catecholborane (**23**) to afford disproportionation product, Cat_3B_2 (**62**) was irreversible and further showed that upon the catalyzed-hydroboration with Wilkinson's catalyst (**58**) this process can be promoted through three different pathways (Scheme 1.39);

- ❖ First promoted by Wilkinson's catalyst (**58**) reaction with catecholborane (step **I**) to afford triphenylphosphine, PPh_3 , the disproportionation product **62**, complex **63** and **64**.
- ❖ Secondly (step **II**) PPh_3 also further catalyze the disproportionation of catecholborane (**23**) to afford **62** and triphenylphosphine borane adduct $\text{Ph}_3\cdot\text{BH}_3$.
- ❖ Lastly (step **IV**), intermediate complex **64** can react with PPh_3 to afford the disproportionation product **58**, complex **63** and regenerate Wilkinson's catalyst **58**.

In section 1.5.3, the disproportionation of some of the heterocyclic reagents was discussed which is a major challenge when working with heterocyclic hydroborating reagents. Furthermore, this process can also be unfortunately promoted by the catalysts.⁶³ Westcott *et al.*,⁶⁹ further gave evidence of disproportionation of the hydroborating reagent promoted by a rhodium catalyst used for hydroboration. Burgers *et al.*,⁶³ then suggested that to develop new hydroboration catalysts and robust hydroborating reagents that were less susceptible to disproportionation needs to be discovered to improve the reaction.

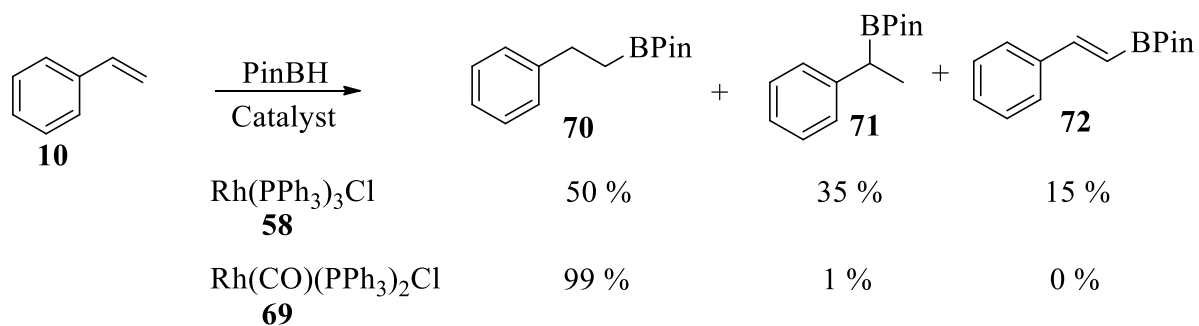
1.6.2. Other rhodium(I) Catalysts employed for Hydroboration

Pereira and Srebnik⁷⁰ discovered that hydroboration of internal alkenes such as *trans*-4-octene (**66**) with pinacolborane (**24**) using Rh(CO)(PPh₃)₂Cl (**69**) afforded internal alkyl pinacolboranates while Wilkinson's catalyst resulted in isomerization-hydroboration to terminal product esters (**67**) (Scheme 1.40).



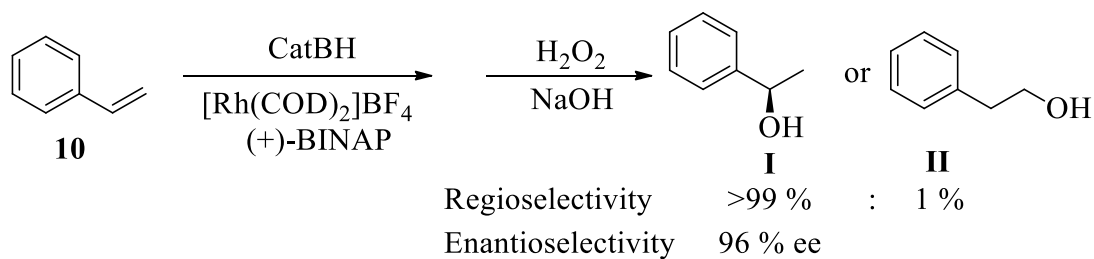
Scheme 1.40: Hydroboration of trans-4-octene (66) with pinacolborane (24) catalyzed by Rh(PPh₃)₃Cl (58) and Rh(CO)(PPh₃)₂Cl (69).

The regioselectivities of hydroboration of styrene (**10**) using these catalysts reported were different, for example, the regioselectivity when Rh(CO)(PPh₃)₂Cl (**69**) was reported to afford predominately the terminal product (**70**) while Wilkinson's catalyst afforded multiple different products (Scheme 1.41).⁷⁰



Scheme 1.41: Hydroboration of styrene (10) with pinacolborane (24) catalyzed by Rh(PPh₃)₃Cl (58) and Rh(CO)(PPh₃)₂Cl (69).

Earlier in section 1.5.2.5 the asymmetric hydroboration of alkene using diisopinocampheylborane was discussed, however, this synthetic approach required high optical purity of the hydroborating reagent and equimolar quantities of the chiral reagent to olefin. Hayashi *et al.*,⁷¹ reported asymmetric synthesis of 1-arylalkanol from styrene derivatives with catecholborane (**23**) catalyzed using a chiral rhodium catalyst which afforded high enantioselectivity (up to 96%), high yields (up to 99%) and high regioselectivity (catalytic amount of optical active reagent was employed opposed to uncatalyzed hydroboration) and an example of the reaction with styrene (**10**) is depicted in Scheme 1.42.



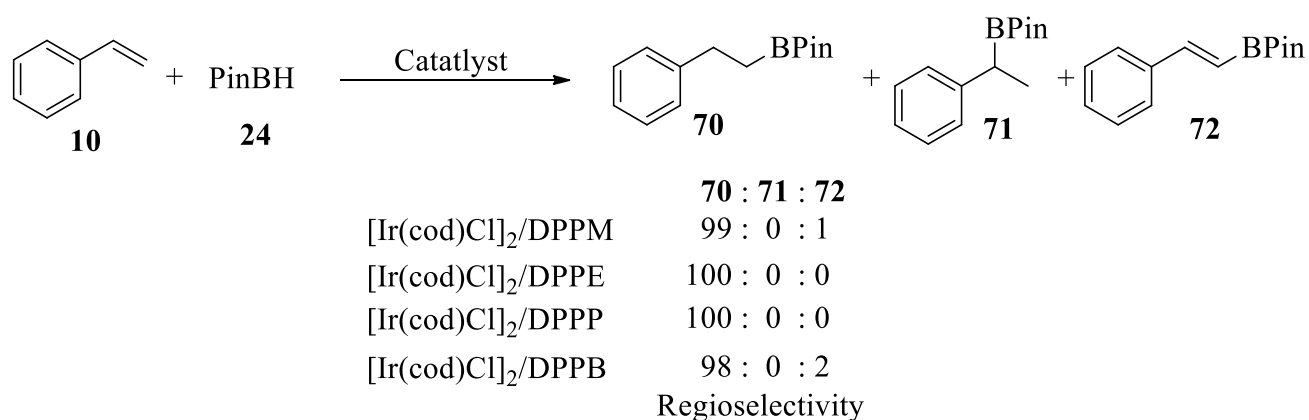
*Scheme 1.42: Hydroboration of styrene (**10**) with catecholborane (**23**) catalyzed by chiral rhodium complex.*

A number of studies have demonstrated that control over chemo, region-, stereo- and enantioselectivity can be afforded through the manipulation of the ligand system around the rhodium metal center.^{42, 43, 70-76}

1.6.3. Iridium-Catalyzed Hydroboration

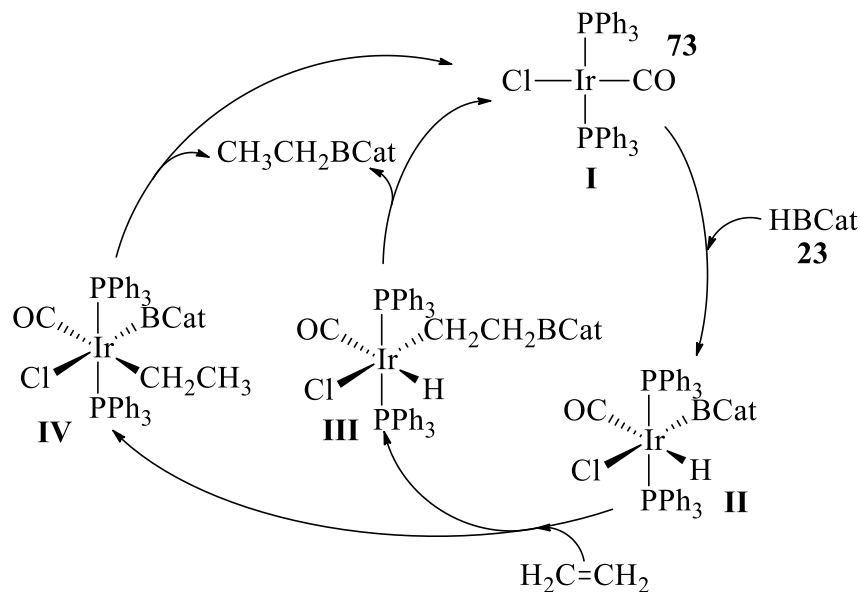
In the initial report of metal-catalyzed hydroboration by Männig and Nöth,³⁶ it was reported that iridium-catalyst exhibited no or minor catalytic activity for hydroboration. However, since this report, a number of iridium-catalyzed hydroboration have been reported that demonstrated enhanced chemo-, region-, stereo-, enatio-selective with efficient yields.⁷² The most often used iridium catalysts are the Vaska's complex ($\text{Ir}(\text{CO})(\text{PPh}_3)_2\text{Cl}$) **73** and derivatives of $[\text{Ir}(\text{cod})\text{Cl}]_2$ complexes.^{43, 57, 72, 77} The Vaska's complex **73** like Wilkinson's catalyst (**58**) was one of the early successful homogenous metal catalyst utilized for processes such as the hydrogenation of olefins.⁷⁸ Iridium-catalyzed hydroboration has also been reported to promote the disproportionation of the hydroborating reagent.⁶⁹

Miyaura *et al.*,⁷⁹ investigated the hydroboration of styrene with pinacolborane using a number of iridium catalysts. In these studies, $[\text{Ir}(\text{cod})\text{Cl}]_2$ coupled 1,1-bis(diphenylphosphino)methane (DPPM), 1,2-bis(diphenylphosphino)ethane (DPPE), 1,3-bis(diphenylphosphino)propane (DPPP) or 1,4-bis(diphenylphosphino)butane catalysts afforded 66 – 97% yield with excellent regioselectivity ranging from 98 – 100% for terminal hydroboration product (Scheme 1.43). Furthermore, these analogues of iridium catalysts series had been reported to be efficient hydroboration catalyst in a number of different publications.^{57, 72, 77}



Scheme 1.43: Hydroboration of styrene (**10**) with catecholborane (**23**) catalyzed by various iridium complexes.

Rablen and Hartwig⁸⁰ investigated the iridium-catalyzed mechanism of hydroboration of olefins. These authors conducted bond dissociation energy calculations and enthalpy measures thereafter proposed the catalytic cycle depicted in Scheme 1.44.



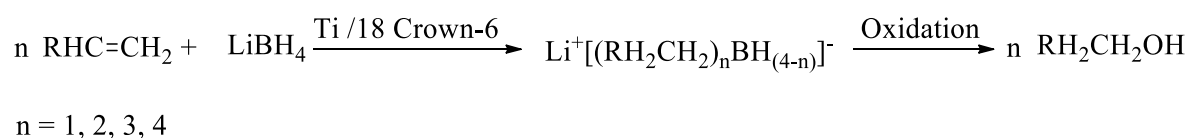
Scheme 1.44: Vaska's complex (73) catalytic cycle for hydroboration.

The catalytic cycle in Scheme 1.44 illustrate:

- **(I → II)** Vaska's complex (73) undergoes oxidative addition with catecholborane (23) in a similar methodology as the Wilkinson's catalyst hydroboration discussed *vide supra*. Evidence of this step had been presented by Westcott *et al.*,⁸¹ after successful isolation of complex II after oxidative addition of Vaska's complex (73) with catecholborane (23). Knorr and Melora⁸² reported a similar observation for an iridium complex similar to the Vaska's complex (73).
- **(II → III)** Illustrates olefin insertion into the Ir-B bond followed by product elimination and regenerating of the catalyst. Similar step **(II → IV)** illustrates the insertion of the olefin into the Ir-H bond. Rablen and Hartwig⁸⁰ reported that step **(II → IV)** was thermodynamically less favourable. However, in this report, it was mentioned that the enthalpies of reaction for both steps are comparable hence, the regular competition between the two pathways.

1.6.4. Titanium catalyzed hydroboration

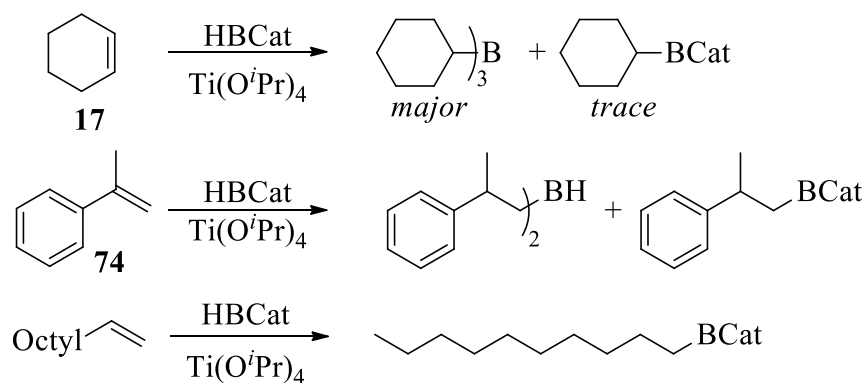
Isagawa *et al.*,⁸³⁻⁸⁵ reported the hydroboration of olefins with AlBH_4 catalyzed with titanium species; titanocene dichloride (Cp_2TiCl_2) or titanium trichloride (TiCl_3) coupled with 18-crown-6 were employed which afforded the corresponding alcohol after oxidation in yield ranging 50 - 80% (Scheme 1.45). In these studies, it was also reported that tetraalkylboron ions were obtained from the hydroboration of less bulky terminal alkenes. The regioselectivity observed after oxidation was similar to the uncatalyzed hydroboration of olefins with B_2H_6 (**1**) such as the hydroboration of 1-octene (**51**) resulted in 94% boron being located at the terminal position.^{11, 85}



Scheme 1.45: Hydroboration of olefins with titanocene dichloride or titanium trichloride (TiCl_3).

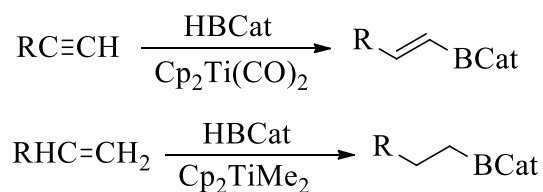
Burgess *et al.*,⁸⁶ further investigated the hydroboration of olefins with catecholborane (**23**) catalyzed with the same titanium catalysts studied discussed above. After careful analysis of the boron-containing compounds before oxidation using ^{11}B -NMR, these authors then concluded that those titanium catalysts only promote the degradation of catecholborane and afforded diborane with other derivatives. Thereafter the hydroboration product obtained from such reactions were ultimate because of the uncatalyzed hydroboration of the olefins with diborane (**1**).

Furthermore, Burgess and van de Donk reported the hydroboration of cyclohexane (**17**) and α -methylstyrene (**74**) with catecholborane (**23**) catalyzed with $\text{Ti}(\text{O}^i\text{Pr})_4$ which afford predominately trialkylborane and dialkylborane (Scheme 1.46). These authors suggested this result of significant degradation of hydroboration reagent which to affords diborane (**1**). However, the catalyst was efficient for the hydroboration of less sterically hindered olefins such as 1-decene.



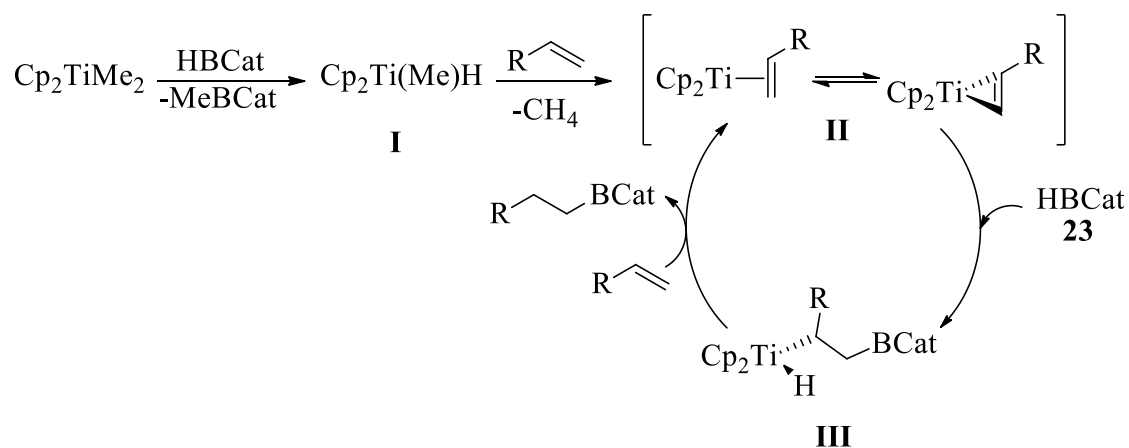
Scheme 1.46: Hydroboration of cyclohexene (**17**), styrene (**10**), 1-decene with catecholborane (**23**) catalyzed with $Ti(O^iPr)_4$.

Hartwig *et al.*,^{87, 88} investigated the hydroboration of olefins with catecholborane (**23**) using dicarbonyltitanocene, $Cp_2Ti(CO)_2$ and dimethyltitanocene, Cp_2TiMe_2 . In these studies, $Cp_2Ti(CO)_2$ was reported to be an efficient and selective catalyst for the hydroboration of alkyne which results in a single addition of catecholborane across the triple bond while Cp_2TiMe_2 was efficient and selective for hydroboration of alkenes (Scheme 1.47). In these studies, both catalysts were reported to afford predominately the less strictly hindered product. However, prior to these studies, the Cp_2TiMe_2 was reported to be inefficient for the hydroboration of olefins with complicated reaction mixtures and promoted degradation of catecholborane **23**.⁸⁹



Scheme 1.47: Hydroboration of alkyne and alkene catalyzed with titanocene derivatives.

He and Hartwig⁹⁰ proposed the mechanism depicted in Scheme 1.48 for the hydroboration of alkenes with titanocene derivatives after careful considerations and analysis of the observed results using $\text{Cp}_2\text{Ti}(\text{CO})_2$ and Cp_2TiMe_2 . In these studies, it was considered that the hydroboration of alkyne with $\text{Cp}_2\text{Ti}(\text{CO})_2$ required the displacement of at least one CO group to afford metallo-alkyne species similar to compound **II**. However, to afford such product species using alkene was too slow. Thereafter it was anticipated that Cp_2TiMe_2 would afford the transient species **II** much easier by reacting with one equivalence of catecholborane and the olefin.



Scheme 1.48: Titanocene derivatives hydroboration cycle.

The above mechanism by He and Hartwig first illustrated how the activated species **II** could be generated from Cp_2TiMe_2 through path **I**. Subsequently:

- (**II** → **III**) bond metathesis of Ti–C and B–H bond to afford metallacyclopentene character. This step was considered to be the regioselective determining step as the boron would prefer to attack the less hindered titanium-carbon bond. An alternative path in which direct bonding of boron to the metal centre was considered less likely as such species were reported inefficient to promote the addition of catecholborane to alkenes.
- (**III** → **II**) Transient species **III** undergo reductive elimination accompanied by olefin binding to regenerate the species **II**.

1.6.5. Iron-catalyzed hydroboration

This section is focused on selected iron complexes shown in Figure 1.11 toward hydroboration.

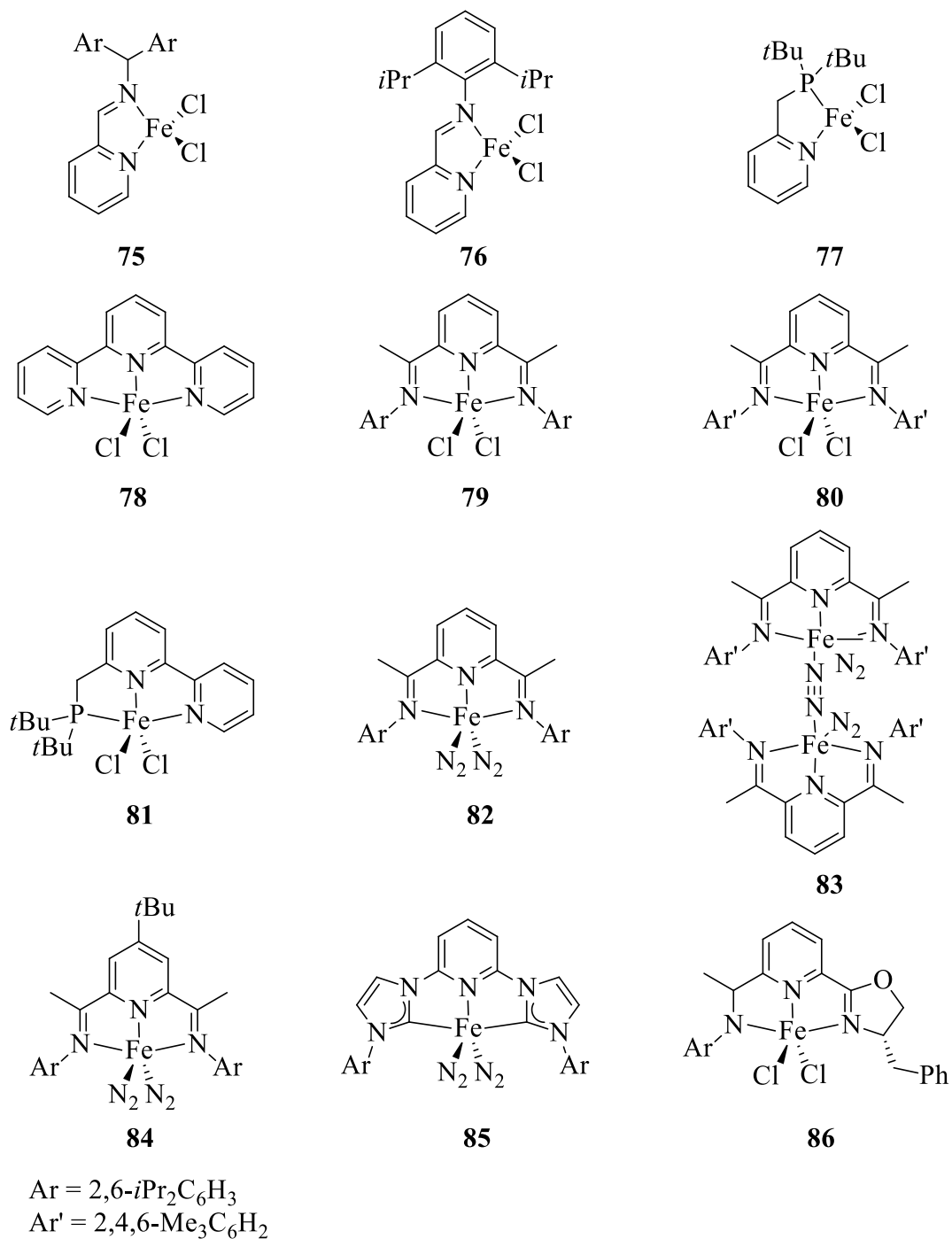
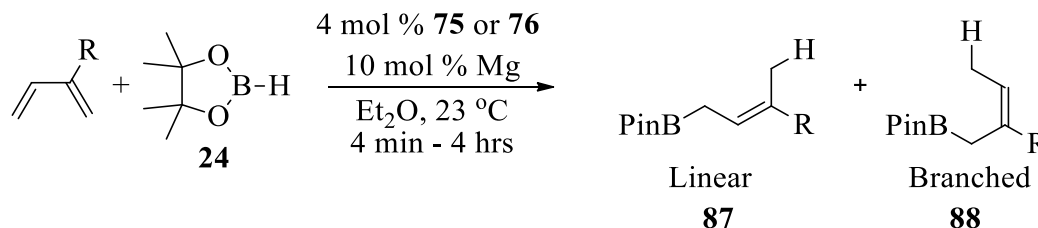


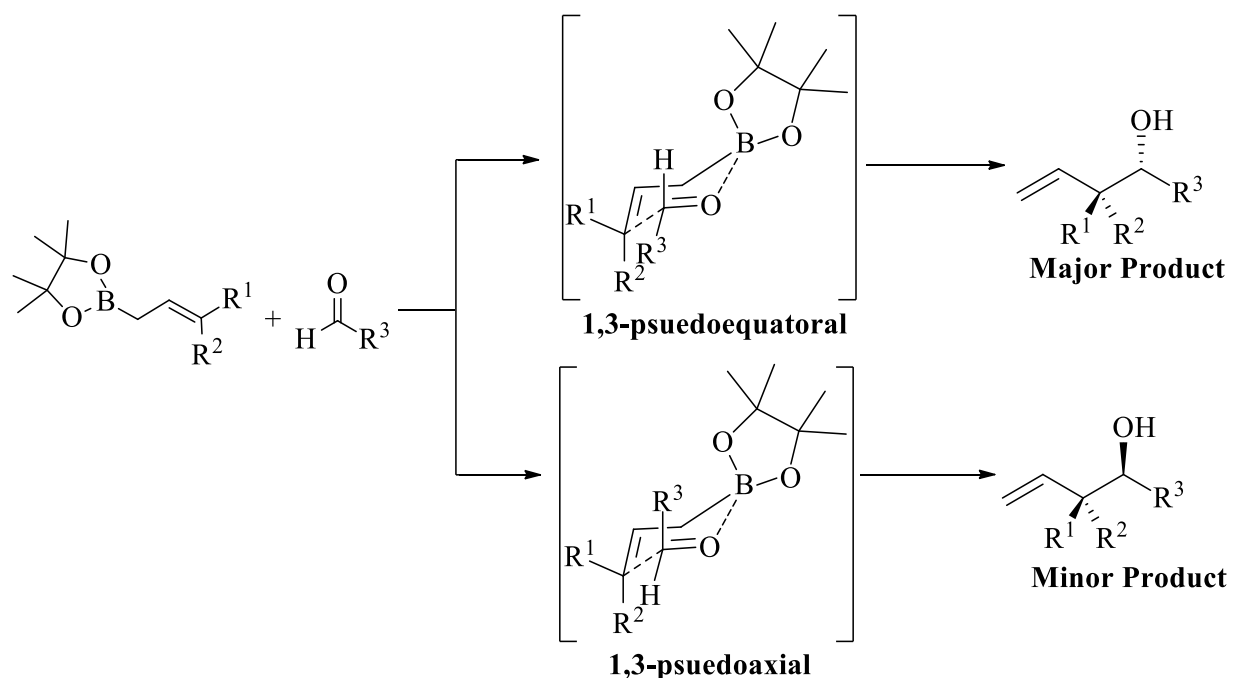
Figure 1.11: Selected iron complexes to be discussed which had been previously investigated for hydroboration.

In 2009, Wu *et al.*,⁹⁰ reported the first iron-catalyzed hydroboration. In this study two iron(II) iminopyridine complex **75** and **76** (Figure 1.11) activated *in-situ* by reduction reaction with an activated magnesium source were employed for hydroboration of 1,3-diene to afford the corresponding allylic boronic esters (Scheme 1.49). In these studies, the esters were afforded with a high regioselectivity 90% more for linear product and excellent stereoselectivity with 99% for the *cis* isomer and the reaction yield range from 66-90%.



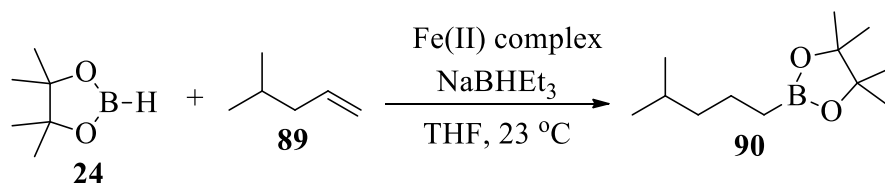
Scheme 1.49: Iron-catalyzed hydroboration of diene with pinacolborane (24).

Hoffmann and Schlapath^{91, 92} reported that allylic boronic esters such as those above (compound **87** and **88**) could react with aldehydes or ketones to afford homoallylic alcohols that can have two stereogenic centres. In this study, the process was reported to proceed with diastereoselectivity (Scheme 1.50). Furthermore, it was indicated that the reaction proceeded *via* a Zimmerman-Traxler transition state. In these studies, it was reported that the transition state was the key for stereoselectivity of the reaction. Mejuch *et al.*,⁹³ further investigated the selectivity of the process in more details using computational modelling of the transition state. In this study, it was demonstrated that the transition state of the 1,3-pseudoequatorial position of R³ was more favourable over 1,3-pseudoaxial position (Scheme 1.50). In this report, the enantioselectivity of the process was not discussed as the transition state did not discriminate each enantiomer over the other, which suggest a racemic mixture of the homoallylic alcohols would be obtained.



Scheme 1.50: Reaction of allylic boronic esters and aldehyde via a Zimmerman-Traxler transition state to homoallyl alcohols.

Zhang *et al.*,⁹⁴ investigated several iron(II) catalysts activated *in-situ* with NaBHET₃ for the hydroboration of 4-methyl-1-pentene (**89**) with pinacolborane (**24**) (Scheme 1.51).

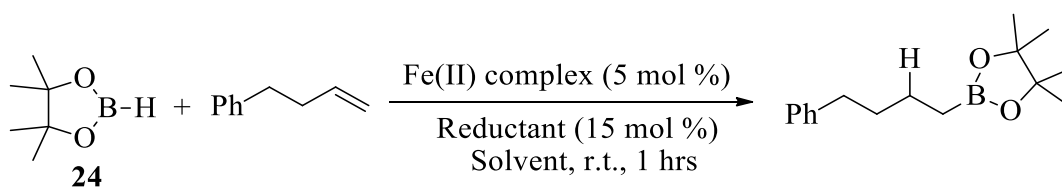


*Scheme 1.51: Iron-catalyzed hydroboration of 4-methyl-1-pentene (**89**) with pinacolborane (**23**)*

From the study reported above by Zhang,⁹⁴ it was discovered that iron(II) complexes with bidentate ligands such as adduct **75** and **77** were unreactive upon hydroboration of 4-methyl-1-pentene (**89**). However, an improvement was observed when tridentate ligands such as adduct (terpy)Fe(II)Cl₂ (**78**) and bis(imino)pyridine iron(II) adduct, (ⁱPrBIP)FeCl₂ (**79**) whereby the reaction yield was 5 and 61%, respectively. Furthermore, Obligacion and Chirik⁹⁵ extended this series of catalysts with (^{Mes}BIP)FeCl₂ (**80**) which resulted in 47% yield. Zhang *et al.*,⁹⁴ established that tridentate ligands were essential for the iron-catalysed hydroboration of alkenes.

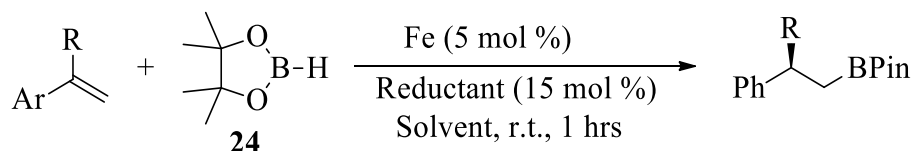
Zhang *et al.*,⁹⁴ suggested that a tridentate electron donating phosphine ligand would be much more effective complex **78** and **79** which lead to the development of the bipyridine-based phosphine ligand iron adduct, (^tBuPNN)FeCl₂ (**81**). In these studies, the adduct was used for the hydroboration of 4-methyl-1-pentene (**89**) which afforded the corresponding ester (**90**) in 99% yield as depicted in Scheme 1.51. These results were much more efficient than the results when the well-studied RhClPPh₃ (**58**) and [Ir(cod)cl]₂/dppe complex were employed which afforded 65 and 75% yield respectively. Hydroboration with (^tBuPNN)FeCl₂ (**81**) was extended to a series of olefins and it was discovered that the reaction was chemoselective could tolerate functional groups such as silyl, ether, acetal, tosylate and amine. However, this catalyst was unreactive toward internal alkenes such as *trans*-3-octene.

Greenhaigh and Thomas⁹⁶ reported an optimisation study for the hydroboration of 4-phenylbutene with pinacolborane using bis(imino)pyridine iron(II) adduct, (ⁱPrBIP)FeCl₂ (**79**) complex activated *in-situ* with tolylmagnesium bromide (TolMgBr), ethylmagnesium bromide (EtMgBr) or *n*-butyllithium (*n*-BuLi) in THF, toluene or solvent-free conditions. It was discovered that the optimum amount of the reducing agents required for efficient hydroboration was 3-folds the amount of the catalyst required with 89 - 94% yield obtained (Scheme 1.52). Thereafter the (ⁱPrBIP)FeCl₂ (**79**) pre-catalyst was investigated for hydroboration of a number of olefins with pinacolborane using EtMgBr which afforded 45 - 95% yield.



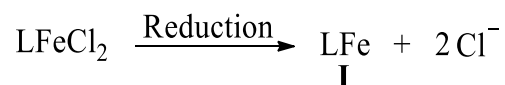
Scheme 1.52: Hydroboration of 4-phenylbutene with pinacolborane (**24**) using (ⁱPrBIP)FeCl₂ (**79**).

Furthermore, Chen *et al.*,⁹⁷ conducted optimization studies for the asymmetric hydroboration of styrene derivatives using chiral iminopyridine oxazoline iron(II) adduct, (IPO)FeCl₂ (**86**) and a number of activating agents or reducing agents were investigated Mg, Et₂Zn, EtMgBr, PhMgBr and NaBHET₃ (Scheme 1.53). In this study, the corresponding asymmetric esters were afforded in excellent enantioselectivity ranging from 80 – 97% ee. It was also reported that sodium triethyl borohydride (NaBHET₃) was more efficient reductant. Zhang *et al.*,⁹⁴ also identified NaBHET₃ to be an efficient reducing agent for the activation of (^tBuPNN)FeCl₂ (**81**) complex.



Scheme 1.53: Asymmetric hydroboration of styrene derivatives (IPO)FeCl₂ (**86**).

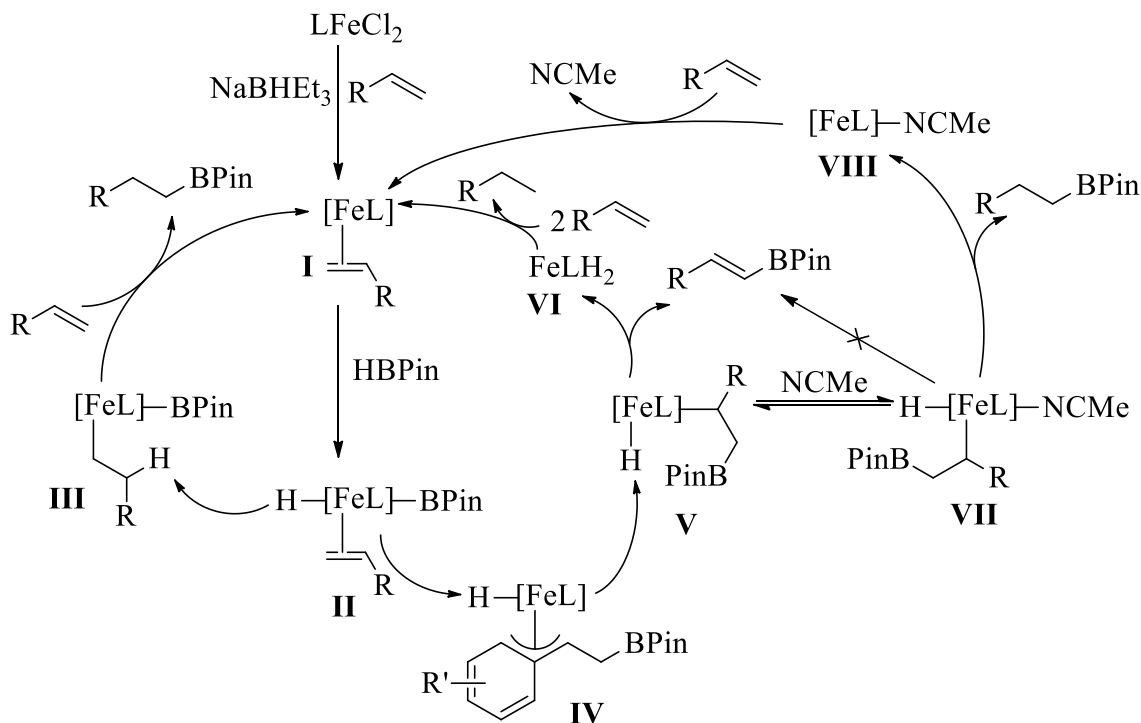
It has been suggested for iron-catalysed olefin hydro-functionalisation that when the iron(II) complexes are being activated *in-situ* by reduction reaction with a reductant to lower oxidation state, it affords activated iron(0) transient adduct (**I**) (Scheme 1.54).⁹⁸



Scheme 1.54: Reduction of iron(II) complexes.

So far Iron(II) complex used to generate the activated iron(0) adduct *in-situ* have been discussed, however, there are a number of adducts for hydroboration such as Fe₂(CO)₉ and [(NHC)Fe(CO)₄].⁹⁹ Most interestingly Obligation and Chirik⁹⁵ reported stable iron(0) nitrogen adducts (ⁱPrBIP)Fe(N₂)₂ (**82**), [(^{Mes}BIP)Fe(N₂)₂](μ-N₂) (**83**), (4-^tBu-ⁱPrBIP)Fe(N₂)₂ (**84**) and (ⁱPrCNC)Fe(N₂)₂ (**85**) which were used to hydroborate a number of olefins under solvent free condition and demonstrated excellent yield up to 98% . In this study, these catalysts were also employed for the hydroboration of 4-methyl-1-pentene (**89**) as represented in (Scheme 1.51). The iron(0) catalysts (ⁱPrBIP)Fe(N₂)₂ (**82**) and [(^{Mes}PDI)Fe(N₂)₂](μ-N₂) (**83**) were highly efficient and afforded a yield of 87% and 86%, respectively as compared to their similar *in-situ* generated catalysts (ⁱPrBIP)FeCl₂ (**79**) and (^{Mes}BIP)FeCl₂ (**80**) which only yielded 61% and 47% respectively.^{94, 95}

Zhang *et al.*,⁹⁴ proposed the only mechanism to date for the iron-catalysed hydroboration as depicted in Scheme 1.55. In this study, a number of hydroboration reactions were conducted which afforded the corresponding esters. However, it was observed that undesired dehydrogenative borylation and hydrogenation products occurred when vinylarenes with no α -substituent were used. Fortunately, it was also discovered that the presence of about 20% acetonitrile suppressed the formation of the undesired products.



Scheme 1.55: Iron-catalyzed hydroboration catalytic cycle.

The initial step of the mechanism (Scheme 1.55) illustrates the activation of the iron complex with the reductant (NaBHET_3) accompanied by olefin binding to afford the transient species **I** which enters the catalytic circle thereafter could follow two catalytic pathways:

The first path (**I** \rightarrow **II** \rightarrow **III**):

- ❖ (**I** \rightarrow **II**) involves the oxidative addition of hydroboration reagent to afford the 18-electron iron(II) intermediate **II**
- ❖ (**II** \rightarrow **III**) depicts olefin 1,2 insertion into the Fe—H bond
- ❖ (**III** \rightarrow **I**) reductive elimination of the hydroboration Markovnikov product accompanied with the bonding of another olefin to regenerate **I**.

The second path (**I** → **II** → **IV** → **V** → **VI**) observed in cases of vinylarenes without an alpha-substituent:

- ❖ (**II** → **IV** → **V**) indicate olefin insertion into the Fe—B bond opposed to Fe—H bond which may be promoted through the formation of **IV**
- ❖ (**V** → **VI**) indicate the elimination of the dehydrogenative borylation product which also afford hydrogenated adducted **VI**. However, in the presence of acetonitrile, it resulted in the formation of **VII** which would be much favoured hence this adduct has no vacant site to permit dehydrogenative borylation product thereby resulted in the elimination of the hydroboration Markovnikov product (**VII** → **VIII**). Thereafter regeneration of **I** through olefin binding with the release of acetonitrile.
- ❖ (**VI** → **I**) adduct **VI** undergoes olefin hydrogenation to+ regenerate **I**.

2. Research rational

2.1. Previous research with the research group.

In this group, there had been studies focused on the design and development of stable and reactive heterocyclic hydroborating reagents, which are more efficient towards hydroboration and a number of reagents have been successfully designed, synthesized and investigated.^{21, 54, 56}

Sample of the reagents are shown in Figure 2.1.

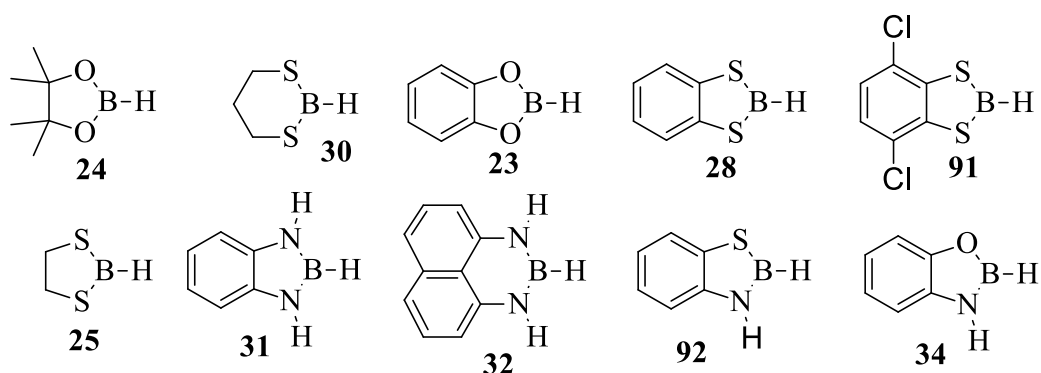
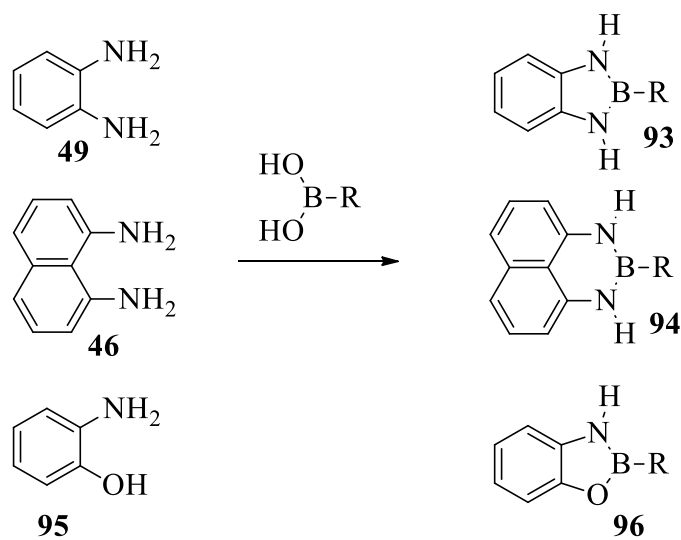


Figure 2.1: Heterocyclic hydroborating reagents previously studied within Robinson's research group.

The hydroboration of a number of selected olefins with the above heterocyclic hydroborating reagents has been studied under uncatalyzed and catalyzed condition.^{21, 100-102} In these studies, a variety of transition metal catalysts have been investigated such as the Wilkinson's catalyst (**58**), $[\text{IrCl}(\text{COD})]_2$ and dimethyltitanocene. There have been studies focused on the green approach to this process whereby reactions are conducted under limited to solvent-free microwave conditions for much lesser reaction times.

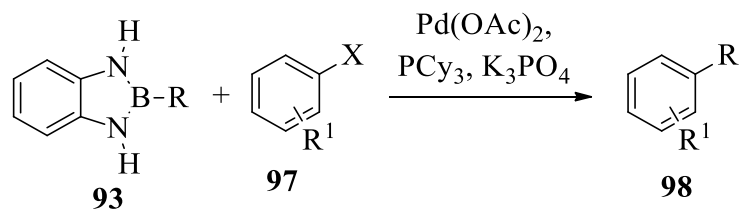
Computational studies for hydroboration processes have been conducted such as the DFT studies of the different hydroborating reagents in an attempt to address the observed stability trends and the hydroboration mechanism of the uncatalyzed process.^{55, 101, 103}

There have been studies focused on the synthesis of *N*-heterocyclic boronic ester derivatives from the condensation reaction of a boronic acid and bidentate nitrogen derivatives (Scheme 2.1).^{58, 101}



Scheme 2.1: Condensation reaction of boronic acids and bidentate nitrogen derivatives to afford N-heterocyclic boronic ester.

Due to the high stability and resistant to oxidation of *N*-heterocyclic boronic ester derivatives (compound like **93**, **94** and **96**), there has been a focused effort on the utilization of these esters as a coupling partner in a number of coupling reactions such as the Suzuki-Miyaura cross-coupling reactions (Scheme 2.2).⁵³



Scheme 2.2: Suzuki-Miyaura cross-coupling reactions with the N-heterocyclic boronic ester.

2.2. Project Aims and Objectives

To further investigate the work done within the group:

- ❖ The project was aimed to investigate the reactivity of heterocyclic borole hydroborating reagents shown in Figure 2.2 toward the olefin hydroboration. This investigation was intended to determine effective hydroborating reagents that could be used for hydroboration. Six different olefins namely, 1-octene (**52**), 1-hexene (**38**), styrene (**10**), α -methylstyrene (**74**), cyclohexene (**17**) and cyclooctene (**117**) were selected for this study. Within this study, it was also aimed to investigate the relative reactivity of the set of catalysts (Figure 2.3) toward hydroboration coupled with the selected set of hydroborating reagents. Thereafter compare the efficiency of the well-studied late transition metal catalyst Wilkinson's catalyst (**58**) against the 3d transition metal catalyst dimethyltitanocene and the two iron complexes **79** and **80**. These set of catalysts was selected to explore the advantages early transition metal catalyst may present over the well-studied Wilkinson's catalyst (**58**). Furthermore, this study was aimed to find new boronic esters which would be afforded from the hydroboration studies.

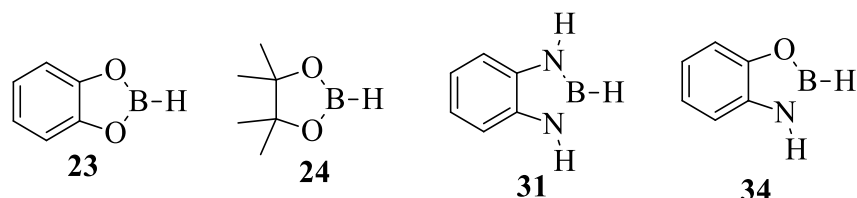
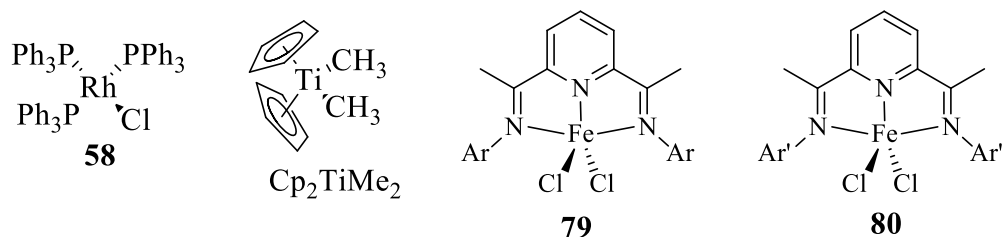


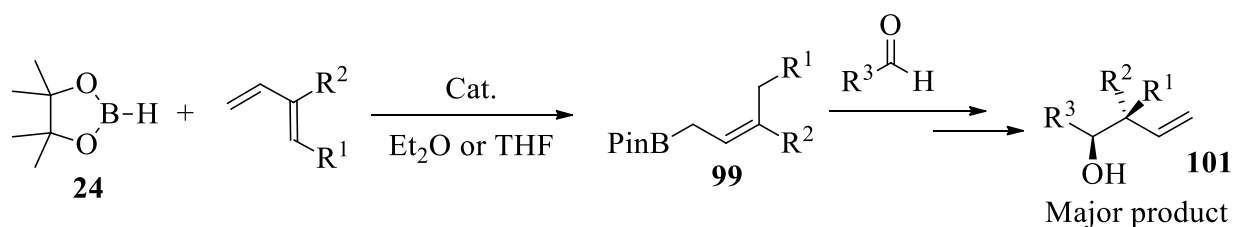
Figure 2.2: Selected hydroborating reagent for the hydroboration studies



Ar = 2,6-*i*Pr₂C₆H₃
Ar' = 2,4,6-Me₃C₆H₂

Figure 2.3: Transition metal catalyst to be used for the hydroboration studies

- ❖ Secondly, it was aimed to apply the hydroboration process toward the diastereoselective synthesis of homoallyl alcohols (**101**). In these studies, it was aimed to conduct hydroboration of 1,3-diene derivatives with the hydroborating reagents shown in Figure 2.2 to afford allylborane esters (**99**) (Scheme 2.3 illustrates an example of the study using pinacolborane (**24**)). Thereafter utilize these esters in a reaction with an aldehyde to afford the corresponding homoallyl alcohol. In these studies, the objective was to investigate the efficiency of each hydroborating reagent towards the diastereoselectivity of the reaction and how the selectivity would vary with each reagent.



Scheme 2.3: Diastereoselective synthesis of homoallylic alcohols via hydroboration.

3. Results and Discussions

3.1. Preparation of Hydroborating reagents.

This section is focused on the preparation of the hydroborating reagents which are intended to be further investigated for hydroboration. These reagents were freshly prepared before each hydroboration study and their yield recorded from the reaction mixture using ^{11}B -NMR spectroscopy. All the yields reported are based on the maximum record yield from ^{11}B -NMR spectroscopy. Isolation of these reagents is technically difficult due to their high sensitivity to moisture and oxygen, however, for our study purposes, isolation was not necessarily required.

3.1.1. Synthesis of catecholborane (23)

In 1977, Brown *et al.*,²⁶ reported an improved method for the preparation of catecholborane (**23**) with a 75% yield using catechol (**41**) and $\text{BH}_3\cdot\text{SMe}_2$ (**16**) in ether at 0 °C. These authors reported that the reaction run-time was reduced from ten hours to four hours with a small decline in yield from 75% to 72% when the reaction was conducted at 25 °C. When the protocols reported by these authors was followed in this study, the results from the ^{11}B -NMR spectroscopy showed multiple undesired products as shown by the signal ranges 17–28 ppm (Figure 3.1). Furthermore, the quartet signal at -20.3 ppm was assigned to unreacted BMS (**16**). The desired product catecholborane (**23**) signal was either insignificantly small or overwhelmed by multiple signals around its resonance frequency for correct assignment.

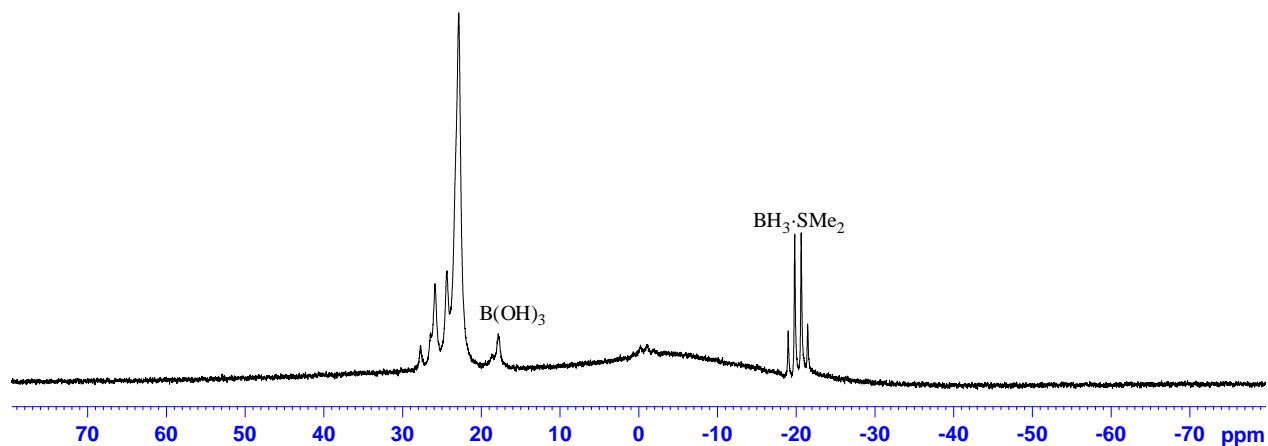


Figure 3.1: ^{11}B -NMR spectrum showing an initial attempt to prepare catecholborane(**23**).

The reaction temperature change from 25 to 0 °C, in this case, only three signals were detected: a doublet at 28.9 ppm indicating a single boron–hydrogen bond (B–H) which was assigned to catecholborane (**23**), a broad singlet at 22.4 ppm which was assigned to the disproportionation product, Cat_3B_2 (**62**) and unreacted BMS (**16**) signal at -20.3 ppm (Figure 3.2). However, a poor yield of 12% was obtained for catecholborane (**23**) after 4 hours with significant disproportionation product Cat_3B_2 (**62**) with 42% and 55% unreacted BMS (**16**).

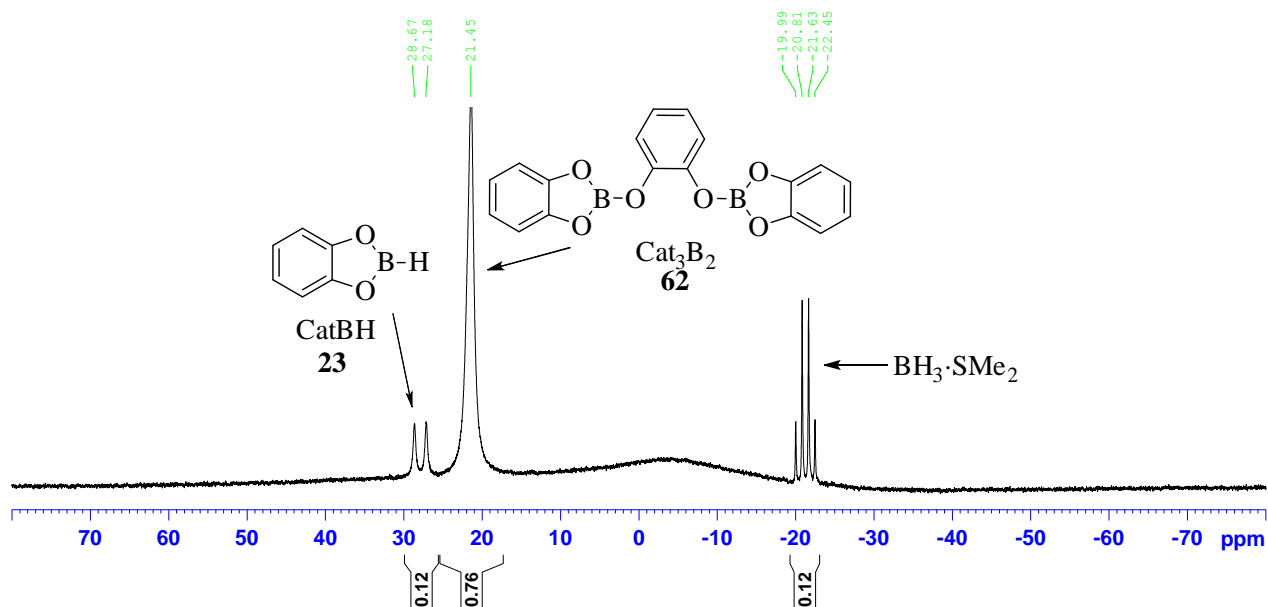
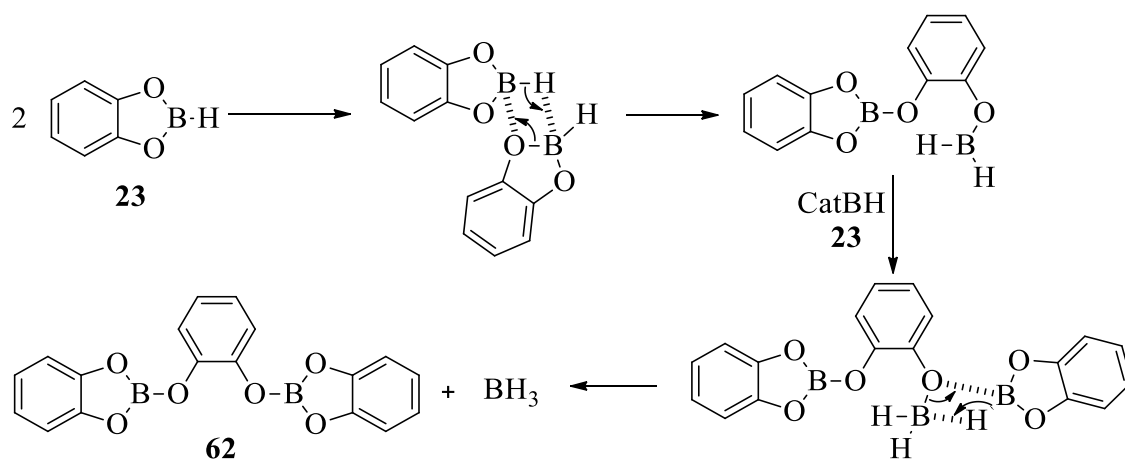


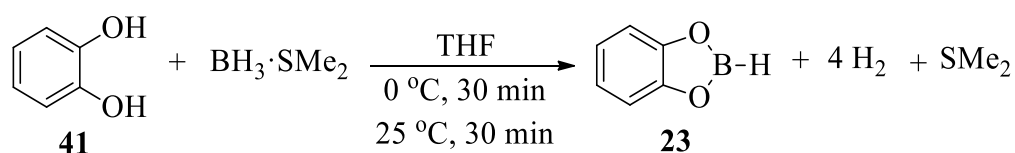
Figure 3.2: ^{11}B -NMR spectrum showing catecholborane (**23**) prepared at 0 °C in THF

The observed disproportionation product Cat_3B_2 (**62**) of catecholborane (**23**) can be afforded from intermolecular catecholborane reaction as depicted in Scheme 3.1. A more detailed discussion of this disproportionation pathway was reported in section 1.5.3.1 using the generalized disproportionation pathway of oxygen based heterocyclic hydroborating reagents.



Scheme 3.1: Disproportionation of catecholborane (23).

In earlier studies to the previous methods, Brown and Gupta,^{45, 52} reported that catecholborane (**23**) could be prepared from catechol and borane-tetrahydrofuran complex ($\text{BH}_3 \cdot \text{THF}$) in THF. According to these authors, a slow addition of catechol (**41**) solution to the borane-tetrahydrofuran complex at 0 °C and subsequently maintained at this temperature for 30 minutes. Thereafter allowed to warm-up slowly to 25 °C and further maintained at this temperature for a further 30 minutes afforded catecholborane (**23**) with 80% yield. Following a modified protocol by these authors, whereby BMS was used instead of $\text{BH}_3 \cdot \text{THF}$ (**12**), catecholborane (**23**) was afforded in a 39% yield (Scheme 3.2).



Scheme 3.2: Synthesis of catecholborane (23).

After the reaction was conducted an ^{11}B -NMR spectrum was recorded which showed a 39% yield catecholborane (**23**), 42% being Cat_3B_2 (**62**) and 19% unreacted BMS (Figure 3.3). The addition of more catechol (**41**) solution and additional reaction run-time had an insignificant change to the yield of catecholborane (**23**) whereas the disproportionation product had increased. Furthermore, reducing the concentration of the reagents also had an insignificant effect on reducing the disproportionation product or the reaction outcome. Hence, the reagent was further investigated for hydroboration.

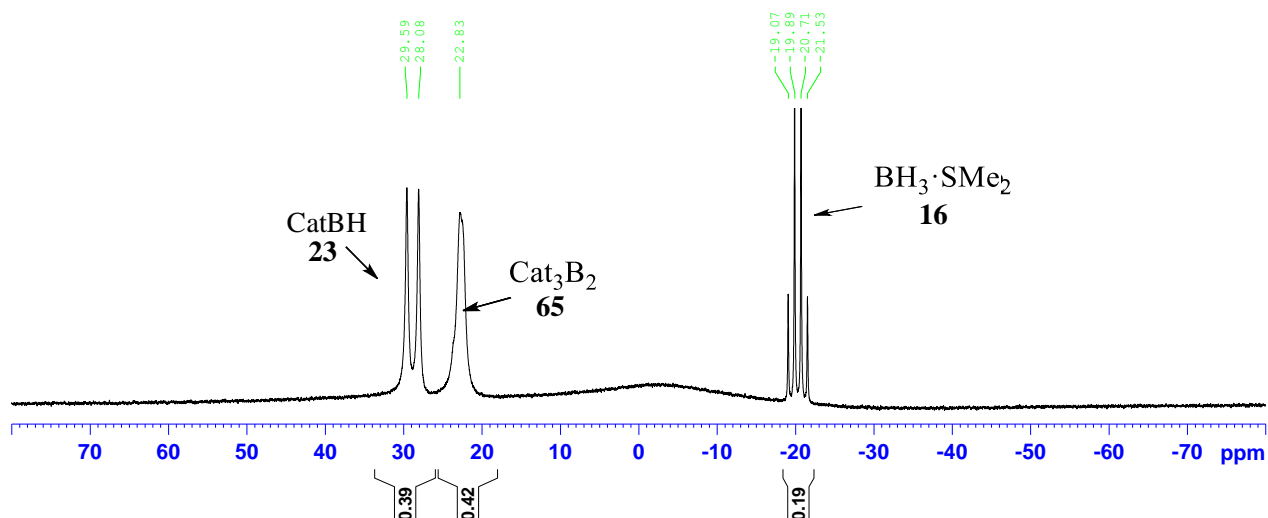
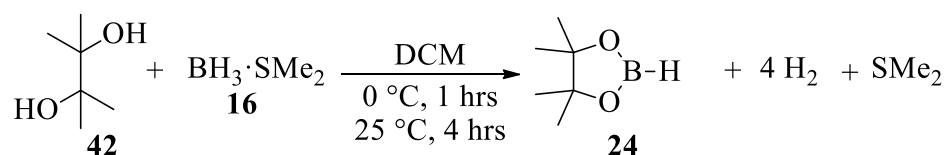


Figure 3.3: ^{11}B -NMR Spectrum for catecholborane (**24**).

3.1.2. Synthesis of Pinacolborane (**24**).

In 1992 Tucker *et al.*,⁴⁹ reported that pinacolborane (**24**) could be easily prepared from pinacol (**42**) and BMS (**16**) in dichloromethane (DCM). According to these authors, a drop-wise addition of BMS (**16**) to a solution of pinacol (**42**) at 0 °C thereafter maintained at this temperature one hour followed by one hour at 25 °C afforded pinacolborane (**24**) with a 63% yield. Following the protocol by these authors, it was observed that the reaction attempted in this study was not completed within the reported time thereafter additional three hours at 25 °C was required for the reaction to be completed and under these conditions, pinacolborane (**24**) was prepared in a yield of 89% (Scheme 3.3).



Scheme 3.3: Synthesis of Pinacolborane (**24**).

The ^{11}B -NMR spectrum obtained showed a doublet at 28.7 ppm indicating single B–H which was assigned to pinacolborane (**24**) (Figure 3.4). A singlet at 23.1 ppm was also detected and it was assigned to the disproportionation product Pin_3B_2 (**101**) that would be afforded in a similar manner as disproportionation product of catecholborane which has been discussed *vide supra*.

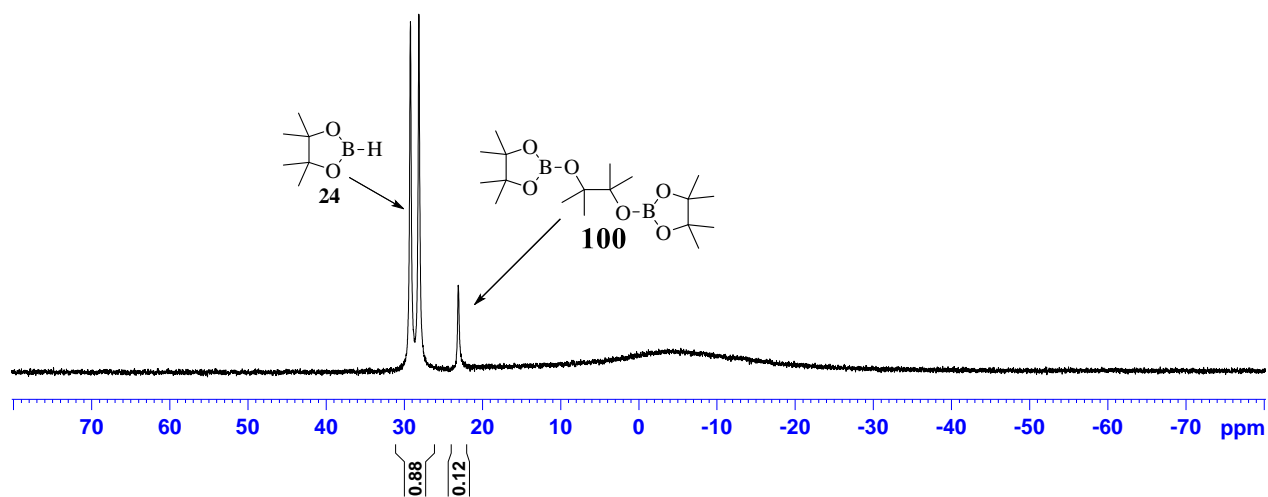
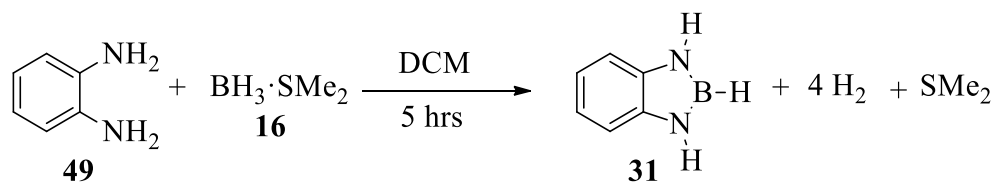


Figure 3.4: ^{11}B -NMR Spectrum of pinacolborane (**24**).

3.1.3. Synthesis of 2,3-dihydro-1,3,2-benzodiazaborole (**31**)

Hadebe *et al.*,⁵⁸ reported a method to prepare 2,3-dihydro-1,3,2-benzodiazaborole (**31**) from *o*-phenylenediamine (**49**) and BMS (**16**) under reflux in DCM for five hours which afforded a 95% yield. Following this method, 2,3-dihydro-1,3,2-benzodiazaborole (**31**) was synthesized in yields exceeding 99%.



Scheme 3.4: Synthesis of 2,3-dihydro-1,3,2-benzodiazaborole (**31**).

The ^{11}B -NMR spectrum indicated a doublet at 23.9 ppm which was assigned to 2,3-dihydro-1,3,2-benzodiazaborole (**31**) (Figure 3.5). These results were in agreement with literature results.⁵⁸

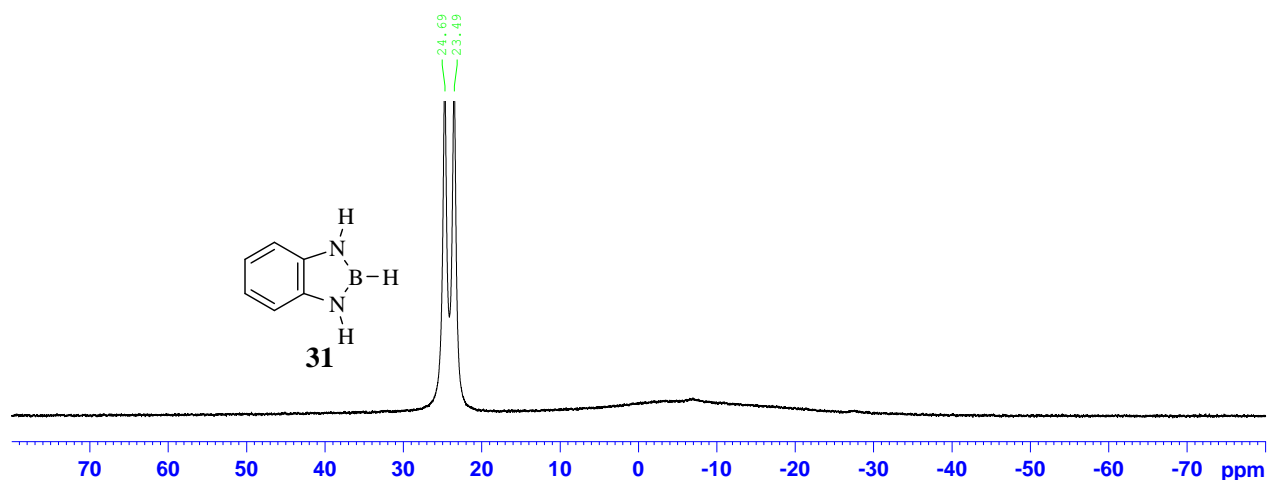


Figure 3.5: ^{11}B -NMR spectrum of 2,3-dihydro-1,3,2-benzodiazaborole (**31**).

High resistance towards disproportionation of 2,3-dihydro-1,3,2-benzodiazaborole (**31**) was observed. This was in agreement with literature report.²¹ Denk *et al.*,¹⁰⁴ reported that an addition π -back bonding exists between boron-hetero atoms (for example Figure 3.6) which are responsible for the enhanced stability of the hetero-boron compounds. These authors further, indicated that this effect was stronger with nitrogen than with oxygen.

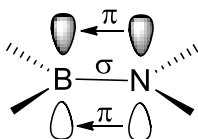
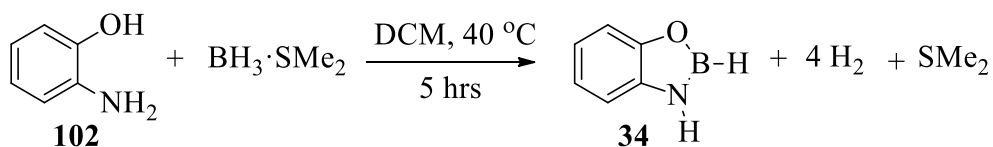


Figure 3.6: π -back bonding between boron-nitrogen sigma-bond.

3.1.4. Synthesis of 2,3-dihydro-1,3,2-benzooxazaborole (**34**).

Slabber⁵⁶ reported that 2,3-dihydro-1,3,2-benzooxazaborole (**34**) can be prepared from 1,2-aminophenol (**102**) and BMS in THF at 25 °C to afford the desired product after 72 hours in 85% yield. In this study, it was discovered that when the reaction was conducted in DCM or THF at 35 - 40 °C, a 97% yield of the desired product was afforded after five hours (Scheme 3.5).



Scheme 3.5: Synthesis of 2,3-dihydro-1,3,2-benzooxazaborole (**34**).

The ^{11}B -NMR spectrum (Figure 3.7) presents a doublet peak at 27.9 ppm which was assigned to 2,3-dihydro-1,3,2-benzoxazaborole (**34**) and a singlet at 23.5 which was assigned to the borazine analogue (**57**) the disproportionation product of 2,3-dihydro-1,3,2-benzoxazaborole (**34**). The disproportionation mechanism to afford the borazine analogue (**57**) was discussed in more details earlier in section 1.5.3.4 (refer to the introduction).

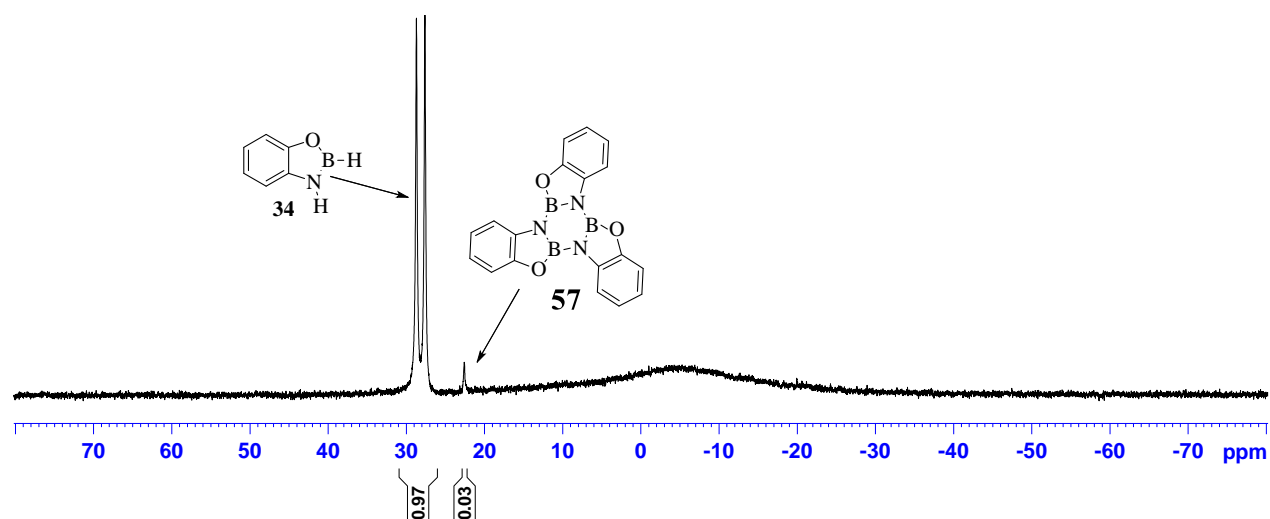


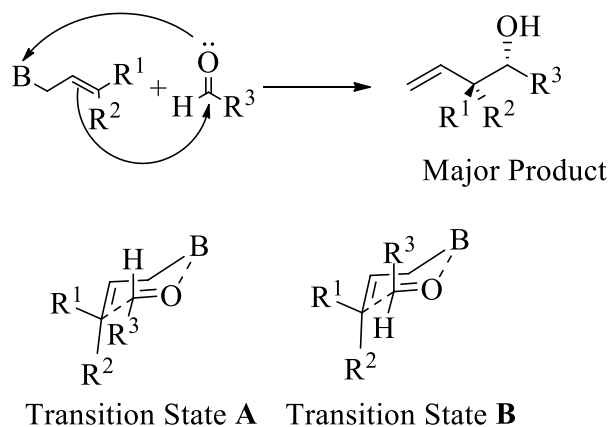
Figure 3.7: ^{11}B -NMR spectrum of 2,3-dihydro-1,3,2-benzoxazaborole (**34**).

3.2. Diastereoselective synthesis of homoallylic alcohols *via* hydroboration.

3.2.1. Background toward the study.

Hadebe *et al.*,²¹ reported the effect of changing the hetero atom using catecholborane (**23**) type analogues (compound **28** and **31**). This study indicated that a reduction in Lewis acidity of these hydroborating reagents when the hetero atom was varying from oxygen to sulfur and subsequently to nitrogen. This effect was attributed to change in the electronic properties which were due to the increased π -back bonding ability to these reagents as the hetero atoms were varied from oxygen, sulfur to nitrogen. Denk *et al.*,¹⁰⁴ discussed similar observations.

In section 1.6.5, the synthesis of homoallylic alcohols from allylboronic esters and aldehydes or ketone was discussed. These reactions have been reported to proceed *via* a Zimmerman-Traxler transition states afforded after the allyl double bond of the ester attacks the carbonyl carbon and carbonyl oxygen overlapping with the boron empty p_z orbital (Scheme 3.6).⁹³ In this study, the major product was reported to proceed *via* transition state A which is more favoured with less 1,3-diaxial interactions as the R^3 -group at the equatorial position opposed to transition state B.



Scheme 3.6: The synthesis of homoallylic alcohols from allylic boronic esters and aldehydes via a Zimmerman-Traxler transition states.

The effect of donor ability on the stability and hydroboration efficiency of hydroboration reagents have been documented earlier in more details at the introduction. However, the effect of changing the Lewis acidity of the boron atom on the reaction mentioned above has never been investigated. The change in the Lewis acidity of the boron atom would influence the B–O interaction transition states (Scheme 3.6) which control the stereoselectivity of the reaction and it would be desired to investigate this effect. Hydroborating reagents with varying acidity were selected for the investigation of this effect (Figure 3.8).

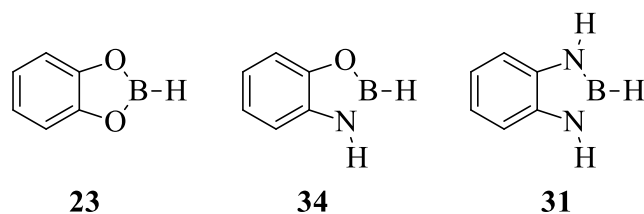
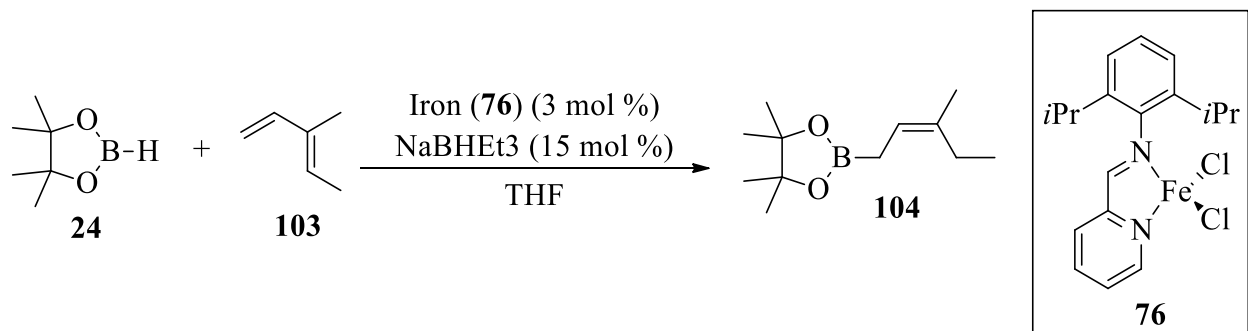


Figure 3.8: Selected hydroborating reagent to prepare allyl heterocyclic boronic esters for investigation of the diastereoselective synthesis of homoallylic

3.2.2. Synthesis of allylic esters to be employed for the preparation of 2-ethyl-2-methyl-1-phenylbut-3-en-1-ol.

Wu *et al.*,⁹⁰ reported a protocol for the hydroboration of *cis*-1,3-diene derivatives with pinacolborane **24** to afford allylic boronic esters catalyzed with iron catalysts (discussed section 1.5.5). A similar protocol was employed for the hydroboration of 3-methyl-1,3-pentadiene (**103**) with pinacolborane (**24**) to afford 4,4,5,5-tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (**104**) (Scheme 3.7). The iron catalyst (iron(II) iminopyridine complex **76**) employed was activated with sodium triethylborohydride in anhydrous ether or THF at 25 °C. The iron(II) iminopyridine complex **76** was prepared using literature procedure and further confirmed using mass spectrum.¹⁰⁵ However, the spectrum indicated several impurities were present and recrystallization was attempted to remove these impurities. Recrystallization was not successful to remove these impurities. Subsequently, this reaction was conducted with the obtained catalyst mixture.



Scheme 3.7: Hydroboration of 3-methyl-1,3-pentadiene (103) with pinacolborane (24).

The above reaction was followed using ^{11}B -NMR spectroscopy as the doublet of pinacolborane (**24**) dissipate a new singlet signal at 33.1 ppm which was formed in a yield of 58% after 24 hours (Figure 3.9). The new signal was suspected to be the desired allylic heterocyclic boronic ester.

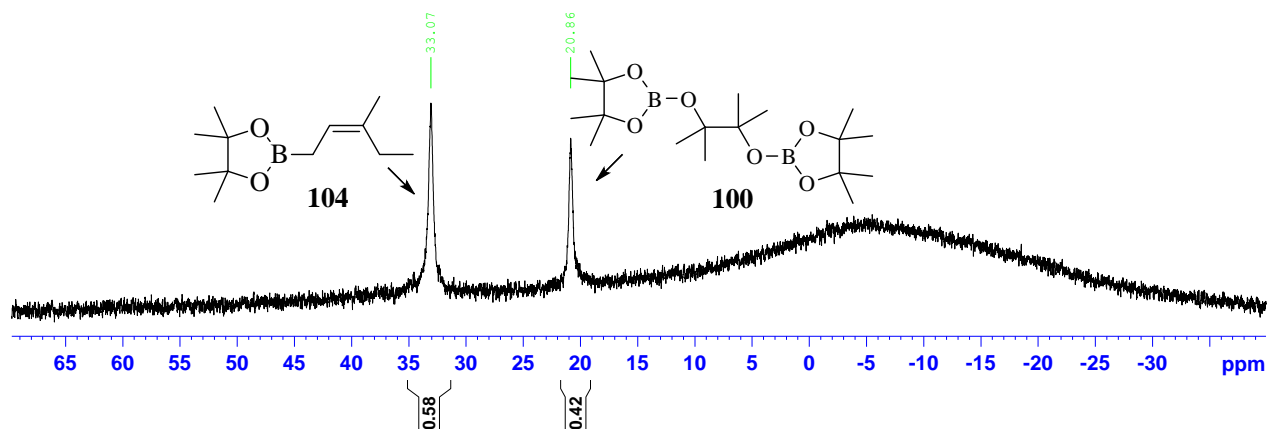
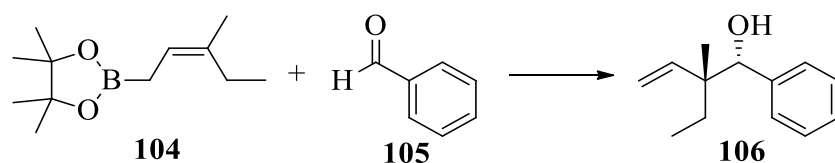


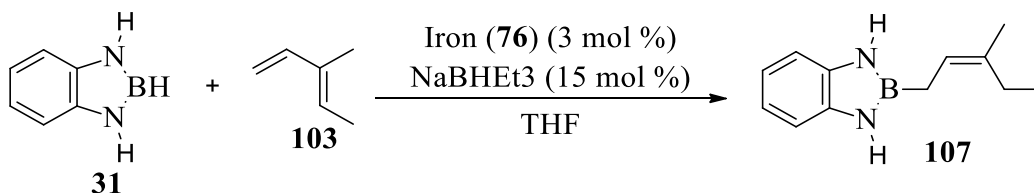
Figure 3.9: ^{11}B -NMR spectrum for the hydroboration of 3-methyl-1,3-pentadiene (103) with pinacolborane (24) after 24 hours.

However, the actual identity and geometry of the above ester were never confirmed due to inefficient isolation attempts of the ester through chromatography despite following the literature procedure.⁹⁰ The isolation process of the product resulted in a mixture of compounds with evidence of degradation of the product after being passed through silica gel with evidence of catalyst fragments on TLC plates and NMR results. Consequently, the reaction of esters with the benzaldehyde to afford (1*S*,2*R*)-2-ethyl-2-methyl-1-phenylbut-3-en-1-ol (**106**) was not conducted (Scheme 3.8). Furthermore, attempts to perform the diastereoselective synthesis of homoallyl alcohols without possibly isolating of the intermediate esters from the initial hydroboration mixture were unsuccessful.



Scheme 3.8: The reaction of 4,4,5,5-tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (104) with the benzaldehyde (105).

After it was observed that pinacolborane (**24**) allylic ester derivatives showed degradation upon isolation another attempt was made using the more stable nitrogen derivative of catecholborane (**24**) to hydroboration of 3-methyl-1,3-pentadiene (**103**) with 2,3-dihydro-1,3,2-benzodiazabolole (**31**) to afford the corresponding intermediate ester 2-(3-methylpent-2-en-1-yl)-1,3,2-benzodiazaborolane (**107**) in THF at 40 °C (Scheme 3.9). This reaction was conducted following protocol like the above. The ¹¹B-NMR spectroscopy indicated that the ester was suspected to have been afforded with a 40% yield after 48 hours. Unfortunately, similar technical problems as the above were encountered during attempts to isolate this ester.



Scheme 3.9: Hydroboration of 3-methyl-1,3-pentadiene (103) with 2,3-dihydro-1,3,2-benzodiazabolole (31).

3.2.3. Summary and conclusion

In this study, it was envisaged that the intermediate esters (Z)-4,4,5,5-tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (**104**) and (Z)-2-(3-methylpent-2-en-1-yl)-2,3-dihydro-1,3,2-benzodiazaborolane (**107**) would be synthesized and subsequently utilized to investigate their diastereoselectivity for the synthesis of homoallyl alcohols such as (1S,2R)-2-ethyl-2-methyl-1-phenylbut-3-en-1-ol (**106**). The study was unsuccessful after multiple attempts towards the preparation and the extraction of the above allyl boronic acid intermediate esters **104** and **107** were inefficient. The ^{11}B -NMR spectroscopic data indicated the formation of a new boron compound which was assumed to be the corresponding desired intermediate esters. However, isolation process of each of these esters was inefficient with product sample showing multi-species and evidence of degradation (observed with TLC plate and NMR-spectroscopy). This study was abandoned as the chances of being prosperous successful were low due to the intermediate esters were not stable enough to be purified.

3.3. Hydroboration Studies

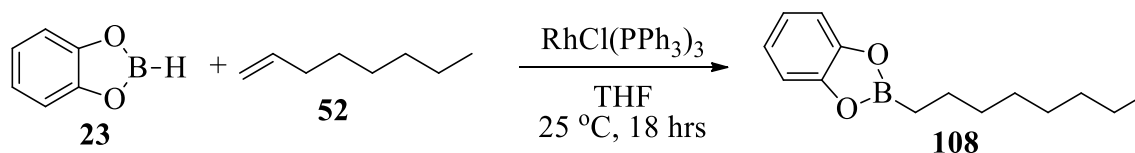
In this section, ^{11}B -NMR spectroscopy was utilized to monitor all hydroboration reactions and measure reaction yields. The reaction yields were calculated from the amount of hydroborating reagent present before the reaction and the amount that was converted to corresponding esters as the hydroborating reagent. The yields were quoted from the maximum observed yield.

3.3.1. Wilkinson's Catalyst ($\text{RhCl}(\text{PPh}_3)_3$) (**58**) Catalyzed Hydroboration

3.3.1.1. $\text{RhCl}(\text{PPh}_3)_3$ -catalysed hydroboration studies with catecholborane

3.3.1.1.1. Hydroboration of 1-octene (**52**) with catecholborane (**23**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**)

Prior to the discovery of catalyzed-hydroboration reactions with transition metals, catecholborane (**24**) had already been successfully used for hydroboration of various olefins.^{45, 48, 52, 61, 106} However, such reactions proceed with poor selectivity at elevated temperature. In the initial report of metal-catalyzed hydroboration report by Männig and Nöth,⁴² the hydroboration of 1-octene (**52**) with catecholborane (**23**) to afford 2-octyl-1,3,2-benzodioxaborolane (**108**) was discussed. In this study, the reaction was conducted in benzene at 25 °C and afforded an 85% yield. However, the yield was recorded after oxidative workup reaction of the hydroboration product to afford the corresponding alcohol. Westcott *et al.*,⁷⁶ conducted this reaction in deuterated tetrahydrofuran which afforded a quantitative yield after 30 minutes. When a similar protocol was followed using THF, 2-octyl-1,3,2-benzodioxaborolane (**108**) was afforded in a 50% yield however after 18 hours



(Scheme 3.10). Furthermore, excessive disproportionation of catecholborane (**23**) was observed.

*Scheme 3.10: Hydroboration of 1-octene (**52**) with catecholborane (**23**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**).*

The reaction was followed using ^{11}B -NMR spectroscopy, the initial borole spectrum showed a doublet peak at 27.9 ppm indicating catecholborane (**23**), a broad singlet at 21.5 ppm indicating the disproportionation product Cat_3B_2 (**62**) and quartet at -21.2 ppm of unreacted BMS (**16**) (Figure 3.10). These results were in agreement with Literature report.²¹

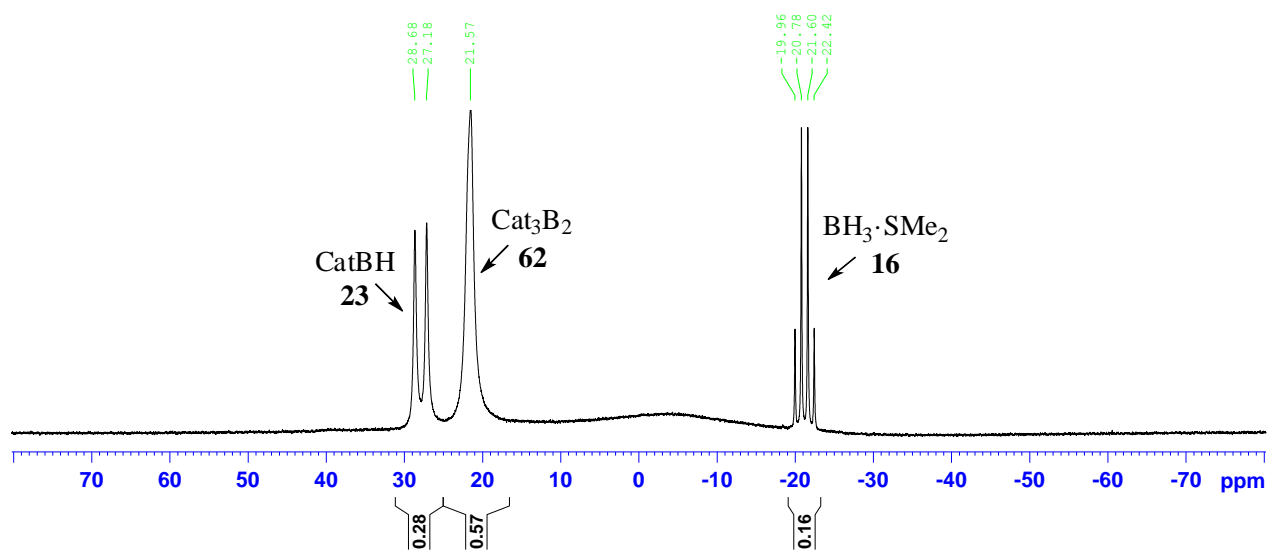


Figure 3.10: ^{11}B -NMR spectrum of the catecholborane (**23**) used before the hydroboration of 1-octene (**52**).

When the hydroboration reaction was completed an ^{11}B -NMR spectrum was recorded which indicated the boronic ester at 34.9 ppm and Cat_3B_2 (**62**) at 21.2 ppm (Figure 3.11). Westcott *et al.*,⁷⁶ reported a similar ^{11}B -NMR spectrum peak for 2-octyl-1,3,2-benzodioxaborolane (**108**).

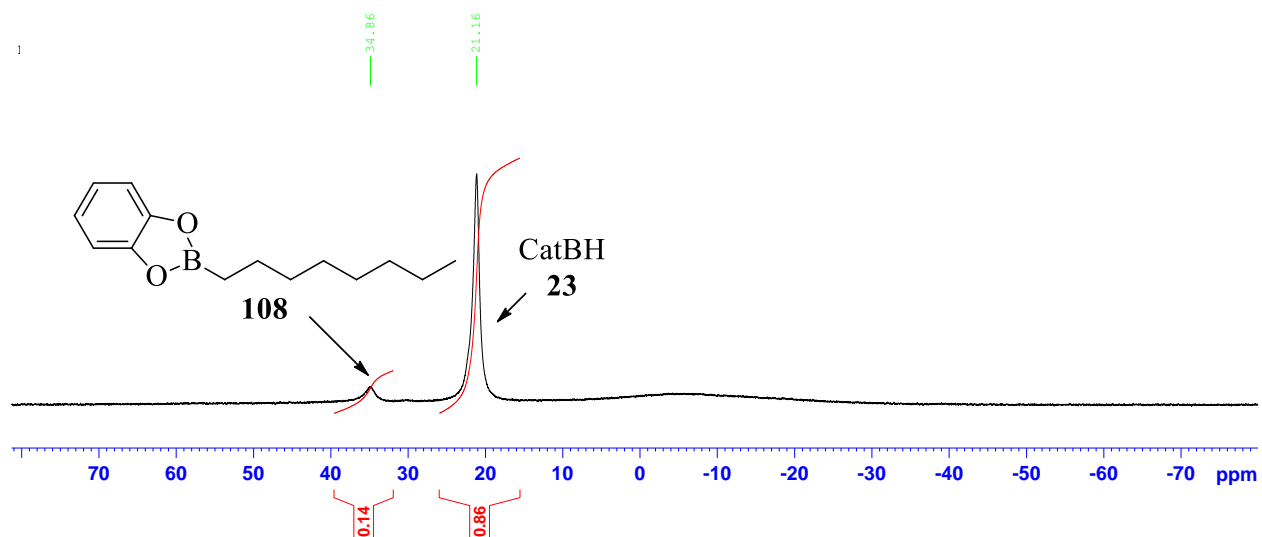
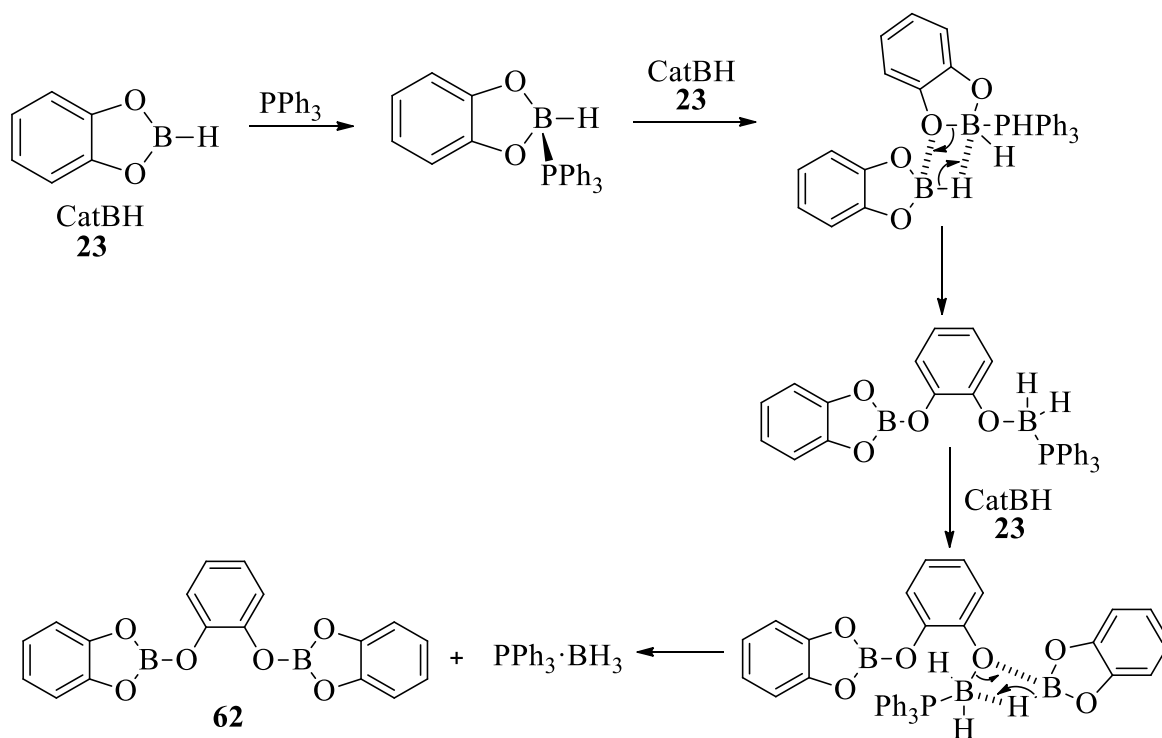


Figure 3.11: ^{11}B -NMR spectrum for the $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed hydroboration 1-octene (**38**) with catecholborane (**23**).

The presence of the Wilkinson's catalyst (**58**) can also promote the disproportionation of the hydroborating reagent which can be used to rationalize the significant amount of disproportionation product observed. In section 1.6.1, a brief discussion of the number of possible pathways toward the disproportionation of the hydroborating reagent in the presence of Wilkinson's catalyst was discussed. For example, the triphenylphosphine (PPh_3) which is liberated from the catalyst before it enters the catalytic cycle initiate the disproportionation process by attacking a hydroborating reagent (Scheme 3.11).⁶³

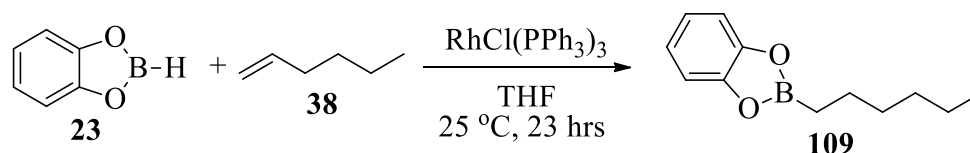


Scheme 3.11: Disproportionation mechanism of catecholborane (23) assisted by triphenylphosphine.

Attempts were made to isolate this alkylboronic acid catechol ester (**106**) afforded from the reaction mixture. However, this ester showed significant degradation when exposed to the atmosphere and when passed through silica gel. Thus, isolation of this ester using simple chromatography was not possible. Numerous literature^{21, 42, 106, 107} about the preparation of above boronic ester have been reported despite that no isolation of was conducted which might be due to high degradation of these esters upon chromatography isolation as observed above. Westcott *et al.*,⁷⁶ was able to report the only ¹H- and ¹³C-NMR spectrum available in the literature of this ester which was recorded when the reaction was conducted in a deuterated solvent and samples were run without any purification.

3.3.1.1.2. Hydroboration of 1-hexene (38) with catecholborane (23) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (58)

A similar approach as above was used for the hydroboration of 1-hexene (38) with catecholborane (23) to afford 2-hexyl-1,3,2-benzodioxaborolane (109). In this case, the ester (109) was afforded in a 25% yield after 24 hours (Scheme 3.12). However, catecholborane (23) signal was also detected indicating the reaction was incomplete. Further reaction time resulted in more disproportionation product (62).



Scheme 3.12: Hydroboration of 1-hexene (38) with catecholborane (23) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (58).

The ^{11}B -NMR spectrum indicated a singlet at 35.7 ppm, a doublet at 23.9 ppm and a singlet at 22.1 ppm which were assigned to 2-hexyl-1,3,2-benzodioxaborolane (109), catecholborane (23) and the disproportionation product Cat_3B_2 (62), respectively (Figure 3.12). Attempts to isolate 2-hexyl-1,3,2-benzodioxaborole (109) were unsuccessful due to technical challenges like those observed with 2-octyl-1,3,2-benzodioxaborole (108) discussed *vide supra*.

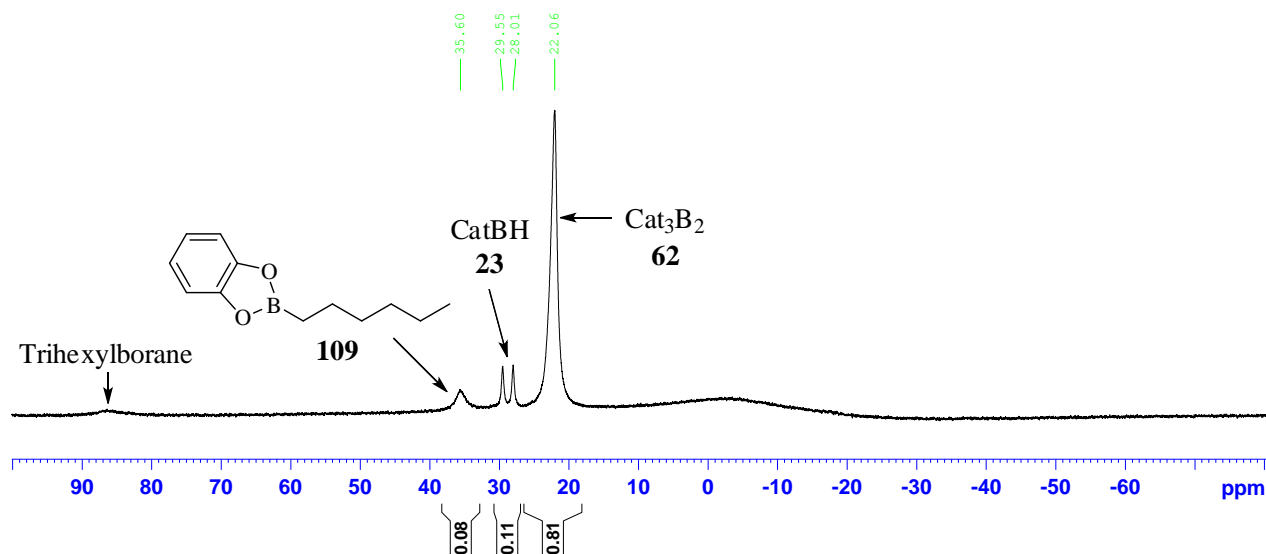


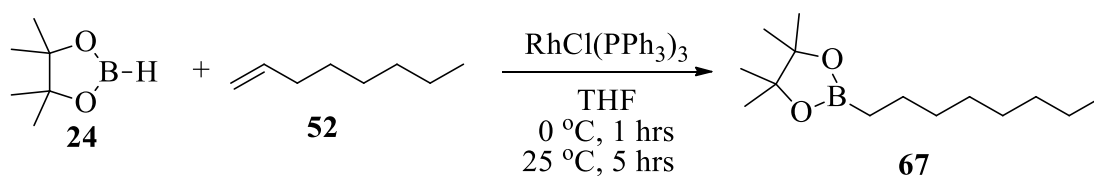
Figure 3.12: ^{11}B -NMR spectrum for the $\text{RhCl}(\text{PPh}_3)_3$ -catalyzed hydroboration of 1-octene (52) with catecholborane (23).

3.3.1.2. *RhCl(PPh₃)₃-catalyzed hydroboration studies with pinacolborane*

Pinacolborane has been used for the hydroboration of several olefins and such reaction can proceed with alkyne at 25 °C and alkenes at 50 °C.⁴⁹ However, when these reactions were conducted in the presence of a Wilkinson's catalyst, hydroboration of alkenes can proceed at room temperature.^{70, 72} In this section, further investigation of pinacolborane (**24**) hydroboration reactions catalyzed with the Wilkinson's catalyst was conducted.

3.3.1.2.1. **Hydroboration of 1-Octene (52) with pinacolborane (24) catalyzed with RhCl(PPh₃)₃ (58)**

The hydroboration of 1-octene (**52**) with pinacolborane (**24**) to afford 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**67**) was investigated using a protocol which has been previously studied within Robinson's research group.^{21, 101} In these studies, the hydroboration of 1-octene (**52**) with pinacolborane (**24**) in the presence of 2 mol% of Wilkinson's catalyst (**58**) that afforded 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**67**) in a quantitative yield after 24 hours was investigated. Pereira and Srebnik¹⁰⁸ reported a similar protocol in which this hydroboration afforded the corresponding ester product (**67**) in a 79% yield. Following a similar protocol, the hydroboration of 1-octene (**52**) with pinacolborane (**24**) in the presence of 1 mol% catalyst afforded the corresponding ester in a 70% yield after 5 hours at 25 °C (Scheme 3.13).



Scheme 3.13: Hydroboration of 1-Octene (52) with pinacolborane (24) catalyzed with RhCl(PPh₃)₃ (58).

The progress of the reaction was followed by ^{11}B -NMR spectroscopy. The initial ^{11}B -NMR spectrum of the pinacolborane (**24**) before the reaction was recorded and depicted in Figure 3.13. The spectrum indicated that 73% of the boron species was pinacolborane (**24**) which was identified by the doublet at 27.8 ppm. It also indicated the disproportionation product of pinacolborane, Pin_3B_2 (**110**) at 22.0 ppm and boric acid 19.06 ppm. The signals were assigned consistent with the literature.^{18, 102}

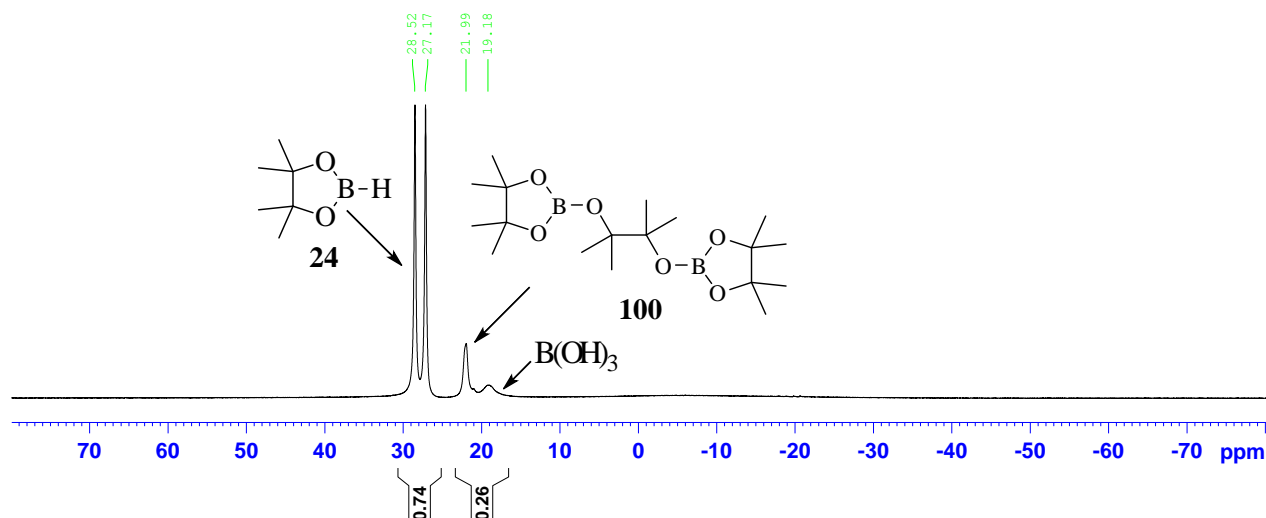


Figure 3.13: The ^{11}B -NMR spectrum of pinacolborane (**24**) before hydroboration.

After the reaction had proceeded at 25 °C for an hour another spectrum was recorded. It indicated the presence of pinacolborane (**24**) which provide evidence that the reaction was incomplete. This contradicted with the observations reported by Pereira and Srebnik¹⁰⁸ suggested that the reaction was fast and required ten minutes to complete.

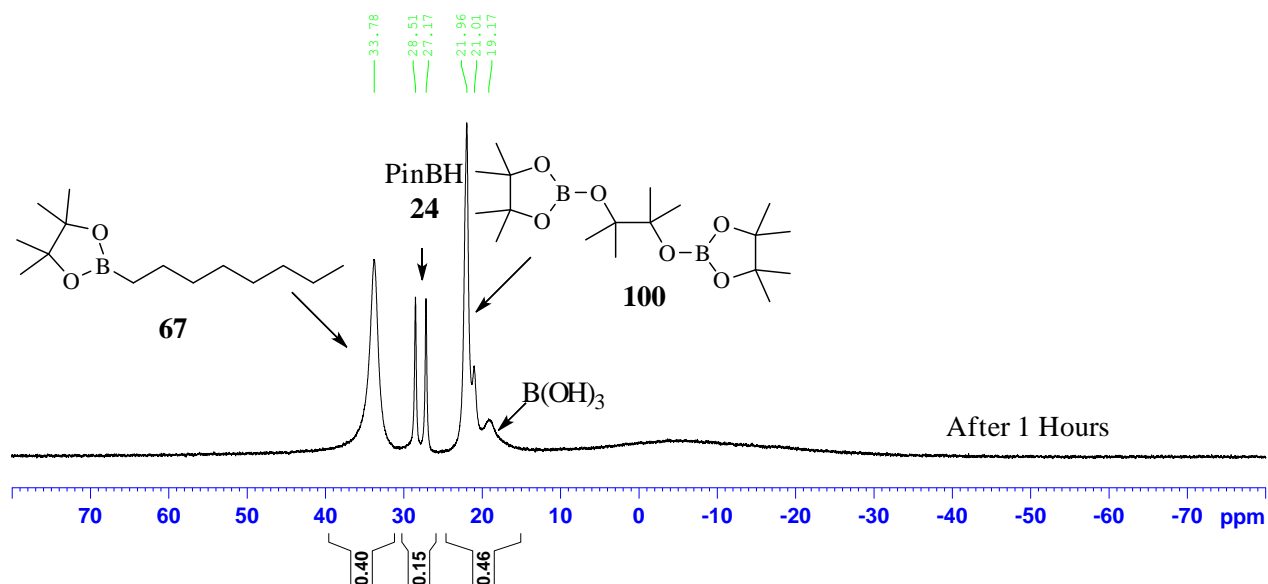


Figure 3.14: ^{11}B -NMR spectrum for the $\text{RhCl}(\text{PPh}_3)_3$ (**58**) catalyzed hydroboration of 1-octene (**52**) with pinacolborane (**24**) after one hour.

An ^{11}B -NMR spectrum was recorded after 5 hours 25°C indicated that the reaction was complete (Figure 3.15). Most interestingly were that the percentages of the Pin_3B_2 (**100**) and boronic acid ($\text{B}(\text{OH})_3$) had only increased slightly since the previous spectrum (Figure 3.14) was recorded. The results indicated that most of the disproportionation occurs at the early stage of the reaction most likely through reagent mixing processes and the catalyst contribution to the disproportionation process was less than attributed. The product was isolated and was further confirmed by ^1H -NMR. The results were in agreement with literature reports.^{101, 108}

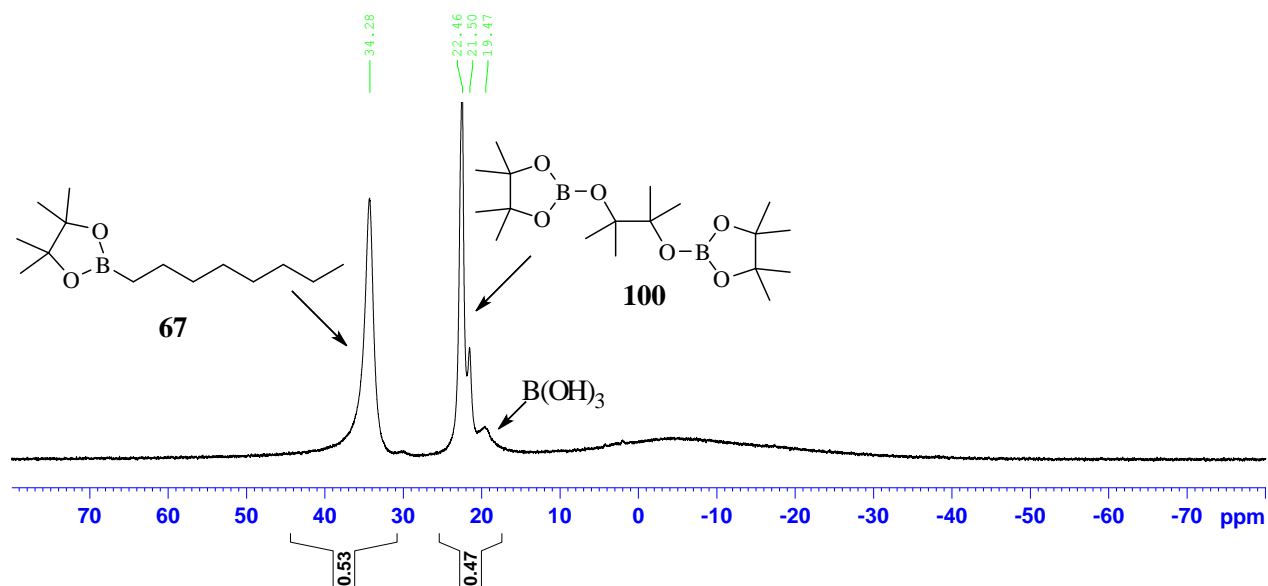


Figure 3.15: ^{11}B -NMR spectrum for the $\text{RhCl(PPh}_3)_3$ (**58**) catalyzed hydroboration of 1-octene (**52**) with pinacolborane (**24**).

3.3.1.2.2. Olefins used for the hydroboration with pinacolborane catalyzed with $\text{RhCl(PPh}_3)_3$ (**58**)

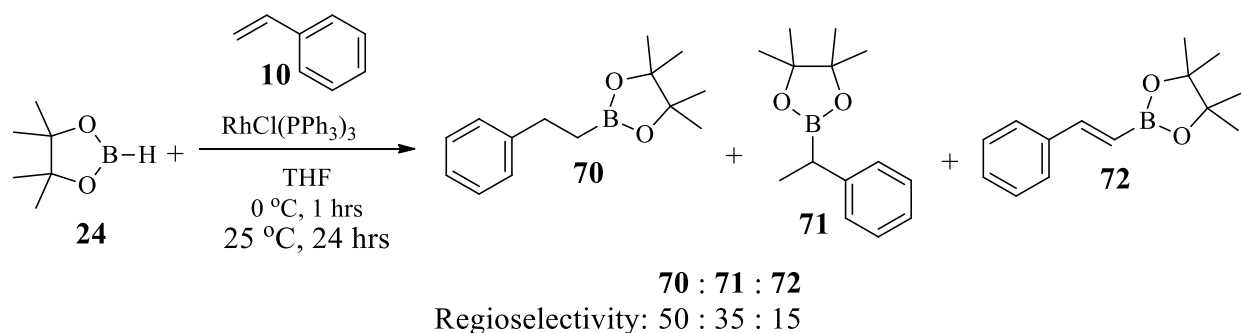
A similar protocol was employed as the hydroboration of 1-octene (**52**) above for the hydroboration 1-hexene (**38**) and styrene (**10**). A summary of the study is shown in Table 3.1.

Table 3.1: Hydroboration of olefins with pinacolborane (**24**) catalyzed with the Wilkinson's catalyst (**58**).

Olefins	Yield(%)
1-Octene (52)	50
1-Hexene (38)	33
Styrene (10)	15 ^a

^aTwo ester products were observed

Pereira and Srebnik¹⁰⁸ demonstrated that the hydroboration of styrene (**10**) with pinacolborane (**24**) catalyzed with 2 mol% $\text{RhCl}(\text{PPh}_3)_3$ (**58**) occurs quantitatively and affords three products (Scheme 3.14). The major product being the terminal hydroboration of the olefin to afford the β -product **70** then internal hydroboration to afford α -product **71** and the minor product hydroboration-elimination type reaction, which affords β -styrenylboronate **72**. An attempt was made to conduct this reaction using the similar protocol. However, the reaction was sluggish with an unsatisfactory yield of 15%.



*Scheme 3.14: Hydroboration of styrene (**10**) with pinacolborane (**24**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**).*

The ^{11}B -NMR spectrum recorded indicated that there were at least two hydroboration products which suggested the formation of ester **70** and **71** that were also reported by Pereira and Srebnik (Figure 3.16).¹⁰⁸ However, isolation of these esters was unsuccessful and no further evidence was obtained.

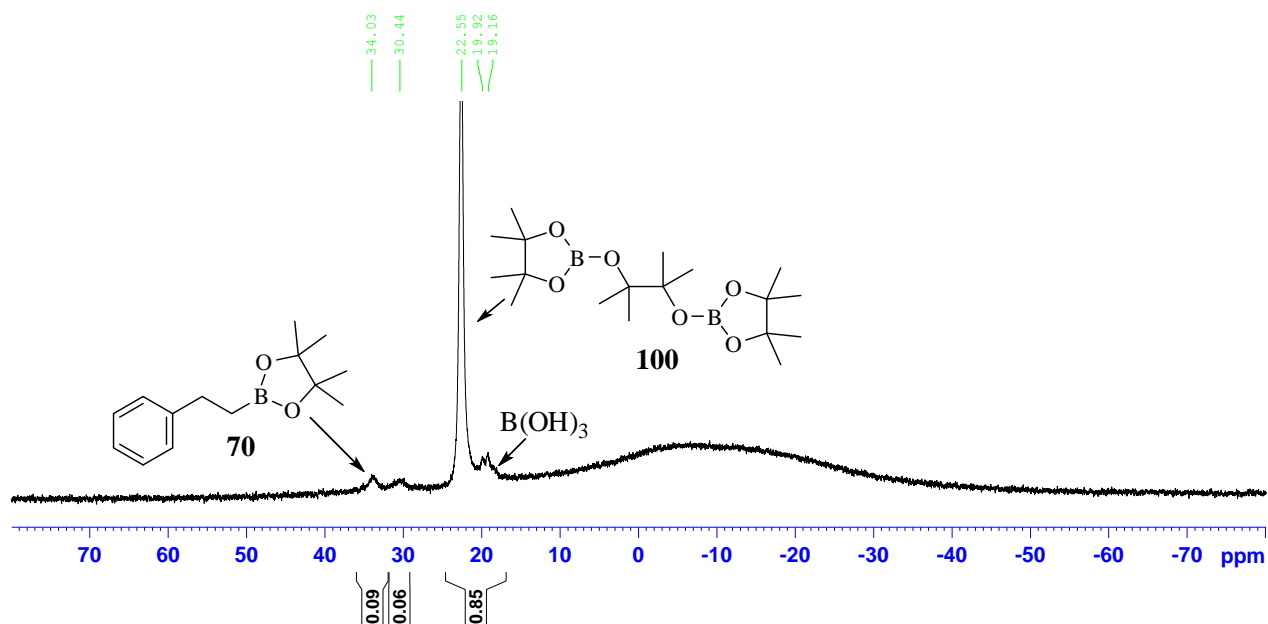


Figure 3.16 ^{11}B -NMR spectrum for the $\text{RhCl}(\text{PPh}_3)_3$ (**58**) catalyzed hydroboration of styrene (**52**) with pinacolborane (**24**).

Disproportionation such as the case of catecholborane (**23**) was the major disadvantage when conducting the reactions reported in Table 3.1. In summary:

- ❖ Reduction in reaction yield was accompanied by severe disproportionation when the olefins were changed from:



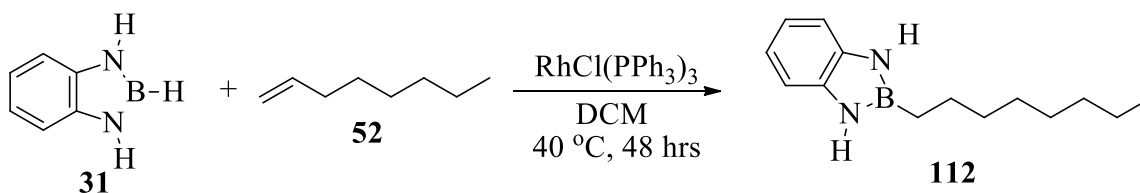
The rate of hydroboration of these olefins with *bis*-(3-methyl-2-butyl)borane (**7**) was reported to follow a similar pattern whereby the relative rates were 108, 100 and 19, respectively.³⁸ A similar relative rate would be expected for the Wilkson's catalyst (**58**) catalyzed hydroboration, Hence the less reactive olefins would result in more disproportionation.

- ❖ Poor regioselectivity was observed for the hydroboration of styrene (**10**). This was in agreement with literature.⁷⁰

3.3.1.3. *RhCl(PPh₃)₃* (58) Catalyzed Hydroboration Studies with 2,3-dihydro-1,3,2-benzodiazaborole (31)

3.3.1.3.1. Hydroboration of 1-octene (52) with 1,3,2-benzodiazaborole (31) catalyzed with *RhCl(PPh₃)₃* (58)

Hadebe *et al.*,^{21, 58} reported that the hydroboration of 1-octene **52** with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with 2 mol% *RhCl(PPh₃)₃* (**58**) in DCM afford 2-octyl-1,3,2-benzoborolane (**112**) in yield ranging from 70 – 92% at 25 °C (Scheme 3.15). In these studies, a higher temperature range of 40 – 60 °C was used to increase the rate of reaction for olefins such as styrene. Following this hydroboration protocol using 1 mol% catalyst at 40 °C, 2-octyl-1,3,2-benzoborolane was afforded in a 55% yield after 48 hours.



Scheme 3.15: Hydroboration of 1-octene (**52**) with 1,3,2-benzodiazaborole (**31**) catalyzed with *RhCl(PPh₃)₃* (**58**).

The initial ^{11}B -NMR spectrum of 2,3-dihydro-1,3,2-benzodiazaborole (**31**) before the hydroboration reaction which has typical for most of the studies conducted with this reagent (Figure 3.17).

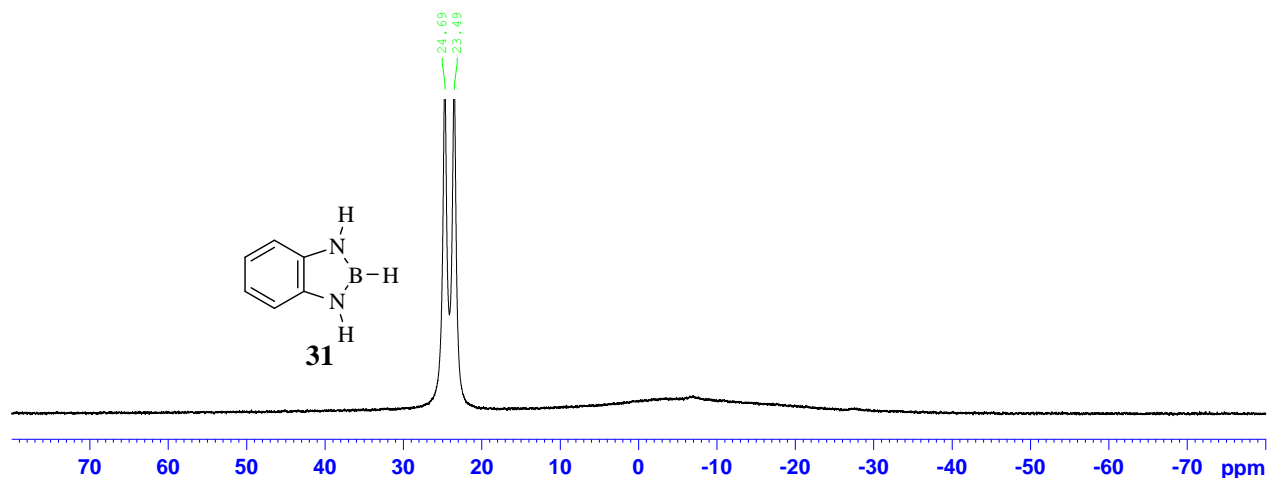


Figure 3.17: A typical ^{11}B -NMR spectrum of 2,3-dihydro-1,3,2-benzodiazaborole (**31**) before hydroboration.

The ^{11}B -NMR spectrum recorded after 48 hours indicated the formation of the product with 55% and unreacted hydroborating reagent. Further reaction time, the addition of more olefin or addition of more catalyst was done to increase reaction yield. Unfortunately, in all these attempts, the ^{11}B -NMR spectrum record showed no improvement.

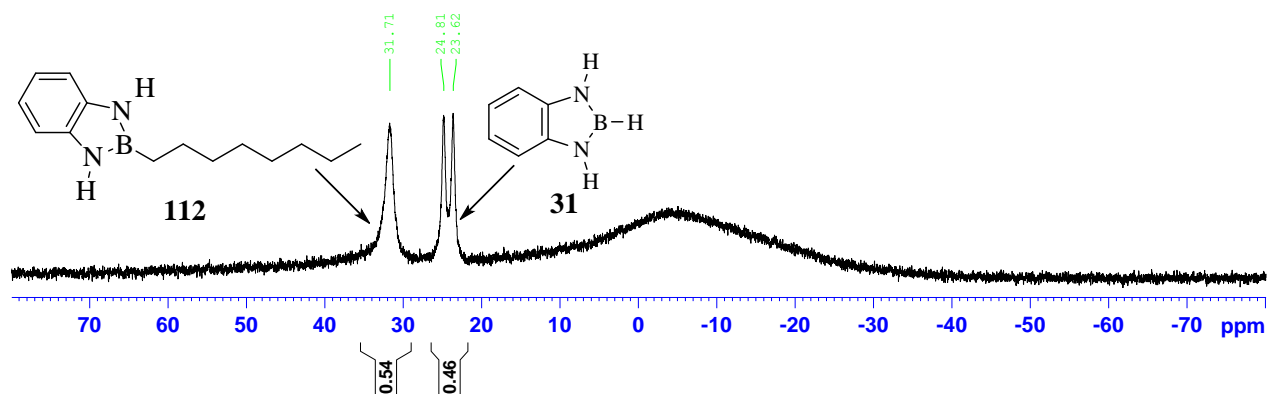


Figure 3.18: ^{11}B -NMR spectrum record for the hydroboration of 1-octene (**52**) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**) after 48 hours.

3.3.1.3.2. Olefins used for the hydroboration with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**)

A similar protocol was employed as the hydroboration of 1-octene (**52**) above for the hydroboration styrene (**10**) and cyclohexene (**17**).⁵⁸ A summary of the study is shown in Table 3.2.

*Table 3.2: Hydroboration of olefins with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with the Wilkinson's catalyst (**58**)*

Olefins	Yield(%)
1-Octene (52)	55
1-Hexene (38)	25
Styrene (10)	19
Cyclohexene (17)	18

Analysis of samples withdrawn from the reaction mixtures after 48 hours using ^{11}B -NMR spectroscopy indicated singlet at 31.4 ppm which was assigned to the of boronic ester product and a doublet at 23.9 ppm of the unreacted hydroborating reagent **31**. For example, Figure 3.19 was obtained for the hydroboration of styrene with 2,3-dihydro-1,3,2-benzodiazaborole catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**).

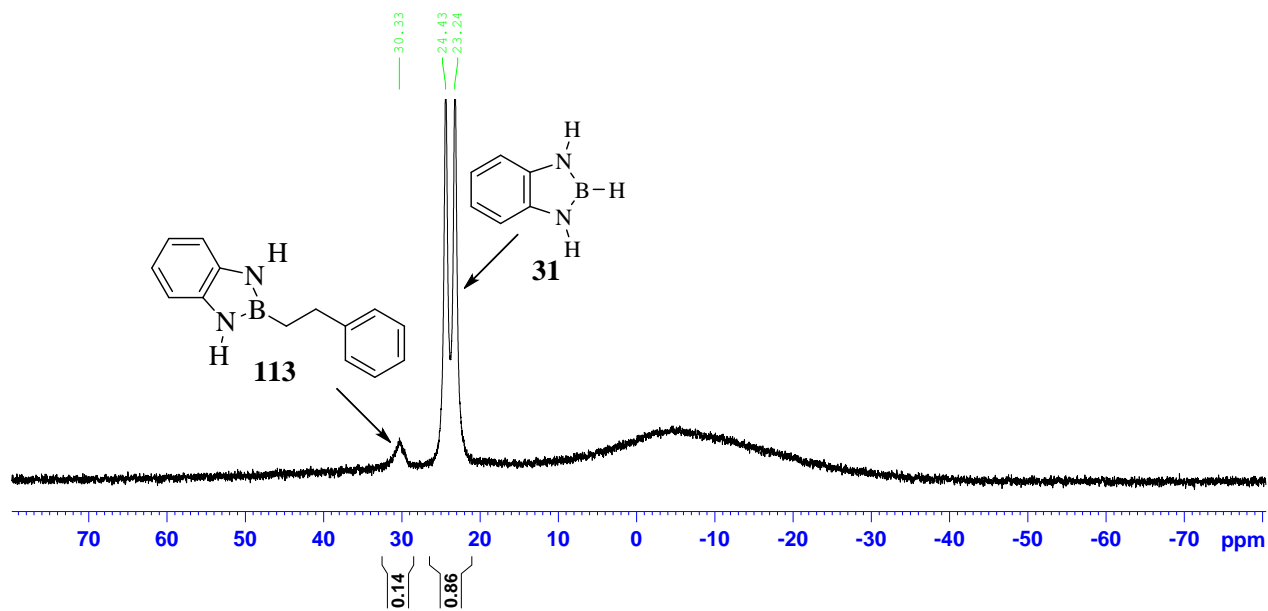


Figure 3.19: ^{11}B -NMR spectrum record for the hydroboration of styrene (**10**) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**) after 48 hours.

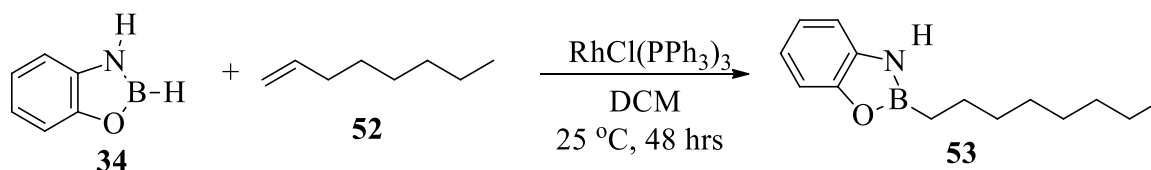
3.3.1.3.3. Summary of hydroboration studies with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with Wilkson's catalyst (**58**)

- ❖ Reduction in reaction yield was observed when the olefins were changed from:
1-Octene (**52**) > 1-Hexene (**38**) > Styrene (**10**) \approx Cyclohexene (**17**)
- ❖ Most interestingly 2,3-dihydro-1,3,2-benzodiazaborole (**31**) demonstrated high stability towards disproportionation. Hadebe and Robison²¹ reported the similar observation of stability for hydroboration with this reagent.

3.3.1.4. *RhCl(PPh₃)₃ Catalyzed Hydroboration Studies with 2,3-dihydro-1,3,2-benzoxazaborole (34)*

3.3.1.4.1. **Hydroboration of 1-octene (52) with 2,3-dihydro-1,3,2-benzoxazaborole (34) catalyzed with RhCl(PPh₃)₃ (58)**

Utilization of 2,3-dihydro-1,3,2-benzoxazaborole (**34**) for hydroboration is not common unlike catecholborane (**23**) and pinacolborane (**24**) hence there is limited literature with this reagent. Slabber,⁵⁶ reported an interesting hydroboration study with this reagent catalyzed with two rhodium catalysts. This author reported that the hydroboration of 1-octene (**52**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with 10 mol% RhCl(PPh₃)₃ (**58**) conducted under microwave radiation condition in DCM and afforded 2-octyl-1,3,2-benzoxazaborolane **53** in 18% yield. A similar protocol was employed in this study, whereby the same reaction was conducted using 1 mol% of the catalyst at 25 °C in DCM and 2-octyl-1,3,2-benzoxazaborolane (**53**) was afforded in an 86% yield (Scheme 3.16). However, no microwave radiation was used.



Scheme 3.16: Hydroboration of 1-octene (52) with 2,3-dihydro-1,3,2-benzoxazaborole (34) catalyzed with RhCl(PPh₃)₃ (58).

Figure 3.20 show a typical ¹¹B-NMR spectrum of 2,3-dihydro-1,3,2-benzoxazaborole (**34**) before hydroboration. The single at about 6 ppm was never identified however, it was suspected to be another product of the hydroborating reagent (**34**) disproportionation.

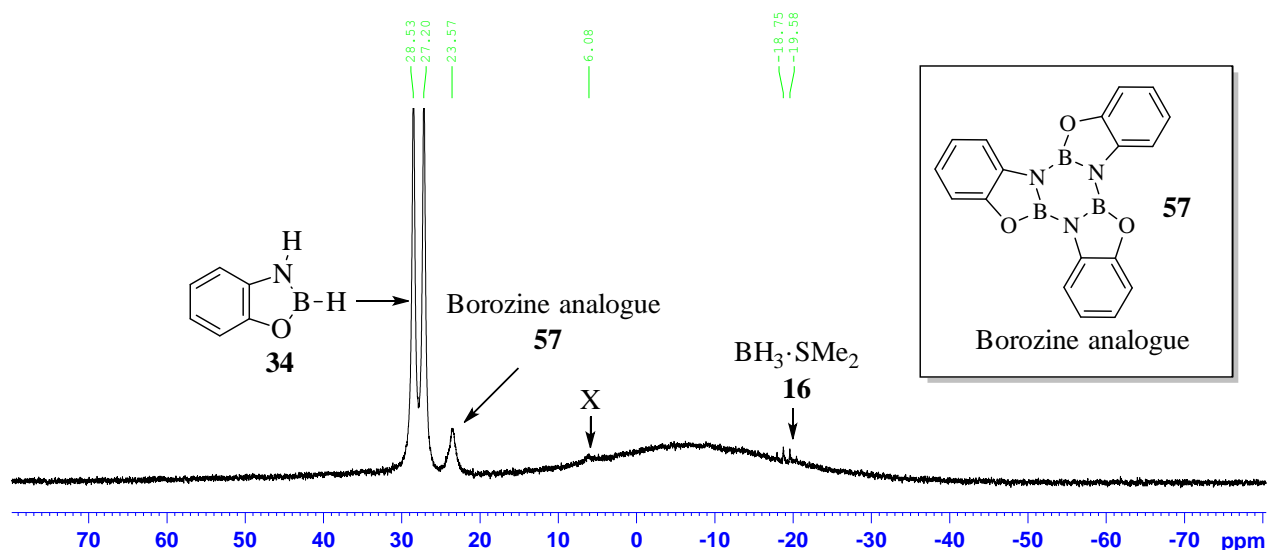


Figure 3.20: Typical ^{11}B -NMR spectrum of 2,3-dihydro-1,3,2-benzoxazaborole (**34**) before hydroboration.

A sample of the reaction mixture after 48 hours indicated the formation of a new major broad singlet at 34.7 ppm which was assigned to 2-octyl-1,3,2-benzoxazaborolane (**53**) using ^{11}B -NMR spectrum (Figure 3.21). However, the peak had a shoulder and it was assigned to a possible hydroboration product whereby the boron atom was being attached at the β -carbon of the olefin to afford the internal hydroboration product. The terminal product 2-octyl-1,3,2-benzoxazaborolane (**53**) was further isolated and confirmed using ^1H and ^{13}C -NMR spectroscopy.

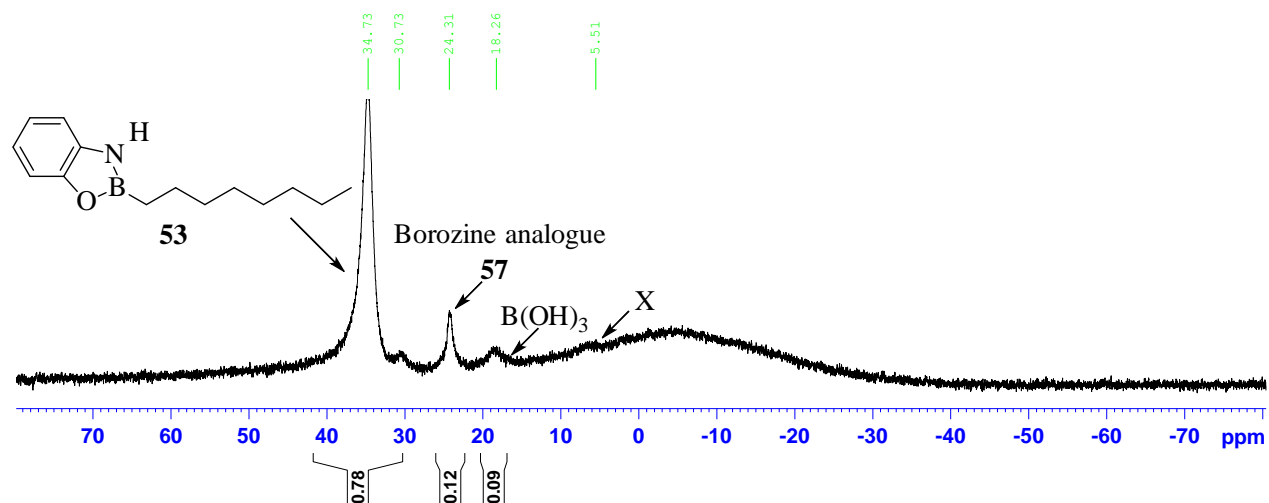


Figure 3.21: ^{11}B -NMR spectrum for the hydroboration of 1-octene (**52**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**).

3.3.1.4.2. Olefins used for the hydroboration with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**)

The protocol for the hydroboration of 1-octene (**52**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**) employed above was further utilized for the hydroboration 1-hexene (**38**), styrene (**10**), cyclohexene (**17**) and cyclooctene (**117**). A summary of the study is shown in **Error! Reference source not found.**

*Table 3.3: Hydroboration of olefins with 2,3-dihydro-1,3,2-benzoxazaborole (**3**) catalyzed with the Wilkinson's catalyst (**58**).*

Olefins	Yield(%)
1-Octene (52)	86
1-hexene (38)	28
Styrene (10)	18
α -methylstyrene (74)	28
Cyclooctene (117)	14

All these hydroboration reactions were accompanied by the disproportionation of 2,3-dihydro-1,3,2-benzoxazaborole (**34**) to afford the undesired borazine analogue (**57**) was discussed in depth in section 1.5.3.4 of the Introduction. For example, Figure 3.22 depicts the spectrum obtained for the hydroboration of 1-hexene (**38**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**) with major disproportion

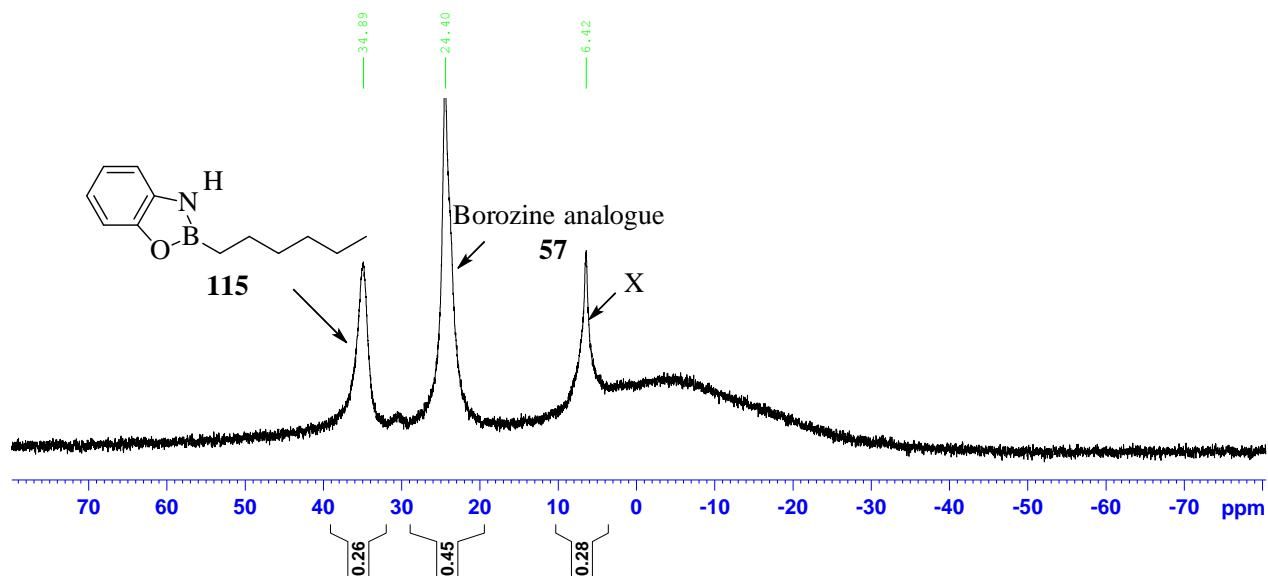


Figure 3.22: ^{11}B -NMR spectrum for the hydroboration of 1-hexene (**38**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with $\text{RhCl}(\text{PPh}_3)_3$ (**58**).

3.3.1.4.3. Observations for the hydroboration of olefins with 2,3-dihydro-1,3,2-benzoxazaborole (34) catalyzed with the Wilkson's catalyst (58).

- ❖ The observation that the reaction rate was reduced when the olefin was changed from linear olefins to branched olefins can be explained using the known reactivity trend.³⁸
- ❖ When product formation was not favored such as the case with 1-octene (117) hydroboration more disproportionation product was obtained.
- ❖ The reaction yields were similar reaction yield obtained by Slabber⁵⁶ with yield difference of no more that 10%. These differences are most likely due to that reaction in this study were conducted using conventional heating method while Slabber⁵⁶ employed microwave conditions.

3.3.1.5. Summary for the hydroboration of olefins using Wilkinson' catalysts

- ❖ Reactions with 2,3-dihydro-1,3,2-benzodiazaborole (31) require high temperature and longer run time and afford poor yields than that of catecholborane (23) and pinacolborane (24).
- ❖ High disproportionation was observed with catecholborane (23), pinacolborane (24) and 2,3-dihydro-1,3,2-benzoxazaborole (34).

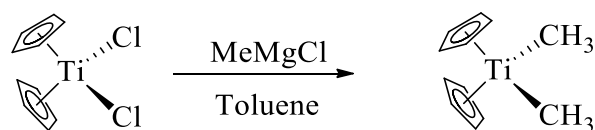
It must be noted that all the results for the hydroboration studies with each of the transition metal catalysts are tabulated and further discussed at the end of this section.

3.3.2. Dimethyltitanocene catalyzed hydroboration

Several publications have reported poor and uncertainty catalytic potential of dimethyltitanocene toward hydroboration.^{42, 83-85, 107} In some cases, it was demonstrated that the observed hydroboration was as a result of the reaction with diborane (**1**) after catalyst facilitate the degradation of hydroborating reagent oppose to hydroboration. However, Hartwig *et al.*,^{87, 88} reported successful hydroboration of olefins with this catalyst and a detailed discussion has been reported *vide supra*. In this section, further investigation of dimethyltitanocene as a hydroboration catalyst was undertaken to develop early transition metal catalysts towards hydroboration.

3.3.2.1. Synthesis of dimethyltitanocene

In 1995, Payack *et al.*,^{109, 110} reported an improved method to prepare dimethyltitanocene. In these studies, titanocene dichloride was reacted with a two-mole equivalence of methylmagnesium chloride in anhydrous toluene to afford dimethyltitanocene with an 85% yield (Scheme 3.17). Following this method dimethyltitanocene was prepared with a high yield ranging from 70 –88%.



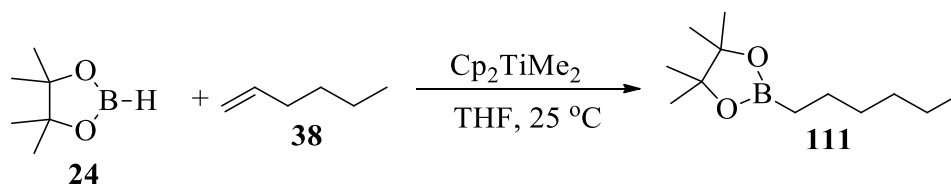
Scheme 3.17: Synthesis of dimethyltitanocene.

Payack *et al.*,¹¹⁰ reported that dimethyltitanocene was less stable in its pure solid state form and further reported that the complex was much more stable when it was kept in toluene:THF mixture. Hence, the ¹H-NMR spectrum of this complex was recorded in a toluene:THF mixture. The NMR results obtained were consistent with the literature reports by Payack *et al.*¹¹⁰

3.3.2.2. *Dimethyltitanocene-catalyzed hydroboration with pinacolborane (24)*

3.3.2.2.1. **Dimethyltitanocene-catalyzed hydroboration of 1-hexene (38) with pinacolborane (24)**

The hydroboration reaction was conducted following the report by He and Hartwig.⁸⁷ These authors reported the hydroboration of 1-hexene (**38**) with catecholborane (**23**) catalyzed with 4 mol% dimethyltitanocene in benzene. A similar protocol to that used by these authors was employed to study the hydroboration of 1-hexene (**38**) with pinacolborane (**24**) with the same catalyst in THF to afford 2-hexyl-4,4,5,5-tetramethyl-1,3,2-borolane (**111**) a 14% yield after 24 hours (Figure 3.22). However, excessive disproportionation of the hydroborating reagent was observed.



*Scheme 3.18: Dimethyltitanocene-catalyzed hydroboration of 1-hexene (**38**) with pinacolborane (**24**).*

The Figure 3.23 shows a typical pinacolborane spectrum recorded before the hydroboration reaction. The spectrum shows that 74% of the boron species being the active hydroborating reagent and 26% being the sum of disproportionation product Pin_3B_2 (**110**) and boronic ester.

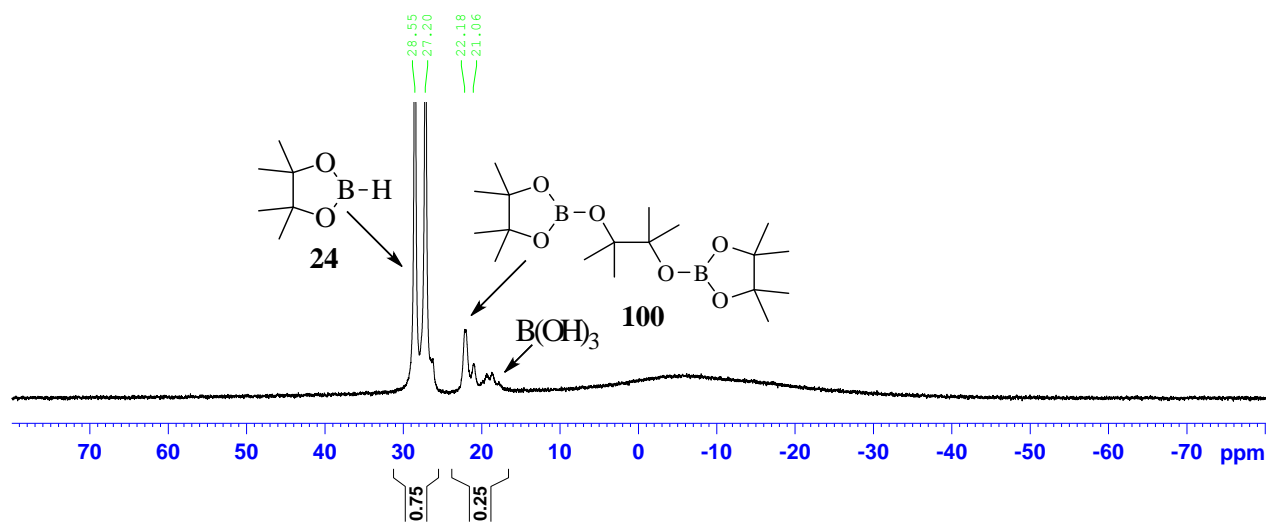


Figure 3.23: ^{11}B -NMR spectrum of pinacolborane (**24**) before Cp_2TiMe_2 catalyzed hydroboration.

Figure 3.24 shows the spectrum recorded after the hydroboration reaction. From these, the hydroborating reagent had been all consumed and only 14% converted to the desired ester **111** while a significant amount being converted to the disproportionation product Pin_3B_2 (**100**).

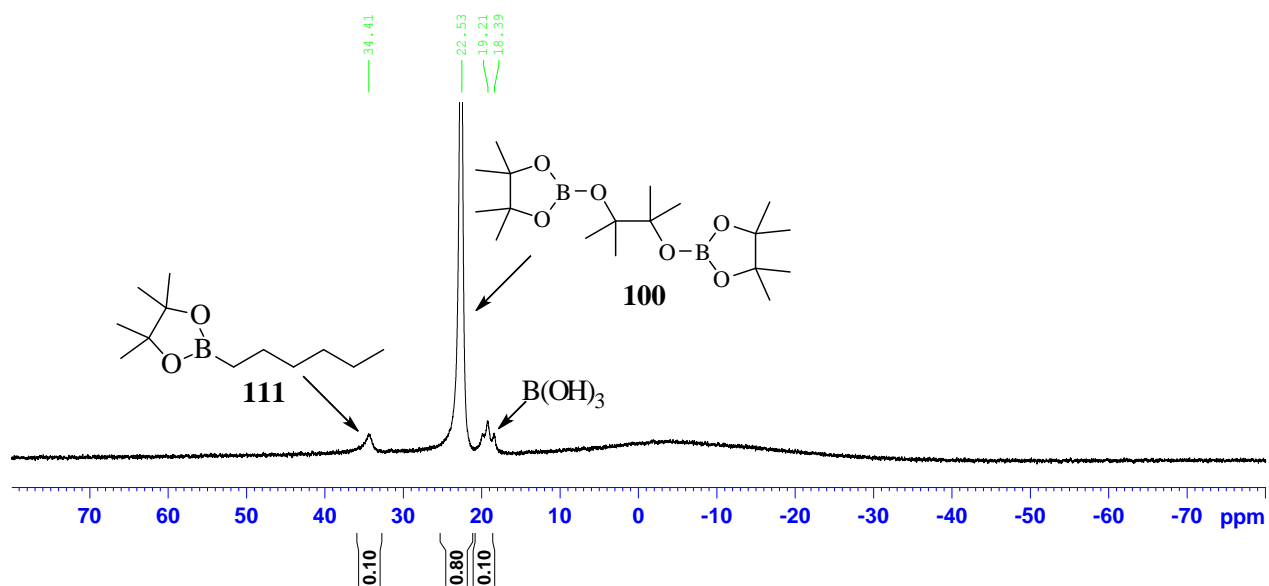
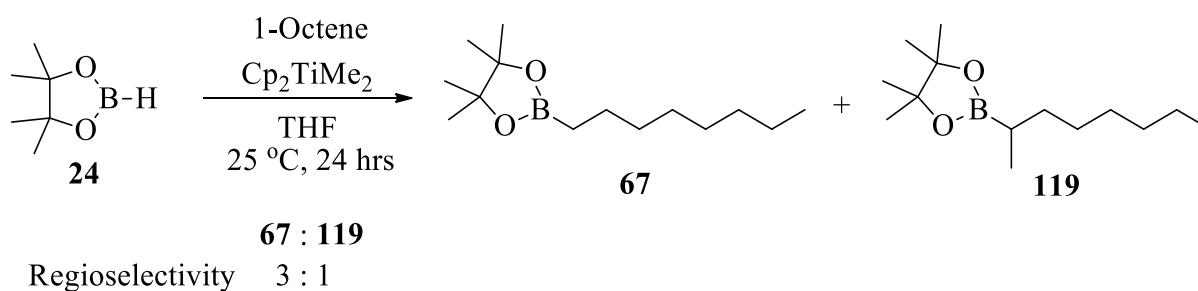


Figure 3.24: ^{11}B -NMR spectrum for the hydroboration of 1-hexene (**38**) with pinacolborane (**24**) catalyzed with Cp_2TiMe_2 .

3.3.2.2.2. Hydroboration of 1-octene with pinacolborane catalyzed with Cp_2TiMe_2

The protocol used above for the hydroboration 1-hexene (**38**) was further employed for the hydroboration of 1-octene (**52**) with pinacolborane (**24**). The reaction was catalyzed with 5 mol% Cp_2TiMe_2 in THF and afforded two boronic esters in a 27% yield. The regioselectivity of the esters was 3:1 (Figure 3.25) whereby the major product was assigned to the linear hydroboration product 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**67**) (thermodynamically favoured product) and the minor product being the branch hydroboration product 4,4,5,5-tetramethyl-2-(oct-2-yl)-1,3,2-dioxaborolane (**119**) (Scheme 3.19). Significant disproportionation of the hydroborating reagent was observed during the reaction which was like the results which were observed with 1-hexene (**38**) hydroboration with pinacolborane (**24**) using this catalyst *vide supra*.



Scheme 3.19: Hydroboration of 1-octene with pinacolborane catalyzed with Cp_2TiMe_2 .

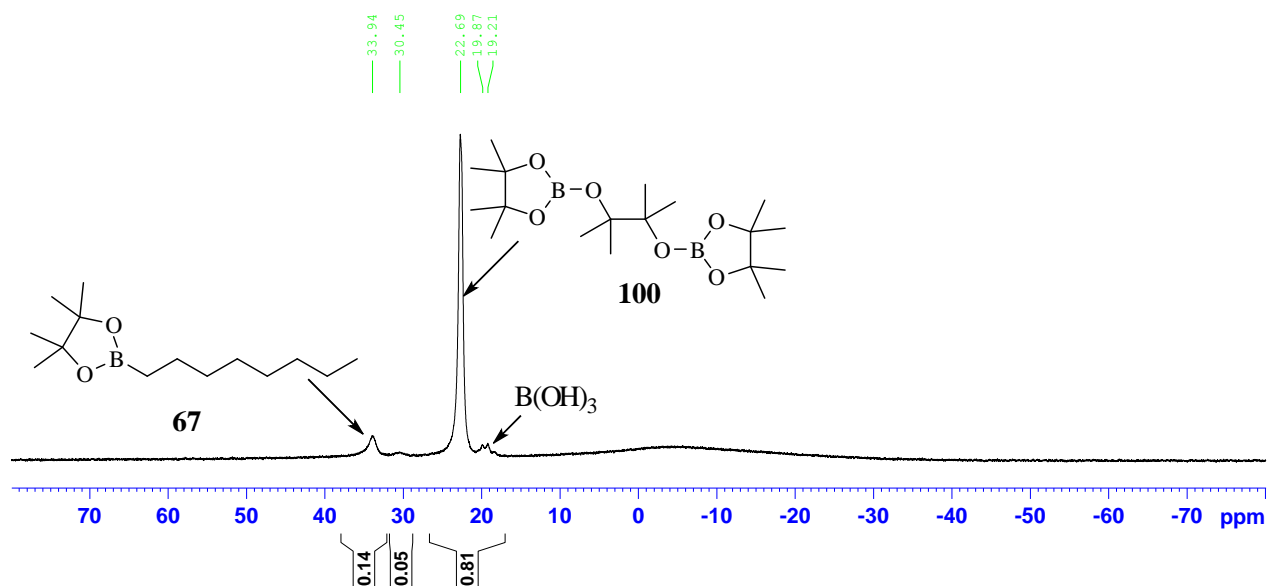
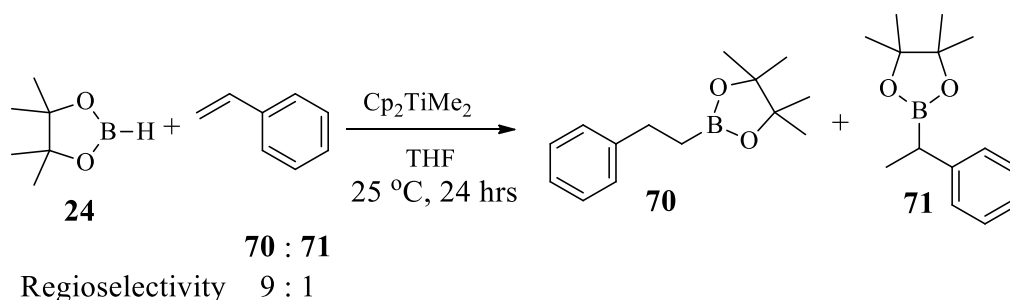


Figure 3.25: ^{11}B -NMR spectrum for the hydroboration of 1-octene (**52**) with pinacolborane (**24**) catalyzed with Cp_2TiMe_2 .

3.3.2.2.3. Dimethyltitanocene-catalyzed hydroboration of styrene (**10**) with pinacolborane (**24**)

The protocol used above was further investigated for the hydroboration of styrene with pinacolborane (**24**). The reaction was catalyzed with 5 mol% Cp_2TiMe_2 in THF and afforded two boronic esters in a 28% yield (Scheme 3.20).



Scheme 3.20: Dimethyltitanocene-catalyzed hydroboration of styrene (**10**) with pinacolborane (**24**).

Attempts were made to isolate the boronic ester using chromatography, unfortunately, the two boronic esters were not isolated (Figure 3.26). The peak at 33.7 ppm was assigned to the linear

hydroboration product **70** with 89:11 selectivity over the branched hydroboration product **71** signal peak at 30.4 ppm was by the boron atom results in the internal position of the olefin.

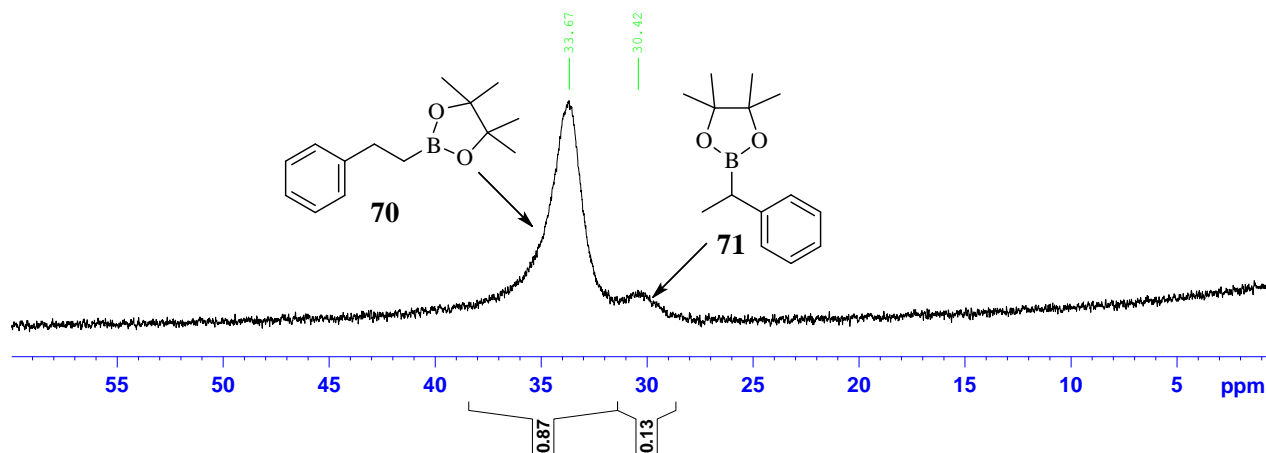


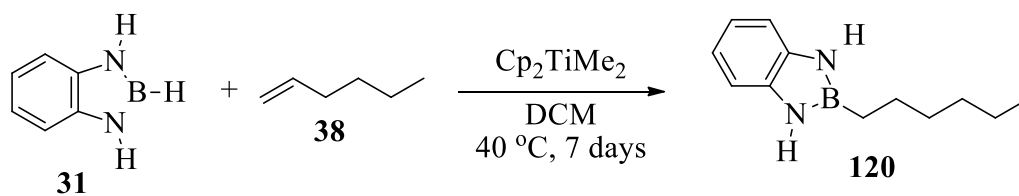
Figure 3.26: ^{11}B -NMR spectrum showing the regioselectivity for the hydroboration of styrene (**10**) with pinacolborane (**24**) catalyzed with Cp_2TiMe_2 .

3.3.2.2.4. Dimethyltitanocene-catalyzed Hydroboration Studies using 2,3-dihydro-1,3,2-benzodiazaborole (**31**)

Pinacolborane hydroboration catalyzed with dimethyltitanocene demonstrated high disproportionation of the hydroborating reagent discussed *vide supra*. Further investigated of this reaction with a more stable hydroborating reagent 2,3-dihydro-1,3,2-benzodiazaborole (**31**) toward disproportionation was much more appealing.

3.3.2.2.5. Hydroboration of 1-hexene (**38**) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with dimethyltitanocene

Hydroboration of 1-hexene (**38**) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed using 5 mol% dimethyltitanocene using a protocol similar to that reported by He and Hartwig⁸⁷ (Scheme 3.21). This reaction afforded the 2-hexyl-1,3,2-benzodiazaborolane (**120**) in a 51% yield after seven days. However, precipitation occurred as the reaction proceeded and the method used to determine the yield in the study is only accurate when all boron species remain dissolved in solution. The formation of a precipitate may have resulted in the removal of boron species which was not accounted for in the recorded spectrum and that would result in the yield not a direct representation of the reaction composition.



Scheme 3.21: Hydroboration of 1-hexene (38) with 2,3-dihydro-1,3,2-benzodiazaborole (31) catalyzed with dimethyltitanocene.

An attempt was made to isolate 2-hexyl-1,3,2-benzodiazaborolane (**120**) and an ¹¹B-NMR spectrum of the ester is depicted by Figure 3.27. However, the isolation was not successful to isolate this ester as ¹H-NMR spectroscopy showed several impurities which were not identified.

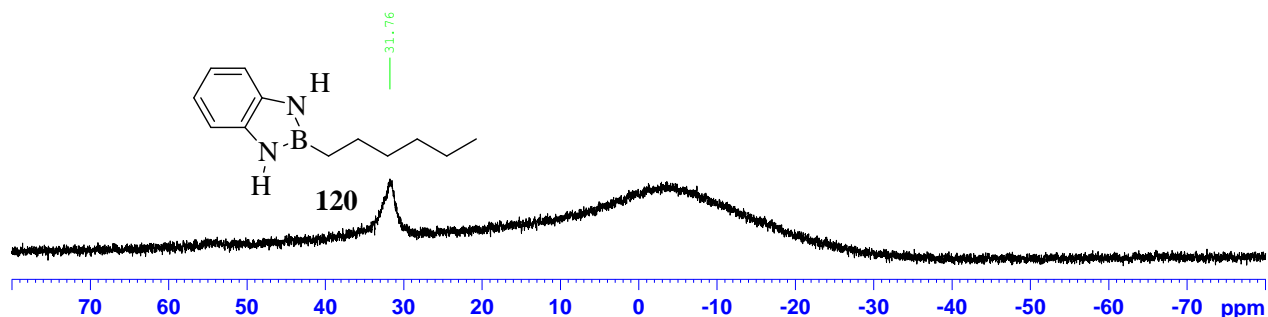
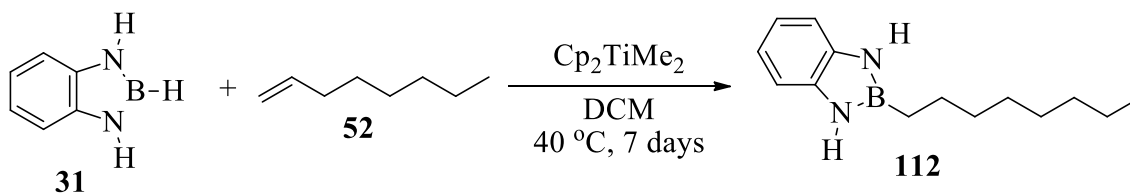


Figure 3.27: ^{11}B -NMR spectrum isolation attempt after isolation attempts for the hydroboration of 1-hexene (**38**) with 2.3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with Cp_2TiMe_2 .

3.3.2.2.6. Hydroboration of 1-octene (**52**) with 2.3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with dimethyltitanocene

A protocol like the above was employed for the hydroboration of 1-octene **52** with the 2.3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed using 5 mol% dimethyltitanocene and afford 2-octyl-1,3,2-benzodiazaborolane (**112**) with a 16% yield after 7 days (Scheme 1.27). Two new peaks were observed after the period, one at 30.7 and the other 28.9 ppm which were assigned to the hydroboration product whereby the boron atom being attached at the terminal position and at the internal position of the double bond, respectively. Similar results were observed for the hydroboration of styrene which results in a 5% yield. The regioselectivity of these reactions was not determined due to their low yield outcome.



Scheme 3.22: Hydroboration of 1-octene (**52**) with 2.3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with dimethyltitanocene.

Figure 3.28 below depicts the ^{11}B -NMR spectroscopic results obtained for the hydroboration of 1-octene (**52**) with 2.3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with dimethyltitanocene

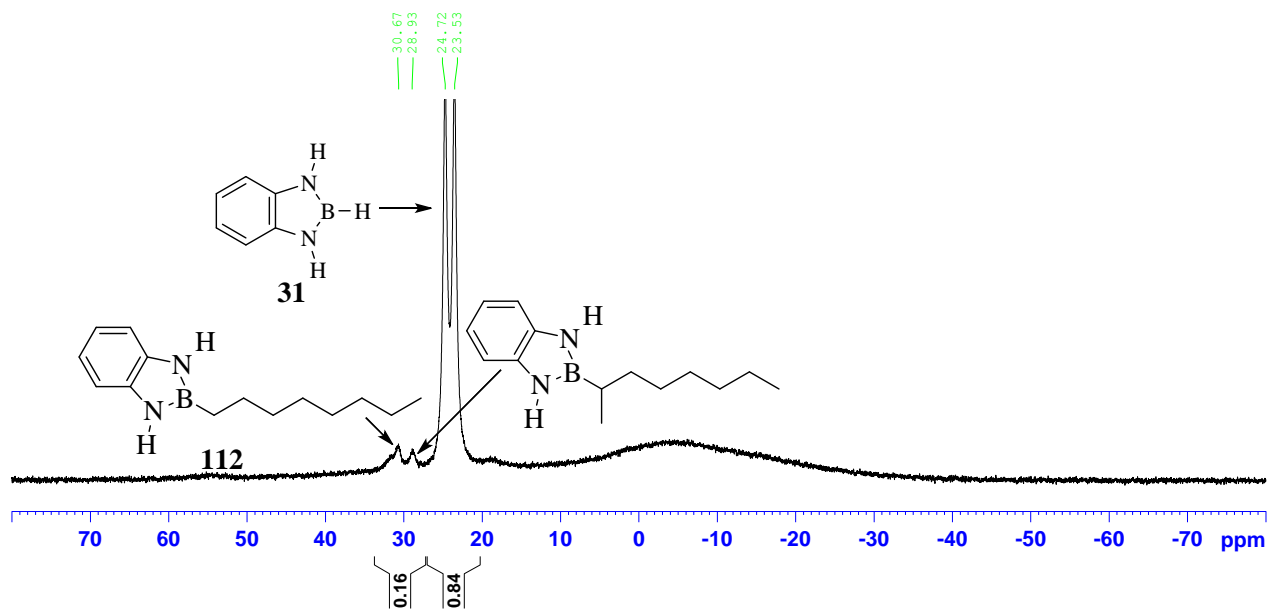


Figure 3.28: ^{11}B -NMR spectrum for the hydroboration of 1-octene (**52**) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with dimethyltitanocene.

3.3.2.3. Dimethyltitanocene catalyzed hydroboration Studies 2,3-dihydro-1,3,2-benzoxazaborole (**34**)

3.3.2.3.1. Hydroboration of 1-octene with benzo-1,3,2-oxazaborole catalyzed with dimethyltitanocene

Hydroboration of 1-octene (**52**) with 2,3-dihydro-benzo-1,3,2-oxazaborole (**34**) catalyzed with dimethyltitanocene was investigated following the protocol similar to that employed above. However, no product was observed while the disproportionation of the hydroborating reagent was enhanced. Figure 3.29 indicate that no hydroboration ester formed after 24 and 48 hours while a significant amount of hydroborating reagent was converted to borazine analogue (**57**) disproportionation product. Similar results were observed with 1-hexene (**38**) and styrene (**10**).

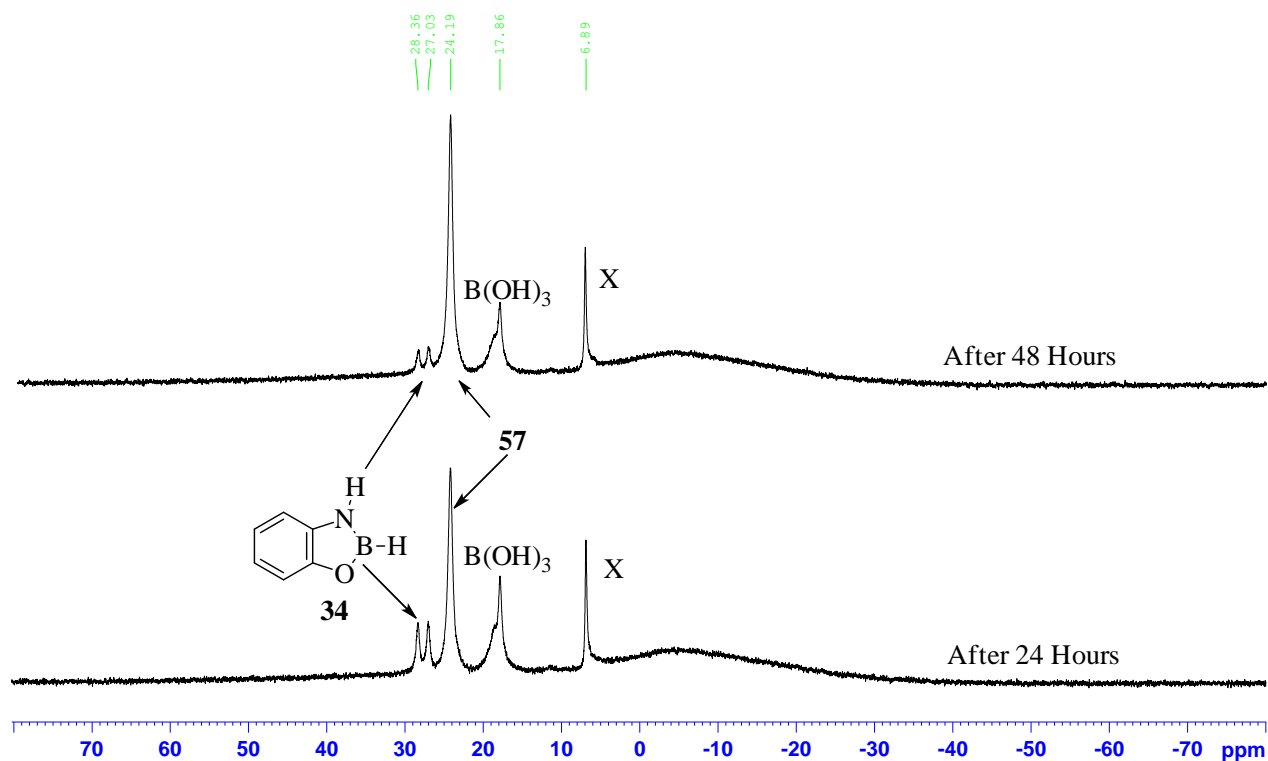


Figure 3.29: ^{11}B -NMR spectrum for the hydroboration of 1-octene (**52**) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with Cp_2TiMe_2

3.3.3. Summary and conclusions

- ❖ The catalyst demonstrated poor catalytic activity for hydroboration as reaction required long reaction run-times and afforded poor yields. Furthermore, the catalyst favoured promoting the degradation of the hydroboration reagents to afford their corresponding disproportionation products over the hydroboration process.
- ❖ Attempts to hydroborate olefins using 2,3-dihydro-benzo-1,3,2-oxazaborole (**34**) showed significant disproportionation.

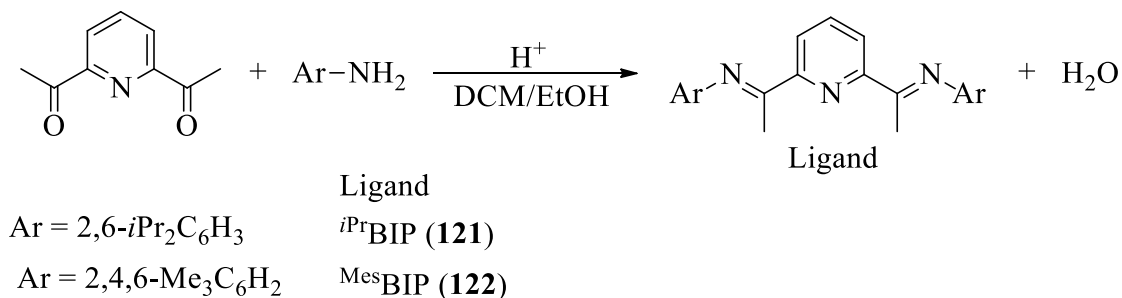
3.3.4. Iron-catalyzed hydroboration

Recently iron-catalyzed hydro-functionalization had gained much interest and a review of this work has been published recently by Greenhalgh *et al.*¹¹¹ In this report, the iron-catalyzed hydroboration studies were conducted using either catecholborane (**23**) or pinacolborane (**24**). In this study, further investigation of these iron catalysts towards hydroboration of more olefins has been conducted. In chapter 1 we have discussed highly active iron(0) dinitrogen complexes which were used for the hydroboration of a number of olefins to afford quantitative yields.⁹⁵ However, iron(0) species are known to be highly reactive, less stable air and moist.¹¹¹ In the section, the iron catalyst used were generated *in-situ* from the most stable iron(II) pre-catalysts (^{*i*}PrBIP)FeCl₂ **79** or (^{TMc}BIP)FeCl₂ (**80**) with sodium triethylborohydride (NaBHET₃) to afford the active iron(0) complex (See Scheme 1.54 at the introduction). Furthermore, the iron-catalyzed hydroboration of olefins with 1,3,2-benzodiazaborolane (**31**) or 1,3,2-benzoxazaborolane (**34**) reactions was being investigated here for the first time.

3.3.4.1. Preparation of the iron catalysts

3.3.4.1.1. Preparation of the iron pincer ligands

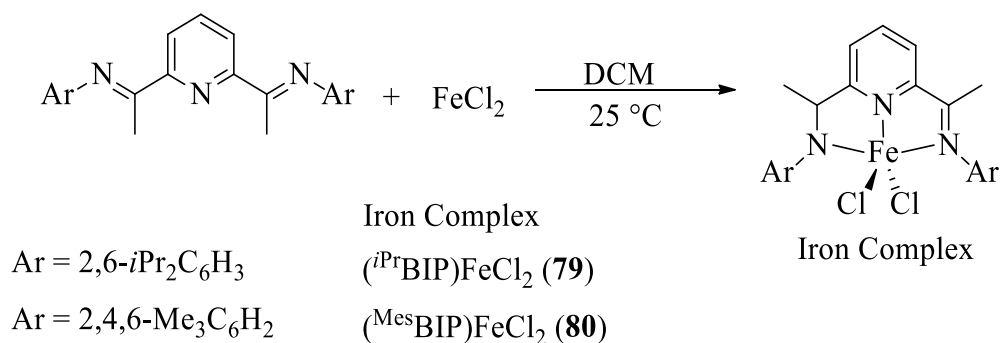
The pincer ligands 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine (^{*i*}PrBIP) (**121**) and 2,6-bis-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine (^{Mes}BIP) (**122**) were prepared following modified literature procedures (Scheme 3.23).^{112, 113} They were either prepared DCM or ethanol and activated with glacial acetic acid and were afforded in yield 60% to 85%. Both ligands were confirmed using ¹H-NMR spectroscopy and the literature.¹¹¹



Scheme 3.23: Preparation of the 2,6-bis-[(imino)ethyl]pyridine (BIP) pincer ligands.

3.3.4.1.2. Synthesis of the iron(II) pre-catalyst complexes

The Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron(II) chloride ($(^{iPr}\text{BIP})\text{FeCl}_2$) (**79**) was conducted using literature procedure.^{112, 113} A similar procedure was also used for the synthesis of 2,6-bis-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine iron(II) chloride ($(^{\text{Mes}}\text{BIP})\text{FeCl}_2$) (**80**). In this study, pincer ligand ^{iPr}BIP (**121**) or $^{\text{Mes}}\text{BIP}$ (**122**) was reacted with iron(II) chloride in anhydrous DCM under a dry argon atmosphere to afford the quantitatively corresponding iron complex (Scheme 3.24).



Scheme 3.24: Synthesis of the iron(II) pre-catalyst complexes.

Both complexes were confirmed using mass spectrum. In both cases, the m/z for the corresponding complex minus chloride ion $[\text{M}^+ - \text{Cl}]$ mass was observed. For example, calculated m/z for $(^{\text{Mes}}\text{BIP})\text{FeCl}_{2-1}$ was 488.864 while the observed is 488.1561 (Figure 3.30). These results agreed with literature.¹¹² The loss of one chloride in the mass spectrum indicating that one chloride likely a counter ion to the complex.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 5.0 PPM / DBE: min = -1.5, max = 100.0

Element prediction: Off

Number of isotope peaks used for i-FIT = 3

Monoisotopic Mass, Even Electron Ions

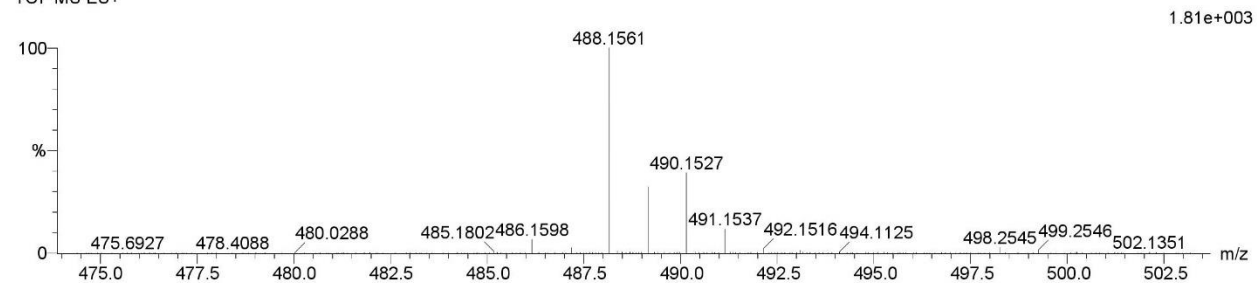
8 formula(e) evaluated with 1 results within limits (up to 20 closest results for each mass)

Elements Used:

C: 25-30 H: 30-35 N: 0-5 Cl: 0-1 Fe: 0-1

FeL3 11 (0.170)

TOF MS ES+



Minimum:

Maximum: 5.0 5.0 -1.5

Mass	Calc. Mass	mDa	PPM	DBE	i-FIT	i-FIT (Norm)	Formula
488.1561	488.1556	0.5	1.0	13.5	101.0	0.0	C27 H31 N3 Cl Fe

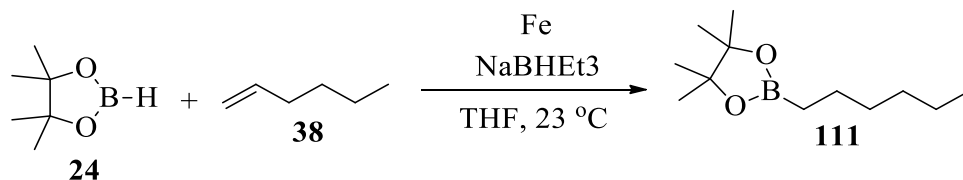
Figure 3.30: mass spectrum obtained for (^{Me}BIP)FeCl₂ (**80**).

3.3.4.2. Iron-catalyzed hydroboration studies with pinacolborane (24)

Most of the iron-catalyzed hydroboration studies have been conducted using pinacolborane (**24**) up to date.^{94-97, 111, 114} In this section, the hydroboration of olefins with pinacolborane using (ⁱPrBIP)FeCl₂ (**79**) or (^{Mes}BIP)FeCl₂ (**80**) activated *in-situ* with NaEt₃BH were investigated. Such hydroboration studies using these pairs of catalysts and activating agent have only been reported twice.^{94, 95} In both these cases, the catalysts were only employed for the hydroboration of 4-methylpent-1-en (**89**) with pinacolborane (**24**) to afford 61% and 46%, respectively with each catalyst. Hence in this section, further hydroboration investigation of these catalysts and hydroborating reagent was conducted with several olefins.

3.3.4.2.1. Iron-catalyzed hydroboration of 1-hexene with pinacolborane

The hydroboration of 1-hexene (**38**) was conducted using a similar protocol to that employed for the hydroboration of 4-methylpent-1-en (**89**) with pinacolborane (**24**) catalyzed with 5 mol% (ⁱPrBIP)FeCl₂ (**79**) activated with 15 mol% NaBHEt₃ in THF (Scheme 3.25).^{94, 95} In this study, hydroboration of 1-hexene (**38**) with pinacolborane (**24**) showed poor yields.



Scheme 3.25: Iron-catalyzed hydroboration of 1-hexene (**38**) with pinacolborane (**24**).

When the reaction was conducted with (ⁱPrBIP)FeCl₂ (**79**), two esters were obtained 2-hexyl-4,4,5,5-tetramethyl-1,3,2-borolane (**111**) and its isomer obtained from hydroboration from opposite regioselectivity with a 7% yield after 24 hours (Figure 3.31). When (^{Mes}BIP)FeCl₂ (**80**) complex was employed, no hydroboration product was observed. In both these cases, major disproportionation was observed.

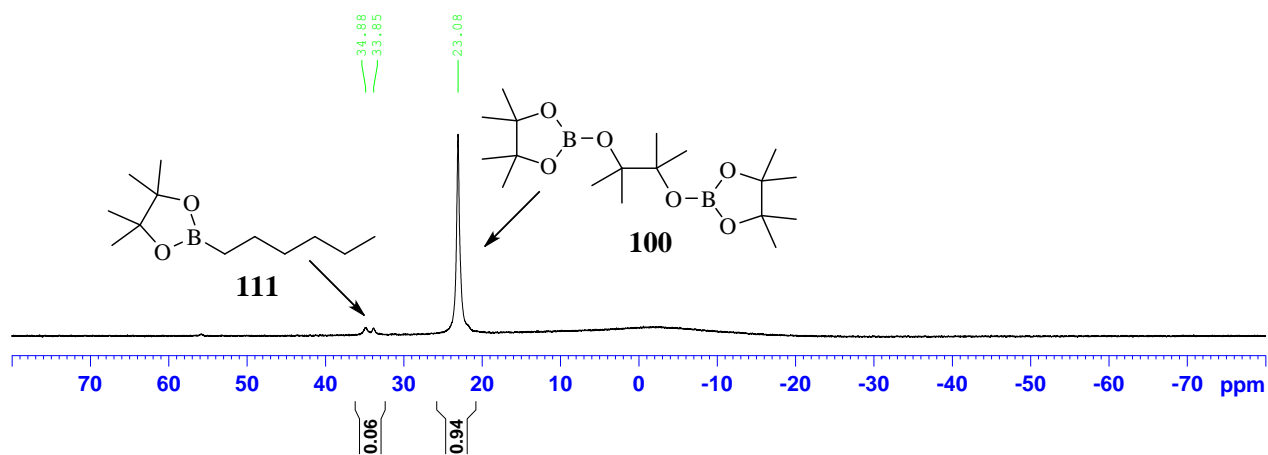
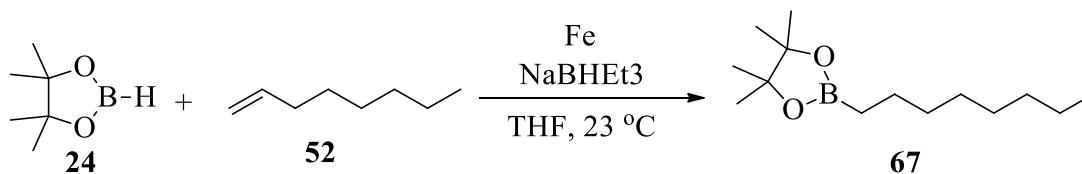


Figure 3.31: ^{11}B -NMR spectrum for the hydroboration of 1-hexene (**38**) with pinacolborane (**24**) catalyzed with $(i\text{PrBIP})\text{FeCl}_2$ (**79**).

3.3.4.2.2. Iron-catalyzed hydroboration of 1-octene with pinacolborane

Hydroboration of 1-octene (**52**) with pinacolborane (**24**) was conducted using the protocol discussed above and 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (**67**) was afforded in a 9% yield when $(i\text{PrBIP})\text{FeCl}_2$ **79** was employed and no ester observed when the reaction was catalyzed with $(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (**80**). In both cases, high disproportionation levels of pinacolborane to afford Pin_3B_2 (**100**) were observed.



Scheme 3.26: Iron-catalyzed hydroboration of 1-octene (**52**) with pinacolborane (**24**).

When an ^{11}B -NMR spectroscopy was recorded after 4 hours of reaction (Figure 3.32). The spectrum indicated that $>80\%$ of the hydroborating reagent had already undergone disproportionation.

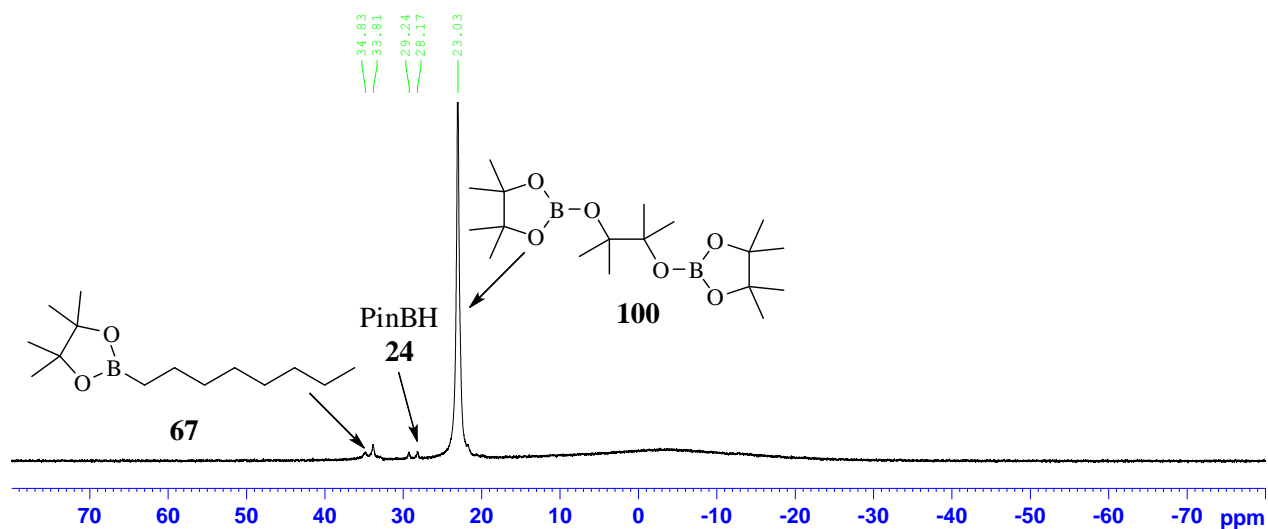


Figure 3.32: ^{11}B -NMR spectrum for the hydroboration of 1-octene (**52**) with pinacolborane (**24**) catalyzed with $(i\text{Pr}^r\text{BIP})\text{FeCl}_2$ (**79**)

3.3.4.2.3. Further iron-hydroboration of more olefins with pinacolborane(**24**)

When further hydroboration of olefins such as styrene (**10**), α -methylstyrene (**74**), cyclohexene (**17**) and cyclooctene (**117**) afforded similar results (Table 3.4).

Table 3.4: Corresponding ester yield for the iron-catalyzed hydroboration of olefins with pinacolborane (**24**).

Olefins	$(i\text{Pr}^r\text{BIP})\text{FeCl}_2$ Yield(%)	$(\text{Mes}^s\text{BIP})\text{FeCl}_2$ Yield(%)
Styrene (10)	24	<5
α -Methylstyrene (74)	9	0
Cyclohexene (17)	8	0
Cyclooctene (117)	6	0

3.3.4.2.4. Summary of observations for the iron-catalyzed hydroboration with pinacolborane (24).

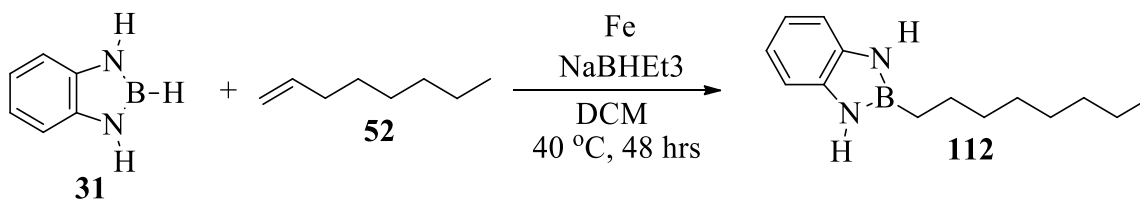
- ❖ The hydroboration of olefins with pinacolborane (24) using (ⁱPrBIP)FeCl₂ (79) and (^{Mes}BIP)FeCl₂ (80) resulted in poor hydroboration selectivity and facilitate the formation of the disproportionation of pinacolborane over hydroboration of olefin (see Figure 3.31 and Figure 3.32). These results differ from the literature reports for the hydroboration of 4-methylpent-1-en with these iron catalysts where the corresponding ester was afforded in moderate yields of 61 and 46% for (ⁱPrBIP)FeCl₂ (79) and (^{Mes}BIP)FeCl₂ (80), respectively.⁹⁵

3.3.4.3. Iron-catalyzed hydroboration Studies with 2,3-dihydro-1,3,2-benzodiazaborole (31).

Following the disappointing results from the iron-catalyzed hydroboration with pinacolborane (24) due to excessive disproportionation of hydroborating reagent, an attempt was made to conduct the hydroboration reaction using 2,3-dihydro-1,3,2-benzodiazaborole (31) as this reagent is less susceptible to disproportionation.

3.3.4.3.1. iron-catalyzed hydroboration reactions of 1-octene (52) with 2,3-dihydro-1,3,2-benzodiazaborole (31).

The hydroboration of 1-octene (52) with 2,3-dihydro-1,3,2-benzodiazaborole (31) was conducted following a protocol like that used for the iron-catalyzed hydroboration and the protocol used for hydroboration with 2,3-dihydro-1,3,2-benzodiazaborole (31) discussed *vide supra*. This reaction was catalyzed with catalysts 5 mol% (ⁱPrBIP)FeCl₂ (79) and (^{Mes}BIP)FeCl₂ (80) conducted in DCM at 40 °C and afforded 2-octyl-1,3,2-benzodiazaboralane (112) in 24% and 83% yields, respectively with minimal or undetectable disproportionation (Scheme 3.27).



Scheme 3.27: Iron-catalyzed hydroboration reactions of 1-octene (52) with 2,3-dihydro-1,3,2-benzodiazaborole (31).

When an aliquot of the reaction mixture was used to record an ^{11}B -NMR spectrum after 48 hours indicated a new broad singlet peak at about 31.67 ppm which was assigned to 2-octyl-1,3,2-benzodiazaborolane (**112**) (an example of such a spectrum is depicted by Figure 3.33). Additional reaction run-time yielded no improvement of product yield. Attempts to isolate 2-octyl-1,3,2-benzodiazaborolane (**112**) were unfortunately not successful.

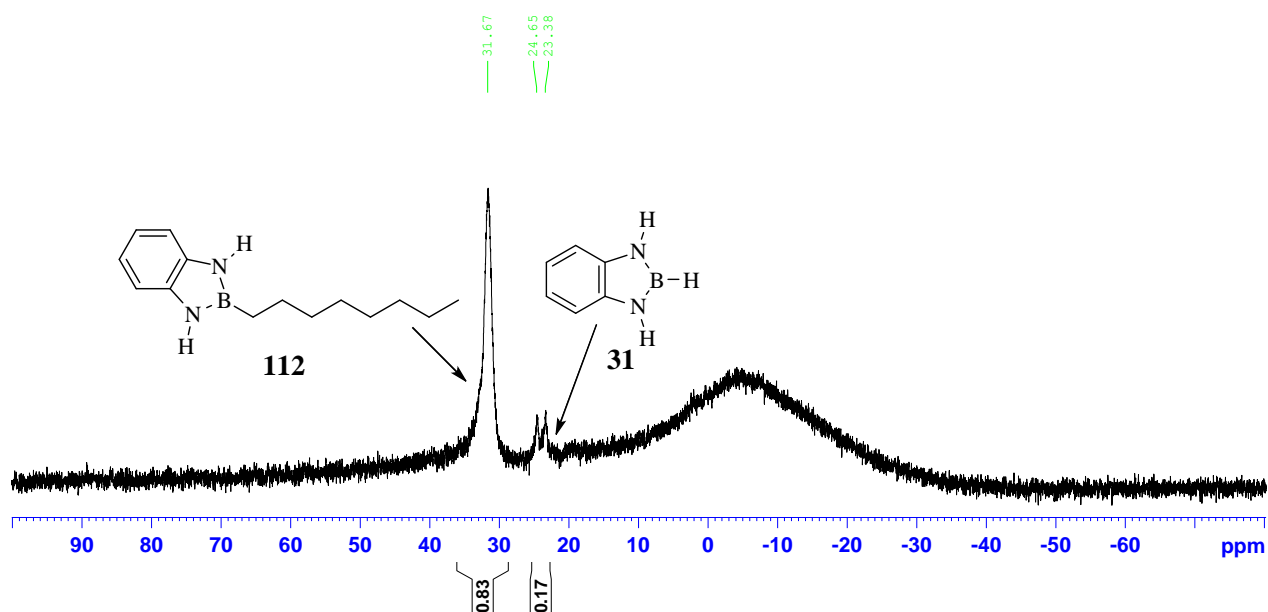


Figure 3.33: ^{11}B -NMR spectrum for the hydroboration of 1-octene (**52**) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with $(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (**80**).

3.3.4.3.2. Further iron-catalyzed hydroboration with 2,3-dihydro-1,3,2-benzodiazaborole (**31**).

A protocol like the above was further utilized for the hydroboration of more olefins to afford their corresponding esters. Similar ^{11}B -NMR spectrums such as the above hydroboration 1-hexene (**38**) with this hydroborating reagent (Figure 3.33) were observed indicating a new broad singlet peak at about 30-33 ppm characteristics of the diazaborolane ester and unreacted starting materials were observed.⁵⁸ A summary of the reaction yields afford with the selected olefins is shown in Table 3.5. The yields were recorded after 48 hours and in all cases the was no reaction progress after this period indicating significantly reduced of catalytic activity.

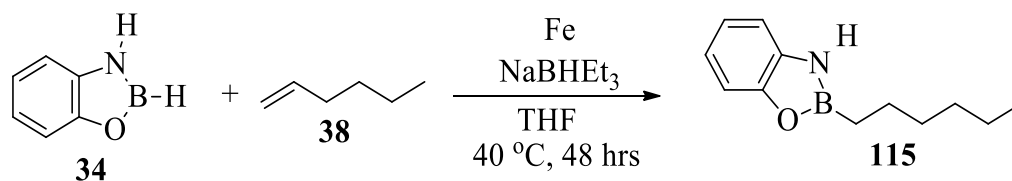
Table 3.5: iron-catalyzed hydroboration of olefins with 2,3-dihydro-1,3,2-benzodiazaborole (**31**).

Entry	olefins	$(^{iPr}\text{BIP})\text{FeCl}_2$ (79)	$(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (80)
		Yield(%)	Yield(%)
1	1-Hexene (38)	28	63
2	1-Octene (52)	24	83
3	Styrene (10)	23	37
4	α -Methylstyrene (74)	20	23
5	Cyclohexene (17)	-	26
6	Cyclooctene (117)	-	28

3.3.4.4. Iron-catalyzed hydroboration Studies with 2,3-dihydro-1,3,2-benzoxazaborole (**34**)

3.3.4.4.1. Iron-catalyzed hydroboration of 1-hexene (**38**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**)

After the positive results obtained from the iron-catalyzed hydroboration studies using 1,3,2-benzodiazaborole (**31**), the methodology from that study was adopted and employed for the investigation of hydroboration with 2,3-dihydro-1,3,2-benzoxazaborole (**34**). The hydroboration of 1-hexene **38** with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) was catalyzed with $(^{iPr}\text{BIP})\text{FeCl}_2$ (**79**) and $(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (**80**) in either THF or DCM at 40 °C (Scheme 3.28).



Scheme 3.28: Iron-catalyzed hydroboration of 1-hexene (**38**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**).

When this reaction was catalyzed with (^{Mes}BIP)FeCl₂ (**80**) it afforded 2-hexyl-1,3,2-benzoxazaborolane (**115**) in 62% yield (Figure 3.34). When the reaction was catalyzed with (^{iPr}BIP)FeCl₂ (**79**), ¹¹B-NMR indicated that 2-hexyl-1,3,2-benzoxazaborolane (**115**) was obtained in a 13% yield. However, a precipitate was observed on the reaction mixture which resulted in a loss of boron species in solution. Therefore, the observed yield may not be a direct representation of the reaction.

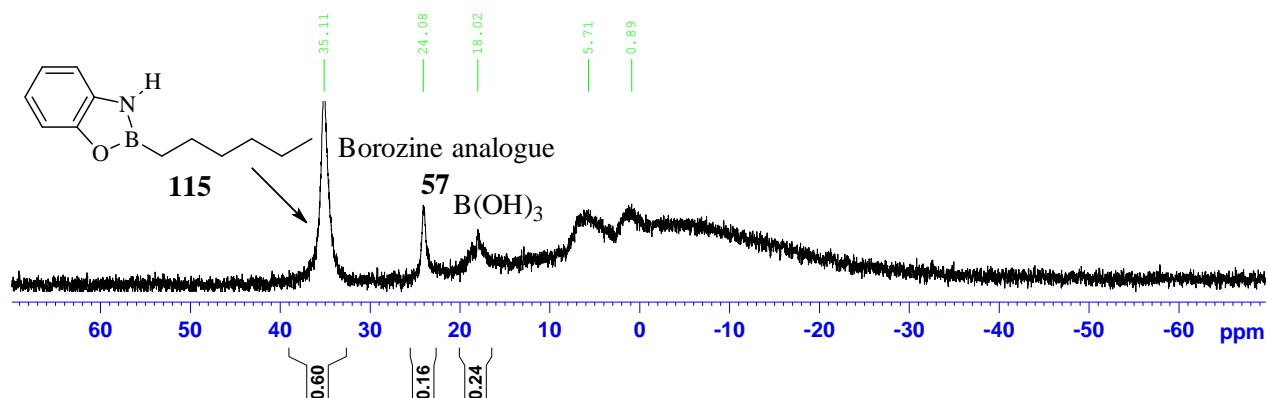


Figure 3.34: ¹¹B-NMR spectrum for the hydroboration of 1-hexene (**38**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalysed with (^{Mes}BIP)FeCl₂ (**79**)

3.3.4.4.2. Further iron-catalyzed hydroboration with 1,3,2-benzoxazaborole.

The hydroboration of olefins with 2,3-dihydro-1,3,2-benzoxazaborole **34** was further investigated using (^{iPr}BIP)FeCl₂ **79** or (^{Mes}BIP)FeCl₂ **80** pre-catalyst. A summary of the findings for the hydroboration of different olefins with 2,3-dihydro-1,3,2-benzoxazaborole **34** to afford the corresponding boronic ester is depicted in Table 3.6.

Table 3.6: iron-catalyzed hydroboration of olefins with 2,3-dihydro-1,3,2-benzoxazaborole (**34**)

Entry	Olefin	$(^{i\text{Pr}}\text{BIP})\text{FeCl}_2$ (79)	$(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (80)
		Yield(%)	Yield(%)
1	1-Hexene (52)	24 ^a	62
2	1-Octene (38)	13 ^b	81
3	Styrene (10)	9 ^b	ppt ^a
4	α -Methylstyrene (74)	9 ^b	ppt ^a
5	Cyclohexene (17)	-	ppt ^a

^a ppt = Reaction occurred with the formation of a precipitate and yield. could not be determined accurately (about 50% yield).

^b Two esters isomers were observed.

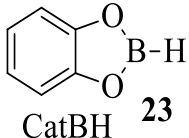
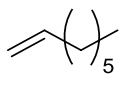
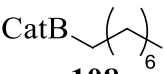
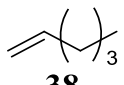
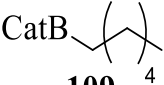
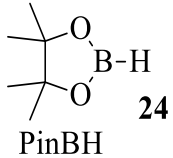
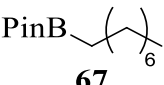
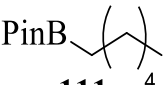
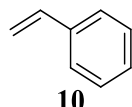
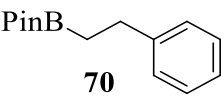
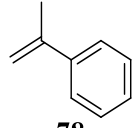
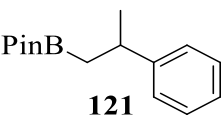

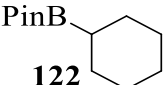
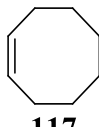
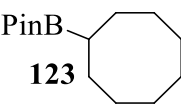
3.3.4.4.3. Observations for the iron-catalyzed hydroboration

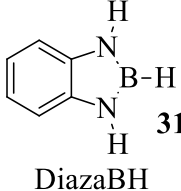
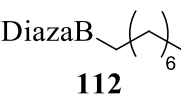
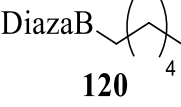
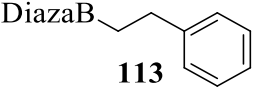
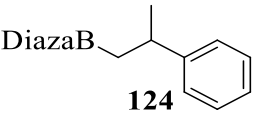
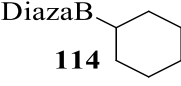
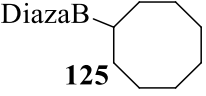
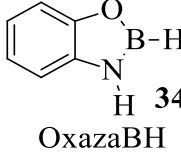
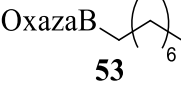
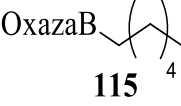
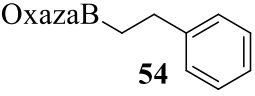
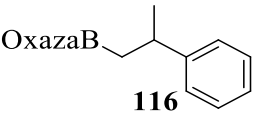
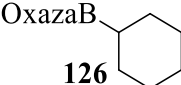
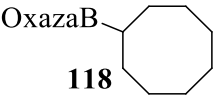
- ❖ Both iron catalysts showed poor reactivity towards hydroboration with pinacolborane (**23**). In this investigation, it was discovered that these catalysts favoured formation of the disproportionation product Pin_3B_2 (**100**). This disproportionation was severe with $(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (**80**) hence the hydroboration ester product was only observed with styrene (**10**) however in a low yield of less than 5%. Unfortunately, similar reactions were reported to afford their corresponding esters in yield 46% to 61% without any difficulty with these catalysts system.^{94, 95}
- ❖ Iron-catalyzed hydroboration with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) and 2,3-dihydro-1,3,2-benzoxazaborole (**34**) were studied here for the first time and demonstrated high efficiency with the highest yield observed with 1-octene (**58**) followed by 1-Hexene (**38**).
- ❖ Hydroboration of olefins which reacts slower such as cyclooctene (**117**), cyclohexene (**17**), α -methylstyrene (**74**), styrene (**10**) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with $(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (**80**) occurred with precipitation. However, this precipitate was never identified.

Most interestingly, the reactivity of $(^{\text{ipr}}\text{BIP})\text{FeCl}_2$ (**79**) and $(^{\text{Mes}}\text{BIP})\text{FeCl}_2$ (**80**) towards hydroboration were different, ligands influence the outcome of the hydroboration reaction (refer to Table 3.5, entry 1-3 and Table 3.6, entry 1, 2) which both analogues of each other.

3.3.5. Summary of hydroboration studies

Table 3.7: Hydroboration studies of olefins with different hydroborating reagents and catalysts.

Entry	Hydroborating reagent	Olefin	Product	58 ^a	Ti ^a	79 ^a	80 ^a
1	 CatBH 23	 52	CatB-  108	50	-	-	-
2	23	 38	CatB-  109	25	-	-	-
3	 PinBH 24	52	PinB-  67	70	35	10	n.p ^b
4	24	38	PinB-  111	33	14	7	n.p ^b
5	24	 10	PinB-  70	21	25 ^c	24	<5
6	24	 78	PinB-  121	-	-	9	n.p ^b
7	24	 17	PinB-  122	-	-	8	n.p ^b
8	24	 117	PinB-  123	-	-	6	n.p ^b

9		52		54	-	28	63
10	31	38		25	16 ^{c, e}	24	83
11	31	10		19	5 ^c	23	37
12	31	78		-	-	20	23
13	31	17		18	-	-	28
14	31	117		-	-	-	28
15		52		86	0 ^b	55 ^c	81
16	34	38		28	0 ^b	13 ^c	62
17	34	10		10	-	11 ^c	ppt ^d
18	34	78		23	-	9	ppt ^d
19	34	17		-	-	-	ppt ^d
20	34	117		14	-	-	ppt ^d

^a**58** = RhCl(PPh₃)₃, Ti = Me₂TiCp₂, **79** = (^{iPr}BIP)FeCl₂, **80** = (^{Mes}BIP)FeCl₂.

^bn.p. = No ester product observed. Excessive disproportionation of the hydroborating agent.

^cTwo ester isomers were formed.

^dppt = Reaction occurred with the formation of a precipitate and yield could not be determined accurately. The corresponding ester was about 50% yield.

^eReaction required 7 days and yield sluggish with precipitation.

Effect of different olefins

Table 3.7 indicates all the hydroboration reaction studied using each of the corresponding hydroborating reagent, catalyst and olefin. In this study, it was observed that 1-octene reacted much more efficiently than all the olefins under different catalytic conditions and hydroborating reagents. Furthermore, the hydroboration yield for different olefins parallels the rate of reaction of each olefin with borane reported Brown *et al.*,^{37,38} irrespective of the catalyst or hydroborating reagent. These observations were rationalized by the consideration that the hydroboration using heterocyclic hydroborating reagents involves a competing disproportionation reaction. If the disproportionation reaction is constant for each hydroborating reagent at the same catalyst condition, therefore, the observed change in the disproportionation products would be because of the different reactivity of the olefins used.

Effect of the different catalysts

The relative reactivity (based on yield) of each catalyst for hydroboration of 1-octene with each of the hydroborating reagent is depicted in Figure 3.35. Similar observations were observed for other some olefins used, refer to entry 4, 10 and 16 for 1-hexene (**38**) (Table 3.7). 2,3-dihydro-1,3,2-benzodiazaborole (**31**) have demonstrated high stability and resistance to disproportionation, hence this presents an advantage for a catalyst to demonstrates their hydroboration reactivity (entry 3, Figure 3.35). The (^{Mes}BIP)FeCl₂ (**80**) catalyst demonstrated high reactivity affording with high yield for example 81% with 1-octene, 63% with 1-hexene. This was followed by the Wilkison's catalyst (**58**) and (^{iPr}BIP)FeCl₂ (**80**) which demonstrated similar reactivity such case with 1-hexene (**38**). Furthermore, poor reactivity was observed with dimethyltitanocene reaction often required extended reaction time and afford low yields.

2,3-Dihydro-1,3,2-benzoxazaborole (**34**) is considered more reactive and more prone to disproportionation than 2,3-dihydro-1,3,2-benzodiazaborole (**31**). In the case of hydroboration with this reagent, it was observed again that the dimethyltitanocene unreactive and better reactivity was observed with Wilkinson's catalyst and (^{Mes}BIP)FeCl₂ (**80**) which showed similar reactivity. The shortcomings of a highly reactive catalyst such as (^{Mes}BIP)FeCl₂ (**80**) were observed upon reaction with pinacolborane as reactions afforded predominately the disproportionation product.

Most interestingly were the outstanding hydroboration efficiency of the iron catalysts for hydroboration compared to the Wilkinson's catalyst (Table 3.7, entry9, 10, 15 and 16). Despite the observed technical challenge with disproportion and precipitation occurring during the hydroboration reaction, the iron catalysts have demonstrated to be efficient hydroboration catalyst (Figure 3.35).

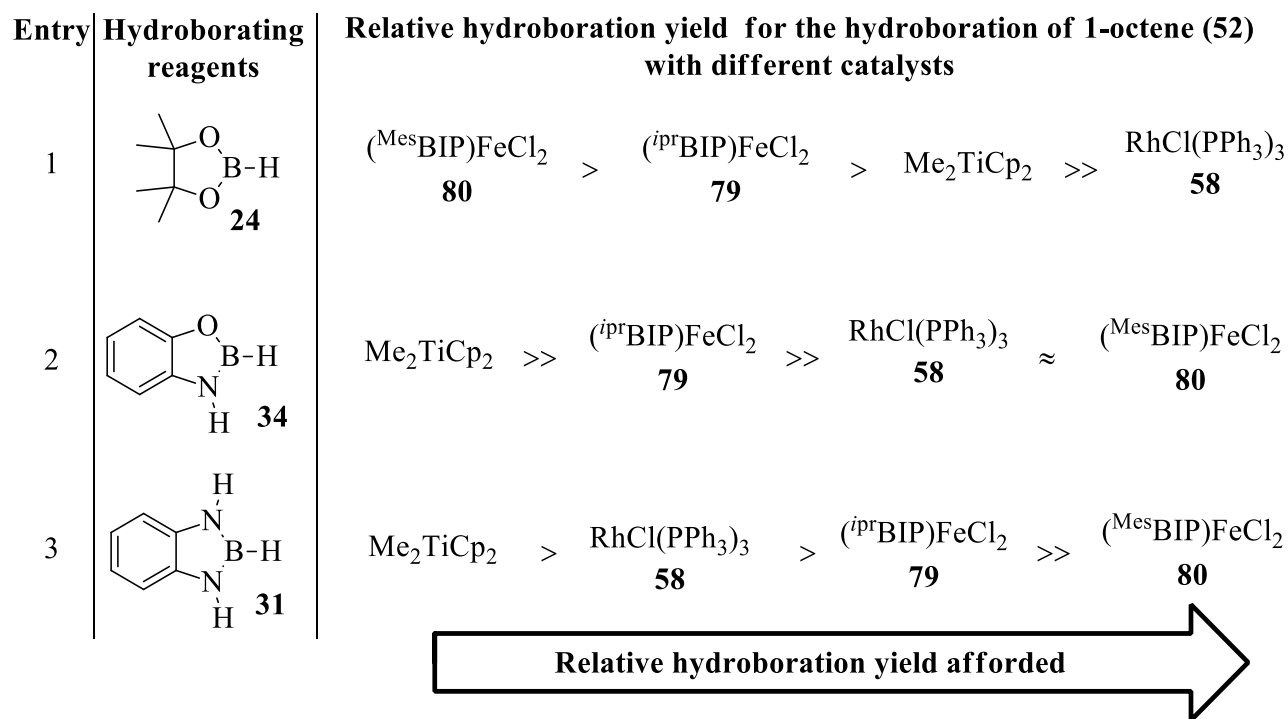


Figure 3.35: Hydroboration efficiency trend observed for the hydroboration of 1-octene (**52**).

3.4. Overall conclusions and recommendations for future works

The first part of this study was intended to prepare heterocyclic hydroborating reagents with single site available for hydroboration and four hydroborating reagents were prepared namely catecholborane (**23**), pinacolborane (**24**), 2,3-dihydro-1,3,2-benzodiazaborole (**31**) and 2,3-dihydro-1,3,2-benzoxazaborole (**34**) with a yield up to 40, 93, 99 and 97% yield respectively.

The second part of this study was aimed to conduct a diastereoselective synthesis of homoallylic alcohol *via* hydroboration. The hydroborating reagent prepared in the first part were to be employed to conduct hydroboration of dienes to afford allylic boronic esters such as (*Z*)-4,4,5,5-tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (**104**) and subsequently reacted with an aldehyde such as benzaldehyde to afford a diastereo homoallyl alcohol 2-ethyl-2-methyl-1-phenylbut-3-en-1-ol (**106**). This study was unsuccessful after failed attempts for preparation and the extraction of the intermediate esters compound such as (**104**). The ^{11}B -NMR spectroscopy result indicated the formation of a new boron compound which was assumed to be the corresponding desired intermediate esters however it could not be isolated for further evidence. In future, diastereoselective synthesis of homoallylic alcohol study maybe conducted using allylic esters (intermediates) being afforded *via* organolithium route opposed to hydroboration which might result in purification mixture.⁹²

The three part of this study, it was intended to investigate the hydroboration efficiency a set of transition metal catalysts and the hydroborating reagents prepared in the first part. The aim was to utilize early transition metal complexes dimethyltitanocene, ($^{i\text{Pr}}$ BIP)FeCl₂ (**79**) and ($^{\text{Mes}}$ BIP)FeCl₂ (**80**) and compare their hydroboration efficiency against the well-studied Wilkinson's catalyst (**58**) on hydroboration. Poor reaction yields were observed in this study compare to other metal catalyzed hydroboration studies.^{21, 55, 58, 94-97, 115} However, careful optimization studies of these reactions would improve the yields. Iron-catalyzed hydroboration with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) and 2,3-dihydro-1,3,2-benzodiazaborole (**31**) has been reported here for the first time and it is worth note that the hydroboration efficiency of both iron catalysts was to be much better than compared to the Wilkinson's catalyst. For example, faster reaction time and better yield for the hydroboration of 1-octen (**52**) with stable 2,3-dihydro-1,3,2-benzodiazaborole (**31**) was observed.

The study has demonstrated that early transition metal catalysts which are usually much cheaper than Wilkinson's catalyst (**58**) can be as effective in hydroboration. Therefore, it is worth further investigation of such metal catalyst for hydroboration whereby different ligand systems and possibly other metals such as cobalt and nickel may be used.

4. Experimental

4.1. General Information

The glassware, glass syringes, metal cannulas and metal needles used in the air- and moist-sensitive reactions were thoroughly dried overnight *ca.* 110 °C. Thereafter store in a desiccator (charged with molecular sieves) to cool prior to use. Glassware was assembled all joints wrapped and sealed with Teflon® tape and Parafilm “M”®. Solid reagents were added thereafter enclose the neck of the flask and condenser were enclosed using Precision Seal® rubber septas. The system was flame dried under reduced pressure and filled with either dry nitrogen or argon. Disposable syringes and needles were discarded after a single use.

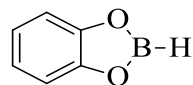
All reactions were conducted in anhydrous solvents which were prepared using Puresolv MD 7 purification system from Innovative Technologies and transferred to the system using a cannula. All other liquid mixture or reagent were introduced to the system using a disposable syringe, glass syringe or cannula.

All NMR spectra were recorded on a Varian Unity-Inova 500 MHz or Bruker 400 MHz UltraShield spectrometers in normal glass NMR tubes. All ¹H-NMR and ¹³C-NMR spectra were quoted relative to corresponding residual solvent signals e.g. CDCl₃: 7.26 ppm and 77.0 ppm or DMSO-d₆: 2.50 ppm and 39.5 ppm respectively. All ¹¹B-NMR were quoted relative to BF₃·OEt₂ (external standard, neat). All high-resolution mass spectra were obtained using a Waters Acquity LCT premier(TOF) ultra-performance liquid chromatography-mass spectrometry.

Merck silica gel 60 F254 pre-coated on an aluminium sheet were used map compounds prior to isolation. Isolation of compounds was performed by flash chromatography using Merck silica gel 60, Grace flash chromatography or centrifugal preparative thin-layer chromatography using plates coated with Merck silica gel 60 F254. All olefins used were initial distilled under nitrogen and store in 0.4 nm molecular sieves. All reagents were purchased from Sigma-Aldrich or Merck.

4.2. Synthesis of Hydroborating Reagents

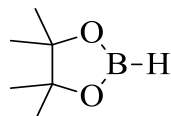
4.2.1. Synthesis of catecholborane (**23**)



Procedure 1

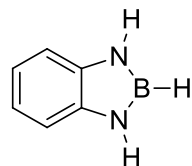
Catechol (110 mg, 1.00 mmol) was dissolved in anhydrous tetrahydrofuran or dichloromethane (50 mL) under a dry nitrogen atmosphere in a flamed dried two neck round bottom flask. The content of the flask was cooled to 0 °C with an ice bath. A slow addition (0.5-1 hour) 10 M solution of borane-dimethylsulfide (**16**) (0.10 mL, 1.0 mmol) was added *via* a disposable syringe. Thereafter, content of the flask was stirred gently allowed warm-up to room temperature. The mixture was stirred for a 1 hour which afforded clear liquid comprising of catecholborane (**23**) (37% yield based on ^{11}B -NMR). ^{11}B -NMR (128 MHz, neat): δ ppm 28.9 (d, $J = 105.6$ Hz).^{45, 52}

4.2.2. Synthesis of Pinacolborane (**24**)



A modified protocol of Procedure 1 was employed whereby catechol was replaced with pinacol (119 mg, 1.00 mmol). After the addition of BMS (**16**) and the reaction mixture allowed to warm-up to room temperature, in this case, the reaction was allowed to proceed for 5 hours. The reaction mixture afforded in a clear liquid comprising of pinacolborane (**24**) as a clear liquid (89% yield based on ^{11}B -NMR). ^{11}B -NMR (128 MHz, neat): δ 28.8 ppm (d, $J = 174.0$ Hz).⁴⁹

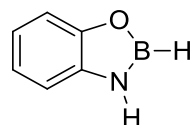
4.2.3. Synthesis of 2,3-dihydro-1,3,2-benzodiazaborole (**31**)



Procedure 2

o-phenylenediamine (109 mg, 1.00 mmol) was dissolved in anhydrous tetrahydrofuran or dichloromethane (50 mL) in a flame dried round bottom flask fitted with a condenser. The flask was reflux at 40 °C with a slow addition (0.5-1 hour) 10 M solution of borane-dimethylsulfide (**16**) (0.10 mL, 1.0 mmol) was added *via* a disposable syringe. The reaction mixture was further stirred der reflux at 40 °C for 5 hours. The reaction mixture resulted in a clear liquid comprising of 2,3-dihydro-1,3,2-benzodiazaborole (**31**) (>99% yield based on ^{11}B -NMR). ^{11}B -NMR (128 MHz, neat): δ 24.18 ppm (d, $J = 155.00$ Hz).⁵⁸

4.2.4. Synthesis of 2,3-dihydro-1,3,2-benzoxazaborole (**34**)

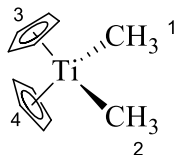


A modified protocol of Procedure 2 as above was employed whereby *o*-phenylenediamine was replaced with 2-aminopheno (108 mg, 1.00 mmol). In this case, the reaction mixture resulted in a clear liquid comprising of 2,3-dihydro-1,3,2-benzoxazaborole (97% yield based on ^{11}B -NMR). ^{11}B -NMR (128 MHz, neat): δ 27.9 ppm (d, $J = 172.0$ Hz).⁵⁶

4.3. Hydroboration studies

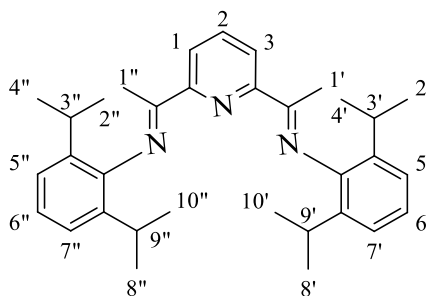
4.3.1. Preparation of metal catalyst complexes

4.3.1.1. *Synthesis of dimethyltitanocene*

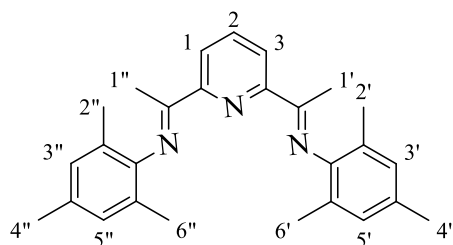


Dimethyltitanocene was prepared using titanocene dichloride (2.075 g, 8.36 mmol) dissolved in anhydrous toluene and 3 M solution of methylmagnesium chloride in THF (6.30 mL, 16.7 mmol) added slowly according to Payack *et al.*^{109, 110} After the reaction, the product was concentrated using a rotor vapor to afford an orange slurry mixture comprising solvent and product (85% yield based on the ¹H-NMR). ¹H-NMR (400 MHz, CDCl₃): δ ppm -0.09 (s, 6 H, 1'-H, 2'-H), 6.04 (s, 10 H, 3-H, 4'-H).

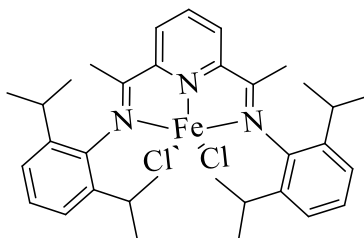
4.3.1.2. *Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine (^{ipr}BIP) (121)*



2,6-diacetylpyridine (100 mg, 0.613 mmol) was reacted with a 98% solution of 2,6-diisopropylaniline (0.26 mL, 1.226 mmol) according to a literature^{112, 113} and activated using glacial acetic acid to afford yellow crystals after recrystallization with 80% yield (236 mg). ¹H-NMR (500 MHz, CDCl₃): δ ppm 1.17 (d, 24 H, 2'-H, 2''-H, 4'-H, 4''-H, 8'-H, 8''-H), 10'-H, 10''-H) 2.27 (s, 6 H) 2.78, (spt, 4 H, 3'-H, 3''-H, 9'-H, 9''-H), 7.11 (t, 2 H, 6'-H, 6''-H), 7.18 (d, 4 H, 5'-H, 5''-H, 7'-H, 7''-H), 7.93 (t, 1 H, 2-H), 8.49 (d, 2 H, 1-H, 3-H).

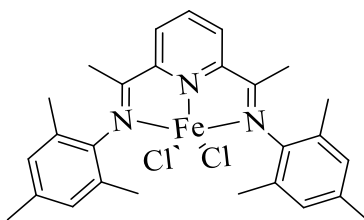
4.3.1.3. *Synthesis of 2,6-bis-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine (^{Mes}BIP) (122)*

2,6-diacetylpyridine (100 mg, 0.613 mmol) and 2,4,6-trimethylaniline (0.18 mL, 1.226 mmol) were reacted according to literature^{112, 113} activated using glacial acetic acid to afford yellow crystals after recrystallization with 80% yield (195 mg). ¹H-NMR (400 MHz, CDCl₃): δ ppm 2.04 (s, 12 H, 2'-H, 2''-H, 6'-H, 6''-H), 2.27 (s, 6 H, 4'-H, 4''-H), 2.33 (s, 6 H, 4'-H, 4''-H), 6.93 (s, 4 H, 3'-H, 3''-H, 4'-H, 5''-H), 7.93 (t, 1 H, 1-H), 8.49 (d, 2 H, 1-H, 3-H).

4.3.1.4. *Synthesis of 2,6-bis-[1-(2,6-diisopropylphenylimino)ethyl]pyridine iron(II) chloride ((^{iPr}BIP)FeCl₂) (79)*

FeCl₂ (50.7 mg, 0.400 mmol) was reacted with ^{iPr}BIP (193 mg, 0.400) according to a literature^{112, 113} to afford the corresponding complex with quantitative yield >80% as blue violet powder. HR-APIMS *m/z* found 573.2500 [M⁺-Cl] or (C₃₃H₄₃N₃FeCl), calculated 573.0260

4.3.1.5. *Synthesis of 2,6-bis-[1-(2,4,6-trimethylphenylimino)ethyl]pyridine iron(II) chloride*
(^{Mes}BIP)FeCl₂ (80)



FeCl₂ (50.7 mg, 0.400 mmol) was reacted with ^{Mes}BIP (159 mg, 0.400 mmol) according to a literature^{111, 112} to afford the corresponding complex with quantitative yield >85% as blue violet powder. HR-APIMS *m/z* found 488.1561 [$M^+ - Cl$] or (C₂₇H₃₁N₃FeCl), calculated 488.864

4.3.2. Hydroboration studies

Procedure 3A: Low-Temperature Approach

The low-temperature approach procedure was conducted to reduce disproportionation with hydroborating reagents that are more susceptible to disproportionation. In this procedure, the resulting mixture afforded using the syntheses protocol employed for preparing hydroborating reagents discussed in section 4.2 is kept in an enclosed system filled with a nitrogen atmosphere and maintained at 0 °C with an ice bath. Equimolar olefin is then added drop-wise to the mixture *via* a disposable syringe through the rubber septa cap. This was followed by addition of each of the catalyst solution (*vide infra*) was introduced to the reaction mixture through the rubber septa cap *via* a syringe or cannula. The content of the flask was then stirred and maintained at 0 °C for 1 hour, thereafter the reaction mixture was gently allowed to warm-up to 25 °C and thereafter maintain at this temperature for the corresponding reported period. All the reaction yields were recorded using ^{11}B -NMR spectroscopy using base on the amount of hydroborating reagent present before reaction over the amount converted to the corresponding boronic ester.

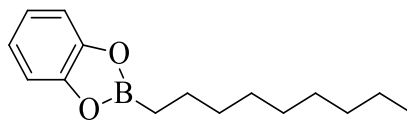
Catalyst solutions

RhClPPh₃ (58): The Wilkinson's catalyst 1 mol% (9.2 mg, 0.01 mmol) is added to a flame dried round bottom flask and dissolved in 5 mL anhydrous THF or DCM. **Iron catalysts**: ($^{i\text{Pr}}\text{BIP}$)FeCl₂ (**79**) (30 mg, 5 mol%) or ($^{\text{Mes}}\text{BIP}$)FeCl₂ (26 mg, 5 mol%) (**79**) was initially prepared as RhClPPh₃ (**58**) catalyst solution followed by addition (0.05 mL, 15 mol%) of a 3 M sodium triethylborohydride in THF solution which was added drop-wise to the mixture using a syringe through the rubber septa cap to activate the iron catalysts. **Cp₂TiMe₂**: The Cp₂TiMe₂ solution was prepared from catalyst solution which has been stored in THF:Toluene mixture under a nitrogen atmosphere according to Payack *et al.*,^{109, 110} and an aliquot equivalent to 5 mol% (calculated using ^1H -NMR spectroscopy) was introduced using a disposable syringe.

Procedure 3B: High-Temperature Approach

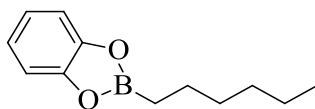
The procedure was conducted to increase reaction rates for hydroborating reagents which are less prone to disproportionation. The procedure is as Procedure 3A however, the temperature of these reactions was maintained at 40 °C.

4.3.2.1. *Synthesis of 2-octyl-1,3,2-benzodioxaboralane (108)*

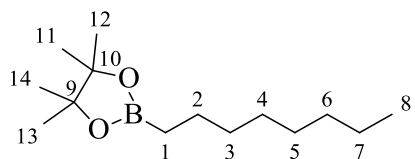


The 2-octyl-1,3,2-benzodioxaboralane (**108**) was prepared from catecholborane (**23**) (1.00 mmol in 50 ml THF) and 98% 1-octene (**52**) (0.16 mL, 1.0 mmol) following the procedure 3A catalyzed with RhClPPh₃ (**58**). After the reaction mixture was allowed to stir for 18 hours at 25 °C which resulted in a clear solution which was containing 2-octyl-1,3,2-benzodioxaboralane (**108**) 50% yield (As indicated above for procedure 3 all reaction yields were based on the ¹¹B-NMR). ¹¹B-NMR (128 MHz, neat): δ ppm 35.6 (br.s.).

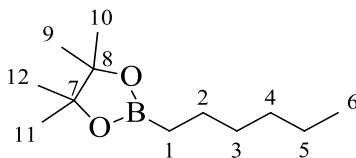
4.3.2.2. *Synthesis of 2-hexyl-1,3,2-benzodioxaboralane (109)*



The 2-hexyl-1,3,2-benzodioxaboralane (**109**) was prepared from catecholborane (**23**) (1.00 mmol in 50 ml THF) and 97% 1-hexene (**38**) (0.14 mL, 1.0 mmol) following the procedure 3A catalyzed with RhClPPh₃ (**58**). After 24 hours at 25 °C the reaction afforded a clear solution which was containing 2-hexyl-1,3,2-benzodioxaboralane (**109**) 25% yield. ¹¹B-NMR (128 MHz, neat) δ ppm 35.7 (br.s.).

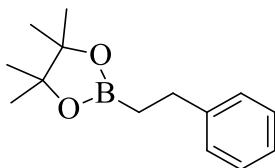
4.3.2.3. *Synthesis of 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane (67)*

Procedure 3A was employed for the hydroboration of 98% 1-octene (**52**) (0.16 mL, 1.0 mmol) with pinacolborane (**24**) to afford 4,4,5,5-tetramethyl-2-octyl-1,3,2-dioxaborolane after 24 hours at 25 °C. The reaction was quenched with water. Ether was used to extract product which was further isolated by column chromatograph with hexane and ethyl ether. The product was afforded in a yield of 70% with RhClPPh₃ (**58**), 35% with Cp₂TiMe₂, 10% with (^{*i*}PrBIP)FeCl₂ (**79**) and no hydroboration product was obtained was observed with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ ppm 34.2 (br.s.), ¹H-NMR (400 MHz, CDCl₃): δ ppm 0.67 (t, 2 H, 1-*H*), 0.71 (t, 3 H, 1-*H*) 1.15 (s, 12 H, 11-*H*, 12-*H*, 13-*H*, 13-*H*), 1.17-1.23 (m, 10 H, 3-*H*, 4-*H*, 5-*H*, 6-*H*, 7-*H*), 1.32 (m, 2 H, 2-*H*)

4.3.2.4. *Synthesis of 2-hexyl 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (111)*

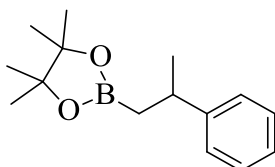
Procedure 3A was employed for the hydroboration of 97% 1-hexene (**38**) (0.14 mL, 1.0 mmol) with pinacolborane (**24**) to afford 2-hexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane after 24 hours at 25 °C. The reaction was quenched with water. Ether was used to extract product which was further isolated by column chromatograph with hexane and ethyl ether. The product was afforded in a yield of 33% with RhClPPh₃ (**58**), 14% with Cp₂TiMe₂, 10% (^{*i*}PrBIP)FeCl₂ (**79**) and no hydroboration product was obtained with (^{Mes}BIP)FeCl₂ (**80**) detected. ¹¹B-NMR (128 MHz, neat): δ ppm 34.1 (br.s.), ¹H-NMR (400 MHz, CDCl₃): δ ppm 0.74 (t, 2 H, 1-*H*), 0.88 (t, 3 H, 6-*H*) 1.23 (s, 12 H, 9-*H*, 10-*H*, 11-*H*, 12-*H*), 1.17-1.23 (m, 6 H, 3-*H*, 4-*H*, 5-*H*), 1.44 (m, 2 H, 2-*H*)

4.3.2.5. *Synthesis of 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane (70)*



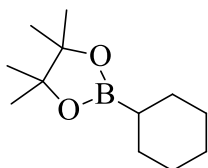
Procedure 3A was employed for the hydroboration of styrene (**10**) (0.11 mL, 1.0 mmol) with pinacolborane (**24**) to afford 4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane after 24 hours at 25 °C. The ester was afforded in a yield of 21% with RhCIPPh₃ (**58**), 25% with Cp₂TiMe₂, 24% with (ⁱPrBIP)FeCl₂ (**79**) and <5% with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ ppm 34.0 (br.s.).

4.3.2.6. *Synthesis of 4,4,5,5-tetramethyl-2-(2-phenylpropyl)-1,3,2-dioxaborolane (121)*



Procedure 3A was employed for the hydroboration of α-methylstyrene (**74**) (0.13 mL, 1.0 mmol) with pinacolborane (**24**) to afford 2-(4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane) after 24 hours at 25 °C. The reaction afforded the corresponding ester with a yield of 9% with (ⁱPrBIP)FeCl₂ (**79**) and no ester product was observed with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ ppm 35.2 (br.s.).

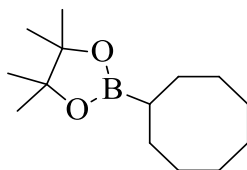
4.3.2.7. *Synthesis of 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (122)*



Procedure 3A was employed for the hydroboration of cyclohexene (**17**) (0.10 mL, 1.0 mmol) with pinacolborane (**24**) to afford 2-cyclohexyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane after 24 hours at 25 °C. The reaction afforded the corresponding ester with a yield of 9% with

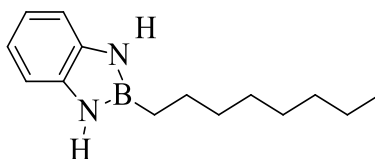
(ⁱPrBIP)FeCl₂ (**79**) and no ester product was observed with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ ppm 34.2 (br.s.).

4.3.2.8. *Synthesis of 2-cyclooctyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (123)*

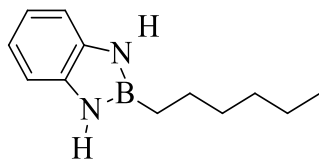


Procedure 23A was employed for the hydroboration of 98% cyclooctene (**77**) (0.16 mL, 1.0 mmol) with pinacolborane (**24**) to afford 2-4,4,5,5-tetramethyl-2-phenethyl-1,3,2-dioxaborolane after 24 hours at 25 °C. The reaction afforded corresponding ester with a yield of 6% with (ⁱPrBIP)FeCl₂ (**79**) and no ester product was observed with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ ppm 34.2 (br.s.).

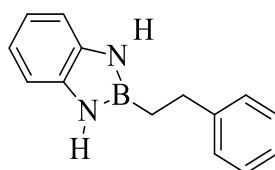
4.3.2.9. *Synthesis of 2-octyl-1,3,2-benzodiazaborolane (112)*



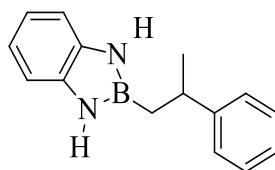
Procedure 3B was employed for the hydroboration of 98% 1-octene (**52**) (0.16 mL, 1.00 mmol) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) to afford 2-octyl-1,3,2-benzodiazaborolane after 48 hours at 40 °C. This reaction afforded the corresponding ester in 28% with (ⁱPrBIP)FeCl₂ **79** and 62% (^{Mes}BIP)FeCl₂ (**80**). The reaction required 7 days to afford 54% with RhCl(PPh₃)₃ (**58**). ¹¹B-NMR (128 MHz, neat): δ ppm 33.7 (br.s.).

4.3.2.10. *Synthesis of 2-hexyl-1,3,2-benzodiazaboralane (120)*

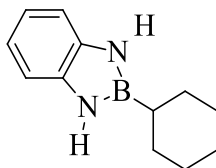
Procedure 3B was employed for the hydroboration of 97% 1-hexene (**38**) (0.14 mL, 1.00 mmol) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) to afford 2-hexyl-1,3,2-benzodiazaboralane after 48 hours at 40 °C. This reaction afforded 24% with (*i*^{Pr}BIP)FeCl₂ (**79**) and 83% with (^{Mes}BIP)FeCl₂ (**80**). This reaction was sluggish required 7 days to afford 28% with RhClPPh₃ (**58**) and 16% with Cp₂TiMe₂. ¹¹B-NMR (128 MHz, neat): δ ppm 33.1 (br.s.).

4.3.2.11. *Synthesis of 2-phenethyl-1,3,2-benzodiazaboralane (113)*

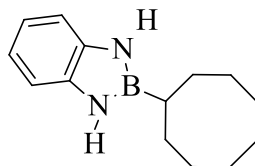
Procedure 3B was employed for the hydroboration of styrene (**10**) (0.11 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) to afford 2-phenethyl-1,3,2-benzodiazaboralane after 48 hours at 40 °C. This reaction afforded 23% (*i*^{Pr}BIP)FeCl₂ (**88**) and 37% (^{Mes}BIP)FeCl₂ (**89**). A similar observation with as above were with RhClPPh₃ (**58**) and Cp₂TiMe₂ and afford 28% and 16% respectively. ¹¹B-NMR (128 MHz, neat): δ ppm 31.7 (br.s.).

4.3.2.12. *Synthesis of 2-(2-phenylpropyl)-1,3,2-benzodiazaboralane (124)*

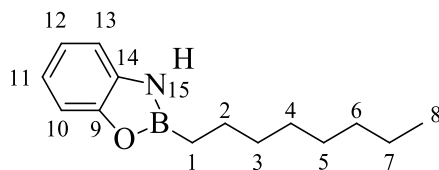
Procedure 3B was employed for the hydroboration of α-methylstyrene (**77**) (0.13 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) to afford 2-(2-phenylpropyl)-1,3,2-benzodiazaboralane after 48 hours. This reaction afforded 20% (*i*^{Pr}BIP)FeCl₂ (**88**) and 23% with (^{Mes}BIP)FeCl₂ (**89**). ¹¹B-NMR (128 MHz, neat): δ ppm 30.3 (br.s.).

4.3.2.13. *Synthesis of 2-cyclohexyl-1,3,2-benzodiazaboralane (114)*

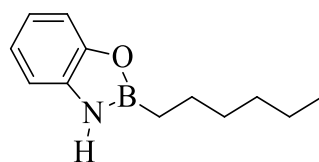
Procedure 3B was employed for the hydroboration of cyclohexene (**17**) (0.10 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) to afford 2-cyclohexyl-1,3,2-benzodiazaboralane. This reaction afforded 18% with RhClPPh₃ (**58**) and 28% (^{Mes}BIP)FeCl₂ (**89**). ¹¹B-NMR (128 MHz, neat): δ ppm 31.6 (br.s.).

4.3.2.14. *Synthesis of 2-cyclooctyl-1,3,2-benzodiazaboralane (125)*

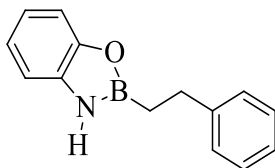
Procedure 3B was employed for the hydroboration of 98% cyclooctene (**77**) (0.16 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzodiazaborole (**31**) catalyzed with (^{Mes}BIP)FeCl₂ (**80**) and afford 2-cyclooctyl-1,3,2-benzodiazaboralane in 28% yield. ¹¹B-NMR (128 MHz, neat): δ ppm 31.8 (s.)

4.3.2.15. *Synthesis of 2-octyl-1,3,2-benzoxazaboralane (53)*

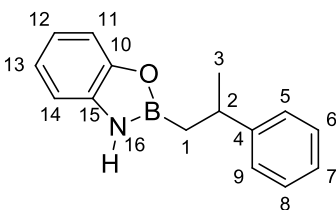
Procedure 3B was employed for the hydroboration of 98% 1-octene (**52**) (0.16 mL, 1.00 mmol) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) to afford 2-octyl-1,3,2-benzoxazaboralane. The reaction was quenched with water. Ether was employed to extract product which was further isolated by column chromatograph with hexane and ethyl ether. This reaction afforded 86% with RhClPPh_3 (**58**), 13% ($^{i\text{Pr}}\text{BIP}$) FeCl_2 (**79**) (with precipitation) and 81% with ($^{\text{Mes}}\text{BIP}$) FeCl_2 (**80**). ^{11}B -NMR (128 MHz, neat): δ 34.7 ppm (br.s); ^1H -NMR (400 MHz, DMSO- d_6): δ ppm 0.56 (t, 2 H, 1-*H*), 0.86 (t, 3 H, 1-*H*), 1.15-1.35 (m, 12 H, (2-7)-*H*), 4.43 (br.s, 1 H, 15-*H*), 6.38 (td, 1 H, 13-*H*), 6.52 (td, 1 H, 11-*H*), 6.58 (dd, 1 H, 10-*H*), 6.62 (dd, 1 H, 12-*H*); ^{13}C -NMR (100 MHz, DMSO- d_6): δ ppm 14.42 (8-*C*), 22.57 (2-*C*), 24.67 (7-*C*), 29.18 (3-*C*), 29.41 (5-*C*), 31.81 (4-*C*), 32.59 (6-*C*), 33.02 (1-*C*), 114.85 (13-*C*), 114.91 (10-*C*), 116.88 (12-*C*), 119.96 (11-*C*), 137.01 (14-*C*), 144.45 (9-*C*).

4.3.2.16. *Synthesis of 2-hexyl-1,3,2-benzodiazaboralane (115)*

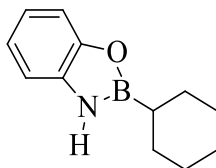
Procedure 3B was employed for the hydroboration of 97% 1-hexene (**38**) (0.14 mL, 1.00 mmol) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) to afford 2-hexyl-1,3,2-benzodiazaboralane. This reaction afforded 28% with RhClPPh_3 (**58**), 13% ($^{i\text{Pr}}\text{BIP}$) FeCl_2 (**79**) and 66% ($^{\text{Mes}}\text{BIP}$) FeCl_2 (**80**). ^{11}B -NMR (128 MHz, neat): δ ppm 34.9 (br.s.).

4.3.2.17. *Synthesis of 2-(2-phenylpropyl)-1,3,2-benzoxazaboralane (54)*

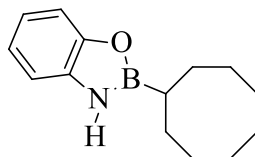
Procedure 3B was employed for the hydroboration of styrene (**10**) (0.11 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) to afford 2-phenethyl-1,3,2-benzoxazaboralane. This reaction afforded 10% with RhClPPh₃ (**58**), 11% (^{iPr}BIP)FeCl₂ (**88**) and precipitate occur during reaction and yield determined with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ 33.7 ppm (br.s.).

4.3.2.18. *Synthesis of 2-(2-phenylpropyl)-1,3,2-benzoxazaboralane (116)*

Procedure 3B was employed for the hydroboration of α -methylstyrene (**74**) (0.13 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) to afford 2-phenethyl-1,3,2-benzoxazaboralane. The reaction was quenched with water. Ether was used to extract product which was further isolated by column chromatograph with hexane and ethyl ether. This reaction afforded 28% with RhClPPh₃ (**58**), 9% (^{iPr}BIP)FeCl₂ (**79**) and precipitate occur during reaction and yield determined with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ 34.2 ppm (br.s.); ¹H-NMR (400 MHz, DMSO-d₆): δ ppm 0.91 (dd, 1 H, 1-*H*), 0.96 (dd, 1 H, 1-*H*), 1.16 (d, 3 H, 3-*H*), 2.98 (m, 1 H, 2-*H*), 7.11 (tt, 1 H, 7-*H*), 7.17 -7.19 (m, 5 H, 6-*H*, 8-*H*, 9-*H*, 11-*H*), 7.34 (m, 1 H, 14-*H*) 7.42 (br.s, 2 H, 12-*H*, 16-*H*) 7.46 (m, 1 H, 13-*H*); ¹³C-NMR (100 MHz, DMSO-d₆): δ ppm 24.73 (3-*C*), 25.57 (1-*C*), 35.20 (2-*C*), 125.31 (11-*C*), 125.34 (7-*C*), 126.29 (5-*C*, 9-*C*), 126.93 (6-*C*, 8-*C*), 127.42 (14-*C*), 128.07 (12-*C*), 128.20 (13-*C*), 143.98 (15-*C*), 149.90 (4-*C*), 151.17 (10-*C*).

4.3.2.19. *Synthesis of 2-cyclohexyl-1,3,2-benzoxazaboralane (126)*

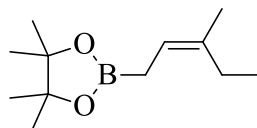
Procedure 3B was employed for the hydroboration of cyclohexene (**17**) (0.10 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with (^{Mes}BIP)FeCl₂ (**80**) to afford 2-cyclohexyl-1,3,2-benzoxazaboralane. Unfortunately, a precipitate was formed during reaction and yield determined. ¹¹B-NMR (128 MHz, neat): δ ppm 34.7 (s).

4.3.2.20. *Synthesis of 2-cyclooctyl-1,3,2-benzoxazaboralane (118)*

Procedure 3B was employed for the hydroboration of 98% cyclooctene (**77**) (0.16 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with (^{Mes}BIP)FeCl₂ (**80**) to afford 2-cyclooctyl-1,3,2-benzoxazaboralane. This reaction afforded 14% with RhClPPh₃ (**58**) and precipitate occur during reaction and yield determined with (^{Mes}BIP)FeCl₂ (**80**). ¹¹B-NMR (128 MHz, neat): δ ppm 34.6 (s).

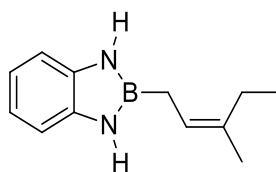
4.4. Diastereoselective synthesis of homoallylic alcohols *via* hydroboration

4.4.1.1. *Synthesis of 4,4,5,5-tetramethyl-2-(3-methylpent-2-en-1-yl)-1,3,2-dioxaborolane (104)*



Procedure 3A was employed for the hydroboration of 98% mixture of *cis* and *trans* 3-methyl-1,3-pentadiene (**103**) (0.11 mL, 1.0 mmol) with pinacolborane (**24**) catalyzed with iron(II) iminopyridine complex (**76**) to afford the corresponding ester with 36% yield after 24 hours. ^{11}B -NMR (128 MHz, neat): δ ppm 33.1 (s).

4.4.1.2. *Synthesis of 2-(3-methylpent-2-en-1-yl)-1,3,2-benzodiazaborolane (107)*



Procedure 3B was employed for the hydroboration of 98% mixture of *cis* and *trans* 3-methyl-1,3-pentadiene (**103**) (0.11 mL, 1.0 mmol) with 2,3-dihydro-1,3,2-benzoxazaborole (**34**) catalyzed with iron(II) iminopyridine complex (**76**) to afford the corresponding ester with 40% yield after 48 hours. ^{11}B -NMR (128 MHz, neat): δ ppm 33.3 (s).

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